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Electronic Supporting Information

High-Efficiency Organic Light-Emitting Diodes of Phosphorescent $PtAg_2$ Heterotrinuclear Acetylide Complexes Supported with Triphosphine

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Table S1. Partial Molecular Orbital Compositions (%) in the Ground State and Absorption Transition Assignment for $PtAg_2$ Complex **1** in Dichloromethane by TD-DFT Method at the PBE1PBE Level.

orbital	energy (eV)	MO contribution (%)			
		Pt (s/p/d)	Ag (s/p/d)	dpmp	C≡C-2-Etcarb-9
LUMO+3	-1.54	0.49 (0/100/0)	4.39 (14/56/30)	68.72	26.41
LUMO+2	-1.55	34.29 (84/0/16)	26.07 (75/24/1)	21.31	18.32
LUMO	-2.48	14.55 (0/100/0)	14.35 (54/33/12)	50.50	20.60
HOMO	-6.04	13.42 (4/0/96)	5.75 (42/20/38)	5.29	75.54
HOMO-1	-6.18	0.93 (0/100/0)	1.11 (71/16/13)	1.52	96.44
HOMO-4	-6.86	25.26 (24/0/76)	33.89 (31/9/60)	38.95	1.90

state	*E*, nm (eV)	O.S.	transition (Contrib.)	assignment	exp. (nm)
S_1	431 (2.88)	0.9039	HOMO→LUMO (96%)	^{1}LLCT/^{1}MC/^{1}LMCT	409
S_5	350 (3.54)	0.5418	HOMO-4→LUMO (96%)	^{1}IL/^{1}MLCT/^{1}MC	327
S_9	317 (3.91)	0.6379	HOMO→LUMO+3 (55%)	^{1}LLCT/^{1}IL/^{1}MLCT	263
			HOMO-1→LUMO+2 (12%)	^{1}LMCT/^{1}LLCT/^{1}IL	

Table S2. Partial Molecular Orbital Compositions (%) in the Lowest Triplet State and Emission Transition Assignment for $PtAg_2$ Complex **1** in Dichloromethane by TD-DFT Method at the PBE1PBE Level.

orbital	energy (eV)	MO contribution (%)			
		Pt (s/p/d)	Ag (s/p/d)	dppm	C≡C-2-Phcarb-9
LUMO+4	-1.50	37.62 (83/0/17)	25.51 (74/25/1)	22.09	14.79
LUMO	-2.70	19.58 (0/100/0)	20.82 (72/18/10)	44.42	15.19
HOMO	-5.85	15.60 (8/0/92)	2.79 (56/12/31)	2.85	78.76
HOMO-3	-6.25	1.08 (0/100/0)	7.80 (38/10/52)	11.07	80.05

state	*E*, nm (eV)	O.S.	transition (contribution)	assignment	exp. (nm)
T_1	605 (2.05)	0.0000	HOMO→LUMO (82%)	^{3}LLCT/^{3}LMCT/^{3}MC	540
T_2	513 (2.42)	0.0000	HOMO-3→LUMO (53%)	^{3}LMCT/^{3}LLCT/^{3}IL	
			HOMO→LUMO+4 (16%)	^{3}LMCT/^{3}LLCT/^{3}MC/^{3}IL	

Table S3. Partial Molecular Orbital Compositions (%) in the Ground State and Absorption Transition Assignment for $PtAg_2$ Complex **2** in Dichloromethane by TD-DFT Method at the PBE1PBE Level.

orbital	energy (eV)	MO contribution (%)			
		Pt (s/p/d)	Ag (s/p/d)	dpmp	C≡C-3-Etcarb-9
LUMO+18	-0.73	6.82 (0/100/0)	16.07 (26/69/4)	73.84	3.27
LUMO+10	-1.14	3.15 (0/100/0)	6.14 (63/32/5)	60.80	29.91
LUMO+8	-1.22	11.17 (0/100/0)	17.32 (86/8/6)	31.36	40.14
LUMO+6	-1.37	4.88 (0/100/0)	7.30 (32/34/34)	85.47	2.36
LUMO+3	-1.47	4.47 (45/0/55)	9.55 (64/18/18)	84.05	1.93
LUMO+2	-1.57	4.64 (0/100/0)	11.47 (50/29/21)	81.94	1.95
LUMO	-2.39	14.35 (0/100/0)	9.75 (25/59/16)	57.91	17.99
HOMO	-5.79	10.65 (1/0/99)	4.17 (2/40/59)	4.08	81.10
HOMO-2	-6.54	6.16 (62/0/38)	4.14 (67/10/23)	1.72	87.98
HOMO-3	-6.57	1.62 (0/100/0)	3.56 (38/16/46)	2.71	92.11
HOMO-4	-6.91	20.72 (24/0/76)	31.62 (31/9/61)	37.46	10.20
HOMO-10	-7.65	4.81 (16/0/84)	6.44 (2/48/50)	88.28	0.47

state	*E*, nm (eV)	O.S.	transition (Contrib.)	assignment	exp. (nm)
S_1	453 (2.73)	0.6504	HOMO→LUMO (96%)	^{1}LLCT/^{1}IL/^{1}MC	455
S_6	338 (3.67)	0.2631	HOMO-4→LUMO (46%) HOMO-2→LUMO (19%) HOMO→LUMO+2 (18%)	^{1}IL/^{1}MLCT/^{1}MC ^{1}LLCT/^{1}IL/^{1}LMCT/^{1}MC ^{1}LLCT/^{1}MC	345
S_7	336 (3.69)	0.1175	HOMO→LUMO+2 (72%) HOMO-4→LUMO (15%)	^{1}LLCT/^{1}MC ^{1}IL/^{1}MLCT/^{1}MC	
S_{18}	306 (4.05)	0.2259	HOMO→LUMO+10 (49%) HOMO→LUMO+8 (24%)	^{1}LLCT/^{1}IL/^{1}MC ^{1}IL/^{1}LLCT/^{1}LMCT/^{1}MC	289
S_{52}	270 (4.59)	0.2222	HOMO-10→LUMO (20%) HOMO-3→LUMO+3 (17%) HOMO→LUMO+18 (17%) HOMO-2→LUMO+6 (11%)	^{1}IL/^{1}LLCT/^{1}LMCT/^{1}MC ^{1}LLCT ^{1}LLCT/^{1}MC ^{1}LLCT/^{1}MC	

Table S4. Partial Molecular Orbital Compositions (%) in the Lowest Triplet State and Emission Transition Assignment for $PtAg_2$ Complex **2** in Dichloromethane Solution by TD-DFT Method at the PBE1PBE Level.

orbital	energy (eV)	MO contribution (%)			
		Pt (s/p/d)	Ag (s/p/d)	dpmp	C≡C-3-Etcarb-9
LUMO	-2.62	18.55 (0/100/0)	14.85 (56/30/14)	52.41	14.19
HOMO	-5.65	11.68 (1/0/99)	2.86 (17/32/51)	3.38	82.08
HOMO-1	-5.99	1.00 (0/100/0)	5.34 (18/19/63)	8.86	84.80

state	*E*, nm (eV)	O.S.	transition (Contrib.)	assignment	exp. (nm)
T_1	608 (2.04)	0.0000	HOMO→LUMO (88%)	^{3}LLCT/^{3}LMCT/^{3}MC	566
T_2	497 (2.49)	0.0000	HOMO-1→LUMO (75%)	^{3}LLCT/^{3}LMCT/^{3}IL	

Table S5. Partial Molecular Orbital Compositions (%) in the Ground State and Absorption Transition Assignment for $PtAg_2$ Complex **3** in Dichloromethane by TD-DFT Method at the PBE1PBE Level.

orbital	energy (eV)	MO contribution (%)			
		Pt (s/p/d)	Ag (s/p/d)	dppm	C≡C-4-Etcarb-9
LUMO+8	-1.30	9.04 (0/100/0)	8.12 (34/40/27)	76.13	6.71
LUMO+4	-1.48	10.60 (39/0/61)	6.53 (52/31/18)	46.10	36.77
LUMO+2	-1.62	4.95 (0/100/0)	10.90 (77/7/16)	22.80	61.34
LUMO	-2.39	15.73 (0/100/0)	20.74 (61/30/9)	53.02	10.51
HOMO	-6.04	6.10 (6/0/94)	0.62 (42/26/32)	3.31	89.98
HOMO-1	-6.12	0.67 (0/100/0)	1.54 (64/21/15)	4.60	93.19
HOMO-2	-6.48	4.28 (13/0/87)	1.98 (76/3 /21)	3.85	89.89
HOMO-3	-6.54	0.58 (0/100/0)	1.02 (48/19/33)	5.54	92.87
HOMO-4	-6.81	20.38 (30/0/70)	33.48 (39/10/52)	38.88	7.26
HOMO-5	-7.09	18.11 (5/0/95)	4.10 (8/15/77)	8.93	68.86
HOMO-9	-7.45	6.29 (4/0/96)	9.51 (4/68/28)	83.44	0.76

state	*E*, nm (eV)	O.S.	transition (Contrib.)	assignment	exp. (nm)
S_1	418 (2.97)	0.0014	HOMO→LUMO (91%)	^{1}LLCT/^{1}LMCT/^{1}IL	435
S_3	357 (3.47)	0.0019	HOMO-2→LUMO (90%)	^{1}LLCT/^{1}LMCT/^{1}IL	
S_4	351 (3.53)	0.2869	HOMO-4→LUMO (96%)	^{1}IL/^{1}MC/^{1}MLCT	
S_6	335 (3.70)	0.529	HOMO→LUMO+2 (61%)	^{1}IL/^{1}LLCT	328
			HOMO-1→LUMO+4 (18%)	^{1}LLCT/^{1}IL/^{1}LMCT	
S_{23}	294 (4.22)	0.1291	HOMO→LUMO+8 (42%)	^{1}LLCT/^{1}LMCT	
			HOMO-1→LUMO+4 (17%)	^{1}LLCT/^{1}IL/^{1}LMCT	
S_{31}	285 (4.35)	0.1388	HOMO-9→LUMO (87%)	^{1}IL/^{1}LMCT/^{1}MC/^{1}LLCT	
S_{70}	264 (4.69)	0.1584	HOMO-5→LUMO+2 (13%)	^{1}IL/^{1}MC	264
			HOMO-3→LUMO+4 (13%)	^{1}LLCT/^{1}IL/^{1}LMCT	

Table S6. Partial Molecular Orbital Compositions (%) in the Lowest Triplet State Emission Transition Assignment for $PtAg_2$ Complex **3** in Dichloromethane by TD-DFT Method at the PBE1PBE Level.

orbital	energy (eV)	MO contribution (%)			
		Pt (s/p/d)	Ag (s/p/d)	dppm	C≡C-4-Phcarb-9
LUMO+3	-1.49	12.00 (55/0/45)	4.98 (50/34/16)	43.41	39.62
LUMO+2	-1.65	2.76 (0/100/0)	9.44 (73/4/23)	22.72	65.09
LUMO	-2.73	22.76 (0/100/0)	31.80 (82/11/7)	38.98	6.46
HOMO	-5.95	6.71 (5/0/95)	1.18 (51/22/27)	3.32	88.79
HOMO-1	-6.05	0.73 (0/100/0)	2.43 (60/18/22)	5.81	91.03

state	*E*, nm (eV)	O.S.	transition (contribution)	assignment	exp. (nm)
T_1	500 (2.48)	0.0000	HOMO→LUMO (85%)	^{3}LLCT/^{3}LMCT	545
T_2	484 (2.56)	0.0000	HOMO→LUMO+2 (41%)	^{3}IL/^{3}LLCT	
			HOMO-1→LUMO+3 (15%)	^{3}IL/^{3}LLCT/^{3}LMCT	

Table S7. Optimization of electroluminescent performance of OLEDs based on complexes **1**–**3** through modifying host materials using 8% $PtAg_2$ complexes as phosphorescent dopants.

complex	host[a]	λ_{EL} (nm)	V_{on}[b] (V)	L_{max}[c] (cd/m^2)	CE_{max}[d] (cd/A)	PE_{max}[e] (lm/W)	EQE_{max}[f] (%)	EQE[g] (%)
1	TCTA	537	6.20	3652	12.7	4.3	3.5	2.3
1	TCTA : OXD-7 = 2 : 1	527	6.10	16166	40.0	14.0	10.3	10.0
1	TCTA : OXD-7= 1.5 : 1	527	5.95	20371	46.2	17.2	11.8	11.7
1	TCTA : OXD-7 = 1 : 1	527	4.75	21975	67.4	33.0	17.4	16.1
1	TCTA : OXD-7 = 0.5 : 1	526	6.35	23392	42.2	15.2	10.8	10.8
1	mCP : OXD-7 = 1 : 1	527	6.15	18447	51.6	18.6	13.4	13.3
1	TAPC : OXD-7 = 1 : 1	526	4.85	10043	36.8	17.4	9.6	9.1
1	CBP : OXD-7 = 1 : 1	527	6.40	25995	35.8	13.0	9.1	9.0
2	TCTA : OXD-7 = 1 : 1	547	5.70	20447	58.4	24.0	15.3	15.2
3	TCTA : OXD-7 = 1 : 1	532	6.80	2965	16.8	6.1	4.6	3.8
3	mCP : OXD-7 = 1 : 1	526	6.50	12363	25.2	9.7	6.8	6.7

[a]The ratio is based on weight and the doping percentage of phosphorescent $PtAg_2$ complex is 8%. [b]Turn-on voltage at 1 cd/m^2. [c]Maximum luminance. [d]Maximum current efficiency. [e]Maximum power efficiency. [f]Maximum external quantum efficiency. [g]Maximum external quantum efficiency at luminance of 1000 cd m^{-2}.

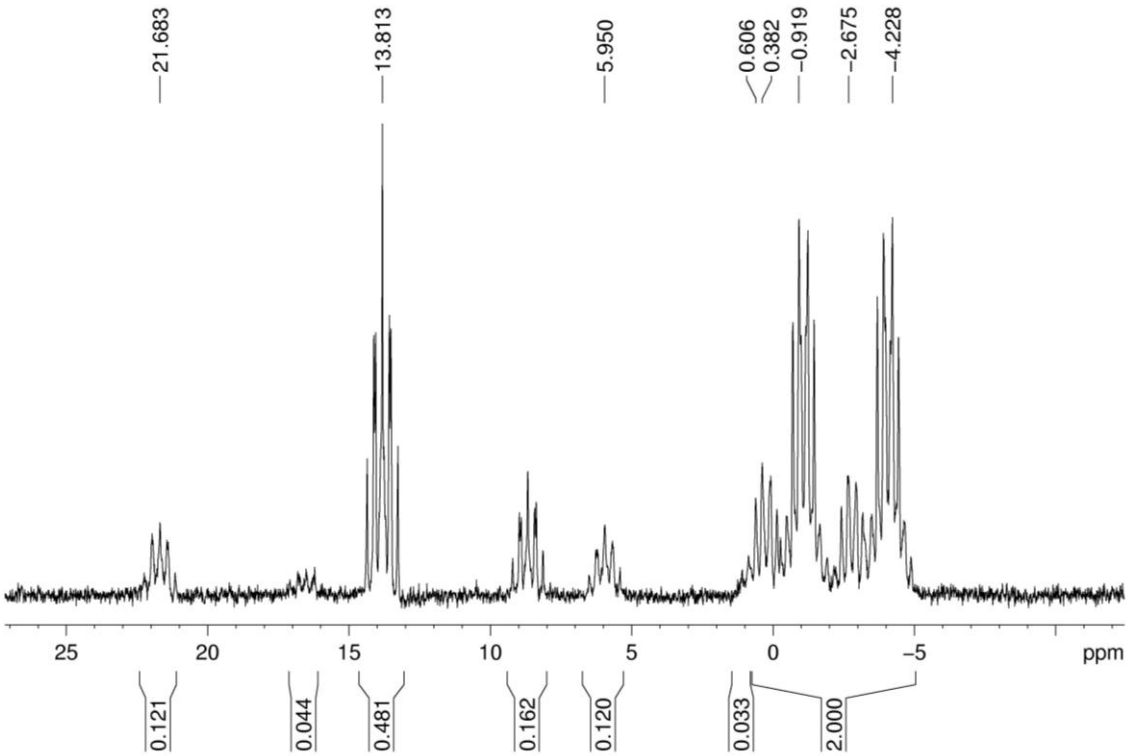

Fig. S1 The ^{31}P NMR of complex **1** in CD_3CN.

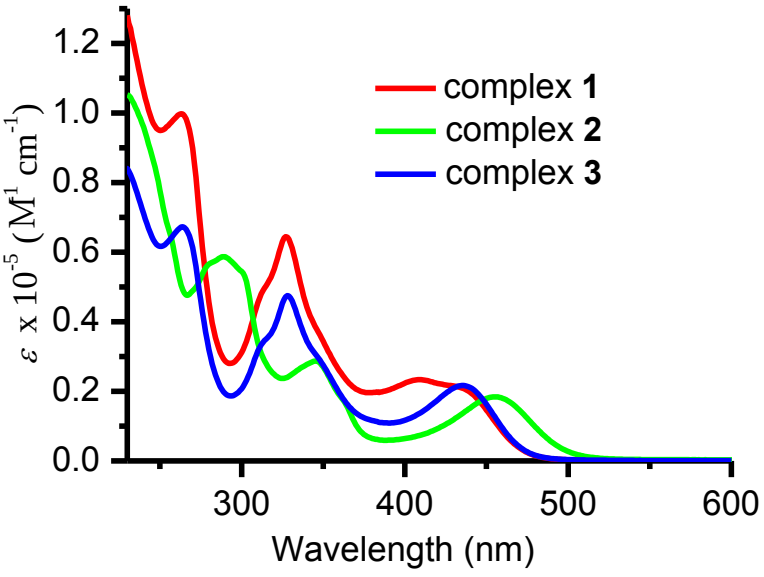

Fig. S2 The UV-Vis absorption spectra of complexes **1-3** in CH_2Cl_2.

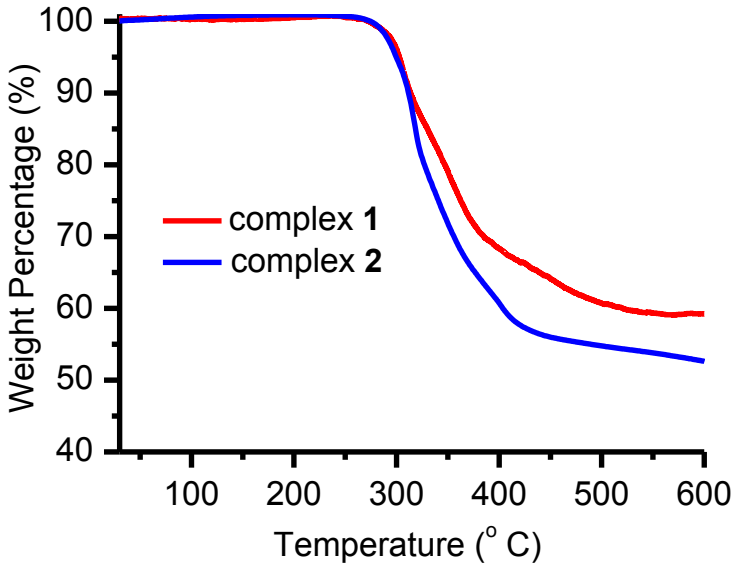

Fig. S3 Plots of thermogravimetric analysis for complexes **1** and **2** in temperature range 30–600 °C.

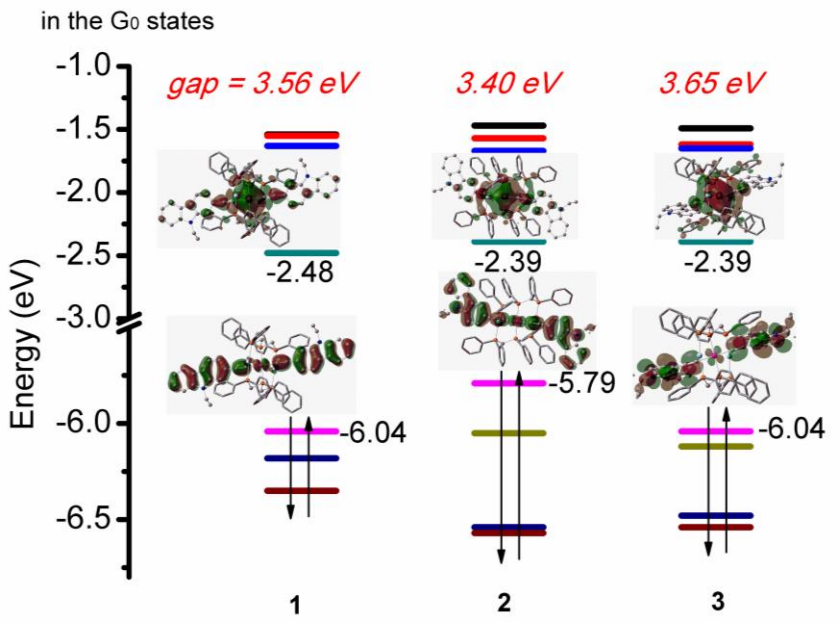

Fig. S4 Plots of energy level of frontier orbitals in the ground states (G_0) for complexes **1–3** in CH_2Cl_2 by TD-DFT method at the PBE1PBE level together with the plots of HOMO and LUMO (isovalue = 0.02).

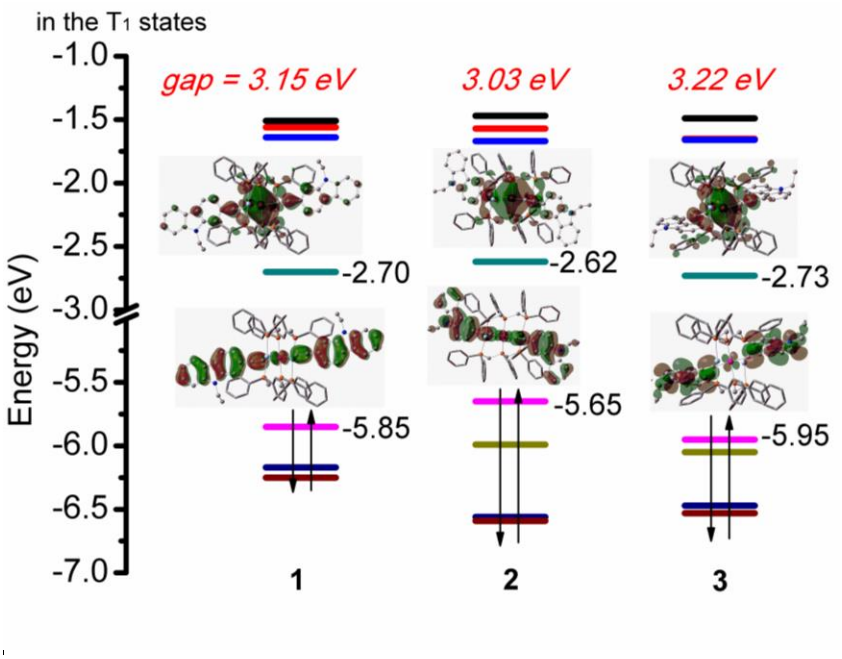

Fig. S5 Plots of energy level of frontier orbitals in the lowest-energy triplet states (T_1) for complexes **1–3** in CH_2Cl_2 by TD-DFT method at the PBE1PBE level together with the plots of HOMO and LUMO (isovalue = 0.02).