Dual-controllable stepwise supramolecular interconversions[†]

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Received (in Cambridge, UK) 14th December 2009, Accepted 16th January 2010 First published as an Advance Article on the web 2nd February 2010 DOI: 10.1039/b926323c

A new unsymmetric guest compound comprising ferrocene and azobenzene moieties was synthesized and can form a host–guest system with β -cyclodextrin (β -CD) complexed. The complexation stoichiometries and sites of the ensembles can be selectively controlled by reversible redox and photoirradiation.

Chemists have been pursuing machinery systems at the molecular level for almost two decades,¹ since these architectures are showing an increasing potential for materials and biological applications.² As a primary prototype of molecular machines, pseudorotaxane-like supramolecular ensembles³ could further undergo many flexible reactions or perform versatile tasks, on account of their unique host-guest construction and the characteristic assembly/disassembly behaviors. Thus far, the replacement of components in an ensemble by competing substances ⁴ has provided a working principle for tunable supramolecular interconversions. However, to the best of our knowledge, control of the host assembly/disassembly behaviors in host-guest systems with multiple stimuli, to selectively modulate the complexation stoichiometries and sites, has rarely been reported. Herein, we demonstrate that a selective control of the host assembly/ disassembly behaviors, and the stepwise interconversion for multi-steady states of ensembles can be driven by redox and photoirradiation.

To modulate the complexation stoichiometries and sites, an unsymmetric guest compound comprising at least two different binding stations is expected to be effective. Ferrocene and azobenzene groups ⁵ are typical electro- and light-active species, respectively, which can also be recognized with high selectivity by host cyclodextrins (CDs).⁶ In this work, they were harnessed to be covalently linked by a viologen unit as a hydrophilic electropositive barrier,⁷ and a 2:1 complex (FVA \subset 2CD) can be formed by encircling of two β -cyclodextrin (β -CD) rings onto both the binding moieties,⁸ as shown in Scheme 1. When one of the binding stations is selectively translated by the external input, the corresponding assembled β -CD will depart from the guest but the other ring remains complexing with the other station, resulting in two different 1:1 complex isomers (FVA- $o \subset CD$, FVA- $p \subset CD$). The 2:1 complex can also be converted to a guest structure (FVA-op) when both the external inputs are present (regardless of the

sequence if they work sufficiently), which leads to the disassembly of the two β -CD rings together. Moreover, the rings can be reassembled to the guest *in situ* for the full reversibility of the redox and the photochemical operations, thus the process of the interconversion for steady states of one 2:1 complex, two 1:1 complexes and one guest compound can be exhibited. The demonstration of such a controllable process might be an important step toward the goal of multi-mode driven supramolecule-to-supramolecule transformations.

FVA⊂2CD was prepared from the guest compound FVA by co-grinding of the guest with 2 equiv. solid β-cyclodextrin for ca. 15 min. Two reference compounds Ref1 and Ref2 were also synthesized for control experiments, to study individually the binding ability and assembly–disassembly process of β -CD to the ferrocene and the azobenzene moieties (Scheme 1). The complexation of β -CD to the ferrocene and azobenzene moieties in FVA was studied with measurement of UV-Vis spectra and cyclic voltammograms (CV). The maximum absorption band for FVA in water at around 325 nm was red-shifted (from Curve a to c, Fig. 1) because of the binding effect of β -CD to the azobenzene moiety. The absorption peak decreases remarkably with the trans-to-cis isomerization of azobenzene. But the near superposition of Curves b and d in Fig. 1 reveals that the isomerized *cis*-azobenzene species was hardly complexed because of a progressive disassemblyphotochemical process.⁹ Adding excess of β-CD led to a shift in the peak potential in CV towards more positive values (Fig. 1, inset), which is indeed connected to the fact that FVA



Scheme 1 The interconversion network of the dual-driven (redoxand light-driven) ensembles between the four states: one 2:1 complex (FVA \subset 2CD), two 1:1 complexes (FVA-o \subset CD, FVA-p \subset CD), and one guest structure (FVA-op).

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[†] Electronic supplementary information (ESI) available: Synthetic details, NMR/²D NOESY NMR spectra, ESI-MS spectra, figures and curves mentioned in the text, reference data for **Ref1** and **Ref2**. See DOI: 10.1039/b926323c



Fig. 1 Absorption spectra of **FVA** (1.01×10^{-4} M) in water at 298 K (a) in the initial state, (b) after irradiation at 365 nm for 30 min, (c) in presence of 20 equiv. β-CD and (d) in presence of 20 equiv. β-CD after irradiation at 365 nm for 30 min. Inset: Cyclic voltammograms of **FVA** (1.01×10^{-4} M) in water at 298 K (a) in the initial state and (b) in presence of 20 equiv. β-CD.

is more difficult to oxidize in the presence of β -CD.^{5c} The trend of the O1 wave with a sigmoidal shape is slightly turned to be flat on the forward scan (Curve b, Fig. 1, inset), indicating a progressive disassembly–electrochemical process according to the observations of Amatore *et al.*^{5d} However, the current on the reverse scan exhibited a peak around the R1 wave rather than a plateau, which confirms that the electrogenerated ferrocenium species was much less complexed. Such assembly/disassembly behaviors can also be illustrated by the huge difference of the association constants between β -CD and the pair of redox species (ESI, Fig. S4†).

The results mentioned above indicate that both the stations in compound **FVA** can be efficiently complexed with a β -CD ring in an aqueous environment, but conditions are unfavourable for complexing when ferrocene is oxidized or the azobenzene is photoisomerized to the *cis*-form. The assembly/ disassembly process could be repeated because of the reversibility of the redox and the photochemical operations (ESI, Fig. S5†). Based on such a controllable assembly/ disassembly effect, next we turn to study the interconversion of β -CD inclusion complexes *via* ¹H NMR spectroscopy.

As shown in Fig. 2B, it clearly reveals one group of proton signals of the guest component in FVA C2CD, which is different from that of FVA (shown in Fig. 2A) and indicates a thorough complexation with 2 equiv. β -CD at the test concentration (ca. 1.0×10^{-2} M). Also, the change in the resonance of the ferrocenvl and the azobenzenvl protons is profound. Before complexing, the proton peaks of $H_{a,b}$ or $H_{k,l}$ in **FVA** are overlapped ($\delta = 4.08$, H_{a,b} and $\delta = 7.90$, H_{k,l} in Fig. 2A). The encapsulation of β -CD caused the splitting of these proton peaks, with $H_{a,b}$ appearing at $\delta = 4.22-4.15$, H_k appearing at $\delta = 7.93$ and H₁ appearing at $\delta = 7.88$ (Fig. 2B). Oxidation of the ferrocenyl moiety generated FVA-o CD. Although the paramagnetism of the oxidized ferrocenium moiety¹⁰ makes its proton signals H_{a,b} greatly shielded in the ¹H NMR spectroscopy, the resonances of the protons $H_{k,l}$ are still split (Fig. 2C). It can be found that the azobenzenyl group remained well complexed by β -CD in the oxidation state. On the other hand, irradiation at 365 nm on the FVA = 2CD caused the trans-to-cis photoisomerization of the azobenzene unit, which generates FVA-p CD. The irradiation led to a



Fig. 2 ¹H NMR spectra (400 MHz in D_2O at 298 K) of (A) **FVA**; (B) **FVA** \subset **2CD**; (C) **FVA-o** \subset **CD**, addition of 1.2 equiv. ferric chloride to **FVA** \subset **2CD**; (D) **FVA-p** \subset **CD**, irradiation on **FVA** \subset **2CD** at 365 nm for 2 h; (E) **FVA-op**, irradiation on **FVA** \subset **2CD** at 365 nm for 2 h, then addition of 1.2 equiv. ferric chloride *in situ*.

cluster of new signals corresponding to the protons of the azobenzenyl group in cis-form, with $H_{j'}$ to $H_{m'}$ appearing at δ = 7.42–6.95 (Fig. 2D). The protons H_{a,b} remain split but $H_{k',l'}$ return to being overlapped ($\delta = 6.97, H_{k',l'}$ in Fig. 2D), which indicates the ferrocenyl group was still encapsulated by β -CD but the *cis*-formed azobenzene was not in the photostationary state. The assembly/disassembly behaviors of the two 1:1 complexes are also confirmed by finding the overlap of corresponding proton peaks of the guest compounds (ESI, Fig. S6[†]). Oxidation of FVA-p⊂CD can generate the disassembled state FVA-op. No distinct β -CD ring induced splitting was found in the ¹H NMR spectroscopy. Fig. 2E features the guest structure of the disassembled state. These interconverted geometries are also confirmed by finding of the corresponding NOEs in 2D NOESY NMR spectra (see ESI, Fig. S7^{\dagger}). The interconversion of β -CD inclusion complexes will cause componential molecular weight alterations, because of the assembly/disassembly process of the β -CD ring to the guest subunit. In this way, the formation of the four states of the supramolecular ensembles was also evidenced by ESI-MS (see ESI, Fig. S8[†]).

Cyclodextrin-based supramolecular complexes are typical species which are very sensitive to generate induced circular dichroism (ICD) signals.¹¹ Specifically, the encapsulation of β -CD to both the ferrocene and the azobenzene stations in **FVA** \subset **2CD** produces a negative Cotton effect of ICD at about 255 nm, and a positive one at around 330 nm (see Fig. 3, curve a), respectively. These signals take place at wavelengths corresponding to their UV-Vis absorptions (ESI, Fig. S9†). The negative ICD signal is attributed to the electronic transitions of the ferrocenyl moiety, which is located in the cavity of β -CD and aligned vertical to the axis of the chiral host, whereas the positive one belongs to transitions of the



Fig. 3 Induced circular dichroism (ICD) spectra $(1.01 \times 10^{-3} \text{ M in})$ water, 298 K) for (a) **FVA** \subset **2CD**; (b) **FVA-o** \subset **CD**; (c) **FVA-p** \subset **CD** and (d) **FVA-op**.

azobenzenyl moiety located in and aligned parallel to the axis of β -CD.¹² As translated to **FVA-o** \subset **CD**, the intensity of the negative band at around 255 nm is drastically weakened from -4.5 to -0.3 mdeg, whereas the positive band at around 330 nm remains almost unchanged (Fig. 3, curve b). Oppositely, the ICD signal of FVA-p CD at 330 nm decreased from 4.7 to 1.8 mdeg, but the peak at around 255 nm varies little (Fig. 3, curve c). The two alternative phenomena signify that the β -CD is greatly released from the ferrocene and the azobenzene station, respectively, weakening the corresponding ICD signals. The β -CD host is disassembled from both stations in the state of FVA-op, which makes both the bands shrink in Fig. 3, curve d, exhibiting the lack of ICD sensitivity of the guest structure. The intensity of the dual-wavelength ICD signals could directly give feedback of the structure information. The numbers of ICD signal bands are just in accordance with the number of rings of the corresponding ensemble states. In this way, the multi-steady states of such a supramolecular system might be used as a novel molecularscale storage medium with optical signal expressions.

In summary, a novel ensemble system of β -CD inclusion complexes was prepared. The assembly/disassembly behaviors of the β -CD ring can be selectively controlled by reversible redox and photochemical operations, thus the modulation of the complexation stoichiometries and sites was realized. Meantime, the ensemble structures are equivalent to the number of ICD signal peaks. Such stepwise supramolecular interconversions provide an effective paradigm for design and development of supramolecule-to-supramolecule transformation processes with easily identifiable optical outputs

This work was supported by NSFC/China (20972053, 20603009), the National Basic Research 973 Program (2006CB806200), and the Scientific Committee of Shanghai. We thank Professor Yitao Long and Mr Wei Song for relevant advice on the electrochemical study.

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- 8 This illustration is based on the tested association constants between the reference compounds and β -CD ($K_1 = 2.42 \times 10^3 \text{ M}^{-1}$, $K_2 = 1.63 \times 10^3 \text{ M}^{-1}$). The oscillation of the ring between the two stations in the 1:1 complex (see ESI) shows that β -CD could bind the two stations of FVA with the same magnitude level.
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