Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Electronic Supporting Information

Using Phosphorescent $PtAu_3$ Clusters for Superior Solution-Processable Organic Light Emitting Diodes with Very Small Efficiency Roll-Off

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Table S1. Partial Molecular Orbital Compositions (%) in the Ground State and Absorption Transitions for $PtAg_3$ complex **1** in CH_2Cl_2 Solution by TD-DFT Method at the PBE1PBE Level.

orbital	energy	MO contribution (%)				
	(eV)	Pt (s/p/d)	Ag (s/p/d)	Cl	tdpmp	C≡C-4-C_6H_4-Carb-9
LUMO+4	-1.48	0.51 (21/74/5)	1.36 (88/10/3)	0.09	81.99	16.05
LUMO+3	-1.55	0.23 (22/51/27)	2.31 (81/17/2)	0.01	93.25	4.19
LUMO+2	-1.63	1.59 (18/60/22)	3.13 (87/10/4)	0.15	75.06	20.07
LUMO+1	-1.73	6.13 (79/9/12)	4.36 (84/14/2)	0.19	65.80	23.53
LUMO	-2.41	15.09 (26/68/6)	14.21 (73/22/5)	3.19	39.61	27.89
HOMO	-5.93	3.30 (8/13/79)	4.51 (15/9/76)	1.55	4.57	86.08
HOMO-1	-6.03	0.98 (5/59/35)	1.94 (61/14/25)	0.04	2.96	94.07
HOMO-2	-6.44	0.61 (17/61/22)	23.26 (20/5/75)	11.61	25.88	38.63
HOMO-5	-6.68	2.97 (74/3/23)	25.62 (41/8/51)	2.59	31.67	37.16

state	*E*, nm (eV)	O.S.	transition (Contrib.)	assignment	exp. (nm)
S_1	431 (2.88)	0.3908	HOMO→LUMO (88%)	LLCT/IL/LMCT	408
S_3	372 (3.33)	0.1575	HOMO-2→LUMO (81%)	IL/MC/LLCT	
S_4	350 (3.54)	0.1750	HOMO→LUMO+1 (36%)	LLCT/IL	340
			HOMO-5→LUMO (33%)	IL/MC	
S_8	334 (3.71)	0.4211	HOMO→LUMO+2 (24%)	LLCT/IL	321
			HOMO-1→LUMO+1 (24%)	LLCT/IL/LMCT	
			HOMO-1→LUMO+2 (17%)	LLCT/IL	
S_{13}	320 (3.87)	0.1634	HOMO-1→LUMO+2 (33%)	LLCT/IL	
			HOMO→LUMO+3 (14%)	LLCT	
			HOMO→LUMO+2 (12%)	LLCT/IL	
			HOMO→LUMO+4 (10%)	LLCT/IL	

Table S2. Partial Molecular Orbital Compositions (%) in the Lowest-Energy Triplet State and the Emission Transition for $PtAg_3$ complex **1** in CH_2Cl_2 Solution by TD-DFT Method at the PBE1PBE Level.

orbital	energy	MO contribution (%)				
	(eV)	Pt (s/p/d)	Ag (s/p/d)	Cl	tdpmp	C≡C-4-C_6H_4-Carb-9
LUMO	-3.08	18.79 (22/59/19)	14.41 (71/19/10)	2.93	35.32	28.55
HOMO	-5.89	3.95 (0/13/87)	3.25 (10/15/75)	1.12	2.57	89.11
HOMO-6	-6.85	17.58 (0/9/91)	14.60 (11/13/76)	3.33	21.52	42.97

state	*E*, nm (eV)	O.S.	transition (contrib.)	assignment	exp. (nm)
T_1	569 (2.18)	0.0000	HOMO→LUMO (74%)	LLCT/IL/LMCT	541
			HOMO-6→LUMO (11%)	IL/MC/LLCT	

Table S3. Partial Molecular Orbital Compositions (%) in the Ground State and Absorption Transitions for $PtAg_3$ complex **3** in CH_2Cl_2 Solution by TD-DFT Method at the PBE1PBE Level.

orbital	energy	MO contribution (%)				
	(eV)	Pt (s/p/d)	Ag (s/p/d)	Cl	tdpmp	C≡C-3-EtCarb–9
LUMO+11	-1.11	5.12 (4 /83/13)	4.00 (87/11/2)	0.58	57.84	32.46
LUMO+10	-1.15	1.40 (79/3/18)	1.83 (68/29/3)	0.15	73.68	22.95
LUMO+5	-1.38	0.47 (37/54/9)	2.24 (85/11/4)	0.09	83.84	13.37
LUMO+3	-1.44	0.27 (46/36/18)	2.20 (80/18/1)	0.08	90.16	7.28
LUMO+2	-1.54	1.41 (29/52/19)	1.98 (87/11/2)	0.07	87.69	8.84
LUMO+1	-1.6	3.53 (84/6/10)	3.83 (84/14/2)	0.27	83.34	9.03
LUMO	-2.27	16.13 (20/73/7)	14.93 (77/18/4)	3.36	45.73	19.84
HOMO	-5.77	5.24 (30/7/63)	6.82 (18/11/70)	1.96	7.17	78.81
HOMO-1	-5.95	2.34 (23/14/63)	3.48 (50/15/35)	0.07	5.83	88.28
HOMO-2	-6.44	0.34 (6/83/12)	20.60 (23/6 /71)	9.74	24.03	45.30
HOMO-4	-6.56	1.85 (12/22/66)	7.27 (25/11/64)	2.76	10.35	77.77

state	*E*,nm (eV)	O.S.	transition (Contrib.)	assignment	exp. (nm)
S_1	445 (2.79)	0.2390	HOMO→LUMO (95%)	LLCT/IL/LMCT/MC	426
S_3	363 (3.41)	0.0818	HOMO-2→LUMO (71%)	IL/LLCT/MC/LMCT	
			HOMO-4→LUMO (18%)	LLCT/IL/LMCT	
S_4	350 (3.54)	0.1403	HOMO→LUMO+1 (74%)	LLCT/IL	
S_9	332 (3.74)	0.1422	HOMO-1→LUMO+1 (17%)	LLCT/IL	334
			HOMO-1→LUMO+2 (15%)	LLCT/IL	
			HOMO→LUMO+5 (13%)	LLCT/IL/MLCT	
			HOMO→LUMO+3 (9%)	LLCT/MLCT	
S_{21}	309 (4.02)	0.1738	HOMO→LUMO+11 (28%)	LLCT/IL	
			HOMO-1→LUMO+3 (15%)	LLCT	
			HOMO→LUMO+10 (9%)	LLCT/IL/MLCT	
S_{53}	278 (4.45)	0.1501	HOMO-2→LUMO+5 (13%)	IL/LLCT/MLCT	262

Table S4. Partial Molecular Orbital Compositions (%) in the Lowest-Energy Triplet State and the Emission Transition for $PtAg_3$ complex **3** in CH_2Cl_2 Solution by TD-DFT Method at the PBE1PBE Level.

orbital	energy	MO contribution (%)				
	(eV)	Pt (s/p/d)	Ag (s/p/d)	Cl	tdpmp	C≡C-3-EtCarb–9
LUMO	-2.95	20.83 (25/52/23)	14.03 (69/21/0)	2.86	36.47	25.81
HOMO	-5.69	7.12 (1/19/80)	4.17 (15/23/1)	0.99	3.12	84.61

state	*E*, nm (eV)	O.S.	transition (Contrib.)	assignment	exp. (nm)
T_1	591 (2.10)	0.0000	HOMO→LUMO (88%)	LLCT/IL/LMCT/MC	585

Table S5. Partial Molecular Orbital Compositions (%) in the Ground State and Absorption Transitions for $PtAu_3$ complex **6** in CH_2Cl_2 Solution by TD-DFT Method at the PBE1PBE Level.

orbital	energy	MO contribution (%)				
	(eV)	Pt (s/p/d)	Au (s/p/d)	Cl	tdpmp	C≡C-4-C_6H_4-Carb-9
LUMO+12	-1.21	2.72 (82/10/8)	1.75 (92/7/1)	0.24	47.56	47.73
LUMO+11	-1.22	2.14 (71/17/12)	1.53 (86/12/2)	0.33	40.61	55.39
LUMO+7	-1.52	0.14 (17/57/26)	3.79 (38/39/23)	0.40	94.61	1.06
LUMO+5	-1.57	1.09 (92/5/3)	1.92 (47/41/12)	0.20	92.91	3.89
LUMO+4	-1.63	0.19 (0/93/6)	1.24 (5/88/7)	0.04	96.37	2.16
LUMO+3	-1.71	3.79 (20/5/75)	4.21 (16/47/36)	0.70	89.02	2.28
LUMO+2	-1.86	0.89 (45/19/35)	8.29 (79/10/10)	0.28	87.39	3.15
LUMO+1	-2.23	13.31 (68/18/14)	15.43 (41/55/4)	3.37	52.16	15.72
LUMO	-2.38	0.88 (0/88/12)	37.05 (31/57/11)	0.44	59.04	2.58
HOMO	-5.91	3.12 (0/5/95)	0.14 (50/41/9)	0.02	1.94	94.78
HOMO-1	-5.93	2.32 (1/5/95)	0.49 (54/11/35)	0.11	1.82	95.26
HOMO-4	-6.59	24.63 (18/3/79)	31.27 (35/3/62)	7.74	17.19	19.17
HOMO-5	-6.62	14.35 (0/0/100)	0.77 (27/44/29)	0.41	3.32	81.15
HOMO-6	-6.72	13.13 (13/3/84)	5.36 (40/4/56)	1.32	8.40	71.78

state	*E*, nm (eV)	O.S.	transition (Contrib.)	assignment	exp. (nm)
S_1	405 (3.06)	0.0086	HOMO→LUMO (94%)	LLCT/LMCT	427
S_3	400 (3.10)	0.3788	HOMO→LUMO+1 (85%)	LLCT/LMCT/IL	
			HOMO-5→LUMO+1 (10%)	LLCT/IL/LMCT/MC	
S_5	372 (3.34)	0.0913	HOMO-4→LUMO (78%)	MC/LLCT/MLCT/IL	368
			HOMO-6→LUMO (14%)	LLCT/LMCT/MC	
S_6	353 (3.51)	0.3308	HOMO-4→LUMO+1 (75%)	IL/MC/MLCT	344
			HOMO-6→LUMO+1 (18%)	LLCT/IL/MC/LMCT	
S_7	345 (3.60)	0.0967	HOMO→LUMO+2 (80%)	LLCT	
			HOMO→LUMO+3 (9%)	LLCT	
S_{16}	326 (3.80)	0.1368	HOMO→LUMO+5 (33%)	LLCT	
			HOMO-1→LUMO+4 (31%)	LLCT	
			HOMO→LUMO+4 (10%)	LLCT	
S_{27}	311 (3.99)	0.5922	HOMO-1→LUMO+4 (17%)	LLCT	292
			HOMO-1→LUMO+7 (17%)	LLCT	
			HOMO-1→LUMO+11 (12%)	IL/LLCT	
			HOMO→LUMO+12 (10%)	IL/LLCT	

Table S6. Partial Molecular Orbital Compositions (%) in the Lowest-Energy Triplet State and the Emission Transition for $PtAu_3$ complex **6** in CH_2Cl_2 Solution by TD-DFT Method at the PBE1PBE Level.

orbital	energy	MO contribution (%)				
	(eV)	Pt (s/p/d)	Au (s/p/d)	Cl	tdpmp	C≡C-4-C_6H_4-Carb-9
LUMO+1	-2.25	11.21 (57/27/16)	15.34 (56/40/4)	3.89	49.18	20.37
LUMO	-2.66	1.08 (4/83/13)	39.02 (33/52/15)	0.48	57.11	2.30
HOMO	-5.95	6.91 (0/4/95)	0.27 (44/51/5)	0.02	1.58	91.22

state	*E*, nm (eV)	O.S.	transition (Contrib.)	assignment	exp. (nm)
T_1	509 (2.44)	0.0000	HOMO→LUMO (48%)	LLCT/LMCT	524
			HOMO→LUMO+1 (24%)	LLCT/LMCT/IL	

Table S7. Partial Molecular Orbital Compositions (%) in the Ground State and Absorption Transitions for $PtAu_3$ complex **8** in CH_2Cl_2 Solution by TD-DFT Method at the PBE1PBE Level.

orbital	energy	MO contribution (%)				
	(eV)	Pt (s/p/d)	Au (s/p/d)	Cl	tdpmp	C≡C-2-PhCarb−9
LUMO+9	-1.37	0.88 (0/81/19)	1.22 (16/77/8)	0.24	30.54	67.12
LUMO+7	-1.48	0.16 (0/87/13)	2.96 (36/47/16)	0.19	95.80	0.89
LUMO+6	-1.50	0.55 (0/92/8)	1.74 (46/53/1)	0.36	90.32	7.04
LUMO+5	-1.54	1.37 (90/6/4)	1.29 (50/40/10)	0.11	90.51	6.72
LUMO+4	-1.61	0.17 (0/91/9)	1.32 (4/90/6)	0.05	92.50	5.96
LUMO+1	-2.18	13.29 (71/16/13)	15.70 (34/61/5)	3.33	53.12	14.56
LUMO	-2.33	0.85 (0/88/12)	36.95 (31/58/11)	0.44	59.32	2.43
HOMO	-6.01	6.09 (4/2/94)	1.00 (55/9/36)	0.20	4.38	88.34
HOMO-1	-6.03	6.77 (0/5/95)	0.26 (41/44/14)	0.04	4.29	88.65
HOMO-3	-6.14	0.25 (47/11/42)	0.04 (42/52/6)	0.01	1.05	98.65
HOMO-4	-6.58	30.06 (19/3/78)	36.37 (35/3/61)	8.16	19.04	6.38

state	*E*, nm (eV)	O.S.	transition (Contrib.)	assignment	exp. (nm)
S_1	400 (3.10)	0.0483	HOMO→LUMO+1 (90%)	LLCT/LMCT/IL	443
S_2	400 (3.10)	0.0524	HOMO→LUMO (91%)	LLCT/LMCT	
S_4	395 (3.14)	0.3303	HOMO-1→LUMO+1 (91%)	LLCT/LMCT/IL	373
S_{10}	352 (3.52)	0.3347	HOMO-4→LUMO+1 (73%)	MLCT/MC/IL	
			HOMO-3→LUMO+1 (20%)	LLCT/LMCT/IL	
S_{17}	322 (3.84)	0.3619	HOMO→LUMO+4 (49%)	LLCT	330
			HOMO→LUMO+6 (20%)	LLCT	
			HOMO-1→LUMO+5 (13%)	LLCT	
S_{29}	308 (4.03)	0.5848	HOMO→LUMO+7 (22%)	LLCT	
			HOMO-1→LUMO+10 (20%)	IL/LLCT	
			HOMO→LUMO+9 (18%)	IL/LLCT	
			HOMO→LUMO+4 (12%)	LLCT	

Table S8. Partial Molecular Orbital Compositions (%) in the Lowest-Energy Triplet State and the Emission Transition for $PtAu_3$ complex **8** in CH_2Cl_2 Solution by TD-DFT Method at the PBE1PBE Level.

orbital	energy (eV)	MO contribution (%)				
		Pt (s/p/d)	Au (s/p/d)	Cl	tdpmp	C≡C-2-PhCarb−9
LUMO	-2.59	13.08 (67/18/15)	21.08 (35/59/6)	1.72	50.06	14.06
HOMO	-5.73	7.70 (1/7/92)	0.97 (27/35/38)	0.10	3.57	87.66

state	*E*, nm (eV)	O.S.	transition (Contrib.)	assignment	exp. (nm)
T_1	522 (2.38)	0.0000	HOMO→LUMO (67%)	LLCT/LMCT	550

Table S9. The energy levels and gaps for $PtAu_3$ complexes **8**-**10**, deduced from electrochemical studies and UV-Vis absorption spectra.

complex	ΔE_g (eV)[a]	HOMO (eV)[b]	LUMO (eV)[b]
8	2.55	−5.25	−2.70
9	2.51	−5.23	−2.76
10	2.47	−5.26	−2.75

[a] Estimated from the onset wavelengths of the absorption spectra in CH_2Cl_2. [b] The HOMO and LUMO energies were determined from CV and the absorption onset. Ferrocene was used as the internal standard in each experiment. The Ferrocene oxidation potential was located at +380 mV, relative to the saturated Ag/AgCl reference electrode.

Table S10. Optimization of Electroluminescent Performance of OLEDs Based on Phosphorescent $PtAu_3$ Cluster Complexes **8**−**10**.

	host materials	doping	ETL	V_{on}[a] V	L[b] cd m^{-2}	CE[c] cd A^{-1}	PE[d] lm W^{-1}	EQE[e] %
8	mCP:OXD-7 (47.5 %:47.5 %)	3%	BmPyPb	5.2	10911	58.3	26.1	14.9
	TCTA:mCP:OXD-7 (23.7 %: 23.7 %: 47.6 %)	3%	BmPyPb	5.4	19643	54.2	25.3	13.8
9	mCP:OXD-7 (48.5 %:48.5 %)	3%	TPBi	4.4	11703	34.2	17.3	9.8
	mCP:OXD-7 (48.5 %:48.5 %)	3%	BCP	5.7	15506	34.1	12.7	9.6
	mCP:OXD-7 (48.5 %:48.5 %)	3%	BmPyPb	5.5	12711	62.8	25.1	17.7
	mcp:oxd-7 (48.5%:48.5%)	8%	BmPyPb	4.95	10430	60.2	28.9	16.8
10	mCP:OXD-7 (48.5 %:48.5 %)	3%	BmPyPb	4.9	19308	45.2	20.3	18.1
	TCTA:OXD-7 (48.5 %:48.5 %)	3%	BmPyPb	4.2	19641	42.8	21.3	17.3

[a]Turn-on voltage at 1 cd m^{-2}. [b]Maximum luminance. [c]Maximum current efficiency. [d]Maximum power efficiency. [e]Maximum external quantum efficiency. Device structure is ITO / PEDOT : PSS (50 nm) / host : $PtAu_3$ complex (50 nm) / ETL (50 nm) / LiF (1 nm) / Al (100 nm).

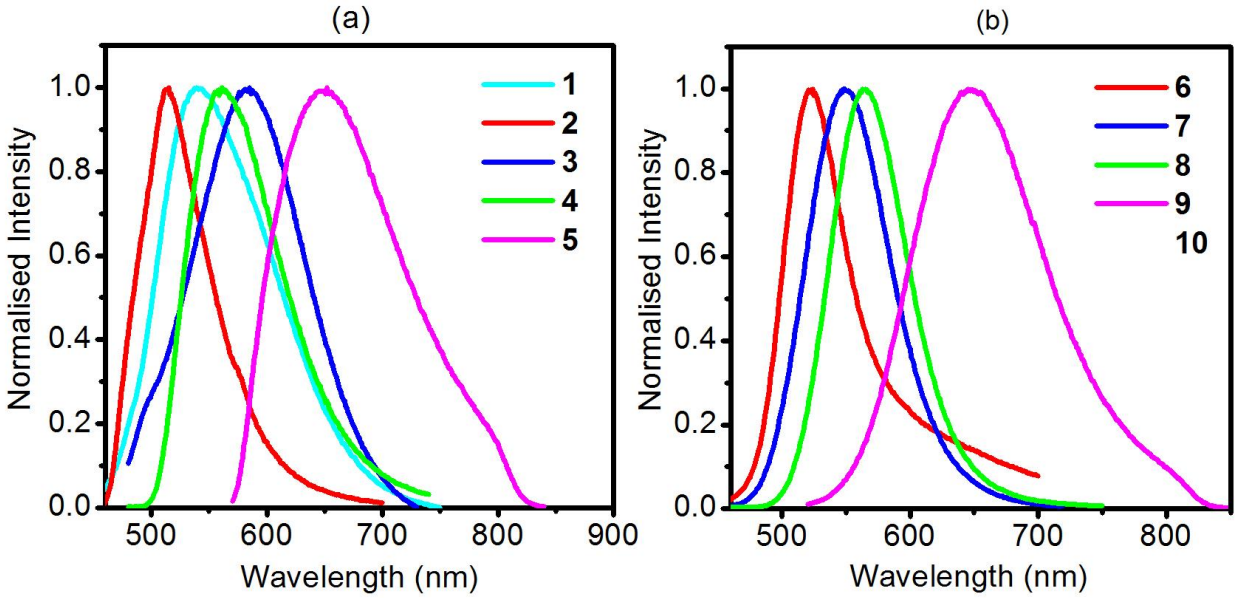


Figure S1. Photoluminescent emission spectra of $PtAg_3$ (a) and $PtAu_3$ (b) complexes in fluid CH_2Cl_2.

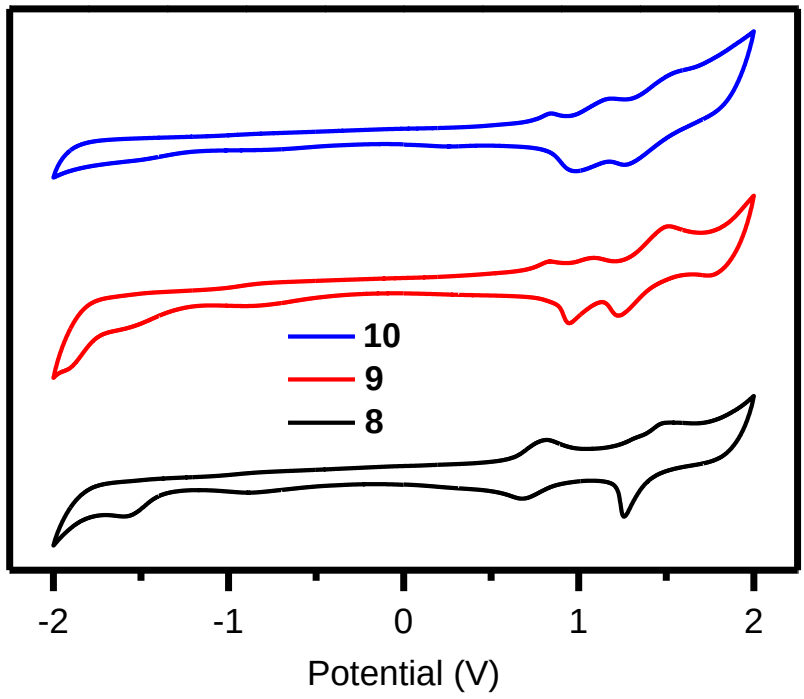


Figure S2. Cyclic voltammogram of $PtAu_3$ complexes **8**–**10** measured in CH_2Cl_2 solution at a scan rate of 100 mV/s.

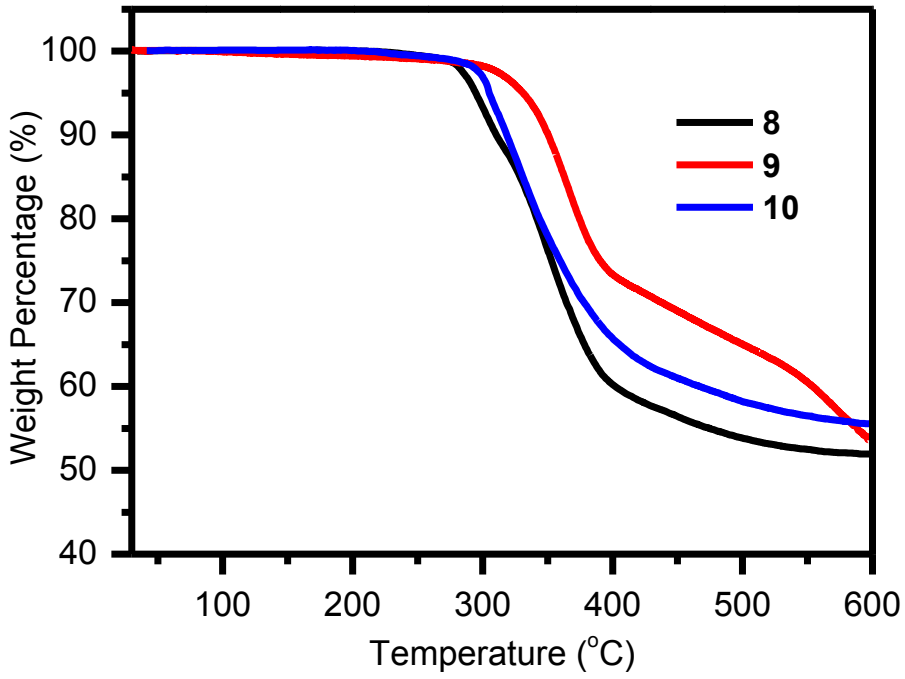


Figure S3. Thermogravimetric curves of $PtAu_3$ complexes **8**–**10**.

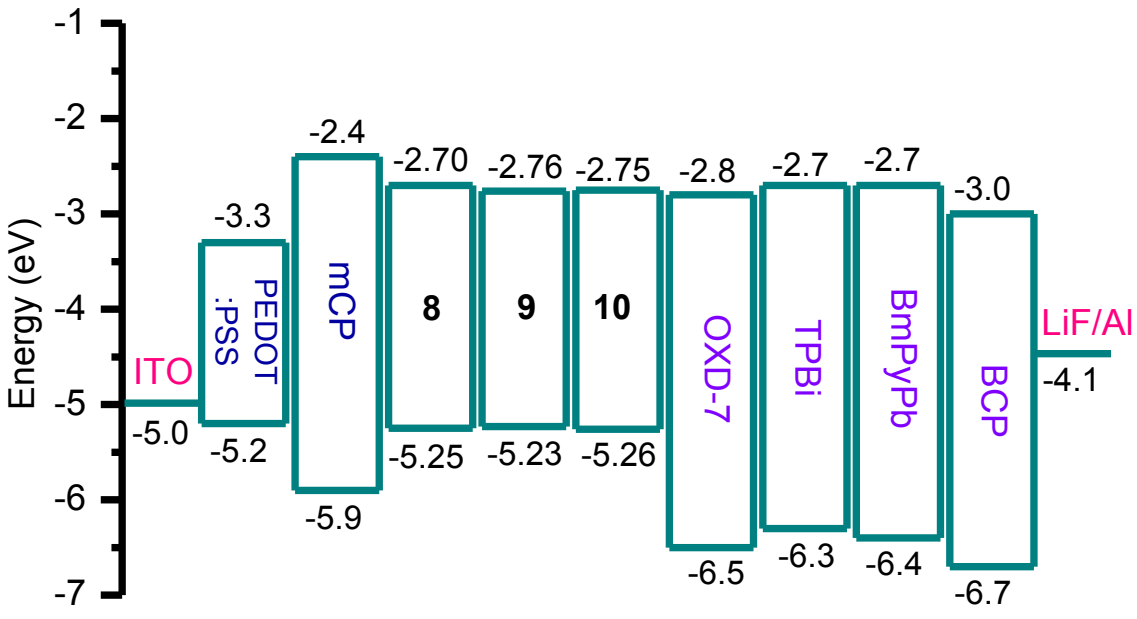


Figure S4. Energy-level diagrams of the transport and emitting materials.

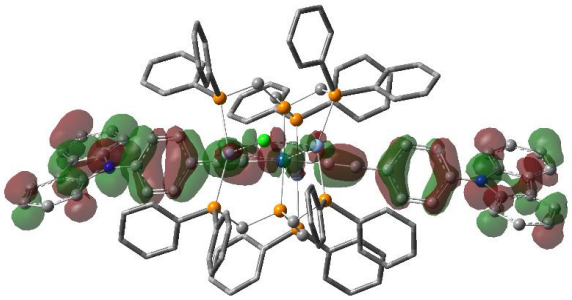
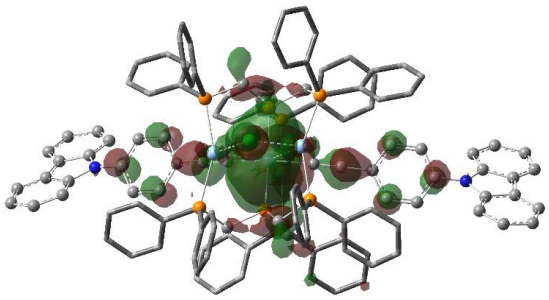
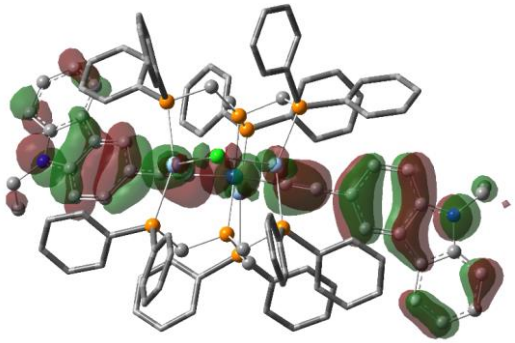
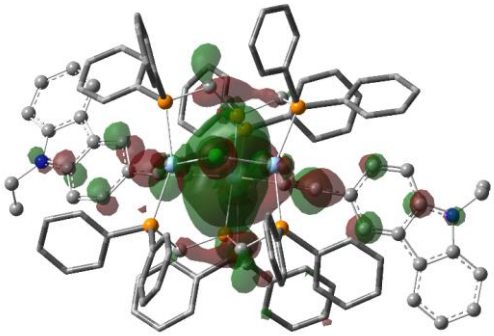
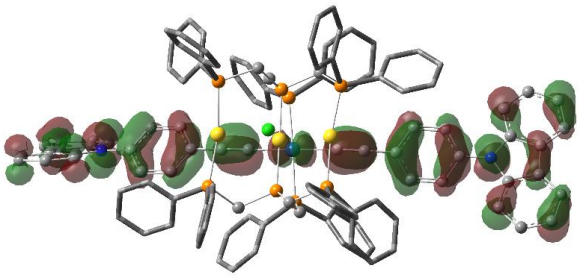
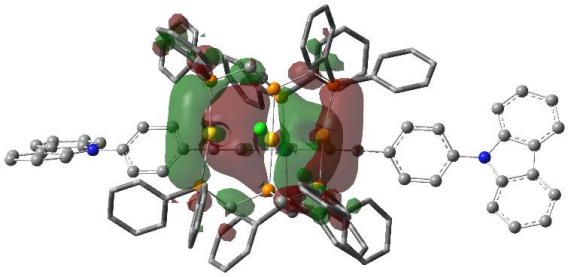
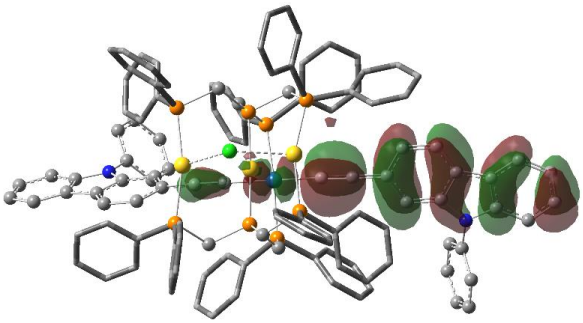
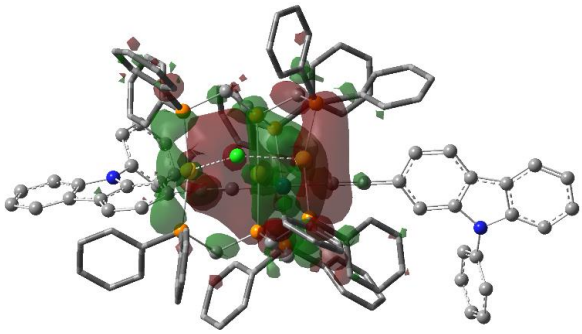
complex	HOMO	LUMO
1		
3		
6		
8		

Figure S5. Plots of the frontier molecular orbitals involved in the emission transition of compounds **1**, **3**, **6** and **8** in CH_2Cl_2 by TD-DFT Method at the PBE1PBE Level (isovalue = 0.02). For clarity, the hydrogen atoms are omitted.

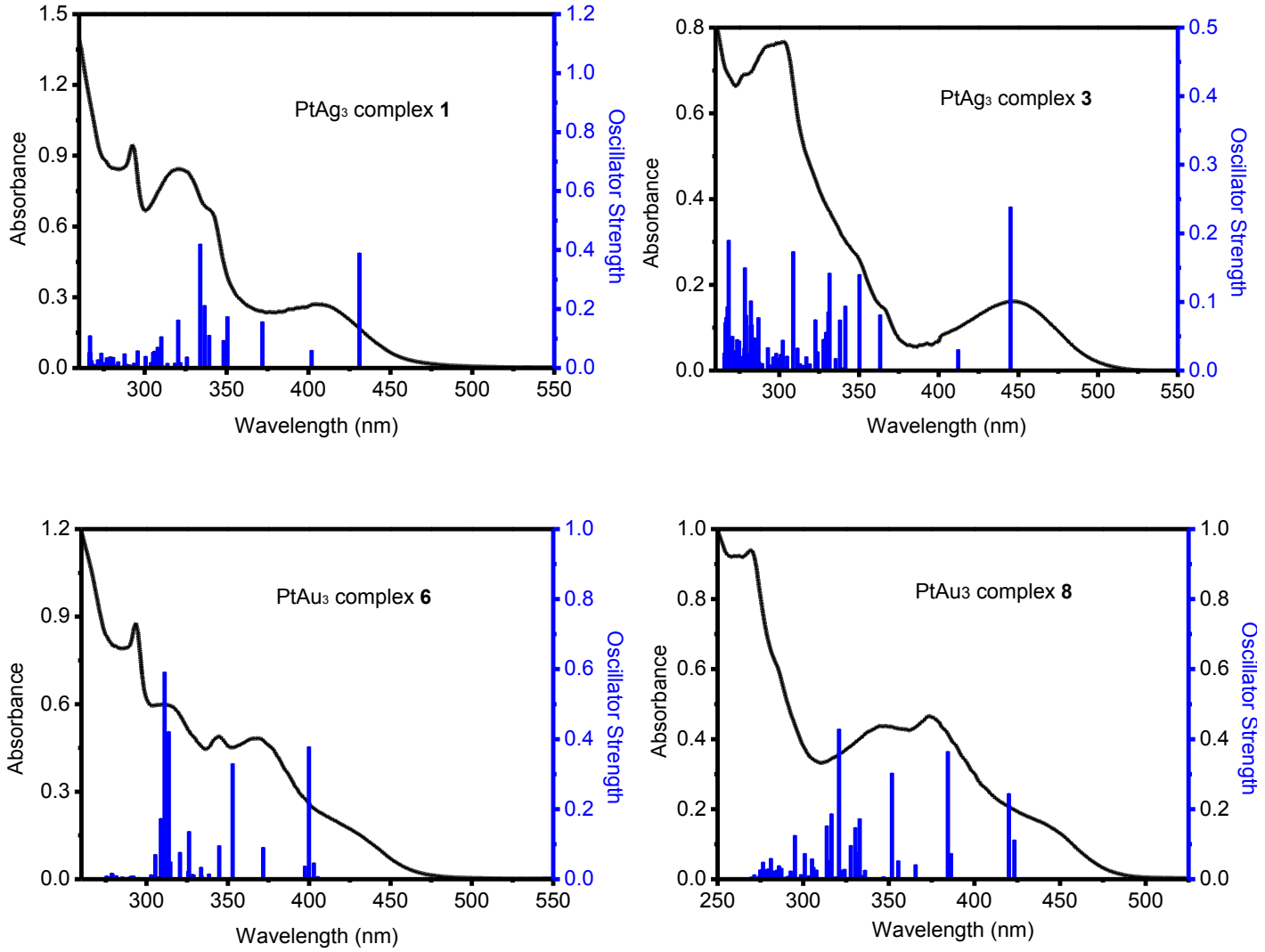


Figure S6. The calculated (blue vertical bars) and measured (black line) absorption spectra of complexes **1**, **3**, and **6** and **8** in dichloromethane at ambient temperature, calculated by TD-DFT method at the PBE1PBE level.