

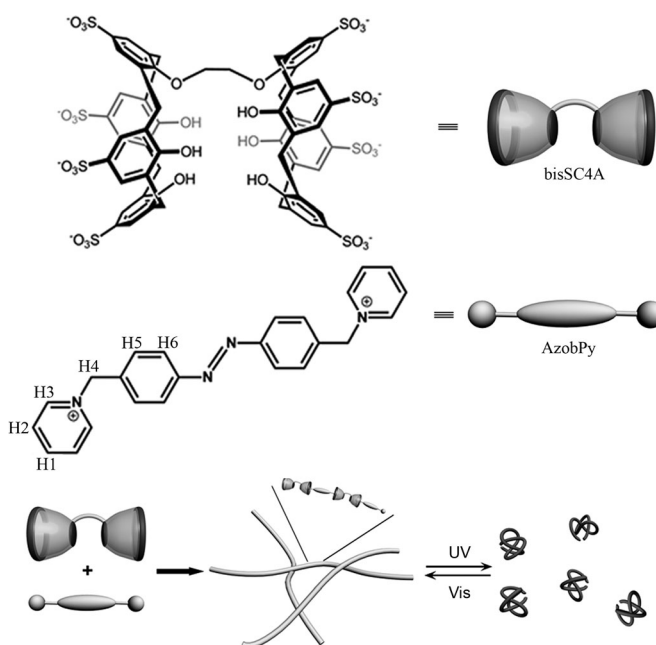
# *p*-Sulfonatocalix[4]arene Supramolecular Polymers: Formation by Host–Guest Interactions and Light Response

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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.<sup>[1]</sup> 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.<sup>[2]</sup> Until now, several noncovalent interactions, including metal coordination,  $\pi$ – $\pi$  stacking, hydrogen bonding, as well as host–guest interactions, have been extensively used to fabricate supramolecular polymers.<sup>[3]</sup> Among the macrocyclic hosts, cyclodextrins and crown ethers are most commonly used in supramolecular polymerization,<sup>[4]</sup> whereas supramolecular polymers directed by host–guest recognition of calixarenes have only occasionally been reported.<sup>[5]</sup> Some typical host–guest pairs are *p*-*tert*-butylcalix[5]arene and primary alkylammonium ions, covalently linked double-calix[5]arenes and C<sub>60</sub>, and water-soluble calixarenes and organic cations.<sup>[6]</sup> 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.<sup>[7]</sup>

*p*-Sulfonatocalix[*n*]arenes (SCnAs) are important biocompatible and water-soluble calixarene derivatives that have fascinating binding properties, especially with organic cations.<sup>[6c]</sup> Consequently, SCnAs are widely used in highly diverse applications in molecular recognition/sensing, crystal engineering, catalysis, amphiphilicity, and biomedical applications.<sup>[8]</sup> 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.<sup>[9]</sup> Subsequent to our study, Tian and co-workers reported a dual-stimulus-responsive supramolecular polymer based on iterative intermolecular inclusion of bisSC4A and a heteroditopic flexible guest.<sup>[10]</sup> Most previous supramolecular polymers consist of

calixarenes and guests with flexible spacers.<sup>[11]</sup> It has been well-established that building blocks with flexible spacers have disadvantages for polymerization.<sup>[12]</sup> 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<sup>[13]</sup> as spacer (Scheme 1). It was anticipated that the isomerization



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).

of AzobPy would result in the morphological conversion of the supramolecular assembly upon irradiation with UV and visible light.

<sup>1</sup>H 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 ( $\Delta\delta$ ) follow the order: H1 > H2 > H3 > H4 > H5 > H6 (Figure 1 and Figure S1). These shifts indicate that AzobPy

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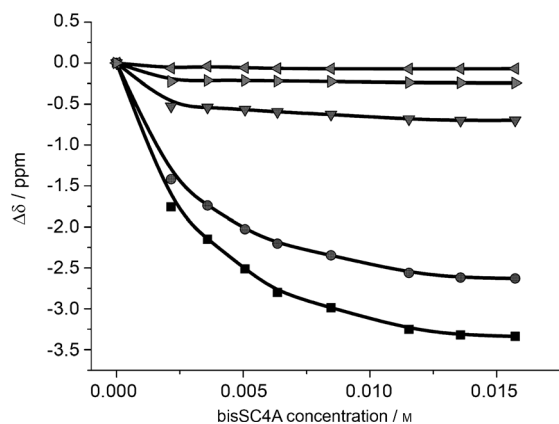


Figure 1. Complexation-induced shifts ( $\Delta\delta$ , ppm, 300 MHz,  $D_2O$ , 303 K) of the H1 (■), H2 (●), H4 (▼), H5 (◄), and H6 (►) protons of AzobPy (3.99 mM) in the presence of various concentrations of bisSC4A. (The chemical shifts of H3 can not be discriminated upon gradual addition of bisSC4A in the NMR spectra).

is captured by bisSC4A with the pyridinium end groups deeply immersed into the cavities, while the azobenzene spacer remains outside.<sup>[14]</sup> The  $n:n$  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  $716M^{-1}$  by using the nonlinear least-squares curve-fitting method<sup>[15]</sup> and fitting the chemical shifts of H1 proton in the  $^1H$  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 aggregate

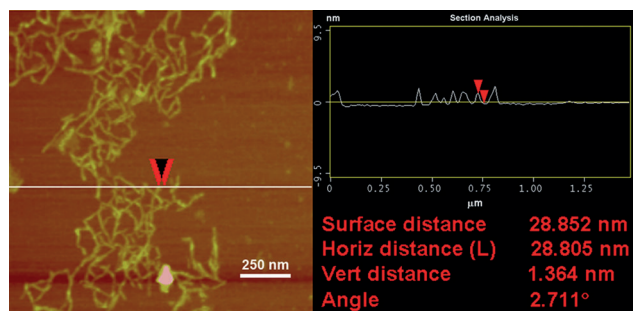


Figure 2. AFM image of the linear AzobPy@bisSC4A.

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.

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-

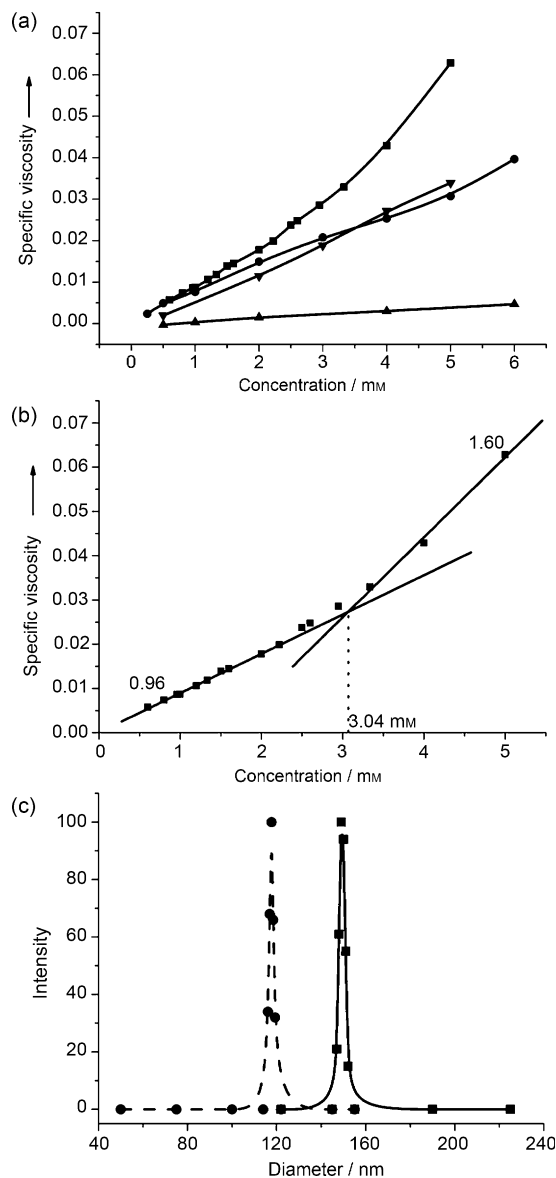


Figure 3. a) Specific viscosity of aqueous solutions of AzobPy@bisSC4A (■), AzobPy (▲), bisSC4A (●), and 2SC4A + AzobPy (▼) mixtures versus monomer concentration at 303 K. b) Slope (values on the curve) of double logarithmic plots of specific viscosity of an aqueous solution of AzobPy@bisSC4A versus concentration. c) Hydrodynamic diameter distribution of AzobPy@bisSC4A (4.5 mM) before (solid line) and after (dashed line) irradiation at 365 nm.

curred. Moreover, a viscosity transition of linear AzobPy@bisSC4A was characterized by a change of slope in the double-logarithmic plots of specific viscosity versus concentration (Figure 3b). The slope of curve in the low concentration region is 0.96, which is close to one. This result indicates that non-interacting monomers and/or oligomers with a constant size predominate in solution.<sup>[16]</sup> When the concentration increases above the critical polymerization concentration (CPC; approximately 3 mM), the double-logarithmic curve has a slope of approximately two, which implies the formation of linear polymers, the size of which continuously increase with concentration.<sup>[17]</sup> We also performed the dynamic light scattering (DLS, Figure 3c) and gel permeation chromatography (GPC, Figure S3) measurements above the CPC to support the theory of supramolecular polymer formation. The DLS result shows that only one relative sharp hydrodynamic diameter distribution of 160 nm was present. GPC measurement shows the degree of polymerization of AzobPy@bisSC4A. Two retention volumes of the assembly were obtained by the refractive index detector. The minor peak at 5.98 mL represents the polymer of AzobPy@bisSC4A. The major peak at 8.07 mL is assumed to be the fragments under high shear forces on the GPC column. Two weight-average molecular weights of  $2.1 \times 10^5$  and  $3.5 \times 10^4$  were obtained, which indicates an average of 19–114 alternating host and guest units in the linear assembly. Compared with the GPC results in our previous two studies,<sup>[9a,b]</sup> the lower stability constants of AzobPy and bisSC4A leads to the larger area of retention volume of the fragments.

It is accepted that azobenzene in AzobPy is a more rigid spacer than any alkyl one in ditopic guest molecule, which leads to the formation of linear supramolecular polymer in aforementioned results.<sup>[18]</sup> Controlling the configurational conversion of the azobenzene spacer by irradiation with UV and visible light is an effective way to modulate the morphology of supramolecular complexes.<sup>[19]</sup> In this case, we wondered whether the morphology of the linear supramolecular assembly could be altered upon UV irradiation and what the resultant structure would be. The photoresponse of AzobPy was examined by UV/vis and <sup>1</sup>H NMR spectroscopy. The UV/vis spectrum of *trans*-AzobPy has a strong absorption maximum at around 322 nm. As shown in Figure 4, irradiation with UV light at 365 nm resulted in bleaching of the main absorption band, accompanied by a slight increase in a new absorption band at around 425 nm. The absorption bands at 322 and 425 nm are ascribed to the  $\pi$ - $\pi^*$  transition of the *trans* form and  $n$ - $\pi^*$  of the *cis* form of the azobenzene spacer, respectively. The spectral changes in Figure 4a clearly show the photoisomerization of AzobPy from the *trans* to the *cis* state. Upon further irradiation of this solution with visible light at 450 nm, the  $\pi$ - $\pi^*$  absorption increases again, and concomitantly the  $n$ - $\pi^*$  absorption decreases slightly, which indicates that the photoisomerization of AzobPy from the *cis* to the *trans* state occurs. Upon irradiating an aqueous solution of AzobPy with light at 365 and 450 nm alternately, this rever-

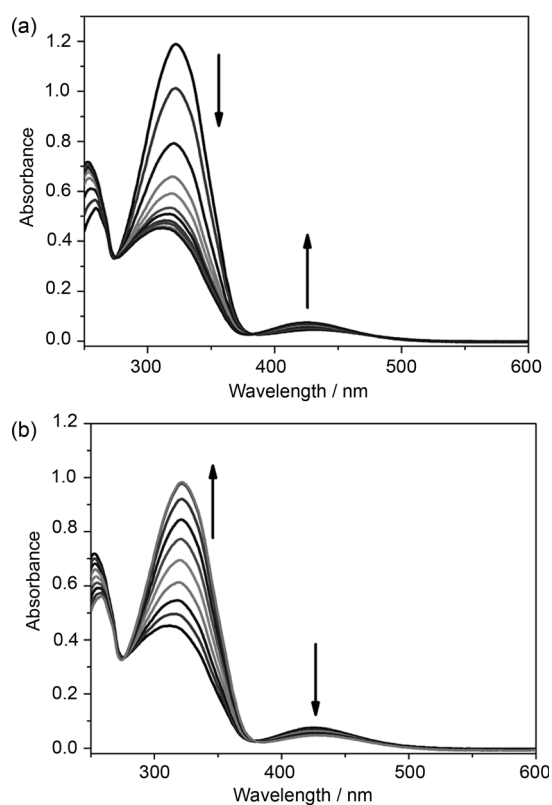


Figure 4. UV/vis absorption spectra of an aqueous solution of AzobPy (0.05 mM) recorded after a) (from bottom to top spectrum) 0, 5, 10, 15, 20, 25, 30, 35, 40, 50, and 60 s of UV irradiation at 365 nm and subsequently b) (from bottom to top spectrum) 0, 10, 20, 35, 60, 100, 150, 240, 540, and 720 s of visible-light irradiation at 450 nm. The spectra were recorded at 303 K and the arrows indicate the spectral evolution with different irradiation time.

sible 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 <sup>1</sup>H NMR spectrum (Figure S5 a–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 <sup>1</sup>H NMR spectrum. These signals are attributed to the protons 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 S5 d–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 5). These globular nanoparticles pre-

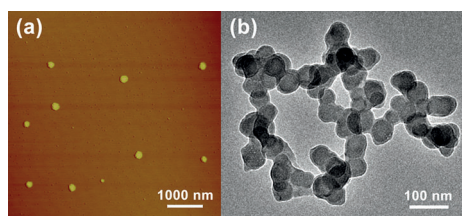


Figure 5. a) AFM and b) TEM images of AzobPy@bisSC4A after irradiation at 365 nm.

sumably 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 from 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 photoresponsive supramolecular systems.

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