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Accelerating the photocatalytic water splitting in catalyst-dye complexes

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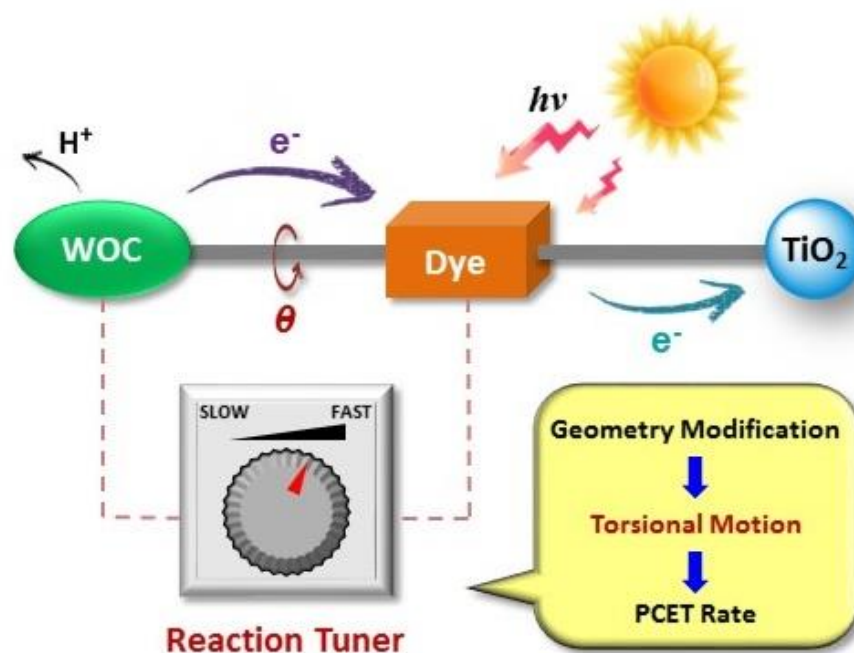
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CHAPTER 4

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



This chapter is based on:

Yang Shao, Huub J.M. de Groot, and Francesco Buda, *ChemSusChem*, **2021**, 14, 479-486, DOI: 10.1002/cssc.202001863.

4

Abstract

In view of the considerably high activation energy barrier of the O–O bond formation photocatalytic step in water oxidation, it is essential to understand if and how nonadiabatic factors can accelerate the PCET rate in this process to find rational design strategies facilitating this step. Here we perform constrained AIMD simulations to investigate this rate-limiting step in a series of catalyst–dye supramolecular complexes functionalized with different alkyl groups on the catalyst component. These structural modifications lead to tuneable thermodynamic driving forces, PCET rates, and vibronic coupling with specific resonant torsional modes. These results reveal that such resonant coupling between electronic and nuclear motions contributes to crossing catalytic barriers in PCET reactions by enabling semiclassical coherent conversion of a reactant into a product. Our results provide insight on how to engineer efficient catalyst–dye supramolecular complexes by functionalization with steric substituents for high-performance DS-PECs.

4.1. Introduction

Solar-driven water splitting via DS-PEC devices is an area of rapid technological growth, and is considered to be a promising scalable, affordable and sustainable technology for direct solar-to-fuel conversion to produce strategically valuable and storable hydrogen, or hydrocarbons from CO₂.¹⁻² Decentralized PEC offers intrinsic advantages since the integration of the PV and electrocatalytic steps in one device operating at low current density reduces overpotential and concentration losses compared to centralized electrolysis driven by PV.³ For one complete water splitting cycle in DS-PECs, four photons are absorbed at the photoanode, generating holes on the light-harvesting dye that should provide sufficient driving force for the four-proton/four-electron water oxidation half-reaction catalyzed by a WOC. The four photo-generated electrons migrate to the (photo)cathode to be consumed for the hydrogen production or for CO₂ reduction.⁴⁻⁵ Despite the effort in the development of novel DS-PECs, which have been improved either in the photoelectrodes⁶⁻⁷ or in the IEM⁸⁻¹⁰, the overall yield of the water oxidation half-reaction is limited. In particular the O–O bond formation step represents a thermodynamic and kinetic bottleneck for productive forward ET.¹¹ This leads to low yield, often less than 20%, due to charge recombination losses at the dye-electrode interface¹²

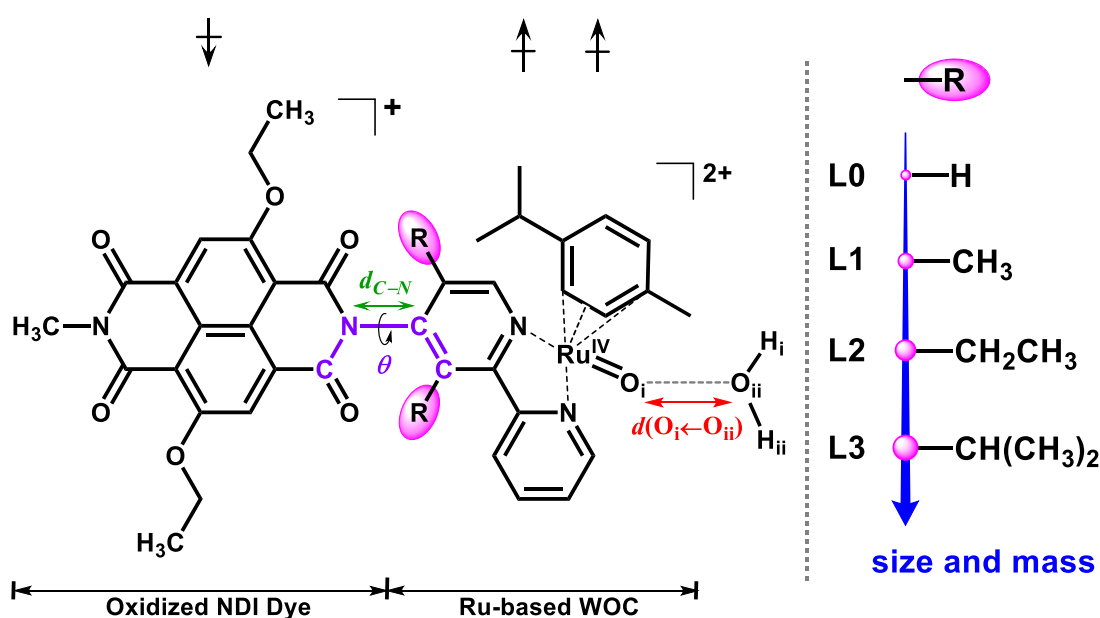
PCET¹³⁻¹⁷ plays an essential role in the photocatalytic four-proton/four-electron oxidation of water. Proper assembly of the components in the WOC–dye supramolecular complex provides channels for PCET steps in which the electron and proton are transferred in different directions and the dye is regenerated to its initial state.^{11, 18} The critical O–O bond formation process with mononuclear catalysts is found to be the most challenging and the rate-limiting step in catalytic water oxidation.¹⁹⁻²⁰ Significant rate enhancement has been achieved either by modifying the ligand of the WOC or by tuning the solvent environment, in which computational studies act as a powerful technique.²¹⁻²⁶

In catalysis, electrons are generally considered to be in equilibrium with their atomic surrounding, and reactions are thought to proceed adiabatically over catalytic barriers. While recent analysis of PCET reactions acknowledge the importance of nonadiabatic terms connecting electronic states, these are usually treated as probabilistic events for the conversion of reactants into products in the

context of nonadiabatic transition state theory.²⁷ However, when reactant and product levels cross due to molecular vibrations, resonant vibronic coupling can be established over an avoided crossing that provides a fast deterministic semiclassical coherent channel from the reactant to the product output, in particular for asymmetric systems that evolve along a torsional degree of freedom.¹¹ While we have found convincing evidence that resonant coupling is important for energy transfer and separation of charges^{28–30}, the purpose of this study is to investigate the possibility for resonant coupling at the crossing of the reactant and product states for the O–O bond formation in water oxidation, and if this offers an attractive chemical engineering principle to achieve near-unity yield in photochemical water oxidation.

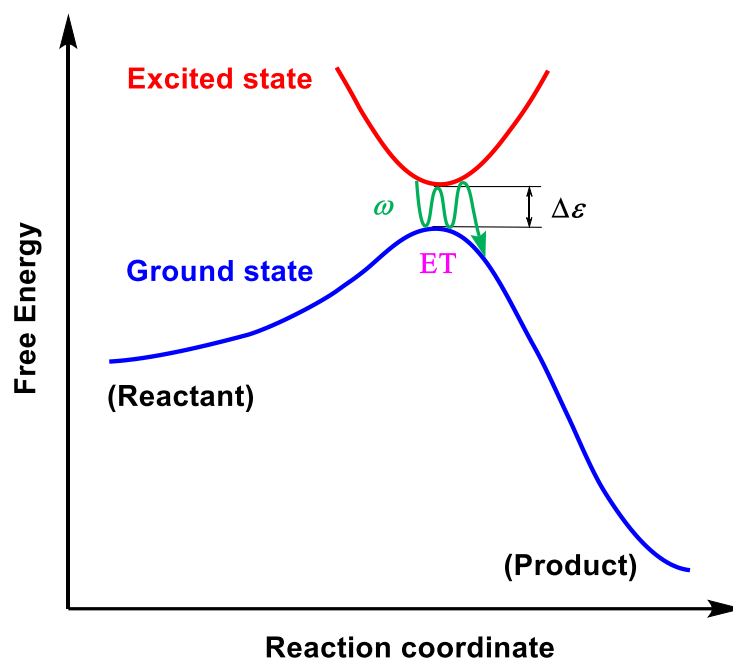
In the context of PCET reactions in artificial photosynthesis, the photocatalytic water splitting cycle in a WOC–dye supramolecular complex $[(\text{cy})\text{Ru}^{\text{II}}\text{bpy}(\text{H}_2\text{O})]^{2+}$ –NDI has recently been systematically investigated *in silico*, providing the driving

Scheme 4.1. Schematic structure of complexes **L0** – **L3** ($^2[(\text{Ru}^{\text{IV}}=\text{O})_i^{2+}\text{–NDI}^{+*}]$, $i = 0 - 3$) after the photooxidation of NDI dye together with the attacking water molecule in the vicinity of Ru center^a



^aThe dihedral angle θ and the C–N bond studied in this work are indicated in purple and green, respectively. The spin multiplicity $2S+1 = 2$ for a net spin $S = 1/2$ in this case corresponds to two unpaired α electrons ($\uparrow$) localized on the catalyst and one unpaired β electron ($\downarrow$) on the oxidized NDI⁺. The red double-sided arrow indicates the reaction coordinate $d(\text{O}_i \leftarrow \text{O}_{ii})$ considered in the constrained MD simulations.

Scheme 4.2. Schematic illustration of the resonant coupling between electronic and nuclear motions in the investigated system. $\Delta\varepsilon$ stands for the excitation energy around the transition state. ω represents the vibrational frequency of the torsional angle θ .



force and the energy barrier of each PCET step by DFT-MD simulations.^{11, 31} The computed energy barrier ($\Delta G^* = 15.9 \text{ kcal mol}^{-1}$) and corresponding reaction rate ($k = 15.7 \text{ s}^{-1}$) confirm that the third catalytic PCET step involving the O–O bond formation is indeed the kinetic bottleneck of the entire catalytic water oxidation half-reaction, which would increase the possibility of deleterious charge recombination and thus lower the quantum yield.^{11, 32}

In this work we explore the possibility of enhancing the rate of this critical PCET step in the WOC–dye complex $[(\text{cy})\text{Ru}^{\text{II}}\text{bpy}(\text{H}_2\text{O})]^{2+}$ –NDI by modifying the bipyridine ligand that is covalently bound to the NDI dye (see Scheme 4.1). Specifically, a series of alkyl groups varying in size and mass were introduced in the bpy residue near the C–N bond connecting the WOC and the NDI dye (**L0** – **L3** in Scheme 4.1). The rationale for this choice is to affect the torsional motion at the interface between the WOC and the dye in order to match the associated nuclear frequency (ω) to the resonance condition for the electron transfer process ($\omega \approx \Delta\varepsilon$, see Scheme 4.2).²⁹ This is inspired by the correlation between the torsional motion and the electron dynamics observed in our previous investigation of the catalytic cycle.¹¹

4.2. Results and Discussion

Understanding the impact of coherent coupling between electron and nuclear motions in catalytic reactions, such as the rate of this PCET reaction in the WOC–dye complex, is of particular interest and great significance.^{33–35} With this aim, we perform DFT-MD simulations following the Car-Parrinello approach to obtain accurate predictions of the activation energy barrier.³⁶ We show how the ET is coherently coupled to a specific torsional motion, and how the reaction rate of this catalytic PCET reaction in the WOC–dye complex ($^2([\text{Ru}^{\text{IV}}=\text{O}]^{2+}-\text{NDI}^+)$, see Scheme 4.1) is affected by the ligand modifications.

4.2.1 Geometry Optimization of the WOC–Dye Complexes

The initial geometry of the photooxidized WOC–dye complexes **L0** – **L3** is optimized at the DFT level employing the OPBE exchange–correlation functional³⁷ and the TZP basis set in implicit solvation (COSMO) with the ADF software package^{38–39} (see Appendix 4.A.1 for more computational details).³¹ The increase in

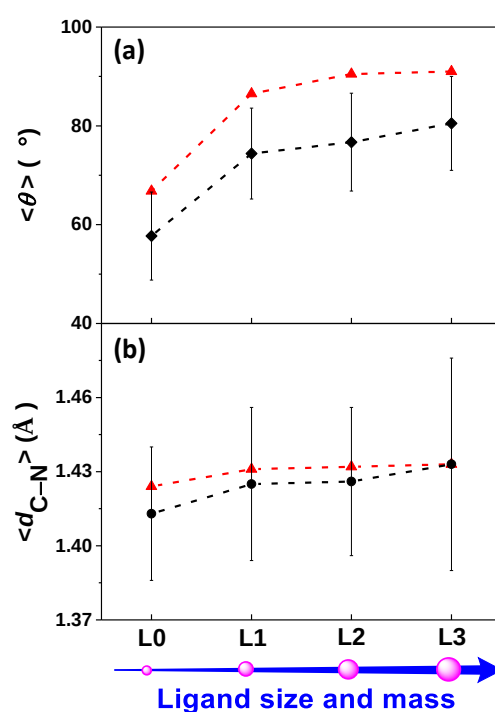


Figure 4.1. (a) Time-averaged dihedral angle ($\langle \theta \rangle$ in °), (b) C–N bond length ($\langle d_{\text{C-N}} \rangle$ in Å), and corresponding standard deviations of complexes **L0** – **L3** during the constrained MD simulations in explicit water solvation. For comparison, the dihedral angle θ (in °) and C–N bond length $d_{\text{C-N}}$ (in Å) of complexes **L0** – **L3** after geometry optimization with the ADF program using the OPBE functional, TZP basis set and implicit solvation (COSMO) are indicated in red triangles.

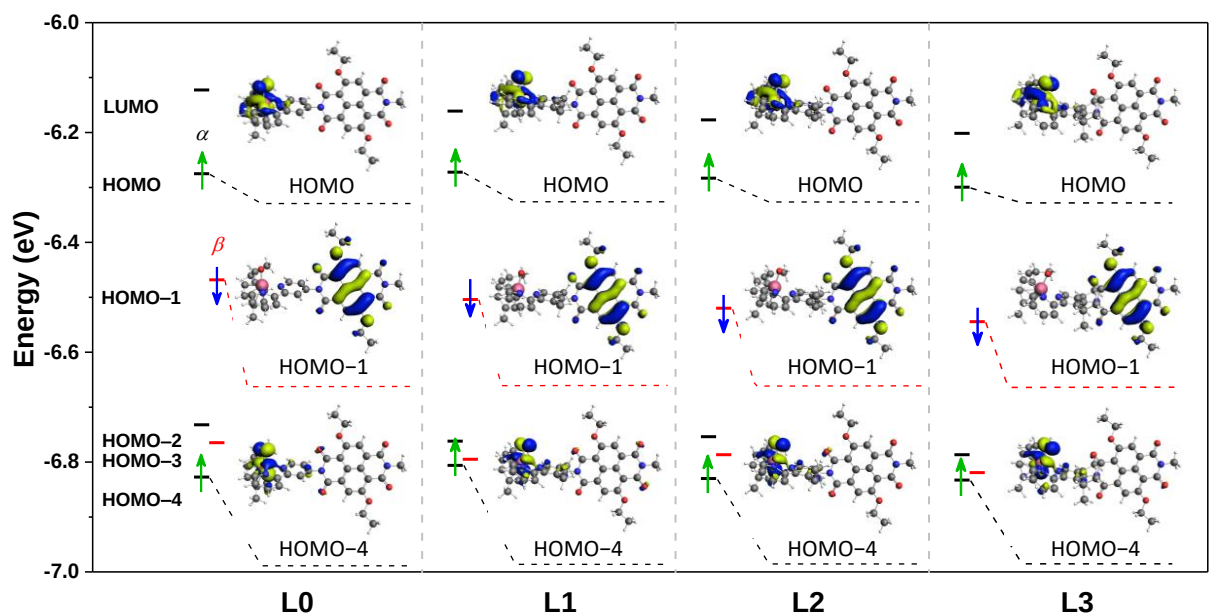


Figure 4.2. Selected frontier molecular orbitals of complexes **L0** – **L3** ($^2([\text{Ru}^{\text{IV}}=\text{O}]_i^{2+}-\text{NDI}^+)$, $i = 0 - 3$) after photooxidation of the NDI dye computed with the ADF program using the OPBE functional and the TZP basis set. The continuum solvation model COSMO is used to describe the water environment. Energy levels are indicated in black for spin α and in red for spin β orbitals, respectively. Only the unpaired electrons are explicitly indicated by vertical arrows (green for an unpaired electron localized on the catalyst and blue for an unpaired electron on the oxidized NDI^+) and the corresponding isosurface representation is shown in the inset. See Table 4.1 for the molecular energy levels.

Table 4.1. Selected frontier molecular orbital energy levels and energy difference ΔE_{SOMO} between SOMO dye and SOMO WOC of complexes **L0** – **L3** ($^2([\text{Ru}^{\text{IV}}=\text{O}]_i^{2+}-\text{NDI}^+)$, $i = 0 - 3$) after the photooxidation of NDI dye.^a

Intermediate		$^2([\text{Ru}^{\text{IV}}=\text{O}]_i^{2+}-\text{NDI}^+)$ ($i = 0 - 3$)			
		$\uparrow$	$\uparrow$	$\downarrow$	
Energy level	Orbital	L0	L1	L2	L3
LUMO	α	-6.123	-6.161	-6.177	-6.202
HOMO (SOMO WOC)	α	-6.275	-6.272	-6.283	-6.299
HOMO-1 (SOMO dye)	β	-6.468	-6.504	-6.520	-6.544
HOMO-2	α	-6.732	-6.762	-6.754	-6.787
HOMO-3	β	-6.765	-6.795	-6.787	-6.819
HOMO-4 (SOMO WOC)	α	-6.827	-6.806	-6.830	-6.833
ΔE_{SOMO}		-0.193	-0.231	-0.237	-0.245

^aThe initial geometry of all the complexes **L0** – **L3** are optimized with the ADF program using the OPBE functional and the TZP basis set. The continuum solvation model COSMO is used to describe the water environment. Only the unpaired electrons are indicated by vertical arrows explicitly (green for unpaired electrons localized on the catalyst and blue for unpaired electrons on the oxidized NDI^+). All energies are in eV.

size and mass of the ligand R leads to an elongation of the C–N bond ($d_{\text{C-N}}$) that links the WOC and dye components. In addition, the dihedral angle (θ) around the C–N bond increases going from **L0** to **L3**, due to the steric hindrance from bulky substituents (see Figure 4.1 and Table A4.1 in Appendix 4.A.2). The initial geometry will determine the sign of the dihedral angle as steric hindrance prevents the system to flip from a positive value of θ to an equivalent geometry with an opposite value, effectively breaking this symmetry.

Using the optimized geometry of the photooxidized WOC–dye complexes, we analyze the electronic structure and in particular the frontier molecular orbitals that play a crucial role in the PCET step and in regenerating the ground state of the dye. Figure 4.2 illustrates the frontier molecular orbital energy levels together with an isosurface corresponding to the SOMOs of complexes **L0** – **L3**. The corresponding energy levels are also listed in Table 4.1. For all these complexes, the SOMO localized on the oxidized NDI⁺ (SOMO dye) is always lower in energy than the HOMO of the supramolecular complex, which is localized on the ruthenium catalyst (SOMO WOC). The energy difference between the SOMO dye and the SOMO WOC (see ΔE_{SOMO} in Table 4.1) is found to systematically increase as the size and mass of the ligand R increases from complex **L0** ($\Delta E_{\text{SOMO}} = -0.193$ eV) to **L3** ($\Delta E_{\text{SOMO}} = -0.245$ eV). This result suggests an increasingly larger driving force for electron transfer from the ruthenium catalyst to the oxidized NDI dye due to the geometrical distortion induced by the steric hindrance from bulky substituents.

4.2.2 Equilibration of WOC–Dye Complexes in the Explicit Solvent Model

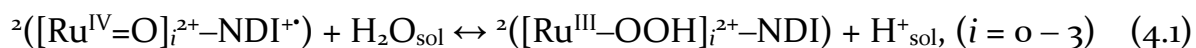
An accurate description of the PCET reaction and corresponding free energy profile requires an explicit inclusion of the water environment as it is crucially involved in the reaction process.^{11, 26, 32} Therefore, an orthorhombic box of dimensions $25.1 \times 17.7 \times 14.4$ Å³ with periodic boundary conditions containing the WOC–dye solute **L0** – **L3** together with 162 explicit water molecules is used in the DFT-MD simulations performed with the CPMD program⁴⁰. The DFT electronic structure is determined by using the OPBE exchange-correlation functional³⁷, GTH pseudopotentials for the ruthenium transition metal⁴¹ and DCACP pseudopotentials for the remaining atoms⁴², together with a plane wave cutoff of 70 Ry (see Appendix 4.A.1). An initial free DFT-MD simulation of 0.6 ps at room temperature is performed for each [WOC]²⁺–dye solvated system to equilibrate the

solvation environment. Prior to this DFT-MD run, the systems have been already pre-equilibrated with a classical force field (see Appendix 4.A.1.2).

In a previous work³¹ we have demonstrated that upon photoexcitation the NDI is able to inject an electron at a dye-sensitized TiO₂ semiconductor surface on a time scale of ~1 ps. It is therefore reasonable to assume in the following analysis that the system is already in its oxidized form [WOC]²⁺–dye⁺ at the beginning of the simulation for this catalytic PCET step driven by the complexes **L0** – **L3**. The photooxidation of the NDI dye is mimicked by removing one electron from the simulation box after the initial equilibration simulation for each system considered. Subsequently, the oxidized state is further equilibrated for another 0.6 ps at room temperature. We show in Figure A4.1 (see Appendix 4.A.3) that the running average of the KS energy reaches a stable value even within this relatively short MD timescale of ~0.6 ps. Notice that during all the MD simulations after the photooxidation of the NDI, we only focus on the most favorable reaction route recently reported¹¹ with a total electron spin angular momentum $S = 1/2$. This is assumed to be conserved along the reaction coordinate since the O–O bond formation is thermodynamically unfavorable for the $S = 3/2$ case.¹¹ When the spin density is tracked along the equilibration MD simulation for the solvated [WOC]²⁺–dye⁺ systems, two unpaired α electrons ($\uparrow$) are observed to localize on the catalyst and one unpaired β electron ($\downarrow$) on the NDI dye in all the systems (see insets in Figure A4.2). Thermal fluctuations of the total spin density localized on the NDI dye, of the dihedral angle θ and C–N bond length d_{C-N} along this FMD trajectory are also collected in Figure A4.2 (see Appendix 4.A.3).

4.2.3 Constrained MD Simulations of the O–O Bond Formation Step

After this equilibration simulation, the constrained MD approach combined with thermodynamic integration is then employed to estimate the free energy profile of the third catalytic water oxidation step (see the redox couple in eq 4.1, where H₂O_{sol} and H⁺_{sol} represent the solvated attacking water molecule and proton respectively):



In eq. 4.1 the total spin multiplicity $2S+1 = 2$ is maintained over the WOC–dye system, with doubly charged WOC catalytic intermediates on both sides of the

redox couple. Hence one electronic spin quantum is internally transferred from the NDI to the WOC, while one unit of charge is released into the solvent environment in the form of a proton. The use of constrained MD is appropriate here since this reaction is a rare event on the typical DFT-MD simulation time scale.⁴³ The constrained reaction coordinate is the distance between the oxygen atoms O_i and O_{ii} indicated by the red double-sided arrow in Scheme 4.1 (see Appendix 4.A.1 for more computational details). In similar computational work on O–O bond formation, metadynamics simulations have been used as an alternative enhanced sampling method.^{44–47} In particular, in a very recent work in addition to the O–O distance, a second collective variable has been included to keep track of the proton transfer.⁴⁷ In our investigation, we didn't introduce additional constraints for the proton transfer to avoid a bias on the proton acceptor.

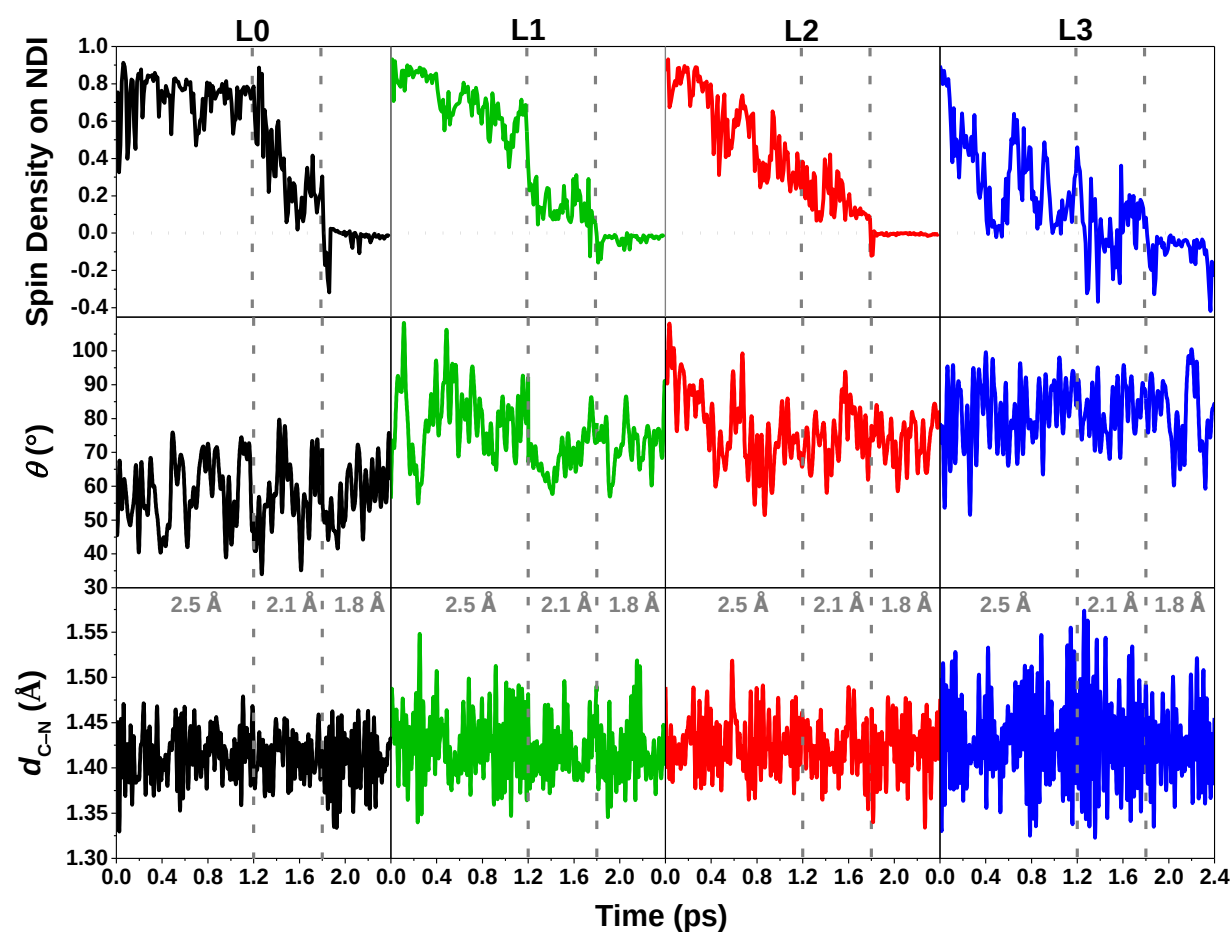


Figure 4.3. Spin density integrated over half of the simulation box including the NDI dye, time evolution of the θ and d_{C-N} of complexes **L0** – **L3** along the constrained MD trajectories. An integrated spin density value of 1 corresponds to one unpaired β electron ($\uparrow$). The value of the constrained reaction coordinate $d(O_i \leftarrow O_{ii})$ in the MD simulations is noted in grey.

In order to explore the correlation between the electronic and nuclear motions in these WOC–dye complexes, the variation of the spin density on the NDI dye together with the time evolution of the dihedral angle θ and C–N bond length $d_{\text{C-N}}$ for complexes **L0** – **L3** along the constrained MD trajectories are collected in Figure 4.3. The time-averaged dihedral angle $\langle\theta\rangle$, C–N bond length $\langle d_{\text{C-N}}\rangle$, and corresponding standard deviations for all complexes **L0** – **L3** during the constrained MD simulations are presented in Table A4.1 and Figure 4.1 for a quantitative comparison. According to the results of our DFT-MD simulations, the introduction of a ligand R larger in size and mass than hydrogen in complexes **L1** – **L3** gives rise to an increasing dihedral angle ($74.7 - 80.5^\circ$), and longer C–N bond ($1.426 - 1.433 \text{ \AA}$) as well as larger fluctuations during the dynamics compared to those of complex **L0** (57.7° , $1.413 \text{ \AA}$). The trend of the computed time average $\langle\theta\rangle$ and $\langle d_{\text{C-N}}\rangle$ when gradually enlarging the size and mass of ligand R from **L0** to **L3** is consistent with the static DFT results (see Table A4.1 and black scatters in Figure 4.1).

The ET is affected by the dynamic structure and starts already in the constrained MD with the reaction coordinate value $d(\text{O}_i \leftarrow \text{O}_{ii}) = 2.5 \text{ \AA}$ in **L1** – **L3**, while it occurs only after further shortening the reaction coordinate $d(\text{O}_i \leftarrow \text{O}_{ii})$ to $2.1 \text{ \AA}$ in the case of **L0** (Figure 4.3, top panels). In particular for **L3** there is oscillatory behaviour. Initially the ET from the WOC to the photoinduced hole on the oxidized NDI occurs very rapidly already with $d(\text{O}_i \leftarrow \text{O}_{ii}) = 2.5 \text{ \AA}$, as it can be visualized by the spin density on the NDI going to zero in about 0.4 ps . This rapid event is then followed by a partial back transfer and pronounced fluctuations. The electron keeps transferring back and forth between the WOC and dye even when we further continue the constrained $2.5 \text{ \AA}$ MD simulation for another $\sim 0.6 \text{ ps}$ (see Appendix 4.A.4). In Figure A4.4 in Appendix 4.A.5, we show that the running average of the constraint force reaches a stable value within the constrained $2.5 \text{ \AA}$ MD timescale of $\sim 1.2 \text{ ps}$ for complexes **L0** – **L3** although large fluctuations on spin density could still be observed at the end of this simulation.

In all cases, the ET is completed at $d(\text{O}_i \leftarrow \text{O}_{ii}) = 1.8 \text{ \AA}$ with a stable integrated spin density value of 0 on the NDI (see also Appendix 4.A.6, where we show a longer constrained simulation with $d(\text{O}_i \leftarrow \text{O}_{ii}) = 1.8 \text{ \AA}$ for **L3**), corresponding to the final state with one unpaired α electron ($\uparrow$) localized on the catalyst and no unpaired electron on the NDI dye, which is regenerated to its initial ground state. The PT

from the attacking water molecule to the solvent only occurs during this constrained 1.8 Å simulation when the ET is completed. In particular, the proton H_i diffuses into the solvent bulk via a “chain” of hydrogen-bonded water molecules, which can be well described by the Grotthuss mechanism⁴⁸⁻⁴⁹ (see Appendix 4.A.7). This mechanism has been already observed in our previous works^{11, 32}. The reaction coordinate $d(O_i \leftarrow O_{ii})$ is then further shortened to 1.6 Å to better explore the complete free energy profile along this reaction pathway and no back reaction occurs (see Appendix 4.A.8). More importantly, no back-transfer of either an electron or a proton is observed even after the release of the constraint between O_i and O_{ii} at the end of the 1.6 Å simulation, confirming the stability of the final product (see eq. 4.1) after the O–O bond formation (see Appendix 4.A.9).

The facilitation of ET by ligand modification can be partially attributed to the larger driving force for bulkier substituents from **L0** to **L3** as discussed earlier in terms of molecular orbital energies (see Figure 4.2). However, another important factor could be a resonant coupling between electronic and nuclear motion that will be discussed further in a next section.

Chapter

4

4.2.4 Free Energy Profile and Reaction Rate Estimation

Based on all the constrained DFT-MD simulations performed, the free energy profile along the reaction coordinate $d(O_i \leftarrow O_{ii})$ of **L0** – **L3** can be computed using the Blue Moon ensemble approach.^{43, 50-51} This will allow for a quantitative evaluation of the effect of the ligand modification on the rate enhancement for this catalytic water oxidation step. The time-averaged forces associated with the applied constraints, the interpolation of the time-averaged mean forces used for this analysis, and the corresponding free energy profile obtained via thermodynamic integration of **L0** – **L3** are presented in Figure 4.4 (see Appendix 4.A.1 for computational details and Appendix 4.A.10 for error bar of each time-averaged mean force).

It is apparent from Figure 4.4b that the obtained activation energy barrier for O–O bond formation decreases systematically as an effect of the increasing steric hindrance by substitution of ligand R in the sequence **L0** → **L1** → **L2** → **L3**. In addition, following the same sequence, the transition state occurs earlier, *i.e.*, at larger values of $d(O_i \leftarrow O_{ii})$ along the reaction coordinate. The key thermodynamic

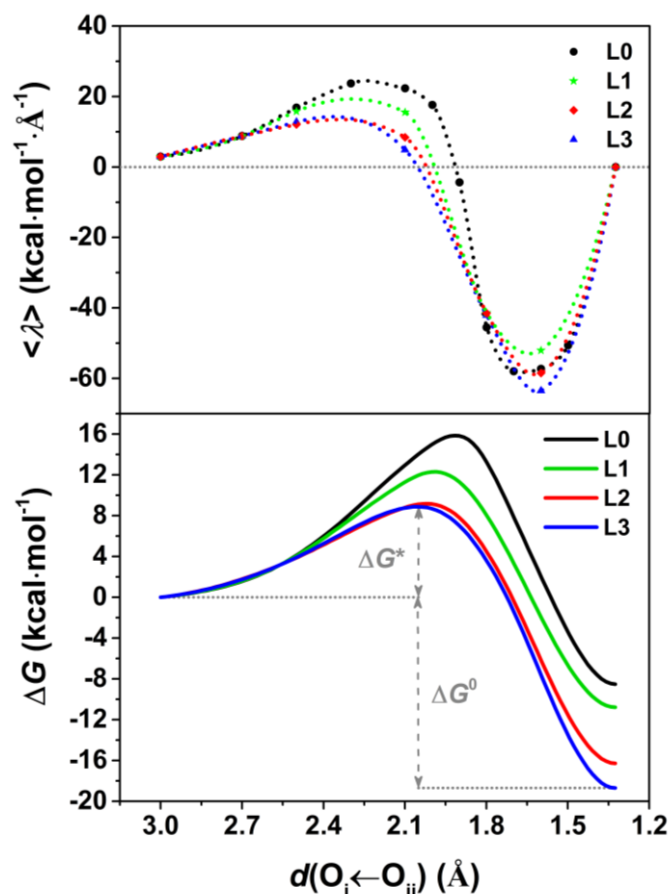


Figure 4.4. (a) Time-averaged constraint force represented by the Lagrangian multiplier $\langle \lambda \rangle$ computed for each constrained MD simulation as a function of the reaction coordinate $d(\text{O}_i \leftarrow \text{O}_{ii})$ for complexes **L0** – **L3**. The Akima splines (100 points) is used to interpolate the mean forces. (b) Free energy profile along the reaction coordinate $d(\text{O}_i \leftarrow \text{O}_{ii})$ computed from thermodynamic integration for complexes **L0** – **L3**. The time-averaged constraint forces and associated free energy profile for **L0** are taken from ref. 11 for comparison.

parameters extracted from the free energy profile of **L0** – **L3** for this water oxidation step are summarized in Table 4.2. The energy difference ΔE_{SOMO} between the SOMO dye and the SOMO WOC of complexes **L0** – **L3** after the photooxidation of the NDI dye is also included in Table 4.2 for comparison. In particular the calculated activation free energy barriers ΔG^* , 9.2 kcal mol^{−1} (~0.40 eV) and 8.9 kcal mol^{−1} (~0.39 eV) for **L2** and **L3** respectively, are dramatically lowered almost by half in comparison with that of **L0** (15.9 kcal mol^{−1} (~0.69 eV)), indicating that this catalytic process is significantly facilitated by the changes in electronic and structural dynamics resulting from the ligand modification. It should be emphasized that the photooxidation of the NDI dye makes this reaction exothermic in all considered cases. However, following the order **L0** → **L1** → **L2** →

L3 the driving force becomes stronger, since ΔG^0 increases systematically from -8.5 to -18.7 kcal mol⁻¹. Table 4.2 shows a clear inverse correlation between the driving force and the activation free energy, which is consistent with Hammond’s postulate.⁵² Interestingly, the variation in ΔG^0 is much larger than the increase in the static molecular orbital energy difference ΔE_{SOMO} (see Table 4.2), pointing to the importance of dynamical (entropic) effects.

Table 4.2. Computed activation energy barrier ΔG^* (in kcal mol⁻¹), thermodynamic driving force ΔG^0 (in kcal mol⁻¹), and estimated reaction rate k (in s⁻¹) of the third PCET step involving the O–O bond formation for the complexes **L0** – **L3**, together with the energy difference (ΔE_{SOMO} in kcal mol⁻¹) between SOMO dye and SOMO WOC of complexes **L0** – **L3** obtained with static DFT calculations. The results for **L0** are taken from ref. 11.

WOC–dye complex	ΔG^*	ΔG^0	ΔE_{SOMO}	k
L0 ¹¹	15.9	−8.5	−4.5	15.7
L1	12.3	−10.8	−5.1	6.6×10 ³
L2	9.2	−16.3	−5.5	1.2×10 ⁶
L3	8.9	−18.7	−5.6	2.0×10 ⁶

The computed activation free energy barrier ΔG^* of **L0** – **L3** can be used to determine the reaction rate k according to transition state theory^{53–55}. The predicted reaction rate reported in Table 4.2 validates the Blue Moon constrained MD approach and shows an enhancement of up to 5 orders of magnitude from **L0** ($k = 15.7$ s⁻¹) to **L3** ($k = \sim 2.0 \times 10^6$ s⁻¹) as an effect of the ligand modification. To address now the crucial question about the origin of this very large effect on the activation energy barrier and hence the reaction rate, we look into the coupling between the electronic and the nuclear motion.

4.2.5 Coupling between Electronic and Nuclear Motions

To resolve possible resonant coupling between the electron transfer process and specific nuclear motions and how this affects the reaction rate of this catalytic water oxidation step, it is convenient to analyze the DFT-MD trajectories in the frequency domain.²⁸ Thus, the Fourier transform of the velocity autocorrelation function is calculated for the time evolution of the spin density and for the thermal fluctuations of θ and $d_{\text{C-N}}$ along the constrained MD trajectories corresponding to Figure 4.3, in which the ET takes place. The Fourier transform of the electron-

transfer time evolution as well as the VDOS of θ and d_{C-N} are presented in Figure 4.5. We focus on the range of 0 – 1000 cm^{-1} since the overlap between nuclear and electronic spectra found at frequencies higher than 1000 cm^{-1} is negligible (see Appendix 4.A.11).

In Figure 4.5 (top panel), the starting complex **L0** shows for each spectrum one main peak, which is located at 566, 726, or 854 cm^{-1} for spin density (red), θ (blue), and d_{C-N} (grey), respectively. The modification of ligand R in complex **L1** – **L3** induces the appearance of a second peak at lower frequencies in the spectrum of the ET and θ , while the spectrum of d_{C-N} stays essentially unchanged. Noticeably,

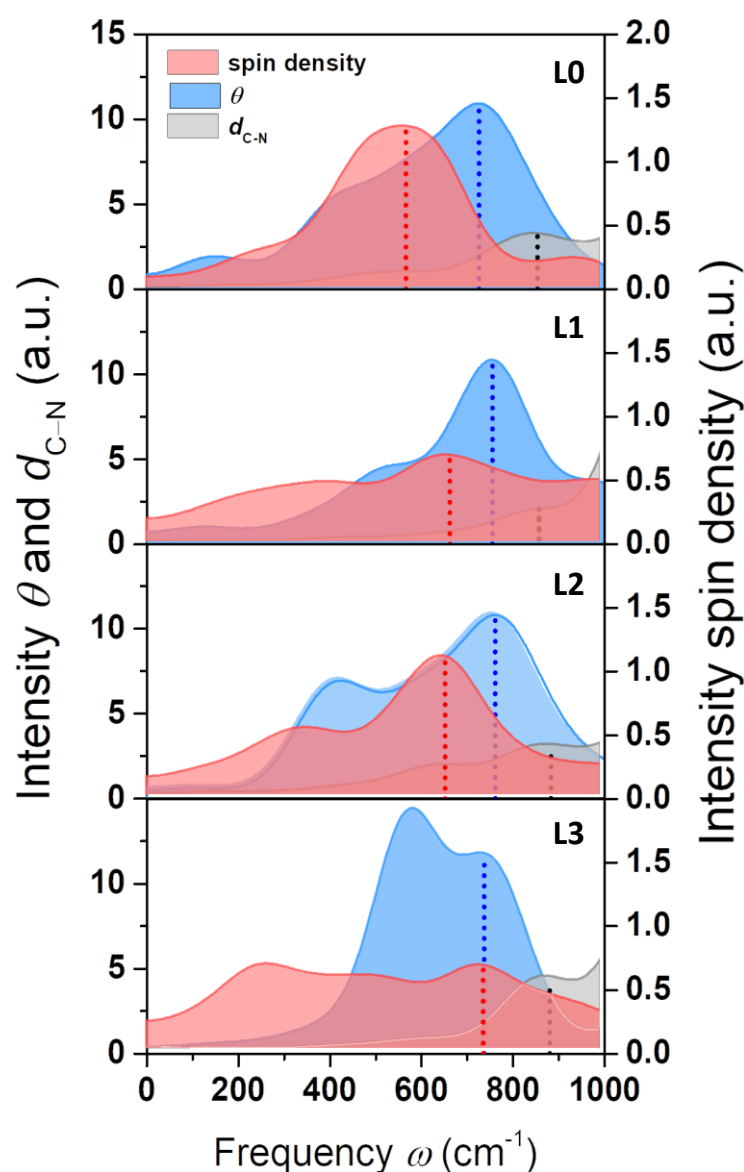


Figure 4.5. Frequency spectrum associated to the ET (red) and the VDOS of θ (blue) and d_{C-N} (grey) for complexes **L0** – **L3** extracted from the constrained 2.5 Å and 2.1 Å MD trajectories corresponding to Figure 4.3.

the main peak of the ET spectrum (red dotted lines in Figure 4.5) is clearly shifted to higher frequency going from **L0** to **L1** – **L3**, leading to increasing overlap with the higher-frequency peak in the spectrum of θ (see blue dotted lines in Figure 4.5). In particular, these two peaks are both centered at around 735 cm^{-1} for the **L3** complex (see Figure 4.5). These results strongly suggest that the ligand modifications induce resonance due to converging timescales of the nuclear vibration of θ and the electronic motion of the charge transfer. The C–N stretching mode instead appears to have less overlap with the ET frequency spectrum. Considering the accelerated reaction rate obtained by modification of the ligand R (see Table 4.2), one is tempted to conclude that the resonance condition achieved between the ET frequencies and the VDOS of θ plays a dominant role in accelerating a catalytic reaction between different electronic states. In other words, the ligand modifications increase the nonadiabatic coupling between reactant and product states, which contributes to the acceleration of the reaction rate in a semiclassical, coherent conversion process that is deterministic instead of probabilistic.

Chapter

4

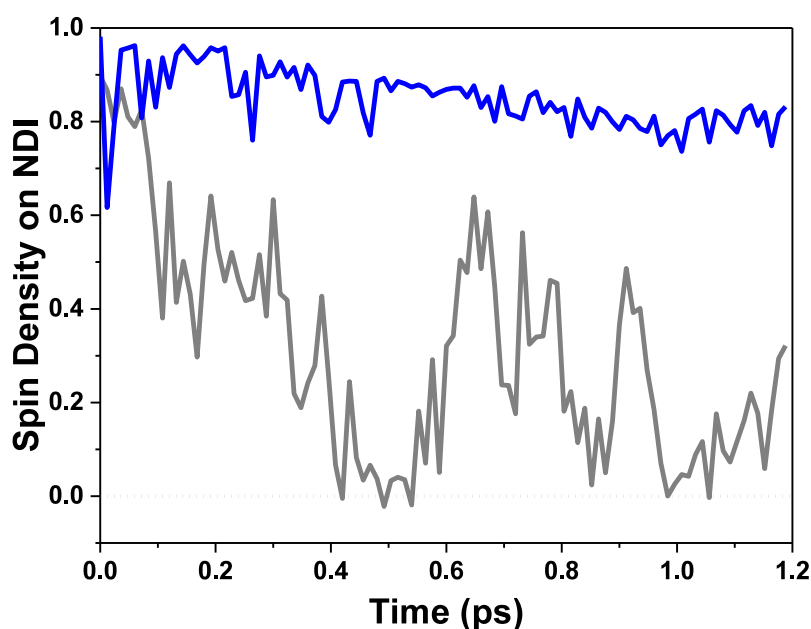


Figure 4.6. Spin density integrated over half of the simulation box including the NDI dye of complex **L3** along the constrained $2.5\text{ \AA}$ MD trajectory with fixed $\theta = 91^\circ$ after the photooxidation of NDI dye (blue line). Before this constrained MD simulation, a simulation of $\sim 0.36\text{ ps}$ with fixed $\theta = 91^\circ$ was performed to equilibrate the solvated system. The data without constraint on the θ of **L3** (grey line) is also presented for comparison, which is extracted from Figure 4.3.

In order to further validate the relevance of vibronic coupling in determining the reaction rate, an additional constrained DFT-MD simulation was carried out for **L3** after the photooxidation of NDI with $d(\text{O}_i\leftarrow\text{O}_{ii}) = 2.5 \text{ \AA}$ and with fixed $\theta = 91^\circ$, as this is the θ obtained from the DFT geometry optimization of **L3** (see Figure 4.1). The time evolution of the spin density localized on the NDI shows that the electron transfer from the WOC to the oxidized NDI dye is strongly inhibited when fixing θ (see Figure 4.6), which highlights the crucial role of this particular nuclear motion in facilitating the ET process. One can also notice that the value of θ extracted from the optimized geometries is about the same for the initial intermediate and for the final product after this catalytic step (see Appendix 4.A.12). Therefore, by fixing the value of θ we are not preventing a specific change in θ from the initial to the final value, but we are only removing the vibrational motion of θ , and thus the coupling with the electronic charge fluctuations.

One further argument supporting the idea of an increased nonadiabatic coupling driving catalysis going from **L0** to **L3** is based on the calculation of the excitation energies near the transition states $\Delta\epsilon$. The results from time-dependent density functional theory (TD-DFT) calculations (see Appendix 4.A.13) show that the energy difference between the ground state and the first excited state $\Delta\epsilon$, which corresponds to the charge transfer state, decreases from $\sim 1.8 \text{ kcal mol}^{-1}$ for **L0** to $\sim 1.3 \text{ kcal mol}^{-1}$ for **L3**. This energy difference is comparable to the energy of the characteristic torsional frequencies ($\omega = 735 \text{ cm}^{-1} = 2.1 \text{ kcal mol}^{-1}$) shown in Figure 4.5.

4.3. Conclusions

In conclusion, we have shown that by changing the mass and size of the ligand **R** at the interface between the WOC and the dye, one can accelerate the PCET reaction step associated to the O–O bond formation by several orders of magnitude. The structural modifications modulate the dihedral angle at the WOC–dye linkage, the electronic structure of the supramolecular complexes, the characteristic frequencies associated with the electron transfer dynamics, and the torsional motion around this link. A similar strategy has been very recently used by synthetically modifying an iron chromophore to interfere with specific atomic motions and resulting in a dramatically different charge transfer lifetime.⁵⁶ This frequency tuning leads to a resonance condition that increases the coupling

between electronic and nuclear motions and facilitates the ET step from the WOC to the oxidized dye in the region of the crossing of reactant and product states, in a process previously denoted NCAP.^{3, 29, 57-58} The computed free energy profiles for this PCET reaction show a considerable decrease in activation energy and increase in the driving force. We expect that the in-depth insight into the acceleration of this specific catalytic water oxidation step provides a general and rational engineering approach for the improvement of the performance of DS-PEC devices from a structural design perspective, which can also be achieved by modifying other ligands around the connecting region or replacing the linker between WOC and dye.

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4.A. Appendix

4.A.1. Computational Details

4.A.1.1 Geometry Optimization at DFT Level

The OPBE exchange-correlation functional¹ and the TZP basis set² were employed in the geometry optimization of the initial and final states of WOC–dye complexes **L0** – **L3**. The OPBE functional has shown to be accurate in describing transition-metal complexes, including Ru-based WOCs.^{3–6} In the geometry optimization, the continuous solvation model COSMO^{7–8} for water was used. These calculations are performed with the ADF software package.^{9–10}

4.A.1.2 Simulation Box

To obtain a realistic description of the catalytic reaction step, the solvent was explicitly introduced in the simulations. The solvent environment for the CPMD simulations was generated using Discovery Studio 2.5.¹¹ The solvent was equilibrated for 0.2 ns using the TIP3P model implemented in the CHARMM force field and CFF partial charge parameters at 300 K,¹² while the [WOC]²⁺–dye complex was kept fixed. The volume was then adjusted using constant pressure for 0.2 ns, after which the system was further allowed to evolve with constant volume for 2 ns. PBC are applied with a time step of $\delta t = 5$ a.u. (1 a.u. = 0.0242 fs).

4.A.1.3 Effect of Periodic Boundary Conditions

In plane wave based AIMD simulations the periodic boundary conditions introduce a spurious Coulomb interaction for charged systems due to the image charges. This effect can be important for charged systems when dealing with isolated molecules/clusters in the simulation box. However, because of the quite large simulation box ($25.1 \times 17.7 \times 14.4 \text{ \AA}^3$) used and the fact that the MD simulation box contains 162 water molecules that will strongly screen the spurious Coulomb interaction, the spurious effect of periodic charges is estimated to be rather small (~ 0.01 eV). We can therefore conclude that the error introduced by the periodic boundary conditions does not affect significantly the conclusions of our work.

4.A.1.4 Free Energy Profile

To estimate the activation free energy barrier of the catalytic reaction step involving the O–O bond formation that is unlikely to occur spontaneously during

the typical AIMD simulation time scale, constrained MD and the so-called Blue Moon approach were employed as a rare event simulation technique.¹³⁻¹⁵ The reaction coordinate (in this case the distance between two oxygen atoms O_i and O_{ii} , $d(O_i \leftarrow O_{ii})$, as shown in Scheme 4.1) is constrained to a series of fixed values in range of 2.5 – 1.6 Å after the initial equilibrium simulation and subsequent photooxidation of NDI along this reaction pathway. A time-averaged constraint force $\langle \lambda \rangle$ for each value of the reaction coordinate is obtained, which should be equal to zero at an equilibrium or for a transition state. In our previous work we learned that the $d(O_i \leftarrow O_{ii}) = 3.0$ Å and 1.325 Å on the reaction coordinates are quite close to the initial/final equilibrium state and far from the transition state. This leads us to conclude that the modification of ligand R has minor effect on the position close to the initial/final equilibrium state and that all the complexes **L0** – **L3** share the same value for the constraint forces at the reaction coordinate $d(O_i \leftarrow O_{ii}) = 3.0$ Å, 2.7 Å, and 1.325 Å.¹⁶ The activation free energy barrier for this catalytic step is then established by interpolating the mean forces with a 100-point Akima splines function and integrating the signed forces $\langle \lambda \rangle$ along the reaction path.¹⁷⁻²⁰ Trajectory analysis and visualization for the CPMD output were carried out using the VMD program.²¹⁻²²

4.A.1.5 Reaction Rate

The computed activation free energy barrier can be used to evaluate to what extent the geometry modification accelerates the rate of the third water oxidation step involving the O–O bond formation. According to transition state theory²³⁻²⁵, the reaction rate k determined by the activation energy barrier ΔG^* can be expressed as

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

One should keep in mind that in DFT-MD simulations protons are treated classically and thus proton tunneling effects are neglected. In the current calculation, only the activation energy barrier is considered as a main factor governing the reaction rate.

4.A.2. Geometrical Parameters

Table A4.1. Calculated geometrical parameters for complexes **L0** – **L3**.

Complex	θ^a	$\langle\theta\rangle^b$	σ_1^b	$d_{\text{C-N}}^a$	$\langle d_{\text{C-N}}\rangle^b$	σ_2^b
L0	66.8	57.7	8.9	1.424	1.413	0.027
L1	86.5	74.4	9.2	1.431	1.425	0.031
L2	90.5	76.7	9.9	1.432	1.426	0.030
L3	91.0	80.5	9.5	1.433	1.433	0.043

^aDihedral angle θ (in $^\circ$) and C–N bond length $d_{\text{C-N}}$ (in Å) of complexes **L0** – **L3** extracted from the static DFT calculations. ^bTime-averaged dihedral angle $\langle\theta\rangle$ (in $^\circ$), C–N bond length $\langle d_{\text{C-N}}\rangle$ (in Å), and corresponding standard deviations of complexes **L0** – **L3** during the free and constrained MD simulations after the photooxidation of NDI dye. See Scheme 4.1 for the identification of the dihedral angle and the C–N bond.

4.A.3. FMD Equilibration Simulation after Photooxidation of **L0** – **L3**

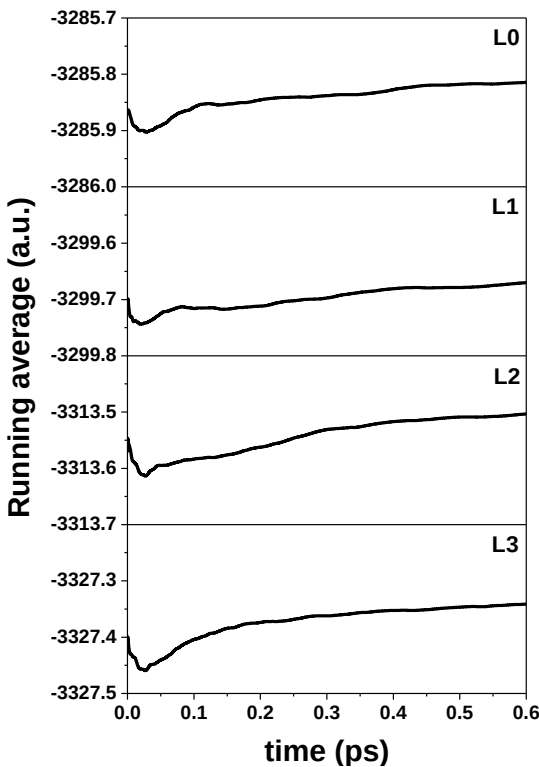


Figure A4.1. The running average of the Kohn-Sham (KS) energy (in a.u.) as a function of time for the equilibration simulation of the photooxidized complexes **L0** – **L3**, respectively. The running average reaches a stable value even within this relatively short MD timescale of ~0.6 ps.

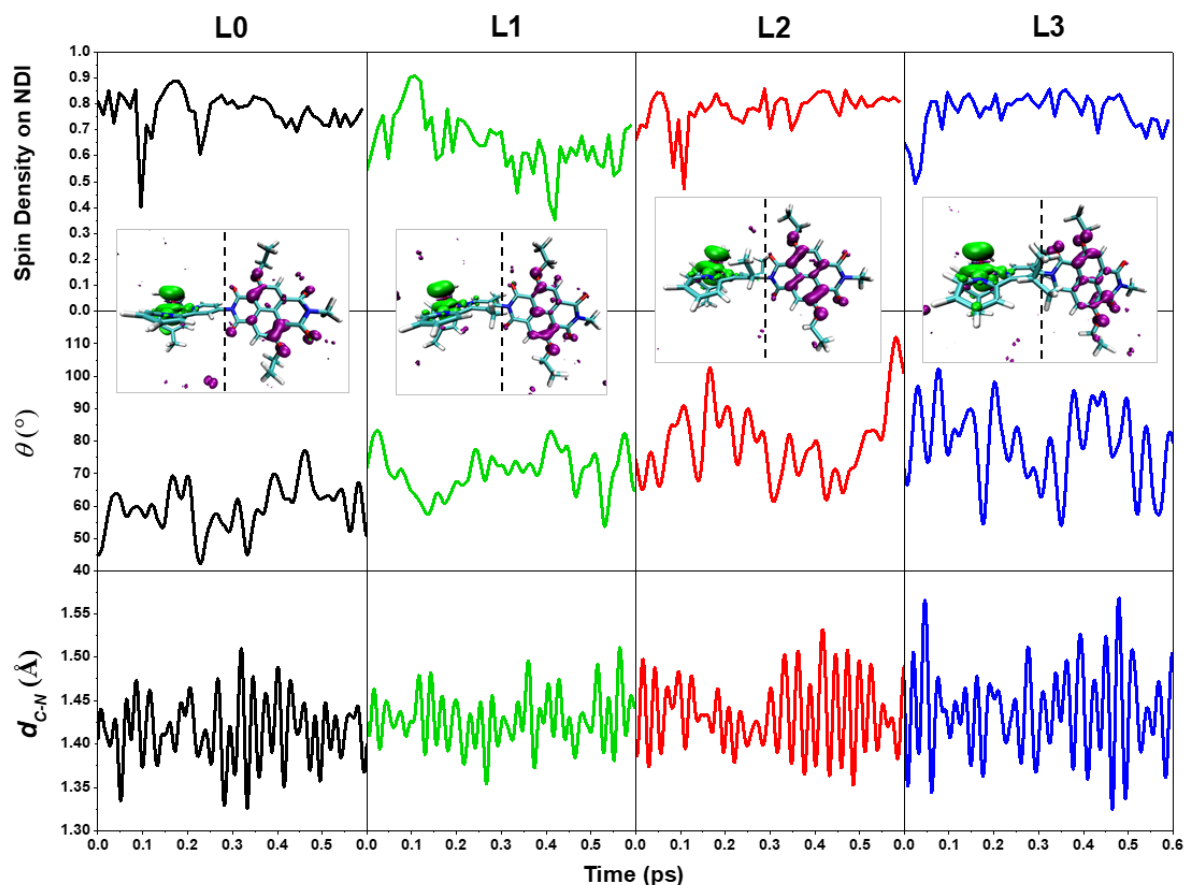


Figure A4.2. Spin density integrated over half of the simulation box including the NDI dye (right-hand side of the dashed black line in the insets), time evolution of θ and d_{C-N} of complexes **L0** – **L3** ($^2([Ru^{IV}=O])_i^{2+}-NDI^+$, $i = 0 - 3$) along the FMD trajectories after the photooxidation of NDI dye. The insets show the spin density isosurface computed at a snapshot taken at the end of each FMD simulation of complexes **L0** – **L3**, respectively, in the doublet state with two unpaired α electrons localized on the catalyst (green spin density isosurface) and one unpaired β electron on the NDI dye (purple spin density isosurface). An integrated spin density value of 1 corresponds to one unpaired β electron ($\uparrow$).

4.A.4. Continued Constrained 2.5 Å MD Simulation for L1

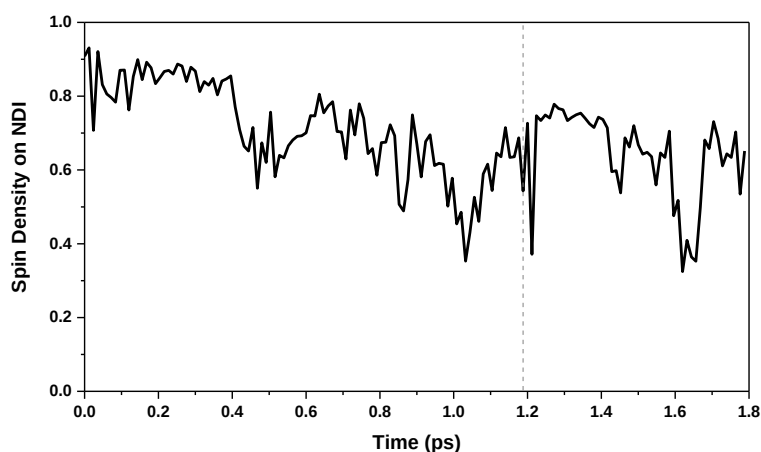


Figure A4.3. Spin density integrated over half of the simulation box including the NDI dye of complex **L1** along the longer constrained 2.5 Å MD trajectory. This figure clearly shows that the spin density fluctuates considerably during the overall constrained 2.5 Å MD simulation, indicating that the electron transfers back and forth between the WOC and dye. In other words, the ET is not completed in such a MD timescale at the current stage of the reaction coordinate $d(\text{O}_i \leftarrow \text{O}_{ii}) = 2.5 \text{ Å}$.

4.A.5. Running Average of the Constraint Force as a Function of Time

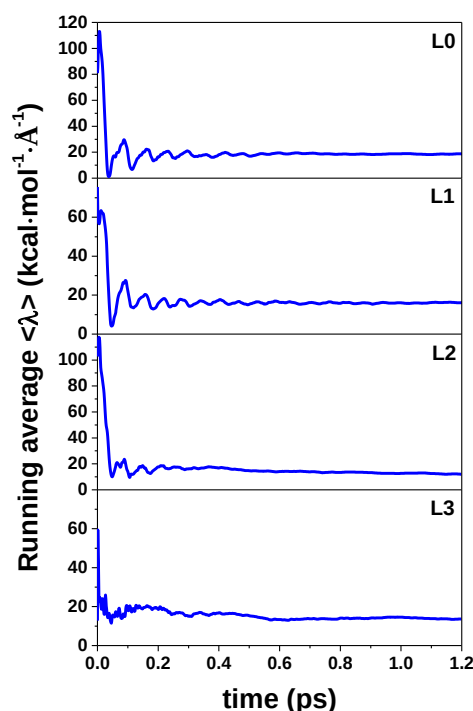


Figure A4.4. The running average of the constraint force $\langle \lambda \rangle$ (in $\text{kcal mol}^{-1} \text{ Å}^{-1}$) as a function of time for the distance constraint $d(\text{O}_i \leftarrow \text{O}_{ii}) = 2.5 \text{ Å}$ of complexes **L0** – **L3**, respectively. The running average reaches a stable value within this MD timescale of $\sim 1.2 \text{ ps}$.

4.A.6. Continued Constrained 1.8 Å MD Simulation for L3

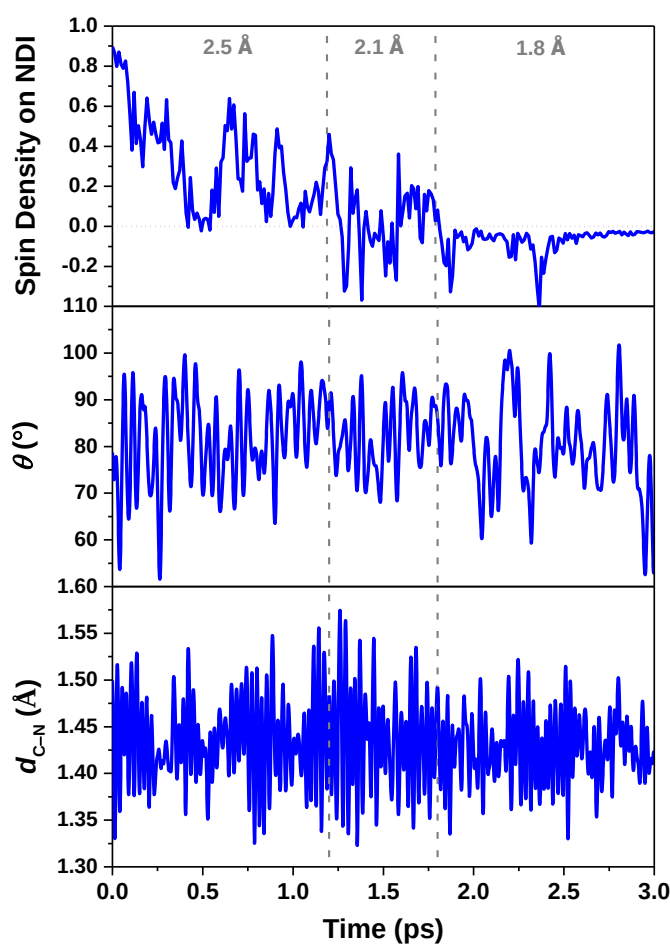


Figure A4.5. Spin density integrated over half of the simulation box including the NDI dye (top panel), time evolution of θ (middle panel) and d_{C-N} (bottom panel) of complex **L3** only along the constrained MD trajectories after the photooxidation of NDI dye. The value of the constrained reaction coordinate $d(O_i \leftarrow O_{ii})$ in the MD simulations is noted in grey.

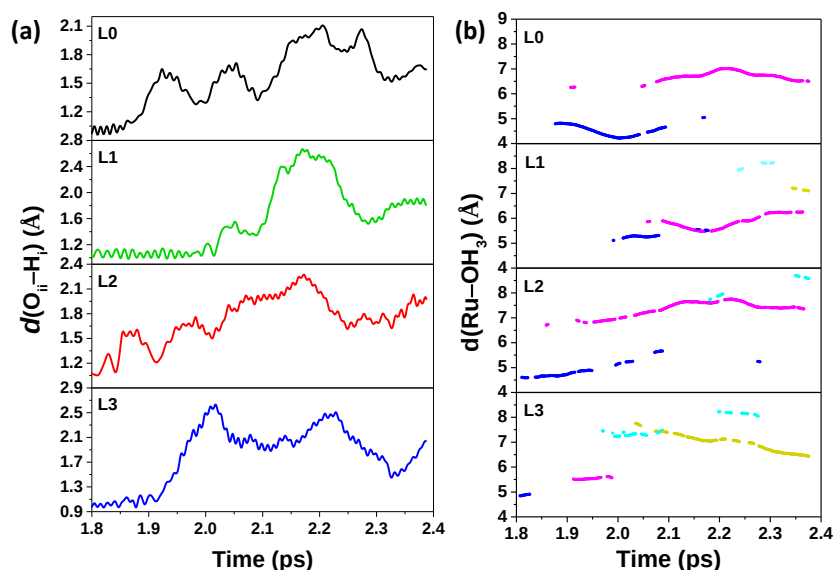
4.A.7. Proton Transfer for L0 – L3 at $d(\text{O}_i \leftarrow \text{O}_{ii}) = 1.8 \text{ \AA}$ 

Figure A4.6. (a) Time evolution of the geometrical parameter $d(\text{O}_{ii}-\text{H}_i)$ along the constrained MD trajectory with $d(\text{O}_i \leftarrow \text{O}_{ii}) = 1.8 \text{ \AA}$ for complexes **L0** – **L3**. (b) The distance between Ru and H_3O^+ , defined as an oxygen atom with 3 H within a radius of $1.2 \text{ \AA}$, illustrating the proton diffusion during the constrained $1.8 \text{ \AA}$ MD simulations for complexes **L0** – **L3**. The analysis of the trajectories shows that only one oxygen is in the H_3O^+ form at any time, and the excess proton associates primarily to 2 – 4 different oxygens (indicated with different colours) during the simulation. This figure clearly shows that the proton diffuses from the first solvation shell of the ruthenium center to the second or even third and fourth solvation shell rapidly within this relatively short MD timescale of $\sim 0.6 \text{ ps}$. The time range is consistent with that in **Figure 4.3**.

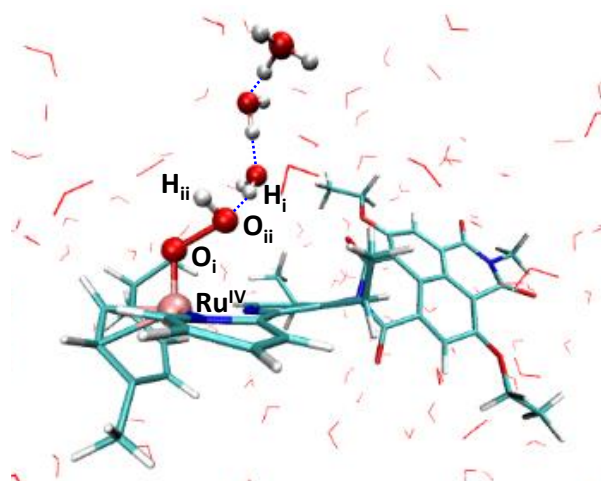


Figure A4.7. Snapshot taken at the end of the constrained $1.8 \text{ \AA}$ simulation for complex **L2**. The attacking water molecule and the neighboring water molecules forming the hydrogen-bonded chain are represented with ball & stick. The dashed blue lines indicate the hydrogen bonds. This figure clearly shows that the proton H_i has been totally released by the attacking water molecule and diffuses rapidly into the solvent bulk via a “chain” of hydrogen-bonded water molecules even within the MD timescale of $\sim 0.6 \text{ ps}$.

4.A.8. Constrained 1.6 Å MD Simulation

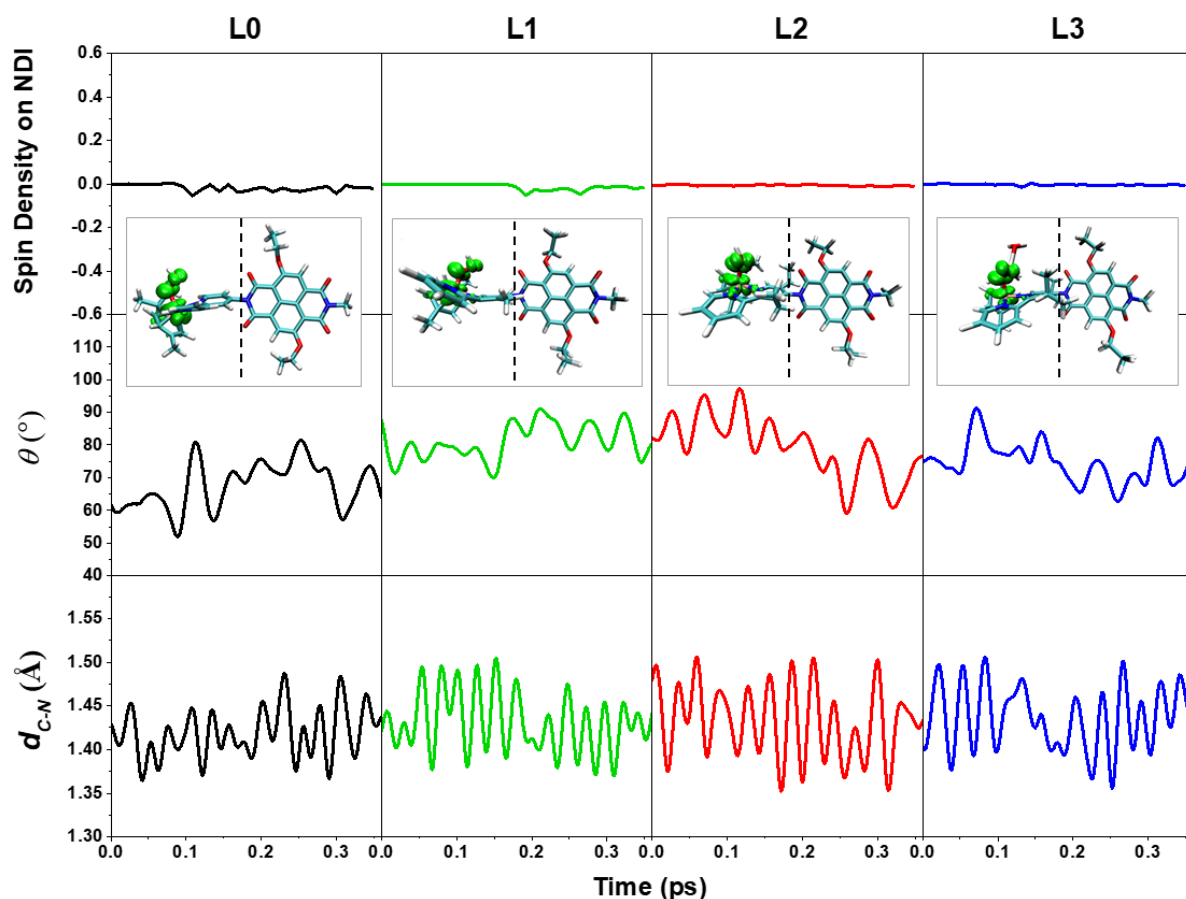


Figure A4.8. Spin density integrated over half of the simulation box including the NDI dye (right-hand side of the dashed black line in the insets), time evolution of θ and d_{C-N} of complexes **L0** – **L3** along the constrained 1.6 Å MD trajectories after the PCET process. The insets show the spin density isosurface computed at a snapshot taken at the end of each MD simulation of complexes **L0** – **L3**, respectively, in the doublet state with one unpaired α electron localized on the catalyst (green spin density isosurface) and no unpaired β electron on the NDI dye. An integrated spin density value of -1 corresponds to one unpaired α electron ($\uparrow$).

4.A.9. O–O Bond Formation during the FMD Simulation

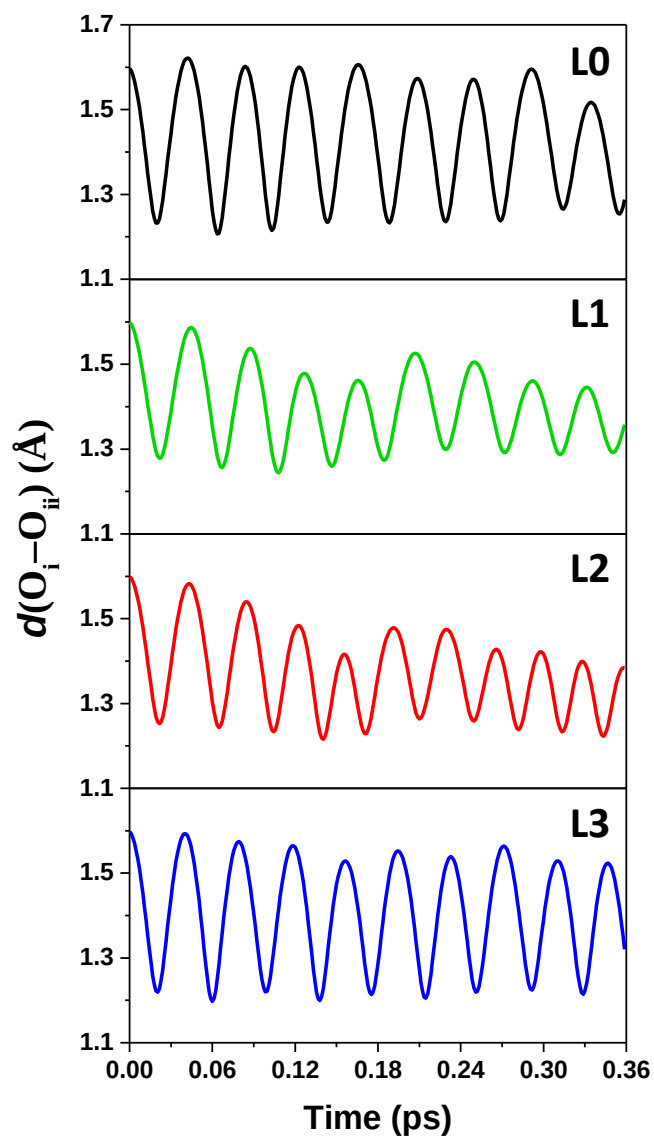


Figure A4.9. Time evolution of the distance between two oxygen atoms O_i and O_{ii} ($d(O_i-O_{ii})$) along the FMD trajectory after the release of constraint at the end of the constrained 1.6 Å MD simulation of complexes **L0** – **L3**.

4.A.10. Time-averaged Constraint Force and Standard Deviation

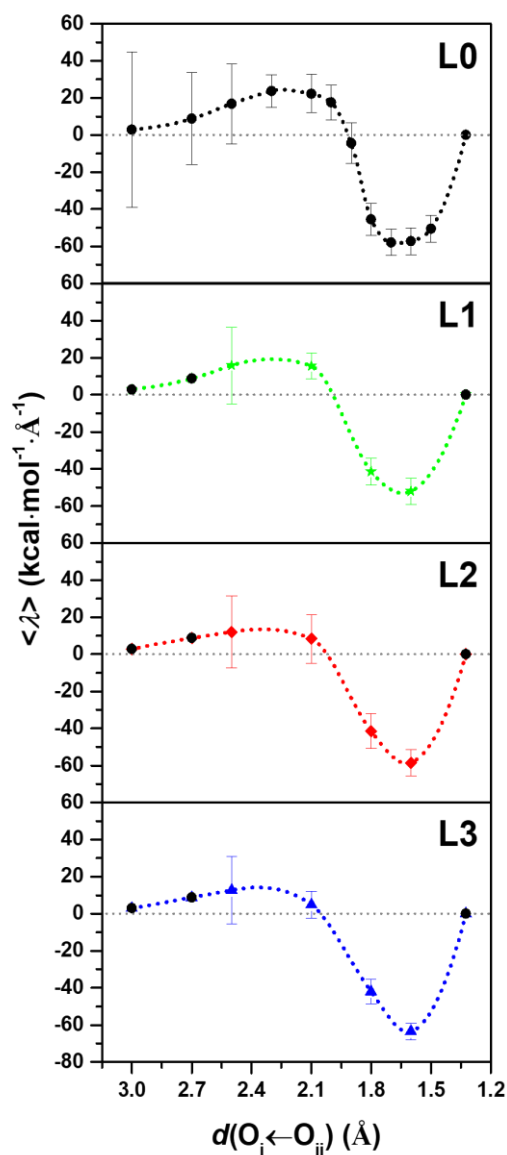


Figure A4.10. Time-averaged constraint force represented by the Lagrangian multiplier $\langle \lambda \rangle$ computed for each constrained MD simulation as a function of the reaction coordinate $d(O_i \leftarrow O_{ii})$ for complexes **L0** – **L3**. The Akima splines (100 points) is used to interpolate the mean forces. The error bars indicate the standard deviations.

4.A.11. Fourier Transform and VDOS

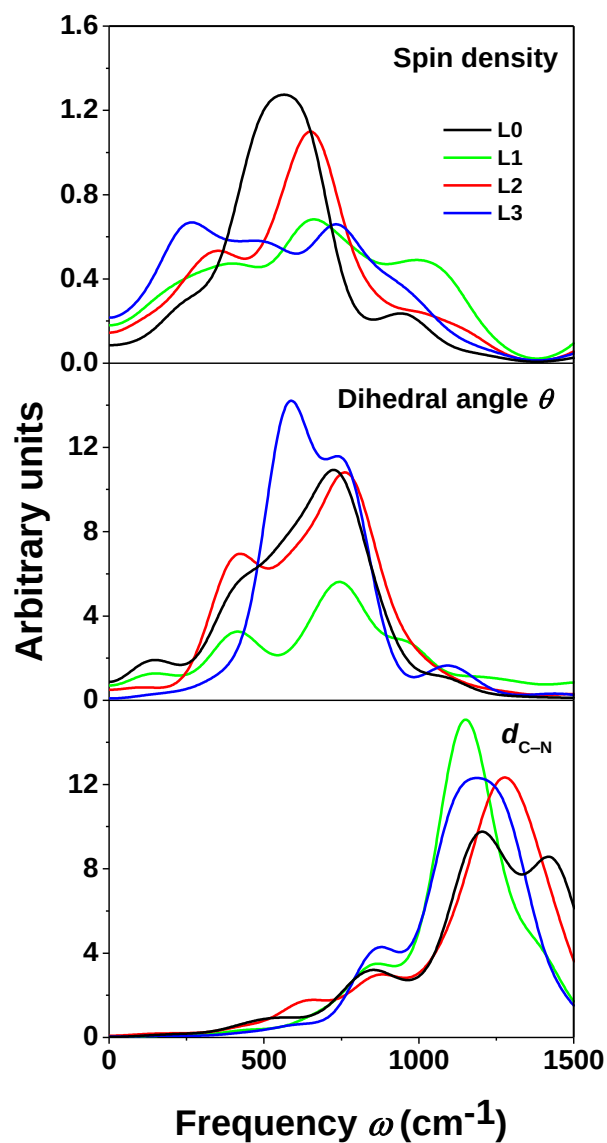


Figure A4.11. Frequency spectrum associated to the ET (top) and the VDOS of the θ (middle) and the $d_{\text{C-N}}$ (bottom) for complexes **L0** – **L3** extracted from the constrained 2.5 Å and 2.1 Å MD trajectories corresponding to **Figure 4.3**.

4.A.12. Geometry Optimization after PCET

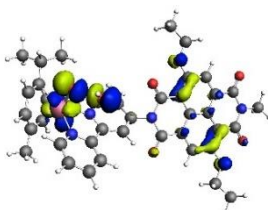
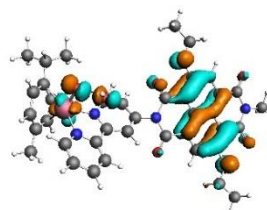
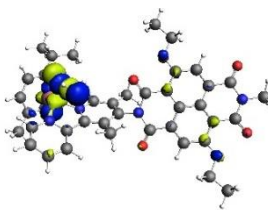
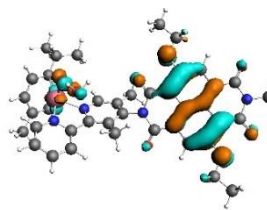
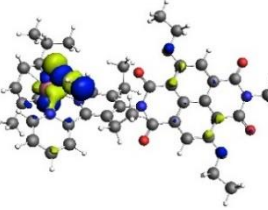
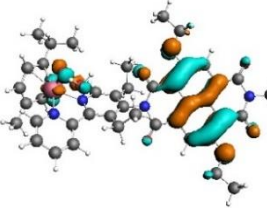
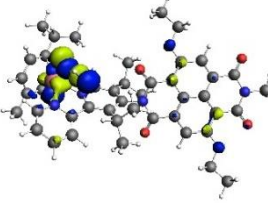
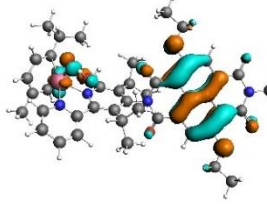
Table A4.2. Calculated geometrical parameters of the initial and final intermediates after geometry optimization for complexes **L0** – **L3**.

Complex	Intermediate			
	Ru=O ^a		Ru-OOH ^b	
	θ_{ini}	$d_{\text{C-N}_{\text{ini}}}$	θ_{fin}	$d_{\text{C-N}_{\text{fin}}}$
L0	66.8	1.424	66.5	1.422
L1	86.5	1.431	86.7	1.428
L2	90.5	1.432	90.3	1.428
L3	91.0	1.433	90.3	1.428

^a θ_{ini} (in °) and $d_{\text{C-N}_{\text{ini}}}$ (in Å) of the initial intermediate (Ru=O) after geometry optimization for complexes **L0** – **L3** extracted from the static DFT calculations. ^b θ_{fin} (in °) and $d_{\text{C-N}_{\text{fin}}}$ (in Å) of the final intermediate (Ru-OOH) after the third PCET step for complexes **L0** – **L3** extracted from the static DFT calculations. See **Scheme 4.1** for the atomic labeling.

4.A.13. TD-DFT Calculation of the Excitation Energies near Transition State

Table A4.3. Excitation energy $\Delta\epsilon$ (in kcal mol⁻¹), oscillator strengths f , and related molecular orbitals for the first excitation of **L0** – **L3** together with the attacking water molecule.^a

Complex	$d(\text{O}_i\text{--O}_{ii})$	$\Delta\epsilon$	f	HOMO	LUMO
L0	1.9	1.788	0.011		
L1	2.0	1.646	0.009		
L2	2.0	1.307	0.006		
L3	2.0	1.291	0.005		

^aThe geometry of all the complexes **L0** – **L3** together with the attacking water molecule are first optimized with the ADF program using OPBE functional and the TZP basis set. The TD-DFT calculations are then performed at the same level. The continuum solvation model COSMO is used to describe the water environment. The distance between the two oxygen atoms O_i and O_{ii} ($d(\text{O}_i\text{--O}_{ii})$, Å) is fixed to certain values which is taken around the transition state according to **Figure 4.4**. The first excitation is mainly related to the transition from HOMO (SOMO WOC) to LUMO (SOMO dye).

4.A.14. References

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