

A fluorescent platinum(II) metallacycle-cored supramolecular network formed by dynamic covalent bonds and its application in halogen ions and picric acid detection

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Supporting Information

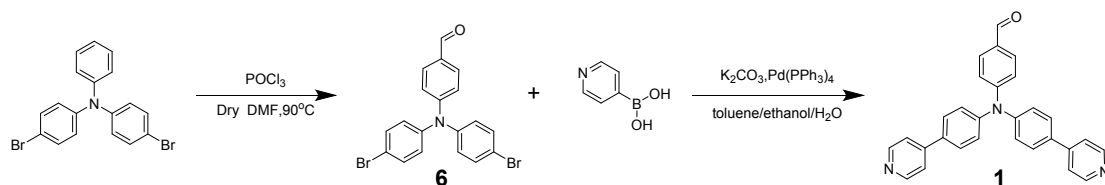
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1. Material and methods

All reagents and deuterated solvents were commercially available and used without further purification. Compounds **1**^{S1, S2}, **2**^{S3} and **4**^{S4} were synthesized according to the published procedure. NMR spectra were recorded on a Bruker Avance 400 MHz or 600 MHz spectrometer. ¹H NMR chemical shifts are reported relative to residual solvent signals, and ³¹P{¹H} NMR chemical shifts are referenced to an external unlocked sample of 85% H₃PO₄ (δ 0.0). Mass spectra were recorded on a Micromass Quattro II triple-quadrupole mass spectrometer using electrospray ionization with a MassLynx operating system. The melting points were collected on a Mettler FP-82 HT hot stage. The UV-vis experiments were conducted on a Lambda 950 absorption spectrophotometer. The fluorescent experiments were conducted on a Hitachi F-7100 fluorescence spectrophotometer. The absolute fluorescence quantum yields were conducted on an Edinburgh FLS9 fluorescence spectrophotometer. Scanning electron microscope (SEM) investigations were carried out on a GeminiSEM 500 instrument.

The samples for fluorescent titration measurements were prepared as follows. The solution of FSN **5** ([FSN **5**] = 10 μ M in metallacycle concentration) was first prepared. Then different concentrations of halide ions or picric acid were added into the solution of FSN **5**.

2. Synthesis of ligand 1



Scheme S1. Synthetic routes of ligand **1**.

2.1 Synthesis of compound 6

A solution of POCl_3 (3.50 ml) in DMF was added to a solution of 4,4'-dibromotriphenylamine (1.00 g, 2.40 mmol) in DMF at 0°C . After addition, the reaction mixture was stirred at room temperature for 1 h and then heated at 90°C under argon for another 10 h. After cooling to room temperature, the reaction mixture was quenched with cool water, and 1M NaOH solution was added. The system was extracted with CHCl_3 ($100\text{ mL} \times 3$), the combined organic layer was dried over anhydrous MgSO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica: dichloromethane/*n*-hexane, 1:1) to give compound **6** (0.75 g, 78%) as a yellow solid. ^1H NMR (400 MHz, CDCl_3 , 295 K) δ 9.84 (s, 1H), 7.71 (d, $J = 8.8$ Hz, 2H), 7.45 (d, $J = 8.8$ Hz, 4H), 7.06 – 6.99 (m, 6H). The ^1H NMR spectrum of **6** matches well with the reported data.^{S1}

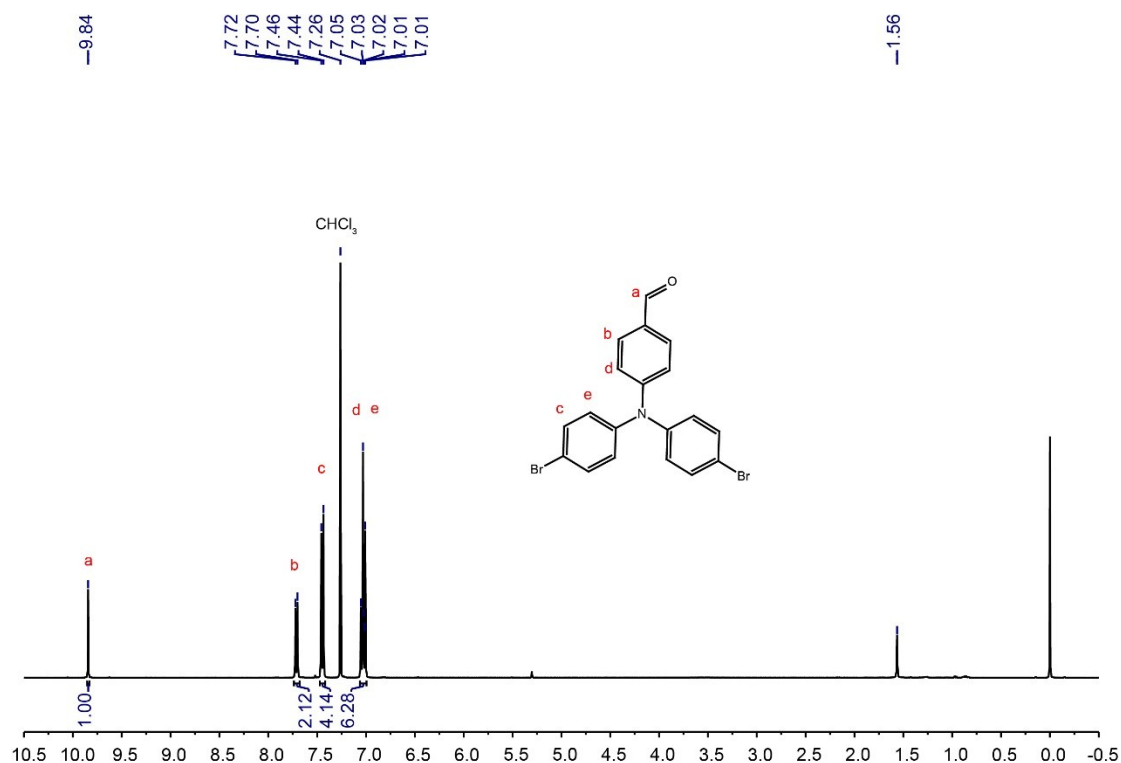


Fig. S1. Partial ^1H NMR (400 MHz, CDCl_3 , 295 K) spectrum recorded for compound **6**.

2.2 Synthesis of ligand **1**

Compound **6** (0.82 g, 1.91 mmol), pyridin-4-ylboronic acid (1.41 g, 11.5 mmol), K_2CO_3 (3.17 g, 22.9 mmol), tetrabutylammonium bromide (TBAB) (38.0 mg, 0.12 mmol) and $Pd(PPh_3)_4$ (0.22 g, 0.19 mmol) were added to a mixture of toluene (32.0 ml), ethanol (8.0 mL) and water (8.0 mL). The reaction mixture was stirred at 80 °C for 48 h under nitrogen atmosphere. After cooling to room temperature, the product was concentrated and purified by flash column chromatography with dichloromethane/methanol (100:1, v/v) as the eluent to afford compound **1** (0.57 g, 70 %) as yellow powder. M. P. 119.2–121°C. 1H NMR (400 MHz, CD_2Cl_2 , 295 K) δ 9.87 (s, 1H), 8.64 (d, J = 6.1 Hz, 4H), 7.77 (d, J = 8.7 Hz, 2H), 7.69 (d, J = 8.6 Hz, 4H), 7.58 (d, J = 6.1 Hz, 4H), 7.30 (d, J = 8.6 Hz, 4H), 7.20 (d, J = 8.7 Hz, 2H). ^{13}C NMR (151 MHz, CD_2Cl_2 , 295 K) δ 190.65, 152.81, 150.73, 147.40, 134.71, 131.52, 130.94, 128.67, 126.50, 121.68, 121.46. The 1H NMR spectrum of **1** matches well with the reported data.^{S2}

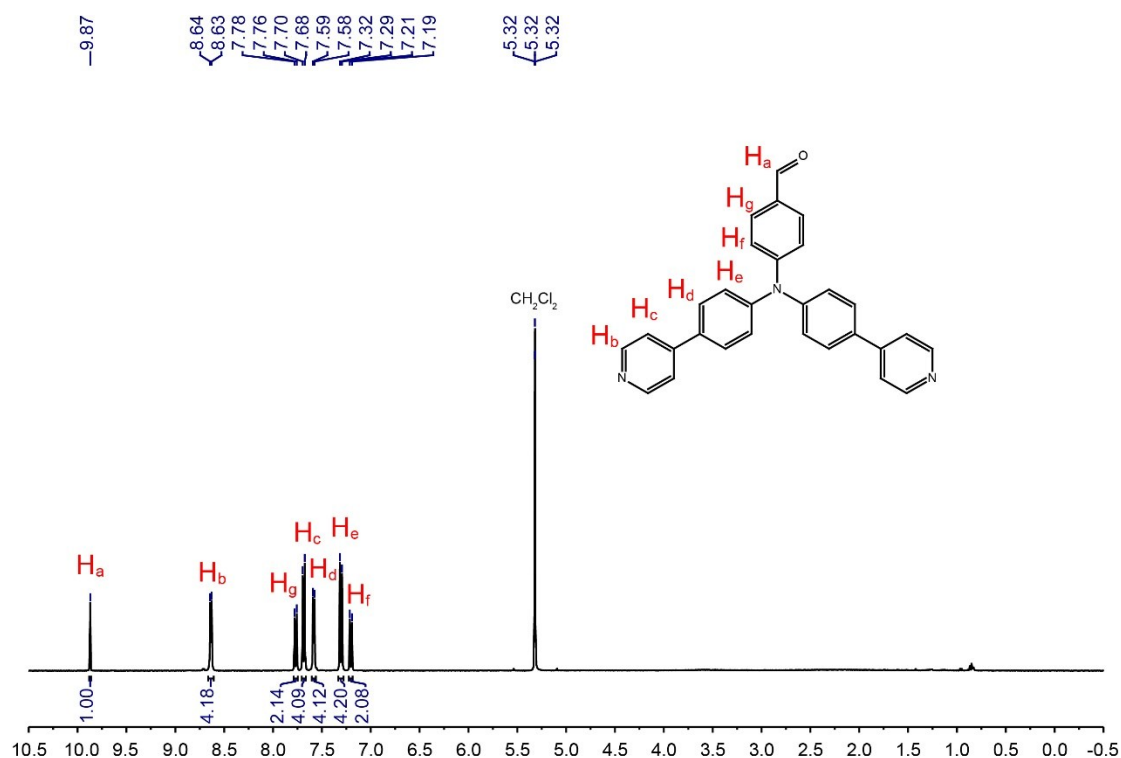


Fig. S2. Partial 1H NMR (400 MHz, CD_2Cl_2 , 295 K) spectrum recorded for ligand **1**.

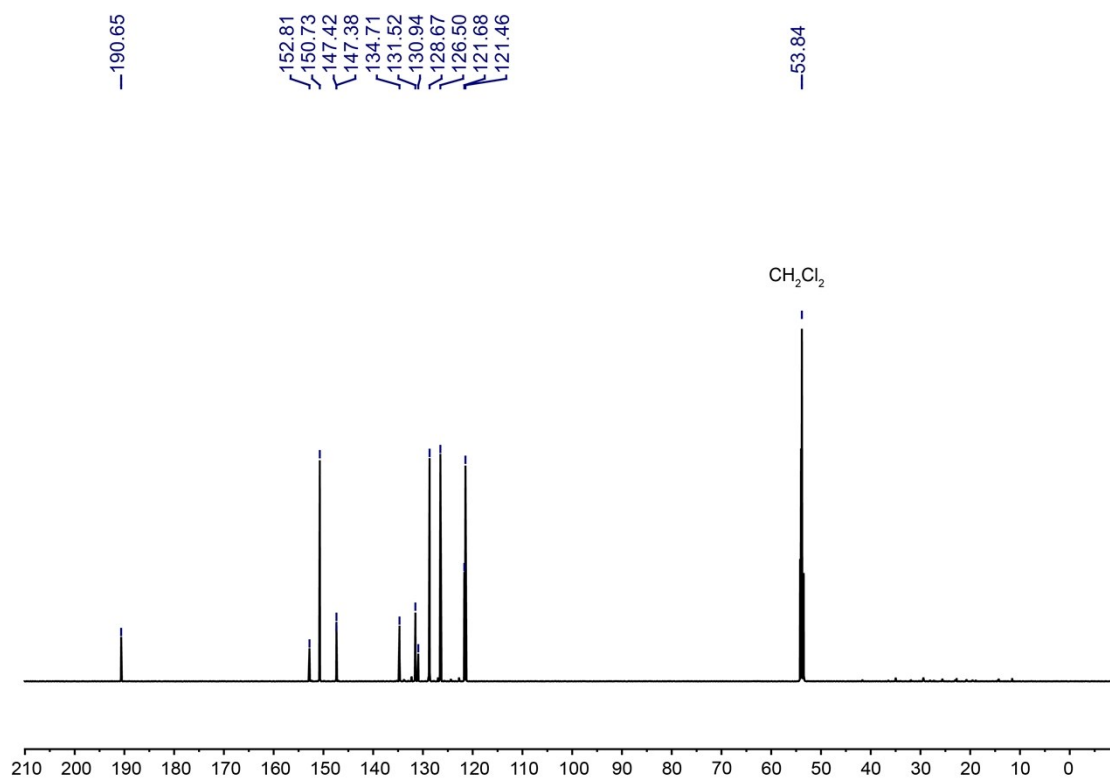


Fig. S3. Partial ^{13}C NMR (400 MHz, CD_2Cl_2 , 295 K) spectrum recorded for ligand **1**.

3. Synthesis of compound **2**

Compound **2** was synthesized according to literature procedure.^{S3} The ^1H NMR and ^{31}P NMR of **2** match well with the reported data.

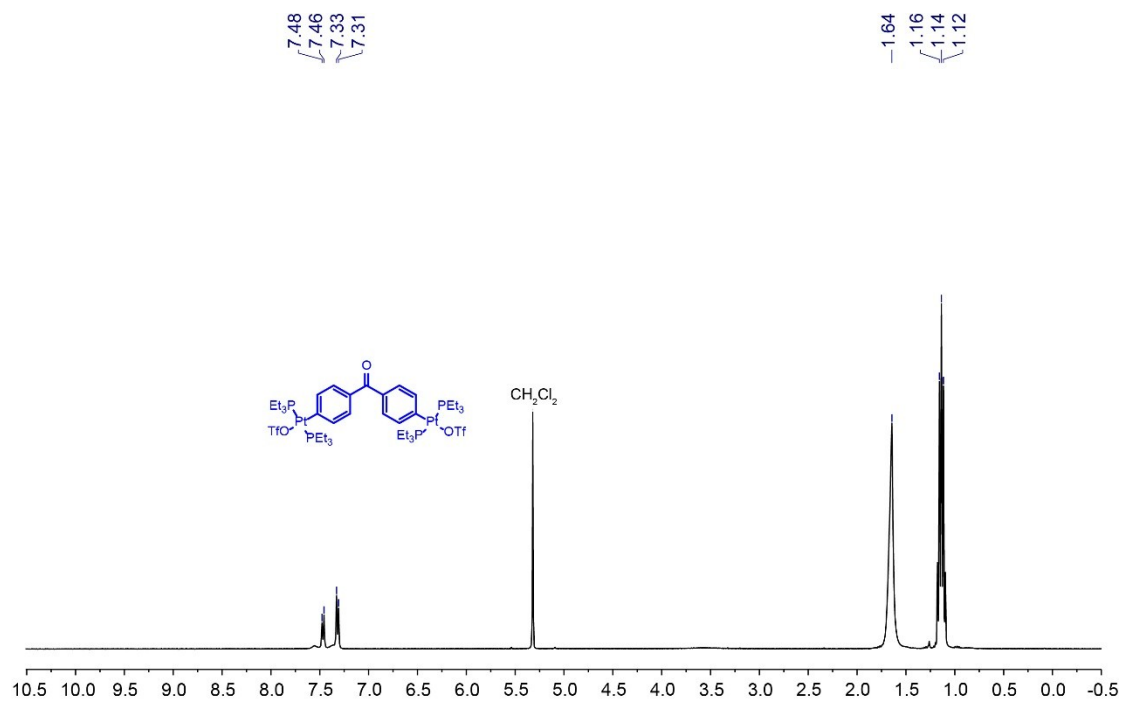


Fig. S4. Partial ^1H NMR spectrum (400 MHz, CD_2Cl_2 , 295 K) recorded for **2**.

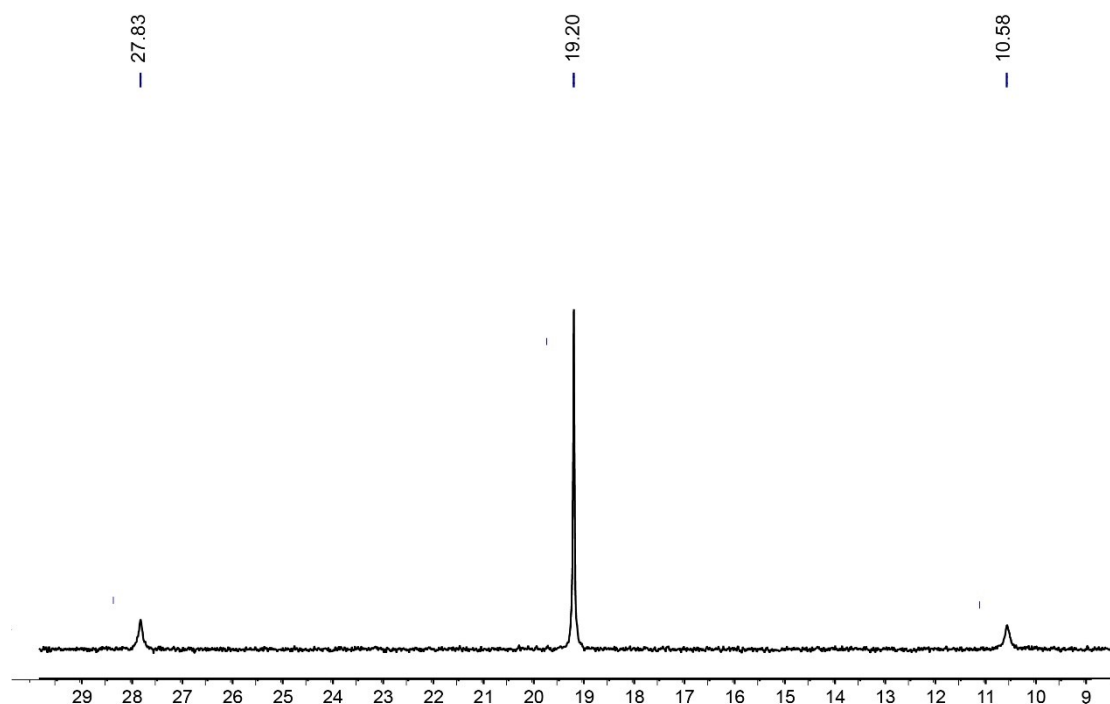
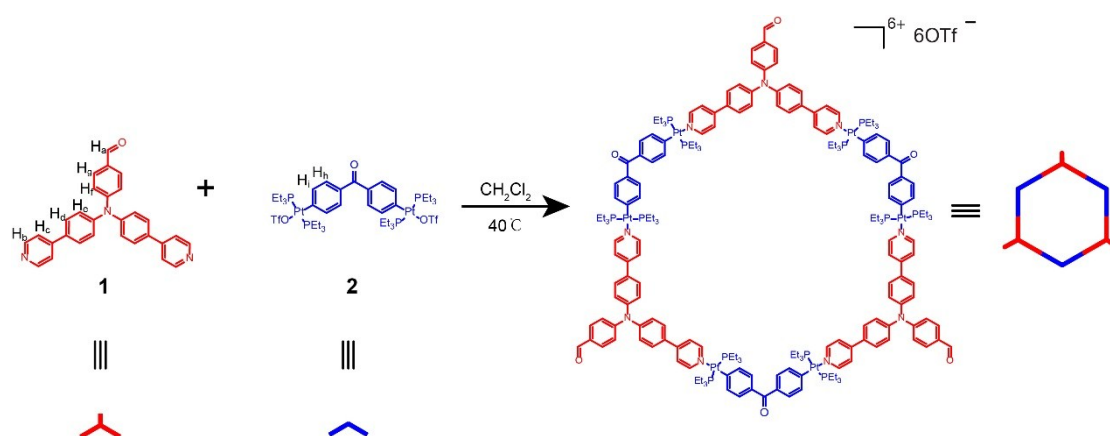


Fig. S5. Partial $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, CD_2Cl_2 , 295K) recorded for **2**.

4. Self-assembly of hexagonal metallacycle **3**



In a 1:1 molar ratio, 4-(bis(4-(pyridin-4-yl)phenyl)amino)benzaldehyde **1** (3.14 mg, 0.007 mmol) and 120° diphosphine acceptor **2** (9.85 mg, 0.007 mmol) were dissolved in 4.0 mL dichloromethane in a sealed vial. The reaction mixture was stirred at 40 °C for 8 h and then cooled to room temperature. The solution was filtered and the solvent was removed by nitrogen flow. The orange solid **3** (11.27 mg, 91 %) was gained by recrystallization through dichloromethane/diethyl ether twice. ^1H NMR (400 MHz, CD_2Cl_2 , 295 K) δ 9.92 (s, 1H), 8.67 (d, J = 6.2 Hz, 4H), 7.99 (d, J = 6.2 Hz, 4H), 7.89 (d, J = 8.6 Hz, 4H), 7.83 (d, J = 8.6 Hz, 2H),

7.55 (dd, $J = 18.8, 7.9$ Hz, 8H), 7.37 (d, $J = 8.5$ Hz, 5H), 7.28 (d, $J = 8.5$ Hz, 2H), 1.46 – 1.31 (m, 24H), 1.19 – 1.11 (m, 36H). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2 , 295 K) δ (ppm): 13.13 ppm (s, ^{195}Pt satellites, $^1J_{\text{Pt-P}} = 2658.42$ Hz). ESI-TOF-MS: m/z 735.2419 [**3** – 6OTf] $^{6+}$, 912.1045 [**3** – 5OTf] $^{5+}$, 1177.4525 [**3** – 4OTf] $^{4+}$, 1619.6833 [**3** – 3OTf] $^{3+}$.

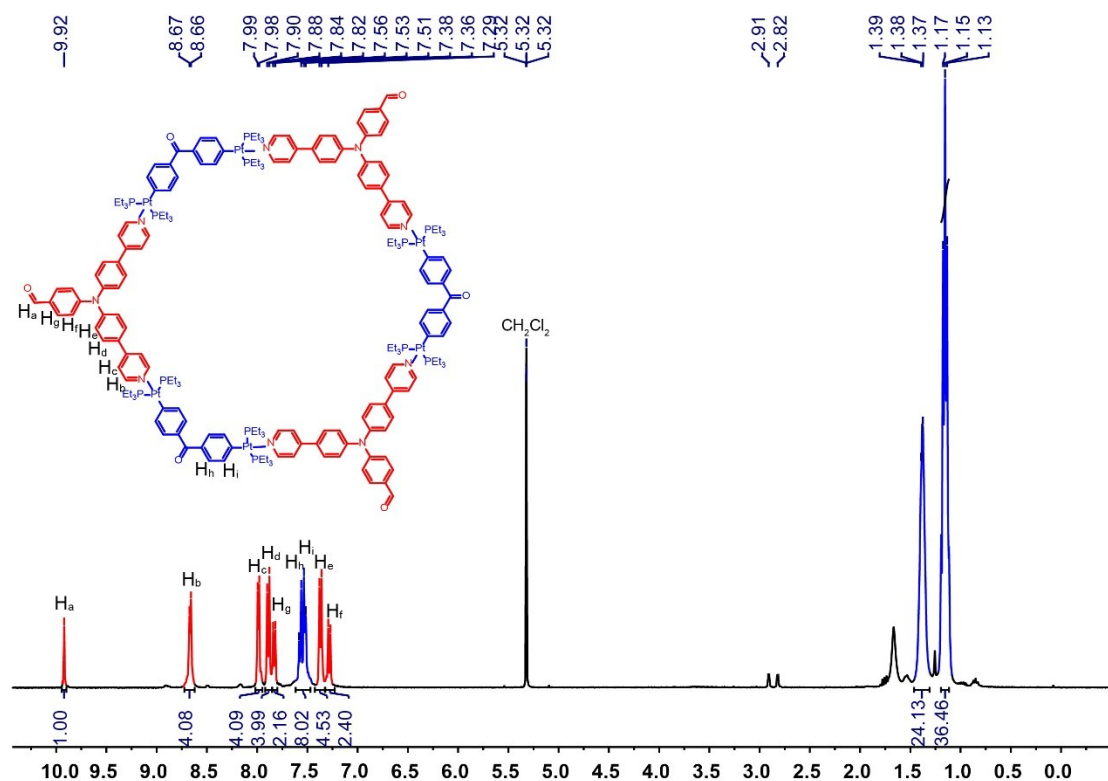


Fig. S6. Partial ^1H NMR spectrum (400 MHz, CD_2Cl_2 , 295 K) recorded for metallacycle **3**.

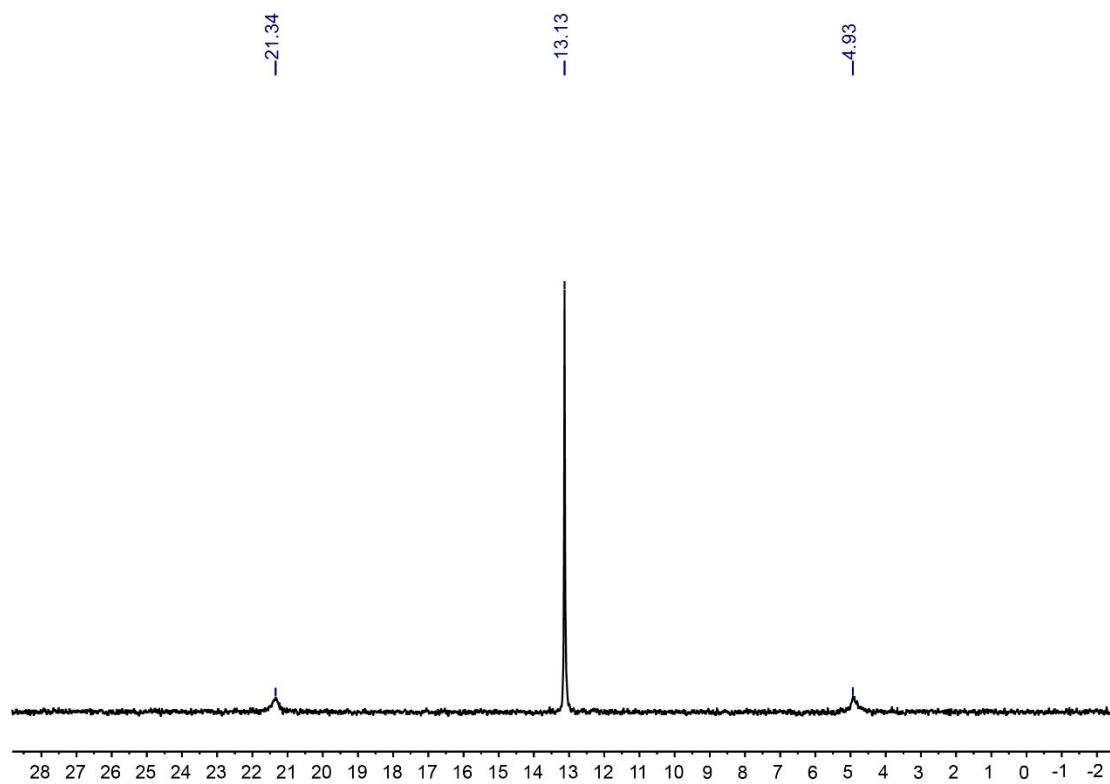


Fig. S7. Partial $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, CD_2Cl_2 , 295K) recorded for metallacycle **3**.

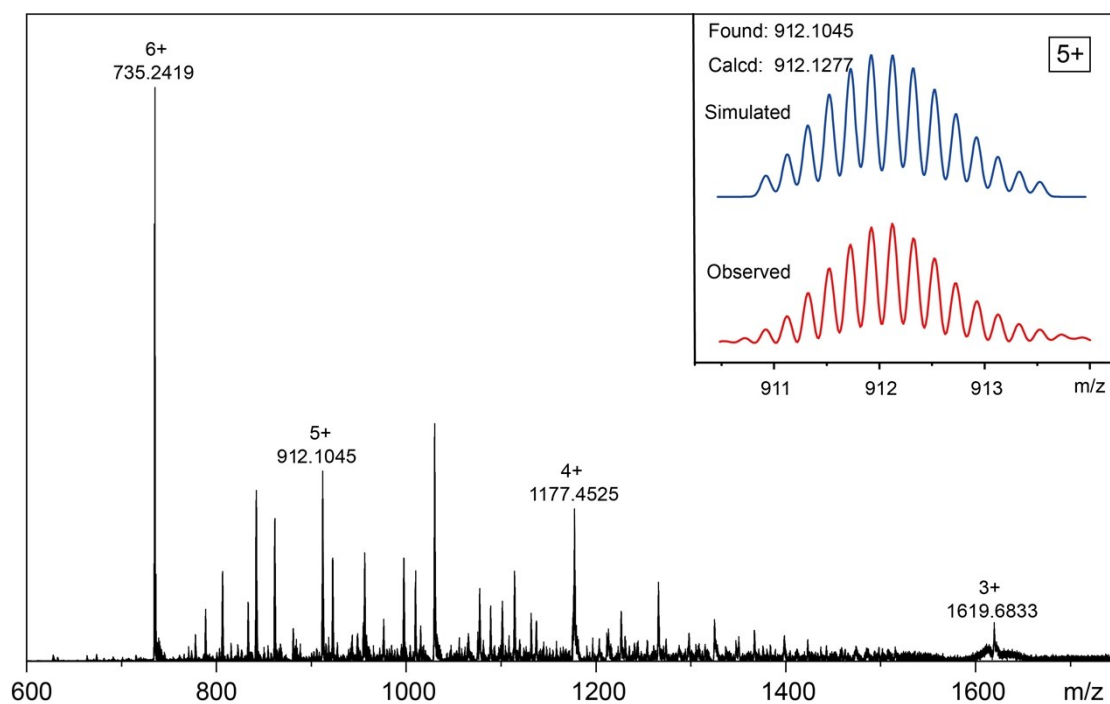
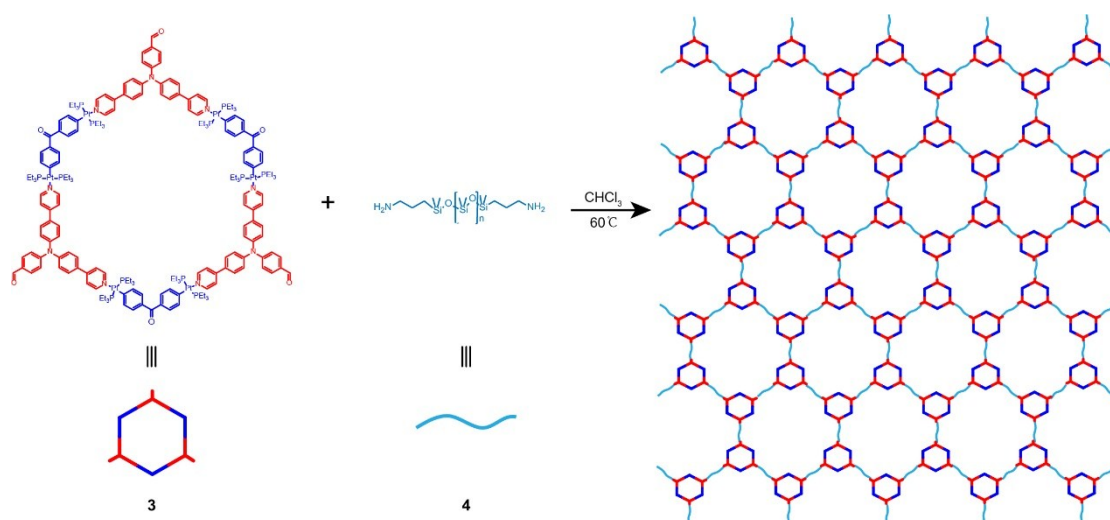


Fig. S8. ESI-TOF-MS spectrum of metallacycle **3**.

5. Synthesis of FSN 5



In a 2:3 molar ratio, a solution of metallacycle **3** (53.20 mg, 0.01 mmol) in CHCl_3 (2.00 mL) was added dropwise into a solution of linker **4** ($M_n = 2000$, PDI = 1.18, 30.00 mg, 0.015 mmol) in CHCl_3 (2.00 mL). The reaction mixture was stirred at 60 °C for 8 h, then dried under vacuum at 40 °C. A yellow polymer (80.85 mg, 98 %) was obtained. ^1H NMR (400 MHz, CD_2Cl_2 , 295 K) δ 8.63 (s, 4H), 8.27 (s, 1H), 7.96 (s, 4H), 7.86 – 7.62 (m, 6H), 7.61 – 7.37 (m, 8H), 7.36 – 7.09 (m, 6H), 3.59 (s, 2H), 2.62 (t, $J = 7.0$ Hz, 3H). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2 , 295 K) δ (ppm): 13.15 ppm (s, ^{195}Pt satellites, $^1J_{\text{Pt-P}} = 2668.14$ Hz).

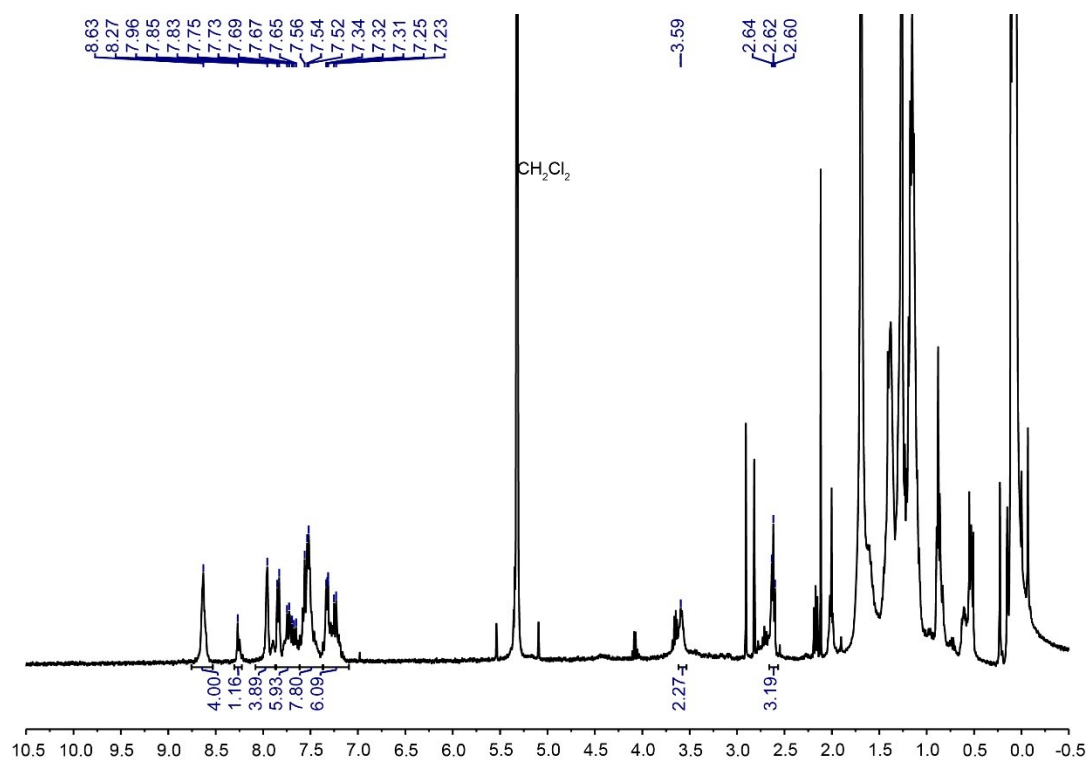


Fig. S9. Partial ^1H NMR spectrum (400 MHz, CD_2Cl_2 , 295 K) recorded for FSN **5**.

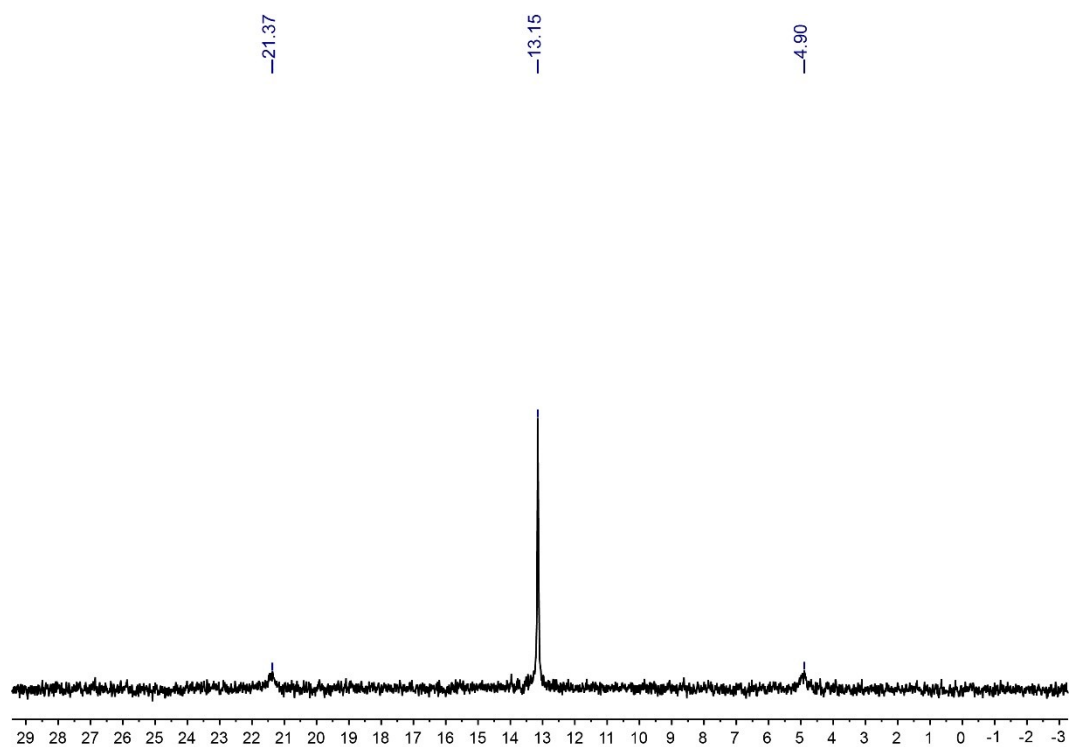


Fig. S10. Partial $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, CD_2Cl_2 , 295K) recorded for FSN **5**.

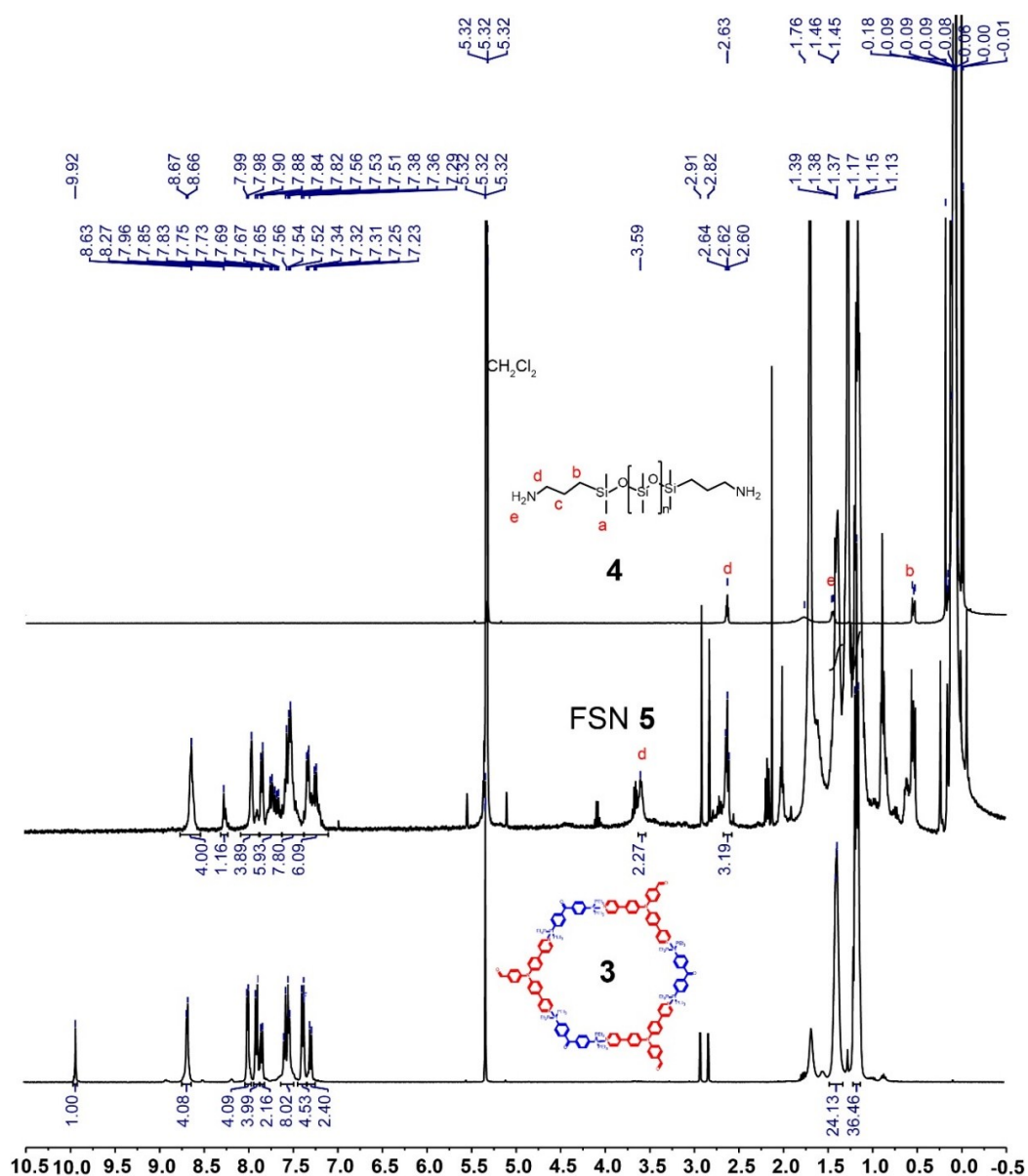


Fig. S11. ^1H NMR spectra (400 MHz, CD_2Cl_2 , 295 K) recorded for metallacycle **3** (bottom), linker **4** (top), and FSN **5** (middle).

6. Absolute fluorescence quantum yields

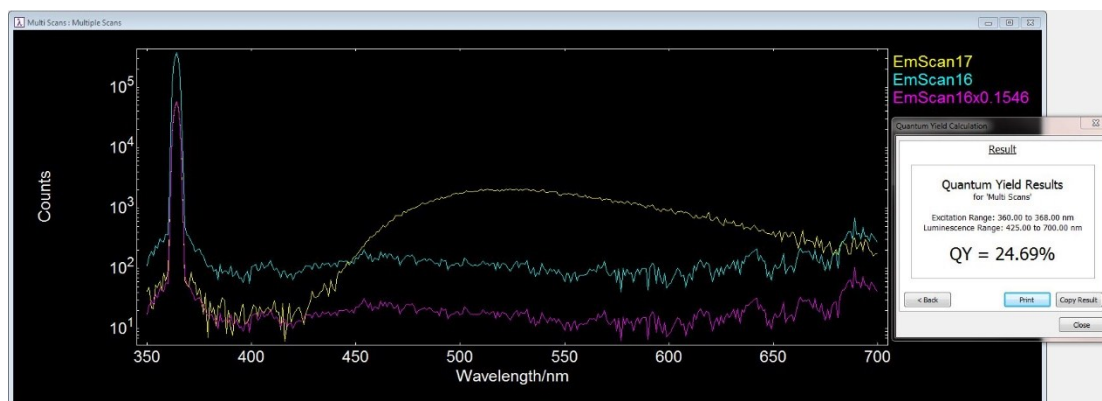


Fig. S12. Absolute fluorescence quantum yield of ligand **1** in the solid state.

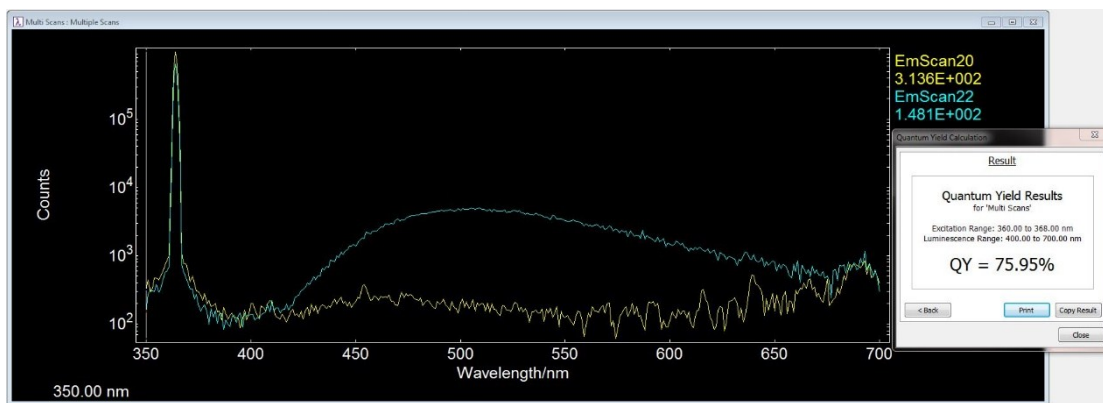


Fig. S13. Absolute fluorescence quantum yield of ligand **1** in CH_2Cl_2 .

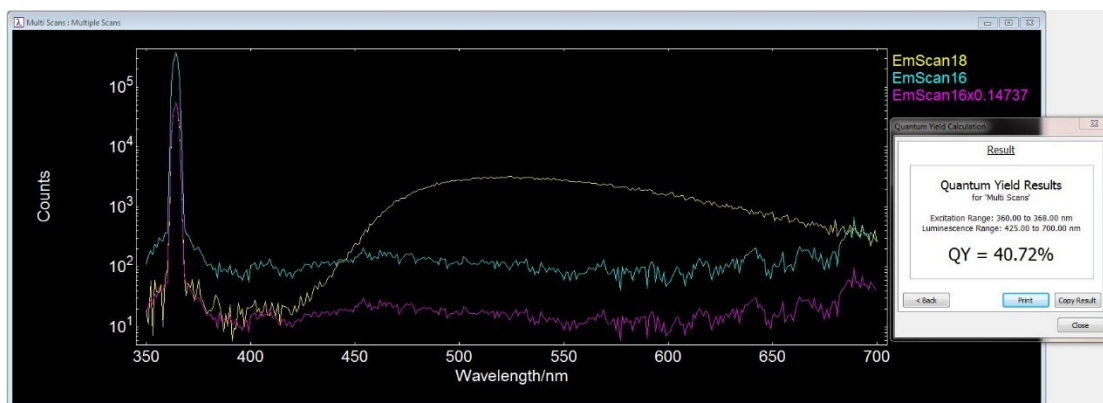


Fig. S14. Absolute fluorescence quantum yield of metallacycle **3** in the solid state.

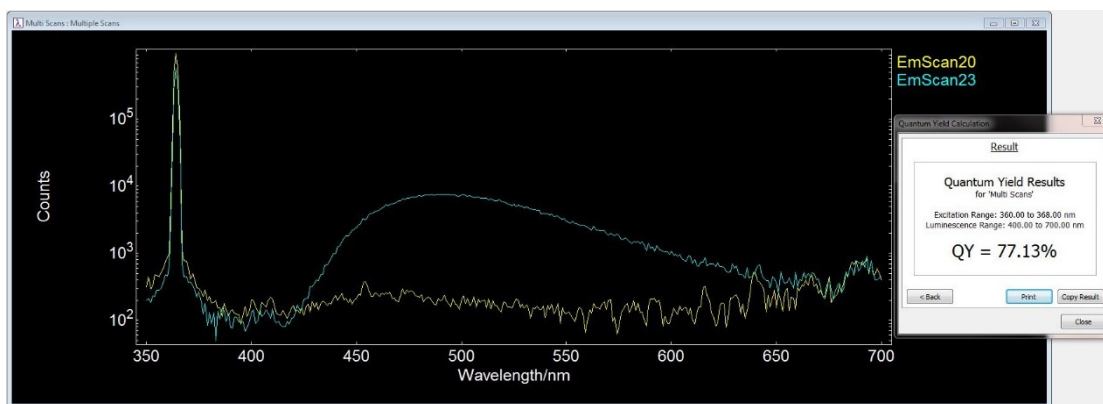


Fig. S15. Absolute fluorescence quantum yield of metallacycle **3** in CH_2Cl_2 .

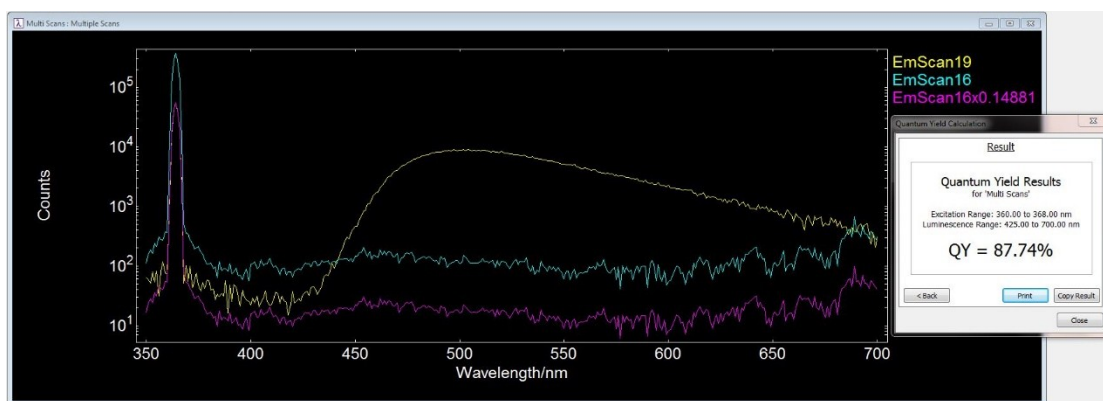


Fig. S16. Absolute fluorescence quantum yield of FSN **5** in the solid state.

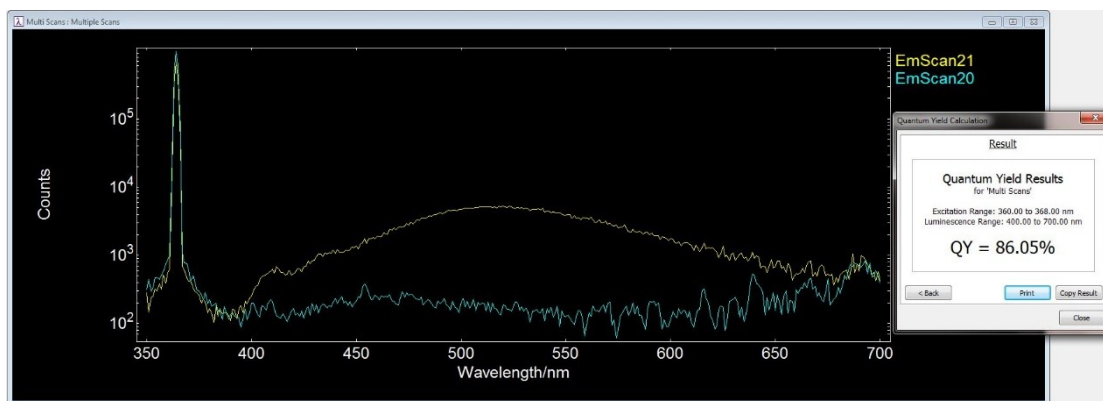


Fig. S17. Absolute fluorescence quantum yield of solid FSN **5** in CH₂Cl₂.

7. NMR characterization of FSN **5** after the addition of halide ions

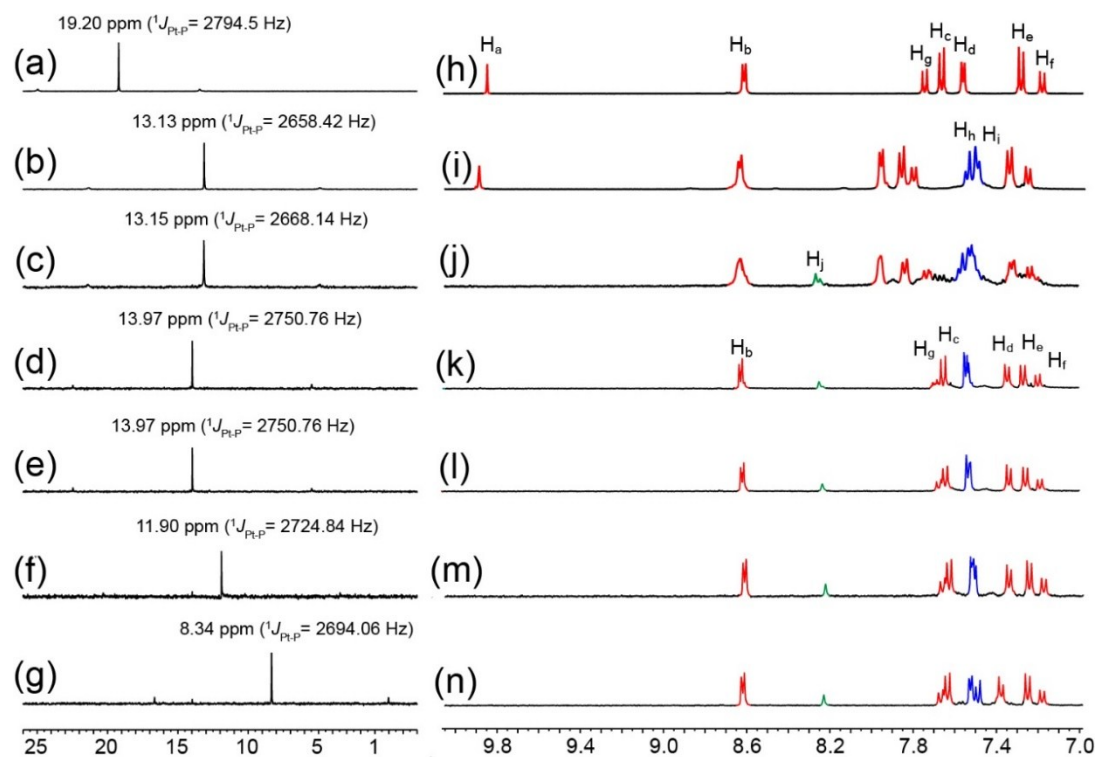


Fig. S18. Partial (a–g) ³¹P{¹H} and (h–n) ¹H NMR spectra (162 or 400 MHz, CD₂Cl₂, 298 K) of ligand **1** (h), platinum acceptor **2** (a), metallacycles **3** (b and i), FSN **5** (c and j), and FSN **5** after the addition of TBAF (d and k), TBAC (e and i), TBAB (f and m), and TBAI (g and n).

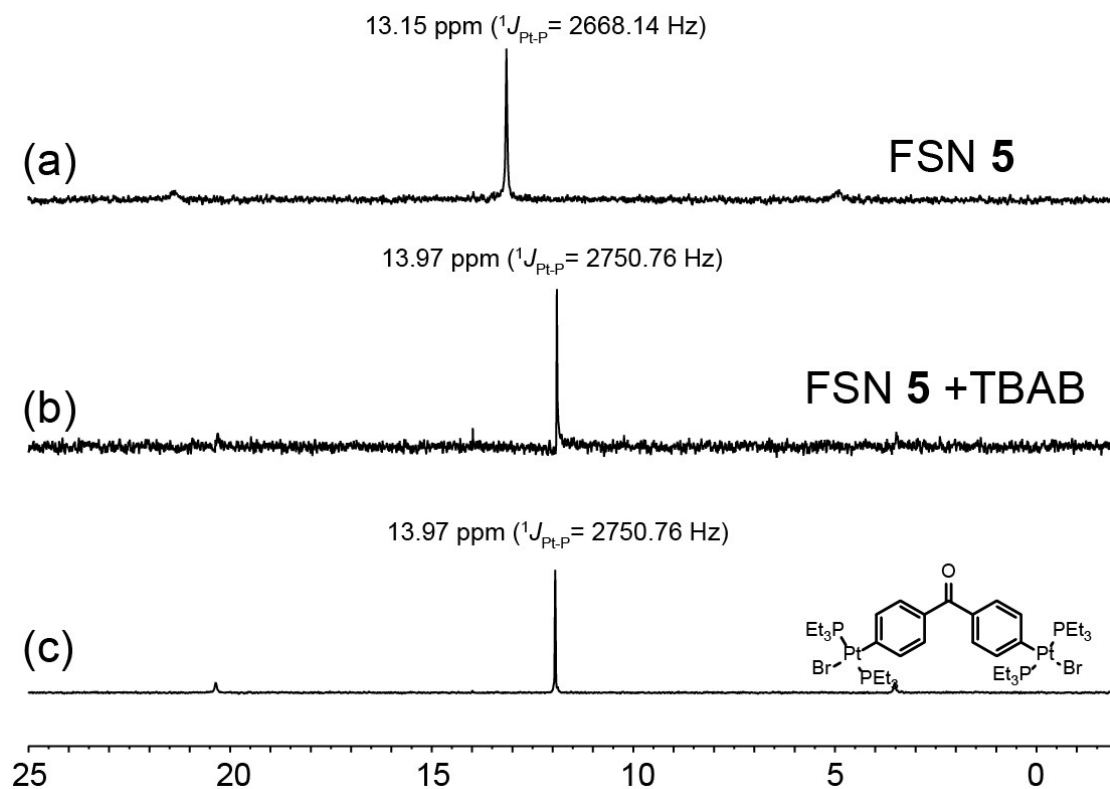


Fig. S19. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, CD_2Cl_2 , 295K) of FSN **5** (a), FSN **5** after the addition of TBAB (b) and the bromide precursor of diplatinum(II) ligand **2** (c).

References

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