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Pillar[5]arene Based Pseudo[1]rotaxane Operating as Acid/Base-Controllable Two State Molecular Shuttle

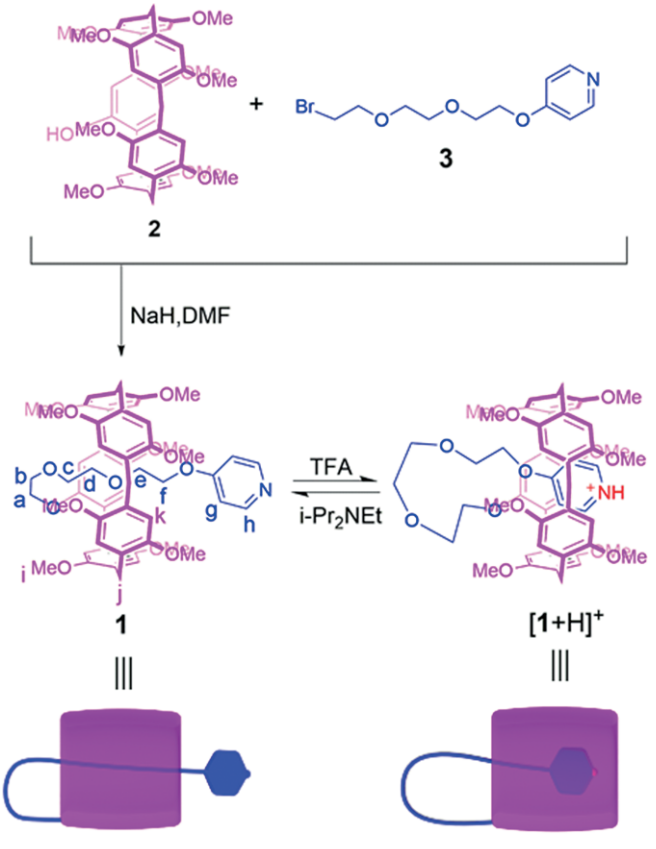
Qian Zhao,[a] Yuan Chen,[a] Baobao Sun,[a] Cheng Qian,[a] Ming Cheng,*[a] Juli Jiang,*[a] Chen Lin,[a] and Leyong Wang[a,b]

Abstract: A ethylene glycol bridged pyridine and pillar[5]arene based mechanically selflocked pseudo[1]rotaxane was constructed successfully. The structure and selflocked conformation of pseudo[1]rotaxane were confirmed by ^{1}H, 2D NMR spectrum and HR-ESI-MS. It was found that in dilute solution the pseudo[1]rotaxane could be operated as an acid/base-controllable two state molecular shuttle while In concentrated solution, the pseudo[1]rotaxane existed as a dimer and could be operated from shrinking state to extension state.

Introduction

The 2016 Nobel Prize in Chemistry was awarded to Jean-Pierre Sauvage, J. Fraser Stoddart and Bernard L. Feringa for their outstanding contributions in the design and synthesis of molecular machines.[1] Particularly, Jean-Pierre Sauvage took the first step towards the synthesis of molecular machine in 1983,[2] from then on, various artificial molecular machines based on mechanically interlocked molecules (MIMs) were fabricated in the past decades.[3] Among them, rotaxanes based molecular shuttles represent the fundamental archetypes of molecular machines and have attracted increasing public attention due to their diverse functions and great applications in smart materials, information storage, sensors and biological science and so on.[4] Pseudorotaxanes, in which the axle components could threaded into/out rings reversibly, play an important role in MIMs based molecular machines. Thus, different kinds of macrocyclic hosts have been employed to construct pseudorotaxane.[5]

Pillararenes, as a kind of macrocyclic hosts, were firstly reported in 2008.[6] After that, pillararenes have been widely used to fabricate pseudo[1]rotaxanes with different guests,[7] not only due to the highly symmetrical and rigid structure, but also for the electron-donating cavities.[8] For example, Xue et al. fabricated the first pillar[5]arene-based pseudo[1]rotaxane by combining C–H···π and ion-pair interactions together in 2014.[9] Yang et al. reported a pillar[5]arene-based pseudo[1]rotaxane which could be used as a catalyst for the Knoevenagel reaction in $CHCl_3$.[10] Recently, our group prepared series of pillar[5]-arene-based pseudo[1]rotaxanes and the relationships between the self-locked behaviors and lengths of bridging chains were investigated.[11] However, although numerous pillar[5]arene based pseudo[1]rotaxane have been constructed so far, it is still a big challenge to fabricate the controllable pillar[5]arene based pseudo[1]rotaxane due to the lack of enough way to regulate



Scheme 1. Synthesis and shuttling process of pseudo[1]rotaxane **1**.

[a] *Jiangsu Key Laboratory of Advanced Organic Materials, School of Chemistry and Chemical Engineering, Nanjing University, 163 Xianlin Avenue, Nanjing 210023, China*
E-mail: ming.cheng2015@foxmail.com
jjl@nju.edu.cn
hysz.nju.edu.cn/supramol
[b] *School of Petrochemical Engineering, Changzhou University, Changzhou, 213164, China*

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host–guest interaction between pillar[5]arene and different guests. Therefore, the introduction of stimuli responsive units into pillar[5]arene based pseudo[1]rotaxanes would greatly expand the application and development prospects of pillar[5]-arene based pseudo[1]rotaxanes.

Considering that, acid/base-controllable two state pseudo-[1]rotaxane **1** were designed (Scheme 1), which incorporated ethylene glycol, pyridine in the thread and 1,4-dimethoxy-pillar[5]arene (MeP5A) as the macrocycle. By addition of acid/base, pseudo[1]rotaxane **1** exists in two possible states, the ethylene glycol bridged pyridine thread could shrink or expand in the pillar[5]arene cavity as an acid/base-controllable two state molecular shuttle (Scheme 1).

Results and Discussion

The first step to design pillar[5]arene based acid/base-controllable molecular shuttle is the appropriate choice of acid/base-controllable guest unit. According to previous report,[12] electron poor pyridinium salts could form very stable host–guest complexes with pillar[5]arenes. Thus, we chose pyridine as the acid/base-controllable guest unit and the host–guest properties between pyridine and pillar[5]arene were investigated by ^{1}H NMR. As shown in Figure 1, upon addition of MeP5A (1.0 equiv.) to a solution of pyridine, no obvious proton signal changes could be observed. In contrast, upon addition of MeP5A (1.0 equiv.) to a solution of protonated pyridine, proton signals of the protonated pyridine are shifted upfield significantly ($\Delta\delta_{H1}$ = –0.21 ppm, $\Delta\delta_{H2}$ = –0.40 ppm, $\Delta\delta_{H3}$ = –0.44 ppm) due to strong shielding effects of MeP5A cavity, indicating the formation of a stable host–guest complex between protonated pyridine and MeP5A in acidic condition.

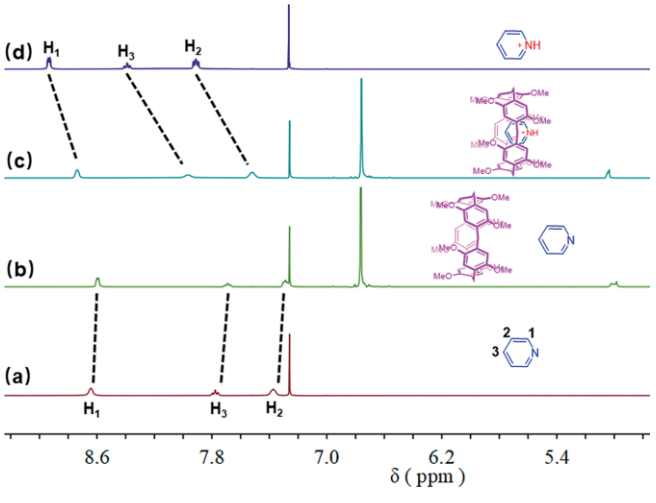


Figure 1. Partial ^{1}HNMR spectra (400 MHz, $CDCl_3$, 298 K): (a) 5.00 mM **pyridine**; (b) 5.00 mM **pyridine** + 5.00 mM **MeP5A**; (c) 5.00 mM **pyridine** + 10.00 mM **TFA** + 5.00 mM **MeP5A**; (d) 5.00 mM **pyridine** + 10.00 mM **TFA**.

Then, we investigated the acid/base-controllable threading/dethreading processes of complex between pyridine and MeP5A. As shown in Figure 2, Upon addition of trifluoroacetic acid (TFA, 2.0 equiv.) to a 1:1 mol ratio mixture of MeP5A and pyridine, the ^{1}H NMR spectrum was recorded (Figure 2b). Proton signals of the protonated pyridine shifted upfield obviously due to aromatic shielding effect of the MeP5A cavity, suggesting the formation of host–guest complex MeP5A⊃protonated pyridine. Moreover, after addition of *N,N*-diisopropylethylamine (iPr$_2$NEt, 3.0 equiv.) to the above solution, in order to remove proton from the protonated pyridine, a ^{1}H NMR spectrum (Figure 2c) similar to 1:1 mol ratio mixture of pyridine and MeP5A was obtained, indicating that the guest pyridine had move out of MeP5A's cavity and the host–guest complex between MeP5A and pyridine had dethreaded. All the above results demonstrated that the threading/dethreading processes between pyridine and MeP5A could be well-regulated by the addition of acid/base.

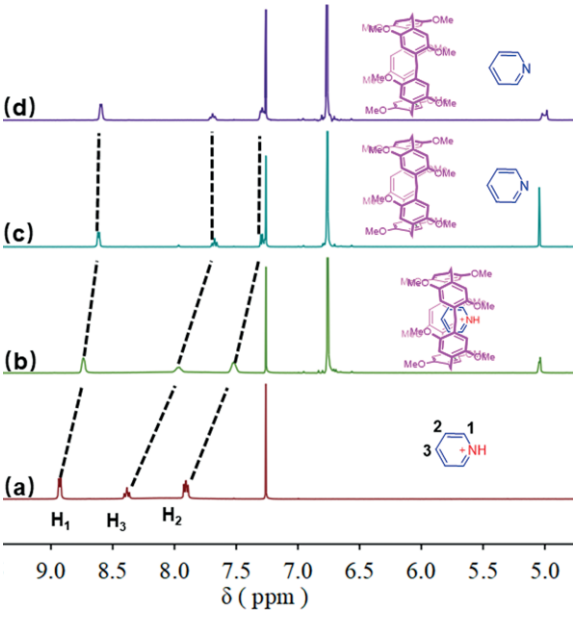


Figure 2. Partial ^{1}HNMR spectra (400 MHz, $CDCl_3$, 298 K): (a) 5.00 mM **pyridine** + 10.00 mM **TFA**; (b) 5.00 mM **pyridine** + 5.00 mM **MeP5A** + 10.00 mM **TFA**; (c) 5.00 mM **pyridine** + 5.00 mM **MeP5A** + 10.00 mM **TFA** + 15.00 mM iPr$_2$**NEt**; (d) 5.00 mM **pyridine** + 5.00 mM **MeP5A**.

On the basis of above host–guest investigation, we designed pillar[5]arene based pseudo[1]rotaxane **1**. The association constant of complexation between protonated pyridine and MeP5A in $CDCl_3$ was determined to be 57.0 ± 1.3 M^{-1} at 25 °C using a nonlinear curve-fitting analysis based on the ^{1}H NMR titration experiments (see SI, section 4 in detail). Considering the association constant was not high as expected, so we chose ethylene glycol chain rather than alkyl chain as a linker connected pyridine and pillar[5]arene.[13] As shown in Scheme 1, by reacting monohydroxy pillar[5]arene **2** with ethylene glycol bridged pyridine **3**, pseudo[1]rotaxane **1** was synthesized successfully in 20 % yields in anhydrous DMF (Scheme 1). The detailed route was displayed in supporting information section 2. Pseudo[1]-rotaxane **1** was further characterized by ^{1}H, ^{13}C, 2D NMR spectrum, high-resolution electrospray ionization mass spectrum (HR-ESI-MS). In the HR-ESI-MS of the **1** (see SI, Fig S6), peaks were found at *m/z* 946.4378 and 968.4192 corresponding to [**1** + H]$^+$ (calcd. 946.4372) and [**1** + Na]$^+$ (calcd. 968.4192) respectively, which preliminarily supported the formation of **1**. In the ^{1}H NMR spectrum (see SI, Fig S4), a broad peak in upfield

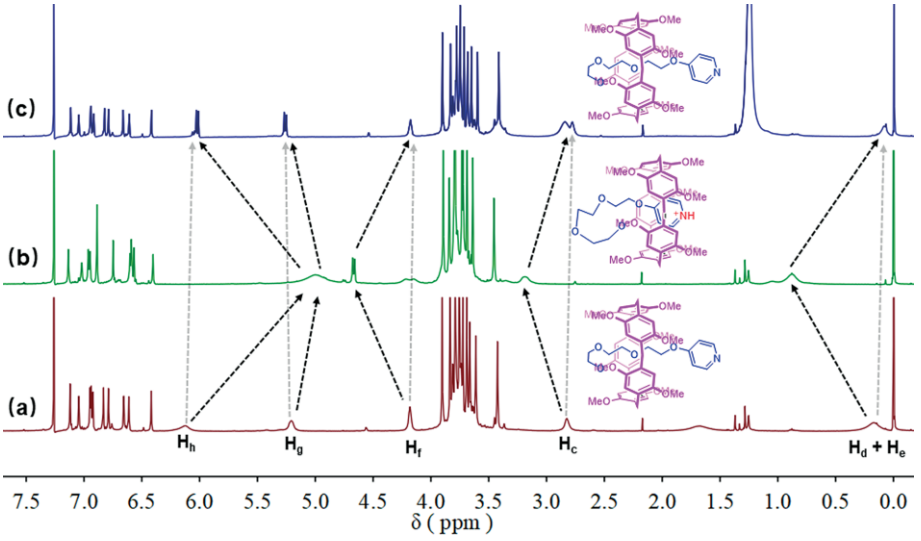


Figure 3. Partial ^{1}HNMR spectra (400 MHz, $CDCl_3$, 298 K): (a) 10.00 mM **1**; (b) 10.00 mM **1** + 20.00 mM **TFA**; (c) 10.00 mM **1** + 20.00 mM **TFA** + 30.00 mM *i*Pr$_2$**NEt**.

chemical shift (δ = 0.19) were observed which was caused by the strong shielding effects of pillar[5]arene cavity, indicating ethylene glycol chain stay in the cavity of pillar[5]arene and the formation of selflocked structure. Besides, NOE correlations were observed clearly between ethylene glycol chain protons H_e, H_d and pillararene protons H_i, H_j, H_k from 2D NOESY analysis (see SI, Fig S11), which further confirmed the formation of selflocked pseudo[1]rotaxane **1**.

The shuttling properties of pseudo[1]rotaxane **1** among ethylene glycol chain and pyridine unit were investigated by ^{1}H NMR. Firstly, we tested the response of pseudo[1]rotaxane **1** to acid. Upon addition of TFA, 2.0 equiv. to a solution of pseudo[1]rotaxane **1**. The signals belonging to ethylene glycol chain (Figure 3a and 3b) showed significant downfield shifts ($\Delta\delta_{Hd,He}$ = 0.88 ppm and $\Delta\delta_{Hc}$ = 0.36 ppm), due to the aromatic shielding effect of the macrocycle weaken, indicating that part of the ethylene glycol chain moved out from the cavity of pillar[5]arene. In contrast, the signals belonging to pyridine shifted upfield obviously ($\Delta\delta_{Hh}$ = −1.12 ppm, $\Delta\delta_{Hg}$ = −0.21 ppm) due to aromatic shielding effect of the pillar[5]arene cavity, suggesting protonated pyridine moved into the cavity of pillar[5]arene.

Furthermore, when addition of 3.0 equiv. *i*Pr$_2$NEt to the above solution, which was used as base to remove proton from the protonated pyridine. A spectrum (Figure 3c) similar to the original pseudo[1]rotaxane **1** was obtained, suggesting that deprotonated pyridine unit left the cavity of pillar[5]arene and ethylene glycol chain back to the cavity of pillar[5]arene. Consequently, all above results confirmed that the switchable process between ethylene glycol chain and pyridine unit have been realized by acid/base control. Therefore, our pseudo[1]rotaxane **1** could be operated as acid/base-controllable two state molecular shuttle.

In addition, diffusion-ordered ^{1}H NMR spectroscopy (DOSY) experiments were performed to investigate self-assembly behavior and aggregation sizes of pseudo[1]rotaxane **1** in both low concentration (10 mM), high concentration (100 mM) and acidic condition (100 mM + 200.0 mM TFA). As shown in Figure 4, the diffusion coefficients of pseudo[1]rotaxane **1** at both low concentration and high concentration were recorded. For pseudo[1]rotaxane **1** at both low concentration (10 mM) and high concentration (100 mM), only one set of signals was observed, indicating only one type of assembly exist in both condition. Then, the radius of pseudo[1]rotaxane **1** in both concentration were calculated by Stokes–Einstein relationship.[14] As shown in Table 1, the calculated radius in high concentration (100 mM, 4.70 Å) is about twice of low concentration (10 mM, 2.86 Å), indicating pseudo[1]rotaxane **1** performed as selflocked monomer **1** in low concentration and interlocked-dimer **4** in high concentration (Scheme 2).

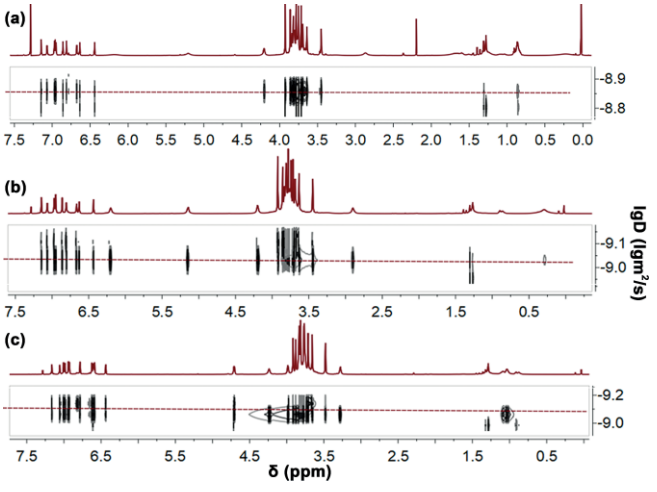
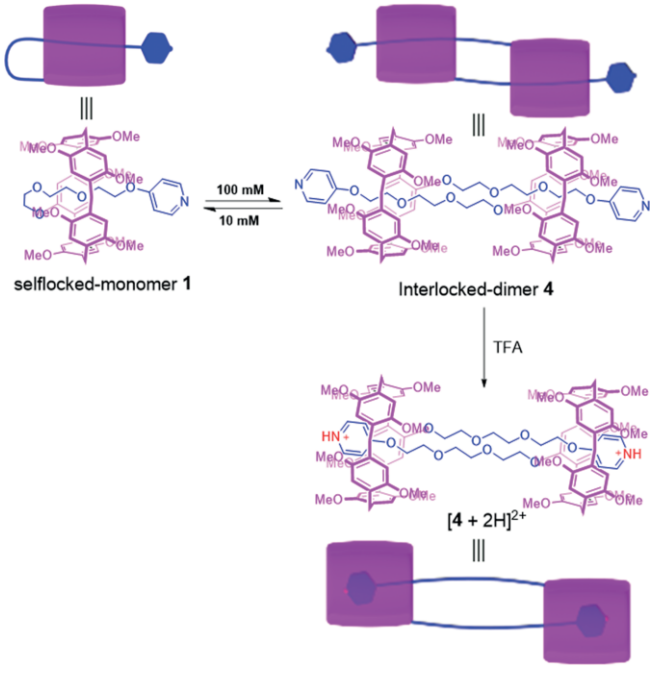


Figure 4. Partial DOSY spectra (600 MHz, $CDCl_3$, 298 K): (a) 10.00 mM **1**; (b) 100.00 mM **1**; (c) 10.00 mM **1** + 200.00 mM **TFA**. Notice that only one set of signals could be observed from the DOSY spectrum and full spectrum was given in SI.

Moreover, after further addition of TFA (2.0 equiv.) to the above high concentration solution, the calculated radii extend from 4.70 Å to 5.30 Å (Table 1), indicating that after the proto-

Table 1. The hydrodynamic radius calculated from the DOSY experiments.

Sample	lg D (lg m^2 s^{-1})	D (10^{-10} m^2 s^{-1})	r [Å]
1	–8.858	1.390	2.86
4	–9.072	0.847	4.70
$[\mathbf{4} + 2H]^{2+}$	–9.125	0.750	5.30



Scheme 2. Assemble process of **1** in different condition.

nation of pyridine the interlocked-dimer **4** changed from shrinking state to extension state (Scheme 2).

Conclusions

In summary, the host–guest interaction and acid/base controllable properties between pyridine and MeP5A were investigated. On the basis of that, an ethylene glycol bridged pyridine and pillar[5]arene based mechanically selflocked pseudo[1]rotaxane **1** was synthesized. Furthermore, MeP5A unit of pseudo[1]rotaxane **1** could shuttle between ethylene glycol chain and pyridine unit as an acid/base-controllable molecular shuttle. Moreover, DOSY experiments indicated that pseudo[1]rotaxane **1** performed as selflocked-monomer in low concentration (10 mM) and interlocked-dimer (100 mM) in high concentration. After addition of TFA (2.0 equiv.) to concentrated solution (100 mM) of **4**, interlocked-dimer **4** could change from shrinking state to extension state.

Experimental Section

General Procedure for the Synthesis of Pseudo[1]rotaxane 1: To a solution of NaH (0.082 g, 3.40 mmol) in 10 mL of anhydrous DMF, slowly added a solution of compound **2** (0.50, 0.68 mmol) in 5 mL of anhydrous DMF. Then the mixture was stirred at room temperature for 0.5 h. After that, compound **3** (0.20 g, 0.68 mmol) was added to the above mixture and continued stirred at room temperature for 24 h. The reaction was quenched by water. The DMF was removed in vacuo and the residue was dissolved in CH_2Cl_2. The organic phase was washed with water, dried with anhydrous Na_2SO_4 and concentrated under vacuum. The residue was purified by silica-gel column chromatography (CH_2Cl_2/MeOH = 50:1) to afford pseudo[1]rotaxane **1** (0.26 g, 20 %) as a white solid. Mp. 142–143 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.12 (s, 1 H), 7.04 (s, 1 H), 6.95–6.92 (m, 3 H), 6.83 (s, 1 H), 6.79 (s, 1 H), 6.65 (s, 1 H), 6.61 (s, 1 H), 6.42 (s, 1 H), 6.17 (s, 2 H), 5.18 (s, 2 H), 4.18 (s, 2 H), 3.94–3.59 (m, 38 H), 3.43 (s, 2 H), 2.84 (s, 2 H), 0.19 (s, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ = 178.1, 151.2, 150.9, 150.8, 150.6, 150.4, 150.1, 150.1, 149.9, 149.4, 149.3, 141.2, 129.1, 129.0, 128.9, 128.7, 128.5, 127.9, 127.8, 127.7, 127.2, 116.5, 115.4, 115.2, 114.5, 114.5, 114.2, 113.6, 113.5, 113.1, 112.8, 112.2, 70.9, 69.9, 69.4, 66.6, 65.6, 56.5, 56.4, 56.4, 56.1, 55.8, 55.7, 55.6, 55.4, 54.6, 51.7, 30.5, 30.5, 29.7, 28.8, 28.0, 27.8. HR-MS (ESI): calcd. for $[\mathbf{1} + H]^+$: 946.4372, found m/z = 946.4378; calcd. for $[\mathbf{1} + Na]^+$: 968.4192, found m/z = 968.4192.

Acknowledgments

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Keywords: Self-assembly · Pseudo[1]rotaxanes · Acid/base-control · Molecular shuttle

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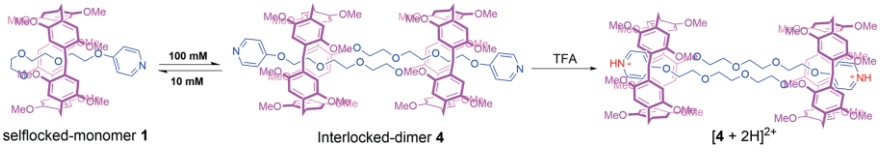
Rotaxane



A ethylene glycol bridged pyridine and pillar[5]arene based mechanically self-locked pseudo[1]rotaxane was successfully constructed. It was found that in dilute solution the pseudo[1]rotaxane could be operated as an acid/base-controllable two state molecular shuttle. In concentrated solution, the pseudo[1]rotaxane existed as a dimer and could be operated from shrinking state to extension state.

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