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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**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 13C NMR 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 preparation:**

   The mixture of AP5 (8.5 mg) and TA (1.5 mg) were added into a binary solution of DMSO and H₂O (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. **¹H NMR experiment:**

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

   A series of DMSO-d₆ 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 ¹H NMR respectively.

3. **Fluorescence titration:**

   Fluorescence titration based on different equivalent Fe³⁺:

   The supramolecular hydrogel SHG with different equivalent Fe³⁺ were prepared by dissolve SHG (5 mg) and proper equivalent of Fe³⁺ in binary solution of DMSO and H₂O (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.

\[
\text{4-Methoxyphenol (1.24 g, 10.0 mmol), K}_2\text{CO}_3 (6.91 g, 50 mmol), KI (1.66 g, 10 mmol), 1,10-dibromodecane (12.0 g, 40 mmol) and acetone (300.0 mL) were added to a 500 mL round-bottom flask in nitrogen atmosphere. The reaction mixture was stirred at 65 °C for 72 h. After the solid was filtered off, the solvent was evaporated and the residue was dissolved in CHCl}_3. The crude product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (v/v = 50 : 1) as the eluent, and compound P as white solid (3.07 g, yield 90%) was isolated. M.p.: 60–62 °C. } \\
^1\text{H-NMR (CDCl}_3, 600 MHz), } \delta/\text{ppm: } 6.83 (s, 4H), 3.91–3.89 (t, } J = 6.6 \text{ Hz, 2H}), 3.76 (s, 3H), 3.41–3.39 (t, } J = 6.9 \text{ Hz, 2H}), 1.86–1.82 (m, 2H), 1.77–1.72 (m, 2H), 1.45–1.41 (m, 2H), 1.35–1.30 (m, 10H). \ \\
^13\text{C-NMR (CDCl}_3, 151 MHz), } \delta/\text{ppm: } 153.64, 153.27, 115.41, 114.59, 68.62, 55.73, 34.01, 32.81, 30.47, 29.42, 29.36, 29.33, 28.72, 28.14, 26.02.
\]
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 CHCl₃ (300 mL) and washed thrice with H₂O (600 mL). The organic layer was dried over anhydrous Na₂SO₄ 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. ¹H-NMR (CDCl₃, 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). ¹³C-NMR (CDCl₃, 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 + NH₄]⁺ calcd for C₅₄H₉₁BrNO₁₀: 972.4256; found: 972.4250.

Fig. S3 ¹H NMR spectra of compound P₅ (CDCl₃, 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.
**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 C₂H₅OH (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 ¹H NMR (600 MHz, DMSO-d₆) 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). ¹³C NMR (151 MHz, DMSO-d₆) δ (ppm): 164.28, 157.55, 134.72, 130.34, 127.32, 123.07, 115.82.

![Diagram of the reaction](image)

**Fig. S6** ¹H NMR spectra of compound NA (DMSO–d₆, 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$_2$CO$_3$ (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$_3$) $\delta$ (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$_3$) $\delta$ (ppm): 164.59, 159.28, 150.67, 150.48, 149.86, 149.19, 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$_2$O$_{13}$ 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, 0.025 g) was dropwise added into the mixture of 4-aminopyridine (0.33 mmol, 0.031 g) 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$_6$O$_3$: 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.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>State</th>
<th>CGC(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ethyl acetate</td>
<td>P</td>
<td>\</td>
</tr>
<tr>
<td>2</td>
<td>Ethyl alcohol</td>
<td>P</td>
<td>\</td>
</tr>
<tr>
<td>3</td>
<td>CCl₄</td>
<td>P</td>
<td>\</td>
</tr>
<tr>
<td>4</td>
<td>Isopropyl alcohol</td>
<td>P</td>
<td>\</td>
</tr>
<tr>
<td>5</td>
<td>Ethylene glycol</td>
<td>P</td>
<td>\</td>
</tr>
<tr>
<td>6</td>
<td>Acetone</td>
<td>P</td>
<td>\</td>
</tr>
<tr>
<td>7</td>
<td>DMSO</td>
<td>S</td>
<td>\</td>
</tr>
<tr>
<td>8</td>
<td>n-Propyl alcohol</td>
<td>P</td>
<td>\</td>
</tr>
<tr>
<td>9</td>
<td>Methyl alcohol</td>
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<td>10</td>
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<td>P</td>
<td>\</td>
</tr>
<tr>
<td>11</td>
<td>Glycerol</td>
<td>P</td>
<td>\</td>
</tr>
<tr>
<td>12</td>
<td>Isoamyl alcohol</td>
<td>P</td>
<td>\</td>
</tr>
<tr>
<td>13</td>
<td>n-Butyl alcohol</td>
<td>P</td>
<td>\</td>
</tr>
<tr>
<td>14</td>
<td>Cyclohexanol</td>
<td>P</td>
<td>\</td>
</tr>
<tr>
<td>15</td>
<td>Tetrahydrofuran</td>
<td>P</td>
<td>\</td>
</tr>
<tr>
<td>16</td>
<td>Acetic acid</td>
<td>P</td>
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</tr>
<tr>
<td>17</td>
<td>n-Butanol</td>
<td>P</td>
<td>\</td>
</tr>
<tr>
<td>18</td>
<td>Cyclohexane</td>
<td>P</td>
<td>\</td>
</tr>
</tbody>
</table>

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

### Table S2. Gelation Property of SHG.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Water(%)</th>
<th>State</th>
<th>CGC(%)</th>
<th>Tgel(°C,wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMSO/ H₂O</td>
<td>0</td>
<td>S</td>
<td>\</td>
<td>\</td>
</tr>
<tr>
<td>DMSO/ H₂O</td>
<td>5</td>
<td>S</td>
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<td>\</td>
</tr>
<tr>
<td>DMSO/ H₂O</td>
<td>10</td>
<td>S</td>
<td>\</td>
<td>\</td>
</tr>
<tr>
<td>DMSO/ H₂O</td>
<td>15</td>
<td>C</td>
<td>\</td>
<td>\</td>
</tr>
<tr>
<td>DMSO/ H₂O</td>
<td>20</td>
<td>C</td>
<td>\</td>
<td>\</td>
</tr>
<tr>
<td>DMSO/ H₂O</td>
<td>25</td>
<td>G</td>
<td>2</td>
<td>53–56°C (2%)</td>
</tr>
<tr>
<td>DMSO/ H₂O</td>
<td>30</td>
<td>P</td>
<td>\</td>
<td>\</td>
</tr>
</tbody>
</table>

*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$_2$O ($f_w = 25\%$) solution with different concentration ($10^{-3}$–$10^{-6}$ M).

**Fig. S14** Absorption spectrum of AP5 (10 $\mu$M) 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 $1.35 \times 10^6$ M$^{-1}$.

\[
\frac{I - I_{\text{min}}}{I_{\text{max}} - I} = \log \text{Ka} + \log[C]
\]
\[ K = 1.35 \times 10^6 \text{ M}^{-1}. \]

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

3. Characterization of SHG.

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

**Fig. S17** Partial \( ^1 \text{H} \) 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

![Graph showing fluorescent spectrum linear range for Fe$^{3+}$](image)

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

**Linear Equation:** $Y = a + bX = 796.67669 - 8007.5188X$ \hspace{1cm} $R^2 = 0.99645$

\[
\delta = \frac{\sum (F_i - F_0)^2}{N - 1} = 2.39 \ (N = 20)
\]

\[
S = 8007.5188 \times 10^6 \sqrt{N - 1}
\]

**LOD =** $K \times \frac{\delta}{S} = 0.9 \text{ nM} \ (K = 3)$

$\delta$ 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.
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 $2.34 \times 10^6$ M$^{-1}$.

$$K = 2.34 \times 10^6 \text{ M}^{-1}.$$  

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

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

<table>
<thead>
<tr>
<th>Ions</th>
<th>Initial concentration (M)</th>
<th>Residual concentration (M)</th>
<th>Adsorption percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$^{3+}$</td>
<td>$1 \times 10^{-5}$</td>
<td>$1.42 \times 10^{-8}$</td>
<td>99.8 %</td>
</tr>
</tbody>
</table>

※Calculation method of adsorption percentage:

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

(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.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Material used</th>
<th>Adsorption percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>S7</td>
<td>Aluminum based MOFs</td>
<td>98.2%</td>
</tr>
<tr>
<td>S8</td>
<td>Pillar[5]arene-based SOFs</td>
<td>99.4%</td>
</tr>
<tr>
<td>S9</td>
<td>Supramolecular Gel</td>
<td>99.42%</td>
</tr>
<tr>
<td>This work</td>
<td>Pillar[5]arene-based Gel</td>
<td>99.8%</td>
</tr>
</tbody>
</table>

Reference:

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.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Dyes</th>
<th>Uptake %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Methyl orange</td>
<td>96.7</td>
</tr>
<tr>
<td>2</td>
<td>Methylene blue</td>
<td>97.4</td>
</tr>
<tr>
<td>3</td>
<td>Sudan I</td>
<td>83.8</td>
</tr>
</tbody>
</table>

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

\[
E = \left( \frac{C_0 - C_t}{C_0} \right) \times 100\%
\]

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 The regeneration 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 orange: (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.