The Effects of Extended π-Conjugation in Bipyridyl Ligands on the Tunable Photophysics, Triplet Excited State and Optical Limiting Properties of Pt(II) Naphthalimidyl Acetylide Complexes

Senqiang Zhu, [a] Hao Liu, [a] Qian Cheng, [a] Zhenxing Ma, [a] Rui Liu *[a] and Hongjun Zhu *[a]

Synthesis and Characterization

Preparation of the compound 3. 1 (2.26 g, 5.97 mmol), 8 (4.41 g, 8.96 mmol) and $Pd(PPh_3)_4$ (0.60 g, 0.52 mmol) were added to 60 mL of toluene. Then 38 mL 2M K_2CO_3 aqueous solution was added. The mixture was heated to reflux under argon for 48 h. The mixture was then extracted with CH_2Cl_2, washed by brine and then combined organic layer dried over $MgSO_4$. After removal of the solvent, the crude product was purified by column chromatography (silica gel, hexane) to afford white solid (2.195g, 49% yield). ^{1}H NMR(400MHz，$CDCl_3$): δ 7.79-7.76 (d, J = 7.81 Hz, 1H,), 7.75-7.70 (d J = 7.65 Hz, 2H), 7.67-7.55 (m, 5H), 7.50-7.45 (m, 2H,), 7.39-7.28 (m, 3H), 2.09-1.90 (m, 8H) 1.19-0.98 (m, 24H), 0.81-0.60 (m, 20H).

Preparation of the compound 4. 2 (2.99 g, 10.12 mmol), 8 (7.00 g, 15.1 mmol) and $Pd(PPh_3)_4$ (0.80 g, 0.86 mmol) were added to 100 mL of toluene. Then 60 mL 2M K_2CO_3 aqueous solution was added. The mixture was heated to reflux under argon for 48 h. The mixture was then extracted with CH_2Cl_2, washed by brine and then combined organic layer dried over $MgSO_4$. After removal of the solvent, the crude product was purified by column chromatography (silica gel, hexane) to afford white solid (2.85 g, 42 % yield).

Preparation of the compound 5. To a stirred solution of 3 (2.195 g, 2.94 mmol) in anhydrate THF (30 mL) was added dropwise a solution of *n*-BuLi (1.3 mL, 1.6 M in hexane,) at -78 ^{o}C under N_2. The mixture was stirred at this temperature for 30 min, and then $B(OMe)_3$ (0.5 mL, 3.83 mmol) was added dropwise, then the mixture was allowed to warm to room temperature gradually and stirred overnight. Then 3 mL 3M HCl was added and the mixture and stirred for 30 min. The mixture was extracted with CH_2Cl_2,

washed with brine, dried over $MgSO_4$. After removal of the solvent, the crude product was purified by column chromatography(silica gel, hexane/EA=1:1, v/v) to afford light yellow solid (0.86g, 41% yield). ^{1}H NMR(400MHz，$CDCl_3$): δ 8.42 (d, J = 7.69 Hz, 1H), 8.33 (s, 1H,), 8.00 (d, J = 7.55 Hz, 1H), 7.97 (d, J = 7.83 Hz, 1H), 7.90–7.66 (m, 6H), 7.48–7.35 (m, 3H), 2.34–2.00 (m, 8H), 1.30–1.06 (m, 24H), 0.94–0.72 (m, 20H).

Preparation of the compound 6. To a stirred solution of 4 (1.9 g, 2,87 mmol) in anhydrate THF (20 mL) was added dropwise a solution of *n*-BuLi (2.87 mL, 1.6 M in hexane,) at -78 ^{o}C under N_2. The mixture was stirred at this temperature for 30 min, and then $B(OMe)_3$ (0.8 mL, 8.61 mmol) was added dropwise, then the mixture allowed to warm to room temperature gradually and stirred overnight. 3 mL 3M HCl was added and the mixture was stirred for 0.5 h, The mixture was extracted with CH_2Cl_2, washed with brine and dried over $MgSO_4$. After removal of the solvent, the crude product was purified by column chromatography (silica gel, hexane/ethyl acetate =2:1, v/v) to afford light yellow solid (1.1g, 54% yield).

Preparation of the compound L3. 5 (0.2 g, 0.28 mmol), 4,4'-dibromo-2,2'-dipyridyl (0.029 g, 0.094 mmol) and $Pd(PPh_3)_4$ (0.04 g, 0.035 mmol) were added to 15 mL of toluene. Then 6 mL 2M K_2CO_3 aqueous solution was added. The mixture was heated to reflux under argon for 24 h. This mixture was then reduced in vacuo, extracted with CH_2Cl_2, washed by brine and then combined organic layer dried over $MgSO_4$. After removal of the solvent, the crude product was purified by column chromatography (Al_2O_3, hexane/ethyl acetate = 40:1, v/v) to afford faint yellow solid. (0.089 g, 21% yield). ^{1}H NMR (400MHz，$CDCl_3$): δ 8.82 (d, J = 5.4 Hz, 2H), 7.88-7.74 (m, 6H), 7.69-7.63 (m, 5H), 7.38-7.31(m, 3H), 2.15-2.03 (m, 8H), 1.13-1.10 (m, 24H), 0.77 – 0.74 (m, 20H).

Preparation of the compound L4. 6 (0.3 g, 0.48 mmol), 4,4'-dibromo-2,2'-dipyridyl (0.05 g, 0.159 mmol) and $Pd(PPh_3)_4$ (0.05 g, 0.048 mmol) were added to 15 mL toluene. Then 6 mL 2M K_2CO_3 aqueous solution was added. The mixture was heated to reflux under argon for 24 h. This mixture was then reduced in vacuo, extracted with CH_2Cl_2, washed by brine, combined organic layer and dried over $MgSO_4$. After removal of the solvent, the crude product was purified by column chromatography (Al_2O_3,

hexane/ethyl acetate = 40:1, v/v) to afford faint yellow solid. (0.144 g, 67 % yield). ^{1}H NMR(400MHz，$CDCl_3$): δ 8.82 (d, J = 5.2 Hz, 2H), 8.40 (s,1 H), 8.21 (d, J = 7.6 Hz, 1H), 7.88-7.79 (m, 5H), 7.75-7.68 (m, 3H), 7.52-7.44 (m, 3H), 7.28 (d, J = 7.4 Hz,1H), 4.36(t, J = 7.1 Hz, 2H), 2.15-2.11 (m, 4H), 1.95-1.88(m, 2H), 1.43-1.30 (m,6H), 1.16-1.10 (m, 12H), 0.88 (t, J = 7.0 Hz, 3H), 0.79-0.75 (m, 10H).

Photophysical properties

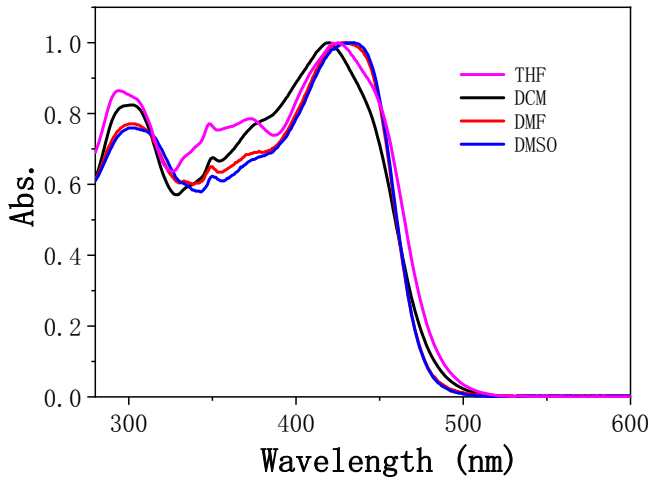


Fig. S1. Normalized UV-vis absorption spectra of Pt-1 in different solvents

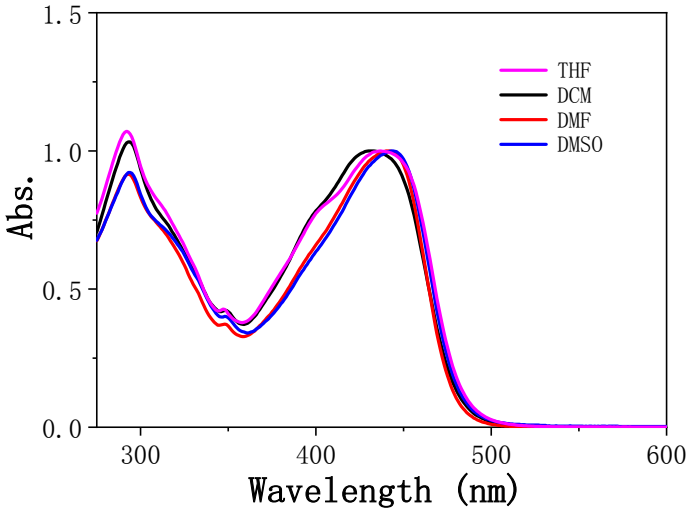


Fig. S2. Normalized UV-vis absorption spectra of Pt-2 in different solvents

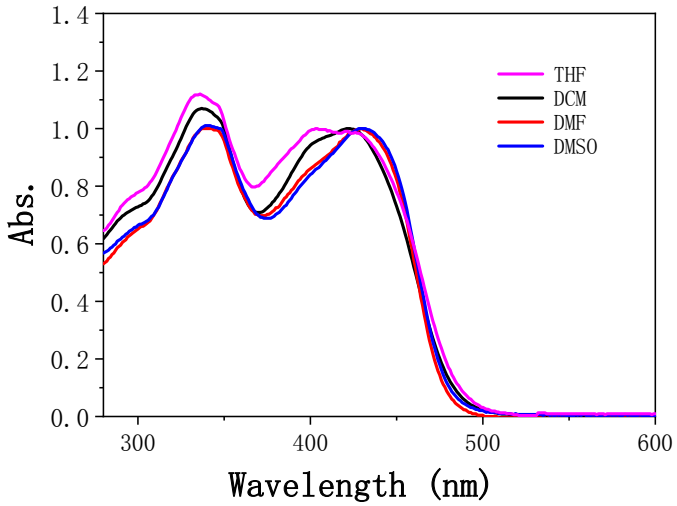


Fig. S3. Normalized UV-vis absorption spectra of Pt-3 in different solvents

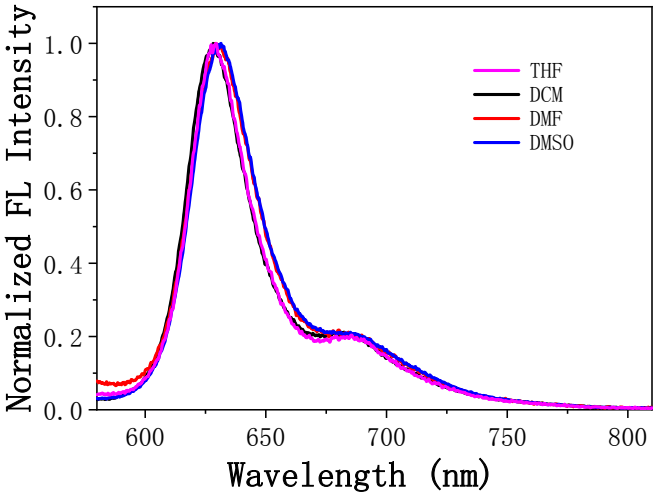


Fig. S4.Normalized emission spectra of Pt-1 (λ_{ex} = 420 nm) in different solvents

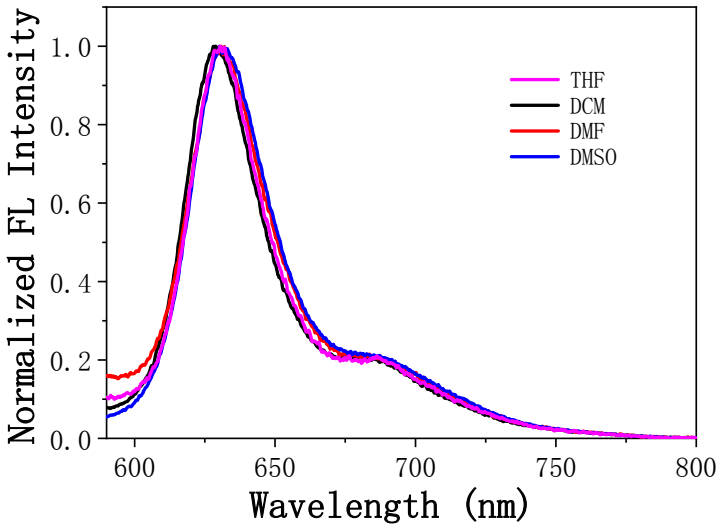


Fig. S5.Normalized emission spectra of Pt-2 (λ_{ex} = 420 nm) in different solvents

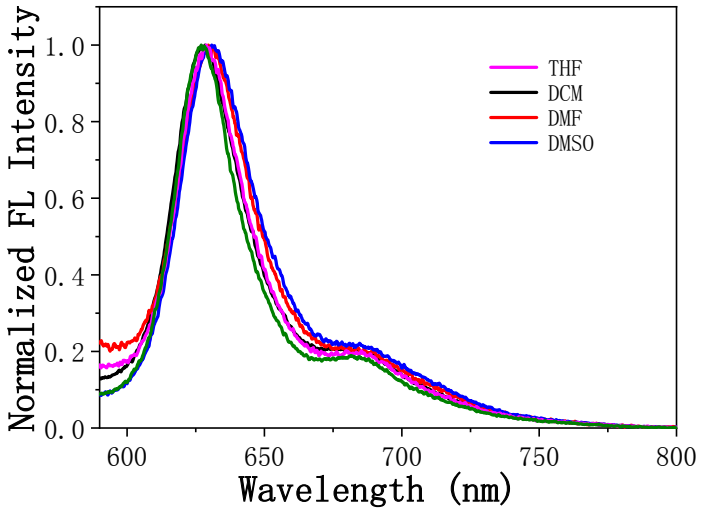


Fig. S6.Normalized emission spectra of Pt-3 (λ_{ex} = 420 nm) in different solvents

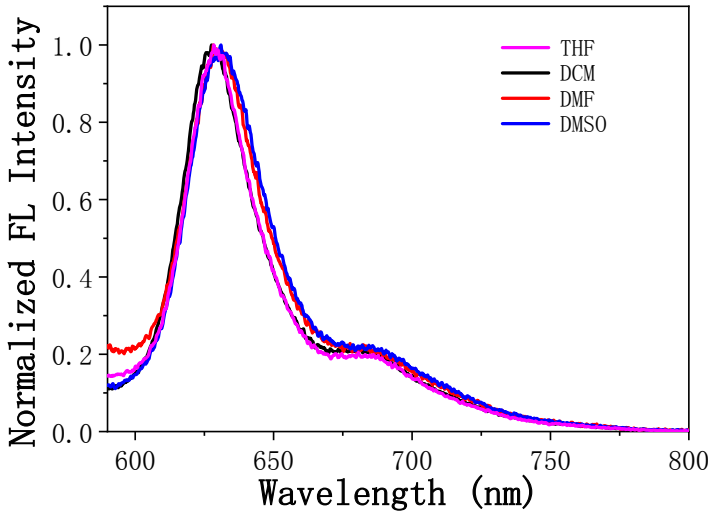


Fig. S7.Normalized emission spectra of Pt-4 (λ_{ex} = 420 nm) in different solvents

Closed Z-scan

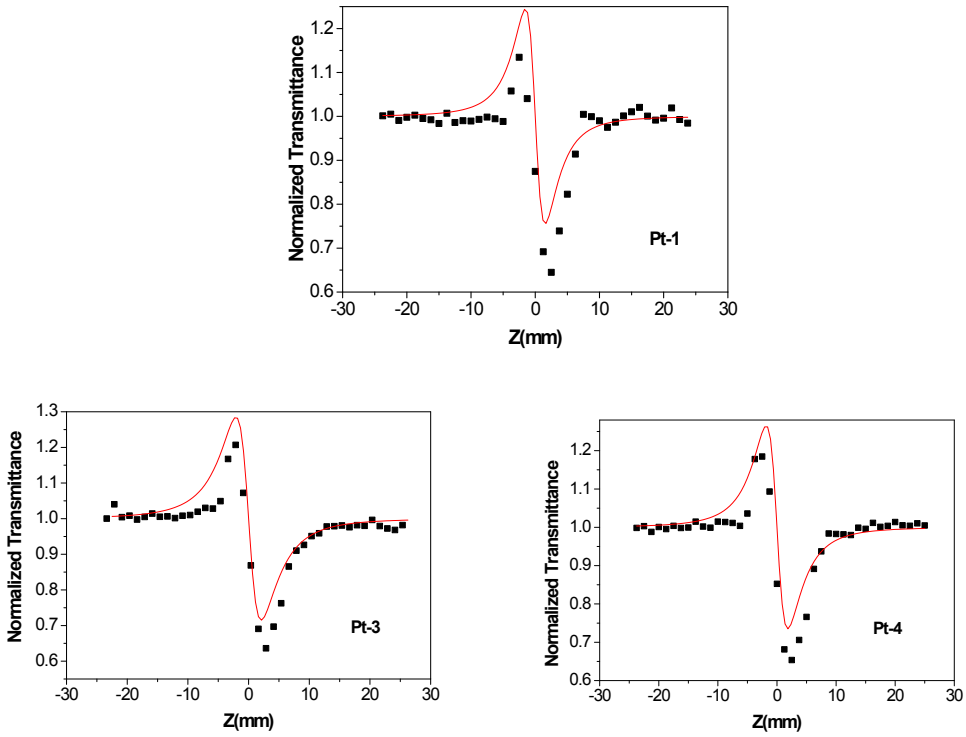


Fig.S8 Closed-aperture Z-scans results of Pt-1, Pt-3 and Pt-4 under 532 nm laser excitation.

^{1}H NMR spectra

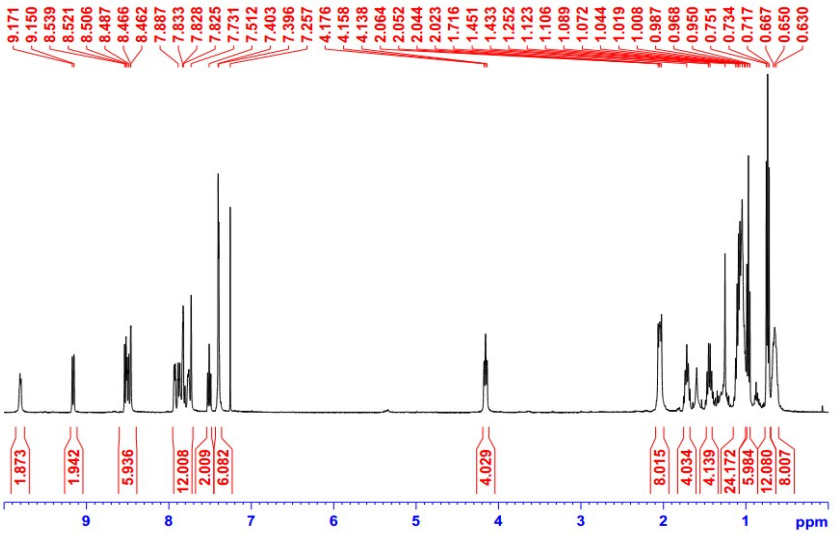


Fig. S9. ^{1}H NMR spectra of Pt-1

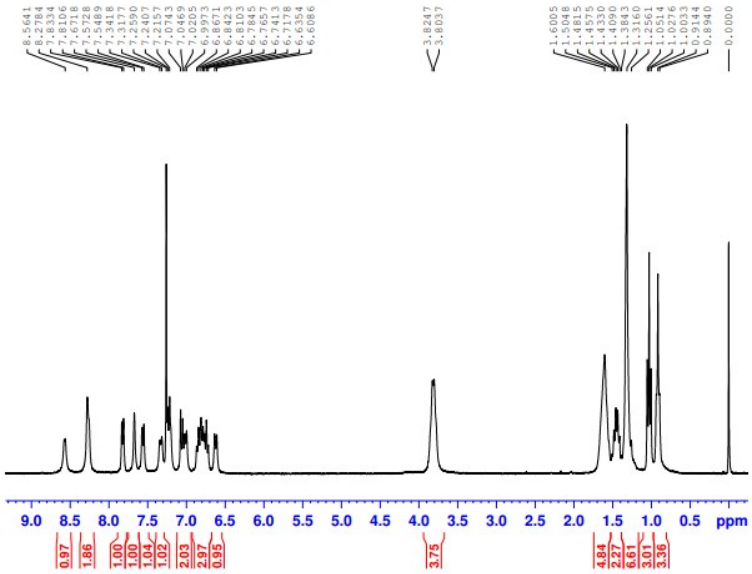


Fig. S10. ^{1}H NMR spectra of Pt-2

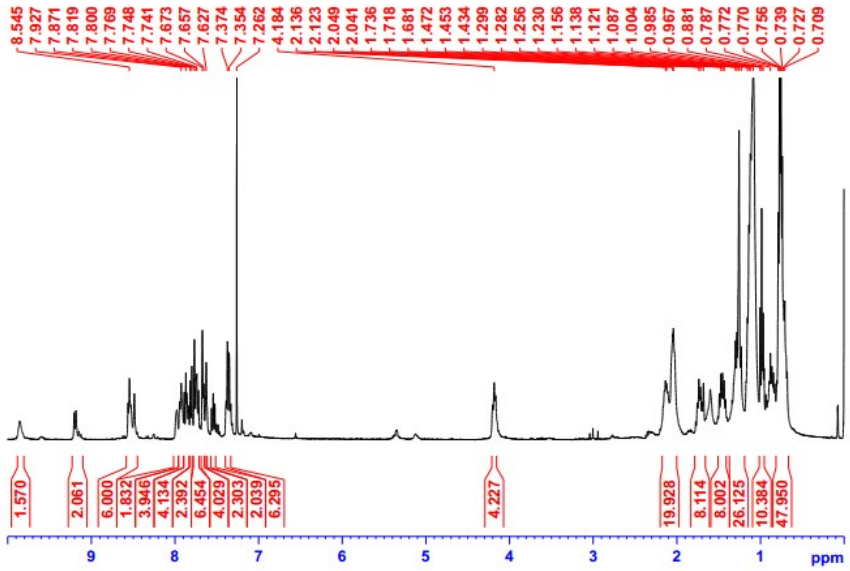


Fig. S11. [1]H NMR spectra of Pt-3

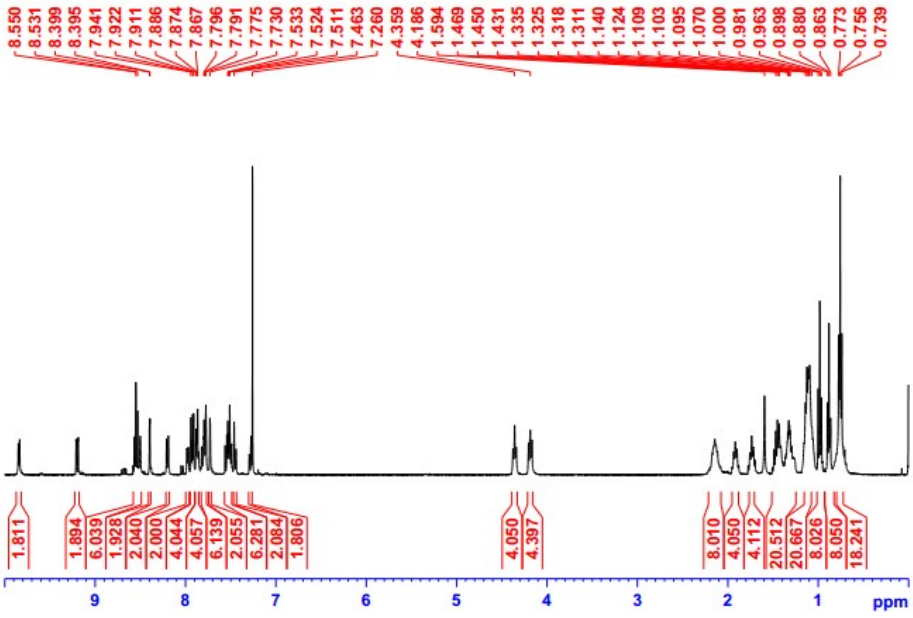
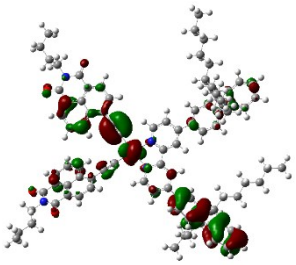
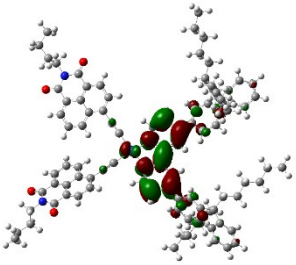
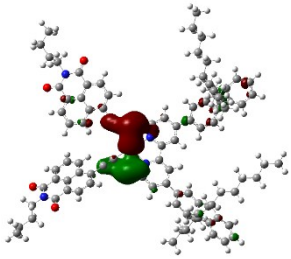
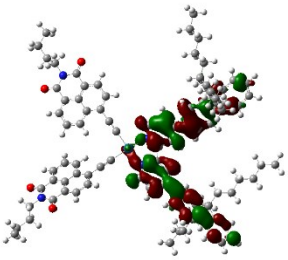
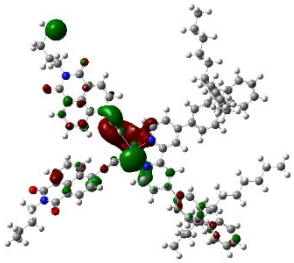
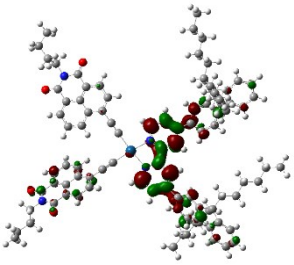
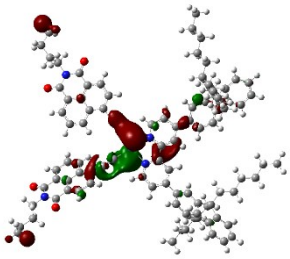
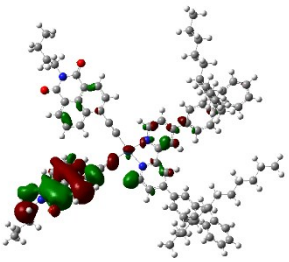
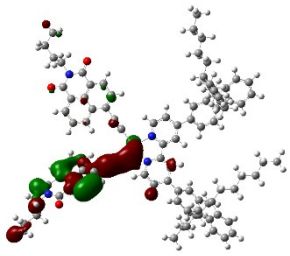
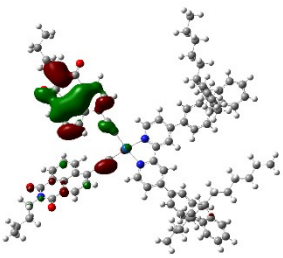


Fig. S12. [1]H NMR spectra of Pt-4

Table S1.Contour plots of the six highest occupied molecular orbitals (HOMOs) and six lowest unoccupied molecular orbitals (LUMOs) for **Pt-1** in CH_2Cl_2.

HOMO-5		LUMO	
HOMO-4		LUMO+1	
HOMO-3		LUMO+2	
HOMO-2		LUMO+3	
HOMO-1		LUMO+4	

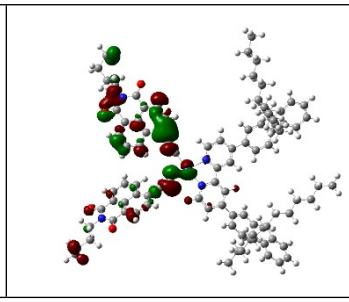
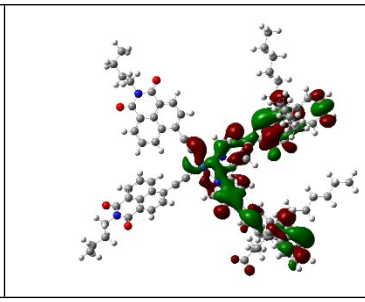
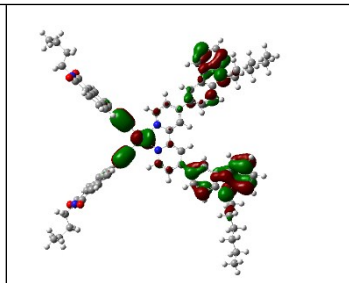
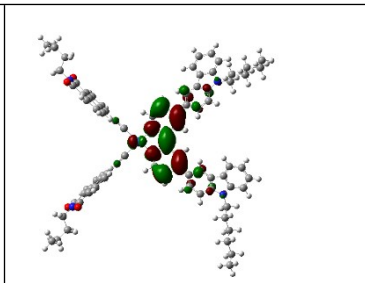
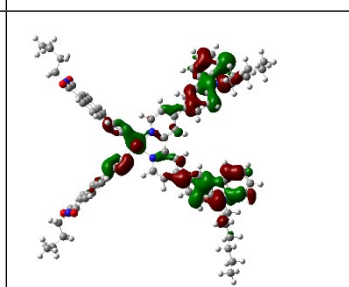
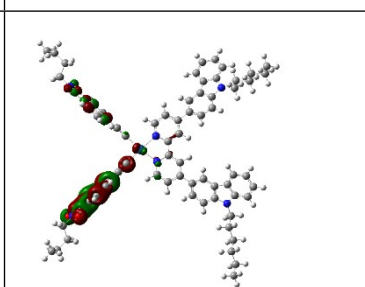
HOMO		LUMO+5	

Table S2 Excitation Energies (eV), Wavelengths (nm), Oscillator Strengths, Main Configurations, the Associated Configuration Coeffcients and Assignments of Complexes **Pt-1**

States	E/eV	λ/nm	f	Main configurations	assignment
S1	2.0018	619.36	0.0574	HOMO ---> LUMO 94.8%	^{1}MLCT/^{1}LLCT
S2	2.1256	583.28	0.1494	HOMO-1 ---> LUMO 95.2%	^{1}MLCT/^{1}LLCT
S3	2.5758	481.34	0.0386	HOMO-4 ---> LUMO 72.9%	^{1}MLCT/^{1}LLCT
S4	2.5935	478.05	0.1685	HOMO-2 ---> LUMO 72.1%	^{1}MLCT/^{1}LLCT
S5	2.7424	452.10	0.0184	HOMO-3 ---> LUMO 88.9%	^{1}MLCT/^{1}LLCT
T1	1.8925	655.14	0.0000	HOMO ---> LUMO 81.4%	^{3}MLCT/^{3}LLCT
T2	1.9742	628.01	0.0000	HOMO-1 ---> LUMO 64.4%	^{3}MLCT/^{3}LLCT
				HOMO-1 ---> LUMO+3 28.5%	
T3	2.0945	591.96	0.0000	HOMO ---> LUMO+3 12.1%	^{3}MLCT/^{3}LLCT
				HOMO ---> LUMO+4 13.9%	
T4	2.1070	588.45	0.0000	HOMO ---> LUMO+4 44.1% HOMO-1 ---> LUMO 16.1%	^{3}MLCT/^{3}LLCT
T5	2.4159	513.21	0.0000	HOMO-2 ---> LUMO 85.1%	^{3}MLCT/^{3}LLCT

Table S3.Contour plots of the six highest occupied molecular orbitals (HOMOs) and six lowest unoccupied molecular orbitals (LUMOs) for **Pt-2** in CH_2Cl_2.

HOMO-5		LUMO	
HOMO-4		LUMO+1	

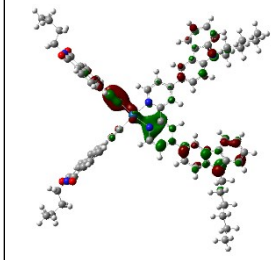
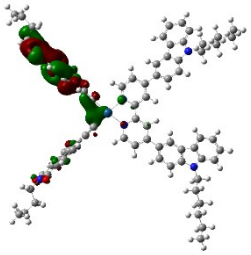
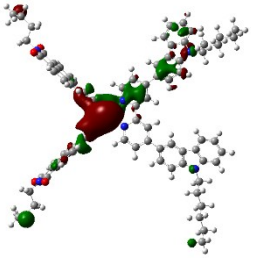
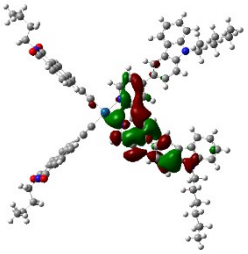
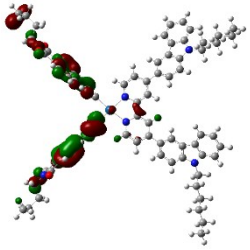
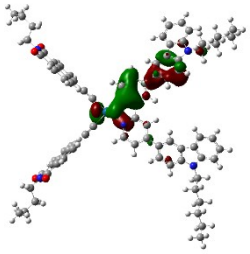
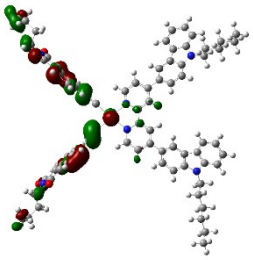
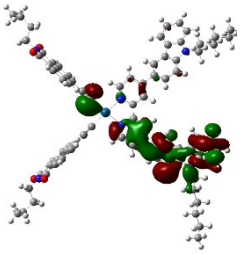
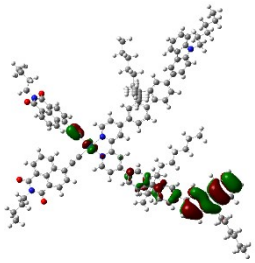
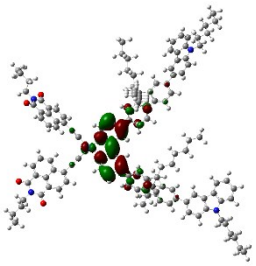
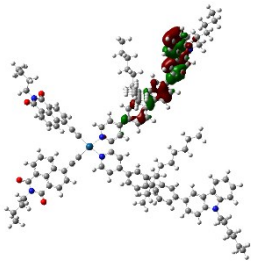
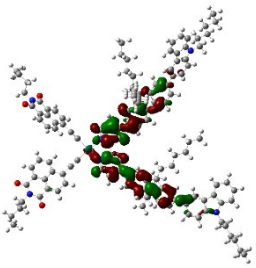
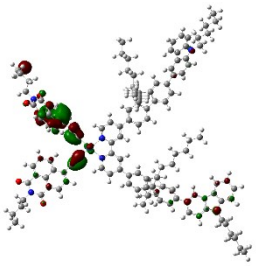
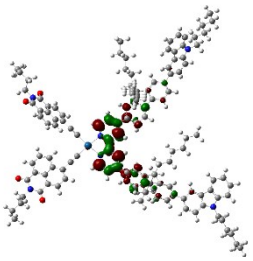
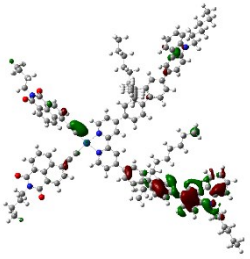
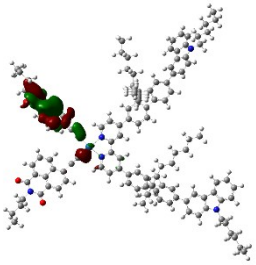
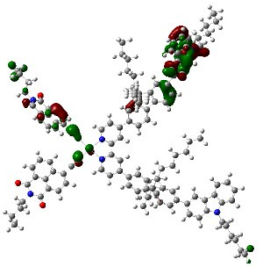
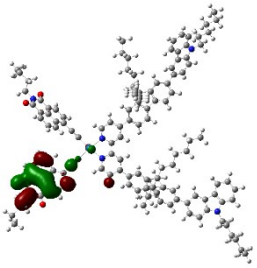
HOMO-3		LUMO+2	
HOMO-2		LUMO+3	
HOMO-1		LUMO+4	
HOMO		LUMO+5	

Table S4 Excitation Energies (eV), Wavelengths (nm), Oscillator Strengths, Main Configurations, the Associated Configuration Coeffcients and Assignments of Complexes **Pt-2**

States	E/eV	λ/nm	f	Main configurations	Assignments
S1	2.1201	584.79	0.0035	HOMO ---> LUMO 97.7%	^{1}MLCT/^{1}LLCT
S2	2.2692	546.38	0.0160	HOMO-1 ---> LUMO 98.3%	^{1}MLCT/^{1}LLCT
S3	2.4396	508.22	0.0563	HOMO-2 ---> LUMO 84.0%	^{1}MLCT/^{1}LLCT
S4	2.6147	474.18	0.0407	HOMO-6 ---> LUMO 84.9%	^{1}MLCT/^{1}LLCT
S5	2.6452	468.71	0.4615	HOMO-3 ---> LUMO 73.6%	^{1}MLCT/^{1}LLCT
T1	2.0521	604.17	0.0000	HOMO ---> LUMO+2 28.0% HOMO-1 ---> LUMO+1 32.1%	^{3}MLCT/^{3}LLCT
T2	2.0568	602.79	0.0000	HOMO-1 ---> LUMO+2 30.1% HOMO ---> LUMO+1 30.4%	^{3}MLCT/^{3}LLCT
T3	2.1068	588.50	0.0000	HOMO ---> LUMO 82.8%	^{3}MLCT/^{3}LLCT
T4	2.2354	554.64	0.0000	HOMO-1 ---> LUMO 77.3%	^{3}MLCT/^{3}LLCT
T5	2.2788	544.08	0.0000	HOMO-2 ---> LUMO 86.4%	^{3}MLCT/^{3}LLCT

Table S5.Contour plots of the six highest occupied molecular orbitals (HOMOs) and six lowest unoccupied molecular orbitals (LUMOs) for **Pt-1** in CH_2Cl_2.

HOMO-5		LUMO	
HOMO-4		LUMO+1	
HOMO-3		LUMO+2	
HOMO-2		LUMO+3	
HOMO-1		LUMO+4	

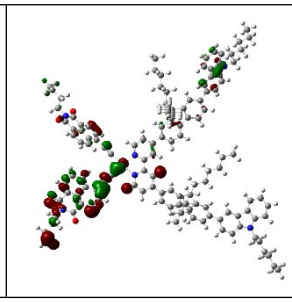
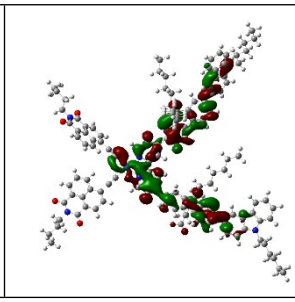
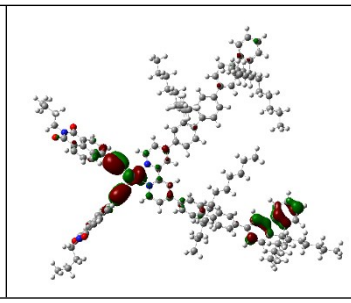
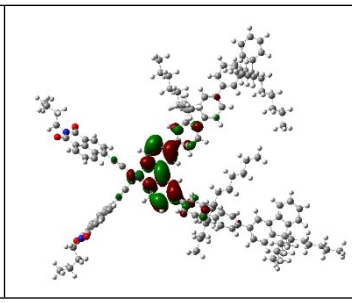
HOMO		LUMO+5	

Table S6 Excitation Energies (eV), Wavelengths (nm), Oscillator Strengths, Main Configurations, the Associated Configuration Coeffcients and Assignments of Complexes **Pt-3**

States	E/eV	λ/nm	f	Main configurations	Assignments
S1	2.0158	615.05	0.0994	HOMO ---> LUMO 89.2%	^{1}MLCT/^{1}LLCT
S2	2.1535	575.75	0.2287	HOMO-3 ---> LUMO 56.8%	^{1}MLCT/^{1}LLCT
S3	2.3178	534.93	0.1105	HOMO-2---> LUMO 59.4% HOMO-1 ---> LUMO 37.0%	^{1}MLCT/^{1}LLCT
S4	2.3403	529.79	0.1555	HOMO-3 ---> LUMO 38.5% HOMO-2 ---> LUMO 24.2% HOMO-1 ---> LUMO 33.0%	^{1}MLCT/^{1}LLCT
S5	2.5583	484.64	0.0714	HOMO-6 ---> LUMO 72.3%	^{1}MLCT/^{1}LLCT
T1	1.8906	655.80	0.0000	HOMO ---> LUMO 78.2%	^{3}MLCT/^{3}LLCT
T2	2.0087	617.25	0.0000	HOMO-3 ---> LUMO 30.5% HOMO-3 ---> LUMO+3 20.9%	^{3}MLCT/^{3}LLCT
T3	2.0987	590.77	0.0000	HOMO ---> LUMO+4 39.0% HOMO ---> LUMO 10.8%	^{3}MLCT/^{3}LLCT
T4	2.1074	588.33	0.0000	HOMO-3 ---> LUMO+3 22.3% HOMO ---> LUMO+4 16.9%	^{3}MLCT/^{3}LLCT
T5	2.2230	557.74	0.0000	HOMO-2 ---> LUMO 41.9% HOMO-1 ---> LUMO 35.9%	^{3}MLCT/^{3}LLCT

Table S7.Contour plots of the six highest occupied molecular orbitals (HOMOs) and six lowest unoccupied molecular orbitals (LUMOs) for **Pt-4** in CH_2Cl_2.

HOMO-5		LUMO	

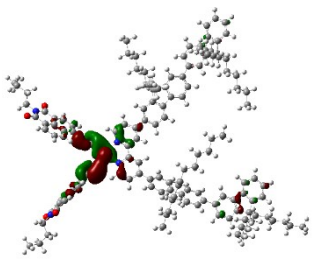
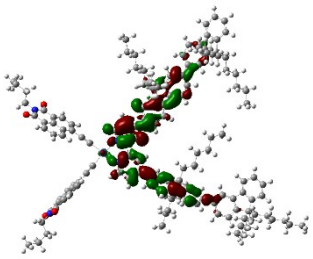
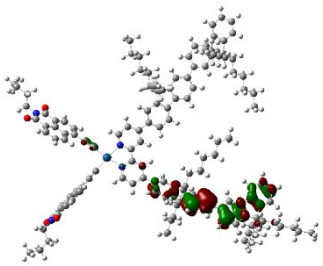
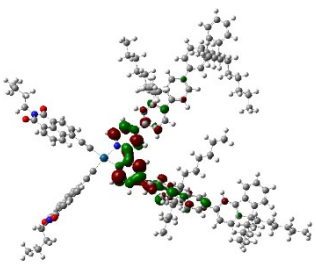
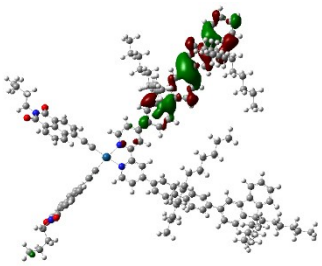
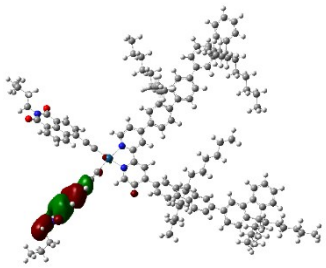
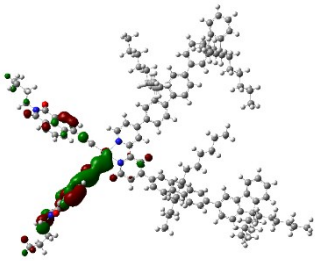
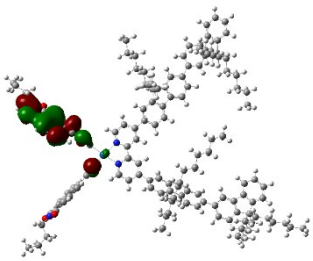
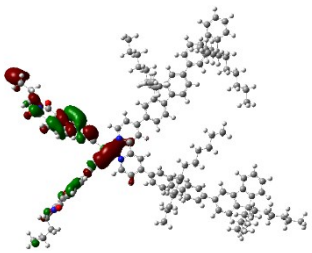
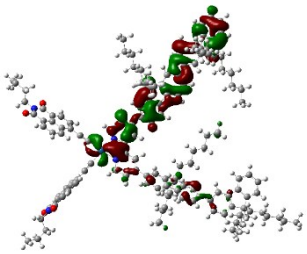
HOMO-4		LUMO+1	
HOMO-3		LUMO+2	
HOMO-2		LUMO+3	
HOMO-1		LUMO+4	
HOMO		LUMO+5	

Table S8 Excitation Energies (eV), Wavelengths (nm), Oscillator Strengths, Main Configurations, the Associated Configuration Coeffcients and Assignments of Complexes **Pt-4**

States	E/eV	λ/nm	f	Main configulations	assignment
S1	2.0075	617.60	0.0435	HOMO ---> LUMO 94.6%	^{1}MLCT/^{1}LLCT
S2	2.1610	573.75	0.0964	HOMO-1 ---> LUMO 95.2%	^{1}MLCT/^{1}LLCT
S3	2.4125	513.93	0.1160	HOMO-4 ---> LUMO 75.4%	^{1}MLCT/^{1}LLCT
S4	2.5547	485.31	0.3578	HOMO-2 ---> LUMO 63.7% HOMO-5 ---> LUMO 10.6%	^{1}MLCT/^{1}LLCT
S5	2.5636	483.63	0.0348	HOMO-7 ---> LUMO 89.6%	^{1}MLCT/^{1}LLCT

T1	1.9310	642.06	0.0000	HOMO ---> LUMO 82.4%	^{3}MLCT/^{3}LLCT
T2	2.0417	607.27	0.0000	HOMO-1 ---> LUMO 29.6% HOMO-1 ---> LUMO+3 45.3%	^{3}MLCT/^{3}LLCT
T3	2.0850	594.64	0.0000	HOMO ---> LUMO+4 45.4% HOMO-1 ---> LUMO+3 17.2%	^{3}MLCT/^{3}LLCT
T4	2.1136	586.61	0.0000	HOMO-1 ---> LUMO 45.7% HOMO ---> LUMO+4 14.9%	^{3}MLCT/^{3}LLCT
T5	2.2402	553.44	0.0000	HOMO-2 ---> LUMO 32.1% HOMO-4 ---> LUMO 37.6%	^{3}MLCT/^{3}LLCT