Energy Conversion

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The Direct Conversion of Light into Continuous Mechanical Energy by Photoreversible Self-Assembly: A Prototype of a Light-Powered Engine**

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There is general agreement on the need for alternative sources of energy owing to the continuous growth in the consumption and the depletion of fossil fuel reserves.[1] In this context the production of clean energy from renewable sources is particularly attractive. Several forms of renewable energy are available, and most of them originate more or less directly from the sun.[2,3] Solar energy conversion systems fall into three categories[4] according to their primary product: solar electricity, solar fuels, and solar thermal systems. The challenge is to improve these technologies or to try and devise new ones with the goal of converting as much of this energy as possible. Herein, we describe a new strategy for the continuous production of clean energy in the form of mechanical work from light. The method relies on the photoreversible isomerization of an azobenzene (diphenyldiazene) derivative.

Several classes of compounds that can undergo photoreversible transformations are known in the literature,[5] and, among these, azobenzene-based systems are possibly the most widely studied.[6,7] Azobenzene can be photoisomerized reversibly from the more stable *E* to the *Z* isomer. When this happens, the molecule is modified in several ways (e.g. size, shape, electronic properties, polarity), and this has been exploited to control material properties.[7] One intriguing aspect of this photoreversible isomerization is that the *Z* isomer has an energy content higher (about $50\,\mathrm{kJ\,mol^{-1}}$) than the *E* form, meaning that, during photoisomerization, some energy is "harvested" from light and "stored" in the *Z* isomer in the form of a potential. Usually this energy is dissipated thermally during the back-isomerization to the *E* form, and the thermal effects of this process are so weak that they are useless for practical purposes. With the aim of finding a way to collect this energy and transform it into a useful form, one can reason that the energy content of a chemical system depends on several factors besides temperature, and in particular, it depends on the number of particles which constitute it. Thus, if the photoisomerization can be coupled to a change in system concentration, this could pave the way to the conversion of the stored energy into an exploitable form (e.g. mechanical work). If a continuous conversion of energy is sought, this concentration change must be reversible, like photoisomerization itself. In addition, the variation of the number of particles does not necessarily imply that matter enters or leaves the system: the system just has to be fooled to believe it. A supramolecular approach is best suited to implement these qualities into an azobenzene-based molecular structure.

The first step was therefore to design an azobenzene derivative with a built-in capability of undergoing an aggregation change as a consequence of photoisomerization. The idea which has been developed is that of an azobenzene derivative able to form polymeric supramolecular aggregates[8] when in the *E* form but unable to self-assemble when in the *Z* form.

It is known that in (*Z*)-azobenzene the two phenyl rings are roughly facing each other: the N=N-C-C dihedral angle is 53° according to X-ray diffraction experiments.[9] Inspection of models indicates that, upon the introduction of two 2′-carboxyphenyl residues (thin line in Figure 1) in the 4-positions of diphenyldiazene (thick line in Figure 1), the distances and geometries might be conducive for the formation of two intramolecular hydrogen bonds between the two carboxylic groups, as long as the *Z* isomer adopts the conformation in which the two groups point towards each other (Figure 1, structure **B**). In order to populate preferen-

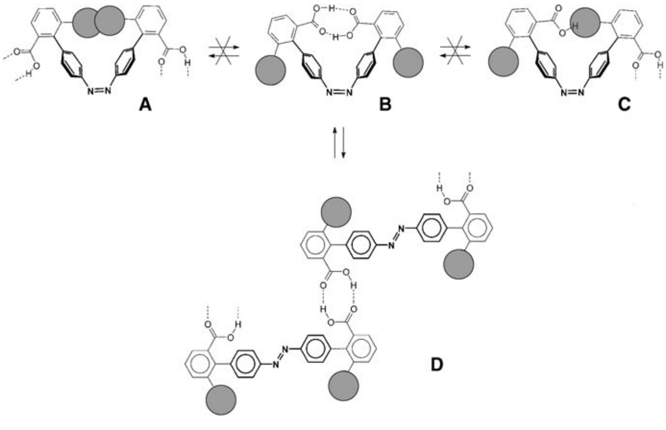

Figure 1.

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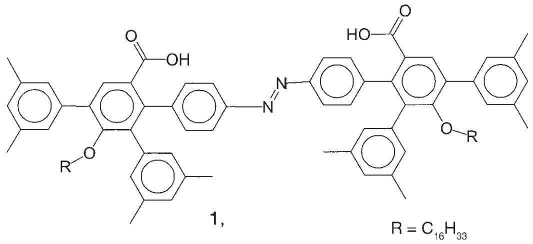
tially this “closed” conformation during photoisomerization to the *Z* form, appropriate bulky groups (gray spheres in Figure 1) must be located at the 6′-positions. In this way, interactions leading to intermolecular self-assembly (“open” conformations, Figure 1, structures **A** and **C**) should be inhibited. On the other hand, this kind of structure could form supramolecular aggregates through intermolecular H-bonding when in the *E* geometry (Figure 1, structure **D**).

Some compounds have been synthesized according to this model. In particular, bis{4-[6′-carboxy-3′-hexadecyloxy-2′,4′-bis(3′′,5′′-dimethylphenyl)]phenyl}diazene **1** has been prepared in the *E* form from commercially available 2-bromo-4-nitrotoluene by standard procedures following a convergent synthetic scheme (Scheme S1 in the Supporting Information).



1, R = $C_{16}H_{33}$

As expected, compound **1** shows a strong tendency, for example, in CH_2Cl_2, to form large supramolecular aggregates when in the *E* form, as evinced from line broadening in its ^1H NMR spectrum, while the *Z* isomer seems much less prone to self-assembly (Figure S1 in the Supporting Information). But a very peculiar behavior was observed when acetone was used as a solvent. When acetone (1 mL) is added to (*E*)-**1** (7.4 mg), most of the solid remains undissolved (Figure 2a). Prolonged sonication generates a turbid orange suspension (Figure 2b). Irradiation of this heterogeneous mixture at 365 nm[10] leads to solubilization of the suspended solid (Figure 2c) until a clear solution is obtained (Figure 2d). Irradiation at 436 nm reverts the *Z* back to the *E* isomer, and a suspension forms again (Figure 2e). This photoinduced solubilization–crystallization cycle has been repeated ten times on the same sample without any evidence of degradation of the system on the NMR spectrum.

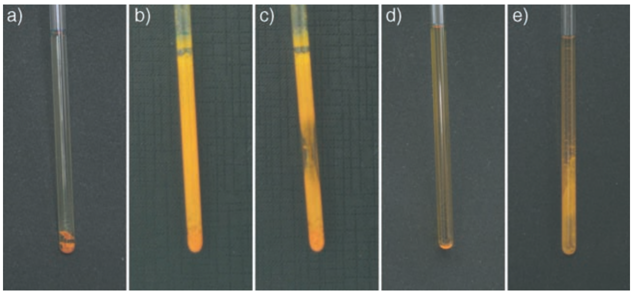
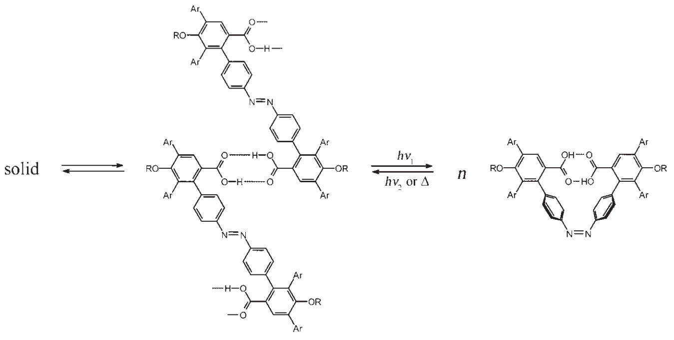


Figure 2. Pictures of the **1**/acetone mixture at various stages of photoisomerization.

A closer inspection by ^1H NMR, IR, ESI-MS, DOSY, and NOESY experiments revealed that the phenomenon is not simply a result of the different polarity of the two isomers,[11] the *Z* being polar while the *E* is apolar,[12] but is the combined outcome of polarity effects and differences in the self-assembly behavior of the two isomers with respect to the hydrogen-bonding properties of the solvent.

While these experiments are described and discussed in the Supporting Information, the resulting conclusions concerning the behavior of azodicarboxylic acid **1** in acetone can be summarized as follows. Conformational constrictions make the *Z* isomer exist as an intramolecularly H-bonded, soluble monomer. On the other hand, owing both to the solvent polarity and its ability to compete for H-bonding, the *E* isomer exists in solution as a dynamic distribution of intermolecularly H-bonded, low order supramolecular oligomers. These oligomers, on growing, become insoluble and precipitate to form an extensively H-bonded solid (Scheme 1). Hence, there is a twofold control operated by light on the number of particles in solution, as the *E* isomer seems aggregated in solution while the *Z* isomer is not and, most of all, because light can control the solubility of the molecule. Although crystallization itself is a self-assembly process, this particular solubility behavior (which has been sought for but of course was not planned) is a direct consequence of the self-assembly propensity of the *E* isomer and suits perfectly well the ultimate goal of the present work.[13]



Scheme 1.

The energy harvested from light and stored in the molecules upon photoisomerization can now be converted into a macroscopic form by taking advantage of colligative properties and, in particular, of osmosis. Natural osmosis is the net, spontaneous flow of solvent from a more diluted to a more concentrated solution separated by a semipermeable membrane. An osmotic cell has been built, in which photoisomerization could be carried out in both compartments (Figure 3).

Both compartments were loaded with a suspension of unirradiated (*E*)-**1** in acetone so that levels were the same. One compartment was alternately irradiated with UV and Vis light, while the opposite was done on the other side (see Figure 4 and Movie S1 in the Supporting Information). In the compartment where the *E*-to-*Z* photoisomerization occurs, dissolution and disaggregation produce an increase in con-

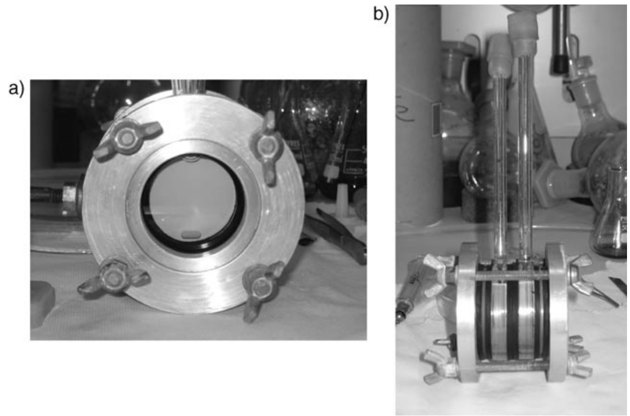


Figure 3. Side (a) and front (b) views of the osmotic cell.

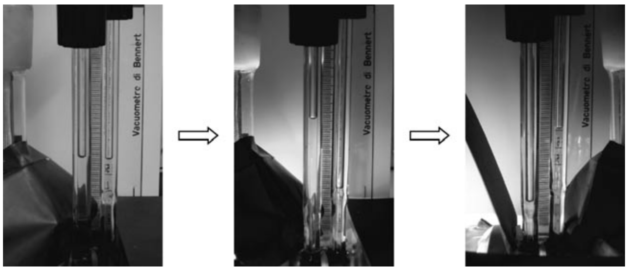


Figure 4. Pictures of the osmotic cell taken during isomerizations. Left: Starting condition, unirradiated **1** suspended in acetone in both sides. Middle: *E*-to-*Z* isomerization by UV light in the left compartment and *Z*-to-*E* isomerization by Vis light in the right compartment. Right: *Z*-to-*E* isomerization by Vis light in the left compartment and *E*-to-*Z* isomerization by UV light in the right compartment.

centration which makes the solution hypertonic with respect to the solution in the other compartment. In contrast, in the compartment where the *Z*-to-*E* retroisomerization takes place, aggregation and crystallization lower the net concentration of the solution, making it hypotonic with respect to the other. Thus, a flow of solvent takes place from the latter to the first compartment. Inverting the wavelengths shone onto the two compartments reverts the flow, and the overall result is an alternate flow of solvent from one side to the other, with a continuous variation of solvent levels. A movie showing the process is available online in the Supporting Information. Thus, the energy harvested from light is transformed continuously into mechanical energy in the form of work necessary to raise and to lower the solvent level.

The solvent-level movement in the two sides of the cell reminds one of an engine: a bicylindrical, two-stroke (*E* and *Z*) and, in the present case, zero-emission, light-powered engine, which could be a prototype for solar mechanical devices. The device, in the present configuration, displaces at each cycle a weight of solvent about three times the weight of the azo derivative loaded in the cell. Although this corresponds to a pressure lower than that which one could calculate from the van't Hoff equation,[14] it should be pointed out that, regardless of performance, this system has been developed to demonstrate the feasibility of the idea of converting light into mechanical energy by means of a photoreversible self-assembly/disassembly process.

Controlled disassembly can be in some instances a valuable process itself, and the use of colligative properties can be a way to link dynamic phenomena that occur at a molecular or nanoscopic level with the macroscopic world. Many improvements can be devised for both the solvent–solute system and cell design and materials, and we are currently moving along these lines. On considering that, according to the van't Hoff equation, a 1 mol$\,L^{-1}$ solution of a non-electrolyte develops a pressure of about 24 atm (i.e. 18 mHg) at room temperature, we believe there is room for future development of such systems.

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[1] International Energy Agency, *World Energy Outlook 2006 Edition* (http://www.worldenergyoutlook.org/2006.asp).
[2] D. M. Kammen, *Sci. Am.* **2006**, *9*, 84.
[3] N. Armaroli, V. Balzani, *Angew. Chem.* **2007**, *119*, 52–67; *Angew. Chem. Int. Ed.* **2007**, *46*, 52–66.
[4] U.S. Department of Energy, Office of Science *Basic Research Needs for Solar Energy Utilization* , **2005**, (http://www.sc.doe.gov/bes/reports/files/SEU_rpt.pdf).
[5] a) B. L. Feringa, *Molecular Switches*, Wiley-VCH, Weinheim, **2001**; b) N. Katsonis, M. Lubomska, M. M. Pollard, B. L. Feringa, P. Rudolf, *Prog. Surf. Sci.* **2007**, *82*, 407; c) H. Rau in *Photochromism: Molecules and Systems* (Eds.: H. Dürr, H. Bouas-Laurent), Elsevier, Amsterdam, **2003**; d) M. Irie et al., *Chem. Rev.* **2000**, *100*; e) V. Balzani, M. Clemente-Leon, A. Credi, B. Ferrer, M. Venturi, H. Flood Amar, J. F. Stoddart, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 1178; f) V. Balzani, M. Venturi, A. Credi, *Molecular Devices and Machines: A Journey into the Nanoworld*, Wiley-VCH, Weinheim, **2004**.
[6] a) R. H. El Halabieh, O. Mermut, C. J. Barret, *Pure Appl. Chem.* **2004**, *76*, 1445; b) Y. Yu, M. Nakano, T. Ikeda, *Nature* **2003**, *425*, 145; c) A. Natansohn, P. Rochon, *Chem. Rev.* **2002**, *102*, 4139.
[7] a) T. Muraoka, K. Kinbara, T. Aida, *Nature* **2006**, *440*, 512; b) A. Vesperinas, J. Eastoe, P. Wyatt, I. Grillo, R. K. Heenan, J. M. Richards, G. A. Bell, *J. Am. Chem. Soc.* **2006**, *128*, 1468; c) D. Takamatsu, Y. Yamakoshi, K. Fukui, *J. Phys. Chem. B* **2006**, *110*, 1968; d) M. Camacho-Lopez, H. Finkelmann, P. Palffy-Muhoray, M. Shelley, *Nat. Mater.* **2004**, *3*, 307; e) Y. Norikane, N. Tamaoki, *Org. Lett.* **2004**, *6*, 2595; f) S. Pieraccini, G. Gottarelli, R. Labruto, S. Masiero, O. Pandoli, G. P. Spada, *Chem. Eur. J.* **2004**, *10*, 5632; g) Y. Yu, M. Nakano, T. Ikeda, *Nature* **2003**, *425*, 145; h) T. Hugel, N. B. Holland, A. Cattani, L. Moroder, M. Seitz, H. E. Gaub, *Science* **2002**, *296*, 1103; i) K. Ichimura, S. K. Oh, M. Nakagawa, *Science* **2000**, *288*, 1624.
[8] a) J.-M. Lehn in *Supramolecular Polymers*, 2nd ed. (Ed.: A. Ciferri), CRC, Boca Raton, **2005**; b) L. Brunsveld, B. J. B. Folmer, E. W. Meijer, R. P. Sijbesma, *Chem. Rev.* **2001**, *101*, 4071; c) A. Harada, *Acc. Chem. Res.* **2001**, *34*, 456.
[9] a) A. Mostad, . C. Romming, *Acta Chem. Scand.* **1971**, *25*, 3561; b) N. Kurita, S. Tanaka, S. Itoh, *J. Phys. Chem. A* **2000**, *104*, 8114.
[10] Photoisomerizations in NMR tubes were carried out at 20 °C with a medium-pressure Hg lamp. Bandpass (10 nm) filters (Andover Co., USA) with a 2.5-cm diameter were used to select wavelengths. As can be seen from Figure 2 c and e, dissolution and precipitation occur where the light beam crosses the sample.

[11] To the best of our knowledge, very few examples of such macroscopic behavior have been described in the literature for azobenzene-containing systems. No example refers to a single, low-molecular-weight compound: a) H. Sakai, A. Matsumura, S. Yokoyama, T. Saji, M. Abe, *J. Phys. Chem. B* **1999**, *103*, 10737; b) K. Arai and Y. Kawabata, *Macromol. Rapid Commun.* **1995**, *16*, 875; c) H. Yamamoto, A. Nishida, T. Takimoto, A. Nagai, *J. Polym. Sci. Part A* **1990**, *28*, 67.

[12] It should be pointed out that (*E*)-**1** is insoluble in DMSO as well as in cyclohexane.

[13] For other photoswitchable self-assembling systems developed by design see, for example, a) J. J. D. de Jong, P. R. Hania, A. Pugzlys, L. N. Lucas, M. de Loos, R. M. Kellogg, B. L. Feringa, K. Duppen, J. H. van Esch, *Angew. Chem.* **2005**, *117*, 2425; *Angew. Chem. Int. Ed.* **2005**, *44*, 2373; b) K. Murata, M. Aoki, T. Nishi, A. Ikeda, S. Shinkai, *J. Chem. Soc. Chem. Commun.* **1991**, 1715.

[14] According to van't Hoff equation, the osmotic pressure π is given by: $\pi = cRTi$, where c is the molar concentration of the solution, R is the gas constant, T is the absolute temperature of the system, and i is the van't Hoff coefficient for electrolytes, which in the present case is inversely related to the extent of association of the solute.