Electronic Supplementary Information (ESI) For

Hierarchical Self-Assembly of Discrete Hexagonal Metallacycle into the Ordered Nanofibers and Stimuli-Responsive Supramolecular Gels

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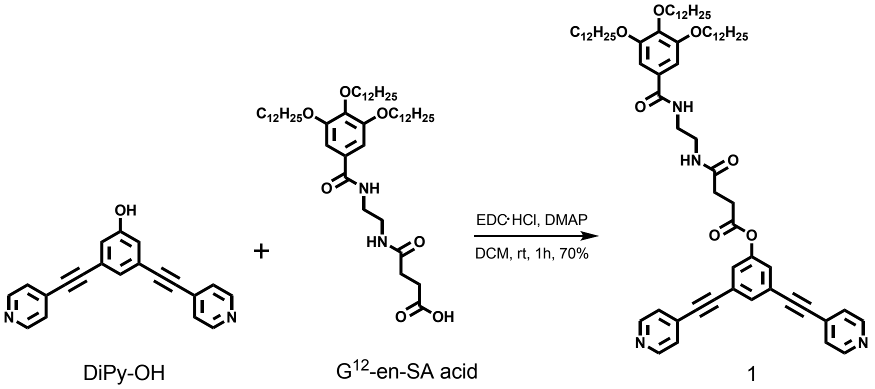
1. General Information.

All solvents were dried according to standard procedures. Reagents were used as purchased. All air-sensitive reactions were carried out under argon atmosphere. ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectra were recorded on Bruker 400 MHz Spectrometer (^{1}H: 400 MHz; ^{13}C: 100 MHz; ^{31}P: 161.9 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.

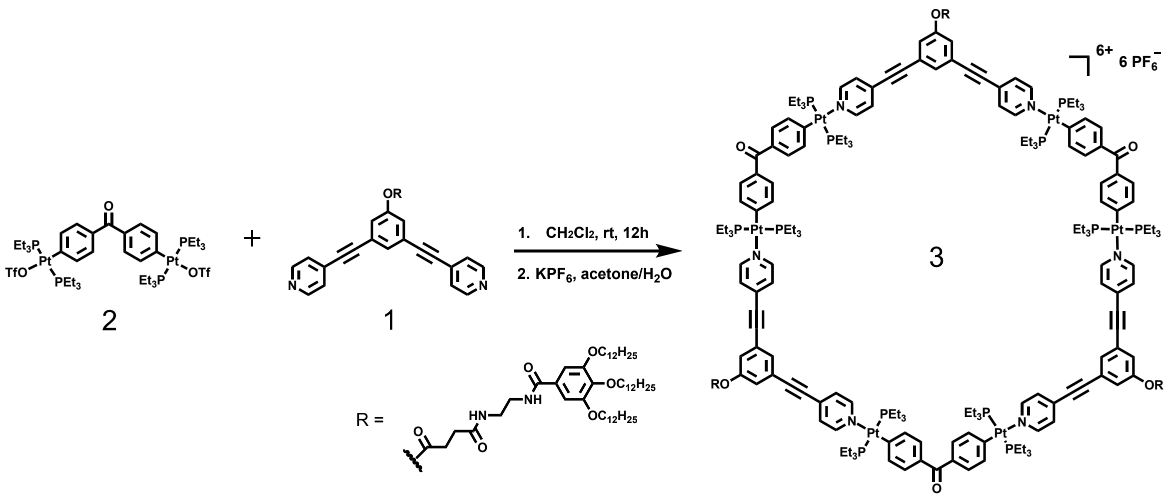
2. Synthetic Experimental Details of New Compounds.



Scheme S1. Synthetic route for the preparation of 120° donor **1**.

Compounds **DiPy-OH**[1] and **G^{12}-en-SA acid**[2] were prepared according to previously reported synthetic procedures and showed identical spectroscopic properties to those reported therein.

Synthesis of compound **1**: A 100 ml of Schlenk flask was charged with **DiPy-OH** (150 mg, 0.51 mmol), **G^{12}-en-SA acid** (413 mg, 0.51 mmol) and N-Ethyl-N'-(3-dimethylaminopropyl)carbodimide hydrochloride (EDC·HCl) (194 mg, 1.01 mmol), 4-Dimethylaminopyridine (DMAP) (12 mg, 0.098 mmol), degassed, and back-filled there times with N_2. A solvent of dried CH_2Cl_2 (30 mL) was added into the reaction flask by syringe. The reaction was stirred at room temperature for 12 hours. The solvent was removed by evaporation on a rotary evaporator and the residue was purified *via* column chromatography on silica gel afforded **1** as an off-white solid (289 mg, 70%). R*f* = 0.43 (CH_2Cl_2/acetone 4/1). M.p. 108 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.63 (d, J = 5.6 Hz, 4H), 7.59 (s, 1H), 7.38 (d, J = 6.0 Hz, 4H), 7.29 (s, 2H), 6.99 (s, 2H), 6.52 (t, J = 5.2Hz, 1H), 3.99-3.94 (m, 6H), 3.60-3.59 (m, 2H), 3.58-3.54 (m, 2H), 2.91 (t, J = 6.4 Hz, 2H), 2.63 (t, J = 6.8 Hz, 2H), 1.81-1.70 (m, 6H), 1.45-1.40 (m, 6H), 1.24 (br, 54H), 0.87 (t, J = 6.4 Hz, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.39, 171.05, 168.22, 153.07, 150.40, 149.61, 141.15, 132.56, 130.92, 128.61, 125.65, 125.61, 123.84, 105.50, 91.77, 88.08, 73.48, 69.21, 40.91, 40.42, 31.90, 30.62, 30.31, 29.73, 29.69, 29.67, 29.64, 29.57, 29.51, 29.42, 29.35, 26.10, 26.06, 22.67, 14.09. MALDI-TOF-MS: m/z calcd for $C_{69}H_{98}N_4O_7$ ($[M+H]^+$) 1095.74, found: 1095.48.

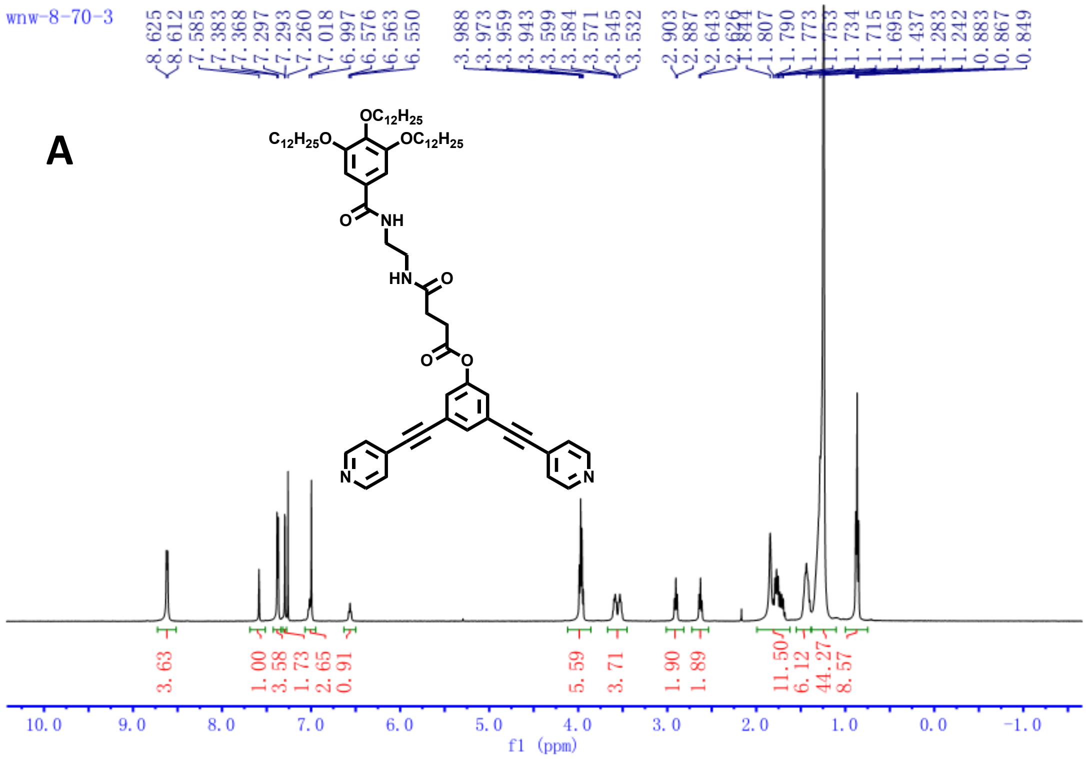


Scheme S2. Self-assembly route for the preparation of hexagon **3**.

Self-Assembly of Hexagon 3. A mixture of 120º donor **1** (10.19 mg, 9.30 μmol) and the equimolar amount of 120° acceptor di-Pt(II) acceptor **2** (11.18 mg, 9.30 μmol) were placed in a glass vial. The reaction mixture was stirred overnight at room time in CH_2Cl_2, upon which the starting materials completely dissolved and the reaction mixture attained a colorless solution. The OTf salt of hexagon **3** was easily obtained by removing solvent under a flow of nitrogen. The PF_6 salt of hexagon **3** was synthesized by dissolving the OTf 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%; off-white solid; ^{1}H NMR (acetone-d_6, 400 MHz) δ 9.08 (d, J = 6.0 Hz, 12H), 7.94 (d, J = 6.4Hz, 12H), 7.71 (d, J = 8.0 Hz, 12H), 7.59 (d, J = 7.6 Hz, 12H), 7.44 (s, 3H), 7.26 (s, 6H), 7.09 (s, 6H), 4.04-3.96 (m, 18H), 3.67 (t, J = 5.2 Hz, 6H), 3.54-3.50 (m, 6H), 1.82-1.70 (m, 18H), 1.52 (br, 90H), 1.30 (br, 162H), 1.24-1.16 (m, 108H), 0.89-0.86 (m, 27H); ^{31}P NMR (acetone-d_6, 161.9 MHz) δ 14.25 (s, $J_{Pt–P}$ = 2652.24 Hz); ESI-TOF-MS: $[M – 4OTf]^{4+}$, 1678.43, $[M – 5\ OTf]^{5+}$, 1312.85. Anal. Calcd for $C_{318}H_{498}F_{36}N_{12}O_{24}Pt_6P_{18}$: C, 52.43; H, 6.89; N, 2.31. Found: C, 52.75; H, 6.54; N, 2.30.

3. Multiple Nuclear NMR (^{1}H, ^{31}P, and ^{13}C NMR) Spectra of New Compounds.

Fig S1. (A) ^{1}H NMR, (B) ^{13}C NMR spectra of precursor **1** in $CDCl_3$.



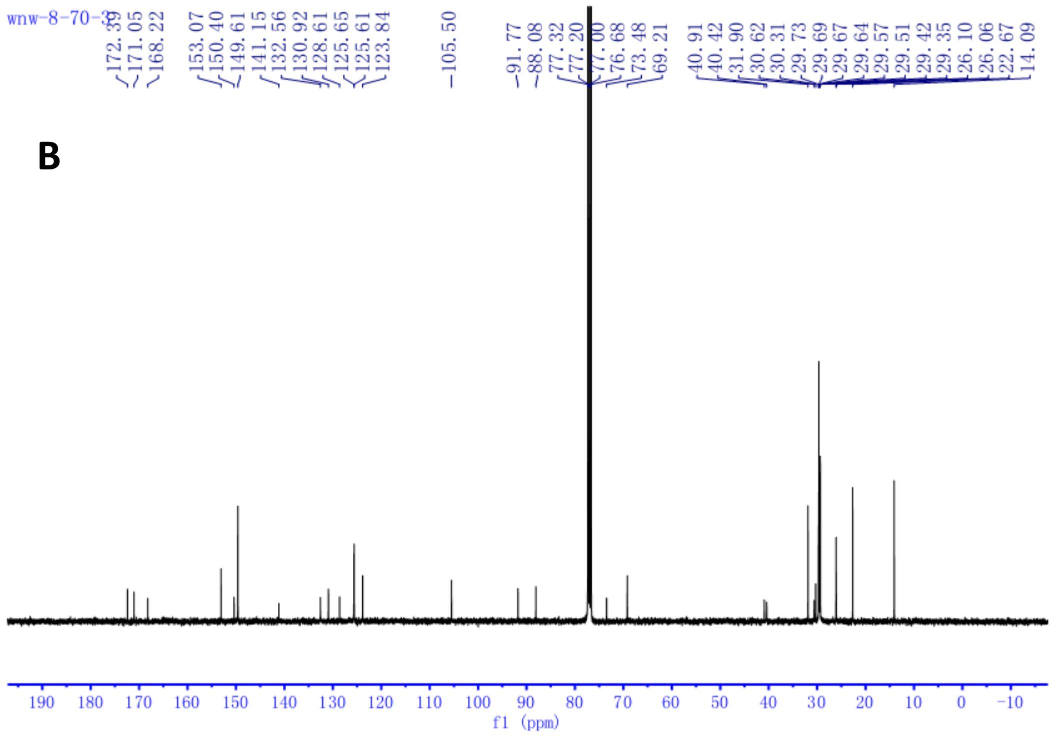
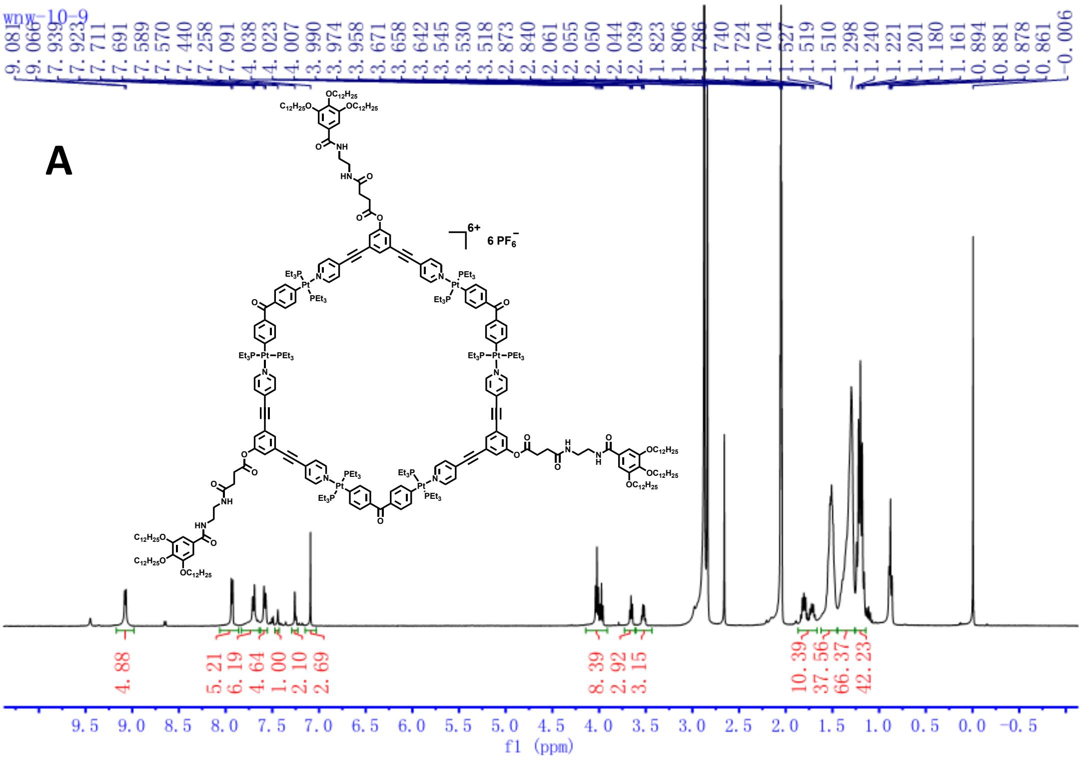


Fig S2. (A) ^{1}H NMR, (B) ^{31}P NMR spectra of hexagon **3** in acetone-*d*$_6$.



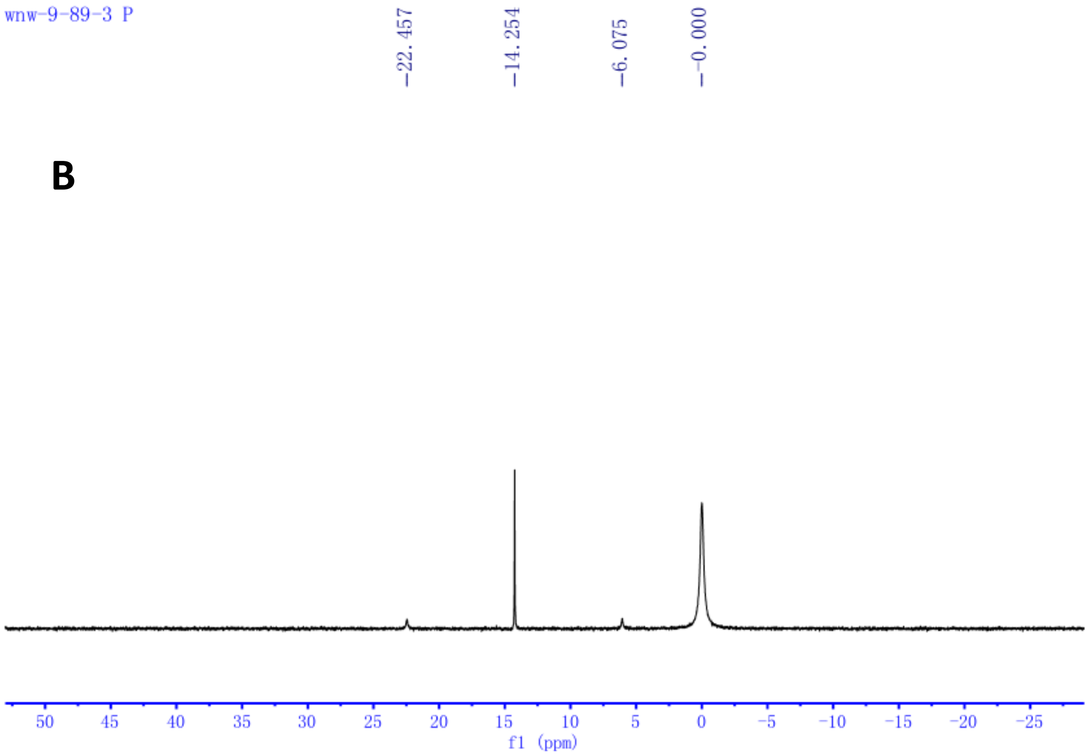


Fig S3. Comparison of partial ^{1}H NMR spectra of the aromatic portion of 120° precursor **1** (a) and the self-assembled [3 + 3] hexagon **3** (b).

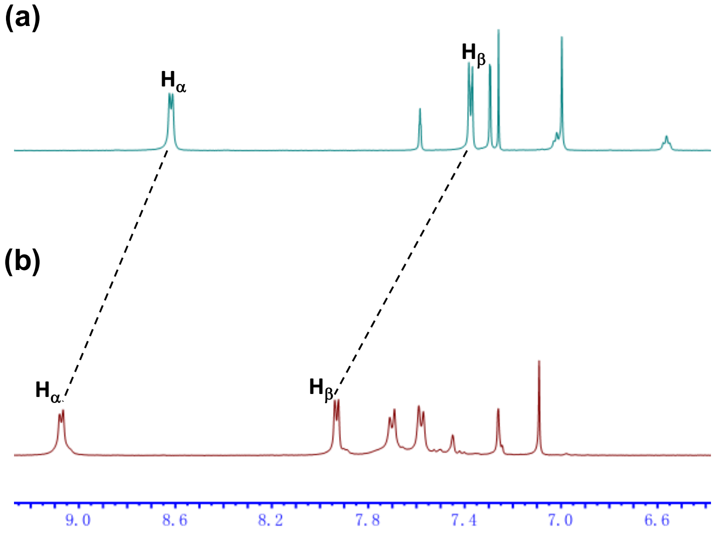
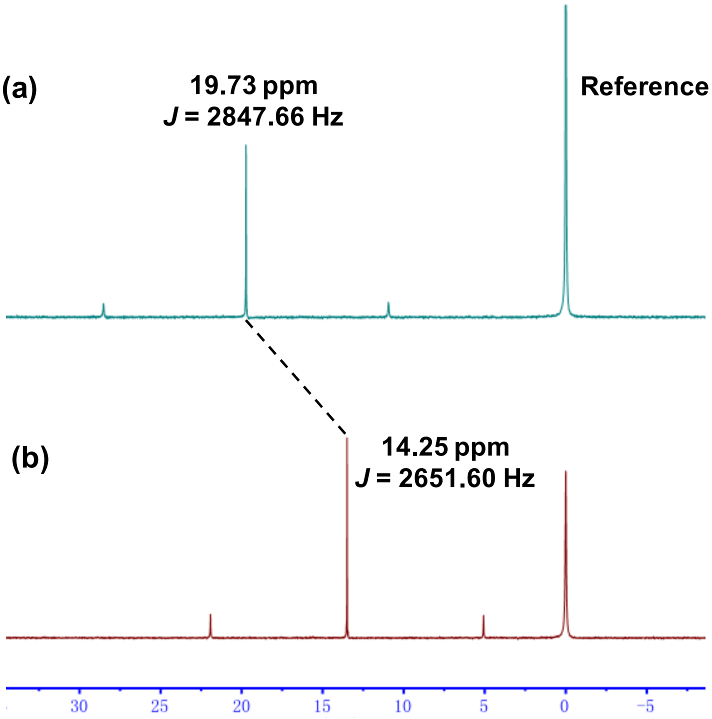
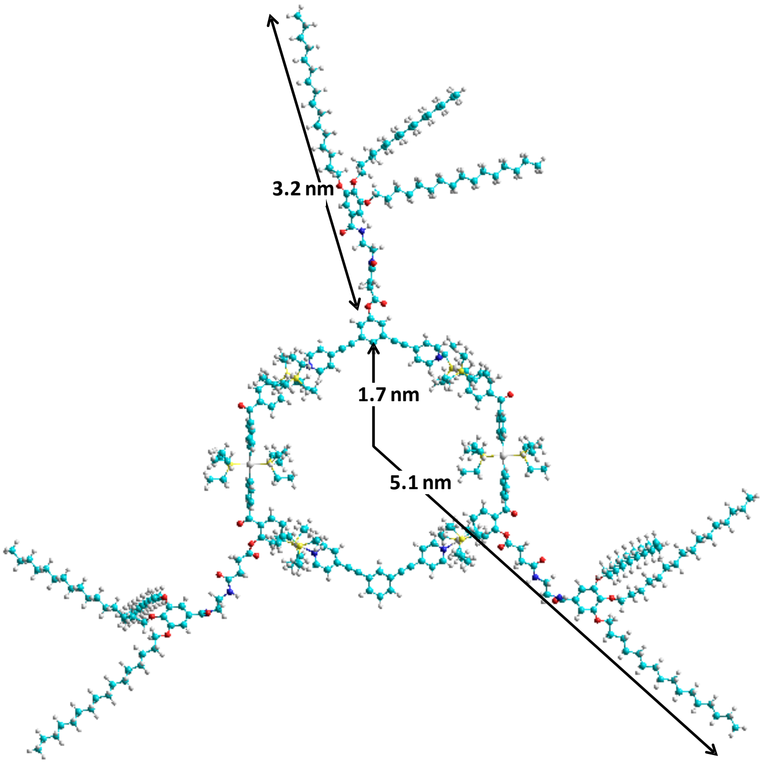


Fig S4. Comparison of ^{31}P {^{1}H} NMR spectra of the 120° di-Pt(II) acceptor **2** (a) and the self-assembled [3 + 3] hexagon **3** (b).

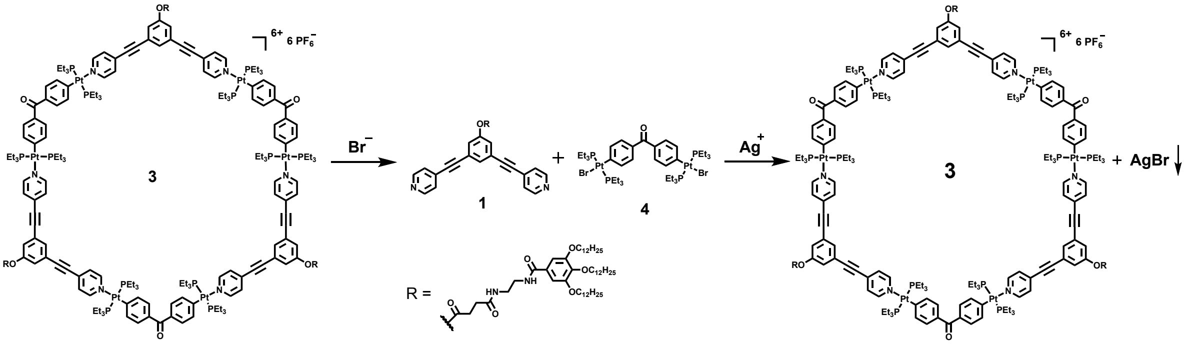


4. PM6 semi-empirical simulated molecular model of hexagon 3.

Fig S5. PM6 semi-empirical simulated molecular model of hexagon **3.**



5. Additional Stimuli-responsive experiments of hexagon 3.



Scheme S3. Stimuli-responsive disassembly and reassembly of hexagon **3** in acetone-*d*$_6$ solution.

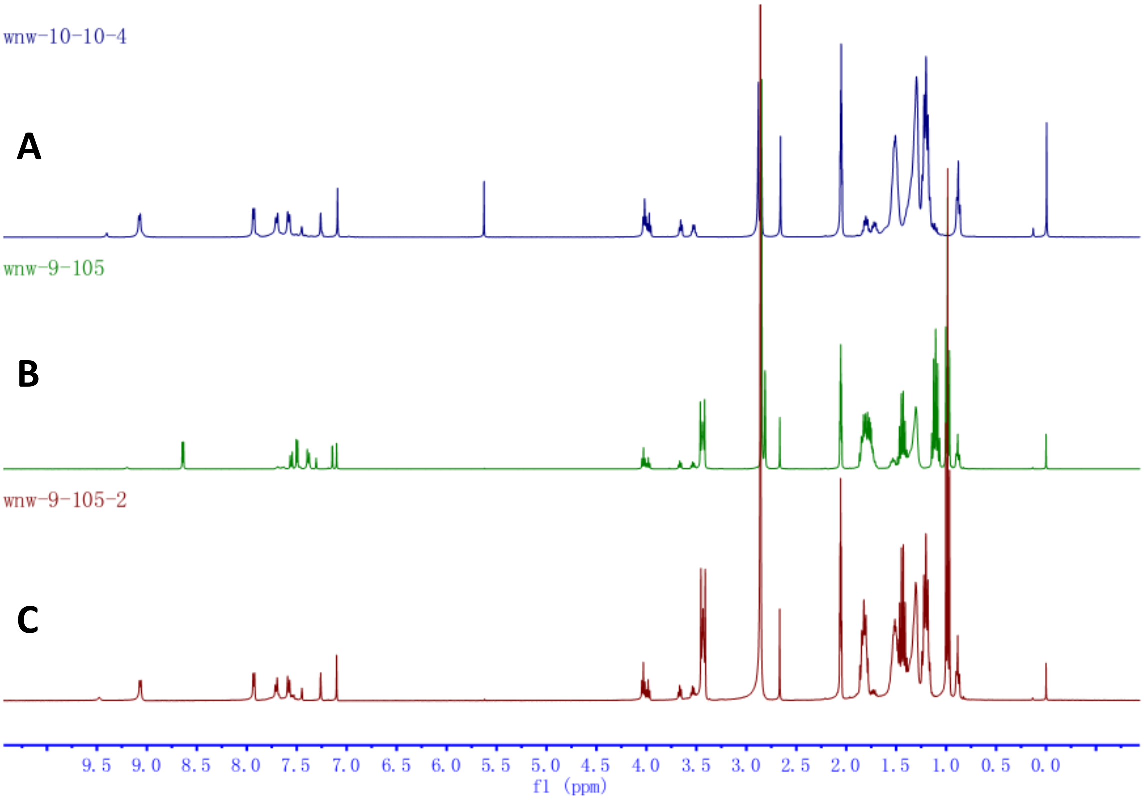


Fig S6. ^{1}H NMR spectras showing the disassembly and reassembly of **3** in acetone-*d*$_6$ (A) ^{1}H NMR spectra of hexagon **3** (B) ^{1}H NMR spectra of adding Bu_4NBr to the acetone-*d*$_6$ solution of the hexagon **3** in a NMR tube and shaking for one minute (C) ^{1}H NMR spectra of further adding of $AgPF_6$ to the same NMR tube and shaking for one minute.

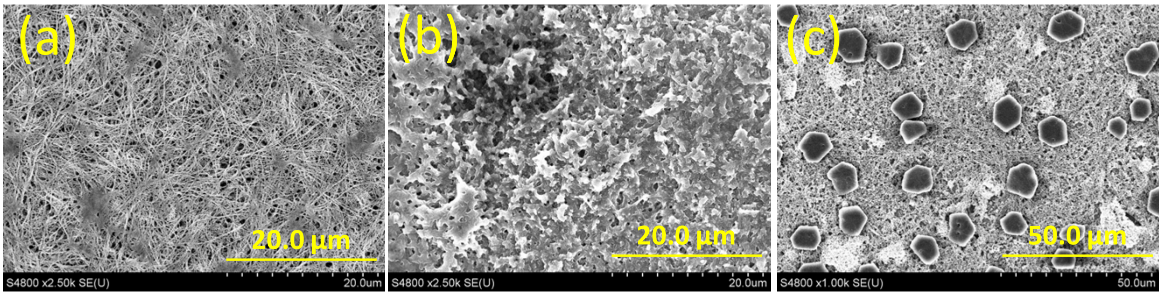


Fig S7. SEM images of xerogels of **3** prepared in acetone/water (v/v 2/1) at 0.9 mM (a) and 5.0 mM (b). SEM image of regenerated hybirdgel of **3** with AgBr precipitate (c).

6. Molecular model of the ring-to-ring interaction.

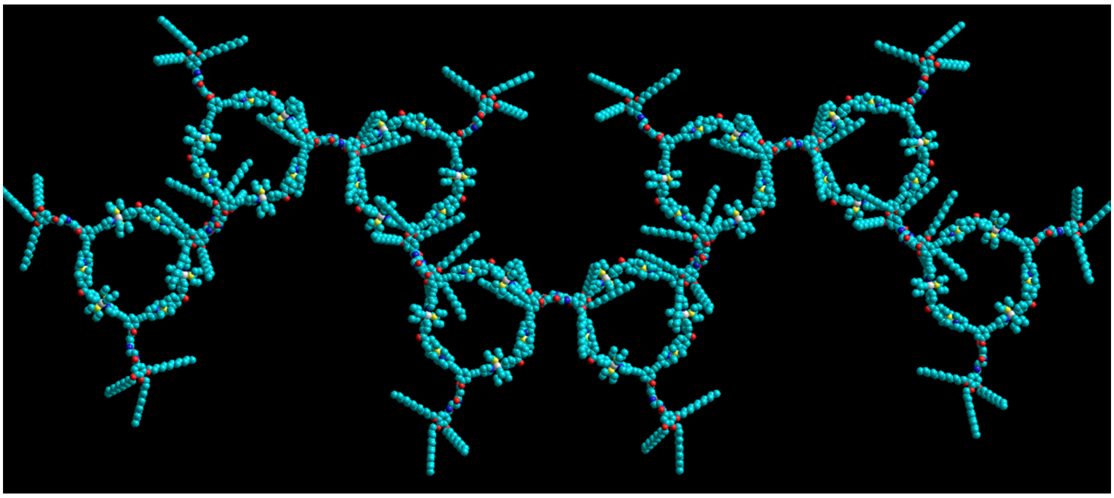


Fig S8. Simulated molecular model of the ring-ring interaction of the hexagon **3.**

7. FTIR spectroscopic studies of hexagon 3 in gel and solution state.

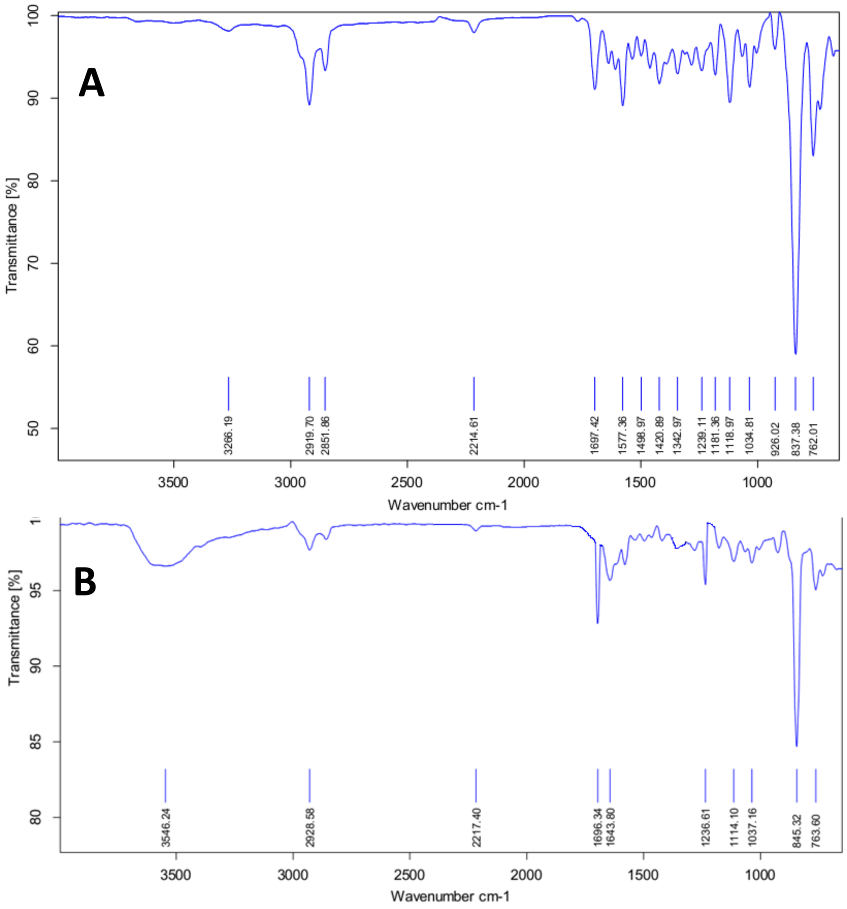


Fig S9. FTIR spectra of the xerogel of hexagon **3** obtained from acetone/water (A) and hexagon **3** in acetone solution (B).

8. ESI-TOF-MS spectrum of hexagon 3.

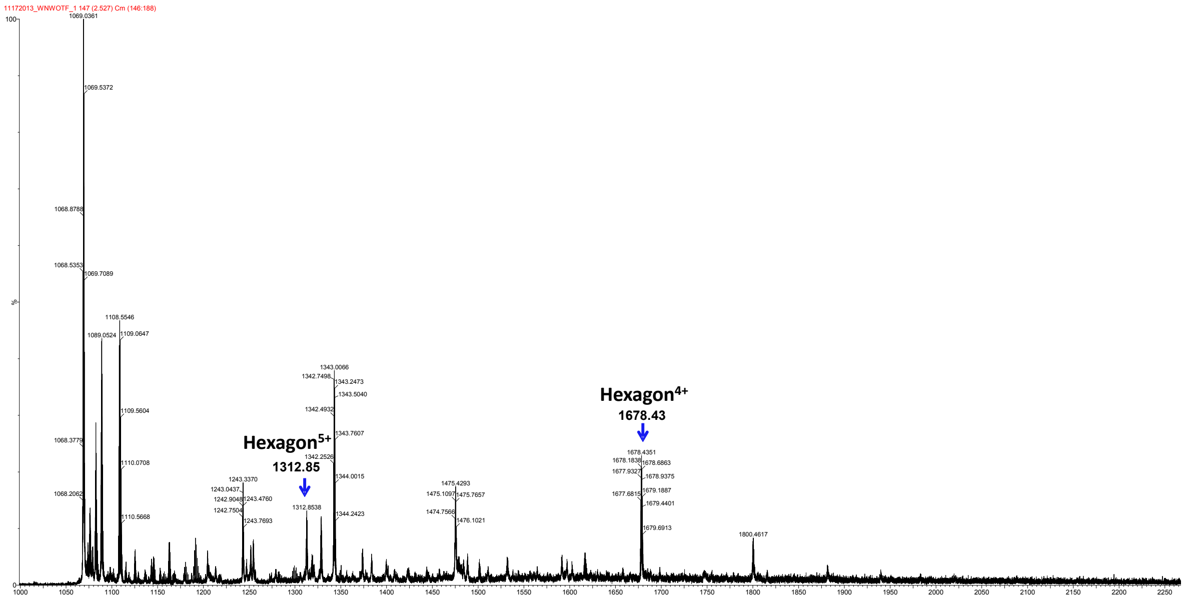


Fig S10. Full ESI-TOF-MS spectrum of the hexagon **3**.

9. References.

1. H.-B. Yang, N. Das, F. Huang, A. M. Hawkridge, D. C. Muddiman, P. J. Stang, *J. Am. Chem. Soc.*, 2006, **128**, 10014.

2. Y. Li, K. M.-C. Wong, A. Y.-Y. Tam, L.Wu, V. W.-W Yam, *Chem.–Eur. J.*, 2010, **29**, 8690.