Supplementary information

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

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Table of Contents

(a) Free; (b) 0.5; (c)1; (d) 2 equiv. of S^{2-}.

Fig. S13. ^1H 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_2S 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–hexad – ecane(11 mmol, 3.36 g), K_2CO_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 $CHCl_3$ and then being washed by H_2O 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%). ^{1}H NMR ($CDCl_3$, 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, -OCH_2), 2.37 (s, 3H, O=C-CH_3), 1.83(m, 4H, -CH_2), 1.47~1.26 (m, 52H, -CH_2), 0.88 (t, J = 16.0 Hz, 6H, -CH_3) (Fig. S1). ^{13}C-NMR ($CDCl_3$, 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 $C_{42}H_{74}O_3$ [**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.

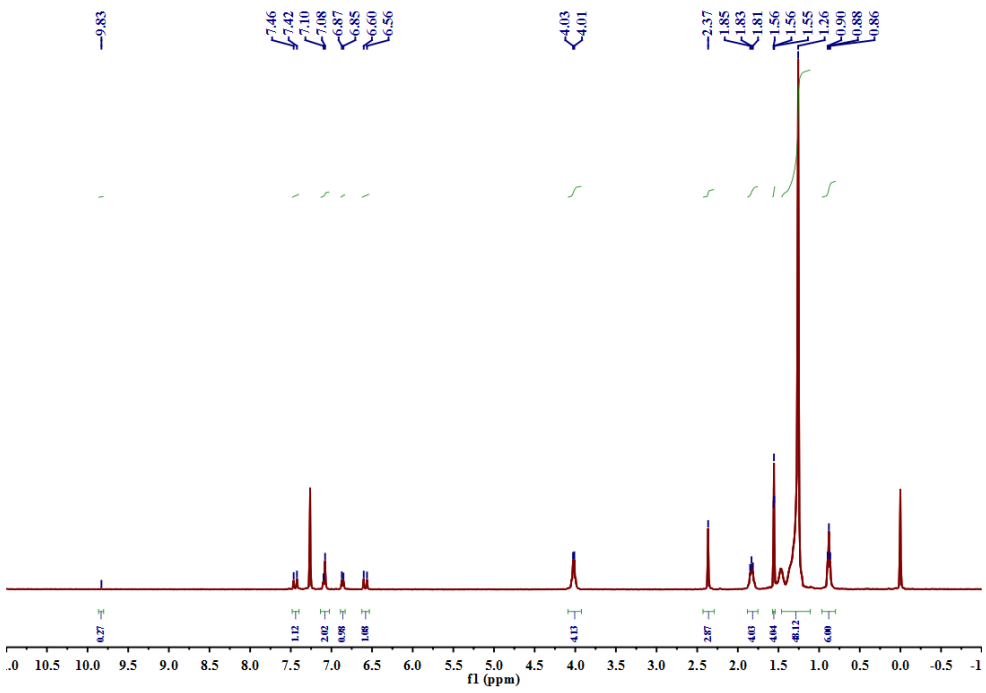

Fig. S1. ^{1}H NMR Spectrum of **G3**

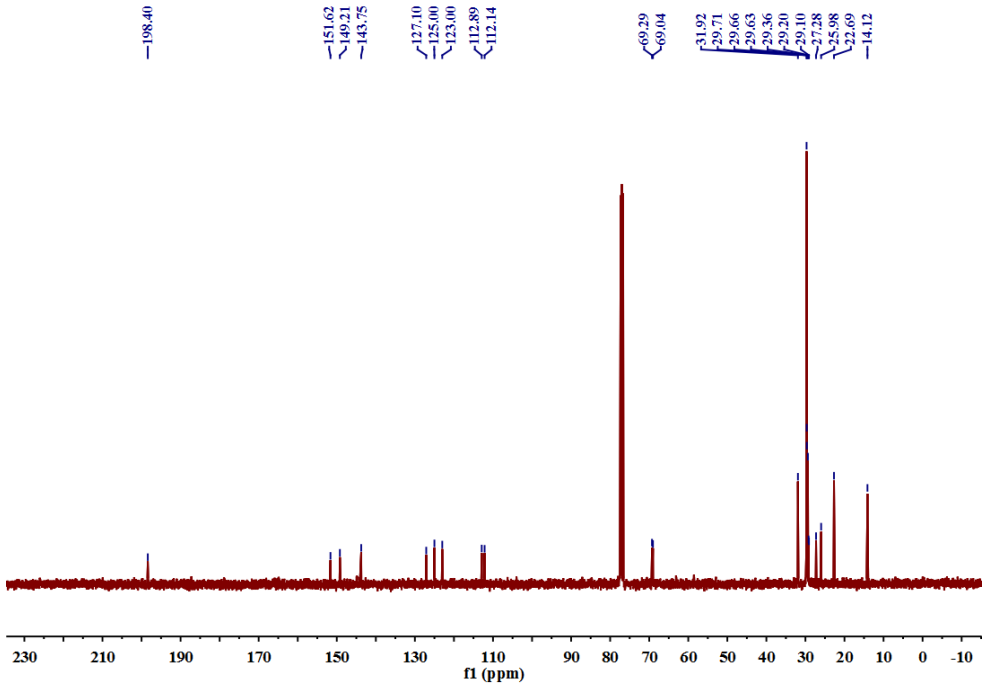

Fig. S2. ^{13}C NMR Spectrum of **G3**

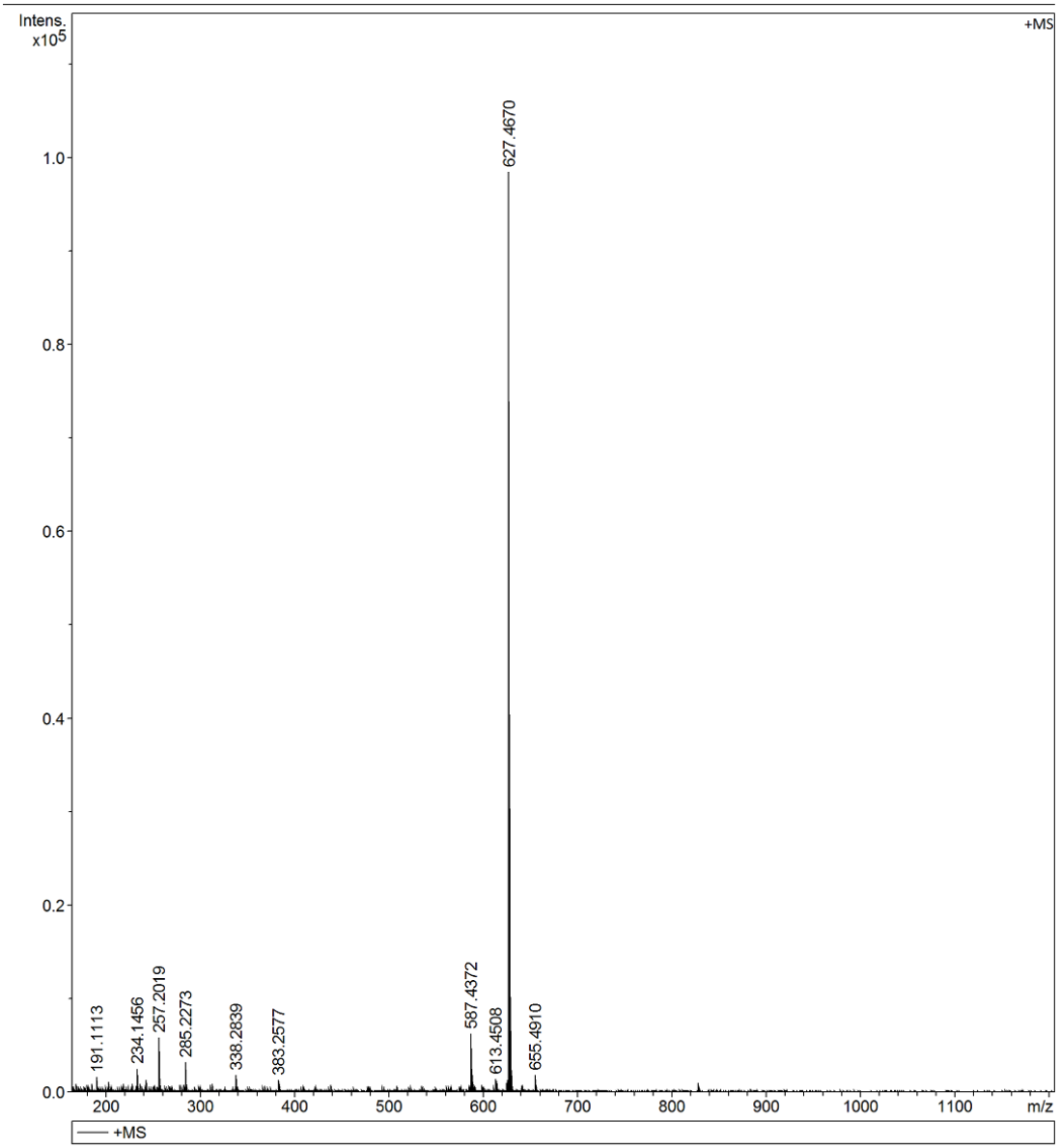

Fig. S3. Mass spec trace for **G3**

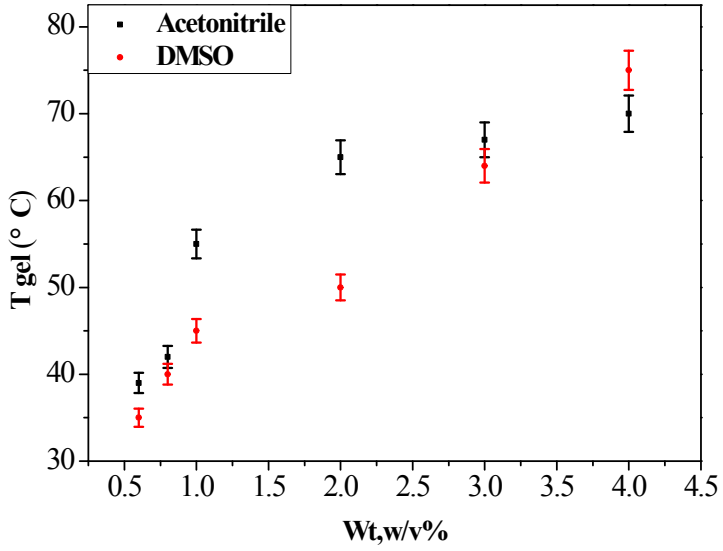

Fig. S4. Plots of T_{gel} against the concentrations of organogel **OG3** in DMSO and acetonitrile.

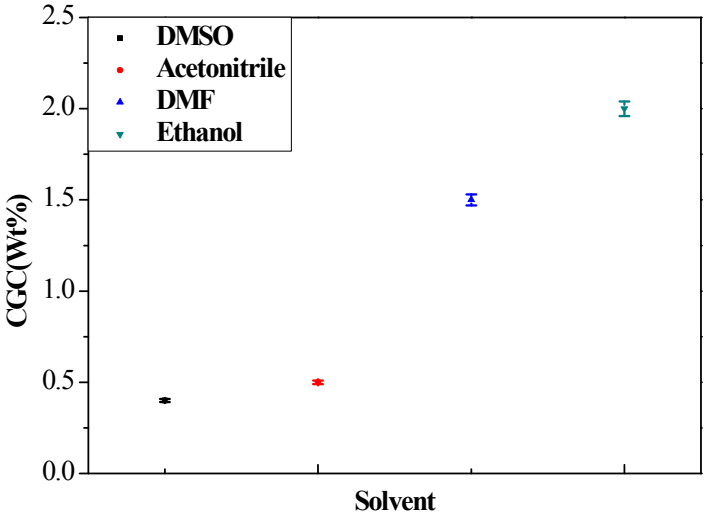

Fig. S5. Plots of CGC of **G3** in the different solvents.

Table S1. Gelation properties of **G3**

Entry	Solvent	State[a]	CGC[b]	Tgel[c] (℃, wt%)
1	Ethyl acetate	p	\	\
2	Isopropanol	p	\	\
3	Petroleum ether	P	\	\
4	THF	S	\	\
5	Chloroform	S	\	\
6	Dichloromethane	S	\	\
7	Acetone	P	\	\
8	Acetonitrile	G	0.5	39(0.6%)
9	DMF	G	1.5	45(2.0%)
10	DMSO	G	0.4	35(0.6%)
11	Methanol	P	\	\
12	Ethanol	G	2.0	40(3.0%)

[a]G, P and S denote gelation, precipitation and solution, respectively, c = 0.8%.
[b]The critical gelation concentration (wt%, 10mg/mL = 1.0%).
[c]The gelation temperature(℃).

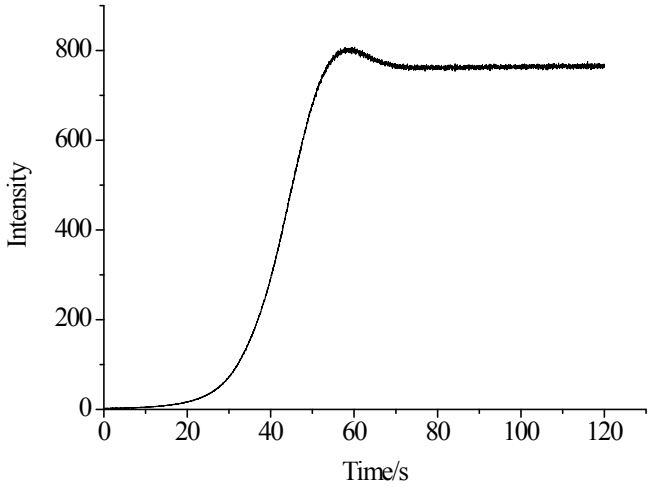

Fig. S6. Fluorescent spectra changed over time (λ_{ex} = 365 nm, λ_{em} = 490 nm).

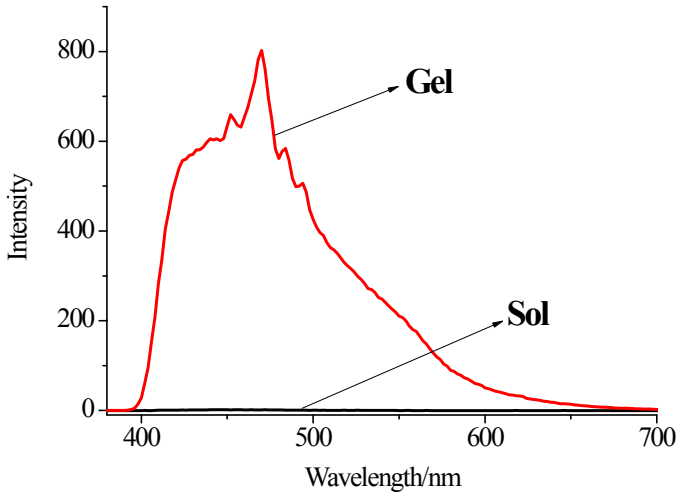

Fig. S7. Fluorescence spectra of organogel and sol (1.5%, in DMSO, λ_{ex} = 365 nm).

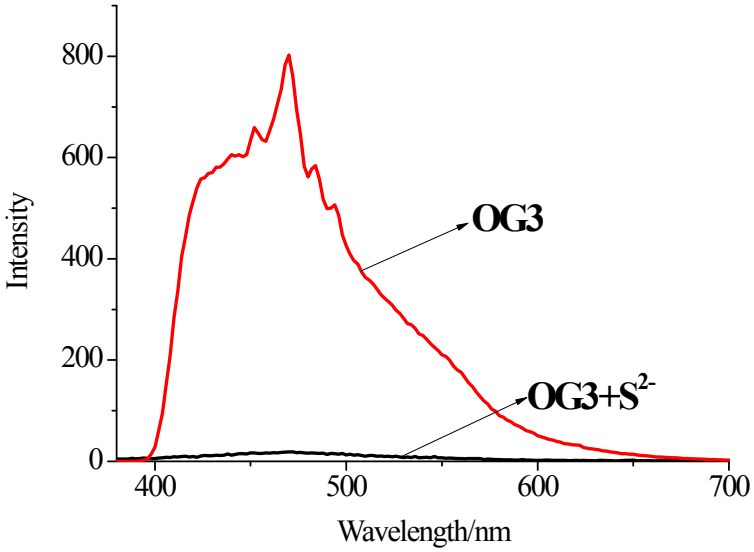

Fig. S8. Fluorescence spectra of organogel **OG3** (1.5%, in DMSO), **OG3** + S^{2-} (1.5%, in DMSO, **G3** : anions = 1 : 2).

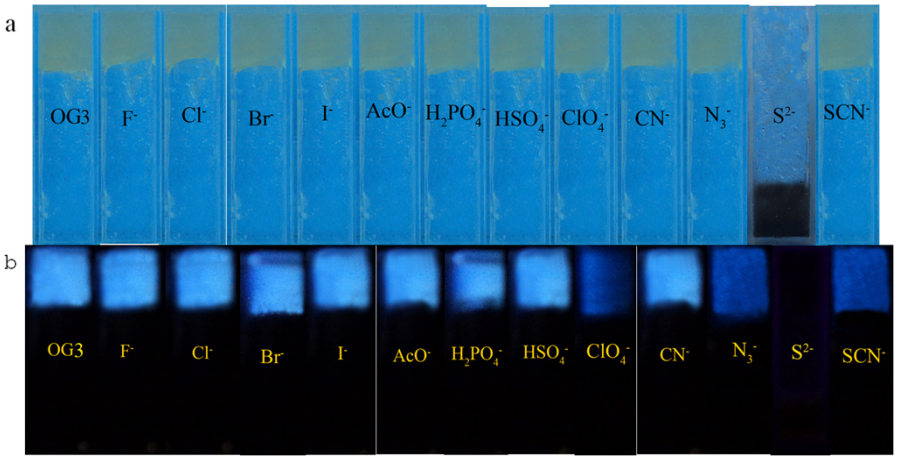

Fig. S9. Photographs of organogel of **G3** in DMSO (1.5% w/v) and organogels of **G3** in the presence of various metal ions (using their perchlorate salts as the sources, **G3**: anions =1 : 2) under (a) room (b) UV light.

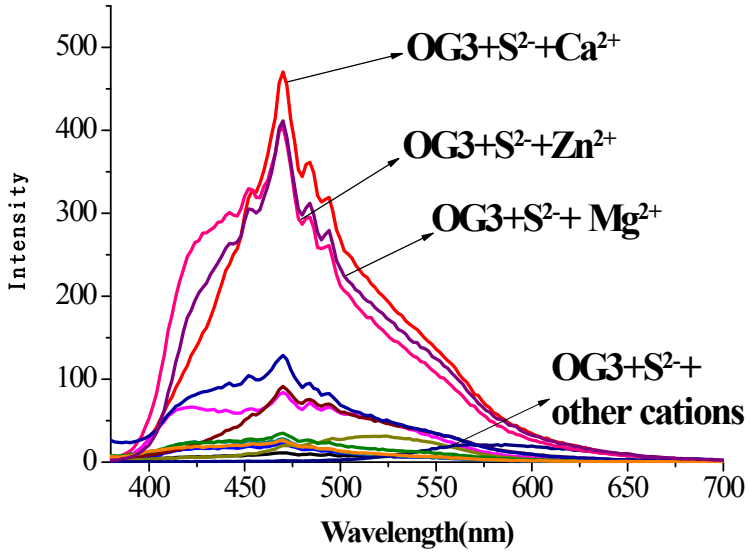

Fig. S10.Fluorescence spectra of OG3+S^{2-} (1.5%, in DMSO) in the presence of various cations (Fe^{3+}, Hg^{2+}, Ag^{+}, Ca^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Cr^{3+} and Mg^{2+}) at room temperature.

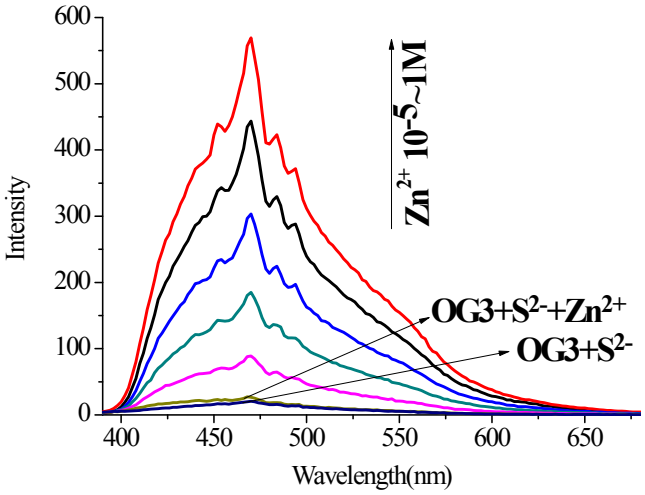

Fig. S11. Fluorescence spectra of **OG3**+S^{2-} (1.5%, in DMSO) with increasing concentration of Zn^{2+} (using 0.1 mol L^{-1} zinc perchlorate DMSO solution as the Zn^{2+} sources), λ_{ex} = 365 nm.

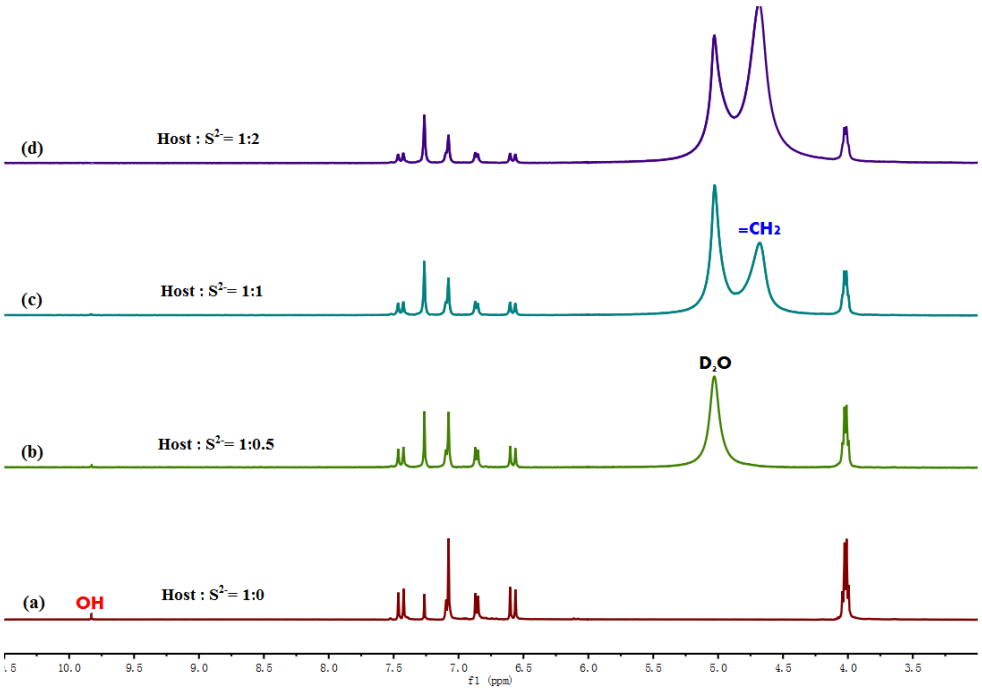

Fig. S12. Partial ^1H NMR spectra of **G3** (0.016 M) in $CDCl_3$ upon the addition of S^{2-} (a) Free; (b) 0.5; (c)1; (d) 2 equiv. of S^{2-}.

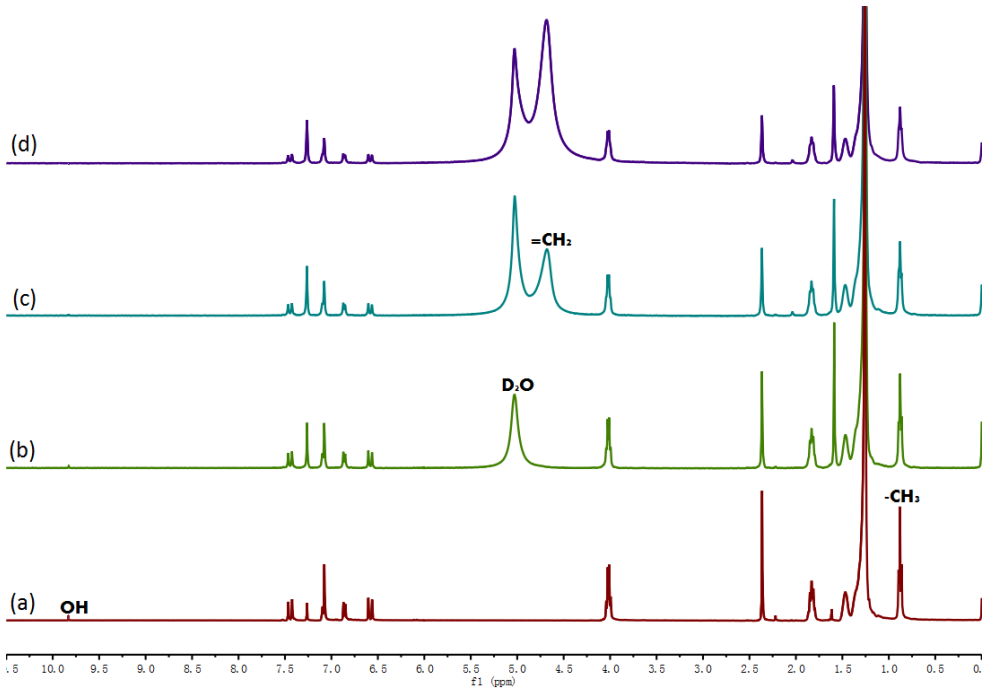

Fig. S13. ^{1}H NMR spectra of **G3** (0.016 M) in $CDCl_3$ upon the addition of S^{2-} (a) Free; (b) 0.5; (c)1; (d) 2 equiv. of S^{2-}.

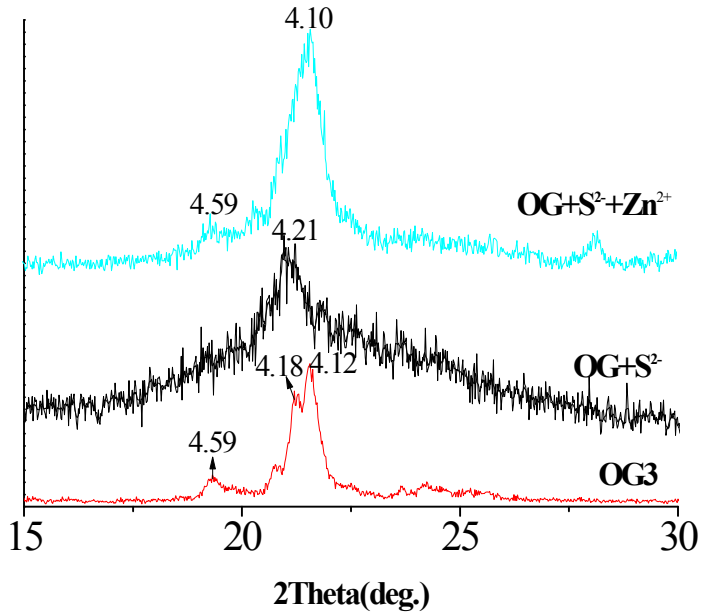

Fig. S14. Powder XRD patterns of xerogels of **OG3** (obtained from 1.5% **OG3** in DMSO), **OG3** xerogel treated with S^{2-}(2 equiv, 0.1 mol/L aqueous Na_2S solution as S^{2-} source) and **OG3** + S^{2-} + Zn^{2+}(1.5%, in DMSO, **G3** : S^{2-} : Zn^{2+} = 1 : 2 : 2, 0.1 mol L^{-1} zinc perchlorate DMSO solution as the Zn^{2+} sources).

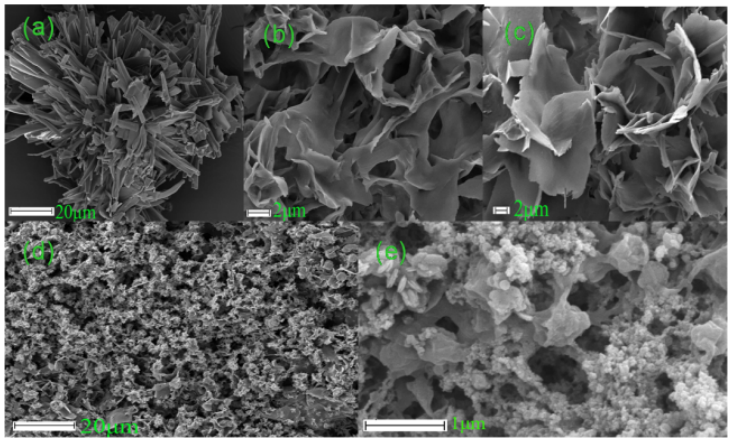

Fig. S15. SEM images of (a) powder; (b) and (c) **OG3** xerogel in DMSO and acetonitrile; (d) **OG3** xerogel treated with S^{2-} in situ; (e) **OG3**+S^{2-} treated with Zn^{2+} in situ.