



Ion-controlled switchable complexation between pentiptycene-based tweezer-like hosts and self-folding guests



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ARTICLE INFO

Article history:

Received 7 February 2013

Received in revised form 26 March 2013

Accepted 8 April 2013

Available online 13 April 2013

Keywords:

Pentiptycene

Complexation

Tweezer-like host

Self-folding guest

Ion-controlled

ABSTRACT

A couple of self-folding A-D-A guests were synthesized, and it was found that the guests could be included by the pentiptycene-based tweezer-like hosts to form stable 1:1 complexes in solution, which have been evidenced by the ¹H NMR, ROESY 2D NMR and ESI MS spectra. Moreover, a potassium ion-controlled switchable process between the host and the self-folding guest was further achieved.

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1. Introduction

In host–guest chemistry, a permanent and challenging topic is to develop novel hosts with the capability of binding specific substrate species strongly and selectively.¹ During the past decades, chemists have designed and synthesized various macrocyclic hosts, including crown ethers,² cryptands,³ calix[n]arenes,⁴ cucurbit[n]urils⁵ and other macrocycles.⁶ Undoubtedly, a new synthetic host could often provide a lot of opportunities in molecular recognition and self-assembly.

On the other hand, it was known that paraquat derivatives⁷ have become some of the most common guests, and they have also been utilized for construction of different kinds of interlocked assemblies, such as pseudorotaxanes, rotaxanes and catenanes. In addition, the foldamers have attracted much attention during the past two decades for they could not only mimic the structural features of biological macromolecules, but are also important in materials science.^{8,9} However, the applications of the foldamers as guests in host–guest chemistry are still very limited. It might be because that the foldamer used as a guest is too large to complex with a classic macrocyclic host. Consequently, tweezer-like hosts¹⁰ could be utilized for the purpose of inclusion with foldamer guests with large structures.

Recently, we found that the pentiptycene derivatives might be utilized as useful building blocks for the design and synthesis of

novel hosts with specific structures and properties.¹¹ As a result, two pentiptycene-based tweezer-like hosts **1** and **2** (Fig. 1) were synthesized.¹² They showed open central cavities, and thus could

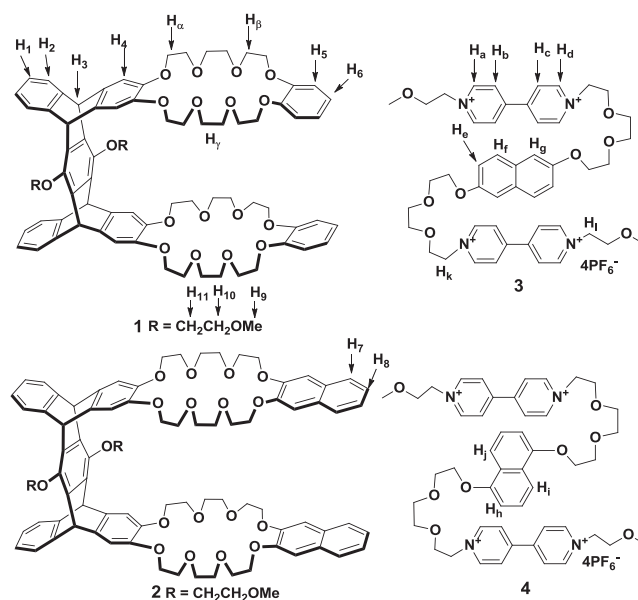


Fig. 1. Structures and proton designations of hosts **1**, **2** and guests **3**, **4**.

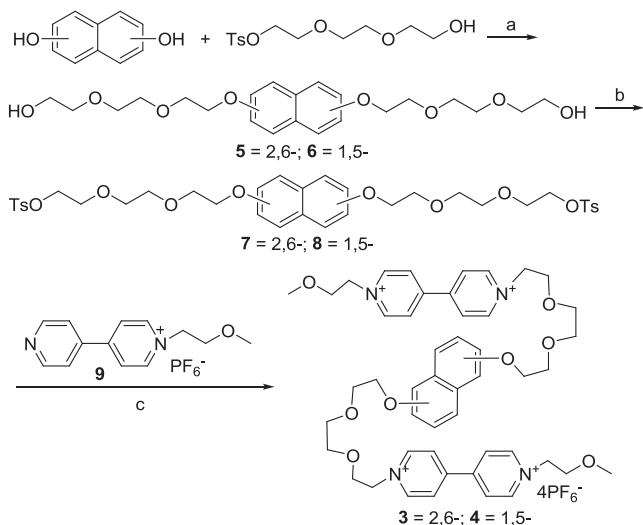
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form stable complexes with tetracationic cyclobis(paraquat-*p*-phenylene) (CBPQT⁴⁺) in different complexation modes.^{12b} To further study the complexation of these synthetic hosts with large open cavities towards different kinds of organic guests, we herein report the complexation between two pentiptycene-based tweezer-like hosts **1** and **2** with self-folding A-D-A guests **3** and **4** in solution in details. Thus, we found that they could form 1:1 stable complexes, respectively, in which the guests with 'S' folding structures could all be included inside the central cavities of the hosts (Fig. 1). Formation of the complexes was all proved by the ¹H NMR, ROESY 2D NMR, and ESI MS spectra. Moreover, it was also found that the binding and release of the guests in the complexes could be easily controlled by the addition and removal of potassium ions.

2. Results and discussion

2.1. Synthesis of self-folding A-D-A guests **3** and **4**

Synthesis of guests **3** and **4** is outlined in Scheme 1. Starting from the dihydroxynaphthalene, the self-folding A-D-A guests **3** and **4** linked by polyether chains could be conveniently synthesized in three steps. First, the reaction of dihydroxynaphthalene with 2-(2-(2-hydroxyethoxy)-ethoxy)ethyl 4-methylbenzenesulfonate in CH₃CN in the presence of K₂CO₃ could give compound **5** or **6**. Then, the reaction of **5** or **6** and tosyl chloride in the presence of Et₃N and DMAP gave bistosylate **7** or **8**, which was further reacted with 1-(2-methoxyethyl)-4-(pyridin-4-yl)pyridinium **9** to afford the target compound **3** or **4**. Compounds **3** and **4** were all characterized by the ¹H NMR, ¹³C NMR, MS spectra, elemental analysis, and X-ray crystal structures.



Scheme 1. Synthesis of guests **3** and **4**. Reagents and conditions: (a) K₂CO₃, CH₃CN, reflux; (b) *p*-TsCl, Et₃N, DMAP, CH₂Cl₂, reflux; (c) (i) CH₃CN, reflux; (ii) NH₄PF₆, acetone.

2.2. Complexation between pentiptycene-based tweezer-like hosts and self-folding A-D-A guests in solution

Complexation between pentiptycene-based tweezer-like hosts and the self-folding A-D-A guests were first studied in solution by the ¹H NMR spectroscopic method. When we mixed the host **1** (3.0 mM) and 1.0 equiv of **3** in 1:1 (v/v) CD₃CN/CDCl₃, a deep orange solution formed immediately because of charge transfer between the electron-rich aromatic rings of the host and the electron-poor pyridinium rings of the guest.¹³ As shown in Fig. 2, the ¹H NMR spectrum of a 1:1 mixture of **1** and **3** showed only one set of

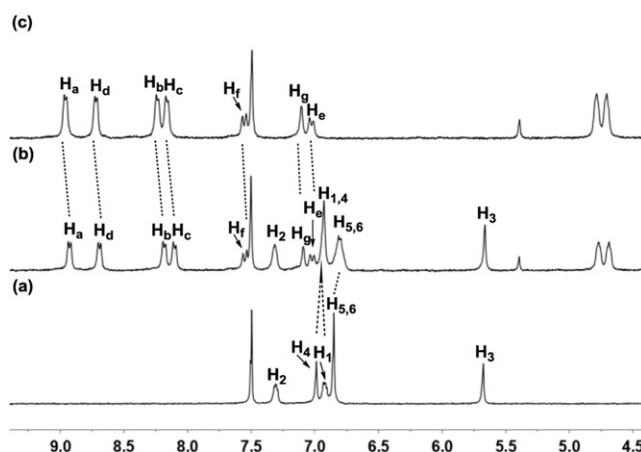


Fig. 2. Partial ¹H NMR spectra (300 MHz, CD₃CN/CDCl₃=1:1, v/v, 295 K) of (a) free host **1**, (b) **1** and 1.0 equiv of **3**, (c) free guest **3**. [1]₀=2.0 mM.

different signals from those of the separated host and guest, which suggested that a new complex **1·3** was formed, and the complexation between **1** and **3** was a fast exchange process. Especially, it was found that the protons H_a, H_b, H_c and H_d of the paraquat ring showed an upfield shift due to the shielding effect of aromatic rings in **1**, and H₄ proton signals of the host also shifted upfield. These observations suggested that a stable complex between host **1** and guest **3** might be formed in solution. The ¹H NMR spectroscopic titrations further afforded a quantitative estimate for the complexation between host **1** and guest **3** by monitoring the changes of the chemical shift of the proton H₄ of **1**. The results showed that 1:1 complex between **1** and **3** was formed by a mole ratio plot. Accordingly, the apparent association constant $K_{a,exp}$ was calculated to be $0.5(\pm 0.01) \times 10^3 \text{ M}^{-1}$ by the Scatchard plot.^{13,14}

Moreover, we identified all protons of pentiptycene-based tweezer-like host **1** and the self-folding A-D-A guest **3** by the ¹H–¹H COSY spectrum.¹³ The 2D ROESY spectral experiment¹³ of complex **1·3** was further carried out to investigate the complexation between the host and the guest. The results showed that the cross-peaks between protons H_a and H_d in the bipyridinium ring of **3** and the proton H_γ in crown ether units, H₁₀ in R group of **1** were found (Fig. 3), which suggested that the guest could thread the

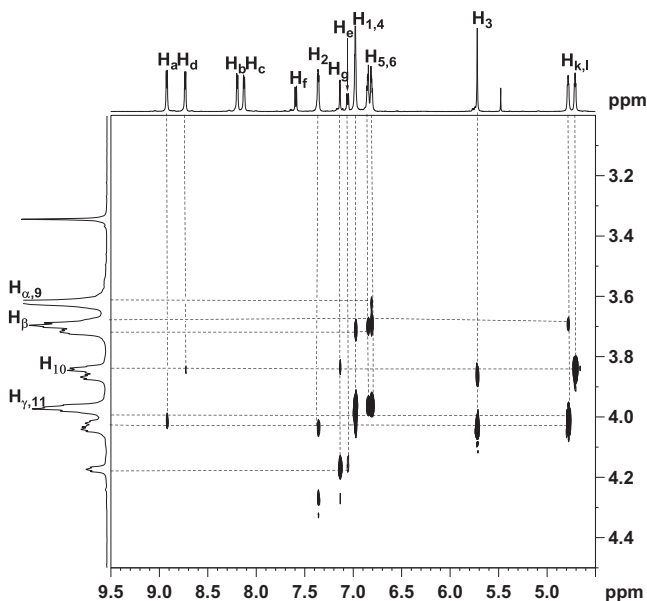


Fig. 3. ¹H–¹H ROESY spectrum (300 MHz, CD₃CN, v/v, 295 K) of **1** and 1.0 equiv of **3**. [1]₀=2.0 mM.

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