Supporting Information for

Hierarchical self-assembly of fluorescence emission-enhanced organogelator and its multiple stimuli-responsive behaviors

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Contents:

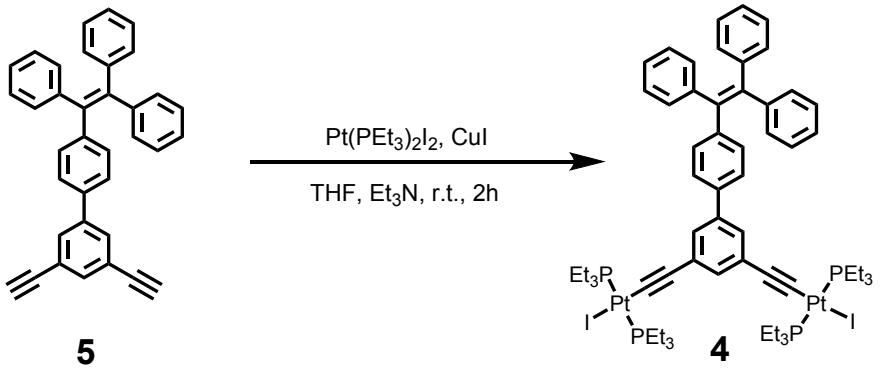
1. General information

All reagents were analytical reagents and used without further treatment. All solvents used were dried according to standard procedures and degassed under N_2 for 30 minutes. All air-sensitive reactions were carried out under argon atmosphere. TLC analysis were performed on silica-gel plates, and column chromatography was conducted by using silica-gel column.

^{1}H NMR, ^{31}P NMR, and ^{13}C NMR spectra were recorded on Bruker 400 MHz Spectrometer (^{1}H: 400 MHz; ^{31}P: 161.9 MHz; ^{13}C: 100 MHZ) at 298 K. The ^{1}H and ^{13}C NMR chemical shifts are reported relative to residual solvent signals, and ^{31}P NMR resonances are referenced to an internal standard sample of 85% H_3PO_4 (δ 0.0). Coupling constants (*J*) are denoted in Hz and chemical shifts (δ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, m = multiplet, br = broad. Fluorescence spectra were recorded on Varian Cary Eclipse.

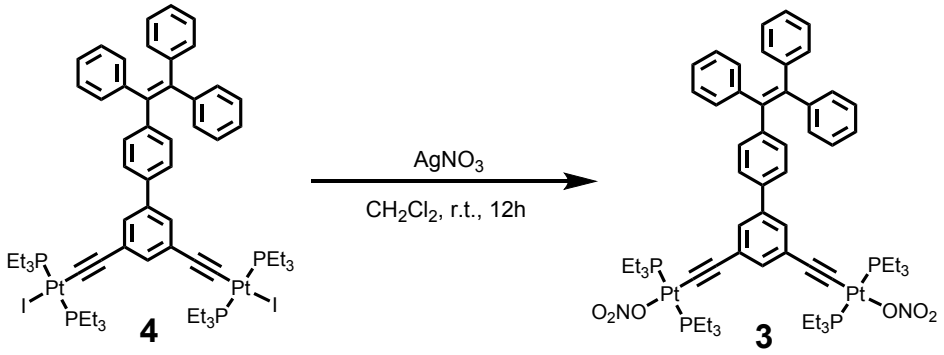
The compound **2** was prepared according to our previous reported method (*Chem. Commun.*, 2014, **50**, 4231).

2. The preparation of hexagonal metallacycle 1 and the structure of complex TPA



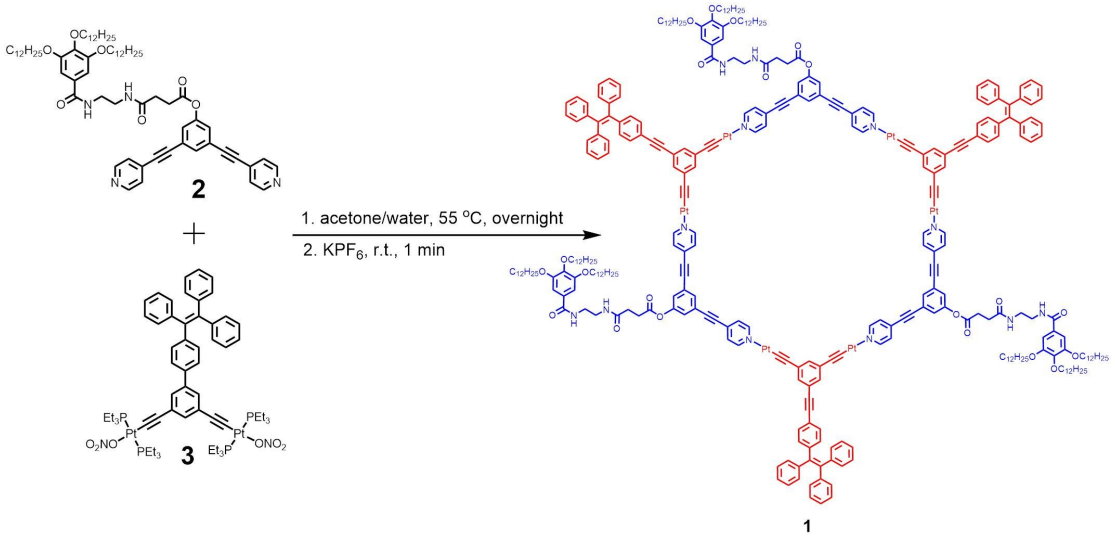
Scheme S1 The synthesis of compound **4**

Synthesis of compound **4**: To a solution of $Pt(PEt_3)_2I_2$ (1.14 g, 1.66 mmol) and CuI (11 mg, 10 mol%) in dried THF (60 mL) and Et_2NH (40 mL) was added compound **5** (200 mg, 0.416 mmol) dropwise with stirring under an atmosphere of nitrogen, the reaction was stirred at room temperature for 2 h yielded compound **4** (433 mg, 75.3%) as a yellow solid after purification by column chromategraphy (dichloromethane/petroleum ether). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.18 (s, 2H), 7.11 (dd, J_1 = 7.2 Hz, J_2 = 4.8 Hz,11H), 7.06–6.99 (m, 8H), 2.21 (m, 24H), 1.21–1.12 (m, 36H). ^{31}P NMR ($CDCl_3$, 161.9 MHz): δ = 9.12 (s, $J_{Pt\text{-}P}$ = 1159.2Hz). ^{13}C NMR ($CDCl_3$, 400 MHz) δ 143.48, 131.38, 130.99, 127.84, 126.64, 77.37, 77.05, 76.73, 29.72, 16.63, 8.33. MS(MALDI): Calcd for $[M + H]^+$ 1595.53; found: 1495.53.



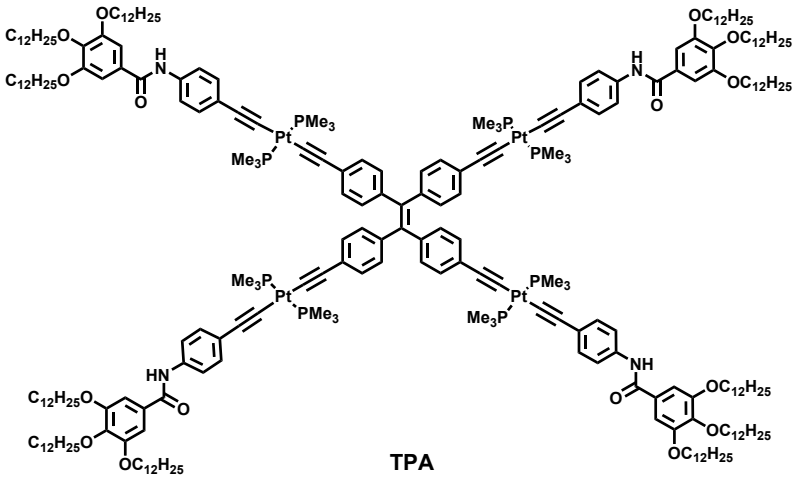
Scheme S2 The synthesis of compound **3**

Synthesis of compound **3**: A 50 ml of Schlenk flask was charged with compound **4** (150 mg, 0.07 mmol), $AgNO_3$ (200 mg, 0.07 mmol) degassed, and back-filled there times with N_2. A solvent of dried CH_2Cl_2 (10 mL) was added into the reaction flask by syringe. The reaction was stirred at room temperature for 12 hours under the condition of avoiding light. The solvent was removed by evaporation, then, recrystallization by ethylether and CH_2Cl_2. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 7.26 (dd, J_1 = 2.0, J_2 = 6.8 Hz, 2H), 7.15-7.11 (m, 11H), 7.06–7.02 (m, 8H), 1.91-1.98 (m, 24H), 1.23–1.17 (m, 36H). ^{31}P NMR (CD_2Cl_2, 161.9 MHz): δ = 20.59 (s, J_{Pt-P} = 1235.3 Hz).^{13}C NMR (100 MHz, CD_2Cl_2): δ 144.70, 143.89, 143.69, 142.27, 140.65, 133.92, 131.63, 131.22, 128.41, 127.91, 127.03, 123.49, 121.11, 54.38, 54.11, 53.84, 53.57,53.30, 30.09, 14.85, 7.99. MS (MALDI): Calcd for $[M + H]^+$ 1465.44; found: 1465.



Scheme S3 The synthesis of complex **1**

Synthesis of hexagon **1**: A mixture of 120º donor **2** (4.5 mg, 4.1 μmol) and the equimolar amount of 120º acceptor di-Pt(II) acceptor compound **3** (618 mg, 4.1 μmol) were placed in a glass vial. The reaction mixture was stirred at 55 ºC in acetone/H_2O (2 mL/0.4 mL). After stirring 12 hours, The ONO_2 salt of hexagon **4** was easily obtained by removing solvent under a flow of nitrogen. The PF_6 salt of hexagon **4** was synthesized by dissolving the ONO_2 salt in acetone/H_2O and adding a saturated aqueous solution of KPF_6 to precipitate the product, which was collected by vacuum filtration. Yield: 97%. ^{1}H NMR (acetone-d_6,400 MHz): δ 9.03 (d, J = 6.0 Hz, 12H), 8.03 (br, 3H), 7.93-7.89 (m, 15H), 7.65 (br, 3H),7.56 (d, J = 1.2 Hz, 3H), 7.32 (d, J = 8 Hz, 6H), 7.28 (d, J = 1.2 Hz, 6H), 7.19-7.13 (m, 33H),7.10-7.03 (m, 27H), 4.03-3.95 (m, 18H), 3.48 (br, 6H), 2.71-2.68 (m, 6H), 1.99-1.95 (m, 72H), 1.83-1.69 (m, 18H), 1.56-1.49 (m, 18H), 1.36-1.19 (m, 252H), 0.89-0.86 (m, 27H). ^{31}P NMR (acetone-d_6, 161.9 MHz): δ = 17.41 (s, $J_{Pt\text{-}P}$ = 1165.68 Hz).



Scheme S4 The structure of complex **TPA**

3. Partial ^{1}H and ^{31}P NMR spectra of the ligands 2-3 and hexagon 1

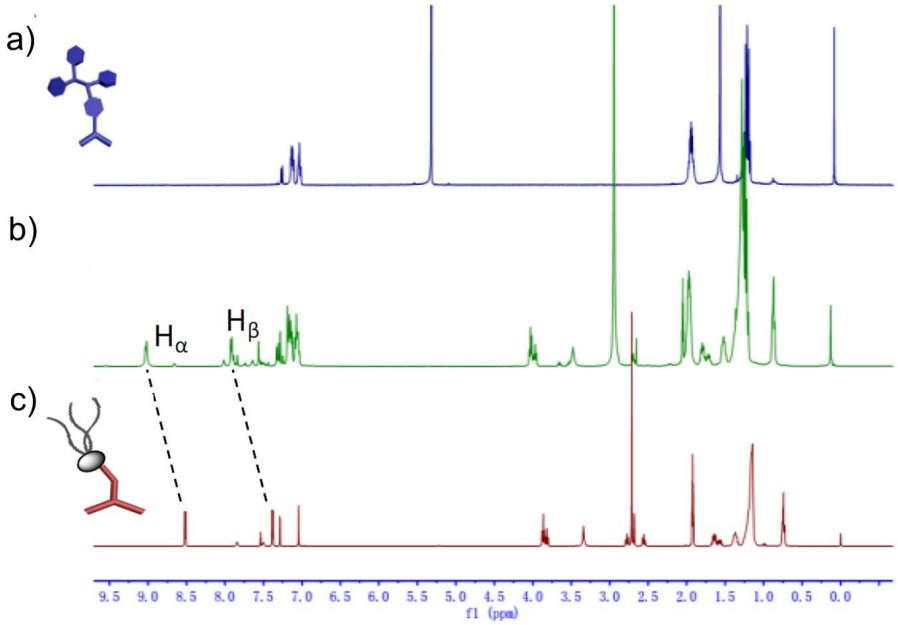


Fig. S1 Partial ^{1}H NMR spectra of the 120° ligand **3** (a), [3 + 3] hexagon **1** (b), and 120° ligand **2** (c).

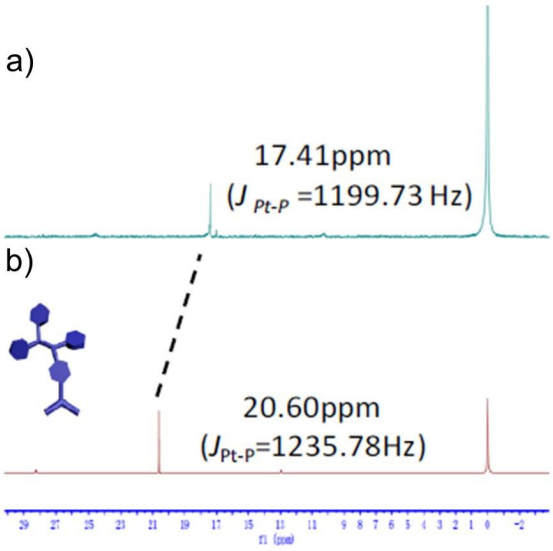


Fig. S2 Partial ^{31}P NMR spectra of the [3 + 3] hexagon **1** (a) and 120° acceptor ligand **3** (b).

4. ESI-TOF-MS of hexagon 1

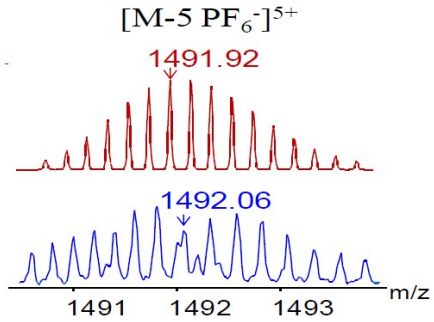


Fig. S3 Theoretical (top) and experimental (bottom) ESI-TOF-MS results of hexagon **1**.

5. SEM image of hexagon 1

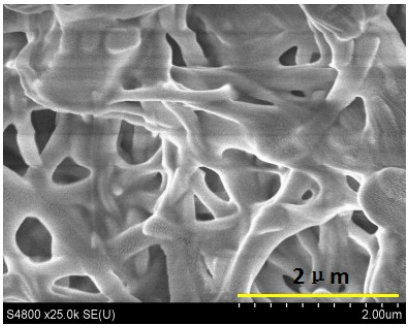


Fig. S4 SEM image of hexagon **1** in gel state.

6. The partial ^{1}H NMR spectra of hexagon 1 with different concentrations

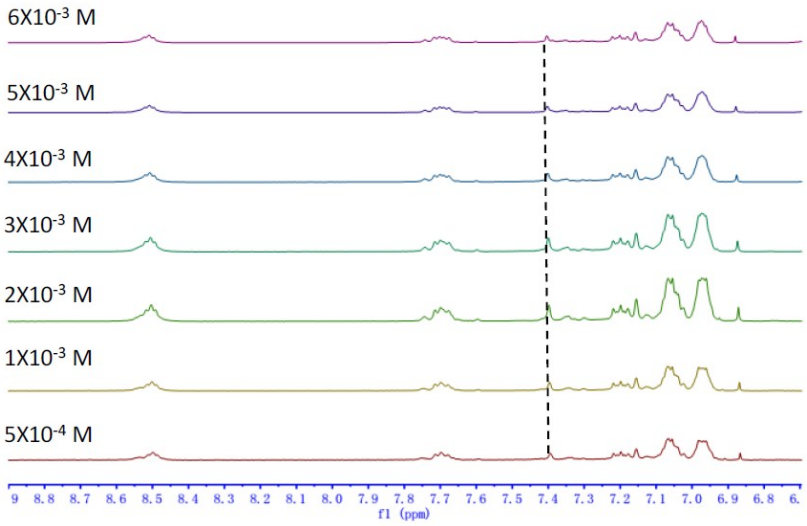
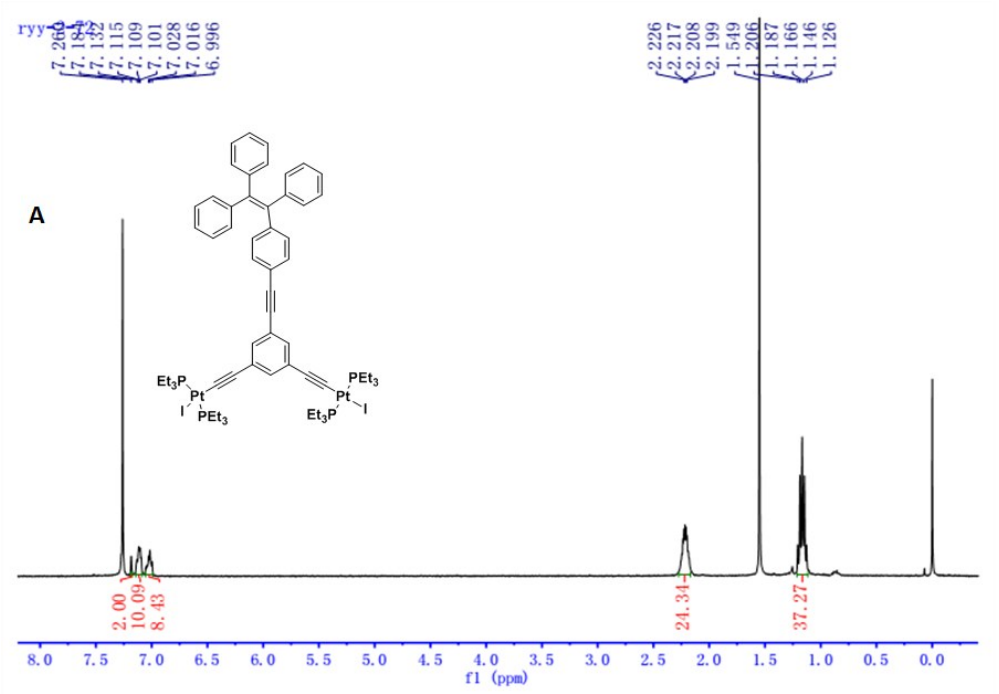
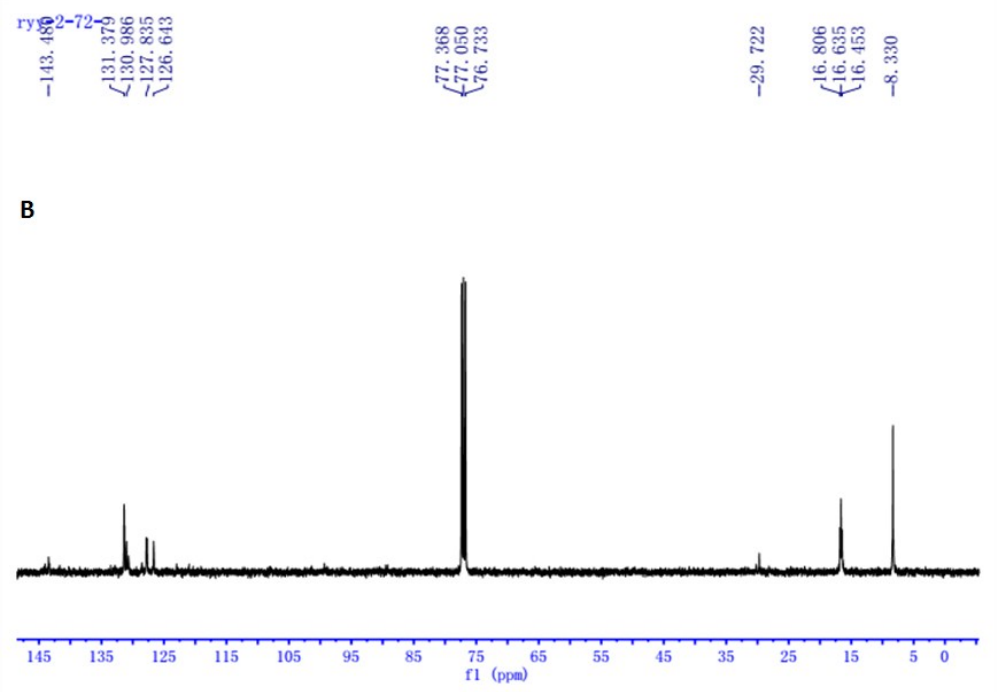


Fig. S5 The partial ^{1}H NMR spectra of hexagon **1** with different concentrations.

7. The ^{1}H, ^{13}C, and ^{31}P NMR spectra of compounds 3-4 and hexagon 1





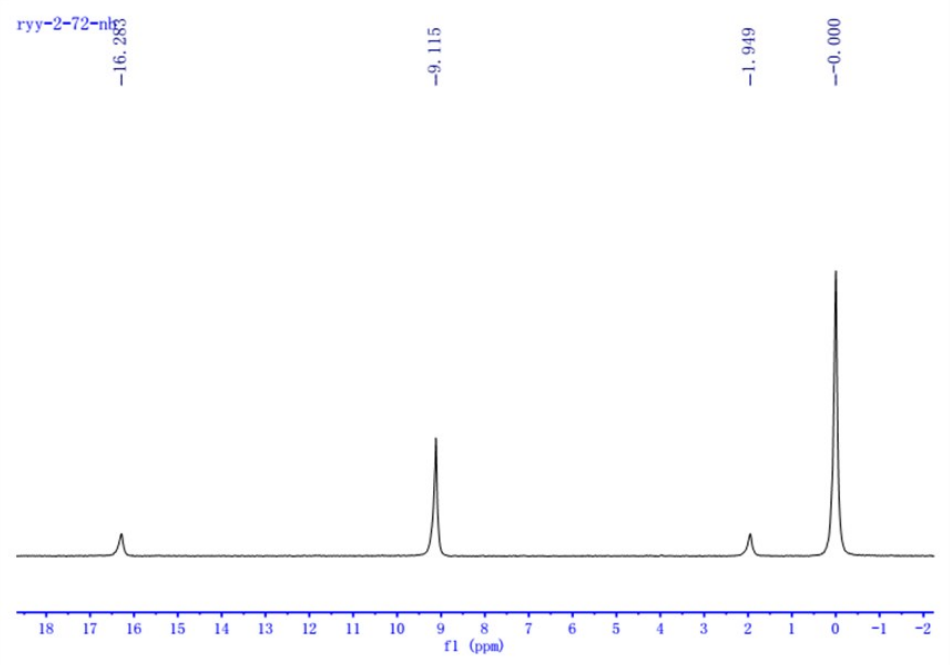
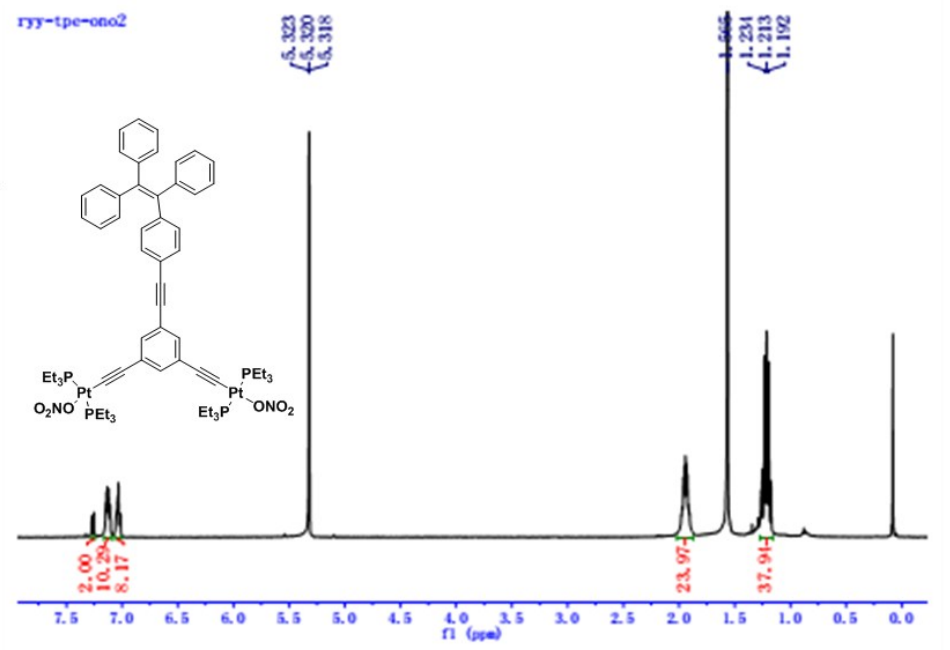


Fig. S6 The ^{1}H NMR (a), ^{13}C NMR (b), and ^{31}P NMR (c) spectra of compound **4** in $CDCl_3$.



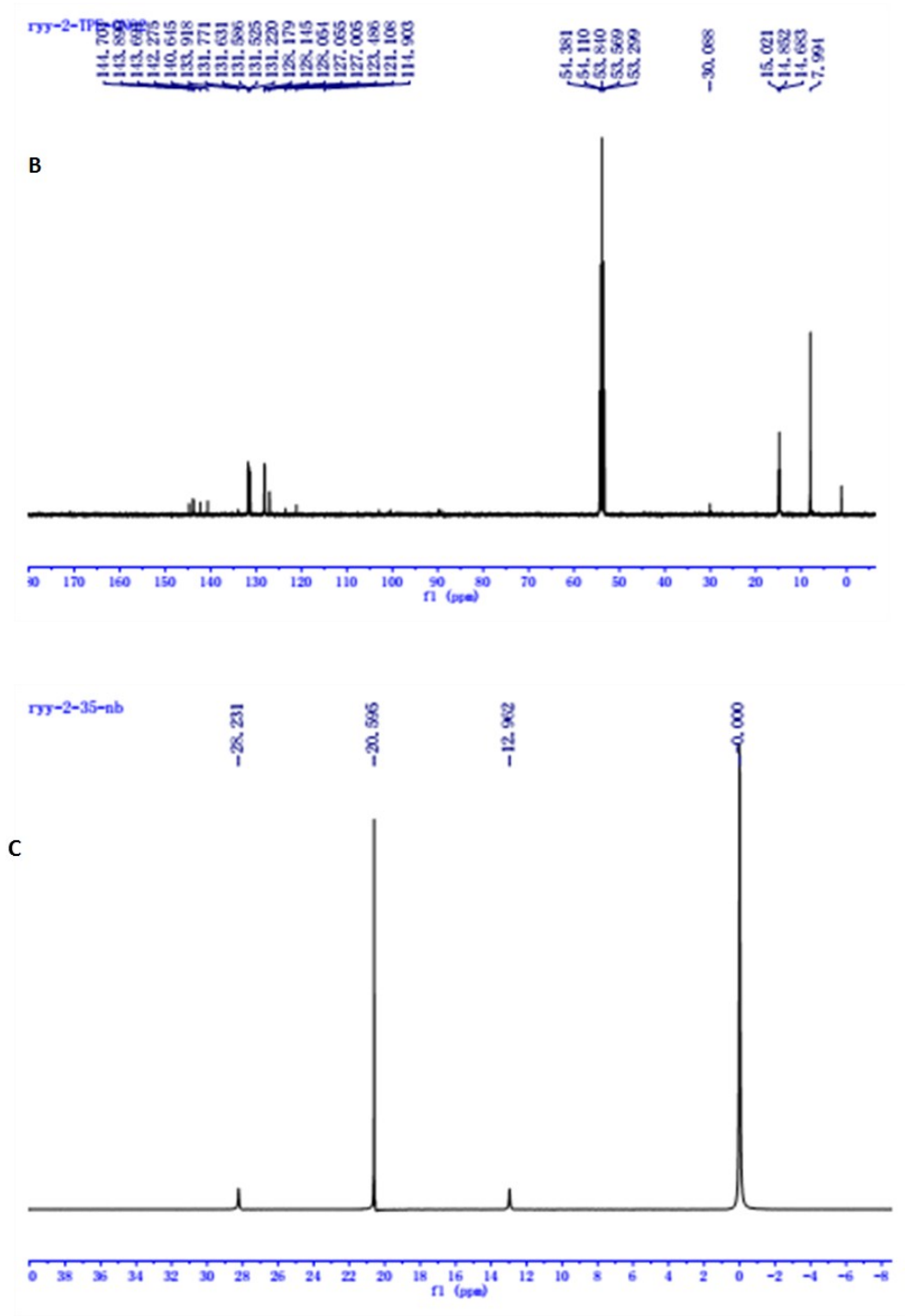


Fig. S7 The ^{1}H NMR (a), ^{13}C NMR (b), and ^{31}P NMR (c) spectra of compound **3** in CD_2Cl_2.

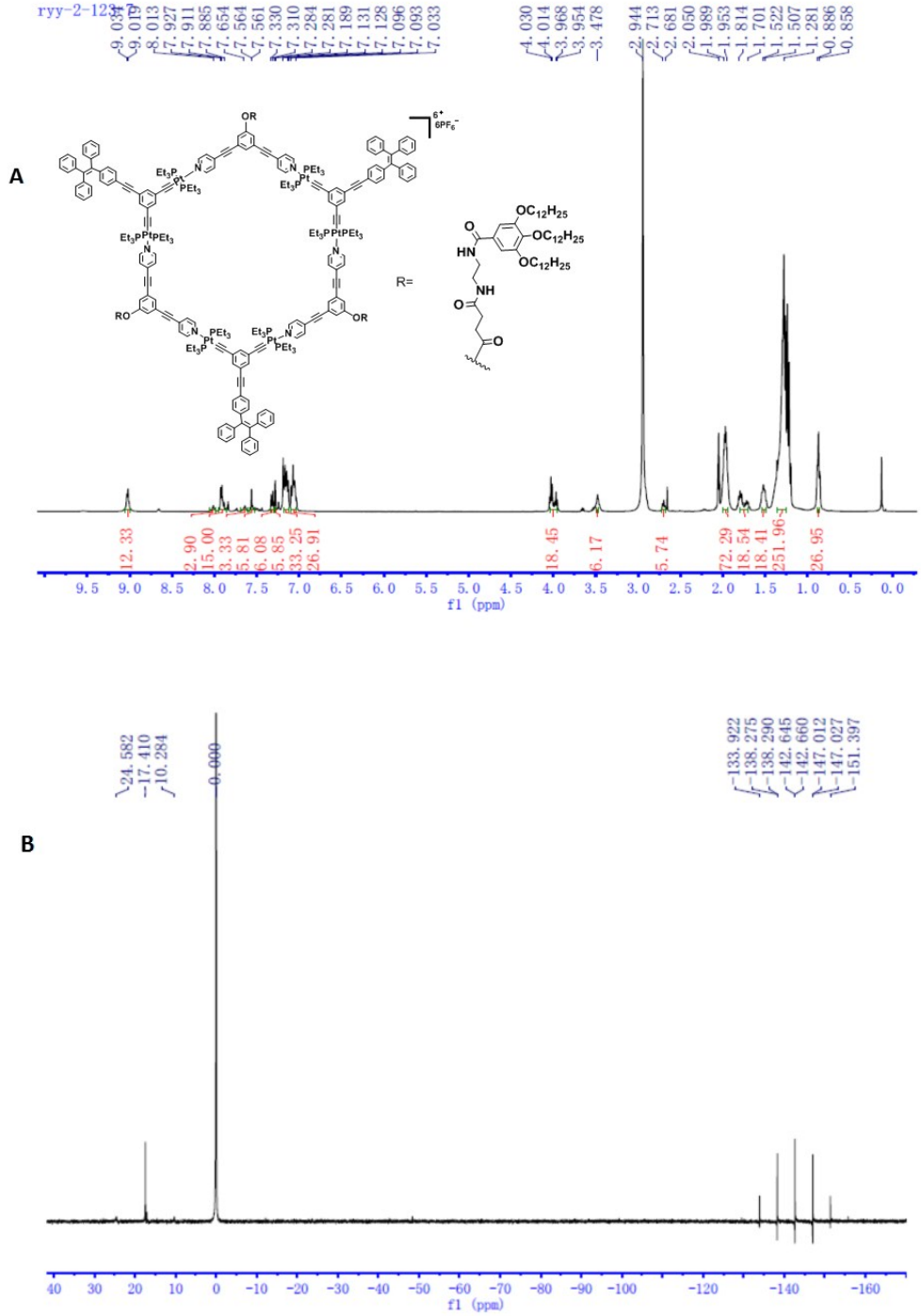


Fig. S8 The ^{1}H NMR (a) and ^{31}P NMR (c) spectra of hexagon **1** in acetone-d_6.