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## Accelerating the photocatalytic water splitting in catalyst-dye complexes

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# **Accelerating the Photocatalytic Water Splitting in Catalyst–Dye Complexes**

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Accelerating the Photocatalytic Water Splitting in Catalyst–Dye Complexes

Ph.D. thesis, Leiden University

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# **Accelerating the Photocatalytic Water Splitting in Catalyst–Dye Complexes**

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in 1990

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Prof. dr. Sandra Luber (University of Zurich)

*For my parents, my wife, and my son*



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# Table of Contents

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<b>List of Abbreviations .....</b>	<b>ii</b>
<b>List of Symbols .....</b>	<b>iv</b>

## Chapter 1

<b>Introduction &amp; Computational Tools .....</b>	<b>1</b>
1.1. Introduction .....	3
1.1.1 Moving toward Sustainable Energy Sources .....	3
1.1.2 Natural Photosynthesis.....	4
1.1.3 Artificial Photosynthesis.....	5
1.1.4 Dye-sensitized Photoelectrochemical Cell .....	7
1.1.5 Catalytic Water Oxidation Mechanism .....	9
1.2. Computational Tools .....	14
1.2.1 Density Functional Theory (DFT) .....	14
1.2.2 Exchange-Correlation Functionals and Other Approximations.....	17
1.2.3 Car-Parrinello Molecular Dynamics (CPMD) .....	18
1.2.4 Free Energy Calculations.....	20
1.3. Aim and Outline of This Thesis .....	21
1.4. References .....	23

## Chapter 2

<b>Photocatalytic Water Splitting Cycle in a Catalyst–dye Supramolecular Complex .....</b>	<b>27</b>
2.1. Introduction.....	29
2.2. Computational Details.....	32
2.2.1 Geometry Optimization at DFT level .....	32
2.2.2 Constrained <i>ab initio</i> Molecular Dynamics .....	33
2.3. Results and Discussion .....	35
2.3.1 Second Catalytic Water Oxidation Step.....	36
2.3.2 Third Catalytic Water Oxidation Step: O–O Bond Formation .....	41

2.3.2.1	Attacking Water Rearrangement and Electron Transfer.....	42
2.3.2.2	Proton Diffusion .....	45
2.3.3	Fourth Catalytic Water Oxidation Step.....	49
2.4.	Conclusions.....	51
2.5	References.....	53
A.	Appendix .....	57

## Chapter 3

### **A Proton Acceptor near the Active Site Lowers Dramatically the O–O Bond Formation Energy Barrier .....**

3.1.	Introduction.....	71
3.2	Computational Details.....	74
3.3.	Results and Discussion.....	74
3.3.1	Inclusion and Equilibration of an OH <sup>-</sup> Ion in the Simulation Box.....	74
3.3.2	Photooxidation of the NDI and O–O Bond Formation.....	77
3.3.3	Spontaneous Proton Transfer Following OOH Ligand Formation .....	79
3.3.4	Activation Free Energy Barrier and Reaction Rate Evaluation.....	80
3.4.	Conclusions .....	83
3.5	References.....	84
3.A.	Appendix.....	87

## Chapter 4

### **Tuning the Proton-Coupled Electron Transfer Rate by Ligand Modification in Catalyst–Dye Supramolecular Complexes .....**

4.1.	Introduction.....	93
4.2.	Results and Discussion .....	96
4.2.1	Geometry Optimization of the WOC–dye Complexes .....	96
4.2.2	Equilibration of WOC–dye Complexes in the Explicit Solvent Model .....	98
4.2.3	Constrained MD Simulations of the O–O Bond Formation Step.....	99
4.2.4	Free Energy Profile and Reaction Rate Estimation .....	102
4.2.5	Coupling between Electronic and Nuclear Motions .....	104
4.3.	Conclusions .....	107
4.4	References .....	109
4.A.	Appendix .....	111

## **Chapter 5**

<b>Two-Channel Model for Electron Transfer in a Dye–Catalyst–Dye Supramolecular Complex .....</b>	<b>125</b>
5.1. Introduction.....	127
5.2. Results and Discussion .....	130
5.2.1 Geometry Optimization of the Dye–WOC–Dye Complex with DFT .....	130
5.2.2 Equilibration of the System and Photooxidation of two NDI Dyes. ....	131
5.2.3 Constrained AIMD Simulations and Catalytic Water Oxidation Steps. ....	132
5.2.4 Free Energy Profile and Reaction Rate Evaluation. ....	136
5.3. Conclusions .....	139
5.4. References .....	140
5.A. Appendix.....	142

## **Chapter 6**

<b>Conclusions and Outlook .....</b>	<b>153</b>
6.1. Conclusions .....	155
6.2. Outlook .....	159
6.3. References .....	161

## **Appendices**

<b>Summary .....</b>	<b>163</b>
<b>Samenvatting .....</b>	<b>165</b>
<b>List of Publications .....</b>	<b>169</b>
<b>Curriculum Vitae .....</b>	<b>171</b>
<b>Acknowledgments .....</b>	<b>173</b>

# List of Abbreviations

<b>ADF</b>	Amsterdam Density Functional
<b>AIMD</b>	<i>Ab Initio</i> Molecular Dynamics
<b>APT</b>	Concerted Atom-Proton Transfer
<b>BO</b>	Born-Oppenheimer approximation
<b>BOMD</b>	Born-Oppenheimer Molecular Dynamics
<b>bpy</b>	2,2'-bipyridine
<b>CB</b>	Conduction Band
<b>CFF</b>	Consistent Force Field
<b>CHARMM</b>	Chemistry at HARvard Macromolecular Mechanics
<b>COSMO</b>	Conductor-like Screening Model
<b>CPMD</b>	Car-Parrinello Molecular Dynamics
<b>cy</b>	<i>p</i> -cymene
<b>DCACP</b>	Dispersion-Correcting Atom-Centered Potential
<b>DFT</b>	Density Functional Theory
<b>DFT-MD</b>	DFT-based Car-Parrinello Molecular Dynamics
<b>DS-PEC</b>	Dye-Sensitized Photoelectrochemical Cell
<b>DSSC</b>	Dye-sensitized Solar Cells
<b>EPT</b>	Concerted Electron-Proton Transfer
<b>ET</b>	Electron Transfer
<b>FMD</b>	Free Molecular Dynamics
<b>FS</b>	Final State
<b>GEA</b>	Gradient Expansion Approximation
<b>GGA</b>	Generalized Gradient Approximation
<b>GTH</b>	Goedecker-Teter-Hutter
<b>HEC</b>	Hydrogen-Evolving Catalyst
<b>HOMO</b>	Highest Occupied Molecular Orbital
<b>IEM</b>	Ion Exchange Membrane
<b>IS</b>	Initial State
<b>I<sub>2</sub>M</b>	Oxo-oxo Coupling
<b>KS</b>	Kohn-Sham
<b>LDA</b>	Local Density Approximation
<b>LUMO</b>	Lowest Unoccupied Molecular Orbital
<b>MD</b>	Molecular dynamics
<b>NCAP</b>	Nonadiabatic Conversion by Adiabatic Passage
<b>NDI</b>	2,6-diethoxy-1,4,5,8-diimide-naphthalene
<b>NPT</b>	Isothermal-isobaric Ensemble

<b>NVT</b>	Canonical Ensemble
<b>OEC</b>	Oxygen Evolving Center
<b>OPBE</b>	OPTX-Perdew-Burke-Ernzerhof
<b>OPTX</b>	Handy's Optimized Exchange
<b>PBC</b>	Periodic Boundary Conditions
<b>PBE</b>	Perdew-Burke-Ernzerhof
<b>PCET</b>	Proton-Coupled Electron Transfer
<b>PEC</b>	Photoelectrochemical Cell
<b>PEM</b>	Proton Exchange Membrane
<b>PSI</b>	PhotoSystem I
<b>PSII</b>	PhotoSystem II
<b>PV-E</b>	PV-Electrolysis
<b>PT</b>	Proton Transfer
<b>PV</b>	Photovoltaics
<b>SOMO</b>	Singly Occupied Molecular Orbital
<b>TD-DFT</b>	Time-Dependent Density Functional Theory
<b>TIP<sub>3</sub>P</b>	Transferable Intermolecular Potential with 3 Points
<b>TS</b>	Transition State
<b>TZP</b>	Triple-Zeta Polarized Basis Set
<b>VDOS</b>	Vibrational Density of States
<b>VMD</b>	Visual Molecular Dynamics
<b>WNA</b>	Water Nucleophilic Attack
<b>WOC</b>	Water Oxidation Catalyst

# List of Symbols

$A$	pre-exponential frequency factor
$d_{C-N}$	C–N bond length
$d_{C-N\_ini}$	C–N bond length of the initial intermediate
$d_{C-N\_fin}$	C–N bond length of the final intermediate
$\langle d_{C-N} \rangle$	time-averaged C–N bond length
$e$	Euler's number
$\eta$	overpotential
$E[\rho]$	ground state energy
$E_{xc}[\rho]$	exchange-correlation functional
$E_{\text{tot}}$	total bonding energy
$\Delta E_{\text{SOMO}}$	energy difference between molecular orbitals
$\Delta E_{\text{int}}$	energy difference between intermediates
$\Delta \varepsilon$	excitation energy around the transition state
$f$	oscillator strength
$g(r)$	radial distribution function
$\Delta G^*$	activation free energy barrier
$\Delta G^\circ$	thermodynamic driving force
$\Delta G$	free energy change
$\Delta G_{\text{calc}}$	calculated free energy change
$\Delta G_{\text{exp}}$	experimentally measured free energy change
$h$	Planck constant
$J[\rho]$	classical Coulomb interaction
$k$	reaction rate
$k_B$	Boltzmann constant
$\phi_i$	Kohn-Sham orbital
$n(r)$	coordination number
$r$	O···O distance
$R$	Universal gas constant
$\rho(\mathbf{r})$	electron density
$S$	total spin angular momentum
$2S+1$	spin multiplicity
$T$	thermodynamic temperature
$T[\rho]$	kinetic energy
$\sigma$	standard deviation
$\theta$	dihedral angle
$\theta_{\text{ini}}$	dihedral angle of the initial intermediate

$\theta_{\text{fin}}$	dihedral angle of the final intermediate
$\langle \theta \rangle$	time-averaged dihedral angle
$\lambda$	constraint force
$\langle \lambda \rangle$	time-averaged constraint force
$\langle \lambda \rangle_r$	running average of constraint force
$\mu$	fictitious mass of the electronic degrees of freedom
$\Lambda_{ij}$	Lagrange multipliers
$V_{ee}[\rho]$	electron-electron interaction
$V_{\text{ext}}[\rho]$	nucleus-electron interaction
$v_{\text{ext}}(\mathbf{r})$	external potential
$\omega$	vibrational frequency

