

Supporting Information

Construction of stimuli-responsive supramolecular gel via bispillar[5]arene-based multiple interactions

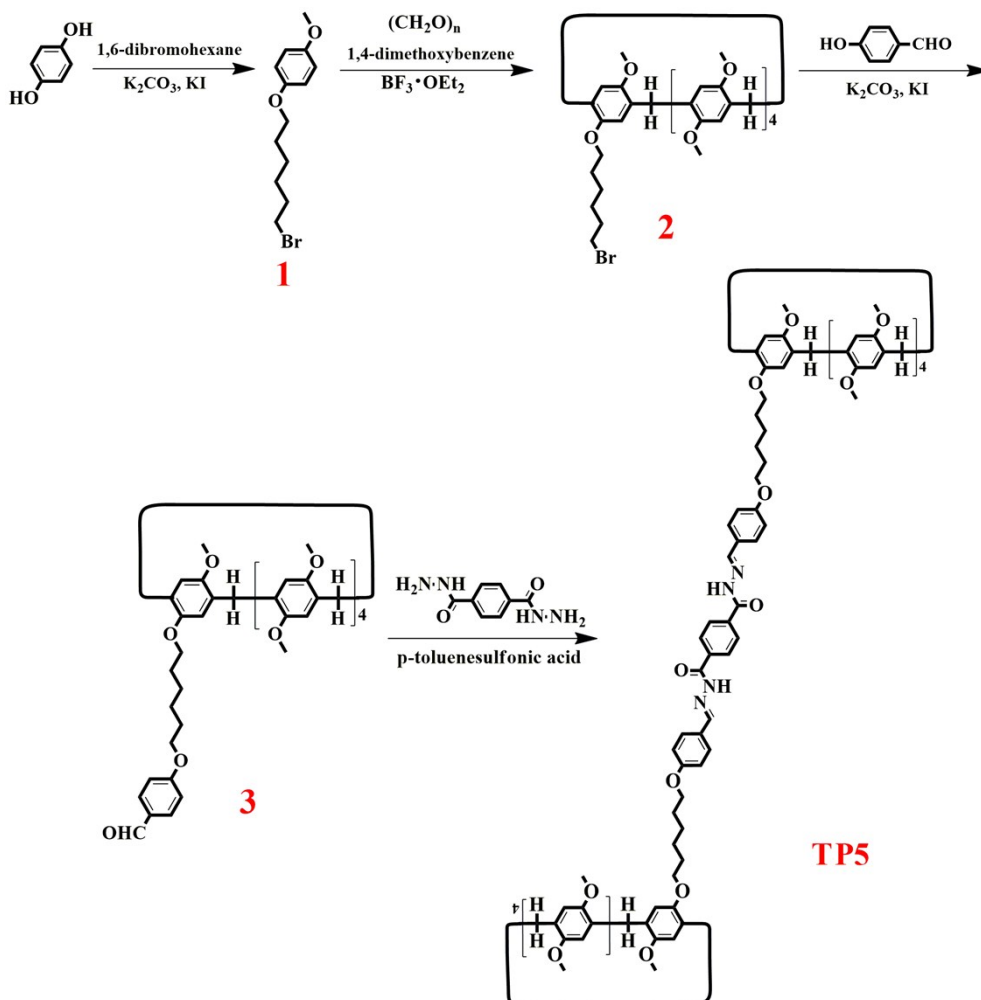
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1. Materials and methods

1,4-Dimethoxybenzene, boron trifluoride ethyl ether complex, 1,6-dibromohexane, and 1,10-dibromodecane were reagent grade and used as received. Solvents were either employed as purchased or dried by CaCl_2 . ^1H NMR spectra were recorded on a Mercury-600BB spectrometer at 600 MHz and ^{13}C NMR spectra were recorded on a Mercury-600BB spectrometer at 150 MHz. Chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale with solvent resonances as internal standards). Mass spectra were performed on a Bruker Esquire 3000 plus mass spectrometer (Bruker-FranzenAnalytik GmbH Bremen, Germany) equipped with ESI interface and ion trap analyzer. The X-ray diffraction analysis (XRD) was performed in a transmission mode with a Rigaku RINT2000 diffractometer equipped with graphite monochromated CuK α radiation ($\lambda = 1.54073 \text{ \AA}$). The morphologies and sizes of the xerogels were characterized using field emission scanning electron microscopy (FE-SEM, JSM-6701F) at an accelerating voltage of 8 kV.

2. Synthesis of bispillar[5]arene TP5



Scheme S1 Synthesis of bispillar[5]arene **TP5**.

Synthesis of compound 1: In a 500 mL round-bottom flask, 4-Methoxyphenol (2.48 g, 20.0 mmol), K_2CO_3 (8.4 g, 60 mmol), KI (3.3 g, 20mmol), 1,6-dibromohexane (12.2 g, 50 mmol) and acetone (400.0 mL) were added. The reaction mixture was stirred at reflux for 2 days. After the solid was filtered off, the solvent was evaporated and the residue was dissolved in CH_2Cl_2 . Column chromatography (silica gel; petroleum ether : ethyl acetate=20:1) afforded a white solid (4.46 g, 78%). 1H NMR (600 MHz, $DMSO-d_6$) δ 6.82 (s, 4H), 3.86 (s, 2H), 3.67 (s, 3H), 3.52 (s, 2H), 1.88–1.71 (m, 2H), 1.71–1.62 (m, 2H), 1.54–1.30 (m, 4H).

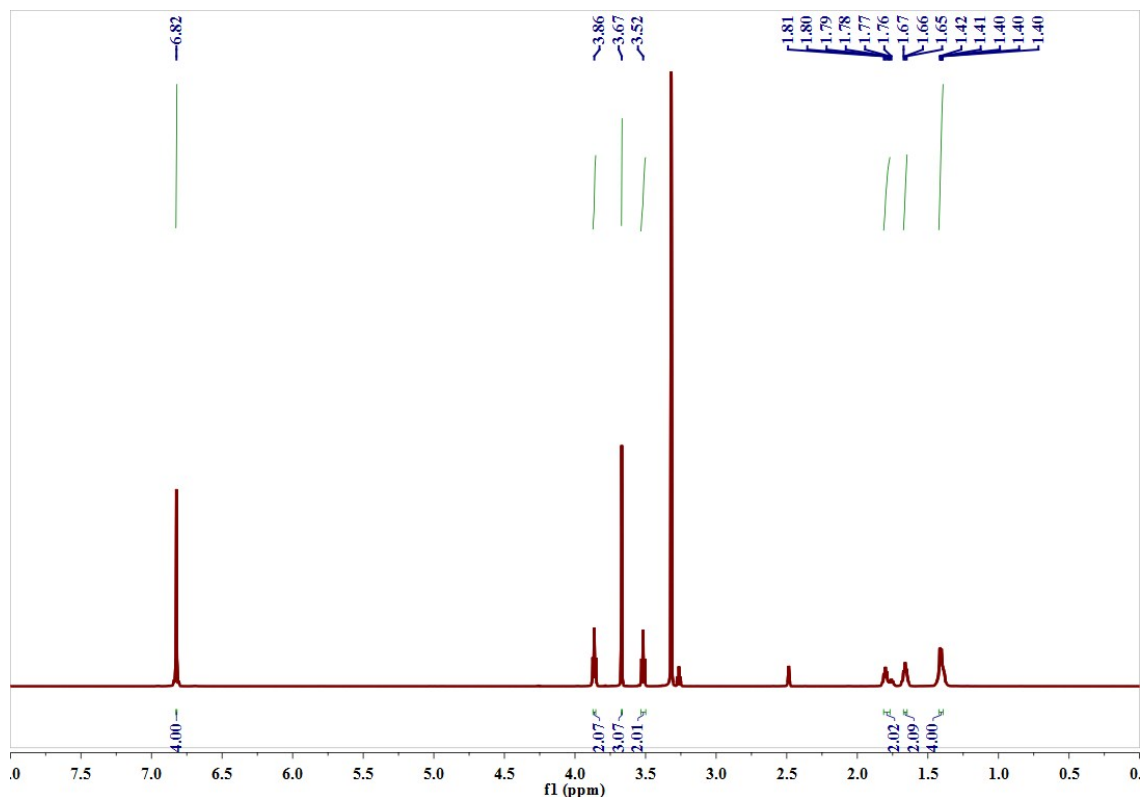


Fig. S1 ^1H NMR spectra (600 MHz, $\text{DMSO-}d_6$) of compound **1**.

Synthesis of a copillar[5]arene **2:** To a solution of compound **1** (1.43 g, 5.0 mmol) and 1,4-dimethoxybenzene (2.76 g, 20.0 mmol) in 1,2-dichloroethane (80 mL), paraformaldehyde (0.75 g, 25.0 mmol) was added under nitrogen atmosphere. Then boron trifluoride diethyl etherate (6.75 mL, 25 mmol) was added to the solution and the mixture was stirred at room temperature for 2 h and concentrated by rotary evaporation. The resultant oil was dissolved in CH_2Cl_2 and washed twice with H_2O . The organic layer was dried over anhydrous Na_2SO_4 and evaporated to afford the crude product, which was isolated by flash column chromatography using petroleum ether/ethyl acetate (20 : 1, v/v) to give **2** (1.3 g, 29%) as a white solid. ^1H NMR (600 MHz, CDCl_3) δ 6.96–6.79(m, 10H), 3.78(t, $J=10.7\text{Hz}$, 37H), 3.70(d, $J=7.0\text{Hz}$, 6H), 1.54–1.46(m, 2H), 1.26(s, 2H), 0.88(d, $J=7.0\text{Hz}$, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 150.64(s), 128.07(s), 113.98(s), 55.62(s), 29.57(s). ESI-MS m/z : $(\text{M}+\text{H})^+$ Calcd for $\text{C}_{50}\text{H}_{60}\text{O}_{10}\text{Br}$ 900.9; Found 901.1.

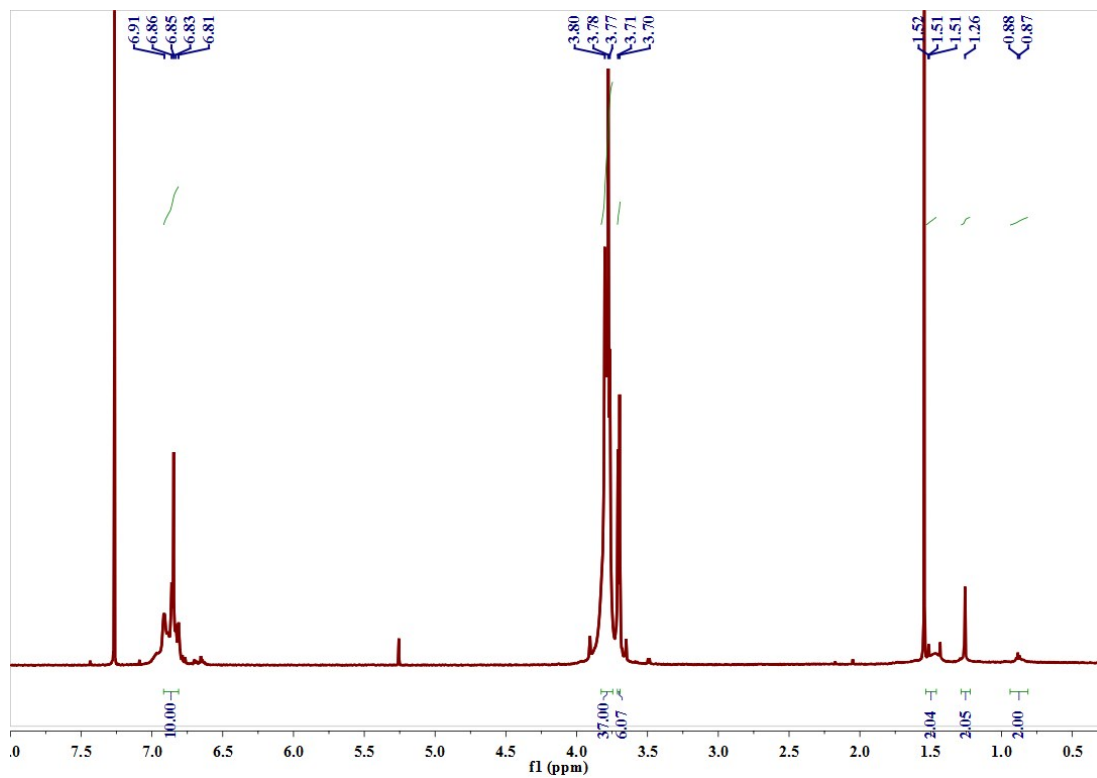


Fig. S2 ^1H NMR spectra(600 MHz, CDCl_3) of a copillar[5]arene **2**.

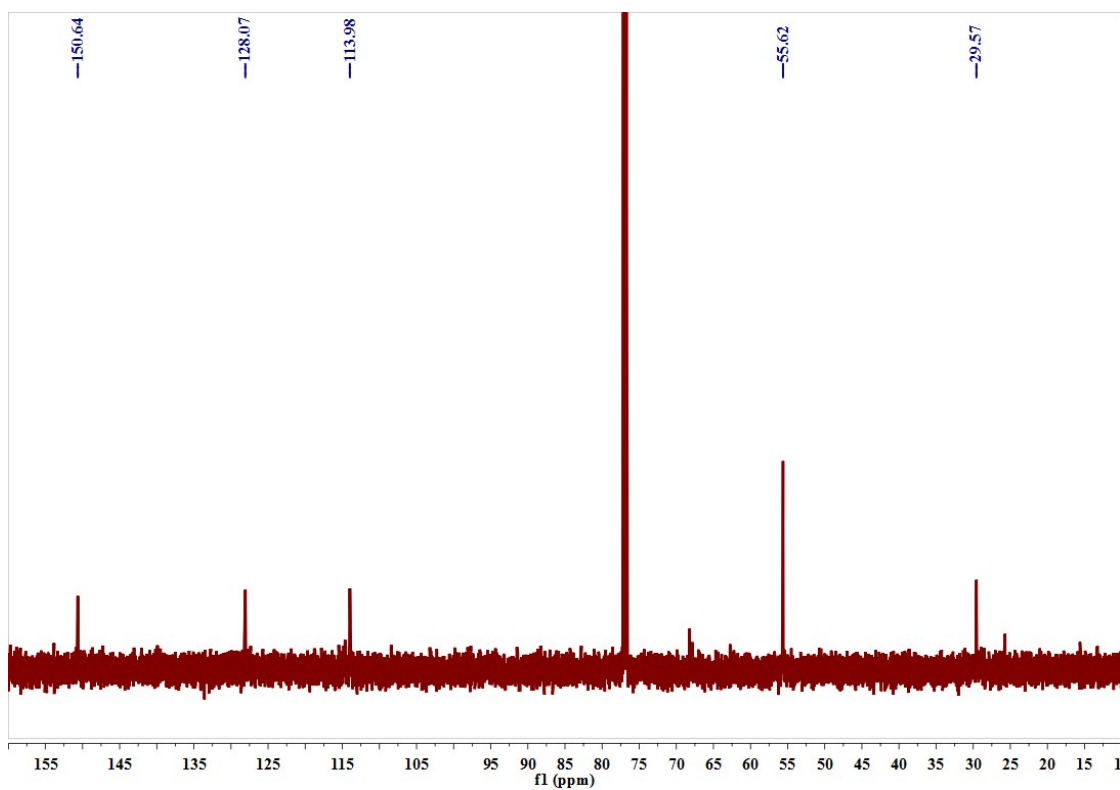


Fig. S3 ^{13}C NMR spectra(151 MHz, CDCl_3) of a copillar[5]arene **2**.

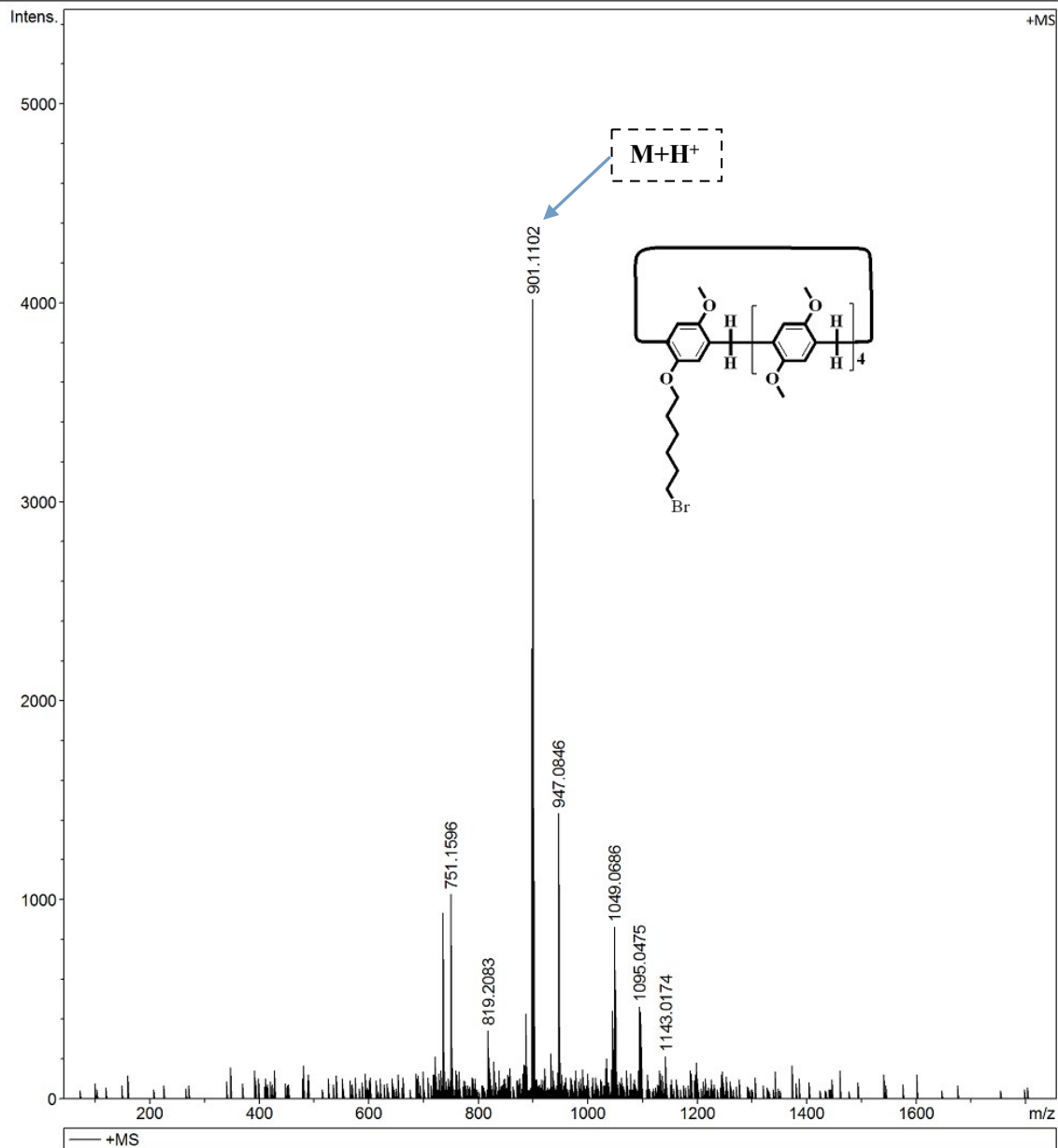
Generic Display Report

Analysis Info

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Operator LZU
Instrument micrOTOF



Bruker Compass DataAnalysis 4.1

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by: LZU

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Fig. S4 mass data of a copillar[5]arene **2**.

Synthesis of compound intermediate 3: Copillar[5]arene **2** (0.9 g ,1mmol), and 4-Hydroxybenzaldehyde (0.122g , 1mmol) was dissolved in THF (80

mL). K_2CO_3 (0.138 g, 1mmol) was added and the reaction mixture was stirred at reflux for 2 days. After solvent was evaporated and the residue was dissolved in CH_2Cl_2 . Column chromatography (silica gel; petroleum ether : ethyl acetate=20:1) afforded a white solid (0.42 g, 45%). 1H NMR (600 MHz, $CDCl_3$) δ 9.88(s, 1H), 7.82(d, $J=8.5$ Hz, 2H), 6.94(d, $J=8.6$ Hz, 2H), 6.77(d, $J=9.7$ Hz, 10H), 3.87(s, 4H), 3.77(s, 10H), 3.65(d, $J=7.1$ Hz, 27H), 3.60(s, 4H), 1.76(s, 2H), 1.25(s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 128.21 (s), 114.71 (s), 114.05 (s), 55.74 (s), 29.64 (s). ESI-MS m/z : $(M+NH_4)^+$ Calcd for $C_{57}H_{68}O_{12}N$ 958.4736; Found 958.4744.

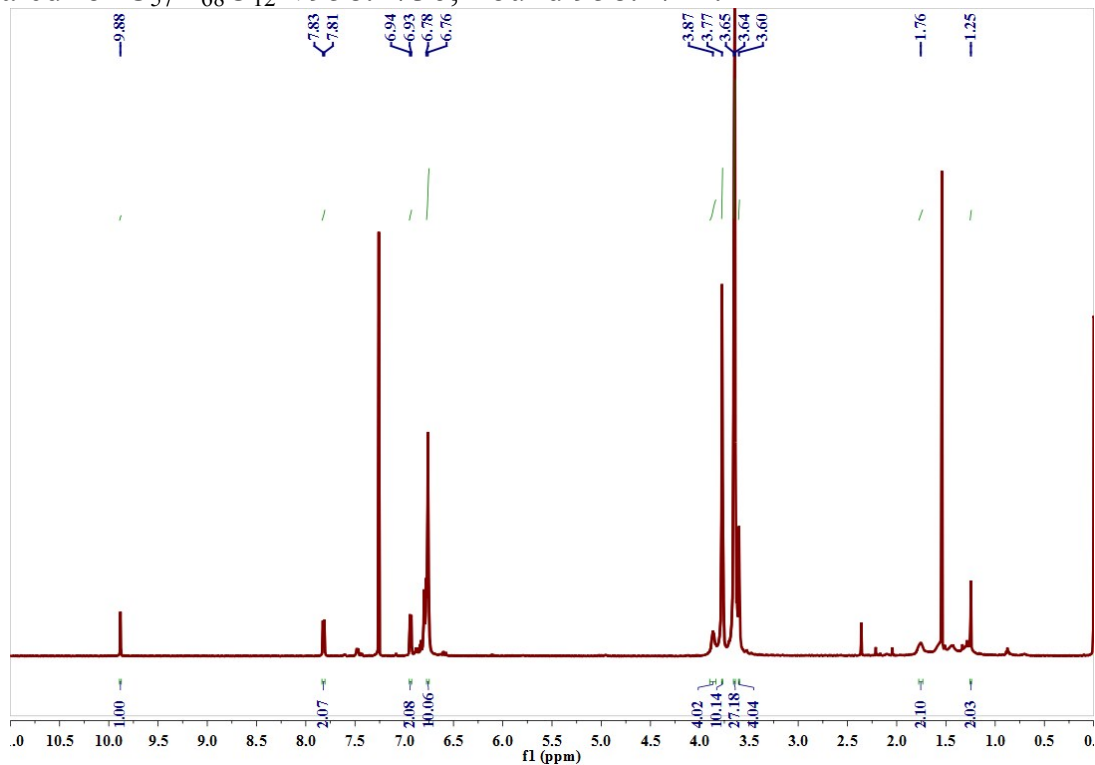


Fig. S5 1H NMR spectra(600 MHz, $CDCl_3$) of compound intermediate **3**.

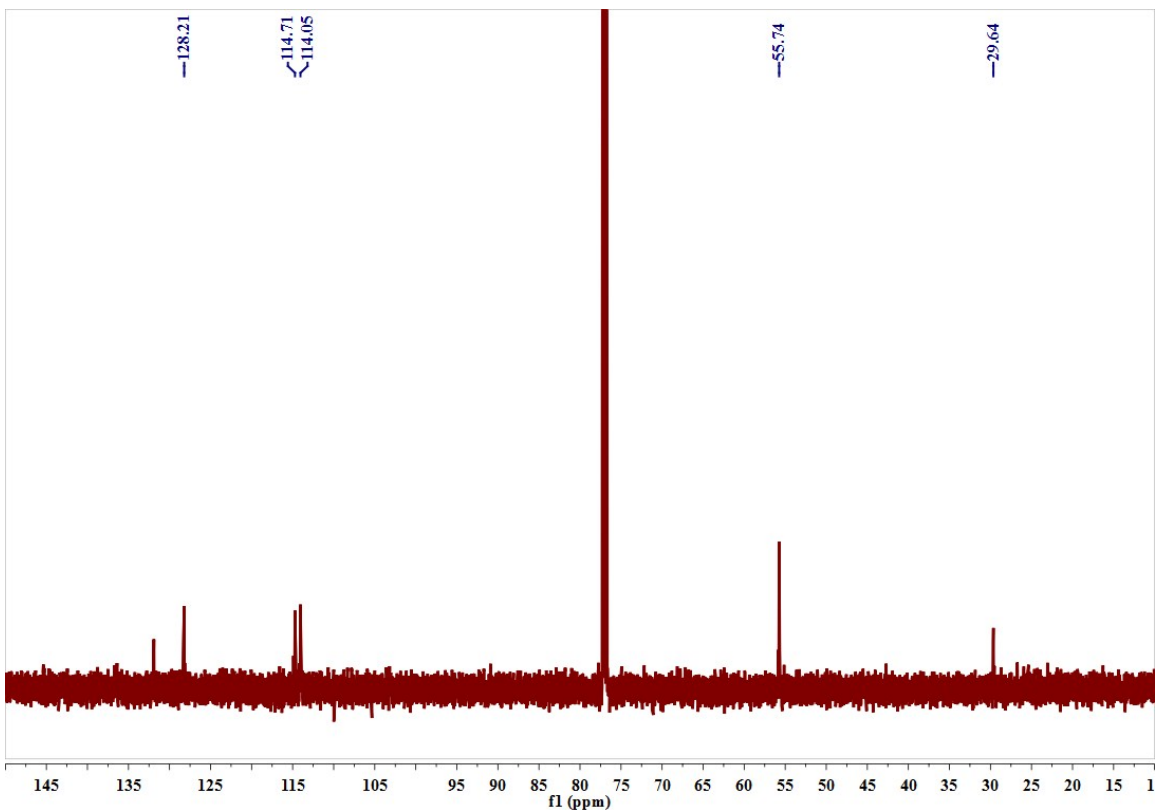


Fig. S6 ^{13}C NMR spectra(151 MHz, CDCl_3) of compound intermediate **3**.

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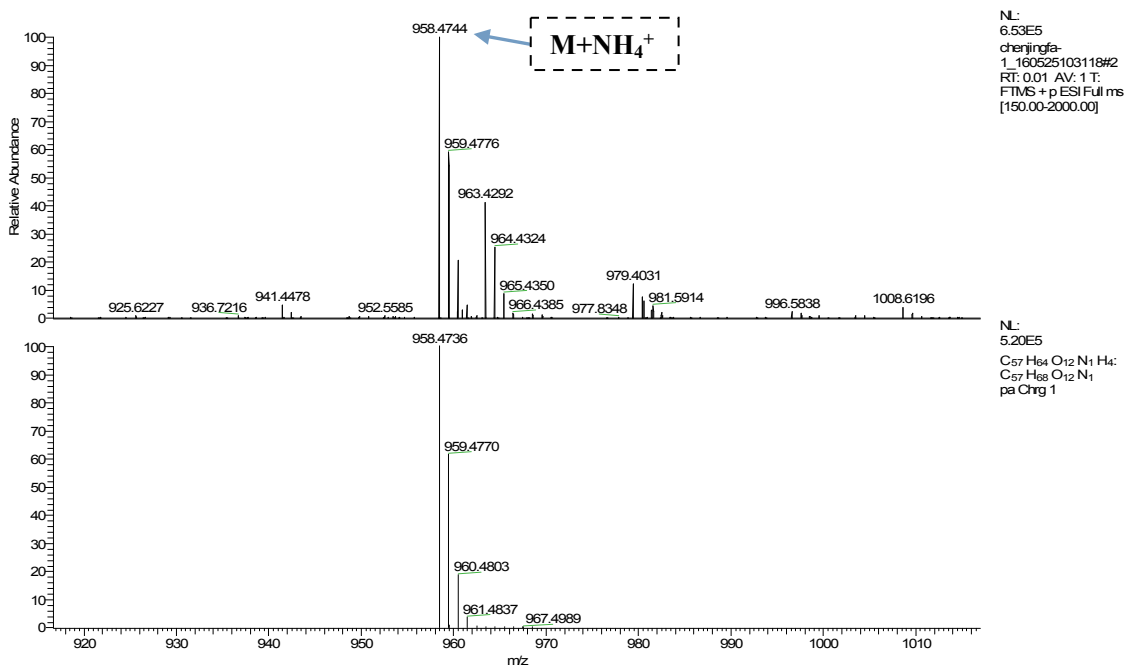


Fig. S7 High resolution mass data of compound intermediate **3**.

Synthesis of bispillar[5]arene TP5: Compound intermediate **3** (1.5 mmol), terephthalic dihydrazide (0.5 mmol) and p-toluenesulfonic acid (0.05 mmol, as a catalyst) were added to ethanol (50 mL) and chloroform (10 mL). Then the reaction mixture was stirred under refluxed conditions for 24 hours, after the solvent was evaporated and the residue was dissolved in CH₂Cl₂. Column chromatography (silica gel; petroleum ether : ethyl acetate=1:1) afforded a slightly yellow solid (0.97 g, 95%). ¹H NMR (600 MHz, CDCl₃) δ 8.29(d, J=63.0Hz, 2H), 8.03(d, J=45.1Hz, 2H), 7.75(d, J=35.0Hz, 6H), 7.51(d, J=15.5Hz, 2H), 6.87(s, 4H), 6.77(dd, J=14.4, 7.6Hz, 20H), 3.87(d, J=6.2Hz, 8H), 3.77(d, J=6.0Hz, 20H), 3.63(dd, J=14.5, 4.9Hz, 54H), 1.81–1.76(m, 4H), 1.70(d, J=6.6Hz, 4H), 1.54–1.50(m, 4H), 1.43(s, 4H). ¹³C NMR (151 MHz, CDCl₃) δ 150.70(s), 128.14(s), 114.07(s), 111.38–109.26 (m), 68.62–67.16(m), 55.71(s), 29.67(s), 25.81(s). ESI-MS m/z: (M+H)⁺ Calcd for C₁₂₂H₁₃₅O₂₄N₄ 2040.9494; Found 2040.9457.

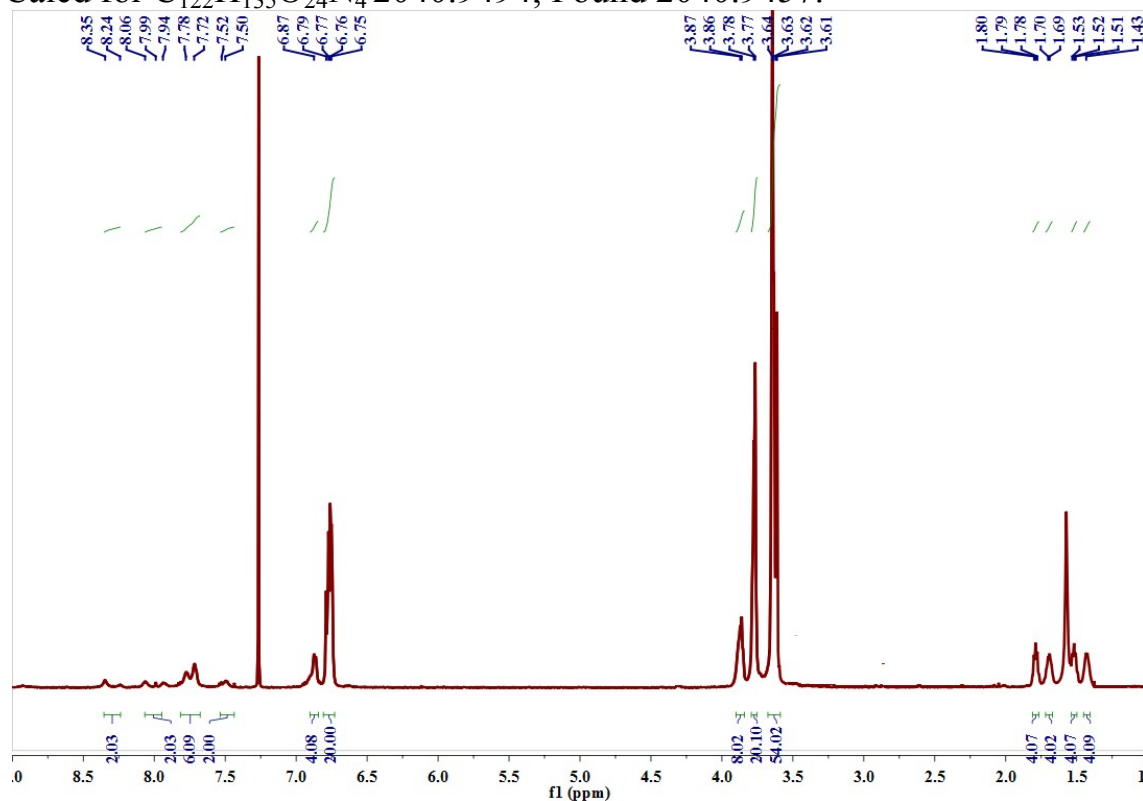


Fig. S8 ¹H NMR spectra(600 MHz, CDCl₃) of bispillar[5]arene **TP5**.

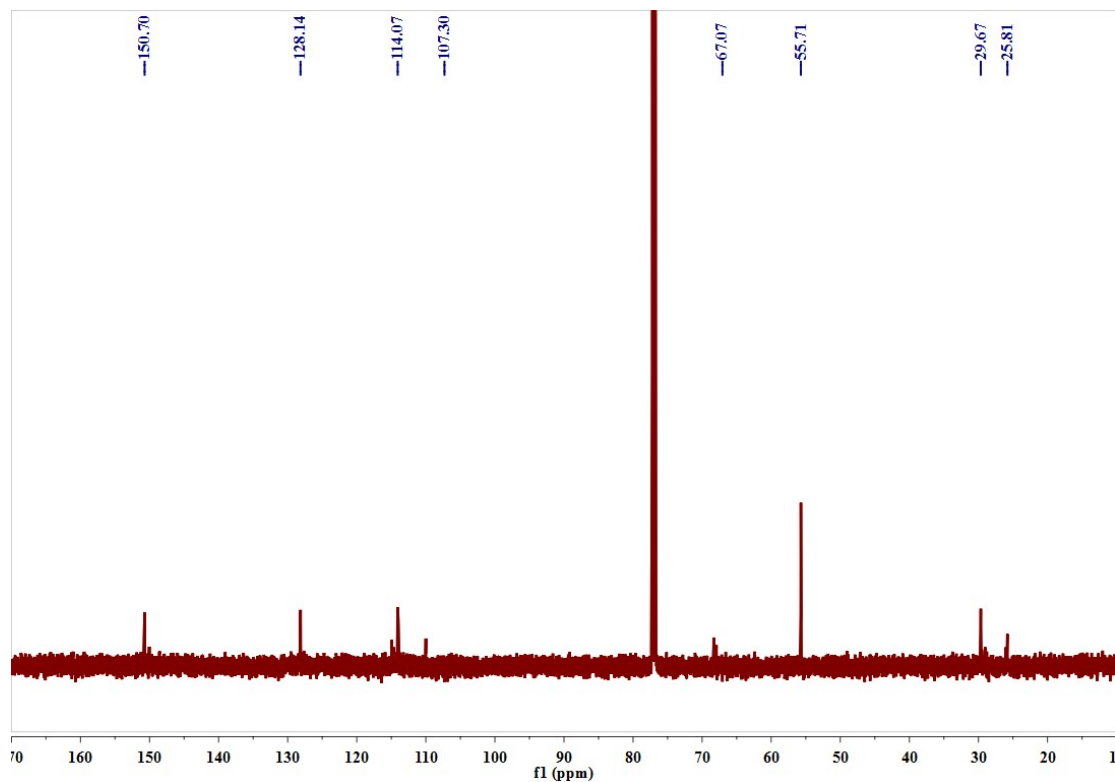


Fig. S9 ^{13}C NMR spectra(151 MHz, CDCl_3) of bispillar[5]arene **TP5**.

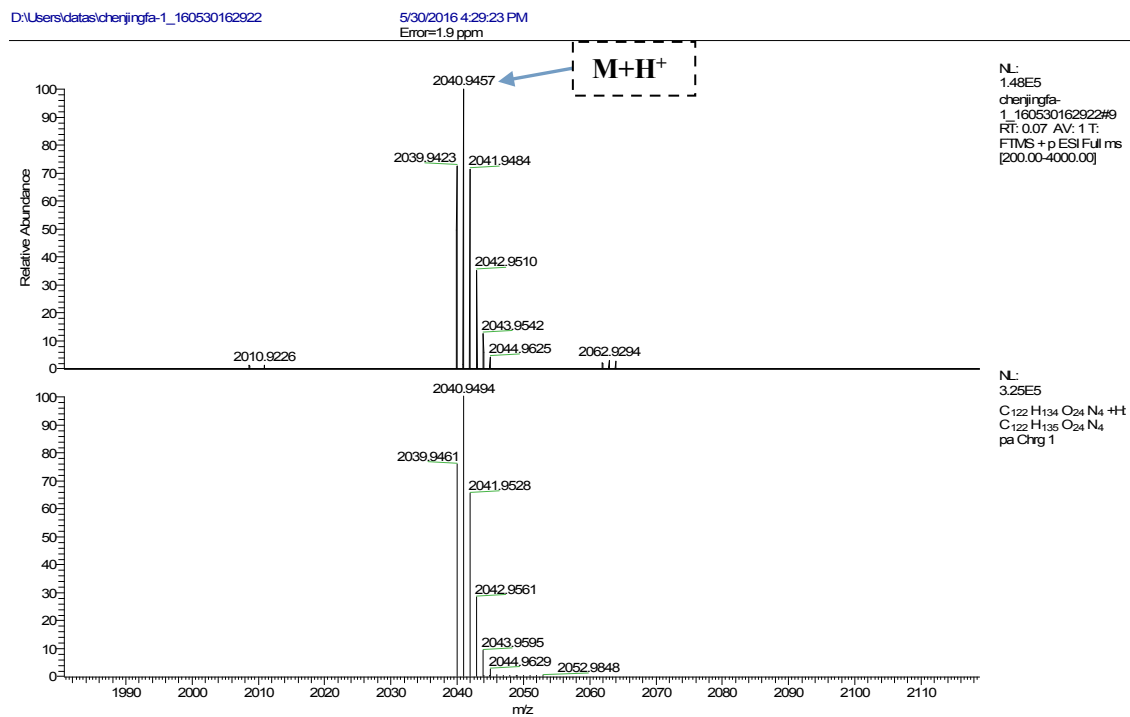
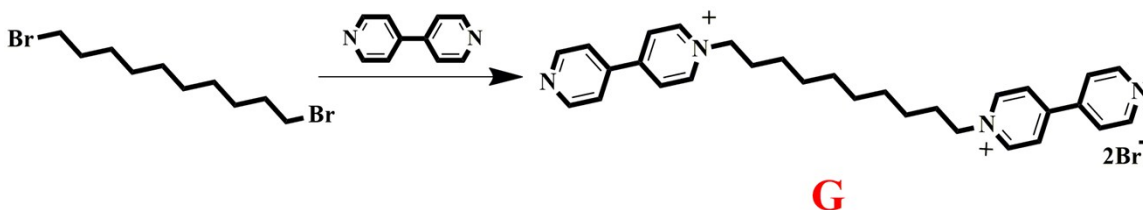


Fig. S10 High resolution mass data of bispillar[5]arene **TP5**.

3. Synthesis of G



Scheme S2 Synthesis of G.

Synthesis of compound G: A solution of 1,10-dibromodecane (1.89 g, 6.3 mmol) in CH₃CN (30 mL) was added dropwise into a stirred solution of 4,4'-bipyridine (5.56 g, 35.7 mmol) in CH₃CN (50 mL) and refluxed over night. After it cooled, the suspension was filtered. The solid was washed with CH₃CN and then dried in an oven to afford a pale green solid **G** (3.3 g, 86%).
¹H NMR (600 MHz, D₂O) δ 8.81(t, J=7.0Hz, 4H), 8.62(d, J=1.4Hz, 4H), 8.25(s, 4H), 7.76(d, J=1.5Hz, 4H), 4.50(d, J=7.3Hz, 4H), 1.90(d, J=6.8Hz, 4H), 1.17(d, J=38.2Hz, 12H).

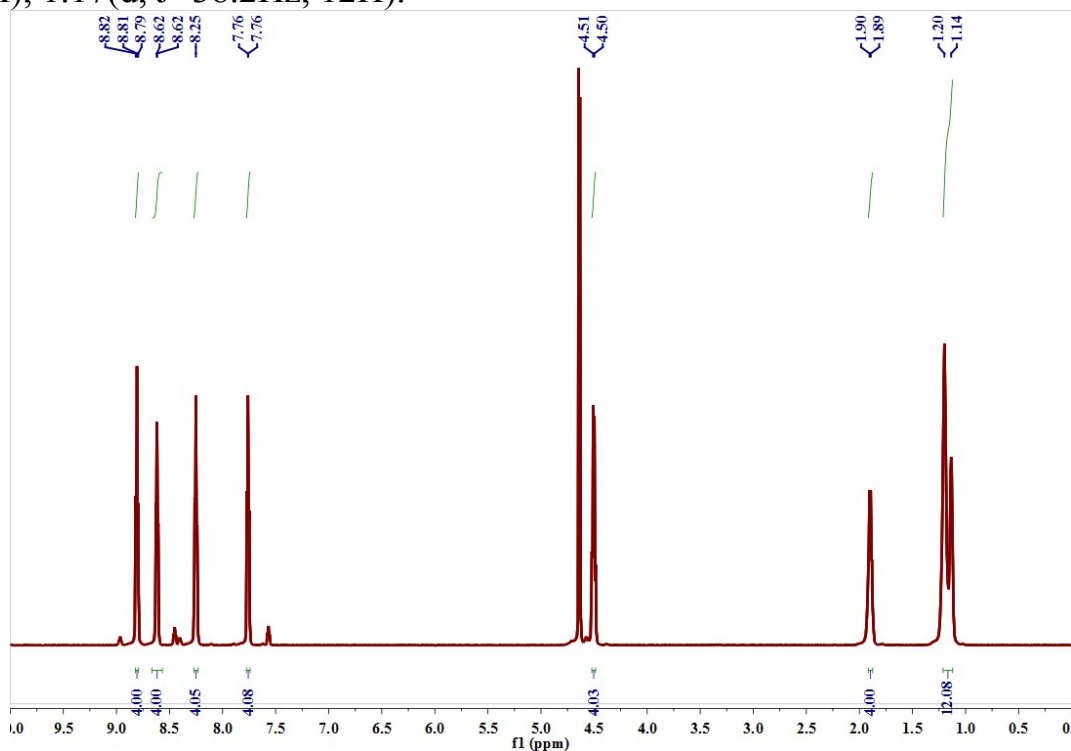


Fig. S11 ¹H NMR spectra(600 MHz, D₂O) of **G**.

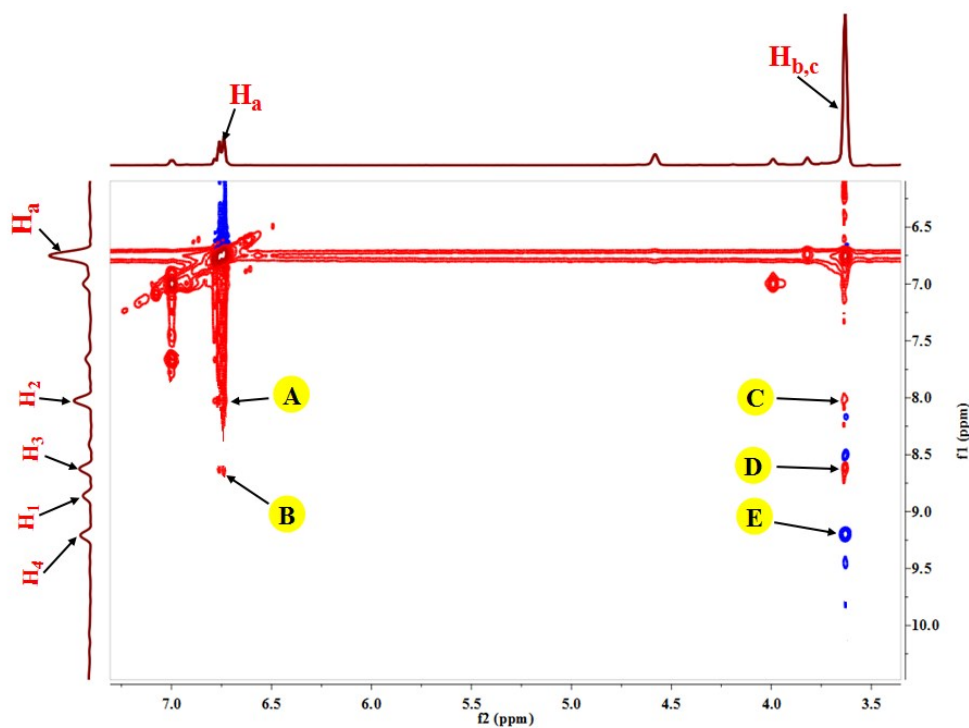


Fig. S12 2D NOESY NMR spectrum (600 MHz, 298 K) of 2.0 mM TP5 and G in DMSO- d_6 solution.

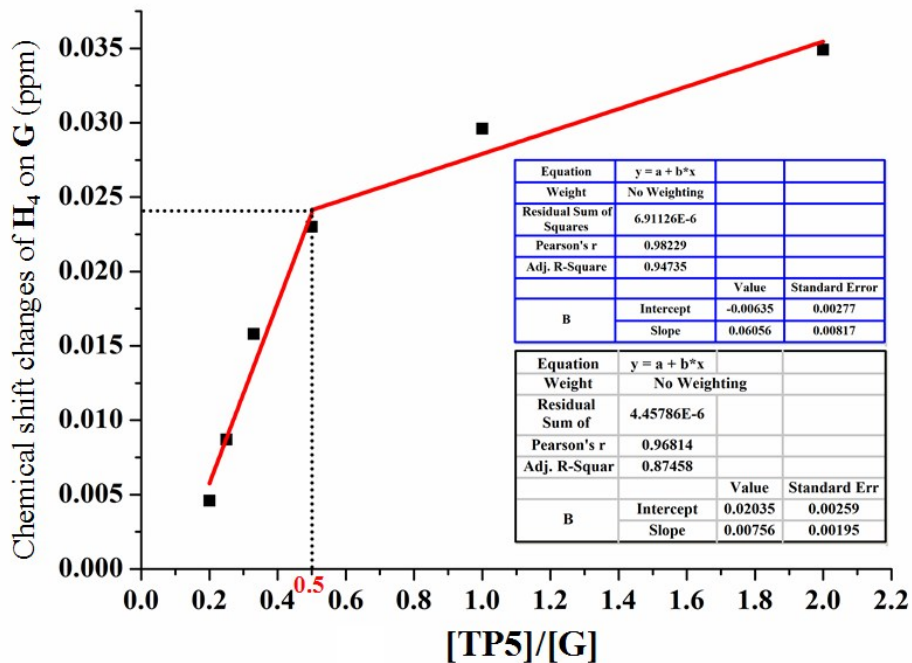


Fig. S13 a mole ratio plot for the complexation between TP5 and G, indicating a 1:2 stoichiometry.

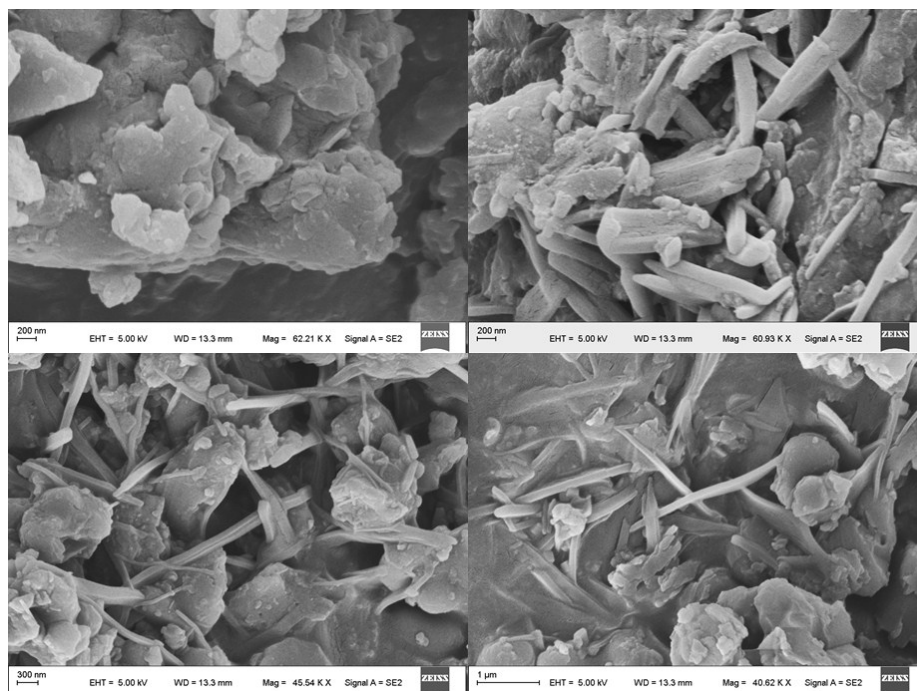


Fig. S14 SEM images of TP5·G gel.

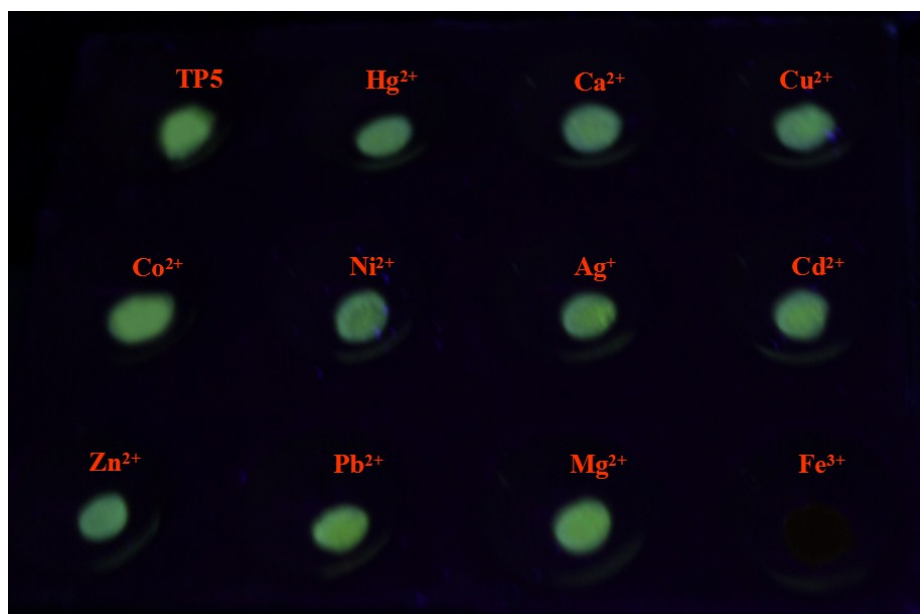


Fig. S15 Fluorescence responses of the supramolecular gel to the presence of various cations.

Determination of the detection limit

We use the 3δ way to figure out the detection limit. The process of the analysis as follows.

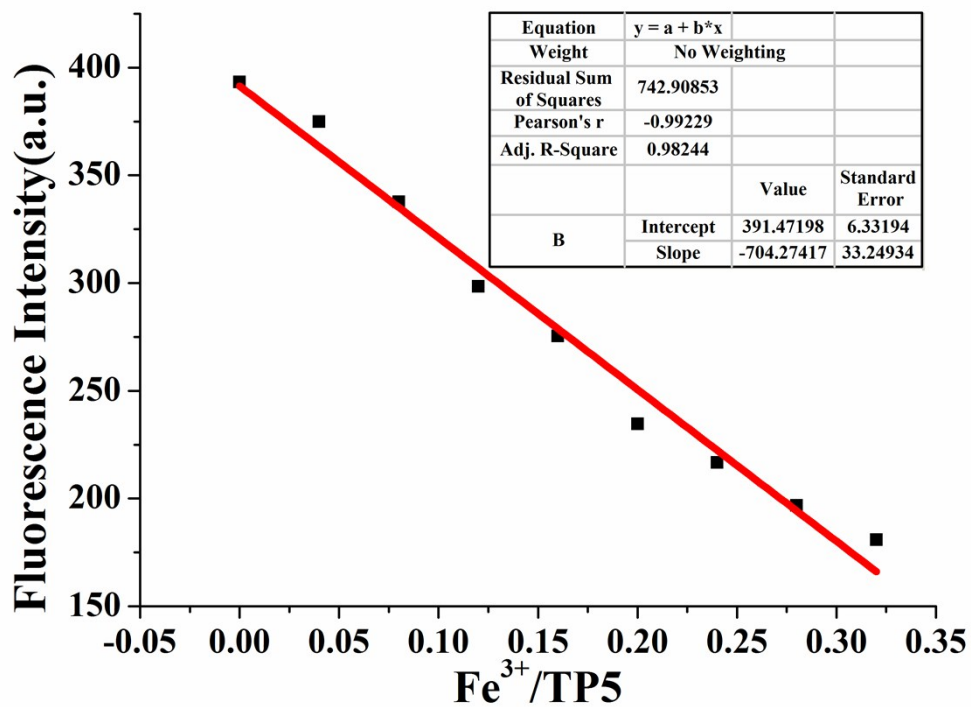


Fig. S16 The photograph of the linear range.

Linear Equation: $Y = -704.27417X + 319.47198$ $R^2 = 0.98244$

$S = 704.27 \times 10^6$

$$\delta = \sqrt{\frac{\sum(x_i - \bar{x})^2}{n-1}} = 36.51 (n = 20)$$

$K = 3$

$LOD = K \times \delta / S = 1.56 \times 10^{-7} M$

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