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Original article

Monofunctionalized pillar[5]arene-based stable [1]*pseudo*rotaxane

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ABSTRACT

We reported a new monofunctionalized pillar[5]arene bearing imidazolium moiety that formed stable [1]*pseudo*rotaxane even at high concentration (100 mmol/L) in chloroform. The self-assembly was detailed investigated by multiple methods, including varying concentration ^{1}H NMR, 2D COSY NMR, 2D NOESY NMR, viscosity measurements, 2D DOSY NMR, and HR-ESI-MS analysis. [1]Rotaxane was obtained efficiently through photo thiol-ene reaction which further confirmed the formation of [1]*pseudo*rotaxane.

1. Introduction

Pillararenes are a novel kind of macrocyclic host for supramolecular chemistry composed of hydroquinone units linked by methylene bridges at *para* positions [1,2]. They have held the spotlight in this field owing to their unique highly rigid structure and easy functionalization with various substituents at the hydroquinone unit [3–6]. Because of the electron-rich property, their cavities can encapsulate many types of cationic guests and neutral molecules [7–16]. These features make them good candidate to construct various assemblies with intriguing properties. Hitherto, many pillararene-based supramolecular architectures have been built, such as the first pillararene-based [c2]daisy chain containing two mirror image monomers reported by Huang's group [17], [2]rotaxane whose motions could be triggered by solvent and temperature [18], and the double-switchable pillararene-based supramolecular polymer reported by our group [19].

*Pseudo*rotaxanes, a self-assembly threaded structure in which macrocyclic components encircle linear components, have been investigated with great interest. They are the building blocks for the preparation of artificial molecular machines, supramolecular polymers, supramolecular gels, and other functional supramolecular materials [20–23]. Some of them are promising in preparation of molecular sensors and in drug delivery [24–28]. [1]*pseudo*rotaxanes are one of the basic threaded structures for *pseudo*rotaxane. However, stable pillar[5]arene-based [1]*pseudo*rotaxanes are still rarely reported because they mostly exist in dilute solutions mixt with linear oligomers, cyclic dimers and so on [29]. In 2011, Ogoshi *et al.* presented firstly the [1]*pseudo*rotaxanes based on pillar[5]arene with octyltrimethylammonium group, which exhibited self-inclusion complexation in chloroform. But it was uncertain whether this [1]*pseudo*rotaxane could form at high concentration due to the restriction of solubility [30]. Stoddart *et al.* investigated detailedly the assembling behavior of a monofunctionalized pillar[5]arene derivative containing a viologen moiety. It behaved as self-complexation at low concentration, assembled into supramolecular daisy chain polymers and eventually organogels upon the increasing of its concentration [31]. Herein, we report a stable pillar[5]arene-based [1]*pseudo*rotaxane even in concentrated chloroform solution (100 mmol/L) by reasonable monofunctionalization. The self-complexation was demonstrated by the research of ^{1}H NMR, 2D COSY NMR, 2D NOESY NMR, viscosity measurements and HR-ESI-MS. Furthermore, [1]rotaxane was obtained efficiently through thiol-ene reaction confirming the formation of [1]*pseudo*rotaxane.

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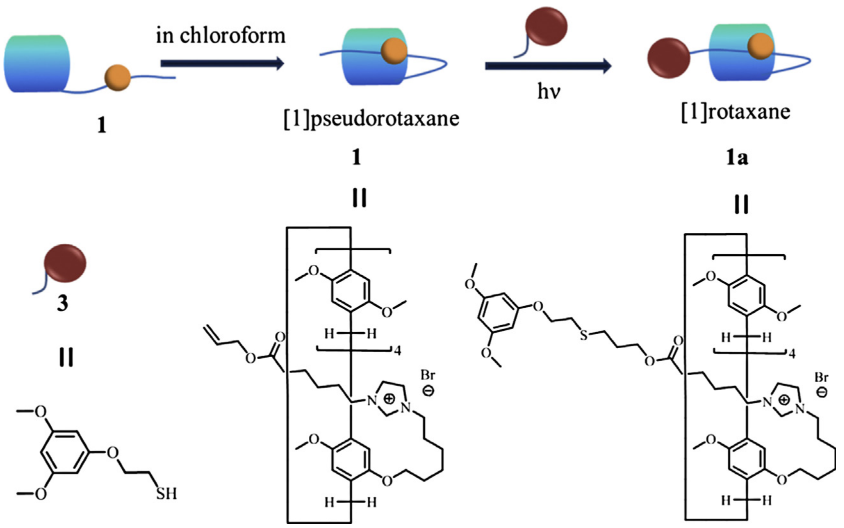

Scheme 1. Illustration of the self-complexation of monofunctionalized pillar[5]arene **1** and the formation of [1]rotaxane.

2. Experimental

All the experimental procedures including materials and methods, synthesis and characterization details, and copies of NMR spectra were present in Supporting information.

3. Results and discussion

As shown in Scheme 1, monofunctionalized pillar[5]arene with imidazolium was exploited in our system due to the strong complexation ($K_a = 1.0 \times 10^4$ L/mol) between pillar[5]arene and imidazolium cation [32]. To ensure the formation of self-complexation assemblies, there were two long alkyl chain linked to imidazolium. One of them was designed to provide the flexibility and the other one appeared as the guest part. Moreover, an allyl group was added at the end of the alkyl guest as a reactive site, which offered the possibility to prepare [1]rotaxane through thiol-ene reaction. Compound **1** was synthesized in five steps with moderate overall yield (Scheme S1 in Supporting information). By similar method, compound **2**, which had the same linear guest part but without pillar[5]arene unit, was synthesized as a reference guest (Scheme S1).

The self-assembled behavior of **1** in solution was first examined by ^{1}H NMR spectroscopy at 40 mmol/L in $CDCl_3$. The ^{1}H NMR spectrum of compound **1** showed quite different from compound **2** at the same concentration. The signals of protons on the imidazolium unit (H_7, H_8, H_9) and alkyl chain (H_{10}, H_{11}, H_{12}, H_{13}) became broader and shifted upfield, including two obvious broadened peaks (H_{11}, H_{12}) located at minus ppm. These upfield shifts resulted from the threading of imidazolium guest into the pillar[5]arene macrocycle (Fig. 1). In order to confirm the proton assignments clearly, two-dimensional correlation spectroscopy ^{1}H NMR (COSY) was performed in combination with ^{1}H NMR (Fig. S5 in Supporting information). It was demonstrated that the signals of protons H_7–H_{12} on or next to the imidazolium ring revealed more than 2 ppm upfield chemical shift, and those of H_{13}, H_{14} showed a

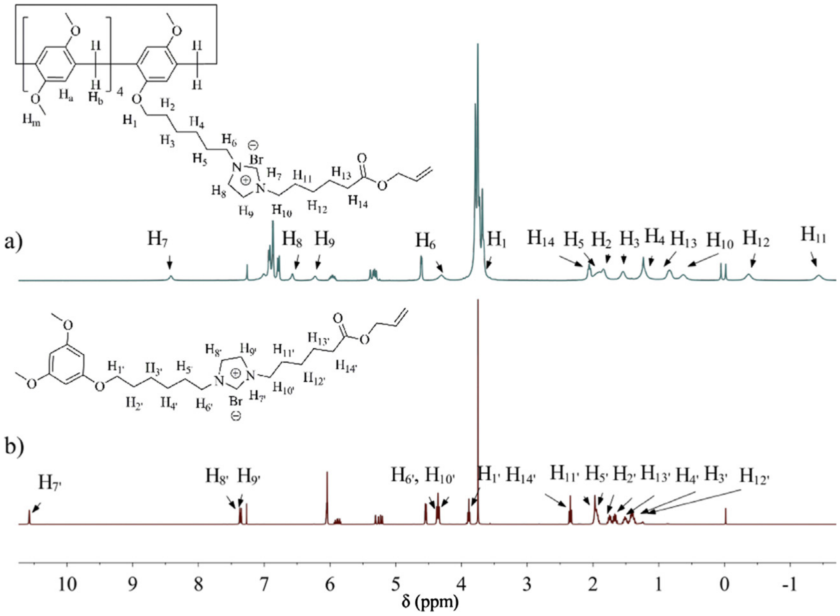

Fig. 1. ^{1}H NMR (40 mmol/L in $CDCl_3$, 400 MHz) spectrum and structure of **1** (a), and **2** (b).

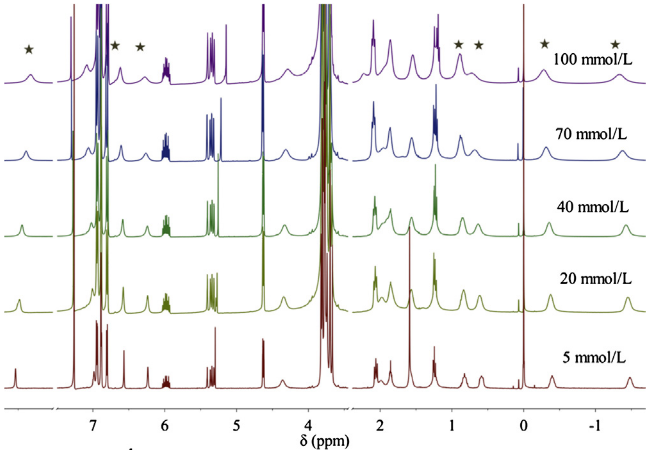

Fig. 2. Partial ^1H NMR ($CDCl_3$, 400 MHz) spectra of **1** at different concentrations (the peaks of complexed part are denoted by asterisks).

fraction of change, while the protons on the other alkyl chain showed little change. This result indicated that imidazolium moiety and adjacent alkyl chain, the one distant from pillar[5]-arene unit, were threaded into the electron-rich cavity and the other protons were located outside the cavity. In addition, the NOESY analyst was consistent with this result in which strong NOE correlation signals were presented between the protons H_{10}, H_{11}, H_{12}, H_{13} and the aromatic or methylene hydrogen atoms of pillar[5]arene (Fig. S6 in Supporting information).

The above spectra validated the complexation of compound **1** undoubtedly, but could not supply us the exact information about whether the assembly was intra- or inter-molecule. To verify the structure of [1]*pseudo*rotaxane, the ^1H NMR spectroscopy of compound **1** at variable concentration (from 5 mmol/L to 100 mmol/L) were measured, which did not show any apparent changes (Fig. 2). Along with the increase of concentration, only some signals gave slight broadened trend, indicating that compound **1** did not form intermolecular complexes in $CDCl_3$.

The self-complexation behavior of **1** in chloroform was further studied by viscosity measurements. As presented in Fig. 3a, the curve in the double logarithmic plots of specific viscosity *vs.* concentration at 5–200 mmol/L had a slope of 1.103, suggesting a linear relationship between specific viscosity and concentration, which is characteristic for non-interacting assemblies of constant size, in agreement with the intramolecular-threading even at high concentrations [33]. Meanwhile, two-dimensional diffusion-ordered ^1H NMR (DOSY) experiments were also employed to investigate the self-assembly of compound **1** at different concentrations (Fig. 3b). The DOSY spectrum at every concentration revealed one set of signals, manifesting only one aggregate size in solutions. As the concentration of **1** increased from 5 mmol/L to 100 mmol/L, the value of weight average diffusion coefficients (D) decreased from 6.28×10^{-10} to 5.02×10^{-10} m^2/s ($D_5/D_{100} = 1.25$). This slight decrease was insufficient to suggest the change of the average dimension of aggregates. That was to say as the concentration increased, the self-assembly kept the same. The high resolution ESI mass spectrometry of a mixture of **1** revealed the molecular peak at m/z 1041.5331 corresponding to the monomer, backing up the result of intramolecular complexation (Fig. S1c in Supporting information).

The above result indicated the existed complexation but no intermolecular aggregates in the chloroform solution of compound **1** at the concentration of 5–100 mmol/L. It was reasonably deduced that stable [1]*pseudo*rotaxane was formed by the new monofunctionalized pillar[5]arene, which was different from the usual assembly as reported by literature when bearing such a long side chain [17,34–36]. It was probably because this molecule held two long flexible chains linked to imidazolium, which ensured the intramolecular interaction between the alkyl chain distant from the pillar[5]arene and the pillar[5]arene cavity.

Finally, the formation of [1]*pseudo*rotaxane was proved considerably by the preparation of [1]rotaxane. Considering the terminal group of compound **1**, we came up with the photo thiol-ene radical reaction. As an important member of thiol-click family, thiol-ene reaction possessed the merits of facile condition, rapid reaction rate, excellent yield, along with strong tolerance for many kinds of functional groups [37]. Here, compound **3** was selected as the stopper and dichloromethane was employed as the solvent (Scheme 1). [1]Rotaxane was obtained successfully both at the concentration of 20 mmol/L and 100 mmol/L in relatively high isolated yield (57% and 54%) (Scheme S2 in Supporting information). Fig. S7 in Supporting information showed the ^1H NMR spectra of [1]*pseudo*rotaxane and [1]rotaxane. Except the new peaks from the added stopper as well as the disappearance of double bond signals, ^1H NMR spectrum kept almost same after reaction, demonstrating no change of complexation. Besides, we prepared the control compound **2a** through thiol-ene reaction between **2** and **3** (Scheme S2). In comparison with the ^1H NMR spectrum of **2a**, the assembly of **1a** was clear (Fig. S8 in Supporting information). In this regard, the convenience and efficiency of thiol-ene reaction might supply a new synthesis strategy for rotaxane.

4. Conclusion

In summary, we described a stable monofunctionalized pillar[5]arene-based [1]*pseudo*rotaxane whose self-inclusion structure was exhaustively proved *via* varying concentration ^1H NMR, 2D COSY NMR, 2D NOESY NMR, viscosity measurements, 2D DOSY NMR, and HR-ESI-MS analysis. [1]Rotaxane, which was prepared efficiently through thiol-ene reaction confirmed the

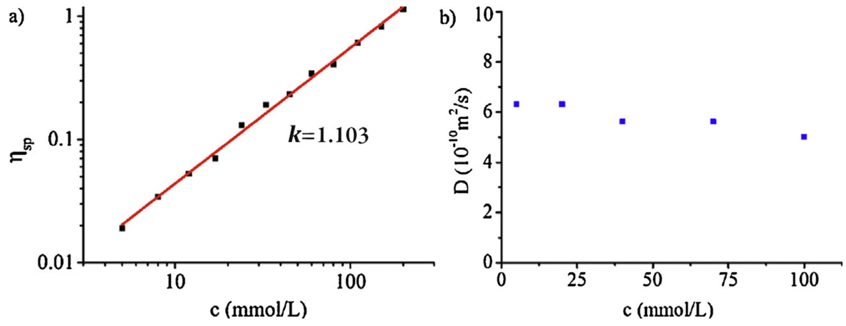

Fig. 3. (a) Specific viscosity of **1** in $CHCl_3$ solutions *vs.* the concentration (293 K). (b) Concentration dependence of diffusion coefficient D ($CDCl_3$, 298 K, 600 MHz) of **1**.

formation of the stable [1]*pseudo*rotaxane. We suspect that this [1]*pseudo*rotaxane and the corresponding [1]rotaxane are potential in developing novel functional molecular machines.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cclet.2015.05.030.

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