Electronic Supplementary Material (ESI) for Dalton Transactions.

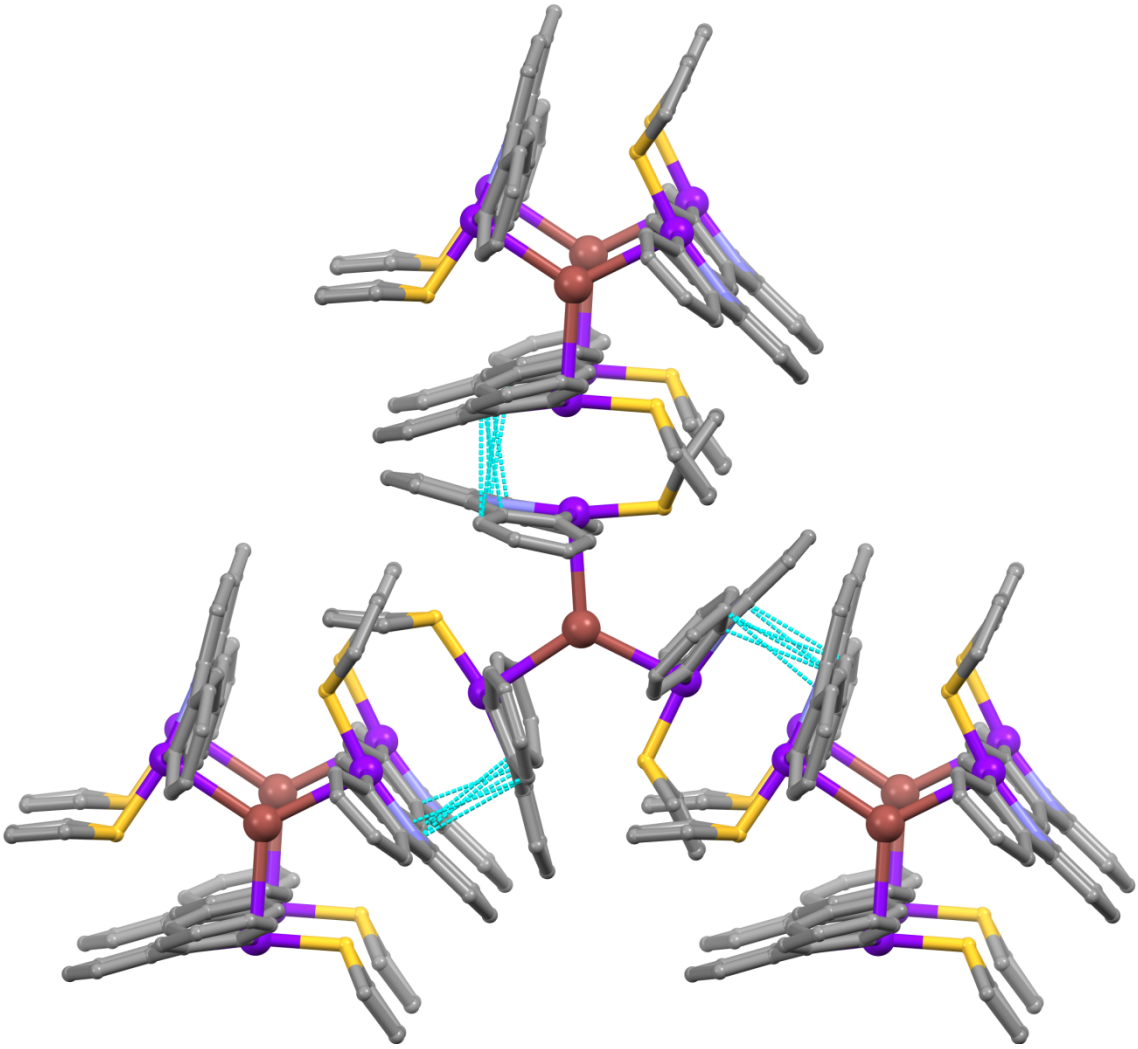
Preparation of Pt–Tl Clusters Showing New Geometries. X-ray, NMR and Luminescence Studies

Úrsula Belío, Sara Fuertes† and Antonio Martín*

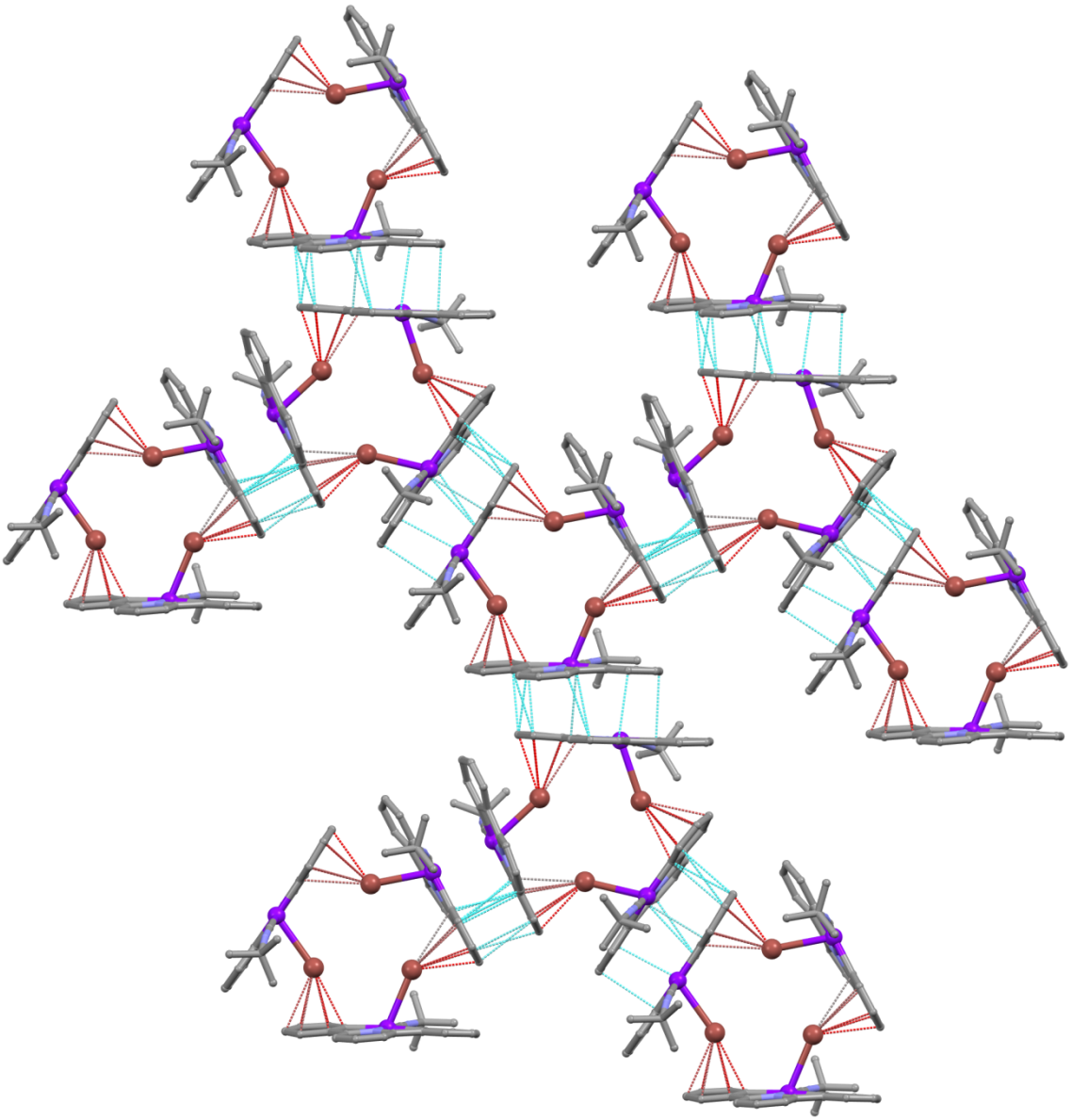
Instituto de Síntesis Química y Catálisis Homogénea (ISQCH). Departamento de Química Inorgánica. Universidad de Zaragoza – CSIC. 50009 Zaragoza, Spain.

† *ARAID Researcher*

SUPPLEMENTARY INFORMATION



a



b

Figure S1. Supramolecular arrangement of the cations of complex **3** (a) and **4** (b). The cyan lines show the intermolecular π···π interactions.

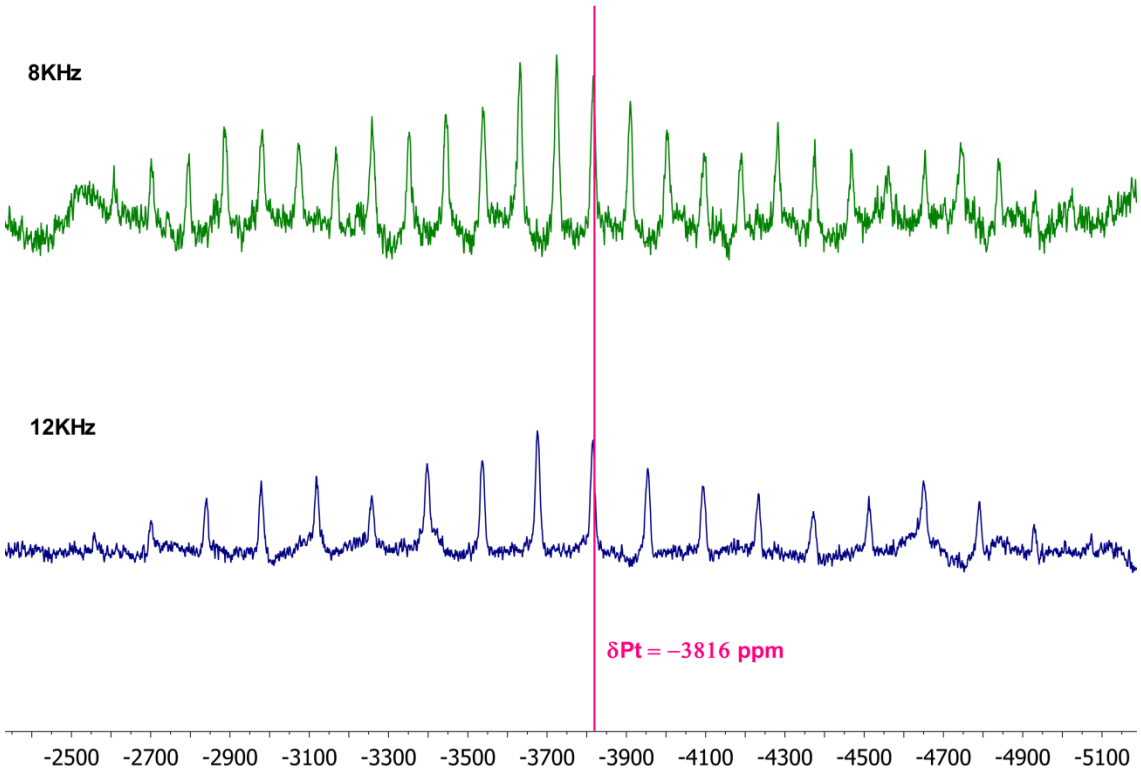


Figure S2. Solid state ^{195}Pt NMR spectra of compound **1** registered at spinning speeds of 8 and 12 kHz.

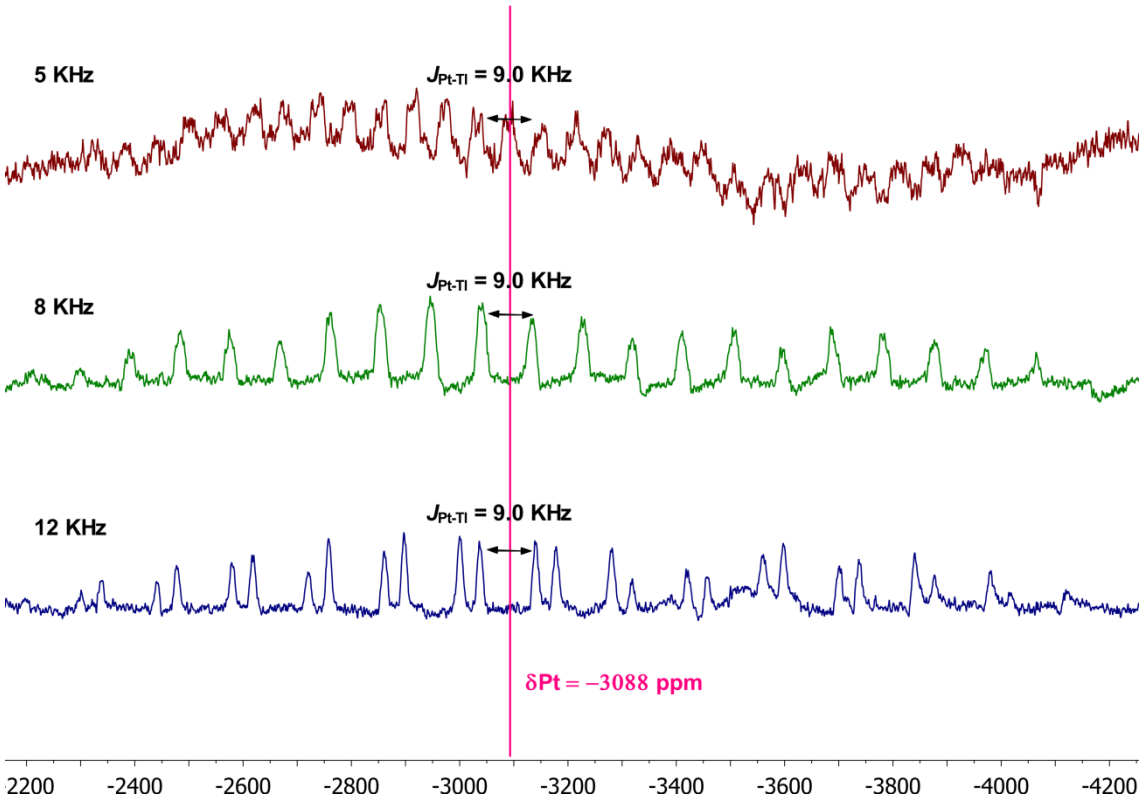


Figure S3. Solid state ^{195}Pt NMR spectra of compound **3** registered at spinning speeds of 5, 8 and 12 kHz.

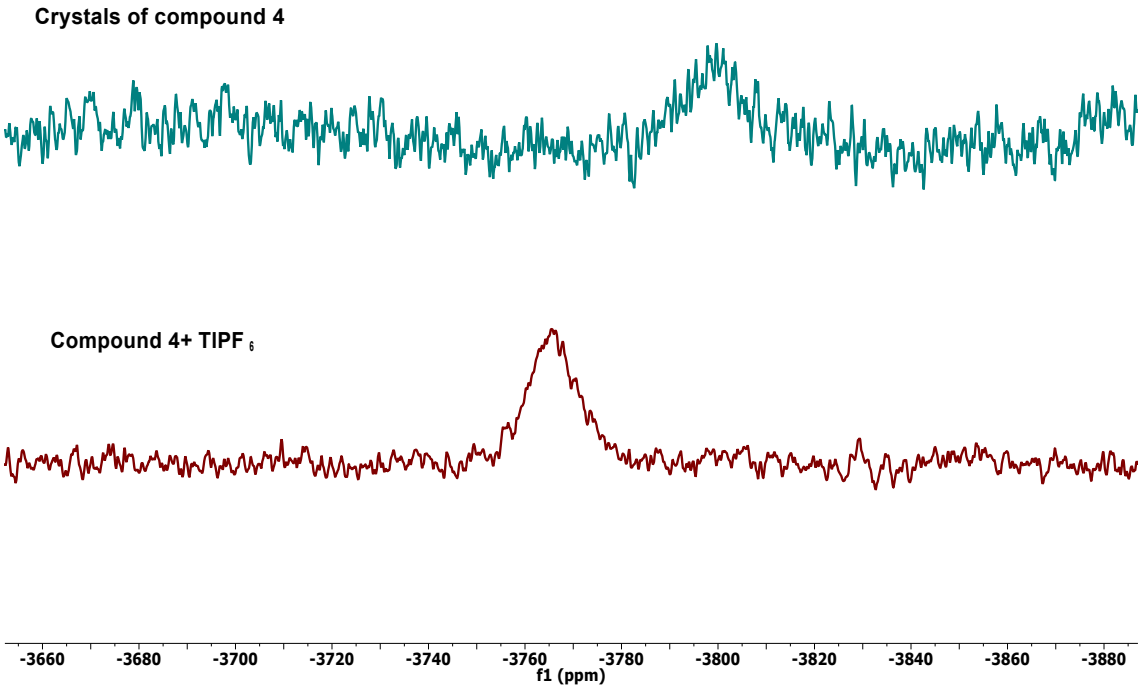


Figure S4. ^{195}Pt NMR spectra of crystals of compound **4** and **4** + $TlPF_6$ exc. in CD_2Cl_2 at room temperature.

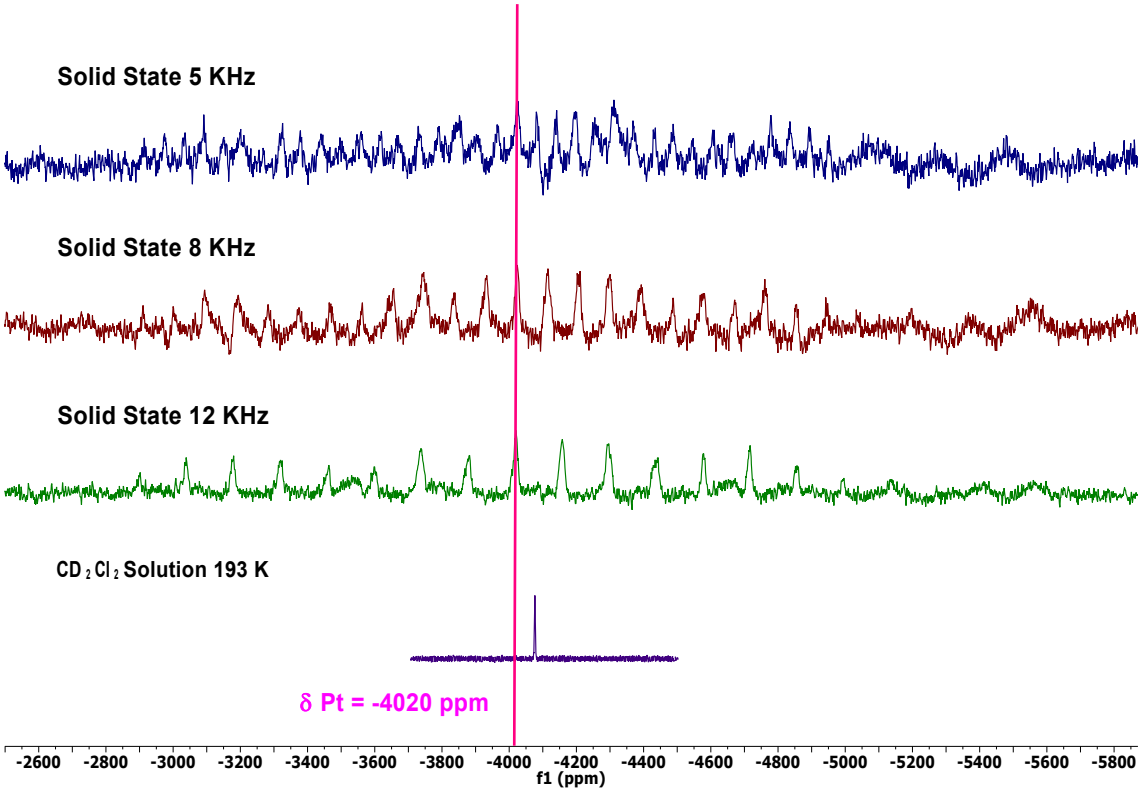


Figure S5. Solid state ^{195}Pt NMR spectra of compound 2 registered at spinning speeds of 5, 8 and 12 kHz. and ^{195}Pt NMR spectra of compound **2** in CD_2Cl_2 at 193K.

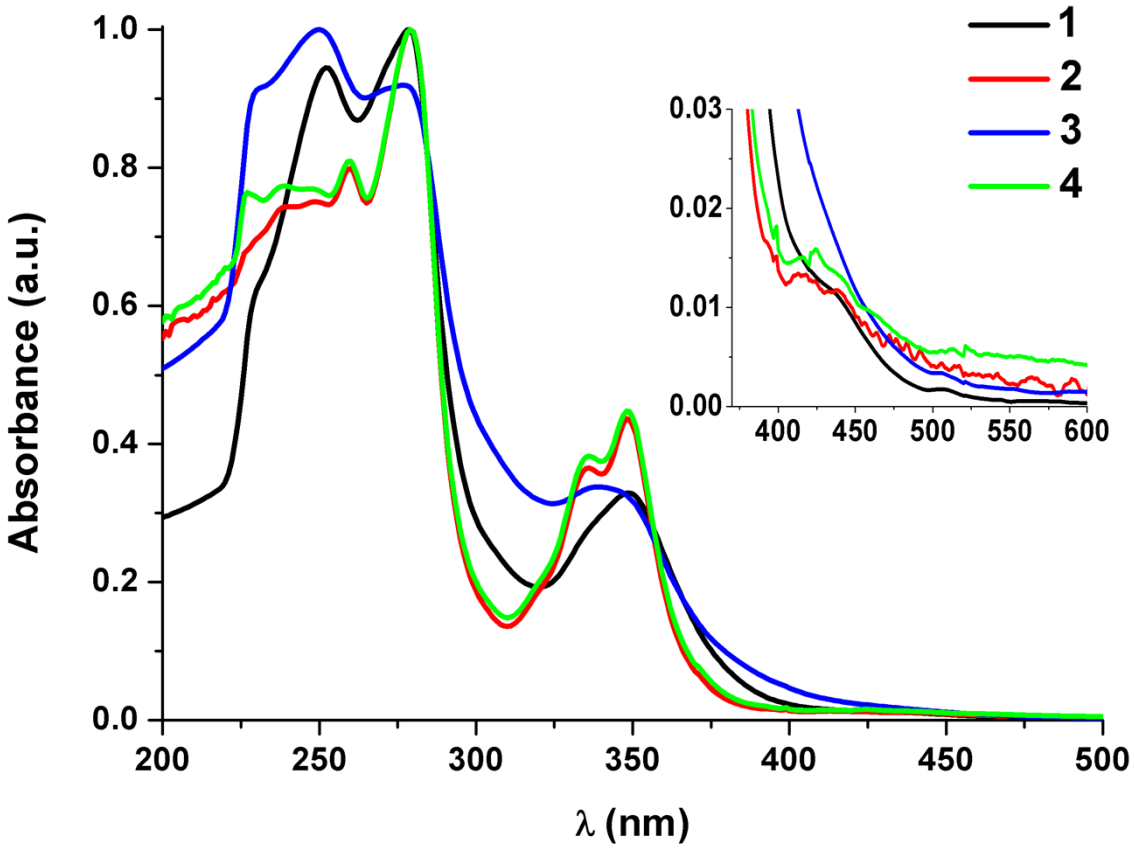


Figure S6. Normalized UV-Vis absorption spectra of **1**-**4** in CH_2Cl_2 at 298 K

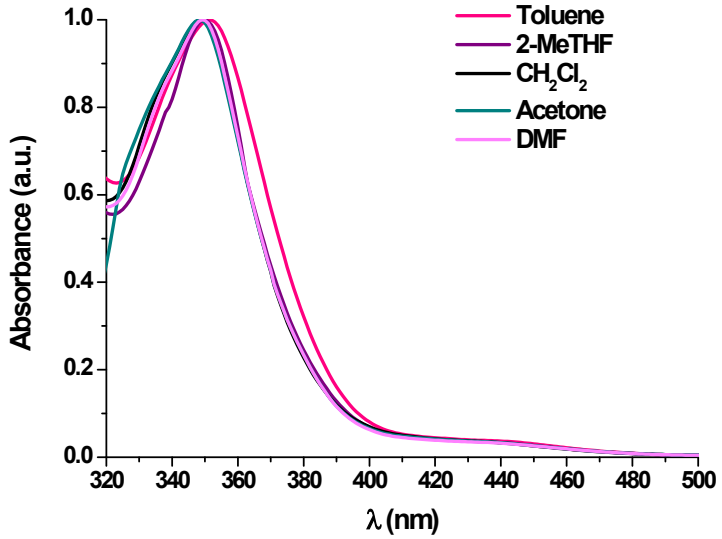


Figure S7. Normalized UV-vis spectra of **1** in different solvents

Table S1. Absorption data for **1-4** in solid state and in solution (10^{-5}M) at 298K.

Comp.	Media	λ_{abs} / nm (10^3 ε M^{-1} cm^{-1})
1	Solid	278, 351, 436, 509
	Toluene	282 (34.1), 304 (9.1), 351 (12.1), 441 (0.3)
	2-Me-THF	271 (105.5), 303 (34.2), 351 (35.5), 436 (1.3)
	CH_2Cl_2	281 (27.6), 300 (20.8), 334 (13.3), 348 (16.2), 435 (0.2)
	Acetone	348 (13.6), 438 (0.3)
	DMF	277 (36.5), 349 (11.9), 434 (0.4)
2	Solid	277, 345, 416, 439, 514
	Toluene	285 (44.4), 338 (19.1), 350 (22.4), 420 (0.7), 443 (0.5)
	2-Me-THF	290 (25.8), 322 (11.9), 336 (16.5), 350 (19.2), 418 (0.6), 442 (0.4)
	CH_2Cl_2	279 (43.7), 318 (6.8), 336 (15.4), 348 (18.7), 414 (0.3), 439 (0.2)
	Acetone	319 (26.6), 336 (16.7), 346 (19.8), 417 (0.5), 437 (0.4)
	DMF	279 (37.1), 319 (7.5), 335 (14.3), 347 (17.0), 417 (0.4), 436(0.3)
3	Solid	277, 347, 432, 512
	Toluene	284 (76.9), 306 (24.7), 352 (33.0), 440 (1.6)
	2-Me-THF	281 (98.6), 339 (32.3), 351 (36.5), 437 (1.4)
	CH_2Cl_2	277 (106.3), 341 (38.6), 430 (0.3)
	Acetone	348 (41.4), 435 (1.1)
	DMF	279 (117.8), 338 (33.9), 349 (39.0), 434 (1.3)
4	Solid	277, 344, 419, 443, 520
	Toluene	285 (39.9), 312 (14.8), 338 (18.9), 350 (21.4), 418 (0.6), 441 (0.5)
	2-Me-THF	278 (63.5), 310 (11.9), 336 (17.9), 349 (18.7) , 416 (0.9), 441 (0.8)
	CH_2Cl_2	278 (37.8), 335 (13.6), 348 (16.2), 413 (0.4), 438 (0.3)
	Acetone	336 (17.6), 346 (23.1), 416 (0.6), 438 (0.5)
	DMF	278 (42.5), 334 (16.1), 347 (18.9), 416 (0.5), 438 (0.4)

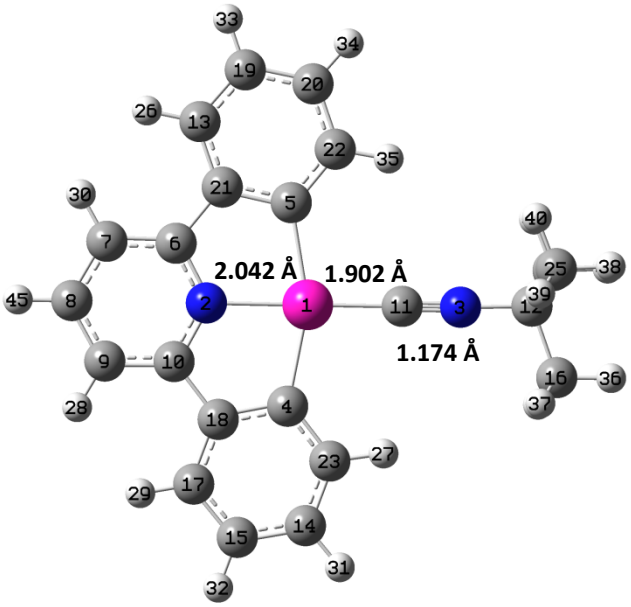


Figure S8. DFT-Optimized structure of [Pt(CNC)(CN^{t}Bu)] (**2**)

Table S2. DFT-Optimized coordinates of **2**, in the Ground State, S_0

Center		Coordinates (Angstroms)	
	X	Y	Z
Pt	0.042705	-0.011545	0.005030
N	-1.998753	0.041599	-0.000999
N	3.118132	-0.084148	0.008046
C	-0.381043	-2.056951	0.002927
C	-0.272536	2.054699	0.003920
C	-2.597777	1.252690	-0.003662
C	-3.991660	1.303603	-0.008549
C	-4.706232	0.111583	-0.010364
C	-4.054552	-1.116149	-0.007560
C	-2.659994	-1.136763	-0.002860
C	1.943992	-0.057842	0.007849
C	4.557515	-0.071861	-0.006454
C	-2.096286	3.706748	-0.003624
C	-0.042791	-4.472775	0.002329
C	-1.416890	-4.698562	-0.000150
C	5.045436	-1.515084	-0.085062
C	-2.285507	-3.615380	-0.001664
C	-1.781288	-2.312250	-0.000294
C	-1.174568	4.745069	-0.001139
C	0.186647	4.451240	0.003991
C	-1.658589	2.380036	-0.001134
C	0.623283	3.127029	0.006526
C	0.459751	-3.172339	0.003747
C	5.006927	0.723482	-1.228574
C	5.035490	0.595943	1.279431
H	-3.162480	3.937919	-0.007558

H	1.542460	-3.028627	0.005301
H	-4.619579	-2.044642	-0.009194
H	-3.362219	-3.791349	-0.003956
H	-4.506973	2.260682	-0.010999
H	0.643262	-5.320164	0.003180
H	-1.809653	-5.713957	-0.001074
H	-1.515643	5.778962	-0.003145
H	0.914565	5.263003	0.006081
H	1.697670	2.928355	0.010859
H	6.142815	-1.533925	-0.102491
H	4.700496	-2.090629	0.782957
H	6.132518	0.631377	1.288726
H	4.697024	0.035862	2.159637
H	4.651785	1.621361	1.350842
H	4.673387	-2.001402	-0.995373
H	4.628322	1.752335	-1.182097
H	6.103550	0.755680	-1.264066
H	4.640838	0.260102	-2.152851
H	-5.794733	0.140437	-0.014211

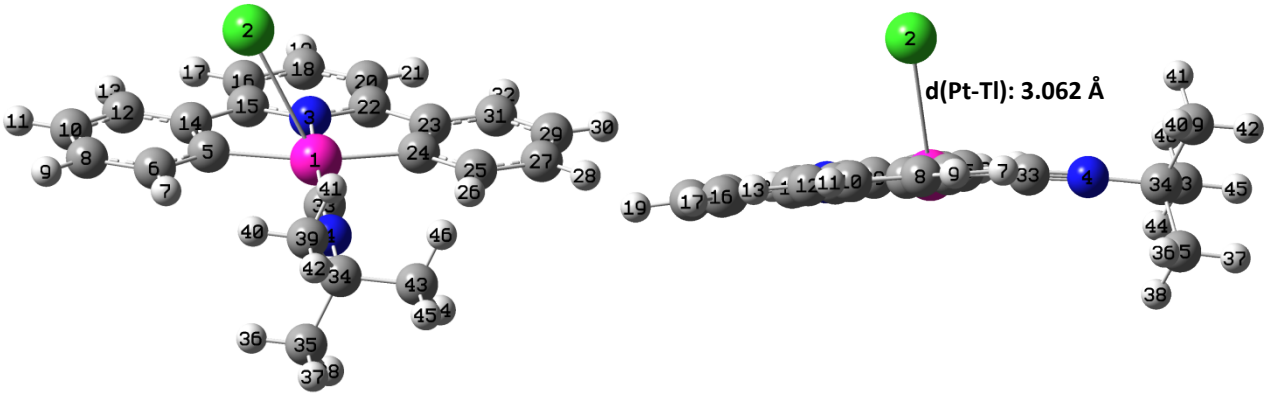


Figure S9. DFT-Optimized structure of $[Pt(CNC)(CN^tBu)Tl]^+$ (**4'**)

Table S3. DFT-Optimized coordinates of **4'**, in the Ground State, S_0

Center		Coordinates (Angstroms)	
	X	Y	Z
Pt	0.253050	0.414867	-0.483461
Tl	-0.720046	-1.475510	1.719763
N	-1.667720	1.095859	-0.609456
N	3.232390	-0.441840	-0.493270
C	-0.751161	-1.356202	-1.105919
C	-0.283020	-2.654486	-1.343623
H	0.782897	-2.869229	-1.232989
C	-1.140651	-3.684921	-1.736837
H	-0.744997	-4.682914	-1.919276
C	-2.501647	-3.438181	-1.893345
H	-3.173042	-4.239730	-2.193260
C	-3.004223	-2.160611	-1.670531
H	-4.070047	-1.977772	-1.806142
C	-2.148501	-1.126692	-1.280284
C	-2.629842	0.244260	-1.038122
C	-3.923462	0.725932	-1.203413
H	-4.718922	0.072384	-1.550900
C	-4.177803	2.068896	-0.934175
H	-5.184818	2.460113	-1.064522
C	-3.164518	2.918600	-0.511701
H	-3.368370	3.967846	-0.316703
C	-1.874713	2.410456	-0.354146
C	-0.669220	3.135081	0.051881
C	0.545248	2.393489	0.075397
C	1.704150	3.069822	0.451194
H	2.658027	2.540715	0.480526
C	1.676973	4.423711	0.790137
H	2.598304	4.928166	1.077874
C	0.481519	5.134580	0.759867
H	0.463018	6.189769	1.023183
C	-0.692030	4.489937	0.390435
H	-1.625096	5.052770	0.368455
C	2.104821	-0.135849	-0.460503
C	4.649948	-0.749528	-0.595445

C	4.934765	-1.114837	-2.048291
H	4.354827	-1.993655	-2.355512
H	6.000874	-1.349182	-2.156388
H	4.694280	-0.281492	-2.719014
C	4.940779	-1.921490	0.334904
H	4.363380	-2.808378	0.045523
H	4.707895	-1.667750	1.376504
H	6.006824	-2.172169	0.274410
C	5.423845	0.494972	-0.175415
H	5.188118	1.343493	-0.829320
H	6.499333	0.291848	-0.247396
H	5.193130	0.772085	0.860833

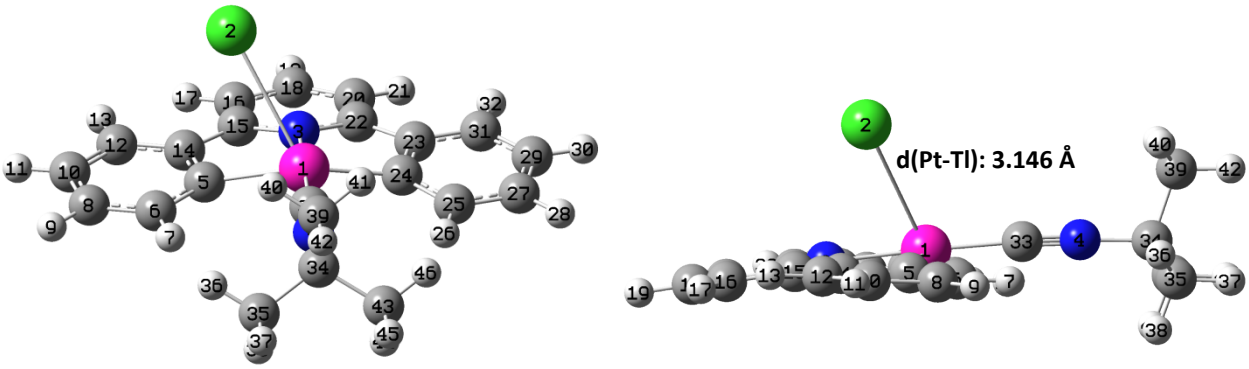


Figure S10. DFT-Optimized structure of **4'** in the Excited State, T_1

Table S4. DFT-Optimized coordinates of **4'** in the Excited State, T_1

Center		Coordinates (Angstroms)	
	X	Y	Z
Pt	0.436488	0.339954	-0.348849
Tl	-1.409798	-1.209928	1.673153
N	-1.452730	1.025910	-0.632783
N	3.375617	-0.654380	-0.066798
C	-0.431123	-1.267399	-1.337917
C	0.179156	-2.475120	-1.709894
H	1.263330	-2.578193	-1.657693
C	-0.592329	-3.546940	-2.132985
H	-0.113012	-4.484804	-2.407752
C	-1.988111	-3.423432	-2.226039
H	-2.583424	-4.267455	-2.567591
C	-2.611489	-2.233465	-1.898007
H	-3.695572	-2.150837	-1.974522
C	-1.849480	-1.131250	-1.473186
C	-2.392700	0.177740	-1.160174
C	-3.680092	0.659110	-1.386344
H	-4.441254	0.001032	-1.799200
C	-3.965759	1.997639	-1.134295
H	-4.964625	2.383240	-1.322313
C	-2.957398	2.862756	-0.697583
H	-3.157848	3.924081	-0.571876
C	-1.683966	2.366300	-0.468488
C	-0.481299	3.102274	-0.132106
C	0.740881	2.371678	-0.197085
C	1.962330	3.040959	-0.064744
H	2.903778	2.507942	-0.196404
C	1.971324	4.384921	0.281304
H	2.919981	4.897302	0.430998
C	0.768130	5.086649	0.433002
H	0.788472	6.142817	0.692759
C	-0.447777	4.454188	0.226349
H	-1.375773	5.016133	0.328725
C	2.265928	-0.293412	-0.135097
C	4.766348	-1.073317	-0.038873

C	4.939351	-2.152297	-1.102332
H	4.305729	-3.021817	-0.886639
H	5.984855	-2.483928	-1.111296
H	4.690004	-1.768859	-2.099190
C	5.067277	-1.615946	1.353603
H	4.434110	-2.480324	1.587775
H	4.913409	-0.846275	2.119528
H	6.115322	-1.937123	1.393844
C	5.617381	0.153283	-0.349294
H	5.368483	0.566981	-1.334266
H	6.675893	-0.134417	-0.352488
H	5.475990	0.931969	0.410590

Table S5. Population Analysis (%) of Frontier MOs in the Ground State for **2** and **4'**

MO	eV		Pt		CNC		CN^tBu		Tl
	2	**4'**	**2**	**4'**	**2**	**4'**	**2**	**4'**	**4'**
L+1	-1.19	-4.28	0	1	97	53	3	1	45
L	-1.79	-4.97	13	16	79	62	8	8	14
H	-5.85	-8.80	24	14	74	86	2	0	0
H-1	-6.22	-9.30	19	7	72	92	8	1	0
H-2	-6.52	-9.34	8	17	79	77	13	5	1
H-3	-6.81	-9.81	93	5	5	92	2	0	3
H-4	-6.83	-10.02	5	8	94	88	1	1	3
H-5	-7.00	-10.34	11	79	72	10	17	2	9
H-6	-7.41	-10.62	52	52	34	35	14	13	0

Table S6. Selected electronic transitions calculated by TD-DFT for **2** and **4'** in gas phase

State	λ_{exc} (calc.)/nm	o.s.	Transition (Percentage contribution)
[Pt(CNC)(CN^{t}Bu)] (2)			
S1	433.5	0.0011	H → L (98.5%)
S2	386.3	0	H-1 → L (98.8%)
S3	330.5	0.0999	H → L+1 (87.1%); H-6 → L (4.4%); H-3 → L (3.9%)
S4	326.4	0.0082	H-3 → L (70.2%); H-1 → L+1 (2.8%)
[Pt(CNC)(CN^{t}Bu)Tl]$^+$ (4')			
S1	452.9	0.0003	H → L (97.6%)
S2	388.0	0.0007	H-2 → L (89.1%); H-1 → L (9.4%)
S3	353.3	0.1252	H-1 → L (84.8%); H-2 → L (9.1%)
S4	335.9	0.0332	H → L+1 (88.9%); H-4 → L (2.1%)

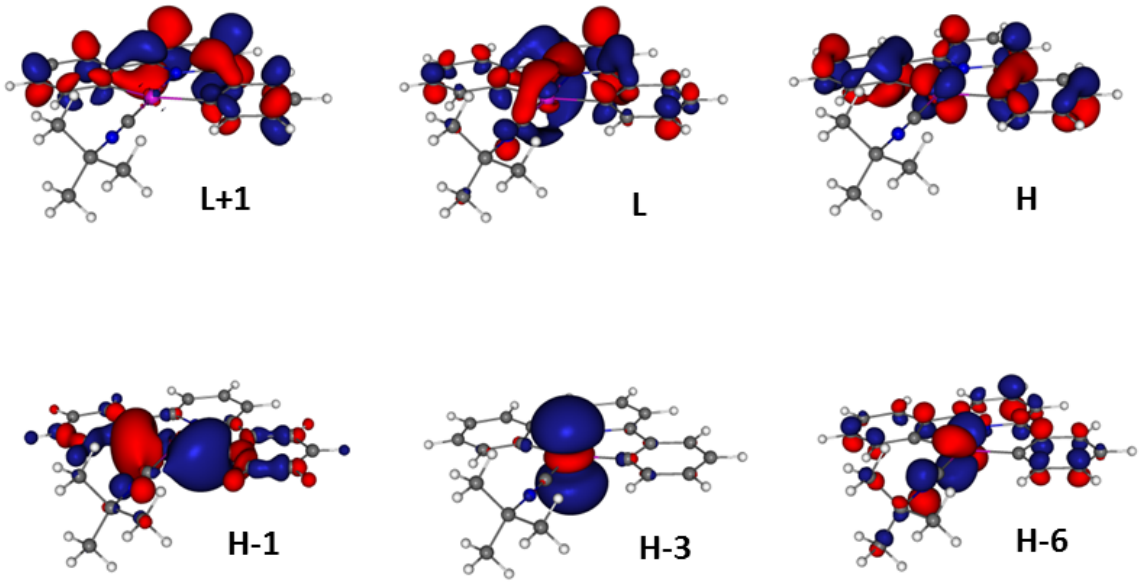


Figure S11. Representative frontier orbitals for **2**

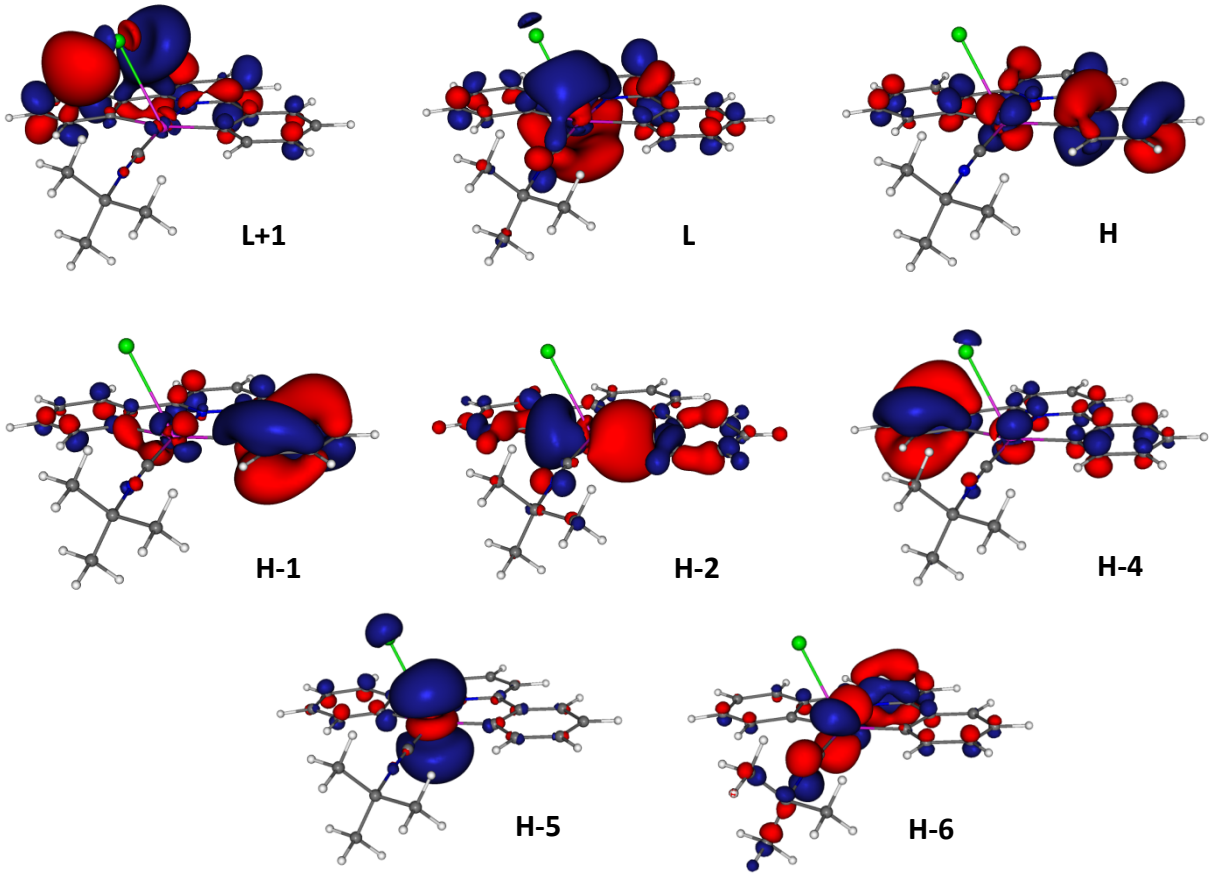


Figure S12. Representative frontier orbitals for **4'**

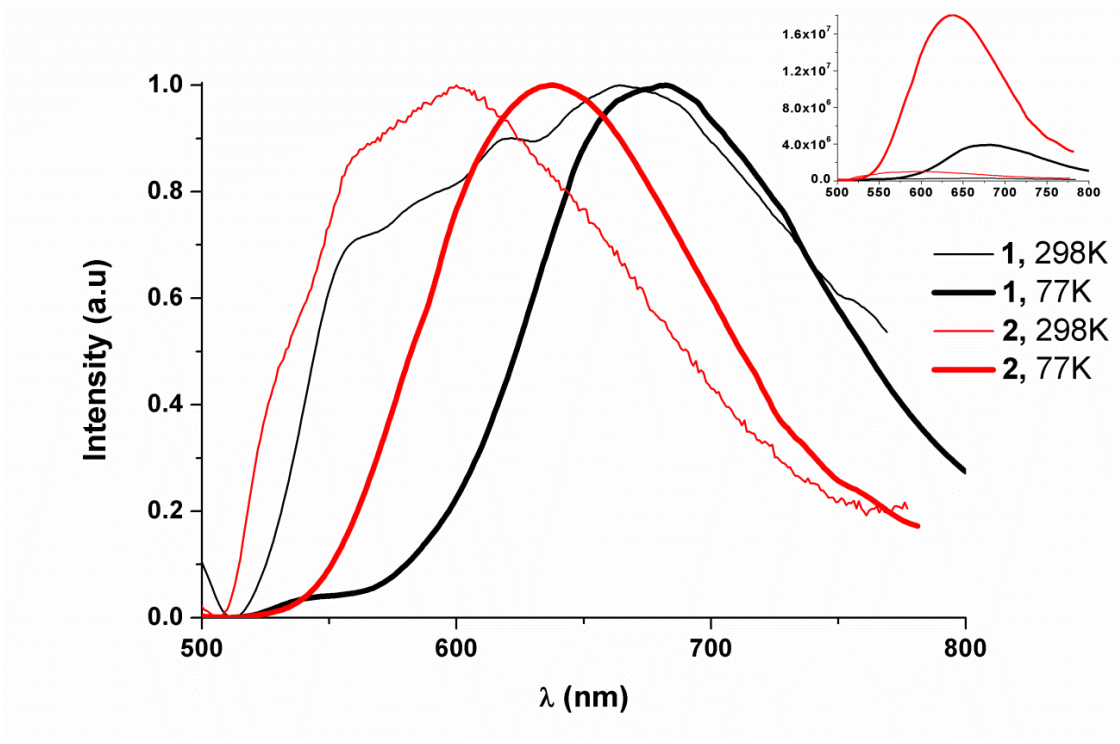


Figure S13. Normalized solid state emission spectra. Inset: Unnormalized spectra

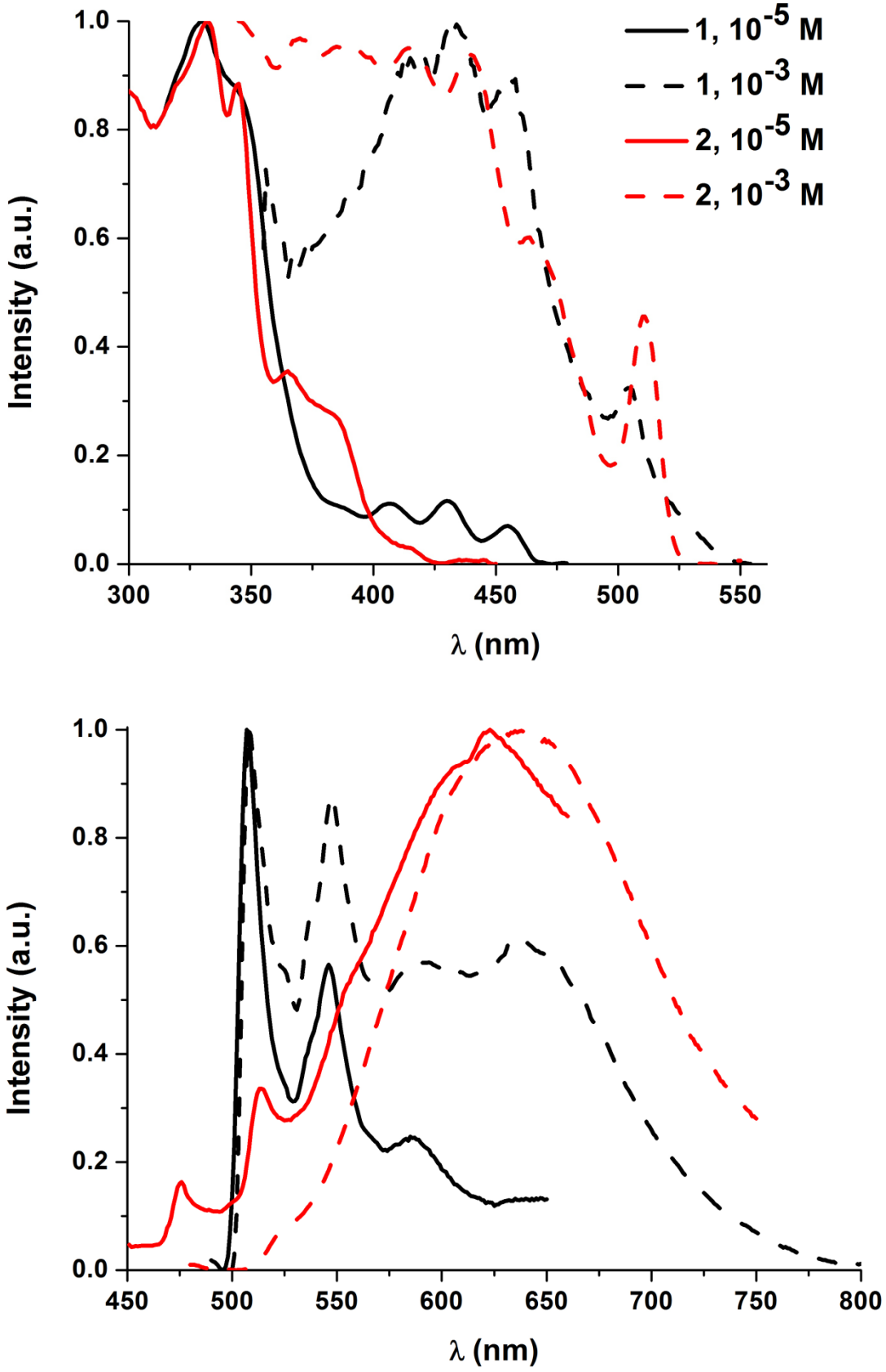


Figure S14. Normalized excitation (above) and emission (below) spectra of **1** and **2**.

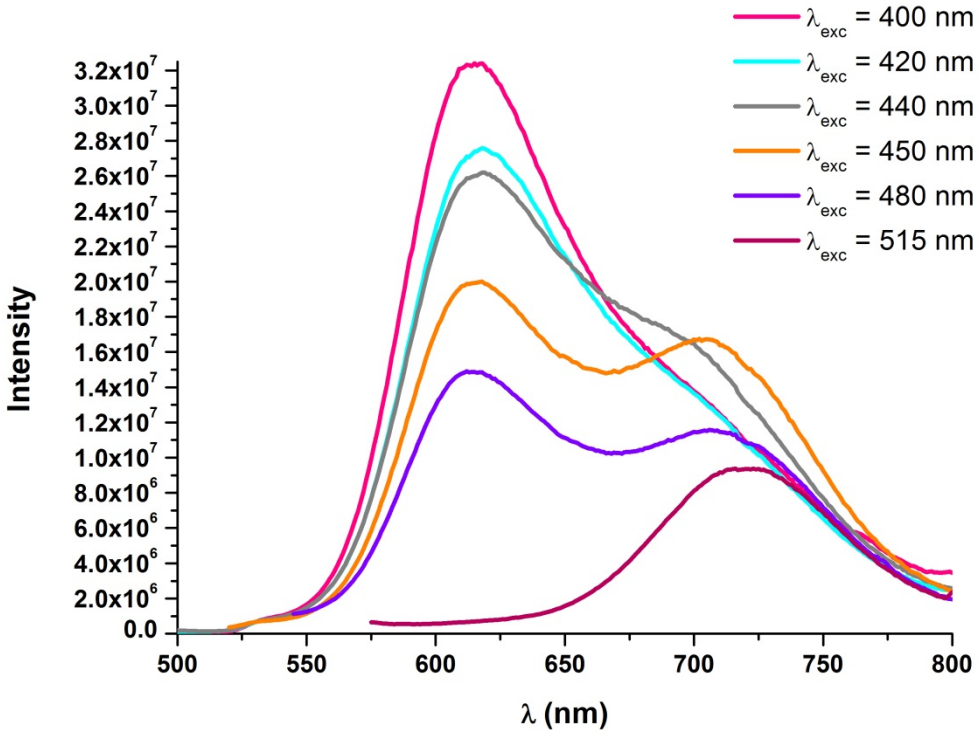
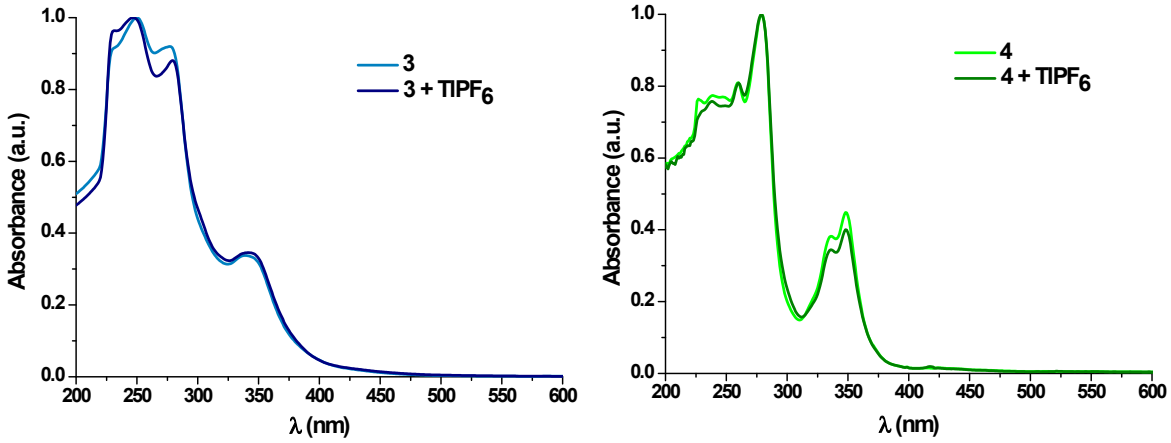


Figure S15. Unnormalized emission spectra of **4** in CH_2Cl_2 (10^{-3} M) at 77 K



(a) (b)

Figure S16. Normalized UV-vis spectra of **3** (a) and **4** (b) in CH_2Cl_2 solution upon adding excess of TlPF6.

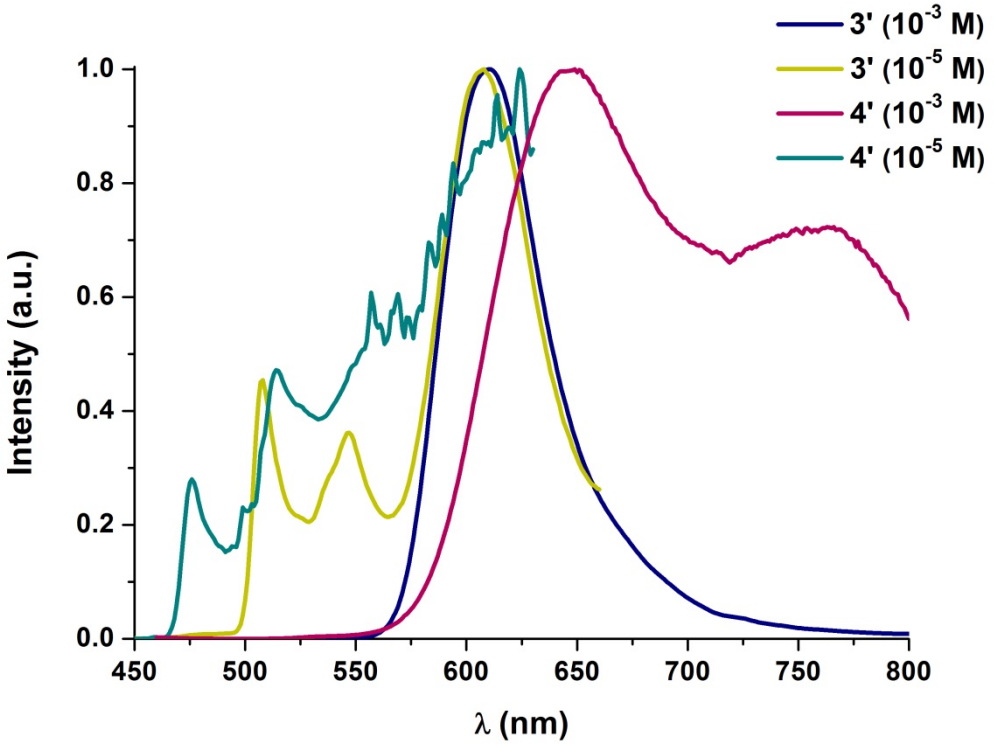


Figure S17. Normalized emission spectra of **3'** (**3** + $TlPF_6$) and **4'** (**4** + $TlPF_6$) in CH_2Cl_2 at 77 K