Supplementary information

“Keto-enol tautomerization”-based response mechanism, a novel approach to stimuli-responsive supramolecular gel

Qi Lin,*a Tao-Tao Lu,a Jin-Chao Lou,a Gui-Yuan Wu,a Tai-Bao Wei,a and You-Ming Zhang*a,b

*aKey Laboratory of Eco-Environment-Related Polymer Materials, Ministry of Education of China, Key Laboratory of Polymer Materials of Gansu Province, College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou, Gansu, 730070, P. R. China.

bKey Laboratory of Hexi Corridor Resources Utilization of Gansu, Hexi University, Zhangye, Gansu, 734000, P. R. China.
Table of Contents

Materials and instruments

Fig. S1. $^1$H NMR Spectrum of G3

Fig. S2. $^{13}$C NMR Spectrum of G3

Fig. S3. Mass spec trace for G3

Fig. S4. Plots of $T_{gel}$ against the concentrations of organogel OG3 in DMSO and acetonitrile.

Fig. S5. Plots of CGC of G3 in different solvents.

Table S1. Gelation properties of G3

Fig. S6. Fluorescent spectra changed over time($\lambda_{ex} = 365$ nm, $\lambda_{em} = 490$ nm).

Fig. S7. Fluorescence spectra of organogel and sol (1.5%, in DMSO, $\lambda_{ex} = 365$ nm).

Fig. S8. Fluorescence spectra of organogel OG3 (1.5%, in DMSO), OG3 $+$ S$^2-$ (1.5%, in DMSO, G3 : anions $=$ 1 : 2).

Fig. S9. Photographs of organogel of G3 in DMSO (1.5% w/v) and organogels of G3 in the presence of various metal ions (using their perchlorate salts as the sources, G3: anions $=$ 1 : 2) under (a) room (b) UV light.

Fig. S10. Fluorescence spectra of OG3$+$S$^2-$ (1.5%, in DMSO) in the presence of various cations (Fe$^{3+}$, Hg$^{2+}$, Ag$^+$, Ca$^{2+}$, Cu$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Cd$^{2+}$, Pb$^{2+}$, Zn$^{2+}$, Cr$^{3+}$, and Mg$^{2+}$) at room temperature.

Fig. S11. Fluorescence spectra of OG3$+$S$^2-$ (1.5%, in DMSO) with increasing concentration of Zn$^{2+}$ (using 0.1 mol L$^{-1}$ zinc perchlorate DMSO solution as the Zn$^{2+}$ sources), $\lambda_{ex} = 365$ nm.

Fig. S12. Partial $^1$H NMR spectra of G3 (0.016 M) in CDCl$_3$ upon the addition of S$^2-$.
Fig. S13. $^1$H NMR spectra of G3 (0.016 M) in CDCl$_3$ upon the addition of S$^{2-}$: (a) Free; (b) 0.5; (c) 1; (d) 2 equiv. of S$^{2-}$.

Fig. S14. Powder XRD patterns of xerogels of OG3 (obtained from 1.5% OG3 in DMSO), OG3 xerogel treated with S$^{2-}$ (2 equiv, 0.1 mol L$^{-1}$ aqueous Na$_2$S solution as S$^{2-}$ source) and OG3+S$^{2-}$+Zn$^{2+}$ (1.5%, in DMSO, G3 : S$^{2-}$ : Zn$^{2+}$ = 1 : 2 : 2, 0.1 mol L$^{-1}$ zinc perchlorate DMSO solution as the Zn$^{2+}$ sources).

Fig. S15. SEM images of (a) powder; (b) and (c) OG3 xerogel in DMSO and acetonitrile; (d) OG3 xerogel treated with S$^{2-}$ in situ; (e) OG3+S$^{2-}$ treated with Zn$^{2+}$ in situ.
Materials and instruments

All anions were used as sodium or potassium salts, the sodium or potassium salt which were purchased from Alfa Aesar and used as received. 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. $^1$H NMR spectra were recorded on Mercury-400BB spectrometer (400MHz) and Bruker Digital RF spectrometer (300MHz). $^1$H chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale with the solvent resonances as internal standards). Low-resolution mass spectra were recorded on a Bruker Esquire 6000 MS instrument. 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. Elemental analyses were performed by Thermo Scientific Flash 2000 organic elemental analyzer.

Synthesis of gelator G3

The synthesis process of gelator G3 is demonstrated in Scheme 1. Synthesis of gelator G3: 3,4-bis-hexadecyloxy-benzaldehyde (5 mmol, 5.76g), 1-bromo–hexadecane (11 mmol, 3.36 g), K$_2$CO$_3$ (40 mmol, 5.52 g) and KI (2 mmol, 0.332 g) were
added to 40 ml acetone. The reaction mixture was stirred under refluxing conditions and nitrogen protection for 48 hours. After removing the solvent, the precipitate was dissolved in CHCl₃ and then being washed by H₂O and saturated sodium chloride aqueous solution successively. The product G₃ was obtained after evaporating the solvent. Then, the G₃ was purified by column chromatography (Petroleum ether : Ethyl acetate =50:1) (Yield: 60%). ¹H NMR (CDCl₃, 400 MHz): δ, 9.83 (s, 1H, -OH), 7.46~7.42 (d, 1H, J = 16.0 Hz, =CH-Ar), 7.10~7.08 (d, 2H, J = 8.0 Hz, -ArH), 6.87~6.85 (d, 1H, J = 8.0 Hz, -C=CH), 6.60~6.56 (d, 1H, J = 16.0 Hz, -ArH), 4.03~4.01 (d, 4H, J = 8.0 Hz, -OCH₂), 2.37 (s, 3H, O=C-CH₃), 1.83 (m, 4H, -CH₂), 1.47~1.26 (m, 52H, -CH₂), 0.88 (t, J = 16.0 Hz, 6H, -CH₃) (Fig. S1). ¹³C-NMR (CDCl₃, 150 MHz) δ/ppm 190.56, 154.28, 149.05, 129.48, 126.16, 111.37, 110.60, 68.75, 68.72, 31.53, 29.31, 29.27, 29.22, 29.21, 29.20, 28.99, 28.98, 28.68, 28.59, 25.59, 25.55, 22.29, 13.71. IR (KBr, cm⁻¹) v: 1668 (C=O), 1591 (C=C) (Fig. S2); MS-ESI calcd for C₄₂H₇₄O₃ [G₃ + H⁺]: 627.5600; found: 627.4670 (Fig. S3).
**General procedure for fluorescence experiments**

Fluorescence spectroscopy was carried out keeping the host concentration constant in DMSO solution on a Shimadzu RF-5301PC spectrofluorophotometer. The S\(^2\) was prepared from its sodium salts.

**General procedure for \(^1\)H NMR titrations**

For \(^1\)H NMR titrations, two stock solutions were prepared in CDCl\(_3\): one of them contained the host only and the second one contained an appropriate concentration of guest. Aliquots of the two solutions were mixed directly in NMR tubes.

**General procedure for concentration-dependent \(^1\)H NMR measurements**

The concentration-dependent \(^1\)H NMR was carried out by gradually increasing the concentration of the CDCl\(_3\) solution of \(G3\). The initial concentration of the \(G3\) is 0.5 mM, the concentration was adjusted by directly addition right amount of powdery \(G3\) into the CDCl\(_3\) solution.
**Fig. S1.** $^1$H NMR Spectrum of G3

**Fig. S2.** $^{13}$C NMR Spectrum of G3
Fig. S3. Mass spec trace for G3
Fig. S4. Plots of $T_{gel}$ against the concentrations of organogel OG3 in DMSO and acetonitrile.

Fig. S5. Plots of CGC of G3 in the different solvents.
**Table S1. Gelation properties of G3**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>State&lt;sup&gt;a&lt;/sup&gt;</th>
<th>CGC&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Tgel&lt;sup&gt;c&lt;/sup&gt; (℃, wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ethyl acetate</td>
<td>p</td>
<td>\</td>
<td>\</td>
</tr>
<tr>
<td>2</td>
<td>Isopropanol</td>
<td>p</td>
<td>\</td>
<td>\</td>
</tr>
<tr>
<td>3</td>
<td>Petroleum ether</td>
<td>P</td>
<td>\</td>
<td>\</td>
</tr>
<tr>
<td>4</td>
<td>THF</td>
<td>S</td>
<td>\</td>
<td>\</td>
</tr>
<tr>
<td>5</td>
<td>Chloroform</td>
<td>S</td>
<td>\</td>
<td>\</td>
</tr>
<tr>
<td>6</td>
<td>Dichloromethane</td>
<td>S</td>
<td>\</td>
<td>\</td>
</tr>
<tr>
<td>7</td>
<td>Acetone</td>
<td>P</td>
<td>\</td>
<td>\</td>
</tr>
<tr>
<td>8</td>
<td>Acetonitrile</td>
<td>G</td>
<td>0.5</td>
<td>39(0.6%)</td>
</tr>
<tr>
<td>9</td>
<td>DMF</td>
<td>G</td>
<td>1.5</td>
<td>45(2.0%)</td>
</tr>
<tr>
<td>10</td>
<td>DMSO</td>
<td>G</td>
<td>0.4</td>
<td>35(0.6%)</td>
</tr>
<tr>
<td>11</td>
<td>Methanol</td>
<td>P</td>
<td>\</td>
<td>\</td>
</tr>
<tr>
<td>12</td>
<td>Ethanol</td>
<td>G</td>
<td>2.0</td>
<td>40(3.0%)</td>
</tr>
</tbody>
</table>

<sup>a</sup>G, P and S denote gelation, precipitation and solution, respectively, c = 0.8%.

<sup>b</sup>The critical gelation concentration (wt%, 10mg/mL = 1.0%).

<sup>c</sup>The gelation temperature(℃).

---

**Fig. S6.** Fluorescent spectra changed over time ($\lambda_{ex} = 365$ nm, $\lambda_{em} = 490$ nm).
**Fig. S7.** Fluorescence spectra of organogel and sol (1.5%, in DMSO, $\lambda_{ex} = 365$ nm).

**Fig. S8.** Fluorescence spectra of organogel OG3 (1.5%, in DMSO), OG3 $+$ S$^{2-}$ (1.5%, in DMSO, G3 : anions $= 1 : 2$).
Fig. S9. Photographs of organogel of G3 in DMSO (1.5% w/v) and organogels of G3 in the presence of various metal ions (using their perchlorate salts as the sources, G3: anions = 1 : 2) under (a) room (b) UV light.

Fig. S10. Fluorescence spectra of OG3+S²⁻ (1.5%, in DMSO) in the presence of various cations (Fe³⁺, Hg²⁺, Ag⁺, Ca²⁺, Cu²⁺, Co²⁺, Ni²⁺, Cd²⁺, Pb²⁺, Zn²⁺, Cr³⁺ and Mg²⁺) at room temperature.
**Fig. S11.** Fluorescence spectra of OG3+S²⁻ (1.5%, in DMSO) with increasing concentration of Zn²⁺ (using 0.1 mol L⁻¹ zinc perchlorate DMSO solution as the Zn²⁺ sources), λ<sub>ex</sub> = 365 nm.

**Fig. S12.** Partial <sup>1</sup>H NMR spectra of G3 (0.016 M) in CDCl₃ upon the addition of S²⁻ (a) Free; (b) 0.5; (c) 1; (d) 2 equiv. of S²⁻.
Fig. S13. $^1$H NMR spectra of G3 (0.016 M) in CDCl$_3$ upon the addition of S$^2^-$ (a) Free; (b) 0.5; (c) 1; (d) 2 equiv. of S$^2^-$.

Fig. S14. Powder XRD patterns of xerogels of OG3 (obtained from 1.5% OG3 in DMSO), OG3 xerogel treated with S$^2^-$ (2 equiv, 0.1 mol/L aqueous Na$_2$S solution as S$^2^-$ source) and OG3 + S$^2^-$ + Zn$^{2+}$ (1.5%, in DMSO, G3 : S$^2^-$ : Zn$^{2+}$ = 1 : 2 : 2, 0.1 mol L$^{-1}$ zinc perchlorate DMSO solution as the Zn$^{2+}$ sources).
Fig. S15. SEM images of (a) powder; (b) and (c) OG3 xerogel in DMSO and acetonitrile; (d) OG3 xerogel treated with S$^{2-}$ in situ; (e) OG3+S$^{2-}$ treated with Zn$^{2+}$ in situ.