SUPPLEMENTARY INFORMATION

Theoretical Investigation of Solvent and Oxidation/Deprotonation effects on the Electronic Structure of a Mononuclear Ru-Aqua-Polypyridine Complex in Aqueous Solution

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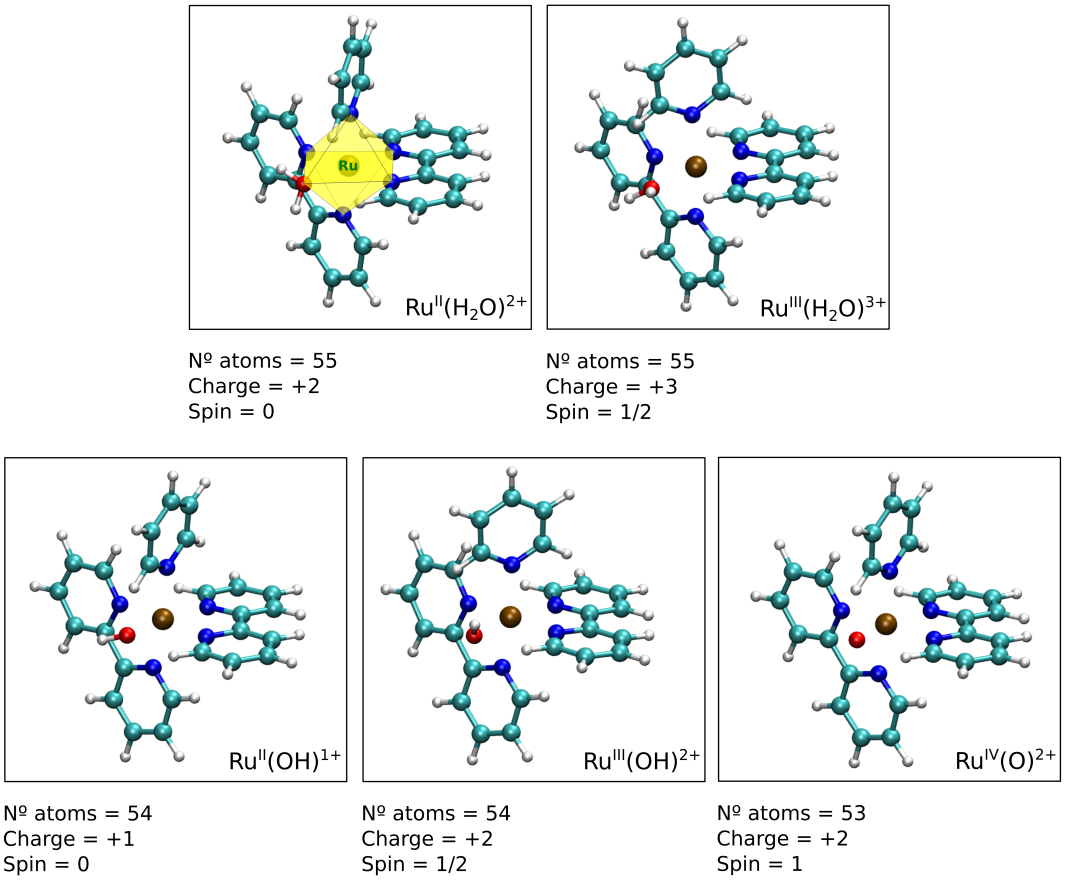
1 Supplementary Information

1.1 Experimental

The cis-[Ru(H2O)(py)(bpy)2](NO3)2 complex was prepared by dispersing 1 g of cis-[Ru(bpy)2Cl2] (Sigma-Aldrich) in 50 ml of 1:1 v/v water/ethanol mixture, reacting with 1.0 equivalent of AgNO3 (0.35 g) at 70-80 ^{o}C, and filtering off the AgCl precipitate using a CeliteTM bed. Then, 1.0 equivalent of pyridine (0.164 g) was reacted with the filtrate solution for 1 hr under reflux to generate the cis-[RuCl(py)(bpy)2](NO3) complex, and 1.0 equivalent of AgNO3 (0.350 g) added into and reacted for 30 min at 70-80 ^{o}C. The white-grey AgCl precipitate was filtered out from the desired cis-[Ru(H2O)(py)(bpy)2](NO3)2 complex bright orange solution, which was concentrated in a flash evaporator, and kept in a refrigerator for 3 hrs. The precipitate was filtered out, washed with a minimum amount of cold acetone, and kept in a desiccator under vacuum. Elemental analysis for (RuC25H23N7O7)H2O, exp.(calc.): C= 46.27 (46.01), H= 3.81 (3.86), N= 14.93 (15.02), ESI-MS: molecular peak at m/z 510.20 [Ru(OH)(py)(bpy)2]+. The complex and the oxidized RuIII aqua/hydroxo and the RuIVO species were generated in situ by reaction with suitable amounts of cerium(IV) ammonium nitrate (CAN). The solution of cis-[RuII(H2O)(py)(bpy)2](NO3)2 used to register the UV-Vis absorption spectrum was prepared by dissolving 3.50 mg of complex in 100 mL of 0.1 mol L1 HNO3 solution, pH = 1. Another solution was prepared by dissolving 3.50 mg of cis-[Ru(H2O)(py)(bpy)2](NO3)2 in 100 mL of 0.1 mol L1 of aqueous HNO3, pH=1, and the first solution was carefully added (volume corresponding to 2.90 mg of CAN) into the stirred RuII complex solution. Considering that the pKa of coordinated water molecule is 0.85, it must contain 40.2 mol L1 of cis-[RuIII(OH)(py)(bpy)2]2+ and 13.4 mol L1 of cis-[RuIII(H2O)(py)(bpy)2]3+. The RuIVO species was generated by reacting the RuII complex as above but using double of the volume of CAN solution (5.80 mg of CAN). The UV-Vis absorption spectra were obtained in a Hewlett Packard 8453A diode array spectrophotometer using a quartz cuvette with a path length of 10.0 mm, at 25 ^{o}C.

1.2 Figures and Tables



Nº atoms = 55
Charge = +2
Spin = 0

Nº atoms = 55
Charge = +3
Spin = 1/2

Nº atoms = 54
Charge = +1
Spin = 0

Nº atoms = 54
Charge = +2
Spin = 1/2

Nº atoms = 53
Charge = +2
Spin = 1

Figure S1: Chemical structure of the Ru-Aqua/Oxo complexes.

Table S1: Structural comparison between the B3LYP/(aug)-cc-pVDZ(PP-*Ru*) optimized geometry of $Ru^{II}(H_2O)$ and the crystallographic geometry of $Ru^{II}Tris(2,2'-bpy)$ [1]. Distances (r) in Å and angles (a) in degree. The parameter $|\Delta|$ represents the module of the difference between the theoretical and experimental values.

par	$Ru^{II}(H_2O)$	Ru^{II}Tris(2,2'-bpy)	$\|\Delta\|$
$r(Ru-N_{11})$	2.043	2.056(3)	0.013
$r(Ru-N_3)$	2.084	2.056(3)	0.028
$r(Ru-N_{19})$	2.107	2.059(3)	0.048
$r(Ru-O)$	2.242	2.059(3)*	0.183
$r(Ru-N_{25})$	2.088	2.060(3)	0.028
$r(Ru-N_{45})$	2.149	2.060(3)*	0.089
$a(N_{11}-Ru-N_3)$	78.9	78.7(2)	0.2
$a(N_{11}-Ru-N_{19})$	99.1	97.9(1)	1.2
$a(N_{11}-Ru-O)$	174.2	172.6(1)*	1.6
$a(N_{11}-Ru-N_{25})$	90.4	92.0(1)	1.6
$a(N_3-Ru-N_{25})$	97.8	94.9(1)	2.9
$a(N_{19}-Ru-N_{25})$	78.1	78.5(1)	0.4
$a(O-Ru-N_{19})$	86.5	86.3(1)	0.2
$a(N_{19}-Ru-N_{45})$	97.5	94.8(1)*	2.7
$a(N_{25}-Ru-N_{45})$	175.4	171.0(1)*	4.4

(*) Non identical atoms.

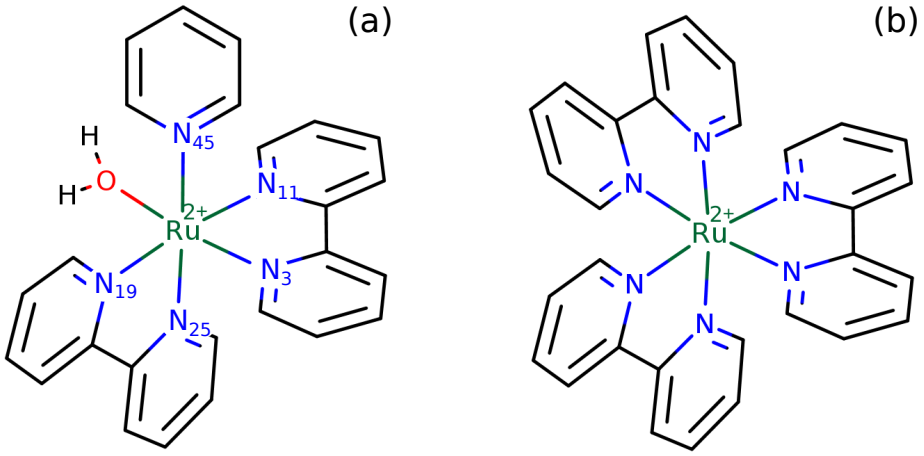


Figure S2: Molecular structure of $Ru^{II}(H_2O)$ (a) and $Ru^{II}Tris(2,2'-bpy)$ (b).

Table S2: Structural comparison between the vacuum (VAC) and solution (SOL) optimized geometries of the *Ru*-Aqua/Oxo complexes, using the B3LYP/(aug)-cc-pVDZ(PP-*Ru*) approach and the continuous PCM model to address the solvent effects. Distances (r) in Å, angles (a) and dihedrals (d) in degrees. The parameter Δ represents the difference between the geometric (par) parameters of the optimized geometries in vacuum and in solution, ie $\Delta = par^{SOL} - par^{VAC}$. At the bottom of the table there is a legend for all the geometric parameters shown. The numbers of atoms follow the numbering shown in the figure S3.

	$Ru^{II}(H_2O)$			$Ru^{III}(H_2O)$			$Ru^{II}(OH)$			$Ru^{III}(OH)$			$Ru^{IV}(O)$		
par	VAC	SOL	Δ	VAC	SOL	Δ	VAC	SOL	Δ	VAC	SOL	Δ	VAC	SOL	Δ
r_1	2.242	2.214	-0.03	2.173	2.148	-0.03	2.044	2.074	0.03	1.930	1.944	0.01	1.762	1.768	0.01
r_2	0.968	0.968	0.00	0.970	0.970	0.00	0.964	0.965	0.00	0.968	0.968	0.00			
r_3	0.969	0.969	0.00	0.971	0.971										
r_4	2.150	2.143	-0.01	2.156	2.140	-0.02	2.162	2.152	-0.01	2.152	2.147	-0.01	2.163	2.159	0.00
r_5	2.043	2.043	0.00	2.061	2.038	-0.02	2.081	2.077	0.00	2.133	2.124	-0.01	2.211	2.198	-0.01
r_6	2.107	2.099	-0.01	2.134	2.106	-0.03	2.071	2.077	0.01	2.094	2.089	0.00	2.103	2.100	0.00
r_7	2.088	2.081	-0.01	2.112	2.084	-0.03	2.058	2.060	0.00	2.089	2.084	-0.01	2.105	2.098	-0.01
r_8	2.084	2.077	-0.01	2.119	2.088	-0.03	2.067	2.067	0.00	2.109	2.107	0.00	2.108	2.106	0.00
a_1	86.5	86.6	0.1	84.5	84.4	-0.1	91.1	89.6	-1.5	89.7	89.5	-0.3	92.4	92.6	0.2
a_2	89.3	89.7	0.4	87.4	89.0	1.6	89.4	89.5	0.0	83.8	85.0	1.2	90.8	91.7	0.9
a_3	105.5	105.1	-0.4	111.1	105.9	-5.2									
a_4	115.7	114.7	-1.0	127.8	120.3	-7.5	114.9	111.0	-4.0	115.7	114.2	-1.6			
d_1	179.6	179.0	-0.6	177.8	176.2	-1.6	178.6	178.7	0.1	178.1	177.7	-0.4	177.7	176.8	-0.9
d_2	177.5	178.0	0.5	180.0	180.0	0.0	176.7	177.2	0.5	180.0	179.8	-0.2	177.7	177.4	-0.3
d_3	178.2	178.4	0.2	179.0	178.3	-0.8	176.6	177.0	0.4	176.1	177.4	1.3	176.7	178.1	1.4
d_4	178.8	179.0	0.2	-177.4	-177.7	-0.3	-177.0	-178.2	-1.2	-172.7	-174.9	-2.2	-176.6	-179.8	-3.2
d_5	179.6	179.3	-0.2	178.7	179.3	0.6	179.0	178.1	-0.9	178.0	178.7	0.7	179.8	179.2	-0.6
d_6	-66.3	-69.8	-3.5	-122.1	-113.1	9.0	-84.4	-75.2	9.2	-125.7	-124.1	1.5	-91.6	-88.0	3.6
d_7	8.9	17.0	8.0	121.7	68.6	-53.1	-59.5	-81.8	-22.4	156.8	153.2	-3.6			

$r_1 = r(ORu)$ $r_5 = r(RuN_{11})$ $a_1 = a(ORuN_{19})$ $d_1 = d(RuN_{11}C_{10}C_9)$ $d_5 = d(RuN_{45}C_{46}C_{47})$

$r_2 = r(OH_{54})$ $r_6 = r(RuN_{19})$ $a_2 = a(ORuN_{25})$ $d_2 = d(RuN_3C_2C_1)$ $d_6 = d(N_3RuN_{45}C_{46})$

$r_3 = r(OH_{55})$ $r_7 = r(RuN_{25})$ $a_3 = a(H_{54}OH_{55})$ $d_3 = d(RuN_{19}C_{18}C_{17})$ $d_7 = d(N_{25}RuOH_{54})$

$r_4 = r(RuN_{45})$ $r_8 = r(RuN_3)$ $a_4 = a(RuOH_{54})$ $d_4 = d(RuN_{25}C_{24}C_{23})$

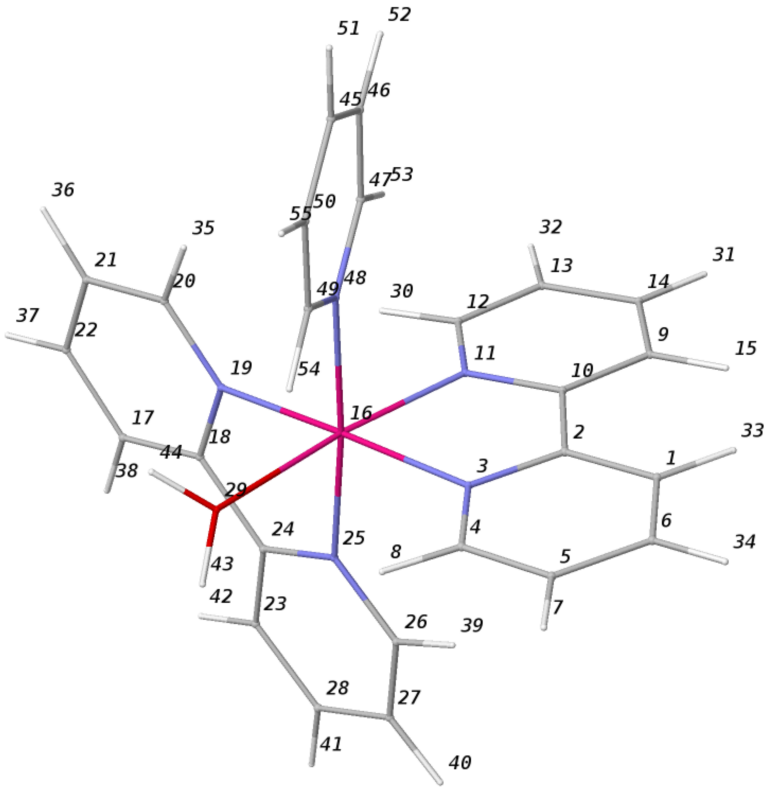


Figure S3: Atomic numbering of $Ru^{II}(H_2O)$.

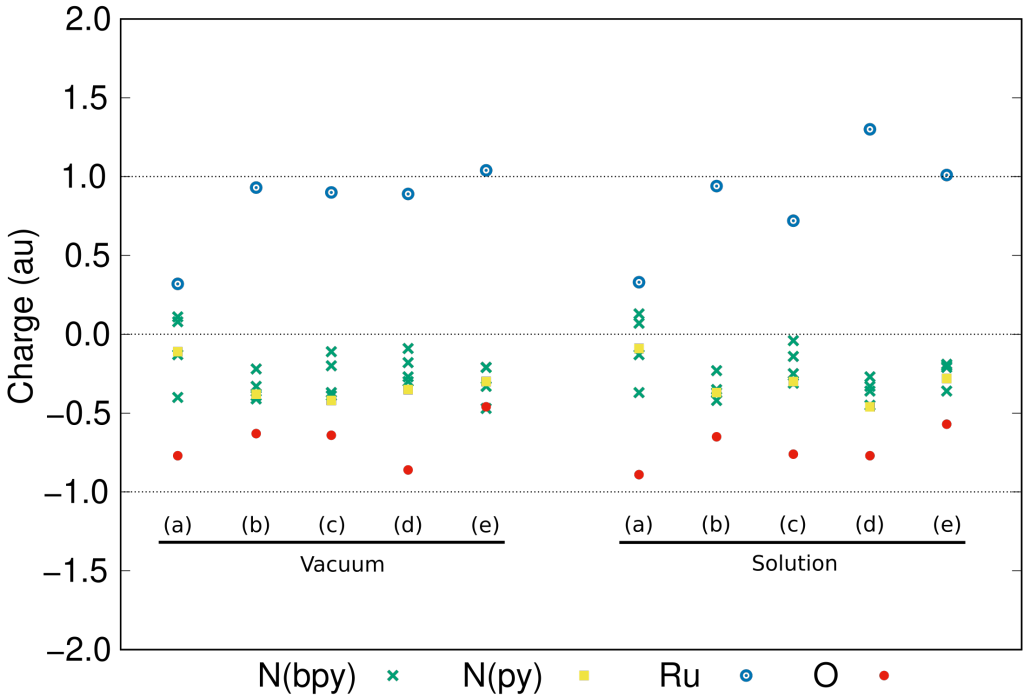


Figure S4: Diagram of the N, Ru and O charges (in au) of the *Ru*-Aqua/Oxo complexes in vacuum (VAC) and in aqueous solution (SOL). The complexes are represented by letters: (a) $Ru^{II}(H_2O)$; (b) $Ru^{III}(H_2O)$; (c) $Ru^{II}(OH)$; (d) $Ru^{III}(OH)$; (e) $Ru^{IV}(O)$.

Table S3: Atomic charges (in au) of the most relevant atoms and group of atoms of the *Ru*-Aqua/Oxo complexes in vacuum (VAC) and in aqueous solution (SOL). The complexes are represented by letters: (a) $Ru^{II}(H_2O)$; (b) $Ru^{III}(H_2O)$; (c) $Ru^{II}(OH)$; (d) $Ru^{III}(OH)$; (e) $Ru^{IV}(O)$.

		Ru	*O*	N_3	N_{11}	N_{19}	N_{25}	N_{45}	$\sum N$	bpy1	bpy2	py	Aqua
	VAC	0.93	-0.63	-0.22	-0.33	-0.39	-0.41	-0.38	-1.74	0.46	0.33	0.19	0.10
$Ru^{II}(H_2O)$	SOL	0.94	-0.65	-0.23	-0.42	-0.37	-0.35	-0.37	-1.75	0.39	0.36	0.18	0.13
	Δq	0.01	-0.02	-0.01	-0.09	0.02	0.06	0.01	-0.01	-0.07	0.03	-0.01	0.03
	VAC	0.89	-0.86	-0.18	-0.27	-0.09	-0.30	-0.35	-1.20	0.81	0.82	0.37	0.12
$Ru^{III}(H_2O)$	SOL	1.30	-0.77	-0.36	-0.27	-0.33	-0.45	-0.46	-1.87	0.68	0.58	0.28	0.16
	Δq	0.41	0.09	-0.18	0.00	-0.24	-0.15	-0.11	-0.67	-0.13	-0.24	-0.09	0.04
	VAC	0.32	-0.77	0.08	-0.40	0.11	-0.13	-0.11	-0.47	0.37	0.55	0.25	-0.50
$Ru^{II}(OH)$	SOL	0.33	-0.89	0.08	-0.37	0.13	-0.13	-0.09	-0.39	0.43	0.58	0.27	-0.61
	Δq	0.01	-0.12	0.00	0.03	0.02	0.00	0.02	0.07	0.06	0.03	0.02	-0.11
	VAC	0.90	-0.64	-0.20	-0.39	-0.11	-0.37	-0.42	-1.49	0.53	0.65	0.22	-0.30
$Ru^{III}(OH)$	SOL	0.72	-0.76	-0.14	-0.31	-0.04	-0.25	-0.30	-1.03	0.63	0.74	0.27	-0.37
	Δq	-0.18	-0.12	0.06	0.08	0.07	0.12	0.12	0.46	0.10	0.09	0.05	-0.07
	VAC	1.04	-0.46	-0.21	-0.47	-0.21	-0.33	-0.30	-1.52	0.51	0.63	0.28	-0.46
$Ru^{IV}(O)$	SOL	1.01	-0.57	-0.20	-0.36	-0.21	-0.19	-0.28	-1.24	0.58	0.68	0.30	-0.57
	Δq	-0.03	-0.11	0.01	0.11	0.00	0.14	0.02	0.28	0.07	0.05	0.02	-0.11

Table S4: Atomic charge variations (in au) of the *Ru*-Aqua/Oxo complexes in solution due to oxidation and deprotonation processes, indicated by arrows.

	$Ru^{II}(H_2O)$ $-e\downarrow$ $Ru^{III}(H_2O)$	$Ru^{II}(OH)$ $-e\downarrow$ $Ru^{III}(OH)$	$Ru^{II}(H_2O)$ $\downarrow -H^+$ $Ru^{II}(OH)$	$Ru^{III}(H_2O)$ $\downarrow -H^+$ $Ru^{III}(OH)$	$Ru^{III}(OH)$ $-e\downarrow -H^+$ $Ru^{IV}O$
Ru	0.36	0.39	-0.61	-0.58	0.29
O	-0.12	0.13	-0.24	0.01	0.19
$\sum N$	-0.12	-0.63	1.35	0.84	-0.21
$bpy1$	0.29	0.20	0.04	-0.05	-0.05
$bpy2$	0.22	0.16	0.22	0.16	-0.06
py	0.10	0.00	0.09	-0.01	0.03
Aqua	0.03	0.61	-0.74	-0.53	-0.20

Table S5: Potential energy profile of $Ru^{II}(H_2O)$ for the dissociation of H_2O. Energies calculated using B3LYP/(aug)-cc-pVDZ(PP-Ru) under the restricted and unrestricted self-consistent field (SCF) approaches. The SCF energy for the complete system and for the sum of the fragments (H_2O and the remaining complex) and the basis set superposition error (BSSE) calculated using the Counter-Poise method are presented. The scan is done varying linearly the distance between Ru and the oxygen of H_2O (Ow) from 1.72691 to 5.0 Angstrom.

	Energies in Hartree					
Ru-Ow	SCF Energy (complete system)		SCF Energy (sum of fragments)		BSSE energy	
Distance (Å)	Restricted	Unrestricted	Restricted	Unrestricted	Restricted	Unrestricted
1.72691	-1409.8696	-1409.869581	-1409.905166	-1409.905158	0.003315	0.0033
1.82691	-1409.905257	-1409.905249	-1409.905165	-1409.905159	0.003072	0.003068
1.92691	-1409.925743	-1409.925748	-1409.905163	-1409.905159	0.002812	0.002819
2.02691	-1409.936607	-1409.936617	-1409.905162	-1409.905159	0.002581	0.002592
2.12691	-1409.94151	-1409.941526	-1409.90516	-1409.905159	0.002386	0.002403
2.22691	-1409.942845	-1409.942858	-1409.905159	-1409.905159	0.00223	0.002242
2.32691	-1409.942134	-1409.942132	-1409.905157	-1409.90516	0.002099	0.002095
2.42691	-1409.940316	-1409.940309	-1409.905156	-1409.90516	0.001965	0.001951
2.52691	-1409.93799	-1409.937989	-1409.905154	-1409.90516	0.001822	0.001815
2.62691	-1409.935512	-1409.935525	-1409.905152	-1409.90516	0.001682	0.001686
2.72691	-1409.933106	-1409.933118	-1409.90515	-1409.90516	0.001557	0.001561
5.0	-1409.913516	-1409.913509	-1409.905144	-1409.905136	0.000394	0.000394

Table S6: Binding energy profile for the dissociation of H_2O from $Ru^{II}(H_2O)$. Energies calculated using B3LYP/(aug)-cc-pVDZ(PP-Ru) under the restricted and unrestricted self-consistent field (SCF) approaches. The raw binding energy refer to the interacting energy between the fragments (H_2O and the remaining complex), but without the BSSE correction. Corrected binding energy is calculated as the difference between the energy of the complete system minus the energy of the sum of the fragments summed to the BSSE energy. The scan is done varying linearly the distance between Ru and the oxygen of H_2O (Ow) from 1.72691 to 5.0 Angstrom.

	Energies in kcal/mol			
Ru-Ow	Binding Energy (raw)		Binding Energy (corrected)	
Distance (Å)	Restricted	Unrestricted	Restricted	Unrestricted
1.72691	22.317731	22.325113	24.397621	24.395924
1.82691	-0.057819	-0.056742	1.870096	1.868502
1.92691	-12.914061	-12.919956	-11.149562	-11.150884
2.02691	-19.732278	-19.739929	-18.112599	-18.113187
2.12691	-22.809746	-22.820121	-21.312397	-21.312251
2.22691	-23.64828	-23.655883	-22.249101	-22.248783
2.32691	-23.203223	-23.20072	-21.886143	-21.8863
2.42691	-22.063648	-22.056369	-20.830615	-20.831904
2.52691	-20.605166	-20.600497	-19.461948	-19.46126
2.62691	-19.051173	-19.054197	-17.9956	-17.995912
2.72691	-17.542804	-17.543969	-16.566059	-16.564526
5.0	-5.252928	-5.253768	-5.005749	-5.006684

Table S7: Energies, in eV, of the HOMO or SOMO (E_{HS}) and LUMO (E_L) orbitals of the *Ru*-Aqua/Oxo complexes, in vacuum and in solution. $\Delta E_{HS}^{VAC/SOL}$ and $\Delta E_L^{VAC/SOL}$ represent the energetic variations of E_{HS} and E_L due to the solvent (PCM) effect. ΔE_{HSL} represents the fundamental gap HOMO(or SOMO)-LUMO.

	E_{HS}			E_L			ΔE_{HSL}	
	VAC	SOL	$\Delta E_{HS}^{VAC/SOL}$	VAC	SOL	$\Delta E_L^{VAC/SOL}$	VAC	SOL
$Ru^{II}(H_2O)$	-11.43	-6.11	5.32	-7.97	-2.73	5.24	3.46	3.38
$Ru^{III}(H_2O)$	-15.81	-7.92	7.89	-11.34	-3.37	7.97	4.47	4.55
$Ru^{II}(OH)$	-7.35	-5.02	2.33	-4.96	-2.44	2.52	2.39	2.58
$Ru^{III}(OH)$	-12.26	-7.12	5.14	-8.24	-2.96	5.28	4.02	4.16
$Ru^{IV}(O)$	-12.18	-7.05	5.13	-8.24	-3.03	5.21	3.94	4.02

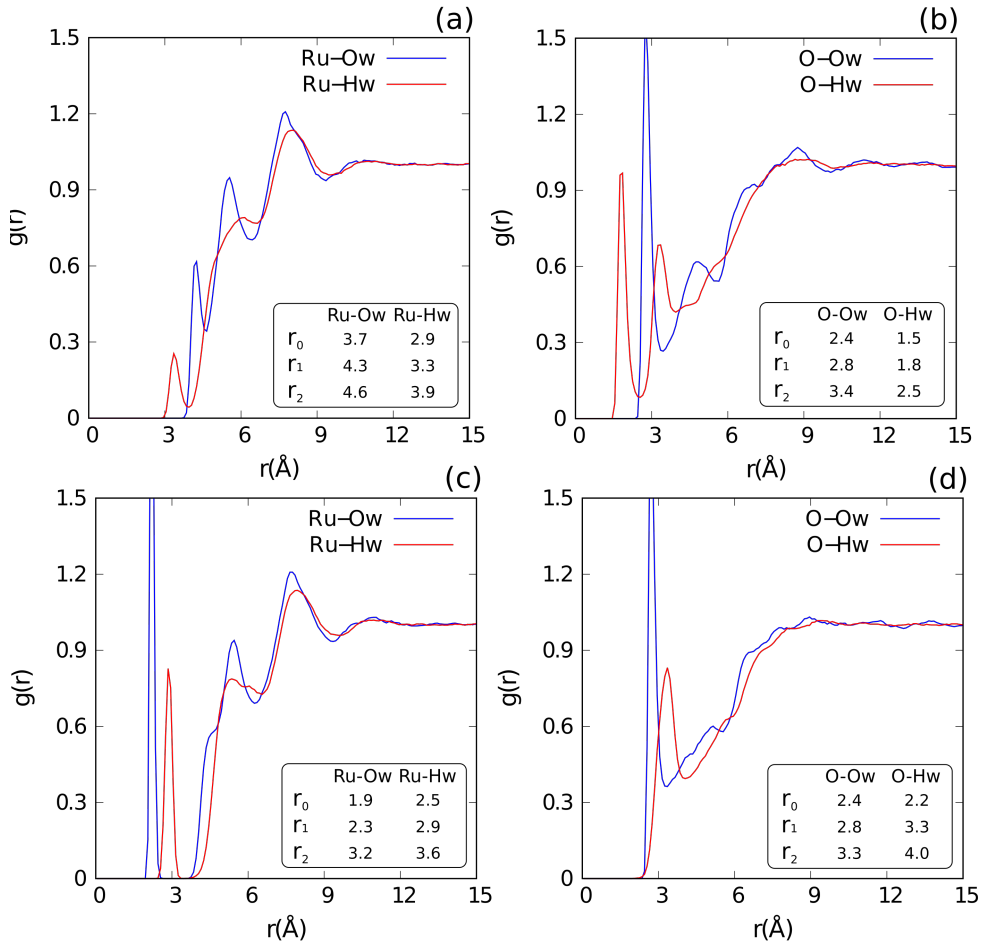


Figure S5: Radial distribution functions between Ru, O, and the oxygens (Ow) and hydrogens (Hw) of the solvent molecules for $Ru^{III}(OH)^{2+}$ (a, b) and $Ru^{III}(H_2O)^{3+}$ (c, d). The characteristic distances that demarcate the beginning of each RDF, the position of the first peak and the position of the first valley are indicated in the graphs by the labels r_0, r_1 and r_2, respectively.

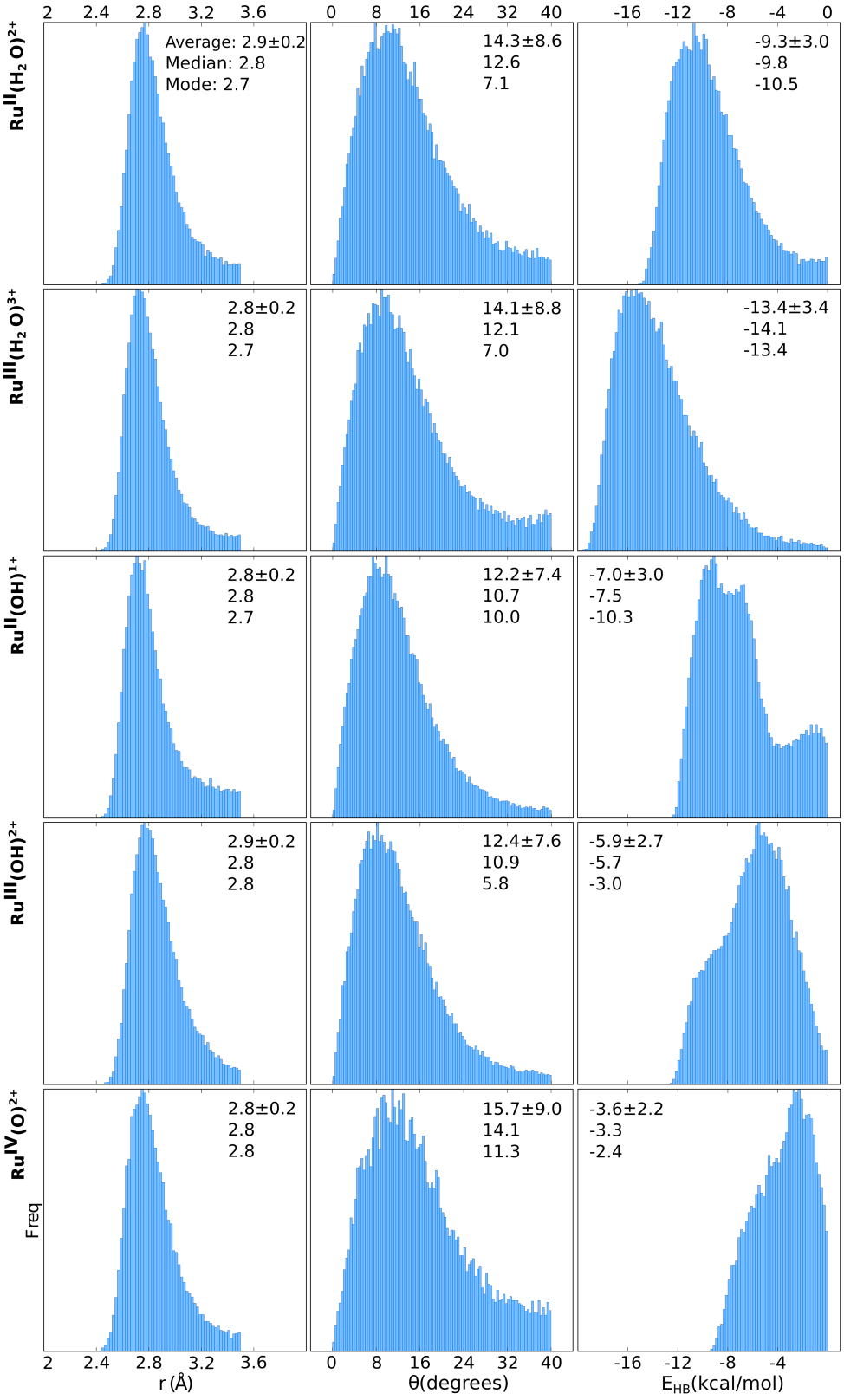


Figure S6: Distance *r* (Å), angle θ (degrees) and energy E (kcal/mol) distributions of the hydrogen bonds formed between the *Ru*-Aqua/Oxo complexes and the solvent. Distributions generated from the MC simulations.

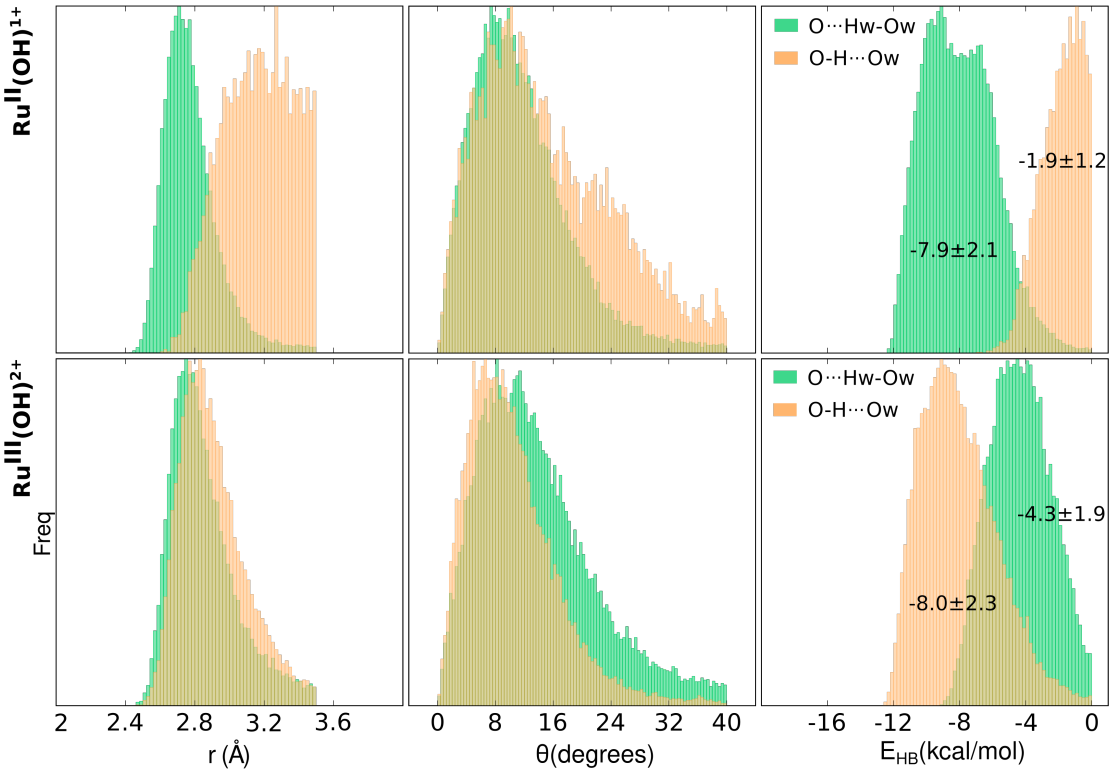


Figure S7: Distance r (Å), angle θ (degrees) and energy E (kcal/mol) distributions of the hydrogen bonds formed between the *Ru*-hydroxo complexes and the solvent. In green and yellow, the distributions relative to hydrogen bonds of the types $O\cdots Hw-Ow$ and $O-H\cdots Ow$, respectively. Distributions generated from the MC simulations.

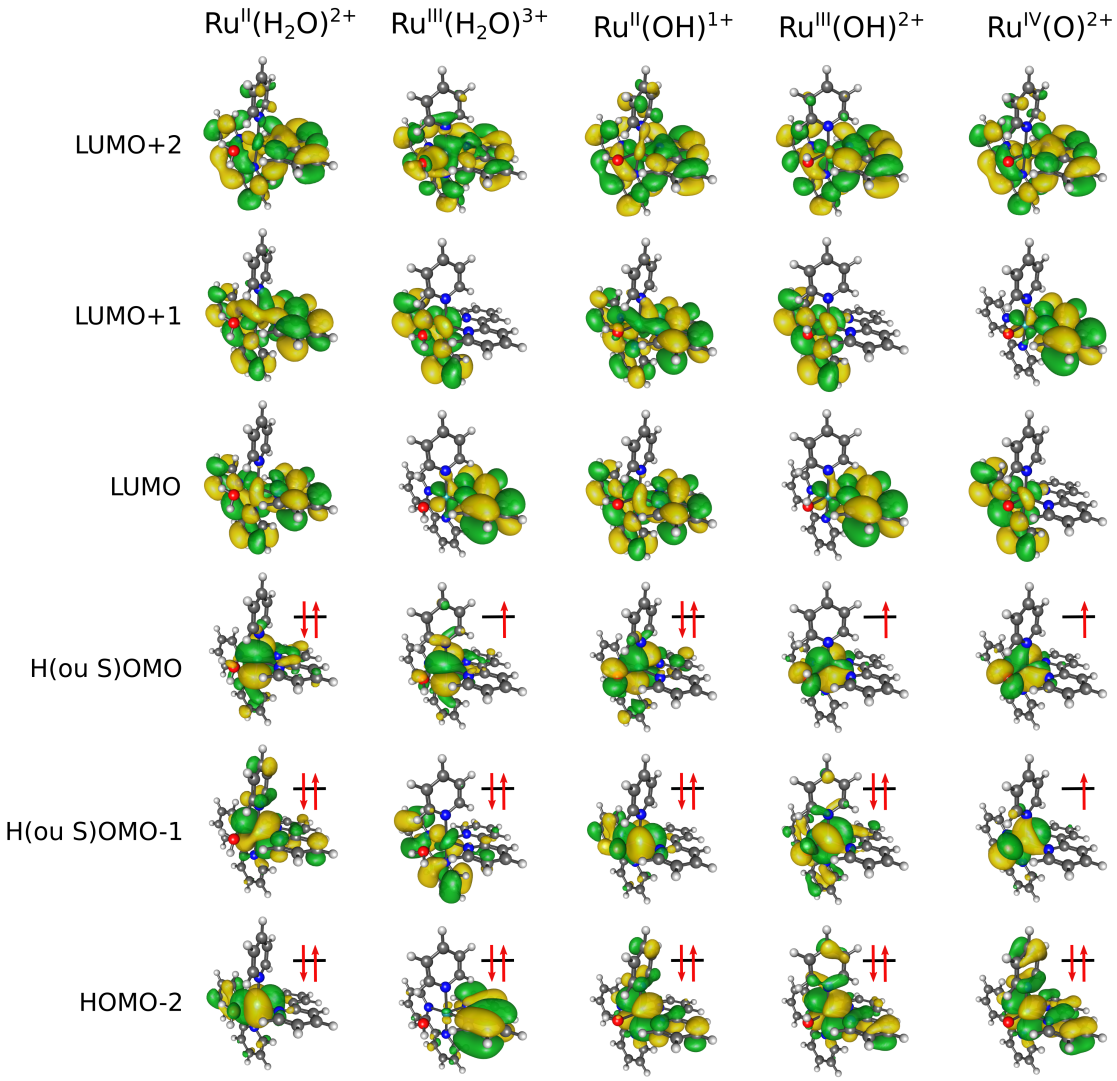


Figure S8: Frontier molecular orbitals of the Ru-Aqua/Oxo complexes.

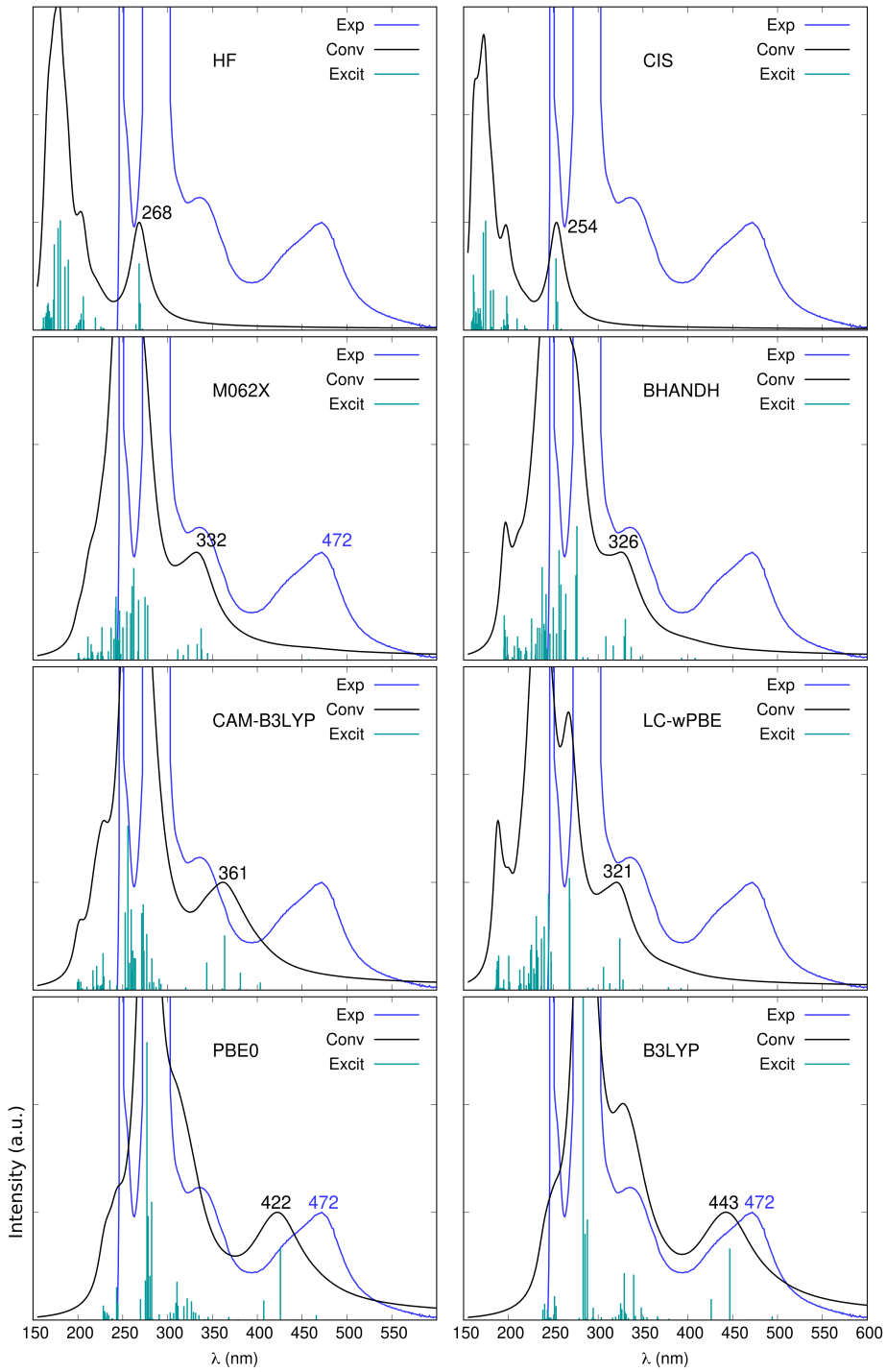


Figure S9: Theoretical UV-Vis absorption spectrum of the $Ru^{II}(H_2O)$ complex in aqueous solution, obtained with different methods, and using the basis set (aug)-cc-pVDZ/(PP-*Ru*). The first 50 calculated electronic excitations are represented by vertical bars, and the convoluted spectrum was obtained from the sum of Lorentzian functions of width 0.15 eV centered on each excitation. Solvent effects were included in the calculations using the continuous PCM model. Experimental spectrum presented for comparison.

Table S8: Wavelength value λ (*nm*) of the absorption peak of the lower energy band of the complex $Ru^{II}(H_2O)$ in aqueous solution, using the B3LYP functional and several sets of basis set. Solvent effects included via the PCM model. Deviation of λ from experimental value ($\Delta\lambda = \lambda^{exp} - \lambda^{teo}$), and actual processing time (in hours) using 10 Intel(R) processors Xeon(R) 2.40GHz E7-2870 CPU and 100GB RAM.

Tipo	Base	λ (nm)	$\Delta\lambda$ (nm)	Tempo (h)
All-electron/ECP	cc-pVDZ/(PP-*Ru*)	438.36	33.64	0.7
	cc-pVTZ/(PP-*Ru*)	448.26	23.74	24.4
	cc-pVQZ/(PP-*Ru*)	450.89	21.11	91.2
	(aug)-cc-pVDZ/(PP-*Ru*)	446.80	25.20	16.8
	(aug)-cc-pVTZ/(PP-*Ru*)	451.26	20.74	182.4
	LANL2DZ	435.95	36.05	0.4
	DEF2TZVP	442.73	35.31	19.2
	DEF2QZVP	447.76	29.27	379.2
	DEF2QZVPP	447.92	24.24	412.8
All-electron	Sapporo-DZP-2012	422.00	50.0	4.8
	Sapporo-TZP-2012	431.84	40.16	45.6
	Sapporo-QZP-2012	433.49	38.51	278.4
All-electron DKH	Jorge-ADZP	517.96	-45.96	2.1
	Jorge-ATZP	458.94	13.06	26.4
	Jorge-AQZP	450.31	21.69	340.8
	ANO-RCC-VDZP	440.67	31.33	45.6
Experimental		472.0		

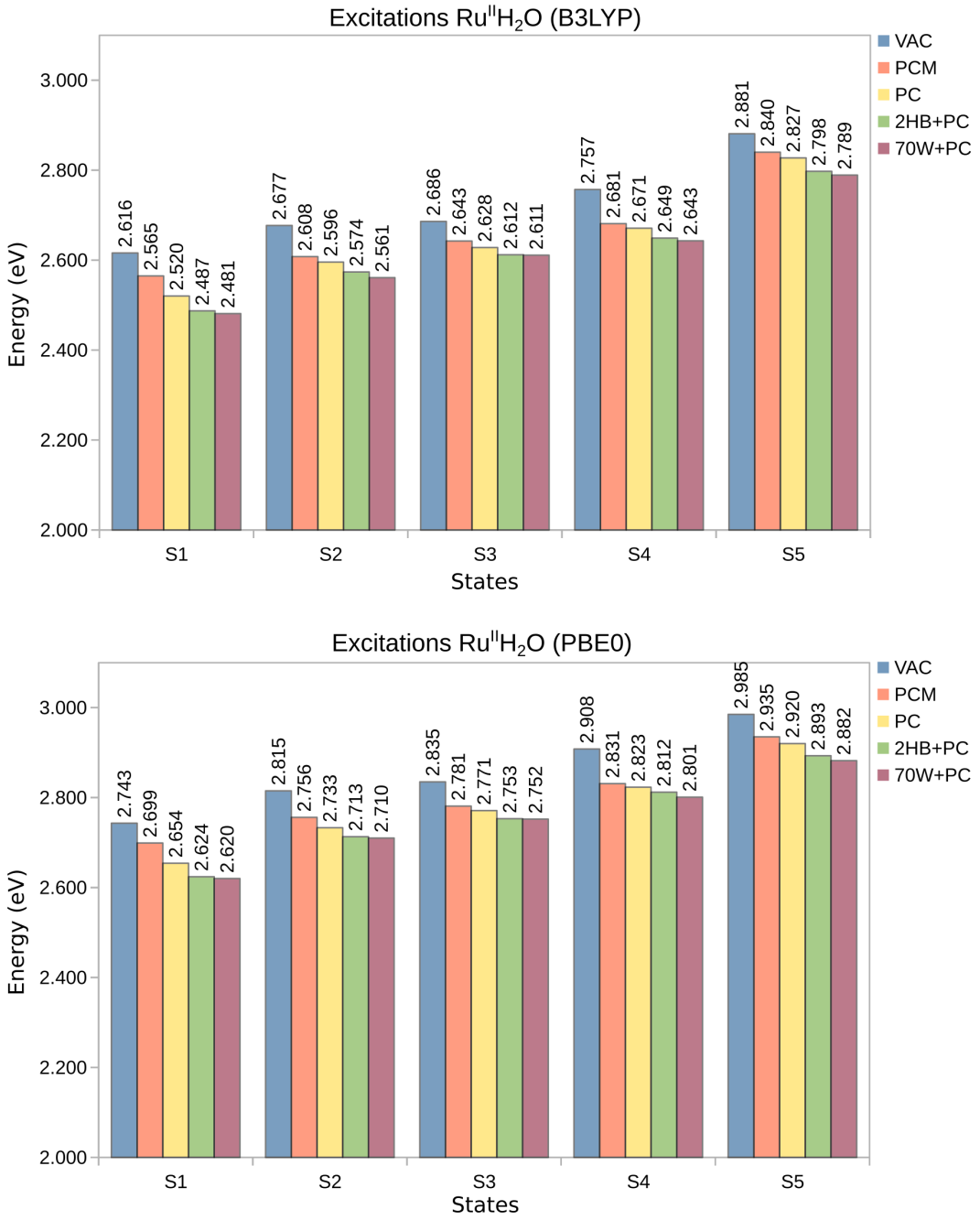


Figure S10: Comparisson of implic and explicit solvation effects on the electronic excitation energies of $Ru^{II}H_2O$. Excitation energies calculated for the first 5 excited states for five configurations extracted from the MC simulation, using B3LYP and PBE0, and the basis sets (aug)-cc-pVDZ(PP for Ru) for the complex and cc-pVDZ for the solvent molecules. VAC, PCM, PC, 2HB+PC and 70W+PC stands for vacuum, polarized continuum model, point charges, two explicit hydrogen bonds plus point charges, seventy explict solvent molecules plus point charges, respectively. Standard deviation of the calculated energies are smaller than 20 meV for all excitations. Excitation S5 is the most intense one, responsible for the low-lying MLCT band in the visible range.

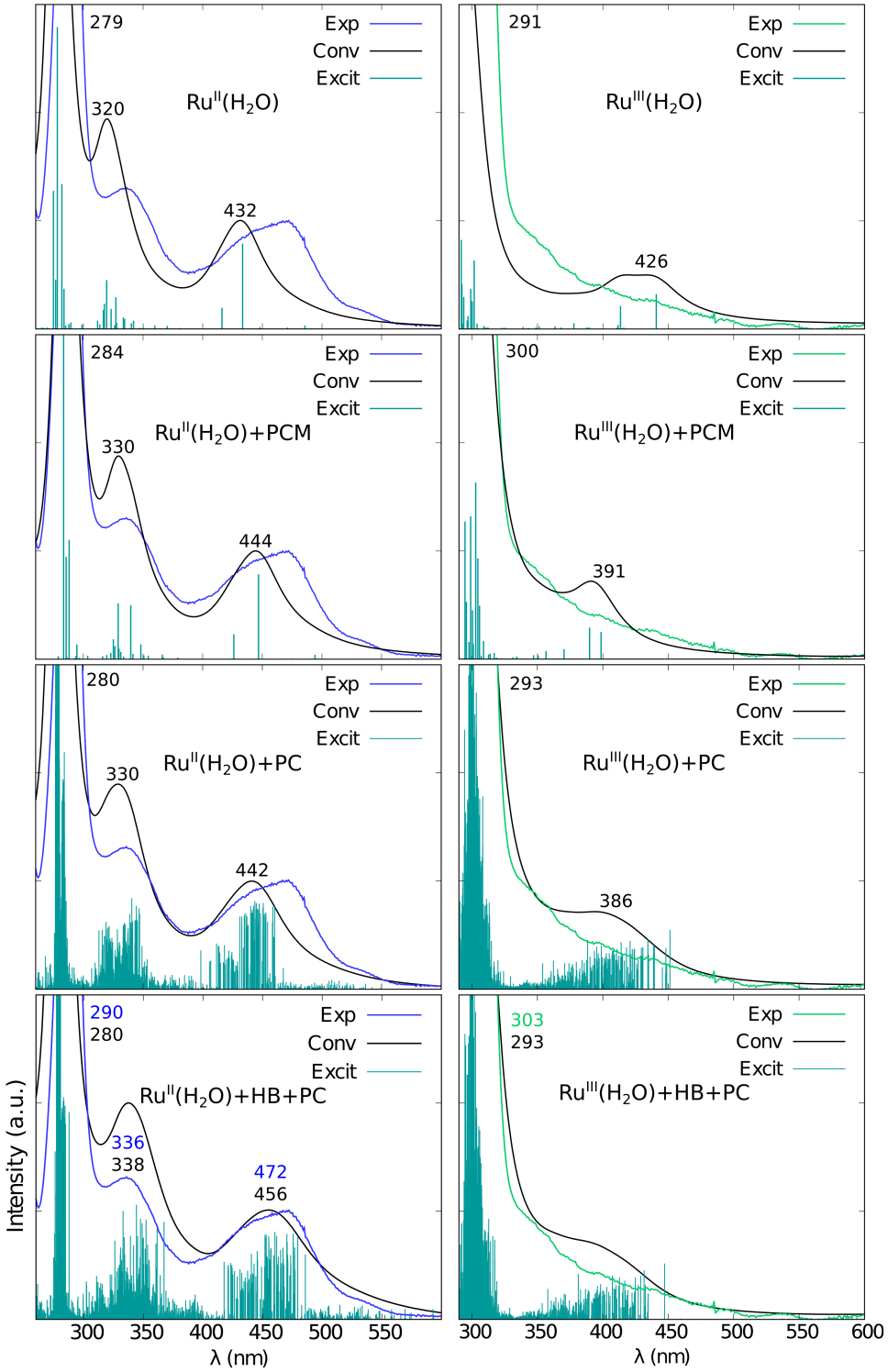


Figure S11: Theoretical UV-Vis absorption spectra of the *Ru*-Aqua complexes in vacuum and in aqueous solution. Electronic excitations, represented by vertical bars, calculated with the TD-DFT method and using B3LYP/(aug)-cc-pVDZ(PP-*Ru*). Theoretical spectra generated from the Lorentzian convolution of width 0.15 *eV* centered on each excitation. Solvent effects treated with PCM, PC and PC+HB models. Experimental spectra presented for comparison.

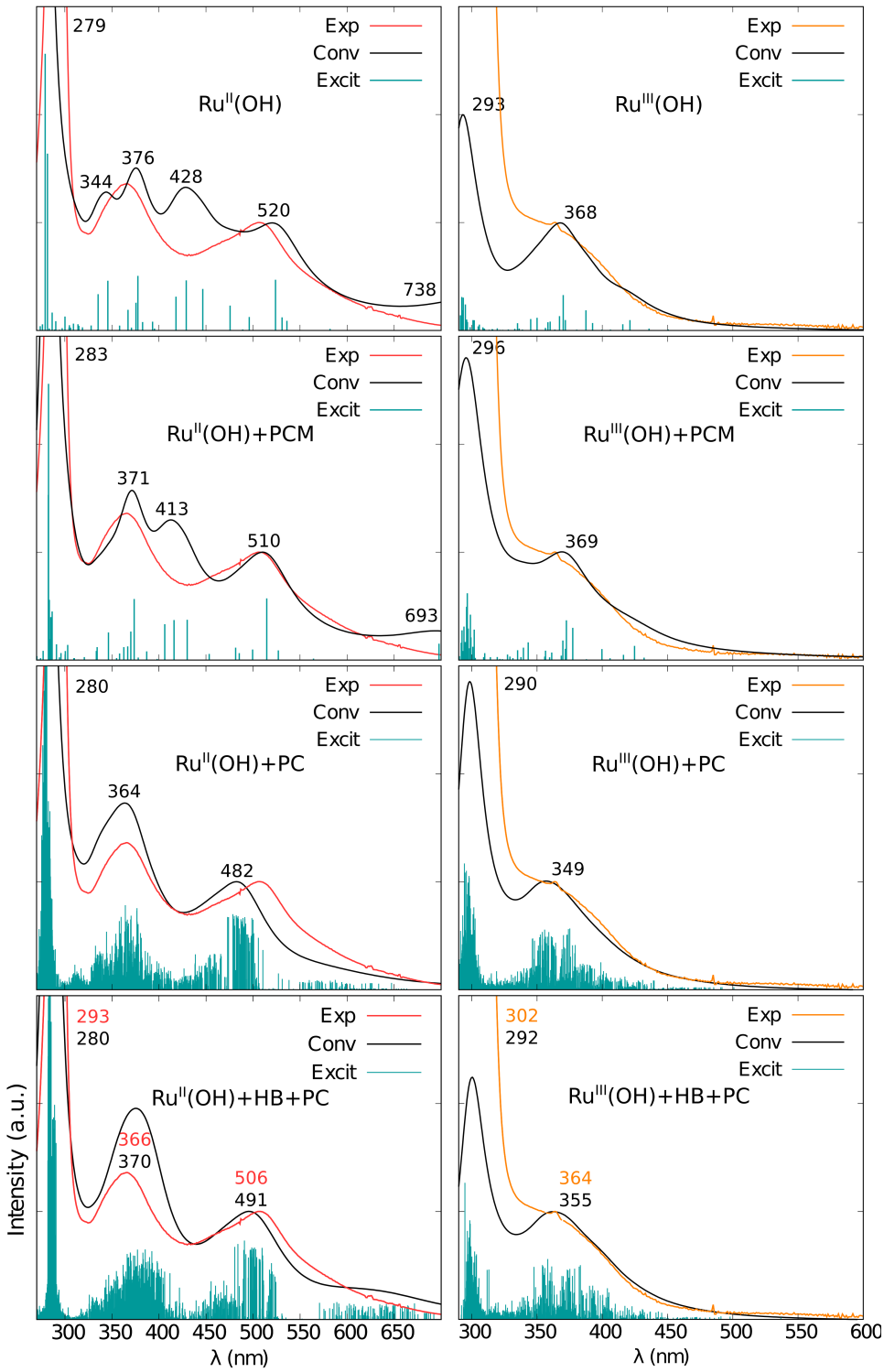


Figure S12: Theoretical UV-Vis absorption spectra of the *Ru*-hydroxo complexes in vacuum and in aqueous solution. Electronic excitations, represented by vertical bars, calculated with the TD-DFT method and using B3LYP/(aug)-cc-pVDZ(PP-*Ru*). Theoretical spectra generated from the Lorentzian convolution of width 0.15 *eV* centered on each excitation. Solvent effects treated with PCM, PC and PC+HB models. Experimental spectra presented for comparison.

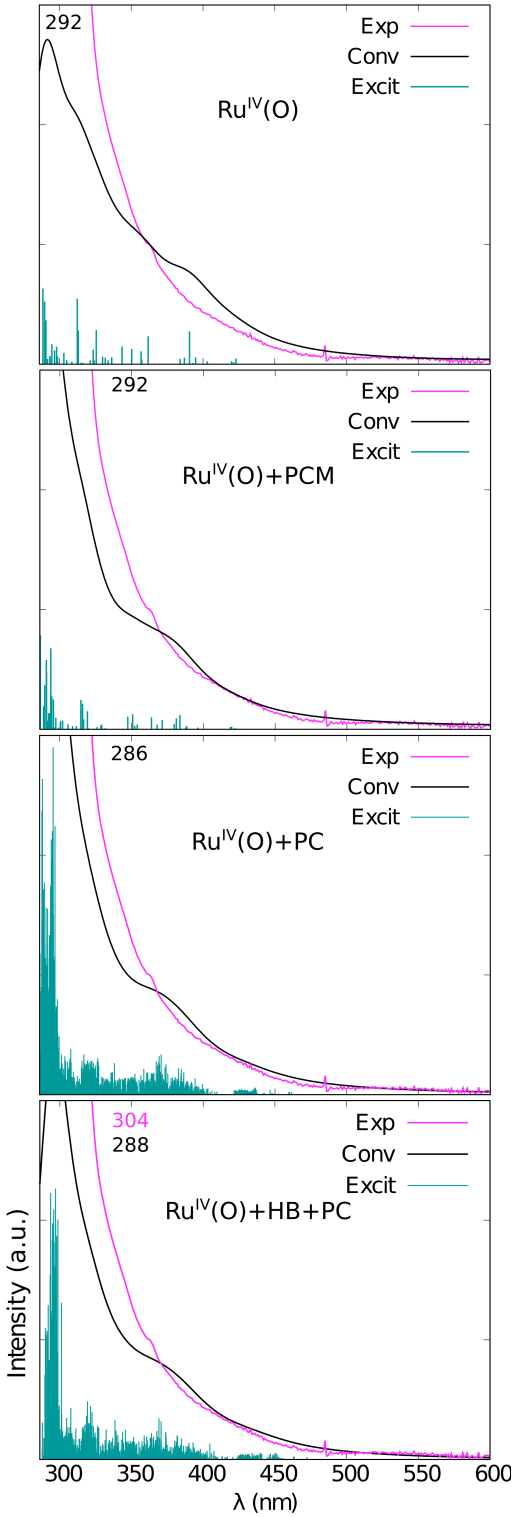


Figure S13: Theoretical UV-Vis absorption spectra of the *Ru*-oxo complexes in vacuum and in aqueous solution. Electronic excitations, represented by vertical bars, calculated with the TD-DFT method and using B3LYP/(aug)-cc-pVDZ(PP-*Ru*). Theoretical spectra generated from the Lorentzian convolution of width 0.15 *eV* centered on each excitation. Solvent effects treated with PCM, PC and PC+HB models. Experimental spectra presented for comparison.

Table S9: Wavelength λ (in *nm*) and intensity *I* ($\times 10^{-3}$) of the first 50 electronic excitations of the *Ru*-Aqua/Oxo complexes in the oxidation state *II*, calculated with the TD-DFT method, using B3LYP/(aug)-cc-pVDZ(PP-*Ru*). Solute-solvent interactions treated with PCM, PC and PC+HB methods.

	$Ru^{II}(H_2O)$							
	VAC		PCM		PC		HB+PC	
States	λ(*nm*)	*I*	λ(*nm*)	*I*	λ(*nm*)	*I*	λ(*nm*)	*I*
1	485.7	4	494.2	7	512.3	4	537.5	6
2	471.1	2	489.9	1	493.0	2	516.4	4
3	468.3	1	474.4	1	476.5	5	496.0	5
4	448.0	2	467.2	1	456.2	19	474.8	20
5	433.4	103	446.8	134	442.3	73	460.1	57
6	416.2	25	426.1	40	421.3	31	435.9	38
7	381.3	1	379.2	3	390.2	7	401.7	8
8	370.2	4	367.0	3	376.5	5	388.2	7
9	359.8	4	366.2	7	368.2	4	377.3	6
10	350.3	2	362.1	0	362.0	4	370.9	7
11	347.2	1	354.4	6	356.5	4	364.7	11
12	342.0	10	350.6	6	351.5	9	358.7	13
13	340.1	7	348.2	24	346.6	10	353.8	23
14	334.5	12	341.5	9	342.4	29	349.3	28
15	333.4	14	339.7	85	338.8	35	345.3	26
16	327.8	7	333.8	4	335.1	21	341.8	17
17	327.1	38	331.4	12	332.2	26	338.2	20
18	326.2	4	329.9	17	329.9	17	335.1	21
19	323.2	24	329.2	88	327.1	16	332.2	24
20	319.5	59	326.4	21	324.6	16	329.2	16
21	317.5	30	325.1	31	321.7	21	325.7	17
22	316.7	23	323.0	10	319.0	25	321.0	11
23	313.7	5	319.6	7	315.6	14	316.2	13
24	311.9	10	316.2	5	311.0	7	310.8	13
25	298.8	5	303.6	6	304.8	4	306.2	4
26	297.2	0	296.7	2	300.5	4	301.7	4
27	289.4	8	294.6	23	294.9	4	297.0	4
28	287.8	6	293.8	5	291.9	6	293.9	3
29	285.1	4	292.2	1	289.2	23	290.2	12
30	283.7	48	288.1	189	286.2	52	286.0	52
31	282.0	174	286.2	4	283.7	106	283.6	80
32	278.1	363	285.6	162	280.7	176	281.3	165
33	276.7	59	283.4	727	278.7	253	279.3	255
34	274.8	166	278.9	5	276.6	207	276.8	180
35	269.7	2	266.3	1	267.7	7	270.8	33
36	267.1	1	260.7	1	263.3	7	265.6	7
37	265.2	2	255.0	2	257.4	9	261.5	6
38	259.6	2	253.1	26	254.9	17	258.8	10
39	257.8	5	251.4	45	252.7	13	256.4	10
40	252.2	30	250.0	2	251.0	17	254.4	13
41	250.4	49	248.7	1	249.4	10	252.7	13
42	245.6	3	247.9	2	248.0	9	251.2	12
43	244.5	2	247.5	5	246.6	9	249.7	17
44	242.3	2	245.6	5	244.9	11	248.3	12
45	241.2	3	244.1	7	243.7	14	247.1	12
46	240.7	8	243.6	20	242.5	12	245.8	10
47	239.3	28	242.4	3	241.4	10	244.8	12
48	237.8	13	240.9	2	240.3	12	243.4	10
49	236.9	6	240.5	31	239.2	11	242.2	12
50	236.5	11	238.4	19	238.1	12	241.3	8

	$Ru^{II}(OH)$							
	VAC		PCM		PC		HB+PC	
Estados	λ(*nm*)	*I*	λ(*nm*)	*I*	λ(*nm*)	*I*	λ(*nm*)	I
1	808.2	5	745.6	4	621.9	3	647.5	13
2	738.3	21	697.8	25	576.7	7	605.4	10
3	581.9	2	564.4	2	536.0	1	545.0	0
4	536.0	10	526.9	15	506.2	8	509.1	16
5	530.9	14	514.7	93	487.7	74	497.5	63
6	523.9	53	499.6	16	457.3	28	469.9	22
7	496.0	14	485.4	10	435.5	15	455.7	14
8	489.1	1	481.6	19	416.4	12	438.4	9
9	475.6	26	453.5	9	397.6	13	413.0	7
10	446.6	43	430.1	61	392.1	9	402.1	6
11	429.0	52	416.1	60	385.8	14	393.9	29
12	418.2	35	406.2	54	379.0	20	387.3	33
13	395.3	2	398.1	2	374.5	29	380.6	36
14	393.3	9	387.1	13	370.4	24	375.3	44
15	382.6	9	378.1	4	366.0	23	365.7	41
16	377.6	57	373.8	92	360.2	24	360.6	25
17	375.6	29	370.2	43	355.9	27	356.3	16
18	370.8	3	366.8	21	350.7	17	353.7	14
19	367.1	22	362.7	20	346.5	17	351.1	19
20	359.7	0	358.2	10	342.7	16	347.4	15
21	358.2	5	355.0	3	336.7	22	342.8	15
22	345.7	52	346.3	42	331.7	19	336.4	13
23	335.4	38	334.4	20	327.2	13	328.0	10
24	334.9	1	333.5	14	319.2	5	324.8	10
25	327.9	5	320.7	4	315.1	9	316.5	3
26	318.8	3	314.3	1	307.8	6	310.7	2
27	314.9	5	310.1	3	304.5	4	306.9	3
28	314.0	7	309.5	3	300.8	3	300.4	2
29	309.2	7	303.1	23	296.9	3	295.8	2
30	306.0	3	300.6	14	293.7	4	291.2	6
31	304.9	6	297.2	1	287.9	56	287.8	19
32	304.5	3	295.9	11	283.3	116	285.0	28
33	300.2	15	294.3	4	281.2	165	283.3	92
34	297.2	2	291.2	24	279.7	197	281.6	143
35	294.4	1	289.8	1	277.0	99	279.7	201
36	290.4	10	286.6	73	274.4	62	277.7	113
37	289.2	1	285.1	65	272.0	46	276.0	113
38	286.6	19	284.6	32	269.2	23	273.0	39
39	283.4	2	283.6	91	266.8	6	270.2	16
40	281.6	185	282.7	416	264.3	6	267.5	6
41	279.1	290	282.5	249	262.1	5	265.4	4
42	276.2	6	276.9	14	260.1	6	263.5	4
43	273.9	4	274.2	3	258.8	7	261.6	4
44	270.4	1	272.4	1	257.5	10	260.0	5
45	269.7	1	270.3	6	256.3	9	258.7	3
46	268.8	190	268.6	3	255.1	8	257.4	5
47	266.4	16	263.4	4	253.8	6	256.5	5
48	265.5	31	263.4	0	252.4	11	255.1	5
49	264.5	6	259.7	3	251.1	13	253.8	8
50	262.1	5	258.6	1	250.0	13	252.4	13

Table S10: Wavelength λ (in *nm*) and intensity *I* ($\times 10^{-3}$) of the first 50 electronic excitations of the *Ru*-Aqua/Oxo complexes in the oxidation state *III*, calculated with the TD-DFT method, using B3LYP/(aug)-cc-pVDZ(PP-*Ru*). Solute-solvent interactions treated with PCM, PC and PC+HB methods.

	$Ru^{III}(H_2O)$							
	VAC		PCM		PC		HB+PC	
States	λ(*nm*)	*I*	λ(*nm*)	*I*	λ(*nm*)	*I*	λ(*nm*)	*I*
1	746.1	1	677.5	1	717.6	0	698.4	0
2	735.9	0	667.2	0	707.3	0	688.1	0
3	725.6	2	657.0	3	697.1	2	677.9	2
4	683.1	2	636.5	2	644.8	1	623.7	1
5	603.6	0	532.9	0	549.7	0	534.4	0
6	440.8	32	419.9	0	437.1	3	438.5	1
7	425.2	0	417.3	0	429.2	4	425.7	2
8	416.0	1	415.3	0	416.6	6	418.3	4
9	413.5	21	412.4	0	411.8	3	411.6	4
10	411.7	4	398.7	27	407.1	6	405.0	6
11	410.7	1	389.8	31	393.9	14	395.5	8
12	389.7	2	375.1	1	382.6	6	382.6	8
13	387.8	2	370.3	10	372.8	5	372.8	7
14	377.9	5	360.5	0	365.6	5	366.0	5
15	368.0	2	356.6	8	360.0	3	361.3	4
16	363.4	3	350.6	4	355.7	2	356.8	3
17	359.4	3	348.7	1	352.2	2	353.1	3
18	351.3	3	347.0	4	348.7	1	350.1	2
19	348.8	2	343.7	0	345.2	1	347.1	2
20	343.2	1	339.6	1	341.6	1	344.3	1
21	342.5	1	337.6	0	338.1	1	341.3	1
22	339.0	2	334.2	3	335.2	1	338.6	1
23	334.3	0	331.4	2	332.3	2	335.3	1
24	325.3	1	329.9	0	329.1	1	332.8	1
25	323.3	1	324.0	1	325.1	1	329.6	1
26	318.6	0	322.4	1	321.8	1	326.7	1
27	317.5	0	320.4	1	319.4	1	323.7	1
28	312.2	2	318.7	2	316.8	1	320.5	1
29	311.4	1	317.0	6	314.9	1	318.5	1
30	310.3	1	313.9	5	312.6	2	316.5	1
31	309.1	3	312.6	5	310.1	3	314.6	1
32	305.7	0	308.7	18	307.1	4	312.4	2
33	303.8	5	307.1	3	304.6	13	309.8	6
34	301.7	63	305.7	52	302.7	18	307.5	6
35	300.1	26	304.4	98	300.9	24	305.3	11
36	299.0	37	302.8	172	299.5	31	303.2	18
37	297.0	2	301.0	15	298.2	32	301.2	24
38	297.0	12	300.4	48	297.0	31	299.8	24
39	296.3	8	299.6	3	295.8	35	298.6	29
40	293.7	30	299.0	139	294.5	44	297.2	44
41	292.9	5	297.7	17	293.0	47	296.1	29
42	292.2	42	295.7	56	291.9	69	294.7	37
43	291.8	82	294.6	134	290.6	69	293.3	49
44	288.8	88	289.3	39	289.0	43	292.3	58
45	287.3	29	287.7	4	287.7	31	291.1	57
46	286.8	50	287.5	5	286.4	22	289.8	57
47	286.1	6	286.6	4	285.3	19	288.5	51
48	285.2	16	284.8	6	284.2	13	286.8	22
49	285.0	48	283.3	19	283.2	11	285.4	21
50	282.4	4	280.5	2	282.0	11	284.3	14

	$Ru^{III}(OH)$							
	VAC		PCM		PC		HB+PC	
Estados	λ(*nm*)	*I*	λ(*nm*)	*I*	λ(*nm*)	*I*	λ(*nm*)	I
1	470.9	1	459.6	1	473.8	0	476.4	1
2	460.7	0	449.4	0	463.6	0	466.2	0
3	450.4	1	439.1	0	453.3	1	455.9	1
4	435.8	2	432.0	2	437.0	2	441.2	2
5	421.2	10	424.7	13	417.0	3	422.7	3
6	415.7	6	416.3	5	410.0	2	412.9	3
7	406.2	1	405.9	2	401.9	4	406.1	3
8	399.6	1	399.7	10	393.6	8	397.9	7
9	395.4	0	393.4	0	387.2	3	391.3	6
10	392.6	7	387.8	1	382.0	5	387.2	7
11	387.5	19	377.4	30	377.6	11	382.5	9
12	380.5	1	372.5	37	370.7	6	376.3	9
13	371.7	10	371.8	10	365.2	8	369.9	10
14	370.1	33	369.8	18	362.3	8	365.4	8
15	367.2	13	368.6	4	359.5	9	362.2	9
16	363.6	1	361.2	7	355.3	12	359.6	9
17	360.0	8	359.6	3	351.1	21	355.8	12
18	358.3	8	356.5	9	347.3	14	352.7	15
19	356.4	2	355.9	3	342.7	8	349.1	11
20	350.0	12	343.2	16	337.9	7	345.2	6
21	345.1	11	339.6	12	333.8	4	341.3	7
22	338.8	1	337.7	3	330.1	3	336.6	4
23	336.3	2	335.1	9	327.6	3	333.3	5
24	335.0	7	331.6	2	325.7	2	329.8	3
25	332.9	2	329.2	3	323.9	3	327.5	4
26	328.0	1	327.4	5	321.9	2	325.4	3
27	323.7	1	323.4	1	320.1	2	323.0	2
28	321.6	1	321.5	1	318.6	1	321.3	2
29	319.5	2	319.5	3	316.9	2	319.5	2
30	316.0	1	317.4	0	315.2	2	317.8	1
31	315.6	1	314.3	3	312.3	3	316.1	2
32	313.3	1	309.9	6	310.0	3	313.7	3
33	309.8	1	309.1	3	307.5	3	311.6	4
34	309.4	2	302.7	2	305.2	3	309.7	2
35	308.5	3	301.9	28	303.3	3	307.4	3
36	305.8	5	300.7	12	301.2	4	305.4	3
37	304.9	4	299.3	21	299.5	4	303.3	3
38	301.9	10	298.9	42	298.0	5	301.8	4
39	300.9	10	298.3	11	296.5	10	300.1	6
40	298.7	3	297.3	29	295.2	14	299.0	8
41	296.7	8	296.6	62	293.9	19	297.6	9
42	296.1	10	296.0	49	293.0	22	296.2	16
43	295.1	24	295.0	17	291.9	20	295.2	13
44	293.5	30	294.0	31	291.0	24	294.1	15
45	292.6	19	293.3	8	290.1	34	293.2	19
46	292.3	31	292.5	28	289.2	37	292.2	19
47	291.3	14	291.9	16	288.3	28	291.4	28
48	289.8	2	290.5	4	287.1	25	290.4	24
49	289.2	8	289.9	50	286.0	15	289.5	21
50	288.6	35	288.9	41	285.1	17	288.5	20

Table S11: Wavelength λ (in *nm*) and intensity *I* ($\times 10^{-3}$) of the first 50 electronic excitations of the *Ru*-Aqua/Oxo complexes in the oxidation state *IV*, calculated with the TD-DFT method, using B3LYP/(aug)-cc-pVDZ(PP-*Ru*). Solute-solvent interactions treated with PCM, PC and PC+HB methods.

	$Ru^{IV}(O)$							
	VAC		PCM		PC		HB+PC	
States	λ	*I*	λ	*I*	λ	*I*	λ	I
1	626.0	1	651.2	1	675.2	1	683.1	0
2	606.4	0	628.1	0	637.2	0	646.9	0
3	433.3	0	434.1	0	439.3	0	442.3	1
4	423.0	3	422.1	1	425.4	1	427.9	1
5	421.5	1	419.6	2	421.8	1	423.5	2
6	420.1	1	418.8	2	418.1	2	419.4	2
7	403.0	1	396.1	2	393.3	1	398.2	1
8	394.9	3	388.4	3	389.1	2	392.6	2
9	392.9	1	387.6	2	383.5	3	386.1	3
10	390.6	15	383.6	12	379.7	3	381.5	3
11	389.4	0	381.1	9	375.8	3	377.9	4
12	387.0	3	379.6	5	373.3	5	374.8	4
13	384.1	2	376.7	1	370.2	3	371.9	3
14	378.9	3	371.3	8	366.9	3	369.1	3
15	361.8	12	367.7	4	362.0	7	365.7	4
16	357.4	2	363.8	10	358.2	5	361.7	4
17	356.9	6	353.8	4	354.4	5	357.8	5
18	350.3	7	352.1	3	350.3	4	354.0	5
19	343.6	8	350.7	13	342.9	4	349.7	4
20	336.4	3	347.3	11	338.0	3	345.1	4
21	333.9	2	331.7	1	334.3	3	339.5	5
22	331.9	3	329.1	4	328.7	4	335.6	4
23	330.0	3	328.5	3	324.9	3	331.1	3
24	325.6	15	325.9	2	322.6	3	327.9	3
25	324.2	2	319.8	1	319.3	4	324.3	3
26	323.5	6	319.1	15	316.6	7	322.1	3
27	321.4	2	316.5	8	314.4	6	319.5	4
28	316.6	1	315.8	21	312.5	7	316.9	7
29	316.1	1	314.6	25	310.8	9	314.8	7
30	314.7	1	314.5	16	309.0	7	312.8	8
31	313.1	15	311.4	3	306.2	4	310.7	9
32	312.4	29	308.8	3	304.1	3	308.7	7
33	308.6	1	305.7	4	302.1	5	306.4	5
34	305.0	2	301.9	7	300.2	4	304.4	4
35	303.1	5	300.4	7	298.1	3	302.2	4
36	298.7	3	299.1	1	296.5	4	300.4	4
37	298.0	8	297.1	10	295.1	4	298.5	4
38	297.0	1	296.5	2	293.8	4	297.2	5
39	296.6	6	295.5	25	292.9	5	295.9	3
40	295.5	0	294.2	28	291.9	6	294.8	4
41	294.7	9	293.6	68	291.0	11	293.7	6
42	293.5	4	292.9	14	289.9	13	292.9	8
43	293.3	4	292.1	13	288.8	22	291.9	6
44	291.7	2	291.4	7	287.9	36	290.8	17
45	291.0	1	290.7	49	286.9	44	289.8	26
46	290.6	19	290.5	58	285.7	50	288.7	23
47	289.7	28	289.4	37	284.3	40	287.8	38
48	288.5	33	288.6	19	282.7	27	286.8	40
49	285.8	15	286.3	79	281.2	30	285.5	33
50	285.6	11	285.4	7	280.0	35	284.2	30

Table S12: Wavelength, λ (*nm*), of the UV-Vis absorption peaks of the *Ru*-Aqua/Oxo complexes in vacuum and in aqueous solution, using B3LYP/(aug)-cc-pVDZ/(PP-*Ru*) and different approaches for the solute-solvent interaction (PCM, PC, HB+PC).

	$Ru^{II}(H_2O)$			$Ru^{II}(OH)$			$Ru^{III}(H_2O)$		$Ru^{III}(OH)$		$Ru^{IV}(O)$
	picos			picos			picos		picos		picos
	I	II	III	I	II	III	II	III	II	III	III
VAC	432	320	279	520	376	279	426	291	368	293	292
PCM	444	330	284	510	371	283	391	300	369	296	292
PC	442	330	280	482	364	280	386	293	349	290	286
HB+PC	456	338	280	491	370	280	-	293	355	292	288
EXP	472	336	290	506	366	293	-	303	364	302	304

Table S13: Percentage of MC, MLCT, LMCT, LC and LLCT contributions for electronic excitation groups (1-30 and 31-50).

	$Ru^{II}(H_2O)$		$Ru^{III}(H_2O)$		$Ru^{II}(OH)$		$Ru^{III}(OH)$		$Ru^{IV}(O)$	
	1-30	31-50	1-30	31-50	1-30	31-50	1-30	31-50	1-30	31-50
MC	9	9	15	5	8	12	16	5	11	4
MLCT	60	30	16	18	58	30	34	24	25	21
LMCT	3	5	32	8	4	8	15	10	17	7
LC	9	23	24	41	7	15	21	30	25	36
LLCT	19	33	13	28	23	35	14	31	22	32

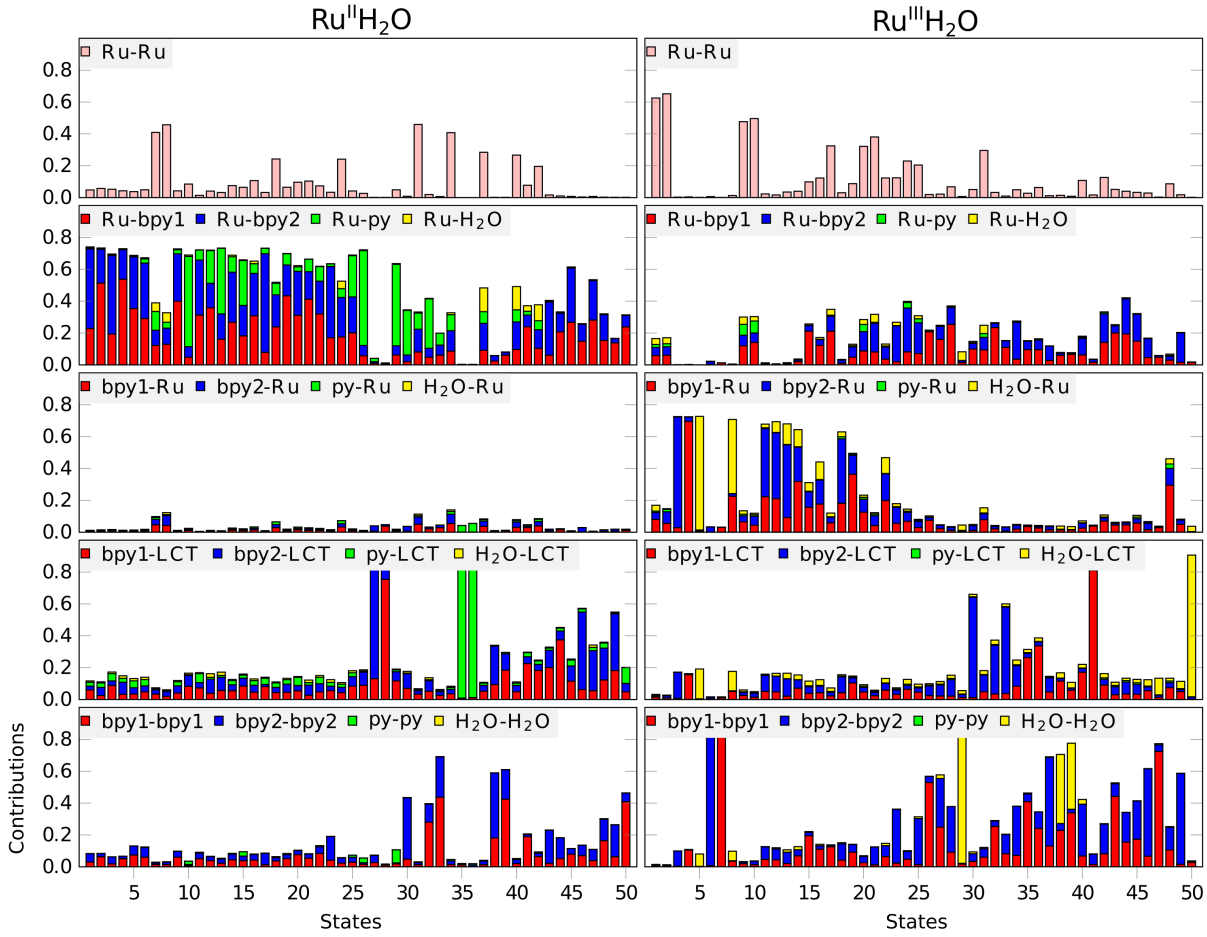


Figure S14: Detailed map of MC, MLCT, LMCT, LLCT and LC contributions in the electronic excitations of the $Ru^{II}(H_2O)$ and $Ru^{III}(H_2O)$ complexes in aqueous solution.

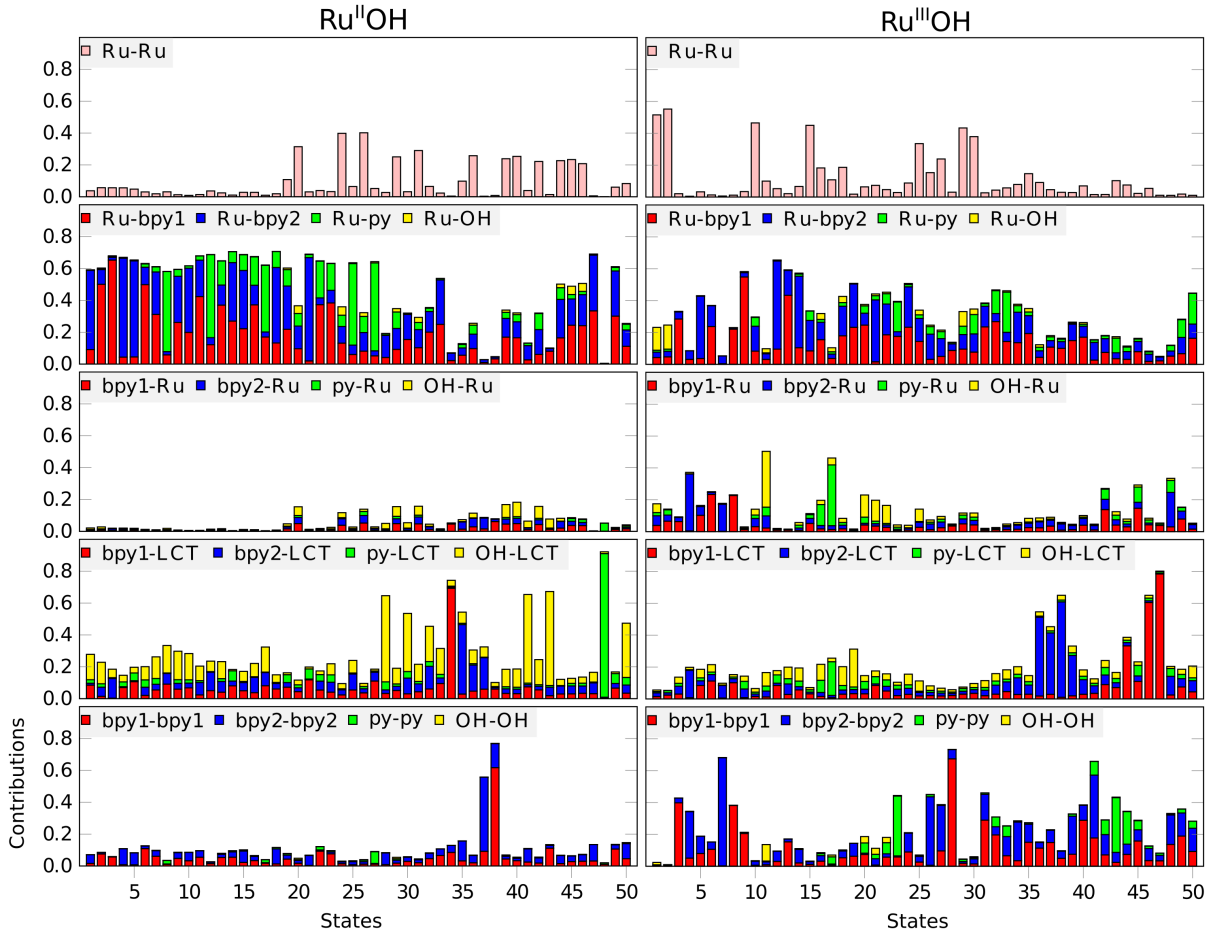


Figure S15: Detailed map of MC, MLCT, LMCT, LLCT and LC contributions in the electronic excitations of the $Ru^{II}(OH)$ and $Ru^{III}(OH)$ complexes in aqueous solution.

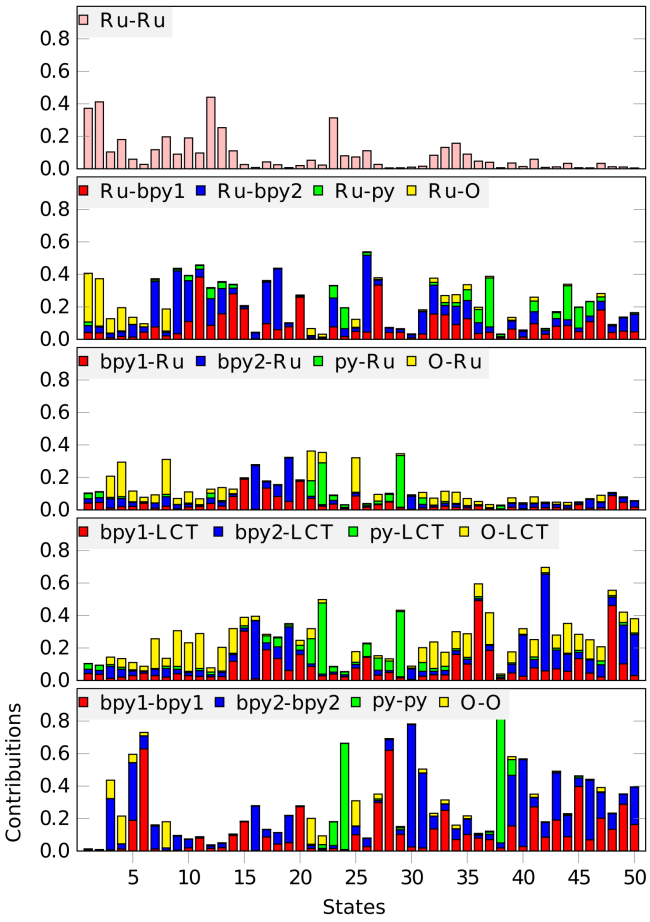


Figure S16: Detailed map of MC, MLCT, LMCT, LLCT and LC contributions in the electronic excitations of the $Ru^{IV}(O)$ complex in aqueous solution.

1.3 Parameters for MC simulations

Geometry and Lennard-Jones Coulomb parameters of $[Ru^{II}(H_2O)(py)(bpy)_2]^{2+}$

	X	Y	Z	Q(e)	E(kcal/mol)	S(Ang.)
C	-3.241264	-2.490441	0.270253	-0.151	0.07	3.55
C	-2.117089	-1.662292	0.346317	0.122	0.07	3.55
N	-1.577458	-1.100252	-0.772114	-0.234	0.17	3.25
C	-2.145056	-1.351254	-1.967101	0.099	0.07	3.55
C	-3.264207	-2.166825	-2.109481	-0.128	0.07	3.55
C	-3.824039	-2.746455	-0.969261	0.042	0.07	3.55
H	-3.682532	-2.338070	-3.100066	0.133	0.03	2.42
H	-1.679183	-0.881454	-2.830618	0.095	0.03	2.42
C	-1.767906	-1.850075	2.848328	-0.199	0.07	3.55
C	-1.412783	-1.334770	1.597776	0.249	0.07	3.55
N	-0.351592	-0.485176	1.459639	-0.420	0.17	3.25
C	0.366001	-0.161574	2.555520	0.233	0.07	3.55
C	0.063305	-0.646694	3.823400	-0.164	0.07	3.55
C	-1.027047	-1.505171	3.975796	0.072	0.07	3.55
H	-2.617447	-2.522417	2.940270	0.148	0.03	2.42
Ru	0.048736	0.148231	-0.440563	0.944	0.40	1.80
C	4.177470	1.222272	0.100447	-0.176	0.07	3.55
C	2.949626	0.584468	-0.103696	0.197	0.07	3.55
N	1.775444	1.277776	-0.055857	-0.371	0.17	3.25
C	1.818845	2.605053	0.173897	0.220	0.07	3.55
C	3.007737	3.298052	0.382389	-0.167	0.07	3.55
C	4.211355	2.592502	0.349454	0.076	0.07	3.55
C	3.901472	-1.737327	-0.452014	-0.187	0.07	3.55
C	2.816665	-0.856467	-0.390443	0.207	0.07	3.55
N	1.541888	-1.291571	-0.603867	-0.354	0.17	3.25
C	1.338267	-2.594715	-0.879237	0.170	0.07	3.55
C	2.375327	-3.519559	-0.955005	-0.146	0.07	3.55
C	3.683006	-3.083250	-0.736397	0.065	0.07	3.55
H	1.204811	0.511774	2.402070	0.046	0.03	2.42
H	-1.295162	-1.903065	4.953878	0.107	0.03	2.42
H	0.678588	-0.348764	4.670893	0.134	0.03	2.42
H	-3.661812	-2.933032	1.170179	0.139	0.03	2.42
H	-4.700716	-3.389265	-1.041472	0.111	0.03	2.42
H	0.863826	3.123441	0.189520	0.047	0.03	2.42
H	2.978937	4.370986	0.565350	0.134	0.03	2.42
H	5.162689	3.098793	0.509858	0.105	0.03	2.42
H	5.104240	0.655183	0.061715	0.141	0.03	2.42
H	0.308190	-2.898450	-1.044659	0.060	0.03	2.42
H	2.150749	-4.560706	-1.181230	0.131	0.03	2.42
H	4.521045	-3.777767	-0.785679	0.109	0.03	2.42
H	4.912266	-1.376969	-0.277646	0.145	0.03	2.42
C	-3.264599	3.818474	-0.134445	0.073	0.07	3.55
C	-2.586100	3.382026	1.004608	-0.185	0.07	3.55
C	-1.656003	2.352829	0.888223	0.222	0.07	3.55
N	-1.369539	1.747772	-0.286885	-0.368	0.17	3.25
C	-2.036847	2.171091	-1.384275	0.204	0.07	3.55
C	-2.979929	3.194966	-1.350016	-0.199	0.07	3.55
H	-3.997679	4.623118	-0.075467	0.105	0.03	2.42
H	-2.768200	3.827718	1.981615	0.136	0.03	2.42

H	-1.122018	1.998208	1.765641	0.030	0.03	2.42
H	-1.797569	1.673043	-2.320335	0.051	0.03	2.42
H	-3.479317	3.490485	-2.271844	0.147	0.03	2.42
O	0.337714	0.673429	-2.571305	-0.834	0.1521	3.1506
H	0.818405	0.011311	-3.089368	0.417	0.0000	0.0000
H	0.803348	1.507281	-2.734042	0.417	0.0000	0.0000

Geometry and Lennard-Jones Coulomb parameters of $[Ru^{II}(OH)(py)(bpy)_2]^{1+}$

	X	Y	Z	Q(e)	E(kcal/mol)	S(Ang.)
C	-3.292231	-2.427922	0.129935	-0.143	0.07	3.55
C	-2.150358	-1.631563	0.278874	-0.010	0.07	3.55
N	-1.535585	-1.079177	-0.805189	0.066	0.17	3.25
C	-2.032972	-1.308646	-2.036023	0.032	0.07	3.55
C	-3.163659	-2.092254	-2.247149	-0.145	0.07	3.55
C	-3.806942	-2.660801	-1.143452	0.020	0.07	3.55
H	-3.529949	-2.249354	-3.260850	0.124	0.03	2.42
H	-1.484579	-0.836483	-2.849878	0.103	0.03	2.42
C	-1.929262	-1.863119	2.791908	-0.217	0.07	3.55
C	-1.502469	-1.333637	1.567894	0.291	0.07	3.55
N	-0.415601	-0.505294	1.489433	-0.374	0.17	3.25
C	0.255698	-0.223973	2.628468	0.234	0.07	3.55
C	-0.115146	-0.724555	3.871046	-0.172	0.07	3.55
C	-1.234752	-1.558194	3.959194	0.033	0.07	3.55
H	-2.797844	-2.516984	2.831087	0.144	0.03	2.42
Ru	0.085104	0.144313	-0.418512	0.331	0.40	1.80
C	4.196048	1.230052	0.104366	-0.167	0.07	3.55
C	2.969951	0.583013	-0.091841	0.072	0.07	3.55
N	1.786536	1.258817	0.000989	0.127	0.17	3.25
C	1.822674	2.579066	0.278767	-0.016	0.07	3.55
C	3.007258	3.277726	0.485966	-0.107	0.07	3.55
C	4.221110	2.590557	0.397898	-0.003	0.07	3.55
C	3.926888	-1.725182	-0.510172	-0.192	0.07	3.55
C	2.839325	-0.850411	-0.398327	0.166	0.07	3.55
N	1.557184	-1.289244	-0.561738	-0.129	0.17	3.25
C	1.353321	-2.594401	-0.834436	0.047	0.07	3.55
C	2.391120	-3.512107	-0.956881	-0.124	0.07	3.55
C	3.707000	-3.070163	-0.793417	0.026	0.07	3.55
H	1.117141	0.431852	2.524261	-0.016	0.03	2.42
H	-1.557166	-1.966386	4.916577	0.098	0.03	2.42
H	0.467540	-0.458998	4.752251	0.129	0.03	2.42
H	-3.778051	-2.862583	1.000652	0.127	0.03	2.42
H	-4.696035	-3.277892	-1.271210	0.100	0.03	2.42
H	0.861789	3.083780	0.332338	0.084	0.03	2.42
H	2.970173	4.343190	0.708667	0.116	0.03	2.42
H	5.169580	3.104305	0.552019	0.108	0.03	2.42
H	5.127596	0.674300	0.025075	0.139	0.03	2.42
H	0.319097	-2.903440	-0.960225	0.082	0.03	2.42
H	2.163036	-4.553620	-1.179400	0.115	0.03	2.42
H	4.546021	-3.759446	-0.883899	0.102	0.03	2.42
H	4.941502	-1.357247	-0.376324	0.138	0.03	2.42
C	-3.220616	3.838247	-0.263974	0.028	0.07	3.55
C	-2.676703	3.335104	0.919774	-0.139	0.07	3.55
C	-1.738805	2.307955	0.850992	0.069	0.07	3.55
N	-1.319983	1.770433	-0.316118	-0.093	0.17	3.25

C	-1.848434	2.261154	-1.459320	0.042	0.07	3.55
C	-2.793165	3.285789	-1.472557	-0.149	0.07	3.55
H	-3.958019	4.641311	-0.243502	0.097	0.03	2.42
H	-2.969850	3.727657	1.892861	0.112	0.03	2.42
H	-1.302810	1.899524	1.759085	0.067	0.03	2.42
H	-1.457660	1.809331	-2.369969	0.124	0.03	2.42
H	-3.182593	3.641232	-2.426310	0.112	0.03	2.42
O	0.324644	0.564824	-2.434806	-0.895	0.1521	3.1506
H	1.072207	1.158418	-2.577181	0.285	0.000	0.0000

Geometry and Lennard-Jones Coulomb parameters of $[Ru^{III}(H_2O)(py)(bpy)_2]^{3+}$

	X	Y	Z	Q(e)	E(kcal/mol)	S(Ang.)
C	-3.255285	-2.502354	0.062112	-0.171	0.07	3.55
C	-2.131602	-1.685629	0.204145	0.236	0.07	3.55
N	-1.654657	-0.958325	-0.846484	-0.365	0.17	3.25
C	-2.294509	-1.007323	-2.028547	0.170	0.07	3.55
C	-3.418997	-1.800671	-2.231940	-0.120	0.07	3.55
C	-3.902889	-2.565971	-1.170142	0.093	0.07	3.55
H	-3.898950	-1.808546	-3.208664	0.148	0.03	2.42
H	-1.902726	-0.391031	-2.833727	0.090	0.03	2.42
C	-1.692496	-2.167948	2.652551	-0.108	0.07	3.55
C	-1.392525	-1.506232	1.461491	0.150	0.07	3.55
N	-0.364528	-0.604390	1.408900	-0.270	0.17	3.25
C	0.361852	-0.349223	2.517343	0.138	0.07	3.55
C	0.097127	-0.973385	3.729660	-0.088	0.07	3.55
C	-0.943274	-1.901446	3.797149	0.065	0.07	3.55
H	-2.505906	-2.887764	2.689219	0.144	0.03	2.42
Ru	0.033672	0.194549	-0.422721	1.300	0.40	2.00
C	4.194471	1.089220	0.190084	-0.146	0.07	3.55
C	2.950412	0.507945	-0.061939	0.191	0.07	3.55
N	1.801758	1.234817	0.053904	-0.325	0.17	3.25
C	1.871402	2.526939	0.427067	0.202	0.07	3.55
C	3.081666	3.158680	0.695526	-0.116	0.07	3.55
C	4.263072	2.428069	0.571383	0.070	0.07	3.55
C	3.815801	-1.805344	-0.618675	-0.160	0.07	3.55
C	2.766602	-0.900508	-0.452753	0.232	0.07	3.55
N	1.473539	-1.295604	-0.636596	-0.449	0.17	3.25
C	1.205456	-2.572486	-0.973055	0.203	0.07	3.55
C	2.210440	-3.515661	-1.153408	-0.133	0.07	3.55
C	3.537596	-3.124252	-0.974276	0.112	0.07	3.55
H	1.163006	0.376621	2.422941	0.066	0.03	2.42
H	-1.172167	-2.414227	4.730524	0.128	0.03	2.42
H	0.705176	-0.730512	4.598841	0.146	0.03	2.42
H	-3.628528	-3.079012	0.904483	0.163	0.03	2.42
H	-4.780088	-3.199623	-1.294411	0.120	0.03	2.42
H	0.930346	3.061312	0.519046	0.050	0.03	2.42
H	3.083810	4.204194	0.997643	0.144	0.03	2.42
H	5.228789	2.890569	0.771636	0.126	0.03	2.42
H	5.105345	0.504389	0.092870	0.152	0.03	2.42
H	0.161691	-2.839369	-1.107067	0.067	0.03	2.42
H	1.945670	-4.534634	-1.428849	0.150	0.03	2.42
H	4.350795	-3.837054	-1.106041	0.117	0.03	2.42
H	4.844609	-1.487326	-0.472611	0.154	0.03	2.42
C	-3.087111	3.989461	0.079615	0.112	0.07	3.55
C	-3.116186	2.927410	0.984507	-0.158	0.07	3.55

C	−2.225851	1.873371	0.821248	0.224	0.07	3.55
N	−1.318820	1.835751	−0.182601	−0.459	0.17	3.25
C	−1.292347	2.868888	−1.059345	0.259	0.07	3.55
C	−2.156927	3.952194	−0.960490	−0.168	0.07	3.55
H	−3.775585	4.828124	0.182199	0.109	0.03	2.42
H	−3.819233	2.903931	1.815317	0.143	0.03	2.42
H	−2.233738	1.042601	1.518148	0.043	0.03	2.42
H	−0.567736	2.811202	−1.865070	0.075	0.03	2.42
H	−2.091781	4.751287	−1.697004	0.144	0.03	2.42
O	0.449875	0.833762	−2.431118	−0.834	0.1521	3.1506
H	0.208531	0.271426	−3.182979	0.417	0.0000	0.0000
H	1.331668	1.184979	−2.633486	0.417	0.0000	0.0000

Geometry and Lennard-Jones Coulomb parameters of $[Ru^{III}(OH)(py)(bpy)_2]^{2+}$

	X	Y	Z	Q(e)	E(kcal/mol)	S(Ang.)
C	−3.342197	−2.397488	0.131457	−0.147	0.07	3.55
C	−2.196936	−1.607068	0.264183	0.141	0.07	3.55
N	−1.654239	−0.973519	−0.813177	−0.138	0.17	3.25
C	−2.231138	−1.118449	−2.020165	0.091	0.07	3.55
C	−3.372643	−1.889867	−2.215047	−0.114	0.07	3.55
C	−3.939461	−2.540366	−1.118802	0.042	0.07	3.55
H	−3.798060	−1.974583	−3.213430	0.133	0.03	2.42
H	−1.751214	−0.611741	−2.852826	0.093	0.03	2.42
C	−1.888179	−1.976329	2.751231	−0.151	0.07	3.55
C	−1.497629	−1.388390	1.544803	0.211	0.07	3.55
N	−0.423210	−0.553051	1.487092	−0.307	0.17	3.25
C	0.265004	−0.289069	2.613343	0.173	0.07	3.55
C	−0.080142	−0.834409	3.845810	−0.124	0.07	3.55
C	−1.173986	−1.697772	3.914641	0.058	0.07	3.55
H	−2.742859	−2.646894	2.786301	0.138	0.03	2.42
Ru	0.066285	0.184209	−0.443483	0.723	0.40	1.80
C	4.220380	0.984533	0.225388	−0.138	0.07	3.55
C	2.967449	0.428932	−0.047778	0.101	0.07	3.55
N	1.829819	1.166672	0.095015	−0.041	0.17	3.25
C	1.919331	2.439492	0.525539	0.102	0.07	3.55
C	3.136492	3.044801	0.820097	−0.115	0.07	3.55
C	4.308957	2.305346	0.659354	0.035	0.07	3.55
C	3.810035	−1.874392	−0.676984	−0.196	0.07	3.55
C	2.766080	−0.967750	−0.470370	0.236	0.07	3.55
N	1.469231	−1.345063	−0.634586	−0.248	0.17	3.25
C	1.191002	−2.609529	−0.995601	0.156	0.07	3.55
C	2.184690	−3.560114	−1.210416	−0.152	0.07	3.55
C	3.518880	−3.183867	−1.052155	0.072	0.07	3.55
H	1.114528	0.381700	2.519838	0.033	0.03	2.42
H	−1.469865	−2.150594	4.860341	0.110	0.03	2.42
H	0.507574	−0.584304	4.727277	0.134	0.03	2.42
H	−3.768077	−2.898413	0.996911	0.142	0.03	2.42
H	−4.832706	−3.153532	−1.232362	0.115	0.03	2.42
H	0.985603	2.982025	0.640676	0.075	0.03	2.42
H	3.153260	4.076629	1.166171	0.129	0.03	2.42
H	5.281424	2.746816	0.874785	0.120	0.03	2.42
H	5.123086	0.390759	0.106686	0.139	0.03	2.42
H	0.142431	−2.863093	−1.122132	0.069	0.03	2.42
H	1.906317	−4.571391	−1.501710	0.135	0.03	2.42
H	4.324330	−3.898560	−1.217786	0.111	0.03	2.42

H	4.843480	-1.562543	-0.549628	0.151	0.03	2.42
C	-2.911491	4.135201	-0.252134	0.053	0.07	3.55
C	-3.139778	3.040704	0.582619	-0.141	0.07	3.55
C	-2.282328	1.946760	0.516614	0.145	0.07	3.55
N	-1.227982	1.892865	-0.326208	-0.301	0.17	3.25
C	-1.006013	2.960931	-1.127313	0.210	0.07	3.55
C	-1.820292	4.088778	-1.121063	-0.154	0.07	3.55
H	-3.567012	5.005596	-0.224310	0.107	0.03	2.42
H	-3.972171	3.022790	1.284481	0.126	0.03	2.42
H	-2.442333	1.091237	1.164911	0.061	0.03	2.42
H	-0.143738	2.903774	-1.787630	0.037	0.03	2.42
H	-1.590092	4.915192	-1.791713	0.131	0.03	2.42
O	0.457317	0.546616	-2.313170	-0.764	0.1521	3.1506
H	-0.270837	0.961939	-2.796714	0.391	0.0000	0.0000

Geometry and Lennard-Jones Coulomb parameters of $[Ru^{IV}(O)(py)(bpy)_2]^{2+}$

	X	Y	Z	Q(e)	E(kcal/mol)	S(Ang.)
C	-3.194061	-2.547517	0.189697	-0.148	0.07	3.55
C	-2.071924	-1.720005	0.288314	0.144	0.07	3.55
N	-1.592354	-1.070576	-0.807077	-0.203	0.17	3.25
C	-2.198767	-1.229303	-1.997599	0.096	0.07	3.55
C	-3.316699	-2.042599	-2.156566	-0.121	0.07	3.55
C	-3.824728	-2.710523	-1.042295	0.066	0.07	3.55
H	-3.773252	-2.141767	-3.139758	0.130	0.03	2.42
H	-1.759098	-0.685804	-2.830986	0.118	0.03	2.42
C	-1.630511	-2.144898	2.747132	-0.151	0.07	3.55
C	-1.330466	-1.493295	1.547392	0.205	0.07	3.55
N	-0.306017	-0.602960	1.473216	-0.360	0.17	3.25
C	0.431845	-0.351691	2.569536	0.200	0.07	3.55
C	0.186023	-0.965807	3.793808	-0.116	0.07	3.55
C	-0.866018	-1.878300	3.881872	0.058	0.07	3.55
H	-2.447798	-2.859316	2.800651	0.141	0.03	2.42
Ru	0.052136	0.215899	-0.534871	1.013	0.40	1.80
C	4.152231	1.292992	0.129111	-0.176	0.07	3.55
C	2.938318	0.651033	-0.125501	0.213	0.07	3.55
N	1.763320	1.336781	-0.060718	-0.205	0.17	3.25
C	1.770745	2.646187	0.243542	0.108	0.07	3.55
C	2.947799	3.340061	0.507957	-0.092	0.07	3.55
C	4.158429	2.649796	0.450158	0.057	0.07	3.55
C	3.920076	-1.639330	-0.582574	-0.133	0.07	3.55
C	2.825374	-0.777334	-0.483699	0.123	0.07	3.55
N	1.563892	-1.226662	-0.726154	-0.191	0.17	3.25
C	1.368638	-2.507680	-1.079728	0.074	0.07	3.55
C	2.419128	-3.413014	-1.199942	-0.097	0.07	3.55
C	3.716436	-2.970567	-0.942774	0.059	0.07	3.55
H	1.239963	0.368044	2.459122	0.034	0.03	2.42
H	-1.090338	-2.381628	4.821840	0.112	0.03	2.42
H	0.810402	-0.727851	4.653076	0.129	0.03	2.42
H	-3.579371	-3.059615	1.067560	0.138	0.03	2.42
H	-4.700938	-3.352379	-1.127023	0.109	0.03	2.42
H	0.806088	3.144422	0.273565	0.082	0.03	2.42
H	2.904137	4.400034	0.751084	0.124	0.03	2.42
H	5.100578	3.159258	0.649736	0.115	0.03	2.42
H	5.088810	0.744105	0.074658	0.154	0.03	2.42
H	0.343622	-2.810969	-1.273655	0.093	0.03	2.42

H	2.211919	-4.441421	-1.490044	0.129	0.03	2.42
H	4.563889	-3.650546	-1.023144	0.111	0.03	2.42
H	4.925548	-1.278859	-0.382048	0.136	0.03	2.42
C	-3.285445	3.839164	0.038791	0.071	0.07	3.55
C	-2.816919	3.137724	1.150344	-0.139	0.07	3.55
C	-1.875954	2.129164	0.968576	0.142	0.07	3.55
N	-1.389695	1.797354	-0.248387	-0.281	0.17	3.25
C	-1.844764	2.478954	-1.324021	0.119	0.07	3.55
C	-2.785592	3.498495	-1.218713	-0.133	0.07	3.55
H	-4.022744	4.634192	0.150739	0.099	0.03	2.42
H	-3.169220	3.360958	2.156201	0.123	0.03	2.42
H	-1.495327	1.574708	1.820633	0.065	0.03	2.42
H	-1.425663	2.189100	-2.284242	0.110	0.03	2.42
H	-3.113972	4.013551	-2.120251	0.120	0.03	2.42
O	0.156952	0.629306	-2.250805	-0.570	0.21	2.96

Geometry and Lennard-Jones Coulomb parameters of H_2O

	X	Y	Z	Q(e)	E(kcal/mol)	S(Ang)
O	0.62050961	-1.46679902	-2.34634898	-0.834	0.1521	3.1506
H	0.79418961	-2.38063902	-2.07210898	0.417	0.0000	0.0000
H	1.21937961	-1.20438902	-3.06320898	0.417	0.0000	0.0000

References

[1] Harrowfield JM, Sobolev AN. The crystal structure of tris (2, 2'-bipyridine) ruthenium (II) perchlorate. Australian Journal of Chemistry. 1994;47(4):763–767.