Synthesis, characterisation and photochemistry of Pt^{IV} pyridyl azido complexes

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Supplementary Information

Tables S1 – S11

Figures S1 – S10

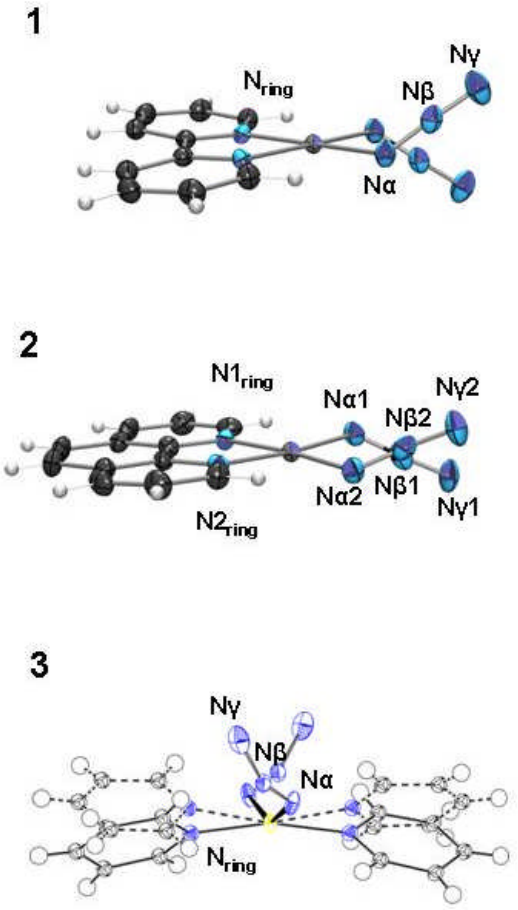


Figure S1. ORTEP plots of [Pt(bpy)(N_3)$_2$] (**1**) and [Pt(phen)(N_3)$_2$] (**2**). PLATON[1] was used to generate the plot for [Pt(py)$_2$(N_3)$_2$] (**3**). Non-hydrogen atoms are represented by Gaussian ellipsoids at the 50% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters.

[1] 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_{ring}; $N(_{\alpha1)} = N_{(\alpha2)}$, $N_{(\beta1)} = N_{(\beta2)}$, $N_{(\gamma1)} = N_{(\gamma2)}$. 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
$Pt–N_{(\alpha1)}$	2.034	2.037	2.036	2.022(3)	2.033	2.049
$Pt–N_{(\alpha2)}$	2.034	2.022	2.036	2.022(3)	2.033	2.049
$N_{(\alpha1)}–N_{(\beta1)}$	1.191	1.182	1.188	1.225	1.174	1.224
$N_{(\beta1)}–N_{(\gamma1)}$	1.148	1.164	1.520	1.148	1.155	1.142
$N_{(\alpha2)}–N_{(\beta2)}$	1.191	1.179	1.188	1.225	1.174	1.224
$N_{(\beta2)}–N_{(\gamma2)}$	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
$N_{(\alpha1)}–Pt–N_{(\alpha2)}$	91.29(18)	95.0(2)	146.7(7)	89.5(2)	96.1(2)	179.994
$Pt\text{-}N_{(\alpha1)}–N_{(\beta1)}–N_{(\gamma1)}$ †	176.81	179.65	-106.70	167.93	167.93	179.80
$N1–Pt–N_{(\alpha1)}–N_{(\beta1)}$ †	-125.45	-164.38	-167.97*	142.39	155.71	123.42
$N2–Pt–N_{(\alpha2)}–N_{(\beta2)}$ †	-125.45	-175.37	-167.97*	142.39	155.71	123.42
$Pt\text{-}N_{(\alpha2)}–N_{(\beta2)}–N_{(\gamma2)}$ †	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
† 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 5.12º. The centroid-centroid distance (4.036 Å) and angle (5.12º) indicate that π-π stacking does not play a major role in the crystal packing of **1**. The structure of [Pt(phen)(N_3)$_2$] (**2**) consists of dimers which are π-π 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^{II} complexes, with linear chains being commonly reported.[1,2] The Pt…Pt distance is however considerably longer than that which is found in complexes with well-defined Pt–Pt bonds.[3]

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–Nα1	2.022	2.020	2.081	2.058	2.055	2.111
Pt–Nα2	2.022	2.020	2.081	2.058	2.055	2.111
Nα1–Nβ1	1.223	1.223	1.223	1.230	1.230	1.226
Nβ1–Nγ1	1.151	1.151	1.154	1.147	1.147	1.150
Nα2–Nβ2	1.223	1.223	1.223	1.230	1.230	1.226
Nβ2–Nγ2	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
Nα1–Pt–Nα2	99.28	100.78	177.41	93.31	94.05	180
Pt–Nα1–Nβ1–Nγ1	176.16	176.76	173.44	178.32	179.16	169.97
Pt–Nα2–Nβ2–Nγ2	176.16	177.57	173.50	-178.32	-179.16	-169.97
N1–Pt–Nα1–Nβ1	-162.16	-166.64	-141.51	133.43	136.12	-77.09
N2–Pt–Nα2–Nβ2	-162.16	-166.64	-141.48	133.43	136.25	77.09
O1–Pt–O2	-	-	-	168.08	167.19	180

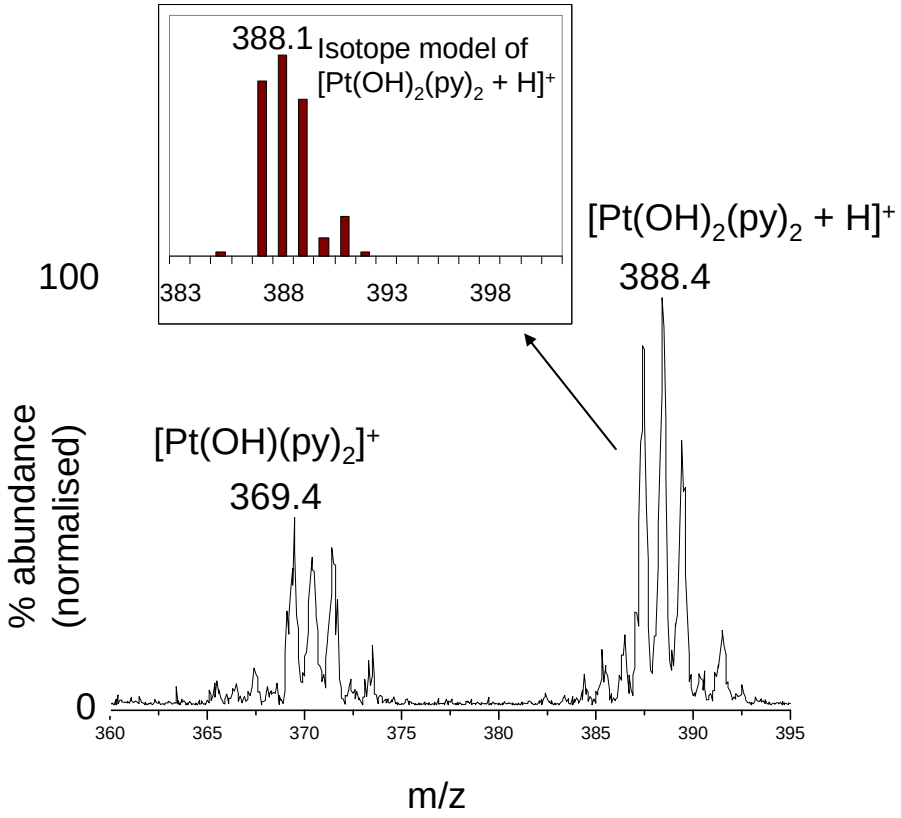


Figure S2. ESI-MS of compound **6** following UVA irradiation for 2 h showing species in which the py ligand is still attached but from which the acetate group has dissociated.

Calculations with Gaussian

Figure S3: Theoretical UV-vis spectrum of 1

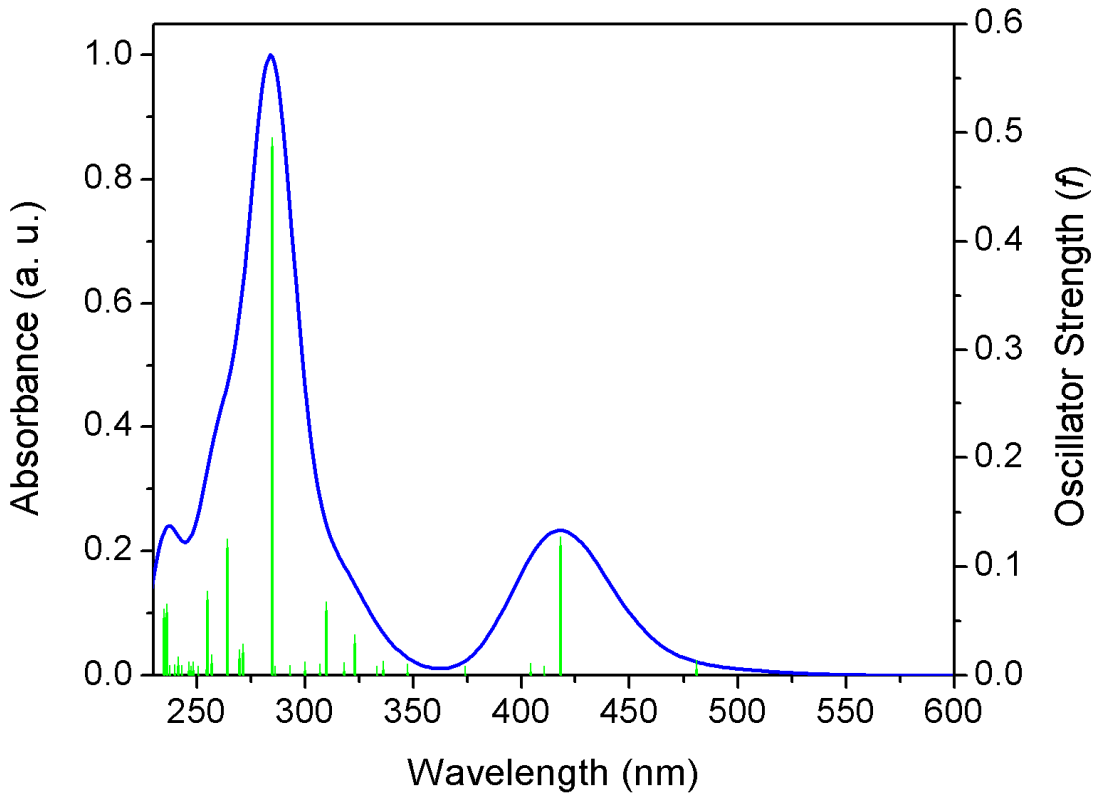


Table S8: Complex 1, selected singlet transitions

No.	Energy (eV)	λ (nm)	Osc. Strength	Major contribs
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	0523	H-6->L+2 (47%), H-1->L+6 (-16%)

Figure S4: Theoretical UV-vis spectrum of 2

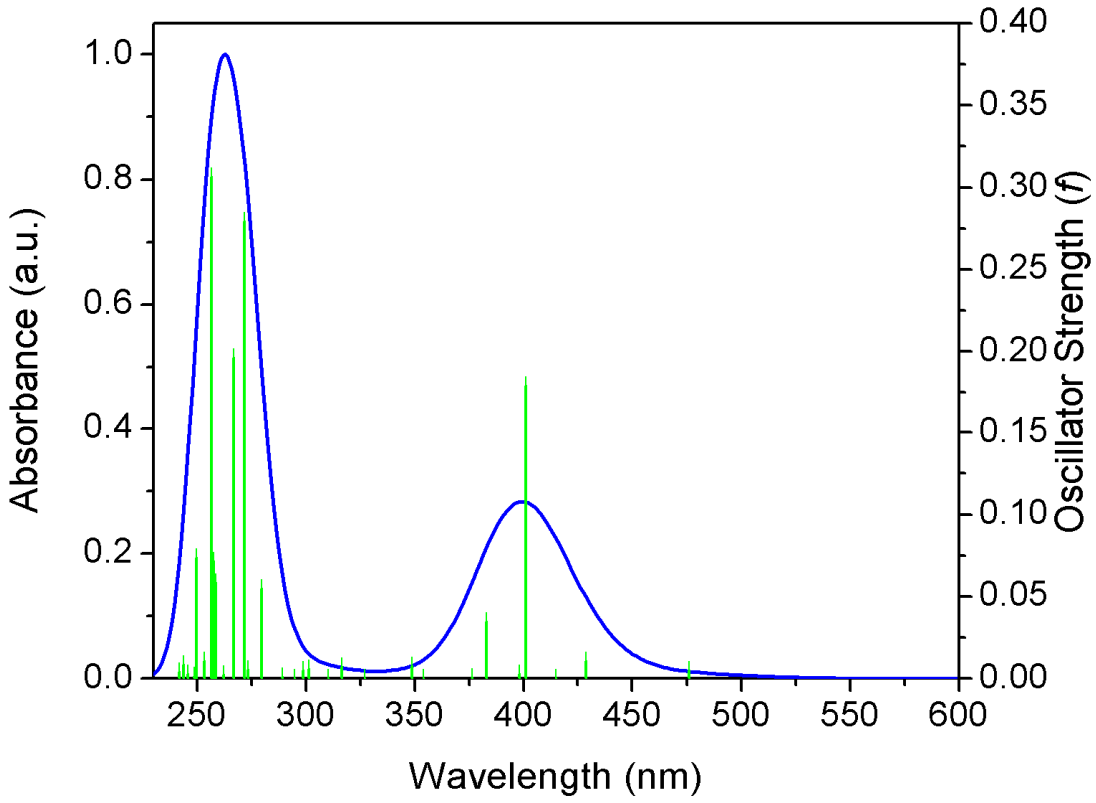


Table S9: Complex 2, selected singlet transitions

No.	Energy (eV)	λ (nm)	Osc. Strength	Major contribs
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

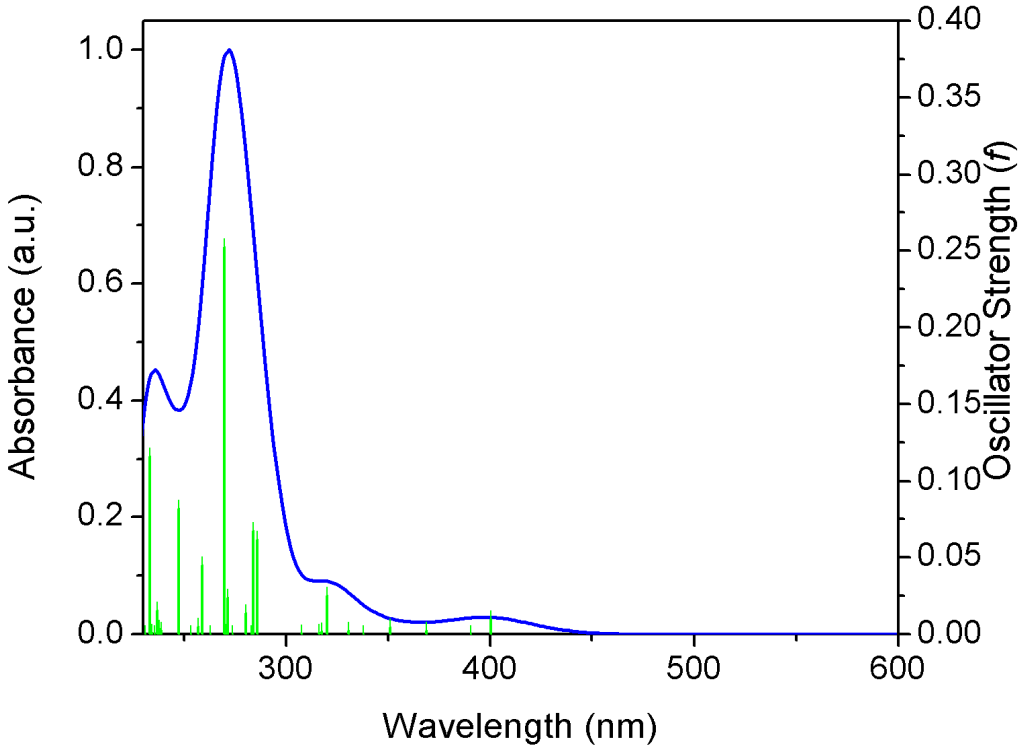
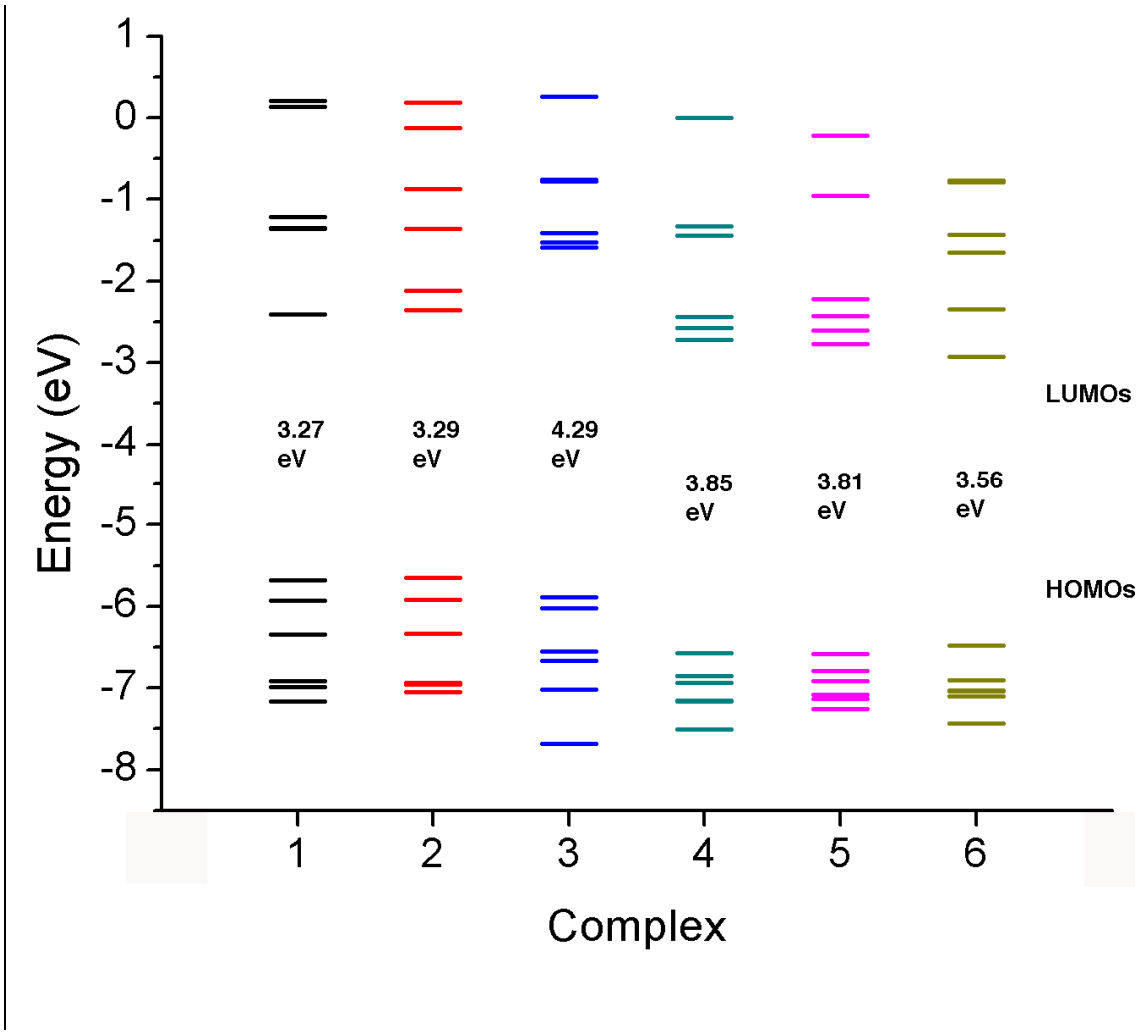


Table S10: Complex 3, selected singlet transitions

No.	Energy (eV)	λ (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

λ_{max}, nm ε (M^{-1} cm^{-1})	Tr[a]	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%) HOMO−8→LUMO+4 (13%)			MMCT
	50	HOMO-9→LUMO+4 (94%)	4.51 (275)	0.0098	LLCT

[a]Tr = transition number as obtained in the TDDFT calculation output.

Figure S7: Complex 4, LUMO

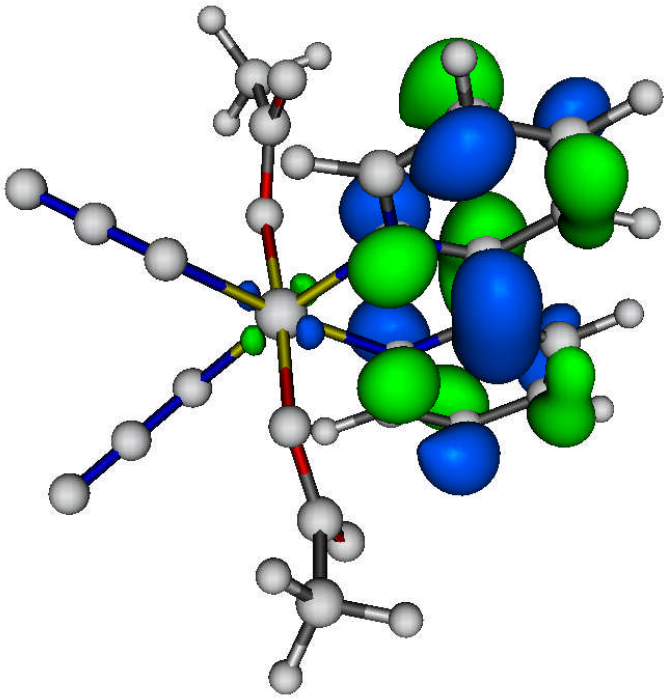


Figure S8: Complex 4, LUMO+1

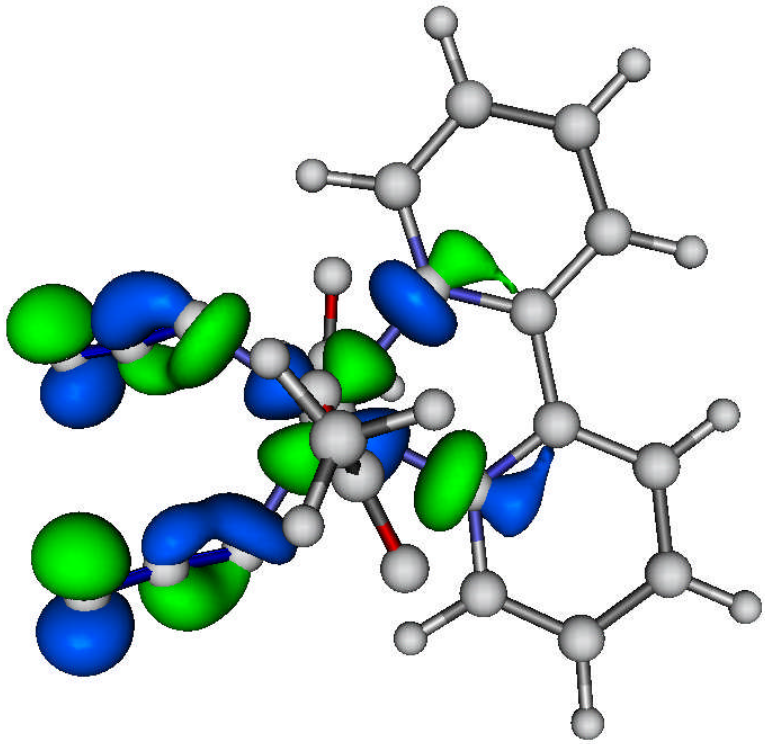


Figure S9: Complex 4, LUMO+2

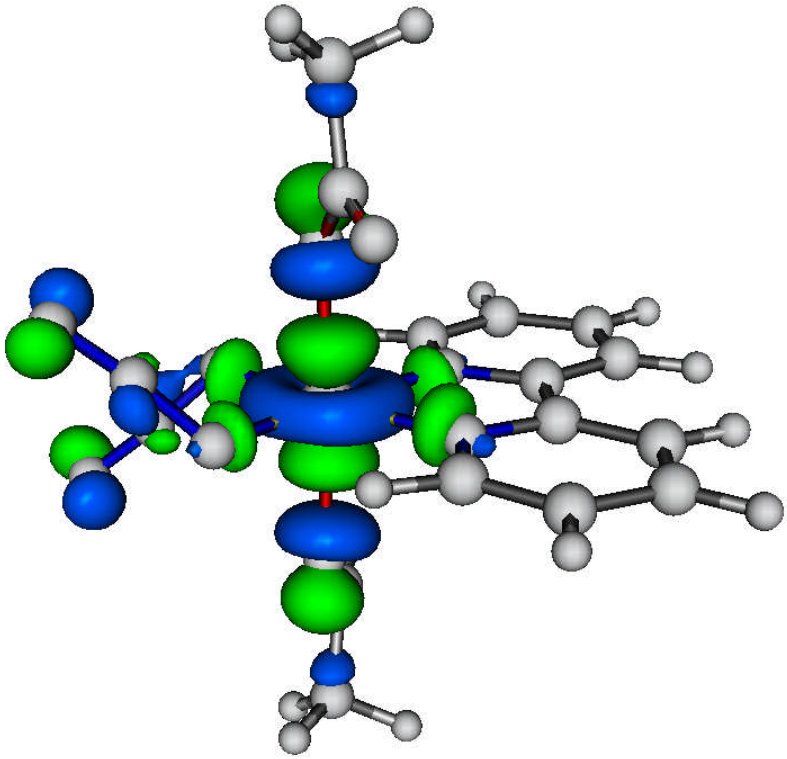
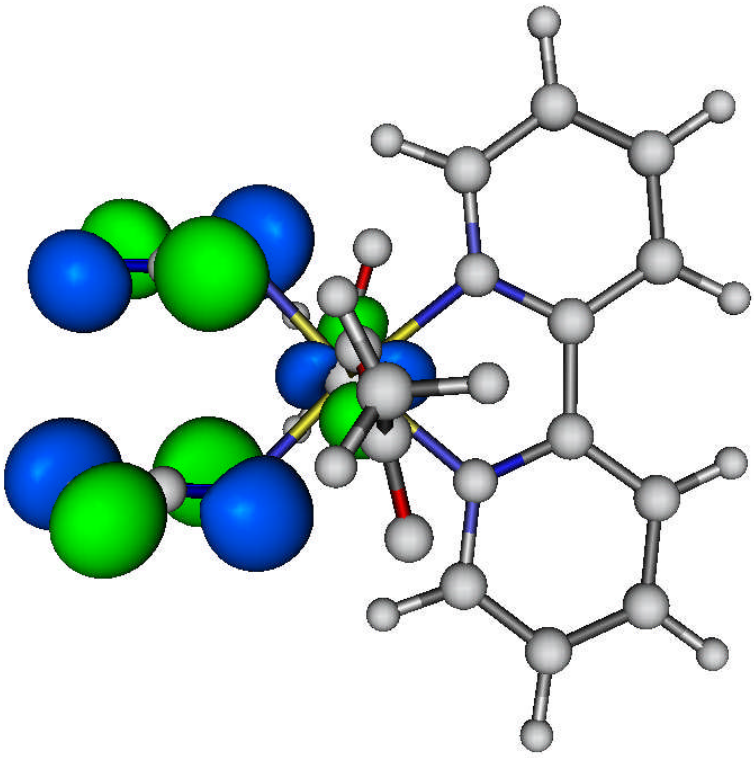


Figure S10: Complex 4, HOMO



(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.