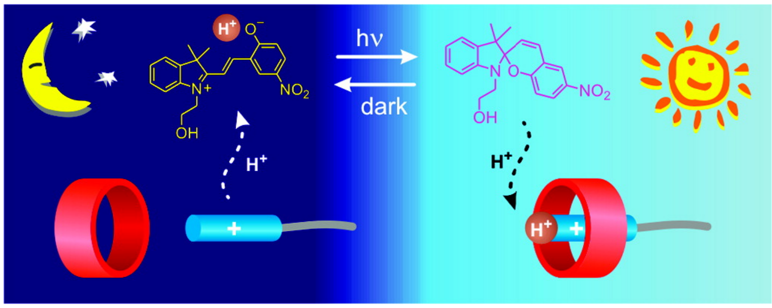
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

A Simple Molecular Machine Operated by Photoinduced Proton Transfer

Serena Silvi, Arturo Arduini, Andrea Pochini, Andrea Secchi, Massimiliano
Tomasulo, Franisco M. Raymo, Massimo Baroncini, and Alberto Credi

J. Am. Chem. Soc., **2007**, 129 (44), 13378-13379• DOI: 10.1021/ja0753851 • Publication Date (Web): 13 October 2007



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 10 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

ACS Publications
High quality. High impact.

Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

A Simple Molecular Machine Operated by Photoinduced Proton Transfer

Serena Silvi,† Arturo Arduini,‡ Andrea Pochini,‡ Andrea Secchi,‡ Massimiliano Tomasulo,§
Françisco M. Raymo,§ Massimo Baroncini,† and Alberto Credi*,†

Dipartimento di Chimica "G. Ciamician", Università di Bologna, via Selmi 2, 40126 Bologna, Italy, Dipartimento di Chimica Organica e Industriale, Università di Parma, via Usberti 17/a, 43100 Parma, Italy, and Center for Supramolecular Science, Department of Chemistry, University of Miami, 1301 Memorial Drive, Coral Gables, Florida 33146-0431

Received July 19, 2007; E-mail: alberto.credi@unibo.it

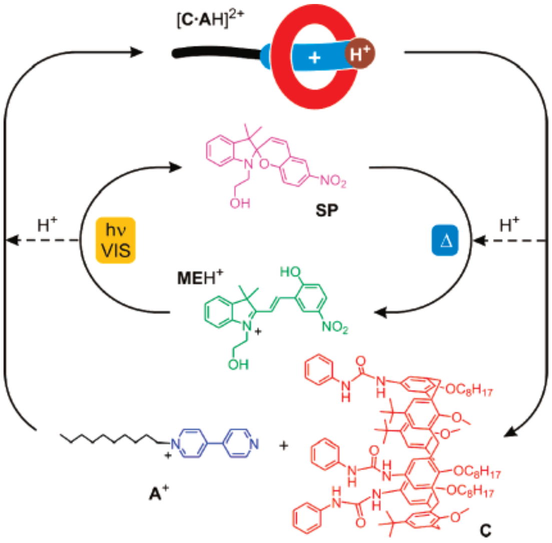
Molecular machines—(supra)molecular systems in which large-amplitude motions of some components can be controlled by appropriate stimuli—can be operated by means of chemical, electrochemical, or photochemical processes.[1] However, the use of light stimulation[2] has several advantages. For example, photons can be used to supply energy to the system and to gather information about its state without physically touching it. Light excitation can be carried out by a variety of sources (including the sun), with the possibility of a fine resolution in space and time.

Many artificial molecular machines reported so far are powered by exoergonic chemical reactions, most typically acid−base reactions.[1,3] A modular construction of light-driven molecular machines, usually pursued by integrating photochemical functions with mechanically switchable systems,[4] is in general more difficult to carry out. It would therefore be useful to identify viable strategies for using light to operate "stand alone" chemically driven molecular machines.[5] Here we show that the acid−base controlled threading−dethreading of a pseudorotaxane in solution can be operated by photoinduced intermolecular proton transfer[6] with a molecular switch. Pseudorotaxanes whose molecular components can be threaded and dethreaded in response to external signals may be regarded as very simple prototypes of chemical machinery[7,8] and are important for the development of less trivial unimolecular machines based on rotaxanes,[9] catenanes,[10] and related interlocked compounds.[11]

The calix[6]arene wheel **C** (Scheme 1) forms fairly stable pseudorotaxane complexes with 4,4′-bipyridinium compounds in apolar solvents.[12] Therefore, we envisaged that compound **A**H^{2+}, obtained by protonation of the pyridine nitrogen of the 4,4′-pyridylpyridinium axle-like $\mathbf{A}^+$ (as PF_6^- salt; Scheme 1), could thread into the cavity of **C** as well. In fact, spectrophotometric titrations and voltammetric experiments show that a very stable [$K = (6 \pm 2) \times 10^6\ M^{-1}$] pseudorotaxane complex is formed between **C** and **A**H^{2+} in CH_2Cl_2 (see Supporting Information). For the present discussion, it is important to note that the pseudorotaxane [**C**·**A**H]$^{2+}$ exhibits a broad and weak charge-transfer (CT) absorption band in the visible region ($\lambda_{max} = 478$ nm, $\epsilon = 500\ M^{-1}\ cm^{-1}$), where none of the isolated molecular components exhibit absorption features. Deprotonation of **A**H^{2+} with a base (e.g., tributylamine) in CH_2Cl_2 leads to dethreading of the pseudorotaxane.

In order to trigger the self-assembly and disassembly of this pseudorotaxane by light, a suitable species whose acid−base properties can be photocontrolled should be identified. Specifically, such a compound must occur in two forms, interconvertible into one another by light irradiation, exhibiting smaller and larger acid strength than that of **A**H^{2+}, respectively. A species that fulfils these requirements is the spiropyran photochrome **SP** (Scheme 1).[13,14] In the presence of an acid, the colorless **SP** is converted into the yellow protonated merocyanine form **ME**H^+.[15] Upon irradiation with visible light, **ME**H^+ releases a proton, isomerizing back to **SP**.[16] The coupled operation expected for the pseudorotaxane and spiropyran switches is represented in Scheme 1.

Scheme 1. Control of Threading−Dethreading Processes in Pseudorotaxane [**C**·**A**H]$^{2+}$ by Means of Light-Induced Proton Exchange with a Spiropyran−Merocyanine Photochromic System



The absorption spectrum of a 1:1 mixture of the protonated axle **A**H^{2+} and the calixarene wheel **C** shows the typical[12] CT absorption band of the [**C**·**A**H]$^{2+}$ complex (Figure 1, black curve). In our conditions (1×10^{-4} M), more than 95% of the molecular components are associated together in the pseudorotaxane superstructure. The CT band of [**C**·**A**H]$^{2+}$ does not change soon after the addition of 1 equiv of **SP** (blue curve). By keeping the solution in the dark, the absorption band typical[16] of **ME**H^+ at 417 nm gradually appears. Although the **ME**H^+ band partially overlaps with the much weaker CT band of the complex, it can be noticed that the absorbance at $\lambda > 520$ nm decreases concomitantly with the formation of **ME**H^+ (Figure 1, red curve). This change cannot be ascribed to the **SP**-**ME**H^+ transformation and has to be assigned to the dethreading of the [**C**·**A**H]$^{2+}$ pseudorotaxane. When the equilibration is completed (after 7 days), it can be estimated on the basis of the **ME**H^+ absorption band at 417 nm that the **SP**:**ME**H^+ ratio is about 60:40; however, the decrease of the CT absorption would correspond to disassembling of 15% of the [**C**·**A**H]$^{2+}$ species, instead of the 40% expected from the amount of **ME**H^+ formed. Most likely, the decrease in the CT band is partially offset by the absorbance increase originating from the formation

---

† Universitá di Bologna.
‡ Universitá di Parma.
§ University of Miami.

10.1021/ja0753851 CCC: $37.00

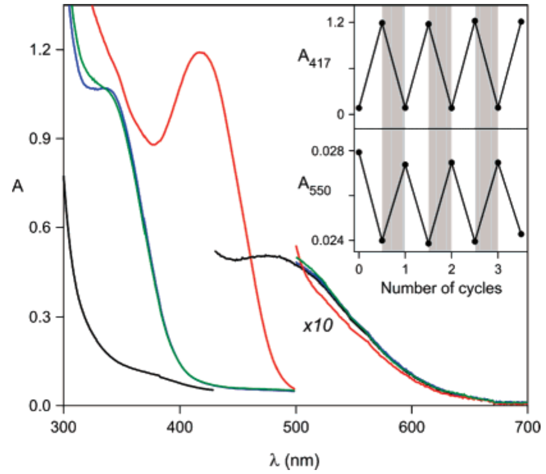


Figure 1. Absorption spectra in CH_2Cl_2 at room temperature of (i) the pseudorotaxane [**C**·**A**H]$^{2+}$, black curve; (ii) [**C**·**A**H]$^{2+}$ and **SP**, immediately after the addition of the latter, blue curve; (iii) solution (ii) after 7 days of rest in the dark, red curve; (iv) solution (iii) after 10 min of irradiation at $\lambda > 450$ nm, green curve. Inset: absorbance changes at 417 nm (a) and 550 nm (b) of a CH_2Cl_2 solution containing [**C**·**A**H]$^{2+}$ and **SP** observed upon several cycles of thermal equilibration (7 days in the dark at room temperature, white areas) and visible light irradiation (10 min with a 150 W tungsten−halogen lamp, $\lambda > 450$ nm, gray areas). The concentration of all the components was 1.0×10^{-4} M.

of a small amount of the nonprotonated merocyanine **ME** (which absorbs strongly in the 500−600 nm region)[15,16] in equilibrium with **ME**H$^+$. By irradiating the solution with visible light, the **ME**H$^+$ band disappears completely, and the initial CT band is fully restored (Figure 1, green curve). The inset of Figure 1 shows the absorbance changes observed at 417 nm (**ME**H$^+$ band) and 550 nm (pseudorotaxane CT band) by repeated thermal equilibration−light irradiation cycles, indicating that the switching process is fully reversible.

The observed changes can be interpreted in terms of the reactions shown in Scheme 1. Starting from a mixture of the complex [**C**·**A**H]$^{2+}$ and **SP**, a thermal proton transfer occurs from **A**H^{2+} to the photochrome, yielding **ME**H$^+$ and the deprotonated axle **A**$^+$ which is not appreciably complexed by **C** in our conditions. Hence, a slow dark reaction that leads to dethreading of the pseudorotaxane takes place. Subsequent light irradiation of the **ME**H$^+$ species in the visible region causes an opposite proton transfer converting **A**$^+$ into **A**H^{2+}, which rethreads into the calixarene wheel. Since the reset of the system occurs thermally, its operation under continuous light irradiation can give rise to autonomous behavior; in other words, the dethreading−rethreading process is repeated without intervention of an operator as long as the energy source (i.e., light) is available. In practice, because of the large difference in the time scale of the dark and light parts of the cycle, the photostationary state is strongly displaced toward the **SP**-[**C**·**A**H]$^{2+}$ state, unless irradiation is carried out with very low intensity and/or the temperature is increased. Nevertheless, this behavior could be employed to implement a memory effect in the system.[6]

In conclusion, we have shown that the threading−dethreading of a pH-switchable calix[6]arene bipyridinium pseudorotaxane in solution can be controlled by visible light irradiation using a merocyanine compound as a photoacid. Such a coupling between the two molecular switches that communicate with one another by intermolecular proton transfer provides a general principle for the operation of photoinactive acid−base controllable molecular machines with light. Investigations aimed at elucidating the switching mechanism in more detail, improving the performances of the system, and applying this strategy to more complex nanodevices are underway.

Acknowledgment. This work was supported by the EU Biomach project, Ministero dell'Università e della Ricerca (PRIN 2006034123), Regione Emilia-Romagna (NANOFABER), and the National Science Foundation (CAREER Award CHE-0237578).

Supporting Information Available: Experimental methods and additional spectroscopic results. This material is available free of charge via Internet at http://pubs.acs.org.

References

(1) (a) Balzani, V.; Credi, A.; Venturi, M. *Molecular Devices and Machines*; Wiley-VCH: Weinheim, Germany, 2003. (b) Browne, W. R.; Feringa, B. L. *Nat. Nanotechnol.* **2006**, *1*, 25−35. (c) Kay, E. R.; Leigh, D. A.; Zerbetto, F. *Angew. Chem., Int. Ed.* **2007**, *46*, 72−191.

(2) (a) Credi, A. *Aust. J. Chem.* **2006**, *59*, 157−169. (b) Tian, H.; Wang, Q. C. *Chem. Soc. Rev.* **2006**, *35*, 361−364. (c) Saha, S.; Stoddart, J. F. *Chem. Soc. Rev.* **2007**, *36*, 77−92.

(3) For recent examples of pH-driven molecular machines, see: (a) Cheng, K.-W.; Lai, C.-C.; Chiang, P.-T.; Chiu, S.-H. *Chem. Commun.* **2006**, 2854−2856. (b) Ooya, T.; Inoue, D.; Choi, H. S.; Kobayashi, Y.; Loethen, S.; Thompson, D. H.; Ko, Y. H.; Kim, K.; Yui, N. *Org. Lett.* **2006**, *8*, 3159−3162. (c) Nguyen, T. D.; Leung, K. C. F.; Liong, M.; Pentecost, C. D.; Stoddart, J. F.; Zink, J. I. *Org. Lett.* **2006**, *8*, 3363−3366. (d) Leigh, D. A.; Thomson, A. R. *Org. Lett.* **2006**, *8*, 5377−5379. (e) Koo, C.-K.; Lam, B.; Leung, S.-K.; Lam, M. H.-W.; Wong, W.-Y. *J. Am. Chem. Soc.* **2006**, *128*, 16434−16435. (f) Sindelar, V.; Silvi, S.; Parker, S. E.; Sobransingh, D.; Kaifer, A. E. *Adv. Funct. Mater.* **2007**, *17*, 694−701.

(4) (a) Balzani, V.; Clemente-León, M.; Credi, A.; Ferrer, B.; Venturi, M.; Flood, A. H.; Stoddart J. F. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 1178−1183. (b) Muraoka, T.; Kinbara, K.; Aida, T. *Nature* **2006**, *440*, 512−515. (c) Saha, S.; Flood, A. H.; Stoddart, J. F.; Impellizzeri, S.; Silvi, S.; Venturi, M.; Credi, A. *J. Am. Chem. Soc.* **2007**, *129*, 12159−12171.

(5) (a) Liu, H.; Xu, Y.; Li, F.; Yang, Y.; Wang, W.; Song, Y.; Liu, D. *Angew. Chem., Int. Ed.* **2007**, *46*, 2515−2517. (b) Wu, H.; Zhang, D.; Su, L.; Ohkubo, K.; Zhang, C.; Yin, S.; Mao, L.; Shuai, Z.; Fukuzumi, S.; Zhu, D. *J. Am. Chem. Soc.* **2007**, *129*, 6839−6846.

(6) (a) Raymo, F. M.; Giordani, S. *Org. Lett.* **2001**, *3*, 3475−3478. (b) Raymo, F. M.; Alvarado, R. J.; Giordani, S.; Cejas, M. A. *J. Am. Chem. Soc.* **2003**, *125*, 2361−2364. (c) Giordani, S.; Cejas, M. A.; Raymo, F. M. *Tetrahedron* **2004**, *60*, 10973−10981.

(7) Balzani, V.; Credi, A.; Venturi, M. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4814−4817.

(8) For interesting pseudorotaxane-based molecular devices, see: Saha, S.; Leung, K. C.-F.; Nguyen, T. D.; Stoddart, J. F.; Zink, J. I. *Adv. Funct. Mater.* **2007**, *17*, 685−693.

(9) Recent example: Serreli, V.; Lee, C.-F.; Kay, E. R.; Leigh, D. A. *Nature* **2007**, *445*, 523−527.

(10) Recent example: Ikeda, T.; Saha, S.; Aprahamian, I.; Leung, K. C.-F.; Williams, A.; Deng, W. Q.; Flood, A. H.; Goddard, W. A.; Stoddart, J. F. *Chem. Asian J.* **2007**, *2*, 76−93.

(11) (a) Jimenez-Molero, M. C.; Dietrich-Buchecker, C.; Sauvage, J.-P. *Chem.—Eur. J.* **2002**, *8*, 1456−1466. (b) Liu, Y.; Flood, A. H.; Bonvallett, P. A.; Vignon, S. A.; Northrop, B. H.; Tseng, H.-R.; Jeppesen, J. O.; Huang, T. J.; Brough, B.; Baller, M.; Magonov, S.; Solares, S. D.; Goddard, W. A.; Ho, C.-M.; Stoddart, J. F. *J. Am. Chem. Soc.* **2005**, *127*, 9745−9759. (c) Badjic, J. D.; Ronconi, C. M.; Stoddart, J. F.; Balzani, V.; Silvi, S.; Credi, A. *J. Am. Chem. Soc.* **2006**, *128*, 1489−1499.

(12) Credi, A.; Dumas, S.; Silvi, S.; Venturi, M.; Arduini, A.; Pochini, A.; Secchi, A. *J. Org. Chem.* **2004**, *69*, 5881−5887.

(13) Dürr, H., Bouas-Laurent, H., Eds. *Photochromism: Molecules and Systems*; Elsevier: Amsterdam, 2003.

(14) Recent examples of photoswitchable systems based on spiropyrans: (a) Andreasson, J.; Straight, S. D.; Kodis, G.; Park, C. D.; Hambourger, M.; Gervaldo, M.; Albinsson, B.; Moore T. A.; Moore A. L.; Gust, D. *J. Am. Chem. Soc.* **2006**, *128*, 16259−16265. (b) Wen, G. Y.; Yan, J.; Zhou, Y. C.; Zhang, D. Q.; Mao, L. Q.; Zhu, D. B. *Chem. Commun.* **2006**, 3016−3018. (c) Zhu, L. Y.; Wu, W. W.; Zhu, M. Q.; Han, J. J.; Hurst, J. K.; Li, A. D. Q. *J. Am. Chem. Soc.* **2007**, *129*, 3524−3525. (d) Niazov, T.; Shlyahovsky, B.; Willner, I. *J. Am. Chem. Soc.* **2007**, *129*, 6374−6375.

(15) Wojtyk, J. T. C.; Wasey, A.; Xiao, N.-N.; Kazmaier, P. M.; Hoz, S.; Yu, C.; Lemieux, R. P.; Buncel, E. *J. Phys. Chem. A* **2007**, *111*, 2511−2516.

(16) (a) Raymo, F. M.; Giordani, S. *J. Am. Chem. Soc.* **2001**, *123*, 4651−4652. (b) Raymo, F. M.; Giordani, S.; White, A. J. P.; Williams, D. J. *J. Org. Chem.* **2003**, *68*, 4158−4169.

JA0753851