Electronic Supplementary Information

A computational mechanistic investigation of hydrogen production in water with the $[Rh^{III}(dmbpy)_2Cl_2]^+ / [Ru^{II}(bpy)_3]^{2+} / ascorbic acid photocatalytic system$

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Optimized structures of $[Ru^{II}(bpy)_3]^{2+}$ **and** $[Ru^{II}(bpy)_2(bpy^{-})]^+$ **in water.** The most important calculated structural parameters, obtained after complete DFT geometry optimization in water solvent, of the electronic ground states of the Ru^{II} photosensitizer and of its reduced state in water are reported in Table S1. The experimental values of $[Ru^{II}(bpy)_3]^{2+}$ obtained by single-crystal X-ray crystallographic analysis^{1,2} are also reported in Table S1 for comparison. The optimized and crystal structures are depicted in Figure S1. Note that geometry optimization and electronic transitions of $[Ru^{II}(bpy)_3]^{2+}$ complex at DFT level was previously reported in the literature.³⁻⁹



Figure S1. Optimized structure in water (a) and crystal structure² (b) of $[Ru(bpy)_3]^{2+}$ complex in the electronic ground state.

Table S1. Calculated bond lengths (Å) and bond angles (°) of the optimized structures of $[Ru^{II}(bpy)_3]^{2+}(D_3 \text{ symmetry})$ and $[Ru^{II}(bpy)_2(bpy^{-})]^+(C_2 \text{ symmetry})$ in the electronic ground state in water and experimental values of $[Ru^{II}(bpy)_3](PF_6)_2$ from its X-Ray crystallographic structure.

	1		
	[Ru ^{II}	$(bpy)_{3}^{2+}$	$[Ru''(bpy)_2(bpy')]$
	Optimized	Experimental ²	Optimized
	Во	nd lengths (Å)	-
Ru-N1	2.113	2.056	2.102
Ru-N2	2.113	2.056	2.102
Ru-N3	2.113	2.056	2.115
N1-C1	1.363	1.354	1.393
N2-C2	1.363	1.354	1.365
N3-C3	1.363	1.354	1.365
N1-C4	1.346	1.354	1.349
N2-C5	1.346	1.354	1.348
N3-C6	1.346	1.354	1.347
C1-C1'	1.477	1.474	1.430
C2-C2'	1.477	1.474	1.472
	В	ond angles(°)	
N1-Ru-N1'	77.72	78.7	78.62
N1-Ru-N2	88.40	89.1	89.12
N1-Ru-N3	172.92	173.0	171.71
N1'-Ru-N2	97.13	96.3	95.67
Ru-N1-C1	115.60	115.9	114.39
Ru-N1-C4	125.28	126.0	126.47

The theoretical and experimental data (reported in Table S1) agree rather well with a small overestimation (< 3%) of the Ru-N bond length by DFT/B3LYP. The optimized structures of $[Ru^{II}(bpy)_3]^{2+}$ and of its reduced state are very similar. The most significant structural change due to the symmetry breaking in the reduced complex is a shortening of the C1-C1' bond with

respect to the other C-C bridging bonds of the bpy ligands, consequence of the relocalization of the electronic density. The additional electron of $[Ru^{II}(bpy)_2(bpy^{\bullet})]^+$ occupies a Kohn-Sham orbital which is mainly localized on one bpy ligand and has bonding character on C1-C1' bond (see Figure S2 for the SOMO of $[Ru^{II}(bpy)_2(bpy^{\bullet})]^+$). This is illustrated by the values reported in Table S1 for the length of C1-C1' (1.430 Å) shorter than those of other two bpy ligands of $[Ru^{II}(bpy)_2(bpy^{\bullet})]^+$, namely C2-C2' (1.472 Å). The question of localisation of the electron density on one bpy ligand for $[Ru^{II}(bpy)_2(bpy^{\bullet})]^+$ has been extensively investigated in literature by EPR and absorption spectroscopies.¹⁰⁻¹⁶

The possible structures of $[Ru^{II}(bpy)_3]^{2+}$ in the lowest triplet state have been optimized under D₃ and C₂ symmetries. Both of them converge to MLCT excited states and the C₂ structure is slightly more stable than the D₃ structure by 1.1 kJ/mol. The C₂ structure has been used as reference in the discussion of the catalytic cycle.



Figure S2. Singly occupied molecular orbital (SOMO) of [Ru^{II}(bpy)₂(bpy[•])]⁺.

Optimized structures of Rh complexes in water. The most important calculated bond lengths and bond angles of the electronic ground states of the Rh^{III} initial catalyst and of some important Rh^I, Rh^{II} and Rh^{III} key intermediates are reported in Tables S2-S6 (*i.e.* [Rh^{III}(dmbpy)₂(Cl)₂]⁺, [Rh^{III}(dmbpy)₂(H₂O)₂]³⁺ [Rh^{III}(dmbpy)₂(Cl)(H₂O)]²⁺, [Rh^{III}(dmbpy)₂(Cl)₂]⁰, [Rh^{III}(dmbpy)₂(H₂O)₂]²⁺, [Rh^{III}(dmbpy)₂(Cl)]⁺, [Rh^{III}(dmbpy)₂(H₂O)]²⁺, [Rh^{III}(dmbpy)₂]⁺, [Rh^{III}(dmbpy)₂(H₂O)]²⁺, [Rh^{III}(dmbpy)₂]⁺, [Rh^{III}(dmbpy)₂(H₂O)]²⁺, [Rh^{III}(H)(dmbpy)₂]⁺, [Rh^{III}(H)(dmbpy)₂(H₂O)]²⁺, [Rh^{III}(H)(dmbpy)₂(Cl)]⁺, [Rh^{III}(H)(dmbpy)₂(Cl)]⁰ and [Rh^{III}(H)(dmbpy)₂(H₂O)]⁺). All of these optimized structures are depicted in Figures S3-S4.

The initial $[Rh^{III}(dmbpy)_2(Cl)_2]^+$ catalyst adopts an octahedral geometry with a C₂ symmetry (Figure S3). Slightly overestimation (2-4%) of the Rh-N and Rh-Cl bond distances by the calculation are observed for this catalyst (Table S2) compared to the crystallographic data obtained for the $[Rh^{III}(bpy)_2(Cl)_2]^+$ analogue.¹⁷ This is a general trend observed in similar studies.¹⁸ When one or two chloride ligands are substituted by aquo ligands in the initial Rh^{III} complex, the distances separating the rhodium and the nitrogen atoms which are coordinated to the opposite side of the aquo ligands (*i.e.* Rh-N" for $[Rh^{III}(bpy)_2(Cl)(H_2O)]^{2+}$ and Rh-N and Rh-N" for $[Rh^{III}(dmbpy)_2(H_2O)_2]^{3+}$) become shorter by 0.04 Å. $[Rh^{III}(dmbpy)_2(H_2O)_2]^{3+}$ is slightly distorted from C₂ symmetry due to hydrogen atoms of aquo ligands.

DFT calculation show that the reduction of the initial Rh^{III} catalyst leads to the

 $[Rh^{II}(dmbpy)_2(Cl)]^+$ complex, in which one chloride is released (Table S3 and Figure S3). In this pentacoordinated Rh^{II} complex, the structure is basically unchanged despite of the loss one Cl⁻ and it possesses a C₁ symmetry. The Rh-Cl and Rh-N" bonds undergo an elongation, the N-Rh-N" and N'-Rh-N" angles increased while the N-Rh-N' and N-Rh-N" angles slightly decreased. The aquo derivative $[Rh^{II}(dmbpy)_2(H_2O)]^+$ displays the same C₁ symmetry with shorter Rh-N and Rh-N' bond which locate in the same plane of aquo ligand. The DFT study shows that the Rh^{II} oxidation state is more stable within a penta-coordinated structure than in a hexa-coordinated structure since, when $[Rh^{III}(dmbpy)_2(X)_2]^{n+}$ (X = H₂O or Cl⁻) is reduced, the added electron occupies an metal-localized orbital which is the sixth coordination site of $[Rh^{II}(dmbpy)_2(X)]^{n+}$. In the hexa-coordinated structure of Rh^{II}, one Cl⁻ or H₂O ligand weakly coordinates to Rh with Rh-Cl/O distance of 3.033 and 2.565 Å, respectively.

Then $[Rh^{II}(dmbpy)_2(CI)]^+$ is reduced into $[Rh^I(dmbpy)_2]^+$ concomitantly with the loss of the last CI⁻ ligand. During this reduction, a significant change of geometry is calculated and observed experimentally.¹⁸ The most important bond lengths and bond angles of $[Rh^I(dmbpy)_2]^+$ are given in Table S4, and this calculated values match well to the experimental data.¹⁸ As previously observed by Fujita et al.¹⁸ in crystal structure and by DFT calculation of the analogue $[Rh^I(bpy)_2]^+$ complex, $[Rh^I(dmbpy)_2]^+$ exhibits a tetrahedrally distorted square-planar geometry with a D₂ symmetry. Even if the bond lengths in the structure of the Rh^I state are almost unchanged compared to those of Rh^{II} state, the N-Rh-N", N-Rh-N" and N'-Rh-N" angles are subject to drastic changes induced by the change in geometry of the rhodium complex. The $[Rh^I(dmbpy)_2]^+$ complex can be potentially reduced into $[Rh^I(dmbpy)(dmbpy^{-})]^0$, even if its reduction by $[Ru^{II}(bpy)_2(bpy^{-})]^+$ is an endergonic reaction. This reduction generates small changes in the structure with decrease of coordination bond and C1-C1' bond of dmbpy ligands (Figure S3, Table S4).

This opened coordination sphere of the rhodium allows the oxidative addition of a proton on the $[Rh^{I}(dmbpy)_{2}]^{+}$ species to give the penta-coordinated $[Rh^{III}(H)(dmbpy)_{2}]^{2+}$ hydride, which induces a small structural perturbation (Figure S4 and Table S5). The only noticeable changes are an elongation of the Rh-N bond by 0.02 Å due to the weakening of the $d\pi_{Rh}/\pi_{bpv}$ bonding interaction by formation of the σ_{Rh-H} bond, and a increase of the N-Rh-N" angle by 1.9°. The calculated Rh-H value of 1.497 Å in [Rh^{III}(H)(dmbpy)₂]²⁺ is in the range of the distance between 1.45 Å and 1.55 Å observed in the literature for rhodium(III) hydrides.¹⁹ However, the formation of the Rh^{III}(H) hydride could be also coupled to the coordination of Cl⁻ or H₂O $[Rh^{III}(H)(dmbpy)_2(Cl)]^+$ vielding the octahedral hydrides ligand or $[Rh^{III}(H)(dmbpy)_2(H_2O)]^{2+}$. Indeed, the theoretical study reveals that the $Rh^{III}(H)$ hydride species is more stable with a hexa-coordinated environment rather than a penta-coordinated one. As shown in Table S5, both hexa-coordinated Rh^{III}(H) hydrides structures display similar optimized bond lengths and bond angles especially with Rh-H bond distances of about 1.543 and 1.546 Å in $[Rh^{III}(H)(dmbpy)_2(Cl)]^+$ and $[Rh^{III}(H)(dmbpy)_2(H_2O)]^{2+}$, respectively. These distances are also comparable to those reported for other Rh^{III}(H) hydrides.¹⁹

In fine, the reduction of the hexacoordinated $[Rh^{III}(H)(dmbpy)_2(X)]^{n+}$ complexes (X = H₂O or Cl⁻) is accompanied by a loss the X ligand to give the penta-coordinated $[Rh^{II}(H)(dmbpy)_2]^+$, as already observed for the reduction of the initial $[Rh^{III}(dmbpy)_2(X)_2]^{n+}$ catalyst (*vide supra*) (Figure S4). Calculations demonstrate that the Rh^{II}(H) hydride species is more stable in a penta-coordinated structure displaying a distorted square-pyramidal geometry. Thus, this

reduction involves a real change of geometry coupled to a weak elongation of both the Rh-H bond (1.585 Å, Table S6) and of Rh-N and Rh-N' bonds (by about 10% and 1% respectively). Besides, the N-Rh-N" and N-Rh-N" angles undergo an increase respectively of 0.6° and 8.8° after the reduction of $[Rh^{III}(H)(dmbpy)_2(H_2O)]^{2+}$, while after the reduction of $[Rh^{III}(H)(dmbpy)_2(Cl)]^{+}$, these angles decrease respectively of 1.18° and 0.72° .



Figure S3. Optimized structures of $[Rh^{III}(dmbpy)_2(Cl)_2]^+$ (C₂ symmetry) (a), $[Rh^{III}(dmbpy)_2(H_2O)_2]^{3+}$ (C₁ symmetry) (b), $[Rh^{II}(dmbpy)_2(Cl)_2]^0$ (C₁ symmetry) (c), $[Rh^{III}(dmbpy)_2(Cl)(H_2O)_2]^{2+}$ (C₁ symmetry) (d), $[Rh^{II}(dmbpy)_2(Cl)]^+$ (C₁ symmetry) (e), $[Rh^{II}(dmbpy)_2(H_2O)_2]^{2+}$ (C₁ symmetry) (f), $[Rh^{II}(dmbpy)_2]^+$ (D₂ symmetry) (g), $[Rh^{II}(dmbpy)_2(H_2O)_2]^{2+}$ (C₁ symmetry) (h) and $[Rh^{II}(dmbpy)(dmbpy^{\bullet})]^0$ (D₂

symmetry) (i) complexes in the electronic ground state in water.



Figure S4. Optimized structures of $[Rh^{III}(H)(dmbpy)_2(Cl)]^+$ (C₁ symmetry) (a), $[Rh^{III}(H)(dmbpy)_2(H_2O)]^{2+}$ (C₁ symmetry) (b), $[Rh^{III}(H)(dmbpy)_2]^{2+}$ (C₂ symmetry) (c), $[Rh^{II}(H)(dmbpy)_2]^+$ (C₂ symmetry) (d), $[Rh^{II}(H)(dmbpy)_2(Cl)]^0$ (C₁ symmetry) (e) and $[Rh^{II}(H)(dmbpy)_2(H_2O)]^+$ (C₁ symmetry) (f) complexes in the electronic ground state in water.

Table S2. Calculated bond lengths (Å) and bond angles (°) of the optimized structures of $[Rh^{III}(dmbpy)_2(Cl)_2]^+$, $[Rh^{III}(dmbpy)_2(H_2O)_2]^{3+}$ and $[Rh^{III}(dmbpy)_2(Cl)(H_2O)]^{2+}$ complexes in the electronic ground state in water and experimental values of $[Rh^{III}(bpy)_2(Cl)_2](ClO_4)$ from its X-Ray crystallographic structure.

5	0 1	[Rh ^{III} (dmbpy) ₂ (Cl) ₂] ⁺	[Rh ^{III} (bpy) ₂ (Cl) ₂] ⁺ Experimental ¹⁷	[Rh ^{III} (dmbpy) ₂ (H ₂ O) ₂] ³⁺	[Rh ^{III} (dmbpy) ₂ (Cl)(H ₂ O)] ²⁺
		optimized	Bond lengths (Å)	Optimized
Rh-N		2.066	2 038	2.028	2.070
Rh-N'		2.000	2.030	2.067	2.084
Rh-N''		2.072	2.037	2.028	2.026
Rh-N'''		2.000	2.013	2.067	2.056
Rh-Cl/O		2.423	2.329	2.152	2.405
Rh-Cl'/O'		2.423	2.334	2.152	2.152
N-C1		1.358	1.359	1.366	1.361
N'-C1'		1.359	1.343	1.360	1.361
C1-C2		1.394	1.380	1.390	1.393
C2-C3		1.399	1.365	1.401	1.400
C3-C4		1.401	1.362	1.400	1.400
C4-C5		1.387	1.356	1.387	1.387
C5-N		1.342	1.332	1.345	1.343
C1-C1'		1.475	1.469	1.473	1.476
			Bond angles (°)	
N-Rh-N'		79.32	80.32	79.98	79.20
N-Rh-N"		91.25	90.41	90.57	91.27
N-Rh-N""		97.32	94.74	97.92	97.17
N'-Rh-N'"	,	175.26	174.22	177.05	175.64
Cl/O-Rh-C	Cl'/O'	91.86	91.18	87.98	85.37

Table S3. Calculated bond lengths (Å) and bond angles (°) of the optimized structures of $[Rh^{II}(dmbpy)_2(Cl)_2]^0$, $[Rh^{II}(dmbpy)_2(H_2O)_2]^{2+}$, $[Rh^{II}(dmbpy)_2(Cl)]^+$ and $[Rh^{II}(dmbpy)_2(H_2O)]^{2+}$ complexes in the electronic ground state in water.

	[Rh ^{II} (dmbpy) ₂ (Cl) ₂] ⁰	[Rh ^{II} (dmbpy) ₂ (H ₂ O) ₂] ²⁺	[Rh ^{II} (dmbpy) ₂ (Cl)] ⁺	[Rh ^{II} (dmbpy) ₂ (H ₂ O)] ²⁺
	Optimized	Dand langths (Å)	Optimized	Optimized
	2 001	Bond lengths (A)		2.0.02
Rh-N	2.091	2.082	2.088	2.062
Rh-N'	2.080	2.062	2.079	2.062
Rh-N''	2.351	2.311	2.283	2.282
Rh-N'''	2.098	2.093	2.084	2.093
Rh-Cl/O	2.496	2.237	2.455	2.205
Rh-Cl'/O'	3.033	2.565	-	-
N-C1	1.359	1.362	1.360	1.363
N'-C1'	1.360	1.359	1.361	1.360
C1-C2	1.397	1.395	1.396	1.394
C2-C3	1.397	1.398	1.397	1.399
C3-C4	1.401	1.401	1.401	1.400
C4-C5	1.388	1.388	1.387	1.388
C5-N	1.344	1.344	1.345	1.344
C1-C1'	1.476	1.476	1.476	1.475
		Bond angles (°)		
N-Rh-N'	78.59	78.93	78.68	79.29
N-Rh-N"	92.26	96.12	93.32	96.92
N-Rh-N'"	97.05	98.01	97.26	97.77
N'-Rh-N'"	174.96	176.34	175.91	177.01
Cl/O-Rh-Cl'/O'	93.64	85.30	-	-

1	L		5 5 0
	[Rh ^I (dmbpy) ₂] ⁺	[Rh ^I (bpy) ₂] ⁺	[Rh ^I (dmbpy)(dmbpy [•])] ⁰
	Optimized	Experimental ^{18,a}	Optimized
		Bond lengths (Å)	
Rh-N	2.082	2.03, 2.01	2.069
Rh-N'	2.082	2.00, 2.00	2.069
Rh-N''	2.082	1.97, 2.01	2.069
Rh-N'''	2.082	2.03, 2.03	2.069
N-C1	1.363	1.36, 1.36	1.381
N'-C1'	1.363	1.36, 1.38	1.381
C1-C2	1.396	1.42, 1.45	1.411
C2-C3	1.397	1.39, 1.25	1.385
C3-C4	1.401	1.40, 142	1.416
C4-C5	1.387	1.40, 1.46	1.380
C5-N	1.348	1.29, 1.38	1.356
C1-C1'	1.472	1.50, 1.45	1.443
		Bond angles (°)	
N-Rh-N'	78.15	79.3, 77.01	78.11
N-Rh-N"	104.11	103.9, 103.2	103.91
N-Rh-N'"	164.05	160.8, 161.4	164.94
N'-Rh-N'"	104.11	103.4, 103.0	103.91

Table S4. Calculated bond lengths (Å) and bond angles (°) of the optimized structures of $[Rh^{I}(dmbpy)_{2}]^{+}$ and $[Rh^{I}(dmbpy)(dmby \cdot)]^{0}$ complexes in the electronic ground state in water and experimental values of $[Rh^{I}(bpy)_{2}](ClO_{4})$ from its X-Ray crystallographic structure.

^a Values corresponding to the two crystallographic independent structures in the unit cell.

Table S5. Calculated bond lengths (Å) and bond angles (°) of the optimized structures of $[Rh^{III}(H)(dmbpy)_2(H_2O)]^{2+}$, $[Rh^{III}(H)(dmbpy)_2(Cl)]^+$, $[Rh^{III}(H)(dmbpy)_2]^{2+}$ complexes in the electronic ground state in water.

	$[Rh^{III}(H)(dmbpy)_2(H_2O)]^{2+}$	$[Rh^{III}(H)(dmbpy)_2(Cl)]^+$	[Rh ^{III} (H)(dmbpy) ₂] ²⁺
	Optimized	Optimized	Optimized
	Be	ond lengths (Å)	
Rh-N	2.032	2.064	2.102
Rh-N'	2.055	2.072	2.088
Rh-N"	2.238	2.246	2.088
Rh-N""	2.084	2.075	2.102
Rh-Cl/O	2.159	2.433	-
Rh-H	1.546	1.543	1.497
N-C1	1.363	1.360	1.360
N'-C1'	1.358	1.359	1.360
C1-C2	1.393	1.395	1.394
C2-C3	1.399	1.398	1.399
C3-C4	1.400	1.401	1.400
C4-C5	1.387	1.387	1.387
C5-N	1.344	1.343	1.345
C1-C1'	1.474	1.475	1.472
	E	Bond angles (°)	
N-Rh-N'	79.90	79.21	78.02
N-Rh-N"	94.13	92.73	103.82
N-Rh-N""	97.65	97.17	164.71
N'-Rh-N'"	176.61	175.66	103.82
Cl/O-Rh-H	89.72	88.10	-

Table S6. Calculated bond lengths (Å) and bond angles (°) of the optimized structures of $[Rh^{II}(H)(dmbpy)_2]^+$, $[Rh^{II}(H)(dmbpy)_2(Cl)]^0$ and $[Rh^{II}(H)(dmbpy)_2(H_2O)]^+$ complexes in the electronic ground state in water.

	[Rh ^{II} (H)(dmbpy) ₂] ⁺ Optimized	[Rh ^{II} (H)(dmbpy) ₂ (Cl)] ⁰ Optimized	[Rh ^{II} (H)(dmbpy) ₂ (H ₂ O)] ⁺ Optimized
	- p	Bond lengths (Å)	-F
Rh-N	2.289	2.048	2.021
Rh-N'	2.101	2.059	2.042
Rh-N''	2.209	2.258	2.259
Rh-N'''	2.090	2.097	2.107
Rh-Cl/O	-	2.479	2.195
Rh-H	1.585	1.544	1.546
N-C1	1.350	1.394	1.396
N'-C1'	1.357	1.392	1.390
C1-C2	1.400	1.425	1.423
C2-C3	1.397	1.377	1.377
C3-C4	1.402	1.428	1.429
C4-C5	1.389	1.379	1.377
C5-N	1.339	1.348	1.351
C1-C1'	1.486	1.420	1.420
		Bond angles (°)	
N-Rh-N'	75.14	80.01	80.51
N-Rh-N"	94.71	91.55	93.03
N-Rh-N'"	106.48	96.45	97.44
N'-Rh-N'''	176.84	174.35	175.41
Cl/O-Rh-H	-	88.93	90.46

Theoretical absorption spectrum of $[Ru^{II}(bpy)_3]^{2+}$ **in water.** The TD-DFT absorption spectrum of $[Ru(bpy)_3]^{2+}$ calculated in water is represented in Figure S5 and the corresponding transitions energies are reported in Table S7.



Figure S5. TD-DFT absorption spectrum of $[Ru(bpy)_3]^{2+}$ in water.

Table S7. TD-DFT transition energies (nm) to the low-lying MLCT/MC and IL excited states of $[Ru(bpy)_3]^{2+}$ in water and associated oscillator strengths *f*.

Transition	Character	Transition energies (nm)	f
$e \rightarrow e$	MLCT/MC	430	2×0.123
$a_1 \rightarrow e$	MLCT/MC	327	2×0.025
$e \rightarrow e$	MLCT/MC	319	2×0.088
$e \rightarrow e$	IL	288	2×0.023
$a_1 \rightarrow e$	IL	282	2×0.268
$e \rightarrow e$	IL	278	0.998
$e \rightarrow a_2$	IL	253	2×0.026
$a_1 \rightarrow a_2$	IL	251	0.056

The intense MLCT/MC transition calculated at 430 nm corresponds to the band observed at 450 nm in alcoholic solution and it is very sensitive to the solvent nature.²⁰ The two next MLCT states are calculated at 327 and 319 nm and can be attributed to the weak shoulders observed at 344 and 322 nm in the experimental spectrum. In excellent agreement with the experimental spectrum that shows an intense band at 285 nm, the upper bpy localized IL states are calculated at about 288 and 282 nm, the later being the most intense.

Theoretical absorption spectra of Rh^I, Rh^{II} and Rh^{III} complexes in water. The TD-DFT absorption spectra of the initial catalyst $[Rh^{III}(dmbpy)_2(Cl)_2]^+$ and the other intermediates $[Rh^{II}(dmbpy)_2(Cl)]^+$, $[Rh^{I}(dmbpy)_2]^+$ and $[Rh^{III}(H)(dmbpy)_2(Cl)]^+$ calculated in water are represented in Figure S6. When they are available, the experimental absorption maxima of some rhodium complexes in various solvents are reported in Table S8. The corresponding calculated transition energies are reported in Tables S9-S11. Since the chloride ligands can be substituted by aquo ligand in course of the photocatalytic cycle, we also calculated the

absorption spectra of the aquo derivatives $(i.e. [Rh^{III}(dmbpy)_2(H_2O)_2]^{3+}$, $[Rh^{II}(dmbpy)_2(H_2O)]^{2+}$ and $[Rh^{III}(H)(dmbpy)_2(H_2O)]^{2+}$) (Figures S6 and Tables S9-S11).



Figure S6. TD-DFT absorption spectra (in water) of $[Rh^{III}(dmbpy)_2(Cl)_2]^+$, $[Rh^{II}(dmbpy)_2(Cl)]^+$, $[Rh^{III}(dmbpy)_2]^+$ and $[Rh^{III}(H)(dmbpy)_2(Cl)]^+$ (left) and of $[Rh^{III}(dmbpy)_2(H_2O)_2]^{3+}$, $[Rh^{II}(dmbpy)_2(H_2O)]^{2+}$, and $[Rh^{III}(H)(dmbpy)_2(H_2O)]^{2+}$ (right).

Overall, the agreement of the calculated and experimental absorption spectra was rather well. The theoretical absorption spectrum of the initial $[Rh^{III}(dmbpy)_2(Cl)_2]^+$ catalyst (Figure S6 and Table S9) starts at 360 nm and is characterized by one weak MLCT state at 341 nm and two intense peaks centred at about 290 and 270 nm. The calculated band around 290 nm which was measured at about 300 - 310 nm in dilute aqueous solution²¹ covers several IL transitions. Two other transitions calculated at 272 and 252 nm were ascribed to MLCT states, the later one being observed experimentally in water²¹ for the $[Rh^{III}(bpy)_2(Cl)_2]^+$ analogue and in CH₃CN²² for $[Rh^{III}(dmbpy)_2(Cl)_2]^+$. The theoretical absorption spectrum of aquo derivative of the initial Rh^{III} catalyst, *i.e.* $[Rh^{III}(dmbpy)_2(H_2O)_2]^{3+}$ (Figure S6 and Table S9), is similar to that of $[Rh^{III}(dmbpy)_2(Cl)_2]^+$ catalyst (Figure S6) and characterized by two intense peaks centred at 290 and 270 nm which are attributed to IL transitions and IL/MLCT transitions, respectively. The shoulder at 341 nm seen in the chloro complex is very small in the aquo complex.

The theoretical absorption spectrum of the $[Rh^{II}(dmbpy)_2(CI)]^+$ intermediate (Figure S6 and Table S10) exhibits a large and weak band centred around 550 nm due to MLCT states. Calculations also gave two other broad bands of low intensities between 450 and 320 nm ascribed to mixed MLCT/IL/MC states, and a large MLCT/IL/LLCT states mixing in the in the UV energy domain between 320 and 250 nm. This is the result of an important electronic density delocalization that characterizes this Rh^{II} intermediate. The theoretical absorption spectrum of the $[Rh^{II}(dmbpy)_2(H_2O)]^+$ intermediate (Figure S6 and Table S10) is similar to that of corresponding chloro complex though shifted to the blue, and characterized by one moderate peak of MLCT transition at 330 nm and two intense peaks centred at 290 and 250, which are attributed to IL/MLCT transitions and MLCT transitions, respectively.

The analysis of the absorption spectrum of the key intermediate $[Rh^{1}(dmbpy)_{2}]^{+}$ is not easy because the lowest band is known to be very sensitive to the experimental conditions.^{18,23,24} Its theoretical spectrum (Figure S6) displays a large band between 650 and 475 nm with a

maximum calculated at 542 nm (Table S9). This band has been amply discussed in the literature because it can be shifted by about 40 nm depending on the concentrations, pH and other experimental parameters as illustrated by the values reported in parenthesis in Table S8. When going from the solvent PCM model to a discrete model with two water molecules coordinated to the intermediate in $[Rh^{I}(dmbpy)_{2}(H_{2}O)_{2}]^{+}$ (one H atom of each water molecule directs to Rh with Rh-H distance of 2.305 Å), the maximum calculated at 542 nm is shifted to the blue at 494 nm. In agreement with the experimental spectrum, the theoretical spectrum of $[Rh^{I}(dmbpy)_{2}]^{+}$ is characterized by three other bands centred at 364 nm, 298 nm, and 269 nm of increasing intensities. The lowest transition (364 nm) corresponds to a MLCT state with a small contribution of MC character, whereas the transition at 298 nm is mainly a IL state with a small MLCT contribution. The transition calculated at 269 nm is assigned to a mixed IL/MLCT state.

The theoretical spectrum of the $[Rh^{III}(H)(dmbpy)_2(Cl)]^+$ hydride in water (Figure S6 and Table S11) is very similar to that of the initial Rh^{III} catalyst with two weak absorptions at about 371 and 332 nm, both being MLCT transitions. Note that these both transitions were experimentally observed at 331 and 362 nm in CH₃CN with a [Rh^{III}(H)(dmbpy)₂(Cl)]⁺ hydride electrogenerated in presence of formic acid (Table S8).²² Otherwise, this Rh^{III}(H) hydride species exhibits in the UV part a IL transition calculated at 288 nm (with an additional peak at 286 nm that corresponds to the mixture of MLCT transition (from metal center to H-localized orbital) and IL transition) and a MLCT transition at 266 nm. In fact, the strong absorption band calculated at 288 nm is blue shifted compared to the experimental spectrum in water²⁴ of the [Rh^{III}(H)(bpy)₂(Cl)]⁺ analogue which exhibits a intense transition at 308 nm. The theoretical spectrum of the aquo derivative of the hydride, i.e. $[Rh^{III}(H)(dmbpy)_2(H_2O)]^{2+}$ (Figure S6 and Table S11), is different from that of $[Rh^{III}(H)(dmbpy)_2(Cl)]^+$ hydride, since it does not display any band between 400 and 320 nm. In contrast, The theoretical spectrum of $[Rh^{III}(H)(dmbpy)_2(H_2O)]^{2+}$ is relatively similar to that of the initial aquo complex $[Rh^{III}(dmbpy)_2(H_2O)_2]^{3+}$ with an intense peak at 289 nm which is characterized by a mixture of IL and MLCT transitions.

Complexes	Solvant	$\lambda_{abs}/nm (\epsilon/M^{-1} cm^{-1})^a$
$[Rh^{III}(dmbpy)_2(Cl)_2]^+,^{22}$	CH ₃ CN	251 (21700), 263 (sh, 17700), 300 (21000), 310 (25300)
$[Rh^{III}(bpy)_2(Cl)_2]^+,^{21}$	H ₂ O	252 (23200), 302 (sh, 23500), 311 (27300), 384 (sh, 100)
$[Rh^{III}(bpy)_2(H_2O)_2]^{3+,21}$	H ₂ O	243 (27700), 299 (sh, 19900), 306 (27500), 319 (26800)
$[Rh^{I}(dmbpy)_{2}]^{+,22 b}$	CH ₃ CN	364, 504 (sh), 548, 633
$[Rh^{I}(bpy)_{2}]^{+},^{18}$	МеОН	246 (24500), 298 (32100), 362 (6800), 518 (sh, 8500), 552 (13100), 656 (sh, 2500), 750 (sh, 500)
$[Rh^{I}(bpy)_{2}]^{+}, ^{18}$	Acetone	514 (sh, 5100), 552 (12500), 648 (sh, 2500), 750 (sh, 500)
$[Rh^{I}(bpy)_{2}]^{+,24}$	H ₂ O 0.1M aq NaOH	523 (9100)
$[Rh^{III}(H)(dmbpy)_2(Cl)]^+$, ²²	CH ₃ CN	252 (29700), 298 (sh, 19600), 307 (19900), 331 (sh, 5000), 362 (sh, 2500)
$[Rh^{III}(H)(bpy)_2(Cl)]^+$, ²⁴	МеОН	247 (35000), 303 (sh, 29000), 310 (32000)
[Rh ^{III} (H)(bpy) ₂ (Cl)] ⁺ , ²⁴	H ₂ O 0.1M aq HCl	248 (48000), 308 (43000)

Table S8. Experimental UV/Visible transition energies (nm) for the Rh complexes in various solvents.

^aShoulder is denoted sh. ^bNo extinction coefficient (ϵ) was done since the Rh^I species was not sufficiently stable in solution.

[Rh ^{II}	I(dmbpy) ₂ (Cl)	2]+	$[Rh^{III}(dmbpy)_2(H_2O)_2]^{3+}$			[Rh ^I (dmbpy) ₂] ⁺		
Character	Transition energies	ſ	Character	Transition energies	f	Character MLCT	Transition energies 542	f 0.28
						MLCT/MC	386	0.03
						MLCT	374	0.04
						MLCT/MC	364	0.15
MLCT	341	0.02	MC/IL	301	0.02	MLCT	355	0.06
MLCT	322	0.03	IL/MC/LMCT	300	0.05	IL/MLCT	301	0.03
IL	292	0.21	IL/LMCT	296	0.05	IL/MLCT	298	0.36
IL	291	0.11	IL	293	0.14	MLCT/IL	295	0.02
IL	290	0.03	IL	292	0.35			
IL	289	0.14				MLCT	288	0.06
LMCT	288	0.02				MLCT	278	0.04
MLCT	272	0.10				IL	271	0.03
			269	IL/MLCT	0.02	MLCT	270	0.05
IL/LMCT	267	0.07	265	IL/MLCT	0.15	IL/MLCT	269	0.31
LMCT/IL	266	0.04				MLCT/IL	267	0.24
LMCT/LLCT	263	0.04				MLCT/MC	265	0.04
MLCT	252	0.06				MC/MLCT	264	0.14
LLCT/MLCT	252	0.05				MC	255	0.07

Table S9. TD-DFT transition energies (nm) to the low-lying singlet excited states of $[Rh^{III}(dmbpy)_2(Cl)_2]^+$, $[Rh^{III}(dmbpy)_2(H_2O)_2]^{3+}$ and $[Rh^{I}(dmbpy)_2]^+$ in water with significant oscillator strengths *f*.

		[P])2(20)]			enguis).	
[R	h ^{II} (dmbpy) ₂ (Cl)]	+	$[Rh^{II}(dmbpy)_2(H_2O)]^{2+}$			
Character	Transition energies	f	Character	Transition energies	f	
MLCT	543	0.01	MLCT	495	0.01	
MLCT/IL	402	0.02				
MLCT/IL	372	0.02	MLCT	329	0.04	
MLCT	345	0.04	MLCT	329	0.03	
MLCT/IL	302	0.04	LMCT/IL	312	0.02	
MLCT/IL	301	0.02	MLCT/IL	303	0.03	
IL/MLCT/LLCT	294	0.02	MLCT/IL	303	0.03	
MLCT/IL	291	0.07	IL/MLCT	300	0.07	
MLCT/IL	289	0.09	IL/MLCT	296	0.02	
MLCT/IL	286	0.04	MLCT/IL	290	0.06	
IL/MLCT	284	0.05	IL/MLCT	288	0.18	
IL/MLCT	282	0.06	IL/MLCT	286	0.05	
MLCT/IL	281	0.05	IL/MLCT	283	0.04	
IL/MLCT	279	0.06	IL/MLCT	281	0.02	
MLCT/IL	278	0.03	IL/MLCT	277	0.02	
MLCT/LMCT	277	0.03	IL/MLCT/LMCT	275	0.02	
MLCT/IL	273	0.03				
LMCT/IL/LMCT	271	0.04	MLCT	269	0.04	
MLCT/IL	270	0.04	MLCT/IL/LMCT	267	0.04	
MLCT/IL	269	0.05	MLCT	266	0.03	
MLCT/LLCT/IL	268	0.07	MLCY	262	0.04	
MLCT/LLCT	265	0.08	MLCT	261	0.04	
LLCT/MLCT	264	0.03	MLCT	258	0.06	
MLCT	262	0.08	MLCT	258	0.04	
MLCT	260	0.03	MLCT	254	0.05	
MLCT/LLCT	255	0.04	MLCT	253	0.05	
MLCT/IL	254	0.06	MLCT	251	0.11	

Table S10. TD-DFT transition energies (nm) to the low-lying singlet excited states of $[Rh^{II}(dmbpy)_2(Cl)]^+$ and $[Rh^{II}(dmbpy)_2(H_2O)]^{2+}$ in water and associated oscillator strengths *f*.

	(11)(unitep))2((11)(unitep))2(11			arei su enginsj.
	$[Rh^{II}]$	^I (H)(dmbpy) ₂ (Cl	l)] ⁺	[Rh	^{III} (H)(dmbpy) ₂ (H ₂ O	$[0]^{2+}$
	Character	Transition energies	f	Character	Transition	f
	MLCT	371	0.01	MLCT/IL	304	0.08
	MLCT	332	0.04	MLCT/IL	300	0.06
	MC/MLCT	323	0.02			
	MLCT/MC	317	0.05			
	IL/MLCT	294	0.08	MLCT/IL	297	0.04
	IL	288	0.20	IL/MLCT	291	0.21
	MC/IL	286	0.16	MLCT/IL	290	0.08
Ι	LLCT/MLCT	285	0.05			
Ι	LLCT/MLCT	281	0.12	IL/MLCT	289	0.24
	MLCT	275	0.03	MLCT/IL	281	0.08
	MC/MLCT	269	0.03	IL/MLCT	280	0.04
Ι	LLCT/MLCT	267	0.03	MC/MLCT	260	0.02
	MLCT	266	0.09	IL	257	0.02
N	MLCT/LLCT	263	0.05	IL	253	0.03
	MLCT	261	0.06			
	MC/MLCT	259	0.06			

Table S11. TD-DFT transition energies (nm) to the low-lying singlet excited states of $[Rh^{III}(H)(dmbpy)_2(Cl)]^+$ and $[Rh^{III}(H)(dmbpy)_2(H_2O)]^{2+}$ in water and associated oscillator strengths *f*.



Figure S7. Potential energy curve for the proton transfer reaction from H_3O^+ to $[Rh^{I}(dmbpy)_2]^+$ by changing R_{Rh-H} bond length from 3.0 to 1.4 Å with all other parameters optimized.

Table S12. Free energies (kJ mol⁻¹) of reactions involved in H_2 production with the water molecule existing near the complex in the product state. The numbering of the reaction corresponds to that in Table 1. The corresponding values which are calculated as dissociated system (the water molecule is calculated separately) are shown in parenthesis.

		∆G°
8	$[Rh^{I}(dmbpy)_2]^{*} + H_3O^{*} \rightarrow \{[Rh^{III}(H)(dmbpy)_2]^{2*} H_2O\}$	-72.2 (-95.2)
9	${[Rh^{III}(H)(dmbpy)_2]^{2+} H_2O} \rightarrow {[Rh^{III}(H)(dmbpy)_2(H_2O)]^{2+}}$	-59.4 (-7.3)
17	$[Rh^{III}(H)(dmbpy)_2(CI)]^+ + H_3O^+ \rightarrow \{[Rh^{III}(dmbpy)_2(CI)]^{2+} H_2O\} + H_2$	-22.4 (-50.9)
18	$[Rh^{III}(dmbpy)_2(CI)]^{2*} + H_2O \rightarrow [Rh^{III}(dmbpy)_2(CI)(H_2O)]^{2*}$	-63.5 (-35.0)
31	${[Rh^{II}(H)(dmbpy)_2]}^{+} H_2O} \rightarrow {[Rh^{II}(H)(dmbpy)_2(H_2O)]}^{+}$	+57.0(+81.6)

Calculation details for λ value

The global reorganization energy (λ) of a system, in which an electron transfer occurs, can be expressed as sum of the inner and outer reorganization energies (respectively denoted λ_i and λ_o) which correspond respectively to the changes of bond lengths and angles within the donor and the acceptor of electron and to the solvent reorientation around the donor and the acceptor after the electron transfer.²⁵ The outer reorganization energy has been calculated for each electron transfer step from the equation:

$$\lambda_o = e^2 \left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s} \right) \left(\frac{1}{2R_D} + \frac{1}{2R_A} - \frac{1}{R_{DA}} \right)$$

Where ϵ_{op} and ϵ_s are respectively the optical and the static dielectric constants of the solvent (for water, $\varepsilon_{op} = 1.34$ and $\varepsilon_s = 78.35$), and R_D, R_A and R_{DA} are respectively the mean van der Waals radii of the donor and the acceptor and the inter-reactants center-to-center distance (in Å) (see Table S13). Herein, the R_{DA} value is considered as the sum of radii of the donor and the acceptor, since it is a bimolecular redox reaction. So, for the reductive quenching of the excited state ${}^{3}[Ru^{III}(bpy)_{2}(bpy^{-})]^{2+}$ by HA⁻ (entry 1 in Table 1), the λ_{0} value was estimated to be 1.24 eV. For the other electron transfers involving the $[Ru^{II}(bpy)_2(bpy^{-})]^+$ species and the different forms of rhodium catalyst (*i.e.* entries 2, 3, 4, 5, 28 and 29 in Table 1), the λ_0 value was calculated to be ~1.00 eV. The inner reorganization energy within a lot of artificial photosystems in literature is considered negligible or inferior to 0.1 eV. By contrast, in our photocatalytic system, λ_i has been estimated to be superior to 0.1 eV since the electron transfers are associated with chemical reactions (e.g. loss of ligand for the rhodium catalyst and loss of proton for the HA⁻ salt) and a significant structural reorganization for the catalyst (*i.e.* a geometry change between the octahedral Rh(III) complex and the square planar Rh(I) complex). Considering the sum of λ_i and λ_o values, the global reorganization energy (λ) for occurring each electron the photocatalytic system transfers in [Rh^{III}(dmbpy)₂Cl₂]⁺/[Ru^{II}(bpy)₃]²⁺/H₂A/HA⁻ could be estimated largely higher than 1.1 eV (*i.e.* superior to $106.1 \text{ kJ mol}^{-1}$).

	$\overline{r}\left(\AA ight) ^{a}$
[Ru(bpy) ₃] ²⁺	5.373
[Ru(bpy) ₃] ²⁺ (triplet)	5.378
[Ru(bpy)₃] ⁺	5.375
HA	3.719
HA	3.720
[Rh ^{III} (dmbpy) ₂ (Cl) ₂] ⁺	5.254
[Rh ^{II} (dmbpy) ₂ (Cl) ₂]	5.291
[Rh ^{II} (dmbpy)₂(CI)]⁺	5.188
[Rh ^I (dmbpy) ₂ (CI)]	5.198
[Rh ^l (dmbpy) ₂] ⁺	5.080
[Rh ^{III} (H)(dmbpy)₂(CI)] ⁺	5.202
$[Rh^{III}(H)(dmbpy)_2(H_2O)]^{2+}$	5.189
[Rh ^{II} (H)(dmbpy)₂] ⁺	5.126
[Rh ^{II} (H)(dmbpy) ₂ (Cl)]	5.205
[Rh ^{II} (H)(dmbpy) ₂ (H ₂ O)] ⁺	5.191

Table S13. Mean radii of the molecules which compose the photocatalytic system $[Rh^{III}(dmbpy)_2Cl_2]^+/[Ru^{II}(bpy)_3]^{2+}/H_2A/HA^-$.

^aThe mean radii of molecules are calculated from the cavity size (V) of molecules used in PCM calculation, in which the molecular surfaces representing the solute-solvent boundaries are treated as van der Waals surface:

$$\bar{r} = \sqrt[3]{\frac{3V}{4\pi}}$$



Figure S8. The optimized structure of $\{[Rh^{II}(dmbpy)_2]^{2^+}--(H_3O^+)--3(H_2O)\}$ (a), $\{[Rh^{III}(H)(dmbpy)_2]^{2^+}--(H_2O)--3(H_2O)\}$ (b), and the transition state between them (c). Their relative energies are 0, +7.1, and +9.9 kJ mol⁻¹, respectively.

Table S14. Free energies (kJ mol⁻¹) of reactions involved in H_2 production with an explicit water molecule. The numbering of the reaction corresponds to that in Table 1. The values without the explicit water molecules are shown in parenthesis.

		ΔG°
10	$[Rh^{III}(H)(dmbpy)_2]^{2+} + CI^{-} \rightarrow [Rh^{III}(H)(dmbpy)_2(CI)]^{+}$	-31.3 (-51.1)
9-12	$[Rh^{III}(H)(dmbpy)_2]^{2+} + AH^- \rightarrow [Rh^{III}(H)(dmbpy)_2(AH)]^+$	-17.5 (-37.6)

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