

Photoresponsive self-assembly of a β -cyclodextrin derivative with an azobenzene terminal group in water

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ABSTRACT

We report the photoresponsive self-assembly of a β -cyclodextrin derivative containing an azobenzene terminal group with an oligoethylene glycol linker (Azo-EG- β CD). Azo-EG- β CD was synthesized, and its aggregation was investigated using several techniques including TEM analysis, DLS and other spectral measurements. In a freshly prepared aqueous solution, Azo-EG- β CD self-assembled into a network-like structure by forming intermolecular host–guest inclusions that transformed into vesicles upon aging because of hydrogen bonding. Transformation from *trans*-azo to *cis*-azo using UV light induced the dissociation of azobenzene in the β -CD cavity, and the aggregate transformed into vesicles. The construction of a photoresponsive self-assembly may provide a unimolecular host–guest complexation model in stimuli-responsive host–guest self-assembly.

1. Introduction

Stimuli-responsive supramolecular self-assembly based on host–guest interactions has drawn much attention in recent years because of their potential applications in various fields such as drug delivery, smart supramolecular materials, and functional nanodevices [1–3]. Numerous external stimuli such as light [4–7], pH change [8,9], redox [10,11], and temperature change [12] have been used to fabricate stimuli-responsive self-assemblies. Light is very useful because of easy operation, cleanness, and low cost. Molecules with photoresponsive groups can undergo structural transition due to steric hindrance after light stimulus, leading to a change in their molecular configuration, polarity, and aggregation behavior [6,13–18]. Therefore, light-stimulus-responsive self-assembly systems can be fabricated by incorporating light-active moieties in the system. Azobenzene is the most frequently used chromophore in the preparation of light-responsive self-assembly based system because of its photoisomerization tendency in response to UV and visible-light irradiation [19]. The difference in the polarity and size of the *trans* and *cis* form of azobenzene provides adjustable microscopic structures and tunable functions for self-assembly systems [20–22].

Because host–guest interaction is a noncovalent interaction, it is dynamic and reversible. Various stimuli-responsive self-assemblies have been constructed based on host–guest complexation [21,23–25]. Host–guest recognition usually occurs between two components, *i.e.*,

the host and guest moieties. Cyclodextrins (CDs) are one of the most extensively used hosts [26,27]. CDs are donut-like oligosaccharides, composed of 6, 7, or 8 D-glucose units. These are named as α -, β -, and γ -CD, respectively. The inner cavities of CDs are hydrophobic, and the outer surfaces are hydrophilic [28]. They can incorporate hydrophobic moieties into the cavities by size-selective complexation [1]. The adjustable binding ability of CDs endows CD-guest inclusion complexes with the possibility to construct stimuli-active self-assembly systems [29–31]. β -CD is the most frequently used host because of its low cost, moderate size, and good modifiability.

In host–guest chemistry, azobenzene moiety is a typical guest for β -CD. This has received much attention due to its photomodulated characteristics [32–34]. β -CD can form host–guest complexes with the *trans*-azo group, while the *cis*-azo group does not form such complexes because of size mismatch [25,32,35]. Therefore, environmentally adjustable host–guest complexation has been widely used to construct photoresponsive host–guest supramolecular self-assemblies. In previous studies, a commonly used strategy was used: An azobenzene derivative was synthesized, and then host–guest inclusion complex was obtained when β -CD or its derivatives were added [3,34,36,37]. Therefore, the self-assembly behavior could be tuned with light irradiation based on the formation or dissociation of the β -CD/azo inclusion complex resulting from photoisomerization.

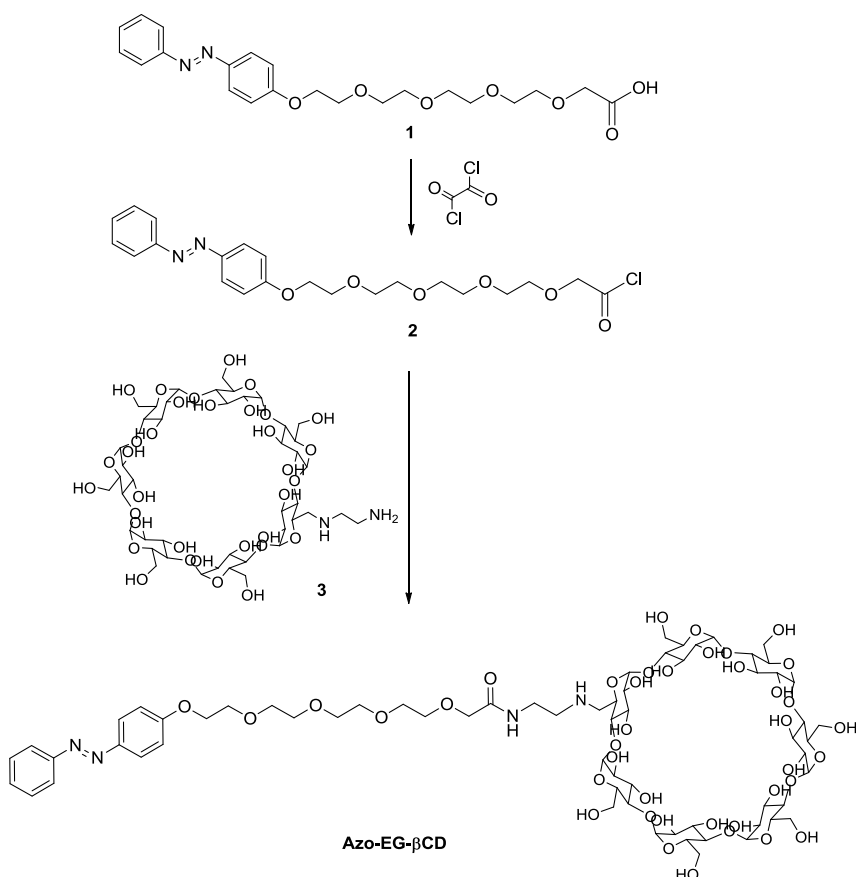
Different from above strategy, we turned our attention to the construction of photoresponsive β -CD/azo self-assembly based on a

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Scheme 1. Synthesis of Azo-EG-βCD.

unimolecular platform. One molecule bearing β-CD and azo moieties in two termini linked by a hydrophilic group has not been reported before, which may form intermolecular host-guest complexes in the aqueous solution and therefore supramolecular polymers were fabricated. As a special kind of self-assembly systems, supramolecular polymers form by monomers interconnecting through noncovalent interactions [38–40]. Thereinto, supramolecular polymers based on recognition between β-CD and guest molecules had been reported extensively [41,42]; however, few samples were explored in a unimolecular solution by forming intermolecular host-guest complexes. Therefore, we made an attempt to construct a unimolecular photoresponsive supramolecular polymerical self-assembly based on β-CD/azo complexation in this study. This is important for the fundamental researches and application prospects.

Therefore, Azo-EG-βCD was designed and synthesized, as shown in Scheme 1 β-CD containing hydrophilic groups is the host, whereas the hydrophobic azobenzene moiety is the guest. These two parts are linked with a hydrophilic spacer, oligoethylene glycol (EG), to improve the solubility of the target molecule in water. Azo-EG-βCD formed network-like structures by intermolecular host-guest complexation. These structures were reversibly transformed into vesicles upon UV irradiation. Interestingly, the network-like structures gradually turned into vesicles with aging time because of hydrogen binding. The fabrication of this unimolecular supramolecular polymer system may provide a new route for the design of more stimuli-responsive supramolecular polymers.

2. Experimental section

2.1. Materials

Triethylamine (TEA), oxalyl chloride, *p*-hydroxyazobenzene, ethyl diazoacetate, *p*-toluenesulfonyl chloride, tetraethylene glycol, boron trifluoride ether adduct, 1, 2-diaminoethane, 1-adamantanamine

hydrochloride, and β-cyclodextrin were purchased from J&K Chemical Ltd. All the solvents and reagents were of analytical grade and used as received.

2.2. Synthesis of Azo-EG-βCD

Azo-EG-βCD was designed and synthesized as shown in Scheme 1. Compounds 1 and 3 were synthesized following the literature procedure [43,44]. Compound 1 (0.554 g, 1.28 mmol) was dissolved in CH₂Cl₂ (250 mL), and then 0.33 mL oxalyl chloride (3.85 mmol) was slowly added. The resulting mixture was stirred at room temperature for 3 h, producing a yellow solution. The solution was evaporated under vacuum, affording a yellow oil (compound 2). This yellow oil was dissolved in DMF (150 mL) and slowly added into a solution containing 1.445 g compound 3 (1.23 mmol), 1.247 g TEA (12.3 mmol), and 100 mL DMF at 0 °C. After the addition, the mixture was stirred at room temperature overnight. After the completion of the reaction, the DMF solution of the resulting mixture was slowly poured into cold acetone (500 mL), affording a yellow solid. The precipitate was repeatedly dissolved in 50 mL DMF and poured into cold acetone (250 mL) several times, furnishing the pure product, Azo-EG-βCD. The product was dried in a vacuum oven. ¹H NMR (D₂O, 500 MHz): δ 7.98 (s, 1H, -CONH-), 7.82–7.73, 7.59, 7.32, 7.20, 6.81 (m, 9H, protons of Azo moiety), 5.05–4.94 (s, 7H, H1 of CD), 4.27 (s, 2H, Azo-O-CH₂-), 4.00 (s, 2H, -OCH₂CONH), 3.90–3.37 (b, 56H, protons of EO chain and H2-6 of CD), 3.17 (s, 2H, -CONHCH₂), 2.91 (s, 2H, -CONHCH₂CH₂), 2.14 (s, 1H, -CH₂NHCH₂).

2.3. Characterization

Transmission electron microscopy (TEM) observations. One drop of each prepared solution was placed on a carbon-coated copper grid (230 mesh), and the excess liquid was removed using a filter paper.

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