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# Solvent-dependent photophysical and anion responsive properties of one glutamide gelator<sup>†</sup>

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One gelator consisting of four amide units and one chromophore was designed and synthesized. These four amide groups could induce the self-assembly of the gelator molecules in one-dimensional (1-D) direction. Two cyano and one nitro terminal groups were also appended into the chromophore as electron withdrawing groups to make the gelator's own typical D– $\pi$ –A electron structure. As a result, it was found that the color of the gel phases, the sol–gel phase transition temperature, microscopic morphologies, emission behaviour and response to anions were dependent on the solvent because of the different packing models and solvation effect in different solvents. For example, the color of the DMSO gel was orange, but ODCB gel possessed a yellow color. In addition, multicolor emission could be realized in DMSO gel systems, but ODCB gels only emitted yellow fluorescence. Moreover, the gelator was responsive to F<sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and OAc<sup>-</sup> in DMSO, but in ODCB it selectively responded to F<sup>-</sup>.

# Introduction

Smart materials and systems have been attracting increasing attention because they can significantly change their mechanical properties (such as shape, stiffness, and viscosity), or their thermal, optical, or electromagnetic properties, in a predictable or controllable manner in response to their environment, such as stress, temperature, moisture, pH, electric or magnetic fields.1 In particular, smart functional organogels, formed by a large amount of organic solvents and a low-molecular mass compound with low concentration (typically <2 wt%), have been widely developed in recent years, because their bulk shape and properties can be either switched or tuned by an external chemical or physical stimulus, such as metal ions, anions, small organic compounds, proton, light irradiation, oxidation or reduction reaction, sound and temperature by introducing unique functional moieties.<sup>2</sup> It is well known that a given gelator can only gelatinize some special solvents. Sometimes, a little difference between solvent structures can lead to obvious differences in gel properties, such as the sol-gel phase transition temperature, morphologies of the molecular aggregates and rheological behaviour.<sup>3</sup> In this paper, we would like to show how the selected

solvents can influence the thermotropic, photophysical and anion-responsive properties of the gels formed by a glutamide derivative with electron-withdrawing groups.

Based on the results obtained in our previous works,<sup>4</sup> in which two gelators with electron withdrawing and donating groups were reported and their photophysical properties in gel phases could be tuned by solvents. It can be confirmed that  $D-\pi-A$ structure of chromophores in gelator molecules is an important factor to achieve adjustable photophysical properties of gels through changing solvents with different polarities. In addition, so far most of the anion-responsive gels reported comprise anion receptors, such as amide, amine or urea units, which also act as hydrogen bond sites that support molecular assembly. Moreover, the works reported by other groups suggested that it was a sensible choice that the anion acceptor was directly linked to chromophores so that the response of the gels to anion stimulus was visible to the naked eye due to obvious color changes.<sup>5</sup> Therefore, we designed and synthesized one new gelator 1, as shown in Scheme 1. It contains three aliphatic amide groups and one aromatic amide moiety, which induce the self-assembly of gelator molecules in one-dimensional (1-D) direction.<sup>6</sup>



Scheme 1 Molecular structure of 1 and markings of anion-binding sites and electron withdrawing units.

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Moreover, four NH units can also act as anion acceptors. Two cyano and one nitro terminal groups were also appended as electron withdrawing groups to enhance the acidity and responsive activity of aromatic NH toward anions, and give **1** its own typical D– $\pi$ –A electron structure (Fig. S1†). The results indicate that the color of the gel phases, microscopic morphologies, emission behavior and response to anions could be adjusted by solvents, which makes us further understand the role of solvent on controlling extraordinary properties of the gelator.

# **Experimental section**

# Instruments

Infrared spectra were measured using a Nicolet-360 FT-IR spectrometer by incorporating the samples in KBr disks. The UV-vis spectra were determined on a Mapada UV-1800pc spectrophotometer. The absorption spectra of the DMSO and DMF system at high concentration were measured with 0.1 mm glass cell. C, H, and N elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. Photoluminescence measurements were taken on a Shimadzu RF-5301 Luminescence Spectrometer. X-Ray diffraction (XRD): diffraction patterns were carried out on a Rigaku D/max-rA X-ray diffractometer with graphite monochromatized Cu-Ka radiation  $(\lambda = 1.5418 \text{ Å})$ . The accelerating voltage was set at 50 kV, with 100 mA fluxes at a scanning rate of 0.02 deg.  $s^{-1}$  in the 2  $\theta$  range of 1-10°. The XRD patterns of the xerogel were obtained by casting wet gel samples in a glass flask followed by evaporation of the solvent naturally. <sup>1</sup>H NMR spectra were recorded on a Mercury plus 500 MHz. SEM images were carried out on a Japan Hitachi model X-650 scanning electron microscope. TEM images were observed with a Hitachi H-8100 apparatus by wiping the samples onto a 200-mesh carbon coated copper grid followed by naturally evaporating the solvent.

# Gelation test of organic fluids

The solution containing certain weighed gelator 1 and organic solvent in a sealed test tube was heated with 1 cm diameter in an oil bath until the solid was dissolved completely. After the solution was allowed to stand at room temperature for 6 h, the state of the mixture was evaluated by the "stable to inversion of a test tube" method.

# Synthetic procedures and characterizations

Molecule 3 was synthesized according to the literature procedures.<sup>6</sup> The synthesis route of 1 was shown in Scheme 2.

(*Z*)-3-(4-Formylphenyl)-2-(4-nitrophenyl)acrylonitrile (2). A mixture of 4-nitro phenylacetonitrile (1.4 g, 8.6 mmol), terephthalaldehyde (2.35 g, 14.5 mmol) and ethanol (20 mL) was heated until the solid was completely dissolved. A few drops of tetrabutylammonium hydroxide (TBAOH) (2 M solution in water) were added and the solution was further refluxed for 2 h. Yellow solid (1.4 g, 58% in yield) was obtained by heat filtration and washing several times by ethanol. Mp 196–198 °C. IR: 3110, 3057, 2233, 1689, 1604 and 1514 cm<sup>-1</sup>. Elemental analysis (%): calculated for  $C_{16}H_{10}N_2O_3$ : C, 69.06; H, 3.62; N, 10.07; found: C



Scheme 2 Synthesis route of 1.

69.12, H 3.56, N 10.20. <sup>1</sup>H NMR (500 MHz, TMS, CDCl<sub>3</sub>): 10.10 (s, 1 H), 8.34 (d, *J* = 9.0 Hz, 2 H), 8.09 (d, *J* = 8.0 Hz 2 H), 8.02 (d, *J* = 8 Hz 2 H), 7.89 (d, *J* = 19.0 Hz, 2H), 7.89 (s, 1H).

N1-((1,3-Bis(dodecylcarbamoyl))propylcarbamoyl))-N5-(4-(1cyano-2-(4-(2-cyano-2-(4-nitrophenyl)vinyl)phenyl) vinyl)phenyl) glutaramide (1). Compound 3 (0.48 g, 0.68 mmol) and 2 (0.19 g, 0.68 mmol) were dissolved in ethanol (50 mL). After the solution was heated and refluxed for 30 min, a few drops of tetrabutylammonium hydroxide (TBAOH) (2 M solution in water) were added. The mixture was refluxed overnight. Orange solid was obtained after filtration and washing using water and ethanol. After dried under vacuum, orange product (0.5 g, 76%) was obtained. Mp >200 °C, IR: 3285, 3067, 2922, 2852, 2218, 1645, 1637, 1521 cm<sup>-1</sup>. Element analysis (%): calculated for C<sub>58</sub>H<sub>79</sub>N<sub>7</sub>O<sub>6</sub>: C, 71.80; H, 8.21; N, 10.10; found: C, 71.70; H, 8.31; N, 10.02. <sup>1</sup>H NMR (500 MHz, TMS, DMSO-d<sub>6</sub>, 60 °C): 10.01 (s, 1 H, NH), 8.36 (d, J = 8.5 Hz, 2 H), 9.30 (s, 1 H), 8.12 (d, J = 8 Hz, 2 H), 8.07 (d, J = 8.5 Hz, 4 H), 7.96 (s, 1 H), 7.76–7.72 (m, 5 H), 7.62 (m, 1 H), 7.55 (m, 1 H), 4.19 (m, 1 H), 3.01 (m, 4 H), 2.36 (t, J = 7 Hz, 2 H), 2.22 (t, J = 7 Hz, 2 H), 2.06 (t, J = 7 Hz, 2 H), 1.88-1.68 (m, 4 H), 1.37 (m, 4 H), 1.22 (m, 36 H), 0.84 (t, J = 7 Hz, 6 H).

# **Results and discussion**

# Gelation properties investigation

The gelation ability of 1 in organic solvents was checked by the standard heating-and-cooling method. We found that 1 was insoluble in many solvents, such as cyclohexane, benzene, THF, butyl acetate *etc*, even upon heating (Table 1). However, it could be dissolved in hot ethanol and *n*-octanol. Moreover, the transparent yellow gel phase could be observed when the hot solutions of 1 in aromatic solvents with high boiling point, such as *o*-dichlorobenzene (ODCB), mesitylene and anisole, were cooled to room temperature. Furthermore, hot bright yellow DMSO and DMF solutions of 1 could be also transformed into opaque orange gels at high concentration.

It is well known, the type of gelation solvent strongly depends on the solvation degree of solvent to gelators or its solubility in solvent. However, their solubility in a given solvent indeed depends on the molecular structures of the gelators. For example, T. Yi reported two gelators with amide and cholesterol

 Table 1 Gelation ability of 1 in various solvents.<sup>a</sup>

Solvent	Status	Solvent	Status
Cyclohexane	Ι	Ethyl acetate	Ι
<i>n</i> -Hexane	Ι	Ethanol	S
Petroleum ether	Ι	Methanol	Ι
Benzene	Ι	n-Octanol	S
Toluene	Ι	Xylene	Ι
THF	Ι	DMSO	G $(1.5^{b})$
Chloroform	Ι	DMF	G (3)
Dichloromethane	Ι	Mesitylene	G (0.5)
Acetone	Ι	Anisole	G (0.5)
Butyl acetate	Ι	o-Dichlorobenzene	G (0.5)

"G: gel; S: soluble; I: insoluble. "Minimum gel concentration (mM) necessary for gelation.

units, which could form a gel in apolar and polar solvents.7 It indicates that the existence of polar and apolar moieties in gelator molecules is important to induce the gelator to gelatinize a wide range of solvents. Another typical example is amino acid gelators with long alkyl chains.<sup>2</sup> For example, M. Suzuki reported L-valine and L-isoleucine gelators, which also gelatinized many types of solvents, such as hexane, menthol, ethyl acetate, toluene, DMSO, and so on.8 In our case, the gelator 1 has four polar amide units, an apolar long alkyl chain and aromatic moieties. Considering the existence of four amide units, which makes the gelator more polar, 1 has poor solubility in apolar solvents, such as benzene, toluene, even on heating. Eventually, 1 can only be dissolved in aromatic solvents with high boiling point and gelatinizes them at low concentration. On the other hand, 1 has large solubility in DMSO and DMF, so minimum gel concentrations necessary for gelation in DMSO and DMF are higher than those in aromatic solvents.

The color difference of the gels in two kinds of solvents with different polarities suggests that photophysical properties of gels should be different and influenced by the solvent. DMSO and ODCB were selected as testing solvents to observe the influence of the solvent on the photophysical and anion-responsive properties of gels.

# Thermotropic behaviors

First, we examined the influence of solvent on the sol-gel phase transition temperature  $(T_{gel})$ .  $T_{gel}$  was determined by a convenient ball-drop method. The result shows that the  $T_{gel}$  values rise nonlinearly with increasing gelator concentration in two solvent systems (Fig. 1). However, the increasing  $T_{gel}$  of the ODCB gel with concentration is more rapid than that of the DMSO gel. For example, ODCB gel at a concentration of 1.0 mM transformed into solution when temperature reached 66 °C.  $T_{gel}$  of the ODCB gel at a concentration of 2.0 mM increased by 57 °C and reached 123 °C. On the other hand, when the gelator concentration was increased from 1.4 mM to 2.8 mM, the corresponding  $T_{gel}$  of the DMSO gel slowly went up from 56 °C to 88 °C. Moreover, it is also evident that  $T_{gel}$  of ODCB gel is higher than that of the DMSO gel at the same concentration of 1. For example, when the concentration of 1 was maintained at 2.0 mM,  $T_{gel}$  of the ODCB gel reached 123 °C, while T<sub>gel</sub> of the DMSO gel was 78 °C. Therefore, the thermotropic behavior of gel could be



Fig. 1 Plots of  $T_{gel}$  versus the concentration of 1 in DMSO and ODCB.

influenced by the solvent. Because 1 has low solubility in ODCB, the  $T_{gel}$  is relatively higher. On the other hand, 1 has large solubility in DMSO. As a result, DMSO gel possesses low  $T_{gel}$  at the same concentration.<sup>9</sup>

# Self-assembled characteristic in gel phases

Because a visible color change was observed in DMSO during the gelation, the gelation processes in the two solvents were investigated by their absorption spectra. As shown in Fig. 2, the maximal absorption peak of 1 in hot DMSO (3 mM) was located at 399 nm, which decreased and blue shifted to 364 nm after the gel phase was formed, indicating a shift of 35 nm. The peak at 399 nm in hot ODCB solution (0.5 mM) disappeared and a new peak at 347 nm (blue-shift of 52 nm) appeared when the sample was cooled down and transformed into the gel phase. It suggests that the H-aggregate (face-to-face packing) between aromatic moieties is formed during gelation in DMSO and ODCB, and the  $\pi$ - $\pi$  interactions between chromophores of 1 in the ODCB gel phase is stronger than that in the DMSO gel.<sup>10</sup> In other words, the distance between adjacent aromatic moieties in the ODCB gel phase is smaller than that in the DMSO gel. It is worth noting that during the gelation process in DMSO the absorption band was gradually broadened accompanied with a blue shift of the absorption band, and the visible absorption band from 460 to 535 nm (maxmium at 458 nm) became stronger and stronger, which can explain why the color of the DMSO solution is yellow, but the DMSO gel is orange. On the other hand, ODCB gel only possessed very weak absorption in this region, so its color remained vellow.

Owing to the formation of H-aggregate and molecular chirality, CD spectroscopy might be considered an appropriate method for further researching the assembly process. Strong bisignated induced CD band (negative Cotton effect) in the region of 300–500 nm ( $\lambda_{max} = 335$ ,  $\lambda_{min} = 375$ , and  $\lambda_{\theta} = 0 = 350$  nm) was found in ODCB gel. DMSO gel also possessed negative Cotton effect, in which the zero-crossing was located at 374 nm. The results of the UV-vis and CD spectral investigation indicate that the chromophores in molecule **1** are packed in a counter-clockwise direction in DMSO and ODCB gel phases.<sup>11</sup> Interestingly, DMSO gel showed a strong additional



**Fig. 2** Absorption spectral change of 1 during cooling process in DMSO (a, 90-20  $^{\circ}$ C, 3.0 mM) and in ODCB (b, 160-20  $^{\circ}$ C, 0.5 mM), (c) and CD spectra of DMSO (3.0 mM) and ODCB (0.5 mM) gels at 20  $^{\circ}$ C.

peak at 500 nm, which is consistent with its absorption spectrum in this region. It further suggests that the absorption band from 460–540 nm originates from the molecules aggregating and packing models in DMSO and ODCB are different.

Furthermore, FT-IR spectra were measured to investigate the interaction between amide units in the gel phase. To exactly clarify the hydrogen bonds in different solvents, IR spectra of wet gels and hot solution were obtained. It was found that in hot

solution the absorption peaks of amide I located at 1687 and 1665 cm<sup>-1</sup>, which shifted to 1660 and 1637 cm<sup>-1</sup>, respectively, in DMSO wet gel, and shifted to 1657 and 1634 cm<sup>-1</sup>, respectively, in ODCB wet gel. Moreover, the absorption bands of NH appeared at 3299 and 3288 cm<sup>-1</sup> in DMSO and ODCB wet gels, respectively. The result indicates that all the amide groups are involved in intermolecular hydrogen bonds,<sup>12</sup> and the interaction between amide units in ODCB gel is stronger than that in DMSO gel, and the closer distance between adjacent amide groups in ODCB gel than that in DMSO gel is present.<sup>13</sup>

NMR spectra were also used to study the hydrogen bonds between amide units. Fig. 3 shows the temperature-dependent <sup>1</sup>H NMR spectra of **1** in DMSO- $d_6$ . The peaks of the chromophore and amide moieties were invisible at 20 °C, suggesting that these groups existed in aggregated form at this temperature. They appeared and gradually became sharper and stronger with increasing temperature, indicating that more and more gelator molecules were detached from aggregation and present in monomeric form. Notably, NMR signals for the four kinds of amide N–H proton not only became stronger, but also shifted toward higher field with increasing temperature because of weakening of hydrogen bond strength. Moreover, the NMR



**Fig. 3** (a) Variable temperature <sup>1</sup>H NMR spectra of DMSO- $d_6$  gel from 20 to 60 °C, [1] = 1.67 mM. (b) Concentration-dependent <sup>1</sup>H NMR spectra of 1 in DMSO- $d_6$  at 60 °C.

spectra of the samples at different concentrations were also compared and were shown in Fig. 3b. It is very clear that the peaks of the four types of amide groups from the low-concentration sample are located at a higher field region relative to those observed at a high concentration. These results support the fact that all the amide groups form unidirectional intermolecular hydrogen bonds,<sup>14</sup> being in agreement with the results obtained by FT-IR spectra. These observations exhibit that the hydrogen bonds between amide moieties in both solvents play an important role on the gel formation.

The morphologies of gels in DMSO and ODCB were investigated by using scanning and transmission electron microscopes (SEM and TEM). SEM images showed that the extended fibrillar network structure was formed by numerous intertwined fibers with high aspect ratio in both gels. It suggests that gelator molecules tend to self-assemble along the 1-D fibrillar direction. Moreover, the width of fibers from the DMSO gel are larger than those from the ODCB gel. TEM images of DMSO and ODCB xerogels also displayed fibrous structures. The fibers in DMSO held solid morphology. On the other hand, the thick fibers were composed of many thin fibers with a width of about 4.5 nm in ODCB, which were loosely stacked together (Fig. 4d).

XRD spectra can be used to detect the regularity of molecular packing. The samples were prepared by casting wet gels on glass plates and further natural evaporation. As shown in Fig. 5, the XRD diffraction pattern of DMSO xerogel was characterized by four reflection peaks at 5.08, 2.54, 1.67 and 1.31 nm in the low angle region, illustrating that a lamellar organization with 5.08 nm of interlayer distance is formed in the DMSO gel phase.<sup>15</sup> On the other hand, two weak diffraction peaks for ODCB xerogel at about 5.08 and 2.54 nm could be observed, implying that it is possible that gelator molecules adopt the similar packing types in long range in DMSO and ODCB. Moreover, it was very clear that the full width at half maximum (FWHM) of the ODCB xerogel was larger than that of the DMSO gel. The weaker diffraction and wider FWHM of the



Fig. 5 Small-angle XRD patterns of xerogels of 1 from DMSO and ODCB.

ODCB xerogel are also indicative of poorer long-range ordering of molecular stacking than that in the DMSO gel.

Once the 1-D self-assembly in the gel phase had been established, the question arose as to why the colors of DMSO and ODCB gels are different and how the molecules are packed within the superstructures. The results of the UV-vis and IR absorption spectra, NMR and electron microscopy experiments clearly illuminate that many aromatic and amide groups interact with each other to form one-dimensional stacking along the direction of fibrous growth. To further reveal detailed information of molecular stacking, the geometric optimization of the gelator molecule was performed by using the AM1 force field. It was found that the molecular length of 1 in extended conformation was about 4.4 nm (Fig. S3<sup>†</sup>), which is shorter than the layer period (5.08 nm). It is possible that gelators adopt a bimolecular layer structure. Considering the fact the formation of H-aggregation in DMSO and ODCB gels and the present of an additional absorption peak at 458 nm in DMSO gel, we give the molecular stacking models in DMSO and ODCB gels. As shown in Fig. 6, when the hot DMSO and ODCB solutions are cooled down, gelator molecules aggregate together to form 1-D face-toface packing (H-aggregate) driven by the  $\pi$ - $\pi$  interaction and



**Fig. 4** SEM and TEM images of xerogels from DMSO (a, c) and ODCB (b, d), respectively.



**Fig. 6** The schematic representation of stacking models in DMSO and ODCB gels.

hydrogen bonds. Because of the solvophobic effect of the aromatic chromophore group of gelator to polar DMSO, such 1-D H-aggregates further construct tilting and interpenetrating bimolecular superstructure, leading to J-aggregates (head-to-tail) in another direction (Fig. 6). Therefore, a red-shifted absorption band at 458 nm can be found in the DMSO gel.<sup>16</sup> On the other hand, in ODCB, better solvation of ODCB to the aromatic moiety of gelator induces a large distance between the 1-D H-aggregates and results in poor J-aggregation in another direction. Finally, a weak absorbance above 450 nm is observed. This assumption can be confirmed by the observations for DMF and anisole gels (Fig. S4 and Fig. S5†). In polar DMF, morphologies and absorption spectra are similar to those in DMSO. Anisole gel possesses similar behaviors to the ODCB gel.

#### Fluorescence properties of gels

When the orange powder of 1 in DMSO was heated to form a clear bright vellow solution (6.6 mM), strong green fluorescence with a emission maxima of 530 nm, ascribed to the emission of molecules in monomeric form, was observed. When the hot solution was naturally cooled, the fluorescence color of the sample showed a substantial color change from green to yellow, and to orange, accompanied by a gradual decrease in emission intensity. Finally weak red emission with a maxima at 605 nm was observed in the gel phase (Fig. 7 and S6<sup>†</sup>). On the other hand, the hot solution of 1 in ODCB (4.0 mM) emitted intense bluish-green fluorescence with a maxima at 512 nm, and the gel showed enhanced yellow emission ( $\lambda_{em} = 567$  nm, Fig. 7, Fig. S7<sup>†</sup>). The large red shift in the emission spectra during the self-assembly of 1 in two solvent systems indicates the delocalization of the exciton across the self-assembled aggregates. Because exciton can be migrated efficiently within the aggregates of different HOMO-LUMO levels, fluorescence originates mainly from aggregates of lower energy, resulting in a red shift in emission wavelength.<sup>17</sup> Interestingly, it also was found that the DMSO gels with various emission color (green, yellow, orange and red) could be realized by simply varying the concentration of 1 (Fig. 8a). On the contrary, in the range of the measured concentration of 1 the ODCB gels possessed similar emission bands (Fig. 8b, Fig. S7<sup>†</sup>). To further understand the fluorescence difference in the two solvents, their concentration-dependent UV-vis spectra were measured. As shown in Fig. 8c, the maximal absorption peaks of the DMSO gels related to gelator concentration are gradually shifted to the longer wavelength region with decreasing concentration. It indicates the weakening  $\pi - \pi$  interaction between chromophores or the larger distance between adjacent chromophores at lower concentration because the



**Fig. 7** Photos of the gelation process of **1** in DMSO (6.0 mM) and ODCB (2.0 mM) under irradiation by 365 nm light.



Fig. 8 Concentration-dependent fluorescence and absorption spectra of 1 in DMSO (a, c) and ODCB (b, d), respectively, at room temperature.  $\lambda_{ex} = 400$  nm.

gelator has higher solubility, or lower aggregation tendency in DMSO, which induces inefficient exciton migration to lower aggregates of lower energy and promotes blue shift of emission band relative to those in high concentration.<sup>18</sup> On the other hand, the maximal absorption peaks of ODCB gels with different concentrations of 1 kept unchanged other than a slight increase in the range of 400 to 500 nm (Fig. 8d). In other words, the aggregated trend of 1 in ODCB is very strong so that almost gelator molecules self-assemble together to form aggregates and the distances between adjacent chromophores are similar at different concentrations, inducing similar exciton migration within one-dimensional aggregates and further resulting in similar emission bands for ODCB gels with different concentrations. By carefully observing emission spectra of ODCB gels, a small blue shift of emission peaks at low concentration could be found and the fluorescence intensity of gels with lower concentration generally are stronger than those of gels with higher concentration. It further proves the delocalization of the exciton across the self-assembled aggregates. These results declare that the solvent system is important in driving the gelator associations and then controlling the photophysical properties of gels. To further give more compelling evidences, concentration-dependent UV-vis and emission spectra of DMF and anisole were also measured. As shown in Fig. S4, the absorption and emission spectra of 1 in DMF strongly depends on the gelator concentration, which is similar to those in DMSO.<sup>†</sup> In another aromatic solvent, anisole, the spectroscopic behaviors of 1 look like those in ODCB. More interestingly, when a small amount of polar DMSO was added into the ODCB gel, yellow ODCB gel was changed into orange gel (Fig. S8<sup>†</sup>). For example, while 50 µL of DMSO was injected into ODCB gel (1 mL) and the mixture was heated and cooled down to form a gel, the maximal absorption peak exhibited at 369 nm and a new band from 450 to 500 nm appeared, which resembles that in neat DMSO. Moreover, the fluorescence was guenched and shift to 600 nm. When additional 50 µL of DMSO was added, the mixture had analogous absorption and emission spectra to those with low concentration in DMSO. This result further confirms the important role of the interaction between solvent and gelator on controlling photophysical characteristics.

#### Anion responsive properties

The anion responsive properties of the gels of 1 toward a number of selected target anions (F-, Cl-, Br-, I-, AcO-, H2PO4- and HSO4<sup>-</sup> as tetrabutylammonium (TBA) slats) were examined in DMSO and ODCB.<sup>19</sup> As we expected, the organogel of 1 exhibited excellent gel-sol transition according to the stimuli of anions. In DMSO, the hot solution of 1 (3 mM) could not be changed into a gel upon the addition of 10 eq. TBAF even when the sample was left over one day. Moreover, the solution turned into a dense red (Fig. 9). However, the gel state of 1 in DMSO could be preserved after adding the same amount of other halide anions, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, AcO<sup>-</sup> and HSO<sub>4</sub><sup>-</sup>. It suggests that the anions, not the TBA cation, are responsible for the transform of the gel to solution and color change.<sup>20</sup> Interestingly, the DMSO gel changed its color from orange to red upon the addition of H<sub>2</sub>PO4<sup>-</sup>, and the color of the gel only became deeper after adding AcO<sup>-</sup> (Fig. S9<sup>†</sup>). The addition of other anions did not



Fig. 9 The absorption spectra of 1 in DMSO (a, 0.5 mM) and ODCB (b, 0.5 mM) upon the addition of different amounts of TBAF, and photos of 1 in DMSO (3.3 mM) and ODCB (1.0 mM) with and without anions. Insets show the plots of absorbance at 590 nm (a), and 510 nm (b) *vs.* [TBAF]/[1].

influence the gel color. More interestingly, the hot yellow DMSO solution with less than 6 eq. TBAF could still transform into red gel, but the color of the red gel became deeper and deeper with increasing TBAF concentration (Fig. S9†). To further take insight into the anion response in DMSO, their UV-vis spectra were obtained. Consequently, it was found that a broad absorption band with two maxima at 560 and 595 nm appeared upon the addition of TBAF and gradually raised with the simultaneous decrease in absorbance of the band at 399 nm as the concentration of TBAF was increased. Finally, the

absorption band at 399 nm completely disappeared upon the addition of 10 eq. TBAF. This result suggests that more and more gelator molecules were bound with F<sup>-</sup> while TBAF was continuously added. Therefore, the gel phase could be preserved in the condition of low TBAF concentration because of enough free gelator molecules to self-assemble and gelatinize the solvent. When more than 6 eq. TBAF was added, the amount of free gelators was too little to form gel phase. At the same time, it was found that the absorption band at 399 nm was still very strong even after adding 10 eq.  $H_2PO_4^-$  and AcO<sup>-</sup>, and the bands at 560 and 595 nm were weak (Fig. S10<sup>†</sup>), which can explain the existence of gel after the addition of 10 eq.  $H_2PO_4^-$  and AcO<sup>-</sup>. According to the absorbance at 560 nm, the anion affinities sequence of 1 is  $F^- > H_2PO_4^- > AcO^- \gg Cl^-$ ,  $Br^-$ ,  $I^-$  and HSO<sub>4</sub><sup>-.21</sup> It is well known that the size of anions is an important factor when organic ligands, which can form a cavity by the receptor binding sites, are used to selectively recognize these anions because of the complementary size of cavity and anion.<sup>22</sup> However, in our case, due to the absence of such a cavity for the gelator, basicity of the anion determines the association constant. Therefore, fluoride anion has the largest binding ability.

In ODCB, only F<sup>-</sup> was able to prevent gel formation. Similarly to those in DMSO, a small amount of TBAF could not prohibit the formation of gel phase (Fig. S9<sup>†</sup>). 10 eq. TBAF led to a brown solution. Moreover, the absorption spectrum was different from that in DMSO. Two new peaks at 490 and 650 nm in the visible region in the ODCB solution with F<sup>-</sup> were found (Fig. 9b). In contrast, the UV-vis spectra showed negligible changes after the addition of other anions (Fig. S12). This spectral observation indicates that 1 has weaker affinity to anions in ODCB than that in DMSO, but possesses excellent selectivity to anions.<sup>23</sup> It is well known that the anions generally have stronger basicity in DMSO than that in ODCB.<sup>24</sup> Therefore, 1 in DMSO can respond to three anions (F<sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, AcO<sup>-</sup>), but in ODCB it selectively responds to F<sup>-</sup>. Furthermore, the different responses of gels to different anions in the same solvent originate from the difference of inherent basicity of anions.<sup>25</sup>

#### Conclusions

In conclusion, **1** was designed and synthesized. It was found that ODCB gel possessed higher  $T_{gel}$  relative to DMSO gel at the same concentration. Hot DMSO solution of **1** could transform into an orange gel, but the color of the ODCB gel was yellow. Moreover, tunable multicolor emission from green to red could be easily achieved by adjusting concentration of gelator in DMSO. In contrast, ODCB gels only emitted yellow fluorescence, being independent of concentration of the gelator. In addition, the anion-responsive behaviors of gels were also relative to solvent. **1** could respond to three anions in DMSO, but only F<sup>-</sup> could bind with **1** and transform the yellow gel into a brown solution in ODCB. This result is fascinating because it supports a strategy to design a novel gelator whose smart properties can be adjusted by solvents.

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