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A combination of the advantages of supramolecular chemistry and materials science has expedited the emergence of supramolecular polymers, in which the repetition of monomeric units is mainly governed by highly directional and dynamic noncovalent interactions.[1] The noncovalent route is a promising approach towards highly functional materials, and has led to a recent surge in the production of self-healing and adaptive supramolecular polymers.[2] Until now, several noncovalent interactions, including metal coordination, π–π stacking, hydrogen bonding, as well as host–guest interactions, have been extensively used to fabricate supramolecular polymers.[3] Among the macrocyclic hosts, cyclodextrins and crown ethers are most commonly used in supramolecular polymerization,[4] whereas supramolecular polymers directed by host–guest recognition of calixarenes have only occasionally been reported.[5] Some typical host–guest pairs are p-tert-butylcalix[5]arene and primary alkylammonium ions, covalently linked double-calix[5]arenes and C60, and water-soluble calixarenes and organic cations.[6] Previously reported calixarene-based supramolecular polymers have been formed mainly through the preorganized scaffolds of calixarenes, and host–guest interactions offered by calixarene cavities were not exploited as the dominant driving force for polymerization.[7]

p-Sulfonatocalix[n]arenes (SCnAs) are important biocompatible and water-soluble calixarene derivatives that have fascinating binding properties, especially with organic cations.[6c] Consequently, SCnAs are widely used in highly diverse applications in molecular recognition/sensing, crystal engineering, catalysis, amphiphilicity, and biomedical applications.[8] By using homoditopic bis-p-sulfonatocalix[n]arenes (bisSCnA, n = 4, 5), we previously designed a series of water-soluble supramolecular polymers based on the molecular recognition of SCnAs by organic cations.[9] Subsequent to our study, Tian an co-workers reported a dual-stimulus-responsive supramolecular polymer based on iterative intermolecular inclusion of bisSC4A and a heteroditopic flexible guest.[10] Most previous supramolecular polymers consist of calixarenes and guests with flexible spacers.[11] It has been well-established that building blocks with flexible spacers have disadvantages for polymerization.[12] Herein, we report a linear supramolecular polymer based on molecular recognition of bisSC4A by a homoditopic bis-4-(N-methylpyridinium)azobenzene (AzobPy) with rigid azobenzene[13] as spacer (Scheme 1). It was anticipated that the isomerization of AzobPy would result in the morphological conversion of the supramolecular assembly upon irradiation with UV and visible light.

Scheme 1. Structural illustration of bisSC4A and AzobPy, and schematic of the morphological conversion between linear supramolecular polymer and spherical nanoparticle based on the trans–cis photoisomerization of AzobPy induced by light stimulus (counterions are omitted for clarity).

1H NMR titration was used to investigate the binding behavior of the supramolecular assembly AzobPy@bisSC4A. As a result of the ring-current effect of the aromatic nuclei in the calixarene, the signals of the AzobPy protons shift upfield from where they occur in free solution as the host concentration increases. The complexation-induced shifts (Δδ) follow the order: H1 > H2 > H3 > H4 > H5 > H6 (Figure 1 and Figure S1). These shifts indicate that AzobPy...
We performed viscosity measurements to validate the formation of the supramolecular polymer derived from the two ditopic building blocks AzobPy and bisSC4A in aqueous solution. As shown in Figure 3a, the specific viscosity of a solution of AzobPy@bisSC4A varies exponentially with its concentration, which indicates the formation of a supramolecular polymer of increasing size. In contrast, under the same conditions solutions of the monomer and complex have linear relations between specific viscosity and concentration, which indicates that no significant physical entanglements or noncovalent intermolecular interactions oc-

is captured by bisSC4A with the pyridinium end groups deeply immersed into the cavities, while the azobenzene spacer remains outside.[14] The $n\pi$ supramolecular polymerization can be simplified by the isodesmic or equal-K model. Therefore, the complexation stability constant between ditopic host and guest can be calculated as $716 \text{m}^{-1}$ by using the nonlinear least-squares curve-fitting method[15] and fitting the chemical shifts of H1 proton in the $^1$H NMR spectra upon gradual addition of bisSC4A (Figure S2). Furthermore, the morphology of AzobPy@bisSC4A was investigated by atomic force microscopy (AFM), as shown in Figure 2. As expected, the resultant supramolecular aggre-

gate has different lengths and widths of 1D linear structures. Those linear arrays overlap together to form a 2D planar netlike morphology with a size in the micron range. The average height is 1.3 nm, which is identical to the upper-rim size of SC4A. AzobPy@bisSC4A has a negative charge, which attracts guest counterions aligned at the profile of polymeric assembly. This significant electrostatic interaction between linear assemblies and guest counterions may cause the formation of different width arrays fabricated from a single-molecule linear assembly.
Further irradiation of this solution with visible light at 450 nm, the spectra changes in Figure 4a clearly show the photoisomerization of AzobPy from the trans to the cis state. Upon irradiating an aqueous solution of AzobPy with light at 365 and 450 nm alternately, this reversible photoisomerization process could be repeated several cycles without any fatigue (Figure S4). Moreover, the trans–cis conversion of AzobPy, which can be calculated by integration of the signals in the 1H NMR spectrum (Figure S5a–c), is quantifiable. When a solution of stable trans-AzobPy was irradiated with UV light for 10 min, a series of new signals appeared in the 1H NMR spectrum. These signals are attributed to the prottons of cis-AzobPy. The trans/cis ratio changed to approximately 40:60. In contrast, a photostationary state with a trans/cis isomer ratio of 67:33 was reached after subsequent irradiation of the already UV-irradiated solution with visible light for 30 min. Irradiation of AzobPy@bisSC4A with UV and visible light induces isomerization conversion between the trans and cis forms of the azobenzene derivative (Figure S5d–g). Upon irradiation at 365 nm for 10 min, the new set of resonances shown in Figure S5e appear, which belong to cis-AzobPy with two pyridinium groups still located inside of the cavity of sulfonatocalixarenes. This indicates that the photoisomerization process does not cause the disassembly of the binary polymer AzobPy@bisSC4A. In the photostationary state, approximately 59% of the guest units of the initial trans-AzobPy@bisSC4A assembly have been converted into the...
cis form, and further irradiation of this solution with visible light leads to a trans/cis isomer ratio of 68:32. The photostationary state shown in trace e in Figure S5 was regenerated from trace f after UV irradiation for 10 min, which indicates the morphological reversibility of the supramolecular assembly (Figure S5g). These results for the assembly are in good accord with the photoisomerization of AzobPy, which suggests that the complexation of the pyridinium group with bisSC4A does not affect the photochromic properties of the azobenzene spacer in AzobPy.

The morphology changes of AzobPy@bisSC4A upon UV irradiation at 365 nm were investigated by AFM and TEM. The aforementioned result shows that AzobPy with a rigid trans-isomer spacer can form a linear supramolecular polymer with ditopic bisSC4A. When the above system was irradiated by UV light at 365 nm, spherical nanoparticles were observed (Figure S5). These globular nanoparticles presumably came from the curved and folded linear assembly of AzobPy with bisSC4A, which was attributed to photoinduced isomerization conversion from trans-AzobPy to cis-AzobPy molecules. Upon irradiation with UV light, the straight trans-AzobPy bends and converts into the curved cis-AzobPy, which leads to the morphological folding and shrinking conversion of linear to irregularly winding globular structure. More powerful evidence for the contraction process of the linear polymer was derived from the DLS result. The average hydrodynamic diameter changed to 124 nm from 160 nm upon irradiation of AzobPy@bisSC4A at 365 nm. This value is a little larger than the diameter of approximately 57 nm measured in the TEM image because of the solvation effect of compact globular nanoparticles.

In conclusion, we successfully constructed a linear supramolecular polymer based on the intrinsically rigid guest trans-AzobPy and the ditopic host bisSC4A. Upon irradiation with UV light, the configuration of AzobPy changes from the trans to the cis form, which results in bending of the straight spacer. This isomerization of guest molecules further leads to folding of the linear assembly and the subsequent formation of supramolecular globular nanoparticles. The morphological conversion could be reversed by the configurational change of the azobenzene spacer between the trans and cis isomers upon alternate UV and visible irradiation. These results pave an alternative way for the future fabrication of more sophisticated photosensitive supramolecular systems.

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