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Original article

A cucurbit[8]uril recognized rigid supramolecular polymer with photo-stimulated responsiveness

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ABSTRACT

A rigid supramolecular polymer was constructed in aqueous solution *via* cucurbit[8]uril (CB[8]) host recognition with a rigid monomer containing an azobenzene unit and two 4,4′-bipyridin-1-ium (BP) moieties in the two ends, which also exhibited photo-responsiveness owing to the photoinduced *trans*–*cis* isomerization of azobenzene group.

1. Introduction

Supramolecular polymers have been prevailing since Jean-Marie Lehn's report in 1990 [1]. Unlike conventional polymers formed by the covalent bonds, the construction of supramolecular polymers is mainly based on non-covalent interactions, such as hydrogen bonds [2], metal–ligand bonds [3], host–guest recognition [4], aromatic stacking [5], and so forth. One typical branch of supramolecular polymers is constructed based on macrocycle recognition and interlocked structures. Supramolecular polymers based on macrocyclic molecules are formed generally by holding monomers or components in the big cavity of macrocycles *via* the highly directional non-covalent interactions. A myriad of macrocyclic components such as crown ether [6], cyclodextrin [7], cucurbituril (CB) [8], calixarene [9], pillararene [10], and their derivatives are usually employed to construct supramolecular polymers based on their recognition.

Cucurbit[*n*]urils (CB[*n*]s), a family of versatile macrocyclic hosts, can usually put the cationic guest molecules into their hydrophobic cavities through the ion dipole, hydrophobic effect and hydrogen bonding interactions between hosts and guests. The CB[*n*]s can include the cationic guest in their cavities with high binding constants in aqueous solution [11]. Comparing with the other members of CB[*n*]s family, CB[8] with bigger cavity makes it the ideal candidate being the host of the supramolecular polymers. Recently, two new rigid supramolecular polymers were constructed *via* the self-assembly of rigid monomers and cucurbit[8]uril (CB[8]) in water [12]. These supramolecular polymers possessed rigid backbones and further aggregated into stick-like bunched fibers. The constructed supramolecular polymers with specific functional group usually exhibit intriguing properties under external environmental stimuli [13], such as light [14], pH [15], temperature [16], and so forth. Herein, we report the construction of a simple supramolecular host–guest polymer system APCB that is stabilized by intermolecular interactions among CB[8] and 4,4′-bipyridin-1-ium (BP) units of a rigid monomer Azopy in aqueous solution, which provided a useful strategy for fabricating supramolecular polymers with significant structural rigidity. Interestingly, this rigid supramolecular polymer also exhibited intriguing photo-responsiveness owing to the photoinduced *trans*–*cis* isomerization of azobenzene [17] units of the monomers (Scheme 1), accompanying with its distinct morphology change. The linear suparmolecular polymers transformed into coiled ones in morphology under alternative light stimuli.

2. Experimental

^{1}H NMR spectra were measured on a Brüker AV-400 spectrometer. The electronic spray ionization (ESI) high-resolution mass spectra were tested on a HP 5958 mass spectrometer. The

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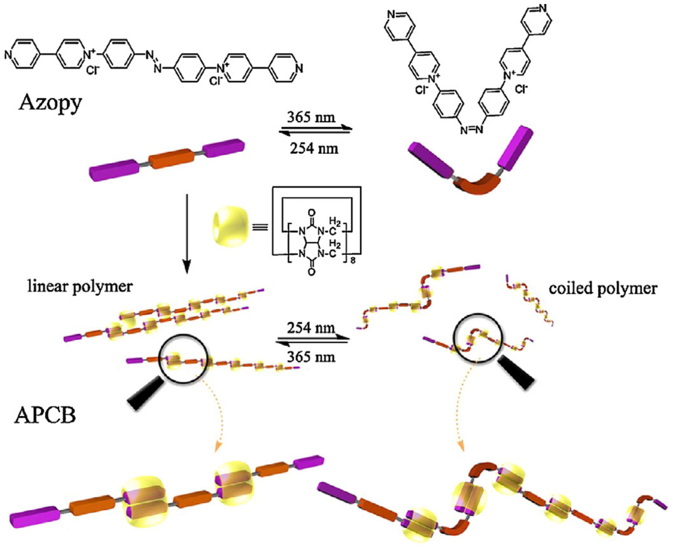

Scheme 1. Schematic representation for the construction of the supramolecular polymer APCB *via* host–guest interaction between Azopy and CB[8], and the photo-responsive morphology changes of APCB by alternative light irradiation.

UV–vis absorption spectra were obtained on a Varian Cary 100 spectrometer and a Varian Cary Eclipse (1-cm quartz cell was used). The nanoparticle size was measured on NanoSight NS 300 supplied by Malvern. TEM images were recorded on JEOL JEM-1400 and JEM-2100 apparatus (droplets of the sample solution (5×10^{-5} mol/L) were applied to a perforated copper grid (400 mesh) covered with a carbon film). The UV irradiations were performed by a handheld UV lamp with an output power of 6 W.

Chloro-2,4-dinitrobenzene, 4,4′-bipyridine, 4,4′-diaminoazobenzene and butyl alcohol were commercially available and used without further purification. 2,4-Dinitrophenyl-4,4′-bipyridinium chloride was synthesized according to the previous report [18]. 4,4′-Bipyridine was added (6.41 g, 41 mmol) to a solution of chloro-2,4-dinitrobenzene (8.31 g, 41 mmol) in 60 mL EtOH and the solution was refluxed for 24 h. The dark brown solution after cooling at room temperature was added to diethyl ether (400 mL) with stirring. A golden-brown precipitate was obtained which was then filtered by suction and washed several times with diethyl ether. The solid was stored under vacuum over anhydrous $CaCl_2$ (highly hygroscopic solid which turns to a sticky brown solid when exposed to air) to give *N*-(2,4-dinitrophenyl)-4,4′-bipyridinium chloride 12.08 g (33.67 mmol, 82%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.57 (d, 2H, J = 6.3 Hz), 9.15 (d, 1H, J = 2.3 Hz), 9.01 (dd, 1H, J = 8.7, 2.3 Hz), 8.96 (d, 4H, J = 4.4 Hz), 8.46 (d, 1H, J = 8.6 Hz), 8.20 (d, 2H, J = 5.2 Hz). ^{13}C NMR (101 MHz, DMSO-d_6): δ 154.99 (s), 150.19 (s), 149.67 (s), 147.21 (s), 143.56 (s), 142.37 (s), 138.92 (s), 132.54 (s), 130.73 (s), 125.89 (s), 123.40 (s), 121.91 (s). TOF-MS: $[M-Cl^-]^+$ 323.0775, found 323.0781.

N-(2,4-dinitrophenyl)-4,4′-bipyridinium chloride (2.03 g, 5.65 mmol) and 4,4′-diaminoazobenzene (0.40 g, 1.88 mmol) were suspended in butyl alcohol (50 mL) in a round bottomed flask under a nitrogen atmosphere. The solution was refluxed for 3 days. After that, the reaction mixture was cooled and the solvent was removed with rotavapor, the resulting residue was subjected to column chromatography (acetonitrile/potassium nitrate solution 10:1) to give the mixture of compound Azopy and potassium nitrate. Then the compound Azopy was recrystallized from H_2O. Next the mixture was cooled and filtrated to give orange solid compound Azopy (0.11 g, 0.2 mmol, 11%). ^{1}H NMR (400 MHz, D_2O): δ 9.29 (d, 4H, J = 6.9 Hz), 8.83–8.77 (m, 4H), 8.61 (d, 4H, J = 6.9 Hz), 8.25 (d, 4H, J = 8.8 Hz), 8.06–7.95 (m, 8H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 154.69–153.58 (m), 153.26 (s), 151.63 (s), 145.90 (s), 144.74 (s), 141.01 (s), 126.99 (s), 125.78 (s), 124.78 (s), 122.58 (s). MASS (ESI) m/z: $([M-2Cl^-]^{2+})/2$ calcd. 246.1026, found 246.1025.

3. Results and discussion

The rigid supramolecular polymer APCB was constructed employing azobenzene derivative Azopy and CB[8] *via* a relatively longer binding process (stirred overnight) in aqueous solution. The two BP units from two independent Azopy monomers were entrapped together inside the cavity of CB[8] in a head-to-tail orientation [19]. The guest monomer Azopy was synthesized simply *via* a Zincke reaction of *N*-(2,4-dinitrophenyl)-4,4′-bipyridinium chloride with 4,4′-diaminoazobenzene and characterized using ^{1}H NMR, ^{13}C NMR and MS spectra (Figs. S10–S12 in, Supporting information). The formation of the APCB between Azopy and CB[8] was explicitly stated by the ^{1}H NMR spectroscopy (Fig. 1) and ^{1}H NOESY spectroscopic experiments in D_2O (Fig. S4 in Supporting information). Diffusion-ordered NMR spectroscopy (DOSY) was further utilized to evaluate the polymerization efficiency of the supramolecular polymerization system (Figs. S2, S3 in Supporting information). The average diffusion coefficients of Azopy and APCB were measured to be 3.16×10^{-10} m^2/s and 1.79×10^{-10} m^2/s, respectively. The decrease of diffusion coefficient of APCB implies that bulky polymeric species are formed. As we can see from Fig. 1, the NMR signal of H_a, H_b, H_c, H_d, H_e and H_f shifted upfield by 0.49 ppm, 0.70 ppm, 0.56 ppm, 0.10 ppm, 0.40 ppm, 0.25 ppm, respectively, owing to the inclusion interaction of CB[8]. Besides, the envisaged inclusion pattern of Azopy and CB[8] was specifically observed from 2D ^{1}H NMR NOESY. The NOE correlations between H_a and H_c, H_b and H_d were observed. This fact also demonstrated that two 4,4′-bipyridin-1-ium units were included inside the cavity of CB[8] in a manner of head-to-tail orientation perfectly. Also, the 1:1 binding stoichiometry was clearly confirmed by Job's plot (Fig. S1 in Supporting information) investigation.

The UV–vis absorption spectra of Azopy and supramolecular polymer APCB were also employed to further illustrate the interaction between CB[8] and Azopy. As seen in Fig. S5 (Supporting information), under the same conditions, the absorption peaks at 268 nm and 335 nm corresponding to Azopy showed red-shifts to 272 nm and 347 nm, respectively, as a result of the formation of APCB.

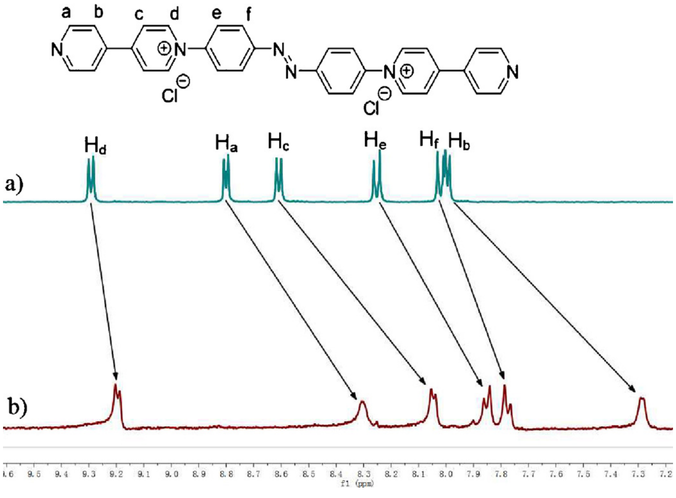

Fig. 1. Partial ^{1}H NMR spectra of (a) Azopy, (b) APCB (Azopy: CB[8] = 1:1) in D_2O at 25 °C, both concentrations were 1.0 mmol/L.