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Preparation of two new [2]rotaxanes based on the pillar[5]arene/alkane recognition motif

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ABSTRACT

Based on the pillar[5]arene/alkane recognition motif, two [2]rotaxanes were successfully prepared. Their formation was confirmed by NMR spectroscopy and ESI mass spectrometry. We also demonstrated that 3,5-dinitrophenyl group and 3,5-bis(trifluoromethyl)phenyl group are big enough to work as stoppers for DPPillar[5]arene, which lays a foundation for the preparation of more complex and functional supramolecular structures.

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The creation of artificial supramolecular assemblies with fascinating structures and desired properties has been fundamental to supramolecular chemistry and material science.¹ Rotaxane, as the basic representative of mechanically interlocked threaded structures, has been one of the most active frontiers in supramolecular chemistry and received a great deal of attention.² Due to their unique topological structures and physical and mechanical properties, rotaxanes have been widely used in the preparation of molecular devices, molecular machines, and supramolecular polymers.³ Pillar[5]arenes, as a new type of macrocyclic hosts, are expected to show many advantages over traditional macrocyclic hosts due to their symmetrical pillar-shaped architectures.⁴ Though, pillar[5]arenes have been used in the field of supramolecular assemblies and host-guest chemistry based on their unique structures, rotaxanes based on pillar[5]arenes have been rarely reported. The only example was reported by the Stoddart's group.^{4r} They exploited a new guest molecule, 1,8-diaminooctane, to prepare a [2]rotaxane with DMPillar[5]arene by reacting the primary amino groups of the guest with 3,5-di-tertbutylbenzaldehyde. However, the yield of this [2]rotaxane was quite low (7%).

In our previous work, we demonstrated that pillar[5]arenes could form [2]pseudorotaxanes with long alkyl chains driven by C-H··· π interactions^{4d} and this recognition motif was successfully applied for the formation of supramolecular assemblies including linear supramolecular polymers^{4o} and a [c2]daisy chain.^{4q} Later, alkyl chains with different substitutes have also been used to

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mixture of 5.00 mM DPP5 and 1 (b) and 5.00 mM 1 (c).







Scheme 1. Synthetic route of [2]rotaxane 3.



Figure 2. Partial ¹H NMR spectra (400 MHz, CDCl₃, 22 °C) of dumbbell-shaped component **2** (a), [2]rotaxane **3** (b) and **DPP5** (c).

state.^{4s} To further explore the possible application of the pillar[5]arene/alkane recognition motif and to develop new synthetic methods to efficiently prepare [2]rotaxanes, we are interested in the fabrication of pseudorotaxane- and rotaxane-type threaded structures based on the pillar[5]arene/alkane recognition motif. Herein, we report the preparation of two new [2]rotaxanes by the complexation between a DPPillar[5]arene and a 1,10-decanediol with 3,5-dinitrophenyl or 3,5-bis(trifluoromethyl)phenyl as stoppers.

DPPillar[5]arene (1,4-dipropoxypillar[5]arene, **DPP5**) was successfully synthesized by the condensation of 1,4-dipropoxybenzene and paraformaldehyde with $[BF_3 \cdot O(C_2H_5)_2]$ as a catalyst according to the literature.^{4c} First of all, we have to confirm which kind of block group is big enough to work as a stopper for DPPillar[5]arene. On the basis of the analysis of previously reported crystal structures of pillar[5]arenes,^{4d,e} we chose easily available 3,5-dinitrophenyl as stoppers and synthesized the semi-blocked rod-like component **1** and the dumbbell-shaped component **2** (Scheme S1 in Supplementary data) via the esterification reaction of 3,5-dinitrobenzoic acid with decane-1,10-diol.



Scheme 2. Synthetic route of [2]rotaxane 4.

The complexation between DPPillar[5]arene and the semiblocked rod-like component 1 in chloroform was first investigated. The ¹H NMR spectrum of an equimolar solution of compound **1** and DPPillar[5]arene in chloroform-*d* shows a fast-exchange complexation on the ¹H NMR time scale at 22 °C (Fig. 1). After complexation, phenyl protons H₁ and H₂ of compound **1** shifted downfield slightly due to the deshielding effect of the electron-rich cavity of DPPillar[5]arene. Methylene protons H_{β} of DPPillar[5]arene shifted upfield from 3.78 to 3.74 ppm while H_{12} in compound $\mathbf{1}$ shifted upfield from 3.62 to 3.52 ppm. Larger chemical shift changes were observed for the alkyl chain protons of compound **1**. Methylene protons H_{11} and H_{5-10} moved upfield from 1.55 and 1.25–1.40 ppm, to 1.38 ppm and 1.10–1.25 ppm, respectively. These chemical shift changes demonstrated that DPPillar[5]arene and the semi-blocked rod-like component 1 can form a pseudorotaxane with the alkyl chain of compound 1 locating in the electronrich cavity of DPPillar[5]arene in chloroform. However, no chemical shift changes were found for compound 2 (dumbbell-



Scheme 3. Cartoon representation of the formation of pseudorotaxanes and [2]rotaxanes.

shaped component) and DPPillar[5]arene in the ¹H NMR experiment when an equimolar solution of them in chloroform-*d* was made (Fig. S12). This indicated that 3,5-dinitrophenyl groups are big enough to work as stoppers for DPPillar[5]arene, which lays a foundation for the following [2]rotaxane preparation.

We then prepared [2]rotaxane **3** using 3,5-dinitrophenyl groups as the stoppers (Scheme 1).^{5,6} A mixture of DPPillar[5]arene and the semi-blocked rod-like component **1** in chloroform was stirred at room temperature for two hours. Then the solution was treated with 3,5-dinitrobenzoic acid in the presence of DMAP and EDC to afford [2]rotaxane 3 as a red solid in a yield of 7%. If 3,5-dinitrobenzoyl chloride and triethylamine were used, [2]rotaxane 3 was obtained in 35% yield. Partial proton NMR spectra of the dumbbell-shaped component 2, [2]rotaxane and DPPillar[5]arene in chloroform-d are shown in Figure 2. The aromatic protons H_a and H_b in component **2** and H_{α} in DPPillar[5]arene shifted downfield. Furthermore, methylene protons H_c in the dumbbell-shaped units shifted upfield from 4.45 to 3.90 ppm due to the shielding effect. While methylene protons H_{γ} in DPPillar[5]arene shifted upfield for about 0.05 ppm, methylene protons H_{δ} shifted downfield for about 0.1 ppm. Methylene protons H_d and H_{e-g} in the alkyl chain of the dumbbell-shaped molecule were located in the cavity of the DPPillar[5]arene. Therefore, due to the shielding effect, these protons moved upfield greatly after the formation of [2]rotaxane **3**. Protons H_d moved upfield from 2.75 to 0.90 ppm, and H_{e-f} and H_g shifted upfield from 1.50 and 1.40 ppm to -0.25 and -0.35 ppm, respectively.^{4,5} We also found similar chemical shift changes from the ¹H NMR spectrum of [2]rotaxane **3** in DMSO- d_6 (Fig. S6 and S17), a highly polar solvent. In DMSO- d_{6} , H_{e-f} and H_{g} shifted upfield from 1.41 and 1.32 ppm to -0.29, -0.45 and -0.62 ppm, respectively, indicating that the alkyl chain still located in the cavity of DPPillar[5]arene. From the 2D NOESY NMR spectrum of [2]rotaxane 3 in chloroform-d (Fig. S15 in Supplementary data), protons H_b on the dumbbell-shaped units were correlated with protons H_{β} , H_{δ} , H_{ϵ} on DPPillar[5]arene, and the aromatic protons H_{α} on DPPillar[5]arene were correlated with H e-f, confirming the formation of a stable mechanically interlocked structure between DPPillar[5]arene and the dumbbell-shaped component 2.

The ¹³C NMR spectra of the dumbbell-shaped component **2**, [2]rotaxane **3** and DPPillar[5]arene also showed consistent changes with the ¹H NMR spectra (Fig. S13 and S14 in Supplementary data). For example, $C_{\rm f}$ moved downfield from 67.1 to 67.9 ppm, and $C_{\rm h}$ shifted upfield from 25.7 to 24.7 ppm, respectively.

The ESI mass spectrum of [2]rotaxane **3** has a peak at m/z 1616.8 (100%) corresponding to [**3** + Na]⁺ (Fig. S8 in Supplementary data), which further confirmed the formation of the mechanically interlocked structure.^{4m}

3,5-Bis(trifluoromethyl)phenyl group was also applied as stoppers to prepare a [2]rotaxane.⁷ [2]rotaxane **4** was successfully synthesized with a yield of 20% in a similar way (Scheme 2). Furthermore, differences between [2]rotaxanes **3** and **4** were investigated by ¹H NMR spectra. In ¹H NMR spectrum of [2]rotaxane **4**, protons of DPPillar[5]arene split into two sets of peaks due to the non-symmetric structure of its dumbbell-shaped component (Fig. S18 in Supplementary data). For example, the signal of protons H_{α} in DPPillar[5]arene was observed to split into two peaks at 6.95 ppm and 6.85 ppm, respectively.⁴

In summary, we successfully synthesized two new [2]rotaxanes based on the pillar[5]arene/alkane recognition motif by efficient and convenient esterification reactions (Scheme 3). Considering that the formation of the related pseudorotaxane-type threaded structure intermediates during the preparation of these [2]rotaxanes were mainly driven by weak C-H··· π interactions, their yields (35% and 20%) are reasonable. Furthermore, we showed that the 3,5-dinitrophenyl group and the 3,5-bis(trifluoromethyl)phenyl group are big enough to work as stoppers for DPPillar[5]arene. Considering the easy availability of pillar[5]arenes, alkane derivative rod components, and these stoppers, the convenient synthetic route, and the elegant mechanically interlocked structure, this kind of [2]rotaxanes will be widely used in the construction of novel fascinating supramolecular structures including molecular machines, molecular devices, and supramolecular polymers.

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Supplementary data

Supplementary data (Synthetic procedures, characterizations, and other materials) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2012.05. 028.

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