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A Light-Fueled "Piston Cylinder" Molecular-Level Machine

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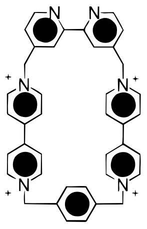
[2]Pseudotaxanes[1] are supermolecules in which a "cylindrical" host is penetrated by a pistonlike guest. They may be viewed as simple molecular-level machines[2−8] since they can undergo assembly/disassembly processes reminiscent of the movement of a piston in a cylinder. Molecular-level machines, like macroscopic ones, require energy to work and signals to communicate with the operator. Light can provide an answer to this dual requirement since mechanical movement can be induced by a photochemical reaction and its occurrence can be followed by absorption or emission spectroscopy.[5]

Our first attempt at designing[9] a photochemically driven dethreading of a pseudorotaxane was based (Figure 1a) on the use of an external electron-transfer photosensitizer. Subsequently, we synthesized[10] the cyclophane L_1^{4+} which contains a 2,2′-bipyridine coordinating ligand along with two 4,4′-bipyridinium electron-acceptor units. Coordination of L_1^{4+} to $[Ru(bpy)_2]^{2+}$ and $[Re(CO)_3Cl]$ moieties, respectively, has allowed the construction of cyclophanes $[Ru(bpy)_2L_1]^{6+}$ and $[Re(CO)_3L_1Cl]^{4+}$ incorporating metal-based photosensitizers (Figure 1b). Self-assembly of these cylindrical-like components with 1,5-bis(2-(2-hydroxyethoxy)-ethoxy)naphthalene (1/5BHEEN) as a pistonlike component provides us with the blueprint for a "second-generation" light-driven molecular-level machine of a pseudorotaxane type.[11]



L_1^{4+}

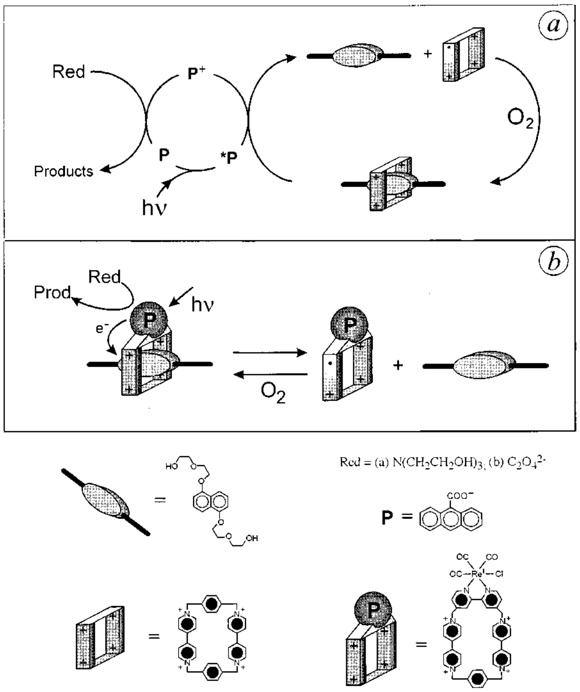


Figure 1. Schematic representation of the light-induced disassembly of (a) a [2]pseudorotaxane by means of an external photosensitizer P and (b) a [2]pseudorotaxane incorporating the photosensitizer in the cyclophane component. In both cases, if oxygen is allowed to enter the irradiated solution, the pistonlike component re-enters the cyclophane.

The 1/5BHEEN guest,[12] the ligand L_1^{4+} (as the PF_6^- salt),[10] and the complexes $[Re(CO)_3L_1Cl]^{4+}$ and $[Ru(bpy)_2L_1]^{6+}$ (as their Cl^- salts)[10] were all prepared according to literature procedures. Experiments were performed in aqueous or acetonitrile solutions using procedures and equipment already described.[9] The 1/5BHEEN guest shows an intense fluorescent band (in acetonitrile: $\lambda_{max} = 345$ nm, $\tau = 7.5$ ns, $\Phi = 0.35$),[9] whereas L_1^{4+}, $[Re(CO)_3L_1Cl]^{4+}$, and $[Ru(bpy)_2L_1]^{6+}$ do not show any emission in solution at room temperature.[10] On mixing aqueous or acetonitrile solutions of 1/5BHEEN and L_1^{4+} (6.5×10^{-5} M in both components), the emission of 1/5BHEEN is quenched and a new, broad absorption band, typical of charge-transfer (CT) transitions, appears in the visible region ($\lambda_{max} = 497$ nm). These results show that there are noncovalent bonding interactions between the dioxynaphthalene electron-donor unit of the guest and the 4,4′-bipyridinium electron-acceptor units of the host—as observed previously[9] in the 1:1 complex formed between 1/5BHEEN and cyclobis(paraquat-*p*-phenylene). The same behavior was observed upon mixing solutions of 1/5BHEEN and $[Re(CO)_3L_1Cl]^{4+}$ or $[Ru(bpy)_2L_1]$.$^{6+}$ In the case of the Ru complex, however, an intense Ru → bpy absorption band, with a maximum around 450 nm, obscures the CT band arising from

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(1) Amabilino, D. B.; Stoddart J. F. *Chem. Rev.* **1995**, *95*, 2725−2828.

(2) de Silva, A. P.; McCoy, C. P. *Chem. Ind.* **1994**, 992−996.

(3) Gómez-López, M.; Preece, J. A.; Stoddart, J. F. *Nanotechnology* **1996**, *7*, 183−192.

(4) (a) Benniston, A. C. *Chem. Soc. Rev.* **1996**, *25*, 427−435. (b) Ward, M. D. *Chem. Ind.* **1997**, 640−645.

(5) Balzani, V.; Credi, A.; Scandola, F. *Chim. Ind. (Rome)* **1997**, *79*, 751−759.

(6) de Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515−1566.

(7) Balzani, V.; Gómez-López, M.; Stoddart, J. F. *Acc. Chem. Res.* **1998**, *31*, 405−414.

(8) Chambron, J.-C.; Sauvage, J.-P.; *Chem. Eur. J.* **1998**, *4*, 1362−1366.

(9) (a) Ballardini, R.; Balzani, V.; Gandolfi, M. T.; Prodi, L.; Venturi, M.; Philp, D.; Ricketts, H. G.; Stoddart, J. F. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1301−1303. (b) Ashton, P. R.; Ballardini, R.; Balzani, V.; Boyd, S. E.; Credi, A.; Gandolfi, M. T.; Gómez-López, M.; Iqbal, S.; Philp, D.; Preece, J. A.; Prodi, L.; Ricketts, H. G.; Stoddart, J. F.; Tolley, M. S.; Venturi, M.; White, A. J. P.; Williams, D. J. *Chem. Eur. J.* **1997**, *3*, 152−170.

(10) Ashton, P. R.; Balzani, V.; Credi, A.; Kocian, O.; Pasini, D.; Prodi, L.; Spencer, N.; Stoddart, J. F.; Tolley, M. S.; Venturi, M.; White, A. J. P.; Williams, D. J. *Chem. Eur. J.* **1998**, *4*, 590−607.

(11) An alternative approach toward a "second-generation" light-driven pseudorotaxane-type machine involves the incorporation of the photosensitizer in the pistonlike component: Ashton, P. R.; Ballardini, R.; Balzani, V.; Constable, E. C.; Credi, A.; Kocian, O.; Langford, S. J.; Preece, J. A.; Prodi, L.; Shofield, E. R.; Spencer, N.; Stoddart, J. F.; Wenger, S.; *Chem. Eur. J.*, in press.

(12) For the synthesis of 1/5BHEEN, see: Brown, C. L.; Philp, D.; Spencer, N.; Stoddart, J. F. *Isr. J. Chem.* **1992**, *32*, 61−67.

10.1021/ja981889a CCC: $15.00

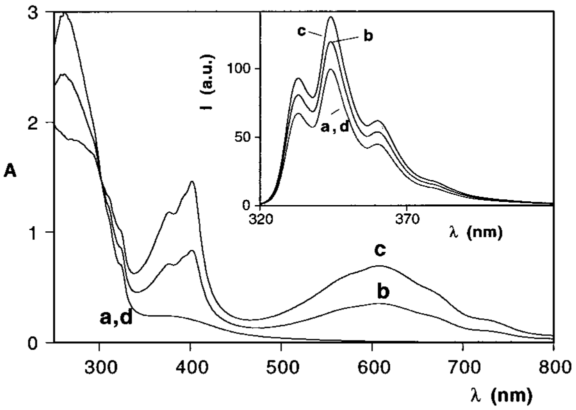

Figure 2. Changes observed in the absorption and (inset) corrected fluorescence ($\lambda_{exc} = 295$ nm) spectra upon irradiation of a deaerated aqueous solution containing 6.5×10^{-5} M 1/5BHEEN and $[Re(CO)_3L_1Cl]^{4+}$ and 1.0×10^{-2} M sodium oxalate. (a) Solution before irradiation; (b) and (c) the same solution irradiated for 7 and 15 min, respectively. (d) solution c after oxidation with air.

the donor−acceptor interaction. The Re complex, which does not show such an interfering band, was therefore chosen for further photochemical experiments.

Both the increase in intensity of the CT absorption band and the decrease in the fluorescence intensity of 1/5BHEEN were used for measuring the association constants of 1/5BHEEN with L_1^{4+} and $[Re(CO)_3L_1Cl]^{4+}$. The values obtained were 5.1×10^3 and 4.4×10^3 M^{-1} for 1/5BHEEN−L_1^{4+} and 1/5BHEEN−$[Re(CO)_3L_1Cl]^{4+}$ in acetonitrile solutions, respectively, and 7.1×10^4 M^{-1} for 1/5BHEEN−$[Re(CO)_3L_1Cl]^{4+}$ in water. Clear evidence for a pseudorotaxane superstructure for the 1/5BHEEN−$[Re(CO)_3L_1Cl]^{4+}$ complex was obtained from mass spectrometry and ^{1}H NMR spectroscopy; see the Supporting Information.

The photochemical and electrochemical properties of the $[Re(CO)_3L_1Cl]^{4+}$ complex have been investigated in detail.[10] Although the bpy-type moiety of L_1^{4+} behaves substantially as a bpy ligand, the photochemical behavior of $[Re(CO)_3L_1Cl]^{4+}$ is quite different from that of the parent $Re(CO)_3(bpy)Cl$ complex because of the presence of the appended bipyridinium units. For both complexes, light excitation leads to the population of the lowest triplet Re → bpy excited state, whose emission in rigid butyronitrile matrix at 77 K takes place at 561 nm for $[Re(CO)_3L_1Cl]^{4+}$ and at 530 nm for $Re(CO)_3(bpy)Cl$. In fluid solution at room temperature, however, the emission of the Re-based chromophoric moiety ($\lambda_{max} = 622$ nm for $Re(CO)_3(bpy)Cl$) is quenched in $[Re(CO)_3L_1Cl]^{4+}$ by electron transfer to one of the appended bipyridinium units.

The photochemical experiments (3-mL reaction cell) were performed in deaerated aqueous solutions containing 6.5×10^{-5} M 1/5BHEEN and $[Re(CO)_3L_1Cl]^{4+}$ with 1.0×10^{-2} M sodium oxalate as a sacrificial electron donor. Under such conditions, 63% of the 1/5BHEEN and $[Re(CO)_3L_1Cl]^{4+}$ species are associated in a pseudorotaxane superstructure. Figure 2 shows the changes observed in the absorption and fluorescence spectra upon irradiation at 365 nm, which corresponds to a Re → bpy absorption band.[13] On the basis of the demonstrated properties of the 1/5BHEEN and $[Re(CO)_3L_1Cl]^{4+}$ species, the results obtained can be interpreted straightforwardly as follows. Light excitation of the $[Re(CO)_3L_1Cl]^{4+}$ component of the pseudorotaxane causes the formation of the lowest triplet Re → bpy excited state, which transfers an electron to one of the 4,4′-bipyridinium units contained in the L_1^{4+} cyclophane ligand, thereby decreasing the noncovalent-bonding interactions responsible for the assembly of the two components. As a consequence, one might expect disassembly to occur, but this process involves slow nuclear motions and therefore it cannot compete with the very fast (picosecond time scale[14]) back electron-transfer reaction. However, when a sufficiently large amount of a sacrificial reductant is present—as in the experimental conditions used here—the oxidized Re-based units produced by the excited-state electron-transfer reaction can be, in part, scavenged. In such a case, the back electron-transfer reaction is prevented and a 4,4′-bipyridinium unit of the pseudorotaxane remains reduced, as indicated by the appearance (Figure 2) of the characteristic absorption bands of the reduced bipyridinium units.[15]

Under such conditions, the interaction between the pistonlike guest and the cyclophane host is *permanently* weakened: disassembly takes place as demonstrated by the increase in the intensity of the dioxynaphthalene fluorescence (Figure 2, inset), which can only take place from “free” 1/5BHEEN. After 15 min of irradiation with 365-nm light (absorbed light intensity, 7×10^{-7} $Nh\nu$/min), 30% of the pseudorotaxane had disassembled (Figure 2c). Since the efficiency of the primary photoinduced electron-transfer process is close to unity,[10] the rather low quantum yield ($\approx 10^{-2}$) of the overall process has to be attributed to the competition between the scavenging of the oxidized Re-based moiety and the fast back electron-transfer reaction. When oxygen was allowed to enter the irradiated solution, the reduced host was promptly reoxidized and the guest re-entered it. The light-induced disassembly/dioxygen-induced assembly processes have been repeated five times without any apparent change in the spectroscopic properties of the system.

In conclusion, we have incorporated a photosensitizer (i.e., a “light-fueled” motor) into a pseudorotaxane (cf. a “piston cylinder”) superstructure, and we have shown that it behaves as a light-driven supramolecular machine. Other kinds of rudimentary molecular-level machines are under investigation in our laboratories.

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Supporting Information Available: The mass spectrometry and ^{1}H NMR spectroscopy carried out on the 1/5BHEEN-$[Re(CO)_3L_1Cl]^{4+}$ pseudorotaxane (3 pages, print/PDF). See any current masthead page for ordering information and Web access instructions. See any current masthead page for ordering information and Web access instructions.

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(13) When irradiation was performed in the visible region (CT band arising from the donor−acceptor interaction), no effect was observed.

(14) Benniston, A. C.; Harriman, A.; Lynch, V. M. *J. Am. Chem. Soc.* **1995**, *117*, 5275−5291. Benniston, A. C.; Mackie, P. R.; Harriman, A. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 354−356.

(15) Watanabe, T.; Honda, K. *J. Phys. Chem.* **1982**, *86*, 2617.