Supporting Information

Trifluoromethyl Substitution Enhances Photoinduced Activity Against Breast Cancer Cells but Reduces Ligand Exchange in Ru(II) Complex

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NMR Data

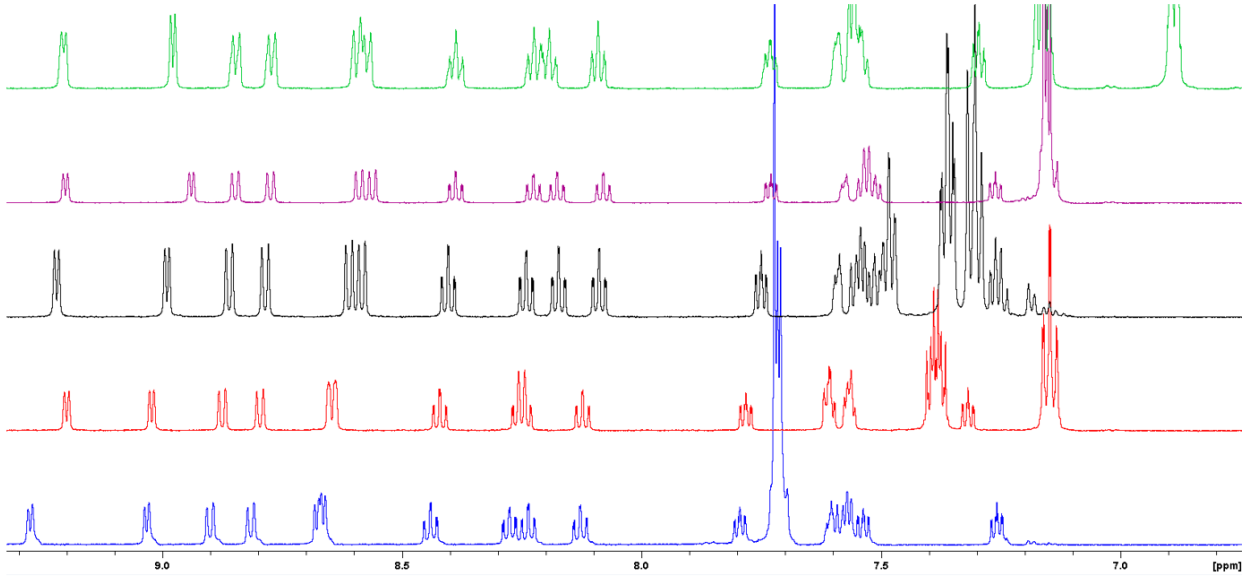


Figure S1. ^{1}H-NMR of the aromatic region of **1** (green), **2** (purple), **3** (black), **4** (red) and **5** (blue) in acetone-d_6.

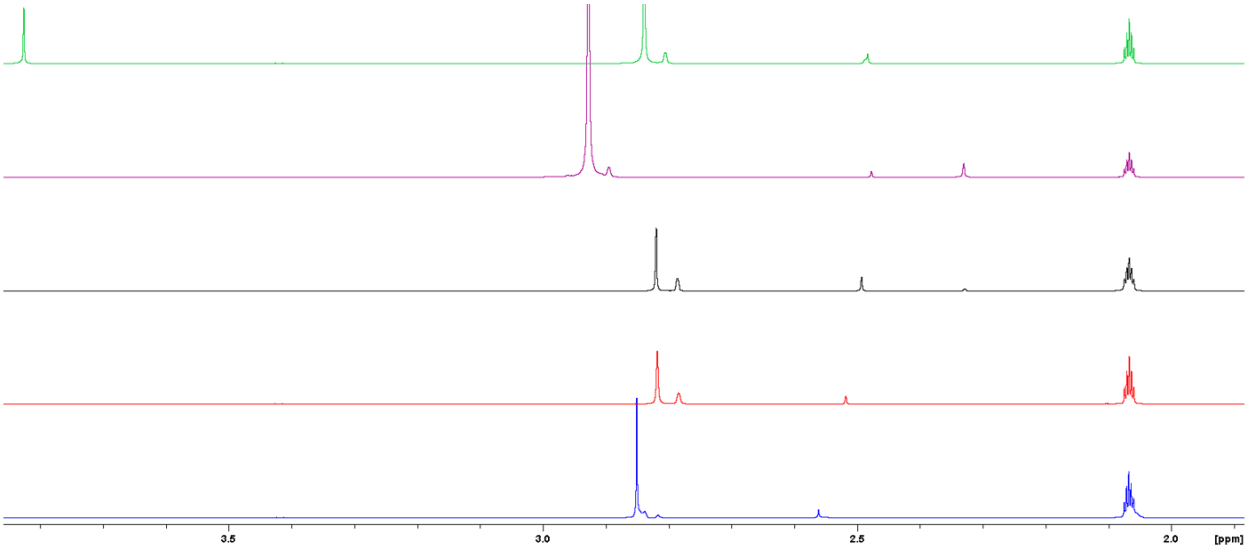


Figure S2. ^{1}H-NMR of the aliphatic region of **1** (green), **2** (purple), **3** (black), **4** (red) and **5** (blue) in acetone-d_6.

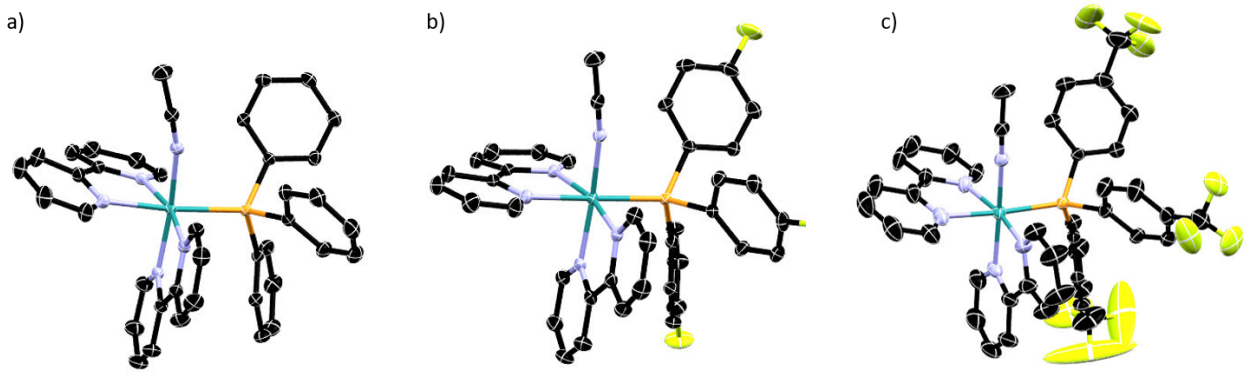


Figure S3. Thermal ellipsoid plots of (a) **1**, (b) **2**, and (c) **3**; H atoms, PF_6^- ions and co-crystallized solvent molecules omitted for clarity.

Table S1. Selected Crystallographic Bond Lengths, Bond Angles, and Phosphine Cone Angles.

	Ru-N / Å					Ru-P / Å	Angles	
Complex	Bpy[a]		Bpy[b]		ACN		ACN-Ru-P	Cone Angle
1	2.100	2.080	2.063	2.063	2.048	2.352	91.72°	142°
2	2.121	2.106	2.058	2.053	2.037	2.347	91.68°	143°
3	2.114	2.100	2.050	2.062	2.040	2.338	93.46°	142°
4	2.106	2.095	2.047	2.057	2.039	2.340	95.10°	142°
5	2.107	2.093	2.046	2.061	2.017	2.333	91.91°	141°

[a]Bpy positioned *trans* to the phosphine. [b]Bpy positioned *trans* to the acetonitrile.

Table S2. Crystallographic Parameters for **1** – **5**.

Compound	**1**	**2**	**3**	**4**	**5**
CCDC Number	200988	2005084	2009191	2009189	2009190
Empirical formula	$C_{43}H_{40}O_3N_5PRu$	$C_{43}H_{40}N_5PRu$	$C_{40}H_{34}N_5PRu$	$C_{40}H_{31}F_3N_5PRu$	$C_{43}H_{31}F_9N_5PRu$
Formula weight	1096.78	1048.80	1080.84	1060.68	1214.71
Temperature (K)	150	150	150	150	150
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/n$
a/ Å	10.3218(6)	20.9185(7)	19.0877(3)	10.8997(3)	11.6837(5)
b/ Å	20.5556(14)	11.1390(4)	12.5735(2)	20.6970(6)	24.9343(11)
c/ Å	21.4000(14)	21.6643(7)	19.8551(4)	19.6616(5)	17.5584(8)
α/°	90	90	90	90	90
β/°	91.670(2)	117.906(10)	105.015(1)	100.5230(10)	90.019(2)
γ/°	90	90	90	90	90
Volume/$Å^3$	4538.5(5)	4461.0(3)	4602.51(14)	4360.9(2)	5115.2(4)
Z	4	4	4	4	4
Density (calc). g/cm^3	1.605	1.5615	1.5597	1.616	1.577
μ/ mm^{-1}	0.547	0.547	0.535	0.571	0.514
F(000)	2218	2117	2189	2120	2416
Crystal size/mm^3	0.12 x 0.15 x 0.31	0.08 x 0.15 x 0.27	0.09 x 0.20 x 0.25	0.11x 0.17 x 0.31	0.13 x 0.18 x 0.26
Radiation	MoKα	MoKα	MoKα	MoKα	MoKα
Reflections collected	123501	201564	134812	115617	101022
Theta range for data collection (deg)	2.797 – 27.890	2.80 – 27.89	2.74 – 27.88	2.736 – 27.884	2.838 – 27.907
Independent reflections	10035	8764	10271	9388	10876
Data/restraints/parameters Goodness-of-fit on F^2	1.701	1.126	1.090	1.049	2.384
Final R indexes [all data]	R_1 0.0397 wR_2 0.1829	R_1 0.0747 wR_2 0.1915	R_1 0.0237 wR_2 0.1478	R_1 0.0293 wR_2 0.1194	R_1 0.0790 wR_2 0.2867
Largest diff. peak/hole/ e $Å^{-3}$	4.8/-0.6	1.7/-1.2	0.6/-0.6	0.7/-0.9	3.7/-1.4

Emission, Excitation, and Absorption Spectra

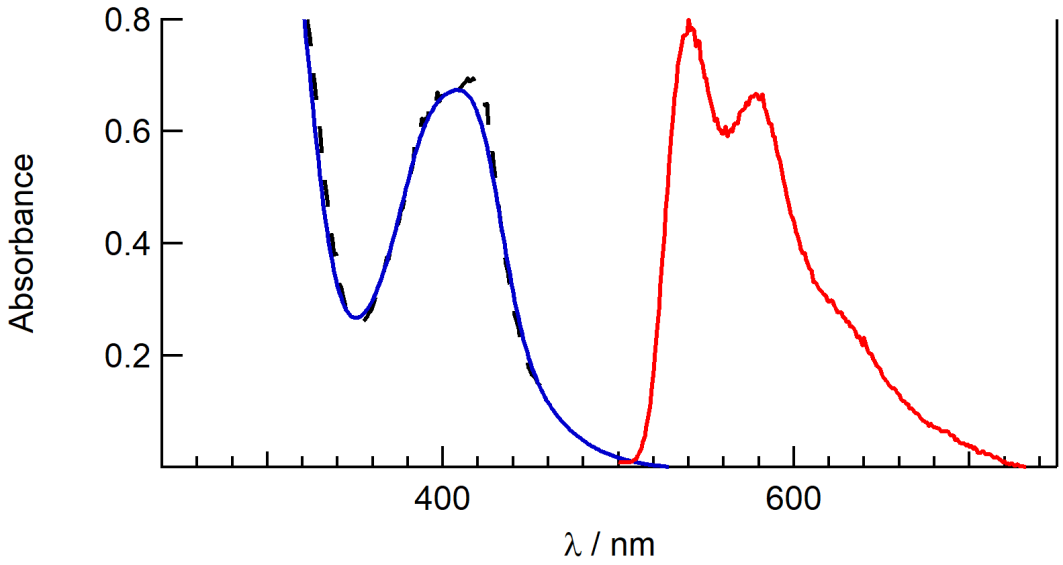


Figure S4. Emission (red, λ_{ex} = 410 nm), excitation (black dash, λ_{em} = 550 nm), and absorption spectra (blue) of **1** in CH_3CN at 77K.

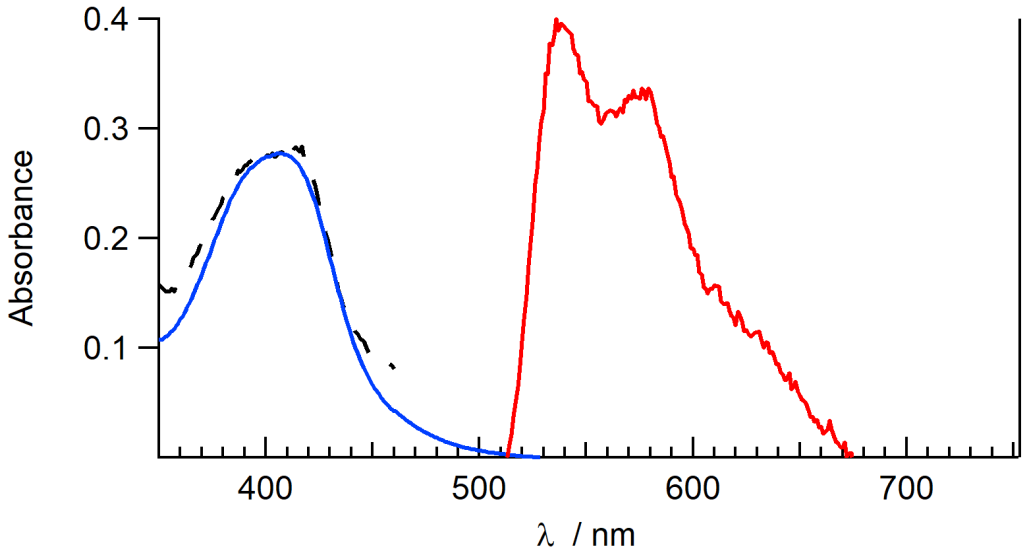


Figure S5. Emission (red, λ_{ex} = 400 nm), excitation (black dash, λ_{em} = 540 nm), and absorption spectra (blue) of **2** in CH_3CN at 77K.

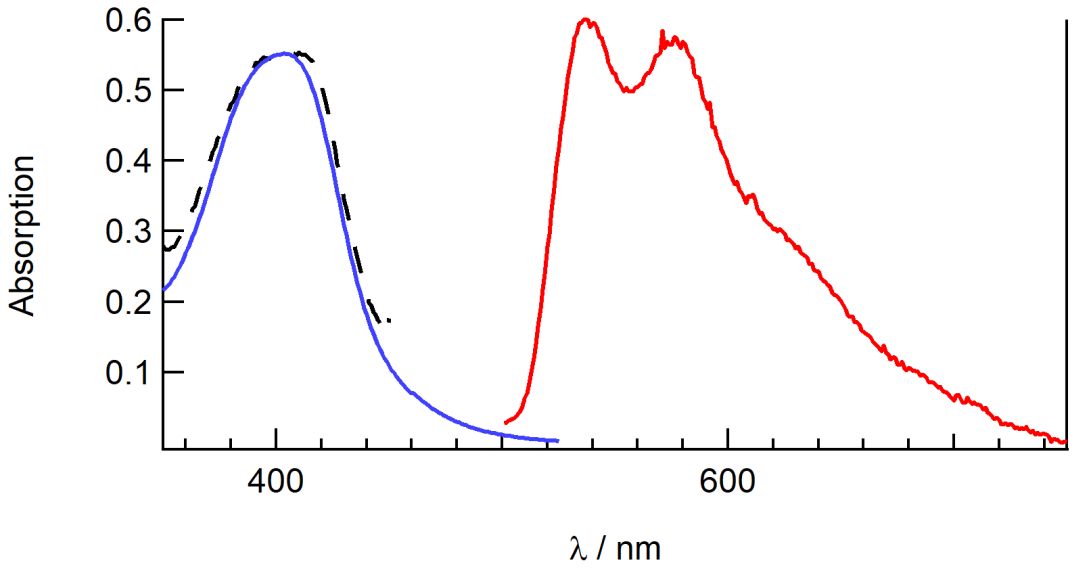


Figure S6. Emission (red, λ_{ex} = 400 nm), excitation (black dash, λ_{em} = 540 nm), and absorption spectra (blue) of **3** in CH_3CN at 77K.

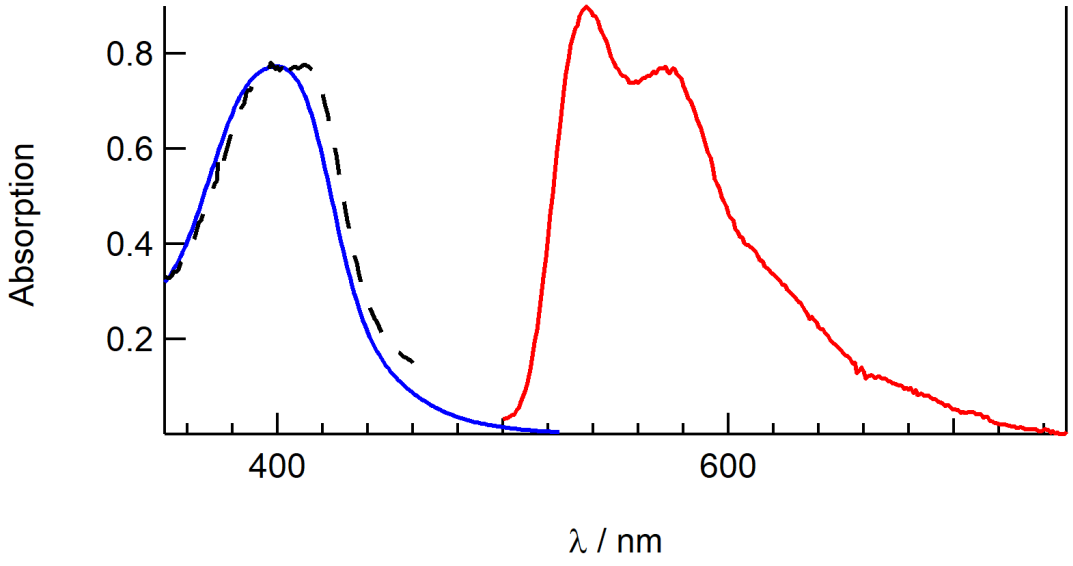


Figure S7. Emission (red, λ_{ex} = 400 nm), excitation (black dash, λ_{em} = 540 nm), and absorption spectra (blue) of **4** in CH_3CN at 77 K.

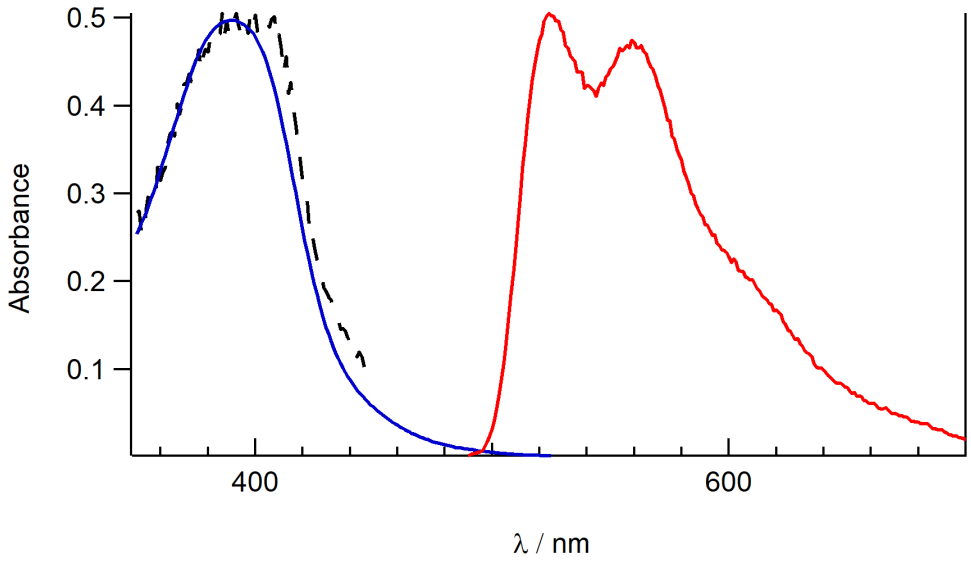


Figure S8. Emission (red, λ_{ex} = 390 nm), excitation (black dash, λ_{em} = 525 nm), and absorption spectra (blue) of **5** in CH_3CN at 77 K.

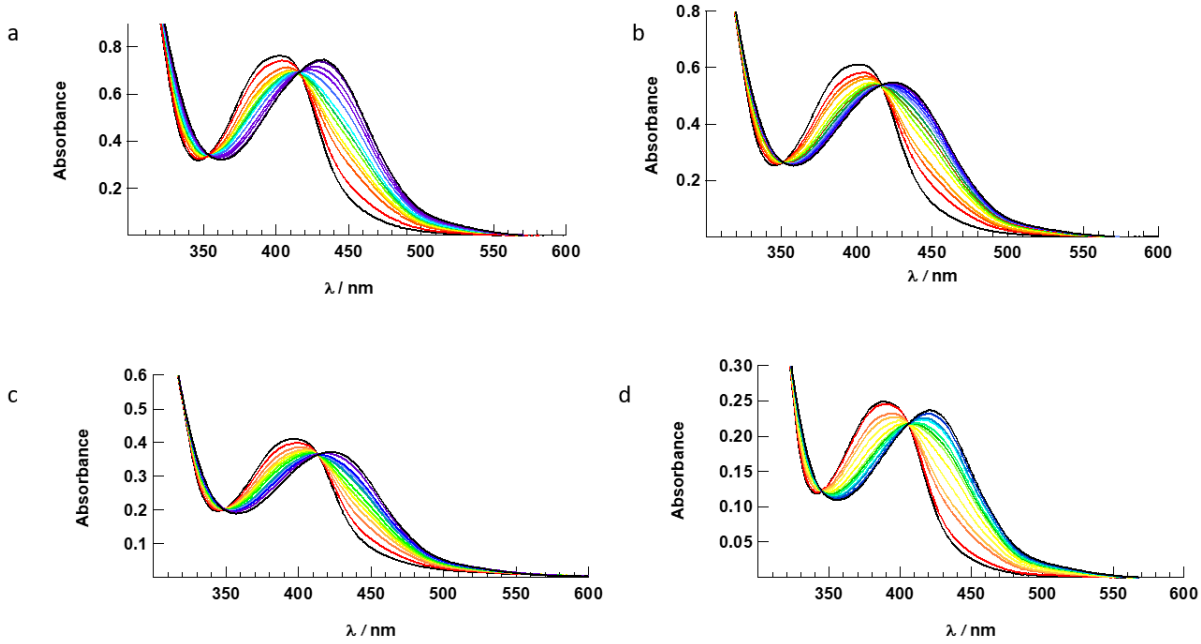


Figure S9. Changes to the electronic absorption spectra upon irradiation of (a) **2** (0 – 60 s), (b) **3** (0 – 70 s), (c) **4** (0- 80 s), and (d) **5** (0 – 240 s) in H_2O (<5% acetone) with λ_{irr} >395 nm.

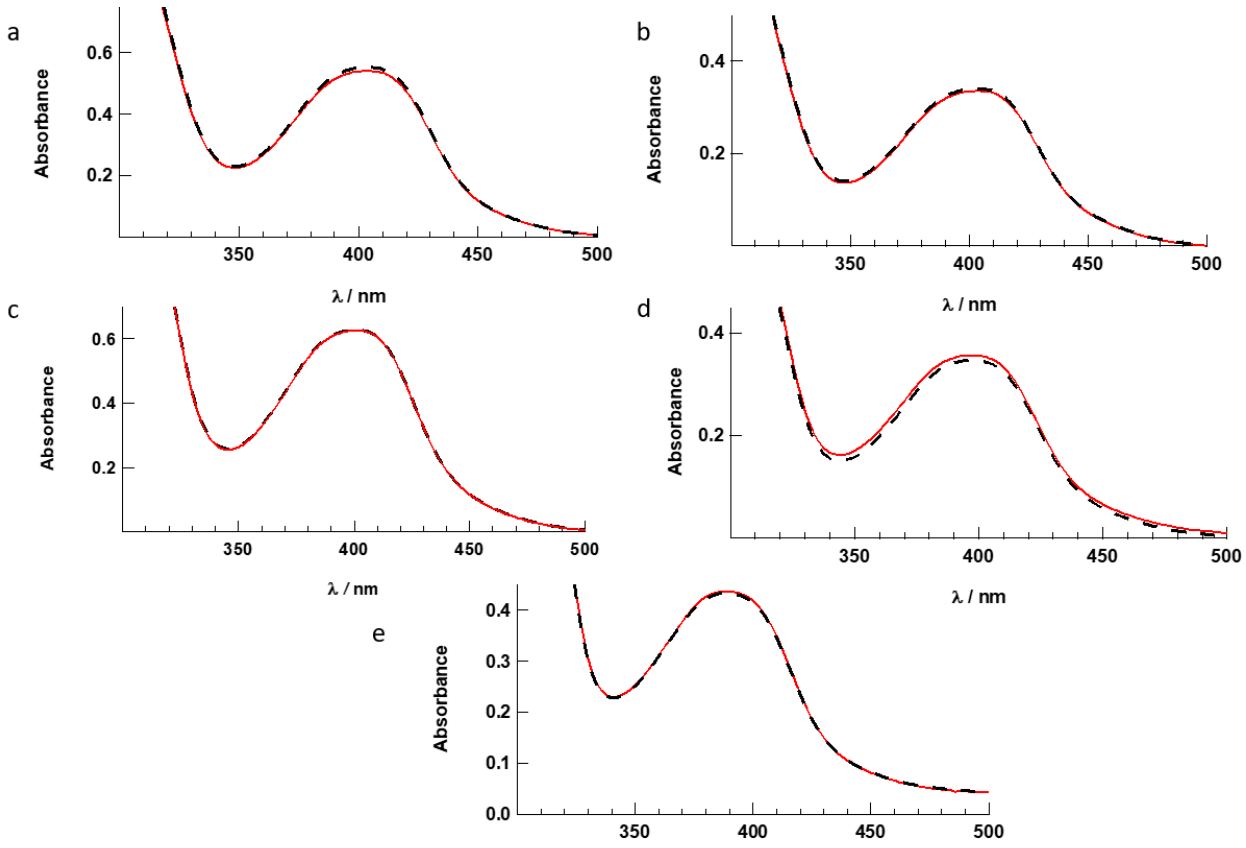


Figure S10. Changes to the electronic absorption spectra for (a) **1**, (b) **2**, (c) **3**, (d) **4**, (e) **5** when kept in the dark, showing the initial spectrum (black, dashed) and after 2 h (red, solid) in H_2O (< 5% acetone) at 298 K.

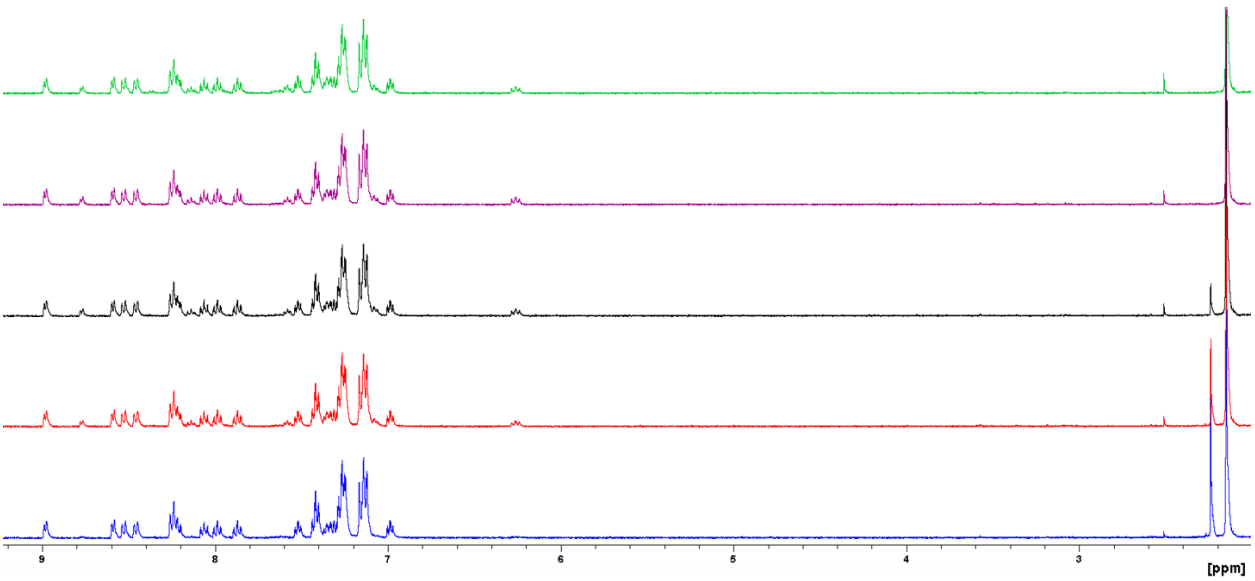


Figure S11. Changes to the ^{1}H NMR spectrum of **3** in CD_3CN upon irradiation with λ_{irr} >395 nm for 0 (blue), 15s (red), 30s (black), 45s (purple) and 1 min (green).

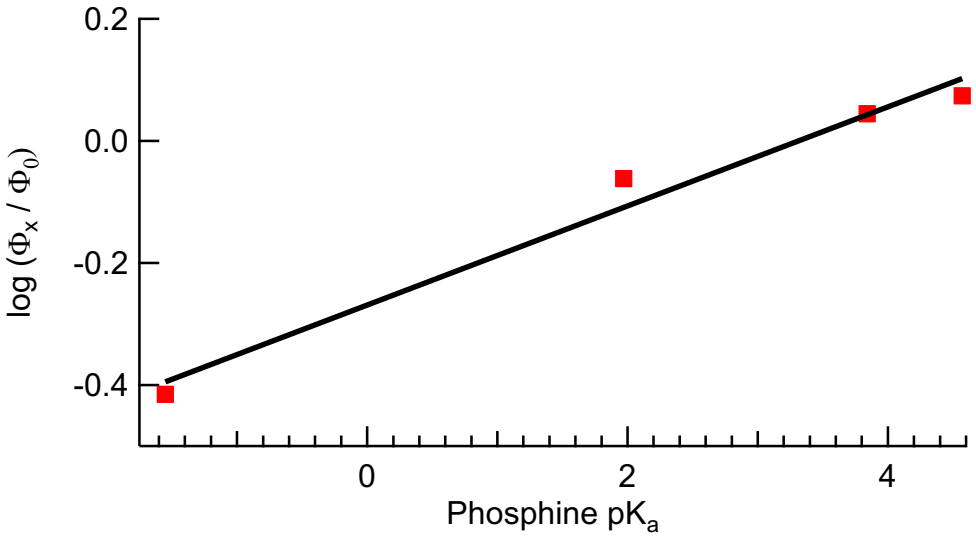


Figure S12. Plot of the quantum yield values, Φ_x, relative to that of **3**, Φ_0, as a function of phosphine pK_a.

DTF Optimized Structures

Table S3. Experimental and calculated bond lengths (Å) for **1**.

	Ru-N/ Å					Ru-N/ Å	N-RuP/ °
	bpy[a]		bpy[b]		ACN	Ru-P	ACN-Ru-P
Exper.	2.078	2.102	2.065	2.060	2.045	2.352	91.69
^{1}GS	2.101	2.133	2.072	2.072	2.072	2.424	89.28
^{3}MLCT	2.099	2.103	2.083	2.046	2.040	2.458	85.81

[a]Bpy positioned *trans* to the phosphine. [b]Bpy positioned *trans* to the acetonitrile.

Table S4. Experimental and calculated bond lengths (Å) for **2**.

	Ru-N/ Å					Ru-N/ Å	N-RuP/ °
	bpy[a]		bpy[b]		ACN	Ru-P	ACN-Ru-P
Exper.	2.121	2.106	2.053	2.058	2.037	2.347	91.68
^{1}GS	2.128	2.108	2.071	2.073	2.009	2.433	88.48
^{3}MLCT	2.121	2.097	2.063	2.043	2.053	2.494	91.51

[a]Bpy positioned *trans* to the phosphine. [b]Bpy positioned *trans* to the acetonitrile.

Table S5. Experimental and calculated bond lengths (Å) for **3**.

	Ru-N/ Å					Ru-N/ Å	N-RuP/ °
	bpy[a]		Bpy[b]		ACN	Ru-P	ACN-Ru-P
Exper.	2.100	2.115	2.062	2.050	2.039	2.337	93.48
^{1}GS	2.103	2.127	2.073	2.074	2.011	2.418	89.54
^{3}MLCT	2.105	2.116	2.031	2.076	2.054	2.470	86.84

[a]Bpy positioned *trans* to the phosphine. [b]Bpy positioned *trans* to the acetonitrile.

Table S6. Experimental and calculated bond lengths (Å) for **4**.

	Ru-N/ Å					Ru-N/ Å	N-RuP/ °
	bpy[a]		Bpy[b]		ACN	Ru-P	ACN-Ru-P
Exper.	2.106	2.095	2.047	2.057	2.039	2.340	95.10
^{1}GS	2.104	2.128	2.073	2.075	2.012	2.418	89.88
^{3}MLCT	2.104	2.112	2.033	2.078	2.056	2.470	86.94

[a]Bpy positioned *trans* to the phosphine. [b]Bpy positioned *trans* to the acetonitrile.

Table S7. Experimental and calculated bond lengths (Å) for **5**.

	Ru-N/ Å					Ru-N/ Å	N-RuP/ °
	bpy[a]		Bpy[b]		ACN	Ru-P	ACN-Ru-P
Exper.	2.046	2.062	2.092	2.108	2.017	2.333	91.93
^{1}GS	2.074	2.078	2.104	2.124	2.015	2.413	89.86
^{3}MLCT	2.029	2.072	2.118	2.139	2.053	2.476	90.87

[a]Bpy positioned *trans* to the phosphine. [b]Bpy positioned *trans* to the acetonitrile.

Atomic Coordinates

Table S8. Optimized atomic coordinates (x,y,z) for ^{1}GS and ^{3}MLCT excited state of **1** using PBE.

^{1}GS				^{3}MLCT			
44	4.086978	13.53362	16.39322	44	4.180369	13.53314	16.33232
15	5.670746	15.2891	15.86045	15	5.668168	15.42971	15.85269
8	6.828938	19.01432	20.45182	8	6.717438	19.11624	20.47621
8	4.140443	19.46632	11.79631	8	4.17647	19.50707	11.69827
7	3.8459	12.76589	14.45274	7	3.841849	12.77385	14.40496
8	10.97935	13.36632	13.74038	8	10.94701	13.34489	13.88095
7	2.587116	14.84175	16.12988	7	2.653572	14.8664	16.10526
7	2.567254	12.06161	16.66371	7	2.634167	12.15747	16.70615
7	4.294991	13.8967	18.42266	7	4.444932	13.87027	18.37088
7	5.5211	12.13274	16.9165	7	5.547619	12.07865	16.77971
6	7.733111	15.12348	13.90602	6	7.731125	15.14538	13.92264
1	7.128007	15.81098	13.31295	1	7.142863	15.82264	13.30206
6	5.098768	16.54157	14.62247	6	5.111016	16.65032	14.5901
6	6.11161	16.38051	17.2898	6	6.076902	16.51838	17.283
6	5.160402	13.06693	19.09018	6	5.232538	12.91857	19.00201
6	3.711794	17.24847	12.73715	6	3.736979	17.31227	12.68242
1	2.910718	17.02141	12.03387	1	2.940973	17.0705	11.97855
6	7.288734	14.71052	15.17286	6	7.272925	14.78764	15.20517
6	5.405392	18.15211	18.8082	6	5.352941	18.31466	18.75972
1	4.663168	18.87448	19.15187	1	4.620409	19.06207	19.06802
6	2.825737	11.8604	14.29148	6	2.867666	11.78895	14.34538
6	5.831457	12.07068	18.25117	6	5.844007	11.94775	18.13334
6	2.092829	11.50025	15.51396	6	2.178127	11.49567	15.58185
6	4.071291	16.30018	13.70096	6	4.087632	16.38574	13.66737
1	3.525255	15.35808	13.72385	1	3.545671	15.44179	13.70607
6	8.119395	13.83667	15.90884	6	8.062998	13.90701	15.97939
1	7.822447	13.49713	16.9019	1	7.725113	13.58109	16.96374
6	1.986421	11.73668	17.83707	6	2.022146	11.95193	17.89411
1	2.398798	12.21188	18.72635	1	2.419457	12.5089	18.74127
6	4.425612	12.46676	12.12631	6	4.315165	12.43536	12.0623
1	5.09657	12.72776	11.30768	1	4.915654	12.712	11.19629
6	8.955892	14.6949	13.38368	6	8.954775	14.68858	13.43882
1	9.266899	15.0483	12.40104	1	9.293177	15.00948	12.45411
6	4.63185	13.03151	13.38044	6	4.537029	13.06308	13.27817
1	5.460842	13.71721	13.55107	1	5.317812	13.81567	13.37971
6	5.136912	17.288	17.75757	6	5.109982	17.46228	17.69637

1	4.167557	17.3526	17.25767	1	4.169472	17.55653	17.14913
6	9.341621	13.41321	15.40824	6	9.285424	13.4542	15.5151
1	9.99193	12.75573	15.98737	1	9.910413	12.79352	16.1174
6	6.66643	18.13232	19.43949	6	6.577907	18.24314	19.46043
6	5.771673	17.78297	14.55291	6	5.786765	17.89005	14.50113
1	6.576249	18.00705	15.25509	1	6.58738	18.12871	15.20327
6	0.915411	10.85307	17.92795	6	0.957604	11.07867	18.04807
1	0.486241	10.62243	18.90313	1	0.513817	10.93645	19.03276
6	2.566774	11.27284	13.04642	6	2.609742	11.12253	13.12863
1	1.751268	10.55879	12.9402	1	1.85432	10.33848	13.09409
6	4.393867	18.4769	12.68007	6	4.421065	18.53998	12.60376
6	1.67676	15.55777	15.99396	6	1.700327	15.52922	16.01645
6	7.364084	16.37609	17.916	6	7.293482	16.46049	17.98007
1	8.159053	15.72263	17.55547	1	8.077476	15.77069	17.66696
6	9.776285	13.83625	14.13539	6	9.748931	13.84008	14.23642
6	5.427984	18.73258	13.60435	6	5.451544	18.81685	13.52865
1	5.948604	19.68997	13.55276	1	5.974625	19.77147	13.45585
6	1.006704	10.61472	15.54161	6	1.09027	10.60315	15.69243
1	0.625449	10.18115	14.61804	1	0.721437	10.08767	14.80652
6	3.361223	11.58238	11.94664	6	3.321673	11.44168	11.98566
1	3.163702	11.12775	10.97518	1	3.123609	10.92059	11.04843
6	11.49977	13.79099	12.46877	6	11.49896	13.68979	12.59428
1	10.84633	13.46676	11.64352	1	10.85085	13.33127	11.78037
1	12.47494	13.3029	12.37571	1	12.46531	13.17889	12.54881
1	11.63112	14.8838	12.43972	1	11.65021	14.77675	12.51252
6	6.721953	11.10672	18.74035	6	6.707993	10.91738	18.56362
1	6.958306	11.07228	19.80312	1	6.943644	10.82115	19.62296
6	3.613789	14.82072	19.13843	6	3.850862	14.82581	19.12057
1	2.937158	15.45494	18.57079	1	3.242165	15.54505	18.57616
6	0.410869	10.28627	16.75613	6	0.48178	10.3887	16.91663
1	-0.43422	9.59737	16.7868	1	-0.35918	9.699216	16.99946
6	3.753196	14.96575	20.51386	6	3.976046	14.89491	20.49944
1	3.176226	15.73107	21.03306	1	3.462476	15.68299	21.04899
6	7.647487	17.23705	18.98134	6	7.551073	17.30874	19.05698
1	8.64055	17.2181	19.42929	1	8.514523	17.25159	19.56241
6	5.347271	13.17768	20.47335	6	5.387653	12.94974	20.40521
1	6.042957	12.51357	20.98473	1	5.994549	12.19068	20.89767
6	4.64055	14.13312	21.1977	6	4.76282	13.92909	21.15637
1	4.778856	14.22454	22.27551	1	4.874927	13.94686	22.241
6	6.093502	11.23701	16.08041	6	6.087114	11.19751	15.89984
1	5.832881	11.32792	15.02834	1	5.823738	11.34453	14.8544

6	3.112187	19.26832	10.81413	6	3.152714	19.29471	10.71072
1	3.099624	20.18474	10.21579	1	3.150104	20.2	10.09594
1	2.128206	19.12866	11.28986	1	2.166227	19.16911	11.18389
1	3.342501	18.40903	10.16448	1	3.38565	18.42214	10.0808
6	6.976122	10.25504	16.51484	6	6.93128	10.17222	16.28508
1	7.40367	9.561269	15.79094	1	7.330985	9.493398	15.53275
6	0.577017	16.47807	15.79604	6	0.52593	16.36351	15.8888
1	0.907926	17.32708	15.17856	1	0.753268	17.2364	15.25828
1	0.211556	16.86404	16.75921	1	0.192987	16.71775	16.87562
1	-0.25756	15.97521	15.28559	1	-0.29466	15.79671	15.42472
6	8.11241	19.09253	21.09371	6	7.950505	19.13292	21.22053
1	8.897807	19.37749	20.37638	1	8.799744	19.38473	20.5672
1	8.374329	18.139	21.57937	1	8.125115	18.1655	21.71599
1	8.011348	19.87365	21.85377	1	7.822625	19.91526	21.97471
6	7.301207	10.18724	17.87063	6	7.250105	10.03016	17.65229
1	7.991559	9.430713	18.24545	1	7.910951	9.230379	17.9885

Table S9. Optimized atomic coordinates (x,y,z) for ^{1}GS and ^{3}MLCT excited state of **2** using PBE.

^{1}GS				^{3}MLCT			
44	-0.76336	5.481167	10.19445	44	-0.71212	5.390014	10.21023
15	1.58689	5.238679	9.614048	15	1.717144	5.144994	9.703096
7	-2.80684	5.498224	10.78777	7	-2.75882	5.570959	10.73794
7	-0.30745	7.212205	11.23635	7	-0.23309	6.940171	11.48481
7	-1.18966	6.938813	8.783039	7	-1.03504	6.988027	8.979199
7	-1.58594	3.908635	9.056192	7	-1.60392	3.972886	8.947791
7	-0.44972	4.254069	11.75432	7	-0.61021	3.942592	11.66326
6	-0.47828	8.387569	10.54787	6	-0.53675	8.202192	10.97767
6	-3.56798	4.475524	10.30178	6	-3.61472	4.861812	9.920754
6	2.70965	5.671713	11.02746	6	2.871897	5.795172	10.98539
6	3.343542	4.666955	11.77692	6	3.719731	4.916004	11.68056
6	2.939132	7.012185	11.38571	6	2.935363	7.168912	11.28545
6	2.207812	6.247815	8.190349	6	2.12065	6.032183	8.12934
6	-0.96421	8.232408	9.174315	6	-0.93642	8.229295	9.600302
6	1.496346	6.201407	6.979395	6	1.493854	5.595258	6.944875
6	2.160632	3.526534	9.16726	6	2.356014	3.440752	9.359375
6	-2.90326	3.615215	9.313567	6	-2.99031	4.023092	8.920844
6	3.887142	7.611805	7.080163	6	3.355939	7.655776	6.814149
6	3.421536	6.954673	8.220575	6	3.054976	7.076999	8.047073
1	4.025205	6.97743	9.127688	1	3.58429	7.419724	8.935432

6	3.16559	0.929624	8.588128	6	3.502159	0.876999	8.926826
6	3.791589	7.331398	12.44349	6	3.84124	7.644207	12.23219
6	-3.36079	6.367813	11.65836	6	-3.26311	6.304697	11.75434
1	-2.71427	7.16675	12.01867	1	-2.53842	6.829152	12.37559
6	-1.74457	6.724668	7.568075	6	-1.44355	6.924481	7.689543
6	1.623813	2.38867	9.794056	6	1.852144	2.307774	10.01864
6	3.174107	7.581656	5.871243	6	2.740495	7.22243	5.625211
6	-0.96594	3.211394	8.074333	6	-0.97351	3.072115	8.153932
6	-1.58742	2.204405	7.342346	6	-1.64264	2.255399	7.256
6	2.120187	1.115894	9.507659	6	2.416307	1.049507	9.800882
6	3.201231	3.347835	8.239369	6	3.442329	3.277492	8.477927
6	1.972534	6.853891	5.843043	6	1.805548	6.176217	5.71875
1	1.407406	6.7892	4.909911	1	1.318819	5.809454	4.811957
6	-3.57238	2.601129	8.616777	6	-3.70748	3.230322	8.002855
6	4.180976	4.996193	12.84456	6	4.609313	5.402657	12.63888
6	-0.3368	3.580788	12.70027	6	-0.74507	3.193176	12.54419
6	4.431648	6.33237	13.19529	6	4.699411	6.774314	12.92676
6	-0.26291	9.624619	11.16791	6	-0.43496	9.33607	11.81538
1	-0.39618	10.54734	10.60454	1	-0.69	10.31993	11.42261
6	3.687897	2.071071	7.957499	6	3.998721	2.017449	8.27028
6	0.061118	7.276241	12.53733	6	0.197929	6.830666	12.76528
6	-4.89837	4.312036	10.71225	6	-5.00788	4.941383	10.13186
1	-5.49497	3.485089	10.32961	1	-5.68629	4.380928	9.489978
6	-2.064	7.752889	6.689911	6	-1.74273	8.050268	6.942867
1	-2.51153	7.514491	5.724878	1	-2.06032	7.939789	5.90685
6	-2.9136	1.879269	7.625885	6	-3.04237	2.354809	7.160685
6	-4.67904	6.264071	12.0903	6	-4.62329	6.403728	12.00382
6	-0.16294	2.742858	13.86809	6	-0.89456	2.253247	13.63235
1	-0.40574	1.696416	13.63053	1	-1.49395	1.38928	13.30921
1	-0.82053	3.07525	14.68501	1	-1.40279	2.734644	14.48142
1	0.880473	2.790678	14.21447	1	0.09115	1.898207	13.9686
6	0.258658	8.478374	13.20732	6	0.297725	7.9151	13.61888
6	-5.46175	5.210968	11.6131	6	-5.51489	5.712328	11.16348
1	-6.49654	5.091588	11.9366	1	-6.59153	5.77143	11.32757
6	-1.7964	9.071099	7.064403	6	-1.6259	9.32005	7.548097
6	0.10449	9.677802	12.50998	6	-0.03216	9.198797	13.13056
1	0.26327	10.63818	13.00173	1	0.03098	10.07214	13.78066
6	3.676167	8.307148	4.653808	6	3.101498	7.829983	4.301365
1	3.353575	9.360984	4.667759	1	3.32266	8.902195	4.394494
1	3.292329	7.859239	3.727495	1	2.302674	7.698017	3.559713
1	4.773799	8.307431	4.609459	1	4.007411	7.350902	3.893716

6	-1.24703	9.305998	8.320328	6	-1.22616	9.402621	8.867212
1	-1.04713	10.32694	8.643006	1	-1.13285	10.37466	9.350123
6	3.721849	-0.43744	8.302538	6	4.127381	-0.47181	8.712009
1	4.633064	-0.61467	8.896577	1	5.062964	-0.55884	9.288107
1	4.002184	-0.54682	7.245812	1	4.387431	-0.63156	7.656204
1	3.005814	-1.23022	8.556567	1	3.464527	-1.28516	9.034511
6	5.384829	6.681241	14.30487	6	5.700981	7.296568	13.91773
1	6.413683	6.760974	13.91801	1	6.65715	7.518656	13.41625
1	5.393985	5.912079	15.08905	1	5.913037	6.561657	14.7059
1	5.137043	7.646661	14.76653	1	5.359479	8.227679	14.38972
1	0.572474	5.625387	6.908134	1	0.779662	4.770189	6.969744
1	-4.61618	2.384434	8.839526	1	-4.79354	3.303194	7.9604
1	3.209752	3.617338	11.51114	1	3.701659	3.846977	11.46541
1	0.801576	2.490978	10.50196	1	1.00679	2.401072	10.69777
1	1.685036	0.245809	10.00572	1	2.004763	0.180267	10.31941
1	0.075993	3.463387	7.892837	1	0.109376	3.01994	8.256381
1	0.545763	8.463499	14.25877	1	0.633665	7.764798	14.64412
1	-1.92715	5.685163	7.301744	1	-1.51964	5.926947	7.260981
1	-3.43015	1.089007	7.079855	1	-3.59864	1.74352	6.449244
1	3.637678	4.207826	7.730189	1	3.859581	4.137708	7.953236
1	4.671976	4.194977	13.40262	1	5.26082	4.700353	13.16419
1	2.47706	7.823184	10.81909	1	2.283589	7.881255	10.77694
1	4.495735	1.959907	7.230228	1	4.841203	1.916099	7.582023
1	4.837987	8.147962	7.128688	1	4.101313	8.453491	6.770947
1	-1.02349	1.684059	6.567966	1	-1.07552	1.558891	6.639056
1	3.971132	8.382026	12.68545	1	3.883676	8.716601	12.43711
1	0.201545	6.321052	13.03837	1	0.457948	5.826042	13.09478
1	-2.02245	9.90185	6.395081	1	-1.85183	10.22537	6.983554
1	-5.07692	6.997574	12.79173	1	-4.9774	7.016268	12.83224

Table S10. Optimized atomic coordinates (x,y,z) for ^{1}GS and ^{3}MLCT excited state of **3** using PBE.

^{1}GS				^{3}MLCT			
44	0.393733	3.47772	4.304272	44	0.381974	3.455552	4.226848
7	1.582639	2.088908	3.265192	7	1.589259	2.044095	3.237186
7	0.523993	1.863054	5.683316	7	0.499335	1.918347	5.675896
7	-1.38616	2.692725	3.589308	7	-1.35421	2.646153	3.551312
7	-0.99875	4.51533	5.439051	7	-0.9876	4.515823	5.372086
6	2.213929	5.91049	2.283005	6	2.238148	6.006214	2.298138
6	2.337884	7.171569	1.669157	6	2.371952	7.288621	1.731647

1	1.452558	7.782947	1.487056	1	1.496284	7.924633	1.594441
6	3.591642	7.652343	1.288125	6	3.626642	7.756218	1.336962
1	3.671261	8.631439	0.812662	1	3.716021	8.75131	0.897994
6	4.738908	6.884608	1.512547	6	4.76095	6.954572	1.499023
1	5.717803	7.262577	1.212837	1	5.739935	7.322787	1.187758
6	4.625412	5.631921	2.119509	6	4.635111	5.67903	2.054737
1	5.516796	5.025495	2.292316	1	5.515791	5.044861	2.173491
6	3.37018	5.147113	2.503471	6	3.380728	5.205268	2.452593
1	3.300493	4.170598	2.979767	1	3.301218	4.206732	2.879293
6	-0.23009	4.931072	1.038318	6	-0.19966	4.97567	1.058742
6	-1.5882	4.577387	0.927365	6	-1.54816	4.583084	0.959866
1	-2.22093	4.522867	1.813988	1	-2.1677	4.490885	1.852478
6	-2.15367	4.313153	-0.32198	6	-2.11333	4.317471	-0.28804
1	-3.21382	4.062779	-0.3934	1	-3.16539	4.035415	-0.35524
6	-1.36919	4.373537	-1.47731	6	-1.33478	4.4059	-1.44658
1	-1.8126	4.167512	-2.45283	1	-1.7772	4.191216	-2.42073
6	-0.01696	4.70655	-1.37643	6	0.011584	4.768675	-1.35279
1	0.602002	4.763321	-2.2736	1	0.622743	4.846276	-2.25365
6	0.550556	4.987696	-0.12987	6	0.58187	5.050998	-0.10939
1	1.602035	5.272355	-0.07614	1	1.626544	5.358657	-0.05753
6	-0.29482	6.865718	3.276998	6	-0.30414	6.935766	3.299067
6	-1.52051	7.331235	2.780749	6	-1.57794	7.323288	2.857151
1	-2.04044	6.791833	1.989083	1	-2.10555	6.74324	2.100329
6	-2.06663	8.527024	3.261032	6	-2.16516	8.492409	3.350628
1	-3.0122	8.887699	2.852154	1	-3.14857	8.794487	2.986499
6	-1.39584	9.270138	4.234307	6	-1.48962	9.283199	4.282754
1	-1.81651	10.21117	4.592509	1	-1.94545	10.20279	4.653292
6	-0.16844	8.815978	4.727596	6	-0.21614	8.90524	4.72143
1	0.37502	9.405014	5.468984	1	0.326091	9.531107	5.432586
6	0.375751	7.619373	4.258149	6	0.372647	7.736233	4.238257
1	1.352223	7.294874	4.625052	1	1.379985	7.469458	4.565159
6	1.971678	2.170845	1.969265	6	2.042343	2.117851	1.962014
1	1.637867	3.050448	1.421437	1	1.786089	3.022472	1.411808
6	2.74302	1.198752	1.34123	6	2.762171	1.101077	1.352757
1	3.021473	1.331991	0.295643	1	3.092004	1.219923	0.321073
6	3.145531	0.078253	2.068907	6	3.035364	-0.06667	2.085174
1	3.759545	-0.69913	1.612712	1	3.592647	-0.88957	1.636218
6	2.725066	-0.03747	3.390466	6	2.566972	-0.16445	3.385277
1	2.998275	-0.9189	3.968933	1	2.746067	-1.07367	3.957721
6	1.937648	0.965373	3.970698	6	1.841166	0.894772	3.965872
6	1.377146	0.859616	5.325463	6	1.302113	0.856231	5.310859

6	1.644822	-0.20146	6.201024	6	1.547389	-0.18144	6.232732
1	2.336161	-0.99227	5.913046	1	2.194468	-1.01248	5.954892
6	1.024171	-0.24659	7.44635	6	0.97663	-0.14506	7.494447
1	1.226568	-1.06929	8.133322	1	1.16653	-0.94883	8.206832
6	0.141577	0.77701	7.795436	6	0.1572	0.943508	7.844555
1	-0.37213	0.783398	8.7569	1	-0.31962	1.008253	8.822017
6	-0.07529	1.811891	6.890934	6	-0.04458	1.949821	6.913332
1	-0.74449	2.636625	7.132288	1	-0.66413	2.815219	7.144034
6	-1.50339	1.735715	2.641047	6	-1.46243	1.666325	2.615638
1	-0.58098	1.425075	2.155433	1	-0.53561	1.3544	2.138833
6	-2.72299	1.172308	2.283629	6	-2.67136	1.102829	2.259604
1	-2.75149	0.402057	1.512814	1	-2.69762	0.323479	1.499056
6	-3.88535	1.612908	2.918486	6	-3.8527	1.557504	2.893455
1	-4.8587	1.192597	2.662709	1	-4.82131	1.13101	2.630374
6	-3.77793	2.602038	3.892051	6	-3.76302	2.543885	3.854886
1	-4.67094	2.960361	4.402611	1	-4.66277	2.901921	4.3541
6	-2.52298	3.130389	4.219791	6	-2.50831	3.092898	4.205343
6	-2.30951	4.162984	5.237803	6	-2.30443	4.096592	5.20613
6	-3.33933	4.754721	5.979141	6	-3.32785	4.66197	6.001761
1	-4.3749	4.467275	5.801627	1	-4.35553	4.321792	5.879022
6	-3.04095	5.709689	6.946822	6	-3.02809	5.631996	6.938585
1	-3.83721	6.174536	7.529153	1	-3.81594	6.062518	7.557553
6	-1.70438	6.055061	7.153055	6	-1.68972	6.052894	7.085205
1	-1.41717	6.797064	7.898124	1	-1.40833	6.813128	7.81283
6	-0.72159	5.444096	6.382517	6	-0.71716	5.477537	6.283848
1	0.329781	5.691122	6.509244	1	0.32716	5.77163	6.369259
15	0.511607	5.288352	2.705864	15	0.536421	5.397023	2.707851
7	2.000863	4.230281	5.250767	7	2.048952	4.202129	5.166619
6	2.929362	4.610051	5.845255	6	2.981655	4.538959	5.775526
6	4.09799	5.103499	6.542559	6	4.152364	4.969078	6.504893
1	4.692898	5.741567	5.871293	1	4.786052	5.590909	5.853907
1	3.807157	5.693702	7.424207	1	3.863247	5.560083	7.386543
1	4.726143	4.265296	6.878545	1	4.735016	4.097835	6.838787

Table S11. Optimized atomic coordinates (x,y,z) for ^{1}GS and ^{3}MLCT excited state of **4** using PBE.

^{1}GS				^{3}MLCT			
44	0.398999	3.483356	4.301959	44	0.387083	3.460967	4.217609
7	1.58133	2.09157	3.257821	7	1.594415	2.049757	3.22863
7	0.530197	1.867185	5.679956	7	0.50758	1.930494	5.668152

7	-1.38638	2.701172	3.596247	7	-1.35029	2.64697	3.546791
7	-0.98633	4.52334	5.444813	7	-0.98462	4.522794	5.36216
6	2.208339	5.916687	2.283716	6	2.235342	6.012266	2.287496
6	2.338094	7.181462	1.674931	6	2.37406	7.292548	1.71272
1	1.455485	7.796313	1.492169	1	1.500768	7.930757	1.570895
6	3.586245	7.671825	1.296821	6	3.622245	7.765834	1.314492
1	3.695139	8.649457	0.825617	1	3.740192	8.754121	0.868341
6	4.714236	6.88459	1.530728	6	4.738037	6.946269	1.491391
6	4.624378	5.628646	2.128174	6	4.636303	5.672799	2.050571
1	5.529904	5.041728	2.287754	1	5.531539	5.059504	2.161294
6	3.365425	5.152272	2.501215	6	3.379117	5.211815	2.444641
1	3.296231	4.173195	2.971722	1	3.30046	4.215875	2.87705
6	-0.22576	4.933676	1.033348	6	-0.20649	4.986821	1.06271
6	-1.58041	4.565129	0.916855	6	-1.55511	4.58653	0.970298
1	-2.21561	4.499785	1.800676	1	-2.17026	4.493142	1.865592
6	-2.15026	4.297958	-0.32723	6	-2.13529	4.313659	-0.26527
1	-3.20318	4.032266	-0.4289	1	-3.18242	4.022226	-0.35345
6	-1.3458	4.377001	-1.46394	6	-1.34405	4.40699	-1.41251
6	0.000497	4.725677	-1.38775	6	0.000986	4.773892	-1.35506
1	0.597108	4.786635	-2.2988	1	0.583273	4.843369	-2.27472
6	0.552749	5.005479	-0.13671	6	0.56618	5.058698	-0.11362
1	1.601386	5.299787	-0.08357	1	1.610588	5.368179	-0.07097
6	-0.30494	6.866742	3.258681	6	-0.29599	6.94614	3.29149
6	-1.52714	7.329693	2.748369	6	-1.57453	7.33319	2.857998
1	-2.03656	6.790532	1.949919	1	-2.10636	6.754939	2.102975
6	-2.09352	8.518428	3.215747	6	-2.1715	8.494417	3.349652
1	-3.03407	8.896266	2.812928	1	-3.15596	8.816119	3.007905
6	-1.42268	9.241406	4.198851	6	-1.47734	9.264183	4.281626
6	-0.19804	8.818985	4.717018	6	-0.19948	8.915444	4.723064
1	0.312182	9.429542	5.463196	1	0.321663	9.559479	5.432475
6	0.349097	7.626251	4.247325	6	0.380999	7.749746	4.229479
1	1.322439	7.308838	4.627701	1	1.390021	7.487247	4.553688
6	1.966007	2.172315	1.960424	6	2.047957	2.120614	1.953268
1	1.629296	3.051646	1.413836	1	1.790173	3.024022	1.401802
6	2.734635	1.199703	1.329975	6	2.769135	1.103785	1.346027
1	3.009619	1.33151	0.283253	1	3.09922	1.220208	0.314106
6	3.138712	0.079187	2.056962	6	3.043666	-0.0622	2.08112
1	3.750735	-0.69877	1.599047	1	3.602499	-0.88514	1.634176
6	2.722086	-0.03582	3.379782	6	2.574544	-0.15774	3.381072
1	2.996441	-0.91744	3.957411	1	2.755103	-1.06544	3.955481
6	1.937156	0.967706	3.962417	6	1.846909	0.901658	3.959211

6	1.379994	0.862127	5.318654	6	1.305776	0.864741	5.303386
6	1.647055	-0.20085	6.192058	6	1.544372	-0.17488	6.224747
1	2.335345	-0.99332	5.901369	1	2.186257	-1.00982	5.946569
6	1.029379	-0.24606	7.438932	6	0.973376	-0.13601	7.486315
1	1.231275	-1.07031	8.124218	1	1.158325	-0.94128	8.1983
6	0.150274	0.779236	7.791575	6	0.159873	0.956824	7.836437
1	-0.36111	0.785552	8.754293	1	-0.31677	1.023984	8.813839
6	-0.06621	1.815949	6.88897	6	-0.03676	1.964398	6.905432
1	-0.73291	2.641776	7.13334	1	-0.65242	2.832433	7.13622
6	-1.50948	1.737957	2.654774	6	-1.45778	1.660388	2.61764
1	-0.58906	1.419102	2.170575	1	-0.53057	1.346531	2.142686
6	-2.73237	1.178219	2.302445	6	-2.66584	1.091776	2.266609
1	-2.76583	0.402415	1.537341	1	-2.69143	0.306958	1.511609
6	-3.89184	1.629234	2.935523	6	-3.84708	1.547067	2.900075
1	-4.86765	1.212385	2.683367	1	-4.81503	1.115889	2.642149
6	-3.77809	2.623176	3.903638	6	-3.75783	2.539126	3.856035
1	-4.66871	2.98796	4.413854	1	-4.65746	2.895965	4.356412
6	-2.51999	3.146916	4.227146	6	-2.50402	3.093864	4.200689
6	-2.29939	4.179331	5.244169	6	-2.30107	4.103728	5.196454
6	-3.32497	4.775868	5.987824	6	-3.32519	4.673436	5.988066
1	-4.36258	4.495563	5.810666	1	-4.35318	4.334212	5.864941
6	-3.0199	5.725399	6.958894	6	-3.0262	5.646403	6.922378
1	-3.81272	6.19382	7.543114	1	-3.81474	6.080241	7.538181
6	-1.68069	6.060006	7.166724	6	-1.68734	6.06516	7.071093
1	-1.3884	6.795476	7.916414	1	-1.40619	6.824945	7.799424
6	-0.70258	5.445455	6.392935	6	-0.71436	5.485447	6.273292
1	0.350832	5.683223	6.521789	1	0.330902	5.775877	6.361869
15	0.509829	5.291581	2.701156	15	0.539077	5.406408	2.70412
7	2.012051	4.227253	5.247724	7	2.053845	4.205811	5.163062
6	2.941084	4.593348	5.850294	6	2.980601	4.52734	5.789626
6	4.108261	5.066609	6.564109	6	4.142093	4.935473	6.546395
1	4.698891	5.735337	5.919526	1	4.781126	5.584832	5.928491
1	3.815483	5.618421	7.469711	1	3.840601	5.4905	7.447171
1	4.742486	4.219518	6.864735	1	4.725279	4.054646	6.853324
9	5.922243	7.350442	1.17292	9	5.943819	7.39544	1.113302
9	-1.96073	10.38768	4.652742	9	-2.04549	10.38269	4.758258
9	-1.88756	4.109276	-2.66388	9	-1.89376	4.130488	-2.60234

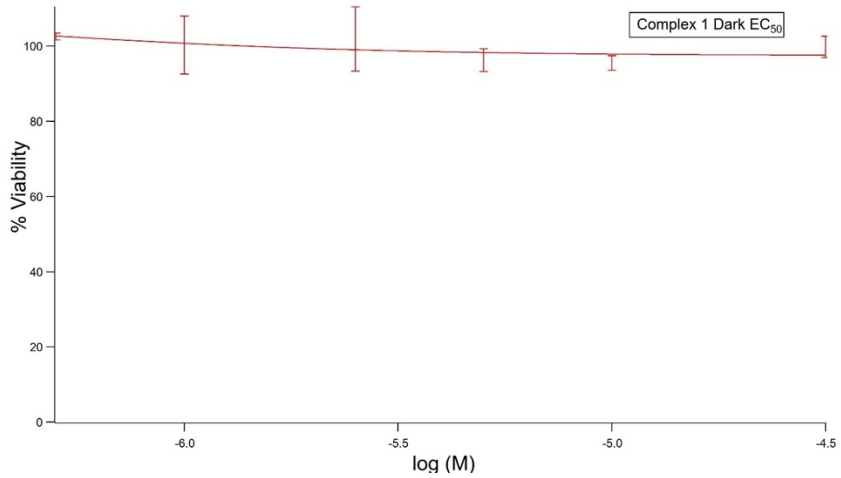
Table S12. Optimized atomic coordinates (x,y,z) for ^{1}GS and ^{3}MLCT excited state of **5** using PBE

^{1}GS				^{3}MLCT			
44	7.076493	16.15682	2.560078	44	7.265496	16.27626	2.678039
15	7.428251	17.70799	4.375031	15	7.510932	17.91705	4.516669
7	8.297575	17.25456	1.391958	7	8.81857	17.14502	1.653617
7	5.631953	15.02839	3.53099	7	5.591122	15.38096	3.392345
7	8.62706	14.80862	3.012631	7	8.633513	14.7768	3.284642
7	6.992117	14.80175	0.927093	7	7.150963	14.87505	1.066432
7	5.335701	17.14523	2.001392	7	5.803013	17.49267	1.857006
9	4.552061	23.80683	3.370073	9	3.634283	23.49637	4.233609
6	8.990419	17.83131	0.652034	6	9.682871	17.58818	1.0119
6	6.354646	19.2276	4.281694	6	6.212095	19.23434	4.59011
6	7.167693	17.02682	6.087115	6	7.471364	17.12346	6.196616
9	3.048843	22.96922	4.727955	9	2.48735	22.3803	5.731711
6	8.886177	13.86104	2.053085	6	8.889687	13.81069	2.330649
6	9.111601	18.49565	4.492691	6	9.114116	18.85153	4.528429
9	3.030817	22.42756	2.602841	9	2.229456	21.93809	3.599358
6	8.205618	17.01402	7.033614	6	8.478057	17.38586	7.141359
9	13.07033	21.23438	5.884998	9	12.85052	22.11111	5.268188
6	6.695244	20.20387	3.327284	6	6.226177	20.25681	3.624067
6	4.332065	15.39214	3.286551	6	4.39599	16.08019	3.164552
6	5.922773	16.47424	6.443275	6	6.407616	16.27147	6.545954
6	10.33486	13.81094	4.402559	6	10.29184	13.77365	4.721317
6	10.23512	17.94894	3.854829	6	10.3103	18.17656	4.2261
6	5.717938	15.94095	7.714247	6	6.352449	15.69368	7.813519
1	4.741677	15.53686	7.987162	1	5.517592	15.04487	8.082439
6	5.21593	19.42159	5.074378	6	5.21426	19.23691	5.575753
6	9.336666	14.74997	4.166175	6	9.318465	14.72554	4.452662
9	13.25884	21.05469	3.707928	9	13.35538	21.08188	3.397906
6	9.270811	19.65293	5.276398	6	9.172274	20.19513	4.930155
6	7.999525	13.88171	0.8809	6	8.023738	13.81949	1.160232
6	5.90488	21.33847	3.157945	6	5.252453	21.25197	3.63634
1	6.188209	22.10132	2.430744	1	5.278028	22.0512	2.893881
6	5.863016	13.93124	4.287274	6	5.543495	14.16243	3.996112
1	6.906592	13.68181	4.466435	1	6.496627	13.64947	4.113674
6	4.414885	20.55405	4.89813	6	4.231364	20.22991	5.581507
6	5.260783	18.23406	1.202278	6	5.977606	18.47431	0.939505
6	4.166613	16.58768	2.453824	6	4.514038	17.23047	2.32703
6	10.52312	20.25357	5.41054	6	10.39922	20.86274	4.992217
6	11.63395	19.70005	4.766216	6	11.57817	20.18744	4.67197

6	11.48982	18.54596	3.989833	6	11.53462	18.83722	4.301295
6	4.751639	21.50617	3.9338	6	4.245505	21.2318	4.609213
6	9.869648	18.56153	-0.23649	6	10.76483	18.15573	0.241326
1	9.290093	19.1825	-0.93571	1	10.37061	18.70033	-0.6298
1	10.48637	17.86376	-0.8222	1	11.43993	17.36325	-0.11391
1	10.53726	19.21546	0.345165	1	11.33729	18.85898	0.866151
6	8.0065	16.46392	8.302796	6	8.423624	16.80145	8.408492
9	13.98125	19.44411	5.006151	9	13.85869	20.16529	5.323918
6	6.103038	14.84966	-0.08657	6	6.263264	14.92248	0.049779
1	5.319921	15.60216	-0.00697	1	5.591984	15.78008	0.036395
6	6.169262	13.99905	-1.18589	6	6.210322	13.94946	-0.93813
1	5.42193	14.07822	-1.97557	1	5.489856	14.04166	-1.75052
6	10.63313	12.876	3.410415	6	10.60733	12.82973	3.732474
1	11.41629	12.13101	3.555853	1	11.38756	12.08583	3.897658
6	9.890045	12.90071	2.233995	6	9.898448	12.85263	2.540635
1	10.082	12.16009	1.458866	1	10.12035	12.12186	1.763771
6	4.841824	13.15481	4.823645	6	4.369824	13.61759	4.475917
1	5.0926	12.28068	5.424868	1	4.389015	12.64437	4.965197
6	2.924763	17.13922	2.115667	6	3.433789	18.04329	1.903613
1	2.006333	16.6886	2.489904	1	2.435501	17.86043	2.300315
6	3.265837	14.64823	3.807614	6	3.184265	15.56583	3.682491
6	6.763172	15.92905	8.644852	6	7.364685	15.95307	8.74411
6	7.203571	13.06411	-1.25098	6	7.097149	12.86462	-0.86251
1	7.293061	12.38707	-2.10151	1	7.074945	12.07539	-1.61513
6	3.516041	13.51847	4.581911	6	3.162959	14.34942	4.333604
6	8.12386	13.00811	-0.20772	6	7.995369	12.79778	0.193682
1	8.936855	12.28421	-0.24304	1	8.666973	11.94454	0.280338
6	3.844858	22.69279	3.672082	6	3.14503	22.27561	4.556801
6	2.861298	18.26514	1.299312	6	3.634984	19.04012	0.971802
1	1.898555	18.70341	1.034022	1	2.801016	19.65641	0.634506
6	4.054398	18.81706	0.829933	6	4.935828	19.24598	0.455562
1	4.058268	19.69787	0.187616	1	5.132466	20.00234	-0.30371
6	12.99599	20.36562	4.853724	6	12.91914	20.90007	4.678713
6	6.54196	15.27973	9.99876	6	7.335374	15.26047	10.09629
9	5.317757	15.58315	10.49631	9	8.025607	15.95255	11.02909
9	6.608386	13.92142	9.884567	9	6.065667	15.10015	10.54068
9	7.47111	15.66156	10.90195	9	7.895433	14.02199	9.998734
1	6.211464	18.6377	0.861344	1	6.999136	18.625	0.592249
1	9.177272	17.44782	6.795854	1	9.304201	18.05559	6.903398
1	9.078652	15.48468	4.92686	1	9.050461	15.47165	5.199547
1	5.095137	16.46488	5.733811	1	5.608405	16.0608	5.836817

1	2.23902	14.94876	3.602759	1	2.259981	16.12473	3.538268
1	10.86689	13.82381	5.354103	1	10.79434	13.77816	5.688416
1	10.13817	17.05496	3.241668	1	10.29514	17.12444	3.941549
1	12.36078	18.10955	3.49764	1	12.46089	18.30241	4.082649
1	4.953348	18.71228	5.858815	1	5.202092	18.48007	6.359543
1	3.536711	20.7029	5.527897	1	3.463259	20.23107	6.355857
1	8.818479	16.4672	9.031154	1	9.201899	17.01979	9.141146
1	7.603352	20.09613	2.730658	1	7.01148	20.29583	2.867768
1	10.63616	21.14973	6.021915	1	10.43467	21.90824	5.300884
1	2.69038	12.93154	4.986161	1	2.225245	13.9466	4.717812
1	8.414664	20.09662	5.787058	1	8.265115	20.73378	5.203272

EC_{50} Curves



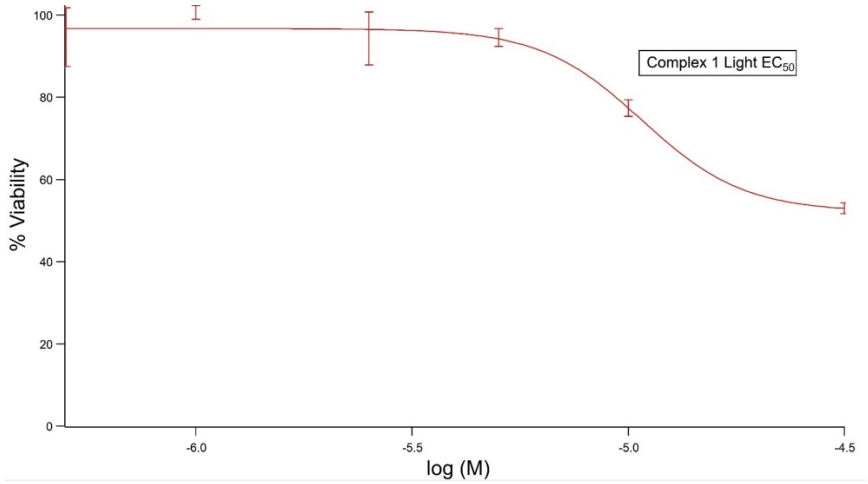
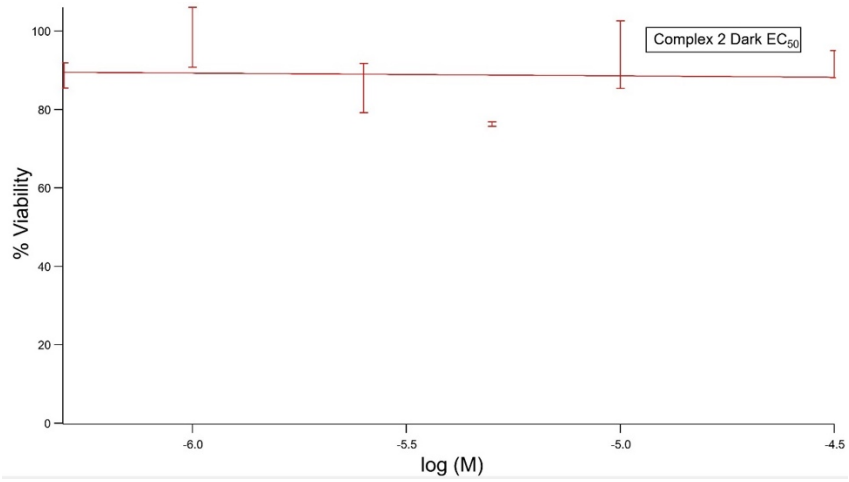


Figure S13. EC_{50} curves of **1** kept in the dark (top) and upon irradiation (bottom, t_{irr} = 20 min, λ_{irr} = 460–470 nm, 56 J/cm). Data are representative of three different experiments.



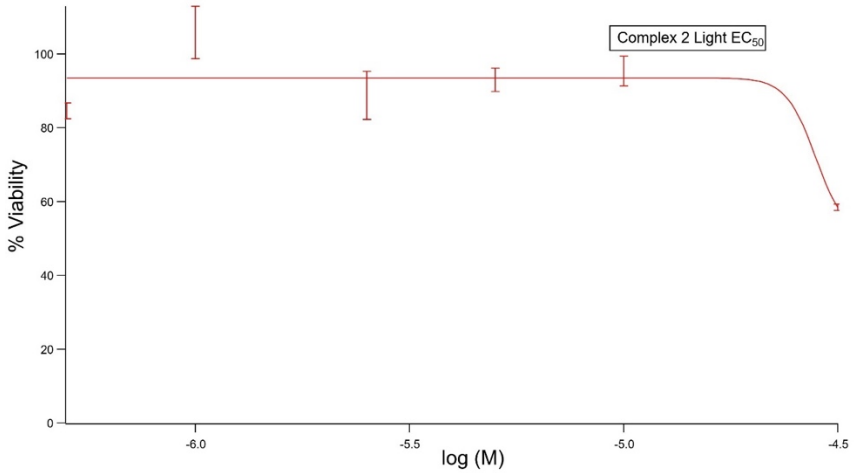


Figure S14. EC_{50} curves of **2** kept in the dark (top) and upon irradiation (bottom, t_{irr} = 20 min, λ_{irr} = 460–470 nm, 56 J/cm). Data are representative of three different experiments.

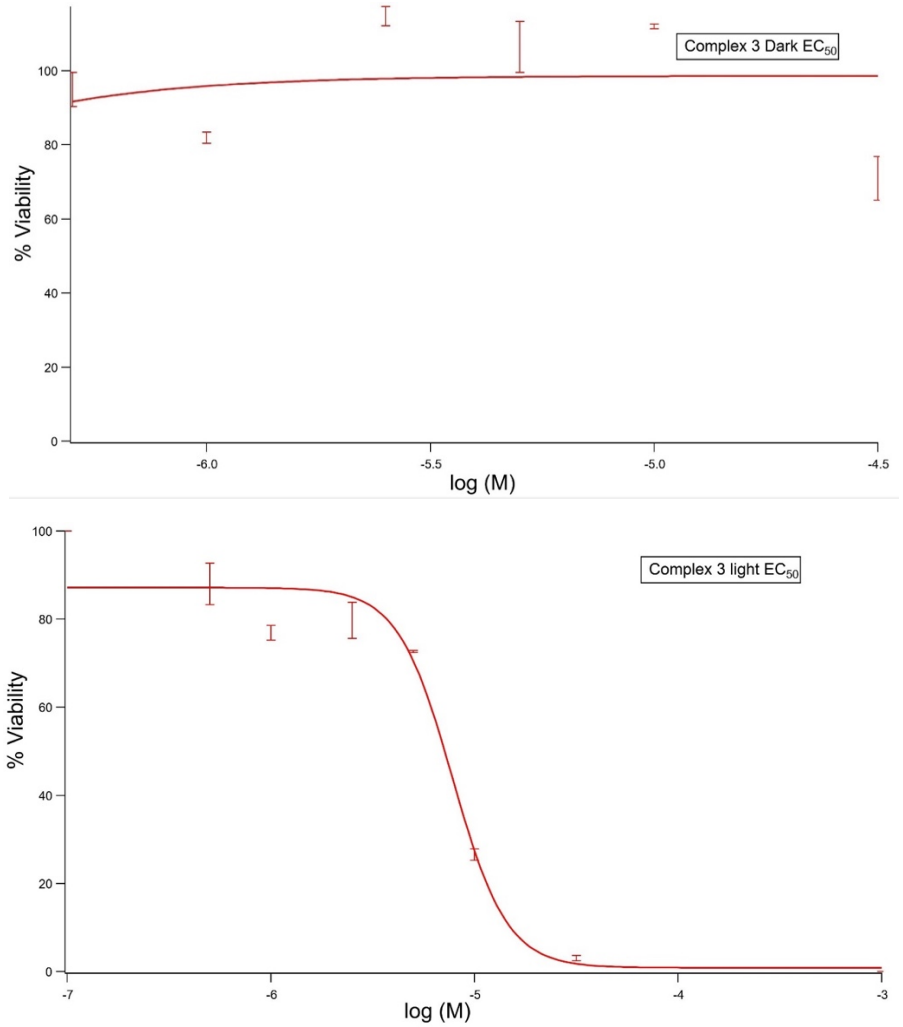


Figure S15. EC_{50} curves of **3** kept in the dark (top) and upon irradiation (bottom, t_{irr} = 20 min, λ_{irr} = 460–470 nm, 56 J/cm). Data are representative of three different experiments.

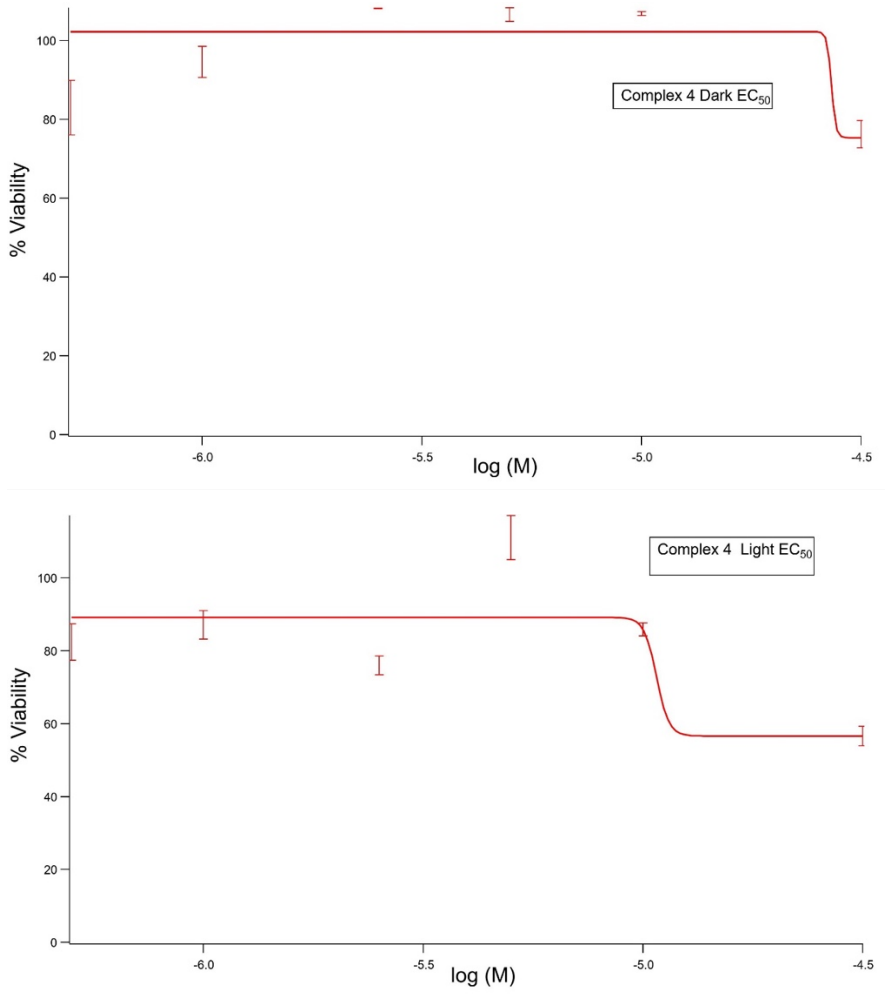


Figure S16. EC_{50} curves of **4** kept in the dark (top) and upon irradiation (bottom, t_{irr} = 20 min, λ_{irr} = 460–470 nm, 56 J/cm). Data are representative of three different experiments.

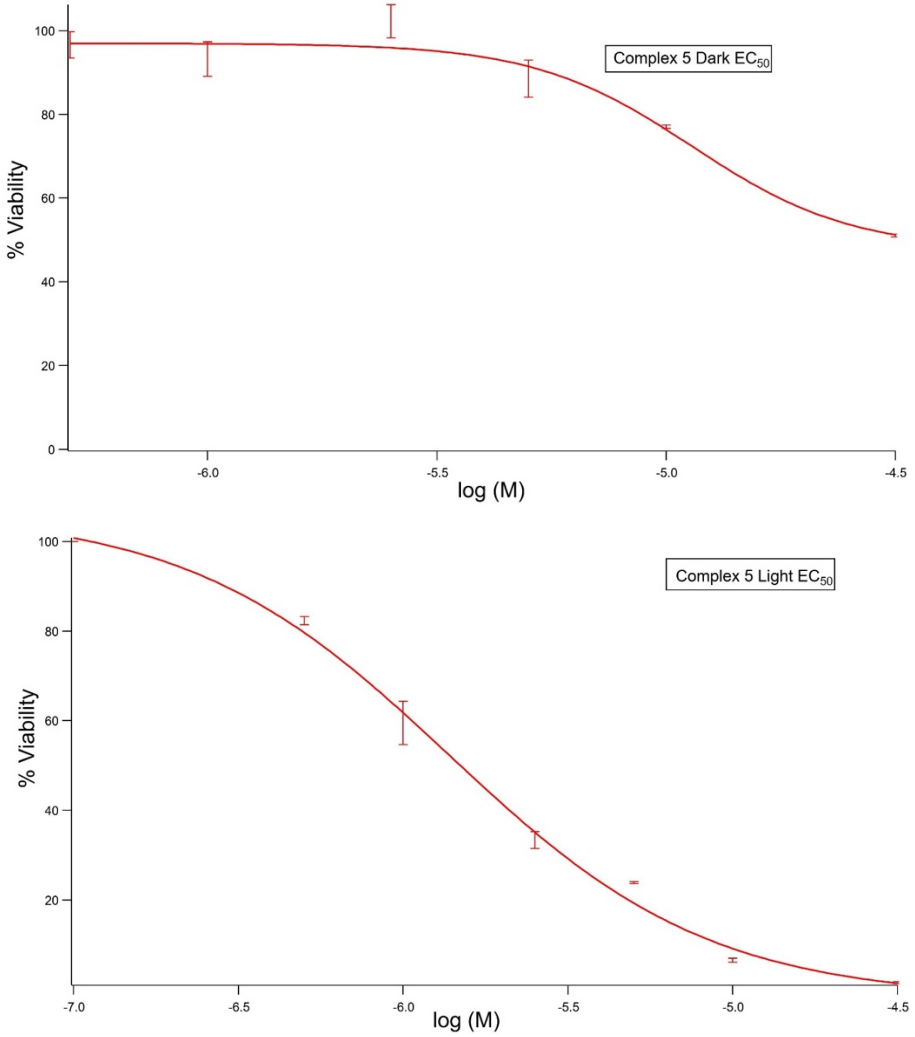


Figure S17. EC_{50} curves of **5** kept in the dark (top) and upon irradiation (bottom, t_{irr} = 20 min, λ_{irr} = 460–470 nm, 56 J/cm). Data are representative of three different experiments.

Cell Death Mechanism Studies

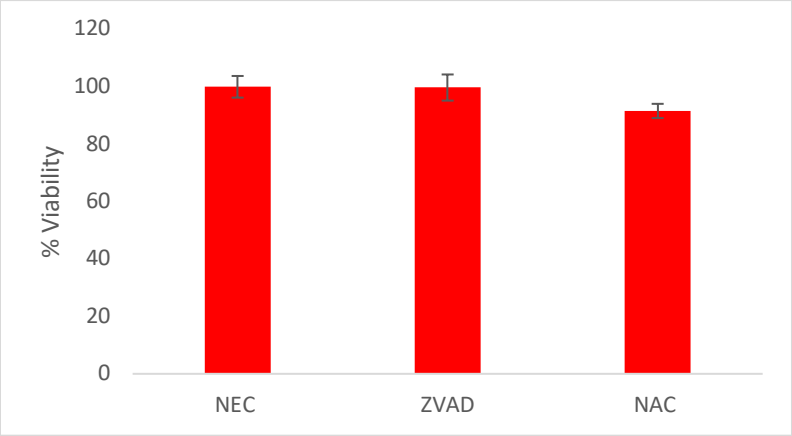


Figure S18. Viability of MDA-MB-231 cells when treated with necrostatin (NEC), ZVAD-FMK (ZVAD) or N-acetyl cysteine (NAC) followed by irradiation (t_{irr} = 20 min, λ_{irr} = 460–470 nm, 56 J/cm^2). Data are representative of three different experiments.

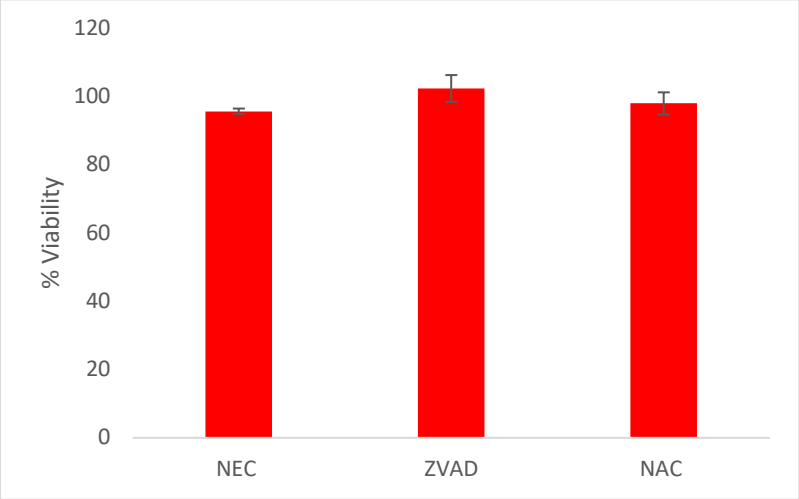


Figure S19. Viability of MDA-MB-231 cells when treated with nectrostatin (NEC), ZVAD-FMK (ZVAD) or N-acetyl cysteine (NAC) and kept in the dark. Data are representative of three different experiments

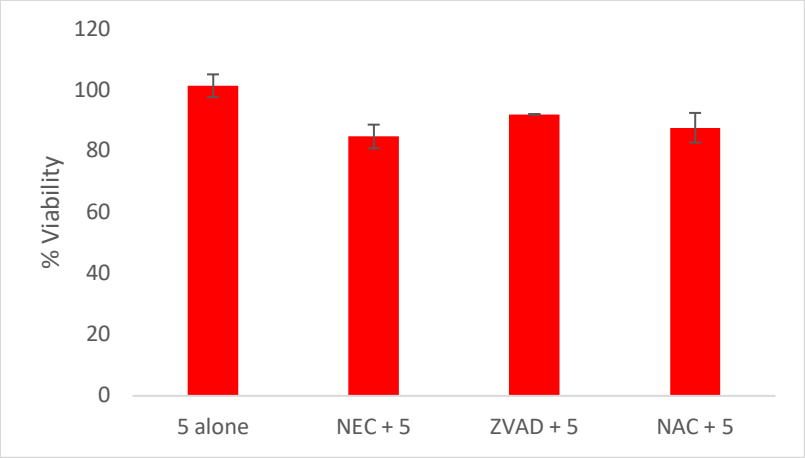


Figure S20. Viability of MDA-MB-231 cells when treated with complex **5** (2 μM) alone and co-treated with Necrostatin (NEC), Z-VAD-FMK (ZVAD), N-Acetyl Cysteine (NAC) and complex **5** (2 μM) and kept in the dark. Data are representative of three different experiments.