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Photoactivated Directionally Controlled Transit of a Non-Symmetric Molecular Axle Through a Macrocycle**

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Dedicated to Professor Vincenzo Balzani on the occasion of his 75th birthday

The control of motion on the molecular scale is of fundamental importance for living organisms,[1] and one of the most fascinating challenges in nanoscience.[2,3] Artificial molecular machines have been realized on the laboratory scale,[4] and utilization of such systems to construct responsive materials[5] and surfaces,[6] control catalytic processes,[7] and develop test structures for information storage devices[8] and drug delivery[9] has been investigated. Nevertheless, the construction of synthetic nanoscale motors capable of showing directionally controlled linear or rotary movements still poses a considerable challenge to chemists.[10] Moreover, the use of such systems to perform the tasks that natural molecular motors do,[11] namely active transport of substrates over long distances or across membranes, remains a very difficult endeavor that is further complicated by the fact that most currently available synthetic molecular motors are based on sophisticated chemical structures and/or operation procedures.[4,10] In this context, the development of (supra)molecular systems that exhibit directionally controlled relative motions of their components based on a minimalist design and activated by convenient inputs is of the highest importance.

Herein we describe the construction and operation of a simple supramolecular assembly in which a molecular axle passes unidirectionally through the cavity of a molecular ring in response to photochemical and chemical stimulation. A system of this kind constitutes a first step towards the construction of an artificial molecular pump; it can also lead to the realization of molecular linear motors based on rotaxanes and rotary motors based on catenanes.[12]

The strategy that we have tackled is illustrated in Figure 1. The system is composed of a molecular ring and a non-symmetric molecular axle that comprises 1) a passive pseudo-stopper (D) at one end; 2) a central recognition site (S) for the ring; and 3) a bistable photoswitchable unit (P) at the other end. Under the conditions employed, the axle pierces the ring exclusively with the photoactive gate in its initial form (α) for kinetic reasons,[13] affording a pseudorotaxane in which the molecular ring encircles the recognition site S. Subsequently, light irradiation converts the α-P end group into the bulkier β form, a process which also causes a destabilization of the supramolecular complex. Therefore, a dethreading of the system is expected, which should occur by extrusion of the D moiety of the axle. Reset is obtained by photochemical or thermal conversion of the β-P gate back to the α state, thereby regenerating the starting form of the axle. Overall, the photoinduced directionally controlled transit of the axle through the ring would be obtained according to a flashing energy ratchet mechanism (Figure 1 b).[4b,14]

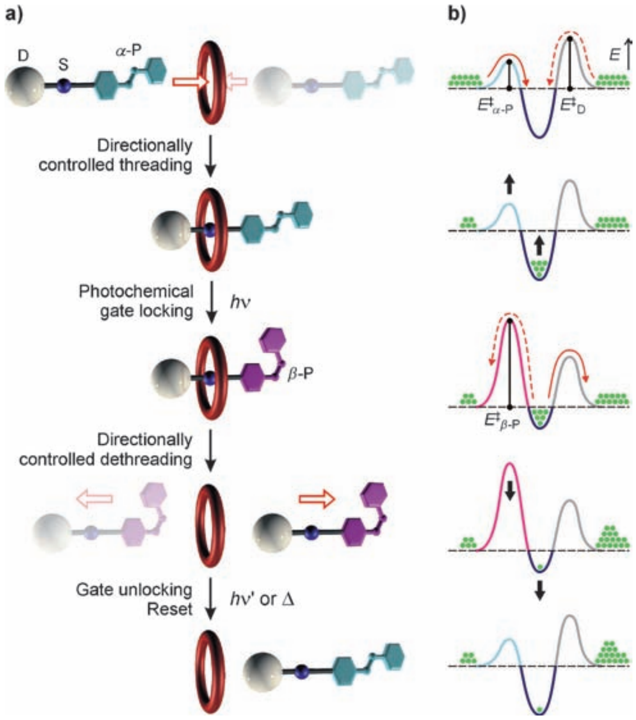

Figure 1. a) Strategy for the photoinduced unidirectional transit of a non-symmetric axle through a molecular ring. b) Simplified potential energy curves (free energy versus ring–axle distance) for the states shown in (a) describing the operation of the system in terms of a flashing ratchet mechanism. Slower processes that do not take place under our conditions are represented by shaded cartoons and dashed lines.

Clearly, the success of such a strategy relies on two basic requirements: 1) the kinetic barriers for the slippage of the axle end groups through the ring[15] should follow the order: $E^{\ddagger}_{\alpha\text{-P}} < E^{\ddagger}_{\mathrm{D}} < E^{\ddagger}_{\beta\text{-P}}$; and 2) the ring should form a more

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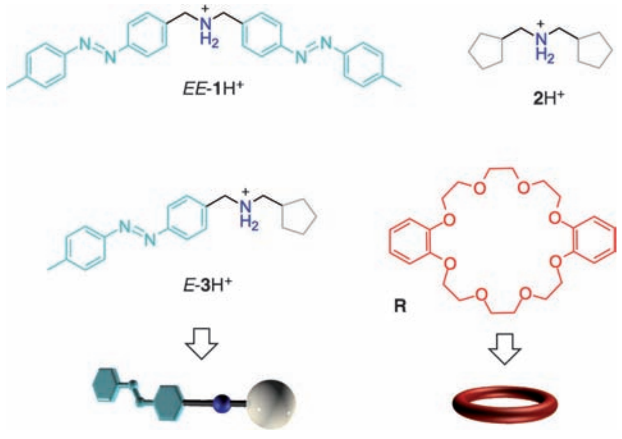
stable pseudorotaxane with the axle bearing the α-P unit compared to that bearing the β-P unit. From a practical viewpoint, to enable a clean operation and characterization of the system, it is important that the differences in the energy barriers and stability constants are sufficiently large, and that the photochemical interconversion of the P gate between α and β forms is fast, efficient, and reversible.

In a previous investigation,[16] we studied the threaded complex of axle *EE*-**1**H$^+$, composed of a dialkylammonium hydrogen-bonding site equipped with two azobenzene end units, with the dibenzo[24]crown-8 ring **R** (Scheme 1).[17] We found that the threading–dethreading rate constants are slowed down by at least four orders of magnitude when the *E*-azobenzene end units are photoisomerized to the *Z* form, practically transforming the complex into a rotaxane; moreover, the stability constant drops by a factor of two (Table 1).[18] The system exhibits excellent photoswitching and reversibility, and it is easy to synthesize. Encouraged by these results, we looked for a passive pseudo-stopper (D in Figure 1) with steric hindrance for slippage through **R** that is intermediate between that of the *E*- and *Z*-azobenzene end units of **1**H$^+$.



Scheme 1. Structure formulas and cartoon representation of the examined axle and ring components.

It was shown earlier by Stoddart and co-workers[19] that in chloroform/acetonitrile 3:1 the bis(cyclopentylmethyl)ammonium ion **2**H$^+$ (Scheme 1) is complexed by **R** in a pseudorotaxane fashion, with threading and dethreading rate-constant values that fall in between those observed for *EE*-**1**H$^+$ and *ZZ*-**1**H$^+$ with **R**.[16] Therefore, we envisaged that the strategy shown in Figure 1 could be implemented with a non-symmetric axle such as *E*-**3**H$^+$ (Scheme 1).

The synthesis of *E*-**3**H$^+$ was performed by reductive amination of cyclopentanecarbaldehyde with (4-nitrophenyl)methanamine, reduction of the nitro group to amine through hydrogenation and subsequent Mill's coupling with *p*-methylnitrosobenzene in acetic acid followed by anion exchange with NH_4PF_6. The *E*-**3**H$^+$·PF_6 salt was fully characterized by ^{1}H and ^{13}C NMR, DQF-COSY, ESI-MS, and UV/Vis absorption spectroscopy.

^{1}H NMR spectroscopic titration experiments in acetonitrile show that *E*-**3**H$^+$ and **R** self-assemble to yield a pseudorotaxane (Supporting Information). The corresponding thermodynamic and kinetic data are reported in Table 1, together with those for the threading–dethreading of the symmetric axles *EE*-**1**H$^+$, *ZZ*-**1**H$^+$ and **2**H$^+$ with **R**. It can be noted that the threading rate constant k_{in} for *E*-**3**H$^+$ is nearly half that for *EE*-**1**H$^+$, and two orders of magnitude larger than that for **2**H$^+$. This observation clearly indicates that on the observed timescale, *E*-**3**H$^+$ pierces the ring exclusively with its *E*-azobenzene terminus. The decrease of the threading constant by a factor of two compared with that for *EE*-**1**H$^+$, which can thread the ring with both its extremities, is fully consistent with this picture.

Irradiation of *E*-**3**H$^+$ at 365 nm affords *Z*-**3**H$^+$ with a quantum efficiency of 0.17 and a yield of over 95 % at the photostationary state. Also *Z*-**3**H$^+$ forms a pseudorotaxane with **R**, and it has a threading rate constant that is nearly half that of **2**H$^+$ and almost 20 times larger than that of *ZZ*-**1**H$^+$ (Table 1). These results show that *Z*-**3**H$^+$ threads **R** from its cyclopentyl terminus. It is noteworthy that the *E*→*Z* photoisomerization of the azobenzene end group of **3**H$^+$ also takes place efficiently when this compound is surrounded by **R**. Therefore, we can kinetically control the threading–dethreading side of **3**H$^+$ by photoadjusting the steric hindrance of its

Table 1: Kinetic and thermodynamic data for the self-assembly of the investigated complexes in CD_3CN at 298 K.[a]

Complex	K[b] [L mol^{-1}]	$-\Delta G°$[c] [kcal mol^{-1}]	k_{in}[d] [L mol^{-1} s^{-1}]	$-\Delta G^{\#}_{in}$[e] [kcal mol^{-1}]	k_{out}[d] [s^{-1}]	$-\Delta G^{\#}_{out}$[e] [kcal mol^{-1}]	$t_{1/2}$[f]
[*EE*-**1**H⊂**R**]PF_6	820	3.9	37[g]	15	4.5×10^{-2}[h]	19.3	15.4 s
[*ZZ*-**1**H⊂**R**]PF_6	400	3.5	2.9×10^{-3}	20.9	7.2×10^{-6}	24.5	27 h
[**2**H⊂**R**]PF_6	ca. 30	2	1.3×10^{-1}	18.6	4.4×10^{-3}	20.7	2.6 min
[*E*-**3**H⊂**R**]PF_6	225	3.2	22[g]	15.6	0.1[h]	18.8	6.3 s
[*Z*-**3**H⊂**R**]PF_6	230	3.2	5.1×10^{-2}	19.2	2.6×10^{-4}	22.3	46 min

[a] The reactions were followed with ^{1}H NMR spectroscopy by monitoring the changes in the relative intensities of the signals associated with the probe protons in the complexed and uncomplexed ammonium ions. [b] The K values were obtained from four single-point measurements of the concentrations of the complexed and uncomplexed cations, in the relevant ^{1}H NMR spectrum, by using the expression $K=[\text{complex}]/[\text{ring}][\text{axle}]$. [c] The free energies of association ($\Delta G°$) were calculated from the K values by using the expression $\Delta G° = -RT\ln K$. [d] The threading (k_{in}) and dethreading (k_{out}) rate constants were calculated by fitting the concentrations of complexed and uncomplexed ammonium ions, extracted from ^{1}H NMR kinetics experiments. [e] The free energies of activation for the threading ($-\Delta G^{\neq}_{in}$) and dethreading ($-\Delta G^{\neq}_{out}$) processes were calculated by using the relationships $-\Delta G^{\neq}_{in} = -RT\ln(k_{in}h/kT)$ and $-\Delta G^{\neq}_{out} = -RT\ln(k_{out}h/kT)$, respectively, where R, h, and k correspond to the gas, Planck, and Boltzmann constants, respectively. [f] The half-life of the complexes were calculated from k_{out} values by using the expression $t_{1/2} = \ln 2/k_{out}$. [g] Determined by stopped flow UV/Vis absorption spectroscopy. [h] Calculated from the k_{in} and K values by using the expression $k_{out} = k_{in}/K$.

azobenzene end group below and above that of the photo-inactive cyclopentyl pseudo-stopper located at the other end.

Unfortunately, in contrast with the results found for the $[EE\text{-}\mathbf{1}\mathrm{H}\subset\mathbf{R}]^+$ and $[ZZ\text{-}\mathbf{1}\mathrm{H}\subset\mathbf{R}]^+$ pseudorotaxanes, the stability constants of $[E\text{-}\mathbf{3}\mathrm{H}\subset\mathbf{R}]^+$ and $[Z\text{-}\mathbf{3}\mathrm{H}\subset\mathbf{R}]^+$ are identical within errors (Table 1). Therefore, the dethreading of $Z\text{-}\mathbf{3}\mathrm{H}^+$ from the ring cannot be caused by the same photochemical stimulus that triggers the azobenzene $E \rightarrow Z$ isomerization. To promote the disassembly of the complexes[20] we used K^+ ions, which act as competitive guests for **R**.[21,22] The addition of three equivalents of KPF_6 causes the complete dethreading of both $[E\text{-}\mathbf{3}\mathrm{H}\subset\mathbf{R}]^+$ and $[Z\text{-}\mathbf{3}\mathrm{H}\subset\mathbf{R}]^+$; however, while the K^+-induced disassembly of the former complex is fast, the latter exhibits a dethreading half-life of 51 min (Figure 2a). This value is much shorter than the half-life of $[ZZ\text{-}\mathbf{1}\mathrm{H}\subset\mathbf{R}]^+$ in the presence of K^+ (ca. 25 h, Figure 2b)[16] and is in excellent agreement with the half-life of $Z\text{-}\mathbf{3}\mathrm{H}^+$ determined from the self-assembly data (46 min, Table 1). These observations indicate that the chemically induced disassembly of $Z\text{-}\mathbf{3}\mathrm{H}^+$ and **R** takes place by extrusion of the cyclopentyl unit of the former from the cavity of the latter.

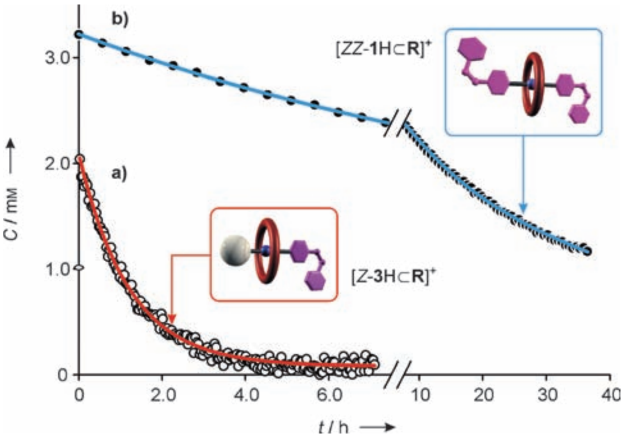


Figure 2. Concentration–time profiles, obtained from ^{1}H NMR data in CD_3CN at 298 K, showing the K^+-induced dethreading of a) $[Z\text{-}\mathbf{3}\mathrm{H}\subset\mathbf{R}]^+$ and b) $[ZZ\text{-}\mathbf{1}\mathrm{H}\subset\mathbf{R}]^+$. Conditions: a) 5.1 mM $Z\text{-}\mathbf{3}\mathrm{H}^+$, 5.4 mM **R** (about 40% complexation of the axle molecules), 15.2 mM KPF_6; b) 4.8 mM $ZZ\text{-}\mathbf{1}\mathrm{H}^+$, 7.6 mM **R** (about 65% complexation of the axle molecules), 16.7 mM KPF_6.

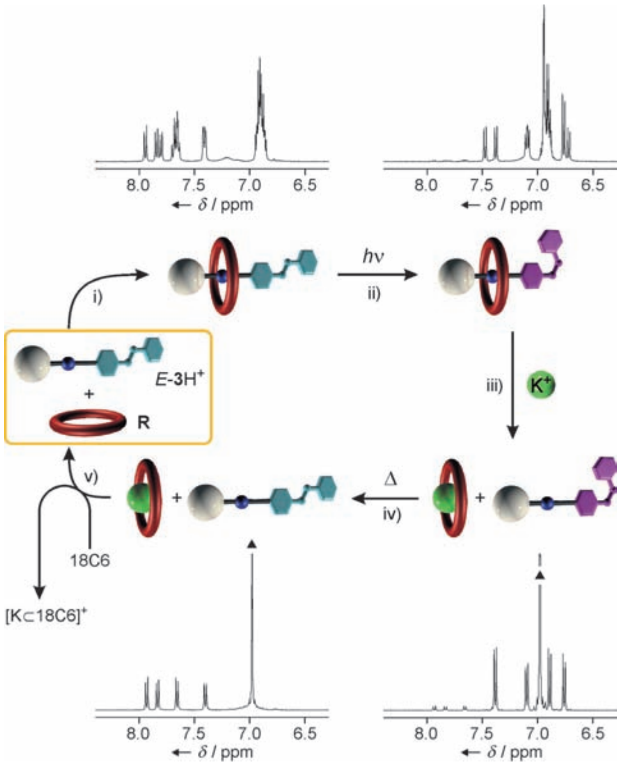


Figure 3. Representation of the photochemically and chemically controlled transit of $\mathbf{3}\mathrm{H}^+$ through **R** and relevant ^{1}H NMR spectra (400 MHz, CD_3CN, 298 K). Conditions: i) 5.0 mM $E\text{-}\mathbf{3}\mathrm{H}^+$ and 5.0 mM **R**; ii) 365 nm, 15 min; iii) 10 mM KPF_6; iv) 344 K, 2 h; v) 30 mM [18]crown-6. Marked signals are due to the $[K\subset\mathbf{R}]^+$ complex.

The results of a summarizing experiment that illustrates the directional transit of the axle through the ring are shown in Figure 3. $E\text{-}\mathbf{3}\mathrm{H}^+$ pierces **R** with its E-azobenzene side to form the $[E\text{-}\mathbf{3}\mathrm{H}\subset\mathbf{R}]^+$ pseudorotaxane complex, which equilibrates rapidly with its separated components. Irradiation in the near UV converts quantitatively $[E\text{-}\mathbf{3}\mathrm{H}\subset\mathbf{R}]^+$ into $[Z\text{-}\mathbf{3}\mathrm{H}\subset\mathbf{R}]^+$, which has much slower assembly–disassembly kinetics. The successive addition of K^+ ions promotes the dethreading of $Z\text{-}\mathbf{3}\mathrm{H}^+$ from **R** by the passage of the cyclopentyl moiety through the cavity of the ring. It should be noted that equilibration of the $[Z\text{-}\mathbf{3}\mathrm{H}\subset\mathbf{R}]^+$ complex with its separated components, which would cause the loss of the information on the threading direction of $E\text{-}\mathbf{3}\mathrm{H}^+$, is much slower than the time required for the activation of the dethreading stimulus (addition of K^+). Therefore, after the threading event the system is "locked" by photoisomerization, and the successive addition of potassium ions causes dethreading in the same direction along which threading of $E\text{-}\mathbf{3}\mathrm{H}^+$ has initially occurred. The starting species $E\text{-}\mathbf{3}\mathrm{H}^+$ can be fully regenerated by thermal $Z \rightarrow E$ isomerization (half-life of 8 days at room temperature; see the Supporting Information). Sequestration of K^+ by an excess (3 equiv) of [18]crown-6 affords the re-assembly of $[E\text{-}\mathbf{3}\mathrm{H}\subset\mathbf{R}]^+$ and the full reset of the system.

This molecular device, however, if it would be incorporated in a compartmentalized structure (for example, embedded in the membrane of a vesicle), could not be used to pump the molecular axle and generate a transmembrane chemical potential[12] because the ring component has two identical faces. However, we are ready to apply the strategy developed in this work to supramolecular assemblies based on three-dimensional non-symmetric macrocycles with lengths that can approach the thickness of a bilayer membrane[23] and in which face-selective threading can be realized.[24] Indeed, the present system is characterized by a minimalist design, facile synthesis, convenient switching, and reversibility: all of these features can foster further research developments and constitute essential requirements for future real-world applications.

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