

## Electronic Supplementary Information

### **A carboxylic acid functionalized benzimidazole-based supramolecular gel with multi-stimuli responsive properties**

Hong Yao, Hong-Ping Wu, Jing Chang, Qi Lin, Tai-Bao Wei\* and You-Ming Zhang\*

*Key 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*

## Supporting Information List:

### Apparatus and chemicals

Melting points were measured on an X-4 digital melting-point apparatus (uncorrected).  $^1\text{H}$  NMR spectra were recorded with a Mercury-400BB spectrometer at 400 MHz, with tetramethylsilane (TMS) as an internal standard. NMR spectra were referenced to the solvent. The infrared spectra were recorded on a Digilab FTS-3000 FT-IR spectrophotometer. The fluorescence spectra were recorded with a Shimadzu RF-5301 spectrofluorimeter. The xerogel of MOGs was coated on a glass plate and the solvent was slowly evaporated. The glass plates with dry gels were then fixed on a sample holder and subjected to XRD analysis at room temperature on a Japan Rigaku D/MAX-2400/PC diffractometer. XRD patterns were recorded at a scanning rate of 5 °/min in the  $2\theta$  range of 2° to 60 ° with Cu-K $\alpha$  radiation. The morphologies and sizes of the MOGs were characterized using field emission scanning electron microscopy (FE-SEM, JSM-6701F) at an accelerating voltage of 8 kV. All reagents of analytical grade were purchased from Alfa Aesar.

**General procedures for synthesis of organogel (C11-OG).** Compounds C11 (0.01 g) were dissolved in 1 mL appropriate mixing solvents (such as MeOH-H<sub>2</sub>O, EtOH-H<sub>2</sub>O and *i*-PrOH-H<sub>2</sub>O; v/v= 1 : 1) in sealed test tubes with applied heat until dissolution was complete. Upon cooling to room temperature (25 °C), white stable organogels (C11-OG) were formed in the test tubes, which were allowed to stand for some weeks. Gel formation was evaluated by its stability to the inversion of the test tube. The corresponding gelator concentrations was 1 wt %.

**General procedures for synthesis of metallogel (Pb-MG).** On addition of lead nitrate as Pb<sup>2+</sup> source to the C11-OG or mixing powder C11 and Pb(NO<sub>3</sub>)<sub>2</sub> in appropriate mixing solvents (such as MeOH-H<sub>2</sub>O, EtOH-H<sub>2</sub>O and *i*-PrOH-H<sub>2</sub>O; v/v= 1 : 1), heating to dissolve and then cooling to room temperature (25 °C), a stable white Pb<sup>2+</sup>-coordinated metallogel (Pb-MG) was formed in the test tubes, which were allowed to stand for some weeks. Gel formation was evaluated by its stability to the inversion of the test tube. The corresponding gelator concentrations was 1 wt %.

**Disassembly procedures of metallogel (Pb-MG) by chemical stimuli.** The metallogel shows a quick response to some anions, leading to macroscopic transformation from gel to sol through destroying the coordination of metal ion with C11. As an example, when the proper amount of the Na<sub>2</sub>S aqueous solution (0.1 mL, 2 eqv.) was added to the surface of Pb-MG (0.5 wt %), the gel was dissolved and transformed into a sol after several hours, while black precipitate was observed, which could be clearly assigned to the PbS precipitate. If we add excess lead ion to the fluid solution again after the PbS precipitate has been filtrated off, the gel was re-formed (Fig. S6). The same result could be observed if the corresponding

equivalents of EDTA were added to the gel as the equivalents of the metal salt in the gel, a white precipitate was observed after several hours. If we add excess lead ion to the fluid solution again after the precipitate has been filtrated off, the gel was re-formed(**Fig. S5**).

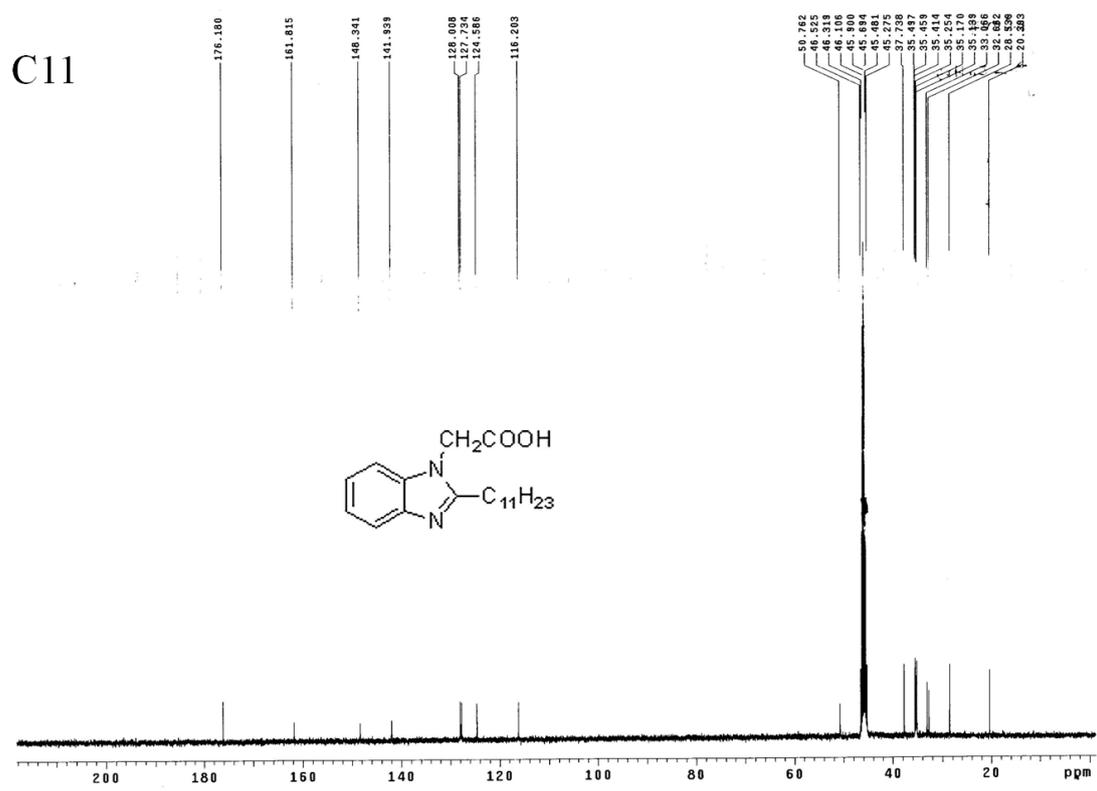


Fig. S1  $^{13}\text{C}$  NMR spectra of C11..

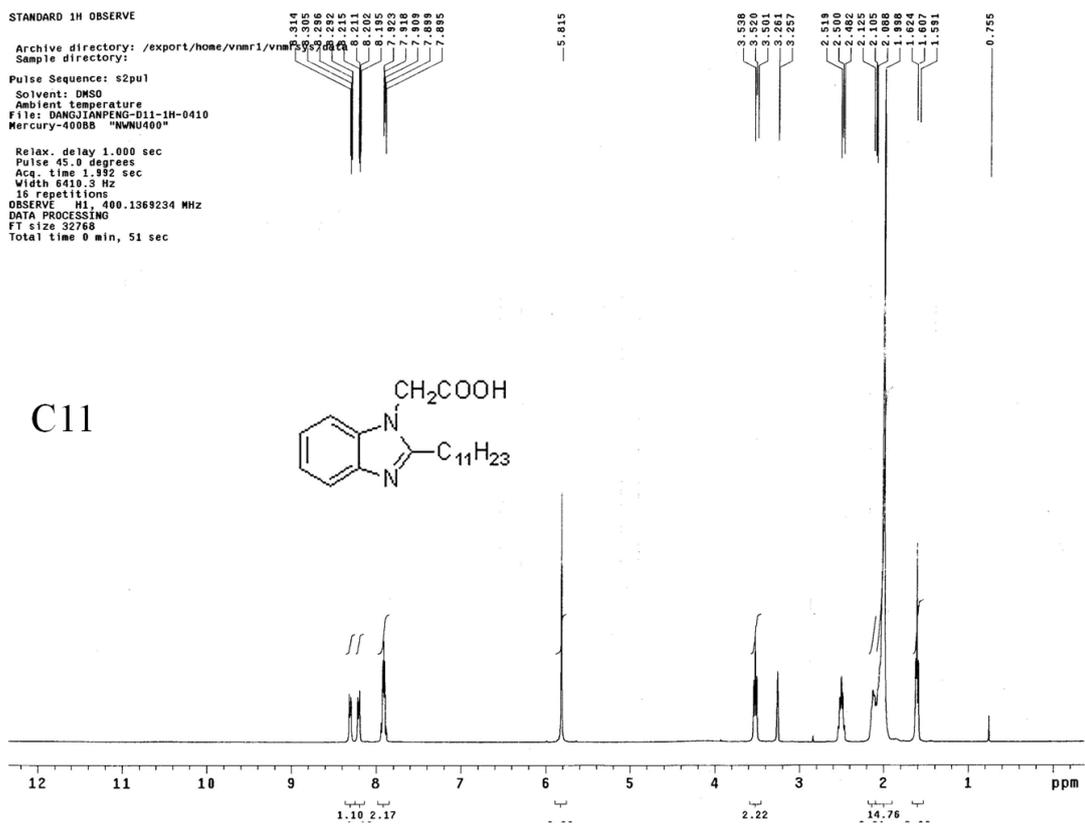
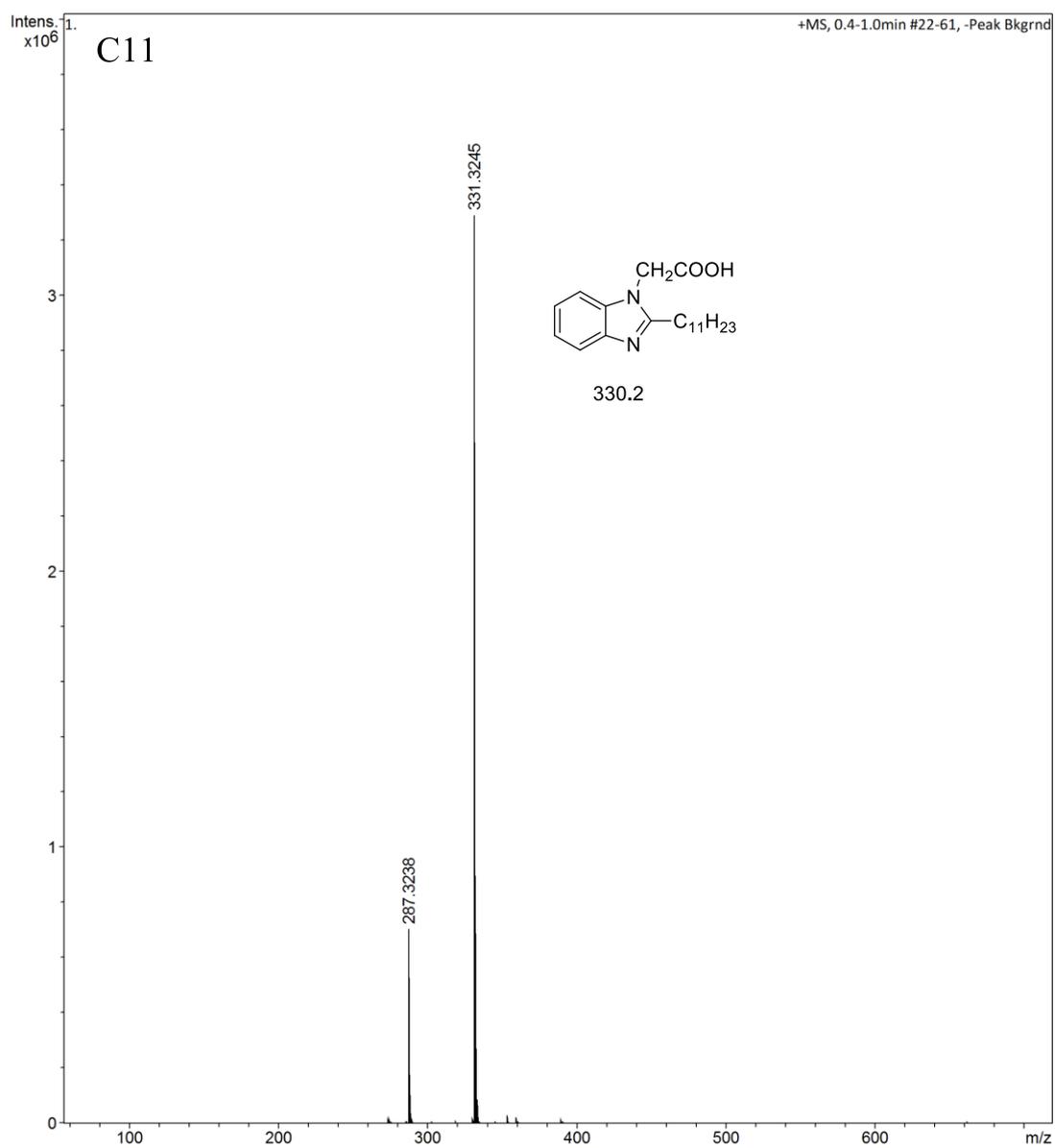
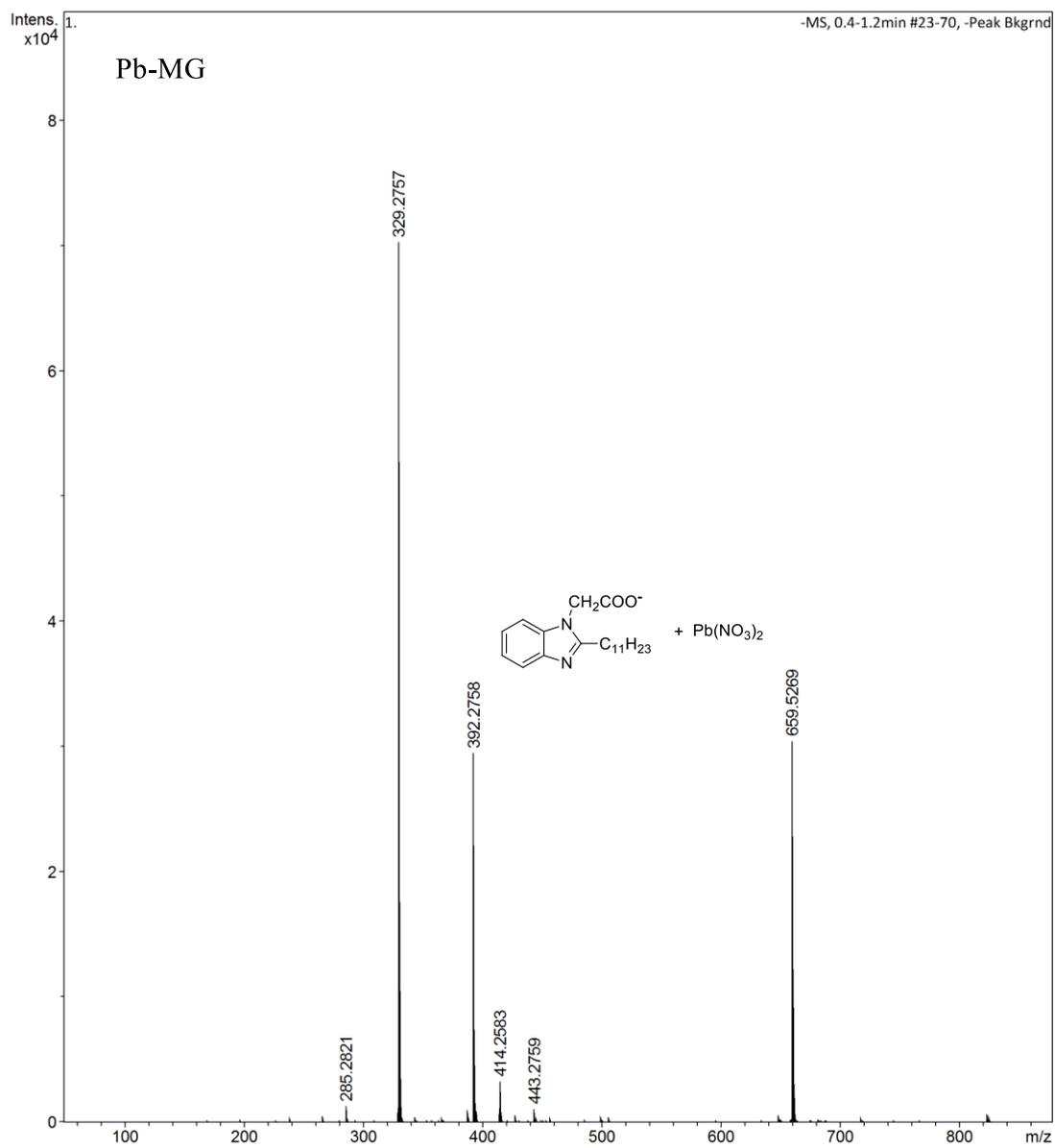


Fig. S2 <sup>1</sup>H NMR spectra of C11.



**Fig. S3** mass spectra of gelator C11.

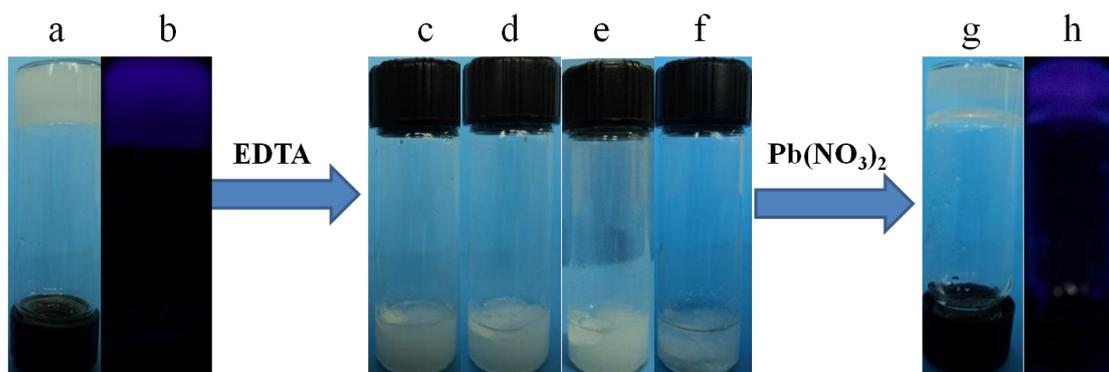


**Fig. S4** mass spectra of organogel Pb-MG.

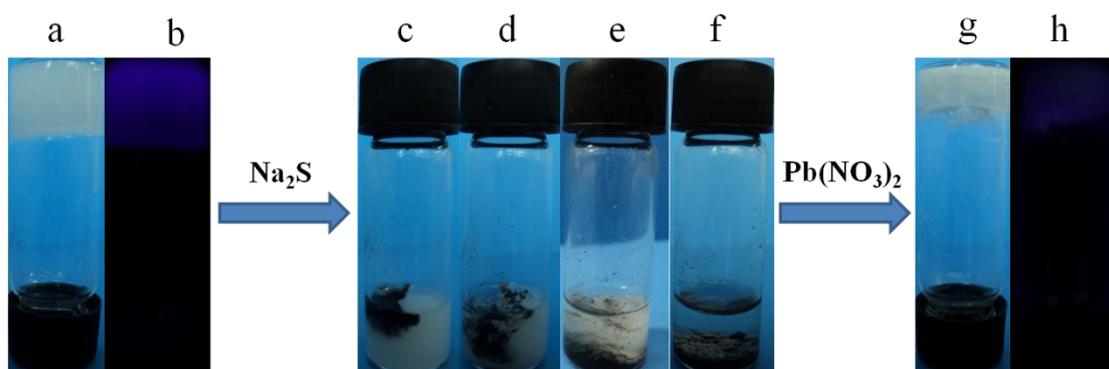
Table S1. The gel formation ability of Pb-MG in different solvents(v/v=1:1)

	MeOH-H <sub>2</sub> O	EtOH-H <sub>2</sub> O	Acetone-H <sub>2</sub> O	DMSO-H <sub>2</sub> O	DMF-H <sub>2</sub> O	Acetonitrile-H <sub>2</sub> O
Pb(NO <sub>3</sub> ) <sub>2</sub>	G	G	SP	P	WG	SP

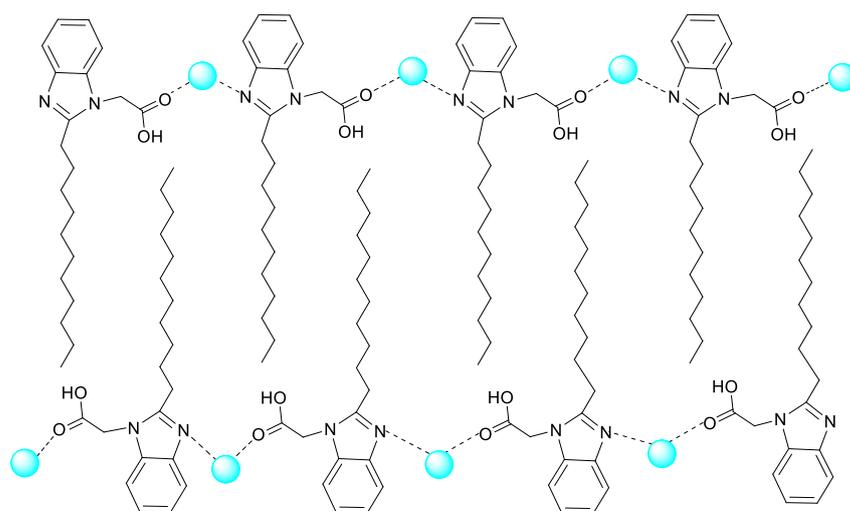
G=gel; WG=weak gel; SP=solution precipitate



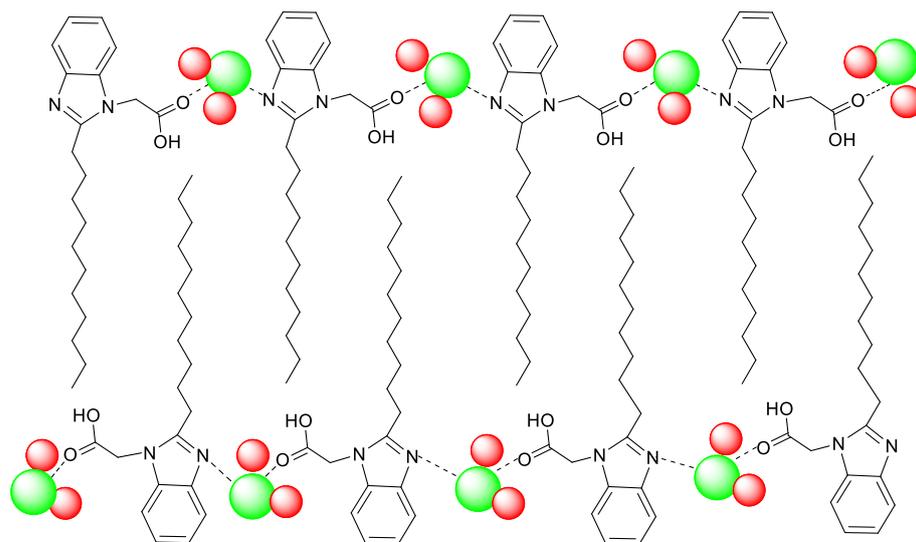
**Fig. S5.** The EDTA response of the Pb-MG. (a) The Pb-MG formed from C11 same equivalent  $\text{Pb}(\text{NO}_3)_2$  in 1:1 EtOH- $\text{H}_2\text{O}$  at 0.5 wt%; (b) photograph of the gel under 365 nm with a hand-held UV lamp.; (c) immediately after addition of EDTA aqueous solution (1 eqv.); (d) after 4 h; (e) after 12 h; (f) after 25h; (g) after addition of  $\text{Pb}(\text{NO}_3)_2$  (3 eqv.) to (f); (h) the photograph of the gel under 365 nm with a hand-held UV lamp.



**Fig. S6.** The  $\text{Na}_2\text{S}$  response of the Pb-MG. (a) The Pb-MG formed from C11 same equivalent  $\text{Pb}(\text{NO}_3)_2$  in 1:1 EtOH- $\text{H}_2\text{O}$  at 0.5 wt%; (b) photograph of the gel under 365 nm with a hand-held UV lamp.; (c) immediately after addition of  $\text{Na}_2\text{S}$  aqueous solution (0.1mL, 2 eqv.); (d) after 4 h; (e) after 12 h; (f) after 25h; (g) after addition of  $\text{Pb}(\text{NO}_3)_2$  (3 eqv.) to (f); (h) the photograph of the gel under 365 nm with a hand-held UV lamp.



**Scheme S1** Schematic representation of the possible arrangement of organogel C11-OG.



**Scheme S2** Schematic representation of the possible arrangement of metallogels Pb-MG.