

ChemComm

Accepted Manuscript



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 [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) 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.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

COMMUNICATION

Formation of fluorescent supramolecular polymeric assemblies via orthogonal pillar[5]arene-based molecular recognition and metal ion coordination

Bingbing Shi, Kecheng Jie, Yujuan Zhou, Danyu Xia and Yong Yao*

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

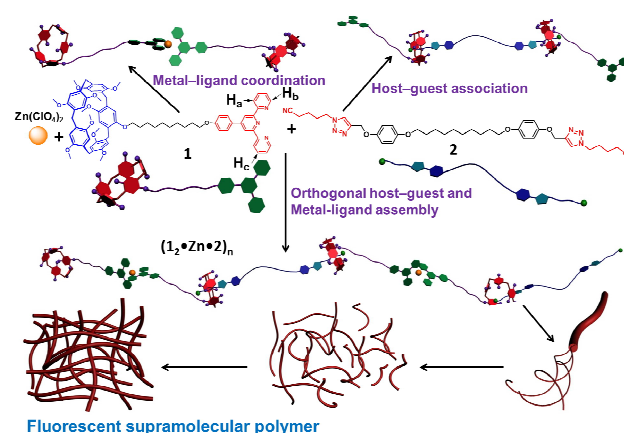
A fluorescent supramolecular polymer was efficiently constructed by pillar[5]arene-based host-guest molecular recognition and zinc ion coordination.

Fluorescent self-assembled materials are an important class of smart materials that are widely used in optoelectronics, fluorescence sensors, memory chips and security inks.¹ These materials have attracted considerable interest over the past ten years. Among various fluorescent self-assembled materials, fluorescent supramolecular polymers, which can be defined as polymeric arrays of low molecular weight monomeric units that are brought together by noncovalent interactions, have found a wide range of applications in materials science.² Due to the combined dynamic and reversible nature of noncovalent interactions and fluorescent property, fluorescent supramolecular polymers have been expected to hold great promise for applications in developing luminescence soft materials and their resulting optoelectronic devices.

Pillararenes, which were firstly found in 2008,³ are a new class of supramolecular hosts after crown ethers,⁴ cyclodextrins,⁵ calixarenes,⁶ and cucurbiturils.⁷ Their syntheses, functionalizations, conformations, host-guest properties and applications in different areas have been widely investigated.⁸ Up to now, thanks to the arduous efforts made by supramolecular chemists, several good examples of supramolecular polymers constructed by pillararene-based molecular recognitions have been reported.⁹ However, recent studies about pillararene-based supramolecular polymers mainly focus on their external stimuli, self-healing and sol-gel transition properties. Comparatively, little effort has been made to investigate their fluorescent properties.¹⁰ Moreover, pillararene-based metal ion responsive fluorescent supramolecular polymers have not been reported. This may greatly impede the application of fluorescent supramolecular polymers. Therefore, it is quite necessary to design and synthesize novel metal ion responsive fluorescent supramolecular polymers constructed by pillararene-based molecular recognitions.

In the previous report, Li's group and Wang's group have demonstrated that the neutral guest bearing a cyano site and a triazole site at its ends (TAPN) is an effective guest for pillar[5]arene, with an association constant (K_a) of 10^4 M^{-1} in the case of an alkylated derivative.¹¹ On the other side, terpyridyl groups can form stable coordination compounds with zinc ions

and have interesting fluorescent properties with significant potential for applications in the fields of self-assembled molecular devices.¹² In view of this and as a part of our research effort devoted to supramolecular polymers, we report a novel zinc ion responsive fluorescent pillar[5]arene-based supramolecular polymer constructed by a neutral guest possessing two triazole binding sites for pillar[5]arene cavities and the coordination between zinc ions and terpyridyl groups. As such, the component $1_2 \cdot \text{Zn}$ (Scheme 1) may be thought of as an unusual homoditopic AA-type monomer. A ditopic connector (**2**, Scheme 1) containing two triazole binding sites was used as a BB-type monomer to interact with $1_2 \cdot \text{Zn}$, forming a linear supramolecular ternary polymer $(1_2 \cdot \text{Zn} \cdot 2)_n$, as suggested in Scheme 1. The phase transitions of the fluorescent supramolecular polymer could be realized by subsequent alteration of heating and cooling. Moreover, the fluorescent supramolecular polymer exhibited base-stimulus responsiveness and concentration controllable fluorescent emissions.



Scheme 1 Cartoon representation of the formation of the fluorescent supramolecular polymer based on orthogonal host-guest association and metal ion coordination.

The linear supramolecular polymer was first envisioned to be driven by host-guest interactions and metal coordination in $\text{CH}_3\text{CN}/\text{CHCl}_3$ ($v/v = 1/1$). Then these linear supramolecular

polymers self-assembled into bundles, which subsequently self-organized to form a cross-linked network. Thus three-dimensional networks were constructed *via* the entanglement of the supramolecular bundles (Scheme 1).

The concentration-dependent ^1H NMR spectra of $\mathbf{1}_2\cdot\text{Zn}\cdot\mathbf{2}$ (500 MHz, $\text{CD}_3\text{CN}/\text{CDCl}_3 = 1/1$, 298 K) provided important insights into their self-assembly behaviors in solution (Fig. 1). As the concentration increased, the signals of protons H_a , H_b and H_c on the terpyridyl groups shifted down field. Furthermore, all the signals became broad at high concentration, indicating that the monomers self-assembled into high-molecular-weight aggregates (Fig. S12 and S13, ESI †).

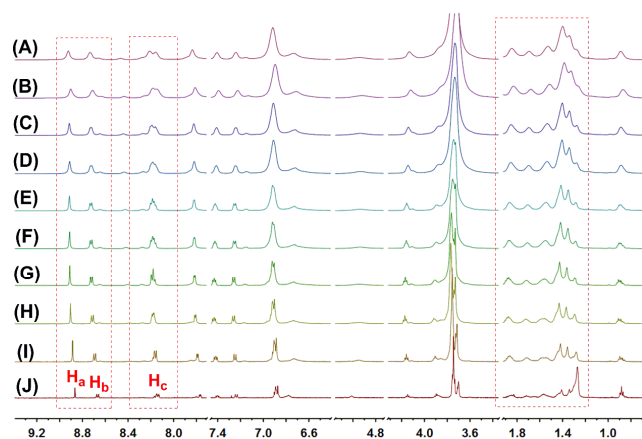


Fig. 1 ^1H NMR spectra (500 MHz, 298 K) of $\mathbf{1}_2\cdot\text{Zn}\cdot\mathbf{2}$ in $\text{CD}_3\text{CN}/\text{CDCl}_3$ ($v/v = 1/1$) at various concentrations: (A) 100 mM; (B) 80 mM; (C) 61.5 mM; (D) 44 mM; (E) 30 mM; (F) 22 mM; (G) 11 mM; (H) 5.5 mM; (I) 2.8 mM; (J) 0.5 mM.

Two-dimensional diffusion-ordered ^1H NMR spectroscopy (DOSY) experiments were performed to investigate the self-aggregation of $\mathbf{1}_2\cdot\text{Zn}\cdot\mathbf{2}$ during linear supramolecular polymerization. We found that different aggregates exchanged on the DOSY timescale. As the

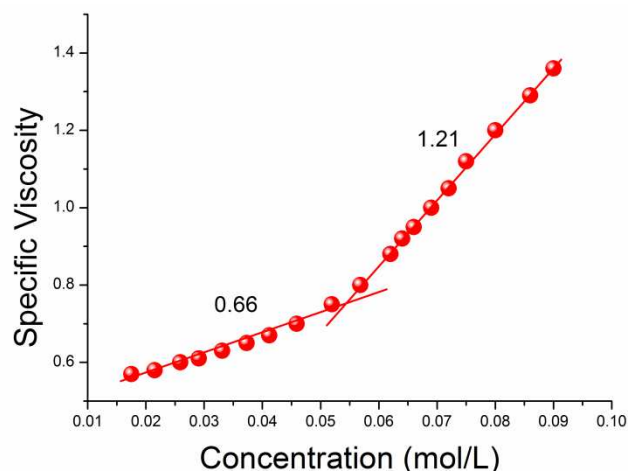


Fig. 2 Specific viscosity (298 K) of a 2:1:1 molar mixture of $\mathbf{1}$, Zn^{2+} and $\mathbf{2}$ in $\text{CH}_3\text{CN}/\text{CHCl}_3$ ($v/v = 1/1$) solutions versus the concentration of $\mathbf{1}_2\cdot\text{Zn}\cdot\mathbf{2}$.

concentration of $\mathbf{1}_2\cdot\text{Zn}\cdot\mathbf{2}$ increased from 2.5 to 100 mM, the measured weight average diffusion coefficient (D) of $\mathbf{1}_2\cdot\text{Zn}\cdot\mathbf{2}$ in $\text{CD}_3\text{CN}/\text{CDCl}_3$ ($v/v = 1/1$) solution decreased almost 8 folds,

from 6.73×10^{-10} to $8.18 \times 10^{-11} \text{ m}^2\text{s}^{-1}$, suggesting the concentration dependence of the linear supramolecular polymerization of the monomers (Fig. S14, ESI †). Based on previous reports, it is well-known that a high degree of polymerization for the repeating unit is necessary to observe a sharp decrease in the diffusion coefficient. Thus, the current measurements clearly indicate the formation of an extended high-molecular-weight polymeric structure.

Viscometry is a convenient method to test the propensity of monomers to self-assemble into large aggregates. Therefore, viscosity measurements were carried out in $\text{CH}_3\text{CN}/\text{CHCl}_3$ ($v/v = 1/1$) using a Cannon Ubbelohde semi-microdilution viscometer. As presented in Fig. 2, the linear supramolecular polymer assembled from the monomers exhibited a viscosity transition that is characterized by a change in slope in the double logarithmic plots of specific viscosity versus concentration. In the low concentration range, the slopes approximated unity, which is characteristic for cyclic oligomers with constant size. When the concentration exceeded the critical polymerization concentration (CPC; approximately 55.0 mM), a sharp rise in the viscosity was observed.

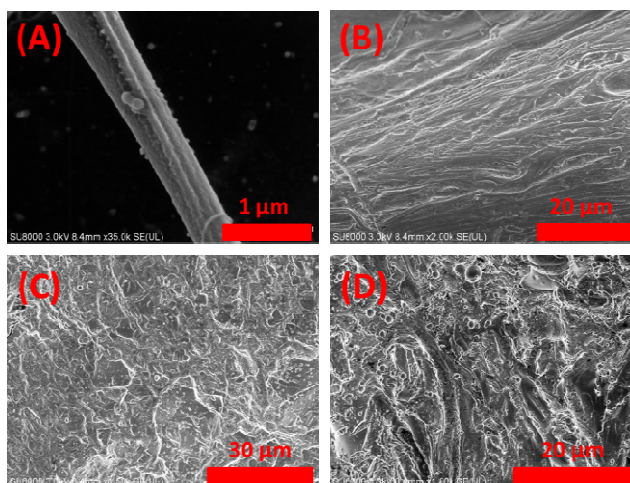


Fig. 3 (A) SEM images of a rod-like fiber drawn from a high concentration solution of $\mathbf{1}_2\cdot\text{Zn}\cdot\mathbf{2}$ in $\text{CH}_3\text{CN}/\text{CHCl}_3$ ($v/v = 1/1$); (B–D) SEM images of the three-dimensional network of the supramolecular polymers.

Furthermore, the morphology of the supramolecular polymers was investigated by scanning electron microscopy (SEM) studies. As shown in Fig. 3, a three-dimensional network was obtained from a highly concentrated solution. Moreover, a rod-like fiber with a regular diameter of 400 nm was drawn from a high concentration solution and observed by SEM (Fig. 3A). These images provide direct evidence for the formation of a supramolecular polymer with high molecular weight.

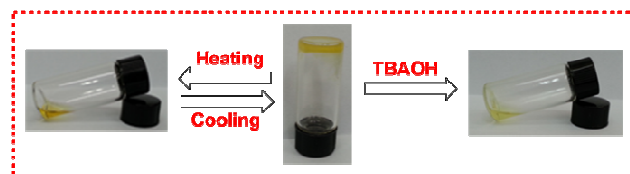


Fig. 4 The glue-sol transitions of the supramolecular polymer triggered by different stimuli.

The macroscopic properties of the high concentration supramolecular polymer were also investigated. Glue-like viscous liquids were prepared by dissolving the monomers in $\text{CH}_3\text{CN}/\text{CHCl}_3$ ($v/v = 1/1$) at 60°C followed by cooling to room temperature. Upon increasing the concentration of the monomers, the high concentration supramolecular polymers finally formed at phase-transition temperature of approximately $42^\circ\text{C} \sim 46^\circ\text{C}$ for $\mathbf{1}_2\cdot\mathbf{Zn}\cdot\mathbf{2}$ at the concentration of 200 mM. In addition, the high concentration supramolecular polymers showed reversible glue-sol phase transitions by heating and cooling. On the other side, the glue-like supramolecular polymers showed base responsive property. It is well-known that OH^- ions can bind strongly to Zn^{2+} ions. As shown in Fig. 4, after the addition of several drops of the $\text{CH}_3\text{CN}/\text{CHCl}_3$ ($v/v = 1/1$) solution of TBAOH, the coordination between terpyridyl groups and zinc ions was decomposed and inorganic zinc hydroxide was formed. In corresponding, the glue-like supramolecular polymers dissociated into a transparent solution within a short time.

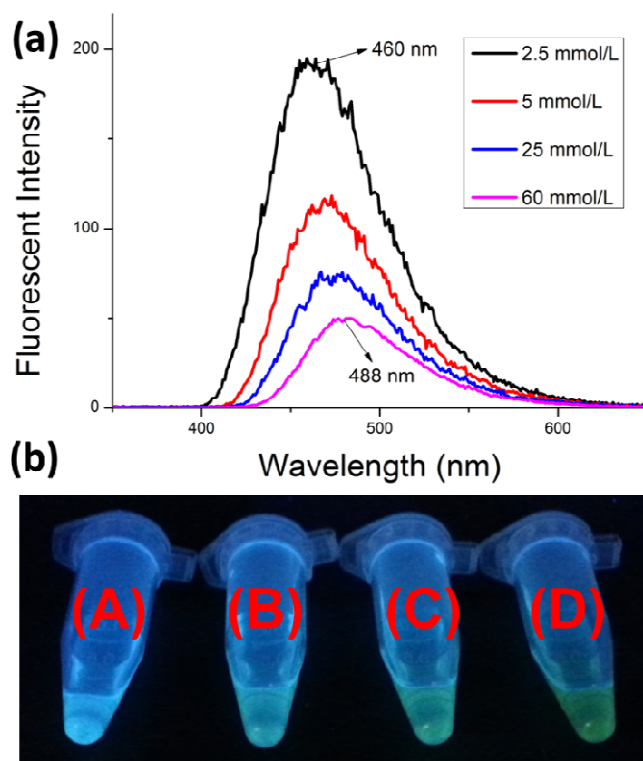


Fig. 5 (a) Fluorescence emission data for $\mathbf{1}_2\cdot\mathbf{Zn}\cdot\mathbf{2}$ at different concentrations. (b) Photos of $\mathbf{1}_2\cdot\mathbf{Zn}\cdot\mathbf{2}$ at different concentrations under irradiation at 365 nm by a UV lamp: (A) 2.5 mM; (B) 5 mM; (C) 25 mM; (D) 60 mM.

Next, the fluorescent properties of the supramolecular polymers were investigated. The absorption spectrum of $\mathbf{1}_2\cdot\mathbf{2}$ in $\text{CH}_3\text{CN}/\text{CHCl}_3$ ($v/v = 1/1$) solution exhibited one absorption band at 293 nm. When 0.5 equivalents of Zn^{2+} were added to the $\text{CH}_3\text{CN}/\text{CHCl}_3$ ($v/v = 1/1$) solution of $\mathbf{1}_2\cdot\mathbf{2}$, the band at 293 nm was red-shifted to 342 nm, and the solution of $\mathbf{1}_2\cdot\mathbf{Zn}\cdot\mathbf{2}$ showed a color change from colorless to yellow. (Fig S15, ESI[†]). In the fluorescence spectrum, the emission of $\mathbf{1}_2\cdot\mathbf{2}$ appeared at the maximum emission wavelength was 388 nm in $\text{CH}_3\text{CN}/\text{CHCl}_3$ ($v/v = 1/1$) solution when excited at 293 nm. When 0.5 equivalents of Zn^{2+} were added to the $\text{CH}_3\text{CN}/\text{CHCl}_3$ ($v/v = 1/1$)

solution of $\mathbf{1}_2\cdot\mathbf{2}$, the fluorescence emission band at 388 nm was red-shifted to 460 nm. The fluorescent color of the solution of $\mathbf{1}_2\cdot\mathbf{Zn}\cdot\mathbf{2}$ indicated a blue emission under UV illumination at 365 nm (Fig S16, ESI[†]). Moreover, after $\mathbf{1}_2\cdot\mathbf{2}$ was coordinated with Zn^{2+} ions, the supramolecular polymer ($\mathbf{1}_2\cdot\mathbf{Zn}\cdot\mathbf{2}$)_n showed concentration controllable fluorescence. At a concentration of 2.5 mM, one emission band was clearly recognized at 460 nm. Under UV illumination at 365 nm, this solution indicated a blue emission. When the concentration was increased from 2.5 mM to 60.0 mM, the fluorescence emission band at 460 nm was red-shifted to 488 nm, directly leading to a yellow emission (Fig. 5). In fluorescent polymers, an increase in repeating unit concentrations generally results in the red shift of the emission band.¹³ Therefore, the red shift from 460 nm to 488 nm was derived from the increasing degree of polymerization at the high concentration.

Finally, to investigate the practical application of the fluorescent supramolecular polymer, a thin film was prepared by immersing a glass sheet into a high concentration solution of $\mathbf{1}_2\cdot\mathbf{Zn}\cdot\mathbf{2}$ (100 mM) and then drying it in air. The thin film of the fluorescent supramolecular polymer was utilized to sense OH^- anions. As shown in Fig. 6, when OH^- anions were added on the thin film, the coordination between terpyridyl group and zinc ions was decomposed and inorganic zinc hydroxide was formed. Then, the obvious color change was observed under irradiation at 365 nm by a UV lamp. Therefore, the thin film could be a convenient test kit for detecting OH^- anions.

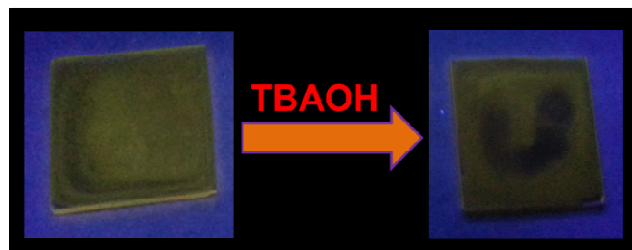


Fig. 6 Photos of the thin film utilized to sense OH^- anions under irradiation at 365 nm by a UV lamp.

In conclusion, we have constructed a fluorescent supramolecular polymer driven by pillararene-based molecular recognition and metal coordination. Various characterization methods, including ^1H NMR, DOESY, UV-Vis spectrum, fluorescence spectrum and viscosity measurements, were performed to investigate the polymerization process of the monomers. The phase transitions of the fluorescent supramolecular polymer can be realized by subsequent alteration of heating and cooling, and the fluorescent supramolecular polymer showed base-stimulus responsive property. Furthermore, the supramolecular polymer has concentration controllable fluorescent emissions. Moreover, a thin film of the fluorescent supramolecular polymer was prepared, which was confirmed to be a convenient test kit for detecting OH^- anions. In the end, this new type of pillar[5]arene-based fluorescent supramolecular polymer may be of highly importance for developing novel functional fluorescent materials and molecular devices in the future.

Acknowledgements

This work was supported by the Fundamental Research Funds for the Central Universities.

Notes and references

Department of Chemistry, Zhejiang University, Hangzhou, Zhejiang 310027 (China)

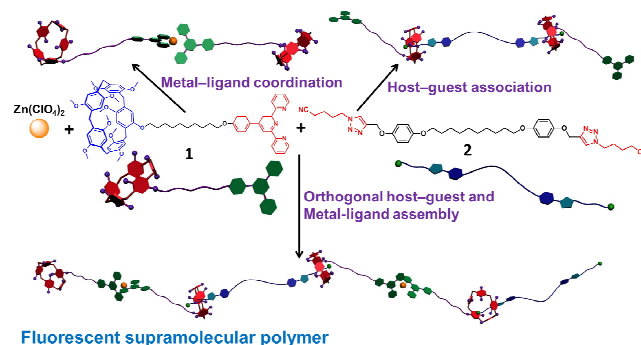
Fax: (+86) 571-8795-3189; Email address: yaoyong@zju.edu.cn

† Electronic Supplementary Information (ESI) available: Synthetic procedures, characterizations and other materials. See DOI: 10.1039/b000000x/

- 1 (a) A. Ajayaghosh, C. Vijayakumar, V. Praveen, S. Babu and R. Varghese, *J. Am. Chem. Soc.*, 2006, **128**, 7174; (b) A. Ajayaghosh, R. Varghese, V. Praveen and S. Mahesh, *Angew. Chem., Int. Ed.*, 2006, **45**, 3261; (c) V. Praveen, S. George, R. Varghese, C. Vijayakumar and A. Ajayaghosh, *J. Am. Chem. Soc.*, 2006, **128**, 7542; (d) S. Babu, S. Prasanthkumar and A. Ajayaghosh, *Angew. Chem., Int. Ed.*, 2012, **51**, 1766; (e) Y. Li, T. Liu, H. Liu, M. Tian and Y. Li, *Acc. Chem. Res.*, 2014, **47**, 1186; (f) R. T. K. Kwok, C. W. T. Leung, J. W. Y. Lamab and B. Z. Tang, *Chem. Soc. Rev.*, 2015, DOI: 10.1039/C4CS00325J.
- 2 (a) F. Wang, C. Han, C. He, Q. Zhou, J. Zhang, C. Wang, N. Li and F. Huang, *J. Am. Chem. Soc.*, 2008, **130**, 11254; (b) X. Ji, Y. Yao, J. Li, X. Yan and F. Huang, *J. Am. Chem. Soc.* 2013, **135**, 74; (c) Y. Ding, P. Wang, Y. Tian, Y. Tian and F. Wang, *Chem. Commun.*, 2013, **49**, 5951; (d) Y.-M. Zhang, B.-B. Shi, H. Li, W.-J. Qu, G.-Y. Gao, Q. L. H. Yao and T.-B. Wei, *Polym. Chem.*, 2014, **5**, 4722; (e) N.-L. Strutt, H. Zhang, M.-A. Giesener, J. Leia and J.-F. Stoddart, *Chem. Commun.*, 2012, **48**, 1647; (f) X. Ma and H. Tian, *Acc. Chem. Res.*, 2014, **47**, 1971; (g) Z. Li, Y. Zhang, C. Zhang, L. Chen, C. Wang, H. Tan, Y. Yu, X. Li and H.-B. Yang, *J. Am. Chem. Soc.*, 2014, **136**, 8577; (h) B. Zhu, H. X. Chen, W. Lin, Y. Ye, J. Wu and S. J. Li, *J. Am. Chem. Soc.*, 2014, **136**, 15126.
- 3 T. Ogoshi, S. Kanai, S. Fujinami, T. Yamagishi and Y. Nakamoto, *J. Am. Chem. Soc.*, 2008, **130**, 5022.
- 4 (a) F. Huang, L. Zhou, J.-W. Jones and H.-W. Gibson, *Chem. Commun.*, 2004, **12**, 2670; (b) F. Huang, L. N. Zakharov, A. L. Rheingold, M. Ashraf-Khorassani and H.-W. Gibson, *J. Org. Chem.*, 2005, **70**, 809; (c) Y.-S. Su, J.-W. Liu, Y. Jiang and C.-F. Chen, *Chem. Eur. J.*, 2011, **17**, 2435; (d) S. Li, G. Weng, W. Lin, Z. Sun, M. Zhou, B. Zhu, Y. Yea and J. Wu, *Polym. Chem.*, 2014, **5**, 3994.
- 5 A. Harada, Y. Takashima and H. Yamaguchi, *Chem. Soc. Rev.*, 2009, **38**, 875.
- 6 (a) D.-S. Guo and Y. Liu, *Chem. Soc. Rev.*, 2012, **41**, 5907; (b) Y. Yao, Y. Sun, Y. Han and C. Yan, *Chin. J. Chem.*, 2010, **5**, 705.
- 7 (a) J. M. Zayed, N. Nouvel, U. Rauwald and O. A. Scherman, *Chem. Soc. Rev.*, 2010, **39**, 2806; (b) X. Tan, L. Yang, Y. Liu, Z. Huang, H. Yang, Z. Wang and X. Zhang, *Polym. Chem.*, 2013, **4**, 5378; (c) X. Tan, L. Yang, Z. Huang, Y. Yu, Z. Wang and X. Zhang, *Polym. Chem.*, 2015, DOI: 10.1039/c4py01440e.
- 8 (a) D.-R. Cao, Y.-H. Kou, J.-Q. Liang, Z.-Z. Chen, L.-Y. Wang and H. Meier, *Angew. Chem. Int. Ed.*, 2009, **48**, 9721; (b) Z. Zhang, B. Xia, C. Han, Y. Yu and F. Huang, *Org. Lett.*, 2010, **12**, 3285; (c) C. Han, F. Ma, Z. Zhang, B. Xia, Y. Yu and F. Huang, *Org. Lett.*, 2010, **12**, 4360; (d) X. Hu, L. Chen, W. Si, Y. Yu and J.-L. Hou, *Chem. Commun.*, 2011, **47**, 4694; (e) X. B. Hu, Z.-X. Chen, G.-F. Tang, J.-L. Hou and Z.-T. Li, *J. Am. Chem. Soc.*, 2012, **134**, 8384; (f) Y. Yao, M. Xue, Z. Zhang, M. Zhang, Y. Wang and F. Huang, *Chem. Sci.*, 2013, **4**, 3667; (g) M. Holler, N. Allenbach, J. Sonet and J.-F. Nierengarten, *Chem. Commun.*, 2012, **48**, 2576; (h) G. Yu, M. Xue, Z. Zhang, J. Li, C. Han and F. Huang, *J. Am. Chem. Soc.*, 2012, **134**, 13248; (i) C. Li, J. Ma, L. Zhao, Y. Zhang, Y. Yu, X. Shu, J. Li and X. Jia, *Chem. Commun.*, 2013, **49**, 1924; (j) X. Wang, H. Deng, J. Li, K. Zheng, X. Jia and C. Li, *Macromol. Rapid Commun.*, 2013, **34**, 1856; (k) J.-F. Xu, Y. -Z. Chen, L.-Z. Wu, C.-H. Tung and Q. Yang, *Org. Lett.*, 2013, **15**, 6148; (l) H. Li, D.-X. Chen, Y.-L. Su, Y.-B. Zheng, L.-L. Tan, P.-S. Weiss and Y.-W. Yang, *J. Am. Chem. Soc.*, 2013, **135**, 1570; (m) L. Chen, Z. Li, Z. Chen and J. -L. Hou, *Org. Biomol. Chem.*, 2013, **11**, 248; (n) R.-R. Kothur, J. Hall, B.-A. Patel, C.-L. Leong, M.-G. Boutelle and P.-J. Cragg, *Chem. Commun.*, 2014, **50**, 852; (o) L. Wu, Y. Fang, Y. Jia, Y. Yang, J. Liao, N. Liu, X. Yang, W. Feng, J. Ming and L. Yuan,

- Dalton Trans.*, 2014, **43**, 3835; (p) X. Shu, W. Chen, D. Hou, Q. Meng, R. Zheng and C. Li, *Chem. Commun.*, 2014, **50**, 4820; (q) Y. Wang, J. Xu, Y. Chen, L. Niu, L. Wu, C. Tung and Q. Yang, *Chem. Commun.*, 2014, **50**, 7001; (r) W. Hu, H. Yang, W. Hu, M. Ma, X. Zhao, X. Mi, Y. Liu, J. Li, B. Jiang and K. Wen, *Chem. Commun.*, 2014, **50**, 10460; (s) Y. Yao, X. Chi, Y. Zhou and F. Huang, *Chem. Sci.*, 2014, **5**, 2778; (t) Q. Z. Zhou, B. Zhang, D. M. Han, R. N. Chen, F. L. Qiu, J. S. Wu and H. J. Jiang, *Chem. Commun.*, 2015, DOI: 10.1039/C4CC09778E; (u) H. Chen, J. Fan, X. Hu, J. Ma, S. Wang, J. Li, Y. Yu, X. Jia and C. Li, *Chem. Sci.*, 2015, **6**, 197.
- 9 (a) Z. Zhang, Y. Luo, J. Chen, S. Dong, Y. Yu, Z. Ma and F. Huang, *Angew. Chem., Int. Ed.*, 2011, **50**, 1397; (b) Y. Guan, M. Ni, X.-Y. Hu, T. Xiao, S. Xiong, C. Lin and L. Wang, *Chem. Commun.*, 2012, **48**, 8529; (c) X.-Y. Hu, P. Zhang, X. Wu, W. Xia, T. Xiao, J. Jiang, C. Lin and L. Wang, *Polym. Chem.*, 2012, **3**, 3060; (d) K. Wang, C. Wang, Y. Wang, H. Li, C. Bao, J. Liu, S. Zhang and Y.-W. Yang, *Chem. Commun.*, 2013, **49**, 10528; (e) C. Li, *Chem. Commun.*, 2014, **50**, 12420; (f) S. Wang, Y. Wang, Z. Chen, Y. Lin, L. Weng, K. Han, J. Li, X. Jia and C. Li, *Chem. Commun.*, 2015, DOI: 10.1039/c4cc08820d; (g) Y. Yao, Y. Wang and F. Huang, *Chem. Sci.*, 2014, **5**, 4312.
- 10 (a) N. Song, D. Chen, Y. Qiu, X. Yang, B. Xu, W. Tian and Y.-W. Yang, *Chem. Commun.*, 2014, **50**, 8231; (b) N. Song, D. Chen, M. Xia, Xi. Qiu, K. Ma, B. Xu, W. Tian and Y.-W. Yang, *Chem. Commun.*, 2014, DOI: 10.1039/C4CC08205B.
- 11 (a) X. Shu, S. Chen, J. Li, Z. Chen, L. Weng, X. Jia and C. Li, *Chem. Commun.* 2012, **48**, 2967; (b) C. Li, K. Han, J. Li, Y. Zhang, W. Chen, Y. Yu and X. Jia, *Chem. Eur. J.*, 2013, **19**, 11892; (c) J. Wu, S. Sun, X. Feng, J. Shi, X. Hu and L. Wang, *Chem. Commun.*, 2014, **50**, 9122.
- 12 (a) M. Schmittel, V. Kalsani, P. Mal, J. W. Bats, *Inorg. Chem.*, 2006, **45**, 6370; (b) S.-C. Yuan, H.-B. Chen, J. Pei, *Org. Lett.*, 2006, **8**, 5701; (c) A. Winter, C. Friebe, M. Chipper, U. S. Schubert, M. Presselt, B. Dietzek, M. Schmitt and J. Popp, *ChemPhysChem.*, 2009, **10**, 787; (d) Y.-K. Tian and F. Wang, *Macromol. Rapid Commun.*, 2014, **35**, 337.
- 13 (a) T. L. Andrew and T. M. Swager, *J. Polym. Sci., Part B: Polym. Phys.*, 2011, **49**, 476; (b) L. P. He, J. J. Liang, Y. Cong, X. Chen and W. F. Bu, *Chem. Commun.*, 2014, **50**, 10841.

Colour Graphic:



Text:

- 115 A fluorescent supramolecular polymer was efficiently constructed by pillar[5]arene-based host-guest molecular recognition and zinc ion coordination.