RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Journal Name

RSCPublishing

ARTICLE

Water tuned nano/micro-structures in redox-responsive supramolecular gel

Cite this: DOI: 10.1039/x0xx00000x

Yuxia Gao,[a] Jinrong Lu,[a] Jindan Wu,[a] Jun Hu*[b] and Yong Ju*[a]

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

A redox-responsive chiral supramolecular gel based on coumarin-tailed cholesterol linked with disulfide was reported. It was found that the gelation was primarily driven by the combination of hydrogen bonding, π-π stacking, and van der Waals forces. Moreover, its assembled morphology could be regulated from nanofibers to micro flowers and ribbons by water on account of its amphiphilic nature.

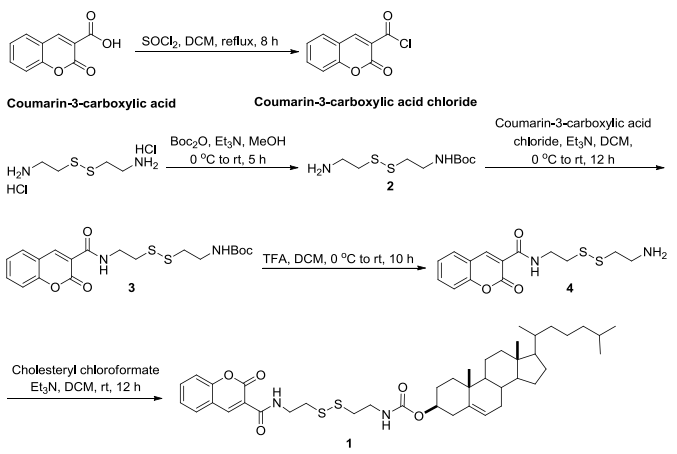
Introduction

Supramolecular gels, which utilize the self-assembly of organic molecules into entangled structures to immobilize the solvents, have attracted immense interests over the past decades for their potential applications in drug delivery, hybrid materials, oil recovery, and electronic devices.[1] In the family of supramolecular gels, low-molecular-weight organogels (LMOGs) show more superiorities because of their accurate molecular weight, easy modification, multifarious nanostructures, and stimuli-responsive properties.[2] Specifically, the stimuli-responsive gels are particularly appealing since their morphologies can be regulated easily in response to the external stimuli, such as light, pH, ultrasound, ion, and oxidation/reduction.[3] Although various assembly morphologies of gels have been reported, including fibers, ribbons, sheets, tubes, and flowers,[4] the regulation of the morphologies is still challengeable. For example, Liu and co-workers reported that metal ions including Na^+, Li^+, Ni^{2+}, Eu^{3+} and Tb^{3+} could turn the assembled nanostructure into a uniform helical twist in organogel.[5a] They also found that water could be used to tune the assembled nanostructures from nanofibers to helical tapes, helical tubes, and chiral nanotwists in organic solvents.[5b] Fang and co-workers discovered nanofibers and microballs could be obtained by changing the volume ratio of pyridine-methanol.[6]

As a continuance of our previous works,[7] herein we exploited a novel redox-responsive gelator **1** based on coumarin-tailed cholesterol linked with disulfide (Scheme 1) and its self-assembly behavior was investigated (Figure 1). In such a molecule, coumarin, cholesterol, and disulfide are used as the sensor, gelation skeleton, and redox-responsive linker, respectively. It is known that disulfide can be reduced by dithiothreitol (DTT), glutathione (GSH) or PPh_3 to sulfhydryl, which could be oxidized back to disulfide with the treatment of oxidants, such as oxygen, peroxide, and iodine.[8] Therefore, disulfide has already been adopted in the self-healing materials, controlled release, and biosensor.[9] Up to date, although many redox-responsive LMOGs based on ferrocene group,[10] Cu(I)/Cu(II),[3i] or tetrathiafulvalene (TTF) group[3j] have been reported, the disulfide involved redox-responsive LMOGs are still rare.[11]

Results and Discussion

The gelator **1** was synthesized in multiple steps as shown in Scheme 1. Reaction between cystamine dihydrochloride and Boc anhydride afforded mono-protected amine **2**,[12] followed by the treatment with coumarin-3-carboxylic acid chloride to give **3**. Subsequently **3** was deprotected by trifluoroacetic acid to give **4**. Finally, the reaction between **4** and cholesteryl chloroformate was carried out in the presence of triethylamine to yield the coumarin-cholesterol conjugate **1**, which was confirmed by ^1H-, ^{13}C NMR, ESI-MS, and HRMS (details see Supporting Information).



Scheme 1 The synthetic route of compound **1**

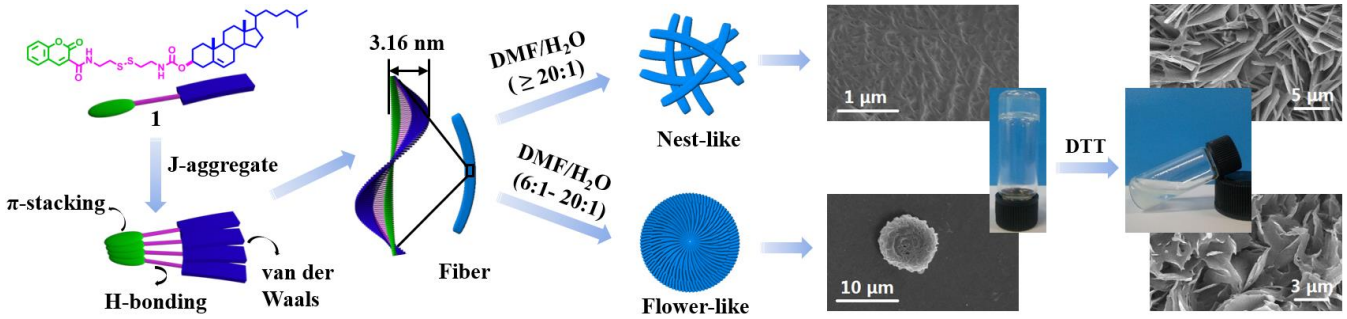


Figure 1 Schematic illustration of the self-assembly process of the aggregates and the redox-responsive gel-sol transition triggered by DTT. The insets are photographs of gel and collapsed sol.

As a general protocol, **1** was dissolved in various solvents, and tested by "stable to inversion of the test tube" method.[7b, 13] The results showed that **1** can form stable gel in DMF/H_2O from the ratio of volume 20:1 to 5:1 (Table S1 and Figure S1). Its viscoelastic behaviour was characterized by the rheological measurements, in which the storage modulus *G′* and the loss modulus *G″* were measured as functions of angle frequency and time sweep at 25 °C, respectively. As shown in Figure 2a, *G′* is around eight times greater than *G″*, revealing the indispensable elastic behaviour of the gel.[7c, 14] The fact that *G′* and *G″* decreased with the extension of time indicates that gel collapsed into the quasi-liquid state gradually (Figure 2b).[14a] Moreover, the concentration-dependent sweep shows that *G′* and *G″* ascended with the increase of gelator concentration (Figure S2).

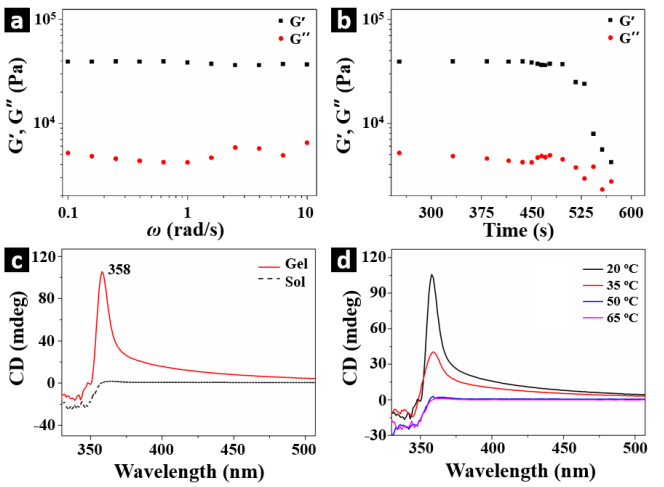


Figure 2 Evolution of *G′* (black cube) and *G″* (red dot) as functions of the (a) angle frequency, and (b) time of the gel **1** (13 mg/mL, DMF/H_2O =10:1, v/v); (c) CD spectra of **1** in solution and gel; (d) temperature-dependent CD spectra of **1** (8 mg/mL, DMF/H_2O=10:1, v/v).

Generally, the chirality of supramolecular systems can be generated through the assembly of chiral molecules.[15] The CD spectra of **1** revealed a strong positive Cotton effect at 358 nm in gel state, while no signal was detected in solution (Figure 2c). The signal intensity of the gel decreased gradually until disappeared completely with the temperature increasing from

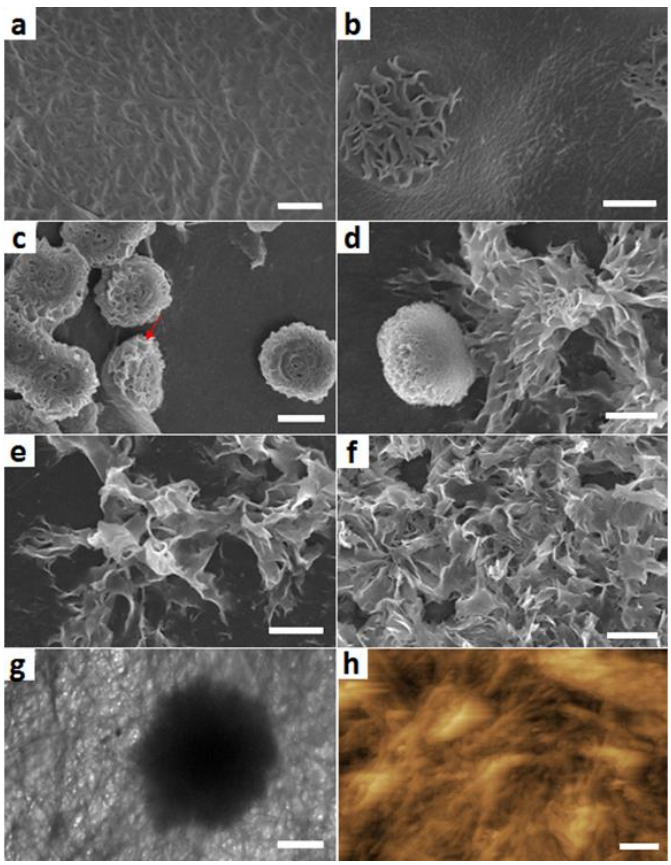


Figure 3 SEM images of xerogels from **1** (10 mg/mL) at different volume ratio of DMF/H_2O (v/v): (a) 25:1, (b) 20:1, (c) 10:1, (d) 6:1, (e) 5:1, (f) 4:1; (g) TEM, and (h) AFM images of xerogels from **1** (10 mg/mL, DMF/H_2O=10:1, v/v). Scale bars are 500 nm for (a), 2 μm for (b, g), 5 μm for (c, d, e), 10 μm for (f), and 1 μm for (h).

20 to 50 °C (Figure 2d). It indicates that the chirality is transformed from gelator **1** to the assembled aggregates during its chiral packing process.[5, 15]

It is clearly seen that the gel turned opaque gradually with the increase of water (Figure S1). Studies on the thermal stability revealed that with the increase of water the minimum gelation concentration (MGC) decreased, while the gel-to-sol transition temperature (T_{gel}) increased (Figure S3). In order to investigate how the water tunes the gel morphologies, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM) were performed. The results showed that a partial gel formed with the nanofibers ~30-50 nm in diameter when water is less than 5% in DMF/H_2O (Figure 3a). Whereas a few micro-scale flower-like structures appeared co-existing with the nanofibers in the stable gel when the ratio of water reached 5% (Figure 3b). The number of uniformed micro-scale flower-like architectures increased continuously with the increase of water in the mixed solvents (Figure 3c). The flower-like architectures are ~5-40 μm in diameter, and the thickness of the 'flower petals' (arrow in figure 3c) is ~30-60 nm, which is close to fiber diameter. However, the further addition of water (6:1) led to collapse of the flowers, consequently generating micro-scale thick ribbons until all the flowers disappeared (Figure 3d-e). When water was more than 20% in DMF/H_2O, ribbons broke into fragments resulting in the collapse of gel (Figure 3f). Moreover, the co-existing of nanofibers and micro-flowers in Figure 3c can be further confirmed by TEM and AFM (Figure 3g-h), in which both of them have the similar sizes as the ones under SEM. Apparently, the transformation from nanofibers to microflowers is a result of the anisotropic arrangement of molecules induced by the water content, consequently leading to the transformation between partial gel, stable gel, opaque gel, and collapsed gel.

To study the driving forces in the gelation process of **1**, we investigated the temperature-dependent ^{1}H NMR, IR, UV-Vis, and fluorescence spectroscopy. As the temperature increases, the protons of coumarin (H_1, H_2, H_3, H_4, H_5) shifted upfield gradually as a result of the shielding effect, which strongly revealed the π-π stacking between the coumarin moieties (Figure 4a), while no change was observed of the aliphatic protons (Figure S4). UV-Vis and fluorescence spectra provided more information about the π-π stacking. As shown in Figure 4b, the absorption bands underwent a significant red shift from 295 to 300 nm with the increase of water content. Meanwhile, the addition of water to DMF solution of **1** led to a gradual decrease in the intensity at 413 nm and an appearance of a new band at 460 nm in fluorescence spectra (Figure 4c). Apparently, the red shift ~47 nm of emission band should be due to the excimer formation caused by π-π stacking between coumarin groups.[14a] Both red shifts in UV-Vis and fluorescence spectra strongly indicate the formation of "J"-type aggregates.[16]

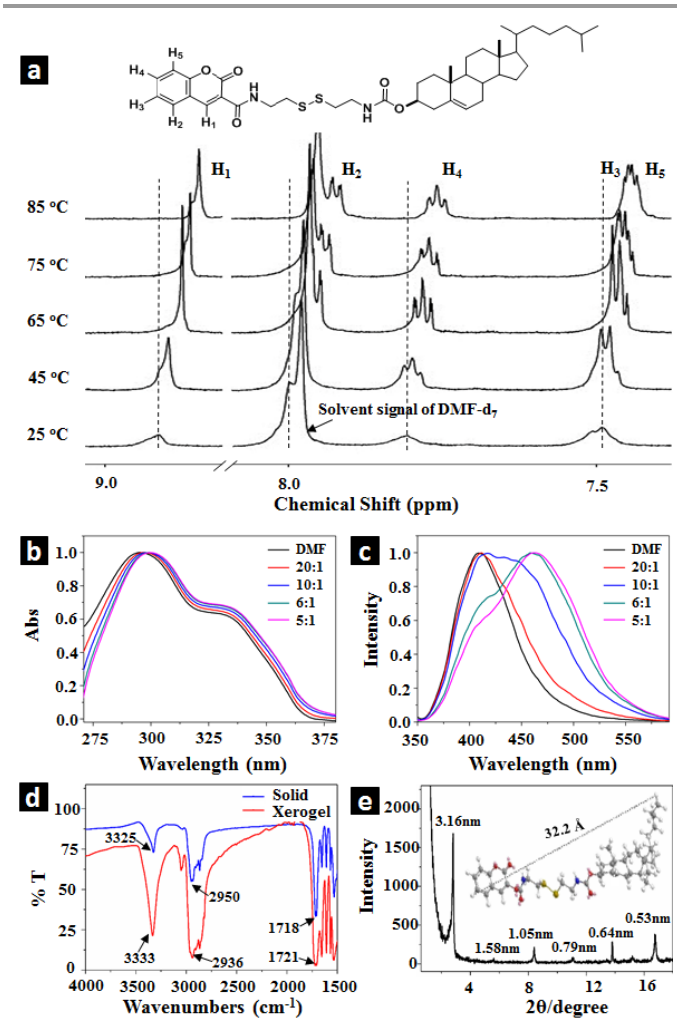


Figure 4 (a) Temperature-dependent ^{1}H NMR (600MHz) of **1** (10 mg/mL) in DMF-d_7/D_2O (10:1, v/v); (b) normalized UV-Vis and (c) fluorescence spectra of **1** (10^{-4} M) in different volume ratio of DMF/H_2O; (d) IR spectra of **1** in solid and xerogel (10 mg/mL) made from DMF/H_2O (10:1, v/v); (e) XRD patterns of the xerogel (10 mg/mL) from **1** in DMF/H_2O (10:1, v/v). The inset is calculated 3D structure of **1**. Carbon atoms are presented in grey, oxygen atoms in red, nitrogen atoms in blue, sulfur atoms in yellow, and hydrogens in white.

Additionally, IR spectra of a powder sample and xerogel of **1** were compared (Figure 4d). It showed that the stretching vibrations of N-H moiety and C=O shifted from 3325, 1718 cm^{-1} to 3333, 1721 cm^{-1}, respectively, upon the gelation. This result implied the formation of the intermolecular hydrogen bonding during the gelation process.[4b] Furthermore, the C-H stretching vibrations of alkyl groups appeared at a lower wavenumber (2936 cm^{-1}) in the xerogel compared with that in the powder sample (2950 cm^{-1}). It is known that the stretching vibrations of alkyl groups can be used as a sensitive sensor for the order of alkyl chains because of the association between the increase in frequencies and band widths with the increasing numbers of gauche defects and disorder.[17] Therefore, the decrease in wavenumbers from the powder sample to xerogel revealed an increase of the van der Waals interactions among the neighboring alkyl chains. It is apparent that the intermolecular hydrogen bonding and van der Waals forces of alkyl chains

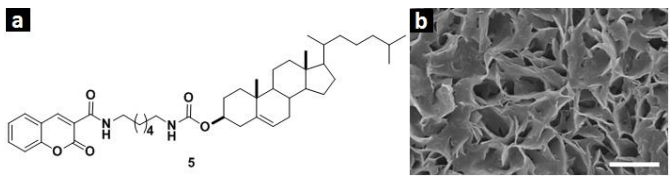


Figure 5 (a) Molecular structure of compound **5**; (b) SEM image of xerogel from **5** in DMF/H_2O (10:1, v/v, 10 mg/mL), scale bar is 10 μm.

play crucial roles in the formation of supramolecular gel besides the π-π stacking between the aromatic rings.

X-ray diffraction (XRD) afforded the direct insight into the molecular packing pattern. As shown in Figure 4e, the reflection peaks corresponding to d-spacing of 3.16, 1.58, 1.05, 0.79, 0.64 and 0.53 nm in the small angle region were observed, following the ratio of 1: 1/2: 1/3: 1/4: 1/5: 1/6. It strongly reveals the lamellar structure of the supramolecular gel. The fact that the interlayer distance (3.16 nm) is close to the extended molecular length of **1** (3.22 nm, Figure 4e, inset) indicates that the "J"-type aggregates are formed by using the single molecule as a basic building block. Based on all the above results, it is apparent that the free molecule **1** in DMF is promoted to form ordered fibers upon the addition of water primarily driven by van der Waals forces, hydrogen bondings, and π-π stacking. These fibers can further entangle each other to form 3D nest-like networks to trap solvent molecules (Figure 1, left). Whereas, on account of its amphiphilic nature, the fibers tend to arrange more closely to form flower-like aggregates bearing less hydrophobic areas with the increase of water in the system.

Due to the involvement of disulfide bond in the gelator, the supramolecular gel showed excellent redox-responsive to reductants. Upon the continuous addition of DTT solution (DMF/H_2O) on the gel surface, the transparent gel gradually turned turbid until collapsed completely (Figure 1, photography). After the cleavage of disulfide, fibers and flowers were destroyed to fragments as shown in SEM images (Figure 1, right). The more direct evidence comes from ESI-MS analysis, in which the ion peak of compound **1** decreased notably companied with several new peaks corresponding to sulfhydryl compounds (Figure S5). For better understanding the role of disulfide in the redox-responsive process, the control molecule **5** (Figure 5a, details see supporting information) was synthesized, in which the disulfide was replaced by the alkyl chain. Though **5** could also form gel in DMF/H_2O (Figure 5b), it didn't display any changes in the presence of DTT, highlighting the importance of disulfide bond to such a redox-responsive supramolecular gel.

Conclusions

We have exploited a novel redox-responsive chiral supramolecular gel based on coumarin-tailed cholesterol linked with disulfide, primarily driven by the combination of hydrogen bonding, π-π stacking, and van der Waals forces. The gel morphology could be regulated by water from nanofibers to microflowers and microribbons on account of its amphiphilic characteristic. Moreover, such supramolecular gel exhibited excellent redox-responsive properties, which may be used in controlled release and drug delivery. Our results point out the potential self-assembled morphological control in area of supramolecular gel.

Acknowledgements

This work was supported by NNSF of China (nos. 21172130, 21472108) and NBRP of China (no. 2012CB8210601). JH is thankful for the support of State Key Laboratory of Polymer Physics and Chemistry, CIAC, China.

Notes and references

[a] *Key Laboratory of Bioorganic Phosphorus Chemistry & Chemical Biology, Ministry of Education, Department of Chemistry, Tsinghua University, Beijing 100084, China. E-mail: juyong@tsinghua.edu.cn.*

[b] *State Key Lab of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China. E-mail: jhu@ciac.ac.cn*

† Electronic Supplementary Information (ESI) available: Synthesis and structure characterization of compounds **1** and **5**; Gelation behaviour of **1** in various solvents; Plots of T_{gel} against the concentration of **1**; Temperature-dependent ^{1}H NMR of **1**; Concentration-dependent rheological measurements of the gel; SEM images of **5**; ESI-MS spectrum of the gel **1** after the DTT addition. See DOI: 10.1039/c000000x/

1 (a) N. M. Sangeetha and U. Maitra, *Chem. Soc. Rev*., 2005, **34**, 821; (b) A. Ajayaghosh, V. K. Praveen and C. Vijayakumar, *Chem. Soc. Rev*., 2008, **37**, 109; (c) S. R. jadhav, P. K. Vemula, R. Kumar, S. R. Raghavan and G. John, *Angew. Chem. Int. Ed*., 2010, **49**, 7695; (d) A. R. Hirst, B. Escuder, J. F. Mairavet and D. K. Smith, *Angew. Chem. Int. Ed*., 2008, **47**, 8002; (e) A. Friggeri, B. L. Feringa and J. van Esch, *J. Controlled Release*, 2004, **97**, 241; (f) M. Cametti and Z. Džolić, *Chem. Commun*., 2014, **50**, 8273; (g) J. W. Steed, *Chem. Commun*., 2011, **47**, 1379.

2 (a) P. Terech and R. G. Weiss, *Chem. Rev.*, 1997, **97**, 3133; (b) M. Geroge and R. G. Weiss, *Acc. Chem. Res*., 2006, **39**, 489; (c) X. Y. Hou, D. Gao, J. L. Yan, Y. Ma, K. Q. Liu and Y. Fang, *Langmuir*, 2011, **27**, 12156; (d) J. R, A. Z. Cardoso and D. J. Adams, *Chem. Soc. Rev*., 2013, **42**, 5143; (e) B. G. Bag and S. S. Dash, *Nanoscale*, 2011, **3**, 4564; (f) B. G. Bag and K. Paul, *Asian J. Org. Chem*., 2012, **1**, 150; (g) B. G. Bag and R. Majumdar, *RSC Adv*., 2012, **2**, 8623.

3 (a) M. D. Segarra-Maset, V. J. Nebot, J. F. Miravet and B. Escuder, *Chem. Soc. Rev*., 2013, **42**, 7086; (b) X. D. Yu, L. M. Chen, M. M. Zhang and T. Yi, *Chem. Soc. Rev*., 2014, **43**, 5346; (c) K. Murata, M. Aoki, T. Suzuki, T. Harada, H. Kawabata, T. Komori, F. Ohseto, K. Ueda and S. Shinkai, *J. Am. Chem. Soc*., 1994, **116**, 6664; (d) S. Sumiya, Y. Shiraishi and T. Hirai, *New J. Chem*., 2013, **37**, 2642; (e) C. Y. Zhou, W. X. Gao, K. W. Yang, L. Xu, J. C. Ding, J. X. Chen, M. C. Liu, X. B. Huang, S. Wang and H. Y. Wu, *Langmuir*, 2013, **29**, 13568; (f) X. D. Yu, Q. Liu, J. C. Wu, M. M. Zhang, X. H. Gao, S. Zhang, Q. Wang, L.M. Chen and T. Yi, *Chem. Eur. J*., 2010, **16**,

9099; (g) X. D. Yu, Y. J. Li, Y. B. Yin and D. C. Yu, *Mater. Sci. Eng., C*, 2012, **32**, 1695; (h) K. Ghosh and D. Kar, *Org. Biomol. Chem*., 2012, **10**, 8800; (i) S. Kawano, N. Fujita and S. Shinkai, *J. Am. Chem. Soc*., 2004, **126**, 8592; (j) C. Wang, D. Q. Zhang and D. B. Zhu, *J. Am. Chem. Soc*., 2005, **127**, 16372.

4 (a) A. Vidyasagar, K. Handore and K. M. Sureshan, *Angew. Chem*., 2011, **123**, 8171; (b) Y. F. Zhou, T. Yi, T. C. Li, Z. G. Zhou, F. Y. Li, W. Huang and C. H. Huang, *Chem. Mater*., 2006, **18**, 2974; (c) P. Y. Xing, X. X. Chu, M. F. Ma, S. Y. Li and A. Y. Hao, *Phys. Chem. Chem. Phys*., 2014, **16**, 8346; (d) V. Lozano, R. Hernandez, C. Mijangos and M. Pérez-Pérez, *Org. Biomol. Chem*., 2009, **7**, 364; (e) S. Ghosh and S. Verma, *Tetrahedron*, 2008, **64**, 6202; (f) A. Ajayaghosh, R. Varghese, V. K. Praveen and S. Mahesh, *Angew. Chem. Int. Ed*., 2006, **45**, 3261; (g) N. S. S. Kumar, S. Varghese, G. Narayan and S. Das, *Angew. Chem*., 2006, **118**, 6465; (h) G. S. Lim, B. M. Jung, S. J. Lee, H. H. Song, C. Kim and J. Y. Chang, *Chem. Mater*., 2007, **19**, 460.

5 (a) X. F. Wang, P. F. Duan and M. H. Liu, *Chem. Commun*., 2012, **48**, 7501; (b) C. X. Liu, Q. X. Jin, K. Lv, L. Zhang and M. H. Liu, *Chem. Commun*., 2014, **50**, 3702.

6 Z. Y. Xu, J. X. Peng, N. Yan, S. S. Zhang, K. Q. Liu and Y. Fang, *Soft Matter*, 2013, **9**, 1091.

7 (a) J. Hu, M. Zhang and Y. Ju, *Soft Matter*, 2009, **5**, 4971; (b) J. R. Lu, J. Hu, Y. Song and Y. Ju, *Org. Lett.*, 2011, **13**, 3372; (c) J. R. Lu, J. Hu, C. L. Liu, H. X. Gao and Y. Ju, *Soft Matter*, 2012, **8**, 9576; (d) J. R. Lu, Y. X. Gao, J. D. Wu and Y. Ju, *RSC Adv*., 2013, **3**, 23548; (e) J. Hu, J. D. Wu, Q. Wang and Y. Ju, *Beilstein J. Org. Chem*., 2013, **9**, 2877; (f) J. R. Lu, J. D. Wu and Y. Ju, *New J. Chem*., 2014, DOI: 10.1039/c4nj01146e.

8 (a) V. Haridas, S. Sahu and A. R. Sapala, *Chem. Commun*., 2012, **48**, 3821; (b) Z. G. Tao, Z. Y. Xiao, X. Zhao, X. K. Jiang and Z. T. Li, *Tetrahedron Lett*., 2012, **53**, 4447.

9 (a) B. Khorsand, G. Lapointe, C. Brett and J. K. Oh, *Biomacromolecules*, 2013, **14**, 2103; (b) J. Canadell, H. Goossens and B. Klumperman, *Macromolecules*, 2011, **44**, 2536; (c) G. H. Deng, F. Y. Li, H. X. Yu, F. Y. Liu, C. Y. Liu, W. X. Sun, H. F. Jiang and Y. M. Chen, *ACS Macro Lett*., 2012, **1**, 275; (d) R. Liu, X. Zhao, T. Wu and P. Y. Feng, *J. Am. Chem. Soc*., 2008, **130**, 14418; (e) R. Liu, Y. Zhang and P. Y. Feng, *J. Am. Chem. Soc*., 2009, **131**, 15128; (f) M. H. Lee, Z. G. Yang, C. W. Lim, Y. H. Lee, S. Dongbang, C. Kang and J. S. Kim, *Chem. Rev*., 2013, **113**, 5071; (g) M. M. Pires and J. Chmielewski, *Org. Lett*., 2008, **10**, 837; (h) M. H. Lee, J. H. Han, P. Kwon, S. Bhuniya, J. Y. Kim, J. L. Sessler, C. Kang and J. S. Kim, *J. Am. Chem. Soc*., 2012, **134**, 1316; (i) J. Ryu, S. Park, B. Kim, A. Klaikherd, T. P. Russell and S. Thayumanavan, *J. Am. Chem. Soc*., 2009, **131**, 9870.

10 (a) J. Liu, J. L. Yan, X. W. Yuan, K. Q. Liu, J. X. Peng and Y. Fang, *J. Colloid Interface Sci*., 2008, **318**, 397; (b) P. L. He, J. Liu, K. Q. Liu, L. P. Ding, J. L. Yan, D. Gao and Y. Fang, *Colloids Surf., A*, 2010, **362**, 127; (c) R. Afrasiabi and H. Kraatz, *Chem. Eur. J*., 2013, **19**, 17296; (d) B. Adhikari and H. Kraatz, *Chem. Commun*., 2014, **50**, 5551; (e) B. Adhikari, R. Afrasiabi and H. Kraatz, *Organometallics*, 2013, **32**, 5899.

11 (a) J. Chen, W. W. Wu and A. J. McNeil, *Chem. Commun*., 2012, **48**, 7310; (b) C. H. Ren, Z. J. Song, W. T. Zheng, X. M. Chen, L. Wang, D. L. Kong and Z. M. Yang, *Chem. Commun*., 2011, **47**, 1619.

12 J. Niu, Z. H. Liu, L. Fu, F. Shi, H. W. Ma, Y. Ozaki and X. Zhang, *Langmuir*, 2008, **24**, 11988.

13 D. G. Velázquez, D. D. Díaz, Á. G. Ravelo and J. J. Marrero-Tellado, *Eur. J. Org. Chem*., 2007, **11**, 1841.

14 (a) M. Dubey, A. Kumar and D. S. Pandey, *Chem. Commun*., 2014, **50**, 1675; (b) M. Dubey, A. Kumar, R. K. Gupta and D. S. Pandey, *Chem. Commun*., 2014, **50**, 8144; (c) H. B. Wei, N. Shi, J. L. Zhang, Y. Guan, J. Zhang, and X. H. Wan, *Chem. Commun*., 2014, **50**, 9333.

15 (a) D. K. Smith, *Chem. Soc. Rev*., 2009, **38**, 684; (b) P. F. Duan, H. Cao, L. Zhang and M. H. Liu, *Soft Matter*, 2014, **10**, 5428; (c) H. Cao, X. F. Zhu and M. H. Liu, *Angew. Chem. Int. Ed*., 2013, **52**, 4122; (d) X. F. Wang, F. F. Duan and M. H. Liu, *Chem. Asian J*., 2014, **9**, 770.

16 (a) S. Abraham, R. K. Vijayaraghavan and S. Das, *Langmuir*, 2009, **25**, 8507; (b) A. Ajayaghosh, C. Vijayakumar, R. Varghese and S. J. George, *Angew. Chem. Int. Ed*., 2006, **45**, 456; (c) K. Jang, L. V. Brownell, P. M. Forster and D. C. Lee, *Langmuir*, 2011, **27**, 14615; (d) H. Yao, T. Isohashi and K. Kimura, *J. Phys. Chem. B*, 2007, **111**, 7176.

17 (a) M. J. Hostetler, J. J. Stokes and R. W. Murray, *Langmuir*, 1996, **12**, 3604; (b) N. Yamada, K. Ariga, M. Naito, K. Matsubara and E. Koyama, *J. Am. Chem. Soc*., 1998, **120**, 12192; (c) S. E. Paramonov, H. -W. Jun and J. D. Hartgerink, *J. Am. Chem. Soc*., 2006, **128**, 7291.