

Supporting Information For
Supramolecular hydrogel with tunable strength switched by
host-guest interaction

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1. General Information.

The compounds **1**^{S1}, **D**^{S2} and **G**^{S3}, were prepared as the reported procedures in literatures. Solvents were either employed as purchased or dried according to procedures described in the literature.

¹H NMR, ¹³C NMR, ³¹P NMR, and ¹⁹F NMR spectra were recorded on Bruker 400 MHz Spectrometer (¹H: 400 MHz; ¹³C: 100 MHz; ¹⁹F: 376 MHz; ³¹P: 161.9 MHz) and Bruker 500 MHz Spectrometer (¹H: 500 MHz; ¹³C: 125 MHz) at 298 K. The ¹H and ¹³C NMR chemical shifts are reported relative to residual solvent signals, and ³¹P NMR resonances are referenced to an internal standard sample of 85% H₃PO₄ (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. IR spectra were recorded on a Bruker Tensor 27 infrared spectrophotometer.

Dynamic Light Scattering (DLS) Studies. DLS measurements were performed under a Malvern Zetasizer Nano-ZS light scattering apparatus (Malvern Instruments, U.K.) with a He-Ne laser (633 nm, 4 mW).

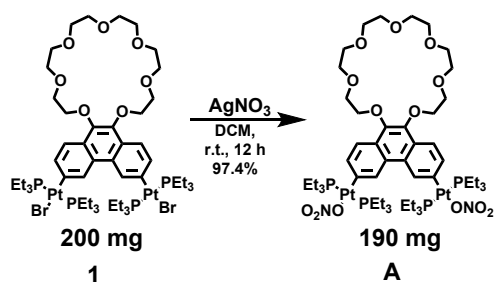
Scanning Electron Microscopy (SEM) Experiments. The SEM samples were prepared on clean Si substrates. To minimize sample charging, a thin layer of Au was deposited onto the samples before SEM examination. All the SEM images were obtained using an S-4800 (Hitachi Ltd.) with an accelerating voltage of 3.0-10.0 kV.

Rheological Experiments. Rheological measurements were performed under a MARS III (HAAKE MARS III) device at 293K.

Gel Permeation Chromatography (GPC) Protocols. A gel permeation chromatograph equipped with a Waters 1515 isocratic HPLC pump and a Waters 2414 refractive index detector was used to perform GPC measurements at 40 °C using THF containing 5 mM LiTFSI, 5 mM 1-butylimidazole, and 0.02 wt % BHT as eluent with a flow rate of 1.0 mL/min. The system was calibrated with polystyrene standards. THF and sample solutions were filtered over a filter with a pore size of 0.22 μ m (PTFE, Millex-HN 13 mm Syringes Filters, Millipore, US).

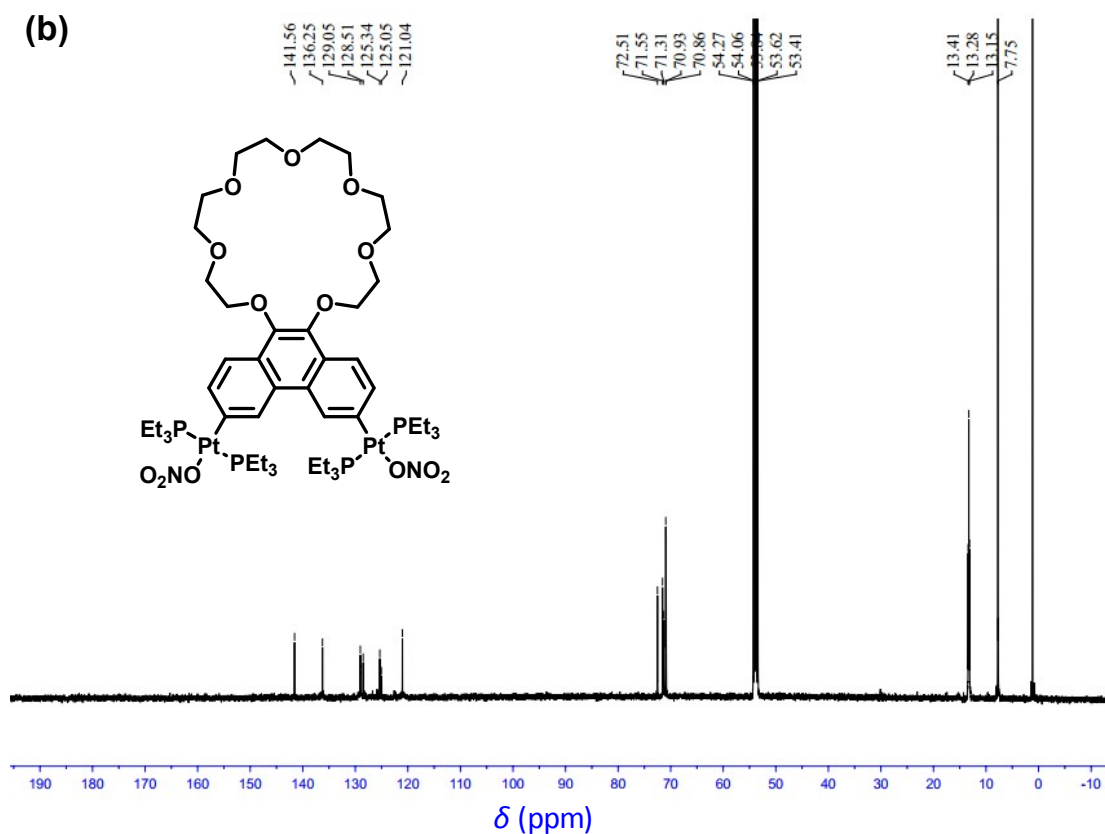
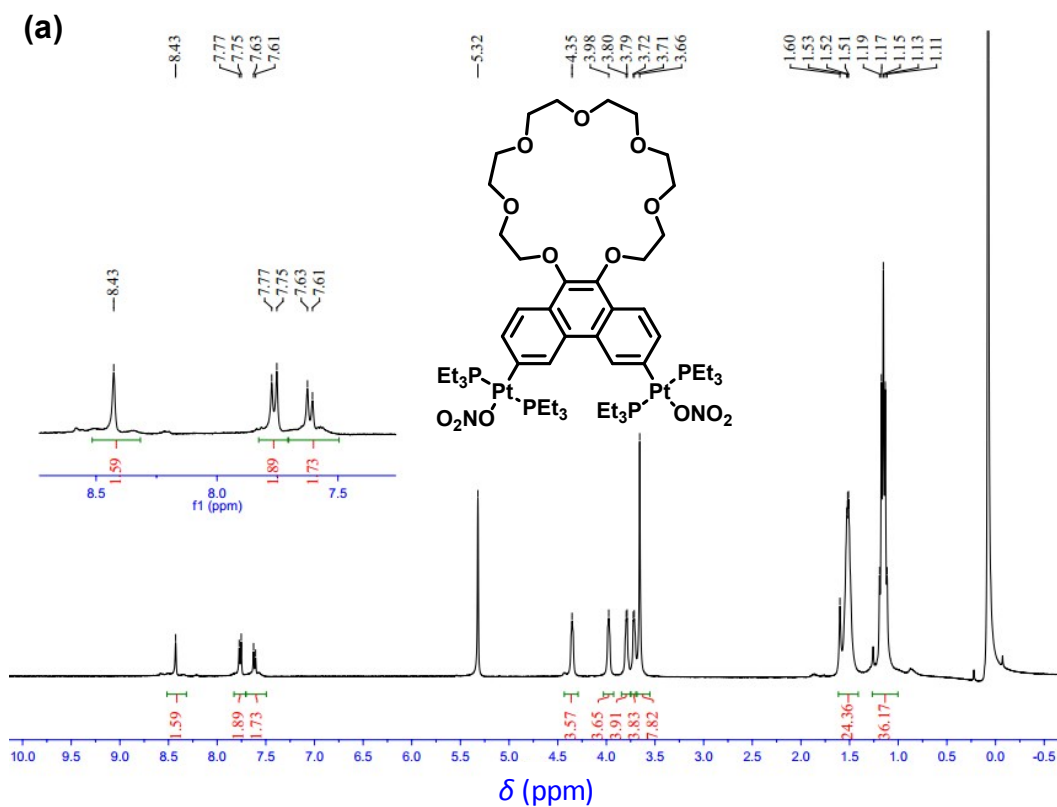
2. Experimental details for synthesis and characterization of new compounds

Synthesis of compound A.



Scheme S1 Synthetic route of compound A.

A 25 mL Schlenk flask was charged with compound **1** (200 mg, 0.14 mmol), degassed, and back-filled three times with N_2 . Anhydrous dichloromethane (10 mL) was introduced into the reaction flask by syringe. Then AgNO_3 (69 mg, 0.41 mmol) was added into the flask under nitrogen atmosphere. The resulting mixture was stirred in the dark at room temperature for 12 h. After filtering off the heavy creamy precipitate, a clear solution was obtained. Then the solvent was removed under a flow of nitrogen to afford **A** as brown solid. Yield: 190 mg, 97.4%. ^1H NMR (CD_2Cl_2 , 400 MHz): δ 8.43 (s, 2H), 7.76 (d, $J = 8.4$ Hz, 2H), 7.62 (d, $J = 8.3$ Hz, 2H), 4.35 (s, 4H), 3.98 (s, 4H), 3.79 (d, $J = 3.8$ Hz, 4H), 3.72 (d, $J = 4.1$ Hz, 4H), 3.66 (s, 8H), 1.54 (br, 24H), 1.27-1.00 (br, 36H). ^{13}C NMR (CD_2Cl_2 , 125 MHz): δ 141.6, 136.3, 129.1, 128.5, 125.3, 125.1, 121.0, 72.5, 71.6, 71.3, 70.9, 13.4, 13.3, 13.2, 7.8. ^{31}P NMR (162 MHz, CD_2Cl_2) δ 19.22 (d, $J = 2881.3$ Hz). IR (neat): 2964, 1730, 1701, 1610, 1577, 1467, 1448, 1379, 1348, 1193, 1174, 1114, 1085, 1033, 993, 921, 763, 732, 557 cm^{-1} . ESI-TOF-MS of **A**: calcd for $[\text{M} - \text{HNO}_3 + \text{K}^+]^+$: 1419.4563, found: 1419.5203; calcd for $[\text{M} - \text{NO}_3^-]^+$: 1378.4771, found: 1378.4856; calcd for $[\text{M} - \text{NO}_3^- + \text{Na}^+]^{2+}$: 700.7334, found: 700.6279; calcd for $[\text{M} - \text{HNO}_3 - \text{NO}_3^- + \text{K}^+]^{2+}$: 678.7343, found: 678.6464; calcd for $[\text{M} - 2\text{NO}_3^-]^{2+}$: 658.2446, found: 658.1268.



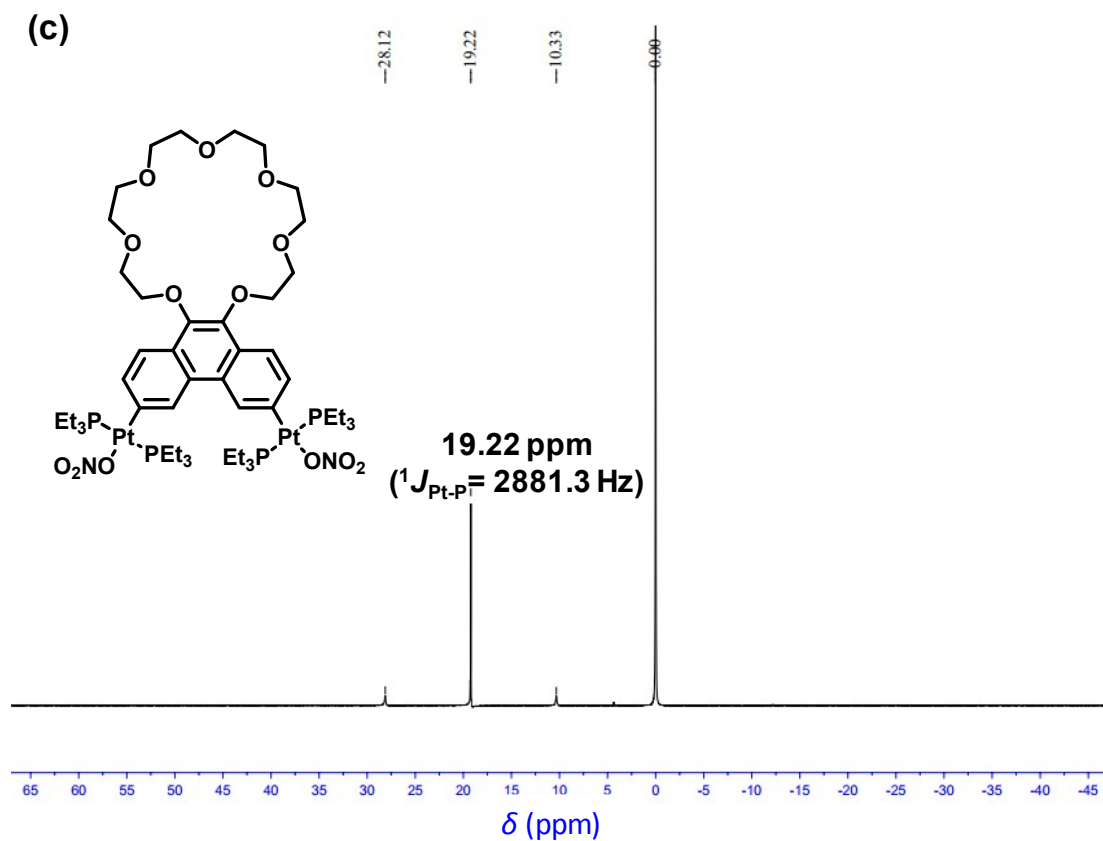


Fig. S1 (a) ^1H , (b) ^{13}C and (c) ^{31}P NMR spectra of A in CD_2Cl_2 .

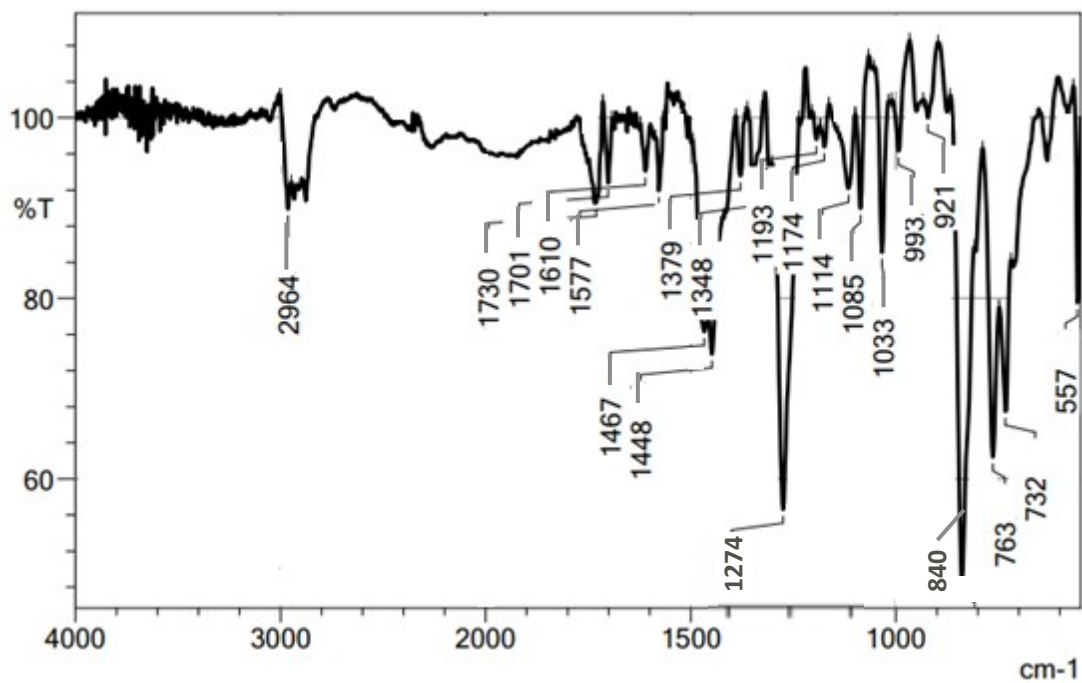


Fig. S2 IR spectrum of A.

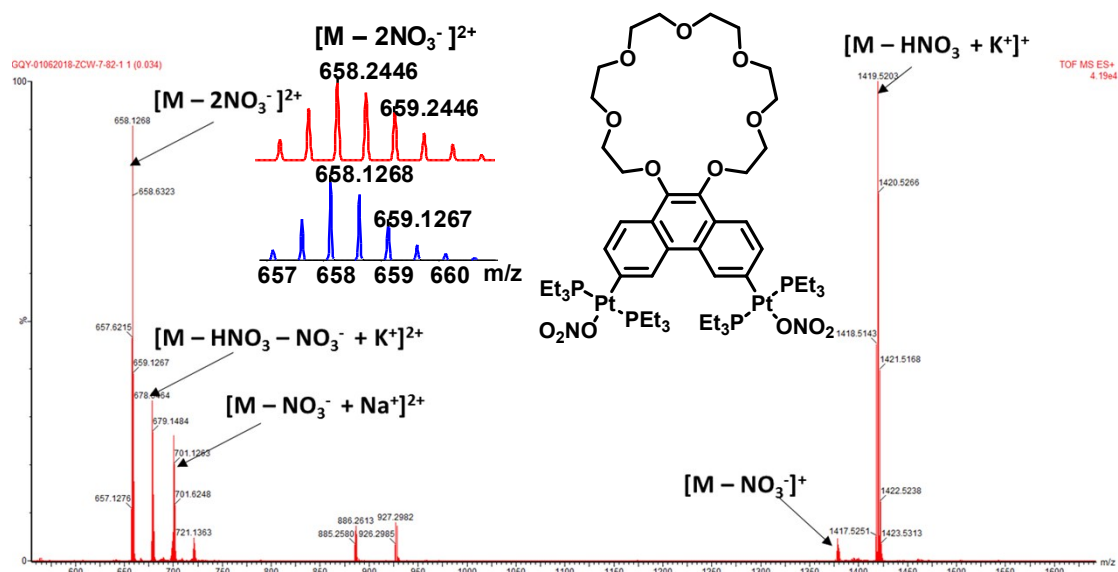
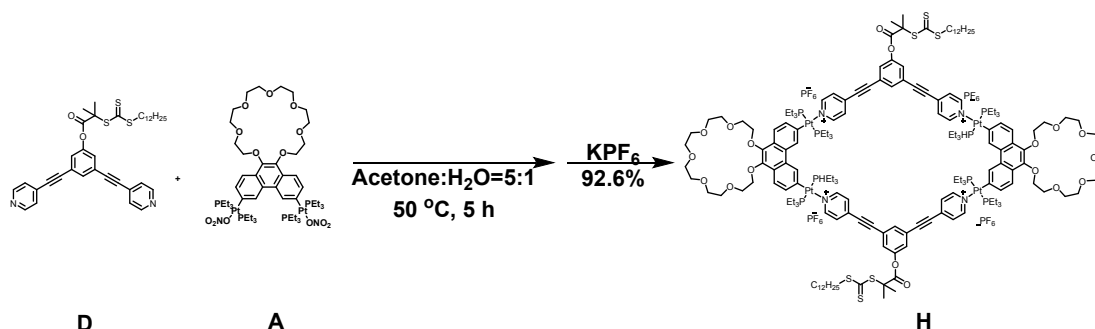


Fig. S3 Experimental ESI-TOF-MS spectra of **A** (Theoretical (red) and experimental (blue)): calcd for $[M - HNO_3 + K^+]^+$: 1419.4563, found: 1419.5203; calcd for $[M - NO_3^-]^+$: 1378.4771, found: 1378.4856; calcd for $[M - NO_3^- + Na^+]^{2+}$: 700.7334, found: 700.6279; calcd for $[M - HNO_3 - NO_3^- + K^+]^{2+}$: 678.7343, found: 678.6464; calcd for $[M - 2NO_3^-]^{2+}$: 658.2446, found: 658.1268.

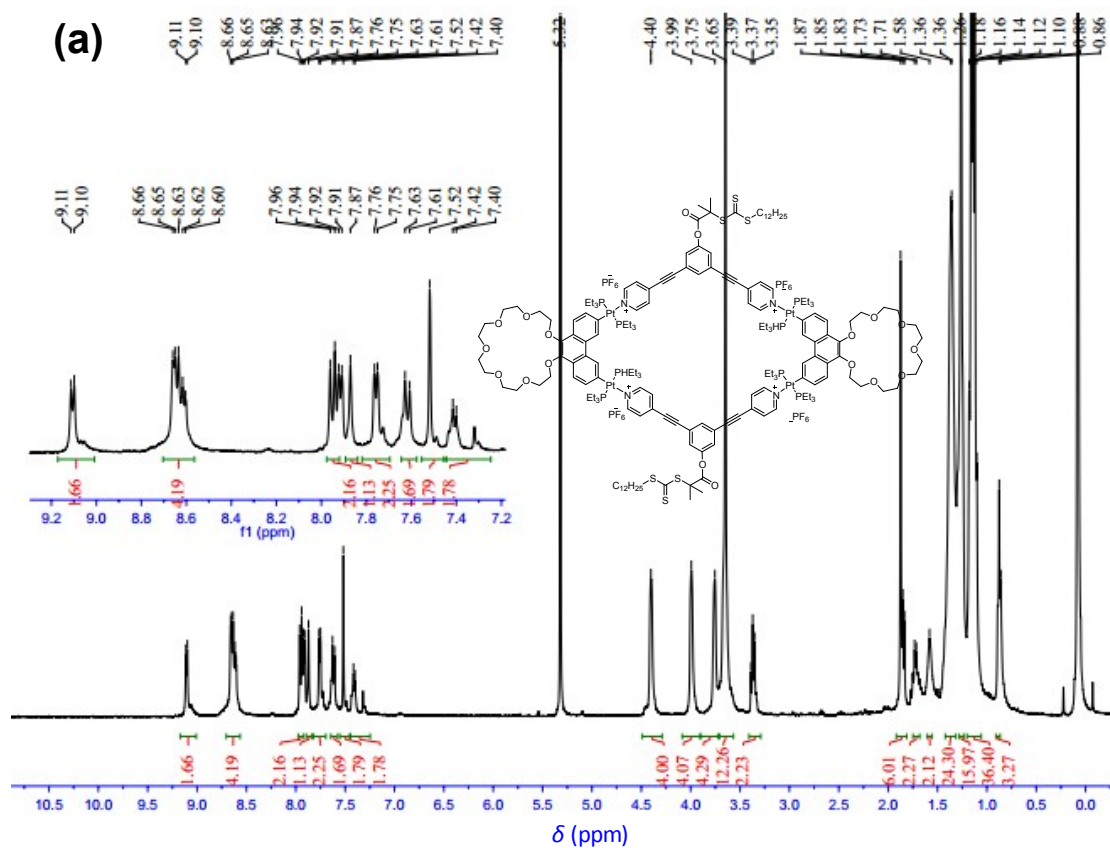
Synthesis of rhombic metallacycle **H**.



Scheme S2 Synthetic route of rhombic metallacycle **H**.

The dipyriddyldon ligand **D** (5.1 mg, 7.95 μ mol) and the organoplatinum 60° acceptor **A** (11.5 mg, 7.95 μ mol) were weighed accurately into a glass vial. To the vial was added 2.5 mL acetone and 0.5 mL water. The reaction solution was then stirred at 50 °C for 6 h to yield a homogeneous pale yellow solution. Then KPF_6 was added into the bottle with continuous stirring (5 min) to precipitate the product. The reaction mixture was centrifuged, washed for several times with water and dried. The yellow product **H** was collected and re-dissolved in CD_2Cl_2 for NMR analysis. Yield: 16.6 mg, 92.6%. 1H NMR (400 MHz, CD_2Cl_2) δ 9.11 (d, $J = 5.6$ Hz, 2H), 8.70 – 8.56 (m, 4H), 7.98 – 7.92 (m, 2H), 7.87 (s, 1H), 7.76 (d, $J = 5.5$ Hz, 2H), 7.62 (d, $J = 8.2$ Hz, 2H), 7.52 (s, 2H), 7.41 (d, $J = 6.0$ Hz, 2H), 4.40 (s, 4H), 3.99 (s, 4H), 3.75 (s, 4H), 3.65 (s, 12H), 3.37 (t, $J =$

7.3 Hz, 2H), 1.92 – 1.81 (m, 6H), 1.72 (d, $J = 7.4$ Hz, 2H), 1.58 (s, 2H), 1.36 (br, 24H), 1.26 (br, 16H), 1.20 – 1.06 (br, 36H), 0.88 (s, 3H). ^{31}P NMR (162 MHz, CD_2Cl_2) δ 12.64 (d, $J = 2691.7$ Hz). ^{13}C NMR (125 MHz, CD_2Cl_2) δ 171.7, 153.3, 151.6, 150.2, 142.0, 135.7, 134.5, 130.1, 129.4, 129.2, 128.9, 127.4, 126.0, 123.5, 121.9, 96.4, 87.2, 72.4, 71.3, 70.8, 70.6, 70.5, 32.3, 30.1, 30.0, 29.9, 29.7, 29.5, 25.3, 23.1, 14.3, 13.3, 13.1, 13.0, 7.9. IR (neat): 2929, 2216, 1753 1701, 1608, 1577, 1458, 1417, 1348, 1309, 1247, 1197, 1138, 1089, 1033, 763, 731, 557 cm^{-1} . ESI-TOF-MS of **7-H**: calcd for $[\text{M-PF}_6^- + 2\text{K}^+]^{3+}$: 1477.7614, found: 1477.7880; calcd for $[\text{M-2PF}_6^- + \text{K}^+]^{3+}$: 1416.4521, found: 1416.4703; calcd $[\text{M-3PF}_6^-]^{3+}$: 1355.1449, found: 1355.1462; calcd for $[\text{M-2PF}_6^- + 2\text{K}^+]^{4+}$: 1072.3301, found: 1072.2902; calcd for $[\text{M-3PF}_6^- + \text{K}^+]^{4+}$: 1026.3481, found: 1026.2883; calcd for $[\text{M-4PF}_6^-]^{4+}$: 980.3657, found: 980.3080; calcd for $[\text{M-3PF}_6^- + 2\text{K}^+]^{5+}$: 828.8743, found: 828.7962.



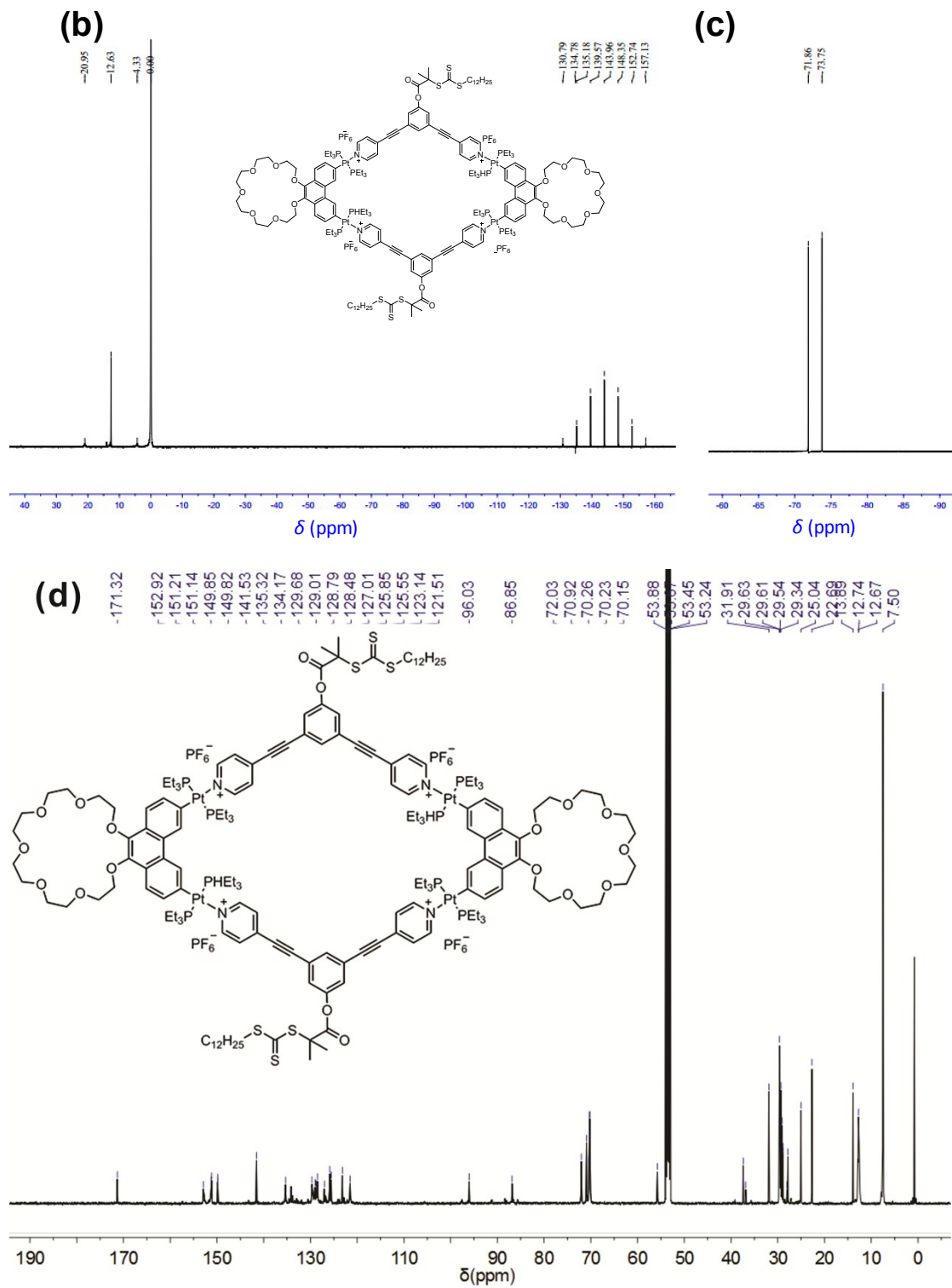


Fig. S4 (a) ¹H, (b) ³¹P, (c) ¹⁹F and (d) ¹³C NMR spectra of **H** in CD₂Cl₂

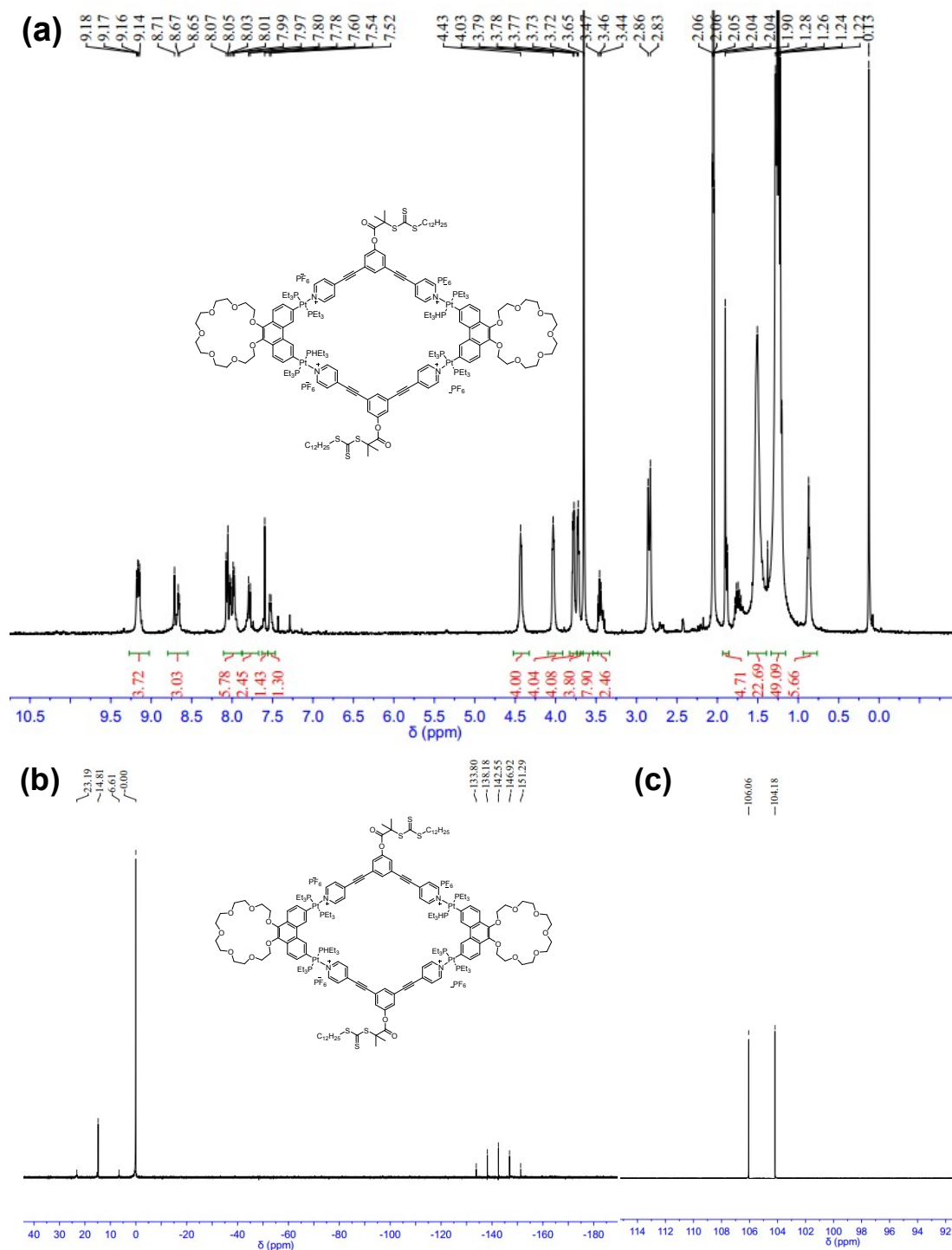


Fig. S5 (a) ^1H , (b) ^{31}P and (c) ^{19}F NMR spectra of **H** in acetone- d_6 .

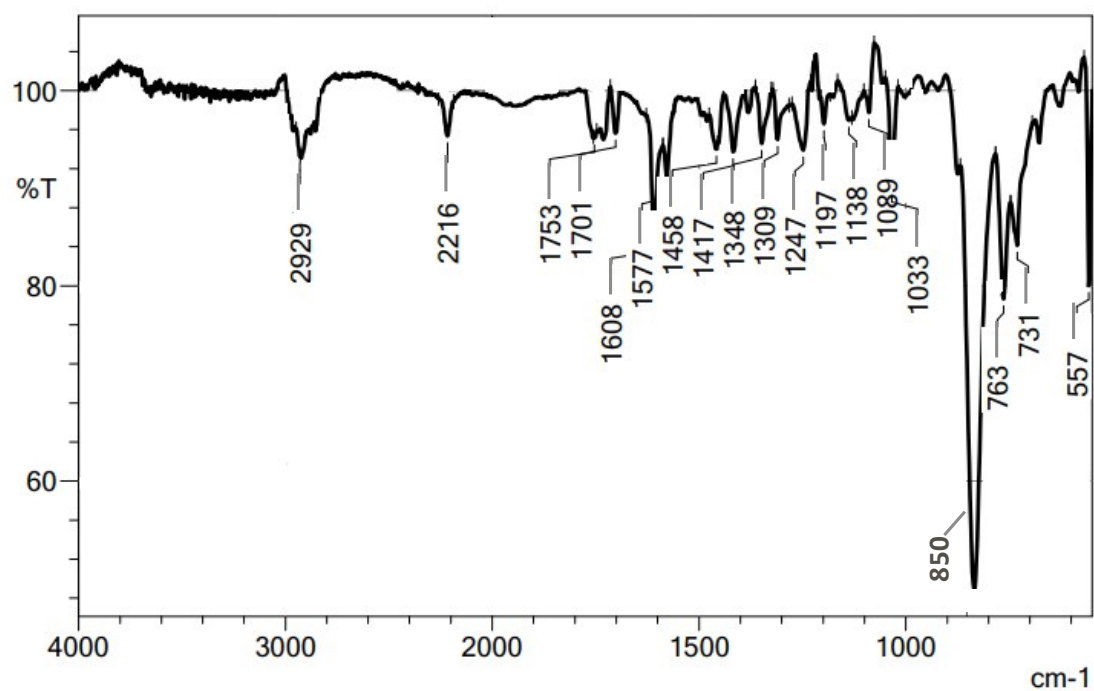


Fig. S6 IR spectrum of H.

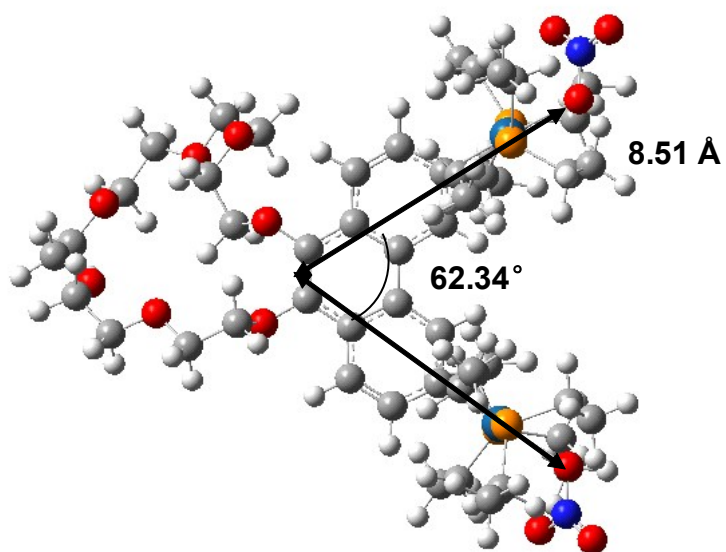


Fig. S7 The geometry structures of A optimized by PM6 semiempirical molecular orbital method.

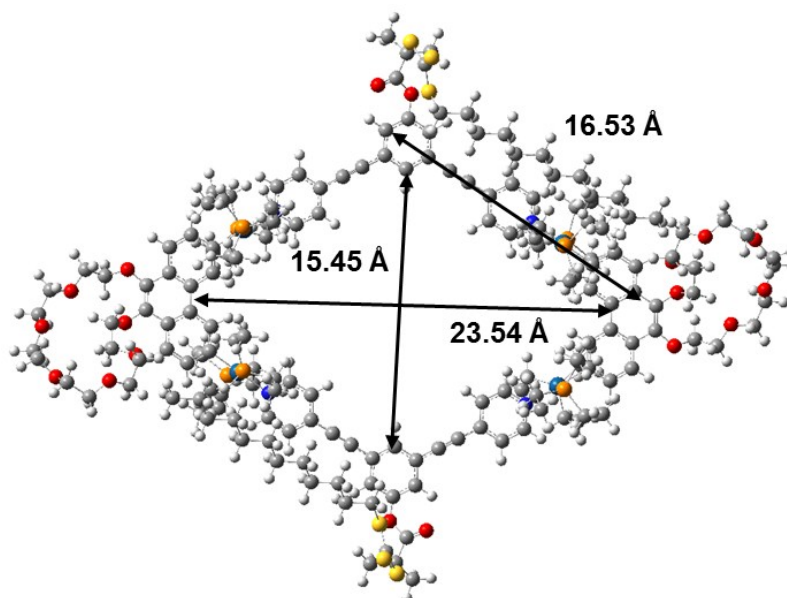
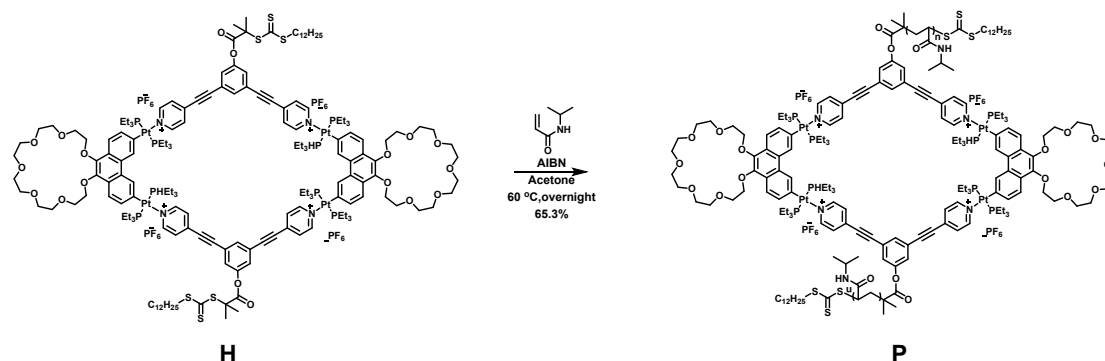


Fig. S8 The geometry structures of **H** optimized by PM6 semiempirical molecular orbital method.

Synthesis of polymer **P**.



Scheme S3 Synthetic route of polymer **P**.

Supramolecular [2+2] rhombic metallacycle **H** (40 mg, 8.88 μmol), AIBN (1.19 mg, 7 μmol), N-isopropylacrylamide (150 mg, 1.33 mmol), and 1.0 mL of acetone were added to a 10 mL flask equipped with a magnetic stirring bar. After being degassed by freeze-pump-thaw cycles three times, the mixed solution was immediately transferred to a preheated 60 $^{\circ}\text{C}$ oil bath to initiate the polymerization. After 5 h, the polymerization was quenched by liquid N_2 , and the resulting mixture was precipitated in diethyl ether. The precipitate was dissolved in acetone and then precipitated again into an excess of diethyl ether. The above dissolution–precipitation cycle was repeated three times. The final product was dried in a vacuum, yielding a yellow solid (124 mg, 65.3%, $M_{n,\text{NMR}} = 2.4 \times 10^4$ g/mol, $M_{n,\text{GPC}} = 2.1 \times 10^4$ g/mol, PDI = 1.22). ^1H NMR (acetone- d_6 , 400 MHz) δ 9.16 (s, 2H), 8.68 (s, 1H), 8.03 (br, 10H), 7.77–6.48 (br, 141H, –NH), 4.01 (br, 152H, –NCH), 2.21 (br, 116H), 1.57 (br, 288H, backbone), 1.14 (br, 987H, backbone). ^{31}P NMR

(acetone- d_6 , 162 MHz): δ 14.83 (s, $J_{\text{Pt-P}} = 2701$ Hz). IR (neat): 2976, 1735, 1691, 1654, 1560, 1460, 1388, 1240, 1211, 1170, 1130, 1039, 842, 669 cm^{-1} .

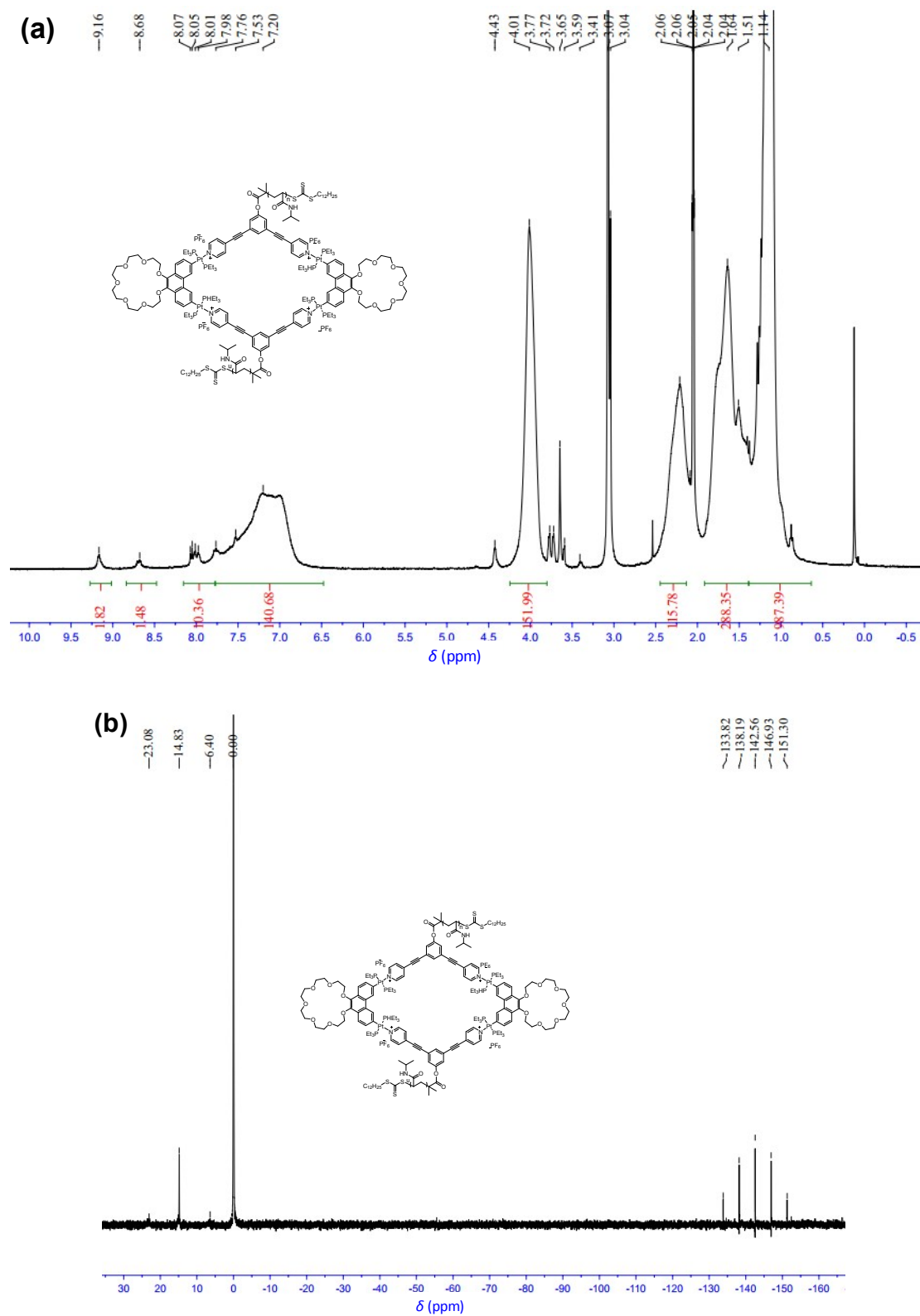


Fig. S9 (a) ^1H and (b) ^{31}P NMR spectra of **P** in acetone- d_6 .

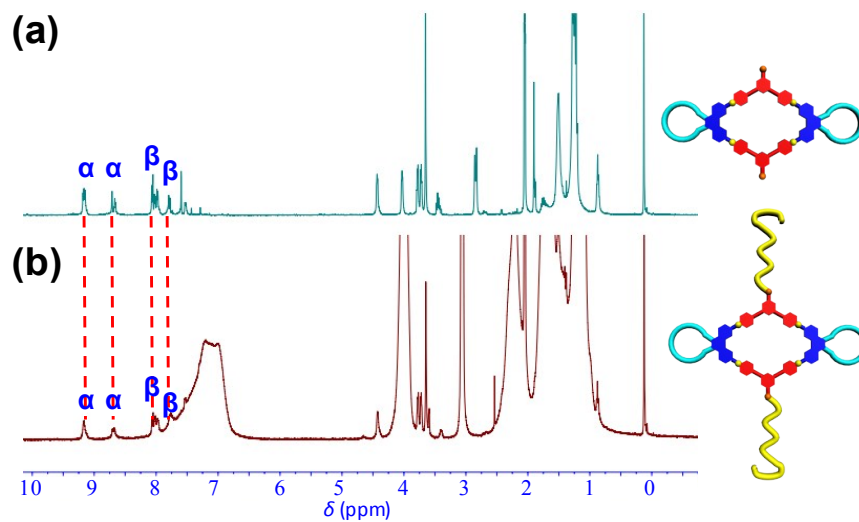


Fig. S10 ^1H NMR spectra of (a) **H** and (b) **P** (400 MHz, acetone- d_6 , 295 K).

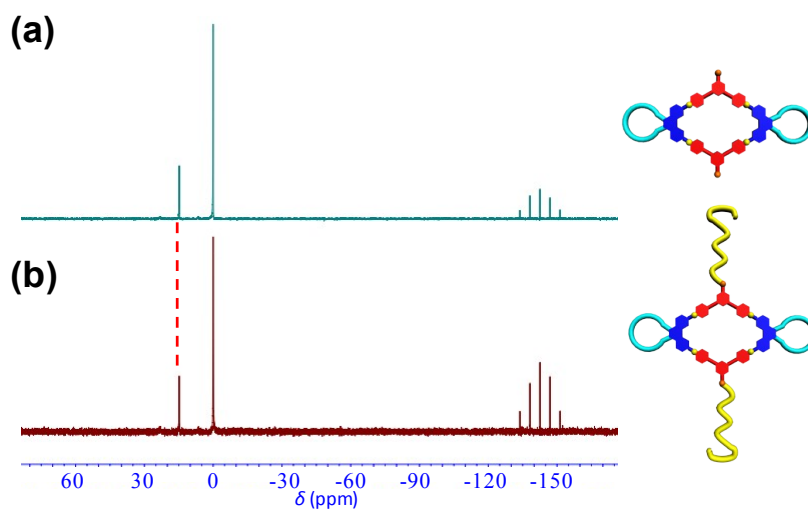


Fig. S11 ^{31}P NMR spectra of (a) **H** and (b) **P** (400 MHz, acetone- d_6 , 295 K).

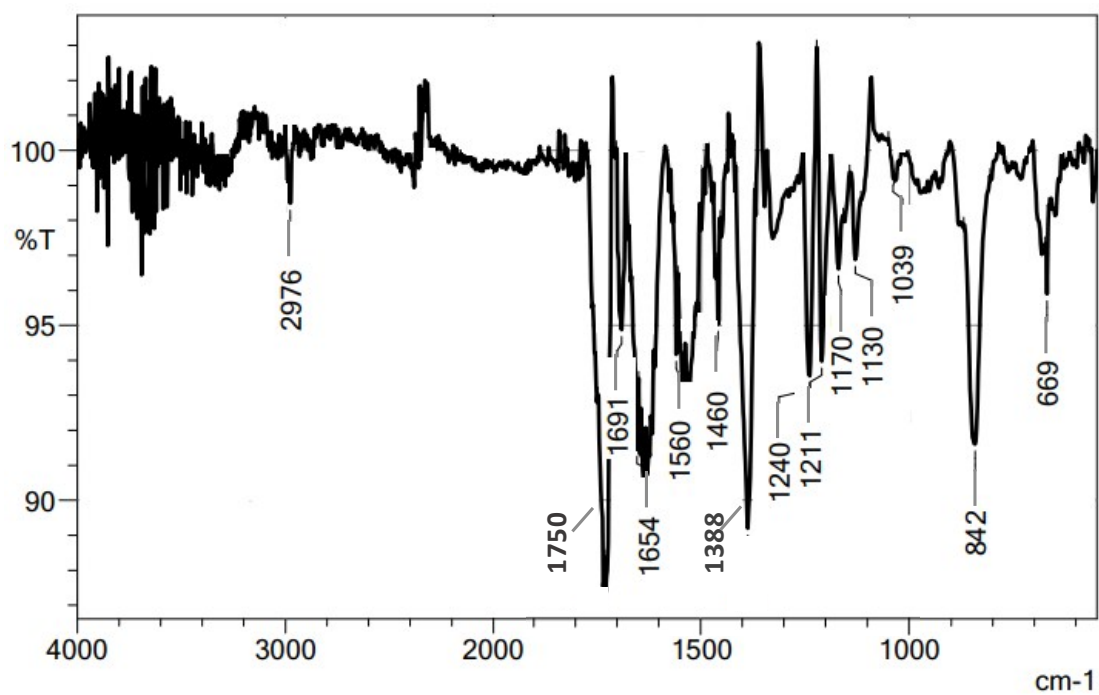


Fig. S12 IR spectrum of P.

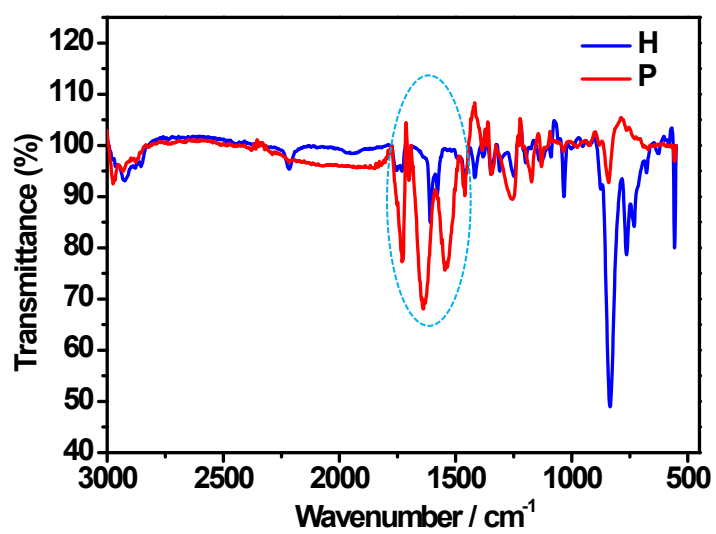


Fig. S13 IR spectra of rhomboidal metallacycle H (blue) and supramolecular polymer P (red).

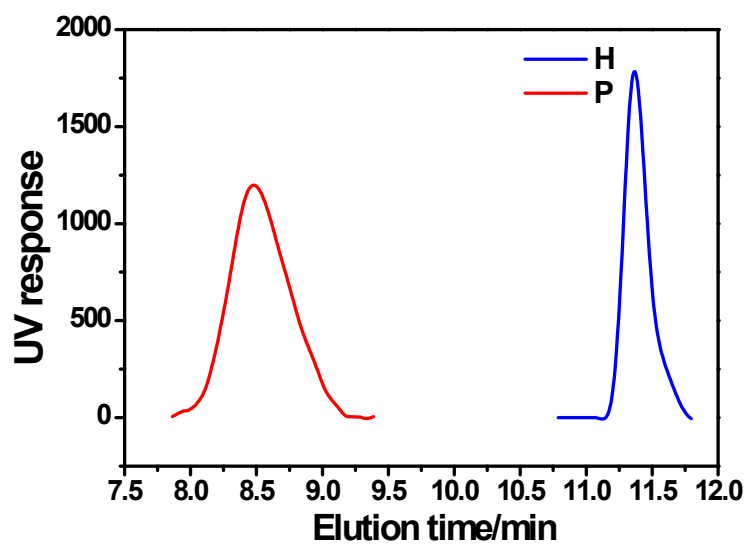


Fig. S14 GPC traces of rhomboidal metallacycle **H** (blue) and supramolecular polymer **P** (red).

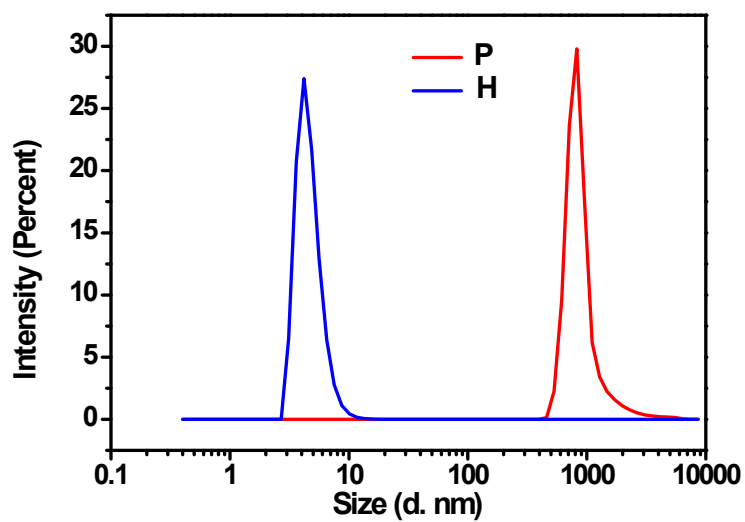


Fig. S15 DLS results of rhomboidal metallacycle **H** (blue) and supramolecular polymer **P** (red) at 1 mg/mL in acetone.

3. Host-guest complexation studies in dilute solution.

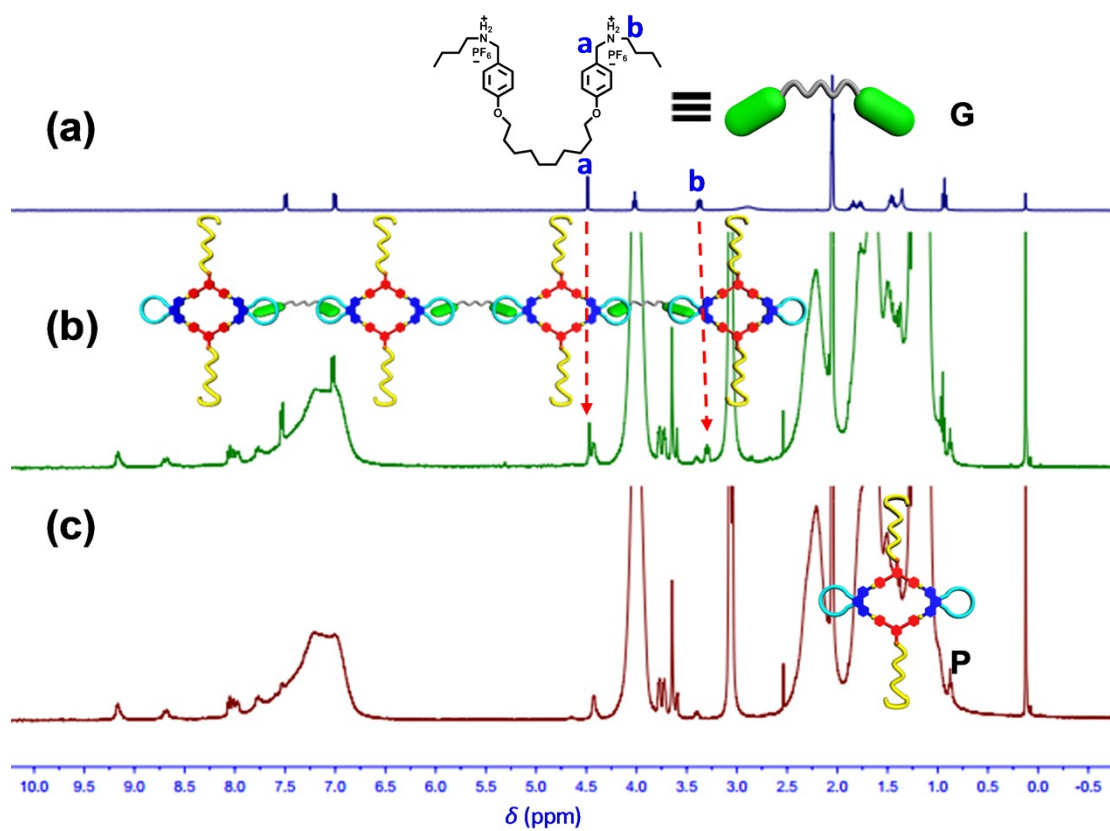
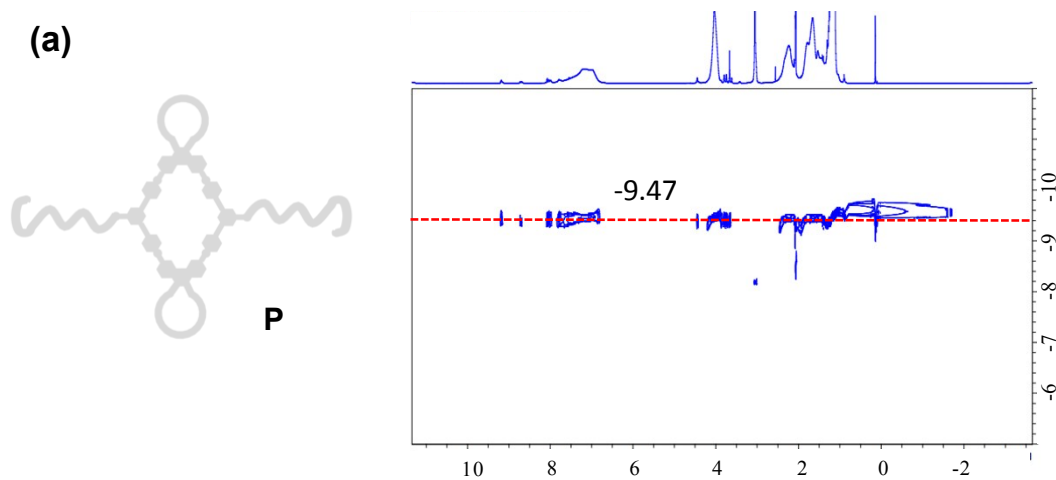


Fig. S16 ^1H NMR spectra (400 MHz, acetone- d_6 , 295 K) of (a) 4.0 mM G, (b) 4.0 mM P>G, (c) 4.0 mM P.



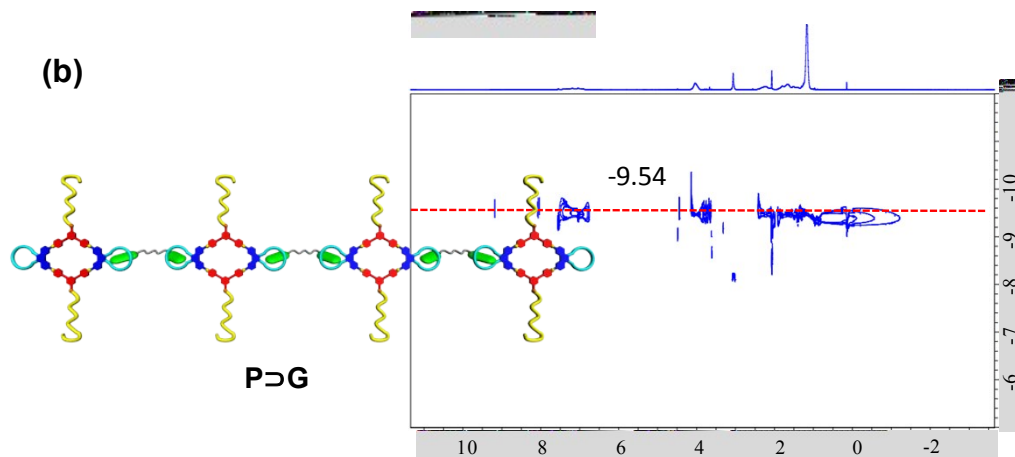


Fig. S17 2-D DOSY (500 MHz, acetone- d_6 , 295 K) spectra for **P** and **P>G** at 4.0 mM.

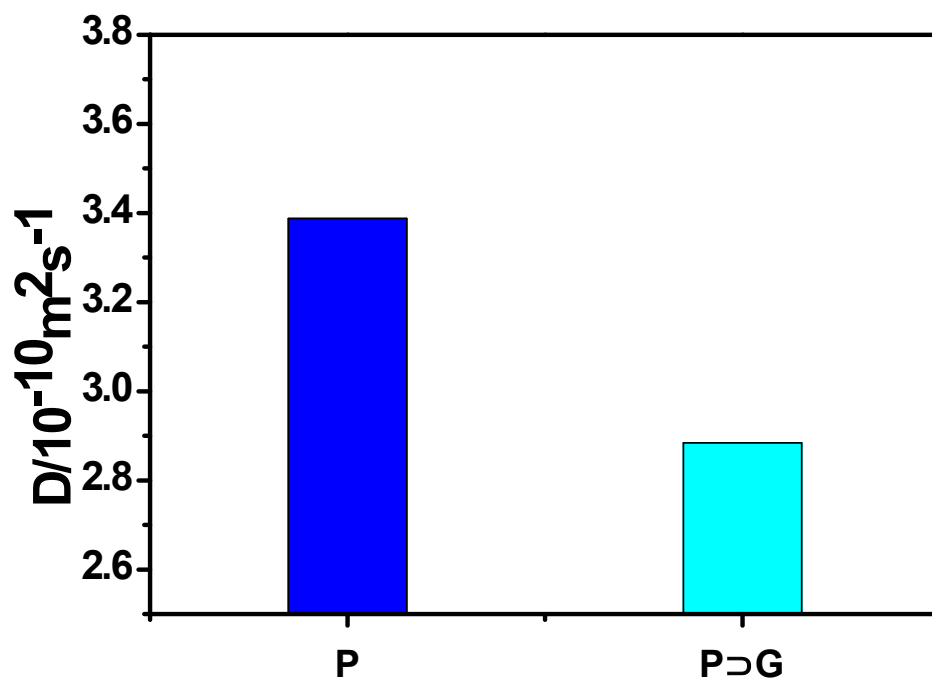


Fig. S18 2-D DOSY (500 MHz, acetone- d_6 , 295 K) value for **P** and **P>G** at 4.0 mM.

4. Rheological measurements studies of different processes.

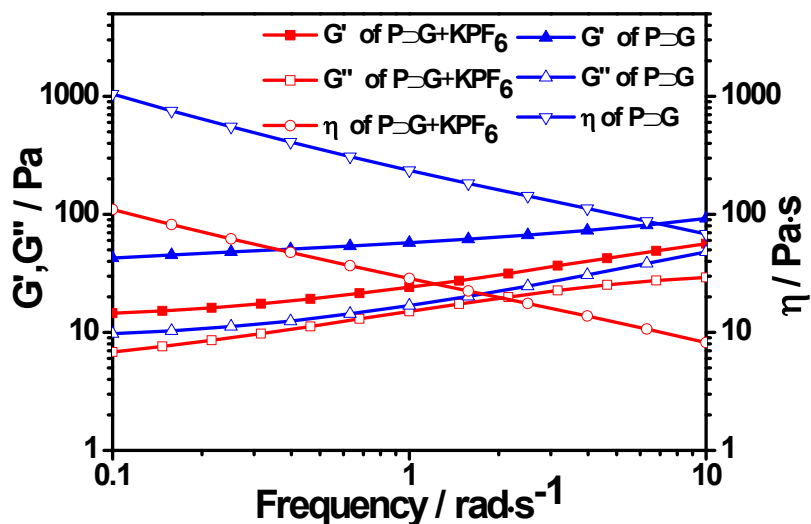


Fig. S19 Rheological data of the supramolecular polymer gels $P\supset G$ before (blue) and after (red) the addition of KPF_6 at 20 °C.

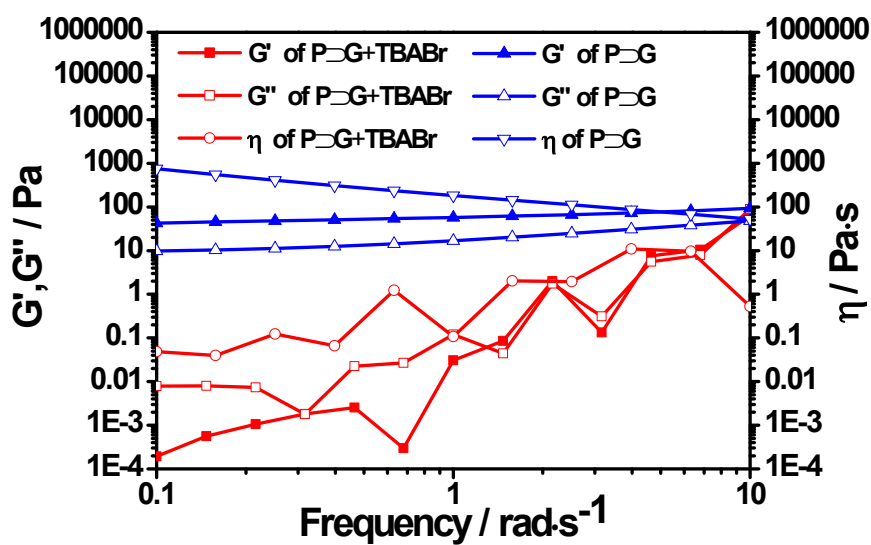


Fig. S20 Rheological data of the supramolecular polymer gels $P\supset G$ before (blue) and after (red) the addition of $TBABr$ at 20 °C.

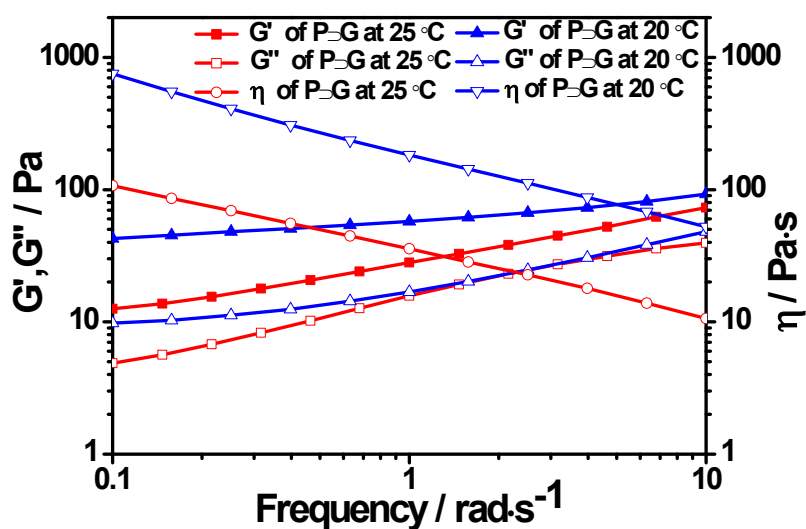


Fig. S21 Rheological data of the supramolecular polymer gels P-G at 20 °C (blue) and 25 °C (red).

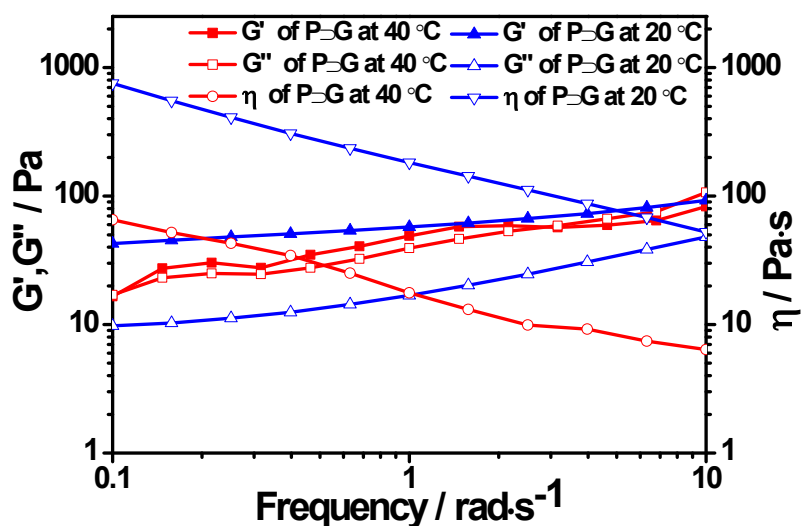


Fig. S22 Rheological data of the supramolecular polymer gels P-G at 20 °C (blue) and 40 °C (red).

Reference:

- S1. M. Zhang, S. Yin, J. Zhang, Z. Zhou, M. L. Saha, C. Lu and P. J. Stang, *Proc. Natl. Acad. Sci. U. S. A.*, 2017, **114**, 3044.
- S2. W. Zheng, L.-J. Chen, G. Yang, B. Sun, X. Wang, B. Jiang, G.-Q. Yin, L. Zhang, X. Li, M. Liu, G. Chen and H.-B. Yang, *J. Am. Chem. Soc.*, 2016, **138**, 4927.
- S3. T. Xiao, X. Feng, Q. Wang, C. Lin, L. Wang and Y. Pan, *Chem. Commun.*, 2013, **49**, 8329.