

Spontaneous Formation of a Cross-Linked Supramolecular Polymer Both in the Solid State and in Solution, Driven by Platinum(II) Metallacycle-Based Host–Guest Interactions

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1. Materials, methods and instruments

All reagents were commercially available and used as supplied without further purification. Solvents were either employed as purchased or dried according to procedures described in the literature. ^1H NMR and ^{13}C NMR spectra were recorded with a Bruker Avance DMX-600 spectrometer, a Bruker Avance DMX-500 spectrometer or a Bruker Avance III-400 spectrometry using the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. DOSY and NOESY spectra were collected on a Bruker Avance DMX-500 spectrometer with internal standard TMS. The $^{31}\text{P}\{^1\text{H}\}$ NMR chemical shifts are referenced to an external unlocked sample of 85% H_3PO_4 (δ 0.0). High-resolution mass spectrometric experiments were performed with a Bruker 7-Tesla FT-ICR mass spectrometer equipped with an electrospray source (Billerica, MA, USA). Scanning electron microscopy investigations were carried out on a JEOL 6390LV instrument. Dynamic light scattering was carried out on a Malvern Nanosizer S instrument at room temperature. The single crystals data were collected on an Oxford Diffraction Xcalibur Atlas Gemini captra.

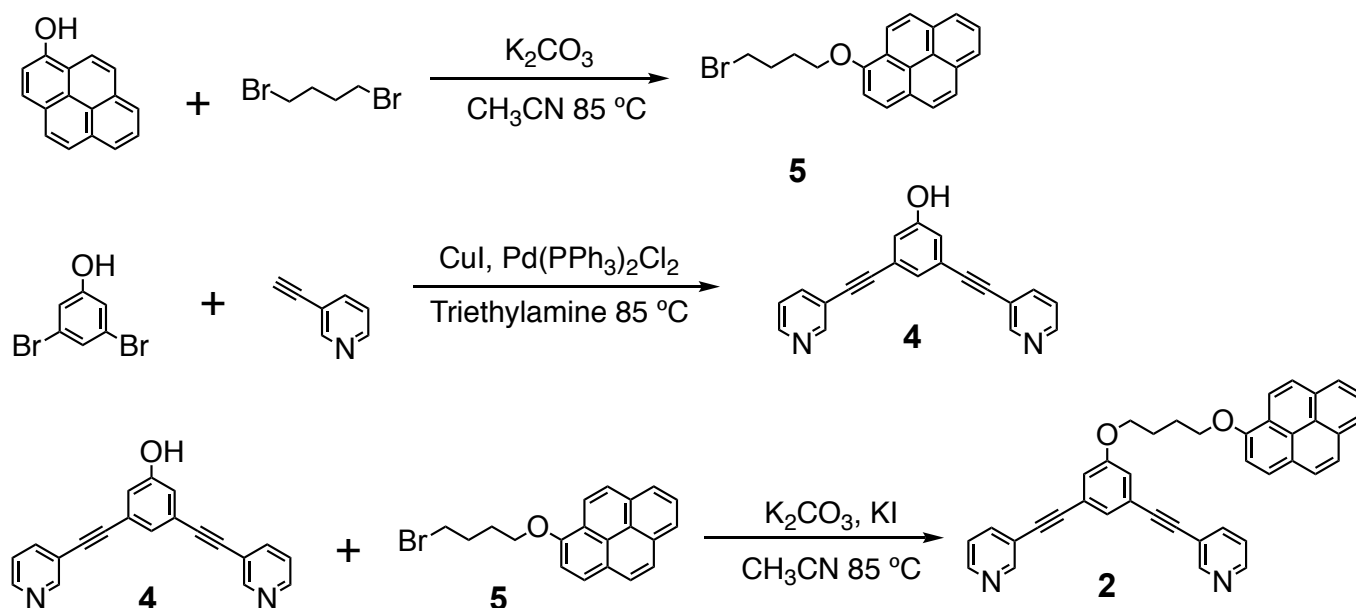
Single-crystal growth: single-crystal growth was performed *via* the following method: 5.0 mg of dry **1** powder was put in a small vial where 3 mL of acetone was added. Light-yellow crystal of **1** was obtained by slow diffusion of ether into the acetone solution of **1** in 2 to 3 days.

Dynamic light scattering (DLS) study: the solutions of **1** (1.0×10^{-3} M and 5.0×10^{-2} M) were left to stand about 10 min before being used for DLS tests.

Scanning electron microscopy (SEM): the morphologies of the self-assemblies were investigated by SEM which helped in the visualization of the self-assembled structures. SEM samples were prepared by drop-coating acetone solutions containing **1** (5.0×10^{-2} M) onto silicon wafers *via* the vacuum freeze-drying methodology.

2. Synthesis of ligand 2

Scheme S1. Synthetic route to 2.



1-(4-bromobutoxy)pyrene (5)

In a 200 mL round bottom flask, 1-pyrenol (2.20 g, 10.0 mmol), K_2CO_3 (5.50 g, 40.0 mmol), 1,4-dibromobutane (4.30 g, 20.0 mmol) and acetonitrile (100.0 mL) were added. The reaction mixture was stirred at reflux for 12 hours. After the solid was filtered off, the solvent was removed. The solid was dissolved in $CHCl_3$ (150 mL) and washed twice with H_2O (200 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated to afford the crude product, which was recrystallized with CH_3CN to give 2.60 g of 1-(4-bromobutoxy)pyrene 5 (yield: 73%) as a light-yellow solid. Mp: $147.4\text{--}148.3\text{ }^\circ C$. 1H NMR spectrum of 5 is shown in Figure S1. 1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.43–8.45 (d, $J = 12$ Hz, 1H), 8.04–8.12 (m, 4H), 7.95–7.98 (m, 2H), 7.88–7.90 (d, $J = 12$ Hz, 1H), 7.47–7.48 (d, $J = 6$ Hz, 1H), 4.29–4.32 (t, $J = 12$ Hz, 2H), 3.56–3.58 (t, $J = 12$ Hz, 2H), 2.21–2.23 (m, 2H), 2.13–2.15 (m, 2H). ^{13}C NMR spectrum of 5 is shown in Figure S2. ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 155.49, 134.49, 134.33, 129.88, 129.09, 128.77, 128.49, 128.11, 127.96, 127.69, 127.60, 126.95, 126.84, 123.76, 123.02, 111.64, 70.46, 36.22, 32.36, 30.78. Anal. Calcd for $C_{20}H_{17}BrO$: C, 68.00; H, 4.85; Found C, 67.89; H, 4.80. HRESIMS: m/z calcd for $[M - H]^- C_{20}H_{16}BrO^-$, 351.0385, found 351.0383, error -5.7 ppm.

3,5-Bis(pyridin-3-ylethynyl)phenol (4)

Compound 4 was prepared according to previously reported procedures.^{S1} 3,5-Dibromophenol (2.60 g, 10.0 mmol), 3-ethynylpyridine (4.10 g, 40 mmol), $[Pd(PPh_3)_2Cl_2]$ (2.80 g, 4.0 mmol) and CuI (0.80 g, 4.0 mmol) were added to 50.0 mL of triethylamine and heated under an argon atmosphere at $70\text{ }^\circ C$. After 72 hours, the reaction mixture was diluted with ethylacetate (100 mL) and filtrated over celite. The solvent was removed

under reduced pressure and the crude residue was further purified by column chromatography (CH₂Cl₂:MeOH = 20:1) to give 1.10 g of 3,5-bis(pyridin-3-ylethynyl)phenol **4** as an off-white solid (yield: 38%). Mp: 235.4–235.9 °C. ¹H NMR spectrum of **4** is shown in Figure S3. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 9.70 (s, 1H), 8.83 (s, 2H), 8.58 (d, *J* = 4 Hz, 2H), 7.89 (d, *J* = 8 Hz, 2H), 7.36–7.39 (m, 2H), 7.29 (d, *J* = 8 Hz, 1H), 7.12 (s, 2H). ¹³C NMR spectrum of **4** is shown in Figure S4. ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 151.68, 148.14, 139.04, 126.41, 123.83, 123.54, 120.68, 119.70, 92.22, 85.93.

3,5-bis(3'-pyridylalkynyl)-1-(pyrenyl-1''-oxybutoxy)benzene (2)

In a 200 mL round-bottom flask, compound **4** (1.50 g, 5.0 mmol), K₂CO₃ (2.80 g, 20 mmol), KI (0.20 g, 1.0 mmol), compound **5** (1.90 g, 5.5 mmol) and acetonitrile (100.0 mL) were added. The reaction mixture was stirred at reflux for 12 hours. After the solid was filtered off, the solvent was removed. The solid was dissolved in CHCl₃ (150 mL) and washed twice with H₂O (200 mL). The organic layer was dried over anhydrous Na₂SO₄ and evaporated to afford the crude product, which was recrystallized with CH₃CN to give 1.80 g of 3,3'-((5-(4-(pyren-1-yloxy)butoxy)-1,3-phenylene)bis(ethyne-2,1-diyl))dipyridine **2** (yield: 63%) as a yellow solid. Mp: 135.7–136.5 °C. ¹H NMR spectrum of **2** is shown in Figure S5. ¹H NMR (600 MHz, CDCl₃) δ (ppm): 8.68 (s, 2H), 8.46–8.47 (d, *J* = 6 Hz, 2H), 8.35–8.36 (d, *J* = 6 Hz, 1H), 7.92–8.00 (m, 4H), 7.83–7.86 (t, *J* = 18 Hz, 2H), 7.77–7.78 (d, *J* = 6 Hz, 1H), 7.67–7.68 (d, *J* = 6 Hz, 2H), 7.42–7.43 (d, *J* = 6 Hz, 1H), 7.24 (s, 1H), 7.16–7.18 (m, 2H), 7.01 (s, 2H), 4.28–4.30 (t, *J* = 12 Hz, 2H), 4.06–4.08 (t, *J* = 12 Hz, 2H), 2.07–2.10 (m, 4H). ¹³C NMR spectrum of **2** is shown in Figure S6. ¹³C NMR (125 MHz, CDCl₃) δ (ppm): 161.40, 155.55, 154.87, 151.37, 141.18, 134.37, 134.31, 130.06, 129.87, 129.06, 128.75, 128.49, 128.12, 127.92, 127.66, 127.59, 126.92, 126.81, 126.58, 125.72, 123.77, 123.02, 122.77, 120.95, 111.68, 94.31, 89.06, 71.00, 70.58, 28.86, 28.82. Anal. Calcd for C₄₀H₂₈N₂O₂: C, 84.48; H, 4.96; N, 4.93; Found C, 84.42; H, 4.90; N, 4.96. HRESIMS: *m/z* calcd for [M + H]⁺ C₄₀H₂₉N₂O₂⁺, 569.2229, found 569.2230, error 1.8 ppm.

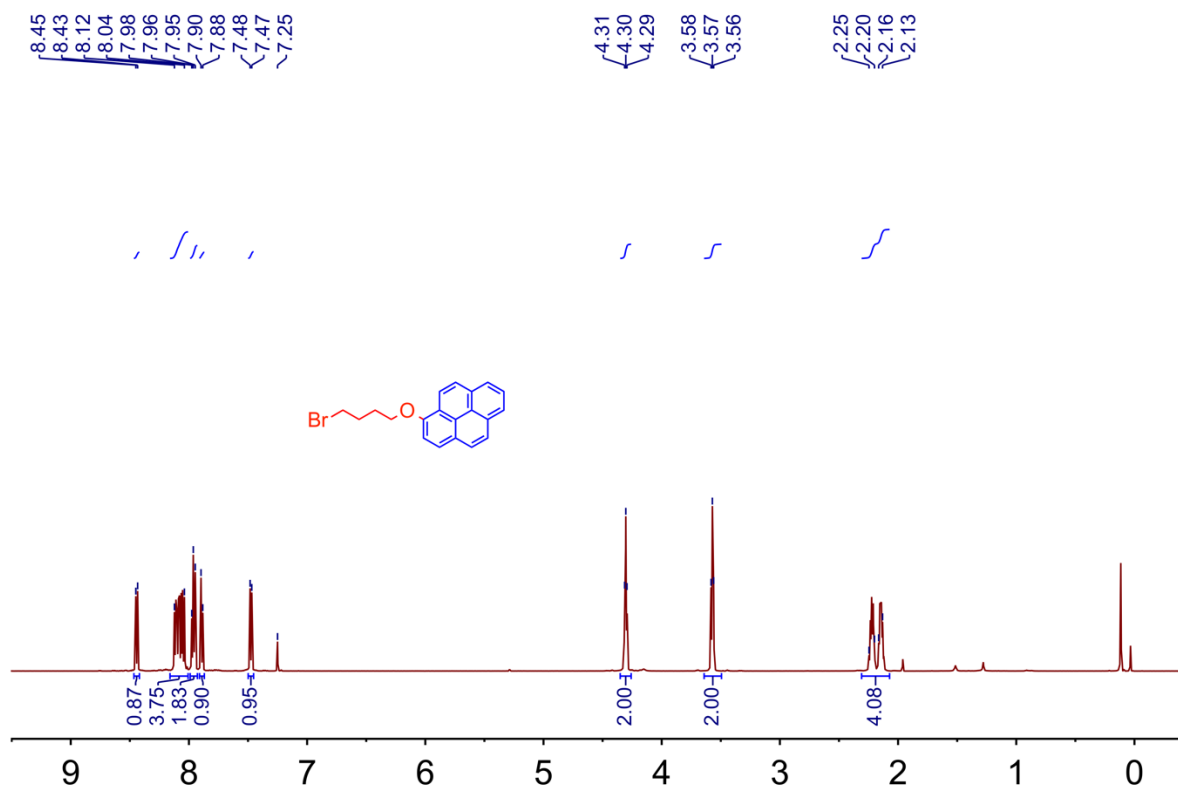


Figure S1. ¹H NMR spectrum (600 MHz, CDCl₃, 293 K) of 5.

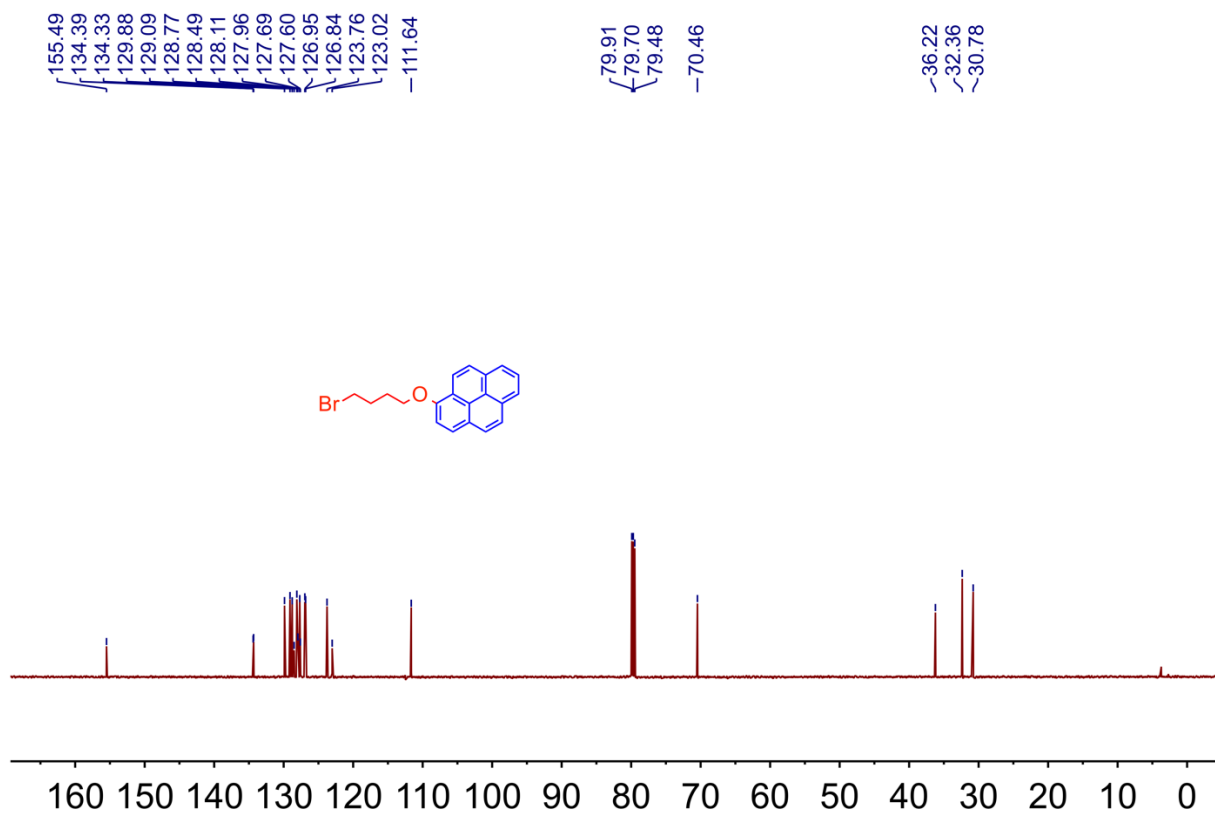


Figure S2. ¹³C NMR spectrum (125 MHz, CDCl₃, 293K) of 5.

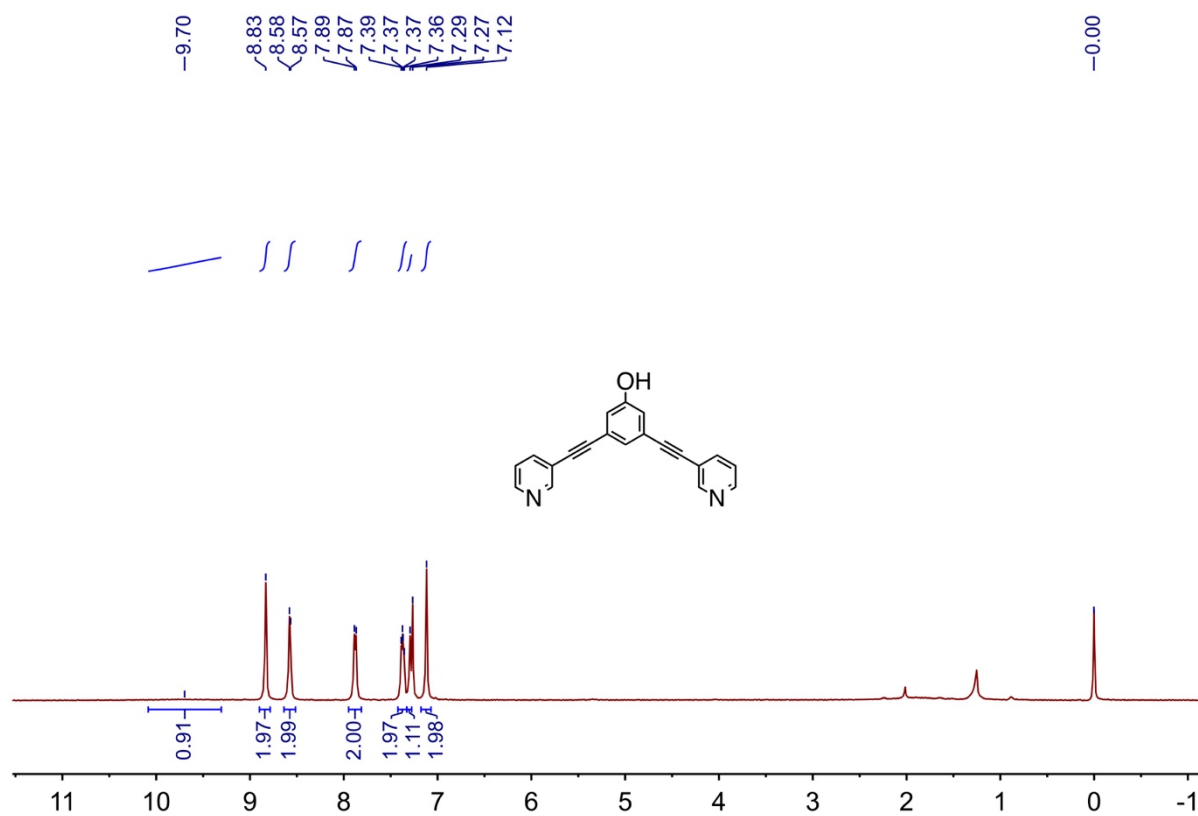


Figure S3. ¹H NMR spectrum (400 MHz, CDCl₃, 293 K) of 4.

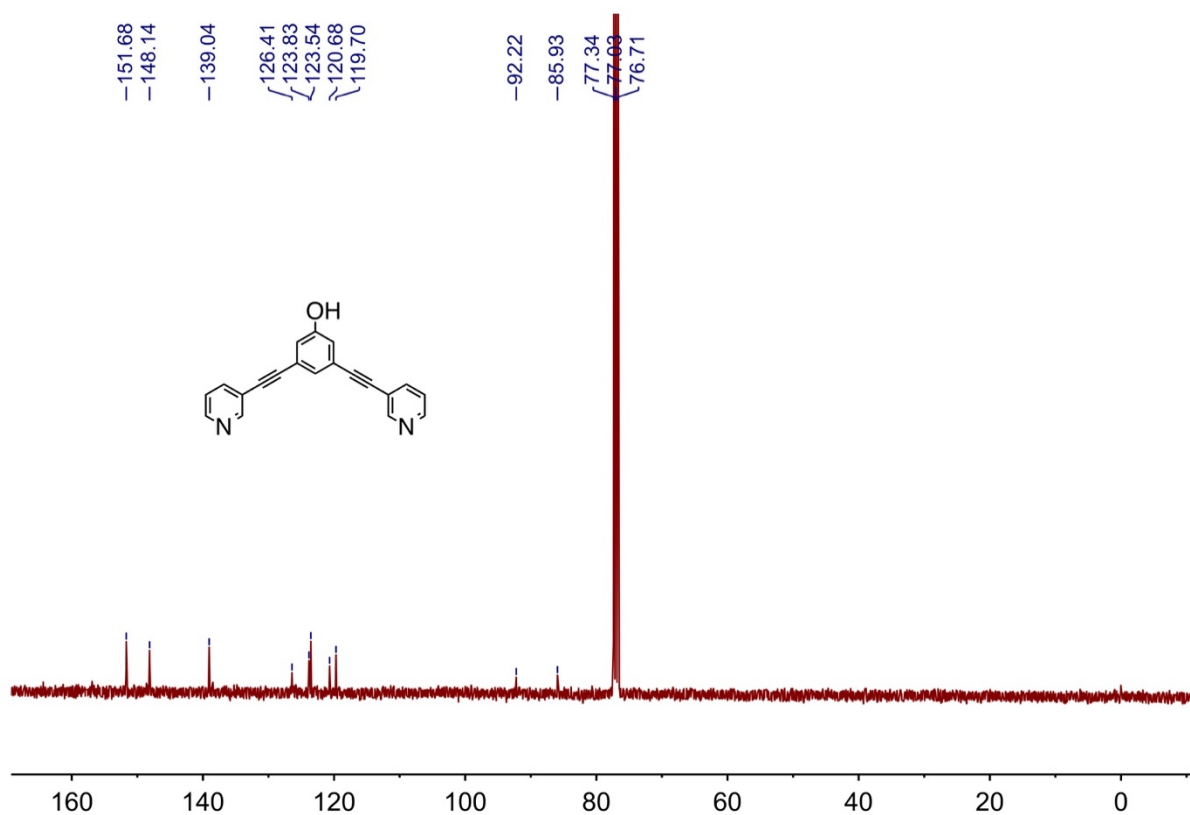


Figure S4. ¹³C NMR spectrum (100 MHz, CDCl₃, 293K) of 4.

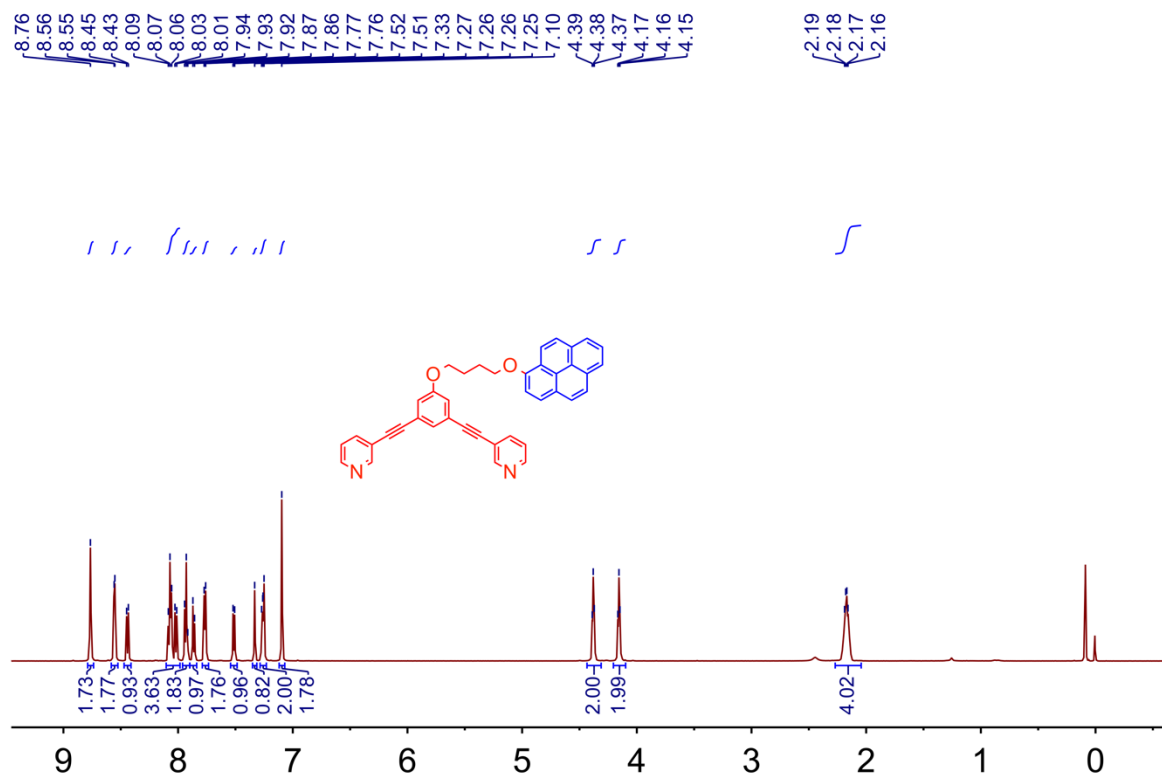


Figure S5. ^1H NMR spectrum (600 MHz, CDCl_3 , 298 K) of **2**.

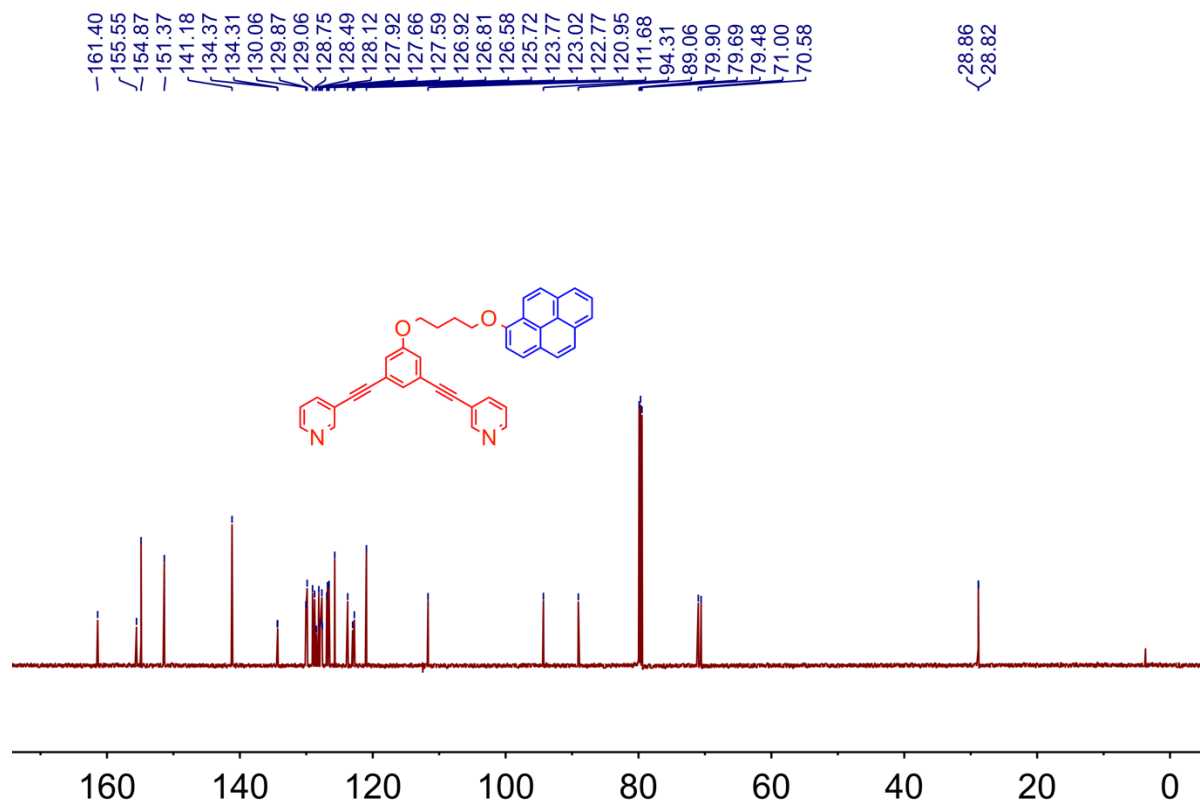


Figure S6. ^{13}C NMR spectrum (125 MHz, CDCl_3 , 298 K) of **2**.

3. Preparation of metallacycle **1**

180° di-Pt (II) acceptor **3** was prepared according to the literature procedure published before.^{S2}

Ligand **2** (3.41 mg, 6.00 μmol) and 180° organic di-Pt(II) **3** (7.42 mg, 6.00 μmol) were placed in a 2-dram vial, followed by addition of acetone (1.00 mL). The mixture was stirred at 25 °C for 8 hours. Then, all solvent was removed by N₂ flow and the solid was dried under vacuum. Acetone (0.50 mL) was then added into the resultant mixture, and the solution was stirred for 2 h at room temperature. Then, the mixture was filtered to remove insoluble materials. The resulting metallacycle **1** was precipitated with diethyl ether, isolated and dried under reduced pressure and dissolved in deuterated acetone for characterization. ¹H NMR spectrum of **1** is shown in Figure S7. ¹H NMR (acetone-*d*₆, 298K, 500 MHz) δ (ppm): 9.20–9.21 (d, *J* = 5 Hz, 4H), 9.02–9.03 (d, *J* = 5 Hz, 4H), 8.47–8.49 (d, *J* = 10 Hz, 2H), 8.24–8.26 (m, 6H), 8.15–8.18 (m, 4H), 8.10–8.12 (d, *J* = 10 Hz, 2H), 8.05–8.07 (d, *J* = 10 Hz, 2H), 8.00–8.01 (d, *J* = 5 Hz, 2H), 7.95–7.98 (t, *J* = 15 Hz, 2H), 7.87–7.90 (m, 4H), 7.77–7.79 (d, *J* = 10 Hz, 2H), 7.46 (m, 2 H), 7.35–7.36 (d, *J* = 5Hz, 4H), 7.32 (m, 4H), 7.18 (m, 4H), 4.54–4.57 (t, *J* = 15 Hz, 4H), 4.36–4.38 (t, *J* = 10 Hz, 4H), 2.23–2.30 (m, 8H), 1.52–1.56 (m, 48H), 1.18–1.25 (m, 78H). ³¹P{¹H} NMR spectrum of **1** is shown in Figure S8. ³¹P{¹H} NMR (acetone-*d*₆, 298 K, 121.4 MHz) δ (ppm): 15.60 (s, ¹⁹⁵Pt satellites, *J*_{Pt-P} = 2705.56 Hz). ESI-TOF-MS is shown in Figure 2: *m/z* 753.2523 [M – 4OTf]⁴⁺, *m/z* 1054.7294 [M – 3 OTf]³⁺.

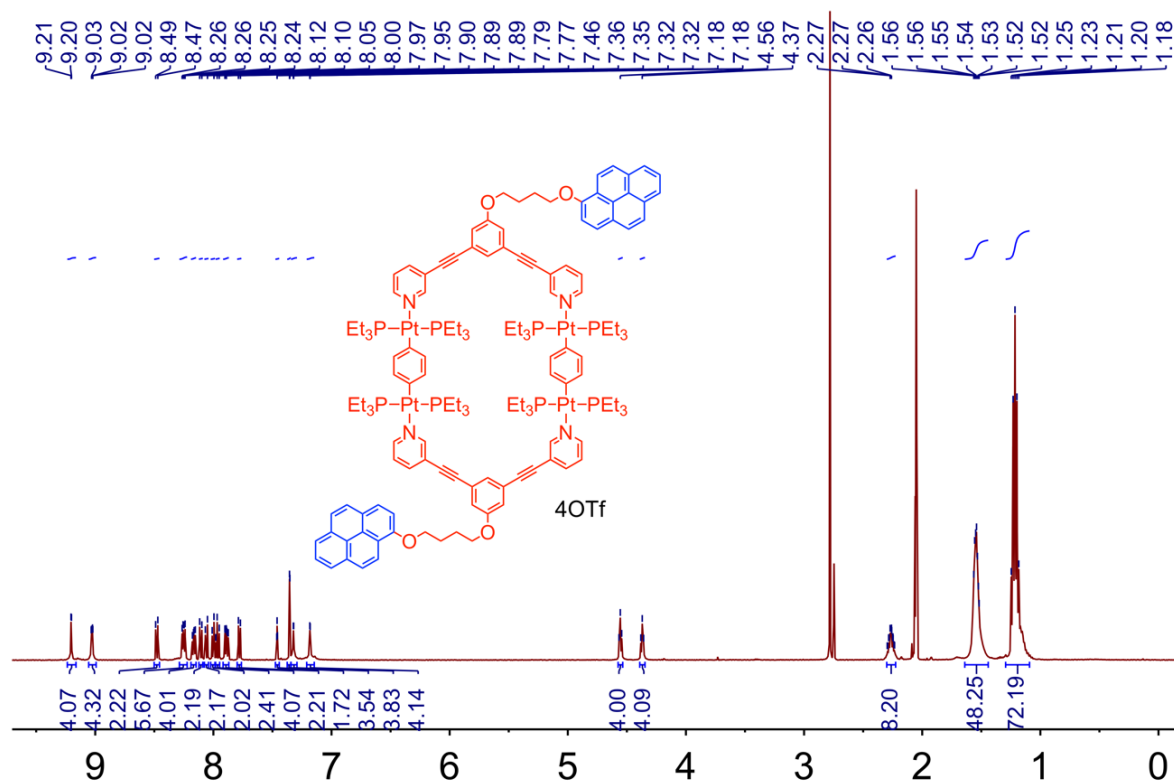


Figure S7. ¹H NMR spectrum (500 MHz, acetone-*d*₆, 298 K) of **1**.

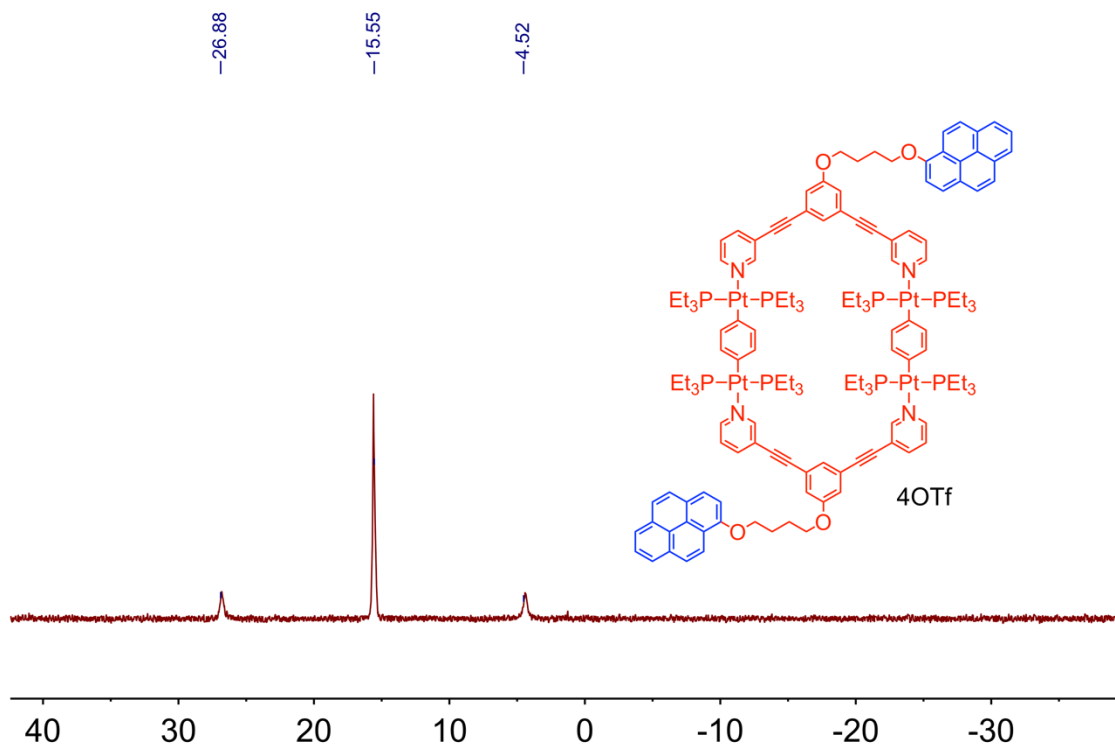


Figure S8. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (acetone- d_6 , 298 K, 121.4 MHz) of **1**.

4. Single-crystal structure of metallacycle **1**

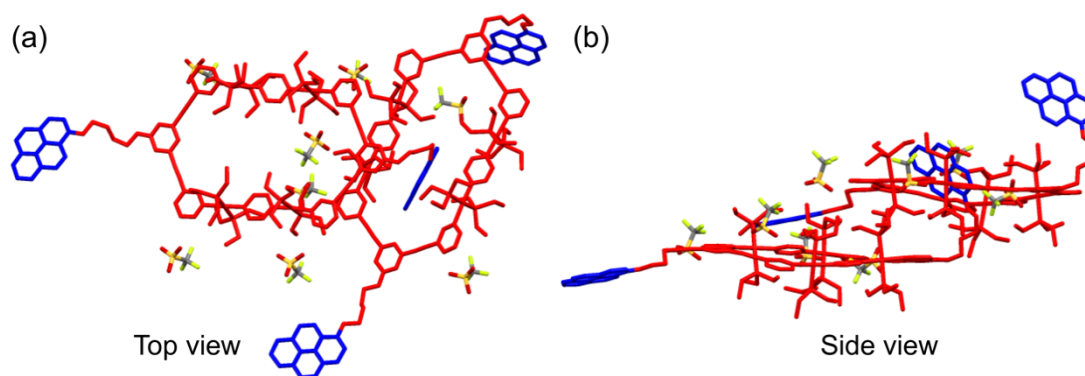


Figure S9. Assembled single-crystal structure driven by the host-guest complexation of monomer **1**. Hydrogen atoms are omitted for clarity.

5. 2D NOESY NMR spectra of metallacycle **1**

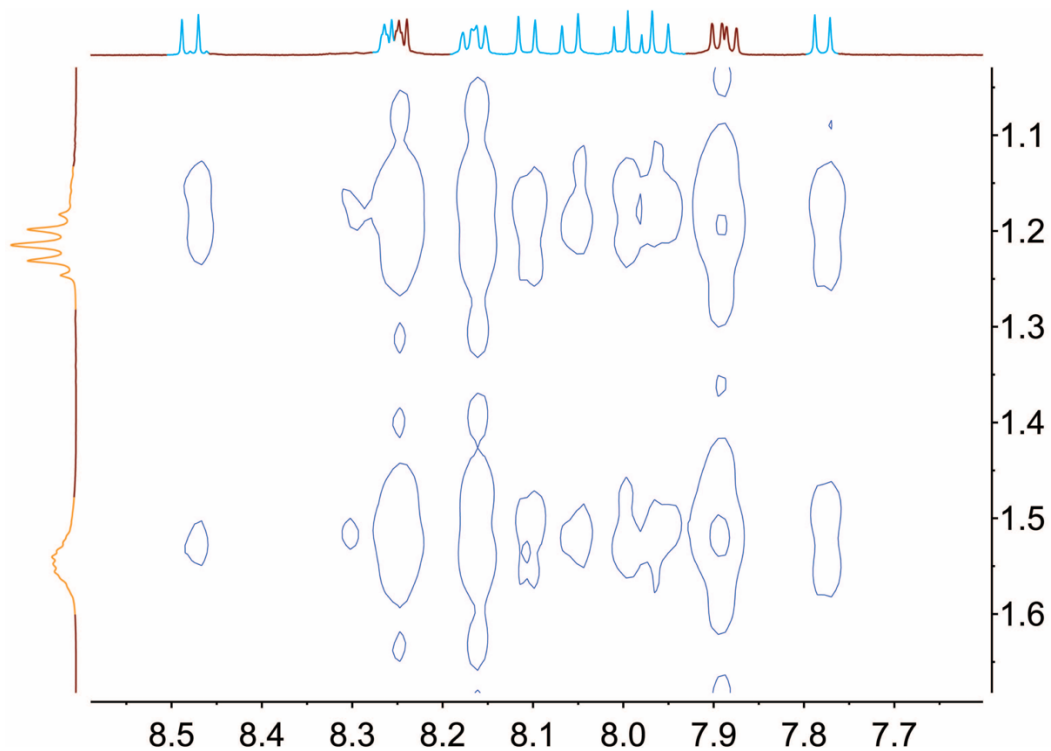


Figure S10. Partial 2D NOESY NMR (500 MHz, acetone- d_6 , 298 K) spectrum of a solution of **1** (1.00 mM).

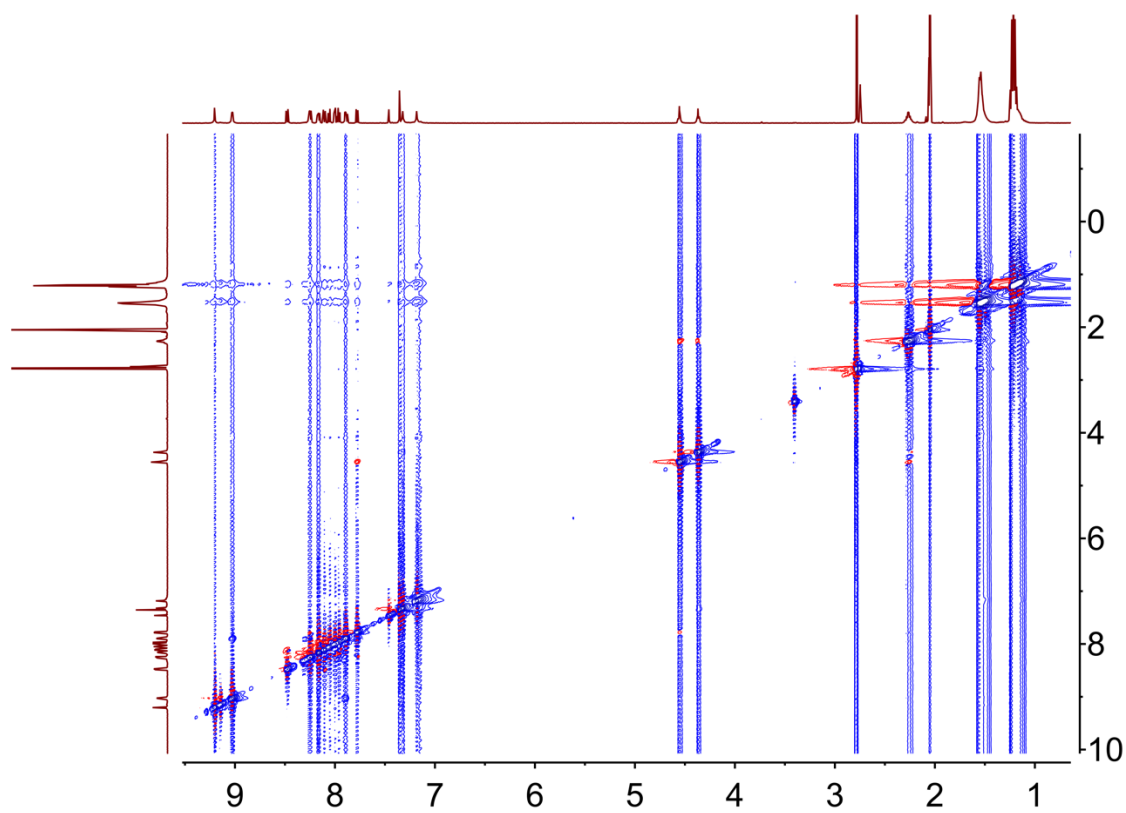


Figure S11. 2D NOESY NMR (500 MHz, acetone- d_6 , 298 K) spectrum of a solution of **1** (1.00 mM).

6. ^1H NMR spectra of metallacycle **1** at various concentrations

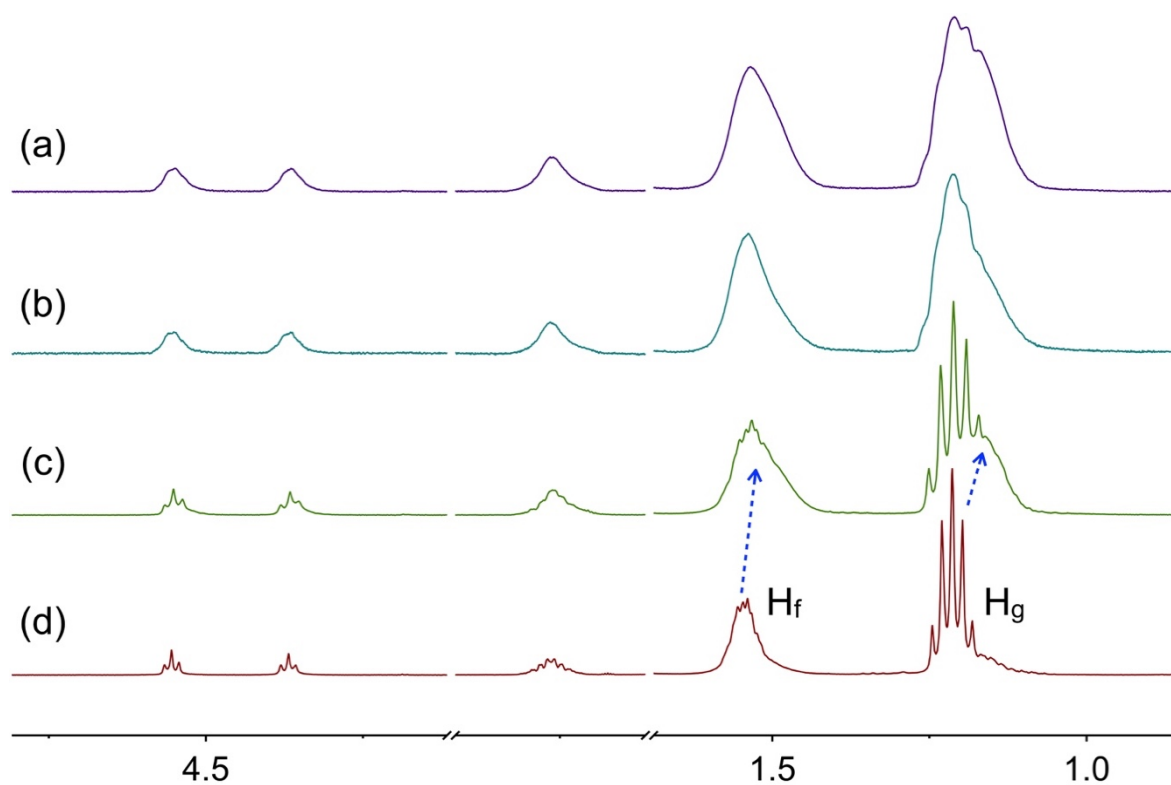


Figure S12. Partial ^1H NMR spectra (400 MHz, 298 K) of **1** in acetone- d_6 at various concentrations: (a) 60.0 mM; (b) 50.0 mM; (c) 25.0 mM; (d) 1.00 mM.

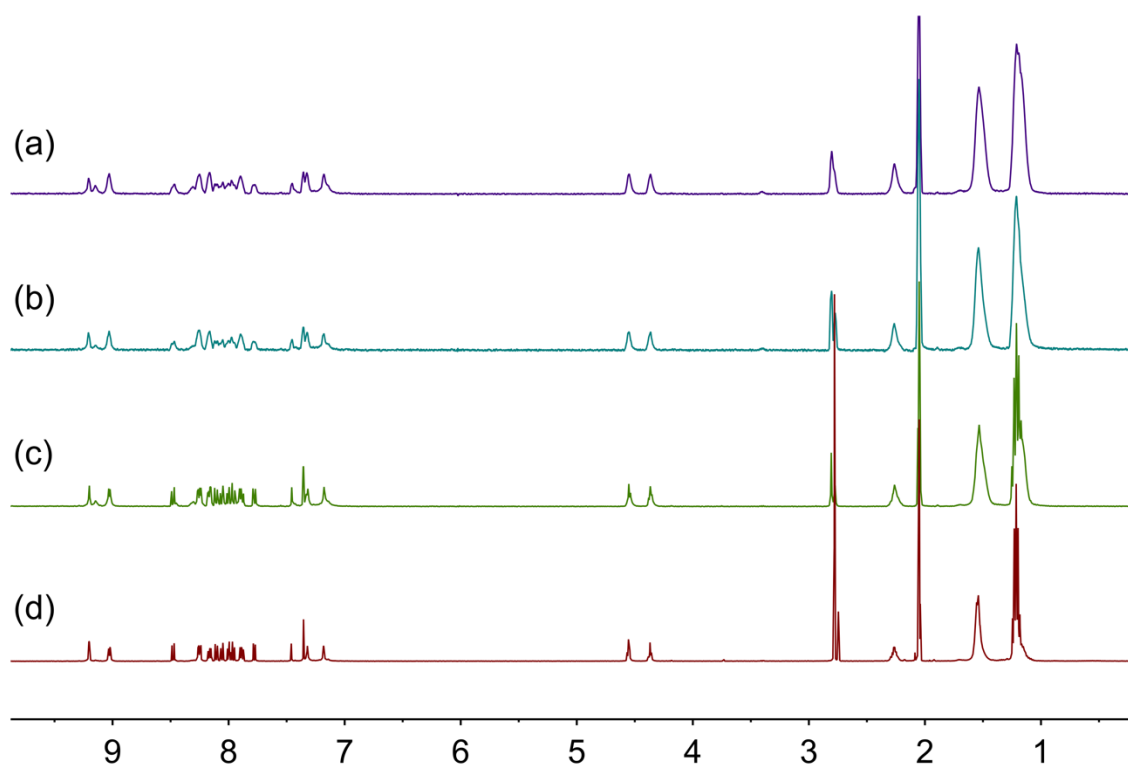


Figure S13. ^1H NMR spectra (400 MHz, 298 K) of **1** in acetone- d_6 at various concentrations: (a) 60.0 mM; (b) 50.0 mM; (c) 25.0 mM; (d) 1.00 mM.

7. Stimuli-responsiveness of the cross-linked supramolecular polymer

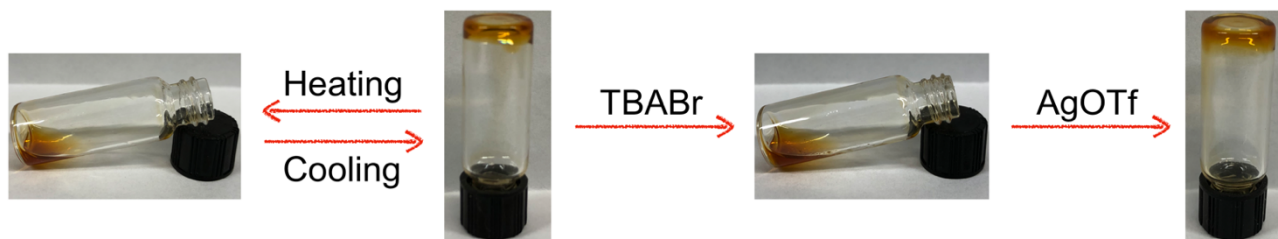


Figure S14. Photographs showing phase transitions of the cross-linked supramolecular polymer triggered by stimuli.

8. X-ray crystal data for metallacycle 1

Crystal Structure Determination: Single-crystal X-ray diffraction data was collected on a Nonius KappaCCD diffractometer equipped with Mo K-alpha radiation ($\lambda = 0.71073 \text{ \AA}$) and a BRUKER APEXII CCD. Throughout data collection, the crystal was cooled to 103(2) K with an Oxford Cryosystem. The APEX3 software suite was used to manage data collection, reduction (SAINT V8.38A1), absorption correction by the Multi-scan method (SADABS), structure determination *via* direct methods (SHLEXT) and model refinement (SHELXL). All non-hydrogen atoms were refined anisotropically though many atoms required anisotropic displacement parameter restraints. All hydrogen atoms were refined with isotropic displacement coefficients and their positions ideally constrained. Squeeze was used to account for regions of heavily disordered solvent. The crystal structure was deposited into the Cambridge Structural Database, deposition 1891639.

Crystallographic data: rectangular block, clear and colorless, $0.085 \times 0.120 \times 0.220 \text{ mm}$, $\text{C}_{140}\text{H}_{184}\text{N}_4\text{O}_4\text{P}_8\text{Pt}_4$, $4[\text{CF}_3\text{O}_3\text{S}]$, FW 3611.30, space group $\text{P}2_1/m$, $a = 14.2760(13)$, $b = 43.860(4)$, $c = 26.515(2) \text{ \AA}$, $\alpha = 90.00^\circ$, $\beta = 101.185(3)^\circ$, $\gamma = 90.00^\circ$, $V = 16287.2(2) \text{ \AA}^3$, $Z = 9$, $D_c = 1.473 \text{ g cm}^{-3}$, $T = 103.3 \text{ K}$, $\mu = 3.62 \text{ mm}^{-1}$, 152,817 measured reflections, 18626 independent reflections, 1639 parameters, 1737 restraints, $F(000) = 7232.0$, $R_{(\text{int})} = 0.0348$, $R_1 = 0.1001 [F_o > 4\text{sig}(F_o)] / 0.1174 [\text{ALL}]$, $wR_2 = 0.2254$ (all data), max. residual density $3.334 \text{ e}\cdot\text{\AA}^{-3}$, and goodness-of-fit (F^2) = 1.228. CCDC 1891639.

9. References

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- S2 Manna, J.; Kuehl, C. J.; Whiteford, J. A.; Stang, P. J.; Muddiman, D. C.; Hofstadler, S. A.; Smith, R. D. Nanoscale Tectonics: Self-Assembly, Characterization, and Chemistry of a Novel Class of Organoplatinum Square Macrocycles. *J. Am. Chem. Soc.* **1997**, *119*, 11611–11619.