

Light-Driven Linear Helical Supramolecular Polymer Formed by Molecular-Recognition-Directed Self-Assembly of Bis(*p*-sulfonatocalix[4]arene) and Pseudorotaxane

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S Supporting Information

ABSTRACT: A light-driven, linear, chiral supramolecular polymer was constructed in water by host–guest molecular recognition between bis(*p*-sulfonatocalix[4]-arene) and the α -cyclodextrin-based pseudo[3]rotaxane containing axially chiral 1,1'-binaphthyl and photoresponsive azobenzene moieties. The successful supramolecular polymerization by non-covalent host–guest molecular recognition was confirmed by ¹H NMR spectroscopy and dynamic light scattering (DLS) measurements, and its photoresponsive behavior was investigated by UV–vis absorption spectroscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM), and transmission electron microscopy (TEM). The chirality of this supramolecular polymer was confirmed by circular dichroism spectroscopy. The dramatic morphology change of this chiral polymer driven by light was observed in SEM, AFM and TEM images. More interestingly, dynamically self-assembled, light-driven, single-helical linear supramolecular polymer molecules with lengths of hundreds of nanometers to micrometers in water were directly observed in their native state using cryo-TEM measurements. The observation of considerably lengthy individual supramolecular polymer molecules indicates that the molecular self-assembly in water by non-covalent host–guest molecular recognition is sufficiently strong to form the supramolecular polymer. Moreover, preliminary molecular modeling was performed to substantiate this interesting photoresponsive supramolecular structure.

The ability to control molecular self-assembly with tailored properties by non-covalent interactions is a major driving force in the bottom-up nanofabrication of molecular devices.¹ Supramolecular polymers, that is, discrete small monomers held together by reversible non-covalent interactions such as hydrogen bonding, π – π stacking, and host–guest molecular recognition, represent a striking example because of their intrinsic non-covalent self-assembled nature and the resultant unique properties, such as self-healing of structural defects.^{2–5} The functional groups of individual monomers can not only provide linkages for the creation of supramolecular polymers but also confer well-defined functionalities to these polymers.⁶ For example, photoresponsive monomer molecules can provide

a path for remote control of the resulting supramolecular polymer morphology or formation by light.^{7–12} Chiral monomers can impart chirality into the supramolecular polymers, leading to the formation of chiral suprastructures that may exhibit some fascinating chirooptical properties.¹³

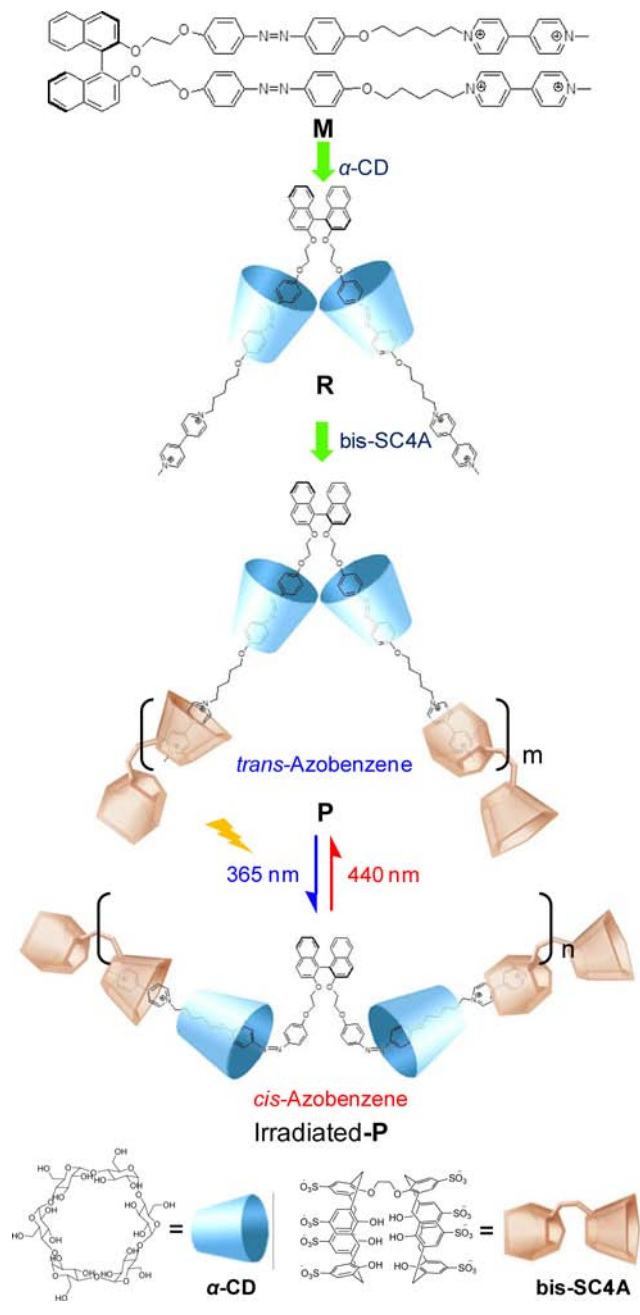
It is well-established that molecular self-assembly usually requires high-affinity binding recognition motifs between small molecular monomers to form truly supramolecular polymers in solution. A challenge in this field is to find complementary small molecules capable of strong self-assembly by non-covalent interactions in solution to furnish multifunctional supramolecular polymers. Here we report the design, construction, and characterization of a novel light-driven linear chiral supramolecular polymer formed by the molecular-recognition-directed self-assembly of bis(*p*-sulfonatocalix[4]arene) (**bis-SC4A**) and the α -cyclodextrin (α -CD)-based pseudo[3]-rotaxane **R** (Scheme 1). The dynamically self-assembled single-helical structure of the resulting light-driven chiral supramolecular polymer molecules in water was observed in its native state using cryo-TEM measurements. To the best of our knowledge, these are the first dynamically self-assembled, light-driven single-helical linear supramolecular polymer molecules with lengths of hundreds of nanometers to micrometers in solution to be directly observed in the native state. The interest behind the design of the new light-driven supramolecular polymer based on the **bis-SC4A**/4,4'-bipyridinium host/guest pair mainly results from their very high host–guest complexation stability to form a truly main-chain supramolecular polymer in water.^{11,14} The inclusion of hydrophilic α -CD onto the azobenzene moieties of monomer molecule **M** can increase the monomer's water solubility and change the hydrophilicity position upon light irradiation. The introduction of photoresponsive azobenzene building blocks in the monomer can induce a dramatic configuration change upon light irradiation and change the α -CD inclusion position, allowing the supramolecular self-assembly to be tuned. Meanwhile, the axially chiral 1,1'-binaphthyl helps to introduce chirality into the linear polymer to form the helical supramolecular polymer.

The construction and synthesis of the supramolecular polymer **P** was straightforward [see the Supporting Information

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Scheme 1. Molecular Structures of Monomers M, α -CD, and bis-SC4A and a Schematic Description of the Self-Assembly Process for Forming α -CD-Based Pseudo[3]rotaxane R, the Supramolecular Polymer P with Azobenzene in the Trans Configuration, and the Corresponding UV-Irradiated P Containing *cis*-Azobenzene (Br⁻, I⁻, and Na⁺ Ions Have Been Omitted for Clarity)



(SI)]. The successful inclusion of α -CDs onto the azobenzene moieties of monomer M and the successful complexation between the host bis-SC4A and the guest 4,4'-bipyridinium moieties in M were confirmed by ¹H NMR spectroscopy (Figure 1). The monomer M with no α -CDs included onto the azobenzene groups showed two sets of peaks (H_e, H_h and H_f, H_g) with similar positions that were assigned to the aromatic protons of the azobenzene units (Figure 1A). However, in the supramolecular polymer P with α -CDs included onto the azobenzene groups, the corresponding protons lost their

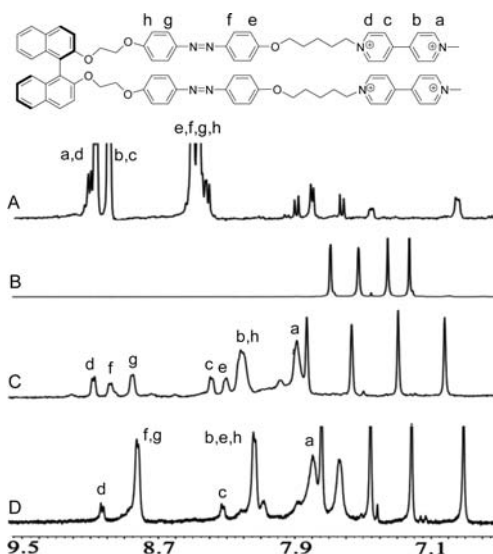


Figure 1. Partial ¹H NMR spectra (D₂O, 400 MHz, 293 K) of (A) guest monomer M, (B) host monomer bis-SC4A, (C) supramolecular polymer P, and (D) P after irradiation with 365 nm light.

symmetry dramatically, and an obvious splitting appeared: H_f and H_g exhibited visible downfield shifts, while H_e and H_h were shifted upfield. The presence of bis-SC4A in the supramolecular polymer P made all of the 4,4'-bipyridinium protons (H_a–H_d) undergo pronounced upfield shifts as a result of shielding due to the ring-current effect of the aromatic nuclei of bis-SC4A (Figure 1C).^{11,14} This confirmed that each 4,4'-bipyridinium moiety in monomer M was successfully encapsulated into a cavity of bis-SC4A. As described in Scheme 1, UV irradiation induces the trans–cis photoisomerization of azobenzene, which makes the α -CDs move away from the azobenzenes as a result of the shape change.⁷ Thus, the peaks H_f, H_g and H_e, H_h that were split in the supramolecular polymer P were observed to recombine, forming two peaks in the spectrum of the corresponding UV-irradiated supramolecular polymer P (Figure 1D). However, since α -CDs still partially affected the azobenzenes, they had an impact on the peak positions. Compared with H_e–H_h, the H_a–H_d signals of the 4,4'-bipyridinium groups exhibited only small shifts after UV irradiation. Therefore, from the ¹H NMR analysis we infer that there was an azobenzene configuration change upon UV irradiation.

UV–vis absorption and circular dichroism spectra were also used to illustrate the formation of the supramolecular polymer. Monomer M and α -CD-based pseudo[3]rotaxane R showed very similar UV–vis absorption spectra, indicating that the inclusion of α -CDs on monomer M did not influence its absorption much (Figure S2 in the SI). The successful complexation of R and bis-SC4A to form supramolecular polymer P could be observed because the P curve was the sum of the R and bis-SC4A curves. As a result of azobenzene trans–cis photoisomerization upon light irradiation, the pseudorotaxane R and supramolecular polymer P showed the expected photoresponsive behavior (Figures S3–S6). It took about 10 and 15 min of 365 nm light irradiation for pseudorotaxane R and supramolecular polymer P, respectively, to reach their photostationary states. This is a result of the fact that the larger size of supramolecular polymer P compared with pseudorotaxane R makes it more difficult to isomerize the azobenzene units by light irradiation accompanied by driving the α -CD

macrocycle to shuttle back and forth along the chain. Moreover, supramolecular polymer **P** showed chirality, as evidenced by the circular dichroism spectra (Figure S6).

To investigate the morphology changes induced by light, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) measurements were undertaken. Neither the host **bis-SC4A** nor the guest pseudorotaxane **R** individually showed any discernible suprastructure (Figure 2A,B). When

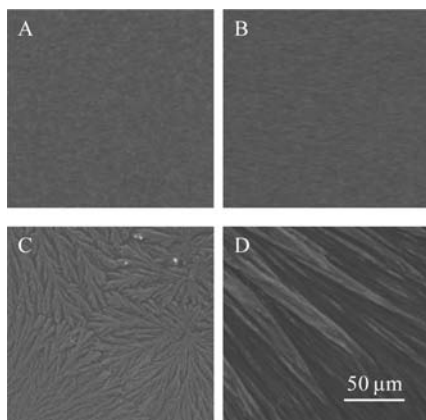


Figure 2. SEM images of dried cast films of (A) guest pseudorotaxane **R**, (b) host **bis-SC4A**, (C) supramolecular polymer **P**, and (D) **P** after irradiation at 365 nm on glass slides.

they combined through the inclusion and complexation process to form supramolecular polymer **P**, an obvious starlike morphology with multiple branches appeared (Figure 2C), indicating successful supramolecular self-assembly. However, the morphology changed significantly after **P** was irradiated with UV light, appearing as linear belts (Figure 2D).

Dynamic light scattering (DLS) measurements in water were performed to characterize the polymer further. A hydrodynamic radius of ca. 200 nm was found, clearly indicating the existence of the highly polymerized supramolecular assemblies in water (Figure S8). The morphology of the supramolecular polymer before and after UV irradiation was also investigated by atomic force microscopy (AFM). As expected, a linear polymer with a length of ca. 2 μm was observed after light irradiation (Figure S12).

To explore the dynamic self-assembly of supramolecular polymer **P** in its native state in water, we used cryogenic TEM (cryo-TEM), in which the dynamic self-assembled structure in water was accurately preserved by a rapid-plunge freezing method. The cryo-TEM images of supramolecular polymer **P** in water before and after UV irradiation showed distinctly different supramolecular self-assembled morphologies (Figure 3A,B). Interestingly, linear single-helical supramolecular polymer molecules with diameters of ca. 2 nm (in agreement with the molecular modeling results) and lengths of hundreds of nanometers to micrometers in water were clearly observed after UV irradiation of **P**. This could be ascribed to the fact that UV-irradiated **P** containing *cis*-azobenzene has a more straight structure compared with **P** containing *trans*-azobenzene, providing a feasible path for the formation of a linear polymer as described in Scheme 1. Moreover, it is interesting to point out that the single-helical structure of irradiated supramolecular polymer **P** can be seen in Figure 3C, where dark and light areas appear alternatively in the polymer chains. The helical structure

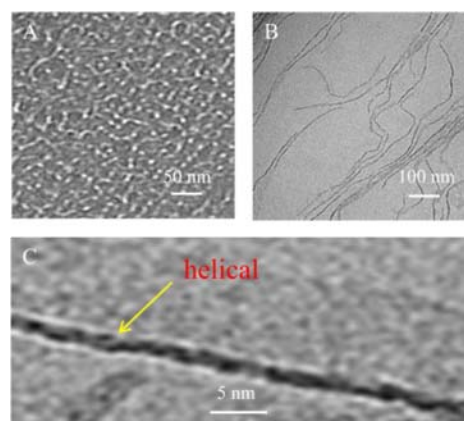


Figure 3. (A, B) Cryo-TEM images of supramolecular polymer **P** (20 μM) in H_2O (A) before and (B) after UV irradiation at 365 nm. (C) Magnified image of (B) in which an obvious linear single-helical supramolecular polymer can be observed.

results from the introduction of the axially chiral 1,1'-binaphthyl units in supramolecular polymer **P**.

To provide further corroboration of the photoresponsive supramolecular structure change, preliminary molecular modeling was performed. On the basis of density functional theory calculations at the B3LYP level, the most stable states of the two core structures composed of the chiral 1,1'-binaphthyl center combined with two azobenzene arms in either the *trans* or *cis* configuration were obtained (Figure S13).¹⁵ The *trans* structure had two very close arms (V shape), while the *cis* structure had two very open arms (linear shape). With inclusion of an α -CD onto each of the *trans*-azobenzene units, the distance between the two arms became slightly broader because of the large steric hindrance, but the structure was still V-shaped. When the 4,4'-bipyridinium and **bis-SC4A** were also taken into consideration, the complete supramolecular structure could be proposed by molecular modeling, providing an explanation of why the supramolecular polymer **P** formed the linear morphology after UV irradiation. On one hand, for **P** containing *trans*-azobenzene, the supramolecular polymer would have less chance to form a linear main-chain structure because of the limitations of the structure. On the other hand, the supramolecules after UV irradiation clearly displayed a *cis* configuration leading to a linear structure.

In conclusion, a novel light-driven, linear, helical, chiral supramolecular polymer was successfully constructed in water by non-covalent host–guest molecular recognition between the calixarene **bis-SC4A** and the pseudorotaxane **R** containing an axially chiral 1,1'-binaphthyl unit and two α -CD-included azobenzene arms terminated with 4,4'-bipyridinium units. The resulting chiral supramolecular polymer was investigated by ¹H NMR, UV–vis absorption, and circular dichroism spectra, DLS, SEM, AFM, and TEM measurements. The dramatic light-driven morphology change of this chiral polymer was observed in SEM, AFM, and TEM images. More interestingly, dynamically self-assembled, light-driven, single-helical supramolecular polymer molecules with lengths of hundreds of nanometers to micrometers in water were for the first time observed in the native state using cryo-TEM measurements. Preliminary molecular modeling was performed to substantiate this photoresponsive supramolecular structure. This work provides an exciting impetus for building controllable supramolecular polymers with tailored functionalities

■ ASSOCIATED CONTENT

■ Supporting Information

Synthesis of intermediates and supramolecular polymers; ¹H NMR, UV–vis, and circular dichroism spectra; DLS measurements; SEM, cryo-TEM, and AFM images; and molecular modeling results for supramolecular structures in different configurations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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- (15) With α -CD, viologen, and bis-SC4A, it was too complicated to do the accurate calculation. However, on the basis of the simulated results, reasonable supramolecular structures were proposed that could still provide valuable information to explain the experimental observations.