Electronic Supplementary Material (ESI) for Dalton Transactions.

Efficiently luminescent heteroleptic neutral platinum(II) complexes based on N^O and N^P benzimidazole ligands

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Synthesis

General syntheses of the ligands (1a-4a and 1b-4b). The corresponding 2-nitroaniline (5 mmol), 2-(diphenylphosphino)benzaldehyde (1.74 g, 6 mmol) and sodium hydrosulfite (3.48 g, 20 mmol) in a 5:1 (v/v) mixture of the ethanol and water were heated at 75°C for 5 h. The mixture was concentrated under reduced pressure and was extracted with ethyl acetate. Further, the crude product was purified by column chromatography with ethyl acetate/petroleum ether as the eluent to give the pure white solid 1a-4a.

The compound 1a-4a (2 mmol) and trichlorosilane (0.81 g, 6 mmol) in anhydrous toluene were heated at 120°C for 6 h under an argon atmosphere. The mixture was naturally cooled down to room temperature, and the resulting white precipitate was collected by quickly filtered under reduced pressure, then dried under vacuum to obtain the ligands 1b-4b.

1a: Yield: 47%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 13.37 (s, 1H; N-H), 8.63-8.52 (m, 1H; Ar-H), 7.72 (t, *J* = 7.7 Hz, 1H; Ar-H), 7.68-7.63 (m, 1H; Ar-H), 7.63-7.52 (m, 4H; Ar-H), 7.49-7.40 (m, 3H; Ar-H), 7.40-7.30 (m, 5H; Ar-H), 7.20-7.08 (m, 3H; Ar-H). ^{31}P NMR (162 MHz, $CDCl_3$) δ = 37.80 (s). elemental analysis calcd (%) for $C_{25}H_{19}N_2OP$: C 76.13, H 4.86, N 7.10; found: C 76.08, H 4.80, N 7.14.

2a: Yield; 43%; ^{1}H NMR (400 MHz, DMSO-d_6) δ = 13.38 (s, 1H; N-H), 8.34 (dd, *J* = 7.5, 4.1 Hz, 1H; Ar-H), 7.81 (t, *J* = 7.6 Hz, 1H; Ar-H), 7.64-7.56 (m, 5H; Ar-H), 7.55-7.49 (m, 2H; Ar-H), 7.49-7.42 (m, 4H; Ar-H), 7.39 (d, *J* = 8.7 Hz, 1H; Ar-H), 7.30 (dd, *J* = 14.6, 7.6 Hz, 1H; Ar-H), 7.04 (s, 1H; Ar-H), 6.86-6.70 (m, 1H; Ar-H), 3.76 (s, 3H; $-OCH_3$). ^{31}P NMR (162 MHz, DMSO-d_6) δ = 34.41 (s). elemental analysis calcd (%) for $C_{26}H_{21}N_2O_2P$: C 73.58, H 4.99, N 6.60; found: C 73.52, H 5.14, N 6.55.

3a: Yield: 44%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 13.82 (s, 1H; N-H), 8.63-8.55 (m, 1H; Ar-H), 7.93 (s, 1H; Ar-H), 7.79-7.68 (m, 2H; Ar-H), 7.65-7.50 (m, 4H; Ar-H), 7.50-7.34 (m, 8H; Ar-H), 7.16 (dd, *J* = 15.0, 7.7 Hz, 1H; Ar-H). ^{31}P NMR (162 MHz, $CDCl_3$) δ = 38.16 (s). elemental analysis calcd (%) for $C_{26}H_{18}F_3N_2OP$: C 67.53, H 3.92, N 6.06; found: C 67.47, H 3.88, N 6.00.

4a: Yield: 41%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 13.49 (s, 1H; N-H), 8.83-8.47 (m, 1H; Ar-H), 7.75-7.66 (m, 1H; Ar-H), 7.66-7.52 (m, 4H; Ar-H), 7.50-7.42 (m, 2H; Ar-H), 7.42-7.27 (m, 5H; Ar-H), 7.18-7.00 (m, 3H; Ar-H), 6.65-6.55 (m, 1H; Ar-H), 3.98 (s, 3H; $-OCH_3$). ^{31}P NMR (162 MHz, $CDCl_3$) δ = 38.28 (s). elemental analysis calcd (%) for $C_{26}H_{21}N_2O_2P$: C 73.58, H 4.99, N

6.60; found: C 73.49, H 5.02, N 6.55.

1b: Yield: 81%; ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.93 (s, 1H; N-H), 7.81-7.75 (m, 2H; Ar-H), 7.74-7.67 (m, 2H; Ar-H), 7.65-7.45 (m, 3H; Ar-H), 7.40-7.30 (m, 6H; Ar-H), 7.29-7.12 (m, 5H; Ar-H). ^{31}P NMR (162 MHz, DMSO-d_6) δ = -12.26 (s). elemental analysis calcd (%) for $C_{25}H_{19}N_2P$: C 79.35, H 5.06, N 7.40; found: C 79.21, H 5.17, N 7.31.

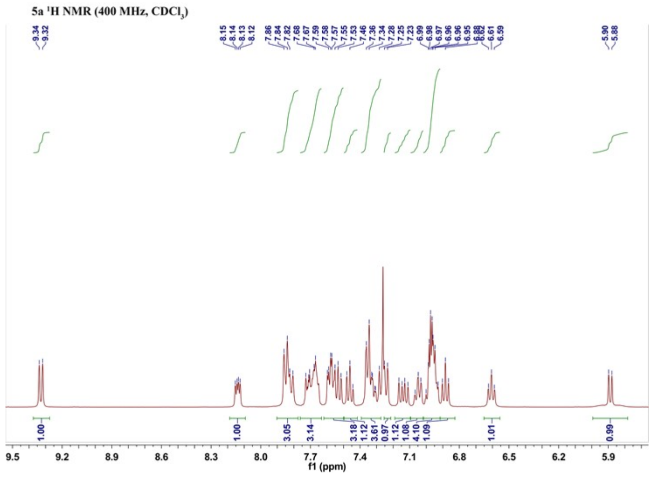
2b: Yield: 80%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.37 (s, 1H; N-H), 7.67 (d, *J* = 9.0 Hz, 1H; Ar-H), 7.47-7.37 (m, 3H; Ar-H), 7.36-7.27 (m, 10H; Ar-H), 7.25-7.23 (m, 1H; Ar-H), 7.15-7.09 (m, 1H; Ar-H), 7.02 (dd, *J* = 9.0, 2.3 Hz, 1H; Ar-H), 3.81 (s, 3H; -OCH_3). ^{31}P NMR (162 MHz, $CDCl_3$) δ = -12.71 (s). elemental analysis calcd (%) for $C_{26}H_{21}N_2OP$: C 76.46, H 5.18, N 6.86; found: C 76.61, H 5.04, N 6.67.

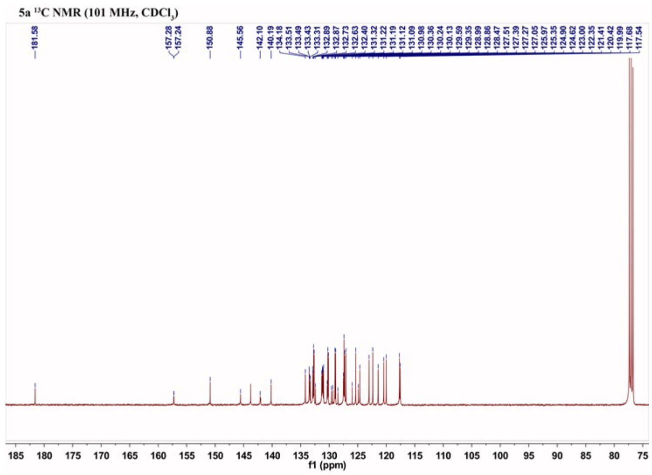
3b: Yield: 75%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.13 (s, 1H; N-H), 7.92 (d, *J* = 8.6 Hz, 1H; Ar-H), 7.80 (dd, *J* = 7.2, 3.4 Hz, 1H; Ar-H), 7.51 (d, *J* = 8.7 Hz, 1H; Ar-H), 7.37 (t, *J* = 7.5 Hz, 1H; Ar-H), 7.30-7.27 (m, 1H; Ar-H), 7.26-7.10 (m, 12H; Ar-H). ^{31}P NMR (162 MHz, $CDCl_3$) δ = -11.90 (s). elemental analysis calcd (%) for $C_{26}H_{18}F_3N_2P$: C 69.95, H 4.06, N 6.28; found: C 70.11, H 4.21, N 6.22.

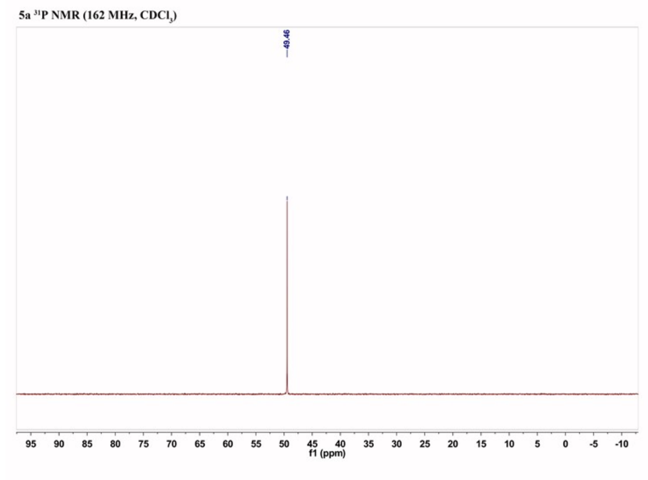
4b: Yield: 77%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.35 (s, 1H; N-H), 7.40 (tt, *J* = 5.8, 2.9 Hz, 1H; Ar-H), 7.30-7.27 (m, 3H; Ar-H), 7.25-7.15 (m, 7H; Ar-H), 7.13-7.04 (m, 4H; Ar-H), 7.02-6.96 (m, 1H; Ar-H), 6.60 (d, *J* = 8.5 Hz, 1H; Ar-H), 3.90 (s, 3H; -OCH_3). ^{31}P NMR (162 MHz, $CDCl_3$) δ = -10.98 (s). elemental analysis calcd (%) for $C_{26}H_{21}N_2OP$: C 76.46, H 5.18, N 6.86; found: C 76.30, H 5.32, N 6.74.

General syntheses of the Pt(bt)(N^O) and Pt(bt)(N^P) complexes (5a-8a and 5b-8b). 2-Phenylbenzothiazole (1.27 g, 6 mmol) and K_2PtCl_4 (1.22 g, 3 mmol) in 2-ethoxyethanol (15 mL) and water (5 mL) was heated at 80°C for 16 h under an argon atmosphere. The mixture was naturally cooled down to room temperature, and filtered to collect the precipitate. The precipitate was washed with methanol, then dried under vacuum to give the μ-chlorobridged cyclometalated platinumdimer as a yellow solid. The prepared μ-chlorobridged dimer $[Pt(bt)Cl]_2$ (0.88 g, 1 mmol), corresponding ancillary ligand (1a-4a and 1b-4b) (2 mmol) and sodium carbonate (1.06 g, 10 mmol) in 2-ethoxyethanol (30 ml) were heated at 120° for 24 h under the protection of argon. The mixture was concentrated under reduced pressure and was extracted with dichloromethane. Further, the pure product (**5a-8a** and **5b-8b**) was obtained by column chromatography with ethyl acetate/dichloromethane as the eluent.

Complex 5a: Yield: 35%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.33 (d, *J* = 8.2 Hz, 1H; Ar-H), 8.14 (dd, *J* = 7.4, 4.0 Hz, 1H; Ar-H), 7.90-7.77 (m, 3H; Ar-H), 7.76-7.63 (m, 3H; Ar-H), 7.62-7.50 (m, 3H; Ar-H), 7.46 (t, *J* = 7.2 Hz, 1H; Ar-H), 7.39-7.27 (m, 4H; Ar-H), 7.25-7.21 (m, 1H; Ar-H), 7.14 (dd, *J* = 14.2, 7.6 Hz, 1H; Ar-H), 7.09-7.01 (m, 1H; Ar-H), 7.02-6.92 (m, 4H; Ar-H), 6.88 (t, *J* = 7.4 Hz, 1H; Ar-H), 6.61 (t, *J* = 7.1 Hz, 1H; Ar-H), 5.89 (d, *J* = 7.8 Hz, 1H; Ar-H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 181.58, 157.26, 150.88, 145.56, 143.77, 142.10, 140.19, 134.18, 133.43, 132.70, 131.15, 130.24, 129.59, 129.35, 128.92, 128.47, 127.39, 127.05, 125.97, 125.35, 124.90, 124.62, 123.00, 122.35, 121.41, 120.42, 119.99, 117.61. ^{31}P NMR (162 MHz, $CDCl_3$) δ = 49.46 (s). elemental analysis calcd (%) for $C_{38}H_{26}N_3OPPtS$: C 57.14, H 3.28, N 5.26; found: C 57.10, H 3.23, N 5.30. LRMS (ESI): m/z calcd for $C_{38}H_{26}N_3OPPtS+H^+$: 799.1 $[M+H]^+$; found: 799.1.

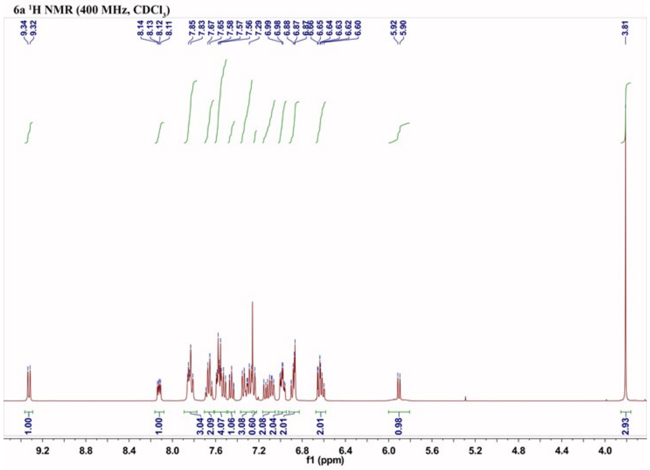




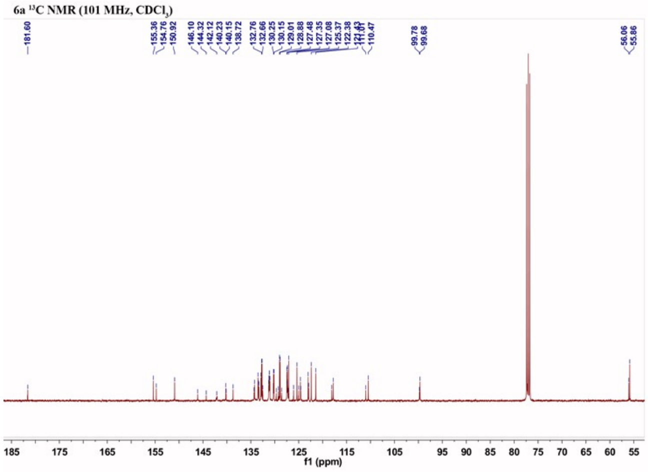


Complex 6a: Yield: 29%; ^1H NMR (400 MHz, $CDCl_3$) δ = 9.33 (d, J = 8.1 Hz, 1H; Ar-H), 8.12

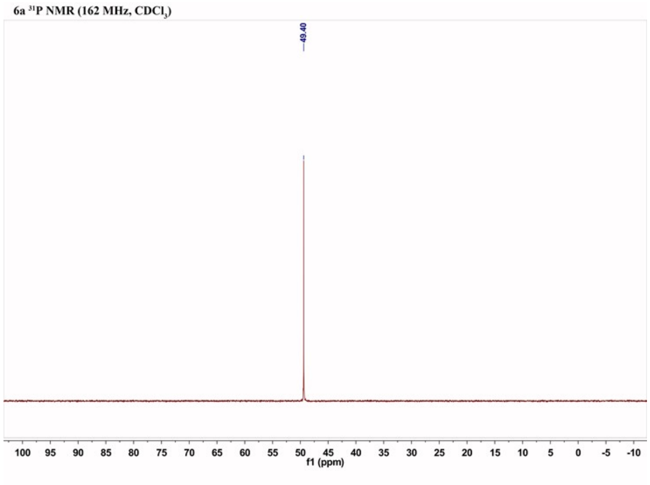
(dd, J = 7.2, 4.1 Hz, 1H; Ar-H), 7.89-7.77 (m, 3H; Ar-H), 7.70-7.62 (m, 2H; Ar-H), 7.61-7.50 (m, 4H; Ar-H), 7.49-7.42 (m, 1H; Ar-H), 7.37-7.26 (m, 3H; Ar-H), 7.25-7.22 (m, 1H; Ar-H), 7.17-7.07 (m, 2H; Ar-H), 6.98 (td, J = 7.6, 3.4 Hz, 2H; Ar-H), 6.92-6.83 (m, 2H; Ar-H), 6.67-6.58 (m, 2H; Ar-H), 5.92 (dd, J = 13.7, 7.9 Hz, 1H; Ar-H), 3.81 (s, 3H; $-OCH_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 181.60, 155.36, 154.76, 150.92, 146.10, 144.32, 142.12, 140.19, 138.72, 134.27, 133.42, 132.70, 131.15, 130.20, 129.69, 129.28, 128.95, 128.57, 127.30, 126.07, 125.37, 125.00, 124.61, 122.99, 122.38, 121.43, 118.09, 117.78, 111.01, 110.47, 99.73, 56.06, 55.86. ^{31}P NMR (162 MHz, $CDCl_3$) δ = 49.40 (s). elemental analysis calcd (%) for $C_{39}H_{28}N_3O_2PPtS$: C 56.52, H 3.41, N 5.07; found: C 56.49, H 3.44, N 5.12. LRMS (ESI): m/z calcd for $C_{39}H_{28}N_3O_2PPtS+H^+$: 829.1 $[M+H]^+$; found: 829.1.



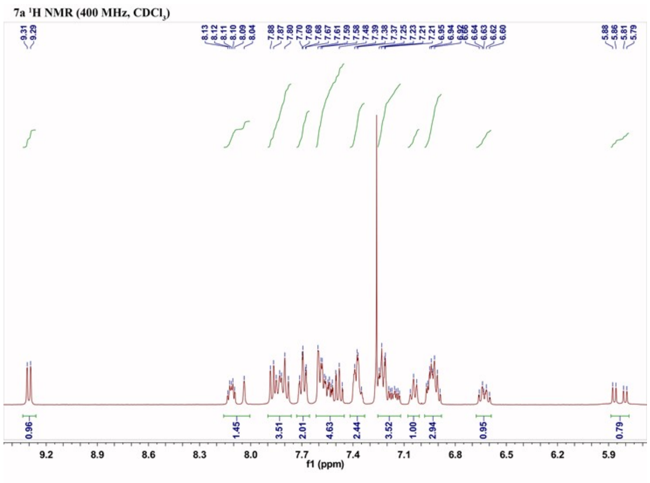
6a ^1H NMR (400 MHz, $CDCl_3$)

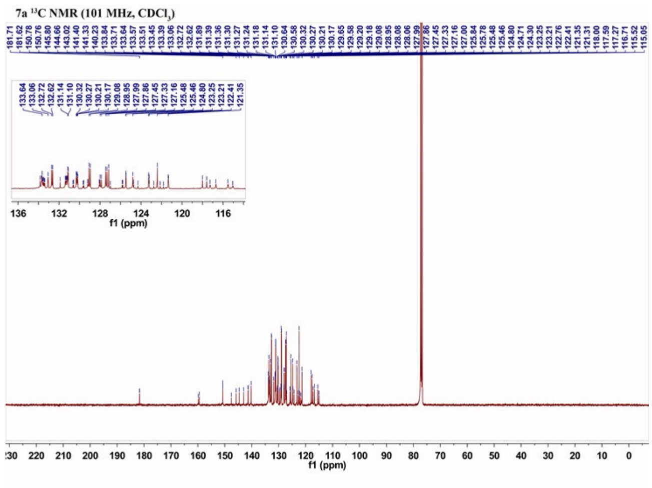


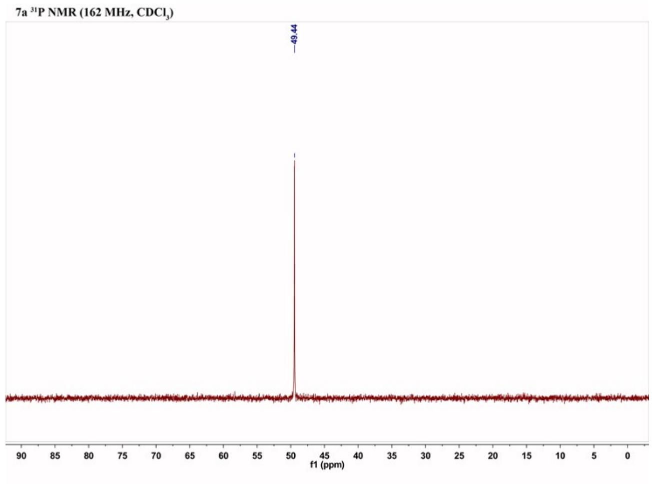
6a ^{13}C NMR (101 MHz, $CDCl_3$)



Complex 7a: Yield: 33%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.30 (d, J = 7.7 Hz, 1H; Ar-H), 8.16-8.00 (m, 1H; Ar-H), 7.90-7.76 (m, 4H; Ar-H), 7.73-7.65 (m, 2H; Ar-H), 7.62-7.45 (m, 5H; Ar-H), 7.42-7.33 (m, 2H; Ar-H), 7.25-7.12 (m, 4H; Ar-H), 7.08-7.00 (m, 1H; Ar-H), 6.98-6.88 (m, 3H; Ar-H), 6.68-6.59 (m, 1H; Ar-H), 5.83 (dd, J = 25.5, 7.6 Hz, 1H; Ar-H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 181.66, 159.69, 150.77, 147.59, 145.80, 144.66, 143.02, 141.36, 140.23, 133.59, 133.06, 132.67, 131.89, 131.25, 130.61, 130.24, 129.61, 129.10, 128.00, 127.23, 125.81, 125.47, 124.76, 124.30, 123.23, 122.76, 122.41, 122.13, 121.81, 121.33, 118.00, 117.59, 117.27, 116.71, 115.52, 115.05. ^{31}P NMR (162 MHz, $CDCl_3$) δ = 49.44 (s). elemental analysis calcd (%) for $C_{39}H_{25}F_3N_3OPPtS$: C 54.04, H 2.91, N 4.85; found: C 53.99, H 2.87, N 4.82. LRMS (ESI): m/z calcd for $C_{39}H_{25}F_3N_3OPPtS+H^+$: 867.1 $[M+H]^+$; found: 867.1.

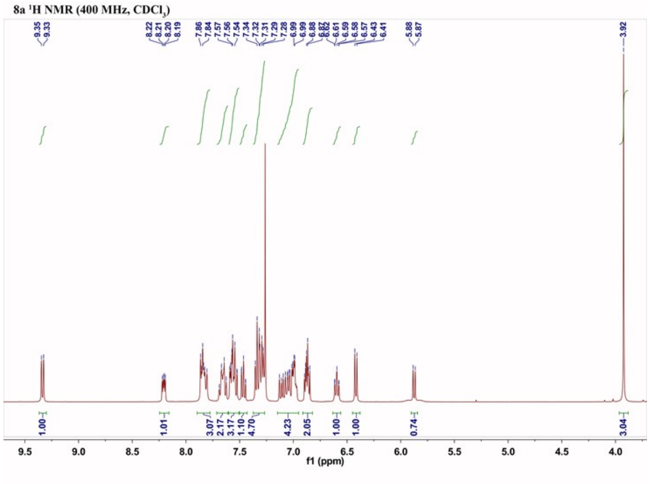




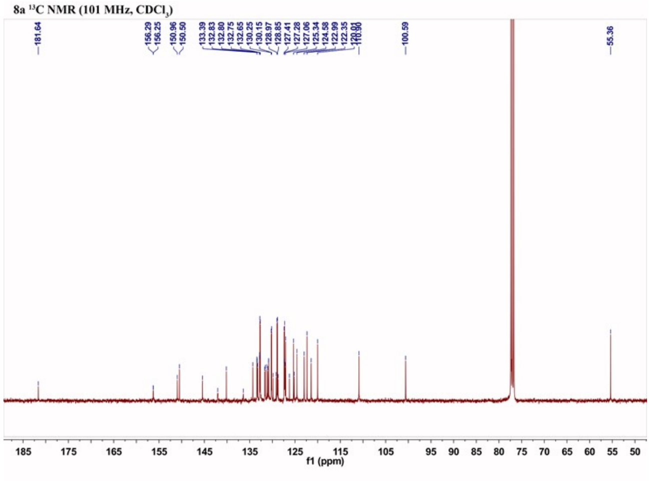


Complex 8a: Yield: 30%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.34 (d, *J* = 8.2 Hz, 1H; Ar-H), 8.21 (dd, *J* = 7.4, 4.0 Hz, 1H; Ar-H), 7.90-7.78 (m, 3H; Ar-H), 7.71-7.61 (m, 2H; Ar-H), 7.59-7.51 (m, 3H; Ar-H), 7.50-7.43 (m, 1H; Ar-H), 7.37-7.27 (m, 5H; Ar-H), 7.14-6.95 (m, 4H; Ar-H), 6.92-6.82 (m, 2H; Ar-H), 6.63-6.56 (m, 1H; Ar-H), 6.42 (d, *J* = 7.6 Hz, 1H; Ar-H), 5.87 (d, *J* = 7.8 Hz, 1H; Ar-H), 3.92 (s, 3H; $-OCH_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 181.64, 156.27, 150.96, 150.50, 145.42, 142.05, 140.14, 136.40, 134.31, 133.34, 132.76, 131.62, 131.22, 130.88, 130.20, 129.84, 129.16, 128.85, 127.25, 126.23, 125.34, 125.16, 124.58, 122.99, 122.35, 121.44, 120.01, 110.90, 100.59, 55.36. ^{31}P NMR (162 MHz, $CDCl_3$) δ = 49.68 (s). elemental analysis calcd (%) for $C_{39}H_{28}N_3O_2PPtS$: C 56.52, H 3.41, N 5.07; found: C 56.47, H 3.46, N 5.13. LRMS (ESI): m/z calcd for $C_{39}H_{28}N_3O_2PPtS+H^+$: 829.1 $[M+H]^+$; found: 829.1.

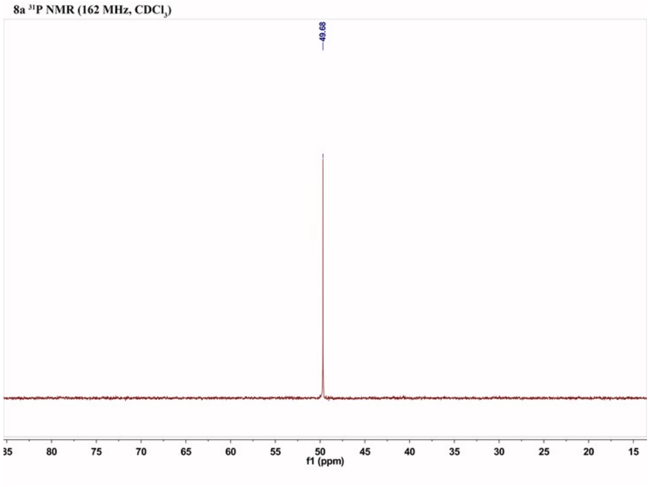
8a ^{1}H NMR (400 MHz, $CDCl_3$)



8a ^{13}C NMR (101 MHz, $CDCl_3$)

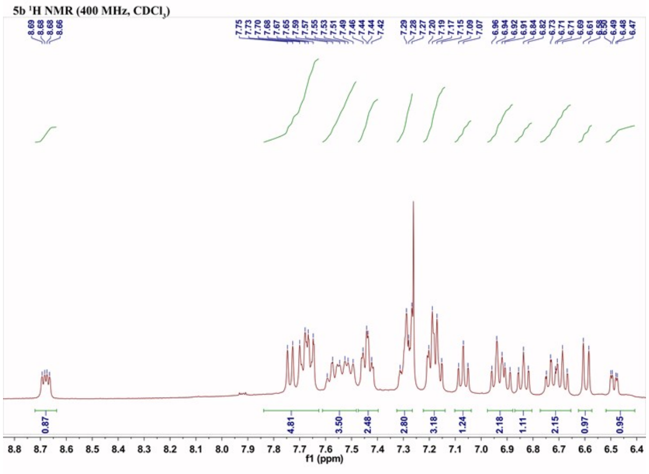


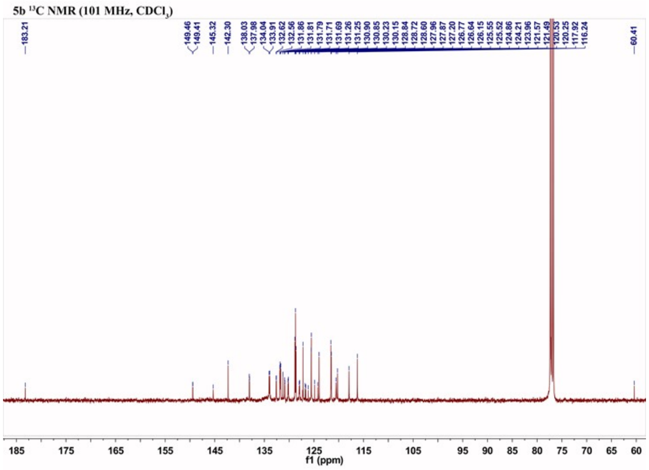
8a ^{31}P NMR (162 MHz, $CDCl_3$)

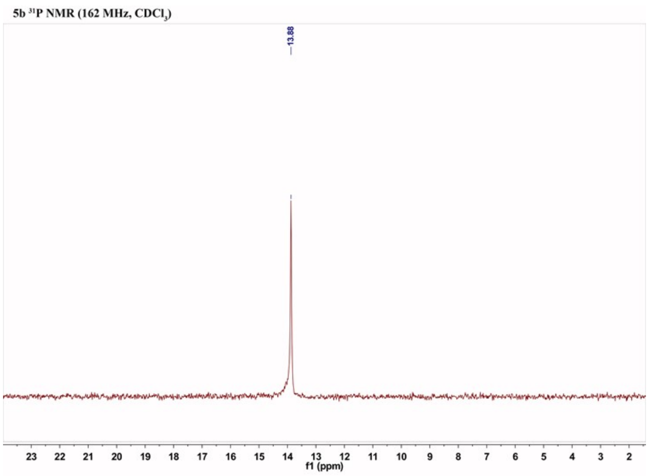


Complex 5b: Yield: 35%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.68 (dd, *J* = 7.2, 4.0 Hz, 1H; Ar-H), 7.85-7.62 (m, 5H; Ar-H), 7.61-7.48 (m, 4H; Ar-H), 7.47-7.40 (m, 2H; Ar-H), 7.33-7.27 (m, 3H; Ar-H), 7.22-7.14 (m, 3H; Ar-H), 7.07 (t, *J* = 7.1 Hz, 1H; Ar-H), 6.98-6.88 (m, 2H; Ar-H), 6.84 (t, *J* = 7.4 Hz, 1H; Ar-H), 6.77-6.65 (m, 2H; Ar-H), 6.60 (d, *J* = 8.5 Hz, 1H; Ar-H), 6.49 (dd, *J* = 7.7, 2.3 Hz, 1H; Ar-H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 183.21, 149.43, 145.32, 142.30, 138.01,

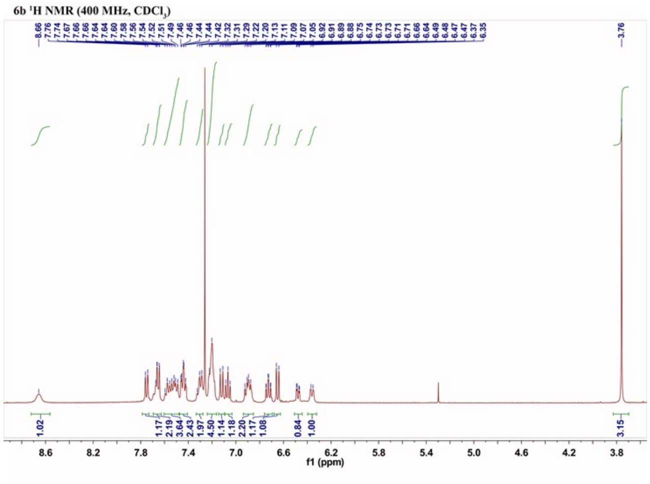
133.97, 132.59, 131.77, 131.25, 130.87, 130.19, 128.72, 127.92, 127.20, 126.77, 126.64, 126.15, 125.53, 124.86, 124.21, 123.96, 121.53, 120.53, 120.25, 117.92, 116.24. ^{31}P NMR (162 MHz, $CDCl_3$) δ = 13.88 (s). elemental analysis calcd (%) for $C_{38}H_{26}N_3PPtS$: C 58.31, H 3.35, N 5.37; found: C 58.37, H 3.39, N 5.31. LRMS (ESI): m/z calcd for $C_{38}H_{26}N_3PPtS+H^+$: 783.1 $[M+H]^+$; found: 783.1.

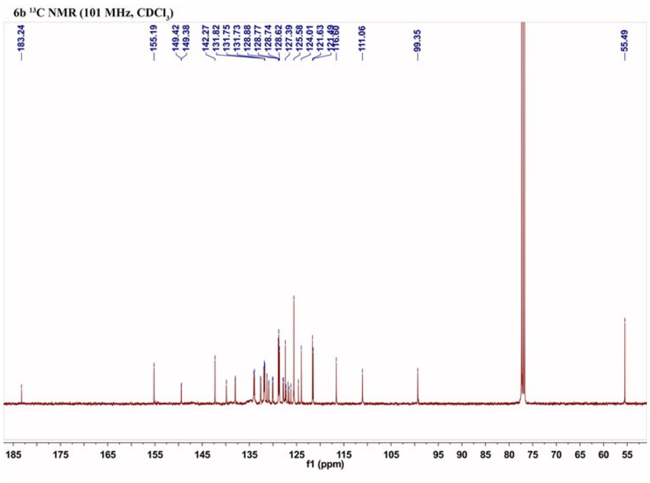


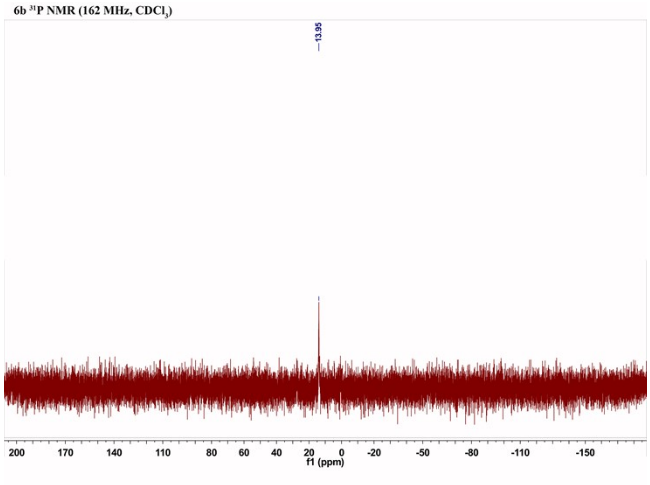




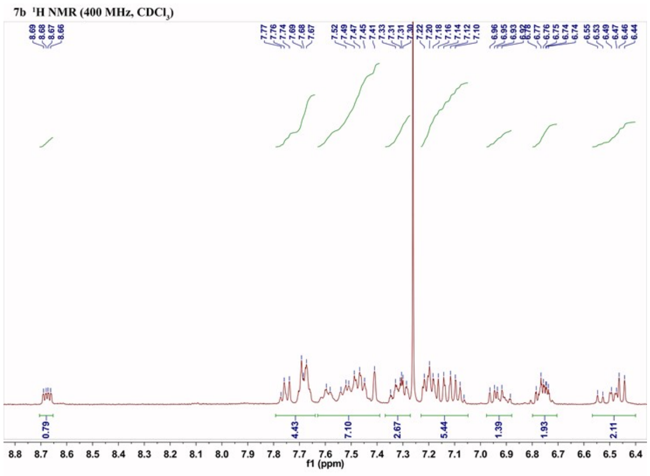
Complex 6b: Yield: 31%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.66 (s, 1H; Ar-H), 7.75 (d, *J* = 8.0 Hz, 1H; Ar-H), 7.70-7.63 (m, 2H; Ar-H), 7.60-7.48 (m, 4H; Ar-H), 7.47-7.41 (m, 2H; Ar-H), 7.33-7.28 (m, 2H; Ar-H), 7.24-7.16 (m, 5H; Ar-H), 7.12 (d, *J* = 8.8 Hz, 1H; Ar-H), 7.07 (t, *J* = 7.1 Hz, 1H; Ar-H), 6.95-6.85 (m, 2H; Ar-H), 6.73 (td, *J* = 7.6, 1.4 Hz, 1H; Ar-H), 6.65 (d, *J* = 8.5 Hz, 1H; Ar-H), 6.48 (dd, *J* = 7.7, 2.3 Hz, 1H; Ar-H), 6.36 (d, *J* = 6.8 Hz, 1H; Ar-H), 3.76 (s, 3H; $-OCH_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 183.24, 155.19, 149.40, 142.27, 139.86, 137.99, 133.99, 132.60, 131.83, 131.29, 130.89, 130.06, 128.75, 127.82, 127.31, 126.82, 126.58, 126.20, 125.58, 124.63, 124.01, 121.56, 116.60, 111.06, 99.35, 55.49. ^{31}P NMR (162 MHz, $CDCl_3$) δ = 13.95 (s). elemental analysis calcd (%) for $C_{39}H_{28}N_3OPPtS$: C 57.63, H 3.47, N 5.17; found: C 57.69, H 3.44, N 5.11. LRMS (ESI): m/z calcd for $C_{39}H_{28}N_3OPPtS+H^+$: 813.1 $[M+H]^+$; found: 813.1.

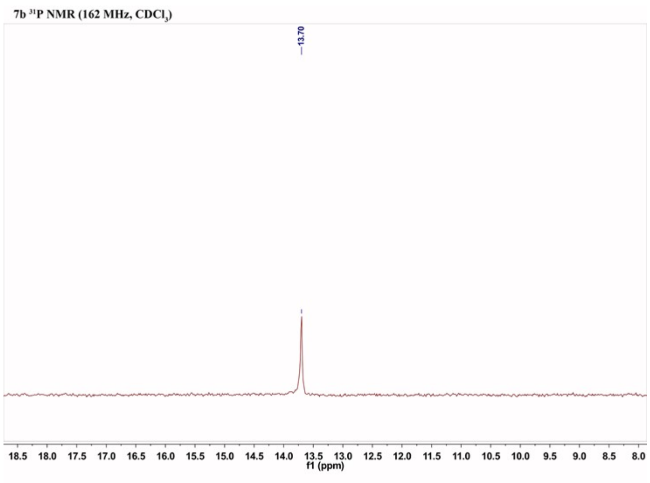




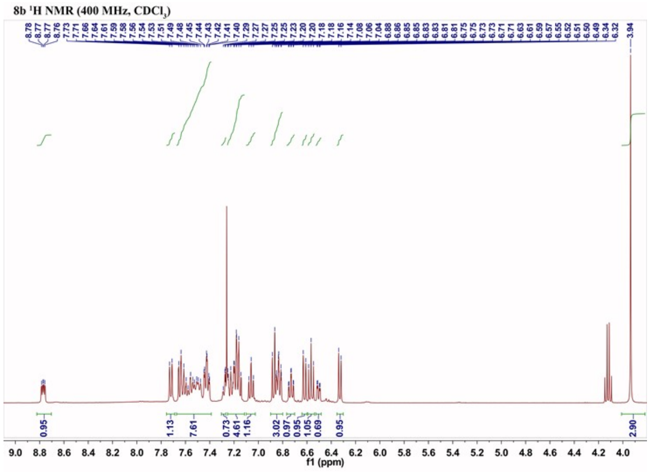


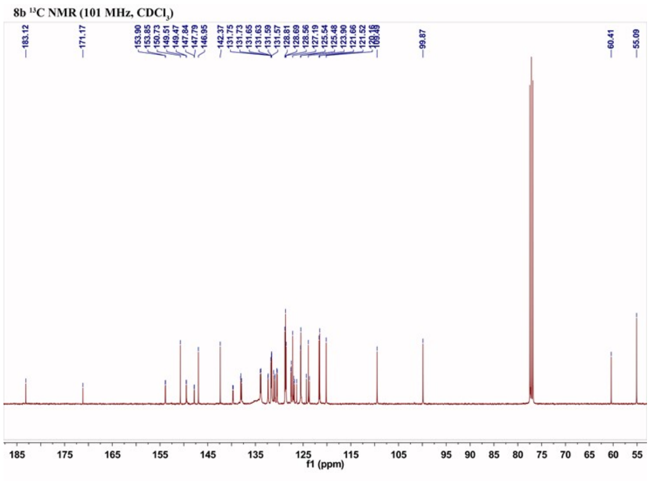
Complex 7b: Yield: 43%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.68 (dd, *J* = 6.8, 4.1 Hz, 1H; Ar-H), 7.79-7.64 (m, 4H; Ar-H), 7.63-7.39 (m, 7H; Ar-H), 7.36-7.28 (m, 3H; Ar-H), 7.23-7.07 (m, 5H; Ar-H), 6.98-6.88 (m, 1H; Ar-H), 6.80-6.70 (m, 2H; Ar-H), 6.61-6.40 (m, 2H; Ar-H). ^{31}P NMR (162 MHz, $CDCl_3$) δ = 13.70 (s). elemental analysis calcd (%) for $C_{39}H_{25}F_3N_3PPtS$: C 55.06, H 2.96, N 4.94; found: C 55.20, H 3.19, N 4.86. LRMS (ESI): m/z calcd for $C_{39}H_{25}F_3N_3PPtS+H^+$: 852.1 $[M+H]^+$; found: 852.1.

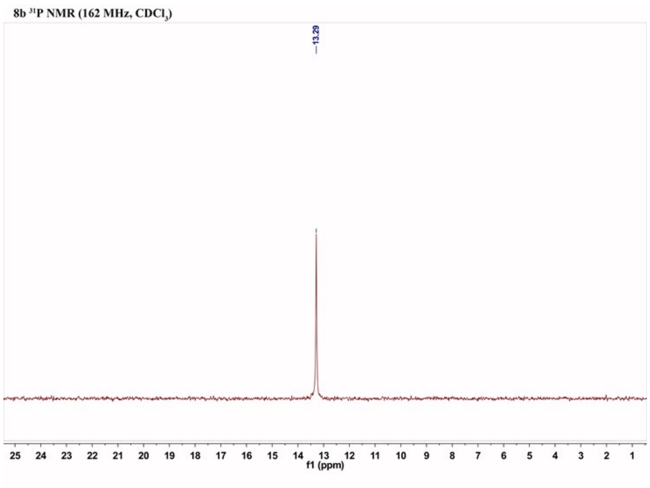




Complex 8b: Yield: 30%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.77 (dd, *J* = 7.0, 4.1 Hz, 1H; Ar-H), 7.72 (d, *J* = 8.0 Hz, 1H; Ar-H), 7.67-7.39 (m, 8H; Ar-H), 7.30-7.27 (m, 1H; Ar-H), 7.25-7.11 (m, 5H; Ar-H), 7.06 (t, *J* = 4.5, 1H; Ar-H), 6.90-6.80 (m, 3H; Ar-H), 6.73 (td, *J* = 7.6, 1.4 Hz, 1H; Ar-H), 6.62 (d, *J* = 8.4 Hz, 1H; Ar-H), 6.57 (t, *J* = 7.9 Hz, 1H; Ar-H), 6.50 (dd, *J* = 7.7, 2.1 Hz, 1H; Ar-H), 6.33 (d, *J* = 7.6 Hz, 1H; Ar-H), 3.94 (s, 3H; -OCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 183.12, 153.87, 150.73, 149.49, 147.82, 146.95, 142.37, 139.69, 138.01, 133.91, 132.35, 131.65, 131.20, 130.90, 130.46, 128.69, 127.51, 127.19, 126.98, 126.83, 126.36, 125.51, 124.33, 123.90, 123.68, 121.59, 120.16, 109.49, 99.87, 55.09. ^{31}P NMR (162 MHz, $CDCl_3$) δ = 13.29 (s). elemental analysis calcd (%) for $C_{39}H_{28}N_3OPPtS$: C 57.63, H 3.47, N 5.17; found: C 57.82, H 3.36, N 5.09. LRMS (ESI): m/z calcd for $C_{39}H_{28}N_3OPPtS$+H^+: 813.1 [M+H]$^+$; found: 813.1.







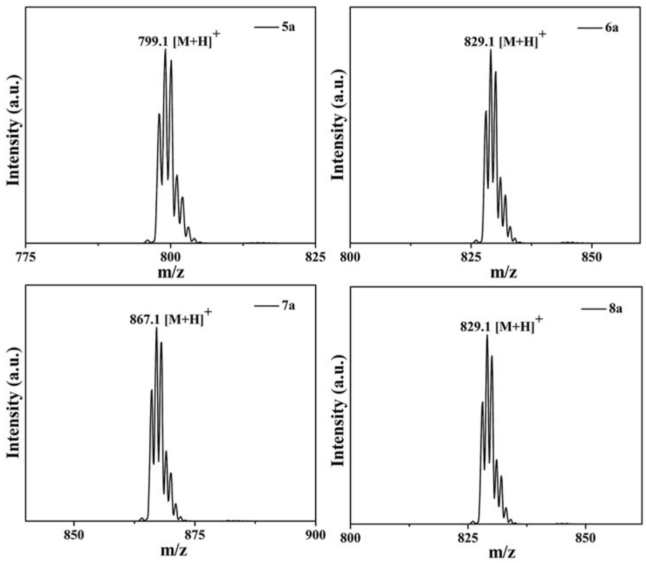


Fig. S1 Low-resolution mass spectra (LRMS) of complexes **5a-8a**.

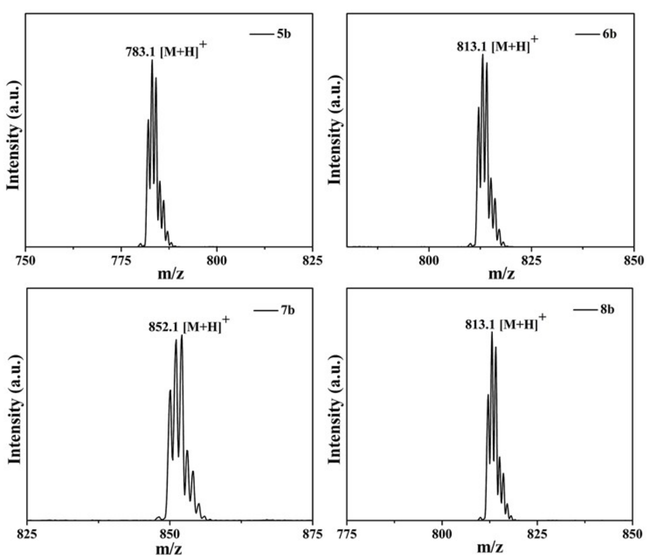


Fig. S2 Low-resolution mass spectra (LRMS) of complexes **5b-8b**.

Table S1. Crystal data details and data collection of the complexes **5a** and **6a**

Compound reference	**5a**	**6a**
Empirical formula	$C_{40}H_{32}Cl_2N_3O_2PPtS$	$C_{39.5}H_{28.5}Cl_{1.5}N_3O_2PPtS$
Formula weight	915.70	888.45
Temperature/K	200(2)	291.15
Crystal system	triclinic	monoclinic
Space group	P-1	$P2_1/c$
a/Å	11.946(6)	12.6337(2)
b/Å	12.473(3)	13.0147(2)
c/Å	12.753(4)	22.8683(4)
α/°	89.885(9)	90
β/°	78.801(14)	102.644(2)
γ/°	72.895(15)	90
Volume/Å^3	1778.5(11)	3668.91(11)
Z	2	4
ρ_{calc}g/cm^3	1.710	1.608
μ/mm^{-1}	4.240	9.410
F(000)	904.0	1748.0
Crystal size/mm^3	0.2 × 0.18 × 0.17	0.19 × 0.18 × 0.17
Radiation	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)
2Θ range for data collection/°	4.37 to 53.466	7.17 to 133.19
Reflections collected	30444	15519
Independent reflections	7355 [R_{int} = 0.0489, R_{sigma} = 0.0405]	6486 [R_{int} = 0.0284, R_{sigma} = 0.0318]
Data/restraints/parameters	7355/0/453	6486/0/461
Goodness-of-fit on F^2	1.041	1.118
Final R indexes [I>=2σ (I)]	R_1 = 0.0290, wR_2 = 0.0754	R_1 = 0.0377, wR_2 = 0.0972
Final R indexes [all data]	R_1 = 0.0315, wR_2 = 0.0767	R_1 = 0.0422, wR_2 = 0.1004
CCDC number	2101050	2101053

Table S2. Crystal data details and data collection of the complexes **7a** and **8a**

Compound reference	**7a**	**8a**
Empirical formula	$C_{39}H_{25}F_3N_3OPPtS$	$C_{41}H_{33}Cl_3N_3O_3PPtS$
Formula weight	866.74	980.17
Temperature/K	293(2)	150.00(10)

Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a/Å	8.8714(2)	14.02219(7)
b/Å	27.0432(4)	13.13260(6)
c/Å	15.3762(3)	21.37276(10)
α/°	90	90
β/°	105.911(2)	100.1698(4)
γ/°	90	90
Volume/Å^3	3547.59(12)	3873.91(3)
Z	4	4
ρ_{calc}g/cm^3	1.623	1.681
μ/mm^{-1}	8.805	9.924
F(000)	1696.0	1936.0
Crystal size/mm^3	0.22 × 0.21 × 0.2	0.16 × 0.14 × 0.12
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.536 to 133.188	7.012 to 134.148
Reflections collected	14586	21243
Independent reflections	6268 [R_{int} = 0.0394, R_{sigma} = 0.0466]	6897 [R_{int} = 0.0275, R_{sigma} = 0.0247]
Data/restraints/parameters	6268/26/442	6897/0/481
Goodness-of-fit on F^2	1.069	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0451, wR_2 = 0.1145	R_1 = 0.0279, wR_2 = 0.0719
Final R indexes [all data]	R_1 = 0.0518, wR_2 = 0.1199	R_1 = 0.0288, wR_2 = 0.0725
CCDC number	2101087	2101059

Table S3. Crystal data details and data collection of the complexes **5b**, **6b** and **8b**

Compound reference	**5b**	**6b**	**8b**
Empirical formula	$C_{39}H_{27}Cl_3N_3PPtS$	$C_{40}H_{31}N_3O_2PPtS$	$C_{39}H_{29}N_3O_{1.5}PPtS$
Formula weight	902.10	843.80	821.77
Temperature/K	291.15	291.15	291.15
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	C2/c
a/Å	11.30060(10)	11.1632(2)	38.3206(9)
b/Å	13.78120(10)	18.2105(4)	7.5249(2)
c/Å	23.3186(2)	18.5907(3)	23.6650(5)
α/°	90	90	90

β/°	100.5730(10)	103.612(2)	109.508(2)
γ/°	90	90	90
Volume/Å^3	3569.88(5)	3673.10(12)	6432.3(3)
Z	4	4	8
ρ_{calc}g/cm^3	1.678	1.526	1.697
μ/mm^{-1}	10.646	8.385	9.546
F(000)	1768.0	1668.0	3240.0
Crystal size/mm^3	0.22 × 0.2 × 0.19	0.22 × 0.2 × 0.2	0.2 × 0.19 × 0.17
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.484 to 141.764	8.15 to 133.192	7.926 to 130.158
Reflections collected	14881	15942	11550
Independent reflections	6757 [R_{int} = 0.0351, R_{sigma}= 0.0447]	6487 [R_{int} = 0.0304, R_{sigma} = 0.0396]	5432 [R_{int} = 0.0310, R_{sigma} = 0.0395]
Data/restraints/parameters	6757/12/433	6487/1/436	5432/0/421
Goodness-of-fit on F^2	1.017	1.031	1.082
Final R indexes [I>=2σ (I)]	R_1 = 0.0439, wR_2 = 0.1203	R_1 = 0.0361, wR_2 = 0.0904	R_1 = 0.0369, wR_2 = 0.0956
Final R indexes [all data]	R_1 = 0.0498, wR_2 = 0.1262	R_1 = 0.0483, wR_2 = 0.0988	R_1 = 0.0413, wR_2 = 0.0996
CCDC number	2101051	2101055	2101060

Table S4. Selected bond lengths (Å) and angles (deg) for the complexes

Complex		Length/Å		Angle/°
5a	Pt1-O1	2.163(2)	N1-Pt1-O1	95.80(10)
	Pt1-N1	2.050(3)	N2-Pt1-O1	88.52(10)
	Pt1-N2	2.022(3)	N2-Pt1-N1	174.09(11)
	Pt1-C1	1.976(4)	C1-Pt1-O1	176.75(10)
			C1-Pt1-N1	81.02(13)
			C1-Pt1-N2	94.61(13)
6a	Pt1-O1	2.158(4)	N1-Pt1-O1	95.47(16)
	Pt1-N1	2.033(4)	N2-Pt1-O1	89.81(16)
	Pt1-N2	2.023(4)	N2-Pt1-N1	171.68(17)
	Pt1-C1	1.973(5)	C1-Pt1-O1	173.86(18)
			C1-Pt1-N1	81.7(2)
			C1-Pt1-N2	93.66(19)
7a	Pt1-O1	2.149(5)	N1-Pt1-O1	97.4(2)
	Pt1-N1	2.039(5)	N2-Pt1-O1	87.41(18)
	Pt1-N2	2.013(4)	N2-Pt1-N1	173.3(2)
	Pt1-C1	1.989(6)	C1-Pt1-O1	178.4(2)
			C1-Pt1-N1	81.0(2)

			C1-Pt1-N2	94.2(2)
8a	Pt1-O1	2.171(2)	N1-Pt1-O1	96.17(11)
	Pt1-N1	2.027(3)	N2-Pt1-O1	88.47(10)
	Pt1-N2	1.997(3)	N2-Pt1-N1	175.01(11)
	Pt1-C1	1.968(4)	C1-Pt1-O1	172.25(12)
			C1-Pt1-N1	81.79(14)
			C1-Pt1-N2	93.84(13)
5b	Pt1-C1	2.042(6)	C1-Pt1-N1	80.1(2)
	Pt1-N1	2.091(5)	N2-Pt1-P1	86.51(13)
	Pt1-N2	2.097(4)	C1-Pt1-N2	163.5(2)
	Pt1-P1	2.2140(14)	N1-Pt1-P1	170.39(14)
			C1-Pt1-P1	99.85(18)
			N1-Pt1-N2	96.12(18)
6b	Pt1-C1	2.028(5)	C1-Pt1-N1	80.39(19)
	Pt1-N1	2.106(4)	N2-Pt1-P1	83.78(11)
	Pt1-N2	2.082(4)	C1-Pt1-N2	167.14(19)
	Pt1-P1	2.2001(12)	N1-Pt1-P1	167.75(12)
			C1-Pt1-P1	100.75(15)
			N1-Pt1-N2	97.77(16)
8b	Pt1-C1	2.000(5)	C1-Pt1-N1	80.15(19)
	Pt1-N1	2.103(4)	N2-Pt1-P1	85.75(13)
	Pt1-N2	2.084(4)	C1-Pt1-N2	166.1(2)
	Pt1-P1	2.2064(12)	N1-Pt1-P1	166.99(14)
			C1-Pt1-P1	102.37(15)
			N1-Pt1-N2	94.48(17)

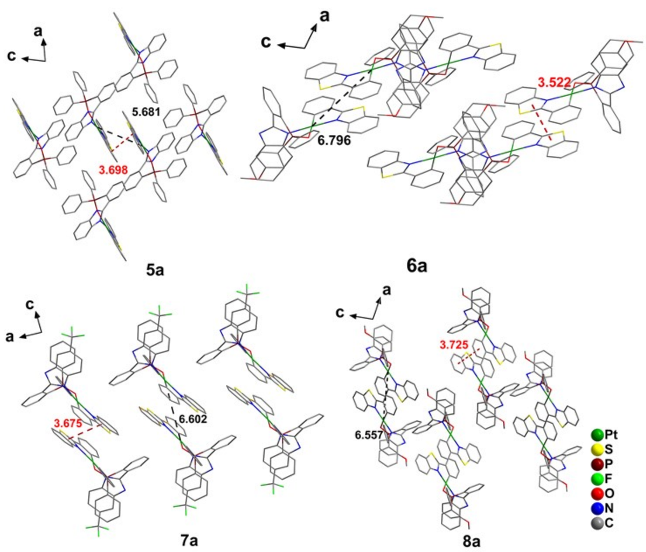


Fig. S3 Packing diagram of the complexes (**5a-8a**) viewed along the b-axis. Solvent molecules and hydrogen atoms are omitted for clarity.

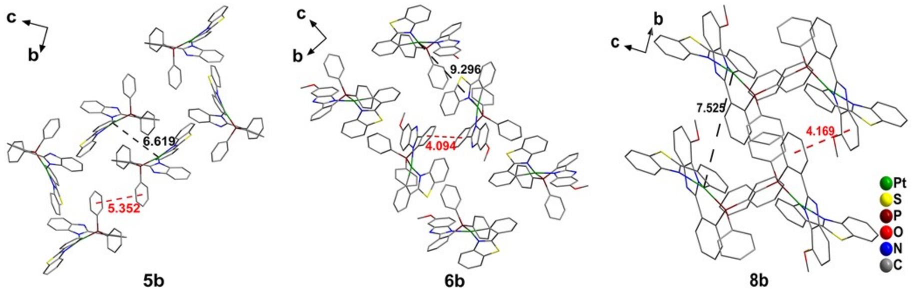


Fig. S4 Packing diagram of the complex **5b**, **6b** and **8b** viewed along the a-axis. Solvent molecules and hydrogen atoms are omitted for clarity.

Table S5. Selected bond lengths (Å) and angles (deg) for the complexes in S_0 state

Complex		Length/Å		Angle/°
5a	Pt1-O1	2.240(0)	N1-Pt1-O1	97.27(5)
	Pt1-N1	2.089(5)	N2-Pt1-O1	88.52(9)
	Pt1-N2	2.041(5)	N2-Pt1-N1	174.89(0)
	Pt1-C1	1.990(8)	C1-Pt1-O1	174.49(2)
			C1-Pt1-N1	80.43(8)
			C1-Pt1-N2	95.58(9)
6a	Pt1-O1	2.246(7)	N1-Pt1-O1	97.44(6)
	Pt1-N1	2.088(8)	N2-Pt1-O1	86.75(5)
	Pt1-N2	2.040(2)	N2-Pt1-N1	174.92(1)
	Pt1-C1	1.990(0)	C1-Pt1-O1	173.55(6)
			C1-Pt1-N1	80.47(9)
			C1-Pt1-N2	95.64(7)
7a	Pt1-O1	2.245(5)	N1-Pt1-O1	97.24(4)
	Pt1-N1	2.087(4)	N2-Pt1-O1	86.78(3)
	Pt1-N2	2.043(1)	N2-Pt1-N1	175.25(1)
	Pt1-C1	1.991(3)	C1-Pt1-O1	174.19(2)
			C1-Pt1-N1	80.50(7)
			C1-Pt1-N2	95.71(8)
8a	Pt1-O1	2.238(0)	N1-Pt1-O1	97.21(2)
	Pt1-N1	2.089(2)	N2-Pt1-O1	86.72(3)
	Pt1-N2	2.041(3)	N2-Pt1-N1	175.17(2)
	Pt1-C1	1.990(4)	C1-Pt1-O1	174.42(3)
			C1-Pt1-N1	80.46(9)
			C1-Pt1-N2	95.85(7)
5b	Pt1-C1	2.039(2)	C1-Pt1-N1	79.52(1)
	Pt1-N1	2.165(9)	N2-Pt1-P1	82.56(2)
	Pt1-N2	2.156(1)	C1-Pt1-N2	166.93(9)
	Pt1-P1	2.280(6)	N1-Pt1-P1	167.52(9)
			C1-Pt1-P1	102.43(7)
			N1-Pt1-N2	98.23(6)
6b	Pt1-C1	2.038(9)	C1-Pt1-N1	79.53(5)
	Pt1-N1	2.165(5)	N2-Pt1-P1	82.77(5)

	Pt1-N2	2.150(1)	C1-Pt1-N2	166.75(3)
	Pt1-P1	2.280(0)	N1-Pt1-P1	167.32(7)
			C1-Pt1-P1	102.41(8)
			N1-Pt1-N2	98.10(5)
7b	Pt1-C1	2.037(6)	C1-Pt1-N1	79.60(4)
	Pt1-N1	2.162(6)	N2-Pt1-P1	82.94(0)
	Pt1-N2	2.159(0)	C1-Pt1-N2	166.34(1)
	Pt1-P1	2.280(3)	N1-Pt1-P1	167.74(8)
			C1-Pt1-P1	102.16(0)
			N1-Pt1-N2	98.13(4)
8b	Pt1-C1	2.036(8)	C1-Pt1-N1	79.48(7)
	Pt1-N1	2.171(9)	N2-Pt1-P1	82.54(5)
	Pt1-N2	2.164(6)	C1-Pt1-N2	168.37(5)
	Pt1-P1	2.273(8)	N1-Pt1-P1	165.30(5)
			C1-Pt1-P1	102.32(4)
			N1-Pt1-N2	98.51(9)

Table S6. Cartesian coordinates for optimized ground state structure of the complexes by theoretical calculations.

complex	atom	x	y	z	complex	atom	x	y	z
5a	Pt	-1.00503	-0.41206	-0.09731	**6a**	Pt	-0.55516	-0.94366	-0.03812
	S	-5.18786	1.33448	-0.07333		S	-4.49365	-3.17789	-0.22824
	P	1.96515	1.07872	0.08041		P	0.0617	2.31626	0.08399
	O	0.58057	1.08887	-0.59781		O	-0.71873	1.21064	-0.65454
	N	-2.64793	0.86463	-0.28906		O	6.03354	-2.75396	-1.88932
	N	0.49379	-1.79272	0.02631		N	-2.54545	-1.47573	-0.38289
	N	2.15384	-3.08621	0.91285		N	1.43408	-0.59101	0.24603
	C	-2.45108	-1.64151	0.50344		N	3.38618	-0.0576	1.30198
	C	-2.32816	-2.96559	0.94899		C	-0.53121	-2.79638	0.68775
	H	-1.35819	-3.44897	0.94971		C	0.54392	-3.47899	1.27518
	C	-3.44515	-3.68307	1.38858		H	1.52049	-3.01143	1.323
	H	-3.319	-4.70897	1.72475		C	0.37891	-4.76541	1.79832
	C	-4.72033	-3.1043	1.40235		H	1.23124	-5.27073	2.24507
	H	-5.57861	-3.67365	1.74474		C	-0.86245	-5.41241	1.75628
	C	-4.87665	-1.79026	0.97591		H	-0.97565	-6.41114	2.16591
	H	-5.8596	-1.32594	0.98572		C	-1.95115	-4.76194	1.18645
	C	-3.75531	-1.06969	0.53554		H	-2.92168	-5.25051	1.15069
	C	-3.78919	0.29986	0.0788		C	-1.786	-3.47066	0.6613
	C	-2.81418	2.16827	-0.7498		C	-2.83865	-2.69384	0.04932
	C	-1.81617	3.01551	-1.25171		C	-3.6235	-0.84653	-0.99953
	H	-0.79438	2.65996	-1.30538		C	-3.62431	0.41953	-1.60207
	C	-2.18066	4.29123	-1.67002		H	-2.71325	1.00556	-1.60954
	H	-1.41932	4.95866	-2.06181		C	-4.80615	0.87795	-2.17538
	C	-3.51375	4.73099	-1.59916		H	-4.8227	1.85565	-2.64695

H	-3.7697	5.73202	-1.93162	C	-5.9764	0.09954	-2.15937
C	-4.51647	3.89442	-1.114	H	-6.88486	0.48256	-2.61335
H	-5.54794	4.22691	-1.06707	C	-5.98513	-1.16482	-1.57446
C	-4.15374	2.61309	-0.69623	H	-6.88393	-1.77228	-1.56922
C	1.96324	0.41631	1.78431	C	-4.79973	-1.62859	-1.00193
C	2.23762	1.28637	2.85268	C	0.41408	1.95087	1.83955
H	2.42315	2.33648	2.65999	C	-0.22038	2.71615	2.83252
C	2.2915	0.81826	4.16507	H	-0.9326	3.48284	2.55076
H	2.50147	1.50887	4.9757	C	0.06284	2.51793	4.18325
C	2.08961	-0.53751	4.42344	H	-0.44205	3.11776	4.93389
H	2.14182	-0.91461	5.44038	C	1.00643	1.56083	4.5573
C	1.81585	-1.41245	3.3739	H	1.2457	1.40883	5.60555
H	1.65879	-2.46832	3.56507	C	1.64034	0.79106	3.58414
C	1.72712	-0.95727	2.05044	H	2.37234	0.04207	3.8662
C	1.4521	-1.9555	0.99548	C	1.34424	0.95	2.22209
C	1.64412	-3.71296	-0.20494	C	2.05889	0.09281	1.25516
C	2.00253	-4.93396	-0.80107	C	2.46145	-1.22577	-0.43063
H	2.79483	-5.54313	-0.3749	C	2.47112	-2.06835	-1.55239
C	1.31795	-5.33152	-1.94413	H	1.55043	-2.33503	-2.0624
H	1.57616	-6.27098	-2.4253	C	3.69656	-2.54645	-1.99118
C	0.28956	-4.53484	-2.49765	H	3.76153	-3.19708	-2.85757
H	-0.2212	-4.87661	-3.39372	C	4.90542	-2.20277	-1.33091
C	-0.07961	-3.32299	-1.92202	C	4.90763	-1.37175	-0.21463
H	-0.86845	-2.70938	-2.34616	H	5.81818	-1.09594	0.30334
C	0.61058	-2.91714	-0.77052	C	3.66477	-0.88478	0.23703
C	3.18308	0.15102	-0.89764	C	7.28462	-2.44982	-1.29031
C	4.34539	-0.39254	-0.32997	H	7.33251	-2.80064	-0.25142
H	4.51724	-0.32521	0.73971	H	7.49098	-1.37206	-1.30984
C	5.28147	-1.03459	-1.14176	H	8.04013	-2.97128	-1.88036
H	6.17792	-1.45713	-0.69859	C	-0.94594	3.83617	0.03693
C	5.05966	-1.14236	-2.51668	C	-0.36367	5.11298	0.01339
H	5.78814	-1.6463	-3.14484	H	0.71579	5.22328	0.00612
C	3.89878	-0.61035	-3.08367	C	-1.17171	6.25018	-0.01102
H	3.72139	-0.70154	-4.15088	H	-0.71422	7.23452	-0.03268
C	2.96104	0.03606	-2.27863	C	-2.5627	6.12216	-0.01457
H	2.05355	0.44349	-2.71257	H	-3.18913	7.00893	-0.03636
C	2.55439	2.8023	0.17002	C	-3.14793	4.85386	0.00498
C	3.91449	3.13165	0.06628	H	-4.22879	4.75117	-0.00204
H	4.65616	2.3551	-0.08936	C	-2.34487	3.71313	0.03006
C	4.31969	4.4642	0.15283	H	-2.8005	2.729	0.03614
H	5.37327	4.71219	0.06833	C	1.63039	2.70407	-0.74912
C	3.37365	5.47438	0.34097	C	1.71207	2.46216	-2.1294
H	3.6921	6.51054	0.40565	H	0.87673	1.99799	-2.64376
C	2.01779	5.15278	0.44147	C	2.86755	2.80588	-2.8308

	H	1.27975	5.93624	0.5839		H	2.92833	2.61233	-3.89738
	C	1.60688	3.82247	0.35601		C	3.94415	3.39265	-2.16093
	H	0.55326	3.5751	0.42661		H	4.84352	3.65881	-2.70826
						C	3.86878	3.63061	-0.78657
						H	4.70857	4.07691	-0.26296
						C	2.71676	3.28599	-0.07816
						H	2.67182	3.46107	0.99209
7a	Pt	-0.52498	-1.02272	0.03885	**8a**	Pt	-0.73572	-0.87487	-0.09482
	S	-3.65	-4.27593	-0.37478		S	-5.05035	-2.26272	-0.11639
	P	-0.87323	2.2925	0.06343		P	0.50869	2.20116	0.08998
	F	6.76197	-0.53081	-2.51937		O	-0.49901	1.2845	-0.63307
	F	7.00368	-2.08924	-1.03347		O	5.72141	-2.1832	-0.05782
	F	7.42182	-0.01983	-0.50773		N	-2.8095	-0.97716	-0.32659
	O	-1.23557	0.98613	-0.6697		N	1.29795	-0.93564	0.07085
	N	-2.25176	-2.09512	-0.43572		N	3.37902	-0.80634	0.99521
	N	1.25326	-0.11361	0.46937		C	-1.04667	-2.73607	0.5385
	N	2.85873	1.01701	1.63514		C	-0.09981	-3.65549	1.01256
	C	6.57259	-0.81051	-1.20277		H	0.95206	-3.39472	1.01683
	C	-2.26639	3.45032	-0.1383		C	-0.49084	-4.91548	1.47637
	C	-0.03557	-2.79171	0.81111		H	0.26603	-5.60835	1.83489
	C	-3.56944	2.9257	-0.16477		C	-1.83773	-5.29927	1.48641
	H	-3.72338	1.85561	-0.07692		H	-2.12661	-6.28072	1.84889
	C	-3.72898	-0.58427	-1.77065		C	-2.80349	-4.40956	1.0295
	H	-3.02237	0.2356	-1.72828		H	-3.85303	-4.69295	1.03484
	C	-4.94698	-0.48022	-2.43488		C	-2.41108	-3.14475	0.56358
	H	-5.204	0.45192	-2.92843		C	-3.31789	-2.13671	0.06587
	C	-4.32068	-2.87898	-1.20576		C	-3.77238	-0.10929	-0.83497
	C	-3.41522	-1.79681	-1.14061		C	-3.55242	1.16512	-1.37645
	C	-5.54345	-2.77111	-1.87003		H	-2.54321	1.55597	-1.42267
	H	-6.23244	-3.60801	-1.9129		C	-4.64871	1.88416	-1.84196
	C	0.74674	1.33118	3.74253		H	-4.49429	2.87223	-2.26439
	H	1.62617	0.81631	4.11382		C	-5.94957	1.3557	-1.77962
	C	-2.07411	4.83398	-0.26883		H	-6.78697	1.9391	-2.14908
	H	-1.07277	5.25142	-0.26264		C	-6.1796	0.08539	-1.25596
	C	1.9743	3.43314	-2.62028		H	-7.18085	-0.33009	-1.2157
	H	2.21084	3.20548	-3.65512		C	-5.08099	-0.63921	-0.79118
	C	-1.04439	-3.79214	0.7095		C	0.89833	1.70147	1.8056
	C	-3.17293	5.68122	-0.41862		C	0.50241	2.53701	2.86355
	H	-3.01685	6.75047	-0.52323		H	-0.05625	3.44235	2.6573
	C	-4.46649	5.15507	-0.44043		C	0.83032	2.23007	4.18368
	H	-5.31932	5.81666	-0.55952		H	0.51046	2.88798	4.98555
	C	-2.22326	-3.34498	0.005		C	1.58053	1.08728	4.46086
	C	1.30343	-4.4214	2.03163		H	1.85317	0.84616	5.48395
	H	2.22643	-4.66438	2.55152		C	1.97817	0.24758	3.4224

	C	-0.58555	2.08423	1.85728		H	2.56138	-0.64337	3.62829
	C	0.30076	-5.39184	1.91531		C	1.63248	0.52088	2.09076
	H	0.44144	-6.38073	2.33989		C	2.10609	-0.4155	1.05099
	C	1.56037	0.75626	1.48702		C	2.1375	-1.71677	-0.70104
	C	-1.28207	2.57749	4.13955		C	1.89556	-2.49318	-1.84863
	H	-1.99342	3.03314	4.82105		H	0.90545	-2.5563	-2.28745
	C	-0.15674	1.91522	4.62892		C	2.98207	-3.16482	-2.38822
	H	0.01866	1.85054	5.69847		H	2.8463	-3.77322	-3.27826
	C	-5.8484	-1.55759	-2.48238		C	4.27772	-3.08755	-1.82155
	H	-6.79216	-1.44814	-3.00717		H	5.08509	-3.63621	-2.29183
	C	2.45012	4.63804	-0.57428		C	4.51429	-2.32138	-0.68173
	H	3.05733	5.34544	-0.0181		C	3.42245	-1.62542	-0.11101
	C	0.59189	3.08627	-0.66097		C	6.83514	-2.87079	-0.61354
	C	3.4583	0.28688	0.63304		H	7.04373	-2.53818	-1.63796
	C	4.81228	0.17914	0.28667		H	6.67796	-3.95653	-0.61629
	H	5.57333	0.71649	0.84098		H	7.68788	-2.63179	0.02366
	C	2.46844	-0.42007	-0.10372		C	2.06704	2.33998	-0.83388
	C	5.1433	-0.63726	-0.79032		C	3.27641	2.69529	-0.21713
	C	2.81079	-1.24375	-1.18692		H	3.32395	2.8367	0.85802
	H	2.05037	-1.77937	-1.74571		C	4.42925	2.85638	-0.98697
	C	0.89719	2.79964	-2.00054		H	5.36402	3.12652	-0.5056
	H	0.29814	2.0774	-2.54571		C	4.38187	2.66032	-2.36916
	C	4.15358	-1.34138	-1.52017		H	5.28169	2.78274	-2.96466
	H	4.45552	-1.96328	-2.35698		C	3.18094	2.29984	-2.98563
	C	2.74777	4.35424	-1.90938		H	3.14486	2.13985	-4.05887
	H	3.58633	4.84591	-2.39341		C	2.02435	2.14038	-2.22264
	C	1.37679	4.00437	0.05331		H	1.09126	1.85401	-2.69703
	H	1.15991	4.21855	1.0952		C	-0.21555	3.87331	0.16622
	C	-4.66376	3.77759	-0.31416		C	0.57136	5.03137	0.07512
	H	-5.668	3.36557	-0.3351		H	1.64509	4.95528	-0.06123
	C	1.13956	-3.14182	1.49122		C	-0.02561	6.2906	0.15103
	H	1.93897	-2.41851	1.60195		H	0.5892	7.1823	0.07653
	C	0.54323	1.3851	2.35658		C	-1.40793	6.40264	0.31618
	C	-0.87996	-5.07604	1.25234		H	-1.86987	7.38376	0.37335
	H	-1.66885	-5.81817	1.15865		C	-2.19713	5.25297	0.40328
	C	-1.48658	2.66798	2.76287		H	-3.27251	5.33682	0.52721
	H	-2.34987	3.20863	2.39299		C	-1.60596	3.99174	0.32787
						H	-2.22159	3.10072	0.38694
5b	Pt	0.28307	0.44337	0.07703	**6b**	Pt	0.20675	0.66484	-0.05713
	P	-1.92547	-0.06853	-0.17068		P	1.92621	-0.81738	0.15438
	N	2.36947	0.97617	-0.15583		N	-1.34273	2.15468	0.20543
	N	0.50081	-1.70006	-0.00434		N	-0.98778	-1.08372	0.31584
	C	0.22178	2.41577	0.59119		C	1.13512	2.30539	-0.83399
	C	-2.0657	-1.23021	-1.59932		C	-0.9864	3.32751	-0.28659

C	-2.67931	-0.93119	1.26079	C	1.64642	-1.76553	1.71359
C	-3.06238	1.30663	-0.60279	C	2.04526	-2.06736	-1.18219
C	2.59534	2.23618	0.16972	C	3.61059	-0.11478	0.35621
C	3.48748	0.35249	-0.70718	C	-2.55558	2.20233	0.89033
C	-0.13405	-2.65214	-0.7528	C	-0.80758	-2.14395	1.1563
C	1.32496	-2.41935	0.83952	C	-2.15056	-1.38375	-0.37044
C	-0.85519	3.1742	1.07683	C	2.38361	2.40272	-1.4689
C	1.49706	3.05351	0.63865	C	0.30928	3.46615	-0.91618
C	-3.08167	-1.04683	-2.55138	S	-2.15334	4.60578	-0.02697
C	-1.19142	-2.33897	-1.72789	C	2.72102	-2.00874	2.58445
C	-3.70081	-1.87948	1.09528	C	0.36954	-2.29811	2.02534
C	-2.22893	-0.61821	2.55285	C	2.53154	-3.36115	-0.9366
C	-4.29076	1.49359	0.04577	C	1.6565	-1.71042	-2.4828
C	-2.68033	2.19316	-1.62474	C	4.7133	-0.59319	-0.36461
S	4.24141	2.76834	-0.09481	C	3.78888	0.93851	1.27006
C	4.63258	1.18026	-0.73652	C	-3.17019	3.47443	0.85261
C	3.55851	-0.94468	-1.23503	C	-3.16671	1.15967	1.60141
N	0.23621	-3.91446	-0.50627	N	-1.76874	-3.07929	1.1094
C	1.16147	-3.79431	0.50449	C	-2.62964	-2.61813	0.14435
C	2.20087	-2.01828	1.86	C	-2.84804	-0.71082	-1.38612
H	-1.85367	2.75437	1.09011	H	3.06253	1.55871	-1.46488
C	-0.68764	4.47889	1.55311	C	2.79536	3.57028	-2.12025
C	1.67062	4.36529	1.10918	C	0.7196	4.64337	-1.56285
H	-3.76217	-0.209	-2.45975	H	3.70275	-1.61361	2.35272
C	-3.2418	-1.93227	-3.61718	C	2.55382	-2.76157	3.74662
C	-1.37664	-3.22508	-2.80235	C	0.22582	-3.06491	3.19456
H	-4.04981	-2.13809	0.10061	H	2.8248	-3.65301	0.06683
C	-4.26568	-2.50072	2.21016	C	2.63144	-4.28109	-1.98134
C	-2.79979	-1.23927	3.66438	C	1.7616	-2.63296	-3.52458
H	-1.42733	0.10276	2.68251	H	1.26512	-0.71547	-2.67306
H	-4.60004	0.81938	0.83689	H	4.59302	-1.40433	-1.07427
C	-5.12548	2.55224	-0.32397	C	5.97648	-0.02556	-0.17354
C	-3.52025	3.24043	-1.99682	C	5.0515	1.49407	1.46461
H	-1.72359	2.06488	-2.12237	H	2.93741	1.32538	1.82213
C	5.85169	0.73207	-1.24739	C	-4.39458	3.71867	1.47674
C	4.77083	-1.38768	-1.75235	C	-4.38194	1.40599	2.23082
H	2.67864	-1.57367	-1.23629	H	-2.68867	0.19075	1.65239
C	1.88642	-4.78305	1.19211	C	-3.81799	-3.19796	-0.34459
C	2.9067	-3.01225	2.53136	C	-4.01452	-1.28804	-1.86563
H	2.31833	-0.9708	2.1204	H	-2.48736	0.22981	-1.79112
H	-1.55199	5.02746	1.91843	H	3.77131	3.59756	-2.59806
C	0.57232	5.08523	1.56458	C	1.97106	4.69892	-2.16505
H	2.66038	4.81478	1.12878	H	0.05875	5.50569	-1.60441
H	-4.03419	-1.76626	-4.34044	H	3.40059	-2.93237	4.40418

	C	-2.38467	-3.02632	-3.74076		C	1.2994	-3.29247	4.04985
	H	-0.70887	-4.0757	-2.87883		H	-0.75251	-3.47855	3.41167
	H	-5.05171	-3.23739	2.07442		H	3.00376	-5.28157	-1.78284
	C	-3.81735	-2.18095	3.49403		C	2.24807	-3.91829	-3.27479
	H	-2.44391	-0.9937	4.66035		H	1.45608	-2.34991	-4.52729
	H	-6.07332	2.69107	0.18718		H	6.82367	-0.40025	-0.73998
	C	-4.74385	3.42358	-1.34438		C	6.14766	1.01474	0.73999
	H	-3.21751	3.9178	-2.78953		H	5.17908	2.30557	2.1746
	H	6.72364	1.37727	-1.25972		H	-4.85773	4.69885	1.43596
	C	5.90954	-0.5643	-1.75295		C	-4.99658	2.66791	2.16457
	H	4.83634	-2.38991	-2.16388		H	-4.86345	0.60602	2.78428
	H	1.7627	-5.83254	0.93926		H	-4.16693	-4.1405	0.05973
	C	2.75404	-4.37819	2.20036		C	-4.4992	-2.51845	-1.34958
	H	3.58878	-2.73398	3.33021		H	-4.58757	-0.81025	-2.65412
	H	0.69503	6.09938	1.93139		H	2.29742	5.60287	-2.66954
	H	-2.49994	-3.72295	-4.56586		H	1.15665	-3.88135	4.95114
	H	-4.2559	-2.66922	4.35921		H	2.32282	-4.63773	-4.08479
	H	-5.39449	4.24452	-1.63057		H	7.12993	1.45375	0.88699
	H	6.84416	-0.93692	-2.16008		H	-5.94729	2.83137	2.66207
	H	3.32421	-5.12238	2.74983		O	-5.66727	-2.95591	-1.92731
						C	-6.21471	-4.18164	-1.46457
						H	-6.46525	-4.13577	-0.39695
						H	-5.52704	-5.02075	-1.63067
						H	-7.12689	-4.34542	-2.04075
7b	Pt	0.5834	0.6757	-0.0289	**8b**	Pt	-0.14936	0.48754	0.01547
	P	2.00685	-1.09875	0.12752		P	2.03357	-0.12592	-0.15285
	N	-0.62707	2.44525	0.25405		N	-2.18047	1.15272	-0.37078
	N	-0.88917	-0.79626	0.5422		N	-0.47031	-1.64537	-0.16724
	C	1.72915	2.06195	-0.98655		C	-0.01013	2.44432	0.56318
	C	-0.10362	3.5013	-0.34248		C	-2.34689	2.42313	-0.05783
	C	1.69192	-1.91416	1.75493		C	2.16017	-1.1659	-1.67476
	C	1.76718	-2.39892	-1.14263		C	2.67382	-1.15794	1.22118
	C	3.80388	-0.72662	0.1586		C	3.27662	1.20011	-0.41838
	C	-1.74086	2.76032	1.03033		C	-3.30843	0.59077	-0.96314
	C	-0.82927	-1.85003	1.4143		C	0.11809	-2.53937	-1.017
	C	-2.13359	-0.90222	-0.03782		C	-1.3494	-2.41354	0.57559
	C	2.91069	1.88275	-1.72291		C	1.06407	3.12085	1.1627
	C	1.13224	3.35448	-1.0808		C	-1.23669	3.16882	0.49646
	S	-0.98094	4.99149	-0.07634		S	-3.94365	3.05383	-0.40714
	C	2.77473	-2.32058	2.55113		C	3.21804	-0.96519	-2.57603
	C	0.3725	-2.18337	2.1977		C	1.21794	-2.19306	-1.93396
	C	2.01422	-3.7526	-0.86496		C	3.68088	-2.11367	1.01326
	C	1.34327	-2.02251	-2.42682		C	2.15526	-0.97006	2.51158
	C	4.73059	-1.44627	-0.60804		C	4.46901	1.2669	0.31511

C	4.25509	0.31524	0.98755	C	3.01508	2.17529	-1.39692
C	-2.10654	4.12344	0.95642	C	-4.39913	1.48566	-1.05491
C	-2.46834	1.8932	1.85808	C	-3.43642	-0.70775	-1.47658
N	-1.93578	-2.59792	1.48413	N	-0.33216	-3.79644	-0.92494
C	-2.78009	-2.01812	0.56855	C	-1.26443	-3.74415	0.08197
C	-2.7738	-0.14364	-1.03107	C	-2.22066	-2.10214	1.64428
H	3.41676	0.92514	-1.71613	H	2.02277	2.6287	1.27281
C	3.47416	2.91427	-2.48174	C	0.94379	4.43299	1.63262
C	1.69672	4.39545	-1.83559	C	-1.36142	4.48899	0.9587
H	3.78858	-2.12959	2.22093	H	3.9507	-0.19089	-2.38368
C	2.57314	-2.97827	3.76469	C	3.35301	-1.75133	-3.72039
C	0.19068	-2.85766	3.41641	C	1.3775	-2.97978	-3.08729
H	2.33131	-4.05779	0.12718	H	4.08125	-2.277	0.01759
C	1.84432	-4.71351	-1.86274	C	4.16605	-2.86384	2.08536
C	1.17862	-2.98688	-3.42185	C	2.64623	-1.72036	3.58107
H	1.13642	-0.97806	-2.64003	H	1.3624	-0.24577	2.67222
H	4.39875	-2.25197	-1.25363	H	4.68666	0.52399	1.07441
C	6.09028	-1.12779	-0.54548	C	5.38691	2.29301	0.07177
C	5.61234	0.62201	1.05428	C	3.93752	3.18954	-1.64354
H	3.54174	0.88806	1.57272	H	2.08685	2.1412	-1.95941
C	-3.19994	4.6309	1.65989	C	-5.61837	1.10516	-1.61754
C	-3.55246	2.40094	2.5655	C	-4.64968	-1.08498	-2.0421
H	-2.17619	0.85488	1.93948	H	-2.59837	-1.38946	-1.42944
C	-4.08029	-2.38063	0.18971	C	-2.05194	-4.77834	0.6267
C	-4.0586	-0.51542	-1.40016	O	-2.23506	-0.80929	2.09103
H	-2.28096	0.70018	-1.50268	C	-2.99242	-3.13385	2.17603
H	4.39058	2.72788	-3.03564	H	1.80417	4.91658	2.08805
C	2.87671	4.17716	-2.53697	C	-0.26416	5.12881	1.5235
H	1.2089	5.3659	-1.88233	H	-2.3146	5.00722	0.88813
H	3.42831	-3.27885	4.36205	H	4.179	-1.57286	-4.40196
C	1.27462	-3.24793	4.19721	C	2.42622	-2.76236	-3.97568
H	-0.82419	-3.06908	3.73357	H	0.65812	-3.7713	-3.26379
H	2.03229	-5.75932	-1.63944	H	4.94186	-3.60445	1.91617
C	1.42798	-4.33218	-3.14058	C	3.65112	-2.667	3.36916
H	0.84814	-2.68797	-4.41194	H	2.23812	-1.57057	4.57604
H	6.80011	-1.68802	-1.14647	H	6.30606	2.33744	0.64813
C	6.5324	-0.09759	0.28483	C	5.12492	3.25184	-0.90689
H	5.95136	1.42684	1.69937	H	3.72718	3.93529	-2.40416
H	-3.47149	5.67884	1.59105	H	-6.44736	1.80221	-1.67878
C	-3.92261	3.75268	2.46365	C	-5.73377	-0.19351	-2.10752
H	-4.12201	1.73849	3.20956	H	-4.75845	-2.08844	-2.44138
H	-4.57692	-3.22956	0.64598	H	-1.97834	-5.79087	0.24191
C	-4.70529	-1.62089	-0.79454	C	-2.90668	-4.45169	1.66552
H	-4.57833	0.04333	-2.17201	C	-3.10302	-0.48146	3.16921

H	3.32067	4.97411	-3.12503	H	-3.6683	-2.93726	2.99956
H	1.10535	-3.76014	5.13961	H	-0.34978	6.14888	1.88452
H	1.29254	-5.08284	-3.9135	H	2.51939	-3.381	-4.86341
H	7.58922	0.14748	0.33202	H	4.02798	-3.25479	4.20091
H	-4.7754	4.12173	3.02449	H	5.84024	4.04683	-1.09546
C	-6.10526	-1.93679	-1.22133	H	-6.67039	-0.51485	-2.55209
F	-6.99306	-0.98859	-0.81575	H	-3.52976	-5.21941	2.11622
F	-6.22685	-1.9986	-2.57336	H	-4.15266	-0.66609	2.91054
F	-6.55184	-3.11653	-0.73212	H	-2.95905	0.58303	3.35833
				H	-2.8517	-1.0485	4.07389

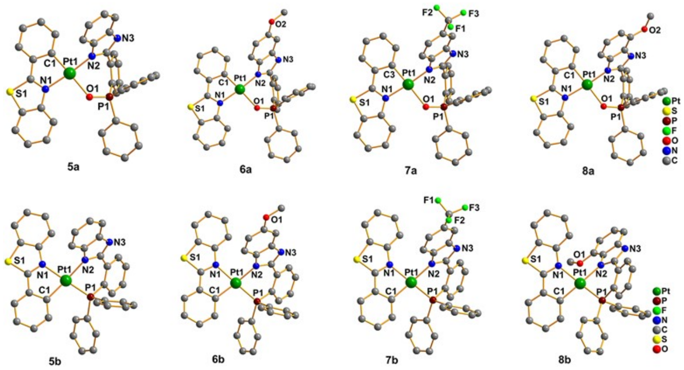


Fig. S5 The optimized structures of the complexes in the ground state (S_0). Hydrogen atoms are omitted for clarity.

Table S7. UV/Vis absorption data of the complexes in DCM (10^{-5} M) at 298K.

complex	λ_{abs}/nm ($\varepsilon \times 10^4$ /M^{-1} cm^{-1})
5a	230 / 4.49, 268 / 2.87, 320 / 2.34, 401 / 0.53
6a	230 / 4.16, 269 / 2.91, 322 / 2.39, 408 / 0.58
7a	230 / 4.60, 266 / 2.87, 319 / 2.25, 378 / 0.51, 408 / 0.40
8a	230 / 4.49, 267 / 2.90, 321 / 2.34, 407 / 0.49
5b	229 / 4.91, 319 / 2.33, 396 / 0.26
6b	229 / 5.87, 320 / 2.59, 404 / 0.38
7b	229 / 5.10, 315 / 2.28, 399 / 0.26
8b	229 / 5.24, 317 / 2.31, 401 / 0.19

Table S8. Calculated energies (eV) and energy gaps of HOMO and LUMO orbitals of complexes.

complex	**5a**	**6a**	**7a**	**8a**
HOMO	-5.499	-5.140	-5.777	-5.141
LUMO	-1.975	-1.969	-2.008	-1.967
ΔE	3.524	3.171	3.769	3.174
complex	**5b**	**6b**	**7b**	**8b**
HOMO	-5.441	-5.071	-5.687	-5.128
LUMO	-1.998	-1.991	-2.033	-1.928
ΔE	3.443	3.080	3.654	3.200

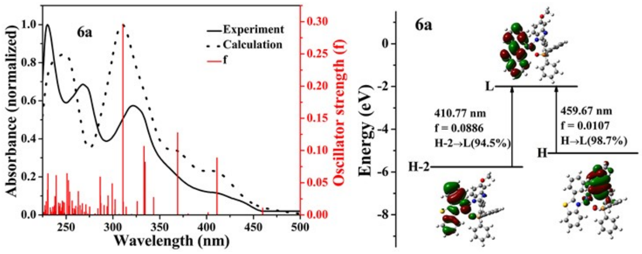


Fig. S6 Comparisons between the simulated and experimental absorption spectra of the complex **6a** (left). The calculated low-energy transitions for the complex **6a** and the relative frontier molecular orbitals (contributions > 35%) (right).

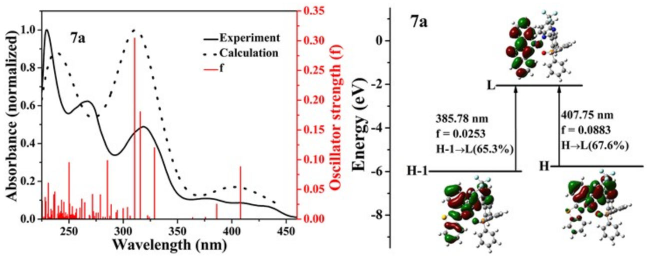


Fig. S7 Comparisons between the simulated and experimental absorption spectra of the complex **7a** (left). The calculated low-energy transitions for the complex **7a** and the relative frontier molecular orbitals (contributions > 35%) (right).

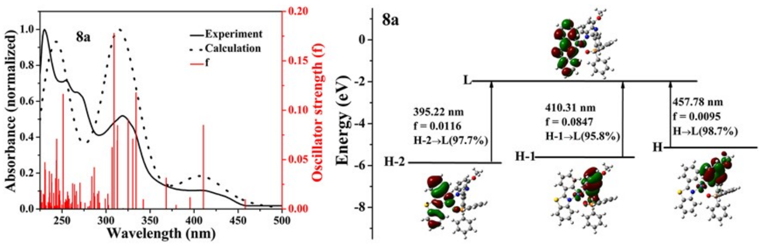


Fig. S8 Comparisons between the simulated and experimental absorption spectra of the complex **8a** (left). The calculated low-energy transitions for the complex **8a** and the relative frontier molecular orbitals (contributions > 35%) (right).

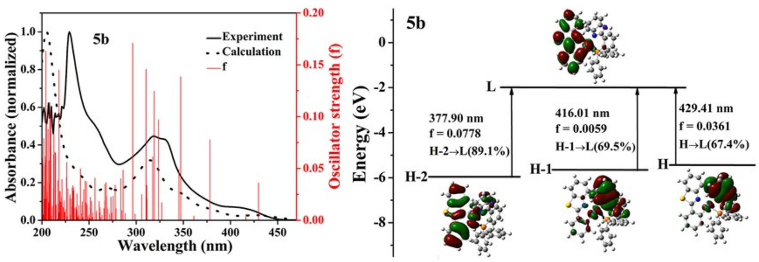


Fig. S9 Comparisons between the simulated and experimental absorption spectra of the complex **5b** (left). The calculated low-energy transitions for the complex **5b** and the relative frontier molecular orbitals (contributions > 35%) (right).

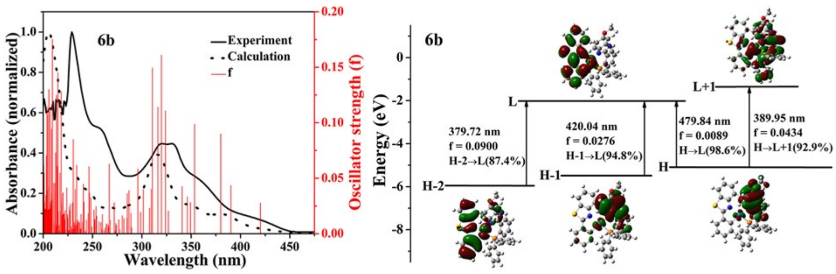


Fig. S10 Comparisons between the simulated and experimental absorption spectra of the complex **6b** (left). The calculated low-energy transitions for the complex **6b** and the relative frontier molecular orbitals (contributions > 35%) (right).

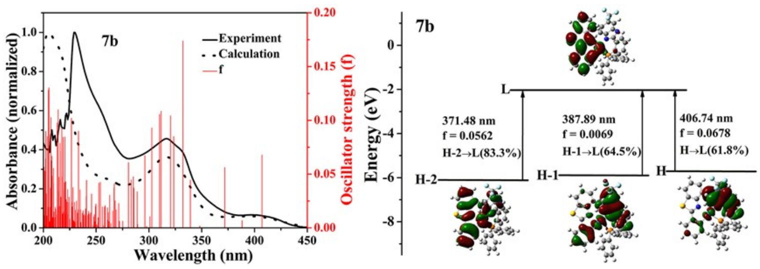


Fig. S11 Comparisons between the simulated and experimental absorption spectra of the complex **7b** (left). The calculated low-energy transitions for the complex **7b** and the relative frontier molecular orbitals (contributions > 35%) (right).

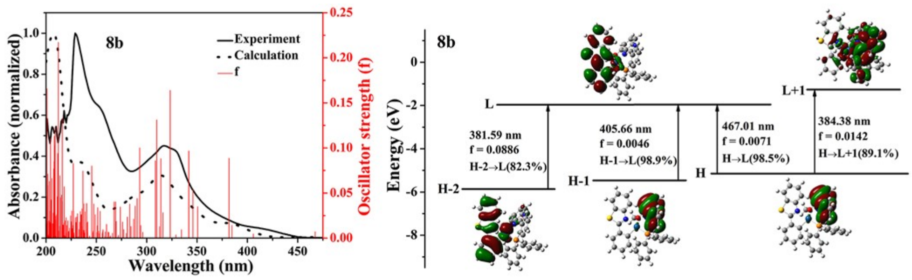


Fig. S12 Comparisons between the simulated and experimental absorption spectra of the complex **8b** (left). The calculated low-energy transitions for the complex **8b** and the relative frontier molecular orbitals (contributions > 35%) (right).

Table S9. Calculated electronic transitions in the range of 300-350 nm for complexes along with the corresponding wavelengths (λ) and oscillator strengths (f).

Complex	λ (nm)	f [a]	Contribution [b]	Assignment
5a	331.06	0.1019	H-4→L (86.2%)	MLCT, ILCT(bt-localized)
	330.09	0.1823	H-1→L+1 (93.2%)	ILCT(L-localized)
	310.42	0.2883	H-5→L (88.2%)	MLCT, ILCT(bt-localized)
6a	332.90	0.1065	H-4→L (62.0%)	MLCT, ILCT(bt-localized)
	310.48	0.2960	H-5→L (88.3%)	MLCT, ILCT(bt-localized)
7a	328.50	0.1202	H-4→L (85.7%)	MLCT, ILCT(bt-localized)
	315.35	0.1805	H-2→L+1 (91.4%)	ILCT(L-localized)
	310.23	0.3046	H-5→L (86.6%)	MLCT, ILCT(bt-localized)

8a	333.81	0.1177	H-4→L (85.6%)	MLCT, ILCT(bt-localized)
	308.95	0.1777	H-6→L(55.4%)	MLCT, ILCT(bt-localized)
5b	346.89	0.1386	H→L+1 (67.4%)	ILCT(L-localized)
	318.86	0.1246	H-1→L+2 (31.4%)	ILCT(L-localized)
	310.04	0.1457	H-1→L+3 (34.0%)	MLCT, ILCT(L-localized)
6b	353.10	0.0987	H→L+2 (42.0%)	ILCT(L-localized)
			H-1→L+1 (30.3%)	ILCT(L-localized)
	323.60	0.1107	H-4→L (55.7%)	MLCT, ILCT(bt-localized)
	319.59	0.1609	H→L+4 (44.3%)	ILCT(L-localized)
	316.08	0.1141	H-1→L+2 (55.3%)	ILCT(L-localized)
	310.52	0.1495	H-5→L (73.7%)	MLCT, ILCT(bt-localized)
7b	331.89	0.1739	H→L+1 (57.1%)	ILCT(L-localized)
	320.09	0.1044	H-4→L (43.8%)	MLCT, ILCT(bt-localized)
	311.40	0.1086	H-5→L (45.2%)	MLCT, ILCT(bt-localized)
	309.94	0.1056	H-5→L (38.8%)	MLCT, ILCT(bt-localized)
8b	323.12	0.1639	H-4→L (68.5%)	MLCT, ILCT(bt-localized)
	309.69	0.1312	H-5→L (69.1%)	MLCT, ILCT(bt-localized)

[a] Oscillator strength (f) ≥ 0.1. [b] Contribution > 25%.

Table S10. Calculated low-energy (>370 nm) transitions for the complexes along with their wavelengths (λ) and Oscillator Strengths (f).

Complex	λ (nm)	f [a]	Contribution	Main assignment
5a	415.46	0.0150	H→L (93.8%)	LLCT
	409.57	0.0914	H-2→L (94.3%)	MLCT, ILCT
6a	459.67	0.0107	H→L (98.7%)	LLCT
	410.77	0.0886	H-2→L (94.5%)	MLCT, ILCT
7a	407.75	0.0883	H→L (67.6%)	LLCT
			H-1→L (28.4%)	MLCT, LLCT, ILCT
	385.78	0.0253	H-1→L (65.3%)	MLCT, LLCT, ILCT
8a	457.78	0.0095	H→L (98.7%)	LLCT
	410.31	0.0847	H-1→L (95.8%)	LLCT
	395.22	0.0116	H-2→L (97.7%)	MLCT
5b	429.41	0.0361	H→L (67.4%)	LLCT
	416.01	0.0059	H-1→L (69.5%)	LLCT
	377.90	0.0778	H-2→L (89.1%)	MLCT, ILCT
6b	479.84	0.0089	H→L (98.6%)	LLCT
	420.04	0.0276	H-1→L (94.8%)	LLCT
	389.95	0.0434	H→L+1 (92.9%)	ILCT
	379.72	0.0900	H-2→L (87.4%)	MLCT, ILCT
7b	406.74	0.0678	H→L (61.8%)	LLCT
	387.89	0.0069	H→L (34.3%)	LLCT
			H-1→L (64.5%)	MLCT, LLCT
	371.48	0.0562	H-2→L (83.3%)	MLCT, ILCT

8b	467.01	0.0071	H→L (98.5%)	LLCT
	405.66	0.0056	H-1→L (98.9%)	LLCT
	384.38	0.0142	H→L+1 (82.9%)	ILCT
	381.59	0.0886	H-2→L (82.3%)	MLCT, ILCT

[a] Oscillator strength (f) ≥ 0.005.

Table S11. Compositions of the frontier molecular orbitals involved in the calculated electronic transitions.

5a			
Orbital	Pt	bt	OL1
HOMO-5	21.5%	72.9%	5.6%
HOMO-4	42.3%	49.8%	7.9%
HOMO-2	36.5%	61.1%	2.4%
HOMO-1	2.4%	-	97.6%
HOMO	14.6%	0.9%	84.5%
LUMO	4.4%	95.6%	-
LUMO+1	1.9%	0.7%	97.4%
6a			
Orbital	Pt	bt	OL2
HOMO-5	21.4%	72.9%	5.7%
HOMO-4	40.1%	47.3%	12.6%
HOMO-2	46.8%	50.5%	2.7%
HOMO	5.5%	-	94.5%
LUMO	4.8%	95.2%	-
LUMO+1	1.9%	0.9%	97.2%
7a			
Orbital	Pt	bt	OL3
HOMO-5	20.8%	75.1%	4.1%
HOMO-4	38.5%	51.8%	9.7%
HOMO-2	7.3%	0.5%	92.2%
HOMO-1	37.8%	36.6%	25.6%
HOMO	26.6%	18.5%	54.9%
LUMO	4.4%	95.6%	-
LUMO+1	1.9%	0.3%	97.8%
8a			
Orbital	Pt	bt	OL4
HOMO-6	38.5%	47.6%	13.9%
HOMO-4	45.1%	45.9%	9.0%
HOMO-2	36.8%	60.7%	2.5%
HOMO-1	7.0%	0.5%	92.5%
HOMO	3.2%	0.6%	96.2%
LUMO	4.9%	95.1%	-
LUMO+1	2.4%	0.3%	97.3%

	5b		
Orbital	Pt	bt	L1
HOMO-2	31.5%	60.1%	8.4%
HOMO-1	13.0%	4.2%	82.8%
HOMO	5.6%	0.9%	93.5%
LUMO	5.0%	93.6%	1.4%
LUMO+1	25.6%	13.9%	60.5%
LUMO+2	15.6%	5.8%	78.6%
LUMO+3	8.5%	0.9%	90.6%
	6b		
Orbital	Pt	bt	L2
HOMO-5	22.2%	76.0%	1.8%
HOMO-4	40.3%	51.8%	7.9%
HOMO-2	32.6%	60.3%	7.1%
HOMO-1	9.0%	3.7%	87.3%
HOMO	4.7%	0.6%	94.7%
LUMO	8.2%	88.4%	3.4%
LUMO+1	25.7%	10.2%	64.1%
LUMO+2	10.6%	5.9%	83.5%
LUMO+4	10.6%	7.6%	81.8%
	7b		
Orbital	Pt	bt	L3
HOMO-5	25.4%	72.3%	2.3%
HOMO-4	28.4%	64.0%	8.6%
HOMO-2	28.2%	51.8%	20.0%
HOMO-1	19.7%	11.5%	68.8%
HOMO	8.3%	3.5%	88.2%
LUMO	4.7%	92.2%	3.1%
LUMO+1	23.4%	8.6%	68.0%
	8b		
Orbital	Pt	bt	L4
HOMO-5	25.8%	71.4%	2.8%
HOMO-4	38.2%	52.6%	9.2%
HOMO-3	62.2%	23.3%	14.5%
HOMO-2	37.0%	58.1%	4.9%
HOMO-1	1.1%	-	98.9%
HOMO	9.4%	2.2%	88.4%
LUMO	4.2%	92.6%	3.2%
LUMO+1	25.8%	10.3%	63.9%

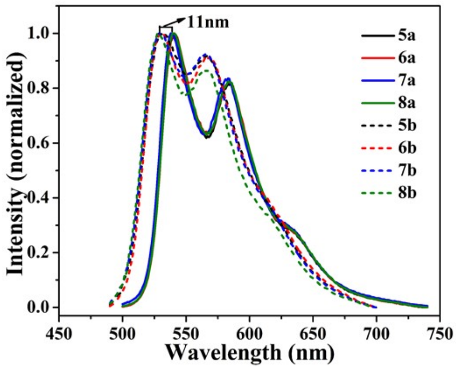


Fig. S13 The shift in emission spectroscopic relevant unit in DCM (10^{-5} M) at 298 K between complexes **7a** and **7b**.

Table S12. The triplet energy and emission wavelength of the complexes (**5a-5b**) calculated with the B3LYP functional.

Complex	Triplet energy (eV)	λ_{em} (nm)
5a	1.8997	652.66
6a	1.8748	661.32
7a	1.9155	647.26
8a	1.8686	663.50

Table S13. Calculated emission results from TD-DFT for the complexes **5a** and **5b**.

Complex	State	λ (nm)	Contribution	Assignment	Orbital	Contribution Pt	bt	L
5a	T_1	652.66	H-2→L (81.8%) H→L (9.4%)	^{3}MLCT, ^{3}ILCT ^{3}LLCT	H-2	26.5	68.4	5.1
					H	7.9	2.9	89.2
					L	5.8	92.6	1.6
5b	T_1	644.96	H-2→L (79.5%) H→L (11.5%)	^{3}MLCT, ^{3}ILCT ^{3}LLCT	H-2	11.4	81.8	6.8
					H	4.6	4.0	91.4
					L	5.1	91.0	3.9

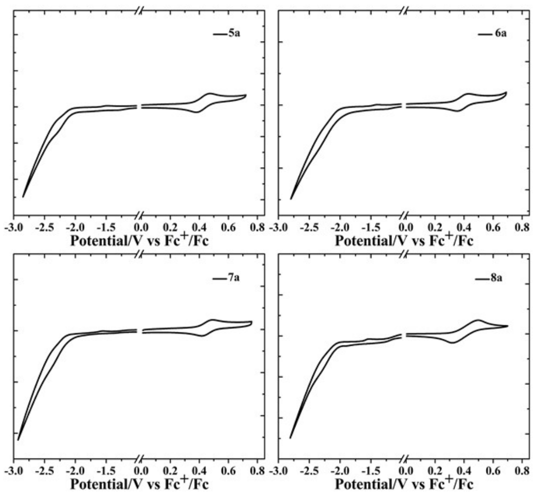


Fig. S14 Cyclic voltammograms of complexes **5a-8a** in CH_2Cl_2 solution in the presence of $[Bu_4N][PF_6]$ (0.1 M) at 298K.

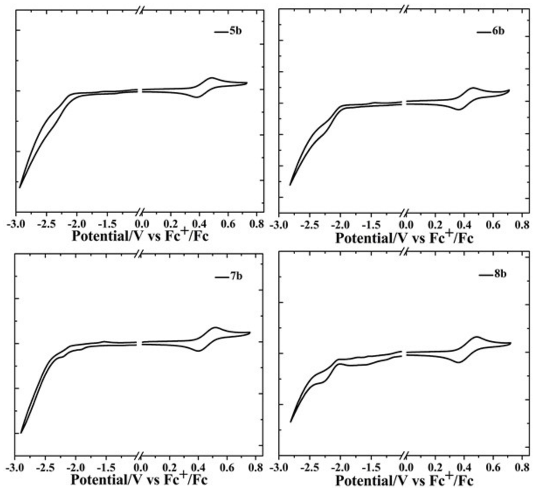


Fig. S15 Cyclic voltammograms of complexes **5b-8b** in CH_2Cl_2 solution in the presence of $[Bu_4N][PF_6]$ (0.1 M) at 298K.