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Communication

Construction of [1]rotaxanes with pillar[5]arene as the wheel and terpyridine as the stopper

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ABSTRACT

The condensation reaction of ω-aminoalkyleneamide-functionalized pillar[5]arenes with 2-(4-([2,2′:6′,2″-terpyridin]-4′-yl)phenoxy)acetic acid or 4-(4-([2,2′:6′,2″-terpyridin]-4′-yl)phenoxy)butanoic acid in dry chloroform at room temperature under the catalysis of HOBT/EDCl resulted in novel pillar[5]arene diamido-bridged terpyridine derivatives. ^{1}H NMR and 2D NOESY spectra clearly indicated that the interesting [1]rotaxanes were formed by longer alkylene such as propylene, butylene and hexylenediamido chains threading into the cavity of the pillar[5]arene and with larger terpyridine acting as the stopper. However, the shorter ethylenediamido chain only exists outer of cavity of pillar[5]arene and the molecule exist on free form.

As one of the basic member of the mechanically interlocked structures, pseudorotaxanes and rotaxanes have become one of the hottest research area in recent years because they are not only able to become the fundamental precursors for novel supramolecular species [1,2], but also realize some functionality and show the response to external stimulus, which could be the prototypes of simple molecular machines [3]. Among various interlocked pseudorotaxanes and rotaxanes, pseudo[1]rotaxane and [1]rotaxanes typically contain the wheel and axle that are connected in one molecule with a fast or slow exchange process between threaded and free forms or with a stable threaded form in solution or solid state [4]. In particular, pseudo[1]rotaxanes and [1]rotaxanes can be extensively utilized as molecular machines to show corresponding response to external stimuli due to their reversible conversion behavior [5]. Therefore, the efficient construction of fascinating [1]rotaxanes attracted continual attentions in supramolecular chemistry [6].

In the past decade, the well-known pillar[5]arenes have been widely used as wheel components in constructing various mechanically interlocked molecules such as pseudorotaxanes, rotaxanes and catananes with diverse functions [7–14]. The mono-functionalized pillar[5]arenes with longer side chains were also employed for construction of various pseudo[1]rotaxanes and [1]rotaxanes [15–20]. For this purpose, various longer chain axels and larger functionalized stopers have been introduced into the rim of pillar[5]arenes [21–26]. Recently, we have successfully synthesized mono-functionalized pillar[5]arene Schiff base, thiourea, pyridylimine and polyamide derivatives and found that these functionalized pillar[5]arene derivatives with longer side chains tending to form stable pesudo[1]rotaxane and [1]rotaxane both in solution and in solid state [27–34]. In order to assembly novel mechanically interlocked structures based on the metal coordination mode, we initialized the project on construction of functionalized [1]rotaxanes with pillar[5]arene as the wheel and versatile ligand terpyridine as the stopper. A literature survey indicated that there are very few reports about the combination of terpyridine and pillararene in supramolecular field [35–37]. Herein, we wish to report the convenient synthesis of a series of pillar[5]arene alkylenediamido-bridged terpyridine derivatives and the efficient formation of the fascinating [1]rotaxanes.

The synthetic rout for pillar[5]arene diamido-bridged terpyridine derivatives was illustrated in Scheme 1. According to our previously established reaction conditions for the synthesis of pilar[5]arene polyamide derivatives [31–33], a mixture of mono-amide-functionalized pillar[5]arenes **1a-d** (m = 2, 3, 4, 6) and (4-([2,2′:6′,2″-terpyridin]-4′-yl)phenoxy)acetic acid **2a** in chloroform in the presence of HOBT/EDCl was stirred at room temperature for 24 h. After workup, the expected pillar[5]arene diamido-bridged terpyridine derivatives **3a-d** (m = 2, 3, 4, 6; n = 1) were successfully prepared in 17%-35% yields. When 4-(4-([2,2′:6′,2″-terpyridin]-4′-yl)phenoxy)butanoic acid was employed in the reaction under same reaction conditions, the corresponding pillar[5]arene diamido-bridged terpyridine derivatives **4a-d** (m = 2, 3, 4, 6; n = 3) were also conveniently synthesized in lower yields. The structures

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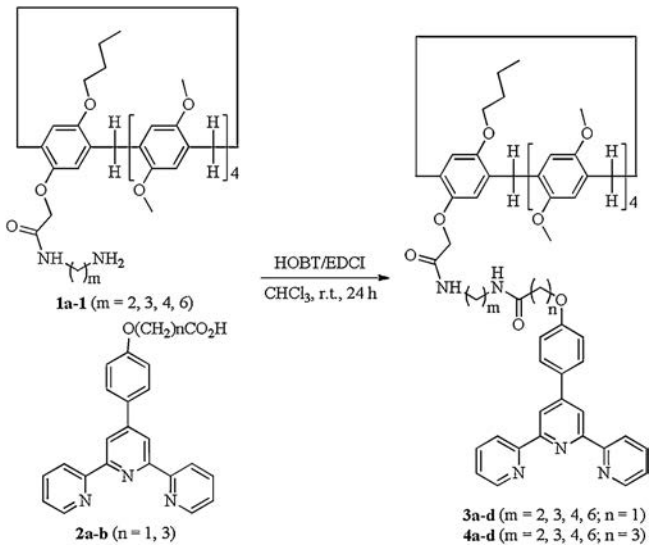

Scheme 1. Synthesis of the terpyridine amide-bridged pillar[5]arenes.

of the obtained pillar[5]arene-terpyridines **3a-d** and **4a-d** were fully characterized by IR, HRMS, ^{1}H and ^{13}C NMR spectroscopy.

The ^{1}H NMR spectra gave the useful information about the interlocked molecular structures of the prepared pillar[5]arene-terpyridnes. In the ^{1}H NMR spectrum of pillar[5]arene-terpyridine **3a** in $CDCl_3$, the methylene unit (OCH_2CO) and ethylenediamido unit ($NHCH_2CH_2NH$) displayed normal absorptions in the range of 4.37-3.58 ppm. There are no any characteristic absorptions in the high magnetic field, which clearly indicated that the ethylenediamido unit did not inserted into the cavity of the pillar[5]arene. Therefore, the scaffold of terpyridine was only connected to the pillar[5]arene by ethylenediamido chain from the outside in pillar[5]arene-terpyridine **3a** (Fig. 1a). On the other hand, the pillar[5]arene-terpyridine **3b-d** clearly showed several absorptions at high magnetic field. There are two peaks at δ -0.38 and δ -1.52 for the propylenediamido unit in compound **3b**, two peaks at δ 0.60 and δ (-1.79)-(-2.07) for butylenediamido unit in compound **3c** and four peaks at δ (-0.07)-(-0.10), δ (-0.90)-(-1.03), δ (-1.61)-(-1.68), δ (-2.25)-(-2.27) for hexylenediamido unit in compound **3d**, respectively. These chemical shift signals in negative field (δ < 0) ambiguously revealed that the alkylenediamido chain inserted into the cavity of pillar[5]arene to form the [1]rotaxane (Fig. 1b). This result is concordance with our previously reported formation of [1]rotaxanes based on the functionalized pillar[5]arene mono-and diamides [27–34], in which the length of the ethylenediamido unit is short for the formation of [1]rotaxane and the relative longer alkylene such as propylene, butylene, and hexylene chains are long enough for the formation of the unique [1]rotaxane.

For providing reliable evidence for the above conclusion, a series of pillar[5]arene-terpyridines with longer diamido-bridge **4a-d** (m = 2, 3, 4, 6; n = 3) were also prepared (Scheme 1). There is still no any chemical shift signals in negative field in ^{1}H NMR spectra of the compound **4a**. This means that the longer $OCH_2CONHCH_2CH_2NHCOCH_2CH_2CH_2O$ chain still did not thread into the cavity of the pillar[5]arene, which is a little beyond of our expectation. A possible reason is that the ethyleneamido unit mainly exist outside of the cavity in starting material mono-amide-functionalized pillar[5]arene **1a** in solution [27]. Then, the catalytic amidation reaction between the amino group and the carboxylic group took place in the outside of the cavity of the pillar[5]arene to give the free form structure (Fig. 1a). The ^{1}H NMR spectra of the pillar[5]arene-terpyridines **4b-d** in $CDCl_3$ indicated that some characteristic absorptions of alkylene unit were clearly observed in the high magnetic field ($\delta < 0$). ^{1}H NMR spectrum of **4b** showed two broad singlets at δ 0.20, and δ -1.61 for the bridging propylene unit. ^{1}H NMR spectrum of **4c** gave a mixed peaks at δ (-2.07)-(-2.30) for the bridging butylene unit. ^{1}H NMR spectrum of **4d** showed four absorptions at δ -0.38, δ (-0.83)-(-1.07), δ (-1.58)-(-1.67), and δ -2.15 for the bridging hexylene unit. Therefore, it can be concluded that the similar [1]rotaxanes was actually formed in the pillar[5]arene-terpyridines **4b-d** as that of the compounds **3b-d** (Fig. 1b).

The stronger evidence for formation of the [1]rotaxanes came from 2D NOESY spectra. For examples, the 2D NOESY spectra of the compounds **3d** and **4d** were listed in Figs. 2 and 3. From Fig. 2, it was clearly seen that the NOE correlations between proton Hm, Hn at the core of pillar[5]arene and protons Hb, Hc, Hd, He of the hexylene chain (Fig. 2, A, B, C, D), between proton Hi at the core of pillar[5]arene and protons Hb, Hc, Hd, He of the hexylene

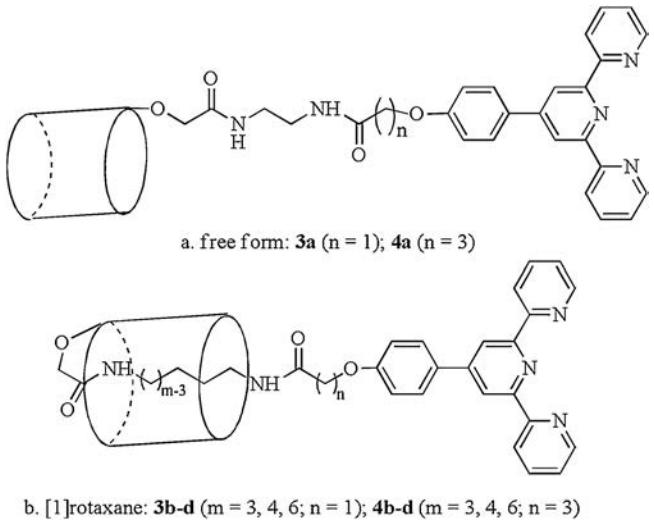

Fig. 1. The illustration of free form (a) and [1]rotaxanes (b) in pillar[5]arene-terpyridines.

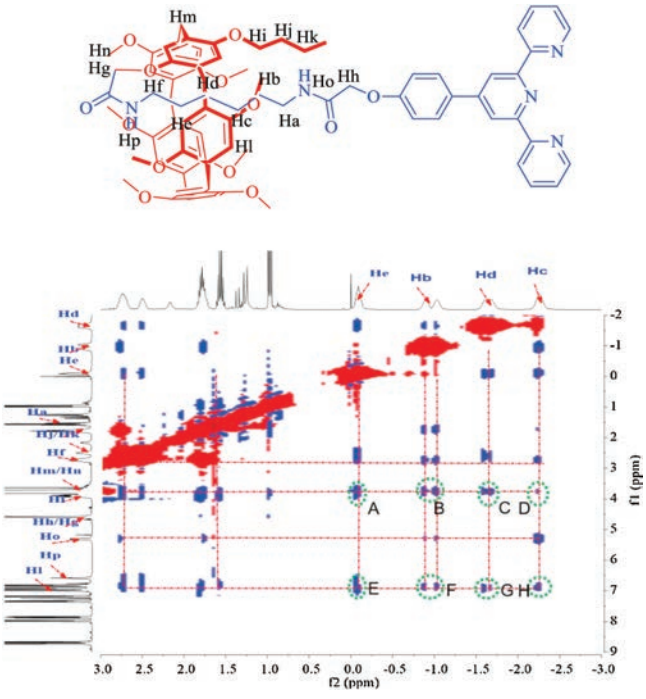

Fig. 2. The NOESY spectrum of compound **3d**.

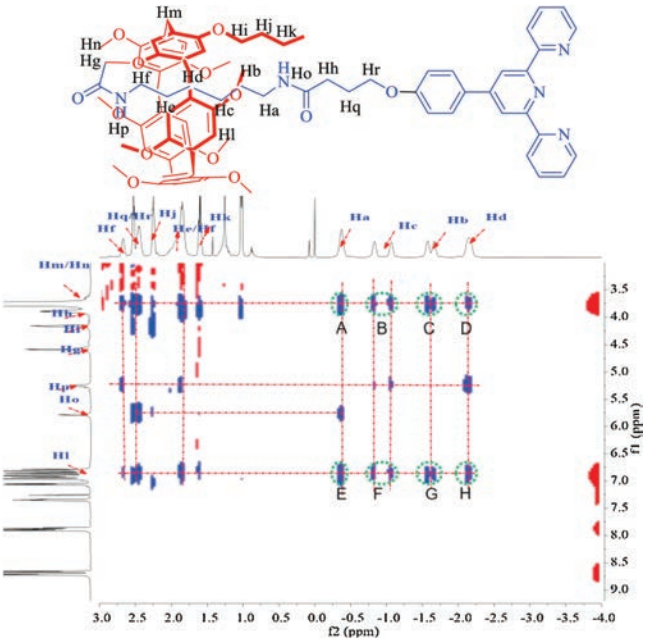

Fig. 3. The NOESY spectrum of compound **4d.**

chain (Fig. 2, E, F, G, H). From the Fig. 3, the correlations between protons Ha, Hb, Hc, Hd of the hexylene unit and protons Hm, Hn at the core of pillar[5]arene (Fig. 3, A, B, C, D), between protons Ha, Hb, Hc, Hd of the hexylene unit and proton Hl at the core of pillar[5]arene (Fig. 3, E, F, G, H) were also observed. Combined the ^{1}H NMR results where the protons of the hexylene unit obviously shifted to high magnetic field, it was confirmed the bridged hexylene chain threading into the cavity of the pillar[5]arene to form [1]rotaxane.

In summary, we have successfully synthesized a series of novel pillar[5]arene diamido-bridged terpyridine derivatives by HOBT/EDCl catalyzed amidation reaction of aminoalkyleneamido-functionalized pillar[5]arenes with terpyridine-substituted acetic acid and butanoic acid. The analysis of ^{1}H NMR and 2D NOESY spectra clearly indicated that the interesting [1]rotaxanes were formed by longer propylene, butylene and hexylenediamido chains threading into the cavity of the pillar[5]arene and with larger terpyridine acting as the stopper, while pillar[5]arenes with the shorter ethylenediamido chain only exists outer of the cavity of pillar[5]arene. The convenient formation of [1]rotaxanes with versatile complexing terpyridine can be easily employed to construct smart mechanically interlocked molecules.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.cclet.2019.04.024.

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