

## **Synthesis, characterisation and photochemistry of Pt<sup>IV</sup> pyridyl azido complexes**

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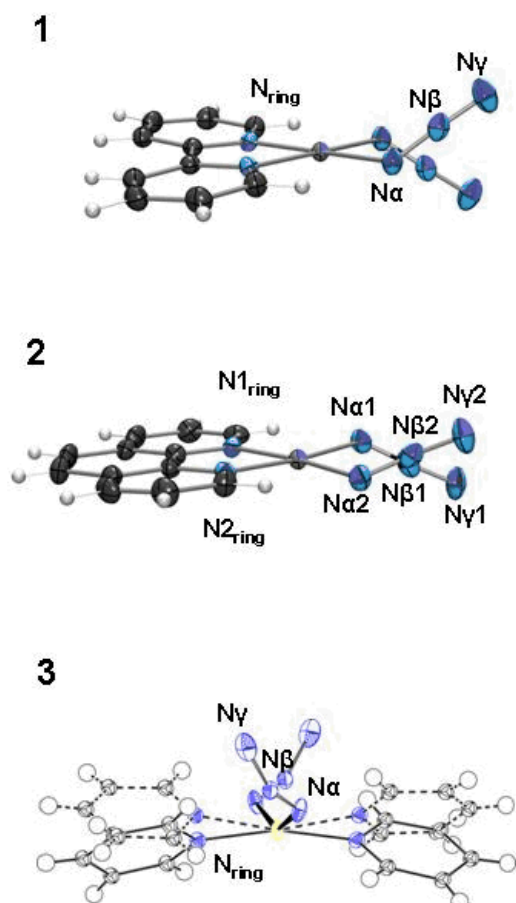
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## **Supplementary Information**

**Tables S1 – S11**

**Figures S1 – S10**



**Figure S1.** ORTEP plots of  $[\text{Pt}(\text{bpy})(\text{N}_3)_2]$  (**1**) and  $[\text{Pt}(\text{phen})(\text{N}_3)_2]$  (**2**). PLATON<sup>1</sup> was used to generate the plot for  $[\text{Pt}(\text{py})_2(\text{N}_3)_2]$  (**3**). Non-hydrogen atoms are represented by Gaussian ellipsoids at the 50% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters.

<sup>1</sup> A. L. Spek, *J. Appl. Cryst.*, 2003, **36**, 7-13.

**Table S1. Selected X-ray bond distances (Å).** For all complexes except **2**; N1 = N2 = N<sub>ring</sub>; N<sub>(α1)</sub> = N<sub>(α2)</sub>, N<sub>(β1)</sub> = N<sub>(β2)</sub>, N<sub>(γ1)</sub> = N<sub>(γ2)</sub>. O1 and O2 are the axially-coordinated oxygens.

Bond	Complex					
	1	2	3	4	5	6
Pt–N1	2.009	2.011	1.992*	2.033(3)	2.051	2.028
Pt–N2	2.009	2.012	1.992*	2.033(3)	2.051	2.028
Pt–N <sub>(α1)</sub>	2.034	2.037	2.036	2.022(3)	2.033	2.049
Pt–N <sub>(α2)</sub>	2.034	2.022	2.036	2.022(3)	2.033	2.049
N <sub>(α1)</sub> –N <sub>(β1)</sub>	1.191	1.182	1.188	1.225	1.174	1.224
N <sub>(β1)</sub> –N <sub>(γ1)</sub>	1.148	1.164	1.520	1.148	1.155	1.142
N <sub>(α2)</sub> –N <sub>(β2)</sub>	1.191	1.179	1.188	1.225	1.174	1.224
N <sub>(β2)</sub> –N <sub>(γ2)</sub>	1.148	1.167	1.520	1.148	1.155	1.142
Pt–O1	-	-	-	2.020	2.001	2.007
Pt–O2	-	-	-	2.020	2.001	2.007

\* disordered bond

**Table S2. Selected X-ray angles (°)**

Angle	Complex					
	1	2	3	4	5	6
N1–Pt–N2	80.40(17)	81.6(2)	165.84*	80.07(17)	81.2(2)	179.994
N <sub>(α1)</sub> –Pt–N <sub>(α2)</sub>	91.29(18)	95.0(2)	146.7(7)	89.5(2)	96.1(2)	179.994
Pt–N <sub>(α1)</sub> –N <sub>(β1)</sub> –N <sub>(γ1)</sub> <sup>†</sup>	176.81	179.65	-106.70	167.93	167.93	179.80
N1–Pt–N <sub>(α1)</sub> –N <sub>(β1)</sub> <sup>†</sup>	-125.45	-164.38	-167.97*	142.39	155.71	123.42
N2–Pt–N <sub>(α2)</sub> –N <sub>(β2)</sub> <sup>†</sup>	-125.45	-175.37	-167.97*	142.39	155.71	123.42
Pt–N <sub>(α2)</sub> –N <sub>(β2)</sub> –N <sub>(γ2)</sub> <sup>†</sup>	176.81	179.50	-106.70	167.93	167.93	179.80
O1–Pt–O2	-	-	-	179.18(14)	165.12(19)	179.994

\*Disordered bonds involved

<sup>†</sup> Torsion angle

**4**: N–Pt–N(bpy) = 80.07°

(Ac)CO⋯H–C contact 2.794 Å

**5**: N–Pt–N(phen) = 81.19°

### Description of crystal packing in **1**.

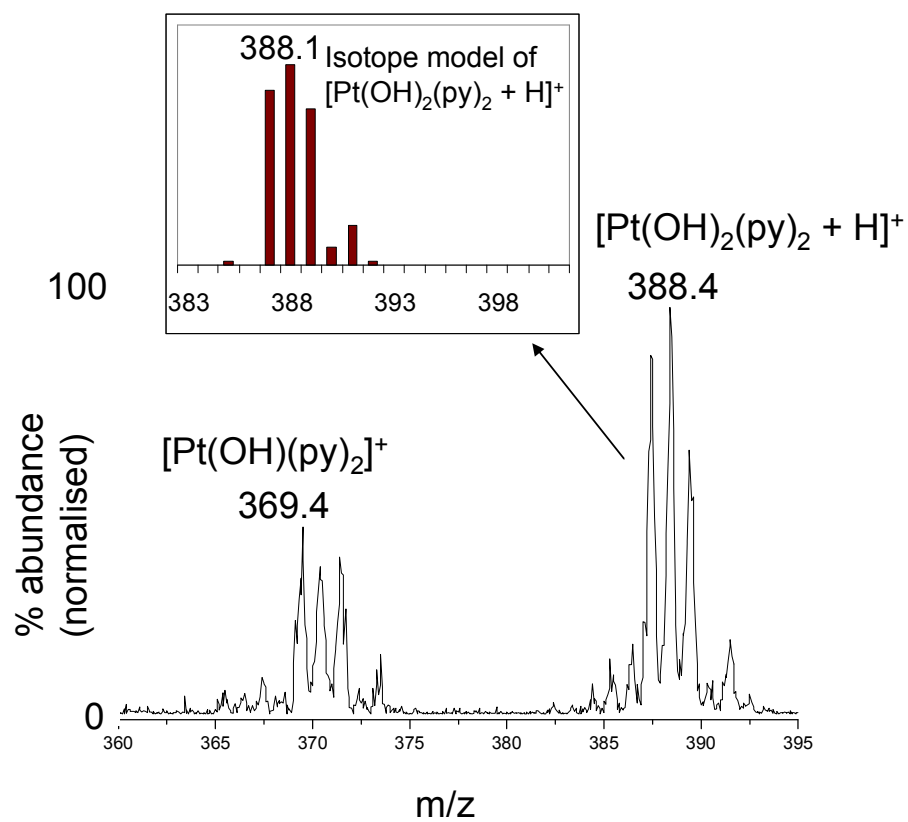
The two aromatic rings within a single molecule of the bpy complex **1** are skewed with respect to each other, at an angle of 5.12°. The centroid-centroid distance (4.036 Å) and angle (5.12°) indicate that  $\pi$ - $\pi$  stacking does not play a major role in the crystal packing of **1**. The structure of [Pt(phen)(N<sub>3</sub>)<sub>2</sub>] (**2**) consists of dimers which are  $\pi$ - $\pi$  stacked at a distance of 3.631 Å with a dihedral angle of 5.27°. The Pt...Pt distance is 3.341 Å; it is not unusual to find such Pt...Pt interactions in square-planar Pt<sup>II</sup> complexes, with linear chains being commonly reported.<sup>1,2</sup> The Pt...Pt distance is however considerably longer than that which is found in complexes with well-defined Pt-Pt bonds.<sup>3</sup>

**Table S3. Selected DFT bond distances (Å)**

Bond	Complex					
	1	2	3	4	5	6
Pt-N1	2.064	2.074	2.063	2.105	2.118	2.076
Pt-N2	2.064	2.074	2.063	2.105	2.118	2.076
Pt-N $\alpha$ 1	2.022	2.020	2.081	2.058	2.055	2.111
Pt-N $\alpha$ 2	2.022	2.020	2.081	2.058	2.055	2.111
N $\alpha$ 1-N $\beta$ 1	1.223	1.223	1.223	1.230	1.230	1.226
N $\beta$ 1-N $\gamma$ 1	1.151	1.151	1.154	1.147	1.147	1.150
N $\alpha$ 2-N $\beta$ 2	1.223	1.223	1.223	1.230	1.230	1.226
N $\beta$ 2-N $\gamma$ 2	1.151	1.151	1.155	1.147	1.147	1.150
Pt-O1	-	-	-	2.058	2.059	2.061
Pt-O2	-	-	-	2.058	2.059	2.061

**Table S4. Selected DFT angles (°)**

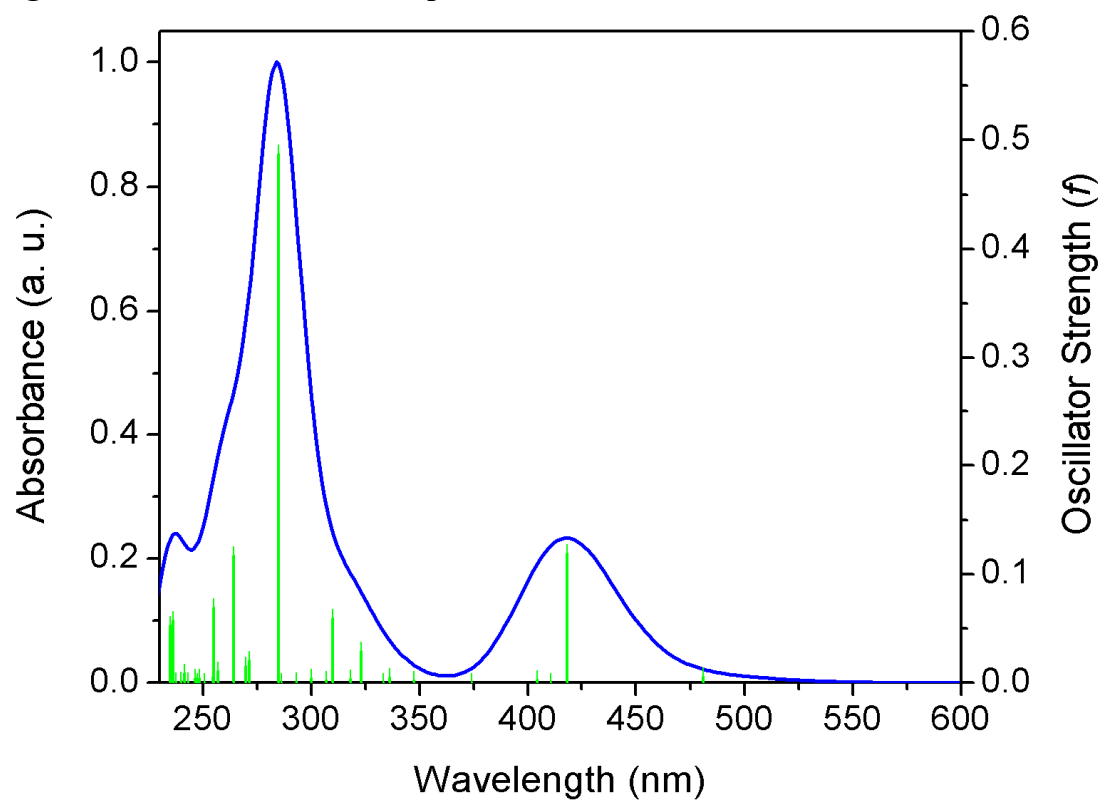
Angle	Complex					
	1	2	3	4	5	6
N1-Pt-N2	79.17	79.97	177.98	78.60	79.06	180
N $\alpha$ 1-Pt-N $\alpha$ 2	99.28	100.78	177.41	93.31	94.05	180
Pt-N $\alpha$ 1-N $\beta$ 1-N $\gamma$ 1	176.16	176.76	173.44	178.32	179.16	169.97
Pt-N $\alpha$ 2-N $\beta$ 2-N $\gamma$ 2	176.16	177.57	173.50	-178.32	-179.16	-169.97
N1-Pt-N $\alpha$ 1-N $\beta$ 1	-162.16	-166.64	-141.51	133.43	136.12	-77.09
N2-Pt-N $\alpha$ 2-N $\beta$ 2	-162.16	-166.64	-141.48	133.43	136.25	77.09
O1-Pt-O2	-	-	-	168.08	167.19	180



**Figure S2.** ESI-MS of compound **6** following UVA irradiation for 2 h showing species in which the py ligand is still attached but from which the acetate group has dissociated.

## Calculations with Gaussian

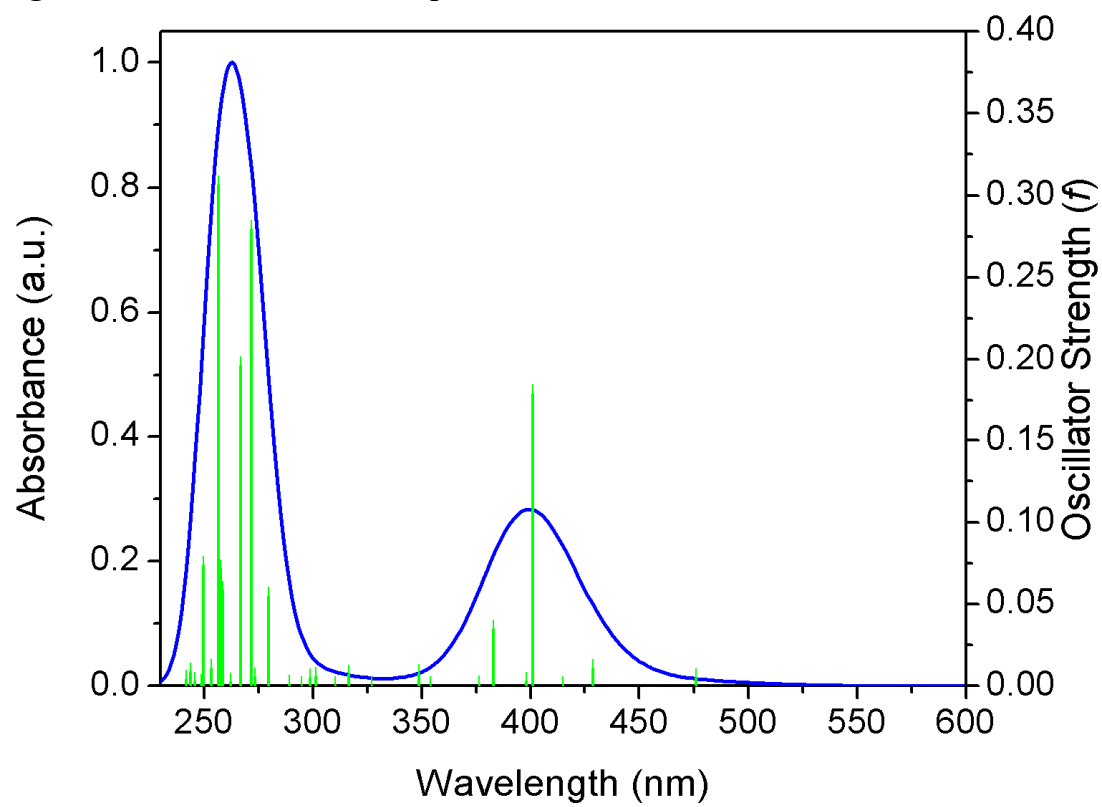
Figure S3: Theoretical UV-vis spectrum of 1



**Table S8: Complex 1, selected singlet transitions**

<b>No.</b>	<b>Energy (eV)</b>	<b><math>\lambda</math> (nm)</b>	<b>Osc. Strength</b>	<b>Major contribs</b>
1	2.5767	481.18	0.0056	HOMO->LUMO (96%)
2	2.9652	418.13	0.1189	H-1->LUMO (92%)
3	3.019	410.69	0.0002	H-2->LUMO (14%), HOMO->L+2 (73%) HOMO->L+1 (-5%)
4	3.0662	404.36	0.0026	H-2->LUMO (83%), HOMO->L+2 (-12%)
9	3.8372	323.11	0.0288	H-1->L+1 (16%), HOMO->L+3 (79%)
10	3.8951	318.31	0.0036	H-4->LUMO (93%)
11	4.0002	309.94	0.0594	H-1->L+1 (70%), HOMO->L+3 (-17%)
16	4.3527	284.85	0.487	H-5->LUMO (62%), H-1->L+3 (-18%)
17	4.5666	271.5	0.0202	H-6->LUMO (92%)
18	4.5934	269.92	0.0152	HOMO->L+6 (73%)
19	4.6943	264.12	0.1168	H-7->LUMO (71%), H-4->L+2 (14%)
20	4.8264	256.89	0.0107	H-6->L+2 (11%), H-3->L+1 (-31%), H-1->L+6 (32%)
21	4.8585	255.19	0.0691	H-7->LUMO (-16%), H-4->L+2 (41%), H-1->L+5 (-16%)
31	5.2475	236.27	0.0571	H-5->L+1 (55%), H-1->L+4 (-15%)
32	5.2757	235.01	0.0523	H-6->L+2 (47%), H-1->L+6 (-16%)

Figure S4: Theoretical UV-vis spectrum of 2

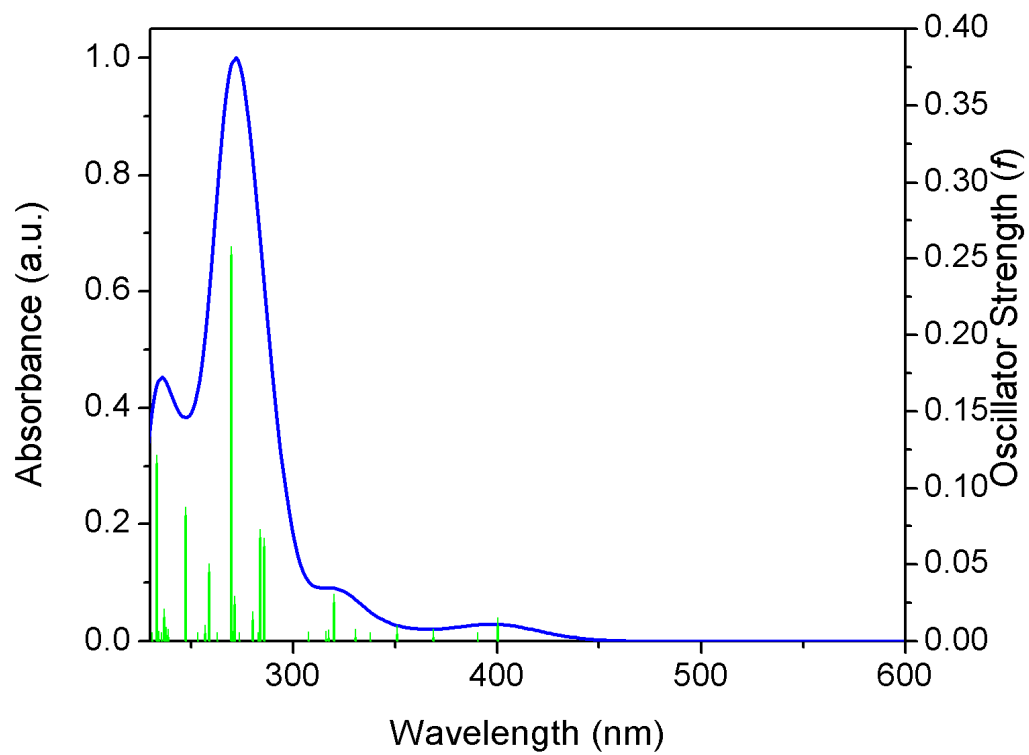




**Table S9: Complex 2, selected singlet transitions**

<b>No.</b>	<b>Energy (eV)</b>	<b><math>\lambda</math> (nm)</b>	<b>Osc. Strength</b>	<b>Major contribs</b>
1	2.6043	476.08	0.005	HOMO->LUMO (96%)
2	2.8917	428.77	0.0104	H-1->LUMO (-36%), HOMO->L+1 (63%)
3	2.9879	414.95	0.0	HOMO->L+2 (90%)
4	3.091	401.12	0.1793	H-1->LUMO (57%), HOMO->L+1 (35%)
5	3.1146	398.07	0.0029	H-2->LUMO (95%)
6	3.238	382.91	0.0346	H-1->L+1 (94%)
18	4.4342	279.61	0.0547	H-1->L+3 (86%)
20	4.5631	271.71	0.2794	H-7->LUMO (-31%), H-6->LUMO (33%), H-5->L+1 (13%)
21	4.6426	267.06	0.1963	H-6->L+1 (61%)
23	4.7911	258.78	0.0583	H-8->LUMO (38%), H-4->L+2 (30%)
24	4.8089	257.82	0.0712	H-7->L+2 (-11%), H-1->L+6 (51%)
25	4.8321	256.58	0.3062	H-7->LUMO (53%), H-1->L+6 (10%)
26	4.8943	253.32	0.0108	H-8->LUMO (34%), H-4->L+2 (-25%), HOMO->L+4 (19%)
28	4.9633	249.8	0.0734	H-5->L+2 (-22%), HOMO->L+4 (59%)

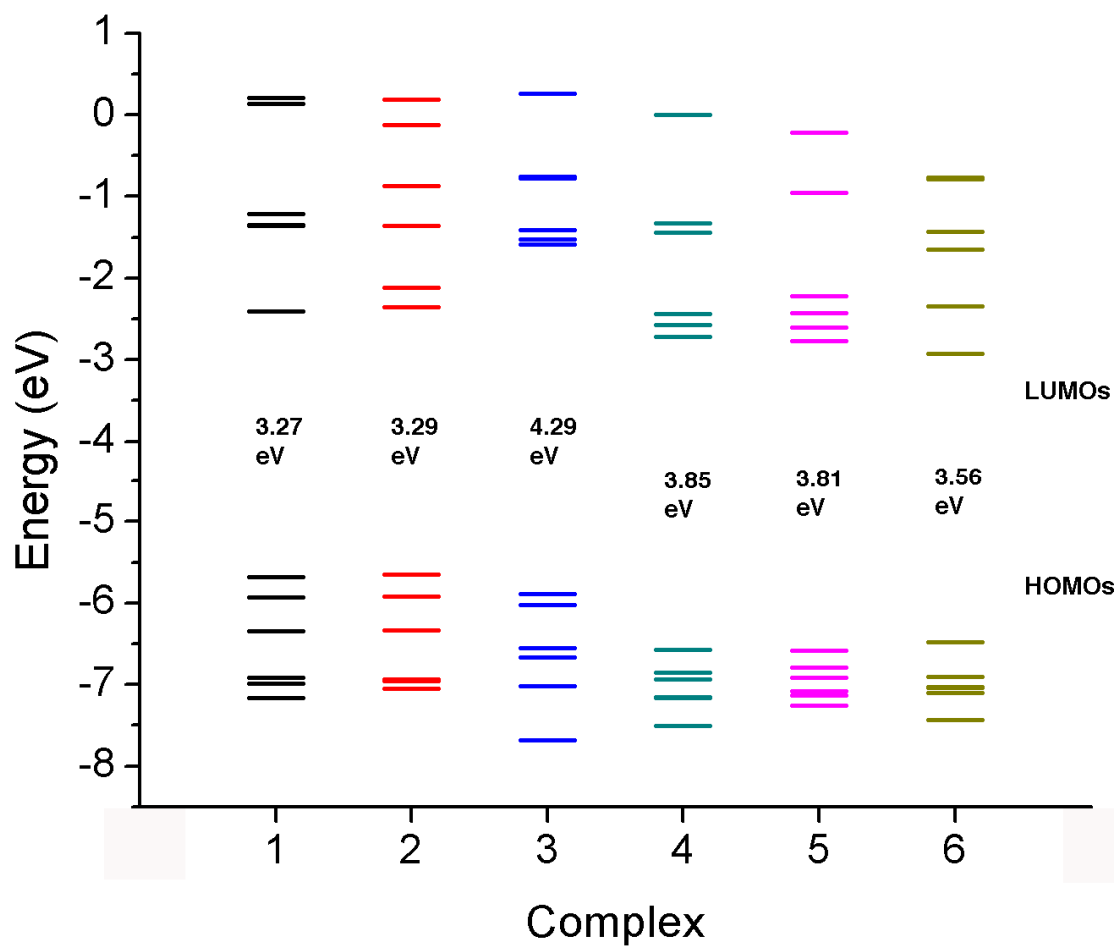
Figure S5: Theoretical UV-vis spectrum of 3



**Table S10: Complex 3, selected singlet transitions**

No.	Energy (eV)	$\lambda$ (nm)	Osc. Strength	Major contribs
1	3.1223	397.09	0.0099A	HOMO->LUMO (43%), HOMO->L+1 (46%)
2	3.1654	391.68	0.0001	H-1->LUMO (40%), H-1->L+1 (53%)
3	3.5748	346.83	0.0021	H-2->LUMO (37%), H-2->L+1 (50%)
4	3.5777	346.55	0.0043	HOMO->LUMO (53%), HOMO->L+1 (-45%)
5	3.7121	334.0	0.0005	HOMO->L+2 (87%)
7	3.8848	319.15	0.026	H-1->L+2 (98%)
11	4.3356	285.97	0.129	H-3->LUMO (25%), H-3->L+1 (43%)
13	4.4197	280.52	0.0248	H-3->LUMO (50%), H-3->L+1 (-16%), HOMO->L+3 (31%)
18	4.7005	263.77	0.2771	H-4->LUMO (54%), H-4->L+1 (-38%)
21	5.0252	246.73	0.0424	H-2->L+4 (96%)
23	5.0422	245.89	0.0614	H-8->LUMO (25%), H-8->L+1 (27%)
26	5.2676	235.37	0.02	H-6->L+2 (-10%), H-5->LUMO (-18%), H-4->L+3 (51%),
29	5.3281	232.7	0.1156	HOMO->L+5 (68%)
31	5.4011	229.55	0.0156	H-5->LUMO (35%), H-5->L+1 (52%)
32	5.4121	229.09	0.0011	H-7->LUMO (33%), H-6->L+1 (26%), H-1->L+5 (17%), HOMO->L+6 (-11%)

Figure S6: Orbital Energy Diagram for complexes 1–6.



## ADF Calculations

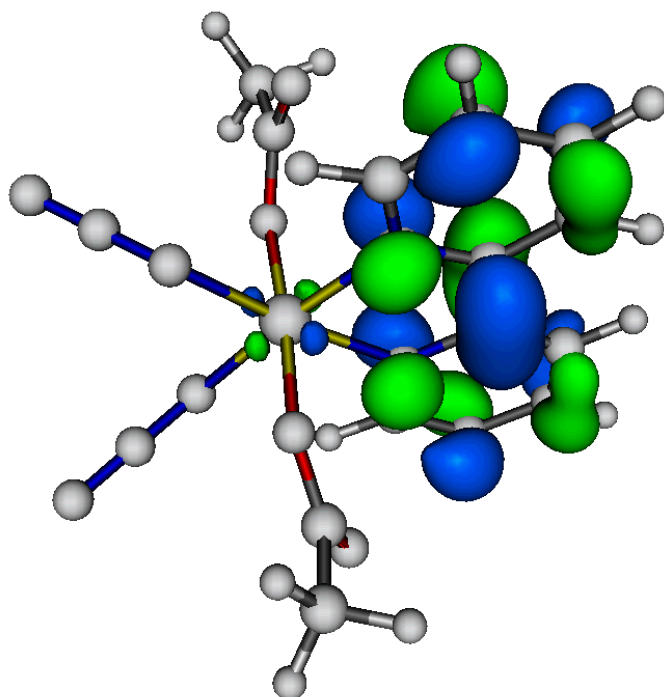
**Table S11. Experimental and calculated absorption properties of 4**

$\lambda_{\max}$ , nm $\epsilon$ ( $M^{-1}$ $cm^{-1}$ )	Tr <sup>a</sup>	Composition	Energy, eV (nm)	Oscillator Strength	Assignment
~350	25	HOMO-9→LUMO (91%) HOMO-4→LUMO+2 (6%)	3.48(361)	0.0052	LLCT/LMCT
304 (11402) and 315 (9756)	35	HOMO-8→LUMO (41%) HOMO-7→LUMO (17%) HOMO-10→LUMO (15%)	3.92 (316)	0.0746	LLCT/MLCT
	40	HOMO-10→LUMO (38%) HOMO-8→LUMO+1 (25%) HOMO-7→LUMO+1 (25%)	4.10 (303)	0.0170	MLCT/LMCT /LLCT
	41	HOMO-8→LUMO+1 (64%) HOMO-10→LUMO (20%)	4.12 (301)	0.0266	MLCT/LMCT /LLCT
	42	HOMO-9→LUMO+1 (58%) HOMO-8→LUMO+2 (23%)	4.17(297)	0.0165	LMCT/LLCT
250 (19102)	43	HOMO-1→LUMO+5 (99%)	4.18(297)	0.0020	LLCT
	44	HOMO-7→LUMO+2 (40%) HOMO-9→LUMO+1 (29%) HOMO-8→LUMO+2 (29%)	4.32 (297)	0.0025	LMCT/LLCT
	45	HOMO-4→LUMO+1 (35%) HOMO-7→LUMO+1 (14%) HOMO-6→LUMO+2 (13%)	4.22 (294)	0.1730	LLCT/LMCT
	46	HOMO-7→LUMO+3 (69%) HOMO-8→LUMO+3 (31%)	4.24 (292)	0.0014	LLCT
	47	HOMO-9→LUMO+3 (97%)	4.35 (285)	0.0027	LLCT
	48	HOMO-7→LUMO+4 (46%) HOMO-8→LUMO+4 (16%) HOMO-5→LUMO+1 (12%)	4.39 (282)	0.0979	LLCT/LMCT
	49	HOMO-7→LUMO+4 (25%) HOMO-5→LUMO+1 (20%)	4.40 (282)	0.1697	LLCT/LMCT/ MLCT/

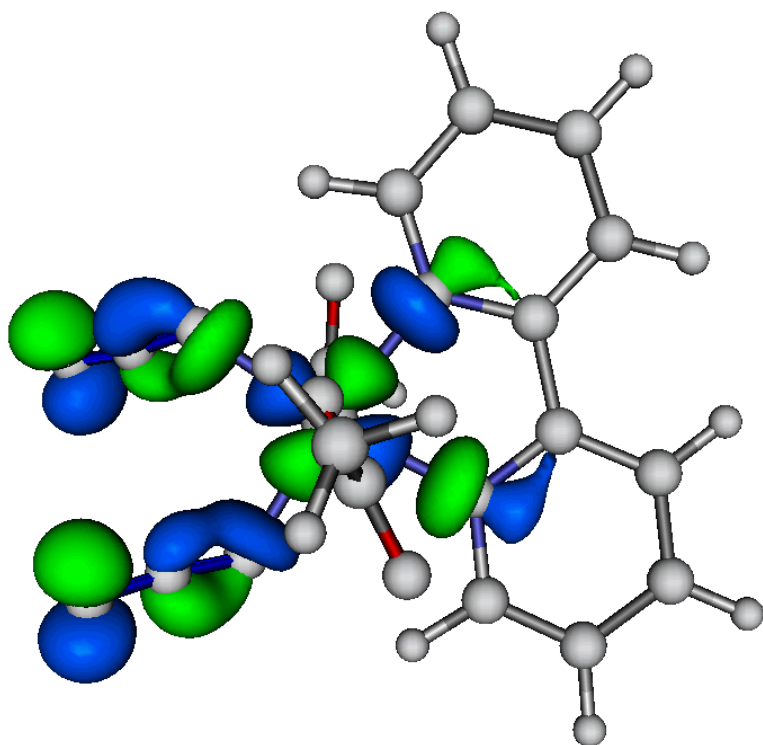
		HOMO-6→LUMO+1 (13%)			MMCT
		HOMO-8→LUMO+4 (13%)			
	50	HOMO-9→LUMO+4 (94%)	4.51 (275)	0.0098	LLCT

<sup>a</sup>Tr = transition number as obtained in the TDDFT calculation output.

**Figure S7: Complex 4, LUMO**



**Figure S8: Complex 4, LUMO+1**



**Figure S9: Complex 4, LUMO+2**

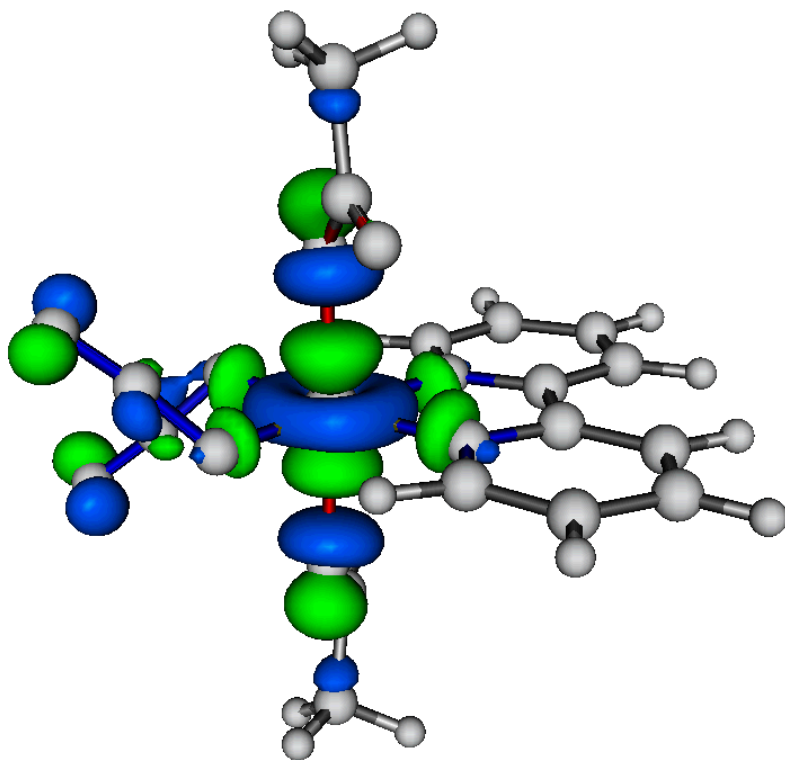
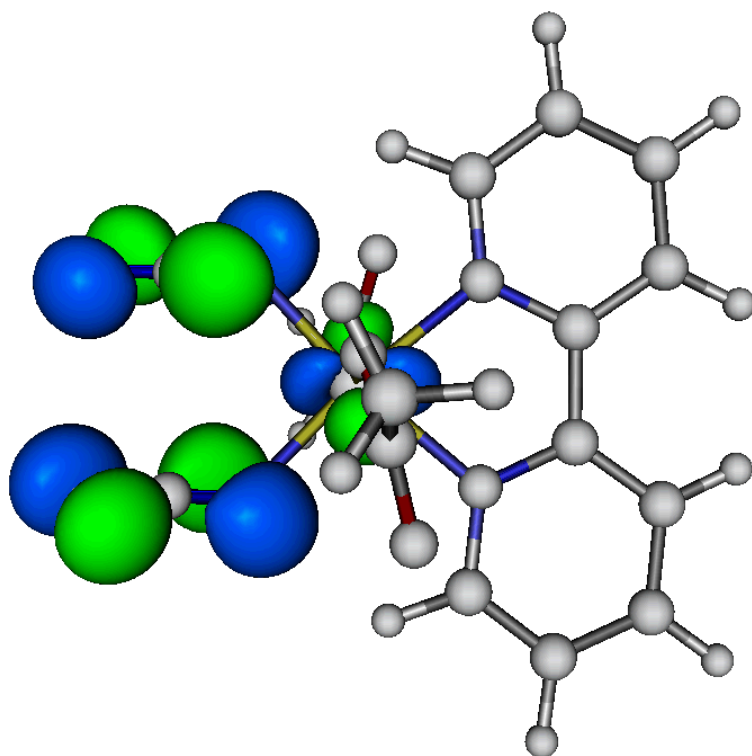


Figure S10: Complex 4, HOMO



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(1) W. B. Connick, L. M. Henling, R. E. Marsh and H. B. Gray, *Inorg. Chem.*, 1996, **35**, 6261–6265.

(2) V. M. Miskowski and V. H. Houlding, *Inorg. Chem.*, 1989, **28**, 1529–1533 and references therein.

(3) R. J. Blau, and J. H. Espenson, *Inorg. Chem.*, 1986, **25**, 878–880.