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Electronic Supporting Information

Anionic cyclometallated Pt(II) and Pt(IV) complexes respectively bearing one or two 1,2-benzenedithiolate ligands

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Calculated geometries

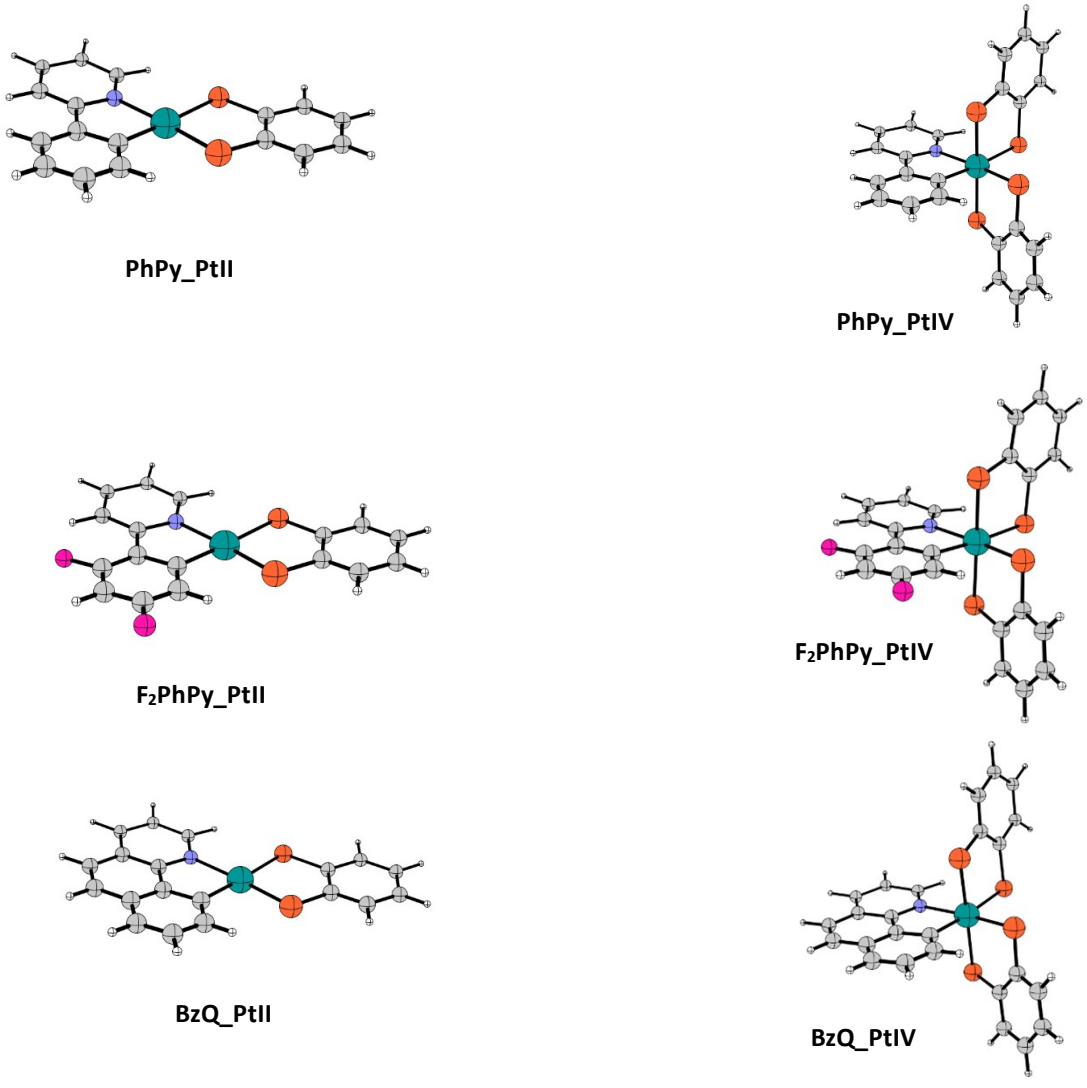


Figure ESI1. Calculated geometrical structures of **1a-c** and **2a-c** complexes

Table ESI1. Main calculated structural parameters: bond lengths (Å) and valence angles (degrees), for **1a-c** and **2a-c** complexes compared with available experimental data

	PhPy_PtII	F_2PhPy_PtII	BzQ_PtII	X-ray	PhPy_PtIV	F_2PhPy_PtIV	BzQ_PtIV	X-ray
Pt-S1	2.422	2.428	2.416	2.306	1.801	1.783	2.358	2.341
Pt-S2	2.321	2.312	2.316	2.280	1.842	1.780	2.412	2.374
Pt-N	2.100	2.050	2.112	2.068	2.022	2.023	2.156	2.140
Pt-C	2.033	2.037	2.040	2.023	2.320	2.216	2.073	2.122
Pt-S3					2.181	2.206	2.484	2.422
Pt-S4					2.172	2.146	2.409	2.369
S1-Pt-S2			88.5	88.9			87.7	89.2
N-Pt-C			80.4	81.6			79.8	81.3
N-Pt-S1			95.6	95.4			91.1	93.3
C-Pt-S2			95.8	94.1			94.6	94.2
S1-Pt-S3							92.7	91.5
S3-Pt-S4							88.3	88.9

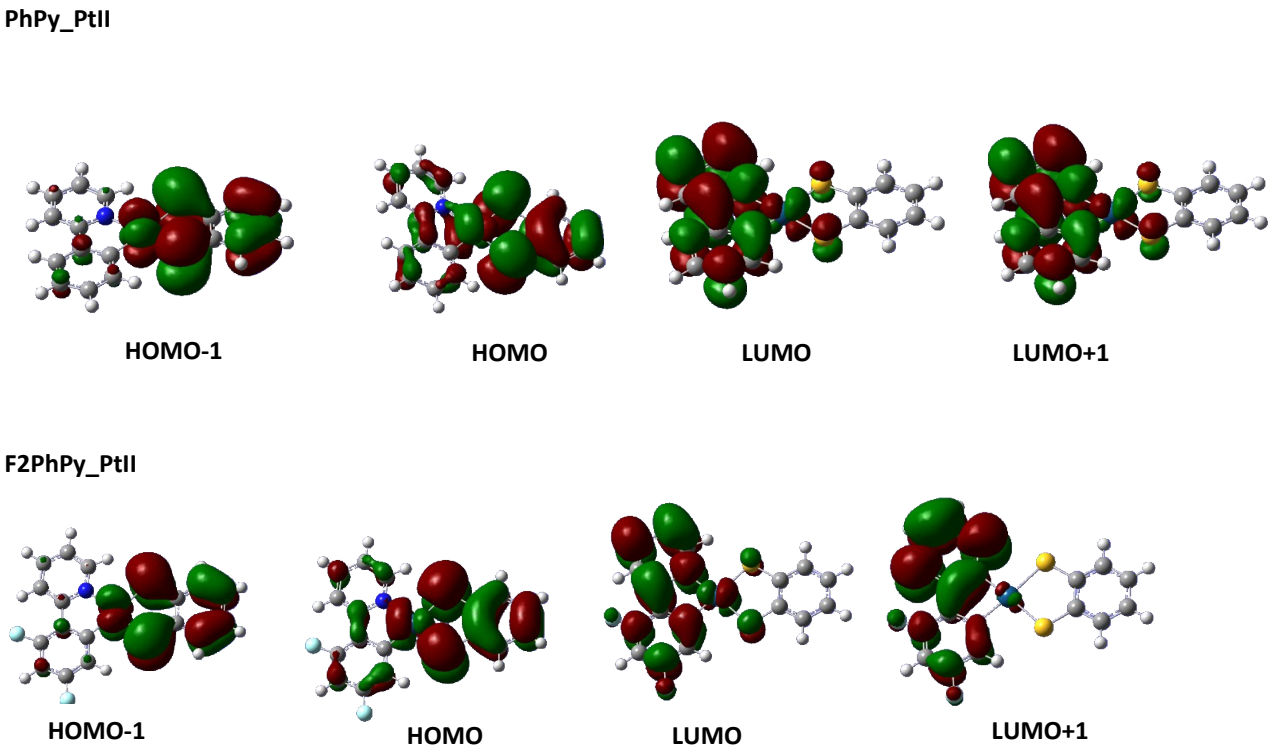


Figure ESI2. Graphical representation of the highest occupied and lowest unoccupied MOs for the **1a,b** complexes

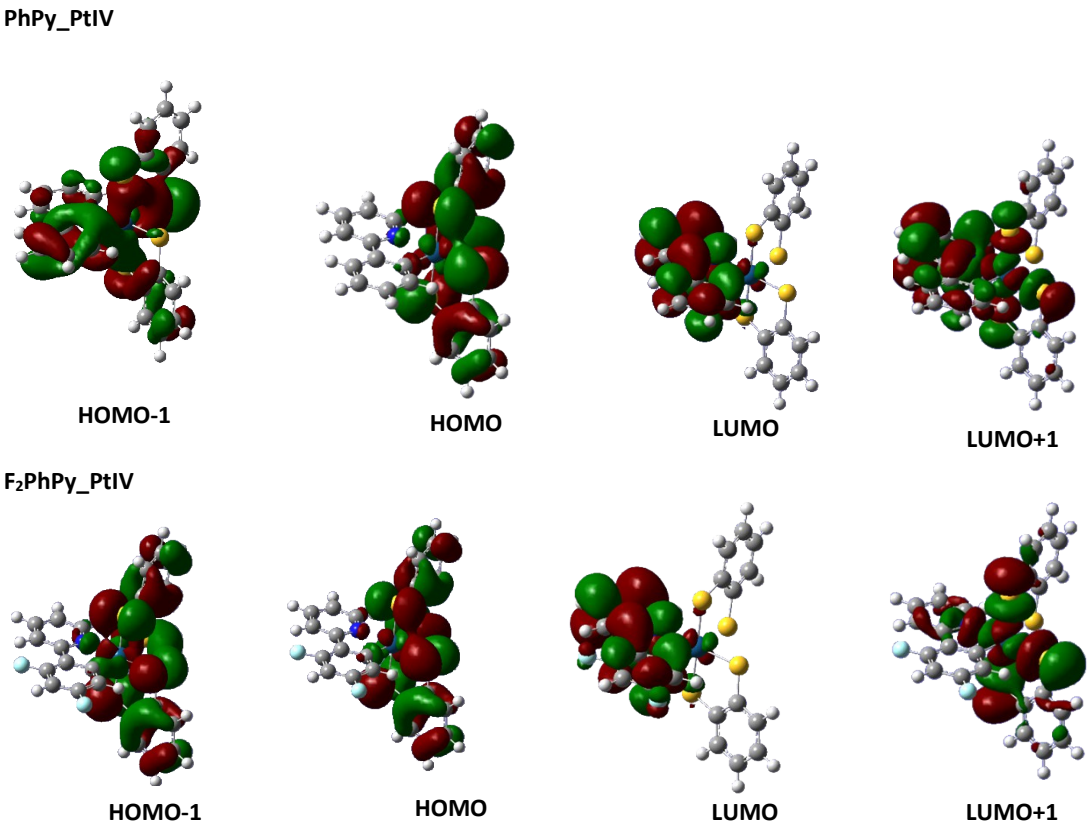


Figure ESI3. Graphical representation of the highest occupied and lowest unoccupied MOs for the **2a,b** complexes

Electrochemistry

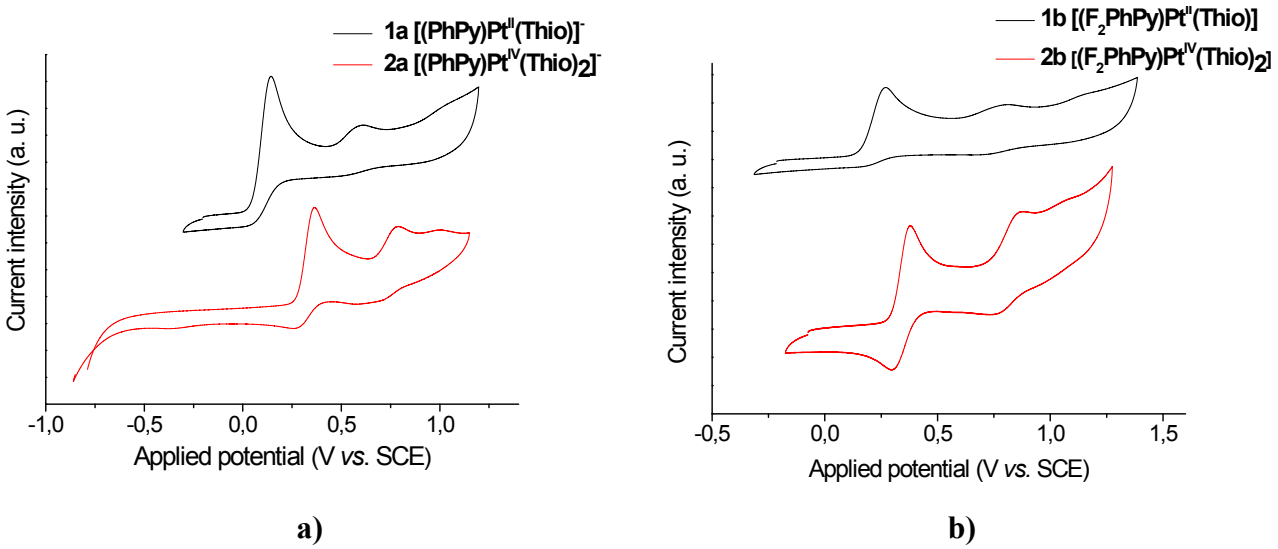
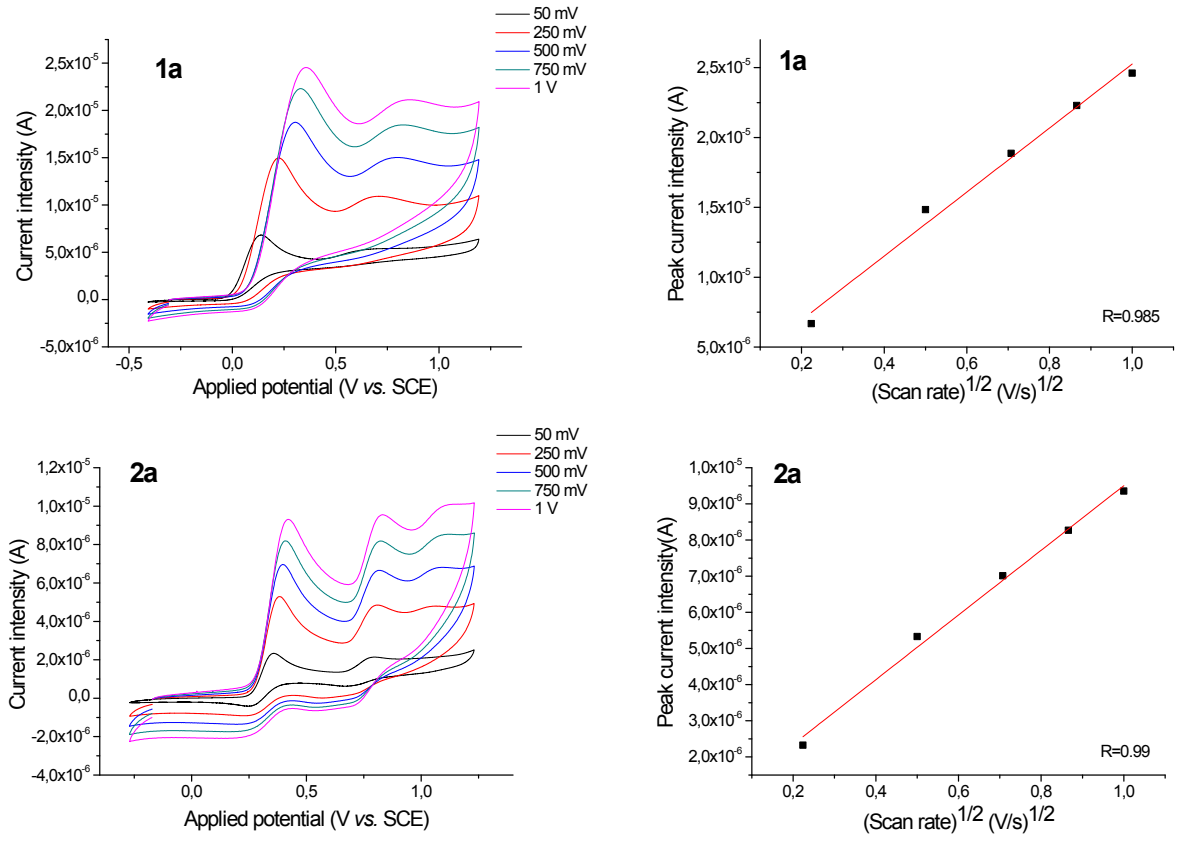


Figure ESI4. Cyclic voltammetry of **a) 1a** $[(PhPy)Pt^{II}(Thio)]^-$ (black curve) and **2a** $[(PhPy)Pt^{IV}(Thio)_2]^-$ and **b) 1b** $[(F_2PhPy)Pt^{II}(Thio)]^-$ (black curve) and **2b** $[(F_2PhPy)Pt^{IV}(Thio)_2]^-$ (red curve). Scan rate 100 mV/s



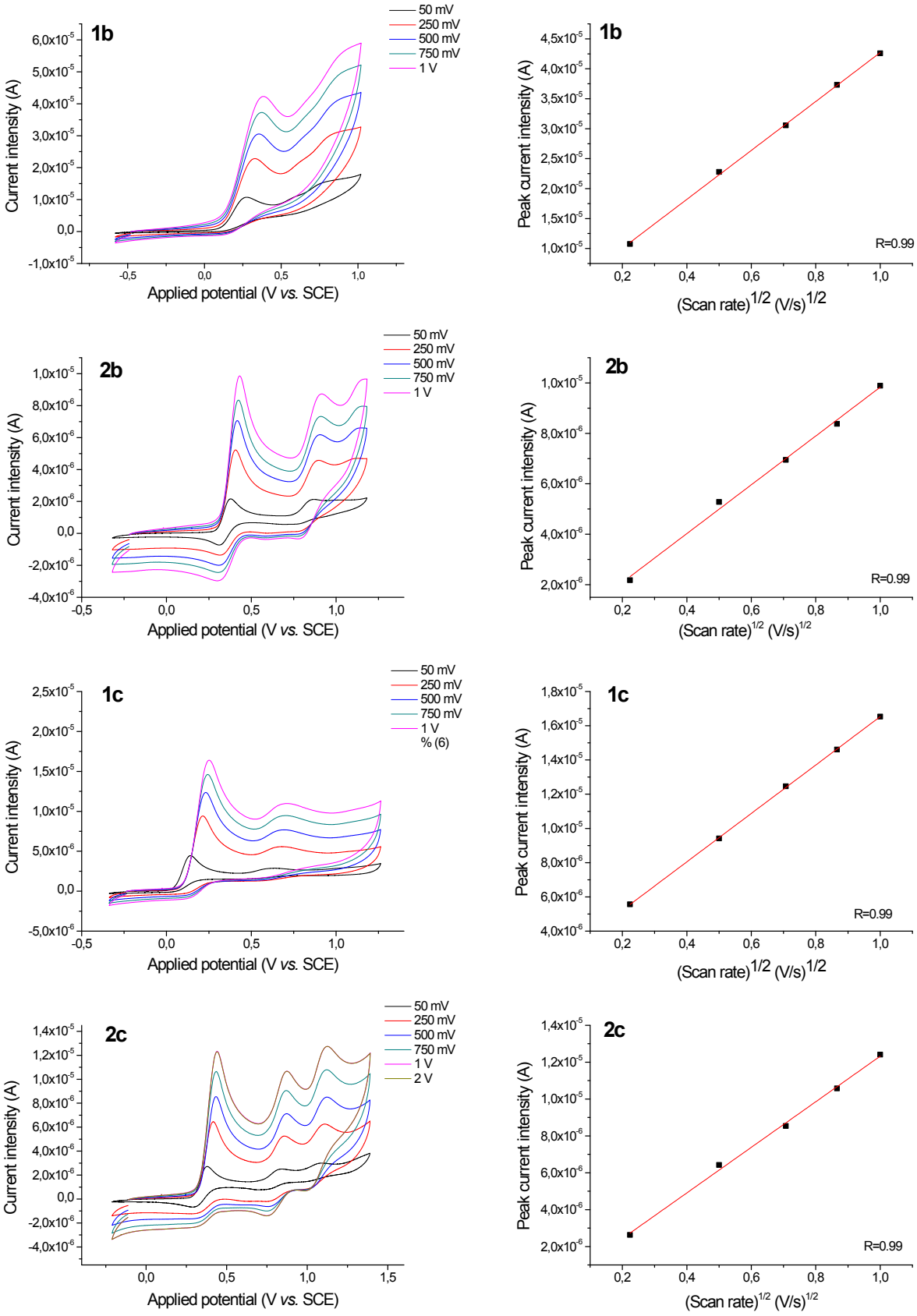


Figure ESI5. Scan rate (50, 250, 500, 750 mV and 1 V) dependencies (left column) and linearity of scan rate of current intensity (right column) of **1,2a-c** complexes

Table ESI2. Main vertical singlet excitation energies ΔE (eV), oscillator strengths f, wavelength λ (nm), and MO contribution to the transitions (%) for all the investigated compounds computed in DMSO solvent

	λ_{abs}/nm	ΔE/eV	*f*	MO contribution
1a	478	2.59	0.1432	H-1→L (3%),H→L (97%),
	433	2.86	0.0229	H-1->L (94%) H->L (3%)
	351	3.52	0.0306	H-1->L+1 (94%) H-3->LUMO (3%)
	310	3.99	0.0962	HOMO->L+3 (90%) H-1->L+6 (4%), HOMO->L+4 (3%)
	293	4.22	0.0451	H-5->LUMO (55%), H-2->L+2 (18%) H-3->L+1 (5%), H-1->L+4 (3%), HOMO->L+4(8%), HOMO->L+6 (3%)
	282	4.39	0.0596	H-6->LUMO (12%), H-5->LUMO (15%), H-3->L+1 (27%), H-2->L+2 (32%) H-4->L+2 (2%), H-2->L+5 (3%), H-1->L+4 (2%)
	275	4.51	0.1661	H-6->LUMO (29%), H-3->L+1 (12%), H-1->L+3 (11%), H-1->L+4 (23%), HOMO->L+6 (16%) H-5->L+1 (3%)
1b	484	2.56	0.227	HOMO->LUMO (98%)
	322	3.84	0.207	H-3->LUMO (90%),H-1->L+1 (2%), HOMO->L+3 (2%)
	314	3.95	0.159	HOMO->L+3 (83%), HOMO->L+4 (11%), H-5->LUMO (2%)
	298	4.156	0.160	H-5->LUMO (80%) H-2->L+2 (5%), H-1->L+3 (6%)
	291	4.25	0.1213	H-2->L+2 (65%), HOMO->L+6 (12%)
	288	4.29	0.1014	H-1->L+3 (46%), HOMO->L+6 (30%) H-6->LUMO (7%), H-5->LUMO (4%), H-2->L+2 (3%), H-1->L+4 (6%)
	282	4.40	0.1206	H-6->LUMO (32%), H-2->L+2 (17%), H-1->L+3 (10%), H-1->L+4 (14%), HOMO->L+6 (15%) H-3->L+1 (6%)
	279	4.44	0.3238	H-6->LUMO (36%), H-1->L+3 (28%), H-1->L+4 (13%) H-5->LUMO (3%), H-3->L+1 (3%), H-1->L+6 (3%), HOMO->L+6 (9%)
1c	515	2.40	0.080	HOMO->LUMO (96%) H-1->LUMO (3%)
	416	2.98	0.126	HOMO->L+1 (96%) H-1->LUMO (2%)
	353	3.51	0.076	H-2->LUMO (92%), H-5->L+1 (2%)
	310	3.99	0.074	HOMO->L+4 (88%) H-5->LUMO (2%), H-2->L+1 (2%), H-1->L+6 (5%)
	287	4.31	0.083	H-7->LUMO (18%), H-6->LUMO (40%), HOMO->L+6 (11%) H-5->LUMO (5%), H-5->L+1 (7%), H-2->L+1 (4%), H-1->L+4 (5%)
2a	558	2.22	0.007	H-1->LUMO (76%), HOMO->LUMO (20%)
	413	3.00	0.011	H-1->L+3 (39%), HOMO->L+3 (53%) H-2->LUMO (6%)
	406	3.05	0.012	H-3->LUMO (50%), H-1->L+3 (25%), HOMO->L+3 (23%)
	336	3.69	0.013	H-5->LUMO (16%), H-4->LUMO (76%) H-6->LUMO (3%)
	328	3.78	0.021	H-5->LUMO (49%), H-4->LUMO (12%),

				H-3->L+3 (15%), H-2->L+3 (11%)
	316	3.92	0.127	H-4->L+1 (90%)
	314	3.94	0.077	H-1->L+4 (18%), HOMO->L+4 (72%) H-3->L+7 (2%)
	307	4.03	0.097	H-3->L+2 (10%), H-1->L+5 (33%), HOMO->L+5 (38%) H-6->LUMO (3%), H-2->L+9 (3%), H-1->L+4 (5%), HOMO->L+4 (3%)
2b	563	2.20	0.007	H-1->LUMO (72%), HOMO->LUMO (24%)
	432	2.87	0.009	H-3->LUMO (26%), H-1->L+2 (33%), H-1->L+3 (17%), HOMO->L+2 (13%)
	428	2.89	0.007	H-2->LUMO (37%), H-1->L+2 (15%), HOMO->L+2 (24%), HOMO->L+3 (13%)
	321	3.86	0.044	H-6->LUMO (28%), H-5->LUMO (32%), H-4->LUMO (32%) H-7->LUMO (2%) H-1->L+4 (17%), HOMO->L+4 (64%)
	315	3.94	0.052	H-2->L+3 (3%), H-1->L+5 (3%), HOMO->L+5 (6%)
	309	4.01	0.085	H-1->L+5 (17%), HOMO->L+4 (12%), HOMO->L+5 (50%) H-6->LUMO (5%), H-5->LUMO (3%), H-4->L+1 (3%),HOMO->L+6 (4%)
	308	4.02	0.082	H-4->L+1 (69%) H-6->LUMO (2%), H-5->LUMO (3%), H-5->L+1 (8%), HOMO->L+5 (6%)
2c	563	2.20	0.008	H-1->L+1 (76%), HOMO->L+1 (22%)
	408	3.03	0.010	H-3->L+1 (47%), H-1->L+3 (30%), HOMO->L+3 (20%)
	356	3.48	0.027	H-4->L+1 (88%) H-4->LUMO (7%)
	352	3.53	0.089	H-4->LUMO (84%) H-6->L+2 (4%), H-4->L+1 (7%)
	321	3.86	0.029	HOMO->L+4 (78%) H-3->L+2 (5%), H-1->L+4 (7%), HOMO->L+5 (5%)

Photophysics

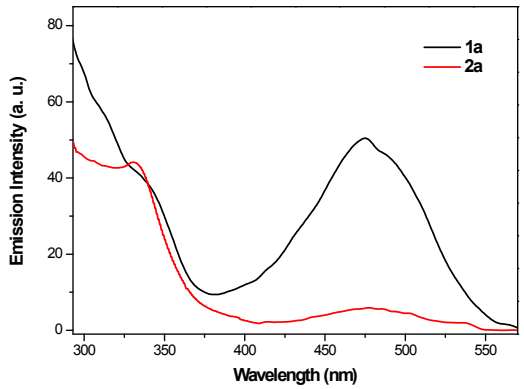


Figure ESI6. Excitation spectra of **1a** and **2a** in DMSO solution at 298K (emission wavelength 645 and 648 nm, respectively)

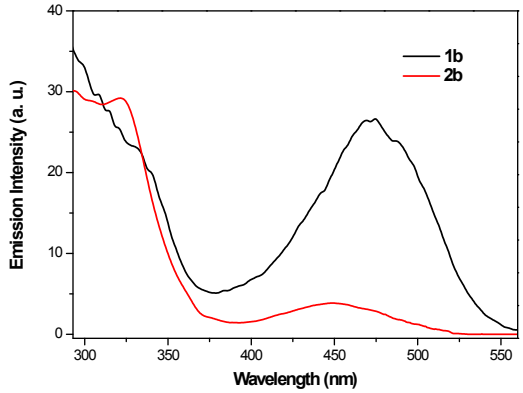


Figure ESI7. Excitation spectra of **1b** and **2b** in DMSO solution at 298K (emission wavelength 649 and 650 nm, respectively)

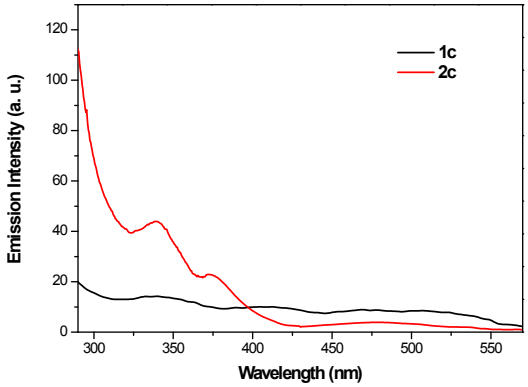


Figure ESI8. Excitation spectra of **1c** and **2c** in DMSO solution at 298K (emission wavelength 690 and 678 nm, respectively