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Electronic Supporting Information

$PtAu_3$ Cluster Complexes with Narrow-band Emission for Solution-Processed Organic Light Emitting Diodes

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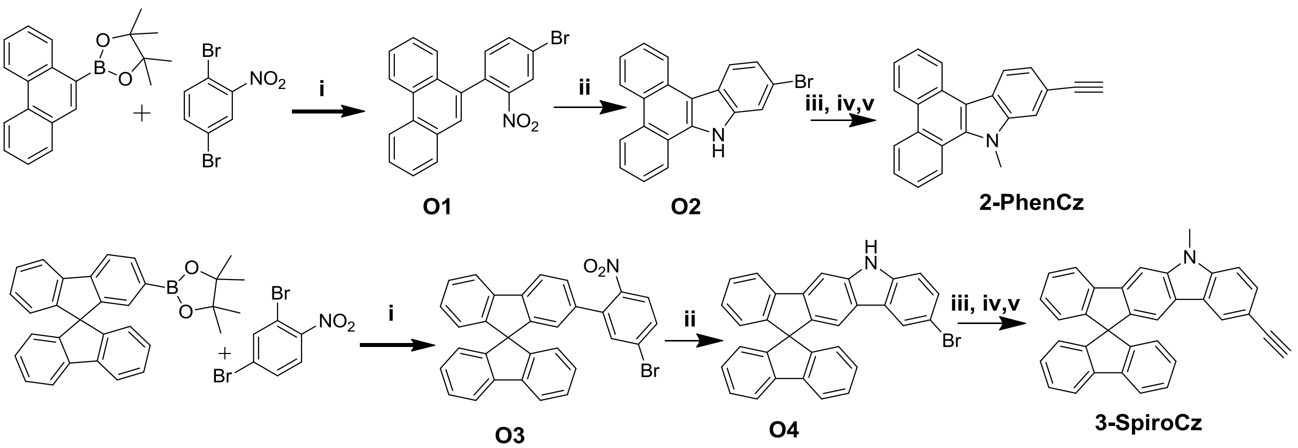

Scheme S1. Synthetic route to aromatic ethynyl ligands HC≡C-2-PhenCarb(NMe) and HC≡C-3-SpiroCarb(NMe). (i) $Pd(PPh_3)_4$, K_2CO_3, THF : water (9:1), 50 ^oC, 24 h, 55%; (ii) 1,2-dichlorobenzene, PPh_3, 180 ^oC, 12 h, 68%; (iii) NaH, MeI, dry DMF, 2 h, 98%; (iv) $Pd(PPh_3)Cl_2$, CuI, PPh_3, TMSA, TEA, 80 ^oC, 12 h, 85%; (v) K_2CO_3, MeOH, THF, RT, 2 h, 99 %.

Synthetic Procedure:

9-(4-Bromo-2-nitrophenyl)phenanthrene (**O1**): 4,4,5,5-Tetramethyl-2-(phenanthren-9-yl)-1,3,2-dioxaborolane (4.7 mmol) was treated with 1,4-dibromo-2-nitrobenzene (5.2 mmol), $Pd[PPh_3]_4$ (0.23 mmol) and K_2CO_3 (9.4 mmol) in THF : water (50 mL) at 50 ^oC under nitrogen atmosphere for 12 h and the reaction was monitored by TLC. The reaction mixture was quenched with water, extracted with CH_2Cl_2 and washed with brine (2 × 50 mL). The organic layer was separated, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using petroleum ether : CH_2Cl_2 (v/v = 9 : 1) to afford the pure 9-(4-bromo-2-nitrophenyl)phenanthrene. ^1H NMR ($CDCl_3$, ppm): 8.81 (d, 1H, J = 8.0 Hz), 8.77 (d, 1H, J = 8.0 Hz), 8.33 (s, 1H), 7.81–7.92 (m, 2H), 7.75–7.81 (m, 2H), 7.64–7.72 (m, 2H), 7.56 (t, 1H, J = 8.0 Hz), 7.47 (t, 2H, J = 8.0 Hz).

11-Bromo-9H-dibenzo[a,c]carbazole (**O2**): The mixture of PPh_3 (15 mmol) and 9-(4-bromo-2-nitrophenyl)phenanthrene (5 mmol) was treated with 1,2-dichlorobenzene (20 mL) and stirred at 180 ^oC under nitrogen atmosphere for 12 h. The reaction mixture was cooled and directly chromatographed on a silica gel column. Initially petroleum ether was only used to remove 1,2-dicholorobenzene and then the mixed petroleum ether : CH_2Cl_2 (v/v = 8 : 2) used as eluent to give pure 11-bromo-9H-dibenzo[a,c]carbazole. ^1H NMR (DMSO-d_6, ppm): 12.60 (s, 1H), 8.94 (d, 2H, J = 8.4 Hz), 8.80 (d, 1H, J = 8.4 Hz), 8.61 (d, 1H, J = 7.6 Hz), 8.56 (d, 1H, J = 8.8 Hz), 7.89 (s, 1H), 7.76–7.84 (m, 3H), 7.64 (t, 1H, J = 7.6 Hz), 7.47 (d, 1H, J = 8.4 Hz).

11-Ethynyl-9-methyl-9H-dibenzo[a,c]carbazole: N-methylated 11-bromo-9H-dibenzo[a,c]carbazole was prepared by treating 11-bromo-9H-dibenzo[a,c]carbazole with MeI and NaH in dry DMF. The reaction mixture was quenched with water and the solid was taken to the Sonogashira coupling. Deprotection of trimethylsilyl group was performed by using K_2CO_3 in MeOH : THF (v/v = 3 : 1) at room temperature for 2 h to afford the pure product 11-ethynyl-9-methyl-9H-dibenzo[a,c]carbazole. ^1H NMR ($CDCl_3$, ppm): 8.86 (d, 1H, J = 8.0 Hz), 8.79 (d, 1H, J = 8.0 Hz), 8.75 (d, 1H, J = 8.4 Hz), 8.68 (d, 1H, J = 8.4 Hz), 8.49 (d, 1H, J = 8.4 Hz), 7.74–7.80 (m, 2H), 7.64–7.72 (m, 2H), 7.61 (t, 1H, *J* = 7.6 Hz), 7.52 (d, 1H, *J* = 8.4 Hz), 4.38 (s, 3H), 2.98 (s, 1H).

2-(5-Bromo-2-nitrophenyl)-9,9'-spirobi[fluorene] (**O3**): This compound was prepared by the same synthetic procedure as that of 9-(4-bromo-2-nitrophenyl)phenanthrene (**O1**) except for the use of 2,4-dibromo-1-nitrobenzene and 2-(9,9'-spirobi[fluoren]-7-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. ^{1}H NMR ($CDCl_3$, ppm): 7.90 (d, 2H, *J* = 8.0 Hz), 7.85 (d, 2H, *J* = 7.6 Hz), 7.67 (d, 1H, *J* = 8.8 Hz), 7.53 (d, 1H, *J* = 8.8 Hz), 7.47 (s, 1H), 7.40 (t, 3H, *J* = 7.6 Hz), 7.31 (d, 1H, *J* = 8.0 Hz), 7.16–7.20 (m, 3H), 6.81 (d, 2H, *J* = 7.6 Hz), 6.75 (d, 1H, *J* = 7.6 Hz), 6.70 (s, 1H).

2'-Bromo-5'H-spiro[fluorene-9,11'-indeno[1,2-b]carbazole] (**O4**): This compound was prepared by the same synthetic procedure as that of **O2** except for the use of 2-(5-bromo-2-nitrophenyl)-9,9'-spirobi[fluorene]. ^{1}H NMR ($CDCl_3$, ppm): 8.11 (br, 1H), 7.91 (d, 4H, *J* = 7.6 Hz), 7.85 (s, 1H), 7.41 (t, 4H, *J* = 7.6 Hz), 7.36 (s, 1H), 7.25 (d, 1H, *J* = 8.8 Hz), 7.12–7.18 (m, 3H), 6.78 (d, 3H).

2'-Ethynyl-5'-methyl-5'H-spiro[fluorene-9,11'-indeno[1,2-b]carbazole]: This compound was prepared by the same synthetic procedure as that of 11-Ethynyl-9-methyl-9H-dibenzo[a,c]carbazole except for the use of 2'-bromo-5'H-spiro[fluorene-9,11'-indeno[1,2-b]carbazole]. ^{1}H NMR ($CDCl_3$, ppm): 7.98 (d, 2H, *J* = 7.6 Hz), 7.92 (d, 2H, *J* = 7.6 Hz), 7.85 (s, 1H), 7.54 (d, 1H, *J* = 8.4 Hz), 7.38–7.42 (m, 4Hz), 7.30 (d, 1H, *J* = 8.4 Hz), 7.10–7.18 (m, 3H), 6.78 (d, 3H, *J* = 7.6 Hz), 3.97 (s, 3H), 2.98 (s, 1H).

Table S1. Photoluminescence Parameters of Compounds **1** and **4** in Doping Films Composed of mCP : OXD-7 (1 : 1) : $PtAu_3$ Complex with Various Doping Concentrations.

$PtAu_3$ complex	**1**			**4**		
	λ_{PL} (nm)	FWHM (nm)	Φ_{PL} (%)	λ_{PL} (nm)	FWHM (nm)	Φ_{PL} (%)
100%	543	49	41.5	564,599	102	9.3
75%	535	43	48.9	582	83	27.1
50%	532	43	55.8	570	66	53.7
20%	531	42	62.5	567	59	67.7
10%	529	41	75.4	560	53	77.8
8%	528	41	87.2	560	53	84.6
5%	528	41	90.1	558	51	87.3
3%	528	41	89.3	558	50	82.5
1%	528	41	78.1	557	50	73.1

Table S2. The Energy Levels and Gaps for $PtAu_3$ Cluster Complexes **1–5**, Deduced from Electrochemical Studies and UV-Vis Absorption Spectra Together with Thermal Decomposition Data.

complex	ΔE_g (eV)[a]	HOMO (eV)[b]	LUMO (eV)[b]	T_d (^{o}C)
1	2.68	−5.86	−3.18	301
2	2.56	−5.52	−2.96	290
3	2.54	−5.74	−3.20	314
4	2.45	−5.38	−2.93	289
5	2.38	−5.30	−2.92	303

[a] Estimated from the onset wavelengths of the absorption spectra in CH_2Cl_2. [b] The HOMO and LUMO energies were determined from the 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 S3. Partial Molecular Orbital Compositions (%) in the Ground State for Complex **1** 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-BI
LUMO+5	-1.63	4.81 (41/3/56)	10.85 (59/14/27)	0.08	60.16	24.10
LUMO+4	-1.70	10.05 (23/3/73)	12.76 (18/51/31)	0.84	70.25	6.10
LUMO+3	-1.72	2.62 (0/72/28)	10.94 (0/96/3)	0.04	24.40	62.00
LUMO+2	-1.88	2.91 (21/28/51)	30.15 (77/12/10)	0.34	61.66	4.94
LUMO+1	-2.29	19.53 (65/20/15)	32.43 (46/50/4)	1.29	39.67	7.07
LUMO	-2.36	2.58 (0/87/13)	28.26 (29/59/12)	0.03	66.16	2.98
HOMO	-6.11	11.37 (0/4/96)	1.45 (44/42/14)	0.07	4.14	82.97
HOMO-1	-6.17	7.90 (5/2/93)	3.66 (47/5/48)	0.44	4.47	83.52
HOMO-2	-6.65	27.09 (19/4/78)	38.63 (35/3/61)	5.83	22.71	5.74

Table S4. The Absorption Transitions for Complex **1** in CH_2Cl_2 Solution by TD-DFT Method at the PBE1PBE Level.

state	*E*, nm (eV)	O.S.	transition (Contrib.)	assignment
S_1	396 (3.13)	0.8075	HOMO→LUMO+1 (90%)	^{1}LMCT/^{1}LLCT/^{1}MC
S_4	383 (3.24)	0.1658	HOMO-1→LUMO (78%)	^{1}LLCT/^{1}LMCT
			HOMO-2→LUMO (19%)	^{1}MLCT/^{1}MC/^{1}IL
S_6	354 (3.51)	0.3081	HOMO-2→LUMO+1 (87%)	^{1}MC/IL/^{1}MLCT
S_7	336 (3.69)	0.7687	HOMO→LUMO+2 (61%)	^{1}LLCT/^{1}LMCT/^{1}MC
			HOMO→LUMO+4 (19%)	^{1}LLCT/^{1}LMCT/^{1}MC
S_{11}	323 (3.83)	0.8537	HOMO-1→LUMO+3 (36%)	^{1}IL/^{1}LLCT
			HOMO→LUMO+5 (33%)	^{1}LLCT/^{1}IL

Table S5. Partial Molecular Orbital Compositions (%) in the Ground State for Complex **2** 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-Cz	C≡C-BI
LUMO+5	-1.59	2.85 (18/66/16)	19.47 (8/82/10)	0.06	72.21	0.37	5.03
LUMO+3	-1.67	2.41 (14/47/39)	11.62 (27/60/13)	0.34	46.18	1.34	38.12
LUMO+1	-2.22	18.77 (66/20/14)	32.41 (45/51/5)	1.41	41.74	1.80	3.87
LUMO	-2.35	2.90 (5/81/13)	26.98 (27/60/14)	0.04	67.08	1.68	1.31
HOMO	-5.82	8.46 (1/5/94)	2.42 (47/25/28)	0.17	3.99	81.75	3.21
HOMO-1	-6.14	9.29 (2/3/95)	2.61 (41/15/45)	0.32	4.24	5.00	78.54
HOMO-3	-6.61	27.88 (19/4/77)	36.70 (35/3/62)	6.25	21.82	3.94	3.41

Table S6. The Absorption Transitions for Complex **2** in CH_2Cl_2 Solution by TD-DFT Method at the PBE1PBE Level.

state	*E*, nm (eV)	O.S.	transition (contrib.)	assignment
S_1	423 (2.93)	0.1131	HOMO→LUMO (89%)	^{1}LLCT/^{1}LMCT
S_2	420 (2.95)	0.2455	HOMO→LUMO+1 (86%)	^{1}LMCT/^{1}LLCT
S_4	384 (3.22)	0.3655	HOMO-1→LUMO (50%)	^{1}LLCT/^{1}LMCT/^{1}MC
			HOMO-1→LUMO+1 (35%)	^{1}LMCT/^{1}LLCT/^{1}MC
S_7	352 (3.52)	0.304	HOMO-3→LUMO+1 (84%)	^{1}MC/^{1}IL/^{1}MLCT
S_{18}	321 (3.86)	0.4294	HOMO→LUMO+5 (44%)	^{1}LLCT/^{1}LMCT/^{1}MC
			HOMO→LUMO+3 (14%)	^{1}LLCT/^{1}MC

Table S7. Partial Molecular Orbital Compositions (%) in the Ground State for Complex **3** 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-Cz
LUMO+17	-0.98	20.23 (83/10/7)	49.88 (73/24/2)	0.01	26.74	3.14
LUMO+16	-1.01	2.39 (26/3/71)	19.81 (16/48/35)	0.25	72.45	5.10
LUMO+15	-1.03	2.47 (0/73/27)	18.88 (51/35/14)	0.46	72.46	5.73
LUMO+7	-1.43	5.83 (0/75/25)	27.29 (62/31/7)	0.02	65.93	0.93
LUMO+1	-2.07	18.04 (69/16/14)	31.13 (41/53/6)	1.88	46.32	2.62
LUMO	-2.38	2.58 (0/89/11)	36.40 (44/47/9)	0.11	58.43	2.49
HOMO	-5.78	7.60 (1/1/98)	1.77 (25/32/43)	0.25	3.69	86.69
HOMO-1	-5.83	5.50 (0/10/90)	2.03 (60/30/10)	0.03	5.86	86.58
HOMO-2	-6.42	25.81 (19/4/76)	34.61 (36/4/61)	10.54	21.21	7.83
HOMO-7	-7.03	1.25 (0/16/84)	32.47 (39/13/48)	39.91	16.89	9.48
HOMO-9	-7.16	1.51 (72/9/19)	48.22 (45/4/51)	23.50	25.65	1.12

Table S8. The Absorption Transitions for Complex **3** in CH_2Cl_2 Solution by TD-DFT Method at the PBE1PBE Level.

states	*E*, nm (eV)	O.S.	transition (contrib.)	assignment
S_1	436 (2.84)	0.0201	HOMO→LUMO (96%)	^{1}LLCT/^{1}LMCT
S_4	398 (3.12)	0.1426	HOMO-1→LUMO+1 (87%)	^{1}LMCT/^{1}LLCT
S_7	355 (3.49)	0.2893	HOMO-2→LUMO+1 (82%)	^{1}MC/^{1}IL/^{1}MLCT/^{1}LLCT
S_{24}	318 (3.90)	0.142	HOMO-9→LUMO (54%)	^{1}MC/^{1}IL/^{1}LLCT/^{1}MLCT
			HOMO→LUMO+7 (22%)	^{1}LLCT/^{1}LMCT
S_{25}	318 (3.90)	0.1321	HOMO→LUMO+7 (37%)	^{1}LLCT/^{1}LMCT
			HOMO-9→LUMO (30%)	^{1}MC/^{1}IL/^{1}LLCT/^{1}MLCT
S_{39}	298 (4.15)	0.4931	HOMO-7→LUMO+1 (39%)	^{1}MC/^{1}LLCT/^{1}IL/^{1}LMCT
			HOMO→LUMO+15 (20%)	^{1}LLCT/^{1}LMC
S_{46}	294 (4.21)	0.2482	HOMO-1→LUMO+17 (40%)	^{1}LMCT/^{1}LLCT
			HOMO→LUMO+15 (14%)	^{1}LLCT/^{1}LMCT

Table S9. Partial Molecular Orbital Compositions (%) in the Ground State for Complex **4** 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-PR
LUMO+21	-0.92	5.69 (70/23/7)	46.10 (88/7/6)	0.22	45.75	2.24
LUMO+19	-0.99	20.88 (65/22/13)	34.06 (64/29/8)	0.05	42.56	2.45
LUMO+7	-1.53	8.30 (77/9/14)	22.53 (37/46/17)	0.12	48.94	20.12
LUMO+4	-1.62	8.98 (13/17/70)	18.22 (24/60/16)	0.52	66.47	5.81
LUMO+3	-1.65	3.99 (17/37/45)	15.66 (29/45/26)	0.03	69.98	10.34
LUMO+2	-1.81	1.45 (17/35/48)	30.84 (75/15/10)	0.30	64.47	2.94
LUMO+1	-2.25	13.67 (49/32/19)	32.39 (53/44/3)	1.04	45.70	7.19
LUMO	-2.38	18.67 (86/9/6)	33.43 (28/65/7)	0.44	45.78	1.67
HOMO	-5.67	7.60 (4/7/89)	8.39 (52/40/8)	0.06	2.92	81.03
HOMO-1	-5.78	3.10 (12/10/78)	3.30 (51/20/30)	0.21	3.11	90.28
HOMO-3	-6.28	2.98 (11/4/85)	4.36 (44/17/39)	0.45	3.38	88.82
HOMO-4	-6.60	26.51 (19/4/78)	37.60 (35/4/62)	6.90	21.58	7.41

Table S10. The Absorption Transitions for Complex **4** in CH_2Cl_2 Solution by TD-DFT Method at the PBE1PBE Level.

states	*E*, nm (eV)	O.S.	transition (contrib.)	assignment
S_1	452 (2.74)	0.2210	HOMO→LUMO (76%)	^{1}LLCT/^{1}LMCT/^{1}MC
			HOMO→LUMO+1 (17%)	^{1}LLCT/^{1}LMCT/^{1}MC
S_2	434 (2.86)	0.5234	HOMO→LUMO+1 (75%)	^{1}LLCT/^{1}LMCT/^{1}MC
			HOMO→LUMO (17%)	^{1}LLCT/^{1}LMCT/^{1}MC
S_5	374 (3.31)	0.0987	HOMO-4→LUMO (66%)	^{1}MC/^{1}IL/^{1}MLCT/^{1}LLCT
			HOMO-3→LUMO (19%)	^{1}LMCT/^{1}LLCT
S_7	365 (3.39)	0.2586	HOMO→LUMO+2 (80%)	^{1}LLCT/^{1}LMCT/^{1}MC
S_{11}	355 (3.50)	0.2146	HOMO→LUMO+4 (32%)	^{1}LLCT/^{1}MC/^{1}LMCT
			HOMO-1→LUMO+2 (16%)	^{1}LLCT/^{1}LMCT
			HOMO→LUMO+3 (16%)	^{1}LLCT/^{1}MC/^{1}IL
			HOMO→LUMO+2 (9%)	^{1}LLCT/^{1}LMCT/^{1}MC
S_{14}	349 (3.55)	0.2284	HOMO→LUMO+3 (30%)	^{1}LLCT/^{1}MC/^{1}IL
			HOMO→LUMO+7 (18%)	^{1}LLCT/^{1}IL/^{1}MC/^{1}LMCT
S_{70}	288 (4.30)	0.2408	HOMO-1→LUMO+19 (14%)	^{1}LMCT/^{1}LLCT
			HOMO→LUMO+21 (10%)	^{1}LLCT/^{1}LMCT

Table S11. Partial Molecular Orbital Compositions (%) in the Ground State for Complex **5** 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-spiro
LUMO+11	-1.28	13.89 (94/4/3)	41.74 (13/83/4)	0.26	41.78	2.34
LUMO+5	-1.53	13.81 (63/30/6)	19.81 (30/62/8)	0.05	37.94	28.39
LUMO+4	-1.60	2.49 (39/48/13)	15.72 (33/48/19)	0.09	77.96	3.74
LUMO+1	-2.17	15.77 (58/25/17)	32.48 (51/47/3)	1.17	46.00	4.57
LUMO	-2.35	17.30 (86/8/5)	34.52 (29/65/6)	0.36	46.42	1.40
HOMO	-5.64	10.97 (0/4/96)	6.84 (52/36/12)	0.07	3.01	79.11
HOMO-1	-5.85	3.56 (9/13/78)	6.28 (61/8/31)	0.52	4.46	85.18
HOMO-2	-6.06	0.76 (11/8/81)	0.57 (12/57/31)	0.01	0.94	97.72
HOMO-3	-6.07	0.98 (32/17/52)	2.87 (29/52/19)	0.08	1.45	94.63
HOMO-5	-6.52	7.24 (20/3/77)	12.15 (39/4/56)	2.03	7.12	71.45
HOMO-6	-6.57	25.87 (19/4/77)	32.59 (34/4/62)	6.10	19.55	15.89

Table S12. The Absorption Transitions for Complex **5** in CH_2Cl_2 Solution by TD-DFT Method at the PBE1PBE Level.

states	*E*, nm (eV)	O.S.	transition (contrib.)	assignment
S_1	462 (2.69)	0.1179	HOMO→LUMO (82%)	^{1}LLCT/^{1}LMCT/^{1}MC
			HOMO→LUMO+1 (13%)	^{1}LLCT/^{1}LMCT/^{1}MC
S_2	439 (2.83)	0.3545	HOMO→LUMO+1 (81%)	^{1}LLCT/^{1}LMCT/^{1}MC
			HOMO→LUMO (14%)	^{1}LLCT/^{1}LMCT/^{1}MC
S_3	423 (2.93)	0.0808	HOMO-1→LUMO (84%)	^{1}LLCT/^{1}LMCT
S_4	404 (3.07)	0.1228	HOMO-1→LUMO+1 (83%)	^{1}LLCT/^{1}LMCT
S_{12}	353 (3.51)	0.2154	HOMO-6→LUMO+1 (56%)	^{1}MC/^{1}IL/^{1}LLCT/^{1}MLCT
			HOMO-5→LUMO+1 (11%)	^{1}LLCT/^{1}LMCT/^{1}MC
			HOMO-3→LUMO+1 (10%)	^{1}LLCT/^{1}LMCT
S_{24}	326 (3.80)	0.7788	HOMO-1→LUMO+4 (20%)	^{1}LLCT
			HOMO-2→LUMO+5 (12%)	^{1}LLCT/^{1}LMCT/^{1}IL
			HOMO→LUMO+11 (12%)	^{1}LLCT/^{1}LMCT/^{1}MC

Table S13. Partial Molecular Orbital Compositions (%) in the Lowest-Energy Triplet State for Complex **1** 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-BI
LUMO	-2.67	20.36 (60/24/17)	25.82 (51/45/4)	0.84	42.82	10.16
HOMO	-5.86	11.92 (1/7/92)	2.89 (40/34/26)	0.11	2.37	82.71

Table S14. Partial Molecular Orbital Compositions (%) in the Lowest-Energy Triplet State for Complex **2** 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-Cz	C≡C-BI
LUMO	-2.67	24.0 (67/16/17)	26.35 (39/58/3)	0.87	42.67	2.77	3.34
HOMO	-5.60	12.41 (0/9/91)	3.34 (45/31/23)	0.08	2.70	72.42	9.05

Table S15. Partial Molecular Orbital Compositions (%) in the Lowest-Energy Triplet State for Complex **3** 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-Cz
LUMO	-2.77	2.28 (0/89/11)	38.28 (45/44/11)	0.12	56.94	2.37
HOMO	-5.58	9.49 (1/1/98)	1.16 (22/47/31)	0.11	3.20	86.05

Table S16. Partial Molecular Orbital Compositions (%) in the Lowest-Energy Triplet State for Complex **4** 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-PR
LUMO	-2.72	25.75 (76/13/11)	28.93 (35/61/5)	0.70	40.80	3.81
HOMO	-5.53	8.53 (1/8/91)	7.44 (55/38/8)	0.03	2.71	81.29

Table S17. Partial Molecular Orbital Compositions (%) in the Lowest-Energy Triplet State for Complex **5** 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-spiro
LUMO	-2.74	8.83 (79/17/5)	38.23 (41/50/9)	0.11	51.09	1.74
HOMO	-5.50	9.98 (3/6/91)	4.11 (56/19/25)	0.29	4.10	81.53

Table S18. The Emission Transitions for Complexes **1–5** in CH_2Cl_2 Solution by TD-DFT Method at the PBE1PBE Level.

	state	*E*, nm (eV)	O.S.	transition (contrib.)	assignment
1	T_1	519 (2.39)	0.0000	HOMO→LUMO (62%)	^{3}LLCT/^{3}LMCT
2	T_1	530 (2.34)	0.0000	HOMO→LUMO (83%)	^{3}LLCT/^{3}LMCT
3	T_1	551 (2.25)	0.0000	HOMO→LUMO (97%)	^{3}LLCT/^{3}LMCT
4	T_1	563 (2.20)	0.0000	HOMO→LUMO (67%)	^{3}LLCT/^{3}LMCT
5	T_1	574 (2.16)	0.0000	HOMO→LUMO (95%)	^{3}LLCT/^{3}LMCT

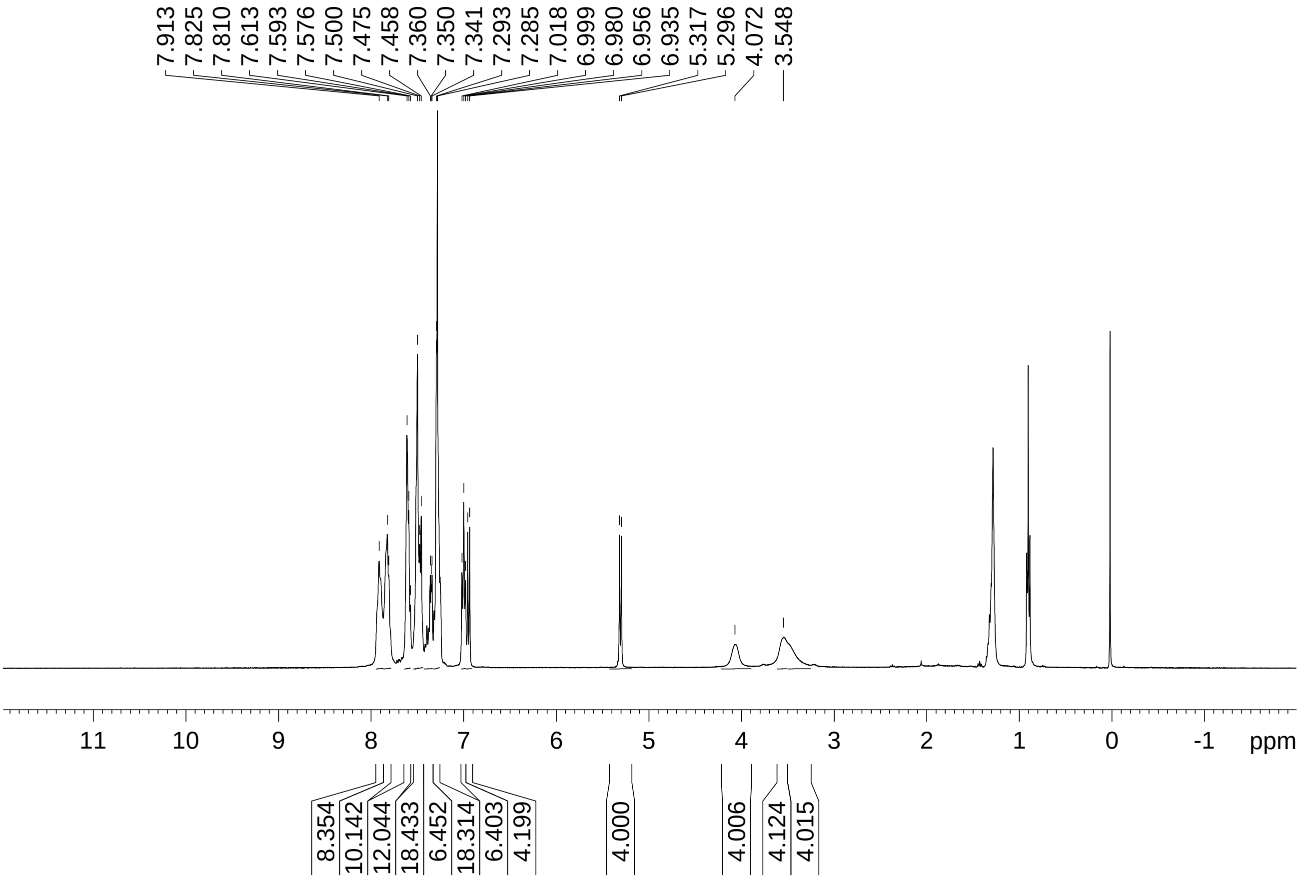

Fig. S1 The ^{1}H NMR spectrum of complex **1** measured in $CDCl_3$ at 298 K.

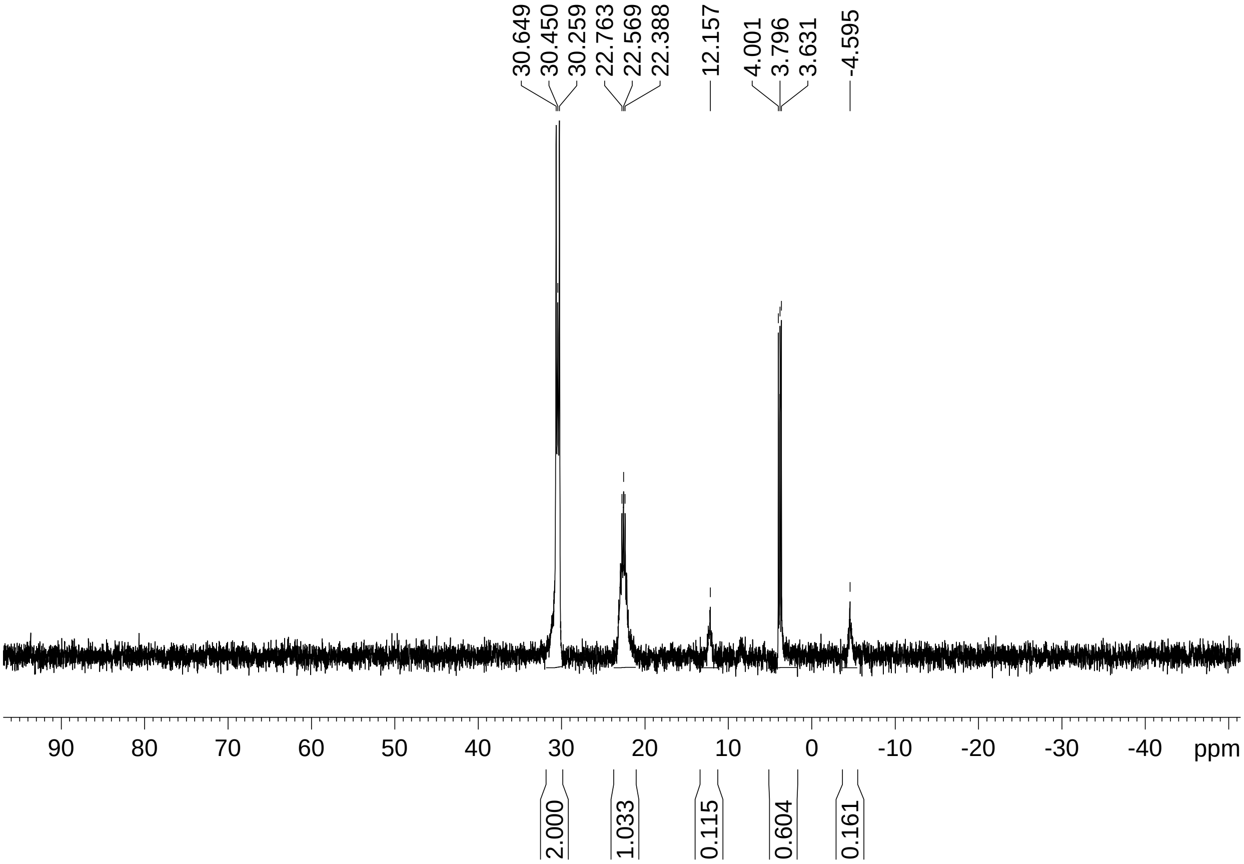

Fig. S2 The ^{31}P NMR spectrum of complex **1** measured in $CDCl_3$ at 298 K.

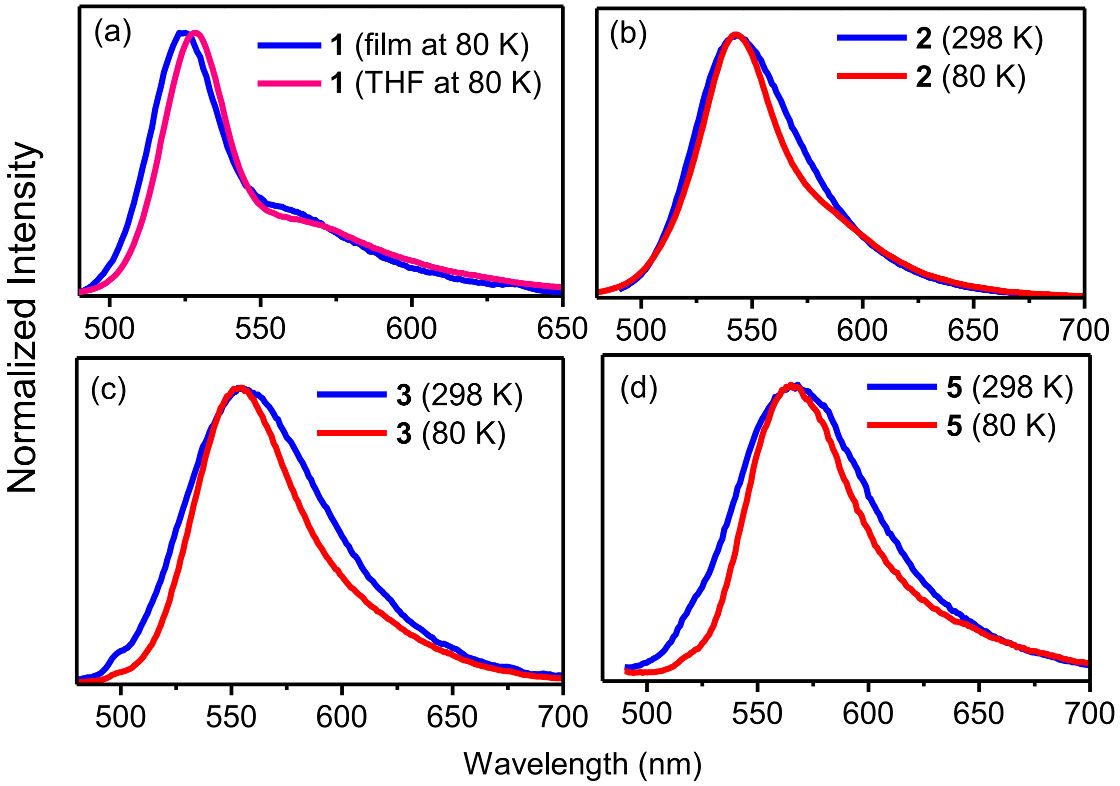

Fig. S3 The photoluminescent emission spectra. (a) Complex **1** in doped film and THF at 80 K; (b) Complex **2** in doping film at 298 and 80 K; (c) Complex **3** in doping film at 298 and 80 K; **(**d) Complex **5** in doping film at 298 and 80 K.

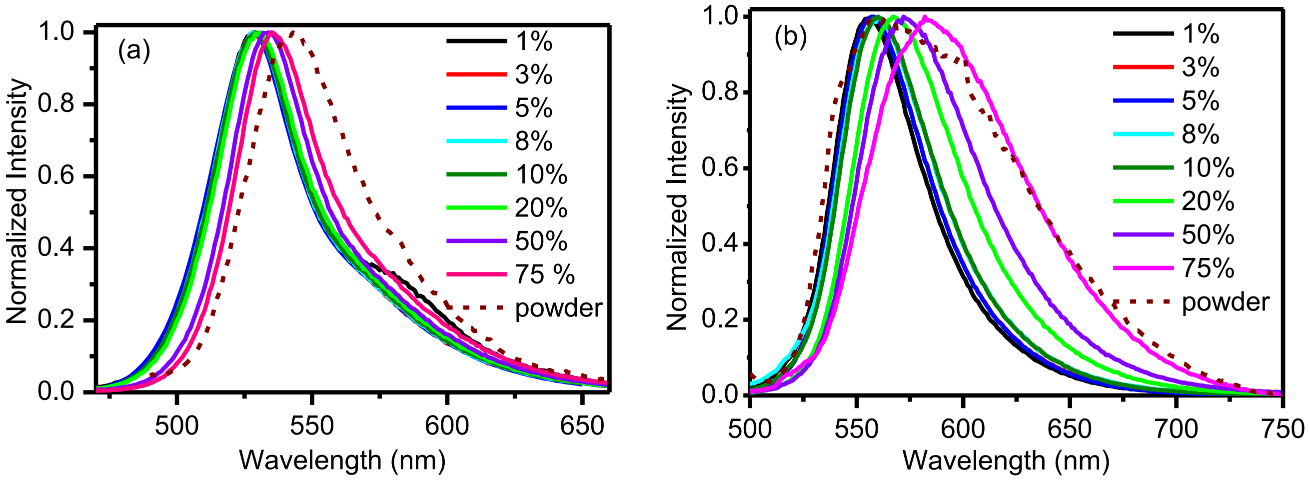

Fig. S4 Normalized photoluminescence spectra of compounds **1** (a) and **4** (b) in mCP : OXD-7 (1 : 1) : PtAu$_3$ doping films at various doping concentrations.

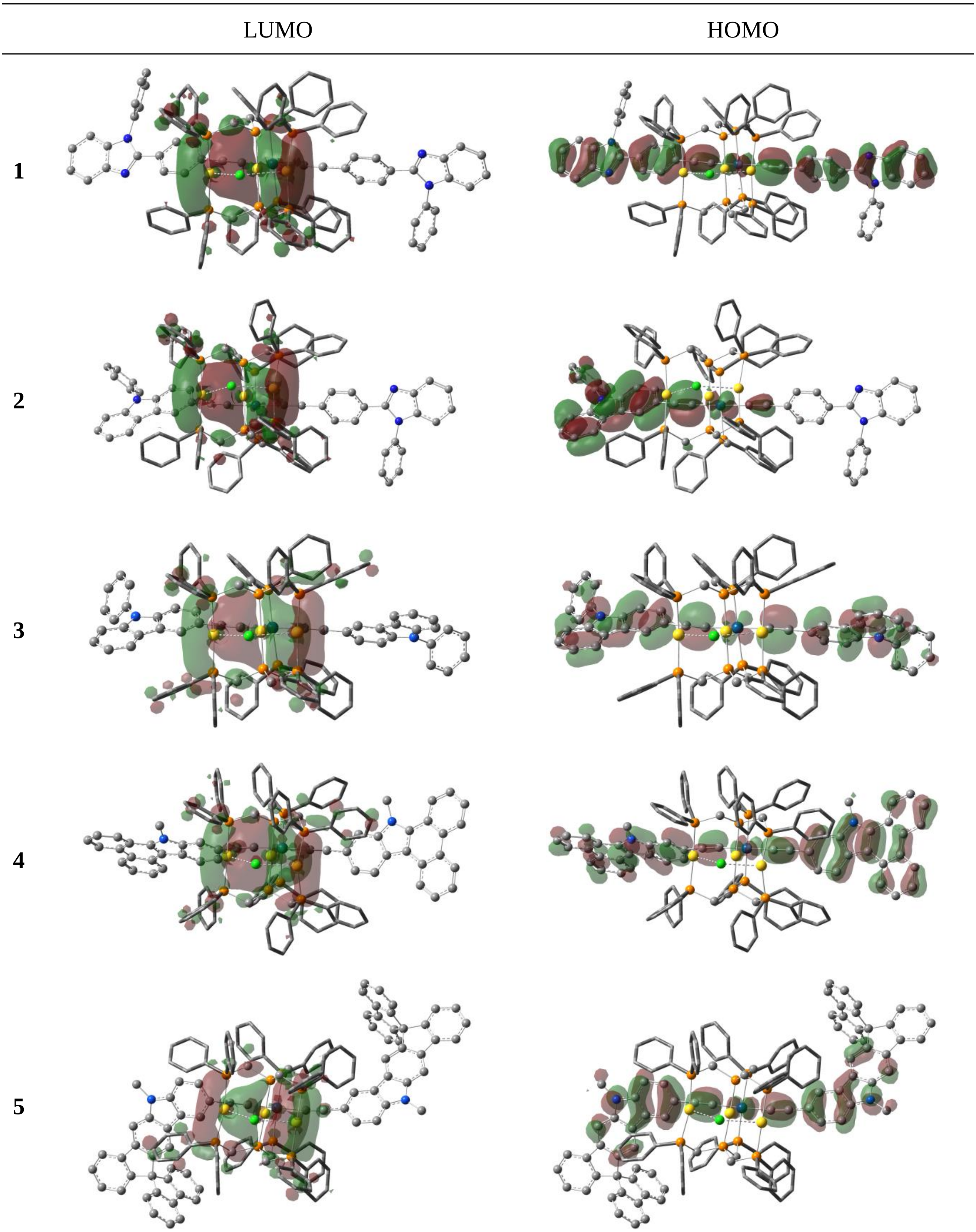

Fig. S5 The plots of HOMO and LUMO (isovalue = 0.02) in the ground states for complexes **1–5** in CH_2Cl_2 solution by TD-DFT method at the PBE1PBE level.

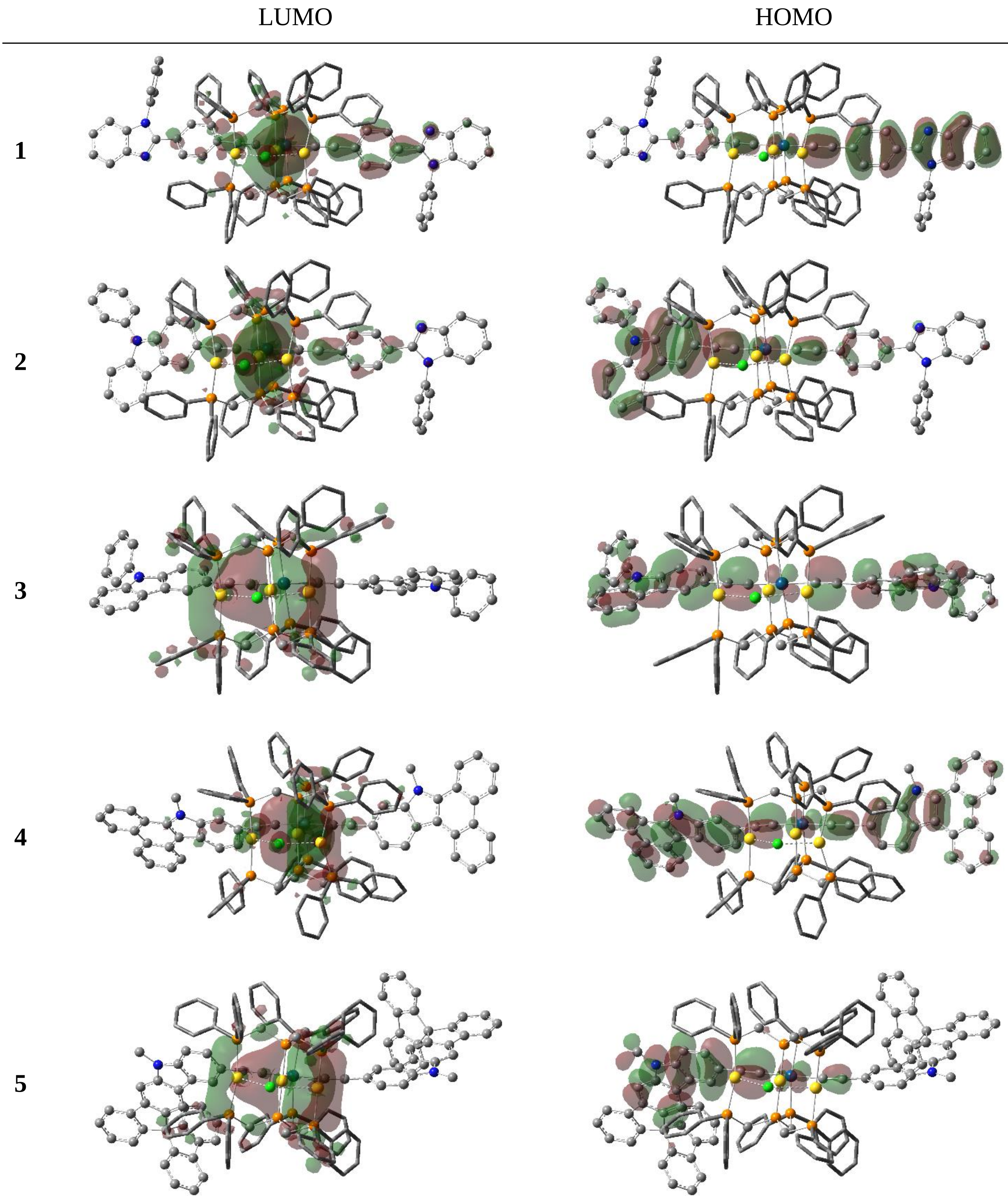

Fig. S6 The plots of HOMO and LUMO (isovalue = 0.02) in the lowest-energy triplet states for complexes **1–5** in CH_2Cl_2 solution by TD-DFT method at the PBE1PBE level.

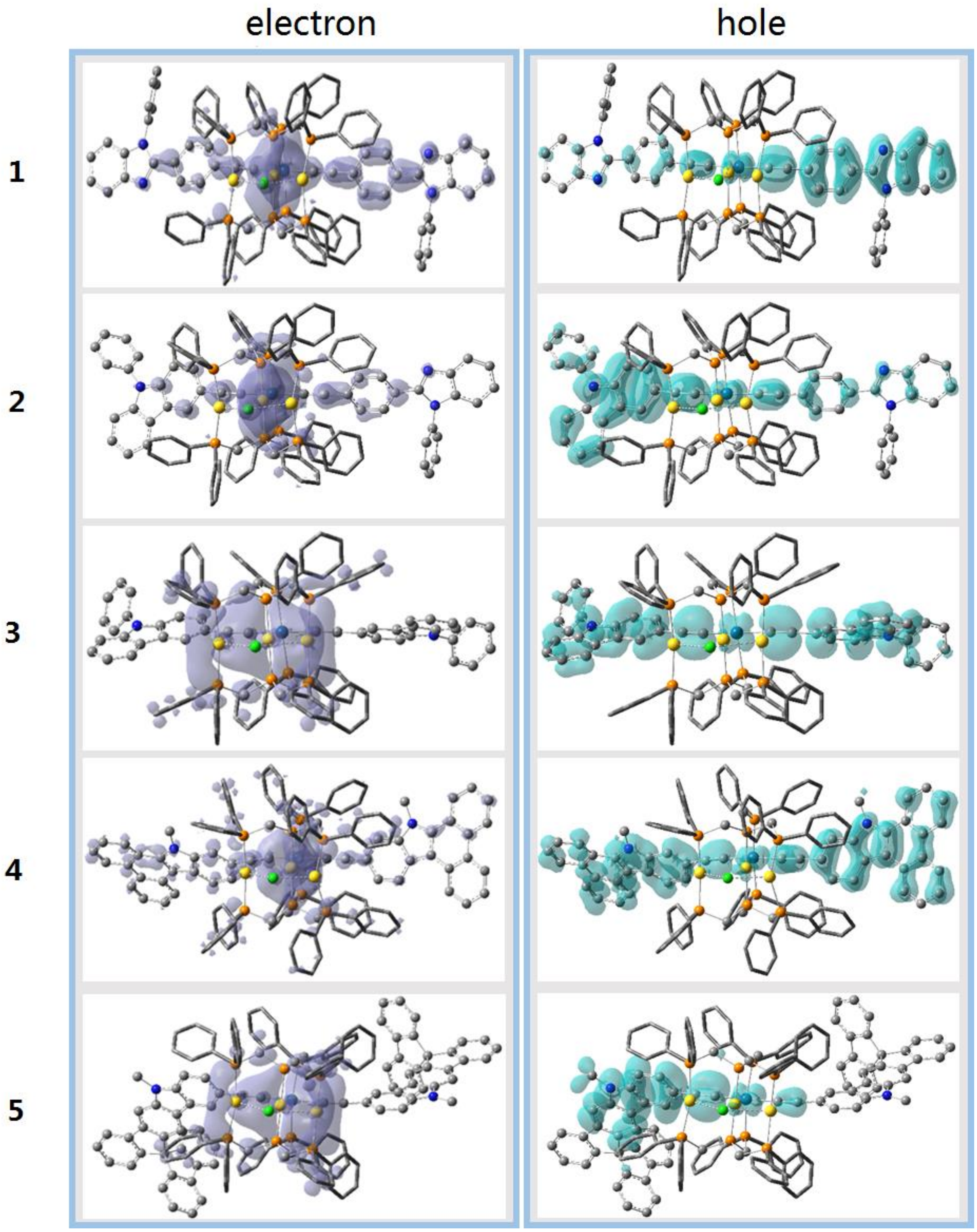

Fig. S7 Plots of the hole and electron in the lowest-energy triplet state for complexes **1–5** by TD-DFT at the PBE1PBE level. The "hole" and "electron" stand for electron lose and acquisition, respectively, in a single electron excitation process.

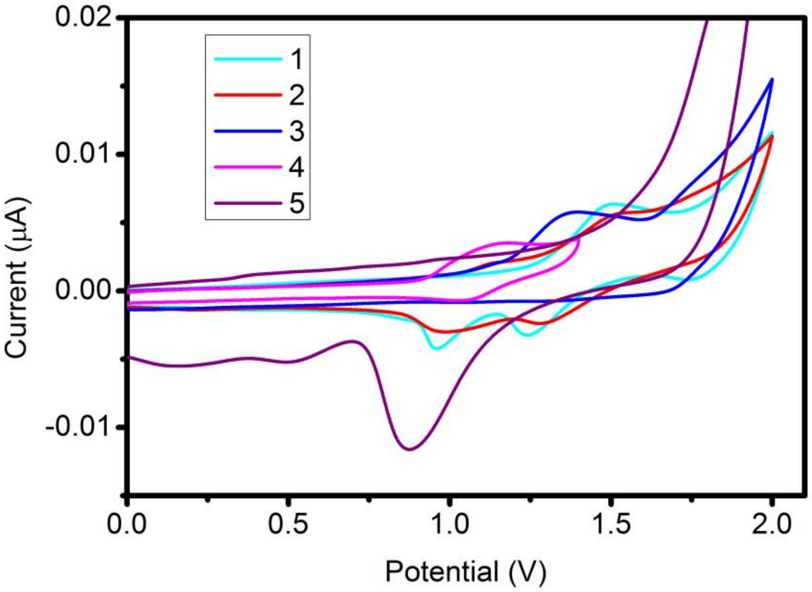

Fig. S8 Cyclic voltammograms for the reductive scans of compounds **1–5** in 0.1 M $Bu^n{}_4NPF_6$ of CH_2Cl_2 solutions.

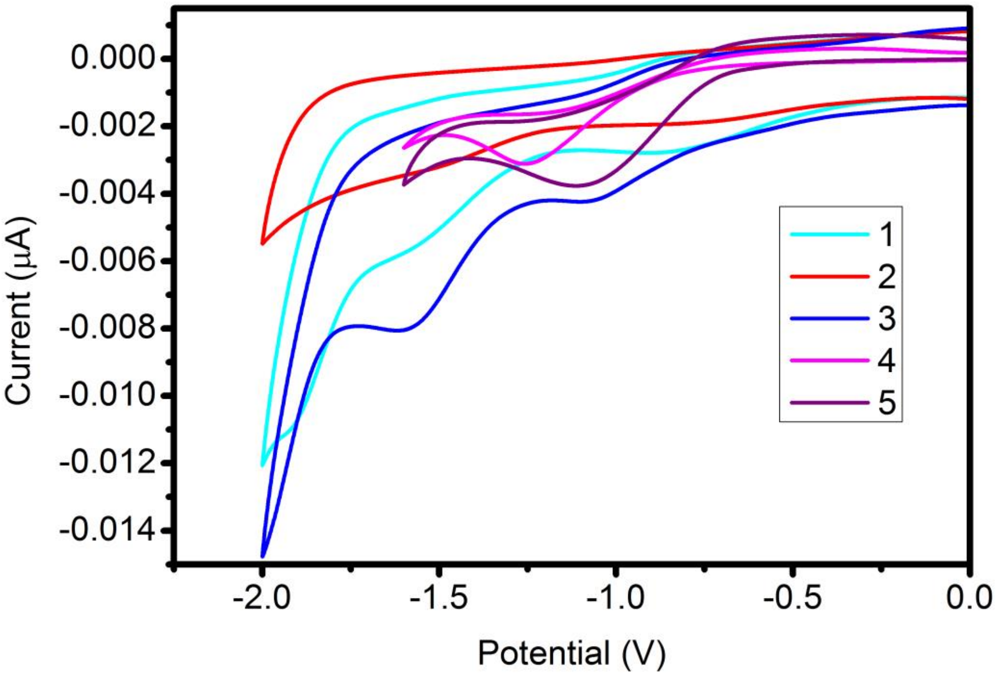

Fig. S9 Cyclic voltammograms for the reductive scans of compounds **1–5** in 0.1 M $Bu^n{}_4NPF_6$ of CH_2Cl_2 solutions.

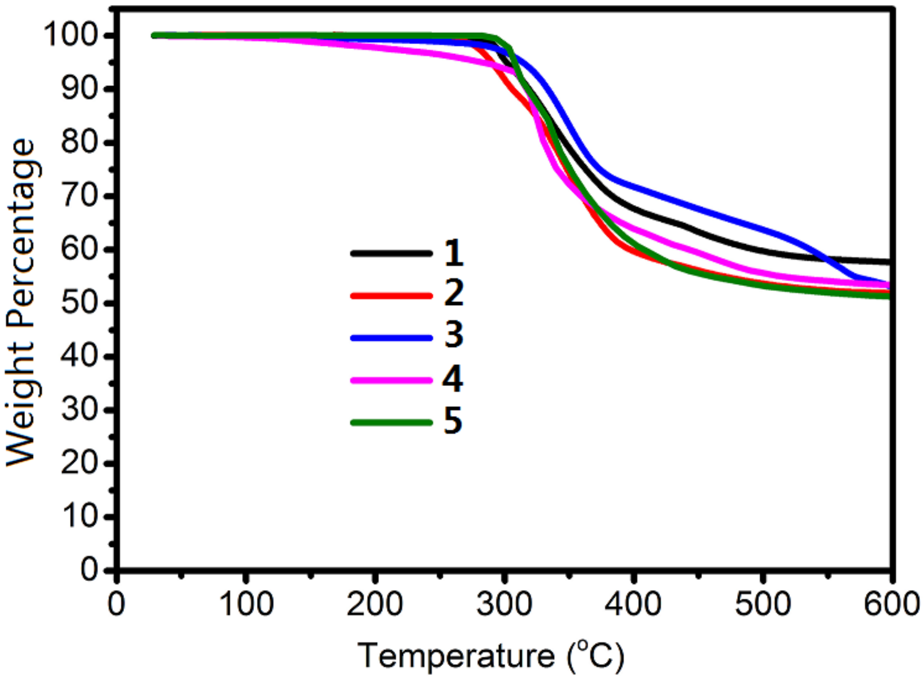

Fig. S10 The plots of thermogravimetric analysis for compounds **1–5**.

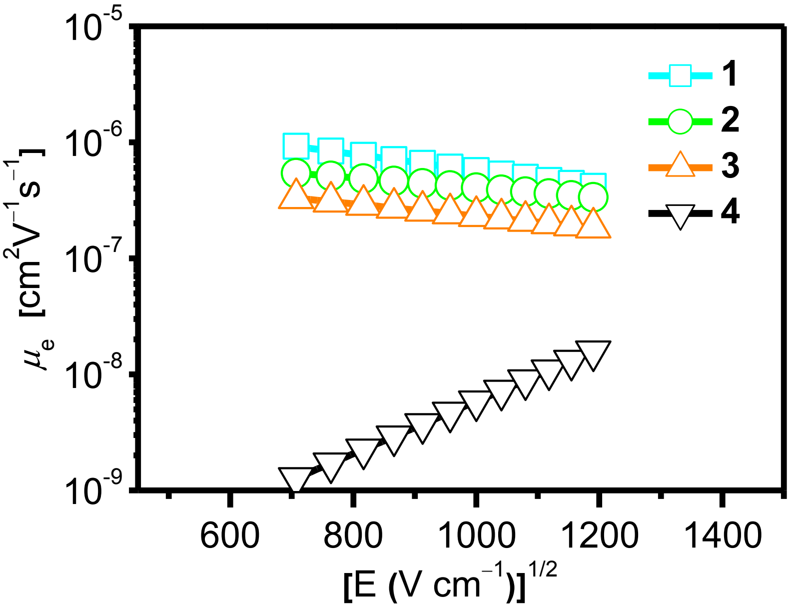

Fig. S11 Electric field dependent electron mobilities of complexes **1–4** in SCLC region.

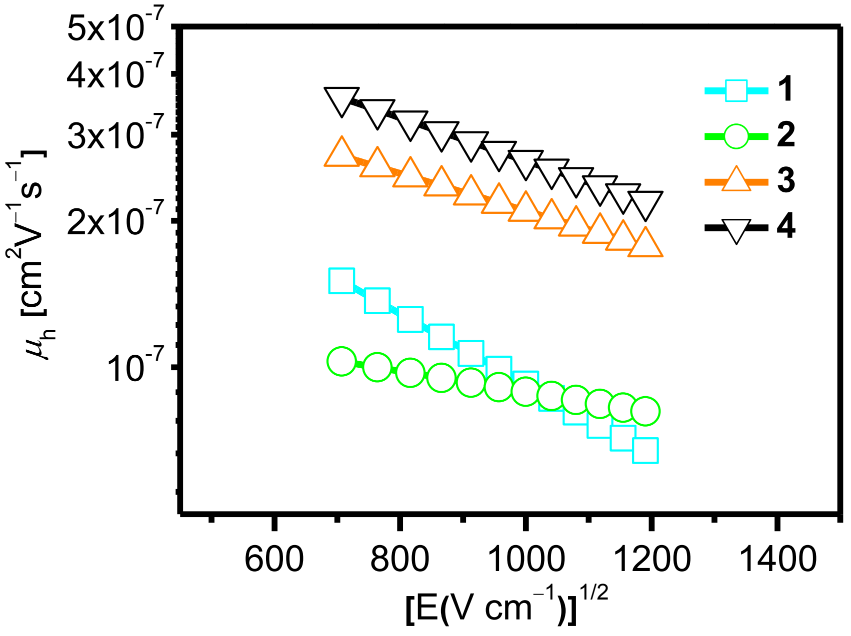

Fig. S12 Electric field dependent hole mobilities of complexes **1–4** in SCLC region.