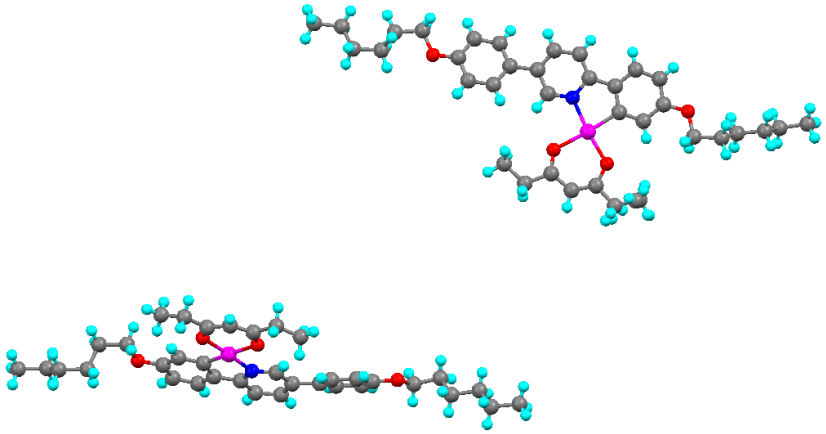
Electronic Supplementary Material (ESI) for Dalton Transactions

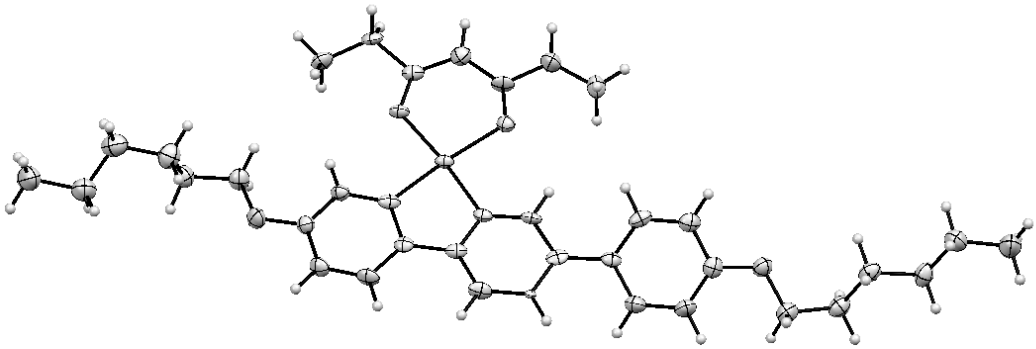
Phosphorescent, Liquid-Crystalline Complexes of Platinum(II): Influence of the β-Diketonate Co-Ligand on Mesomorphism and Emission Properties[§]

Matthew Spencer, Amedeo Santoro, Álvaro Díez, Paul R. Murray, Gemma R. Freeman, Javier Torroba, Adrian C. Whitwood, Lesley J. Yellowlees, J. A. Gareth Williams, and Duncan W. Bruce*

Supplementary Information

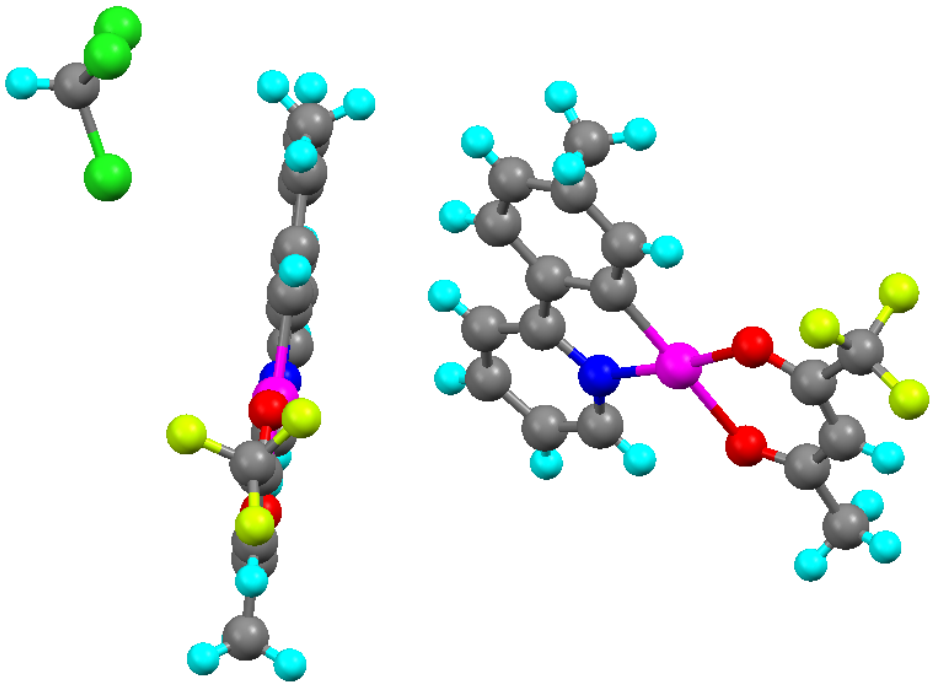


(a)

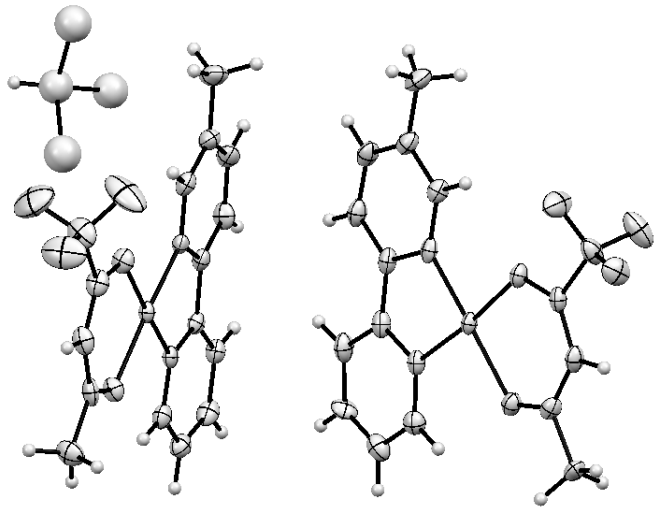


(b)

Figure S1 (a) The asymmetric unit of complex **5**-6 and (b) an ORTEP representation of one of the complexes



(a)



(b)

Figure S2 (a) Asymmetric unit of complex **12** and (b) an ORTEP representation of the same.

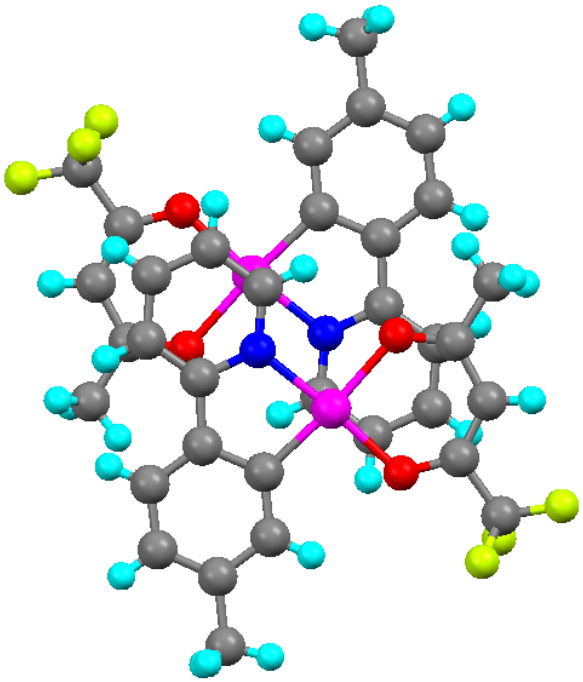
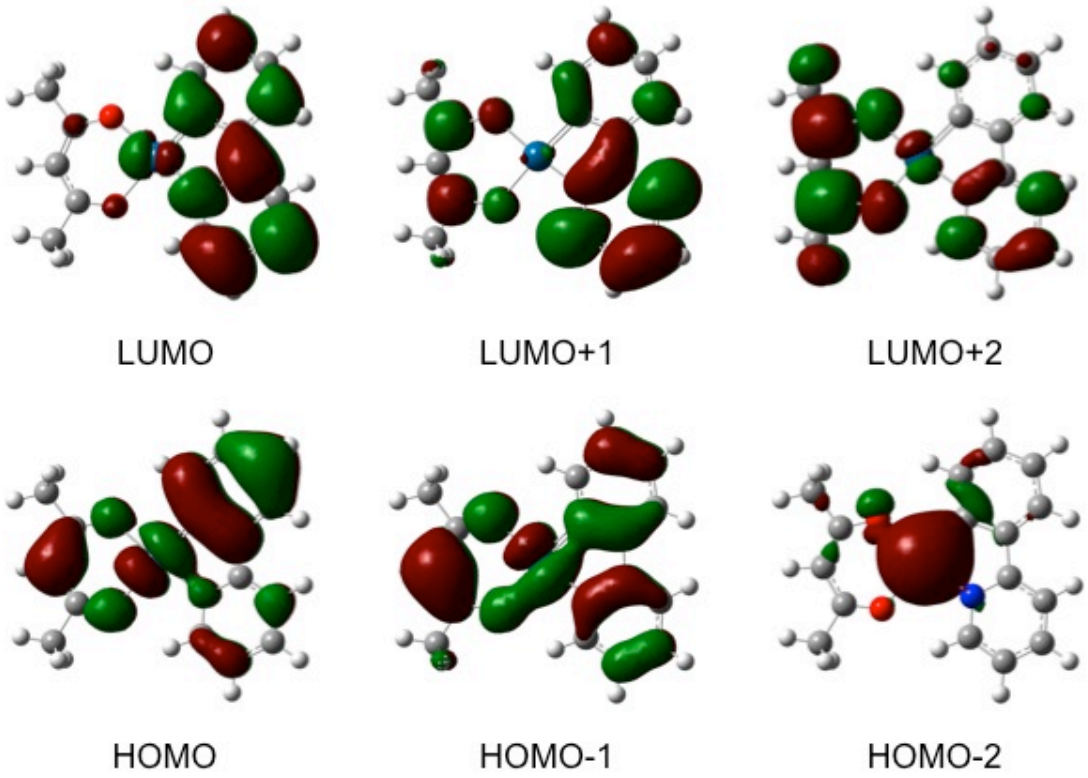
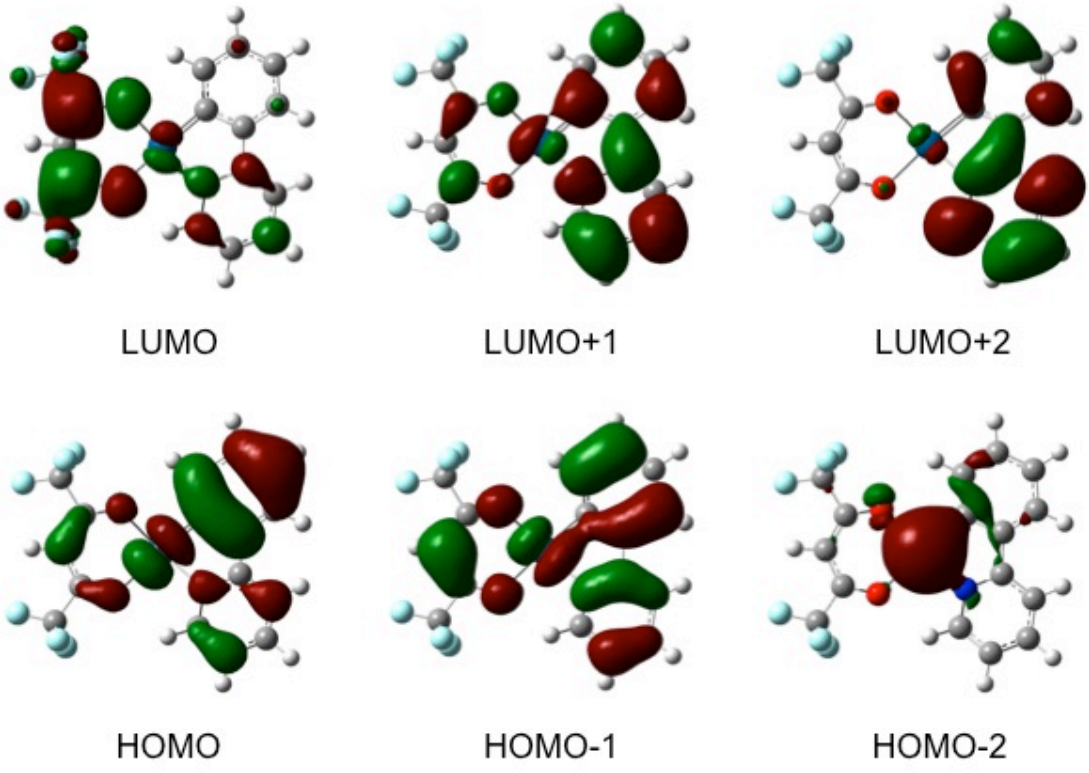


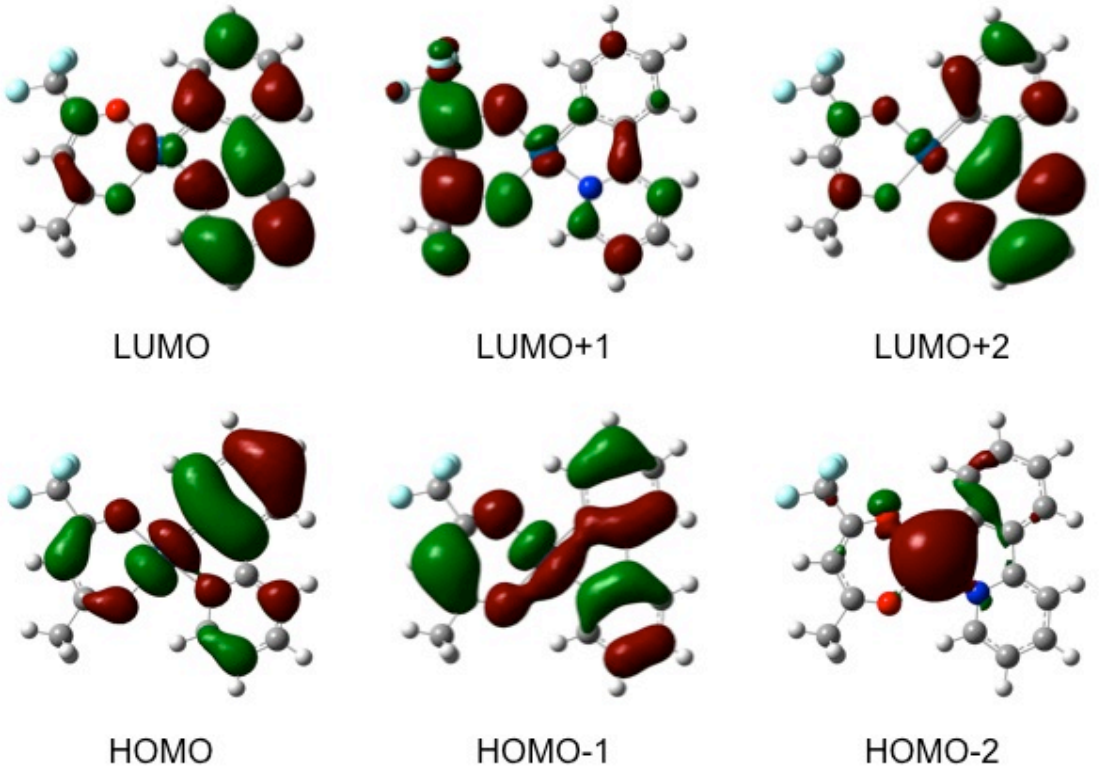
Figure S3 Top view of complex **12** showing the overlay.



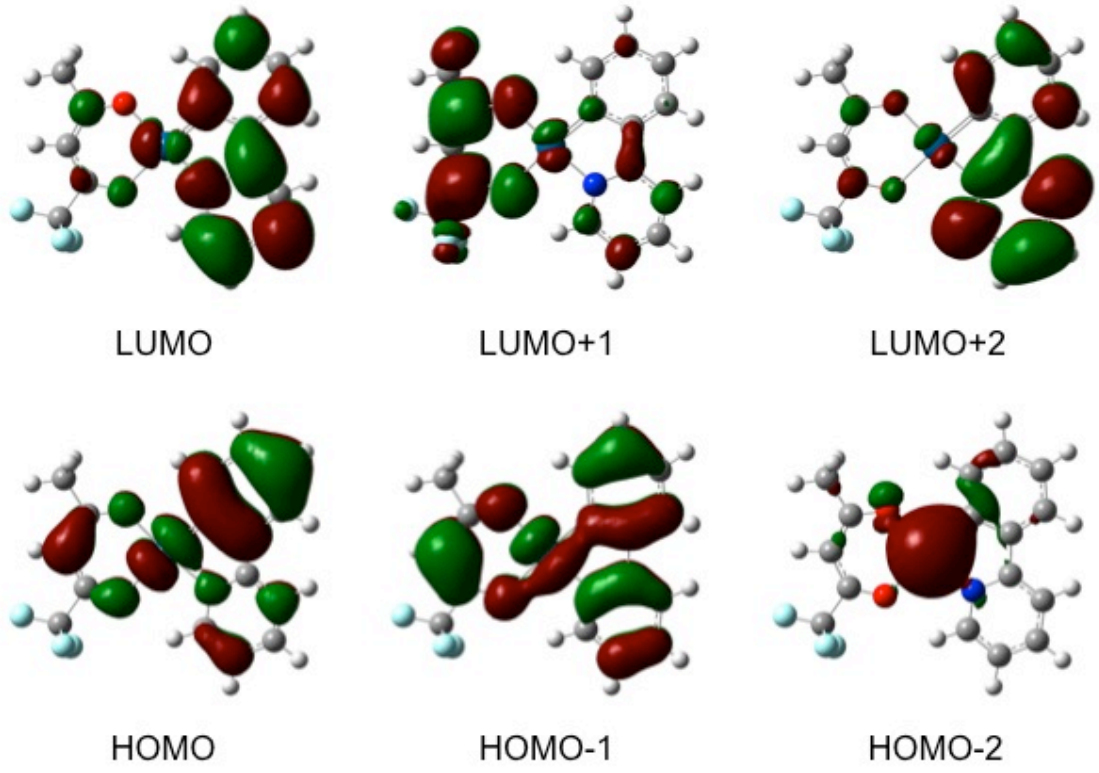
(a) [Pt(ppy)(acac)]



(b) [Pt(ppy)(hfac)]

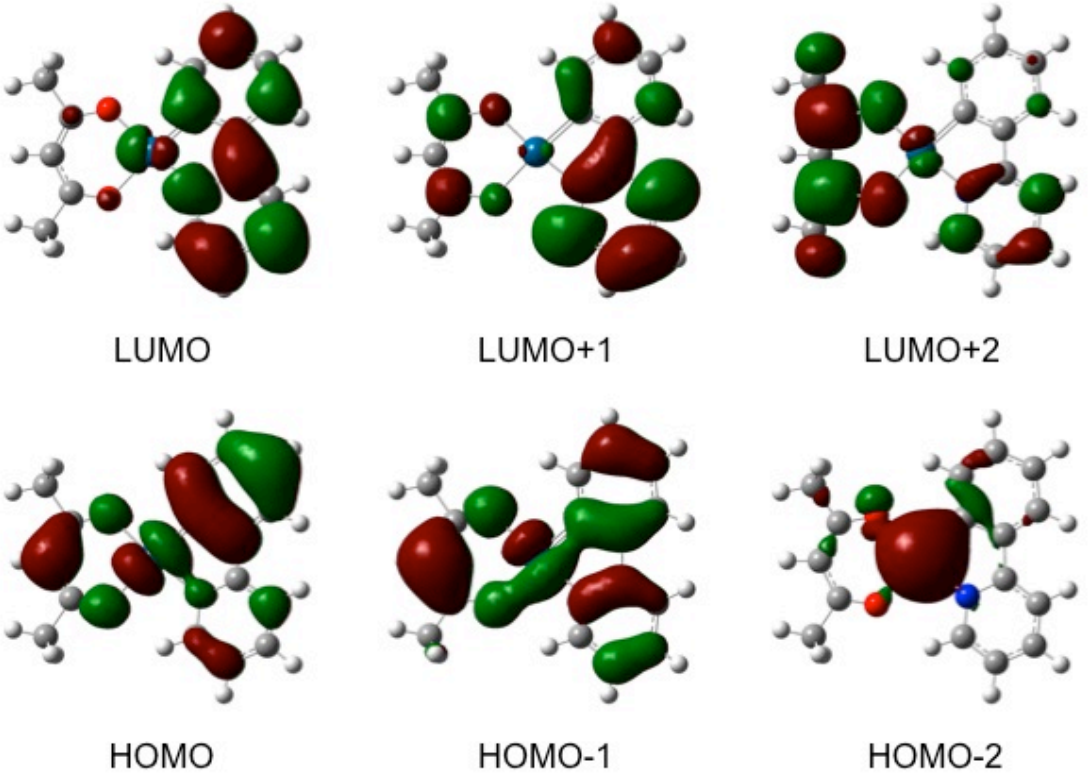


(c) *trans*-[Pt(ppy)(tfac)]

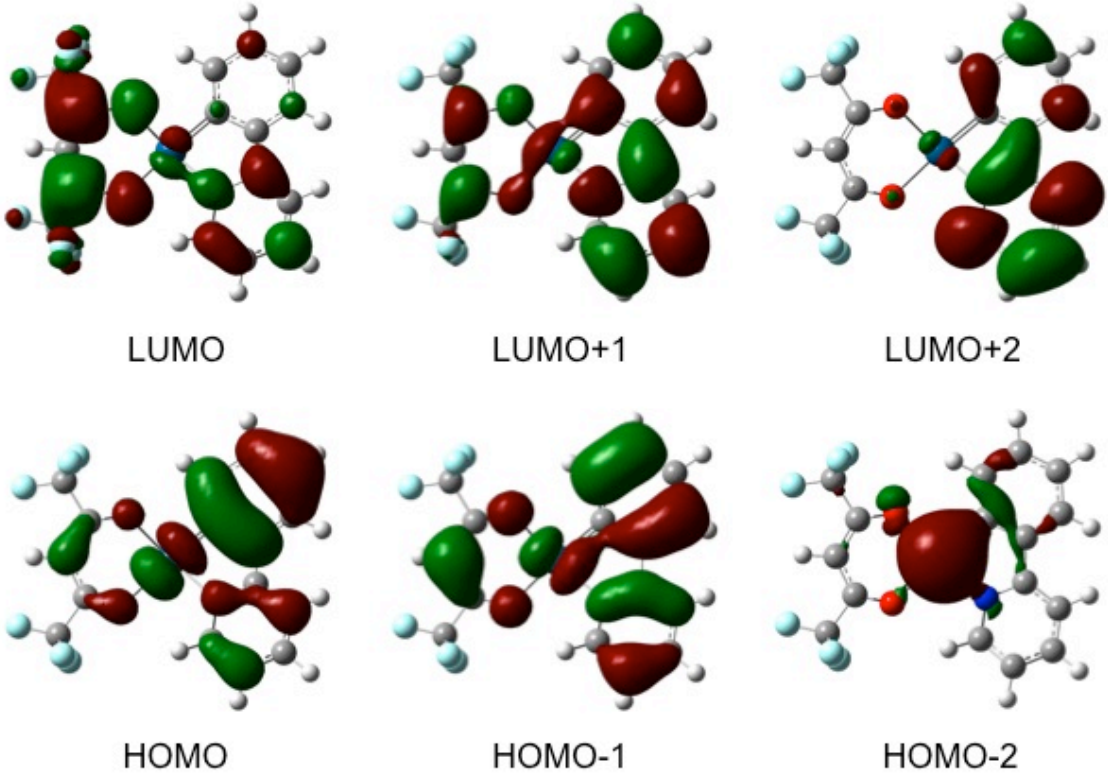


(d) *cis*-[Pt(ppy)(tfac)]

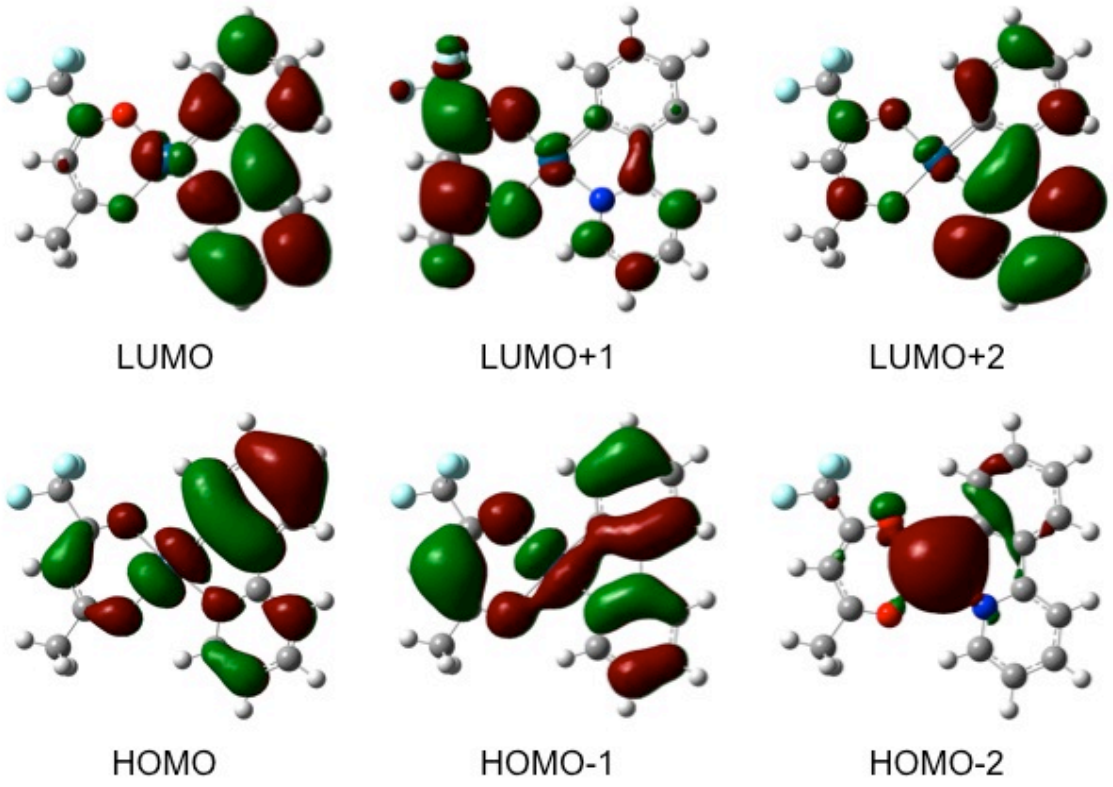
Figure S4 Frontier orbitals calculated using PBE0 in the gas-phase.



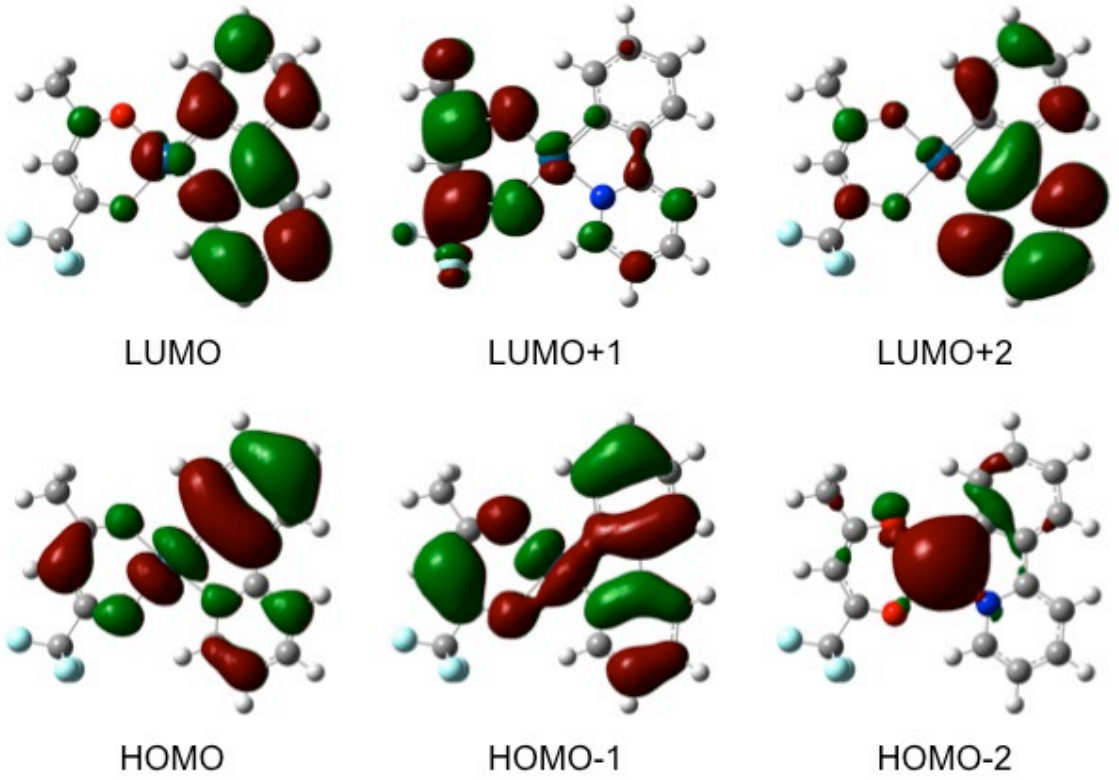
(a) [Pt(ppy)(acac)]



(b) [Pt(ppy)(hfac)]

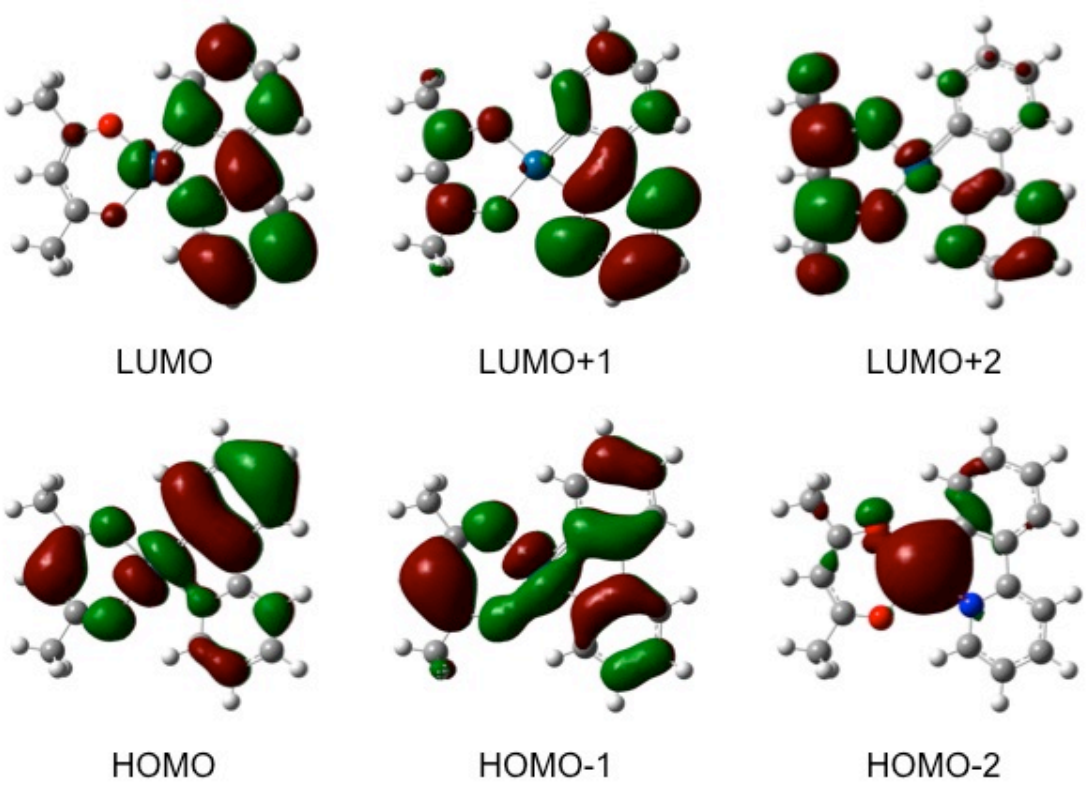


(c) *trans*-[Pt(ppy)(tfac)]

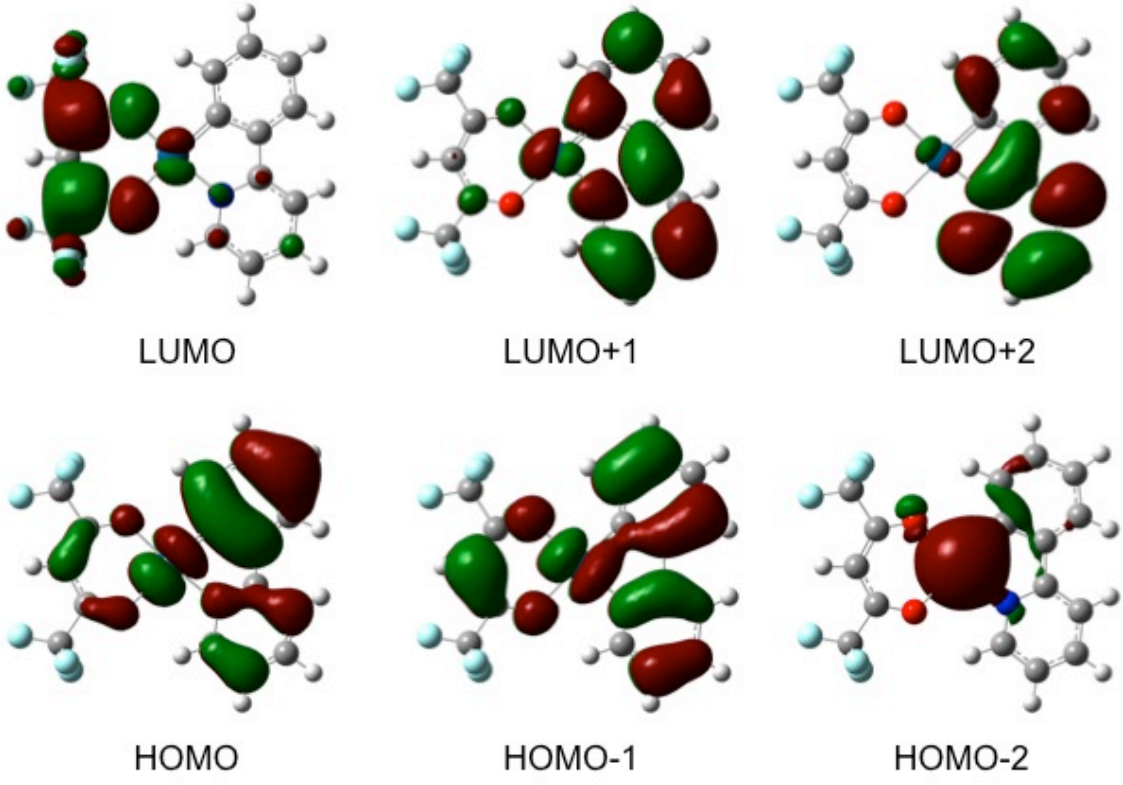


(d) *cis*-[Pt(ppy)(tfac)]

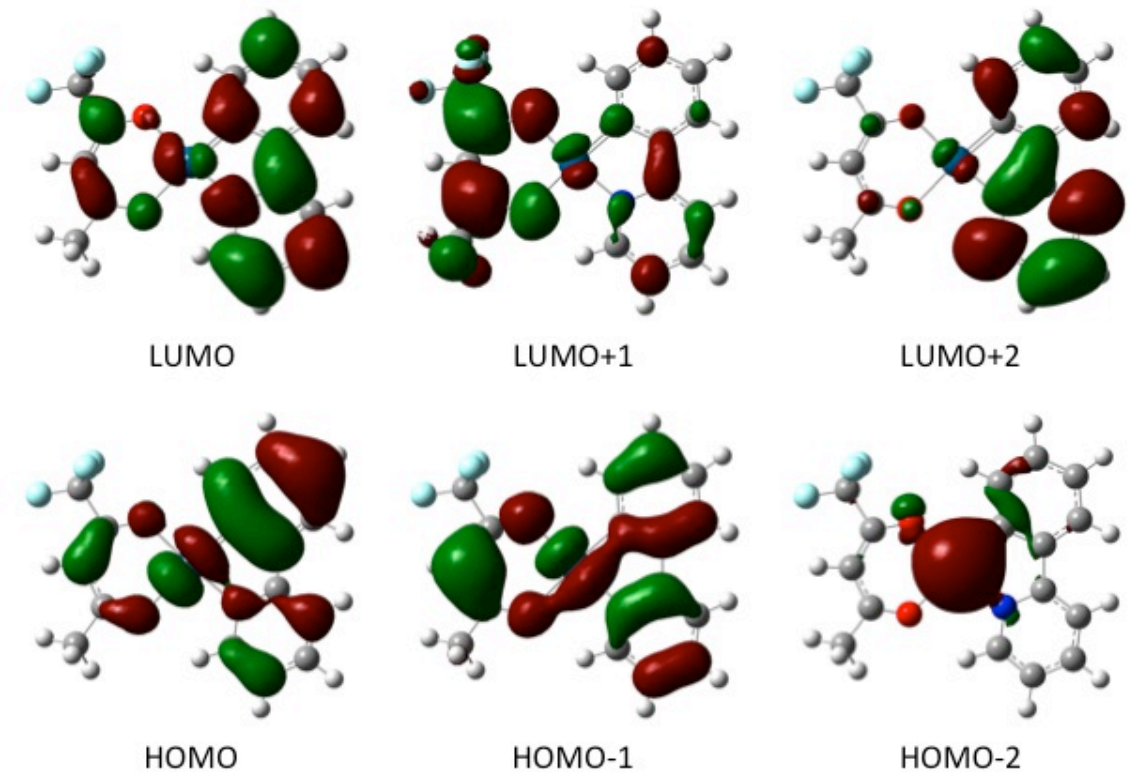
Figure S5 Frontier orbitals calculated using CAM B3LYP in the gas-phase.



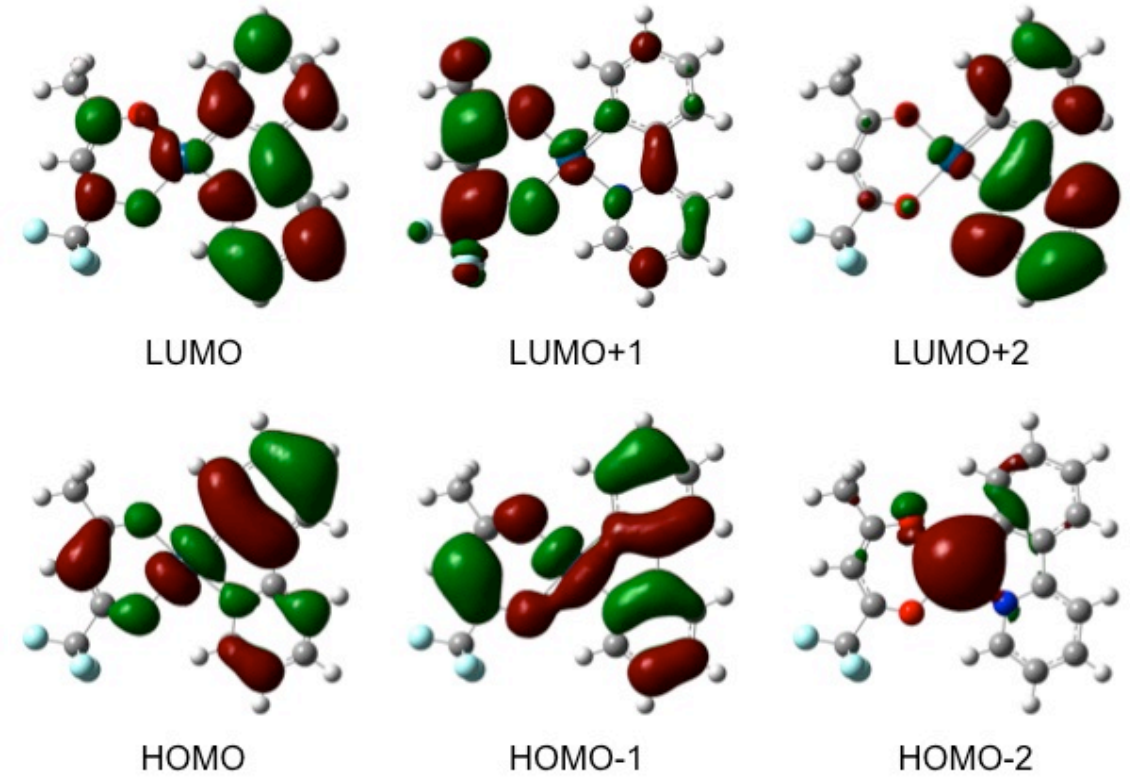
(a) [Pt(ppy)(acac)]



(b) [Pt(ppy)(hfac)]

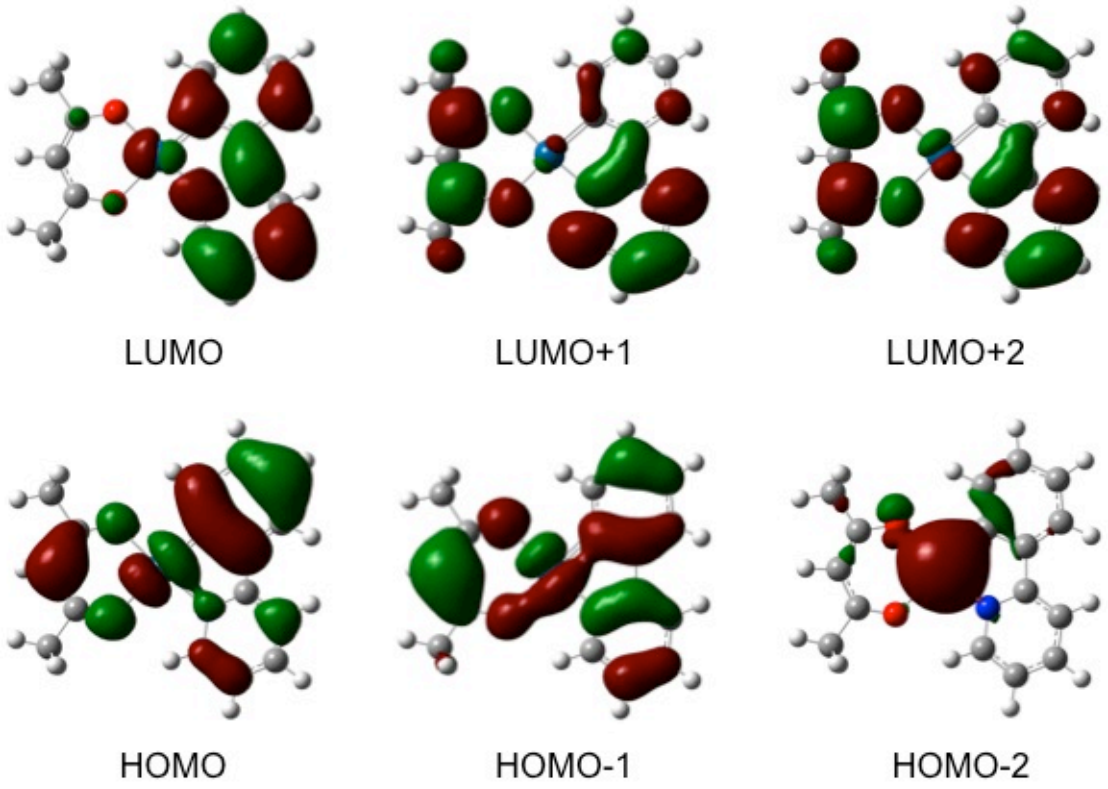


(c) *trans*-[Pt(ppy)(tfac)]

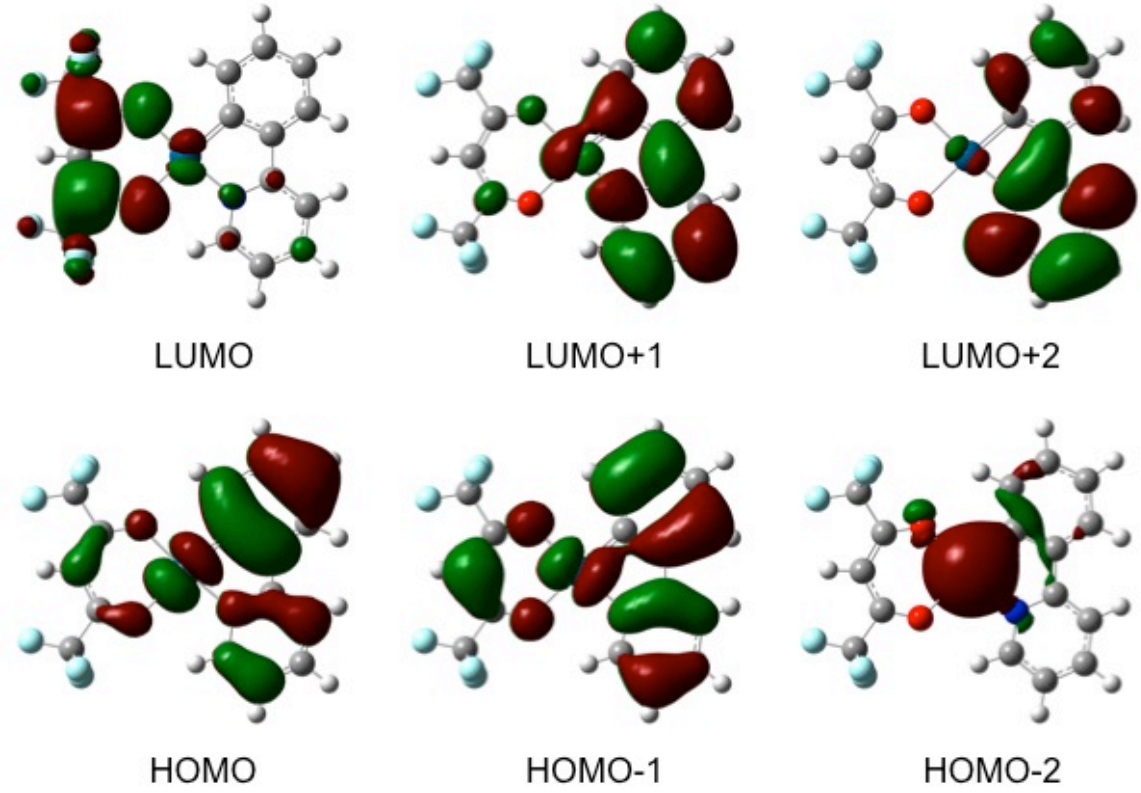


(d) *cis*-[Pt(ppy)(tfac)]

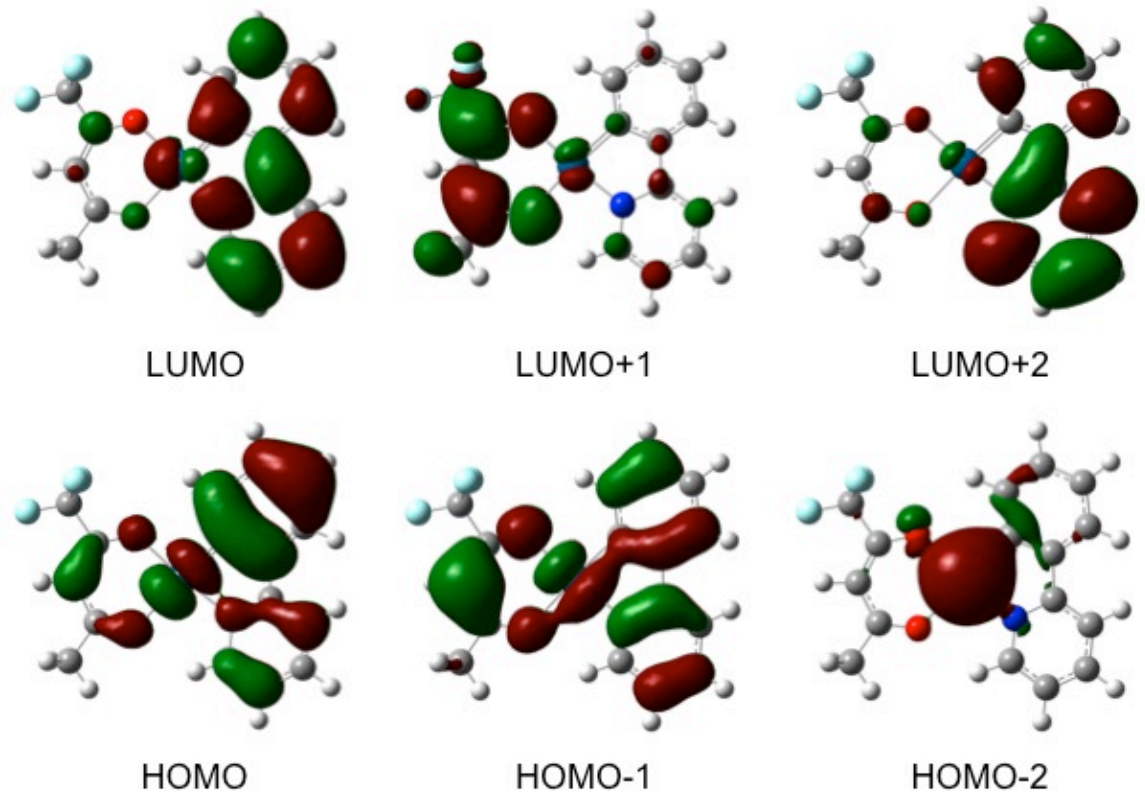
Figure S6 Frontier orbitals calculated using PBE0 with the PCM model for CH_2Cl_2 solvent.



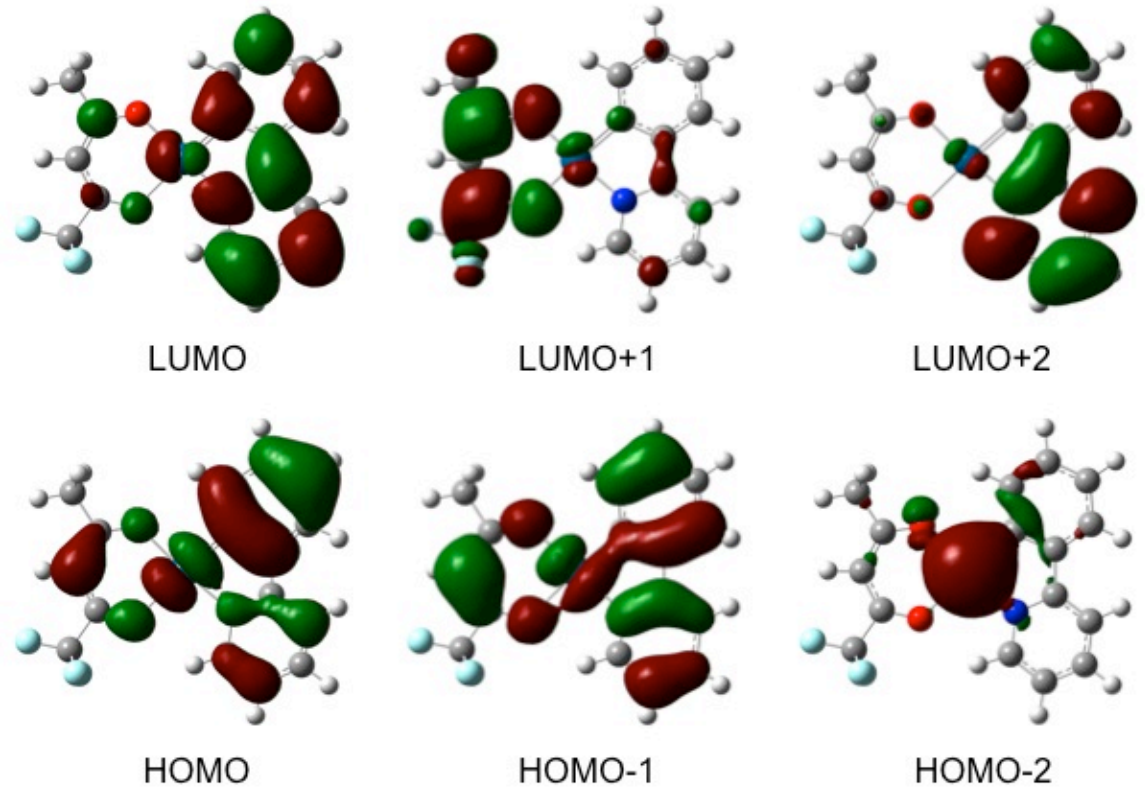
(a) [Pt(ppy)(acac)]



(b) [Pt(ppy)(hfac)]



(c) *trans*-[Pt(ppy)(tfac)]



(d) *cis*-[Pt(ppy)(tfac)]

Figure S7 Frontier orbitals calculated using CAM B3LYP with the PCM model for CH_2Cl_2 solvent.

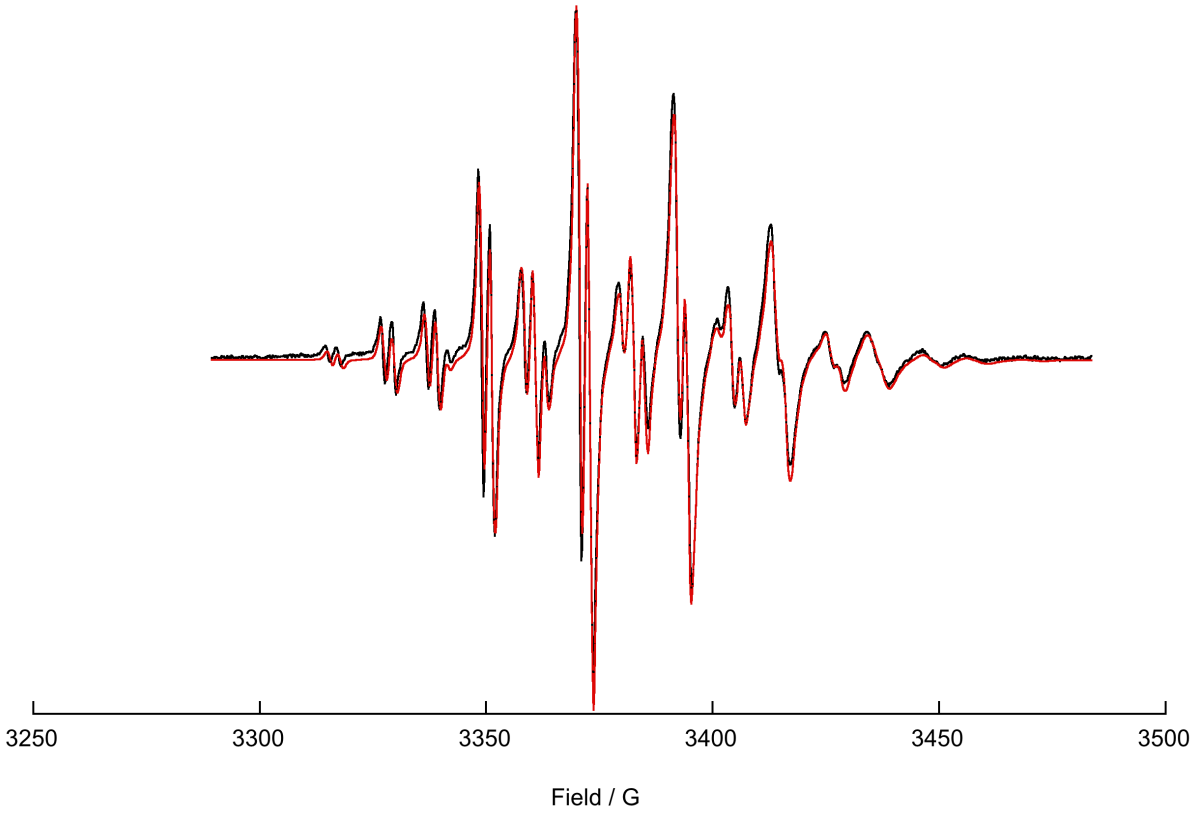


Figure S8 Overlay of experimental (black line) and simulated (red line) EPR spectrum of the monoanion of complex **7**.

Table S1 Orbital energies calculated at the ground state geometry using the functionals and conditions indicated.

(a) PBE0 in the gas phase.

	HOMO-3	HOMO-2	HOMO-1	HOMO	LUMO	LUMO+1	LUMO+2	LUMO+3	LUMO+4
acac	-6.70	-6.39	-6.17	-5.80	-1.63	-1.06	-0.84	0.35	0.52
hfac	-7.18	-7.02	-6.87	-6.37	-2.25	-2.03	-1.40	-0.19	-0.07
trans-tfac	-6.90	-6.70	-6.51	-6.09	-1.85	-1.55	-1.20	0.16	0.18
cis-tfac	-6.94	-6.70	-6.57	-6.09	-1.84	-1.57	-1.18	0.13	0.17

(b) CAM B3LYP in the gas phase.

	HOMO-3	HOMO-2	HOMO-1	HOMO	LUMO	LUMO+1	LUMO+2	LUMO+3	LUMO+4
acac	-7.82	-7.65	-7.34	-6.91	-0.56	0.09	0.35	1.41	1.73
hfac	-8.33	-8.28	-8.01	-7.46	-1.09	-0.94	-0.24	1.01	1.04
trans-tfac	-8.03	-7.96	-7.67	-7.19	-0.77	-0.38	-0.05	1.22	1.40
cis-tfac	-8.08	-7.96	-7.73	-7.19	-0.76	-0.39	-0.03	1.20	1.39

(c) PBE0 using PCM for CH_2Cl_2 as solvent.

	HOMO-3	HOMO-2	HOMO-1	HOMO	LUMO	LUMO+1	LUMO+2	LUMO+3	LUMO+4
acac	-6.92	-6.62	-6.39	-6.05	-1.74	-1.15	-1.00	0.05	0.27
hfac	-7.15	-6.92	-6.86	-6.37	-2.31	-1.90	-1.21	-0.21	-0.12
trans-tfac	-7.01	-6.77	-6.60	-6.23	-1.84	-1.65	-1.13	-0.03	0.04
cis-tfac	-7.04	-6.77	-6.67	-6.21	-1.84	-1.69	-1.13	-0.04	0.03

(d) CAM B3LYP using PCM for CH_2Cl_2 as solvent.

	HOMO-3	HOMO-2	HOMO-1	HOMO	LUMO	LUMO+1	LUMO+2	LUMO+3	LUMO+4
acac	-8.03	-7.86	-7.55	-7.14	-0.64	0.04	0.19	1.10	1.50
hfac	-8.29	-8.16	-7.99	-7.45	-1.13	-0.80	-0.02	0.95	1.03
trans-tfac	-8.11	-8.01	-7.74	-7.32	-0.73	-0.39	0.06	1.03	1.27
cis-tfac	-8.16	-8.02	-7.82	-7.30	-0.73	-0.51	0.05	1.02	1.26

Table 2 Analytical data for the new complexes

Compound	**Found (Expected) / %**		
	C	**H**	**N**
5-6	80.6 (80.7)	8.7 (8.6)	3.4 (3.3)
5-8	81.3 (81.1)	9.3 (9.3)	2.7 (2.9)
5-10	81.8 (81.7)	10.0 (9.8)	2.5 (2.6)

5-12	82.2 (82.1)	10.8 (10.3)	2.1 (2.3)
6-6	81.5 (81.9)	8.7 (8.8)	3.2 (3.0)
6-8	81.7 (81.9)	10.0 (9.4)	2.7 (2.7)
6-10	82.3 (82.1)	9.8 (9.9)	2.4 (2.8)
6-12	82.4 (82.6)	10.4 (10.2)	2.3 (2.2)
7	52.4 (52.6)	5.8 (6.0)	2.2 (2.0)
9	56.9 (57.2)	6.8 (7.1)	1.9 (1.7)
10	56.2 (56.3)	5.8 (6.0)	2.1 (1.9)
11	58.1 (58.5)	6.2 (6.6)	2.0 (1.8)