A novel smart organogel which could allow a two channel anion response by proton controlled reversible sol–gel transition and color changes†

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A super gelator (F3) with an excellent gelation ability was synthesized; the organogel of F3 could allow two channel recognition of F^-, AcO^- and $H_2PO_4^-$ through proton controlled reversible sol–gel transition and color changes.

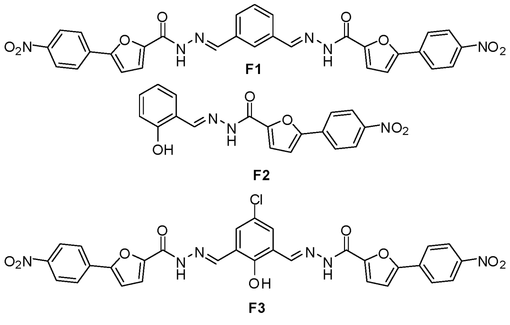
Recently, low-molecular mass organogelators (LMOG) have attracted substantial attention[1] in supramolecular chemistry and materials science due to their unique characteristics and wide range of potential applications. For example, organogels could be used as templates of nano-scale inorganic materials,[2] organic soft materials,[3] optical sensors,[4] slow drug-delivery systems[5] and so on. In an organogel the gelator molecules self-assemble into nanoscale superstructures, such as fibers, rods, and ribbons through weak noncovalent interactions (*i.e.*, hydrogen bonding, π–π stacking, van der Waals, coordination, and charge-transfer interactions).[1,6] Of particular interest for organogel material science are "smart gels", *i.e.* gels whose properties can be controlled reversibly or irreversibly in response to changes in external chemical,[7a–g,8] photochemical,[9] thermal stimuli[6,10] or sound.[7h] To date, there have been reports on organogels that are responsive to pH changes,[8] light,[9] catalysis,[11] and cation[12] recognition. However, only a few reports currently exist on the controllable gelation systems based on reversible changes of a gelator molecule induced by anions stimuli.[7a–g]

Over the past thirty years, more and more interest has been attracted to the selective recognition and sensing of anions *via* artificial receptors, because anions play fundamental roles in chemical, biological and environmental process.[13] Although previous work developed a wide variety of anion sensors based on electrostatic interactions, hydrogen bond donor groups, Lewis acid groups and hydrophobic interactions, it is still a challenge to design and synthesize anion sensors with single selectivity and high sensitivity for certain anions.[13,14] Moreover, most of these anion sensors have been employed in solution by means of spectroscopic instrumentation. This will significantly restrict the practical applications of these anion sensors. For simplicity, convenience and low cost, the fabrication of small molecular anion sensors into colorimetric test kits is highly demanding.[13,15] It is interesting that most of the organogels reported thus far using amide or urea units as hydrogen bonding sites that support molecular assembly. However, amide or urea units often act as anion binding sites in anion receptors. Therefore in organogel, if the hydrogen bonding donor NH sites in the amide or urea units interact with anions, the gelators may not form stable assemblies, resulting in the transformation of the gels, for example, into a solution. In this case, the organogel is so-called anion-responsive gel.[7e]

As an attempt to obtain a smart anion-responsive gel with potential anion sense applications, we have designed and synthesized a gelator (**F3**) bearing phenol O–H and acylhydrazone N–H groups (Scheme 1). Interestingly, **F3** could form very stable organogel in *N*,*N*-dimethyl formamide (DMF). It is exciting that the organogel of **F3** could allow two channels response for F^-, AcO^- and $H_2PO_4^-$ through proton controlled reversible gel–sol transition and color changes.

The most impressive gelation ability of **F3** was observed in polar solvents such as DMF and DMSO (Table 1). As a general procedure, the powdery **F3** was completely dissolved in hot DMF (≥15.6 mM), after cooling to ambient temperature, the vessel was turned upside down and the fluidity of the system was absent, it was denoted as a gel (Fig. 1a). However, much to our surprise, in DMF, the sol–gel transition is very rapid. The whole transition process only takes less than 2 min after stop heating the DMF solution (23.3 mM). The DMF gel is very stable, for example, the gel–sol transition temperature, T_{gel}, was measured by using the 'tilted tube' method and increasing regularly with concentration of **F3** and reaching a limit at 151 °C from a 23.3 mM gel. The gel was quite stable for more than one year at room temperature without phase separation.

Moreover, **F3** could act as a super gelator for dimethylsulfoxide (DMSO). In DMSO, the gelation took place at a low **F3** concentration of only 3.1 mM (0.2 wt%). Such an ability to gelate solvents at concentrations lower than 1 wt% (15.6 mM for **F3**) is classified as super-gelation.[16] Gel formation was not observed in other solvents or solvent mixtures such as aliphatic



Scheme 1

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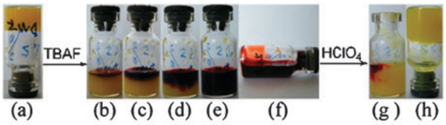

Fig. 1 (a) Organogel formed from a solution of **F3** in DMF (23.3 mM); (b) Immediately after addition of solid TBAF (5 eqv.); (c) after 2 min; (d) after 8 min; (e) and (f) after 15 min; (g) Immediately after addition of 0.30 mL $HClO_4$ (0.1 M) to the above obtained solution; (h) The "stable-to-inversion test" succeeds after addition of $HClO_4$ 2 min.

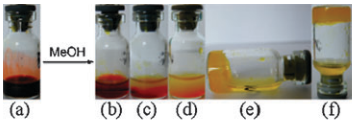

Fig. 2 (a) The solution obtained from the DMF gel reacted with solid TBAF salt (5 eqv.); (b) immediately after addition of methanol (0.20 mL); (c) after 1 min; (d) after 2 min; (e) after 7 min; (f) after 8 min (the small amount of solution is excess methanol).

Table 1 Gelation properties of **F3**

Solvent	Concentration/mM	Phase^a	Gelating time	T_{gel}/°C
DMF	<15.6	SP	—	—
DMF	15.6	OG	5 min	98
DMF	23.3	OG	2 min	151
DMSO	<3.1	S	—	—
DMSO	3.1	TG	*ca.* 1 month	45
DMSO	15.6	GP	*ca.* 1 day	56
DMSO	>62.2	GP	10 min	92

^{a} SP, solution and precipitate; OG, opaque gel; S, solution; TG, translucent gel; GP, gel and precipitate.

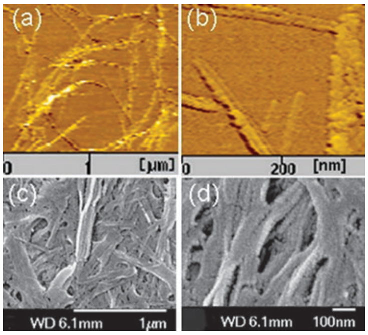

Fig. 3 (a) and (b) AFM images of xerogel from DMSO gel of **F3** (scale bar: (a) = 1 μm; (b) = 200 nm); (c) and (d) SEM images of xerogel from DMF gel of **F3** ((scale bar: (c) = 1 μm; (d) = 100 nm)).

solvents, ethers, ethanol, and tetrahydrofuran due to the poor solubility of **F3**. In order to investigate the influence of the O–H group and the molecular structure on the gelating abilities of **F3**, we also designed **F1** and **F2**. **F1** is an analogue of **F3** but does not contain the O–H groups. **F2** resembles the single arm of **F3**. Compounds **F1** and **F2** could not gelate DMF or DMSO. The results of these comparisons indicate that the molecular structure and phenol O–H group play a critical role in the gelation process.

The morphology of the organogel was investigated by atomic force microscopy (AFM) images and cold field emission scanning electron microscope (SEM). The AFM images of DMSO gel (3.1 mM) show a network structure consisting of many entangled tape-like aggregates of widths between 30–60 nm and lengths of several μm (Fig. 3a,b). In addition, the SEM images of DMF gel (23.3 mM) reveal a well-defined network, tape-like structure as well. These tapes are approximately 50–200 nm in width and several μm long (Fig. 3c,d).

Owing to the fact that **F3** is an efficient gelator of polar solvents, we believe that hydrogen-bonding interactions contribute to the stabilization of the self-assembled aggregates. To obtain further insights we measured FT-IR spectra of **F3** in the solid state, the gel phase and the sol phase (fresh solution in DMF) (Fig. S1 in the ESI†). The FT-IR spectra of the xerogel showed the presence of bands belonging to O–H and N–H groups at 3433 and 3333 cm^{-1} respectively. While, in solution, the bands of O–H and N–H were combined into a broad band which appeared at 3482 cm^{-1}. However, in organogel, the broad band of O–H and N–H shifted to 3450 cm^{-1}, which indicate the O–H and N–H groups participate in the formation of intermolecular hydrogen bonds among the gelator molecules. An optimized hydrogen bonding self-assemble model obtained by DFT studies agrees with the evidences (Fig. S2 in the ESI†). Moreover, the self-assembled structure of the organogel is also supported by XRD analysis (Fig. S3 in the ESI†). The xerogel of **F3** exhibited well-resolved X-ray diffraction patterns that were characteristic of the long-range ordering of the molecules.

As we expected, the organogel of **F3** exhibited excellent reversible gel–sol transition according to the stimulus of anions. As shown in Fig. 1b–f, the addition of F^- (5 equiv.) as its TBA salt (solid Bu_4NF) to the DMF gel of **F3** at 20 °C effected a gradual decomposition of the gelatinous state in *ca.* 15 min, yielding an wine-colored solution. Similarly, the addition of solid TBA salts of AcO^- or $H_2PO_4^-$ also lead to the DMF gel of **F3** decomposed to corresponding red-colored solutions. While, these transition need 10 min for adding AcO^- and 27 min for $H_2PO_4^-$ respectively. In the same conditions, the addition of Cl^-, Br^-, I^-, HSO_4^- and ClO_4^- (all used as solid TBA salts) could not lead to the gel decomposition. These results support the assumption that the anions such as F^-, AcO^- and $H_2PO_4^-$, not TBA cations, are responsible for the transformation of the organogel to solution. On the other hand, according to the speed difference of the gel–sol transition, we could conclude that the anion affinities sequence of the gelator is $AcO^- > F^- > H_2PO_4^- \gg Cl^-$, Br^-, I^-, HSO_4^- and ClO_4^-.

The organogel of **F3** could not only sense F^-, AcO^- and $H_2PO_4^-$ in their solid TBA salts, but also could colorimetrically sense these anions in their DMSO solutions. As shown in Fig. S4 (in the ESI), when adding 0.02 mL DMSO solution (10 mM) of F^-, AcO^- or $H_2PO_4^-$ (tetrabutylammonium was used as a countercation) to the small amount gel (*ca.* 0.01 g), the gels showed dramatic color changes from yellow to nacarat (for F^-), red (for AcO^-) or orange (for $H_2PO_4^-$) respectively. The same tests were applied to Cl^-, Br^-, I^-, HSO_4^- and ClO_4^-, no obvious color change was observed. In addition, As shown in Fig. S5, S6 (in the ESI),† the solution of **F3** could colorimetrically sense F^-, AcO^- or $H_2PO_4^-$ also.

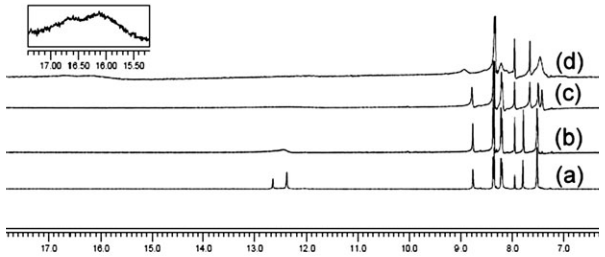

Fig. 4 Partial ^{1}H NMR spectra of compound **F3** (2.5 mM) in DMSO-d_6 upon the addition of F^-. (a) Free, (b) 0.5 equiv. of F^-, (c) 1 equiv of F^-, (d) 4 equiv. of F^-.

The further anion–**F3** reaction mechanism was observed from ^{1}H NMR titration experiments (Fig. 4, S7 in the ESI) in DMSO-d_6. Before the addition of anions, the ^{1}H NMR chemical shifts of the N–H, O–H and $-HC{=}N-$ protons on **F3** were at δ 12.66, 12.39 and 8.75 ppm, respectively. After adding 0.5 equiv. of F^-, the resonances for N–H and O–H protons disappeared, and a weak broad signal appeared at δ 12.44 ppm, which indicated the formation of $N\text{–}H\cdots F^-$ and $O\text{–}H\cdots F^-$ hydrogen bonds. With continuous addition of F^-, this signal disappeared also, which suggested that the O–H and N–H groups perhaps underwent a deprotonation process. Simultaneously, a new weak broad signal appeared at δ 16.15 ppm, which indicated the formation of HF_2^-.[17]

According to the ^{1}H NMR titration experiments we could presume the mechanism of anion induced gel–sol transition. Upon the addition of F^-, AcO^- or $H_2PO_4^-$, owing to the deprotonation of O–H and N–H, the intermolecular hydrogen bonds which assembled the gelator to gel were broken. Hence the gel transitioned to solution. Meanwhile, the deprotonation of phenol O–H group induced the color change of the gelator from orange to red. While, the basicity of Cl^-, Br^-, I^-, HSO_4^-, and ClO_4^- are much weaker than F^-, AcO^- and $H_2PO_4^-$. Therefore Cl^-, Br^-, I^-, HSO_4^-, and ClO_4^- can not lead to the phenol OH group deprotonation. So the organogel can not respond to such anions.

Since the root causes of the anion induced gel–sol transition is deprotonation, we presume that addition of proton could lead to re-gelation of the solution where gel disintegrated. This presumption was confirmed by our experiments. As shown in Fig. 1g, when 0.3 mL of $HClO_4$ (0.1 M) was added to the solution which was obtained from F^- disintegrated gel, the solution re-gelated immediately. Meanwhile, the wine-colored solution changed to yellow gel again. Interestingly, protic solvents such as H_2O and methanol could re-gelate the gel disintegrated solution as well (Fig. 2). The re-gelation speed is depending on the proton concentration of the solvent. For example, at same conditions, the sequence of re-gelation speed is $HClO_4 > H_2O >$ methanol.

In summary, a super gelator **F3** bearing phenol O–H and acylhydrazone N–H groups was synthesized. It has showed an excellent gelation ability towards DMF and DMSO. The organogel of **F3** could allow two channels recognition for F^-, AcO^- and $H_2PO_4^-$ through reversible gel–sol transition and color changes. We have demonstrated that the reversible gel–sol transition processes were controlled by proton. When the gelator reacted with basic anions such as F^-, AcO^- or $H_2PO_4^-$, the gelator was deprotonated, then, the gel disintegrated. While when the solution of disintegrated gel obtained proton from protic solvents, the solution re-gelated to gel again. Due to the smart gel reported here is very stable at room temperature, we believe the gel could act as a convenient and efficient anion test kit.

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