

Supporting Information

Experimental and computational exploration of ground and excited state properties of highly strained ruthenium terpyridine complexes

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Functional Choice

Choosing the best functional for TD-DFT calculations is difficult as there are a myriad of different choices available, each of which has been designed to address specific shortcomings of other functionals or has been designed to use empirical parameters that have been fit to experimental data such that the functional is tailored to a specific class of molecules. As of yet there has not been a clear consensus on which functionals work best for coordination complexes nor more specifically ruthenium polypyridyl complexes. As this project explores geometry and electronic absorption effects, efforts were focused on finding a functional that could reproduce ground state Ru-N bond lengths, as they are important in calculating TD-DFT energies^{1,2}, and correct electronic absorption peaks. The functionals that we chose to explore represent a mixture of local functionals which include no HF exchange (BLYP, PBE, M06-L, and M11-L), popular hybrid functionals which include varying amounts of HF exchange (B3LYP, PBE0, M06), and long range corrected functionals which modify the amount of HF exchange as a function of distance (ω -B97X, LC- ω PBE0, M11).

It is noted that the comparison between gas-phase DFT geometries and crystal structures is not entirely appropriate as the calculations do not account for crystal packing effects. These deviations are on the order of 0.01-0.02 Å for metal-ligand bond distances, but are still smaller than known overestimations made by DFT calculations.³

The optimized geometries for **1** were calculated using the functionals mentioned above with a constant basis set (6-31g(d)) and Ru core pseudopotentials (SDD). The Ru-N1 and Ru-N2 values were compared to the respective experimental bond lengths as determined from a published crystal structure⁴ (data are listed in Table S1). Overall there is no clear pattern to the results according to the different types of functionals. The functionals with Ru-N1 and Ru-N2 errors greater ($>1\%$), included local (BLYP, PBE, M06-L), hybrid (B3LYP), and range corrected (ω B97X, M11). The worst of these functionals was PBE with Ru-N1 and Ru-N2 errors of 3.73% and 5.03% respectively. The hybrid PBE0 had the smallest error of only 0.35% and 0.92%. Addition of dispersion correction with PBE0-D brought this down to 0.05% and 0.19% error, while addition of range correction (LC- ω PBE0) and use of a triple zeta basis set (PBE0-TZ) slightly worsened the error. These results match results which found Ru-N dative bond lengths difficult to reproduce accurately, especially with B3LYP, and inclusion of dispersion or long-range corrections did not drastically improve the results.^{3,5}

Next, MLCT absorption peaks from the simulated absorption spectra (generated using the optimized geometries and the lowest 50 singlet states, as determined using TD-DFT) were compared to the experimental MLCT absorption peaks for **1**. Note that this differs from the technique of only using the lowest non-zero oscillator strength transition as determined by TD-DFT for experimental comparison. The prominent MLCT band and UV band are identified and compared to the experimental solution absorption peaks in Table S1. Most functionals overestimate the UV band and some drastically overestimate the MLCT band. The popular hybrid functionals PBE0, B3LYP, and M06 have errors of 0.58, 0.42, and 0.36 eV respectively for the MLCT band. We found this surprising, as the hybrid functionals – particularly B3LYP – are known to underestimate charge transfer states.⁶ As one might expect from this set of observations, the range corrected functionals show MLCT energies that are even further blue shifted thus resulting in a rather significant overestimation of the MLCT band by more than 1 eV. We point out that overestimation of the MLCT appears throughout the literature for ruthenium polypyridyl complexes and inclusion of solvent through a polarizable continuum model does not significantly improve results.⁷⁻⁹ Interestingly, the electronic absorption spectra of other d^6 metal

complexes, including other ruthenium (II) complexes, have been well reproduced by various hybrid functionals with significantly smaller errors on the order of 0.1 – 0.2 eV.¹⁰⁻¹² In our calculations the local functionals (those that lack any HF exchange), better reproduce the MLCT energy within 0.05-0.16 eV error, but then underestimate the UV band by 0.1-0.5 eV.

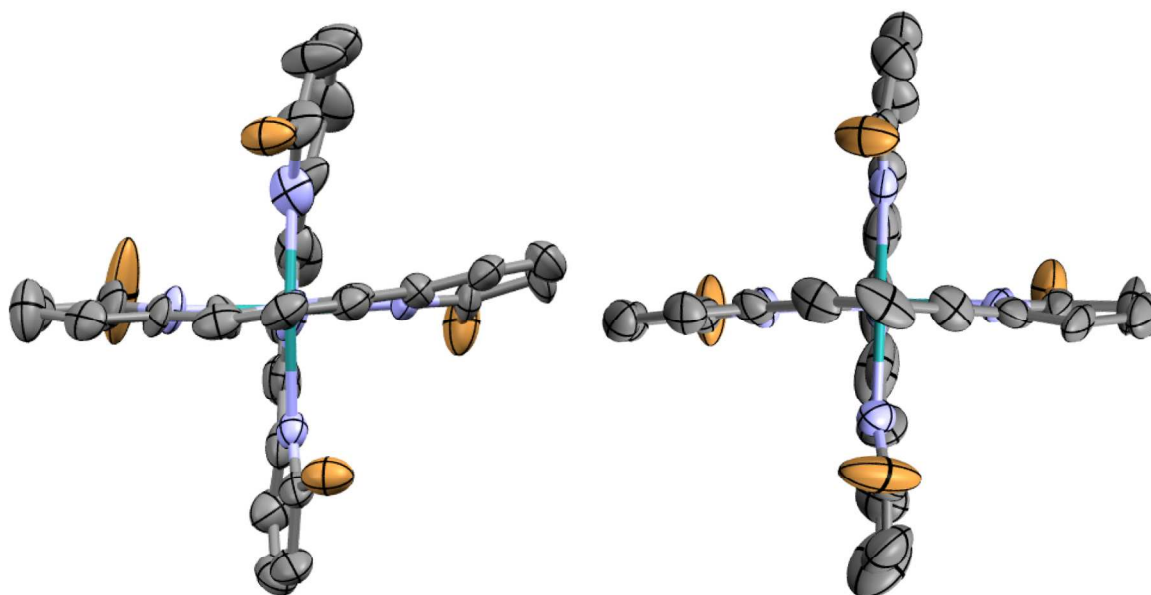
Given that there is no clear functional which accurately reproduces both the geometry and the electronic absorption spectrum, we looked for a compromise. In these studies, the effects of strain on geometry are of central importance. The functional PBE0 captures geometrical properties well, while showing modest overestimation of the MLCT band.

Table S1. Metal-Ligand Bond Distances for Optimized Geometries of 1 with Simulated Electronic Absorption Peaks Using TD-DFT and Experimental Values.

functional	bond length / Å		peaks / eV (extinction coefficient / 10 ⁴ M ⁻¹ cm ⁻¹)	
	Ru-N1 ^a	Ru-N2 ^a	MLCT	UV peak
local				
BLYP	2.019	2.117	2.57 (1.4)	3.66 (4.4)
PBE	2.059	2.171	2.46 (1.4)	3.54 (4.2)
M06-L	2.005	2.110	2.73 (1.6)	3.94 (5.0)
M11-L ^b	1.970	2.063	--	--
hybrid				
B3LYP	2.011	2.113	3.04 (1.9)	4.28 (7.6)
PBE0	1.992	2.086	3.20 (2.2)	4.46 (9.8)
M06	2.003	2.095	2.98 (1.9)	4.30 (8.5)
range-corrected				
ωB97X	2.023	2.128	3.68 (1.0)	4.82 (5.6)
LC-ωPBE0	1.995	2.088	3.70 (1.6)	4.96 (9.5)
M11 ^b	2.023	2.120	--	--
other				
PBE0-D	1.986	2.071	3.20 (1.8)	4.46 (8.4)
PBE0-TZ ^d	1.992	2.087	3.17 (1.8)	4.43 (8.3)
exp.	1.985^c	2.067^c	2.62 (1.6)	4.03 (6.4)

^aN1 and N2 refer to the nitrogens in the central and terminal pyridyl rings respectively in the terpyridine ligand. See Scheme 1 in the main text. ^bTD-DFT code for M11-L and M11 has not yet been implemented in Q-Chem 4.0 as of the time of this writing. ^cReference ⁴. ^dWith triple zeta basis set 6-311g(d).

Comparison of Conformers 3A and 3B



Conformer 3A

Conformer 3B

Figure S1. Crystal structure comparison of **3A** (left) and **3B** (right) showing 40% probability ellipsoids. Counterions and hydrogen atoms have been removed. The relative orientations of the conformers has been adjusted for side-by-side comparison.

Table S2: Selected Average Distances and Angles for Experimental Crystal Conformers of 3.^a

parameter	[Ru(6,6''-Br ₂ -tpy) ₂] ²⁺ (3)	
	crystal 3A	crystal 3B
bond length / Å		
Ru-N1	1.976 (0.007)	1.965 (0.014)
Ru-N2	2.157 (0.050)	2.135 (0.033)
Br-N1'	3.076 (0.062)	3.070 (0.022)
Br-C2'	3.317 (0.124)	3.311 (0.188)
angle / °		
N1-Ru-N2	80.64 (10.10)	79.41 (3.43)
C4-C3-C5	89.03 (0.36)	88.75 (0.99)
dihedral / °		
N1-C2-C1-N2	8.64 (10.42)	5.79 (3.50)
C2-N1-N1'-C2'	74.58 (4.69)	88.76 (1.46)
C2-N1-Ru-N2'	82.67 (5.13)	89.74 (0.31)

^aAtom numbering corresponds to those given in Scheme 1 with the prime marks indicating the same atom position on the opposing ligand. Uncertainties are given in parentheses as $\pm 2\sigma$ by determining the standard deviation of all similar measurements within the crystal structure. ^bReference ⁴.

Full TD-DFT Results for complexes 1-7

Table S3. Lowest 50 Transitions Calculated for Complexes 1-7 with Gas Phase TD-DFT, PBE0 Functional, SDD Pseudopotential and Basis Set for Ru, 6-31g(d) Basis Set for All Other Atoms.

(1) [Ru(tpy) ₂] ²⁺			(2) [Ru(6,6□-Br ₂ -tpy)(tpy)] ²⁺			(3) [Ru(6,6□-Br ₂ -tpy) ₂] ²⁺		
E (eV)	λ (nm)	f	E (eV)	λ (nm)	f	E (eV)	λ (nm)	f
2.715	456.8	0.0124	2.680	462.7	0.0100	2.664	465.4	0.0007
2.715	456.8	0.0124	2.768	448.0	0.0002	2.861	433.5	0.0035
2.777	446.5	0.0000	2.916	425.3	0.0144	2.877	431.0	0.0121
2.856	434.1	0.0000	2.919	424.8	0.0046	2.886	429.7	0.0186
3.013	411.6	0.0275	2.943	421.4	0.0079	2.943	421.3	0.0000
3.044	407.4	0.0000	3.038	408.1	0.0230	3.013	411.6	0.0092
3.203	387.1	0.1849	3.051	406.5	0.0438	3.087	401.7	0.0431
3.204	387.0	0.0114	3.123	397.0	0.0019	3.137	395.3	0.0075
3.204	387.0	0.0113	3.159	392.5	0.0826	3.187	389.1	0.0000
3.218	385.3	0.0261	3.269	379.3	0.0096	3.235	383.3	0.0241
3.218	385.3	0.0261	3.309	374.7	0.0008	3.303	375.4	0.0251
3.603	344.1	0.0000	3.373	367.7	0.0014	3.330	372.3	0.0356
3.604	344.1	0.0000	3.423	362.2	0.0234	3.421	362.5	0.0035
4.044	306.7	0.0009	3.560	348.3	0.0012	3.421	362.5	0.0002
4.044	306.7	0.0009	3.618	342.8	0.0161	3.572	347.2	0.0000
4.083	303.7	0.0097	3.878	319.8	0.1268	3.821	324.5	0.0288
4.083	303.7	0.0097	4.032	307.5	0.0138	3.821	324.5	0.1479
4.131	300.2	0.0556	4.075	304.3	0.0797	3.906	317.4	0.0941
4.175	297.0	0.0000	4.114	301.4	0.0166	3.962	313.0	0.0016
4.175	297.0	0.0000	4.116	301.3	0.0068	4.021	308.4	0.0843
4.237	292.7	0.0000	4.184	296.4	0.0226	4.079	304.0	0.0520
4.237	292.6	0.0000	4.190	296.0	0.0012	4.104	302.1	0.0498
4.281	289.7	0.0000	4.209	294.6	0.0100	4.173	297.2	0.0000
4.286	289.3	0.0117	4.211	294.5	0.0014	4.213	294.3	0.0000
4.289	289.1	0.0114	4.228	293.3	0.0001	4.238	292.6	0.0018
4.289	289.1	0.0113	4.239	292.5	0.0110	4.252	291.6	0.0001
4.368	283.9	0.0006	4.265	290.8	0.3453	4.292	288.9	0.0337
4.368	283.9	0.0006	4.324	286.8	0.0000	4.317	287.3	0.0001
4.453	278.5	0.5210	4.339	285.8	0.0037	4.333	286.2	0.0000
4.453	278.5	0.5212	4.414	280.9	0.0457	4.369	283.8	0.0000
4.530	273.7	0.0000	4.445	279.0	0.0089	4.371	283.7	0.0068
4.535	273.4	0.0006	4.480	276.8	0.0000	4.393	282.3	0.0009
4.630	267.8	0.0474	4.494	275.9	0.0808	4.404	281.6	0.2455
4.630	267.8	0.0474	4.541	273.1	0.3628	4.417	280.7	0.2429
4.682	264.8	0.0000	4.583	270.6	0.0267	4.418	280.6	0.0015
4.817	257.4	0.1626	4.644	267.0	0.0048	4.439	279.4	0.0000

4.845	255.9	0.0000	4.661	266.0	0.0173	4.441	279.2	0.0329
4.870	254.6	0.0000	4.684	264.8	0.0020	4.483	276.6	0.0000
4.981	249.0	0.0145	4.689	264.5	0.0655	4.538	273.2	0.0630
4.981	249.0	0.0145	4.737	261.8	0.0001	4.564	271.7	0.0000
5.082	244.0	0.0000	4.771	259.9	0.1133	4.593	270.0	0.0273
5.090	243.6	0.0000	4.849	255.7	0.0336	4.653	266.5	0.0015
5.091	243.6	0.0000	4.919	252.1	0.0054	4.710	263.3	0.1593
5.114	242.5	0.0000	4.925	251.8	0.0248	4.735	261.9	0.1001
5.134	241.5	0.0156	4.967	249.7	0.0160	4.769	260.0	0.0007
5.223	237.4	0.0000	5.000	248.0	0.0000	4.799	258.4	0.0858
5.299	234.0	0.1821	5.018	247.1	0.0001	4.799	258.4	0.0000
5.299	234.0	0.1821	5.056	245.3	0.0652	4.842	256.1	0.0364
5.326	232.8	0.0000	5.083	244.0	0.0021	4.901	253.0	0.0000
5.349	231.8	0.0531	5.121	242.1	0.0272	4.921	252.0	0.0001
(4) [Ru(5,5□-Br₂-tpy)(tpy)]²⁺			(5) [Ru(5,5□-Br₂-tpy)₂]²⁺			(6) [Ru(4,4□-Br₂-tpy)(tpy)]²⁺		
E (eV)	λ (nm)	f	E (eV)	λ (nm)	f	E (eV)	λ (nm)	f
2.700	459.2	0.0095	2.755	450.1	0.0082	2.646	468.7	0.0276
2.771	447.6	0.0118	2.755	450.1	0.0082	2.705	458.5	0.0122
2.781	445.9	0.0000	2.802	442.6	0.0000	2.761	449.1	0.0000
2.873	431.6	0.0000	2.876	431.1	0.0000	2.854	434.4	0.0000
3.000	413.4	0.0171	3.030	409.2	0.0239	2.960	418.9	0.0085
3.087	401.7	0.0130	3.085	401.9	0.0000	3.037	408.3	0.0120
3.189	388.8	0.0450	3.237	383.1	0.1080	3.151	393.6	0.0518
3.203	387.1	0.0001	3.246	382.0	0.0160	3.155	393.1	0.2021
3.216	385.6	0.1370	3.246	382.0	0.0160	3.161	392.3	0.0002
3.254	381.1	0.0003	3.255	381.0	0.0246	3.230	383.9	0.0009
3.275	378.6	0.0343	3.255	381.0	0.0245	3.246	382.0	0.0357
3.576	346.8	0.0000	3.550	349.3	0.0000	3.561	348.3	0.0021
3.600	344.4	0.0028	3.597	344.7	0.0000	3.561	348.2	0.0000
3.859	321.3	0.1383	3.842	322.8	0.1235	3.995	310.4	0.0028
3.960	313.1	0.0012	3.842	322.8	0.1235	4.022	308.3	0.0000
3.991	310.7	0.0036	3.906	317.5	0.0619	4.026	308.0	0.0006
4.021	308.4	0.0001	3.906	317.5	0.0619	4.067	304.9	0.0594
4.088	303.3	0.0523	3.971	312.3	0.0070	4.075	304.3	0.0102
4.104	302.1	0.0179	3.971	312.3	0.0070	4.139	299.6	0.0000
4.107	302.0	0.0228	4.058	305.6	0.0481	4.143	299.3	0.0072
4.119	301.1	0.0113	4.099	302.5	0.0012	4.162	298.0	0.0000
4.134	300.0	0.0000	4.099	302.5	0.0012	4.195	295.6	0.0048
4.150	298.8	0.0015	4.134	300.0	0.0000	4.215	294.2	0.0031
4.184	296.3	0.2474	4.148	298.9	0.0023	4.259	291.2	0.0000
4.213	294.3	0.0000	4.175	297.0	0.0000	4.315	287.4	0.0037
4.231	293.1	0.1985	4.175	297.0	0.0000	4.335	286.1	0.0750
4.277	289.9	0.0000	4.202	295.1	0.0044	4.366	284.0	0.0022

4.320	287.1	0.0000	4.204	294.9	0.0000	4.368	283.9	0.6942
4.339	285.8	0.0029	4.232	293.0	0.4057	4.390	282.4	0.1595
4.341	285.7	0.0011	4.232	293.0	0.4057	4.435	279.6	0.0019
4.347	285.3	0.0011	4.235	292.8	0.0000	4.439	279.4	0.3199
4.377	283.3	0.0006	4.236	292.7	0.0000	4.499	275.6	0.0103
4.461	278.0	0.4477	4.306	288.0	0.0009	4.562	271.8	0.0003
4.466	277.7	0.0008	4.306	288.0	0.0009	4.587	270.3	0.0000
4.507	275.2	0.2194	4.333	286.2	0.0014	4.587	270.3	0.0199
4.508	275.1	0.2656	4.337	285.9	0.0000	4.639	267.3	0.0013
4.572	271.2	0.1117	4.461	278.0	0.0944	4.642	267.1	0.0105
4.578	270.9	0.1244	4.461	278.0	0.0944	4.649	266.7	0.0007
4.625	268.1	0.0345	4.462	277.9	0.0000	4.686	264.6	0.1490
4.712	263.2	0.1177	4.539	273.2	0.1004	4.705	263.6	0.0757
4.808	257.9	0.0000	4.539	273.2	0.1005	4.713	263.1	0.0000
4.824	257.0	0.0002	4.557	272.1	0.5902	4.716	263.0	0.0001
4.825	257.0	0.0000	4.564	271.7	0.2291	4.716	262.9	0.0179
4.844	256.0	0.0427	4.564	271.7	0.2289	4.798	258.4	0.0000
4.905	252.8	0.0081	4.701	263.8	0.0000	4.819	257.3	0.0918
4.963	249.9	0.0141	4.783	259.3	0.0000	4.819	257.3	0.0042
5.016	247.2	0.0000	4.788	259.0	0.0000	4.855	255.4	0.0403
5.025	246.8	0.0000	4.800	258.4	0.0000	4.887	253.7	0.0441
5.039	246.1	0.0147	4.800	258.4	0.0000	4.940	251.0	0.0005
5.063	244.9	0.0000	4.805	258.1	0.0000	4.972	249.4	0.0137

(7) [Ru(4,4'-Br₂-tpy)₂]²⁺

E (eV)	λ (nm)	f
2.637	470.2	0.0274
2.637	470.2	0.0274
2.767	448.1	0.0000
2.844	436.0	0.0000
2.957	419.3	0.0056
2.980	416.1	0.0000
3.119	397.6	0.2320
3.178	390.2	0.0238
3.178	390.2	0.0238
3.198	387.8	0.0267
3.198	387.8	0.0267
3.519	352.4	0.0000
3.528	351.5	0.0000
3.987	311.0	0.0027
3.988	311.0	0.0027
4.002	309.8	0.0663
4.017	308.7	0.0001
4.017	308.7	0.0001

4.134	300.0	0.0035
4.134	300.0	0.0035
4.188	296.1	0.0000
4.188	296.1	0.0000
4.232	293.0	0.0000
4.234	292.8	0.0056
4.316	287.3	0.0269
4.316	287.3	0.0266
4.320	287.0	0.0947
4.320	287.0	0.0958
4.356	284.7	0.6277
4.356	284.7	0.6285
4.439	279.4	0.0029
4.439	279.3	0.0028
4.449	278.7	0.0000
4.466	277.6	0.0251
4.498	275.7	0.0000
4.501	275.5	0.0000
4.541	273.1	0.0000
4.550	272.5	0.0009
4.568	271.5	0.0008
4.568	271.4	0.0008
4.582	270.6	0.0000
4.634	267.6	0.0000
4.650	266.7	0.0010
4.654	266.5	0.1332
4.654	266.5	0.1333
4.685	264.7	0.0000
4.685	264.7	0.0000
4.732	262.1	0.0364
4.732	262.1	0.0364
4.751	261.0	0.0000

NTO Analysis for Complexes 4-7

Table S4. NTO Analysis for Selected TD-DFT Transitions for Complexes 4-7.

E (eV)	λ (nm)	f	Character (NTO)		
(4) [Ru(5,5'-Br ₂ -tpy _a)(tpy _b)] ²⁺					
3.21	386	0.137	Ru d _{xy,yz}	→ tpy _a π^*	(89.5%)
3.86	321	0.138	tpy _a π , Br p _x	→ tpy _a π^*	(70.0%)
			Ru d _{xy}	→ tpy _a π^*	(25.2%)
4.18	297	0.247	tpy _b π	→ tpy _a π^*	(50.9 %)
			tpy _a π	→ tpy _a π^*	(34.9 %)
			Ru d _{xy}	→ tpy _a π^*	(12.5 %)
4.23	293	0.198	tpy _b π	→ tpy _a π^*	(71.1 %)
			Ru d _{xy}	→ tpy _a π^*	(21.8 %)
4.46	278	0.448	Ru d _{xy}	→ tpy _b π^*	(42.5 %)
			tpy _b π	→ tpy _b π^*	(37.2 %)
			Ru d _{yz}	→ Ru _{x2-y2}	(10.4 %)
(5) [Ru(5,5'-Br ₂ -tpy) ₂] ²⁺					
3.24	383	0.108	Ru d _{xy,yz,xz}	→ tpy π^*	(98.3 %)
3.84	323	0.124	tpy π , Br p _x	→ tpy π^*	(83.0 %)
			Ru d _{xy}	→ tpy π^*	(10.0 %)
3.91	317	0.062	tpy π , Br p _x	→ tpy π^*	(82.3 %)
			Ru d _{xy}	→ tpy π^*	(11.4 %)
4.06	305	0.048	Ru d _{xy} , tpy π	→ tpy π^*	(90.6 %)
4.23	293	0.406	Ru d _{xy, yz}	→ tpy π^*	(74.6 %)
			tpy π , Br p _x	→ tpy π^*	(17.2 %)
4.56	272	0.590	Br p _x , tpy π	→ tpy π^*	(78.1 %)
			Ru d _{xy, yz}	→ tpy π^*	(18.4 %)
(6) [Ru(4,4'-Br ₂ -tpy _a)(tpy _b)] ²⁺					
3.21	386	0.137	Ru d _{xy,yz}	→ tpy _a π^*	(89.5%)
3.86	321	0.138	tpy _a π , Br p _x	→ tpy _a π^*	(70.0%)
			Ru d _{xy}	→ tpy _a π^*	(25.2%)
4.18	297	0.247	tpy _b π	→ tpy _a π^*	(50.9 %)
			tpy _a π	→ tpy _a π^*	(34.9 %)
			Ru d _{xy}	→ tpy _a π^*	(12.5 %)
4.23	293	0.198	tpy _b π	→ tpy _a π^*	(71.1 %)
			Ru d _{xy}	→ tpy _a π^*	(21.8 %)
4.46	278	0.448	Ru d _{xy}	→ tpy _b π^*	(42.5 %)
			tpy _b π	→ tpy _b π^*	(37.2 %)
			Ru d _{yz}	→ Ru _{x2-y2}	(10.4 %)

(7) $[\text{Ru}(\text{4,4'-Br}_2\text{-tpy})_2]^{2+}$

3.24	383	0.108	Ru $d_{xy,yz,xz}$	$\rightarrow$ tpy π^*	(98.3 %)
3.84	323	0.124	tpy π , Br p_x	$\rightarrow$ tpy π^*	(83.0 %)
			Ru d_{xy}	$\rightarrow$ tpy π^*	(10.0 %)
3.91	317	0.062	tpy π , Br p_x	$\rightarrow$ tpy π^*	(82.3 %)
			Ru d_{xy}	$\rightarrow$ tpy π^*	(11.4 %)
4.06	305	0.048	Ru d_{xy} , tpy π	$\rightarrow$ tpy π^*	(90.6 %)
4.23	293	0.406	Ru $d_{xy,yz}$	$\rightarrow$ tpy π^*	(74.6 %)
			tpy π , Br p_x	$\rightarrow$ tpy π^*	(17.2 %)
4.56	272	0.590	Br p_x , tpy π	$\rightarrow$ tpy π^*	(78.1 %)
			Ru $d_{xy,yz}$	$\rightarrow$ tpy π^*	(18.4 %)

Experimental and Simulated Absorption Spectra for 4-7

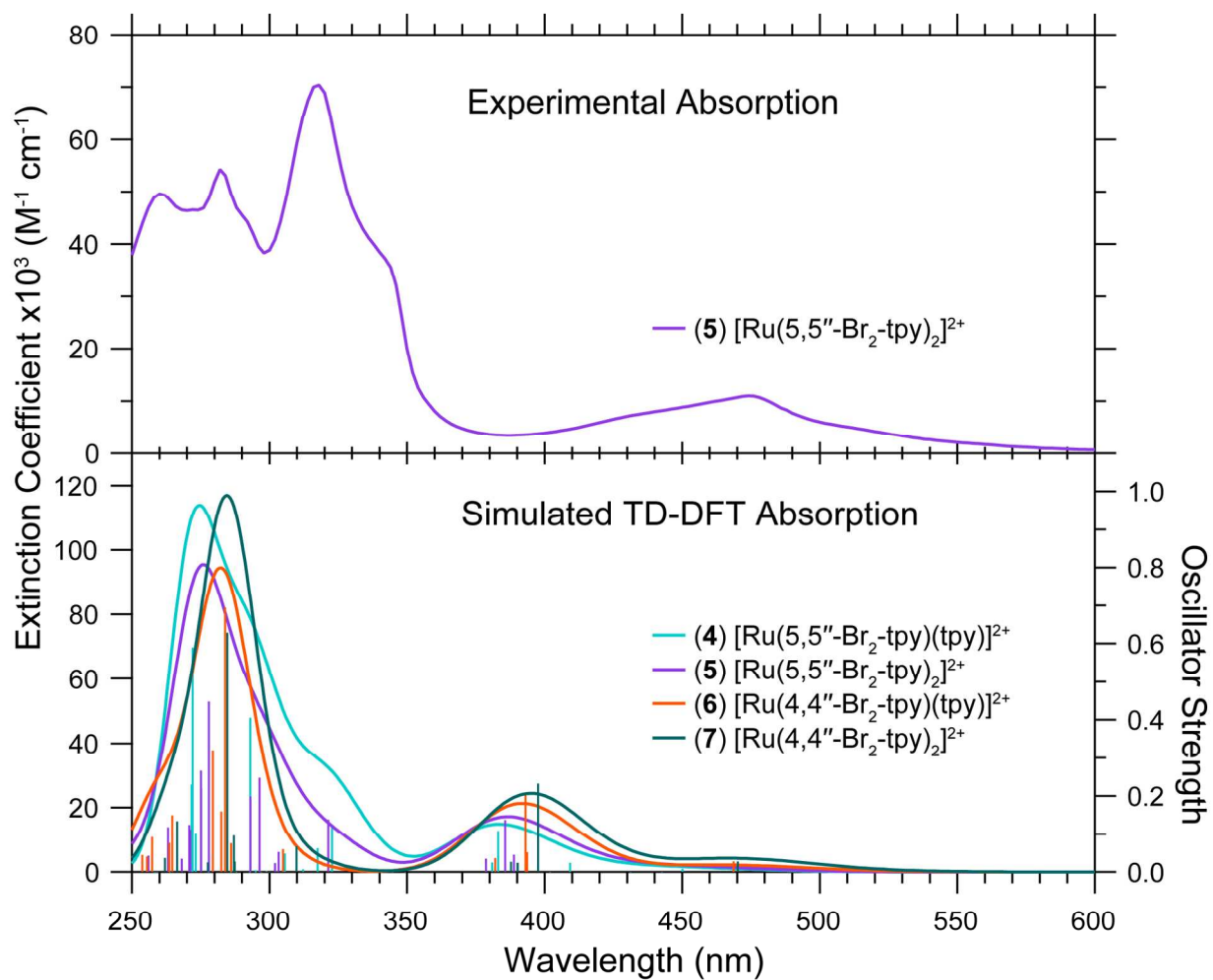


Figure S2. Experimental absorption spectrum for complex **5** (top), along with the simulated absorption spectra from calculated TD-DFT transitions for complexes **4-7** (bottom).

Kohn-Sham Orbital Analysis of **2** and **4**

Kohn-Sham Orbitals

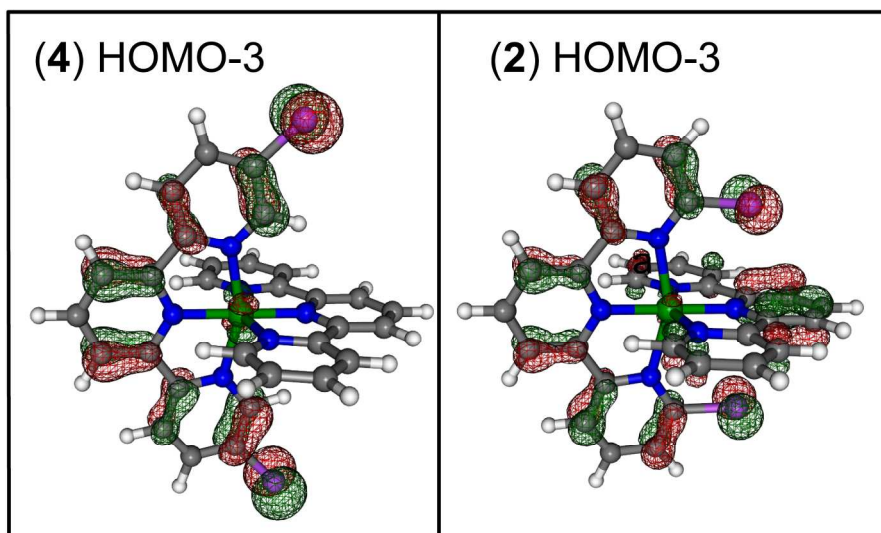


Figure S3. Calculated HOMO-3 Kohn-Sham molecular orbitals at 0.04 isovalue for **2** (right) and **4** (left). Location of the Br in **2** allows the p_x orbitals to overlap and interact with the tpy π orbitals, an effect not observed in **4**.

The observation in **2** (with evidence also in **3**) of interligand CT character in the attachment-detachment densities (main text) led to an examination of occupied Kohn-Sham orbitals of **2** as compared to **4**. The highest occupied ligand orbital is HOMO-3, as HOMO through HOMO-2 are occupied ruthenium d orbitals. As observed in Figure S3, the HOMO-3 Kohn-Sham orbital for **4** is localized on the brominated terpyridine while for **2** the orbital extends onto the central pyridyl ring of the non-brominated terpyridine ligand via out-of-phase overlap with lobes of the bromine p_x orbital that are spatially located directly above. This indicates that there may be enhanced ground state electronic coupling between the π -systems of the terpyridine ligands. The mechanism of interaction can be thought of as being similar to spiroconjugation – a situation that occurs in twisted aromatic systems where an occupied π -system weakly interacts with the unoccupied π^* system of a directly connected but spatially orthogonal system.^{13,14} While a weak effect, spiroconjugation has been employed successfully to modify the

photophysics of various organic and mixed organic/inorganic systems.¹⁵⁻¹⁷ In our case the effect would differ as the interaction is mediated not via a pathway of bonding contact between the two ligand moieties but rather via the proximal halogen atoms and the strength of the effect would depend strongly on halogen-tpy distances.

Details of C-DFT Calculations in Generating Figure 9

Table S5. Calculation Details for Generation of Figure S4 (Figure 9 in Main Text).

point	geom.	state	energy / eV ^a	Ru spin ^b	calc. type ^c	notes
(1) [Ru(tpy)₂]²⁺						
A	¹ GS	¹ GS	0.000	0.000	GO	
B	¹ GS	³ MLCT	2.379	0.959	SP	ΔSCF triplet calculation; no constraint
C	¹ GS	³ MC	2.908	1.786	C-SP	constraint: Ru spin = 1.786
D	³ MLCT	¹ GS	0.518	0.000	SP	singlet calculation
E	³ MLCT	³ MLCT	2.183	0.945	GO	ΔSCF triplet calculation; no constraint
F	³ MLCT	³ MC	2.613	1.786	C-SP	constraint: Ru spin = 1.786
G	³ MC	¹ GS	1.234	0.000	SP	singlet calculation
H	³ MC	³ MLCT	2.506	0.945	C-SP	constraint: Ru spin = 0.945
I	³ MC	³ MC	2.024	1.786	C-GO, GO	constraint: Ru spin = 2, followed by ΔSCF with no constraint
(2) [Ru(6,6''-Br₂-tpy)(tpy)]²⁺						
A	¹ GS	¹ GS	0.000	0.000	GO	
B	¹ GS	³ MLCT	2.492	1.106	SP	ΔSCF triplet calculation; no constraint; excess spin resides on Br ₂ -tpy ligand.
C	¹ GS	³ MC	2.641	1.896	C-SP	constraint: Ru spin = 1.896
D	³ MLCT	¹ GS	0.436	0.000	SP	singlet calculation
E	³ MLCT	³ MLCT	2.102	0.945	GO	ΔSCF triplet calculation; no constraint; excess spin resides on Br ₂ -tpy ligand
F	³ MLCT	³ MC	2.711	1.896	C-SP	constraint: Ru spin = 1.896
G	³ MC	¹ GS	0.845	0.000	SP	singlet calculation
H	³ MC	³ MLCT	2.307	0.945	C-SP	constraint: Ru spin = 0.945, excess spin resides on Br ₂ -tpy ligand.
I	³ MC	³ MC	1.802	1.896	C-GO, GO	constraint: Ru spin = 2, followed by ΔSCF with no constraint
(3) [Ru(6,6''-Br₂-tpy)₂]²⁺						
A	¹ GS	¹ GS	0.000	0.000	GO	
B	¹ GS	³ MLCT	2.384	0.945	C-SP	constraint: Ru spin = 0.945
C	¹ GS	³ MC	1.985	1.775	SP	ΔSCF triplet calculation; no constraint
D	³ MLCT	¹ GS	0.674	0.000	SP	singlet calculation
E	³ MLCT	³ MLCT	1.952	0.945	C-GO	constraint: Ru spin = 0.945 based on results from point E in 1 and 2 ; subsequent ΔSCF calculation with no constraint only found the ³ MC state; freq. analysis for the ³ MLCT returned zero imaginary frequencies.
F	³ MLCT	³ MC	1.703	1.871	C-SP	constraint: Ru spin = 1.871
G	³ MC	¹ GS	0.764	0.000	SP	singlet calculation
H	³ MC	³ MLCT	2.091	0.945	C-SP	constraint: Ru spin = 0.945
I	³ MC	³ MC	1.401	1.871	GO	ΔSCF triplet calculation, no constraint

^aRelative to GS. ^bSpin is reported as Mulliken spin density. ^cGO = geometry optimization, SP = single point energy calculation, C-GO or C-SP = calculation performed with a Ru spin constraint using C-DFT.

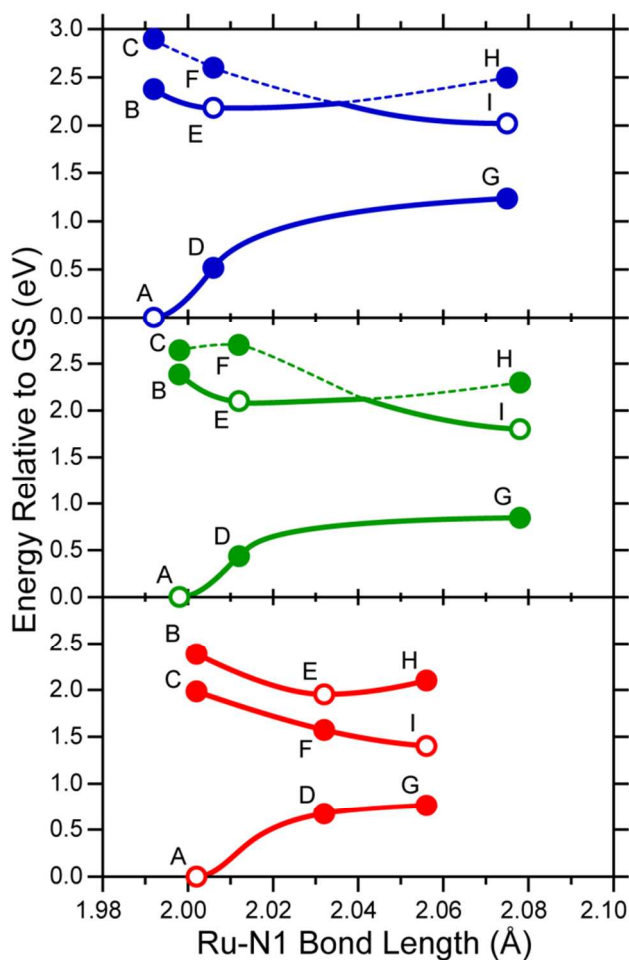


Figure S4. Reproduced version of Figure 9 (main text) with calculated points labeled corresponding to details presented in Table S5.

To generate Figure 9 in the main text (reproduced here as Figure S4) we first calculated optimized structures for the three states of interest: ^1GS , $^3\text{MLCT}$, and ^3MC (points A, E, and I respectively in Figure S4) for each of the complexes **1-3**. A straightforward DFT geometry optimization calculation was used to determine the singlet ground state geometry, and a ΔSCF triplet optimization was used to determine the geometry of one of the two triplets (the one that is found depends on the initial geometry in the calculation as well as the initial SCF guess). The nature of the triplet state found is clear by both the geometry of the complex as well as the spin density in the vicinity of the Ru atom, which differs

significantly for the $^3\text{MLCT}$ versus the ^3MC . The spin density values at the Ru center are not found to be integers (1 for the $^3\text{MLCT}$ and 2 for the ^3MC) because formal partitioning of spin at the boundary of the atom does not adequately capture consequences of delocalization. For example the Ru spin density for **1** in the ^3MC state as determined by ΔSCF calculation is not 2.0 but rather 1.79 with ~ 0.21 residing on the coordinating nitrogen atoms. In order to calculate the geometry of the second triplet, a combination of C-DFT and ΔSCF was used. First, C-DFT with the appropriate spin constraint at the metal center is used to find a geometry and SCF that is close to the correct values for the triplet of interest. Then, the constraint is lifted and a ΔSCF calculation is used to find the optimized geometry.

With optimized geometries for each state in hand, we are able to determine the energy of the other two electronic states at each of those fixed geometries, a procedure in which C-DFT is particularly useful. As an illustration of the process, consider the several points in the energy landscape of **1** that we have explored. At the optimized geometry of the ^1GS (point A) we can calculate the energy of the $^3\text{MLCT}$ (point B) by performing a single-point triplet calculation. The nature of this triplet state is confirmed by examining the spin on the Ru center. In this case it is 0.959 so we confirm that it is the $^3\text{MLCT}$ state. For the ^3MC energy at the ^1GS geometry (point C), we turn to C-DFT and constrain the spin density at the Ru center to a value that is the same as that found in the ΔSCF calculation of the geometry-optimized ^3MC state (in this case 1.79 from point I). Turning to the optimized geometry of the $^3\text{MLCT}$ (point E) it is straightforward to calculate the energy of the ^1GS as there are no other singlets of comparable energy (point D). For the energy of the ^3MC at this geometry (point F), C-DFT is again used to constrain the Ru spin density to 1.79. Finally, at the geometry of the ^3MC (point I), it is again straightforward to calculate the energy of the ^1GS (point G). For the $^3\text{MLCT}$ at this geometry (point H), C-DFT is used to constrain the Ru spin density to a value commensurate with the ΔSCF calculation of that state (in this case 0.945 from point E).

Solving kinetic equations for excited state dynamics of **3**

Restated below in Eq. S1 is the proposed excited state dynamics of **3**, along with the expression for the recovery of the ground state, assuming that the contact ion pair (CIP) and metal-to-ligand-charge-transfer (³MLCT) equilibration occurs much faster than the subsequent step ($k_3+k_4 \gg k_1$).



$$[CIP]_{eq} = k_3 \tau_{eq} [MLCT]_0 \quad (S2)$$

$$\tau_{eq} = (k_3 + k_4)^{-1} \quad (S3)$$

$$\Delta Abs_{465\text{ nm}}(t) \propto - \left\{ \frac{(k_3 + k_4)k_2 [{}^3MLCT]_0}{(k_3 + k_4)k_2 - k_4k_1} \right\} e^{-\frac{k_4k_1}{k_3+k_4}t} - \left\{ \frac{-k_4k_1 [{}^3MLCT]_0}{(k_3 + k_4)k_2 - k_4k_1} + [{}^3MC]_0 \right\} e^{-k_2t} \quad (S4)$$

If we assume that the single wavelength kinetics measured at 375 nm solely arises from the reduced ligand absorption, then those measurements can be taken as a direct measurement of [MLCT]. If the early time component of **3** is attributed to the equilibration time (2.3 ps = τ_{eq}) then the normalized pre-exponential factor of the short-time component measured at 375 nm (0.09) is a measurement of the amount of initial excited ³MLCT population converted to the CIP ($0.09 = [CIP]_{eq}/([{}^3MLCT]_{eq} + [CIP]_{eq})$; $[{}^3MLCT]_{eq} + [CIP]_{eq} = [{}^3MLCT]_0$). Assuming the ³MLCT initial excited state population is normalized ($[{}^3MLCT]_0 = 1$) then using Eq. S2 we can solve for $k_3 = 0.039 \text{ ps}^{-1}$. Again knowing that $\tau_{eq} = 2.3 \text{ ps}$, we can use Eq. S3 to solve for $k_4 = 0.396 \text{ ps}^{-1}$. With k_3 and k_4 we can calculate the equilibrium constant for the formation of the CIP ($K_{eq} = k_3/k_4 = 0.099$).

Examining the relationship for ground state recovery in Eq. S4, k_2 can be readily determined from the measured time constants of the bleach. We assign the shorter time component (21.0 ps, 0.048 ps^{-1}) to k_2 as it is similar to the time constants determined for the same ${}^3MC \rightarrow {}^1GS$ step in complexes **1** and **2** (18 ps

and 16 ps, respectively). Using Eq. S4 the second, longer time constant observed (216 ps, 0.0046 ps⁻¹) is then assigned to $k_4k_1/(k_3+k_4)$. With k_3 and k_4 already determined, we can solve for $k_1 = 0.0051 \text{ ps}^{-1}$ (197 ps). Under the assumption that the signal measured at 465 nm in **3** arises solely from the ground state bleach, Eq. S4 becomes exact and the measured pre-exponential factors along with the rate constants can be used to determine initial excited state partitioning between ³MLCT and ³MC as 71% and 29% respectively.

Coherent Oscillations in Short Time Transient Absorption

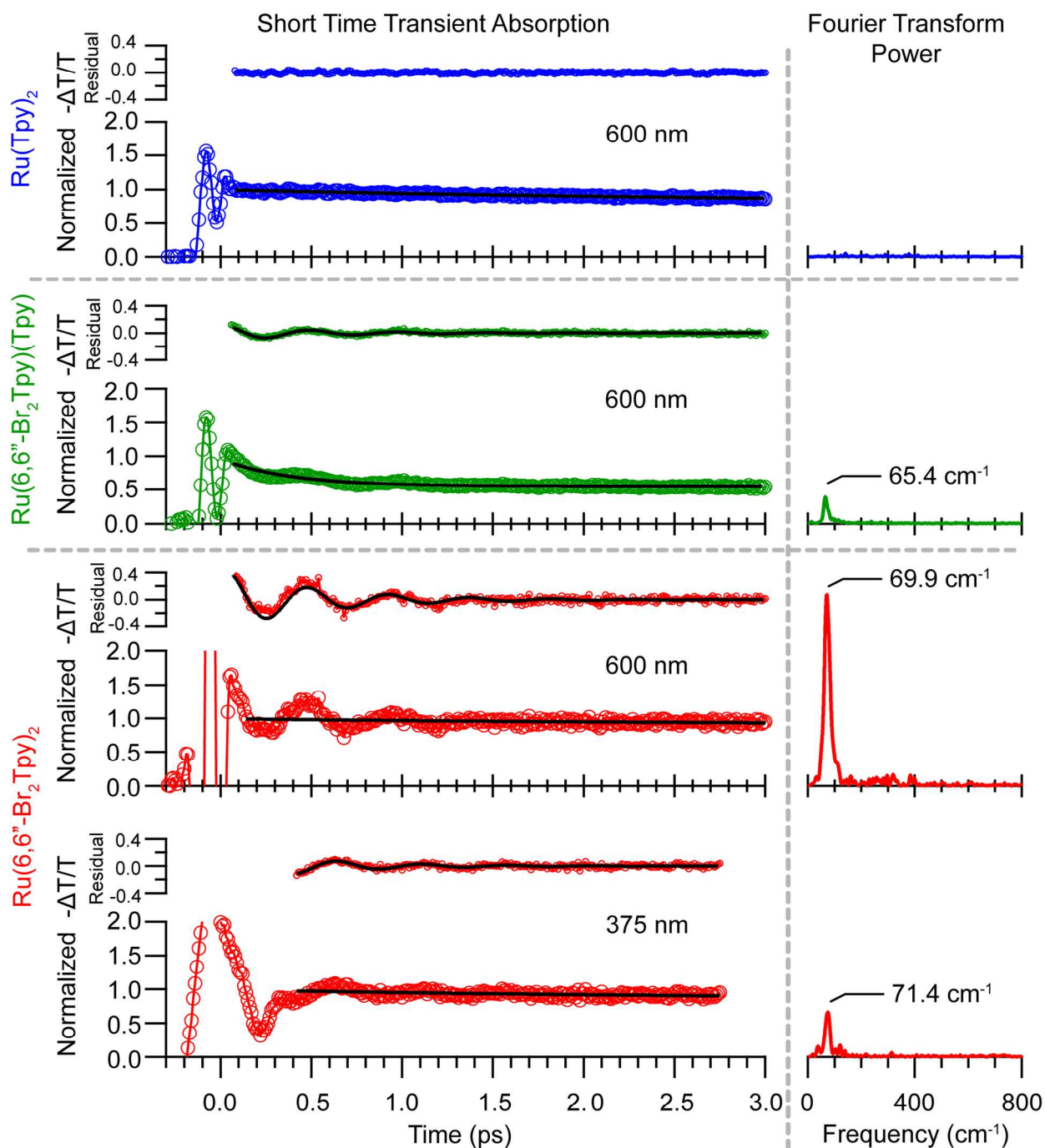


Figure S5. Early time transient absorption dynamics for **1-3** indicating no coherent oscillations in **1** (data shown at 600 nm (top)) but a presence of ~ 70 cm⁻¹ oscillations at 600 nm for **2** and **3** (middle), and also at 375 nm for **3** alone (bottom). TA traces are first fit to a single-exponential decay function. The residuals of that model are then fit to an exponentially decaying sinusoidal function. The Fourier transform power spectra of each residual is presented on the right hand side.

DFT Normal Modes for Triplet States in 2 and 3

Table S6. Selected Calculated Vibrational Frequencies for 2 and 3 at both ³MLCT and ³MC Optimized Geometries that Involve Significant Br Movement.

2 / cm⁻¹ (IR Intensity)		3 / cm⁻¹ (IR intensity)	
³MLCT	³MC	³MLCT	³MC
10.79 (0.054)	16.02 (1.164)	6.93 (2.637)	7.96 (0.291)
11.33 (1.836)	16.33 (1.212)	20.37 (5.001)	16.52 (2.138)
84.12 (0.553)	25.12 (0.009)	24.40 (1.696)	19.45 (0.625)
105.73 (0.755)	45.72 (0.297)	25.05 (1.399)	22.23 (1.512)
121.27 (1.899)	56.23 (0.218)	31.08 (0.546)	24.48 (0.359)
	83.26 (2.002)	47.37 (4.416)	69.02 (0.109)
	87.75 (0.067)	65.68 (0.814)	85.96 (0.516)
		65.93 (0.707)	94.54 (2.217)
		94.15 (0.130)	110.52 (0.986)
		102.29 (0.011)	
		117.18 (2.136)	
		128.85 (0.094)	

DFT Calculated Gas Phase Geometries

Table S7. DFT gas-phase geometries for ¹GS, ³MLCT, and ³MC states for complexes 1-3

(1) [Ru(tpy)₂]²⁺									
Atom	Ground State Coordinate (Å)			³MLCT State Coordinate (Å)			³MC State Coordinate (Å)		
	X	Y	Z	X	Y	Z	X	Y	Z
C	2.64248	-0.83628	0.83624	2.59298	-1.31582	-0.01776	2.70072	-1.16784	0.25732
C	4.03568	-0.85363	0.85364	3.96925	-1.34677	0.09217	4.08868	-1.19553	0.39005
C	4.72953	0.00000	0.00000	4.70826	-0.16513	-0.07998	4.79061	0.00017	0.44953
C	4.03568	0.85363	-0.85364	4.04965	1.05812	-0.28215	4.08877	1.19582	0.38837
C	2.64248	0.83628	-0.83624	2.67303	1.08563	-0.39340	2.70080	1.16805	0.25568
N	1.99171	0.00000	0.00000	1.96730	-0.11624	-0.35499	2.02363	0.00008	0.18194
H	4.57809	-1.51742	1.51754	4.48163	-2.27097	0.33848	4.61324	-2.14013	0.47483
H	4.57809	1.51742	-1.51754	4.62445	1.97762	-0.32233	4.61339	2.14051	0.47180
H	-0.86567	-3.65042	3.64978	-1.06005	-5.05377	0.83498	-0.50100	-5.39056	0.36816
C	-0.10546	-3.10310	3.10258	-0.27178	-4.32957	0.66179	0.19719	-4.56179	0.31526
C	1.24908	-3.32422	3.32359	1.07184	-4.71248	0.59255	1.55443	-4.76883	0.08832
C	-0.48265	-2.15800	2.15774	-0.58500	-2.99259	0.49962	-0.25284	-3.25646	0.47238
C	2.17619	-2.59186	2.59143	2.03953	-3.75008	0.36606	2.40835	-3.67254	0.04771
H	1.58175	-4.05492	4.05407	1.35494	-5.75395	0.70892	1.94600	-5.77125	-0.05503
N	0.40309	-1.44727	1.44716	0.34470	-2.04967	0.28106	0.56244	-2.19985	0.42632
H	-1.52832	-1.95352	1.95346	-1.61135	-2.64260	0.54385	-1.30471	-3.04336	0.64630
C	1.73591	-1.65789	1.65773	1.66696	-2.40869	0.21344	1.87985	-2.39446	0.23436
H	3.23795	-2.74822	2.74774	3.08515	-4.02950	0.29420	3.46663	-3.81817	-0.13889
C	1.24908	3.32422	-3.32359	1.38714	4.59692	-0.87506	1.55475	4.76887	0.08167
C	2.17619	2.59186	-2.59143	2.28487	3.54925	-0.77985	2.40860	3.67248	0.04260
C	-0.10546	3.10310	-3.10258	0.02145	4.34385	-0.71412	0.19749	4.56224	0.30886
H	1.58175	4.05492	-4.05407	1.74183	5.60245	-1.07887	1.94639	5.77107	-0.06305
C	1.73591	1.65789	-1.65773	1.82153	2.25351	-0.52023	1.88001	2.39469	0.23100
H	3.23795	2.74822	-2.74774	3.34655	3.72492	-0.91685	3.46689	3.81778	-0.14417
C	-0.48265	2.15800	-2.15774	-0.38388	3.04542	-0.46338	-0.25262	3.25715	0.46777
H	-0.86567	3.65042	-3.64978	-0.71494	5.13671	-0.78442	-0.50065	5.39112	0.36060
N	0.40309	1.44727	-1.44716	0.47745	2.01962	-0.36641	0.56259	2.20043	0.42319
H	-1.52832	1.95352	-1.95346	-1.43335	2.80166	-0.33180	-1.30452	3.04436	0.64196
H	1.52832	1.95352	1.95346	1.72079	0.38158	2.56031	0.93851	0.00215	2.96196
C	0.48265	2.15800	2.15774	0.70615	0.46569	2.93592	-0.13829	0.00226	3.09269
C	0.10546	3.10310	3.10258	0.44366	0.68983	4.28061	-0.71809	0.00319	4.35416
N	-0.40309	1.44727	1.44716	-0.27445	0.34127	2.03084	-0.85937	0.00146	1.96571
C	-1.24908	3.32422	3.32359	-0.87879	0.78778	4.69812	-2.10635	0.00329	4.45253

H	0.86567	3.65042	3.64978	1.26831	0.78433	4.97890	-0.08876	0.00381	5.23781
C	-1.73591	1.65789	1.65773	-1.57422	0.43333	2.42445	-2.21855	0.00155	2.05214
C	-2.17619	2.59186	2.59143	-1.89575	0.65741	3.75868	-2.86341	0.00246	3.28771
H	-1.58175	4.05492	4.05407	-1.11922	0.96328	5.74202	-2.59445	0.00400	5.42208
C	-2.64248	0.83628	0.83624	-2.56089	0.27922	1.34354	-2.92157	0.00063	0.76241
H	-3.23795	2.74822	2.74774	-2.93330	0.73025	4.06592	-3.94653	0.00253	3.34268
C	-4.03568	0.85363	0.85364	-3.94688	0.32464	1.47307	-4.30438	0.00051	0.57205
N	-1.99171	0.00000	0.00000	-2.00137	0.07557	0.13405	-2.09603	-0.00016	-0.30744
C	-4.72953	0.00000	0.00000	-4.73012	0.15759	0.33451	-4.80444	-0.00043	-0.72304
H	-4.57809	1.51742	1.51754	-4.41421	0.48576	2.43811	-4.98213	0.00113	1.41823
C	-2.64248	-0.83628	-0.83624	-2.73965	-0.08785	-0.97953	-2.56297	-0.00109	-1.57771
C	-4.03568	-0.85363	-0.85364	-4.13088	-0.05081	-0.90387	-3.93190	-0.00124	-1.81223
H	-5.81487	0.00000	0.00000	-5.81231	0.18941	0.41321	-5.87685	-0.00054	-0.89048
C	-1.73591	-1.65789	-1.65773	-1.93373	-0.29660	-2.19439	-1.50404	-0.00186	-2.61206
H	-4.57809	-1.51742	-1.51754	-4.74241	-0.18204	-1.78952	-4.32660	-0.00198	-2.82176
C	-2.17619	-2.59186	-2.59143	-2.46833	-0.48438	-3.46463	-1.76731	-0.00284	-3.97672
N	-0.40309	-1.44727	-1.44716	-0.59034	-0.29480	-1.99693	-0.22174	-0.00157	-2.14750
C	-1.24908	-3.32422	-3.32359	-1.61229	-0.67241	-4.54512	-0.70776	-0.00353	-4.88037
H	-3.23795	-2.74822	-2.74774	-3.54245	-0.48481	-3.61445	-2.78842	-0.00307	-4.34128
C	0.48265	-2.15800	-2.15774	0.23255	-0.47667	-3.03498	0.79126	-0.00223	-3.02196
C	0.10546	-3.10310	-3.10258	-0.23968	-0.66908	-4.32759	0.59467	-0.00322	-4.39726
H	-1.58175	-4.05492	-4.05407	-2.01605	-0.81951	-5.54201	-0.90315	-0.00429	-5.94834
H	1.52832	-1.95352	-1.95346	1.29258	-0.46483	-2.80404	1.78688	-0.00195	-2.59151
H	0.86567	-3.65042	-3.64978	0.46364	-0.81276	-5.14093	1.44826	-0.00373	-5.06658
Ru	0.00000	0.00000	0.00000	0.05604	0.00634	0.01633	-0.12429	0.00002	-0.02876
H	5.81487	0.00000	0.00000	5.78919	-0.18797	0.00328	5.86991	0.00021	0.56532

(2) [Ru(6,6□-Br₂-tpy)(tpy)]²⁺

Atom	Ground State Coordinate (Å)			³ MLCT State Coordinate (Å)			³ MC State Coordinate (Å)		
	X	Y	Z	X	Y	Z	X	Y	Z
C	0.07074	2.25017	-1.17738	1.18293	-3.06016	-0.00086	1.17981	-3.04648	-0.17435
C	0.07232	3.64208	-1.20443	1.18120	-4.41835	-0.26043	1.20469	-4.39944	-0.51104
C	-0.00606	4.33469	0.00127	-0.03338	-5.10647	-0.37058	0.00855	-5.07863	-0.69435
C	-0.08250	3.64087	1.20638	-1.23850	-4.40231	-0.27212	-1.18960	-4.40330	-0.50991
C	-0.07699	2.24898	1.17818	-1.22574	-3.04377	-0.00987	-1.16862	-3.05021	-0.17349
N	-0.00218	1.60371	0.00014	-0.01726	-2.39036	0.18941	0.00457	-2.38130	-0.05026
H	0.12967	4.18558	-2.14086	2.11318	-4.95002	-0.41605	2.14850	-4.90961	-0.66218
H	-0.14139	4.18342	2.14327	-2.17566	-4.92233	-0.43592	-2.13199	-4.91636	-0.66013
H	0.21411	-1.24880	-5.16268	5.37289	0.12770	0.15464	5.60918	-0.20897	0.54720
C	0.19212	-0.49050	-4.38724	4.54317	-0.56827	0.14386	4.73012	-0.83172	0.42763
C	0.23574	0.86445	-4.69416	4.74041	-1.94316	0.24176	4.77808	-2.20853	0.58138

C	0.11939	-0.86906	-3.05331	3.24703	-0.09108	0.03035	3.49397	-0.26916	0.11408
C	0.20093	1.78960	-3.65699	3.63658	-2.76820	0.20186	3.61810	-2.95582	0.39495
H	0.29439	1.19980	-5.72489	5.74088	-2.35018	0.34864	5.71096	-2.69807	0.84413
C	0.08822	0.01513	-2.04806	2.35549	-2.22224	0.06893	2.43744	-2.29691	0.05906
H	0.12600	1.34759	-2.33977	3.75224	-3.84150	0.29321	3.64152	-4.03033	0.53461
C	0.23081	2.85146	-3.87505	-4.76867	-1.87862	0.21868	-4.76862	-2.22369	0.58600
C	-0.23791	0.85990	4.69383	-3.67739	-2.71937	0.17086	-3.60614	-2.96712	0.39966
C	-0.20578	1.78600	3.65742	-4.54934	-0.50462	0.15751	-4.72600	-0.84711	0.42850
H	-0.19047	-0.49467	4.38579	-5.77615	-2.27258	0.30692	-5.69928	-2.71599	0.85144
C	-0.29746	1.19424	5.72483	-2.38653	-2.19086	0.06063	-2.42850	-2.30459	0.06035
H	-0.12966	1.34528	2.33982	-3.81009	-3.79240	0.23874	-3.62515	-4.04138	0.54196
C	-0.23865	2.84758	3.87635	-3.24552	-0.04515	0.06524	-3.49245	-0.28074	0.11162
H	-0.11676	-0.87193	3.05155	-5.36790	0.20394	0.18221	-5.60724	-0.22734	0.54756
H	-0.21026	-1.25366	5.16060	-0.04122	-1.88661	-2.72770	0.00601	-1.66595	-2.79028
C	-0.08815	0.01317	2.04702	-0.03878	-0.84293	-3.02464	0.00406	-0.61721	-3.06840
C	3.22918	-0.06020	0.09081	-0.05259	-0.46636	-4.36041	0.00422	-0.22312	-4.39830
N	4.53825	-0.53357	0.01752	-0.02117	0.05763	-2.03273	0.00142	0.26195	-2.05787
C	2.13351	-0.82994	0.05034	-0.04819	0.88819	-4.67385	0.00153	1.13660	-4.69236
H	4.74706	-1.89505	-0.09456	-0.06624	-1.22833	-5.13224	0.00637	-0.97252	-5.18247
C	5.36294	0.16831	0.05189	-0.01538	1.38697	-2.32238	-0.00130	1.59130	-2.33331
C	2.36059	-2.18442	-0.03082	-0.02914	1.82149	-3.64291	-0.00128	2.05165	-3.64654
H	3.63743	-2.72661	-0.10992	-0.05898	1.21775	-5.70807	0.00157	1.48180	-5.72140
C	5.75187	-2.30033	-0.15973	0.00692	2.27676	-1.15220	-0.00428	2.45450	-1.14849
H	1.17774	-3.05329	-0.02281	-0.02495	2.88222	-3.86782	-0.00345	3.11600	-3.85322
C	3.77033	-3.79842	-0.18676	0.02257	3.66773	-1.17253	-0.00785	3.84591	-1.15232
N	1.20570	-4.44756	-0.02258	0.01354	1.62113	0.02062	-0.00355	1.77407	0.01830
C	0.00289	-2.39289	-0.00116	0.04600	4.35217	0.04015	-0.01072	4.52727	0.06021
H	0.00599	-5.14696	-0.00351	0.01727	4.21586	-2.10796	-0.00847	4.39623	-2.08638
C	2.14241	-4.99131	-0.03316	0.03369	2.25801	1.20091	-0.00609	2.42041	1.20399
C	-1.17046	-3.05598	0.01978	0.05217	3.64975	1.24153	-0.00984	3.81120	1.25181
H	-1.19530	-4.45029	0.01704	0.05935	5.43771	0.04817	-0.01363	5.61240	0.07579
C	0.00721	-6.23222	-0.00463	0.03195	1.34955	2.35731	-0.00474	1.51816	2.35768
H	-2.35527	-2.18979	0.03003	0.07089	4.18237	2.18559	-0.01214	4.33127	2.20298
C	-2.13080	-4.99614	0.02650	0.04424	1.76711	3.68338	-0.00621	1.92886	3.68705
N	-3.63073	-2.73478	0.11203	0.01516	0.02729	2.04624	-0.00176	0.19811	2.03318
C	-2.13135	-0.83479	-0.05123	0.03982	0.81831	4.70059	-0.00465	0.97714	4.69897
H	-4.74218	-1.90558	0.09993	0.05670	2.82418	3.92511	-0.00851	2.98500	3.93302
C	-3.76109	-3.80688	0.18909	0.01167	-0.88650	3.02397	-0.00032	-0.71840	3.01317
C	-3.22877	-0.06744	-0.08923	0.02377	-0.53056	4.36655	-0.00169	-0.37114	4.35593
H	-4.53661	-0.54362	-0.01238	0.04880	1.13264	5.73965	-0.00572	1.28526	5.73975
H	-5.74593	-2.31302	0.16794	-0.00172	-1.92249	2.70264	0.00204	-1.75611	2.69706
H	-5.36289	0.15651	-0.04423	0.02013	-1.30379	5.12739	-0.00038	-1.14862	5.11235
Ru	0.00050	-0.38840	-0.00068	-0.00514	-0.43387	-0.02028	0.00082	-0.24493	-0.01020

Br	-0.00760	5.42025	0.00172	-3.09876	1.86375	-0.02780	-3.42425	1.62837	-0.11536
H	-3.10388	1.82943	-0.28641	-0.03966	-6.16950	-0.58438	0.01012	-6.12501	-0.98425
Br	3.09994	1.83643	0.28725	3.13113	1.81580	-0.12710	3.41800	1.64040	-0.10661
N	0.08359	-1.91469	-2.76594	-2.15262	-0.82590	0.02439	-2.37649	-0.96170	-0.05880
N	-0.07803	-1.91723	2.76332	2.14244	-0.85566	0.00539	2.38042	-0.95393	-0.05669
(3) [Ru(6,6□-Br₂-tpy)₂]²⁺									
Atom	Ground State Coordinate (Å)			³MLCT State Coordinate (Å)			³MC State Coordinate (Å)		
	X	Y	Z	X	Y	Z	X	Y	Z
C	-2.65507	-0.70281	0.93871	1.60884	-1.12949	2.23238	2.56838	-0.98003	1.04779
C	-4.04800	-0.72326	0.96193	2.64456	-1.19194	3.16097	3.73481	-0.94805	1.81158
C	-4.74539	0.00075	0.00170	3.65275	-0.23838	3.09761	4.14011	0.24252	2.39571
C	-4.04844	0.72453	-0.95901	3.60515	0.74674	2.11780	3.36761	1.37778	2.20242
C	-2.65550	0.70366	-0.93676	2.54873	0.75639	1.20860	2.20415	1.28914	1.44000
N	-2.00176	0.00036	0.00077	1.58110	-0.17592	1.28185	1.81064	0.12484	0.88298
H	-4.59105	-1.29624	1.70396	2.64778	-1.94626	3.93954	4.31183	-1.84943	1.97578
H	-4.59183	1.29765	-1.70069	4.38842	1.49339	2.07125	3.64358	2.31382	2.67284
H	0.57525	-3.54412	4.00296	-2.85169	-3.93955	2.42606	0.74728	-5.34234	-1.36199
C	-0.12305	-2.94481	3.43098	-1.89388	-3.43697	2.35553	1.16972	-4.47725	-0.86444
C	-1.46573	-2.88350	3.75567	-0.74461	-3.97813	2.92076	2.46303	-4.47373	-0.36490
C	0.33048	-2.22045	2.33035	-1.80537	-2.20728	1.71915	0.42428	-3.31332	-0.70993
C	-2.30451	-2.13631	2.94082	0.42852	-3.23546	2.88225	2.94213	-3.33207	0.26570
H	-1.85478	-3.42466	4.61241	-0.77626	-4.94553	3.41187	3.09417	-5.35083	-0.47041
N	-0.43741	-1.43691	1.56439	-0.66361	-1.51160	1.57328	0.85570	-2.21210	-0.11503
C	-1.78167	-1.44448	1.85611	0.43924	-2.00737	2.23546	2.11347	-2.21832	0.38710
H	-3.36556	-2.09181	3.15311	1.33345	-3.61156	3.34626	3.95940	-3.31556	0.63652
C	-1.46754	2.88384	-3.75467	3.19969	3.58341	-1.18584	0.89164	4.81912	1.29277
C	-2.30595	2.13693	-2.93919	3.34150	2.73309	-0.09772	1.78677	3.76261	1.42235
C	-0.12461	2.94479	-3.43094	2.14265	3.38027	-2.05833	-0.43939	4.54885	1.01136
H	-1.85705	3.42507	-4.61116	3.91167	4.38422	-1.36012	1.22664	5.84412	1.41979
C	-1.78252	1.44500	-1.85482	2.41371	1.71648	0.10588	1.32678	2.45954	1.25124
H	-3.36717	2.09274	-3.15071	4.17421	2.86494	0.58187	2.83067	3.96008	1.63643
C	0.32950	2.22035	-2.33061	1.25912	2.34161	-1.77962	-0.79753	3.21570	0.83547
H	0.57344	3.54390	-4.00343	1.99816	3.99834	-2.93672	-1.18016	5.33571	0.93003
N	-0.43805	1.43702	-1.56407	1.34890	1.53637	-0.72607	0.04038	2.19440	0.92237
C	-0.33129	-2.31156	-2.24023	-1.30232	2.37998	1.70175	-1.32215	-0.96661	2.73421
C	0.12236	-3.08067	-3.31001	-2.20964	3.40560	1.95094	-2.31180	-1.53527	3.53160
N	0.43678	-1.49819	-1.50617	-1.37597	1.53924	0.67521	-1.47044	-0.66105	1.44569
C	1.46522	-3.03358	-3.63625	-3.27281	3.55647	1.07524	-3.54444	-1.79425	2.95692
H	-0.57608	-3.70232	-3.85746	-2.07751	4.05387	2.80923	-2.10837	-1.75991	4.57202
C	1.78114	-1.51834	-1.79691	-2.44524	1.66915	-0.16003	-2.70555	-0.87507	0.90261
C	2.30403	-2.25409	-2.85231	-3.39574	2.67017	0.01373	-3.74492	-1.44716	1.62835

H	1.85435	-3.60959	-4.46992	-4.00355	4.34498	1.22643	-4.34089	-2.24711	3.53922
C	2.65479	-0.74068	-0.91007	-2.56005	0.67277	-1.23254	-2.88877	-0.45468	-0.49091
H	3.36518	-2.21888	-3.06579	-4.23253	2.76144	-0.66750	-4.70606	-1.63090	1.16500
C	4.04772	-0.76243	-0.93263	-3.61343	0.61818	-2.14375	-4.11409	-0.47694	-1.15758
N	2.00180	-0.00052	-0.00081	-1.57664	-0.24519	-1.27491	-1.78041	-0.00926	-1.11391
C	4.74546	-0.00124	-0.00189	-3.64225	-0.39614	-3.09368	-4.17592	-0.04810	-2.47459
H	4.59054	-1.36451	-1.65141	-4.40832	1.35353	-2.12257	-5.01386	-0.81810	-0.66086
C	2.65589	0.73928	0.90795	-1.58681	-1.22723	-2.19630	-1.82572	0.42166	-2.39099
C	4.04885	0.76031	0.92940	-2.61819	-1.33425	-3.12560	-3.02146	0.40429	-3.10257
H	5.83086	-0.00152	-0.00232	-4.45283	-0.44579	-3.81385	-5.11860	-0.06476	-3.01224
C	1.78335	1.51736	1.79549	-0.40371	-2.08684	-2.17129	-0.54318	0.87384	-2.96250
H	4.59254	1.36211	1.64776	-2.60627	-2.11131	-3.88137	-3.06537	0.72604	-4.13551
C	2.30748	2.25283	2.85047	-0.37350	-3.33312	-2.78191	-0.48429	1.46235	-4.21905
N	0.43874	1.49788	1.50584	0.69005	-1.55543	-1.52267	0.57938	0.66995	-2.20519
C	1.46973	3.03276	3.63509	0.81067	-4.05900	-2.79675	0.74566	1.83190	-4.74984
H	3.36879	2.21707	3.06307	-1.27204	-3.73618	-3.23546	-1.38855	1.64100	-4.78669
C	-0.32829	2.31169	2.24051	1.84189	-2.23835	-1.64496	1.74993	0.99503	-2.75962
C	0.12664	3.08056	3.30992	1.95019	-3.48463	-2.24510	1.89093	1.57913	-4.01623
H	1.85984	3.60858	4.46843	0.85784	-5.03985	-3.25913	0.80934	2.29645	-5.72909
H	-0.57102	3.70259	3.85791	2.91540	-3.97497	-2.29813	2.87743	1.81864	-4.39511
Ru	0.00000	-0.00004	0.00002	0.00238	-0.20505	0.00383	-0.02018	0.03312	-0.13946
Br	2.18081	2.47694	-1.92254	-0.14245	2.07383	-3.06078	-2.65132	2.84726	0.48229
H	-5.83079	0.00091	0.00208	4.46606	-0.25335	3.81626	5.03700	0.28065	3.00591
Br	2.18145	-2.47739	1.92096	-3.45260	-1.43762	1.12984	-1.36077	-3.33165	-1.42450
Br	-2.18025	2.55088	1.82492	3.47631	-1.43070	-1.07135	3.38438	0.61608	-1.84712
Br	-2.18306	-2.54960	-1.82311	0.11128	2.18835	2.98353	0.32555	-0.58020	3.62624

Table S8. DFT gas-phase ground state geometries for complexes 4-7

(4) [Ru(5,5□-Br ₂ tpy)(tpy)] ²⁺				(5) [Ru(5,5□-Br ₂ tpy) ₂] ²⁺			
Coordinate (Å)				Coordinate (Å)			
Atom	X	Y	Z	Atom	X	Y	Z
C	2.64051	-0.83623	0.83626	C	2.64398	-0.83642	0.83652
C	4.03366	-0.85375	0.85369	C	4.03737	-0.85403	0.85402
C	4.72729	-0.00004	-0.00008	C	4.73046	-0.00008	-0.00013
C	4.03365	0.85370	-0.85381	C	4.03736	0.85392	-0.85420
C	2.64050	0.83627	-0.83626	C	2.64396	0.83643	-0.83656
N	1.99030	0.00005	0.00003	N	1.99382	0.00005	0.00003
H	4.57611	-1.51757	1.51749	H	4.58040	-1.51765	1.51767
H	4.57609	1.51747	-1.51767	H	4.58036	1.51747	-1.51794
H	-0.86638	-3.65133	3.65131	C	-0.10690	-3.09565	3.09553

C	-0.10665	-3.10375	3.10373	C	1.24439	-3.32560	3.32559
C	1.24795	-3.32426	3.32415	C	-0.48871	-2.14976	2.14976
C	-0.48451	-2.15879	2.15887	C	2.16871	-2.59264	2.59277
C	2.17472	-2.59168	2.59160	H	1.56920	-4.05771	4.05763
H	1.58115	-4.05477	4.05458	N	0.40416	-1.44624	1.44636
N	0.40085	-1.44801	1.44808	H	-1.53503	-1.94951	1.94948
H	-1.53040	-1.95485	1.95501	C	1.73706	-1.65650	1.65665
C	1.73390	-1.65808	1.65810	H	3.22865	-2.75547	2.75565
H	3.23655	-2.74773	2.74759	C	1.24433	3.32556	-3.32565
C	1.24791	3.32421	-3.32423	C	2.16866	2.59259	-2.59286
C	2.17469	2.59165	-2.59166	C	-0.10696	3.09570	-3.09549
C	-0.10669	3.10374	-3.10376	H	1.56913	4.05763	-4.05775
H	1.58111	4.05468	-4.05471	C	1.73703	1.65652	-1.65667
C	1.73388	1.65811	-1.65810	H	3.22860	2.75536	-2.75582
H	3.23652	2.74767	-2.74769	C	-0.48875	2.14986	-2.14967
C	-0.48454	2.15884	-2.15884	N	0.40413	1.44632	-1.44631
H	-0.86642	3.65132	-3.65134	H	-1.53507	1.94965	-1.94932
N	0.40083	1.44806	-1.44805	H	1.53501	1.94952	1.94958
H	-1.53043	1.95492	-1.95495	C	0.48868	2.14980	2.14981
H	1.53351	1.94787	1.94797	C	0.10685	3.09558	3.09569
C	0.48748	2.14881	2.14882	N	-0.40418	1.44638	1.44630
C	0.10613	3.09451	3.09461	C	-1.24445	3.32563	3.32561
N	-0.40584	1.44535	1.44528	C	-1.73709	1.65668	1.65654
C	-1.24507	3.32526	3.32524	C	-2.16875	2.59281	2.59265
C	-1.73846	1.65636	1.65624	H	-1.56927	4.05769	4.05770
C	-2.16964	2.59274	2.59260	C	-2.64398	0.83655	0.83643
H	-1.56937	4.05744	4.05745	H	-3.22869	2.75569	2.75545
C	-2.64561	0.83653	0.83644	C	-4.03738	0.85412	0.85394
H	-3.22947	2.75586	2.75565	N	-1.99380	0.00003	0.00001
C	-4.03895	0.85403	0.85391	C	-4.73045	0.00004	-0.00009
N	-1.99503	0.00003	0.00002	H	-4.58041	1.51779	1.51754
C	-4.73227	0.00003	-0.00005	C	-2.64392	-0.83648	-0.83646
H	-4.58186	1.51777	1.51762	C	-4.03732	-0.85404	-0.85407
C	-2.64557	-0.83647	-0.83645	H	-5.81577	0.00005	-0.00013
C	-4.03891	-0.85396	-0.85398	C	-1.73698	-1.65662	-1.65651
H	-5.81758	0.00003	-0.00008	H	-4.58032	-1.51770	-1.51770
C	-1.73839	-1.65631	-1.65622	C	-2.16863	-2.59277	-2.59262
H	-4.58179	-1.51770	-1.51771	N	-0.40408	-1.44634	-1.44623
C	-2.16956	-2.59270	-2.59257	C	-1.24430	-3.32565	-3.32550
N	-0.40577	-1.44531	-1.44523	H	-3.22857	-2.75563	-2.75547
C	-1.24498	-3.32527	-3.32514	C	0.48879	-2.14982	-2.14967
H	-3.22939	-2.75579	-2.75565	C	0.10699	-3.09565	-3.09550
C	0.48756	-2.14882	-2.14872	H	-1.56911	-4.05774	-4.05757

C	0.10622	-3.09457	-3.09446	H	1.53512	-1.94954	-1.94940
H	-1.56928	-4.05747	-4.05733	Ru	0.00001	0.00006	0.00005
H	1.53359	-1.94790	-1.94784	H	5.81579	-0.00013	-0.00019
Ru	-0.00351	0.00005	0.00004	Br	1.44721	-4.05023	-4.05016
H	5.81260	-0.00008	-0.00013	Br	1.44704	4.05002	4.05054
Br	1.44679	-4.04912	-4.04913	Br	-1.44723	4.05061	-4.04973
Br	1.44669	4.04893	4.04943	Br	-1.44716	-4.05050	4.04986
(6) [Ru(4,4□-Br₂tpy)(tpy)]²⁺				(7) [Ru(4,4□-Br₂tpy)₂]²⁺			
Coordinate (Å)				Coordinate (Å)			
Atom	X	Y	Z	Atom	X	Y	Z
C	-0.00007	2.36583	-1.18328	C	-0.00008	2.36517	-1.18237
C	-0.00016	3.75901	-1.20739	C	-0.00016	3.75816	-1.20710
C	-0.00023	4.45188	0.00031	C	-0.00023	4.45147	0.00031
C	-0.00023	3.75885	1.20793	C	-0.00023	3.75801	1.20763
C	-0.00014	2.36567	1.18364	C	-0.00014	2.36502	1.18273
N	-0.00007	1.71521	0.00014	N	-0.00007	1.71307	0.00014
H	-0.00016	4.30282	-2.14557	H	-0.00016	4.30267	-2.14494
H	-0.00030	4.30255	2.14618	H	-0.00030	4.30240	2.14554
H	0.00021	-1.14360	-5.16260	H	0.00019	-1.13427	-5.17393
C	0.00015	-0.38316	-4.38895	C	0.00014	-0.37978	-4.39498
C	0.00009	0.97137	-4.70156	C	0.00007	0.97860	-4.69471
C	0.00014	-0.75895	-3.05226	C	0.00013	-0.75328	-3.05931
C	0.00002	1.89954	-3.66660	C	0.00001	1.90797	-3.66010
H	0.00010	1.30386	-5.73485	N	0.00006	0.12608	-2.04876
N	0.00007	0.12769	-2.04847	H	0.00018	-1.80085	-2.77759
H	0.00019	-1.80362	-2.76009	C	0.00000	1.45848	-2.34470
C	0.00001	1.46038	-2.34596	H	-0.00005	2.96844	-3.88281
H	-0.00003	2.96105	-3.88921	C	-0.00014	0.97801	4.69490
C	-0.00014	0.97078	4.70174	C	-0.00016	1.90751	3.66039
C	-0.00016	1.89907	3.66690	C	-0.00008	-0.38033	4.39500
C	-0.00008	-0.38371	4.38897	C	-0.00012	1.45818	2.34495
H	-0.00017	1.30314	5.73507	H	-0.00021	2.96795	3.88324
C	-0.00012	1.46008	2.34620	C	-0.00004	-0.75367	3.05928
H	-0.00021	2.96055	3.88965	H	-0.00006	-1.13492	5.17385
C	-0.00004	-0.75934	3.05222	N	-0.00006	0.12581	2.04883
H	-0.00006	-1.14425	5.16252	H	0.00001	-1.80120	2.77744
N	-0.00006	0.12742	2.04855	H	2.77765	1.24347	0.00019
H	0.00001	-1.80398	2.75994	C	3.05932	0.19587	0.00013
H	2.77573	1.24665	0.00020	C	4.39506	-0.17754	0.00014
C	3.05824	0.19928	0.00014	N	2.04884	-0.68346	0.00005
C	4.39408	-0.17372	0.00015	C	4.69487	-1.53585	0.00007
N	2.04817	-0.68047	0.00005	C	2.34487	-2.01592	-0.00003
C	4.69409	-1.53193	0.00007	C	3.66026	-2.46528	-0.00002

C	2.34454	-2.01283	-0.00003	C	1.18257	-2.92263	-0.00012
C	3.66017	-2.46180	-0.00002	H	3.88310	-3.52571	-0.00008
C	1.18253	-2.91967	-0.00012	C	1.20740	-4.31563	-0.00021
H	3.88333	-3.52215	-0.00008	N	0.00005	-2.27058	-0.00012
C	1.20735	-4.31264	-0.00021	C	0.00008	-5.00907	-0.00029
N	0.00004	-2.26740	-0.00012	H	2.14533	-4.85999	-0.00021
C	0.00007	-5.00614	-0.00029	C	-1.18247	-2.92266	-0.00020
H	2.14533	-4.85692	-0.00021	C	-1.20727	-4.31565	-0.00029
C	-1.18243	-2.91970	-0.00020	H	0.00009	-6.09441	-0.00036
C	-1.20722	-4.31266	-0.00029	C	-2.34479	-2.01598	-0.00018
H	0.00009	-6.09147	-0.00036	H	-2.14518	-4.86004	-0.00035
C	-2.34446	-2.01289	-0.00019	C	-3.66017	-2.46536	-0.00026
H	-2.14518	-4.85697	-0.00036	N	-2.04879	-0.68350	-0.00008
C	-3.66008	-2.46188	-0.00026	C	-4.69481	-1.53596	-0.00023
N	-2.04812	-0.68051	-0.00009	H	-3.88298	-3.52580	-0.00034
C	-4.69403	-1.53204	-0.00024	C	-3.05929	0.19580	-0.00006
H	-3.88322	-3.52224	-0.00035	C	-4.39502	-0.17764	-0.00013
C	-3.05821	0.19921	-0.00006	H	-2.77764	1.24341	0.00002
C	-4.39405	-0.17382	-0.00014	Ru	0.00002	-0.27872	0.00001
H	-2.77573	1.24658	0.00002	H	-0.00030	5.53682	0.00038
Ru	0.00002	-0.27621	0.00001	H	-5.17386	0.57693	-0.00011
H	-0.00030	5.53726	0.00039	H	5.17389	0.57705	0.00021
H	-5.17275	0.58087	-0.00011	Br	-6.49924	-2.12747	-0.00034
H	5.17277	0.58098	0.00022	Br	6.49932	-2.12731	0.00008
Br	-6.49922	-2.12302	-0.00035	Br	-0.00019	1.56924	6.49943
Br	6.49930	-2.12287	0.00008	Br	0.00008	1.57004	-6.49917

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