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Structure–property relationship of a class of efficient organogelators and their multistimuli responsiveness

Jia-Wei Liu [a,b], Jian-Tai Ma [b], Chuan-Feng Chen [a,*]

[a] Department Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Molecular Recognition and Function, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China
[b] College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, 730000, China

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ABSTRACT

A new class of efficient low-molecular-weight gelators composed of a 2-substituted anthraquinone and a hydrazide subunit were synthesized, and the structure–property relationships with respect to their gelation abilities in organic solvents were investigated. The toluene gels showed exceptional thermal stability. Interestingly, it was also found that the ultrasound radiation could promote **1b**–**e** to form a stable organogels instead of precipitates in polar solvent, and the ultrasound could remarkably induce changes of the morphology of the assembly in pyridine. Moreover, the reversible gel to sol phase transition could be achieved by adding TFA and TEA. The gelators **1b**–**e** further showed selective gelation of aromatic solvents or chloroalkanes from their mixtures with water.

1. Introduction

Organogelators are a family of low-molecular-weight organic molecules that can gel organic solvents at low concentrations. These gelators create a three-dimensional network in organic solvents.[1] The subject of organogels has generated enormous interest because of their wide-ranging applications as templated materials, drug delivery agents, cosmetics, sensors, enzyme-immobilization matrices, phase-selective gelation, as well as in art conservation.[2] The first attempts to design molecular gelators originate from the mid-1990 by the group of Hanabusa, Shinkai, van Esch, and Hamilton and several other groups.[3] Consequently, different types of organogelators including anthryl derivatives,[4] steroid,[1d] amino acid,[5] urea, hydrazide, and thiourea derivatives,[6] sugar compounds,[7] linear *p*-systems and chromophores,[8] and others[9] have been developed. Although intense effort has been devoted to establish a structure–property relationship for the development of low-molecular-weight gelators, up to now it has been impossible to predict the gelation efficiency in a given solvent from the molecular structure. Thus, a major challenge in this field is the rational design of gelator molecules together with a proper understanding of the gelation mechanism.[6c,10]

In addition, there has been an increasing interest in the study of functional and stimuli-responsive smart materials during the past few decades.[11] As we know, organogels are formed by assembling low-molecular-weight gelators (LMWGs) into entangled three-dimensional networks with solvent molecules entrapped inside through weak intermolecular interactions (i.e., hydrogen bonding, π-π stacking, van der Waals, coordination, and charge-transfer interactions). Accordingly, the main characteristic of gels formed by LMWGs is their thermo-reversible gel-to-sol transition that occurs by self-assembly and dis-assembly processes, respectively. It is important to obtain organogels whose gel–sol transitions can be further tuned by other environmental stimuli. Thus, some examples on the sol–gel transition tuned by the environmental stimulus, such as light,[12] ionic strength,[13] electric or magnetic fields,[14] mechanical stress,[15] and so on have been reported. One way to generate responsive organogels is to develop LMWGs with physical or chemically reactive groups. For instances, organogels, which respond to anion or acid/base to effect the gel–sol transition have been achieved by incorporating hydrogen-bonding functionalities (e.g., urea and amide)[16] into the corresponding LMWGs. Recently, ultrasound has also begun to play a significant role in the organogel field.[17] The Naota[17a,d] and Zhang[17b] groups independently observed ultrasound-induced gelation in hydrogen-bonded gelators for the first time. The groups of Naota,[17a,d] Sijbesma,[17e] and Bardelang[17f,h] have contributed the majority of the studies on ultrasound-induced reversible gelation. However, the example of ultrasound-induced morphology

* Corresponding author. Tel.: +86 010 62588936; fax: +86 010 62554449; e-mail address: cchen@iccas.ac.cn (C.-F. Chen).

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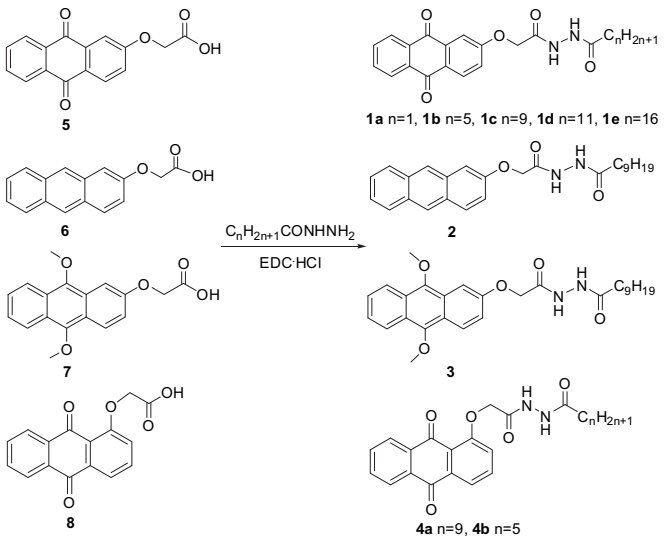
change in a gel system still remains rare.[17f,g] Although some multistimuli responsive organogels have been reported,[18] the design and synthesis of multistimuli responsive LMOGs are still worth intense.

Recently, we[19] reported two novel LMWGs **1c** and **1e** (Scheme 1), and found that they could form stable gels in wide tested solvents. Moreover, the gel systems with dual-channel response could be changed reversibly sol–gel and color by the use of anion (F^-, AcO^-, and $H_2PO_4^-$) stimuli and proton control. In order to systematically explore the relationship of the structure and property on the gelation ability, we further designed and synthesized the hydrazide derived compounds **1a**,**b**, **1d**, and **2**–**4** (Scheme 1). Herein, we report the structure–property relationship of a class of efficient organogelators and their multistimuli responsiveness. Consequently, we found that the gelation abilities of the organogelators depend on a well-balanced relation of the length of the alkyl-chain, the electron density of aromatic part, and the position of the hydrogen-bonding unit (hydrazide) at the anthraquinone ring. It was also found that the toluene gels showed exceptional thermal stability, and such thermo-stable gels could be heated to temperatures exceeding the boiling point of the solvent without gel-to-sol transition. Interestingly, although the gelation of compounds **1b**–**e** could not occur in polar solvents by heating and cooling, they could form stable gels during the cooling process in the presence of ultrasound, and the ultrasound inducement could remarkably change the morphology of the assembly in pyridine. We further found that the reversible gel to sol phase transition could be achieved by adding trifluoroacetic acid (TFA) and triethylamine (TEA). Moreover, gelators **1b**–**e** also showed selective gelation of aromatic solvents or chloroalkanes from their mixture with water, which might have tremendous implications for resolving problems such as an oil spill.



Scheme 1. Synthesis of compounds **1a**–**e**, **2**, **3** and **4a**–**b**.

2. Results and discussion

2.1. Design and synthesis

Although LMWGs have been known a long time, studies on their structure–property relationship are intensifying toward the rational design and development of the LMWGs.[3,20] Recently, we reported that compounds **1c** and **1e** could form stable gels in wide tested solvents.[19] In this case, the organogelators **1c** and **1e** have three regulatory segments responsible for their self-aggregation: (1) an aromatic part, (2) a hydrophobic-chain, and (3) a hydrogen-bonding hydrazide unit at the middle of molecule (Scheme 1). The gelation ability of the synthesized LMWGs in organic solvents depends strongly on the structural fragments of the molecules. Therefore, to understand the influence of the different parts of the synthesized molecules in the gelation, we systematically varied the each segment of the gelator to find a well-balanced situation of the attractive and repulsive forces and to optimize the gelation efficiency. The synthetic routes to the compounds **1**–**4** were shown in Scheme 1. First, compounds **1a**–**e** were easily synthesized by the reaction of (2-anthraquinonoxyl)-acetic acid **5** with the proper hydrazide derivatives in the presence of EDC·HCl. Similarly, compounds **2**,**3** were synthesized starting from the anthracene derivatives **6** and 7, respectively, and compound **4** was prepared starting from the (1-anthraquinonoxyl)acetic acid **8** according to the same methods.

2.2. Structure–property relationships on the gelation ability

The structural variation was first performed at the hydrophobic-chain unit by changing the length of hydrophobic-chain. While keeping the hydrogen-bonding unit (hydrazide) at the middle of molecule fixed and also the aromatic part of anthraquinone at the heads, we altered the hydrophobic-chain length from C-1 to C-16 (**1a**–**e**, Scheme 1). To evaluate their gelation abilities, a weighed amount of the gelator and 1.00 mL solvent were added into a sealed glass vital and heated until the solid was completely dissolved. The solution was then cooled to room temperature and left for 1 h to check the stability of the gel using 'inverse flow' method.[21] This process was repeated many times, demonstrating the thermoreversibility of the gelation and dissolution process. A series of organic solvents was used to test the gelation behavior. In concurrence with the gelation behavior of **1c** and **1e**, the compounds **1b** and **1d** were insoluble in alkane and precipitated out in polar solvents (i.e., methanol, DMF, DMSO, and so on) by heating and cooling (Table 1). As expected, the molecules were also insoluble in water. However, **1b** and **1d** formed stable transparent gels in chloroalkanes and aromatic solvents and yielded opaque gels in alcohol, ketones, and other solvents. All the gels were quite stable for more than six months at room temperature without phase separation. Compound **1a** was insoluble in any test solvents owing to the hydrophobic-chain of one carbon atom at the ends.

Table 1
Organogelation properties of **1**–**4** in organic solvents

Solvent	Status of compounds (MGC) [mM][a]								
	1a	**1b**	**1c**	**1d**	**1e**	**2**	**3**	**4a**	**4b**
Toluene	I	TG (17.4)	TG (12.9)	TG (10.0)	TG (7.8)	P	P	P	P
1,2-Dichloroethane	I	TG (15.2)	TG (13.6)	TG (12.0)	TG (6.3)	P	P	P	P
Chloroform	I	TG (19.4)	TG (14.9)	TG (11.6)	TG (6.8)	P	P	P	P
Chlorobenzene	I	TG (39.6)	TG (36.9)	TG (22.6)	TG (6.2)	P	P	P	P
Bromobenzene	I	TG (30.5)	TG (27.1)	TG (16.4)	TG (6.8)	P	P	P	P
1,2-Dichlorobenzene	I	TG (11.9)	TG (9.8)	TG (8.4)	TG (6.8)	P	P	P	P
Methanol	I	P	P	P	P	P	P	P	P
Ethanol	I	OG (16.5)	OG (10.0)	OG (9.9)	OG (9.9)	P	P	P	P
2-Propanol	I	OG (18.7)	OG (15.6)	OG (14.0)	OG (7.3)	P	P	P	P
1-Butanol	I	OG (15.2)	OG (12.9)	OG (11.0)	OG (8.5)	P	P	P	P
Perchloromethane	I	OG (8.4)	OG (6.5)	OG (5.6)	OG (2.9)	P	P	P	P
Cyclohexanone	I	OG (35.0)	OG (29.7)	OG (26.0)	OG (15.0)	P	P	P	P
Acetone	I	OG (16.2)	OG (13.8)	OG (12.6)	OG (10.9)	P	P	P	P
Ethyl acetate	I	OG (23.9)	OG (20.7)	OG (15.6)	OG (8.3)	P	P	P	P
Methyl benzoate	I	OG (22.1)	OG (18.2)	OG (15.3)	OG (10.2)	P	P	P	P
THF	I	OG (23.0)	OG (19.4)	OG (17.3)	OG (9.9)	P	P	P	P
Hexane	I	I	I	I	I	I	I	I	I
o-Xylene	I	TG (37.6)	TG (35.5)	OG (16.4)	TG (7.9)	P	P	P	P
DMF	I	P	P	P	P	P	P	P	P
DMSO	P	P	P	P	P	S	S	S	S

[a] S, solution; P, precipitate; TG, transparent gel; OG, opaque gel; I, insoluble.

Moreover, the gelation ability in organic solvents was largely dependent on the length of the alkyl-chain at the ends. On the whole, the MGC decreased more two-fold as the length of the alkyl-chain at the ends from **1b** to **1e** steadily decreased, irrespective of the nature of the organic solvents (Table 1). Furthermore, the gelation efficiency for any individual of **1b**–**e** varied to a significant extent in different organic solvents. Compounds **1b**–**e** had the strongest gelation ability in perchloromethane as shown in Table 1. This result indicated that the length of the alkyl-chain at the ends had a pronounced influence on formation of the organogels. It seemed that the alkyl-chain at the ends in **1b**–**e** promoted the intermolecular interactions of the gelators in the required way.

The second structural variation was performed at the aromatic part. The role of the aromatic part was investigated using anthraquinone, 9, 10-dimethoxyanthracene and anthracene. While keeping the hydrogen-bonding unit (hydrazide) at the middle of molecule fixed and also the hydrophobic-chain of 9 carbon atoms at the ends, we substituted the anthraquinone with more electron-deficient in **1c** by anthracene (**2**) and 9, 10-dimethoxyanthracene (**3**) with more electron-rich. Compounds **2** and **3** were either insoluble or precipitated out in all organic solvents, except for DMSO, in which these compounds were soluble (Table 1). Compared to compound **1c**, compounds **2** and **3** had a greater solubility in most organic solvents. This result indicated that the excellent gelator **1c**, but in which the anthraquinone of the aromatic part was truncated to anthracene or 9, 10-dimethoxyanthracene, was not LMWGs for reasons that probably involve diminished π-π stacking. It seemed that the anthraquinone with more electron-deficient as the aromatic part in **1b**–**e** promoted the intermolecular π-π stacking interactions of the gelators compared to the anthracene (**2**) and 9, 10-dimethoxyanthracene (**3**) with more electron-rich.

At last, the third structural variation was performed at the hydrogen-bonding unit at the middle of molecule. The supramolecular organization of **1c** was studied by concentration-dependent and temperature-dependent ^{1}H NMR, FT-IR spectroscopy.[19] It was found that all the NH of the hydrazide unit formed intermolecular hydrogen bonding in the gelation process. To explore the influence of the position of the substituent group at the anthraquinone ring and the intermolecular hydrogen bonding interactions on gelation efficiency, we also synthesized compounds **4a** and **4b** (Scheme 1). Compounds **4a** and **4b** were either soluble or precipitated out in most organic solvents (Table 1). It was noted that **4a** and **4b** could not form gels in any of the tested solvents, which suggested that the position of the substituting group had a pronounced influence on formation of the organogels. Fortunately, the single crystal of **4b**, suitable for X-ray crystallographic analysis, was obtained upon slow evaporation 1, 2-dichloroethane solution of **4b**.[22] As shown in Fig. 1, the distances of O(1)···H(1a) and O(3)···H(1a) were 2.365 and 2.104 Å, respectively. It indicated that **4b** contained a strong intramolecular hydrogen bonding interaction between the adjacent anthraquinone carbonyl oxygen O(1), the ether oxygen O(3), and the proton H(1a) of the hydrazide unit. The intramolecular hydrogen bonding interaction leads to planarization with the hydrazide unit. This implied that only the hydrazide proton H(1b) formed intermolecular hydrogen bonding. Such a hydrogen bond is not possible for **1b**, which makes all the NH of the hydrazide unit form intermolecular hydrogen bonding. These results suggested that the intermolecular hydrogen bonding interactions were the main driving forces for formation of the organogels, and the position of the substituting group had a pronounced influence on formation of the organogels.

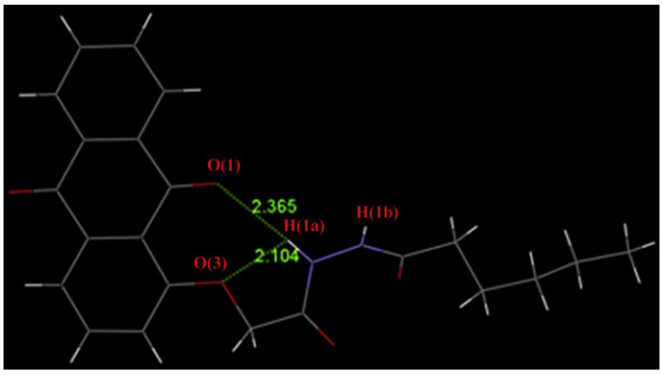


Fig. 1. The crystal structure of **4b**.

2.3. The thermal stability and morphology of organogels

The main characteristic of gels formed by small organic compounds is their thermo-reversible gel-to-sol transition that occurs by self-assembly and dis-assembly processes, respectively. The gel-to-sol transition temperature (T_{gel}) of the gelators having different chain lengths **1b**–**d** in toluene was investigated by the dropping ball method. As shown in Fig. 2, the T_{gel} value is dependent on the concentration of the gelator. In concurrence with the literature, in all investigated gels the sol–gel transition temperatures increased with increasing gelator concentration.[16c,23] Furthermore, at the same concentration, the observed T_{gel} value of **1b**–**d** increased with the length of the alkyl-chain at the ends. This result also indicated that the length of the alkyl-chain at the ends had a pronounced influence on the formation and stability of the organogels. Impressively, some of such thermo-stable **1b**–**d** gels could be heated at up to 20 °C higher (oil bath temperatures) than the boiling point of the toluene (Fig. 2). It indicated the toluene gels of **1b**–**d** were very stable. It may be explained by the less efficient heat transfer through the bulk gel and increased pressure in the micro-compartments filled with toluene molecules.[24]

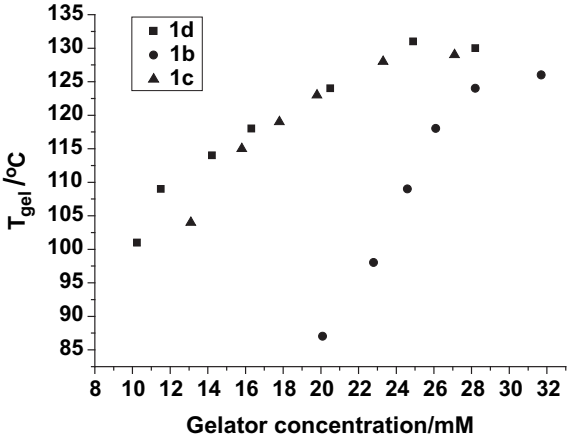


Fig. 2. Effect of concentration on the gel-to-sol transition temperature (T_{gel}) of compounds **1b**–**c** in toluene.

The morphology of the gelators **1b** and **1d** was investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) after evaporation of the solvent. Fig. 3 shows the SEM pictures of the dried three-dimensional network of gelators **1b** and **1d** in toluene and ethyl acetate, respectively. The electron micrographs show differences in the morphology of the same gelator in different solvents. The transparent gels **1b** and **1d** in toluene showed threadlike three-dimensional networks (Fig. 3a, b). Under the same conditions, the gelator **1b** and **1d** could self-assemble into three-dimensional networks composed of rod shaped

fibrous aggregates in ethyl acetate. Moreover, the TEM images of **1b** and **1d** revealed the similar morphologies in toluene (Fig. S1). These different morphological structures show the strong influence of the solvents on formation of the supramolecular structures.

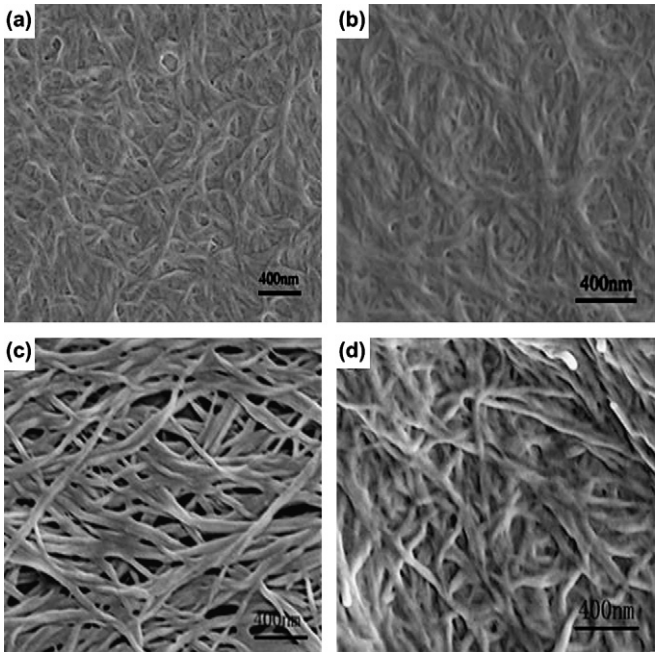


Fig. 3. SEM images obtained from the air-dried gel of **1b** and **1d**, (a) **1b** gel in toluene, (b) **1d** gel in toluene, (c) **1b** gel in ethyl acetate, (d) **1d** gel in ethyl acetate.

2.4. Ultrasound responsive behavior

Recently, ultrasound has also begun to play a significant role in the gelation of low-molecular-weight gelators by promoting the formation of fibrillar network via disruption of aggregates and fast combinatorial exchange of the thermodynamic states.[17] The compounds **1b**–**e** precipitated out in polar solvents (i.e., methanol, DMF, DMSO, and so on) by heating and cooling (Table 1). Interestingly, it was found that when the gelation tests were carried out in polar solvents, ultrasound radiation could promote **1b**–**e** to form a stable organogel (Fig. S2) instead of precipitates during the cooling process as observed in the absence of ultrasound. Both the resulting organogels and precipitates returned to the soluble state by heating. This course can be recycled many times as illustrated in Fig. 4. As shown in Table 2, the gelators **1b**–**e** formed stable opaque gels in polar solvents under ultrasound except that **1b** was soluble in DMF, DMSO, and pyridine. The gels were quite stable for more than one month at room temperature without phase separation. Moreover, the gelation ability in polar solvents under ultrasound was relatively independent on the length of the alkyl-chain at the ends, which suggested that ultrasound played an important role in formation of the organogels.

Fig. 4. Appearance of gelator **1c** in pyridine.

Table 2
Organogelation properties of **1b**–**e** in polar solvents under ultrasound

Solvent	Status of compounds (MGC) [mM][a]			
	1b	**1c**	**1d**	**1e**
Methanol	OG (9.5)	OG (8.3)	OG (8.1)	OG (7.5)
Acetonitrile	OG (10.8)	OG (8.6)	OG (8.4)	OG (8.1)
Pyridine	S	OG (27.4)	OG (26.4)	OG (26.1)
DMF	S	OG (32.1)	OG (28.7)	OG (24.5)
DMSO	S	OG (53.8)	OG (44.0)	OG (39.5)

[a] S, solution; OG, opaque gel.

The morphology of precipitate and xerogel obtained from **1c** were investigated by SEM (Fig. 5). Interestingly, we found that the morphology of **1c** precipitate and xerogel strongly depend on the solvents and external ultrasound stimuli. The **1c** precipitate from pyridine gives flower-like ball of approximate diameter 20–40 μm (Fig. 5a, b). The **1c** xerogel from pyridine under ultrasound gives rod shaped fibrillar network of approximate width 0.5–1.5 μm and approximate length 10–15 μm (Fig. 5c).

The **1c** precipitate from DMF also gives rod shaped fibrillar network of approximate width 0.5–1 μm and approximate length 5–15 μm (Fig. 5d). However, the **1c** xerogel from DMF under ultrasound gives ultralong nanobelts with an aspect ratio higher than 1000 (Fig. 5e, f). These results indicated that ultrasound effectively promoted the formation of the fiber.

2.5. Acid/base responsive behavior

The reversible gel to sol phase transition in response to heat was the intrinsic property of supramolecular gels. Thus, we also studied the acid/base responsive properties of the organogels formed by **1b**–**e**. Consequently, we interestingly found that the transparent gel of **1c** in toluene could be converted into fluid solution upon the addition of 10 equiv of TFA, and the solution could be further converted into gel upon the addition of 12 equiv of TEA (Fig. 6). It can be deduced that TFA intercalates the intermolecular hydrogen bonding, and thus breaks the gel. In the ^{1}H NMR study, the aromatic proton signals shifted downfield when excess TFA was added into the solution of **1** in $CDCl_3$, which was then relapsed when TEA was added (Fig. S3). This result also indicated that π-π stacking was a key element to drive gel formation. The change in the absorption behavior was monitored with UV–vis spectroscopy immediately after TFA was added to the toluene solution of gelator **1** (Fig. S4), which also showed that the absorption intensity of gelator **1** increased upon the addition of TFA and relapsed when TEA was added. These observations indicated that the organogel formed by **1c** exhibited the acid/base responsive property.

2.6. Selective organogelation from oil/water

Realization of phase-selective gelation from water and organic solvent mixtures is valuable but challenging. The reason might be that water competes for the hydrogen bonding sites in the gelator molecules, and thereby disrupting the self-association of the gelator and ruining gelation. To this end, Bhattacharya and Ghosh reported the 'first phase-selective gelation of oil from oil/water mixtures', which has tremendous implications for the dissolution of an oil spill.[25] Interestingly, we found that gelators **1b**–**e** are insoluble in water and have good organogelation abilities in many organic solvents. So, they could display remarkable abilities to gelate selectively chloroform, chlorobenzene, toluene, aniline or 1,2-dichlorobenzene from their mixtures with water (Fig. 7). In a typical procedure, 1 mL of organic solvent and 1 mL of water were mixed in a sample vial to which a weighed amount of the gelator

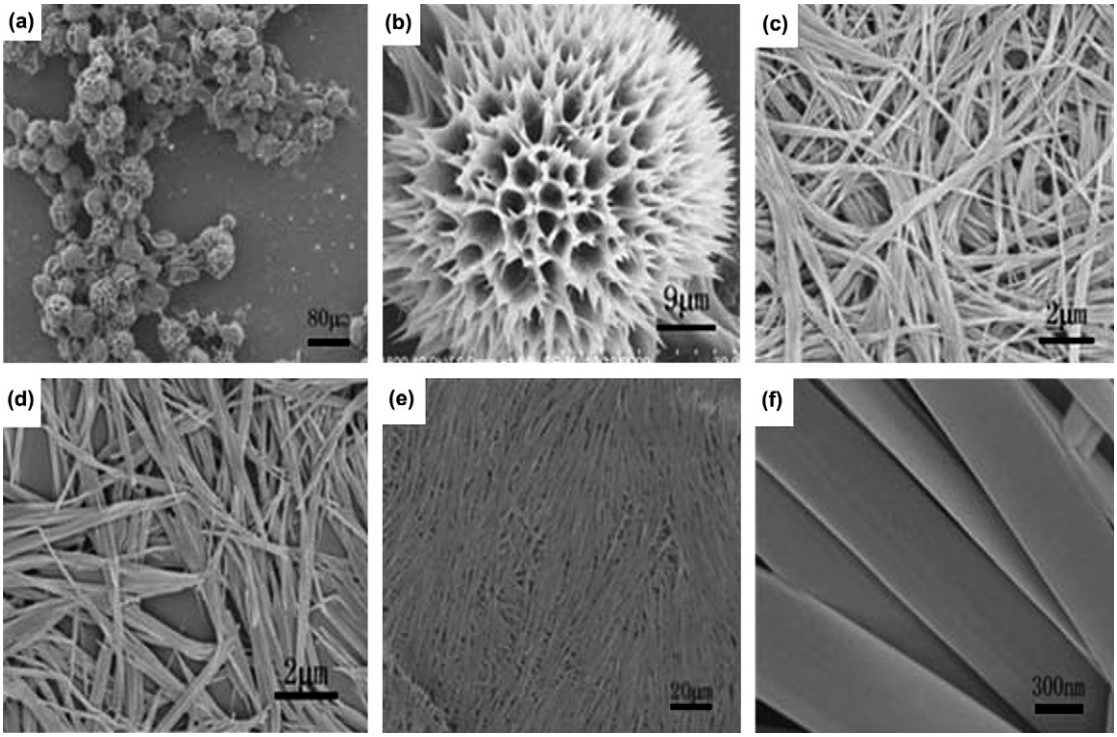


Fig. 5. SEM images of **1c** precipitates and xerogels: (a,b) **1c** precipitates from pyridine; (c) **1c** xerogels from pyridine under ultrasound; (d) **1c** precipitates from DMF; (e,f) **1c** xerogels from DMF under ultrasound.

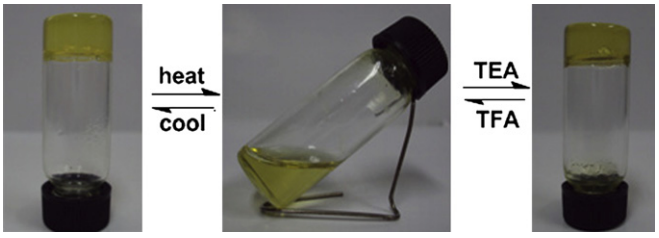


Fig. 6. The same gel of **1c** in toluene implement reversible gel to sol phase transition by heating-cooling and adding TFA/TEA.

was added. The gelator was then solubilized in this two-phase solution by heating and also shaken vigorously to ensure homogeneous dispersion of oil in water. After cooling the mixture to room temperature, the organic layer was gelated, and the water layer remained intact in liquid state (Fig. 7). Next, the organogel was separated from the water simply by filtration.

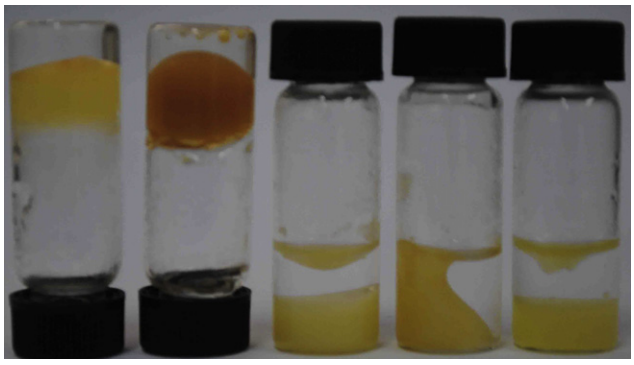


Fig. 7. Selective organic solvents gelation over water (1/1 vol %). From left to right: toluene, aniline, 1,2-dichlorobenzene, chlorobenzene, chloroform.

3. Conclusion

Although intense effort has been devoted to establish a structure–property relationship for the development of low-molecular-weight gelators, a major challenge in this field is the rational design of gelator molecules together with a proper understanding of the gelation mechanism. In the present study, we discussed the influence of the different structural units on the gelation behavior in details. The gelation process was analyzed at the molecular level to explain how changes in the chemical structure influence the self-assembling behavior. We have established a relationship between the different structural components of gelator and their gelation efficiencies, and demonstrated that the electron density of aromatic part, the length of hydrophobic-chain and the position of the substituting group had a pronounced influence on formation of the organogels. We also found that the toluene gels showed exceptional thermal stability, and such thermo-stable gels could be heated to temperatures exceeding the boiling point of the solvent without gel-to-sol transition. Interestingly, although the gelation of compounds **1b**–**e** could not occur in polar solvents by heating and cooling, they could form stable gels during the cooling process in the presence of ultrasound. Especially, the ultrasound inducement could remarkably change the morphology of the assembly in pyridine. Moreover, the reversible gel to sol phase transition could be achieved by adding TFA and TEA. We further found that gelators **1b**–**e** also showed selective gelation of an oil (aromatic solvents and chloroalkanes) in the presence of water.

4. Experimental section

4.1. General methods

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AMX 300 Spectrometer at 298 K. Chemical shifts are reported in parts per million (ppm) relative to the internal standards (tetramethylsilane,

TMS). Mass spectra were obtained by ESI techniques. Melting points, taken on an electrothermal melting point apparatus, are uncorrected. Elemental analyses were performed by the Analytical Laboratory of Institute of Chemistry, CAS. The morphologies and sizes of the xerogels were characterized by field emission scanning electron microscopy (FE-SEM, Hitachi S-4800) at an accelerating voltage of 6 kV. Samples were prepared by drop casting the suspension of freeze-dried gel in hexane on placed on a silicon substrate. To minimize sample charging, a thin layer of Au was deposited onto the samples before SEM examination. TEM was performed on a JEOL JEM-2010 microscope. Samples were prepared by drop casting the suspension of freeze-dried gel in hexane on carbon coated copper grids and the TEM pictures were obtained without staining. Sonication treatment of a sol was performed in a KQ-5200B ultrasonic cleaner (max. power, 200 W, 40 KHz; Kunshang Ultrasound Instrument Co, Ltd., China).

4.2. Synthetic procedures

All starting materials were obtained from commercial supplies and used as received. Compound 2-hydroxyl anthracene was prepared according to the literature procedure.[26a] Compound **7** was prepared according to the literature procedure.[26b] The other compounds were prepared according to the literature procedure.[19]

*4.2.1. Compound **1a**.* Light yellow solid. Yield, 91%. Mp: 244–245 °C; ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C, TMS): δ=10.19 (s, 1H), 9.88 (s, 1H), 8.20 (dd, J=8.8, 3.6 Hz, 3H), 7.94 (dd, J=8.9, 5.2 Hz, 2H), 7.69 (d, J=2.6 Hz, 1H), 7.50 (dd, J=8.6, 2.6 Hz, 1H), 4.88 (s, 2H), 1.88 (s, 3H); ^{13}C NMR (75 MHz, [D$_6$]DMSO, 25 °C, TMS): δ=182.2, 181.3, 168.0, 165.7, 162.4, 134.9, 134.6, 134.2, 133.0, 129.4, 126.9, 126.7, 126.6, 121.0, 111.5, 66.1, 20.4; ESI-MS: m/z: 337.2 [M−H]$^+$; elemental analysis: calcd (%) for $C_{18}H_{14}N_2O_5$: C 63.90, H 4.17, N 8.28; found: C 63.61, H 4.22, N 8.41.

*4.2.2. Compound **1b**.* Light yellow solid. Yield, 94%. Mp: 224–225 °C; ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C, TMS): δ=10.20 (s, 1H), 9.84 (s, 1H), 8.17 (dt, J=10.9, 5.6 Hz, 3H), 8.01–7.84 (m, 2H), 7.67 (d, J=2.6 Hz, 1H), 7.49 (dd, J=8.7, 2.7 Hz, 1H), 4.87 (s, 2H), 2.14 (t, J=7.3 Hz, 2H), 1.68–1.43 (m, 2H), 1.41–1.16 (m, 4H), 0.86 (t, J=6.7 Hz, 3H); ^{13}C NMR (75 MHz, [D$_6$]DMSO, 25 °C, TMS): δ=182.2, 181.3, 171.1, 165.8, 162.4, 134.9, 134.6, 134.2, 133.0, 129.4, 126.9, 126.7, 126.6, 121.0, 111.5, 66.2, 33.1, 30.7, 24.7, 21.8, 13.8; ESI-MS: m/z: 393.2 [MH]$^+$; elemental analysis: calcd (%) for $C_{22}H_{22}N_2O_5$: C 66.99, H 5.62, N 7.10; found: C 66.84, H 5.68, N 7.12.

*4.2.3. Compound **1d**.* Light yellow solid. Yield, 94%. Mp: 231–232 °C; ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C, TMS): δ=10.19 (s, 1H), 9.82 (s, 1H), 8.20 (dd, J=8.8, 3.2 Hz, 3H), 8.05–7.85 (m, 2H), 7.69 (d, J=2.6 Hz, 1H), 7.51 (dd, J=8.7, 2.7 Hz, 1H), 4.87 (s, 2H), 2.13 (t, J=7.3 Hz, 2H), 1.52 (s, 2H), 1.20 (d, J=21.6 Hz, 16H), 0.85 (t, J=6.6 Hz, 3H); ^{13}C NMR (75 MHz, [D$_6$]DMSO, 25 °C, TMS): δ=182.3, 181.3, 171.1, 165.8, 162.4, 135.0, 134.6, 134.2, 133.1, 129.4, 126.9, 126.7, 126.7, 121.1, 111.6, 66.2, 33.1, 31.2, 29.0, 28.9, 28.7, 28.6, 28.5, 25.0, 22.0, 13.9; ESI-MS: m/z: 501.4 [M+Na]$^+$; elemental analysis: calcd (%) for $C_{28}H_{34}N_2O_5$: C 70.27, H 7.16, N 5.85; found: C 70.14, H 7.24, N 5.73.

*4.2.4. Compound **2**.* Light yellow solid. Yield, 90%. Mp: 203–204 °C; ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C, TMS): δ=10.14 (s, 1H), 9.81 (s, 1H), 8.51 (s, 1H), 8.38 (s, 1H), 8.04 (d, J=8.9 Hz, 3H), 7.59–7.09 (m, 4H), 4.76 (s, 2H), 2.14 (t, J=7.3 Hz, 2H), 1.51 (d, J=6.8 Hz, 2H), 1.24 (s, 12H), 0.85 (t, J=6.5 Hz, 3H); ^{13}C NMR (75 MHz, [D$_6$]DMSO, 25 °C, TMS): δ=171.2, 166.4, 155.2, 132.1, 131.7, 130.0, 129.8, 128.08, 127.9, 127.5, 126.1, 125.7, 124.6, 124.1, 120.4, 105.2, 66.0, 33.2, 31.2, 28.9, 28.8, 28.6, 28.5, 25.0, 22.0, 13.9; ESI-MS: m/z: 443.4 [M+Na]$^+$; elemental analysis: calcd (%) for $C_{26}H_{32}N_2O_3\cdot 1/2H_2O$: C 72.73, H 7.69, N 6.53; found: C 72.58, H 7.57, N 6.72.

*4.2.5. Compound **3**.* Yellow solid. Yield, 89%. Mp: 168–169 °C; ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C, TMS): δ=10.19 (s, 1H), 9.83 (s, 1H), 8.20 (m, 3H), 7.52 (m, 3H), 7.35 (dd, J=9.4, 2.4 Hz, 1H), 4.83 (s, 2H), 4.02 (s, 3H), 4.04 (s, 3H), 2.14 (t, J=7.3 Hz, 2H), 1.51 (d, J=7.1 Hz, 2H), 1.24 (s, 12H), 0.85 (t, J=6.5 Hz, 3H); ^{13}C NMR (75 MHz, [D$_6$]DMSO, 25 °C, TMS): δ=171.0, 166.2, 155.5, 148.2, 146.3, 125.9, 125.1, 124.9, 124.4, 122.9, 122.4, 121.9, 120.9, 120.4, 99.8, 66.0, 63.2, 62.4, 33.1, 31.2, 28.9, 28.7, 28.6, 28.5, 25.0, 22.0, 13.9; ESI-MS: m/z: 503.4 [M+Na]$^+$; elemental analysis: calcd (%) for $C_{28}H_{36}N_2O_5$: C 69.98, H 7.55, N 5.83; found: C 69.77, H 7.32, N, 5.76.

*4.2.6. Compound **4a**.* Yellow solid. Yield, 85%. Mp: 196–197 °C; ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS): δ=10.70 (s, 1H), 8.35–8.23 (m, 2H), 8.04 (d, J=7.7 Hz, 1H), 7.78 (dt, J=11.2, 7.8 Hz, 4H), 7.22 (d, J=8.3 Hz, 1H), 4.80 (s, 2H), 2.36 (t, J=7.6 Hz, 2H), 1.75 (dd, J=14.8, 7.3 Hz, 2H), 1.28 (s, 12H), 0.88 (t, J=6.3 Hz, 3H); ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C, TMS): δ=182.7, 171.0, 165.3, 157.3, 135.7, 135.5, 134.6, 134.4, 133.8, 132.6, 127.7, 126.8, 121.4, 121.3, 118.8, 67.5, 34.4, 31.9, 29.5, 29.4, 29.3, 29.3, 25.4, 22.7, 14.1; ESI-MS: m/z: 473.3 [M+Na]$^+$; elemental analysis: calcd (%) for $C_{26}H_{30}N_2O_5\cdot 1/2H_2O$: C 67.97, H 6.75, N 6.10; found: C 68.37, H 6.74, N 6.10.

*4.2.7. Compound **4b**.* Yellow solid. Yield, 87%. Mp: 182–183 °C; ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS): δ=10.7 (s, 1H), 8.35–8.23 (m, 2H), 8.01 (d, J=7.3 Hz, 1H), 7.92–7.61 (m, 2H), 7.20 (d, J=8.2 Hz, 1H), 4.8 (s, 2H), 2.4 (t, J=7.5 Hz, 2H), 1.76 (d, J=6.6 Hz, 2H), 1.39 (s, 4H), 0.93 (t, J=6.3 Hz, 3H); ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C, TMS): δ=182.7, 171.0, 165.3, 157.3, 135.7, 135.5, 134.6, 134.4, 133.8, 132.6, 127.7, 126.8, 121.4, 121.3, 118.8, 67.5, 34.4, 31.42, 25.0, 22.4, 13.9; ESI-MS: m/z: 417.3 [M+Na]$^+$; elemental analysis: calcd (%) for $C_{22}H_{22}N_2O_5$: C 66.99, H 5.62, N 6.10; found: C 67.12, H 5.53, N 6.13.

4.3. Preparation of the organogels

A weighed amount of the gelator and 1.00 mL solvent were added into a sealed glass vial and heated to get a clear solution. The solution was then cooled to room temperature and left for 0.5 h to check the stability of the gel using 'inverse flow' method.[21]

4.4. Determination of gel–sol transition temperature (T_{gel})

Temperatures for the gel-to-sol transition (T_{gel}) were determined by using a conventional 'falling ball' method.[27] In the experiment, a small glass ball (diameter 4 mm) was carefully placed on the top of the gel, which was produced in a test tube (diameter 10 mm). The tube was slowly heated (1 °C/min) in a thermostatted oil bath until the ball fell to the bottom of the tube. The temperature corresponding to the end of the falling process was recorded and taken as the T_{gel} of the system.

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Supplementary data

Supplementary data related to this article can be found online, at doi:10.1016/j.tet.2010.11.027. These data include MOL files and InChIKeys of the most important compounds described in this article.

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