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A kinetically controlled molecular switch based on bistable [2]rotaxane†

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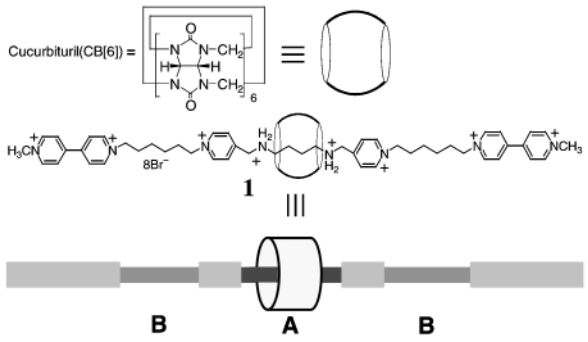
Received (in Cambridge, UK) 17th April 2001, Accepted 30th April 2001
First published as an Advance Article on the web 16th May 2001

A bistable [2]rotaxane that behaves as a kinetically controlled molecular switch is synthesized; switching from one state to the other is driven by pH change but the reverse process requires pH change plus thermal activation.

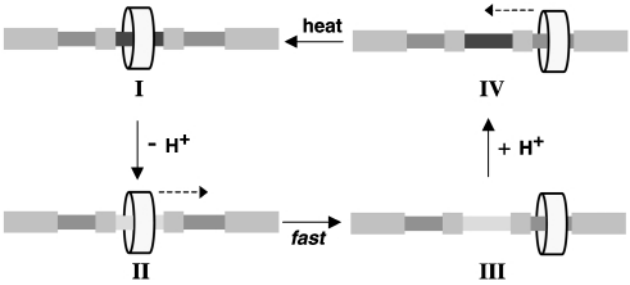
The construction of nanometer-scale devices such as molecular machines and switches from molecular components ('bottom-up' approach) is of much interest in modern science and technology.[1] Mechanically interlocked molecules such as rotaxanes and catenanes have great potential as such molecular devices because the relative positions of their components can be induced to change by external chemical, electrochemical or photochemical stimuli.[2,3] In appropriately designed systems, such mechanical movements occur between two different well-defined states so that they behave as molecular switches that are potentially useful in molecular-scale information storage and processing as well as sensors. In most cases, the molecular switches operate under thermodynamic control. In other words, since such a system is in thermodynamic equilibrium when it responds to a stimulus, it reverts to its initial state upon removal of the stimulus, which means that the new state cannot be 'locked in'.[4] Here we present a novel bistable [2]rotaxane behaving as a kinetically controlled molecular switch—the new state induced by an external stimulus can be 'locked in' after removal of the stimulus.

Cucurbituril (CB[6]),[5] a macrocyclic cage compound forms host–guest complexes with protonated diaminoalkanes (log$K$ = 5.19 at 40 °C for diaminobutane at pH = 1), the stabilities of which, however, depend on pH. Taking advantage of this fact, we[6] and others[7–9] have constructed interlocked species such as rotaxanes, polyrotaxanes, molecular necklaces and molecular switches using CB[6] as a molecular bead. Recently, CB[6] was found to form a stable inclusion complex with 1,6-di(pyridinium)hexane (log$K$ = 4.40 at 25 °C);[10] this complex formation is little affected by the pH of the solution. Taking these inclusion properties of CB[6] into account, we have designed and synthesized a bistable [2]rotaxane (**1**) consisting of CB[6] as a bead, one protonated diaminobutane unit as a station (**A**), two pyridinium groups as linkers, two hexamethylene units as further stations (**B**), and two terminal viologen groups (Scheme 1). [2]Rotaxane **1** is synthesized from the corresponding 'string' and CB[6] by 'slippage'.[11]† The ^{1}H-NMR spectrum of **1** is consistent with the desired [2]rotaxane structure. The signals for the internal CH_2 protons of the protonated diaminobutane unit, which are now located inside CB[6], are up-field-shifted relative to those in the free 'string'. On the other hand, there is no chemical-shift change in the hexamethylene units. These observations are consistent with the structure (state **I**, Scheme 2) in which the CB[6] bead in **1** resides exclusively at station **A**.

Deprotonation of the protonated diaminobutane unit in **1** promotes the movement of CB[6] from station **A** to station **B**.



Scheme 1 Bistable [2]rotaxane **1**.



Scheme 2 Switching cycle of bistable [2]rotaxane **1**.

Diisopropylethylamine (DIEA) was found to be an ideal base to drive the switching process because it is strong enough to deprotonate the NH_2^+ while behaving concurrently as an unreactive nucleophile towards the viologen units. Reprotonation can be performed by addition of a suitable acid such as DCl. The pH-controlled switching processes of **1** have been monitored by ^{1}H NMR spectroscopy (Fig. 1).

In a typical experiment, DIEA (2.1 eq.) is added to a solution of **1** (state **I**) in D_2O. The ^{1}H NMR spectrum shows that, upon base addition, deprotonation of the NH_2^+ in station **A** occurs and CB[6] moves from station **A** to station **B**, while leaving the viologen unit intact but the chemical shifts of viologen and pyridinium units are influenced by the CB[6] movement (Fig. 1b). Resonances for $-NH_2^+CH_2(\bullet)CH_2(\blacklozenge)CH_2CH_2NH_2^+-$ protons disappear and new signals, which can be assigned to $-NHCH_2(\bullet)CH_2(\blacklozenge)CH_2CH_2NH-$ protons without CB[6], become visible as a result of the relocation of CB[6]. At the same time, signals for the hexamethylene units (station **B**) split into *two* sets: one set shows dramatic chemical-shift changes (upfield shifts) whereas the other set shows no change.[12] This observation suggests that the CB[6] bead locates at one of the two **B** stations (state **III**, Scheme 2).

Upon addition of DCl (2.2 eq.), the $-NH_2^+CH_2(\bullet)CH_2(\blacklozenge)$ proton signals shift downfield due to protonation of the amine groups, while the signals for the hexamethylene unit remain unchanged, suggesting that the CB[6] bead *does not* shuttle back quickly to station **A** (state **IV**) (Fig. 1c). In fact, the reverse process is very slow at rt: the CB[6] bead shuttles back ~50%

† Electronic supplementary information (ESI) available: synthetic procedure and characterization data of **1** and colour versions of Schemes 1 and 2. See http://www.rsc.org/suppdata/cc/b1/b103380h/

 DOI: 10.1039/b103380h

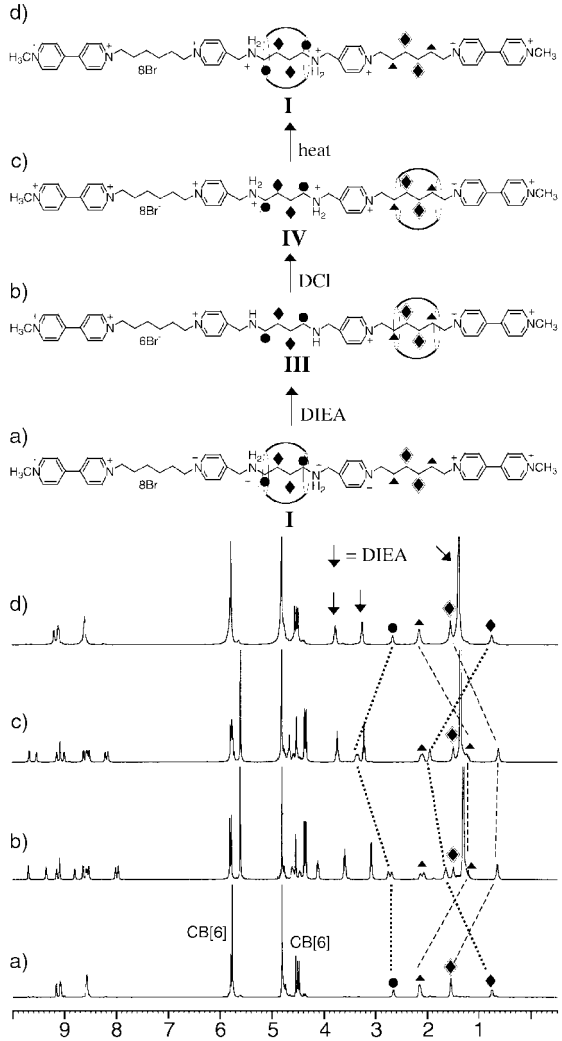


Fig. 1 Comparison of the ^{1}H-NMR spectra (in D_2O at 25 °C) of **1**. (a) **1** (state **I**), (b) after treatment of DIEA (state **III**), (c) after treatment of DCl (state **IV**), and (d) after heating at 80 °C (state **I**); the spectrum was taken after cooling at 25 °C.

to station **A** after two weeks at rt. The extremely slow reverse process at rt indicates that it has a high activation barrier. Indeed, when the same sample is warmed up to 80 °C, the CB[6] bead shuttles back quickly and completely to station **A** (Fig. 1d). The rate of the reverse process is measured to be 7.4×10^{-5} s^{-1} at 60 °C and the activation barrier ($\Delta G^{\ddagger}$) 26 kcal mol^{-1}. Therefore, this novel bistable [2]rotaxane behaves as a kinetically controlled molecular switch in which the kinetically stable new state is maintained at rt after removal of an applied stimulus. The complete cycle of the molecular switch is given in Scheme 2.

In summary, we present a kinetically controlled molecular switch based on [2]rotaxane. The switching of the molecular bead from one site to the other site is driven by pH change, but the reverse process requires pH change plus thermal activation. This novel switching system may thus provide useful insights in designing 'safeguarded' molecular switches.

We gratefully acknowledge Creative Research Initiative Program of the Korean Ministry of Science and Technology for support of this work, Brain Korea 21 Program of Korean Ministry of Education for graduate studentship to Kyungpil Kim, and Professor P. K. Bharadwaj for reading the manuscript.

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12 Upon the movement of CB[6] from station **A** to one of the two **B** stations, the signals for the viologen and pyridinium units also split into two sets due to the disymmetric structure in state **III**. However, the directions of the chemical shift changes are consistent with the idea that the bead is not located *on* the viologen or pyridinium unit but *between* them.