View Article Online View Journal

ChemComm

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: P. Li, B. Lv, D. Han, P. Duan, M. Liu and M. Yin, *Chem. Commun.*, 2019, DOI: 10.1039/C8CC08924H.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/chemcomm

Journal Name



Stoichiometry-controlled inversion of circularly polarized luminescence in co-assembly of chiral gelators with achiral tetraphenylethylene derivative

Pengyu Li,^a Baozhong Lü,^a Dongxue Han,^b Pengfei Duan,^b Minghua Liu^{*b} and Meizhen Yin^{*a}

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Published on 22 January 2019. Downloaded by University of Winnipeg on 1/24/2019 2:33:59 PM

A supramolecular circularly polarized luminescence (CPL) system was constructed based on the cogelation of an achiral tetraphenylethylene derivative and chiral organic gelators of glutamic acid in chloroform. Adjusting the stoichiometric ratio was found to be an effective strategy for regulating the handedness of CPL.

Circularly polarized luminescence (CPL) have drawn great attention¹ due to their potential applications in the fields of devices,² three-dimensional photoelectric displays,³ information storages,⁴ and even catalysts for asymmetric photochemical reactions.⁵ CPL with controllable handedness are eye-catching and useful in many cases.⁶ Realized by a coassembly strategy, supramolecular cogels consisting of achiral fluorophores and chiral units provide a convenient platform for fabricating CPL materials.⁷ In chiral co-assembly systems, the handedness of CPL always follows the chirality of the chiral component. To obtain opposite handedness of CPL, the prevailing approach is changing the chiral component to its enantiomer.⁸ But the synthesis of chiral enantiomers is always tedious and troublesome. Thus, new convenient and efficient strategies to regulate the handedness of CPL needs to be developed. The stoichiometry between the components is the simplest variable to modulate. In general, different stoichiometric ratios of the components will produce different properties, such as morphology^{12b} and mechanical properties^{12c} of the co-assembled system. However, in emissive coassembled systems, the effect of the stoichiometric ratio of the achiral fluorophores on the supramolecular chirality has rarely been discussed.

In co-assembly systems, achiral fluorophores will participate in the formation of chiral supramolecular structure and emit CPL through non-covalent interactions, such as hydrogen bonding and π – π stacking.⁹ Such an interaction, which could be influenced by the interaction positions of the achiral fluorophores, provides great possibilities for regulating the handedness of CPL.¹⁰ It was reported that adjusting the stoichiometry could produce opposite supramolecular chirality.¹¹ However, chirality inversions have been reported only in non-emissive systems, which shows no excited-state chiroptical activity.¹² Therefore, the control of CPL inversion by stoichiometry of achiral fluorophores in co-assembled systems is still a challenge.

Here, a co-assembled supramolecular CPL system composed of chiral amphiphilic D-glutamic acid gelator (DGG) and achiral pyridine-functionalized tetraphenylethylenes (PTPE) was developed (Fig. 1). Because of the strong carboxylic acidpyridine hydrogen bonds, DGG and PTPE can form emissive cogels at various molar ratios in chloroform.¹³ Furthermore, the stoichiometry-induced inversion of supramolecular chirality was observed through chiroptical spectra. At molar ratio of PTPE/DGG=1:100 or smaller, left-handed CPL and positive cotton effect can be observed from the CPL spectrum and the dichroism (CD) spectrum, circular respectively. At



Fig. 1 Molecular structures of PTPE and gelator DGG. At molar ratio of PTPE/DGG =1:100, bunchy-like nanofibers with significant left-handed CPL signals are obtained. At PTPE/DGG=1:16, the handedness of CPL is inverted to mirrored right-handed pattern.

^{a.} State Key Laboratory of Chemical Resource Engineering, Beijing Laboratory of Biomedical Materials, Beijing University of Chemical Technology, Beijing 100029, P. R. China, E-mail: <u>yinmz@mail.buct.edu.cn</u>.

^{b.} CAS Center for Excellence in Nanoscience, CAS Key Laboratory of Nanosystem and Hierarchical Fabrication, Division of Nanophotonics, National Center for Nanoscience and Technology (NCNST), No. 11 ZhongGuanCun BeiYiTiao, Beijing 100190, P. R. China. E-mail: liumh@iccas.ac.cn.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

COMMUNICATION

Published on 22 January 2019. Downloaded by University of Winnipeg on 1/24/2019 2:33:59 PM

PTPE/DGG=1:16, negative cotton effect and right-handed CPL signal can be obtained. The opposite inversion can be observed in the enantiomer cogel systems. Nonetheless, if too much PTPE was added, for instance, at PTPE/DGG=1:8, the intensity of CD signal and CPL signal would decrease sharply. This work aims to provide a better understanding of the influence of achiral molecules on supramolecular chirality and enrich the methodology for regulating the handedness of CPL.^{1a, 14}

DGG was synthesized according to previous reports.¹³ PTPE was synthesized through the Suzuki couple reaction (Scheme S1).¹⁵ The gelation process was performed in chloroform by a heating-cooling method. DGG can form an opaque white organogel in chloroform. Scanning electron microscopy (SEM) reveals that DGG self-assembles into belt-like nanofibers with diameters of about 100 nm (Fig. S13a). The formation of nanofibers is because the abundant carboxyl acid groups and amide groups form a stable and complex hydrogen bond network.^{13a}

PTPE can dissolve in various polar solvents and cannot by itself form a gel. But PTPE can co-assemble with DGG and form cogels. Due to its aggregate-induced emission (AIE) nature, PTPE shows a weak fluorescence with a quantum yield (QY) of 2.55% in chloroform. However, an intense yellow-green emission with a sharply increased QY of 98.83% can be observed from cogels (Fig. 2a). The enhanced emission can be confirmed by the longer fluorescence lifetime of PTPE (see Fig. 2b and Table S1). In chloroform solution, the lifetime of PTPE is 0.40 ns. After co-assembly with DGG, the lifetime of PTPE was extended to 4.07 ns, probably because the rapid intramolecular rotational deactivation pathways were blocked by the tight packing of DGG in aggregates.¹⁶

The ground and the excited supramolecular chirality can be confirmed by the CD and the CPL spectrum, respectively. PTPE is a typical achiral AIE fluorophore. Furthermore, due to lacking of chromophore in DGG gel, no chiroptical activity was detected (Fig. S9).13a However, in the cogel systems, CD and CPL were observed in the absorption and fluorescence region of PTPE (Fig. 2c, 2d, and Fig. S6). A positive cotton effect and a lefthanded CPL signal with yellow-green emission was obtained from the PTPE/DGG cogel with PTPE/DGG=1:100. The magnitude of CPL can be evaluated by the luminescence dissymmetry factor (g_{lum}), which is defined as $g_{lum} = 2(I_L - I_R)/(I_L$ + I_R), where I_L and I_R are the intensity of the left-handed CPL signal and the intensity of the right-handed CPL signal, respectively.^{1a, 9c, 17} Here, the calculated value of g_{lum} of the CPL signals is about 0.011 (Fig. 2e and Fig. S7), which is comparable with those of pure organic supramolecular systems.¹⁸

Furthermore, we varied the content of PTPE to examine the influence of stoichiometric ratio on the induced CPL. And at each ratio, stable cogels can form. The cogels with high PTPE contents have a QY and fluorescence lifetime about the same as those of the cogel with PTPE/DGG=1:100, which are 91.19% and 3.65 nm, respectively (Fig. 2b). The chiroptical activity measured from the CPL spectrum shows an interesting inversion of CPL handedness (Fig. 2c). Fig. 2e shows the CPL spectra of the cogels with various molar ratios from 1:100 to 1:8. At PTPE/DGG=1:32 or higher, left-handed CPL signals with

Journal Name

positive glum were detected, and the molar ratio of PTPE/DGG has almost no influence on the gium value? A 中印尼/如GG=印泊; the left-handed CPL was inverted to a right-handed signal with a g_{lum} value of about -0.015 (Fig. 2c and 2e). In previous coassembled CPL systems, glum decreased with the increase of achiral fluorophore and the handedness of CPL cannot be inverted.^{7a, b, 19} The stoichiometry-controlled inversion of CPL is quite different from the previous co-assembled CPL systems. Furthermore, the chirality inversion can be observed in the CD spectrum. As shown in Fig. 2d, a positive cotton effect at 374 nm can be observed from the cogel with PTPE/DGG=1:100. However, the positive signal will turn negative with increasing content of PTPE (Fig. 2d and 2f), and two new characteristic peaks appear at 287 nm and 335 nm, implying a different content of PTPE would lead to different molecular packing mode of PTPE. Further increases of PTPE/DGG to 1:8 or higher will weaken or even eliminate the chiroptical activity in both the CD and the CPL spectrum, indicating that the optimum molar for inverting the supramolecular ratio chirality is PTPE/DGG=1:16 (Fig. 2e). Further, we measured the CPL spectra between PTPE/DGG=1:8 and 1:40 finely, in which the gels were always formed. As shown in Fig. S8a and c, the CPL gradually inverted and the g_{lum} value showed the corresponding changes from PTPE/DGG=1:40 to 1:16. Between PTPE/DGG=1:28 and 1:20, the critical conversion process was captured (Fig. S8b). In addition, the inversion of the CD and CPL signals follows the molecular chirality of the gelator. We measured the chiroptical activities of the L-enantiomer (LGG). Mirror patterns in the CPL



Fig. 2 (a) Fluorescence spectra of PTPE in cogel (black line) and solution (red line) in chloroform; (b) Fluorescence decay of PTPE in solution (black line) and in PTPE/DGG cogels (red line for PTPE/DGG=1:100 and blue line for PTPE/DGG=1:16). (c) CPL spectrum and (d) CD spectrum of PTPE/DGG cogel at molar ratios of 1:100 and 1:16. (e) Plot of g_{lum} of CPL signal versus PTPE/DGG ratio. (f) Plot of g_{CD} versus PTPE/DGG ratio. (The concentration of DGG was fixed at 20 mg/mL.)

COMMUNICATION

Journal Name

and CD spectra were obtained for the *L*- and *D*-enantiomers. Meanwhile, the opposite inversion of supramolecular chirality can be observed from the cogels of PTPE/LGG (Fig. S6). This unusual chirality inversion motivates us to figure out the mechanism and effect of stoichiometric ratio.

To clarify how the stoichiometric ratio affect the induced CPL, the morphologies of the cogels with various amounts of PTPE was first investigated. Fluorescence microscopy observations show that PTPE is uniformly distributed inside the fibrous structure (Fig. 3c, d). The SEM images for the cogels with low contents of PTPE show bunchy belt-like nanofibers (see Fig. 2a and Fig. S13a). However, in the cogels with high contents of PTPE (PTPE/DGG=1:16), interwoven nanofibers can be observed, indicating that the addition of PTPE affects the formation of supramolecular structure. The SEM image of the cogel with PTPE/DGG=1:8 does not show any fibrous morphology (Fig. S13e). These results agree well with the observations from the CPL and CD spectra.



Fig. 3 SEM images of PTPE/DGG cogels at molar ratio of (a) 1:100 and (b) 1:16 (scale bar: 1 µm). Optical microscopy image (left side) and fluorescence microscopy image (right side) of cogels: (c) PTPE/DGG=1:100 and (d) PTPE/DGG=1:16.

The Fourier transform infrared (FTIR) spectra of the cogels can provide detailed information about the interaction between DGG and PTPE. For DGG gel, the $v_{C=0}$ bands at 1731, 1697, and 1686 cm⁻¹ indicate that carboxyl acid groups are involved in various hydrogen bonds (Fig. S11b).^{11b, 13a} The FTTR spectrum of the cogel with PTPE/DGG=1:100 is similar to that of the DGG gel. As PTPE/DGG increases to 1:16, the intensity of peak at 1697 cm⁻¹ decreases, and the peak at 1686 cm⁻¹ shifts to 1675 cm⁻¹, revealing that some of the acid-acid hydrogen bonds are replaced by acid-pyridine hydrogen bonds. In addition, the peaks at 2918 and 2850 cm⁻¹, corresponding to the stretching vibrations of asymmetric and symmetric CH₂, respectively, were unchanged, indicating that the highly ordered packing mode of alkyl chains are retained in a zigzag conformation (Fig. S11a).

X-ray diffraction (XRD) was used to determine the molecular packing mode of PTPE/DGG systems. According to Bragg's equation, the *d*-spacing was estimated. From the XRD pattern of DGG xerogel, peaks are observed at 2.59°, 5.09°, and 10.04°, corresponding to the *d*-spacing of 3.38, 1.72, and 0.88 nm, respectively (Fig. S12a). The *d*-spacing ratio is about 1:1/2:1/4, indicating the lamellar structure of DGG gel.²⁰ The XRD pattern

of the cogel with PTPE/DGG=1:100 is nearly the same as that of DGG, indicating that the basic packing mode 3 of 90 GC 9 Was preserved. As PTPE/DGG=1:16, although the XRD pattern is similar to that of DGG, an additional weak Bragg peak is observed at 2.10°. The calculated *d*-spacing of 4.2 nm, which corresponds to the sum of the lengths of DGG and PTPE, indicating the formation of complexes based on the hydrogen bonds between DGG and PTPE. Moreover, the slight increase in Bragg angles corresponds to the slight decreased d-spacing of the bilayers. We speculated that the former bilayer structure of DGG was squeezed by the addition of too much PTPE and a slanted molecular packing happened during the formation of new bilayer structure. As shown in Fig. S12b, the disappearance of the peak at 23.68° means that the tight molecular packing between the bilayers is expanded,^{11b} consistent with the FTIR results.

Based on all the above results, possible packing models of the cogels and a mechanism of the inversion of supramolecular chirality were proposed, as illustrated in Fig. 4. The three hydrogen-bond sites, two carboxylic acid groups, and one amide group in DGG can form a complicated hydrogen bond network to stabilize the supramolecular structure. The amide group could form intermolecular hydrogen bond to stabilize the packing of the amphiphile, while the two carboxylic acid groups can form H-bond themselves or with pyridine groups.

On account of the priority of acid-pyridine hydrogen bonds over acid-acid and acid-amide hydrogen bonds, a superstructure of PTPE-4DGG is formed by the introduction of PTPE (Fig. 4a).²¹ However, there still remain four carboxylic acid groups in this superstructure because of the dicarboxylic structure of DGG, resulting in an efficient co-assembly of the supramolecular building block with DGG.



Fig. 4 (a) Formation of PTPE-4DGG and (b) schematic illustration of supramolecular chirality inversion based on PTPE content: At PTPE/DGG=1:100, the H-bond network and lamellar structure are retained, and PTPE is inserted between the bilayers. At PTPE/DGG=1:16, most acid-acid H-bonds were replaced by acid-pyridyl H-bonds, and a slanted bilayer structure was formed.

Published on 22 January 2019. Downloaded by University of Winnipeg on 1/24/2019 2:33:59 PM

emComm Accepted Manusc

Journal Name

COMMUNICATION

At PTPE/DGG=1:100 or lower (Fig. 4b), the small amount of PTPE-4DGG complex is insufficient to form aggregate that their supramolecular chirality followed the chiral supramolecular structure of DGG. This was confirmed from the XRD that almost the same XRD was obtained. In this case, PTPE is just like a fluorescent label²² to report the chirality of the DGG selfassembly. However, at PTPE/DGG=1:16, PTPE/DGG complex plays a dominant role in the formation of supramolecular cogels. These complexes formed chiral aggregates, while such aggregation can sometime inverse the supramolecular chirality of the system. This result is in analogy to the previous report on chirality inversion in mixture of analogue achiral and chiral OPVs due to molecular exciton interactions.²³ Here, we used chiral gelator and achiral chromophore, which are not analogue, and also realized the inversion of the supramolecular chirality. In addition, we showed further the CPL inversion, which has not been reported previously.

In conclusion, we have demonstrated a supramolecular CPL system obtained by the co-gelation of a chiral gelator and an achiral fluorophore. The system shows significant CPL performance and unusual stoichiometry-controlled inversion of supramolecular chirality and CPL handedness. Mirror CPL and CD signals can be observed by increasing the content of the achiral fluorophore because of a delicate balance between the different types of hydrogen bonding interactions and different molecular packing mode. This work is believed to provide new insights for regulating the handedness of CPL.

This work was financially supported by the National Natural Science Foundation of China (grant numbers 21774007, 21574009), the Fundamental Research Funds for the Central Universities (PT1811) and Beihuazhongri United Fund (PYBZ1822).

Conflicts of interest

There are no conflicts to declare.

Notes and references

- (a) J. Roose, B. Z. Tang and K. S. Wong, *small*, 2016, **12**, 6495;
 (b) M. Liu, L. Zhang and T. Wang, *Chem. Rev.*, 2015, **115**, 7304.
- (a) J. Han, S. Guo, H. Lu, S. Liu, Q. Zhao and W. Huang, Adv. Optical Mater., 2018, 6, 1800538; (b) M. Li, S. H. Li, D. Zhang, M. Cai, L. Duan, M. K. Fung, and C. F. Chen, Angew. Chem. Int. Ed., 2018, 57, 2889; (c) F. Song, Z. Xu, Q. Zhang, Z. Zhao, H. Zhang, W. Zhao, Z. Qiu, C. Qi, H. Zhang, H. H. Y. Sung, I.D. Williams, J. W. Y. Lam, Z. Zhao, A. Qin, D. Ma and B. Z. Tang, Adv. Funct. Mater., 2018, 28, 1800051.
- 3 (a) Y. Yang, R. C. da Costa, D. M. Smilgies, A. J. Campbell and M. J. Fuchter, *Adv. Mater.*, 2013, **25**, 2624; (b) Y. H. Geng, A. Trajkovska, S. W. Culligan, J. J. Ou, H. M. P. Chen, D. Katsis and S. H. Chen, *J. Am. Chem. Soc.*, 2003, **125**, 14032; (c) M. Grell, M. Oda, K. S. Whitehead, A. Asimakis, D. Neher and D. D. C. Bradley, *Adv. Mater.*, 2001, **13**, 577.
- 4 (a) C. Wagenknecht, C. M. Li, A. Reingruber, X. H. Bao, A. Goebel, Y. A. Chen, Q. A. Zhang, K. Chen and J. W. Pan, *Nat. Photonics*, 2010, 4, 549; (b) J. Kumar, T. Nakashima, H.

Tsumatori, M. Mori, M. Naito and T. Kawai, *Chem. Eur. J.* 2013, **19**, 14090; (c) J. F. Sherson, H. Krauter, *B. K. Clese States and States and*

- 5 (a) C. Hao, L. Xu, W. Ma, X. Wu, L. Wang, H. Kuang and C. Xu, *Adv. Funct. Mater.*, 2015, **25**, 5816; (b) I. Sato, R. Sugie, Y. Matsueda, Y. Furumura, K. Soai, *Angew. Chem. Int. Ed.*, 2004, **43**, 449.
- (a) M. Deng, L. Zhang, Y. Jiang, M. Liu, Angew. Chem. Int. Ed., 2016, 55, 15062;
 (b) Z. Shen, T. Wang, L. Shi, Z. Tang and M. Liu, Chem. Sci., 2015, 6, 4267;
 (c) Y. Sheng, D. Shen, W. Zhang, H. Zhang, C. Zhu, and Y. Cheng, Chem. Eur. J., 2015, 21, 13196.
- 7 (a) D. Yang, P. Duan and M. Liu, Angew. Chem. Int. Ed., 2018, 57, 9357; (b) D. Han, J. Han, S. Huo, Z. Qu, T. Jiao, M. Liu and P. Duan, Chem. Commun., 2018, 54, 5630; (c) S. K. Samanta and S. Bhattacharya, Chem. Commun., 2013, 49, 1425.
- 8 (a) J. Wu, W. Liang, T. Niu, W. Wu, D. Zhou, C. Fan, J. Ji, G. Gao, J. Men, Y. Yang and C. Yang, *Chem. Commun.*, 2018, **54**, 9206;
 (b) T. Goto, Y. Okazaki, M. Ueki, Y. Kuwahara, M. Takafuji, R. Oda and H. Ihara, *Angew. Chem. Int. Ed.*, 2017, **56**, 2989; (c) Y. Wang, X. Li, F. Li, W. Y. Sun, C. Zhu and Y. Cheng, *Chem. Commun.*, 2017, **53**, 7505.
- 9 (a) P. Duan, H. Cao, L. Zhang and M. Liu, *Soft Matter*, 2014, **10**, 5428; (b) D. Yang, P. Duan, L. Zhang and M. Liu, *Nat. Commun.*, 2017, **8**, 15727; (c) C. Ji, Q. Gao, X. Dong, W. Yin, Z. Gu, Z. Gan, Y. Zhao and M. Yin, *Angew. Chem. Int. Edit.*, 2018, **57**, 11348.
- (a) G. Liu, J. Sheng, H. Wu, C. Yang, G.Yang, Y. Li, R. Ganguly, L. Zhu and Y. Zhao, *J. Am. Chem. Soc.*, 2018, **140**, 6467; (b) P. Xing and Y. Zhao, *Acc. Chem. Res.*, 2018, **51**, 2324.
- 11 F. Wang and C. L. Feng, Chem. Eur. J., 2018, 24, 1509.
- 12 (a) L. E. Buerklea and S. J. Rowan, *Chem. Soc. Rev.*, 2012, 41, 6089; (b) X. Zhu, P. Duan, L. Zhang and M. Liu, *Chem. Eur. J.*, 2011, 17, 3429; (c) Y. Liu, T. Wang and M. Liu, *Chem. Eur. J.*, 2012, 18, 14650.
- 13 (a) P. Gao, C. Zhan, L. Liu, Y Zhou and M. Liu, *Chem. Commun.*, 2004, 1174; (b) J. Bachl, J. Mayr, F. J. Sayago, C. Cativiela and D. Diaz Diaz, *Chem. Commun.*, 2015, **51**, 5294.
- 14 S. Zhang, Nat. Biotechnol., 2003, 21, 1171.
- (a) H. T. Feng, J. B. Xiong, J. Luo, W. F. Feng, D. Yang and Y. S. Zheng, *Chem. Eur. J.*, 2017, **23**, 644; (b) M. Wang, Y. R. Zheng, K. Ghosh and P. J. Stang, *J. Am. Chem. Soc.*, 2010, **132**, 6282; (c) P. P. Kapadia, J. C. Widen, M. A. Magnus, D. C. Swenson and F. C. Pigge, *Tetrahedron Lett.*, 2011, **52**, 2519.
- 16 (a) Y. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Soc. Rev.*, 2011, 40, 5361; (b) P. Wei, J. X. Zhang, Z. Zhao, Y. Chen, X. He, Ming Chen, J. Gong, H. H. Y. Sung, Ian D. Williams, J. W. Y. Lam and B. Z. Tang, *J. Am. Chem. Soc.*, 2018, 140, 1966.
- 17 J. P. Riehl and F. S. Richardson, Chem. Rev., 1986, 86, 1.
- 18 (a) Y. Sheng, J. Ma, S. Liu, Y. Wang, C. Zhu and Y. Cheng, *Chem. Eur. J.*, 2016, **22**, 9519; (b) J. Han, J. You, X. Li, P. Duan and M. Liu, *Adv. Mater.*, 2017, **29**, 1606503; (c) M. Li, C. Zhang, L. Fang, L. Shi, Z. Tang, H. Y. Lu and C. F. Chen, *ACS Appl. Mater. Interfaces*, 2018, **10**, 8225.
- (a) D. Yang, Y. Zhao, K. Lv, X. Wang, W. Zhang, L. Zhang and M. Liu, *Soft Matter*, 2016, **12**, 1170; (b) R. Sethy, J. Kumar, R. Metivier, M. Louis, K. Nakatani, N. Mecheri, A. Subhakumari, K. G. Thomas, T. Kawai and T. Nakashima, *Angew. Chem. Int. Ed.*, 2017, **56**, 15053.
- 20 I. W. Hamley and V. Castelletto, *Prog. Polym. Sci.*, 2004, **29**, 909.
- 21 G. Liu, J. Liu, C. Feng and Y. Zhao, Chem. Sci., 2017, 8, 1769.
- 22 (a) M. Chen and M. Yin, Prog. Polym. Sci., 2014, **39**, 365; (b) K. Liu, Z. Xu and M. Yin, Prog. Polym. Sci., 2015, **46**, 25; (c) M. Sun, K. Müllen and M. Yin, Chem. Soc. Rev., 2016, **45**, 1513.
- 23 A. Ajayaghosh, R. Varghese, S. J. George and C. Vijayakumar, Angew. Chem. Int. Ed., 2006, **45**, 1141.