

Switchable Neutral Bistable Rotaxanes

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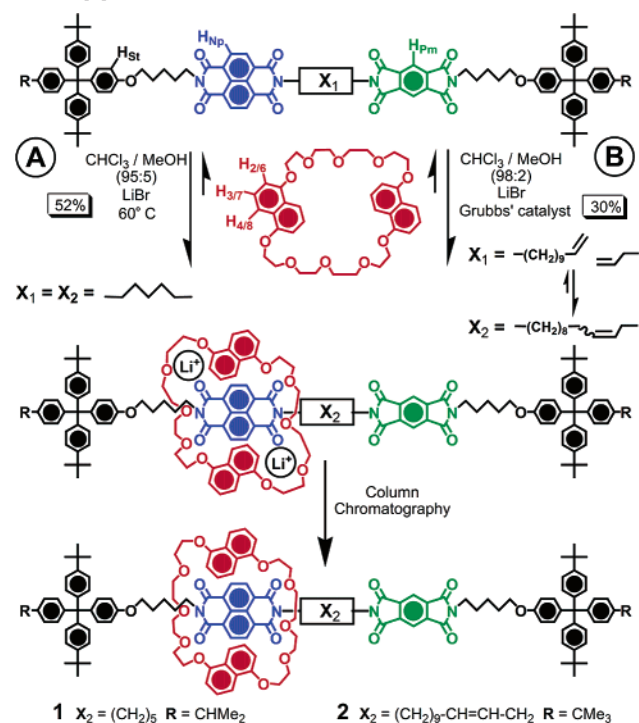
The study of mechanically interlocked molecules¹ in the form of bistable [2]catenanes² and [2]rotaxanes³ and their incorporation ultimately into molecular machines⁴ and switches⁵ has been advancing apace in the past few years. Examples of the attachment of such molecules to surfaces have already been reported,⁶ and the development of molecular actuators^{4,5,7} and switches^{4,5,8} in devices is well underway. Not only is the structural complexity⁹ of these molecules on the increase, but also the degree of control is becoming more precise and predictable, whether light,^{3,10} electricity,¹¹ or chemicals^{9,12,13} are employed as the stimulus.

One of the most common methods of controlling switching in bistable catenanes and rotaxanes is by ion-induced co-conformational changes.¹⁴ Sauvage¹⁵ has demonstrated remarkable control of mechanical movement in exquisitely designed molecules using Cu⁺/Cu²⁺ ions. While the UCLA group has employed variations in pH (base/H⁺) to switch off and on the binding of dialkylammonium centers to crown ethers in bistable interlocked molecules, the Cambridge group has used¹⁶ Li⁺ ions to control mechanical motions in neutral pseudorotaxanes. Here, we report the template-directed syntheses¹⁷ of two neutral bistable [2]rotaxanes and the use of Li⁺ ions and [12]crown-4 to effect their switching between two states in solution.

Utilizing the neutral donor–acceptor recognition system¹⁸ developed by the Cambridge group, two bistable [2]rotaxanes **1** and **2** were designed and made. They both incorporate 1/5DNP38C10 (Scheme 1), with its two π -electron rich 1,5-dioxynaphthalene ring systems, around their dumbbell components, wherein pyromellitic diimide (PmI) and naphtho-diimide (NpI) are present as the two competing π -electron deficient units for interaction with the crown ether. Recognition is achieved by a combination¹⁹ of $[\pi\cdots\pi]$ stacking and $[C-H\cdots O]$ interactions and is expected²⁰ to be expressed in the form of a preference for 1/5DNP38C10 to encircle the NpI unit in both rotaxanes. Addition of Li⁺ ions should lead to the formation of strong 2:1 complexes with the translational isomers in which the 1/5DNP38C10 ring encircles the PmI units, ensuring that the initial preference is reversed. In the knowledge²¹ that [12]-crown-4 is a very strong sequestering agent for Li⁺ ions, we have all the ingredients at hand to render both **1** and **2** chemically switchable in organic solvents.

The template-directed syntheses¹⁷ of **1** and **2** from their immediate precursors were both achieved (Supporting Information) under thermodynamic control—**1** by slippage²² in CHCl₃/MeOH (95:5) at 60 °C of 1/5DNP38C10 over the appropriately chosen stoppers on the preformed dumbbell compound in the presence of an excess of LiBr and **2** by dynamic covalent chemistry,²³ employing olefin metathesis²⁴ performed on appropriate half-dumbbell compounds carrying terminal alkene functions for reaction with the second-

Scheme 1 Final Steps in the Syntheses of the Switchable Bistable Neutral [2]Rotaxanes **1** and **2**^a



^a Two different template-directed approaches were used in the final steps, i.e., namely slippage (A) or dynamic bond formation (B).

generation Grubbs' catalyst^{24c} in CHCl₃/MeOH (98:2), also in the presence of an excess of LiBr. Both bistable [2]rotaxanes were fully characterized following purification by column chromatography on SiO₂ using CHCl₃/EtOAc (8:2) as the eluent.

¹H NMR spectroscopic studies were carried out in solution on both **1** and **2** to ascertain if the preferred translational isomers were indeed those with the 1/5DNP38C10 ring encircling the NpI units. Within the limits of detection (~3%) afforded by ¹H NMR spectroscopy, the anticipated outcome was observed for **1** in CD₂-Cl₂/CD₃COCD₃ (4:1) and **2** in CDCl₃/CD₃OD (98:2). The ¹H NMR spectrum of **1** reveals (Figure 1a) that the signals corresponding to the NpI unit (δ = 8.17 ppm), and the PmI unit (δ = 8.21 ppm) are present: no signals could be identified for free NpI and encircled PmI units. This situation was reversed completely (Figure 1b) on addition of at least 2 equiv of LiClO₄ to the NMR tube: the signals at δ 8.17 and 8.21 ppm disappear and a new pair²⁵ of signals (δ = 8.66 and 8.69 ppm) corresponding to a free NpI unit are observed, leaving the signal for the PmI unit now encircled by 1/5DNP38C10 obscured by other aromatic signals somewhere in the region δ = 6.5–7.5 ppm. Qualitatively, the original ¹H NMR spectrum was

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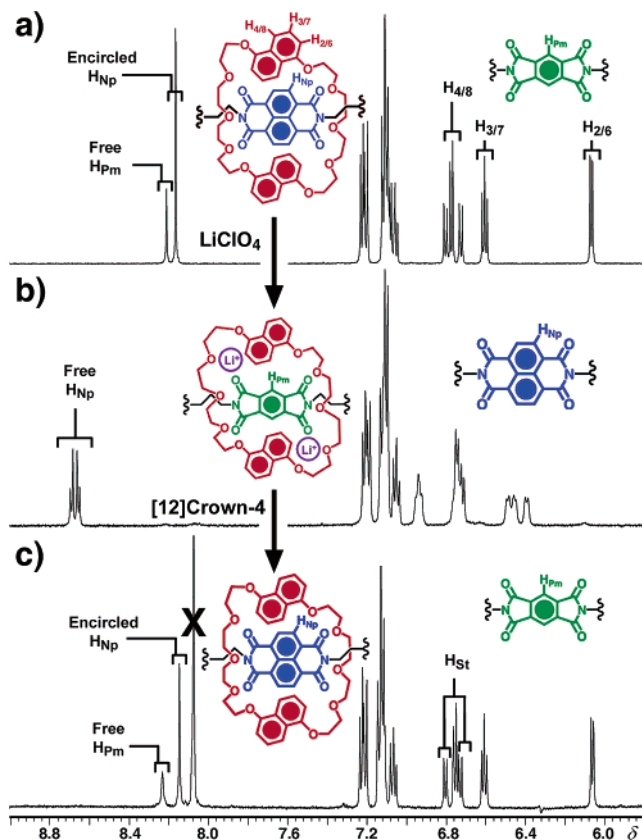


Figure 1. Partial ^1H NMR spectrum recorded at 600 MHz of **1** in $\text{CD}_2\text{Cl}_2/\text{CD}_3\text{COCD}_3$ (80:20) at 273 K in (a) the neutral ground state, after (b) addition of excess of LiClO_4 , and after (c) addition of excess of [12]crown-4. Signals corresponding to the free and encircled PmI and NpI units are labeled to show that the crown ether macrocycle moves from the NpI unit to the PmI unit in the presence of Li^+ ions and back to the NpI unit after the Li^+ ions are removed with [12]crown-4. Peak labels are defined in Scheme 1.

regenerated (Figure 1c) by addition of a large excess²⁶ of [12]crown-4: the two signals corresponding to the encircled NpI unit ($\delta = 8.16$ ppm) and the free PmI unit ($\delta = 8.20$ ppm) were slightly shifted with respect to their chemical shifts in the starting spectrum (Figure 1a). Similar results were obtained (Supporting Information) for **2** using LiBr as the Li^+ ion source and aqueous extraction of the sample to return this chemical switch to its original state.

We have demonstrated the reversible chemical switching of a pair of neutral bistable rotaxanes. Currently, we are investigating the ability of similar compounds to undergo electrochemical switching in solution with every intention of introducing them into solid-state molecule electronic devices^{5,8} at a later date.

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Supporting Information Available: Experimental preparations for **2** and **3** and characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (25) The signal corresponding to the NpI unit is separated into two signals because of the asymmetry of the dumbbell, causing the two ends of the NpI unit to be nonequivalent. This separation is not observed in the neutral ground state because it is small, but the separation is much larger and visible in the 2Li^+ co-complex, probably as a result of the presence of the Li^+ ions in the dumbbell increasing the difference in environments for the two ends of the NpI unit.
- (26) A large excess is used to drive the equilibrium between binding of the Li^+ to the [2]rotaxane versus binding to the crown completely toward binding with [12]crown-4, ensuring all the rotaxane is free from Li^+ ions.

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