

ELECTRONIC SUPPLEMENTARY INFORMATION

for

Ruthenium Catalyst linked to a Redox-Active Ruthenium Polypyridine for Water Oxidation

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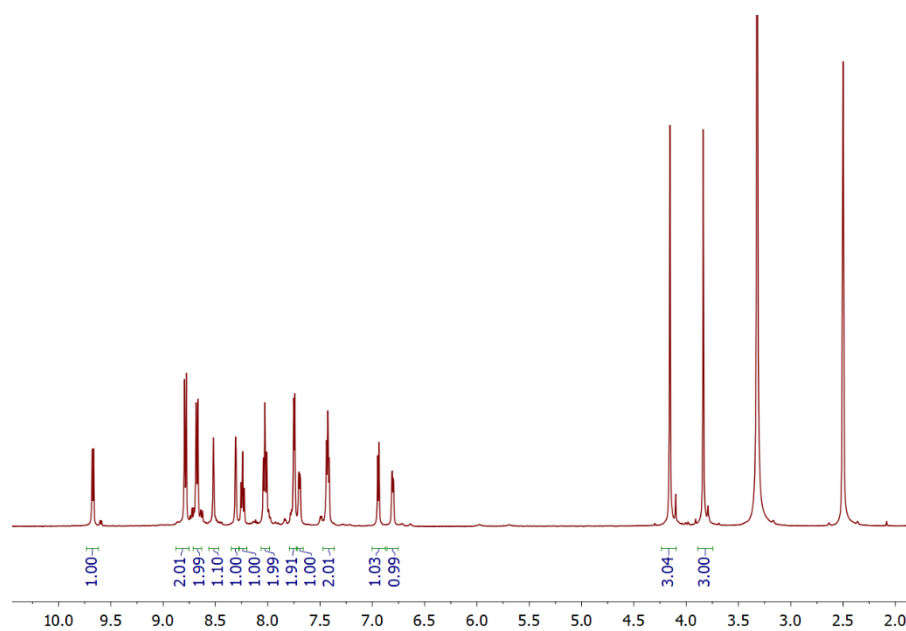
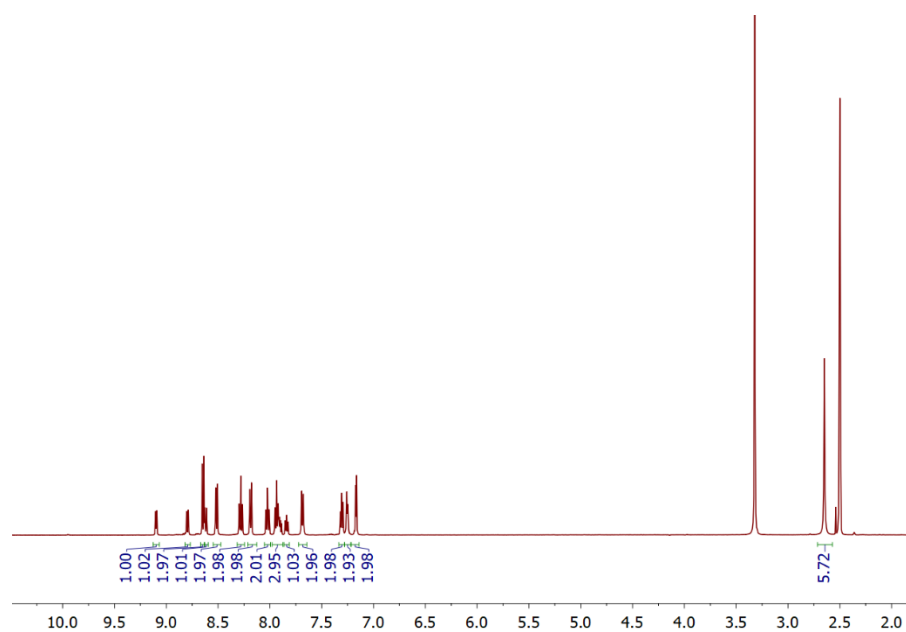


Figure S1. 500 MHz ^1H -NMR spectrum of $[\text{Ru}(\text{tpy})(\text{MeO-bpy})\text{CN}](\text{PF}_6)$ dissolved in $\text{d}_6\text{-DMSO}$.



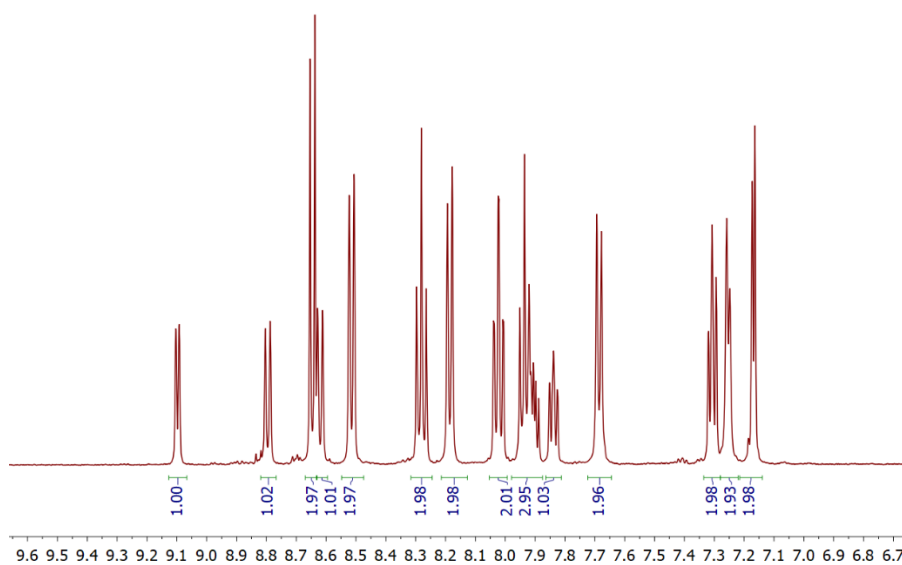


Figure S2. 500 MHz ^1H -NMR spectrum of **(1)** dissolved in d_6 -DMSO. (top) Full scale. (bottom) Aromatic region.

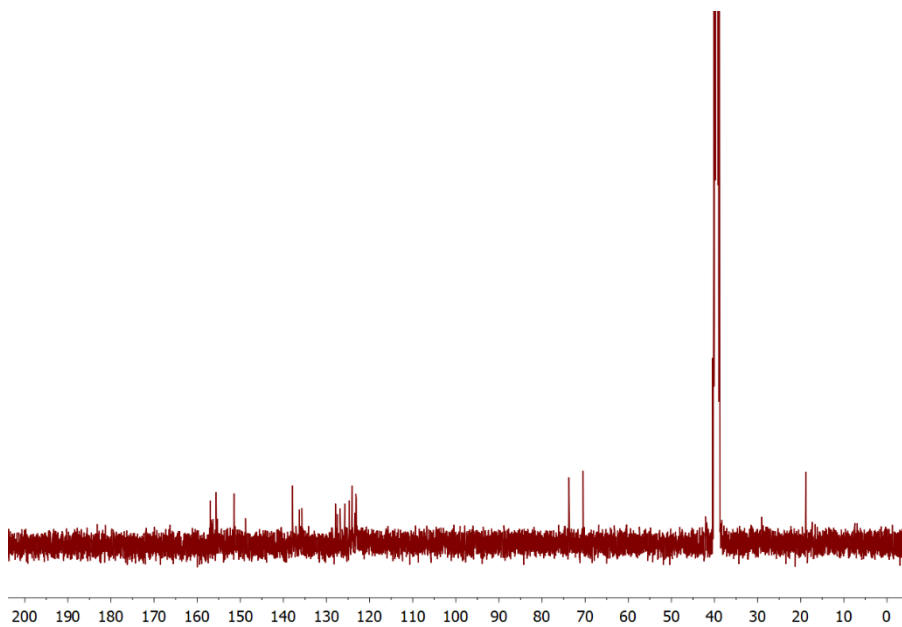


Figure S3. 125 MHz ^{13}C -NMR spectrum of **(1)** dissolved in d_6 -DMSO.

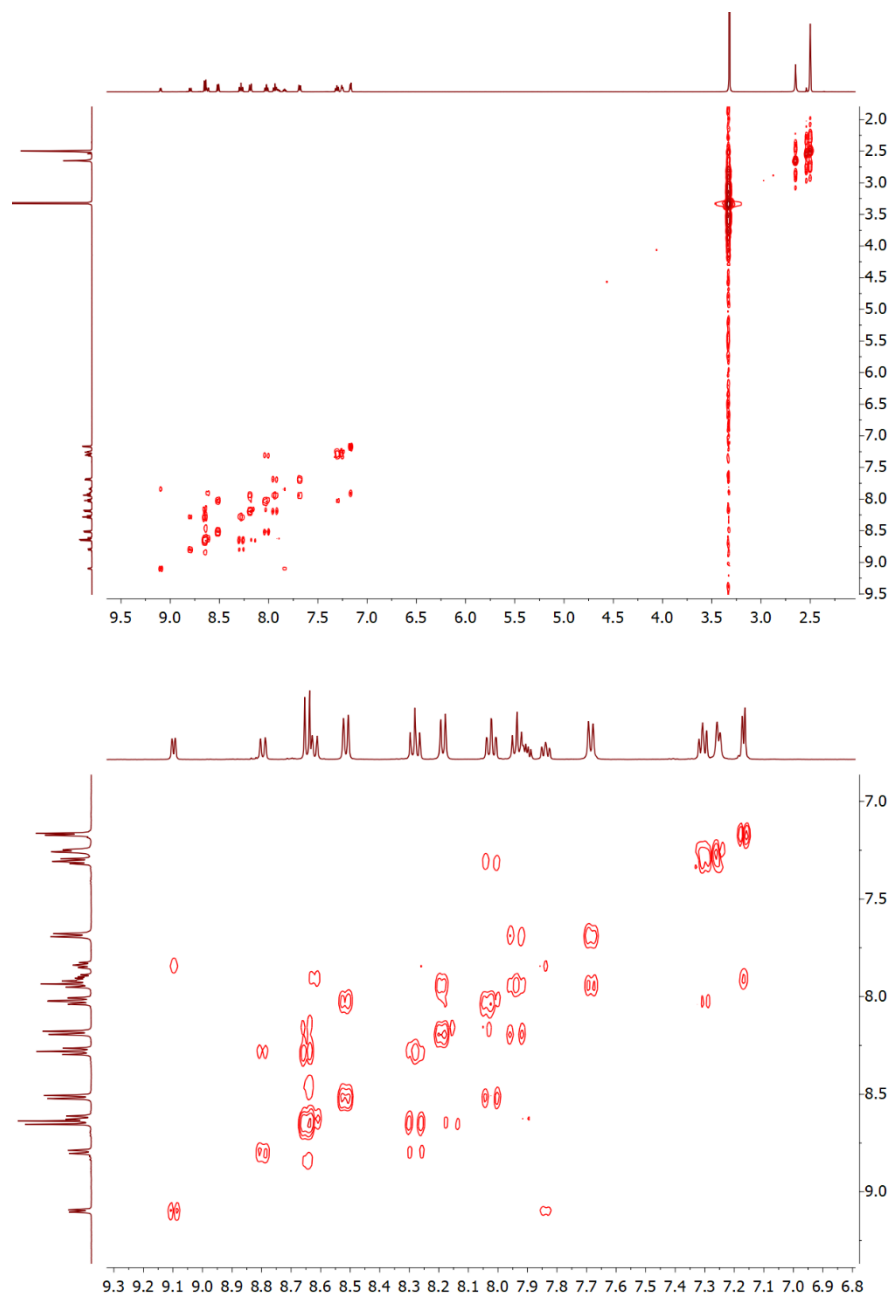


Figure S4. $2\text{D } ^1\text{H}-^1\text{H}$ COSY spectrum of **1** dissolved in d_6 -DMSO. (top) Full scale. (bottom) Aromatic region.

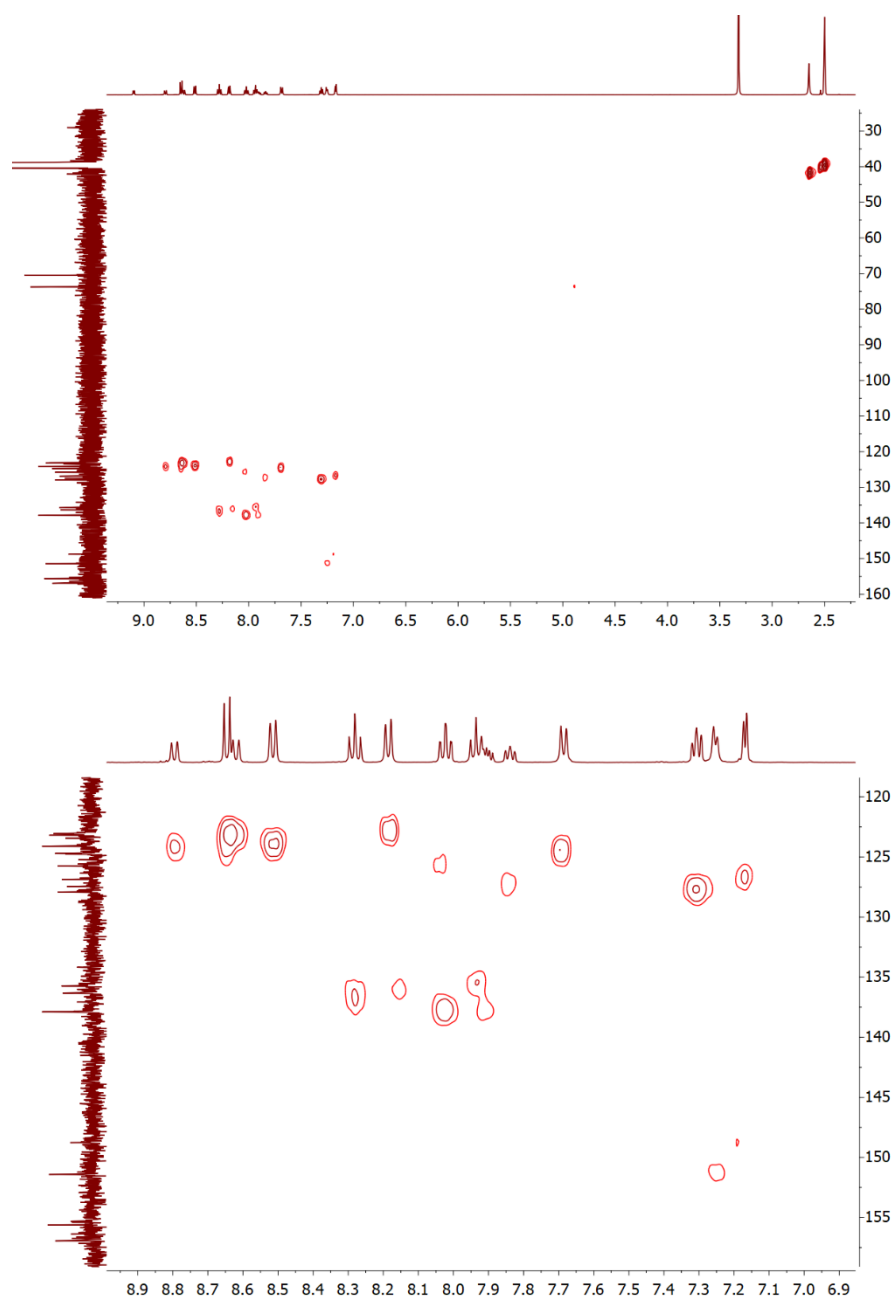


Figure S5. 2D ^1H - ^{13}C HSQC spectrum of **1** dissolved in d_6 -DMSO. (top) Full scale. (bottom) Aromatic region.

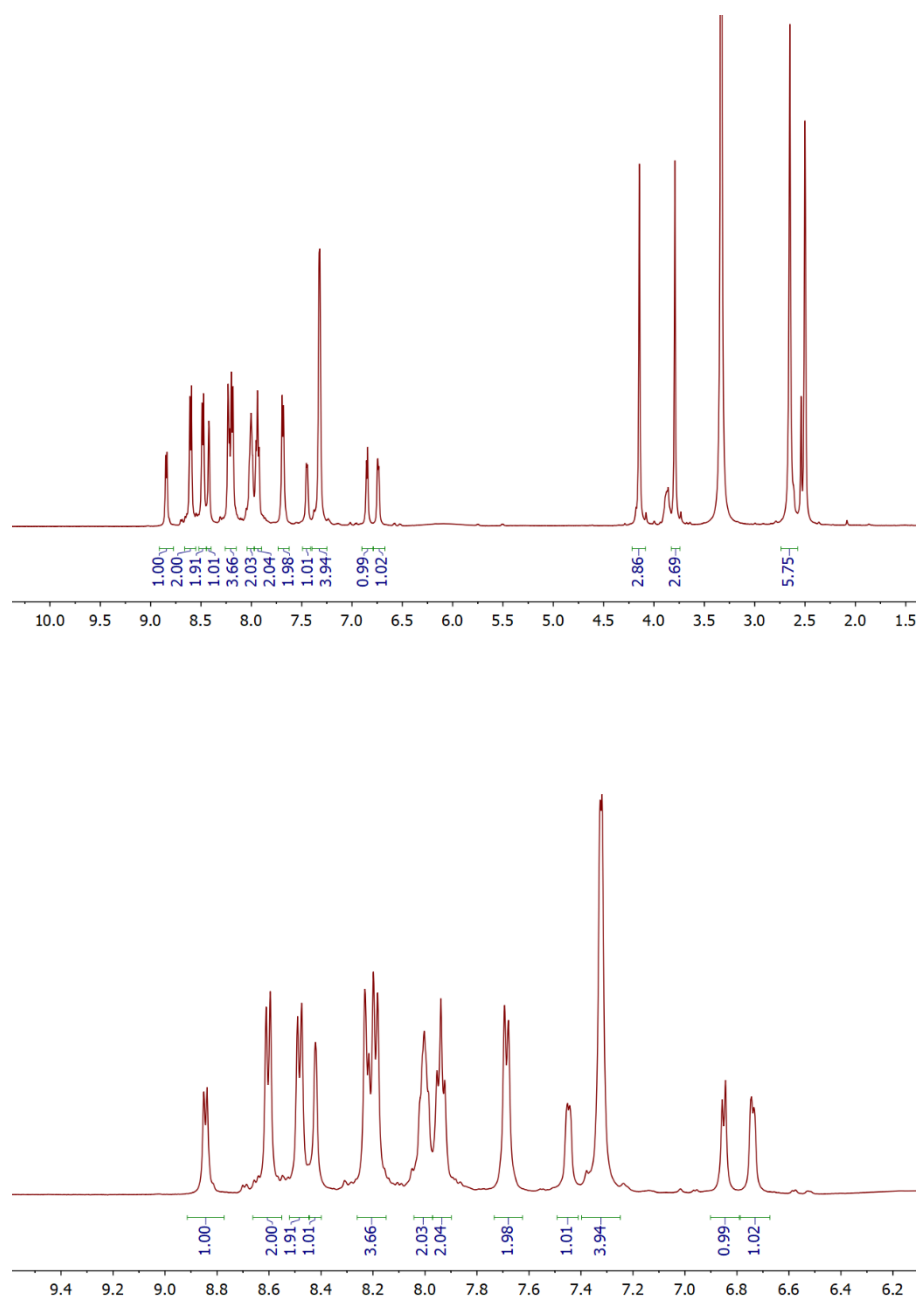


Figure S6. 500 MHz ¹H-NMR spectrum of **(2)** dissolved in d₆-DMSO. (top) Full scale. (bottom) Aromatic region.

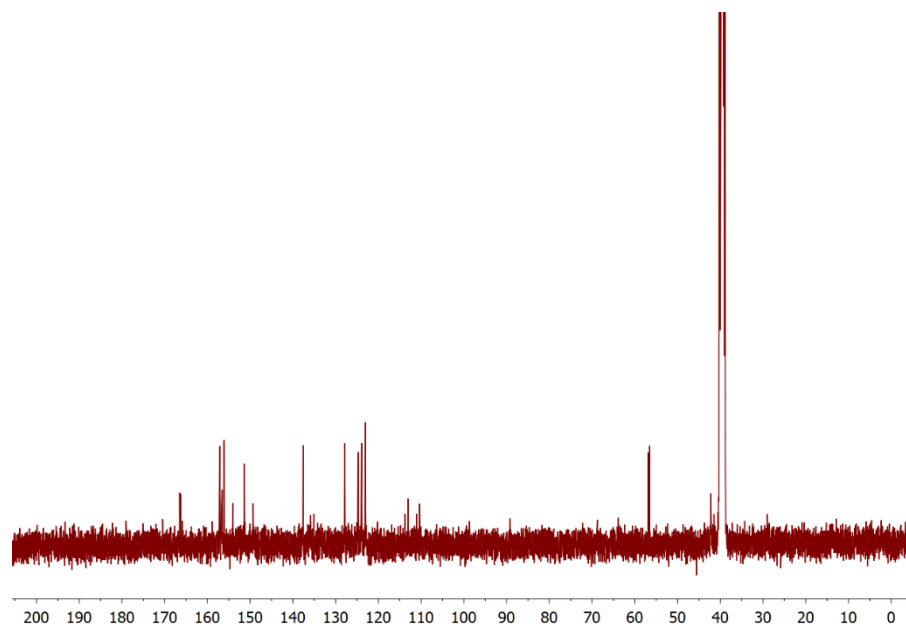
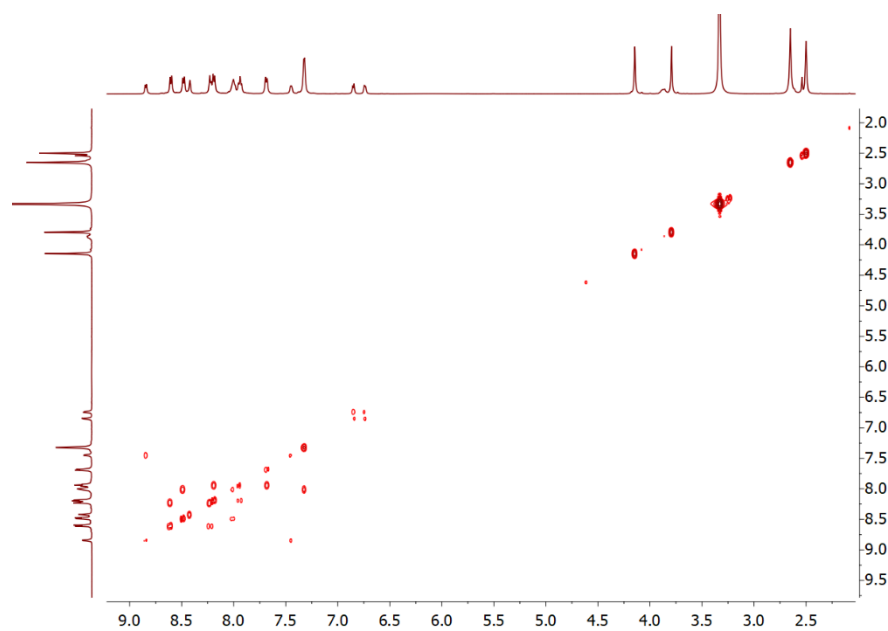


Figure S7. 125 MHz ^{13}C -NMR spectrum of **(2)** dissolved in d_6 -DMSO.



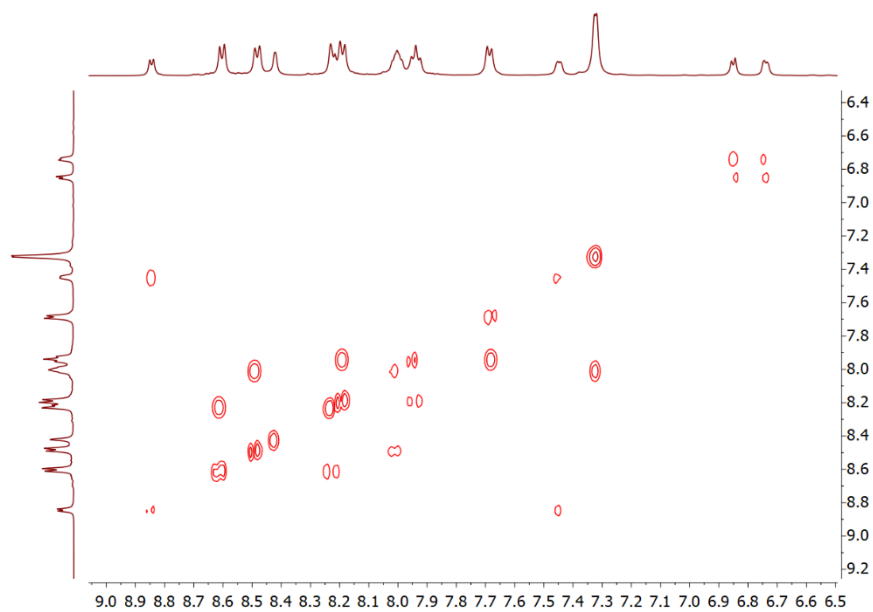
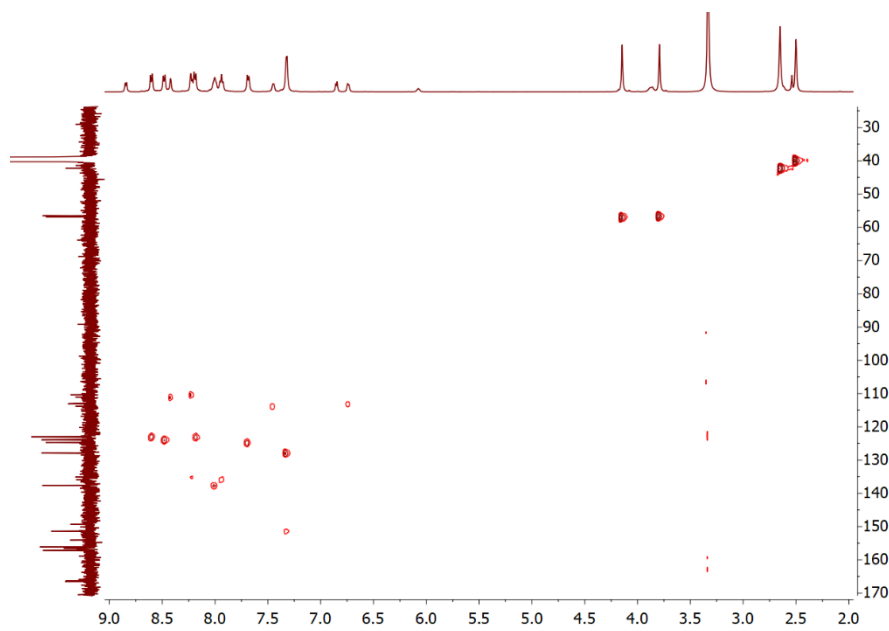


Figure S8. 2D ^1H - ^1H COSY spectrum of **(2)** dissolved in d_6 -DMSO. (top) Full scale. (bottom) Aromatic region.



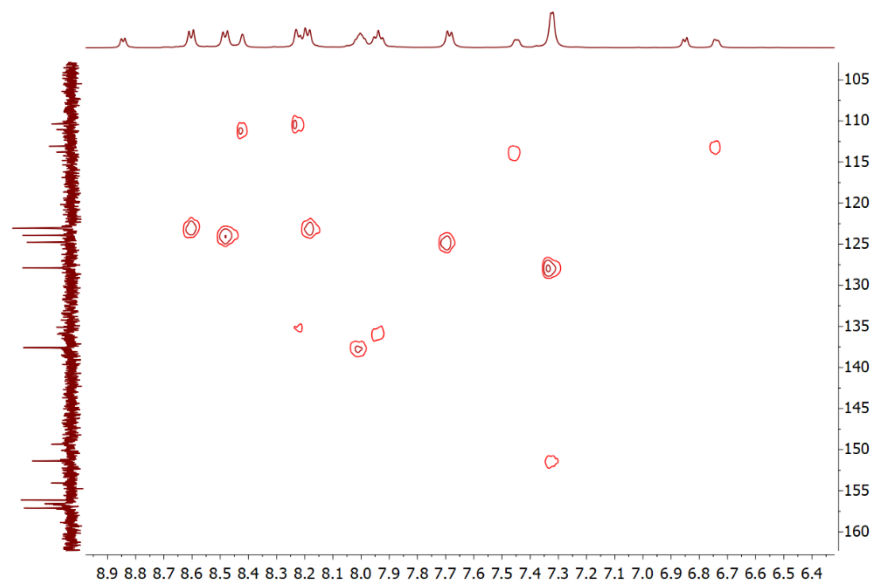


Figure S9. 2D ^1H - ^{13}C HSQC spectrum of **(2)** dissolved in d_6 -DMSO. (top) Full scale. (bottom) Aromatic region.

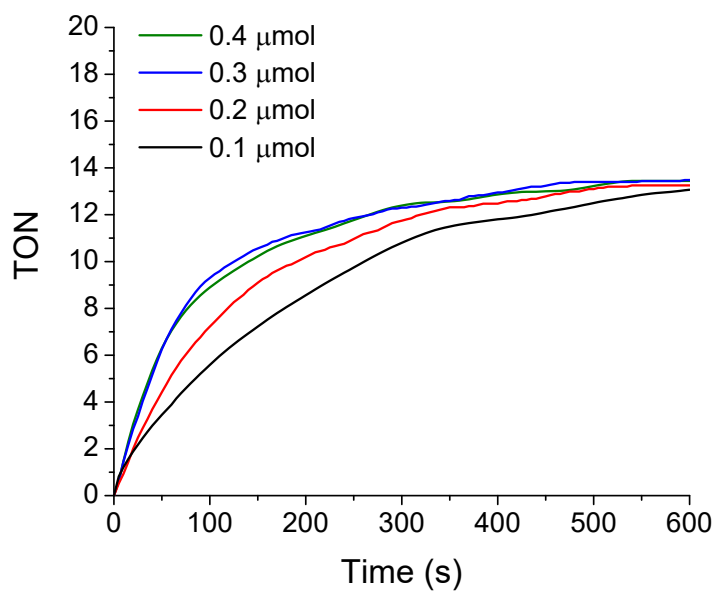


Figure S10. O_2 concentration detected using a Clark electrode vs. time at different concentrations of **(1)** in 0.1M triflic acid ($\text{pH} = 1$) with $[\text{Ce(IV)}] = 0.21 \text{ M}$ as oxidant.

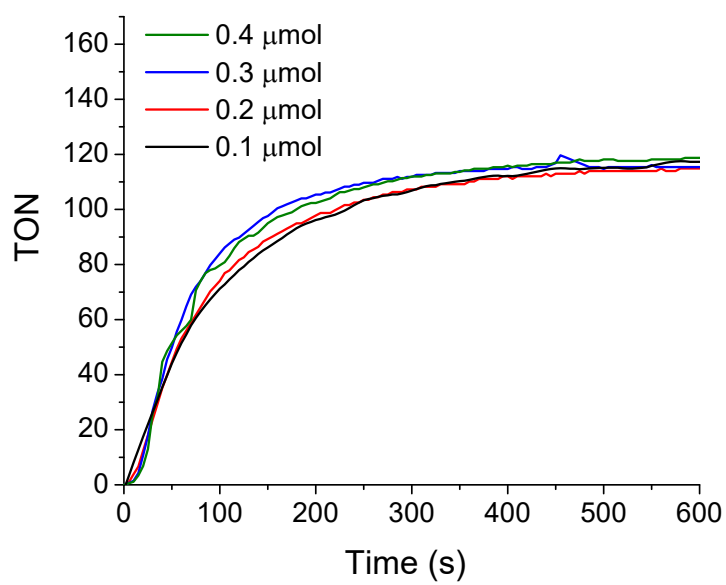
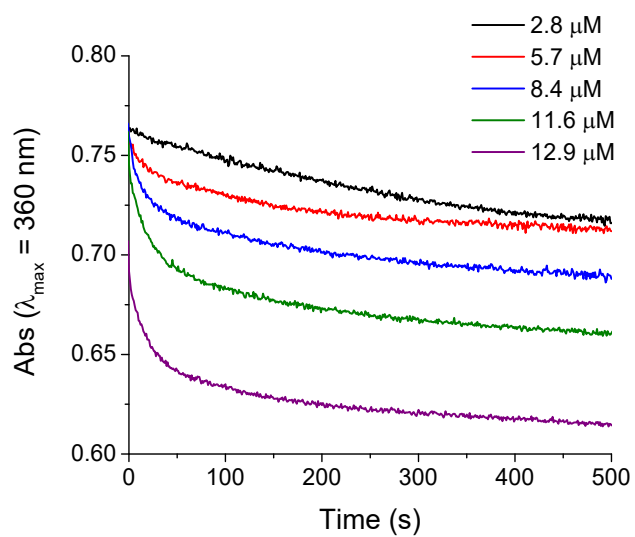


Figure S11. O_2 concentration detected using a Clark electrode vs. time at different concentrations of (**2**) in 0.1M triflic acid ($\text{pH} = 1$) with $[\text{Ce(IV)}] = 0.28 \text{ M}$ as sacrificial oxidant.



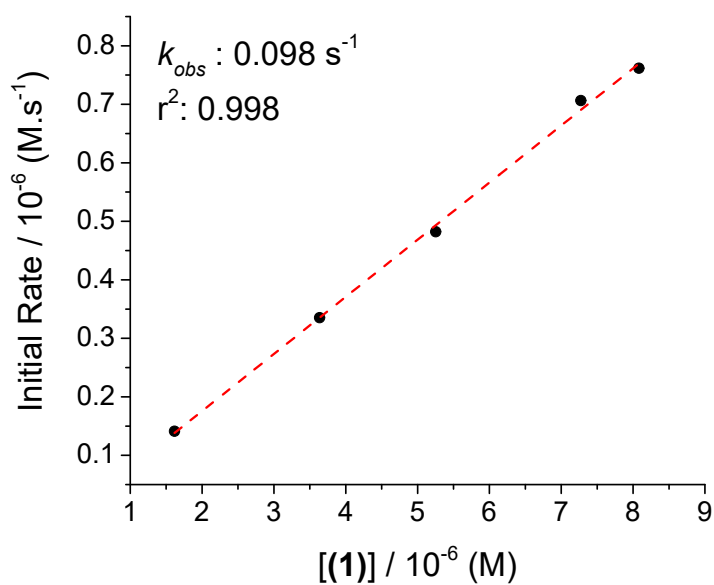
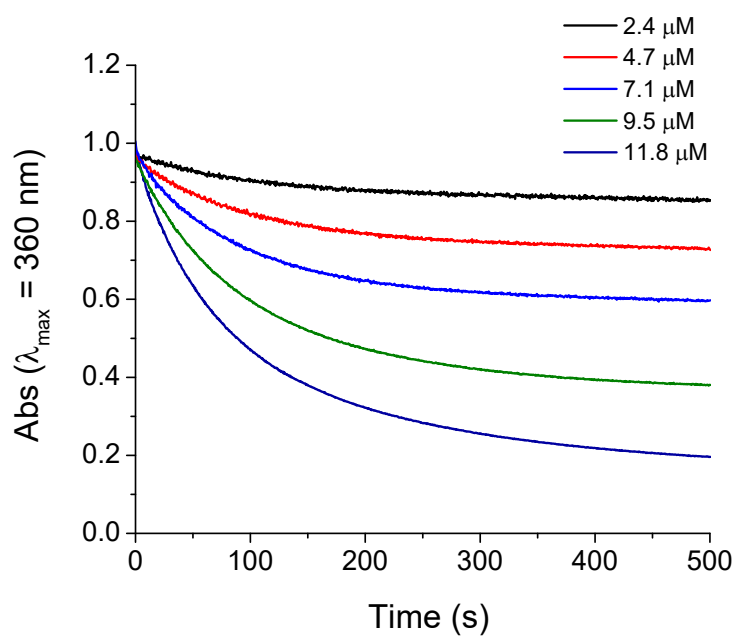


Figure S12. (Top) Absorbance decay monitored at 360 nm in aqueous solution as a function of time for different concentrations of **(1)**. (Bottom) Plot of the rate constant vs concentrations of **(1)**. Conditions: $[\text{Ce(IV)}] = 1.78 \text{ mM}$, $\text{pH} = 1.0$ (aqueous 0.1 M triflic acid) and $T = 298 \text{ K}$.



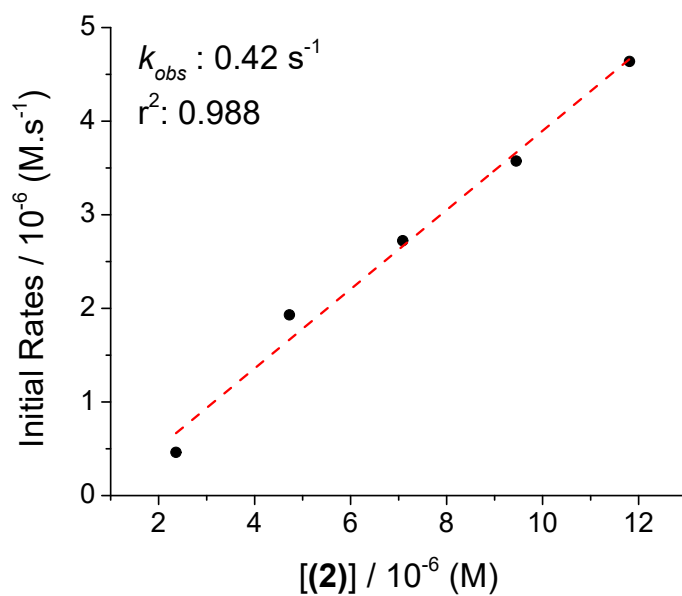


Figure S13. (Top) Absorbance decay monitored at 360 nm in aqueous solution as a function of time for different concentrations of **(2)**. (Middle) Plot of the rate constant vs concentrations of **(2)**. Conditions: $[\text{Ce(IV)}] = 2.89 \text{ mM}$, $\text{pH} = 1.0$ (aqueous 0.1 M triflic acid) and $T = 298 \text{ K}$.

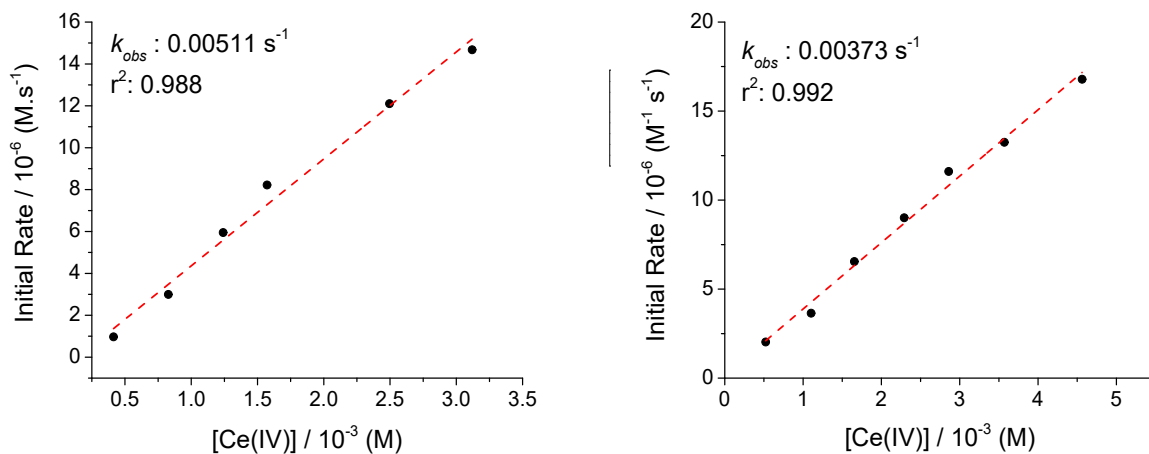


Figure S14. Plot of the rate constant vs concentrations of $[\text{Ce(IV)}]$ for **(1)** (Left) and **(2)** (Right). Conditions: $[(1)] = 35.6 \mu\text{M}$, $[(2)] = 37.5 \mu\text{M}$, $\text{pH} = 1.0$ (aqueous 0.1 M triflic acid) and $T = 298 \text{ K}$.

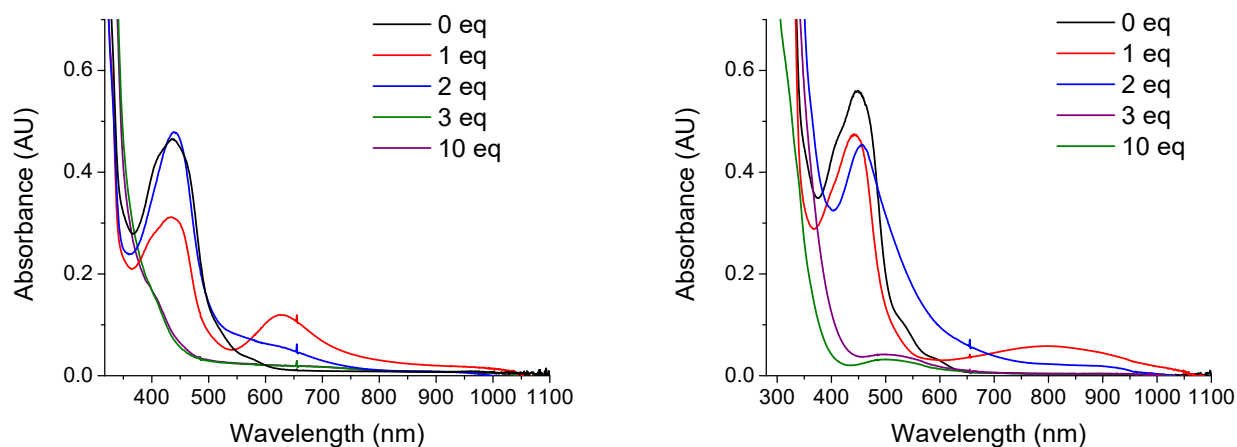


Figure S15. UV-vis spectra for **1** (Left) and **2** (Right) after the addition of 1, 2, 3 and, 10 eq. of Ce(IV) in 0.1M triflic acid (pH = 1).

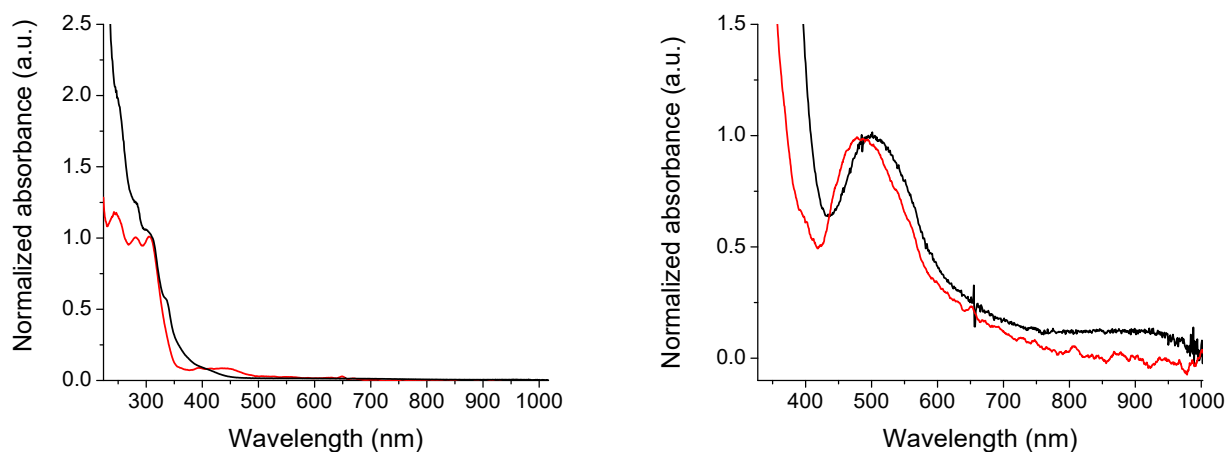


Figure S16. Normalized UV-vis spectra of **1** (Left) and **2** (Right) in the resting state after addition of 240 eq. of Ce(IV) in 0.1M triflic acid (pH = 1) (red trace) and after a three-electron oxidation process in a spectroelectrochemistry experiment.

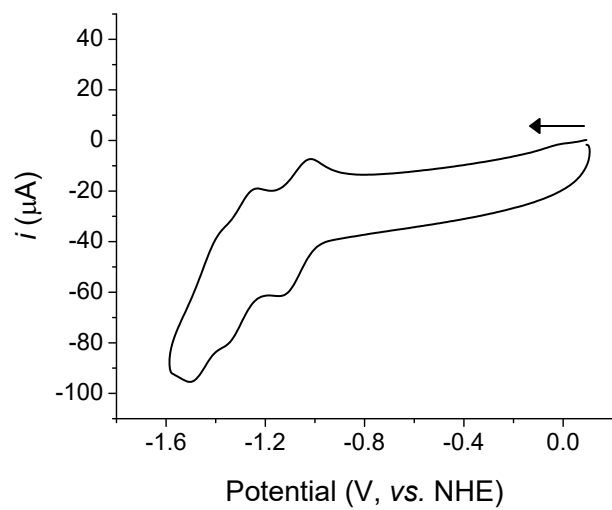
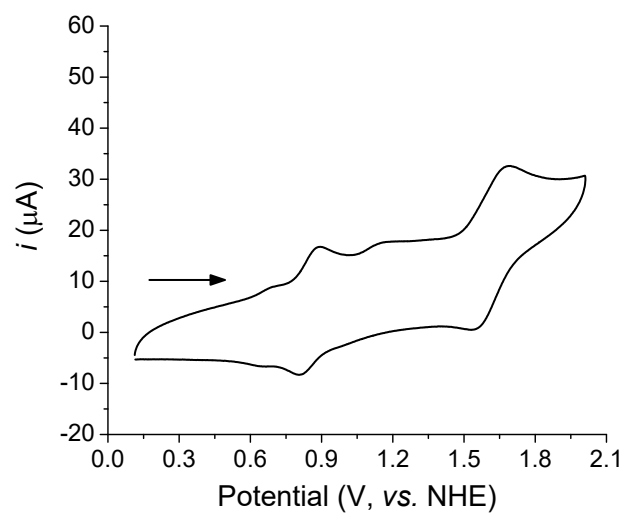


Figure S17. **(Top)** Anodic and **(Bottom)** cathodic cyclic voltammogram of **(2)** in propylene carbonate / 0.1M tetrabutylammonium hexafluorophosphate. ($[(\mathbf{2})] = 3\text{mM}$; $v = 0.1\text{ V.s}^{-1}$).

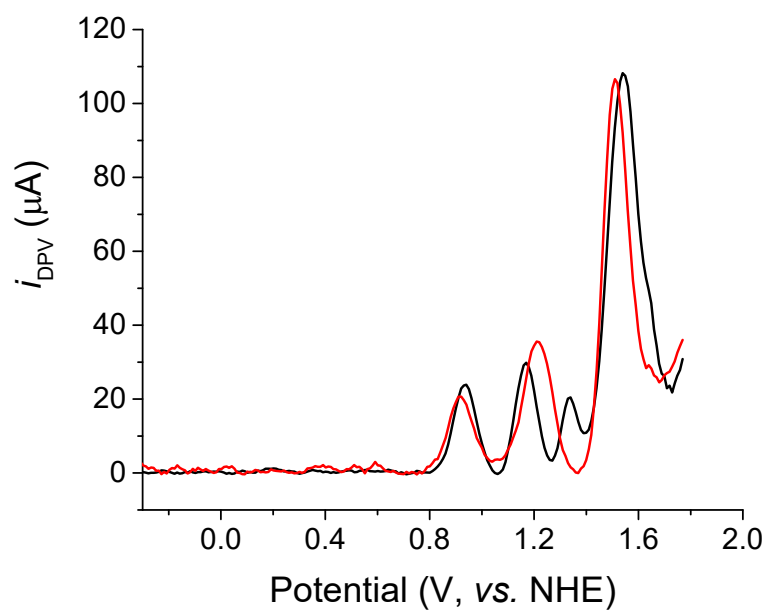


Figure S18. Differential pulse voltammetry experiment of **(1)** (black trace) and **(2)** (red trace) in 0.1 M trifluoromethanesulfonic acid (pH = 1.0). Conditions: WE: glassy carbon electrode, CE: platinum coil, RE: Ag/AgCl 3M NaCl, $[(1)] = 2.0$ mM and, $[(2)] = 2.0$ mM. For **(2)**, 7% propylene carbonate as co-solvent.

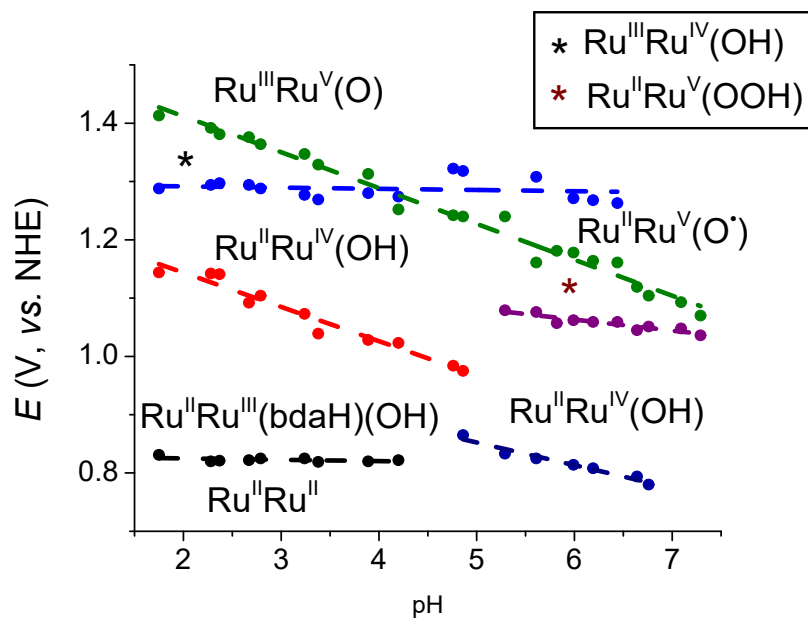
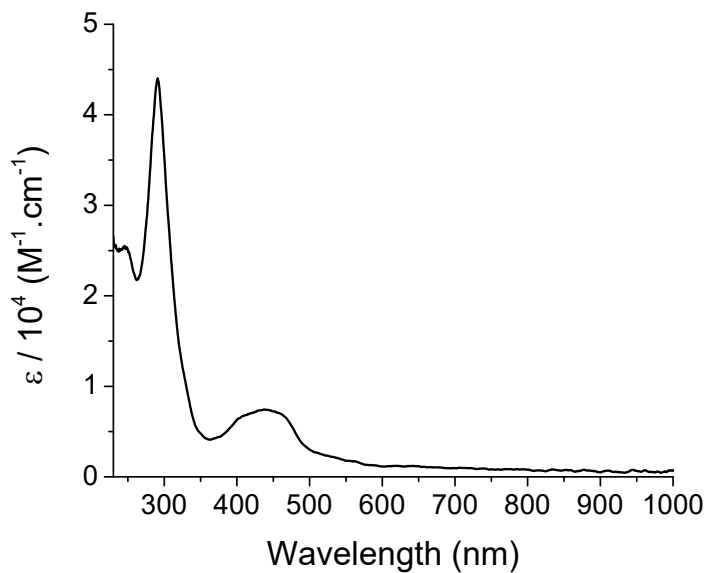
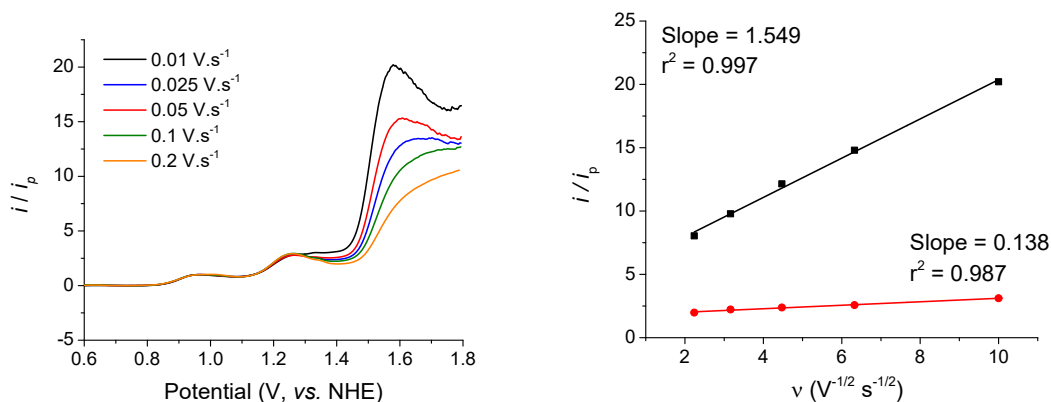
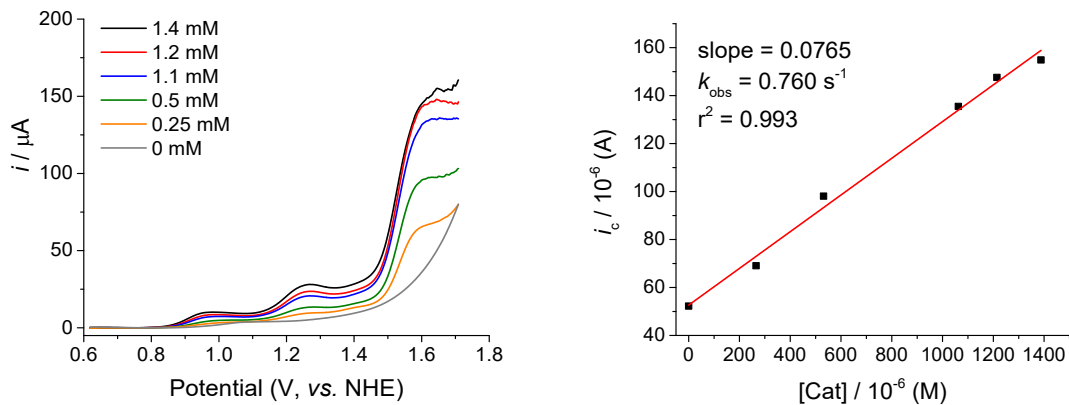


Figure S19. Potential vs pH diagram for **(2)** in aqueous phosphate buffer. Conditions: WE: glassy carbon electrode, CE: platinum coil, RE: Ag/AgCl 3M NaCl.



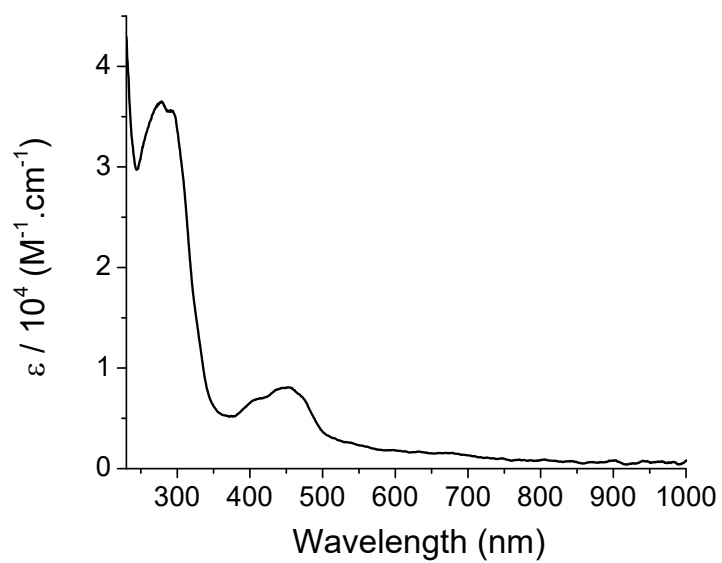


Figure S22. UV-vis spectrum of **(1)** (Top) and **(2)** (Bottom) in 0.1M triflic acid (pH = 1).

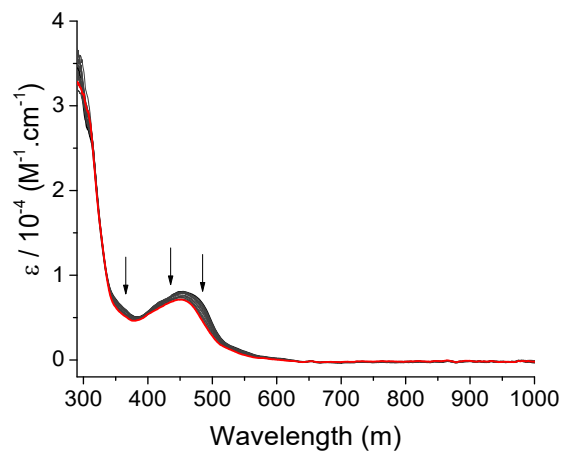


Figure S23. Spectroelectrochemistry experiments of **(2)** in 0.1M tetrabutylammonium hexafluorophosphate in propylene carbonate solution.

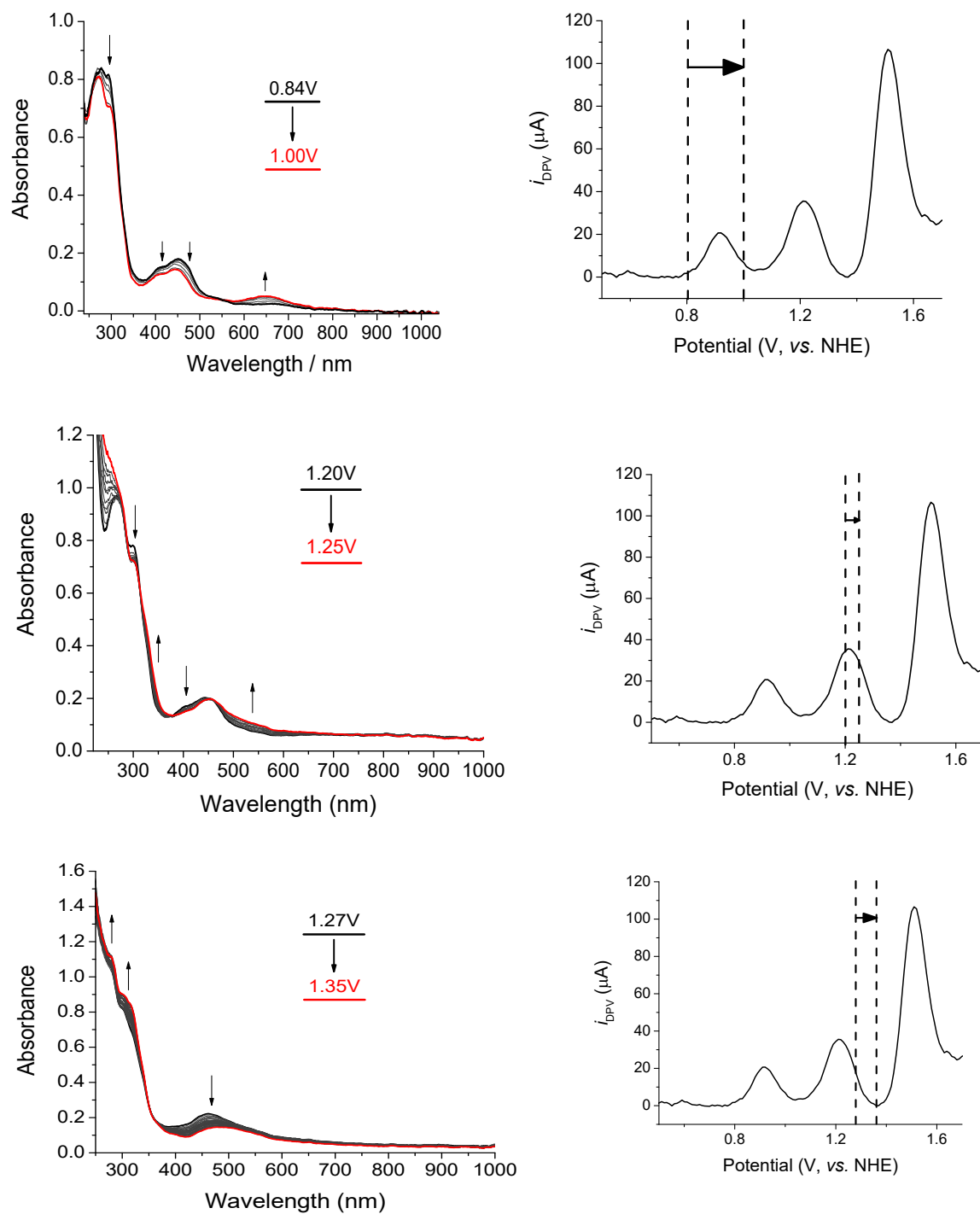


Figure S24. Spectroelectrochemistry of (**2**) in 0.1 M trifluoromethanesulfonic acid (pH = 1) for the first three oxidation processes. The arrows indicate changes during the different oxidation process. Conditions: WE: Pt, CE: Pt, RE: Ag/AgCl 3M NaCl.

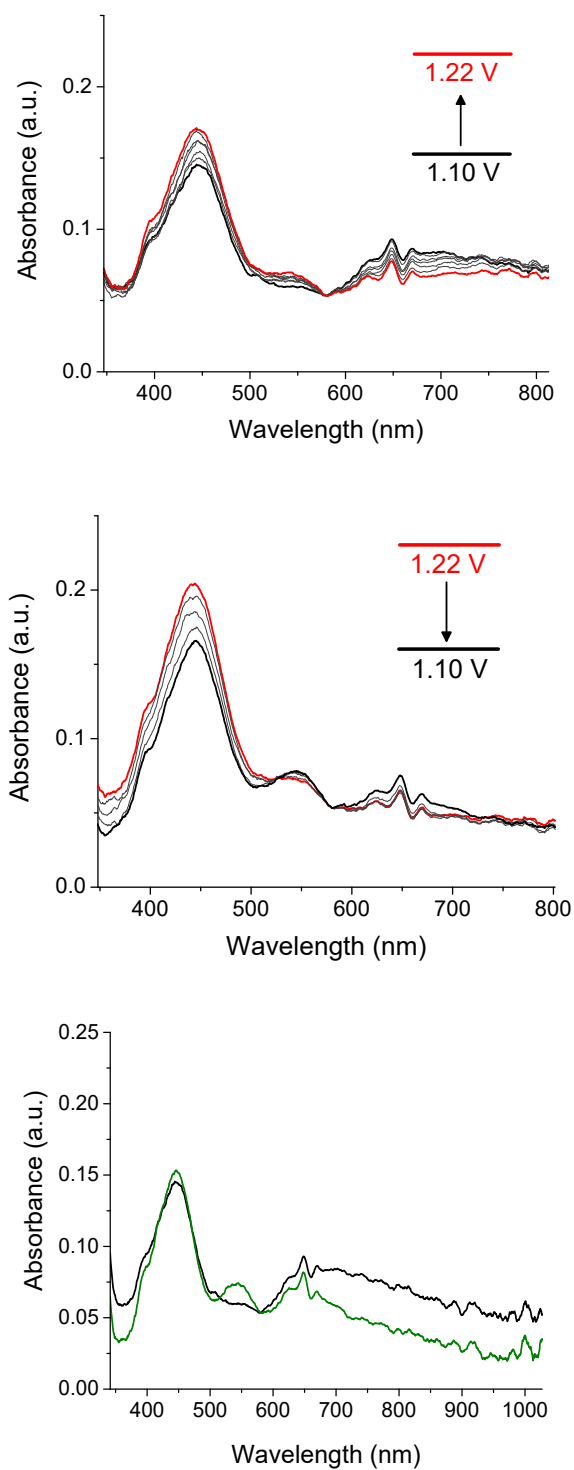


Figure S25. Spectroelectrochemistry experiments of **(1)** in 0.1M triflic acid (pH = 1) sweeping back and forth between 1.10 and 1.22V. (Top) UV-vis spectra collected while changing the applied potential from 1.10V to 1.22V. (Middle) UV-vis spectra collected while changing the applied potential from 1.22V to 1.10V. (Bottom) Comparison between the UV-vis spectra at E=1.10V before (black trace) and after (green trace) the experiment.

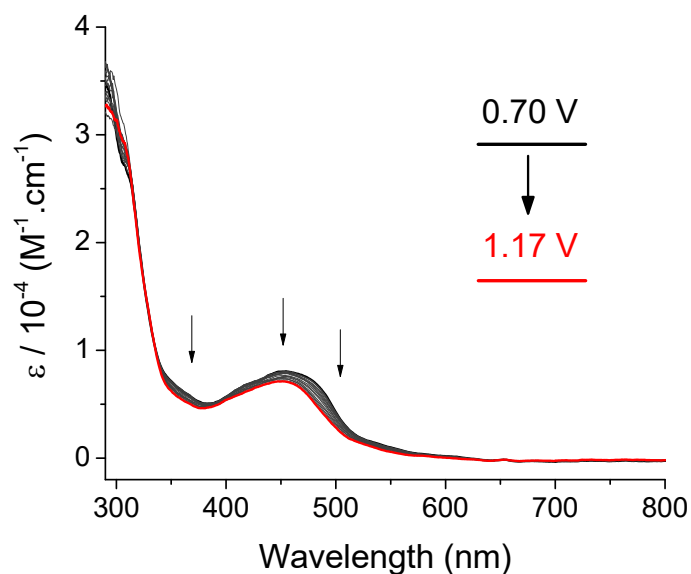
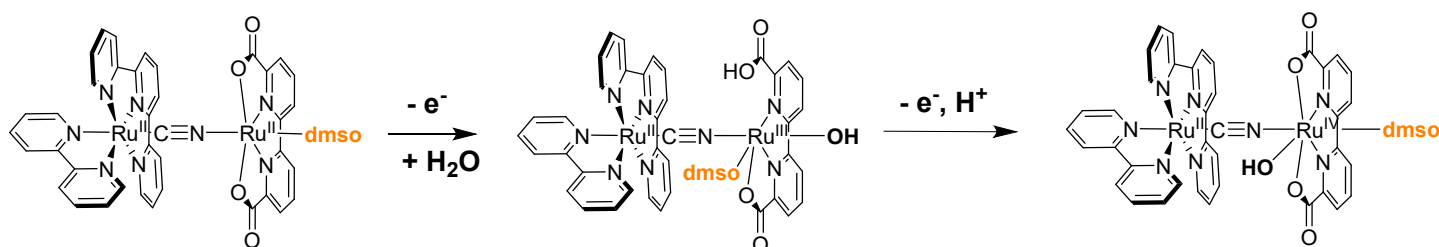


Figure S26. Spectroelectrochemistry experiments of (**1**) in 0.1M tetrabutylammonium hexafluorophosphate in propylene carbonate solution.



Scheme 1. Oxidation steps proposed for the studied complexes including the isomerization in the $\text{Ru}^{\text{II}}\text{-CN-Ru}^{\text{III}}\text{-OH}_2$ specie.

Table S1. Energies values and percentual group contributions of selected MO's of complex $[\text{Ru}^{\text{II}}(\text{bpy})\text{-Ru}^{\text{II}}(\text{bda})]^+$ in their singlet ground state.

MO's	Energy (eV)	Ru_{bda}	bda	DMSO	CN	Ru_{tpy}	tpy	bpy
L+10	-0,82	41	8	18	7	4	20	1
L+9	-1,47	0	0	0	0	4	67	29
L+8	-1,48	0	0	0	0	1	2	97
L+7	-1,58	0	0	0	0	1	99	0
L+6	-1,72	0	0	0	0	1	29	70
L+5	-1,88	4	95	0	0	0	0	0
L+4	-2,22	1	98	1	0	0	0	0
L+3	-2,51	0	0	0	0	4	59	36
L+2	-2,56	3	37	1	0	1	26	32
L+1	-2,57	5	52	1	0	1	14	27
LUMO	-2,71	0	1	0	1	6	91	1
HOMO	-5,16	70	27	0	1	1	0	0

H-1	-5,62	50	20	1	6	18	3	1
H-2	-5,77	51	16	2	7	19	4	1
H-3	-6,08	2	1	0	0	76	8	11
H-4	-6,22	12	10	0	4	54	14	6
H-5	-6,4	18	9	0	5	53	14	2
H-6	-6,92	4	5	89	2	0	0	0
H-7	-7,22	1	3	97	0	0	0	0
H-8	-7,29	1	76	1	0	0	21	1
H-9	-7,3	0	22	0	0	1	72	4
H-10	-7,39	0	19	0	0	1	3	77

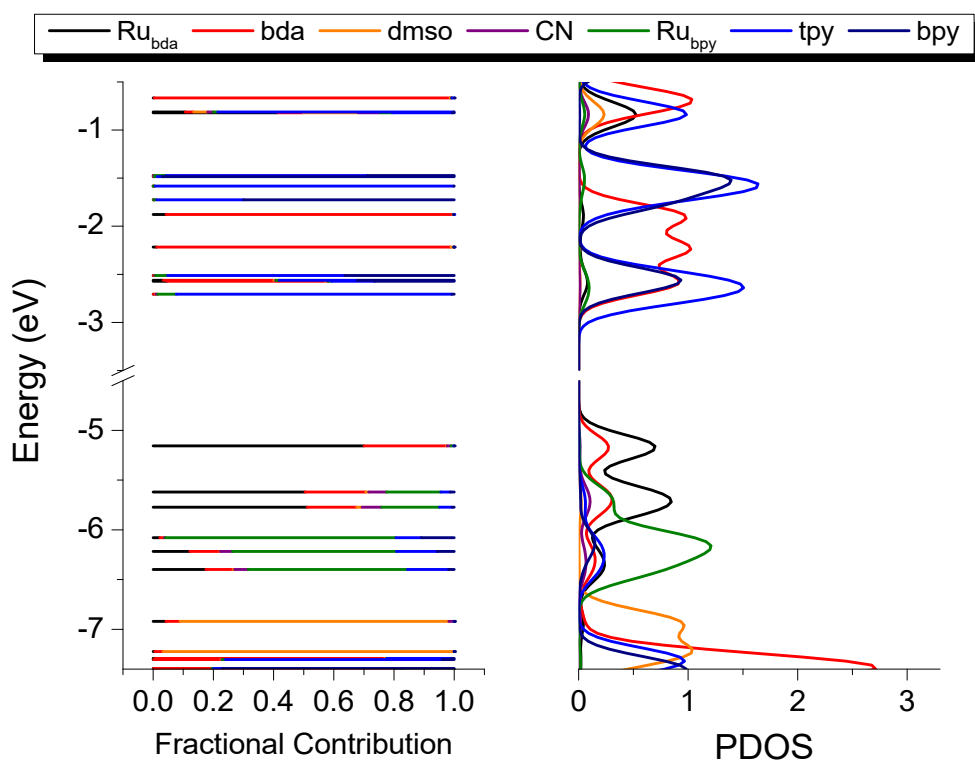


Figure S27. Molecular orbital diagram and partial density of states (PDOS) of complex $[Ru^{II}(bpy)-Ru^{II}(bda)]^+$ in their singlet ground state.

Table S2. (TD)DFT assignments for calculated UV-Vis transitions of the complex $[Ru^{II}(bpy)-Ru^{II}(bda)]^+$.

No.	Wavelength (nm)	Osc. Strength	Major contributions	Assignment
2	548.2	0.01	H-1 -> LUMO (71%) H-3 -> LUMO (12%)	$d(Ru_{bda}) \rightarrow \pi^*(tpy)$
3	538.6	0.01	H-1 -> L+1 (83%)	$d(Ru_{bda}) \rightarrow \pi^*(bda)$
11	479.0	0.01	H-2 -> L+1 (52%)	$d(Ru_{bda}) \rightarrow \pi^*(bda)$
12	465.5	0.05	H-2 -> LUMO (35%) H-1 -> L+3 (17%)	$d(Ru_{bda}) \rightarrow \pi^*(tpy)$ $d(Ru_{bpy}) \rightarrow \pi^*(tpy)$

			H-3 -> L+3 (16%)	$d(Ru_{bpy}) \rightarrow \pi^*(bpy)$
18	430.1	0.10	H-3 -> L+3 (36%) H-3 -> L+2 (20%)	$d(Ru_{bpy}) \rightarrow \pi^*(tpy)$ $d(Ru_{bpy}) \rightarrow \pi^*(bpy)$
64	310.8	0.16	H-9 -> LUMO (62%) H-4 -> L+7 (17%)	$\pi(tpy) \rightarrow \pi^*(tpy)$
76	297.3	0.14	H-4 -> L+7 (40%) H-11 -> LUMO (12%) H-9 -> LUMO (11%)	$\pi(tpy) \rightarrow \pi^*(tpy)$
89	286.3	0.22	H-12 -> L+1 (47%) H-6 -> L+5 (11%)	$\pi(bda) \rightarrow \pi^*(bda)$
104	278.3	0.19	H-12 -> L+2 (27%) H-11 -> L+3 (17%) H-12 -> L+3 (14%)	LLCT ($bda \rightarrow tpy+bpy$)
164	241.1	0.10	H-9 -> L+7 (24%) HOMO -> L+17 (10%)	$\pi(tpy) \rightarrow \pi^*(tpy)$
200	229.0	0.19	H-3 -> L+17 (21%) H-6 -> L+10 (13%)	$d(Ru_{bpy}) \rightarrow \pi^*(tpy)$

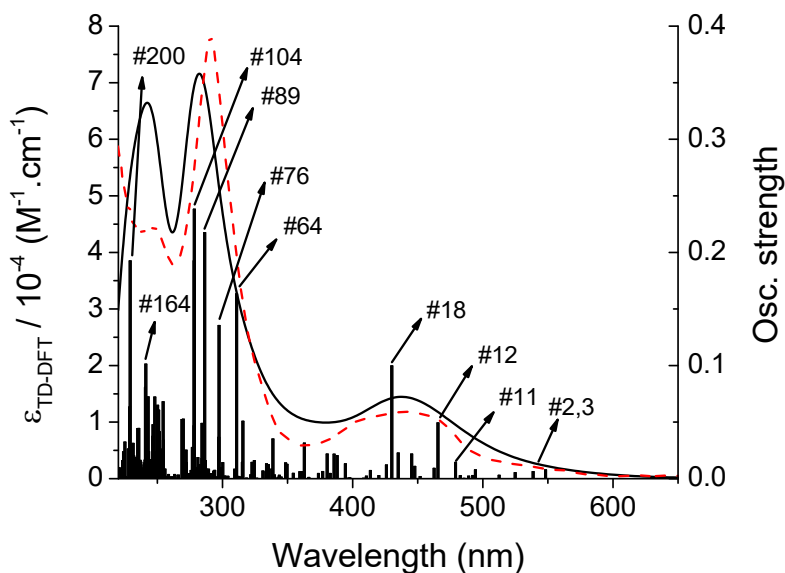


Figure S28. (TD)DFT-calculated (dashed curve) and experimental (solid curve) UV-visible absorption spectra of complex $[Ru^{II}(bpy)-Ru^{II}(bda)]^+$ in their singlet ground state. Calculated transitions are represented by red vertical bars.

Table S3. Energies values and percentual group contributions of selected MO's of complex $[Ru^{II}(MeO-bpy)CNRu^{II}(bda)]^+$ in their singlet ground state.

MO's	Energy (eV)	Ru_{bda}	bda	DMSO	CN	Ru_{tpy}	tpy	MeO-bpy
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L+10	-0,98	56	11	19	10	4	0	1
L+9	-1,28	0	0	0	0	1	0	98
L+8	-1,42	0	0	0	0	4	54	42
L+7	-1,56	0	0	0	0	1	99	0
L+6	-1,64	0	0	0	0	1	44	55
L+5	-1,94	3	96	0	0	0	0	0
L+4	-2,21	2	97	1	0	0	0	0
L+3	-2,36	0	0	0	0	3	4	92
L+2	-2,52	0	0	0	0	1	94	5
L+1	-2,59	7	89	1	0	0	2	0
LUMO	-2,68	0	2	0	1	6	90	1
HOMO	-5,54	69	24	0	2	4	1	0
H-1	-5,69	37	11	1	7	35	6	3
H-2	-5,85	45	13	2	6	27	6	1
H-3	-5,93	1	0	0	0	74	8	16
H-4	-6,21	30	16	1	4	35	9	5
H-5	-6,41	28	12	1	4	41	11	2
H-6	-6,93	5	5	89	2	0	0	0
H-7	-7,21	1	8	92	0	0	0	0
H-8	-7,24	1	91	6	0	0	2	0
H-9	-7,27	0	2	0	0	1	93	4
H-10	-7,32	1	98	0	0	0	1	0

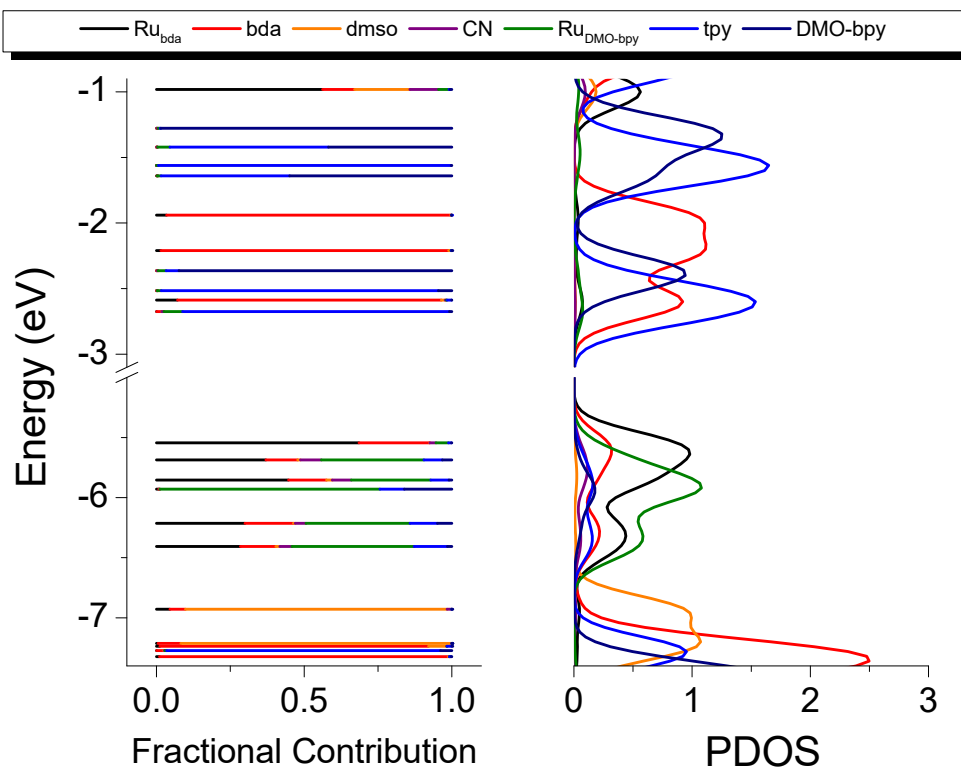


Figure S29. Molecular orbital diagram and partial density of states (PDOS) of complex $[Ru^{II}(MeO-bpy)CNRu^{II}(bda)]^+$ in their singlet ground state.

Table S4. (TD)DFT assignments for calculated UV-Vis transitions of the complex $[\text{Ru}^{\text{II}}(\text{MeO-bpy})\text{CNRu}^{\text{II}}(\text{bda})]^+$.

No.	Wavelength (nm)	Osc. Strength	Major contributions	Assignment
2	561.6	0.01	H-1 -> LUMO (65%) H-3 -> LUMO (19%)	$d(\text{Ru}_{\text{bda}}) + d(\text{Ru}_{\text{MeO-bpy}}) \rightarrow \pi^*(\text{tpy})$
5	521.2	0.01	HOMO -> LUMO (79%)	$d(\text{Ru}_{\text{bda}}) \rightarrow \pi^*(\text{tpy})$
13	460.6	0.05	H-3 -> L+2 (24%) H-2 -> LUMO (21%) H-1 -> L+2 (17%) H-1 -> L+3 (12%)	$d(\text{Ru}_{\text{bda}}) \rightarrow \pi^*(\text{tpy})$ $d(\text{Ru}_{\text{MeO-bpy}}) \rightarrow \pi^*(\text{tpy})$
17	429.4	0.09	H-3 -> L+3 (55%) H-3 -> L+1 (10%)	$d(\text{Ru}_{\text{MeO-bpy}}) \rightarrow \pi^*(\text{MeO-bpy})$
63	310.6	0.10	H-9 -> LUMO (65%) H-4 -> L+7 (19%)	$\pi(\text{tpy}) \rightarrow \pi^*(\text{tpy})$
88	286.5	0.12	H-11 -> L+1 (44%) H-6 -> L+5 (14%) H-11 -> LUMO (14%)	LLCT $\pi(\text{bda}) \rightarrow \pi^*(\text{tpy})$
91	284.4	0.12	H-13 -> LUMO (69%)	LLCT $\pi(\text{MeO-bpy}) \rightarrow \pi^*(\text{tpy})$
130	259.5	0.11	H-12 -> L+1 (47%) H-6 -> L+5 (11%)	LLCT $\pi(\text{MeO-bpy}) \rightarrow \pi^*(\text{tpy})$
149	251.0	0.12	H-18 -> LUMO (31%) H-14 -> L+4 (27%)	$\pi(\text{tpy}) \rightarrow \pi^*(\text{tpy})$ $\pi(\text{bda}) \rightarrow \pi^*(\text{bda})$

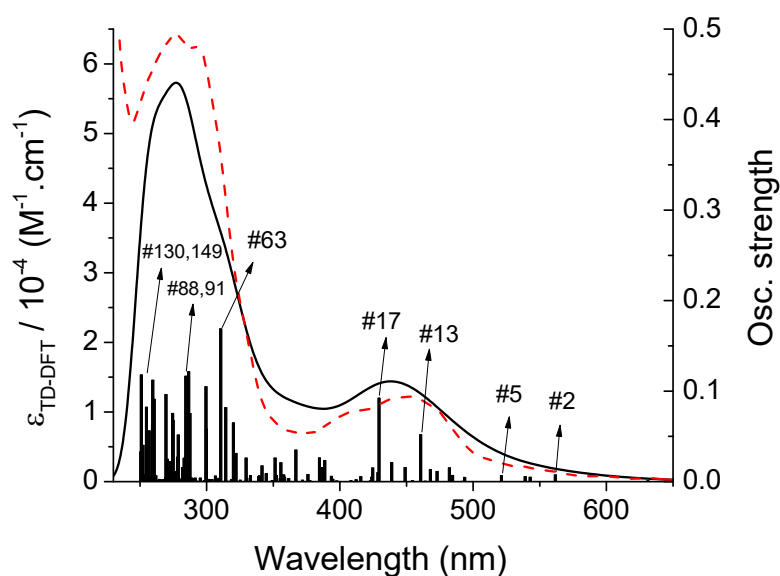


Figure S30. (TD)DFT-calculated (dashed curve) and experimental (solid curve) UV-visible absorption spectra of complex $[\text{Ru}^{\text{II}}(\text{MeO-bpy})\text{CNRu}^{\text{II}}(\text{bda})]^+$ in their triplet ground state. Calculated transitions are represented by red vertical bars.

Table S5. Energies values and percentual group contributions of selected α MO's of complex $[\text{Ru}^{\text{II}}(\text{bpy})\text{-Ru}^{\text{III}}(\text{bdaH})(\text{OH})]^{2+}$.

MO's (α)	Energy (eV)	Ru _{bda}	bdaH	DMSO	CN	Ru _{tpy}	tpy	bpy	OH
L+10	-1.57	1	0	0	0	3	59	36	0
L+9	-1.67	27	8	2	5	1	45	8	5
L+8	-1.68	23	6	2	4	1	56	4	4
L+7	-1.8	0	0	0	0	1	33	65	0
L+6	-2.12	59	31	9	1	0	0	0	0
L+5	-2.62	0	1	0	1	4	50	45	0
L+4	-2.64	1	40	0	0	1	25	33	0
L+3	-2.66	1	56	0	0	1	24	17	0
L+2	-2.78	1	97	0	0	0	2	0	0
L+1	-2.84	0	2	0	1	5	91	1	0
LUMO	-3.22	4	95	0	0	0	0	0	0
HOMO	-6.23	5	1	1	6	70	12	5	1
H-1	-6.33	2	0	0	2	72	11	12	0
H-2	-6.45	7	1	0	8	64	15	2	3
H-3	-7.02	43	18	4	2	6	2	0	24
H-4	-7.07	40	8	21	4	6	6	1	14
H-5	-7.4	1	0	2	0	1	82	13	0
H-6	-7.44	58	23	6	1	1	1	7	1
H-7	-7.47	5	2	0	0	2	12	79	0
H-8	-7.59	26	12	57	1	0	1	0	2
H-9	-7.66	2	1	96	0	0	0	0	0

H-10	-7.93	1	98	0	0	0	0	0	0
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Table S6. Energies values and percentual group contributions of selected β MO's of complex $[\text{Ru}^{\text{II}}(\text{bpy})-\text{Ru}^{\text{III}}(\text{bdaH})(\text{OH})]^{2+}$.

MO's (β)	Energy (eV)	Ru _{bda}	bdaH	DMSO	CN	Ru _{tpy}	tpy	bpy	OH
L+10	-1.58	7	3	0	2	2	27	59	1
L+9	-1.68	0	0	0	0	1	99	0	0
L+8	-1.8	0	0	0	0	1	33	65	0
L+7	-1.84	60	27	10	1	0	0	1	0
L+6	-2.56	7	86	1	0	0	4	1	1
L+5	-2.62	0	4	0	1	4	42	50	0
L+4	-2.65	0	1	0	0	1	54	44	0
L+3	-2.77	1	95	0	0	0	3	0	0
L+2	-2.83	0	4	0	1	5	89	1	0
L+1	-3.19	6	93	0	0	0	0	0	0
LUMO	-3.86	57	14	0	3	1	1	0	24
HOMO	-6.18	11	2	1	7	62	11	4	2
H-1	-6.31	2	0	0	1	74	10	12	0
H-2	-6.48	3	2	0	8	68	16	3	1
H-3	-6.87	43	10	11	4	14	7	1	12
H-4	-7.19	70	22	3	1	2	1	0	1
H-5	-7.4	0	0	1	0	1	85	13	0
H-6	-7.47	0	0	0	0	1	11	87	0
H-7	-7.51	15	7	72	0	0	1	0	5
H-8	-7.6	5	8	74	0	0	0	0	13
H-9	-7.84	6	40	24	0	0	0	0	28
H-10	-7.93	1	92	2	0	0	0	0	5

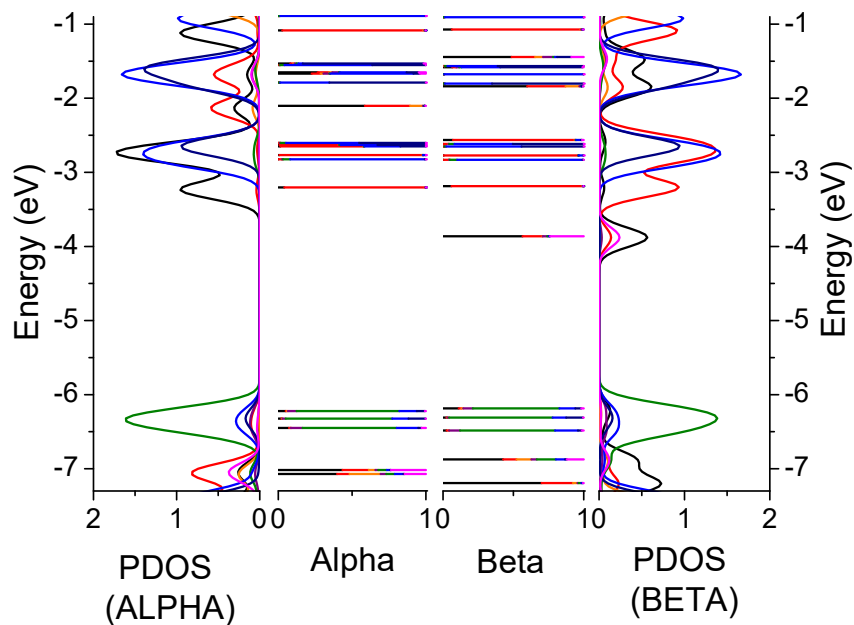


Figure S31. Molecular orbital diagram and partial density of states (PDOS) of complex $[\text{Ru}^{\text{II}}(\text{bpy})\text{-Ru}^{\text{III}}(\text{bdaH})(\text{OH})]^{2+}$.

Table S7. (TD)DFT assignments for calculated UV-Vis transitions of the complex $[\text{Ru}^{\text{II}}(\text{bpy})\text{CNRu}^{\text{III}}(\text{bdaH})(\text{OH})]^{2+}$.

No.	Wavelength (nm)	Osc. Strength	Major contributions	Assignment
5	595.0	0.047	H-2(B) -> LUMO(B)	$d(\text{Ru}_{\text{tpy}}) \rightarrow d(\text{Ru}_{\text{bda}})$
22	458.8	0.026	H-9(B)->LUMO(B) (23%), H-8(B)->LUMO(B) (61%)	$\pi(\text{DMSO}) \rightarrow d(\text{Ru}_{\text{bda}})$
35	420.1	0.060	H-1(A)->L+3(A) (11%), H-1(A)->L+4(A) (15%), HOMO(A)->L+2(A) (12%), H-1(B)->L+4(B) (20%), HOMO(B)->L+6(B) (10%)	$d(\text{Ru}_{\text{tpy}}) \rightarrow \pi^*(\text{bda})$
134	306.7	0.063	H-5(A)->L+1(A) (12%), H-2(A)->L+8(A) (13%)	$d(\text{Ru}_{\text{tpy}}) \rightarrow \pi^*(\text{tpy})$
144	301.9	0.115	H-7(A)->L+1(A) (12%), H-6(B)->L+2(B) (19%), H-4(B)->L+4(B) (21%)	$d(\text{Ru}_{\text{tpy}}) \rightarrow \pi^*(\text{tpy})$
148	300.3	0.131	H-4(B)->L+4(B) (12%)	$d(\text{Ru}_{\text{bda}}) \rightarrow \pi^*(\text{tpy}) + \pi^*(\text{bpy})$

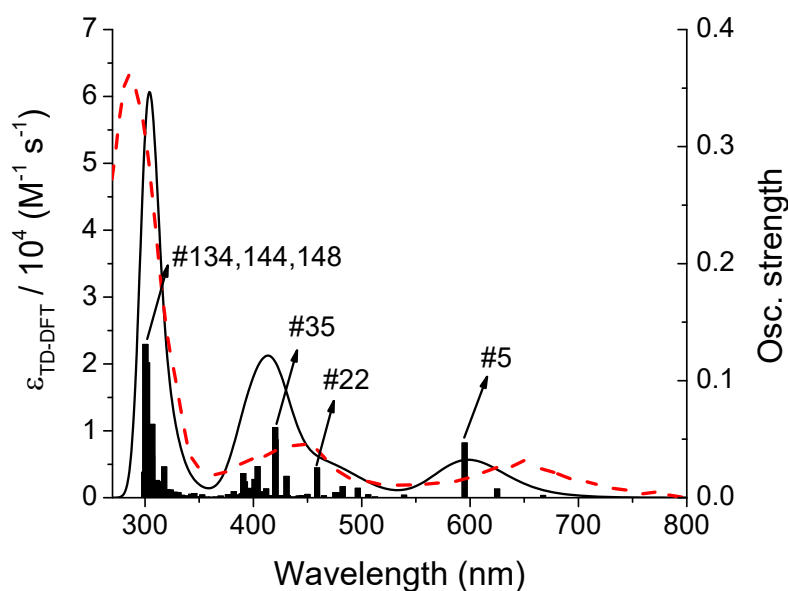


Figure S32. (TD)DFT-calculated (dashed curve) and experimental (solid curve) UV-visible absorption spectra of complex $[\text{Ru}^{\text{II}}(\text{bpy})\text{-Ru}^{\text{III}}(\text{bdaH})(\text{OH})]^{2+}$. Calculated transitions are represented by red vertical bars.

Table S8. Energies values and percentual group contributions of selected α MO's of complex $[\text{Ru}^{\text{II}}(\text{MeO-bpy})\text{-Ru}^{\text{III}}(\text{bdaH})(\text{OH})]^{2+}$.

MO's (α)	Energy (eV)	Ru _{bda}	bdaH	DMSO	CN	Ru _{tpy}	tpy	MeO-bpy	OH
L+10	-1.51	2	1	0	0	4	44	49	0
L+9	-1.65	8	3	1	1	1	84	1	2
L+8	-1.68	47	13	4	8	1	17	3	9
L+7	-1.72	0	0	0	0	1	52	46	0
L+6	-2.1	58	31	9	1	0	0	0	0
L+5	-2.44	0	0	0	1	2	2	95	0
L+4	-2.61	0	4	0	0	1	93	2	0
L+3	-2.66	2	92	1	0	0	4	1	0
L+2	-2.79	1	89	0	0	1	9	0	0
L+1	-2.81	0	10	0	1	5	83	1	0
LUMO	-3.22	4	95	0	0	0	0	0	0
HOMO	-6.11	2	0	0	3	73	10	12	0
H-1	-6.17	4	1	1	5	64	12	13	1
H-2	-6.4	6	1	0	8	65	15	2	2
H-3	-7.02	45	18	3	2	5	2	0	25
H-4	-7.06	41	9	21	4	4	4	2	14
H-5	-7.37	0	0	1	0	1	91	7	0
H-6	-7.46	63	26	6	1	1	1	1	1

H-7	-7.5	0	0	0	0	0	1	98	0
H-8	-7.59	20	9	51	1	0	0	16	2
H-9	-7.64	6	3	8	0	5	8	69	1
H-10	-7.67	2	1	96	0	0	0	0	0

Table S9. Energies values and percentual group contributions of selected β MO's of complex $[\text{Ru}^{\text{II}}(\text{MeO-bpy})-\text{Ru}^{\text{III}}(\text{bdaH})(\text{OH})]^{2+}$.

MO's (β)	Energy (eV)	Ru _{bda}	bdaH	DMSO	CN	Ru _{tpy}	tpy	MeO-bpy	OH
L+10	-1.53	12	4	1	3	2	35	41	2
L+9	-1.66	0	0	0	0	1	99	0	0
L+8	-1.72	0	0	0	0	1	52	47	0
L+7	-1.82	60	28	10	1	0	0	0	0
L+6	-2.44	0	0	0	1	2	2	95	0
L+5	-2.57	7	84	1	0	0	7	0	1
L+4	-2.62	0	6	0	0	1	90	2	0
L+3	-2.78	1	82	0	0	1	16	0	0
L+2	-2.81	0	18	0	1	4	76	1	0
L+1	-3.19	6	92	0	0	0	0	0	0
LUMO	-3.87	56	14	0	3	1	1	0	24
HOMO	-6.09	6	1	1	5	67	10	8	1
H-1	-6.14	4	1	0	3	66	10	16	1
H-2	-6.42	2	2	0	8	68	16	2	1
H-3	-6.85	46	10	11	4	9	5	3	13
H-4	-7.21	71	23	3	1	1	1	0	0
H-5	-7.37	0	0	0	0	1	92	7	0
H-6	-7.5	0	0	3	0	0	1	95	0
H-7	-7.53	14	6	70	0	0	0	5	4
H-8	-7.59	5	9	69	0	0	0	2	15
H-9	-7.63	1	1	3	0	4	8	83	0
H-10	-7.81	0	2	2	0	9	3	82	1

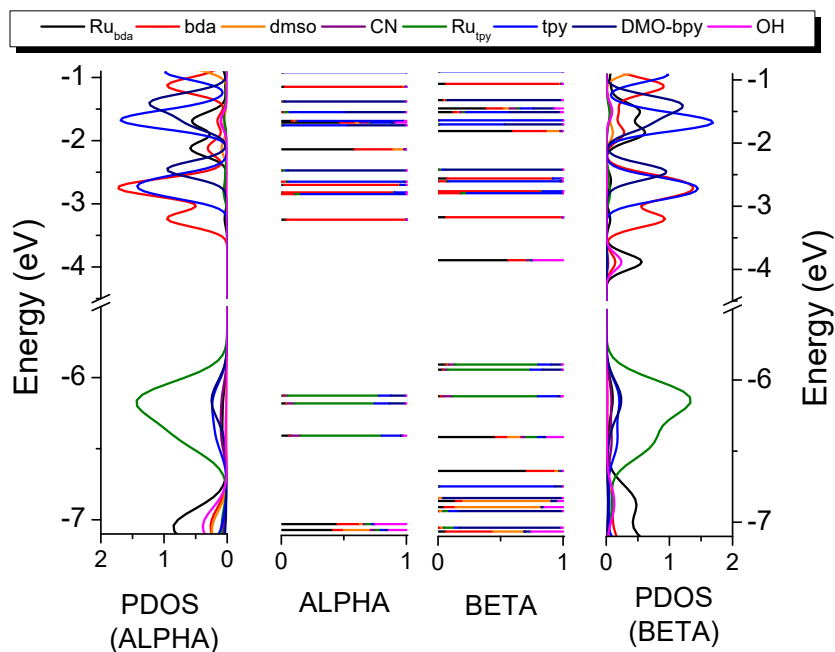


Figure S33. Molecular orbital diagram and partial density of states (PDOS) of complex $[\text{Ru}^{\text{II}}(\text{MeO-bpy})\text{-Ru}^{\text{III}}(\text{bdaH})(\text{OH})]^{2+}$.

Table S10. (TD)DFT assignments for calculated UV-Vis transitions of the complex $[\text{Ru}^{\text{II}}(\text{MeO-bpy})\text{-Ru}^{\text{III}}(\text{bdaH})(\text{OH})]^{2+}$.

No.	Wavelength (nm)	Osc. Strength	Major contributions	Assignment
5	616.5	0.054	H-2(B)->LUMO(B) (86%)	d(Ru_{tpy}) -> d(Ru_{bda})
22	460.7	0.025	H-8(B)->LUMO(B) (58%), H-11(B)->LUMO(B) (18%)	$\pi(\text{DMSO})$ -> d(Ru_{bda})
39	418.7	0.037	HOMO(A)->L+3(A) (27%)	d(Ru_{tpy}) -> $\pi^*(\text{bda})$
42	407.4	0.032	H-2(A)->L+4(A) (31%), H-2(B)->L+4(B) (39%)	d(Ru_{tpy}) -> $\pi^*(\text{tpy})$
139	305.7	0.158	H-5(A)->L+1(A) (15%), H-2(A)->L+9(A) (10%), H-5(B)->L+2(B) (13%), H-2(B)->L+9(B) (15%)	d(Ru_{tpy}) -> $\pi^*(\text{tpy})$

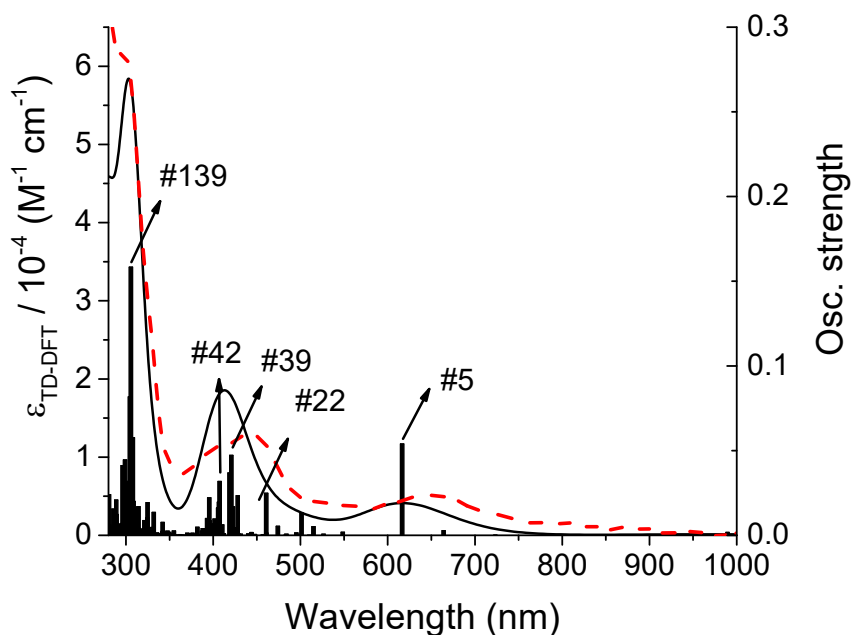


Figure S34. (TD)DFT-calculated (dashed curve) and experimental (solid curve) UV-visible absorption spectra of complex $[\text{Ru}^{\text{II}}(\text{MeO-bpy})-\text{Ru}^{\text{IV}}(\text{bdaH})(\text{OH})]^{2+}$. Calculated transitions are represented by red vertical bars.

Table S11. Energies values and percentual group contributions of selected MO's of complex $[\text{Ru}^{\text{II}}(\text{bpy})-\text{Ru}^{\text{IV}}(\text{bda})(\text{OH})]^{2+}$.

MO's	Energy (eV)	Ru _{bda}	bda	DMSO	CN	Ru _{tpy}	tpy	bpy	OH
L+10	-1.65	0	0	0	0	1	99	0	0
L+9	-1.78	0	0	0	0	1	30	69	0
L+8	-2.41	55	8	14	12	2	0	0	9
L+7	-2.58	0	0	0	0	4	58	37	0
L+6	-2.63	0	0	0	0	2	40	58	0
L+5	-2.71	1	97	0	0	0	1	0	0
L+4	-2.79	0	2	0	1	6	91	1	0
L+3	-2.87	1	97	0	0	0	1	0	0
L+2	-3.42	5	93	1	0	0	0	0	0
L+1	-3.56	55	31	1	1	0	0	0	13
LUMO	-3.89	60	32	0	0	0	0	0	8
HOMO	-6.17	1	0	0	4	77	11	7	0
H-1	-6.26	1	0	0	3	72	13	11	0
H-2	-6.37	2	0	0	8	71	16	2	0
H-3	-7.33	5	2	88	3	0	1	0	1
H-4	-7.37	1	0	1	0	1	91	6	0
H-5	-7.45	0	0	0	0	1	5	94	0
H-6	-7.6	6	6	87	0	0	0	0	1

H-7	-7.69	30	43	12	2	1	2	0	10
H-8	-7.78	7	64	1	1	0	0	0	28
H-9	-8.01	57	17	1	8	1	8	0	8
H-10	-8.04	1	99	0	0	0	0	0	0

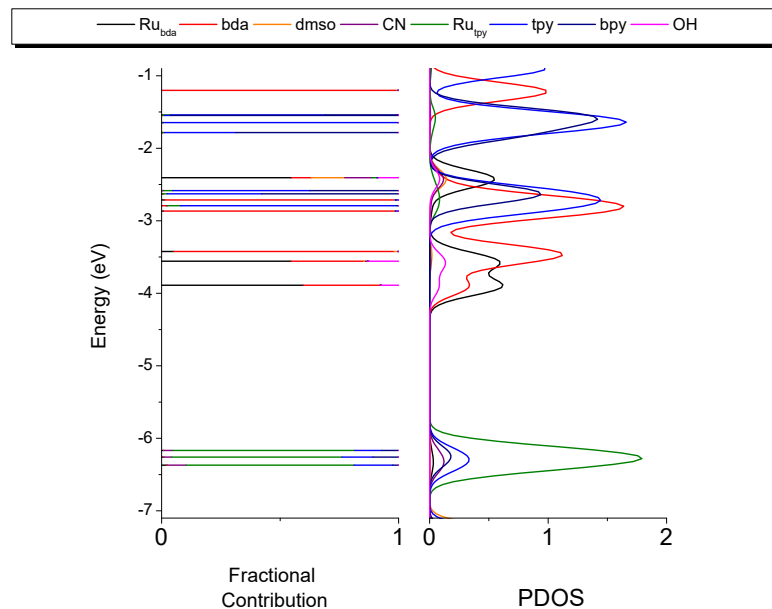


Figure S35. Molecular orbital diagram and partial density of states (PDOS) of complex $[Ru^{II}(bpy)-Ru^{IV}(bda)(OH)]^{2+}$.

Table S12. (TD)DFT assignments for calculated UV-Vis transitions of the complex $[Ru^{II}(bpy)-Ru^{IV}(bda)(OH)]^{2+}$.

No.	Wavelength (nm)	Osc. Strength	Major contributions	Assignment
13	488.3	0.011	H-1->L+4 (91%)	$d(Ru_{tpy}) \rightarrow \pi^*(tpy)$
21	425.5	0.118	H-1->L+6 (79%)	$d(Ru_{tpy}) \rightarrow \pi^*(tpy)$ $d(Ru_{tpy}) \rightarrow \pi^*(bpy)$
33	396.3	0.034	H-1->L+7 (41%), H-2->L+4 (17%), H-8->LUMO (14%)	$d(Ru_{tpy}) \rightarrow \pi^*(tpy)$ $d(Ru_{tpy}) \rightarrow \pi^*(bpy)$
66	319.9	0.060	HOMO->L+11 (77%), H-1->L+12 (10%)	$d(Ru_{tpy}) \rightarrow \pi^*(bpy)$
74	305.4	0.163	H-4->L+4 (31%), H-2->L+12 (21%), H-2->L+11 (16%)	$d(Ru_{tpy}) \rightarrow \pi^*(tpy)$ $d(Ru_{tpy}) \rightarrow \pi^*(bpy)$
81	300.6	0.175	H-1->L+12 (42%), H-3->L+8 (22%)	$d(Ru_{tpy}) \rightarrow \pi^*(tpy)$

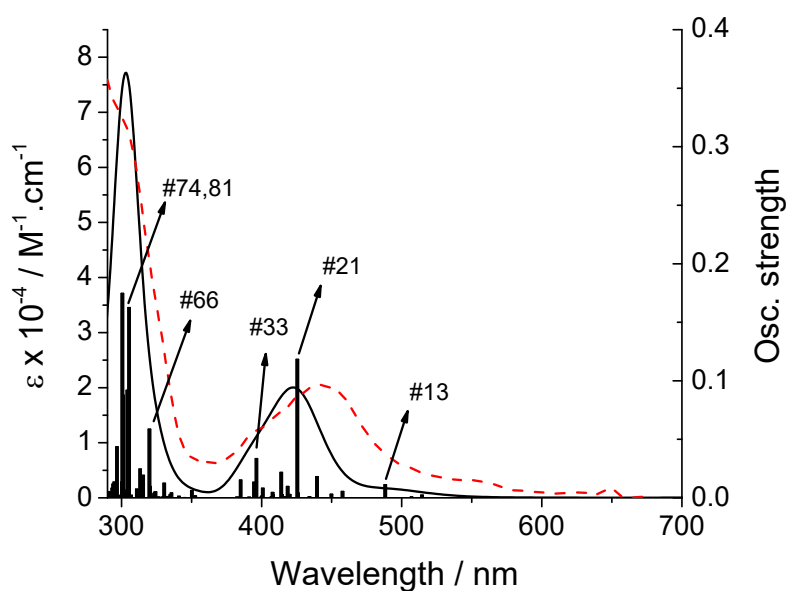


Figure S36. (TD)DFT-calculated (dashed curve) and experimental (solid curve) UV-visible absorption spectra of complex $[\text{Ru}^{\text{II}}(\text{bpy})\text{-Ru}^{\text{IV}}(\text{bda})(\text{OH})]^{2+}$. Calculated transitions are represented by red vertical bars.

Table S13. Energies values and percentual group contributions of selected MO's of complex $[\text{Ru}^{\text{II}}(\text{MeO-bpy})\text{-Ru}^{\text{IV}}(\text{bda})(\text{OH})]^{2+}$.

MO's	Energy (eV)	Ru _{bda}	bda	DMSO	CN	Ru _{tpy}	tpy	MeO-bpy	OH
L+10	-1.62	0	0	0	0	1	99	0	0
L+9	-1.7	0	0	0	0	1	46	52	0
L+8	-2.39	52	8	13	11	2	0	6	8
L+7	-2.42	3	0	1	1	2	3	89	0
L+6	-2.58	0	1	0	0	1	95	3	0
L+5	-2.71	1	96	0	0	0	3	0	0
L+4	-2.76	0	3	0	1	6	90	1	0
L+3	-2.86	1	98	0	0	0	1	0	0
L+2	-3.42	5	93	1	0	0	0	0	0
L+1	-3.55	55	30	1	1	0	0	0	13
LUMO	-3.88	60	32	0	0	0	0	0	8
HOMO	-6.03	0	0	0	1	76	9	14	0
H-1	-6.11	1	0	0	6	67	14	11	0
H-2	-6.29	2	0	0	8	71	17	2	0
H-3	-7.32	5	2	83	3	0	6	0	1
H-4	-7.34	1	0	6	0	1	88	4	0
H-5	-7.49	0	0	0	0	0	0	99	0
H-6	-7.59	8	8	51	1	0	1	29	1
H-7	-7.61	0	0	37	0	2	4	56	0
H-8	-7.69	28	41	11	2	1	2	5	9

H-9	-7.77	7	63	1	1	0	0	0	28
H-10	-7.8	0	0	0	0	9	3	88	0

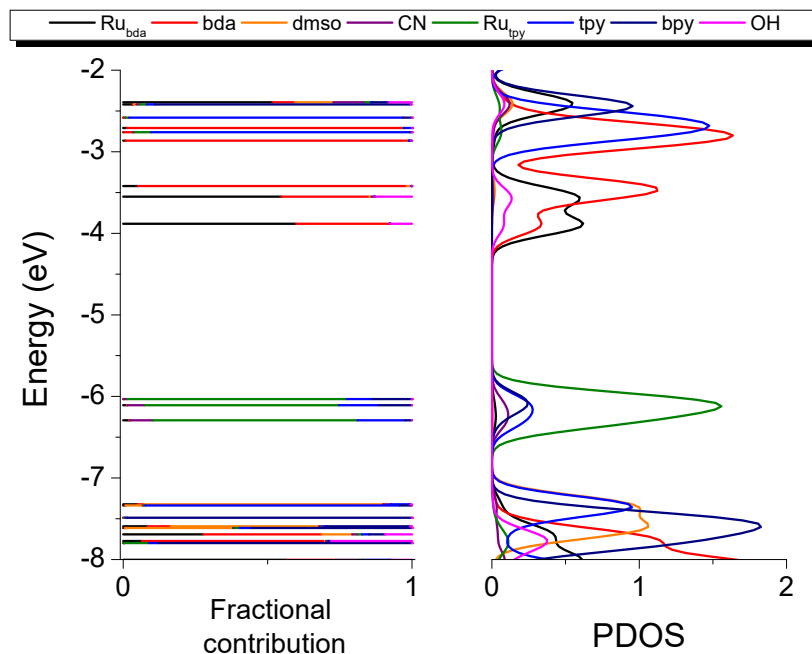


Figure S37. Molecular orbital diagram and partial density of states (PDOS) of complex $[\text{Ru}^{\text{II}}(\text{MeO-bpy})\text{-Ru}^{\text{IV}}(\text{bda})(\text{OH})]^{2+}$.

Table S14. (TD)DFT assignments for calculated UV-Vis transitions of the complex $[\text{Ru}^{\text{II}}(\text{MeO-bpy})\text{-Ru}^{\text{IV}}(\text{bda})(\text{OH})]^{2+}$.

No.	Wavelength (nm)	Osc. Strength	Major contributions	Assignment
13	507.9	0.014	H-1->L+4 (95%)	$d(\text{Ru}_{\text{tpy}}) \rightarrow \pi^*(\text{tpy})$
20	437.5	0.027	HOMO->L+7 (80%)	$d(\text{Ru}_{\text{tpy}}) \rightarrow \pi^*(\text{MeO-bpy})$
22	426.3	0.103	H-1->L+6 (39%), H-1->L+7 (32%), H-2->L+4 (20%)	$d(\text{Ru}_{\text{tpy}}) \rightarrow \pi^*(\text{tpy})$ $d(\text{Ru}_{\text{tpy}}) \rightarrow \pi^*(\text{MeO-bpy})$
33	401.9	0.037	H-1->L+7 (36%), H-2->L+7 (16%), H-2->L+4 (15%)	$d(\text{Ru}_{\text{tpy}}) \rightarrow \pi^*(\text{MeO-bpy})$ $d(\text{Ru}_{\text{tpy}}) \rightarrow \pi^*(\text{tpy})$
38	385.0	0.016	H-3->L+2 (88%)	$\pi(\text{DMSO}) \rightarrow \pi^*(\text{bda})$
79	307.1	0.175	H-4->L+4 (27%), H-4->L+3 (24%), H-1->L+17 (16%)	$\pi(\text{tpy}) \rightarrow \pi^*(\text{tpy})$ $\pi(\text{tpy}) \rightarrow \pi^*(\text{bda})$
81	306.3	0.212	H-4->L+4 (41%), H-4->L+3 (18%), H-1->L+10 (11%)	$\pi(\text{tpy}) \rightarrow \pi^*(\text{tpy})$ $\pi(\text{tpy}) \rightarrow \pi^*(\text{bda})$
83	302.6	0.218	H-1->L+11 (36%), H-1->L+12 (19%),	$d(\text{Ru}_{\text{tpy}}) \rightarrow \pi^*(\text{MeO-bpy})$

HOMO→L+12 (14%),
H-3→L+8 (11%)

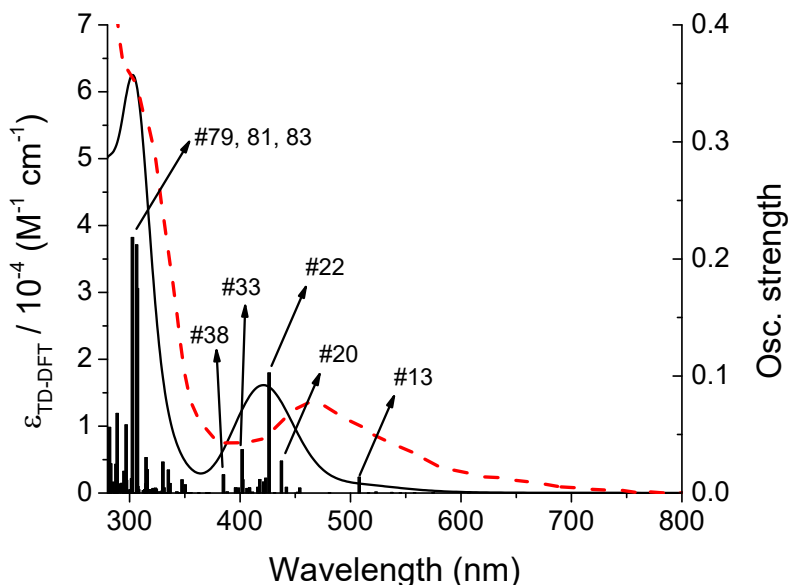


Figure S38. (TD)DFT-calculated (dashed curve) and experimental (solid curve) UV-visible absorption spectra of complex $[\text{Ru}^{\text{III}}(\text{MeO-bpy})-\text{Ru}^{\text{IV}}(\text{bda})(\text{OH})]^{2+}$. Calculated transitions are represented by red vertical bars.

Table S15. Energies values and percentual group contributions of selected α MO's of complex $[\text{Ru}^{\text{III}}(\text{bpy})-\text{Ru}^{\text{IV}}(\text{bda})(\text{OH})]^{3+}$.

MO's (α)	Energy (eV)	Ru _{bda}	bda	DMSO	CN	Ru _{tpy}	tpy	bpy	OH
L+10	-2.29	0	0	0	0	1	55	44	0
L+9	-2.44	5	1	1	2	45	41	5	1
L+8	-2.71	48	10	13	10	7	3	2	8
L+7	-2.79	2	98	0	0	0	0	0	0
L+6	-2.93	2	96	1	0	0	1	0	1
L+5	-3.12	0	1	0	0	1	91	8	0
L+4	-3.2	0	0	0	0	2	8	90	0
L+3	-3.46	0	4	0	0	3	91	1	0
L+2	-3.51	6	88	2	0	0	5	0	0
L+1	-3.71	54	32	1	1	0	0	0	13
LUMO	-4.03	59	33	0	0	0	0	0	8
HOMO	-7.44	6	2	88	2	0	0	0	1
H-1	-7.7	6	6	84	1	1	1	0	1
H-2	-7.77	9	9	8	2	8	57	4	2
H-3	-7.81	18	33	6	1	2	27	0	13
H-4	-7.88	6	46	1	1	1	6	22	18
H-5	-7.89	4	17	0	0	1	1	72	5
H-6	-8.05	37	10	1	9	23	12	4	4

H-7	-8.11	1	98	0	0	0	1	0	0
H-8	-8.24	2	9	0	3	48	24	14	0
H-9	-8.26	2	96	0	0	1	0	0	0
H-10	-8.36	14	11	0	2	33	29	9	2

Table S16. Energies values and percentual group contributions of selected β MO's of complex $[\text{Ru}^{\text{III}}(\text{bpy})-\text{Ru}^{\text{IV}}(\text{bda})(\text{OH})]^{3+}$.

MO's (β)	Energy (eV)	Ru _{bda}	bda	DMSO	CN	Ru _{tpy}	tpy	bpy	OH
L+10	-2.25	1	0	0	1	25	69	3	0
L+9	-2.67	53	10	14	10	4	1	1	9
L+8	-2.79	1	98	0	0	0	0	0	0
L+7	-2.93	1	95	0	0	0	2	0	0
L+6	-3.06	0	2	0	0	3	77	18	0
L+5	-3.17	0	0	0	0	3	19	78	0
L+4	-3.44	0	2	0	0	3	94	1	0
L+3	-3.5	6	90	2	0	0	2	0	0
L+2	-3.71	54	32	1	1	0	0	0	13
L+1	-4.03	59	33	0	0	0	0	0	8
LUMO	-5.28	0	0	0	3	74	15	7	0
HOMO	-7.44	6	2	88	2	0	0	0	1
H-1	-7.68	11	10	51	2	12	10	3	1
H-2	-7.72	2	1	37	1	20	34	4	0
H-3	-7.78	21	28	11	3	11	17	0	9
H-4	-7.87	4	59	0	1	2	6	1	27
H-5	-7.89	2	1	0	1	5	7	82	1
H-6	-7.91	12	4	0	5	26	31	20	2
H-7	-8.02	6	21	0	2	37	26	6	0
H-8	-8.11	2	97	0	0	0	0	0	0
H-9	-8.26	3	95	0	0	0	0	0	1
H-10	-8.29	41	24	1	3	12	12	2	6

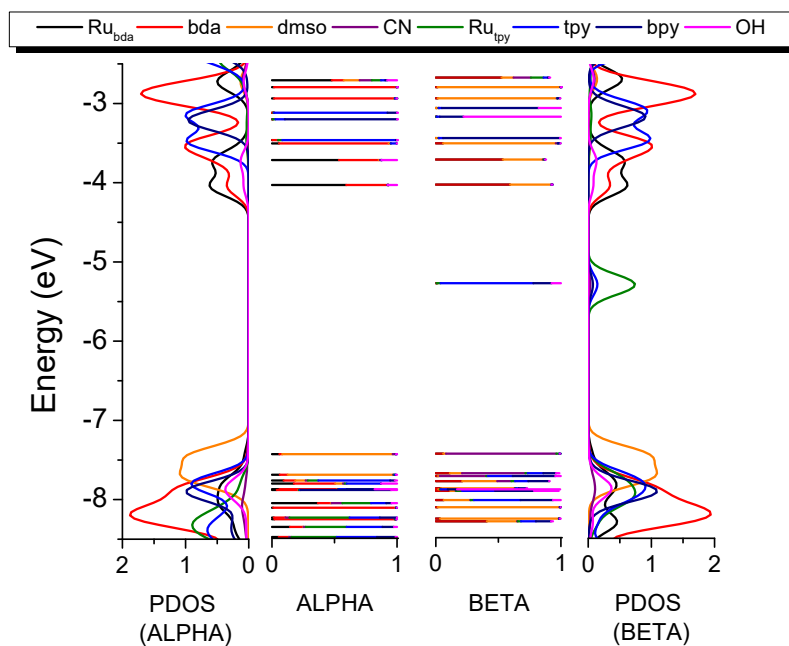


Figure S39. Molecular orbital diagram and partial density of states (PDOS) of complex $[Ru^{III}(bpy)-Ru^{IV}(bda)(OH)]^{3+}$.

Table S17. (TD)DFT assignments for calculated UV-Vis transitions of the complex $[Ru^{III}(bpy)-Ru^{IV}(bda)(OH)]^{3+}$.

No.	Wavelength (nm)	Osc. Strength	Major contributions	Assignment
7	669.1	0.005	H-5(B)->LUMO(B) (73%), H-6(B)->LUMO(B) (24%)	$\pi(bpy) \rightarrow d(Ru_{tpy})$
9	619.9	0.005	H-1(B)->LUMO(B) (44%), H-3(B)->LUMO(B) (29%), H-7(B)->LUMO(B) (23%)	$\pi(DMSO) \rightarrow d(Ru_{tpy})$ $\pi(bda) \rightarrow d(Ru_{tpy})$
15	525.3	0.011	H-10(B)->LUMO(B) (82%)	$d(Ru_{bda}) \rightarrow d(Ru_{tpy})$
41	396.0	0.013	H-17(B)->LUMO(B) (72%)	$\pi(tpy) \rightarrow d(Ru_{tpy})$
46	382.4	0.017	HOMO(B)->L+3(B) (48%), HOMO(A)->L+2(A) (47%)	$\pi(DMSO) \rightarrow \pi^*(bda)$
49	377.9	0.016	H-19(B)->LUMO(B) (57%)	$\pi(bpy) \rightarrow d(Ru_{tpy})$
103	327.0	0.033	H-5(A)->L+1(A) (24%)	$\pi(bpy) \rightarrow d(Ru_{bda})$
134	313.0	0.040	H-2(B)->L+4(B) (15%), H-1(B)->L+4(B) (13%)	$\pi(DMSO) \rightarrow \pi^*(tpy)$
149	307.0	0.023	H-24(B)->LUMO(B) (18%), H-23(B)->LUMO(B) (23%)	$\pi(DMSO) \rightarrow d(Ru_{tpy})$ $\pi(bda) \rightarrow d(Ru_{tpy})$

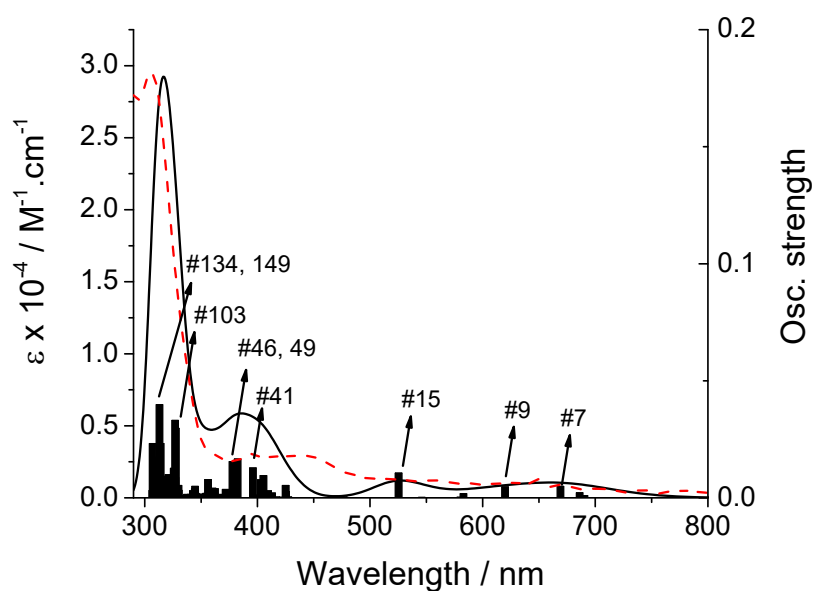


Figure S40. (TD)DFT-calculated (dashed curve) and experimental (solid curve) UV-visible absorption spectra of complex $[\text{Ru}^{\text{III}}(\text{bpy})\text{-Ru}^{\text{IV}}(\text{bda})(\text{OH})]^{3+}$. Calculated transitions are represented by red vertical bars.

Table S18. Energies values and percentual group contributions of selected α MO's of complex $[\text{Ru}^{\text{III}}(\text{MeO-bpy})\text{-Ru}^{\text{IV}}(\text{bda})(\text{OH})]^{3+}$.

MO's (α)	Energy (eV)	Ru _{bda}	bda	DMSO	CN	Ru _{tpy}	tpy	MeO-bpy	OH
L+10	-2.23	0	0	0	0	1	63	36	0
L+9	-2.36	3	0	1	2	47	41	5	0
L+8	-2.67	50	9	13	10	6	2	1	8
L+7	-2.79	1	98	0	0	0	0	0	0
L+6	-2.93	1	92	0	0	0	2	4	0
L+5	-2.94	0	4	0	0	1	1	93	0
L+4	-3.08	0	2	0	0	1	96	1	0
L+3	-3.41	0	1	0	0	3	94	1	0
L+2	-3.5	6	91	2	0	0	1	0	0
L+1	-3.7	54	32	1	1	0	0	0	13
LUMO	-4.02	59	33	0	0	0	0	0	8
HOMO	-7.42	6	2	88	2	0	0	0	1
H-1	-7.56	5	2	1	3	24	14	51	0
H-2	-7.69	4	5	87	0	1	1	2	1
H-3	-7.77	1	1	1	0	11	40	45	0
H-4	-7.79	22	33	10	2	3	19	2	10
H-5	-7.81	3	6	1	0	3	28	55	3
H-6	-7.87	8	63	1	1	1	0	2	24
H-7	-7.95	3	1	0	1	3	3	88	0
H-8	-8.03	30	11	1	8	24	11	13	3

H-9	-8.11	1	97	0	0	0	0	0	0
H-10	-8.25	6	75	0	1	8	7	2	1

Table S19. Energies values and percentual group contributions of selected β MO's of complex $[\text{Ru}^{\text{III}}(\text{MeO-bpy})-\text{Ru}^{\text{IV}}(\text{bda})(\text{OH})]^{3+}$.

MO's (β)	Energy (eV)	Ru _{bda}	bda	DMSO	CN	Ru _{tpy}	tpy	MeO-bpy	OH
L+10	-2.18	0	0	0	1	21	75	3	0
L+9	-2.64	53	9	14	10	3	1	1	9
L+8	-2.79	1	98	0	0	0	0	0	0
L+7	-2.88	0	1	0	0	3	5	91	0
L+6	-2.93	1	94	0	0	0	2	1	0
L+5	-3.05	0	2	0	0	2	92	3	0
L+4	-3.39	0	1	0	0	3	95	1	0
L+3	-3.5	6	91	2	0	0	1	0	0
L+2	-3.69	54	32	1	1	0	0	0	13
L+1	-4.01	59	33	0	0	0	0	0	8
LUMO	-5.15	0	0	0	2	73	13	11	0
HOMO	-7.39	4	1	10	4	35	11	36	0
H-1	-7.43	5	2	79	2	4	2	5	1
H-2	-7.68	8	8	76	1	4	2	1	1
H-3	-7.75	19	18	23	5	22	8	1	5
H-4	-7.79	0	0	0	0	1	73	25	0
H-5	-7.85	3	42	0	2	14	6	8	25
H-6	-7.87	5	20	0	1	3	11	52	7
H-7	-7.92	14	28	1	2	14	8	32	1
H-8	-8.02	1	4	0	1	6	8	80	0
H-9	-8.11	1	98	0	0	0	0	0	0
H-10	-8.24	41	24	1	3	8	7	10	7

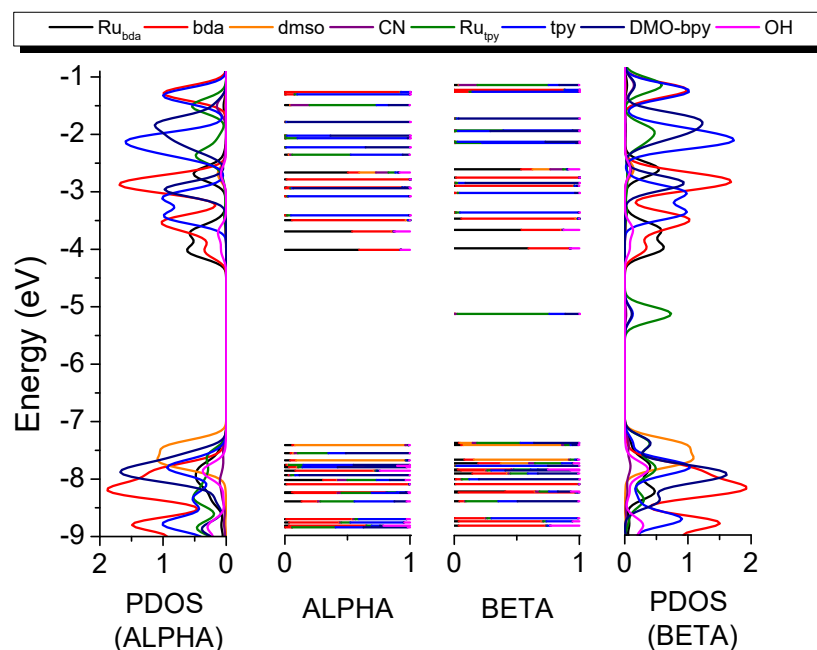


Figure S41. Molecular orbital diagram and partial density of states (PDOS) of complex $[\text{Ru}^{\text{III}}(\text{MeO-bpy})\text{-Ru}^{\text{IV}}(\text{bda})(\text{OH})]^{3+}$.

Table S20. (TD)DFT assignments for calculated UV-Vis transitions of the complex $[\text{Ru}^{\text{III}}(\text{MeO-bpy})\text{-Ru}^{\text{IV}}(\text{bda})(\text{OH})]^{3+}$.

No.	Wavelength (nm)	Osc. Strength	Major contributions	Assignment
9	594.2	0.023	H-8(B)->LUMO(B) (44%), H-6(B)->LUMO(B) (12%), H-7(B)->LUMO(B) (11%), H-2(B)->LUMO(B) (10%)	$\pi(\text{MeO-bpy}) \rightarrow d(\text{Ru}_{\text{tpy}})$
16	528.0	0.070	H-12(B)->LUMO(B) (62%), H-10(B)->LUMO(B) (14%)	$\pi(\text{MeO-bpy}) \rightarrow d(\text{Ru}_{\text{tpy}})$
29	424.1	0.008	HOMO(A)->L+1(A) (46%), H-1(B)->L+2(B) (41%)	$\pi(\text{DMSO}) \rightarrow d(\text{Ru}_{\text{bda}})$
38	403.2	0.008	H-6(A)->LUMO(A) (32%), H-5(B)->L+1(B) (24%)	$\pi(\text{bda}) \rightarrow d(\text{Ru}_{\text{bda}})$ $\pi(\text{OH}) \rightarrow d(\text{Ru}_{\text{bda}})$
46	382.9	0.016	HOMO(A)->L+2(A) (48%), H-1(B)->L+3(B) (40%)	$\pi(\text{DMSO}) \rightarrow \pi^*(\text{bda})$
118	321.5	0.037	H-5(A)->L+3(A) (17%)	$\pi(\text{tpy}) \rightarrow \pi^*(\text{tpy})$ $\pi(\text{MeO-bpy}) \rightarrow \pi^*(\text{tpy})$
165	303.5	0.062	HOMO(A)->L+8(A) (19%), H-1(B)->L+9(B) (15%)	$\pi(\text{DMSO}) \rightarrow d(\text{Ru}_{\text{bda}})$
181	296.6	0.052	H-8(A)->L+4(A) (15%), H-4(A)->L+4(A) (15%)	$d(\text{Ru}_{\text{bda}}) \rightarrow \pi(\text{tpy})$

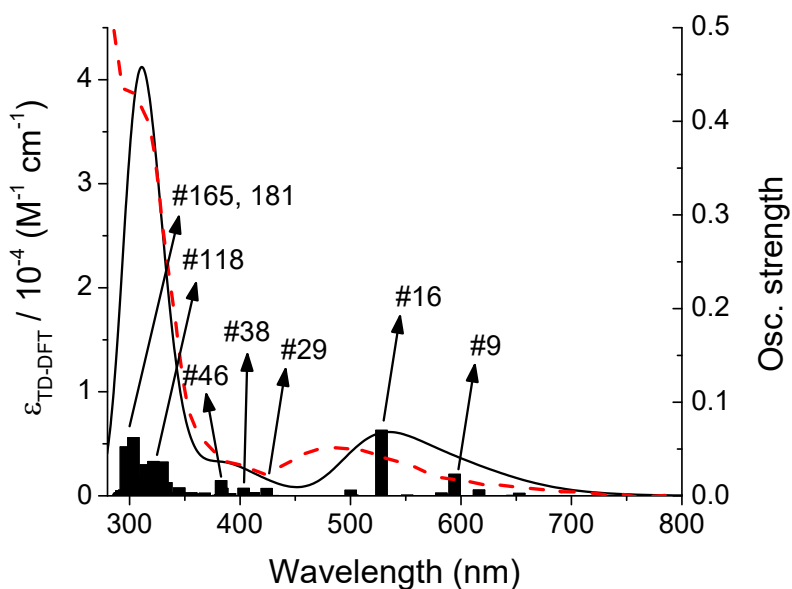


Figure S42. (TD)DFT-calculated (dashed curve) and experimental (solid curve) UV-visible absorption spectra of complex $[\text{Ru}^{\text{III}}(\text{MeO-bpy})-\text{Ru}^{\text{IV}}(\text{bda})(\text{OH})]^{3+}$. Calculated transitions are represented by red vertical bars.

Table S21. Energies values and percentual group contributions of selected α MO's of complex $[\text{Ru}^{\text{III}}(\text{bpy})-\text{Ru}^{\text{V}}(\text{bda})(\text{O})]^{3+}$.

MO's (α)	Energy (eV)	Ru _{bda}	bda	DMSO	CN	Ru _{tpy}	tpy	bpy	O
L+10	-2.3	0	0	0	0	1	55	44	0
L+9	-2.49	1	0	0	2	50	41	6	0
L+8	-2.8	1	99	0	0	0	0	0	0
L+7	-2.89	27	50	5	5	2	1	1	9
L+6	-2.95	23	58	4	3	1	1	0	9
L+5	-3.13	0	1	0	0	1	90	8	0
L+4	-3.21	0	0	0	0	2	8	90	0
L+3	-3.47	0	12	0	0	3	84	1	0
L+2	-3.52	3	84	1	0	0	12	0	1
L+1	-3.96	55	28	7	5	1	0	0	4
LUMO	-4.51	56	32	0	0	0	0	0	12
HOMO	-7.66	6	3	86	3	0	0	0	2
H-1	-7.79	1	0	0	1	7	88	3	0
H-2	-7.9	0	0	1	0	1	4	94	0
H-3	-7.92	1	7	90	0	0	0	1	0
H-4	-8.03	1	86	1	0	0	0	0	11
H-5	-8.06	19	59	6	2	6	3	2	2
H-6	-8.13	7	85	1	1	3	2	1	0
H-7	-8.18	16	18	1	6	31	16	5	6
H-8	-8.25	2	78	0	1	11	5	4	0
H-9	-8.29	4	21	0	3	39	24	9	1

H-10	-8.44	16	7	1	2	28	25	13	7
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Table S22. Energies values and percentual group contributions of selected β MO's of complex $[\text{Ru}^{\text{III}}(\text{bpy})-\text{Ru}^{\text{V}}(\text{bda})(\text{O})]^{3+}$.

MO's (β)	Energy (eV)	Ru _{bda}	bda	DMSO	CN	Ru _{tpy}	tpy	bpy	O
L+10	-2.71	49	10	10	7	2	1	1	22
L+9	-2.8	1	99	0	0	0	0	0	0
L+8	-2.92	1	96	0	0	0	2	0	1
L+7	-3.07	0	2	0	0	3	76	19	0
L+6	-3.18	0	0	0	0	3	20	77	0
L+5	-3.4	5	84	0	0	0	4	0	6
L+4	-3.45	0	3	0	0	3	92	1	0
L+3	-3.78	56	25	6	6	1	0	0	6
L+2	-4.3	54	26	0	0	0	0	0	20
L+1	-4.81	28	11	4	1	1	0	0	55
LUMO	-5.32	0	0	0	3	74	14	8	1
HOMO	-7.65	7	3	83	3	3	1	0	1
H-1	-7.75	1	1	2	1	25	63	6	0
H-2	-7.85	2	71	1	0	1	2	0	23
H-3	-7.9	1	3	3	0	2	4	87	0
H-4	-7.91	5	14	60	1	4	5	11	0
H-5	-7.95	7	10	30	3	21	22	6	0
H-6	-8.01	2	3	2	5	51	31	6	1
H-7	-8.1	2	78	4	0	8	6	1	0
H-8	-8.15	14	64	0	1	12	7	1	0
H-9	-8.27	1	98	0	0	0	0	0	1
H-10	-8.67	4	91	1	1	0	1	0	2

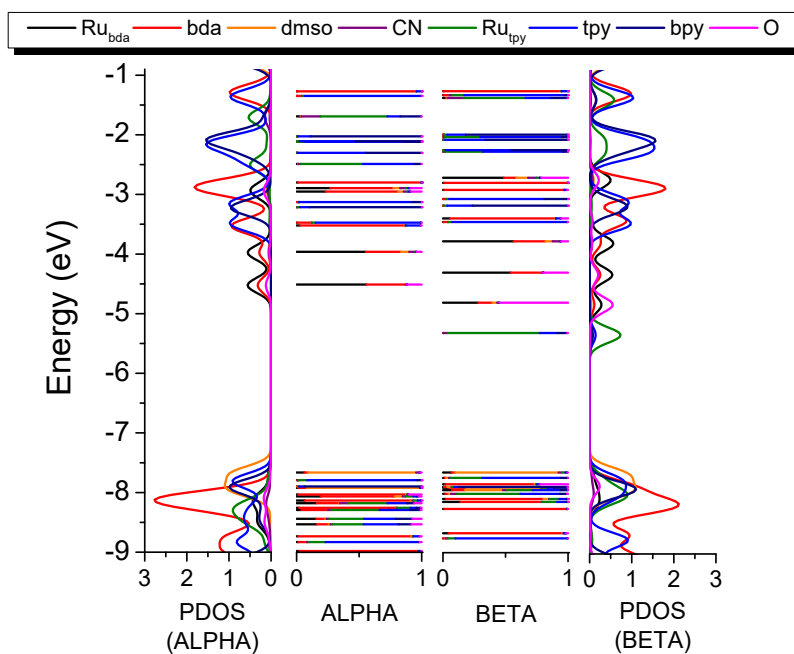


Figure S43. Molecular orbital diagram and partial density of states (PDOS) of complex $[Ru^{III}(bpy)-Ru^V(bda)(O)]^{3+}$.

Table S23. (TD)DFT assignments for calculated UV-Vis transitions of the complex $[Ru^{III}(bpy)CNRu^V(bda)(O)]^{3+}$.

No.	Wavelength (nm)	Osc. Strength	Major contributions	Assignment
7	680.3	0.005	H-3(B)->LUMO(B) (78%), H-4(B)->LUMO(B) (13%)	$\pi(bpy) \rightarrow d(Ru_{tpy})$
9	634.8	0.008	HOMO(B)->LUMO(B) (67%), HOMO(B)->L+1(B) (26%)	$\pi(DMSO) \rightarrow d(Ru_{tpy})$
15	560.0	0.004	H-4(B)->LUMO(B) (53%), H-8(B)->LUMO(B) (17%), H-7(B)->LUMO(B) (17%)	$\pi(DMSO) \rightarrow d(Ru_{tpy})$
24	490.2	0.004	H-7(A)->L+1(A) (24%), H-10(A)->L+1(A) (16%), H-11(A)->L+1(A) (14%), HOMO(A)->L+1(A) (10%)	$d(Ru_{tpy}) \rightarrow d(Ru_{bda})$
51	403.2	0.024	HOMO(B)->L+3(B) (27%), HOMO(A)->L+1(A) (20%)	$\pi(DMSO) \rightarrow d(Ru_{bda})$
54	397.8	0.024	H-3(A)->L+1(A) (19%), HOMO(B)->L+3(B) (15%), H-20(B)->L+1(B) (11%)	$\pi(DMSO) \rightarrow d(Ru_{bda})$
66	380.8	0.014	H-18(B)->LUMO(B) (68%)	$\pi(bpy) \rightarrow d(Ru_{tpy})$

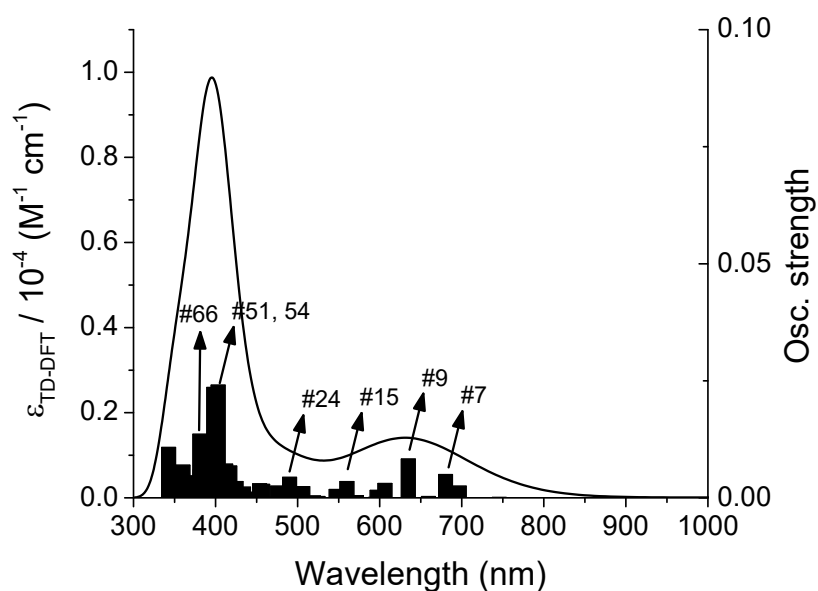


Figure S44. (TD)DFT-calculated UV-visible absorption spectra of complex $[\text{Ru}^{\text{III}}(\text{bpy})\text{-Ru}^{\text{V}}(\text{bda})(\text{O})]^{3+}$. Calculated transitions are represented by black vertical bars.

Table S24. Energies values and percentual group contributions of selected α MO's of complex $[\text{Ru}^{\text{III}}(\text{MeO-bpy})\text{-Ru}^{\text{V}}(\text{bda})(\text{O})]^{3+}$.

MO's (α)	Energy (eV)	Ru _{bda}	bda	DMSO	CN	Ru _{tpy}	tpy	MeO-bpy	O
L+10	-2.23	0	0	0	0	1	62	37	0
L+9	-2.4	1	0	0	2	51	40	6	0
L+8	-2.79	1	99	0	0	0	0	0	0
L+7	-2.87	37	34	7	6	2	1	1	13
L+6	-2.94	13	70	2	1	0	1	7	5
L+5	-2.95	1	5	0	0	1	1	90	1
L+4	-3.09	0	1	0	0	1	97	1	0
L+3	-3.42	0	3	0	0	3	93	1	0
L+2	-3.5	3	92	1	0	0	3	0	1
L+1	-3.94	55	28	7	5	1	0	0	4
LUMO	-4.5	56	32	0	0	0	0	0	12
HOMO	-7.59	1	0	0	2	23	16	57	0
H-1	-7.65	6	3	86	3	0	0	0	2
H-2	-7.79	0	0	0	0	8	61	31	0
H-3	-7.82	0	0	0	0	6	24	69	0
H-4	-7.91	1	6	92	0	0	0	1	0
H-5	-7.96	1	1	1	0	2	3	92	0
H-6	-8.02	2	85	1	0	1	0	1	10
H-7	-8.05	19	54	4	3	9	4	4	3
H-8	-8.11	5	73	2	2	11	6	1	1

H-9	-8.15	16	34	0	5	21	13	6	4
H-10	-8.24	1	89	0	0	5	4	0	0

Table S25. Energies values and percentual group contributions of selected β MO's of complex $[\text{Ru}^{\text{III}}(\text{MeO-bpy})-\text{Ru}^{\text{V}}(\text{bda})(\text{O})]^{3+}$.

MO's (β)	Energy (eV)	Ru _{bda}	bda	DMSO	CN	Ru _{tpy}	tpy	MeO-bpy	O
L+10	-2.69	50	9	10	7	2	0	0	22
L+9	-2.79	1	99	0	0	0	0	0	0
L+8	-2.89	0	2	0	0	3	5	90	0
L+7	-2.91	1	95	0	0	0	1	3	1
L+6	-3.06	0	1	0	0	2	94	3	0
L+5	-3.38	5	72	0	0	1	17	0	5
L+4	-3.41	1	16	0	0	3	78	1	1
L+3	-3.76	57	25	6	6	1	0	0	6
L+2	-4.29	54	25	0	0	0	0	0	21
L+1	-4.79	28	11	4	1	1	0	0	55
LUMO	-5.19	0	0	0	2	73	12	12	1
HOMO	-7.43	1	0	1	3	38	13	43	0
H-1	-7.64	7	3	83	3	3	1	0	1
H-2	-7.8	0	0	0	0	0	75	24	0
H-3	-7.84	2	70	1	0	2	1	2	22
H-4	-7.88	5	14	10	3	16	12	39	1
H-5	-7.9	1	3	37	1	9	10	37	0
H-6	-7.92	1	3	49	3	27	11	6	0
H-7	-8.02	4	8	1	1	6	7	73	0
H-8	-8.08	9	64	4	1	5	4	14	0
H-9	-8.12	11	79	1	1	2	2	4	0
H-10	-8.26	1	98	0	0	0	0	0	1

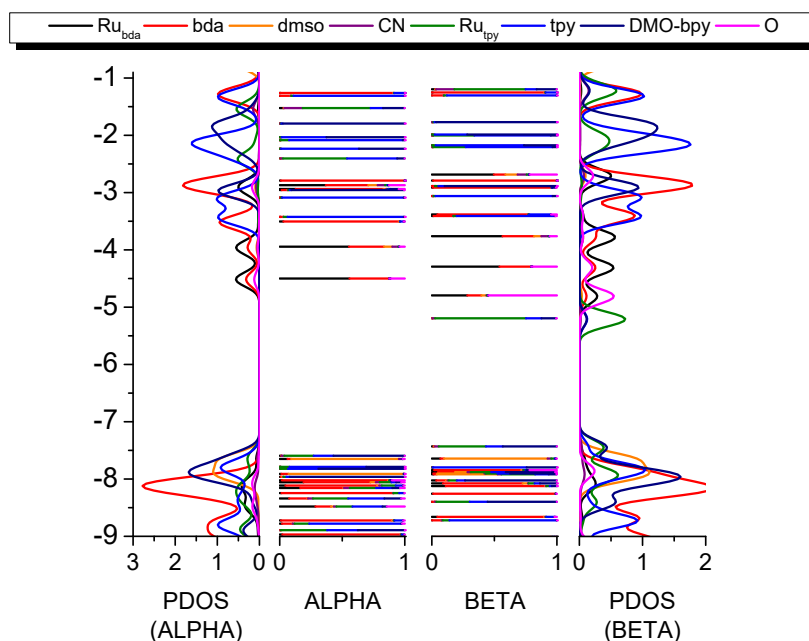


Figure S45. Molecular orbital diagram and partial density of states (PDOS) of complex $[Ru^{III}(MeO-bpy)-Ru^V(bda)(O)]^{3+}$.

Table S26. (TD)DFT assignments for calculated UV-Vis transitions of the complex $[Ru^{III}(MeO-bpy)-Ru^V(bda)(O)]^{3+}$.

No.	Wavelength (nm)	Osc. Strength	Major contributions	Assignment
9	619.5	0.013	H-1(B)->L+1(B) (74%), H-1(B)->LUMO(B) (14%)	$\pi(DMSO) \rightarrow d(Ru_{bda}=O)$
10	601.5	0.018	H-7(B)->LUMO(B) (58%)	$\pi(MeO-bpy) \rightarrow d(Ru_{tpy})$
18	534.8	0.070	H-11(B)->LUMO(B) (63%)	$\pi(MeO-bpy) \rightarrow d(Ru_{tpy})$
53	403.2	0.027	H-1(B)->L+3(B) (30%), H-1(A)->L+1(A) (21%)	$\pi(DMSO) \rightarrow d(Ru_{bda})$
58	397.3	0.024	H-1(B)->L+3(B) (15%), H-22(B)->L+1(B) (14%), H-20(B)->L+1(B) (12%)	$\pi(bda) \rightarrow d(Ru_{bda}=O)$ $\pi(DMSO) \rightarrow d(Ru_{bda}=O)$
135	322.0	0.058	H-3(A)->L+3(A) (28%)	$\pi(MeO-bpy) \rightarrow \pi^*(tpy)$
149	314.9	0.051	HOMO(A)->L+4(A) (13%), H-15(A)->LUMO(A) (12%), HOMO(B)->L+8(B) (11%)	$d(Ru_{tpy}) \rightarrow \pi^*(tpy)$

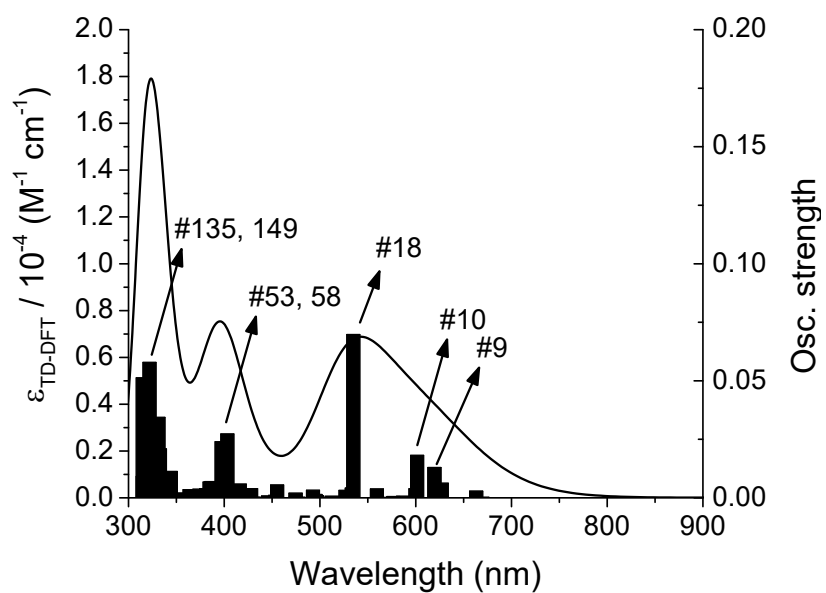


Figure S46. (TD)DFT-calculated UV-visible absorption spectra of complex $[\text{Ru}^{\text{III}}(\text{MeO-bpy})\text{-Ru}^{\text{V}}(\text{bda})(\text{O})]^{3+}$. Calculated transitions are represented by black vertical bars.