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Highly Stable Chiral $(A)_6$−B Supramolecular Copolymers: A Multivalency-Based Self-Assembly Process

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S *Supporting Information*

ABSTRACT: A novel type of chiral layered supramolecular copolymer with high molecular weight has been assembled from a hydrogen bonded C_6-symmetric zinc porphyrin hexamer and chiral C_3-symmetric pyridine hexadentate linkers driven by multivalent zinc porphyrin−pyridine coordination. UV−vis, circular dichroism, and static light scattering experiments revealed that the formation of the layered supramolecular copolymers is at first dynamically controlled and then becomes thermodynamically controlled.

In the past decade, great effort has been devoted to the construction of supramolecular polymers because of their unique structures and potential applications,[1,2] and hydrogen bonding,[3] solvophobicity,[4] metal−ligand coordination,[5] and donor−acceptor interactions[6] have been utilized as the driving forces. The formation of supramolecular polymers with high molecular weight, especially in dilute solution, requires the introduction of highly stable binding motifs into the monomers. However, the development of such highly stable binding motifs has been a great challenge because of the weakness of the noncovalent forces.[7] A straightforward strategy is to introduce multiple simple binding modes into one rationally designed monomer to utilize their binding multivalency.[8,9] This strategy has been perfectly practiced by nature in the assembly of the DNA double helix but rarely exploited for the creation of stable supramolecular (co)-polymers,[10] especially those with hierarchical control of the chirality.[11] Herein we describe the error-correction formation of a new type of highly stable chiral supramolecular $(A)_6$−B copolymer from a hydrogen bonded C_6-symmetric zinc porphyrin hexamer and pyridine-derived chiral hexadentate linkers based on multivalent Zn−N coordination.

It has been established that the heterocyclic unit of **1**[12] forms a hydrogen-bonded C_6-symmetric hexamer (Scheme 1).[13] We envisioned that C_3-symmetric chiral hexadentate linkers **2** might bind the hexamer $(\mathbf{1})_6$ by alternately forming three N−Zn coordination bonds in an induced-fit manner[14] to generate a layered chiral supramolecular copolymer. The chiral tridentate linker **3** was first prepared to test whether it would combine with hexamer $(\mathbf{1})_6$ to form selectively the sandwich-styled complex $\mathbf{3}\cdot(\mathbf{1})_6\cdot\mathbf{3}$. Their binding properties were first investigated in toluene using UV−vis spectroscopy. Adding 0.33 equiv of (*R*)-**3**, corresponding to 1.0 equiv of pyridine, to a 28 μM solution of **1** led to the exclusive formation of the hexamer,[12,13] causing red shifts of 6.5 and 14 nm in the Soret and Q bands, respectively, of the porphyrin unit of **1** (Figure 1). In contrast, adding the same amount of (*R*)-**3** to control **4** caused only a small red shifts (~0.5 nm) in the two bands (Figure S13 in the Supporting Information). Titration of **1** with (*R*)-**3** produced well-defined isosbestic points for the absorption of **1** (Figure 1), implying the formation of a single supramolecular entity. The Job's plot confirmed a 3:1 stoichiometry (Figure 1). The apparent association constant (K_{assoc}) for the complex of the zinc porphyrin of **1** and the single pyridine of (*R*)-**3** was determined to be 3.4×10^7 M^{-1}, which is 4415 times higher than that of the complex of **4** and the single pyridine of (*R*)-**3** (7.7×10^3 M^{-1}). Two-dimensional diffusion-ordered ^1H NMR (DOSY) experiments for **1** and the **1**/(*R*)-**3** (1:0.33) mixture ([**1**] = 4.8 mM) in $CDCl_3$ gave rise to diffusion coefficients (*D*) of 6.1×10^{-9} and 4.5×10^{-9} m^2/s, respectively. The value for the mixture was notably lower than that for **1**, supporting the formation of the complex $\mathbf{3}\cdot(\mathbf{1})_6\cdot\mathbf{3}$ of increased size. The average masses of the samples of **1** and the **1**/(*R*)-**3** (1:0.33) mixture in toluene were further determined by vapor pressure osmometry (VPO) to be 7700 and 10 000 u, respectively, which are also close to the calculated values of hexamer $(\mathbf{1})_6$ (7698 u) and complex $\mathbf{3}\cdot(\mathbf{1})_6\cdot\mathbf{3}$ (9500 u).

The circular dichroism (CD) spectra of **1** in toluene in the presence of (*R*)- and (*S*)-**3** displayed mirror-symmetric bisignate induced circular dichroism (ICD) signals with the positive and negative extrema at 425 and 433 nm, respectively (Figure 2). The intercept with the *x* axis (429 nm) matched the maximum in the UV−vis spectrum (430 nm). The mixture of (*R*)- or (*S*)-**3** with **4** (1:3) did not exhibit any CD signals in the 300−500 nm region. Thus, these ICD signals should be attributed to the orderly through-space exciton coupling of the porphyrin unit of **1** induced by **3** in the sandwich-styled chiral complex. Diluting the solution of **1** and (*R*)-**3** (1:0.33) from 42 to 6.2 μM (referring to **1**) did not lead to an observable decrease in the molar absorption of the ICD signals (Figure S14), and raising the temperature from 10 to 60 °C caused only a slight weakening of the ICD signals (Figure S15), both confirming the high stability of this multivalency-driven chiral complex.

The C_3-symmetric chiral hexadentate linkers (*R*)- and (*S*)-**2**, whose extended size is comparable to that of **3**, were then

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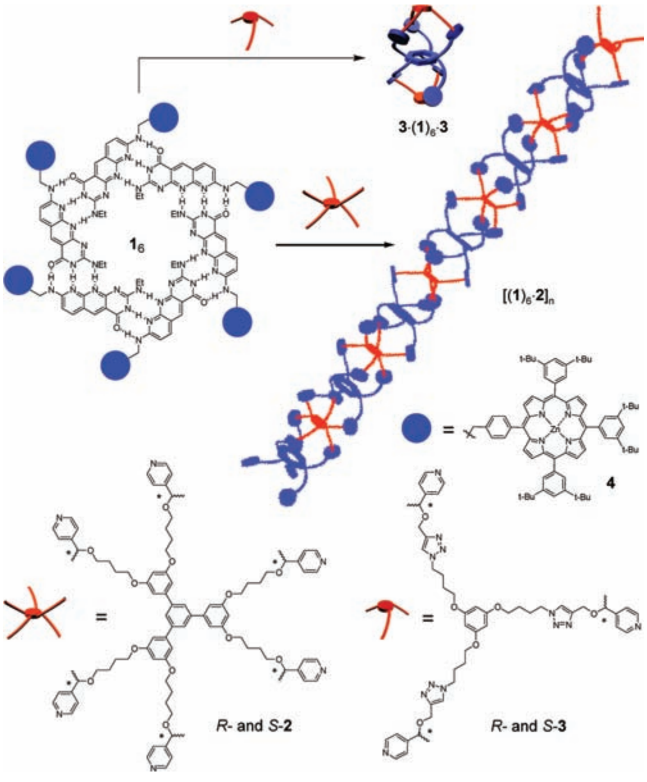
Scheme 1. **Schematic Representation of the Formation of $(A)_6$—B-Type Chiral Supramolecular Copolymers and a Sandwich-Styled Eight-Component Complex from C_6-Symmetric Hexamer $(1)_6$ and Chiral Hexadentate Linker 2 or Tridentate Linker 3**



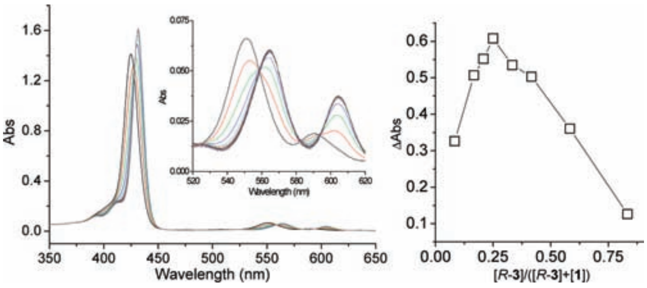


Figure 1. (left) UV—vis spectral changes of **1** (28 μM) in the presence of (*R*)-**3** (0—62 μM) in toluene at 25 °C. (right) Job's plot demonstrating the 3:1 stoichiometry.

prepared. Two chiral pyridine-appended side chains were introduced at the 3 and 5 positions of the three peripheral benzene rings. Such an arrangement would favor the formation of copolymeric structures with $(\mathbf{1})_6$ via a three-to-three binding pattern, as shown by **3**, but not the simple seven-component two-layer complex $(\mathbf{1})_6\cdot\mathbf{2}$ because of twisting of the biphenyl backbone.[15]

Adding (*R*)-**2** to a solution of **1** in toluene caused a time-dependent red shift of the Soret absorption band of the porphyrin unit of **1** (Figure 3). The band first rapidly shifted from 425 to 432 nm in about 1 min and then slowly shifted further to 433 nm, reaching equilibrium after ~6 h. These results indicated that the binding between **2** and hexamer $(\mathbf{1})_6$ increased with time and probably underwent a conversion from being dynamically controlled to being thermodynamically controlled. Thus, for the quantitative evaluation of the binding stability, UV—vis titration experiments were undertaken after the two samples were mixed for 12 h to make sure that the binding equilibrium had been reached (Figure S16). The resulting spectra also gave rise to well-defined isosbestic points, and the apparent K_{assoc} of the complex between the zinc porphyrin unit of **1** and the single pyridine unit of **2** was determined to be 3.0×10^7 M^{-1}.

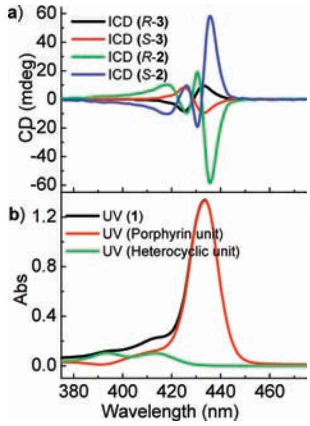


Figure 2. (a) ICD spectra of **1** (45 μM) in the presence of (*R*)- and (*S*)-**2** (7.5 μM) and (*R*)- and (*S*)-**3** (15 μM). (b) UV—vis spectra of **1** (28 μM) in the presence of (*R*)-**2** (0—79 μM). The measurements were performed in toluene after mixing for 10 h at 25 °C.

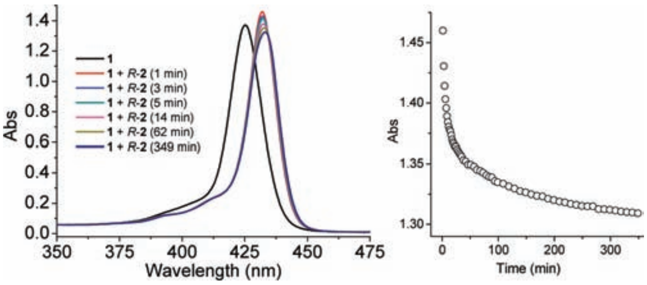


Figure 3. (left) Time-dependent UV—vis spectra of **1** (28 μM) in toluene at 25 °C after mixing with (*R*)-**2** (4.7 μM). (right) Plot of the absorption intensity change at 432 nm vs time.

The ICD spectra of **1** in toluene upon mixing with (*R*)-**2** were also time-dependent (Figure 4). Addition of 0.17 equiv of (*R*)-**2**, corresponding to 1.0 equiv of pyridine, to a solution of **1** in toluene first caused two negative ICD signals centered at 418 and 430 nm and two positive ICD signals centered at 426 and 435 nm. The signals reached maxima after ~4 min and then weakened and vanished almost completely after 23 min. With the elongation of time, the signals were exhibited again, but all increased in the opposite directions and reached equilibrium after ~6.5 h. Notably, the negative ICD signal at 435 nm was substantially stronger than the other three. The ICD spectra of **1** upon mixing with 0.17 equiv of (*S*)-**2** exhibited similar time-dependence, with the final signals being mirror-symmetric to those induced by (*R*)-**2** (Figure 4 and Figure S17). Diluting the solution of **1** and (*R*)- or (*S*)-**2** (1:0.17) in toluene from 36 μM to 1.0 μM (referring to **1**) and then mixing for 12 h did not cause a distinct decrease in the molar absorption of the ICD signals

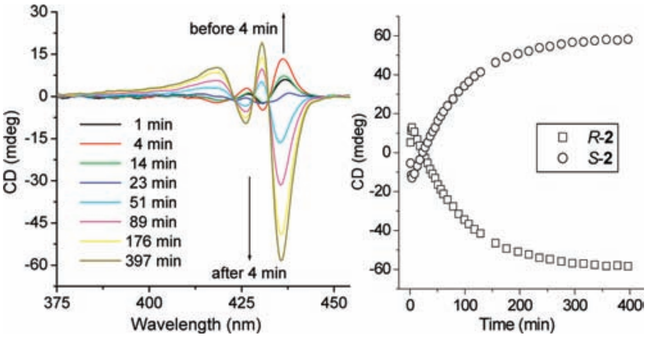


Figure 4. (left) ICD spectra of **1** (45 μM) upon mixing with (*R*)-**2** (7.5 μM) in toluene at 25 °C. (right) ICD intensities of **1** (45 μM) at 435.5 nm in the presence of (*R*)- and (*S*)-**2** (7.5 μM) at different times.

(Figure S18), and raising the temperature from 10 to 60 °C also induced no discernible reduction in the signals (Figure S19), which again showed the high stability of the new layered supramolecular copolymers.

The above CD results were consistent with the UV−vis observations, further indicating that there existed two different binding patterns between hexamer $(\mathbf{1})_6$ and chiral **2** at different assembling stages. The signal at 426 nm matched the Soret absorption of the zinc porphyrin unit of **1**. Similar signals, along with an *x*-axis intercept (429 nm), were also displayed by the sandwich-style complex $\mathbf{3}\cdot(\mathbf{1})_6\cdot\mathbf{3}$ (Figure 2). Thus, **1** and **2** formed similar layered supramolecular substructures that were interlinked to generate the chiral supramolecular copolymer $[(\mathbf{1})_6\cdot\mathbf{2}]_n$. The strongest ICD signal at 435 nm originated from the long-distance through-space exciton coupling of the porphyrin units of different hexamer $(\mathbf{1})_6$ units,[16] induced by chiral **2** in an accumulative manner, which could occur only in the layered supramolecular copolymers, as shown in Scheme 1. The distortional signal at 430 nm might have resulted from the combination of the two exciton couplets at 426 and 435 nm.[17] Since complex $\mathbf{3}\cdot(\mathbf{1})_6\cdot\mathbf{3}$ formed only a very weak shoulder peak of opposite signals in the 410−420 nm region (Figure 2), the broad, strong signal around 418 nm induced by chiral **2** might be ascribed to the long-range exciton coupling of the heterocyclic cores of hexamer $(\mathbf{1})_6$, providing further support for the formation of the layered chiral supramolecular copolymer from **1** and **2**. As expected, mixtures of **1** and (*R*)-**2** in polar methanol and DMSO were CD-silent. In chloroform, the mixture displayed ICD signals similar to those of the mixture of **1** and (*R*)-**3** and were not time-dependent (Figure S20). These results suggest that in chloroform, **1** and (*R*)-**2** did not form long copolymers. Instead, they might just form short layered co-oligomers with a binding pattern similar to that between **1** and (*R*)-**3**.

Static light scattering (SLS) experiments revealed that the scattered intensity of the mixture of **1** and **2** in toluene solution was also time-dependent (Figure 5 left). The experiments were carried out at two scattering angles (45° and 60°). For the first series, the scattered intensity of a solution of pure **1** of the same concentration was measured to be ~26 kcps. Upon addition of (*R*)-**2**, the scattered intensity increased gradually, reflecting an increase in the degree of copolymerization,[18] and reached maximum after ~3 h. The scattered intensity measured at 60° displayed a similar time-dependent increase. These results were consistent with the above UV−vis and CD observations and also implied that the dynamic optimization of the supramolecular chirality occurred simultaneously in the copolymers. SLS experiments were further performed to evaluate the average molecular weight of the supramolecular copolymers in toluene (Figure 5 right),[18] and a value of ≥4.2 × 10^6 g mol^{-1} was obtained. This value corresponded to a copolymerization degree of ≥459, reflecting the high efficiency of the new multicovalency-driven binding motif.

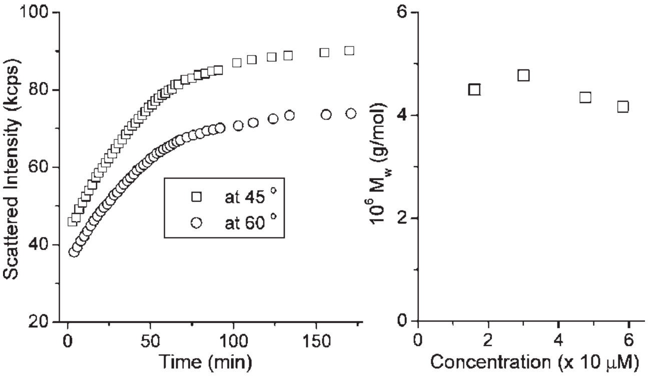


Figure 5. (left) Scattered intensity of the mixture of **1** (90 μM) and (*R*)-**2** (15 μM) in toluene as a function of time. (right) SLS measurements of the apparent molecular weight of the supramolecular copolymer $[(\mathbf{1})_6\cdot(R)\text{-}\mathbf{2}]_n$ at various concentrations of **1** in toluene at 25 °C.

The UV−vis and CD spectra of the solution mixture of **1** and **3** did not display time-dependence. Thus, the remarkable time-dependence of the ICD spectra of the mixture of **1** and **2** might reflect the dynamic features of the coordination and chirality matching during the formation of the chiral supramolecular copolymers. The induced Cotton effects at the early stage should be attributed to the formation of dynamically controlled chiral supramolecular complexes or co-oligomers in which the hexameric cores of **1** are arranged in a less-ordered manner. This process was entropically favored and reached a maximum in ~4 min. The SLS results showed that the resulting coaggregates had relatively small sizes and could not combine to form long copolymers. The following reversal and amplification of the ICD signals indicated that these first-formed short supramolecular structures were less stable and thus were transformed into more stable, thermodynamically controlled chiral supramolecular copolymers in which the bonded zinc porphyrin hexamer substructures were arranged in a more ordered way. This process took several hours to complete because it required the decomposition of the stable hexamer $(\mathbf{1})_6$ as well as the strong cooperative Zn−N coordination bonds in the complexes.[19] In addition, the chirality optimization and the chain increase of the copolymers should occur simultaneously.

In conclusion, we have demonstrated that layered chiral supramolecular copolymers of high molecular weight can be constructed from a C_6-symmetric hydrogen-bonding-driven hexamer and a C_3-symmetric chiral hexadentate linker. The high stability of the new supramolecular copolymers is endowed by the multivalent or cooperative complexation between conventional zinc porphyrin and pyridine units. The high stability of the new binding pattern results in strong supramolecular chirality, the formation of which occurs through self-optimization, which is common in biological systems. One future work will point to the design of chiral pyridine-attached heterocyclic derivatives. An investigation of the assembly behavior of their mixtures with **1** at varying molar ratios might reveal interesting new supramolecular chirality and/or self-sorting phenomena in this type of layered supramolecular copolymers.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. General experimental procedures, synthesis and characterization, ^{1}H and ^{13}C NMR spectra, and additional UV−vis and CD spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) Ciferri, A. *Supramolecular Polymers*; Marcel-Dekker: New York, 2005.

(2) (a) Brunsveld, L.; Folmer, B. J. B.; Meijer, E. W.; Sijbesma, R. P. *Chem. Rev.* **2001**, *101*, 4071. (b) Lehn, J.-M. *Prog. Polym. Sci.* **2005**, *30*, 814. (c) Harada, A.; Takashima, Y.; Yamaguchi, H. *Chem. Soc. Rev.* **2009**, *38*, 875. (d) Huang, F.; Gibson, H. W. *Prog. Polym. Sci.* **2005**, *30*, 982. (e) Rasa, M.; Schubert, U. S. *Soft Matter* **2006**, *2*, 561. (f) Serpe, M. J.; Craig, S. L. *Langmuir* **2007**, *23*, 1626. (g) Rieth, S.; Baddeley, C.; Badjic, J. D. *Soft Matter* **2007**, *3*, 137. (h) Weck, M. *Polym. Int.* **2007**, *56*, 453. (i) De Greef, T. F. A.; Smulders, M. M. J.; Wolffs, M.; Schenning, A. P. H. J.; Sijbesma, R. P.; Meijer, E. W. *Chem. Rev.* **2009**, *109*, 5687. (j) Niu, Z.; Gibson, H. W. *Chem. Rev.* **2009**, *109*, 6024. (k) Fox, J. D.; Rowan, S. J. *Macromolecules* **2009**, *42*, 6823. (l) Fang, L.; Olson, M. A.; Benitez, D.; Tkatchouk, E.; Goddard, W. A., III; Stoddart, J. F. *Chem. Soc. Rev.* **2010**, *39*, 17.

(3) (a) Wietor, J.-L.; van Beek, D. J. M.; Peters, G. W.; Mendes, E.; Sijbesma, R. P. *Macromolecules* **2011**, *44*, 1211. (b) Smulders, M. M. J; Filot, I. A. W; Leenders, J. M. A; van der Schoot, P.; Palmans, A. R. A; Schenning, A. P. H. J; Meijer, E. W. *J. Am. Chem. Soc.* **2010**, *132*, 611. (c) Shokrollahi, P.; Mirzadeh, H.; Huck, W. T. S.; Scherman, O. A. *Polymer* **2010**, *51*, 6303. (d) Todd, E. M.; Zimmerman, S. C. *Tetrahedron* **2008**, *64*, 8558. (e) Leung, K. C.-F.; Mendes, P. M.; Magonov, S. N.; Northrop, B. H.; Kim, S.; Patel, K.; Flood, A. H.; Tseng, H.-R.; Stoddart, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 10707.

(4) (a) Miyawaki, A.; Takashima, Y.; Yamaguchi, H.; Harada, A. *Tetrahedron* **2008**, *64*, 8355. (b) Zhang, Z.; Luo, Y.; Chen, J.; Dong, S.; Yu, Y.; Ma, Z.; Huang, F. *Angew. Chem., Int. Ed.* **2011**, *50*, 1397.

(5) (a) Burnworth, M.; Tang, L.; Kumpfer, J. R.; Duncan, A. J.; Beyer, F. L.; Fiore, G. L.; Rowan, S. J.; Weder, C. *Nature* **2011**, *472*, 334. (b) Xu, D.-H.; Liu, C.-Y.; Craig, S. L. *Macromolecules* **2011**, *44*, 2343. (c) Jeon, S. L.; Loveless, D. M.; Craig, S. L. *Supramol. Chem.* **2010**, *22*, 697. (d) Kumpfer, J. R.; Jin, J.; Rowan, S. J. *J. Mater. Chem.* **2010**, *20*, 145. (e) Weng, W.; Li, Z.; Jamieson, A. M.; Rowan, S. J. *Soft Matter* **2009**, *5*, 4647. (f) Chiper, M.; Hoogenboom, R.; Schubert, U. S. *Macromol. Rapid Commun.* **2009**, *30*, 565.

(6) (a) Niu, Z.; Huang, F.; Gibson, H. W. *J. Am. Chem. Soc.* **2011**, *133*, 2836. (b) Wang, F.; Zhang, J.; Ding, X.; Dong, S.; Liu, M.; Zheng, B.; Li, S.; Wu, L.; Yu, Y.; Gibson, H. W.; Huang, F. *Angew. Chem., Int. Ed.* **2010**, *49*, 1090. (c) Lee, M.; Schoonover, D. V.; Gies, A. P.; Hercules, D. M.; Gibson, H. W. *Macromolecules* **2009**, *42*, 6483. (d) Liu, Y.; Yu, Y.; Gao, J.; Wang, Z.; Zhang, X. *Angew. Chem., Int. Ed.* **2010**, *49*, 6576.

(7) (a) Blight, B. A.; Hunter, C. A.; Leigh, D. A.; McNab, H.; Thomson, P. I. T. *Nat. Chem.* **2011**, *3*, 244. (b) Zhao, X.; Wang, X.-Z.; Jiang, X.-K.; Chen, Y.-Q.; Li, Z.-T.; Chen, G.-J. *J. Am. Chem. Soc.* **2003**, *125*, 15128. (c) Folmer, B. J. B.; Sijbesma, R. P.; Meijer, E. W. *J. Am. Chem. Soc.* **2001**, *123*, 2093. (d) Beijer, F. H.; Sijbesma, R. P.; Kooijman, H.; Spek, A. L.; Meijer, E. W. *J. Am. Chem. Soc.* **1998**, *120*, 6761. (e) Corbin, P. S.; Zimmerman, S. C. *J. Am. Chem. Soc.* **1998**, *120*, 9710.

(8) (a) Martos, V.; Castreno, P.; Valero, J.; de Mendoza, J. *Curr. Opin. Chem. Biol.* **2008**, *12*, 698. (b) Badjic, J. D.; Nelson, A.; Cantrill, S. J.; Turnbull, W. B.; Stoddart, J. F. *Acc. Chem. Res.* **2005**, *38*, 723. (c) Mulder, A.; Huskens, J.; Reinhoudt, D. N. *Org. Biomol. Chem.* **2004**, *2*, 3409.

(9) (a) Badjic, J. D.; Cantrill, S. J.; Stoddart, J. F. *J. Am. Chem. Soc.* **2004**, *126*, 2288. (b) Broeren, M. A. C.; van Dongen, J. L. J.; Pittelkow, M.; Christensen, J. B.; van Genderen, M. H. P.; Meijer, E. W. *Angew. Chem., Int. Ed.* **2004**, *43*, 3557. (c) Huskens, J.; Mulder, A.; Auletta, T.; Nijhuis, C. A.; Ludden, M. J. W.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **2004**, *126*, 6784. (d) Zhu, J.; Lin, J.-B.; Xu, Y.-X.; Shao, X.-B.; Jiang, X.-K.; Li, Z.-T. *J. Am. Chem. Soc.* **2006**, *128*, 12307.

(10) Yang, X.; Hua, F.; Yamato, K.; Ruckenstein, E.; Gong, B.; Kim, W.; Ryu, C. Y. *Angew. Chem., Int. Ed.* **2004**, *43*, 6471.

(11) (a) Besenius, P.; Portale, G.; Bomans, P. H. H.; Janssen, H. M.; Palmans, A. R. A.; Meijer, E. W. *Proc. Natl. Acad. Sci. U.S.A.* **2010**, *107*, 17888. (b) Stals, P. J. M.; Everts, J. C.; de Bruijn, R.; Filot, I. A. W.; Smulders, M. M. J.; Martin-Rapun, R.; Pidko, E. A.; de Greef, T. F. A.; Palmans, A. R. A.; Meijer, E. W. *Chem.—Eur. J.* **2010**, *16*, 810.

(12) Chen, S.-G.; Fu, Y.-C.; Wang, G.-T.; Li, G.-Y.; Ma, Y.; Jiang, X.-K.; Li, Z.-T. *Tetrahedron* **2010**, *66*, 4057.

(13) (a) Kolotuchin, S. V.; Zimmerman, S. C. *J. Am. Chem. Soc.* **1998**, *120*, 9092. (b) Ma, Y.; Kolotuchin, S. V.; Zimmerman, S. C. *J. Am. Chem. Soc.* **2002**, *124*, 13757.

(14) Koshland, D. E. *Proc. Natl. Acad. Sci. U.S.A.* **1958**, *44*, 98.

(15) Nishide, H.; Doi, R.; Oyaizu, K.; Tsuchida, E. *J. Org. Chem.* **2001**, *66*, 1680.

(16) Mammana, A.; Pescitelli, G.; Asakawa, T.; Jockusch, S.; Petrovic, A. G.; Monaco, R. R.; Purrello, R.; Turro, N. J.; Nakanishi, K.; Ellestad, G. A.; Balaz, M.; Berova, N. *Chem.—Eur. J.* **2009**, *15*, 11853.

(17) Berova, N.; Nakanishi, K.; Woody, R. W. *Circular Dichroism*; Wiley-VCH: New York, 2000; p 338.

(18) Wyatt, P. J. *Anal. Chim. Acta* **1993**, *272*, 1.

(19) Scanning electron microscopy and transmission electron microscopy measurements showed that the mixture of **1** and (*R*)-**2** in toluene did not generate fibrous microstructures on the surface upon evaporation of the solvent. In view of the weakness of the hydrogen bonding, it is reasonable to propose that upon transfer from the solution to the surface, the $(A)_6$−B supramolecular copolymers break because the disklike hydrogen-bonded hexamer of **1** is not be stable enough to stand on the surface. As a result, long layered aggregates were not formed on the surface.