

Electronic Supplementary Information

**Novel supramolecular polymer gel based on naphthalimide
functionalized-pillar[5]arene for fluorescent detection Hg²⁺,
I⁻ and recyclable removal of Hg²⁺ *via* cation- π interactions**

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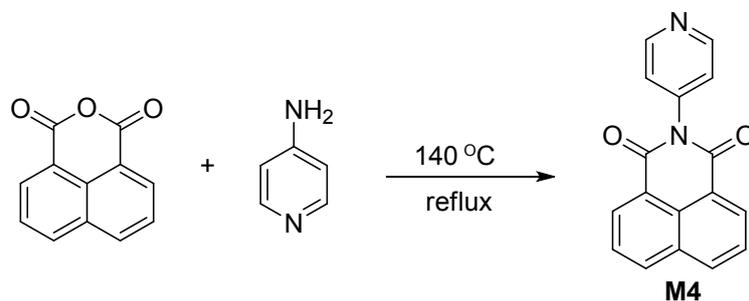
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Materials and physical methods

All anions were used as tetrabutylammonium salts, which were purchased from Alfa Aesar and used as received. All metal ions were prepared from the perchlorate salts. Other reagents used in the study were of analytical grade. Fresh double distilled water was used throughout the experiment. All other reagents and solvents were commercially available at analytical grade and were used without further purification. ^1H NMR spectra were recorded on Mercury-400BB spectrometer (400MHz) and Bruker Digital RF spectrometer (300MHz). ^1H chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, $^{\text{TM}}$ scale with the 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 on a Rigaku D/Max-2400 X-Ray Diffractometer. 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. The infrared spectra were performed on a Digilab FTS-3000 Fourier transform-infrared spectrophotometer. Melting points were measured on an X-4 digital melting-point apparatus (uncorrected). Ultraviolet-visible (UV-vis) spectra were recorded on a Shimadzu UV-2550 spectrometer. Fluorescence spectra were recorded on a Shimadzu RF-5301PC spectrofluorophotometer.

2. Synthesis and characterizations of compound **M4**.



Scheme S1 The synthesis of compound **M4**.

Synthesis of compound **M4**

1,8-Naphthalimide (1.98 g, 10 mmol) and 4-aminopyridine (0.95 g, 10 mmol) was suspended in anhydrous DMF (75 mL) and heated to 140 °C under a N₂ atmosphere in a 100 mL reaction flask equipped with a stir bar. The reaction mixture was then heated under reflux in an N₂ atmosphere overnight. Afterwards, the solution was cooled to room temperature, the mixture was poured into H₂O (15 mL). The precipitate was collected by filtration, washed with ethanol (20 mL × 3) and then dried in vacuum; give a beige powder compound **M4**. Yield: 1.87g (68.2%). m.p.>300 °C. ¹H NMR (400 MHz, DMSO-*d*₆, Fig. S1): δ 8.73 (d, *J* = 4.8 Hz, 2H), 8.53 (t, *J* = 6.8 HZ, 4H), 7.93 (t, *J* = 8.0 Hz, 2H, ArH), 7.53 (m, 2H, ArH). ESI-MS calcd for [C₁₇H₁₀O₂N₂ + H]⁺ = 275.08; found: 275.00.

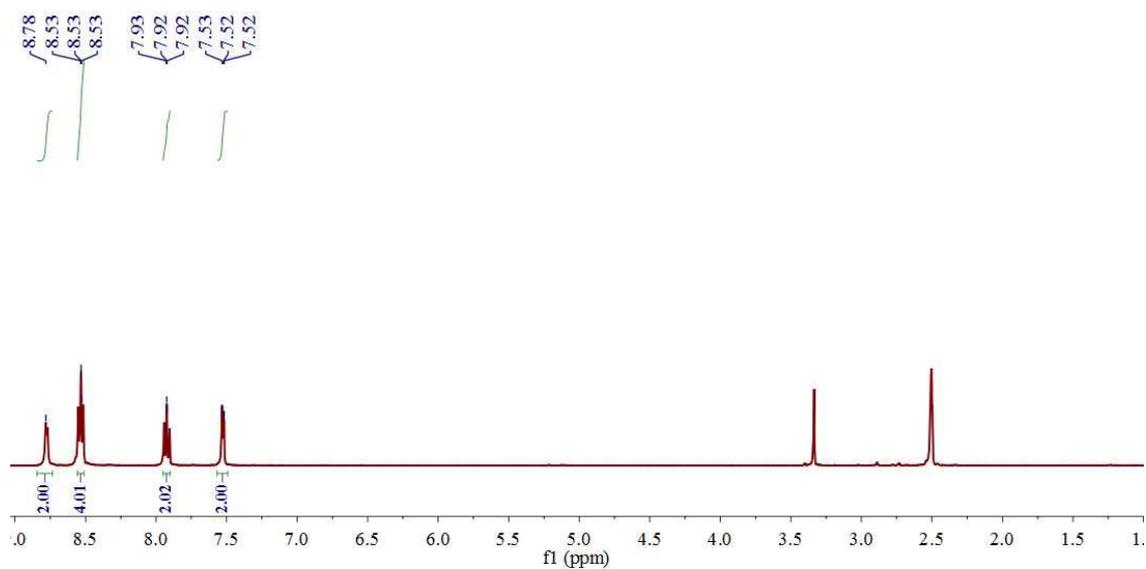


Fig. S1 ^1H NMR spectrum of **M4** in $\text{DMSO-}d_6$.

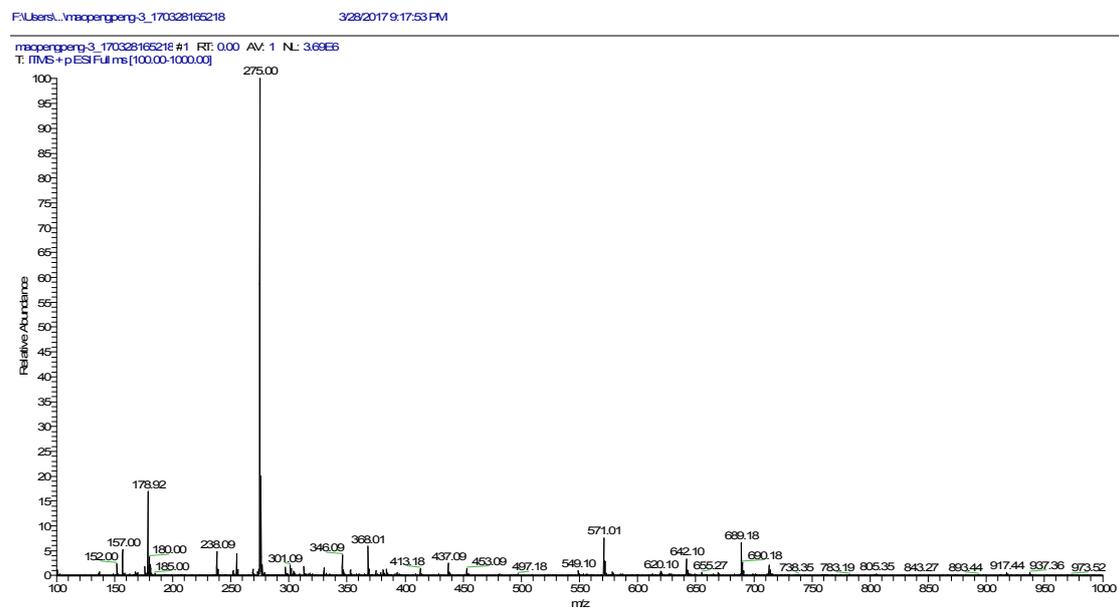
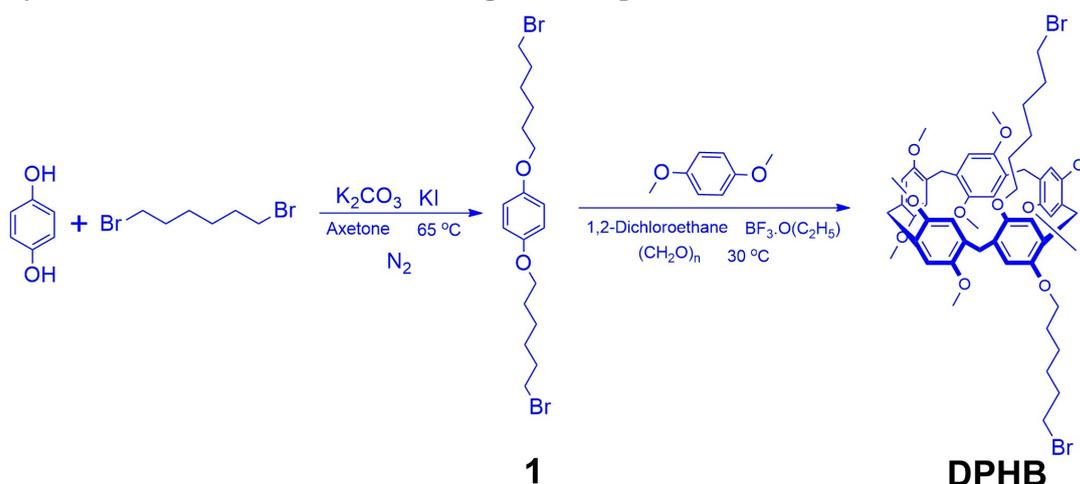


Fig. S2 ESI-MS spectrum of **M4**.

Synthesis and characterizations of guest compound DPMB.



Scheme S2 The synthesis of compound DPMB.

Synthesis of 1, 4-bis(4-bromohexyloxy)benzene 1:

Hydroquinone (2.3 g, 20.0 mmol), K₂CO₃ (16.6 g, 120 mmol), KI (6.6 g, 40 mmol), 1, 4-dibromobutane (34.6 g, 160 mmol) and acetone (400.0 mL) were added in a 500 mL round bottom flask stirred at room temperature. The reaction mixture was stirred at reflux for 1.5 days. After the solid was filtered off, the solvent was evaporated and the residue was dissolved in CH₂Cl₂. Column chromatography (silica gel; petroleum ether: CH₂Cl₂ = 10:1) afforded a white solid (6.0g yield 70%). m.p.: 87 °C. ¹H NMR (400 MHz, DCCl₃, room temperature): δ 6.81(s, 4H, ArH), 3.90(t, *J* = 4.4 Hz, 4H, -CH₂), 3.42(t, *J* = 4.8 Hz, 4H, -CH₂), 1.89(m, 4H, -CH₂), 1.77(m, 4H, -CH₂), 1.50(t, *J* = 2.4Hz, 8H, -CH₂).

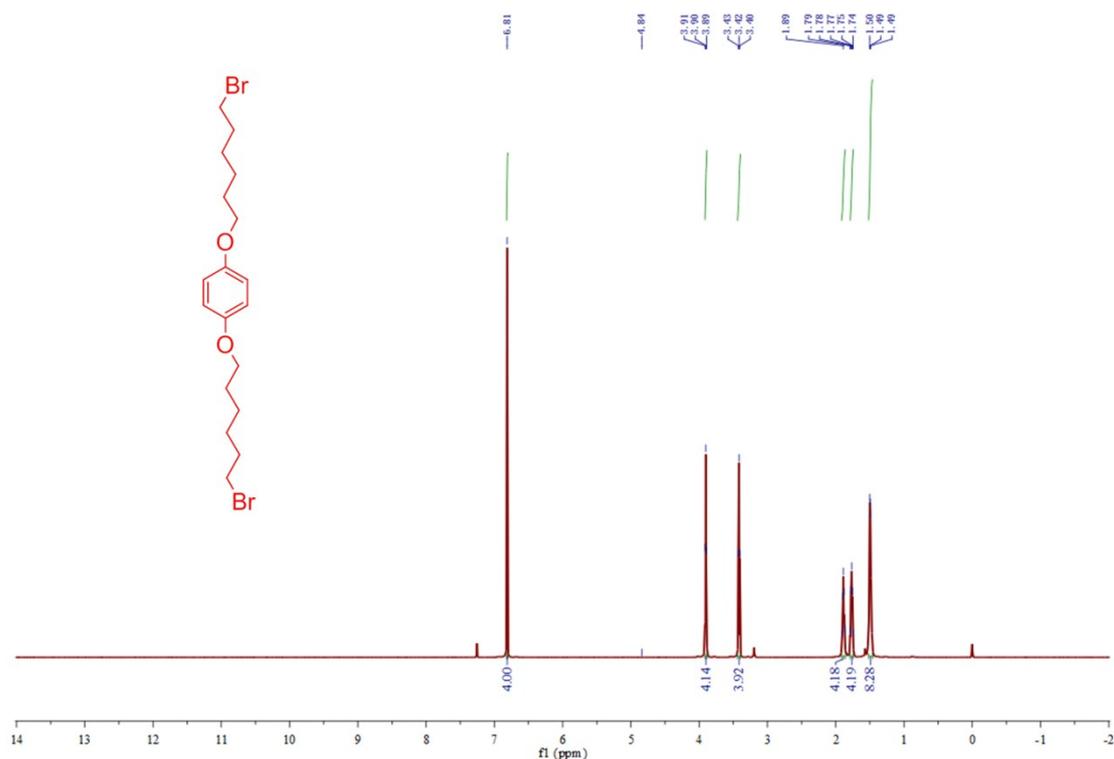
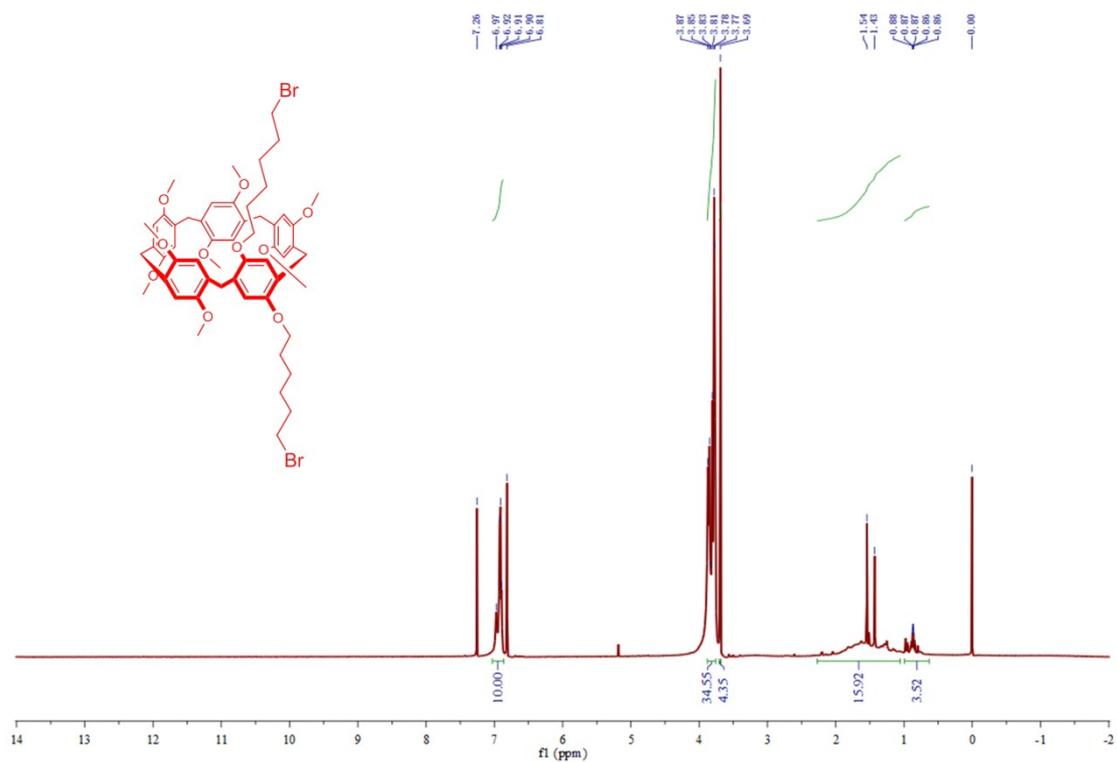


Fig. S3 ^1H NMR spectra (400 MHz, CDCl_3) of 1, 4-bis(4-bromohexyloxy) benzene **1**.

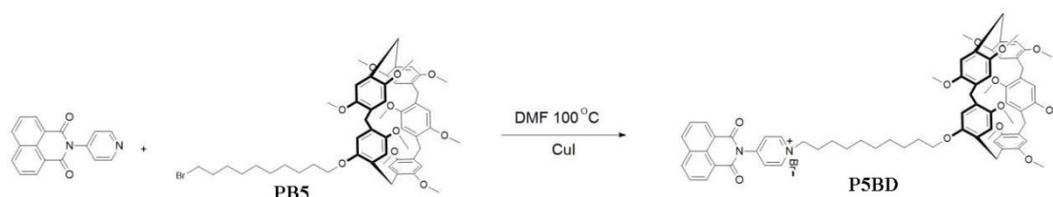
Synthesis of guest compound DPMB.

To a solution of 1, 4-bis (4-bromohexyloxy) benzene (1.9 g, 5.0 mmol) and 1, 4-dimethoxybenzene (2.76 g, 20.0 mmol) in 1, 2-dichloroethane (200 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 4 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 **DPMB** 2.0219g (38.66%) as a white solid. m.p.: 115 °C. ^1H NMR (400 MHz, DCCl_3 , room temperature): δ (ppm): 6.93(m, 10H, ArH), 3.82(m, 34H, $-\text{CH}_2/-\text{OCH}_3$), 3.69(s, 4H, $-\text{CH}_2$), 1.49(m, 16H, $-\text{CH}_2$), 0.87(m, 4H, -

CH₂). HRMS (ESI) m/z [C₅₁H₆₀O₁₀Br₂ + NH₄]⁺ calcd for 1066.3493; Found 1066.3496.



Synthesis of host compound **P5BD**



Scheme S3 The synthesis of compound **P5BD**.

Copillar[5]arene **PB5** was synthesized according to previous literature (yield 30%).^{S1} In a 100 mL round bottom flask, copillar[5]arene **PB5** (0.954, 1.0 mmol), CuI (0.0019g 0.1mmol), **M4** (0.274 g, 1.0 mmol) and DMF (30 ml) was added and the reaction mixture was stirred for 48 h at 100 °C. Then the solvent was removed by evaporation and afford the crude product, which was isolated by flash column chromatography using petroleum ether/ethyl acetate (10:1). The fractions containing the product were combined and concentrated under vacuum to give **P5BD** (0.33 g, 30 %) as a yellow solid. m.p: 85 - 86 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.77 (s, 2H, ArH), 8.65 (m, 2H, -CH), 8.06 (s, 2H, -CH), 7.94 (m, 2H, -CH), 7.52 (d, *J* = 3.6 Hz, 2H, ArH), 6.80 (d, *J* = 11.2 Hz, 10H, -CH₂), 3.83 (s, 4H, -CH₂), 3.70 (m, 37H, CH₂/-OCH₃), 1.76 (s, 2H, -CH₂), 1.44 (s, 2H, CH₂), 1.33 - 1.09 (m, 8H, -CH₂), 0.99 (s, 2H, CH₂), 0.85 (s, 2H, -CH₂). ESI-MS m/z: (C₇₁H₇₇N₂O₁₅ + H)⁺ Calcd for 1151.40; Found 1151.49.

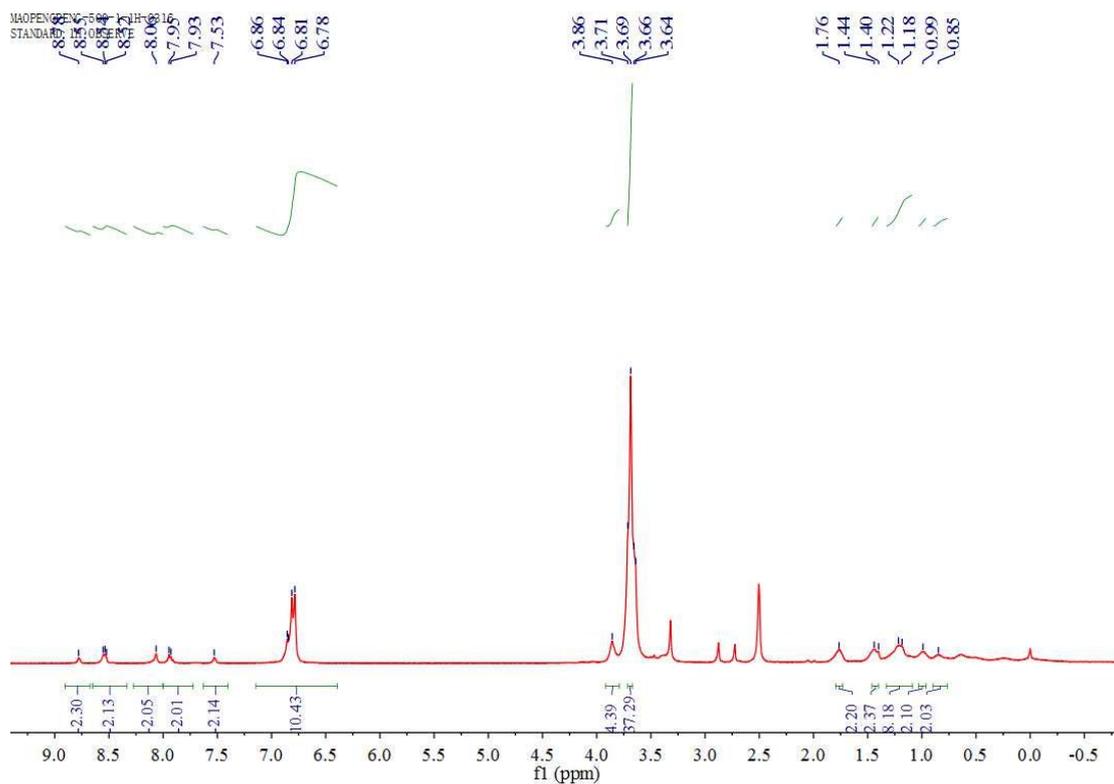


Fig. S6 ^1H NMR spectra (400 MHz, CDCl_3) of host compound **P5BD**.

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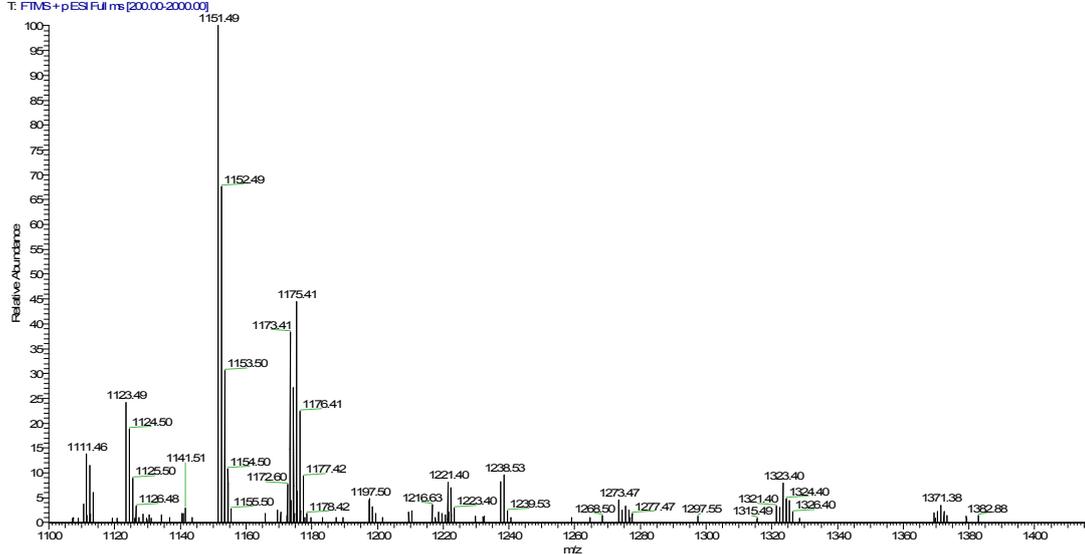


Fig. S7 High resolution mass data of host compound **P5BD**.

Table S1. Gelation Property of supramolecular polymer **P5BD-DPHB**.

Entry	Solvent	State ^a	CGC ^b (%)	Tgel ^c (°C, wt %)
1	water	P	\	\
2	acetone	P	\	\
3	methanol	P	\	\
4	ethanol	G	8	\
5	n-propanol	G	10	\
6	n-butyl alcohol	G	10	42
7	n-Hexanol	P	\	\
8	Acetonitrile	P	\	\
9	Formic acid	S	\	\
9	Propanoic acid	G	8	\
10	DMF/Water	G	10	\
11	DMSO	G	5	38
12	Caproic acid	S	\	\
13	Acetic acid	P	\	\
14	n-pentanoic acid	G	10	\
15	Formic acid	S	\	\
16	CH ₂ Cl ₂	S	\	\
17	CHCl ₃	S	\	\
18	n-Butyric acid	G	8	\
20	ethyl acetate	P	\	\
21	n-propanol	P	\	\
21	n-butyl alcohol	P	\	\
22	Alcohol	P	\	\
23	Heptanoic acid	G	8	\

^aG, P and S denote gelation, precipitation and solution, respectively.

^bThe critical gelation concentration (wt%, 10 mg mL⁻¹ = 1.0%).

^cThe gelation temperature (°C).

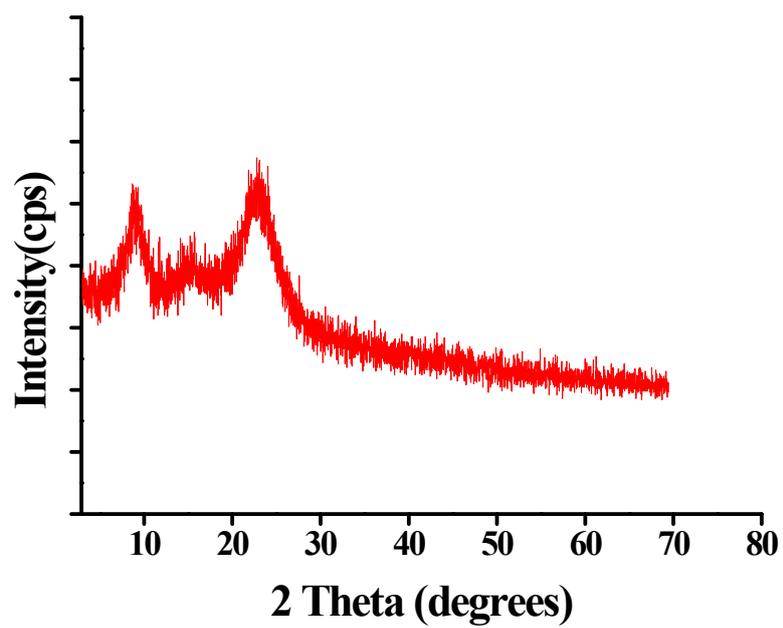


Fig. S8 Powder XRD patterns of xerogel **P5BD-DPHB-G**.

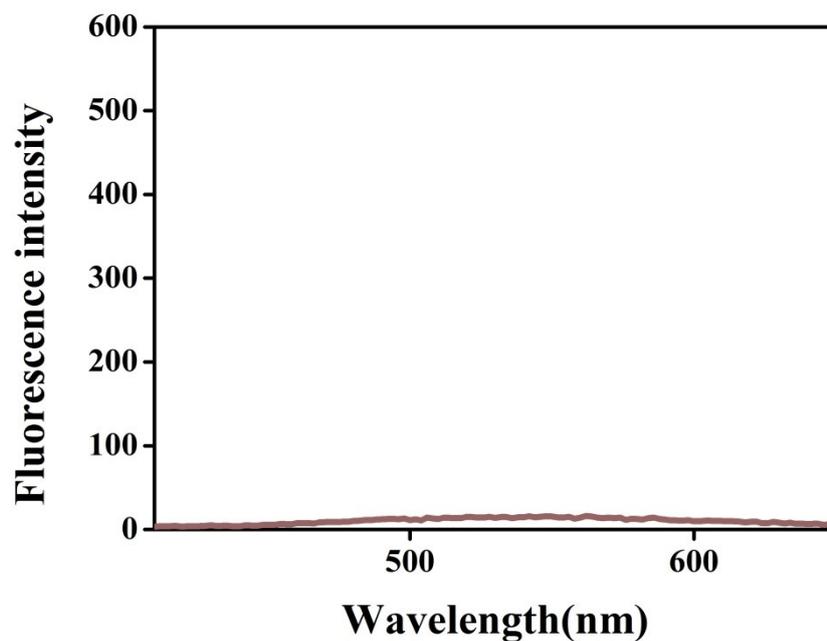


Fig. S9 Fluorescent spectral of blank tests was measured 20 times.

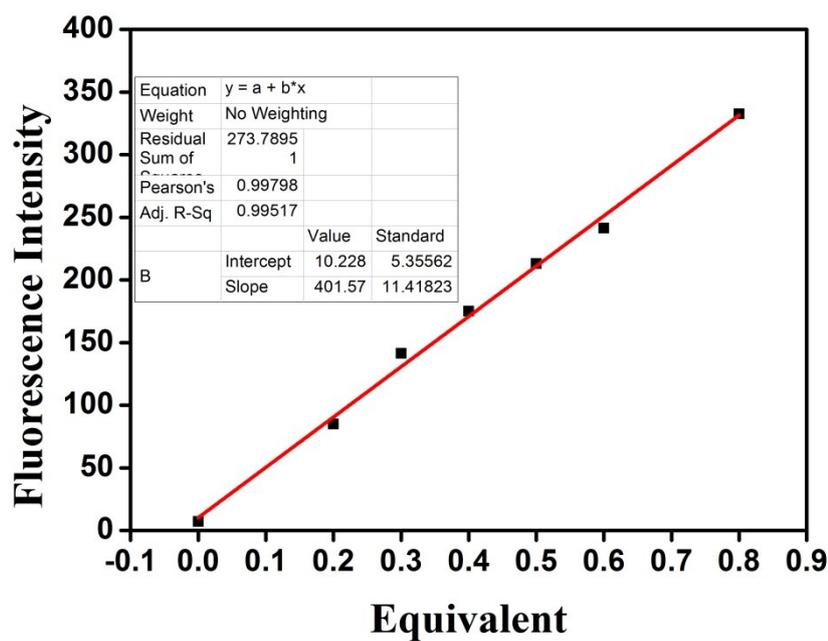


Fig. S10 Plot of the intensity at 380 nm for a mixture of the P5BD-DPHB-G (20 μ M) and Hg^{2+} in DMSO.

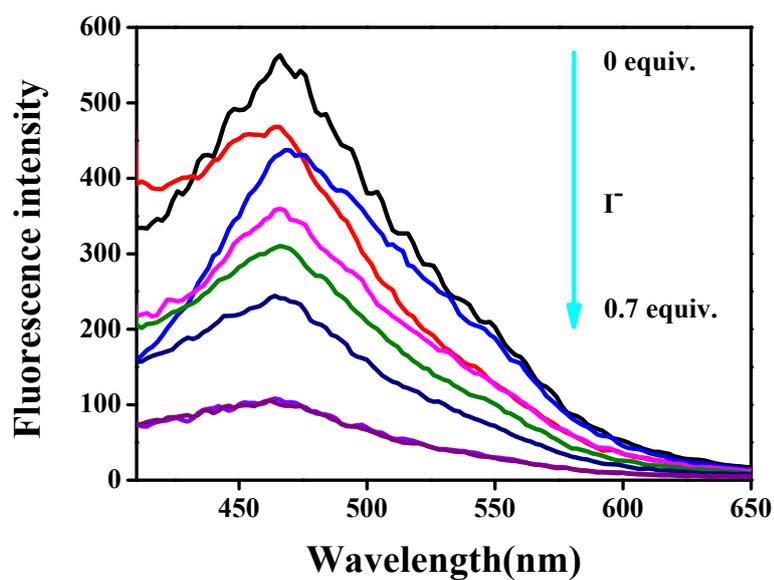


Fig. S11 Fluorescence spectra of HgG (5% in DMSO) with increasing equivalent of I⁻.

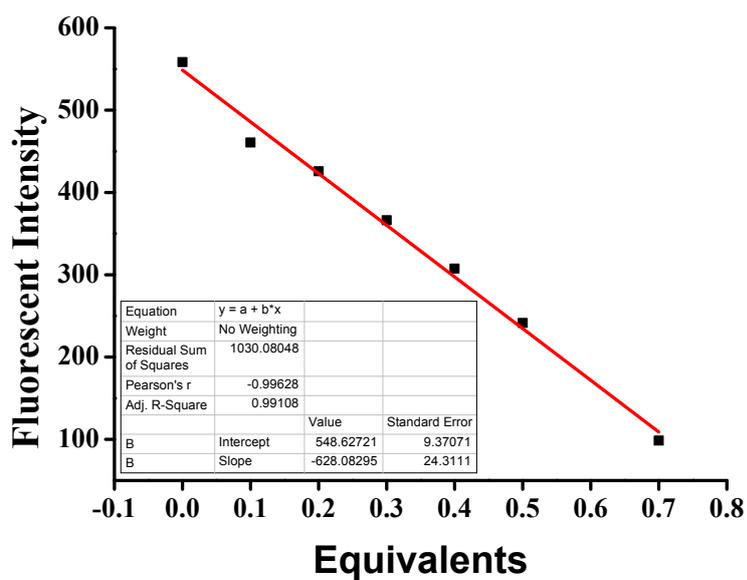


Fig. S12 Plot of the intensity at 380 nm for a mixture of the **P5BD-DPHB-HgG** (20 μM) and I⁻ in DMSO.

Table S2. The ICP data of **P5BD-DPHB-G** with Hg^{2+} .

Entry	Ion	Initial concentration (M)	Residual concentration (M)	Absorbing rate %
1	Hg^{2+}	1.8×10^{-4}	0.27×10^{-5}	97.38 %