Electronic Supplementary Information for:

Synergetic Effect of C*N^N/C^N^N Coordination and the Arylacetylide Ligands on the Photophysical Properties of Cyclometalated Platinum Complexes

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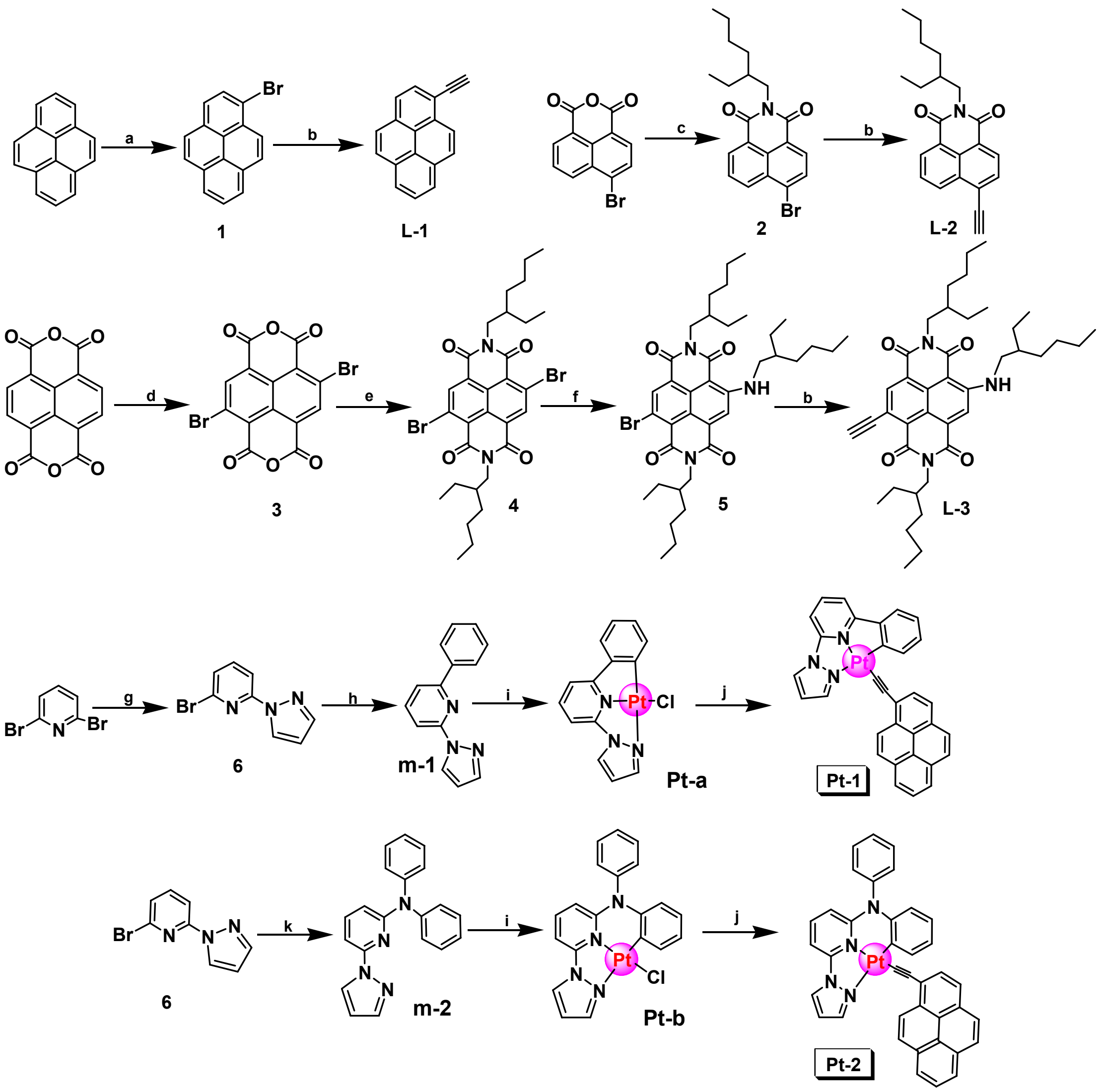
Table of Contents

Synthesis and molecular structural characterization data



Scheme S1. Synthesis of the Pt(II) complexes. (a) NBS, DMF, r.t., 24 h; (b) i) Trimethylsilylacetylene, $Pd(PPh_3)_2Cl_2$, PPh_3, CuI, NEt_3, Ar, 90 °C, 8 h; ii) K_2CO_3, DCM/MeOH (2/1, v/v), r.t.; (c) 2-ethylhexylamine, ethanol, Ar, reflux, 8 h; (d) bromine, oleum, 85 °C, 48 h; (e) 2-ethylhexylamine, acetic acid, Ar, reflux, 120 °C, 2 h; (f) 2-ethylhexylamine, 2-methoxyethanol, Ar, 120 °C, 8 h; (g) diglyme, KOH, 60 °C, 48 h; (h) phenylboronic acid, $Pd(PPh_3)_4$, K_2CO_3, toluene/EtOH/H_2O (2:2:1, v/v/v), Ar, 80°C, 8 h; (i) K_2PtCl_4 (1 equiv), acetic acid, reflux; 22 h;(j) L-1, CuI, CH_2Cl_2, i-Pr_2NH, r.t., 24 h; (k) $Pd(dba)_2$ (4%), DPPF (4%), NaO^tBu (1.2 equiv), toluene, Ar, reflux, 24 h.

Synthesis of 1

A solution of NBS (1.02 g, 5.8 mmol) in DMF (23 mL) was slowly added to a solution of pyrene (1.30 g, 6.0 mmol) in DMF (35 mL) at 0°C. After stirring at room temperature for 24 h, the reaction mixture was poured into ice–water (150 mL) and the reaction mixture was extracted with diethyl ether. The organic layer was dried with anhydrous Na_2SO_4. After removal of the solvent by evaporation the crude white solid was purified by column chromatography (silica gel, petroleum ether). A white solid was obtained 1.98 g; yield: 85.4 %. ^{1}H NMR (400 MHz, $CDCl_3$):δ = 8.40 (d, J = 9.2 Hz, 1 H), 8.20–8.17 (m, 3 H), 8.13 (d, J = 9.2 Hz, 1 H),8.05–7.95 (m, 4 H) ppm. HRMS (ESI): calcd. ($[C_{16}H_9Br]^+$) m/z =279.9888; found m/z =279.9889.

Synthesis of L-1

Under argon, 1-bromopyrene (1.0 g, 3.57 mmol),$[Pd(PPh_3)_2Cl_2]$ (67.6 mg, 0.09 mmol), PPh_3 (50.6 mg, 0.20 mmol) and CuI (36.7 mg, 0.18 mmol) were mixed in TEA (10 mL). Then trimethylsilylacetylene (424 mg, 4.28 mmol) was added. The system was heated for 8 h at 90 °C. The reaction mixture was cooled to room temperature. After removal of the solvent by evaporation the crude white solid was purified by column chromatography (silica gel, petroleum ether/DCM = 15:1, v/v).A yellow powder was obtained. The yellow powder was dissolved in DCM (20 mL). Then methanol (10 mL) and potassium carbonate (1.24 g) were added. The system was stirred at room temperature for 3 h. The mixture was filtered and the filtrate was revolved to dryness. The residue was purified by column chromatography (silica gel, petroleum ether/DCM =30:1, v/v). The product was obtained as a cinereous powder 370 mg; yield: 49.3%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.57 (d, J = 9.2 Hz, 1 H), 8.15 (m, 4 H), 8.10 (m, 2H), 8.04 (m, 2 H), 3.62 (s, 1 H) ppm. HRMS (ESI): calcd. ($[C_{18}H_{10}]^+$) m/z =226.0783, found m/z =226.0790.

Synthesis of 2

A solution of 2-ethylhexylamine (2.33 g, 18 mmol) in ethanol (50 mL) was added dropwise to a mixture of 4-bromo-1,8-naphthalic anhydride (4.0 g, 14 mmol) and ethanol (250 mL) at 60 °C under stirring. The mixture was refluxed for 6 h until the mixture became clear, then cooled to room temperature and filtered to give the crude product as a yellow powder. After recrystallization from anhydrous ethanol, compound 1 was obtained as a white solid 5.23 g; yield 82.6%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.65 (d, J = 7.4 Hz, 1H), 8.55 (d, J = 8.5 Hz, 1H), 8.40 (d, J = 8.0 Hz, 1H), 8.03 (d, J = 7.9 Hz ,1H), 7.83 (t, J = 8.0 Hz ,1H), 4.16−4.05(m, 2H), 1.98−1.88 (m, 1H), 1.41−1.29(m, 8H), 0.95−0.86 (m, 6H)ppm. MALDI-HRMS: calcd ($[C_{20}H_{22}BrNO_2+H]^+$) m/z =388.0912, found, m/z = 388.0890.

Synthesis of L-2

Under Ar atmosphere, 2-ethylhexyl-4-bromonaphthalimide (1.00 g, 3.0 mmol),PPh_3 (32.0 mg, 0.12 mmol) $Pd(PPh_3)_2Cl_2$ (42.0 mg, 0.06 mmol), and CuI (23.0 mg,0.12 mmol) were mixed in TEA (30 mL). Then trimethylsilylacetylene (414 mg, 4.2 mmol) was added. The mixture was heated for 8 h at 90 °C under Ar atmosphere. The reaction mixture was cooled to room temperature. After removal of the solvent by evaporation the crude white solid was purified by column chromatography (silica gel, DCM / ethyl acetate = 10 / 1, v/v). A gray powder was obtained. The gray powder was dissolved in DCM (20 mL). Then methanol (10 mL) and potassium carbonate (1.08 g) were added. The system was stirred at room temperature for 1.5 h. The residue was taken up with DCM, washed with water (2×10 mL). The combined organic layer was dried over anhydrous Na_2SO_4. The residue was purified by column chromatography (silica gel, DCM / ethyl acetate = 10 / 1, v/v), gray powder was obtained 600.0 mg; yield 56.0 %. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.67−8.62 (m, 2H), 8.52 (d, *J* = 10 Hz, 2H), 7.93 (d, *J* = 5.0 Hz , 1H), 7.82 (t, *J* = 15 Hz, 1H), 4.16−4.07 (m, 2H), 3.73 (s, 1H), 1.97−1.91 (m, 1H), 1.40−1.36 (m, 4H), 1.33−1.30 (m, 4H), 0.93 (t,*J*=15Hz, 3H), 0.87 (t, *J* = 15 Hz, 3H) ppm. MS (ESI): calcd.($[C_{22}H_{23}NO_2+H]^+$) *m/z* =335.17, found *m/z* =335.29.

Synthesis of 3

Naphthalenetetracarboxylic dianhydrides (NDA, 10 g, 37.28 mmol) and some iodine were placed reaction bottle equipped with a magnetic stirrer. Oleum (50% SO_3, 150 mL) was used to dissolve the anhydride. Bromine (11.92g, 74.56 mmol) was injected in small portions to the reaction mixture. After completion of the bromine injection the temperature was increased to 50°C and the mixture stirred 48 h. The reaction mixture was then carefully poured into ice. The precipitated solid was filtered off, and washed with water and methanol. The dried yellow product was the mixture of monobromonaphthalene tetracarboxylic diimides (NDIs) and dibromo NDIs, which were used as the starting materials of NDI acetylide ligand without further purification.

Synthesis of 4

The mixture of compound **3** (1.06 g, 2.5 mmol), 2-ethylhexylamine (0.97 g, 7.5 mmol), and acetic acid (25 mL) was refluxed for 2 h. After cooling to room temperature, the precipitate was filtered and washed with water (300 mL). Then the residue was purified with column chromatography (silica gel; DCM / petroleum ether = 1 / 1, v/v) to give an orange crystal 0.785 g; yield: 48.5 %. ^{1}H NMR (400 MHz, $CDCl_3/CD_3OD$) δ = 8.99 (s, 2H), 4.11−4.20 (m, 4H), 1.93−1.96 (m, 2H), 1.25−1.43 (m,16H), 0.94 (t, *J* = 7.2 Hz, 6H), 0.89 (t, *J* = 7.2 Hz, 6H). HRMS (ESI): calcd. ($[C_{30}H_{36}N_2O_4Br_2]$+) m/z = 646.1042. found: m/z = 646.1032.

Synthesis of 5

The mixture of compound **4** (130.0 mg, 0.20 mmol), 2-ethylhexylamine (28.6 mg, 0.22 mmol) in methoxyethanol (5 mL) was stirred at 120 °C for 8 h. The reaction mixture was cooled to room temperature. After removal of the solvent by evaporation the crude red solid was purified by column chromatography (silica gel; DCM / petroleum ether = 1 / 1, v/v) to give a red solid 98.8 mg; yield: 70.6 %. ^{1}HNMR (500 MHz, $CDCl_3$) δ = 10.18 (s, 1H), 8.86 (s, 1H), 8.29 (s, 1H), 4.17– 4.09 (m, 4H), 3.50 (t, J = 10 Hz, 1H), 1.95–1.92(m, 2H), 1.81–1.76 (m, 1H), 1.31–1.24 (m, 24H), 1.00–0.87 (m, 18H) ppm. MALDI-HRMS: calcd ($[C_{38}H_{55}N_3O_4Br+H]^+$) m/z =696.3333, found, m/z =696.3376.

Synthesis of L-3

Compound **5** (78.8 mg, 0.113 mmol), PPh_3(25.4 mg, 0.0057 mmol) and $Pd(PPh_3)_2$ Cl_2(33.4 mg, 0.0029 mmol) were dissolved in 10 mL of TEA under argon atmosphere. Ethynyltrimethylsilane (0.8 mL) was added to the above solution and CuI (20.2 mg, 0.0046 mmol) was added then. The mixture was stirred at 75 °C for 8 h. After removal of triethylamine in vacuum, the residue was purified with column chromatography (silica gel; DCM / petroleum ether = 2 / 1, v/v) to give red solid; yield: 65.5 mg, 81.1 %. The red solid (65.5 mg, 0.092 mmol) was dissolved in 15 ml of mixed solvent (DCM / petroleum ether = 1 / 1, v/v), then K_2CO_3 (50.6 mg, 0.30 mmol) was added. The mixture was stirred at room temperature for 0.5 h. The precipitate was filtered and washed with water (30 mL). Then the residue was purified with column chromatography (silica gel; DCM /methanol= 1 / 1, v/v) to give an red solid 42.5 mg; yield: 72.2 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.25 (s, 1H), 8.79 (s, 1H), 8.29 (s, 1H), 4.15 (t, J = 20 Hz, 4H), 3.75 (s, 1H), 3.51 (t, J = 8.0 Hz, 2H), 1.99 – 1.91(m, 2H), 1.82–1.76 (m, 1H), 1.46–1.25 (m, 24H), 1.00–0.86 (m, 18H) ppm. MALDI-HRMS: calcd ($[C_{40}H_{55}N_3O_4+H]^+$) m/z =642.4222, found, m/z = 642.4271.

Synthesis of 6

The mixture of 2,6-dibromopyridine (2.35 g, 10mmol), pyrazole (0.816g,12mmol) and excess potassium hydroxide were dissolved in 50 ml of diglyme. The mixture was stirred at 60 °C for 24 h. After removal of the solvent by evaporation the crude white solid was purified by column chromatography (silica gel; DCM / petroleum ether = 1 / 1, v/v) to give a white solid 1.33 g; yield: 59.6 %. HRMS (EI) : calcd. ($[C_8H_6N_3Br]^+$) m/z = 222.9750. found: m/z = 222.9745. ^{1}HNMR (500 MHz, $CDCl_3$) δ = 8.52 (d, *J* = 2Hz,1H), 7.93 (d, *J* =10 Hz, 1H), 7.73 (d, *J* = 1Hz, 1H), 7.64 (t, *J* =16Hz, 1H), 7.34 (d, *J* =7.5 Hz,1H), 6.46– 6.45(m, 1H) ppm.

Synthesis of m-1

Complex **6** (223.0 mg, 1.0 mmol), phenylboronic acid (160.0 mg, 1.3 mmol), $Pd(PPh_3)_4$ (45.2 mg, 0.03 mmol) and K_2CO_3 (180.4 mg, 1.3 mmol) was charged in a two-necked flask under nitrogen. Degassed mixed solvent (toluene/ethanol/water = 2 / 2 / 1 v/v/v) 25 mL was added to the mixture, then the mixture was stirred at 80 °C for 8 h. The reaction mixture was cooled to room temperature. After removal of the solvent by evaporation the crude solid was purified by column chromatography (silica gel; DCM / petroleum ether = 2 / 1, v/v) to give a white solid 154.2 mg; yield: 69.7%. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.76 (s, 1H), 8.09 (d, *J* =5.0 Hz, 2H), 7.96 (d, *J* = 5.0 Hz , 2H), 7.89 (t, *J*=15Hz, 1H), 7.78(s, 1H), 7.66 (d, *J* =10 Hz, 1H), 7.50 (t, *J*=15 Hz, 2H), 7.45 (t, *J*=10 Hz, 1H), 6.50 (s,1H) ppm. MS (ESI): calcd.($[C_{14}H_{11}N_3+H]^+$) *m/z* =222.25, found *m/z* =222.29.

Synthesis of m-2

To a 25 mL flask were charged complex **6** (445.9 mg, 2.0 mmol), diphenylamine (508.0 mg, 3 mmol), $Pd(dba)_2$ (46.0 mg, 0.08 mmol), DPPF (44.0 mg, 0.08 mmol), sodium tert-butoxide (463.0 mg, 4.8 mmol), and toluene (15 mL), and the mixture was refluxed for 24 h. After being cooled to room temperature, the reaction mixture was poured into water, and the aqueous phase was extracted with ethyl acetate (3 × 35 mL). The combined organic extracts were washed with water

(50 mL) and then brine (50 mL) and dried over anhydrous Na_2SO_4. The mixture was filtered, concentrated in vacuo, and purified by chromatography (silica gel; DCM) to provide an off-white solid, 204.9 mg, yield 33.4%. ^{1}H NMR (500 MHz, $CDCl_3$) δ =8.09 (d, J=5.0 Hz, 1H), 7.70 (d, J =10 Hz, 1H), 7.55 (t, J =15 Hz, 1H), 7.42 (d, J =5.0Hz, 1H), 7.36(t, J = 20 Hz , 4H), 7.27 (d, J =5.0 Hz , 4H), 7.19 (t, J =15 Hz , 2H), 6.55 (d, J =10 Hz , 1H), 6.32 (s, 1H) ppm. MS (ES): calcd.($[C_{20}H_{16}N_4+Na]^+$) *m/z* =335.1282, found *m/z* =335.1273.

Synthesis of Pt-a.

To a 50 mL dry, argon-flushed flask were charged **m-1** (110.6 mg, 0.5 mmol), K_2PtCl_4 (207.6 mg, 0.5 mmol), and glacial acetic acid (20 mL). The mixture was degassed and refluxed under Ar atmosphere for 22 h. After the mixture was cooled to room temperature, the orange precipitates were collected by filtration, washed with water, and dried in air. The crude material was purified by flash chromatography (silica gel, dichloromethane). The compound was further recrystallized from dichloromethane and hexanes to give an orange solid 126.9 mg, yield 56.4%. ^{1}H NMR (400 MHz, $CDCl_3/CD_3OD$) δ = 8.76 (d, J = 2.4 Hz, 1H), 8.09 (t, J = 7.2 Hz, 2H), 7.93 (d, J = 8.0 Hz , 1H), 7.89 (t, J = 12Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.52−7.43(m, 3H), 6.50 (t, J = 4.0 Hz, 1H) ppm. MALDI-HRMS: calcd ($[C_{14}H_{10}ClN_3Pt]^-$): *m/z* =450.0216, found, *m/z* = 450.0211.

Synthesis of Pt-b.

This complex was prepared from **m-2** (48.9 mg, 0.25 mmol) following the procedure synthesis of **Pt-a.** The crude material was purified by flash chromatography on silica gel with dichloromethane. The compound was further recrystallized from dichloromethane and hexanes to give an orange solid 113.8 mg, yield 84.2%. ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 8.58 (d, J = 7 Hz, 1H), 8.32−8.31 (m, 2H), 7.71−7.58 (m, 4H), 7.36−7.34 (m, 2H), 7.04 (d, J = 8 Hz, 1H), 6.86−6.83 (m, 3H), 6.38 (d, J = 9 Hz, 1H), 6.28−6.26 (m,1H) ppm. MALDI-HRMS: calcd ($[C_{20}H_{15}ClN_4Pt+H]^+$): *m/z* =542.0678, found *m/z* = 542.0711.

Synthesis of Pt-1

To a 25 mL dry, argon-flushed flask were charged complex **Pt-a** (45.0 mg, 0.10 mmol), L-1 (30.0 mg, 0.13 mmol), CuI (3.5 mg, 0.018 mmol), i-Pr_2NH (1 mL), and dichloromethane (10 mL). The mixture was stirred under argon at room temperature for 24 h. The crude material was purified by flash chromatography on silica gel with dichloromethane to give a yellow solid, 34.1 mg, yield 53.2%. MALDI-HRMS: calcd ($[C_{32}H_{20}N_3Pt+H]^+$) *m/z* = 641.1305, found *m/z* = 641.1343.

Synthesis of Pt-2

This compound was prepared following the general procedure for complex **Pt-1** The crude material was purified by flash chromatography on silica gel with dichloromethane to give a yellow solid, 12.4 mg, yield 68.3%. MALDI-HRMS: calcd ($[C_{38}H_{25}N_4Pt]^+$) *m/z* = 732.1727, found *m/z* = 732.1735.

NMR and HRMS spectra

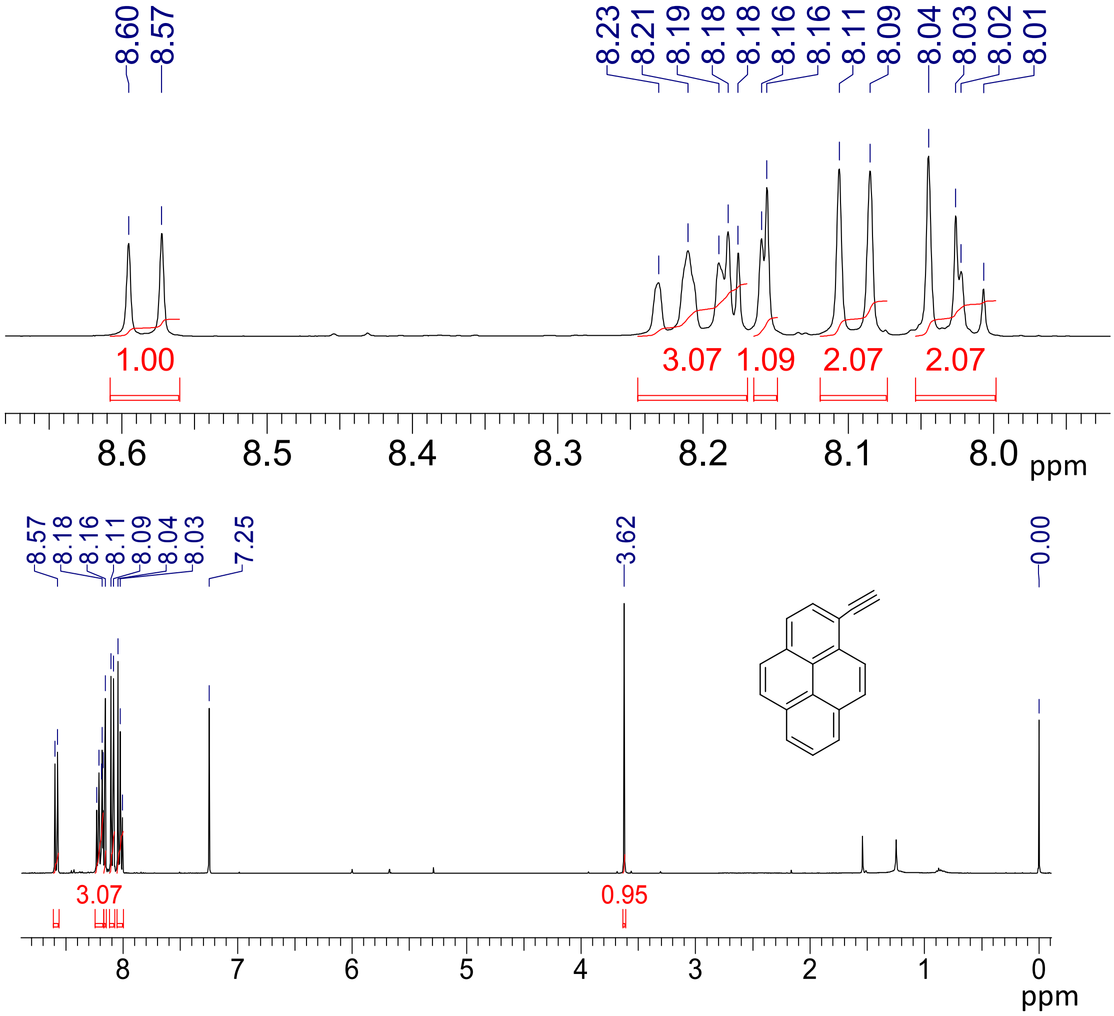


Figure S1. ^{1}H NMR of **L-1** in CDCl$_3$ (400 MHz), 25°C.

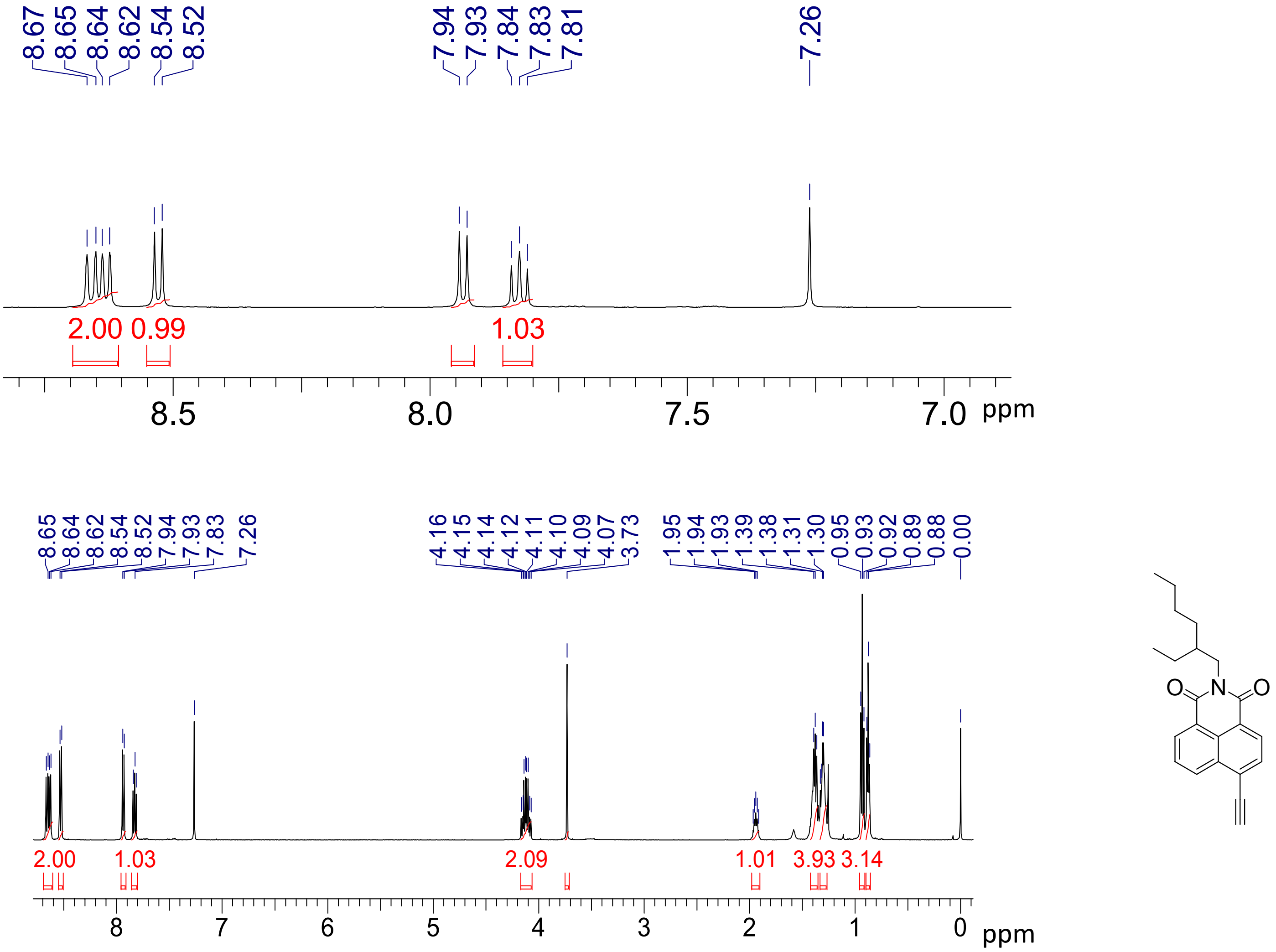


Figure S2. ^{1}H NMR of **L-2** in $CDCl_3$ (500 MHz), 25°C.

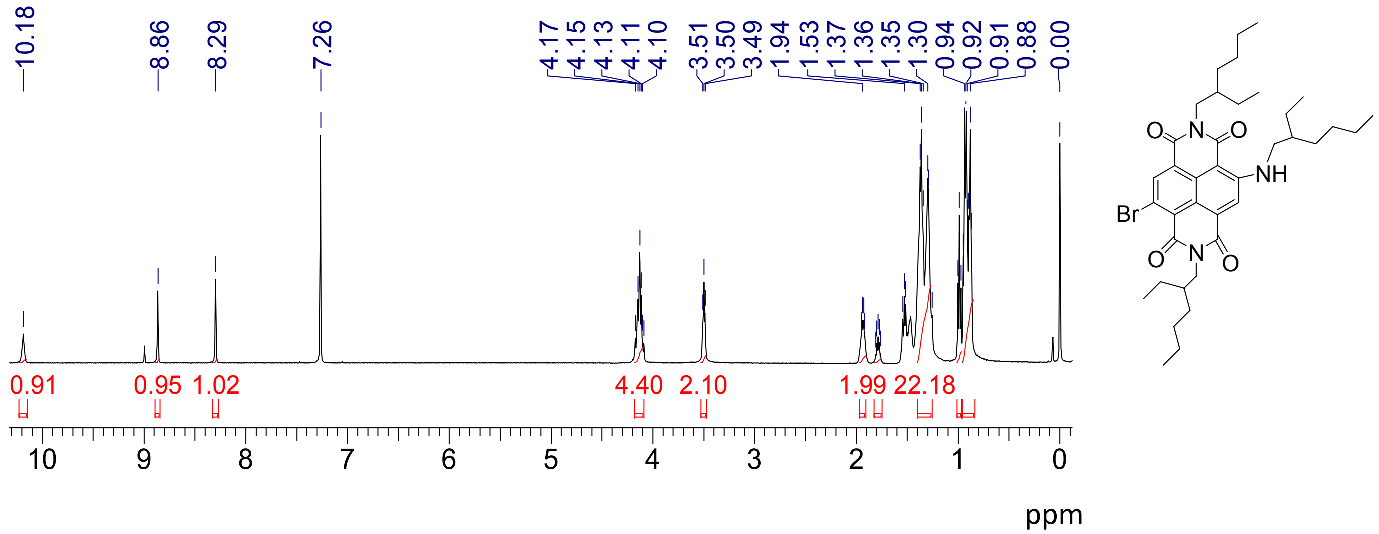


Figure S3. ^{1}H NMR of **5** in $CDCl_3$ (400 MHz), 25°C.

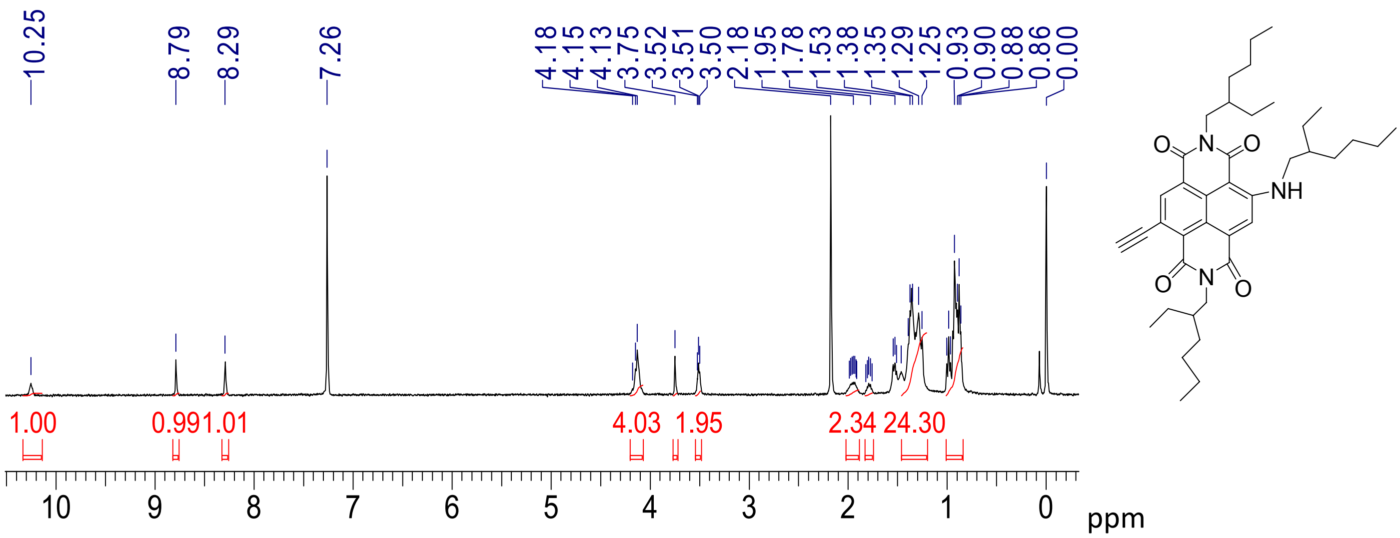


Figure S4. 1H NMR of **L-3** in CDCl3 (400 MHz), 25°C.

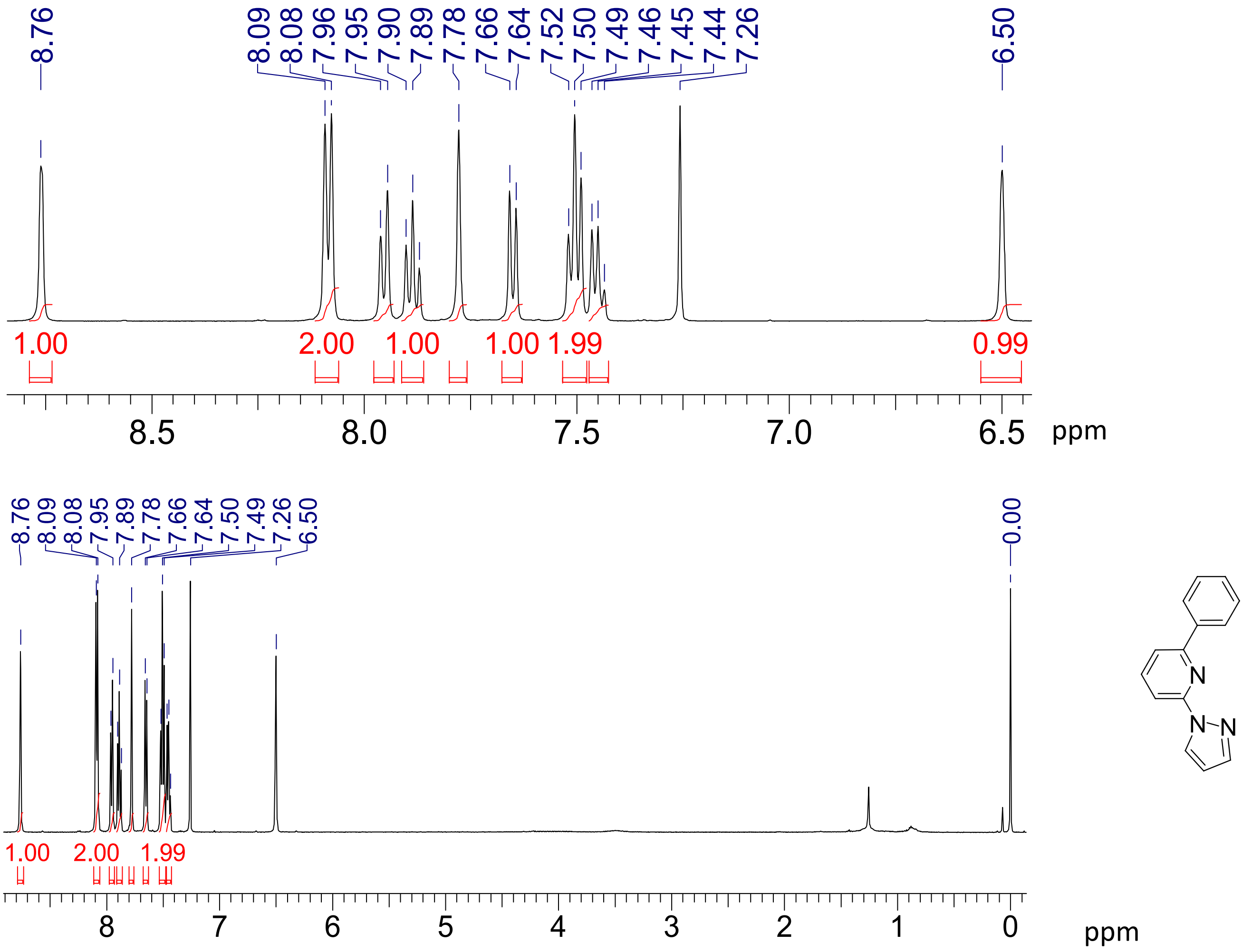


Figure S5. ^{1}H NMR of **7** in $CDCl_3$ (500 MHz), 25°C.

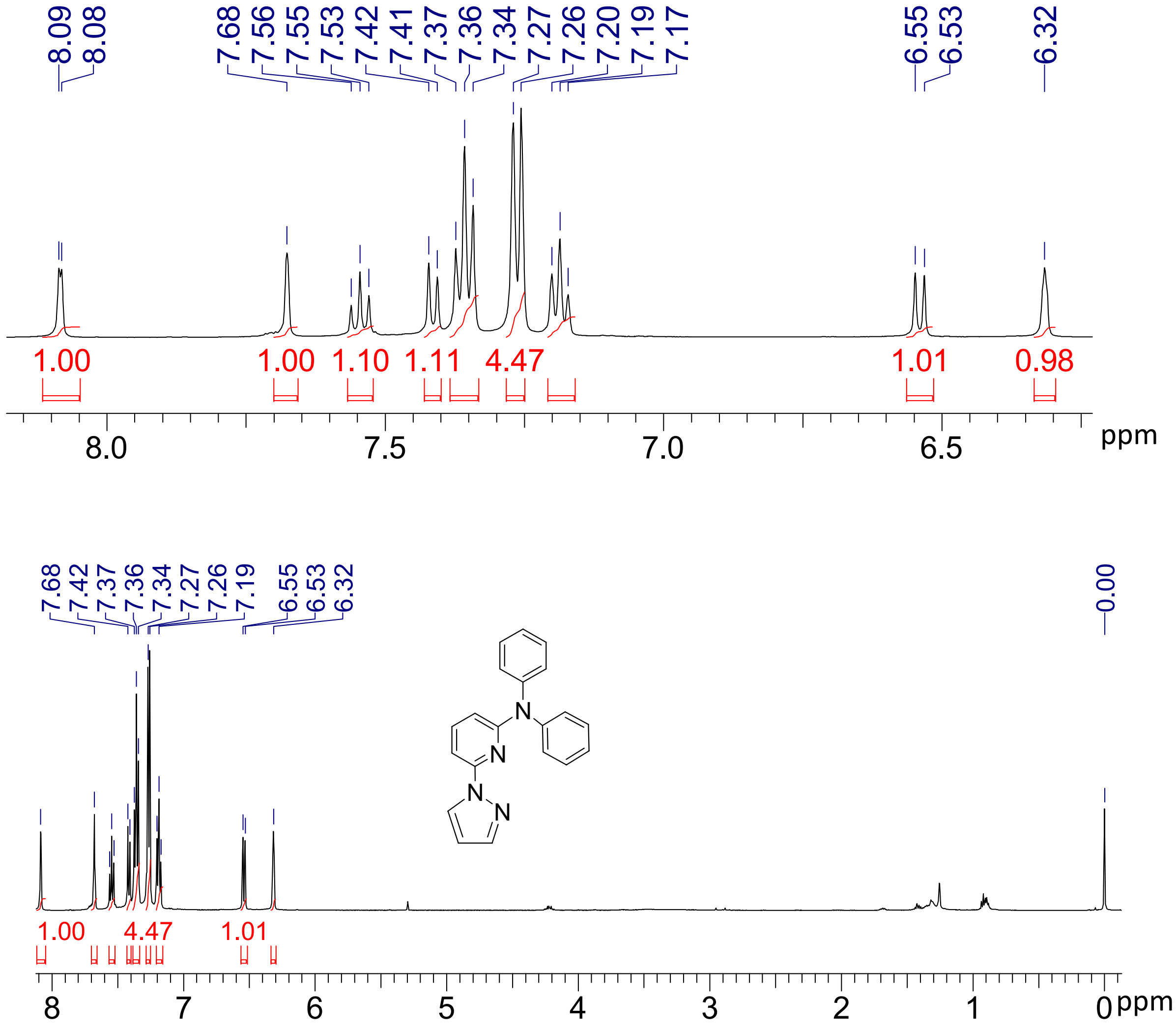


Figure S6. ^{1}H NMR of **8** in $CDCl_3$ (500 MHz), 25°C.

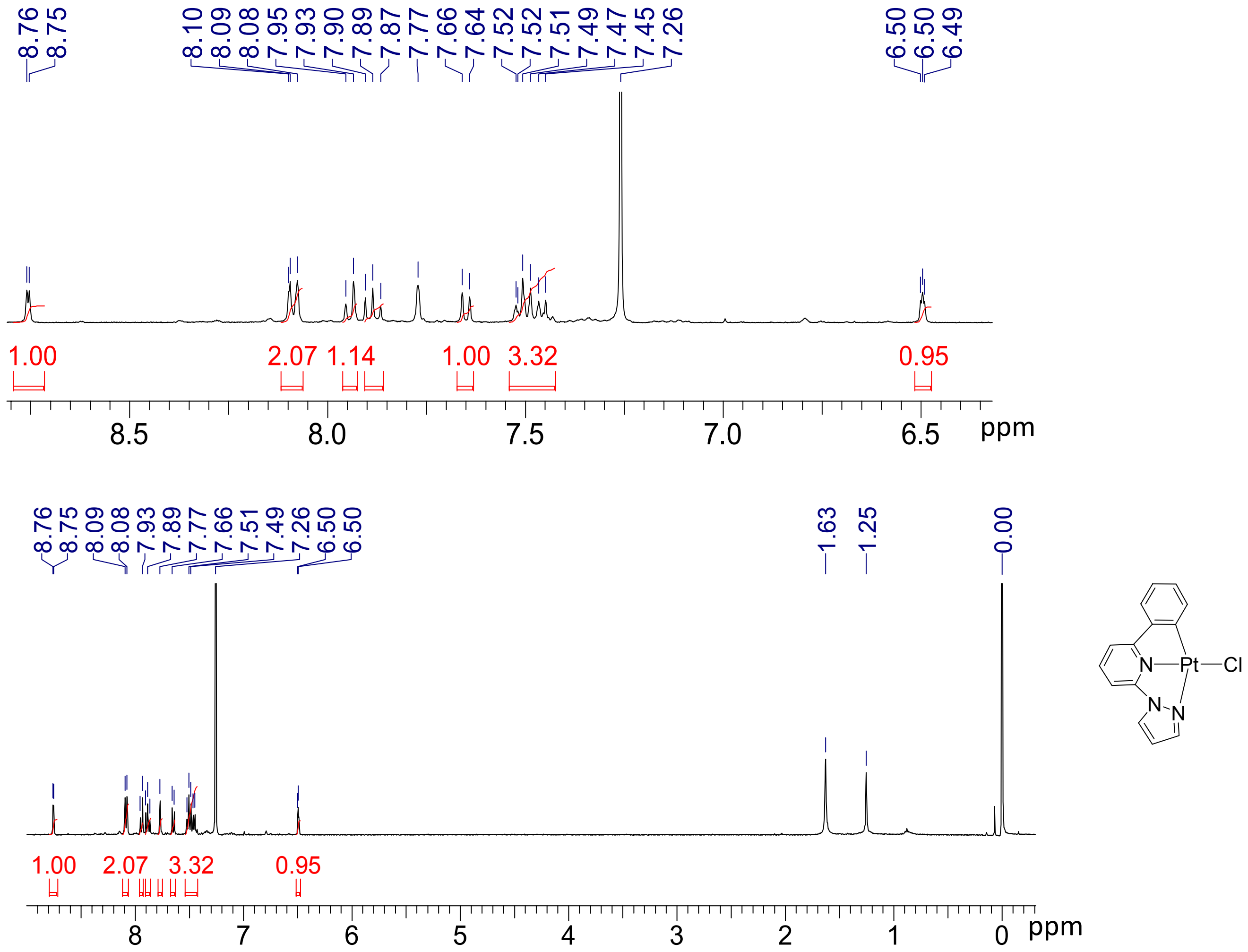


Figure S7. ^{1}H NMR of **Pt-a** in $CDCl_3$/ CD_3OD(400 MHz), 25°C.

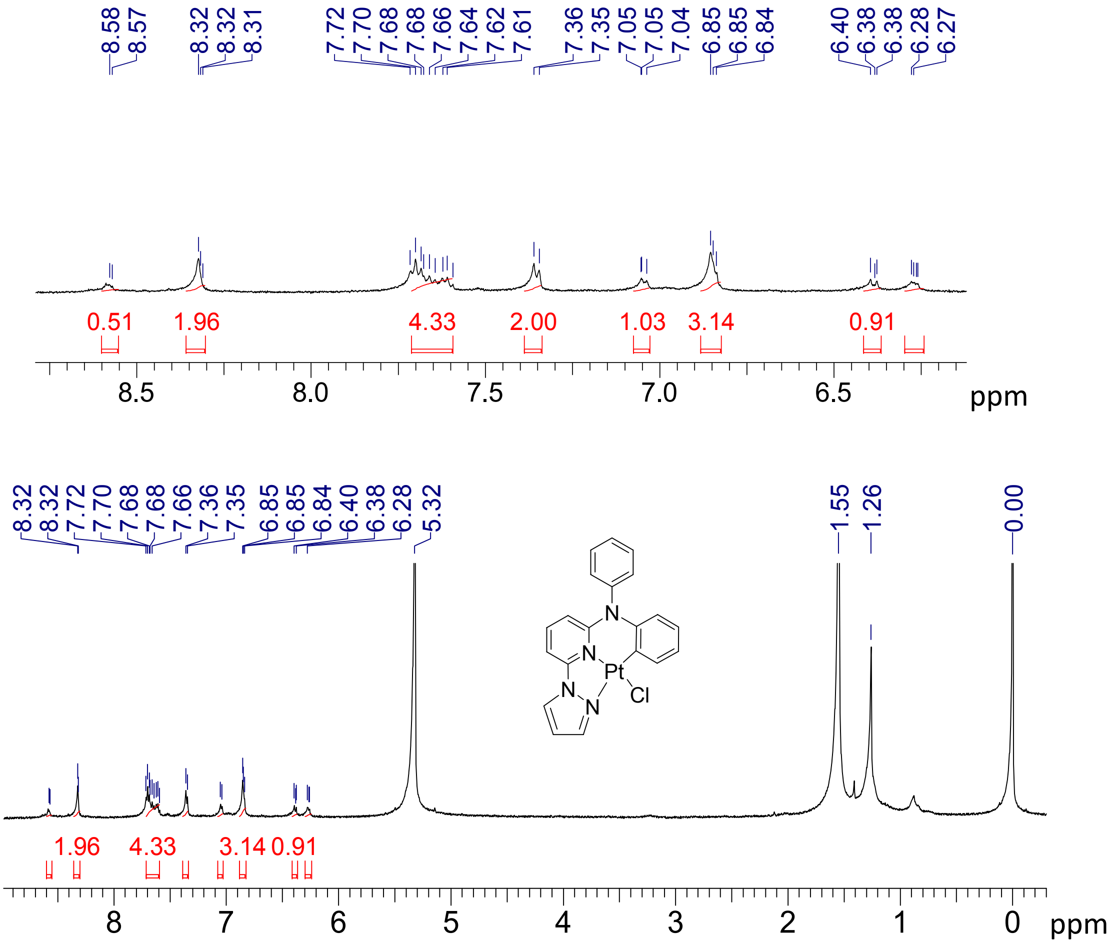


Figure S8. ^{1}H NMR of **Pt-b** in CD_2Cl_2 (500 MHz), 25°C.

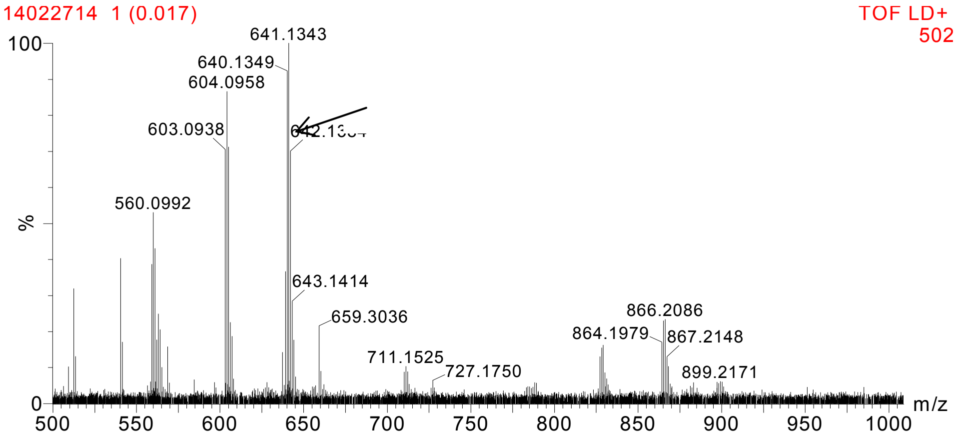


Figure S9. MALDI-HRMS of **Pt-1**.

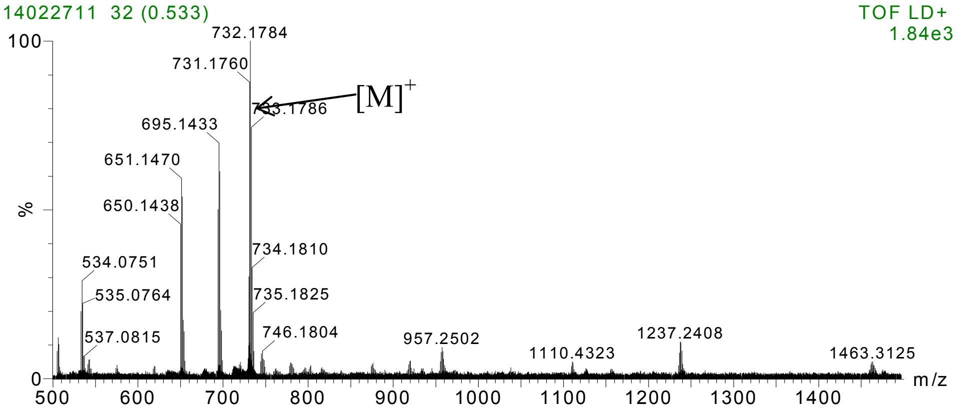


Figure S10. MALDI-HRMS of **Pt-2**.

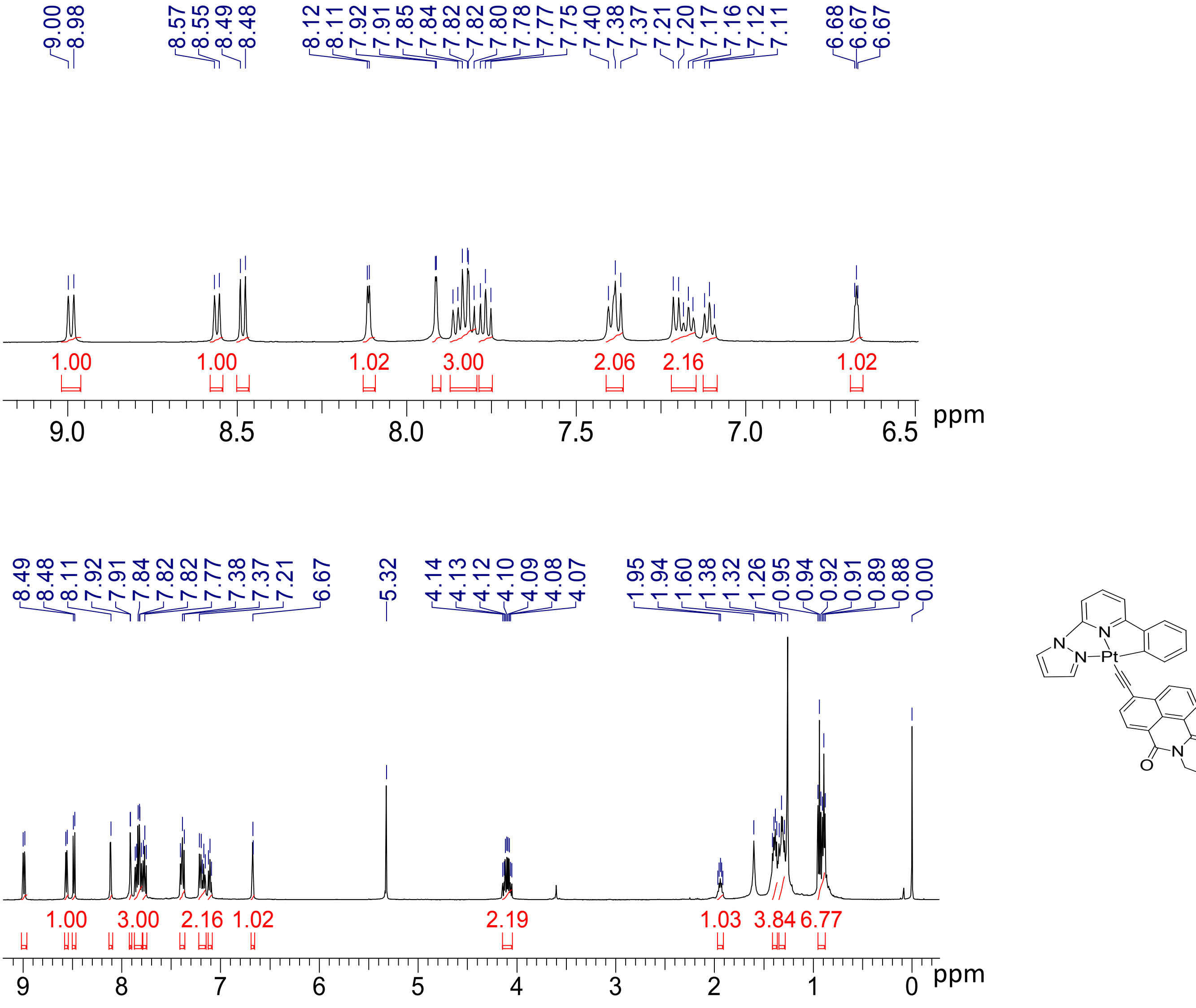


Figure S11. ^{1}H NMR of **Pt-3** in CD_2Cl_2 (400 MHz), 25°C.

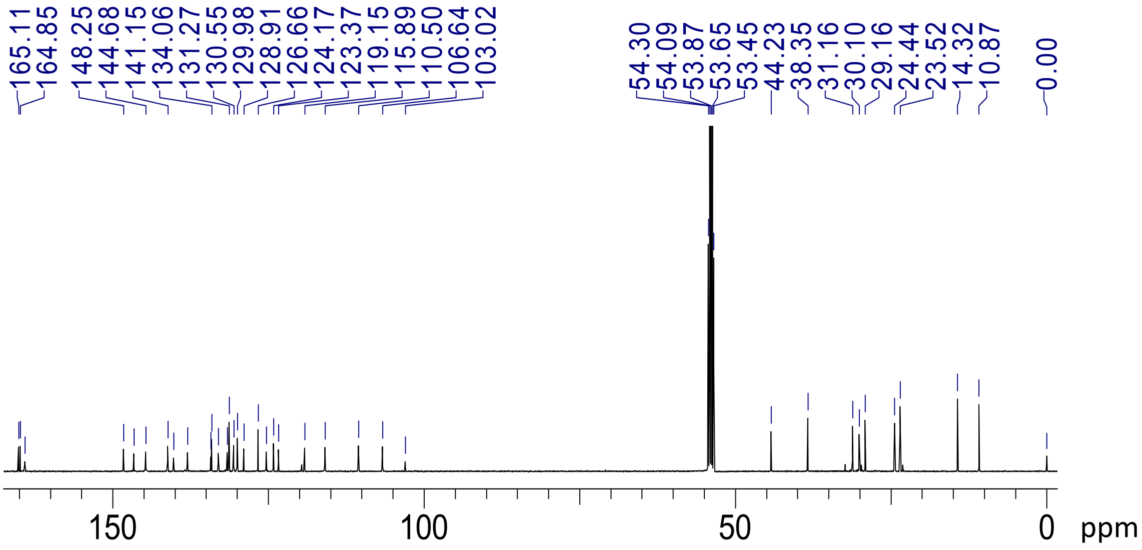


Figure S12. ^{13}C NMR of **Pt-3** in CD_2Cl_2 (100 MHz), 25°C.

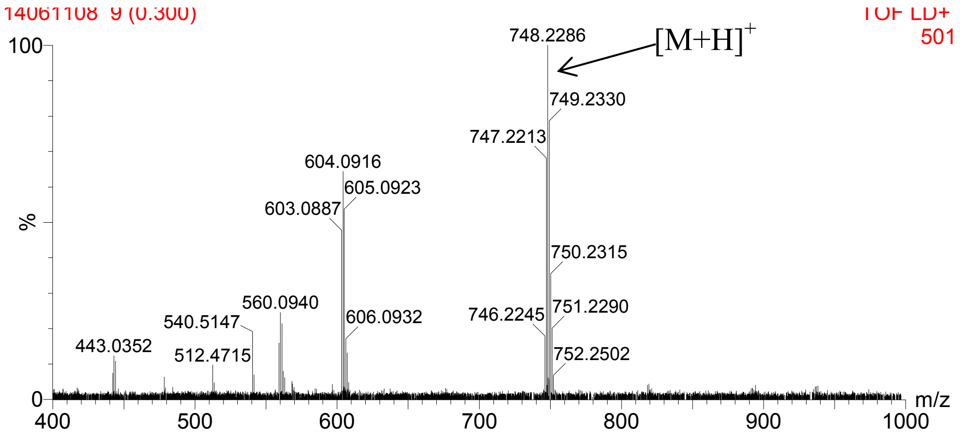


Figure S13. MALDI-HRMS of **Pt-3**.

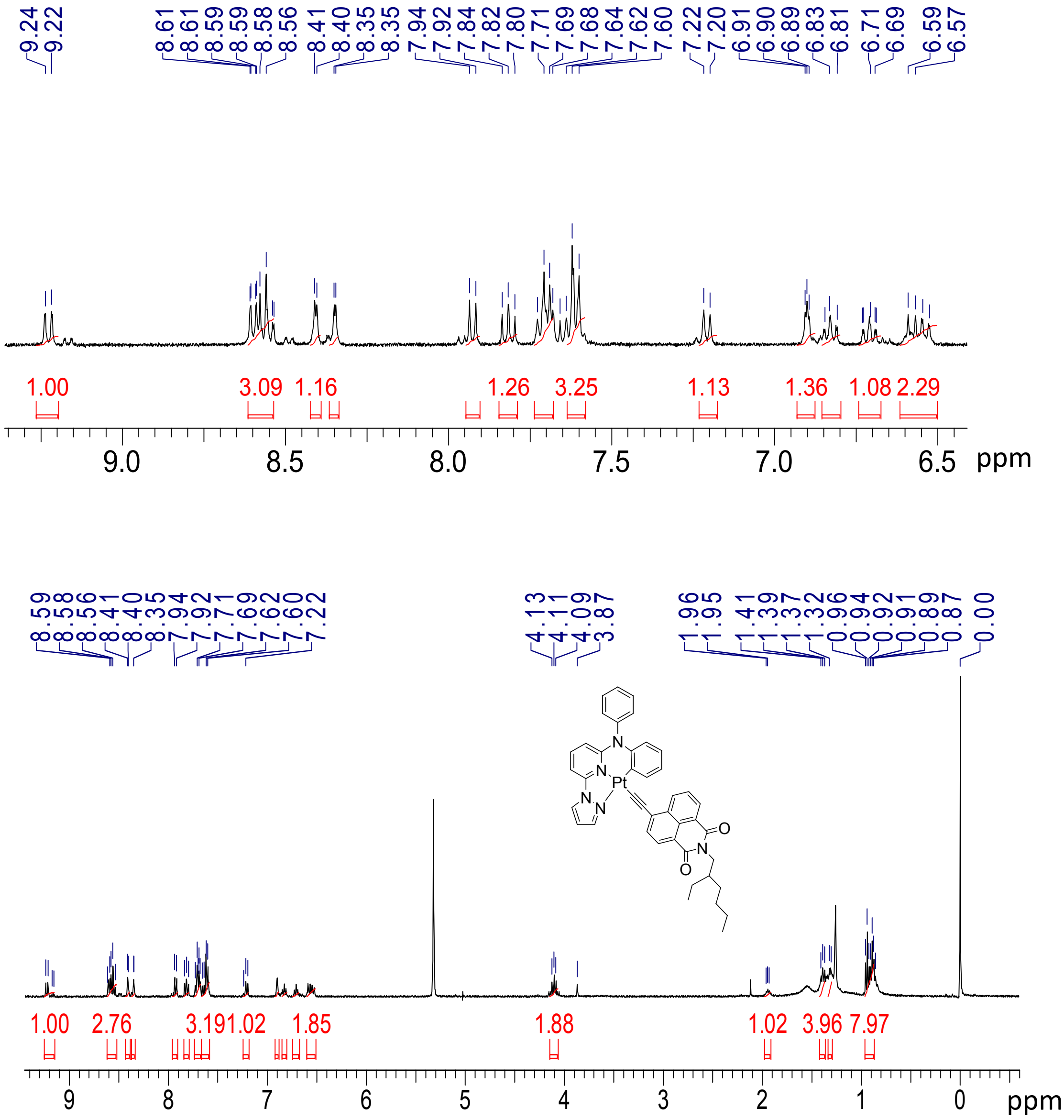


Figure S14. ^{1}H NMR of **Pt-4** in CD_2Cl_2 (400 MHz), 25°C.

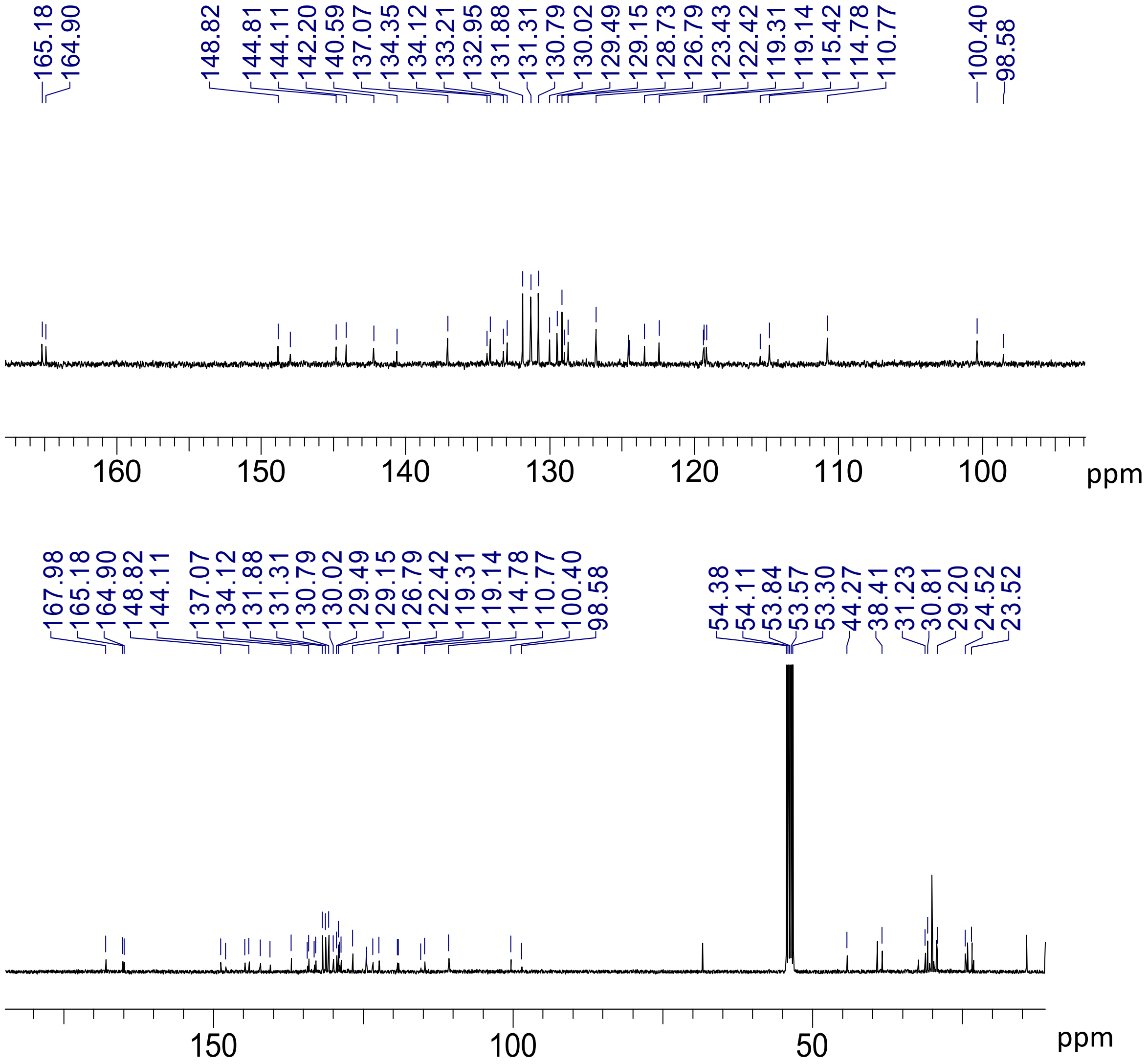


Figure S15. ^{13}C NMR of **Pt-4** in CD_2Cl_2 (100 MHz), 25°C.

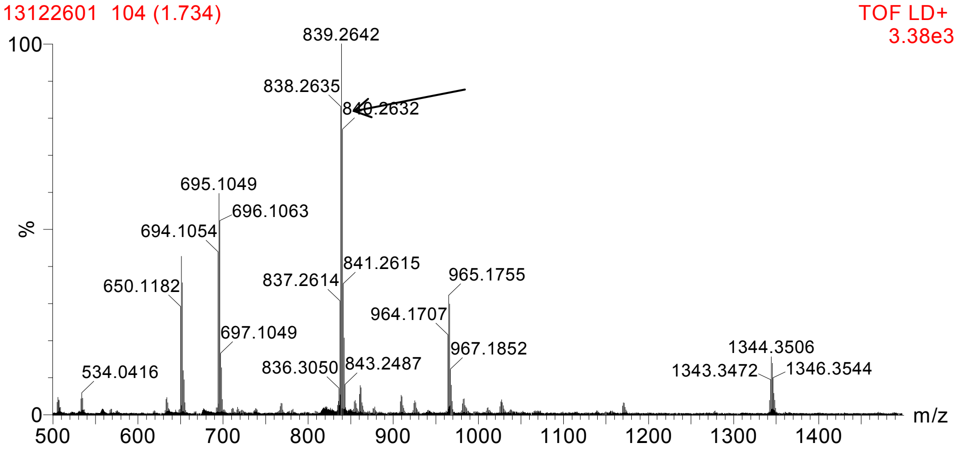


Figure S16. MALDI-HRMS of **Pt-4.**

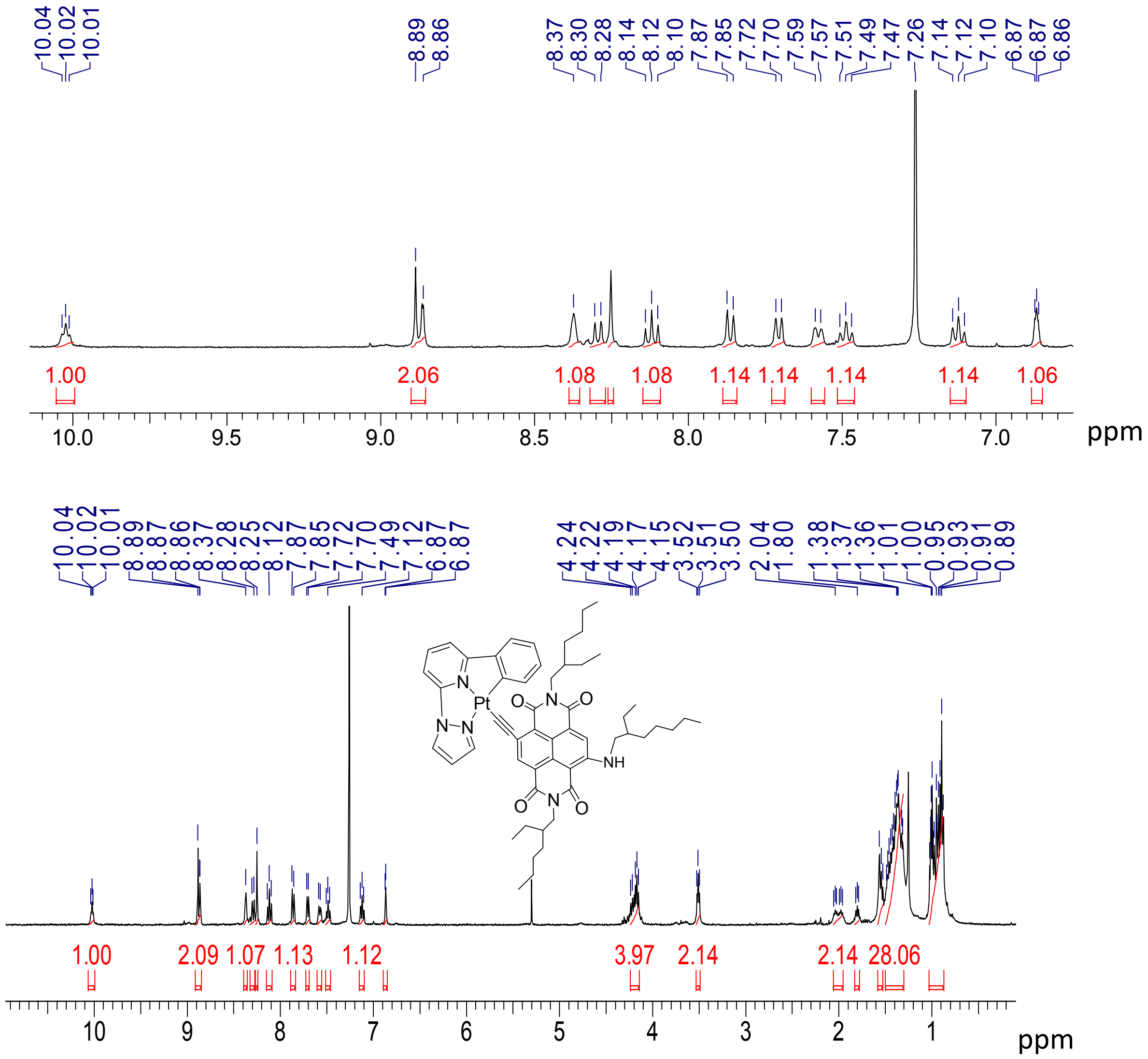


Figure S17. ^{1}H NMR of **Pt-5** in $CDCl_3$ (400 MHz), 25°C.

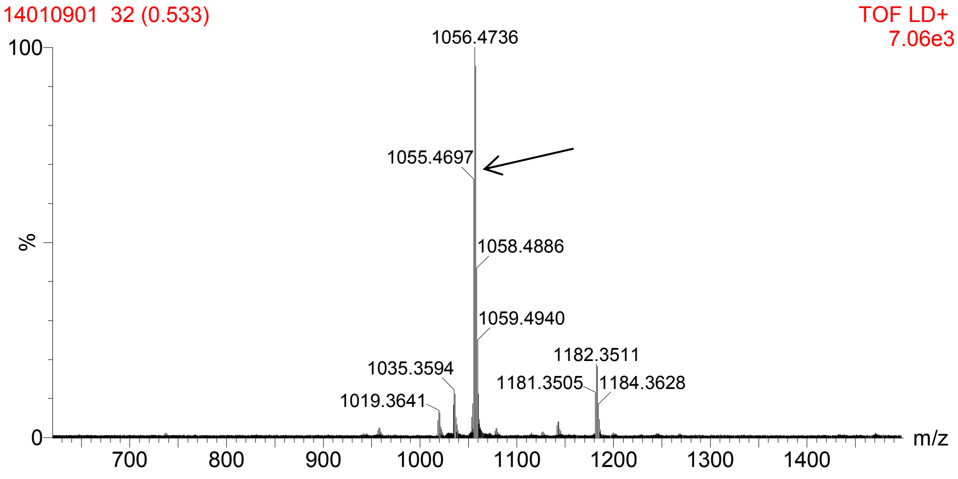


Figure S18. MALDI-HRMS of **Pt-5**.

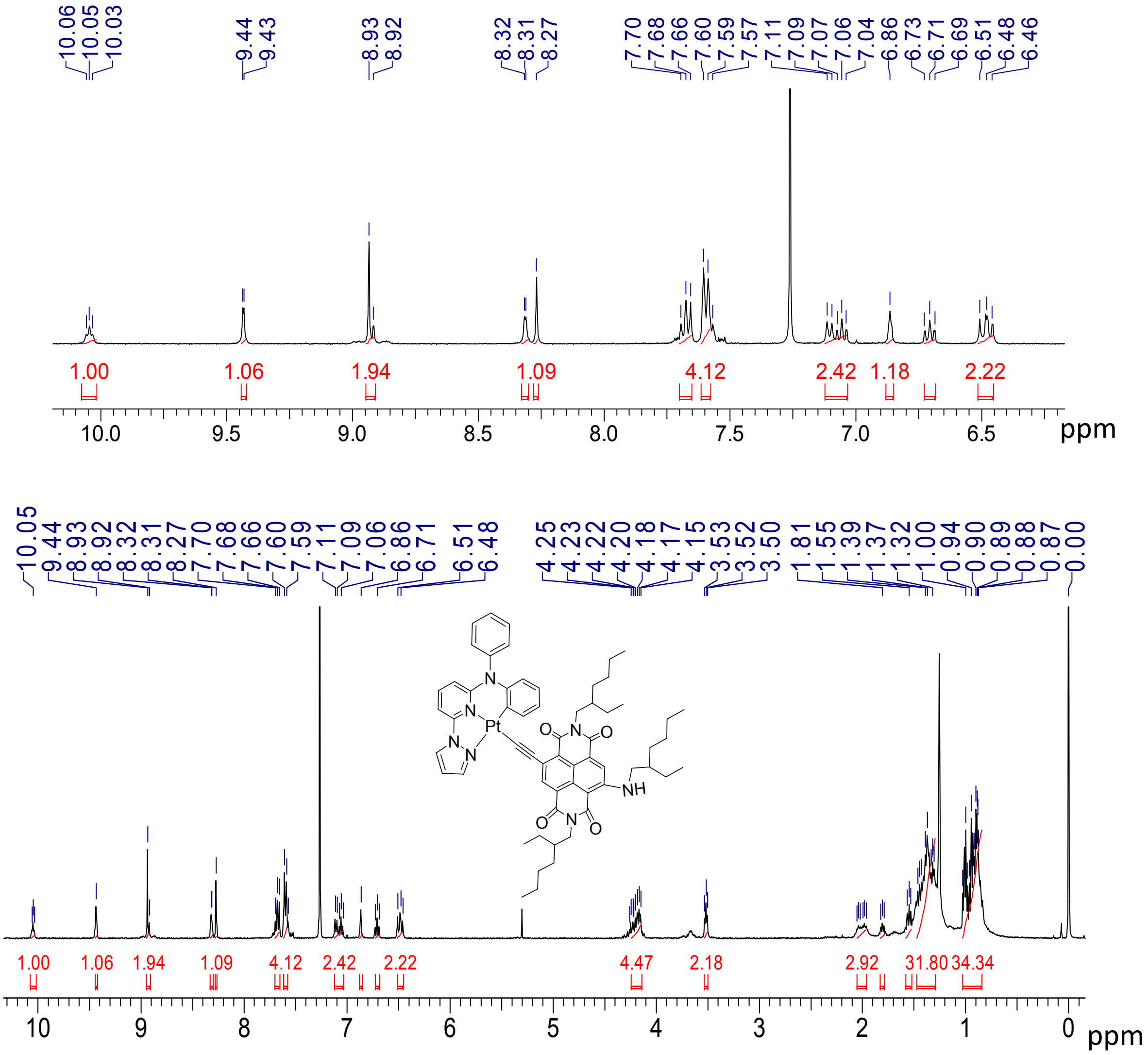


Figure S19. ^{1}H NMR of **Pt-6** in $CDCl_3$ (400 MHz), 25°C.

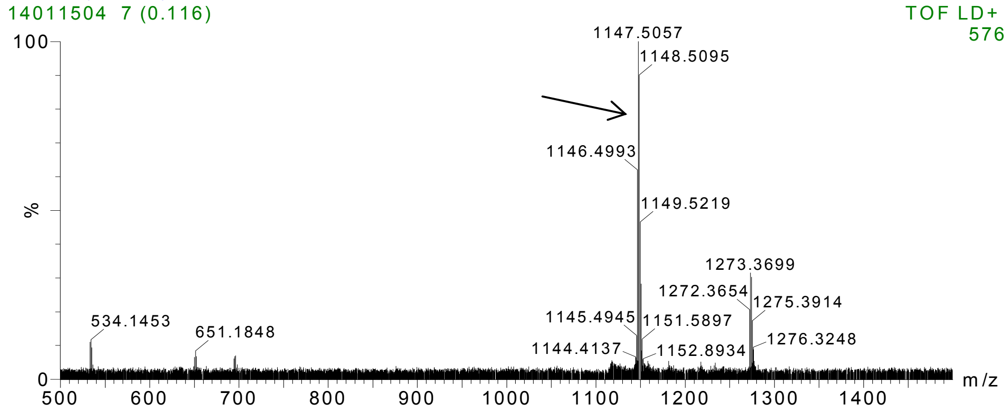


Figure S20. MALDI-HRMS of **Pt-6**.

Electrochemical data of the complexes

Table S1. Parameters used in the calculation of the free energy changes of the potential PET effect with Rehm-Weller Equation [a]

	E_{ox} (eV) [b]	E_{red} (eV) [c]	$E_{0,0}$ (eV) [d]	ΔG° (eV) [e]
Pt-3	+0.77	−1.62	3.12	−0.73
Pt-4	+1.27	−1.61	2.88	0.00
Pt-5	+1.10	−1.16	2.22	0.04
Pt-6	+1.12	−1.15	2.22	−0.05

[a] CH_2Cl_2 as the Solvent. [b] E_{ox}: oxidation potential of the electron donor; [c] E_{red}: reduction potential of the electron acceptor; [d] $E_{0,0}$: excitation energy, which is calculated based on the wavelength of maximum absorption in the visible region; e $\triangle G^{o}$: free energy changes of the potential PET effect with Rehm–Weller Equation.

Steady state absorption and emission spectroscopy

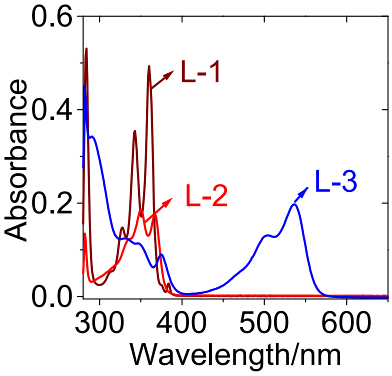


Figure S21. UV-Vis absorption of **L-1**, **L-2** and **L-3**. $c = 1.0 \times 10^{-5}$ M, in Toluene, 20 °C.

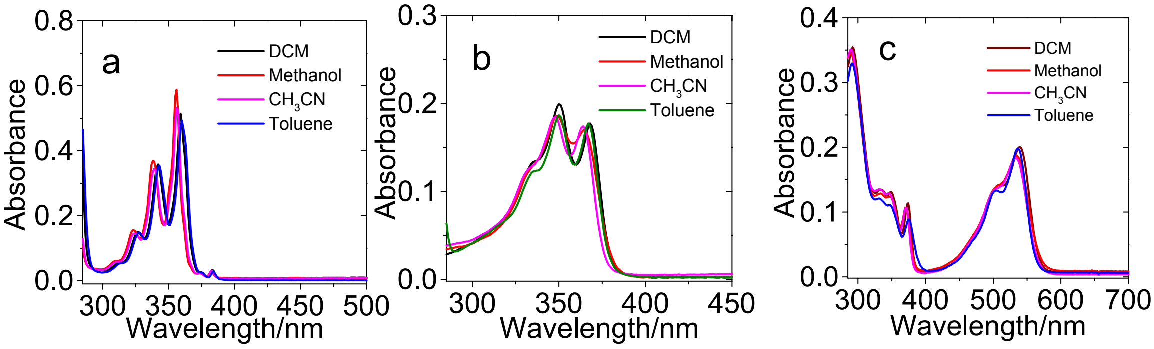


Figure S22. UV-Vis absorption of (a) **L-1**, (b) **L-2**, (c) **L-3**, in DCM, Methanol, CH_3CN and Toluene. $c = 1.0 \times 10^{-5}$ M, 20 °C

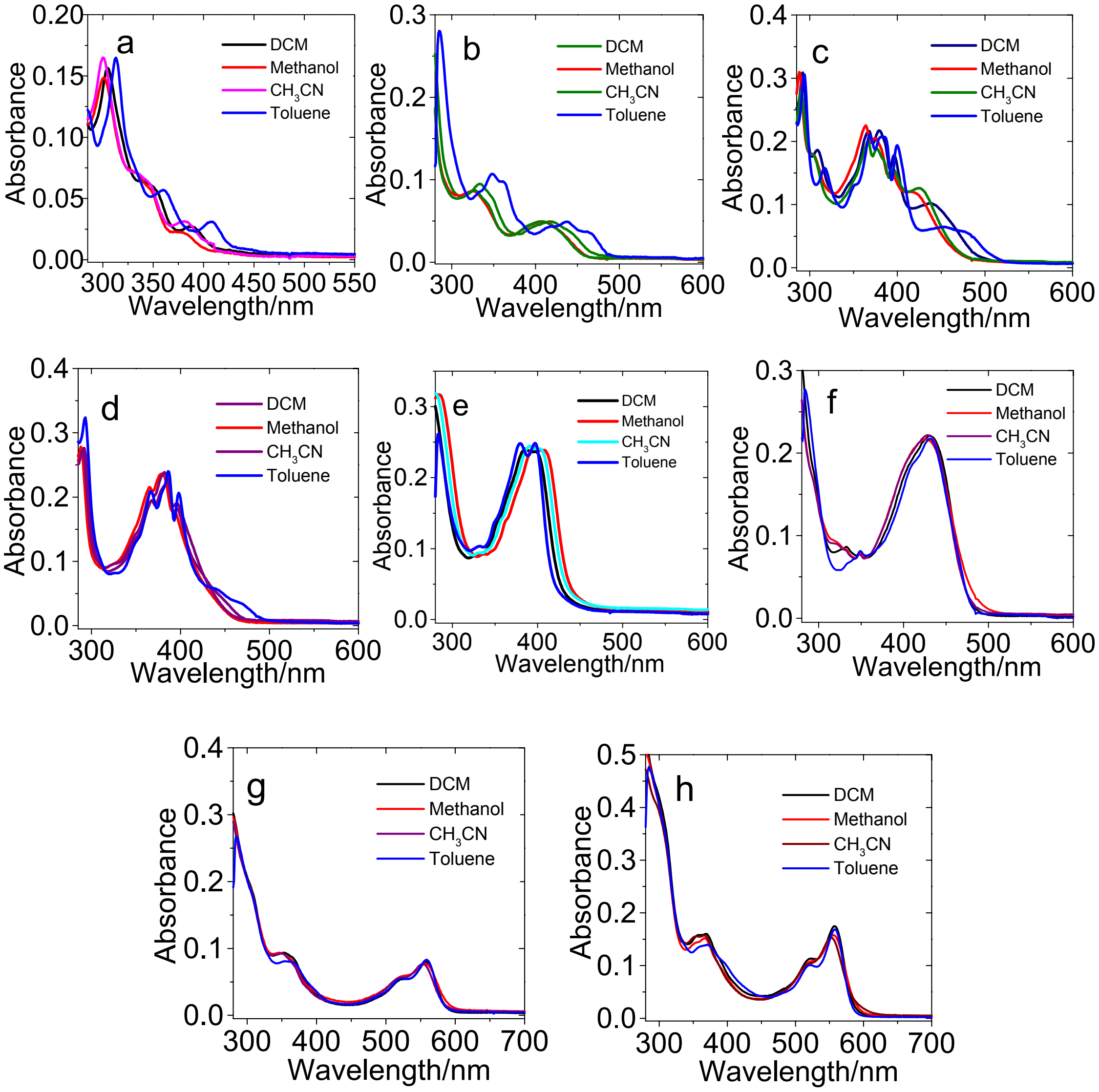


Figure S23. UV-Vis absorption of (a) **Pt-a**, (b) **Pt-b**, (c) **Pt-1**, (d) **Pt-2**, (e) **Pt-3**, (f) **Pt-4**, (g) **Pt-5**, (h) **Pt-6**, in DCM, Methanol , CH_3CN and Toluene. *c* = 1.0×10^{-5} M, 20 °C.

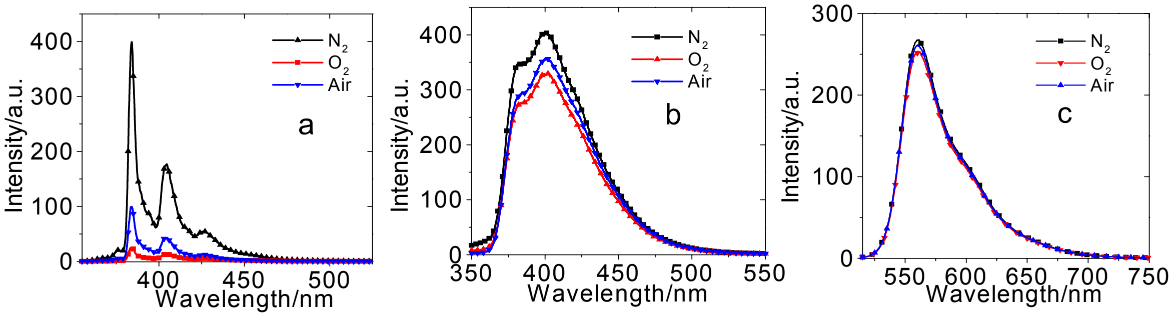


Figure S24. The emission spectra of ligand. (a) **L-1** (λ_{ex} = 350 nm) (b) **L-2** (λ_{ex} = 360 nm), (c) **L-3** (λ_{ex} = 510 nm), under different atmosphere. In Toluene. c = 1.0×10^{-5} M , 20 °C.

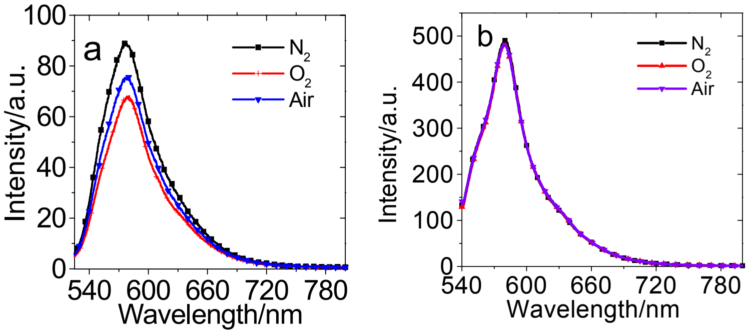


Figure S25. The emission spectra of the Pt(II) complexes. (a) **Pt-5** (λ_{ex} = 515 nm), (b) **Pt-6** (λ_{ex} = 535 nm) under different atmosphere. In Toluene. c = 1.0×10^{-5} M , 20 °C.

Upconversion details

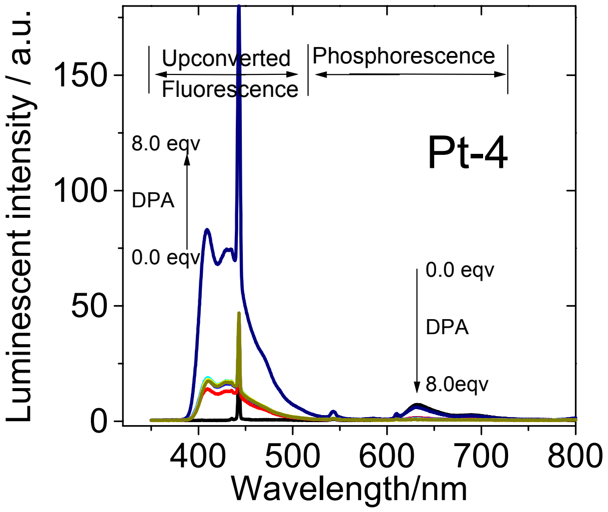


Figure S26. The unconverted DPA fluorescence and the residual phosphorescence of **Pt-4** with increasing DPA concentration following selective excitation at 445 nm. The concentration of complex was 1.0 ×10^{-5} mol dm^{-3} in deaerated Toluene. 20°C.

Table S2. Quenching of the lifetime of the triplet photosensitizers with increasing the concentration of DPA.[a]

c [DPA][b]	0	0.01	0.05	0.1	0.2	0.3	0.5	1.0	2.0	3.0	4.0	6.0	7.0	8.0	10.0
τ_{Pt-4}/μs[c]	90.1	74.0	61.4	54.7	41.9	31.3	18.0	11.3	6.5	4.5	3.5	2.7	–	–	–

[a] In deaerated toluene, pulsed excitation (λ_{ex} = 430 nm), 25 °C. [b] c [DPA] : 10^{-5} M. [c] The lifetime of the triplet excited states of the triplet photosensitizers **Pt-4**.

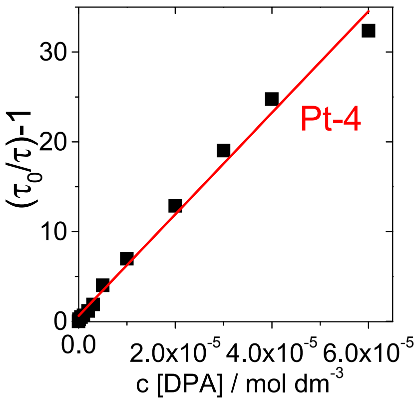
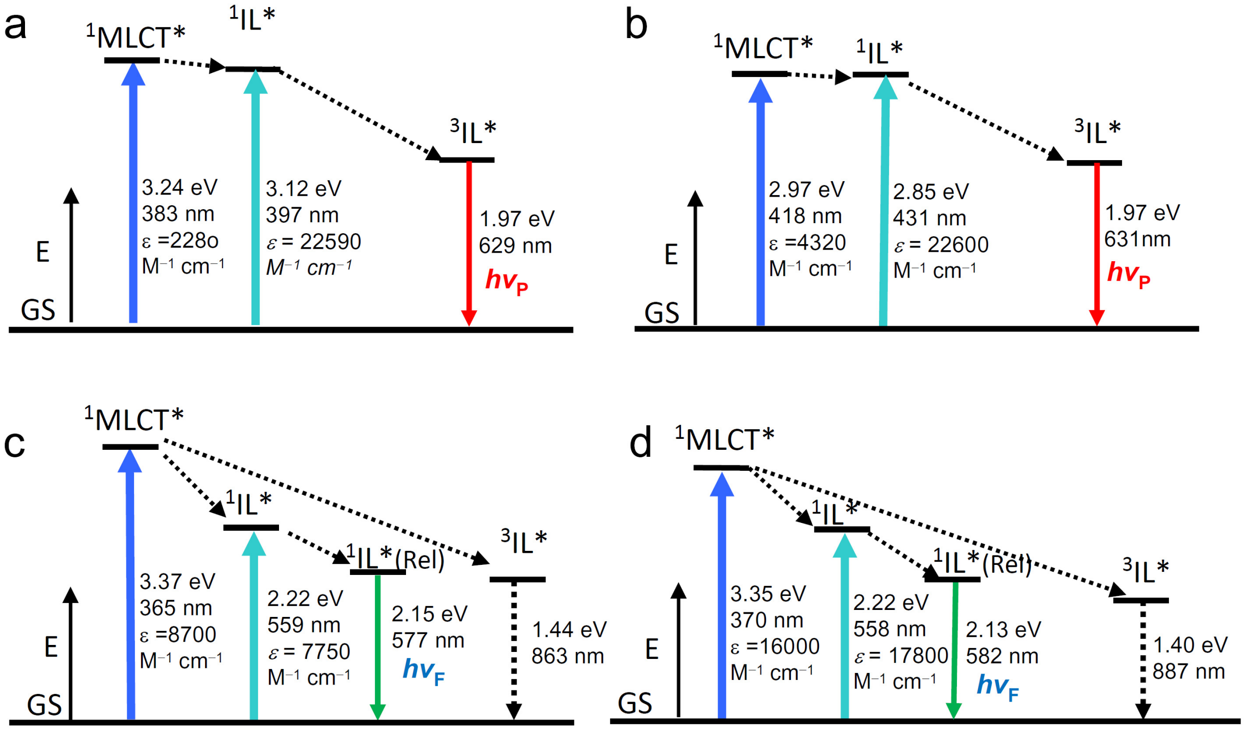


Figure S27. Stern–Volmer plots for lifetime quenching of **Pt-4** with increasing the concentration of DPA after pulsed excitation (λ_{ex} = 430 nm). *c* [sensitizers] = 1.0 × 10^{-5} M in deaerated toluene, 25 °C.

Table S3. Triplet excited state lifetimes (τ_T), Stern-Volmer quenching constant (K_{SV}) and bimolecular quenching constants (k_q) of the Pt(II) sensitizers. In deaerated toluene solution. 25 °C.

	τ_T / μs [b]	K_{sv} / 10^3 M^{-1}	k_q / 10^9 M^{-1} s^{-1}	Φ_{UC} [d]
Pt-4	90.1	565.4	6.3	29.7% [c]

[a] Upconversion quantum yields, with coumarin-6 as the standard (Φ_F =78% in ethanol), [b] Excited with 430 nm. [c] 445 nm (5.2 mW) laser excitation. [d] In toluene.



Scheme S2. Qualitative Jablonski diagram showing the rule for Pt(II) complexes. (a) **Pt-3**, (b) **Pt-4**, (c) **Pt-5**, (d) **Pt-6**. The relative energy levels of the states may vary from complex to complex. GS is the ground state (S_0), ^{1}MLCT* is the metal-to-ligand-charge-transfer excited state (for **Pt-3** and **Pt-4**, the values are approximated with the parent complex **Pt-a** and **Pt-b**, due to overlap of the bands; for **Pt-5** and **Pt-6**, the values are derived from the UV-Vis absorption spectra), ISC is intersystem crossing, ^{3}IL is the arylacetylide localized triplet excited state (for **Pt-3** and **Pt-4**, the energy level was approximated with the phosphorescence emission wavelength; for **Pt-5** and **Pt-6**, the energy levels are the DFT calculation results), ^{1}IL is the arylacetylide-localized singlet excited state, ^{1}IL(Rel) is the vibrationally relaxed arylacetylide-localized singlet excited state (emissive singlet excited state), $h\nu_F$ is the fluorescent emission, $h\nu_P$ is the phosphorescent emission. The spin state of the excited electronic states or the relative energy levels dictates the possibility of a process.

DFT calculations results

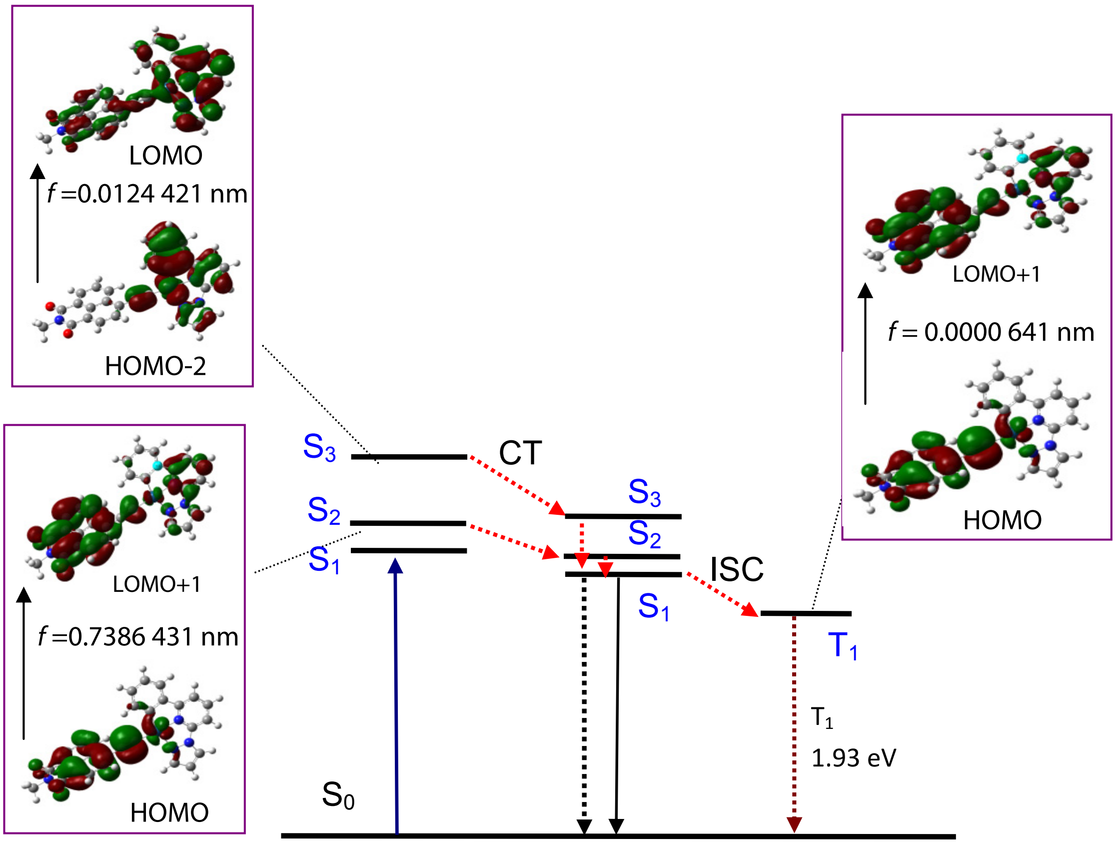


Figure S28. Selected frontier molecular orbitals involved in the excitation and the singlet/triplet excited states of **Pt-3**. CT stands for conformation transformation. The left column is UV/Vis absorption (based on the ground state geometry) and the right column is the triplet excited state (based on the ground state geometry). For clarity, only the selected excited states were presented. The calculations are at the B3LYP/6-31G/LANL2DZ level using Gaussian 09W.

Table S4. Selected Electronic Excitation Energies (eV) and Corresponding Oscillator Strengths (*f*), Main Configurations and CI Coefficients of the Low-lying Electronically Excited States of **Pt-3**. Based on the optimized ground state geometries. Calculated at TDDFT// B3LYP/6-31G/LANL2DZ level.

Pt-3	**Electronic transition**	**TDDFT//B3LYP/6-31G**				
		Energy(eV)[a]	*f*[b]	Composition[c]	CI[d]	Character
Singlet	$S_0 \rightarrow S_1$	2.66eV/467nm	0.0539	H→L	0.6788	MLCT,ILCT
				H→L+1	0.1640	ILCT
	$S_0 \rightarrow S_2$	2.88eV/431nm	0.7386	H→L	0.1603	MLCT,ILCT
				H→L+1	0.6542	ILCT
	$S_0 \rightarrow S_{10}$	3.52eV/352nm	0.1368	H-2→L+2	0.5461	MLCT,ILCT
	$S_0 \rightarrow S1_4$	3.86V/321nm	0.3078	H-4→L	0.6167	MLCT,ILCT
Triplet	$S_0 \rightarrow T_1$	1.93eV/641nm	0.0000	H→L	0.3145	MLCT,ILCT
				H→L+1	0.5954	ILCT
	$S_0 \rightarrow T_2$	2.57eV/482nm	0.0000	H-2→L	0.4977	MLCT,ILCT
				H→L	0.2563	MLCT,ILCT
	$S_0 \rightarrow T_3$	2.63eV/471nm	0.0000	H→L	0.5409	MLCT,ILCT
				H→L+1	0.2782	ILCT

[a] Only selected excited states were considered. The numbers in parentheses are the excitation energy in wavelength. [b] Oscillator strength. [c] H stands for HOMO and L stands for LUMO. Only the main configurations are presented. [d] Coefficient of the wave function for each excitations. The CI coefficients are in absolute values.

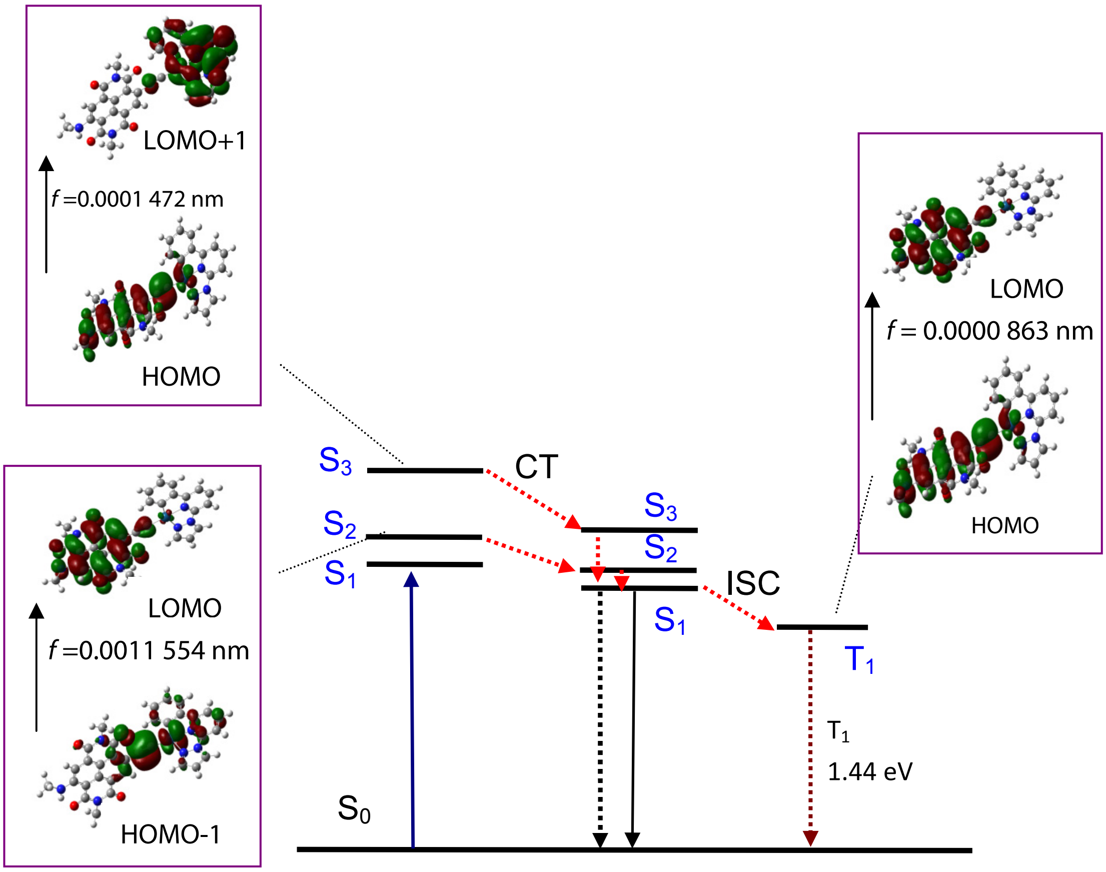


Figure S29. Selected frontier molecular orbitals involved in the excitation and the singlet/triplet excited states of **Pt-5**. CT stands for conformation transformation. The left column is UV/Vis absorption (based on the ground state geometry) and the right column is the triplet excited state (based on the ground state geometry). For clarity, only the selected excited states were presented. The calculations are at the B3LYP/6-31G/LANL2DZ level using Gaussian 09W.

Table S5. Selected Electronic Excitation Energies (eV) and Corresponding Oscillator Strengths (*f*), Main Configurations and CI Coefficients of the Low-lying Electronically Excited States of **Pt-5**. Based on the optimized ground state geometries. Calculated at TDDFT// B3LYP/6-31G/LANL2DZ level.

Pt-5	**Electronic transition**	**TDDFT//B3LYP/6-31G**				
		Energy(eV) [a]	*f* [b]	Composition [c]	CI [d]	Character
Singlet	$S_0 \rightarrow S_1$	2.18eV/569nm	0.3795	H→L	0.7028	MLCT
	$S_0 \rightarrow S_2$	2.24eV/554nm	0.0011	H-1→L	0.6965	MLCT,ILCT
	$S_0 \rightarrow S_6$	2.97eV/417nm	0.2073	H-1→L+1	0.5579	ILCT
	$S_0 \rightarrow S_{14}$	3.49eV/356nm	0.2222	H-2→L+2	0.5849	MLCT
Triplet	$S_0 \rightarrow T_1$	1.44eV/863nm	0.0000	H→L	0.6972	MLCT
	$S_0 \rightarrow T_2$	2.16eV/573nm	0.0000	H-1→L	0.6882	MLCT,ILCT
	$S_0 \rightarrow T_3$	2.42eV/513nm	0.0000	H-6→L	0.6487	MLCT

[a] Only selected excited states were considered. The numbers in parentheses are the excitation energy in wavelength. [b] Oscillator strength. [c] H stands for HOMO and L stands for LUMO. Only the main configurations are presented. [d] Coefficient of the wave function for each excitations. The CI coefficients are in absolute values.

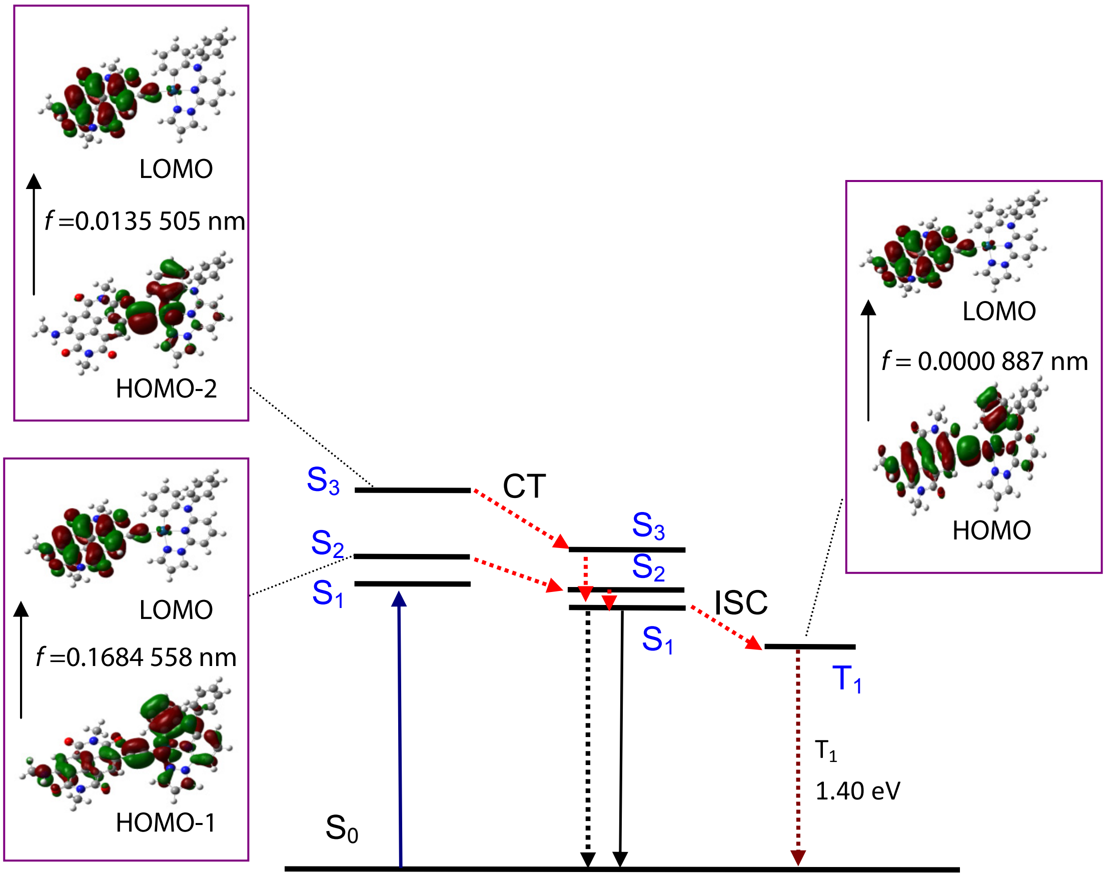


Figure S30. Selected frontier molecular orbitals involved in the excitation and the singlet/triplet excited states of **Pt-6**. CT stands for conformation transformation. The left column is UV/Vis absorption (based on the ground state geometry) and the right column is the triplet excited state (based on the ground state geometry). For clarity, only the selected excited states were presented. The calculations are at the B3LYP/6-31G/LANL2DZ level using Gaussian 09W.

Table S6. Selected Electronic Excitation Energies (eV) and Corresponding Oscillator Strengths (*f*), Main Configurations and CI Coefficients of the Low-lying Electronically Excited States of **Pt-6**. Based on the optimized ground state geometries. Calculated at TDDFT// B3LYP/6-31G/LANL2DZ level.

Pt-6	**Electronic transition**	**TDDFT//B3LYP/6-31G**				
		Energy(eV) [a]	f^b	Composition[c]	CI[d]	Character
Singlet	$S_0 \rightarrow S_1$	2.01eV/617nm	0.2092	H→L	0.6697	MLCT,ILCT
	$S_0 \rightarrow S_2$	2.22eV/558nm	0.1684	H-1→L	0.6059	MLCT,ILCT
	$S_0 \rightarrow S_{14}$	2.46eV/505nm	0.0135	H-2→L	0.6228	ILCT
Triplet	$S_0 \rightarrow T_1$	1.40eV/887nm	0.0000	H→L	0.6333	MLCT,ILCT
	$S_0 \rightarrow T_2$	2.06eV/602nm	0.0000	H-2→L	0.2877	MLCT,ILCT
				H→L	0.2640	MLCT,ILCT
	$S_0 \rightarrow T_3$	2.37eV/522nm	0.0000	H-2→L	0.5288	MLCT,ILCT
				H-1→L	0.2074	MLCT,ILCT

[a] Only selected excited states were considered. The numbers in parentheses are the excitation energy in wavelength. [b] Oscillator strength. [c] H stands for HOMO and L stands for LUMO. Only the main configurations are presented. [d] Coefficient of the wave function for each excitations. The CI coefficients are in absolute values.

Pt-3 (DFT//B3LYP/6-31G(d))

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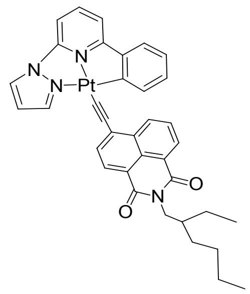

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C	5.93609	-3.95689	-2.84563
C	5.23787	-3.05426	-2.04302
H	7.8816	-4.66782	-3.47761
H	5.38645	-4.66814	-3.47926
H	4.13827	-3.05424	-2.04417
N	7.3298	-2.15274	-1.23739
C	9.49795	-3.05425	-2.03959
C	10.1958	-3.95645	-2.84349
C	10.19536	-2.1523	-1.23606
C	11.59051	-3.95664	-2.84284
H	9.64595	-4.66737	-3.47717
C	11.5905	-2.15196	-1.23627
C	12.28802	-3.05413	-2.03945
H	12.14071	-4.66725	-3.47652
H	12.14009	-1.44069	-0.60288
H	13.38763	-3.05414	-2.03942
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C	5.68885	0.74723	1.02974
C	4.31945	0.38826	0.79577
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H	6.06672	1.47453	1.74043
H	3.45518	0.76324	1.33359
N	6.55698	-0.12994	0.37906
Pt	8.07251	-1.31999	-0.51364
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C	10.61309	4.72332	1.40647
C	10.47484	6.0012	0.80486
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C	10.14469	2.30968	1.45511
C	11.38554	4.57475	2.60466
C	11.52372	3.29691	3.20628
C	10.87589	2.16906	2.5891
C	12.01246	5.70551	3.18981
C	11.12281	7.12903	1.42197

H	8.51121	5.12756	-1.85339
H	8.74651	2.88233	-0.80729
H	9.60627	7.11694	-0.8365
H	10.99506	1.18618	3.07048
O	10.9688	8.40549	0.79601
O	12.76528	5.47661	4.38386
H	12.30287	3.16137	3.97214
C	9.45396	1.09979	0.79886
C	8.76324	-0.1101	0.14261
N	11.85395	6.98843	2.55599
C	12.51344	8.14339	3.1821
H	12.45756	8.05211	4.24674
H	13.53948	8.17513	2.88021
H	12.02332	9.04364	2.87511

Pt-4 (DFT//B3LYP/6-31G(d))

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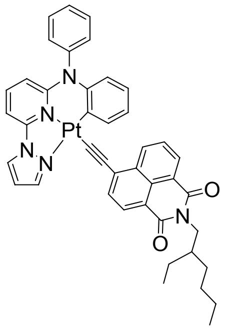

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C	2.71438	-0.83298	2.22691
C	2.95958	-2.2232	1.95011
C	4.01344	-2.54034	1.09267
H	1.88423	-0.58266	2.90329
H	2.34741	-3.02481	2.38847
H	4.2317	-3.59163	0.8554
N	4.47617	0.10659	0.88172
C	3.94189	2.83895	1.44005
C	3.48199	4.2075	1.96244
C	5.12746	2.70217	0.54789
C	3.9719	5.47931	1.66419
H	2.6221	4.09386	2.63843
C	5.58657	4.21655	0.29041
C	5.06327	5.62314	0.80723
H	3.49871	6.36843	2.10556
H	6.44669	4.32989	-0.38521
H	5.44952	6.6256	0.57264
N	5.94111	-1.46179	-0.37565
C	6.51815	-2.51406	-0.86793
C	7.76669	-0.7046	-1.48412
C	7.67784	-2.13329	-1.5831
H	6.01201	-3.47471	-0.78185
H	8.43166	-0.04658	-2.03335
H	8.2376	-2.76713	-2.2626

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Pt	5.39295	1.16876	0.25912
N	2.88003	1.85552	1.99577
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C	10.4942	3.65812	-0.38539
C	10.40615	3.7424	-1.78091
C	11.48132	4.31276	-2.51072
C	12.62905	4.78984	-1.8258
C	12.68415	4.69015	-0.42966
C	9.25548	3.26727	-2.50401
C	11.40813	4.40674	-3.93909
C	10.26045	3.92961	-4.62399
C	9.18618	3.35634	-3.85591
C	12.48338	4.977	-4.66893
C	13.70326	5.36326	-2.59388
H	11.68054	4.05679	1.37551
H	9.66344	3.21688	0.18528
H	13.57149	5.05886	0.10625
H	8.30434	2.99214	-4.40517
O	14.84822	5.83723	-1.88021
O	12.33584	5.03527	-6.09011
H	10.11911	4.22429	-5.67526
C	8.10983	2.64484	-1.68445
C	7.1263	2.11049	-0.98086
N	13.63399	5.45226	-3.94577
C	14.73377	6.03856	-4.72528
H	14.8623	5.48574	-5.63234
H	14.50257	7.05703	-4.95803
H	15.63695	5.99969	-4.15287
C	1.60539	2.13232	2.67367
C	0.44162	2.3096	1.92488
C	1.5591	2.21607	4.0651
C	-0.76822	2.57131	2.56779
H	0.47825	2.2431	0.82789
C	0.34885	2.47839	4.70829
H	2.47624	2.07572	4.65541
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H	-1.68551	2.71123	1.97777
H	0.31261	2.54443	5.80539
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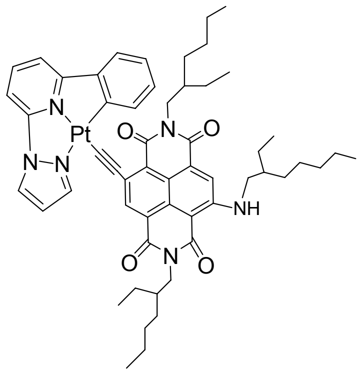
Pt-5 (DFT//B3LYP/6-31G(d))

Charge = 0 Multiplicity = 1



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C	4.92371	15.86752	-2.87388
C	5.77293	16.87722	-2.35118
C	7.15641	16.55994	-2.1104
C	5.24426	18.14704	-2.08571
C	3.05941	17.43069	-2.84481
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C	2.71905	15.10525	-3.65238
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C	-1.53945	7.94344	-8.38325
C	-2.29689	7.07586	-7.59641
C	-2.25628	7.17998	-6.20576
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H	-2.92639	6.30972	-8.07205
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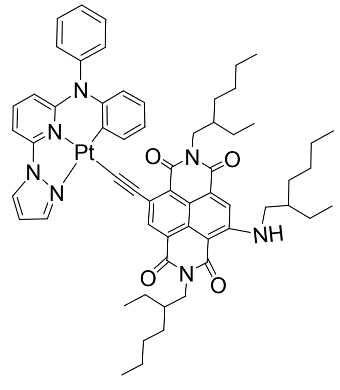
C	0.01522	9.72617	-9.99956
C	0.85568	10.80176	-8.00569
C	0.77229	10.5937	-10.78662
H	-0.61453	8.96017	-10.4749
C	1.61216	11.67012	-8.79316
C	1.5706	11.56601	-10.18348
H	0.73914	10.51238	-11.88276
H	2.24144	12.43628	-8.31762
H	2.16706	12.25017	-10.8042

N	-1.16228	8.55755	-4.22066
C	-1.70086	7.99711	-3.18218
C	-0.49237	9.7855	-2.43794
C	-1.33352	8.70355	-2.01285
H	-2.22786	7.05297	-3.31367
H	0.10181	10.44275	-1.81199
H	-1.4641	8.35181	-0.99499
N	-0.32524	9.77842	-3.82303
Pt	0.07672	9.98079	-5.89847
C	7.00912	10.676	-3.97788
H	6.45953	9.94519	-3.42222
H	6.91888	10.4706	-5.0241
H	8.04025	10.63814	-3.69461
C	9.42725	17.17932	-1.35692
H	9.41944	16.35529	-0.67441
H	9.8219	16.85889	-2.29844
H	10.03878	17.96361	-0.96217
C	3.36235	19.75417	-2.04755
H	3.42258	20.35748	-2.92919
H	2.34038	19.67042	-1.74182
H	3.93274	20.20873	-1.26465

Pt-6 (DFT//B3LYP/6-31G(d))

Charge = 0 Multiplicity = 1

C	6.10621	0.65437	4.39567
C	7.16858	-1.65939	3.78449
C	5.82043	-1.99264	3.65069
C	4.64328	-1.19749	3.87758
C	4.81974	0.13454	4.25305
H	5.68172	-3.04243	3.35402
H	3.62884	-1.60719	3.76562
H	3.94456	0.77436	4.43694
N	7.47517	-0.3083	4.12086
C	9.77049	-1.9216	3.68296
C	10.81778	-2.9838	3.31931
C	10.16156	-0.52572	4.02766
C	12.21001	-2.89388	3.32789
H	10.32949	-3.93275	3.05402
C	11.76415	-0.56145	3.99871
C	12.82917	-1.68971	3.6637
H	12.81947	-3.77174	3.06871
H	12.25216	0.38767	4.26358
H	13.92648	-1.61892	3.66997



N	6.67692	1.95865	4.76162
C	5.95514	3.00145	5.03402
C	8.1361	3.67594	4.99933
C	6.79027	4.13115	5.20034
H	4.8887	2.86611	5.20956
H	9.0524	4.22131	5.19884
H	6.48978	5.08135	5.62887
N	8.22572	1.96225	4.63709
Pt	8.85862	0.34106	4.2648
N	8.42984	-2.69965	3.65447
C	14.36027	4.33724	1.62003
C	14.68273	4.79081	2.90558
C	13.91421	4.3443	4.01189
C	12.83273	3.44816	3.80848
C	12.5376	3.01457	2.50961
C	15.77356	5.69961	3.14394
C	14.23031	4.79809	5.33422
C	15.3118	5.69414	5.53762
C	16.07266	6.12919	4.39548
C	15.60698	6.12771	6.83657
C	13.78442	4.80484	7.7261
C	13.46184	4.35147	6.44058
C	12.37091	3.44275	6.20215
C	12.07178	3.01323	4.95062
H	11.78662	3.10774	7.07303
H	16.35762	6.0347	2.27297
O	16.69534	7.03069	7.04872
O	13.01427	4.35905	8.8455
O	11.4489	2.11201	2.29744
O	15.13043	4.78319	0.5007
N	14.84757	5.68437	7.91674
N	13.29715	3.45778	1.42939
H	16.8355	8.02116	5.13279
N	17.24041	7.10177	4.64459
C	10.90336	2.04153	4.70123
C	9.99669	1.28752	4.50771
C	15.17152	6.14991	9.27293
H	16.16247	5.83849	9.52972
H	15.11319	7.21778	9.30689
H	14.4747	5.73232	9.96932
C	17.90607	7.43707	3.37756
H	18.30252	6.54652	2.93637
H	17.1982	7.88146	2.70947
H	18.70201	8.12729	3.56457
C	12.97284	2.99245	0.07323

H	12.88947	1.9257	0.07258
H	12.04438	3.42295	-0.23906
H	13.74861	3.28999	-0.60098
C	8.18297	-4.14377	3.5341
C	8.14524	-4.94229	4.67752
C	7.98488	-4.71523	2.27736
C	7.91005	-6.31244	4.56382
H	8.301	-4.49147	5.6683
C	7.75009	-6.08605	2.16353
H	8.01398	-4.08579	1.37611
C	7.71285	-6.8844	3.30668
H	7.88045	-6.94198	5.46489
H	7.59399	-6.53642	1.17252
H	7.52785	-7.9648	3.2173