Soft Matter

RSC Publishing

PAPER

View Article Online
View Journal | View Issue

A multi-stimuli responsive organogel based on a tetrapeptide–dithienylcyclopentene conjugate†

Cite this: *Soft Matter*, 2013, **9**, 7538

Yi Jiang,[a] Fei Zeng,[b] Ruiying Gong,[a] Zongxia Guo,[a] Chuan-Feng Chen[b] and Xiaobo Wan*[a]

Multi-stimuli responsive organogels based on low-molecular-weight gelators (LMWGs) have attracted much attention due to their potential applications. Herein, the synthesis and the self-assembly behavior of a novel molecular gelator based on a tetrapeptide–dithienylcyclopentene conjugate is described. This gelator forms stable gels in THF, acetone and acetonitrile, in which the formation of anti-parallel β-sheets of the biomimetic tetrapeptides is the key driving force. Further studies suggest that the organogel is multi-responsive to various external stimuli including temperature, light, chemicals, and mechanical force. Moreover, in the presence of catechol, this gelator forms a more robust organogel, accompanied by a dramatic change of the assembly manner and rheological properties. These prominent features of this conjugate make it an excellent smart soft material with potential applications in areas such as drug encapsulation and release systems.

Received 17th April 2013
Accepted 25th May 2013

DOI: 10.1039/c3sm51052b

www.rsc.org/softmatter

Introduction

Low-molecular-weight gelators (LMWGs) could be assembled into entangled three-dimensional fibrous network structures on the nano-/micro-scale, which entrap and immobilize solvent molecules by capillary forces to form molecular gels.[1] The driving forces towards gelation usually are various weak non-covalent interactions such as hydrogen bonding, electrostatic attraction, metal coordination, and π–π stacking/hydrophobic interactions. Consequently, the weak nature of these non-covalent interactions allows various external stimuli including temperature, light, chemicals and mechanical force, to control the properties of gels easily.[2,3] Therefore, apart from the studies solely on the gel formation and structures, stimuli responsive gels have recently attracted increasing attention, due to their potential applications as new functional materials, such as sensors, actuators, *etc.*[4] For example, a multi-stimuli responsive organogel based on a photo and redox responsive-organic gelator featuring tetrathiafulvalene and azobenzene has been reported by Zhang and coworkers.[5]

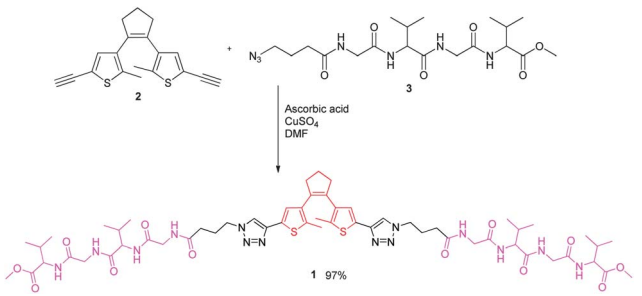
The incorporation of functional groups including photo-responsive, electroactive, or chemically reactive groups to LMWGs could afford responsive organogels. For instance, photo-responsive organogels based on azobenzene[6] or coumarin[7] were widely studied. As a well-known photochromic group, dithienylcyclopentenes,[8] whose structure could be reversibly transformed photochemically between the colorless open-ring and the colored closed-ring forms upon UV/visible irradiation, hold particular promise in smart materials because of their unique fatigue resistance and thermal irreversibility. For example, Feringa and coworkers developed photo-responsive dithienylethene–urea-based organogels with reversible optical transcription of supramolecular chirality into molecular chirality.[9] More recently, Li's group[10] developed a photochromic dithienylcyclopentene organogel, in which dithienylcyclopentene behaved as a bridge between the amide and the long alkyl chains. However, to date, only a few dithienylethene-based organogels were reported.[9–11] Especially, to our surprise, although oligopeptide-based responsive organogels were widely studied,[12,13] to the best of our knowledge, organogels based on a peptide–dithienylcyclopentene conjugate have not been reported, and there has also been no mention the multi-stimuli responsive ones.

Following our continued pursuit of developing peptide-based organogels,[14] herein we report a novel organogel based on peptide–dithienylcyclopentene conjugate **1** (Scheme 1) and its self-assembly behavior. This molecule was designed on the basis of the following considerations. Firstly, the dithienylcyclopentene chromophore has been chosen as the photochemical

[a]*Key Laboratory of Bio-mass based materials, Chinese Academy of Sciences, Qingdao Institute of Bioenergy and Bioprocess Technology, 189 Songling Road, Qingdao, Shandong Province, P. R. China, 266101. E-mail: wanxb@qibebt.ac.cn; Fax: +86-532-806-62741; Tel: +86-532-806-62741*

[b]*Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Molecular Recognition and Function, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China*

† Electronic supplementary information (ESI) available: Synthetic procedure and characterization data for new compound **1**, the morphology and PXRD data of the xerogel after the addition of catechol, frequency sweep experiment, ^{1}H NMR of **1** before and after the addition of catechol, photochromic behavior of **1** after the addition of catechol, and the plausible packing model of **1**. See DOI: 10.1039/c3sm51052b



Scheme 1 The chemical structure of compound **1** and the synthetic approach.

core due to its simple, clean, and efficient photochemical isomerization.[8] Secondly, peptide-based organogels might be responsive to external stimuli such as chemicals and mechanical force as evidenced by the literature.[13] Thirdly, we have shown that an artificial oligopeptide N_3-GVGV-OMe (G = glycine, V = valine) that mimics the repeating sequence in silk proteins could form an organogel by forming anti-parallel β-sheets,[14] and could be used to modify functional molecules easily *via* the well-known "click chemistry". Thus, the formation of multi-responsive organogels based on the tetrapeptide–dithienylcyclopentene conjugate is anticipated. It turned out that this conjugate formed organogels easily. More importantly, the organogel is multi-responsive to various stimuli such as temperature, UV/visible irradiation, chemical (catechol), and mechanical force. Also, interestingly, in the presence of catechol, the assembly behavior of peptide segments is modulated from anti-parallel β-sheets to random coils, resulting in the morphological and rheological changes of the organogel. Such simultaneous modulation of the molecular assembly behavior, morphology and rheological properties remain a challenge, especially in the field of stimuli-responsive supramolecular organogels.[15] This is the first example of a multi-stimuli responsive peptide–dithienylcyclopentene conjugate.

Results and discussion

Molecular synthesis and organogelation behavior

Gelator **1** (Scheme 1) was synthesized by the highly efficient Huisgen 1,3-dipolar cycloaddition of compounds **2** and **3** in the presence of a catalytic amount of $CuSO_4 \cdot 5H_2O$ and ascorbic acid with a yield of 97%. Its purity and chemical structure were confirmed by ^{1}H NMR, ^{13}C NMR, and HR-ESI MS. With gelator **1** in hand, its gelation behavior was then evaluated in different organic solvents. Stable organogels are formed in various solvents such as THF, acetonitrile, and acetone through the heating–cooling process. The critical gelation concentrations (CGCs) are listed in Table 1. A typical sol–gel transition is illustrated in Fig. 1a. A transparent yellow gel was formed by cooling a hot solution of **1** (11.2 mg ml^{-1}) in THF, and the gel was then transformed back into the corresponding solution when reheated. The xerogel structure of **1** was studied using a scanning electron microscope (SEM). Fig. 1b–d show the SEM images of xerogels of **1** obtained from THF, acetone and acetonitrile, respectively. Entangled three-dimensional (3D) fibrous networks with widths of 15–50 nm and lengths of several micrometers were observed. Compared with the xerogel formed in acetone, the xerogels of **1** formed in THF and acetonitrile exhibit more densely packed 3D networks.

Table 1 The gelation experimental results of compound **1** in different solvents[a]

Solvents tested	Gelation results
THF	G_o (11.2 mg ml^{-1})
CH_3CN	G_o (18.6 mg ml^{-1})
Acetone	G_o (7.2 mg ml^{-1})
Toluene, chloroform, DCM, EtOAc	I
Hexane, benzene	I
Methanol, ethanol, 1,4-dioxane	S
DMF, DMSO	S

[a] The gelation test was performed based on the heating–cooling process. G_o: opaque gel; S: solution; I: insoluble; each of the CGCs was measured at 25 °C.

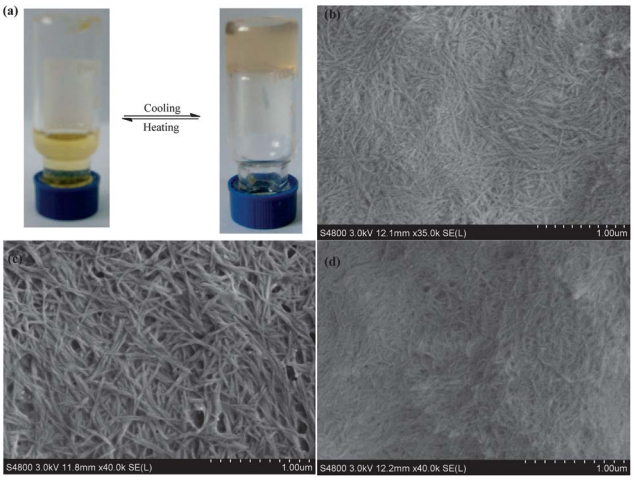


Fig. 1 Illustration of the organogel formation with gelator **1** (12 mg) in 1 ml of THF (a), and SEM images of xerogels of **1** obtained from THF (b), acetone (c), and acetonitrile (d).

Investigation of the driving force of organogelation

We further studied the driving force of **1** toward gelation *via* FT-IR, temperature dependent (TD)-^{1}H NMR and powder X-ray diffraction (PXRD) techniques. FT-IR spectroscopy provides information about the arrangement of tetrapeptide segments. The absorption peaks at 3284 cm^{-1}, 1626 cm^{-1} and 1543 cm^{-1} clearly indicate the formation of β-sheets, as shown in Fig. 2. Moreover, the weak absorption at 1692 cm^{-1} suggests that the β-sheets are anti-parallel.[16] No obvious characteristic peaks of either the α-helix or the random coil were found, suggesting the strong tendency toward anti-parallel β-sheet formation of **1**. In the TD-^{1}H NMR experiments (Fig. 3), the resonance signals for the NH protons H_1–H_4 of **1** are gradually shifted upfield upon the increase of the temperature from 298 to 328 K. In contrast, the signal of H_5 of the dithienylcyclopentene does not change. The above observation suggested that the strength of hydrogen bonding between peptide segments became weak upon heating. In addition, the formation of β-sheets between peptide segments was also evidenced by the

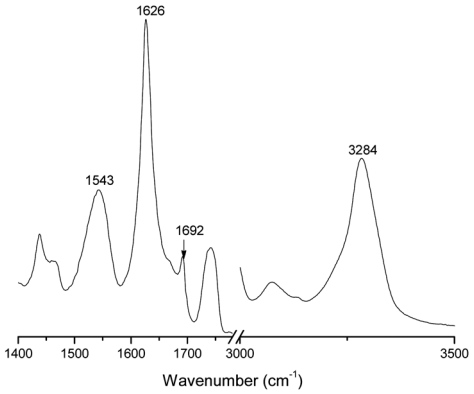


Fig. 2 Partial FT-IR spectrum of **1** in xerogel at 298 K.

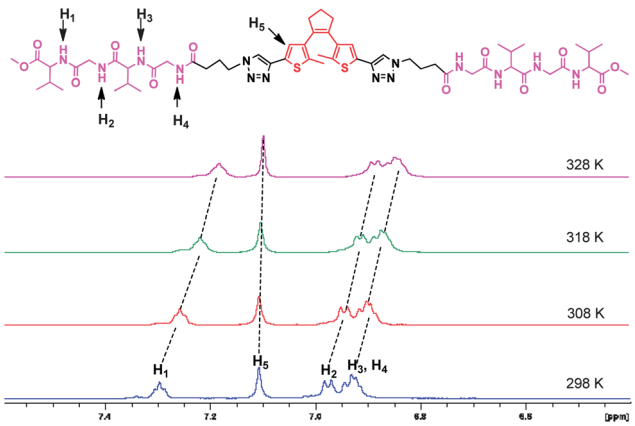


Fig. 3 Partial ^{1}H NMR spectra of the gel formed with **1** (5 mg ml^{-1}) in acetonitrile-d_3 at different temperatures.

PXRD experiment (Fig. 4). The peak that was assigned to a periodic distance of 4.5 Å in the wide-angle region was ascribed to the packing of anti-parallel β-sheets.[17] Based on all these results, we concluded that the strong multiple hydrogen bonding between peptide segments might be the key factor guiding the assembly processes and responsible for the gel formation.

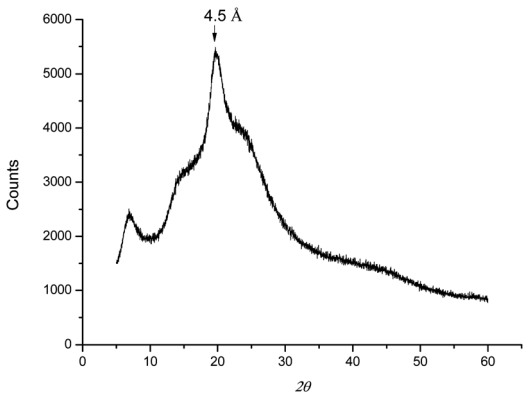


Fig. 4 Powder X-ray powder diffraction pattern (PXRD) of xerogel of compound **1**.

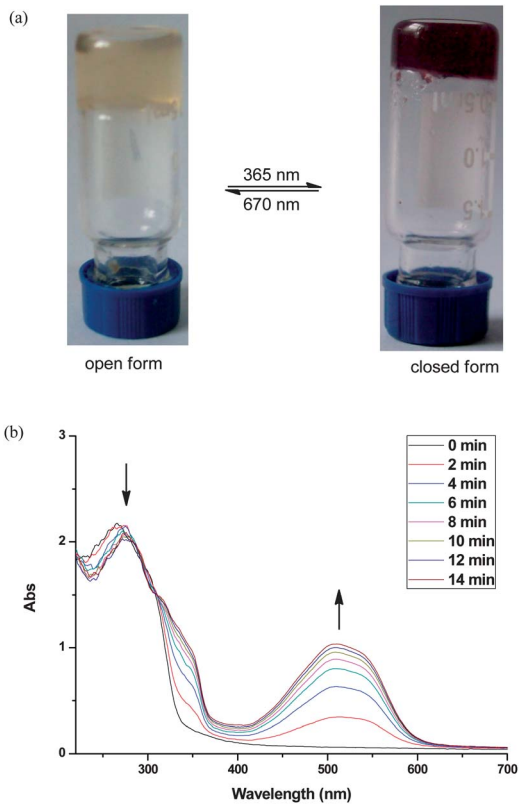


Fig. 5 (a) Image of organogel **1** triggered by UV-vis light; (b) UV-Vis spectra evolution of organogel **1** in THF (9 mg ml^{-1}) under 365 nm irradiation as a function of time.

Tuning the organogel by light

The gel exhibited the reversible photochromic behavior as designed. When the gel was irradiated with UV light (365 nm) for 8 minutes, the color of the gel changed from pale yellow to deep brown (Fig. 5a), suggesting the conformational change of dithienylcyclopentene. The deep brown color could also be reverted to pale yellow upon visible light irradiation. Such transition of the organogel triggered by UV and visible light irradiation was reversible in the tested cycles. The conformational change of the dithienylcyclopentene chromophore of organogel **1** was further confirmed by its UV-vis spectra evolution upon UV irradiation at 365 nm, as evidenced by the appearance of a new broad absorption band at ~510 nm (Fig. 5b), which indicated the photoisomerization from the opened-ring form to the closed-ring form. The isomerization efficiency was calculated to be ~20% by ^{1}H NMR analysis.[9a] The opened-ring sample is almost colorless whereas its closed-ring isomer is deep colored, due to a longer π-conjugation of the closed-ring form than that of the open-ring form. All these results demonstrated the reversible photochromic behavior of this organogel.

Tuning the assembly behavior and morphology of organogel

Inspired by the previous reports,[13a,b] catechol was added to the THF solution of **1** to study the chemical-responsive behavior of the organogel. The addition of catechol might affect the

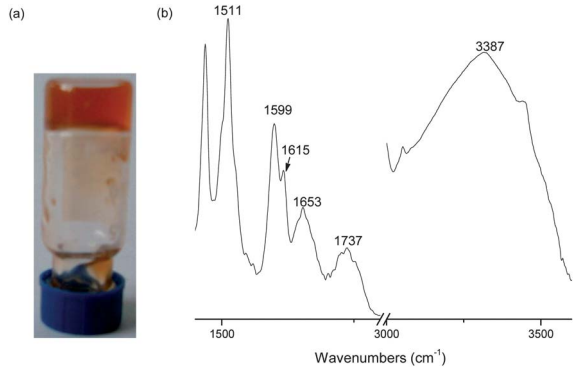


Fig. 6 (a) Illustration of the organogel of **1** (12 mg) in 1 ml of THF formed after the addition of catechol (12 mg); (b) partial FT-IR spectrum of organogel **1** (12 mg) after the addition of catechol (12 mg) at 298 K.

self-assembly behavior of the peptide segments of **1**, hence change its gelation ability because of its strong ability to form hydrogen bonding. Interestingly, the organogel (named as **1**–catechol/THF organogel) was still formed through the heating–cooling process of **1** (12 mg) in THF after the addition of 12 mg catechol, as shown in Fig. 6a. FT-IR, PXRD and SEM experiments of the **1**–catechol/THF organogel were then conducted to analyze the assembly behavior changes of the peptide segments after the addition of catechol. Compared with the FT-IR spectrum of the organogel formed before addition of catechol (Fig. 3), when catechol was embedded in the organogel, all the characteristic peaks of β-sheets disappeared, suggesting the disruption of the anti-parallel β-sheets (Fig. 6b). Meanwhile, a new absorption peak at 1653 cm^{-1} (Amide I) was found, which is the characteristic peak of random coils.[18] Moreover, the PXRD experiment (Fig. S3, ESI†) showed that characteristic peaks assigned to the formation of β-sheets also disappeared, and a new broad peak, which is characteristic for an amorphous structure, was found. The SEM result (Fig. S4, ESI†) also shows the morphological change of the organogel formed after the addition of catechol. The xerogel exhibited a honeycombed structure, and no fibrous structure was observed. ^{1}H NMR spectra show that the resonance signals of –OH of catechol shift downfield and become broad, suggesting the formation of new hydrogen bonding interactions between peptide segments and catechol (Fig. S6, ESI†). These results suggested that catechol participated in the formation of hydrogen bonding interactions and might act as a "glue" to link oligopeptides together to form new network structures, so the gel state was maintained although the assembly manner of the peptide segments of **1** was modulated from the anti-parallel β-sheet to the random coil. UV irradiation at 365 nm of organogel **1** after the addition of catechol also resulted in the photo-isomerization from the opened-ring to the closed-ring (Fig. S7, ESI†). More interestingly, the mechanical strength of the organogel increased upon the addition of catechol, which will be discussed in the following chapter.

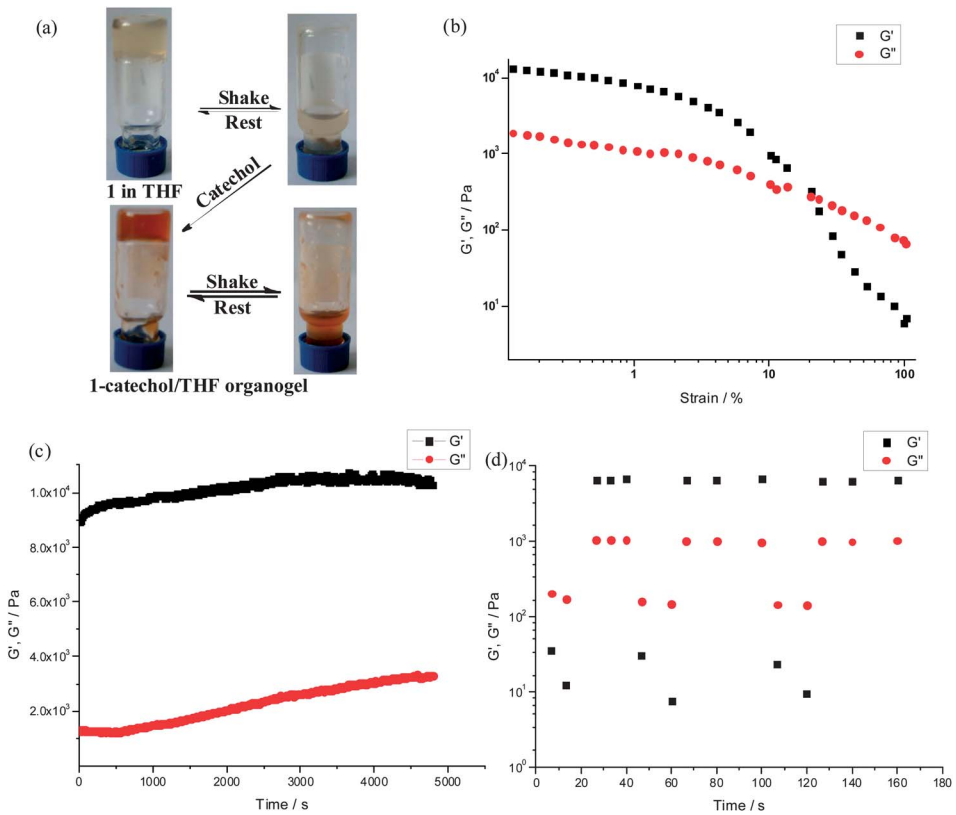


Fig. 7 (a) Reversible sol–gel phase transition of the organogel of **1** in THF before and after the addition of catechol triggered by shear-stress. Storage modulus *G′* and loss modulus *G″* values of the organogel of **1** (14 mg) in 1 ml of THF after the addition of catechol (16 mg) on the rheological experiments of (b) strain sweep; (c) time sweep; (d) three cycles of deformation and recovery processes.

Investigation of thixotropic properties *via* rheological techniques

Serendipitously, we found that the organogel of **1** in THF formed both before and after the addition of catechol exhibited thixotropic properties (Fig. 7a). For example, the organogel of **1** in THF was changed to a solution by vigorous shaking, and then regenerated rapidly upon resting. This reversible gel–sol phase transition could be repeated many times. To the best of our knowledge, there is no reported example of a thixotropic dithienylcyclopentene–oligopeptide organogel. Rheological characterizations of organogels were further performed in dynamic mode to investigate this mechano-responsive behavior in detail. However, the rheological data of the organogel of **1** formed in THF was difficult to obtain since the gel was very soft and its mechanical properties were beyond the test range of the equipment. Surprisingly, although the addition of catechol to the gel broke the well-established anti-parallel β-sheets of tetrapeptides, the **1**–catechol/THF organogel was much stronger while it retained the thixotropic properties.

The rheological experiments on the **1**–catechol/THF organogel were then conducted. The changes in storage modulus (G') and loss modulus (G'') under shear strain were recorded, as shown in Fig. 7b. At low strain values, the G' values are one order of magnitude larger than those of G'', suggesting the dominant elastic character of the organogel. Both G' and G'' remain roughly constant below the critical strain value (*ca.* 1.0%). When the strain value is above 1.0%, both moduli gradually decrease, demonstrating a partial breakup of the gel. The changes of storage modulus (G') and loss modulus (G'') as a function of angular frequency were also determined (Fig. S5, ESI†). The frequency sweep results also show that at low frequency values (*ca.* below 1.0 rad s^{-1}), the G' values are one order of magnitude larger than the values of G'', suggesting the behavior of a "true gel". However, both G' and G'' show obvious frequency dependency in the 1.0–100 rad s^{-1} frequency range, which indicates that the organogel has poor tolerance to external forces in the 1.0–100 rad s^{-1} frequency range.

The recovery property of the **1**–catechol/THF organogel was further studied. As shown in Fig. 7c, after the organogel is continually deformed at 100% deformation for 30 s, its G' and G'' are monitored over 5000 s to follow the structural recovery process of the organogel. The organogel recovers its elastic property quickly and acts as a gel-like material once the external force is removed. Moreover, the thixotropic process of the organogel is fully reproducible for at least 3 cycles (Fig. 7d). Overall, the rheological measurements show that the **1**–catechol/THF organogel is a robust thixotropic gel with a fast-recovery ability, which might be attributed to the quick reorganization of multiple hydrogen bondings between peptide segments and catechol. The fast reformation ability of the gel is important in the applications for injectable gels, where the quick deformation during injection and the timely reformation after injection are critical.[19]

Conclusion

In conclusion, we have designed and synthesized a novel multi-responsive organogelator based on a tetrapeptide–dithienylcyclopentene conjugate. This organogelator forms stable gels in THF, acetone and acetonitrile, and the formation of anti-parallel β-sheets of the biomimetic tetrapeptides is the key driving force. This organogel exhibits a smart multi-stimuli responsive behavior upon exposure to external stimuli such as temperature, light, chemicals (catechol), and mechanical force. Moreover, in the presence of catechol, this gelator forms a more robust organogel, with a dramatic change of the assembly behavior and rheological properties. These prominent features of the organogel system make it an excellent smart soft material with promising potential applications in areas such as drug encapsulation and release, and further studies on its applications are in process.

Experimental

General methods

All starting materials were obtained from commercial suppliers and used as received. All solvents were distilled with suitable drying agents. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AMX 600 spectrometer (^{1}H NMR: 600 MHz; ^{13}C NMR: 150 MHz) at 298 K. The HR-ESI mass spectrum was obtained on a Bruker APEX IV instrument. Powder wide-angle X-ray diffraction (PXRD) patterns of xerogels were obtained using a D/MAX-2500/PC diffractometer (Rigaku Co., Japan) with Cu Kα radiation ($\lambda = 1.54178$ Å).

Synthesis of gelator 1

The mixture of compounds **2** (ref. 14) (61.6 mg, 0.1 mmol) and **3** (ref. 20) (91.0 mg, 0.2 mmol) in 5 ml of DMF was stirred in the presence of a catalytic amount of $CuSO_4 \cdot 5H_2O$ (2.5 mg) and ascorbic acid (7 mg) at room temperature overnight. Et_2O (30 ml) was added to the mixture, and the resulting precipitate was filtered and washed with Et_2O (3 × 30 ml) to afford **1** as a pale yellow solid with a yield of 97%. M.P. = 147–149 °C; ^{1}H NMR (600 MHz, DMSO-d_6): $\delta = 8.40$ (s, 2H), 8.27 (t, $J = 5.8$ Hz, 2H), 8.12 (t, $J = 5.8$ Hz, 2H), 8.03 (d, $J = 8.2$ Hz, 2H), 7.86 (d, $J = 8.2$ Hz, 2H), 7.21 (s, 2H), 4.38 (t, $J = 6.8$ Hz, 4H), 4.19–4.16 (m, 4H), 3.80–3.73 (m, 6H), 3.63 (s, 6H), 2.81 (t, $J = 7.4$, 4H), 2.52–2.50 (m, 4H), 2.17 (t, $J = 7.2$, 4H), 2.08–1.97 (m, 10H), 1.89 (s, 6H), 0.88–0.84 (m, 24H); ^{13}C NMR (150 MHz, DMSO-d_6): $\delta =$ 172.4, 171.9, 171.7, 169.5, 169.4, 142.0, 136.4, 134.4, 133.4, 129.6, 120.8, 58.2, 57.8, 52.2, 49.5, 42.4, 42.0, 32.1, 30.9, 30.5, 26.2, 19.6, 19.4, 18.64, 18.55, 14.4. HR-MS (ESI) calcd: 1219.5750 for [M + H], 1241.5570 for [M + Na]; found: 1219.5786 for [M + H], 1241.5606 for [M + Na].

Field emission scanning electron microscopy (FE-SEM)

The morphologies of the xerogels were characterized by field emission scanning electron microscopy (FE-SEM, Hitachi S-4800) at an accelerating voltage of 15 kV. Samples were prepared by dropping the diluted gels on silicon slices and dried in a vacuum drying oven at room temperature for 2 days. To minimize sample charging, a thin layer of Au was deposited onto the samples before SEM examination.

Photoresponsive measurements

Photo irradiation was carried out using a 300 W Xe lamp (CEL-HXF 300) through a light guide and an appropriate color filter ($330 < \lambda < 390$ nm for UV light and $400 < \lambda < 700$ nm for visible light). UV-vis absorption spectra were obtained using a Varian Cary 100 UV-visible spectrophotometer. Fluorescence spectra were obtained with a 48000 DSCF spectrometer.

Rheological measurements

Rheological research was conducted using a stress-controlled rheometer (TA Instruments, ARG2) equipped with steel parallel-plate geometry (40 mm diameter), when the gap distance was fixed at 750 μm. In order to avoid the evaporation of THF, a solvent-trapping device was placed above the plate. All measurements were carried out at 283 K. To determine the linear viscoelastic region (LVER) of the gel sample, strain sweep at a constant frequency (6.28 rad s^{-1}) was performed in the 0.05–200% range. The frequency sweep was performed from 0.1 rad s^{-1} to 100 rad s^{-1} at a constant strain of 0.1%, well within the linear regime determined by the strain sweep. In order to examine the recovery behavior of the organogel, a thixotropic study was conducted. Just after the strain sweep progress, the recovery of the storage modulus of the destroyed gel was monitored at a constant frequency (6.28 rad s^{-1}) under a low strain (0.1%). The storage modulus G' and the loss modulus G'' were recorded as functions of time in the recovery processes. To conduct the cycle of deformation and recovery, firstly, a constant oscillatory strain (100%), that was enough to destroy the gel, was applied to the fresh gel in the sample holder for 10 s when the frequency of the measurement was 6.28 rad s^{-1}; secondly, the recovery of the storage modulus was monitored at a constant frequency (6.28 rad s^{-1}) under a low strain (0.1%) within 20 s. Both G' and G'' were recorded as functions of time in both processes.

Gelation test

In a test vial, a weighed amount of gelator **1** was mixed with a solvent (0.5 ml), which was sealed and then heated. If the compound was unable to dissolve, it was noted as insoluble (I). After cooling down to room temperature, if a stable and opaque gel was formed, it was noted as undergoing gelation (G_o); if a clear solution was retained, it was marked as soluble (S). The repeated heating and cooling process confirmed the thermo-reversibility of the gelation process. The critical gelator concentration (CGC) was determined by determining the minimum amount of gelator required for the formation of a stable gel at 298 K.

Acknowledgements

The authors thank the "100 Talents Program" from the Chinese Academy of Sciences, the National Natural Science Foundation of China (21174157), the Natural Science Foundation of Shandong Province (ZR2010BZ007) and the National Natural Science Foundation of China for the Youth (21202180) for financial support.

Notes and references

1 (*a*) S. Banerjee, R. K. Das and U. Maitra, *J. Mater. Chem.*, 2009, **19**, 6649; (*b*) L. E. Buerkle and S. J. Rowan, *Chem. Soc. Rev.*, 2012, **41**, 6089; (*c*) M. George and R. G. Weiss, *Acc. Chem. Res.*, 2006, **39**, 489; (*d*) A. M. Jonker, D. W. P. M. Löwik and J. C. M. van Hest, *Chem. Mater.*, 2012, **24**, 759; (*e*) M. O. Piepenbrock, G. O. Lloyd, N. Clarke and J. W. Steed, *Chem. Rev.*, 2010, **110**, 1960; (*f*) N. M. Sangeetha and U. Maitra, *Chem. Soc. Rev.*, 2005, **34**, 821; (*g*) P. Terech and R. G. Weiss, *Chem. Rev.*, 1997, **97**, 3133; (*h*) R. G. Weiss, *Langmuir*, 2009, **25**, 8369, and reviews in this special issue.

2 For selected reviews, see: (*a*) T. Ishi-i and S. Shinkai, *Top. Curr. Chem.*, 2005, **258**, 119; (*b*) G. O. Lloyd and J. W. Steed, *Nat. Chem.*, 2009, **1**, 437; (*c*) M. D. Segarra-Maset, V. J. Nebot, J. F. Miravet and B. Escuder, *Chem. Soc. Rev.*, 2012, DOI: 10.1039/c2cs35436e; (*d*) J. W. Steed, *Chem. Soc. Rev.*, 2010, **39**, 3686; (*e*) X. Yang, G. Zhang and D. Zhang, *J. Mater. Chem.*, 2012, **22**, 38.

3 For selected examples, see: (*a*) X. Ji, Y. Yao, J. Li, X. Yan and F. Huang, *J. Am. Chem. Soc.*, 2013, **135**, 74; (*b*) X. Jiang, S. Jin, Q. Zhong, M. D. Dadmun and B. Zhao, *Macromolecules*, 2009, **42**, 8468; (*c*) S. Kawano, N. Fujita and S. Shinkai, *J. Am. Chem. Soc.*, 2004, **126**, 8592; (*d*) E. Krieg, E. Shirman, H. Weissman, E. Shimoni, S. G. Wolf, I. Pinkas and B. Rybtchinski, *J. Am. Chem. Soc.*, 2009, **131**, 14365; (*e*) J. Liu, Y. Feng, Z. X. Liu, Z. C. Yan, Y. M. He, C. Y. Liu and Q. H. Fan, *Chem.–Asian J.*, 2013, **8**, 572; (*f*) S. Samai and K. Biradha, *Chem. Mater.*, 2012, **24**, 1165; (*g*) T. Suzuki, S. Shinkai and K. Sada, *Adv. Mater.*, 2006, **18**, 1043.

4 (*a*) E. Cheng, Y. Xing, P. Chen, Y. Yang, Y. Sun, D. Zhou, L. Xu, Q. Fan and D. Liu, *Angew. Chem., Int. Ed.*, 2009, **48**, 7660; (*b*) S. Kiyonaka, K. Sada, I. Yoshimura, S. Shinkai, N. Kato and I. Hamachi, *Nat. Mater.*, 2004, **3**, 58; (*c*) X. Li, Y. Kuang and B. Xu, *Soft Matter*, 2012, **8**, 2801; (*d*) H. Lin, Y. Zou, Y. Huang, J. Chen, W. Y. Zhang, Z. Zhuang, G. Jenkins and C. J. Yang, *Chem. Commun.*, 2011, **47**, 9312; (*e*) X. Yang, G. Zhang, L. Li, D. Zhang, L. Chi and D. Zhu, *Small*, 2012, **8**, 578; (*f*) I. Yoshimura, Y. Miyahara, N. Kasagi, H. Yamane, A. Ojida and I. Hamachi, *J. Am. Chem. Soc.*, 2004, **126**, 12204; (*g*) Z. Zhu, C. Wu, H. Liu, Y. Zou, X. Zhang, H. Kang, C. J. Yang and W. Tan, *Angew. Chem., Int. Ed.*, 2010, **49**, 1052.

5 C. Wang, Q. Chen, F. Sun, D. Zhang, G. Zhang, Y. Huang, R. Zhao and D. Zhu, *J. Am. Chem. Soc.*, 2010, **132**, 3092.

6 (*a*) Z.-X. Liu, Y. Feng, Z.-C. Yan, Y.-M. He, C.-Y. Liu and Q.-H. Fan, *Chem. Mater.*, 2012, **24**, 3751; (*b*) S. Yagai, T. Nakajima, K. Kishikawa, S. Kohmoto, T. Karatsu and A. Kitamura, *J. Am. Chem. Soc.*, 2005, **127**, 11134; (*c*) Y. Zhou, T. Yi, T. Li, Z. Zhou, F. Li, W. Huang and C. Huang, *Chem. Mater.*, 2006, **18**, 2974.

7 (*a*) Q. Huang, C. Bao, W. Ji, Q. Wang and L. Zhu, *J. Mater. Chem.*, 2012, **22**, 18275; (*b*) M. Nagata and Y. Yamamoto, *React. Funct. Polym.*, 2008, **68**, 915.

8 (*a*) M. Irie, *Chem. Rev.*, 2000, **100**, 1685; (*b*) F. M. Raymo and M. Tomasulo, *Chem. Soc. Rev.*, 2005, **34**, 327; (*c*) H. Tian and S. Wang, *Chem. Commun.*, 2007, 781; (*d*) T. J. Wigglesworth, A. J. Myles and N. R. Branda, *Eur. J. Org. Chem.*, 2005, 1233.

9 (*a*) J. J. D. de Jong, L. N. Lucas, R. M. Kellogg, J. H. van Esch and B. L. Feringa, *Science*, 2004, **304**, 278; (*b*) J. J. de Jong, P. R. Hania, A. Pugzlys, L. N. Lucas, M. de Loos, R. M. Kellogg, B. L. Feringa, K. Duppen and J. H. van Esch, *Angew. Chem., Int. Ed.*, 2005, **44**, 2373; (*c*) J. J. de Jong, T. D. Tiemersma-Wegman, J. H. van Esch and B. L. Feringa, *J. Am. Chem. Soc.*, 2005, **127**, 13804.

10 K. Rameshbabu, L. Zou, C. Kim, A. Urbas and Q. Li, *J. Mater. Chem.*, 2011, **21**, 15673.

11 (*a*) M. Akazawa, K. Uchida, J. J. de Jong, J. Areephong, M. Stuart, G. Caroli, W. R. Browne and B. L. Feringa, *Org. Biomol. Chem.*, 2008, **6**, 1544; (*b*) S. Wang, W. Shen, Y. Feng and H. Tian, *Chem. Commun.*, 2006, 1497; (*c*) S. Xiao, Y. Zou, M. Yu, T. Yi, Y. Zhou, F. Li and C. Huang, *Chem. Commun.*, 2007, 4758.

12 (*a*) A. Banerjee, G. Palui and A. Banerjee, *Soft Matter*, 2008, **4**, 1430; (*b*) A. M. Jonker, D. W. P. M. Löwik and J. C. M. van Hest, *Chem. Mater.*, 2012, **24**, 759; (*c*) S. Ray, A. K. Das and A. Banerjee, *Chem. Commun.*, 2006, 2816.

13 (*a*) B. Escuder, J. F. Miravet and J. A. Saez, *Org. Biomol. Chem.*, 2008, **6**, 4378; (*b*) J. A. Saez, B. Escuder and J. F. Miravet, *Chem. Commun.*, 2010, **46**, 7996; (*c*) X. Yu, X. Cao, L. Chen, H. Lan, B. Liu and T. Yi, *Soft Matter*, 2012, **8**, 3329.

14 R. Gong, Y. Song, Z. Guo, M. Li, Y. Jiang and X. Wan, *Supramol. Chem.*, 2013, **25**, 269.

15 (*a*) J. T. Cirulis, C. M. Bellingham, E. C. Davis, D. Hubmacher, D. P. Reinhardt, R. P. Mecham and F. W. Keeley, *Biochemistry*, 2008, **47**, 12601; (*b*) L. Donato, E. Kolodziejcyk and M. Rouvet, *Food Hydrocolloids*, 2011, **25**, 734; (*c*) N. Lin and A. Dufresne, *Biomacromolecules*, 2013, **14**, 871; (*d*) A. Petit, B. Muller, P. Bruin, R. Meyboom, M. Piest, L. M. Kroon-Batenburg, L. G. de Leede, W. E. Hennink and T. Vermonden, *Acta Biomater.*, 2012, **8**, 4260; (*e*) P. A. Ruhs, N. Scheuble, E. J. Windhab, R. Mezzenga and P. Fischer, *Langmuir*, 2012, **28**, 12536; (*f*) M. Tsianou and P. Alexandridis, *Langmuir*, 1999, **15**, 8105.

16 N. Yamada, K. Ariga, M. Naito, K. Matsubara and E. Koyama, *J. Am. Chem. Soc.*, 1998, **120**, 12192.

17 (*a*) B. Escuder and J. F. Miravet, *Langmuir*, 2006, **22**, 7793; (*b*) S. Iqbal, J. F. Miravet and B. Escuder, *Eur. J. Org. Chem.*, 2008, 4580.

18 V. K. Kotharangannagari, A. Sánchez-Ferrer, J. Ruokolainen and R. Mezzenga, *Macromolecules*, 2012, **45**, 1982.

19 Z. Li, H. Yin, Z. Zhang, K. L. Liu and J. Li, *Biomacromolecules*, 2012, **13**, 3162.

20 Y. Lin, J. Yuan, M. Hu, J. Cheng, J. Yin, S. Jin and S. H. Liu, *Organometallics*, 2009, **28**, 6402.

