Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supporting Information

Photoluminescence and Electroluminescence of Cationic $PtAu_2$ Heterotrinuclear Complexes with Aromatic Acetylides

Li-Yi Zhang, Liang-Jin Xu,* Jin-Yun Wang, Xian-Chong Zeng, Zhong-Ning Chen*

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China

Table S1. The Partial Molecular Orbital Compositions (%) in the Ground State and the Absorption Transitions for $PtAu_2$ Complex **1** in CH_2Cl_2 Calculated by TD-DFT Method at the PBE1PBE Level.

orbital	energy/eV	MO contribution /%			
		Pt (s/p/d)	Au (s/p/d)	dpmp	$C{\equiv}CC_6H_5$
LUMO+13	-0.98	2.14 (0/100/0)	16.09 (10/76/14)	72.38	9.40
LUMO+10	-1.18	13.55 (0/100/0)	20.57 (48/39/13)	61.03	4.86
LUMO+4	-1.57	3.58 (60/0/40)	10.48 (27/67/6)	83.29	2.65
LUMO+3	-1.63	3.92 (0/100/0)	9.33 (32/50/18)	81.56	5.19
LUMO+2	-1.69	3.45 (0/100/0)	12.87 (43/32/25)	82.58	1.10
LUMO	-2.54	12.10 (0/100/0)	19.31 (47/41/12)	58.67	9.92
HOMO	-6.34	22.97 (3/0/97)	3.31 (45/9/46)	3.49	70.23
HOMO-1	-6.79	34.65 (27/0/73)	38.49 (34/11/55)	25.92	0.94
HOMO-2	-6.81	1.08 (0/100/0)	16.91 (43/8/50)	12.76	69.25

state	*E*/nm (eV)	O.S.	transition	contrib.	assignment	exp./nm
S_1	410 (3.03)	0.3188	HOMO→LUMO	98%	^{1}LLCT/^{1}MC/^{1}IL	432
S_2	363 (3.42)	0.6303	HOMO-1→LUMO	98%	^{1}MLCT/^{1}MC/^{1}IL	382
S_6	309 (4.01)	0.0754	HOMO→LUMO+2	57%	^{1}LLCT/^{1}MC/^{1}MLCT	
			HOMO→LUMO+3	35%	^{1}LLCT/^{1}MC/^{1}MLCT	
S_9	304 (4.08)	0.0872	HOMO→LUMO+3	57%	^{1}LLCT/^{1}MC/^{1}MLCT	
			HOMO→LUMO+2	37%	^{1}LLCT/^{1}MC/^{1}MLCT	
S_{27}	271 (4.58)	0.1361	HOMO→LUMO+10	69%	^{1}LLCT/^{1}MC	267
			HOMO-2→LUMO+4	17%	^{1}LLCT/^{1}MC/^{1}IL	
S_{46}	259 (4.78)	0.1315	HOMO→LUMO+13	75%	^{1}LLCT/^{1}MC	

Table S2. Partial Molecular Orbital Compositions (%) in the Lowest Triplet State and the Emission Transitions for $PtAu_2$ Complex **1** in CH_2Cl_2 Calculated by TD-DFT Method at the PBE1PBE Level.

orbital	energy/eV	MO contribution /%			
		Pt (s/p/d)	Au (s/p/d)	dpmp	$C{\equiv}CC_6H_5$
LUMO	-2.69	13.76 (0/100/0)	20.65 (55/32/13)	54.73	10.87
HOMO	-6.15	22.57 (2/0/98)	2.98 (41/11/47)	3.36	71.09

state	*E*/nm (eV)	O.S.	transition	contrib.	assignment	exp./nm
T_1	511 (2.43)	0.0000	HOMO→LUMO	83%	^{3}LLCT/^{3}MC	494

Table S3. The Partial Molecular Orbital Compositions (%) in the Ground State and the Absorption Transitions for $PtAu_2$ Complex **2** in CH_2Cl_2Calculated by TD-DFT Method at the PBE1PBE Level.

orbital	energy/eV	MO contribution /%			
		Pt (s/p/d)	Au (s/p/d)	dpmp	C≡CC_6H_4Bu-4
LUMO+14	-0.92	7.64 (0/100/0)	19.19 (44/51/5)	61.56	11.60
LUMO+6	-1.39	9.72 (61/0/39)	6.47 (50/41/9)	79.91	3.90
LUMO	-2.51	14.92 (0/100/0)	24.07 (63/29/9)	53.00	8.01
HOMO	-6.24	23.13 (3/0/97)	1.42 (47/19/34)	3.18	72.27
HOMO-1	-6.65	33.91 (23/0/77)	39.11 (37/10/53)	26.06	0.92
HOMO-2	-6.72	1.06 (0/100/0)	11.77 (51/6/42)	10.08	77.08

states	*E*/nm (eV)	O.S.	transition	contrib.	assignment	exp. /nm
S_1	414 (3.00)	0.4146	HOMO→LUMO	98%	^{1}LLCT/^{1}MC	438
S_2	371 (3.34)	0.6896	HOMO-1→LUMO	98%	^{1}MC/^{1}MLCT/^{1}IL	384
S_{43}	262 (4.73)	0.2223	HOMO→LUMO+14	56%	^{1}LLCT/^{1}MC/^{1}IL	263
			HOMO-2→LUMO+6	11%	^{1}LLCT/^{1}MC/^{1}IL	

Table S4. Partial Molecular Orbital Compositions (%) in the Lowest Triplet State and the Emission Transitions for $PtAu_2$ Complex **2** in CH_2Cl_2 Calculated by TD-DFT Method at the PBE1PBE Level.

orbital	energy/eV	MO contribution (%)			
		Pt (s/p/d)	Au (s/p/d)	dpmp	C≡CC_6H_4Bu-4
LUMO	-2.68	13.93 (0/100/0)	21.21 (56/32/12)	54.27	10.58
HOMO	-6.03	20.45 (4/0/96)	2.76 (40/13/47)	3.08	73.71

state	*E*/nm (eV)	O.S.	transition	contrib.	assignment	exp./nm
T_1	522 (2.38)	0.0000	HOMO→LUMO	85%	^{3}LLCT/^{3}MC	502

Table S5. The Partial Molecular Orbital Compositions (%) in the Ground State and the Absorption Transitions for $PtAu_2$ Complex **3** in CH_2Cl_2 Calculated by TD-DFT Method at the PBE1PBE Level.

orbital	energy/eV	MO contribution /%			
		Pt (s/p/d)	Au (s/p/d)	dpmp	C≡C-OXD
LUMO+2	-1.98	4.05 (0/100/0)	9.71 (58/35/8)	41.98	44.25
LUMO+1	-2.11	11.81 (76/0/24)	8.83 (61/37/2)	7.09	72.27
LUMO	-2.74	13.72 (0/100/0)	22.09 (61/29/10)	43.14	21.05
HOMO	-6.37	17.54 (4/0/96)	1.25 (52/15/33)	2.33	78.88
HOMO-1	-6.68	0.58 (0/100/0)	5.72 (50/7/43)	5.02	88.68
HOMO-2	-6.74	33.41 (22/0/78)	39.37 (38/9/53)	26.23	0.98

state	*E*/nm (eV)	O.S.	transition	contrib.	assignment	exp./nm
S_1	420 (2.95)	1.31	HOMO→LUMO	95%	^{1}LLCT/^{1}MC/^{1}IL/^{1}LMCT	439
S_2	380 (3.26)	0.62	HOMO-2→LUMO	96%	^{1}MLCT/^{1}MC/^{1}IL	390
S_6	328 (3.78)	1.66	HOMO→LUMO+	78%	^{1}IL/^{1}LLCT/^{1}MC	329

Table S6. Partial Molecular Orbital Compositions (%) in the Lowest Triplet State and the Emission Transitions for $PtAu_2$ Complex **3** in CH_2Cl_2 Calculated by TD-DFT Method at the PBE1PBE Level.

orbital	energy/eV	MO contribution (%)			
		Pt (s/p/d)	Au (s/p/d)	dpmp	C≡C-OXD
LUMO+1	-2.30	12.04 (50/31/19)	12.12 (65/30/4)	20.74	55.10
LUMO	-2.92	12.93 (2/97/1)	20.19 (62/27/11)	36.76	30.11
HOMO	-6.11	11.58 (2/1/97)	1.92 (51/14/36)	2.69	83.82

state	*E*/nm (eV)	O.S.	transition	contrib.	assignment	exp./nm
T_1	527 (2.35)	0.0000	HOMO→LUMO	63%	^{3}LLCT/^{3}IL/^{3}LMCT/^{3}MC	516
			HOMO→LUMO+1	24%	^{3}IL/^{3}LLCT/^{3}LMCT/^{3}MC	

Table S7. The Partial Molecular Orbital Compositions (%) in the Ground State and the Absorption Transitions for $PtAu_2$ Complex **4** in CH_2Cl_2 Calculated by TD-DFT Method at the PBE1PBE Level.

orbital	energy/eV	MO contribution /%				
		Pt (s/p/d)	Au (s/p/d)	dpmp	C≡C-OXD	C≡C-3-Phcarb-9
LUMO+1	-2.01	6.66 (31/49/20)	9.85 (59/35/6)	29.59	53.19	0.71
LUMO	-2.60	14.67 (2/97/2)	23.25 (63/29/9)	46.05	12.62	3.40
HOMO	-5.88	9.21 (2/4/94)	1.91 (43/16/41)	3.14	4.77	80.96
HOMO-1	-6.48	8.18 (6/4/90)	2.03 (50/12/38)	3.14	51.43	35.21
HOMO-2	-6.59	1.46 (11/19/70)	3.55 (60/9/31)	3.95	26.53	64.51
HOMO-3	-6.67	33.80 (23/0/77)	39.21 (37/10/53)	25.98	0.51	0.50

states	*E*/nm (eV)	O.S.	transition	contrib.	assignment	exp./nm
S_1	458 (2.70)	0.5714	HOMO→LUMO	94%	^{1}LLCT/^{1}LMCT/^{1}MC	457
S_2	379 (3.27)	0.4005	HOMO-1→LUMO	76%	^{1}LLCT/^{1}LMCT/^{1}IL/^{1}MC	383
			HOMO-2→LUMO	14%	^{1}LLCT/^{1}LMCT/^{1}IL	
S_3	375 (3.30)	0.6848	HOMO-3→LUMO	94%	^{1}MC/^{1}MLCT/^{1}IL	
S_{12}	318 (3.90)	0.6006	HOMO-1→LUMO+1	52%	^{1}IL/^{1}LLCT	303
			HOMO-2→LUMO+1	15%	^{1}IL/^{1}LLCT/^{1}LMCT	

Table S8. Partial Molecular Orbital Compositions (%) in the Lowest Triplet State and the Emission Transitions for $PtAu_2$ Complex **4** in CH_2Cl_2 Calculated by TD-DFT Method at the PBE1PBE Level.

orbital	energy/eV	MO contribution /%				
		Pt (s/p/d)	Au (s/p/d)	dpmp	C≡C-OXD	C≡C-3-Phcarb-9
LUMO	-2.78	15.82 (1/98/1)	24.99 (68/23/10)	44.96	10.07	4.16
HOMO	-5.72	10.34 (1/4/95)	2.81 (49/16/35)	3.79	5.64	77.43

state	*E*/nm (eV)	O.S.	transition	contrib.	assignment	exp./nm
T_1	611 (2.03)	0.0000	HOMO→LUMO	77%	^{3}LLCT/^{3}LMCT/^{3}MC	570

Table S9. The Partial Molecular Orbital Compositions (%) in the Ground State and the Absorption Transitions for $PtAu_2$ Complex **5** in CH_2Cl_2 Calculated by TD-DFT Method at the PBE1PBE Level.

orbital	Energy/eV	MO contribution /%			
		Pt (s/p/d)	Au (s/p/d)	dpmp	C≡C-3-Phcarb-9
LUMO+26	-0.44	3.31 (0/100/0)	22.90 (81/17/2)	43.90	29.89
LUMO+17	-0.86	19.73 (95/0/5)	10.17 (41/53/6)	69.16	0.94
LUMO	-2.45	13.96 (0/100/0)	22.66 (60/31/9)	55.91	7.47
HOMO	-5.72	12.52 (3/0/97)	1.51 (56/13/30)	2.67	83.29
HOMO-1	-6.00	0.59 (0/100/0)	4.39 (47/12/41)	5.23	89.79
HOMO-4	-6.62	33.74 (23/0/77)	39.19 (36/11/53)	26.08	0.99

state	*E*/nm (eV)	O.S.	transition	contrib.	assignment	exp./nm
S_1	470 (2.64)	0.4896	HOMO→LUMO	97%	^{1}LLCT/^{1}LMCT/^{1}MC	473
S_3	369 (3.36)	0.6872	HOMO-4→LUMO	97%	^{1}MC/^{1}MLCT/^{1}IL	380
S_{77}	265 (4.69)	0.5901	HOMO-1→LUMO+17 HOMO→LUMO+26	22% 15%	^{1}LLCT/^{1}LMCT ^{1}IL/^{1}LLCT/^{1}MC/^{1}LMCT	288

Table S10. Partial Molecular Orbital Compositions (%) in the Lowest Triplet State and the Emission Transitions for $PtAu_2$ Complex **5** in CH_2Cl_2 Calculated by TD-DFT Method at the PBE1PBE Level.

orbital	energy/eV	MO contribution /%			
		Pt (s/p/d)	Au (s/p/d)	dpmp	C≡C-3-Phcarb-9
LUMO	-2.64	15.69 (0/100/0)	25.31 (67/23/10)	51.41	7.58
HOMO	-5.60	13.20 (1/0/99)	1.99 (63/13/24)	2.76	82.05

state	*E*/nm (eV)	O.S.	transition	contrib.	assignment	exp./nm
T_1	605 (2.05)	0.0000	HOMO→LUMO	88%	^{3}LLCT/^{3}LMCT/^{3}MC	558

Table S11. The energy levels and gaps for $PtAu_2$ complexes **1**–**5**, deduced from electrochemical studies and UV-Vis absorption spectra.

complex	ΔE_g [a] /eV	HOMO [b] /eV	LUMO [c] /eV
1	2.66	5.49	2.83
2	2.64	5.61	2.97
3	2.62	5.63	3.01
4	2.49	5.51	3.02
5	2.42	5.41	2.99

[a] Estimated from the onset wavelengths of the absorption spectra in CH_2Cl_2.

[b] Calculated from the oxidation potentials of cyclic voltammetry.

[c] Calculated from the HOMO energy levels and ΔE_g.

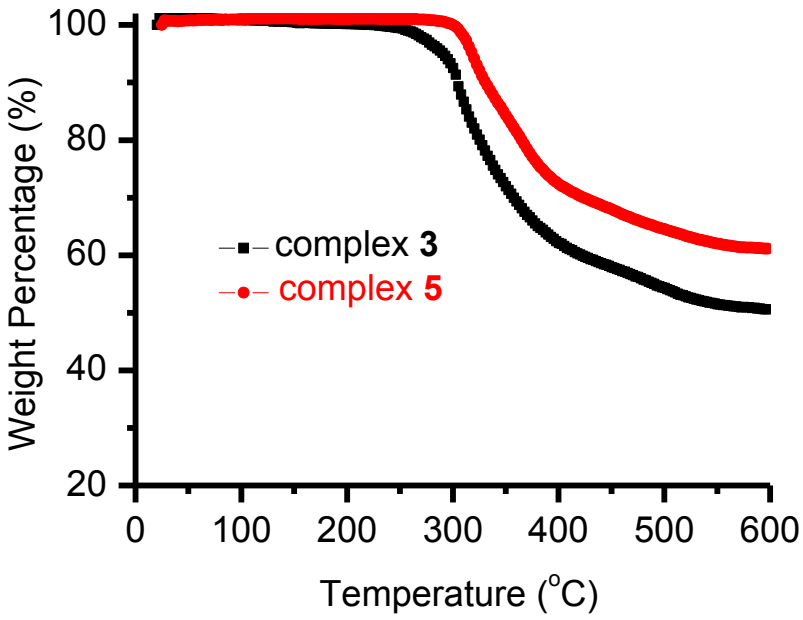

Fig. S1. Plots of thermogravimetric analysis for complexes **3** and **5** at temperature range 25–600 °C.

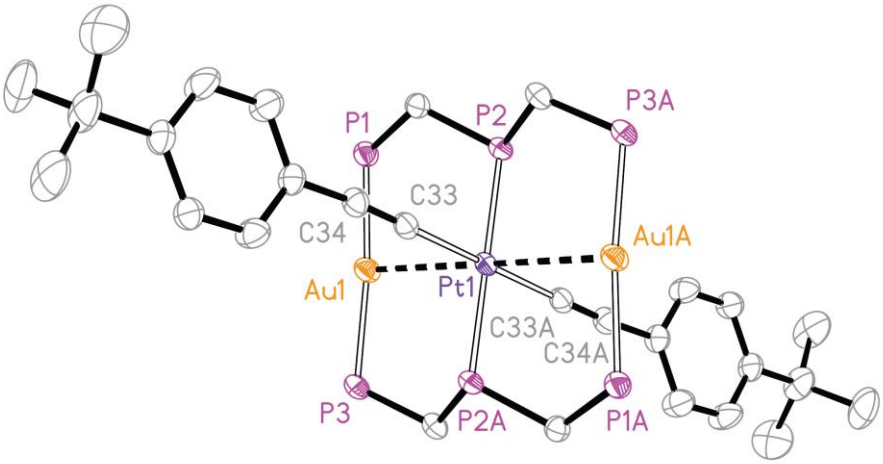

Fig. S2. A perspective drawing (30% thermal ellipsoids) of complex **2**. Phenyl rings on the phosphorus atoms are omitted for clarity.

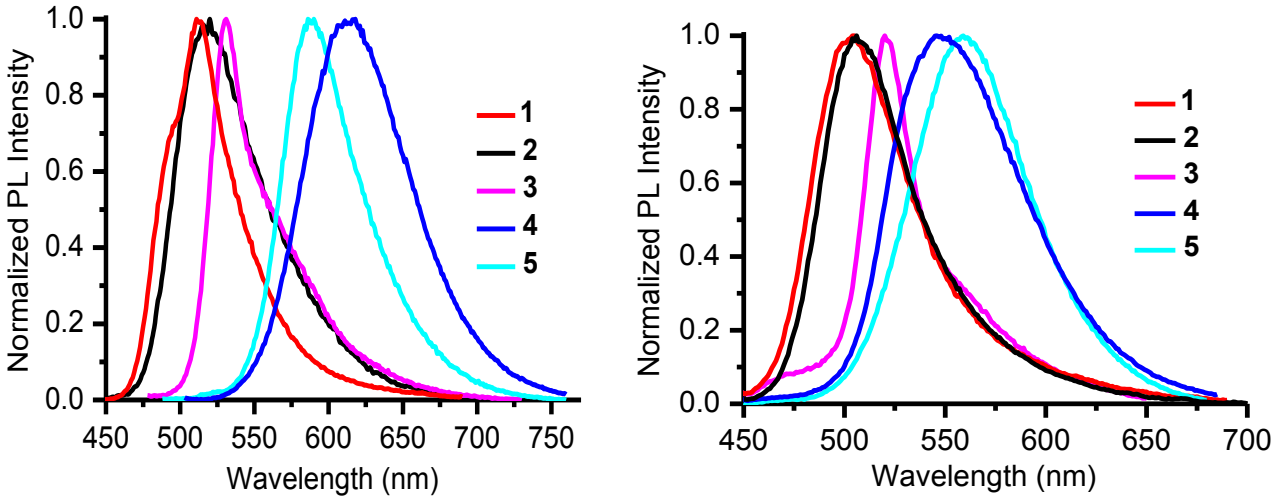

Fig. S3. The emission spectra of complexes **1**–**5** in solid state (left) and doping film (right) with mixed host (61% TCTA : 31% OXD-7) at ambient temperature.

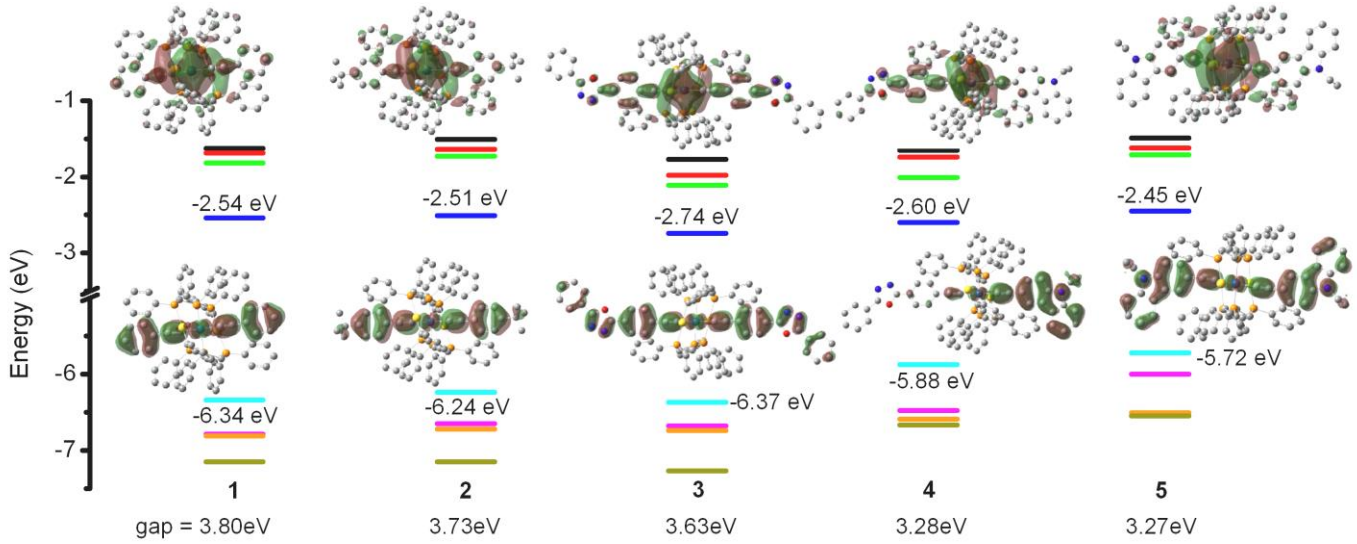

Fig. S4. Plots of the HOMO and LUMO and their energy level for complexes **1**–**5** in the ground state in dichloromethane by TD-DFT method at the PBE1PBE level (isovalue = 0.02).

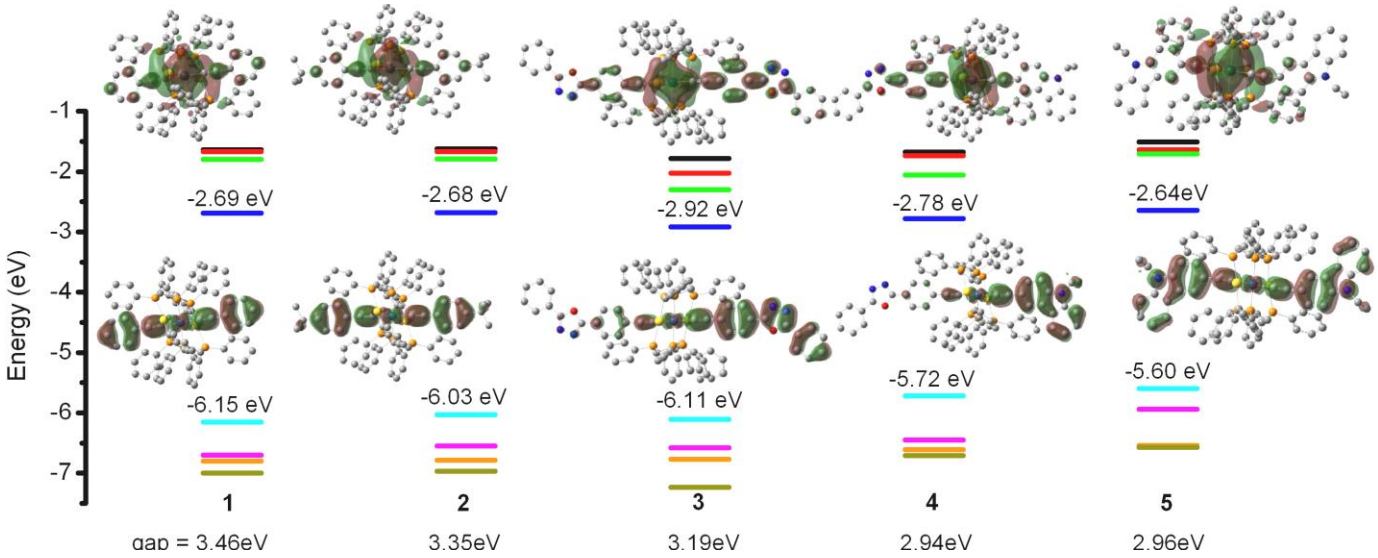

Fig. S5. Plots of the HOMO and LUMO and their energy level for complexes **1**–**5** in the lowest triplet state in dichloromethane by TD-DFT method at the PBE1PBE level (isovalue = 0.02).

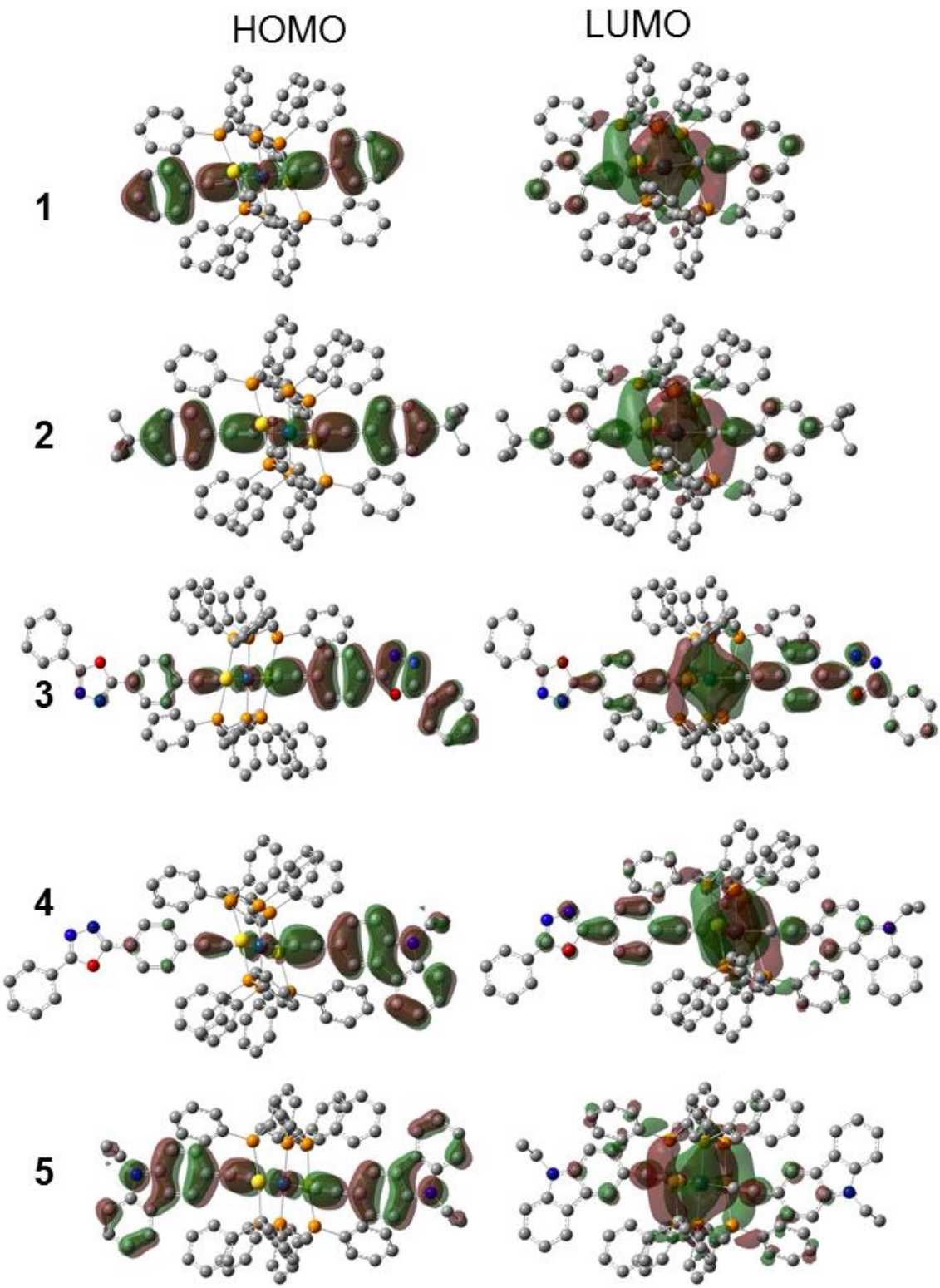

Fig. S6. Plots of the HOMO and LUMO involved in emission transition of complexes **1–5** in dichloromethane, calculated by TD-DFT method at the PBE1PBE level (isovalue = 0.02).

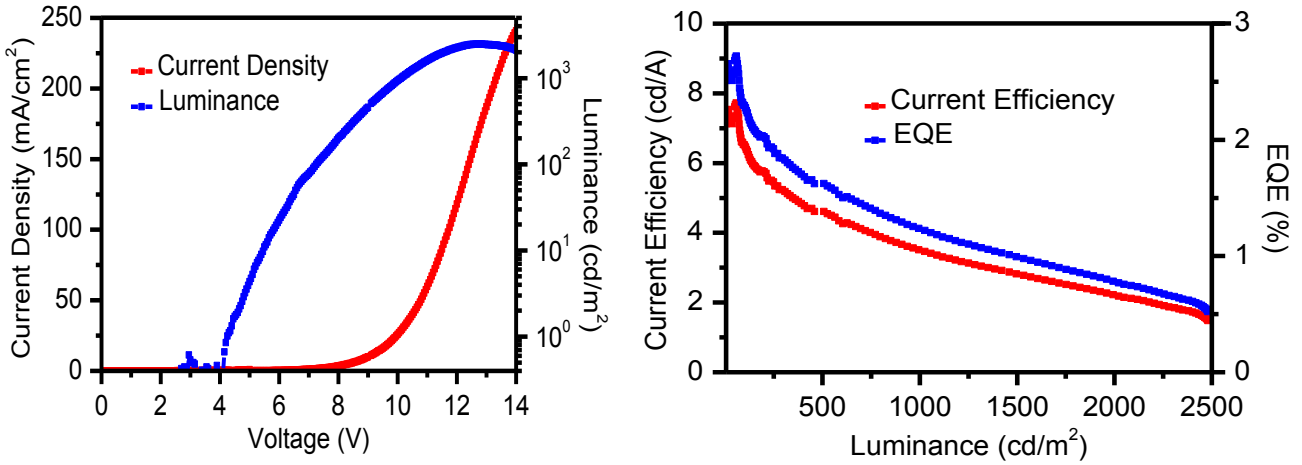

Fig. S7. (a) Current density-voltage-luminance characteristics. (b) Current efficiency/external quantum efficiency *vs* luminance for complex **1**.

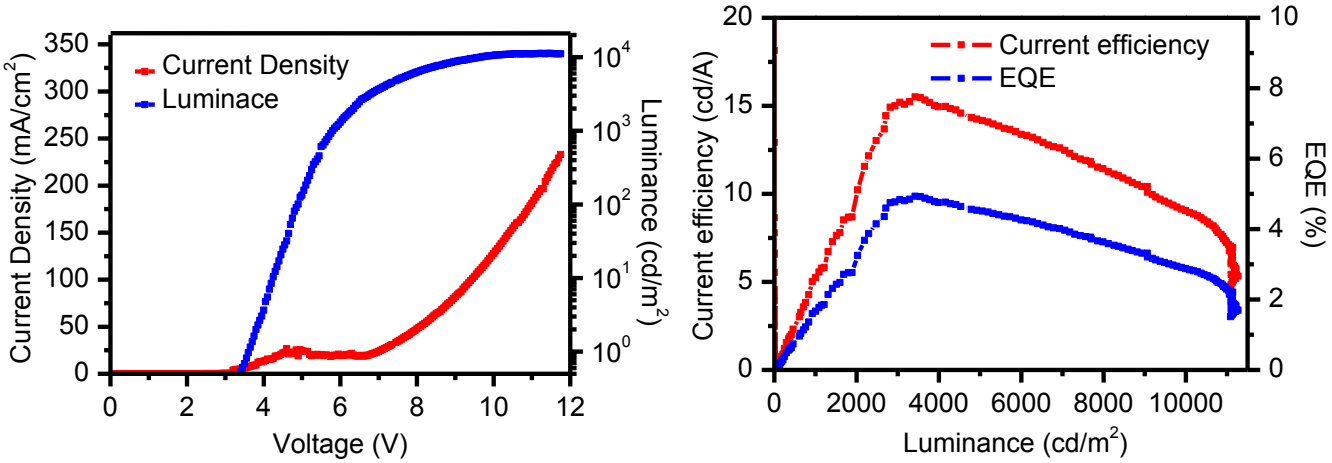

Fig. S8. (a) Current density-voltage-luminance characteristics. (b) Current efficiency/external quantum efficiency *vs* luminance for complex **2**.

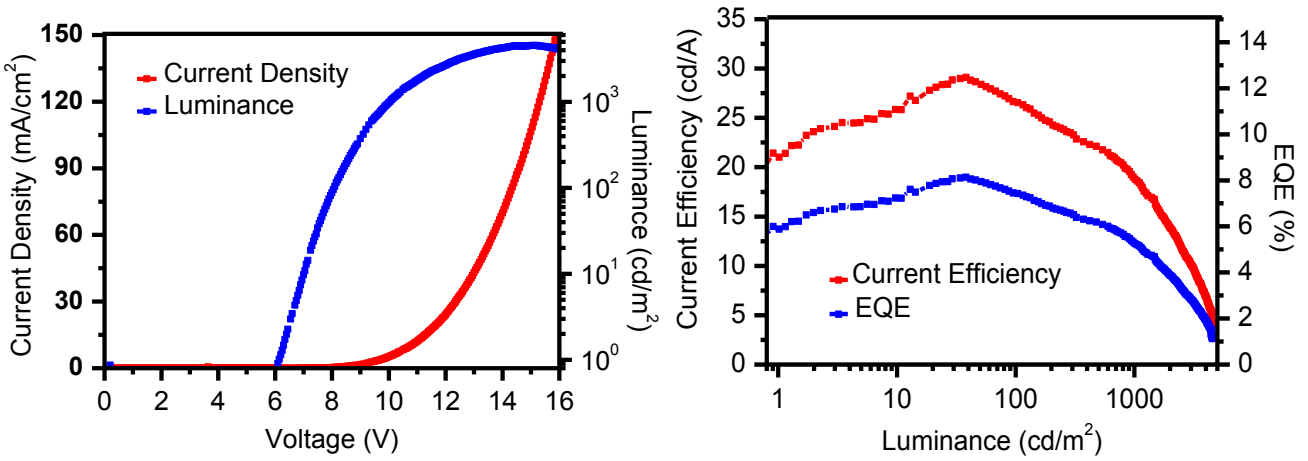

Fig. S9. (a) Current density-voltage-luminance characteristics. (b) Current efficiency/external quantum efficiency *vs* luminance for complex **3**

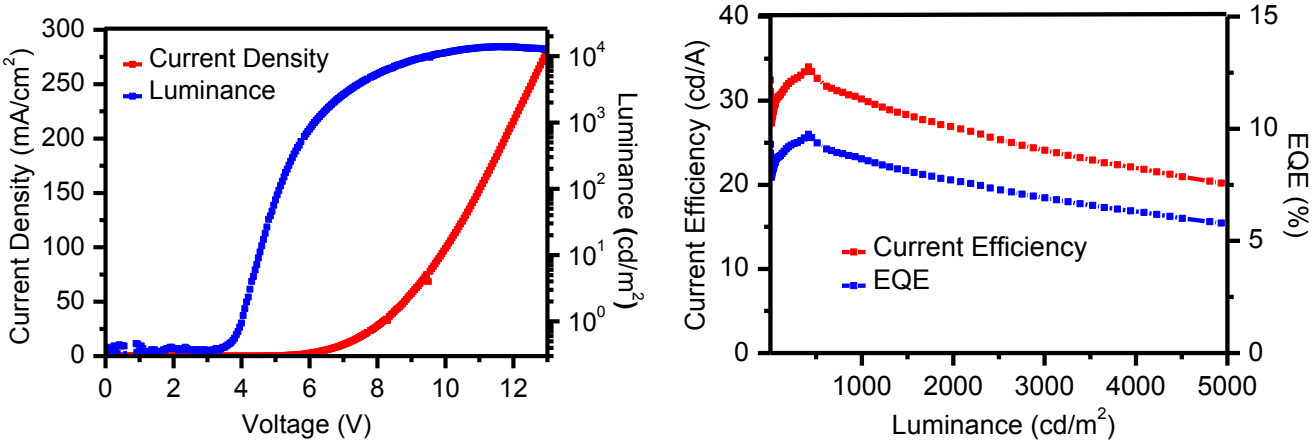

Fig. S10. (a) Current density-voltage-luminance characteristics. (b) Current efficiency/external quantum efficiency *vs* luminance for complex **4**.