Electronic Supplementary Information for:

Tuning the Emissive Triplet Excited States of Platinum(II) Schiff base Complexes with Pyrene and Application for Enhanced Triplet-triplet Energy Transfer: Luminescent Oxygen Sensing and Triplet-triplet-annihilation Based Upconversions

Wanhua Wu,[a] Jifu Sun, Shaomin Ji,[a] Wenting Wu,[a] Jianzhang Zhao[a]* and Huimin Guo,[a]*

State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, 2 Ling-gong Road, Dalian 116024, P. R. China.

E-mail: zhaojzh@dlut.edu.cn (J. Zhao) guohm@dlut.edu.cn (H. Guo)

Fax: +86 (0) 411 8498 6236; Tel: +86 (0) 411 8498 6236;

Group homepage: http://finechem.dlut.edu.cn/zhaojianzhang/guohm/index.htm

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1.0 General

All the chemicals are analytical pure and were used as received. Solvents were dried and distilled for synthesis. NMR spectra were recorded on a 400 MHz Varian Unity Inova NMR spectrophotometer. Carbon NMR spectra were recorded on the same instrument (at 100 MHz) with total proton decoupling. Mass spectra were recorded with Q-TOF Micro MS spectrometer. UV-Vis absorption spectra were measured with a HP8453 UV-visible spectrophotometer. Fluorescence spectra were recorded on JASCO FP-6500 or a Sanco 970 CRT spectrofluorometer (modified for the upconversion experiments). Fluorescence quantum yields were measured with $Ru(bpy)_2(Phen)$ as the reference (Φ= 6.0 %, in CH_3CN, under deaerated condition). Lifetimes were measured on a Horiba Jobin Yvon Fluoro Max-4 (TCSPC) instrument and Edinburgh analytical instruments (LP900, Edinburgh Instruments, U.K.). Flash chromatography was carried out using silica gel, particle size 0.04-0.063 mm.

Typical film preparation was undertaken by dissolving 10.0 mg of IMPEK-C polymer in 0.5 mL $CHCl_3$ to which was added 0.4 mL of **Pt-3** complex solution in CH_2Cl_2 (1×10^{-3} M). After thorough mixing, about 0.25 mL of the solution was applied to a quartz glass disk (diameter: 1.6 cm), The solvent was evaporated at r.t. and a transparent film was obtained. The thickness of the film of complex **Pt-3** was estimated as 12.7 μm, by the weight of the film (2.9 mg) and the density of the polymer (1.14 g cm^{-3}). Similarly the thickness of the film of **Pt-1, Pt-2, Pt-4, Pt-5** and **Pt-6** were estimated as 11.3 μm, 12.1μm, 10.3μm, 11.5μm and 10.5 μm, respectively.

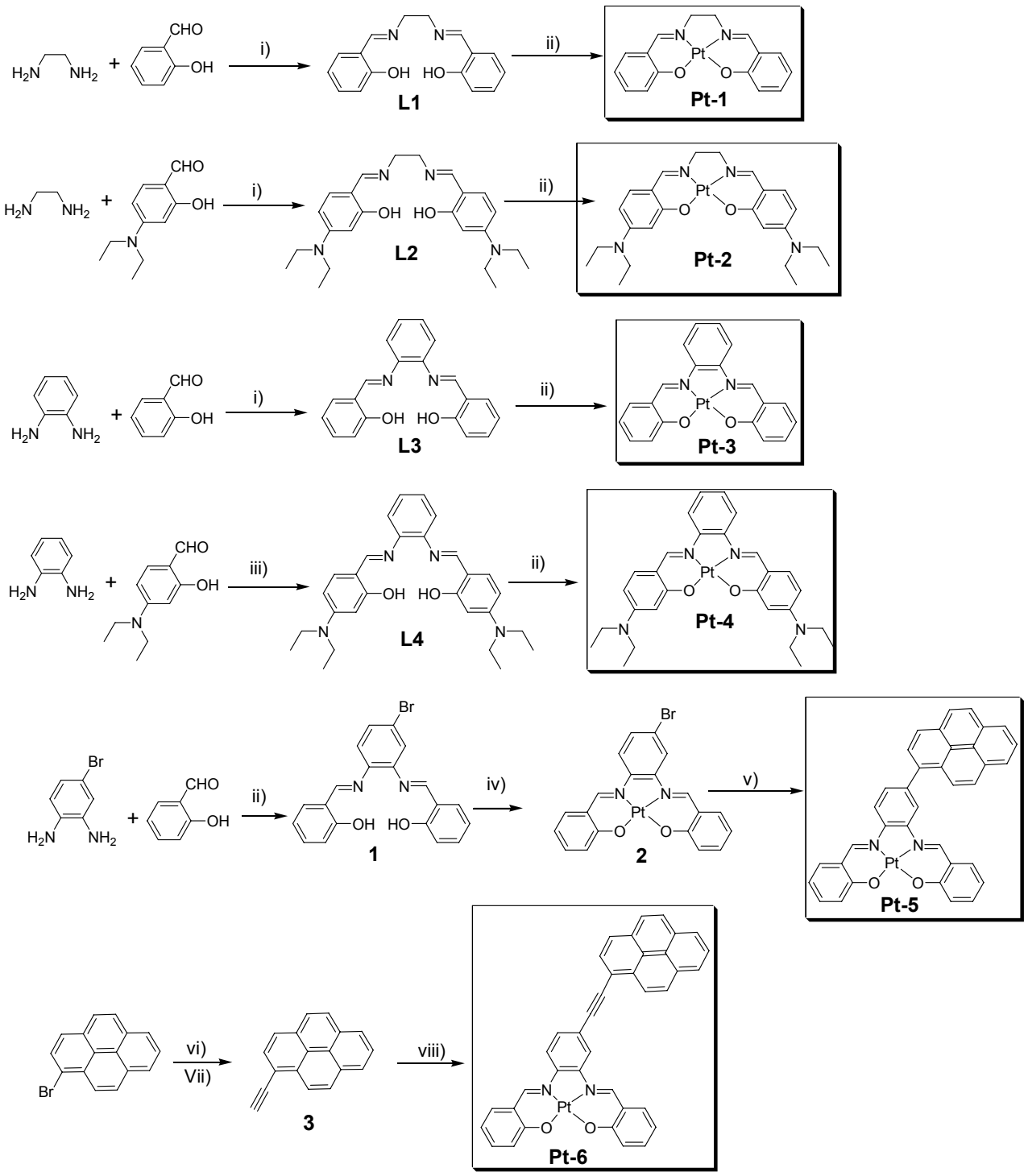
All these calculations were performed with Gaussian 09W.[1] The structures of the complexes were optimized using density functional theory (DFT)[2] with B3LYP functional and 3-21G/LanL2DZ basis set. The spin density surfaces of the complexes were carried out with the optimized triplet state geometry. The 3-21G basis set was employed for C, H, N, O and the LanL2DZ basis set was used for Pt^{II}. There are no imaginary frequencies for all optimized structures.

Reference:

1. Hohenberg P, Kohn W. *Phys. Rev.* 1964; **136**: B864.

2. M. J. Frisch, G. W. Trucks, H. B. Schlegel, et al. Gaussian 09 Revision A.1, Gaussian Inc., Wallingford CT, 2009.

2.0 Experimentation section



i) Ethanol, r.t.; ii) NaOAc, K_2PtCl_4, DMSO; iii) Ethanol, reflux, pH=4; iv) K_2CO_3, K_2PtCl_4, DMSO; v) 1-Pyrenylboronic acid, $Pd(PPh_3)_4$, K_2CO_3, vi) Trimethylsilylacetylene, $Pd(PPh_3)_4$, CuI, TEA, reflux, 8 h; vii) K_2CO_3, MeOH; viii) **2**, $Pd(PPh_3)_4$, CuI, TEA , DMF.

N,N'-bis(salicylidene) ethylenediamine (L1)

Salicylaldehyde (1.0 g, 8.2 mmol) was dissolved in EtOH (30 mL), ethylenediamine (246.0 mg, 4.1 mmol) was added, the mixture was stirred at room temperature until the precipitate did not increase any more (about 1h). The yellow solid was collected by filtration and crystallized from EtOH to give orange needle crystals (1.6 g, 3.47 mmol) in 84.6% yield. ^{1}H NMR (400 MHz, CDCl3): 13.22 (s, 2H), 8.35 (s, 2H), 7.29 (t, 2H, J = 8.4Hz), 7.23 (d, 2H, *J* = 7.6Hz), 6.95 (d, 2H, *J* = 8.2Hz), 6.85 (t, 2H, *J* = 7.5Hz), 3.93(s, 4H).

N,N'-bis(4- *N,N'*-diethylaminosalicylidene) ethylenediamine (L2)

4- *N, N'*-diethylsalicylidene (1.0 g, 5.2 mmol) was dissolved in EtOH (30 mL), ethylenediamine (155.4 mg, 2.6 mmol) was added, the mixture was stirred at room temperature over night, after removal of the solvent, the residue was crystallized from EtOH to give orange crystals (1.3 g, 2.2 mmol) in 82.9% yield. ^{1}H NMR (400 MHz, CDCl3): 13.65 (s, 2H), 7.97 (s, 2H), 6.92 (d, 2H, *J* = 8.7Hz), 6.08 (d, 2H, *J* = 8.7Hz), 6.04 (s, 2H), 3.69 (s, 4H), 3.32 – 3.27 (m, 8H), 1.11(t, 12H, *J* = 7.1Hz).

N,N'-bis(salicylidene) phenylenediamine (L3)

Compound **3** was prepared by a similar procedure as that used for **1**, but with phenylenediamine (442.8 mg, 4.1 mmol). ^{1}H NMR (400 MHz, CDCl3): 13.06 (s, 2H), 8.63 (s, 2H), 7.38 – 7.33 (m, 6H), 7.25 – 7.22 (m, 2H), 7.06 (d, 2H, *J* = 7.1Hz), 6.92 (t, 2H, *J* = 7.1Hz).

N,N'-bis(4- *N,N'*-diethylaminosalicylidene) phenylenediamine (L4)

4-(*N,N'*-diethylamino)salicylaldehyde(1.0 g, 5.2 mmol) and o-phenylenediamine (280.8 mg, 2.6 mmol) were dissolved in 80 mL of chloroform. The pH of the mixed reaction was adjusted to 4–5 with acetic acid, and then the mixture was stirred at 60 ^{o} C for about 3 days. After the reaction was complete, the solvent was removed from the reaction mixture in vacuo. The crude product was purified by column chromatography using dichloromethane as eluent and evaporation of solvent from the solution gave a yellow solid (900 mg, 1.96 mmol), yield: 75.4%. ^{1}H NMR (400 MHz, CDCl3): 8.38 (s, 2H), 7.21 – 7.17 (m, 4H), 7.13 (d, 2H, *J* = 8.5 Hz), 6.22 (s, 3H), 6.20 (d, 1H, *J* = 2.5Hz), 3.40 – 3.35 (m, 8H), 1.19 (t, 12H, *J* = 7.3Hz).

N,N'-bis(salicylidene)-4-bromo-phenylenediamine (1)

Compound **1** was prepared by a similar procedure as that used for **L1**, but with 4-bromo-phenylenediamine (762.6 mg, 4.1 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): 12.85 (s, 1H), 12.74 (s, 1H), 8.61 (s, 2H), 7.46 – 7.44 (m, 1H), 7.40 – 7.37 (m, 5H), 7.12 (d, 1H, *J* = 7.1Hz), 7.05 (d, 2H, *J* = 7.1Hz), 6.95 – 6.90 (m, 2H).

Compound 2

K_2PtCl_4 (523.8 mg, 1.27 mmol), **1** (500 mg, 1.27 mmol) and K_2CO_3 (525.8 mg, 3.81 mmol) were dissolved in degassed DMSO (10 mL), the flask was vacuumed and back-filled with argon for several times, then the mixture was stirred at 75 ^{o}C for 12 h. The red precipitation was collected and further purified by column chromatography using dichloromethane as eluent, after removal of the solvent the red solid (450.5 mg, 0.77 mmol) was collected in 60.6% yield. ^{1}H NMR (400 MHz, $CDCl_3$): 8.68 (s, 1H), 8.66 (s, 1H), 7.98 (s, 1H), 7.77 (d, 1H, *J* = 8.9 Hz), 7.48 – 7.39 (m, 4H), 7.32 (d, 1H, *J* = 8.4 Hz), 7.19 (d, 2H, *J* = 8.5 Hz), 6.68 – 6.63 (m, 2H).

Complex Pt-3

Complex **Pt-3** was prepared by modification of the literature procedures. Sodium acetate (52.5 mg, 0.64 mmol) was suspended in a solution of L**3** (100 mg, 0.32 mmol) in MeCN (15 mL). the mixture was stirred under r.t. for about 5 min, then K_2PtCl_4 (132.1 mg, 0.32 mmol) and DMSO (2 mL) was added, the flask was vacuumed and back-filled with argon for several times, and heated to 70^{o}C, the resulting mixture was stirred at the same temperature for 15 h. Upon cooling, the majority of the solvent was removed from the reaction mixture in vacuo then diethyl ether (50 mL) was added to the mixture to afford a dark red precipitate. The solid product was filtered and washed with Et_2O (5—10 mL). the product as red solid. Yield: 80mg(0.16 mmol, 50%).^{1}H NMR (400 MHz, $CDCl_3$): 8.82 (s, 2H), 7.96 – 7.94 (m, 2H), 7.58 – 7.52 (m, 4H), 7.40 (d, 2H, *J* = 8.5 Hz), 7.33 – 7.30 (m, 2H), 6.75 (t, 2H, *J* = 7.5 Hz). MALDI-MS: calcd ($[C_{20}H_{14}N_2O_2Pt]^+$), m/z = 509.0703, found, m/z = 509.0690.

Complex Pt-1

Complex **Pt-1** was prepared by a similar procedure as that used for **Pt-3.** yield: 58%. ^{1}H NMR (400 MHz, $CDCl_3$): 7.96 (s, 2H), 7.46 (t, 3H, *J* = 8.1 Hz), 7.21 (t, 3H, *J* = 8.4 Hz), 6.59 (t, 2H, *J* = 7.5 Hz), 3.82 (s, 4H). MALDI-MS: calcd ($[C_{16}H_{14}N_2O_2Pt]^+$), m/z = 461.0703, found, m/z = 461.0747.

Complex Pt-2

Complex **Pt-2** was prepared by a similar procedure as that used for **Pt-3.** yield: 10%. ^{1}H NMR (400 MHz, $CDCl_3$): 7.70 (s, 2H), 7.06 (d, 2H, *J* = 8.8 Hz), 6.45 (s, 2H), 6.10 (d, 2H, *J* = 8.9 Hz), 3.63 (s, 4H), 3.36 – 3.31 (m, 8H), 1.18 (t, 12H, *J* = 7.0 Hz). MALDI-MS: calcd ($[C_{24}H_{32}N_4O_2Pt]^+$), m/z = 603.2173, found, m/z = 603.2120.

Complex Pt-4

Complex **Pt-4** was prepared by a similar procedure as that used for **Pt-3.** yield: 70%. 1H NMR (400 MHz, CDCl3): 8.41 (s, 2H), 7.79 – 7.77 (m, 2H), 7.29 (d, 2H, *J* = 9.2Hz), 7.13 – 7.11 (m, 2H), 6.56 (s, 2H), 6.27 (d, 2H, J = 9.0Hz), 3.43 – 3.37 (m, 8H), 1.23 (t, 12H, *J* = 7.0Hz). MALDI-MS: calcd ($[C_{28}H_{32}N_4O_2Pt]^+$), m/z = 651.2173, found, m/z = 651.2231.

1-Ethynylpyrene (3)

Under nitrogen atmosphere, 1-Bromopyrene (500.0 mg, 1.79 mmol), $Pd(PPh_3)_2Cl_2$ (8.5 mg, 0.01 mmol), PPh_3 (21.2 mg, 0.08 mmol), and CuI (8.5 mg, 0.05 mmol) were dissolved in TEA (20 ml). the flask was vacuumed and back-filled with argon for several times, The mixture was stirred until a clear yellow solution obtained (ca. 15 min). Then ethynyltrimethylsilane(350.8 mg, 3.58 mmol) was added via syringe. The solution was refluxed for 8 h. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel, dichloromethane/petroleum ether = 1:1, V/V). The above trimethylsilane protected intermediate was dissolved in methanol (30 mL), K_2CO_3 (741.1 mg, 5.37 mmol) was added and the mixture was stirred at r.t. for 3 h. The solvent was removed under reduced pressure. Water was added and the mixture was extracted with diethyl ether. The organic layer was dried over anhydrous Na_2SO_4. After removal the solvent, compound **3** was obtained as light yellow solid, 350.2 mg (1.55mmol), yield: 86.6 %. ^{1}H NMR (400 MHz, CDCl3), 7.36 (d, 2H, J = 8.0 Hz), 6.61 (d, 2H, J = 8.0 Hz), 2.97 (s, 7H).

3.0 Structure characterization data

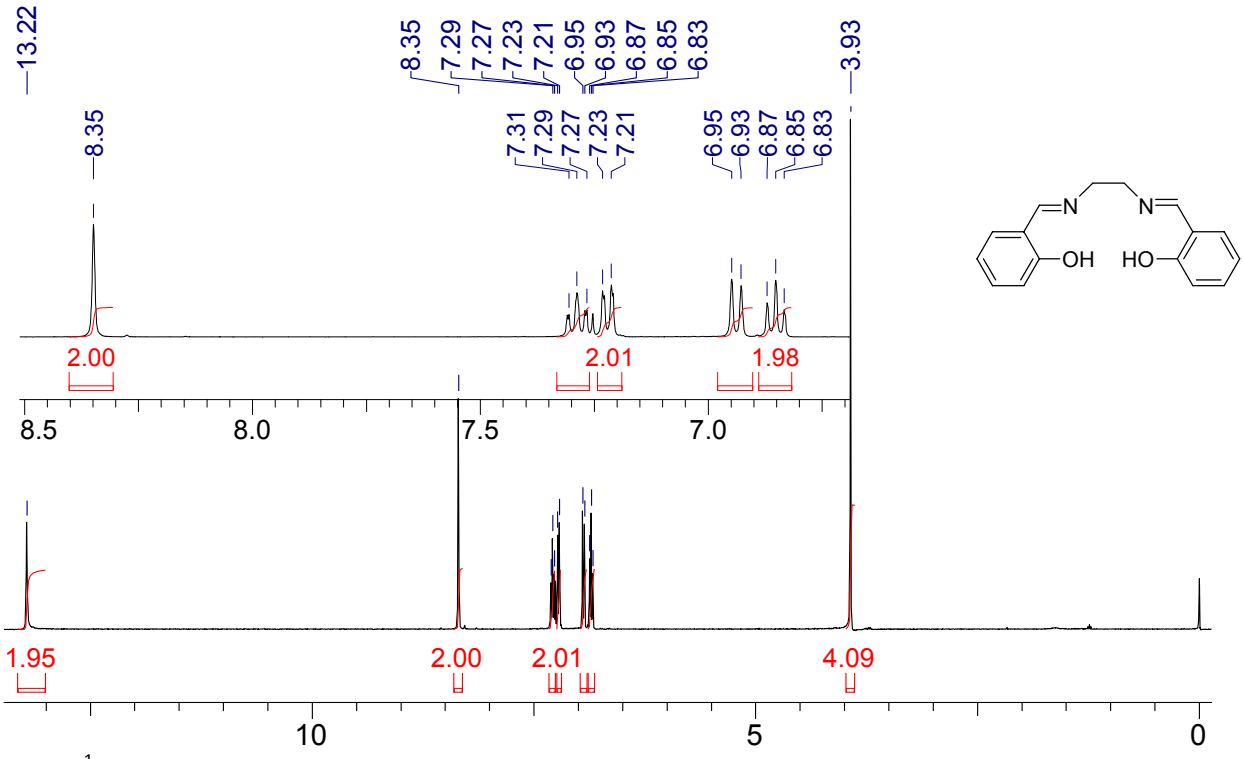


Fig. S1 ^{1}H NMR of **L1** in $CDCl_3$ (400 MHz) at room temperature.

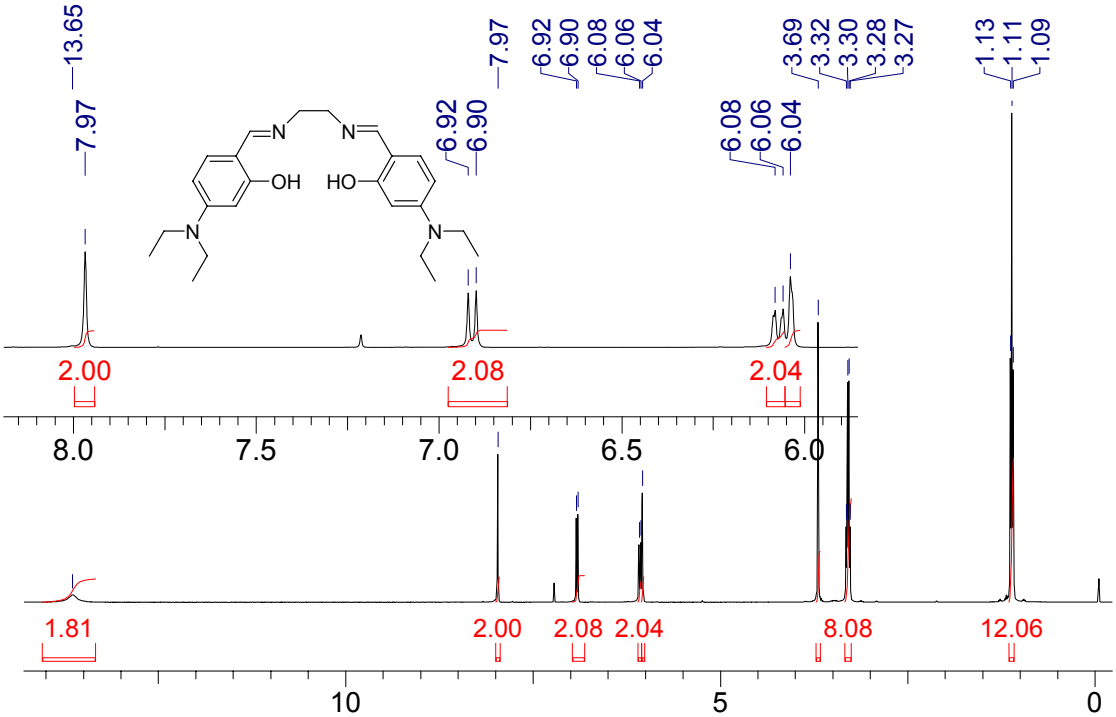


Fig. S2 ^{1}H NMR of **L2** in $CDCl_3$ (400 MHz) at room temperature.

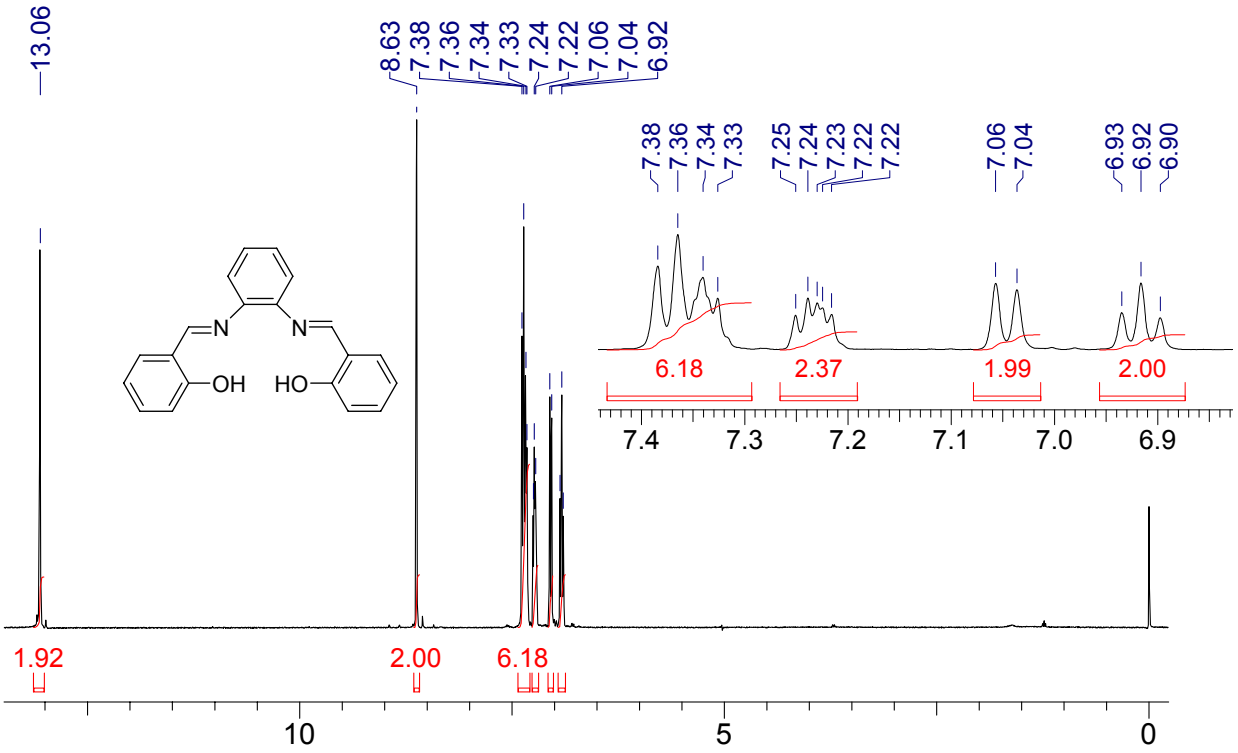


Fig. S3 ^{1}H NMR of **L3** in $CDCl_3$ (400 MHz) at room temperature.

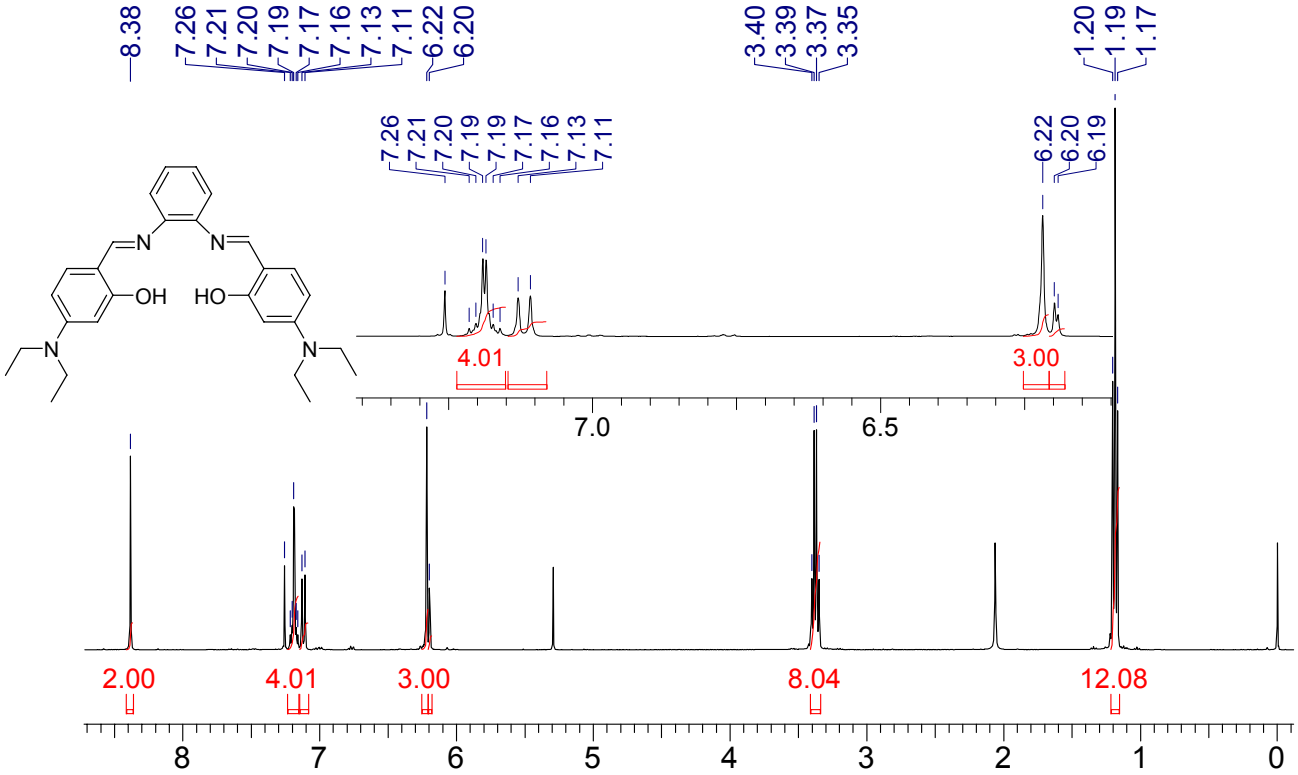


Fig. S4 ^{1}H NMR of **L4** in $CDCl_3$ (400 MHz) at room temperature.

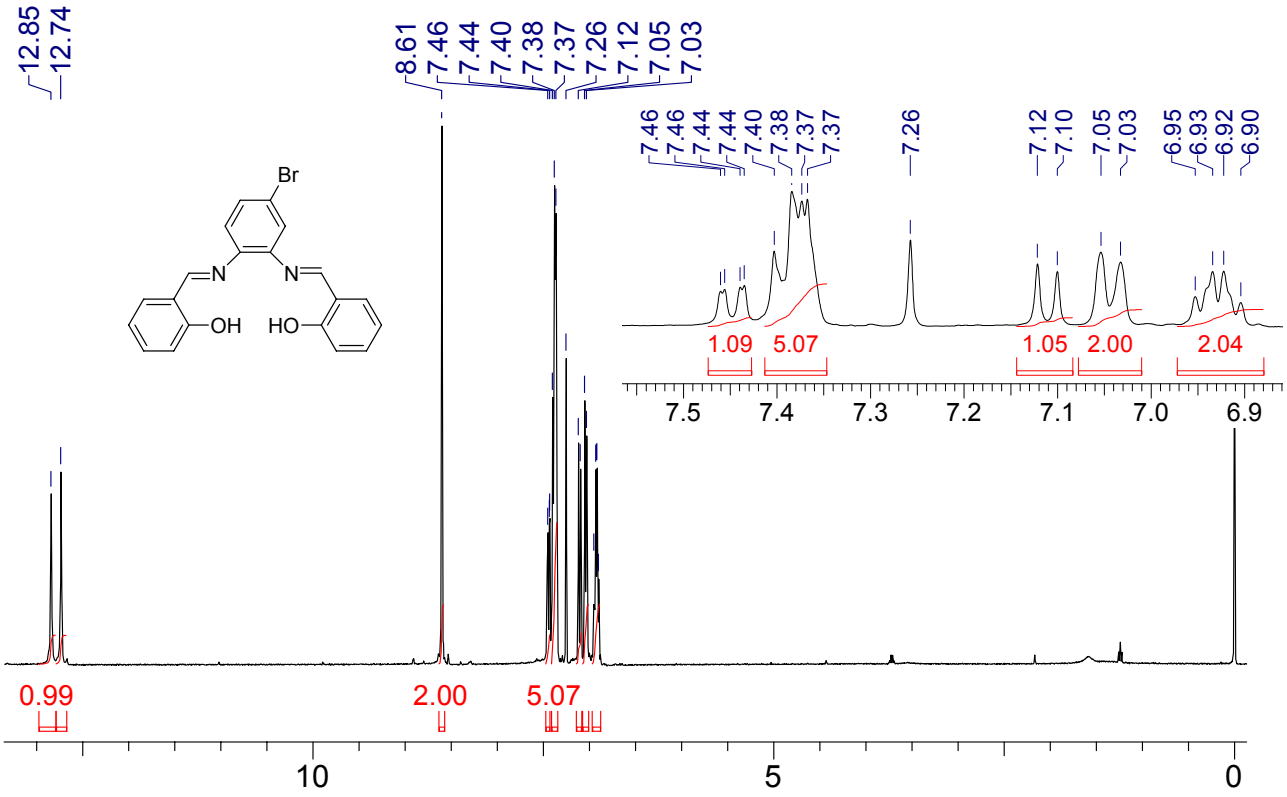


Fig. S5 ^{1}H NMR of **5** in $CDCl_3$ (400 MHz) at room temperature.

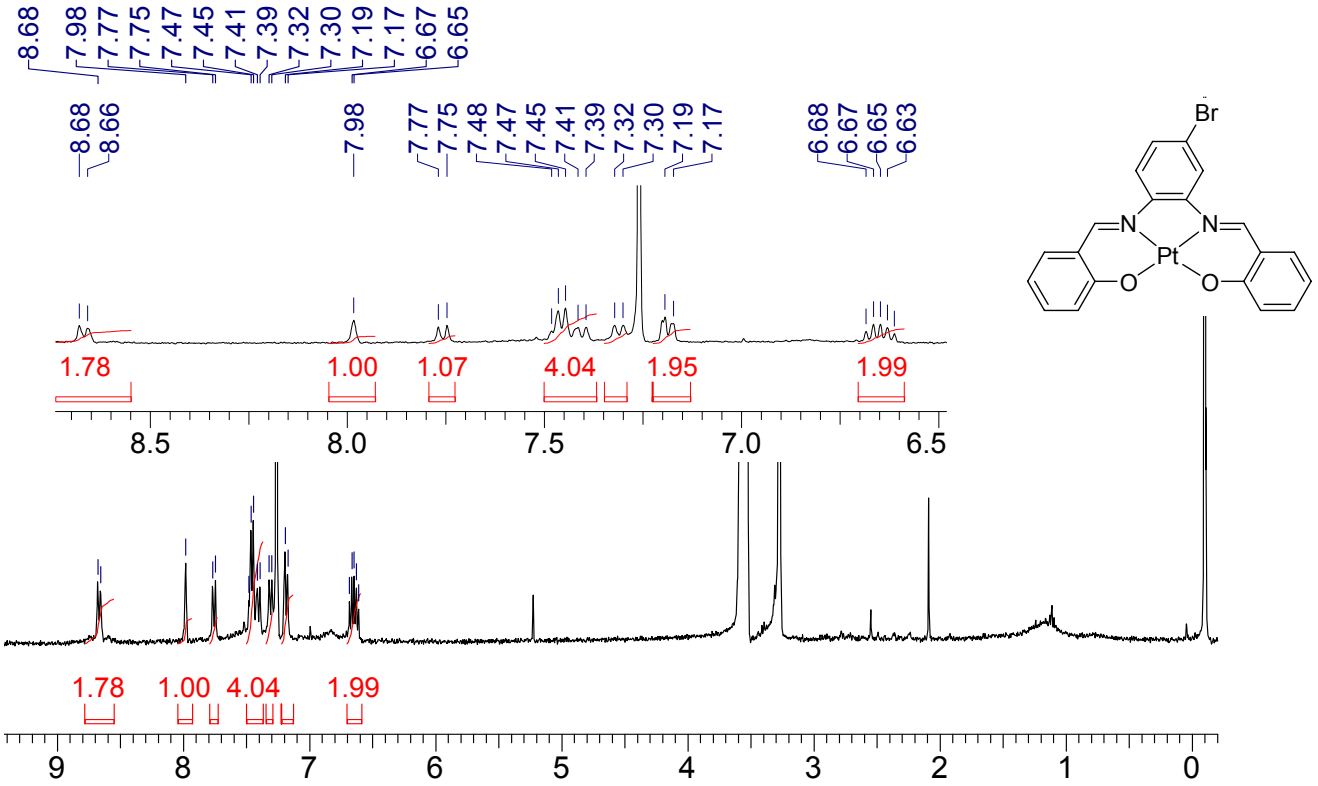


Fig. S6 ^{1}H NMR of **6** in $CDCl_3$ (400 MHz) at room temperature.

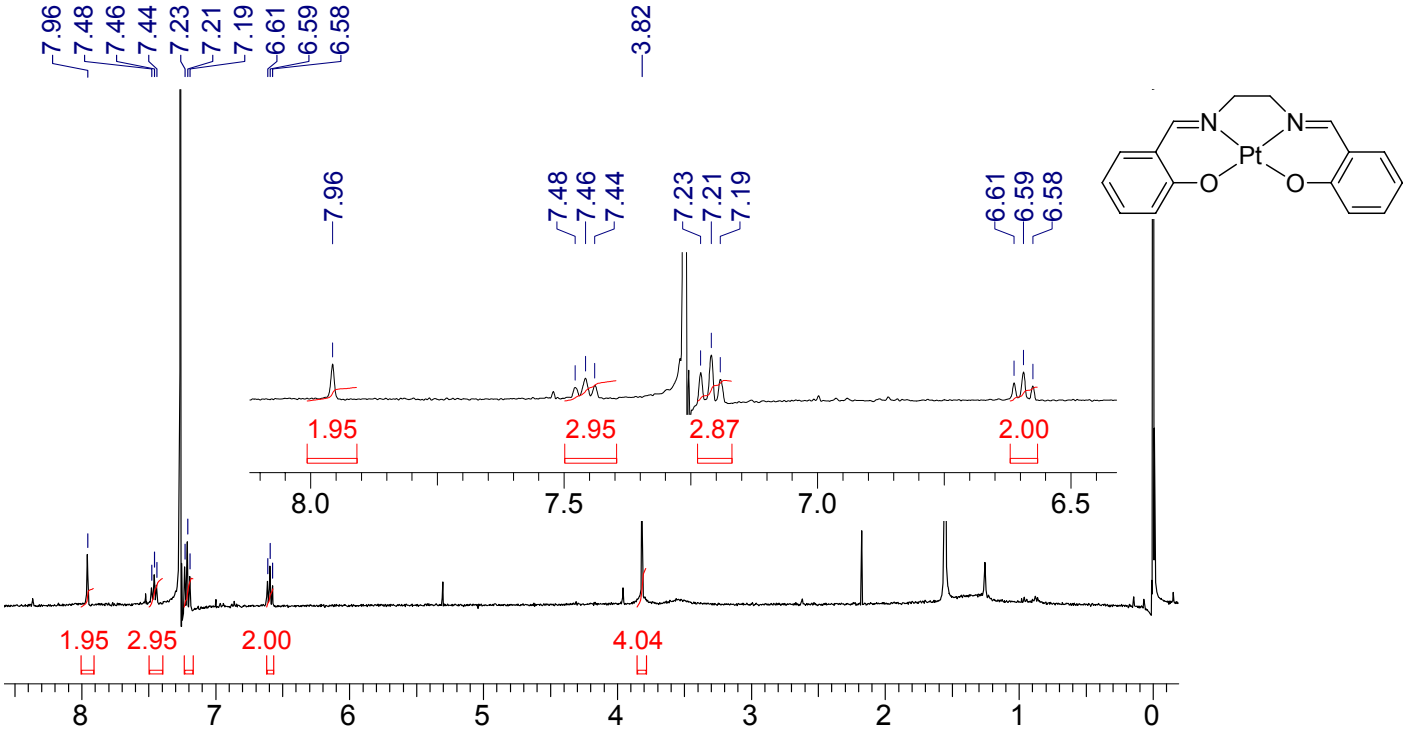


Fig. S7 ^{1}H NMR of **Pt-1** in $CDCl_3$ (400 MHz) at room temperature.

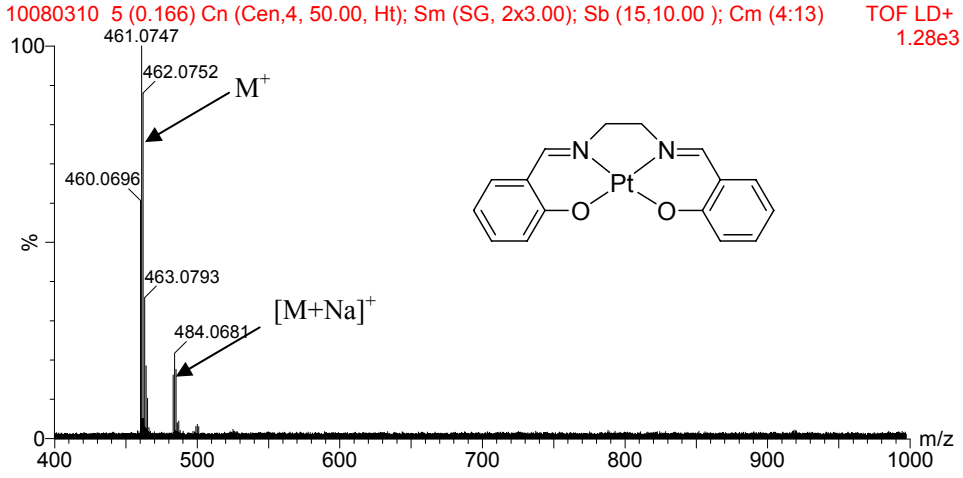


Fig. S8 MALDI-MS of **Pt-1**.

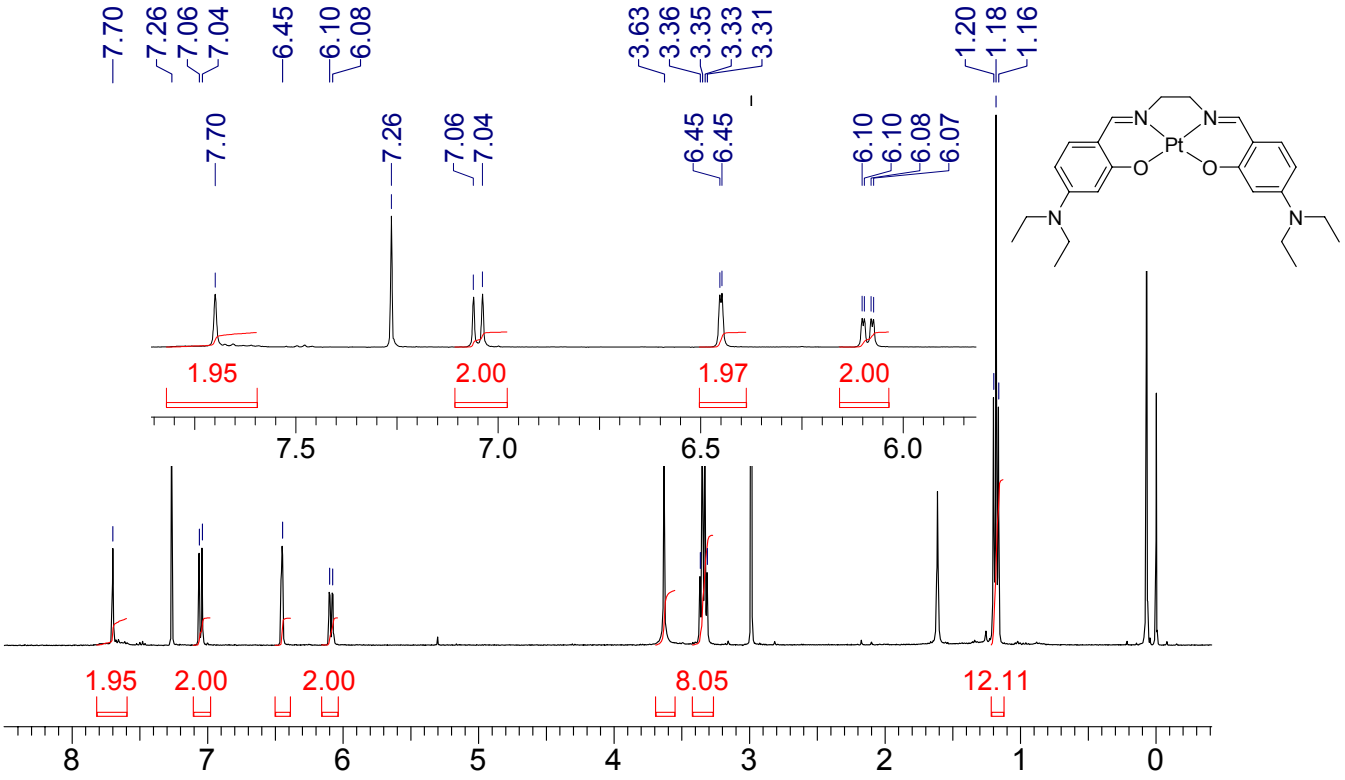


Fig. S9 ^{1}H NMR of **Pt-2** in $CDCl_3$ (400 MHz) at room temperature.

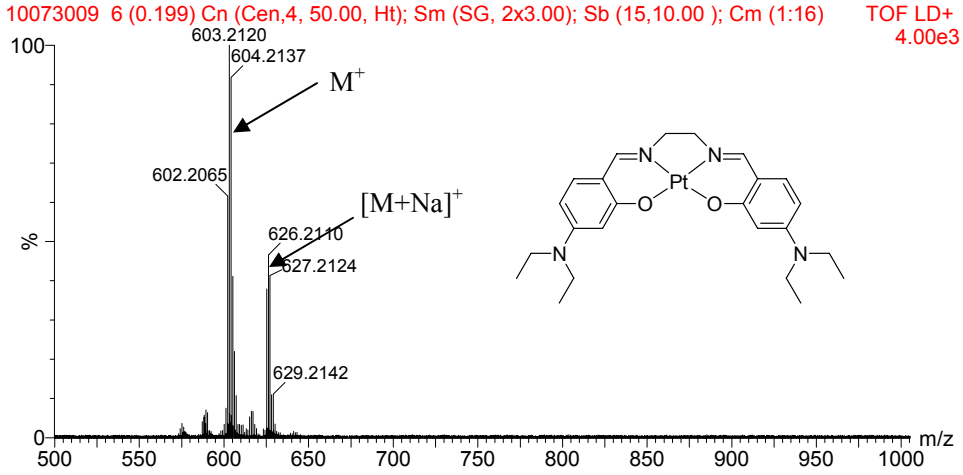


Fig. S10 MALDI-MS of **Pt-2.**

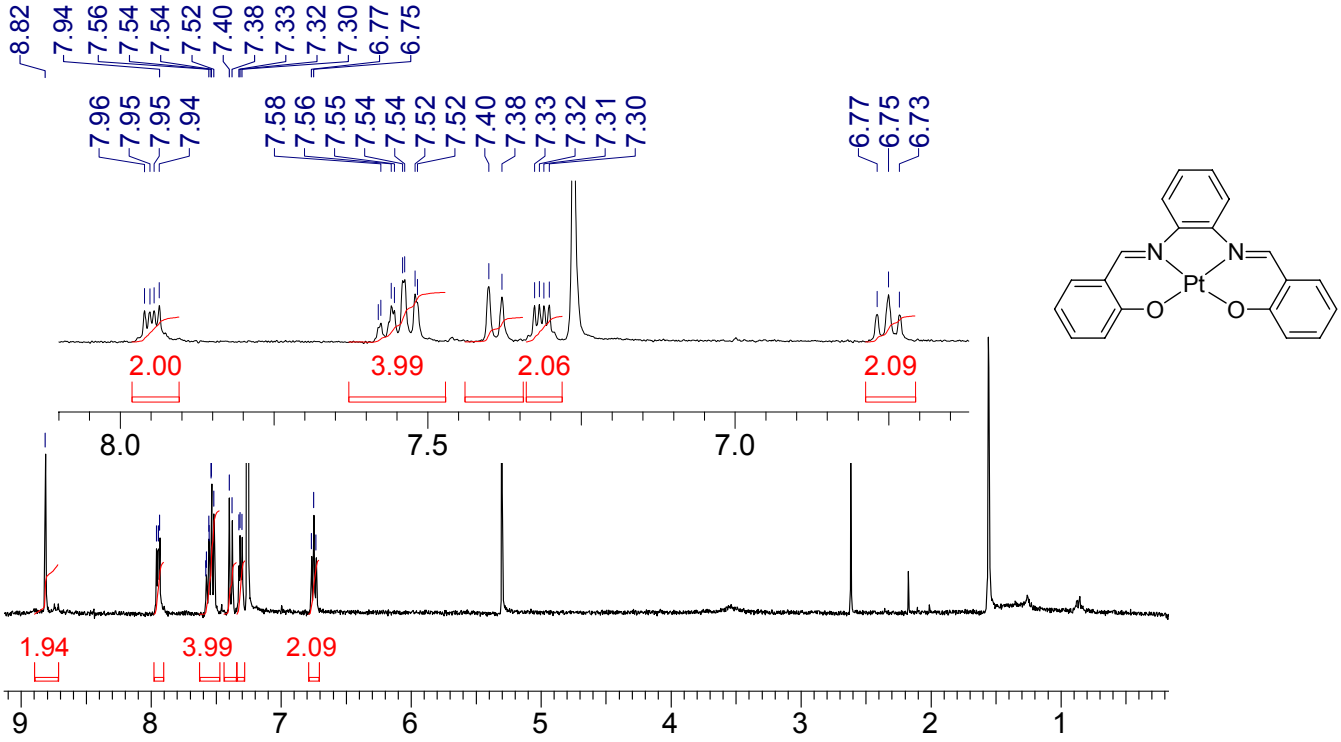


Fig. S11 ^{1}H NMR of **Pt-3** in $CDCl_3$ (400 MHz) at room temperature.

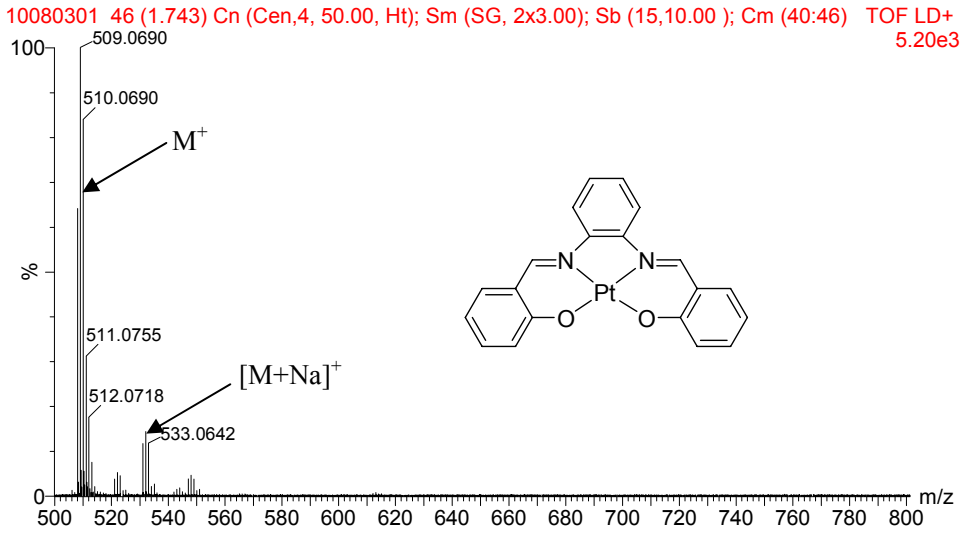


Fig. S12 MALDI-MS of **Pt-3.**

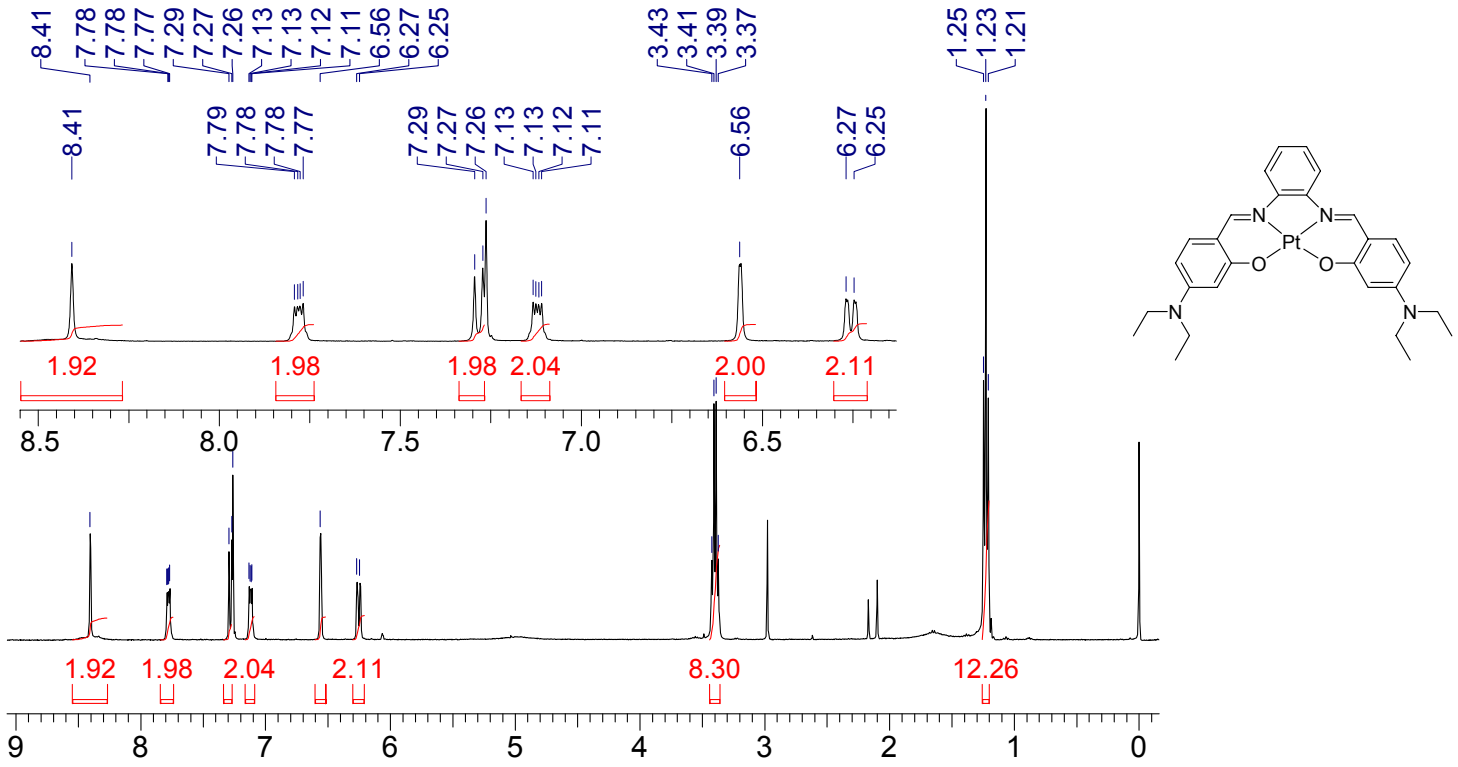


Fig. S13 ^{1}H NMR of **Pt-4** in $CDCl_3$ (400 MHz) at room temperature.

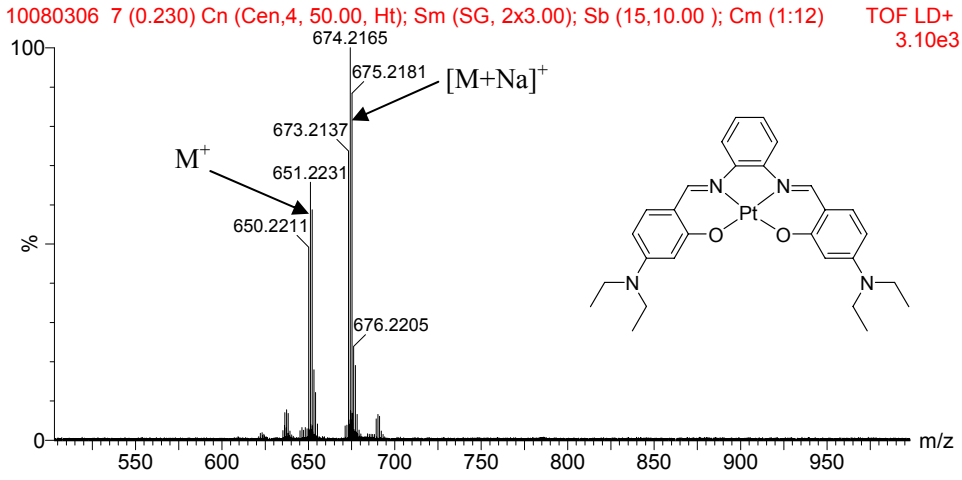


Fig. S14 MALDI-MS of **Pt-4.**

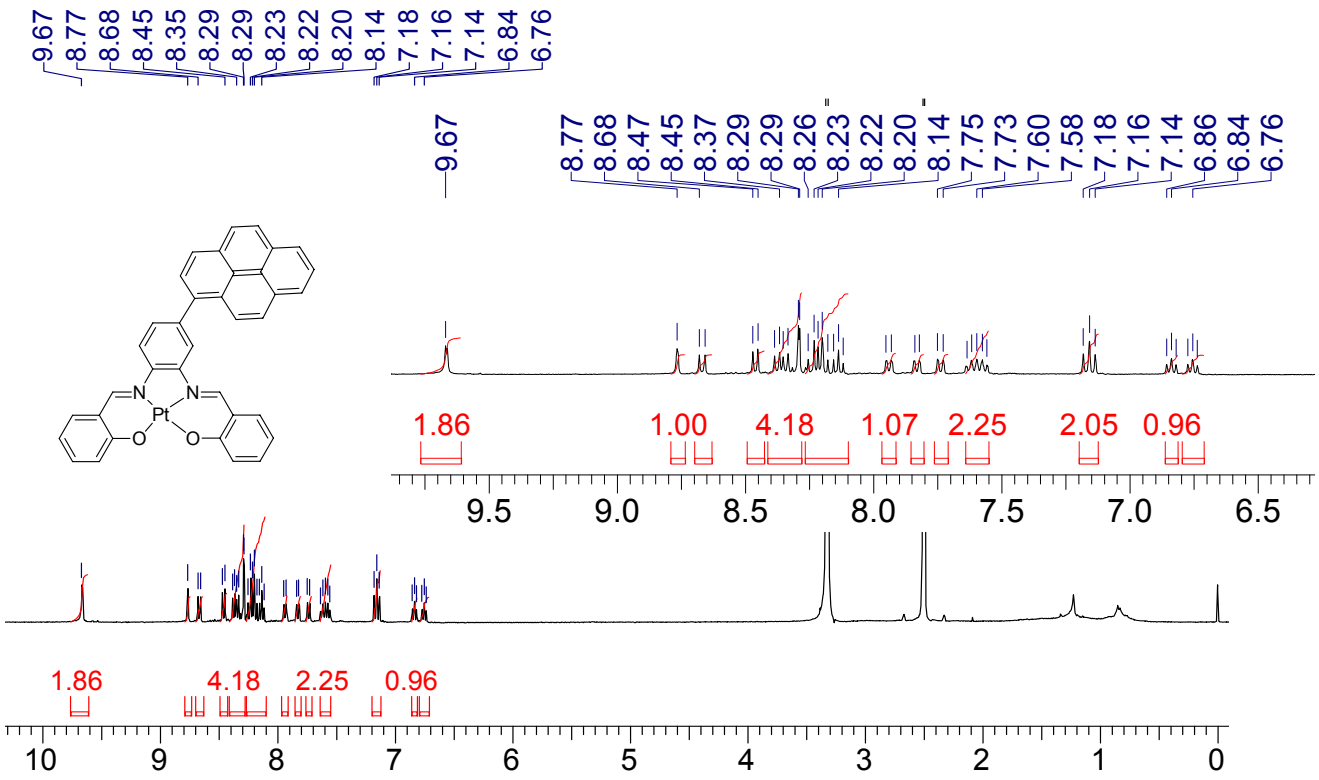


Fig. S15 ^{1}H NMR of **Pt-5** in d_6-DMSO (400 MHz) at room temperature.

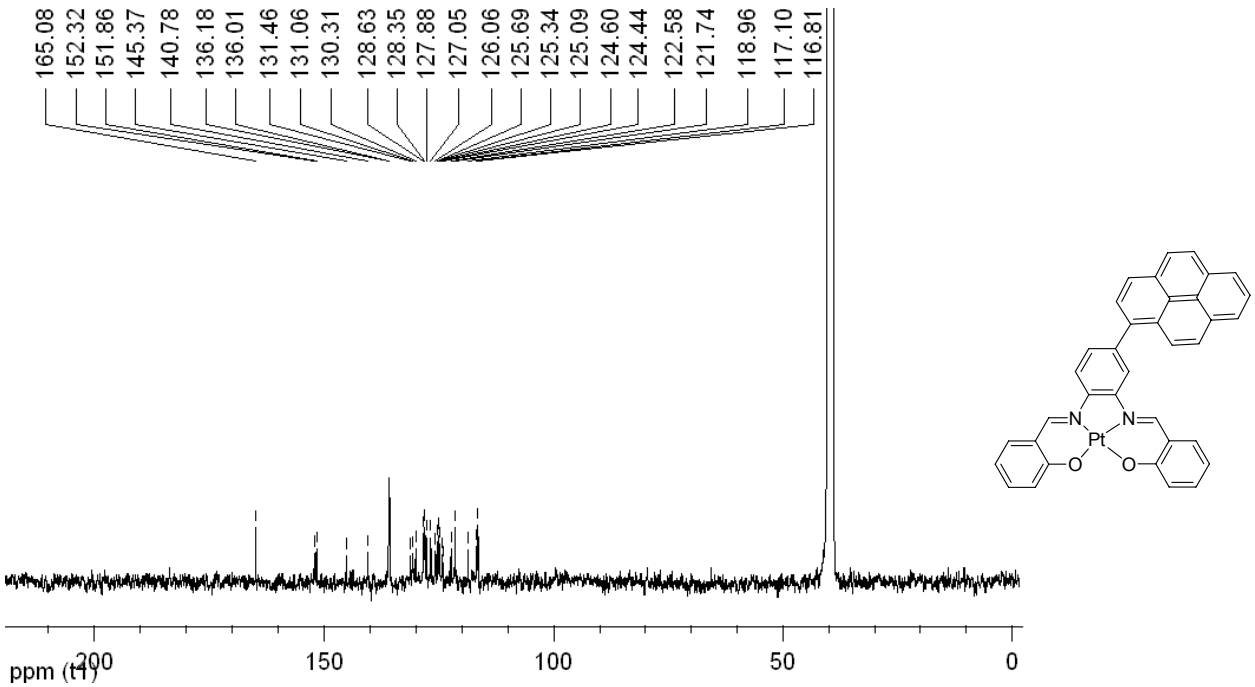


Fig. S16 ^{13}C NMR of **Pt-5** in d^6-DMSO (100 MHz) at room temperature.

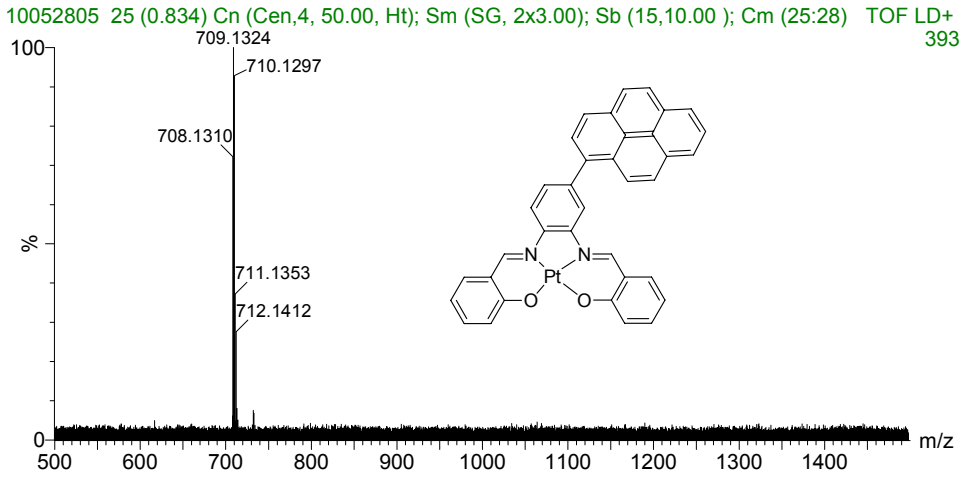


Fig. S17 MALDI-MS of **Pt-5.**

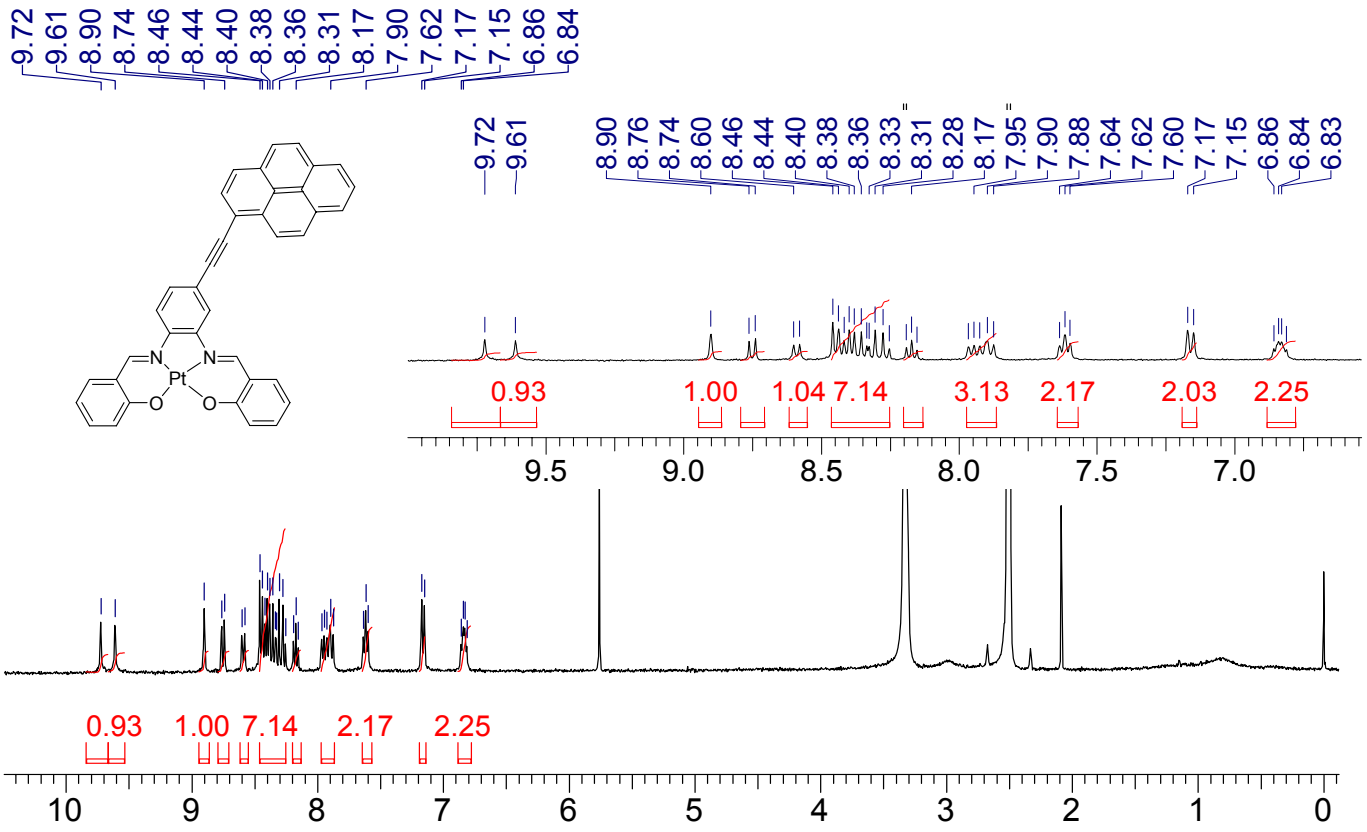


Fig. S18 ^{13}C NMR of **Pt-6** in d^{6}-DMSO (100 MHz) at room temperature.

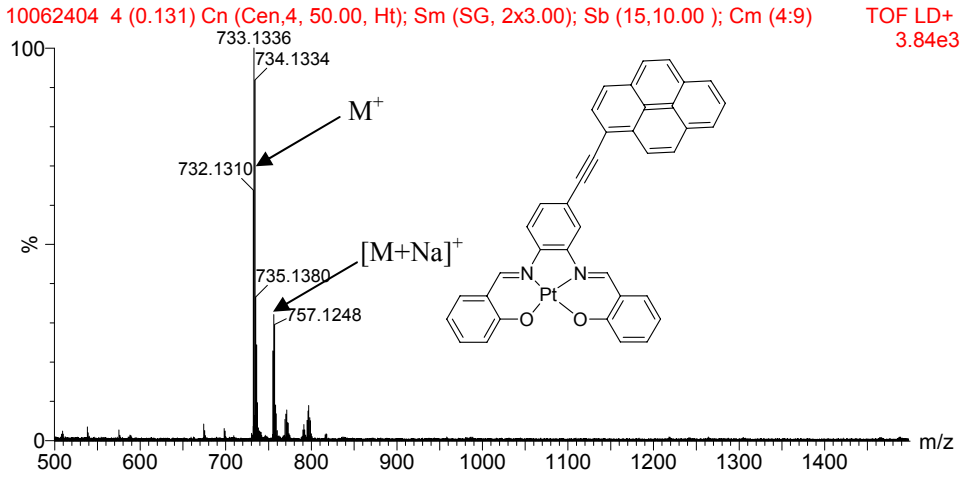


Fig. S19 MALDI-MS of **Pt-6.**

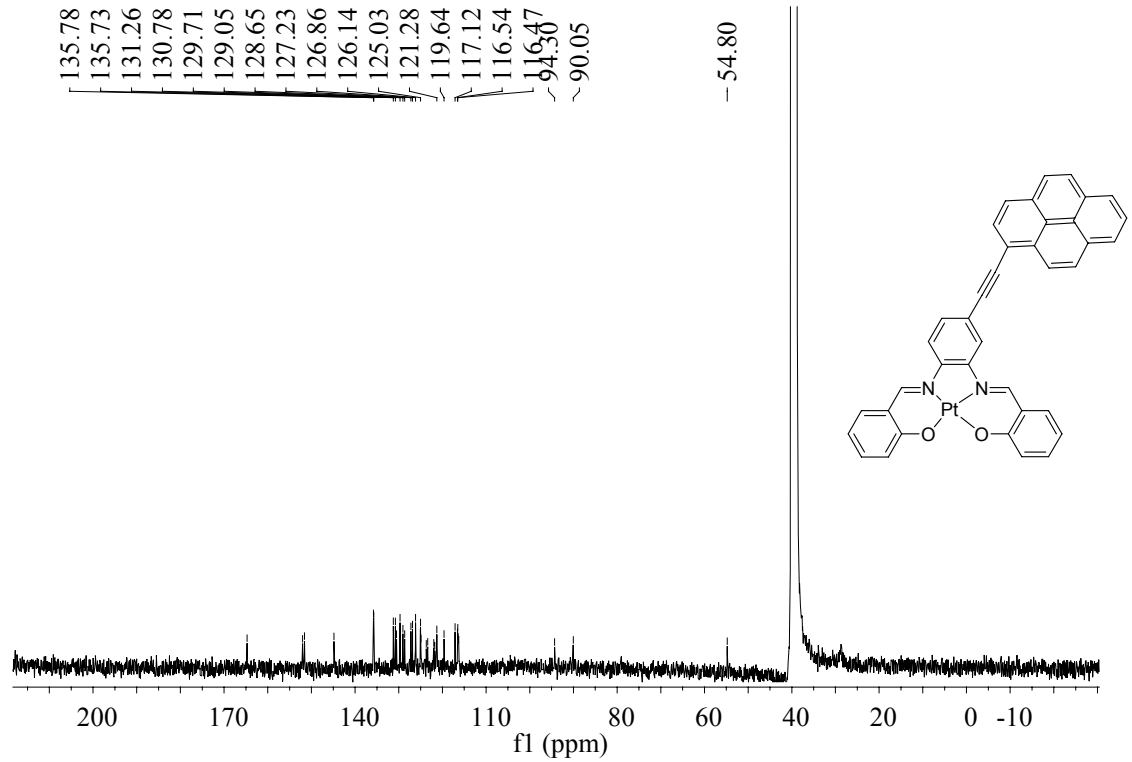


Fig. S20 ^{13}C NMR of **Pt-6** in d_6-DMSO (100 MHz) at room temperature.

4.0 Photophysical properties

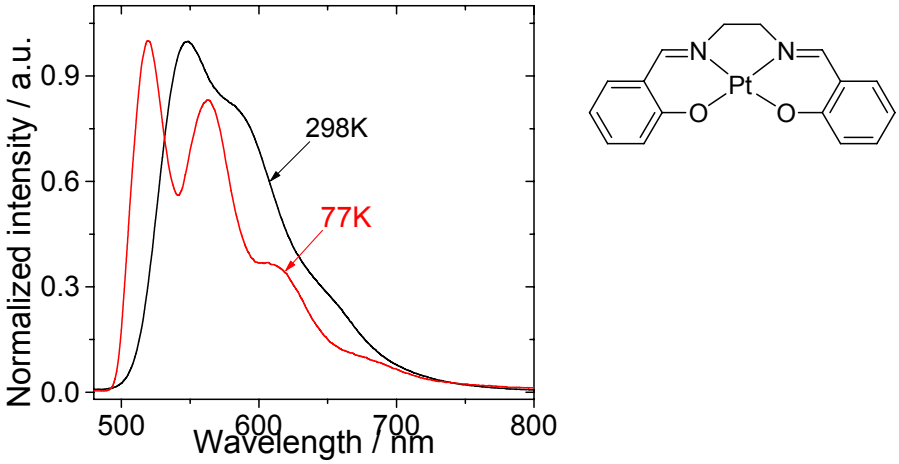


Fig. S21 Emission spectra of **Pt-1** in ethanol-methanol (4:1, V/V) glass at 77K and solution at 298K. Excitation wavelength at 420 nm.

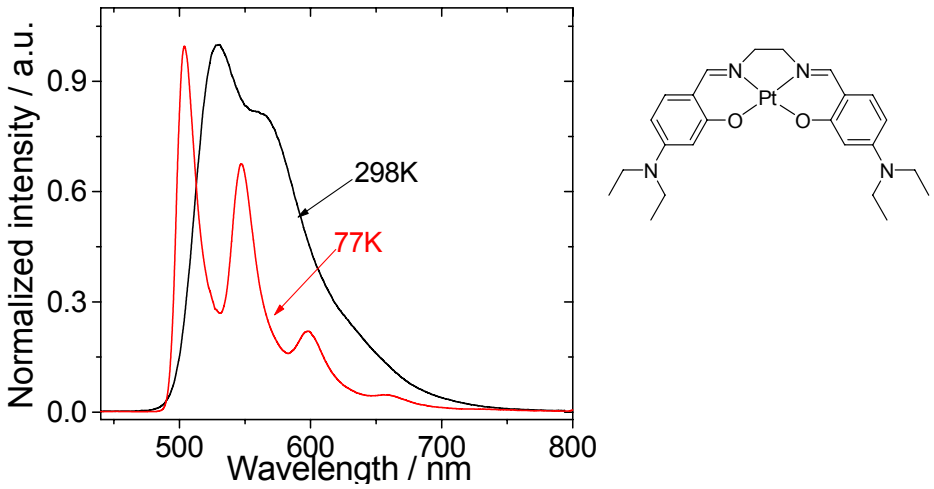


Fig. S22 Emission spectra of **Pt-2** in ethanol-methanol (4:1, V/V) glass at 77K and solution at 298K. Excitation wavelength at 400 nm.

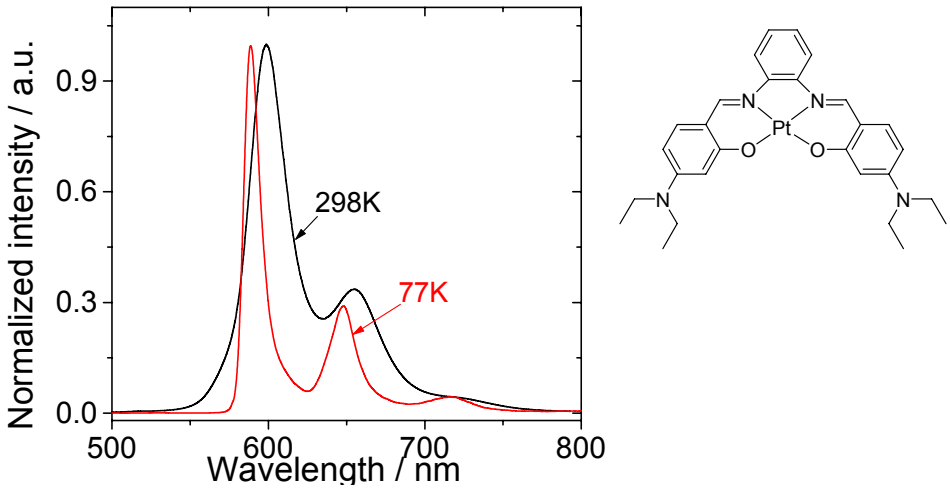


Fig. S23 Emission spectra of **Pt-4** in ethanol-methanol (4:1, V/V) glass at 77K and solution at 298K. Excitation wavelength at 480 nm.

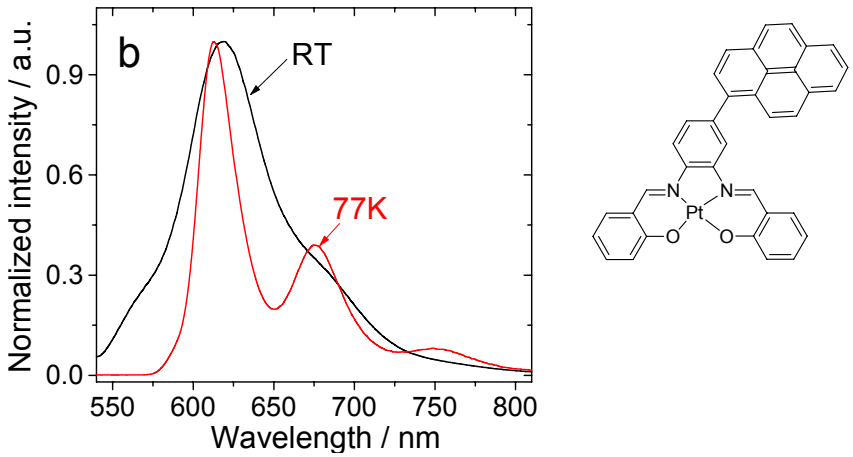


Fig. S24 Emission spectra of **Pt-5** in ethanol-methanol (4:1, V/V) glass at 77K and solution at 298K. Excitation wavelength at 520 nm.

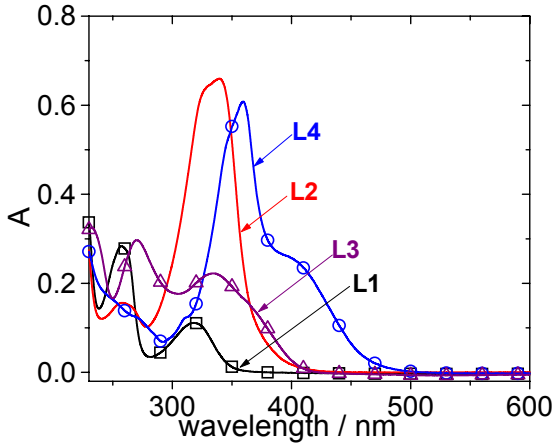
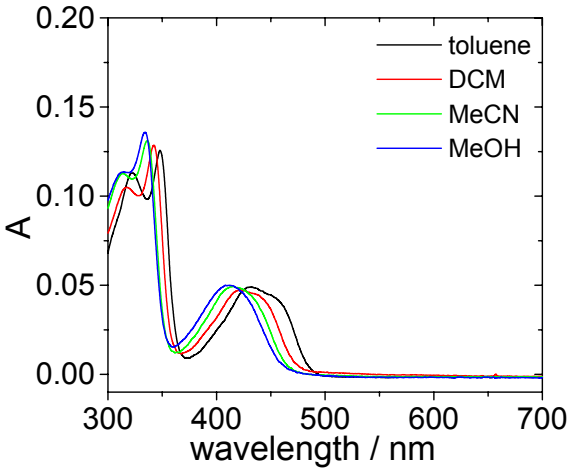


Fig. S25 Absorption spectra of **L1**, **L2**, **L3** and **L4** in DCM (1.0×10^{-5} mol dm^{-3}).



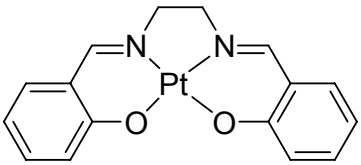


Fig. S26 Absorption spectra of **Pt-1** in various solvents.

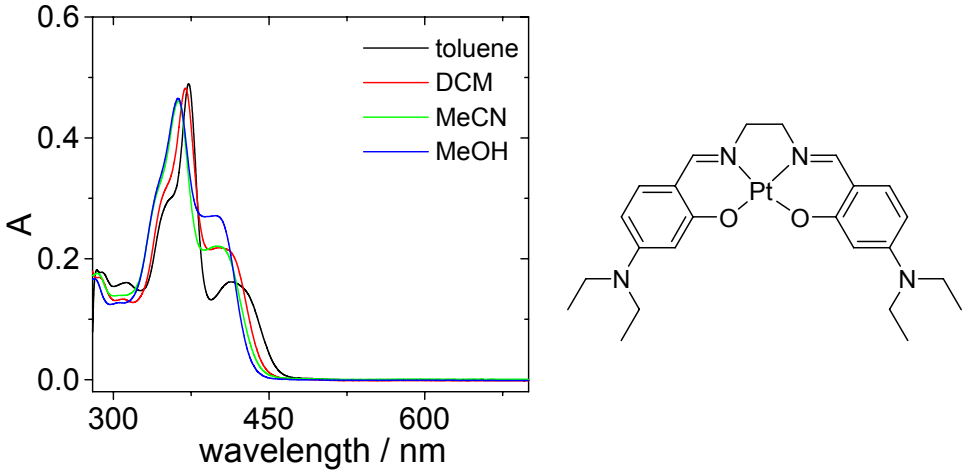


Fig. S27 Absorption spectra of **Pt-2** in various solvents.

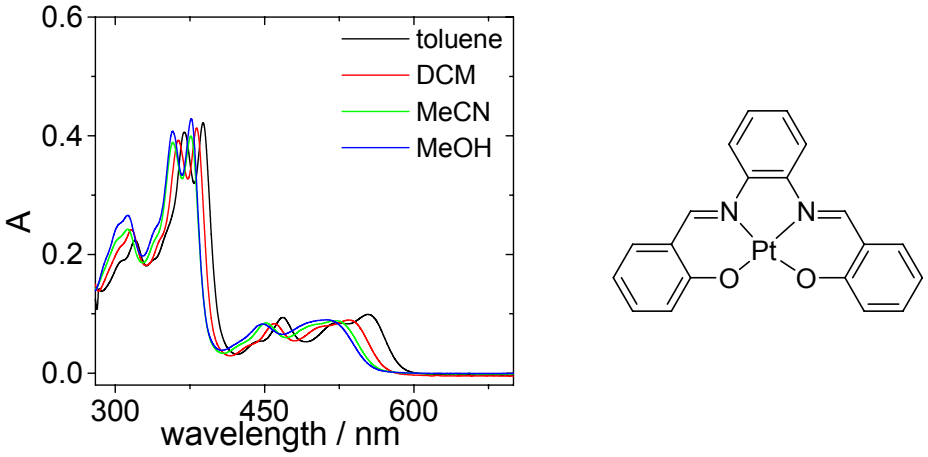


Fig. S28 Absorption spectra of **Pt-3** in various solvents.

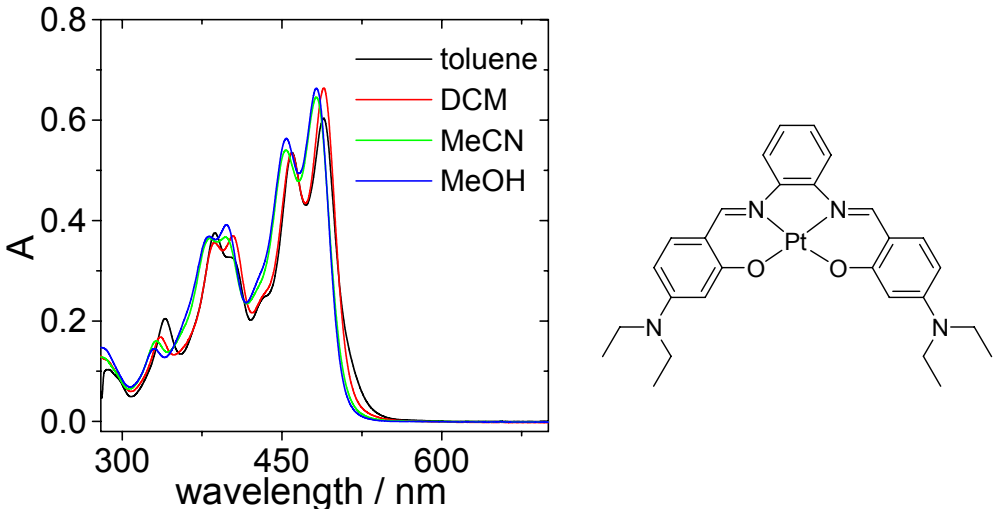


Fig. S29 Absorption spectra of **Pt-4** in various solvents.

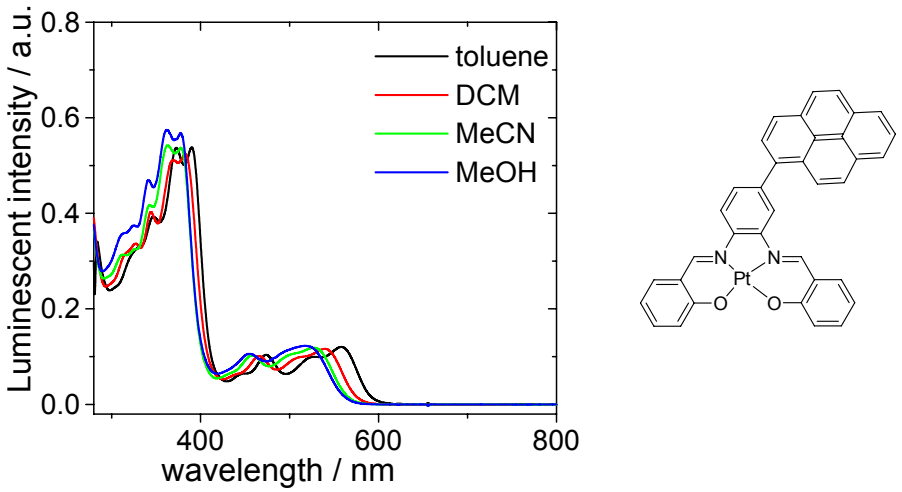


Fig. S30 Absorption spectra of **Pt-5** in various solvents.

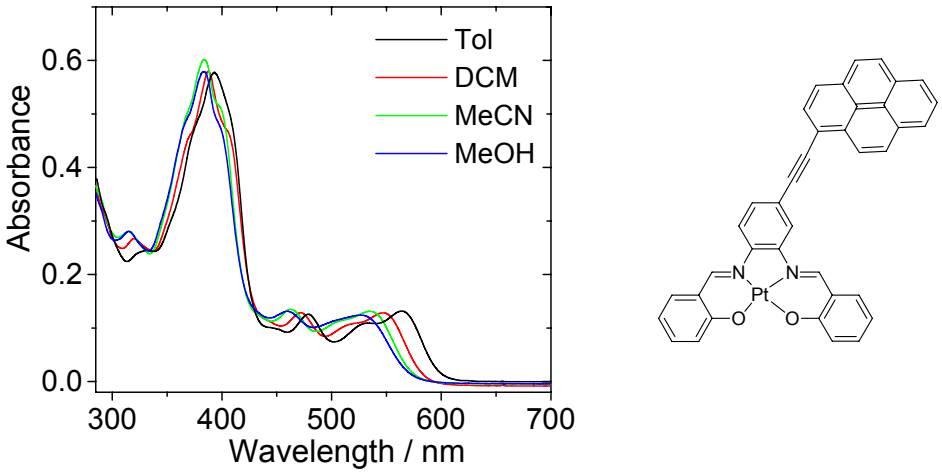


Fig. S31 Absorption spectra of **Pt-6** in various solvents.

5.0 Calculation details

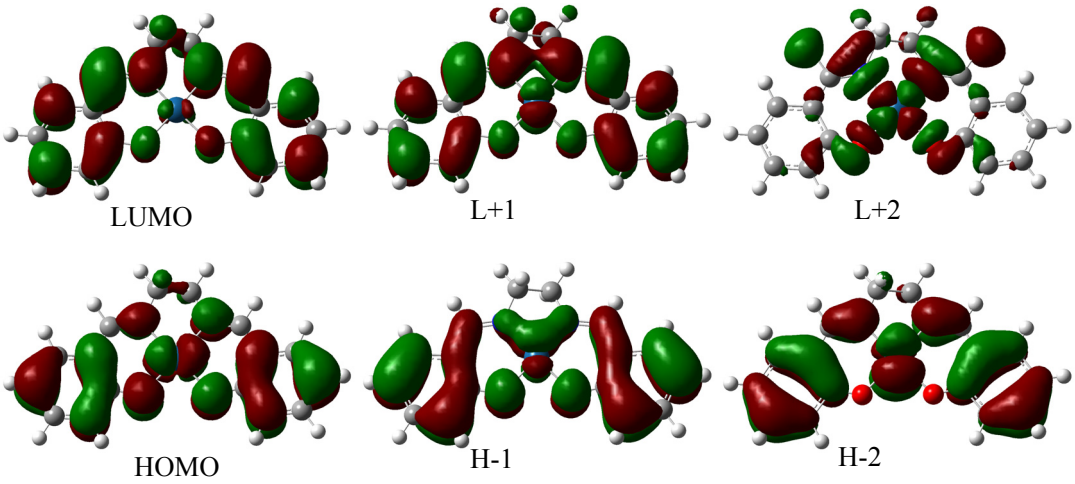


Fig. S32 Frontier molecular orbitals of **Pt-1**. H stands for HOMO and L stands for LUMO. Calculated by DFT at the B3LYP/6-31G((d)/ LanL2DZ level using Gaussian 09.

Table S1. Electronic Excitation Energies (eV) and corresponding Oscillator Strengths (*f*), main configurations and CI coefficients of the Low-lying Electronically Excited States of complex **Pt-1,** Calculated by TDDFT//B3LYP/6-31G(d)/LanL2DZ, based on the DFT//B3LYP/6-31G(d)/LanL2DZ Optimized Ground State Geometries

	Electronic transition	TDDFT//B3LYP/6-31G(d)				
		Energy (eV) [a]	*f* [b]	Composition [c]	CI [d]	character
Singlet	$S_0 \rightarrow S_1$	2.74 eV 452 nm	0.0323	HOMO → LUMO	0.6773	MLCT
	$S_0 \rightarrow S_2$	2.90 eV 427 nm	0.0414	HOMO→LUMO+1	0.6661	MLCT, ILCT
	$S_0 \rightarrow S_5$	3.69 eV 335 nm	0.0562	HOMO-1→LUMO+1	0.6600	ILCT
	$S_0 \rightarrow S_8$	4.13 eV 300 nm	0.2546	HOMO-3→LUMO+2	0.1654	MLCT
				HOMO-2→LUMO	0.6461	MLCT, ILCT
Triplet	$S_0 \rightarrow T_1$	2.18 eV 568 nm	0.0000	HOMO-2 → LUMO+1	0.1347	MLCT, ILCT
				HOMO-1→ LUMO+1	0.2509	ILCT
				HOMO → LUMO	0.6988	MLCT
	$S_0 \rightarrow T_2$	2.25 eV 551 nm	0.0000	HOMO-2 → LUMO	0.1410	MLCT, ILCT
				HOMO-1→ LUMO	0.3098	MLCT, ILCT
				HOMO → LUMO+1	0.6784	MLCT, ILCT

[a] Only the selected low-lying excited states are presented. [b] oscillator strength. [c] H stands for HOMO and L stands for LUMO. Only the main configurations are presented. [d] The CI coefficients are in absolute values. [e]No spin-orbital coupling effect was considered, thus the f values are zero.

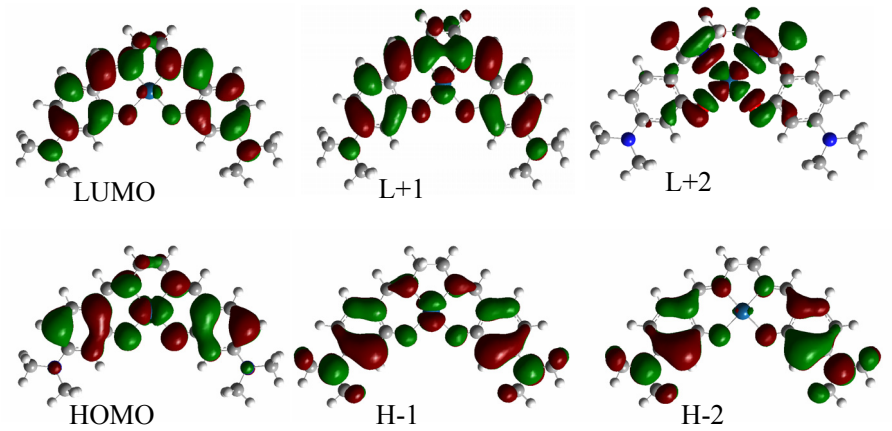


Fig. S33 Frontier molecular orbitals of **Pt-2**. H stands for HOMO and L stands for LUMO. Calculated by DFT at the B3LYP/6-31G((d)/ LanL2DZ level using Gaussian 09.

Table S2. Electronic Excitation Energies (eV) and corresponding Oscillator Strengths (*f*), main configurations and CI coefficients of the Low-lying Electronically Excited States of complex **Pt-2,** Calculated by TDDFT//B3LYP/6-31G(d)/LanL2DZ, based on the DFT//B3LYP/6-31G(d)/LanL2DZ Optimized Ground State Geometries

	Electronic transition	**TDDFT//B3LYP/6-31G(d)**				
		Energy (eV) [a]	***f*** [b]	**Composition** [c]	**CI** [d]	**character**
Singlet	$S_0 \rightarrow S_1$	2.92 eV 425 nm	0.0315	HOMO → LUMO	0.6725	MLCT
	$S_0 \rightarrow S_2$	3.02 eV 411 nm	0.0492	HOMO-1→LUMO	0.1313	MLCT, ILCT
				HOMO→LUMO+1	0.66029	ILCT
	$S_0 \rightarrow S_3$	3.50 eV 355 nm	0.5835	HOMO-3→LUMO	0.13906	ILCT
				HOMO-1→LUMO	0.64729	MLCT, ILCT
				HOMO→LUMO+1	0.11459	ILCT
Triplet	$S_0 \rightarrow T_1$	2.37 eV 523 nm	0.0000	HOMO-3 → LUMO+1	0.24985	ILCT
				HOMO -2→ LUMO	0.10929	ILCT
				HOMO-1 → LUMO+1	0.16681	ILCT
				HOMO → LUMO	0.67927	MLCT

[a] Only the selected low-lying excited states are presented. [b] oscillator strength. [c] H stands for HOMO and L stands for LUMO. Only the main configurations are presented. [d] The CI coefficients are in absolute values. [e]No spin-orbital coupling effect was considered, thus the f values are zero.

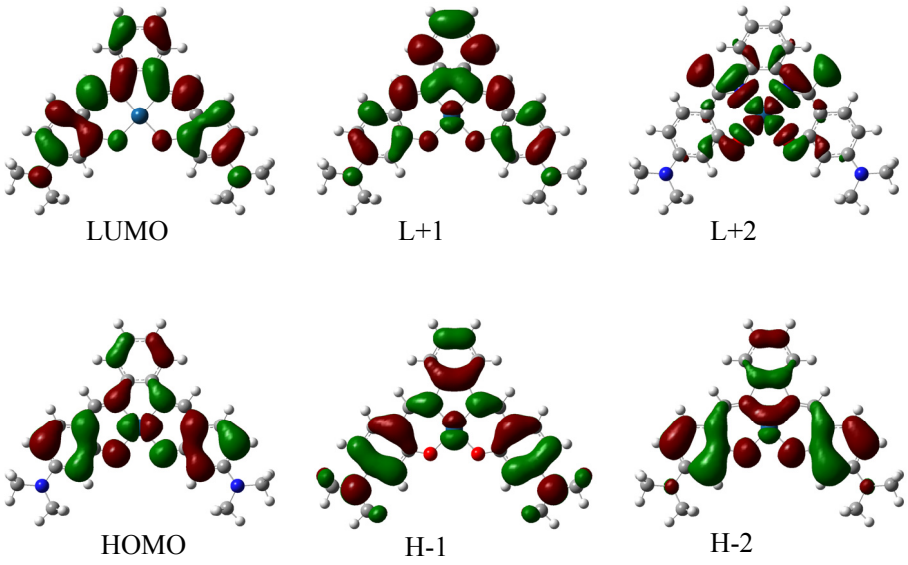


Fig. S34 Frontier molecular orbitals of **Pt-4.** H stands for HOMO and L stands for LUMO. Calculated by DFT at the B3LYP/6-31G((d)/ LanL2DZ level using Gaussian 09.

Table S3. Electronic Excitation Energies (eV) and corresponding Oscillator Strengths (*f*), main configurations and CI coefficients of the Low-lying Electronically Excited States of complex **Pt-2,** Calculated by TDDFT//B3LYP/6-31G(d)/LanL2DZ, based on the DFT//B3LYP/6-31G(d)/LanL2DZ Optimized Ground State Geometries

	Electronic transition	TDDFT//B3LYP/6-31G(d)				
		Energy (eV) [a]	*f* [b]	Composition [c]	CI [d]	character
Singlet	$S_0 \rightarrow S_1$	2.54 eV 489 nm	0.0427	HOMO → LUMO	0.6755	MLCT
	$S_0 \rightarrow S_2$	2.86 eV 433 nm	0.6054	HOMO-1→LUMO	0.6341	MLCT
				HOMO→LUMO+1	0.1998	MLCT, ILCT
	$S_0 \rightarrow S_7$	3.43 eV 362 nm	0.2705	HOMO-3→LUMO	0.4039	ILCT
				HOMO-2→LUMO+1	0.3160	ILCT
				HOMO-1→LUMO+1	0.3960	ILCT
	$S_0 \rightarrow S_8$	3.64 eV 340 nm	0.4045	HOMO-3→LUMO	0.2688	ILCT
				HOMO-2→LUMO+1	0.5935	ILCT
				HOMO-1→LUMO+1	0.1132	ILCT
Triplet	$S_0 \rightarrow T_1$	2.12eV 586 nm	0.0000	HOMO-3 → LUMO+1	0.1655	ILCT
				HOMO-2→ LUMO	0.1862	MLCT, ILCT
				HOMO-1 → LUMO	0.6531	MLCT
				HOMO→ LUMO+1	0.2811	MLCT, ILCT

[a] Only the selected low-lying excited states are presented. [b] oscillator strength. [c] H stands for HOMO and L stands for LUMO. Only the main configurations are presented. [d] The CI coefficients are in absolute values. [e]No spin-orbital coupling effect was considered, thus the f values are zero.

Table S4. Electronic Excitation Energies (eV) and corresponding Oscillator Strengths (*f*), main configurations and CI coefficients of the Low-lying Electronically Excited States of complex **Pt-5,** Calculated by TDDFT//B3LYP/6-31G(d)/LanL2DZ, based on the DFT//B3LYP/6-31G(d)/LanL2DZ Optimized Ground State Geometries.

	Electronic transition	TDDFT//B3LYP/6-31G(d)				
		Energy (eV) [a]	*f* [b]	Composition [c]	CI [d]	character
Singlet	$S_0 \rightarrow S_1$	2.32 eV 533 nm	0.1131	HOMO → LUMO	0.6671	MLCT
	$S_0 \rightarrow S_2$	2.70 eV 459 nm	0.0935	HOMO-2→LUMO	0.2952	ILCT
				HOMO-1→LUMO	0.6062	ILCT
	$S_0 \rightarrow S_6$	3.19 eV 388 nm	0.4385	HOMO-1→LUMO+1	0.6169	ILCT
				HOMO-1→LUMO+2	0.2009	ILCT
				HOMO→LUMO+1	0.1335	MLCT, ILCT
				HOMO→LUMO+2	0.1183	MLCT, ILCT
	$S_0 \rightarrow S_8$	3.39 eV 366 nm	0.4490	HOMO-3→LUMO	0.6520	MLCT, ILCT
Triplet	$S_0 \rightarrow T_1$	1.87 eV 664 nm	0.0000[e]	HOMO-2 → LUMO+1	0.1154	ILCT
				HOMO-2 → LUMO+2	0.1551	ILCT
				HOMO-1 → LUMO+1	0.1493	ILCT
				HOMO → LUMO	0.6983	MLCT
	$S_0 \rightarrow T_2$	2.01 eV 618 nm	0.0000[e]	HOMO-5 → LUMO+3	0.1244	MLCT
				HOMO-2 → LUMO	0.1725	MLCT, ILCT
				HOMO-2 → LUMO+1	0.2299	ILCT
				HOMO-2 → LUMO+2	0.1868	ILCT
				HOMO-1 → LUMO	0.4378	MLCT, ILCT
				HOMO-1→ LUMO+1	0.2448	ILCT
				HOMO-1 → LUMO+2	0.3438	ILCT
				HOMO → LUMO+1	0.3394	MLCT, ILCT

[a] Only the selected low-lying excited states are presented. [b] oscillator strength. [c] H stands for HOMO and L stands for LUMO. Only the main configurations are presented. [d] The CI coefficients are in absolute values. [e]No spin-orbital coupling effect was considered, thus the f values are zero.

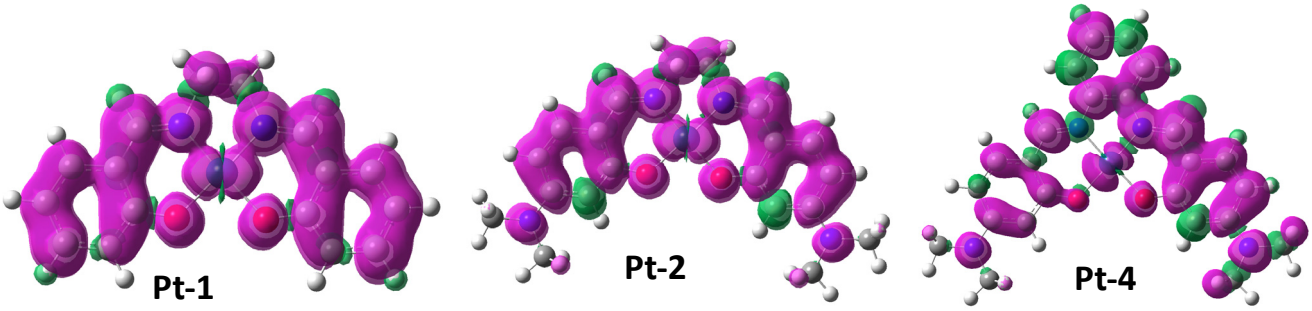


Fig. S35 Spin density surface of Pt(II) Schiff base complexes **Pt-1**, **Pt-2** and **Pt-4** at the optimized T_1 state geometry. Calculated at B3LYP/6-31G/LANL2DZ level with Gaussian 09W.

6.0 Oxygen sensing

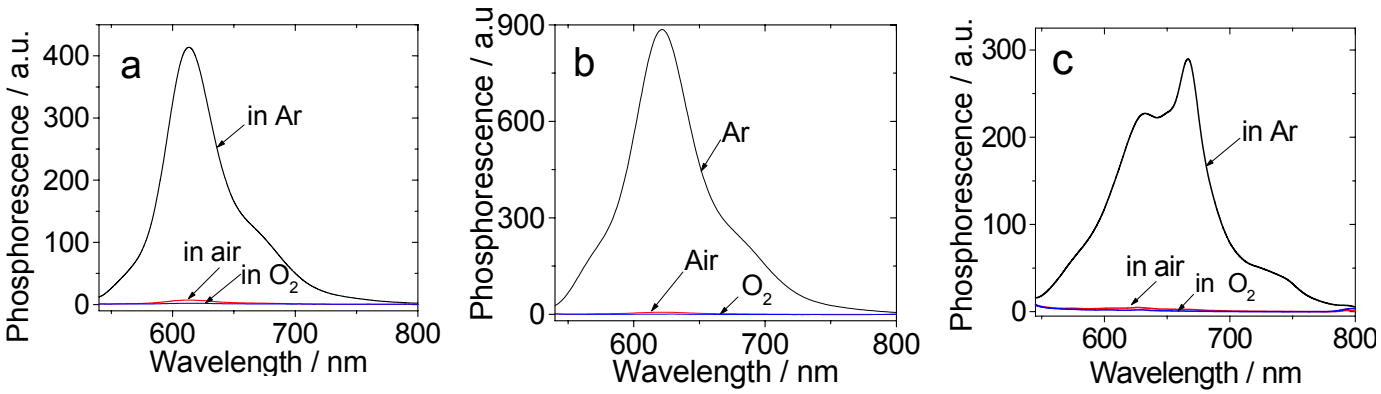


Fig. 36 Emission of complex **Pt-3, Pt-5** and **Pt-6** in solution under air, argon and oxygen atmosphere (1.0×10^{-5} M in MeCN). The solution is purged with Ar or O_2 for about 20 min before measurement. (a) **Pt-3**: λex = 526 nm, (b) **Pt-5**: λex = 520 nm, (c) **Pt-6**: λex = 530 nm.20 °C.

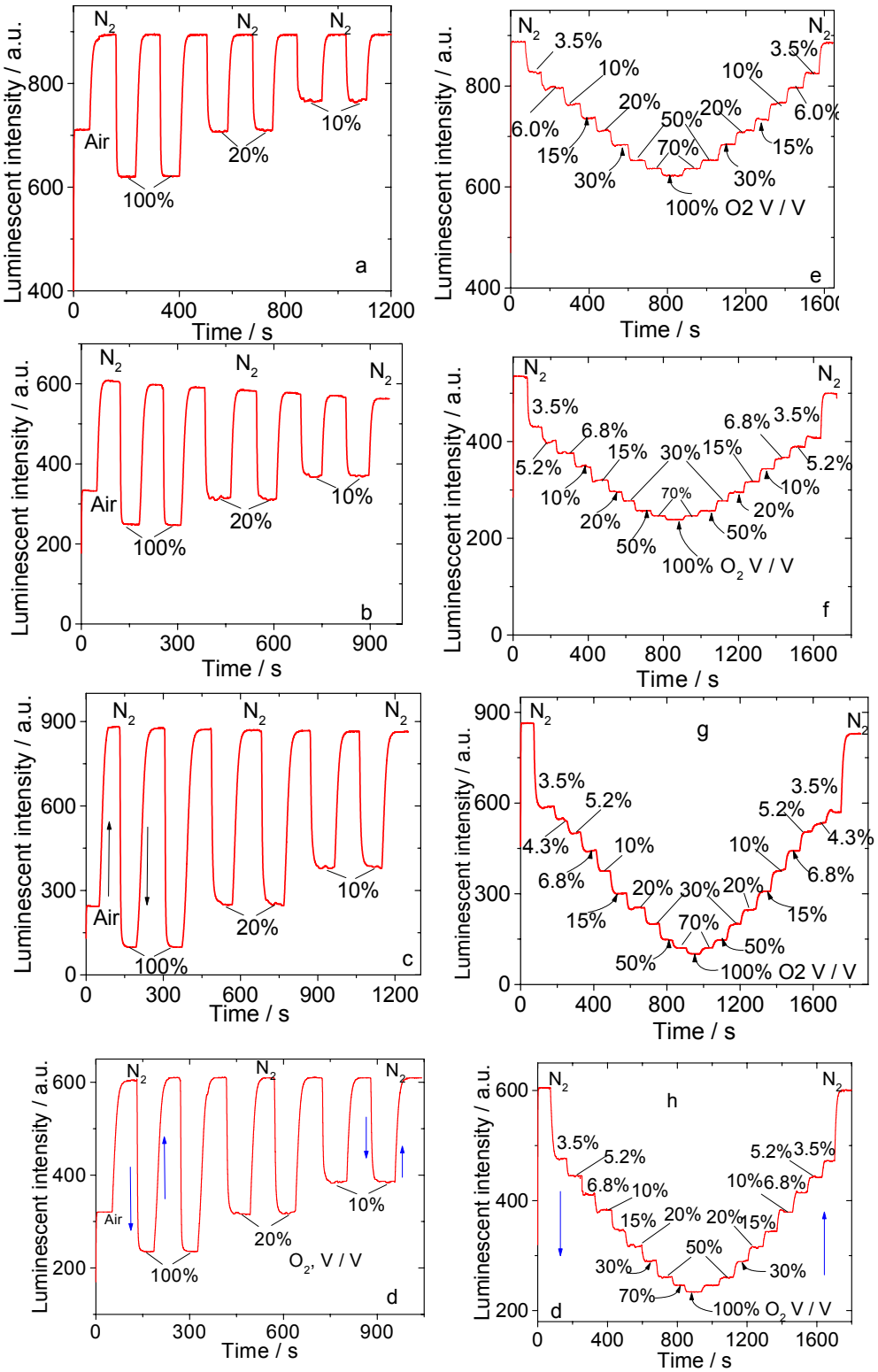


Fig. S37 Phosphorescent emission intensity response of the complexes to step variations of O_2 concentration levels (a-d) emission change of **Pt-1, Pt-2, Pt-4** and **Pt-5** film vs. O_2/N_2 saturation switch, (e-h) dynamic response of the **Pt-1, Pt-2, Pt-4** and **Pt-5** film vs. small steps of variation of O_2 partial pressure. **Pt-1**: λex = 420 nm, λem = 538nm; **Pt-2** λex = 400 nm, λem = 534 nm; **Pt-4**: λex = 485 nm, λem = 600 nm; **Pt-5**: λex = 520 nm, λem = 613 nm. 20 °C.

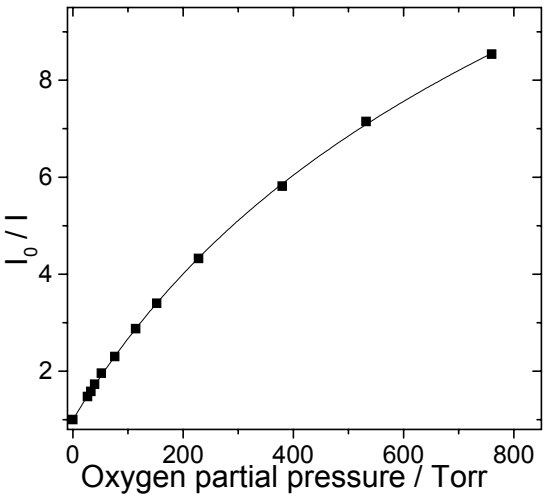


Fig. S38 Fitting of the oxygen sensing property of the IMPEK-C films of complex **Pt-4** based on the two site model

7.0 Transient absorption details

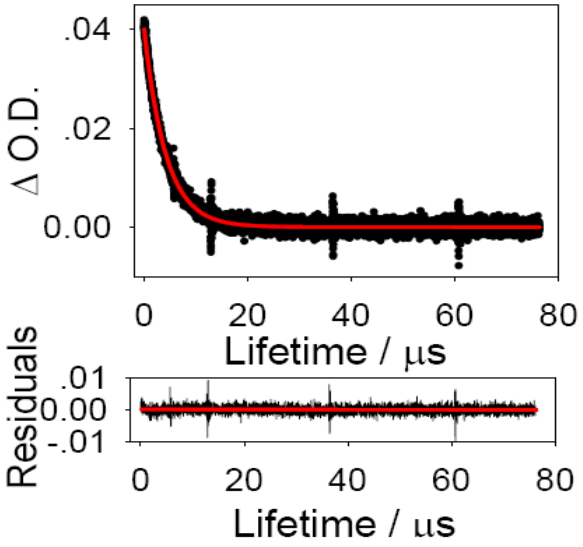


Fig. S39 Decay traces of **Pt-3** at 520 nm, λex = 532 nm, 1.0×10^{-5} M in MeCN.

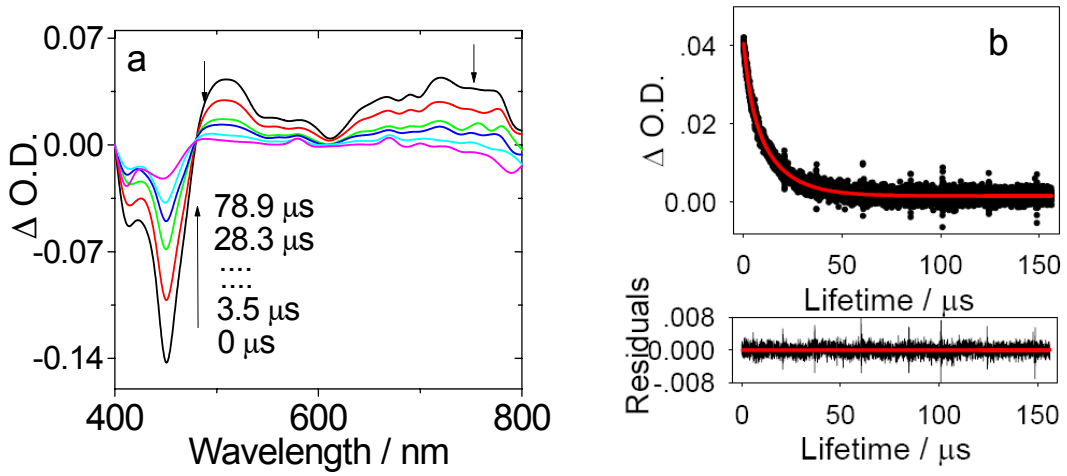


Fig. S40 (a) Transient absorption difference spectra of **Pt-5** in deaerated MeCN at room temperature after pulsed excitation (λex = 532 nm) and (b) Decay traces of **Pt-5** at 520 nm.

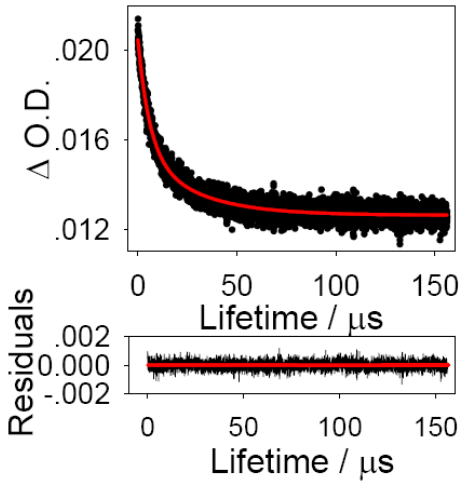


Fig. S41 Decay traces of **Pt-6** at 530 nm, λex = 532 nm, 1.0×10^{-5} M in MeCN.