Polymer Chemistry

ARTICLE TYPE

Construction of muscle-like metallo-supramolecular polymers from a pillar[5]arene-based [c2]daisy chain†

Lingyan Gao, Zibin Zhang, Bo Zheng and Feihe Huang*

A muscle-like metallo-supramolecular polymer based on a solvent-driven [c2]daisy chain was prepared from an amino-modified pillar[5]arene. The integration of terpyridine moieties on both ends of the [c2]daisy chain and the stiff architecture of pillar[5]arene units facilitated the efficient formation of the
_10_ metallo-supramolecular polymer. UV/Vis absorption spectroscopy, dynamic light scattering, transmission electron microscopy and scanning electron microscopy were used to characterize the self-assembly behavior of the resulting polymer chains. From proton NMR studies, we confirmed that the pillar[5]arene-based [c2]daisy chain could change its length continuously in response to changes in the polarity of the solvent so the metallo-supramolecular polymer could change its length continuously by
_15_ varying the solvent polarity based on the individual contraction and extension of each daisy chain repeating unit. The current system can serve as a platform to mimic the muscle movement.

Introduction

In biological systems, biopolymers with exquisite sequences (primary structure) and distinctive architectures resulting from
_20_ folding of their primary structures (secondary structure) have attracted great interest owing to their intriguing functional properties: they can change their shapes or lengths continuously in response to stimuli and amplify their molecular motions by orders of magnitude. For example, in muscle tissues, collective
_25_ molecular motions of gliding of thick myosin filaments along thin actin filaments leads to the contraction of the sarcomere and realizes the muscular movement. To date, increasing endeavors have been devoted to mimicking the natural structural and controlling hierarchical self-assembly in molecular
_30_ nanosciences.[1]

Inspired by ingenious natural constructions, a variety of man-made self-assembled supramolecular polymers based on mechanically interlocked molecules (MIMs) have been designed by employing bottom-up methodologies.[2] These mechanically
_35_ bonded polymers can produce internal individual controllable, stimuli-responsive mechanical motions from one 'station' to the

State Key Laboratory of Chemical Engineering,
Department of Chemistry, Zhejiang University, Hangzhou 310027,
P. R. China. E-mail: fhuang@zju.edu.cn; Fax: 86 571 8795 3189;
Tel: 86 571 8795 3189
† Electronic Supplementary Information (ESI) available: Synthetic procedures, characterizations. See DOI: 10.1039/b000000x/

other 'station' on thread-components of MIMs to mimic biological counterparts.[3] Daisy chains,[3a,b,4] as a unique species of MIMs, have shown potential capability in the alternation of
_40_ macroscopic properties by switching mechanisms on a molecular scale. In particular, through careful design of the recognition sites, intramolecular motions in daisy chains can be triggered by external inputs, which result in controlled elongation mobility for the construction of molecular muscles. Herein we describe the
_45_ design of a new muscle-like metallo-supramolecular polymer based on a tailored pillar[5]arene-based [c2]daisy chain which can be connected by utilizing a metallo-supramolecular polymerization process.[5]

Pillar[n]arenes, mainly including pillar[5]arenes[6] and
_50_ pillar[6]arenes,[7] are a new class of macrocyclic hosts with symmetrical pillar architectures and electron-donating cavities, which have proved to be versatile macrocycles in the fabrication of dynamic supramolecular assemblies, mechanically interlocked structures and controlled release systems, and so forth.[8] Recently,
_55_ a novel pillar[5]arene-based solvent-driven molecular spring has been reported by our group; it can change its length continuously in response to changes in the polarity of the solvent.[5d] The continuous contraction/stretching property of this pillar[5]arene-based [c2]daisy chain forms the basis for the construction of an
_60_ environmentally responsive interlocked polymer that can mimic the muscle movement. Thus, we employed a solvent-driven pillar[5]arene-based [c2]daisy chain with terpyridine stoppers to prepare a muscle-like supramolecular polymer. The integration of terpyridine moieties on both ends of the [c2]daisy chain and the

stiff architecture of pillar[5]arene units facilitated the efficient formation of the metallo-supramolecular polymer. From proton NMR studies and the property of previously reported molecular spring, we confirmed that the pillar[5]arene-based [c2]daisy chain could change its length continuously in response to changes in the polarity of the solvent and thus the current polymer system could extend or contract in a continuous fashion by varying the solvent polarity based on the individual contraction and extension of each daisy chain repeating unit. Therefore, it can serve as a platform to mimic the muscle movement.

Experimental section

Synthetic procedure (see scheme 1a). Copillar[5]arenes **2** and **3** were reported previously.[5d]

For the synthesis of [c2]daisy chain **1**, a chloroform solution of carbonyldiimidazole (0.310 g, 2.00 mmol) was added dropwise into a mixture of triethylamine (0.210 mL, 1.50 mmol) and **3** (0.890 g, 1.00 mmol) in 20.0 mL of chloroform at 0 °C over 30 minutes, and the mixture was stirred for further 24 hours. Then the solvent was evaporated to get an intermediate. As reported before,[5d] copillar[5]arene **3** forms a cyclic dimer in chloroform, driven by the dispersion force between the *exo* cavity parts of the alkyl groups. Thus, to strengthen the self-complexation of **3** and increase the yield of the capping process, a mixture of the intermediate and aminoterpyridine **4** (0.450 g, 1.55 mmol) in 10.0 mL of chloroform was stirred at 0 °C for 2 days. Later, the crude product was purified by column chromatography using dichloromethane/methanol (20:1 to 10:1) as the eluent to give **1** as a white powder (0.150 g, 12%). mp: 115.8–116.0 ºC. The proton NMR spectrum of compound **1** is shown in Fig. S1. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ (ppm): 8.68–8.61 (m, 8H), 8.04 (m, 4H), 7.86–7.82 (m, 4H), 7.32 (m, 4H), 6.87–6.69 (m, 20H), 6.64 (br, 2H), 3.75–3.63 (m, 92H), 3.43–3.39 (m, 4H), 1.79 (m, 4H), 1.53 (m, 4H), 1.22 (m, 4H), 1.19 (br, 6H), 0.80 (br, 4H), 0.32 (br, 4H), (–0.10) to (–0.69) (br, 8H). The ^{13}C NMR spectrum of **1** is shown in Fig. S2. ^{13}C NMR (125 MHz, CDCl$_3$, 298 K) δ (ppm): 167.28, 157.43, 156.25, 150.70, 149.27, 137.07, 128.50, 121.59, 113.46, 107.55, 66.37, 56.34, 55.92, 55.45, 40.64, 37.67, 29.79, 29.38, 28.25, 25.79. The MALDI–TOF MS is shown in Fig. S3: m/z 2471.2 [M + Na]$^+$ (100%).

UV/Vis spectroscopic investigations. UV/Vis spectra were obtained on a UV-2550PC instrument. Titration experiments and Job plot were performed in quartz cuvettes scanning in the range of 250−700 nm.

Transmission electron microscopic (TEM) studies. The self-assembly structures of metallo-supramolecular polymer **Fe1** in different solvents were revealed using TEM. Samples were prepared from 1.00 mM solutions of **Fe1** in different solvents [chloroform, a mixture of chloroform and DMSO (ν/ν, 1:1), and DMSO]. Each of them was made by drop-coating the corresponding solution onto a carbon-coated copper grid. TEM investigations were carried out on a JEM-1200EX instrument.

Scanning electron microscopic (SEM) investigations. SEM investigations were carried out on a JEOL 6390LV instrument. The SEM samples were prepared on clean Si substrates. They were freeze-dried before use.

Dynamic light scattering (DLS) investigations. DLS experiments were carried out on a Malvern Nanosizer S instrument at room temperature.

Results and discussion

Structural characterization. The proton NMR spectrum of **1** (Fig. S1) in chloroform-*d* contains broad peaks from −0.10 ppm to −0.69 ppm, corresponding to the eight protons on the decyl chains. Based on this phenomenon and the MALDI-TOF mass spectrometric result [m/z 2471.2 [M + Na]$^+$ (100%)], we conclude that **1** is a doubly threaded daisy chain rather than a singly threaded rotaxane.[5d]
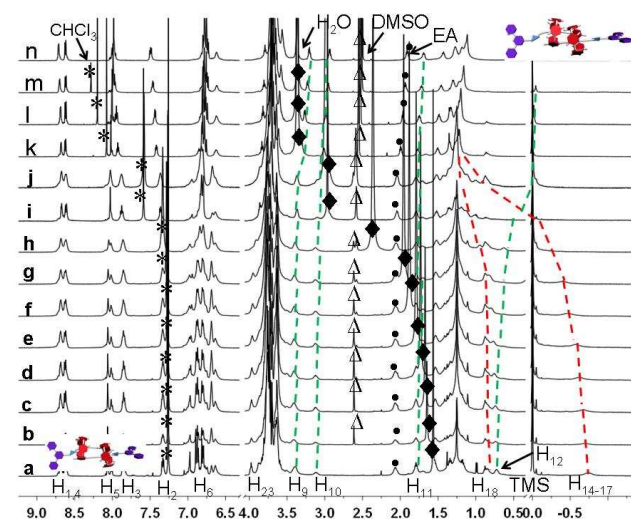
Fig. 1 Partial ^{1}H NMR spectra of **1** (500 MHz, 298 K) in different solvents. (a) Chloroform-*d*. Mixtures of chloroform-*d* and DMSO-d_6 (v/v): (b) 600:1; (c) 300:1; (d) 200:1; (e) 150:1; (f) 100:1; (g) 75:1; (h) 25:1; (i) 10:1; (j) 5:1; (k) 1:1; (l) 1:2; (m) 1:5. (n) DMSO-d_6.

Contraction/stretching movements of monomer 1 monitored by ^{1}H NMR spectroscopy. Monomer **1** is inclined to show muscle-like contraction/stretching movements by changing the polarity of the solvent, similar to the molecular spring based on an amino-modified copillar[5]arene previously reported by us.[5d] According to the literature, we postulated that **1** would be in a contracted state in chloroform and the copillar[5]arene cavities were statistically located on the four methylenes adjacent to the urea group, driven by the dispersion forces between the *exo* cavity parts of the alkyl groups. And it stretched when a polar solvent was introduced, such as DMSO, in which monomer **1** also showed good solubility. Thus, we performed proton NMR studies to confirm our hypotheses. From the ^{1}H NMR spectrum of **1** in different solvent mixtures (Fig. 1), we found that the signals from H$_{14−18}$ (the red dashed lines) of **1** shifted downfield gradually as the solvent polarity increased, indicating that H$_{14}$, H$_{15}$, H$_{16}$, H$_{17}$ and H$_{18}$ were gradually moving out of the cavities. On the contrary, peaks from H$_{9−12}$ (the green dashed lines) shifted upfield,
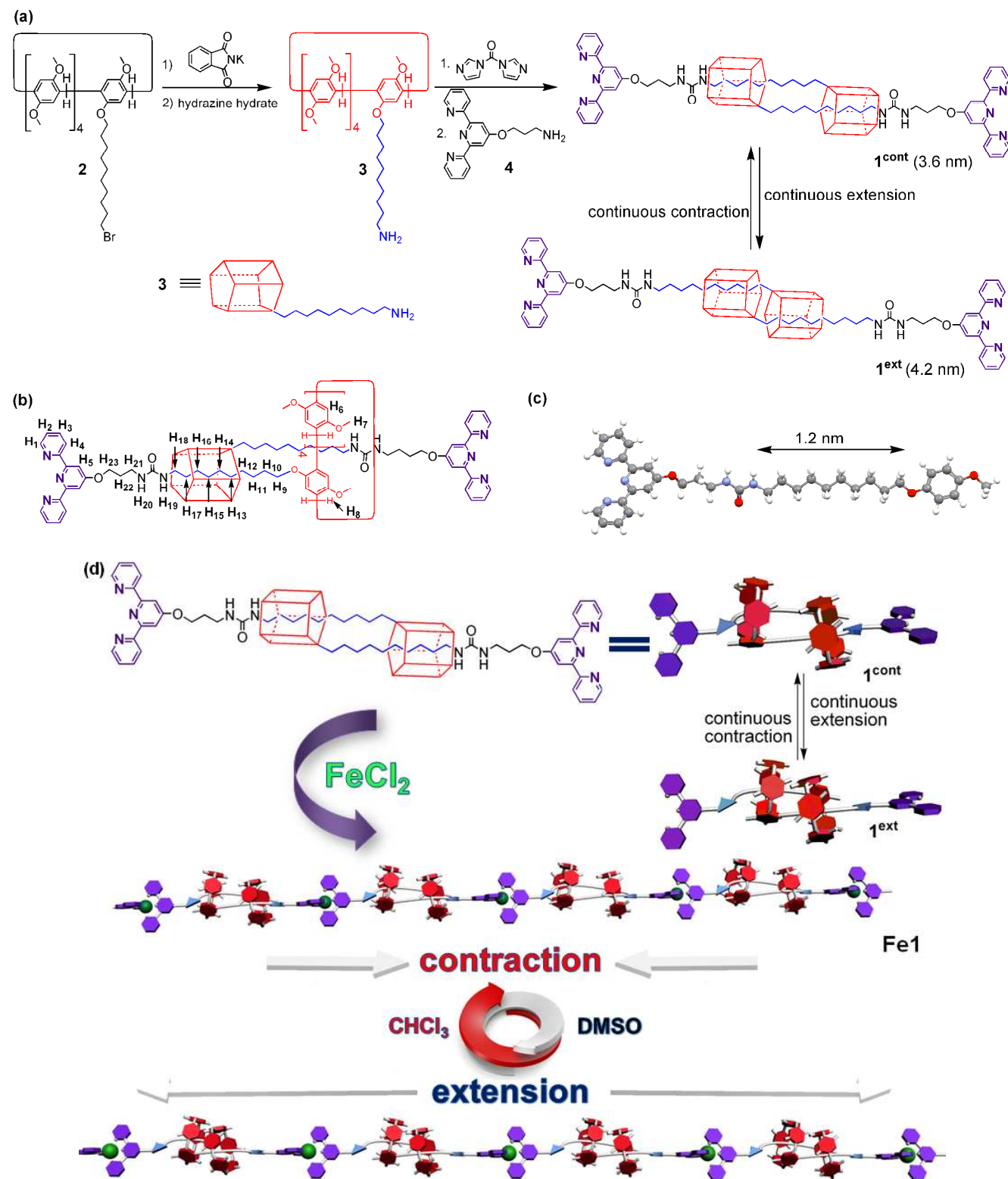
Scheme 1. (a) Synthesis of [c2]daisy chain **1**, whose length can vary continuously between 4.2 nm (**1^{ext}**) and 3.6 nm (**1^{cont}**). (b) Assignment of protons on **1**. (c) Length of the decyl chain (Δd = 1.2 nm) as determined by molecular modeling. (d) Cartoon representation for the formation of supramolecular polymers and the corresponding integrated translational motion based on the individual contraction and extension of each daisy chain repeating unit.

indicating that they were gradually moving into the cavities. These results verified that monomer **1** was in a contracted form (**1^cont**, 3.6 nm) in chloroform, and stretched continuously to reach an extended state (**1^ext**, 4.2 nm) as the volume ratio of chloroform-*d* and DMSO-*d₆* decreased, in excellent agreement with the previous study.[5d] Here the lengths (**1^cont** and **1^ext**) of the[*c*2]daisy chain monomer **1** were estimated by molecular modeling.[5d]

a

b

c
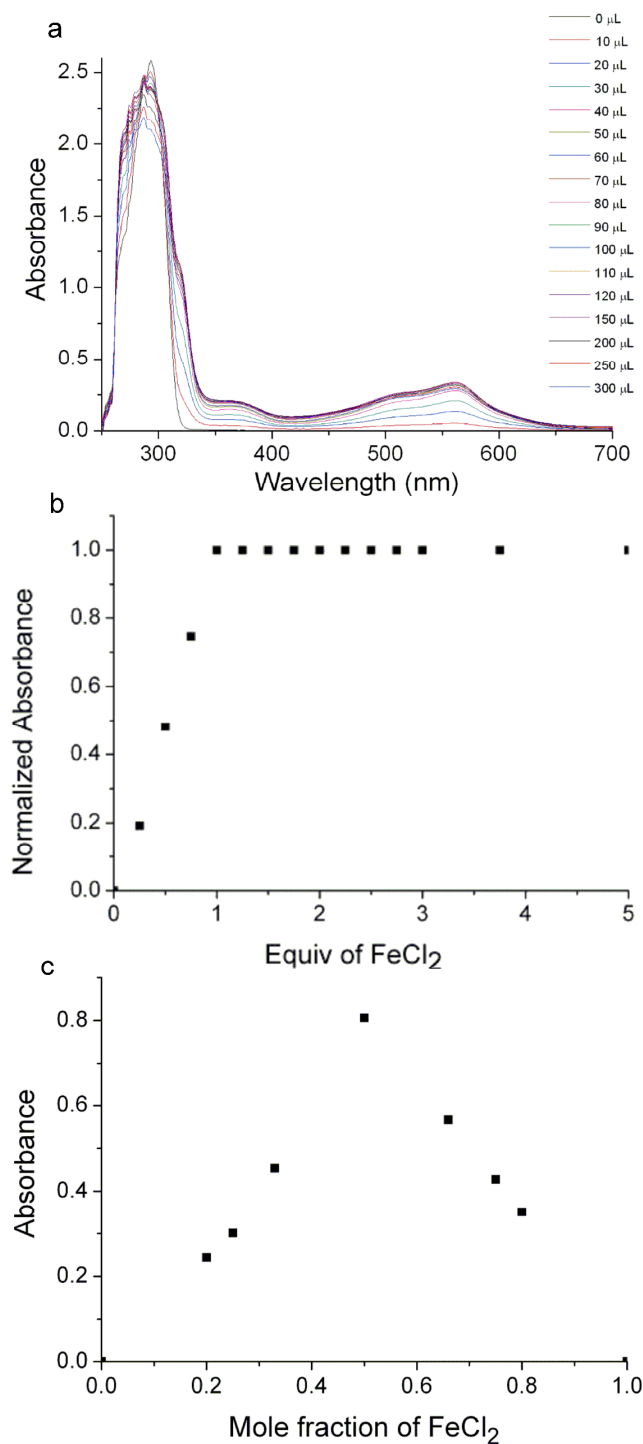
Fig. 2 (a) UV/Vis titration of **1** with $FeCl_2$ (in DMSO). (b) Plot of the normalized absorbance at 563 nm versus equivalents of $FeCl_2$. (c) Job plot, $[FeCl_2]_0 + [1]_0 = 0.200$ mM.

Metal–ligand complex formation monitored by UV/Vis absorption spectroscopy. Then we turned to study the coordination interactions between the terminal terpyridines and the metal ion. UV/Vis measurements were carried out to monitor the coordination between monomer **1** and Fe^{2+}. A remarkable metal-to-ligand charge transfer (MLCT) band ($\lambda_{max} = 563$ nm, Fig. 2a) appeared along with an immediate color change of the solution (from colorless to purple), indicating its formation.[5a,i,k] Moreover, we proceeded to perform UV/Vis titrations by stepwise addition of a DMSO solution of $FeCl_2$ to a solution of **1** (Fig. 2). The MLCT absorption band achieved the maximum absorbance when the $FeCl_2$/**1** molar ratio reached 1 and there was no significant change upon further addition, suggesting 1:1 complexation stoichiometry (Fig. 2a and b). The 1:1 complexation stoichiometry was also confirmed by the Job plot based on UV/Vis absorption data (Fig. 2c). These UV/Vis results gave strong evidence for the efficient complexation between [*c*2]daisy chain **1** and Fe^{2+}, which results in the formation of coordination polymer **Fe1** in solution (Scheme 1d).

Self-assembly behavior of polymer Fe1 revealed by TEM, SEM and DLS. Then, we proceeded to perform TEM and SEM studies to get deeper understanding of the self-assembly behavior of coordination polymer **Fe1**. Samples for TEM and SEM measurements were prepared in different solvents [chloroform (Fig. S4a and d), a mixture of chloroform and DMSO (ν/ν, 1:1) (Fig. 3 and Fig. S4b and e) and DMSO (Fig. S4c and f)] with the same concentration of 1.00 mM. Interestingly, both TEM (Figs. 3a–c and S4a–c) and SEM (Figs. 3d–f and S4d–f) results revealed that polymer **Fe1** formed filamentous structures on average 10 nm in diameter with three different solvent compositions. As shown in Figs. 3 and S4, **Fe1** spontaneously assembled into a bunch of fibres much like myofibrils. The length of the fibres can be over 40 micrometers (Fig. 3d).
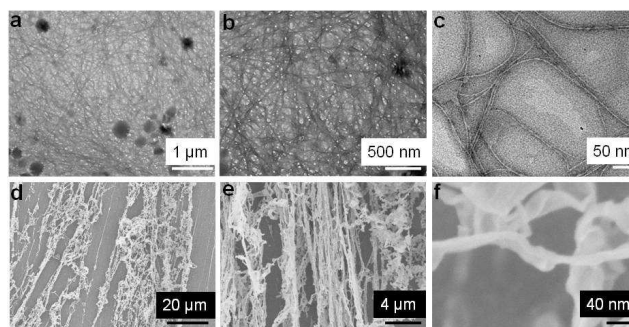
Fig. 3 (a, b and c) TEM and (d, e and f) SEM images of fibrous networks prepared from 1.00 mM **Fe1** in a mixture of chloroform and DMSO (ν/ν, 1:1).

Further, DLS experiments were carried out to confirm the formation of coordination polymer **Fe1** in solution. As shown by the DLS results given in Fig. 4, **Fe1** all presented a single polymer population in different solvents with the same concentration of 1.50 mM at room temperature. Moreover, when the polarity of the solvent increased (both $CHCl_3$ and DMSO are good solvents for supramolecular polymer **Fe1** and the self-assembly morphologies of **Fe1** in these two solvents show the same filamentous aggregates revealed by TEM and SEM), the hydrodynamic radius (R_h) of the aggregates became larger

correspondingly (from an average R_h of 104 nm in $CHCl_3$ gradually to an average R_h of 254 nm in DMSO). As mentioned before (Fig. 1), the increase of the solvent polarity would cause the movement of the pillar[5]arene cavities on **1** and lead to its extension. Besides the possible swelling process of the polymer which might increase the hydrodynamic radius, we considered that the main reason for the increase of the hydrodynamic radius was the integrated motion from the extensions of a number of interlocked [*c*2]daisy chain **1** units along the single polymer chains. Furthermore, from the DLS results, we found that **Fe1** could form a metallo-supramolecular polymer even at low monomer concentration when compared with other muscle-like supramolecular polymers reported previously.[3b] We speculate that two factors are responsible for this distinctive property. On the one hand, the stiff architecture of pillar[5]arene units endows mechanically interlocked [*c*2]daisy chain monomer **1** with a rigid and stretched structure that allows it to undergo coordination polymerization with Fe^{2+} efficiently even in dilute solutions,[4c,7c] since the conventional approach to the construction of linear metallo-supramolecular polymers are usually based on flexible chain linked building blocks, which will cause the formation of cyclic oligomers and simultaneous reduction of the degree of polymerization.[2a] On the other hand, the strong coordination interaction between Fe^{2+} and the terpyridine ligands ($\log\beta = 20.9$ M^{-2} in water) acts a predominant role in the polymerization process undoubtedly.[3b]
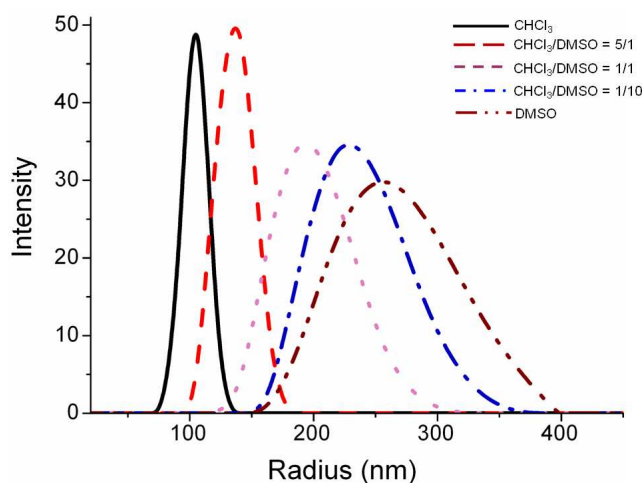
Fig. 4 Distributions of the scattering intensity with the R_h values obtained for supramolecular polymer **Fe1** in different solvents at the same concentration of 1.50 mM.

Conclusions

In conclusion, the preparation of metallo-supramolecular polymer **Fe1** based on a [*c*2]daisy chain from an amino-modified copillar[5]arene was described. The integration of terpyridine moieties on both ends of the [*c*2]daisy chain and the stiff architecture of pillar[5]arene units facilitated the efficient formation of the metallo-supramolecular polymer. UV/Vis absorption spectroscopy, dynamic light scattering, transmission electron microscopy and scanning electron microscopy were used to characterize the self-assembly behavior of the resulting polymer chains. From proton NMR studies and the property of previously reported molecular spring, we confirmed that the

pillar[5]arene-based [*c*2]daisy chain could change its length continuously in response to changes in the polarity of the solvent and thus the current polymer system could change its length continuously by varying the solvent polarity based on the individual contraction and extension of each daisy chain repeating unit, which provides a new pathway to supplement the design of artifical molecular machines to mimic living systems.
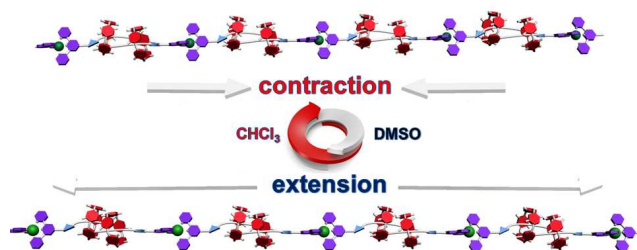
Notes and references

1 (a) T. Park, S. C. Zimmerman, *J. Am. Chem. Soc.*, 2006, **128**, 14236; (b) A. M. Kushner, J. D. Vossler, G. A. Williams, Z. Guan, *J. Am. Chem. Soc.*, 2009, **131**, 8766; (c) M. Chen, W. Zhang, R. Jiang and G. Diao, *Anal. Chim. Acta*, 2011, **687**, 177; (d) H. Y. Kuchelmeister, A. Gutschmidt, S. Tillmann, S. Knauer, C. Schmuck, *Chem. Sci.*, 2012, **3**, 996; (e) J. D. Fox, J. R. Capadona, P. D. Marasco, S. J. Rowan, *J. Am. Chem. Soc.*, 2013, **135**, 5167; (f) Z. Qi, C. Wu, P. Malo de Molina, H. Sun, A. Schulz, C. Griesinger, M. Gradzielski, R. Haag, M. B. Ansorge-Schumacher, C. A. Schalley, *Chem. Eur. J.*, 2013, **19**, 10150; (g) K. Liu, Y. Kang, Z. Wang, X. Zhang, *Adv. Mater.*, 2013, **25**, 5530; (h) J.-F. Xu, Y.-Z. Chen, D. Wu, L.-Z. Wu, C.-H. Tung and Q.-Z. Yang, *Angew. Chem. Int. Ed.*, 2013, **52**, 9738.

2 (a) N. Yamaguchi, D. S. Nagvekar, H. W. Gibson, *Angew. Chem. Int. Ed.*, 1998, **37**, 2361; (b) K. Kim, *Chem. Soc. Rev.*, 2002, **31**, 96; (c) H. W. Gibson, N. Yamaguchi, J. W. Jones, *J. Am. Chem. Soc.*, 2003, **125**, 3522; (d) F. Huang, H. W. Gibson, *Prog. Polym. Sci.*, 2005, **30**, 982; (e) S. J. Loeb, *Chem. Soc. Rev.*, 2007, **36**, 226; (f) W. Jiang, H. D. F. Winkler, C. A. Schalley, *J. Am. Chem. Soc.*, 2008, **130**, 13852; (g) P. G. Clark, M. W. Day and R. H. Grubbs, *J. Am. Chem. Soc.*, 2009, **131**, 13631; (h) S. Li, B. Zheng, J. Chen, S. Dong, Z. Ma, F. Huang and H. W. Gibson, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 4067; (i) M. Zhang, S. Li, S. Dong, J. Chen, B. Zheng and F. Huang, *Macromolecules*, 2011, **44**, 9629; (j) S. F. M. van Dongen, S. Cantekin, J. A. A. W. Elemans, A. E. Rowan, R. J. M. Nolte, *Chem. Soc. Rev.*, 2014, **43**, 99; (k) M. Arunachalam, H. W. Gibson, *Prog. Polym. Sci.*, 2014, **39**, 1043.; (l) S. Li, G.-H. Weng, W. Lin, Z.-B. Sun, M. Zhou, B. Zhu, Y. Ye and J. Wu, *Polym. Chem.*, 2014, DOI: 10.1039/C4PY00409D.

3 (*a*) J.-P. Collin, C. Dietrich-Buchecker, P. Gaviña, M. C. Jimenez-Molero, J.-P. Sauvage, *Acc. Chem. Res.*, 2001, **34**, 477; (b) G. Du, E. Moulin, N. Jouault, E. Buhler, N. Giuseppone, *Angew. Chem. Int. Ed.*, 2012, **51**, 12504; (c) B. Lewandowski, G. De Bo, J. W. Ward, M. Papmeyer, S. Kuschel, M. J. Aldegunde, P. M. E. Gramlich, D. Heckmann, S. M. Goldup, D. M. D'Souza, A. E. Fernandes, D. A. Leigh, *Science*, 2013, **339**, 189.

4 (*a*) M. C. Jiménez, C. Dietrich-Buchecker, J.-P. Sauvage and A. De Cian, *Angew. Chem. Int. Ed.*, 2000, **39**, 1295; (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) J. Rotzler and M. Mayor, *Chem. Soc. Rev.*, 2013, **42**, 44.

5 (*a*) Z. Zhang, B. Xia, C. Han, Y. Yu, F. Huang, *Org. Lett.*, 2010, **12**, 3285; (b) J. R. Kumpfer, S. J. Rowan, *J. Am. Chem. Soc.*, 2011, **133**, 12866; (c) V. N. Vukotic, S. J. Loeb, Chem. Soc. *Rev.*, 2012, **41**, 5896; (d) Z. Zhang, C. Han, G. Yu, F. Huang, *Chem. Sci.*, 2012, **3**, 3026; (e) Y. Ding, P. Wang, Y.-K. Tian, Y.-J. Tian, F. Wang, *Chem. Commun.*, 2013, **49**, 5951; (f) Y.-K. Tian, L. Chen, Y.-J. Tian, X.-Y. Wang and F. Wang, *Polym. Chem.*, 2013, **4**, 453; (g) X. Yan, S. Li, J. B. Pollock, T. R. Cook, J. Chen, Y. Zhang, X. Ji, Y. Yu, F. Huang, P. J. Stang, *Proc. Nati. Acad. Sci. U.S.A.*, 2013, **110**, 15585; (h) S. Li, J. Huang, F. Zhou, T. R. Cook, X. Yan, Y. Ye, B. Zhu, B. Zheng and P. J. Stang, *J. Am. Chem. Soc.*, 2014, **136**, 5908.

6 (a) T. Ogoshi, Y. Nishida, T. Yamagishi and Y. Nakamoto, *Macromolecules*, 2010, **43**, 7068; (b) C. Li, L. Zhao, J. Li, X. Ding, S. Chen, Q. Zhang, Y. Yu and X. Jia, *Chem. Commun.*, 2010, **46**, 9016; (c) W. Si, X.-B. Hu, X.-H. Liu, R. Fan, Z. Chen, L. Weng and J.-L. Hou, *Tetrahedron Lett.*, 2011, **52**, 2484; (d) Y. Yao, M. Xue, J. Chen, M. Zhang and F. Huang, *J. Am. Chem. Soc.*, 2012, **134**,

15712; (e) H. Deng, X. Shu, X. Hu, J. Li, X. Jia and C. Li, *Tetrahedron Lett.*, 2012, **53**, 4609; (f) L. Gao, C. Han, B. Zheng, S. Dong and F. Huang, *Chem. Commun.*, 2013, **49**, 472; (g) Y. Yao, M. Xue, Z. Zhang, M. Zhang, Y. Wang and F. Huang, *Chem. Sci.*, 2013, **4**, 3667; (h) L. Gao, B. Zheng, Y. Yao and F. Huang, *Soft Matter*, 2013, **9**, 7314; (i) H. Li, D.-X. Chen, Y.-L. Sun, Y. Zheng, L.-L. Tan, P. S. Weiss and Y.-W. Yang, *J. Am. Chem. Soc.*, 2013, **135**, 1570; (j) J.-F. Xu, Y.-Z. Chen, L.-Z. Wu, C.-H. Tung and Q.-Z. Yang, *Org. Lett.*, 2013, **15,** 6148; (k) 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; (l) Y. Fang, L. Wu, J. Liao, L. Chen, Y. Yang, N. Liu, L. He, S. Zou, W. Feng and L. Yuan, *RSC Adv.*, 2013, **3**, 12376; (m) L. Gao, S. Dong, B. Zheng and F. Huang, *Eur. J. Org. Chem.*, 2013, 1209; (n) S. Dong, J. Yuan and F. Huang, *Chem. Sci.*, 2014, **5**, 247; (o) D.-D. Zheng, D.-Y. Fu, Y. Wu, Y.-L. Sun, L.-L. Tan, T. Zhou, S.-Q. Ma, X. Zha and Y.-W. Yang, *Chem. Commun.*, 2014, **50**, 3201; (p) K. Jie, Y. Yao, X. Chi and F. Huang, *Chem. Commun.*, 2014, **50**, 5503; (q) Z.-Y. Li, Y. Zhang, C.-W. Zhang, L.-J. Chen, C. Wang, H. Tan, Y. Yu, X. Li and H.-B. Yang, *J. Am. Chem. Soc.*, 2014, DOI: 10.1021/ja413047r.

7   (a) D. Cao, Y. Kou, J. Liang, Z. Chen, L. Wang and H. Meier, *Angew. Chem. Int. Ed.*, 2009, **48**, 9721; (b) C. Han, F. Ma, Z. Zhang, B. Xia, Y. Yu and F. Huang, *Org. Lett.*, 2010, **12**, 4360; (c) M. Xue, Y. Yang, X. Chi, Z. Zhang and F. Huang, *Acc. Chem. Res.*, 2012, **45**, 1294; (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) P. J. Cragg and K. Sharma, *Chem. Soc. Rev.*, 2012, **41**, 597; (f) G. Yu, X. Zhou, Z. Zhang, C. Han, Z. Mao, C. Gao and F. Huang, *J. Am. Chem. Soc.*, 2012, **134**, 19489; (g) W. Chen, Y. Zhang, J. Li, X. Lou, Y. Yu, X. Jia and C. Li, *Chem. Comm.*, 2013, **49**, 7956; (h) C. Han, L. Gao, G. Yu, Z. Zhang, S. Dong and F. Huang, *Eur. J. Org. Chem.*, 2013, 2529; (i) I. Nierengarten, S. Guerra, M. Holler, L. Karmazin-Brelot, J. Barberá, R. Deschenaux and J.-F. Nierengarten, *Eur. J. Org. Chem.*, 2013, 3675; (j) X. Chi, M. Xue, Y. Ma, X. Yan and F. Huang, *Chem. Commun.*, 2013, **49**, 8175; (k) D. Xia, G. Yu, J. Li and F. Huang, *Chem. Commun.*, 2014, **50**, 3606; (l) J. Yang, G. Yu, D. Xia and F. Huang, *Chem. Commun.*, 2014, **50**, 3993; (m) P. Wang, X. Yan and F. Huang, *Chem. Commun.*, 2014, **50**, 5017.

8   (a) Z. Zhang, G. Yu, C. Han, J. Liu, X. Ding, Y. Yu and F. Huang, *Org. Lett.*, 2011, **13**, 4818; (b) N. L. Strutt, R. S. Forgan, J. M. Spruell, Y. Y. Botros and J. F. Stoddart, *J. Am. Chem. Soc.*, 2011, **133**, 5668; (c) Z. Zhang, Y. Luo, J. Chen, S. Dong, Y. Yu, Z. Ma and F. Huang, *Angew. Chem. Int. Ed.*, 2011, **50**, 1397; (d) 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; (e) L. Liu, L. Wang, C. Liu, Z. Fu, H. Meier and D. Cao, *J. Org. Chem.*, 2012, **77**, 9413; (f) Y. Guan, M. Ni, X. Hu, T. Xiao, S. Xiong, C. Lin and L. Wang, *Chem. Commun.*, 2012, **48**, 8532; (g) X. Wang, K. Han, J. Li, X. Jia and C. Li, *Polym. Chem.*, 2013, **4**, 3998; (h) X.-Y. Hu, X. Wu, S. Wang, D. Chen, W. Xia, C. Lin, Y. Pan and L. Wang, *Polym. Chem.*, 2013, **4**, 4292; (i) L. Chen, W. Si, L. Zhang, G. Tang, Z.-T. Li and J.-L. Hou, *J. Am. Chem. Soc.*, 2013, **135**, 2152; (j) Q. Duan, Y. Cao, Y. Li, X. Hu, T. Xiao, C. Lin, Y. Pan and L. Wang, *J. Am. Chem. Soc.*, 2013, **135**, 10542; (k) G. Yu, Y. Ma, C. Han, Y. Yao, G. Tang, Z. Mao, C. Gao and F. Huang, *J. Am. Chem. Soc.*, 2013, **135**, 10310; (l) Z. Zhang, Q. Zhao, J. Yuan, M. Antonietti and F. Huang, *Chem. Commun.*, 2014, **50**, 2595; (m) Z. Li, J. Yang, G. Yu, J. He, Z. Abliz and F. Huang, *Chem. Commun.*, 2014, **50**, 2841; (n) Z. Li, J. Yang, G. Yu, J. He, Z. Abliz and F. Huang, *Org. Lett.*, 2014, **16**, 2066.

TOC

5 A muscle-like metallo-supramolecular polymer based on a solvent-driven [c2]daisy chain was prepared from an amino-modified pillar[5]arene. The integration of terpyridine moieties on both ends of the [*c2*]daisy chain and the stiff architecture of pillar[5]arene units facilitated the efficient formation of the metallo-supramolecular polymer.