Polymer
Chemistry

RSCPublishing

PAPER

View Article Online
View Journal | View Issue

Cite this: *Polym. Chem.*, 2013, **4**, 3998

Pillar[5]arene–neutral guest recognition based supramolecular alternating copolymer containing [c2] daisy chain and bis-pillar[5]arene units†

Xiaoyang Wang,[a] Kang Han,[a] Jian Li,[a] Xueshun Jia*[a] and Chunju Li*[ab]

Received 10th April 2013
Accepted 29th April 2013

DOI: 10.1039/c3py00462g

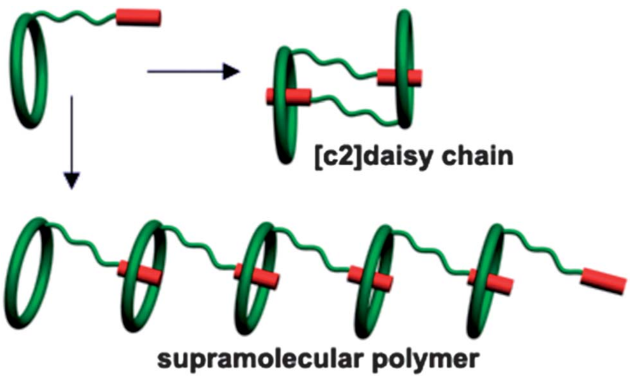
www.rsc.org/polymers

A novel supramolecular alternating copolymer with [c2]daisy-chain dimer and macrocycle host dimer as repeating units has been fabricated. A key factor for this new assembly strategy is based on a [c2]daisy-chain pseudorotaxane bearing additional unbound recognition sites at both ends, which was successfully achieved from a careful designed heterotritopic (AB$_2$-type) copillar[5]arene. By utilizing the intermolecular host–guest interactions between the double-threaded dimer and a pillar[5]arene dimer, a linear supramolecular polymer was prepared. These results provided not only a convenient approach for the construction of [c2]daisy chain based supramolecular polymers, but also a novel method for building supramolecular alternating copolymers.

Introduction

Supramolecular polymers, fabricated by connecting repeating units into a polymeric architecture *via* noncovalent interactions, have attracted extensive interest because of their novel properties such as self-healing, recycling, and degradability owing to the reversible and tunable nature of noncovalent interactions.[1] Additionally, such approaches based on molecular recognition can provide a facile way to achieve large-scale structures. The development of new assembly strategies/methodologies and the production of novel building blocks are always the hot and important topics in the area. As shown in Scheme 1, one of the most efficient assembly strategies relies on the supramolecular polymerization of self-complementary AB-type heteroditopic monomers *via* iterative intermolecular inclusion complexation.[2,3] Nevertheless, self-assembly to linear supramolecular polymers have to compete with the formation of cyclic analogues, especially for dimeric [c2]daisy chains (Scheme 1). In fact, the formation of such cyclic interwoven dimers is thermodynamically favored, thus suppressing the assembly to polymeric species in many cases.[4,5] Although [c2] daisy chains are an important kind of topological motifs in supramolecular chemistry, supramolecular polymers based on them are less explored. Polymerization of [c2]daisy-chain rotaxanes, which are functionalized with various different end groups, using traditional covalent coupling or metal coordination has been previously demonstrated,[6] carving out a promising route towards functional polymeric materials. However, the synthesis of mechanically interlocked [c2]daisy-chain rotaxanes with functionalized groups does not always give high yields due to the accompanying formation of unwanted byproducts and sometimes requires multiple-step reactions. On the other hand, the covalent coupling approaches involve irreversible, conventional, covalent linkages between rotaxane monomers, making such materials hardly degradable, just like traditional polymers.

Herein, we describe the formation of a novel supramolecular alternating copolymer based on the host–guest complexation between a [c2]daisy-chain pseudorotaxane (**1**·**1**) bearing additional unbound recognition sites at its ends, and a pillar[5]arene[7–10] dimer (**2**), as shown in Scheme 2. Generally, highly regular alternating copolymers possess unique properties



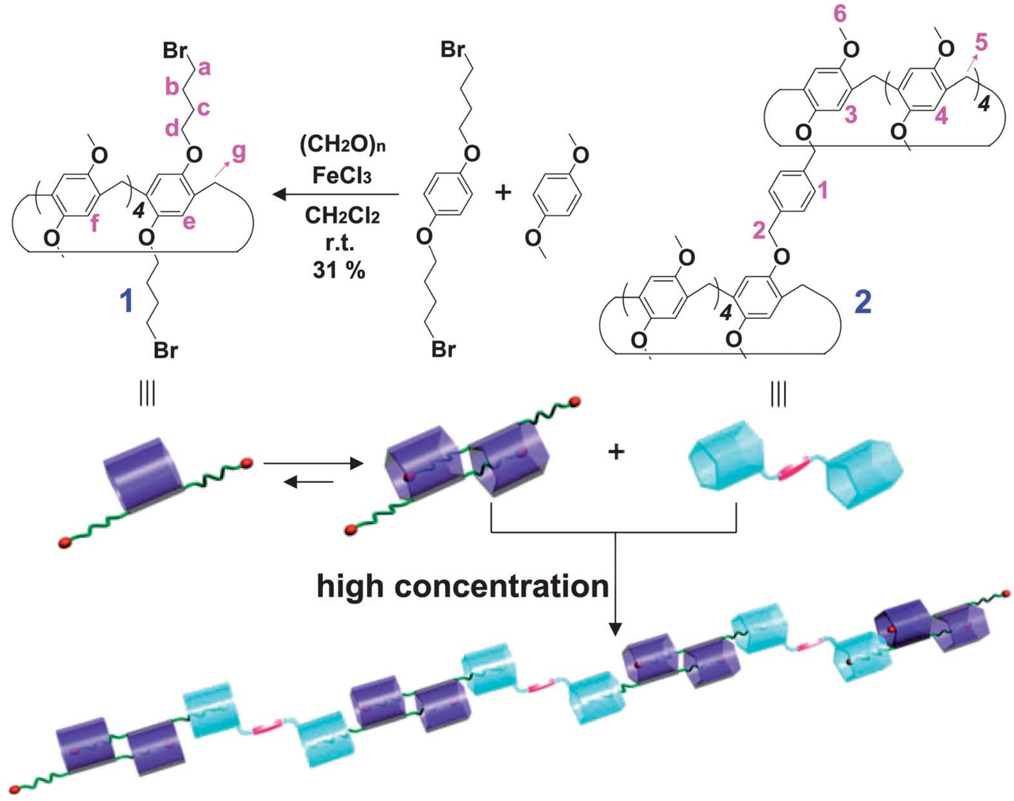
Scheme 1 Schematic depiction of [c2]daisy chain and supramolecular polymer formed by AB-type heteroditopic monomer.

---

[a]Department of Chemistry, Shanghai University, Shanghai, 200444, P. R. China. E-mail: cjli@shu.edu.cn; xsjia@mail.shu.edu.cn

[b]Beijing National Laboratory for Molecular Sciences, Beijing, P. R. China

† Electronic supplementary information (ESI) available: Synthesis, ^{1}H NMR spectra, and X-ray crystal data. CCDC reference number 921428. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3py00462g



Scheme 2 Synthesis of copillar[5]arene **1**, structure and proton designations of **1** and **2**, and schematic illustration of the supramolecular polymerization.

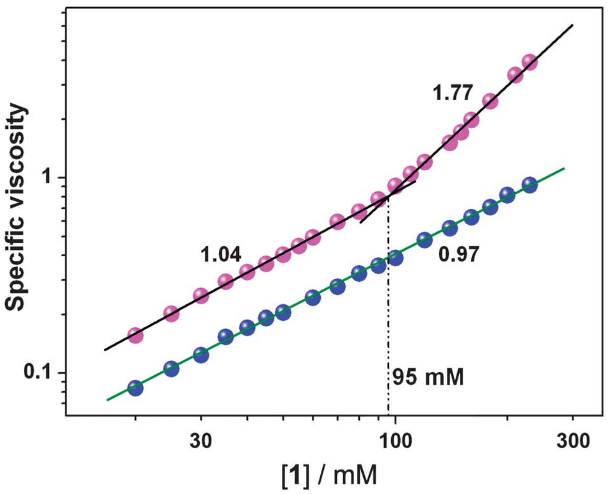


Fig. 1 Specific viscosity of chloroform solutions of **1** alone (blue) and 2 : 1 molar ratio of **1** and **2** (magenta) *versus* the concentration of **1** (298 K).

different from those of random copolymers and polymers with uniform backbones.[11] Therefore, supramolecular alternating copolymers have gained considerable attention recently.[12] The present new methodology, which is to utilize readily available [c2]daisy-chain pseudorotaxanes as the monomers and exploit non-covalent host–guest interactions as the linkages, can be employed to achieve facile fabrication of a previously undocumented kind of supramolecular alternating copolymers with two dimers, *i.e.*, [c2]daisy-chain dimer and macrocycle host dimer, as repeating units.

Results and discussion

Very different to the general supramolecular polymerization of AB-type monomers, the formation of double-threaded dimers in this strategy is not an unfavourable factor, but a necessary precondition. To obtain a [c2]daisy-chain pseudorotaxane containing additional free guest moieties at both ends, we designed and synthesized a dimeric self-complex precursor **1**, an AB_2-type heterotritopic copillar[5]arene, which contains complementary recognition sites, a pillar[5]arene, and two 4-bromobutyl $[Br(CH_2)_4–]$ moieties. Several important considerations were taken into account in designing **1**, including: (a) this copillar[5]arene can be easily prepared by one-step co-oligomerization reaction using commercial or readily available reagents; (Scheme 2) (b) by taking advantage of the efficient binding between peralkylated pillar[5]arenes and halogenated alkanes,[10c] which is mainly on account of the multiple hydrogen bonds, C–H⋯π, and van der Waals interactions, $Br(CH_2)_4$– group is employed as a guest moiety; (c) other substituents on the copillar[5]arene portals are methyls, hence, weak steric hindrance will occur in the [c2]daisy-chain motif and there may exist host–host C–H⋯O hydrogen bonding, which can favor the ability to form [c2]daisy chain;[4a,b] and (d) the length of the binding site is appropriate (four methylenes), ensuring that self-complexation is unfavorable.

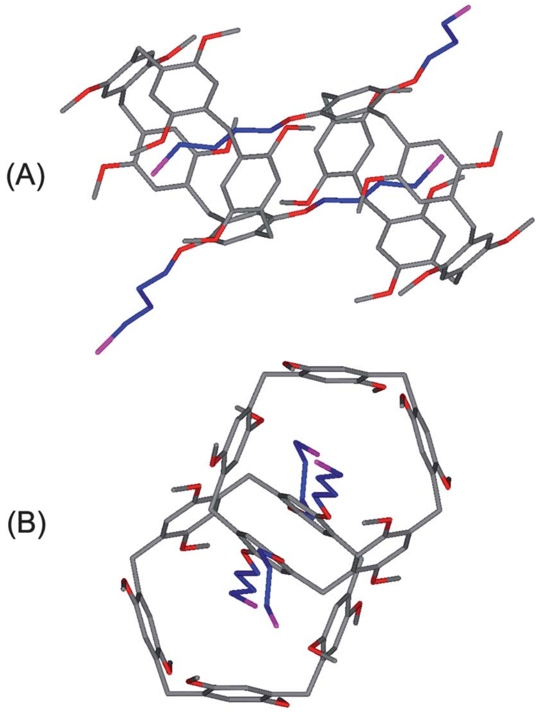


Fig. 2 Side and top views of the crystal structure of **1**·**1** dimer.

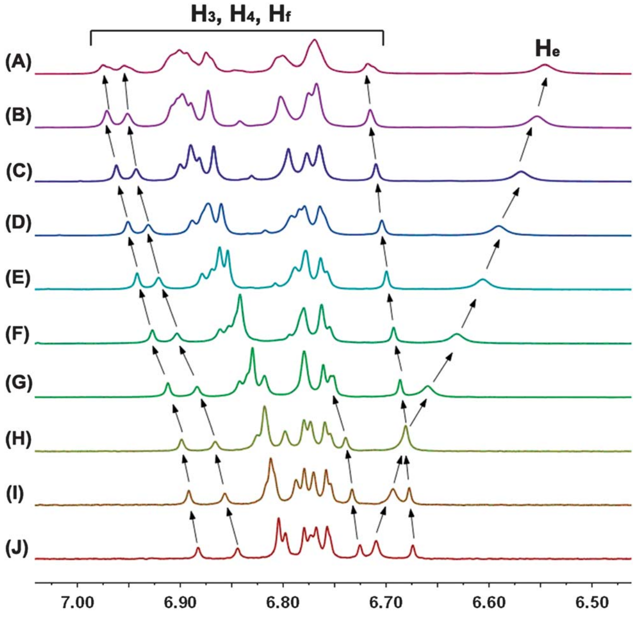


Fig. 3 Partial ^{1}H NMR spectra (500 MHz, $CDCl_3$, 298 K) of 2 : 1 molar ratio of **1** and **2** at different concentrations of **1**: (a) 200, (b) 150, (c) 100, (d) 60, (e) 40, (f) 20, (g) 10, (h) 5.0, (i) 3.0, and (j) 1.0 mM.

The self-assembly behavior of the [c2]daisy chain-forming compound **1** was firstly examined. Theoretically, except for the dimeric geometry, there are another two kinds of molecular topologies: self-inclusion complex caused by intramolecular complexation and hyperbranched supramolecular polymer caused by irregular intermolecular complexation. Previously, we have systematically investigated the considerable guest's length effect upon complexation with pillar[5]arenes,[9c,10a–c] showing that a four-methylene (butylidene) axle is the most suitable length for an pillar[5]arene wheel in most cases and the decrease of axle length will lead to a dramatically unfavorable effect on the complex stability.[13] Since the recognition site in **1** is $Br(CH_2)_4$– group, maybe only two (or at most three) methylenes could locate inside the copillar[5]arene cavity for the intramolecular self-inclusion mode. Thus, self-complexation is theoretically inhibited because the formation of such a complex is thermodynamically unfavorable. The assembly to cyclic interwoven dimer was first investigated by viscosity measurements. A double-logarithmic plot of specific viscosity *versus* the initial concentrations of copillar[5]arene **1** is shown in Fig. 1. The slope of **1** in the whole range of concentration closes to one, which is characteristic for cyclic oligomers with constant size, implying that no hyperbranched supramolecular polymers are formed and [c2]daisy chains predominate in solution. Meanwhile, there is a possibility for the formation of trimers, tetramers and other small cyclic oligomers, but they are not predominant.[14]

From variable-concentration ^{1}H NMR spectra of **1**, (Fig. S7†) it could be found that the complexation-induced upfield shifts and broadening effects for the butylidene signals ($H_{a–d}$) were concentration-dependent, reflecting the involvement of fast-exchanging noncovalent interactions in solution. At 1.0 mM and 0.50 mM, no obvious signal broadening was observed, indicating that free **1** predominated in solution at very low concentration. As the concentration increased, the ^{1}H NMR spectra revealed upfield shifts for butylidene $H_{a–d}$. These results suggested that the aggregates of co-pillarene **1** changed from self-encapsulation monomers into [c2]daisy chain dimers as the concentration increased. From variable-temperature (VT) ^{1}H NMR spectra of **1** (Fig. S11†), the complexation induced broadening effects of butylidene signals in higher temperatures were less remarkable than those at lower temperatures. This implies that the complexation events are enthalpy-driven processes, which are similar to those observed in the 1,4-bis(imidazol-1-yl)butane ⊂ pillararene complexes, as previously reported by us.[10a]

The double-threaded topological structure was then unambiguously confirmed by X-ray crystallographic analysis (Fig. 2 and S14†) of a colorless single-crystal obtained by slow evaporation of its solution in a chloroform–ethyl acetate mixture. The crystal structure of **1** showed a [c2]daisy-chain pseudorotaxane geometry, which is consistent with the result in solution. And as expected, the dimer **1**·**1** possesses two additional free recognition sites at both ends. There are octuple C–H···π interactions with the distances of 2.55–3.07 Å (Fig. S14a, C–F†), quadruple C–H···Br hydrogen bonding interactions with the distances of 2.97–3.23 Å (Fig. S14a, A–B†), as well as sextuple C–H···O hydrogen bonds with the distances of 2.76–2.93 Å (Fig. S14b, a–c†) between the host moieties and the guest moieties, indicating the good size fit between them. These multiple noncovalent interactions certainly play an important role in the formation of the double-interpenetrated geometry and its strong stability. More interestingly, it is also found that there

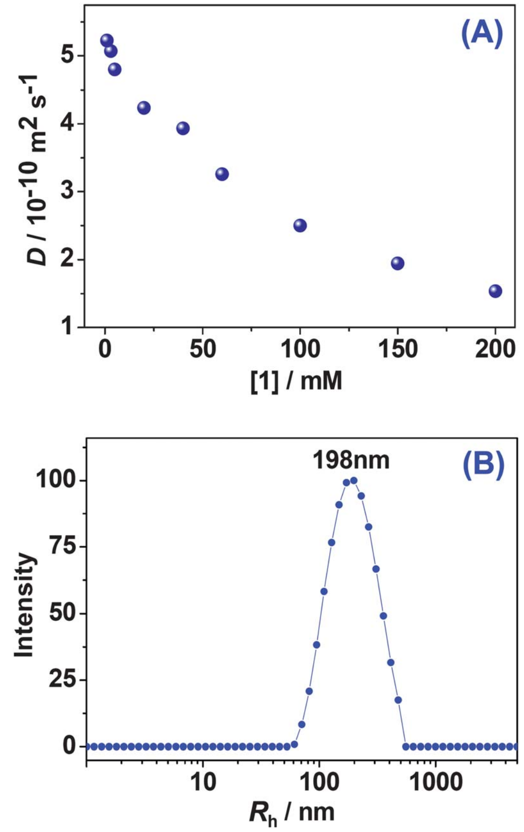


Fig. 4 (A) Concentration dependence of weight average diffusion coefficient *D* (from ^{1}H NMR spectroscopy; 500 MHz, $CDCl_3$, 298 K) of 2 : 1 molar ratio of **1** and **2** at multiple **1** concentrations. (B) Hydrodynamic diameter distribution of chloroform solution of 2 : 1 molar ratio of **1** and **2**; [**1**] = 150 mM.

exists double C–H···O hydrogen bonding interactions between the two host moieties with a distance of 2.71 Å (Fig. S14b, d†). The host–host hydrogen bonds further improve the ability to produce cyclic dimers. To our knowledge, this is the first [c2] daisy chain formed by a AB_2-type heterotritopic monomer, although AB-type heteroditopic monomer based cyclic dimers are much documented.

Since [c2]daisy chain **1·1** has two unbound sites, this dimer can be regard as a nontypical homoditopic BB-type monomer. It is anticipated that the combination of **1·1** and a homoditopic AA-type monomer, *i.e.*, pillar[5]arene dimer **2**, will provide a new assembly strategy for supramolecular polymerization and produce a supramolecular alternating copolymer **1·1** ⊂ **2** with two types of dimer blocks: [c2]daisy-chain dimer and pillar[5] arene dimer. From ^{1}H NMR measurements, the addition of 0.5 equiv. amount of **2**, to a $CDCl_3$ solution of **1** lead to clear broadening and upfield shifts for the butylidene signals H_{a-d}, (Fig. S9, S11e and S12e†) suggesting the intermolecular complexation between **1** and **2**. The concentration-dependent ^{1}H NMR spectra of 2 : 1 molar ratio of **1** and **2** provided significant insights into the assembly behavior. As shown in Fig. 3, the complexation is a fast-exchanging system on the proton NMR time scale. As the concentration increased, the proton signals of $H_{3,4}$ on **2** and H_f on **1** moved downfield progressively, while those for H_e on the 1,4-bis(4-bromobutoxy) benzene unit of co-pillararene **1** shifted upfield. At high concentrations, all of the proton signals became broad, suggesting the formation of high-molecular-weight assemblies.

Viscosity is a convenient method to test the supramolecular polymerization. As mentioned above, the double-logarithmic curve slope of **1** in the whole concentration region was close to one, while for **1·1** ⊂ **2**, when the concentrations of **1** increased above the critical polymerization concentration (CPC, about 95 mM), the curve had a slope value of 1.77 (Fig. 1). This revealed the formation of supramolecular polymers of increasing sizes.[15] Diffusion-ordered NMR spectroscopy (DOSY) provides reliable information about the dimensions of the polydisperse supramolecular aggregate systems. From Fig. 4A, the measured weight average diffusion coefficient (*D*) of 2 : 1 molar ratio of **1** and **2** in $CDCl_3$ solution decreased remarkably from 5.22×10^{-10} to 1.53×10^{-10} m^2 s^{-1}, as the monomer concentration increased from 1.0 mM to 200 mM, further suggesting that the formation of high-molecular-weight polymeric species was intrinsically concentration-dependent. The maximum possible polymerization degree n_{max} of supramolecular alternating copolymer **1·1** ⊂ **2** with **1** concentration of 200 mM was calculated to be 15.4 ($p = 93.5\%$). That is to say, there are 61.6 (15.4 × 4) pillararene units in the copolymer and the molar mass is 54.7 kDa. Dynamic light scattering (DLS) experiments were also conducted to support the theory of supramolecular polymer formation and estimate the size of the assembly in solution. As shown in Fig. 4B, a chloroform solution of **1·1** ⊂ **2** with **1** concentration of 150 mM has a hydrodynamic radius of 198 nm, manifesting the formation of large sized aggregates.

In addition, although no fibers can be drawn from the individual high concentration solutions of **1** and **2**, long and thin fibers with a regular diameter of approximately 7 μm could easily be drawn from a highly concentrated solution of **1** and **2** (2 : 1 molar ratio) and observed by scanning electron microscopy (SEM) (Fig. 5), providing further direct evidence for the formation of supramolecular polymer with high molecular weight.

Conclusions

In summary, a heterotritopic copillar[5]arene **1** containing complementary recognition sites, a pillar[5]arene, and two 4-bromobutyl [$Br(CH_2)_4$–] moieties, was found to preferentially assemble to [c2]daisy-chain geometry as a consequence of the specially designed recognition site and the host–host interactions, ruling out both intramolecular interactions leading to self-encapsulation and irregular intermolecular interactions leading to the formation of hyperbranched supramolecular polymer. Very different with traditional [c2]daisy chains, **1·1** contains additional free guest moieties at both ends. By utilizing the intermolecular host–guest interactions between **1·1** and a pillar[5]arene dimer **2**, a first example of a supramolecular polymer with [c2]daisy-chain pseudorotaxane as monomer was fabricated.

The new strategy provides not only a convenient approach for the construction of [c2]daisy chain-based supramolecular

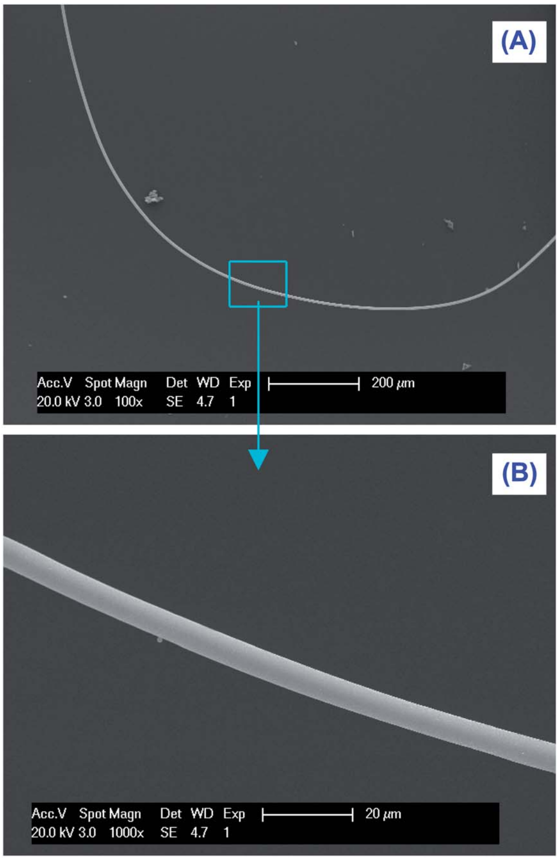


Fig. 5 Scanning electron micrograph of a gold-coated fiber drawn from a high-concentration solution of 2 : 1 molar ratio of **1** and **2** in chloroform. Scale bar: 200 µm (A), 20 µm (B).

polymers, but also a method for building novel supramolecular alternating copolymers with two dimers, [c2]daisy-chain dimer and macrocycle host dimer, as repeating units. The next challenge is to design and produce stimuli-responsive supramolecular copolymers based on [c2]daisy-chain pseudorotaxanes with bistability.

Acknowledgements

This work was supported by the NNSFC (no. 21272155, 21272147, and 20902057), the Innovation Program of Shanghai Municipal Education Commission (no. 13YZ010) and the Beijing National Laboratory for Molecular Sciences. The authors thank Dr Hongmei Deng (Laboratory for Microstructures, Shanghai University) for NMR measurements.

Notes and references

1 (*a*) T. F. A. De Greef, M. M. J. Smulders, M. Wolffs, A. P. H. J. Schenning, R. P. Sijbesma and E. W. Meijer, *Chem. Rev.*, 2009, **109**, 5687; (*b*) A. Harada, Y. Takashima and H. Yamaguchi, *Chem. Soc. Rev.*, 2009, **38**, 875; (*c*) E. A. Appel, J. Barrio, X. J. Loh and O. A. Scherman, *Chem. Soc. Rev.*, 2012, **41**, 6195; (*d*) X. Yan, F. Wang, B. Zheng and F. Huang, *Chem. Soc. Rev.*, 2012, **41**, 6042; (*e*) C. Schmuck, T. Rehm, F. Gröhn, K. Klein and F. Reinhold, *J. Am. Chem. Soc.*, 2006, **128**, 1430; (*f*) R. Nally and L. Isaacs, *Tetrahedron*, 2009, **65**, 7249; (*g*) A. Farcas, I. Ghosh, V. C. Grigoras, I. Stoica, C. Peptu and W. M. Nau, *Macromol. Chem. Phys.*, 2011, **212**, 1022; (*h*) D.-S. Guo and Y. Liu, *Chem. Soc. Rev.*, 2012, **41**, 5907; (*i*) Y.-S. Su, J.-W. Liu, Y. Jiang and C.-F. Chen, *Chem.–Eur. J.*, 2011, **17**, 2435; (*j*) C. J. Bruns and J. F. Stoddart, *Nat. Nanotechnol.*, 2013, **8**, 9.

2 Linear supramolecular polymers can also be conveniently prepared from two-component equimolar mixtures of AA–BB-type heterocomplementary homoditopic monomers.

3 It is well documented that cucurbit[8]uril can accommodate two guest molecules in its cavity. Recently, Scherman and Zhang *et al* have developed a new method for supramolecular polymerization based on the complexation of cucurbit[8]uril with an electron-acceptor guest and an electron-donor guest to form a 1 : 1 : 1 ternary complex. See: (*a*) Y. Liu, Y. Yu, J. Gao, Z. Wang and X. Zhang, *Angew. Chem., Int. Ed.*, 2010, **49**, 6576; (*b*) U. Rauwald and O. A. Scherman, *Angew. Chem., Int. Ed.*, 2008, **47**, 3950.

4 (*a*) J. Rotzler and M. Mayor, *Chem. Soc. Rev.*, 2013, **42**, 44; (*b*) P. R. Ashton, I. Baxter, S. J. Cantrill, M. C. T. Fyfe, P. T. Glink, J. F. Stoddart, A. J. P. White and D. J. Williams, *Angew. Chem., Int. Ed.*, 1998, **37**, 1294; (*c*) D. Cao, C. Wang, M. A. Giesener, Z. Liu and J. F. Stoddart, *Chem. Commun.*, 2012, **48**, 6791.

5 (*a*) M. C. Jiménez, C. Dietrich-Buchecker and J. Sauvage, *Angew. Chem., Int. Ed.*, 2000, **39**, 3284; (*b*) N. H. Evans and P. D. Beer, *Chem.–Eur. J.*, 2011, **17**, 10542; (*c*) B. Zheng, M. Zhang, S. Dong, J. Liu and F. Huang, *Org. Lett.*, 2011, **14**, 306.

6 (*a*) E. N. Guidry, J. Li, J. F. Stoddart and R. H. Grubbs, *J. Am. Chem. Soc.*, 2007, **129**, 8944; (*b*) L. Fang, M. Hmadeh, J. Wu, M. A. Olson, J. M. Spruell, A. Trabolsi, Y.-W. Yang, M. Elhabiri, A.-M. Albrecht-Gary and J. F. Stoddart, *J. Am. Chem. Soc.*, 2009, **131**, 7126; (*c*) S. Tsuda, Y. Aso and T. Kaneda, *Chem. Commun.*, 2006, 3072; (*d*) G. Du, E. Moulin, N. Jouault, E. Buhler and N. Giuseppone, *Angew. Chem., Int. Ed.*, 2012, **51**, 12504.

7 Pillararenes, made up of hydroquinone units linked by methylene bridges, are a new family of macrocyclic host molecules that exhibit intriguing and peculiar host–guest properties (see ref. 8–10). Compared with other macrocyclic hosts, the most peculiar host–guest properties of pillararenes are their strong affinities towards neutral guests in organic medium, (see ref. 10) since crown ethers, calixarenes and resorcarenes generally interact strongly with cationic guests.

8 (*a*) P. J. Cragg and K. Sharma, *Chem. Soc. Rev.*, 2012, **41**, 597; (*b*) M. Xue, Y. Yang, X. Chi, Z. Zhang and F. Huang, *Acc. Chem. Res.*, 2012, **45**, 1294; (*c*) G. Yu, C. Han, Z. Zhang, J. Chen, X. Yan, B. Zheng, S. Liu and F. Huang, *J. Am. Chem. Soc.*, 2012, **134**, 8711; (*d*) Y. Ma, X. Chi, X. Yan, J. Liu, Y. Yao, W. Chen, F. Huang and J.-L. Hou, *Org. Lett.*, 2012, **14**, 1532; (*e*) C. Han, G. Yu, B. Zheng and F. Huang, *Org. Lett.*, 2012, **14**, 1712; (*f*) W. Si, L. Chen, X.-B. Hu, G. Tang, Z. Chen, J.-L. Hou and Z.-T. Li, *Angew. Chem., Int.*

Ed., 2011, **50**, 12564; (*g*) T. Ogoshi, S. Kanai, S. Fujinami, T. A. Yamagishi and Y. Nakamoto, *J. Am. Chem. Soc.*, 2008, **130**, 5022; (*h*) T. Ogoshi, Y. Nishida, T. Yamagishi and Y. Nakamoto, *Macromolecules*, 2010, **43**, 3145; (*i*) D. Cao, Y. Kou, J. Liang, Z. Chen, L. Wang and H. Meier, *Angew. Chem., Int. Ed.*, 2009, **48**, 9721.

9 (*a*) N. L. Strutt, R. S. Forgan, J. M. Spruell, Y. Y. Botros and J. F. Stoddart, *J. Am. Chem. Soc.*, 2011, **133**, 5568; (*b*) H. Zhang, N. L. Strutt, R. S. Stoll, H. Li, Z. Zhu and J. F. Stoddart, *Chem. Commun.*, 2011, **47**, 11420; (*c*) C. Li, Q. Xu, J. Li, F. Yao and X. Jia, *Org. Biomol. Chem.*, 2010, **8**, 1568; (*d*) C. Li, L. Zhao, J. Li, X. Ding, S. Chen, Q. Zhang, Y. Yu and X. Jia, *Chem. Commun.*, 2010, **46**, 9016; (*e*) C. Li, J. Ma, L. Zhao, Y. Zhang, Y. Yu, X. Shu, J. Li and X. Jia, *Chem. Commun.*, 2013, **49**, 1924; (*f*) Q. Duan, W. Xia, X. Hu, M. Ni, J. Jiang, C. Lin, Y. Pan and L. Wang, *Chem. Commun.*, 2012, **48**, 8532; (*g*) K. Wang, L.-L. Tan, D.-X. Chen, N. Song, G. Xi, S. X.-A. Zhang, C. Li and Y.-W. Yang, *Org. Biomol. Chem.*, 2012, **10**, 9405; (*h*) H. Zhang, X. Ma, J. Guo, K. T. Nguyen, Q. Zhang, X.-J. Wang, H. Yan, L. Zhu and Y. Zhao, *RSC Adv.*, 2013, **3**, 368; (*i*) Z. Zhang, Y. Luo, J. Chen, S. Dong, Y. Yu, Z. Ma and F. Huang, *Angew. Chem., Int. Ed.*, 2011, **50**, 1397; (*j*) G. Yu, X. Zhou, Z. Zhang, C. Han, Z. Mao, C. U. Gao and F. Huang, *J. Am. Chem. Soc.*, 2012, **134**, 19489.

10 Our group have found the surprising host–guest properties of pillar[5]arenes toward the neutral substituted alkane guests. See: (*a*) C. Li, S. Chen, J. Li, K. Han, M. Xu, B. Hu, Y. Yu and X. Jia, *Chem. Commun.*, 2011, **47**, 11294; (*b*) X. Shu, S. Chen, J. Li, Z. Chen, L. Weng, X. Jia and C. Li, *Chem. Commun.*, 2012, **48**, 2967; (*c*) X. Shu, J. Fan, J. Li, X. Wang, W. Chen, X. Jia and C. Li, *Org. Biomol. Chem.*, 2012, **10**, 3393; (*d*) C. Li, K. Han, J. Li, H. Zhang, J. Ma, X. Shu, Z. Chen, L. Weng and X. Jia, *Org. Lett.*, 2012, **14**, 42.

11 (*a*) K. Satoh, S. Saitoh and M. Kamigaito, *J. Am. Chem. Soc.*, 2007, **129**, 9586; (*b*) V. Berl, M. Schmutz, M. J. Krische, R. G. Khoury and J.-M. Lehn, *Chem.–Eur. J.*, 2002, **8**, 1227; (*c*) W. C. Yount, H. Juwarker and S. L. Craig, *J. Am. Chem. Soc.*, 2003, **125**, 15302; (*d*) S. Sivakova, D. A. Bohnsack, M. E. Mackay, P. Suwanmala and S. J. Rowan, *J. Am. Chem. Soc.*, 2005, **127**, 18202; (*e*) M. N. Higley, J. M. Pollino, E. Hollembeak and M. Weck, *Chem.–Eur. J.*, 2005, **11**, 2946; (*f*) S. De, T. Pascher, M. Maiti, K. G. Jespersen, T. Kesti, F. Zhang, O. Inganas, A. Yartsev and V. Sundstrom, *J. Am. Chem. Soc.*, 2007, **129**, 8466.

12 (*a*) *Supramolecular Polymer Chemistry*, ed. A. Harada, Wiley-VCH, 2011; (*b*) M. Miyauchi and A. Harada, *J. Am. Chem. Soc.*, 2004, **126**, 11418; (*c*) S. K. Yang, A. V. Ambade and M. Weck, *J. Am. Chem. Soc.*, 2010, **132**, 1637; (*d*) T. Park and S. C. Zimmerman, *J. Am. Chem. Soc.*, 2006, **128**, 13986; (*e*) L. Brunsveld, B. J. B. Folmer, E. W. Meijer and R. P. Sijbesma, *Chem. Rev.*, 2001, **101**, 4071; (*f*) T. Ogoshi, H. Kayama, D. Yamafuji, T. Aoki and T.-A. Yamagishi, *Chem. Sci.*, 2012, **3**, 3221; (*g*) H.-X. Zhao, D.-S. Guo, L.-H. Wang, H. Qian and Y. Liu, *Chem. Commun.*, 2012, **48**, 11319; (*h*) F. Wang, C. Han, C. He, Q. Zhou, J. Zhang, C. Wang, N. Li and F. Huang, *J. Am. Chem. Soc.*, 2008, **130**, 11254.

13 For example, the association constant for 1,3-dibromopropane guest and perethylated pillar[5]arene host is reduced by a factor of 16, compared with that for 1,4-dibromobutane. See ref. 10*c*.

14 (*a*) S. H. M. Söntjens, R. P. Sijbesma, M. H. P. Van Genderen and E. W. Meijer, *Macromolecules*, 2001, **34**, 3815; (*b*) H. Xu and D. M. Rudkevich, *Chem.–Eur. J.*, 2004, **10**, 5432; (*c*) T. Xiao, S.-L. Li, Y. Zhang, C. Lin, B. Hu, X. Guan, Y. Yu, J. Jiang and L. Wang, *Chem. Sci.*, 2012, **3**, 1417.

15 (*a*) R. P. Sijbesma, F. H. Beijer, L. Brunsveld, B. J. B. Folmer, J. H. K. K. Hirschberg, R. F. M. Lange, J. K. L. Lowe and E. W. Meijer, *Science*, 1997, **278**, 1601; (*b*) O. A. Scherman, G. B. W. L. Ligthart, H. Ohkawa, R. P. Sijbesma and E. W. Meijer, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 11850; (*c*) F. Huang, D. S. Nagvekar, X. Zhou and H. W. Gibson, *Macromolecules*, 2007, **40**, 3561.