Pillar[5]arene-based spongy supramolecular polymer gel and its properties in multi-responsiveness, dyes sorptions, ultrasensitive detection and separation of Fe^{3+}

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Contents

Experimental Procedures ***and Characterizations***

Water used throughout was triply distilled. All reagents were commercially available and used as supplied without further purification.1H NMR (600 MHz) and 13CNMR spectra (151 MHz) were carried out with a Mercury-600 BB spectrometer. High-resolution mass spectra were recorded with a Bruker Esquire 3000 Plus spectrometer. The fluorescence spectra were recorded on a Shimadzu RF-5301PC fluorescence spectrophotometer. The infrared spectra were performed on a Digilab FTS-3000 FT-IR spectrophotometer. Melting points were measured on an X-4 digital melting-point apparatus. The X-ray diffraction (XRD) pattern was generated using a Rigaku RINT2000 diffract meter equipped (copper target; λ = 0.154073 nm). Scanning electron microscopy (SEM) images of the xerogels were investigated using JSM-6701F instrument.

1. Gel preperation:

The mixture of **AP5** (8.5 mg) and **TA** (1.5 mg) were added into a binary solution of DMSO and H_2O (V/V, 3:1) (0.2 ml), the mixture was heated dissolve, then cooled to room temperature, obtaining stable (i.e. stagnant) gel (light yellow).

2. ^{1}H NMR experiment:

(1) **The concentrations-dependent ^{1}H NMR of the mixture of TA:**

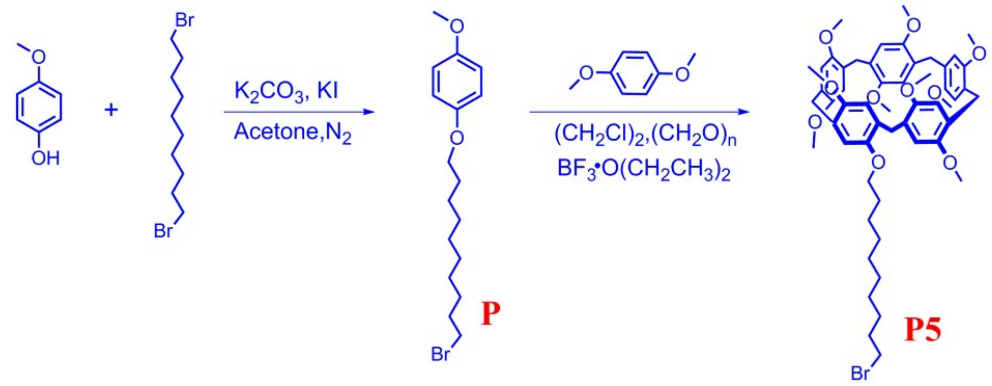
A serious of DMSO-d_6 solutions of **TA** with different concentrations [(a) 1.0×10^{-3} M **TA**; (b) 2.0×10^{-3} M **TA**; (c) 5.0×10^{-3} M **TA**; (d) 1.0×10^{-2} M **TA**] were prepared. Then record their ^{1}H NMR respectively.

3. Fluorescence titration:

Fluorescence titration based on different equivalent Fe^{3+}:

The supramolecular hydrogel **SHG** with different equivalent Fe^{3+} were prepared by dissolve **SHG** (5 mg) and proper equivalent of Fe^{3+} in binary solution of DMSO and H_2O (V/V, 3:1) (0.2 mL). Then record their fluorescence intensity at the 280 nm wavelength and the limit of detection (LOD) calculated on the basis of 3σ/m method.

1. Characterization Spectra of compounds **P**, **P5**, **NA**, **AP5** and **TA**.



***Synthesis and characterization of P*:** 4-Methoxyphenol (1.24 g, 10.0 mmol), K_2CO_3 (6.91 g, 50 mmol), KI (1.66 g, 10 mmol), 1,10-dibromodecane (12.0 g, 40 mmol) and acetone (300.0 mL) were added to a 500 mL round-bottom flask in nitrogen atmosphere. The reaction mixture was stirred at 65 °C for 72 h. After the solid was filtered off, the solvent was evaporated and the residue was dissolved in $CHCl_3$. The crude product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (v/v = 50 : 1) as the eluent, and compound **P** as white solid (3.07 g, yield 90%) was isolated. M.p.: 60–62 °C. ^{1}H-NMR ($CDCl_3$, 600 MHz), δ/ppm: 6.83 (s, 4H), 3.91–3.89 (t, J = 6.6 Hz, 2H), 3.76 (s, 3H), 3.41–3.39 (t, J = 6.9 Hz, 2H), 1.86–1.82 (m, 2H), 1.77–1.72 (m, 2H), 1.45–1.41 (m, 2H), 1.35–1.30 (m, 10H). ^{13}C-NMR ($CDCl_3$, 151 MHz), δ/ppm: 153.64, 153.27, 115.41, 114.59, 68.62, 55.73, 34.01, 32.81, 30.47, 29.42, 29.36, 29.33, 28.72, 28.14, 26.02.

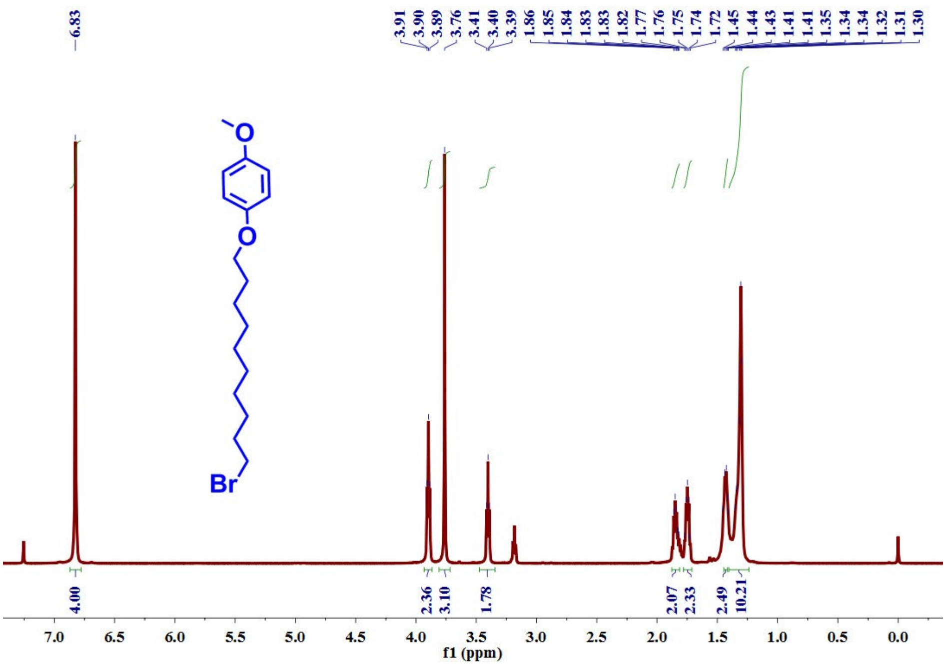


Fig. S1 ^{1}H NMR spectra of compound **P** ($CDCl_3$, 600 MHz, 298 K).

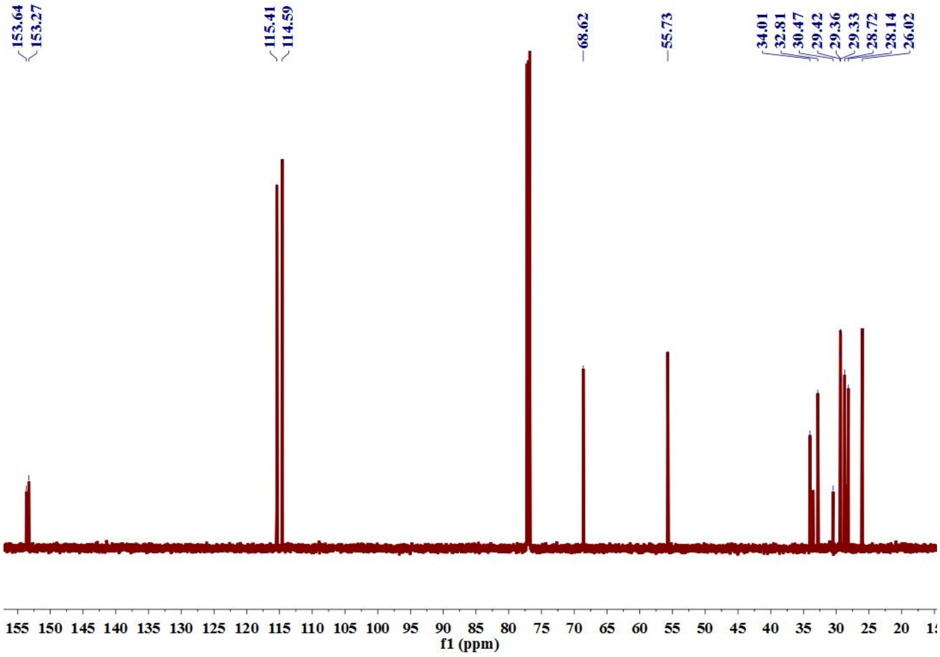


Fig. S2 ^{1}H NMR spectra of compound **P** ($CDCl_3$, 151 MHz, 298 K).

Synthesis and characterization of P5: Compound **P** (1.72 g, 5 mmol), 1,4-dimethoxybenzene (8.29 g, 60 mmol) and paraformaldehyde (3.00 g, 100 mmol) were added to a solution of 1,2-dichloroethane (200 mL). First, the mixture was stirred for 30 min. Then, boron trifluoride diethyletherate (6 mL, 47.6 mmol) was added to the solution, and the mixture was stirred at 30 °C for 40 min. After the reaction was complete, the reaction mixture was dissolved in $CHCl_3$ (300 mL) and washed thrice with H_2O (600 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated to afford the crude product. After purification by column chromatography using petroleum ether/ethyl acetate (v/v = 50 : 1) as the eluent, compound **P5** as a white solid (1.67 g, yield 35%) was isolated. M.p.: 170–172 °C. ^{1}H-NMR ($CDCl_3$, 600 MHz), δ/ppm: 6.95–6.80 (m, 10H), 3.98–3.96 (t, *J* = 6.2 Hz, 2H), 3.80–3.70 (m, 37H), 2.93–2.61 (m, 2H), 1.83–1.71 (m, 4H), 1.34–1.31 (m, 2H), 1.25–0.68 (m, 10H). ^{13}C-NMR ($CDCl_3$, 151 MHz), δ/ppm: 150.56, 150.40, 150.32, 150.22, 150.12, 149.54, 128.39, 128.23, 128.08, 127.90, 127.83, 114.60, 113.91, 113.27, 113.19, 113.08, 68.10, 55.69, 55.36, 55.26, 33.62, 31.56, 29.30, 29.27, 29.24, 29.15, 29.08, 27.59. ESI-MS m/z: [**P5** + NH_4]$^+$ calcd for $C_{54}H_{71}BrNO_{10}$: 972.4256; found: 972.4250.

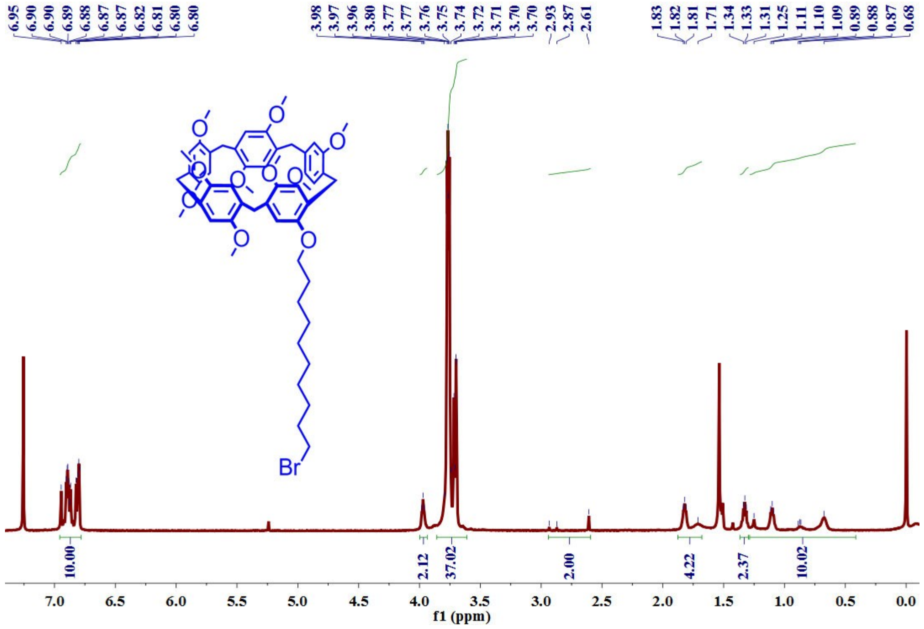


Fig. S3 ^{1}H NMR spectra of compound **P5** ($CDCl_3$, 600 MHz, 298 K).

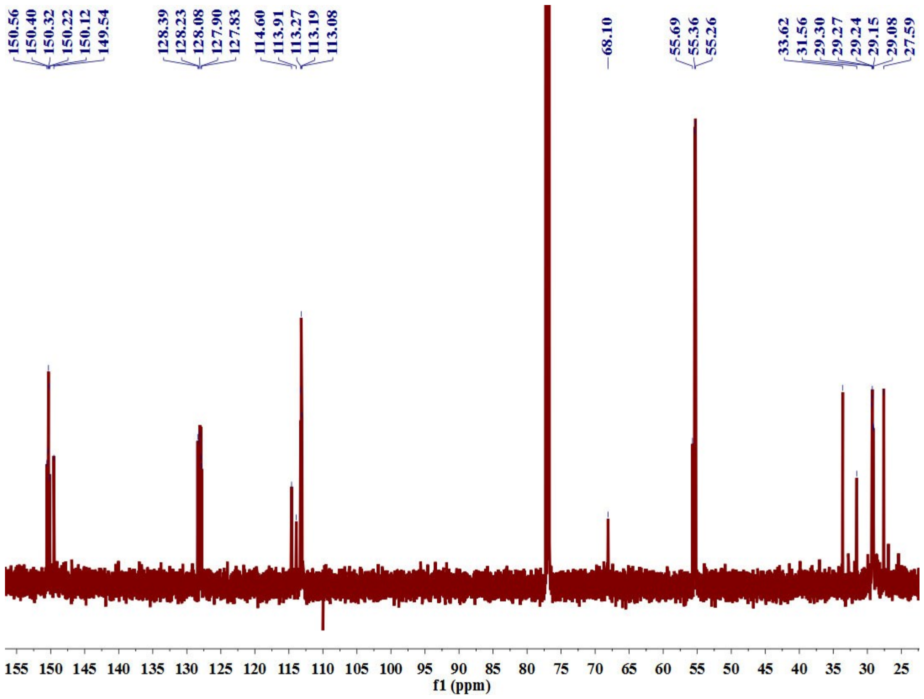


Fig. S4 ^{13}C NMR spectra of compound **P5** ($CDCl_3$, 151 MHz, 298 K).

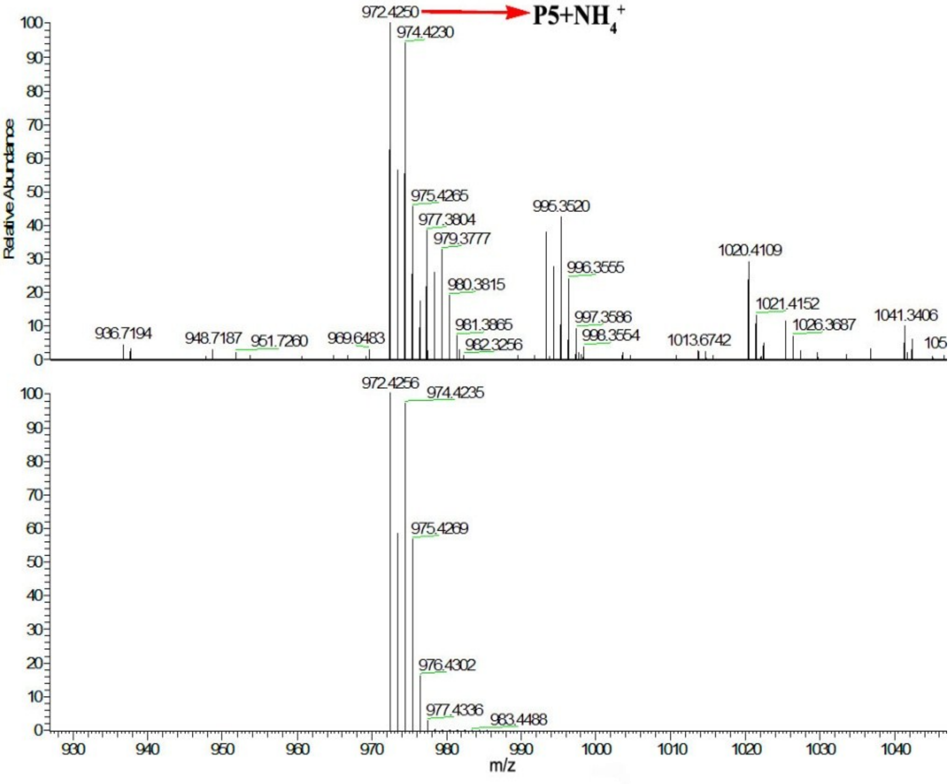
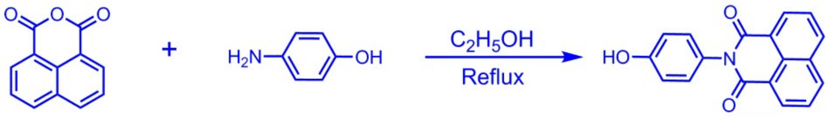


Fig. S5 Mass spectra of **P5.**



NA

Synthesis of compound NA: 1,8-naphthalic anhydride (0.19 g, 1.0 mmol) was added to a mixture of 4-aminophenol (0.22 g, 2.0 mmol) in C_2H_5OH (60 mL), and the reaction mixture was stirred and refluxed for 48 h. After reaction was finished, the solvent was filtered under reduced pressure. The crude product was washed with ethanol to give **NA** as a white solid (0.28 g, 96 %). M.p.: > 290 °C. The ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm): 9.63 (s, 1H), 8.45-8.44 (t, J = 5.2 Hz, 4H), 7.85 (t, J = 5.2 Hz, 2H), 7.13-7.11 (d, J = 5.6 Hz, 2H), 6.86-6.85 (d, J = 5.6 Hz, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ (ppm): 164.28, 157.55, 134.72, 130.34, 127.32, 123.07, 115.82.

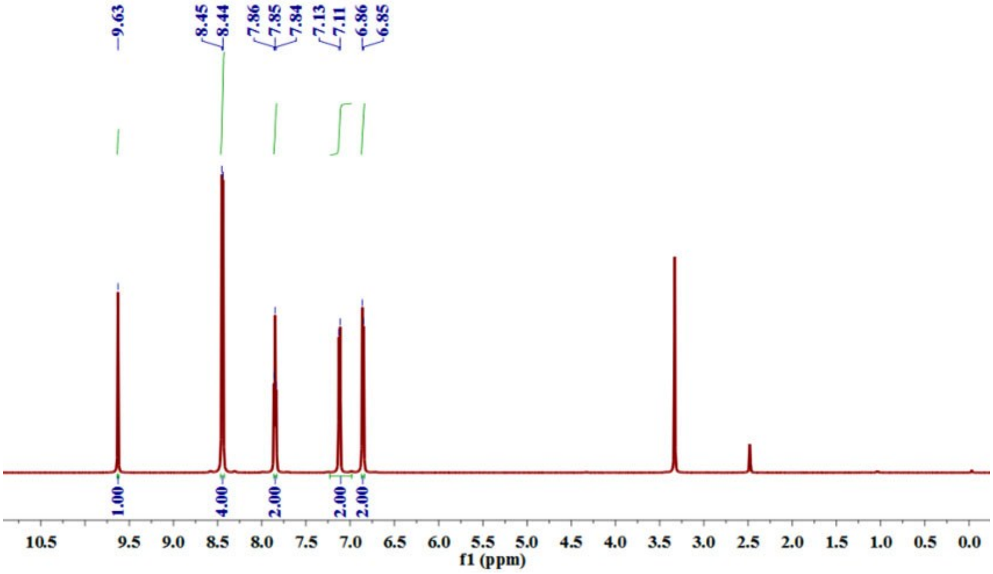


Fig. S6 ^{1}H NMR spectra of compound **NA** (DMSO–d_6, 600 MHz, 298 K).

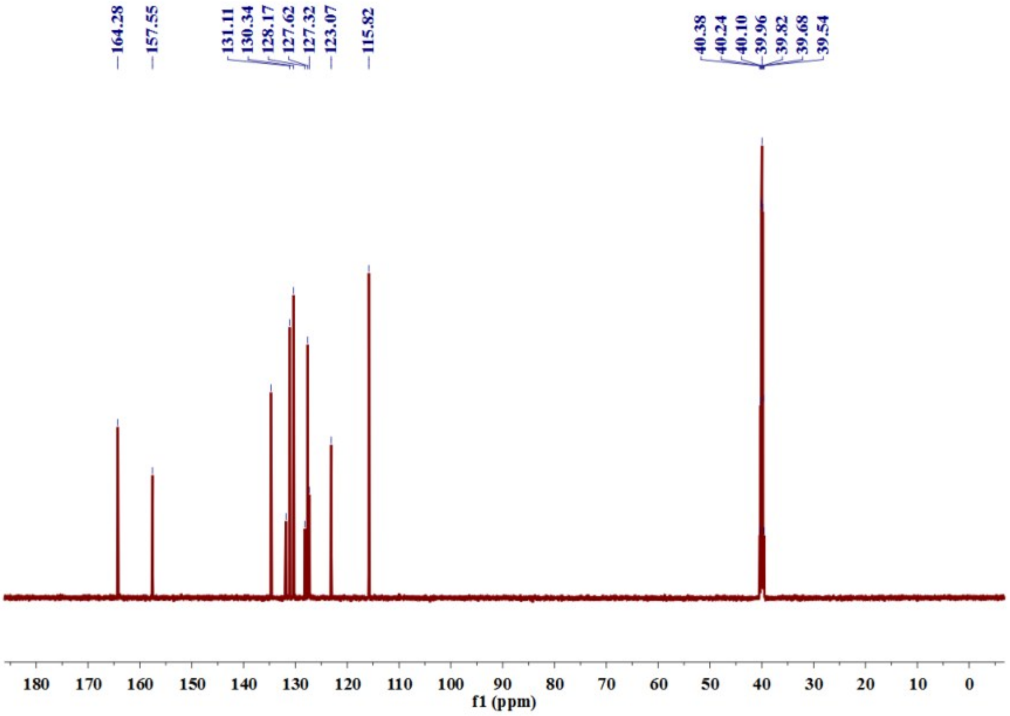
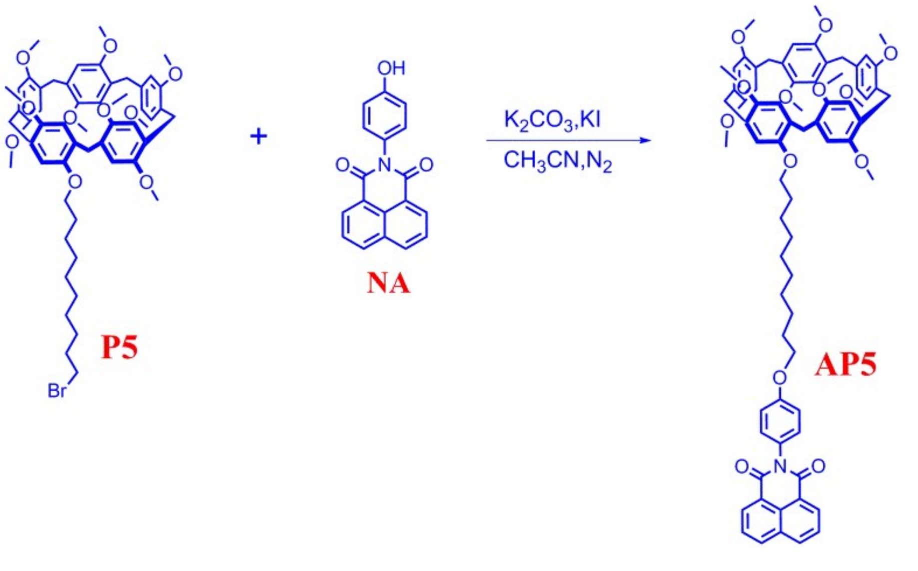


Fig. S7 ^{13}C NMR spectra of compound **NA** (DMSO–d_6, 151 MHz, 298 K).



Synthesis of compound AP5: Compound **P5** (0.95 g, 1.0 mmol) was added to a mixture of compound **NA** (0.29 g, 1.0 mmol) and K_2CO_3 (0.42 g, 3.0 mmol) in acetonitrile (50 mL), and the resulting mixture was stirred and refluxed for 48 h. After reaction was finished, the solvent was evaporated under reduced pressure. The crude product was purified by chromatography on silica gel. Elution with a mixture of petroleum ethers/ethyl acetate (v/v, 30:1) afforded **AP5** as a yellow solid (1.02 g, 86 %). M.p.: 86-

88 °C. The ^{1}H NMR (600 MHz, CDCl$_3$) δ (ppm): 8.67-8.65 (d, *J* = 7.2 Hz, 2H), 8.29-8.27 (d, *J* = 8.3 Hz, 2H), 7.82-7.78 (t, *J* = 7.2 Hz, 2H), 7.24-7.22 (d, *J* = 8.7 Hz, 2H), 7.05-7.03 (d, *J* = 8.8 Hz, 2H), 6.83-6.77 (m, 10H), 3.92-3.77 (m, 13H), 3.68-3.66 (m, 28H), 1.35-1.19 (m, 11H), 0.88-0.86 (m, 5H). The ^{13}C NMR (151 MHz, CDCl$_3$) δ (ppm): 164.59, 159.28, 150.67, 150.48, 149.86, 134.19, 131.54, 129.51, 129.50, 127.00, 122.91, 114.56, 114.17, 114.10, 113.98, 113.96, 113.78, 113.70, 68.38, 68.10, 55.73, 55.64, 55.63, 55.52, 29.70, 29.59, 29.54, 29.48, 29.46, 28.95, 28.78, 25.61, 25.34. ESI-MS m/z: $[M+NH_4]^+$ calcd. for $C_{72}H_{81}N_2O_{13}$ 1181.5733, found 1181.5702.

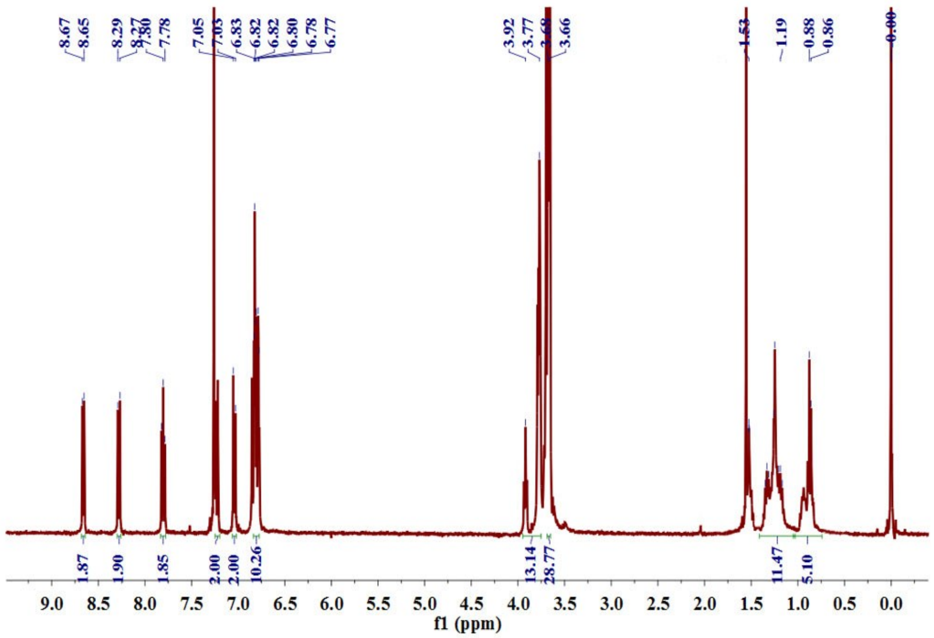


Fig. S8 ^{1}H NMR spectra of compound **AP5** (CDCl$_3$, 600 MHz, 298 K).

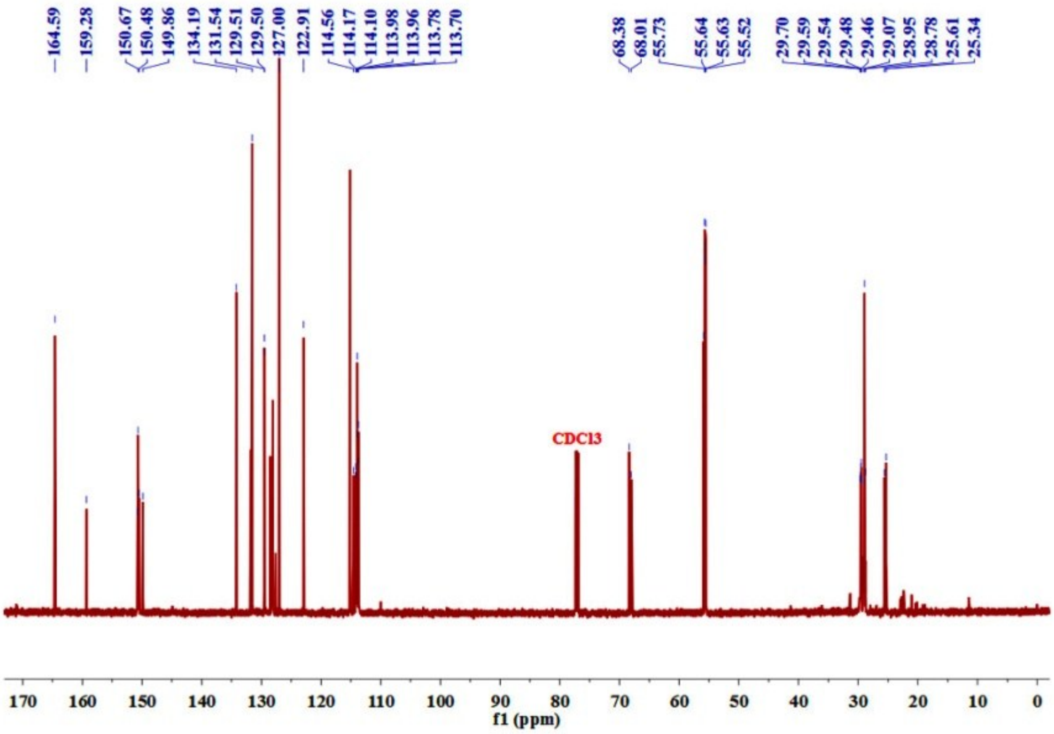


Fig. S9 ^{13}C NMR spectra of compound **AP5** ($CDCl_3$, 151 MHz, 298 K).

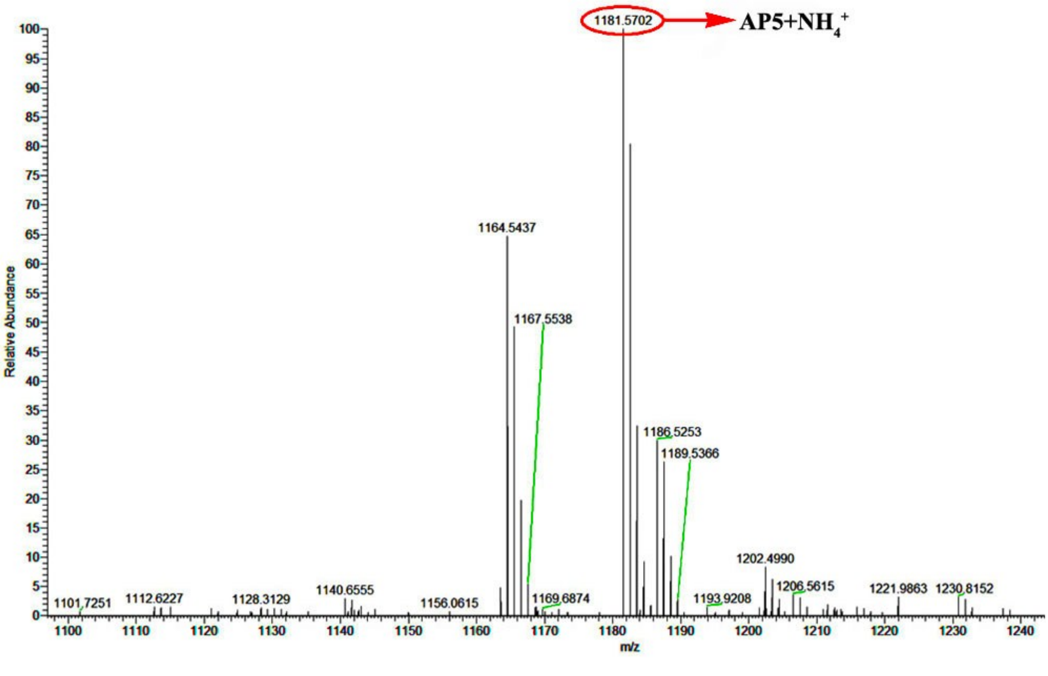
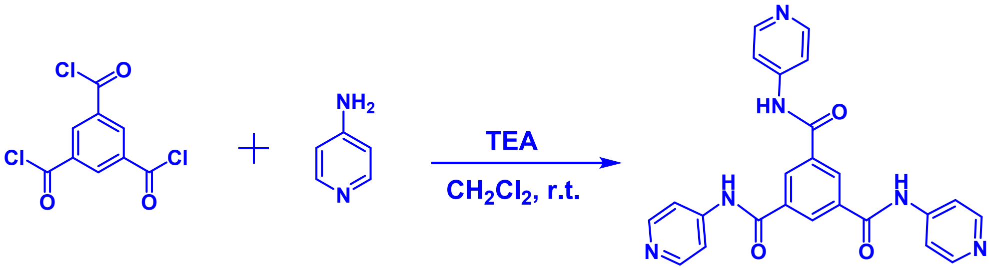


Fig. S10 Mass spectra of **AP5.**



Syntheses of TA: To a solution of 1, 3, 5-benzenetricarbonyl trichloride (0.1 mmol, 0.025g) was dropwise added into the mixture of 4-aminopyridine (0.33 mmol, 0.031g) and TEA (1 mL) in dichloromethane. The mixture was stirred at room temperature for 20 h. The product **TA** was collected by filtration, washed by water, and dried under vacuum (0.0421 g, 96%). M.p.: 167-169 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ/ppm: 11.78 (s, 3 H), 8.99 (s, 3 H), 8.68 (m, 6 H), 8.25 (m, 6 H). ESI-MS m/z: [**TA**]$^+$ calcd for $C_{24}H_{18}N_6O_3$: 439.1474, found 439.1932.

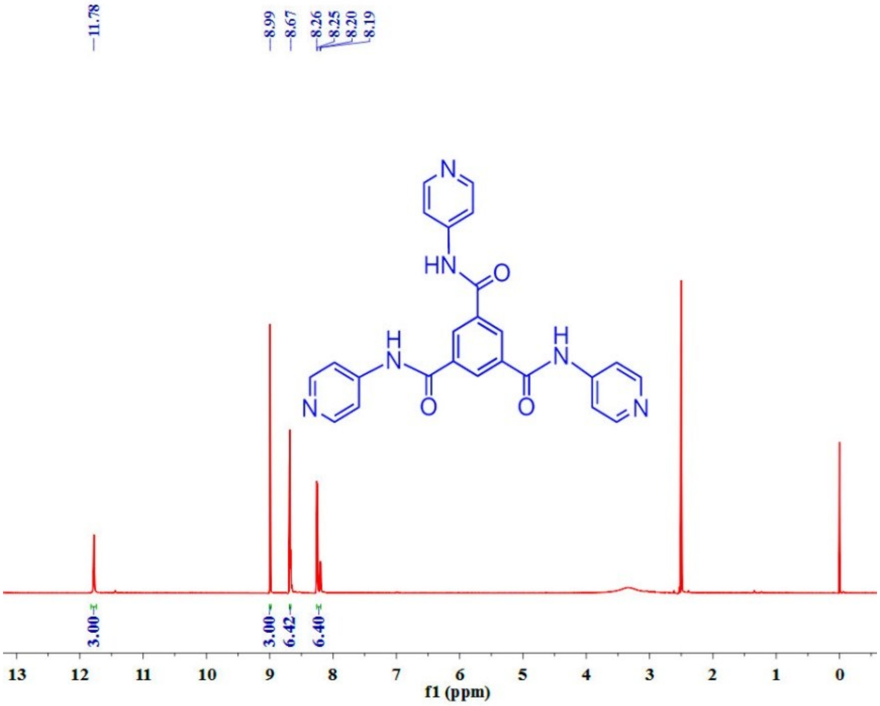


Fig. S11 ^{1}H NMR spectrum of **TA** (DMSO-d_6, 600 MHz, 298 K).

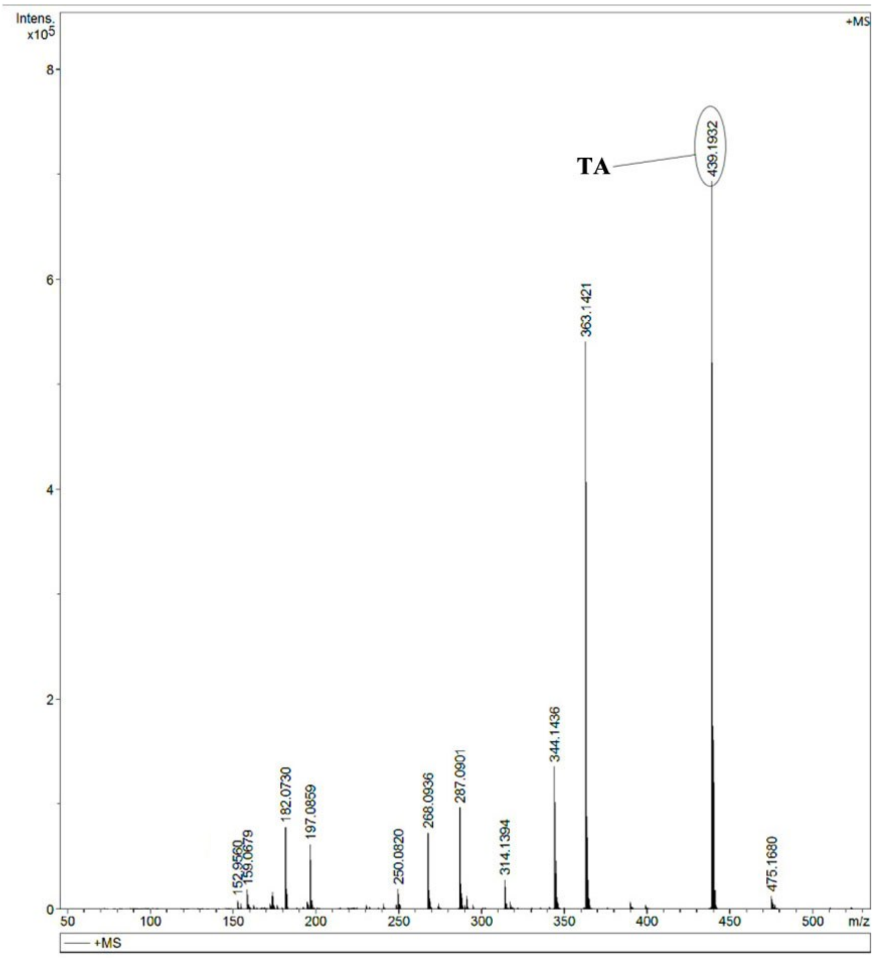


Fig. S12 Mass spectrum of **TA**.

2. Gelation property of **SHG**

Table S1. Gelation Property of **SHG.**

Entry	**Solvent**	**State**	CGC(%)
1	Ethyl acetate	P	\
2	Ethyl alcohol	P	\
3	CCl_4	P	\
4	Isopropyl alcohol	P	\
5	Ethylene glycol	P	\
6	Acetone	P	\
7	DMSO	S	\
8	n-Propyl alcohol	P	\
9	Methyl alcohol	P	\
10	Tert-butyl alcohol	P	\
11	glycerol	P	\
12	Isoamyl alcohol	P	\
13	n-Butyl alcohol	P	\
14	Cyclohexanol	P	\
15	Tetrahydrofuran	P	\
16	Acetic acid	P	\
17	n-Butanol	P	\
18	Cyclohexane	P	\

State： G=gelation, S=Solution, P=Precipitation

Table S2. Gelation Property of **SHG.**

Solvent	**Water**(%)	**State**	CGC(%)	Tgel(°C,wt%)
DMSO/ H_2O	0	S	\	\
DMSO/ H_2O	5	S	\	\
DMSO/H_2O	10	S	\	\
DMSO/ H_2O	15	C	\	\
DMSO/ H_2O	20	C	\	\
DMSO/ H_2O	25	G	2	53~56°C (2%)
DMSO/ H_2O	30	P	\	\

[a] G=gelation, S=Solution, P=Precipitation, C=Collosol;

[b] The critical gelation concentration (wt%, 10 mg/ml = 1.0 %);

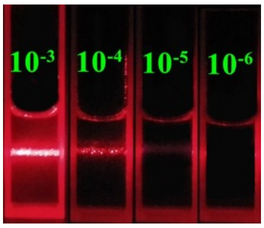


Fig. S13 Tyndall effect photos of **SHG** in DMSO/H_2O (f_w = 25%) solution with different concentration(10^{-3}~10^{-6} M).

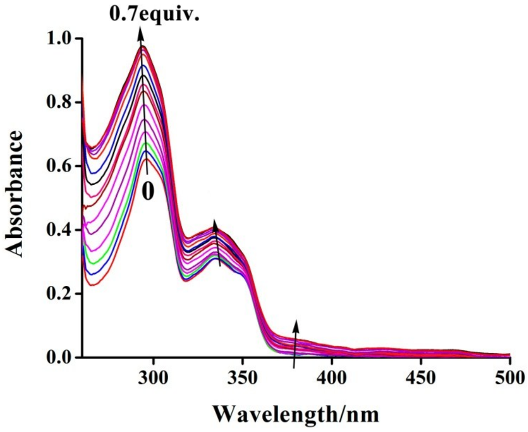


Fig. S14 Absorption spectrum of **AP5** (10 μM) in the presence of different equiv of **TA** in DMSO solutions.

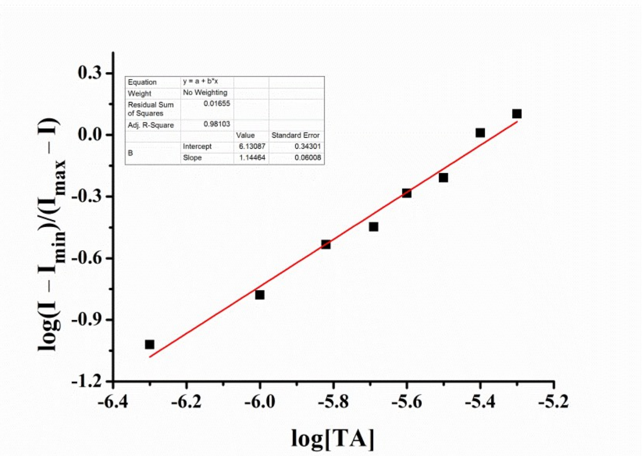


Fig. S15 The photograph of the Absorption spectrum linear range for **TA**.

The association constant (Ka) for the complexation of **AP5** and **TA** was estimated by means of absorption titration experiments at room temperature in DMSO. The Ka for **SHG** was obtained as 1.35 × 10^6 M^{-1}.

$$\log\frac{I - I_{min}}{I_{max} - I} = \log Ka + \log[C]$$

$K = 1.35 \times 10^{6}\ M^{-1}$.

I is the observed the absorbance of **TA** at the fixed concentrations of **AP5**. $\mathbf{I_{max}}$ and $\mathbf{I_{min}}$ are the corresponding maximum and minimum, respectively. I is the observed the absorbance of **TA** at the fixed concentrations of **AP5**. [C] is the the concentration of **TA**.

3. Characterization of **SHG.**

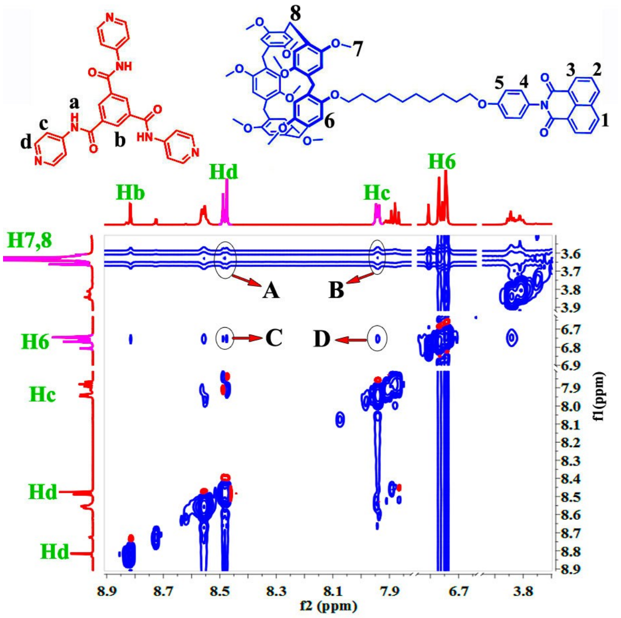


Fig. S16 NOESY-NMR spectrum of mixture of **AP5** and **TA** (600 MHz, DMSO-d_6, 298 K).

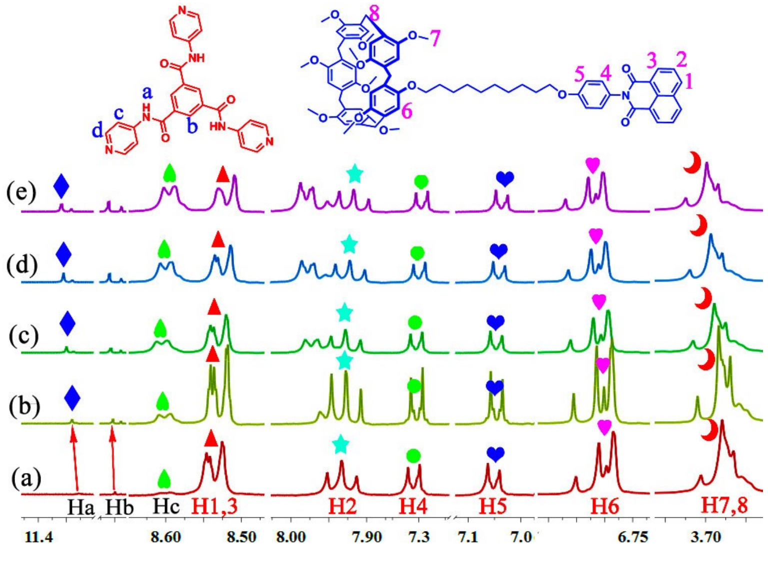


Fig. S17 Partial ^{1}H NMR spectra (600 MHz, DMSO-d_6, 298 K) of mixtures of 3:1

molar ratio of **AP5**, **TA** at different concentrations: (a) 2.0 mM; (b) 5.0 mM; (c) 10.0 mM; (d)20.0 mM; (e) 30.0 mM.

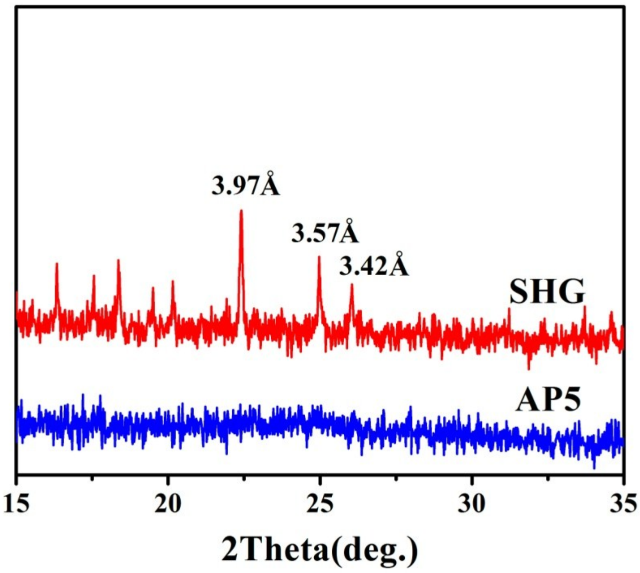


Fig. S18 Powder XRD patterns of **AP5** and xerogel of **SHG**.

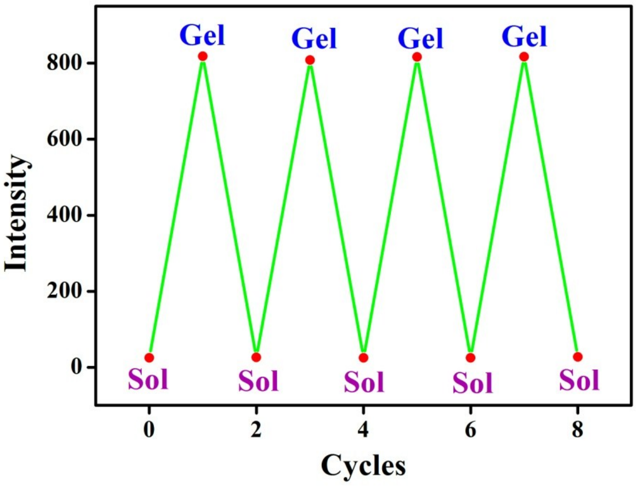


Fig. S19 Fluorescence intensity for the reversibility of gel-sol transformation shown for four cycles.

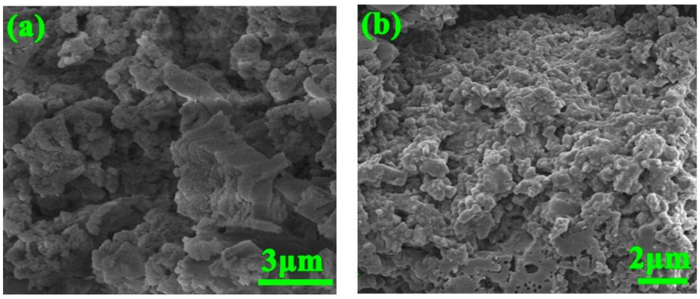


Fig. S20 SEM images of (a) **SHG** treated with adiponitrile; (b) **SHG** treated with Fe^{3+}.

4. Interaction study of **SHG** for Fe^{3+} and dyes

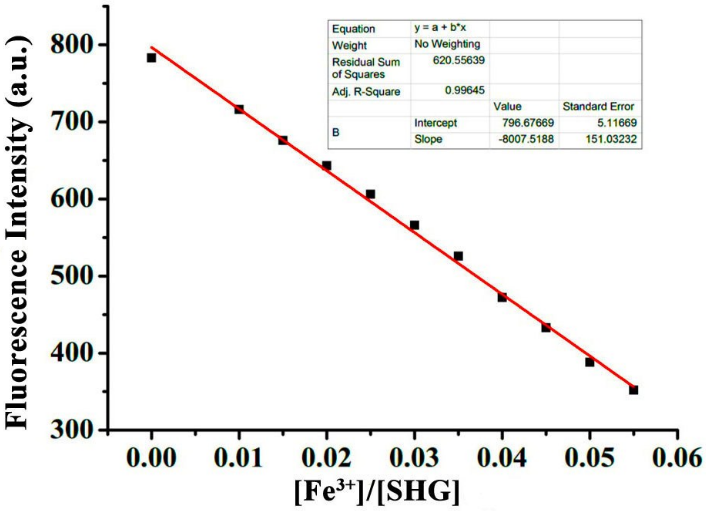


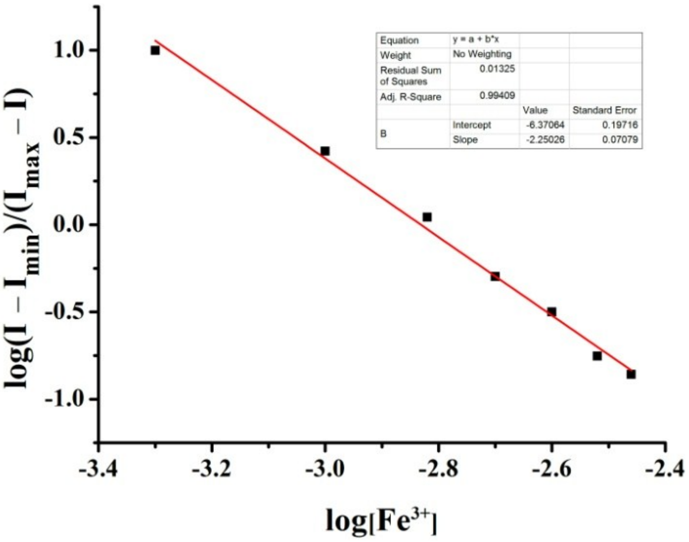
Fig. S21 The photograph of the fluorescent spectrum linear range for Fe^{3+} (from 0 to 0.055 equiv.).

Linear Equation: Y = a + bX = 796.67669 −8007.5188X R^2 = 0.99645

$$S = 8007.5188 \times 10^6 \qquad \delta = \sqrt{\frac{\sum (F_i - F_0)^2}{N-1}} = 2.39\ (N = 20)$$

$$\mathrm{LOD} = K \times \delta/S = 0.9\ \mathrm{nM}\ (K = 3)$$

δ is the standard deviation of the fluorescence intensity of **SHG** in the presence of Fe^{3+}; **S** is the slope of the calibration curve of the fluorescence emission.



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0.01325		
Adj. R-Square	0.99409		
		Value	Standard Error
B	Intercept	-6.37064	0.19716
	Slope	-2.25026	0.07079

Fig. S22 The photograph of the fluorescence spectrum linear range for Fe^{3+}.

The association constant (Ka) for the complexation of **SHG** and Fe^{3+} was estimated by means of fluorescence titrations experiment at room temperature. The Ka was obtained 2.34×10^6 M^{-1}.

K = 2.34×10^6 M^{-1}.

I is the observed the fluorescence intensity of Fe^{3+} at the fixed concentrations of **SHG**. I_{max} and I_{min} are the corresponding maximum and minimum, respectively. [C] is the the concentration of Fe^{3+}.

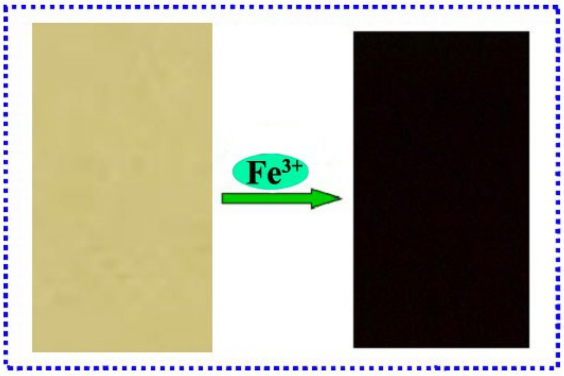


Fig. S23 Photos of the thin film utilized to sense Fe^{3+} under irradiation at 365 nm using a UV lamp.

Table S3. Adsorption percentage of supramolecular gel **SHG** for Fe^{3+}.

Ions	**Initial concentration (M)**	**Residual concentration (M)**	**Adsorption percentage (%)**
Fe^{3+}	1×10^{-5}	1.42×10^{-8}	99.8 %

※**Calculation method of adsorption percentage:**

Adsorption percentage (%) = $\left(1 - \frac{C_R \times V_R}{C_I \times V_I}\right) \times 100\%$

(state: C_R is the residual concentration of Fe^{3+}, C_I is the initial concentration of Fe^{3+} $V_R = V_I$)

Table S4. A part of the literatures about the uptake of Fe^{3+} were provided in the followed table.

Ref.	**Material used**	**Adsorption percentage**
S7	Aluminum based MOFs	98.2%
S8	Pillar[5]arene-based SOFs	99.4%
S9	Supramolecular Gel	99.42%
This work	Pillar[5]arene-based Gel	99.8%

Reference:

(S7) C. X. Yang, H-B. Ren, X-P. Yan, *Anal. Chem.* 2013, **85**, 7441.

(S8) Q. Lin, Y. Q. Fan, P. P. Mao, L. Liu, J. Liu, Y. M. Zhang, H. Yao, T. B. Wei, *Chem. Eur. J.* 2018, **24**, 777.

(S9) Y. M. Zhang, W. Zhu, W. J. Qu, K. P. Zhong, X. P. Chen, H. Yao, T. B. Wei, Q. Lin, *Chem. Commun.*, 2018, **54**, 4549.

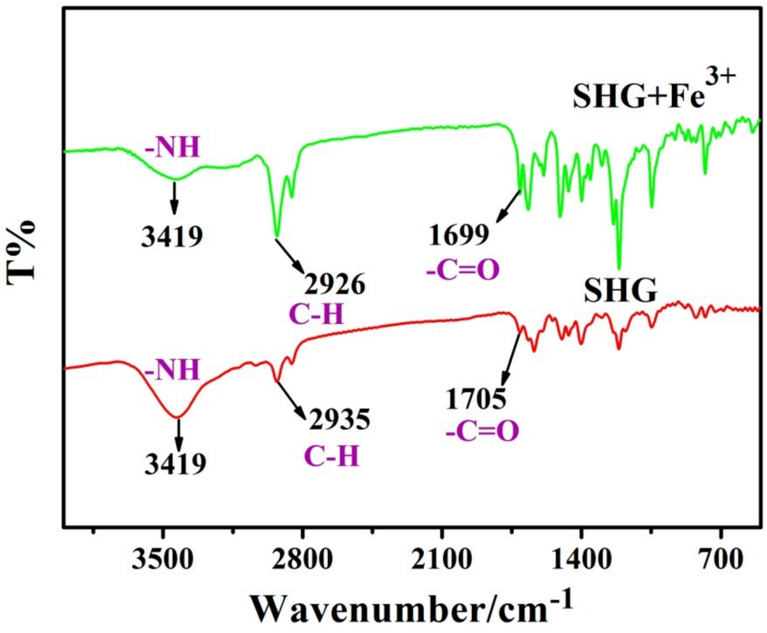


Fig. S24 FT-IR spectra of xerogel **SHG** and **SHG** + Fe^{3+}.

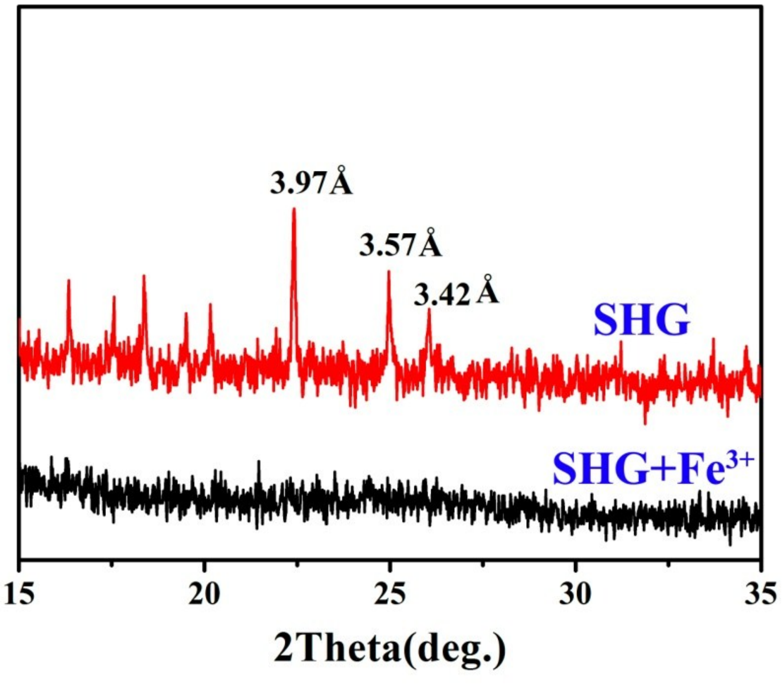


Fig. S25 Powder XRD patterns of powder **SHG** and **SHG** + Fe^{3+}.

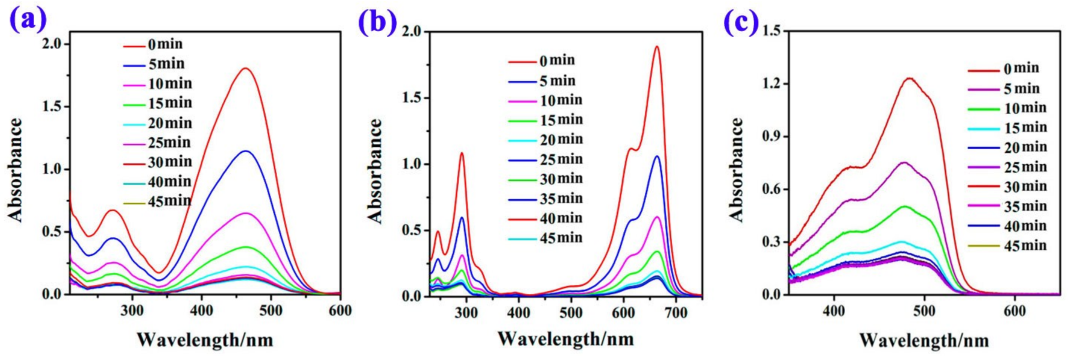


Fig. S26 UV-vis spectra a recorded as a function of contact times with **SHG**: (a) methyl orange; (b) methylene blue; (c) sudan I.

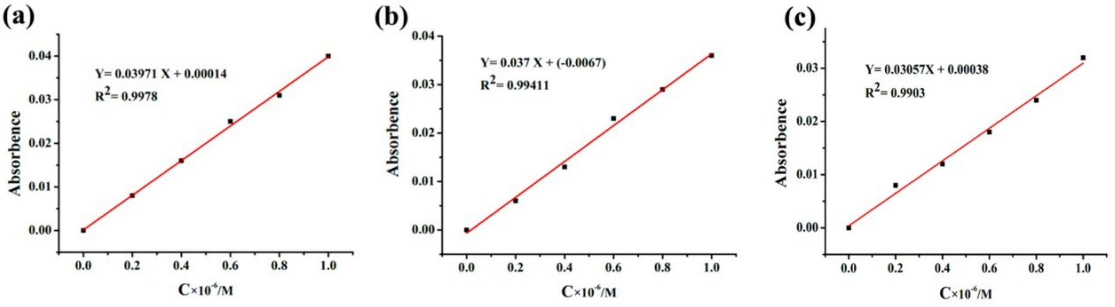


Fig. S27 A plot of concentration vs. absorbance intensity is shown. (a) methyl orange; (b) methylene blue; (c) sudan I.

Table S5. The equilibrium uptake percentage and amount of bound dyes of **SHG.**

Entry	Dyes	Uptake %
1	Methyl orange	96.7
2	Methylene blue	97.4
3	Sudan I	83.8

※ The efficiency of pollutant removal (%) by the adsorbent **SHG** was determined by the following equation:

$$E = \frac{(C_0 - C_t)}{C_0} \times 100\%$$

Where C_0 (mM) is the initial solution concentration, C_t (mM) is the residual concentrations after adsorption, E is the percentage of adsorption. Meanwhile, the amount of pollutant bound to the adsorbent was determined by the following equation.

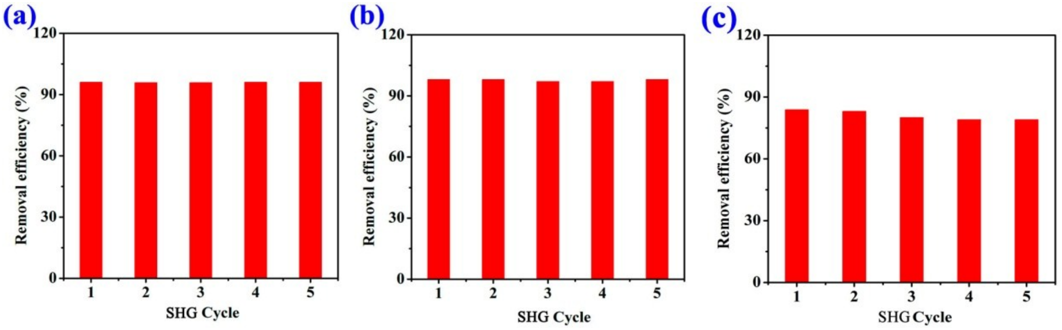


Fig. S28 Theregeneration cycles of SHG after the adsorption of (a) methyl orange (b) methylene blue and (c) sudan I.

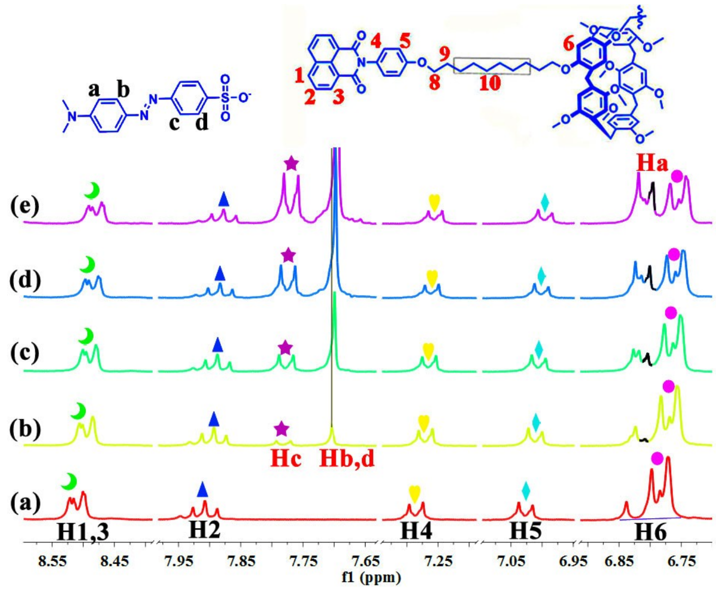


Fig. S29 Partial ^{1}H NMR spectra of **SHG** (DMSO-d_6) with various equivalents of methyl orangel: (a) 0 equiv, (b) 0.5 equiv.; (c) 1.0 equiv.; (d) 2.0 equiv.; (d) 3.0 equiv.

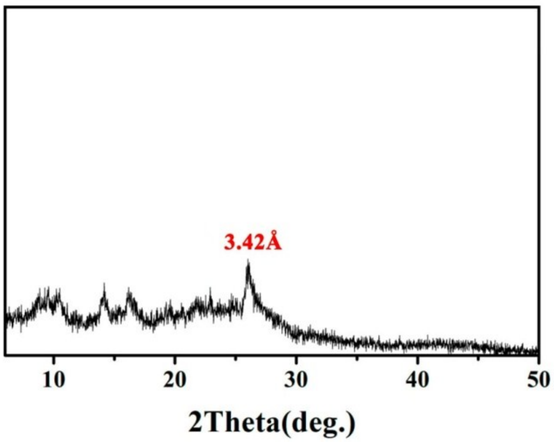


Fig. S30 Powder XRD patterns xerogel of **SHG** + methyl orangel.