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Tetrapeptide–coumarin conjugate 3D networks based on hydrogen-bonded charge transfer complexes: gel formation and dye release†

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Oligopeptide-based derivatives are important synthons for bio-based functional materials. In this article, a Gly-(L-Val)-Gly-(L-Val)-coumarin (GVGV-Cou) conjugate was synthesized, which forms 3D networks in ethanol. The gel nanostructures were characterized by UV-vis spectroscopy, FT-IR spectroscopy, X-ray diffraction (XRD), SEM and TEM. It is suggested that the formation of charge transfer (CT) complexes between the coumarin moieties is the main driving force for the gel formation. The capability of the gel to encapsulate and release dyes was explored. Both Congo Red (CR) and Methylene Blue (MB) can be trapped in the CT gel matrix and released over time. The present gel might be used as a functional soft material for guest encapsulation and release.

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Introduction

Supramolecular gels are fabricated through noncovalent interactions, such as hydrogen bonding, π - π stacking, van de Waals interactions, *etc.*, and they can be used as functional materials in many fields.¹ Peptide-based gels have been attracting much interest due to their ability to form various organized secondary nanostructures (α -helices, β -sheets, β -turns), and their biocompatibility, which is important for fabricating bio-based materials.² One of the most important applications for peptide-based gels is drug encapsulation and release. A lot of fantastic work has been done in this field.³ Stupp and coworkers synthesized peptide amphiphiles containing the V2A2E2K peptide sequence, which could be used for Prodan release.⁴ Zhang *et al.* have developed an acetyl-(Arg-Ala-Asp-Ala)₄-CONH₂ (Ac-(RADA)₄-CONH₂) peptide hydrogel that could efficiently encapsulate and release small dye molecules and proteins.⁵ Xu *et al.* have designed supramolecular hydrogels composed of the FFKY sequence connected to Taxol, which could be released in the presence of an enzyme.⁶ Such gel matrices could find potential use in therapeutic medicines.

Despite these fabulous examples, the design of novel peptide-based gel matrices still needs to meet different requirements

for guest capsulation and release. The Gly-(L-Ala)-Gly-(L-Ala) peptide segment plays an important role in forming β -sheet secondary structures, which facilitate the strength of the silk protein.⁷ Inspired by such a structure, we have developed a biomimetic tetrapeptide Gly-(L-Val)-Gly-(L-Val), which was proved to have a strong tendency to form β -sheets.⁸ In the present investigation, we further explore the potential application of Gly-(L-Val)-Gly-(L-Val) based supramolecular polymers as matrices for guest encapsulation and release. A conjugate of Gly-(L-Val)-Gly-(L-Val) with coumarin (GVGV-Cou) was designed and successfully synthesized. Coumarin was selected as an end group since: (i) it could provide π - π interactions, which facilitate gel formation for peptide based molecules;⁹ (ii) moreover, it can perform a reversible [2+2] photoaddition reaction under certain conditions, and thus a soft material with light stimuli-responsive properties is expected.¹⁰

GVGV-Cou can indeed form a stable gel composed of 3D entangled nanofibers in ethanol. Unexpectedly, a strong charge transfer (CT) interaction between the coumarin groups was observed.¹¹ Normally, such an interaction is observed between a donor and an acceptor,¹² and nanostructures based on single-component CT complex, especially gels, have rarely been reported. Furthermore, the formation of CT complexes between coumarin groups has not been reported before. The only related example in the literature is the formation of CT complexes of a tetraphenylethene–coumarin hybrid (TPE-Cou), which showed a new CT band at 450 nm, but the tetraphenylethene part dominated this CT absorption.¹³ According to the newly published review on supramolecular charge transfer nanostructures by Subi J. George *et al.*, the GVGVCou gel could be considered as hydrogen-bonded CT complexes.¹¹ Although the formation of such CT

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complexes prohibits the occurrence of the photoaddition reaction of the coumarin group in the present work, which is critical for preparing light stimuli-responsive drug delivery materials, the GVG–Cou gel is still able to be used as a soft material for dye encapsulation. Two dyes, Congo Red (CR) and Methylene Blue (MB), were used to probe the dye release and the impact of the type of molecule on this process. The mechanisms of gel formation and dye release were systematically investigated. The molecular packing in the gel assemblies and why the [2+2] photoaddition reaction does not happen are discussed as well.

Results and discussion

Synthesis of the gelator

The synthesis of the Gly-(L-Val)-Gly-(L-Val)-coumarin (GVG–Cou) conjugate is shown in Scheme 1. GVG–Cou was obtained by coupling 7-hydroxy coumarin decorated with an alkyne group and a Gly-(L-Val)-Gly-(L-Val) peptide segment with an azide terminal by click chemistry. Details of the synthesis are discussed in the ESI.†

Gelation of GVG–Cou and morphology observations

The gelation of GVG–Cou was tested both in organic solvents and water (Table 1). It was found that GVG–Cou can form a stable peachy beige gel in ethanol (inset in Fig. 1). The gel formation was confirmed by the vial inversion method. The sol–gel transformation can be realized by heating and cooling treatments. The critical gel concentration (CGC) is 15 mg mL^{−1} at room temperature (~25 °C). SEM and TEM measurements (Fig. 1A–C) showed that fibers with widths ranging from tens to hundreds of nanometers were formed. Such fibers further entangled into 3D networks. When checking the fibers in detail, it was found that the thick fibers were actually composed of thinner wires, which are indicated by the yellow arrows in Fig. 1B and C. It is clear that the thin wires hierarchically assembled into thick fibers. It is suggested that fiber–fiber interactions facilitated this hierarchical self-assembly. It needs to be noted that the coumarin group plays a key role in the gelation of GVG–Cou in ethanol, since if the coumarin group in GVG–Cou is replaced by an alkyl chain (Scheme S2 in the ESI†), it could not form a gel in ethanol.

Scheme 1 The chemical structure of GVG–Cou and the synthetic approach.

Table 1 Gelation tests for GVG–Cou

Solvent	State ^a
Hexane	I
Toluene	I
1,4-Dioxane	S
CH ₂ Cl ₂	WG
THF	S
CHCl ₃	S
Ethanol	G (CGC; 15 mg mL ^{−1})
Ethyl acetate	I
Acetone	WG
CH ₃ CN	S
DMF	S
Methanol	S
DMSO	S
H ₂ O	P

^a G = gel; WG = weak gel; S = soluble; I = insoluble; P = precipitate.

Spectral characterization of the organogel

The self-assembly of the gelator was investigated by FT-IR, X-ray diffraction (XRD) and UV-vis spectroscopic techniques. The formation of β -sheets can be clearly observed from the FT-IR spectrum (Fig. 2), where the N–H stretching vibration is positioned at 3284 cm^{−1} and the C=O stretching vibration is at 1633 cm^{−1}. Furthermore, anti-parallel β -sheets were confirmed by the weak absorption at 1693 cm^{−1} from the derivative of the FT-IR spectrum (inset in Fig. 2).¹⁴ This speculation was further proved by the temperature-dependent ¹H NMR experiments (Fig. 3). In the temperature-dependent ¹H NMR spectra, the resonance signals from H₁ to H₄ are gradually shifted upfield when the temperature increased from 298 to 313 K. The signals for H₅ and H₆ from the coumarin group, however, do not show an obvious shift. We came to the conclusion that the strength of the H-bonds between adjacent GVG peptide segments became weaker when increasing the temperature. Based on the FT-IR and temperature-dependent ¹H NMR results, it can be deduced that hydrogen bonding also plays an important role in the formation of the gel.

In the XRD spectrum of the xerogel film (Fig. 4A), peaks were observed at $2\theta = 33.7^\circ, 33.1^\circ, 23.7^\circ, 20.5^\circ, 17.4^\circ, 16.7^\circ, 15.5^\circ, 13.6^\circ, 11.8^\circ, 10.4^\circ, 7.7^\circ$, and 4.6° , which indicated the formation of ordered molecular packing in the fiber structures. According to the Bragg equation, the corresponding d values are 2.65 Å, 2.7 Å, 3.7 Å, 4.3 Å, 5.1 Å, 5.3 Å, 5.7 Å, 6.5 Å, 7.5 Å, 8.5 Å, 11.4 Å, and 19.3 Å. It is obvious that (2.65 or 2.7 Å and 5.3 Å), (3.7 Å, 7.5 Å, and 11.4 Å), and (4.3 Å and 8.5 Å) are basically diploid, suggesting long range ordering of the molecular packing. The d values of 2.65 and 2.7 Å are the distances between neighbouring coumarin groups, and the two peaks might be due to the coumarin packing in different domains. One characteristic peak with a d spacing of 4.3 Å is in accordance with the distance between adjacent peptide strands, indicating the formation of H-bonds.¹⁵ The characteristic peak with a d spacing of 3.7 Å is assigned to the distance between adjacent layers.¹⁵ The d value of 5.7 Å might be the triazole–triazole distance within one layer. The d values of 6.5 and 5.1 Å are very close to the length and the width of a coumarin group (6.7 and 5.0 Å). In addition, the

Fig. 1 (A) SEM image of a large area containing fiber structures and (B) high resolution image of the fiber networks of the GVGV-Cou xerogel. (C) TEM image of the fibrous nanostructures. Inset in (A) is a photo of the GVGV-Cou gel.

d value of $19.3 \text{ \AA}$ is close to the length of the peptide segment with the three methylene groups ($21 \text{ \AA}$). Based on the FT-IR, ^1H NMR, and XRD data, the molecular packing is proposed in Fig. 4B.

The UV-vis spectra were used to check if there were electronic interactions during the self-assembly process (Fig. 5). First, the molecularly dissolved GVGV-Cou was explored in a

Fig. 2 FT-IR spectrum of the GVGV-Cou xerogel. Inset: the red line is the derivative of the FT-IR spectrum.

Fig. 3 A section of the ^1H NMR spectra of the GVGV-Cou weak gel in acetone- d_6 (15 mg mL^{-1}) at different temperatures.

dilute solution where methanol was used as the good solvent (0.013 mg mL^{-1}). The maximum absorption is at 316 nm , which is assigned to the coumarin group.^{10d,16} When the concentration was increased to 1.3 mg mL^{-1} , a new band with two peaks centred at 478 and 505 nm appeared, which indicates the formation of certain supramolecular interactions at a higher concentration. In the xerogel film from ethanol, the band absorption at 316 nm was broadened and showed a 15 nm red shift compared to that in the molecular state. Moreover, a new band ranging from 430 to 520 nm with the maximum peak at 510 nm showed up, similar to the new absorption band observed at the higher concentration in methanol. From the UV-vis spectra, it can be concluded that J-type aggregates were formed within the fibers, specific neighbouring coumarin groups adopted an edge-on-edge packing orientation,¹⁷ and charge transfer (CT) interactions occurred.¹⁸ The CT complex formation is also proved by the generation of the peachy beige color of the gel.

As reported before, peptide segments with a strong tendency to form β -sheets might facilitate or manipulate the self-assembly of the connected π -conjugated systems. In such situations, the

Fig. 4 (A) XRD spectrum of the GVG-Cou xerogel film. (B) Proposed molecular packing.

Fig. 5 UV-vis spectra of GVG-Cou in methanol solutions and as a xerogel film.

formation of β -sheets brings the aromatic groups or π -conjugated oligomers closer to each other, which facilitates π - π interactions.⁹ Similarly, in our system it is suggested that the formation of anti-parallel β -sheet secondary structures is the first step. After the H-bonded assembly was formed, the coumarin groups were forced to get close to each other and can interact *via* π - π interactions. As a result, CT complexes were formed. It has been reported that CT interactions are an important noncovalent interaction, which can drive the formation of gels.¹¹ Normally, donor and

Fig. 6 Proposed mechanism of the GVG-Cou self-assembly. The green atoms in (A) are the positions where the [2+2] photoaddition reaction would happen if the relative spatial location of the double bonds meets the reaction requirements.

acceptor molecules are both needed and two-component CT gels have been obtained.¹² CT gels formed from a single building block are rare. In the present investigation, a single component CT gel driven by H-bonds and π - π interactions was obtained from a peptide-coumarin conjugate (GVG-Cou).

Since the coumarin group can perform dimerization, light stimuli materials can be prepared. Therefore, the GVG-Cou gel was illuminated by using 365 nm UV light, but unfortunately, no dimerization was observed in our present system.

Proposed mechanism of the hierarchical self-assembly

Based on the above results, the hierarchical self-assembly process of GVG-Cou is proposed (Fig. 6). First, hydrogen-bonded β -sheet nanostructures are formed based on the H-bonds between neighbouring peptide segments, and then coumarin groups from adjacent β -sheets interact by π - π interactions.¹³ More specifically, the electron-deficient part of one coumarin molecule interacts with the electron-rich part of another coumarin molecule to form a CT complex. The synergistic effects of H-bonding and such π - π interactions play an important role in the formation of the CT gel. The anti-parallel β -sheet secondary structures bring the coumarin groups into appropriate positions and the CT interactions occur. The formation of such CT complexes also prevents the [2+2] cyclization normally observed in many other coumarin derivatives from occurring, since the coumarin groups are aligned in a head-to-tail manner, and therefore the double bonds are far away from each other. This is in accordance with our observations. Nanofibers are formed based on the synergy of hydrogen bonding, π - π interactions and charge transfer interactions. Furthermore, the fiber bundles are fabricated through fiber-fiber interactions, and finally the hierarchical fiber bundles and the fibers entangle with each other into three dimensional networks.

Encapsulation and release of guest molecules

Gel networks have been used for guest molecule encapsulation and release for potential use in applications, such as drug controlled release.^{1,19} We have investigated the dye encapsulation and release properties for the present GVG-Cou gel.

Fig. 7 Molecular structures of CR and MB, and the pictures of before (A) and after (B) the release of CR. (C) A picture where the upper ethanol solution has been removed to show that the stable gel film is not dissolved during the release of CR.

Congo Red (CR) and Methylene Blue (MB) are not only biological markers but also therapeutic drugs, for instance, MB can be used to treat methemoglobinemia and CR can be used to treat Huntington's disease. Both CR and MB (Fig. 7) were selected as the guest molecules to check: (i) the guest encapsulation and release abilities of the GVGVCou gel; and (ii) the encapsulation and release abilities for different drug molecules.

The dye molecule and GVGVCou were dissolved in ethanol by heating and the solution was then cooled down to form a cogel. After the stable cogels with CR or MB were formed, ethanol solutions without dye molecules were put on top of the cogels. Fig. 7A and B show pictures of before and after the release of CR. Fig. 7C shows that the GVGVCou gel film is very stable and it cannot be dissolved by the upper ethanol solution during the dye release. The release of the dye molecules was monitored by fluorescence (FL) spectra. Fig. 8 shows the time-dependent release rates of the dyes from the cogels *via* diffusion. It is obvious that both CR and MB can be released

from the gel structures. However, the release processes for the two dyes are different. Within the first 5 min, the release rates of MB and CR seem to be similar. After that, the release of CR slows down. After 90 min, about 85% of MB was released, while only 58% of CR can be released from the gel matrices.

To investigate the mechanism for forming the cogels from GVGVCou and the dyes, the assembled structures and the molecular packing were characterized by SEM and XRD spectra. Many spherical aggregates were observed besides the fibre nanostructures in the SEM images, both for the GVGVCou&CR cogel and the GVGVCou&MB cogel (Fig. S3 in the ESI†). In addition, the XRD spectra of the GVGVCou&CR and GVGVCou&MB cogels were found to be almost the same as that of the GVGVCou xerogel (Fig. S4 in the ESI†). However, the peaks corresponding to the coumarin-coumarin packing distances disappeared in the cogels. Based on the SEM and XRD results, it can be concluded that the dyes do not change the overall packing in the gels and are simply trapped inside the 3D fiber networks of GVGVCou. In addition, a few dyes intercalate into the coumarin packs *via* π - π stacking.

The different release ratios in ethanol for CR and MB might be explained by the following factors: (i) the length of CR is about 2.6 nm, while the length is only 1.4 nm for MB. Such different molecular sizes would lead to different mechanisms of interactions between the gel fibers and dye molecules, *i.e.* CR may have stronger dipole-dipole interactions with the gel fibers than MB does; (ii) in addition, the amino and S=O groups on CR might form hydrogen bonds with GVGVCou and such interactions would retard the release of the CR molecules from the gel networks. In short, the GVGVCou gel can be used as a matrix for guest molecule encapsulation and release, and the release ratio depends on the guest molecule properties, which can affect the interactions between the gel and guest molecules, and thus the release ratio.

Conclusions

A tetrapeptide-coumarin conjugate (GVGVCou) was synthesized and the gel behavior of GVGVCou was investigated as well as its ability for encapsulation and release of guest molecules. Anti-parallel β -sheets can be formed between the peptide segments *via* the formation of H-bonds. It is worth noting that in our study, an unexpected charge transfer (CT) interaction between the coumarin groups was observed and this prohibited the occurrence of [2+2] photoaddition reaction of the coumarin, which has not been reported before. The formation of such a strong CT complex might be facilitated by the strong ability of the GVGVCou peptides to form β -sheets. Based on the collaborative interactions of hydrogen bonding and CT interactions, GVGVCou assembled into a stable gel composed of fibrous structures. Furthermore, the gel can be used as a matrix for the encapsulation and release of dye molecules. The present soft material may find potential applications in materials science as a reservoir for trapping and the controlled release of guest molecules.

Fig. 8 Release of the dye molecules from the GVGVCou gel.

Experimental section

Compounds

All starting materials were obtained from commercial suppliers and were used as received. All solvents were distilled with suitable drying agents. GVG–Cou was synthesized according to the following steps: GVG–Cou was obtained by coupling 7-hydroxy coumarin decorated with an allylene group and a Gly-(L-Val)-Gly-(L-Val) peptide segment by click chemistry. The chemical structure and the purity of GVG–Cou were confirmed by ^1H NMR spectroscopy and HR-ESI MS. The synthesis of GVG–alkyl was carried out following the above procedure.

Gel formation

The typical gel preparation method is as follows: 15 mg of GVG–Cou was dissolved in 1 mL of ethanol by heating and then cooling down slowly to form a stable gel within 5 min. The gel formation was confirmed by the vial inversion method.

Dye encapsulation and release

Cogels consisting of a dye and GVG–Cou were prepared by the following steps: first, CR or MB was dissolved in ethanol to make a 1 mg mL $^{-1}$ stock solution; second, 3 mg of GVG–Cou was dissolved in 0.2 mL of the CR or MB ethanol solution (1 mg mL $^{-1}$) by heating and then cooling down to form a cogel film in a 5 mL bottle. After the cogel was formed, 2 mL of ethanol solution was put on top of the gel film and the release of the dye molecules was monitored by FL spectroscopy. 0.2 mL of the CR or MB ethanol solution (1 mg mL $^{-1}$) was diluted with 1.8 mL of ethanol and this served as the FL reference.

Characterization

^1H NMR spectra were recorded on a Bruker AMX 600 spectrometer (^1H NMR: 600 MHz) at 298 K. HR-ESI mass spectra were obtained on a Bruker APEX IV instrument. UV-vis spectra were recorded in a quartz cuvette with an optical path length of 1 cm or on a quartz slide using a Varian Cary 50 UV-vis spectrophotometer. FT-IR spectra were measured on a Nicolet 6700 FT-IR spectrometer (Thermo Electron Corporation). Xerogels for the SEM and XRD characterization were prepared *via* evaporating the solvent in the natural atmosphere first and then drying under vacuum overnight. XRD was performed on a Bruker d8 advance X-ray diffractometer with Cu K α ($\lambda = 1.54178 \text{ \AA}$) radiation. SEM measurements were performed on a Hitachi S-4800 with an accelerating voltage of 3.0 kV on freshly cleaved mica and the samples were coated with gold before imaging. TEM measurements were performed on a Hitachi H-7650. The solutions were cast onto Cu grids without staining and dried at room temperature before the TEM observations.

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Notes and references

- (a) S. S. Babu, V. K. Praveen and A. Ajayaghosh, *Chem. Rev.*, 2014, **114**, 1973–2129; (b) P. Dastidar, *Chem. Soc. Rev.*, 2008, **37**, 2699–2715; (c) M. O. Piepenbrock, G. O. Lloyd, N. Clarke and J. W. Steed, *Chem. Rev.*, 2010, **110**, 1960–2004; (d) N. M. Sangeetha and U. Maitra, *Chem. Soc. Rev.*, 2005, **34**, 821–836; (e) M. D. Segarra-Maset, V. J. Nebot, J. F. Miravet and B. Escuder, *Chem. Soc. Rev.*, 2013, **42**, 7086–7098; (f) D. K. Smith, *Chem. Soc. Rev.*, 2009, **38**, 684–694; (g) J. W. Steed, *Chem. Commun.*, 2011, **47**, 1379–1383; (h) X. Yang, G. Zhang and D. Zhang, *J. Mater. Chem.*, 2012, **22**, 38–50; (i) L. Zhang, L. Qin, X. Wang, H. Cao and M. Liu, *Adv. Mater.*, 2014, **26**, 6959–6964.
- (a) C. A. Hauser and S. Zhang, *Chem. Soc. Rev.*, 2010, **39**, 2780–2790; (b) A. M. Jonker, D. W. P. M. Löwik and J. C. M. van Hest, *Chem. Mater.*, 2012, **24**, 759–773; (c) S. Kiyonaka, K. Sada, I. Yoshimura, S. Shinkai, N. Kato and I. Hamachi, *Nat. Mater.*, 2004, **3**, 58–64; (d) P. Koley and A. Pramanik, *Adv. Funct. Mater.*, 2011, **21**, 4126–4136.
- (a) W. A. Petka, *Science*, 1998, **281**, 389–392; (b) H. Wang and Z. Yang, *Nanoscale*, 2012, **4**, 5259–5267; (c) Z. Yang and B. Xu, *J. Mater. Chem.*, 2007, **17**, 2385–2393; (d) S. Young, M. Wong, Y. Tabata and A. G. Mikos, *J. Controlled Release*, 2005, **109**, 256–274; (e) F. Zhao, M. L. Ma and B. Xu, *Chem. Soc. Rev.*, 2009, **38**, 883–891.
- J. B. Matson, C. J. Newcomb, R. Bitton and S. I. Stupp, *Soft Matter*, 2012, **8**, 3586–3595.
- (a) S. Koutsopoulos, L. D. Unsworth, Y. Nagai and S. Zhang, *Proc. Natl. Acad. Sci. U. S. A.*, 2009, **106**, 4623–4628; (b) Y. Nagai, L. D. Unsworth, S. Koutsopoulos and S. Zhang, *J. Controlled Release*, 2006, **115**, 18–25.
- Y. Gao, Y. Kuang, Z. F. Guo, Z. Guo, I. J. Krauss and B. Xu, *J. Am. Chem. Soc.*, 2009, **131**, 13576–13577.
- F. Vollrath and D. P. Knight, *Nature*, 2001, **410**, 541–548.
- (a) R. Gong, Y. Song, Z. Guo, M. Li, Y. Jiang and X. Wan, *Supramol. Chem.*, 2013, **25**, 269–275; (b) Z. Guo, R. Gong, Y. Mu, X. Wang and X. Wan, *Chem. – Asian J.*, 2014, **9**, 3245–3250; (c) Z. Guo, Y. Song, R. Gong, Y. Mu, Y. Jiang, M. Li and X. Wan, *Supramol. Chem.*, 2014, **26**, 383–391.
- (a) R. Matmour, I. De Cat, S. J. George, W. Adriaens, P. Leclere, P. H. Bomans, N. A. Sommerdijk, J. C. Gielen, P. C. Christianen, J. T. Heldens, J. C. van Hest, D. W. Lowik, S. De Feyter, E. W. Meijer and A. P. Schenning, *J. Am. Chem. Soc.*, 2008, **130**, 14576–14583; (b) M. Ma, Y. Kuang, Y. Gao, Y. Zhang, P. Gao and B. Xu, *J. Am. Chem. Soc.*, 2010, **132**, 2719–2728; (c) S. Bai, S. Debnath, N. Javid, P. W. Frederix, S. Fleming, C. Pappas and R. V. Ulijn, *Langmuir*, 2014, **30**, 7576–7584; (d) S. R. Diegelmann, N. Hartman, N. Markovic and J. D. Tovar, *J. Am. Chem. Soc.*, 2012, **134**, 2028–2031;

- (e) R. Marty, R. Nigon, D. Leite and H. Frauenrath, *J. Am. Chem. Soc.*, 2014, **136**, 3919–3927; (f) Y. Sun, L. Jiang, K. C. Schuermann, W. Adriaens, L. Zhang, F. Y. Boey, L. De Cola, L. Brunsveld and X. Chen, *Chem. – Eur. J.*, 2011, **17**, 4746–4749.
- 10 (a) E. Abe, S. J. Pennycook and A. P. Tsai, *Nature*, 2003, **421**, 347–350; (b) Q. Huang, C. Bao, W. Ji, Q. Wang and L. Zhu, *J. Mater. Chem.*, 2012, **22**, 18275; (c) M. Nagata and Y. Yamamoto, *React. Funct. Polym.*, 2008, **68**, 915–921; (d) S. R. Trenor, A. R. Shultz, B. J. Love and T. E. Long, *Chem. Rev.*, 2004, **104**, 3059–3077.
- 11 M. Kumar, K. V. Rao and S. J. George, *Phys. Chem. Chem. Phys.*, 2014, **16**, 1300–1313.
- 12 (a) U. Maitra, P. Vijay Kumar, N. Chandra, L. J. D'Souza, M. D. Prasanna and A. R. Raju, *Chem. Commun.*, 1999, 595–596; (b) P. Babu, N. M. Sangeetha, P. Vijaykumar, U. Maitra, K. Rissanen and A. R. Raju, *Chem. – Eur. J.*, 2003, **9**, 1922–1932; (c) A. Das, M. R. Molla, A. Banerjee, A. Paul and S. Ghosh, *Chem. – Eur. J.*, 2011, **17**, 6061–6066; (d) J. Hu, J. Wu, Q. Wang and Y. Ju, *Beilstein J. Org. Chem.*, 2013, **9**, 2877–2885; (e) C. Kulkarni, G. Periyasamy, S. Balasubramanian and S. J. George, *Phys. Chem. Chem. Phys.*, 2014, **16**, 14661–14664; (f) S. Prasanthkumar, S. Ghosh, V. C. Nair, A. Saeki, S. Seki and A. Ajayaghosh, *Angew. Chem., Int. Ed.*, 2015, **54**, 946–950.
- 13 X. Lou, Z. Zhao, Y. Hong, C. Dong, X. Min, Y. Zhuang, X. Xu, Y. Jia, F. Xia and B. Z. Tang, *Nanoscale*, 2014, **6**, 14691–14696.
- 14 (a) Z. Ke, H. F. Chow, M. C. Chan, Z. Liu and K. H. Sze, *Org. Lett.*, 2012, **14**, 394–397; (b) A. Banerjee, G. Palui and A. Banerjee, *Soft Matter*, 2008, **4**, 1430; (c) G.-C. Kuang, X.-R. Jia, M.-J. Teng, E.-Q. Chen, W.-S. Li and Y. Ji, *Chem. Mater.*, 2012, **24**, 71–80; (d) T. B. Yu, J. Z. Bai and Z. Guan, *Angew. Chem., Int. Ed.*, 2009, **48**, 1097–1101.
- 15 B. Escuder and J. F. Miravet, *Langmuir*, 2006, **22**, 7793–7797.
- 16 Z. Guo, T. Jiao and M. Liu, *Langmuir*, 2007, **23**, 1824–1829.
- 17 (a) W. F. Mooney, P. E. Brown, J. C. Russell, L. G. Pedersen and D. G. Whitten, *J. Am. Chem. Soc.*, 1984, **106**, 5659–5667; (b) S. Yagai, Y. Goto, X. Lin, T. Karatsu, A. Kitamura, D. Kuzuhara, H. Yamada, Y. Kikkawa, A. Saeki and S. Seki, *Angew. Chem., Int. Ed.*, 2012, **51**, 6643–6647.
- 18 (a) K. Liu, C. Wang, Z. Li and X. Zhang, *Angew. Chem., Int. Ed.*, 2011, **50**, 4952–4956; (b) S. Basak, S. Bhattacharya, A. Datta and A. Banerjee, *Chem. – Eur. J.*, 2014, **20**, 5721–5726.
- 19 F. Zeng, Y. Shen and C.-F. Chen, *Soft Matter*, 2013, **9**, 4875–4882.