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Rationally Designed Anion-Responsive-Organogels: Sensing F^- via Reversible Color Changes in Gel-Gel States with Specific Selectivity

Qi Lin,^{*a} Xin Zhu,^a Yong-Peng Fu,^a You-Ming Zhang,^a Ran Fang,^b Li-Zi Yang^b and Tai-Bao Wei^{*a}

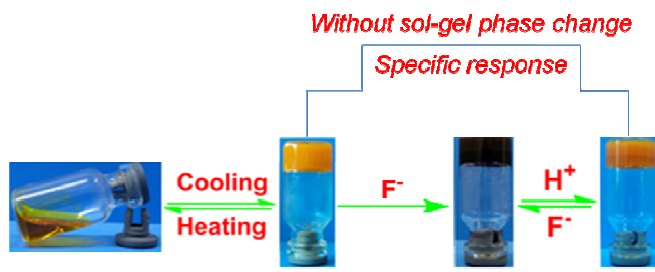
^a Key Laboratory of Eco-Environment-Related Polymer Materials, Ministry of Education of China; Key

Laboratory of Polymer Materials of Gansu Province; College of Chemistry and Chemical Engineering, Northwest

Normal University, Lanzhou, Gansu, 730070, P. R. China

^b College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, Gansu, 730070, P. R. China

Graphical Abstract



Anion-responsive organogel **OGL1** could reversibly sense F^- via dramatic color changes under gel-gel states with specific selectivity. **OGL1** could act as a facile and reusable smart materials for rapid detection F^- .

* Corresponding author. e-mail: linqi2004@126.com (Dr. Q. Lin), weitaobao@126.com (Prof. T.-B. Wei)

Rationally Designed Anion-Responsive-Organogels: Sensing F⁻ via Reversible Color Changes in Gel-Gel States with Specific Selectivity

Qi Lin,^{*a} Xin Zhu,^a Yong-Peng Fu,^a You-Ming Zhang,^a Ran Fang,^b Li-Zi Yang^b and Tai-Bao Wei^{*a}

^a Key Laboratory of Eco-Environment-Related Polymer Materials, Ministry of Education of China; Key

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Normal University, Lanzhou, Gansu, 730070, P. R. China

^b College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, Gansu, 730070, P. R. China

Abstract: Through the rational introduction of the multi self-assembly driving forces and F⁻ sensing sites into gelator molecule, low-molecular-weight organogelators **L1** and **L2** were designed and synthesized. **L1** and **L2** showed excellent gelation ability in DMF and DMSO. They could form stable organogels (**OGL1** and **OGL2**) in DMF and DMSO with very low critical gelation concentrations. **OGL1** and **OGL2** could act as anion-responsive organogels (AROGs). Unlike most of the reported AROGs showing gel-sol phase transition according to the anions' stimulation, **OGL1** could colorimetrically sense F⁻ under gel-gel states. Upon the addition of F⁻, **OGL1** showed dramatic color changes, while the color could be recovered by adding H⁺. Moreover, **OGL1** showed specific selectivity for F⁻, other common anions and cations couldn't lead to any similar response. What deserves to be mentioned is that the report on specific sensing of anions under gel-gel states is very scarce. The gel-gel state

* Corresponding author. e-mail: linqi2004@126.com (Dr. Q. Lin), weitaibao@126.com (Prof. T.-B. Wei)

recognition can endow the organogel **OGL1** with the merits of facile and efficient properties for rapid detection of F⁻. Therefore, **OGL1** could act as F⁻ responsive smart materials.

Keywords: sense in gel-gel states; anion-responsive organogel; specific selectivity; fluoride recognition

1. Introduction

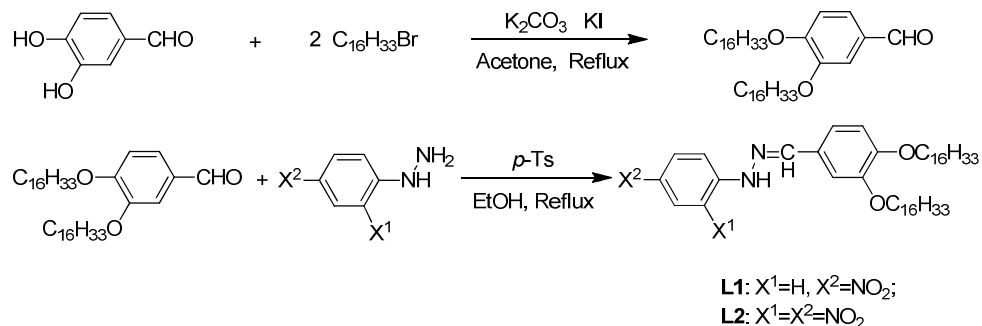
Smart materials which can sense, process, and actuate a response to an external change without assistance have been attracting considerable attentions due to their wide ranges of potential applications in sensors, biomaterials, surface science, displays, etc.^[1-3] Among them, stimuli-responsive supramolecular organogels are one kind of the most attractive examples.^[4-10] Supramolecular organogels are formed by assembling low-molecular-weight gelators (LMWGs) into physically crosslinked three-dimensional networks with solvent molecules entrapped inside through noncovalent intermolecular interactions, such as hydrogen bonding, π - π stacking, van der Waals (vdW), electrostatic interactions, and so on.^[11-19] Due to the weak nature of these forces, the gel-sol transition for organogels is thermally reversible and can be further tuned by other physical and chemical stimuli. These intriguing properties of organogels endow them with promising applications in optoelectronic devices, template syntheses, drug delivery, tissue engineering, catalysis, and biomimetic systems.^[20-24] Despite the great progress made recently in this field, there are two big

challenges in the field of designing novel organogels. One is how to improve the gelator's gelation ability and make sure that the designed gelator can self-assemble to desired organogel in certain solutions, the other is how to selectively detect a given chemical stimulus.

In addition, anions play a fundamental role in chemical, biological and environmental processes. More and more interests have been attracted in selective recognition and sensing of anions via artificial receptors. [25-35] Among the anions, fluoride anions are one of the most attractive targets because of their considerable significance for health and environmental issues. [36] Therefore, there is great demand for the development of methods that can rapidly, sensitively, and selectively detect the fluoride anion. [37-38] As we all know, an important feature of the chemosensor is its specific selectivity toward the analyte. Although considerable efforts have been made for the development of anion-responsive organogel (AROG) [4-10,12,15,39-44], few of AROGs could detect fluoride anions with specific selectivity.

Moreover, common AROGs realize the anion recognition *via* a reversible or irreversible gel-sol phase transition because the anion could be competitively bound to the gelator's self-assembly sites (e.g., hydrogen bonds or electrostatic interactions sites) and induce the dis-assembly of the organogel. To date, the reports of supramolecular organogel which could colorimetrically or fluorescently detect anions under gel-gel states without sol-gel phase change are very scarce. What's more the

gel-gel state recognition can endow the AROGs with the merits of facile and efficient properties for rapid detection of target anion.



Scheme 1. Structure and synthesis of the gelator **L1** and **L2**.

In view of this, as a part of our research interest in molecular recognition,^[43,45-49] herein, we report an AROG which could selectively recognize F^- via a dramatic color change under gel-gel states, the color could be recovered by adding H^+ . It is interesting to note that in the F^- recognition process, the organogel didn't carry out gel-sol phase change. In addition, other anions (such as AcO^- , $H_2PO_4^-$, Cl^- , Br^- , I^- , HSO_4^- and ClO_4^-) and common cations (such as Mg^{2+} , Ca^{2+} , Cr^{3+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Ag^+ , Cd^{2+} , Hg^{2+} and Pb^{2+}) couldn't lead to any similar response. Our strategy for the design of gelator **L1** (scheme 1) has been shown as follows. Firstly, in order to achieve specific selectivity for F^- , we rationally selected and introduced an F^- sensing group into the gelator molecule. There are lots of functional groups having been reported as F^- sensing groups, like urea, thiourea, amide, phenol, pyrrole, acylhydrazone and arylhydrazone and so on^[37-38]. Among them, the hydrazone group ($-CH=N-NH-$), as a sense site, possesses several merits. For example, there are two

different hydrogen bond donor sites (H-C=N- and -N-H) in the same group, both of which can act as anion binding sites as well as self-assembly sites. Furthermore, owing to the truth that the acidity of the “-N-H” is stronger than “H-C=N-”, the hydrazone group can sense F^- not only by forming hydrogen bonds ($F^- \cdots H-C=N-$) but also by a deprotonation process (deprotonation of -N-H). As a result, it can afford two kinds of sense approaches and enhance the sense selectivity for F^- . In the light of these considerations, we introduced hydrazone group into the gelator as F^- sensing sites and hydrogen bond donor groups. Secondly, in order to obtain an easy gelation and relative stable gelator, we introduced 3,4-bis(hexadecyloxy)phenyl group as a self-assembly group to provide strong vdW forces. In addition, since the arylhydrazone group and the 3,4-bis(hexadecyloxy)phenyl group were introduced into the same gelator molecule, the gelator possesses three kinds of self-assembly driving forces, including vdW forces, hydrogen bonding and $\pi-\pi$ stacking interactions. These designs provided the gelator **L1** with stronger gelation ability. Finally, with the aim to achieve colorimetric sense for F^- , a nitrophenyl group was introduced into the gelator as a colorimetric signal group.

2. Experimental Section

Synthesis of **L1**. 3,4-Bis(hexadecyloxy)benzaldehyde was synthesized according to literature methods.^[50, 51] 3,4-bis(hexadecyloxy)benzaldehyde (5.0 mmol), 4-nitrobenzenehydrazine (5.0 mmol) and catalytic amount of *p*-toluenesulfonic acid (*p*-Ts) were mixed in hot absolute ethanol (30 mL). The solution was stirred under

reflux conditions for 8 hours. After being cooled to room temperature, the yellow precipitate was filtrated and then recrystallized with CHCl_3 -EtOH to get compound **L1** (yield, 72%) as an orange powdery product: ^1H NMR (CDCl_3 , 400 MHz) δ 8.18 (d, $J = 6.9$ Hz, 2H, ArH), 7.91 (s, 1H, -NH), 7.70 (s, 1H, -N=CH-), 7.33 (s, 1H, ArH), 7.10-7.07 (m, 3H, ArH), 6.87 (d, $J = 6.3$ Hz, 1H, ArH), 4.06 (m, 4H, -OCH₂), 1.86 (m, 4H, -OCH₂CH₂), 1.51 (m, 4H, -CH₂CH₃), 1.35 (m, 48H, -C₁₂H₂₄), 0.87 (t, $J = 5.4$ Hz, 6H, -CH₂CH₃); ^{13}C NMR (CDCl_3 , 150 MHz) δ 150.85, 149.56, 149.37, 141.75, 139.93, 126.86, 126.25, 121.29, 112.75, 111.43, 110.26, 69.23, 31.88, 29.36, 25.99, 22.65, 14.10; IR (KBr, cm^{-1}) ν : 3505 (N-H), 2919, 2850 (C-H), 1596 (C=N), 1516, 1468 (C=C), 1111 (Ar-O-C). Anal. Calcd. for $\text{C}_{45}\text{H}_{75}\text{N}_3\text{O}_4$: C 74.85, H 10.47, N 5.82; Found C, 74.88, H, 10.41, N, 5.85. MS: m/z : 722.9 [**L1**+H]⁺; Calcd. for $\text{C}_{45}\text{H}_{76}\text{N}_3\text{O}_4$: 722.6.

Synthesis of **L2**. The compound **L2** (yield, 85%) was prepared by the similar procedure: ^1H NMR (CDCl_3 , 400 MHz) δ 11.30 (s, 1H, -NH), 9.16 (s, 1H, -N=CH-), 8.35 (d, $J = 7.2$ Hz, 1H, ArH), 8.06 (d, $J = 11.6$ Hz, 2H, ArH), 7.38 (s, 1H, ArH), 7.19 (d, $J = 8.4$ Hz, 1H, ArH), 6.91 (d, $J = 8.4$ Hz, 1H, ArH), 4.10-4.04 (m, 4H, -OCH₂), 1.89-1.84 (m, 4H, -OCH₂CH₂), 1.53-1.49 (m, 4H, -CH₂CH₃), 1.37-1.25 (m, 48H, -C₁₂H₂₄), 0.89 (t, $J = 6.4$ Hz, 6H, -CH₂CH₃). ^{13}C NMR (CDCl_3 , 150 MHz) δ 152.09, 149.46, 148.35, 144.72, 137.79, 137.23, 129.93, 128.97, 125.67, 122.76, 116.56, 112.60, 110.82, 69.32, 31.91, 29.66, 29.36, 25.99, 22.68, 14.11; IR (KBr, cm^{-1}) ν : 3443 (N-H), 2920, 2849 (C-H), 1616 (C=N), 1508, 1466 (C=C), 1133 (Ar-O-C). Anal.

Calcd. for $C_{45}H_{74}N_4O_6$: C 70.46, H 9.72, N 7.30; Found C, 70.48, H, 9.70, N, 7.25.

MS: m/z : 767.9 [$L2+H$]⁺; Calcd. for $C_{45}H_{75}N_4O_6$: 767.6.

Table 1. Gelation Properties of **L1** and **L2**.

	L1	L2
Solvent	State ^a (CGC ^b , CGT ^c)	State (CGC, CGT)
n-amyl alcohol	I	I
Ethanol	P	I
Acetone	S	I
Acetonitrile	P	I
DMSO	OG (0.6%, 58 °C)	OG (0.2%, 75 °C)
Toluene	S	S
Petroleum ether	P	P
THF	S	S
Chloroform	S	P
Dichloromethane	WG	P
Cyclohexanol	I	I
DMF	OG (3.1%, 38 °C)	OG (1.7%, 65 °C)

^aOG, opaque gel; S, solution; I, insoluble; WG, weak gel; P, precipitate.

^bCGC is the critical gelation concentration (w/v%, 10 mg/mL = 1%).

^cCGT is the gelation temperature (°C) at critical gelation concentration.

3. Results and Discussion

The gelation abilities of gelators **L1** and **L2** were examined in various solvents by means of the “stable to inversion of a test tube” method. The corresponding critical gelation concentrations (CGCs) at room temperature were also measured (Table 1). Gelators **L1** and **L2** could gel polar aprotic solvents dimethyl sulfoxide (DMSO) and N,N-dimethylformamide (DMF). More interestingly, **L1** and **L2** exhibited excellent

gelation abilities and very low CGCs in DMSO, and the CGCs of **L1** and **L2** were 0.6 % (for **L1**) and 0.2 % (for **L2**) respectively. Moreover, in DMSO, the sol-gel transition was very rapid. The whole transition process only took less than 3 mins after stopping heating the DMSO solution. The gel-sol transition temperature (T_{gel}) was measured by using the ‘tilted tube’ method. With regularly increasing the concentration of **L1** and **L2**, the T_{gel} reached a limit of 79 °C and 111 °C respectively (**Figure 1**). These gels were found stable in closed tubes for at least 3 months at 25 °C. According to the CGCs and T_{gel} of **L1** and **L2**, we could find that **L2** was more stable than **L1**, because the **L2** contained more nitro groups than **L1** and the nitro groups could act as the hydrogen bonds acceptor for these gelators.

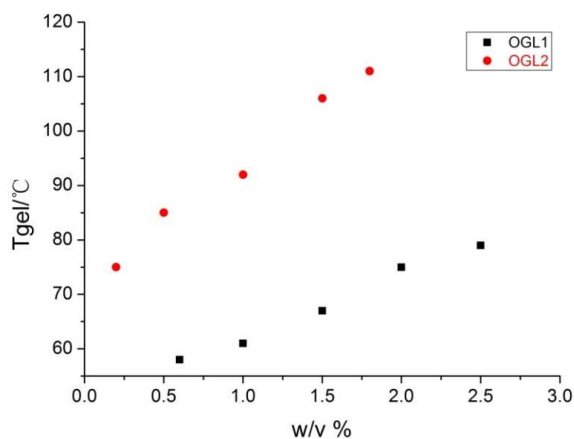


Figure 1. Plots of T_{gel} versus the concentration of **OGL1** and **OGL2** obtained from DMSO.

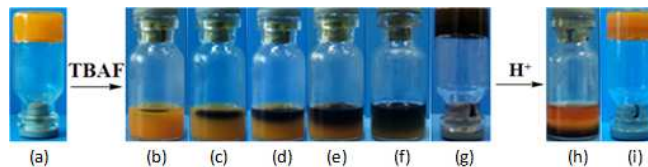


Figure 2. a) Organogel **OGL1** (0.8 %, in DMSO); b) immediately after addition of solid TBAF (5 equiv.); c) after 30 min; d) after 90 min; e) 150 min; f) and g) after 220 min; h) addition of 0.05 mL HClO₄ (0.01 M) after 10 min; i) after 20 min.

Since gelators **L1** and **L2** could form stable organogel in DMSO, a series of experiments were carried out to investigate the anion response capability of the organogels formed by gelators **L1** and **L2** in DMSO (named **OGL1** and **OGL2** respectively). As we expected, the **OGL1** and **OGL2** exhibited excellent color changes according to the stimulus of fluoride ion. As is shown in **Figure 2**, upon the addition of F⁻ (5 equiv., solid Bu₄NF) to the **OGL1** at 25 °C, a dramatic color change from yellow to dark brown instantly took place on the surface of **OGL1**. The color of whole gels changed in ca. 4 hours with the F⁻ diffusion into the gels. Additionally, the color of the **OGL1** could be recovered by adding proton solutions such as HClO₄ solution, MeOH or water. It is very interesting that unlike most of the reported AROGs which showed gel to solution phase transition according to the fluoride anion's stimulation, the gel state of **OGL1** didn't show any changes in the whole F⁻ response process. The T_{gel} of F⁻-contained gel is 52 °C and the hot solution of F⁻-contained gel could recover to the gel states after cooling the sol to room temperature. This special stability could be attributed to the cooperation of the above-mentioned multi self-assembly forces (vdW forces, hydrogen bonding and π - π

stacking interactions) we rationally introduced to the gelators. Simply stated, because there are three kinds of self-assembly driving forces in the same gelator, even if the hydrogen bonds were destroyed by F^- , the remaining two forces could maintain the organogels' gel states. Meanwhile, owing to the breaking of hydrogen bonds, the T_{gel} of **OGL1** changed from 79 °C to 52 °C. Under the same conditions, **OGL2** showed similar response for F^- .

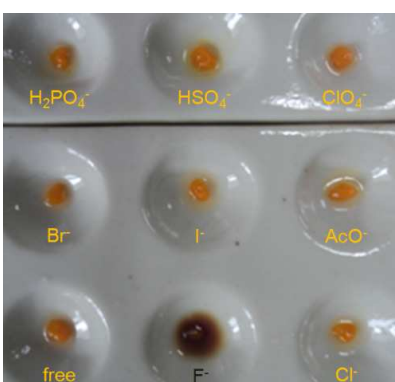


Figure 3. Color changes immediately after the addition of various anions (one drop, ca 0.02 mL) to organogel **OGL1** (0.8 %, in DMSO) on a spot plate respectively.

The selectivity of organogels for anions was also investigated. As is shown in **Figure 3**, when DMSO solutions of various anions (F^- , Cl^- , Br^- , I^- , AcO^- , $H_2PO_4^-$, HSO_4^- and ClO_4^-) were added to the small amounts of organogel **OGL1** on a spot plate, respectively, only F^- could induce an instant color change of **OGL1**. Other anions couldn't induce any color or organogels' state change, which indicated that **OGL1** could instantly sense F^- with specific selectivity. The selectivity tests were also carried out in the DMSO solution of gelator **L1**. As is shown in **Figure 4**, in DMSO

solution, the gelator **L1** could selectively response F^- by color change. In the corresponding UV-vis spectra, upon addition of F^- , the absorption of **L1** at 430 nm shifted to 570 nm. Similarly, the color and the UV-vis absorption could be restored by adding proton solutions (Figure S1a in ESI). As is shown in **Figure 4&5**, other anions (Cl^- , Br^- , I^- , AcO^- , $H_2PO_4^-$, HSO_4^- and ClO_4^-) and common cations (such as Mg^{2+} , Ca^{2+} , Cr^{3+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Ag^+ , Cd^{2+} , Hg^{2+} and Pb^{2+}) couldn't cause any significant color or spectra response. Therefore, the gelator **L1** could response F^- with specific selectivity. However, under similar conditions, the addition of AcO^- or $H_2PO_4^-$ also led to the color of **OGL2** changing from yellow to red (**Figure 4**) and the color and UV-vis absorption could be restored by adding proton solutions too (Figure S1b in ESI). Thus, the **OGL2** could response F^- , AcO^- and $H_2PO_4^-$ without specific selectivity.

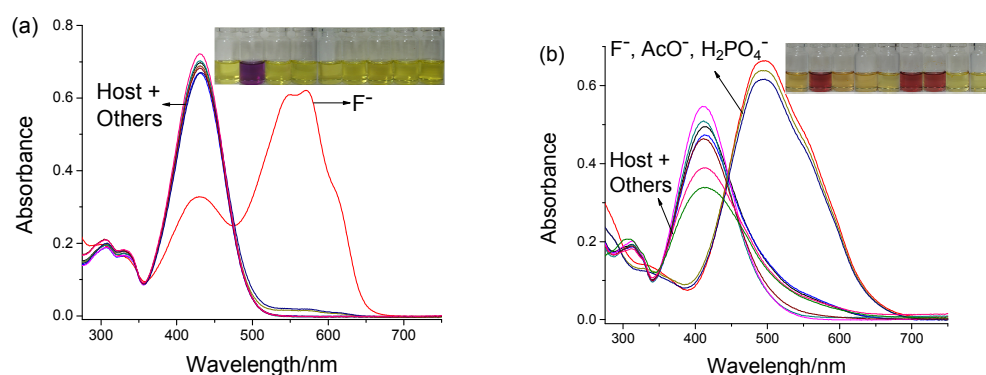


Figure 4. UV-vis spectra response of a) **L1**; b) **L2** (2.0×10^{-5} M) in DMSO upon the addition of 50 equiv. of various anions. Inset: photograph of a) **L1**; b) **L2** (2.0×10^{-5} M) upon adding 50 equiv. of various anions in DMSO, from left to right: none, F^- , Cl^- , Br^- , I^- , AcO^- , $H_2PO_4^-$, HSO_4^- , ClO_4^- .

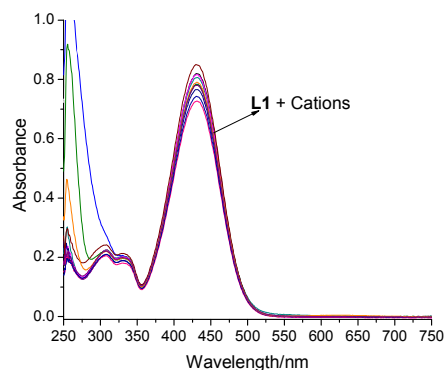


Figure 5. UV-vis spectra of **L1** (2.0×10^{-5} M) in DMSO upon the addition of 10 equiv. of various cations (Mg^{2+} , Ca^{2+} , Cr^{3+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Ag^{+} , Cd^{2+} , Hg^{2+} and Pb^{2+}).

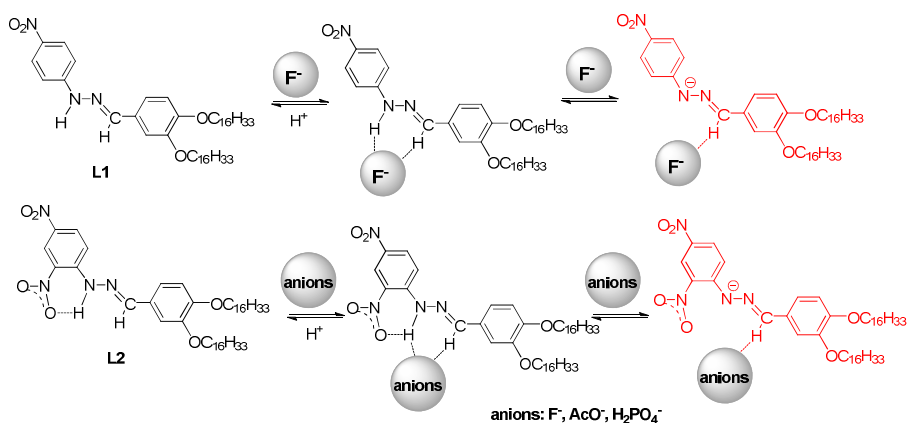


Figure 6. A possible mechanism of the **L1** and **L2** response to F^- or anions.

According to these results we can find that the **L1** and **L2** showed different anion response selectivity. Because in the molecule of **L2**, there is an intramolecular hydrogen bond between hydrazone $-\text{N}-\text{H}$ and ortho nitro group (**Figure 6**). This hydrogen bond enhanced the acidity of the $-\text{N}-\text{H}$ group. Therefore, the $-\text{N}-\text{H}$ group in **L2** could carry out a deprotonation process not only with F^- but also with AcO^- and

H_2PO_4^- . This assumption was confirmed by the ^1H NMR. The -N-H proton chemical shift of **L1** appeared at 7.91 ppm, while in the **L2** the -N-H signal appeared at 11.30 ppm, which indicated that the -N-H group of the **L2** is more easily to deprotonate than the **L1**.

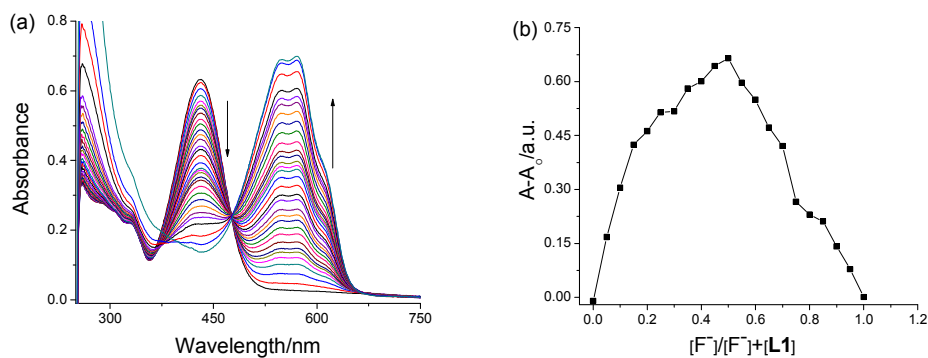


Figure 7. a) UV-vis spectral titration of **L1** (2.0×10^{-5} M) with F^- in DMSO solution. b) Job's plot for complex of **L1** and F^- (in DMSO solution), which indicated that the stoichiometry of **L1**- F^- is 1:1.

The anions response mechanisms of **L1** and **L2** were carefully investigated by various methods. According to the absorption titration experiments (**Figure 7a**), upon the gradual addition of F^- to the solution of **L1**, an isosbestic point at 475 nm was observed. Moreover, in the Job's plots (**Figure 7b**), the absorbance value approached the maximum when the molar fraction of **L1** was 0.5, which demonstrated the formation of a 1:1 complex between **L1** and F^- . By the Benesi–Hildebrand equation fitting^[52] at $\lambda_{\text{max}} = 571$ nm for **L1**, the association constant K_a of **L1** with F^- was obtained as $1.67 \times 10^3 \text{ M}^{-1}$.

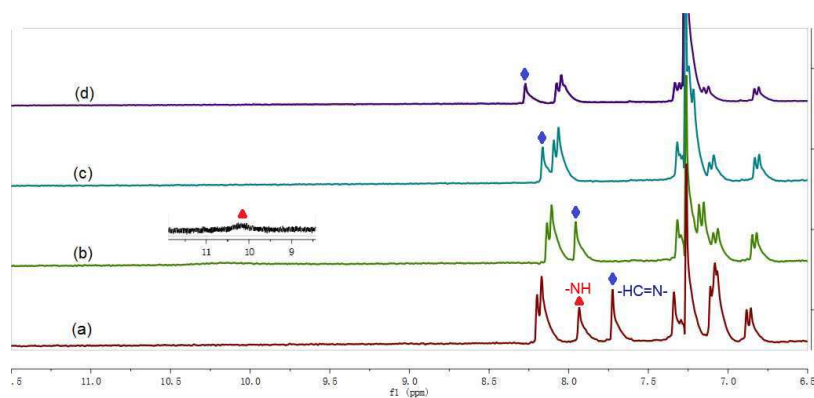


Figure 8. Partial ^1H NMR spectra of **L1** (0.01 M) in CDCl_3 upon the addition of F^- a) Free; b) 0.2 equiv. of F^- ; c) 0.5 equiv. of F^- ; d) 1.0 equiv. of F^- .

The further **L1**- F^- reaction mechanism was investigated by F^- - ^1H NMR titration, ^{19}F NMR and ESI-MS experiments. As shown in **Figure 8**, in the F^- - ^1H NMR titration spectra, before the addition of F^- , chemical shifts of the N-H and -HC=N- protons on **L1** appeared at δ 7.91 and 7.70 ppm. After the addition of 0.2 equiv. of F^- , the signal of these two protons shifted downfield. With the continuous addition of F^- , the N-H signal completely disappeared; meanwhile, the -HC=N- signal shifted downfield at δ 8.30 ppm. These phenomena indicated that the N-H group might undergo a deprotonation process and the -HC=N- group formed a $\text{F}^- \cdots \text{H-C=N-}$ hydrogen bond (**Figure 6**). The deprotonation process induced the color changes of the **L1** solution and **OGL1**. This process could be confirmed by adding proton solutions to the **OGL1** containing F^- . After adding proton solutions, the color of the solution or gel turned yellow again.

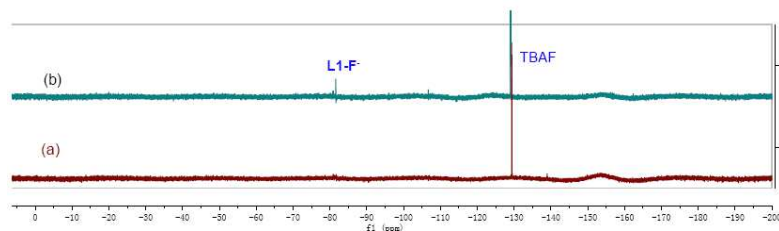


Figure 9. Partial ^{19}F NMR spectra of a) TBAF, b) **L1** + TBAF (50 equiv.).

The presumed F^- response mechanism was also supported by the ^{19}F NMR and EI-Mass respectively. As shown in the **Figure 9**, in the ^{19}F NMR spectra of TBAF, the signal of F^- appeared at -129.36 ppm. While after the addition of 50 equiv. TBAF into the $\text{DMSO-}d_6$ solution of **L1**, two ^{19}F signals appeared in the corresponding ^{19}F NMR spectra at -129.03 and -81.56 ppm respectively. The signal at -129.03 was attributed to the excess TBAF and the signal at -81.56 was attributed to the **L1-F $^-$** complex. Meanwhile, in the ESI-MS spectra of sensor **L1**, the [**L1** + H] $^+$ peak appeared at 722.9 (m/z calcd = 722.6). However, when 50 equiv. of F^- was added to the solution of **L1**, a new peak appeared at 764.7, coinciding well with that for the species [**L1** + F^- + Na^+ + H] $^+$ (m/z calcd = 764.6) and indicating the formation of the stabilized anionic species **L1-F $^-$** .

Moreover, in order to provide more adequate evidence for the possible anions response mechanism, the ^1H NMR titration experiments of **L1** and **L2** with AcO^- were carried out. As shown in **Figure S2**, chemical shifts of the N-H and -HC=N- protons on **L1** appeared at δ 7.91 and 7.70 ppm. After the addition of 0.5 equiv. of AcO^- , the signal of these two protons shifted downfield. After the addition of 2 equiv. of AcO^- ,

the signal of these two protons shifted to 10.66 and 8.03 ppm, respectively. These results indicated that the N-H and -HC=N- protons on **L1** formed stable hydrogen bonds with AcO⁻. Thus, unlike that F⁻ could induce the deprotonation of N-H on **L1**, AcO⁻ could not deprotonate N-H of **L1**. Therefore, AcO⁻ couldn't lead to the color change of **L1** and **OGL1**. The similar experiments were carried out for **L2** with AcO⁻. As shown in **Figure S3**, in the ¹H NMR of **L2**, the N-H and -HC=N- protons on **L2** were at δ 11.3 and 9.16 ppm. Upon the addition of AcO⁻, the N-H signal at 11.3 ppm disappeared, indicating the deprotonation of the -N-H group. Usually, the deprotonation of the N-H on hydrazone moiety would induce the proton signal of -HC=N- shifted to upfield while the formation of hydrogen bonds would induce the proton signal of -HC=N- shifted to lowfield. When the two events took place simultaneously, the signal of -HC=N- group would not show obvious shift. Upon the addition of AcO⁻, the -HC=N- proton signal of **L2** didn't show obvious upfield-shift, which indicated that the AcO⁻ formed hydrogen bonds with -HC=N- group (**Figure 6**).

The self-assembly mechanism was investigated by ¹H NMR, FT-IR, DFT calculations, X-ray diffraction and SEM. According to the results of concentration dependent ¹H NMR experiments (**Figure 10**), the NH resonance signals gradually shifted downfield as the concentration of **L1** rose. Moreover, in the FT-IR (**Figure 11**) the N-H vibration absorption of powdery **L1** appeared at 3505 cm⁻¹ while it shifted to 3470 cm⁻¹ in xerogel. These results revealed that the NH groups formed hydrogen bonds in the gelation process.

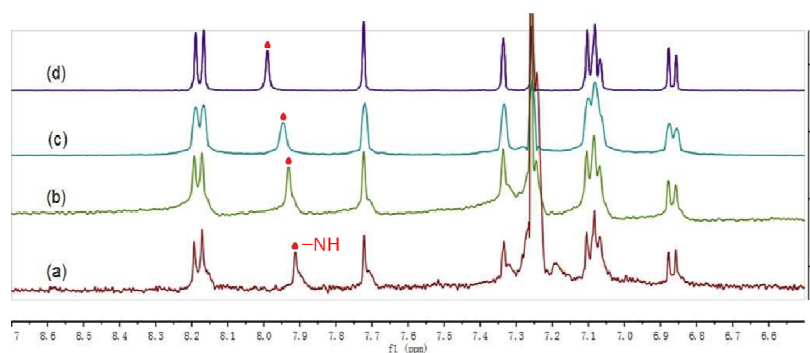


Figure 10. Partial ^1H NMR spectra of **L1** in CDCl_3 with different concentrations a) 0.6 mM; b) 2.8 mM; c) 13.9 mM; d) 27.7 mM.

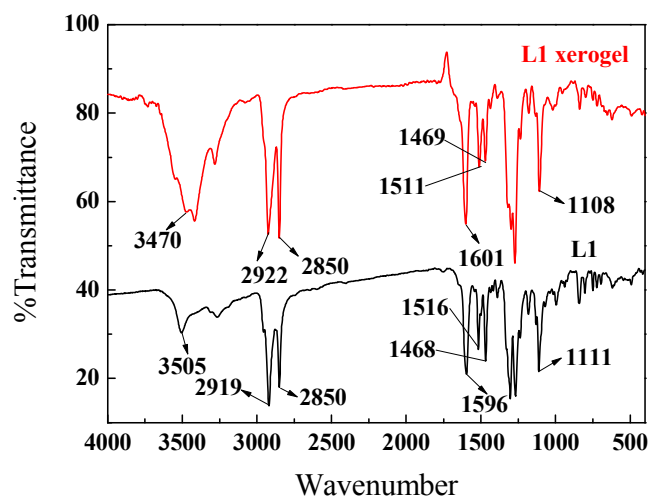


Figure 11. FT-IR spectra for powdered **L1** and xerogel of **OGL1** (0.8 % in DMSO).

These presumptions were confirmed by the optimized self-assembly model obtained by DFT calculations. As is shown in **Figure 12**, the nitro group on one gelator formed two intermolecular hydrogen bonds with the NH and CH group on the other gelator molecule (bond length: $-\text{N}-\text{H}\cdots\text{O}$, 14 Å; $-\text{C}-\text{H}\cdots\text{O}$, 2.508 Å).

There were π - π stacking interactions in neighbouring nitrophenyl groups, and the distance between the two phenyl groups was 3.84 Å. Therefore, the gelator **L1** could self-assemble to stable organogel via the hydrogen bonds, π - π stacking interactions, and vdW interactions.

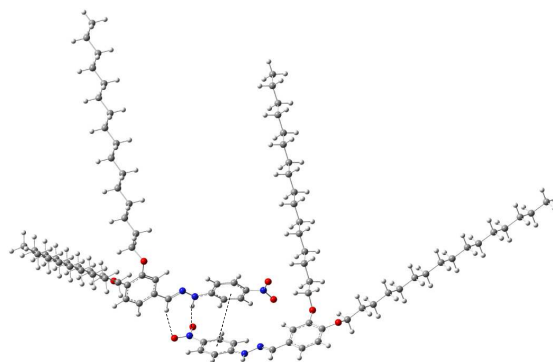


Figure 12. Optimized self-assembly model of **OGL1** obtained by DFT calculations.

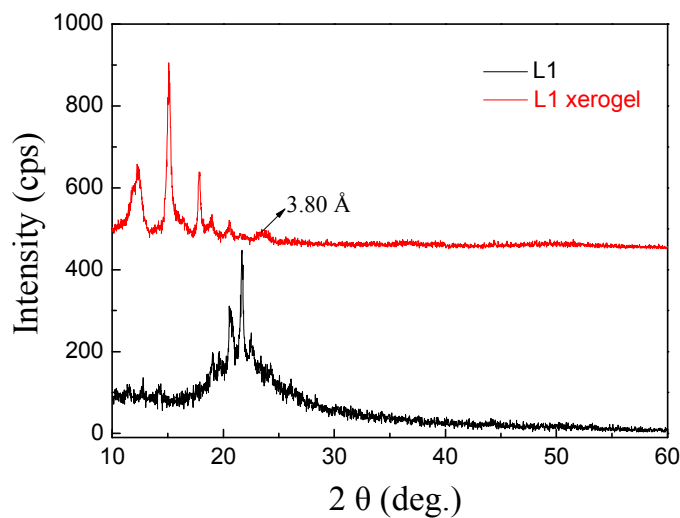


Figure 13. Powder X-ray diffraction patterns for powdered **L1** and xerogel of **OGL1** (0.8 % in DMSO).

Moreover, the X-ray diffraction patterns (**Figure 13**) of **OGL1** xerogel showed periodical diffraction peaks, indicating that **L1** indeed assembled into an ordered structure. The d-spacing of 3.80 Å at $2\theta = 23.42$ suggested that π - π stacking existed between the phenyl groups of gelator **L1**, which also supported the self-assembly assumption.

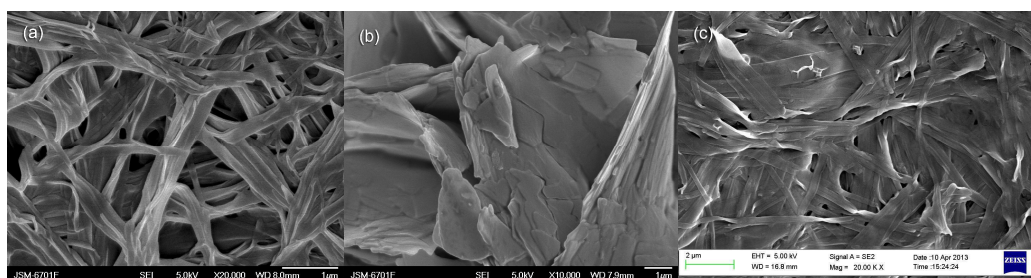


Figure 14. SEM images of a) xerogel of **OGL1** (0.8 %, in DMSO); b) **OGL1** xerogel treated with F^- in situ; c): **OGL1** xerogel treated with F^- in situ, then added $HClO_4$ (0.01 M).

The SEM images of **OGL1** showed a network structure consisting of many entangled tape-like structures. These tapes were approximately 10-30 nm in width and several μm long (**Figure 14a**). It was very interesting that although the macro phase of **OGL1** couldn't change under the stimulation of F^- , on micro level, the self-assembly process was actually influenced by F^- . As is shown in (**Figure 14b**), upon the addition of the F^- , the entangled tape-like structure (**Figure 14a**) of **OGL1** changed to a rugate layer structure (**Figure 14b**). This phenomenon could be attributed to the deprotonation of N-H group by the attack of F^- . When the N-H group was deprotonated, the hydrogen bonds between the gelators were destroyed, and the

gelators were assembled by vdW forces among long alkyl chains and π - π stacking interactions among nitrophenyl groups. Therefore, the micro morphology of **OGL1** changed as is mentioned above. When adding the proton solutions (HClO_4 , H_2O etc.) to the **OGL1** containing F^- , the micro morphology restored (**Figure 14c**).

Conclusion

In summary, we have developed an excellent organogel **OGL1** which could act as F^- responsive smart material for instant colorimetric detecting F^- with specific selectivity under gel-gel states as well as in DMSO solutions. The color change induced by F^- could be recovered by adding proton solutions. Other anions and common cations did not cause any similar stimuli response. With the cooperation of multi self-assembly driving forces we rationally introduced into the gelator, **L1** showed excellent gelation capability in DMSO and DMF. Of particular significance, in the F^- sensing process, the organogel didn't carry out any gel-sol phase change on macro level, which is very rare in the research of anion responsive organogels. The gel-gel state recognition has the merits of facile and efficient properties. The experimental study presented herein has important potentials for the fabrication of smart materials in anion sensing applications.

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