Supporting Information for:

Photocatalytic Water Splitting Cycle in a Dye-catalyst Supramolecular Complex: *Ab initio* Molecular Dynamics Simulations

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Step	Intermediates		$\Delta G_{\text{calc}} (\text{eV})$	$\Delta G_{\mathrm{exp}} (\mathrm{eV})$
1 st	$[\mathrm{Ru}^{\mathrm{II}}\!\!-\!\!\mathrm{OH}_2]^{2\scriptscriptstyle +}\!\rightarrow [\mathrm{Ru}^{\mathrm{III}}\!\!-\!\!\mathrm{OH}]^{2\scriptscriptstyle +}$	$(I_1 \rightarrow I_2)$	0.87	0.67
2^{nd}	$[Ru^{III}\!\!-\!\!OH]^{2+}\!\rightarrow [Ru^{IV}\!\!=\!\!O]^{2+}$	$(I_2 \rightarrow I_3)$	1.38	1.27
3 rd	$[\mathrm{Ru}^{\mathrm{IV}}\!\!=\!\!\mathrm{O}]^{2+}\!\rightarrow [\mathrm{Ru}^{\mathrm{III}}\!\!-\!\!\mathrm{OOH}]^{2+}$	$(I_3 \rightarrow I_4)$	2.19	1.83
4^{th}	$[\mathrm{Ru^{III}}\text{-}\mathrm{OOH}]^{2+} \rightarrow [\mathrm{Ru^{II}}\text{-}\mathrm{OO}]^{2+}$	$(I_4 \rightarrow I_0)$	0.73	
	$[\mathrm{Ru^{II}}\text{-}\mathrm{OO}]^{2+} \rightarrow [\mathrm{Ru^{II}}\text{-}\mathrm{OH_2}]^{2+}$	$(\mathrm{I}_0 \to \mathrm{I}_1)$	-0.15	
	$2H_2O \rightarrow 2H_2 + O_2$		5.02	4.92



Figure S1. Free energy difference (ΔG) between intermediates along the catalytic pathway of the $[Ru^{II}-OH_2]^{2+}$ catalyst. DFT results (dashed blue line) are compared with the values extracted from electrochemical data (dashed red line). We also show for comparison the optimal catalyst case (black line) corresponding to a change in free energy of 1.23 eV for all four steps (adapted from Ref. 44 in the main text).



Figure S2. Schematic diagram of (a) a proposed dye-sensitized photoelectrochemical cell (DS-PEC) for solar-energy conversion and (b) WOC-dye supramolecular complex considered in this work in the photooxidized state.

Table S2. Selected frontier molecular orbital energy levels and energy difference between SOMO WOC (HOMO WOC for ${}^{2}([Ru^{II}-OH_{2}]^{2+}-NDI^{+}))$ and SOMO dye (ΔE , in eV) of four intermediates along the catalytic pathway of the $[Ru^{II}-OH_{2}]^{2+}$ catalyst following route (1) in Scheme 1 computed with the ADF program using the OPBE (and PBE for comparison) 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 electron localized on the catalyst and blue for unpaired electron on the oxidized NDI⁺⁺). SOMO stands for singly occupied molecular orbital. All energies are in eV.

Intermediate	² ([Ru ^{II} -OH ₂] ²⁺ -	NDI+•)	³ ([Ru ^{III} -OH] ²	²⁺ -NDI ^{+•})	² ([Ru ^{IV} =O] ²⁺ ·	·NDI+•)	³ ([Ru ^{III} -OOH]	²⁺ -NDI ^{+•})
		<u>+</u>	<u>+</u>	1	<u>↑</u> †	ŧ	+	1
	OPBE							
Energy levels	Orbital	Energy	Orbital	Energy	Orbital	Energy	Orbital	Energy
LUMO	β	-6.1172	β	-6.1144	α	-6.1226	β	-6.1008
НОМО	β] (HOMO WOO)	-6.2913	α (SOMO WOC)	-6.3430	α (SOMO WOC)	-6.2750	α (SOMO WOC)	-6.1607
HOMO-1	α { (HOMO WOC)	-6.2940	α (SOMO dye)	-6.4600	β (SOMO dye)	-6.4682	α (SOMO dye)	-6.4491
HOMO-2	α (SOMO dye)	-6.4628	eta	-6.6804	α	-6.7321	β	-6.7675
НОМО-3	β	-6.6995	eta	-6.7566	β	-6.7648	α	-6.8002
HOMO-4	α	-6.6995	α	-6.7920	α	-6.8274	β	-6.8437
ΔΕ		0.1714		0.1170		0.1932		0.2884
				PB	E			
Energy levels	Orbital	Energy	Orbital	Energy	Orbital	Energy	Orbital	Energy
LUMO	β	-6.1172	β	-6.1226	α	-6.1281	β	-6.1281
НОМО	β] (HOMO WOO)	-6.2723	α (SOMO WOC)	-6.3512	α (SOMO WOC)	-6.2641	α (SOMO WOC)	-6.1852
HOMO-1	α { (HOMO WOC)	-6.2723	α (SOMO dye)	-6.4355	β (SOMO dye)	-6.4383	α (SOMO dye)	-6.4410
HOMO-2	α (SOMO dye)	-6.4301	eta	-6.6886	α	-6.7213	β	-6.7321
НОМО-3	β	-6.5716	eta	-6.7349	α	-6.7430	α	-6.7539
HOMO-4	α	-6.5743	α	-6.7566	β	-6.7458	β	-6.8954
ΔE		0.1578		0.0844		0.1742		0.2558



Figure S3. Selected frontier molecular orbitals of involved intermediates after photooxidation of NDI during the four consecutive catalytic steps in route (1) computed with the ADF program using the OPBE functional and the TZP basis set. The continuum solvation model (COSMO³⁻⁴) is used to describe the water environment. The left (black) and right (red) columns refer to as the α orbitals and β orbitals, respectively. Only the unpaired electrons are indicated by vertical arrows explicitly (green for unpaired electron localized on the catalyst and blue for unpaired electron on the oxidized NDI⁺⁺). See Table S2 for the molecular energy levels.

For all these intermediates, the partially occupied molecular orbital localized on the NDI is always lower in energy than the HOMO of the supramolecular complex, which is localized on the ruthenium catalyst. This result suggests that for all the oxidized intermediates there is a driving force for electron transfer from the ruthenium catalyst to the NDI dye in continuum solvation model. The ab initio MD simulations presented in this work show that this is also the case in explicit solvent.



Figure S4. Time evolution of the geometrical parameter $d(H_i-O_i)$ (black line) and $d(H_i-O_{ii})$ (blue line) along the free MD simulation for the oxidized intermediate ${}^{3}([Ru^{III}-OH]^{2+}-NDI^{++})$ in route (1). See scheme 2 for the atomic labelling. We can observe a shortened $d(H_i-O_{ii}) \approx 1.3$ Å and a corresponding stretched $d(H_i-O_i) \approx 1.1$ Å at several time intervals (~0.25 ps, ~0.71 ps, and ~1.84 ps), which can be interpreted as spontaneous attempts of proton transfer from the hydroxide to the neighboring water molecule. The inset shows the spin density isosurface (green) computed at a snapshot taken at ~1.4 ps, clearly indicating that one unpaired α electron is localized on the catalyst and the other unpaired α electron on the oxidized NDI⁺⁺.



Figure S5. The constraint force (λ , in kcal mol⁻¹ Å⁻¹) and running average of the constraint force ($\langle \lambda \rangle$, in kcal mol⁻¹ Å⁻¹) as a function of time for two different distance constraints $d(H_i \leftarrow O_{ii}) = 1.6$ Å (**a**, **c**) and $d(H_i \leftarrow O_{ii}) = 1.4$ Å (**b**, **d**), respectively. The running average reaches a stable value even within this relatively short MD timescale of ~0.5 ps.



Figure S6. (top) Maximum (red) and minimum (blue) interpolations of the Lagrangian multiplier $\langle \lambda \rangle$ reproduced from Figure 2. The error bars indicate the standard deviations. (**bottom**) Free energy profiles along the reaction coordinate d(H_i \leftarrow O_{ii}) computed from thermodynamic integration of the interpolated time-averaged mean forces.



Figure S7. (top) The constraint mean force represented by the Lagrangian multiplier $\langle \lambda \rangle$ computed for each constrained MD simulation as a function of the reaction coordinate $d(H_i \leftarrow O_{ii})$ along route (2) (blue triangles) and (1) (red squares), for comparison. The mean force at the equilibrium distance $d(H_i - O_{ii}) = 0.98$ Å evaluated in the free MD has been set to 0. The 100-point Akima spline interpolation (dotted lines) is used to interpolate the mean forces including also the zero point at equilibrium. (**bottom**) Free energy profile along the reaction coordinate $d(H_i \leftarrow O_{ii})$ of route (2) (blue line) and (1) (red line) computed from thermodynamic integration of the interpolated time-averaged mean forces. The initial and final intermediates are also indicated.



Figure S8. Time evolution of the Kohn-Sham energy of the product intermediates ${}^{3}([Ru^{IV}=O]^{2+}-NDI)$ (red line) and ${}^{1}([Ru^{IV}=O]^{2+}-NDI)$ (blue line) along the free MD trajectories after the second catalytic step. Although large energy fluctuations are observed during the MD simulations, the product intermediate ${}^{3}([Ru^{IV}=O]^{2+}-NDI)$ is on average lower in energy than ${}^{1}([Ru^{IV}=O]^{2+}-NDI)$ (see Table S3).

Table S3. Time-averaged Kohn-Sham energy (KS energy) of the product intermediates ³ ([$Ru^{IV} = O]^{2+-1}$	NDI) and
¹ ([Ru ^{IV} =O] ²⁺ –NDI) along the free MD trajectories (see Figure S6).		

2S+1	Intermediate	KS energy	Energy difference
	$[Ru^{IV}=O]^{2+} - NDI$	eV	eV
3	↑ ↑	-89429.615	1 212
1	↑ ↓	-89428.302	1.313



Figure S9. (top) The spin density integrated over the half of the simulation box including the catalyst (left-hand side of the dashed black line in the inset **b** and **c**) along the MD trajectories starting from the oxidized intermediate ¹([Ru^{III}-OH]²⁺-NDI⁺) (see route 2) in Scheme 1). An integrated spin density value of -1 corresponds to one unpaired α electron. The starting configuration at $d(H_i \leftarrow O_{ii}) = 1.6$ Å has been extracted from a previous unconstrained simulation of the first catalytic intermediate for ~1 ps (with an average $d(H_i-O_{ii}) \approx 1.7$ Å). (middle) Time evolution of the geometrical parameter $d(H_i - O_i)$ along the constrained and free MD (FMD) trajectory. (bottom) The distance between Ru and H_3O^+ , defined as an oxygen atom with 3 H within a radius of 1.2 Å, as measured for a sequence of MD simulations. According to the simulations, only one oxygen is in the H_3O^+ form at any time, and although the proton associates with a number of different oxygens (indicated with different colours) during the simulation, it is primarily bonded to four oxygens (blue, gold, red and purple). The value of the constrained reaction coordinate $d(H_i \leftarrow O_{ii})$ applied in the MD simulations is noted in grey. Inset (a) shows the schematic structure of the first few water molecules along the hydrogen-bonding network coordinated to the hydroxide ligand. The red double sided arrow indicates the reaction coordinate considered for oxidized intermediate ${}^{1}([Ru^{III}-OH]^{2+}-NDI^{+})$ during the constrained MD simulations. **Inset** (b) and (c) show snapshots from the FMD and constrained MD trajectories, in which the spin density isosurface of α and β electrons in green and purple respectively. The labels refer to the time at which the snapshot has been taken along the collected trajectory.



Figure S10. (a) Configuration of the attacking water molecule during the free MD at room temperature. (b) – (f) Snapshots from the constrained MD trajectories at different $d(O_i \leftarrow O_{ii})$ (in purple) with spin multiplicity 2S+1 = 2. Only the attacking water molecule, the ruthenium metal center and the oxygen coordinating to it are shown explicitly. The orientation rearrangement of the attacking water molecule during this process is clearly visible.



Figure S11. The attacking water molecule and the neighboring water molecules along the hydrogen-bonding network (dashed blue lines) at the beginning of the constrained simulation with $d(O_i \leftarrow O_{ii}) = 2.0$ Å.



Figure S12. Time evolution of the geometrical parameter $d(H_{ii}-O_{ii})$ (black line) and $d(H_{ii}-O_{iii})$ (blue line) along the constrained MD simulations (route 1). See **Figure S9** for the atomic labels. The value of the constrained reaction coordinate $d(O_i \leftarrow O_{ii})$ in the MD simulations is noted in grey. The red vertical arrow indicates a first proton transfer attempt during the constrained 1.9 Å simulation followed by fast back reaction.



Figure S13. (top-left) Average constraint force represented by the Lagrangian multiplier $\langle \lambda \rangle$ computed for each constrained MD simulation of route (2) (blue triangles) and (1) (red squares, for comparison) as a function of the reaction coordinate $d(O_i \leftarrow O_{ii})$. The Akima spline (100 points) is used to interpolate the mean forces. The point at $d(O_i - O_{ii}) = 1.32$ Å corresponds to the equilibrium product state and thus its $\langle \lambda \rangle$ is assumed to be zero. (top-right) Free energy profile along the reaction coordinate $d(O_i \leftarrow O_{ii})$ of route (2) computed from thermodynamic integration, compared to the results for route (1). (bottom) The spin density integrated over the half of the simulation box that includes the catalyst along the constrained and free MD (FMD) trajectory of route (2). The value of the constrained reaction coordinate $d(O_i \leftarrow O_{ii})$ in the MD simulations is noted in grey. Inset (a) shows the schematic structure of the first water molecule along the hydrogen-bonding network coordinated to the oxygen ligand. The red double sided arrow indicates the reaction coordinate considered for $[Ru^{IV}=O]^{2+...}(H_2O)$ during the constrained MD simulations. Inset (b) and (c) show snapshots from the constrained MD trajectory, in which the spin density isosurface of α and β electrons in green and purple respectively. The labels refer to the time at which the snapshot has been taken along the collected trajectory.



Figure S14. Combination of free energy profiles computed from thermodynamic integration for all steps in the catalytic cycle. For the first step (black line) only one spin state is possible. For the second and third step two different spin alignments are considered: route (1) (red line) and route (2) (blue line). The 4th step (black dotted arrow) is found to proceed spontaneously at room temperature for both spin alignments (S = 0 / S = 1), which implies no significant activation barrier. The black squares indicate the stable intermediates, while the green triangles correspond to the supramolecular complex after photooxidation of the NDI dye, leading to NDI⁺⁺. The dashed grey break arrow (not in scale) indicates the change in energy due to the photoinduced electron transfer from the NDI to the semiconductor. For the second and fourth step the two possible spin alignments after photooxidation are found to be essentially degenerate (see **Table S4**). The product ²([Ru^{III}–OOH]²⁺–NDI) at the end of the third step can be only in the S = 1/2 state. The small free energy difference found between the two routes is due to statistical/numerical errors in the thermodynamic integration procedure.

Table S4. Total bonding energy (*E* in kcal mol⁻¹) computed for each catalytic intermediate at the DFT level. Computational details are described in section 2.1 of the main manuscript. The spin alignment of the unpaired electron on the Ru-based catalyst and NDI (\ddagger for α electron and \ddagger for β electron) and the spin multiplicity of the system (2S+1) are also shown. ΔE (kcal mol⁻¹) is the computed energy difference between different spin alignments and is calculated with respect to the lowest energy spin state for each catalytic step.

Step		Intermediate	2S+1	E	ΔE
	Reactant	[Ru ^{II} –OH ₂] ²⁺ –NDI ^{+•}			
1^{st}		<u></u>	2	-13408.4	
	Product	[Ru ^{III} –OH] ²⁺ –NDI			
		<u> </u>	2	-13424.2	
	Reactant	[Ru ^{III} –OH] ²⁺ –NDI ^{+•}			
		$\uparrow \qquad \downarrow \qquad \qquad \downarrow$	1	-13292.1	0
		$[Ru^{m} OH]^{2} - NDI^{*}$	3	-13292.0	0.1
2^{nd}	Product	[Ru ^{IV} =O] ²⁺ -NDI	5	15272.0	0.1
	Tioudet	↓ ↓	1	-13298.1	7.5
		[Ru ^{IV} =O] ²⁺ -NDI	-		
		÷ ÷	3	-13305.6	0
	Reactant	[Ru ^{IV} =O] ²⁺ –NDI ^{+•}			
		↑ ↑ ↓	2	-13173.6	0
3rd		$[Ru^{IV}=O]^{2+}-NDI^{+}$			
5		<u>+ + +</u>	2	-13167.6	6.0
	Product	[Ru ^{III} –OOH] ²⁺ –NDI			
		<u>+</u>	2	-13532.4	
	Reactant	[Ru ^{III} –OOH] ²⁺ –NDI ^{+•}			_
4 th			1	-13400.9	0
		[Rum=OOH] ²⁺ -NDI ⁺	2	12400.2	0.6
	Decduct	+ +	3	-13400.3	0.0
	Flouuet		1	13421 4	9.4
		$\uparrow \downarrow \downarrow$ [Bu ^{II} -OO1 ²⁺ -NDI	1	-13421.4	7.4
			3	-13430.8	0
		1 1	-		~



Figure S15. Spin density localization at different snapshots along the free MD trajectory for the final step in the catalytic cycle (see **Figure 6**). The hole (spin density) localized on the NDI immediately after photooxidation (0.36 ps) is very quickly filled by the electron from the catalyst within approximately 50 fs. In the snapshot taken at 0.4 ps the proton has been already transferred to the solvent neighbouring water molecules temporarily forming a $(O_2H_5)^+$ complex (see inset above). The spin density at the end of the process is mostly localized on the O_2 ligand and shows the characteristic shape expected for the oxygen molecule (see also enlargement in the inset). A small amount of spin density can be seen localized on a few water molecules due to transient solvent polarization effects.



Figure S16. (top) The spin density integrated over the half of the simulation box including the catalyst before and after the photoinduced electron injection, which is mimicked by removing one electron from the system at 0.36 ps (indicated by the grey dotted line) to generate an oxidized ¹($[Ru^{III}-OOH]^{2+}-NDI^{++}$) in the S = 0 state (see Scheme 1). The inset shows the spin density isosurface computed at a snapshot taken at ~0.66 ps, clearly indicating that one unpaired α electron (green spin density isosurface) and one unpaired β electron (purple spin density isosurface) are localized on the catalyst. (**middle**) The distance between Ru and H₃O⁺ measured for the free MD simulations. According to the simulations, the proton primarily bonds to three oxygens (green, purple and magenta). (**bottom**) Time evolution of the geometrical parameter d(Ru–O_i) (blue line) and d(O_i–O_{ii}) (black line) along the free MD trajectory (see labeling in Scheme 2c).



Figure S17. Time evolution of the Kohn-Sham energy of the product intermediates ${}^{3}([Ru^{II}-OO]^{2+}-NDI)$ (red line) and ${}^{1}([Ru^{II}-OO]^{2+}-NDI)$ (blue line) along the free MD trajectories after the fourth catalytic step. Although large fluctuations are observed during the MD simulations, the intermediate ${}^{3}([Ru^{II}-OO]^{2+}-NDI)$ indicates a relatively more stable product much lower in energy most of the time compared to the ${}^{1}([Ru^{II}-OO]^{2+}-NDI)$.

Table S5. Time-averaged Kohn-Sham energy (KS energy) of the product intermediates ³ ([Ru ^{II} –OO] ²⁺ –NDI) and
$([Ru^{II}-OO]^{2+}-NDI)$ along the free MD trajectories after the fourth catalytic step. The triplet state is on average
almost 1 eV lower in energy than the singlet state.

2S+1	Intermediate	KS energy	Energy difference
	$[Ru^{II}-OO]^{2+} - NDI$	eV	eV
3	 ↑ ↑	-89395.046	0.062
1	↑ ↓	-89394.084	0.902



Figure S18. The spin density integrated over the half of the simulation box including the catalyst (red line) and time evolution of the geometrical parameter dihedral angle \angle C1-N1-C2-C3 (blue line) along the MD trajectories of (a) second and (b) third catalytic step (see labelling in Scheme 1), respectively. An integrated spin density value of -1 corresponds to one unpaired α electron. The value of the constrained reaction coordinate applied in the MD simulations for the second (a) and third (b) steps is noted in grey.

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