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Artificial molecular-level machines. Dethreading–rethreading of a pseudorotaxane powered exclusively by light energy

Vincenzo Balzani,*[a] Alberto Credi,[a] Filippo Marchioni[a] and J. Fraser Stoddart[b]

[a] *Dipartimento di Chimica 'G. Ciamician', Università degli Studi di Bologna, via Selmi 2, 40126 Bologna, Italy. E-mail: vbalzani@ciam.unibo.it; Fax: 39 051 2099456; Tel: 39 051 2099560*
[b] *Department of Chemistry and Biochemistry, University of California at Los Angeles, 405 Hilgard Avenue, Los Angeles, CA 90095-1569, USA. E-mail: stoddart@chem.ucla.edu; Fax: +1 310 2061843; Tel: +1 310 2067078*

Received (in Cambridge, UK) 12th June 2001, Accepted 3rd August 2001
First published as an Advance Article on the web 4th September 2001

The reversible light-driven dethreading–rethreading of a pseudorotaxane is obtained in solution by exploiting the (*E*)–(*Z*) photoisomerisation of azobenzene, and monitored through fluorescence signals.

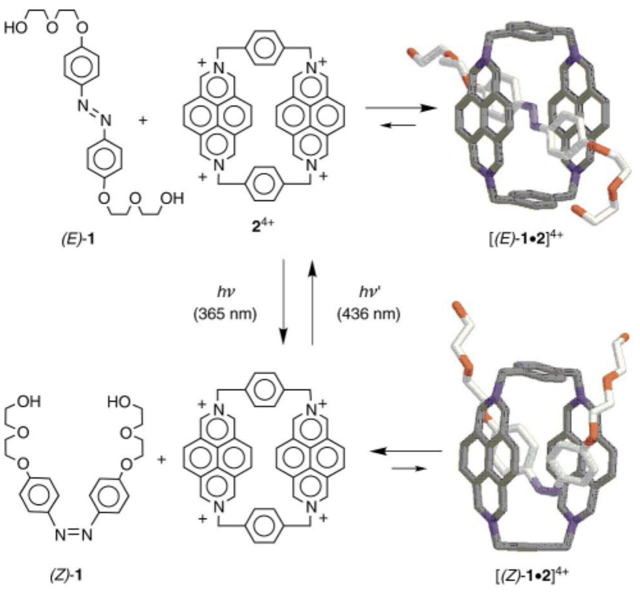
An artificial molecular-level machine[1–3] can be defined as an assembly of a discrete number of molecular components designed to perform mechanical-like movements (output) as a consequence of appropriate external stimuli (input).[1] The problem of the energy supply to make an artificial molecular-level machine work is, of course, of the greatest importance.[4] If chemical energy has to be used, addition of fresh reactants ('fuel') at any step of its working cycle is needed, with the concomitant formation of waste products whose accumulation will compromise the operation of the machine, unless they are removed from the system. Chemical fuel, however, is not the only means by which energy can be supplied to make molecular-level machines work. In green plants, the energy needed to sustain the machinery of life is supplied by sunlight. In this paper, we show that light energy inputs can indeed make an artificial piston/cylinder molecular-level machine work without the formation of waste products.

Dethreading–rethreading of the thread and ring components of a pseudorotaxane is reminiscent of the movement of a piston in a cylinder and can therefore be considered as a very simple molecular machine.[1] In pseudorotaxanes which are primarily stabilised by π-electron donor–acceptor (D–A) interactions, charge-transfer (CT) absorption bands appear in the visible region of the spectrum. Light excitation in these bands leads formally to the transfer of an electron from the donor to the acceptor component and is therefore expected to destabilise the D–A interaction responsible for the self-assembly. This simple approach to photoinduced dethreading, however, is precluded by the fact that the back electron transfer—that is, the deactivation of the CT excited state to the ground state—is much faster than the separation of the molecular components,[5] a process which requires extended nuclear motions. In order to obtain photoinduced dethreading, a photosensitizer was then incorporated into the pseudorotaxane structure,[6,7] and light excitation was performed in the presence of a sacrificial reductant in order to prevent the back electron-transfer process. Rethreading could be obtained by back oxidation (*e.g.* with dioxygen) of the reduced electron-acceptor component. Clearly, in such sysytems, the dethreading–rethreading process is powered by *both* light *and* chemical energy, with formation of waste products deriving from the reactions of the sacrificial reductant and dioxygen.

A system in which dethreading–rethreading is controlled exclusively by light energy, without generation of any waste product, is illustrated in Scheme 1. The thread-like species (*E*)-**1**,[8] which contains an azobiphenoxy electron-donor unit in the (*E*)-isomeric form, and cyclophane $\mathbf{2}^{4+}$,[9] which contains two 2,7-diazapyrenium electron-acceptor units, self-assemble very efficiently in acetonitrile solution, as demonstrated by the quenching, caused by the CT interaction, of the fluorescence of $\mathbf{2}^{4+}$ (λ_{max} = 434 nm) on addition of (*E*)-**1**. The association constant K_a, obtained by fluorescence titration, is $(1.5 \pm 0.2) \times 10^5$ L mol^{-1}.

The adduct formed by (*E*)-**1** and $\mathbf{2}^{4+}$, hereafter indicated by $[(E)\text{-}\mathbf{1}\cdot\mathbf{2}]^{4+}$, has a pseudorotaxane superstructure (Scheme 1), which allows maximisation of the donor–acceptor stabilising interactions.[8] Such a superstructure has been confirmed by electrochemical experiments. Macrocycle $\mathbf{2}^{4+}$ shows two reduction waves, at −0.32 and −0.96 V *vs*. SCE, that can be assigned to the first and second reductions of both diazapyrenium units. This result shows that the two electron-acceptor units of $\mathbf{2}^{4+}$ are equivalent. When macrocycle $\mathbf{2}^{4+}$ is engaged in the adduct, its first reduction process is displaced by *ca*. 40 mV to more negative potential values, but remains bielectronic in nature. The shift is a consequence of the formation of the adduct, in which the electron-acceptor diazapyrenium units of $\mathbf{2}^{4+}$ undergo CT interactions with the (*E*)-**1** electron donor.† The fact that the process remains bielectronic shows that the two diazapyrenium units of $[(E)\text{-}\mathbf{1}\cdot\mathbf{2}]^{4+}$ are equivalent, as expected for a pseudorotaxane-type superstructure.‡

The absorption spectrum of the $[(E)\text{-}\mathbf{1}\cdot\mathbf{2}]^{4+}$ pseudorotaxane shows both the bands of the (*E*)-**1** and $\mathbf{2}^{4+}$ components, and a broad and weak CT band in the visible region that appears as a tail extending up to 550 nm. Irradiation§ at 295 K of an acetonitrile solution containing 1×10^{-4} mol L^{-1} (*E*)-**1** and $\mathbf{2}^{4+}$



Scheme 1 Controllable dethreading–rethreading processes, based on a (*E*)–(*Z*) photoisomerisation reaction, of the pseudorotaxanes formed by self-assembly of (*E*/*Z*)-**1** with $\mathbf{2}^{4+}$. The structures shown are energy-minimised MM2 (CS Chem3D Pro) geometries of pseudorotaxanes $[(E)\text{-}\mathbf{1}\cdot\mathbf{2}]^{4+}$ and $[(Z)\text{-}\mathbf{1}\cdot\mathbf{2}]^{4+}$ (hydrogen atoms have been omitted for clarity).

DOI: 10.1039/b105160c

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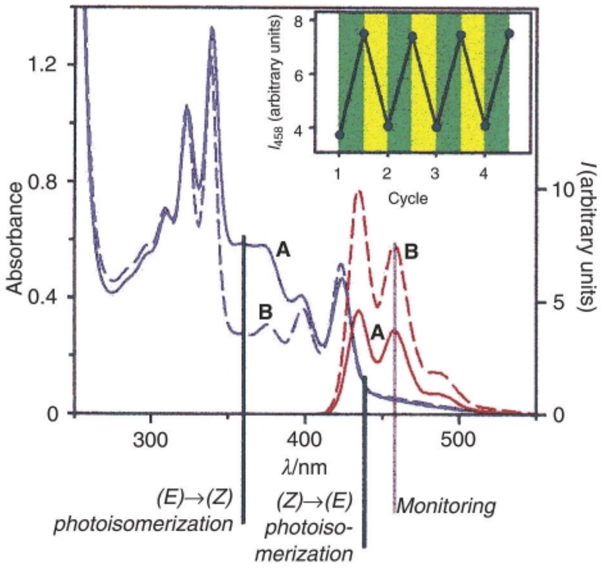

Fig. 1 Absorbance (left scale) and luminescence (right scale) spectroscopic evidence of the photoinduced dethreading–rethreading processes (acetonitrile solution, 295 K). Curves A, equimolar mixture (1×10^{-4} mol L^{-1}; pathlength 2.0 mm) of (*E*)-**1** and $\mathbf{2}^{4+}$; curves B, same mixture after irradiation (20 min) at 365 nm. Inset: changes in intensity of the fluorescence associated with the free macrocyclic ring $\mathbf{2}^{4+}$ for an equimolar mixture (1×10^{-4} mol L^{-1}) of (*E*/*Z*)-**1** and $\mathbf{2}^{4+}$ upon consecutive (*E*)→(*Z*) (20 min of irradiation at 365 nm, green areas) and (*Z*)→(*E*) (10 min of irradiation at 436 nm, yellow areas) photoisomerization cycles. The wavelength employed for dethreading (365 nm), rethreading (436 nm) and monitoring (458 nm) the system are indicated.

(*ca.* 80% complexed species) with 365 nm light—almost exclusively absorbed by the (*E*)-azobiphenoxy unit—causes strong spectral changes (Fig. 1), as expected for the well known[10] (*E*)→(*Z*) photoisomerisation of the azobenzene-type moiety. Such spectral changes are accompanied by a parallel increase in the intensity of the fluorescence band with λ_{max} = 434 nm, characteristic of free $\mathbf{2}^{4+}$ (*vide supra*). This behaviour shows that photoisomerisation is accompanied by dethreading (Scheme 1), a result which is confirmed by the finding that the association constant of $\mathbf{2}^{4+}$ with (*Z*)-**1** is much smaller [K_a = $(1.0 \pm 0.1) \times 10^4$ L mol^{-1}] than that with (*E*)-**1**.

When the (*E*)-**1**→(*Z*)-**1** photoisomerisation and the consequent pseudorotaxane dethreading have been performed, irradiation of the same solution at 436 nm causes the reverse (*Z*)-**1**→(*E*)-**1** photoisomerisation. This process is accompanied by a parallel decrease in the fluorescence intensity at λ_{max} = 434 nm, indicating that the (*E*)-**1** isomer rethreads inside the cyclophane $\mathbf{2}^{4+}$. Owing to the full reversibility of the photoisomerisation process, the light-driven dethreading–rethreading cycle can be repeated at will (Fig. 1, inset). The system described in this paper is in some aspects similar to that previously described by Murakami *et al.*,[11] with the advantage of exhibiting profound changes of a strong fluorescence signal (Fig. 1).

Molecular-level machines, based on pseudorotaxanes, rotaxanes and catenanes, have been proposed as possible components of chemical computers,[12] and are currently being exploited for the construction of practical devices.[13] They also constitute the starting basis for the design of more sophisticated molecular-level devices.[4,14] The system described in this paper is of particular interest because *the dethreading–rethreading process is powered only by light and does not produce any waste products*. Photochemical energy inputs offer a further advantage over chemical energy inputs: they can be switched on and off easily and rapidly. It should also be noted that excitation with lasers provides the opportunity of working in very small spaces and in extremely short time domains. Finally, two other important properties exhibited by the system described in this paper should be emphasized—namely, full reversibility and the presence of a strong fluorescence signal.

This work was supported by the EU through the Molecular-Level Devices and Machines (MLDM) network, the University of Bologna (Funds for selected research topics), and MURST (Supramolecular devices project).

Notes and references

† Evidence for adduct formation comes also from the redox processes of (*E*)-**1**. Both its reduction and oxidation processes are shifted to more negative and more positive potential values, respectively, indicating that (*E*)-**1** is stabilized by the insertion into the cavity of $\mathbf{2}^{4+}$.

‡ The second reduction peak of $\mathbf{2}^{4+}$ does not shift upon addition of (*E*)-**1**. This indicates that, upon monoreduction of both diazapyrenium units of the cylophane and in consequence of the decreased electron-acceptor capability of such units, the pseudorotaxane dethreads.

§ Photoisomerisation was carried out by irradiation with the 365 and 436 nm lines of a medium-pressure Hg lamp (Hanau Q400, 150 W), isolated by means of interference filters (incident light intensity of the order of 3×10^{-7} *N hν* min^{-1}). For the fluorescence spectra, excitation was performed in an isosbestic point at 411 nm, and the emission intensity was monitored with front-face geometry in the band peaking at 458 nm.

1 V. Balzani, A. Credi, F. M. Raymo and J. F. Stoddart, *Angew. Chem., Int. Ed.*, 2000, **39**, 3348.

2 *Acc. Chem. Res.*, 2001, **34**, n. 6 (Special Issue on Molecular Machines).

3 T. R. Kelly, H. De Silva and R. A. Silva, *Nature*, 1999, **401**, 150; N. Koumura, R. W. J. Zijlstra, R. A. van Delden, N. Harada and B. L. Feringa, *Nature*, 1999, **401**, 152; P. R. Ashton, R. Ballardini, V. Balzani, A. Credi, K. R. Dress, E. Ishow, C. J. Kleverlaan, O. Kocian, J. A. Preece, N. Spencer, J. F. Stoddart, M. Venturi and S. Wenger, *Chem. Eur. J.*, 2000, **6**, 3558; A. M. Brouwer, C. Frochot, F. G. Gatti, D. A. Leigh, L. Mottier, F. Paolucci, S. Roffia and G. W. H. Wurpel, *Science*, 2001, **291**, 2124.

4 R. Ballardini, V. Balzani, A. Credi, M. T. Gandolfi and M. Venturi, *Acc. Chem. Res.*, 2001, **34**, 445.

5 A. C. Benniston, A. Harriman and D. S. Yufit, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2356.

6 P. R. Ashton, V. Balzani, O. Kocian, L. Prodi, N. Spencer and J. F. Stoddart, *J. Am. Chem. Soc.*, 1998, **120**, 11190.

7 P. R. Ashton, R. Ballardini, V. Balzani, E. C. Constable, A. Credi, O. Kocian, S. J. Langford, J. A. Preece, L. Prodi, E. R. Schofield, N. Spencer, J. F. Stoddart and S. Wenger, *Chem. Eur. J.*, 1998, **4**, 2411.

8 M. Asakawa, P. R. Ashton, V. Balzani, C. L. Brown, A. Credi, O. A. Matthews, S. P. Newton, F. M. Raymo, A. N. Shipway, N. Spencer, A. Quick, J. F. Stoddart, A. J. P. White and D. J. Williams, *Chem. Eur. J.*, 1999, **5**, 860.

9 P. R. Ashton, S. E. Boyd, A. Brindle, S. J. Langford, S. Menzer, L. Pérez-García, J. A. Preece, F. M. Raymo, N. Spencer, J. F. Stoddart, A. J. P. White and D. J. Williams, *New J. Chem.*, 1999, **23**, 587.

10 H. Rau, in *Photochromism: Molecules and Systems*, ed. H. Dürr and H. Bouas-Laurent, Elsevier, Amsterdam, 1990, p. 165.

11 H. Murakami, A. Kawabuchi, K. Kotoo, M. Kunitake and N. Nakashima, *J. Am. Chem. Soc.*, 1997, **119**, 7605.

12 D. Rouvray, *Chem. Brit.*, 1998, **34**(2), 26; P. Ball, *Nature*, 2000, **406**, 118; A. P. de Silva and N. D. McClenaghan, *J. Am. Chem. Soc.*, 2000, **122**, 3965.

13 C. P. Collier, G. Mattersteig, E. W. Wong, Y. Luo, K. Beverly, J. Sampaio, F. M. Raymo, J. F. Stoddart and J. R. Heath, *Science*, 2000, **289**, 1172.

14 M. C. Jimenez, C. Dietrich-Buchecker and J.-P. Sauvage, *Angew. Chem., Int. Ed.*, 2000, **39**, 3284.