

Molecular Devices

Intermittent Molecular Shuttle as a Binary Switch**

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Rotaxanes have attracted intensive attention as potential molecular switching devices.^[1] Most of the studies have so far focused on nondegenerate molecular shuttles in which two recognition sites (stations) are nonequivalent.^[2] Thus, fixation of a bead at one station gives rise to state 1 while fixation at the other gives state 2 and these two bistable states could constitute a binary logic system. In addition to such a protocol based on the differentiation between nonequivalent stationary states, a dynamic/static binary mode may be feasible if the shuttling and stationary processes could be switched freely in a degenerate rotaxane (Figure 1). Leigh and co-workers reported that shuttling in a degenerate rotaxane bearing a sulfide linkage at the center of the thread could be interrupted

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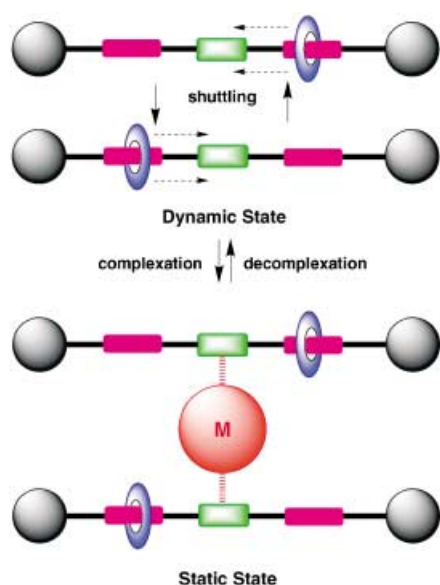


Figure 1. Schematic representation of a dynamic/static binary mode.

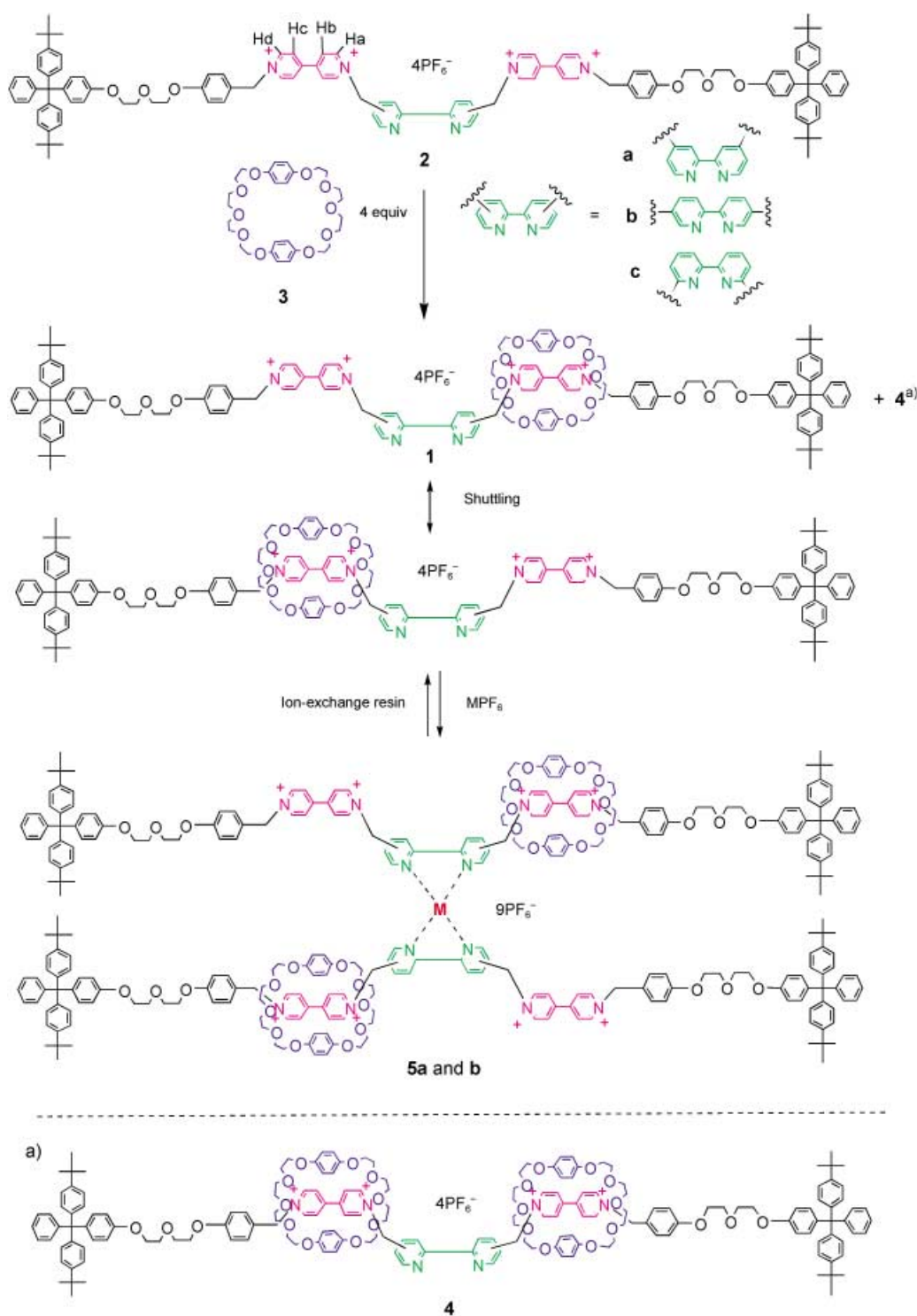
by introduction of a bulky tosylimino group on the sulfur atom.^[3] Reduction of the resulting sulfinylimine with P_4S_{10} regenerated the original sulfide to re-start the shuttling process. However, no mention was made of whether these events could be repeated.^[4] Herein, we report on novel molecular shuttles which can be converted repeatedly between dynamic and static states through alternating intermolecular complexation and decomplexation processes.

We designed degenerate [2]rotaxanes **1** containing a central bipyridine moiety for effective formation of a chelate and bipyridinium units to act as stations for a crown ether bead. The requisite molecules were prepared according to the slippage method^[5] as shown in Scheme 1. [2]Rotaxane **1a** bearing a central 2,2'-bipyridine moiety substituted at the 4,4'-positions was obtained in 38% yield together with [3]rotaxane **4a** (25%) by heating a solution of thread **2a** and bead **3** in acetonitrile at 55 °C for 6 days.^[6] The 1H NMR spectrum of **1a** exhibited a pattern consistent with a centrosymmetric molecular structure at room temperature (Figure 2a). Thus, the crown ether bead moves back and forward between the two equivalent bipyridinium stations at a rate which cannot be followed on the NMR time scale. Addition of a solution of $[Cu(CH_3CN)_4]PF_6$ (0.5 equiv) in acetone to a solution of **1a** (1.0 equiv) in the same solvent resulted in the solution immediately turning from orange to dark red.^[7] Evaporation of the solvent afforded the 2:1 complex **5a**, which is formed by chelation of the central bipyridine ligands to a Cu^I ion. The stoichiometry of the complex was confirmed by MALDI-TOF mass spectrometry.^[6,8] The 1H NMR spectrum of this complex in $(CD_3)_2CO$ showed a desymmetrization of the original pattern of **1a**, and is most evident for the ring protons of the bipyridinium moieties (Figure 2b). Each of the four relevant proton signals was split into two parts with equal intensity: one encircled by the crown ether ring (Ha', Hb', Hc', or Hd') and the other bearing no crown ether (Ha'', Hb'', Hc'', or Hd''). This

observation shows that the shuttling of the macrocycle is apparently hampered by the blockade in its path. Treatment of the complex (0.005 mmol) with a suspension of ion-exchange resin (Murochelat B-1,^[9] which is equivalent to Dowex A-1; 400 mg) in acetone at pH 5.5 led to complete decomplexation in 15 minutes and resulted in the original color as well as the 1H NMR spectrum being restored as **1a** was recovered. Adjusting the pH value of the commercially available resin (pH 8.5) to 5.0–6.0 was crucial for this process.^[10] At higher pH values the quaternary pyridinium-carbon bond to the central bipyridine unit in **1a** was cleaved, while at lower pH values decomplexation took place, but the released **1a** could not undergo further complexation because of protonation on the bipyridine unit.

The same behavior towards the Cu^I ion was essentially observed with rotaxane **1b**, in which the central 2,2'-bipyridine unit is substituted at the 5,5'-positions.^[6] The solution of **1b** changed from orange to dark-red upon addition of the copper salt. However, rotaxane **1c** with a central 2,2'-bipyridine unit substituted at the 6,6'-positions failed to give a 2:1 complex because of the steric congestion resulting from the side arms located in proximity to the nitrogen atoms.^[11]

With these results in hand, we turned our attention to devise a system that would enable alternate complexation and decomplexation. Figure 3a shows the apparatus used for this purpose. A glass cylinder was separated into two compartments by a filter. The ion-exchange resin (pH 5.5, 400 mg) was added to one compartment (A) while a solution of **1a** (17.2 mg, 0.006 mmol) in acetone (3.0 mL) was introduced into the other (B). A solution of $[Cu(CH_3CN)_4]PF_6$ (1.1 mg, 0.003 mmol) in acetone (0.2 mL) was added through the inlet connected to compartment B and the color of the solution changed instantaneously from orange to dark red (Figure 3b). The apparatus was then inverted to allow the solution to transfer to compartment A.^[12] The color of the solution gradually changed and in 15 minutes became the original orange color (Figure 3c). Inverting the apparatus again resulted in the solution returning to compartment B, where further addition of the Cu^I solution regenerated the complex. These operations were repeated 10 times and resulted in alternating color changes (Table 1). Longer times were understandably required for decomplexation as the repetition number increased because of reduction of the active sites on the resin surface. The accumulation of copper salts was apparent from the gradual green coloration of the resin. Although the switching process could be readily judged by the color change of the solution, the formation of complex **5a** in compartment B followed by regeneration of free rotaxane **1a** in compartment A was further confirmed on the basis of 1H NMR spectra obtained by analysis after the fifth and tenth runs. The spectra could be entirely superimposed on those of the respective pure species, thus indicating that perfect switching was realized between the two states. It should also be noted that the rotaxane was recovered quantitatively (ca. 100%) after the tenth run, and is thus indicative that no loss of the materials occurs during the complexation and decomplexation process or on filtration. The switching events also occurred with **1b**, and the times required for decomplexation are also given in Table 1.^[13]



Scheme 1. Synthesis of the rotaxanes by the slippage method.

In summary, a novel switching system has been devised, namely, a dynamic state in which free shuttling occurs is completely interrupted by complex formation and the bead sticks on either of the two stations. The switching can be achieved simply by treating rotaxanes containing chelating sites with Cu^{I} ions followed by exposing the complexes to an ion-exchange resin. Hence, no redundant reagents are

accumulated in the system during the process, thus keeping the system clean. Although the switching time is not quick at present, we believe that the protocol of complexation/decomplexation in combination with an immobilized resin has potential as a new type of molecular switch.

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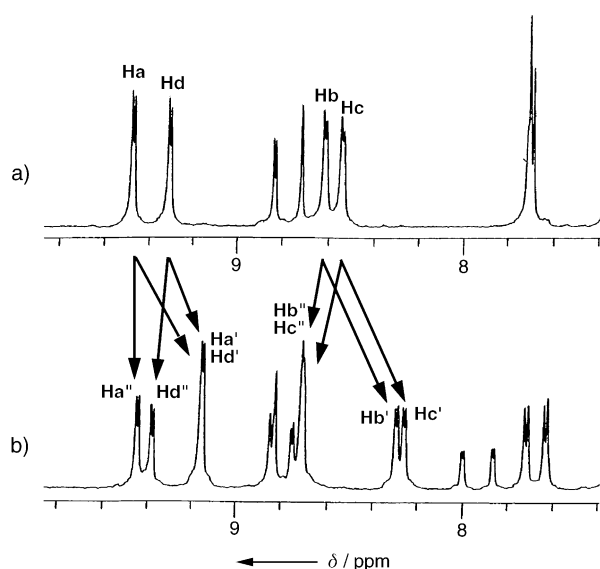


Figure 2. ^1H NMR spectra of a) rotaxane **1a** and b) the Cu^{I} complex of rotaxane **5a**.



Figure 3. a) Apparatus used for the complexation and decomplexation process, with b) complex **5a** in compartment B and c) rotaxane **1a** in compartment A after decomplexation.

Table 1: Time required for the decomplexation of **5**.

Entry	t [min]		Entry	t [min]	
	5a ^[a]	5b ^[b]		5a ^[a]	5b ^[b]
1	12	12	6	20	34
2	15	14	7	24	38
3	15	15	8	28	44
4	15	18	9	35	55
5	18	24	10	45	70

[a] Murochelate B-1 (pH 5.5) was used as the resin for decomplexation.

[b] Murochelate B-1 (pH 5.0) was used as the resin for decomplexation.

Keywords: chelation · coordination modes · copper · molecular devices · rotaxanes

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- [6] For detailed information, see the Supporting Information.
- [7] All manipulations should be carried out under argon to avoid oxidation of the Cu^{I} salt. The choice of the solvent is crucial for the formation of the complex; only acetone and acetonitrile can be used, as the complex does not form in other solvents.
- [8] For rotaxanes dimerized through complexation with a copper ion at their wheel peripheries, see X.-y. Li, J. Illigen, M. Nieger, S. Michel, C. A. Schalley, *Chem. Eur. J.* **2003**, *9*, 1332.
- [9] Available from Muromachi Technos Co., Tokyo.
- [10] A 2.5N solution of HCl (0.2 mL) was added to a suspension of the resin (5.0 g) in water (15 mL). The mixture was stirred for 14 h and then the resin filtered off and dried. The resin thus obtained had a pH value of 5.5.
- [11] A 1:1 complex was formed even in the presence of excess **1c**.
- [12] To facilitate the filtration a small amount of argon was removed from the lower compartment by syringe while the upper compartment was pressurized with an argon balloon.
- [13] In this case, the pH value of the resin should be adjusted to 5.0. Above this value, the rotaxane returned to **2b** and a small amount of **3** (ca. 6 %).