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# Construction of a pillar[5]arene-based linear supramolecular polymer and a photo-responsive supramolecular network<sup>†</sup>

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A linear supramolecular polymer has been constructed from selfassembly of two complementary homoditopic monomers, an azobenzene-bridged pillar[5]arene dimer and a bisammonium salt, at high concentration based on the pillar[5]arene/secondary ammonium salt molecular recognition motif. This supramolecular polymer exhibited photo and pH dual-responsiveness. Polymer– oligomer and polymer–monomer transitions were reversibly regulated by UV/vis light irradiation and changing the solution pH, respectively. Furthermore, a photo-responsive supramolecular crosslinked liquid-crystalline polymer network based on the host– guest interactions between the azobenzene-bridged pillar[5]arene dimer and a secondary ammonium salt-functionalized poly(methyl acrylate) was fabricated.

## Introduction

Self-assembly is the autonomous organization of components into patterns or structures without human intervention.<sup>1</sup> Nature provides a wide range of ingenious and efficient selfassembly processes, such as the formation of proteins with precisely controlled nanostructures.<sup>2</sup> Inspired by these examples, scientists have tried their best to construct many dynamic, multicomponent systems with novel properties and intriguing functions.<sup>3</sup> Supramolecular polymers, which emerged from the combination of traditional polymer science and supramolecular chemistry, are polymeric arrays based on low molecular weight monomeric units brought together by noncovalent interactions, such as metal-ligand coordination, hydrophobic interactions, multiple hydrogen bonding and host-guest recognition,<sup>4</sup> and have captured more and more attention of scientists in recent years not only because they can exhibit partial properties of traditional polymers, but also because their controllable structures and functions make them excellent candidates for accommodative and

exquisite materials and enable their various applications, such as molecular sensing, membrane separation, or drugdelivery.<sup>5</sup> Therefore, supramolecular polymers are expected to strongly contribute to the development of materials science *via* the spontaneous but controlled generation of welldefined, functional nanostructures through the manipulation of the noncovalent forces that hold the monomeric units together.

Supramolecular polymers based on host-guest interactions exhibit novel properties and potential applications, not only for the formation of various well-defined macromolecular architectures but also for the preparation of responsive materials with properties that can be tuned by varying the environmental conditions such as temperature-change, pHchange, light irradiation, redox, or concentration change. Pillararenes,<sup>6</sup> a kind of emerging macrocyclic host next to crown ethers,<sup>7</sup> cyclodextrins,<sup>8</sup> calixarenes,<sup>9</sup> and cucurbiturils,<sup>10</sup> have been studied actively since they were found in 2008. Their intrinsic characteristics, including the unique symmetrical scaffold, facile functionalization and adjustable inclusion property, indicate prominent potential for the preparation of supramolecular polymers.

On account of its easy operation, non-invasiveness, low cost, remarkable sensitivity, and excellent penetration depth, a photo-stimulus is especially attractive among the multitudinous external stimuli.<sup>11</sup> Herein, we employed two complementary homoditopic monomers, an azobenzene-bridged pillar[5]arene dimer (*trans*-**DP5**) and a bisammonium salt (**G**), to construct a linear supramolecular polymer which possesses both photo-responsive and pH-responsive properties. Furthermore, a crosslinked supramolecular network was fabricated based on the host-guest interactions between the azobenzene-bridged pillar[5]arene dimer *trans*-**DP5** and a secondary ammoniumfunctionalized poly(methyl acrylate) **CP1**.

## **Results and discussion**

In previous studies,  $^{12}$  it has been demonstrated that long connections between the host and guest moieties of  $A_2B_2\mbox{-type}$ 



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Scheme 1 Chemical structures of *trans*-DP5, G, G1, and DMP5 and schematic representation of photo-responsive transformation of the azobenzene-bridged pillar[5]arene dimer.



heterocomplementary homoditopic monomers not only prohibit the formation of cyclic oligomers efficiently, but also lead to low critical polymerization concentrations. On the other hand, it has been reported that pillar[5]arenes can bind secondary ammonium derivatives to form 1:1 threaded structures in chloroform.<sup>6g</sup> Inspired by this, we employed a homoditopic A2B2 monomer containing an azobenzene-bridged pillar[5]arene dimer and its complementary secondary ammonium guest to construct a linear supramolecular polymer at high concentration (Scheme 1). It is worth noting that the efficient complexation of the host-guest moieties would contribute to the formation of supramolecular polymer with stimuli-responsive behaviors. The resulting supramolecular polymer can not only exhibit UV-responsiveness due to the presence of an azobenzene moiety acting as a molecular bridge but also possess pH-responsiveness resulting from the pH-controlled reversible host-guest complexation (Scheme 2).

Due to the formation of supramolecular polymer, it is difficult for us to study the host-guest complexation between



Fig. 1 Partial <sup>1</sup>H NMR (500 MHz,  $CDCl_3-CD_3CN = 1:1, 293$  K) spectra of equimolar mixtures of G and *trans*-DP5 at different concentrations: (a) 300 mM; (b) 150 mM; (c) 75.0 mM; (d) 37.5 mM; (e) 13.8 mM; (f) 7.00 mM; (g) 3.50 mM; (h) 1.80 mM; (i) 1.00 mM; and (j) 0.500 mM.

*trans*-**DP5** and **G**, so **DMP5** and **G1** were selected as a model system to investigate the host–guest interactions between *trans*-**DP5** and **G** (Scheme 1). The association constant  $K_a$  of **DMP5**  $\supset$  **G1** was determined to be 81.6 ± 2.7 M<sup>-1</sup> in 1 : 1 complexation in the mixture of CDCl<sub>3</sub> and CD<sub>3</sub>CN (v/v, 1 : 1) by a proton NMR titration method.

<sup>1</sup>H NMR spectra of the G and trans-DP5 mixture were obtained from samples with concentrations ranging from 0 mM to 300 mM (Fig. 1). As expected, the <sup>1</sup>H NMR spectra were concentration-dependent, reflecting the involvement of fast-exchanging noncovalent interactions in solution on the NMR time scale. The signals related to the protons of G showed upfield chemical shift changes, indicating that these protons were located within the electron-rich cavity of the trans-DP5 host. Moreover, the peaks related to all protons of G became broad when the concentration was increased, demonstrating the formation of high-molecular-weight supramolecular polymer aggregates. In addition, the signals of protons H<sub>1-2</sub> shifted upfield quickly at first and then slowly tended to a constant value, illustrating that the percentage of the cyclic species decreased while the percentage of the linear polymer increased.12

The concentration-dependent viscosity changes provided convincing insight into the aggregation behavior. A double logarithmic representation of specific viscosity *versus* concentration of monomer **G** and *trans*-**DP5** in CHCl<sub>3</sub>-CH<sub>3</sub>CN (v/v, 1:1) was obtained (Fig. 2a). In the low concentration range, the slope of the curve was 1.18, indicating a linear relationship between specific viscosity and concentration, which demonstrated the presence of cyclic oligomers in dilute solutions. As the concentration increased, a sharp increase in the viscosity was observed (slope = 2.42 at 298 K). This stronger concentration dependence indicated the formation of a supramolecular polymer of increasing size.<sup>12</sup> The critical polymerization



**Fig. 2** (a) Specific viscosity of equimolar monomers **G** and *trans*-**DP5** in CHCl<sub>3</sub>-CH<sub>3</sub>CN at 298 K *versus* monomer concentration ( $\blacktriangle$ ), after adding Et<sub>3</sub>N ( $\bullet$ ), after adding CF<sub>3</sub>COOH ( $\blacksquare$ ). (b) Specific viscosity of equimolar monomers **G** and *trans*-**DP5** in CHCl<sub>3</sub>-CH<sub>3</sub>CN at 298 K *versus* monomer concentration ( $\bigstar$ ), after UV light (365 nm) irradiation ( $\bullet$ ), after visible light (435 nm) irradiation ( $\blacksquare$ ).

concentration of monomer G and *trans*-DP5 in  $CHCl_3-CH_3CN$  was about 100 mM as evidenced by the change of slope occurring at this concentration, indicating a ring-chain transition from cyclic oligomers to linear supramolecular polymers.

A 2D NOESY NMR study of a mixture of trans-DP5 (10.0 mM) and G (10.0 mM) in CDCl<sub>3</sub>-CH<sub>3</sub>CN was carried out to investigate the relative spatial positions of this host-guest complex. As shown in Fig. S7,† clear correlation signals were observed between protons  $H_{\alpha}$  on trans-DP5 and protons  $H_{6.7}$ on G, indicating that G penetrated through the cavity of trans-DP5. The concentration dependence of the diffusion coefficient D gives important information on the aggregation behavior. As the monomer concentration increased from 10.0 mM to 175 mM in solution, the measured weighted average diffusion coefficient decreased considerably from  $3.17 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  to  $1.57 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$  (Fig. S16<sup>†</sup>), providing direct evidence for the formation of supramolecular polymers with high molecular weight and high degree of linear chain extension. Furthermore, microscopic fibers with an average diameter of 270 nm were drawn from a high concentration solution of monomer G and trans-DP5 and observed by scanning electron microscopy (SEM), which was consistent with the decrease of diffusion coefficient (Fig. 3a and b).

It is well known that the recognition motif based on secondary ammonium possesses excellent pH-responsive properties because the secondary ammonium unit could be easily protonated and deprotonated by adjusting the solution pH.<sup>13</sup> As expected, upon addition of 1.5 equiv. triethylamine, the elevated pH value gave rise to the deprotonation of the secondary ammonium, further resulting in the immediate transition from the linear supramolecular polymer to monomers. In contrast, the newly formed secondary amine turned back to the charged state and hence reformed the supramolecular polymers after the addition of trifluoroacetic acid (1.7 equiv.). As shown in Fig. 2a, when the value of the solution pH increased, a decrease of the slope of the curve was observed, indicating the transition from the linear supramolecular polymer to monomers (deprotonated G and trans-DP5). While the solution pH was adjusted to acid again, the slope rose as expected,



**Fig. 3** SEM images of products electrospun from a high concentration solution of equimolar **G** and *trans*-**H** in  $CDCl_3-CD_3CN$  (v/v, 1:1): (a) rod-like fibers; (b) enlarged image of (a); (c) the linear supramolecular polymer after irradiation with UV light at 365 nm for 10 min; (d) after further irradiation with visible light at 435 nm for 10 min of (c); (e) the linear supramolecular polymer after addition of 1.5 equiv. of triethylamine; and (f) after addition of 1.7 equiv. of trifluoroacetic acid in (e).

demonstrating the reversible transition between the monomers and linear supramolecular polymer. Similarly, the assembly and disassembly of the supramolecular polymer could also be proved by SEM. As shown in Fig. 3e, rod-like fibers could not be drawn after the addition of 1.5 equiv. triethylamine, and only electrospun droplets could be observed under SEM, while after addition of trifluoroacetic acid, electrospun supramolecular polymer fibers could be drawn again, which also suggested the reversible transition from the monomers to linear supramolecular polymer.

Due to the presence of an azobenzene moiety on the host, the assembly and disassembly of the supramolecular polymer could also be switched by alternating between UV and visible light irradiation. When an equimolar trans-DP5 and G mixture was irradiated with UV light at 365 nm for 10 min, the specific viscosity of the mixture decreased significantly (Fig. 2b). The reason may be that the host-guest complexation was weakened by the steric hindrance generated by the photo-isomerization from the trans to cis form and further giving rise to the transformation from supramolecular polymers to oligomers.<sup>14</sup> After irradiation with visible light, the specific viscosity increased again, suggesting the re-assembly of the supramolecular polymer. As shown in Fig. 3c, electrospun droplets and fibers could be reversible observed by alternating between UV and visible light irradiation, from which the same conclusion could also be drawn.



**Fig. 4** (a) Cartoon representation of the formation of a crosslinked liquid-crystalline polymer based on the host-guest interactions between the azobenzene-bridged pillar[5]arene dimer and a secondary ammonium-functionalized poly(methyl acrylate) **CP1**. (b) A heart-shaped thin film moulded from the cross-linked supramolecular polymer. Polarized optical microscopy images: (c) the thin film before UV irradiation; (d) the thin film after UV irradiation.

Azobenzene-containing liquid crystals possess photoinduced isomerization, good stability, tunable reversibility and other characteristics,<sup>15</sup> which exhibited great potential applications in optical storage and nonlinear optical materials. We further employed this host-guest molecular recognition to construct a supramolecular crosslinked network by using the azobenzene-bridged pillar[5]arene dimer trans-DP5 and a secondary ammonium-functionalized poly(methyl acrylate) CP1 as the building blocks (Fig. 4). Interestingly, this cross-linked network exhibited liquid crystal properties. In this side chain liquid crystal polymers, the azobenzene moieties were designed to be the mesogenic units as well as the cross-linking agents for the main chain which is functionalized with secondary ammonium. It is well known that the azobenzene derivatives in trans form is a rod and tends to stabilize the phase structure of liquid crystals while the cis form of the azobenzenes is bent and tends to destabilize the phase structure. Therefore, trans-cis photoisomerization of the azobenzene can disorganize the phase structure of liquid crystals, resulting in a photochemical phase transition.<sup>15b,c</sup> The optical properties of this crosslinked liquid-crystalline polymer film at room temperature were evaluated by polarized optical microscopy

(Fig. 4b and c). It was clearly observed that the film showed optical anisotropy when the azobenzene was in the *trans* state, indicating the formation of the supramolecular liquid crystal. After UV irradiation, a dark image was observed, demonstrating the optical isotropy property of the film due to the *trans*-*cis* isomerization of the azobenzene moieties. Therefore, this novel photo-switchable crosslinked liquid-crystalline polymer probably has many potential photonic applications such as optical switching, optical image storage, optical display, and optical computing.

#### Conclusions

In summary, we prepared a novel linear supramolecular polymer and a supramolecular network based on the pillar[5]-arene/secondary ammonium salt molecular recognition motif in CDCl<sub>3</sub>-CH<sub>3</sub>CN. The presence of an azobenzene moiety acting as a molecular bridge and the pH-controlled reversible host-guest complexation played essential roles for the supramolecular polymer to show UV and pH-responsiveness, making it possible to achieve reversible polymer–oligomer and polymer–monomer transitions, respectively. More interestingly, the crosslinked supramolecular network exhibited a liquid crystal property, and could be easily controlled by photo irradiation, bringing about lots of potential photonic applications.

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Communication

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