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One platform solid multicolour emission of terthiophene compounds controlled by mixed self-assembly†

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Via the mixed self-assembling procedure, solid multicolour emission materials based on an amphiphilic terthiophene compound are obtained from a unimolecular platform. Upon controlling the concentration of the cationic surfactant dodecyltriethyl ammonium bromide (DEAB) in the precipitate–monomer equilibrium system of the terthiophene compound TTC4L, mixed self-assembly of TTC4L–DEAB results in diverse structures (including plates, spheres, and needles) with different emission colours. The multicolour emissions are triggered by the different distances between the terthiophene groups in these mixed self-assemblies. Each distance corresponds to a specific molecular state of terthiophene groups, so that emissions corresponding to the monomers, excimers, and aggregates are obtained. Upon variation of the ratio of DEAB and TTC4L, the relative fraction of emissions corresponding to the monomers, excimers, and aggregates of TTC4L changes. This approach may act as a simple method to control the stacking mode of the oligothiophene group which is anticipated to realize unimolecular-platform multicolour emissions.

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Introduction

Oligothiophene compounds have received increasing attention in recent years in the fields of light emitting diodes (LEDs),^{1–5} because they exhibit different emission colours corresponding to monomers, aggregates, and excimers, respectively.^{6–11} This makes it possible to obtain multicolour emission from the same molecule simply by changing the intermolecular distance, namely one platform multicolour emission.^{12–15} However, so far the multicolour emissions of thiophene have been mainly obtained through synthetic chemistry by modifying the number of conjugated thiophene groups or the replacing groups that are covalently connected to the thiophene skeleton.^{16–20} This is to a large extent due to the difficulty in tuning the states of thiophene compounds in solids since it is hard to change the intermolecular distance in such cases. As a result, to date solid state multicolour emission of thiophene compounds remains a challenging task.

On the other hand, the control over solution based molecular assemblies has burst into flourishing developments in the

last few decades. The change of molecular states or molecular packing can be achieved upon exerting external stimuli, such as light,²¹ enzyme,²² pH,²³ temperature,²⁴ redox,²⁵ and so forth. However, for the oligothiophene derivatives, the molecular states corresponding to various emissions highly depend on the intermolecular distances, which can hardly be tuned through external stimuli. In order to solve this problem, we proposed a strategy of mixed self-assembly in our previous work,²⁶ which is similar to the formation of self-assembled structures in the oppositely charged surfactant systems.^{27–31} The main idea for this strategy is to form mixed self-assembly with the thiophene compound and another amphiphilic component. In case that no specific recognition occurs, the two components will averagely distribute in the mixed self-assembly,^{30,32,33} so that the distance between molecules of the same kind is governed by the mixing ratio between the two components.^{34–37} Using this strategy, we have obtained multicolour emissions of the amphiphilic TTC4L in solution simply by tuning the self-assembly of TTC4L with an oppositely charged surfactant DEAB.²⁶

The solution based mixed self-assembly inspires that if the mixed self-assemblies were allowed to grow up to reach the meso- or macro-scale, they may precipitate out from the solution so as to form solid materials. In this way, the control over the intermolecular distance in solids can be achieved also by variation of the mixing ratio between the components when they are in solution. In this work, we report that the multicolour emission of TTC4L in solid states is indeed obtained by co-crystallization of the TTC4L with the surfactant dodecyltriethyl

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ammonium bromide (DEAB). At a lower pH than in our previous work, variation of the ratio of DEAB and TTC4L leads to various crystalline structures, including plates, spheres and needles, which exhibit different emission colours. Most interestingly, the starting TTC4L is a solid suspension which is in equilibrium with its monomers in this study. The co-crystallization of TTC4L with DEAB shifts the solubilization equilibrium of TTC4L toward monomers, so that the TTC4L solid was transformed into the mixed self-assembly, which allows tuning the intermolecular distance between TTC4L. We expect that this strategy will be generalized to other intermolecular distance dependent emitting systems.

Experimental section

Materials

TTC4L was synthesized according to the procedure reported in our previous work.^{26,38} Dodecyltriethyl ammonium bromide (DEAB) was prepared by the reaction of 1-bromododecane with triethylamine, followed by recrystallizing five times from ethanol–acetone. The purity of the surfactant was examined by the lack of minima in its surface tension curve. The water used was purified by the Millipore filtration system. The other chemicals were of analytical reagent grade.

Sample preparation

The TTC4L solutions were obtained by dissolving the solid TTC4L powder in ultrapure water (Milli-Q, 18.2 MΩ cm). The pH of TTC4L solutions was controlled around 7.0 using concentrated hydrochloric acid solution. Mixed assembly of TTC4L and DEAB was performed *via* mixing certain amounts of TTC4L solutions with concentrated DEAB solutions at desired molar ratios. These samples were vortex mixed and kept at 20 °C for at least 3 days before further analysis. The pH values were measured using a SevenMulti type pH meter with InLab Semi-Micro electrodes (Mettler Toledo, Switzerland). All analytical measurements were performed at room temperature.

Spectroscopic measurements

The UV-vis absorbance measurements were carried out on a UV-1800 SHIMADZU spectrophotometer in the range of 200–700 nm. A Hitachi F-7000 fluorescence spectrometer was used to measure the fluorescence emission of TTC4L–DEAB mixed systems. The excitation wavelength was set at 365 nm. Emission spectra were recorded in the range of 380–700 nm. Quantum efficiencies of TTC4L in various assemblies were recorded on a Horiba-Jobin Yvon Nanolog FL3-2iHR infrared fluorescence spectrometer with a calibrated integrating sphere system. The time-resolved fluorescence spectrum measurement was performed with a Lifespec Red spectrofluorometer of Edinburgh Instruments equipped with a Hamamatsu picosecond light pulser C8898 using a 372 nm laser with a repetition rate of 1 MHz as the light source. For each measurement, at least 5000 photon counts were collected in the peak channel to ensure the decay quality. The quality of the fit for the decay curves was supported by the fact that the fitting parameter χ^2 was less than 1.3.

Scanning electron microscopy (SEM)

Field-emission scanning electron microscopy (FE-SEM) images were taken with a Hitachi S4800. For the SEM measurements, a drop of dispersion was placed on a clean silicon wafer and then dried freely under ambient conditions.

Confocal laser scanning microscopy (CLSM)

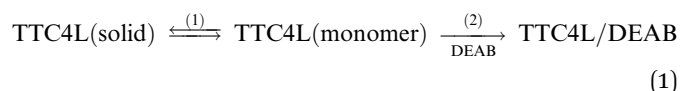
An A1R-si inverted confocal laser scanning microscope (Nikon, Japan) was used to conduct experiments in fluorescence (irradiated at 405 nm, collection wavelength range: 420.75–740.75 nm) and differential interference contrast (DIC) modes. For CLSM measurements, a drop of dispersion was loaded onto a clean glass slide, followed by drying naturally.

X-ray diffraction (XRD)

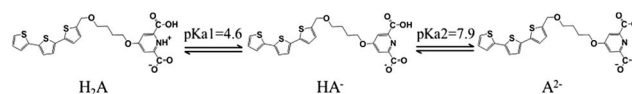
Reflection XRD studies were carried out on the film with a model Rigaku Dmax-2000 diffractometer. The X-ray beam was generated with a Cu anode and the wavelength of the $K_{\alpha 1}$ beam was 1.5406 Å. The X-ray beam was directed toward the film edge, and scanning was performed in the range of 2–35°. For XRD measurements, several drops of the dispersion were loaded on a clean glass slide and dried in air.

Results and discussion

The molecular forms of TTC4L are pH dependent. H_2A , HA^- , and A^{2-} occur one by one with increasing pH (Scheme 1). In our previous work, we report that the A^{2-} form dominates at pH > 8.0, and addition of oppositely charged surfactant DEAB leads to water soluble mixed self-assembly, such as vesicles and micelles.²⁶ However, in this work, we are interested in the HA^- form, which exists predominantly in the pH range of 4.6–7.9. All the studies in this work were carried out at pH 7.0, where the TTC4L molecules in the HA^- form are slightly dissolved. We expect that the presence of precipitate–monomer equilibrium allows us to rearrange the packing of TTC4L molecules upon addition of the oppositely charged surfactant DEAB, as demonstrated in the following equation:



Since the TTC4L in the HA^- form averagely carries only one elementary charge, addition of the aqueous solution of positively charged DEAB may shift the equilibrium (1) toward the right side, and the mixed self-assembly of TTC4L–DEAB is apt to grow up and finally precipitates out from the solution. Then



Scheme 1 Illustration of the three forms of TTC4L.

changing the amount of DEAB may lead to mixed self-assemblies with various TTC4L–DEAB ratios.

Fig. 1 shows the optical observations of the precipitates in the 0.10 mM TTC4L system. Without DEAB, rectangular plates of several micrometers are formed, which are obviously self-assembled from TTC4L. In the ratio of 2 : 1, spherical particles of several micrometers are observed, which seem to be hollow under optical microscopy. As the ratio of TTC4L and DEAB increases to 1 : 1, needle-like structures about 1000 μm long and 80 μm wide are formed. Both the length and the width of the needles decrease with an increase in the ratio of TTC4L and DEAB. At the ratio of 1 : 20, the length has been decreased to about 60 μm and the width is about 5 μm . No needles are available as the ratio of TTC4L and DEAB is over 1 : 50. Similar results are observed from SEM images (see Fig. S1[†]).

Fig. 2 shows that the X-ray diffraction pattern of the TTC4L–DEAB precipitates formed at different ratios of TTC4L and DEAB are obviously different from that of the single TTC4L and DEAB systems, suggesting that both the hollow spheres and the needles are the mixed self-assembly of TTC4L–DEAB. It is noticed that the XRD patterns of the 2 : 1 system is drastically different from the mixed systems with 1 : 1 and 1 : 20, suggesting that the molecular packing mode in the spherical particles is completely different from that in the needles. It is also striking that the pattern in the 1 : 20 system contains both the feature of pure DEAB crystals and that of the mixed self-assembly in the ratio of 1 : 1, indicating that there are some domains of DEAB in the needles formed in the ratio of the 1 : 1–1 : 20 system.

Nevertheless, the difference in the XRD patterns is a reflection of changes in the intermolecular distance or packing mode of the molecules.^{34,39} According to our design principle introduced in the previous text, we expect that this should lead to emissions of different colours. In Fig. 3, we show the CLSM observations of these precipitates. As indicated in Fig. 3, the polydispersed plates formed by TTC4L alone emit green light. In the ratio of 2 : 1, yellow-green emission was observed in the matrix of green emission for the hollow microspheres. As the ratio reaches 1 : 1 where the long and wide needles were observed, blue-emissive needles were generated. Interestingly, the colour of the needles changes to cyan as the ratio of TTC4L

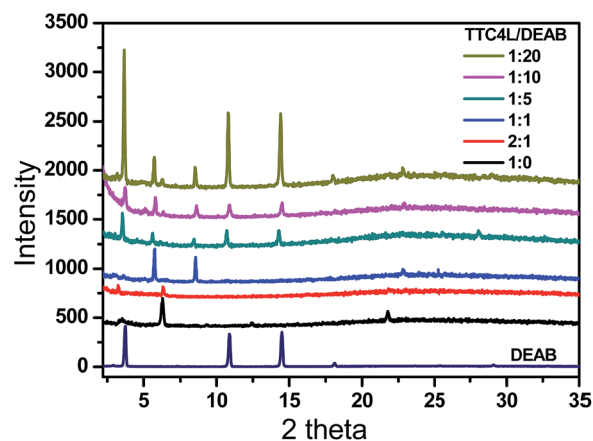


Fig. 2 XRD patterns of DEAB solid powder and assemblies of 0.10 mM TTC4L in the different ratios of TTC4L and DEAB (1 : 0, 2 : 1, 1 : 1, 1 : 5, 1 : 10 and 1 : 20).

and DEAB increases to 1 : 5, which is accompanied by the decreased needle length and width. Obviously, the emission colours for TTC4L in solid states have been successfully changed simply by varying the ratio of TTC4L and DEAB.

In order to explore the origins of the different emission colours, the photophysical data for the different emission forms were measured (details can be seen in Table S1[†]). Additionally, the fluorescence decays were measured (see Fig. S2–S4[†]) It was found that TTC4L exhibited three lifetimes at all DEAB concentrations, but the fraction of different lifetimes varies as the ratio between TTC4L and DEAB changes (see Fig. 4). According to the literature, the longest lifetime is attributed to emissions from the excimers, which are formed at an intermolecular distance being 4–7 \AA .^{6,14} The medium lifetime is from the aggregates, where the intermolecular distance is about 3 \AA .^{7,8} The shortest lifetime belongs to the monomers dispersed in the molecular state in the system.^{10,11} The fluorescence decay data suggest that without DEAB, most TTC4L molecules in the precipitates are in the form of excimers (41.1%), while those in the form of aggregates and monomers are 31.2%, 27.7%, respectively. Upon increasing the fraction of DEAB in the range of 1 : 0–1 : 1, where the morphology of the precipitates changes

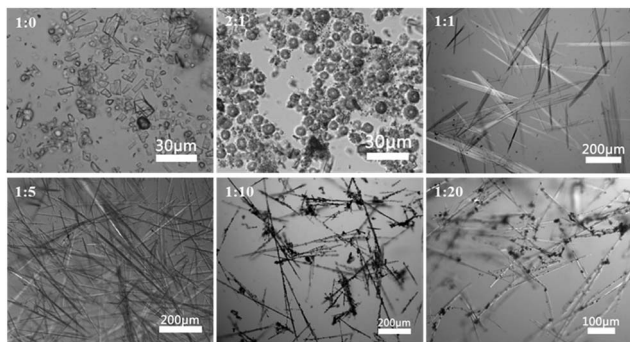


Fig. 1 CLSM images in DIC mode of the assembled structures of 0.10 mM TTC4L in the different ratios of TTC4L and DEAB (1 : 0, 2 : 1, 1 : 1, 1 : 5, 1 : 10 and 1 : 20).

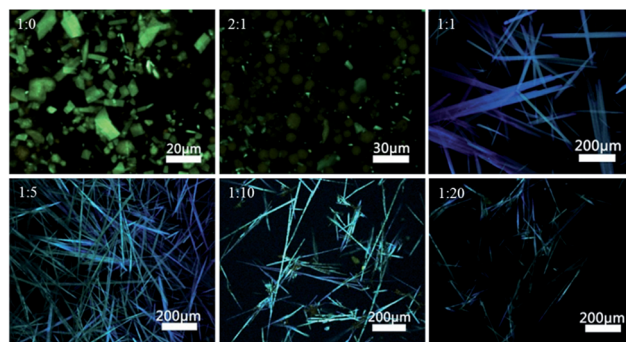


Fig. 3 CLSM images in fluorescence mode of the self-assembled structures of 0.10 mM TTC4L in the presence of different ratios of TTC4L and DEAB (1 : 0, 2 : 1, 1 : 1, 1 : 5, 1 : 10 and 1 : 20).

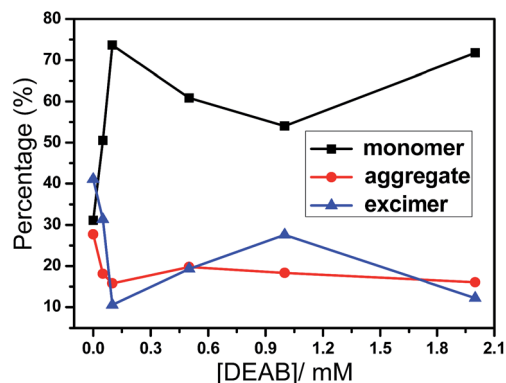


Fig. 4 Variation of the percentage of different fluorescent species of the self-assembled structures in the 0.10 mM TTC4L solutions with increasing the concentration of DEAB. The lines are simply to guide the eyes.

from rectangular *via* spherical to needle-like, the fraction of excimers drops steeply whereas that of both the monomers and aggregates increase sharply. This is in line with the disappearance of the bright green emissions. Upon an increase in the ratio of DEAB in the range of 1 : 1–1 : 10 where the size of the needles decreases only, the fraction of the monomers decreases slightly while that of the excimers increases. Interestingly, a further increase of the ratio of DEAB up to 1 : 20 may lead to a slight increase of the fraction of monomers again. Correspondingly, the fraction of excimers decreases slightly. In the latter two DEAB concentration ranges, the fraction of aggregates is nearly constant. This explains that the colour of the needles changes from blue to cyan as the ratio of TTC4L and DEAB increases from 1 : 1 to 1 : 10, whereas the blue hue is strengthened again as DEAB increases from 1 : 10 to 1 : 20. Moreover, the solid fluorescence spectra were measured (Fig. S5†). Corresponding to the variation of the fraction of TTC4L in different states, three lifetimes obtained for the different emission assemblies can also be ascribed.

The morphology and emission change of TTC4L with the increasing ratio of TTC4L and DEAB is attributed to the change at the molecular scale. Without DEAB, the charged TTC4L molecules are amphiphilic, so that they aggregate *via* self-assembly. The electrostatic repulsion between the head groups leads to a larger intermolecular distance, which allows the formation of excimers. In the presence of a small amount of DEAB, where the positive charges provided by DEAB is not enough to balance the negative charges of TTC4L, the self-assembly of TTC4L with an apparent form of precipitates gradually changes into the mixed self-assembly of TTC4L–DEAB. This process may be mediated by a precipitate dissolution process, as demonstrated in eqn (1). Because DEAB and TTC4L carry opposite charges, the electrostatic interaction in the mixed assembly is reduced so that the self-assembly may grow into large scales, which finally precipitates out from the aqueous media.⁴⁰ Meanwhile, the presence of DEAB separates the TTC4L molecules so that it makes them difficult to aggregate together. Therefore, at this stage the increased fraction of monomers is accompanied by the decrease of excimers and

aggregates. However, as the ratio of TTC4L and DEAB is increased in the range of 1 : 0–1 : 20, where the DEAB becomes dominant, the DEAB molecules tend to self-aggregate, as revealed in the XRD patterns in Fig. 2, since they attract themselves better than TTC4L. This implies that there might be two kinds of islands that are rich in DEAB and TTC4L, respectively. This inevitably leads to a slight increase of the fraction of TTC4L in the form of excimers and decrease of monomers. As the fraction of DEAB further increases, the amount of DEAB becomes prevailingly dominant so that the TTC4L molecules can hardly form islands and most of them are dissolved in the island of DEAB. Therefore, the fraction of monomers increases again and that of the excimers decreases. Because the water solubility of DEAB is very good, the islands that is rich in DEAB tend to enter into water. As a result, the size of the needles keeps decreasing. In fact, all the needles disappear as the ratio of TTC4L and DEAB is over 1 : 100. This was clearly reflected in the evolution of UV-vis spectra (Fig. 5) upon addition of DEAB. Fig. 5 shows that the UV absorbance keeps decreasing as the ratio of TTC4L and DEAB increases from 1 : 0 to 1 : 10, whereas it starts to increase at the ratio of TTC4L and DEAB increases above 1 : 10. It is noticeable that the UV absorbance is not zero at a longer wavelength as the ratio of TTC4L and DEAB up to 1 : 20, which is a reflection of the presence of scattering particles. In this study, these scatters are hollow spheres or needles. However, the tail absorption falls to zero at the ratio of TTC4L and DEAB above 1 : 100 and the UV absorbance in the system finally reaches a stable value as the ratio of TTC4L and DEAB is beyond 1 : 200.

The formation of ‘island’ of TTC4L in the needles was confirmed by the observation of the needles with a CLSM under lasers of various wavelengths (Fig. 6). We can see that under 405, 488, and 543 nm, the needles emit blue, green, and yellow light, respectively. It is worth noting that domain-like structures are observed in the needles, suggesting that the green and orange emitting species form small islands in the crystals. In contrast, the blue-violet hue for the needles under 405 nm looks very homogeneous, indicating the monomers that emit corresponding light is dominant and averagely distributed in the

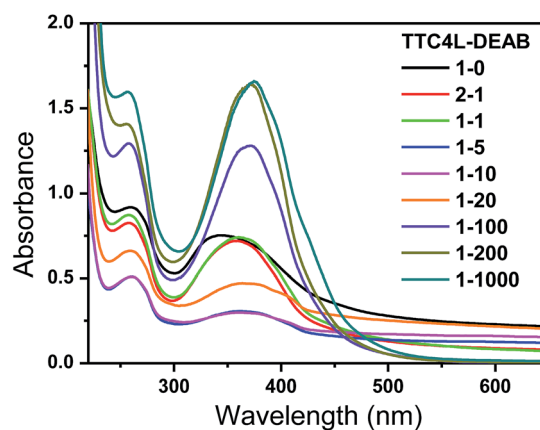


Fig. 5 UV-vis absorption spectra of the self-assembled structures of 0.10 mM TTC4L in the different ratios of TTC4L and DEAB.

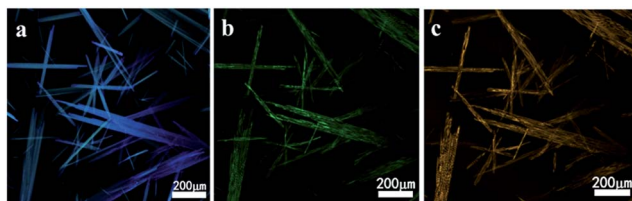
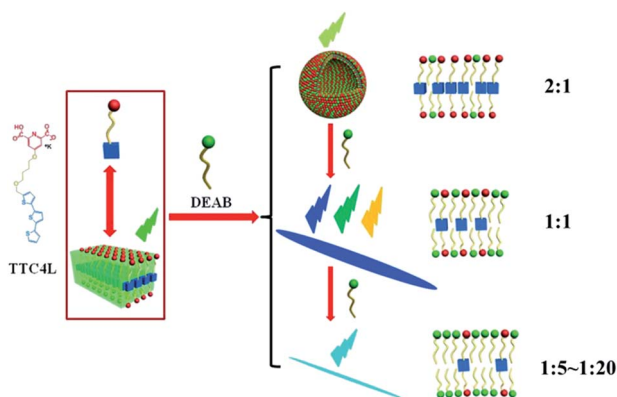


Fig. 6 CLSM images in fluorescence mode of the self-assembled structures of 0.10 mM TTC4L in the ratio of TTC4L and DEAB 1 : 1 excited by the laser of (a) 405 nm, (b) 488 nm and (c) 543 nm.



Scheme 2 Illustration of the self-assembly of TTC4L into various forms in the different ratios of TTC4L and DEAB.

crystals. This observation not only verifies the origins of the different emissions, but also allows us to obtain different emission colours from exactly the same platform, namely the same emitting molecule in its same solid state, simply by variation of exciting wavelengths.^{41,42} The complete scenario for the creation of one-platform solid multicolour emission is illustrated in Scheme 2.

Conclusions

In summary, we developed solid state one-platform multicolour emission of terthiophene compounds TTC4L by the strategy of mixed self-assembly. TTC4L is weakly soluble in water, which allows the presence of equilibrium between TTC4L monomers and solid self-assembled structures. Upon addition of oppositely charged surfactant DEAB, the equilibrium shifts and the self-assembly of TTC4L gradually transforms into mixed assembly of TTC4L–DEAB. This effectively changes the intermolecular distance between TTC4L, so that emissions corresponding to monomers, excimers, and aggregates of TTC4L were generated simply by controlling the ratio between TTC4L and DEAB. Since we have successfully developed solution based multicolour emission of TTC4L using the same principle, we expect that this strategy may be a general approach to achieve one-platform multicolour emission of oligothiophene compounds, which may shed light on the design and development of devices with multicolour emissions.

Acknowledgements

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Notes and references

- 1 F. Geiger, M. Stoldt, H. Schweizer, P. Bauerle and E. Umbach, *Adv. Mater.*, 1993, **5**, 922–925.
- 2 M. Mazzeo, V. Vitale, F. Della Sala, M. Anni, G. Barbarella, L. Favaretto, G. Sotgiu, R. Cingolani and G. Gigli, *Adv. Mater.*, 2005, **17**, 34–39.
- 3 G. Horowitz, P. Delannoy, H. Bouchriha, F. Deloffre, J. L. Fave, F. Garnier, R. Hajlaoui, M. Heyman, F. Kouki, P. Valat, V. Wintgens and A. Yassar, *Adv. Mater.*, 1994, **6**, 752–755.
- 4 T. Noda, H. Ogawa, N. Noma and Y. Shirota, *J. Mater. Chem.*, 1999, **9**, 2177–2181.
- 5 M. S. Song, Q. P. B. Nguyen, C. H. Song, D. Lee and K. Y. Chai, *Molecules*, 2013, **18**, 14033–14041.
- 6 S. DeFeyter, J. vanStam, F. Imans, L. Viaene, F. C. DeSchryver and C. H. Evans, *Chem. Phys. Lett.*, 1997, **277**, 44–50.
- 7 M. Fujitsuka, D. W. Cho, J. Ohshita, A. Kunai and T. Majima, *J. Phys. Chem. C*, 2007, **111**, 1993–1998.
- 8 W. W. Tsai, L. S. Li, H. G. Cui, H. Z. Jiang and S. I. Stupp, *Tetrahedron*, 2008, **64**, 8504–8514.
- 9 V. Percec, M. Glodde, T. K. Bera, Y. Miura, I. Shiyonovskaya, K. D. Singer, V. S. K. Balagurusamy, P. A. Heiney, I. Schnell, A. Rapp, H. W. Spiess, S. D. Hudson and H. Duan, *Nature*, 2002, **417**, 384–387.
- 10 S. Saito, K. Nakakura and S. Yamaguchi, *Angew. Chem., Int. Ed.*, 2012, **51**, 714–717.
- 11 V. D. Deepak and P. R. Sundararajan, *J. Phys. Chem. B*, 2011, **115**, 8458–8464.
- 12 K. Y. Musick, Q. S. Hu and L. Pu, *Macromolecules*, 1998, **31**, 2933–2942.
- 13 H. Meng, J. Zheng, A. J. Lovinger, B. C. Wang, P. G. Van Patten and Z. N. Bao, *Chem. Mater.*, 2003, **15**, 1778–1787.
- 14 W. Mroz, J. P. Bombenger, C. Botta, A. O. Biroli, M. Pizzotti, F. De Angelis, L. Belpassi, R. Tubino and F. Meinardi, *Chem.–Eur. J.*, 2009, **15**, 12791–12798.
- 15 G. Barbarella, M. Melucci and G. Sotgiu, *Adv. Mater.*, 2005, **17**, 1581–1593.
- 16 P. Xiao, F. Dumur, D. Thirion, S. Fagour, A. Vacher, X. Sallenave, F. Morlet-Savary, B. Graff, J. P. Fouassier, D. Gigmes and J. Lalevee, *Macromolecules*, 2013, **46**, 6786–6793.
- 17 J. P. Lu, P. F. Xia, P. K. Lo, Y. Tao and M. S. Wong, *Chem. Mater.*, 2006, **18**, 6194–6203.
- 18 G. Gigli, O. Ingnas, M. Anni, M. De Vittorio, R. Cingolani, G. Barbarella and L. Favaretto, *Appl. Phys. Lett.*, 2001, **78**, 1493–1495.
- 19 M. Anni, G. Gigli, V. Paladini, R. Cingolani, G. Barbarella, L. Favaretto, G. Sotgiu and M. Zambianchi, *Appl. Phys. Lett.*, 2000, **77**, 2458–2460.

- 20 S. Hachiya, K. Asai and G. Konishi, *Tetrahedron Lett.*, 2013, **54**, 3317–3320.
- 21 F. P. Hubbard, G. Santonicola, E. W. Kaler and N. L. Abbott, *Langmuir*, 2005, **21**, 6131–6136.
- 22 Y. Gao, Y. Kuang, Z. F. Guo, Z. H. Guo, I. J. Krauss and B. Xu, *J. Am. Chem. Soc.*, 2009, **131**, 13576–13577.
- 23 M. Johnsson, A. Wagenaar and J. Engberts, *J. Am. Chem. Soc.*, 2003, **125**, 757–760.
- 24 T. S. Davies, A. M. Ketner and S. R. Raghavan, *J. Am. Chem. Soc.*, 2006, **128**, 6669–6675.
- 25 S. Ghosh, K. Irvin and S. Thayumanavan, *Langmuir*, 2007, **23**, 7916–7919.
- 26 L. Zhao, X. H. Cheng, Y. Ding, Y. Yan and J. B. Huang, *Soft Matter*, 2012, **8**, 10472–10478.
- 27 A. Ajayaghosh, C. Vijayakumar, V. K. Praveen, S. S. Babu and R. Varghese, *J. Am. Chem. Soc.*, 2006, **128**, 7174–7175.
- 28 C. Vijayakumar, V. K. Praveen and A. Ajayaghosh, *Adv. Mater.*, 2009, **21**, 2059–2063.
- 29 S. S. Babu, K. K. Kartha and A. Ajayaghosh, *J. Phys. Chem. Lett.*, 2010, **1**, 3413–3424.
- 30 C. Wang, Y. S. Guo, Y. P. Wang, H. P. Xu, R. J. Wang and X. Zhang, *Angew. Chem., Int. Ed.*, 2009, **48**, 8962–8965.
- 31 L. M. Zhai, B. Herzog, M. Drechsler and H. Hoffmann, *J. Phys. Chem. B*, 2006, **110**, 17697–17701.
- 32 A. Ajayaghosh, C. Vijayakumar, V. K. Praveen, S. S. Babu and R. Varghese, *J. Am. Chem. Soc.*, 2006, **128**, 7174–7175.
- 33 D. F. Yu, Q. Zhang, C. X. Wu, Y. X. Wang, L. H. Peng, D. Q. Zhang, Z. B. Li and Y. L. Wang, *J. Phys. Chem. B*, 2010, **114**, 8934–8940.
- 34 X. G. Gu, J. J. Yao, G. X. Zhang and D. Q. Zhang, *Small*, 2012, **8**, 3406–3411.
- 35 H. C. Ma, J. B. Fei, Y. Cui, J. Zhao, A. H. Wang and J. B. Li, *Chem. Commun.*, 2013, **49**, 9956–9958.
- 36 H. Hoffmann, C. Thunig, U. Munkert, H. W. Meyer and W. Richter, *Langmuir*, 1992, **8**, 2629–2638.
- 37 Y. Y. Lin, A. D. Wang, Y. Qiao, C. Gao, M. Drechsler, J. P. Ye, Y. Yan and J. B. Huang, *Soft Matter*, 2010, **6**, 2031–2036.
- 38 L. Zhao, L. X. Jiang, Y. C. Han, Z. Y. Xian, J. B. Huang and Y. Yan, *Soft Matter*, 2013, **9**, 7710–7717.
- 39 H. Maeda, Y. Haketa and T. Nakanishi, *J. Am. Chem. Soc.*, 2007, **129**, 13661–13674.
- 40 L. T. Kang, Z. C. Wang, Z. W. Cao, Y. Ma, H. B. Fu and J. N. Yao, *J. Am. Chem. Soc.*, 2007, **129**, 7305–7312.
- 41 Z. J. Zhao, Z. M. Wang, P. Lu, C. Y. K. Chan, D. D. Liu, J. W. Y. Lam, H. H. Y. Sung, I. D. Williams, Y. G. Ma and B. Z. Tang, *Angew. Chem., Int. Ed.*, 2009, **48**, 7608–7611.
- 42 J. Z. Liu, Y. C. Zhong, J. W. Y. Lam, P. Lu, Y. N. Hong, Y. Yu, Y. N. Yue, M. Faisal, H. H. Y. Sung, I. D. Williams, K. S. Wong and B. Z. Tang, *Macromolecules*, 2010, **43**, 4921–4936.