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A photochromic supramolecular polymer based on bis-*p*-sulfonatocalix[4]arene recognition in aqueous solution†

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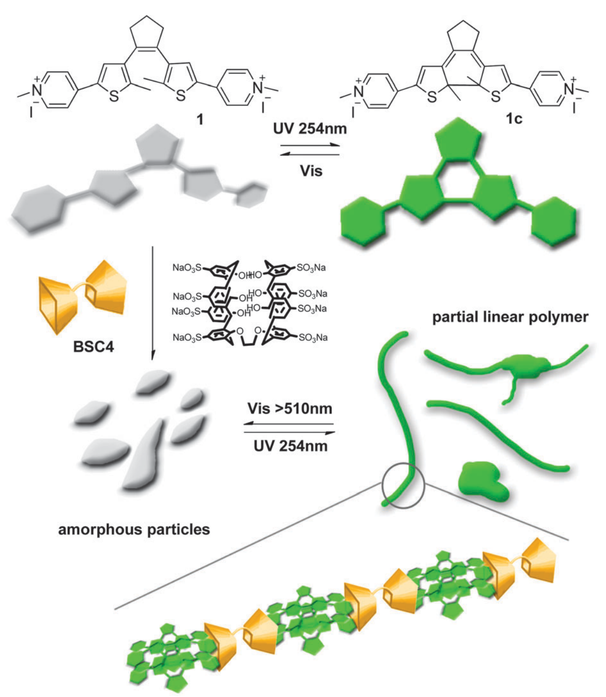
A photochromic supramolecular polymer based on bis-*p*-sulfonatocalix[4]arene recognition with a dithienylethene derivative in aqueous solution was fabricated. The resultant polymer showed good photochromic behaviour with obvious colour switching and a morphology change under alternative UV/Vis light stimuli.

Supramolecular chemistry provides a convenient way to bring monomers together into supramolecular structures by directional and reversible non-covalent interactions, including host–guest recognition,[1] hydrogen bonds,[2] metal–ligand interaction,[3] donor–acceptor interaction,[4] and so forth. The constructed supramolecular structures with organized functional moieties usually exhibit intriguing behaviours under external environmental stimuli,[5] such as light,[6] pH,[7] temperature,[8] redox,[9] enzyme,[10] and so forth. Among these external stimuli, light is regarded as an excellent way capable of remote controlling and leading no waste into the system.

Dithienylethene derivatives, with good reversibility, stability and remarkable absorption change under light stimuli, were fabricated into a variety of photochromic materials[11] including switches,[12] sensors and supramolecular cages[13] and so forth. Constructing their supramolecular polymers provides a new approach to functional materials with light responsiveness. In the past decade, photochromic supramolecular polymers were constructed *via* hydrogen bonding to realize significant visual, morphology and size switching under light stimuli based on dithienylethene derivatives.[14] However, to the best of our knowledge, photochromic supramolecular polymers with dithienylethene derivatives based on host–guest interaction have been rarely reported. Since host–guest interaction may provide the supramolecular structures with higher selectivity, more responsiveness and well-sorted structures by modifying host or guest moieties, it is interesting to introduce dithienylethene derivatives into supramolecular polymers based on host–guest recognition and investigate their properties.

Herein, we combined a water soluble dithienylethene derivative 2-bis[2-methyl-5-(4-methylpyridyl)-3-thienyl] cyclopentene (**1**) with bis-*p*-sulfonatocalix[4]arene (**BSC4**) in aqueous solution and obtained a photochromic supramolecular polymer (**PSP**) based on calixarene-induced aggregation (CIA) (Scheme 1).[15] The photochromic supramolecular polymer was obtained by mixing **1** and **BSC4** in water sufficiently under stirring. The complexation



Scheme 1 Schematic representation for the preparation of the photochromic supramolecular polymer (**PSP**) by host–guest interaction between dithienylethene derivative **1** and **BSC4**, and the photoswitching of colour and morphology changes by alternative UV/Vis light irradiation.

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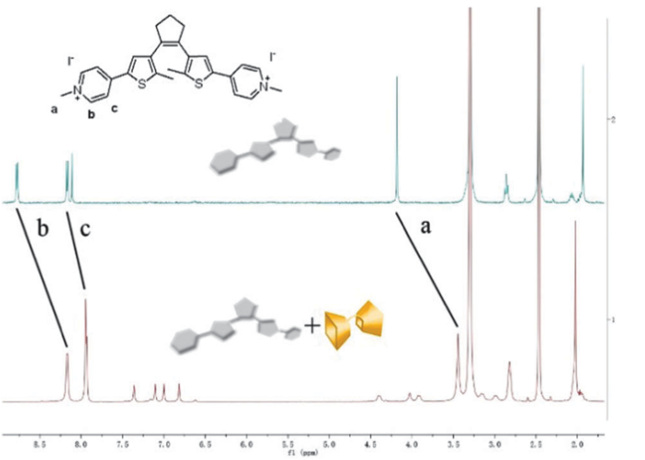

Fig. 1 Partial ^{1}H NMR spectra of **1** (3.6×10^{-3} mol L^{-1}, top) and **PSP** (9.0×10^{-4} mol L^{-1}, bottom) in DMSO-d_6.

behaviour was validated by ^{1}H NMR spectroscopy both in D_2O and DMSO-d_6. The proton signals of the methyl pyridine moiety in **1** underwent a significant upfield shift as a result of the shielding effect of the calixarene cavity. In D_2O, however, the **PSP** was not soluble enough to show a qualified NMR spectrum. In DMSO-d_6, the $\Delta\delta$ values were 0.79, 0.59 and 0.20 for protons H_a, H_b and H_c, respectively (Fig. 1). The order of $\Delta\delta$ $H_a > H_b > H_c$ suggested the proposed inclusion behaviour of the host and guest moieties, in which the methyl pyridines were included in the sulfonated cavity of **BSC4** induced by electrostatic interactions. Rotating Frame Overhauser Effect Spectroscopy (ROESY) was also carried out to confirm the host–guest interaction (ESI,† Fig. S1). Diffusion-ordered spectroscopy (DOSY) further validated the formation of an assembly, displaying a slower diffusion rate of **1** in **PSP** (7.212×10^{-11} m^2 s^{-1}) than that of free **1** (1.725×10^{-10} m^2 s^{-1}) (Fig. S2 and S3, ESI†).

The stoichiometry is essential to predict the binding behaviour in host–guest self-assembly supramolecular polymers. A Job's plot method was used to confirm the binding stoichiometry between monomer **1** and **BSC4** (ESI,† Fig. S4a). The change in the absorption reached the maximum at a ratio of 0.8 for [**1**]/([**1**] + [**BSC4**]), suggesting the 4 : 1 complex between **1** and **BSC4**. To investigate whether the stoichiometry would change after **1** turned into its closed form **1c**, another Job's plot for **1c** and **BSC4** was also carried out to confirm the same stoichiometry as 4 : 1 (ESI,† Fig. S4b). The 4 : 1 stoichiometry accords with charge matching between **1** and **BSC4**, in which the total number of positive charges of **1** was equal to that of negative charges of **BSC4**. Dynamic light-scattering (DLS) measurement was employed to identify the formation of **PSP** with the average hydrodynamic diameter increase from undetectable to ~135 nm by adding **BSC4** into the solution of **1** (0.015 mM).

The photochromic property of the **PSP** was investigated by UV-Vis spectroscopy. Both **1** and **PSP** in aqueous solution (Fig. 2a and b) and the solid state (Fig. 2c and d) displayed a significant colour switching with major absorption change from ~360 nm to ~680 nm. However, compared with monomer **1** itself, **PSP** underwent a slower photochromic process with a

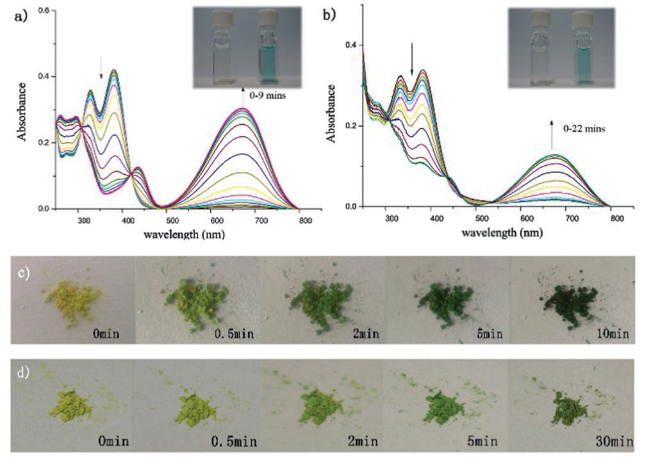

Fig. 2 UV-Vis spectra of (a) monomer **1** and (b) **PSP** under 254 nm UV irradiation (inset: corresponding photographic images). The photographic images of (c) **1** and (d) **PSP** in the solid state and its colour change under 254 nm UV irradiation. (The solid sample of **PSP** was prepared by centrifuging the mixture of **1** and **BSC4** (molar ratio 4 : 1) in aqueous solution at a concentration of 0.05 M.)

lower conversion rate under the same experimental conditions (Fig. 2). The time required for monomer **1** to reach the steady state was 9 minutes, while it was 22 minutes for **PSP**. The prolonged transforming time and the lower conversion rate (Fig. S5 and S6, ESI†) are reasonable and ascribed to the restriction effect of the formed photoswitchable supramolecule.[6d] The photochromic switching of both **1** and **PSP** was reversible in aqueous solution (Fig. S7, ESI†).

It would be intriguing if supramolecular polymers underwent a morphology change under environmental stimuli. The morphology change of the **PSP** before and after UV irradiation was demonstrated by atomic force microscopy (AFM).

The **PSP** in a state of amorphous nanoparticles was observed before UV irradiation possibly because of the flexibility of monomer **1** (Fig. 3a). Another sample was prepared from the same solution after UV irradiation for 30 min. It was obvious that the partial **PSP** particles turned to exhibit linear morphology (Fig. 3b, for more AFM images see Fig. S8, ESI†). As shown in the transmission electron microscopy (TEM) images, the linear supramolecular polymers with length of hundreds of nanometres were also observed both in single form (Fig. 3e) and in assembly (Fig. 3g). Electrostatic interactions in linear **PSP** were the probable reason for the assembly, which was observed in a similar supramolecular polymer.[16] It is deduced that connections between small units of stacked **1c** might be the formation mode of linear polymers, which was observed in an enlarged TEM view (Fig. 3f). Besides, a new peak representing smaller assemblies with an average size of ~60 nm and an intensity of ~30% appeared in the DLS result after UV irradiation (Fig. 3d). Taking the above results and the conformational change between **1** and **1c** into consideration, we can infer that the increase of rigidity was the reason for the appearance of linear **PSP** and the partial morphology change was ascribed to the incomplete transformation from **1** to **1c** as well as the possible assembly of linear polymers.

In summary, we fabricated a photochromic supramolecular polymer **PSP** based on host–guest interaction between a

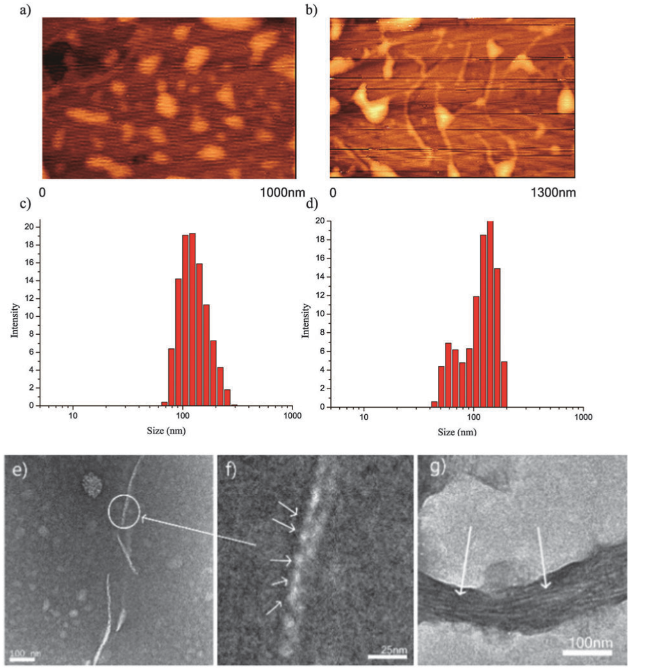

Fig. 3 AFM images of **PSP** (a) before UV irradiation; (b) after UV irradiation for 30 min under 254 nm light. DLS results of **PSP** (c) before UV irradiation; (d) after UV irradiation for 30 min under 254 nm light. Negative-staining TEM images of (e) separate linear **PSP**; (f) enlarged view of part of separate linear **PSP**; (g) assembly of linear **PSP**.

dithienylethene derivative and a bis-sulfonatocalixarene in aqueous solution and investigated its photochromic property and morphology transition. **PSP** showed a good photochromic property and morphology change under alternative UV/Vis light stimuli in aqueous solution. Potential applications of supramolecular systems based on the water soluble dithienylethene derivative and sulfonatocalixarene in light storage and optical sensors as smart soft materials are in progress.

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