Interlocked Molecules

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Molecular Shuttling of a Compact and Rigid H-Shaped [2]Rotaxane**

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Bistable [2]rotaxanes (molecular shuttles) are mechanically interlocked molecules (MIMs) that can be switched between different translational co-conformations in response to an external stimulus.[1] Chemical, electrochemical, and photochemical inputs have been used to control the actions of these systems in solution and some very efficient and sophisticated examples are known, including those that occupy non-equilibrium states and function using a ratchet-type mechanism.[2] Since most [2]rotaxane molecular shuttles are large, flexible molecules with multiple functional groups they operate with efficiency in solution where the interlocked components enjoy a high degree of structural and dynamic freedom. The size and flexibility of the molecular structure are rarely a problem,[3] however, these attributes make them much less practical for highly condensed phases where the size, positional orientation and degree of aggregation of the MIM components are crucial to optimum switching efficiency.[4] To incorporate efficient molecular switches into materials and devices with a high density of functional components, a compact structure with a rigid axle and short, linear track for translational motion would be most desirable.[5]

We report herein a compact MIM-based switch with well-defined geometry, rigid backbone, and efficient switching characteristics for future application in highly dense media. Highlights include 1) the development of a new recognition template for [2]pseudorotaxane formation built around a 24-membered crown ether wheel and a benzimidazolium axle with extended aromatic substituents, 2) a high yielding, modular synthesis of [2]rotaxane molecular shuttles with a compact and rigid, H-shaped molecular structure, 3) access to three distinct molecular states and corresponding molecular shuttling rates through acid–base chemistry, and 4) control of the rate of molecular shuttling through lithium ion "ferrying" between neutral binding sites.[6]

The interaction of dibenzo[24]crown-8 (**DB24C8**) with the imidazolium ($K_a = 8\,\text{M}^{-1}$)[7] or phenylbenzimidazolium, [**1**-H]$^+$ ($K_a = 5.0 \times 10^1\,\text{M}^{-1}$) cation is weak but this can be drastically increased by adding aromatic groups to the 4- and 7-positions of the benzimidazolium unit. The benzimidazolium salt [**2**-H][BF_4] was synthesized by reacting 4,7-dibromo-2-phenyl-1*H*-benzimidazole[8] with 2 equivalents of 4-fluorophenylboronic acid under Suzuki coupling conditions followed by protonation with HBF_4 (see the Supporting Information). The ^{1}H NMR spectrum of a solution comprised of equimolar amounts of [**2**-H]$^+$ and **DB24C8** ($1.0 \times 10^{-3}\,\text{M}$, CD_3CN, 298 K) shows the efficient formation of [2]pseudorotaxane [**2**-H⊂**DB24C8**]$^+$ (Figure 1). The association constant of $1.0 \times 10^3\,\text{M}^{-1}$ is two orders of magnitude larger than for simple imidazolium or benzimidazolium derivatives. Significant shifts to higher frequency were observed for the NH (+0.73 ppm) and proton *a* resonances (+0.37 ppm) indicating hydrogen-bonding interactions while shifts to lower frequency for peaks *b* and *c* on the axle as well as *e* and *f* on the wheel (−0.31 to −0.63 ppm) are the result of efficient π-stacking. While [2]pseudorotaxane formation between **DB24C8** and axles containing two benzimidazolium groups linked by an ethane chain was reported previously,[9,10] this new templating motif shows much stronger association and the modular synthesis should allow for the incorporation of a wide variety of functionalized aromatics into the molecular scaffold.[11]

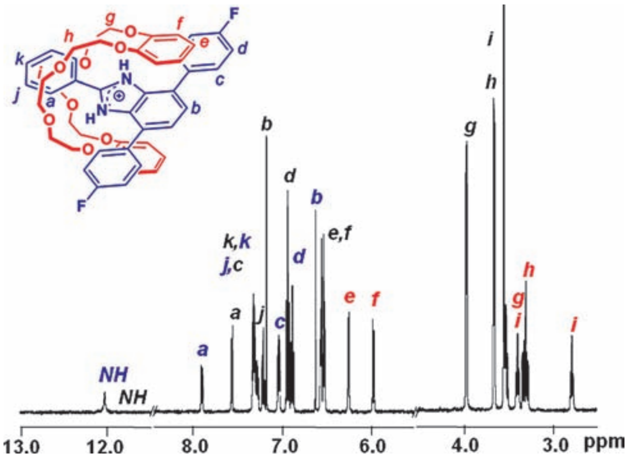

Figure 1. ^{1}H NMR spectrum of an equimolar solution of [**2**-H][BF_4] and **DB24C8** showing formation of [2]pseudorotaxane [**2**-H⊂**DB24C8**]$^+$ (the NH resonance for the uncomplexed axle is very broad). Conditions: $1.0 \times 10^{-3}\,\text{M}$ in CD_3CN at 298 K. Blue labels = complexed [**2**-H]$^+$ axle, red labels = complexed **DB24C8** wheel, black labels = uncomplexed components.

The X-ray structure of [**2**-H⊂**DB24C8**][BF_4] was consistent with the non-covalent interactions observed in solution. Figure 2 shows views emphasizing the primary NH···O hydrogen bonding (2.90 Å, 163°; 2.83 Å, 164°) between benzimidazolium NH groups and **DB24C8** ether oxygen atoms and $N^+\cdots O$ ion–dipole interactions (2.96–3.29 Å) as well as the π-

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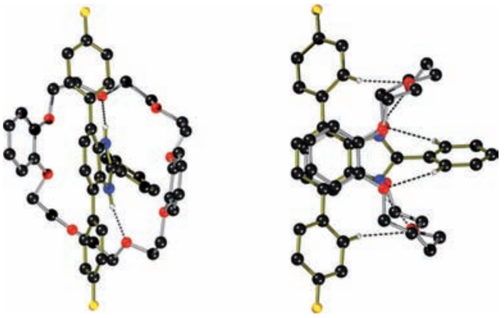

Figure 2. Ball-and-stick representations of the single-crystal X-ray structure of the cationic [2]pseudorotaxane [**2**-H⊂**DB24C8**]$^{+}$. Left: emphasizing the primary NH···O hydrogen bonds. Right: emphasizing the π-stacking and additional CH···O hydrogen bonds to the aromatic rings. F = yellow, O = red, N = blue, C = black, H = white, axle = gold bonds, wheel = silver bonds.

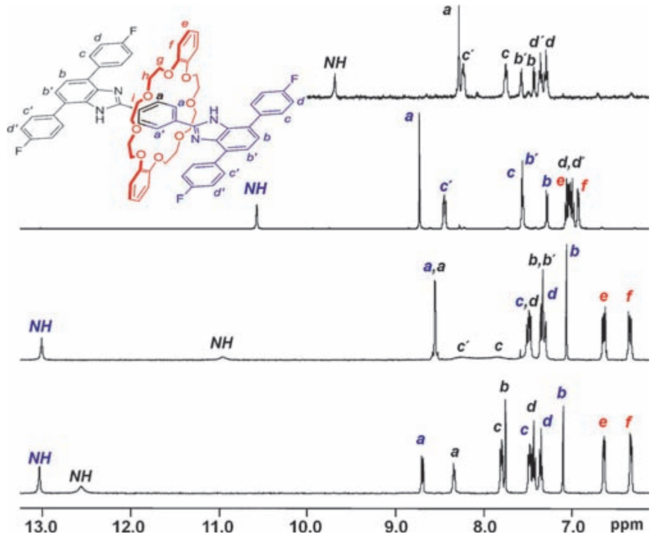

Figure 3. ^{1}H NMR spectra from top to bottom: the neutral axle in CD_2Cl_2; the neutral [2]rotaxane, [**3**⊂**DB24C8**] in CD_2Cl_2; the monoprotonated [2]rotaxane, [**3**-H⊂**DB24C8**]$^{+}$ in CD_3CN; and the diprotonated [2]rotaxane, [**3**-H_2⊂**DB24C8**]$^{2+}$ in CD_3CN. Blue labels = complexed portion of the axle, red labels = complexed **DB24C8** wheel, black labels = uncomplexed portion of the axle.

stacking of the benzimidazolium ring between the catechol rings of **DB24C8**. Four additional CH···O interactions (3.38–3.76 Å, 155–161°) are observed between **DB24C8** oxygen atoms and aromatic protons reinforcing the premise that the addition of these groups contributes significantly to the increase in association between axle and wheel. The C-shape conformation adopted by the **DB24C8** macrocycle allows efficient π-stacking interactions by clamping around the electron-poor benzimidazolium ring (3.44–4.40 Å).

Utilization of this new [2]pseudorotaxane templating motif to prepare a permanently interlocked [2]rotaxane was accomplished by taking advantage of the mild conditions used to prepare the original benzimidazole unit through condensation of a diamine with an aldehyde followed by catalytic oxidation.[12]

Substituting terephthalaldehyde for benzaldehyde in the axle synthesis allowed formation of a [2]pseudorotaxane similar to [**2**-H⊂**DB24C8**]$^{+}$, but with an exposed aldehyde functional group ($K_a = 9.7\times10^{3}\,\text{M}^{-1}$ in 10% $CH_3NO_2/CHCl_3$). In a one-pot reaction, this [2]pseudorotaxane was condensed with an equivalent of 1,2-diamino-3,6-di(4′-fluorophenyl)benzene[13] and then oxidized with a catalytic amount of $ZrCl_4$ to produce a [2]rotaxane which was isolated as the monoprotonated species [**3**-H⊂**DB24C8**][BF_4] in 93% yield. This methodology also provides a facile method to produce [2]rotaxane molecular shuttles without nuisance of [3]rotaxane side-products.[6,14,15]

The presence of two benzimidazole recognition sites on a single axle means that there are three potential forms of the [2]rotaxane accessible by acid–base chemistry: neutral, monocation, and dication. Each of these forms might be expected to adopt a different structure and undergo molecular shuttling at a different rate. Figure 3 shows the ^{1}H NMR spectra of the neutral axle (no crown), the neutral [2]rotaxane [**3**⊂**DB24C8**], the monoprotonated [2]rotaxane [**3**-H⊂**DB24C8**]$^{+}$, and the diprotonated [2]rotaxane [**3**-H_2⊂**DB24C8**]$^{2+}$. The spectrum of the neutral species is the simplest as both ends of the axle appear to be equal due to fast exchange between complexed and uncomplexed species. This is because the benzimidazole units are not protonated which eliminates both the ion–dipole and π-stacking interactions and reduces the degree of hydrogen bonding between axle and wheel. A comparison of the chemical shifts of the NH group in the neutral axle, **3** ($\delta = 9.65$ ppm), and the neutral [2]rotaxane, [**3**⊂**DB24C8**] ($\delta = 10.53$ ppm), shows that residual hydrogen bonding between the neutral benzimidazole NH group and crown ether oxygen atoms remains.

Conversely, the diprotonated species [**3**-H_2⊂**DB24C8**]$^{2+}$ contains two strongly binding recognition sites each reminiscent of that observed for the [2]pseudorotaxane. The ^{1}H NMR spectrum shows two sets of peaks that can be clearly assigned as complexed and uncomplexed axle undergoing slow exchange at 298 K. The monoprotonated [2]rotaxane, [**3**-H⊂**DB24C8**]$^{+}$, contains both protonated and neutral recognition sites and the ^{1}H NMR spectrum appears to be static showing only resonances due to a protonated site which is complexed and a neutral site which is uncomplexed.

Single-crystal X-ray structures were determined for the neutral [**3**⊂**DB24C8**] and diprotonated [**3**-H_2⊂**DB24C8**]$^{2+}$ [2]rotaxanes. For both structures, the rigid axle measures 14 Å between F atoms on the same benzimidazole group (upright of the H) and 12 Å between centroids of the benzimidazole phenyl rings (crossbar of the H).

Figure 4 (top) shows that for the diprotonated form the arrangement of axle and wheel are almost identical to that observed for the [2]pseudorotaxane in which the **DB24C8** wheel clamps around one of the benzimidazolium recognition sites. The primary NH···O hydrogen bonding (2.78 Å, 167°; 2.82 Å, 165°), N^{+}···O ion–dipole (3.03–3.82 Å), π-stacking, and CH···O interaction parameters are similar. The structure of the neutral [2]rotaxane [**3**⊂**DB24C8**] shown in Figure 4 (bottom) is very different. Since the benzimidazole units are no longer charged, there are no ion–dipole interactions and no significant driving force for π-stacking. The **DB24C8** macrocycle adopts a more open conformation and only

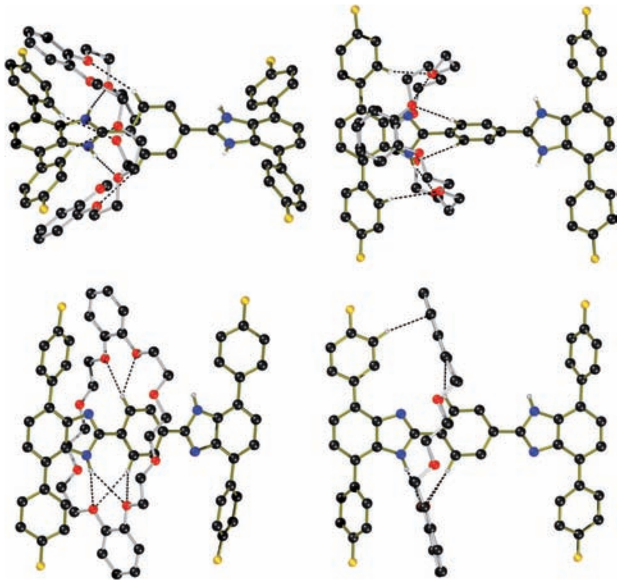

Figure 4. Ball-and-stick representations of single-crystal X-ray structures. Top: [**3**-H_2⊂**DB24C8**]$^{2+}$; left, showing primary NH⋯O hydrogen bonds; right, the π-stacking. Bottom: [**3**⊂**DB24C8**]; left, showing hydrogen bonds; right, the additional CH⋯π hydrogen bonds. F = yellow, O = red, N = blue, C = black, H = white, axle = gold bonds, wheel = silver bonds.

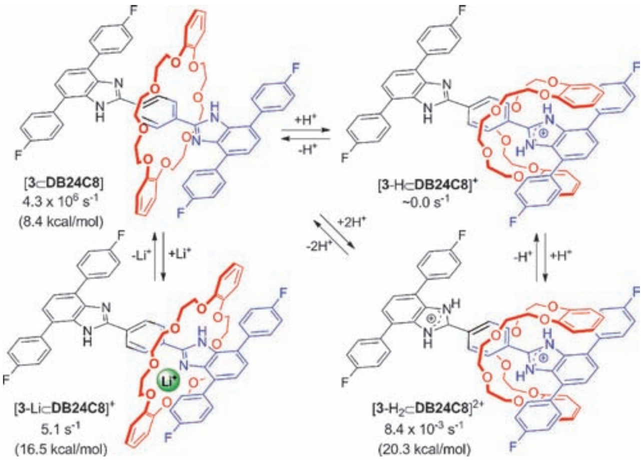

Figure 5. Four states of a new compact and rigid, H-shaped [2]rotaxane molecular shuttle are accessible. The rate of translational motion (shuttling) along the short, linear axle between benzimidazole recognition sites can be controlled by facile addition and removal of either protons or lithium ions. Rates shown are those in measured in CD_2Cl_2 solution with $\Delta G^{\neq}$ at 298 K.

participates in hydroge-bonding to the neutral NH group (3.24 Å, 160°) and two adjacent CH groups on the central phenyl ring (3.38 Å, 151°; bifurcated 3.29 Å, 136°; 3.33 Å, 136°). Importantly, this demonstrates that even when the templating charge is removed from the axle there remains enough residual non-covalent interaction to allow the benzimidazole unit to act as a recognition site for the **DB24C8** macrocycle.

Since these three [2]rotaxanes contain an axle with two recognition sites but only a single macrocyclic wheel, each should function as a molecular shuttle.[16] 2D EXSY[17] and VT ^{1}H NMR spectroscopy were employed to determine the rate of molecular shuttling at 298 K. The dicationic system [**3**-H_2⊂**DB24C8**]$^{2+}$ exhibits the lowest rate of shuttling ($8.4\times10^{-3}\,s^{-1}$, CD_2Cl_2; $3.8\times10^{-1}\,s^{-1}$, CD_3NO_2) since the non-covalent interactions between axle and wheel are the strongest and thus the barrier (20.3 kcal mol^{-1}, CD_2Cl_2; 17.8 kcal mol^{-1}, CD_3NO_2) to motion is the highest (Figure 5). Removal of the charges by deprotonation eliminates the great majority of these non-covalent interactions and the neutral species shows a high rate of shuttling ($4.3\times10^{6}\,s^{-1}$, CD_2Cl_2)[18] and correspondingly lower barrier (8.4 kcal mol^{-1}).[5c,19] When the [2]rotaxane is singly charged there is the potential for competition between the charged benzimidazolium and neutral benzimidazole recognition sites for the wheel, but NMR experiments showed the crown ether is essentially static (approximately 0.00 s^{-1}, CD_2Cl_2) preferring the charged state to such an extent that the rate of shuttling appears to be negligible.

Although the demonstration of facile acid–base control between three states of molecular shuttling[20] was gratifying, the access to a rare, neutral molecular shuttle motivated further investigation into other methods to affect the rate of shuttling in this system. Since the structure of the neutral [2]rotaxane contains a residual donor nitrogen atom on the benzimidazole ring in close proximity to several oxygen atoms from the **DB24C8** macrocycle, it was reasoned that this convergence of donor atoms might be an effective chelating site for metal ions.[21] Given the donor set and compact nature of the site, Li^+, Na^+ and Zn^{2+} were tested for coordination. Only the smallest Li^+ ion showed binding[22] as evidenced by significant changes in the ^{1}H NMR spectrum.

Adding one equivalent of Li^+ to a solution of the neutral [2]rotaxane [**3**⊂**DB24C8**] in CD_2Cl_2 showed chemical shift changes consistent with strong binding of Li^+ to the benzimidazole nitrogen atom and adjacent crown ether oxygen atoms. 2D EXSY spectra showed that the addition of Li^+ ions results in a slowing of the shuttling (5.1 s^{-1}, CD_2Cl_2) and raising of the barrier to motion (16.5 kcal mol^{-1}). However, unlike the monoprotonated [2]rotaxane which showed no evidence of translational motion, [**3**-Li⊂**DB24C8**]$^+$ shuttles at a rate intermediate between those observed for the neutral and dicationic molecules. Since the rate of shuttling was determined to be independent of the concentration of Li^+ ion (see the Supporting Information), the shuttling process is best described as an intramolecular "ferrying" of the cation between benzimidazole sites utilizing residual Li^+⋯O interactions between the cation and the crown ether. Addition of an equivalent of [12]crown-4 ether (**12C4**) completely sequesters the Li^+ ion and completely reverts the ^{1}H NMR spectrum back to that of the neutral species [**3**⊂**DB24C8**] (see the Supporting Information).

In summary, a new rigid and compact, H-shaped [2]rotaxane was prepared using a new templating motif and a new high yield capping methodology. The [2]rotaxane design provides an axle with an exactly linear shuttling trajectory that is the shortest known (7.5 Å) and goal-post style end groups that shelter the macrocycle. The neutral form of the molecular shuttle [**3**⊂**DB24C8**] undergoes extremely rapid shuttling between two equivalent recognition sites on the ends of the rigid axle. Addition of one equivalent of acid to give [**3**-H$\subset$**DB24C8**]$^{+}$ arrests the shuttling by biasing the molecule in favor of a single co-conformer to the point that the wheel interacts only with one end of the axle. Diprotonation produces [**3**-H$_2$$\subset$**DB24C8**]$^{2+}$ containing two equivalent recognition sites and the shuttling is resumed but at a much lower rate due to an increased barrier to translational motion. Furthermore, addition of a single equivalent of Li^{+} to [**3**$\subset$**DB24C8**] yields [**3**-Li$\subset$**DB24C8**]$^{+}$ in which a lithium cation provides a braking action slowing the rapid shuttling of the neutral [2]rotaxane to an intermediate rate by participating in the ferrying of the lithium ion between recognition sites. Conversion between these four states of this new [2]rotaxane molecular shuttle is straightforward (Figure 5). Control over the rates of translational motion coupled with a rigid and compact design should find application in condensed-phase materials. This system is particularly well suited for inclusion into metal–organic frameworks[23] where the size and rigidity of individual MIM components and the nature of the translational pathway are important for unperturbed motion and efficient switching.

Experimental Section

DB24C8 was purchased from Aldrich Chemicals and used as received. NMR experiments were recorded on a Bruker Avance 300 and 500 MHz NMR spectrometers. Details of the syntheses and spectroscopic characterization of all new compounds can be found in the Supporting Information.

X-ray data: [**2**-H$\subset$**DB24C8**][BF$_4$]: $C_{51}H_{52}BN_3O_8F_6$, $M=959.77$, colorless prisms ($0.18\times0.20\times0.26$ mm), triclinic, $P\bar{1}$, $a=11.3489(14)$, $b=12.4327(15)$, $c=17.633(2)$ Å, $\alpha=76.400(2)$, $\beta=79.367(2)$, $\gamma=88.120(2)°$, $U=2376.6(5)$ Å^3, $Z=2$, $\rho_{calcd}=1.341\,g\,cm^{-3}$, $\mu=0.105\,mm^{-1}$, min/max trans. = 0.8552, $\lambda(Mo_{K\alpha})=0.71073$ Å, $T=173.0(2)$ K, 23201 total reflections ($R(int)=0.0826$), $R1=0.0777$, $wR2=0.1773$ [$I>2\sigma I$], $R1=0.1469$, $wR2=0.2173$ [all data], GoF(F^2) = 1.010, data/variables/restraints = 8309/623/0. X-ray data for [**3**$\subset$**DB24C8**]·(CHCl$_3$)(CH$_3$COOCH$_2$CH$_3$): $C_{73}H_{67}Cl_3F_4O_{10}N_4$, $M=1342.66$, colorless prisms ($0.30\times0.26\times0.20$ mm), triclinic, $P\bar{1}$, $a=12.718(2)$, $b=17.456(2)$, $c=17.499(2)$ Å, $\alpha=106.241(2)$, $\beta=109.040(2)$, $\gamma=106.716(2)°$, $U=3203.8(7)$ Å^3, $Z=2$, $\rho_{calcd}=1.392\,g\,cm^{-3}$, $\mu=0.220\,mm^{-1}$, min/max trans. = 0.7905, $\lambda(Mo_{K\alpha})=0.71073$ Å, $T=173.0(2)$ K, 31108 total reflections ($R(int)=0.0796$), $R1=0.0915$, $wR2=0.2543$ [$I>2\sigma I$], $R1=0.1334$, $wR2=0.2934$ [all data], GoF(F^2) = 1.038, data/variables/restraints = 11235/847/12. X-ray Data for [**3**-H$_2$$\subset$**DB24C8**][BF$_4$]$_2$: $C_{68}H_{60}F_{12}O_8N_4B_2$, $M=1310.82$, colorless prisms ($0.34\times0.24\times0.18$ mm), triclinic, $P\bar{1}$, $a=11.182(2)$, $b=16.755(3)$, $c=17.568(3)$ Å, $\alpha=86.127(2)$, $\beta=77.189(2)$, $\gamma=74.007(2)°$, $U=3085.1(8)$ Å^3, $Z=2$, $\rho_{calcd}=1.411\,g\,cm^{-3}$, $\mu=0.116\,mm^{-1}$, min/max trans. = 0.7919, $\lambda(Mo_{K\alpha})=0.71073$ Å, $T=173.0(2)$ K, 28860 total reflections ($R(int)=0.0657$), $R1=0.0642$, $wR2=0.1715$ [$I>2\sigma I$], $R1=0.0918$, $wR2=0.1906$ [all data], GoF(F^2) = 1.066, data/variables/restraints = 10772/847/0. The SHELXTL library of programs[24] was used for X-ray solutions and figures were drawn with DIAMOND software.[25] CCDC 855552, 855553, and 855554 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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