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Stimuli responsive gels based on low molecular weight gelators

Xingyuan Yang,^{ab} Guanxin Zhang^a and Deqing Zhang^{*a}

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In this feature article we summarize the recent developments of stimuli responsive gels based on low molecular weight gelators (LMWGs) for which the gel-sol transitions can be triggered by other stimuli besides heating. These include gels responsive to redox reactions and light irradiations.

Chemoresponsive gels are also introduced, including those for which the gel-sol transitions can be induced by reactions with neutral molecules and those for which the gel strength is improved following the addition of neutral molecules. Perspectives for such stimuli responsive gels are discussed with regard to their potential applications and remaining challenging issues.

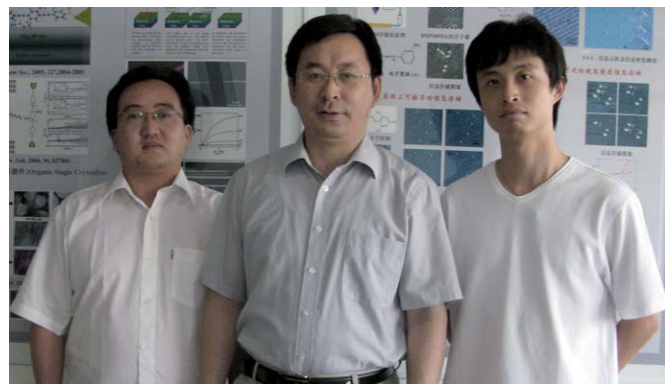
1. Introduction

Gels as soft materials are continuous in structure and solid-like in rheological behavior.^{1–7} They can be categorized into chemical gels and physical gels.^{8–16} Usually, chemical gels are covalently cross-linked polymers and not able to be redissolved, whereas physical gels based on intermolecular interactions can be redissolved again showing cycled reversibility. Self-assembly of certain molecules, referred to as low-molecular weight gelators (LMWGs),^{1,2,9} through weak intermolecular interactions such as H-bonding, π - π stacking and van der Waals interactions, can lead to solvent gelation and formation of physical gels. In the gel phase, molecules of LMWGs are self-assembled into entangled

three-dimensional networks, which entrap and immobilize solvent molecules by capillary forces. These physical gels are characterized by the following unique features: (1) they are generally composed of hierarchically fiber-like structures, which cross-link to form a three-dimensional (3D) network;^{6,8} (2) they are thermally responsive, namely, the gels are transformed into solutions after heating and they can be recovered after cooling, since molecules of LMWGs within the fibril structures are associated through weak non-covalent interactions such as H-bonding, π - π stacking and van der Waals;^{8,9,11} (3) they are viscoelastic owing to the fact that solvent molecules are macroscopically immobilized by surface tensions and capillary forces;^{1,2,17} (4) they possess the respective critical gelation temperatures (T_{gel}), at which the gel-sol transitions occur, and the respective critical gelator concentrations (CGC), above which gels form in certain solvents at room temperature.^{1,2,8,17}

^aBeijing National Laboratory for Molecular Sciences, Organic Solids Laboratory, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190, China. E-mail: dqzhang@iccas.ac.cn; Tel: +86 6263 9355

^bGraduate School of Chinese Academy of Sciences, Beijing, 100190, China



(Right) Xingyuan Yang received his B.S. in chemistry from Beijing Normal University in 2005 and Ph.D. in organic chemistry from the Institute of Chemistry, Chinese Academy of Sciences in 2011 under the supervision of Prof. Deqing Zhang and Prof. Daoben Zhu. Currently he is an engineer at the Research Institute of Petroleum Processing (RIPP). His research interests include design and synthesis of organic functional molecules.

(Left) Guanxin Zhang was born in 1976 and received his M.Sc. in chemistry from Beijing Normal University in 2002 and Ph.D. in organic chemistry from ICCAS in 2005 under the supervision of Prof. Deqing Zhang and Prof. Daoben Zhu. He is now an Associated Professor at the Institute. His research interests include design, synthesis and self-assembly of organic functional molecules, chemobiosensors and nanomaterials.

Gels based on LMWGs have been investigated for tens of years. However a key question, “what are the structural requirements for a molecule to gel an organic liquid”, still remains. This is because the process of gelation is complicated and often in competition with other kinds of molecular aggregations such as crystallization. Development of LMWGs is usually regarded as serendipitous discovery. However, rational design of LMWGs is eagerly pursued and has played an important role in generation of new LMWGs. Chemical segments such as cholesterol and urea have been found favorable for gelation of solvents and thus they are widely employed for designing new LMWGs.

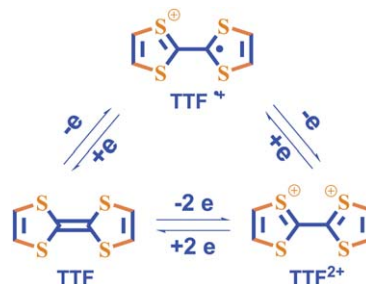
Recent studies have demonstrated that these physical gels may have potential applications in a number of areas including nanomaterials and delivery or modification agents for paints, inks, cleaning agents, drugs, *etc.*^{17–21} As a result, they have received increasing attention in recent years. Apart from studies on the gel formation and structures, extensive efforts have been made to investigate functional and stimuli responsive gels. Applications of these physical gels, for example as microreactors for chemo- and biotransformation, have also been intensively addressed. Several critical reviews have been published highlighting the advances of gel chemistry from different aspects.^{8,17,22–24} In this paper, we want to focus on recent developments of stimuli-responsive gels based on LMWGs.

Stimuli-responsive physical gels offer us promising opportunities for designing and constructing new functional materials, such as sensors, actuators, *etc.* Apart from thermal responsiveness, various physical gels also respond to other stimuli including light irradiation and redox reactions which can also trigger the gel-sol (solution) transitions. The molecular design rationale for these stimuli-responsive gels is to incorporate photoresponsive-/electroactive-/chemical reactive segments into the respective LMWGs derived from cholesterol, urea and other gelating moieties. For instance, organogels which respond to light irradiation have been achieved by incorporating photoresponsive moieties (*e.g.* azobenzene and stilbene)^{8,23} into the corresponding LMWGs. By designing LMWGs with electroactive moieties, organogels showing responsiveness to redox reactions have been described.²³ In the following, we will introduce the representative examples of stimuli-responsive gels based on LMWGs with responsive groups to demonstrate the molecular design principle and perspectives for these fascinating physical gels.

(Middle) Deqing Zhang received his Ph.D. from Ruprecht-Karls University Heidelberg in 1996 under the supervision of Prof. Dr H. A. Staab. He is currently a Research Professor at ICCAS. His research interests include development of external stimuli-responsive molecular systems for molecular switches, logic gates and chemobiosensors. He is also interested in the design and synthesis of organic conjugated molecules toward functional assemblies and materials. He serves as an Editorial Advisory Board member of several scientific journals.

2. Redox-responsive gels based on LMWGs with electroactive groups

It is known that tetrathiafulvalene (TTF) and its derivatives can be reversibly transformed into the respective radical cations (TTF^{•+}) and dication (TTF²⁺) by either chemical or electrochemical redox reactions.^{25,26}



By taking advantage of this unique feature, we and other groups have reported the TTF-based gelators and the resulting gels that show responsiveness to redox reactions. LMWG **1**²⁷ is one of such TTF-derived gelators. Apart from electroactive TTF segment it also contains a urea group that can form intermolecular extended H-bonding and accordingly is widely employed as one of gelating groups. LMWG **1** can gel several solvents such as cyclohexane and 1,2-dichloroethane. Either addition of Fe³⁺ or applying of an oxidation potential to the gel of **1** can lead to the gel-sol transition. Spectroscopic investigations show that TTF unit in **1** is oxidized into the corresponding TTF^{•+} after inputs of either Fe³⁺ or an oxidation potential. Interestingly, the gel state can be restored by electrochemical reduction, followed by heating and cooling (see Fig. 1). Therefore, the gel-sol transition can be tuned as a function of the redox state of the TTF moiety in LMWG **1**. Alternatively, the gel-phase of LMWG **1** can also be modulated by reaction with tetracyanoquinodimethane (TCNQ) which is a strong electron acceptor. Addition of TCNQ to the gel of **1** from 1,2-dichloroethane results in the

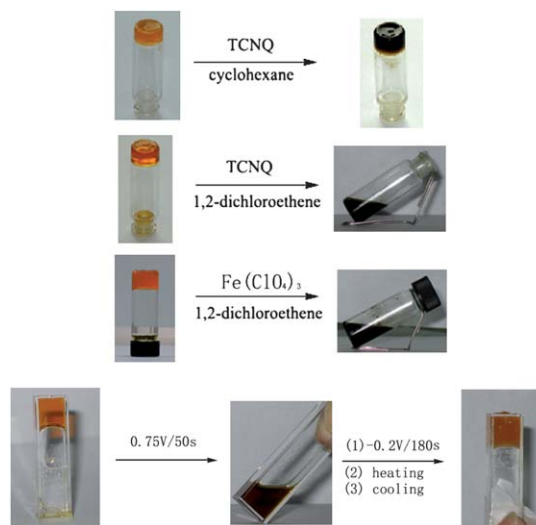
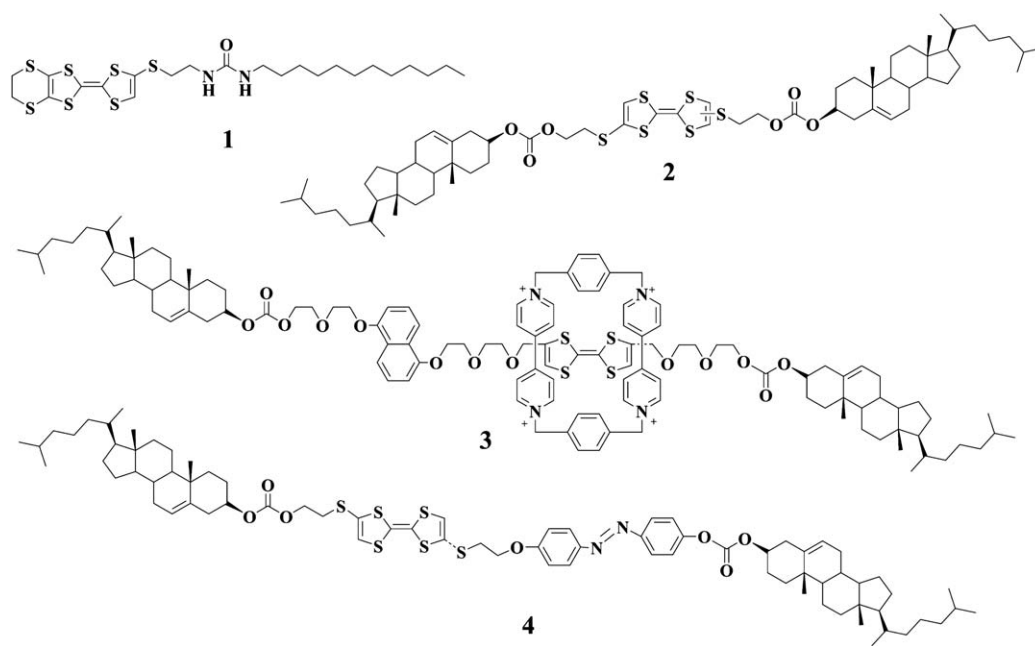


Fig. 1 Gel formation with **1** and tuning by the formation of charge-transfer complexes and chemical or electrochemical oxidation and reduction.



destruction of the gel state, but the reaction of **1** with TCNQ in cyclohexane leads to a dark-green gel. This may be attributed to the fact that 1,2-dichloroethane is more polar than cyclohexane and as a result the TTF unit in **1** interacts more strongly with TCNQ in 1,2-dichloroethane. Apart from urea group cholesterol units were incorporated into TTF unit to generate the TTF-based gelator **2**.²⁸ The gel of **2** from hexane can be destroyed upon addition of I_2 which can oxidize the TTF unit in **2**. This result provides another example of organogels that respond to redox reactions.

Stoddart and coworkers have built a fascinating chemistry of TTF-based rotaxanes.^{29–31} They have recently described a new gelator **3** with TTF-based bistable [2]rotaxane framework.³² The cholesterol units in **3** have dual functions, *i.e.* as stopper groups and gelating segments. LMWG **3** can gel a mixture of $CH_2Cl_2/MeOH(3 : 2, v/v)$, moreover, the gel can be transformed into the solution after oxidations with $Fe(ClO_4)_3$. This is likely due to the oxidation of the TTF unit and in turn the cyclobis(paraquat-*p*-phenylene) (CBPQT⁴⁺) ring is switched from TTF station to 1,5-dioxynaphthalene (NDP) station as reported earlier.^{29–31} Accordingly, the intermolecular interactions may be altered, leading to the gel-sol transition. Although it has not been mentioned whether the gel phase can be restored by further reduction, it is expected that the gel-sol transition of LMWG **3** can be reversibly tuned by redox reactions of the TTF unit.

Some of us³³ have just recently described a new gelator **4** featuring both electroactive TTF and photoresponsive azobenzene units with the end to generate multistimuli responsive gels. LMWG **4** can lead to gelation of several solvents and the gels become CD active because of the formation of chiral assemblies probably due to the cholesterol units in LMWG **4**. The *cis-trans* photoisomerization can take place smoothly. As anticipated, the gel-sol transitions for gels of LMWG **4** can be reversibly tuned by either chemical or electrochemical oxidation/reduction reactions (Fig. 2). Additionally, the

photoisomerization of the azobenzene group in **4** can also trigger the gel-sol transition (Fig. 3). Therefore, the gel-sol transition for gels of LMWG **4** induced by redox reactions and light irradiations can be operated separately. Physical gels of **4** respond not only to thermal stimuli but also to redox reactions and light irradiation.

Other LMWGs with TTF units have also been reported in recent years. However, the motivation is to generate conducting nanostructures through gel formation. For instance, Kato and coworkers³⁴ studied TTF derivatives **5a–c** containing amino acid moieties. Gelation of **5a–c** occurred for aromatic liquid crystals to form stable fibrous aggregates. Iodine-doping was successfully carried out for the solid-state self-assembled fibers, which showed conductivities in the range of 10^{-5} – 10^{-6} S cm^{-1} after doping. Meanwhile, Shinkai and coworkers³⁵ reported another TTF-based gelator **6** bearing one 3,4,5-trialkoxybenzene group and two amide groups. Gelation of hydrocarbon solvents with LMWG **6** induced the formation of 1D nanostructures, which again could become conductive after exposure to I_2 vapor. The TTF-driven gelator **7** containing one amide unit and one long alkyl chain can gel both hexane and decane.^{36,37} The resulting xerogel is composed of nanofibers in which a mixed-valence state due to the TTF unit in **7** is formed after doping with I_2 . Compound **8**, the analogue of **7**, can function as a gelator too.³⁸ Direct casting of gel samples formed with **8** on the surface of HOPG led to the formation of fibrous materials. TTF-containing compounds **9** and **10** were also investigated as new gelators.^{39,40}

Apart from TTF there are other electroactive units such as ferrocene and thiophene, which can also be reversibly transformed into the respective cations by either chemical or electrochemical means; thus, the corresponding gels from LMWGs with these electroactive segments may also show responsiveness to redox reactions. For instance, Fang and coworkers⁴¹ studied LMWG **11** bearing a ferrocene segment. Their results manifest that the gel-sol transition of **11** can be reversibly tuned by

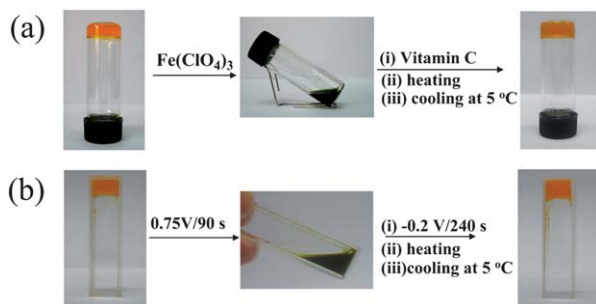
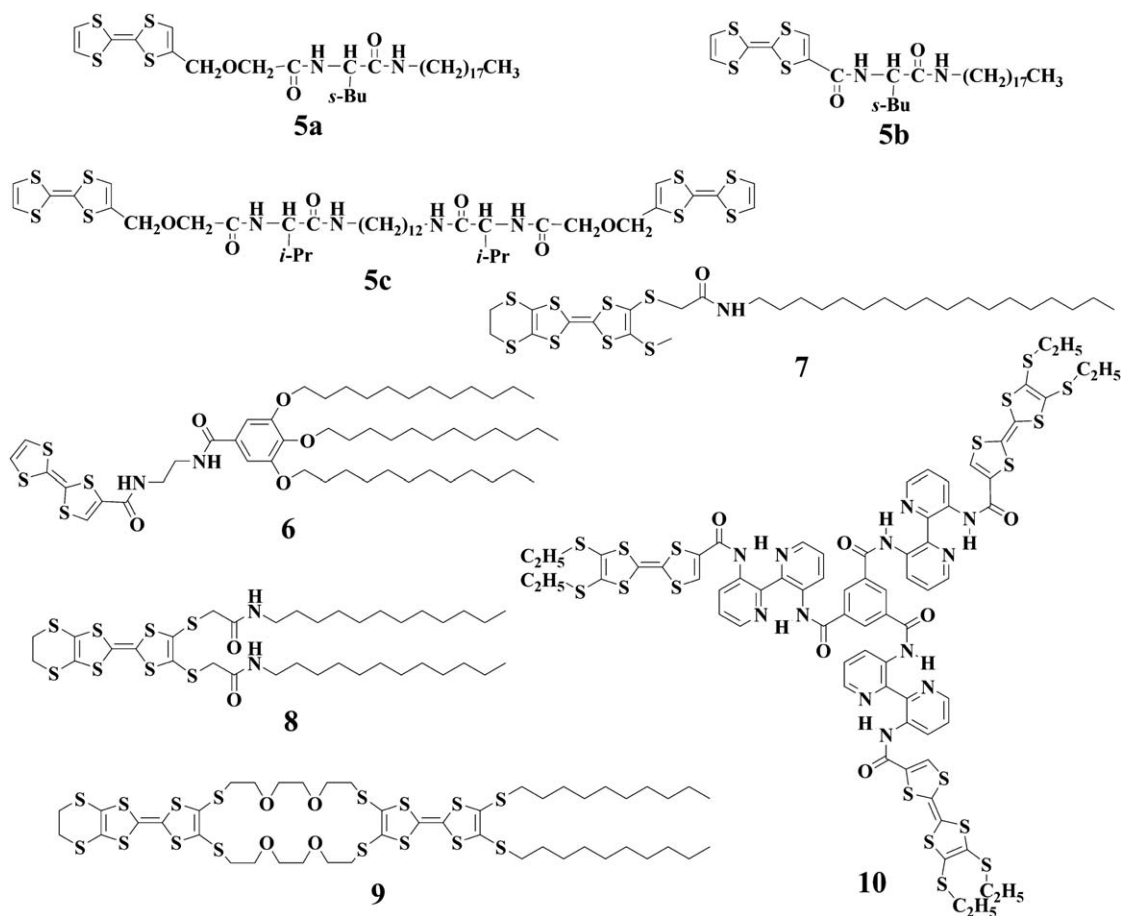


Fig. 2 Reversible tuning of the gel formation of **4** (8.0 mg mL⁻¹) in CH₂Cl₂/CH₃OH (3/1, v/v) (a) by chemical oxidation and reduction and (b) by sequential electrochemical oxidation and reduction.

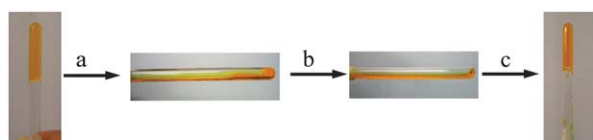


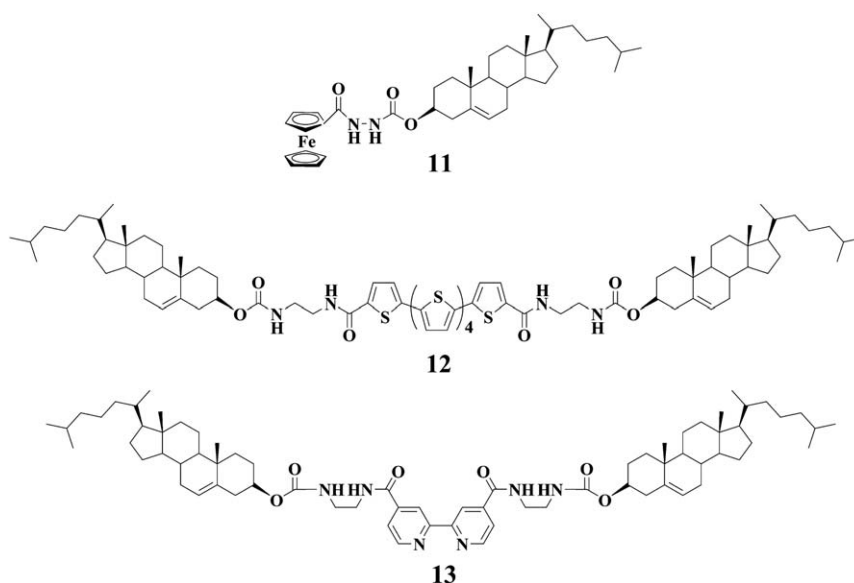
Fig. 3 Reversible tuning of the gel formation of **4** (8.0 mg mL⁻¹) in CH₂Cl₂/CH₃OH (3/1, v/v) by UV light irradiation and further visible light irradiation: (a) UV light irradiation for 30 min; (b) UV light irradiation for 1.0 h; (c) further visible light irradiation for 2.0 h and then being left in the dark at 5.0 °C for 18 h.

chemical redox reactions with (NH₄)₂Ce(NO₃)₆ as oxidant and NH₂·NH₂ as reductant. In addition, the gel-sol transition is also affected by shear stress and sonication, and as a result the gels of **11** are multistimuli responsive.

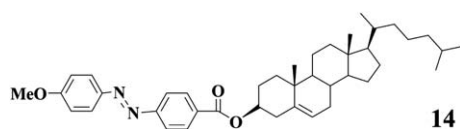
Shinkai and his co-workers have also reported redox-stimuli responsive gels based on compounds **12**⁴² and **13**.⁴³ Gelator **12** entails a redox active sexithiophene segment which enables gels of **12** to be responsive to redox reactions. For example, gel of **12** from 1,1,2,2-tetrachloroethane was changed to the corresponding solution by oxidation with FeCl₃, and the gel state can be restored by further addition of ascorbic acid which can reduce the radical cation of sexithiophene segment to neutral. By taking advantage of the redox switching of Cu(I)/Cu(II) complexes, they reported another example of a heat-free sol-gel phase transition that can be induced by a redox stimulus. The Cu(I) coordination complex of **13** can gel solvents, and transformation of Cu(I) complex to the respective Cu(II) complex will induce structural distortion for the complex which in turn may destabilize the fibril structures leading to gel-sol transition.

3. Photoresponsive gels based on LMWGs

Azobenzene as a photoisomerization unit was incorporated into LMWGs to generate photoresponsive gels. Shinkai and coworkers⁴⁴ initially designed LMWG **14** bearing an azobenzene segment and the gel-sol transitions for the resulting gels could be



tuned by light irradiation. Later, Koumura and coworkers⁴⁵ reported an azobenzene compound **15** with two urethane moieties linked to two cholesterol ester units. They also found that the gel-sol transition for gels of **15** can take place upon photoirradiation as a result of *trans-cis* isomerization of the azobenzene unit. Further studies manifested that intermolecular H-bonding which was partly responsible for stabilizing the gels was broken or reformed during gel-sol transition induced by light irradiation.



Yagai and coworkers⁴⁶ described a gelator **16** derived from *N,N'*-disubstituted-4,6-diaminopyrimidin-2(1*H*)-one with two azobenzene units. ¹H-NMR, absorption and dynamic light scattering studies clearly indicated that the self-assembly structures of **16** are strongly affected by the photoisomerization of the azobenzene units. This was ascribed to the variation of intermolecular H-bonding after *trans-cis* isomerization of azobenzene units. In fact, exposure of the gel of **16** from heptane resulted in the collapse of gel within a few hours. Further studies showed that the *trans-cis* isomerization of the azobenzene moieties induced the collapse of the lamellar structures into soluble supramolecular tapes. They also investigated the self-assembly structures from the mixture of **17** and **18**.⁴⁷ It was found that the concentrated cyclohexane solution of **17** and **18** gradually became viscous at room temperature and eventually a transparent gel was obtained after 24 h (Fig. 4). When the gel was irradiated by UV light for more than 15 min, the gel was transformed into the corresponding solution; the gel phase was regenerated after the photoinduced solution was kept in the dark for 48 h.

It usually takes a long period for the gel-sol transition of LMWGs with azobenzene moieties to complete by

photoirradiation. However, rapid and reversible gel-sol transition was reported for gels derived from a bis-dendritic gelator **19** consisting of azobenzene dendron and aliphatic amide units; the collapse of the gel occurred in 2.0 min upon UV light irradiation, and gel regeneration was achieved by subsequent irradiation of visible light in just 5.0 s (Fig. 5).⁴⁸ Another dendritic gelator **20** with one azobenzene unit was synthesized and the resulting gels were responsive to light irradiations as expected.⁴⁹

Kato and coworkers^{50,51} designed a chiral gelator **21** with photochromic azobenzene moieties. Interestingly, they investigated the gelation of a liquid crystal, 4-cyano-4'-pentyl-biphenyl with **21**. Nematic gel state was obtained by cooling the isotropic liquid state, and was transformed into the cholesteric liquid crystal phase after UV light irradiation. Cholesteric gel state was generated after keeping the cholesteric liquid state or visible light irradiation. Such photoresponsive soft materials may have potential applications in re-writable information recording.

Gels that respond to light irradiation were also constructed with LMWGs containing stilbens moieties. As an example, compound **22** is composed of a *cis*-stilbenes group and one oxamide moiety, which can be dissolved in ethanol.^{52,53} However, the clear solution of **22** turned into an opaque gel after light irradiation with a high-pressure mercury lamp. Prolonged irradiation led to the crystallization of the gelator (the corresponding *trans*-form of **22**) from the system with time. Heating a gel or a crystallized precipitate and further cooling resulted in the repeated gel formation. Compound **23** can gelate toluene-*d*₈ with the aid of a small amount of *N,N'*-dimethyldodecylamine.⁵⁴ The gel can be transformed into the solution after UV light irradiation. Interestingly, when the gel was irradiated through a mask, only within the illuminated areas did the gel-sol transition occur. ¹H-NMR studies indicated that this gel-sol transition was due to the formation photodimer of **23** upon UV light irradiation.

Das and coworkers⁵⁵ studied the self-assembly of the butadiene **24** and its analogues. The resulting gel of **24** from *n*-butanol was composed of globular aggregates rather than interconnected

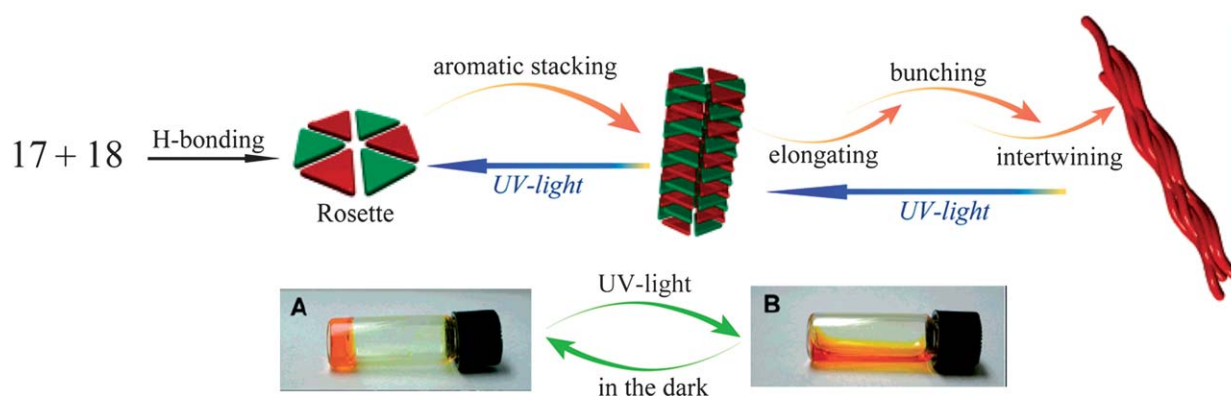
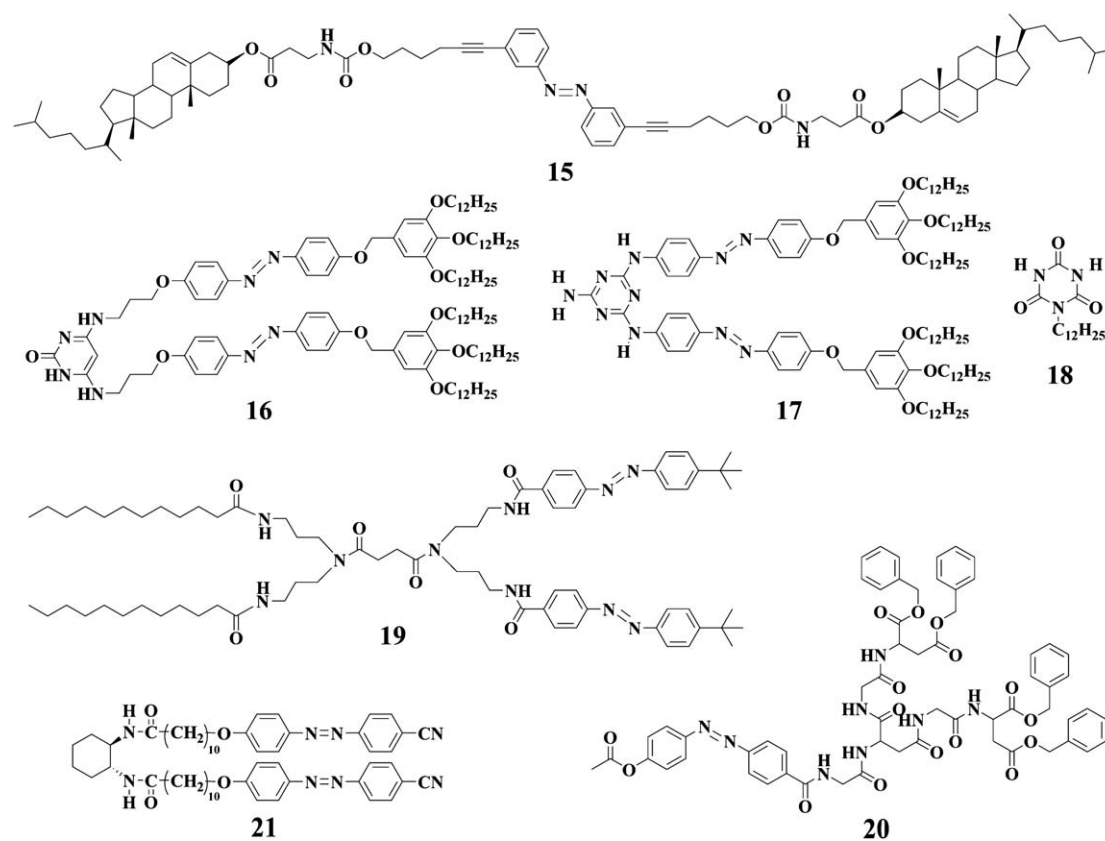


Fig. 4 Illustration of the hierarchical self-assembly structures of **17** and **18**, and the gel-sol transition under UV light irradiation.

nanofibers. Rheological studies indicated the gels were stable and not thixotropic. Irradiation of the gel at wavelength longer than 385 nm led to gel-sol transition, as observed by the free-flowing nature of the irradiated sample. This is believed to be due to the *trans-cis* isomerization of one C=C bond in **24** as shown in Chart 1. Keeping the irradiated solution in the dark for 24 h resulted in the re-generation of the gel.

Photodimerization may occur to anthracene-derived compounds when intermolecular arrangements are appropriate. Shinkai and coworkers⁵⁶ described binary gelators **25a-c** which were prepared from equimolar amounts of anthracene-9-carboxylic acid and the corresponding alkylamine. Their gelation

abilities were found to be dependent on the lengths of the respective alkyl chains. The gels were converted to the solutions after UV light irradiation because of the generation of photodimers as shown in Chart 2. These photodimers can be dissociated by heating, but the gels cannot be regenerated directly. However, the gel phase can be recovered by further cooling the solution. Some of us reported gelator **26**⁵⁷ with an anthracene moiety. However, photodimerization did not happen for the gels of **26** and indeed the gel-sol transition did not take place for these gels upon UV light irradiation. Interestingly, gelator **26** became strongly emissive (green emission) after gelation (Fig. 6). This was attributed to the formation of emissive intermolecular

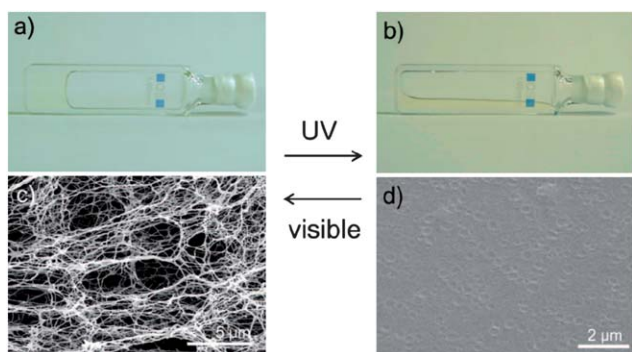


Fig. 5 Photographs of the cyclohexane gel of **19** (0.05% w/v) (a) before and (b) after UV irradiation for 120 s, and FE-SEM images after drying (c) from the gel state and (d) from the sol state.

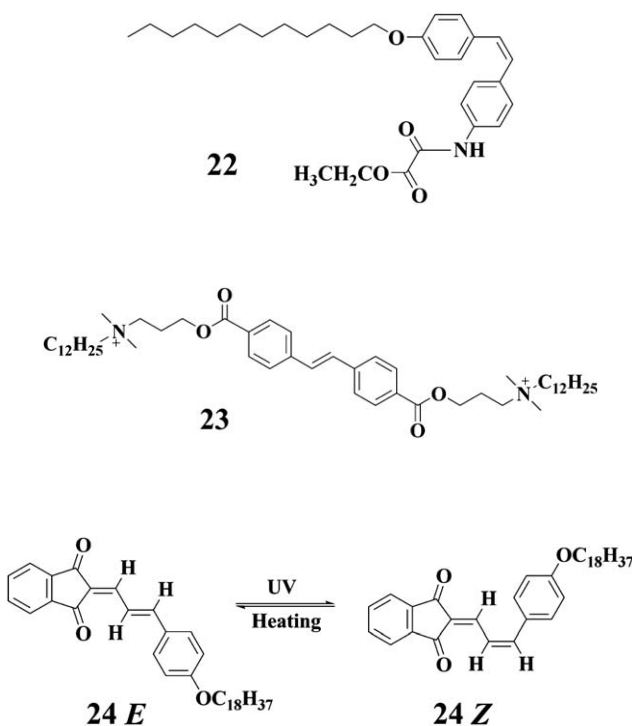


Chart 1 Photo- and thermal isomerization of **24**.

anthracene-excimer in the gel phase, and as a result the photodimerization was inhibited.

Compounds **27** and **28**⁵⁸ are photochromic because of the presence of *2H*-chromene moieties which can be reversibly transformed between the closed and open forms as shown in Chart 3. The neutral carboxylic acid derivatives of **27** and **28** can be easily dissolved in DMF and DMSO. However, the corresponding sodium salts can gelate DMF and DMSO. Upon UV light irradiation the gels became rapidly colored and transformed into the solutions. The studies show that the transformation of the closed form into the open form of the *2H*-chromene moieties in **27** and **28** affects strongly the intermolecular H-bonding interactions. The gel-phases can be restored by heating and further cooling the solutions. In addition, the gel-sol transitions for gels of **27** and **28** can also be triggered by lowering the pH values of the systems.

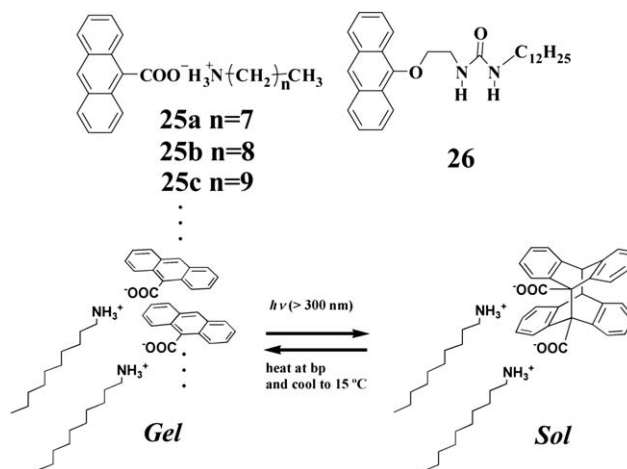


Chart 2 Photodimerization and dissociation of **25c** under UV light irradiation and heating.

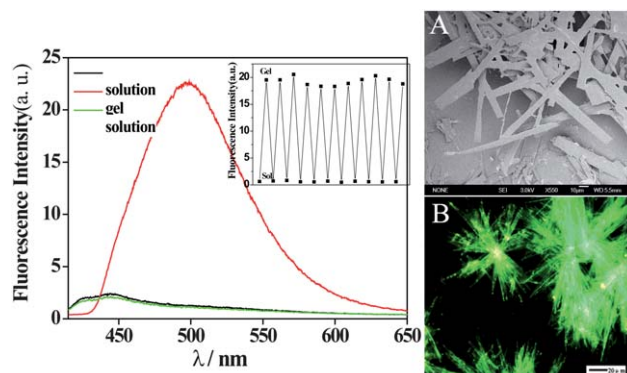


Fig. 6 (Left) Fluorescence spectra of **26** (20 mg mL⁻¹) in 1,2-dichloroethane (black), the gel phase (red), and the solution formed after heating the gel phase (green); (Right) SEM image of the xerogel based on **26** (A) and fluorescence microscopy image of the xerogel (B) from 1,2-dichloroethane.

Spiropyran (SP) is another type of photochromic molecules. The respective closed form and open form (merocyanine form) can be reversibly interconverted by alternating UV and visible light irradiations. By taking advantage of the photochromic behavior of spiropyran, Zhang and her coworkers developed a photoresponsive hydrogelator **29**⁵⁹ in which the spiropyran unit was converted to the corresponding merocyanine form (MC). The gel-sol transition occurred upon exposure of the gel to visible light irradiation, and the gel phase could be regenerated by further UV light irradiation (Fig. 7). The light responsiveness of the hydrogel based on **29** is due to the fact that merocyanine moiety has a strong tendency to form π - π stacking compared to the closed form (spiropyran).

Some of us reported a spiropyran-functionalized dendron **30**⁶⁰ which can gel toluene and benzene. Multivalent π - π interactions due to the dendron segment in **30** may be the driving force for the gelation. Absorption spectral studies showed that the photochromic reaction of the spiropyran unit in **30** could take place both in solution and gel phase. However, the gel phase was not destroyed after UV light irradiation, and the yellow gel was transformed into the purple-blue gel as illustrated in Fig. 8.

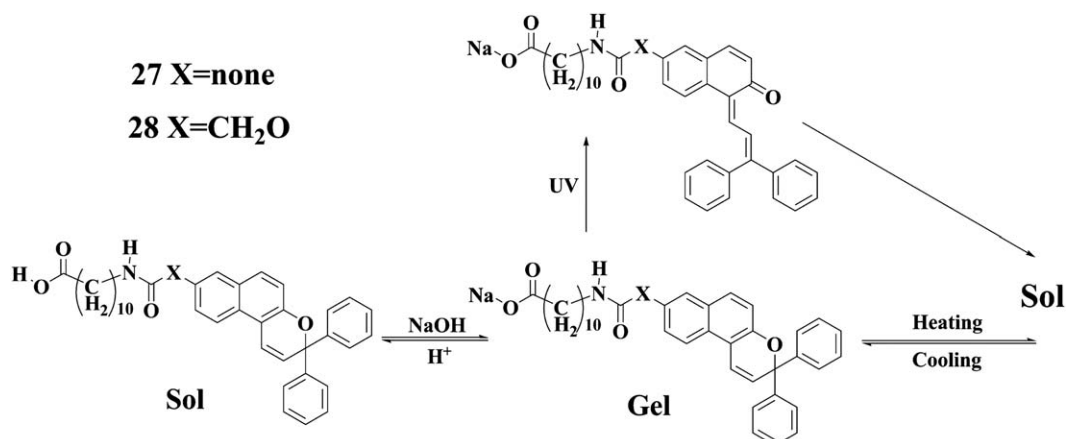


Chart 3 Illustration of interconversion of compounds 27 and 28.

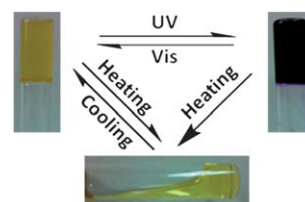
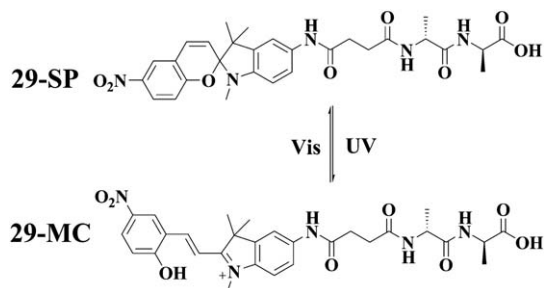


Fig. 8 Illustration of the gel-to-gel transformation after heating, cooling, UV and visible light irradiations.

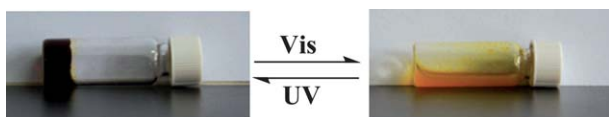
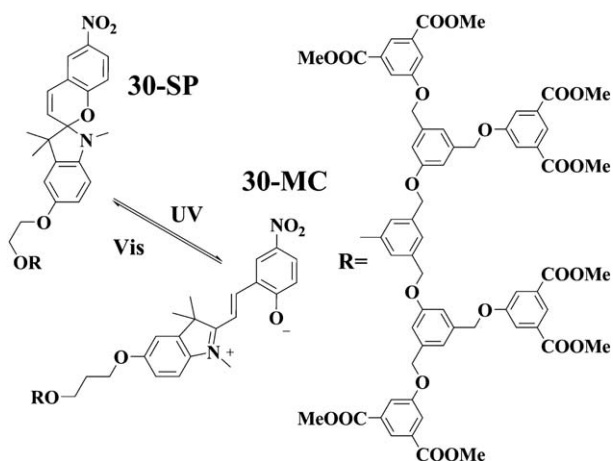


Fig. 7 Reversible transformation of the SP and MC forms of 29, and an illustration of the gel-sol transition after photoirradiation.

Further visible light irradiation of the purple-blue gel led to the yellow gel again. The results also manifest that the merocyanine form in the gel phase becomes more stable compared to that in solution. Of particular interest the purple-blue gel exhibits relatively strong red fluorescence and the red fluorescence of the gel can be switched off by visible light irradiation.



Dithienylethene derivatives as photochromic molecules have been extensively investigated. Gelators containing photochromic dithienylethene units are available. For instance, Feringa and coworkers reported gelator **31**⁶¹ featuring one dithienylethene moiety. Photochromic transformations can easily take place for **31** both in the solution and gel states accompanying the reversible spectral changes. However, the gel-sol transition cannot be triggered by light irradiation. Interestingly, the chirality of the gel phase is preserved during the photochromic reactions; moreover, the chirality is lost after gel-sol transition, and gels with opposite chirality are generated after further cooling the respective solutions as illustrated in Chart 4. Tian and his co-workers⁶² described another dithienylethene-derived gelator **32**. Similarly, photochromic transformations can occur for **32** both in the solution and gel states. Again, the gel-sol transition cannot be induced by light irradiations. However, the gel can be converted to the solution after introducing F⁻, and the gel phase can be restored by addition of acid (Fig. 9).

4. Chemoresponsive gels based on LMWGs

Chemoresponsive gels based on LMWGs are herein referred to as gels that exhibit responsiveness to chemical species (neutral molecules or metal ions or anions). Clarke, Steed and their coworkers¹⁷ have just recently published a detailed review on the progresses of metal- and anion-binding supramolecular gels, and they have already introduced various gels based on LMWGs which respond to metal- and anion-binding. Xu and coworkers⁶³⁻⁶⁹ have reported series of hydrogels in the presence of enzymes. In this section we will just focus on gels that are

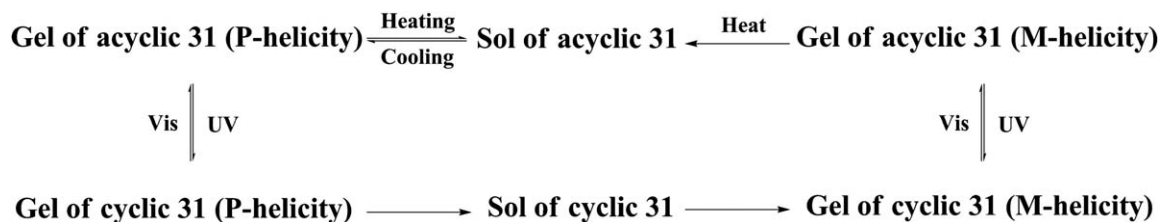
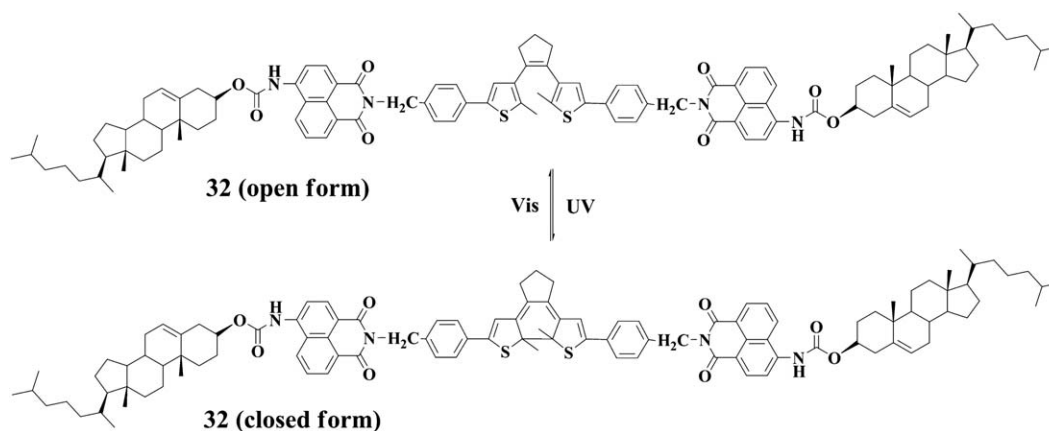
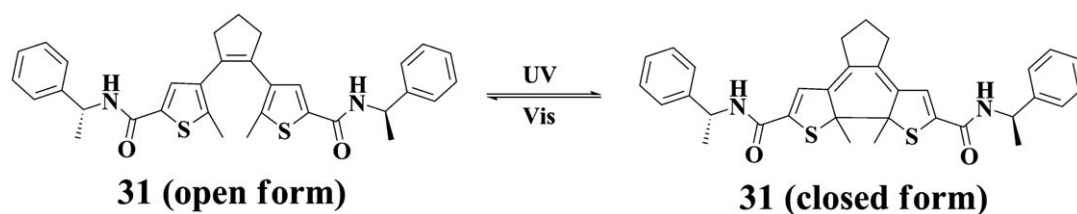


Chart 4 Reversible transformation of the open and closed forms of **31**, and the gel-sol transitions with chirality variation.

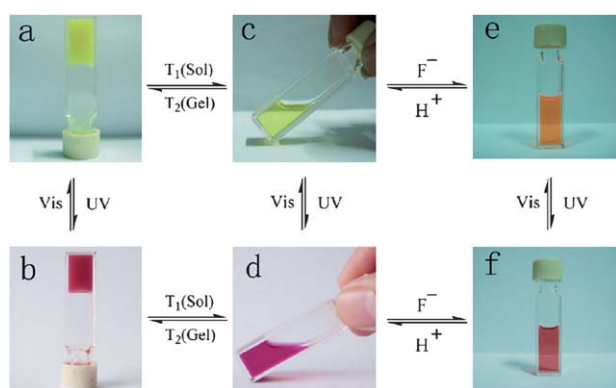


Fig. 9 Reversible transformation of the open and closed forms of **32**, and the gel-sol transitions under the cooperative effects of light, thermal, fluoride anions, protons: (a) Gel(open); (b) Gel(closed); (c) Sol(open); (d) Sol(closed); (e) Sol(open) + F^- ; (f) Sol(closed) + F^- .

responsive to neutral molecules through either chemical reactions or intermolecular interactions with LMWGs.

Some of us⁷⁰ designed the cholesterol-based gelator **33** with maleimide unit which can easily react with thiols under basic

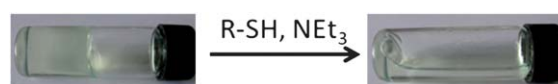
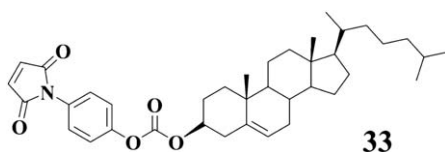
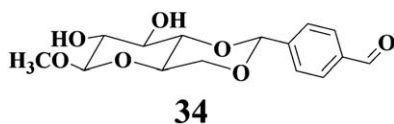


Fig. 10 Chemical structure of **33** and gel-sol phase transition triggered by the addition of n-hexylthiol and triethylamine after 2 h for the organogel of **33** (5.0 mg mL^{-1}) in cyclohexane.

conditions to form the corresponding Michael adducts. Gelator **33** can gel several solvents including cyclohexane leading to transparent gels. It is interesting to note that the gel of **33** from cyclohexane can be gradually transformed into the solution after addition of n-hexylthiol (ca. 2.1 eq.) and triethylamine (ca. 2.1 eq.) onto the top layer of the gel as demonstrated in Fig. 10. Such gel-sol transition is attributed to the Michael reaction between the maleimide unit in **33** and thiol, which is facilitated by the presence of triethylamine; accordingly the intermolecular interactions of **33** will be altered. However, if n-hexylthiol is added alone, the gel-sol transition can not occur even after several days under the same conditions. This is probably because the Michael reaction between maleimide and thiol is slow in the absence of bases such as triethylamine. When only triethylamine is added the gel phase can not be destroyed either.



Compound **34** was a saccharide-derived hydrogelator containing an aldehyde group which can react with cysteine to form thiazolidine derivative.⁷¹ Fig. 11 displays the variation of hydrogels of **34** after the careful addition of the corresponding aqueous solution of amino acids on the top of the hydrogels and further incubation at 37 °C for 4 h. The hydrogel in the vial containing cysteine was completely transformed into solution, and the hydrogels in other vials were unaffected as demonstrated in Fig. 11. Such selective responsiveness of the hydrogel toward cysteine should be related to the specific reaction of aldehyde with cysteine to form the thiazolidine derivative. The aldehyde group cannot react with other amino acids including the acidic and basic ones under the same conditions. In addition, the hydrogel of **34** is sensitive to acidic solutions. The hydrogel of **34** can be converted to the solution after mixing the aqueous solution with pH = 1.18 at 37 °C for 60 h.



Alkylamines are generally nongelators or inefficient ones. However, Weiss and coworkers^{72,73} found that the amines can react with carbon dioxide to afford ammonium carbamates (see Chart 5) which are more efficient LMWGs than the respective amines. In fact, these ammonium carbamates from the reaction between the respective amines and CO₂ can gel several solvents. Interestingly, the ammonium carbamates can be transformed into the corresponding amines again by slight heating. In this manner, reversible formation of organogels is realized by employing 'latent' gelators (amines) and CO₂.

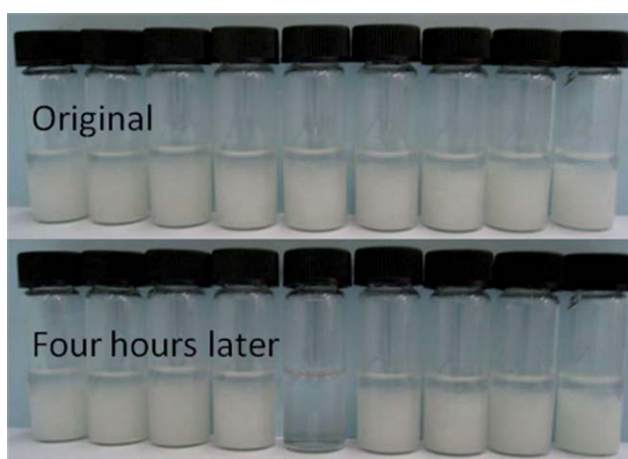


Fig. 11 Hydrogels with **34** covered with the aqueous solutions of different amino acids; the sequence of amino acids added to the hydrogels from left to right is as follows: aspartic acid, lysine, alanine, serine, cysteine, histidine, arginine, proline, and phenylalanine.

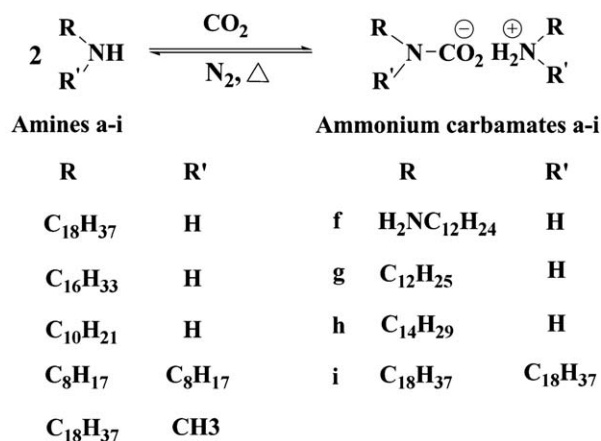
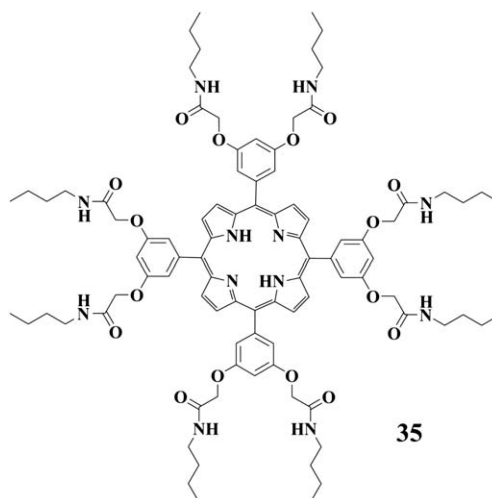
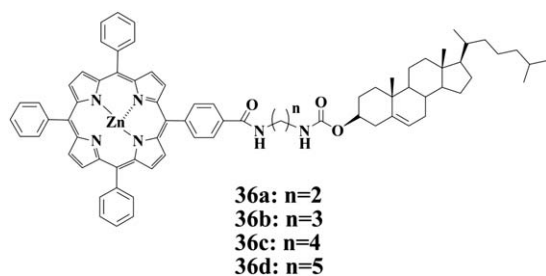


Chart 5 The reaction of amines and carbon dioxide generating ammonium carbamates.

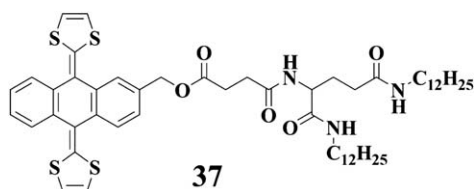
Several reports indicate that it is possible to improve the gel stabilities by introducing certain molecules to the systems. For instance, Shinkai and coworkers⁷⁴ reported porphyrin-derived gelator **35** with amide groups. Compound **35** can gel benzene and toluene, but not *p*-xylene and anisole. However, all four of the solvents noted above can be gelled by **35** in the presence of C₆₀. Moreover, the gel-to-sol transition temperature for the gel of **35** from benzene was enhanced from 79 to 120 °C after addition of C₆₀. A striking morphological change was induced for the self-assembly structures of **35** after introducing C₆₀. They attributed these changes to the strong porphyrin-C₆₀ interactions.



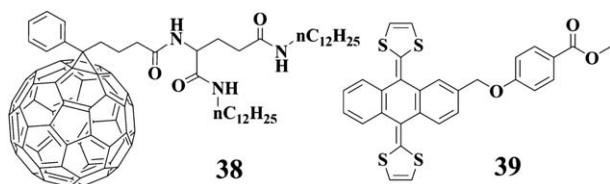
Compounds **36a–d** are series of Zn(II) porphyrin-based gelators with cholesterol segments reported by Shinkai and coworkers.⁷⁵ Interestingly, the influence of C₆₀ on the gelation abilities of **36a–d** are dependent on the spacer groups in **36a–d**. The gelation abilities of **36a** and **36c** in which -(CH₂)₂- and -(CH₂)₄- are the spacer groups, respectively, are enhanced in the presence of C₆₀. For **36b** and **36d** in which the spacer groups are -(CH₂)₃- and -(CH₂)₅-, respectively, however, their gelation abilities are not obviously affected by C₆₀. The influence of C₆₀ on the gelation abilities of **36a** and **36c** is ascribed to the binding of Zn(II) porphyrin units with C₆₀, forming a 2 : 1 Zn(II) porphyrin/C₆₀ sandwich complex.



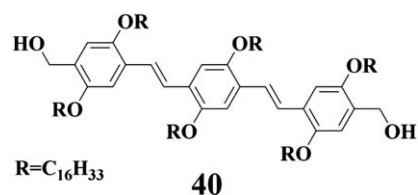
9,10-bis(1,3-Dithiol-2-ylidene)-9,10-dihydroanthracene, which is usually referred to as ex-TTF, is unique in terms of its structure and electrochemical behavior. Martín *et al.*^{76–81} have presented series of reports with regard to the binding of ex-TTF with fullerene and assembly of ex-TTF-fullerene derivatives into nanostructures comprising supramolecular dendrimers. We have very recently reported an ex-TTF derived gelator **37** with *L*-glutamid-derived lipid segment which can facilitate the gelation through hydrophobic and H-bonding interactions.⁸² Compound **37** can gel several organic solvents such as toluene, DMSO and ethanol. Notably, the gelation ability of **37** can be enhanced after addition of C₆₀. The gel melting temperature increases gradually by introducing C₆₀ reaching the maximum after addition of 0.5 eq. of C₆₀.



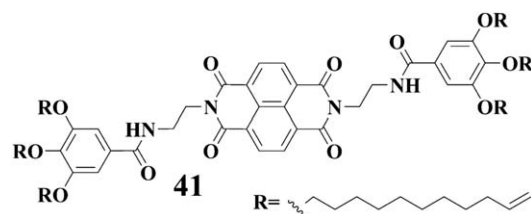
Compound **38** is a new C₆₀-derived gelator with *L*-glutamid-derived lipid unit reported by us just recently.⁸³ The results manifest that the gelation ability of **38** can be improved by addition of an exTTF compound **39**, for which the intermolecular interaction between the C₆₀ unit in **38** and exTTF unit in **39** is responsible based on the absorption and ¹H-NMR spectral studies.



Ajayaghosh and his collaborators⁸⁴ have intensively investigated the self-assembly and gel formation of oligo(*p*-phenylene vinylene)s (OPVs). For instance, compound **40**^{84d} with two –OH groups can gel several nonpolar solvents, but the gels of **40** from relatively polar solvents are thixotropic and mechanically unstable. They have recently shown that the self-assembly of OPV molecules is accelerated in the presence of carbon nanotubes (CNTs) through the interactions of OPV molecules and CNTs. In this way, CNTs which are dispersed and aligned within the gel can on one hand reinforce the self-assembly structures of OPV molecules, and may on the other hand act as physical cross-links between these self-assembly structures, thus enhancing the gel stability.



Shinkai and coworkers⁸⁵ have described a versatile gelator **41** with an electron accepting naphthalenediimide moiety. It is interesting to note that gels of **41** can form charge-transfer complexes with dihydroxynaphthalenes, but not with alkoxy- and hydroxynaphthalenes. Moreover, different color gels are generated with different isomers of dihydroxynaphthalenes. Thus, naked-eye differentiation of positional isomers of dihydroxynaphthalenes becomes possible with the gels of **41**. The authors also mentioned that the gel superstructure was extremely sensitive to the amount of dihydroxynaphthalene compounds added to the gel system. For example, when more than 1.2 equiv of dihydroxynaphthalene were added, the gel-sol transition occurred easily.



5. Conclusion and perspectives

In summary, we have introduced recent developments of stimuli-responsive gels based on LMWGs for which the gel-sol transitions can be triggered by other stimuli except heating. These stimuli-responsive gels are prepared from LMWGs with electroactive or photoresponsive or reactive groups. However, molecular design of LMWGs leading to stimuli-responsive gels is still not straightforward since incorporation of functional groups into gelator-frameworks may perturb the self-assembly processes in a destructive way. Additional studies will be required, especially those dealing with the kinetics and mechanisms of gel formation. These studies may offer guiding principles for rationally designing functional LMWGs and responsive gels.

Clearly, stimuli-responsive gels based on LMWGs deserve more exploitations since their potential applications are enormous. For instances, such gels may find uses in areas where on-demand flow is desirable. They may also be useful as reversibly formed membranes or media for the controlled release of drugs. When functional solvents such as cholesteric or ferroelectric liquid crystals are gelled with these functional gelators, more advanced applications can be imagined.

Further studies in this attractive area need the endeavours of scientists of different disciplines including organic chemistry, physical chemistry, nanoscience and materials science. Stability and mechanical strength are among the issues that must be well addressed for realizing the practical applications of such gels. Design and synthesis of functional gelators that will lead to gels

responsive to more than two external stimuli still remain challenging.

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