



**Universiteit
Leiden**
The Netherlands

Coupled electronic and nuclear dynamics at interfaces of artificial photosynthesis devices

Haas, T. de

Citation

Haas, T. de. (2025, September 4). *Coupled electronic and nuclear dynamics at interfaces of artificial photosynthesis devices*. Ridderprint, Leiden. Retrieved from <https://hdl.handle.net/1887/4259657>

Version: Publisher's Version

License: [Licence agreement concerning inclusion of doctoral thesis in the Institutional Repository of the University of Leiden](#)

Downloaded from: <https://hdl.handle.net/1887/4259657>

Note: To cite this publication please use the final published version (if applicable).

Coupled Electronic and Nuclear Dynamics at Interfaces of Artificial Photosynthesis Devices

Proefschrift

ter verkrijging van
de graad van doctor aan de Universiteit Leiden,
op gezag van rector magnificus prof.dr.ir. H. Bijl,
volgens besluit van het college voor promoties
te verdedigen op donderdag 4 september 2025
klokke 14:30 uur

door

Titus de Haas

geboren te Amsterdam, Nederland
in 1996

Promotores:

Prof. dr. H.J.M. de Groot

Dr. F. Buda

Promotiecommissie:

Prof. dr. M. Ubbink

Prof. dr. S.A. Bonnet

Prof. dr. M.A.G.J. Orrit

Prof. dr. G.J. Kroes

Prof. dr. E.J. Meijer (Universiteit van Amsterdam)

Prof. dr. ir. V. Van Speybroeck (Universiteit Gent)

Copyright © 2025 Titus de Haas

ISBN 978-94-6522-528-9

Printing: Ridderprint, www.ridderprint.nl

Table of Contents

Table of Contents	5
Chapter 1: Introduction.....	12
1.1 Dye-Sensitized Photoelectrochemical Cells.....	14
1.2 Outline of the thesis.....	17
1.3 References	20
Chapter 2: Theory and Methodology	22
2.1 Introduction	24
2.2 Electronic structure theory and the Born-Oppenheimer approximation.....	25
2.3 Molecular Dynamics and Thermodynamics.....	28
2.4 Excited States and Non-Adiabatic Dynamics.....	31
2.5 Obtaining Thermodynamic Properties from Static Calculations.....	36
2.6 Electronic Structure Methods.....	38
2.6.1 <i>Density Functional Theory</i>	38
2.6.2 <i>Time-Dependent Density Functional Theory</i>	41
2.7 References	42
Chapter 3: Strategies to Enhance the Rate of Proton-Coupled Electron Transfer Reactions in Dye-Water Oxidation Catalyst Complexes	45
3.1 Abstract	46
3.2 Introduction	47
3.3 Results and Discussion.....	50
3.3.1 <i>Search for the PCET reaction path using the Intrinsic Reaction Coordinate method</i>	50
3.3.2 <i>Tracking the electron transfer during the PCET reaction</i>	52
3.3.3 <i>Exploring the excited state potential energy surfaces with TDDFT</i>	54
3.4 Conclusion.....	63
3.5 Experimental Section	64
3.6 References	65
3A. Appendix	68
Chapter 4: Hybrid-DFT Molecular Dynamics Simulations of Photocatalytic Water Oxidation in a [Ru-bda]–Dye Complex.....	84
4.1 Abstract	86
4.2 Introduction	87
4.3 Computational methods.....	90
4.4 Results and discussion.....	92
4.4.1 <i>Probing the equilibrium dynamics of the low-valent Ru^{III}-bda intermediate</i>	95
4.4.2 <i>Blue Moon simulations of the rate-determining O-O bond formation step</i>	97

4.4.3 Dioxygen dissociation after the fourth PCET step	103
4.5 Conclusions	105
4.6 References	107
4A. Appendix	110
Chapter 5: Electron-Withdrawing Effects of Cobalt Porphyrin Catalysts Boost Homogeneous Photocatalytic Hydrogen Evolution in Neutral Aqueous Solutions	133
5.1 Abstract	134
5.2 Introduction	135
5.3 Results	138
5.3.1 Synthesis	138
5.3.2 Electrochemical properties	139
5.3.3 Photocatalysis	143
5.3.4 Photostability.....	146
5.3.5 Kinetic study.....	147
5.3.6 Density functional theory calculations	149
5.4 Discussion	157
5.5 Conclusions	163
5.6 experiments and methods	164
5.6.1 Synthesis	165
5.6.2 Cyclic voltammetry, differential pulse voltammetry and linear sweep voltammetry	169
5.6.3 Photo-induced hydrogen evolution.....	170
5.6.4 Calculating the turnover number and turnover frequency.....	171
5.6.5 Calculation of photochemical H ₂ production quantum yield	171
5.6.6 Computational details	172
5.6.7 Thermodynamic calculations.....	173
5.7 References	175
5A. Appendix	178
Chapter 6: Effects of Nuclear Motion on the Photoinduced Interfacial Charge Transfer Dynamics at a NiO/P1 Photocathode.....	194
6.1 Abstract	196
6.2 Introduction	197
6.3 Methods.....	199
6.3.1 Sample preparation and transient absorption experiments	199
6.3.2 Computational Methods	199
6.4 Results	201
6.4.1 Femtosecond transient absorption results.....	201
6.4.2 Quantum chemical modeling.....	205
6.4.3 Electronic structure of the NiO/P1 interface.....	206
6.4.4 Hole injection simulations.....	208
6.5 Discussion	215
6.6 Conclusions	218
6.7 References	219

6A. Appendix	221
Chapter 7: Charge Transfer-Induced Weakening of Vibronic Coupling for Single Terrylene Molecules Adsorbed onto hBN..	237
7.1 Abstract	240
7.2 Introduction	241
7.3 Results and discussion.....	242
7.3.1 <i>Single-Molecule Fluorescence Spectroscopy</i>	242
7.3.2 <i>Quantum Chemical Calculations</i>	246
7.3.3 <i>Calculation of the Vibrationally Resolved Fluorescence Spectra</i>	252
7.4 Conclusion.....	254
7.5 References	255
7A. Appendix	257
Chapter 8: Conclusions and Outlook	273
8.1 Conclusions	276
8.2 Outlook.....	278
8.2.1 <i>Non-adiabatic surface hopping simulations of photo-activated proton transfer in a supramolecular water oxidation catalyst-dye complex</i> .	278
8.3 References	281
Summary	284
Samenvatting	287
Acknowledgements.....	292
Curriculum vitae	295
List of Publications.....	297

List of abbreviations

AA	Ascorbic Acid
ADMM	Auxiliary Density Matrix Method
AIMD	<i>Ab Initio</i> Molecular Dynamics
B3LYP	XC-functional approximation by Becke, Lee, Yang and Parr
bda ²⁻	2,2'-bipyridine-6,6'-dicarboxylic acid
BO	Born-Oppenheimer
bpy	2,2'-bipyridine
CB	Conduction Band
CBM	Conduction Band Minimum
COSMO	COnductor like Screening MOdel
CSVR	Canonical Sampling Through Velocity Rescaling
CT	Charge Transfer
CV	Cyclic Voltammetry
cy	p-cymene
D-A	Donor-Acceptor
DFT	Density Functional Theory
DMF	Dimethylformamide
DOS	Density of States
DS-PEC	Dye-Sensitized Photoelectrochemical Cell
DVP	Differential Pulse Voltammetry
DZP	Double- ζ Polarized
ED	Electron Donor
EH	Extended Hückel
EPR	Electronic Paramagnetic Resonance
ET	Electron Transfer
FCDW	Franck-Condon-Debye-Waller
FES	Free Energy Surface
FSSH	Fewest Switches Surface Hopping
GGA	Generalized Gradient Approximation
GSB	Ground State Bleach
HAT	Hydrogen Atom Transfer
hBN	Hexagonal Boron Nitride
HEC	Hydrogen Evolution Catalyst
HER	Hydrogen Evolution Reaction
HFX	Hartree-Fock exchange
HOMO	Highest Occupied Molecular Orbital
HSE06	XC-functional approximation by Hyed, Scuseria and Ernzerhof
I2M	Interaction of two Metal centers

IRC	Internal Reaction Coordinate
LDA	Local Density Approximation
LSV	Linear Sweep Voltammetry
LUMO	Lowest Unoccupied Molecular Orbital
MD	Molecular Dynamics
NDI	2,6-diethoxy-1,4,5,8-diimidenapthalene
NHE	Normal Hydrogen Electrode
NMR	Nuclear Magnetic Resonance
NTO	Natural Transition Orbital
OER	Oxygen Evolution Reaction
OPBE	XC-functional approximation which combines Handy's Optimized exchange with PBE correlation
OT	Orbital Transformation
P1	4-(bis-4-(5-(2,2-dicyano-vinyl)-thiophene-2-yl)- phenyl-amino)-benzoic acid
PBC	Periodic Boundary Conditions
PBE	XC-functional approximation by Perdew, Burke and Ernzerhof
PCET	Proton-Coupled Electron Transfer
PDOS	Projected Density of States
PEG	Polyethylene Glycol
PEM	Proton Exchange Membrane
pic	4-picoline
PS	Photosensitizer
PV	Photovoltaic
PW	Plane Wave
RDS	Rate-Determining Step
SAS	Species Associated Spectra
SE	Stimulated Emission
SF-TDDFT	Spin-Flip Time-Dependent Density Functional Theory
SHE	Standard Hydrogen Electrode
SP	Survival Probability
TA	Transient Absorption Spectroscopy
TBAPF6	tetrabutylammonium hexafluorophosphate
TCEP	tris(2-carboxyethyl)phosphine hydrochloride
TDDFT	Time-Dependent Density Functional Theory
TOF	Turnover Frequency
TON	Turnover Number
TS	Transition State
TZP	Triple- ζ Polarized
UEG	Uniform Electron Gas
VB	Valence Band
VBM	Valence Band Maximum

VDOS	Vibrational Density of States
WNA	Water Nucleophilic Attack
WOC	Water Oxidation Catalyst
XC	Exchange-Correlation
ZORA	Zeroth Order Regular Approximation
ZPL	Zero Phonon Line

Chapter 1: Introduction

Solar-to-fuel production stands as a promising strategy to reduce CO₂ emissions from fossil fuel combustion. However, the realization of devices that can effectively store solar energy into chemicals has proven to be difficult. This chapter highlights some of the challenges in this field and places the contents of this dissertation in a broader perspective.

Chapter 1: Introduction

1.1 Dye-Sensitized Photoelectrochemical Cells

Fossil fuel combustion has been identified as a major driver for human-induced global warming, creating urgent need for alternative energy sources and effective means of energy storage.^[1–3] Solar light offers an unparalleled energy resource, with an hourly global flux sufficient to meet the world annual energy demand.^[4] Over the last decades, highly efficient photovoltaic (PV) cells have been developed^[5], which nowadays supply a substantial share of consumed electricity.^[3] Nevertheless, the discontinuous supply of solar energy necessitates large-scale energy storage solutions if we aim to fully transition to solar power. While batteries are promising for many applications, their heavy weight and limited capacity prompt a need for innovative energy storage technologies. One strategy is to perform electrolysis using green electricity to generate hydrogen or carbon-based fuels. However, this decentralized PV plus electrochemical approach is costly and the photon to product yield is intrinsically limited by concentration and overpotential losses.^[6,7]

Inspired by natural photosynthesis, researchers have been investigating the possibility of storing solar energy directly into chemical bonds. Ideally, one would like to mimic algae and plants by using sunlight to convert water and carbon dioxide into hydrocarbons with a high energy-density. Through billions of years of evolution, the natural photosynthetic system achieves this transformation with remarkable efficiencies, but reproducing these efficiencies in an artificial setting and at a meaningful scale remains challenging.^[4,8]

The first photoelectrochemical cell for water splitting was developed in the early 70s by Fujishima and Honda, who employed TiO_2 as a photoanode.^[9] Although their system was capable of driving hydrogen evolution, the wide TiO_2 bandgap of 3 eV firmly restricted the range of the solar spectrum that they could capture, lowering the cells efficiency. In addition, the catalytic activity of TiO_2 towards water oxidation is sluggish compared to molecular catalysts developed in recent years.^[10–14]

Nature employs a sophisticated assembly of molecular pigments, proteins, enzymes and co-enzymes, each individually optimized and interlinked to efficiently capture photons and use that energy to oxidize water and reduce CO_2 .^[15,16] Dye-sensitized photoelectrochemical cells (DS-PEC), mimic this functional separation in specialized units, thereby overcoming some of the fundamental limitations encountered in early water splitting devices. The photon absorption, water oxidation, proton reduction, and charge separation and transport, are addressed by separate chemical components or materials that can be tailored to meet desired criteria.^[17] A schematic overview of a DS-PEC is provided in Figure 1.1.

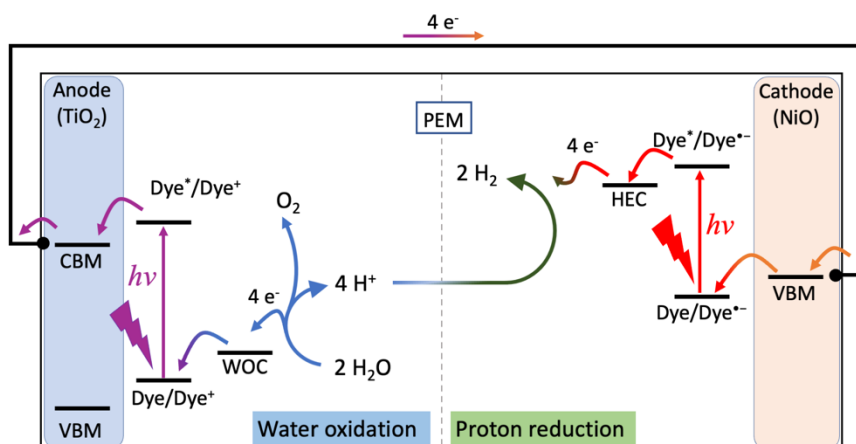


Figure 1.1. Schematic overview of a tandem dye-sensitized photoelectrochemical cell (DS-PEC) for water splitting. Photoexcitation of the dye at the cell's photoanode results in electron injection into the TiO_2 conduction band (CBM stands for conduction band minimum, while VBM stands for valence band maximum) and the resulting hole is used to drive the OER in a water oxidation catalyst (WOC). The obtained protons and electrons are transported to the photocathode through the proton exchange membrane (PEM) and through a conducting medium attached to the TiO_2 , respectively. Excitation of the photocathode dye generates additional reduction potential, which provides a driving force for the hydrogen evolution catalyst (HEC) to produce hydrogen. For

Chapter 1: Introduction

clarity, the energy level heights are depicted schematically; however, the actual water-splitting process requires 1.23 eV under standard conditions ($pH = 0$).

DS-PECs are composed of two compartments separated by a proton-exchange membrane (PEM). These membranes are designed such that they can conduct protons while keeping the produced hydrogen and oxygen separated.^[18] At the cell's photoanode, sunlight is absorbed by a dye molecule (see Figure 1.1, purple photon absorption). Upon photoexcitation, an electron is injected from the excited dye (dye*) into the conduction band (CB) of an *n*-type semiconductor, typically TiO₂. This process leaves an electron hole on the oxidized dye (dye⁺) molecule, which then transfers to a water oxidation catalyst (WOC), where it drives water oxidation. Through four consecutive photoinduced oxidation steps, water is converted into O₂ four protons and a reduction potential in the form of four electrons. The electrons and protons are transferred to the cathode side of the DS-PEC, where they are used to generate hydrogen by a hydrogen evolution catalyst (HEC) or reduce CO₂ to produce carbon-based solar-fuels (Figure 1.1).

Early DS-PEC devices for water splitting employed dark cathodes that do not absorb a second photon to drive the hydrogen evolution reaction (HER). In these cells, solar harvesting is limited to the UV spectrum, and a small additional potential is often required to drive the HER catalysis.^[4,19–21] Tandem DS-PECs overcome these limitations by using dye-sensitized p-type semiconductors. Ideally, the cathode dye absorbs at a higher wavelength than the anode dye, thereby capturing a broader range of the solar spectrum (see Figure 1.1, red photon absorption).

Despite the great potential of DS-PECs, current devices are still severely limited in their photon-to-fuel efficiency. A major reason for this poor performance is the considerable energy loss due to electron-hole recombination after photoexcitation of the dye. To have efficient charge separation at the dye-catalyst interface, the catalyst needs to operate at high turnover frequency with low the chemical

conversion barriers. Additionally, it is critical that the photoexcited dye* injects charge efficiently into the semiconductor surface. Although these topics are active areas of research, mechanistic insights in these photoinduced processes are still limited for many systems.

The aim of this thesis is to gain insights into charge transfer phenomena at dye-semiconductor and dye-catalyst interfaces and to better understand the catalytic mechanisms of specific WOCs and HECs. The coupling between nuclear and electronic motion is a central and common theme. Several chapters of this thesis include experimental collaborations. The important role of molecular dynamics simulations and density functional theory calculations in complementing and clarifying experimental data is evident. The following section provides an outline of this thesis.

1.2 Outline of the thesis

An extensive theoretical background is provided in **Chapter 2** of this dissertation. Starting from the Born-Oppenheimer approximation, the basic principles of molecular dynamics calculations and thermodynamics are explained. The discourse then extends to excited states, and finally density functional theory (DFT) and time-dependent density functional theory (TD-DFT) are discussed.

Chapter 3 investigates the catalytic cycle of a supramolecular [Ru-bda]-dye complex using DFT-based Born-Oppenheimer molecular dynamics. The performed simulations shed light on the equilibrium dynamics of the low-valent Ru^{III}-bda intermediate and further investigate whether this specific Ru-based WOC is efficient also following the water nucleophilic attack mechanism.

Because the proton-coupled electron transfer (PCET) steps that constitute the photocatalytic water oxidation cycle can involve non-adiabatic effects, it is interesting to investigate these reactions while considering several electronically excited states.^[22–24] **Chapter 4** maps out the electronic reactant and product states for two key reaction steps in two supramolecular dye-catalyst complexes. It is shown that these PCET reactions evolve through a reaction path where the two

Chapter 1: Introduction

states get very close in energy and are strongly coupled. Based on these results, a strategy is suggested to dramatically accelerate the PCET processes by optically populating a specific electronic state.

Another challenging aspect of DS-PEC's is that the oxygen evolution reaction (OER) and HER typically proceed in acidic and alkaline conditions, respectively. HER catalysts that perform efficiently at high pH conditions are limited, and known examples rely heavily on rare metals such as platinum.^[25] Therefore, further research into catalysts based on earth-abundant materials that perform well in alkaline media is warranted.^[26,27] **Chapter 5** of this thesis presents a combined theoretical and experimental investigation into photocatalytic hydrogen formation catalyzed by a series of cobalt porphyrin complexes. It was shown that through synthetic modification of the catalyst with electron withdrawing groups, the charge density on the cobalt metal center could be controlled. Interestingly, the catalysts with low electron density on the metal preferred to catalyze the HER via the ligand rather than the metal. In alkaline to neutral conditions, the ligand-based catalysis appears considerably more efficient than the metal-based catalysis, effectively opening a new avenue for HER catalyst design.

As mentioned above, dye-semiconductor interfaces present an important aspect in DS-PEC design. Tandem cells are presently limited by poor hole-conductance of the p-type semiconductor materials. Therefore, insights into the photoinduced hole-injection process, from the dye* into the semiconductor surface, are highly desirable. **Chapter 6** presents a combined theoretical and experimental study into the charge transfer dynamics at the P1/NiO interface, which serves as a benchmark for dye-sensitized photocathodes. Through means of quantum-classical molecular dynamics simulations and transient absorption (TA) spectroscopy, it was shown that the hole-injection dynamics are affected considerably by the thermal nuclear motion of the dye. In addition, two different surface species were identified and tentatively assigned to dye molecules either standing perpendicular or parallel to

the surface. These results provide valuable insights that can inform the design of future DS-PECs.

The idea that electronic and nuclear dynamics are strongly coupled is a recurring theme in this dissertation. While the first chapters show that these coupled dynamics are important in the context of artificial photosynthesis, the importance of this coupling emerges also in vibrationally resolved spectroscopy. Low-temperature spectroscopy of single molecules can provide highly resolved spectra with very sharp 0-0 zero phonon lines (ZPL), up to a few tens of megahertz in width. Recently, it was shown that hexagonal boron nitride (hBN) can be used as a host matrix for fluorescence spectroscopy studies of single-molecules of terrylene.^[28] Interestingly, a fraction of the molecules displayed considerable redshifts in their 0-0 ZPL and showed very weak vibronic coupling. These features, in combination with the very high sensitivity of these fluorescence spectra to the chemical environment of the dye molecule, render the reported terrylene/hBN system promising for applications in quantum technologies and quantum sensing.^[29,30] These promising applications make a deep understanding of the physics behind the observed phenomena highly desirable. **Chapter 7** of this thesis presents a combined theoretical and experimental study of terrylene molecules adsorbed on hBN. It is shown that the redshift of the 0-0 ZPL and the reduced vibronic coupling can be explained by terrylene chemisorption on specific charge donating defect sites in hBN. These insights provide a strategy for the design of material-molecule interfaces which can emit photons with extremely narrow lines at highly specific wavelengths.

Chapter 8 presents an outlook, in which the conclusions of this work are summarized, and future lines of research are suggested. Special emphasis is placed on the systems discussed in chapter 3 and chapter 4 of this thesis. In chapter 4 it was proposed that populating the electronic product state in the studied dye-catalyst complex could accelerate the key catalytic step in the water oxidation cycle. This hypothesis has been further explored through excited state surface-hopping simulations. These simulations show that population of the electronic

Chapter 1: Introduction

product state is indeed accompanied by ultrafast proton transfer, suggesting a promising avenue for increasing the rate of water oxidation in dye-catalyst systems.

1.3 References

- [1] S. A. Bandh, S. Shafi, M. Peerzada, T. Rehman, S. Bashir, S. A. Wani, R. Dar, *Environ. Sci. Pollut. Res.* **2021**, 28, 24872–24888.
- [2] L. Al-Ghussain, *Env. Prog. and Sustain. Energy* **2019**, 38, 13–21.
- [3] K. Calvin, D. Dasgupta, G. Krinner, A. Mukherji, P. W. Thorne, C. Trisos, J. Romero, P. Aldunce, K. Barrett, G. Blanco, *et al.*, *IPCC, 2023: Climate Change 2023: Synthesis Report. Contribution of Working Groups I, II and III to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change [Core Writing Team, H. Lee and J. Romero (Eds.)]. IPCC, Geneva, Switzerland.*, Intergovernmental Panel On Climate Change (IPCC), **2023**.
- [4] A. B. Muñoz-García, I. Benesperi, G. Boschloo, J. J. Concepcion, J. H. Delcamp, E. A. Gibson, G. J. Meyer, M. Pavone, H. Pettersson, A. Hagfeldt, M. Freitag, *Chem. Soc. Rev.* **2021**, 50, 12450–12550.
- [5] N. Rathore, N. L. Panwar, F. Yettou, A. Gama, *Int. J. Ambient Energy* **2021**, 42, 1200–1217.
- [6] R. L. Purchase, H. J. M. De Groot, *Interface Focus* **2015**, 5, 1–16.
- [7] S. Ardo, D. Fernandez Rivas, M. A. Modestino, V. Schulze Greiving, F. F. Abdi, E. Alarcon Llado, V. Artero, K. Ayers, C. Battaglia, J. P. Becker, D. Bederak, A. Berger, F. Buda, E. Chinello, B. Dam, V. Di Palma, T. Edvinsson, K. Fujii, H. Gardeniers, H. Geerlings, S. M. Hashemi, S. Haussener, F. Houle, J. Huskens, B. D. James, K. Konrad, A. Kudo, P. P. Kunturu, D. Lohse, B. Mei, E. L. Miller, G. F. Moore, J. Muller, K. L. Orchard, T. E. Rosser, F. H. Saadi, J. W. Schütttauf, B. Seger, S. W. Sheehan, W. A. Smith, J. Spurgeon, M. H. Tang, R. Van De Krol, P. C. K. Vesborg, P. Westerik, *Energy Environ. Sci.* **2018**, 11, 2768–2783.
- [8] Z. Wang, Y. Hu, S. Zhang, Y. Sun, *Chem. Soc. Rev.* **2022**, 51, 6704–6737.
- [9] A. Fujishima, K. Honda, *Nature* **1972**, 238, 37–38.
- [10] L. Duan, F. Bozoglian, S. Mandal, B. Stewart, T. Privalov, A. Llobet, L. Sun, *Nat. Chem.* **2012**, 4, 418–423.
- [11] B. Zhang, L. Sun, *J. Am. Chem. Soc.* **2019**, 141, 5565–5580.
- [12] P. Garrido-Barros, C. Gimbert-Suriñach, R. Matheu, X. Sala, A. Llobet, *Chem. Soc. Rev.* **2017**, 1, DOI 10.1039/C7CS00248C.
- [13] P. Garrido-Barros, I. Funes-Ardoiz, S. Drouet, J. Benet-Buchholz, F. Maseras, A. Llobet, *J. Am. Chem. Soc.* **2015**, 137, 6758–6761.
- [14] A. Ghaderian, J. Holub, J. Benet-Buchholz, A. Llobet, C. Gimbert-Suriñach, *Inorg. Chem.* **2020**, 59, 4443–4452.
- [15] S. Eberhard, G. Finazzi, F.-A. Wollman, *Annu. Rev. Genet.* **2008**, 42, 463–515.
- [16] A. Stirbet, D. Lazár, Y. Guo, G. Govindjee, *Annals of Botany* **2020**, 126, 511–537.
- [17] M. Grätzel, *Nature*. **2001**, 414, 338–344.
- [18] S. Ahmad, T. Nawaz, A. Ali, M. F. Orhan, A. Samreen, A. M. Kannan, *Int. J. Hydrogen Energy* **2022**, 47, 19086–19131.
- [19] W. J. Youngblood, S.-H. A. Lee, Y. Kobayashi, E. A. Hernandez-Pagan, P. G. Hoertz, T. A. Moore, A. L. Moore, D. Gust, T. E. Mallouk, *J. Am. Chem. Soc.* **2009**, 131, 926–927.
- [20] L. Li, L. Duan, Y. Xu, M. Gorlov, A. Hagfeldt, L. Sun, *Chem. Commun.* **2010**, 46, 7307.
- [21] L. Duan, L. Tong, Y. Xu, L. Sun, *Energy Environ. Sci.* **2011**, 4, 3296.
- [22] B. Auer, A. V. Soudackov, S. Hammes-Schiffer, *J. Phys. Chem. B* **2012**, 116, 7695–7708.
- [23] S. Hammes-Schiffer, *Acc. Chem. Res.* **2001**, 34, 273–281.

- [24] J. Y. Fang, S. Hammes-Schiffer, *J. Chem. Phys.* **1997**, *107*, 5727–5739.
- [25] J. Li, J. Zhang, J. Zhang, K. Pan, H. Xu, H. Chen, G. Liu, N. Wu, C. Yuan, X. Liu, *J. Mater. Chem. A* **2023**, *11*, 19812–19844.
- [26] Y. Sun, J. Sun, J. R. Long, P. Yang, C. J. Chang, *Chem. Sci.* **2013**, *4*, 118–124.
- [27] M. Vennampalli, G. Liang, L. Katta, C. E. Webster, X. Zhao, *Inorg. Chem.* **2014**, *53*, 10094–10100.
- [28] R. Smit, A. Tebyani, J. Hameury, S. J. Van Der Molen, M. Orrit, *Nat. Commun.* **2023**, *14*, 7960.
- [29] S. Faez, S. J. Van Der Molen, M. Orrit, *Phys. Rev. B* **2014**, *90*, 205405.
- [30] C. Toninelli, I. Gerhardt, A. S. Clark, A. Reserbat-Plantey, S. Götzinger, Z. Ristanović, M. Colautti, P. Lombardi, K. D. Major, I. Deperasińska, W. H. Pernice, F. H. L. Koppens, B. Kozankiewicz, A. Gourdon, V. Sandoghdar, M. Orrit, *Nat. Mater.* **2021**, *20*, 1615–1628.

Chapter 2: Theory and Methodology

Molecular simulation methods rely on a broad array of approximations to efficiently describe the dynamics of nuclei and electrons. This chapter provides a brief outline of the methods relevant for this dissertation and discusses advantages and disadvantages of each method.

Chapter 2: Theory and Methodology

2.1 Introduction

The work described in this dissertation hinges on a simple, yet powerful concept: that the complex behavior of a system of interest can be studied by applying the laws of physics on a representative model. This implies that the dynamical behavior and photochemical response of molecules and materials can be predicted from their elementary structure by applying the laws of quantum mechanics. Unfortunately, the quantum mechanical calculations resulting from those laws are associated with a numerical cost that scales exponentially with the system size. Quantum computers hold promise to crack this exponential scaling problem, but for now their hardware is insufficiently developed to be practically useful. Therefore, modern quantum chemistry still relies on a broad range of approximations, and the difficulty in this field often lies in finding a workable compromise between computational efficiency and accuracy.

This chapter provides an introduction into the conceptual frameworks used in this dissertation for studying a range of molecular phenomena. Section 2.2 deals with the quantum-mechanical laws of physics that describe the behavior of electrons and atomic nuclei. Application of these laws results in a recipe to calculate interatomic forces, which can be used to study the dynamics of molecular systems as well as bond formation and breaking. Section 2.3 concentrates on how the equations of motion can be integrated over time, yielding a description of molecular dynamics in the ground state. In Section 2.4, the discourse extends to an electronic excited state situation, which is crucial for capturing the physics of light-induced processes. Section 2.5 deals with extracting thermodynamic properties from molecules in their minimum energy structure. The final section 2.6 goes more in-depth on the electronic structure methods used in this work.

2.2 Electronic structure theory and the Born-Oppenheimer approximation

In this chapter, we assume that the physics relevant for chemistry is described by the non-relativistic, time-dependent Schrödinger equation, which in atomic units ($\hbar = m_e = 4\pi\epsilon_0 = e = 1$) takes the form:

$$\hat{H} \Phi(\mathbf{r}, \mathbf{R}, t) = i \frac{\partial}{\partial t} \Phi(\mathbf{r}, \mathbf{R}, t) \quad (2.1)$$

where i is the imaginary unit, Φ represents a wavefunction that depends on time t and on both electronic coordinates $\mathbf{r}$ and nuclear coordinates $\mathbf{R}$, and $\hat{H}$ is the Hamiltonian describing the system. Note that throughout this dissertation, vectors and matrices are written in bold, and operators are written with a circonflexe (“little hat”). $\mathbf{r}$ and $\mathbf{R}$ thus represent a column vector containing all electronic and nuclear positions, respectively. For chemical purposes, it is sufficient to model the atomic nucleus as a point charge Z_I located at the position $\mathbf{R}_I$. The Hamiltonian for a chemical system with N nuclei and n electrons is thus given by:

Here, M_I and m_i represent the nuclear and electronic masses, respectively. In this

$$\begin{aligned} \hat{H} = & - \sum_{I=1}^N \frac{1}{2M_I} \nabla_{\mathbf{R}_I}^2 - \sum_{i=1}^n \frac{1}{2m_i} \nabla_{\mathbf{r}_i}^2 \\ & + \left[\sum_{i < j}^n \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{I,i}^{N,n} \frac{Z_I}{|\mathbf{R}_I - \mathbf{r}_i|} + \sum_{I < J}^N \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \right]. \end{aligned} \quad (2.2)$$

equation, we can identify in order, the kinetic energy operator for the nuclei, the kinetic energy operator for the electrons and the Coulomb operators for the electron-electron, electron-nuclei and nuclei-nuclei interactions. It is useful to regroup these terms into an electronic Hamiltonian, $\hat{H}_e$, and a nuclear Hamiltonian, $\hat{H}_n$. By convention, this separation is defined such that the nuclear Hamiltonian contains the nuclear kinetic energy operator, while the electronic Hamiltonian contains all the other terms:

$$\hat{H} = - \sum_{I=1}^N \frac{1}{2M_I} \nabla_{\mathbf{R}_I}^2 + \hat{H}_e \quad (2.3)$$

Chapter 2: Theory and Methodology

Using the electronic Hamiltonian, we can also define the electronic wavefunctions $\Psi_i(\mathbf{r}; \mathbf{R})$ as the set of functions that satisfy the following eigenvalue problem, also known as the time-independent electronic Schrödinger equation:

$$\hat{H}_e \Psi_i(\mathbf{r}; \mathbf{R}) = E_i \Psi_i(\mathbf{r}; \mathbf{R}) . \quad (2.4)$$

The eigenfunctions $\Psi_i(\mathbf{r}; \mathbf{R})$ form a complete and orthonormal basis, in which the nuclear dependence is included parametrically. This is convenient because most chemical calculations do not require a full quantum-mechanical description of both nuclei and electrons.

In the work presented in this thesis, the electronic system is treated quantum mechanically, while the atomic nuclei are treated classically. This is generally justifiable, as quantum effects become less prominent for heavier particles. To show that a mixed quantum-classical description can be derived neatly from the above equations, we follow a route proposed by Doltsinis and Marx.^[1] This route also sets up the framework of equations from which we can later derive the surface hopping algorithm proposed by Tully.^[2] The following multiconfigurational ansatz for the wavefunction is proposed:

$$\Phi(\mathbf{r}, \mathbf{R}, t) = \sum_j^{\infty} \Psi_j(\mathbf{r}; \mathbf{R}) X_j(\mathbf{R}, t) . \quad (2.5)$$

This ansatz separates the total wavefunction $\Phi(\mathbf{r}, \mathbf{R}, t)$ into an electronic part, $\Psi_j(\mathbf{r}; \mathbf{R})$, and a nuclear part, $X_j(\mathbf{R}, t)$. The subscript j runs over the electronic basis functions, effectively associating to each electronic basis state a nuclear wavefunction. The solutions to equation (2.4) present a convenient basis for the electronic wavefunction. The nuclear wavefunctions do not need to be orthogonal or normalized. When equation (2.5) is inserted into equation (2.1) we can derive an expression for the time-evolution of $X_i(\mathbf{R}, t)$. By inserting the ansatz, multiplying from the left with $\Psi_i^*(\mathbf{r}; \mathbf{R})$, and subsequently integrating over $\mathbf{r}$, the following equation is obtained for the time-evolution of the nuclei:

$$\begin{aligned}
 i \frac{\partial X_j(\mathbf{R}, t)}{\partial t} = & \left[- \sum_{I=1}^N \frac{1}{2M_I} \nabla_{R_I}^2 + E_j(\mathbf{R}) \right] X_j(\mathbf{R}, t) \\
 & + \sum_i^\infty \left[\sum_I^N \frac{1}{2M_I} D_{ji}^I - \sum_I^N \frac{1}{M_I} d_{ji}^I \nabla_{R_I} \right] X_i(\mathbf{R}, t) \quad (2.6)
 \end{aligned}$$

Note that, subscript i and j run over the electronic state indexes, while I runs over the nuclear particle indexes. E_j represents the matrix element $\langle \Psi_j(\mathbf{r}; \mathbf{R}) | \hat{H}_e | \Psi_j(\mathbf{r}; \mathbf{R}) \rangle$ while d_{ji}^I and D_{ji}^I represent the first and second order non-adiabatic coupling terms, given by:

$$d_{ji}^I = \langle \Psi_j(\mathbf{r}, \mathbf{R}) | \nabla_{R_I} | \Psi_i(\mathbf{r}, \mathbf{R}) \rangle \quad (2.7)$$

and

$$D_{ji}^I = \langle \Psi_j(\mathbf{r}, \mathbf{R}) | \nabla_{R_I}^2 | \Psi_i(\mathbf{r}, \mathbf{R}) \rangle \quad (2.8)$$

The bra-ket notation signifies an integral over the space of all electronic coordinates.^[3] We can simplify equation (2.6) considerably by invoking the adiabatic approximation, which neglects all the non-diagonal terms in d_{ji}^I and all the second order terms D_{ji}^I :

$$i \frac{\partial X_j(\mathbf{R}, t)}{\partial t} = \left[- \sum_{I=1}^N \frac{1}{2M_I} \nabla_{R_I}^2 + E_j(\mathbf{R}) + \sum_{I=1}^N \frac{1}{2M_I} d_{jj}^I \right] X_j(\mathbf{R}, t) \quad (2.9)$$

The Born-Oppenheimer approximation is now recovered by neglecting also the diagonal terms d_{jj}^I :

$$i \frac{\partial X_j(\mathbf{R}, t)}{\partial t} = \left[- \sum_{I=1}^N \frac{1}{2M_I} \nabla_{R_I}^2 + E_j(\mathbf{R}) \right] X_j(\mathbf{R}, t) \quad (2.10)$$

This equation evolves the nuclear wavefunction in an average potential generated by the electronic sub-system, which is quenched to a specific eigenstate of the electronic Hamiltonian E_j . Despite invoking several approximations, equation (2.10) remains prohibitively expensive to solve numerically for most problems

Chapter 2: Theory and Methodology

encountered in chemistry. However, as stated before, in most cases it is reasonable to describe the nuclear motion classically. By assuming classical behavior of the atomic nuclei, equation (2.10) can be rewritten^[1] to yield Newtons equations of motion for the classic nuclei evolving in a quantum mechanical potential generated by the electrons:

$$M_I \frac{d^2}{dt^2} \mathbf{R}_I(t) = -\nabla_I E_j(\mathbf{R}) = \mathbf{F}_I(t) \quad (2.11)$$

Here, E_j is found by solving the eigenvalue equation (2.4). Typically, we are interested in the behavior of a system in the electronic ground state, where $j=0$. Equation (2.11) demonstrates that the time-evolution of the nuclear positions $\mathbf{R}_I$ can be computed using only the gradient of the electronic energy with respect to the nuclei $\nabla_I E_j(\mathbf{R})$. The next section will focus on integrating these equations of motion in an efficient manner.

2.3 Molecular Dynamics and Thermodynamics

One of the most popular algorithms to numerically integrate equations (2.11) is the Velocity Verlet algorithm.^[4] Since the computation of equation (2.4) depends only on the nuclear positions and not on the velocities, the algorithm can be divided in an initiation step followed by a 5 step cycle according to:

1. Initiate the system at t_0 by providing an initial set of nuclear positions $\mathbf{R}_I(t)$ and velocities $\mathbf{v}_I(t)$, and calculate the accelerations $\mathbf{a}_I(t)$ from equation (2.11) as $\mathbf{F}_I(t)/M_I$.

2. Calculate the new positions:

$$\mathbf{R}_I(t + \Delta t) = \mathbf{R}_I(t) + \mathbf{v}_I(t)\Delta t + \frac{1}{2} \mathbf{a}_I(t)\Delta t^2$$

3. With the newly obtained set of positions compute the accelerations at the next time step $\mathbf{a}_I(t + \Delta t)$.
4. Calculate the new velocities:

$$\mathbf{v}_I(t + \Delta t) = \mathbf{v}_I(t) + \frac{1}{2} (\mathbf{a}_I(t) + \mathbf{a}_I(t + \Delta t)) \Delta t$$

5. Set the current time step t to the new time step $t + \Delta t$.
6. If the simulation time exceeds the desired simulation time t_{final} , terminate the simulation. Otherwise, go back to step 2.

After initialization, this algorithm iteratively computes the nuclear positions $\mathbf{R}_I(t + \Delta t)$ at the next time step, $t + \Delta t$, from the nuclear velocities and accelerations at the current time t , until the total simulation time reaches a satisfactory length. Due to its third order numerical precision in Δt and low memory intensity, this algorithm has become the default molecular dynamics (MD) propagator in state-of-the-art computational chemistry codes. A critical parameter for any integration scheme is the time step Δt , which is chosen such that the total energy, *i.e.* the combination of the potential and the kinetic energy in the simulation is conserved. Typically, this means that the shortest oscillation period in the system of interest is described with *ca.* 10 time steps. For a molecular system in the ground state, these oscillations are the vibrations of C-H or O-H bonds, whose characteristic stretching frequencies are properly described with a time step of 0.5 fs. If the time-evolution of the electronic subsystem is considered explicitly, a much shorter time step of 0.01 fs is generally required.^[5]

Despite the numerical robustness of the Velocity Verlet Algorithm, tracing the exact trajectory of a molecular system on longer timescales is impossible. Fortunately, we are interested in the collective properties of a molecular ensemble rather than the precise dynamics of an individual molecule. The basic assumption underpinning all MD simulations is that the ensemble average of an observable in a macroscopic system is equivalent to the time average of this observable in a microscopic system.

The most straightforward way to perform a MD simulation, is to initialize a predefined number of particles in a box with fixed dimensions and start integrating the equations (2.11). Such a simulation at constant volume (V), constant particle number (N), and constant total energy (E) of the system, reproduces the NVE ensemble or microcanonical ensemble. Often, one would like to sample an

Chapter 2: Theory and Methodology

ensemble at thermal equilibrium with an external heat bath, to mimic experimental conditions. This ensemble is referred to as the NVT or canonical ensemble. To achieve this desired phase space distribution, a range of different thermostats have been developed which all try to obey physical constraints such as microscopic reversibility and continuous trajectories without requiring a large computational overhead. Notable examples of commonly applied thermostats are the Nose-Hoover Chain and the Canonical Sampling through Velocity Rescaling thermostats.^[6–8] Besides temperature constraints, performing dynamics simulations at constant pressure by changing the box volume can often be useful. Such isoenthalpic-isobaric (NPH) or isothermal-isobaric (NPT) simulations can be used to achieve a realistic density of molecules in the simulation. Finally, for chemical purposes it is useful to define the grand canonical ensemble with constant chemical potential (μ), volume (V) and temperature (T).

All statistical ensembles are associated with an intrinsic thermodynamic potential, which measures the internal energy change when the system evolves from one microstate to the other. For the NVT ensemble, this property is called the Helmholtz free energy, F , which is defined as:

$$F \equiv U - TS \quad (2.12)$$

where U is the internal energy of the system, T is the temperature and S is the entropy. The probability, p , assigned to a specific microstate in the canonical ensemble is subsequently given by:

$$p(\mathbf{r}^N \mathbf{p}^N) = e^{(F-E)/k_B T} = \frac{1}{Q} e^{-E/k_B T},$$

$$Q = e^{-F/k_B T} = \sum_i e^{-E_i/k_B T} \quad (2.13)$$

where E is the energy associated with the specific microstate of interest, k_B is the Boltzmann constant and Q is the canonical partition function. The index i in the summation runs over all possible microstates of the system within the canonical ensemble and each microstate is associated with a specific energy E_i . These equations show that the Helmholtz free energy intrinsically carries information

about the probability distribution of accessible microstates, while taking entropy effects explicitly into account. This renders NVE ensemble simulations extremely useful for predicting the internal dynamics of (bio-) molecular systems and materials. Equation (2.13) also plays an integral role in enhanced sampling simulations such as Metadynamics, or Blue Moon sampling, which are extensively used in chapter 4 of this thesis.^[9–12] However, going into the details of these enhanced sampling methods is beyond the scope of this introduction. Chemical experiments are typically performed at constant pressure rather than constant volume. Hence, the driving force for chemical reactions is the gradient of the so-called Gibbs Free energy, which is defined as

$$G \equiv U + PV - TS = H - TS, \quad (2.14)$$

in which the pressure P and volume V term, together with the internal energy U sum to the enthalpy H . The main difference with the Helmholtz free energy is thus the inclusion of the PV term, which measures the work related to the volume change associated to the simulated phenomenon. Although this difference can be very important for studying phase transitions or other physical processes, the effect is rather small for most chemical conversions encountered in this thesis. As the critical MD simulations described in this dissertation are performed at constant volume, the terms *Helmholtz* and *Gibbs* free energies are used interchangeably.

A final point to address in this section on MD is how to deal with the finite size effects introduced by the boundaries of the simulation box. An effective way of avoiding finite size effects is to impose periodic boundary conditions (PBC). The idea behind PBC is that a periodic *image* of the unit cell is projected at all edges of the simulation cell, subsequently allowing particles to move through the boundary and re-appear on the other side of the box. Invoking periodic boundary conditions is associated with a neglectable computational cost, since each particle interacts only with the nearest image of all other particles in the system.

2.4 Excited States and Non-Adiabatic Dynamics

The previous discussion has focused on describing the nuclear dynamics of a molecular system in the electronic ground state. These simulations are interesting for a wide range of applications ranging from computation of thermodynamic quantities to probing the dynamics of ground state chemical reactions. However, in the context of solar-fuel production it is critical to investigate electronically excited states and explicitly calculate the coupling between nuclear and electronic degrees of freedom.

To describe excited state phenomena, we need to follow the time-evolution of the wavefunction as dictated by equation (2.1). The time-evolution of the electronic wavefunction is typically computed in terms of time-dependent wavefunction coefficients $c_i(t)$, in a basis of adiabatic eigenstates of the electronic Hamiltonian:

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_i c_i(t) \Psi_i(\mathbf{r}; \mathbf{R}; t), \quad (2.15)$$

where $\Psi_i(\mathbf{r}; \mathbf{R}; t)$ are the eigenfunctions obtained from solving equation (2.4), and include a parametric time-dependence to account for the changing nuclear positions.^[13] By inserting equation (2.15) into equation (2.1) and multiplying from the left by $\Psi_j^*(\mathbf{r}; \mathbf{R}; t)$ we obtain:

$$\frac{\partial}{\partial t} c_j(t) = - \sum_i [iH_{ji} + T_{ji}] c_i, \quad (2.16)$$

where T_{ji} is the time-derivative coupling, calculated as $T_{ji} = \mathbf{v} \cdot \mathbf{d}_{ji}$, in which $\mathbf{v}$ collects all the nuclear velocities and $\mathbf{d}_{ji}$ is now a column vector containing the non-adiabatic coupling contributions for all nuclear coordinates (see equation (7)). In practice, the quantum chemistry method of choice can affect the nature of the basis states $\Psi_i(\mathbf{r}; \mathbf{R}; t)$ and the computation of $\mathbf{d}_{ji}$. For Time-Dependent DFT based approaches (see section 2.6.2), the basis states are generally not adiabatic, and the non-adiabatic couplings are either numerically intensive or analytically difficult to obtain. Therefore, the work discussed in this dissertation relies on a propagation scheme in which the eigen basis is obtained by diagonalizing the

Hamiltonian matrix at each time step, and the wavefunction coefficients are propagated based on the overlap matrix between subsequent time steps.^[14,15]

Now that we have established a practical approach to evolve the quantum mechanical wavefunction coefficients for the electronic subsystem, the classical propagation of the nuclear coordinates can be discussed. One of the easiest approaches is to completely ignore electronic structure effects on the nuclear motion and simply evolve the nuclei on a potential energy surface generated by a single electronic eigenstate as described by equation (2.11). This approach is justifiable if the electronic motion is very fast compared to the nuclear response or if the nuclear response is generally negligible. Such scenarios are often encountered when studying interfacial electron or hole transfer processes in dye-semiconductor heterostructures. In Chapter 6 of this dissertation such a study is presented.

In many cases the nuclear response to the electronic wavefunction change cannot be ignored and needs to be considered explicitly. The main assumption in the Born-Oppenheimer approximation is that the classical motion of the nuclear subsystem is subject exclusively to a single potential energy surface generated by a single quantum mechanical electronic eigenstate $|j\rangle$. The main challenge thus lies in addressing situations where multiple electronic eigenstates contribute to the electronic wavefunction simultaneously. Historically, two approaches have been proposed to solve this problem. In the first approach, an averaged potential energy surface is defined in which all considered electronic states contribute according to their electronic wavefunction coefficient. This mean-field approach is referred to as the Ehrenfest method and captures the coherent motion between the nuclei and electrons naturally, while preserving a normalized wavefunction.^[16] However, the mean-field character of this approach renders it impossible to describe trajectory-branching that occurs due to different trajectories being subject to different quantum states. This is specifically relevant when one is interested in a low probability channel that will never be accessed with the mean-field approach.^[17]

Chapter 2: Theory and Methodology

With this issue in mind, John C. Tully developed an alternative method for simulating excited state molecular dynamics, which is now known as Fewest Switches Surface Hopping (FSSH).^[2] The idea behind his approach is that instead of propagating a single trajectory on an averaged potential energy surface, an ensemble of trajectories is propagated on potential energy surfaces belonging to specific electronic eigenstates. The trick is to allow trajectories to “hop” between surfaces, based on a stochastic algorithm. In this way the population of trajectories subject to a specific quantum state remains approximately equal to the wavefunction amplitude associated with that state. Trajectories are allowed to switch to any coupled state at any point during the simulations, and the switching probability is governed by the quantum probabilities. The switching probability g_{ij} , for a trajectory to switch from state i to state j is calculated as:

$$g_{ij} = \frac{\Delta\tau [2 \operatorname{Im}(c_j^* c_i H_{ji}) - 2 \operatorname{Re}(c_j^* c_i \mathbf{R} \cdot \mathbf{d}_{ji})]}{c_j c_j^*}. \quad (2.17)$$

where $\Delta\tau$ is the time step at which the electronic subsystem is propagated. In most surface hopping implementations, the electronic subsystem is propagated with a time step at least one order of magnitude smaller than the classical time step Δt . For a trajectory in active state $|\lambda\rangle$, the hopping probabilities $g_{\lambda j}$ are calculated at each quantum time step $\Delta\tau$. Transition probabilities lower than zero are set to zero. This minimizes the number of hops, hence *Fewest Switches*. Subsequently, a random number ζ is drawn between 0 and 1. At each quantum time step, the following equation is evaluated for all states $|k\rangle$:

$$\sum_{j=1}^{k-1} g_{\lambda j} < \zeta < \sum_{j=1}^k g_{\lambda j} \quad (2.18)$$

If the equation holds for any state $|k\rangle$, then a hop to potential energy surface E_k is attempted at the next classical time step. Once a state is found for which equation (2.18) is satisfied, no further hopping attempts are undertaken until the new time step $t + \Delta t$ is reached. Figure 2.1 presents a schematic overview of the FSSH algorithm.

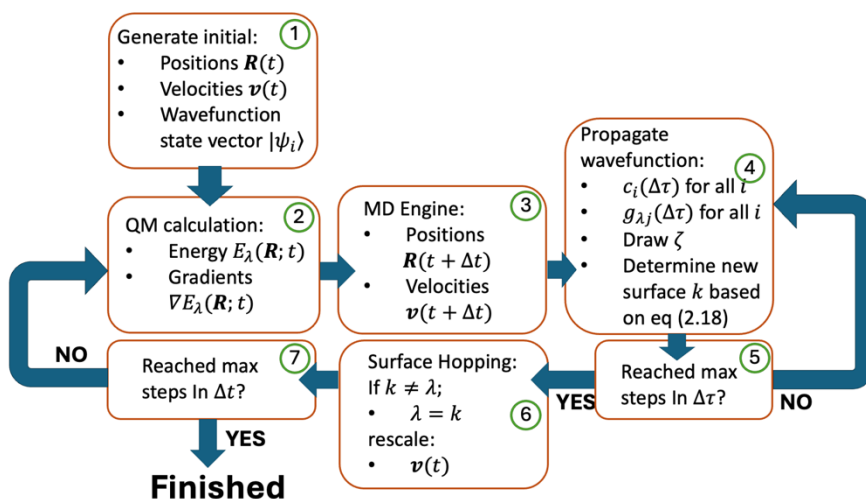


Figure 2.1. Schematic overview of the typical FSSH algorithm.

Analogous to ground state MD simulations, the first step in a FSSH simulation requires generating a set of initial positions and velocities. Additionally, FSSH also requires preparation of an initial electronic state vector. Here one may choose to initiate the wavefunction in a specific electronic eigenstate, or one can calculate explicitly the wavefunction coefficients based on the interaction of a molecule with an external electromagnetic field. Steps 2 and 3 in Figure 2.1 do not deviate from a normal MD scheme, except for the fact that the energies and gradients are not only calculated for the ground state but also for one or more excited states. The exact number of required gradients depends on the decoherence correction schemes.^[18] In step 4, the newly obtained positions and velocities are used to evolve the electronic wavefunction. At each new sub-time step $\tau + \Delta\tau$, the hopping probabilities to all states are evaluated using equation (2.17). Then, a random number ζ is drawn, and the label k is saved for which equation (2.18) holds. A hop to the new state is invoked in step 6, after the electronic wavefunction propagation is finished. The change in potential energy in the system is adjusted for by scaling the nuclear velocities such that the sum of potential and kinetic energies remains constant. Finally, the trajectory is truncated after a desired

Chapter 2: Theory and Methodology

simulation time has been reached, or the algorithm goes back to step 2.

One of the most prominent issues with the FSSH is that the coherences between different electronic eigenstates are insufficiently damped. Because the nuclear motion is subject only to a single electronic energy surface, wavefunction branching due to diverging nuclear trajectories is not captured. In the past three decades a range of hopping algorithms have been derived which try to address this issue.^[18–20] Recently, a pedagogical paper on FSSH was published that discusses the issue of decoherence in an intuitive manner.^[21]

2.5 Obtaining Thermodynamic Properties from Static Calculations

Although molecular dynamics is an elegant way of including solvent and entropy effects explicitly into the computational study of chemical reactions, the associated computational cost is often a limiting factor when high accuracy in the interatomic potentials is required. In such cases it is common practice to consider only the molecule of interest in its minimal potential energy structure without explicit solvent molecules. The assumption is that the potential energy minimum is representative for the average structure of the molecule, which in many cases is reasonable especially for relatively rigid systems. Solvent and thermodynamic effects can subsequently be added a posteriori using a few simple approximations. The internal energy U can be approximated as the sum of the electronic energy E_{scf} and the nuclear internal energy E_{NI} , which in turn is partitioned in translational, rotational and vibrational contributions. The first two contributions can easily be shown to amount to $\frac{3}{2} k_{\text{B}}T$, where each translational and rotational degree of freedom contributes $\frac{1}{2} k_{\text{B}}T$. The vibrational zero-point energy is

$$E_{\text{ZP}} = R \sum_j^{3N-6} v_j \left(\frac{1}{2} + \frac{1}{(e^{v_j/T} - 1)} \right), \quad (2.19)$$

where v_j is the angular frequency of the j 'th eigenmode, $3N - 6$ is the number of vibrational modes for a non-linear molecule and R is the gas constant.^[22] The

internal vibrations are calculated as the eigenvectors of the Hessian within the harmonic approximation. The vibrational entropy is calculated as:

$$S_v = R \sum_j^{3N-6} \left[\frac{v_j/T}{(e^{v_j/T} - 1)} - \ln(1 - e^{-v_j/T}) \right], \quad (2.20)$$

where the low frequency modes are often scaled down to reduce numerical noise which may become large due to the first term on the right hand side of the equation.^[23,24] In addition, small corrections might be imposed to account for thermal occupation of vibrational excited states. Finally, the PV contribution in equation (2.14) can be approximated by the ideal gas law, *i.e.* $PV = NRT$. Solvent corrections may be calculated completely a posteriori or may be considered during the geometry optimization and frequency calculations. However, the studies in this dissertation, and specifically chapter 5, use optimizations in the gas phase. Therefore, the solvation term, ΔG_{solv}^0 , covers the solvation energy associated with moving from the gas phase to the solution phase. This term is calculated with implicit continuous solvation models such as COSMO, or SMD.^[25–27] The Gibbs free energy of a molecule in solution, $G^0(\text{solv})$, is calculated as:

$$G^0(\text{solv}) = E_{\text{scf}}(\text{gas}) + E_{\text{NI}}(\text{gas}) - TS(\text{gas}) + \Delta G_{\text{solv}}^0 + \Delta G^{0/*} \quad (2.21)$$

Here, the $E_{\text{scf}}(\text{gas})$ contribution is taken as the energy obtained from the electronic structure theory calculation and the $E_{\text{NI}}(\text{gas})$ variable is the sum of the E_{ZP} , translational and rotational internal energy contributions. The $\Delta G^{0/*}$ contribution quantifies the Gibbs free energy difference related to changing from standard state conditions (1 Atm in the gas phase) to the desired concentration in solution. For a chemical reaction in solution, this term is calculated as:

$$\Delta G^{0/*} = RT \ln(24.46 * [\text{molecule}]) \quad (2.22)$$

where $[\text{molecule}]$ is the molecular concentration.^[28] Having the flexibility to easily take into account concentration differences is a big advantage of this *static* approach, especially when dealing with reactions that are driven by Chatelier's principle such as ligands that coordinate to metal complexes or protonation

Chapter 2: Theory and Methodology

reactions. However, disadvantages of the static approach arise when the solvent interactions need to be sampled explicitly or when anharmonic terms dominate the vibrational spectrum.

2.6 Electronic Structure Methods

2.6.1 Density Functional Theory

The previous sections have focused on describing the mixed quantum-classical dynamics of atomic nuclei on the electronic potential energy surfaces, without explicitly addressing how the stationary Schrödinger equation is solved. We now shift our attention to finding solutions to the electronic structure problem stated in equation (2.4). In the past three decades, density functional theory (DFT) has established itself as the workhorse of quantum chemical calculations, because of its reasonable accuracy and limited numerical cost. Given the wealth of books and review papers available on the theory and application of DFT, we will focus here strictly on the fundamental concepts.^[29–32]

The foundation for DFT was laid in 1964 by Hohenberg and Kohn,^[33] who showed that the ground state energy of an inhomogeneous interacting electron gas, subject to an external potential $v(\mathbf{r})$,

$$E[\rho] = \int_{\mathbb{R}^3} d\mathbf{r} v(\mathbf{r})\rho(\mathbf{r}) + \frac{1}{2} \int_{\mathbb{R}^3} d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + G[\rho], \quad (2.23)$$

is a unique functional of the electronic density $\rho(\mathbf{r})$. Here, $\mathbb{R}^3$ signifies the integral over all real space. The first term in this equation covers the interaction of the electronic system with the external potential, while the second term represents the coulomb energy. The functional $G[\rho]$ is defined as the difference between the exact density functional and the first two terms. It is important to note that $G[\rho]$ depends uniquely on the density ρ and not on the external potential $v(\mathbf{r})$. Hohenberg and Kohn demonstrated that inserting the true electron density $\rho(\mathbf{r})$ into equation (2.23) yields an absolute minimum for $E[\rho]$, corresponding to the system's ground state. This implies that the ground state energy E_{GS} can be found

by minimization of the energy functional with respect to the density

$$E_{\text{GS}} = \min_{\rho} E[\rho] , \quad (2.24)$$

subject to the constraint that the total density integral is conserved, thus ensuring conservation of particle number. Soon after publication of the Hohenberg Kohn theorem, Kohn and Sham introduced a practical approximation to $G[\rho]$, which allowed them to derive a set of self-consistent equations that can be used to perform calculations on chemically relevant systems.^[34] They first separated $G[\rho]$ into two parts:

$$G[\rho] \equiv T_s[\rho] + E_{\text{xc}}[\rho] \quad (2.25)$$

where $T_s[\rho]$ represents the electronic kinetic energy and $E_{\text{xc}}[\rho]$ represents the so-called exchange-correlation (XC) functional. The key insight now lies in recognizing that the true electron density of the system can be expressed in terms of a set of fictitious non-interacting electrons. The density of this fictitious system is described as a sum of squared single-particle wavefunctions according to

$$\rho(\mathbf{r}) = 2 \sum_{i=1}^{n/2} |\varphi_i(\mathbf{r})|^2 . \quad (2.26)$$

Here n is the number of electrons and the factor 2 accounts for the double occupancy of each spatial orbital $\varphi_i(\mathbf{r})$, assuming a closed shell spin configuration. The single-particle spatial orbitals are constrained to remain orthonormal. Equation (2.26) simplifies the evaluation of the electronic kinetic energy functional, allowing equation (2.23) to be written as

$$\begin{aligned} E[\rho] = & \int_{\mathbb{R}^3} d\mathbf{r} v(\mathbf{r})\rho(\mathbf{r}) + \frac{1}{2} \int_{\mathbb{R}^3} d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\ & + 2 \sum_{i=1}^{N/2} \left\langle \varphi_i(\mathbf{r}) \left| -\frac{1}{2} \nabla^2 \right| \varphi_i(\mathbf{r}) \right\rangle + E_{\text{xc}}[\rho] . \end{aligned} \quad (2.27)$$

Kohn and Sham showed that, by minimizing this functional with respect to the density, one can obtain a set of single particle eigenvalue equations

Chapter 2: Theory and Methodology

$$\left\{ -\frac{1}{2}\nabla^2 + v(\mathbf{r}) + \int_{\mathbb{R}^3} \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{\text{xc}}(\mathbf{r}) \right\} \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r}) \quad (2.28)$$

that can be solved in a self-consistent manner. The $v_{\text{xc}}(\mathbf{r}) = \delta(E_{\text{xc}}(\mathbf{r}))/\delta\rho$ is the XC potential, and the ε_i are the Kohn-Sham energy eigenvalues. In theory, equation (2.28) is exact within the Born-Oppenheimer approximation. However, in practice the exact XC potential for any practically useful system is unknown. Finding numerically tractable and physically accurate approximations to $v_{\text{xc}}(\mathbf{r})$ is an active research area and a very large number of functionals have been proposed.^[35]

The first XC functional, introduced by Kohn and Sham in their seminal paper, is now known as the Local Density Approximation (LDA).^[34] They derived the exact functional for the XC energy of a uniform electron gas (UEG) and used this functional to approximate the XC energy density of the inhomogeneous system under study. The XC energy with the LDA approximation is thus calculated as

$$E_{\text{xc}}^{\text{LDA}}[\rho] = \int_{\mathbb{R}^3} e_{\text{xc}}^{\text{UEG}}(\rho(\mathbf{r})) \rho(\mathbf{r}) d\mathbf{r}, \quad (2.29)$$

where $e_{\text{xc}}^{\text{UEG}}(\rho)$ is a functional that returns for any given density the energy per particle of the UEG with that density.

Although the LDA approximation yields reasonable results for specific problems in solid state physics, it is generally not accurate enough to study properties of molecular systems. A considerable improvement over LDA-DFT can be achieved with generalized gradient approximations (GGA) that consider explicitly the local gradient of the electron density. Later, meta-GGA functionals have been proposed that account also for the Laplacian of the density and hybrid-functionals were developed that incorporate an empirically determined fraction of exact Hartree-Fock exchange (HFX) into the XC potential. While GGA-functionals are generally effective at producing accurate bonding energies and molecular structures, they suffer from a large delocalization error due to self-interaction of

the electronic density.^[36] Consequently, transition states and band gaps are underestimated and charge tends to be over-delocalized. Chapter 4 of this dissertation assesses how the inclusion of HFX affects the localization of spin densities in DFT-based MD simulations of a supramolecular water oxidation catalyst-dye complex.

2.6.2 Time-Dependent Density Functional Theory

The Hohenberg-Kohn theorem proves that the external potential $v(\mathbf{r})$ uniquely determines the ground state electron density distribution $\rho(\mathbf{r})$ of a many-body system, and that the ground state wavefunction is a unique functional of $\rho(\mathbf{r})$.^[33] This implies that any ground state property of interest can be calculated as a functional of the ground state density. However, as mentioned before, we are also interested in properties of molecules in electronically excited states. In 1984, Runge and Gross demonstrated that a similar unique mapping exists between the time-dependent density of a many-body system subject to a time-dependent potential $v(\mathbf{r}, t)$.^[37] This theory provides a formal basis extending the application of DFT to the calculation of excited state properties, and nowadays, linear response time-dependent DFT (LR-TDDFT) has become one of the most popular methods of choice to calculate optical properties in molecules.^[38] The main idea is to calculate the first order density response $\delta\rho$ to a small change in $v(\mathbf{r}, t)$ in a basis of fully converged ground state Kohn-Sham orbitals. A more elaborate derivation of LR-TDDFT can be found in literature.^[39] As we are interested in excitation energies, the response function is calculated in the frequency (ω) domain:

$$\delta\rho(\mathbf{r}, \omega) = \int_{\mathbb{R}^3} \chi(\mathbf{r}, \mathbf{r}'; \omega) \delta v_{\text{eff}}(\mathbf{r}', \omega) d\mathbf{r}'. \quad (2.30)$$

Here, $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ is the response function, which can be expressed in terms of occupied (φ_i) and virtual (φ_a) Kohn-Sham orbitals and energy eigenvalues:

Chapter 2: Theory and Methodology

$$\chi(\mathbf{r}, \mathbf{r}'; \omega) = \sum_{i=1}^{\frac{n}{2}} \sum_{a=1}^{\frac{m}{2}} 2 \frac{\omega_{ai}}{\omega - \omega_{ai}} \varphi_i(\mathbf{r}) \varphi_{ja}(\mathbf{r}) \varphi_i(\mathbf{r}') \varphi_{ja}(\mathbf{r}'), \quad (2.31)$$

where n is the number of occupied spatial orbitals, m the number of empty spatial orbitals, and $\omega_{ai} \equiv \varepsilon_a - \varepsilon_i$ is the difference of Kohn-Sham energies between state i and a . The perturbation in the effective potential is

$$\begin{aligned} \delta v_{\text{eff}}(\mathbf{r}', \omega) = & \delta v(\mathbf{r}, \omega) + \int_{\mathbb{R}^3} \frac{\delta \rho(\mathbf{r}', \omega)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \\ & + \int_{\mathbb{R}^3} \delta f_{\text{xc}}(\mathbf{r}, \mathbf{r}'; \omega) \delta \rho(\mathbf{r}, \omega) d\mathbf{r}'. \end{aligned} \quad (2.32)$$

The first and second term on the right-hand side of the equation represent the perturbation in the external potential and the electronic density, respectively. The third term contains the time-dependent XC kernel

$$\delta f_{\text{xc}}(\mathbf{r}, \mathbf{r}'; \omega) = \left. \frac{\delta v_{\text{xc}}(\mathbf{r}, \omega)}{\delta \rho(\mathbf{r}', \omega)} \right|_{\rho=\rho_0}. \quad (2.33)$$

Here the functional derivative is taken with respect to the ground state density. Analogous to the XC potential in ground state DFT, the XC kernel in linear response TDDFT needs to be approximated. In practice, the Adiabatic Local Density Approximation (ALDA) is commonly applied, and it is also the approximation of choice in this dissertation.^[40]

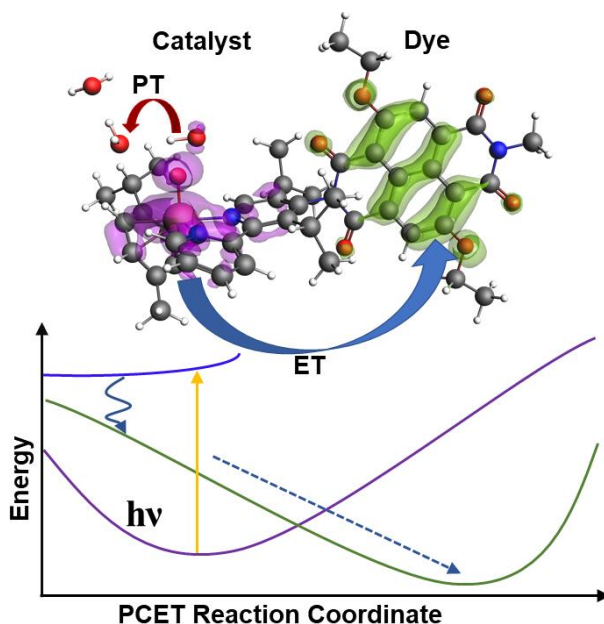
2.7 References

- [1] N. L. Doltsinis, D. Marx, *J. Theor. Comput. Chem.* **2002**, 01, 319–349.
- [2] J. C. Tully, *J. Chem. Phys.* **1990**, 93, 1061–1071.
- [3] P. A. M. Dirac, *Math. Proc. Camb. Phil. Soc.* **1939**, 35, 416–418.
- [4] W. C. Swope, H. C. Andersen, P. H. Berens, K. R. Wilson, *J. Chem. Phys.* **1982**, 76, 637–649.
- [5] A. Torres, R. S. Oliboni, L. G. C. Rego, *J. Phys. Chem. Lett.* **2015**.
- [6] S. Nosé, *J. Chem. Phys.* **1984**, 81, 511–519.
- [7] W. G. Hoover, *Phys. Rev. A* **1985**, 31, 1695–1697.
- [8] G. Bussi, D. Donadio, M. Parrinello, *J. Chem. Phys.* **2007**, 126, 014101.
- [9] A. Laio, F. L. Gervasio, *Rep. Prog. Phys.* **2008**, 71, 12660.
- [10] A. Barducci, M. Bonomi, M. Parrinello, *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2011**, 1, 826–843.
- [11] G. Bussi, A. Laio, *Nat. Rev. Phys.* **2020**, 2, 200–212.
- [12] G. Ciccotti, M. Ferrario, *Mol. Simul.* **2004**, 30, 787–793.

- [13] S. Mai, P. Marquetand, L. González, *WIREs Comput Mol Sci.* **2018**, *8*, e1370.
- [14] S. Mai, P. Marquetand, L. González, *Int. J. Quantum Chem.* **2015**, *115*, 1215–1231.
- [15] G. Granucci, M. Persico, A. Toniolo, *J. Chem. Phys.* **2001**, *114*, 10608–10615.
- [16] S. Choi, J. Vaníček, *J. Chem. Phys.* **2021**, *155*, 124104.
- [17] J. C. Tully, *Faraday Discuss.* **1998**, *110*, 407–419.
- [18] A. Jain, E. Alguire, J. E. Subotnik, *J. Chem. Theory Comput.* **2016**, *12*, 5256–5268.
- [19] H. M. Jaeger, S. Fischer, O. V. Prezhdo, *J. Chem. Phys.* **2012**, *137*, 22A545.
- [20] J. E. Subotnik, N. Shenvi, *J. Chem. Phys.* **2011**, *134*, 30–45.
- [21] A. Jain, A. Sindhu, *ACS Omega* **2022**, *7*, 45810–45824.
- [22] J. W. Ochterski, “Thermochemistry in Gaussian”, 2000, Gaussian, Inc., 1-19, June 2, 2000.
- [23] S. Grimme, *Chem. - Eur. J.* **2012**, *18*, 9955–9964.
- [24] Y.-P. Li, J. Gomes, S. Mallikarjun Sharada, A. T. Bell, M. Head-Gordon, *J. Phys. Chem. C* **2015**, *119*, 1840–1850.
- [25] A. Klamt, *J. Phys. Chem.* **1995**, *99*, 2224–2235.
- [26] A. Klamt, V. Jonas, *J. Chem. Phys.* **1996**, *105*, 9972–9981.
- [27] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2009**, *113*, 6378–6396.
- [28] C. P. Kelly, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2006**, *110*, 16066–16081.
- [29] E. Cancès, G. Friesecke, Eds., *Density Functional Theory: Modeling, Mathematical Analysis, Computational Methods, and Applications*, Springer International Publishing, Cham, **2023**.
- [30] N. Argaman, G. Makov, *Am. J. Phys.* **2000**, *68*, 69–79.
- [31] R. Car, *Quant. Struct.-Act.Relat.* **2002**, *21*, 97–104.
- [32] M. Orio, D. A. Pantazis, F. Neese, *Photosynth. Res.* **2009**, *102*, 443–453.
- [33] P. Hohenberg, W. Kohn, *Phys. Rev.* **1964**, *136*, B864–B871.
- [34] W. Kohn, L. J. Sham, *Phys. Rev.* **1965**, *140*, A1133–A1138.
- [35] N. Mardirossian, M. Head-Gordon, *Mol. Phys.* **2017**, *115*, 2315–2372.
- [36] K. R. Bryenton, A. A. Adeleke, S. G. Dale, E. R. Johnson, *WIREs Comput. Mol. Sci.* **2023**, *13*, e1631.
- [37] E. Runge, E. K. U. Gross, *Phys. Rev. Lett.* **1984**, *52*, 997–1000.
- [38] C. Adamo, D. Jacquemin, *Chem. Soc. Rev.* **2013**, *42*, 845–856.
- [39] C. A. Ullrich, *Time-Dependent Density-Functional Theory: Concepts and Applications*, Oxford University Press, **2011**.
- [40] S. J. A. Van Gisbergen, J. G. Snijders, E. J. Baerends, *J. Chem. Phys.* **1995**, *103*, 9347–9354.

Chapter 3: Strategies to Enhance the Rate of Proton-Coupled Electron Transfer Reactions in Dye-Water Oxidation Catalyst Complexes

Excited state calculations on two supramolecular catalyst-dye complexes for water oxidation reveal an avoided crossing in the region of the transition state for the rate-limiting proton coupled electron transfer steps. Two strategies are discussed to exploit this excited state energy landscape to accelerate the water splitting process.



This chapter is based on:

T. de Haas, H. van Overeem, H.J.M. de Groot, F. Buda. Strategies to Enhance the Rate of Proton-Coupled Electron Transfer Reactions in Dye-Water Oxidation Catalyst Complexes. *ChemPhotoChem* **2023**, e202200274.

Chapter 3: Strategies to Enhance the Rate of Proton-Coupled Electron Transfer Reactions in Dye-Water Oxidation Catalyst Complexes

3.1 Abstract

A thorough understanding of the Proton Coupled Electron Transfer (PCET) steps that are involved in photocatalytic water oxidation is of crucial importance to increase the efficiency of dye-sensitized photoelectrochemical cells (DS-PEC) for solar to fuel conversion. This work provides a computational investigation of the ground and excited state potential energy surfaces of PCET reactions in two supramolecular dye-catalyst complexes for photocatalytic water splitting. The Intrinsic Reaction Coordinate path is computed for the rate limiting PCET step in the catalytic cycle for both complexes. Using time-dependent density functional theory calculations, it is shown that the ground and excited state potential energy surfaces have a near-degeneracy in the region of the PCET transition state. We discuss two possible strategies that take advantage of this feature to accelerate the PCET reaction: (i) through optimizing the conditions for vibronic coupling by chemical design and synthesis or (ii) through populating the product state with appropriately tuned laser pulses.

3.2 Introduction

The increase of carbon dioxide levels in the earth's atmosphere, a by-product of the combustion process of fossil fuels, has shown to be one of the driving forces behind global warming. To reduce the fierce consequences of climate change, the world has to turn entirely to environmentally benign resources of energy within the next three decades.^[1] Dye-Sensitized Photoelectrochemical Cells (DS-PECs) are a promising instrument to contribute to the transition towards net zero carbon emissions.^[2] These devices harness the technology to convert solar-light and water directly into hydrogen gas by integrating the photovoltaic (PV) and electrochemical process in a single cell, thereby reducing overpotential and current losses of a decentralized PV and electrocatalytic process.^[3,4] At the heart of a DS-PEC device lays the process of photo-induced water oxidation. In this sunlight-driven catalytic reaction, two water molecules are converted into molecular oxygen, four protons and four electrons in a series of four Proton Coupled Electron Transfer (PCET) steps. Each PCET step is initiated by photoinduced electron transfer from a light-absorbing dye to an anode, usually TiO₂. Subsequently, bidirectional PCET takes place at the Water Oxidation Catalyst (WOC), where the electron moves to the dye and the proton transfers to the water environment.

In the recent decades substantial progress has been made in the development of catalysts that can facilitate the water splitting reaction.^[5-7] Generally, two classes of WOC's can be distinguished^[8], WOC's that operate via the mononuclear Water Nucleophilic Attack (WNA) pathway^[9-12] and WOC's that operate via the binuclear interaction of two metal centers (I2M) pathway.^[13-17] In the WNA mechanism, the rate determining (PCET) step is the nucleophilic attack of a solvent water molecule on the metal-oxo species at the centre of the catalyst and simultaneous O-H dissociation to form a high-energy peroxo-intermediate and a hydronium ion. In the I2M mechanism, the formation of this intermediate is circumvented by forming the O-O bond directly from two metal-oxo species in an intermolecular fashion.^[18,19] Although remarkable turnover frequencies have been

Chapter 3: Strategies to Enhance the Rate of Proton-Coupled Electron Transfer Reactions in Dye-Water Oxidation Catalyst Complexes

reported with WOC's that work via I2M,^[13,14] it remains questionable whether this type of mechanism would still apply once the molecular catalyst is immobilized on a surface in a DS-PEC device. Therefore, also research into the optimization of the WNA mechanism is important.

Often, PCET reactions can proceed over a non-adiabatic path, coupling reactant and product adiabatic electronic states.^[20–23] Inclusion of vibronically excited states in calculations is critical for recovering experimental data from computations.^[24] Earlier studies in our group have shown that nuclear modes that are resonant with electronic motion can enhance non-adiabatic coupling between the reactant and product states, opening a channel between such states for deterministic charge transfer at high yield, beyond adiabatic practices where yields are limited by back reaction and recombination losses.^[3] In order to engineer systems for artificial photosynthesis with a near unity quantum yield, taking into account properly the interplay between nuclear and electronic motion will thus be of crucial importance. In a recent study from our group, it was shown that vibronic coupling plays a central role in the rate limiting O-O bond forming PCET step in a WOC-dye complex.^[25,26] In particular, it was shown that a specific torsional motion was coupled to the electron transfer (ET) process. Through rational functionalization of the catalyst ligand backbone, the characteristic frequencies associated with this mode were tuned to achieve faster charge transfer. Interesting advances have been made in exploiting non-adiabatic decay pathways to trigger PCET events.^[27–31] Recently, Schlenkler et al. showed that PCET between trianisoheptazine and a series of phenol-derivatives can selectively be controlled by irradiating the complex in solution with laser pulses.^[32] The driving force for this reaction is the result of the intermolecular charge transfer excitation from the phenol to the heptazine core. Ab initio non-adiabatic molecular dynamics (AIMD) simulations indicate that a H-atom can be extracted from water using laser irradiation with the trianisoheptazine complex.^[33] Although this type of hydrogen atom abstraction (HAT) mechanism is different from the bidirectional

PCET steps that take place in water-oxidation, it represents a new paradigm in reactivity with promise for solar fuel production.

The challenge is now to design artificial photosynthesis systems that can optimally exploit these non-adiabatic phenomena for PCET reactions. With this goal in mind, we have computationally explored the ground and excited state potential energy surfaces for different catalyst-dye models for photocatalytic water oxidation.

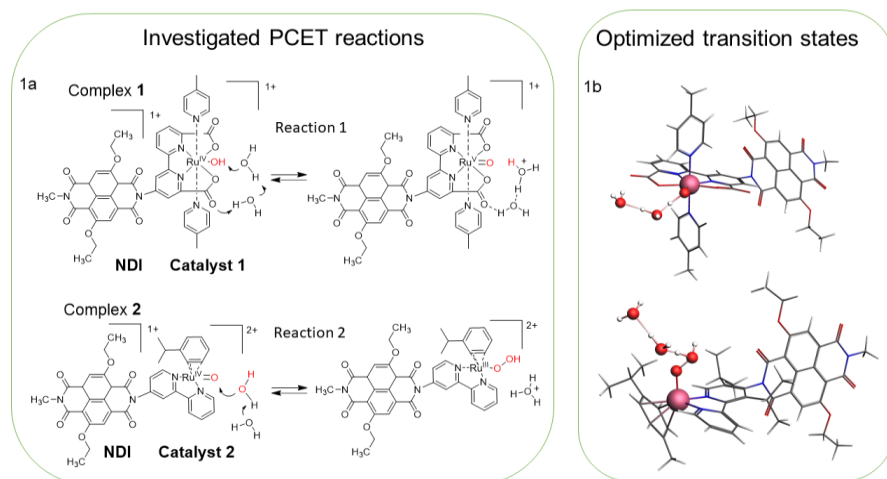


Figure 3.1. A schematic depiction of the investigated reaction steps for complex 1 (**1**) and complex 2 (**2**) are provided in (a). Earlier work has shown that these two reaction steps are thermodynamically the most demanding steps in the water oxidation cycle for these two catalysts.^[25,34] The local charge on the WOC, dye and proton accepting water molecule are also indicated. For both complexes the overall charge is conserved over the reaction, but locally a plus charge moves from the NDI to the excess solvated proton. (b) Shows the optimized transition states for **1** and **2**. The transition state structures clearly show the formation of a hydrogen bonded water molecules chain to distribute the excess charge.

The general outline of this chapter is as follows: In the first section, the generation of the PCET reaction path using the Intrinsic Reaction Coordinate (IRC)^[35,36]

Chapter 3: Strategies to Enhance the Rate of Proton-Coupled Electron Transfer Reactions in Dye-Water Oxidation Catalyst Complexes

method is discussed. Then, it is demonstrated that the electron and hole transfer along the obtained reaction path can be followed by plotting the spin-density. In the subsequent section the excited state potential energy surface along the generated reaction path is analysed. To this end, time dependent DFT (TDDFT) and spin-flip TDDFT (SF-TDDFT) were employed. Normal TDDFT fails to properly describe regions of strong coupling, due to the multiconfigurational nature of the electronic ground state. Instead, in SF-TDDFT both ground and excited states are treated as spin-flip excitations from a state with different multiplicity. Hence this single determinant method is able to describe near degeneracies and conical intersections.^[37–39] It has been demonstrated that SF-TDDFT can describe dissociation reactions, avoided crossings and conical intersections reasonably well, and with a relatively low computational cost.^[40–44] For both investigated photo-induced PCET steps, a conical intersection is found between the ground state and a higher lying excited state in the region near the transition state. A discussion is provided on plausible strategies to exploit this characteristic energy landscape, either by appropriately shaped laser pulses as done in the emerging field of optochemistry^[45], or through optimizing the resonance conditions for vibronic coupling by synthetically tuning molecular properties, with the goal of reducing back-reaction and recombination losses.^[46]

3.3 Results and Discussion

3.3.1 Search for the PCET reaction path using the Intrinsic Reaction Coordinate method

Two particular ruthenium based catalysts are considered, $[\text{Ru}^{\text{II}}(\text{bda})(\text{pic})_2(\text{H}_2\text{O})]^+$ (bda = 2,2'-bipyridine-6,6'-dicarboxylic acid, pic = 4-picoline; Figure 3.1a, catalyst 1) and $[(\text{cy})\text{Ru}^{\text{II}}\text{bpy}(\text{H}_2\text{O})]^{2+}$ (cy = p-cymene, bpy = 2,2'-bipyridine; Figure 3.1a, catalyst 2), which operate via the I2M and WNA mechanism, respectively.^[11,13,47] 2,6-diethoxy-1,4,5,8-diimidenaphthalene (Figure 3.1a, NDI) was selected as the light absorbing dye. The redox and light absorbing properties

of this specific NDI dye, and other core substituted derivatives, have been investigated extensively.^[48–50] Recent computational investigations have shown that this molecule has suitable absorption and redox properties to drive the four PCET steps that are required to complete the water oxidation process.^[25,51] The dye was considered to be covalently bound to the WOC via the nitrogen atom as depicted in Figure 3.1. For the remainder of this paper, the bound WOC-Dye complexes in Figure 3.1a will be referred to as **1** and **2**. Coupling of the dye via the non-substituted carbon atom at the naphthalene core was also considered. As this case yielded results very similar to the other binding mode, the obtained results for that system are provided in the appendix (see appendix, 3A.1.1). In order to properly describe the solvation of the hydronium cation after each PCET step, explicit water molecules were included in the model system, *i.e.* two water molecules for **1** and three water molecules for **2** (Figure 3.1b). Addition of explicit water stabilizes the product significantly, as it allows for the formation of a Zundel cation. Taking into account the WOC, the dye and explicit water molecules, allows for a study of the entire PCET process after photo-oxidation of the dye. The TiO₂ semiconductor surface is not considered explicitly as previous work has shown that the photo-induced electron injection process from the NDI to the conduction band of TiO₂ is fast compared to the water oxidation reaction timescale.^[52] The systems are thus optimized in their oxidized form ([WOC]⁺-dye^{•+} for **1**, and [WOC]²⁺-dye^{•+} for **2**). For both complexes, the catalytic step that was shown to be thermodynamically most demanding has been investigated. Earlier work has shown that for **1**, this involves a PCET step where the proton transfers from the Ru(IV)-hydroxo intermediate to bulk water^[13,34] (Figure 3.1a, reaction 1) and for **2** this involves the O-O bond formation via the WNA mechanism (Figure 3.1a, reaction 2).^[11,25]

For both WOC-dye complexes, a transition state (TS) was located, and its saddle point character was verified with vibrational analysis. For the TS of **1**, the imaginary normal mode features the displacement of the proton from the OH ligand to the nearest water molecule (see Figure 3.1b, top). In the case of **2**, the

Chapter 3: Strategies to Enhance the Rate of Proton-Coupled Electron Transfer Reactions in Dye-Water Oxidation Catalyst Complexes

TS captures both the formation of the O-O bond and simultaneous release of the proton to the bulk water (see Figure 3.1b, bottom). Starting from the optimized TS, a ground state IRC path was generated, which corresponds to a minimum energy path in mass-weighted coordinates.^[35,36] The IRC paths feature a Grotthuss-type mechanism for the proton diffusion to the solvent water (xyz trajectory files of the IRC paths can be found as supplementary material to the original publication).^[53,54] For **1**, the IRC calculations yield a reaction path in which the ruthenium hydroxide O-H bond is broken and the hydronium is subsequently stabilized by coordinating to the carboxylate group of the bda²⁻ ligand. It will be interesting to further investigate if the stabilizing role of the ligand in this catalytic cycle is consistently observed when explicit solvation is included in AIMD. The IRC for **2** yields a path involving simultaneous O-O bond formation and O-H bond dissociation to form a hydronium cation. In this system, the propagation of the IRC path converged when the O-O distance was elongated from 1.75 Å in the TS, to 2.05 Å in the reactant geometry. To obtain a comprehensive picture of the water molecule approaching the Ru-OXO species, the IRC path was extended with a series of ten constrained geometry optimizations in which the O-O bond length was increased stepwise. Detailed descriptions of the procedures used to obtain the reaction paths, the obtained xyz trajectory files and the ground state energy profile are provided in the appendix, 3A.2.2.

3.3.2 Tracking the electron transfer during the PCET reaction

The obtained IRC paths were used as input structures for DFT calculations with the hybrid B3LYP functional, to study ET along the PCET reaction. Due to the presence of unpaired electrons in the ground state, ET can be analyzed by visualizing the spin density. The spin densities of **1** and **2**, in the reactant and product geometries, are depicted in Figure 3.2. For **1**, the unpaired electron is initially localized on the NDI, as a result of the excited state electron injection into the TiO₂ semi-conductor. After proton transfer, the whole spin density is

transferred to the catalyst, indicating that the catalyst has been oxidized leading to electron pairing on the NDI ($[\text{WOC}]^+-\text{dye}^{\bullet+} \rightarrow [\text{WOC}]^{2+}-\text{dye}$). The situation for **2** is slightly different. Although a doublet multiplicity is imposed over the entire reaction path, **2** has three unpaired electrons after electron injection into the semiconductor: specifically, two unpaired electrons on the catalyst and one unpaired electron with opposite spin on the NDI (see Figure 3.2, bottom left). In Figure 3.2 it is seen that after the PCET step, **2** has only one unpaired electron on the WOC in the product structure. Further investigations show that the $S=3/2$ and $S=1/2$ states in the reactant geometry are nearly degenerate ($\Delta E < 0.01 \text{ kcal mol}^{-1}$), which is plausible since the ruthenium center and the NDI are spatially separated by about 5 Å. This quasi degeneracy is also the reason for serious spin contamination in the calculations on these initial structures. The expectation value for the $\hat{S}^2$ operator is about 1.77 for the reactant structure of **2**, while a pure $S=1/2$ state would yield a value of 0.75 for this operator and a pure $S=3/2$ state would yield a value of 3.75. The α and β spin density are, however, localized exclusively on the WOC and NDI respectively, corresponding to the expected electronic state in which a local triplet is formed on the WOC and a local doublet on the NDI. The spin contamination disappears as soon as the $S=3/2$ and $S=1/2$ degeneracy is lifted. Nevertheless, we note that the spin contamination could still affect the obtained energies.^[55] A figure with the $\hat{S}^2$ expectation value plotted over the reaction coordinate is provided in the appendix (3A.2.3, Figure 3A.7).

Chapter 3: Strategies to Enhance the Rate of Proton-Coupled Electron Transfer Reactions in Dye-Water Oxidation Catalyst Complexes

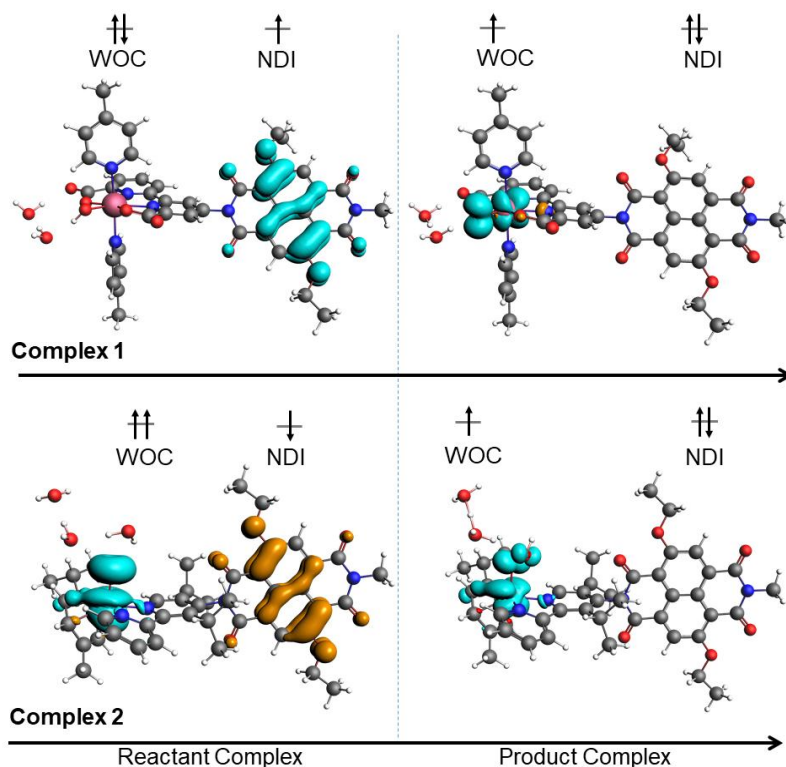


Figure 3.2. Reactant and product geometries of **1** and **2** obtained with the IRC method at the OPBE/TZP/COSMO level of theory. The spin densities have been calculated at the B3LYP/TZ2P/COSMO level of theory and the isosurface value was set at 0.002. The schematic electronic configurations with the unpaired electrons are indicated. Cyan corresponds to spin up and orange corresponds to spin down electrons. Although for both systems the overall charge is conserved over the entire reaction path, locally a plus charge moves from the NDI to the excess solvated proton.

3.3.3 Exploring the excited state potential energy surfaces with TDDFT

With the aim of gaining insights into the excited state potential energy surfaces along the obtained IRC reaction coordinates, TDDFT was employed. Excited state calculations were performed on a selection of structures along the IRC path. In

Figure 3.3, the ground state and excited state profile for the two systems are projected along a specific geometrical parameter that represents the main bonding rearrangement during the PCET step. For **1**, the selected reaction coordinate is the difference between the O_I -H and the O_{II} -H distances, with O_I being the oxygen of the OH ligand and O_{II} the oxygen of the proton acceptor water molecule (see inset in Figure 3.3, upper panel). For **2**, the selected reaction coordinate is the difference between the O_I - O_{II} and the O_{II} -H distances, with O_I being the oxygen of the oxo ligand and O_{II} the oxygen of the attacking water molecule (see inset in Figure 3.3, lower panel).

AIMD simulations on **2** in explicit solvation have convincingly shown that reaction 2 is exothermic upon photo-oxidation of the NDI.^[25,26] It is noted that in these static calculations the ground state reaction (red line in Fig. 3) is endothermic. Given the fact that an implicit solvation model is used with only a few explicit water molecules and that the IRC method does not necessarily yield a fully optimized structure, it is plausible that these calculations underestimate the stability of the solvated hydronium cation in the product structure. Nevertheless, this will not affect the main conclusions of this work, as we are here primarily interested in exploring the behavior of the ground and excited state energy profile along the reaction coordinate, especially in the region of near degeneracy.

Chapter 3: Strategies to Enhance the Rate of Proton-Coupled Electron Transfer Reactions in Dye-Water Oxidation Catalyst Complexes

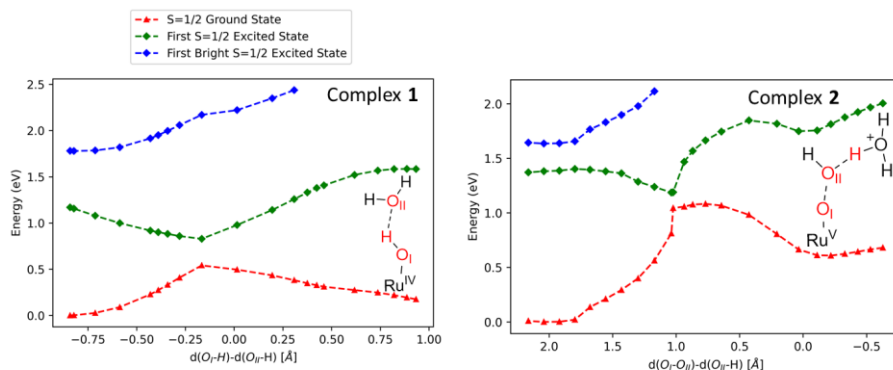


Figure 3.3. The obtained $S=1/2$ ground state (red), first $S=1/2$ excited state (green) and “bright” $S=1/2$ excited state (blue) potential energy surfaces along the reaction coordinates for the rate determining PCET step of **1** (top) and **2** (bottom). The energy for the ground state and the first excited states for each point is evaluated at the B3LYP/TZ2P/COSMO level of theory within the TDDFT framework.

The calculations reveal an avoided crossing between the ground state and first excited state at the PCET transition state for **1**. Also **2** moves through an avoided crossing, yet a key difference is that this crossing does not completely coincide with the transition state for the PCET reaction. The reason for this is that the reaction coordinate involves two molecular rearrangements, namely, formation of the O-O bond and dissociation of the O-H bond. Conversely, the PCET step investigated in **1** involves only proton transfer from the ruthenium hydroxo species to the water environment. Additionally, it is also observed that the barrier for the rate determining step of the reaction with **1** is significantly lower than the rate determining step for the reaction with **2** (ca. 13 kcal mol⁻¹ against 20 kcal mol⁻¹ evaluated at the B3LYP/TZ2P/COSMO level of theory). This is in agreement with prior studies that have shown the catalyst in **1** to have higher turnover frequencies than the catalyst in **2**.^[11,13] It is noted that the B3LYP/TZ2P setup here estimates a barrier significantly higher than the OPBE/TZP/COSMO

calculations (>7 kcal mol⁻¹ for both complexes, see appendix, 3A.2.2). It is emphasized again that our calculations are not aimed at precisely estimating reaction rates. In addition to the analysis of the excited state profile along the ground state PCET reaction coordinate, also an excited state geometry relaxation was performed from the Franck-Condon point at the reactant structure of **1**. These calculations are discussed in the appendix, 3A.1.4.

To gain further insights into the characteristics of the ground and excited state, the Natural Transition Orbitals (NTOs) at the reactant and product geometries for **1** and **2** are depicted in Figure 3.4. NTOs are a practical way of transforming the transition density matrix to obtain a set of compact orbitals that describe the transitions of interest in as few as possible terms.^[56] Starting from the reactant complex, it was found that the first excited state of the oxidized complex corresponds to a charge transfer excitation from the catalyst to the NDI, for both **1** and **2**. Then, in the product structure, again for both investigated complexes, the first excited state is described as a charge transfer excitation from the dye to the catalyst. Instead of mixing of the involved NTOs prior to approaching the avoided crossing, a sudden rearrangement is observed upon moving over the barrier. For the reactant and product structures of **1**, the occupied and virtual NTO's correspond entirely to the spin α HOMO and LUMO. For the product structure of **2**, this is also the case. The observed transitions correspond for $>99.5\%$ to the HOMO-LUMO excitation. For the reactant structure of **2**, the HOMO-LUMO orbital excitation constitutes 96.1% of the displayed transition.

Chapter 3: Strategies to Enhance the Rate of Proton-Coupled Electron Transfer Reactions in Dye-Water Oxidation Catalyst Complexes

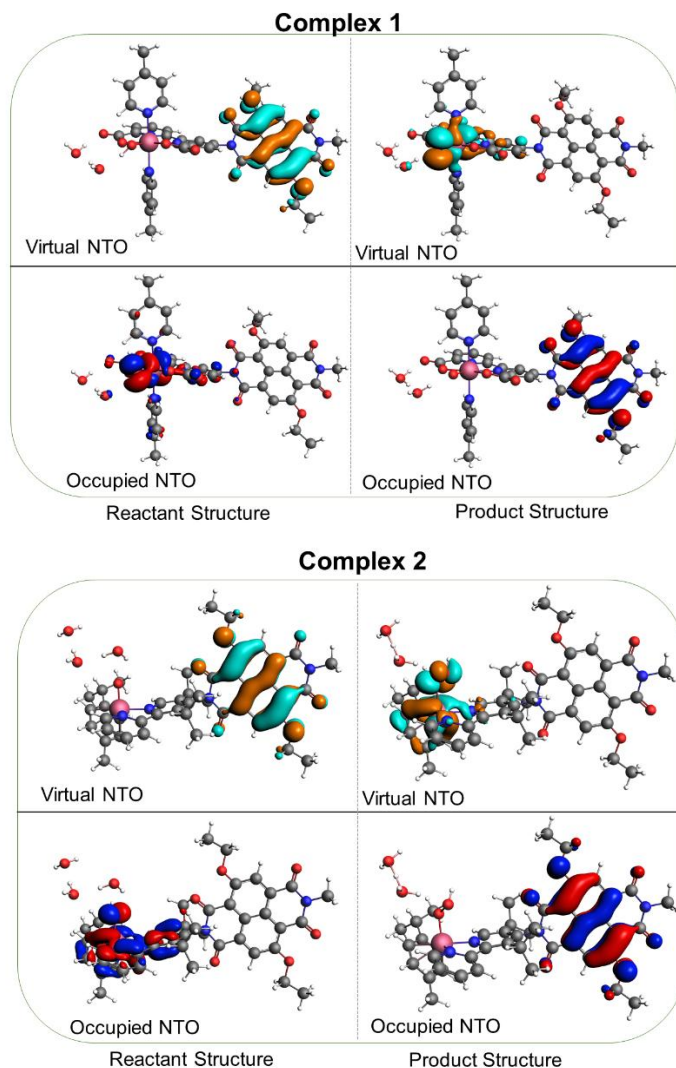


Figure 3.4. The Natural Transition Orbitals (NTO's) of the first excitation, calculated at the B3LYP/TZP/COSMO level of theory on the reactant and product geometries of **1** (top) and **2** (bottom). It is observed that for the reactant structure, the first excited state is a charge transfer excitation from the ruthenium catalyst to the NDI, while for the product structure, the excitation corresponds to a charge transfer from the NDI to the ruthenium center.

One strategy to optimize PCET steps in artificial photosynthetic systems is to utilize the interplay between nuclear and electronic motion. Interestingly, our calculations sketch a potential energy landscape where the ground and excited state get within a 0.4 eV energy gap, which is the typical domain of molecular vibrational energies. This indicates that in these systems the two electronic states could be coupled vibronically, if a nuclear mode is available with the appropriate vibrational frequency. Earlier constrained AIMD simulations in our group have shown that electron transfer in **2** is strongly inhibited once the C-N-C-C torsional mode at the WOC-dye interface is fixed.^[25,26] The results presented in this paper provide a rationale behind this observation: The energy gap between the two adiabatic states in the region of the transition state is around 0.1 eV, which is indeed comparable to the energy associated with the torsional mode discussed in ref.^[26] The resonance between the torsional mode frequency and the electronic energy gap between the reactant and product states, leads to a deterministic conversion pathway from the reactant to the product. These results show that vibronic coupling is an important mechanistic aspect to consider, to properly understand the catalytic performance of artificial photosynthetic devices.

In a recent publication, Schlenkler and co-workers have shown that PCET between a series of phenol and heptazine derivatives can be driven and controlled using laser pulses.^[32] The authors use quantum chemical calculations to show that the probed decay process involves excitation to a short lived excited state and subsequent population of a charge transfer state. In this article, we argue that this idea can be extended to catalyst-dye complexes that are useful for water oxidation. The results in Figure 3.3 highlights two important observations. The first is that only two electronic states are relevant for the ET transfer, the reactant state, where the electron is still on the catalyst, and the product state, where the unpaired electron is transferred to the NDI. This implies that the product state could be accessed by exciting the systems at their reactant geometry. Second, for both complexes, the product state PES in the geometry corresponding to the reactant has a gradient towards the product geometry. These observations support the idea

Chapter 3: Strategies to Enhance the Rate of Proton-Coupled Electron Transfer Reactions in Dye-Water Oxidation Catalyst Complexes

that the PCET reaction can be initiated by irradiating the complex solution with appropriately tuned laser pulses, accelerating the reaction and preventing back reaction.

To explore this idea in more detail, the oscillator strengths between the ground state and higher lying excited states were assessed. The excitation energies and oscillator strengths at the reactant and product geometries for **1** and **2** are given in the appendix, 3A.3.1, table 3A.2 and 3A.3. Additionally, we have also examined the coupling between reactant and product states based on the generalized Mulliken-Hush ansatz. This analysis is provided in the appendix, 3A.3.2.^[57,58] Similar to the work of Schlenkler *et al.*, the charge transfer state that triggers PCET is optically dark. This would imply that once this state is populated, it will be unlikely that it will decay to the ground state through light emission. The first bright excitation from the ground state is found at 1.78 eV (number 7, 3A.3.1 table 3A.2) for **1** and at 1.63 eV (number 5, 3A.3.1 table 3A.3) for **2** at their initial structures on the computed reaction paths (see also table 3A.2 and 3A.3 and Figure 3.3, the first bright $S=1/2$ excited state). The calculations do not provide information on radiative or non-radiative decay pathways from these states to the first $S=1/2$ excited state. Ab initio non-adiabatic molecular dynamics simulations could provide insights into non-radiative pathways, while radiative pathways could be explored by calculating oscillator strengths between excited states.

The region around the avoided crossing was further investigated with SF-TDDFT. In traditional TDDFT, the ground state is optimized self-consistently, opening the gap between occupied and unoccupied orbitals. In the spin-flip approach, a state of different spin symmetry than the ground state is self-consistently optimized and used subsequently as a reference, to obtain the ground state and excited states electronic configurations of interest, by a spin-flip excitation. In Figure 3.5, the diabatic potential energy surfaces obtained with SF-TDDFT are plotted along the same reaction coordinates used for Figure 3.3. For both systems, a diabatic relaxation pathway (green line) is found along the PCET reaction coordinate.

Spin-flip excitations to the $S=1/2$ ground and $S=1/2$ excited states are calculated from the $S=3/2$ reference state, which is also shown in grey in Figure 3.5. Notice that this is not the same state as the $S=1/2$ ‘bright state’ that was found earlier with TDDFT, shown in Figure 3.3.

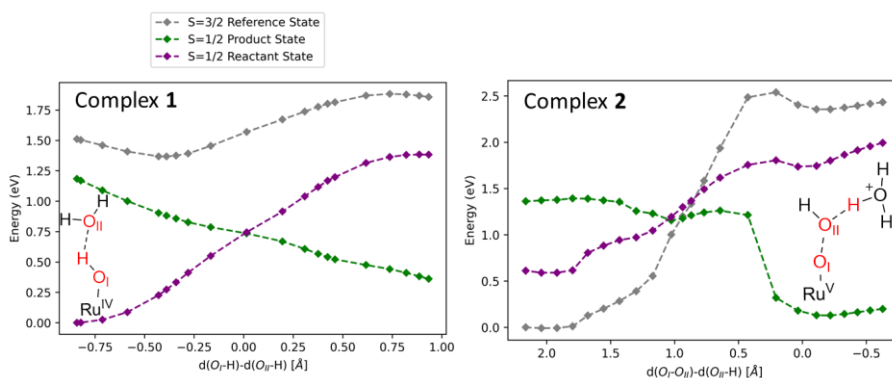


Figure 3.5. SF-TDDFT potential energy surfaces along the reaction coordinates for the rate determining PCET step of **1** (top) and **2** (bottom). A clear intersection is observed for the reactant (purple) and product (green) states. The $S=3/2$ reference state is also reported in grey. The energy for the reactant and product states is evaluated at the B3LYP/TZ2P/COSMO level of theory.

Both the reactant and product state yield a smooth energy profile when calculated as a spin-flip excitation from the $S=3/2$ reference state (dots in grey) in **1**. The $S=3/2$ reference state was found to be energetically separated by at least 0.3 eV from the investigated $S=1/2$ ground and excited states, along the entire reaction path. Also, the smoothness of the curve indicates that the same electronic configuration is retained. As was discussed earlier in this work, we know that for **2** the lowest $S=1/2$ and $S=3/2$ states are degenerate if separately optimized in a self-consistent manner. However, when using the $S=3/2$ state as a reference state, the spin-flip excitation energies to the $S=1/2$ ground state are non-zero. Interestingly, the spin-flip calculations indicate that there are two additional states very close in energy around the crossing region. For clarity, these states are not

Chapter 3: Strategies to Enhance the Rate of Proton-Coupled Electron Transfer Reactions in Dye-Water Oxidation Catalyst Complexes

depicted in Figure 3.5, however, a complete picture is provided in the appendix, 3A.4.1.

The product state energy profile of **2** (green line in Figure 3.5, bottom panel) features a significant jump around a reaction coordinate value of ~ 0.5 Å. This is because, initially the lowest $S=3/2$ state in this system has two unpaired electrons on the catalyst and one unpaired electron on the NDI, while later in the reaction path, the state with one unpaired electron on the catalyst and two on the NDI is favourable. The observed discontinuity in the product state of **2** (Figure 3.5, bottom panel, green line) is thus a consequence of the changing nature of the reference $S=3/2$ state. Nevertheless, the region of near degeneracy between reactant and product states is still well described by this reference state. Tables with the spin configurations on the WOC and NDI part of the complexes, and the spin orbital transitions associated with the excitations to the reactant and product states are provided in the appendix, 3A.4.2 and 3A.4.3.

Our results show that, for both systems, the electron transfer process can be described as population transfer between two electronically well characterized reactant and product states. TDDFT calculations show that this charge transfer state is optically dark, therefore, once populated it is unlikely that the system would relax to the ground state via a radiative pathway. As shown schematically in Figure 3.6, one could excite the system to one of the bright, higher lying excited states, after which the system could relax to the charge transfer state ($S=1/2$ ES in Figure 3.6). Our calculations show that the charge transfer state has a gradient in the direction of the PCET product, suggesting that this could lead to a barrierless, fast process. Further research using non-adiabatic molecular dynamics could shed light on excited state relaxation pathways.

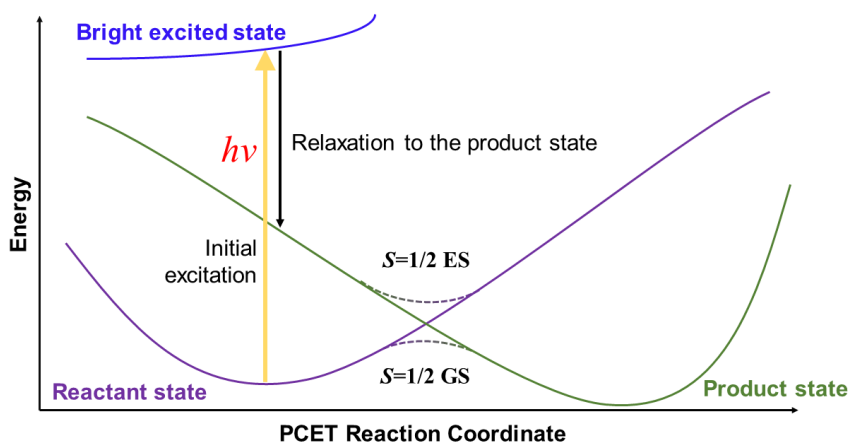


Figure 3.6. Schematic depiction of the hypothetical laser pump scheme. An initial, appropriately tuned laser pulse populates a bright excited state. The system then relaxes to the dark product state, either via a radiative or a non-radiative decay pathway. If this process is fast enough, subsequent relaxation along the non-adiabatic product state energy surface could then result in formation of the desired PCET product.

3.4 Conclusion

This work computationally explores the excited state potential energy surfaces of two water oxidation catalyst-dye systems, which can be used as a module in a DS-PEC device. Using static DFT calculations, an Intrinsic Reaction Coordinate path was computed for the rate limiting step in the photocatalytic cycle of both complexes. By calculating the spin density along the obtained reaction coordinate, it was possible to follow precisely at what stage the electron transfer process takes place. Subsequently, TDDFT was employed to gain insights into the excited state potential energy profile along the obtained reaction coordinates.

Two approaches are discussed which could exploit the observed potential energy profiles to accelerate the PCET step. Earlier works suggest that vibronic coupling between the reactant and product states could be facilitated by thermal activation

Chapter 3: Strategies to Enhance the Rate of Proton-Coupled Electron Transfer Reactions in Dye-Water Oxidation Catalyst Complexes

of a torsional mode at the catalyst-dye interface. The normal frequency associated with such a mode can be tuned by chemical design and synthesis to match the energy gap between the ground and excited state, facilitating a deterministic non-adiabatic pathway from the reactant to the product. Our calculations show that indeed, around the transition state for PCET, two electronic states have an energy gap that is comparable to the energy associated with typical nuclear vibrational modes in molecules. Alternatively, the PCET rate could be enhanced by populating the charge transfer (CT) state with an appropriately tuned laser pulse sequence. We propose a scheme in which first a higher lying bright state is populated through irradiating the sample with an appropriately tuned laser pulse. If in a subsequent step, relaxation to the charge transfer state is competitive against other decay pathways, this could trigger a photo-induced proton coupled electron transfer process. TDDFT calculations suggest that radiative decay to the ground state is unlikely once the CT state is populated. Our calculations establish a qualitative view of the excited state energy surfaces involved in PCET reactions in realistic catalyst-dye complexes, showing that photo-initiation is feasible for the bidirectional PCET that occurs during the water oxidation process.

3.5 Experimental Section

All structure optimizations and (SF-) TD-DFT calculations were performed within the AMS2020 program by SCM.^[59] Structures were optimized using the OPBE functional.^[60] A triple- ζ polarized (TZP) Slater-type basis set was employed with a small core for all atoms with the scalar zeroth order regular approximation (ZORA) to account for relativistic effects.^[61] The solvation of the complexes in water was modelled by the implicit conductor like screening model (COSMO).^[62,63] Vibrational analysis was performed for verification of the local minima and saddle points. We note that the used transition state for 2 contained an additional imaginary frequency of -0.004 eV, corresponding to a soft mode in

the ligand backbone. Despite numerous attempts to optimize this mode, it remained present in the final structure.

Ground and excited state energies of the obtained structures were then re-evaluated at the B3LYP/TZ2P level of theory without a frozen core and including COSMO water solvation.^[64–67] The Tamm-Dancoff approximation was applied for the calculation of excitation energies within the TDDFT framework.^[68] This was also the level of theory at which the spin densities were examined. TDDFT calculations were also performed with the long-range separated hybrid CAM-B3LYP and wb97-X functionals (see appendix, 3A.1.2 and 3A.1.3).^[69,70] Although, these functionals reproduce the same HOMO and LUMO orbitals as B3LYP, the specific HOMO-LUMO transition, associated with the reactant to product state excitation, was not recovered by the subsequent TDDFT calculations. Therefore, it was decided to discuss the B3LYP results in the article.

3.6 References

- [1] UNFCCC. Conference of the Parties (COP), *Adoption of the Paris Agreement. Proposal by the President*. **2015**, 21932, 32.
- [2] M. Grätzel, *Nature*. **2001**, 414, 338–344.
- [3] R. L. Purchase, H. J. M. De Groot, *Interface Focus* **2015**, 5, 1–16.
- [4] S. Ardo, D. Fernandez Rivas, M. A. Modestino, V. Schulze Greiving, F. F. Abdi, E. Alarcon Llado, V. Artero, K. Ayers, C. Battaglia, J. P. Becker, D. Bederak, A. Berger, F. Buda, E. Chinello, B. Dam, V. Di Palma, T. Edvinsson, K. Fujii, H. Gardeniers, H. Geerlings, S. M. Hashemi, S. Haussener, F. Houle, J. Huskens, B. D. James, K. Konrad, A. Kudo, P. P. Kunturu, D. Lohse, B. Mei, E. L. Miller, G. F. Moore, J. Muller, K. L. Orchard, T. E. Rosser, F. H. Saadi, J. W. Schüttauf, B. Seger, S. W. Sheehan, W. A. Smith, J. Spurgeon, M. H. Tang, R. Van De Krol, P. C. K. Vesborg, P. Westerik, *Energy Environ. Sci* **2018**, 11, 2768–2783.
- [5] J. D. Blakemore, R. H. Crabtree, G. W. Brudvig, *Chem. Rev.* **2015**, 115, 12974–13005.
- [6] S. Ye, C. Ding, M. Liu, A. Wang, Q. Huang, C. Li, *Adv. Mater.* **2019**, 31, 1902069.
- [7] L. H. Zhang, S. Mathew, J. Hessels, J. N. H. Reek, F. Yu, *ChemSusChem*. **2021**, 14, 234–250.
- [8] D. W. Shaffer, Y. Xie, J. J. Concepcion, *Chem. Soc. Rev.* **2017**, 46, 6170–6193.
- [9] J. J. Concepcion, J. W. Jurss, J. L. Templeton, T. J. Meyer, *J. Am. Chem. Soc.* **2008**, 130, 16462–16463.
- [10] H. Wang, E. Mijangos, S. Ott, A. Thapper, *Angew. Chem. Int. Ed.* **2014**, 1, 14499–14502.
- [11] J. M. De Ruiter, R. L. Purchase, A. Monti, C. J. M. Van Der Ham, M. P. Gullo, K. S. Joya, M. D’Angelantonio, A. Barbieri, D. G. H. Hetterscheid, H. J. M. De Groot, F. Buda, *ACS Catal.* **2016**, 6, 7340–7349.
- [12] T. Nakazono, A. R. Parent, K. Sakai, *Chem. Comm.* **2013**, 49, 6325.
- [13] L. Duan, F. Bozoglian, S. Mandal, B. Stewart, T. Privalov, A. Llobet, L. Sun, *Nat. Chem.* **2012**, 4, 418–423.

Chapter 3: Strategies to Enhance the Rate of Proton-Coupled Electron Transfer Reactions in Dye-Water Oxidation Catalyst Complexes

- [14] J. Yang, L. Wang, S. Zhan, H. Zou, H. Chen, M. S. G. Ahlquist, L. Duan, L. Sun, *Nat. Commun.* **2021**, *12*, 373.
- [15] D. Wang, J. T. Groves, *Proc. Natl. Acad. Sci. U. S. A.* **2013**, *110*, 15579–15584.
- [16] S. W. Gersten, G. J. Samuels, T. J. Meyer, *J. Am. Chem. Soc.* **1982**, *104*, 4029–4030.
- [17] B. Zhang, S. Zhan, T. Liu, L. Wang, A. Ken Inge, L. Duan, B. J. J. Timmer, O. Kravchenko, F. Li, M. S. G. Ahlquist, L. Sun, *J. Energy Chem.* **2021**, *54*, 815–821.
- [18] J. Hessels, R. J. Detz, M. T. M. Koper, J. N. H. Reek, *Chem. Eur. J.* **2017**, *23*, 16413–16418.
- [19] M. J. Craig, G. Coulter, E. Dolan, J. Soriano-López, E. Mates-Torres, W. Schmitt, M. García-Melchor, *Nat. Commun.* **2019**, *10*, 4993.
- [20] S. Hammes-Schiffer, *Acc. Chem. Res.* **2001**, *34*, 273–281.
- [21] J. Y. Fang, S. Hammes-Schiffer, *J. Chem. Phys.* **1997**, *107*, 5727–5739.
- [22] C. J. Gagliardi, B. C. Westlake, C. A. Kent, J. J. Paul, J. M. Papanikolas, T. J. Meyer, *Coord. Chem. Rev.* **2010**, *254*, 2459–2471.
- [23] P. Goyal, C. A. Schwerdtfeger, A. V. Soudackov, S. Hammes-Schiffer, *J. Phys. Chem. B.* **2015**, *119*, 2758–2768.
- [24] R. E. Warburton, A. V. Soudackov, S. Hammes-Schiffer, *Chem. Rev.* **2022**, *122*, 10599–10650.
- [25] Y. Shao, J. M. De Ruiter, H. J. M. De Groot, F. Buda, *J. Phys. Chem. C.* **2019**, *123*, 21403–21414.
- [26] Y. Shao, H. J. M. de Groot, F. Buda, *ChemSusChem.* **2021**, *14*, 479–486.
- [27] E. J. Rabe, K. L. Corp, A. L. Sobolewski, W. Domcke, C. W. Schlenker, *J. Phys. Chem. Lett.* **2018**, *9*, 6257–6261.
- [28] J. J. Concepcion, M. K. Brennaman, J. R. Deyton, N. V. Lebedeva, M. D. E. Forbes, J. M. Papanikolas, T. J. Meyer, *J. Am. Chem. Soc.* **2007**, *129*, 6968–6969.
- [29] F. Weber, J. C. Tremblay, A. Bande, *J. Phys. Chem. C.* **2020**, *124*, 26688–26698.
- [30] J. C. Lennox, D. A. Kurtz, T. Huang, J. L. Dempsey, *ACS Energy Lett.* **2017**, *2*, 1246–1256.
- [31] J. Leier, N. C. Michenfelder, A. N. Unterreiner, M. Olzmann, *Mol. Phys.* **2021**, *119*, e1975051.
- [32] K. L. Corp, E. J. Rabe, X. Huang, J. Ehrmaier, M. E. Kaiser, A. L. Sobolewski, W. Domcke, C. W. Schlenker, *J. Phys. Chem. C.* **2020**, *124*, 9151–9160.
- [33] X. Huang, W. Domcke, *J. Phys. Chem. A* **2021**, *125*, 9917–9931.
- [34] J. P. Menzel, M. Kloppenburg, J. Belić, H. J. M. de Groot, L. Visscher, F. Buda, *J. Comput. Chem.* **2021**, *42*, 1885–1894.
- [35] L. Deng, T. Ziegler, L. Fan, *J. Chem. Phys.* **1993**, *99*, 3823–3835.
- [36] L. Deng, T. Ziegler, *Int. J. Quantum Chem.* **1994**, *52*, 731–765.
- [37] F. Wang, T. Ziegler, *J. Chem. Phys.* **2004**, *121*, 12191–12196.
- [38] F. Wang, T. Ziegler, *J. Chem. Phys.* **2005**, *122*, 074109.
- [39] Y. Shao, M. Head-Gordon, A. I. Krylov, *J. Chem. Phys.* **2003**, *118*, 4807–4818.
- [40] N. Minezawa, M. S. Gordon, *J. Phys. Chem. A.* **2009**, *113*, 12749–12753.
- [41] M. Huix-Rotllant, B. Natarajan, A. Ipatov, C. Muhavini Wawire, T. Deutsch, M. E. Casida, *Phys. Chem. Chem. Phys.* **2010**, *12*, 12811–12825.
- [42] Z. Rinkevicius, O. Vahtras, H. Ågren, *J. Chem. Phys.* **2010**, *133*, 114104.
- [43] E. Salazar, S. Faraji, *Mol. Phys.* **2020**, *118*, e1764120.
- [44] K. G. Moghaddam, G. Giudetti, W. Sipma, S. Faraji, *Phys. Chem. Chem. Phys.* **2020**, *20*, 26944–26954.
- [45] H. Li, X. Gong, H. Ni, P. Lu, X. Luo, J. Wen, Y. Yang, X. Qian, Z. Sun, J. Wu, *J. Phys. Chem. Lett.* **2022**, 5881–5893.
- [46] B. C. Paulus, S. L. Adelman, L. L. L. Jamula, J. K. K. McCusker, *Nature.* **2020**, *582*, 214–218.
- [47] J. Nyhlén, L. Duan, B. Åkermark, L. Sun, T. Privalov, *Angew. Chem. Int. Ed.* **2010**, *49*, 1773–1777.
- [48] C. Röger, F. Würthner, *J. Org. Chem.* **2007**, *72*, 8070–8075.

- [49] N. Sakai, J. Mareda, E. Vauthey, S. Matile, *Chem. Commun.* **2010**, 46, 4225.
- [50] M. Al Kobaisi, S. V. Bhosale, K. Latham, A. M. Raynor, S. V. Bhosale, *Chem. Rev.* **2016**, 116, 11685–11796.
- [51] J. Belić, B. van Beek, J. P. Menzel, F. Buda, L. Visscher, *J. Phys. Chem. A* **2020**, 124, 6380–6388.
- [52] A. Monti, J. M. De Ruiter, H. J. M. De Groot, F. Buda, *J. Phys. Chem. C* **2016**, 120, 23074–23082.
- [53] C. J. D. T. von Grotthuss, *Ann. Chim. (Paris)* **1806**, 58, 54–74.
- [54] N. Agmon, *Chem. Phys. Lett.* **1995**, 244, 456–462.
- [55] J. Baker, A. Scheiner, J. Andzelm, *Chem. Phys. Lett.* **1993**, 216, 380–388.
- [56] R. L. Martin, *J. Chem. Phys.* **2003**, 118, 4775–4777.
- [57] R. J. Cave, M. D. Newton, *Chem. Phys. Lett.* **1996**, 249, 15–19.
- [58] R. J. Cave, M. D. Newton, *J. Chem. Phys.* **1997**, 106, 9213–9226.
- [59] AMS2021.101, SCM, Theoretical Chemistry. Vrije Universiteit: Amsterdam, The Netherlands. <https://www.scm.com>.
- [60] M. Swart, A. W. Ehlers, K. Lammertsma, *Mol. Phys.* **2004**, 102, 2467–2474.
- [61] E. Van Lenthe, *J. Chem. Phys.* **1999**, 110, 8943–8953.
- [62] A. Klamt, *J. Phys. Chem.* **1995**, 99, 2224–2235.
- [63] A. Klamt, V. Jonas, *J. Chem. Phys.* **1996**, 105, 9972–9981.
- [64] A. D. Becke, *Phys. Rev. A* **1988**, 38, 3098.
- [65] A. D. Becke, *J. Chem. Phys.* **1993**, 98, 1372–1377.
- [66] S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* **1980**, 58, 1200–1211.
- [67] P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, 98, 11623–11627.
- [68] S. Hirata, M. Head-Gordon, *Chem. Phys. Lett.* **1999**, 314, 291–299.
- [69] T. Yanai, D. P. Tew, N. C. Handy, *Chem. Phys. Lett.* **2004**, 393, 51–57.
- [70] J.-D. Chai, M. Head-Gordon, *J. Chem. Phys.* **2008**, 128, 084106.

3A. Appendix

3A.1 Additional TDDFT calculations

3A.1.1 TDDFT results for the C-bound $[Ru(bda)(pic)_2(H_2O)]^+-NDI$ complex

The obtained $S=1/2$ GS and ES energy profiles of the carbon bound WOC-NDI complex look similar to the profiles obtained for **1**. Only in the region of the transition state, two TDDFT calculations do not find the HOMO-LUMO excitation that describes the excited state PES of interest.

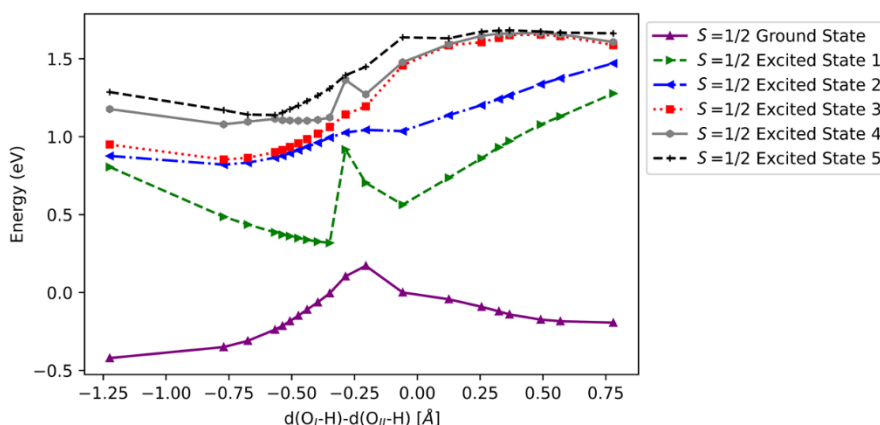


Figure 3A.1. Ground and excited state energy profile for the carbon bound $[Ru(bda)(pic)_2]^+$ ($bda = 2,2'$ -bipyridine-6,6'-dicarboxylic acid, $pic = 4$ -picoline) 2,6-diethoxy-1,4,5,8-diimidenaphthalene complex. Excitation energies are calculated at the B3LYP/TZ2P/COSMO level of theory.

3A.1.2 TDDFT results on **1** using the CAM-B3LYP functional

Calculations with the CAM-B3LYP functional do not always converge to the proper electronic state, especially in the region of the transition state. For the entire IRC path, the CAM-B3LYP TDDFT calculations do not find the charge transfer HOMO-LUMO excitation that was investigated in this article.

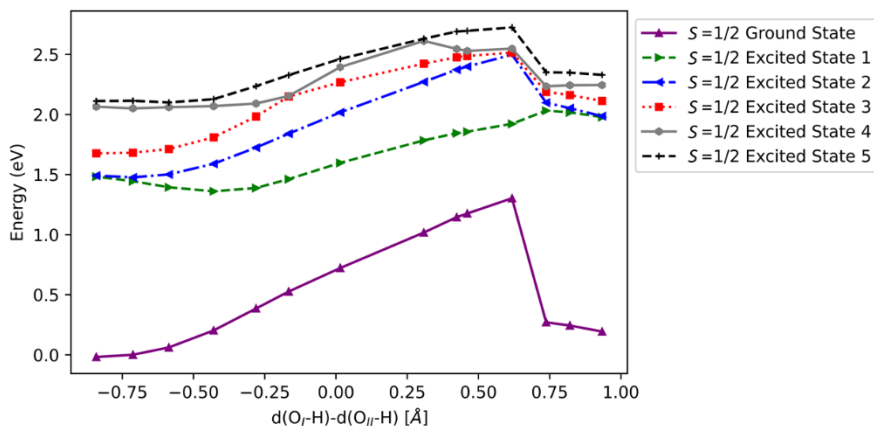


Figure 3A.2. Ground and excited states energy profile for **1**. Excitations calculated at the CAM-B3LYP/TZ2P/COSMO level of theory.

3A.1.3 TDDFT results on **1** using the wB97-X functional

The calculations with the wB97-X functional do recover for all investigated geometries along the PCET IRC path the proper electronic ground state. However, also for this range separated functional, the investigated HOMO-LUMO excitations are not recovered in the performed TDDFT calculations.

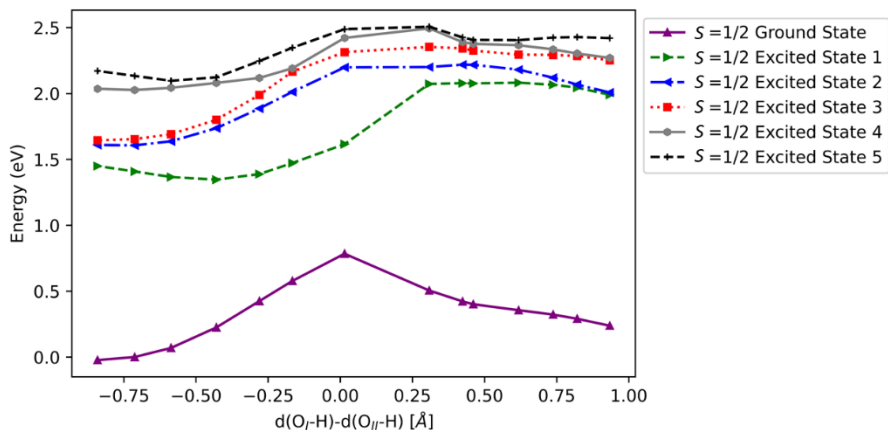


Figure 3A.3. Ground and excited states energy profile for **1**. Excitations calculated at the wB97X/TZ2P/COSMO level of theory.

Chapter 3: Strategies to Enhance the Rate of Proton-Coupled Electron Transfer Reactions in Dye-Water Oxidation Catalyst Complexes

3A.1.4 Excited state geometry optimization of **1**

In addition to the excited state analysis on the ground state IRC reaction path, also an excited state geometry relaxation from the Franck-Condon point was performed for **1**. The optimized geometries at the Franck-Condon point, the PCET transition state and the $S = \frac{1}{2}$ excited state are visualized in Figure 3A.4 (top). The first optimization steps from the Franck-Condon point mainly affected the orientation of the dye fragment with respect to the WOC. In the subsequent relaxation steps, the hydroxide oxygen-proton distance (O_I-H) is elongated from 0.99 Å to 1.08 Å and the distance from the hydroxide proton to the nucleophilic water oxygen atom ($O_{II}-H$) is shortened significantly from 1.83 Å to 1.42 Å (see table 3A.1). It was found that the same reaction coordinate that was used to describe the ground state PCET reaction could also be used to track the excited state geometry optimization. This geometry optimization supports the finding that the excited state has a gradient in the direction of the product of the PCET reaction. The $S=1/2$ excited state and ground state energy profile along the $d(O_I-H)$ - $d(O_{II}-H)$ reaction coordinate is plotted in Figure 3A.4 (bottom).

The excited state geometry optimization was performed at the same level of theory as the excited state calculations from the main paper, except for the basis set, which was scaled down from TZ2P to TZP quality in order to make the computation more efficient. The geometry was optimized up to an energy convergence of 1×10^{-3} H Bohr⁻¹, a max gradient convergence of 1×10^{-3} H Bohr⁻¹ and a root mean square gradient convergence of $2 \cdot 10^{-4}$ H Bohr⁻¹.

Table 3A.1. Distances of the dissociating and forming O-H bonds at Franck-Condon point, transition state and optimized excited state structures.

Structure	O _I – H distance (Å)	O _{II} – H distance (Å)
Franck-Condon point	0.991	1.832
Transition State	1.219	1.204
Optimized Excited State	1.077	1.422

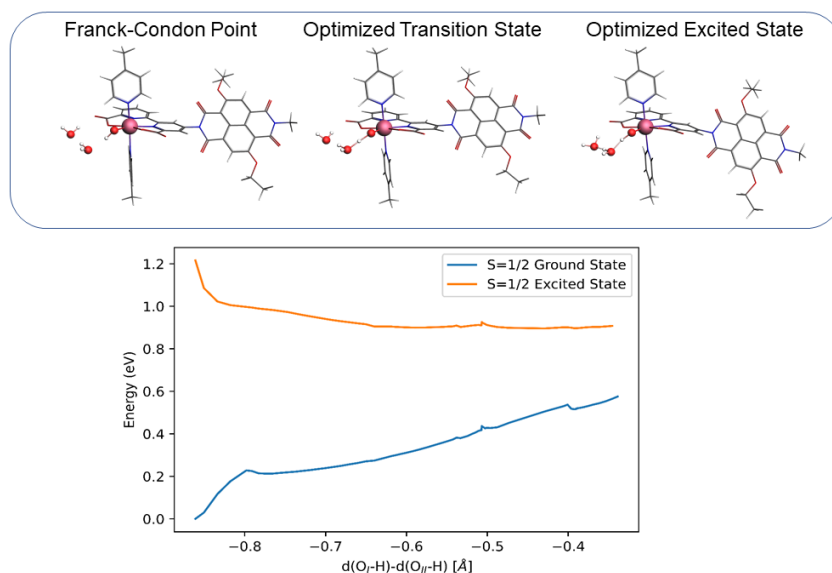


Figure 3A.4. On top, the optimized structures of **1** at the Franck-Condon point, at the optimized transition state and at the optimized excited state. On the bottom, a plot of the ground and excited states energy profile along an excited state geometry optimization for **1**. The calculation was performed at the B3LYP/TZP/COSMO level of theory.

Chapter 3: Strategies to Enhance the Rate of Proton-Coupled Electron Transfer Reactions in Dye-Water Oxidation Catalyst Complexes

3A.2.1 Obtaining the IRC paths

As a starting point for the investigation, an unconstrained geometry optimization was carried out of the two model systems. Performing a series of geometry optimizations then allowed for the search of a single normal mode that describes either the proton coupled electron transfer reaction from the Ru(IV)-OH species to form the Ru(V)=O intermediate (see Figure 3.1, Reaction 1) or O-O bond formation between the Ru(IV)=O intermediate and a H₂O molecule (see Figure 3.1, reaction 2). By performing a hessian calculation on a structure close to the TS, the normal modes corresponding to these geometric rearrangements were obtained. A transition state (TS) for each WOC-dye complex was located by optimization of the found normal mode without any constraints. Even though at this stage the constraints were lifted, no large structural changes were observed for the chain of water molecules in either system. Once a TS was located and characterized by a frequency calculation, the IRC method was employed to obtain the steepest descent path in mass-weighted coordinates from the TS to the reactant and product complexes. In the case of complex 2, the range of the reaction coordinate was extended by performing a series of 10 constrained optimizations with a O-O distance between 2.05 and 3.14 Å. The xyz trajectory files of the obtained IRC paths are provided as supplementary materials to the original publication, IRC_traj_1.xyz and IRC_traj_2.xyz.^[1]

3A.2.2 Ground state IRC reaction paths for 1 and 2

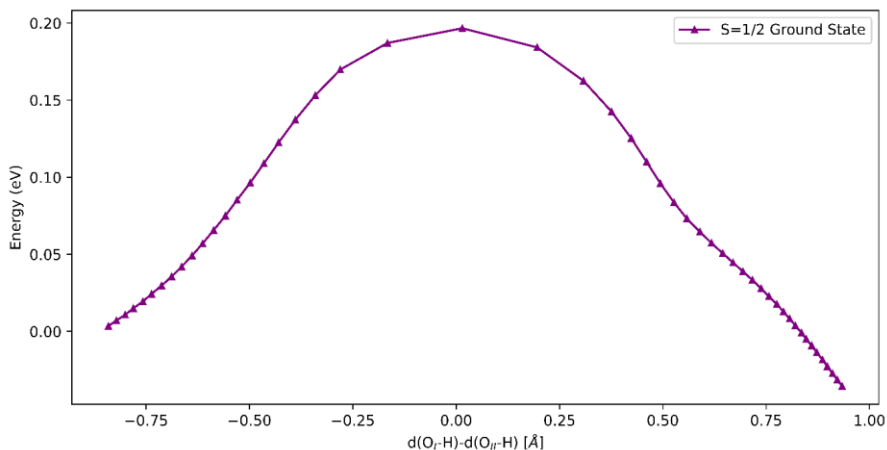


Figure 3A.5. Ground state energy profile for **1**, as obtained from the IRC calculation performed at the OPBE/TZP/COSMO level of theory.

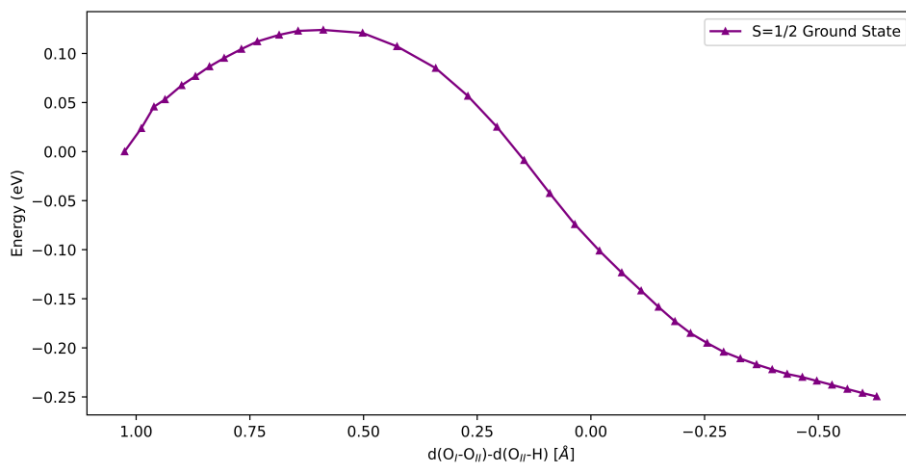


Figure 3A.6. Ground state energy profile for **2**, as obtained from the IRC calculation performed at the OPBE/TZP/COSMO level of theory.

3A.2.3 Expectation value for the $\hat{S}^2$ operator along the PCET reaction coordinate for 2

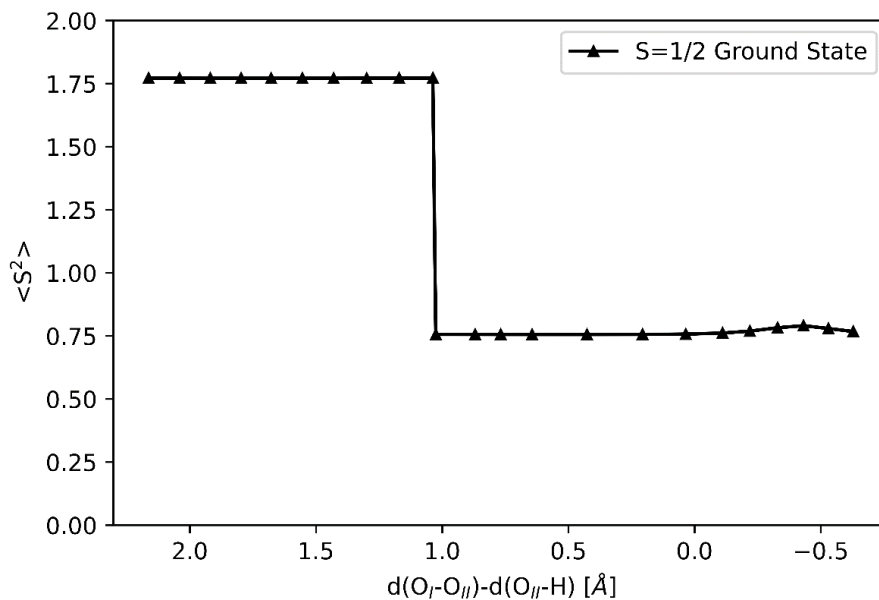


Figure 3A.7. Expectation value of the $\hat{S}^2$ operator along the PCET reaction coordinate for 2.

3A.3.1 Excitation energies and oscillator strengths of 1 and 2 at initial and final structures of the investigated reaction path

Table 3A.2. Excitation energies and oscillator strengths for complex 1 in the initial and final geometry on the IRC path. Excitations are computed at the B3LYP/TZ2P/COSMO level of theory within the Tamm-Dancoff TDDFT framework.

Number	Reactant structure		Product structure	
	Excitation energies (eV)	Oscillator strengths	Excitation Energies (eV)	Oscillator strengths
1	1.15	0.0001	1.41	0.0002
2	1.30	0.0002	1.69	0.0012
3	1.36	0.0004	1.76	0.0089
4	1.60	0.0000	1.79	0.0000
5	1.60	0.0000	1.84	0.0001
6	1.76	0.0000	1.93	0.0000
7	1.78	0.0171	2.08	0.0003
8	1.78	0.0036	2.16	0.0000
9	1.85	0.0000	2.33	0.0003

Chapter 3: Strategies to Enhance the Rate of Proton-Coupled Electron Transfer Reactions in Dye-Water Oxidation Catalyst Complexes

Table 3A.3. Excitation energies and oscillator strengths for complex 2 in the initial and final geometry on the IRC path. Excitations are computed at the B3LYP/TZ2P/COSMO level of theory within the Tamm-Dancoff TDDFT framework.

Reactant structure		Product structure	
Excitation energies (eV)	Oscillator strengths	Excitation Energies (eV)	Oscillator strengths
1.28	0.0017	1.32	0.0000
1.36	0.0008	1.44	0.0016
1.56	0.0193	1.64	0.0015
1.57	0.0008	1.75	0.0072
1.63	0.1069	2.03	0.0036
1.82	0.0101	2.27	0.0001
1.88	0.1032	2.36	0.0277
1.94	0.0060	2.55	0.0055
2.11	0.0006	2.63	0.0034

3A.3.2 Transition dipole moment, dipole moment, excitation energy and the H_{ab} coupling element of 1 and 2 along the investigated reaction path

In order to gain further insights into the coupling between the reactant and product states, the electronic coupling elements were calculated following the Generalized Mulliken-Hush ansatz.^[2,3]

$$V_{\text{et}} = \frac{\Delta E_{12} |\vec{\mu}_{12}|}{[(\vec{\mu}_{11} - \vec{\mu}_{22})^2 + 4(\vec{\mu}_{12})^2]^{\frac{1}{2}}}$$

In this equation, ΔE_{12} and μ_{12} are the vertical excitation energy and transition dipole moment between states 1 and 2, and μ_{11} and μ_{22} are the dipole moments for state 1 and 2, respectively. In the AMS2020 program, ΔE_{12} , μ_{11} and μ_{12} are readily obtained from an unrestricted open-shell TDDFT calculation. However, as of yet, it is not possible to calculate the excited state dipole moment, μ_{22} . Therefore, we approximate the μ_{22} parameter as the dipole moment of the first structure along the reaction coordinate, where the electronic ground state corresponds to the product state (and vice-versa for the coupling after the PCET event). For **1**, the coupling remains relatively constant. Along the entire reaction path a value around $1.5 \cdot 10^{-4}$ H is found (corresponding to 32 cm^{-1}). For **2**, the calculated matrix elements do change significantly along the reaction coordinate, particularly the first four reactant structures show a higher coupling around $4.5 \cdot 10^{-4}$ H (corresponding to 99 cm^{-1}). These structures were not part of the initial IRC reaction path, but correspond the constraint geometry optimizations that were used to elongate the reaction path. Likely, this caused larger distortions in the geometry, resulting in a larger changes in the parameters that were used to calculate the coupling. The Larger coupling in these structures is caused mainly by a larger transition dipole moment, as can be seen in Figure 3A.8.

The magnitude of μ_{12} and μ_{11} vectors, the electronic excitation energy and the calculated electronic coupling elements along the investigated reaction coordinate for **1** and **2** are presented in figures 3A.8 and 3A.9.

Chapter 3: Strategies to Enhance the Rate of Proton-Coupled Electron Transfer Reactions in Dye-Water Oxidation Catalyst Complexes

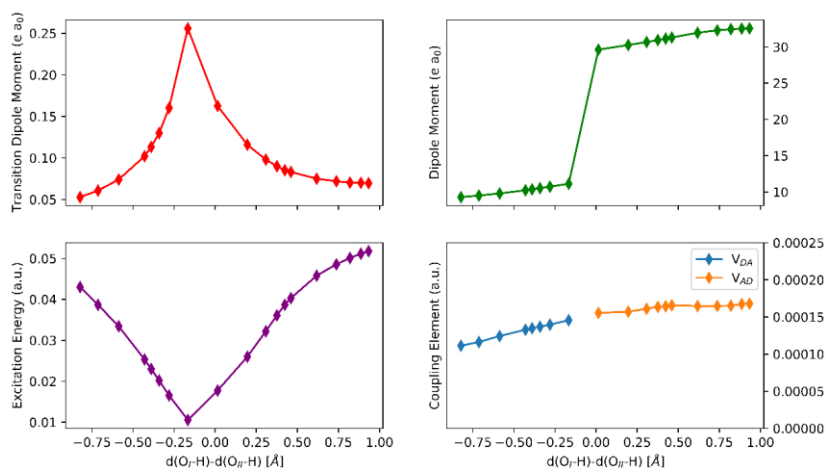


Figure 3A.8. Calculated transition dipole moment between $S=1/2$ ground and excited state (upper left panel), $S=1/2$ ground state dipole moment (upper right panel) and the first excitation energy (lower left panel) along the investigated reaction coordinate for **1**. The electronic coupling between reaction and product states (first half of the reaction, in blue) and product and reactant states (second half of the reaction, orange) are plotted in the bottom right panel.

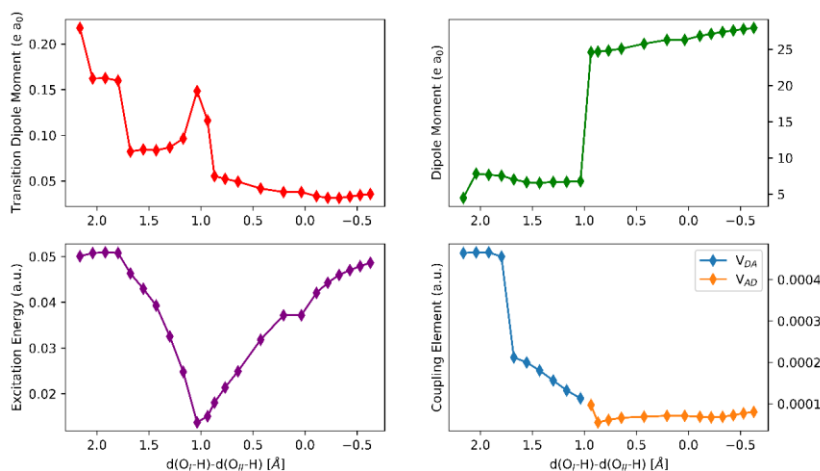


Figure 3A.9. Calculated transition dipole moment between $S=1/2$ ground and excited state (upper left panel), $S=1/2$ ground state dipole moment (upper right panel) and the first excitation energy (lower left panel) along the investigated reaction coordinate for **2**. The electronic coupling between reaction and product states (first half of the reaction, in blue) and product and reactant states (second half of the reaction, orange) are plotted in the bottom right panel.

3A.4.1 SF-TDDFT results for **2**

SF-TDDFT calculations on **2** reveal that at the beginning of the reaction path (longer O-O distance), previously not found electronic states are present beneath the doublet product state that was displayed in Figure 3.3. By analyzing the spin-orbital transitions associated with each excitation, the diabatic reactant and product states could be assigned at each frame in the IRC path. The other excitations all featured significant mixed orbital character, making it hard to consistently assign excited states for different frames.

Chapter 3: Strategies to Enhance the Rate of Proton-Coupled Electron Transfer Reactions in Dye-Water Oxidation Catalyst Complexes

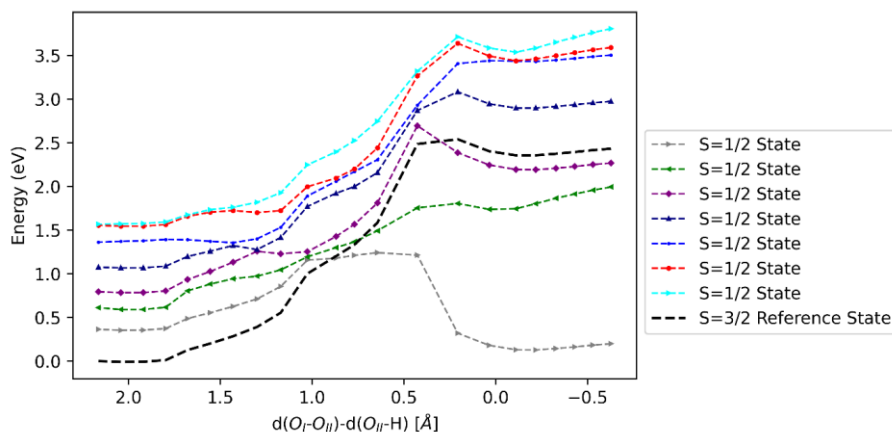


Figure 3A.10. Spin-flip TDDFT results for **2**. Excitations calculated at the B3LYP/TZ2P/COSMO level of theory.

3A.4.2 Interpretation of the spin-orbital transitions in the SF-TDDFT calculations for **1**

The $S=1/2$ ground state and $S=1/2$ excited states were computed as spin-flip excitations from the $S=3/2$ reference state (^4QRS). The reactant and product states can be identified by analyzing the spin-orbitals associated with the spin-flip transitions. In Table 3A.4 the interpretation of the calculated transitions is provided. Note that the indicated ruthenium d orbitals actually contain large oxygen p-orbital character as well as contributions from the ligand π -system (see Figure 3A.11). The HOMO and LUMO labels on the NDI refer to the HOMO and LUMO in the $S=3/2$ reference electronic state, not the HOMO and LUMO of the $S=1/2$ diabatic reactant and product states.

Table 3A.4. Spin configurations of different diabatic reactant and product states on WOC and Dye for complex 1 used in the SF-TDDFT. See also Figure 3A.11 for the visualization of the orbitals.

Diabatic state	Spin configuration on WOC	Spin configuration on NDI	Transition	Total spin
^4QRS (quartet reference state)	$d_{xy}(\alpha), d_{yz}(\alpha)$	$\text{NDI}_{\text{HOMO}}(\alpha)$	Reference state	3/2
^2RS (reactant state)	$d_{yz}(\alpha), d_{xz}(\beta)$	$\text{NDI}_{\text{HOMO}}(\alpha)$	$d_{xy}(\alpha) \rightarrow d_{xz}(\beta)$	1/2
^2PS (product state)	$d_{yz}(\alpha)$	$\text{NDI}_{\text{HOMO}}(\alpha)$ $\text{NDI}_{\text{LUMO}}(\beta)$	$d_{xy}(\alpha) \rightarrow \text{NDI}_{\text{LUMO}}(\beta)$	1/2

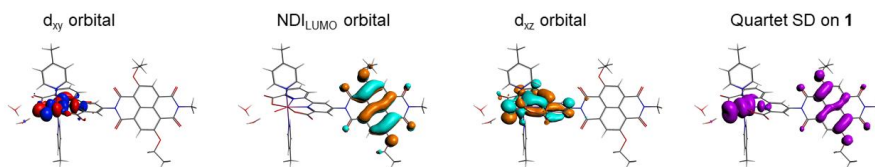


Figure 3A.11. Orbitals involved with the spin-flip excitations to the diabatic reactant and product states and the spin density of the quartet reference state. Isosurface values are set at 0.03 for the visualized orbitals and at 0.002 for the spin density.

Chapter 3: Strategies to Enhance the Rate of Proton-Coupled Electron Transfer Reactions in Dye-Water Oxidation Catalyst Complexes

3A.4.3 Interpretation of the spin-orbital transitions in the SF-TDDFT calculations for **2**

Table 3A.5. Spin configurations of different diabatic reactant and product states on WOC and Dye for **2** before change of reference state

Diabatic state	Spin configuration on WOC	Spin configuration on NDI	Transition	Total spin
⁴ QRS (quartet reference state)	$d_{xz}(\alpha), d_{yz}(\alpha)$	$\text{NDI}_{\text{HOMO}}(\alpha)$	Reference state	3/2
² RS (reactant state)	$d_{xz}(\alpha), d_{yz}(\beta)$	$\text{NDI}_{\text{LUMO}}(\alpha)$	$d_{xz}(\alpha) \rightarrow d_{yz}(\beta)$	1/2
² PS (product state)	$d_{xz}(\alpha)$	$\text{NDI}_{\text{HOMO}}(\alpha)$ $\text{NDI}_{\text{LUMO}}(\beta)$	$d_{xz/yz}(\alpha) \rightarrow \text{NDI}_{\text{LUMO}}(\beta)$	1/2

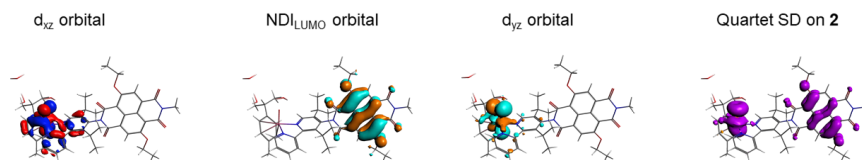
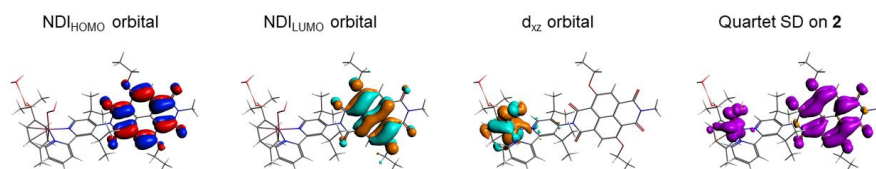


Figure 3A.12. Orbitals involved with the spin-flip excitations to the diabatic reactant and product states and the spin density (SD) of the quartet reference state for the first frames. Isosurface values are set at 0.03 for the visualized orbitals and at 0.002 for the spin density.

Table 3A.6. Spin configurations of different diabatic reactant and product states on WOC and Dye for **2** after change of reference state

Diabatic state	Spin configuration on WOC	Spin configuration on NDI	Spin transition	Total spin
⁴ QRS (quartet reference state)	Ru- $d_{xz/yz}(\alpha)$	NDI _{HOMO-1} (α), NDI _{HOMO} (α)	Reference state	3/2
² RS (reactant state)	Ru- $d_{xz/yz}(\alpha)$, O- $p_{x/y}(\alpha)$	NDI _{LUMO} (β)	NDI _{HOMO} (α) → $d_{yz/xz}(\beta)$	1/2
² PS (product state)	Ru- $d_{xz/yz}(\alpha)$	NDI _{HOMO-1} (α), NDI _{LUMO} (β)	NDI _{HOMO} (α) →NDI _{LUMO} (β)	1/2

**Figure 3A.13.** Orbitals involved with the spin-flip excitations to the diabatic reactant and product states and the spin density (SD) of the quartet reference state after the reference state switch. Isosurface values are set at 0.03 for the visualized orbitals and at 0.002 for the spin density.

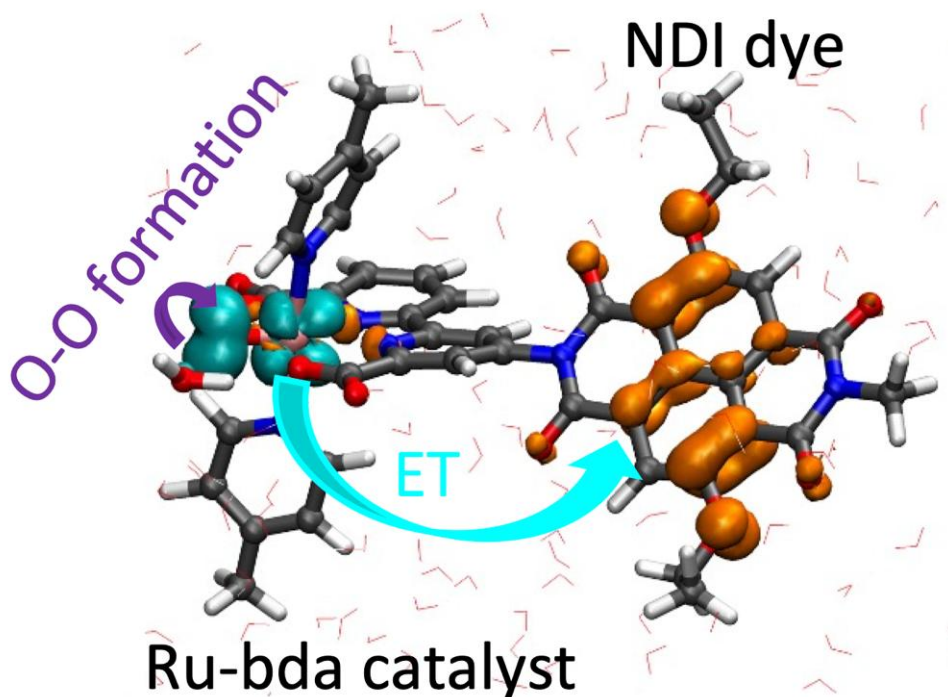
3A.5. References

- [1] T. de Haas, H. van Overeem, H. J. M. de Groot, F. Buda, *ChemPhotoChem* **2022**, e202200274.
- [2] R. J. Cave, M. D. Newton, *Chem. Phys. Lett.* **1996**, 249, 15–19.
- [3] R. J. Cave, M. D. Newton, *J. Chem. Phys.* **1997**, 106, 9213–9226

Chapter 4: Hybrid-DFT Molecular Dynamics

Simulations of Photocatalytic Water Oxidation in a [Ru-bda]–Dye Complex

The catalytic cycle of a dye-catalyst supramolecular complex for water oxidation is investigated using DFT-MD simulations.



This chapter is based on:

T. de Haas, D. Calvani, A. Zaaruolo, T. de Jong, J. Rutgers, B. Kreupeling, H.J.M. de Groot, F. Buda. Hybrid-DFT Molecular Dynamics Simulations of Photocatalytic Water Oxidation in a [Ru-bda]–Dye Complex. *J. Phys. Chem. C*. **2024**, 128 (47), 20093-20103.

Chapter 4: Hybrid-DFT Molecular Dynamics Simulations of Photocatalytic Water Oxidation in a [Ru-bda]–Dye Complex

4.1 Abstract

In the past decade, Ru-bda (bda = 2,2'-bipyridine-6,6'-dicarboxylic acid) complexes have emerged as extremely effective water oxidation catalysts, rendering them a potential candidate for incorporation into dye-sensitized photoelectrochemical cells. However, the performance of these catalysts declines dramatically when anchored to a photoanode surface due to their catalytic mechanism involving the interaction of two metal centers (I2M). This reduced performance prompts an investigation into the catalytic cycle following an alternative mechanism in which the O-O bond is formed through a water nucleophilic attack (WNA). In this work, we have performed hybrid-DFT based molecular dynamics simulations of the rate-determining O-O bond formation following the WNA mechanism in a [Ru-bda]-dye dyad model in explicit water solvation. In addition, our study probes oxygen dissociation from the Ru^{III}-O₂ intermediate, and the equilibrium dynamics of the low-valent Ru^{III}-bda intermediate. Our simulations demonstrate that including a fraction of exact Hartree-Fock exchange impacts the electron and hole localizations in the catalyst-dye complex, which can in specific instances affect the dynamics of the system. This study contributes to a fundamental understanding of water oxidation catalysis with the Ru-bda catalyst family and highlights the relevance of modeling catalytic processes at the hybrid-DFT level.

4.2 Introduction

In view of an escalating global climate crisis, harnessing solar energy for fuel production stands as a promising endeavor, offering a potential route towards the mitigation of greenhouse gas emissions.^[1-4] Dye-sensitized photoelectrochemical cells (DS-PEC) are devices that use sunlight to convert water and other abundant chemical resources into solar fuels.^[5,6] Typically, a DS-PEC contains two compartments. At the anode compartment, four photons are used to oxidize two molecules of water into four protons, four electrons, and one molecule of oxygen (O_2). At the cathode of the cell, the acquired reduction potential and the protons are used to generate molecular hydrogen or reduce a carbon-based feedstock into a denser energy carrier such as ethanol or ethylene.^[7]

At the anode of the DS-PEC, three chemical components are responsible for the water-splitting process: the semiconductor surface, a water oxidation catalyst (WOC) and a dye molecule. Photon absorption by a dye molecule initiates a charge separation process. The excited dye can donate an electron to the semiconductor surface, usually TiO_2 , and inject a hole into the WOC. This last step provides the driving force for one of the proton-coupled electron transfer (PCET) steps that constitute the water oxidation catalytic cycle. In practice, many photo-responsive anodes are based on solid state materials with an activity which is often hampered by slow reaction kinetics and inefficient photoactivity of the semiconductors.^[8] In contrast to solid state catalysts, specific molecular catalysts have been reported that perform at much lower overpotentials, in some cases even reaching higher activities than photosystem II.^[9,10] In light of this, it becomes highly compelling to adopt a design wherein the catalyst and dye molecules are present in a homogeneous solution or co-deposited on the semiconductor surface. However, a major disadvantage of such approaches is that the charge recombination reaction, in which the oxidized dye is quenched by electron-hole recombination from the TiO_2 surface, becomes competitive with the hole-scavenging of the catalyst.^[11] To overcome this issue, intermolecularly linked dye-catalyst complexes have been synthesized, either through covalent

Chapter 4: Hybrid-DFT Molecular Dynamics Simulations of Photocatalytic Water Oxidation in a [Ru-bda]–Dye Complex

interactions,^[12,13] or through supramolecular assembly strategies.^[11] In these photo-anodes, the interfacial electron transfer is typically very fast and the efficiency is proposed to be hampered by the chemical conversion rate of the catalyst.^[14]

One class of water oxidation catalysts that has shown to be particularly promising was developed in the labs of Sun and Llobet.^[9,15] This family of complexes employs a ruthenium center bearing a bda^{2-} (= 2,2'-bipyridine-6,6'-dicarboxylic acid) ligand in the equatorial plane and two monodentate pyridyl-type ligands on the axial positions. Because the Ru valence shell in the Ru^{II} -bda complex is completely occupied, the complex becomes catalytically active only after an initial oxidation to form a Ru^{III} species. The tetra-coordinated bda^{2-} backbone leads to a distorted octahedral environment around the ruthenium atom, leaving space for a water molecule to coordinate. However, whether that leads to a 7-coordinated environment around the Ru^{III} center remains a matter of debate, as the flexible bda^{2-} ligand has also been shown to be able to lower its coordination number, either by elongation of one of the equatorial $\text{Ru-N}_{\text{bda}^{2-}}$ bonds ($k^3\text{-O}^2\text{N}^1$ binding mode) or by elongation of the $\text{Ru-O}_{\text{COO}^-}$ distance ($k^3\text{-O}^1\text{N}^2$ binding mode).^[16–18] As the dynamic behavior of this low-valent complex in solution is still not entirely understood, a DFT-based Molecular Dynamics (DFT-MD) investigation of the coordination chemistry of this complex is desirable.

The Ru-bda family of catalysts typically performs the rate-limiting oxygen-oxygen bond-forming step through a bimolecular mechanism in which two $\text{Ru}^{\text{V}}=\text{O}$ species couple to form a $\text{Ru}^{\text{IV}}\text{-O-O-Ru}^{\text{IV}}$ complex that can eventually dissociate O_2 .^[9,19] This interaction of two metal (I2M) mechanism is postulated to be the major reason for a high catalytic activity of this catalyst class. As a result of its excellent performance, the Ru-bda catalyst has been used as a prototype to study water oxidation in systems where catalysts have been immobilized on surfaces, in supramolecular structures, and even in lipid bilayers and metal-organic frameworks.^[20–24] It remains questionable, however, whether the high

performance of this catalyst is preserved once the intermolecular collision frequency is significantly reduced as a result of catalyst immobilization. A recent study has shown that after immobilization on TiO_2 , the catalyst activity was quenched significantly, even though a second-order kinetics in the catalyst concentration was preserved.^[22] This is particularly interesting, since under such conditions a different mechanism is typically expected to become dominant in ruthenium based catalysts.^[25] In this alternative mechanism, the O-O bond is formed through a nucleophilic attack of a solvent water molecule on the high valent $\text{Ru}^{\text{V}}=\text{O}$, culminating in formation of the $\text{Ru}^{\text{IV}}-\text{O}-\text{OH}$ intermediate (WNA pathway). After a fourth PCET step, a $\text{Ru}^{\text{III}}-\text{O}_2$ species could be formed, leading to dissociation of the dioxygen ligand to recover the initial catalyst. The amount of work published on the WNA mechanism is significantly less than that on the I2M mechanism in the Ru-bda family, and an in-depth investigation of this alternative catalytic cycle, as well as an estimation of the reaction barriers, is appropriate.

In this work, we performed DFT-MD simulations of all four, proton-coupled electron transfer steps of the WNA mechanism in a Ru-bda catalyst, covalently bound to a naphthalene diimide (NDI) dye in explicit water solvation. Including the electron-accepting NDI and the proton-accepting water environment explicitly, allowed us to study the proton and electron transfer events during the simulation. This work addresses two questions regarding the catalytic cycle of the Ru-bda^{2-} catalyst class. First, we aim to establish a comprehensive picture of the equilibrium dynamics of the low-valent Ru^{III} intermediate, which is a debated topic in literature. Second, we evaluate the suitability of this catalyst for DS-PEC devices. Specifically, we determine the barrier for O-O bond formation following a nucleophilic attack of a water molecule on the $\text{Ru}^{\text{V}}=\text{O}$ intermediate, and we investigate the O_2 dissociation from the catalyst after the final PCET step.

Over the past three decades, density functional theory (DFT) based on the generalized gradient approximation (GGA) has become the workhorse of DFT-MD due to its numerical efficiency and accurate predictive power when it comes

Chapter 4: Hybrid-DFT Molecular Dynamics Simulations of Photocatalytic Water Oxidation in a [Ru-bda]–Dye Complex

to thermodynamic properties and structures. Despite its extensive use in modeling molecular water oxidation catalysis,^[26–31] GGA-DFT is known to suffer from a large self-interaction error, which leads to over-delocalized charge distributions.^[32–34] This has been clearly demonstrated for Cl[–] ions in water and ineffective hole-localizations in materials and surfaces.^[33,35] By applying the Auxiliary Density Matrix Method (ADMM),^[36] we could afford to include exact exchange and perform simulations at the hybrid-DFT level, which can correct the over-delocalization errors.^[35] Next to addressing the previously posed questions regarding the Ru-bda catalyst, this study also aims to assess the effects of including a fraction of screened-Hartree-Fock exchange in the description of the electronic structure.

The applied computational methodologies are described in section 4.3. The performed DFT-based molecular dynamics simulations of PCET reactions are discussed in detail in paragraphs 4.4.1 – 4.4.4. Section 4.4.1 describes the equilibrium dynamics of the low-valent Ru^{III}-bda intermediate. Section 4.4.2 deals with the enhanced sampling simulations of the O-O bond formation step, while section 4.4.3 investigates the oxygen dissociation from the catalyst after the fourth PCET reaction. The conclusions of this paper are presented in section 4.5.

4.3 Computational methods

The optimized initial structure of the dye-[Ru(bda)(pic)(OH)]⁺ complex was already obtained in a previous computational work.^[37] The complex was placed in a cubic box with periodic boundary conditions. 199 explicit water molecules were added using the PACKMOL^[38] builder tool in the AMS2022.102 package by SCM.^[39] Subsequently, GROMACS was used to perform classical molecular dynamics (MD) simulations in which the water solvent molecules were equilibrated.^[40] In these simulations, the water molecules were modeled with the TIP-3P force field, while the LigParGen tool was used to generate a set of OPLS-AA parameters for the non-metal atoms in the WOC-dye complex.^[41–45] As this

tool does not allow for metal parameter optimization, the ruthenium atom was replaced with a seven-coordinated sulfur atom during the optimization run, and the ϵ and σ Van der Waals parameters for ruthenium were obtained from Bernardes *et al.* (the employed OPLS-AA force field parameters can be found attached to the publication by de Haas *et al.*).^[46] Partial charges for all atoms of the WOC-dye complex were obtained from the Mulliken charges calculated at the B3LYP-D3(BJ)/TZP level on the optimized geometry.^[37] In these classical MD equilibration runs, the atoms in the WOC-dye complex were kept at fixed positions. After an initial geometry relaxation, 5 ns of NVT ensemble simulation followed by 10 ns of NPT ensemble simulation were performed, each with a 2 fs timestep. These simulations employed the Berendsen thermostat and the Parrinello-Rahman barostat, respectively.^[47–49] The volume equilibration yielded a cubic box with a side length of 20.343 Å and the temperature was stable around 300 K (see Appendix, Figure 4A.1). This system was subsequently used as the input for the DFT-MD simulations. Before the production runs, additional NVT simulations were performed at the DFT-MD level to equilibrate the whole system including the WOC-dye complex at 300 K. These calculations were performed with the Canonical Sampling Through Velocity Rescaling (CSVR) thermostat with a time constant set to 20 fs. The production runs were performed with a time constant of 150 fs. The time evolution of the temperatures of these runs is provided in the Appendix, Figure 4A.2.

All Kohn-Sham density functional theory simulations were carried out with the Quickstep routine in the CP2K8.2 software package.^[50] All pure-DFT calculations were performed with the PBE exchange-correlation functional, while hybrid-DFT simulations were performed at the B3LYP level. All simulations included Grimme's pairwise additive D3 dispersion corrections with a cut-off of 22 Å and grid-smoothening.^[51–54] The valence electrons for ruthenium were modelled with the DZVP-MOLOPT-SR-GTH basis set, while all other elements were modelled with the DZVP-MOLOPT-GTH basis.^[55] The core electrons were described using the GTH pseudopotentials optimized for the PBE functional.^[56–58] A value of 280

Chapter 4: Hybrid-DFT Molecular Dynamics Simulations of Photocatalytic Water Oxidation in a [Ru-bda]–Dye Complex

Ry was used as cut-off for the auxiliary plane wave (PW) basis. The PW integration was performed on a 5-layer multi-grid with the relative cut-off parameter set to 40 Ry. The orbital transformation (OT) method was used for the SCF procedure, employing a preconditioner based on diagonalization and inversion of the complete $\mathbf{H} - \epsilon^0 \mathbf{S}$ matrix in conjunction with the conjugated gradient minimizer.^[59] The convergence accuracy was set to 10^{-6} Hartree, which was found to conserve the total energy in the molecular dynamics simulations. Hybrid-DFT calculations were performed with the B3LYP functional containing a 0.2 fraction of screened Hartree-Fock exchange (HFX).^[60–63] The HFX part was computed in an auxiliary density matrix using the AUX_FIT cFIT11 basis for ruthenium and the AUX_FIT cFIT3 basis for all other elements.^[36] To reduce the computational cost, the Coulomb operator for the HFX calculation was truncated at a radius of $8.0 a_0$ and the threshold for the $\epsilon_{\text{Schwartz}}$ screening parameter was set to 10^{-6} , with screening of the initial density matrix enabled.^[64] Level of theory benchmarks on the structural and electronic properties of the complexes and on the oxygen-oxygen radial distribution function are provided in the Appendix, section 4A.7. These tests demonstrate that the level of theory employed is sufficiently accurate for the system of interest in this work.

4.4 Results and discussion

In this work, the $[\text{Ru}^{\text{II}}(\text{bda})(\text{pic})_2(\text{H}_2\text{O})]^+$ (bda = 2,2'-bipyridine-6,6'-dicarboxylic acid, pic = 4-picoline) complex was considered as the water oxidation catalyst. This catalyst has been reported to operate with a catalytic turnover frequency (TOF) of 32 s^{-1} and is representative of a class of ruthenium-based catalysts developed in the groups of Sun and Llobet.^[9] Although other catalysts have been reported to perform at higher turnover frequencies, these catalysts typically rely on different axial ligands which increase π - π stacking interactions, leading to higher intermolecular collision frequencies that favor the I2M pathway.^[15,19] Since the purpose of this work is to study the mononuclear WNA mechanism, it is

reasonable to consider the smaller 4-picoline ligand, as this saves computational resources. We note that the catalyst with 4-picoline axial ligands has been reported to perform very similarly to its phenylpyridine counterpart once it had been immobilized in a supramolecular assembly on a TiO_2 surface (see ref ^[11], Figure 4.2b). This type of catalyst has been adopted in several studies on catalyst and photosensitizer functionalized photoanodes.^[11,20,21,65–74]

The organic 2,6-diethoxy-1,4,5,8-diimidenaphthalene (NDI) dye was employed as photon absorber. This dye has been studied extensively and computational work has shown that it has the appropriate redox properties to provide a driving force for all four PCET steps in the water oxidation process in similar catalysts.^[75–77]

The NDI molecule was covalently bound to the catalyst on the nitrogen position of one of the imide moieties (see Figure 4.1). Computational work in our group has shown that photo-induced electron injection from the NDI to the TiO_2 surface is fast compared to the kinetics of the catalyst,^[78,79] which is consistent with experimental works on other dye- TiO_2 interfaces.^[80–82] The TiO_2 was, therefore, not taken into account explicitly and the photoinduced electron injection was simulated by instantaneous oxidation of the dye molecule. Experimental works, as well as *in silico* efforts, have focused on elucidating the reaction mechanism for the $[\text{Ru}^{\text{II}}(\text{bda})(\text{pic})_2(\text{H}_2\text{O})]^+$ catalyst.^[15] Based on these investigations and the research reported in this work, a reaction mechanism is proposed for the catalyst-dye complex. The proposed catalytic cycle is depicted in Figure 4.1. The catalyst is activated by oxidation of the Ru^{II} complex to form a $\text{Ru}^{\text{III}}\text{-OH}_2$ intermediate. Subsequently, a series of four proton coupled electron transfer steps lead to formation of $\text{Ru}^{\text{IV}}\text{-OH}$, $\text{Ru}^{\text{V}}\text{=O}$, $\text{Ru}^{\text{IV}}\text{-OOH}$ and finally again the $\text{Ru}^{\text{III}}\text{-OH}_2$. It has been found in earlier research that during the entire catalytic cycle the ruthenium remains in the low-spin electronic configuration.^[83] In this work, we have simulated with DFT based molecular dynamics all four PCET steps of the catalyst-dye complex. Simulations of the first and second PCET step were found to proceed on a fast timescale and are discussed in the Appendix, sections 4A.3 and 4A.4. The first section in the results concerns the equilibrium dynamics of the

Chapter 4: Hybrid-DFT Molecular Dynamics Simulations of Photocatalytic Water Oxidation in a [Ru-bda]–Dye Complex

Ru^{III}-bda intermediate before the first PCET step, as the nature of this equilibrium is still under debate in literature. Subsequently, the paper focusses on the rate-limiting third PCET step and the fourth PCET step which is rapidly followed by release of the dioxygen ligand.

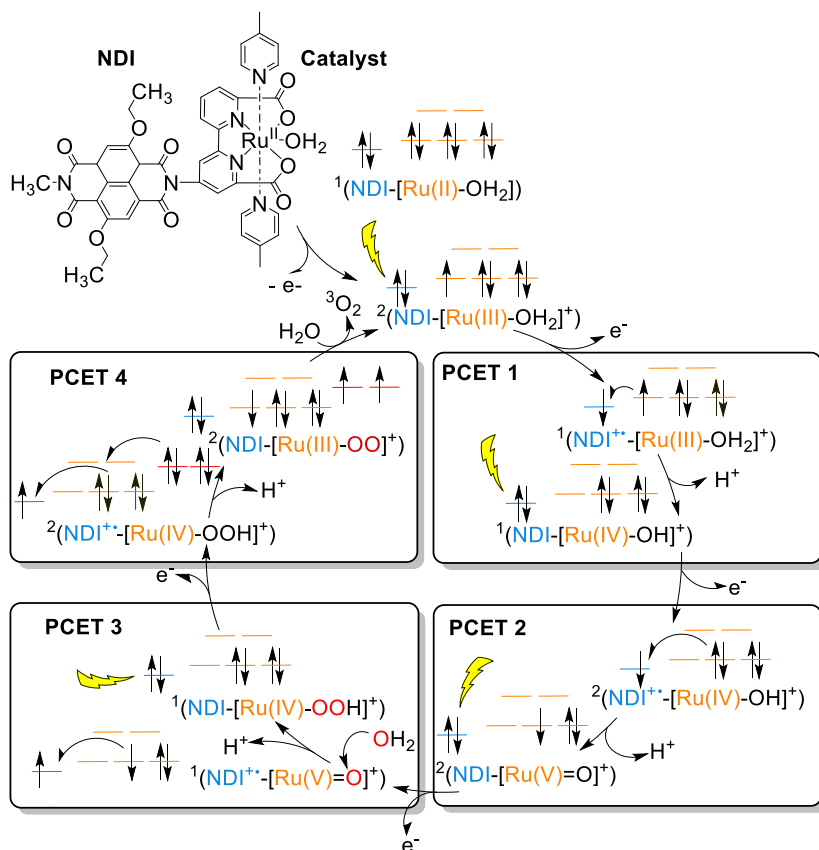


Figure 4.1. The proposed catalytic cycle for the studied WOC-dye system. Initially, the Ru(II) complex is oxidized to Ru(III). Then, four photo-induced PCET steps lead to formation of one dioxygen molecule, four protons and four electrons. A schematic representation of the electronic configuration on the ruthenium center at each intermediate is depicted in orange and the HOMO energy level of the dye is depicted in blue. The photo-oxidation events are highlighted by the yellow flash symbols. In the third and fourth PCET steps, the high valent ruthenium is reduced with electrons coming from the hydroperoxo/oxygen ligand.

Those orbitals are depicted in red. Both in PCET step 1 and step 3, the singlet spin-multiplicity is preserved during the reaction, despite the initial open shell character of the system.

4.4.1 Probing the equilibrium dynamics of the low-valent Ru^{III}-bda intermediate

From a combination of X-ray, NMR, and EPR studies, three distinct binding modes have been resolved for Ru^{III}-bda complexes.^[16–18] In the first binding mode, one of the carboxylate groups is reported to dissociate from the ruthenium, leading to a $k^3\text{-O}^1\text{N}^2$ coordination, whereas in the second binding mode the $\text{Ru-N}_{\text{bda}^{2-}}$ is elongated, leading to a $k^3\text{-O}^2\text{N}^1$ coordination.^[17,18] Recently, also a complex has been isolated in which the aqua ligand exhibits a weak interaction with the ruthenium, while the bda^{2-} backbone binds symmetrically in a $k^4\text{-O}^2\text{N}^2$ binding mode.^[16] In order to gain insights into the dynamic behavior of the catalyst in this low-valent oxidation state, we performed simulations both employing the PBE and the B3LYP exchange-correlation functionals. The $^2(\text{NDI-}[\text{Ru(III)-OH}_2])^+$ complex was equilibrated at the GGA-PBE level for 3 ps and subsequently propagated for another 5 ps at room temperature. Then the simulation was continued for another 4.6 ps at the hybrid level.

Interestingly, the complex was found to exhibit a dynamic equilibrium in which all binding modes discussed above participate. Snapshots of the trajectory where the system is in the $k^4\text{-O}^2\text{N}^2$, $k^3\text{-O}^1\text{N}^2$ and $k^3\text{-O}^2\text{N}^1$ binding modes are provided in Figure 4.2a, b and c, respectively. These figures also indicate with colors the $\text{Ru-O}_{\text{H}_2\text{O}}$, $\text{Ru-O}_{\text{COO}^-}$ and $\text{Ru-N}_{\text{bda}^{2-}}$ bonds that coordinate and dissociate from the ruthenium center. The time evolution of these bonds during the PBE and B3LYP simulations is visualized in Figure 4.2d. The other $\text{Ru-O}_{\text{COO}^-}$ and $\text{Ru-N}_{\text{bda}^{2-}}$ distances, as well as the axial Ru-N_{pic} distances, were found to remain relatively stable during the MD simulation and are provided in the Appendix, Figure 4A.3 and Figure 4A.4. In the performed PBE-based simulations, it was found that the system resides in a dynamic equilibrium between two six-coordinated, pseudo-

Chapter 4: Hybrid-DFT Molecular Dynamics Simulations of Photocatalytic Water Oxidation in a [Ru-bda]–Dye Complex

octahedral complexes, where the aqua ligand and one of the bda-carboxyl groups rapidly coordinate and dissociate to the Ru^{III} center on the sub-ps timescale. Interestingly, the binding of the aqua ligand was paired with the formation of strong hydrogen bonding interactions between the aqua ligand and the surrounding water molecules. Remarkably, at the B3LYP level of theory the dynamic behavior of the complex was preserved, but now also involving the $\text{k}^3\text{-O}^2\text{N}^1$ binding mode, where the equatorial $\text{Ru-N}_{\text{bda}^{2-}}$ distance is elongated, see parts of the trajectory between 5.2-5.4 ps and 9.1-9.5 ps in Figure 4.2. It was also attempted to equilibrate this $\text{k}^3\text{-O}^2\text{N}^1$ complex at the PBE level by constraining the equatorial $\text{Ru-N}_{\text{bda}^{2-}}$ distance to 2.54 Å and equilibrating the system for 2.5 ps. However, after lifting the constraint the system was found to relax instantaneously to the $\text{k}^3\text{-O}^1\text{N}^2$ coordination mode.

It can be concluded that the barriers associated with the transitions between the different binding modes are low. The aqua ligand is found to remain close to the metal center (< 3.0 Å) at all times during the simulation, even in the case of $\text{k}^4\text{-O}^2\text{N}^2$ coordination of the bda^{2-} ligand. This pseudo-7-coordinated environment implies that the first step in the catalytic cycle is not limited by slow coordination of the aqua ligand to the Ru(III) center. These results underscore how DFT-MD with explicit solvent can help to understand the dynamical flexibility in the coordination sphere of transition metal complexes.

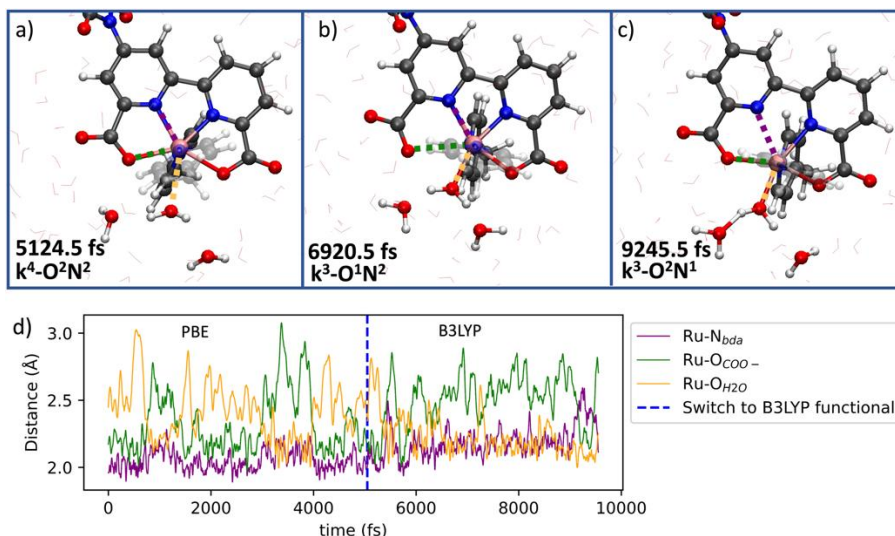


Figure 4.2. Snapshots from the AIMD simulations that represent the three binding modes, $k^4-O^2N^2$ (a), $k^3-O^1N^2$ (b) and $k^3-O^2N^1$ (c), are displayed in the top panel. The time evolution of Ru-N_{bda}²⁻, Ru-O_{COO}⁻ and Ru-O_{H₂O} bonds are plotted in d). In panel d), the first half of the trajectory is propagated at the GGA-PBE level, while the second half of the trajectory is propagated at the hybrid-B3LYP level of theory.

4.4.2 Blue Moon simulations of the rate-determining O-O bond formation step

The first and second photo-induced proton-coupled electron transfer (PCET) steps in the catalytic cycle of the investigated catalyst-dye dyad were found to proceed fast, on the ab initio MD time scale of several picoseconds (see Appendix, section 4A.3 and 4A.4). Consequently, we shift our attention to the third PCET event (PCET 3 in Figure 4.1). We employed a similar strategy as in the previous section: the equilibration of the system and exploratory Metadynamics (MetaD) and Blue Moon ensemble simulations were performed at the GGA-PBE level of theory, followed by an additional ~ 1 ps propagation of the Blue Moon ensemble trajectories at the hybrid-B3LYP level to refine the results. This approach enables us to compare the obtained free energy surface (FES) at both levels of theory. This section describes in more detail the performed enhanced sampling simulations.

Chapter 4: Hybrid-DFT Molecular Dynamics Simulations of Photocatalytic Water Oxidation in a [Ru-bda]–Dye Complex

The high-valent $^2(\text{NDI}[\text{Ru}(\text{V})=\text{O}])^+$ complex was equilibrated at room temperature for ~ 4 ps at the GGA-PBE level of theory. During this simulation, the spin density was localized exclusively on the ruthenium t_{2g} and the oxygen p orbitals (see Appendix, section 4A.5, Figure 4A.8). Despite the considerable electron deficient character of the oxygen, essentially no nucleophilic coordination of water molecules was observed in the performed simulations. This is in accordance with other *in silico* studies that reported the $\text{Ru}=\text{O}$ moiety to be hydrophobic.^[19] The Ru-O distance was found to fluctuate around 1.72 ± 0.05 Å, which is in excellent agreement with in-situ X-ray absorption spectroscopy studies on this catalyst class, that report a value of 1.75 ± 0.02 Å.^[84] At this stage, the complex was found strictly in the 7-coordinated environment with a symmetric binding of the carboxyl groups, although both Ru-O bonds fluctuated appreciably. After the removal of one alpha-spin electron from the dye, the system was found to equilibrate to a stable open-shell singlet with one unpaired alpha-electron on the catalyst and one unpaired beta-electron on the dye (see Figure 4A.9). This complex was found to remain stable over the course of 3 ps, without attempting electron transfer or interaction with nearby water molecules.

In order to observe the slow O-O bond formation, the water nucleophilic attack was accelerated by employing the well-tempered MetaD enhanced sampling method, of which the details are discussed in the appendix, 4A.6.1.^[85] The O-O distance between the oxo ligand and the nearest water molecule in the solvent was chosen as collective variable (CV), similar to previous studies.^{26,29,75} We argue that this choice of the CV is justified, given that one cannot discriminate between different water molecules in the simulation and the system is sufficiently equilibrated before we start the MetaD. Notably, the carboxylate group of the bda^{2-} ligand acted as a hydrogen bond acceptor towards one of the protons of the nucleophilic water molecule during the final ~ 22 ps of the MetaD simulation, even though this interaction was not included in the collective variable along which the reaction was biased (see Figure 4.3). Nevertheless, the PCET event consistently

involved dissociation of the proton facing the water environment, and not the one involved in this interaction. Although the MetaD simulations yielded a reactive trajectory, the statistical error in the obtained free energy surface (FES) remained large within the timescale that we could afford to run the simulation (see Appendix, Figure 4A.10).

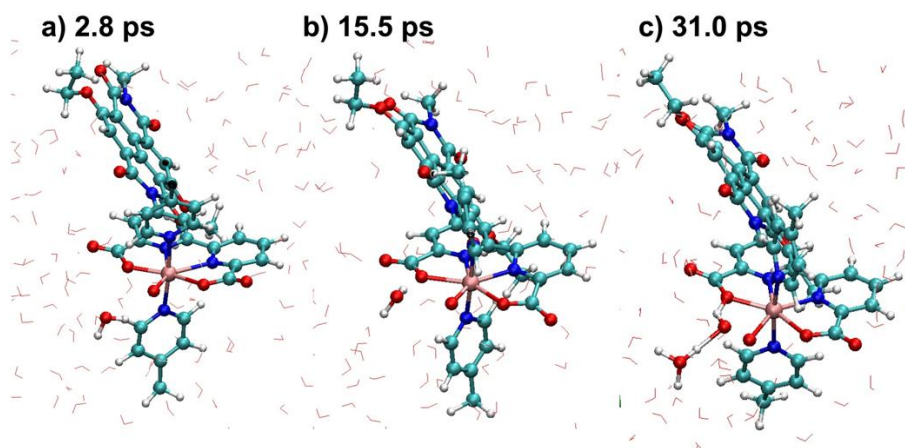


Figure 4.3. Three stages during the third PCET reaction, forming the O-O bond. (a) The water molecule roams around freely. (b) One of the protons on the water molecule forms a hydrogen bond with the carboxylate group of the bda^{2-} ligand. (c) The O-O bond is formed, while simultaneously the water facing proton is abstracted following a Grotthüs mechanism.

The FES was further refined following the Blue Moon approach using the O-O distance as collective variable.^[86,87] Nine structures were sampled from the MetaD simulation with O-O distances between 3.0 and 1.4 Å at 0.2 Å intervals. These structures were subsequently used as input for GGA-PBE based MD simulations, in which their O-O distance was constrained. After the averaged constraint force λ for each MD simulation had converged to a stable value, the trajectories were propagated for another $1.5 < t < 3$ ps, after which a constraint force profile was constructed from the averaged λ values (see Appendix, Figure 4A.11 a). Two

Chapter 4: Hybrid-DFT Molecular Dynamics Simulations of Photocatalytic Water Oxidation in a [Ru-bda]–Dye Complex

additional points were added to this profile at 1.45 Å and 3.3 Å. Unconstrained DFT-MD simulations showed that these values present the equilibrium O-O distances in the reactant and product states of the complex (see Appendix, section 4A.6.2). The profile was fitted with a 100-point Akima spline, and subsequently numerically integrated to obtain the FES (see Appendix, Figure 4A.11 b). The equilibrated GGA-PBE trajectories were further propagated for another ~ 1 ps at the hybrid-B3LYP level, after which this procedure was repeated to generate the force profile and FES at the hybrid-DFT level (Figure 4.4a and b). To improve the resolution in the region of the transition state, two additional points, at 2.1 and 1.9 Å, were considered at the hybrid-level. Errors on the λ -profile and FES were obtained from block averaging. Details on this procedure and further details on the Blue Moon approach are provided in the Appendix, 4A.6.2.

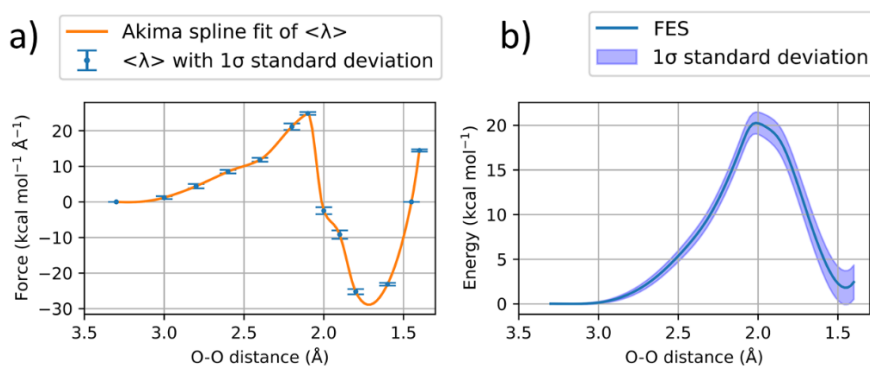


Figure 4.4. FES calculated at the B3LYP level, plotted as a function of the O-O distance reaction coordinate. The free energy was obtained by thermodynamic integration of a 100-point Akima spline fit of the averaged constraint forces, $\langle \lambda \rangle$, at different values of the constrained O-O bond distance. The error bars on $\langle \lambda \rangle$ are obtained by block averaging. The error on the FES is calculated by integrating the upper and lower bounds of the $\langle \lambda \rangle$ profile.

The hybrid-B3LYP based Blue Moon ensemble simulations predict a 20.3 ± 1.2 kcal mol⁻¹ free energy barrier governing the O-O bond formation. The overall

reaction has a free energy difference of $1.8 \pm 1.9 \text{ kcal mol}^{-1}$, indicating that, within the statistical error, the reaction is endothermic with the selected NDI dye. Previous studies from our group on different catalysts with the same dye showed a larger driving force for the O-O bond formation, likely because those catalysts involved Ru in a lower oxidation state.^[75,76] Experimentally, the half wave potential $E_{1/2}$ for the employed NDI dye has been measured at 1.36 V vs Fc/Fc⁺,^[88] which thus appears to be the minimum required oxidation potential for mononuclear water oxidation catalysis with this Ru-bda catalyst.^[77] While the relatively low barrier suggests the viability of the WNA mechanism as a potential route, the associated rate constant of $\sim 0.008 \text{ s}^{-1}$ (min = 0.001 s^{-1} , max = 0.06 s^{-1}) is four to eight orders of magnitude slower than the rates achieved through the I2M mechanism with this catalyst.^[15] We have also calculated the reaction profile at the GGA-PBE level (see the Appendix, Figure 4A.11). Interestingly, the overall reaction is found to be endothermic at that level with a $\Delta G = 2.9 \pm 0.9 \text{ kcal mol}^{-1}$. The barrier at the GGA-level is lower than at the hybrid-level, with the $\Delta G^\ddagger = 14.9 \pm 0.9 \text{ kcal mol}^{-1}$. Note that the error bar at the GGA-level is smaller than at the hybrid-B3LYP level since the GGA is computationally more efficient and simulations can be run over a longer timescale.

To get an understanding of the observed differences between the two functional set-ups, we have evaluated the proton and electron transfer dynamics during the Blue Moon ensemble simulations. In these simulations, the proton involved in the PCET reaction was not constrained and, therefore, free to dissociate from the nucleophilic water molecule. In addition, the electron could move freely from the catalyst to the photo-oxidized dye. In Figure 4.5, panel a, the spin density of the initial state corresponding to an open-shell singlet spin configuration with an unpaired electron on the catalyst and a hole on the dye is shown (see also Figure 4.1, PCET 3). After the third PCET step, a singlet closed shell configuration is obtained, where the unpaired electron on the catalyst has recombined with the hole (Figure 4.5, panel b). In Figure 4.5, panels c and d, the hybrid-B3LYP and GGA-PBE spin density evolution is visualized for the duration of 400 fs during the Blue

Chapter 4: Hybrid-DFT Molecular Dynamics Simulations of Photocatalytic Water Oxidation in a [Ru-bda]-Dye Complex

Moon simulations with constrained O-O distances of 3.0 Å, 2.2 Å, 2.0 Å and 1.4 Å. Figure 4.5c displays the first 400 fs for the hybrid simulations, while Figure 4.5d provides the 400 fs in which the PCET event takes places in the 2.0 Å GGA-based simulation.

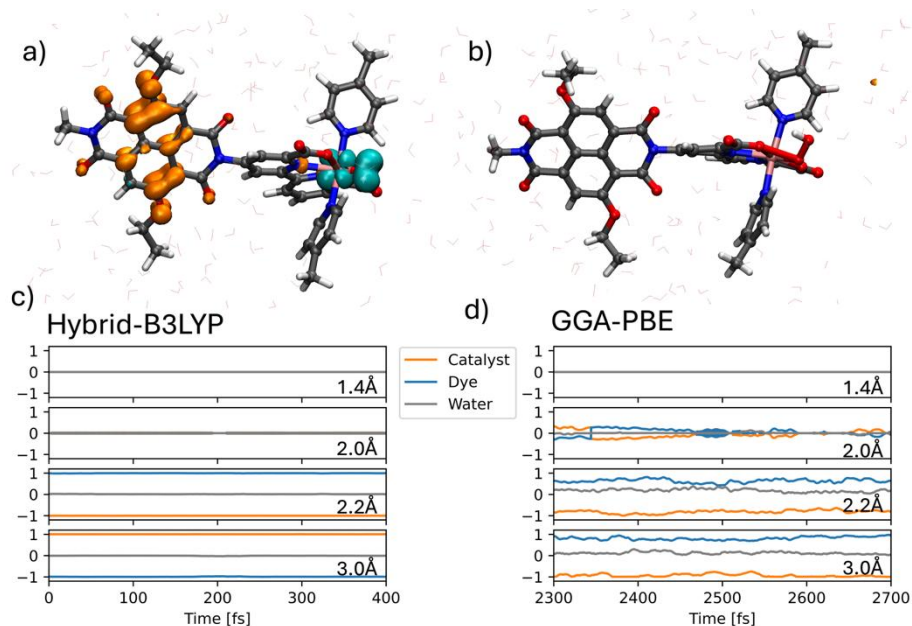


Figure 4.5. The top panels provide a visualization of the spin density of snapshots taken from the hybrid-B3LYP simulations with constrained O-O distances of 3.0 Å (a) and 1.4 Å (b), where the isosurface values were set to 0.003 for positive, and -0.003 for negative spin density contributions. Panels c) and d) plot the spin density population analysis on the catalyst (orange), dye (blue) and water (grey) as a function of simulation time. The local spin density on the specified fragments was obtained by summing over the atomic Mulliken spin density contributions.

Figure 4.5 shows that the simulations with constrained O-O distances longer than 2.0 Å exhibit consistently an open shell singlet spin-multiplicity, where the hole is located on the dye. The application of the pure-DFT functional leads to a

considerable fraction of spin density on the water solvent molecules. This is a commonly known artifact of GGA-based DFT.^[33,34] Interestingly, this spin delocalization is virtually eliminated in the simulations with the hybrid-B3LYP functional. The tendency of B3LYP to localize the spin density better than PBE becomes particularly apparent when the O-O distance is shortened to 2.2 Å. At that point, the integrated spin density on the dye is reduced to ~0.6 at the GGA level, indicating that the electron and hole are formed only partially. In contrast, the spin localization on the dye is preserved at the hybrid-B3LYP level. The GGA simulation at 2.0 Å shows that the electron-hole pair separation collapses after 2500 fs, which was found to coincide with the proton transfer event. In the simulations with an O-O bond distance shorter than 2.0 Å, the system forms consistently a closed-shell singlet, where the electron has transferred to the dye.

4.4.3 Dioxygen dissociation after the fourth PCET step

The initial structure for the equilibration simulations of the $^1\text{[Ru(IV)-OOH]-NDI}^+$ intermediate was extracted from the final part of the trajectory of the third PCET step, where the excess proton was removed from the water solvation environment. The system was equilibrated at the PBE level at room temperature for 2 ps before once more the photooxidation of the NDI was simulated by removing an electron from the simulation box. The evolution of the spin density on the dye, catalyst, and the water environment are plotted over time in Figure 4.6a in the top panel, while the dissociating O-H distance from the hydroperoxo ligand is shown in the bottom panel.

Chapter 4: Hybrid-DFT Molecular Dynamics Simulations of Photocatalytic Water Oxidation in a [Ru-bda]–Dye Complex

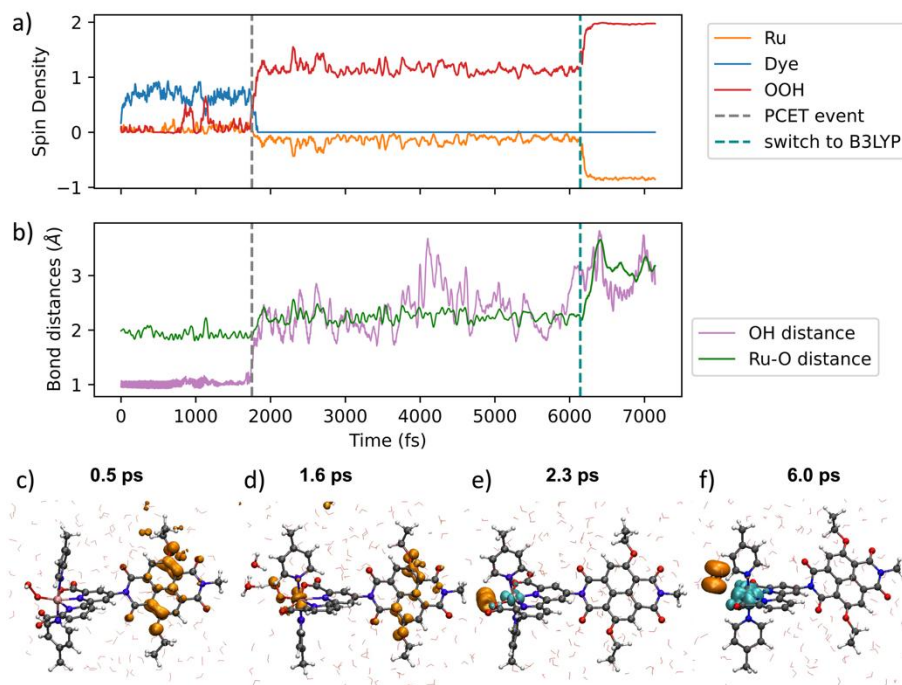


Figure 4.6. a) The red, blue, and orange traces represent the integrated spin moments on the O-O ligand, NDI dye, and ruthenium center, respectively. b) The purple line represents the length of the dissociating O-H bond, while the green line represents the Ru-O distance. c), d), e), and f) provide visualizations of the spin density at four stages which are characteristic for the PCET reaction. Isosurface values were set to 0.003 for positive, and -0.003 for negative spin density contributions.

Although the hole is initially delocalized over the solvent water molecules, most of the spin density localizes on the NDI within the first ~100 fs after oxidation of the system (Figure 4.6a and c). In the following ~1.7 ps the system remains in a stable state with the proton attached to the O-O ligand. Interestingly, two attempted electron transfers are observed prior to the final PCET event, at around 0.9 ps and 1.1 ps. At this stage, a water molecule is closely coordinated to the hydroperoxo ligand, however, there is no chain of water molecules to facilitate

long-range proton transfer. Subsequently, a second water molecule was observed to form a hydrogen bond interaction with the water molecule coordinating to the hydroperoxo ligand, allowing for the PCET event to occur (see Figure 4.6d). After the PCET, significant oscillations are observed of the spin density moving between the metal center and the oxygen ligand. Nevertheless, the performed simulations employing the PBE functional eventually appeared to favor a configuration where one of the triplet oxygen electrons recombines with the anti-ferromagnetically coupled ruthenium electron, forming what is best described as a doublet spin configuration on the oxygen ligand (see Figure 4.6e). This species remained stable over more than 4 ps of simulation time. Since GGA functionals are known to overestimate charge delocalization, it was decided to propagate the system for another 1 ps with the B3LYP functional.^[32–34] By including a fraction of screened-Hartree-Fock exchange, the two unpaired electrons localized on the dioxygen ligand exclusively, forming a local triplet (see Figure 4.6f). Consequently, the O₂ ligand dissociated rapidly from the catalyst after switching to the hybrid functional. This observation underlines the importance of including a fraction of exact exchange in this type of simulations and should be kept in mind for future studies on similar systems.

4.5 Conclusions

In summary, DFT-based molecular dynamics simulations were performed of the four proton-coupled electron transfer (PCET) steps in the catalytic water oxidation cycle of a [Ru^{III}(bda)(pic)₂(H₂O)]⁺ (bda = 2,2'-bipyridine-6,6'-dicarboxylic acid, pic = 4-picoline) catalyst, covalently bound to the 2,6-diethoxy-1,4,5,8-diimidenaphthalene (NDI) dye. The first part of this work addresses the coordination environment of the ruthenium center at the beginning of the catalytic cycle. The dynamics simulations reveal that the low valent [Ru^{III}(bda)(pic)₂(H₂O)]⁺ intermediate adopts a six-coordinated configuration, wherein coordination of the aqua ligand is followed by a lowering of the coordination number of the bda²⁻ ligand, either by elongation of the equatorial Ru-

Chapter 4: Hybrid-DFT Molecular Dynamics Simulations of Photocatalytic Water Oxidation in a [Ru-bda]–Dye Complex

$N_{bda^{2-}}$ bond or by elongation of the equatorial $Ru-O_{COO^-}$ bond. Following the first PCET step, the resulting $[Ru^{IV}(bda)(pic)_2(OH)]^+$ complex consistently maintained a 7-coordinated environment. This 7-coordinated environment is preserved also after the second, third, and fourth PCET steps.

To gain an understanding of the behavior of this catalyst when anchored to a surface, the O-O bond-forming step was considered to involve the nucleophilic attack of a water molecule on a single, high valent $Ru^V=O$ species. Using Blue Moon ensemble simulations at the B3LYP level, the barrier for this process was determined to be 20.3 ± 1.2 kcal mol⁻¹, corresponding to a catalytic rate of approximately 0.008 s⁻¹ (min = 0.001 s⁻¹, max = 0.06 s⁻¹) at 300 K. This rate represents a realistic estimate for systems where the catalyst is immobilized, and is four to eight orders of magnitude slower than the rates that have been reported in studies where the catalyst followed the binuclear mechanism.^[9,15] The oxidation potential of the employed NDI dye, which has been measured at 1.36 V vs Fc/Fc^+ ,^[88] was found to be slightly insufficient to drive the O-O bond formation. We found that the subsequent and final PCET step, in which the hydroperoxo ligand is oxidized to form O₂, happened spontaneously on the ab initio molecular dynamics timescale and will, therefore, not affect much the kinetics of the catalyst. Finally, we have evaluated the performance of the widely used GGA-PBE and the hybrid-B3LYP functionals in determining the reaction barriers, energetics, and description of spin localizations in the DFT-based molecular dynamics simulations. In addition to the slight changes in the relative energies of reactant and product states for the rate-determining O-O bond formation, it was found that the GGA functional exhibits a tendency to overestimate delocalization of spin density, leading to significant spin polarizations on the water environment and unphysical pairing of electrons on the O₂ ligand with an electron on the ruthenium center. The inclusion of exact exchange quenches delocalization, leading to the electron and hole densities that are localized on the catalyst and dye fragments of the system. The most notable effect of this correction on the dynamics was

observed for the dissociation of the O₂ ligand at the end of the catalytic cycle, which happened spontaneously with the hybrid functional while in the simulations with the GGA functional the oxygen molecule remained bound to the ruthenium complex.

4.6 References

- [1] S. Ardo, D. Fernandez Rivas, M. A. Modestino, V. Schulze Greiving, F. F. Abdi, E. Alarcon Llado, V. Artero, K. Ayers, C. Battaglia, J. P. Becker, D. Bederak, A. Berger, F. Buda, E. Chinello, B. Dam, V. Di Palma, T. Edvinsson, K. Fujii, H. Gardeniers, H. Geerlings, S. M. Hashemi, S. Haussener, F. Houle, J. Huskens, B. D. James, K. Konrad, A. Kudo, P. P. Kunturu, D. Lohse, B. Mei, E. L. Miller, G. F. Moore, J. Muller, K. L. Orchard, T. E. Rosser, F. H. Saadi, J. W. Schüttauf, B. Seger, S. W. Sheehan, W. A. Smith, J. Spurgeon, M. H. Tang, R. Van De Krol, P. C. K. Vesborg, P. Westerik, *Energy Environ. Sci.* **2018**, *11*, 2768–2783.
- [2] H. Tian, *Sustain. Energy Fuels* **2019**, *3*, 888–898.
- [3] J. H. Kim, D. Hansora, P. Sharma, J.-W. Jang, J. S. Lee, *Chem. Soc. Rev.* **2019**, *48*, 1908–1971.
- [4] S. Haussener, *Sol. Energy* **2022**, *246*, 294–300.
- [5] M. Grätzel, *Nature* **2001**, *414*, 338–344.
- [6] A. Vilanova, P. Dias, T. Lopes, A. Mendes, *Chem. Soc. Rev.* **2024**, *53*, 2388–2434.
- [7] S. Nitopi, E. Bertheussen, S. B. Scott, X. Liu, A. K. Engstfeld, S. Horch, B. Seger, I. E. L. Stephens, K. Chan, C. Hahn, J. K. Nørskov, T. F. Jaramillo, I. Chorkendorff, *Chem. Rev.* **2019**, *119*, 7610–7672.
- [8] J. Seo, H. Nishiyama, T. Yamada, K. Domen, *Angew. Chem. Int. Ed.* **2018**, *57*, 8396–8415.
- [9] L. Duan, F. Bozoglian, S. Mandal, B. Stewart, T. Privalov, A. Llobet, L. Sun, *Nat. Chem.* **2012**, *4*, 418–423.
- [10] J. Yang, L. Wang, S. Zhan, H. Zou, H. Chen, M. S. G. Ahlquist, L. Duan, L. Sun, *Nat. Commun.* **2021**, *12*, 373.
- [11] H. Li, F. Li, Y. Wang, L. Bai, F. Yu, L. Sun, *ChemPlusChem* **2016**, *81*, 1056–1059.
- [12] D. L. Ashford, W. Song, J. J. Concepcion, C. R. K. Glasson, M. K. Brennaman, M. R. Norris, Z. Fang, J. L. Templeton, T. J. Meyer, *J. Am. Chem. Soc.* **2012**, *134*, 19189–19198.
- [13] L. Alibabaei, M. K. Brennaman, M. R. Norris, B. Kalanyan, W. Song, M. D. Losego, J. J. Concepcion, R. A. Binstead, G. N. Parsons, T. J. Meyer, *Proc. Natl. Acad. Sci. U.S.A.* **2013**, *110*, 20008–20013.
- [14] J. T. Kirner, J. J. Stracke, B. A. Gregg, R. G. Finke, *ACS Appl. Mater. Interfaces* **2014**, *6*, 13367–13377.
- [15] B. Zhang, L. Sun, *J. Am. Chem. Soc.* **2019**, *141*, 5565–5580.
- [16] T. Liu, G. Li, N. Shen, L. Wang, B. J. J. Timmer, S. Zhou, B. Zhang, A. Kravchenko, B. Xu, M. S. G. Ahlquist, L. Sun, *CCS Chem.* **2022**, *4*, 2481–2490.
- [17] R. Matheu, A. Ghaderian, L. Francàs, P. Chernev, M. Z. Ertem, J. Benet-Buchholz, V. S. Batista, M. Haumann, C. Gimbert-Suriñach, X. Sala, A. Llobet, *Chem. Eur. J.* **2018**, *24*, 12838–12847.
- [18] Q. Daniel, P. Huang, T. Fan, Y. Wang, L. Duan, L. Wang, F. Li, Z. Rinkevicius, F. Mamedov, M. S. G. Ahlquist, S. Styring, L. Sun, *Coord. Chem. Rev.* **2017**, *346*, 206–215.
- [19] S. Zhan, D. Mårtensson, M. Purg, S. C. L. Kamerlin, M. S. G. Ahlquist, *Angew. Chem. Int. Ed.* **2017**, *56*, 6962–6965.
- [20] D. Wang, S. L. Marquard, L. Troian-Gautier, M. V. Sheridan, B. D. Sherman, Y. Wang, M. S. Eberhart, B. H. Farnum, C. J. Dares, T. J. Meyer, *J. Am. Chem. Soc.* **2018**, *140*, 719–726.

Chapter 4: Hybrid-DFT Molecular Dynamics Simulations of Photocatalytic Water Oxidation in a [Ru-bda]–Dye Complex

- [21] D. Wang, M. S. Eberhart, M. V. Sheridan, K. Hu, B. D. Sherman, A. Nayak, Y. Wang, S. L. Marquard, C. J. Dares, T. J. Meyer, *Proc. Natl. Acad. Sci. U.S.A.* **2018**, *115*, 8523–8528.
- [22] X. Yan, K. Sakai, H. Ozawa, *ACS Catal.* **2023**, *13*, 13456–13465.
- [23] H. Song, A. Amati, A. Pannwitz, S. Bonnet, L. Hammarström, *J. Am. Chem. Soc.* **2022**, *144*, 19353–19364.
- [24] J. Feng, X. Li, Y. Luo, Z. Su, M. Zhong, B. Yu, J. Shi, *Chinese J. Catal.* **2023**, *48*, 127–136.
- [25] D. W. Shaffer, Y. Xie, J. J. Concepcion, *Chem. Soc. Rev.* **2017**, *46*, 6170–6193.
- [26] N. Govindarajan, A. Tiwari, B. Ensing, E. J. Meijer, *Inorg. Chem.* **2018**, *57*, 13063–13066.
- [27] M. Schilling, R. A. Cunha, S. Lubner, *J. Chem. Theory Comput.* **2020**, *16*, 2436–2449.
- [28] M. Schilling, R. Ketkaew, S. Lubner, *Chimia* **2021**, *75*, 195–201.
- [29] M. Schilling, R. A. Cunha, S. Lubner, *ACS Catal.* **2020**, *10*, 7657–7667.
- [30] K. R. Gorantla, B. S. Mallik, *J. Phys. Chem. C* **2020**, *124*, 205–218.
- [31] K. R. Gorantla, B. S. Mallik, *J. Phys. Chem. A* **2022**, *126*, 3301–3310.
- [32] Aron J. Cohen, Paula Mori-Sánchez, Weitao Yang, *Science* **2008**, *321*, 792–794.
- [33] C. Li, X. Zheng, N. Q. Su, W. Yang, *Natl. Sci. Rev.* **2018**, *5*, 203–215.
- [34] K. R. Bryenton, A. A. Adeleke, S. G. Dale, E. R. Johnson, *WIREs Comput. Mol. Sci.* **2023**, *13*, e1631.
- [35] J. Cheng, M. Sulpizi, J. VandeVondele, M. Sprik, *ChemCatChem* **2012**, *4*, 636–640.
- [36] M. Guidon, J. Hutter, J. VandeVondele, *J. Chem. Theory Comput.* **2010**, *6*, 2348–2364.
- [37] T. de Haas, H. van Overeem, H. J. M. de Groot, F. Buda, *ChemPhotoChem* **2022**, e202200274.
- [38] L. Martínez, R. Andrade, E. G. Birgin, J. M. Martínez, *J. Comput. Chem.* **2009**, *30*, 2157–2164.
- [39] AMS2022.102, SCM, Theoretical Chemistry. Vrije Universiteit: Amsterdam, The Netherlands. <https://www.scm.com>.
- [40] D. Van Der Spoel, E. Lindahl, B. Hess, G. Groenhof, A. E. Mark, H. J. C. Berendsen, *J. Comput. Chem.* **2005**, *26*, 1701–1718.
- [41] W. L. Jorgensen, J. Chandrasekhar, J. D. Madura, R. W. Impey, M. L. Klein, *J. Chem. Phys.* **1983**, *79*, 926–935.
- [42] W. L. Jorgensen, D. S. Maxwell, J. Tirado-Rives, *J. Am. Chem. Soc.* **1996**, *118*, 11225–11236.
- [43] L. S. Dodda, I. Cabeza de Vaca, J. Tirado-Rives, W. L. Jorgensen, *Nucleic Acids Res.* **2017**, *45*, W331–W336.
- [44] W. L. Jorgensen, J. Tirado-Rives, *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 6665–6670.
- [45] L. S. Dodda, J. Z. Vilseck, J. Tirado-Rives, W. L. Jorgensen, *J. Phys. Chem. B* **2017**, *121*, 3864–3870.
- [46] C. E. S. Bernardes, José. N. Canongia Lopes, M. E. M. Da Piedade, *J. Phys. Chem. A* **2013**, *117*, 11107–11113.
- [47] H. J. C. Berendsen, J. P. M. Postma, W. F. Van Gunsteren, A. DiNola, J. R. Haak, *J. Chem. Phys.* **1984**, *81*, 3684–3690.
- [48] M. Parrinello, A. Rahman, *J. Appl. Phys.* **1981**, *52*, 7182–7190.
- [49] S. Nosé, M. L. Klein, *Mol. Phys.* **1983**, *50*, 1055–1076.
- [50] T. D. Kühne, M. Iannuzzi, M. Del Ben, V. V. Rybkin, P. Seewald, F. Stein, T. Laino, R. Z. Khaliullin, O. Schütt, F. Schiffrmann, D. Golze, J. Wilhelm, S. Chulkov, M. H. Bani-Hashemian, V. Weber, U. Borštnik, M. Taillefumier, A. S. Jakobovits, A. Lazzaro, H. Pabst, T. Müller, R. Schade, M. Guidon, S. Andermatt, N. Holmberg, G. K. Schenter, A. Hehn, A. Bussy, F. Belleflamme, G. Tabacchi, A. Glöß, M. Lass, I. Bethune, C. J. Mundy, C. Plessl, M. Watkins, J. VandeVondele, M. Krack, J. Hutter, *J. Chem. Phys.* **2020**, *152*, 194103.
- [51] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1997**, *78*, 1396–1396.
- [52] S. Grimme, *J. Comput. Chem.* **2004**, *25*, 1463–1473.
- [53] S. Grimme, *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2011**, *1*, 211–228.

- [54] S. Grimme, *Chem. - Eur. J.* **2012**, *18*, 9955–9964.
- [55] J. VandeVondele, J. Hutter, *J. Chem. Phys.* **2007**, *127*, 114105.
- [56] S. Goedecker, M. Teter, J. Hutter, *Phys. Rev. B* **1996**, *54*, 1703–1710.
- [57] C. Hartwigsen, S. Goedecker, J. Hutter, *Phys. Rev. B* **1998**, *58*, 3641–3662.
- [58] M. Krack, *Theor. Chem. Acc.* **2005**, *114*, 145–152.
- [59] J. VandeVondele, J. Hutter, *J. Chem. Phys.* **2003**, *118*, 4365–4369.
- [60] A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098.
- [61] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 1372–1377.
- [62] S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* **1980**, *58*, 1200–1211.
- [63] P. J. Stephen, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623–11627.
- [64] M. Guidon, F. Schiffmann, J. Hutter, J. VandeVondele, *J. Chem. Phys.* **2008**, *128*, 214104.
- [65] L. Li, L. Duan, Y. Xu, M. Gorlov, A. Hagfeldt, L. Sun, *Chem. Commun.* **2010**, *46*, 7307.
- [66] Y. Gao, X. Ding, J. Liu, L. Wang, Z. Lu, L. Li, L. Sun, *J. Am. Chem. Soc.* **2013**, *135*, 4219–4222.
- [67] H. Li, F. Li, B. Zhang, X. Zhou, F. Yu, L. Sun, *J. Am. Chem. Soc.* **2015**, *137*, 4332–4335.
- [68] F. Li, K. Fan, L. Wang, Q. Daniel, L. Duan, L. Sun, *ACS Catal.* **2015**, *5*, 3786–3790.
- [69] Y. Gao, L. Zhang, X. Ding, L. Sun, *Phys. Chem. Chem. Phys.* **2014**, *16*, 12008.
- [70] B. D. Sherman, Y. Xie, M. V. Sheridan, D. Wang, D. W. Shaffer, T. J. Meyer, J. J. Concepcion, *ACS Energy Lett.* **2017**, *2*, 124–128.
- [71] M. S. Eberhart, D. Wang, R. N. Sampaio, S. L. Marquard, B. Shan, M. K. Brennaman, G. J. Meyer, C. Dares, T. J. Meyer, *J. Am. Chem. Soc.* **2017**, *139*, 16248–16255.
- [72] L. Zhang, Y. Gao, X. Ding, Z. Yu, L. Sun, *ChemSusChem* **2014**, *7*, 2801–2804.
- [73] D. Wang, M. V. Sheridan, B. Shan, B. H. Farnum, S. L. Marquard, B. D. Sherman, M. S. Eberhart, A. Nayak, C. J. Dares, A. K. Das, R. M. Bullock, T. J. Meyer, *J. Am. Chem. Soc.* **2017**, *139*, 14518–14525.
- [74] M. Yamamoto, Y. Nishizawa, P. Chábera, F. Li, T. Pascher, V. Sundström, L. Sun, H. Imahori, *Chem. Commun.* **2016**, *52*, 13702–13705.
- [75] Y. Shao, J. M. De Ruiter, H. J. M. De Groot, F. Buda, *J. Phys. Chem. C* **2019**, *123*, 21403–21414.
- [76] Y. Shao, H. J. M. D. Groot, F. Buda, *ChemSusChem* **2020**, *13*, 1–9.
- [77] J. Belić, A. Förster, J. P. Menzel, F. Buda, L. Visscher, *Phys. Chem. Chem. Phys.* **2022**, *24*, 197–210.
- [78] J. P. Menzel, A. Papadopoulos, J. Belić, H. J. M. de Groot, L. Visscher, F. Buda, *J. Phys. Chem. C* **2020**, *124*, 27965–27976.
- [79] A. Monti, C. F. A. Negre, V. S. Batista, L. G. C. Rego, H. J. M. De Groot, F. Buda, *J. Phys. Chem. Lett.* **2015**, *6*, 2393–2398.
- [80] M. Hilgendorff, V. Sundström, *J. Phys. Chem. B* **1998**, *102*, 10505–10514.
- [81] R. J. Ellingson, J. B. Asbury, S. Ferrere, H. N. Ghosh, J. R. Sprague, T. Lian, A. J. Nozik, *J. Phys. Chem. B* **1998**, *102*, 6455–6458.
- [82] J. B. Asbury, N. A. Anderson, E. Hao, X. Ai, T. Lian, *J. Phys. Chem. B* **2003**, *107*, 7376–7386.
- [83] J. P. Menzel, M. Kloppenburg, J. Belić, H. J. M. de Groot, L. Visscher, F. Buda, *J. Comput. Chem.* **2021**, *42*, 1885–1894.
- [84] D. Lebedev, Y. Pineda-Galvan, Y. Tokimaru, A. Fedorov, N. Kaeffer, C. Copéret, Y. Pushkar, *J. Am. Chem. Soc.* **2018**, *140*, 451–458.
- [85] A. Barducci, G. Bussi, M. Parrinello, *Phys. Rev. Lett.* **2008**, *100*, 020603.
- [86] M. Sprik, G. Ciccotti, *J. Chem. Phys.* **1998**, *109*, 7737–7744.
- [87] G. Ciccotti, M. Ferrario, *Mol. Sim.* **2004**, *30*, 787–793.
- [88] R. S. K. Kishore, O. Kel, N. Banerji, D. Emery, G. Bollot, J. Mareda, A. Gomez-Casado, P. Jonkheijm, J. Huskens, P. Maroni, M. Borkovec, E. Vauthey, N. Sakai, S. Matile, *J. Am. Chem. Soc.* **2009**, *131*, 11106–11116.

4A. Appendix

4A.1 Calculation of the reaction rates from the activation free energies

The reaction rates reported in this paper were calculated according to the following equation from transition state theory:^[1,2]

$$k = \frac{k_B T}{h} e^{\frac{-\Delta G}{RT}}$$

Where k is the reaction rate, k_B is the Boltzmann constant, T is the temperature, h is Planck's constant, ΔG is the activation energy and R is the universal gas constant.

4A.2 Equilibrations of the $^2(\text{NDI-}[\text{Ru(III)-OH}_2]^+)$, $^1(\text{NDI-}[\text{Ru(IV)-OH}]^+)$, $^2(\text{NDI-}[\text{Ru(V)=O}]^+)$, and $^1(\text{NDI-}[\text{Ru(IV)-OOH}]^+)$ intermediates

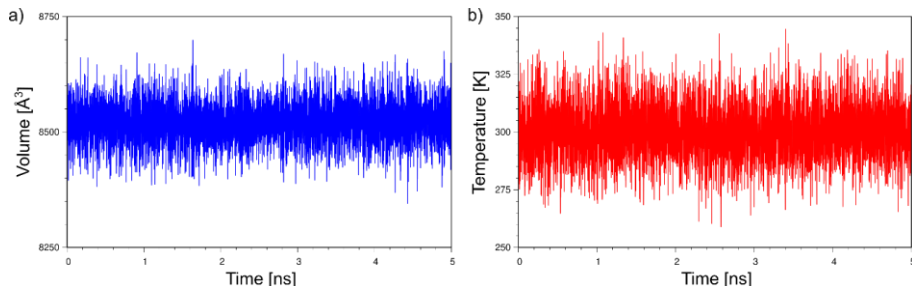


Figure 4A.1. Panels a and b provide the simulation box volume in Å³ (blue line) and the simulation temperature in K (red line) along the last 5 ns of classical MD NPT equilibration, respectively.

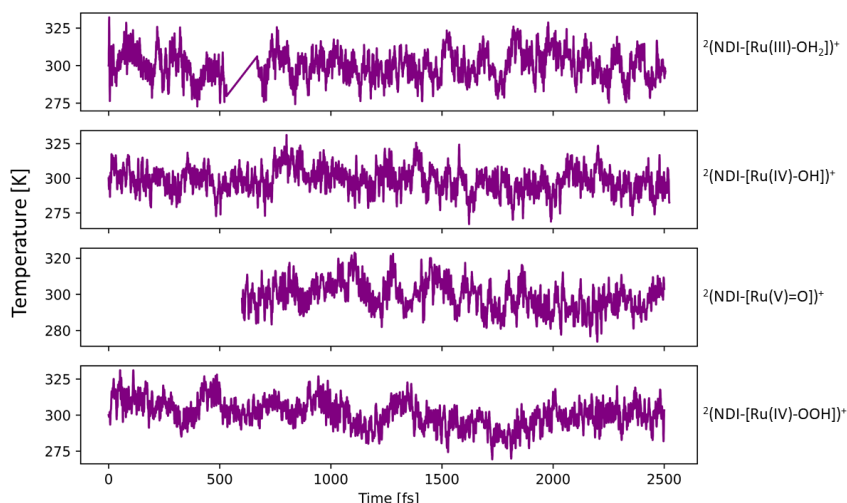


Figure 4A.2. Temperatures of the equilibration runs at the DFT (PBE) level for the $^2(\text{NDI}[\text{Ru}(\text{III})\text{-OH}_2])^+$, $^1(\text{NDI}[\text{Ru}(\text{IV})\text{-OH}])^+$, $^2(\text{NDI}[\text{Ru}(\text{V})\text{=O}])^+$, and $^1(\text{NDI}[\text{Ru}(\text{IV})\text{-OOH}])^+$ intermediates.

4A.3 Additional information on the simulations on the $^2(\text{NDI}[\text{Ru}(\text{III})\text{-OH}_2])^+$ complex

4A.3.1 Time evolution of ligand bond distances in $^2(\text{NDI}[\text{Ru}(\text{III})\text{-OH}_2])^+$ complex

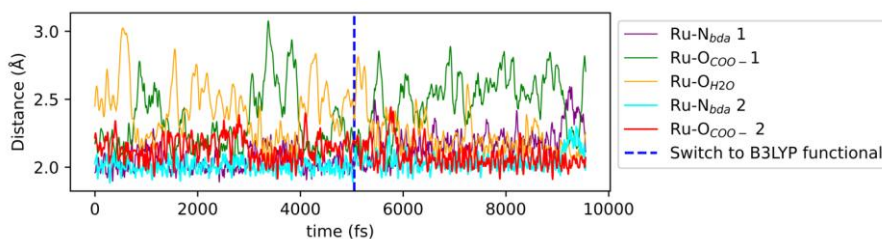


Figure 4A.3. Time evolution of the bond distances between the ruthenium center, the nitrogen backbone atoms and the carboxylate oxygen atoms of the equatorial bda^{2-} ligand, and the aqua ligand.

Chapter 4: Hybrid-DFT Molecular Dynamics Simulations of Photocatalytic Water Oxidation in a [Ru-bda]–Dye Complex

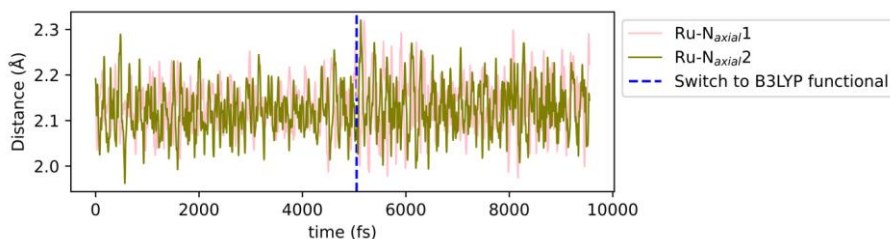


Figure 4A.4. Time evolution of the bond distances between the ruthenium center and the nitrogen atoms of the axial picoline ligands.

4A.3.2 First PCET step

The first PCET reaction was simulated at the PBE level of theory. One α -electron was removed from the dye fragment of the molecule, leading to an open-shell-singlet configuration with one unpaired α -electron on the catalyst and one unpaired β -electron on the dye. The spin-densities on the dye and on the catalyst part of the complex as well as the O-H₁ and O-H₂ bond lengths are plotted in Figure 4A.5. Interestingly, the open-shell state was found to form only partially, with a total spin-moment of only 0.4 on the dye and -0.6 on the catalyst and decayed within 50 fs to the closed-shell spin-configuration. A single point energy calculation performed after removing the electron and using tighter SCF convergence criteria converges to an electronic state where the open shell character is almost negligible ($<|0.1|$ Mulliken spin density accumulation on the catalyst and dye fragments of the molecule). This suggests that the reactant and product electronic states are already very close in energy, and this electron transfer step in the catalytic cycle is essentially instantaneous upon oxidation of the dye and does not depend on nuclear rearrangements.

After the electron has transferred to the dye, the resulting Ru^{IV}-bda complex was found reside consistently in a 7-coordinated configuration, where both carboxylate ligands, as well as the aqua ligand bind strongly to the ruthenium and the bond distances are ~ 2.0 Å. As a response to the oxidation event and binding

of the aqua ligand, the O-H bonds of the ligand are activated, leading to alternating elongations of their respective bond lengths (named O-H₁ and O-H₂ in Figure 4A.5). The dissociated proton remains within close proximity of the hydroxide ligand during the remainder of the simulation, instead of long-range transfer by a Grotthuss mechanism. The fact that the proton does not diffuse further from the hydroxide ligand within the simulated time domain could be due to limited sampling or to finite box size effects.

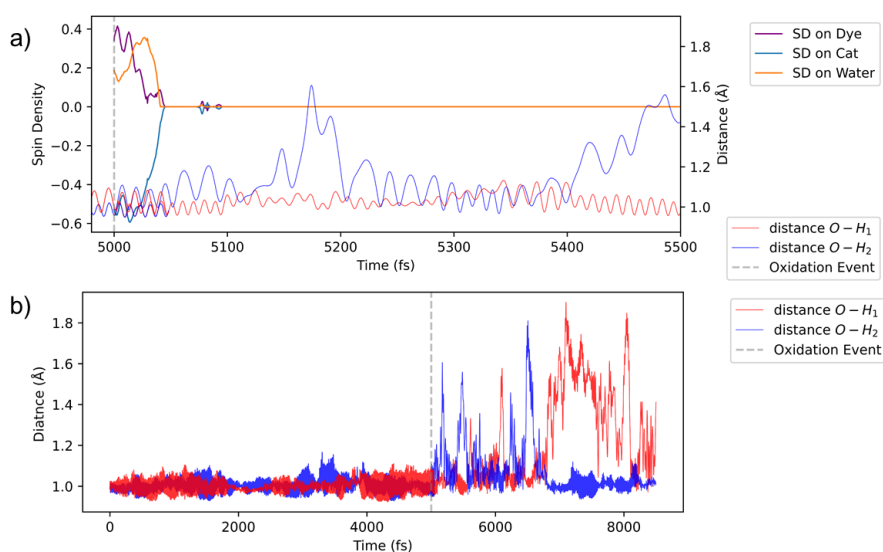


Figure 4A.5. Panel a provides the time-evolution of the spin-densities (SD) on the catalyst, dye, and water environment, as well as the two O-H bond distances of the aqua ligand for the first 0.5 ps after the oxidation event. The O-H bond distances of the aqua ligand are also plotted in b for the duration of the entire simulation.

4A.4 Additional information on the simulations of the $^1(\text{NDI}[\text{Ru(IV)}\text{-OH}]^+)$ complex

4A.4.1 The second PCET step

As for the first PCET step, the $^1(\text{NDI}[\text{Ru(IV)}\text{-OH}]^+)$ system was equilibrated for 5 ps, where now one proton was removed from the simulation box. At this stage, the complex strongly binds the OH^- ligand in a symmetric 7-coordinated environment of the Ru^{IV} ion with $d_{\text{Ru-O}} \approx 1.90 \text{ \AA}$. A strong hydrogen bonding network emerged near the hydroxide ligand, where a nucleophilic water was coordinated to the proton, which was in turn also coordinated by two water molecules (see Figure 4A.7).

The photooxidation process was simulated by removing one electron from the simulation box, now resulting in a doublet $^2(\text{NDI}^+[\text{Ru(IV)}\text{-OH}]^+)$ species with the unpaired electron found predominantly on the NDI. In Figure 4A.6, the integrated spin density on the dye, catalyst, and water environment are plotted over time in blue, orange, and green respectively. In the same plot, also the length of the dissociating O-H bond is plotted. It is observed that the two quantities evolve in a highly correlated manner, underlining the concerted nature of this PCET step. The photoexcited state was found to live significantly longer in the second PCET step than for the first PCET step, indicating that the electronic state in which the dye is oxidized, and not the ruthenium, does present a minimum on the potential energy surface in this catalytic step. Completion of the electron transfer from the Ru^{IV} -bda complex to the dye was observed in $\sim 400 \text{ fs}$. Immediately after removal of the electron on the dye, some spin density on the catalyst has already recombined with the excess hole density on the NDI. Also, a significant fraction was found to delocalize on the water environment. This was also observed for the first PCET step. Given the tendency of GGA-functionals to overemphasize charge delocalization, it was decided to replicate this PCET step at the B3LYP level of theory.^[3–6] Contrarily to the simulations with the PBE functional, the excess spin localized exclusively on the dye component of the

complex post-oxidation, as depicted in Figure 4A.6, panels b and c. The system was observed to remain in the reactant state for the duration of 2.5 ps, without undergoing a spontaneous PCET event. To obtain a reactive trajectory, Metadynamics (metaD) was used, as implemented in the Plumed library. A constant bias potential characterized by a height of $0.621 \text{ kcal mol}^{-1}$ and width $0.1 \text{ \AA}$, was deposited every 10 fs, acting along a collective variable defined by the dissociating O-H bond distance. Interestingly, the electron transfer event was observed to unfold on an ultrashort timescale, with the total spin density on the dye transferring to the catalyst within a few femtoseconds. This observation aligns with the expectation that in Born-Oppenheimer molecular dynamics simulations, the electronic system remains strictly quenched to the absolute ground state. In previous work, we have shown that the electron transfer in this catalyst-dye system can be described by two electronic states that cross along the proton transfer reaction coordinate.^[7] The proton and electron dynamics in this PCET event are strongly coupled, as it is observed that the electron transfer takes place as soon as the dissociating O-H bond is elongated to about $\sim 1.4 \text{ \AA}$. Due to the aggressive biasing, it is not meaningful to analyze the obtained free energy surface associated with the MetaD simulation.

In summary, a GGA-based simulation predicted the PCET event to occur spontaneously, while the hybrid-functional-based simulation does not show this event on the few picoseconds timescale. This observation aligns with benchmark tests that show that GGA functionals consistently underestimate proton transfer barriers in water by about 3 to $3.5 \text{ kcal mol}^{-1}$.^[8] Based on previous work in our group, we expect the GGA-DFT predicted barrier for ruthenium-catalyzed oxidation of the hydroxide ligand to be of the order of 2 kcal mol^{-1} .^[9] With hybrid functionals this would thus increase to $\sim 5 \text{ kcal mol}^{-1}$. Therefore, the apparent discrepancy between the GGA and hybrid-DFT simulations can be attributed to the difference in the predicted activation barriers.

Chapter 4: Hybrid-DFT Molecular Dynamics Simulations of Photocatalytic Water Oxidation in a [Ru-bda]–Dye Complex

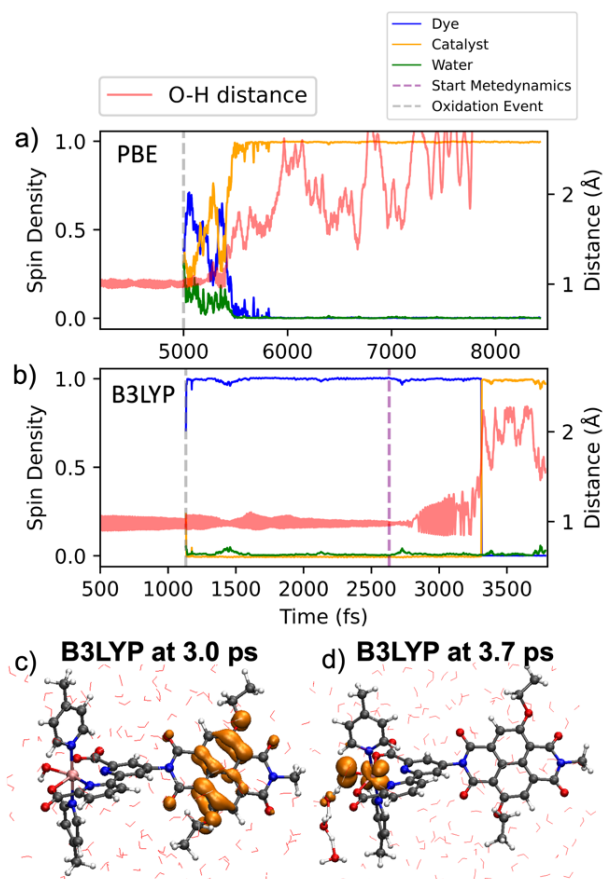


Figure 4A.6. The evolution of the spin density on the dye (blue), catalyst (yellow), and water (green) components of the system are plotted over time as calculated with the PBE functional (a) and with the B3LYP functional (b). The dissociation O-H bond lengths are plotted in red. In the simulations with the B3LYP functional, the spin densities are localized exclusively on the dye and on the catalyst, whereas with the PBE functional the spin density is delocalized significantly on the water. The oxidation event is indicated with a vertical dashed line in both figures. The vertical purple dashed line in b indicates the moment from which bias potentials were deposited. Figures c) and d) provide a visualization of the spin density right before and after the PCET event in the simulation performed with the B3LYP functional.

4A.4.2 Manifestation of a hydrogen bonding network around the $^1(\text{NDI-}[\text{Ru(IV)}\text{-OH}]^+)$ intermediate

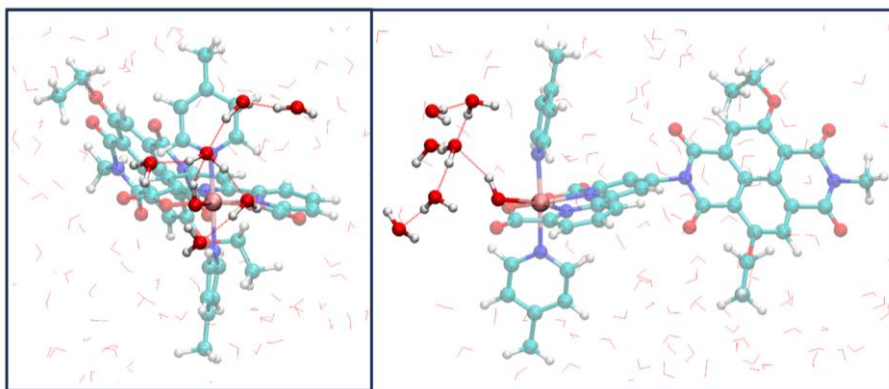


Figure 4A.7. Front- (left) and side-view (right) of the hydrogen bonding network that form around the hydroxide ligand during the equilibration run of the $^1(\text{NDI-}[\text{Ru(IV)}\text{-OH}]^+)$ intermediate.

4A.5 Spin-densities of $^2(\text{NDI-}[\text{Ru(III)}\text{-OH}_2]^+)$, $^2(\text{NDI-}[\text{Ru(V)}\text{=O}]^+)$ and $^2(\text{NDI}^{\bullet+}\text{-}[\text{Ru(V)}\text{=O}]^+)$ intermediates

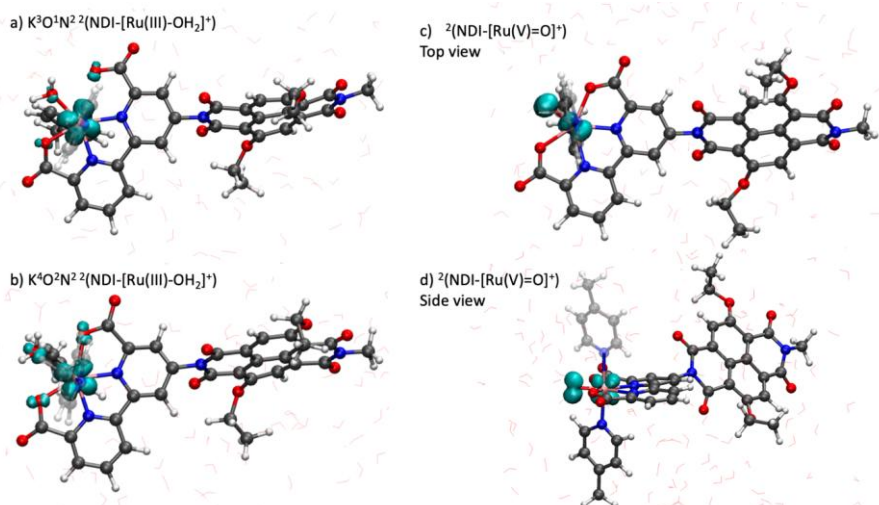


Figure 4A.8. Spin-densities on the $^2(\text{NDI-}[\text{Ru(III)}\text{-OH}_2]^+)$ (a and b) and $^2(\text{NDI-}[\text{Ru(V)}\text{=O}]^+)$ intermediates (c and d).

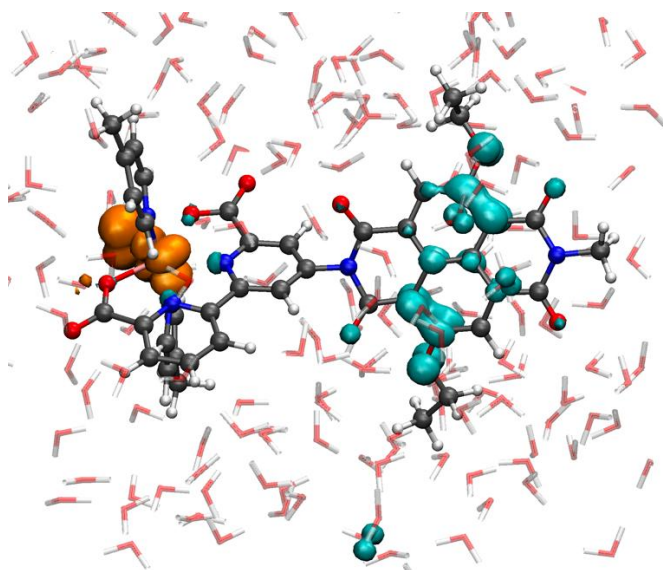


Figure 4A.9. Spin-density on the $^2(\text{NDI}^{+}\text{-}[\text{Ru}(\text{V})=\text{O}]^{+})$ intermediate.

4A.6 Enhanced sampling methods to accelerate the rate determining O-O formation step

4A.6.1 Metadynamics Simulations of O-O bond formation

As collective variable (CV), the O-O distance between the oxo ligand and the nearest water molecule in the solvent shell was chosen.^{3,12} A quadratic wall was employed at a CV value of 3.1 Å to restrict the explorable configuration space to a minimum by preventing the nucleophilic water molecule from drifting away. The initial bias with a height 0.5 kcal mol⁻¹ and width of 0.1 Å was adaptively scaled during the simulation based on a target bias factor of 35 $k_{\text{B}}T$. After 22.7 ps, the initial bias height had decreased to about ~0.15 kcal mol⁻¹, while the fluctuations in the collective variable did not yet get close to a transition, which we expected to be around 1.75 Å. At that point, it was decided to continue the simulation with a constant Gaussian height of 0.2 kcal mol⁻¹. The Gaussians were deposited along the CV every 50 fs. The Metadynamics simulation terminated

after the first crossing event, which took place after 31.0 ps. This is justifiable since the purpose of this study was to investigate the activation barrier and mechanism for the PCET step in question and not the free energy difference between the reactant and product states.

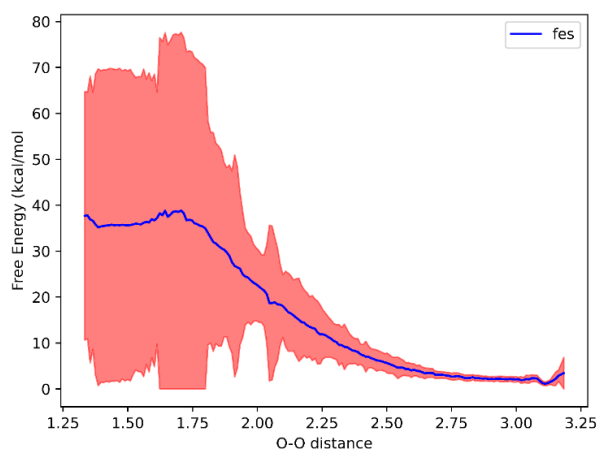


Figure 4A.10. Plot of the free energy profile obtained from the Metadynamics simulations (blue) performed at the GGA-PBE level of theory. The total simulation time amounted to ~ 31 ps. The error (1 standard deviation) for the free energy is given in the red shaded area. The barrier of O-O bond formation was found to amount to ~ 40 kcal mol $^{-1}$. The high uncertainty in the obtained free energy profile indicates that a considerably longer simulation needs to be carried out to obtain a converged result.

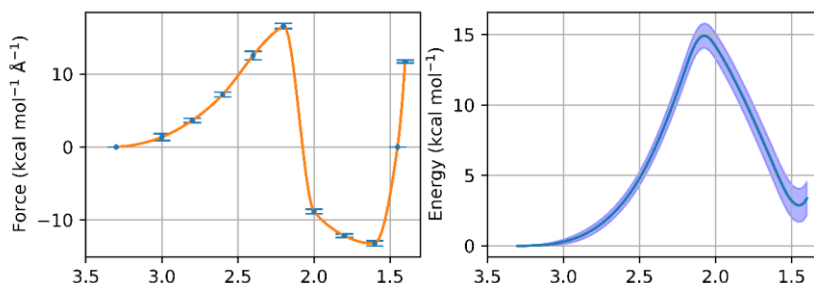


Figure 4A.11. FES calculated at the PBE-level, plotted as a function of the O-O distance reaction coordinate. The free energy was obtained by thermodynamic integration of a 100-point Akima spline fit of the averaged constraint forces, $\langle \lambda \rangle$, at different values of the O-O bond distance. The error bars on $\langle \lambda \rangle$ are obtained by block averaging. The error on the FES is calculated by integrating the upper and lower bounds of the $\langle \lambda \rangle$ profile.

4A.6.2 Blue moon simulations of O-O bond formation

The Blue Moon Ensemble Free energy profile was constructed from nine AIMD simulations performed with a constrained O-O distance of 3.0, 2.8, 2.6, 2.4, 2.2, 2.0, 1.8, 1.6 and 1.4 Å. In addition, simulations in the reactant and product states were performed to determine the equilibrium O-O bond lengths. The average bond length in the product state was found to fluctuate around 1.45 Å. To improve the FES integral quality, an additional point was added on the y-axis at an x-value of 1.45 Å. The radial distribution function of the oxo-ligand with all oxygen atoms of the solvent water molecules is plotted in Figure 4A.12. The data for this figure were extracted from the 2.5 ps equilibration of the open-shell singlet state. It is observed that the function reaches its first maximum in the range from 3.3 to 4.0. It was, therefore, decided to add another point in the force profile at 3.3 Å. The final free energy profile was obtained by thermodynamic integration of a 100-point Akima spline interpolation of the mean forces along the reaction path.

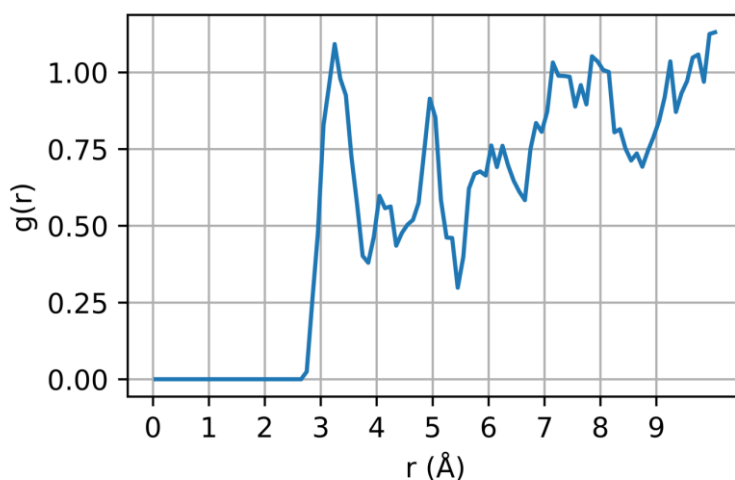


Figure 4A.12. Radial pair distribution function, $g(r)$, of the oxo ligand with all solvent water oxygen atoms. The distance r is given in Å.

Plots of the temperature during the constrained AIMD simulations are provided in Figure 4A.13 for the PBE simulations. It is observed that all simulations equilibrated within 0.5 ps. Figure 4A.14 provides a plot of the temperature evolution in the B3LYP simulations, which appear to be properly equilibrated from the start. The time evolutions of the constraint forces are plotted in Figure 4A.15 (PBE) and Figure 4A.16 (B3LYP), as well as the running average which culminates in the mean force for each specific run.

Chapter 4: Hybrid-DFT Molecular Dynamics Simulations of Photocatalytic Water Oxidation in a [Ru-bda]–Dye Complex

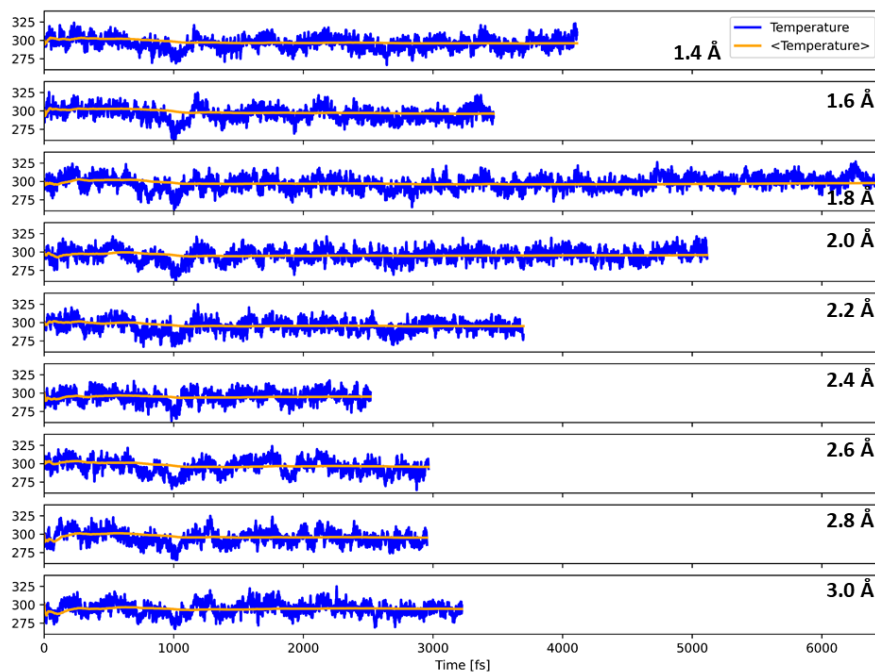


Figure 4A.13. Temperature evolution during Blue Moon ensemble simulations (PBE) of the $^1(\text{NDI}^{+\bullet}\text{-}[\text{Ru}(\text{V})=\text{O}]^+)$ intermediate and an H_2O molecule with constrained intramolecular O-O distances.

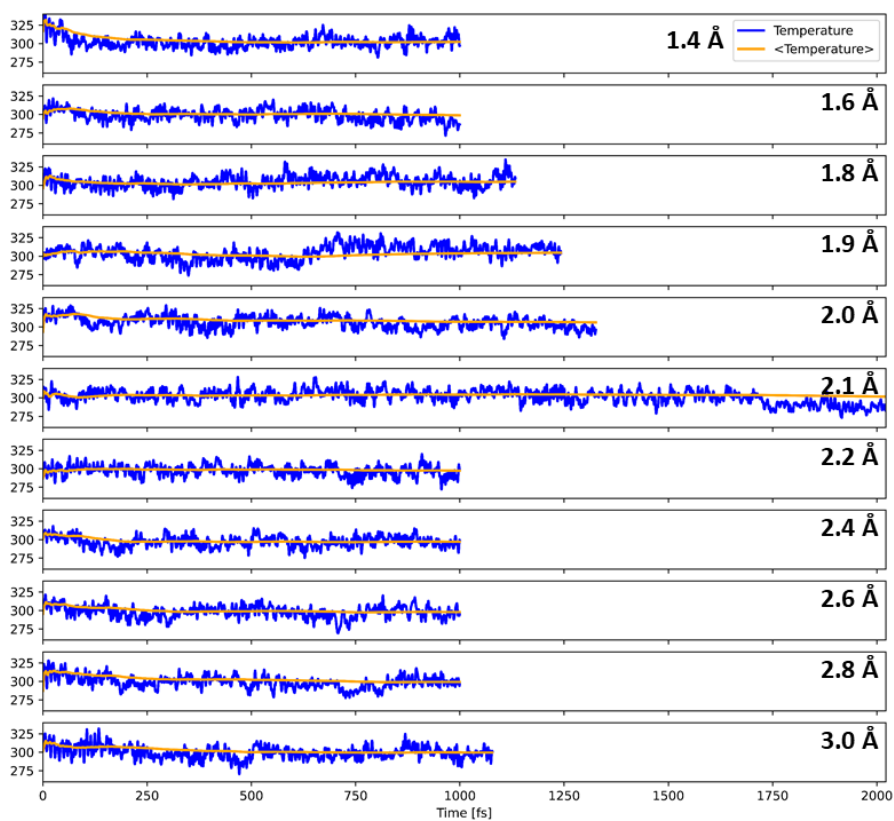


Figure 4A.14. Temperature evolution during Blue Moon ensemble simulations (B3LYP) of the $^1(\text{NDI}^{+\bullet}-[\text{Ru}(\text{V})=\text{O}]^+)$ intermediate and an H_2O molecule with constrained intramolecular O-O distances.

Chapter 4: Hybrid-DFT Molecular Dynamics Simulations of Photocatalytic Water Oxidation in a [Ru-bda]–Dye Complex

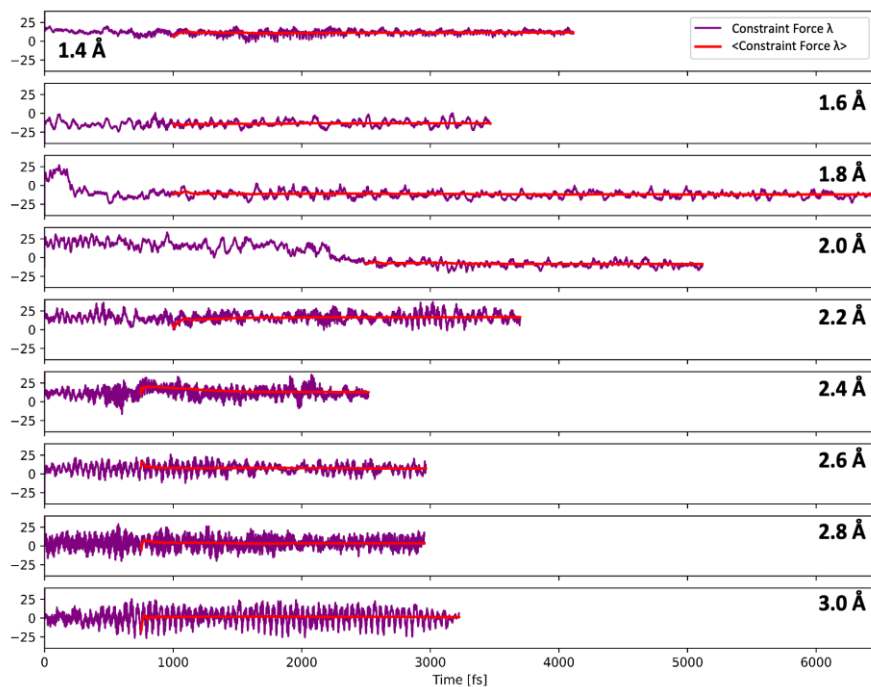


Figure 4A.15. Constraint force evolution during Blue Moon ensemble simulations (PBE) of the $^1(\text{NDI}^{+\bullet}-[\text{Ru}(\text{V})=\text{O}]^+)$ intermediate and an H_2O molecule with constrained intramolecular O-O distances.

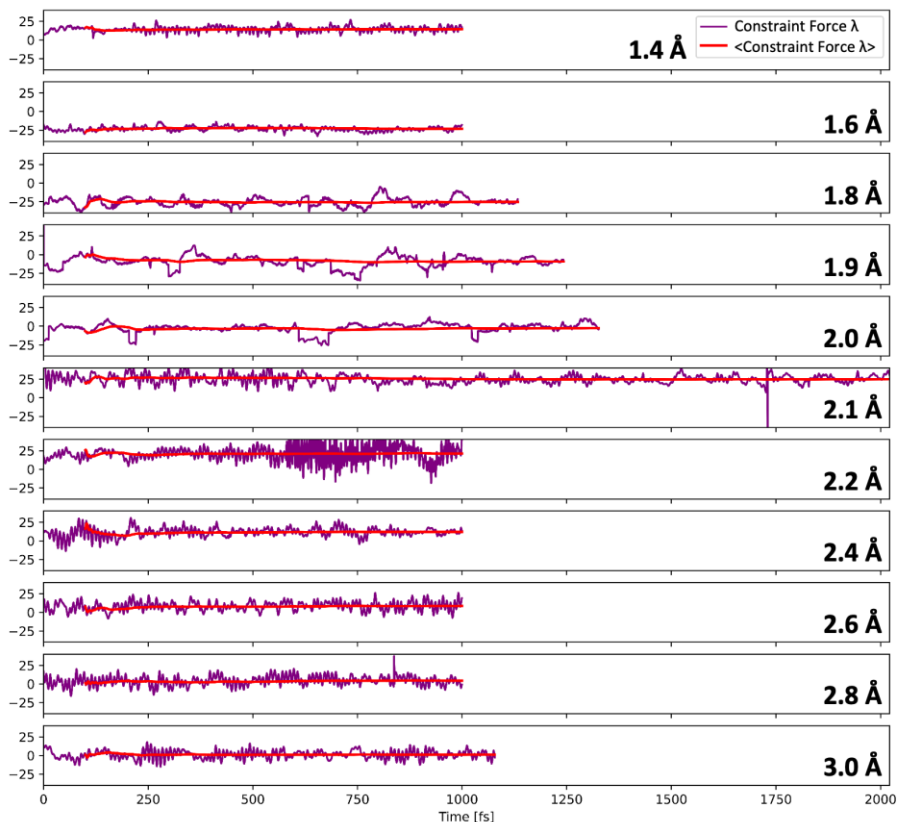


Figure 4A.16. Constraint force evolution during Blue Moon ensemble simulations (B3LYP) of the $^1(\text{NDI}^+ \cdots [\text{Ru}(\text{V})=\text{O}]^+)$ intermediate and an H_2O molecule with constrained intramolecular O-O distances.

4A.6.3 Estimation of error bars using block averaging

To reduce the time correlation effects in the error estimate of the mean forces, the total trajectory was cut in blocks. The error was then estimated as one standard deviation in the averaged constrain force values among all blocks:

$$\sigma = \sqrt{\frac{1}{N} \sum_{i=1}^N (x_i - \mu)^2}$$

Where i runs over the block indexes, N is the total number of blocks, x_i is the λ average of the block, and μ is the mean λ over all blocks.

Chapter 4: Hybrid-DFT Molecular Dynamics Simulations of Photocatalytic Water Oxidation in a [Ru-bda]–Dye Complex

In Figure 4A.17 (PBE) and A18 (B3LYP), the calculated error is plotted as a function of the block size for all simulations. Due to time correlations, the errors initially increase steeply with the block size, however, when the block size increases to ~ 100 time steps, the errors plateau. Most of the calculations display some noise in the error estimates with larger block sizes, which can be attributed to the decreasing number of blocks at that stage. Nevertheless, all error estimates appear to converge within the given simulation time, and the error bar estimates were extracted by taking the maximum value running average of the error.

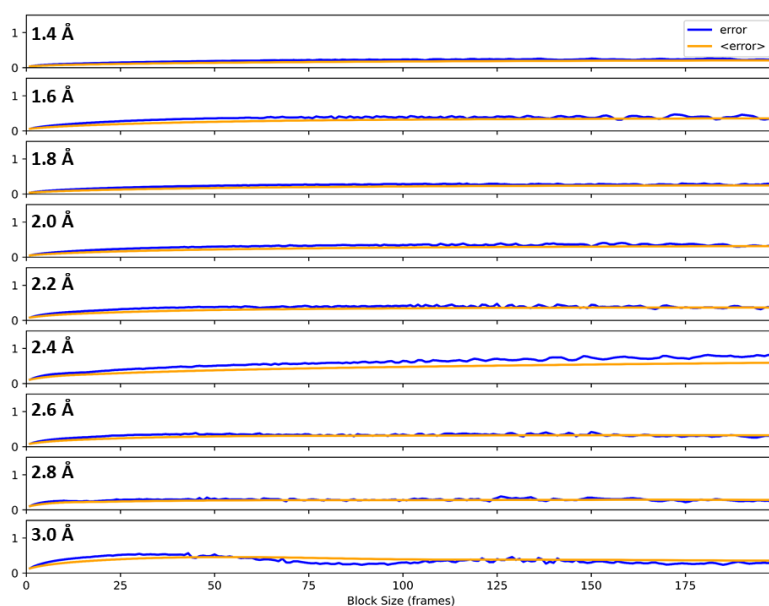


Figure 4A.17. Convergence of the mean force error with increasing block lengths for the different constrained simulations (PBE). The error is quantified as one standard deviation in the value of λ calculated between different blocks.

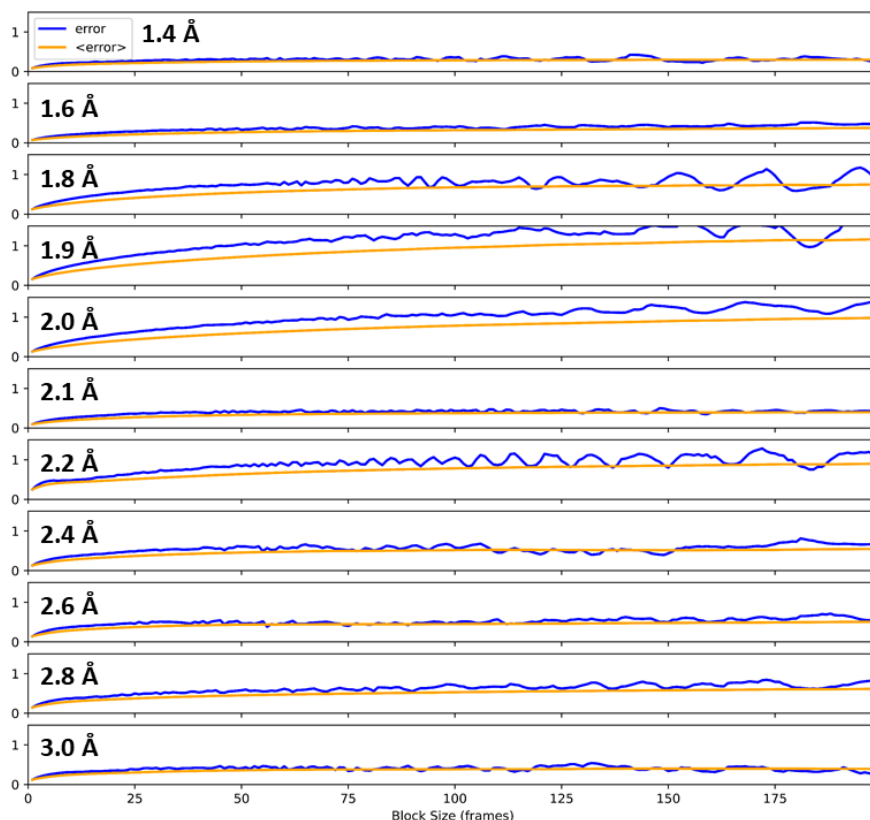


Figure 4A.18. Convergence of the mean force error with increasing block lengths for the different constrained simulations (B3LYP). The error is quantified as one standard deviation in the value of λ calculated between different blocks.

4A.7 Level of theory benchmarks

To justify the applied level of theory, several benchmark studies were performed. The first benchmark involved geometry optimization of the $^1(\text{NDI}^+[\text{Ru}(\text{IV})\text{-OH}])^+$ and $^1(\text{NDI}^+[\text{Ru}(\text{V})\text{=O}])^{2+}$ intermediates. The calculations were performed at four different levels of theory, which are outlined in Table 4A.1. The geometry optimizations were carried out with convergence criteria of $1 \cdot 10^{-4}$ Hartree Bohr $^{-1}$ and $5 \cdot 10^{-5}$ Hartree Bohr $^{-1}$ for the max and RMS changes in the forces, and $1 \cdot 10^{-4}$ Bohr and $5 \cdot 10^{-5}$ Bohr for the max and RMS changes in the atomic displacements. A similar test has been carried out by Meijer and coworkers, who found that the

Chapter 4: Hybrid-DFT Molecular Dynamics Simulations of Photocatalytic Water Oxidation in a [Ru-bda]–Dye Complex

geometry of a similar ruthenium based water oxidation catalyst was properly described with the DZVP basis in conjunction with a plane wave cut-off of 280 Ry.^[10] After the optimization, we compared the bond distances from the Ru center to all atoms in the first coordination sphere. For the $^1(\text{NDI}^+-[\text{Ru}(\text{V})=\text{O}])^{2+}$ intermediate, we investigated also the Mulliken spin accumulation on the combined Ruthenium atom and oxo ligand. The investigated bond distances for the $^1(\text{NDI}-[\text{Ru}(\text{IV})-\text{OH}])^+$ complex are provided in Table 4A.2, while the investigated bond distances and Mulliken spin accumulations for the $^1(\text{NDI}^+-[\text{Ru}(\text{V})=\text{O}])^{2+}$ complex are provided in Table 4A.3.

Table 4A.1. The four different sets of numerical parameters that were benchmarked.

	GGA lower setting	GGA higher setting	Hybrid lower setting	Hybrid higher setting
Functional	PBE	PBE	B3LYP	B3LYP
Gaussian basis	DZVP-MOLOPT-GTH ^a	TZVP-MOLOPT-GTH ^a	DZVP-MOLOPT-GTH ^a	TZVP-MOLOPT-GTH ^a
PW basis	280Ry	400Ry	280Ry	400Ry
EPS Schwartz	-	-	10E–6	10E–8
ADMM basis	-	-	cFIT3 ^b	pFIT3 ^b

^a In all cases the DZVP-SR-MOLOPT-GTH basis was employed for ruthenium, as no larger basis was available.

^b For ruthenium the cFIT11 and FIT11 ADMM basis sets were used for the low and high settings calculations, respectively.

Table 4A.2. Comparison of coordination bond lengths to Ru(IV)-OH intermediate computed at different levels of theory. See Figure 4A.19. a) for the atomic labeling in the Ru complex.

	GGA lower setting	GGA higher setting	Hybrid lower setting	Hybrid higher setting	Experiment [11] Ru(IV)- OH
Ru-N _{bda} 1	2.13	2.12	2.16	2.17	2.09
Ru-N _{bda} 2	2.13	2.13	2.17	2.17	2.09
Ru-O _{coo-} 1	2.10	2.10	2.10	2.11	2.04
Ru-O _{coo-} 2	2.09	2.08	2.06	2.08	2.03
Ru-N _{pic} 1	2.11	2.11	2.11	2.11	2.08
Ru-N _{pic} 2	2.10	2.10	2.10	2.11	2.08
Ru-O _{OH}	1.93	1.93	1.92	1.91	1.96

Table 4A.3. Comparison of coordination bond lengths to Ru(V)=O computed at different levels of theory. See Figure 4A.19. a) for the atomic labeling in the Ru complex.

	GGA lower setting	GGA higher setting	Hybrid lower setting	Hybrid higher setting	Experiment ^[12] Ru(V)=O
Ru-N _{bda} 1	2.27	2.27	2.29	2.30	~2.1 Å
Ru-N _{bda} 2	2.26	2.26	2.28	2.30	~2.1 Å
Ru-O _{coo-} 1	2.15	2.15	2.16	2.14	~2.1 Å
Ru-O _{coo-} 2	2.13	2.13	2.11	2.13	~2.1 Å
Ru-N _{pic} 1	2.12	2.12	2.13	2.12	~2.1 Å
Ru-N _{pic} 2	2.12	2.12	2.12	2.12	~2.1 Å
Ru-O _{oxo}	1.70	1.70	1.70	1.70	1.75±0.02 Å
Spin Moment on Ru(V)=O	0.744	0.748	1.047	1.045	-

Chapter 4: Hybrid-DFT Molecular Dynamics Simulations of Photocatalytic Water Oxidation in a [Ru-bda]–Dye Complex

Table 4A.2 shows that the investigated bond distances are in close agreement with the available X-ray data of the $[(\text{bda})(\text{pic})_2\text{Ru}(\text{IV})\text{-OH}]^+$ complex. Minor differences, on the order of 0.05 Å, may arise from covalent binding of the NDI-dye to the bda^{2-} backbone, intrinsic DFT errors or limited X-ray resolution.

Importantly, the overall trends in bond lengths within the $^1(\text{NDI}[\text{Ru}(\text{IV})\text{-OH}])^+$ complex are reproduced, including the shortening of the Ru-O bond distance from ~1.96 in Ru(IV)-OH to ~1.75 Å in Ru(V)=O. Increasing the computational settings did not significantly affect the Mulliken spin accumulation on the Ru(V)=O intermediate, although a difference between functionals is observed. Overall, this test thus shows that accurate structural and electronic properties are produced with a Gaussian basis of DZVP quality, in conjunction with a plane wave basis with a cutoff of 280 Ry.

The second benchmark involved DFT-MD simulations of the $^1(\text{NDI}^{\bullet+}[\text{Ru}(\text{V})=\text{O}])^{2+}$ intermediate. All benchmark DFT-MD simulations were equilibrated for 300 fs and subsequently propagated for another ~0.5 to 1 ps. To verify the quality of the performed MD simulations, we computed the oxygen-oxygen radial pair distribution function (RDF). The RDF's obtained at the different levels of theory are displayed in Figure 4A.19b. We do not observe significant changes between the RDF's computed at various levels of theory, further validating the level of theory employed in this paper.

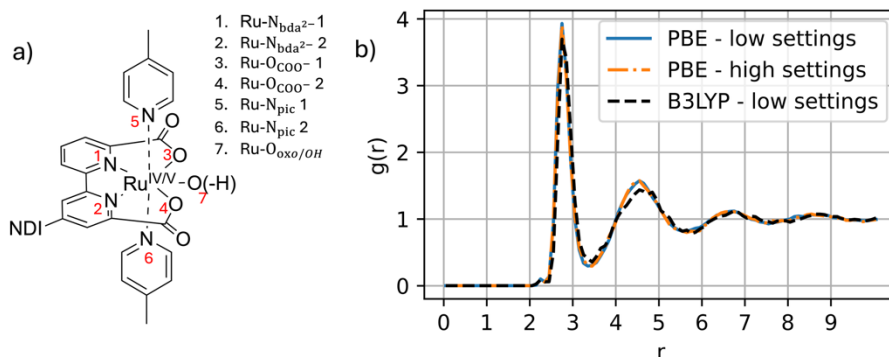


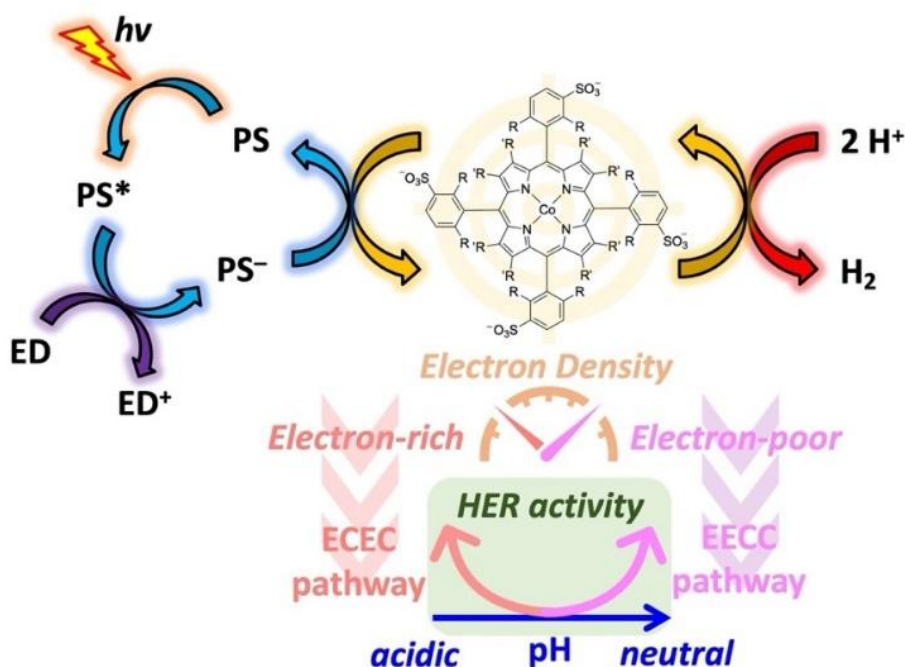
Figure 4A.19. a) Schematic structure and atomic labeling of the Ru complex; b) O-O radial distribution function computed from molecular dynamics simulation with PBE/DZVP+280Ry (blue), PBE/TZVP+400Ry (red) and B3LYP/DZVP/+280Ry (black). The distance r is given in Å.

4A.8 References

- [1] H. Eyring, *J. Chem. Phys.* **1935**, 3, 107–115.
- [2] E. Pollak, P. Talkner, *Chaos* **2005**, 15, 026116.
- [3] J. Cheng, M. Sulpizi, J. VandeVondele, M. Sprik, *ChemCatChem* **2012**, 4, 636–640.
- [4] Aron J. Cohen, Paula Mori-Sánchez, Weitao Yang, *Science* **2008**, 321, 792–794.
- [5] C. Li, X. Zheng, N. Q. Su, W. Yang, *Natl. Sci. Rev.* **2018**, 5, 203–215.
- [6] K. R. Bryenton, A. A. Adeleke, S. G. Dale, E. R. Johnson, *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2023**, 13, e1631.
- [7] T. de Haas, H. van Overeem, H. J. M. de Groot, F. Buda, *ChemPhotoChem* **2023**, e202200274.
- [8] A. Hassanali, F. Giberti, J. Cuny, T. D. Kühne, M. Parrinello, *Proc. Natl. Acad. Sci. U.S.A.* **2013**, 110, 13723–13728.
- [9] Y. Shao, J. M. De Ruiter, H. J. M. De Groot, F. Buda, *J. Phys. Chem. C* **2019**, 123, 21403–21414.
- [10] N. Govindarajan, A. Tiwari, B. Ensing, E. J. Meijer, *Inorg. Chem.* **2018**, 57, 13063–13066.
- [11] L. Duan, A. Fischer, Y. Xu, L. Sun, *J. Am. Chem. Soc.* **2009**, 131, 10397–10399.
- [12] D. Lebedev, Y. Pineda-Galvan, Y. Tokimaru, A. Fedorov, N. Kaeffer, C. Copéret, Y. Pushkar, *J. Am. Chem. Soc.* **2018**, 140, 451–458.

Chapter 5: Electron-Withdrawing Effects of Cobalt Porphyrin Catalysts Boost Homogeneous Photocatalytic Hydrogen Evolution in Neutral Aqueous Solutions

DFT calculations show that the mechanism for photocatalytic hydrogen evolution in cobalt porphyrins depends on the ligand substituents. This change in mechanism results in two distinct optimal pH conditions for the catalysis to occur.



This chapter is based on:

C. Liu*, T. de Haas*, F. Buda, S. Bonnet. Electron-Withdrawing Effects of Cobalt Porphyrin Catalysts Boost Homogeneous Photo-catalytic Hydrogen Evolution in Neutral Aqueous Solutions. *ACS Catal.* **2025**, 15 (6), 4681-4697 (*contributed equally).

Chapter 5: Electron-Withdrawing Effects of Cobalt Porphyrin Catalysts Boost Homogeneous Photocatalytic Hydrogen Evolution in Neutral Aqueous Solutions

5.1 Abstract

Molecular catalysts offer an ideal platform for conducting mechanistic studies of the hydrogen evolution reaction (HER) due to their electronic tunability. This study explores a series of anionic Co(III)- and Zn(II)-porphyrin complexes with electron-donating ($[M(\text{OMeP})]^{n-}$, $[M(\text{MeP})]^{n-}$) and electron-withdrawing ($[M(\text{F8P})]^{n-}$, $[M(\text{F16P})]^{n-}$) substituents. The activity of these complexes for the HER was analyzed in homogeneous photocatalytic conditions using $[\text{Ru}(\text{bpy})_3]^{2+}$ as a photosensitizer under blue light (450 nm) irradiation. The substituent-induced electronic effects were found to tightly control the activity and mechanism of the photocatalytic HER. The electron-rich $[\text{Co}(\text{OMeP})]^{3-}$ catalyst showed higher activity in acidic media (pH 4.1) with a maximum TOF of $7.2 \pm 0.4 \text{ h}^{-1}$ and TON of 175 ± 5 after 39.5 hours. DFT calculations were performed to investigate the HER mechanism. H_2 formation was found to initiate following proton-coupled reduction of a $\text{Co}^{\text{III}}\text{-H}$ hydride intermediate in such conditions. In contrast, the electron-poor $[\text{Co}(\text{F16P})]^{3-}$ catalyst was most active at neutral pH (7.0), achieving a maximum TOF of $6.7 \pm 0.3 \text{ h}^{-1}$ and TON of 70 ± 3 after 39.5 hours. Instead of forming the $\text{Co}^{\text{III}}\text{-H}$ hydride, an additional ligand-based reduction led to a ligand-protonated intermediate. This work demonstrates that electron-poor HER catalysts can outperform electron-rich catalysts near neutral pH conditions.

5.2 Introduction

Light-induced H_2 evolution in aqueous solutions has attracted much attention since it could contribute to providing a sustainable and environmentally friendly energy conversion system.^[1] In order to drive this photoreaction efficiently, well-performing hydrogen-evolving catalysts (HECs) must be prepared, the design of which remains challenging.^[2–4] Recently, studies on molecular hydrogen evolution catalysts have multiplied due to their numerous advantages: 1) they mimic the active sites of heterogeneous catalysts and allow to approach catalytic mechanisms with atomic precision;^[5–7] 2) ligand functionalization allows for fine-tuning the coordination sphere and electronic density of the metal center, which is a powerful tool to establish relationships between the properties of the metal center and its photocatalytic performances;^[7,8] and 3) they can be integrated in supramolecular water-splitting systems, also in combination with solid-state materials and catalysts.^[9–11]

In the last decade, molecular HECs have been extensively studied for photocatalytic hydrogen evolution, especially those made of first-row transition metals.^[12–28] Many of those catalysts are based on cobalt, which is particularly attractive as it is available in larger quantities on Earth than platinum or ruthenium, and because it has more than five accessible oxidation states.^[29,30] Usually, these catalysts show better catalytic properties in mildly acidic conditions (pH 4–5), where more protons are available for the fast generation of H_2 . On the other hand, coupling proton reduction and water oxidation to achieve a full water splitting scheme, may be more favorable in neutral conditions, because water oxidation becomes more challenging at acidic pH. Still, examples of cobalt-based HECs working at pH 7.0 in homogeneous aqueous solutions are very rare.^[31,32]

Photocatalytic H_2 -evolving systems contain, next to the catalyst, a photosensitizer (PS) and a sacrificial electron donor (ED). In such 3-component systems the much higher concentration of the ED, compared to the hydrogen evolution catalyst (HEC), usually favors kinetically the excited photosensitizer PS^* to be quenched reductively by the ED to produce the reduced photosensitizer PS^- (Step 2 in Figure

Chapter 5: Electron-Withdrawing Effects of Cobalt Porphyrin Catalysts Boost Homogeneous Photocatalytic Hydrogen Evolution in Neutral Aqueous Solutions

5.1a).^[4] PS⁻ then reduces the HEC to HEC⁻ (Step 3), an electron-transfer step driven by the driving force E_{dr} (in V), defined as the difference between the redox potential of the PS/PS⁻ couple and the catalytic onset potential, itself defined as the potential at which electrocatalytic H₂ evolution catalyzed by HEC becomes significant. This process, when repeated twice, leads to the formation of an H₂ molecule (Step 4). In such a system a good balance between E_{dr} and the overpotential of the catalyst (η) is needed to keep both Step 3 and Step 4 fast.^[8] Functionalization of the catalyst with electron-donating or electron-withdrawing groups in principle allows for optimization of E_{dr} and η . However, for synthetic reasons it is not always easy to vary systematically the redox properties of a cobalt complex to optimize its redox potential for catalytic hydrogen reduction.^[19,33]

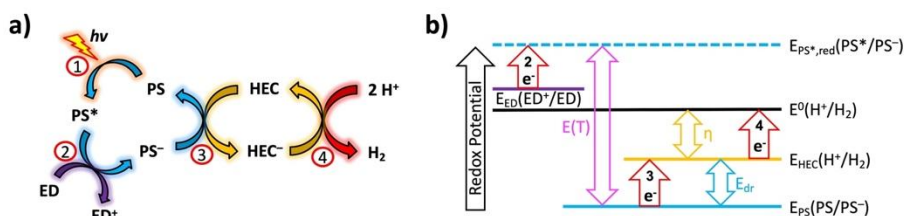


Figure 5.1. a) Simplified photocatalytic mechanism and b) relation between the redox potentials (in V) of different redox couples of the reductive quenching pathway in a three-component molecular photocatalytic hydrogen-evolution system. ED: sacrificial electron donor; PS: photosensitizer; HEC: hydrogen evolution catalyst; $E(T)$: triplet excited state energy of the PS; η : overpotential of the catalyst; E_{dr} : driving force (in V) of the electron-transfer step from the reduced photosensitizer PS⁻ to the catalyst (see text for exact definition).

Porphyrin ligands offer stable and rigid coordination sites for metal centers, while being readily tunable with functional substituents. This makes cobalt porphyrin a very attractive compound for HEC development.^[1,33–35] Importantly, two hydrogen evolution mechanisms for Step 4 (Figure 5.1a) have been reported with

cobalt porphyrin catalysts.^[36] In the first one, initial electroreduction of the Co^{II} center to Co^{I} is followed directly by a chemical oxidative protonation (EC mechanism), forming a Co^{III} hydride ($\text{Co}^{\text{III}}\text{-H}$). The second electrochemical reduction step then leads to fast formation of dihydrogen via the protonolysis pathway.^[37–40] Weak acids, typically do not protonate the Co^{I} metal center and a second reduction step is required before oxidative protonation and subsequent protonolysis can occur.^[35–38,41] Similar behavior has been observed for copper porphyrins and aminopyridine cobalt complexes.^[42,43] The first mechanism is referred to as an ECEC mechanism, while the second is usually denoted as EECC. As the formal $\text{Co}^{\text{I}}/\text{Co}^0$ couple has been shown to be partially ligand based, the EECC mechanism can involve catalysis on the ligand rather than on the metal center.^[37] Therefore, the activity of a cobalt catalyst (Step 4 in Figure 5.1a) may depend strongly on the pH, and the different mechanisms may be contingent on the electron-density on the metal catalyst. In general, it remains poorly understood which influence electron-withdrawing or electron-donating groups have on the (photo)catalytic activity of HEC, and in particular on the pH dependence.

To bridge this knowledge gap, in this work a family of sulfonated, water-soluble $\text{Co}(\text{III})$ -porphyrin complexes was prepared bearing either electron-donating ($[\text{Co}(\text{OMeP})]^{3-}$, $[\text{Co}(\text{MeP})]^{3-}$) or electron-withdrawing ($[\text{Co}(\text{F8P})]^{3-}$, $[\text{Co}(\text{F16P})]^{3-}$) substituents (Figure 5.2). This series of compounds was used to investigate the effect of the electron density of the ligand on homogeneous photocatalytic hydrogen evolution in presence of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ as photosensitizer (PS), and ascorbic acid (AA) in combination with tris(2-carboxyethyl)phosphine hydrochloride (TCEP) as sacrificial electron donor (ED). Using TCEP as final electron donor allows ascorbate to be recycled, enabling it to function as a reversible electron relay. This additional donor is known to significantly suppress electron back transfer from PS^- to the ascorbate radical, sometimes leading to much higher turnover numbers in photocatalytic hydrogen evolution compared with using ascorbate only.^[12,44] The pH dependence of the (photo)catalytic properties of these systems was investigated and compared to those of the Zn^{2+}

Chapter 5: Electron-Withdrawing Effects of Cobalt Porphyrin Catalysts Boost Homogeneous Photocatalytic Hydrogen Evolution in Neutral Aqueous Solutions

analogues, in which the metal center cannot accommodate any changes of the oxidation state, while the ligand remains potentially redox active. The mechanism of cobalt-porphyrin catalyzed hydrogen evolution is here clarified with DFT calculations, which show a change from an ECEC to an EECC mechanism by reducing the electron richness of the cobalt center. Consequently, the electron-poor catalyst favors a ligand-based mechanism over a metal-centered mechanism, resulting in increased catalytic activity at higher pH, highlighting a new design principle for proton reduction catalysts for solar-to-fuel devices.

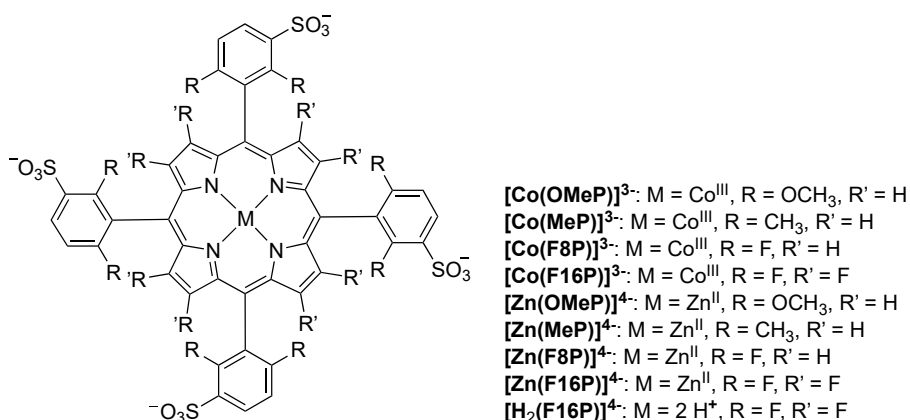


Figure 5.2. Chemical structures of the water-soluble metal porphyrin complexes and free base ligands used in this work. All compounds were isolated as Na^+ salts.

5.3 Results

5.3.1 Synthesis

The tetra-sulfonated, free-base porphyrin ligands $\text{Na}_4[\text{H}_2(\text{OMeP})]$,^[8] $\text{Na}_4[\text{H}_2(\text{MeP})]$,^[45] $\text{Na}_4[\text{H}_2(\text{F8P})]$,^[46] $\text{Na}_4[\text{H}_2(\text{F16P})]$,^[47] and their metal complexes $\text{Na}_3[\text{Co}(\text{F8P})]$,^[48,49] $\text{Na}_4[\text{Zn}(\text{F8P})]$,^[50] $\text{Na}_4[\text{Zn}(\text{F16P})]$,^[47] were synthesized according to reported methods. The other Co(III) and Zn(II) porphyrin compounds described in this work are new and were synthesized via refluxing the free-base ligands with Co(II) sulfate or Zn(II) dichloride in Milli-Q water for 12 h. Na^+ -

loaded ion exchange resin was used to exchange the counter ions with Na^+ , and the complexes were purified by size-exclusion chromatography in order to remove excess inorganic salts. According to NMR all cobalt compounds were diamagnetic and hence contained low-spin Co(III) ions. The Co(III) porphyrin complexes were formed by aerial oxidation of Co(II) during purification.^[48,49,51] A full characterization is given in the Supplementary Information (Figure 5A.1-5A.6).

5.3.2 Electrochemical properties

The electron-richness of a ligand influences the redox and electrocatalytic properties of its metal complex.^[7,32] A classical idea in hydrogen-evolution catalysis is that lowering the pH values renders most catalysts more efficient at catalyzing the HER. The redox properties of the Co(III)- and Zn(II)-porphyrin complexes were hence studied with electrochemical methods in pH 7.0 and pH 4.1 aqueous solutions and N,N-Dimethylformamide (DMF) solution. Cyclic voltammetry (CV), linear sweep voltammetry (LSV), and differential pulse voltammetry (DPV), were recorded using a glassy-carbon (GC) working electrode in an aqueous phosphate buffer or a tetrabutylammonium hexafluorophosphate (TBAPF₆) DMF solution.

The initial reduction of Co(III)-porphyrin ($\text{Co}^{\text{III}}(\text{P})$) complexes to Co(II)-porphyrin ($\text{Co}^{\text{II}}(\text{P})$) takes place at positive potentials vs NHE. While this reduction was difficult to detect in aqueous solution, a distinct reduction wave was clearly observable in DMF. This behavior is illustrated in Figure 5A.7a, which presents the CV of $[\text{Co}(\text{F8P})]^{3-}$ in DMF with increasing water content. Based on this analysis, after the first reduction, the DPV traces of the four cobalt porphyrin complexes at pH 7.0 (Figure 5.3a) are assigned to reduction of the $\text{Co}^{\text{II}}(\text{P})$ to Co(I)-porphyrin ($\text{Co}^{\text{I}}(\text{P})$). Lowering the electron density of the complex led to a more negative potential of this second reduction wave, which was observed at -0.53 V vs NHE for the most electron-poor complex $[\text{Co}(\text{F16P})]^{3-}$ and at -0.75 V vs NHE for the most electron-rich compound $[\text{Co}(\text{OMeP})]^{3-}$. Figure 5A.7b in the Appendix 5 demonstrates that a 1-electron process induces a current change of ~ 8

Chapter 5: Electron-Withdrawing Effects of Cobalt Porphyrin Catalysts Boost Homogeneous Photocatalytic Hydrogen Evolution in Neutral Aqueous Solutions

μA . Based on this, a catalytic onset is defined as a current increase exceeding $-16 \mu\text{A}$, corresponding to a process involving more than two electrons. Cyclic voltammograms recorded at pH 7.0 revealed that the third reduction of the cobalt porphyrin complexes induced electrocatalytic hydrogen evolution with an onset potential between -0.84 and -1.04 V vs NHE depending on the substituents (Figure 5.3b). Interestingly, the trend in the variation of the third reduction potential does not align with the electron-richness of the cobalt center, as the onset potential for the $[\text{Co}(\text{MeP})]^{3-}$ catalyst was found to be more positive than that found for the $[\text{Co}(\text{F8P})]^{3-}$ catalyst. This observation suggested that the HER catalytic mechanism may have changed when switching from an electron-rich $[\text{Co}(\text{MeP})]^{3-}$ to an electron-poor $[\text{Co}(\text{F8P})]^{3-}$ catalyst. A control CV measurement was conducted using $[\text{Co}(\text{F8P})]^{3-}$ in 0.1 M KCl (Figure 5A.7b). The reduction of Co(II) to Co(I) occurred at -0.62 V vs NHE, and the reduction of Co(I) to Co(0) was observed at -1.06 V vs NHE. These values closely correspond to -0.64 V and -1.01 V vs NHE, respectively, measured in a pH 7.0 buffer. As a conclusion, the phosphate buffer did not significantly affect the potentials of the catalytic waves for this complex, hence our data in buffer solution can be used for comparison with DFT calculations (see below). The redox potential of the $[\text{Ru}(\text{bpy})_3]^{2+}/[\text{Ru}(\text{bpy})_3]^+$ couple lies between -1.26 and -1.32 V vs NHE depending on the reports.^[13,52,53] Therefore, the one-electron reduced species PS^- is thermodynamically capable of driving the reduction of all four Co(III)-porphyrin compounds to a potential where catalytic HER occurs, with an electron-transfer driving force E_{dr} (Figure 5.1b) exceeding 160 mV. It is worth noting that for $[\text{Co}(\text{F16P})]^{3-}$ a small reduction wave was observed at -0.80 V vs. NHE at the foot of the catalytic wave (Figure 5.3b), which is attributed to a ligand-based reduction. At a similar potential, a reduction wave was observed for the $[\text{Zn}(\text{F16P})]^{4-}$ analogue, for which metal-based reduction is unlikely (Figure 5.3c).

The LSV traces of the Zn porphyrin complexes were measured at pH 7.0, focusing on reduction. As expected, the electron-poor $[\text{Zn}(\text{F16P})]^{4-}$ showed the least negative reduction potential (-0.80 V vs NHE, see 5.3c). There is little increase of reduction current with increasingly negative potential until -1.10 V vs NHE, which suggested that this process concerns a reductive polarization of the complex without catalysis. In addition, the reduction current was approximately -8 μA , which was similar to the current of the -7 μA single electron reduction of Co^{II} to Co^{I} (see Figure 5A.8). Thus, this first reduction of this Zn porphyrin most likely involves 1 electron. For $[\text{Zn}(\text{F8P})]^{4-}$, more than one but less than two electrons were needed to form the species active for the further HER, which took place at -1.20 V vs NHE. Reduction of the electron-rich $[\text{Zn}(\text{MeP})]^{4-}$ and $[\text{Zn}(\text{OMeP})]^{4-}$ was observed below -1.20 V vs NHE with reduction currents higher than -16 μA (Figure 5A.9). Hence, we tentatively attribute these currents to electrocatalytic hydrogen evolution. In aqueous solution at pH 7.0, the reduced form of the photosensitizer is capable of driving the 2-electron reduction of the Zn-porphyrin complexes and HER catalyzed by the Zn compounds, with E_{dr} exceeding 60 mV.

Chapter 5: Electron-Withdrawing Effects of Cobalt Porphyrin Catalysts Boost Homogeneous Photocatalytic Hydrogen Evolution in Neutral Aqueous Solutions

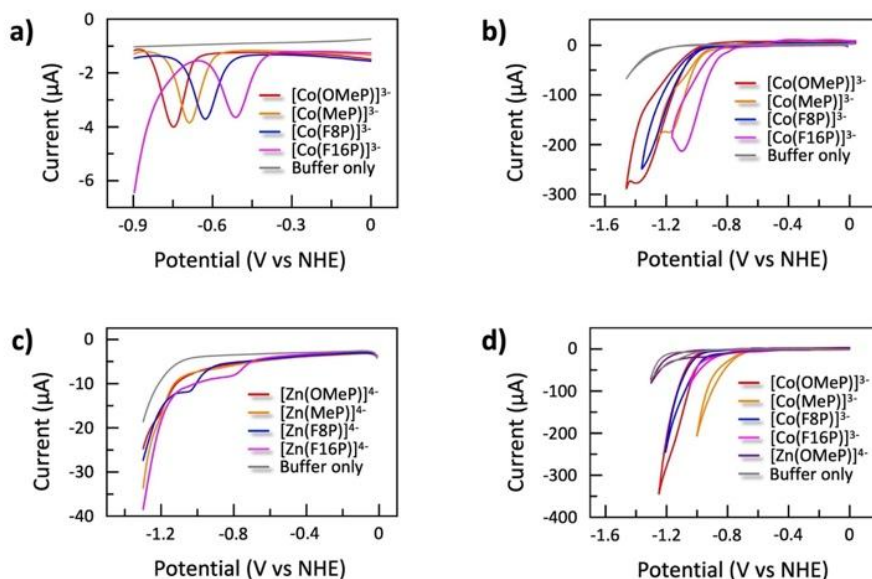


Figure 5.3. Electrochemistry at pH 7.0 and 4.1 of the water-soluble metal porphyrin complexes studied in this work. a) Differential pulse voltammetry (DPV) and b) cyclic voltammetry (CV) of the Co-porphyrin complexes at pH 7.0; c) linear sweep voltammetry (LSV) of the Zn porphyrin complexes at pH 7.0 and d) CV of the Co-porphyrin complexes at pH 4.1. Conditions: 0.1 M phosphate buffer for pH 7.0 and 1.0 M phosphate buffer for pH 4.1, 0.07 cm² glassy-carbon working electrode, Pt wire auxiliary electrode, Ag/AgCl reference electrode, CV and LSV scan rate 50 mV s⁻¹, T = 298 K. DPV experimental parameters: 0.004 V increase potential, 0.05 V amplitude, 0.05 s pulse width, 0.0167 s sampling width, 0.5 s sample period.

At pH 4.1, CVs showed that all cobalt porphyrin complexes were also electrocatalytically active for the HER (Figure 5.3d). As expected, the compounds [Co(OMeP)]³⁻, [Co(MeP)]³⁻ and [Co(F8P)]³⁻ showed a higher catalytic current at pH 4.1 than at pH 7.0 with the same overpotential. However, the electrocatalytic current obtained with [Co(F16P)]³⁻ was lower at pH 4.1 (< -100 μA) than at pH

7.0 ($> -200 \mu\text{A}$), with 200 mV overpotential. This result strongly suggested that the most electron-poor catalyst of the series may catalyze the HER at neutral pH more efficiently than at pH 4.1, possibly by following a different mechanism than the other complexes.

5.3.3 Photocatalysis

Considering the encouraging electrocatalytic results described above, the photocatalytic activity of all metal porphyrin complexes in HER was tested in homogeneous aqueous solutions using $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ as PS (0.5 mM), AA and TCEP (100 mM each) as sacrificial electron donors, and under blue light irradiation (450 nm, 16 mW). Importantly, all these cobalt and zinc porphyrin complexes have very weak absorption at 450 nm (Figure 5.4), therefore, negligible photons would be absorbed by the catalyst instead of the photosensitizer during photocatalysis. Unlike in electrocatalytic conditions where all cobalt porphyrins showed catalytic activity for proton reduction, in photocatalytic conditions at pH 7.0 only the most electron-poor and the most electron-rich complexes showed significant HER activity (Figure 5.5a). In contrast, the most electron-rich complex $[\text{Co}(\text{OMeP})]^{3-}$ had a lower activity than the electron-poor complex $[\text{Co}(\text{F16P})]^{3-}$, which showed the highest turnover number in the series ($\text{TON} = 70 \pm 3 \text{ mol}_{\text{H}_2}/\text{mol}_{\text{HEC}}$ after 39.5 h irradiation) and the highest maximum turnover frequency ($\text{TOF} = 6.7 \pm 0.3 \text{ h}^{-1}$, defined in section 5.6.4). At that stage, it was surprising to find $[\text{Co}(\text{F16P})]^{3-}$ so active at pH 7.0. Although this complex had the highest driving force for electron transfer E_{dr} (Figure 5.1b) in the four cobalt porphyrins according to their onset potentials (Table 5A.1), this was not the key reason for its high performance, as $[\text{Co}(\text{MeP})]^{3-}$ had a E_{dr} 90 mV stronger than that of $[\text{Co}(\text{OMeP})]^{3-}$ while $[\text{Co}(\text{MeP})]^{3-}$ showed no better photocatalytic HER activity than $[\text{Co}(\text{OMeP})]^{3-}$ under such conditions.

Chapter 5: Electron-Withdrawing Effects of Cobalt Porphyrin Catalysts Boost Homogeneous Photocatalytic Hydrogen Evolution in Neutral Aqueous Solutions

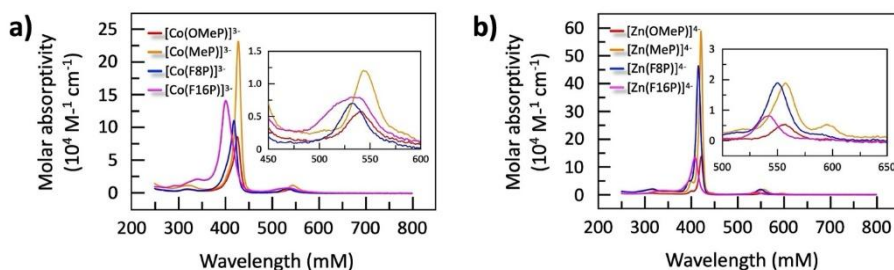


Figure 5.4. UV-vis spectra of Co(III)- (a) and Zn(II)-Porphyrins (b) used in this work.

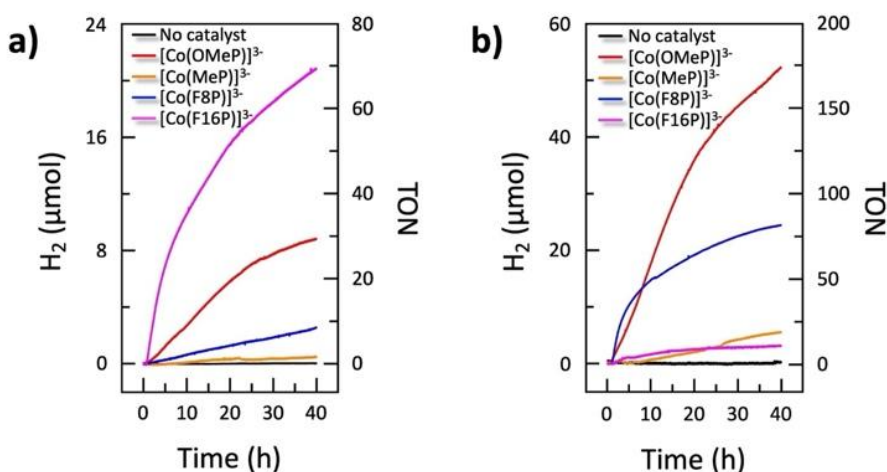


Figure 5.5. Hydrogen evolution during photocatalytic water reduction in homogeneous aqueous solution in presence of 0.1 mM catalyst [Co(OMeP)]³⁻, [Co(MeP)]³⁻, [Co(F8P)]³⁻ or [Co(F16P)]³⁻, 0.5 mM [Ru(bpy)₃]Cl₂ as photosensitizer, 0.1 M ascorbate and TCEP as electron donor, at pH 7.0 (a) or 4.1 (b), using blue light irradiation (450 nm, 16 mW). Conditions: *T* = 298 K, 0.1 M phosphate aqueous buffer.

At pH 4.1, the photocatalytic HER activity of electron-rich compounds [Co(OMeP)]³⁻ and [Co(MeP)]³⁻ as well as the electron-poor compound [Co(F8P)]³⁻, all improved compared to their performance at pH 7.0 (Figure 5.5b). After 39.5 h irradiation, [Co(OMeP)]³⁻ showed the highest TON of the series (175

$\pm 5 \text{ mol}_{\text{H}_2}/\text{mol}_{\text{HEC}}$ after 39.5 h) and a maximum TOF of $7.2 \pm 0.4 \text{ TON/h}$. By contrast, $[\text{Co}(\text{MeP})]^{3-}$ was not active at pH 7.0, but showed at pH 4.1 a TON of 22. $[\text{Co}(\text{F8P})]^{3-}$ showed the fastest turnover frequency at the beginning of the reaction (12.7 h^{-1}), but the system was not stable, resulting in a TON of only 80 after 39.5 h. In contrast to the other compounds, the electron-poorest complex $[\text{Co}(\text{F16P})]^{3-}$ showed significantly lower photocatalytic activity at pH 4.1 than at pH 7 (Figure 5.5b). At pH 4.1, it achieved a TON of 10 after 39.5 h irradiation, compared to a TON of 70 at pH 7.0.

Overall, these photocatalytic results are consistent with those observed in electrochemical conditions. The electron-withdrawing fluorine substituents appear to influence the electron density at the metal center and change the pH dependence of the catalytic activity. This suggested that the mechanism of catalytic proton reduction at the porphyrin complexes were different for the electron-rich and electron-poor cobalt compounds.

Photocatalytic hydrogen evolution using the Zn-porphyrin complexes as catalysts was also investigated using the same conditions as described above. In the zinc complexes, only the ligand may lead to HEC activity, as the metal center is unable to accommodate different redox states. At pH 7.0 the electron-poor Zn porphyrin complex were the only ones to show significant HER activity: $[\text{Zn}(\text{F16P})]^{4-}$ reached a TON of 9.5 after 39.5 h irradiation (Figure 5A.10), while $[\text{Zn}(\text{F8P})]^{4-}$ showed lower activity (TON = 6.5). This observation confirmed that a ligand-based catalytic pathway for HER is possible with these porphyrins and that catalysis becomes faster when more electron-withdrawing groups are added to the porphyrin ring. We note that in these pH neutral conditions, $[\text{Zn}(\text{F16P})]^{4-}$ and its free-base analogue $[\text{H}_2(\text{F16P})]^{4-}$ showed lower photocatalytic activity than $[\text{Co}(\text{F16P})]^{3-}$ (Figure 5A.11a). This suggests that the redox activity of the cobalt center does play a role in the catalytic cycle of the $[\text{Co}(\text{F16P})]^{3-}$ catalyst. In contrast, at pH 4.1 $[\text{Zn}(\text{OMeP})]^{4-}$ was found to be inactive (Figure 5A.11b), while $[\text{Co}(\text{OMeP})]^{3-}$ showed the highest photocatalytic activity of the cobalt

Chapter 5: Electron-Withdrawing Effects of Cobalt Porphyrin Catalysts Boost Homogeneous Photocatalytic Hydrogen Evolution in Neutral Aqueous Solutions

compounds. This suggests that for the most electron-rich cobalt catalyst of this series the high activity in acidic conditions involves mainly the metal center.

$[\text{Co}(\text{OMeP})]^{3-}$ and $[\text{Co}(\text{F16P})]^{3-}$ gave the highest TON at pH 4.1 and pH 7.0, respectively. Therefore, the influence of pH on the photocatalytic activity of these two complexes was further studied at different pH values between 4.1 and 9.0, using otherwise identical conditions. Upon increasing the pH from 4.1 to 7.0, the TON after 39.5 h for $[\text{Co}(\text{F16P})]^{3-}$ increased from 10 to 70, while the TON decreased to 12 upon further increase of the pH to 9.0 (Figure 5A.12a and 5A.13a). For this complex, pH 7.0 thus appears to be optimal for the stability of the photocatalytic system, although a higher maximum TOF of 8.9 TON/h was found at pH 6.0 (Figure 5A.13b). By contrast, the electron-rich complex $[\text{Co}(\text{OMeP})]^{3-}$ clearly showed increasing TON and maximum TOF with more acidic pH, culminating in a TON of 175 and a maximum TOF of 7.2 TON/h at pH 4.1 (Figure 5A.12b and 5A.13).

Overall, classical behavior was observed for the electron-richest complex of the series $[\text{Co}(\text{OMeP})]^{3-}$, with more efficient H_2 generation at low pH values. In contrast, the most electron poor $[\text{Co}(\text{F16P})]^{3-}$ catalysts performed optimally in pH-neutral solution, where its TON was twice that of $[\text{Co}(\text{OMeP})]^{3-}$. Finally, the photocatalytic activity of $[\text{Co}(\text{F16P})]^{3-}$ was inhibited both at pH values higher and lower than 7.0.

5.3.4 Photostability

In order to check the photostability of $[\text{Co}(\text{F16P})]^{3-}$ and $[\text{Co}(\text{OMeP})]^{3-}$, the UV-vis spectra of solutions of complexes in 0.1 M phosphate buffer (pH 7.0) were monitored both in the dark and upon blue light irradiation for 48 h (450 nm, 16 mW). After 48 h irradiation, the UV-vis spectra of $[\text{Co}(\text{F16P})]^{3-}$ and $[\text{Co}(\text{OMeP})]^{3-}$ had changed only slightly (Figure 5A.14 and 5A.15), in contrast with $[\text{Zn}(\text{OMeP})]^{4-}$, which lost 80% of its absorption properties after 48 h of

irradiation at 423 nm. In another experiment using $[\text{Co}(\text{F16P})]^{3-}$ or $[\text{Co}(\text{OMeP})]^{3-}$ as the catalyst, two consecutive photocatalytic runs were performed, adding a fresh batch of PS between the two runs to compensate for possible PS decomposition. A 3-5% lower TON were found after the second photocatalytic run compared to the first (Figure 5A.16). As widely reported, $[\text{Ru}(\text{bpy})_3]^{2+}$ decomposes quickly in photocatalytic aqueous conditions,^[13,54] which is responsible for deactivation of HER photocatalytic systems. However, clearly both electron-rich and electron-poor Co catalysts had not decomposed during the first photocatalytic run. Overall, these results confirm the excellent photostability of both $[\text{Co}(\text{F16P})]^{3-}$ and $[\text{Co}(\text{OMeP})]^{3-}$ in such conditions.

5.3.5 Kinetic study

A full kinetic study was performed for the photocatalytic system comprising the catalyst $[\text{Co}(\text{F16P})]^{3-}$ at pH 7.0. Starting at standard photocatalytic conditions of 0.1 mM $[\text{Co}(\text{F16P})]^{3-}$, 0.5 mM $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$, 0.1 M ascorbate and TCEP, and a light source set at 450 nm and 16 mW power, the results were studied of systematic variations in the light intensity, the concentrations of the electron donors, the PS, and the catalyst (Figure 5A.17). We observed the maximum rate of hydrogen evolution of the system to plateau when the light power was higher than 10 mW (Figure 5A.17a), when the concentration of ascorbate and TCEP were higher than 0.075 M (Figure 5A.17b), or with a PS concentration higher than 0.25 mM (Figure 5A.17c). However, a first-order dependence of the maximum H_2 evolution rate was found on catalyst concentration (Figure 5A.17d). These observations suggests that Step 1, Step 2 and Step 3 in Figure 5.1 can proceed well independent of the photocatalytic reaction rate. The rate-determining step (RDS) of the system appeared to be Step 4, i.e., the catalytic H_2 -evolving step. Considering the linear dependence of the H_2 production rate with catalyst concentration, it appeared that in the conditions investigated here, the rate-determining step of the catalytic cycle involves one molecule of $[\text{Co}(\text{F16P})]^{3-}$. Though we can formally not exclude that at high concentration a binuclear mechanism may take place, it is hard to obtain

Chapter 5: Electron-Withdrawing Effects of Cobalt Porphyrin Catalysts Boost Homogeneous Photocatalytic Hydrogen Evolution in Neutral Aqueous Solutions

such information as we do expect to reach a plateau, like we did for $[\text{Co}(\text{OMeP})]^{3-}$ at concentrations higher than 0.05 mM. As the catalyst molecules are heavily negatively charged, they most probably strongly avoid each other in solution. Using 0.1 mM $[\text{Co}(\text{F16P})]^{3-}$ in the standard conditions described above at pH 7.0, the quantum yield for H_2 evolution was calculated to be $0.10 \pm 0.01\%$. This low quantum yield highlights the occurrence of many charge-recombination events that are characteristic of homogeneous photocatalytic systems, where PS^- and the catalyst roam free in solution.

A similar kinetic study was performed at pH 4.1 using the catalyst $[\text{Co}(\text{OMeP})]^{3-}$, for which significantly different results were obtained than for the study on $[\text{Co}(\text{F16P})]^{3-}$. A first-order dependence of the maximum H_2 evolution rate on light power was found (Figure 5A.17a), indicating that the RDS of this catalytic system involved light, and is thus related to Step 1 of the photocatalytic mechanism shown in Figure 5.1a. Step 4 is relatively fast for this electron-rich catalyst at that low pH at concentrations $[\text{HEC}] > 0.05$ mM. At low concentrations of $[\text{Co}(\text{OMeP})]^{3-}$, i.e. 0.05 mM or lower (Figure 5A.17d), a first-order dependence of the maximum hydrogen evolution rate on the catalyst concentration was found. This suggests that the catalytic H_2 evolution involves one molecule of catalyst. The observation that at higher HEC concentrations the photon flux becomes limiting, aligns with results reported by Alberto and coworkers.^[55] Using 0.1 mM $[\text{Co}(\text{OMeP})]^{3-}$ in the standard conditions at pH 4.1, the quantum yield for H_2 evolution was calculated to be $0.12 \pm 0.01\%$, which is very similar to that for $[\text{Co}(\text{F16P})]^{3-}$ at pH 7.0.

Overall, the performed kinetic experiments suggest that, under the conditions of our photocatalytic experiments, the RDS for the $[\text{Co}(\text{F16P})]^{3-}$ system is the catalytic H_2 -evolving step (step 4 in Figure 5.1a). In contrast, the photon flux appears to be the RDS for the $[\text{Co}(\text{OMeP})]^{3-}$ system (step 1 in Figure 5.1a). For both systems the RDS appears different from the electron transfer from PS^- to the catalyst in the photocatalytic cycle. Most likely the observed pH dependence in

the photocatalytic activity of the two systems is linked to variations in their catalytic mechanisms, instead of differences in their driving forces for electron transfer. While the mechanisms of the two investigated catalysts thus appear to be different, their performances in optimized conditions were comparable.

5.3.6 Density functional theory calculations

To get an understanding of the mechanisms responsible for the hydrogen evolution catalysis with these cobalt catalysts, a detailed density functional theory (DFT) study was performed with GGA functionals and implicit solvation models (see computational details section 5.6.6). The aim of these calculations was to establish reaction mechanisms and to identify the most probable reaction intermediates. We performed calculations on the $[\text{Co}(\text{F16P})]^{3-}$ and $[\text{Co}(\text{OMe})]^{3-}$ complexes, as those two catalysts represent the two most extreme cases of electron-poor and electron-rich cobalt centers. Additional information on the used theoretical methodologies is provided in sections 5.6.6 and 5.6.7 of this chapter.

First, the coordination environment of the $^1[\text{Co}^{\text{III}}(\text{P})]^{3-}$ ($\text{P} = \text{OMeP}$ or F16P) pre-catalyst systems was investigated, specifically addressing whether they exhibited a preference for a square planar environment or if axial water ligands could effectively coordinate to the cobalt center. Interestingly, the two investigated complexes were found to strongly bind water molecules at the metal center. The short $\text{Co}-\text{OH}_2$ bond distances of $\sim 1.9 \text{ \AA}$ suggest that the aqua ligands form a covalent bond with the cobalt center, thereby acting as redox non-innocent ligand. The reaction $^1[\text{Co}^{\text{III}}(\text{P})(\text{H}_2\text{O})_2]^{3-} \rightarrow ^1[\text{Co}^{\text{III}}(\text{P})(\text{H}_2\text{O})]^{3-} + \text{H}_2\text{O}$ is energetically uphill by $4.2 \text{ kcal mol}^{-1}$ for the OMeP complex, and $8.4 \text{ kcal mol}^{-1}$ uphill for the F16P complex, indicating that two water molecules coordinate each complex (see Appendix, Table 5A.2). Repeated attempts to optimize geometries of the Co^{III} complexes without water ligands did not converge to a local minimum. As explained later in this section, protonation of the cobalt center becomes thermodynamically feasible for these systems after two reductions to form the Co^{I}

Chapter 5: Electron-Withdrawing Effects of Cobalt Porphyrin Catalysts Boost Homogeneous Photocatalytic Hydrogen Evolution in Neutral Aqueous Solutions

species. Therefore, the protonated states of the non-reduced and $1e^-$ reduced compounds are not discussed here.

The same analysis was then carried out for the $1e^-$ reduced form of the cobalt porphyrin complexes, which corresponds to the catalysts resting state. It appears that the square-planar low-spin $^2[\text{Co}^{\text{II}}(\text{P})]^{4-}$ complex was slightly more stable than a five-coordinated, low-spin $^2[\text{Co}^{\text{II}}(\text{P})(\text{H}_2\text{O})]^{4-}$ complex by 3.5 and 1.7 kcal mol $^{-1}$ for the F16P and OMeP catalysts, respectively. The compounds with two water ligands were found to be higher in energy (detailed in Appendix, Table 5A.2). The DFT calculations thus suggest that the aqua ligands dissociate upon the first reduction for both compounds. We also optimized the high-spin $^4[\text{Co}^{\text{II}}(\text{OMeP})]^{4-}$ complex, which was found to be significantly higher in energy than the low-spin analogue, by 16.4 kcal mol $^{-1}$ (Table 5A.2). Optimization of the high-spin $^4[\text{Co}^{\text{II}}(\text{F16P})]^{4-}$ complex failed due to convergence issues in the self-consistent field optimization, however, this species is believed to be higher in energy than the low-spin complex. For the remainder of the paper, the $^2[\text{Co}^{\text{II}}(\text{P})]^{4-}$ complexes, without water ligands are considered as the catalysts resting states.

We then analyzed the coordination environment of these complexes after the third reduction. During the optimization of the 3-electron reduced $^1[\text{Co}^{\text{I}}(\text{P})(\text{H}_2\text{O})]^{5-}$ species, the axial water ligand dissociated, underlining the preference of the d8 metal complex for a square planar environment. We also considered the triplet analogues of the $3e^-$ reduced species, however, our calculations reveal a preference of over 13 kcal mol $^{-1}$ for the low-spin $^1[\text{Co}^{\text{I}}(\text{P})]^{5-}$ complexes over the high-spin $^3[\text{Co}^{\text{I}}(\text{P})]^{5-}$ analogues in both systems (see Table 5A.2). This is in line with NMR measurements reported in the literature, where Co(I)-porphyrins exhibited a singlet spin multiplicity.^[37]

After establishing the most favorable spin states and coordination environment, the electronic structure and geometries of two investigated systems were analyzed in the Co^{II} , Co^{I} and formal Co^0 oxidation states. Figure 5.6 presents the optimized

geometries of the three intermediates of the $[\text{Co}(\text{F16P})]^{3-}$ catalyst, while the structures for the $[\text{Co}(\text{OMeP})]^{3-}$ catalyst can be found in the Figure 5A.18. Visualization of the spin-density of the species upon a third reduction to what is formally a Co^0 complex, revealed that the added electron was delocalized over the π -system of the porphyrin ring and the d orbital of the cobalt center (Figure 5.6, right panel), which can hence be interpreted as an intermediate species between the two localized forms $^2[\text{Co}^{\text{I}}(\text{P}^{\cdot-})]^{6-}$ and $^2[\text{Co}^0(\text{P})]^{6-}$.

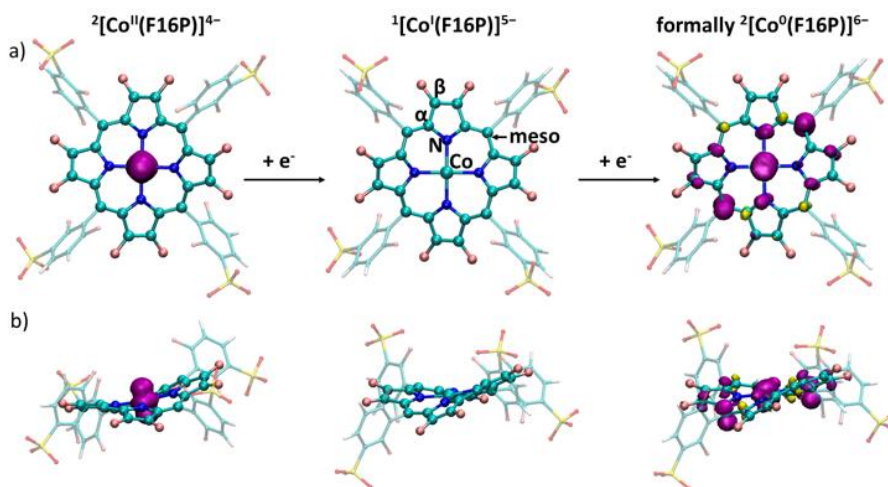


Figure 5.6. Top (a) and side (b) views of the optimized structures of the $[\text{Co}(\text{F16P})]^{n-}$ catalyst complex in the Co^{II} , Co^{I} and formal Co^0 oxidation states. For the complexes with unpaired electrons, the spin density is visualized with an isosurface value of 0.003. The $^1[\text{Co}^{\text{I}}(\text{F16P})]^{5-}$ intermediate contains atom labels that are used in the text to distinguish the five distinct protonation sites on the cobalt porphyrin complex.

As in principle all reduction steps might be coupled to proton transfer, the $\text{p}K_{\text{b}}$ values were calculated for the two catalysts in the Co^{I} and formal Co^0 oxidation states, considering five plausible protonation sites. The considered protonation sites were the cobalt center, the nitrogen on the porphyrin ligand, the porphyrin α -position, the β -position as well as the *meso*-position. These different positions

Chapter 5: Electron-Withdrawing Effects of Cobalt Porphyrin Catalysts Boost Homogeneous Photocatalytic Hydrogen Evolution in Neutral Aqueous Solutions

susceptible to protonation are indicated with specific labels in Figure 5.6, top middle panel. For the pK_b calculations of the $2e^-$ reduced Co^I species, we considered high- and low-spin options, as well as potential coordination of an axial aqua ligand to the complex. The calculated pK_b values are presented in Table 5.1, while the relative energies of all considered intermediates are detailed in Appendix 5, Table 5A.2.

Table 5.1. Calculated pK_b values for protonation on the metal center and on the nitrogen, α -, β - and *meso*-position on the porphyrin ligand.

	Co	N	α	β	<i>meso</i>
$^1[Co^I(F16P)]^{5-}$	15.8	22.9	24.5	20.9	23.9
$^2[Co^0(F16P)]^{6-}$	6.7	12.6	3.3	-2.5	3.7
$^1[Co^I(OMeP)]^{5-}$	9.7	17.9	20.1	13.7	12.8
$^2[Co^0(OMeP)]^{6-}$	2.0	10.9	2.5	-2.9	-5.9

Table 5.1 shows that the metal center of the $^1[Co^I(P)]^{5-}$ species emerges as the most basic site for both catalysts after the second reduction, with pK_b values of 15.8 and 9.7 for the $^1[Co^I(F16P)]^{4-}$ and the $^1[Co^I(OMeP)]^{4-}$ systems, respectively. This is interesting, as it indicates that at pH 4.1 conditions, the electron-rich $^1[Co^I(OMeP)]^{4-}$ catalyst will be protonated at the metal center, while the electron-poor analogue will remain unprotonated. The most favorable protonation site in both systems shifts to the porphyrin macrocycle after the third reduction, forming the formal $^2[Co^0(P)]^{6-}$ intermediate. At this stage our calculations showed that protonation of the complexes was exothermic at both pH 7.0 and pH 4.1, with the ligand being more basic than the metal center by about ~ 8 and ~ 9 pK_b units for the F16P and OMeP systems, respectively. This is qualitatively consistent with other DFT studies on cobalt porphyrin-catalyzed hydrogen evolution.^[37] Our calculations show that the most favorable protonation site for the electron-poor complex $^2[Co^0(F16P)]^{6-}$, is the β -pyrrole position with a value of -2.5 pK_b units.

In contrast, the *meso*-position appeared to be more basic for the $^2[\text{Co}^0(\text{OMeP})]^{6-}$ system, with a value of $-5.9 \text{ p}K_{\text{b}}$ units. We attribute the shift towards a preference for the *meso*-position to the nearby methoxy group in the *ortho*-position of the benzo-4-sulfonic acid substituent. In the optimized structure, the distance between the added hydrogen atom and the oxygen atom of the methoxy group was $2.32 \text{ \AA}$, indicating the formation of a hydrogen bond to stabilize the protonated state. Visualization of the spin-densities of the ligand protonated intermediates showed that the excess electron was still largely delocalized over both the Co center and the ligand (Figure 5A.19), indicating once more an intermediate species between the two localized forms $^2[\text{Co}^{\text{I}}(\text{P-H}^{\cdot-})]^{5-}$ and $^2[\text{Co}^0(\text{P-H})]^{5-}$. For the remainder of this paper, we will refer to these complexes as formal $^2[\text{Co}^0(\text{P-H})]^{5-}$, in which the P-H ligand represents a hydride bound to a cation radical porphyrin ligand P^+ .

Figure 5.7 summarizes the most probable mechanistic pathways according to our experimental and theoretical results. It starts from the 1e^- reduced, activated catalyst in the Co^{II} oxidation state. The relative Gibbs free energies have been calculated assuming optimal pH values and the experimentally observed catalytic onset potential for both catalysts: $\text{pH} = 7.0$ and a potential of -0.84 V vs. NHE for the $[\text{Co}(\text{F16P})]^{3-}$ system, and $\text{pH} = 4.1$ and a potential of -0.95 V vs. NHE for the $[\text{Co}(\text{OMeP})]^{3-}$ system.

Chapter 5: Electron-Withdrawing Effects of Cobalt Porphyrin Catalysts Boost Homogeneous Photocatalytic Hydrogen Evolution in Neutral Aqueous Solutions

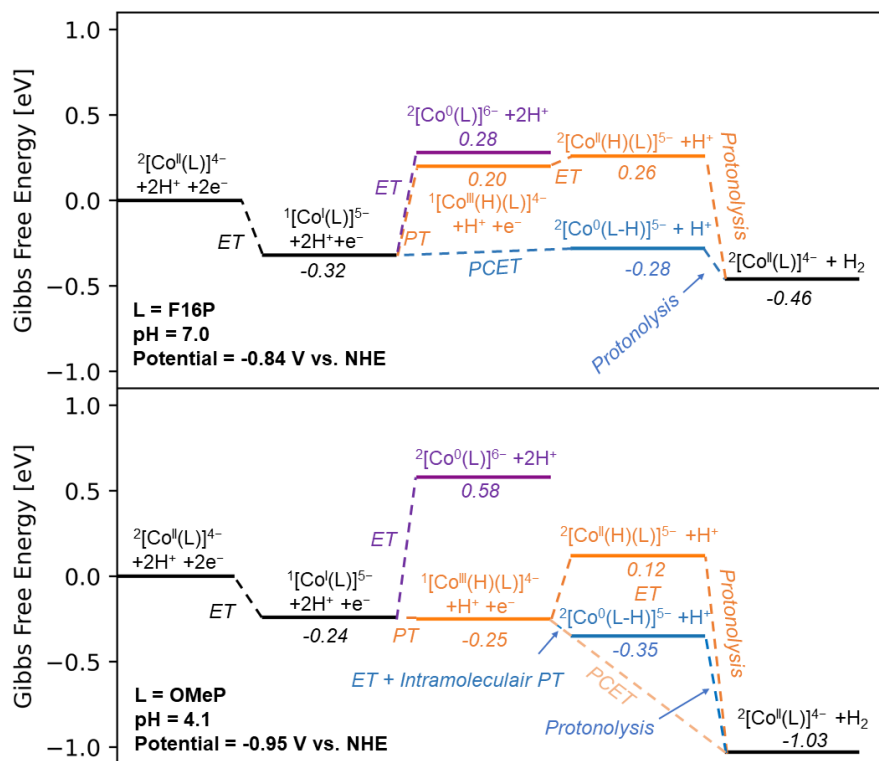


Figure 5.7. Calculated Gibbs free energy diagrams for the $[\text{CoF16P}]^{3-}$ (top) and $[\text{CoOMeP}]^{3-}$ (bottom) systems. In the Gibbs free energy diagrams the first reduction step from Co^{III} to Co^{II} is not shown for clarity. $^2[\text{Co}^{\text{I}}(\text{P})]^{6-}$ notation is formal and the added charge is delocalized between Co and the Ligand. In the $^2[\text{Co}^{\text{I}}(\text{P-H})]^{5-}$ notation, P-H formally corresponds to a cation radical porphyrin ligand P^+ and a hydride. The Gibbs free energy diagrams are calculated at the pH for which the catalysts achieved the highest TON, and at the onset potential of the catalytic wave for each catalyst. For the electron-poor $[\text{Co}(\text{F16P})]^{3-}$ system this is at pH 7.0 and a potential of -0.84 V vs NHE, while for the $[\text{Co}(\text{OMeP})]^{3-}$ system this is at pH 4.1 and a potential of -0.95 V vs NHE. Due to the different proton and electron potentials, formation of H_2 is more exothermic in the bottom panel than for the top panel.

Figure 5.7 shows that after the Co^{II} to Co^{I} reduction, protonation of the electron-poor catalyst $^1[\text{Co}^{\text{I}}(\text{F16P})]^{5-}$ to generate a $^1[\text{Co}^{\text{III}}(\text{H})(\text{F16P})]^{4-}$ metal hydride is thermodynamically unfavorable by 0.52 eV (orange pathway in top panel). Similarly, the purely electronic reduction to form the formal Co^0 intermediate is energetically uphill by 0.60 eV (purple pathway). DFT thus predicts the purely electronic reduction of $^1[\text{Co}^{\text{I}}(\text{F16P})]^{5-}$ to $^2[\text{Co}^0(\text{F16P})]^{6-}$ to lay at -1.44 V vs. NHE, in line with CV measurements of the $[\text{Co}(\text{F8P})]^{3-}$ -complex in DMF, which shows an onset at ca. -1.4 V (see Appendix, Figure 5A.7a). As both reactions involving only proton or only electron transfer are endergonic, the most favorable pathway involves a concerted process, in which the reduction is coupled to protonation of the porphyrin macrocycle (blue PCET pathway in top panel of Figure 5.7). We emphasize that the ligand is more basic than the cobalt by 9.2 pK_a units for the 3-electron reduced $[\text{Co}^0(\text{F16P})]^{6-}$ complex (see Table 5.1). Therefore, the proton attaches to the ligand, and not to the cobalt. Subsequently, dihydrogen formation can occur by protonolysis of the hydride ligand, which is exothermic by 0.18 eV.

In contrast, for the electron-rich $^1[\text{Co}^{\text{I}}(\text{OMeP})]^{5-}$ catalyst, metal hydride formation following the Co^{II} to Co^{I} reduction is exothermic, although only by 0.01 eV (orange pathway in bottom panel of Figure 5.7). DFT thus indicates that for this complex a Co^{III} hydride is formed, after the Co^{II} to Co^{I} reduction step. Subsequently, the purely electronic reduction from this Co^{III} hydride to the Co^{II} hydride is endothermic by 0.37 eV (see Figure 5.7, orange pathway, formation of $^2[\text{Co}^{\text{II}}(\text{H})(\text{OMeP})]^{5-}$). This highly endothermic purely electronic reduction suggests once more that this reduction is coupled to proton transfer. The process becomes exothermic by 0.78 eV once we consider the reduction to be coupled with protonolysis of the metal hydride, yielding H_2 and regenerating the initial catalyst (Figure 5.7, orange PCET pathway in bottom panel). Alternatively, the reduction may be coupled with intramolecular proton/hydride transfer from the

Chapter 5: Electron-Withdrawing Effects of Cobalt Porphyrin Catalysts Boost Homogeneous Photocatalytic Hydrogen Evolution in Neutral Aqueous Solutions

metal to the porphyrin ligand (Figure 5.7, blue pathway in bottom panel), which would be exothermic by 0.10 eV.

To verify that H₂ formation for all hydride intermediates is exothermic, hydricity values for these species were calculated following a thermodynamic cycle proposed in literature (see Appendix A5, Table 5A.5 and Table 5A.6).^[56,57] All considered intermediates have hydricity values below 34.2 kcal mol⁻¹, indicating that hydrogen formation is thermodynamically favorable.

Overall, pK_b calculations of the [Co^I(P)]⁵⁻ and the formal [Co⁰(P)]⁶⁻ complexes showed that after formation of Co^I, the electron-rich ¹[Co^I(OMeP)]⁵⁻ catalyst is protonated at the metal, while the ¹[Co^I(F16P)]⁵⁻ porphyrin is unprotonated. Considering that the experiments were performed in aqueous conditions, it is reasonable to assume that if protonation of the reduced species is thermodynamically downhill, the electron transfer is coupled to proton transfer. Table 5.2 presents the assignment of the experimental redox couples, based on these assumptions.

Table 5.2. Assignment of the redox couples observed in experiment.

Assigned couple	Redox potential (V vs NHE)	
	Calculated	Measured
$^2[\text{Co}^{\text{II}}(\text{OMeP})]^{4-} + \text{e}^- + \text{H}^+ \rightleftharpoons ^1[\text{Co}^{\text{III}}(\text{H})(\text{OMeP})]^{4-}$	-0.70	-0.78
$^1[\text{Co}^{\text{III}}(\text{H})(\text{OMeP})]^{4-} + \text{e}^- \rightleftharpoons ^2[\text{Co}^{\text{II}}(\text{H})(\text{OMeP})]^{5-}$ $\rightleftharpoons ^2[\text{Co}^{\text{II}}(\text{OMeP-H}_{\text{meso}})]^{5-}$	-1.31 (-0.85)[b]	-0.95
$^2[\text{Co}^{\text{II}}(\text{F16P})]^{4-} + \text{e}^- \rightleftharpoons ^1[\text{Co}^{\text{I}}(\text{F16P})]^{5-}$	-0.52	-0.53
$^1[\text{Co}^{\text{I}}(\text{F16P})]^{5-} + \text{e}^- + \text{H}^+ \rightleftharpoons ^2[\text{Co}^{\text{I}}(\text{F16P-H}_{\beta})]^{5-}$	-0.88	-0.84

[a] data according to CV, V vs NHE, measured at pH 4.1 for the [Co(OMe)]³⁻ complex and pH 7.0 for the [Co(F16P)]³⁻ complex.

[b] -1.31 V corresponds to the purely electronic reduction to form 2[Co^{II}(H)(OMeP)]⁵⁻, without taking proton transfer into account. The number between brackets corresponds to the 1 e⁻ reduction coupled to intramolecular proton transfer from the cobalt to the meso-position on the porphyrin ligand.

For the electron-rich $^1[\text{Co}^{\text{II}}(\text{OMeP})]^{4-}$ system, the first reversible redox couple is assigned to the proton-coupled reduction of the Co^{II} species to the Co^{III} hydride. The calculated -0.70 V redox potential matches closely the experimentally observed -0.78 V vs NHE. The second catalytic reduction is attributed to the reduction of the Co^{III} hydride to the Co^{II} hydride. At this stage the calculated potential of -1.31 V is more anodic than the measured potential of -0.95 V. The reduction could be coupled to intramolecular proton transfer from the metal center to the porphyrin macrocycle, as this site becomes more basic upon reduction of the complex. Accounting for this stabilization, the redox potential for the second couple was calculated to lay at -0.85 V, closely matching the experimentally measured value of -0.95 V. Alternatively, the reduction could be coupled protonolysis of the metal centered hydride. This may also explain the lower experimental redox potential compared to the calculated value of -1.31 V which does not account for proton transfer effects.

After the second reduction, an electron-poor complex $^1[\text{Co}^{\text{I}}(\text{F16P})]^{5-}$ is produced, which is stable against oxidative protonation. Therefore, the current increase at -0.53 V was assigned to the reduction of $^2[\text{Co}^{\text{II}}(\text{F16P})]^{4-} + \text{e}^- \rightarrow ^1[\text{Co}^{\text{I}}(\text{F16P})]^{5-}$, and the catalytic wave at -0.84 V is attributed to the proton-coupled electrochemical reduction of $^1[\text{Co}^{\text{I}}(\text{F16P})]^{5-} + \text{e}^- + \text{H}^+ \rightarrow ^2[\text{Co}^0(\text{F16P-H}_\beta)]^{5-}$ and subsequent hydrogen evolution. The calculated potentials of -0.52 V and -0.88 V vs NHE very closely match the measured values. In addition, they accurately reproduce the difference between the two onset potentials within an error of 0.05 V. A schematic illustration of the proposed mechanisms is provided in Figure 5.8.

5.4 Discussion

Our electrochemical study of this series of Co-porphyrin complexes reveals that the electron-richness of the ligand controls the onset potential for the $[\text{Co}^{\text{II}}(\text{P})]^{4-}$ to $[\text{Co}^{\text{I}}(\text{P})]^{5-}$ reduction, after the initial $[\text{Co}^{\text{III}}(\text{P})]^{3-}$ to $[\text{Co}^{\text{II}}(\text{P})]^{4-}$ reduction. However, catalysis starts at a later stage, and a third reduction is needed for catalytic hydrogen evolution. The dependence of this third reduction step on the

Chapter 5: Electron-Withdrawing Effects of Cobalt Porphyrin Catalysts Boost Homogeneous Photocatalytic Hydrogen Evolution in Neutral Aqueous Solutions

electronic properties of the porphyrin ring substituents was less straightforward to establish than for the first two reductions. As expected, the electron-richest complex $[\text{Co}(\text{OMeP})]^{3-}$ had the most cathodic onset potentials of -1.04 and -0.95 V vs NHE at pH 7.0 and pH 4.1, respectively (Table 5A.1). However, the electron-poorest complex $[\text{Co}(\text{F16P})]^{3-}$ showed the least negative onset potential of -0.84 V vs NHE only at pH 7.0. Surprisingly at pH 4.1, it was the electron rich $[\text{Co}(\text{MeP})]^{3-}$ that showed the least negative onset potential of -0.74 V vs NHE.

We then proceeded to perform photocatalytic experiments using standard concentrations of 0.1 mM catalyst, 0.5 mM $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$, 0.1 M ascorbate and TCEP, and light power at 450 nm of 16 mW. Given that the system has a large excess of electron donor (0.1 M) over photosensitizer (0.5 mM), it is reasonable to assume that the photosensitizer is reductively quenched during the photocatalytic process. This is in line with the literature, which shows that photocatalytic experiments with ascorbate and TCEP favor reductive quenching of the $\text{Ru}(\text{bpy})_3$ photosensitizer.^[12] We have experimentally determined the driving force E_{dr} value (in V) for electron transfer from the reduced photosensitizer PS^- to the Co-porphyrins from the difference between $E_{\text{PS}}(\text{PS}/\text{PS}^-)$ and the hydrogen evolution onset potential of the catalyst in electrochemical conditions. We find that all investigated cobalt complexes have a catalytic onset potential that is higher than the $E_{\text{PS}}(\text{PS}/\text{PS}^-)$ value. This implies that the reduced photosensitizer can act as electron source for all reductions in the catalytic cycles of the investigated cobalt catalysts.

The decrease in E_{dr} for $[\text{Co}(\text{F16P})]^{3-}$ from 420 mV at pH 7.0 to 380 mV at pH 4.1 suggests that electron transfer from the photo-reduced species PS^- to $[\text{Co}(\text{F16P})]^{3-}$ may be faster at pH 7.0 than at pH 4.1. However, our kinetic studies in photocatalytic conditions demonstrated that the rate of the photocatalytic system using $[\text{Co}(\text{F16P})]^{3-}$ as HEC at pH 7.0 was limited by the activity of the catalyst rather than the electron transfer between PS^- and the HEC. At pH 4.1, using

identical concentrations and light intensity, the photocatalytic system using $[\text{Co}(\text{OMeP})]^{3-}$ as HEC was limited by the photon flux, which appears to be slower than electron transfer and the activity of the catalyst. Overall, at both pH 7.0 and 4.1, the onset potential of the catalyst in electrocatalytic conditions had very little predictive value in terms of its activity in photocatalytic conditions. The different performances of the photocatalytic systems using $[\text{Co}(\text{OMeP})]^{3-}$ at pH 4.1 and of $[\text{Co}(\text{F16P})]^{3-}$ at pH 7.0 is primarily attributed to differences in their HER catalytic mechanisms, as is further supported by DFT calculations. A schematic illustration of the proposed mechanisms is provided in Figure 5.8.

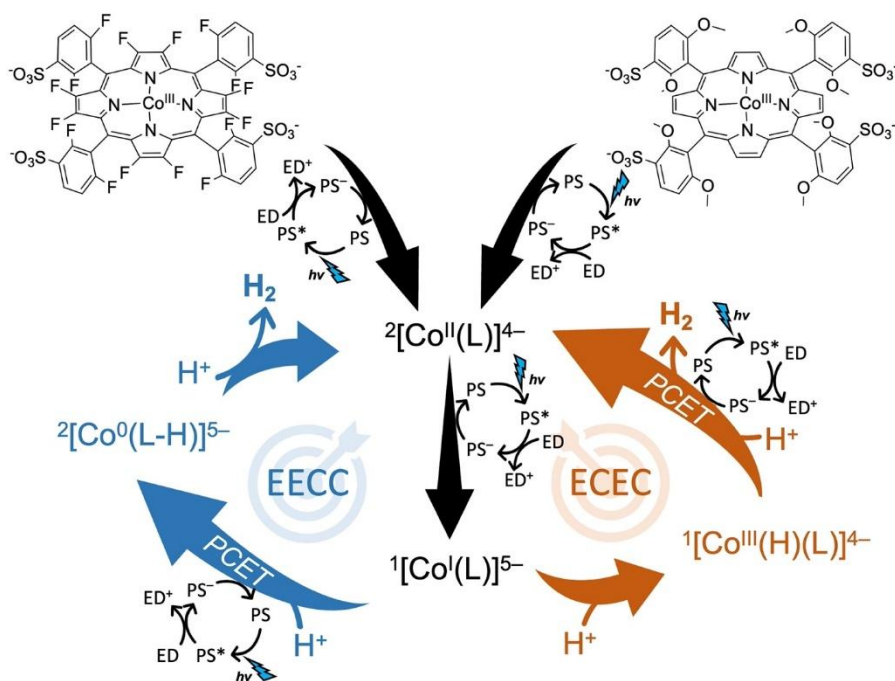


Figure 5.8. Reaction mechanism for photocatalytic hydrogen evolution starting from $[\text{Co}^{\text{III}}(\text{F16P})]^{3-}$ (Left) and $[\text{Co}^{\text{III}}(\text{OMe})]^{3-}$ (Right).

Consistent with CV experiments, our DFT calculations indicated that the first steps in the catalytic cycle for the two catalysts are identical. After an initial Co^{III} to Co^{II} reduction, the low-spin $2[\text{Co}^{\text{II}}(\text{P})]^{4-}$ complexes are reduced to form a low-spin $1[\text{Co}^{\text{I}}(\text{P})]^{5-}$ intermediate. Subsequently, the mechanisms of the two

Chapter 5: Electron-Withdrawing Effects of Cobalt Porphyrin Catalysts Boost Homogeneous Photocatalytic Hydrogen Evolution in Neutral Aqueous Solutions

investigated catalysts diverge. The pK_b value of 9.7 of the $[Co^I(OMeP)]^{5-}$ metal center suggested that at pH 4.1 the metal center is protonated, thus forming the metal hydride species $^1[Co^{III}(H)(OMeP)]^{4-}$ (Table 5.1). At pH 7.0, most complexes remain unprotonated according to our calculations, although we note that pK_b calculations are very sensitive to the accuracy in the DFT method and the calculated solvation energies, introducing potential errors up to 2-3 pK_a units.^[58,59] Distinctively, the much higher pK_b value of 15.8 of the low-spin $^1[Co^I(P)]^{5-}$ intermediate for $[Co(F16P)]^{5-}$ reveals that this complex remains unprotonated in both buffer solutions. This bifurcation in the mechanisms after the second $Co^{II} \rightarrow Co^I$ reduction, explains the observed trend in the third reduction waves in electrochemical measurements. At pH 4.1, the $[Co(MeP)]^{3-}$ catalyst was found to have the lowest catalytic onset potential, followed by $[Co(F16P)]^{3-}$, then $[Co(F8P)]^{3-}$, and finally $[Co(OMeP)]^{3-}$ (see Appendix A5, Table 5A.1). From this, we thus conclude that for the electron-poor $[Co(F16P)]^{3-}$ and $[Co(F8P)]^{3-}$ catalyst, the third reduction corresponds to the $^1[Co^I(P)]^{5-} \rightarrow ^2[Co^0(P-H)]^{5-}$ proton-coupled reduction step (EECC mechanism, Figure 5.8, left). In contrast, we conclude that for the electron-rich catalysts $[Co(MeP)]^{3-}$ and $[Co(OMeP)]^{3-}$, the proton-coupled reduction of $^1[Co^{III}(H)(P)]^{4-}$ is observed, which then yields the $^2[Co^{II}(P)]^{4-}$ complex and H_2 (ECEC mechanism, Figure 5.8, right).

The divergence in the mechanisms is further supported by the following arguments. The calculated redox potentials for the second and third reduction steps with the electron poor $[Co(F16P)]^{3-}$ catalyst closely match the measured potentials, validating the correct assignment of these redox couples shown in Table 5.2. A reduction wave was observed at the foot of the catalytic onset for the electron-poor complexes, which we attribute to a proton-coupled reduction of $^1[Co^I(F16P)]^{5-} \rightarrow ^2[Co^0(F16P-H)]^{5-}$. The observation of this reduction wave at a similar potential in the LSV of both $[Co(F16P)]^{3-}$ and $[Zn(F16P)]^{4-}$ (Figure 5.3) validates the DFT prediction that both the electron and the proton react with the

ligand rather than the metal. Since the Zn metal is redox inactive, this reduction must be ligand-based. Based on the DFT calculations of the cobalt complex, we expect that the $[\text{Zn}(\text{F16P})]^{4-}$ complex is also protonated at the ligand, most likely again at the β -pyrrole position. This ligand-based reductive protonation explains the photocatalytic activity of the electron-poor zinc $[\text{Zn}(\text{F16P})]^{4-}$ complex, which we would otherwise expect to be redox inactive. CV measurements of the Zn complexes show a catalytic onset around -1.2 V (see Figure 5.3d), which we thus assign to electron transfer coupled to proton transfer, generating H_2 . Finally, also the CV measurements of the electron poor $[\text{Co}(\text{F8P})]^{3-}$ in DMF solution, support the idea that the measured third reduction is strongly coupled to proton transfer in the presence of water. For this complex, the purely electronic reduction from $[\text{Co}^{\text{I}}(\text{P})]^{5-}$ to formal $[\text{Co}^0(\text{P})]^{6-}$ was observed at *ca.* -1.4 V in pure DMF (Figure 5A.7a), which aligns well with DFT calculations predicting a value of -1.44 V for the purely electronic reduction of $[\text{Co}(\text{I})(\text{F16P})]^{5-} \rightarrow [\text{Co}(\text{0})(\text{F16P})]^{6-}$. With increasing water content, the reduction shifted towards positive potentials, indicating that electron transfer is coupled to proton transfer in water. Our DFT results further demonstrate that the complex with a protonated ligand can act as a hydride source for hydrogen formation (see Appendix 5, Table 5A.5). Although the hydricity of carbons is generally very weak, the system studied here presents an exception. The third reduction of the complex breaks the aromaticity of the porphyrin ring, which is subsequently restored upon hydride donation. This restored aromaticity provides a strong thermodynamic driving force for hydrogen evolution.

On the other hand, our DFT calculations support the idea that the electron-rich $[\text{Co}(\text{OMe})]^{3-}$ is protonated after the second reduction to form the Co^{III} hydride species, demonstrated by the $\text{p}K_{\text{b}}$ calculations as well as the calculated redox potential, which again closely matches the assigned redox couple $\text{Co}^{\text{II}} \rightarrow \text{Co}^{\text{III}}\text{-H}$. In addition, the quenching of the catalytic activity of the $[\text{Zn}(\text{OMe})]^{4-}$ system strengthens our conclusion that catalytic hydrogen generation with $[\text{Co}(\text{OMe})]^{3-}$,

Chapter 5: Electron-Withdrawing Effects of Cobalt Porphyrin Catalysts Boost Homogeneous Photocatalytic Hydrogen Evolution in Neutral Aqueous Solutions

occurs *via* a metal-based pathway, which is a characteristic of many metal-based catalysts.^[4,9]

The DFT results reported in this paper qualitatively agree with prior studies by Hammes-Schiffer *et al.*, who showed that electrochemical reduction of a Co(I)-porphyrin complex breaks aromatization in the porphyrin ring, thereby making the ligand more basic than the metal center.^[37] Similarly, Nocera and coworkers have spectroscopically shown that in HER conditions, Ni(II)-porphyrins are readily protonated at the *meso*-carbon position following two initial reduction steps.^[60] Interestingly, the resulting species does not produce hydrogen, but rather undergoes further hydrogenation. In weakly acidic conditions, the reported complex intermolecularly produced Ni isobacteriochlorin that is hydrogenated 4 times on the β -carbon positions, while in strongly acidic conditions also higher hydrogenation products were obtained. This is particularly interesting as it gives us a clue as to why the electron-poor [Co(F16P)]³⁻ system loses activity in conditions with pH lower than 6. Even though for the highly anionic intermediate ²[Co^{II}(F16P-H _{β})]⁵⁻ any intermolecular electron or proton transfer will probably be difficult, acidic conditions might still trigger further hydrogenation of the macrocycle, lowering the yield for hydrogen evolution.

Overall, the electrochemical, photocatalytic and kinetic experiments presented in this work, in combination with the detailed DFT analysis, show that the synthesized complexes can photocatalytically evolve hydrogen *via* two distinct mechanisms. The first mechanism is characterized by a metal hydride formation after the Co^{II} $\rightarrow$ Co^I reduction and performs better in acidic conditions, which is typical for proton reduction catalysis. The data provide converging evidence that this mechanism is active for the electron-rich complexes in acidic conditions. In contrast, the second mechanism without a metal hydride, catalyzes the hydrogen evolution *via* the ligand following a third reduction of the [Co^{III}(P)]³⁻ complex. Interestingly, this ligand-based mechanism allows for considerable hydrogen

evolution rates at neutral pH conditions with the electron-poor $[\text{Co}(\text{F16P})]^{3-}$ catalyst. In more acidic conditions, however, the performance of the electron-poor catalyst was strongly diminished. We tentatively attribute this to the detrimental hydrogenation of the porphyrin macrocycle, which has been extensively reported in previous studies on similar porphyrins complexes bearing Ni.^[60]

5.5 Conclusions

A series of water-soluble, tetra-sulfonated Co(III)- and Zn(II)-porphyrin complexes were prepared and tested as catalysts for homogeneous photocatalytic hydrogen evolution from water in neutral and acid conditions. Their catalytic activity and catalytic mechanisms were found to be strongly dependent on the presence of electron-withdrawing or electron-donating substituents on the porphyrin. For the electron-richest catalyst $[\text{Co}(\text{OMeP})]^{3-}$, which in theory has a stronger driving force to reduce water than the electron poor complex, higher photocatalytic activities were observed only at low pH (4.1). In neutral conditions, its activity was much lower and vanished when the cobalt center was replaced by zinc. In contrast, the electron-poorest catalyst $[\text{Co}(\text{F16P})]^{3-}$ showed low photocatalytic hydrogen evolution at pH 4.1 and outperformed $[\text{Co}(\text{OMeP})]^{3-}$ at neutral pH. Overall, comparable photocatalytic H_2 production quantum yields were obtained with $[\text{Co}(\text{OMeP})]^{3-}$ at pH 4.1 and $[\text{Co}(\text{OMeP})]^{3-}$ at pH 7.0. Based on a combination of electrochemical studies, kinetic investigations and extensive DFT modeling, we explain these differences as follows: starting from the $^2[\text{Co}^{\text{II}}(\text{P})]^{4-}$ resting state, the first reduction to $^1[\text{Co}^{\text{I}}(\text{P})]^{5-}$ is common to both catalyst types. However, in the next step the catalytic mechanisms diverged. In the electron-rich catalyst the metal center was basic enough to be protonated to form a metal hydride intermediate $^1[\text{Co}^{\text{III}}(\text{H})(\text{P})]^{5-}$. Subsequently, the catalytic wave observed experimentally was assigned to a proton-coupled reduction of $^1[\text{Co}^{\text{III}}(\text{H})(\text{P})]^{5-}$ to recover the $^2[\text{Co}^{\text{II}}(\text{P})]^{4-}$ resting state and H_2 , which corresponded overall to a ECEC mechanism. The electron-poor catalyst was much less basic at the metal center than the electron rich catalyst and needed to be

Chapter 5: Electron-Withdrawing Effects of Cobalt Porphyrin Catalysts Boost Homogeneous Photocatalytic Hydrogen Evolution in Neutral Aqueous Solutions

reduced by an additional electron before it could accept a proton. This model was consistent with electrochemical experiments showing a second reduction wave at the foot of the catalytic onset. It thus formed a ligand-protonated intermediate formally written ${}^2[\text{Co}^0(\text{P-H})]^{5-}$ where P-H corresponds to a cation radical porphyrin ligand P^+ and a hydride. This intermediate in turn can react with a second proton to form H_2 and recover the resting state in a EECC mechanism. This second mechanism was confirmed by the observation that when using $[\text{Zn}(\text{F16P})]^{3-}$ instead of $[\text{Co}(\text{F16P})]^{3-}$, part of the photocatalytic activity was retained. Overall, this work represents a significant advance in the understanding of how molecular hydrogen evolution catalyst should be designed. Although for catalytic H_2 evolution systems at low pH it is better, as usually acknowledged, to use electron-rich catalysts, for neutral conditions (pH 7.0) it is in fact better to have electron-poor cobalt H_2 evolution catalysts. In water splitting systems coupling photocatalytic HEC and oxygen evolution catalyst near pH 7.0, electron-poor proton reduction catalysts may represent a better optimum than the usually proposed electron-rich catalysts.

5.6 Experiments and Methods

All reagents were purchased from Sigma-Aldrich and used as received unless otherwise noted. ${}^1\text{H}$ NMR spectra were recorded with a Bruker 400DPX-liq spectrometer operating at 400 MHz. ${}^{19}\text{F}$ NMR spectra were recorded with a Bruker 500DPX spectrometer operating at 500 MHz. High-resolution mass spectrometric measurements were performed with a Bruker Fourier Transform Ion Cyclotron Resonance Mass Spectrometer APEX IV installed at Leiden University. Elemental analyses were performed at the Mikroanalytisches Laboratorium Kolbe, Germany. Electronic absorption spectra were obtained with a Varian Cary 60 spectrophotometer, with samples kept at 25 °C during the spectrophotometric

measurements. The LED optical power was measured using an OPHIR Nova-display laser power meter.

5.6.1 Synthesis

Trisodium 5,10,15,20-tetrakis(2,6-dimethoxyl-3-sulfonatophenyl)porphyrin cobalt(III) (Na₃[Co(OMeP)]).

The ligand Na₄[H₂(OMeP)] (115 mg, 0.09 mmol) and Milli-Q water (40 mL) were placed under N₂ in a 100 mL round-bottom flask equipped with a magnetic stirring bar and a condenser. A solution of cobalt(II) sulfate heptahydrate (126 mg, 0.45 mmol) in Milli-Q water (10 mL) was added to the stirred solution, and the mixture was refluxed for 12 h under N₂. After cooling to room temperature, water was rotary evaporated at 40 °C and the residue was redissolved in cold methanol (15 mL). After filtration on a filter paper, methanol was rotary-evaporated, the residue was redissolved in cold methanol (5 mL). The solution was filtered by filter paper, rotary-evaporated, and the crude product was redissolved in Milli-Q water (5 mL) then passed onto an Amberlite IR 120 Na⁺ form ion exchange resin column (10 cm), washed with Milli-Q water and further purified on Sephadex-20H size exclusion chromatography to remove excess cobalt sulfate (methanol). Methanol was finally rotary evaporated and the solid dried in vacuo. Yield (115 mg, 88%); ¹H NMR (400 MHz, CD₃OD): δ = 9.37 – 9.19 (m, 8H; β -pyrrole-H), 8.48 – 8.40 (m, 4H; *p*-Ph-H), 7.52 – 7.15 (m, 4H; *m*-Ph-H), 3.92 – 3.49 (m, 12 H; OCH₃), 3.24 – 2.29 ppm (m, 12 H; OCH₃); HRMS (Appendix 5): *m/z* calcd for C₅₂H₄₄N₄CoO₂₀S₄⁺: 1231.0758 [*M*-3Na+4H]⁺; found: 1231.0750; elemental analysis calcd (%) for C₅₂H₄₀N₄Na₃CoO₂₀S₄•Na₂SO₄•H₂O: C 42.86, H 2.91, N 3.85; found: C 43.01, H 2.79, N 3.84. UV-vis (H₂O): λ_{max} (ϵ in M⁻¹ cm⁻¹) 426 nm (8.8×10^4), 542 nm (5.8×10^3).

Trisodium 5,10,15,20-tetrakis(2,6-dimethyl-3-sulfonatophenyl)porphyrin cobalt(III) (Na₃[Co(MeP)]).

Tetrasodium 5,10,15,20-tetrakis(2,6-dimethyl-3-sulfonatophenyl)-21H,23H-porphyrin•9H₂O (130 mg, 0.10 mmol) and Milli-Q water (40 mL) were placed

Chapter 5: Electron-Withdrawing Effects of Cobalt Porphyrin Catalysts Boost Homogeneous Photocatalytic Hydrogen Evolution in Neutral Aqueous Solutions

under N₂ in a 100 mL round-bottom flask equipped with a magnetic stirring bar and a condenser. A solution of cobalt(II) sulfate heptahydrate (141 mg, 0.50 mmol) in Milli-Q water (10 mL) was added to the stirred solution and the mixture was refluxed for 12 h under N₂. After cooling to room temperature, water was rotary evaporated, and the residue was redissolved in cold methanol (15 mL). After filtration on a filter paper, methanol was rotary-evaporated, the residue was redissolved in cold methanol (5 mL), the solution was filtered a second time by filter paper and rotary-evaporated, then the crude product was then passed onto an Amberlite IR 120 Na⁺ form ion exchange resin column (10 cm), washed with Milli-Q water and finally purified on Sephadex-20H size exclusion chromatography (methanol). Methanol was finally rotary evaporated and the solid dried in vacuo. Yield (109 mg, 90%); ¹H NMR (400 MHz, CD₃OD): δ = 9.18 – 9.09 (m, 8H; β -pyrrole-H), 8.43 – 8.38 (m, 4H; *p*-Ph-H), 7.68 – 7.55 (m, 4H; *m*-Ph-H), 2.42 – 2.09 (m, 12H; CH₃), 2.07 – 1.74 ppm (m, 12H; CH₃); HRMS (Appendix 5): *m/z* calcd for C₅₂H₄₃N₄NaCoO₁₂S₄⁺: 1125.0985 [*M*-2Na+3H]⁺; found: 1125.0977; elemental analysis calcd (%) for C₅₂H₄₀N₄Na₃CoO₁₂S₄•2H₂O: C 51.83, H 3.68, N 4.65; found: C 52.08, H 3.43, N 4.66. UV-vis (H₂O): λ_{max} (ϵ in M⁻¹ cm⁻¹) 428 nm (2.3 × 10⁵), 545 nm (1.2 × 10⁴).

Trisodium 2,3,7,8,12,13,17,18-octafluoro-5,10,15,20-tetrakis(2,6-difluoro-3-sulfonato-phenyl)porphyrin cobalt(III) (Na₃[Co(F16P)]). Tetrasodium 2,3,7,8,12,13,17,18-octafluoro-5,10,15,20-tetrakis(2,6-difluoro-3-sulfonatophenyl)-21*H*,23*H*-porphyrin•5H₂O (140 mg, 0.10 mmol) and Milli-Q water (40 mL) were placed under N₂ in a 100 mL round-bottom flask equipped with a magnetic stirring bar and a condenser. A solution of cobalt(II) sulfate heptahydrate (141 mg, 0.50 mmol) in Milli-Q water (10 mL) was added to the stirred solution and the mixture was refluxed for 12 h under N₂. After cooling to room temperature, the water was rotary evaporated, and the residue was redissolved in cold methanol (15 mL). After filtration over a filter paper, methanol

was rotary-evaporated, the residue was redissolved in cold methanol (5 mL), and filtered by filter paper again. The filtrate was rotary-evaporated and the $[\text{Co}(\text{F16P})]^{3-}$ complex was then passed through an Amberlite IR 120 Na^+ form ion exchange resin column (10 cm) and washed with Milli-Q water before being purified on Sephadex-20H size exclusion chromatography (eluent: methanol). Methanol was finally rotary evaporated and the solid dried in vacuo. Yield (135 mg, 90%); ^1H NMR (400 MHz, CD_3OD): δ = 6.80 (s, 4H; *p*-Ph-H), 5.60 – 5.37 ppm (m, 4H; *m*-Ph-H); ^{19}F NMR (471 MHz, CD_3OD): δ = –111.97 (d, J = 236.0 Hz, 8F; β -pyrrole-F), –112.74 (s, 4F; *o*-F), –113.26 ppm (s, 4F; *o*-F); HRMS (Appendix 5): m/z calcd for $\text{C}_{44}\text{H}_{12}\text{F}_{16}\text{N}_4\text{CoO}_{12}\text{S}_4^+$: 1278.8406 $[\text{M}-3\text{Na}+4\text{H}]^+$; found: 1278.8407; elemental analysis calcd (%) for $\text{C}_{44}\text{H}_8\text{F}_{16}\text{N}_4\text{Na}_3\text{CoO}_{12}\text{S}_4\cdot\text{Na}_2\text{SO}_4\cdot\text{H}_2\text{O}$: C 35.12, H 0.67, N 3.72; found: C 35.06, H 0.61, N 3.82. UV-vis (H_2O): $\lambda_{\text{max}}(\epsilon \text{ in } \text{M}^{-1} \text{ cm}^{-1})$ 402 nm (1.4×10^5), 535 nm (6.3×10^3).

Tetrasodium 5,10,15,20-tetrakis(2,6-dimethoxyl-3-sulfonatophenyl)porphyrin zincate(II) ($\text{Na}_4[\text{Zn}(\text{OMeP})]$).

The ligand $\text{Na}_4[\text{H}_2(\text{OMeP})]$ (115 mg, 0.09 mmol) and Milli-Q water (40 mL) were placed under N_2 in a 100 mL round-bottom flask equipped with a magnetic stirring bar and a condenser. A solution of zinc(II) chloride (61 mg, 0.45 mmol) in Milli-Q water (10 mL) was added to the stirred solution, and the mixture was refluxed for 12 h under N_2 . After cooling to room temperature, water was rotary evaporated at 40 °C and the residue was redissolved in cold methanol (15 mL). After filtration on a filter paper, methanol was rotary-evaporated, the residue was redissolved in cold methanol (5 mL). The solution was filtered by filter paper, rotary-evaporated, and the crude product was redissolved in Milli-Q water (5 mL) then passed onto an Amberlite IR 120 Na^+ form ion exchange resin column (10 cm), washed with Milli-Q water and further purified on Sephadex-20H size exclusion chromatography to remove excess zinc chloride (methanol). Methanol was finally rotary evaporated and the solid dried in vacuo. Yield (107 mg, 85%); ^1H NMR (400 MHz, CD_3OD): δ = 8.82 – 8.77 (m, 8H; β -pyrrole-H), 8.40 – 8.35 (m, 4H; *p*-

Chapter 5: Electron-Withdrawing Effects of Cobalt Porphyrin Catalysts Boost Homogeneous Photocatalytic Hydrogen Evolution in Neutral Aqueous Solutions

Ph-H), 7.31 – 7.23 (m, 4H; *m*-Ph-H), 3.67 – 3.54 (m, 12 H; OCH₃), 3.07 – 2.76 ppm (m, 12 H; OCH₃); HRMS (Appendix 5): m/z calcd for C₅₂H₄₅N₄ZnO₂₀S₄⁺: 1237.0796 [$M-4Na+5H$]⁺; found: 1237.0792; elemental analysis calcd (%) for C₅₂H₄₀N₄Na₄ZnO₂₀S₄•4H₂O: C 44.66, H 3.46, N 4.01; found: C 44.79, H 3.19, N 3.99. UV-vis (H₂O): $\lambda_{\max}$ (ϵ in M⁻¹ cm⁻¹) 422 nm (1.4×10^5), 557 nm (6.5×10^3).

Tetrasodium 5,10,15,20-tetrakis(2,6-dimethyl-3-sulfonatophenyl)porphyrin zincate(II) (Na₄[Zn(MeP)]).

Tetrasodium 5,10,15,20-tetrakis(2,6-dimethyl-3-sulfonatophenyl)-21*H*,23*H*-porphyrin•9H₂O (130 mg, 0.10 mmol) and Milli-Q water (40 mL) were placed under N₂ in a 100 mL round-bottom flask equipped with a magnetic stirring bar and a condenser. A solution of zinc(II) chloride (68 mg, 0.50 mmol) in Milli-Q water (10 mL) was added to the stirred solution and the mixture was refluxed for 12 h under N₂. After cooling to room temperature, water was rotary evaporated, and the residue was redissolved in cold methanol (15 mL). After filtration on a filter paper, methanol was rotary-evaporated, the residue was redissolved in cold methanol (5 mL), the solution was filtered a second time by filter paper and rotary-evaporated, then the crude product was then passed onto an Amberlite IR 120 Na⁺ form ion exchange resin column (10 cm), washed with Milli-Q water and finally purified on Sephadex-20H size exclusion chromatography (methanol). Methanol was finally rotary evaporated and the solid dried in vacuo. Yield (110 mg, 90%); ¹H NMR (400 MHz, CD₃OD): δ = 8.63 – 8.59 (m, 8H; β -pyrrole-H), 8.35 (m, 4H; *p*-Ph-H), 7.56 – 7.49 (m, 4H; *m*-Ph-H), 2.40 – 2.26 (m, 12H; CH₃), 1.94 – 1.79 ppm (m, 12H; CH₃); HRMS (Appendix 5): m/z calcd for C₅₂H₄₅N₄ZnO₁₂S₄⁺: 1109.1203 [$M-4Na+5H$]⁺; found: 1109.1204; elemental analysis calcd (%) for C₅₂H₄₀N₄Na₄ZnO₁₂S₄•H₂O: C 51.34, H 3.48, N 4.61; found: C 51.54, H 3.39, N 4.61. UV-vis (H₂O): $\lambda_{\max}$ (ϵ in M⁻¹ cm⁻¹) 423 nm (6.0×10^5), 557 nm (1.8×10^4), 599 nm (4.6×10^3).

5.6.2 Cyclic voltammetry, differential pulse voltammetry and linear sweep voltammetry

Cyclic voltammetry (CV), differential pulse voltammetry (DPV) and linear sweep voltammetry (LSV) measurements were performed using an Autolab PGstart10 potentiostat controlled by GPES4 software. CV, DPV and LSV measurements were recorded in 0.1 M sodium phosphate buffer (pH 7.0), 1.0 M sodium phosphate buffer (pH 4.1) or 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF6) DMF solution, using a three-compartment cell with a 0.07 cm² glassy-carbon electrode as the working electrode, Pt wire as the auxiliary electrode, Ag/AgCl (saturated KCl aq.) as the reference electrode for aqueous solution and saturated calomel electrode (SCE) (saturated KCl aq.) as the reference electrode for DMF solution. To ensure consistency, we followed a rigorous preparation protocol for the glassy-carbon electrode before each test: First, the electrode was polished sequentially with 1.0 μm , 0.3 μm , and 0.05 μm alumina for a total of 6 min. After polishing, the electrode tip was ultrasonicated in distilled water and ethanol for 5 min each. It was then allowed to dry at room temperature in ambient air. To verify cleanliness, we performed cyclic voltammetry (CV) tests in 0.5 M H₂SO₄ using a potential range of -1.0 V to 1.0 V versus Ag/AgCl, at a scan rate of 50 mV/s under an argon atmosphere. If the CV curves remain stable for 20 consecutive cycles, we consider the electrode surface free of impurities. Otherwise, the polishing process was repeated. Finally, we tested the electrode in a 4 mM ferrocyanide solution. The electrode was deemed suitable for use only if the reversible peak separation was less than 80 mV; otherwise, the polishing and testing procedures were repeated. K₃[Fe(CN)₆] was added at the end of the measurements in aqueous solutions as internal standard ($E([\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}) = +0.361$ V vs NHE).^[61] Potential vs SCE is converted $+0.241$ V vs NHE at 298K. Unless otherwise indicated, the potential was converted relative to NHE, the solutions were bubbled with high-purity argon for at least 30 min before analysis.

Chapter 5: Electron-Withdrawing Effects of Cobalt Porphyrin Catalysts Boost Homogeneous Photocatalytic Hydrogen Evolution in Neutral Aqueous Solutions

5.6.3 Photo-induced hydrogen evolution

Photo-induced hydrogen evolution from water was analysed by a hydrogen electrode (Unisense H2-NP) controlled by x-5 UniAmp using Logger software. The irradiation source was an OSRAM Opto Semiconductors LD W5SM LED ($\lambda_{\text{irr}} = 450 \text{ nm}$, $\Delta\lambda_{1/2} = 25 \text{ nm}$) with water cooling. All the photochemical hydrogen evolution measurements were carried out in a thermostatic (298 K) photochemical reactor (total volume 25.0 mL). $[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (1.3 mg, 0.5 mM), the catalyst $\text{Na}_3[\text{Co}(\text{OMeP})]$, $\text{Na}_3[\text{Co}(\text{MeP})]$, $\text{Na}_3[\text{Co}(\text{F8P})]$, $\text{Na}_3[\text{Co}(\text{F16})]$, $\text{Na}_4[\text{Zn}(\text{OMeP})]$, $\text{Na}_4[\text{Zn}(\text{MeP})]$, $\text{Na}_4[\text{Zn}(\text{F8P})]$, and $\text{Na}_4[\text{Zn}(\text{F16P})]$ (0.1 mM), and ascorbic acid (53 mg, 0.1 M) and tris(2-carboxyethyl)phosphine hydrochloride (86 mg, 0.1 M) were added as solids in the reactor, and dissolved using sodium phosphate buffer (0.1 M, pH 7.0, 3.0 mL), the pH value of the mixture solution was then controlled with sodium hydroxide solid by checking pH. Under constant stirring, the reactor was equipped with 1 rubber septum and 2 silicon septa in order to make an air-tight system. The hydrogen electrode was then inserted through the septum, to measure the hydrogen concentration in the head space (gas phase) of the photochemical reactor, and the whole system was deaerated by high-purity argon for at least 30 min. After removing the argon, the hydrogen electrode was calibrated by a four-time injection of 100 μL (4.46 μmol at 1 atm) of high-purity H_2 into the closed system, thereby limiting the overpressure to <5%; the calibration was adapted with the pressure change using Logger software, affording direct reading of the volume of dioxygen (μL) produced in the gas phase of the reactor ($V_{\text{gas}} = 22.0 \text{ mL}$). Following calibration, the three used septa were replaced by new ones and the hydrogen electrode was reinserted into the system. The system was degassed for 30 min with argon, then data recording was started, first keeping the system in the dark for another 30 min prior to starting light irradiation. Unless otherwise indicated, the data recording was stopped after 39.5 h of light irradiation.

5.6.4 Calculating the turnover number and turnover frequency

The turnover number (TON) of oxygen evolution was determined by a hydrogen electrode (Unisense OX-NP) controlled by x-5 UniAmp using Logger software. The amount of oxygen formed during 39.5 h illumination was used to calculate the TON. The TON were calculated from the oxygen production data by the following equation:

$$\text{TON} = \frac{n_{\text{H}_2}}{n_{\text{cat}}}$$

in which n_{H_2} is the number of mol of dihydrogen calculated from the volume of the H_2 produced in the photocatalytic experiment as indicated by the calibrated hydrogen electrode in the gas phase (μL), divided by 22.4 L/mol, and n_{cat} is the number of mol of cobalt or zinc porphyrin catalyst used in the photocatalytic experiment. The TON errors were calculated according to triplicate measurements.

The maximum H_2 evolution rate (in h^{-1}) or the maximum turnover frequency TOF_{max} (in h^{-1}) of photocatalytic hydrogen evolution was obtained using Origin 9.1 software by 1) nonlinear curve fitting of the time evolution of the TON, starting at $t = 30$ min for photocatalytic reactions (category: Growth/Sigmoidal, function: logistic Fit); 2) calculating the first derivative $\text{TOF} = f(t)$ using mathematics, differentiate, and 3) identify the maximum value of the H_2 evolution rate $\text{TOF} = f(t)$, noted TOF_{max} (example of $[\text{Co}(\text{OMeP})]^{3-}$ shown in Figure 5A.20). The maximum H_2 evolution rate and TOF_{max} errors were calculated according to triplicate measurements.

5.6.5 Calculation of photochemical H_2 production quantum yield

The H_2 generation quantum yield was calculated using the TOF_{max} , n_{cat} and the rate of photons absorption:

$$\varphi = \frac{2n_{\text{HEC}}\text{TOF}_{\text{max}}}{3600\Phi(1 - 10^{-A_e})(A_{\text{PS}}/A_e)}$$

Chapter 5: Electron-Withdrawing Effects of Cobalt Porphyrin Catalysts Boost Homogeneous Photocatalytic Hydrogen Evolution in Neutral Aqueous Solutions

in which TOF_{max} (h^{-1}) is the maximum turnover frequency of the photocatalytic hydrogen evolution reaction, n_{HEC} (in μmol) is the number of mol of cobalt catalyst used in the photocatalytic experiment, Φ is the photon flux ($\mu\text{mol s}^{-1}$) determined by standard ferrioxalate actinometry (typically $1.05 \mu\text{mol s}^{-1}$ when using a 16 mW light power),^[62] A_{e} is the total absorption of the photocatalytic solution at 450 nm (in all experiments $A_{\text{e}} > 3$ and the photon absorption probability was ~ 1), A_{PS} is the absorption of photosensitizer only in buffer at 450 nm ($A_{\text{PS}}/A_{\text{e}} \sim 1$), and 3600 is the number of seconds per hour. In this calculation we assumed 2 photons were needed for each molecule of H_2 produced. The quantum yield errors were calculated according to triplicate measurements.

5.6.6 Computational details

Structure optimizations and hessian calculations were performed within the AMS2021.101 package by SCM.^[63] All structures were optimized using the OPBE density functional approximation,^[64] in an all-electron double- ζ polarized (DZP) Slater-type basis set, including scalar relativistic effects by means of the zero-order regular approximation (ZORA).^[65] Grimme's third generation dispersion corrections (D3) were used with the Becke-Johnson damping function.^[66–68] Geometries were confirmed to be local minima on the potential energy surface by a hessian calculation without imaginary frequencies. This vibrational analysis was also used to estimate the thermodynamic corrections in the calculated free energies. The partition function contribution of low frequency vibrations has been modified as described in ref^[69]. Because AMS2022.103 does not provide the absolute energies required for the pK_{a} calculations, Gaussian16.2 single-point energy calculations were performed on the obtained structures.^[70] These calculations were performed using the PBE functional with D3(BJ) dispersion corrections in the def2TZVP basis set.^[71–73] The Gibbs free energy of solvation was calculated with the SMD model and SCF convergence was set to

‘tight’.^[74] To verify the consistency between the Gaussian16 and AMS results, the energies of the obtained geometries were also re-evaluated by performing a single point calculation in AMS2021, employing the OPBE-D3(BJ) functional in a ZORA triple- ζ Slater-type basis with two polarization functions (ZORA-TZ2P). At this point, the solvation of the complexes in water was accounted for by the implicit conductor like screening model (COSMO).^[75–77] For all calculations the integration quality was improved over the default settings by putting the numerical quality to ‘good’. It was found that the change in program and density functional affected the one electron reduction potentials of the $^2[\text{Co}^{\text{II}}(\text{F16P})]^{4-}$ and $^2[\text{Co}^{\text{II}}(\text{OMeP})]^{4-}$ complexes by less than 0.02 V vs NHE (Table 5A.3).

To assess the functional dependence of the calculated results, the $^2[\text{Co}^{\text{II}}(\text{F16P})]^{4-}$ to $^1[\text{Co}^{\text{I}}(\text{F16P})]^{5-}$ reduction potential was re-evaluated with a series of different functionals (see Table 5A.4). These reduction potentials were calculated by performing a single point calculation within the AMS2021.101 program with the functional in question, including D3(BJ) dispersion corrections, in a ZORA-TZ2P basis with COSMO solvation on the OPBE-D3(BJ)/ZORA-DZP structures. Interestingly, all hybrid functionals predict a potential that is significantly more anodic than the experimentally observed potential. This was observed also in earlier DFT studies of cobalt porphyrins.^[78,79] Recent studies have addressed this issue by systematically shifting the calculated reduction potentials to match the experimentally observed potential.^[80] In this work, instead we opted for using a GGA functional, as these functionals have also been shown to correctly predict the singlet Co(I)-porphyrin complexes to be more stable than the triplet analogues.^[37]

5.6.7 Thermodynamic calculations

The Gibbs free energies for all structures in solution were calculated following a Born-Haber thermodynamic cycle:

$$G^0(\text{solv}) = E_{\text{scf}}(\text{gas}) + E_{\text{NI}}(\text{gas}) - TS(\text{gas}) + \Delta G_{\text{solv}}^0 + \Delta G^{0/*}$$

Chapter 5: Electron-Withdrawing Effects of Cobalt Porphyrin Catalysts Boost Homogeneous Photocatalytic Hydrogen Evolution in Neutral Aqueous Solutions

where $G^0(\text{solv})$ is the Gibbs free energy of the solvated structure, $E_{\text{scf}}(\text{gas})$ is the electronic energy from the single point calculation, E_{NI} and TS are the nuclear internal energy and entropy corrections as provided by the vibrational analysis in the gas phase, and ΔG_{solv}^0 is the Gibbs free energy of solvation, given by the solvent model. We note that the E_{NI} term includes both the zero-point energy contribution, as well as rotational and translational contributions. The $\Delta G^{0/*}$ term is introduced to convert the Gibbs free energy in the gas-phase at a pressure of 1 atm to the Gibbs free energy of the solvated molecule at the desired concentration. The term is calculated as

$$\Delta G^{0/*} = RT \ln(24.46 * [\text{molecule}])$$

where R is the universal gas constant, T is temperature (in K) and $[\text{molecule}]$ is the concentration of the molecule.^[81] The Gibbs free energies associated with redox reactions were calculated using

$$\Delta G_{\text{redox}}^0(\text{solv}) = G_{\text{red}}^0(\text{solv}) - G_{\text{ox}}^0(\text{solv}),$$

where G_{red}^0 and G_{ox}^0 were the Gibbs free energies of the relaxed oxidized and reduced species, including protonation steps and ligand dissociations. Subsequently, redox potentials could be calculated directly as

$$E_{\text{redox}}^0 = \frac{-\Delta G_{\text{redox}}^0(\text{solv})}{nF} - 4.281 \text{ eV},$$

with n the number of transferring electrons and F the Faraday constant. The 4.281 eV term is introduced to translate the absolute potentials to potentials against NHE.^[81] $\text{p}K_{\text{a}}$ values were calculated directly from the Gibbs free energy associated with the dissociation reaction $\text{HA} \rightarrow \text{H}^+ + \text{A}^-$

$$\text{p}K_{\text{a}}(\text{HA}) = \frac{\Delta G_{\text{dissociation}}^0(\text{solv})}{2.303 k_{\text{B}}T}$$

where the (translational) free energy of a proton was taken as $-6.23 \text{ kcal mol}^{-1}$ and the solvation energy of a proton in water was taken as $-264.0 \text{ kcal mol}^{-1}$ at 1 atm and 298.15 K standard state conditions.^[82,83] k_{B} is the Boltzmann constant.

The $\Delta G^{0/*}$ term to convert the Gibbs free energy of the proton in the gas-phase to the Gibbs free energy of a proton in solution at 1 mol L⁻¹ is -1.89 kcal mol⁻¹.^[84] Finally, the Gibbs free energies associated with the protonation of a metal complex at a specific pH value was calculated as

$$\Delta G_{\text{PT}}^0(\text{solv}) = 2.303 K_{\text{B}}T [\text{pH} - \text{p}K_{\text{a}}(\text{HA})],$$

where $\Delta G_{\text{PT}}^0(\text{solv})$ is the Gibbs free energy of the proton transfer reaction in solution.

5.7 References

- [1] W. Zhang, W. Lai, R. Cao, *Chem. Rev.* **2017**, *117*, 3717–3797.
- [2] P. Du, R. Eisenberg, *Energy Environ. Sci.* **2012**, *5*, 6012.
- [3] W. T. Eckenhoff, *Coord. Chem. Rev.* **2018**, *373*, 295–316.
- [4] A. Mazzeo, S. Santalla, C. Gaviglio, F. Doctorovich, J. Pellegrino, *Inorganica Chim. Acta* **2021**, *517*, 119950.
- [5] H. I. Karunadasa, E. Montalvo, Y. Sun, M. Majda, J. R. Long, C. J. Chang, *Science* **2012**, *335*, 698–702.
- [6] B. R. Garrett, S. M. Polen, K. A. Click, M. He, Z. Huang, C. M. Hadad, Y. Wu, *Inorg. Chem.* **2016**, *55*, 3960–3966.
- [7] M. Kondo, H. Tatewaki, S. Masaoka, *Chem. Soc. Rev.* **2021**, *50*, 6790–6831.
- [8] C. Liu, D. Van Den Bos, B. Den Hartog, D. Van Der Meij, A. Ramakrishnan, S. Bonnet, *Angew. Chem. Int. Ed.* **2021**, *60*, 13463–13469.
- [9] Y. Han, H. Fang, H. Jing, H. Sun, H. Lei, W. Lai, R. Cao, *Angew. Chem. Int. Ed.* **2016**, *128*, 5547–5552.
- [10] X. Yang, Z. Hu, Q. Yin, C. Shu, X. Jiang, J. Zhang, X. Wang, J. Jiang, F. Huang, Y. Cao, *Adv. Funct. Mater.* **2019**, *29*, 1808156.
- [11] H. Lei, C. Liu, Z. Wang, Z. Zhang, M. Zhang, X. Chang, W. Zhang, R. Cao, *ACS Catal.* **2016**, *6*, 6429–6437.
- [12] C. Bachmann, B. Probst, M. Guttentag, R. Alberto, *Chem. Commun.* **2014**, *50*, 6737–6739.
- [13] B. B. Beyene, C.-H. Hung, *Sustainable Energy Fuels* **2018**, *2*, 2036–2043.
- [14] S. Chakraborty, E. H. Edwards, B. Kandemir, K. L. Bren, *Inorg. Chem.* **2019**, *58*, 16402–16410.
- [15] F. Gärtner, A. Boddien, E. Barsch, K. Fumino, S. Losse, H. Junge, D. Hollmann, A. Brückner, R. Ludwig, M. Beller, *Chem. Eur. J* **2011**, *17*, 6425–6436.
- [16] E. Giannoudis, E. Benazzi, J. Karlsson, G. Copley, S. Panagiotakis, G. Landrou, P. Angaridis, V. Nikolaou, C. Matthaiaki, G. Charalambidis, E. A. Gibson, A. G. Coutsolelos, *Inorg. Chem.* **2020**, *59*, 1611–1621.
- [17] J. G. Kleingardner, B. Kandemir, K. L. Bren, *J. Am. Chem. Soc.* **2014**, *136*, 4–7.
- [18] M. P. McLaughlin, T. M. McCormick, R. Eisenberg, P. L. Holland, *Chem. Commun.* **2011**, *47*, 7989.
- [19] M. Natali, E. Badetti, E. Deponti, M. Gamberoni, F. A. Scaramuzza, A. Sartorel, C. Zonta, *Dalton Trans.* **2016**, *45*, 14764–14773.
- [20] A. Panagiotopoulos, A. M. Douvas, P. Argitis, A. G. Coutsolelos, *ChemSusChem* **2016**, *9*, 3213–3219.
- [21] A. Reynal, E. Pastor, M. A. Gross, S. Selim, E. Reisner, J. R. Durrant, *Chem. Sci.* **2015**, *6*, 4855–4859.
- [22] Y. Yuan, Z. Yu, H. Gao, Z. Zou, C. Zheng, W. Huang, *Chem. Eur. J.* **2013**, *19*, 6340–6349.

Chapter 5: Electron-Withdrawing Effects of Cobalt Porphyrin Catalysts Boost Homogeneous Photocatalytic Hydrogen Evolution in Neutral Aqueous Solutions

- [23] M. Yang, J. E. Yarnell, K. El Roz, F. N. Castellano, *ACS Appl. Energy Mater.* **2020**, *3*, 1842–1853.
- [24] Z.-T. Yu, X.-L. Liu, Y.-J. Yuan, Y.-H. Li, G.-H. Chen, Z.-G. Zou, *Dalton Trans.* **2016**, *45*, 17223–17232.
- [25] J.-M. Lei, S.-P. Luo, S.-Z. Zhan, *Polyhedron* **2018**, *154*, 295–301.
- [26] T. Lazarides, M. Delor, I. V. Sazanovich, T. M. McCormick, I. Georgakaki, G. Charalambidis, J. A. Weinstein, A. G. Coutsolelos, *Chem. Commun.* **2014**, *50*, 521–523.
- [27] R. S. Khnayzer, V. S. Thoi, M. Nippe, A. E. King, J. W. Jurss, K. A. El Roz, J. R. Long, C. J. Chang, F. N. Castellano, *Energy Environ. Sci.* **2014**, *7*, 1477–1488.
- [28] C. Bachmann, M. Guttentag, B. Spingler, R. Alberto, *Inorg. Chem.* **2013**, *52*, 6055–6061.
- [29] M. Natali, *ACS Catal.* **2017**, *7*, 1330–1339.
- [30] A. Mahammed, B. Mondal, A. Rana, A. Dey, Z. Gross, *Chem. Commun.* **2014**, *50*, 2725–2727.
- [31] M. Vennampalli, G. Liang, L. Katta, C. E. Webster, X. Zhao, *Inorg. Chem.* **2014**, *53*, 10094–10100.
- [32] Y. Sun, J. Sun, J. R. Long, P. Yang, C. J. Chang, *Chem. Sci.* **2013**, *4*, 118–124.
- [33] A. Panagiotopoulos, K. Ladomenou, D. Sun, V. Artero, A. G. Coutsolelos, *Dalton Trans.* **2016**, *45*, 6732–6738.
- [34] K. Ladomenou, M. Natali, E. Iengo, G. Charalampidis, F. Scandola, A. G. Coutsolelos, *Coord. Chem. Rev.* **2015**, *304–305*, 38–54.
- [35] B. B. Beyene, S. B. Mane, C.-H. Hung, *Chem. Commun.* **2015**, *51*, 15067–15070.
- [36] H. M. Castro-Cruz, N. A. Macías-Ruvalcaba, *Coord. Chem. Rev.* **2022**, *458*, 214430.
- [37] B. H. Solis, A. G. Maher, T. Honda, D. C. Powers, D. G. Nocera, S. Hammes-Schiffer, *ACS Catal.* **2014**, *4*, 4516–4526.
- [38] M. M. Roubelakis, D. K. Bediako, D. K. Dogutan, D. G. Nocera, *Energy Environ. Sci.* **2012**, *5*, 7737.
- [39] D.-X. Zhang, H.-Q. Yuan, H.-H. Wang, A. Ali, W.-H. Wen, A.-N. Xie, S.-Z. Zhan, H.-Y. Liu, *Transit. Met. Chem.* **2017**, *42*, 773–782.
- [40] H. Lei, Y. Wang, Q. Zhang, R. Cao, *J. Porphyrins Phthalocyanines* **2020**, *24*, 1361–1371.
- [41] B. B. Beyene, S. B. Mane, C.-H. Hung, *J. Electrochem. Soc.* **2018**, *165*, H481–H487.
- [42] A. Call, F. Franco, N. Kandoth, S. Fernández, M. González-Béjar, J. Pérez-Prieto, J. M. Luis, J. Lloret-Fillol, *Chem. Sci.* **2018**, *9*, 2609–2619.
- [43] X. Peng, M. Zhang, H. Qin, J. Han, Y. Xu, W. Li, X. Zhang, W. Zhang, U. Apfel, R. Cao, *Angew. Chem. Int. Ed.* **2024**, *63*, e202401074.
- [44] B. C. M. Martindale, E. Joliat, C. Bachmann, R. Alberto, E. Reisner, *Angew. Chem. Int. Ed.* **2016**, *55*, 9402–9406.
- [45] M. F. Zippies, W. A. Lee, T. C. Bruice, *J. Am. Chem. Soc.* **1986**, *108*, 4433–4445.
- [46] S. Nakagaki, F. L. Benedito, F. Wypych, *J. Mol. Catal. A Chem.* **2004**, *217*, 121–131.
- [47] J. C. Biffinger, H. Sun, A. P. Nelson, S. G. DiMaggio, *Org. Biomol. Chem.* **2003**, *217*, 121–131.
- [48] A. R. Parent, K. Sakai, *ChemSusChem* **2014**, *7*, 2070–2080.
- [49] T. Nakazono, A. R. Parent, K. Sakai, *Chem. Eur. J.* **2015**, *21*, 6723–6726.
- [50] A. Sulek, B. Pucelik, J. Kunciewicz, G. Dubin, J. M. Dąbrowski, *Catal. Today* **2019**, *335*, 538–549.
- [51] T. Nakazono, K. Sakai, *Dalton Trans.* **2016**, *45*, 12649–12652.
- [52] L. Troian-Gautier, C. Moucheron, *Molecules* **2014**, *19*, 5028–5087.
- [53] D. P. Rillema, G. Allen, T. J. Meyer, D. Conrad, *Inorg. Chem.* **1983**, *22*, 1617–1622.
- [54] Y.-J. Yuan, Z.-T. Yu, D.-Q. Chen, Z.-G. Zou, *Chem. Soc. Rev.* **2017**, *46*, 603–631.
- [55] E. Joliat-Wick, N. Weder, D. Klose, C. Bachmann, B. Spingler, B. Probst, R. Alberto, *Inorg. Chem.* **2018**, *57*, 1651–1655.

- [56] J. T. Muckerman, P. Achord, C. Creutz, D. E. Polyansky, E. Fujita, *Proc. Natl. Acad. Sci. U.S.A.* **2012**, *109*, 15657–15662.
- [57] E. S. Wiedner, M. B. Chambers, C. L. Pitman, R. M. Bullock, A. J. M. Miller, A. M. Appel, *Chem. Rev.* **2016**, *116*, 8655–8692.
- [58] B. H. Solis, S. Hammes-Schiffer, *Inorg. Chem.* **2014**, *53*, 6427–6443.
- [59] J. Ho, M. L. Coote, *Theor. Chem. Acc.* **2009**, *125*, 3–21.
- [60] A. G. Maher, M. Liu, D. G. Nocera, *Inorg. Chem.* **2019**, *58*, 7958–7968.
- [61] A. Bettelheim, B. A. White, S. A. Raybuck, R. W. Murray, *Inorg. Chem.* **1987**, *26*, 1009–1017.
- [62] J. G. Calvert, J. N. Pitts, *Photochemistry*, Wiley and Sons: New York, 1967; 780.
- [63] AMS2021.101, SCM, Theoretical Chemistry. Vrije Universiteit: Amsterdam, The Netherlands. <https://www.scm.com>.
- [64] M. Swart, A. W. Ehlers, K. Lammertsma, *Mol. Phys.* **2004**, *102*, 2467–2474.
- [65] E. Van Lenthe, *J. Chem. Phys.* **1999**, *110*, 8943–8953.
- [66] S. Grimme, *J. Comput. Chem.* **2004**, *25*, 1463–1473.
- [67] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104.
- [68] S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456–1465.
- [69] S. Grimme, *Chem. Eur. J.* **2012**, *18*, 9955–9964.
- [70] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, Gaussian 16; Gaussian, Inc.: Wallingford, CT, 2016.
- [71] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1997**, *78*, 1396–1396.
- [72] F. Weigend, *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057.
- [73] R. Weigend, F.; Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.
- [74] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2009**, *113*, 6378–6396.
- [75] A. Klamt, *J. Phys. Chem.* **1995**, *99*, 2224–2235.
- [76] A. Klamt, V. Jonas, *J. Chem. Phys.* **1996**, *105*, 9972–9981.
- [77] C. C. Pye, T. Ziegler, E. Van Lenthe, J. N. Louwen, *Can. J. Chem.* **2009**, *87*, 790–797.
- [78] I. M. B. Nielsen, K. Leung, *J. Phys. Chem. A* **2010**, *114*, 10166–10173.
- [79] K. Leung, I. M. B. Nielsen, N. Sai, C. Medforth, J. A. Shelnutt, *J. Phys. Chem. A* **2010**, *114*, 10174–10184.
- [80] A. Call, M. Ciban, K. Yamamoto, T. Nakazono, K. Yamauchi, K. Sakai, *ACS Catal.* **2019**, *9*, 4867–4874.
- [81] A. A. Isse, A. Gennaro, *J. Phys. Chem. B* **2010**, *114*, 7894–7899.
- [82] M.-K. Tsai, J. Rochford, D. E. Polyansky, T. Wada, K. Tanaka, E. Fujita, J. T. Muckerman, *Inorg. Chem.* **2009**, *48*, 4372–4383.
- [83] M. D. Tissandier, K. A. Cowen, W. Y. Feng, E. Gundlach, M. H. Cohen, A. D. Earhart, J. V. Coe, T. R. Tuttle, *J. Phys. Chem. A* **1998**, *102*, 7787–7787.
- [84] C. P. Kelly, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. A* **2006**, *110*, 2493–2499.

Chapter 5: Electron-Withdrawing Effects of Cobalt Porphyrin Catalysts Boost Homogeneous Photocatalytic Hydrogen Evolution in Neutral Aqueous Solutions

5A. Appendix

5A.1 ^1H -NMR and ^{19}F -NMR

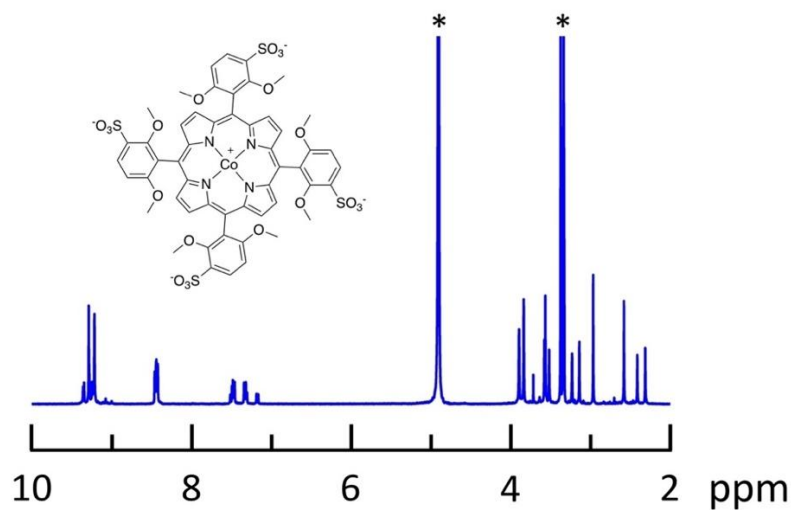


Figure 5A.1. ^1H NMR of $[\text{Co}(\text{OMeP})]^{3-}$ in MeOD . * Methanol and water.

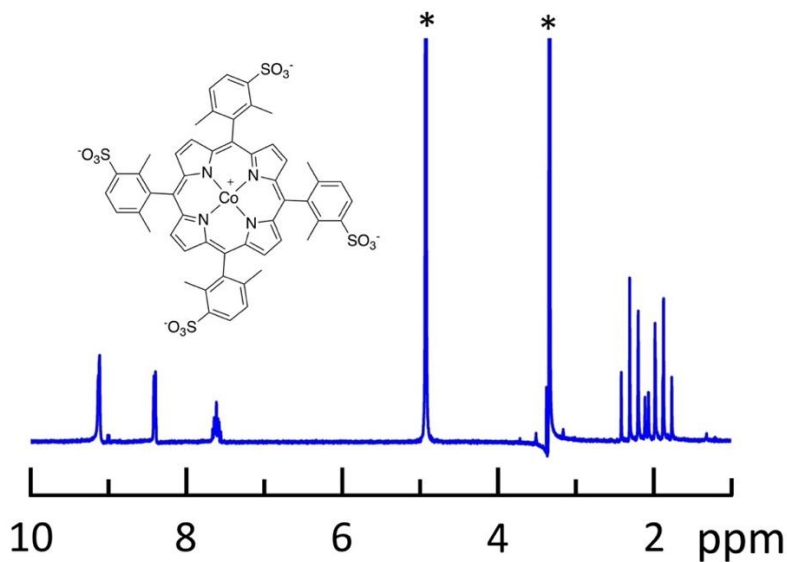


Figure 5A.2. ^1H NMR of $[\text{Co}(\text{MeP})]^{3-}$ in MeOD . * Methanol and water.

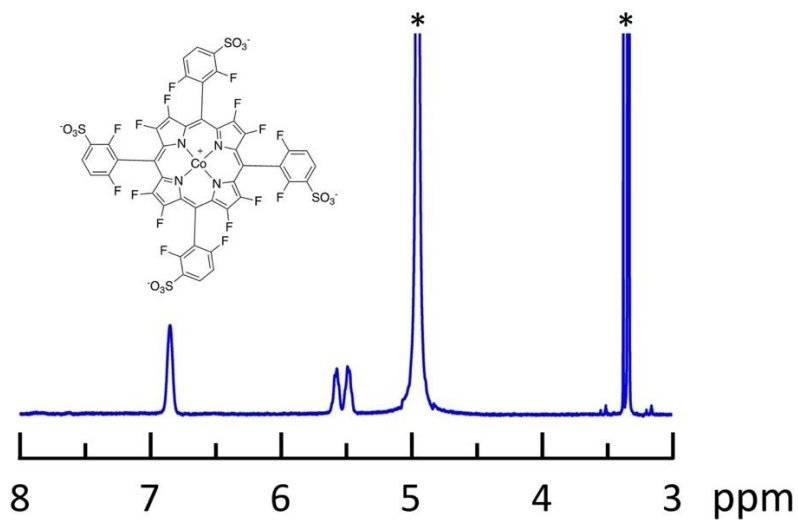


Figure 5A.3. ^1H NMR of $[\text{Co}(\text{F16P})]^{3-}$ in MeOD . * Methanol and water.

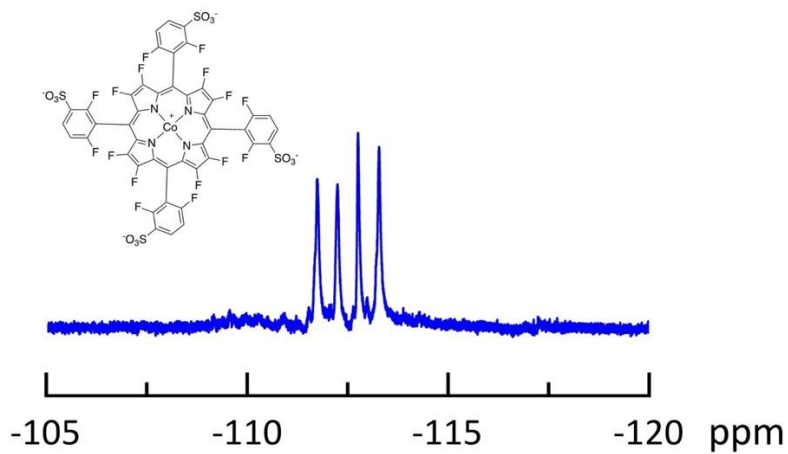


Figure 5A.4. ^{19}F NMR of $[\text{Co}(\text{F16P})]^{3-}$ in MeOD .

Chapter 5: Electron-Withdrawing Effects of Cobalt Porphyrin Catalysts Boost Homogeneous Photocatalytic Hydrogen Evolution in Neutral Aqueous Solutions

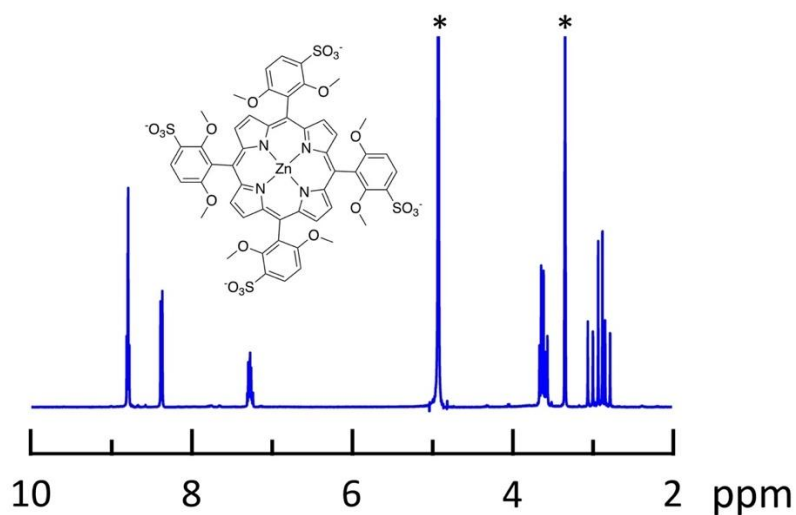


Figure 5A.5. ^1H NMR of $[\text{Zn}(\text{OMeP})]^{4-}$ in MeOD. * Methanol and water.

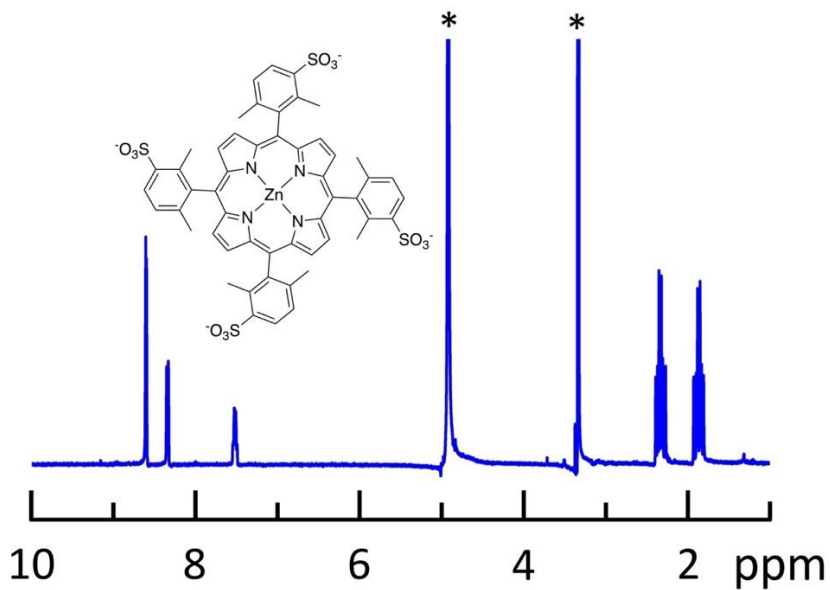


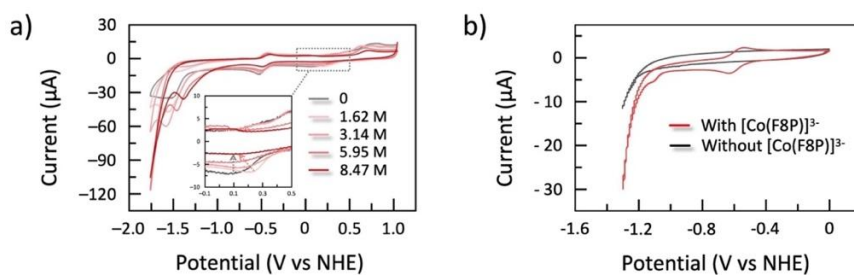
Figure 5A.6. ^1H NMR of $[\text{Zn}(\text{MeP})]^{4-}$ in MeOD. * Methanol and water.

5A.2. Cyclic Voltammetry and Linear Sweep Voltammetry

Table 5A.1. Electrochemical properties of Co-porphyrin complexes at pH 7.0 and pH 4.1.

	2 nd reduction potential at pH 7.0 (at pH 4.1) ^[a]	HER on-set potential at pH 7.0 (at pH 4.1) ^[b]	η at pH 7.0 (at pH 4.1) ^[c]	E_{dr} at pH 7.0 (at pH 4.1) ^[d]
[Co(OMeP)] ³⁻	-0.75 (-0.78)	-1.04 (-0.95)	630 (710)	220 (310)
[Co(MeP)] ³⁻	-0.70 (-0.73)	-0.95 (-0.74)	540 (500)	310 (520)
[Co(F8P)] ³⁻	-0.64 (-0.66)	-1.01 (-0.94)	600 (700)	250 (320)
[Co(F16P)] ³⁻	-0.53 (-0.55)	-0.84 (-0.88)	430 (640)	420 (380)

^[a] data according to DPV, V vs. NHE. ^[b] data according to CV, V vs. NHE. ^[c] calculated according to the HER on-set potential, in mV. ^[d] calculated according to $E_{PS}(PS/PS^-) = -1.26$ V vs. NHE, in mV.



Figure

5A.7. Cyclic voltammetry of the [Co(F8P)]³⁻ **a)** in DMF with addition of 0 to 8.47 M water; **b)** in KCl aqueous solution. Conditions: **a)** 1.0 mM Na₃[Co(F8P)], 0.1 M TBAPF₆, SCE reference electrode, 200 mV s⁻¹ scan rate; **b)** 0.5 mM Na₃[Co(F8P)], 0.1 M KCl, Ag/AgCl reference electrode, 50 mV s⁻¹ scan rate. 0.07 cm² glassy-carbon working electrode, Pt wire auxiliary electrode, $T = 298$ K.

Chapter 5: Electron-Withdrawing Effects of Cobalt Porphyrin Catalysts Boost Homogeneous Photocatalytic Hydrogen Evolution in Neutral Aqueous Solutions

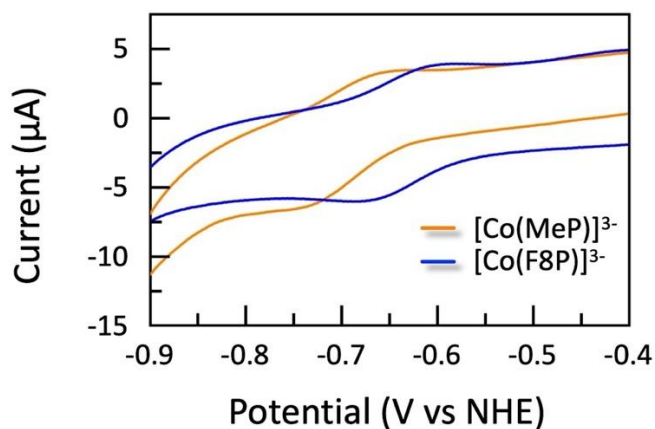


Figure 5A.8. Detailed view of the cyclic voltammograms of $[\text{Co}(\text{MeP})]^{3-}$ and $[\text{Co}(\text{F8P})]^{3-}$ shown in Figure 3b from -0.9 to -0.4 V vs. NHE.

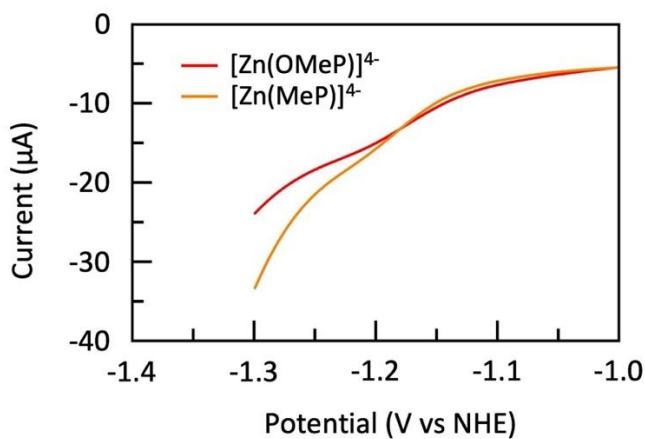


Figure 5A.9. Linear sweep voltammetry from -1.3 to -1.0 V vs. NHE of the $[\text{Zn}(\text{OMeP})]^{4-}$ and $[\text{Zn}(\text{MeP})]^{4-}$ in Figure 5.3c.

5A.3. Photocatalytic Hydrogen Evolution

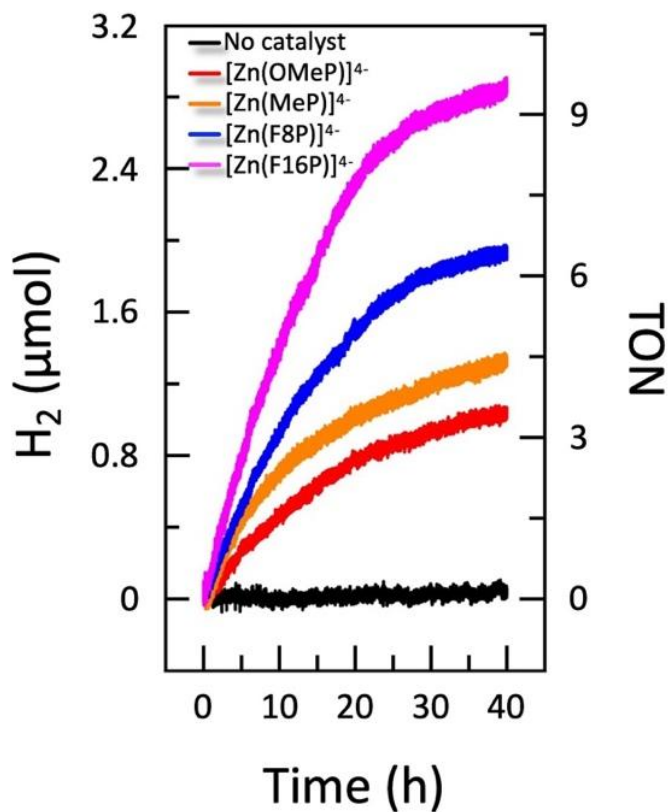


Figure 5A.10. Total amount of hydrogen (in μmol) measured over time (in hours) during photocatalytic water reduction in the presence of 0.1 mM catalyst $[\text{Zn}(\text{OMeP})]^{4-}$, $[\text{Zn}(\text{MeP})]^{4-}$, $[\text{Zn}(\text{F8P})]^{4-}$ and $[\text{Zn}(\text{F16P})]^{4-}$, using 0.5 mM $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ as photosensitizer, 0.1 M ascorbate and TCEP, in pH 7.0 aqueous solution, and LED lamp (450 nm, 16 mW) for irradiation, $T = 298\text{ K}$.

Chapter 5: Electron-Withdrawing Effects of Cobalt Porphyrin Catalysts Boost Homogeneous Photocatalytic Hydrogen Evolution in Neutral Aqueous Solutions

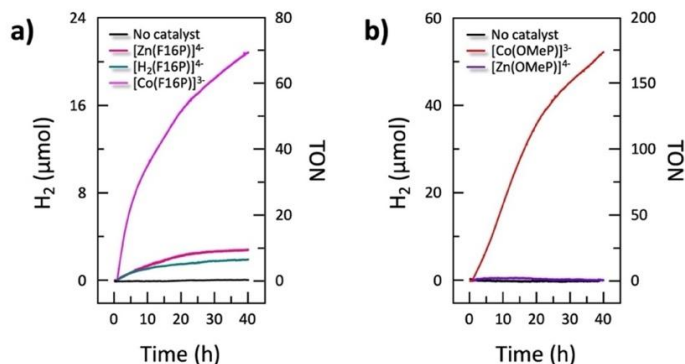


Figure 5A.11. Total amount of hydrogen (in μmol) measured over time (in hours) during photocatalytic water reduction in the presence of a) 0.1 mM catalyst $[\text{Co}(\text{F16P})]^{3-}$, $[\text{H}_2(\text{F16P})]^{4-}$ and $[\text{Zn}(\text{F16P})]^{4-}$ in pH 7.0 aqueous solution, and b) 0.1 mM catalyst $[\text{Co}(\text{OMeP})]^{3-}$ and $[\text{Zn}(\text{OMeP})]^{4-}$ in pH 4.1 aqueous solution using 0.5 mM $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ as photosensitizer, 0.1 M ascorbate and TCEP, and a LED lamp (450 nm, 16 mW) for irradiation, $T = 298 \text{ K}$.

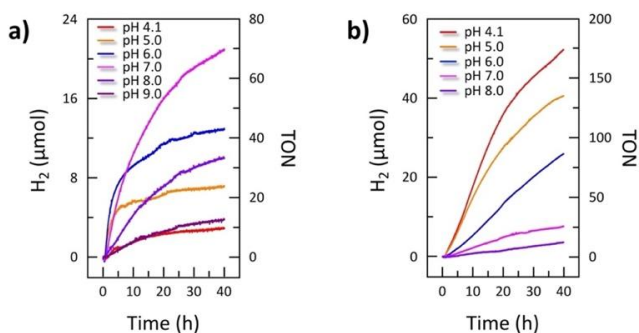


Figure 5A.12. Total amount of hydrogen (in μmol) measured over time (in hours) during photocatalytic water reduction in presence of a) 0.1 mM catalyst $[\text{Co}(\text{F16P})]^{3-}$ and b) $[\text{Co}(\text{OMeP})]^{3-}$ at different pH in aqueous solution using 0.5 mM $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ as photosensitizer, 0.1 M ascorbic acid and TCEP as electron donor, and blue light irradiation (450 nm, 16 mW). Conditions: $T = 298 \text{ K}$, phosphate buffer.

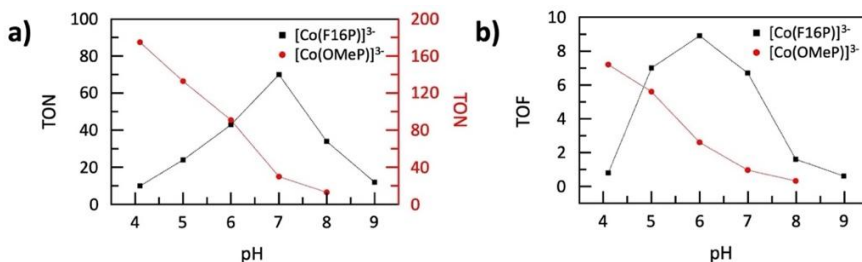


Figure 5A.13. a) Turnover numbers and b) maximum turnover frequencies of photocatalytic H_2 evolution systems in Figure 5A.12 plotted as a function of the pH.

5A.4. Photostability

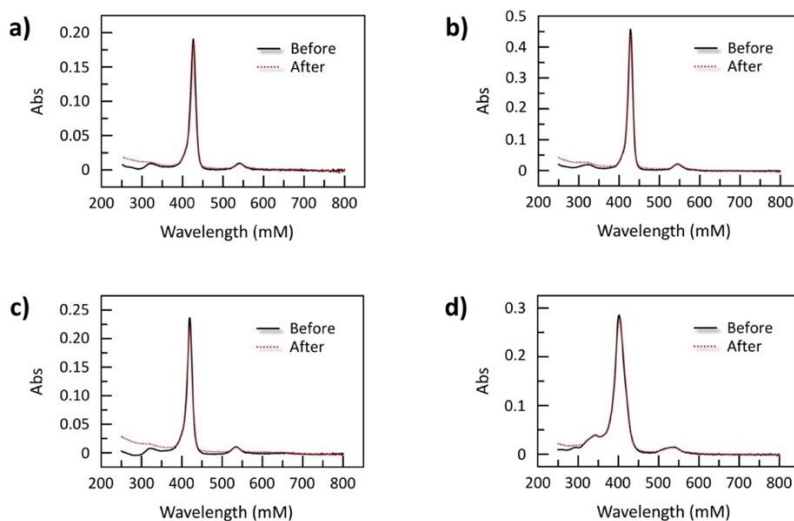


Figure 5A.14. Absorption spectra of 2 μM a) $[Co(OMeP)]^{3-}$, b) $[Co(MeP)]^{3-}$, c) $[Co(F8P)]^{3-}$, and d) $[Co(F16P)]^{3-}$ before (black solid) and after (red short dot) 48 hours irradiation (LED lamp, 450 nm, 16 mW) in 0.1 M sodium phosphate buffer (pH 7.0) under air, $T = 298$ K.

Chapter 5: Electron-Withdrawing Effects of Cobalt Porphyrin Catalysts Boost Homogeneous Photocatalytic Hydrogen Evolution in Neutral Aqueous Solutions

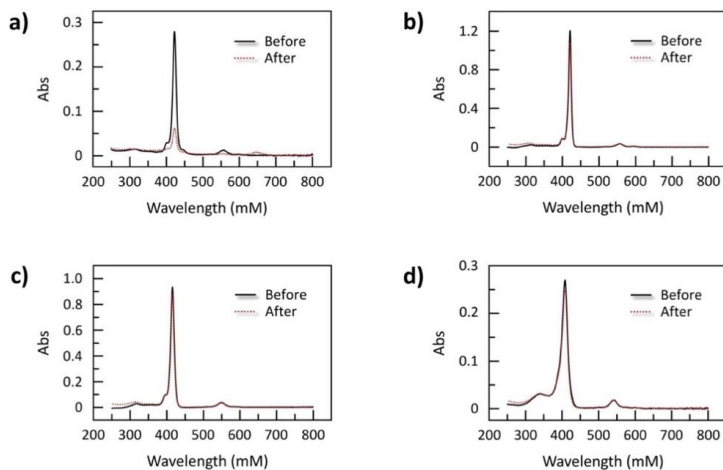


Figure 5A.15. Absorption spectra of 2 μM a) $[\text{Zn}(\text{OMeP})]^{4-}$, b) $[\text{Zn}(\text{MeP})]^{4-}$, c) $[\text{Zn}(\text{F8P})]^{4-}$, and d) $[\text{Zn}(\text{F16P})]^{4-}$ before (black solid) and after (red dots) 48 hours irradiation (LED lamp, 450 nm, 16 mW) in 0.1 M sodium phosphate buffer (pH 7.0) under air, $T = 298\text{ K}$.

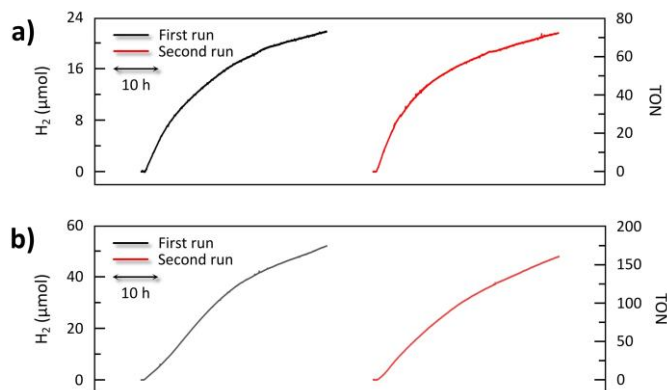


Figure 5A.16. Repetitive photocatalytic hydrogen evolution in presence of a) 0.1 mM $[\text{Co}(\text{F16P})]^{3-}$ in pH 7.0 and b) $[\text{Co}(\text{OMeP})]^{3-}$ in different pH 4.1 aqueous solution using 0.5 mM $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ as photosensitizer, 0.1 M ascorbate and TCEP, and a LED lamp (450 nm, 16 mW) for irradiation, $T = 298\text{ K}$. Between the two irradiation experiments, 1.5 μmol fresh $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ was added as a solid powder.

5A.5. Kinetic Study

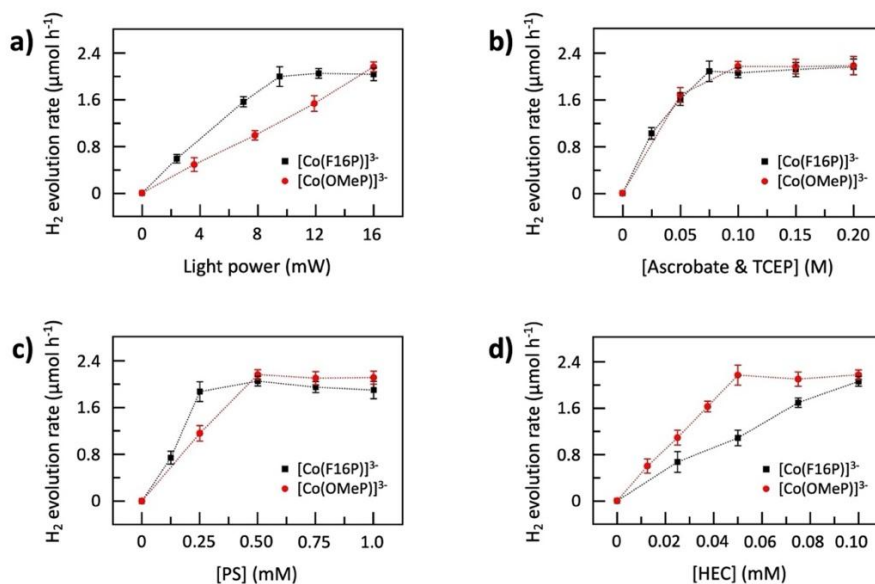


Figure 5A.17. Maximum H_2 evolution rate during photocatalytic H_2 evolution using the catalyst $[\text{Co}(\text{F16P})]^{3-}$ at pH 7.0 (black squares) or $[\text{Co}(\text{OMeP})]^{3-}$ at pH 4.1 (red circles) plotted as a function of a) the light power, b) the concentration of ascorbate and TCEP, c) the concentration of the photosensitizer $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ and d) the concentration of the hydrogen evolution catalyst. Standard conditions: 0.1 mM catalyst, 0.5 mM $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$, 0.1 M ascorbate and TCEP, blue light (450 nm, 16 mW), $T = 298 \text{ K}$.

Chapter 5: Electron-Withdrawing Effects of Cobalt Porphyrin Catalysts Boost Homogeneous Photocatalytic Hydrogen Evolution in Neutral Aqueous Solutions

5A.6. Density Functional Theory

Table 5A.2. Gibbs free energies of all considered 1,2 and 3 electron reduced intermediates (in kcal/mol, relative to $^2[\text{Co}^{\text{II}}(\text{P})]^{4-}$).^[a]

Species	Relative energy (kcal mol ⁻¹)	
	[Co(F16P)]	[Co(OMeP)]
Non-reduced		
$^1[\text{Co}^{\text{III}}(\text{P})]^{3-}$	-	-
$^1[\text{Co}^{\text{III}}(\text{P})(\text{H}_2\text{O})]^{3-}$	21.6 ^[b]	3.4 ^[b]
$^1[\text{Co}^{\text{III}}(\text{P})(\text{H}_2\text{O})_2]^{3-}$	13.2 ^[b]	-0.8 ^[b]
1 e⁻ reduced		
$^2[\text{Co}^{\text{II}}(\text{P})]^{4-}$	0	0
$^4[\text{Co}^{\text{II}}(\text{P})]^{4-}$	-	16.4
$^2[\text{Co}^{\text{II}}(\text{P})(\text{H}_2\text{O})]^{4-}$	3.5	1.7
$^2[\text{Co}^{\text{II}}(\text{P})(\text{H}_2\text{O})_2]^{4-}$	8.0	14.0
2 e⁻ reduced		
$^1[\text{Co}^{\text{I}}(\text{P})]^{5-}$	12.1	16.5
$^3[\text{Co}^{\text{I}}(\text{P})]^{5-}$	26.9	29.0
$^3[\text{Co}^{\text{I}}(\text{P})(\text{H}_2\text{O})]^{5-}$	26.6 ^[c]	29.9 ^[c]
$^1[\text{Co}^{\text{III}}(\text{H})(\text{P})]^{4-}$	14.5	10.5
$^1[\text{Co}^{\text{III}}(\text{H})(\text{P})(\text{H}_2\text{O})]^{4-}$	19.8	13.7 ^[c]
$^1[\text{Co}^{\text{I}}(\text{P}-\text{H}_\text{N})]^{4-}$	24.2	21.8
$^1[\text{Co}^{\text{I}}(\text{P}-\text{H}_\alpha)]^{4-}$	26.4	24.7
$^1[\text{Co}^{\text{I}}(\text{P}-\text{H}_\beta)]^{4-}$	21.4	16.4
$^1[\text{Co}^{\text{I}}(\text{P}-\text{H}_{\text{meso}})]^{4-}$	30.1	20.1
$^3[\text{Co}^{\text{I}}(\text{P}-\text{H}_\alpha)]^{4-}$	31.5 ^[d]	22.6 ^[d]
$^3[\text{Co}^{\text{I}}(\text{P}-\text{H}_\beta)]^{4-}$	25.6 ^[d]	21.1
$^3[\text{Co}^{\text{I}}(\text{P}-\text{H}_{\text{meso}})]^{4-}$	21.9 ^[d]	14.8
$^3[\text{Co}^{\text{I}}(\text{P}-\text{H}_\alpha)(\text{H}_2\text{O})]^{4-}$	33.2	29.7
$^3[\text{Co}^{\text{I}}(\text{P}-\text{H}_\beta)(\text{H}_2\text{O})]^{4-}$	27.3	24.2
$^3[\text{Co}^{\text{I}}(\text{P}-\text{H}_{\text{meso}})(\text{H}_2\text{O})]^{4-}$	24.6	21.9
3 e⁻ reduced		
$^2[\text{Co}^0(\text{P})]^{6-}$	45.3	57.2
$^2[\text{Co}^{\text{II}}(\text{H})(\text{P})]^{5-}$	35.2	40.8
$^2[\text{Co}^0(\text{P}-\text{H}_\text{N})]^{5-}$	43.3	52.9
$^2[\text{Co}^0(\text{P}-\text{H}_\alpha)]^{5-}$	30.6	41.5
$^2[\text{Co}^0(\text{P}-\text{H}_\beta)]^{5-}$	22.7	34.1
$^2[\text{Co}^0(\text{P}-\text{H}_{\text{meso}})]^{5-}$	31.1	30.2

[a] Gibbs free energies assume concentrations of 0.1mM for all metal complexes and 55 M for water. All Gibbs free energies are calculated at pH = 0, at a potential of 0 V vs NHE and a temperature of 298.15 K.

[b] Optimizations were carried out with the COSMO solvation model because geometry optimizations in vacuum did not converge due to non-converging SCF optimizations.

[c] Aqua ligands partially dissociated during optimizations.

[d] Only a single-point calculation in the low-spin optimized geometries were performed, as a geometry optimizations of the high-spin state structures did not converge due to issues with the SCF procedure.

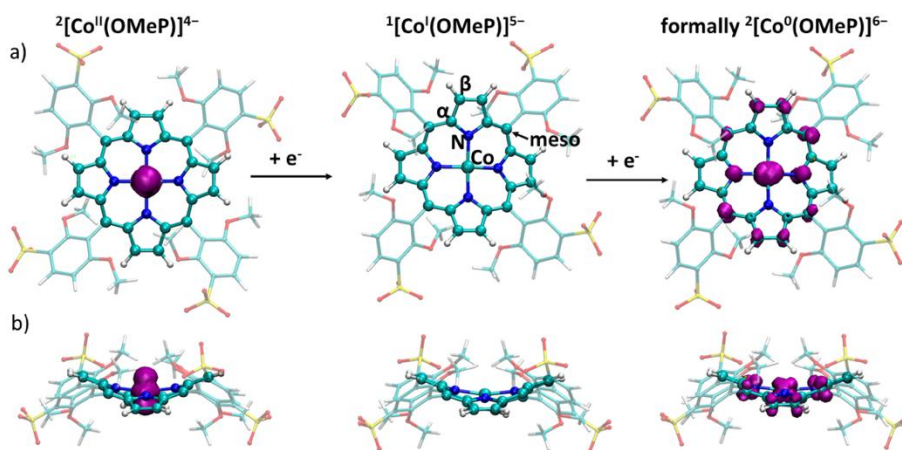


Figure 5A.18. Top (a) and side (b) views of the optimized structures of the $[\text{Co}(\text{OMeP})]^{3-}$ catalyst complex in the Co^{II} , Co^{I} and formally Co^0 oxidation states. For the complexes with unpaired electrons, the spin density is visualized with an isosurface value of 0.003. The five different sites on the cobalt porphyrin complex which are prone to protonation are indicated with insets on the $^1[\text{Co}^{\text{I}}(\text{OMeP})]^{5-}$ intermediate.

Chapter 5: Electron-Withdrawing Effects of Cobalt Porphyrin Catalysts Boost Homogeneous Photocatalytic Hydrogen Evolution in Neutral Aqueous Solutions

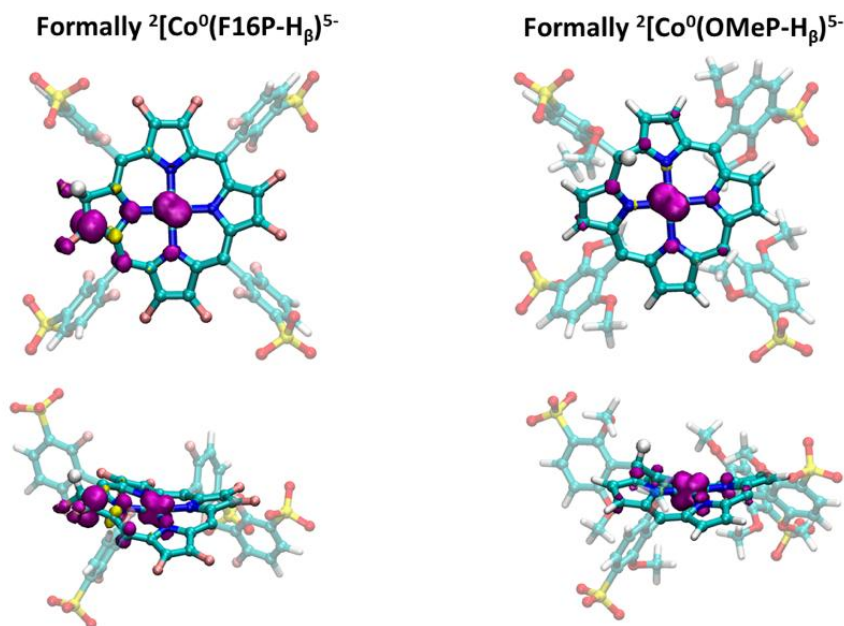


Figure 5A.19. Top and side views of the spin densities of the $^2[\text{Co}^0(\text{F16P}-\text{H}_\beta)]^{5-}$ (b) and $^2[\text{Co}^0(\text{OMeP}-\text{H}_{\text{meso}})]^{5-}$ intermediates. Spin densities were computed at the PBE/def2TZVP/SMD level of theory and the isosurface value was set to 0.003. The hydride hydrogen atom is depicted with a VDW sphere with radius of 0.4, while all other atoms are visualized with radius of 0.2.

Table 5A.3. Calculated one electron reduction potentials of the Co^{II} intermediates at the PBE/def2TZVP/SMD and OPBE/TZ2P/COSMO levels of theory.

Redox couple	PBE/def2TZVP/SMD	OPBE/TZ2P/COSMO
$^2[\text{Co}^{\text{II}}(\text{F16P})]^{4-} \rightarrow ^1[\text{Co}^{\text{I}}(\text{F16P})]^{5-}$	-0.52	-0.50
$^2[\text{Co}^{\text{II}}(\text{OMeP})]^{4-} \rightarrow ^1[\text{Co}^{\text{I}}(\text{OMeP})]^{5-}$	-0.70	-0.70

Table 5A.4. Reduction potentials (in V vs. NHE) of the $^2[\text{Co}^{\text{II}}(\text{F16P})]^{4-}$ to $^1[\text{Co}^{\text{I}}(\text{F16P})]^{5-}$ reduction, calculated with six different exchange correlation functionals on the OPBE-D3BJ/ZORA-DZP geometries.

	OPBE	PBE	wB97X	PBE0	B3LYP	M06 ^[a]	Exp ^[B]
Reduction potential (V vs NHE)	-0.50	-0.27	-1.11	-1.33	-0.98	-1.04	-0.53

^[a] No dispersion corrections were included for the calculations with the M06 functional ^[b] data according to CV, V vs. NHE at pH 7 phosphate buffer as reported in this work.

Table 5A.5. Calculated hydricity values for catalytic intermediates capable of H₂ generation.

Reaction	ΔG hydricity (kcal mol ⁻¹)
$^2[\text{Co}^{\text{II}}(\text{H})(\text{F16P})]^{5-} \rightarrow ^2[\text{Co}^{\text{II}}(\text{F16})]^{4-} + \text{H}^-$	7.8
$^2[\text{Co}^0(\text{F16P-H}_\alpha)]^{5-} \rightarrow ^2[\text{Co}^{\text{II}}(\text{F16})]^{4-} + \text{H}^-$	12.4
$^2[\text{Co}^0(\text{F16P-H}_\beta)]^{5-} \rightarrow ^2[\text{Co}^{\text{II}}(\text{F16})]^{4-} + \text{H}^-$	20.3
$^2[\text{Co}^0(\text{F16P-H}_{\text{meso}})]^{5-} \rightarrow ^2[\text{Co}^{\text{II}}(\text{F16})]^{4-} + \text{H}^-$	11.9
$^2[\text{Co}^0(\text{F16P-H}_\text{N})]^{5-} \rightarrow ^2[\text{Co}^{\text{II}}(\text{F16})]^{4-} + \text{H}^-$	-0.2
$^2[\text{Co}^{\text{II}}(\text{H})(\text{OMe})]^{5-} \rightarrow ^2[\text{Co}^{\text{II}}(\text{OMeP})]^{4-} + \text{H}^-$	2.3
$^2[\text{Co}^0(\text{OMe-H}_\alpha)]^{5-} \rightarrow ^2[\text{Co}^{\text{II}}(\text{OMeP})]^{4-} + \text{H}^-$	1.5
$^2[\text{Co}^0(\text{OMe-H}_\beta)]^{5-} \rightarrow ^2[\text{Co}^{\text{II}}(\text{OMeP})]^{4-} + \text{H}^-$	9.0
$^2[\text{Co}^0(\text{OMe-H}_{\text{meso}})]^{5-} \rightarrow ^2[\text{Co}^{\text{II}}(\text{OMeP})]^{4-} + \text{H}^-$	13.1
$^2[\text{Co}^0(\text{OMe-H}_\text{N})]^{5-} \rightarrow ^2[\text{Co}^{\text{II}}(\text{OMeP})]^{4-} + \text{H}^-$	-9.9

Chapter 5: Electron-Withdrawing Effects of Cobalt Porphyrin Catalysts Boost Homogeneous Photocatalytic Hydrogen Evolution in Neutral Aqueous Solutions

Table 5A.6. Thermodynamic cycle employed for calculating hydricity values.

Number	Reaction	Value
Reaction 1	$\text{D-H} \rightarrow \text{D}^+ + \text{H}^-$	
Reaction 2	$\text{D-H} \rightarrow \text{D}^- + \text{H}^+$	DFT
Reaction 3	$\text{D}^+ + 2\text{e}^- \rightarrow \text{D}^-$	DFT
Reaction 4	$\text{H}_2 \rightarrow \text{H}^- + \text{H}^+$	Reference ^[1]
Reaction 5	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	DFT

$$\Delta G(\text{reaction 1}) = \Delta G(\text{reaction 2}) - \Delta G(\text{reaction 3}) + \Delta G(\text{reaction 4}) + \Delta G(\text{reaction 5}).$$

5A.7. Calculation of Maximum H₂ Evolution Rate and Maximum TOF

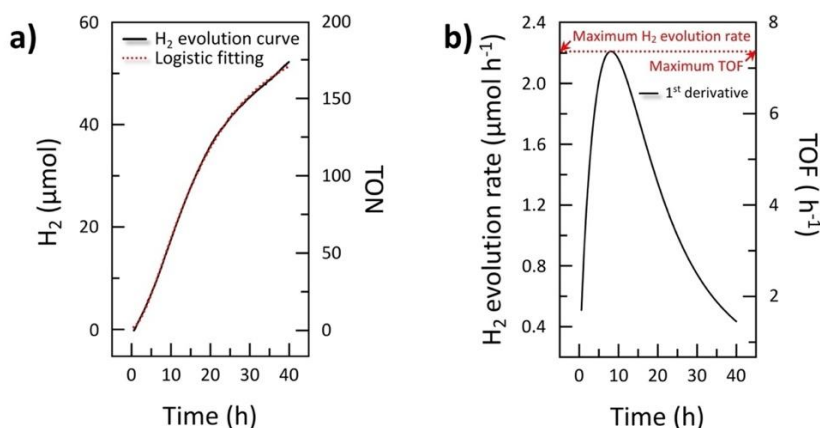


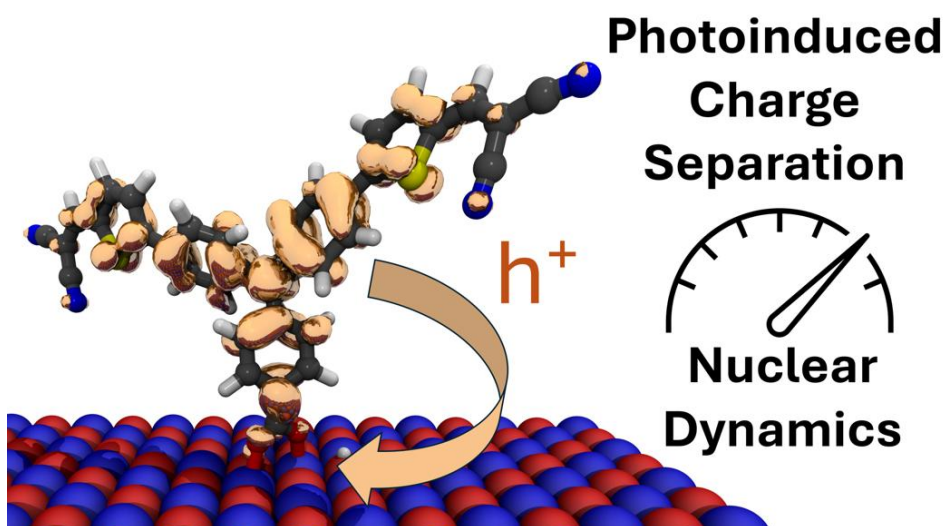
Figure 5A.20 a) Total amount of hydrogen (in μmol) measured over time (in hours). b) First derivative of the curve in a), which was used to calculate the maximum H₂ evolution rate and the maximum TOF of $[\text{Co}(\text{OMeP})]^{3-}$.

5A.7 References

- [1] E. S. Wiedner, M. B. Chambers, C. L. Pitman, R. M. Bullock, A. J. M. Miller, A. M. Appel, *Chem. Rev.* **2016**, *116*, 8655–8692.

Chapter 6: Effects of Nuclear Motion on the Photoinduced Interfacial Charge Transfer Dynamics at a NiO/P1 Photocathode

Quantum/Classical dynamics simulations were employed to interpret transient absorption spectroscopy measurements on a push-pull dye absorbed on NiO.



This chapter is based on:

T. de Haas*, K. Zhu*, J.M. van der Sterre, Y. Luo, G. Mul, F. Buda, A. Huijser. Effects of Nuclear Motion on the Photoinduced Interfacial Charge Transfer Dynamics at a NiO/P1 Photocathode. *J. Phys. Chem. C.* **2025**, 129 (14), 6817-6826 (* contributed equally)

Chapter 6: Effects of Nuclear Motion on the Photoinduced Interfacial Charge Transfer Dynamics at a NiO/P1 Photocathode

6.1 Abstract

The performance of dye-sensitized photoelectrochemical cells is presently limited by the photocathode component. Here, we investigate the impact of nuclear dynamics on the photoinduced charge separation of the benchmark NiO/P1 system (P1 = 4-(bis-4-(5-(2,2-dicyano-vinyl)-thiophene-2-yl)-phenyl-amino)-benzoic acid). Transient absorption (TA) studies in aqueous environments with different viscosities show that photoinduced hole injection either proceeds ultrafast (<100 fs) or in a sub-ps time window. We assign the fastest component to a surface species strongly coupled to the NiO. Interestingly, the slower injection component and charge recombination are slowed down considerably in increasingly viscous media. Quantum-classical dynamics simulations of a system with the dye standing perpendicular to the surface yield an injection lifetime remarkably close to the slow component from kinetic modelling of the TA results. Simulations including nuclear thermal motion yield a two-fold increase in hole transfer rate compared to simulations for which the nuclei were fixed, highlighting the role of nuclear motion and providing new design principles for dye-sensitized photocathodes.

6.2 Introduction

The development of efficient solar conversion devices is essential to advance the energy transition. Dye-sensitized photoelectrochemical cells (DS-PEC) are attractive because of their tunable properties and capability to directly convert solar energy into H_2 through water splitting or into other fuels via CO_2 reduction.^[1,2] In a typical DS-PEC cell, both photoanode and photocathode consist of a wide bandgap nanoporous semiconductor functionalized with light-absorbing dyes and catalysts. However, the efficiency of the photocathode is substantially lower than that of a photoanode,^[3] limiting the overall performance of a DS-PEC and highlighting the importance of developing efficient photocathodes.

The choice for NiO as p-type semiconductor is motivated by its electronic energy levels and chemical stability.^[4] Despite numerous efforts focused on the NiO nanostructure and doping, and the design of new dyes and catalysts,^[5] improving the efficiency of NiO-based photocathodes remains a challenge. Hole injection from the photoexcited dye into the NiO typically occurs on a sub-ps timescale^[6] and should be followed by electron transfer from the dye into the catalyst.^[7] However, hole injection does not necessarily occur with close to unity quantum yield^[8] and also detrimental charge recombination between dye radical anions and holes injected into the NiO occurs fast, typically in a ps-ns time window.^[9] The photocathode performance is well known to depend on the NiO nanostructure,^[10] doping,^[7,9] and the chemical structures of the dye and catalyst.^[7,11–17] Also the nature of the electrolyte and the composition of the electrochemical double layer play an important role in the performance and interfacial photodynamics.^[18]

Theoretical studies by several groups on a variety of molecule-semiconductor photoanode systems have emphasized the key role of the nuclear dynamics in the interfacial photodynamics.^[19–21] These studies highlight that nuclear motion can facilitate non-adiabatic charge transfer channels which dominate the injection process when the electronic coupling between donor and acceptor moieties is low. Prezhdo *et al.* studied Ru complexes chemisorbed onto Ta_2O_5 , either via COOH or PO_3H_2 anchoring groups. Non-adiabatic quantum-classical molecular dynamics

Chapter 6: Effects of Nuclear Motion on the Photoinduced Interfacial Charge Transfer Dynamics at a NiO/P1 Photocathode

(MD) simulations based on Extended Hückel (EH) theory indicate that photoinduced electron transfer from the Ru complex into Ta₂O₅ is faster with COOH anchoring groups than for the same complex with PO₃H₂ anchoring groups, due to a stronger non-adiabatic coupling for the COOH anchored complex. The COOH anchoring groups promote charge transfer with higher frequency vibrational modes than the PO₃H₂ anchoring groups. Quantum decoherence appears to counteract this effect to a small extent, because of a faster decay in the COOH-anchored system compared to the PO₃H₂ tethering.^[22] Monti *et al.* studied the interfacial photoinduced electron transfer for a terrylene dye anchored on TiO₂ by a phenyl-amide-phenyl molecular rectifier bridge. They found that the inclusion of nuclear dynamics is crucial to observe the process, and the electron propagation shows oscillatory features that correlate with interatomic distance fluctuations in the bridge.^[23] Similarly, Torres and co-workers have investigated a TiO₂ surface sensitized with a perylene dye and observed that nuclear motion couples to the electron wave packet propagation.^[19] The role of nuclear-electronic coupling in intramolecular charge transfer has also been studied extensively for ruthenium-based dye compounds. These works have shown through both experimental and computational methods that specific molecular vibrations can couple to electron and hole dynamics in such systems.^[24–27]

The photosensitization of NiO can be achieved with various dye's and has been studied extensively in the context of dye-sensitized solar cells.^[28] Particularly interesting is a class dyes consisting of π -conjugated donor (D) and acceptor (A) moieties, commonly referred to as D-A dyes. Photoexcitation in these complexes is associated with a donor-to-acceptor electron transfer, resulting in a spatial separation of the electron-hole pair, which helps prevent charge recombination. In a previous publication, we have demonstrated that this electron transfer can cause the acceptor moiety of the dye to twist relative to the donor moiety.^[29]

In the present work, we explore the photoinduced hole injection and charge recombination dynamics in a benchmark D-A dye chemisorbed on NiO. In

particular, the role of nuclear motion on the photoinduced interfacial dynamics is investigated by combining EH-based quantum-classical dynamics simulations with femtosecond transient absorption studies in aqueous environments with different viscosities. The NiO is functionalized with the D-A dye P1 [4-(bis-4-(5-(2,2-dicyano-vinyl)-thiophene-2-yl)-phenyl-amino)-benzoic acid] by chemisorption via the COOH anchoring group. The P1 dye combines a triphenylamine donor unit linked via thiophene bridges to two dicyanovinylene acceptors. We observe that photoinduced hole injection either proceeds on an ultrafast timescale, during which the process is driven by electronic coupling, or in a sub-ps time window where nuclear motion is critical for the injection process. Especially the fluctuations in the dihedrals between the donor and acceptor moieties of the dye, and fluctuations in the carboxylate O – surface Ni distance appears to be important for photoinduced hole injection, although other nuclear dynamics likely play a role as well. Also charge recombination depends on the structural dynamics and slows down in viscous media. Our work highlights the importance of understanding the interplay between nuclear dynamics and photoinduced charge separation and recombination, which is essential for the development of photocathodes where structural flexibility is tailored for efficient solar to fuel conversion.

6.3 Methods

6.3.1 Sample preparation and transient absorption experiments

The sample preparation and femtosecond transient absorption setup has been described in detail earlier.^[9] Polyethylene glycol (PEG) was purchased from Sigma Aldrich (BioUltra, 1000, M_n 950-1050) and dissolved into MilliQ water with a concentration of 4.5 wt%.

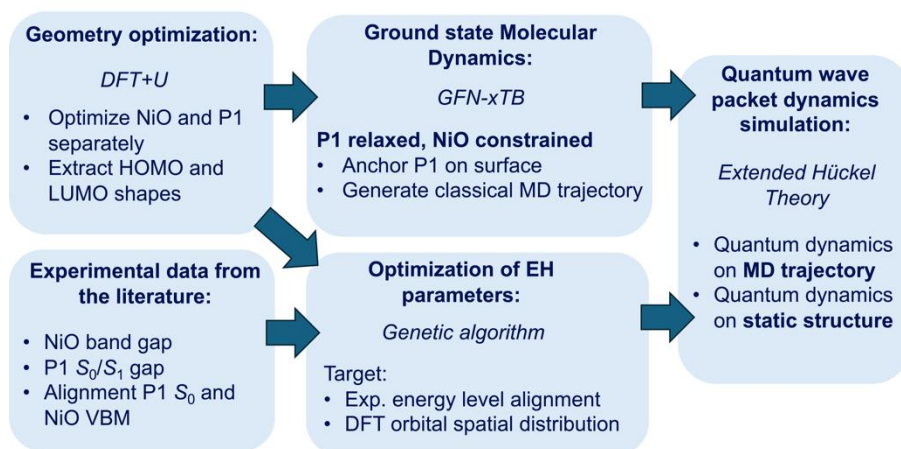
6.3.2 Computational Methods

Multiple computational methodologies were combined to study the electronic and structural factors that govern interfacial hole-transfer dynamics between the

Chapter 6: Effects of Nuclear Motion on the Photoinduced Interfacial Charge Transfer Dynamics at a NiO/P1 Photocathode

photoexcited dye P1* and the NiO surface. A schematic overview of the employed computational workflow is provided in Scheme 1. Density functional theory (DFT) was used to optimize both the geometries and electronic structure of P1 and the NiO semiconductor slab (details provided in the Appendix, A1, A2 and A7). The obtained dye and slab structures were used to build the configurations discussed in section 6.4.4. Then, nuclear classical dynamics simulations were performed of the dye molecule on the fixed DFT-optimized NiO using the self-consistent GFN-xTB tight-binding Hamiltonian.^[30] We note that these simulations did not include explicit solvent. The Coulomb integral parameters of the employed EH model were optimized to reproduce the energy level alignment of the NiO/P1 interface, while that the spatial distribution of the P1 HOMO and LUMO orbitals closely matched the DFT results. This optimization procedure targetted the NiO band gap, the P1 HOMO-LUMO gap and the relative alignment of the P1 HOMO with the NiO valence band maximum (VBM), as discussed further in section 6.3.2.1. Details on the EH parameter optimization are provided in the Appendix, section 6A.8. Finally, the photoexcited electron and hole wave packet quantum dynamics were propagated either on a static nuclear geometry or on a precomputed nuclear trajectory using an EH approach. We have used a similar strategy based on semi-empirical calculations in earlier work to describe photoinduced electron transfer dynamics in a dye-TiO₂ interface.^[21] The details of the wave packet propagation schemes are explained in the papers by Rego and Batista.^[31,32] Details on the applied computational methodologies are provided in the Appendix, sections 6A.1-6A.4.

Scheme 6.1. Schematic overview of the workflow used for photoinduced hole injection simulations on the P1/NiO system. VMB = valence band maximum, MD = molecular dynamics, EH = Extended Hückel.



6.4 Results

6.4.1 Femtosecond transient absorption results

To investigate the effect of nuclear dynamics on photoinduced charge separation and recombination, femtosecond transient absorption (TA) studies have been carried out using 500 nm pump pulses, predominantly exciting the π - π^* transition of the P1 dyes.^[13] We compared the photodynamics of NiO/P1 in H₂O and NiO/P1 in H₂O with 4.5 wt% polyethylene glycol (PEG), with the latter increasing the viscosity of the solvent and, therefore, likely slowing down the nuclear dynamics of the P1 molecule. Anchoring of the P1 dye onto the NiO surface via its COOH group causes deprotonation.^[33,34] The P1 molecules are solvated by H₂O and PEG molecules, and H₂O molecules are likely adsorbed onto the NiO surface.^[18] Dissociative H₂O adsorption onto NiO has been reported to result in the formation of various Ni-OH surface species.^[35]

Chapter 6: Effects of Nuclear Motion on the Photoinduced Interfacial Charge Transfer Dynamics at a NiO/P1 Photocathode

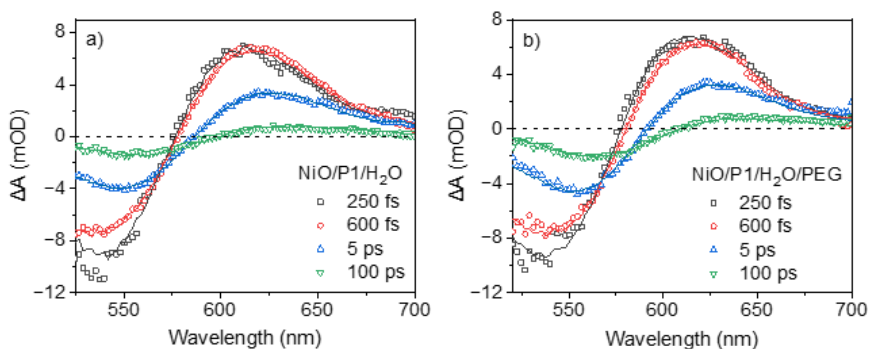


Figure 6.1. TA spectra for NiO/P1/H₂O (a) and NiO/P1/H₂O/PEG (b) at selected time delays after 500 nm excitation. The solid lines indicate fits from target analysis.

Figure 6.1 shows the TA spectra at various time delays for NiO/P1 in H₂O (a) and in H₂O/PEG (b) and fits from photophysical modelling (see below). All spectra show a negative signal below *ca.* 600 nm due to ground state bleach (GSB) of the photoexcited P1 dye (P1*). Also stimulated emission (SE) by P1* may contribute to the early-time negative TA signal. Tian and co-workers observed SE at around 660 nm.^[6] Fluorescence up-conversion studies by Gustavsson *et al.* showed a signal at around 600 nm, decaying on a sub-ps time scale due to electronic relaxation from the bright Franck-Condon state into a low-emitting charge-transfer state.^[36] The positive TA signal around 610 nm at early times and red-shifting in time towards *ca.* 635 nm can be assigned to four distinct species. The first two are related to the dye: P1* has an absorption band centered around 550 nm and the P1 radical anion (P1^{•-}) formed after hole injection into the NiO around 615 nm.^[12,13] The other two are due to redox processes in the NiO induced by photoinduced hole injection, resulting in Ni³⁺ and Ni⁴⁺ centres contributing to the absorption above 650 nm.^[37] Photoinduced hole injection by P1* resulting in P1^{•-} formation occurring beyond the TA time resolution (100-150 fs) contributes to the

red-shift in TA spectrum with time observed here. The TA signals decay on a ps time scale due to charge recombination.

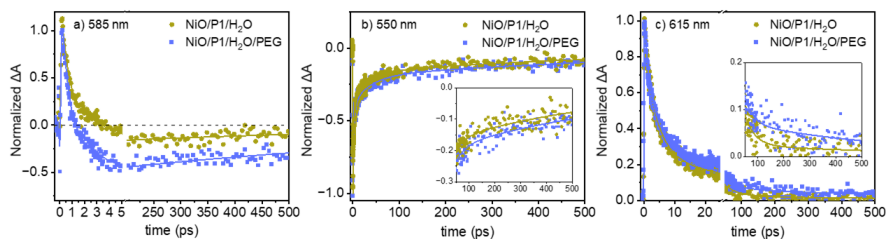


Figure 6.2. Normalized TA kinetic traces following 500 nm excitation for NiO/P1/H₂O and NiO/P1/H₂O/PEG at 585 nm (a), 550 nm (b) and 615 nm (c). The solid lines indicate fits from target analysis.

Figure 6.2a shows the early-time normalized TA kinetic traces at 585 nm of NiO/P1 in H₂O and H₂O/PEG. The P1* signal at this wavelength persisting until a few ps exceeds that of the GSB&SE, resulting in a positive overall TA signal at early times. The signal decays faster in H₂O/PEG, suggesting a shorter P1* lifetime caused by faster hole injection. Figure 6.2 also compares the kinetic traces at 550 nm (b) and 615 nm (c) of NiO/P1 in H₂O and in H₂O/PEG. The signal at 550 nm beyond a few ps is dominated by GSB, which is indicative of charge recombination and seems to decay slightly slower in H₂O/PEG. This difference is clear at *e.g.* 615 nm, which signal is predominantly due to P1*. These observations are consistent with our photophysical modeling discussed below.

Chapter 6: Effects of Nuclear Motion on the Photoinduced Interfacial Charge Transfer Dynamics at a NiO/P1 Photocathode

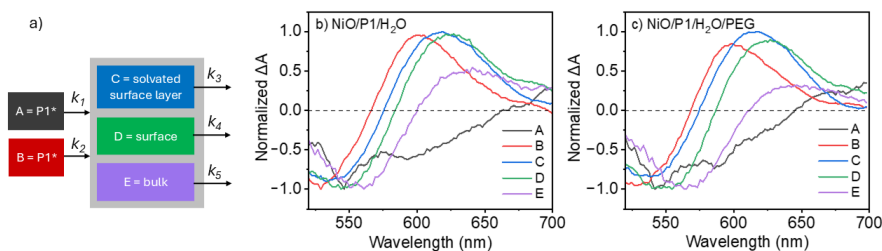


Figure 6.3. Photophysical model used for target analysis of the TA data (a) and obtained species associated spectra (SAS) for NiO/P1/H₂O (b) and NiO/P1/H₂O/PEG (c).

We performed target analysis using the program Glotaran.^[38] Figure 6.3a presents a photophysical model based on five components that explains the TA data well. Photoinduced hole injection by P1* into the NiO either occurs ultrafast with rate constant k_1 or proceeds on a sub-ps time scale with rate constant k_2 . Species A is a result of P1* GSB, SE and absorption, with GSB and especially SE dominating the TA signal. In contrast, species B does not show such strong SE contribution, consistent with the work of Gustavsson *et al.* with the fluorescence of P1* not only being quenched due to hole injection into NiO, but also by intrinsic sub-ps electronic relaxation from the bright Franck-Condon state into a low-emitting charge-transfer state observed for P1 on insulating Al₂O₃.^[36] The time constants (Table 6.1, $\tau_x = 1/k_x$) qualitatively agree with the time constants obtained from quantum-classical dynamics simulations presented in the next section 6.4.4. The species associated spectra for each component are shown in Figures 6.3b and 6.3c. τ_1 is slightly shortened in the presence of PEG, consistent with the faster decay shown in Figure 6.2a. Although the difference is small, it might be a result of a favourable initial P1 geometry for photoinduced hole injection induced by the PEG. In contrast to τ_1 , the value for τ_2 is higher in H₂O/PEG compared to H₂O. We attribute this difference to the higher solvent viscosity in the presence of PEG, which likely slows down the nuclear dynamics of the P1 dye. Slow nuclear

dynamics delays hole injection, as is demonstrated in the quantum-classical dynamics simulations presented in the section 6.4.4.

To properly describe charge carrier recombination, at least three components are needed to get a good fit. The fastest component (k_3) is assigned to charge recombination between $P1^{\bullet-}$ and holes still present in the solvated NiO surface layer, the intermediate component (k_4) to recombination with holes at the NiO surface and the slowest component (k_5) to recombination with holes that have succeeded to escape into the NiO bulk. The spectra of the corresponding species C-E are included in Figures 6.3b and 6.3c and are clearly red-shifted relative to that of species B as a result of charge separation. Charge recombination is slightly slowed down in the presence of PEG, as also evident from Figure 6.2c, likely because of slow nuclear dynamics of the P1 dye due to the higher viscosity of H_2O/PEG compared to H_2O .

Table 6.1. Time scales obtained from target analysis.

	NiO/P1 in H_2O	NiO/P1 in H_2O/PEG
τ_1 (fs)	76 ± 3	60 ± 3
τ_2 (fs)	479 ± 13	506 ± 12
τ_3 (ps)	3.6 ± 0.04	3.9 ± 0.09
τ_4 (ps)	33.3 ± 0.7	37.9 ± 0.7
τ_5 (ps)	628.5 ± 15	725.5 ± 14

6.4.2 Quantum chemical modeling

Motivated by the two chemical species identified through kinetic modeling of the TA results, we considered two configurations of P1 in our quantum chemical modeling studies. In the first configuration (species 1), the dye is oriented perpendicular to the surface, while in the second (species 2), P1 lies flat with both tails physisorbed to the surface. Visual representations of these two P1

Chapter 6: Effects of Nuclear Motion on the Photoinduced Interfacial Charge Transfer Dynamics at a NiO/P1 Photocathode

configurations are shown in Figures 6.4a and 6.4b. DFT-based geometry optimizations, performed on a small representative model system, indicate that species 2 represents a local minimum on the dye-NiO potential energy surface. In vacuum, this configuration is ~ 30 kcal mol⁻¹ lower in energy than the perpendicular configuration (see Appendix section 6A.6, Table 6A.2). The stability of the flat configuration arises from a strong π -stacking interaction between the aniline rings of the model dye and the NiO surface. Although this stabilizing interaction is expected to be significantly reduced in the solvated system due to the saturation of Ni atoms with physisorbed water molecules, these calculations suggest that strong interactions between the surface layer and the P1 tails are likely. We have also performed DFT-based MD on the same model with explicit solvent at room temperature, which show that the dye remains standing perpendicular to the surface on the ps time scale (see Appendix, section 6A.6). Overall, we conclude that both species are likely to coexist on the surface. In both configurations, the carboxylate group is attached to the surface via a bidentate binding mode, with the COOH deprotonated and the excess proton bonded to an oxygen atom on the NiO surface. DFT studies of a similar dye with a carboxylate anchoring group have shown that this is the preferred binding mode on NiO (100).^[33,34]

6.4.3 Electronic structure of the NiO/P1 interface

The quantum wave packet dynamics is described by a semi-empirical EH Hamiltonian.^[39,40] Prior to performing calculations, the parameters of this model were fine-tuned to reproduce the correct energy level alignment on the interface structure.^[41] The HOMO orbital of the P1 has been estimated to be at ≈ 1.4 V vs NHE and the valence band maximum (VBM) for bulk NiO is found to be at ≈ 0.5 V vs NHE, providing a driving force of ≈ 0.9 V for hole injection by the photoexcited dye P1*.^[42,43] The 0-0 absorption of this dye has been estimated to be 2.24 eV, based on the intersection of absorption and emission spectra in

acetonitrile.^[44] Bulk NiO has a band gap in the range of 3.4–4.3 eV, with the value depending on the measurement technique and the preparation method.^[45–50] These values have been employed to define optimization targets for the bulk NiO band gap and for the P1 HOMO and LUMO orbital energies. A genetic algorithm was used to fine-tune the Coulomb integral parameters of the EH model, producing the correct energetic alignment, while simultaneously maintaining the proper symmetry and spatial distribution of the P1 HOMO and LUMO.^[23] The details of the parametrization procedure are provided in section 6A.8.

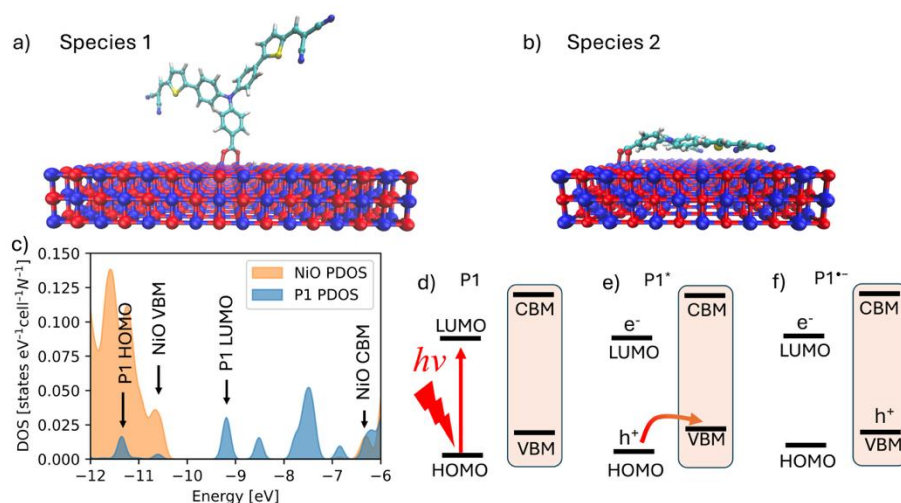


Figure 6.4. Visualizations of the P1 dye in the two configurations considered: a) Species 1, standing perpendicular to the surface and b) Species 2, lying flat on the surface. c) Plot of the electronic density of states (DOS) of the optimized P1 dye on the NiO (100) slab, Species 1. The arrows indicate the positions of the P1 HOMO and LUMO orbitals and the NiO valence band maximum (VBM) and conduction band minimum (CBM) edges. The projected DOS (PDOS) of P1 and NiO were normalized by their respective number of atoms, N . d-f) Schematic overview of the investigated P1 excitation and subsequent hole injection process.

Chapter 6: Effects of Nuclear Motion on the Photoinduced Interfacial Charge Transfer Dynamics at a NiO/P1 Photocathode

Figure 6.4c shows the electronic density of states (DOS) obtained from the EH calculation on the NiO/P1 interface for species 1 shown in Figure 6.4a. The same DOS plot for species 2 can be found in the Appendix, Figure 6A.10 and shows qualitatively the same energy level alignment. The model predicts a NiO band gap of *ca.* 3.9 eV, consistent with experimental data. Furthermore, it shows that the P1 HOMO is 0.9 eV below the NiO valence band maximum (VBM) and the P1 LUMO is 2.2 eV above the P1 HOMO. It should be kept in mind that despite the correct energy level alignment, the model does not reproduce the anti-ferromagnetic alignment of the Ni d-electrons and is, therefore, not able to reproduce the consequential anisotropy in the quantum wave packet dynamics in the semiconductor. However, this model should give a sufficient description of the electronic structure, as our primary focus is elucidating the effects of the P1 structural motions on the photoinduced hole injection rate rather than the diffusion of the wave packet inside the semiconductor itself. We note that despite neglecting the spin, the opening of the NiO band gap was naturally reproduced with the default parameters.^[41] Figure 6.4(d-f) provide a schematic overview of the hole injection simulations discussed in this work. Initially, the ground state P1 dye is exposed to a light flash (Figure 6.4d), which excites the system to the first electronic excited state (Figure 6.4e). This excited state is subsequently quenched by hole transfer from P1* to NiO, forming the reduced dye radical anion P1^{•-} (Figure 6.4f).

6.4.4 Hole injection simulations

After optimizing and equilibrating P1 in the configuration standing perpendicular to the surface (see Figure 6.4a, species 1), a 3 ps ground state MD simulation of the dye was performed at the GFN-xTB level. The obtained trajectory was then divided into three sub-trajectories of equal length. Two EH based quantum dynamics simulations were performed on each sub-trajectory: the first simulation incorporated nuclear motion from the MD, while the second simulation was

performed using only the first MD snapshot as a static structure. By comparing these two simulations, the effect of thermal nuclear motion on the interfacial charge transfer dynamics was analyzed. Additionally, a single photoinduced hole injection simulation was performed on the optimized system where the dye lies flat on the surface (see Figure 6.4b, species 2). As the injection process for this species occurred on an ultrafast timescale, this simulation was carried out without including thermal nuclear motion.

Figure 6.5a presents the averaged hole survival probability (SP) for the species 1 photoexcited dye P1* over time, computed on the dynamic trajectories (blue) and on static structures (orange). Figure 6.5b presents the hole SP for the dye lying flat on the surface, while Figure 6.5c provides the injection traces for the individual trajectories of species 1, without averaging. The electron SP traces are provided in the Appendix, Figure 6A.4. Figures 6.5d and 6.5e display the hole density in Run 2 before and after injection. It is clearly observed that the hole is localized in the P1 HOMO orbital prior to injection, while it is delocalized over the entire NiO surface after injection.

Chapter 6: Effects of Nuclear Motion on the Photoinduced Interfacial Charge Transfer Dynamics at a NiO/P1 Photocathode

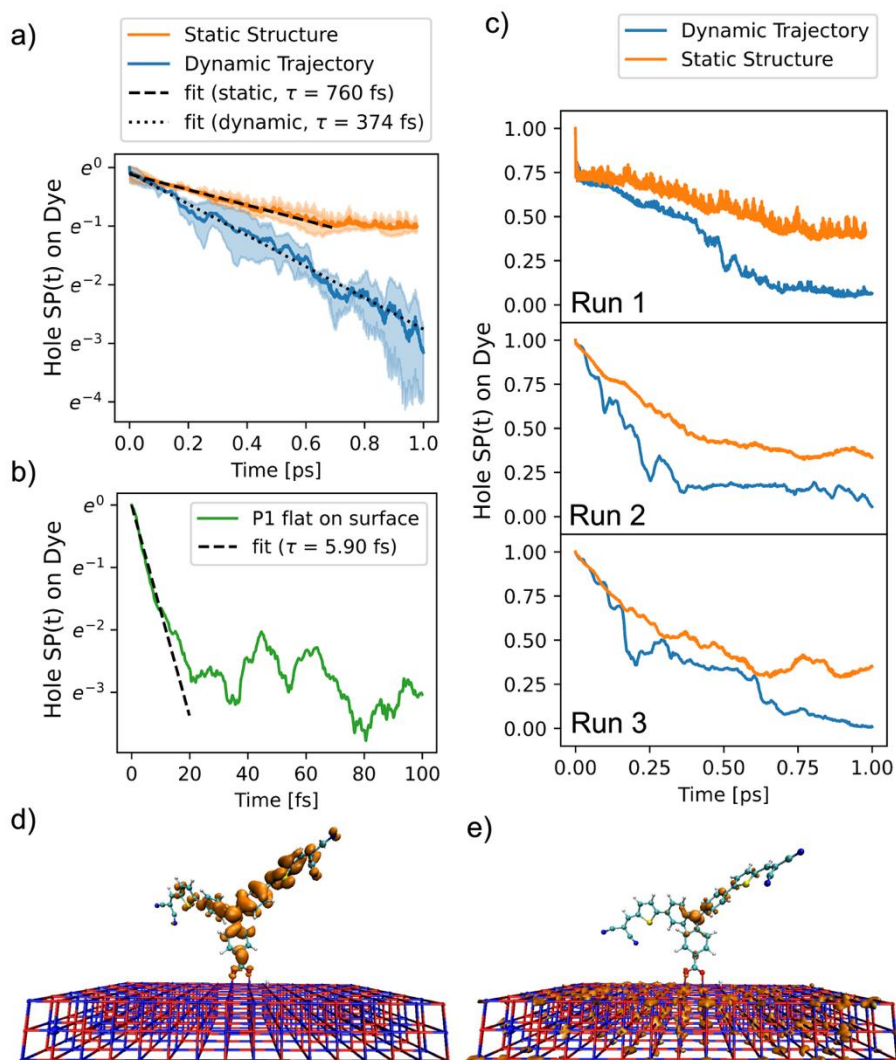


Figure 6.5. a) Time-dependent survival probability (SP) of the hole density on the excited dye $P1^*$ averaged over static structures (red) or dynamic trajectories (blue) for species 1. The transparent areas represent one standard deviation centered around the mean value. Panel b) shows the ultrafast injection in the case of species 2. Panel c) provides the traces of the individual runs for species 1 on a linear y-axis scale. Panels d) and e) present visualizations of the hole wave packet density at 0 and 900 fs extracted from Run 2.

The averaged decay traces of the hole SP were modeled with an exponential decay function $m \cdot \exp\left[\frac{-x}{\tau}\right]$. The m parameter was introduced to account for the initial ultrafast injection on the first *ca.* 5 fs observed in Figure 6.5c, Run1. For P1 standing on the surface, this yielded lifetimes of 760 fs for the injection process on the fixed nuclei and 374 fs for the injection on the moving nuclei. This lifetime is remarkably close to the lifetime obtained for the second component by target analysis of the TA results (see Table 6.1). The fit for the injection on fixed nuclei was performed only on the first 690 fs, as the curve does not follow exponential behavior over the final 310 fs. Figures 6.5a and 6.5c highlight the critical role of nuclear dynamics on photoinduced hole injection in this system. Although all simulations predict a rapid initial injection process, the hole transfer rate on the static structures is rapidly diminished after approximately 66% of the charge density has been injected, resulting in an average SP on the dye of 34% after 1 ps. In contrast, the hole injection along the dynamic trajectories continues without stagnation during the 1 ps simulation, resulting in a 4% hole SP on the dye.

The first injection simulation with P1 standing on the surface (Run 1, Figure 5c) displays a remarkably fast initial injection, causing a 27 % reduction of hole SP on the P1 dye within the first 5 fs. This ultrafast component is attributed to very rapid hole transfer to an electronic orbital which is partly delocalized on the NiO (see Appendix, section 6A.10, Figure 6A.5). It was found that for the initial structure of Run 1, and other nuclear geometries, this orbital energy becomes nearly degenerate with the P1 HOMO energy ($E_{HOMO} - E_{HOMO-1} \approx 0.05$ eV, see Appendix, Figure 6A.5). The strong electronic coupling between these quasi-degenerate orbitals leads to an ultrafast charge transfer channel from the P1 HOMO to the NiO valence band.

Figure 6.5b presents the photo-induced hole-injection trace for the dye lying flat on the NiO surface. The charge transfer process for this species is observed to occur on a significantly faster timescale, with a sub-10 fs lifetime, which is nearly

Chapter 6: Effects of Nuclear Motion on the Photoinduced Interfacial Charge Transfer Dynamics at a NiO/P1 Photocathode

two orders of magnitude shorter than that of the P1 oriented perpendicular to the surface. This much faster injection process occurs because the hole density can diffuse directly from the P1 aniline core into the NiO surface, without evolving through the carboxylate anchoring group.

We now further investigate the role of thermal nuclear motion on the interfacial charge transfer dynamics, specifically for species 1, where the dye stands perpendicular to the surface. To analyze this effect, we look at the hole SP trace in the frequency domain. By Fourier transforming the velocity autocorrelation function of the SP time evolution, power spectra were obtained for the hole SP on fixed and moving nuclei. Similarly, a vibrational density of states (VDOS) was obtained from the nuclear trajectory.

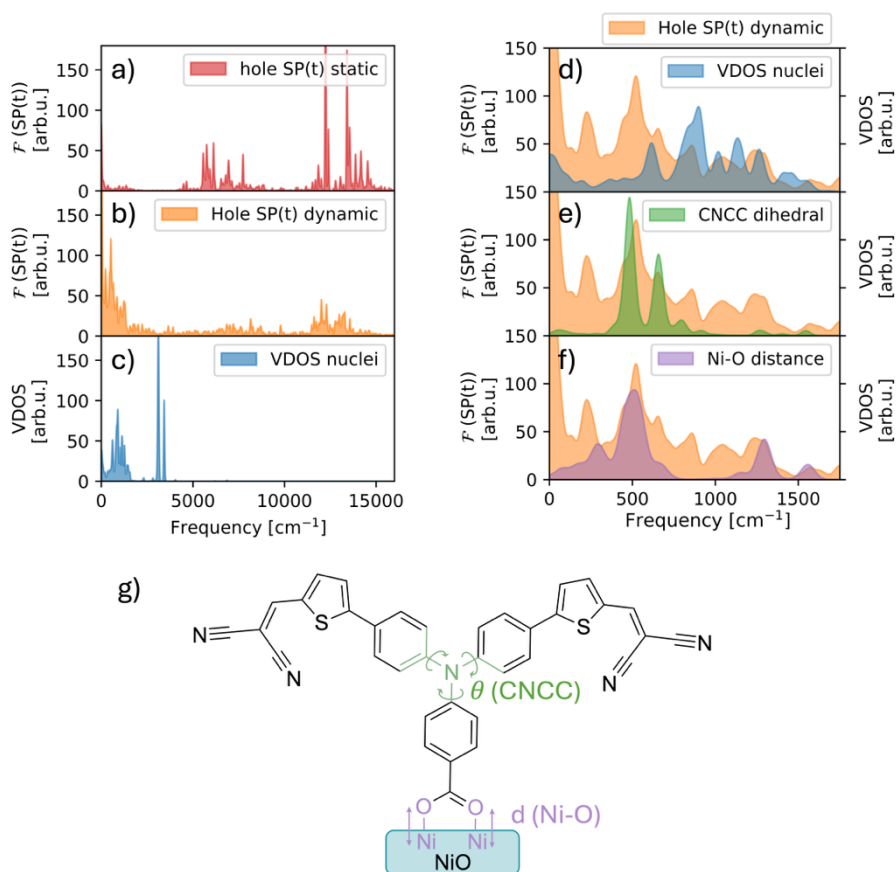


Figure 6.6. Frequency spectra associated with the hole transfer on fixed (a) and moving (b) nuclei, and the vibrational density of states (VDOS) of the nuclear trajectory (c). A frequency spectrum was computed for each run individually and subsequently averaged to obtain the displayed figure. Panel d) provides an overlay of hole SP frequency spectrum on moving nuclei and the VDOS of the entire trajectory. Additional overlays are provided for the same hole injection spectrum but now compared with the VDOS computed by considering only the CNCC dihedral angle torsions (e) or the Ni-O distance (f) fluctuations. The relevant Ni-O distances and CNCC dihedral angles are shown in panel g). Spectra for both Ni-O fluctuations and all three CNCC dihedral torsions (displayed in g) were averaged to produce the spectra displayed in e) and f).

Chapter 6: Effects of Nuclear Motion on the Photoinduced Interfacial Charge Transfer Dynamics at a NiO/P1 Photocathode

Figure 6.6a shows the hole injection frequency spectrum for the quantum dynamics performed on the static structures of species 1. The spectrum is characterized by sharp peaks around 6000 cm^{-1} , 12000 cm^{-1} and 13500 cm^{-1} . These frequencies are associated with fast Rabi oscillations of the hole wave packet between different electronic eigenstates mostly located on the P1 dye, but with a slightly different delocalization on the NiO slab. Such rapid Rabi oscillations were also observed in the simulations by Torres *et al.*^[19] Interestingly, the frequency spectrum of the injection trace on moving nuclei (Figure 6.6b) shows a much stronger signal in the $0\text{--}1700\text{ cm}^{-1}$ region. As evidenced by the vibrational density of states (Figure 6.6c), this is precisely the frequency range where nuclear vibrations are expected to play a role. Evidently, the propagation of the hole wave packet exhibits strong coupling to the nuclear motion in this range. In figure 6.6d, the VDOS and hole SP frequency spectra are overlaid in the $0\text{--}1700\text{ cm}^{-1}$ region. The frequency spectrum of the hole injection peaks around 500 cm^{-1} and also contains several other characteristic frequencies. This observation indicates that a broad range of vibrations couple to the wave packet dynamics. To further investigate which vibrational modes are important, we extracted from the simulations the characteristic frequencies of specific geometrical features and found two modes that appear to be in resonance with the hole dynamics. Particularly, fluctuations of the CNCC dihedral angles (displayed in green in Figure 6.6g) and of the anchoring Ni-O distances (displayed in purple in Figure 6.6g) show high correlations with the injection process as evidenced by the spectra shown in Figure 6.6e and Figure 6.6f.

The influence of the CNCC dihedral angle on hole injection was further examined by visualizing the hole wave packet dynamics in the excited P1^* . A video (supplied in the associated content of the publication by de Haas *et al.*^[51]), shows that the wave packet oscillates several times between the two tails of the P1^* before eventually diffusing into the NiO surface. This behavior suggests that the specific geometric conformation of the dihedral angles at the P1 aniline core plays a

critical role in directing the wave packet. Depending on the alignment of these dihedrals, the wave packet may either evolve towards the surface or remain confined to the opposite tail. Recent studies on ruthenium bipyridine dye complexes show that, upon photoexcitation, electron transfer dynamics between the two bipyridine ligands can occur on a similar sub-100 fs timescale as observed here.^[25]

6.5 Discussion

Quantum-classical dynamics simulations and femtosecond TA spectroscopy experiments were performed to investigate the photoinduced hole injection dynamics at the NiO/P1 interface, which serves as a benchmark system for photocathodes. After excitation of the P1 π - π^* transition using 500 nm pump pulses, the excited dye P1* is quenched by rapid (sub-ps) hole injection into the valence band of NiO. Target analysis of the femtosecond TA data indicates that the photoinduced hole injection process in water is best described by a biexponential decay with lifetimes τ_1 and τ_2 of 76 ± 3 fs and 479 ± 13 fs, respectively. A good model for the subsequent charge carrier recombination process was obtained using three components with lifetimes of a few to several hundred picoseconds. The addition of PEG increases the values of τ_2 - τ_5 , which could be attributed to slower nuclear dynamics of the P1 dye.

Motivated by the observation of two characteristic lifetimes for hole injection in the TA results, two systems were considered in our quantum chemical modelling studies. While in the first system, the P1 dye stands perpendicular to the surface (see Figure 6.4a), the second system considers the dye as it lies flat on the surface (see Figure 6.4b). DFT calculations on a smaller model system confirm that the dye is flexible and could form strong π -stacking interactions with the NiO surface. Although this suggests that the P1 dye could adopt configurations in which the tails come near the surface, the real system probably does not collapse to the surface entirely due to the solvating effect of surrounding water molecules and

Chapter 6: Effects of Nuclear Motion on the Photoinduced Interfacial Charge Transfer Dynamics at a NiO/P1 Photocathode

due to the entropic gain associated with dissociation of the P1 tail from the surface. We attribute the fast component observed in the TA target analysis to a surface species in which the P1 aniline core is strongly coupled to the NiO surface layer. Quantum-classical dynamics simulations show that a P1 molecule that lies flat on the NiO surface exhibits a hole injection process characterized by a sub-10 fs lifetime. For the system with the dye standing on the surface, we observed that in specific geometric conformations, the electronic state corresponding to the hole occupying the P1 HOMO, becomes nearly degenerate with a state where the hole is delocalized on the P1 carboxylate bridge and the NiO surface. It was found that this quasi-degeneracy also leads to strong coupling between the $P1^*$ and the surface, providing a channel for ultrafast injection of roughly 27% of the hole density in ~ 5 fs.

Exponential fitting of the photoinduced hole injection trace for the P1 dye standing perpendicular to the surface yielded a characteristic lifetime of 374 fs, in near-quantitative agreement with the slower component of the injection in H_2O media. The 22% faster decay in the simulation compared to the TA results is within the error margin of the applied computational method and may be explained by several contributing factors.

In a previous study, we demonstrated that including explicit solvent molecules can affect the nuclear conformations visited by the MD simulations, thereby influencing the injection rate in for specific dye molecules.^[21] The absence of explicit solvation in the simulations increases the P1 flexibility, thereby enhancing the non-adiabatic coupling between donor and acceptor states, accelerating the decay process. Recent studies on photoinduced intramolecular charge transfer dynamics in a ruthenium-based chromophore have shown that explicitly accounting for solvent molecules can considerably slow down electron and hole mobility due to solute-solvent polarization effects.^[26] Neglecting such polarization effects in our simulations could therefore lead to an overly fast injection process. Finally, our model system shows a fast and isotropic diffusion of the hole wave

packet into the NiO slab, whereas the actual injection process is constrained by the anti-ferromagnetically coupled spin layers in the NiO (111) plane. Again, this approximation could contribute to the slightly faster injection in the model system compared to the TA measurements.

Both the TA measurements and the quantum-classical dynamics simulations highlight the importance of nuclear motion for the injection process. Our results support the idea that the increase in solvent viscosity is the underlying reason for the higher τ_2 - τ_5 in H₂O + PEG compared to H₂O. We note here that the very small change in solvent reorganization energy due to a change in solvent polarity in the presence of PEG might also decrease the electron transfer rate according to Marcus theory. However, this slight change in polarity is not expected to play a role on the sub-ps timescales at which the solvent has not yet adjusted to the electronic excitation and the system is out of equilibrium.

The performed quantum-classical dynamics simulations of the dye standing perpendicular to the surface reveal that the removal of nuclear motion doubles the injection time scale ($\tau = 374$ fs for simulations on moving nuclei vs. $\tau = 760$ fs for a simulations on a static structure), and that the hole transfer stagnates after *ca.* 69 % injection. Fourier analysis of the hole-transfer simulations on moving nuclei reveals that the spectrum of the injection trace is characterized by frequencies in the 0-1700 cm⁻¹ range. In contrast, the injection on fixed nuclei is characterized by much higher frequencies, around 6000 cm⁻¹ and above 12000 cm⁻¹. It thus appears that the hole dynamics are affected considerably by the nuclear motion of the dye. Specifically, torsional motions around the dihedral angles between the three aniline components in the P1 dye (see Figure 6.6g, green dihedrals), appear to be resonant with the hole density propagation. Prior to injection, the hole wave packet oscillates multiple times between the two P1 tails. We propose that a specific conformation involving the dihedrals between the core aniline units directs the hole wave packet either toward the opposite P1 tail, or toward the NiO surface. In addition to these dihedral angle torsions, also fluctuations in the Ni-O bond lengths at the NiO/P1 interface appear to correlate with the photoinduced

Chapter 6: Effects of Nuclear Motion on the Photoinduced Interfacial Charge Transfer Dynamics at a NiO/P1 Photocathode

injection trace. Overall, the performed calculations underscore how the injection process is strongly coupled to nuclear motion of the dye. These findings align with the literature, where coupled electron-nuclear dynamics is a feature observed for charge transfer in molecules, materials and biological systems.^[21,24–27,52–56]

6.6 Conclusions

In summary, we have performed quantum-classical dynamics simulations in combination with TA spectroscopy to investigate the effects of nuclear motion on the photoinduced hole injection dynamics at the prototype NiO/P1 photocathode interface. The injection process of the excited dye P1* into the NiO surface is best fitted with a biphasic exponential consisting of an ultrafast component (τ_1 of 76 ± 3 ps, within the TA instrument response) and a slower component (τ_2 of 479 ± 13 fs). Based on quantum chemical modeling, we assign the fast component to P1 molecules that are strongly coupled to NiO, possibly through π -stacking interactions of the P1 tails to the surface. The slow component is assigned to P1 molecules standing perpendicular to the surface. Notably, the lifetime of this slow component depends on the solvent viscosity, as was shown by comparing the TA data of the NiO/P1 system in water and in water with 4.5 wt% PEG. Also charge recombination is slightly slowed down in more viscous media.

Quantum-classical dynamics simulations show excellent agreement with the TA results and further highlight the critical role of nuclear motion. Simulations of quantum hole dynamics on moving nuclei predict an approximately two-fold faster injection rate compared to those on fixed nuclei. Subsequent frequency domain analysis shows that the fluctuations of the hole survival probability on the P1* are in resonance with the vibrational fingerprint of the dye molecule. Specifically, torsional degrees of freedom around the P1 tails appear to be correlated with the injection trace. These results provide detailed insights into the fundamental photochemistry at the NiO/P1 interface, offering valuable guidelines for the design of highly efficient dye-sensitized photocathodes.

6.7 References

- [1] K. Fan, F. Li, L. Wang, Q. Daniel, E. Gabrielsson, L. Sun, *Phys. Chem. Chem. Phys.* **2014**, *16*, 25234–25240.
- [2] F. Li, K. Fan, B. Xu, E. Gabrielsson, Q. Daniel, L. Li, L. Sun, *J. Am. Chem. Soc.* **2015**, *137*, 9153–9159.
- [3] S. Wrede, H. Tian, *Phys. Chem. Chem. Phys.* **2020**, *22*, 13850–13861.
- [4] R. J. Dillon, L. Alibabaei, T. J. Meyer, J. M. Papanikolas, *ACS Appl. Mater. Interfaces* **2017**, *9*, 26786–26796.
- [5] K. Zhu, G. Mul, A. Huijser, *Chemical Physics Reviews* **2024**, *5*, 021305.
- [6] L. Zhang, G. Boschloo, L. Hammarström, H. Tian, *Phys. Chem. Chem. Phys.* **2016**, *18*, 5080–5085.
- [7] J. M. Gardner, M. Beyler, M. Karnahl, S. Tschierlei, S. Ott, L. Hammarström, *J. Am. Chem. Soc.* **2012**, *134*, 19322–19325.
- [8] J. Föhlinger, S. Maji, A. Brown, E. Mijangos, S. Ott, L. Hammarström, *J. Phys. Chem. C* **2018**, *122*, 13902–13910.
- [9] K. Zhu, S. K. Frehan, A. M. Jaros, D. B. O'Neill, J. P. Korterik, K. Wenderich, G. Mul, A. Huijser, *J. Phys. Chem. C* **2021**, *125*, 16049–16058.
- [10] C. J. Wood, G. H. Summers, C. A. Clark, N. Kaeffer, M. Braeutigam, L. R. Carbone, L. D'Amario, K. Fan, Y. Farré, S. Narbey, F. Oswald, L. A. Stevens, C. D. J. Parmenter, M. W. Fay, A. La Torre, C. E. Snape, B. Dietzek, D. Dini, L. Hammarström, Y. Pellegrin, F. Odobel, L. Sun, V. Artero, E. A. Gibson, *Phys. Chem. Chem. Phys.* **2016**, *18*, 10727–10738.
- [11] M. G. Gatty, S. Pullen, E. Sheibani, H. Tian, S. Ott, L. Hammarström, *Chem. Sci.* **2018**, *9*, 4983–4991.
- [12] L. J. Antila, P. Ghamgosar, S. Maji, H. Tian, S. Ott, L. Hammarström, *ACS Energy Lett.* **2016**, *1*, 1106–1111.
- [13] P. Qin, J. Wiberg, E. A. Gibson, M. Linder, L. Li, T. Brinck, A. Hagfeldt, B. Albinsson, L. Sun, *J. Phys. Chem. C* **2010**, *114*, 4738–4748.
- [14] C. J. Wood, G. H. Summers, E. A. Gibson, *Chem. Commun.* **2015**, *51*, 3915–3918.
- [15] G. H. Summers, J.-F. Lefebvre, F. A. Black, E. Stephen Davies, E. A. Gibson, T. Pullerits, C. J. Wood, K. Zidek, *Phys. Chem. Chem. Phys.* **2016**, *18*, 1059–1070.
- [16] M. Gennari, F. Légalité, L. Zhang, Y. Pellegrin, E. Blart, J. Fortage, A. M. Brown, A. Deronzier, M.-N. Collomb, M. Boujtita, D. Jacquemin, L. Hammarström, F. Odobel, *J. Phys. Chem. Lett.* **2014**, *5*, 2254–2258.
- [17] K. L. Materna, A. M. Beiler, A. Thapper, S. Ott, H. Tian, L. Hammarström, *ACS Appl. Mater. Interfaces* **2020**, *12*, 31372–31381.
- [18] K. Zhu, S. K. Frehan, G. Mul, A. Huijser, *J. Am. Chem. Soc.* **2022**, *144*, 11010–11018.
- [19] A. Torres, R. S. Oliboni, L. G. C. Rego, *J. Phys. Chem. Lett.* **2015**.
- [20] S. G. Abuabara, L. G. C. Rego, V. S. Batista, *J. Am. Chem. Soc.* **2005**, *127*, 18234–18242.
- [21] J. P. Menzel, A. Papadopoulos, J. Belić, H. J. M. de Groot, L. Visscher, F. Buda, *J. Phys. Chem. C* **2020**, *124*, 27965–27976.
- [22] A. V. Akimov, R. Asahi, R. Jinnouchi, O. V. Prezhdo, *J. Am. Chem. Soc.* **2015**, *137*, 11517–11525.
- [23] A. Monti, C. F. A. Negre, V. S. Batista, L. G. C. Rego, H. J. M. De Groot, F. Buda, *J. Phys. Chem. Lett.* **2015**, *6*, 2393–2398.
- [24] J. D. Gaynor, A. Petrone, X. Li, M. Khalil, *J. Phys. Chem. Lett.* **2018**, *9*, 6289–6295.
- [25] F. Perrella, X. Li, A. Petrone, N. Rega, *JACS Au* **2023**, *3*, 70–79.
- [26] F. Perrella, A. Petrone, N. Rega, *J. Chem. Theory Comput.* **2023**, *19*, 626–639.
- [27] E. Buttarazzi, F. Perrella, N. Rega, A. Petrone, *J. Chem. Theory Comput.* **2023**, *19*, 8751–8766.
- [28] E. Benazzi, J. Mallows, G. H. Summers, F. A. Black, E. A. Gibson, *J. Mater. Chem. C* **2019**, *7*, 10409–10445.

Chapter 6: Effects of Nuclear Motion on the Photoinduced Interfacial Charge Transfer Dynamics at a NiO/P1 Photocathode

- [29] K. Zhu, A. P. Rodríguez, M. B. Brands, T. De Haas, F. Buda, J. N. H. Reek, G. Mul, A. Huijser, *Adv. Sci.* **2024**, 2403454.
- [30] S. Grimme, C. Bannwarth, P. Shushkov, *J. Chem. Theory Comput.* **2017**, *13*, 1989–2009.
- [31] L. G. C. Rego, V. S. Batista, *J. Am. Chem. Soc.* **2003**, *125*, 7989–7997.
- [32] R. Da Silva, D. A. Hoff, L. G. C. Rego, *J. Phys.: Condens. Matter* **2015**, *27*, 134206.
- [33] A. B. Muñoz-García, M. Pavone, *Phys. Chem. Chem. Phys.* **2015**, *17*, 12238–12246.
- [34] M. Wykes, F. Odobel, C. Adamo, I. Ciofini, F. Labat, *J. Mol. Model.* **2016**, *22*, 289.
- [35] M. Alsabet, M. Grdeň, G. Jerkiewicz, *Electrocatalysis* **2015**, *6*, 60–71.
- [36] V. Maffei, B. Jousseme, T. Gustavsson, *Photochem. Photobiol. Sci.* **2021**, *20*, 1257–1271.
- [37] L. D’Amario, J. Föhlner, G. Boschloo, L. Hammarström, *Chem. Sci.* **2018**, *9*, 223–230.
- [38] J. J. Snellenburg, S. P. Laptenok, R. Seger, K. M. Mullen, I. H. M. V. Stokkum, *J. Stat. Soft.* **2012**, *49*, 1–22.
- [39] R. Hoffmann, *J. Chem. Phys.* **1963**, *39*, 1397–1412.
- [40] J. H. Ammeter, H. B. Buergi, J. C. Thibault, R. Hoffmann, *J. Am. Chem. Soc.* **1978**, *100*, 3686–3692.
- [41] Alvarez, S. Table of Parameters for Extended Huckel Calculations. Universitat de Barcelona: Barcelona, 1993.
- [42] F. Odobel, L. Le Pleux, Y. Pellegrin, E. Blart, *Acc. Chem. Res.* **2010**, *43*, 1063–1071.
- [43] J. He, H. Lindstro, S.-E. Lindquist, *Sol. Energy Mater.* **2000**.
- [44] L. Zhu, H. Yang, C. Zhong, C. M. Li, *Chem. Asian J.* **2012**, *7*, 2791–2795.
- [45] D. Adler, J. Feinleib, *Phys. Rev. B* **1970**, *2*, 3112–3134.
- [46] H. Sato, T. Minami, S. Takata, T. Yamada, *Thin Solid Films* **1993**, *236*, 27–31.
- [47] E. L. Miller, R. E. Rocheleau, *J. Electrochem. Soc.* **1997**, *144*, 1995–2003.
- [48] G. A. Sawatzky, J. W. Allen, *Phys. Rev. Lett.* **1984**, *53*, 2339–2342.
- [49] E. Z. Kurmaev, R. G. Wilks, A. Moewes, L. D. Finkelstein, S. N. Shamin, J. Kuneš, *Phys. Rev. B* **2008**, *77*, 165127.
- [50] C. Rödl, F. Fuchs, J. Furthmüller, F. Bechstedt, *Phys. Rev. B* **2009**, *79*, 235114.
- [51] T. de Haas, K. Zhu, Y. Luo, G. Mul, F. Buda, A. Huijser **2025**, *J. Phys. Chem. C* **2025**, *129* (14), 6817–6826.
- [52] Y. Yoneda, S. J. Mora, J. Shee, B. L. Wadsworth, E. A. Arsenault, D. Hait, G. Kodis, D. Gust, G. F. Moore, A. L. Moore, M. Head-Gordon, T. A. Moore, G. R. Fleming, *J. Am. Chem. Soc.* **2021**, *143*, 3104–3112.
- [53] P. You, D. Chen, X. Liu, C. Zhang, A. Selloni, S. Meng, *Nat. Mater.* **2024**, *23*, 1100–1106.
- [54] R. L. Purchase, H. J. M. De Groot, *Interface Focus* **2015**, *5*, 1–16.
- [55] X. Li, F. Buda, H. J. M. De Groot, G. J. Agur. Sevink, *J. Phys. Chem. C* **2019**, *123*, 16462–16478.
- [56] X. Li, F. Buda, H. J. M. De Groot, G. J. A. Sevink, *J. Phys. Chem. B* **2020**, *124*, 4026–4035.

6A. Appendix

6A.1 Computational details on DFT-based NiO slab structure optimizations

All optimizations were carried out using the Quickstep module in the CP2K8.2 software package.^[1] The calculations applied the generalized gradient approximation (GGA) introduced by Perdew, Burke and Ernzerhof for the treatment of the exchange correlation potential with Grimme's third generation of dispersion corrections including a 22 Å cutoff and grid-smoothing.^[2-5] A Mullikan based Hubbard-U parameter of 3.4 eV was applied on the Ni d-electrons to improve the description of the electronic structure over the standard GGA based DFT. Details on the optimization of the Hubbard-U parameter are provided in A.5. The calculations employed a hybrid Gaussian Plane Wave (GPW) scheme as implemented in the Quickstep routine in CP2K8.2.^[6] The Ni and O valence electrons were expanded in the DZVP-MOLOPT-SR-GTH basis, while the core-valence electron interactions were modeled with pseudopotentials developed by Goedecker, Teter and Hutter.^[7-9] A cut-off energy of 400 Ry was used for the auxiliary plane wave basis. All calculations considered only the Γ -point. Optimizations of the electronic structure were converged to $5 \cdot 10^{-7}$ H cycle⁻¹ and geometric structure optimizations were converged to root mean square values of 10^{-4} Bohr⁻¹ in the step size and 10^{-5} H Bohr⁻¹ in the forces.

6A.2 NiO structure optimization.

The bulk structure of NiO was optimized in a rhombohedral cell ($\alpha=\beta=\gamma=60^\circ$) containing 64 nickel and 64 oxygen atoms at the DFT+U level of theory in CP2K8.2.^[1] Cell-optimizations yielded a quasi-perfect rock salt structure with an average cubic lattice parameter of 4.17 Å, which matches lattice parameters reported in literature.^[10-12] Visualization of the spin-density demonstrates that the optimized electronic structure exhibits anti-ferromagnetic spin alignments in the (111) plane (see Figure 6A.1). The bulk optimized rhombohedral was transformed to an orthorhombic box and cut along the (100) direction. The x and y dimensions of the box were preserved, but the z -axis was elongated to 40.0 Å, introducing a vacuum of 28.2 Å above the surface. Subsequently, a structure optimization was

Chapter 6: Effects of Nuclear Motion on the Photoinduced Interfacial Charge Transfer Dynamics at a NiO/P1 Photocathode

carried out in which the lowest layer of nickel and oxide atoms were kept at fixed positions to simulate the constraining effect of the bulk material. In line with previous studies, the (100) surface undergoes only minor rearrangements.^[13–16] As a sanity check, slab optimizations were carried out also for the (111) surface. This yielded a structure that aligns with reports in literature.^[17]

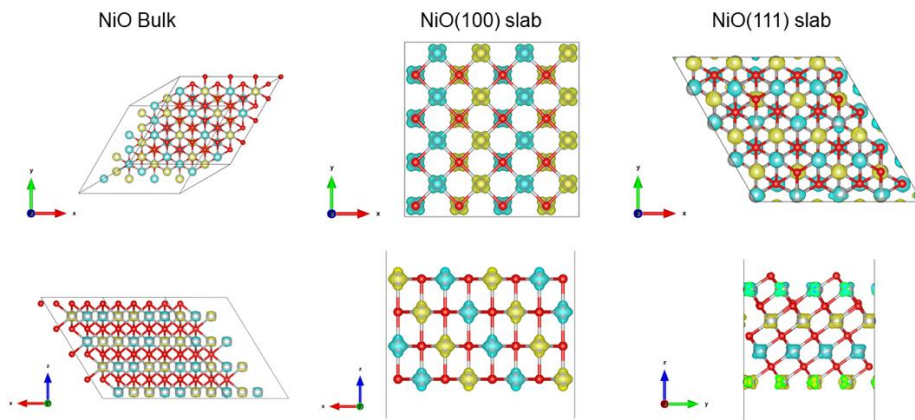


Figure 6A.1: Visualization of the DFT+U optimized bulk and slab NiO structures. Spin densities are plotted in yellow (spin up) and cyan (spin down). The spins are observed to align in the (111) plane for both phases, forming anti-ferromagnetically coupled sheets.

6A.3 Ground state P1/NiO molecular dynamics simulations

The optimized NiO (100) surface slab was used to generate a 3-layer orthorhombic slab of 8 by 4 NiO units (192 Ni and 192 O atoms in total). In the center of the unit cell, the optimized P1 dye was attached to the surface through a bidentate binding mode where both carboxylate oxygens were attached to two distinct nickel atoms (see Figures 6A.2c and 6A.2d for a visualization of the system). Previous DFT studies of a similar dye with a carboxylate anchoring group have shown that this is the preferred binding mode on NiO (100).^[16] Optimizations and

molecular dynamics (MD) simulations of the dye attached to the surface were subsequently performed at the GFN-xTB level of theory, including Grimme's third generation of pairwise additive dispersion corrections.^[4] The P1 structure was optimized on the surface, and initial conditions for a production run were obtained by performing a 5 ps equilibration run at 300 K. The timestep for this equilibration run was set to 0.5 fs and a constant temperature was maintained with the Canonical Sampling through Velocity Rescaling (CSVR) thermostat.^[18] The timestep for the production runs was set to 0.1 fs. During the optimization, equilibration and production runs, the positions of the nickel and oxygen atoms of the NiO slab were kept fixed. We note that we have also attempted MD simulations with fully relaxed Ni and O atoms. However, we found that NiO rock salt structure was unstable during these simulations, resulting in nickel and oxygen dissociation from the surface. These unstable dynamics are likely a result of the limitations of GFN-xTB in properly describing the anti-ferromagnetically coupled spin layers in the NiO (111) plane. To validate the decision to neglect structural relaxations of NiO in response to the P1 dye anchoring, DFT-based MD simulations were performed on a small representative model system. This system consisted of a 4-(diphenylamino)benzoic acid molecule on a NiO (100) slab of four layers of 8x8 NiO units and explicit water solvation. The simulation showed that neither the solvent nor the dye molecule had significant effects on the NiO surface structure, justifying the approach described above. The DFT-based simulations on the small model are further discussed in A.6.

6A.4 Electron and hole wavepacket simulations

After the ground states nuclear trajectories were obtained, the evolution of the excited states electron and hole wave packets were simulated on the basis of the Extended Hückel formalism, as implemented in the DynEMol software.^[19] For all simulations, the photoexcited state was prepared by initiating an electron wave packet in the P1 LUMO and a hole wave packet in the P1 HOMO, which is justifiable considering that the 0-0 excitation in the P1 dye is largely dominated

Chapter 6: Effects of Nuclear Motion on the Photoinduced Interfacial Charge Transfer Dynamics at a NiO/P1 Photocathode

by the HOMO-LUMO transition (see A.7). The time-step for the wave packet propagation was set to 0.1 fs, which is short enough to guarantee proper convergence of the electronic sub-system.^[20] The quantum propagation of the wave packet is followed by calculating the time-dependent survival probability (SP) on the dye and on the NiO slab. This property is calculated by projecting the wave function at time t , on the atomic orbital basis of the molecular sub-system of interest.^[21]

6A.5 Optimization of the Hubbard-U parameter

As mentioned in the section 6A.1.2, the calculations reported in the paper employed a Mulliken-based Hubbard U parameter of 3.4 eV to the Ni d-electrons to improve the description of the NiO electronic structure over standard GGA-DFT. As the goal of the DFT optimizations was only to obtain a structure for the subsequent quantum wave packet simulations, we focused on obtaining a correct geometry rather than reproducing an accurate band gap. With these considerations in mind, a series of 6 bulk phase cell-optimizations were performed, applying a Hubbard parameter of 1, 2, 3, 4, 5 or 6 eV, respectively. These cell-optimizations were performed on a rhombohedral box containing 64 nickel and 64 oxygen atoms. This series was later extended with additional optimizations applying a U parameter of 3.4 and 3.6 eV. Subsequently, a series of electronic structure optimizations was performed on a perfect NiO bulk structure with a lattice parameter of 4.17 Å, to extract the predicted band gap. The obtained lattice parameter and band gap energies are provided in Table 6A.1. Based on these benchmark calculations, it was decided to perform the slab optimizations with a Hubbard U parameter of 3.4 eV, as this yielded a good compromise between the predicted lattice parameter and band gap properties.

Table 6A.1. Lattice parameters and band gap energies for the performed NiO bulk phase optimizations with different Hubbard U values. Experimental data are shown in the last column.

Hubbard U parameter (eV)	1	2	3	3.4	3.6	4	5	6	Exp.
Lattice parameter ($\text{\AA}$)	4.12	4.18	4.17	4.16	4.15	4.18	4.15	4.10	4.17 ^[10–12]
Band Gap (eV)	1.48	1.64	1.93	2.10	2.19	2.39	2.90	2.75	3.4–4.0

6A.6 DFT-based molecular dynamics of a model dye-NiO system in explicit solvation

To investigate the structural response of the NiO surface to the anchoring of P1, DFT-based molecular dynamics were performed using a small model system. In this model system, P1 was represented by a 4-(diphenylamino)benzoic acid (4DPABA) molecule. 4DPABA represents a good model for the P1 dye as it contains the same benzoic acid anchoring group and triphenyl amine core. The same computational settings were employed as described in section 6A.1 The optimized NiO (100) surface was used to generate a slab of 4 layers of 4 by 4 NiO units (total of 128 Ni and 128 O atoms). The 4DPABA molecule was considered to attach to the surface in a bidentate binding mode, as earlier studies from Pavone *et al* have shown that this is energetically more stable than the monodentate binding.^[16] The carboxylate oxygen atoms were considered to bind to two distinct Ni atoms at the surface, while the dissociating carboxylate proton was considered to bind to the adjacent oxygen atom. Since each Ni atom hosts two unpaired electrons, two distinct binding modes are possible: one in which the two carboxylate oxygen atoms bind to two Ni atoms with the same spin polarization ($\alpha\alpha$ -binding), and another where they bind to two Ni atoms with opposite spin polarization ($\alpha\beta$ -binding). Furthermore, we considered two different surface species. The first species stands perpendicular to the NiO surface and is displayed in Figure 6A.2a, while the second species lies flat on the surface and is displayed in Figure 6A.2b. All interface structures were optimized in a cubic box with

Chapter 6: Effects of Nuclear Motion on the Photoinduced Interfacial Charge Transfer Dynamics at a NiO/P1 Photocathode

dimensions 16.6 by 16.6 by 24 Å. The energies associated with each species are reported in Table 6A.2. Interestingly, the species where the 4DPABA dye lies flat on the surface was found to be ~ 30 kcal mol⁻¹ lower in energy than the species where the dye stands perpendicular to the surface. The difference between binding two to nickel atoms of same or opposite spin appears to have an effect in the order of 1 kcal mol⁻¹.

Table 6A.2. Relative energies for the four considered 4DPABA surface species.

	Energy (kcal mol ⁻¹)
<i>standing perpendicular ($\alpha\alpha$)</i>	30.4
<i>standing perpendicular ($\alpha\beta$)</i>	29.3
<i>flat on surface ($\alpha\alpha$)</i>	0
<i>flat on surface ($\alpha\beta$)</i>	0.9

After geometry optimizations of the 4DPABA-NiO interface, 129 water molecules were added to the simulation box with the PACKMOL builder tool as implemented in AMS2021.^[22,23] The system was equilibrated for 1 ps, and subsequently propagated for another 3 ps at the DFT-MD level. During the dynamics, the CSVR thermostat was applied with a timestep of 50 fs.^[18] Figure 6A.2c-d presents a snapshot from the MD simulations. During the dynamics, the 4DPABA dye was found to remain strictly perpendicular to the surface and the bidentate binding mode was found to remain stable for the entire duration of the simulation. This indicates that the interconversion between the conformations - with the dye standing perpendicular or parallel to the surface - is associated with a barrier substantially higher than $k_B T$. Water molecules appeared to be strongly physisorbed to the surface, with the oxygen atoms consistently oriented towards the surface nickel atoms, while the hydrogens atoms formed strong hydrogen bonds with the surface oxygen atoms. During the course of the simulation, two water molecules underwent O-H bond dissociation, resulting in their

chemisorption on the surface. The binding of the 4DPABA molecule has a limited effect on the structure or the dynamics of the Ni and O atoms at the dye-surface interface. This result justifies the assumption of neglecting the structural motion within the NiO slab in the GFN-xTB simulations reported in the main manuscript.

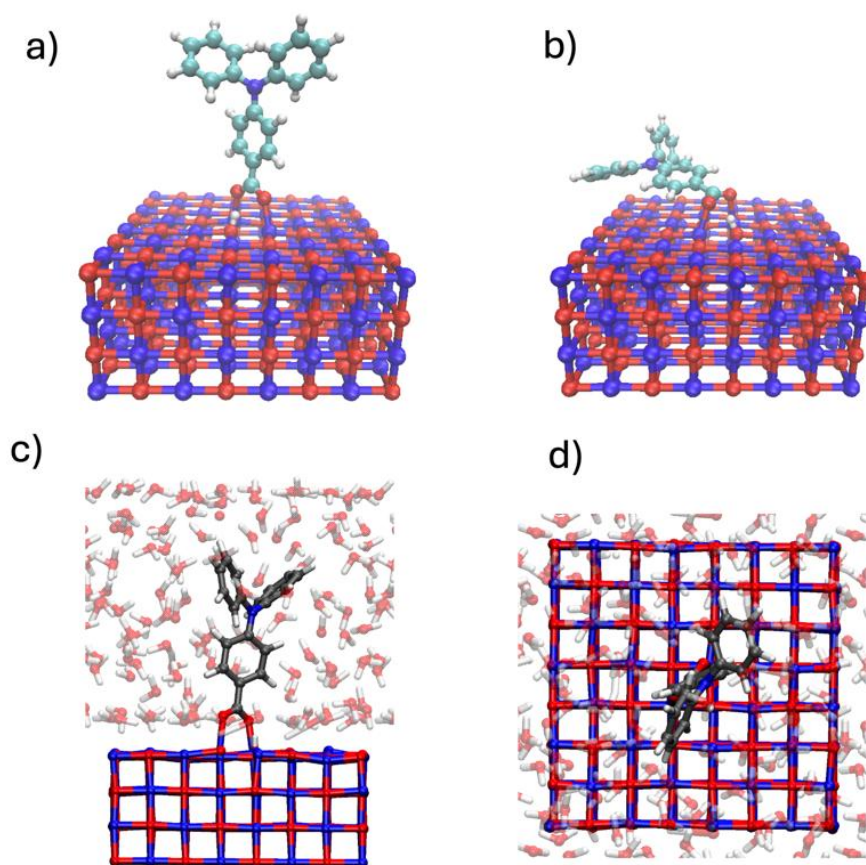


Figure 6A.2. a) and b) present visualizations of the 4DPABA dye in perpendicular orientation towards to surface and in when it lies on the surface, respectively. Top (c) and side (d) view of snapshots from the DFT-based molecular dynamics simulations of 4DPABA on NiO.

6A.7 DFT optimization and TDDFT excitations spectrum of the P1 dye

The P1 geometry was optimized at the DFT level using the AMS2021 program.^[23] The optimizations employed the hybrid B3LYP exchange-correlations functional in an all-electron, triple- ζ (TZP) Slater-type basis. Van der Waals forces were corrected by the third generation of Grimme's dispersion corrections including Becke and Johnsen damping functions (D3BJ),^[3–5,24] and relativistic effects were included by means of the Zeroth Order Regular Approximation (ZORA).^[25] The COnductor like Screening MOdel (COSMO) was employed to take into account the electronic polarization effects of the water environment.^[26–28] The numerical integration was improved over the default setting to “good”, and the self-consistent field convergence was tightened to 10^{-8} H. A frequency calculation on the optimized P1 geometry did not reveal any imaginary eigenmodes, thereby verifying that the obtained structure represents a local minimum on the potential energy surface. The excitation spectrum was calculated by a Time-Dependent DFT (TDDFT) calculation within the Tamm-Dancoff formalism, employing the same settings as described above.^[29]

The lowest 5 electronic excitations calculated by TDDFT are provided in Table 6A.3. According to this calculation at the B3LYP level, the first bright (oscillator strength of 1.51 a.u.) excitation is largely (98.7%) described by the HOMO-LUMO transition.

Table 6A.3. Unrestricted TDDFT (B3LYP-D3BJ/TZP) excitation spectrum of the P1 dye in implicit water solvation (COSMO). Also the first spin-forbidden singlet-triplet excitations are included.

	Spin	Excitation energy (eV)	Oscillator strength (a.u.)	Major MO contributions
1	singlet-triplet	1.73	0.05	α :156 $\rightarrow$ 157 (53%), β :156 $\rightarrow$ 157 (26%)
2	singlet-triplet	1.80	0.00	α :156 $\rightarrow$ 158 (48%), β :156 $\rightarrow$ 157 (22%)
3	singlet-singlet	2.15	1.51	β :156 $\rightarrow$ 157 (64%) α :156 $\rightarrow$ 157 (35%)
4	singlet-singlet	2.35	0.20	β :156 $\rightarrow$ 158 (67%) α :156 $\rightarrow$ 158 (29%)
5	singlet-triplet	2.42	0.01	α :155 $\rightarrow$ 157 (30%), α :156 $\rightarrow$ 158 (19%), β :155 $\rightarrow$ 157 (17%), α :154 $\rightarrow$ 158 (12%)

6A.8 Optimization of the Extended-Hückel parameters

The simulations of electron and hole wave packets described in this work were performed within the framework of Extend-Hückel (EH) theory. A more elaborate overview of this method is provided for instance in ref.^[30] The EH calculations on the NiO-P1 interface using the default EH parameters^[31] did not yield a driving force for the hole transfer from the excited P1* to the NiO surface. A realistic alignment of the P1 frontier orbitals with respect to the NiO valence band (VB), as well as a widening of the P1 HOMO-LUMO gap and a narrowing of the NiO band gap was achieved by fine-tuning the Coulomb integral parameters with a genetic algorithm. The optimization of the NiO parameters was performed on a bulk-phase, cubic NiO structure, containing 32 nickel and 32 oxygen atoms in a perfect rock-salt formation. Periodic boundary conditions were employed in the [100], [010] and [001] directions. The parameters for the P1 dye were optimized by performing the EH calculations on a DFT-optimized structure of the free P1 dye including the proton on the carboxylate group, that would later dissociate

Chapter 6: Effects of Nuclear Motion on the Photoinduced Interfacial Charge Transfer Dynamics at a NiO/P1 Photocathode

upon anchoring to the NiO. During the optimization procedure, a distinction was made between different carbon and nitrogen atoms that were found in different chemical environments. A schematic representation of the different atomic species is provided in Figure 6A.3a. In each optimization run, the genetic algorithm spawned a population of 50 sets of parameters of which the 2 best performing sets were propagated to the next generation. After 10 generations, the best performing set of parameters was assessed by hand to see whether the relevant orbitals still preserved the correct symmetry and spatial distribution. The target values for the optimization procedure are given in Table 6A.4, while the formulation of the cost function is described in an earlier work.^[30] Figure 6A.3b provides a visual comparison between the frontier P1 orbitals calculated with DFT and with the final EH parameters. The obtained EH parameters for all chemical elements, as described in Figure 6A.3a, are provided in the A.11 appendix.

Table 6A.4. The NiO VBM (valence band maximum), NiO CBM (conduction band minimum) and P1 energy level alignment with the original and optimized EH parameters.

	P1 HOMO (eV)	P1 LUMO (eV)	NiO VBM (eV)	NiO CBM (eV)
Original parameters	-11.2	-9.8	-12.3	-5.6
Optimized parameters	-11.4	-9.2	-10.4	-6.4
Optimization targets	-11.4	-9.2	-10.5	-6.5

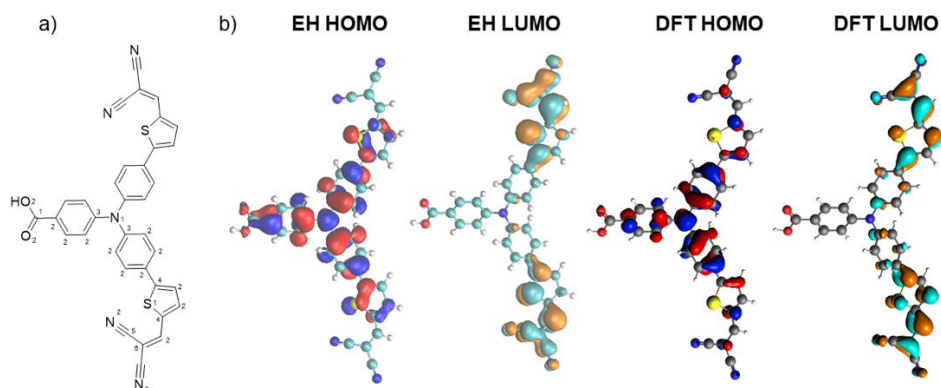


Figure 6A.3. a) provides the distinct atomic species in the EH optimization procedure. A visual comparison between the P1 HOMO and LUMO orbitals calculated at the DFT level and at the EH level is provided in b). The B3LYP functional was used for the DFT calculations. Isosurfaces of the HOMO and LUMO orbitals were plotted at a density value of 0.03.

6A.9 Electron dynamics simulations on static structures and dynamics nuclear trajectories

Figure 6A.4 presents the electron survival probability on the excited $P1^*$ calculated from the quantum wave packet simulations on MD trajectories including nuclear motion (green) and static nuclear structures (red). The three different panels correspond to the three initial conditions sampled from the performed classical MD simulations at $t=0$ fs, $t=1000$ fs and $t=2000$ fs. The electron wave packet remains localized on the dye throughout all three wave packet simulations on the MD trajectories including thermal nuclear motion. In contrast, the simulations on static structures show a gradual electron transfer to the NiO slab after the initial ~ 200 fs of the simulation. This suggests that a recombination pathway becomes accessible, enabling coherent charge transfer from the P1 LUMO to the NiO valence band. Interestingly, nuclear motion

Chapter 6: Effects of Nuclear Motion on the Photoinduced Interfacial Charge Transfer Dynamics at a NiO/P1 Photocathode

appears to quench this coherent transfer and prevents the recombination on the simulated timescale of 1 ps.

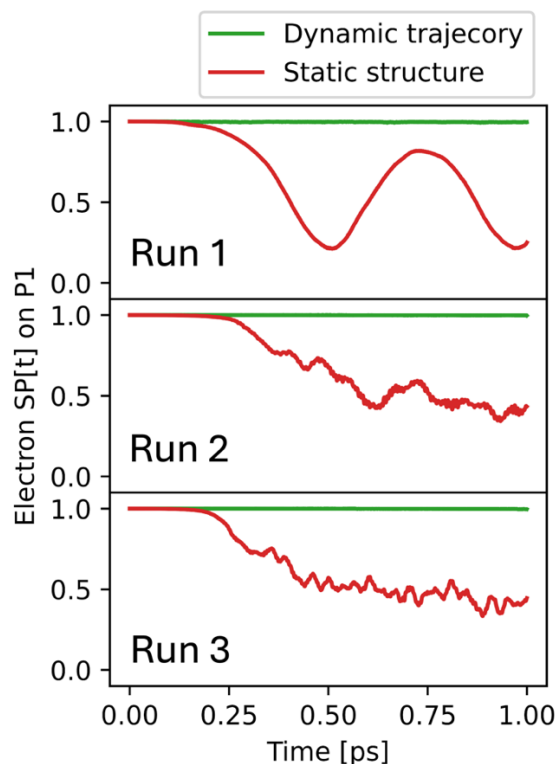


Figure 6A.4: Time-dependent electron survival probability on the P1 dye on the static nuclear structures (red) and dynamic nuclear trajectories (green).

6A.10 Ordering of HOMO and HOMO–1 states for different conformations sampled from MD

Before performing the photoinduced hole injection quantum dynamics simulations, the relative alignment of the HOMO and HOMO–1 orbitals was investigated for a series of 30 different structures sampled from the MD simulations. For each of these structures, we performed two quantum dynamics simulations with the hole initialized in the HOMO or in the HOMO–1 orbital of the system. Subsequently, the hole density was visualized after the first 0.1 fs

timestep. The orbital energies are plotted in Figure 6A.5a, while two representative hole density visualizations are provided in Figure 6A.5b. It was observed that for several conformational structures the HOMO and HOMO-1 orbitals become nearly degenerate and that for four structures their relative alignment is reversed.

Chapter 6: Effects of Nuclear Motion on the Photoinduced Interfacial Charge Transfer Dynamics at a NiO/P1 Photocathode

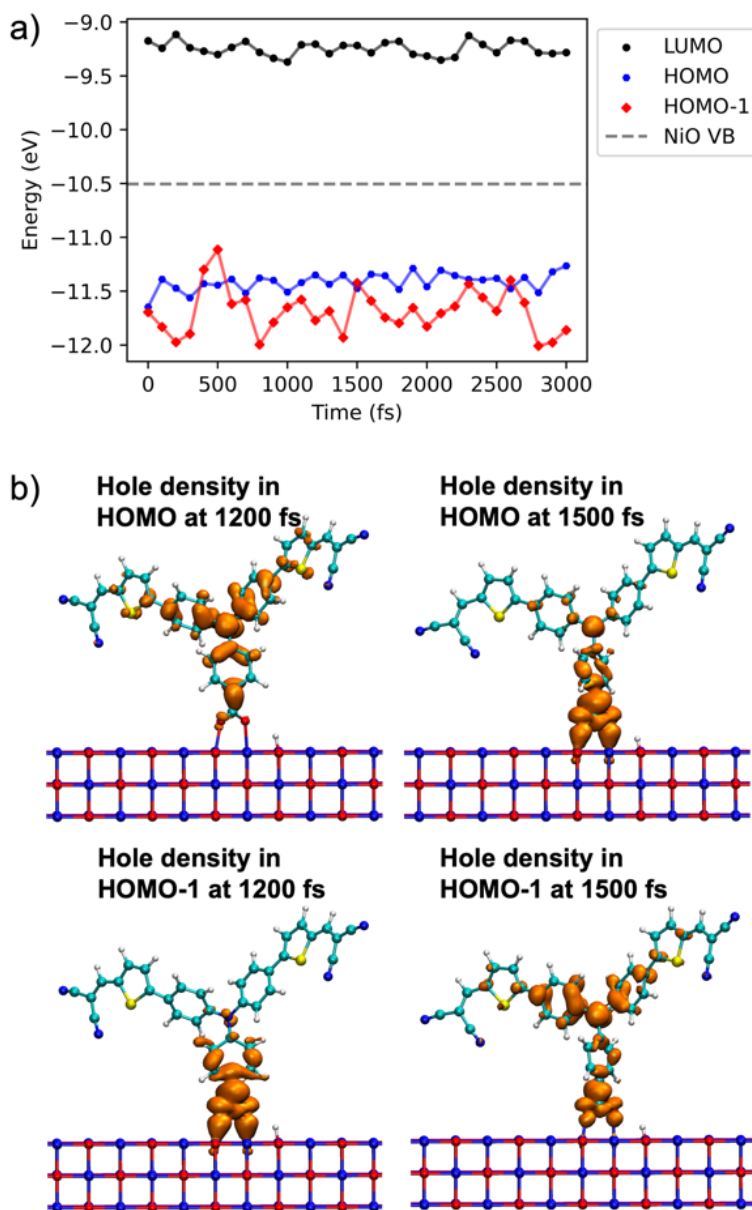


Figure 6A.5. a) The energies of the LUMO, HOMO and HOMO-1 states in the 3 ps time interval. b) Visualizations of the hole wave packet density initiated in the HOMO and HOMO-1 states at 1200 fs and 1500 fs. At this stage, the order of the energy levels is reversed, and the two states are mixed.

6A.11 Extended Hückel-based DOS plot for P1 lying flat on surface

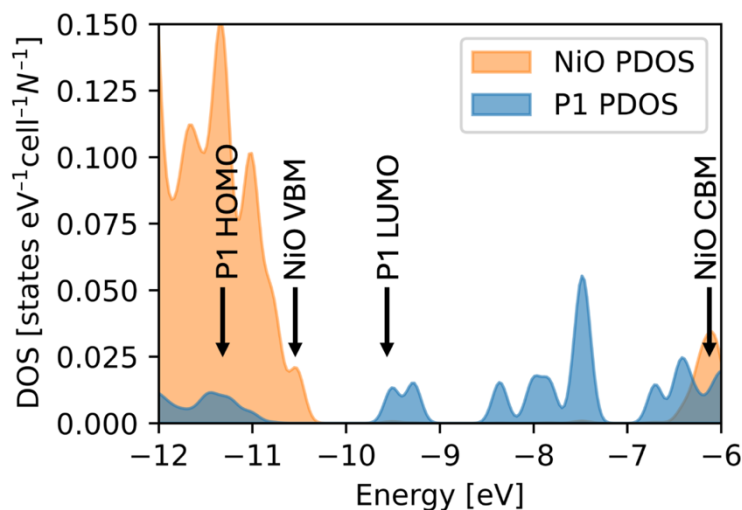


Figure 6A.6. Plot of the electronic density of states (DOS) of the optimized P1 dye on lying flat on the NiO (100) slab (Species 2, Figure 6.4b).

6A.11: The optimized EH parameters

Symbol	MMsymbol	NoAt	Nvalen	Nzeta	n	spdf	IP	zeta1	zeta2	coef1	coef2	k_WH
O	O1	8	6	1	2	s	-31.97708	2.419349	0.000000	1.000000	0.000000	2.388173
O	O1	8	6	1	2	p	-12.44601	2.188920	0.000000	1.000000	0.000000	1.708553
Ni	Ni1	28	10	1	4	s	-8.35691	2.423005	0.000000	1.000000	0.000000	1.726895
Ni	Ni1	28	10	1	4	p	-5.04010	1.550887	0.000000	1.000000	0.000000	3.040000
Ni	Ni1	28	10	2	3	d	-12.95211	5.881614	2.300000	0.568300	0.629200	2.007307
C	C1	6	4	1	2	s	-21.83998	1.502273	0.000000	1.000000	0.000000	1.652710
C	C1	6	4	1	2	p	-11.11776	1.578776	0.000000	1.000000	0.000000	1.271570
C	C2	6	4	1	2	s	-21.64263	1.392992	0.000000	1.000000	0.000000	1.586950
C	C2	6	4	1	2	p	-11.30164	1.592068	0.000000	1.000000	0.000000	2.189580
C	C3	6	4	1	2	s	-21.30227	1.602251	0.000000	1.000000	0.000000	1.399880
C	C3	6	4	1	2	p	-12.56206	1.907199	0.000000	1.000000	0.000000	1.909580
C	C4	6	4	1	2	s	-21.26181	1.652660	0.000000	1.000000	0.000000	1.905050
C	C4	6	4	1	2	p	-11.55636	1.727973	0.000000	1.000000	0.000000	1.932090
C	C5	6	4	1	2	s	-21.79423	1.641574	0.000000	1.000000	0.000000	1.521610
C	C5	6	4	1	2	p	-10.69162	1.507971	0.000000	1.000000	0.000000	2.166900
C	C6	6	4	1	2	s	-21.66886	1.537034	0.000000	1.000000	0.000000	1.718590
C	C6	6	4	1	2	p	-11.56014	1.599292	0.000000	1.000000	0.000000	1.678440
S	S1	16	6	1	3	s	-20.14530	2.069794	0.000000	1.000000	0.000000	2.032820
S	S1	16	6	1	3	p	-11.89877	1.899772	0.000000	1.000000	0.000000	3.837720
N	N1	7	5	1	2	s	-25.46722	2.010008	0.000000	1.000000	0.000000	1.282550
N	N1	7	5	1	2	p	-12.73100	2.281318	0.000000	1.000000	0.000000	1.988070
N	N2	7	5	1	2	s	-26.01483	1.859309	0.000000	1.000000	0.000000	1.817200
N	N2	7	5	1	2	p	-13.46475	2.227766	0.000000	1.000000	0.000000	1.427180
O	O2	8	6	1	2	s	-32.51769	1.823570	0.000000	1.000000	0.000000	1.869520
O	O2	8	6	1	2	p	-14.66009	1.962404	0.000000	1.000000	0.000000	2.132110

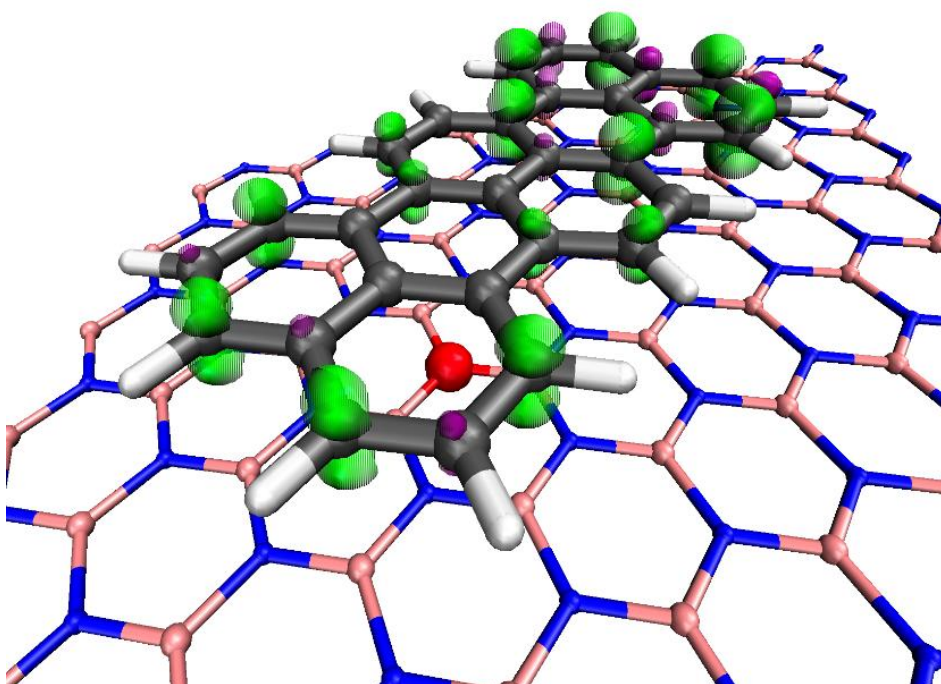
Chapter 6: Effects of Nuclear Motion on the Photoinduced Interfacial Charge Transfer Dynamics at a NiO/P1 Photocathode

6A.12 References

- [1] T. D. Kühne, M. Iannuzzi, M. Del Ben, V. V. Rybkin, P. Seewald, F. Stein, T. Laino, R. Z. Khaliullin, O. Schütt, F. Schiffmann, D. Golze, J. Wilhelm, S. Chulkov, M. H. Bani-Hashemian, V. Weber, U. Borštnik, M. TAILLEFUMIER, A. S. Jakobovits, A. Lazzaro, H. Pabst, T. Müller, R. Schade, M. Guidon, S. Andermatt, N. Holmberg, G. K. Schenter, A. Hehn, A. Bussy, F. Belleflamme, G. Tabacchi, A. Glöß, M. Lass, I. Bethune, C. J. Mundy, C. Plessl, M. Watkins, J. VandeVondele, M. Krack, J. Hutter, *J. Chem. Phys.* **2020**, *152*, 194103.
- [2] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1997**, *78*, 1396–1396.
- [3] S. Grimme, *J. Comput. Chem.* **2004**, *25*, 1463–1473.
- [4] S. Grimme, *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2011**, *1*, 211–228.
- [5] S. Grimme, *Chemistry - Chem. - Eur. J.* **2012**, *18*, 9955–9964.
- [6] J. VandeVondele, M. Krack, F. Mohamed, M. Parrinello, T. Chassaing, J. Hutter, *Comput. Phys. Commun.* **2005**, *167*, 103–128.
- [7] S. Goedecker, M. Teter, J. Hutter, *Phys. Rev. B* **1996**, *54*, 1703–1710.
- [8] C. Hartwigsen, S. Goedecker, J. Hutter, *Phys. Rev. B* **1998**, *58*, 3641–3662.
- [9] M. Krack, *Theor. Chem. Acc.* **2005**, *114*, 145–152.
- [10] R. W. Cairns, E. Ott, *J. Am. Chem. Soc.* **1933**, *55*, 527–533.
- [11] A. K. Cheetham, D. A. O. Hope, *Phys. Rev. B* **1983**, *27*, 6964–6967.
- [12] B. Walls, A. A. Mazilkin, B. O. Mukhamedov, A. Ionov, I. A. Smirnova, A. V. Ponomareva, K. Fleischer, N. A. Kozlovskaya, D. A. Shulyatev, I. A. Abrikosov, I. V. Shvets, S. I. Bozhko, *Sci. Rep.* **2021**, *11*, 3496.
- [13] S. Piccinin, D. Rocca, M. Pastore, *J. Phys. Chem. C* **2017**, *121*, 22286–22294.
- [14] A. Segalina, S. Lebègue, D. Rocca, S. Piccinin, M. Pastore, *J. Chem. Theory Comput.* **2021**, *17*, 5225–5238.
- [15] J. Massin, M. Bräutigam, S. Bold, M. Wächtler, M. Pavone, A. B. Muñoz-García, B. Dietzek, V. Artero, M. Chavarot-Kerlidou, *J. Phys. Chem. C* **2019**, *123*, 17176–17184.
- [16] A. B. Muñoz-García, M. Pavone, *Phys. Chem. Chem. Phys.* **2015**, *17*, 12238–12246.
- [17] W. Zhao, A. D. Doyle, S. E. Morgan, M. Bajdich, J. K. Nørskov, C. T. Campbell, *J. Phys. Chem. C* **2017**, *121*, 28001–28006.
- [18] G. Bussi, D. Donadio, M. Parrinello, *J. Chem. Phys.* **2007**, *126*, 014101.
- [19] A. Torres, R. S. Oliboni, L. G. C. Rego, *J. Phys. Chem. Lett.* **2015**.
- [20] R. Da Silva, D. A. Hoff, L. G. C. Rego, *J. Phys.: Condens. Matter* **2015**, *27*, 134206.
- [21] L. G. C. Rego, V. S. Batista, *J. Am. Chem. Soc.* **2003**, *125*, 7989–7997.
- [22] L. Martínez, R. Andrade, E. G. Birgin, J. M. Martínez, *J. Comput. Chem.* **2009**, *30*, 2157–2164.
- [23] AMS2022.101, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands 2022, <https://www.scm.com>.
- [24] S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456–1465.
- [25] E. Van Lenthe, *J. Chem. Phys.* **1999**, *110*, 8943–8953.
- [26] A. Klamt, *J. Phys. Chem.* **1995**, *99*, 2224–2235.
- [27] A. Klamt, V. Jonas, *J. Chem. Phys.* **1996**, *105*, 9972–9981.
- [28] C. C. Pye, T. Ziegler, E. Van Lenthe, J. N. Louwen, *Can. J. Chem* **2009**, *87*, 790–797.
- [29] S. Hirata, M. Head-Gordon, *Chem. Phys. Lett.* **1999**, *314*, 291–299.
- [30] A. Monti, C. F. A. Negre, V. S. Batista, L. G. C. Rego, H. J. M. De Groot, F. Buda, *J. Phys. Chem. Lett.* **2015**, *6*, 2393–2398.
- [31] Santiago Alvarez. Table of Parameters for Extended Hückel Calculations', Universitat de Barcelona: Barcelona, 1993

Chapter 7: Charge Transfer-Induced Weakening of Vibronic Coupling for Single Terrylene Molecules Adsorbed onto hBN

Adsorption of a terrylene dye on charge donating defect sites in hBN weakens the vibronic intensities in the dye's fluorescence spectrum.



This chapter is based on:

T. de Haas*, R. Smit*, A. Tebeyani, S. Bhattacharyya, K. Watanabe, T. Taniguchi, F. Buda, M. Orrit. Charge Transfer-Induced Weakening of Vibronic Coupling for Single Terrylene Molecules Adsorbed onto Hexagonal Boron Nitride. *J. Phys. Chem. Lett.* **2025**, 16 (1), 349-356 (*contributed equally)

Chapter 7: Charge Transfer-Induced Weakening of Vibronic Coupling for Single Terrylene Molecules Adsorbed onto hBN

7.1 Abstract

Fluorescence spectra of single terrylene molecules adsorbed on hexagonal boron nitride (hBN) flakes were recorded at cryogenic temperatures. The pure electronic transitions of terrylene molecules are spread over a wavelength scale from 570 to 610 nm. Surprisingly, peaks in the vibrationally resolved fluorescence spectrum show intensity variations up to 20-fold between molecules. We find an extreme case where the Debye-Waller-Franck-Condon factor of the zero-phonon line exceeds 0.8. The vibronic intensity correlates both with the spectral position of the electronic transition and with the frequency of the longitudinal stretch mode, which varies between 243 and 257 cm^{-1} . By means of DFT calculations, we show that these observations can be explained by terrylene chemisorption on charge-donating defect sites. The electronic states of molecules at such chemisorption sites would be very attractive for the efficient emission of single photons with narrow lines and for the generation of indistinguishable photons.

7.2 Introduction

The emission of a photon by an excited molecule is generally accompanied by the release of molecular vibration quanta arising from the change in molecular geometry between the molecule's ground and excited state. The larger the change in geometry, the more pronounced are the associated vibronic bands in the fluorescence spectrum (see the theoretical discussion in section 7A.1 of the Appendix). At liquid-helium temperatures, these vibronic fluorescence lines become very sharp, a few cm^{-1} in width or less^[1], and are often used as fingerprints of the single molecule under study. This so-called fluorescence line-narrowing generally works well for molecules embedded in *n*-alkane Shpol'skii matrices^[2], for specific guest molecules in organic matrices^[3] and, as recently demonstrated, for single terrylene molecules adsorbed on the surface of hexagonal boron nitride (hBN).^[4] This latter host system is also currently scrutinized for the many single-photon emitters that it can host, with emission ranging from deep ultraviolet^[5] to the near-infrared.^[6] Recently, in conjunction with our work of terrylene on hBN, new insights were gathered on the potential nature of some of these emitters, namely on the potential formation of aromatic molecules at the hBN/substrate interface during high-temperature annealing.^[7] The same work also summarizes the many defect structures in the hBN crystal lattice that have been proposed in the past to explain the measured emission from hBN. In addition, a recent work on hBN immersed in organic solvents showed that some solvent molecules can potentially bind to defects and display localized fluorescence, while hopping from binding site to binding site.^[8] This work is particularly interesting, as it suggests that molecules can bind more strongly to specific sites on hBN.

In our previous work of single terrylene molecules on hBN, we reported that molecules with redshifted electronic transitions displayed weaker vibronic coupling, and thus show a more intense zero-phonon line in the spectrum, captured by a higher Franck-Condon-Debye-Waller factor α_{FCDW} .^[4] If the interaction of the terrylene molecule with the hBN surface could be engineered so as to maximize this factor, this control method would potentially be much simpler than

Chapter 7: Charge Transfer-Induced Weakening of Vibronic Coupling for Single Terrylene Molecules Adsorbed onto hBN

current methods such as coupling a molecule to an optical cavity.^[9] In this work, we examine potential origins of the weakened vibronic coupling, observed particularly for the most redshifted terrylene molecules. We perform quantum chemical calculations at the DFT level of the interaction of terrylene with a pristine hBN surface and find little change of the vibronic coupling. We then investigate several defects in the hBN lattice and find that some of them, in particular an oxygen substitution at a nitrogen site (O_N) and vacancies at the boron (V_B) or nitrogen site (V_N), can transfer charge to terrylene. Interestingly, we find that this charge transfer reduces the change in geometry between ground and excited state as compared to terrylene in vacuum and strikingly decreases the vibronic coupling of all modes simultaneously in the emission spectrum. This charge donating/accepting behaviour is also relevant to the field of dye-sensitized solar cells, where functionalized terrylenes and similar dyes have been employed for the efficient generation of photocurrents.^[10,11]

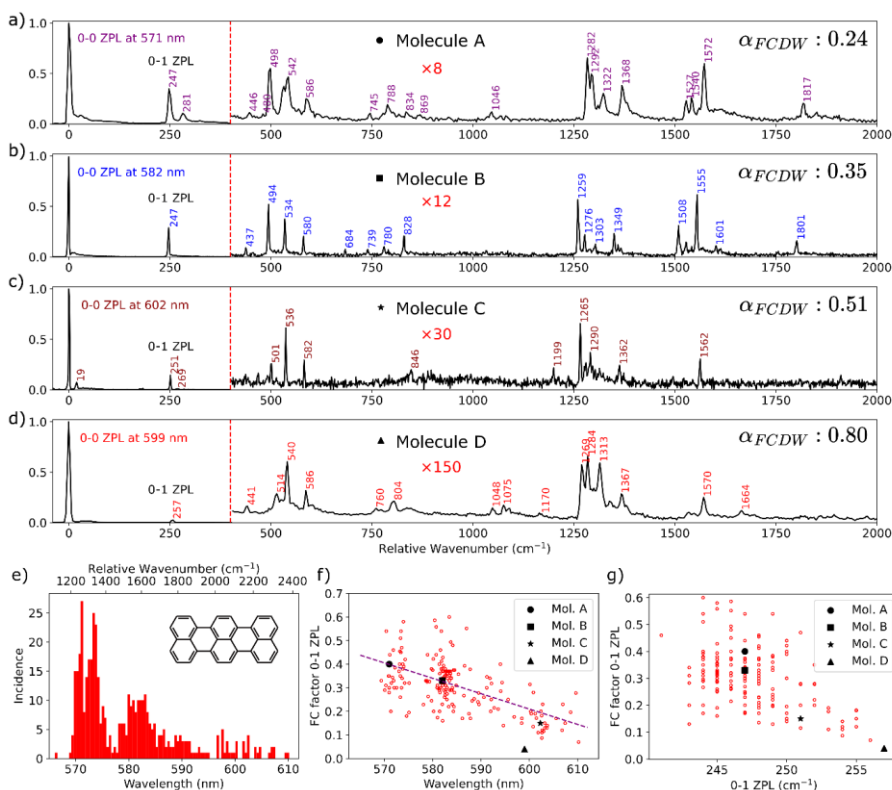
7.3 Results and discussion

7.3.1 Single-Molecule Fluorescence Spectroscopy

Four examples of single-molecule fluorescence spectra obtained from four individual molecules are presented in Figure 7.1a-d and arranged by decreasing intensity of their vibronic lines. All fluorescent molecules were identified as terrylene from their ground state vibrational fingerprint, although slight differences between spectra were observed (see structure in Figure 7.1e). Most of the lines correspond to the release of a single quantum of vibration in various intramolecular modes (0-1), with their intensity related to the Franck-Condon factor of these modes (see section 7A.1 in the Appendix for a short reminder of the theory of vibronic coupling).

In addition to the intramolecular vibrational modes, we also see the phonon wing appearing most clearly between 0 and 100 cm^{-1} to the red of the 0-0 ZPL origin. The intensity of the vibronic fingerprint decreases when going from molecule A

to D, the corresponding values of the Franck-Condon-Debye-Waller factor (α_{FCDW}) being: A: 0.24, B: 0.35, C: 0.51, D: 0.80. Molecule D shows an extremely weak vibronic coupling, with a Franck-Condon-Debye-Waller factor of at least 0.80, which largely exceeds the largest ones observed for organic molecules in a matrix at low temperature. To the best of our knowledge, all factors observed so far for organic molecules were lower than 55 %.^[12] Another surprising observation is that, for each molecule, the coupling strengths of all vibrational modes including lattice phonons vary in a similar way across the spectrum. An alternative formulation of this fact is that the change of geometry of some molecules upon excitation can become very small for all molecular modes simultaneously. This is surprising because, whereas we could expect a weak equilibrium shift for certain modes due to specific interaction with the substrate, we wouldn't expect this to occur simultaneously for all the modes.



Chapter 7: Charge Transfer-Induced Weakening of Vibronic Coupling for Single Terrylene Molecules Adsorbed onto hBN

Figure 7.1. (a)-(d) Fluorescence emission spectra from four different molecules at different wavelengths in the inhomogeneous distribution. The spectra of (A) and (D) were taken at a slightly lower resolution (600 lines/mm grating, 4 cm^{-1} resolution) as compared to (B) and (C), which were taken with a 1200 lines/mm grating (2 cm^{-1} resolution). The first three spectra show decreasing Franck-Condon factors with increase of the 0-0 zero-phonon line (ZPL) wavelength. The fourth spectrum is the most extreme case of ultra-weak vibronic coupling we could find. Note that the intensity of all vibronic lines is reduced by a factor of about 20 with respect to molecule A. Integration times were 10 s in a, 300 s in b, 150 s in c, 600 s in d. The noise in the spectra depends on integration time and mean signal intensities that varied for each molecule. Panel (e) shows the inhomogeneous distribution composed of 452 individual terrylene molecules, with the structure of terrylene in the inset. The relationship between the 0-0 ZPL and FC factor of the 0-1 ZPL is shown in panel (f), while the frequency of the vibration mode responsible for the 0-1 ZPL in relation to its FC factor is shown in panel (g). The corresponding molecules in the spectra of panel (a)-(d) are shown as black markers in the scatter plots. The purple dashed line in (f) is a guide to the eye for the trend, resulting from a linear fit to the data. We note the strong anti-correlation between the Franck-Condon factor and the frequency of the extensional mode at 250 cm^{-1} in (g). This is particularly extreme for molecule D (triangle), which is the one with the highest frequency (257 cm^{-1}) and the lowest 0-1 Franck-Condon factor (0.026) for this mode.

Figure 7.1e presents a histogram of the 0-0 ZPL spectral positions of 452 molecules. The broad distribution in this histogram, extending over a particularly broad range (570-610 nm or more than 1000 wavenumbers), exceeds what is usually observed for terrylene embedded in molecular crystals and presents distinct maxima of around 10 cm^{-1} in width. We assign this structure in the distribution of Figure 7.1e, with maxima around 571, 582 and 600 nm, to selection

within a broad profile through resonance of vibronic lines with the excitation laser. As all molecules were excited with a fixed 532 nm laser, molecules with absorption lines at this wavelength had an increased probability to be selected in the histogram. Indeed, the relative position in wavenumber of the 0-0 zero-phonon lines (ZPLs) with respect to the laser wavelength resembles the mirror image of the vibrational spectra of Figure 7.1a-d. The large inhomogeneous broadening may be the result of significant variations in the environment around the molecule, which might be affected by parameters such as significant tensile strain^[13] or the many types of (charged) defects present.^[14] In addition, the annealing that we perform prior to the deposition of molecules on the hBN, may also hydroxylate parts of the hBN^[15] or create wrinkles in the sheets.^[16]

We now turn to the scatter plots of Figure 7.1f and 7.1g. We observe a clear correlation in Figure 7.1f between the spectral position of a molecule and the intensity of its first vibronic line at $\approx 250\text{ cm}^{-1}$, corresponding to stretching of terrylene along its long axis. Redshifted molecules appear less strongly coupled to vibrations. The correlation is more pronounced in Figure 7.1g when the vibronic coupling of the longitudinal stretch mode is correlated with its frequency: molecules with high stretch frequency exhibit weaker coupling to the electronic system. This correlation reaches an extreme point for molecule D, whose FC factor for the 0-1 ZPL (0.027) is more than 10 times lower than the average over all other molecules, while its stretch mode is the one with the highest frequency at 257 cm^{-1} . As the effective mass of this skeleton mode is not likely to change much from molecule to molecule, the high frequency points to a relatively strong interaction of molecule D with the surface, which appears to change the intramolecular spring constant by about 8%.

As noted above for molecule D, we see that coupling to *all* vibrations decreases in a similar way when going from molecule A to D. Although some minor intensity changes, shifts and splitting of certain modes can be spotted, we observe no major redistribution of intensities between the main modes, so that all of them follow qualitatively the general trend observed on the 250 cm^{-1} stretch mode.

Chapter 7: Charge Transfer-Induced Weakening of Vibronic Coupling for Single Terrylene Molecules Adsorbed onto hBN

7.3.2 Quantum Chemical Calculations

Density functional theory (DFT) was employed to study physisorption of terrylene on a pristine hBN surface, and on hBN including a selection of potential lattice defects. The considered defects include a boron vacancy (V_B), a nitrogen vacancy (V_N), the boron nitride (V_{BN}) divacancy, as well as oxygen substitution at the boron (O_B) or nitrogen (O_N) centres. Indeed, as our samples were annealed in a moderate vacuum of residual air, oxygen substitution appears plausible. Although a comprehensive study of possible defects is beyond the scope of this work, these vacancies and substitutions are representative for a wider range of defects with either electron-accepting or electron-donating properties. Ground state structure optimizations and band structure calculations of the terrylene-hBN interfaces were performed at the HSE06+D3BJ DFT-level using the CP2K software package.^[17–19] Calculations of the vibronic spectra were subsequently performed with FCclasses3 software using geometries, Hessians and dipole moments calculated with Gaussian.^[20,21] In these excited state calculations, a two-layer ONIOM(B3LYP/PM3) approach was employed, as considering the entire interface structure at the time-dependent DFT (TD-DFT) level was too computationally demanding.^[22–30] Details on the computational workflow are provided in A2 and A3 of the Appendix.

Table 7.1: Adsorption energies and properties of terrylene adsorbed on different defects.*

			long-axis length (Å)			short-axis length (Å)		
	Adsorption energy (eV)	Mulliken charge on terrylene (atomic units)	Ground state	Excited state	Δx	Ground state	Excited state	Δx
vacuum	-	-	10.078	10.044	-0.034	4.839	4.883	0.044
pristine hBN	-2.44	0.02	10.089	10.054	-0.035	4.843	4.887	0.044
V_{BN}^{**}	-2.36	0.02	-	-	-	-	-	-
V_B	-2.52	0.83	10.054	10.041	-0.013	4.829	4.854	0.023
V_N	-2.46	-0.68	10.094	10.082	-0.012	4.839	4.860	0.021
O_B^{**}	-2.29	0.01	-	-	-	-	-	-
O_N	-3.96	-0.70	10.095	10.083	-0.012	4.839	4.860	0.021

* Note that adsorption energies and Mulliken charges are calculated at the full-DFT level, while the structural properties are calculated at the ONIOM(B3LYP/PM3) level. Δx indicates the change in axis length from the excited to the ground state.

** As the V_{BN} and O_B defects have a lower binding energy for the terrylene molecule compared to defect-free hBN, we did not further investigate the excited state geometry of terrylene on these defects.

The first two columns of Table 7.1 present physisorption energies and partial Mulliken charge accumulation on terrylene in the presence of defects, calculated at the full DFT-level. The charge analysis has also been performed using Hirshfeld and Intrinsic Orbital Analysis charges, which show the same trend and are provided in the Appendix, Table 7A.2.^[31] The physisorption energy of terrylene on a perfect monolayer of hBN was found to be -2.44 eV, compared to terrylene and hBN in vacuum. This adsorption energy follows the trend reported in literature of increasing adsorption energy with increasing molecule size for polycyclic aromatic hydrocarbons (PAH's) on hBN.^[32] Defect site binding energies were established by comparing adsorption energies on defects with the adsorption energy on the defect-free lattice. It was found that the V_{BN} divacancy and the O_B defects bind the molecule less strongly than pristine hBN, with 0.08 and 0.15 eV, respectively. It is therefore unlikely that the terrylene molecule would be localized on these specific defects. Contrarily, the adsorption energy in

Chapter 7: Charge Transfer-Induced Weakening of Vibronic Coupling for Single Terrylene Molecules Adsorbed onto hBN

the presence of the V_N and V_B vacancies is slightly higher (by 0.02 and 0.08 eV) than the defect-free case, and specifically for the O_N defect the binding is much stronger (by 1.52 eV). Notably, this latter defect has also been proposed as a source for specific features observed in X-ray spectroscopy.^[33] The reported partial Mulliken charges reveal that the three terrylene adsorbing defects (V_N , V_B , O_N) donate a considerable amount of electron (V_N , O_N) or hole (V_B) density to terrylene. This type of charge transfer has been reported before in GGA-based DFT studies on hBN-graphene heterostructures.^[34] Because of the charge transfer, we observe significant changes in the extent to which terrylene elongates or contracts upon excitation from the ground to the excited state. For instance, in the defect-free hBN, the long-axis contraction in the excited state is -0.035 Å, whereas in the presence of the O_N defect, this contraction is reduced to only -0.012 Å (see Table 7.1). Therefore, one can expect the intensity of vibrational modes coupled to the electronic transition to be affected considerably in the fluorescence spectrum.

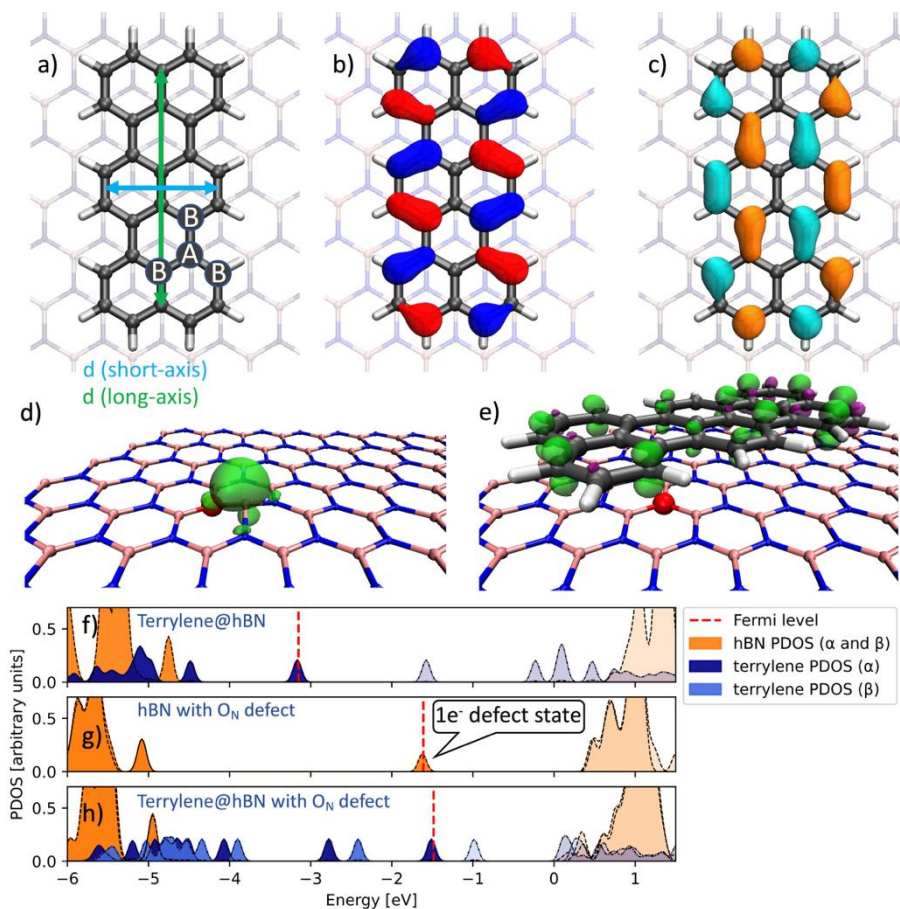


Figure 7.2. (a)-(c) terrylene molecules adsorbed on a single monolayer of pristine hBN. a) shows the longitudinal (green) and short (blue) axis, while the HOMO and LUMO are shown in b) and c), with the isosurfaces plotted at 0.03 a.u. The carbon atoms of the graphene A- and B-sublattices of terrylene are depicted with insets in (a). (d) and (e) show the spin density on the O_N chemisorption site before and after binding of terrylene with an isosurface plotted at 0.005 a.u. Projected density of states (PDOS) of terrylene adsorbed on pristine hBN (f), of hBN with the O_N defect (g) and of terrylene adsorbed on hBN with the O_N defect (h). The PDOS were computed in CP2K at the HSE06+D3(BJ)-level and include a Gaussian broadening of 0.05 eV. Bands with transparent colors correspond to unoccupied levels. The α and β bands for hBN with the O_N defect in (g) and (h)

Chapter 7: Charge Transfer-Induced Weakening of Vibronic Coupling for Single Terrylene Molecules Adsorbed onto hBN

largely overlap and are depicted in the same color (orange). However, it should be noted that the defect state in panel (g) is singly occupied.

Figure 7.2a shows the optimized geometry of terrylene on the hBN single-layer lattice. The two structures are nearly commensurate. The terrylene carbon atoms of the graphene A-sublattice are found to reside on top of monolayer boron atoms, whereas the terrylene carbon atoms of the B-sublattice are placed over the centers of the (BN)₃ hexagons (A- and B-sublattices are indicated in Figure 7.2a). The hBN nitrogens are thus placed underneath the centers of the terrylene aromatic rings. Previous theoretical works have also found this configuration to be most stable for similar PAH's on hBN.^[32,35] Our TD-DFT calculations show that the experimentally observed fluorescence around 600 nm is associated with the electronic transition that involves predominantly (>70%) the HOMO and LUMO orbitals. Figure 7.2b and 7.2c present the HOMO and LUMO orbitals of the terrylene molecule on the hBN surface. Both orbitals are localized on the terrylene molecule and do not hybridize with hBN electronic states. This is in line with Figure 7.2f, which shows that the frontier orbitals of terrylene are found to reside completely isolated within the hBN bandgap. The calculated bandgap of ~5.7 eV is similar to previous studies reporting hBN bandgaps of ~6 eV.^[35,36] The shapes of the HOMO and LUMO orbitals provide a physical interpretation for the observed short-axis elongation and long-axis contraction when terrylene is excited from the ground to the excited state, as electron density is transferred from bonding orbitals along the short-axis to bonding orbitals along the long-axis. Similarly, one can expect that populating the LUMO orbital may affect the spectral position of the long-axis vibration observed around ~250 cm⁻¹.

For the remainder of this discussion, we focus on the terrylene interaction with the O_N defect, as binding to this defect was found to be particularly strong. Figure 7.2d shows the spin density at the O_N defect site. Interestingly, the excess electron is localized almost entirely on the lone-pair of the boron atom adjacent to the

introduced oxygen atom, resulting in an out-of-plane distortion of the boron atom. Figure 7.2g shows that the introduced defect state is localized within the hBN bandgap, at a similar energy as the terrylene LUMO orbital. Upon chemisorption of terrylene, the excess electron is transferred to the terrylene as is made apparent by the spin density in Figure 7.2e and the PDOS plot in Figure 7.2h. Once the excess electron has transferred to terrylene, the hBN relaxes again to its planar structure. A similar electron donor state is introduced by the V_N vacancy, which is shown in the Appendix, Figure 7A.2. We note that the terrylene HOMO-LUMO gap decreases upon charge transfer. This aligns with the redshift of the 0-0 ZPL that was observed for specific terrylene molecules in the single molecule fluorescence experiments. In contrast to the O_N and V_N cases, the V_B vacancy introduces an acceptor state close to the valence band. In this case, it is the terrylene molecule that donates charge to the hBN surface, rather than the opposite (see Appendix, Figure 7A.3). Despite considerable charge transfer at all these chemisorption sites, no single isolated covalent bond is formed between the adsorbate and adsorber. Only a *ca.* 0.2 Å shortening of the terrylene-hBN distance is observed in the case of chemisorption on the O_N and V_N defects (see Appendix, Table 7A.3).

In addition to the geometry optimizations, PBE-DFT-based molecular dynamics simulations were carried out to gain insights into the diffusive behaviour of terrylene on pristine hBN. The optimized structure was used as input for a 5 ps equilibration run at 300 K. Subsequently, the system was propagated for another 5 ps in a production run. Figure 7A.4 shows three structures sampled from the MD production run trajectory at 0, 2 and 4 ps. Despite the relatively high binding energy, the MD simulations show that at 300 K, terrylene can rotate and even translate on the pristine hBN monolayer on the picosecond timescale. This corroborates our interpretation that the observed localized emission at room temperature^[37] originates from terrylene chemisorbed at specific defect sites.

Chapter 7: Charge Transfer-Induced Weakening of Vibronic Coupling for Single Terrylene Molecules Adsorbed onto hBN

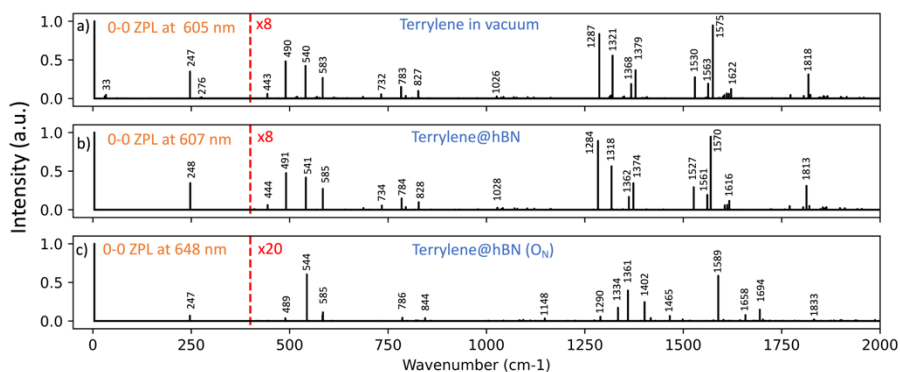


Figure 7.3. Computed vibrationally resolved fluorescence spectra of terrylene in vacuum (a), on hBN (b) and adsorbed onto the O_N defect (c). All spectra are shifted such that their respective 0-0 Zero Phonon Line (ZPL) is centred at 0. The spectra are corrected with a linear scaling function with parameters 0.977 and 4.132, as suggested by Palafox.^[38] All intensities are scaled such that the intensity of the 0-0 ZPL equals 1. The intensities of the peaks observed above 400 cm⁻¹ are multiplied by a factor 8 for a) and b) and a factor of 20 for c).

7.3.3 Calculation of the Vibrationally Resolved Fluorescence Spectra

Figure 7.3 shows the calculated vibrationally resolved fluorescence spectra for terrylene in vacuum, terrylene on hBN and terrylene adsorbed onto the O_N defect site. Both the spectra of terrylene in vacuum and terrylene on pristine hBN match very closely the experimental spectrum reported for molecule A in Figure 7.1a. The most prominent feature in all simulated spectra is the peak observed at around 250 cm⁻¹, which originates from a stretching vibration along the terrylene longitudinal axis (Figure 7A.6, mode 11).^[39,40] Other strong peaks in the spectrum are found around ~1285 and ~1570 cm⁻¹ and also involve nuclear distortions in the same direction and with the same A_g symmetry (Figure 7A.6, mode 86 and mode 108). The peaks around 540 cm⁻¹ are associated with a contraction along the terrylene short-axis and preserve the same A_g symmetry. Table 7A.4 in the

Appendix provides a complete assignment of the fluorescence signals with an intensity above 1% of the 0-0 ZPL intensity. Our interpretation aligns with that of Deperasińska and Kozankiewicz, and of Greiner and Sundholm.^[39,40]

None of the vibrational peak intensities change significantly between the terrylene spectrum in vacuum and the terrylene spectrum on pristine hBN. We thus conclude that the observed ultra-weak vibronic coupling cannot be attributed solely to the adsorption process of terrylene on the defect-free lattice. However, both the fluorescence wavelength and intensity of features in the spectrum change drastically when terrylene is chemisorbed on the O_N defect site (or on the V_N and V_B sites, see Appendix, Figure 7A.5). The effective charge transfer and consequential structural rearrangement in the ground and excited state led to a much weaker vibronic coupling, characterized by an overall diminished intensity of all vibrational features and an increased intensity of the 0-0 ZPL. The intensity ratio of the stretching mode around 250 cm⁻¹ to the ZPL decreases by a factor ≈ 5 when comparing the terrylene on defect-free hBN with the terrylene on the O_N defect (see tables 7A.5 and 7A.6 in Appendix). Interestingly, peaks that originate from vibrational overtones and combinations of vibrational modes are weaker than peaks that originate from a single mode in its lowest vibrational state, as demonstrated by the ~ 490 cm⁻¹ and ~ 1817 cm⁻¹ peaks which almost vanish in spectrum c, Figure 7.3. This diminishing of overtone peaks is also observed in the experimental spectra in Figure 7.1c and Figure 7.1d. The observation that all peaks are simultaneously diminished is explained by the fact that all visible vibrational modes have the same symmetry and involve nuclear displacements along the terrylene short and long axes (see Appendix, Figure 7A.6). The wavelength of the 0-0 ZPL shifts to the red by ~ 43 nm by introducing the O_N and V_N defects (see Figure 7.3 and Figure 7A.5), closely matching the experimentally observed redshift. Terrylene adsorption on the hole-donating V_B vacancy also leads to a diminished vibronic coupling, but to a much larger, *ca.* 100 nm, redshift of the 0-0 ZPL (see Figure 7A.5). Even though this redshift is larger than the experimentally observed redshift, we do not rule out the possibility of electron-

Chapter 7: Charge Transfer-Induced Weakening of Vibronic Coupling for Single Terrylene Molecules Adsorbed onto hBN

withdrawing defects affecting the fluorescence spectrum, as the too large shift could be an artifact of exaggerated charge transfer description within the ONIOM approach. In summary, the significant overall reduction of vibronic coupling, the nearly vanishing vibrational overtones, and the redshifted 0-0 ZPL observed for terrylene on charge-donating defects, strongly suggest that such a defect may be responsible for the experimentally observed large molecule-to-molecule variations.^[41] In the work of Vasilev *et al.*,^[42] large shifts of a 0-0 ZPL were also observed upon localized charging of a phthalocyanine molecule through deprotonation. These shifts were interpreted as an 'internal Stark effect'. In our case, the interaction of terrylene with a particular hBN defect also leads to charge transfer from the defect to the aromatic molecule, and therefore to local electric fields shifting the electronic transition. These effects are naturally included in the DFT calculations that reproduce the redshift of the 0-0 ZPL. In a similar manner, the change in vibronic coupling intensity, which we observe experimentally and confirm through DFT calculations, could be interpreted as a vibrational Stark effect, *i.e.*, a change of coupling due to charge transfer-induced local fields.

7.4 Conclusion

As noted in earlier experiments,^[4] the single terrylene molecules observed through fluorescence on an hBN surface don't diffuse translationally or rotationally at low temperature and even show localized emission at room temperature.^[37] The latter observation is in contrast to the performed molecular dynamics simulations that show that molecules would diffuse rapidly on defect-free hBN. Moreover, many molecules display a comparatively strong redshift of their optical transition (from 570 nm to up to more than 620 nm), and considerable variation in the intensity of their vibronic structure in fluorescence. These observations point to a strong interaction of the molecule with the substrate, although the interaction is not strong enough to radically modify the chemical nature of terrylene. As Van der Waals interactions of terrylene with hBN are not strong enough to account for the

above observations, it is natural to assume that some degree of chemisorption between the molecule and the surface takes place. From quantum chemical calculations, we can select two potential candidate binding sites that are given by chemisorption to a O_N or V_N defect assisted by charge transfer from the defect to terrylene. Moreover, the binding to such defects affects the geometries of terrylene in the ground and excited states in such a way that the vibronic couplings of all modes are affected simultaneously, as observed in experiment. To experimentally investigate the possibility of specific defects to be responsible for chemisorption of terrylene, we propose experiments that involve the engineering of defects, such as oxygen-related defects created by hydrogen plasma irradiation^[43] or vacancies by low-energy ion irradiation^[44].

7.5 References

- [1] J. Zirkelbach, M. Mirzaei, I. Deperasińska, B. Kozankiewicz, B. Gurlek, A. Shkarin, T. Utikal, S. Götzinger, V. Sandoghdar, *J. Chem. Phys.* **2022**, *156*, 104301.
- [2] C. Gooijer, F. Ariese, J. W. Hofstra, *Shpol'skii Spectroscopy and Other Site-Selection Methods. Applications in Environmental Analysis, Bioanalytical Chemistry, and Chemical Physics*, Wiley And Sons, New York, **2000**.
- [3] S. Adhikari, R. Smit, M. Orrit, *J. Phys. Chem. C* **2024**, *128*, 3–18.
- [4] R. Smit, A. Tebyani, J. Hameury, S. J. van der Molen, M. Orrit, *Nat. Commun.* **2023**, *14*, 7960.
- [5] R. Bourrellier, S. Meuret, A. Tararan, O. Stéphan, M. Kociak, L. H. G. Tizei, A. Zobelli, *Nano Lett.* **2016**, *16*, 4317–4321.
- [6] R. Camphausen, L. Marini, S. A. Tawfik, T. T. Tran, M. J. Ford, S. Palomba, *APL Photonics* **2020**, *5*, 076103.
- [7] M. Neumann, X. Wei, L. Morales-Inostroza, S. Song, S.-G. Lee, K. Watanabe, T. Taniguchi, S. Götzinger, Y. H. Lee, *ACS Nano* **2023**, *17*, 11679–11691.
- [8] N. Ronceray, Y. You, E. Glushkov, M. Lihter, B. Rehl, T.-H. Chen, G.-H. Nam, F. Borza, K. Watanabe, T. Taniguchi, S. Roke, A. Keerthi, J. Comtet, B. Radha, A. Radenovic, *Nat. Mater.* **2023**, *22*, 1236–1242.
- [9] D. Wang, H. Kelkar, D. Martin-Cano, D. Rattenbacher, A. Shkarin, T. Utikal, S. Götzinger, V. Sandoghdar, *Nat. Phys.* **2019**, *15*, 483–489.
- [10] T. Edvinsson, N. Pschirer, J. Schöneboom, F. Eickemeyer, G. Boschloo, A. Hagfeldt, *Chem. Phys.* **2009**, *357*, 124–131.
- [11] A. Monti, C. F. A. Negre, V. S. Batista, L. G. C. Rego, H. J. M. de Groot, F. Buda, *J. Phys. Chem. Lett.* **2015**, *6*, 2393–2398.
- [12] R. C. Schofield, P. Burdekin, A. Fasoulakis, L. Devanz, D. P. Bogusz, R. A. Hoggarth, K. D. Major, A. S. Clark, *ChemPhysChem* **2022**, *23*, e202100809.
- [13] N. Mendelson, M. Doherty, M. Toth, I. Aharonovich, T. T. Tran, *Adv. Mater.* **2020**, *32*, 1908316.
- [14] D. Wong, J. Velasco, L. Ju, J. Lee, S. Kahn, H.-Z. Tsai, C. Germany, T. Taniguchi, K. Watanabe, A. Zettl, F. Wang, M. F. Crommie, *Nat. Nanotechnol.* **2015**, *10*, 949–953.
- [15] J. Ren, L. Stagi, P. Innocenzi, *J. Mater. Sci.* **2021**, *56*, 4053–4079.

Chapter 7: Charge Transfer-Induced Weakening of Vibronic Coupling for Single Terrylene Molecules Adsorbed onto hBN

- [16] G. Zhang, Y. Chang, B. Yan, *Cryst.* **2023**, *13*, 304.
- [17] J. Heyd, G. E. Scuseria, M. Ernzerhof, *J. Chem. Phys.* **2003**, *118*, 8207–8215.
- [18] J. Heyd, G. E. Scuseria, *J. Chem. Phys.* **2004**, *121*, 1187–1192.
- [19] T. D. Kühne, M. Iannuzzi, M. Del Ben, V. V. Rybkin, P. Seewald, F. Stein, T. Laino, R. Z. Khaliullin, O. Schütt, F. Schiffmann, D. Golze, J. Wilhelm, S. Chulkov, M. H. Bani-Hashemian, V. Weber, U. Borštnik, M. Taillefumier, A. S. Jakobovits, A. Lazzaro, H. Pabst, T. Müller, R. Schade, M. Guidon, S. Andermatt, N. Holmberg, G. K. Schenter, A. Hehn, A. Bussy, F. Belleflamme, G. Tabacchi, A. Glöß, M. Lass, I. Bethune, C. J. Mundy, C. Plessl, M. Watkins, J. VandeVondele, M. Krack, J. Hutter, *J. Chem. Phys.* **2020**, *152*, 194103.
- [20] J. Cerezo, F. Santoro, *J. Comput. Chem.* **2023**, *44*, 626–643.
- [21] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, Gaussian 16; Gaussian, Inc.: Wallingford, CT, 2016.
- [22] S. Dapprich, I. Komaromi, K. S. Byun, K. Morokuma, M. J. Frisch, **1999**.
- [23] L. W. Chung, W. M. C. Sameera, R. Ramozzi, A. J. Page, M. Hatanaka, G. P. Petrova, T. V. Harris, X. Li, Z. Ke, F. Liu, H.-B. Li, L. Ding, K. Morokuma, *Chem. Rev.* **2015**, *115*, 5678–5796.
- [24] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 1372–1377.
- [25] S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* **1980**, *58*, 1200–1211.
- [26] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789.
- [27] P. J. Stephen, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623–11627.
- [28] J. J. P. Stewart, *J. Comput. Chem.* **1989**, *10*, 209–220.
- [29] J. J. P. Stewart, *J. Comput. Chem.* **1989**, *10*, 221–264.
- [30] J. J. P. Stewart, *J. Comput. Chem.* **1991**, *12*, 320–341.
- [31] G. Knizia, *J. Chem. Theory Comput.* **2013**, *9*, 4834–4843.
- [32] X. Chen, S. Jia, N. Ding, J. Shi, Z. Wang, *Environ. Sci.: Nano* **2016**, *3*, 1493–1503.
- [33] N. L. McDougall, J. G. Partridge, R. J. Nicholls, S. P. Russo, D. G. McCulloch, *Phys. Rev. B* **2017**, *96*, 144106.
- [34] M. K. Prasad, O. A. Al-Ani, J. P. Goss, J. D. Mar, *Phys. Rev. Materials* **2023**, *7*, 094003.
- [35] G. Melani, J. P. Guerrero-Felipe, A. M. Valencia, J. Krumland, C. Cocchi, M. Iannuzzi, *Phys. Chem. Chem. Phys.* **2022**, *24*, 16671–16679.
- [36] C. Elias, P. Valvin, T. Pelini, A. Summerfield, C. J. Mellor, T. S. Cheng, L. Eaves, C. T. Foxon, P. H. Beton, S. V. Novikov, B. Gil, G. Cassabois, *Nat. Commun.* **2019**, *10*, 2639.
- [37] S. Han, C. Qin, Y. Song, S. Dong, Y. Lei, S. Wang, X. Su, A. Wei, X. Li, G. Zhang, R. Chen, J. Hu, L. Xiao, S. Jia, *J. Chem. Phys.* **2021**, *155*, 244301.
- [38] M. A. Palafox, *Phys. Sci. Rev.* **2018**, *3*, DOI 10.1515/psr-2017-0184.
- [39] I. Deperasińska, B. Kozankiewicz, *Chem. Phys. Lett.* **2017**, *684*, 208–211.
- [40] J. Greiner, D. Sundholm, *Phys. Chem. Chem. Phys.* **2020**, *22*, 2379–2385.
- [41] K. Vasilev, B. Doppagne, T. Neuman, A. Rosławska, H. Bulou, A. Boeglin, F. Scheurer, G. Schull, *Nat. Commun.* **2022**, *13*, 677.
- [42] K. Vasilev, B. Doppagne, T. Neuman, A. Rosławska, H. Bulou, A. Boeglin, F. Scheurer, G. Schull, *Nat. Commun.* **2022**, *13*, 677.
- [43] Y. Xiao, H. Yu, H. Wang, X. Zhu, L. Chen, W. Gao, C. Liu, H. Yin, *Appl. Surf. Sci.* **2022**, *593*, 153386.
- [44] M. Längle, B. M. Mayer, J. Madsen, D. Propst, A. Bo, C. Kofler, V. Hana, C. Mangler, T. Susi, J. Kotakoski, *arXiv*, **2024**, DOI: 10.48550/arXiv.2404.07166.

7A. Appendix

7A.1 Theory of vibronic coupling

We will briefly remind the reader of vibronic coupling and of its importance in chemical analysis and cryogenic single-molecule spectroscopy. As a simplifying hypothesis, we assume that only the minimum of the harmonic potential of each mode changes slightly upon an electronic transition from the excited to the ground electronic state, *i.e.* that the vibration frequency does not change. This approximation, called linear vibronic coupling, works well for most intramolecular vibration modes of aromatic molecules. Figure 7A.1a shows a cut of the potential hypersurfaces of the ground (S_0) and excited (S_1) state along the vibrational coordinate, x , of a single vibration mode. At liquid-helium temperature, fluorescence proceeds from the lowest vibronic state of the excited state S_1 to vibrationally excited levels of the ground state S_0 (see downward arrows in Figure 7A.1a). The corresponding lines in the fluorescence spectrum will be the purely electronic transition (hereafter called 0-0 zero-phonon line and denoted with a yellow arrow, or ZPL for short) and a series of vibronic components at longer wavelengths corresponding to the creation of dominantly 1, 2 or more quanta of vibration (arrows of respectively orange and red color).

Chapter 7: Charge Transfer-Induced Weakening of Vibronic Coupling for Single Terrylene Molecules Adsorbed onto hBN

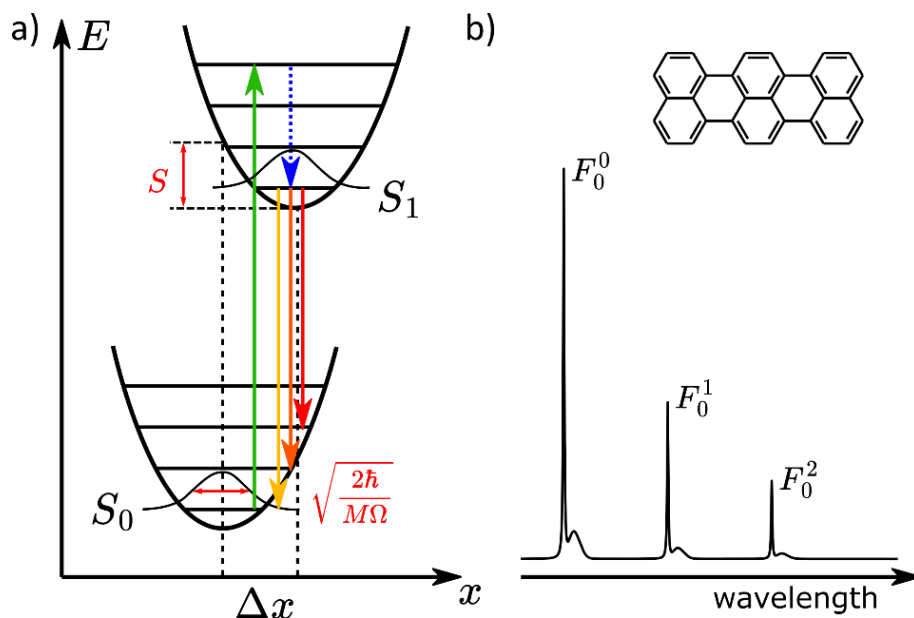


Figure 7A.1: a) Schematic harmonic potentials of the ground and excited molecular electronic states, with associated vibrational levels for a single vibration mode (mode coordinate x) under the linear coupling approximation. The figure displays some quantities used in the text of section 7A.1. The intensity of vibronic bands scales as the overlap of nuclear vibrational wavefunctions and for the 0-1 emission (orange arrow) it increases quadratically with the coordinate displacement Δx , as long as it remains small. The shift Δx can be alternatively represented by the associated energy stabilization S upon relaxation of the ground state geometry in the excited state. b) Schematic structure of terrylene together with a schematic representation of typical emission lines (downward arrows in (a)) whose relative intensities are associated with Franck-Condon factors. The vibronic bands are usually observed to be coupled to phonons by the presence of a phonon sideband, appearing on the red side of each narrow line.

The intensity of the vibronic lines is given by the overlap of nuclear wavefunctions called Franck-Condon factors. For linear coupling to one mode, the Franck-Condon factor F_0^n for the release of n quanta has a simple expression:

$$F_0^n = \frac{\xi^{2n}}{n!} e^{-\xi^2}, F_0^0 = e^{-\xi^2},$$

with

$$\xi = \frac{\Delta x}{\sigma_x},$$

where Δx is the position shift of the mode upon electronic excitation, and $\sigma_x = \sqrt{\frac{2\hbar}{M\Omega}}$ characterizes the coordinate's quantum spread in the ground state of the mode, with effective mass M and frequency Ω . The position shift of the mode is often characterized by the ratio of the reorganization energy or Stokes loss S (see Figure 7A.1) to the vibrational quantum $\hbar\Omega$:

$$\xi^2 = \frac{S}{\hbar\Omega}.$$

For several independent modes, and assuming that the mode decomposition does not change upon excitation, the Franck-Condon factors are simply the products of factors for each mode i . The strength of the 0-0 transition is then $\alpha_{\text{FC}} = \exp(-\xi^2)$,

with

$$\xi^2 = \sum_i \frac{S_i}{\hbar\Omega_i}.$$

It is usual and convenient to distinguish lattice phonons from intramolecular vibrations. For lattice phonons, the above analysis leads to a ratio of the pure electronic transition intensity I_{ZPL} compared to that I_{PW} of the phonon wing $\alpha_{\text{DW}} = I_{\text{ZPL}}/(I_{\text{ZPL}} + I_{\text{PW}})$ called the Debye-Waller factor. The strength of the combined purely electronic transition free from any phonon or intramolecular vibration, the 0-0 ZPL, is thus a combined Franck-Condon-Debye-Waller factor α_{FCDW} :

$$\alpha_{\text{FCDW}} = \alpha_{\text{FC}}\alpha_{\text{DW}}.$$

Chapter 7: Charge Transfer-Induced Weakening of Vibronic Coupling for Single Terrylene Molecules Adsorbed onto hBN

In the case of many weakly coupled modes, this factor can be calculated for a non-zero temperature T , as^[1]:

$$\alpha_{\text{FCDW}}(T) = \exp \left\{ - \sum_i \frac{S_i}{\hbar \Omega_i} \coth \frac{\hbar \Omega_i}{2k_{\text{B}}T} \right\},$$

where the sums run over all modes, intramolecular and lattice phonons. The very fast decay with temperature of this factor explains why the ZPL can only be observed at liquid-helium temperatures in molecular materials, whose vibrations frequencies are low compared to many inorganic materials.

7A.2 Methods section

7A.2.1 Experimental details

The hBN was obtained from two manufacturers: the company HQ-Graphene and the NIMS research institute^[2]. Flakes of hBN were retrieved from a single crystal and deposited on a Si/SiO₂ substrate (University Wafer) through the exfoliation method using scotch tape. After exfoliation, the substrates were annealed in a tube oven (Thermcraft) at 750 °C for 12 hours in a moderate vacuum (rough pumping) and in the presence of oxygen. Subsequently, some terrylene was deposited on the annealed flakes by sublimation in a vacuum sublimation apparatus. These samples were loaded into the cryostat (Janis SVT-200-5) for measurement. After cooldown with liquid helium, the emission spectra were recorded upon excitation with a laser at 532 nm (Sprout-G15W, Lighthouse Photonics) in a confocal setup equipped with a Horiba IHR-320 spectrometer.

7A.2.2 Computational details

All periodic density functional theory (DFT) based geometry optimizations and molecular dynamics simulations were performed within the CP2K.8.2 software package.^[3] The electron density was expanded in a hybrid Gaussian and plane wave scheme as is implemented in the Quickstep module within CP2K.8.2.^[4] The boron valence electrons were described by the DZVP-MOLOPT-SR-GTH basis

set, while the DZVP-MOLOPT-GTH basis set was used for all other atoms.^[5] The atom-centered basis set was augmented with plane waves up to a kinetic energy cutoff of 500 Ry. The Brillouin zone was integrated over the Γ -point only. The core electrons were modeled with the PBE-optimized, norm-conserving pseudopotentials developed by Goedecker, Teter and Hutter.^[6-8] During the geometry optimizations, the electronic structure was consistently converged to a value of 10^{-7} a.u. Geometry optimizations were carried out with the conjugated gradients algorithm until a precision of 10^{-5} Ha Bohr⁻¹ and 10^{-4} Bohr⁻¹ was reached in the root mean squared change of the forces and geometry step size, respectively. The electron density was integrated over a multigrid of size 5. The calculations discussed in the main paper employ the screened hybrid-density functional introduced by Heyd, Scuseria and Ernzerhof (referred to as the HSE06 functional),^[9-12] in combination with Grimme's third generation of atom pairwise dispersion corrections with Becke-Johnson damping (D3(BJ)) and a 22 Å cutoff.^[13-15] The Hartree-Fock exchange was computed in an auxiliary density matrix using the AUX_FIT cFIT3 basis for all elements.^[16]

The employed exchange-correlation functional plus dispersion correction setup has been used successfully in literature to study the electronic structure of polycyclic aromatic hydrocarbons adsorbed on hBN.^[17] To assess the effect of the functional and dispersion corrections on the terrylene adsorption distance, additional calculations were performed with the GGA-PBE functional, the hybrid-B3LYP functional and the non-local dispersion-corrected rVV10 functional. The terrylene-hBN adsorption distances, calculated with these functionals are provided in Table 7A.1. These calculations were all performed in a periodic unit cell which was optimized at the PBE level. This PBE optimization resulted in a lattice parameter of 2.51 Å, which is very close to the experimentally observed lattice parameter of 2.50 Å. It was found that the HSE06 functional produces a terrylene-hBN distance in line with other calculations, while producing a more accurate band gap for hBN. Therefore, this functional plus dispersion correction was employed for the calculations in the main paper. Subsequently, also the cell-

Chapter 7: Charge Transfer-Induced Weakening of Vibronic Coupling for Single Terrylene Molecules Adsorbed onto hBN

optimization was performed again at this level of theory, yielding the correct lattice parameter of 2.50 Å.

Molecular dynamics (MD) simulations were performed at the same level of theory as the geometry optimizations with the PBE functional. However, the plane-wave cutoff was lowered to 400 Ry to speed up the calculations. The MD simulations employed a 0.5 fs timestep and were performed within the NVT ensemble by means of the Canonical Sampling Through Velocity Rescaling (CSVR) thermostat with a time constant of 20 fs for equilibration and 150 fs for production runs.^[18]

Table 7A.1. *Interplanar terrylene-hBN distance calculated with four different functionals plus dispersion corrections.*

	PBE + D3	B3LYP + D3BJ	HSE06 + D3BJ*	rVV10
Terrylene-hBN distance (Å)	3.34	3.21	3.25	3.31

* Cell optimization was performed also at this level of theory. Other calculations used the cell optimized at the PBE+D3 level.

The vibrationally resolved fluorescence spectra were calculated with the FCclasses program,^[19] within the framework of the adiabatic Hessian approximation. The nuclear dependence of the electronic transition dipole is described in constant terms according to the Franck-Condon approximation. As input for the FCclasses program, ground and excited state optimized structures and Hessians, as well as transition dipole moments, were calculated with the Gaussian16.02 software.^[20] The terrylene-hBN interface was described using a two-layer ONIOM procedure,^[21,22] in which the terrylene was modeled at the DFT level, while the hBN electronic structure was described at the PM3 semi-empirical level.^[23] Time-dependent DFT (TDDFT) was employed for the excited state

calculations on terrylene. The high level ONIOM layer utilized the B3LYP exchange correlation functional, expanded in a 6-31G(d,p) basis set.^[24–27] Again, the D3BJ corrections were included to improve the description of dispersion forces. Notably, a very similar setup has been used in literature to interpret the vibronic spectrum of terrylene in naphthalene crystals.^[28] Both ground and excited state ONIOM-based structure optimizations were initiated from the ground state optimized structures, extracted from the previously described periodic DFT calculations. During the ONIOM calculations, the PM3 level hBN layer was constrained except for a set of newly introduced hydrogen atoms, which were added manually to saturate the terminal N and B atoms.

7A.3 Computational workflow

A two-dimensional, single layer of hBN was optimized in a hexagonal periodic unit cell containing 9 x 9 boron nitride units, amounting to a total of 81 boron and 81 nitrogen atoms. During this procedure, both the unit cell size and interatomic forces in the hBN lattice were relaxed, resulting in a hBN lattice constant of 2.50 Å and a B-N bond length of 1.44 Å. These values are within 0.004 Å agreement with X-ray data reported in literature.^[29,30] The preoptimized terrylene molecule was subsequently placed in the unit cell, in a parallel alignment with the surface and an intermolecular distance of ~3.5 Å. The subsequent structure optimization involved only relaxation of the interatomic distances, while the cell dimensions were kept constant.

After optimization of terrylene on the perfect hBN surface, defects were introduced into the hBN monolayer. All single-atom defects were introduced by removing or substituting one atom underneath the adsorbed terrylene molecule and subsequently performing a geometry optimization of the whole terrylene-hBN interface. Separately, an optimization of the hBN monolayer without the terrylene molecule was also performed to calculate the adsorption energy.

The periodic full-DFT optimized ground-state structure of the terrylene-hBN interface was taken as input for the aperiodic ONIOM calculations, where the

Chapter 7: Charge Transfer-Induced Weakening of Vibronic Coupling for Single Terrylene Molecules Adsorbed onto hBN

boron and nitrogen atoms at the box edges were terminated with hydrogen atoms. As the previous full-DFT calculations revealed considerable charge transfer from the V_N and O_N to terrylene, the ONIOM calculations with these defects were initiated with the excess electron transferred from the low-level (PM3) hBN layer to the high-level (TD-DFT) terrylene layer. Similarly, calculations with the V_B vacancy were initiated with one electron transferred from the high level layer to the low level layer. We note here that the defect-induced charge transfer results in the ground and excited states of interest being doublet states. In the presence of defects, additional electronic excitations with very low oscillator strength ($f < 0.05$) appear between the relevant ground and excited states. Throughout this study, we consistently identified the excited state of interest by verifying that the excitation predominantly involved the HOMO to LUMO transition in terrylene, and that the oscillator strength remains large ($f \approx 0.8$). On the perfect monolayer, both the S_0 and S_1 states of terrylene molecules were found to adsorb to the hBN with a bond distance of 3.03 Å (see table 7A.3). This is slightly shorter than in the full-DFT calculation (3.25 Å, see table 7A.3), however, we do not expect that this will affect significantly the fluorescence spectrum. It is known that the wavenumbers for peaks further away from the 0-0 ZPL are increasingly overestimated.^[31] Therefore, all the spectra have been corrected with a linear scaling function of the form $y = ax + b$, where the a and b parameters were fitted such that the spectrum of terrylene in vacuum reproduced accurately the peaks at 247 and 1817 cm^{-1} observed in the spectrum presented in Figure 7.1a. Fitting the spectrum for terrylene on pristine hBN yielded parameters of $a = 0.97655035$ and $b = 4.1319276$, which have subsequently also been used to scale all the other spectra.

Interestingly, transitions at 33 and 276 cm^{-1} are observed for terrylene in vacuum and are quenched for terrylene on hBN. These transitions are associated with a slow, out of plane torsional mode that is inhibited in the adsorbed system (Figure 7A.6, mode 2). Some of the experimental single-molecule fluorescence spectra

show lines in the same region (see for instance, Figure 7.1, molecule A, line at 281 cm^{-1}).

7A.4 Additional results of the quantum chemical calculations

To assess the charge transfer from hBN to terrylene in the presence of different defects, we calculated the partial charge on terrylene by summing the partial charges of all atoms belonging to terrylene. We have performed this analysis with Mulliken charges, Hirshfeld charges and charges obtained from the Intrinsic Atomic Orbital Analysis (IOA).^[32] The obtained values are provided in Table 7A.2. All three analysis methods produce overall the same trend in charge transfer from hBN to terrylene. Only an almost rigid shift in the absolute values is observed from one method to another.

Table 7A.2: Partial charges on terrylene calculated with different charge analysis methods.

Defect site	Mulliken charge on Terryene (e^- units)	IOA charges on Terryene (e^- units)	Hirshfeld charge on Terryene (e^- units)
Pristine hBN	0.02	0.16	0.30
O _N defect	−0.70	−0.59	−0.36
O _B defect	0.01	0.14	0.32
V _N vacancy	−0.68	−0.57	−0.36
V _B vacancy	0.83	1.06	1.11
V _{BN} vacancy	0.02	0.16	0.29

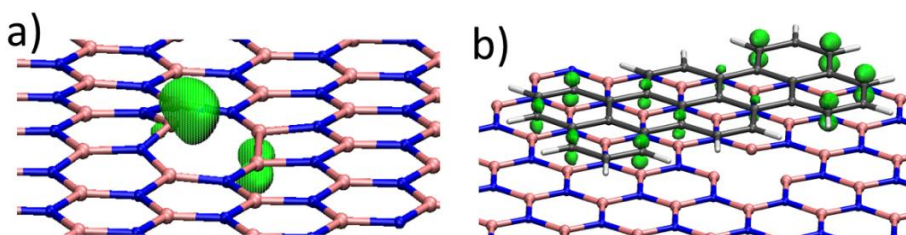


Figure 7A.2. Spin density of hBN with V_N vacancy (a) and spin density of terrylene chemisorbed at the V_N vacancy (b). Isosurfaces are plotted at 0.01 a.u.

Chapter 7: Charge Transfer-Induced Weakening of Vibronic Coupling for Single Terrylene Molecules Adsorbed onto hBN

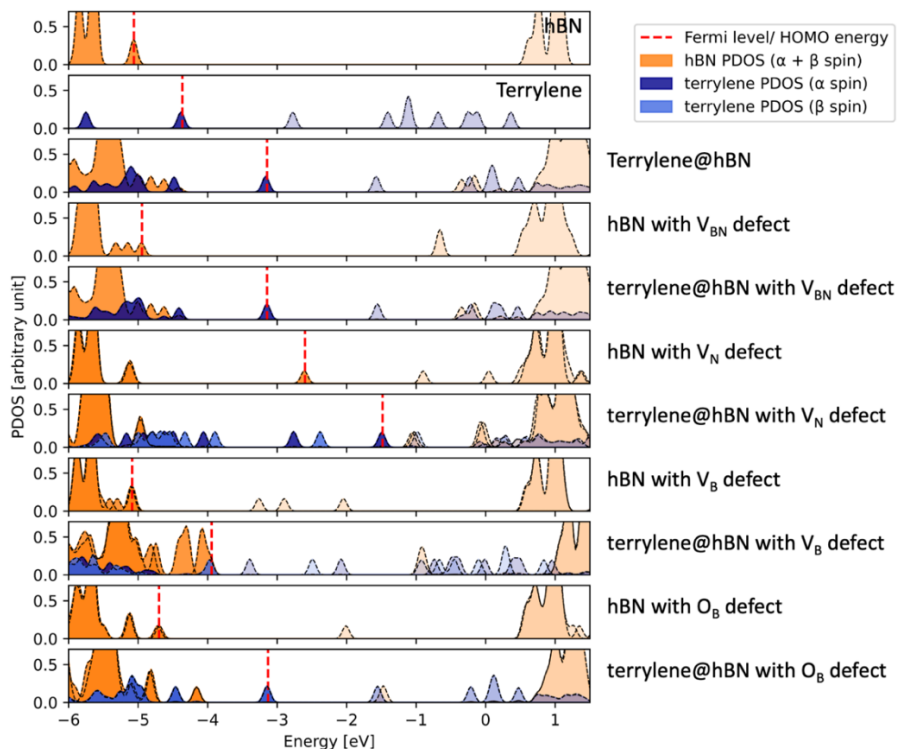


Figure 7A.3. Projected density of states (PDOS) of pristine hBN and hBN with the V_N , V_B , V_{BN} , O_B defects, with and without chemisorbed terrylene. The plotted density of states were computed in CP2K at the HSE06+D3(BJ)-level and include a Gaussian broadening of 0.05 eV. Bands with transparent colors correspond to unoccupied levels.

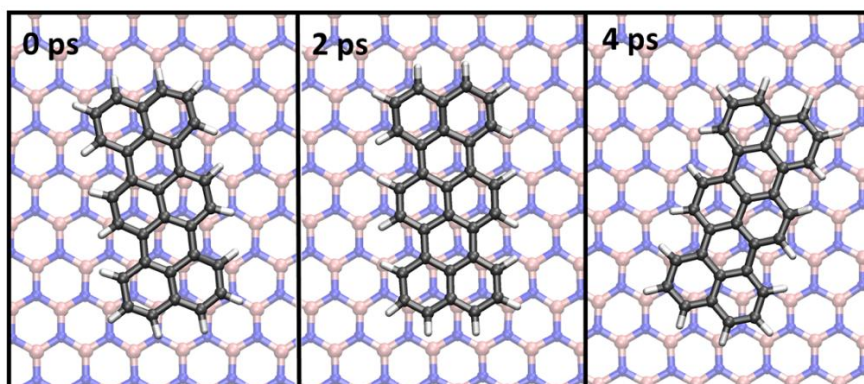


Figure 7A.4. Snapshots from a DFT-based (PBE+D3(BJ)) molecular dynamics trajectory of terrylene on pristine hBN. The simulation was performed at 300 K. Snapshots are taken at 0, 2 and 4 ps after the start of the production run and show that the terrylene molecule is free to diffuse over the surface.

Table 7A.3. Terrylene-hBN distances ($\text{\AA}$), calculated with full-DFT (HSE06+D3BJ) and with the ONIOM(B3LYP+D3BJ/PM3) approach in the ground and excited states.

	HSE06+D3BJ ground state	ONIOM (B3LYP+D3BJ/PM3) ground state	ONIOM (B3LYP+D3BJ/PM3) excited state
hBN	3.25	3.03	3.03
V _N	3.03	3.00	3.00
V _B	3.20	3.04	3.04
O _N	3.03	3.01	3.01

Chapter 7: Charge Transfer-Induced Weakening of Vibronic Coupling for Single Terrylene Molecules Adsorbed onto hBN

Table 7A.4. Interpretation of the simulated vibrationally resolved fluorescence spectrum for D_{2h} terrylene in vacuum.

$h\nu$ (cm ⁻¹)	$h\nu$ (cm ⁻¹) ^[a]	Intensity (a.u.)	Assignment	Symmetry
0.0	0.0	1.000	0-0 ZPL	
26.6	30.1	0.026	1 ²	Ag (Au ²)
30.1	33.5	0.047	2 ²	Ag (B1g ²)
248.7	247.0	0.348	11 ¹	Ag
497.4	489.8	0.060	11 ²	Ag
549.2	540.4	0.053	28 ¹	Ag
593.8	583.0	0.033	33 ¹	Ag
797.9	783.3	0.018	28 ¹ , 11 ¹	Ag
842.5	826.9	0.012	33 ¹ , 28 ¹	Ag
1313.4	1286.7	0.104	86 ¹	Ag
1348.0	1320.5	0.069	91 ¹	Ag
1396.4	1367.8	0.023	94 ¹	Ag
1407.6	1378.7	0.046	96 ¹	Ag
1562.1	1529.6	0.034	86 ¹ , 11 ¹	Ag
1596.7	1563.3	0.024	91 ¹ , 11 ¹	Ag
1608.2	1575.2	0.118	108 ¹	Ag
1656.3	1621.6	0.015	96 ¹ , 11 ¹	Ag
1856.4	1818.0	0.039	108 ¹ , 11 ¹	Ag
2922.2	2857.8	0.011	108 ¹ , 86 ¹	Ag

[a] scaled with parameters (*a*, *b*): [0.97655035 4.1319276]

Table 7A.5. Interpretation of the simulated vibrationally resolved fluorescence spectrum for D_{2h} terrylene on hBN.

$h\nu$ (cm ⁻¹)	$h\nu$ (cm ⁻¹) ^[a]	Intensity (a.u.)	Assignment	Symmetry
0.0	0.0	1.000	0-0 ZPL	
249.3	247.6	0.346	17 ¹	Ag
498.6	491.0	0.059	17 ²	Ag
549.9	541.2	0.052	34 ¹	Ag
594.3	584.5	0.034	39 ¹	Ag
799.2	784.6	0.018	34 ¹ , 17 ¹	Ag
843.6	827.9	0.012	39 ¹ , 17 ¹	Ag
1310.0	1284.4	0.111	92 ¹	Ag
1345.2	1317.8	0.077	97 ¹	Ag
1390.4	1361.9	0.021	100 ¹	Ag
1402.2	1373.5	0.043	101 ¹	Ag
1559.0	1526.9	0.036	92 ¹ , 17 ¹	Ag
1594.5	1561.2	0.024	97 ¹ , 17 ¹	Ag
1603.2	1569.8	0.118	114 ¹	Ag
1651.5	1616.9	0.014	101 ¹ , 17 ¹	Ag
1852.5	1813.2	0.037	114 ¹ , 17 ¹	Ag
2913.3	2849.1	0.012	114 ¹ , 92 ¹	Ag

[a] scaled with parameters (a , b): [0.97655035 4.1319276]**Table 7A.6.** Interpretation of the simulated vibrationally resolved fluorescence spectrum for D_{2h} terrylene on hBN + O_N defect.

$h\nu$ (cm ⁻¹)	$h\nu$ (cm ⁻¹) ^[a]	Intensity (a.u.)	Assignment	Symmetry
0.0	0.0	1.000	0-0 ZPL	
248.3	246.6	0.068	17 ¹	Ag
552.7	543.9	0.030	34 ¹	Ag
594.4	584.6	0.006	39 ¹	Ag
1362.1	1334.3	0.009	97 ¹	Ag
1387.9	1359.5	0.020	100 ¹	Ag
1431.3	1401.9	0.012	103 ¹	Ag
1622.9	1589.0	0.029	113 ¹	Ag
1731.0	1694.5	0.007	119 ¹	Ag
3504.03	3426.0	0.010	121 ²	Ag (B1g ²)

[a] scaled with parameters (a , b): [0.97655035 4.1319276]

Chapter 7: Charge Transfer-Induced Weakening of Vibronic Coupling for Single Terrylene Molecules Adsorbed onto hBN

Table 7A.7. Interpretation of the simulated vibrationally resolved fluorescence spectrum for D_{2h} terrylene on hBN + V_N vacancy.

$h\nu$ (cm ⁻¹)	$h\nu$ (cm ⁻¹) ^[a]	Intensity (a.u.)	Assignment	Symmetry
0.0	0.0	1.000	0-0 ZPL	
248.4	246.7	0.069	17 ¹	Ag
552.7	543.9	0.030	34 ¹	Ag
594.3	584.5	0.008	39 ¹	Ag
1362.1	1334.3	0.008	97 ¹	Ag
1388.9	1360.5	0.019	100 ¹	Ag
1431.4	1402.0	0.013	103 ¹	Ag
1624.1	1590.2	0.030	113 ¹	Ag
1731.2	1694.8	0.008	119 ¹	Ag
2310.1	2260.0	0.005	121 ¹ , 35 ¹	Ag (B1g*B1g)
2933.6	2869.0	0.005	121 ¹ , 84 ¹	Ag (B1g*B1g)
3504.4		0.012	121 ²	Ag (B1g ²)

[a] scaled with parameters (a , b): [0.97655035 4.1319276]

Table 7A.8. Interpretation of the simulated vibrationally resolved fluorescence spectrum for D_{2h} terrylene on hBN + V_B vacancy.

hν (cm ⁻¹)	hν (cm ⁻¹) ^[a]	Intensity (a.u.)	Assignment	Symmetry
0.0	0.0	1.000	0-0 ZPL	
250.4	248.6	0.050	17 ¹	Ag
557.2	548.3	0.018	34 ¹	Ag
601.1	591.2	0.014	39 ¹	Ag
1380.1	1351.8	0.006	96 ¹	Ag
1414.3	1385.3	0.024	100 ¹	Ag
1455.2	1425.2	0.011	103 ¹	Ag
1643.0	1608.6	0.026	113 ¹	Ag
1661.6	1626.8	0.019	55 ²	Ag (B3u ²)
1734.8	1698.2	0.007	119 ¹	Ag
2258.2	2209.4	0.008	101 ¹ , 55 ¹	Ag (B3u*B3u)
2274.4	2225.2	0.032	102 ¹ , 55 ¹	Ag (B3u*B3u)
2553.7	2497.9	0.017	117 ¹ , 55 ¹	Ag (B3u*B3u)
2871.0	2807.8	0.016	102 ¹ , 101 ¹	Ag (B3u*B3u)
2887.2	2823.6	0.007	102 ¹	Ag (B3u ²)
3150.3	3080.5	0.006	117 ¹ , 101 ¹	Ag (B3u*B3u)
3166.4	3096.3	0.017	117 ¹ , 102 ¹	Ag (B3u*B3u)

[a] scaled with parameters (*a*, *b*): [0.97655035 4.1319276]

Chapter 7: Charge Transfer-Induced Weakening of Vibronic Coupling for Single Terrylene Molecules Adsorbed onto hBN

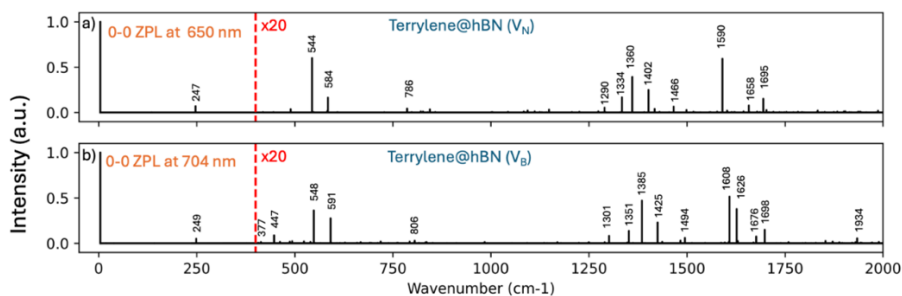


Figure 7A.5. Computed vibrationally resolved fluorescence spectra of terrylene on the V_N defect (a), and on the V_B defect (b). Both spectra are shifted such that their respective 0-0 ZPL is centered at 0. The spectra are corrected with a linear scaling function with parameters 0.977 and 4.132, as suggested by Palafox.^[31] All intensities are scaled such that the intensity of the 0-0 ZPL is 1. The intensities of the peaks observed above 400 cm⁻¹ are multiplied by a factor 20.

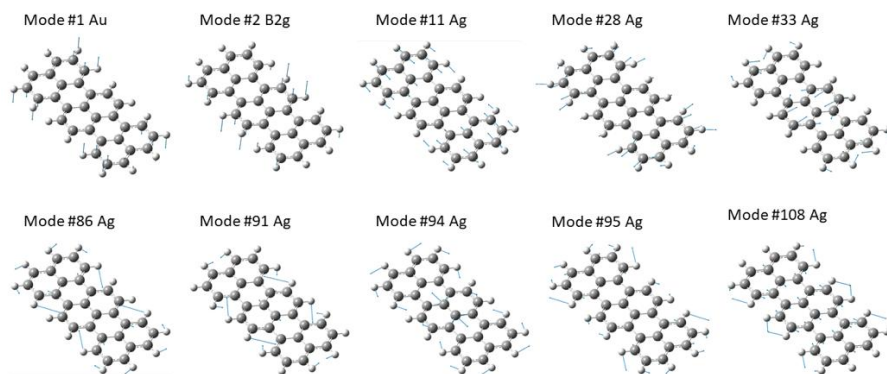


Figure 7A.6. Visualization of the most prominent vibrational modes observed in the $S_1 \rightarrow S_0$ vibrationally resolved fluorescence spectrum for terrylene in vacuum.

7A.5 References

- [1] K. K. Rebane, *Impurity Spectra of Solids*, Plenum New York, **1970**.
- [2] K. Watanabe, T. Taniguchi, H. Kanda, *Nat. Mater.* **2004**, *3*, 404–409.
- [3] T. D. Kühne, M. Iannuzzi, M. Del Ben, V. V. Rybkin, P. Seewald, F. Stein, T. Laino, R. Z. Khaliullin, O. Schütt, F. Schiffmann, D. Golze, J. Wilhelm, S. Chulkov, M. H. Bani-Hashemian, V. Weber, U. Borštnik, M. Taillefumier, A. S. Jakobovits, A. Lazzaro, H. Pabst, T. Müller, R. Schade, M. Guidon, S. Andermatt, N. Holmberg, G. K. Schenter, A. Hehn, A. Bussy, F. Belleflamme, G. Tabacchi, A. Glöß, M. Lass, I. Bethune, C. J. Mundy, C. Plessl, M. Watkins, J. VandeVondele, M. Krack, J. Hutter, *J. Chem. Phys.* **2020**, *152*, 194103.
- [4] J. VandeVondele, M. Krack, F. Mohamed, M. Parrinello, T. Chassaing, J. Hutter, *Comput. Phys. Commun.* **2005**, *167*, 103–128.
- [5] J. VandeVondele, J. Hutter, *J. Chem. Phys.* **2007**, *127*, 114105.
- [6] S. Goedecker, M. Teter, J. Hutter, *Phys. Rev. B* **1996**, *54*, 1703–1710.
- [7] C. Hartwigsen, S. Goedecker, J. Hutter, *Phys. Rev. B* **1998**, *58*, 3641–3662.
- [8] M. Krack, *Theor. Chem. Acc.* **2005**, *114*, 145–152.
- [9] J. Heyd, G. E. Scuseria, M. Ernzerhof, *J. Chem. Phys.* **2003**, *118*, 8207–8215.
- [10] J. Heyd, G. E. Scuseria, *J. Chem. Phys.* **2004**, *121*, 1187–1192.
- [11] J. Heyd, J. E. Peralta, G. E. Scuseria, R. L. Martin, *J. Chem. Phys.* **2005**, *123*, 174101.
- [12] J. Heyd, G. E. Scuseria, M. Ernzerhof, *J. Chem. Phys.* **2006**, *124*, 219906.
- [13] S. Grimme, *J. Comput. Chem.* **2004**, *25*, 1463–1473.
- [14] S. Grimme, *Wiley Interdiscipl. Rev.: Comput. Mol. Sci.* **2011**, *1*, 211–228.
- [15] S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456–1465.
- [16] M. Guidon, J. Hutter, J. VandeVondele, *J. Chem. Theory Comput.* **2010**, *6*, 2348–2364.
- [17] G. Melani, J. P. Guerrero-Felipe, A. M. Valencia, J. Krumland, C. Cocchi, M. Iannuzzi, *Phys. Chem. Chem. Phys.* **2022**, *24*, 16671–16679.
- [18] G. Bussi, D. Donadio, M. Parrinello, *J. Chem. Phys.* **2007**, *126*, 014101.
- [19] J. Cerezo, F. Santoro, *J. Comput. Chem.* **2023**, *44*, 626–643.
- [20] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, Gaussian 16; Gaussian, Inc.: Wallingford, CT, **2016**.
- [21] S. Dapprich, I. Komaromi, K. S. Byun, K. Morokuma, M. J. Frisch, *J. Mol. Struct. THEOCHEM*, **1999**, 461–462, 1–21.
- [22] L. W. Chung, W. M. C. Sameera, R. Ramozzi, A. J. Page, M. Hatanaka, G. P. Petrova, T. V. Harris, X. Li, Z. Ke, F. Liu, H.-B. Li, L. Ding, K. Morokuma, *Chem. Rev.* **2015**, *115*, 5678–5796.
- [23] J. J. P. Stewart, *J. Mol. Model.* **2007**, *13*, 1173–1213.
- [24] A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098.
- [25] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 1372–1377.
- [26] S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* **1980**, *58*, 1200–1211.
- [27] P. J. Stephen, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623–11627.
- [28] I. Deperasińska, B. Kozankiewicz, *Chem. Phys. Lett.* **2017**, *684*, 208–211.
- [29] R. W. Lynch, H. G. Drickamer, *J. Chem. Phys.* **1966**, *44*, 181–184.
- [30] E. K. Sichel, R. E. Miller, M. S. Abrahams, C. J. Buicocchi, *Phys. Rev. B* **1976**, *13*, 4607–4611.
- [31] M. A. Palafox, *Phys. Sci. Rev.* **2018**, *3*, 20170184.
- [32] G. Knizia, *J. Chem. Theory Comput.* **2013**, *9*, 4834–4843

Chapter 8: Conclusions and Outlook

Conclusions of this work are summarized and **future perspectives** are discussed.

Chapter 8: Conclusions and Outlook

8.1 Conclusions

At the photoanode of a dye-sensitized photoelectrochemical cell (DS-PEC), significant electron-hole recombination losses can occur due to the kinetic bottleneck associated with the slow oxygen evolution reaction. The development of efficient water oxidation catalysts (WOCs) continues to be an area of active research, where mechanistic insights into catalytic cycles are highly valuable.

Chapter 3 and 4 of this thesis focus on photocatalytic water oxidation in two model catalyst-dye systems applicable to DS-PECs.

In **Chapter 3**, the proton coupled electron transfer (PCET) steps that comprise the catalytic cycle were found to be characterized by an electronic reactant and product state that cross in the transition state region along the proton transfer reaction coordinate. Based on this finding, we propose a strategy to accelerate these catalytic steps by optically populating specific excited states that would drive the system towards the conical intersection.

In **Chapter 4**, we investigate a specific supramolecular complex comprising the Ru-bda²⁻ catalyst covalently bound to an NDI dye. Through means of hybrid DFT-based molecular dynamics (MD) simulations, we examined the equilibrium dynamics of the low-valent Ru^{III}-OH₂ intermediate. These simulations revealed that the complex maintains a pseudo-seven-coordinated environment, where the aqua ligand remains close to the ruthenium center. Enhanced sampling simulations of the high-valent Ru^V=O intermediate showed that oxygen-oxygen bond formation via the water nucleophilic attack (WNA) mechanism is associated with a free energy barrier of ~20.2 kcal mol⁻¹, indicating that this pathway is considerably slower than the interaction of two metal centers (I2M) pathway. Finally, the effects of including a fraction of Hartree-Fock exchange were investigated for several reaction steps in the catalytic mechanism. In agreement with the literature, the hybrid functional largely corrected the excessive delocalization of the hole observed when using a GGA functional. This improved description of the hole affected the relative energies of intermediates along the

catalytic cycle, slightly increased the barrier for the rate-determining O-O formation step and facilitated the release of the O₂ molecule at the end of the cycle.

Chapter 5 of the dissertation examines the photocatalytic proton reduction activity of a series of cobalt porphyrin complexes in various aqueous solutions with different acidity. Counterintuitively, we find that modification of the catalyst with electron withdrawing substituents leads to an increased photocatalytic activity in pH neutral conditions compared to acidic conditions. A combination of kinetic experiments, electrochemical experiments and extensive DFT modeling shows that this increased activity originates from a substituent-induced change from a metal-catalyzed to a ligand-catalyzed mechanism. These results provide an important guideline for the design of hydrogen evolution catalysts that are highly active at neutral conditions.

In addition to photoinduced water oxidation and proton reduction catalysis, charge transfer processes at the dye-semiconductor interface pose a challenging aspect of DS-PEC design. **Chapter 6** of this thesis presents combined quantum/classical dynamics and transient absorption spectroscopy (TA) study of the photoinduced charge transfer dynamics in a push-pull dye-NiO photocathode interface. Two surface species are identified in the TA measurements. The first species exhibits a photoinduced hole injection lifetime of ~0.5 ps and is assigned to dye molecules standing perpendicular to the surface. The second species injects on a much faster timescale compared to first species, and is assigned to dye molecules that are more strongly coupled to the surface, possibly through π -stacking interactions. Quantum/classical dynamics simulations on a model system with the dye standing perpendicular to the NiO surface yield a lifetime in close agreement with TA and show that dynamics of the hole wave packet are strongly correlated with thermal nuclear motion of the dye. This chapter provides critical insights into the photoinduced charge separation dynamics at the dye-NiO interface, which are important for the design of efficient DS-PEC's.

In a recent article, Smit and coworkers reported the localized emission of single terrylene molecules on hexagonal boron nitride (hBN).^[1] A fraction of molecules

Chapter 8: Conclusions and Outlook

displayed considerable redshifts in their 0-0 zero phonon line, along with exceptionally weak vibronic intensities across all vibrational modes. This latter observation is particularly interesting, as it demonstrates that hBN serves as a compelling host matrix for single-molecule emitters with very sharp spectral lines and potential applications in quantum technologies.^[2] In **Chapter 7** of this thesis, the observed ultra-weak vibronic coupling is further examined through extensive quantum chemical modeling. We show that terrylene adsorbs strongly to specific charge donating defect sites in hBN. This charge donation from the defect to terrylene narrows the dye's HOMO-LUMO gap and considerably reduces the change in its geometry upon electronic excitation. Calculations of terrylene adsorbed on these defect sites show that the vibronic couplings of all modes in the fluorescence spectrum are affected simultaneously, in line with the experimental observations. This chapter provides detailed insights into the physical mechanisms that govern vibronic coupling in dye adsorbate interfaces.

8.2 Outlook

8.2.1 Non-adiabatic surface hopping simulations of photo-activated proton transfer in a supramolecular water oxidation catalyst-dye complex

Chapters 3 and 4 provide detailed insights into the reaction dynamics of supramolecular catalyst-dye complexes for photocatalytic water oxidation. Simulations in chapter 4 show that proton transfer steps are coupled to electron transfer during the catalytic cycle. However, these simulations were carried out within the Born-Oppenheimer (BO) framework, where the electronic system is strictly quenched to the ground state. Chapter 3 suggests that this assumption may break down along the reaction path when the reactant and product electronic states move through a degeneracy in the region of the proton transfer transition state (see Chapter 3, Figure 3.5). These observations are interesting as they suggest that the PCET reaction can be accelerated by populating the electronic product state.

To explore this idea in detail, we have carried out non-adiabatic surface hopping simulations of the supramolecular complex with several explicit water molecules. The excited state surface hopping simulations were carried out with the SHARC version 2.1 molecular dynamics program interfaced with ADF2022.101^[3-6] The WFOverlap program was employed to evolve wavefunction coefficients between consecutive timesteps.^[7-10] Excited state calculations were performed with SF-TDDFT, employing the long-range corrected CAM-B3LYP exchange correlation functional and a double- ζ (DZ) basis set.^[11] Grimme's third generation of dispersion corrections were added to account for van der Waals forces.^[12-14] We note that we employed an in-house version of the ADF-SHARC interface, compatible with the post 2020 environment of the AMS program and with simulations based on spin-flip excitations.

The equilibrated BO molecular dynamics (BOMD) trajectory of the ¹(NDI-[Ru(IV)-OH])⁺ intermediate was taken from chapter 4 of this dissertation and further propagated at the GGA-PBE level for 7.5 ps at 300 K using the CP2K software package.^[15] During this simulation, a stable hydrogen bonding network emerged around the hydroxo ligand, as was also indicated in Chapter 4 (see Figure 4A.4.2). The seven water molecules in closest proximity to the hydroxo ligand are displayed in the Figure 8.1a with a thick ball and stick representation. Initial positions and velocities for a surface-hopping molecular dynamics (SHMD) simulation were taken from the BOMD trajectory. To save computational resources, only the 7 water molecules that actively participated in the hydrogen bonding network around the hydroxo ligand were included. In this proof-of-concept simulation, the lowest three electronic states were considered during the simulations, excluding the spin-flip reference state.

Two assumptions are made regarding the electronic structure of the catalyst-dye complex. First, electron injection from the excited dye into the TiO₂ semiconductor is simulated by removing an electron from the system, effectively oxidizing the dye instantaneously. We have shown in previous work that this injection process is fast on a picosecond timescale, validating this approach.^[16,17]

Chapter 8: Conclusions and Outlook

Second, it is assumed that photoexcitation of the dye-catalyst complex to the electronic product state occurs immediately after photo-oxidation. We thus followed the time evolution of the complex as it is excited directly into the electronic product state (indicated in green in Figure 3.5, Chapter 3), but starting from the nuclear initial conditions corresponding to the complex in the unoxidized state. Figure 8.1b presents the energies associated with the two lowest electronic doublet states in the system along the SHMD simulation time, while Figure 8.1c shows the dissociating and forming O-H bond lengths (see enlarged detail in Figure 8.1a for the atomic labeling).

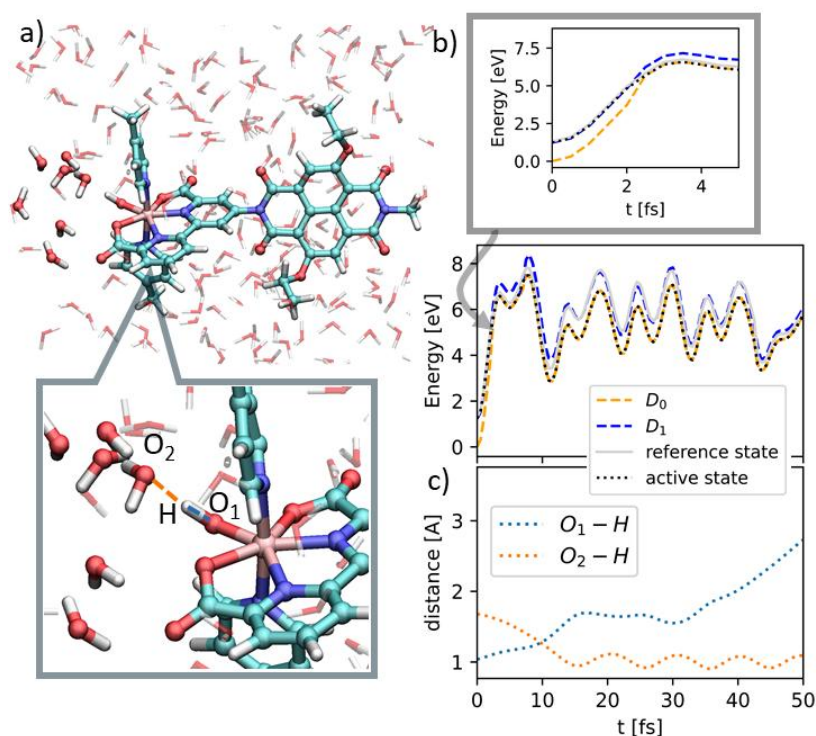


Figure 8.1. a) Snapshot of the Born-Oppenheimer MD simulation from which initial conditions for the surface hopping simulation were taken. The inset shows the relevant atomic labels and $O_1 - H$ and $O_2 - H$ bond distances. The time-evolution of the lowest two doublet state energies is provided in b). c) shows the evolution of the $O_1 - H$ and $O_2 - H$ bond distances.

Figure 8.1b) shows a swift increase in energy of ~ 5 eV in the first 0 to 10 fs of the trajectory, which is slightly larger than the typical fluctuations that are observed after the first 10 fs. We interpret this increase in potential energy to be a consequence of the initial velocity distribution that was extracted from the ground state dynamics of the unoxidized complex in explicit solvation. Overall, the trajectory decays from D_1 to the electronic ground state D_0 within the first ~ 5 fs of the trajectory (see enlarged detail in Figure 8.1b). Figure 8.1c shows that the proton transfer proceeds on a similar timescale, although it is completed only after the electron transfer. The $O_2 - H$ distance decreases immediately after initialization of the reaction and appears to stabilize around ~ 1 Å after less than 20 fs. Simultaneously, the $O_1 - H$ distance is elongated, first to ~ 2 Å, and then to larger distances, indicating that the bond has fully dissociated. Overall, the simulation shows that upon electronic excitation into the electronic product state, ultrafast proton transfer occurs for this complex. However, additional simulations should be performed to assess the influence of the initial starting conditions on this result. Furthermore, simulations should preferably include more electronic states to properly consider other decay pathways that might be missed when accounting only for the lowest two excited states. Nevertheless, this simulation presents an encouraging result that should be studied in further research.

8.3 References

- [1] R. Smit, A. Tebyani, J. Hameury, S. J. Van Der Molen, M. Orrit, *Nat. Commun.* **2023**, *14*, 7960.
- [2] C. Toninelli, I. Gerhardt, A. S. Clark, A. Reserbat-Plantey, S. Götzinger, Z. Ristanović, M. Colautti, P. Lombardi, K. D. Major, I. Deperasińska, W. H. Pernice, F. H. L. Koppens, B. Kozankiewicz, A. Gourdon, V. Sandoghdar, M. Orrit, *Nat. Mater.* **2021**, *20*, 1615–1628.
- [3] M. Richter, P. Marquetand, J. González-Vázquez, I. Sola, L. González, *J. Chem. Theory Comput.* **2011**, *7*, 1253–1258.
- [4] S. Mai, P. Marquetand, L. González, *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2018**, *8*, DOI 10.1002/wcms.1370.
- [5] M. Richter, P. Marquetand, J. González-Vázquez, I. Sola, L. González, *J. Chem. Theory Comp.* **2011**, *7*, 1253–1258.
- [6] AMS2022.101, Theoretical Chemistry, VrijeUniversiteit, Amsterdam, The Netherlands 2022, <https://www.scm.com>.

Chapter 8: Conclusions and Outlook

- [7] F. Plasser, M. Ruckebauer, S. Mai, M. Oppel, P. Marquetand, L. González, *J. Chem. Theory Comput.* **2016**, *12*, 1207–1219.
- [8] F. Plasser, L. González, *J. Chem. Phys.* **2016**, *145*, 021103.
- [9] M. Ruckebauer, S. Mai, P. Marquetand, L. González, *J. Chem. Phys.* **2016**, *144*, 074303.
- [10] M. Ruckebauer, S. Mai, P. Marquetand, L. González, *Sci. Rep.* **2016**, *6*, 35522.
- [11] T. Yanai, D. P. Tew, N. C. Handy, *Chem. Phys. Lett.* **2004**, *393*, 51–57.
- [12] S. Grimme, *J. Comput. Chem.* **2004**, *25*, 1463–1473.
- [13] S. Grimme, *Wiley Interdiscip. Rev. Comp. Mol. Sci.* **2011**, *1*, 211–228.
- [14] S. Grimme, *Chem. - Eur. J.* **2012**, *18*, 9955–9964.
- [15] T. D. Kühne, M. Iannuzzi, M. Del Ben, V. V. Rybkin, P. Seewald, F. Stein, T. Laino, R. Z. Khaliullin, O. Schütt, F. Schiffmann, D. Golze, J. Wilhelm, S. Chulkov, M. H. Bani-Hashemian, V. Weber, U. Borštnik, M. Taillefumier, A. S. Jakobovits, A. Lazzaro, H. Pabst, T. Müller, R. Schade, M. Guidon, S. Andermatt, N. Holmberg, G. K. Schenter, A. Hehn, A. Bussy, F. Belleflamme, G. Tabacchi, A. Glöb, M. Lass, I. Bethune, C. J. Mundy, C. Plessl, M. Watkins, J. VandeVondele, M. Krack, J. Hutter, *J. Chem. Phys.* **2020**, *152*, 194103.
- [16] A. Monti, J. M. De Ruiter, H. J. M. De Groot, F. Buda, *J. Phys. Chem. C* **2016**, *120*, 23074–23082.
- [17] J. P. Menzel, A. Papadopoulos, J. Belić, H. J. M. de Groot, L. Visscher, F. Buda, *J. Phys. Chem. C* **2020**, *124*, 27965–27976.

Summary

Coupled Electronic and Nuclear Dynamics at Interfaces of Artificial Photosynthesis Devices

Reducing greenhouse gas emissions is one of the most pressing challenges that humanity faces in the coming decades. As a platform for generating solar fuels, dye-sensitized photoelectrochemical cells (DS-PECs) offer a promising solution. DS-PECs effectively address the intermittency issues inherent to solar and wind energy by storing solar energy in chemical bonds to generate sustainable fuels. However, the design of efficient DS-PECs remains challenging due to sluggish catalytic turnovers and low charge separation efficiencies. Addressing these limitations requires a deeper understanding of the physical mechanisms that govern these processes. With this goal in mind, this dissertation aims to elucidate at an atomistic level the mechanisms that drive photo-induced charge separation and catalysis in various components of DS-PEC devices. A strong emphasis is placed on the coupled motion of nuclear and electronic degrees of freedom, which I demonstrate to be crucial for many of the investigated systems.

Chapter 1 and 2 provide an introduction into DS-PEC devices and into the computational methodologies relevant to this work. Subsequently, I focus on photocatalytic water oxidation in dye sensitized photoanodes. Slow catalytic turnovers often present a kinetic bottleneck for these systems, making it highly relevant to come up with innovative approaches to accelerate individual catalytic steps. **Chapter 3** explores the excited state potential energy landscape of two dye-catalyst complexes which could be employed in a DS-PEC photoanode. The most intriguing result is that the proton-coupled electron transfer steps that govern the photocatalytic water oxidation cycle are characterized by an electronic reactant and product state which cross along the proton transfer reaction coordinate. This result leads to novel strategies to accelerate these photocatalytic steps. **Chapter 4** examines the dynamic properties of a [Ru-bda]-NDI complex through simulations

Summary

that include explicitly the water environment. These simulations provide critical insights on the equilibrium dynamics of the low-valent $\text{Ru}^{\text{III}}\text{-OH}_2$ intermediate, clarifying EPR observations reported in literature. Detailed analysis of the rate limiting O-O bond forming step following the water nucleophilic attack mechanism (WNA) reveals that this process is viable, though with a slow turnover frequency and minimal driving force. This highlights the need for alternative catalysts optimized for the WNA mechanism in immobilized systems.

The discourse of the dissertation then shifts to DS-PEC photocathode design. A critical challenge in these systems is maintaining a pH gradient to facilitate proton diffusion from photoanode to photocathode. While high-turnover hydrogen evolution catalysts (HECs) exist for neutral pH conditions, they predominantly rely on precious metals. Therefore, identifying first-row transition metal catalysts that operate efficiently in pH neutral conditions is crucial for advancing DS-PEC technologies. In **Chapter 5**, a series of cobalt porphyrin complexes was investigated for their photocatalytic hydrogen evolution activity in a range of different pH conditions. The catalysts were functionalized by either electron withdrawing or electron donating groups, thereby tuning the charge density on the cobalt center. Strikingly, the electron poor catalysts outperformed the electron rich catalysts in neutral conditions. This observation is explained by extensive DFT modeling, which demonstrates that the electron withdrawing substituents promote a ligand-based mechanism, while the electron rich catalysts operate via a metal-based mechanism. These results open a promising new avenue for the design of porphyrin-based HECs that operate with high turnover frequencies in neutral conditions.

Besides catalyst performance, photoinduced charge separation at the dye-semiconductor interface impacts photon-to-product efficiency in photocathodes. While many studies have investigated energetic properties of such systems, the structural effects and the impact of thermal nuclear motion on the interfacial electron and hole-transfer dynamics has remained relatively unexplored. In **Chapter 6**, the photoinduced charge separation dynamics at the dye-NiO

photocathode interface have been studied using a combination of quantum/classical dynamics simulations and transient absorption (TA) spectroscopy. The performed simulations provide an atomistic level interpretation for species observed in TA. It was found that the absorption mode of the dye on the surface dramatically impacts the photoinduced injection rate, and that thermal nuclear motion plays an important role in driving the process, particularly on timescales longer than 100 fs. These findings enhance our understanding of charge-transfer dynamics at dye-semiconductor interfaces and provide guidance for DS-PEC design.

The final section of this dissertation focuses on another system where the nuclear-electronic coupling is critical. Recently, it was shown that hexagonal boron nitride can serve as a host matrix for single-molecule fluorescence studies of organic dye molecules. When certain molecules adsorb onto these matrices, they display distinctive spectral features, including weak vibronic intensities and redshifted 0-0 zero phonon lines (ZPL). The potential applications of these highly sensitive spectra in molecular sensing and quantum technologies renders a physical understanding of the underlying mechanism behind these observations highly desirable. In **Chapter 7**, I employ extensive quantum chemical modeling to investigate these mechanisms. It was found that the ultra-weak vibronic coupling and redshift of the 0-0 ZPL can be explained by adsorption of the molecule on specific charge donating defect sites. These insights establish design principles for material-molecule interfaces capable of emitting highly resolved single photons with minimal vibrational coupling.

Samenvatting

Gekoppelde Dynamica van Elektronen en Kernen op Interfaces van Apparaten voor Kunstmatige Fotosynthese

Het terugdringen van broeikasgasuitstoot is een van de grootste maatschappelijke uitdagingen van de komende decennia. Met kleurstof gesensibiliseerde foto-elektrochemische cellen (*dye-sensitized electrochemical cells*, DS-PEC's) bieden een veelbelovende stap op weg naar de aanpak van dit probleem. Door zonne-energie op te slaan in chemische bindingen zijn DS-PEC's in staat duurzame brandstoffen te genereren. Deze brandstoffen zouden een belangrijke rol kunnen spelen in de transportsector, waar energiedichte opslag essentieel is, of ze zouden kunnen helpen in het afstemmen van een niet synchroon lopend vraag en aanbod van duurzame energie. De ontwikkeling van efficiënte DS-PEC's blijft echter lastig vanwege trage katalytische omzettingen en vanwege de lage efficiëntie van belangrijke ladingsscheidingsprocessen. Om deze horden te nemen moet men de fysica en chemie die hieraan ten grondslag ligt goed begrijpen. Daarom richt dit proefschrift zich op het ontrafelen van de mechanismen achter de door licht geïnduceerde ladingsscheidingsprocessen en katalyse in verschillende componenten van DS-PEC's. Binnen dit kader wordt er een sterke nadruk gelegd op de onderlinge wisselwerking tussen nucleaire en elektronische subsystemen. In het bijzonder de koppeling tussen deze twee vrijheidsgraden speelt een belangrijke rol in veel van de onderzochte systemen in dit proefschrift.

Hoofdstukken 1 en 2 geven een inleiding in DS-PEC's en in de relevante computationele methoden die zijn gebruikt in het onderzoek. Vervolgens richt ik me op fotokatalytische wateroxidatie in met kleurstof gesensibiliseerde fotoanodes. Aangezien trage katalytische omzettingen vaak de beperkende factor zijn in de fotochemische reacties van dit soort systemen, is het belangrijk om deze stappen te optimaliseren.

Samenvatting

Hoofdstuk 3 onderzoekt het potentiële energieoppervlak van de aangeslagen toestand van twee kleurstof-katalysator complexen die inzetbaar zijn in een fotoanode van een DS-PEC. Het onderzoek laat zien dat de proton-gekoppelde elektronoverdracht (*proton-coupled electron transfer*, PCET) processen, die inherent zijn aan de wateroxidatie cyclus, worden gekenmerkt door een elektronische reactant- en producttoestand die elkaar kruisen langs de protonoverdracht reactiecoördinaat. Op basis hiervan stel ik nieuwe strategieën voor om de fotochemie van dit systeem te versnellen.

Hoofdstuk 4 onderzoekt de dynamische eigenschappen van een [Ru-bda]-kleurstof-complex door middel van simulaties die expliciet ook de wateromgeving meenemen. Deze simulaties bieden inzicht in het dynamisch evenwicht dat leidt tot de vorming van het Ru^{III}-OH₂-intermediair, en verklaren daarmee EPR-waarnemingen die zijn gerapporteerd in de literatuur. Een gedetailleerde analyse laat zien dat snelheidsbepalende vorming van de O-O binding kan plaatsvinden via een nucleofiele aanval van een watermolecuul op het Ru^V=O intermediair. Echter, de hoge kinetische barrière en lage thermodynamische drijvende kracht tonen aan dat deze reactiestap erg langzaam verloopt. Voor toepassing in verankerde systemen is het dus belangrijk om katalysatoren te optimaliseren voor dit water nucleofiele aanval mechanisme.

De focus van het onderzoek verschuift daarna naar fotokathodes. Een cruciale uitdaging in DS-PEC's is het in stand houden van een pH-gradiënt voor proton-diffusie van de fotoanode naar de fotokathode. Fotokathodes moeten dus actief zijn in relatief basische omstandigheden ten opzichte van fotoanodes. Hoewel er waterstofevolutiekatalysatoren (*hydrogen evolution catalyst*, HEC's) bestaan die goed werken onder neutrale pH-omstandigheden, bevatten deze meestal zeldzame aardmetalen. Om minder afhankelijk te worden van deze groep elementen is het dus belangrijk om ook katalysatoren op basis van eerste rij overgangsmetalen te identificeren die efficiënt werken onder neutrale pH-omstandigheden. In **Hoofdstuk 5** wordt een reeks kobalt-porfyrinecomplexen onderzocht op hun

fotochemische reactiviteit voor protonreductie tot waterstof onder verschillende pH-condities. De katalysatoren werden voorzien van elektronenzuigende of elektronenstuwende groepen, wat de ladingsdichtheid op het kobalt-centrum beïnvloedt. Opmerkelijk genoeg presteerden de elektronenarme katalysatoren beter dan de elektronenrijke katalysatoren onder pH-neutrale condities. Dit wordt verklaard op basis van uitgebreide DFT-berekeningen die aantonen dat de elektronenzuigende substituenten een ligand-gestuurd mechanisme bevorderen, terwijl de elektronenrijke katalysatoren via een metaal-gestuurd mechanisme opereren. Deze resultaten bieden een veelbelovend nieuw perspectief op het ontwerp van HEC's die gebaseerd zijn op porfyrones en opereren met een bijna kwantitatieve omzetting van reactanten onder pH-neutrale condities.

Naast de katalysator, speelt ook de ladingsoverdracht tussen de aangeslagen kleurstofmoleculen en het halfgeleideroppervlak een prominente rol in de efficiëntie van de fotokathode. Veel studies hebben de energetische eigenschappen van kleurstof-halfgeleider systemen onderzocht, maar zowel de invloed van de moleculaire structuur als de invloed van thermische beweging van de kernen op de dynamica van elektronen en gaten is tot nu toe grotendeels onderbelicht gebleven. **Hoofdstuk 6** onderzoekt de ladingsoverdracht van aangeslagen kleurstofmoleculen naar een NiO halfgeleideroppervlak met behulp van kwantum-klassieke moleculaire dynamica simulaties en *transient* absorptie (TA) spectroscopie. De simulaties bieden een atomaire interpretatie van de verschillende signalen die werden waargenomen in TA. De specifieke manier van absorptie van de kleurstofmoleculen op het oppervlak blijkt een grote invloed te hebben op de injectiesnelheid van de gaten. Daarnaast blijkt ook dat de beweging van de kernen een belangrijke rol speelt in het mechanisme van het ladingsscheidingsproces, vooral op tijdschalen langer dan 100 fs. Deze bevindingen verbeteren ons begrip van ladingsoverdracht tussen kleurstoffen en halfgeleiders, en kunnen gebruikt worden voor het ontwerp van efficiënte DS-PEC's.

Samenvatting

Het laatste deel van dit proefschrift richt zich op een ander systeem waarin koppeling tussen de elektronische en nucleaire subsystemen een zeer belangrijke rol speelt. Recentelijk is aangetoond dat hexagonaal boornitride (hBN) kan functioneren als gastmatrix voor fluorescentiestudies van individuele organische kleurstofmoleculen. Wanneer bepaalde moleculen op deze matrices adsorberen, vertonen ze opmerkelijke spectrale eigenschappen, waaronder zwakke vibronische intensiteiten en een naar het rood verschoven spectraallijn van de puur elektronische transitie tussen de grondtoestand en de eerste aangeslagen toestand. De veelbelovende toepassingen van deze uiterst gevoelige spectrale techniek op het gebied van moleculaire detectie en kwantumtechnologieën, maakt het bijzonder interessant om de onderliggende mechanismen achter deze observaties beter te begrijpen. In **Hoofdstuk 7** gebruik ik uitgebreide kwantumchemische modellen om deze mechanismen te onderzoeken. Het blijkt dat de uiterst zwakke vibronische koppeling en de roodverschuiving van bepaalde spectraallijnen wordt veroorzaakt door adsorptie van het kleurstofmolecuul op vervormingen in het hBN die in staat zijn lading te doneren. Dit inzicht leidt tot een nieuwe strategie voor het ontkoppelen van elektronische transities en nucleaire vibraties in materiaal-molecuul systemen. Deze systemen zijn in staat zeer nauwkeurig gedefinieerde fotonen uit te zenden met minimale koppeling aan vibraties

Acknowledgements

These past four years have been an incredibly exciting experience, from learning about physics and chemistry to solving complex problems and writing research papers. Yet beyond these individual efforts, my fondest memories are the moments of collaboration and exchange with all the exceptional students, PhD candidates, and professors that I have had the privilege of working with. I am truly grateful to all of you.

First and foremost, I want to express my deepest gratitude towards Dr. Francesco Buda for granting me the opportunity to pursue this PhD research and for his unparalleled support throughout these past four years. You have encouraged me to work on challenging projects, entrusted me with several collaborations and provided me the liberty to explore my own ideas. You were patient, meticulous and genuinely kind. I feel lucky to have had you as my mentor!

I also want to thank Prof. Dr. Huub de Groot for serving as my other promotor and for openly welcoming me in the BPOC group. Your critical perspective has been valuable for my dissertation and for shaping my scientific mindset.

In addition, I would like to extend my gratitude towards all colleagues with whom I had the privilege to collaborate during my PhD. I am immensely grateful to Prof. Dr. Sylvestre Bonnet and Dr. Chengy Liu for the chance to contribute to the ACS Catalysis paper that resulted in Chapter 5 of this thesis. Your expertise in catalysis and your scientific drive are a source of inspiration. I also want to thank Drs. Annemarie Huijser, Kaijian Zhu and Yusen Luo for the opportunity to work on the dye-sensitized photocathode system, which led to two publications and Chapter 6 of this dissertation. I am especially grateful for your support on the JPPC paper, on which we spend several afternoons correcting. Finally, I wish to express my gratitude to Prof. Dr. Michel Orrit, and Dr. Robert Smit for the collaboration that resulted in the JPCL paper and Chapter 7 of this thesis. I thoroughly enjoyed our scientific discussions, marked by your deep insights in physical chemistry.

Acknowledgements

From our own computational group in Leiden, I would like to thank Dr. Dario Calvani and Bas Kreupeling for your contributions on Chapter 4 and for the great times that we had, also outside the office. On that note, I also want to thank Dr. Jan Paul Menzel, for helping me with setting up the calculations of Chapter 6 and for being a great advisor for matters related to science and beyond.

I would also like to thank all the students that I had the pleasure of mentoring throughout these years. Hannah van Overeem, Jonas Rutgers, Tjeerd de Jong, Aegir Zaaruolo, and Jos van der Sterre. It was great working with you, and I wish you all the best in your future careers!

In addition to those with whom I worked directly, I am immensely grateful for the many scientific discussions with colleagues and friends at meetings, schools and conferences. In particular, I want to thank Emiel, Stefano, Steven, Wouter and Nicolaas for conversations on topics ranging from the fundamentals of quantum mechanics to climate change. In addition, I want to thank my paranymphs Matthijs and David for helping me in these last stages of the PhD and for standing by my side during the defense!

Besides the scientific research conducted, I hugely appreciate the great times that we had in Leiden. As such, I would very much like to thank my former office mates: Roxanne, Ina, Willemijn, Rick, Alexandra; everyone from the office next-door: Art, Xingmeng, Jeroen; and the rest of the BPOC group: Rico, Anjali, Agur, Alia, Rianne, Suzanne, Tirong, Lolita, Chuang, Padmaja, Karthick, Anouska, Willem, Serkan and of course Liesbeth. Thank you for the great times!

Finally, I would like to thank all my friends, family and specifically Iris. Your support has been invaluable throughout the past four years.

Curriculum vitae



Titus de Haas was born on the 13th of November 1996 in Amsterdam, the Netherlands, where he spent most of his childhood and early adulthood. Titus went to high school between 2009 and 2015 at the Geert Groote College Amsterdam, where he obtained a VWO diploma (pre-university education) with N&T profile (Nature and Technology, emphasis on natural sciences). After graduating, he went on to pursue a chemistry bachelor's degree program hosted between the University of Amsterdam (UvA) and Vrije Universiteit (VU) Amsterdam. He obtained the BSc. degree in 2018, writing a thesis on cobalt catalyzed water oxidation, which he studied with both experimental and theoretical methods. Following the bachelor, Titus pursued a master's degree in molecular sciences, again at the UvA and the VU. For his thesis he conducted DFT-based research on organometallic chemistry under supervision of Prof. Dr. Peter H.M. Budzelaar at the Federico II university of Naples, in Italy.

After the summer of 2020, Titus started as a PhD candidate at the Leiden Institute of Chemistry in Leiden, the Netherlands, where he was supervised by Dr. Francesco Buda and Prof. Dr. Huub J.M. de Groot. His doctoral research focused on photoinduced charge-separation and catalytic processes for solar-to-fuel production. In this context, he employed density functional and semi-empirical methods to simulate the dynamics of molecules, materials and interfaces in both the ground state and excited states.

Titus showcased his work through multiple presentations at national and international conferences during his PhD studies. Highlights include talks at CHAINS (2022), the Kroese-Duijsters symposium (2023 and 2024), and the HRSMC symposium (2024), and posters at IPQC2023 conference in Bratislava, a Gordon Research Conference (2024) in Easton, Massachusetts, USA, and a

Curriculum vitae

CECAM meeting in Varigotti, Italy. He also won the poster award in the section for Physical Chemistry and Spectroscopy at the 2023 HRSMC symposium.

Beyond research, Titus has been actively involved in teaching at various levels, both during his PhD and as a Master student. He mentored three master's and two bachelor's theses, supervised two *Leren Onderzoeken* projects, and served as a teaching assistant for courses on quantum chemistry, classical mechanics, and practical labs on organic chemistry. During his PhD, Titus followed courses on *Academic Writing*, *Scientific Conduct* and on *How to Write an Excellent Research Grant*. In addition, he was an active board member of the LIC73 PhD and Postdoc group in Leiden, where he contributed to community building.

List of Publications

Main author

- 1) **T. de Haas**, T. de Jong, H.J.M. de Groot, F. Buda. Non-adiabatic surface hopping dynamics of ultra-fast proton coupled electron transfer in catalyst-dye complex for water oxidation. *Manuscript in preparation*.
- 2) **T. de Haas***, K. Zhu*, J.M. van der Sterre, Y. Luo, G. Mul, F. Buda and A. Huijser. Effects of Nuclear Motion on the Photoinduced Interfacial Charge Transfer Dynamics at a NiO/P1 Photocathode. *J. Phys. Chem. C*. **2025**, 129 (14), 6817-6826 (* contributed equally)
- 3) C. Lui*, **T. de Haas***, F. Buda, S. Bonnet. Electron-Withdrawing Effects in Cobalt Porphyrin Catalysts Boost Homogeneous Photocatalytic Hydrogen Evolution in Neutral Aqueous Solutions. *ACS Catal.* **2025**, 15 (6), 4681-4697 (* contributed equally)
- 4) **T. de Haas***, R. Smit*, A. Tebyani, S. Bhattacharyya, K. Watanabe, T. Taniguchi, F. Buda, M. Orrit. Charge Transfer-Induced Weakening of Vibronic Coupling for Single Terrylene Molecules Adsorbed onto Hexagonal Boron Nitride. *J. Phys. Chem. Lett.* **2025**, 16 (1), 349-356 (*contributed equally)
- 5) **T. de Haas**, D. Calvani, A. Zaaruolo, T. de Jong, J. Rutgers, B. Kreupeling, H.J.M. de Groot, F. Buda. Hybrid-DFT Molecular Dynamics Simulations of Photocatalytic Water Oxidation in a [Ru-bda]-Dye Complex. *J. Phys. Chem. C*. **2024**, 128 (47), 20093-20103
- 6) **T. de Haas**, H. van Overeem, H.J.M. de Groot, F. Buda. Strategies to Enhance the Rate of Proton-Coupled Electron Transfer Reactions in Dye-Water Oxidation Catalyst Complexes. *ChemPhotoChem.* **2023**, 7 (3), e202200274.

Co-author

- 1) C. Liu, A. Amati, **T. de Haas**, F. Buda, A.M. Brouwer, S. Bonnet. Electronic Effects in Water-soluble Zn(II) and Sn(IV) Porphyrin Photosensitizers for Homogeneous Photocatalytic Hydrogen Evolution at pH 7.0. *To be submitted*.
- 2) K. Zhu, A. P. Rodríguez, M. B. Brands, **T. de Haas**, F. Buda, J. N. H. Reek, G. Mul and A. Huijser. Limiting Molecular Twisting: Upgrading a Donor–Acceptor Dye to Drive H₂ Evolution. *Adv. Sci.* **2024**, *11* (40), 2403454.
- 3) A. Cataffo, **T. de Haas**, C. Ehm, P. H. M. Budzelaar. Between T and Y: Asymmetry in the Interaction of LAu(I) with Bipy and β -Diiminate-like Ligands. *Eur. J. Inorg. Chem.* **2021**, *2021* (4), 314-320.