



Construction and reversible assembly of a redox-responsive supramolecular cyclodextrin amphiphile



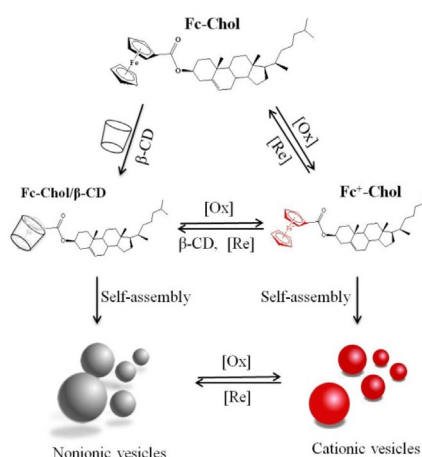
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HIGHLIGHTS

- A supramolecular amphiphile was constructed by host-guest approach, and self assembled into vesicles.
- The vesicles possess reversible redox-responsive properties.
- The aggregates transform between nonionic vesicles and cationic ones triggered by adding the reductant or oxidant.

GRAPHICAL ABSTRACT



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ABSTRACT

We present here the reversible assembly of a redox-responsive supramolecular amphiphile based on a ferrocene-containing molecule Fc-Chol and β -cyclodextrin (β -CD). The supramolecular amphiphile Fc-Chol/ β -CD is constructed by a host-guest approach between ferrocene and β -CD. Upon controlling the change of ferrocene between neutral and positively charged state by the addition of the oxidant and reductant, the host-guest complexes form and fall apart reversibly, resulting in the aggregate transformation between nonionic vesicles and cationic vesicles. The construction of a reversible redox-responsive supramolecular amphiphile system was demonstrated on the basis of host-guest chemistry, which may provide a new route for the fabrication of various stimuli-responsive supramolecular assemblies.

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1. Introduction

Stimuli-responsive self-assembly has attracted much research attention for its wide applications in the fields from chemistry

to materials [1–3]. External stimuli, such as pH-change [4], light [5], redox [6] and temperature [7,8], have been employed for the fabrication of self-assembly systems, while the modulation of these stimuli usually changes the responsive group's polarity or steric structure and further alters the balance of the hydrophobicity and hydrophilicity resulting in the aggregation transformation [9–11]. Different from conventional amphiphiles, supramolecular amphiphiles are constructed by assembling hydrophobic and

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hydrophilic parts with non-covalent interactions or dynamic covalent bonds [12,13], such as host-guest interaction [14], metal-ligand bonding [15], electrostatic interaction [16] and so on [17]. Through these reversible and dynamic weak interactions, discrete functional groups can be introduced into supramolecular amphiphiles to fabricate stimuli-responsive multi-functional self-assembly systems, which provide choices for the design of smart materials and molecular devices [18,19].

Stimuli-responsive supramolecular amphiphiles based on host-guest interactions show great potential applications because of the variability and flexibility of starting materials and availability of fabrication methods [18,20]. Cyclodextrins (CDs) are one type of mostly used host molecules with a hydrophilic outer surface and a hydrophobic cavity, which can include hydrophobic guests into its cavity depending on size-selective complexation [21]. Different from the common situations that CDs destroyed the surfactant assemblies [22], CDs here supply hydrophilic surface as the hydrophilic part to fabricate a host-guest supramolecular amphiphile [23]. For example, Jiang and co-workers have reported a non-covalent amphiphile connected by host-guest interactions between CDs and azobenzene-containing molecule (3C18-Azo), which showed an optical switchable self-assembly behavior [14]. Similar research work was reported by Zou et al. [24]. Among plenty of CD-guest pairs, stimuli-responsive supramolecular amphiphiles can be constructed by choosing guests with environmental adjustable binding abilities with CDs besides the light-sensitive azobenzene moiety mentioned above [25].

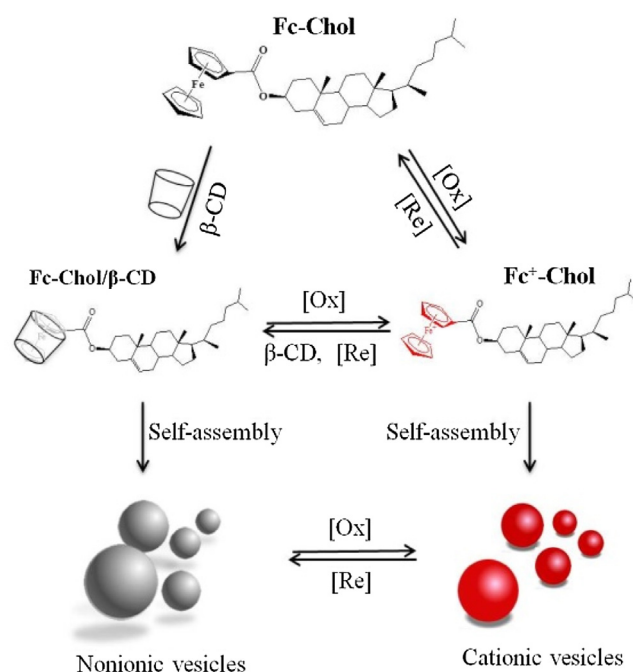
It's well-known that ferrocene (Fc) is one typical guest molecule for β -cyclodextrin (β -CD) and has received lots of attention in host-guest chemistry due to its redox-active characteristics [26–29]. β -CD can exactly form 1:1 inclusion complex with Fc moiety, while no binding of β -CD with oxidation-state Fc species (Fc^+) can be detected [30]. Meanwhile, the charged Fc^+ shows hydrophilic property [31]. Thus the oxidation of Fc can realize the conversion of amphipathy from hydrophobicity to hydrophilicity, which can act as a polar group in an amphiphile [32–34]. Hence, Fc is widely used to prepare reversible redox-responsive supramolecular amphiphile assembly systems [35,36].

Further development of reversible redox-responsive supramolecular amphiphile self-assembly system based on Fc is important and necessary for their promising applications in controlled release and drug delivery. In this work, one cholesterol derivative (Fc-Chol) containing Fc moiety was designed and synthesized for the construction of reversible redox-responsive supramolecular amphiphile system with β -CD (Scheme 1). Cholesterol is an important constituent of animal cell membranes, and it is a good choice as the hydrophobic part due to its sterol skeleton, good biodegradability and biocompatibility [37]. This hydrophobic cholesterol derivative Fc-Chol can form host-guest complexes with β -CD. The resultant complexes are amphiphilic with hydroxyl groups of CDs' outer surface as the hydrophilic part and cholesteryl group as the hydrophobic part. Upon the addition of oxidant, this supramolecular amphiphile will be transferred into a traditional cationic amphiphile, while the host-guest recognition occurs again by adding reductant. This reversible redox-responsive supramolecular amphiphile fabricated by a host-guest approach may provide a new route for the design of smart nanocarriers and devices.

2. Experimental

2.1. Materials

Triethylamine, ferrocenecarboxylic acid, pyrene, oxalyl chloride, glutathione (GSH), 4-dimethylaminopyridine (DMAP) and



Scheme 1. Schematic illustration for the preparation of the supramolecular amphiphile Fc-Chol/ β -CD and its reversible redox-responsive assemblies.

cholesterol were bought from J&K Chemical Ltd. Other reagents are of analytical purity. All the solvents and reagents were used as received.

2.2. Synthesis of Fc-Chol [31]

1.00 g ferrocenecarboxylic acid (4.35 mmol) was dispersed in 100 mL CH_2Cl_2 , and then 1 mL oxalyl chloride (11.6 mmol) was added slowly. The mixture was stirred at room temperature for 3 h to obtain a dark red solution. The solution was evaporated under vacuum to get red oil (chlorocarbonyl ferrocene). The red oil was dissolved in 80 mL benzene and dropped slowly into a solution containing cholesterol (1.68 g, 4.35 mmol), triethylamine (4.40 g, 43.5 mmol), DMAP (0.11 g, 0.89 mmol) and 20 mL benzene at 0°C. After the addition, the mixture was stirred at room temperature and refluxed for 42 h. The red solid was collected by filtering and dissolved in CH_2Cl_2 . The organic phase was washed by dilute hydrochloric acid (pH ~ 4) and water twice, and dried with anhydrous MgSO_4 . After evaporating the solvent, the product was purified by column chromatography (ethyl acetate: *n*-hexane = 1:40). The molecular structure is shown in Scheme 1. ^1H NMR(CDCl_3 , 300MHz): δ 5.43 (m, 1H), 4.84 (s, 2H), 4.78 (m, 1H); 4.42(s, 2H), 4.24(s, 5H), 0.69–2.43(m, 43H). Elemental analysis: calcd(%) for $\text{C}_{38}\text{H}_{54}\text{FeO}_2$: C 76.24, H 9.09; found: C 76.43, H 9.25.

2.3. Samples preparation [21,24]

The Fc-Chol molecules were first dissolved in DMF (1 mM). To prepare Fc-Chol/ β -CD solution, β -CD of equal molar was added. The above solution was diluted with deionized water, obtaining the 50 μM Fc-Chol/ β -CD aqueous solution. To prepare Fc⁺-Chol solution, the oxidant FeCl_3 was dissolved in CH_3CN to give a 0.1 mol/L solution and 20 μL was sucked out and mixed with 1 mL DMF solution of Fc-Chol (1 mM). Similarly, the above solution was injected into deionized water to get a 50 μM Fc⁺-Chol aqueous solution. Fc⁺-Chol/ β -CD solution was prepared by mixing the Fc⁺-Chol DMF solution and β -CD aqueous solution. GSH was dissolved in water (10 mM), and 5 μL was sucked out and injected into 1 mL Fc⁺-

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