



Photo-responsive pseudo[*n*]rotaxanes based on disparate hetero-macrocycle host combination



Ruyi Sun, Xiang Ma*

Key Labs for Advanced Materials and Institute of Fine Chemicals, East China University of Science & Technology, Shanghai 200237, PR China

ARTICLE INFO

Article history:

Received 16 September 2012

Received in revised form 12 November 2012

Accepted 20 November 2012

Available online 24 November 2012

Keywords:

Pseudorotaxane

Cyclodextrin

Cucurbituril

Sulfonatocalixarene

ABSTRACT

A series of novel photo-responsive pseudorotaxanes employing three different hetero-macrocycles combination, α -cyclodextrin (α -CD), cucurbit[7]uril (CB[7]) and *p*-sulfonatocalix[4]arene (SC4), as hosts were obtained. The shuttling of α -CD on the dumbbell can be reversibly driven by alternating irradiation with different lights. ^1H NMR, 2D NOSEY experiments, and MALDI-TOF MS measurement are used to demonstrate the formation of the pseudorotaxanes. UV–vis absorption and induced circular dichroism measurements were carried out to illustrate the reversible photo-responsive properties of the pseudorotaxanes as well.

© 2012 Elsevier Ltd. All rights reserved.

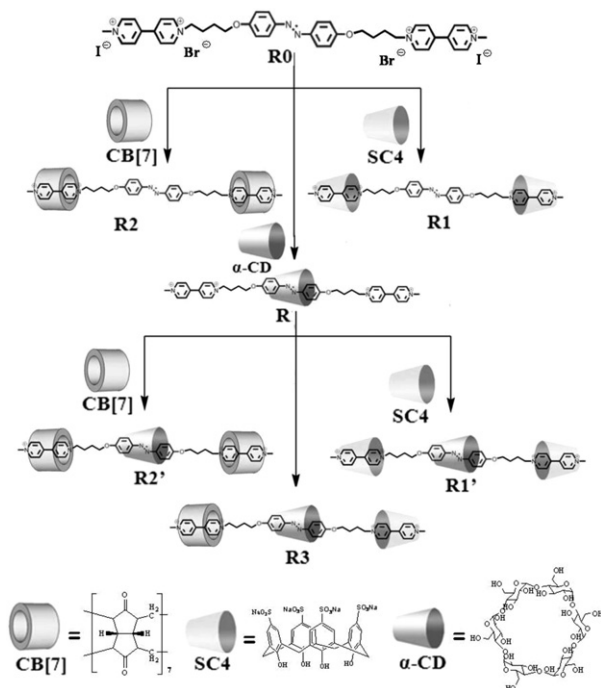
1. Introduction

Pseudorotaxane and rotaxane, as the most representative type of interlocked supramolecular machine,¹ have prevailed since the late 1980s and the early 1990s, with the development of supramolecular chemistry and the better understanding of the processes of the host–guest molecular recognition. Rotaxanes are defined as molecular species consisting of one or more macrocycles encircling the rod portion of dumbbell-like components, in which the dissociation of the ring from the axis is stopped by two bulky terminals (stoppers). The similar species only except for an absence of bulky terminals are called pseudorotaxanes. Multifarious rotaxanes and pseudorotaxanes² have been designed and constructed to achieve specific functions in the areas of nano-structured functional materials, memory devices, and biological applications.³ Cyclodextrin (CD), cucurbituril (CB), and calixarene, as three different host macrocycle compounds provided with special structures and disparate supramolecular inclusion performances, respectively, have been extensively employed to construct rotaxanes and pseudorotaxanes.^{4–6} Many rotaxanes or pseudorotaxanes incorporating two or more components in one interlocked system (either rotaxane oligomer or not) have been constructed in recent years.^{4c,7,8} However, there were only a few rotaxanes or pseudorotaxanes incorporating two or more different host macrocycles in one system. For example, Kim firstly reported a simple pseudo[3]rotaxane holding both α -CD macrocycle and CB[6] macrocycle

together.⁹ And he also prepared another pseudorotaxane polymer whose monomer contained DM- β -CD and CB[7] together and the CB[7] macrocycle could be driven to move by pH change.¹⁰

Previously, a light-driven pseudo[4]rotaxane based on α -CD and CB[7] and their photoisomerized properties in hydrogel have been investigated.¹¹ Herein, based on this work, we constructed several pseudo[*n*]rotaxanes based on disparate hetero-macrocycle host (α -CD, CB[7], and SC4) combination. As shown in Scheme 1, the dumbbell **R0** contains an azobenzene moiety and two 4,4'-bipyridinium (viologen) dication units. The very known phenomena have been reported that α -CD can encircle on such moieties as stilbene and azobenzene in aqueous solution,¹² CB[7]¹³ and SC4¹⁴ prefers to bind 4,4'-bipyridinium (viologen) dication units with very high association constants (about ca. 10^5 L mol⁻¹). Then combining the dumbbell with α -CD, CB[7] and SC4 in various combination modes, we constructed the pseudo[2]rotaxane **R**, pseudo[3]rotaxanes **R1** and **R2**, pseudo[4]rotaxanes **R1'**, **R2'**, and **R3**. The three pseudo[4]rotaxanes could be also regarded as α -CD based rotaxanes to some extent because its two end parts, included by CB[7] or SC4 with very high association constants, could be used to stop α -CD from slipping away from **R0**. In particular, the pseudo[4]rotaxane **R3** consists of one inclusion part between α -CD and the azobenzene moiety and another two inclusion sites between CB[7], SC4, and 4,4'-bipyridinium units, respectively. As far as we know, it is the first example that the three hetero-macrocycle (α -CD, CB[7] and SC4) host are incorporated in one supramolecular pseudorotaxane system. The constructions of these complicated supramolecular systems may set up new basis for exploiting future molecular devices with multiple functions.

* Corresponding author. E-mail address: maxiang@ecust.edu.cn (X. Ma).



Scheme 1. Schematic synthesis of pseudorotaxanes in water, the anions Br^- and I^- of the dumbbell in pseudorotaxanes are omitted here for clarity.

2. Results and discussion

2.1. Pseudorotaxane synthesis and characterizations

Scheme 1 shows the synthetic procedures of the pseudorotaxanes. The dumbbell **R0**, CD based pseudo[2]rotaxane **R**, CB[7] based pseudo[3]rotaxane **R2**, and CD-and-CB based pseudo[4]rotaxane **R2'** were prepared as we reported previously.¹¹ All of the pseudorotaxanes were formed in aqueous solution. Owing to the very effective binding between SC4 and the viologen moieties, SC4 based pseudo[3]rotaxanes **R1** and pseudo[4]rotaxane **R1'** were prepared in the similar way as pseudo[3]rotaxane **R2** and pseudo[4]rotaxane **R2'**, respectively in the absence of CB but SC4.

The inclusion formation of pseudo[3]rotaxanes between the dumbbell and the macrocycles CB[7] and SC4 can be confirmed from the ^1H NMR spectral variances of the dumbbell protons. As shown in Fig. 1, the protons of the symmetrical dumbbell **R0** exhibit obvious split shifts after being included in the cavity of CB[7] and SC4. In the presence of 2 equiv of SC4, all the aromatic protons of viologen dication unit $H_{h(i),g(j),f(k),e(l)}$ exhibit a visible upfield shift ($\Delta\delta$) owing to the inclusion complexation behavior, which suggests that the viologen dication part of the symmetrical dumbbell is included by SC4. The $\Delta\delta$ values between **R0** and **R1** are 2.47 ppm for $H_{h(i)}$, 0.42 ppm for $H_{g(j),f(k)}$. Upon the different $\Delta\delta$ value for each proton, we can infer that **R0** is captured by SC4 with the methyl-pyridium

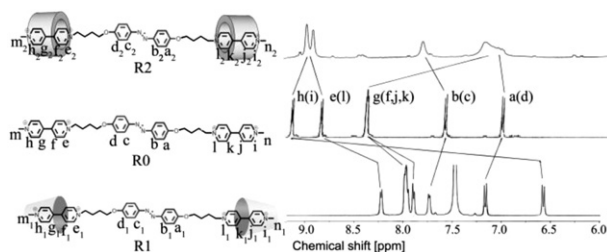


Fig. 1. Partial ^1H NMR spectra in D_2O (400 MHz, 293 K) of **R0**, **R1**, and **R2**, the anions Br^- and I^- of the molecules are omitted here for clarity.

portion immersed into the cavity, which is coincided with Liu's reports.¹⁴ On the other hand, the $\Delta\delta$ values between **R0** and **R2** are very different from that of **R0** and **R1**, with $H_{g(j),f(k)}$ exhibiting a visible upfield shift about 1.2 ppm, while $\Delta\delta$ values for $H_{e(l)}$ and $H_{h(i)}$ are very small. These shifts of protons of viologen dication unit is evident for the interaction between CB[7] and viologen dication, and the different inclusion modes between **R1** and **R2** is due to the disparate cavity structure of SC4 and CB[7].

The formation of the inclusion complex between the dumbbell and α -CD, SC4 and CB[7] is clearly confirmed by ^1H NMR spectroscopy as in Fig. 2. As described in our previous reports, the chemically equivalent aromatic protons located in the same electromagnetic environment of the symmetrical dumbbell molecular **R0** exhibit obvious split shifts with equal intensity after being included by α -CD in pseudo[2]rotaxane **R**. And in the presence of 2 equiv of SC4, all the aromatic protons of viologen dication also exhibit a visible upfield shift ($\Delta\delta$), which is similar to the shift changes of pseudo[3]rotaxane **R1** comparing with the dumbbell **R0**. The $\Delta\delta$ values between **R** and **R1'** are about 2.64 ppm for $H_{h(i)}$, 0.74 ppm for $H_{g(j),f(k)}$. Coinciding with the very characteristic NMR addresses of the inclusion between CB[7] and the viologen reported by Kaifer,¹³ the aromatic protons of the bipyridinium in pseudo[4]rotaxane **R2'** have an upfield shift of more than 1.61 ppm compared with the dumbbell **R** in the presence of 2 equiv of the host CB[7].¹¹ By comparing these NMR spectra with that of **R3**, we can find that the $\Delta\delta$ values of the viologen dication protons show respective similarity with that of both **R1'** and **R2'** to some extent, so the structure of pseudo[4]taxane **R1'**, **R2'** and pseudo[4]rotaxane **R3**, which contains α -CD, SC4, and CB[7] were confirmed.¹⁵

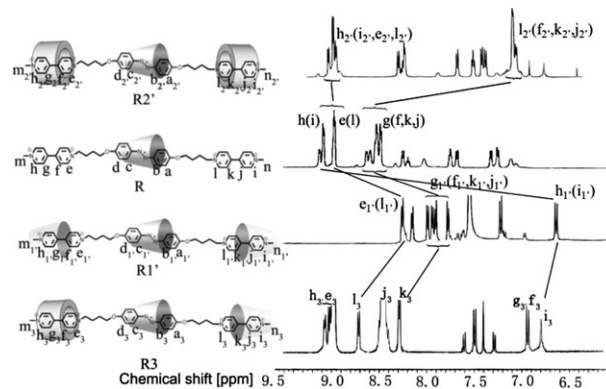


Fig. 2. Partial ^1H NMR spectra of pseudorotaxanes **R**, **R1'**, **R2'**, and **R3** in D_2O (400 MHz, 293 K).

The structure of **R1'** in which α -CD cycles on azobenzene portion and the viologen portion assembles with SC4 at two ends of the dumbbell can be confirmed using 2D ^1H NMR NOESY spectroscopy (Fig. 3). The NOEs between the α -CD protons and the azobenzene protons H_a, H_b, H_c, H_d show that the azobenzene part is embedded in CD cavity. While, the NOE between proton H_h and the proton of SC4 indicates that the two viologen parts, which lay in the two ends are captured in the SC4 cavity.

The structure of **R3**, which contains α -CD, SC4, and CB[7] was also confirmed by 2D ^1H NMR NOESY spectroscopy (Fig. 4). The NOE between H_i proton and the hydrogen atom of SC4 indicates that the viologen part involved in the SC4 cavity. There is no NOE signal between CB[7] and any proton of the dumbbell because the protons of CB[7] lie outside of the cavity. The NOE signals between H_i and SC4 of pseudo[4]rotaxanes **R1'** and **R3** appear at different places in the two spectra Figs. 3 and 4, respectively, since the pseudo[4]rotaxane **R3** contains α -CD in the middle of the dumbbell, and the disparate SC4 and CB[7] including parts lying at two ends, respectively.

Download English Version:

<https://daneshyari.com/en/article/5217990>

Download Persian Version:

<https://daneshyari.com/article/5217990>

[Daneshyari.com](https://daneshyari.com)