Functional Rotaxanes: From Controlled Molecular Motions to Electron Transfer Between Chemically Nonconnected Chromophores

Jean-Claude Chambron and Jean-Pierre Sauvage*

Abstract: Rotaxanes are molecules consisting of a cyclic component threaded onto a dumbbell-shaped linear component. Although first synthesized in the late sixties, they were considered as curiosities until they became relatively easily available through template methods (taking advantage of hydrophobic interactions, or using a transition metal or donor–acceptor interactions between aromatic stacks). This allowed for the development of functional rotaxanes, that is, rotaxanes responding to external stimuli such as injection or removal of electrons, light irradiation, and so forth. Examples are rotaxanes displaying electrochemically triggered intramolecular motions like translation of the ring along the dumbbell axle, or photochemically induced electron transfer from porphyrinic stoppers (electron donors in the excited state) to a gold(III) porphyrin electron acceptor appended to the ring component.

Keywords: electron transfer • mechanical bonds • molecular devices • porphyrinoids • rotaxanes

Introduction

Although catenanes, rotaxanes and, to a lesser extent, molecular knots have recently been popularized through the many publications devoted to their synthesis and to the study of their chemical or physical properties,[1] it might be useful to briefly redefine these species. Their prototypes are represented in Figure 1, and the drawings should be sufficient to convey their structural specificities. Notice simply that, whereas catenanes and knots are composed of rings only, rotaxanes are made up of at least a ring and a dumbbell, the latter component bearing stoppers large enough to prevent unthreading of the ring.

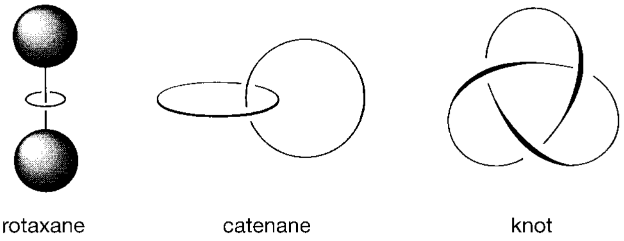
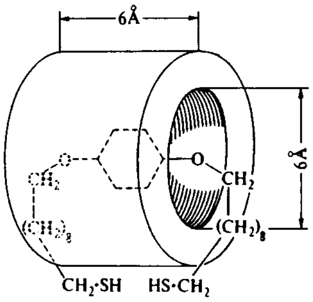


Figure 1. Cartoons of the simplest rotaxane, catenane, and knot.

From a purely topological viewpoint, rotaxanes have never been considered as noble as interlocking ring systems and knots, although they have been associated with these species in the chemist's mind since the very first published discussions and experimental works on catenanes.[1a, 2] The reason for this is the following: whereas in both systems the components are held together by a mechanical bond, in the case of catenanes, the mechanical bond is also a topological bond, since the interlocked rings cannot be separated without cleavage of one ring. In the case of rotaxanes, only deformations of one of the components are required to dissociate the system.

Rotaxanes can be described as threaded species stabilized by steric interactions. The first threaded species in the chemical literature was obtained by Lüttringhaus, Cramer, Prinzbach, and Henglein as early as 1958,[3] and was a host–guest complex (**1**) between a cyclodextrin and a benzene nucleus bearing long-chain dithiols, the latter protruding from the rims of the cyclodextrin (Figure 2). In fact, true rotaxanes based on cyclodextrins as ring components were to be synthesized only in 1981, by Ogino, as discussed below.[4]



1

Figure 2. Reproduction from ref. [3] of the first threaded molecular complex: α-cyclodextrin is threaded onto a benzene nucleus bearing long-chain dithiols.

The introduction of new synthetic methodologies for making rotaxanes, based on templates, has certainly changed our view

---

[*] Dr. J.-P. Sauvage, Dr. J.-C. Chambron
Laboratoire de Chimie Organo-Minérale
C.N.R.S. U.M.R. 7513, Université Louis Pasteur, Institut Le Bel
4, rue Blaise Pascal, F-67070 Strasbourg (France)
Fax: (+33)3-8860-7312
E-mail: sauvage@chimie.u-strasbg.fr

0947-6539/98/0408-1362 $ 17.50+.50/0

of them;[1c–f] they no longer appear as the exotic species which they used to be before those efficient synthetic strategies were proposed. Despite the earlier prevailing view, rotaxanes have been known for several decades thanks to the pioneering work of Schill et al.[5] (directed strategy) and Harrison (threading[6a] or slippage[6b–c]). Examples of these historical rotaxanes (**2** and **3**) are shown in Figure 3.

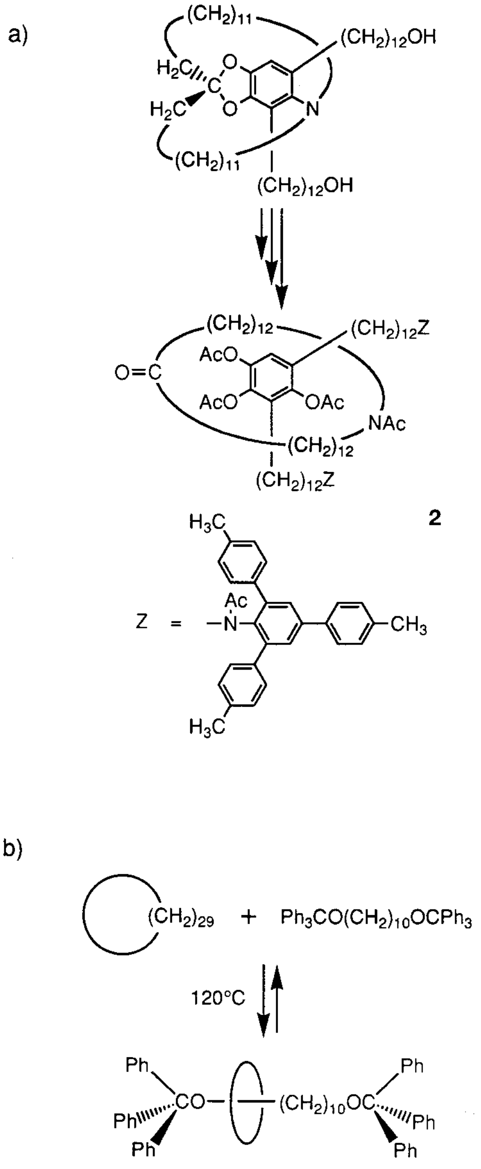
When chemists suddenly achieved greater success in making threaded or interlocked molecular systems, they also rapidly became more ambitious in terms of functionality and complexity of the chemical groups to be introduced. This is especially true for rotaxanes, and we shall discuss the possibilities thus opened up below.

Discussion

Ogino[4] and others[7] used transition metal complexes as stoppers, and this approach is potentially very rich as far as chemical and physical properties are concerned. Figure 4 shows the first rotaxane of this kind (**4**).[4] It is also the first cyclodextrin-based rotaxane. The cyclodextrin ring is threaded onto an alkyl chain ended by amino groups, the latter being able to coordinate to cobalt(III) centres chelated with ethylenediamine ancillary ligands.

The use of electro- and/or photoactive components incorporated in the central part of the linear fragment of the rotaxane or used as stoppers is of particular interest. The compounds will now respond to certain external stimuli (chemical, electrical or photonic signals) in a way dictated by their special structure. The threaded nature of the molecule will govern various processes following the triggering signal, such as molecular motions, electron or energy transfer, etc. The phenomenon of photochemically induced disassembly of a threaded complex without blocking groups, described by Balzani, Stoddart and coworkers, is of particular relevance to these issues.[8]

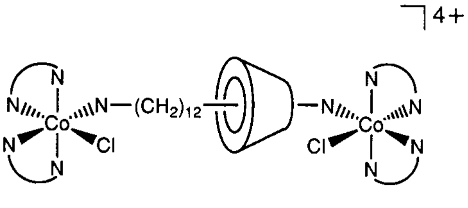
Abstract in French: *Les rotaxanes sont des molécules constituées d'un anneau enfilé sur un constituant linéaire en forme d'haltère. Bien que synthétisés pour la première fois à la fin des années soixante, ils furent considérés comme des curiosités de laboratoire jusqu'à ce que les méthodes de synthèse par effet template (mettant en jeu des interactions de type hydrophobe, ou utilisant un métal de transition ou des interactions donneur–accepteur entre sous-unités aromatiques) les rendirent assez facilement accessibles. Ceci permit la mise au point de rotaxanes fonctionnels, c'est-à-dire des rotaxanes répondant à des stimuli externes, comme l'apport ou le retrait d'électrons, l'excitation lumineuse, etc. Par exemple, des rotaxanes qui sont le siège de mouvements internes déclenchés de façon électrochimique, comme le mouvement de translation de l'anneau le long de l'axe de l'haltère, ou des rotaxanes dans lesquels un transfert d'électron photoinduit a lieu des groupements bloquants de type porphyrine de zinc (donneurs d'électron à l'état excité) vers une porphyrine de Au^{III} greffée au macrocycle (accepteur d'électron).*



2

3

Figure 3. a) The first rotaxane (**2**) prepared by directed synthesis. Also shown is the key precursor, in which a ketal group maintains the plane of the ring orthogonal to the mean plane containing the thread precursor.[5a] b) The first rotaxane (**3**) produced by statistical slippage: it is obtained by heating a mixture of dumbbell and cyclic components. In order to force the threading process, the solvent used was the macrocyclic component itself.[6b]



4

Figure 4. The first rotaxane (**4**) bearing transition metal complex fragments as stoppers. Compound **4** is also the first cyclodextrin-based rotaxane: the α-cyclodextrin ring is threaded onto an alkyl chain ended by amino groups, which bind cobalt(III) centres coordinated to ethylenediamine chelates.[4a]

Before focussing on porphyrin-containing rotaxanes, we shall discuss a few other examples of rotaxanes incorporating redox active groups and thus displaying a specific function associated to an electrochemical response. Two such systems are indicated in Figure 5. The first (Figure 5a) is the molecular shuttle **5** described by Kaifer, Stoddart and their coworkers.[9] It is an interesting example of a molecule whose shape and internal motions can be externally controlled by electrochemical means. The threaded ring is a tetracationic electron-deficient cyclophane. The dumbbell component has two stations able to interact with the ring, but differing in their electron-donating properties: a benzidine group, which is the stronger electron donor, and a biphenol-based moiety. In the initial state, about 84 % of the macrocycles rest at benzidine stations. Upon electrochemical oxidation of the latter, the macrocycle is shifted towards the biphenol station. The process can be reversibly activated by reducing the benzidine station back to its initial state.

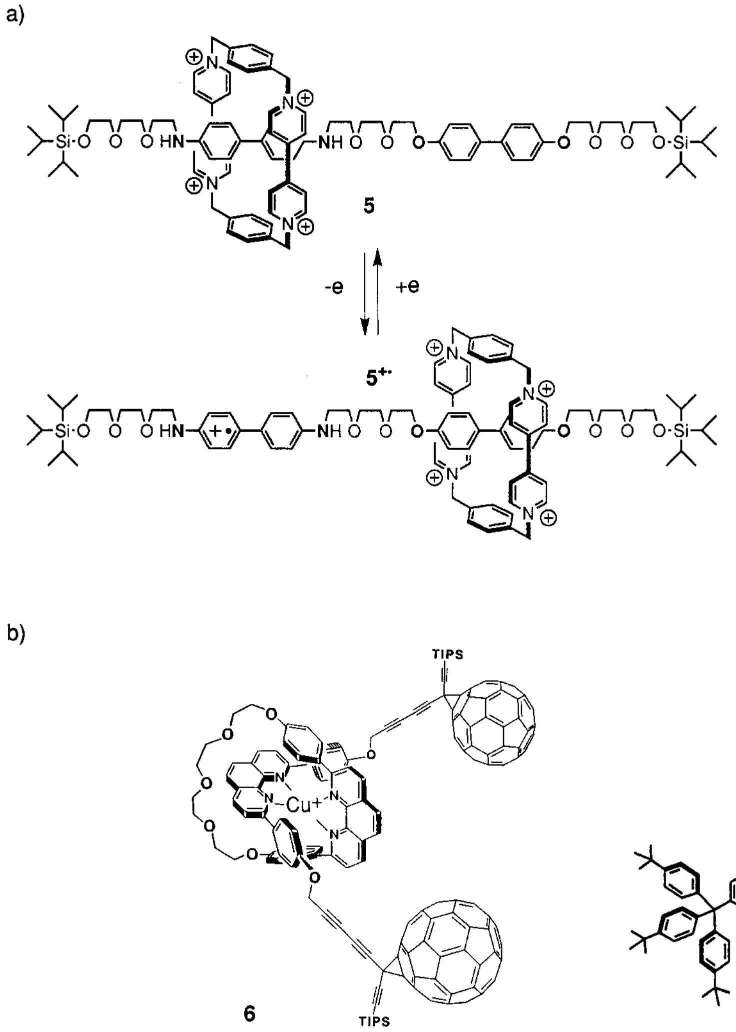


Figure 5. a) A molecular shuttle (**5**).[9] An electron-deficient cyclophane is threaded onto a linear component incorporating two sites with differing electron-donor properties. In the resting state, ≈84 % of the macrocycle is bound to the more powerful electron donor, the benzidine moiety; electrochemical oxidation of the latter triggers the reversible translation of the macrocycle to the biphenol moiety. b) A C_{60}-stoppered rotaxane (**6**),[10] based on a copper(I) dpp complex. Thanks to the electron-donor character of the MLCT excited state of the complex fragment and the electron-acceptor properties of the C_{60} moiety, electron transfer is likely to take place between these two components.

The system of Figure 5b is the C_{60}-stoppered rotaxane **6**.[10] It contains a central copper(I) complex, based on 2,9-diphenyl-1,10-phenanthroline (dpp) chelates, whose metal-to-ligand charge-transfer (MLCT) excited state, generated by visible light irradiation (MLCT absorption band maximum around 500 nm), is a powerful electron donor. Electron transfer under light irradiation is thus likely to take place between the copper(I) central complex of the rotaxane and one of the C_{60} stoppers acting as electron acceptor.

Another nonporphyrinic rotaxane, **7**, is represented in Figure 6.[11] An electrochemical signal is used to set the molecular system in motion. The ring incorporates a dpp fragment and the molecular string consists of a terdentate ligand (terpy = 2,2′,6′,2″-terpyridine) linked to a bidentate coordinating unit (2,9-disubstituted-1,10-phenanthroline). Trityl-derived stoppers are covalently attached to the extremities of the string. Initially the ring threaded onto the molecular string coordinates copper(I) together with the phenanthroline site of the string in a tetrahedral fashion. Since $\mathrm{Cu^{II}}$ requires higher coordination numbers than $\mathrm{Cu^{I}}$,

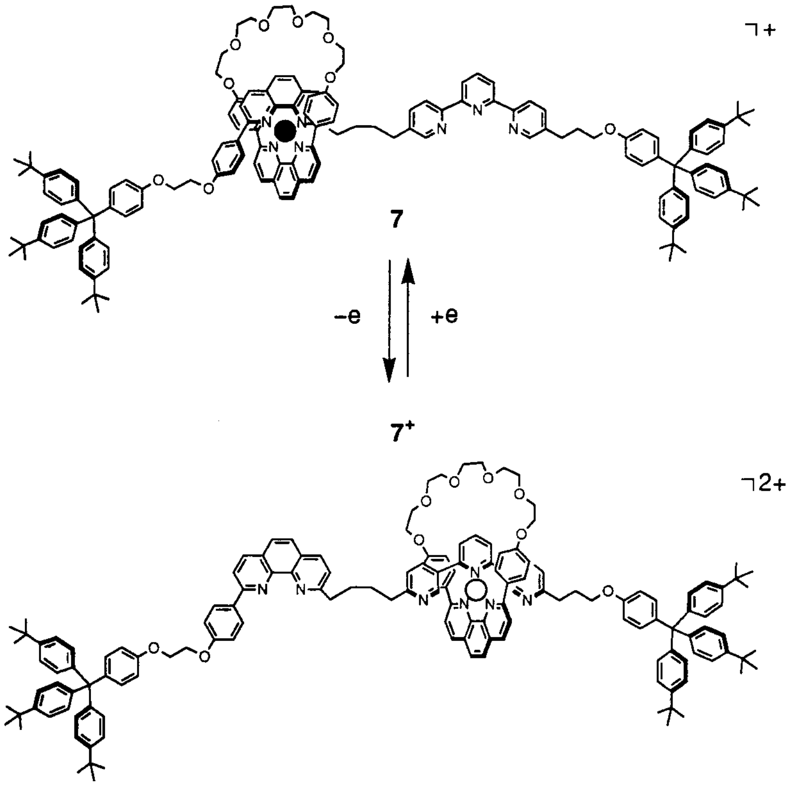
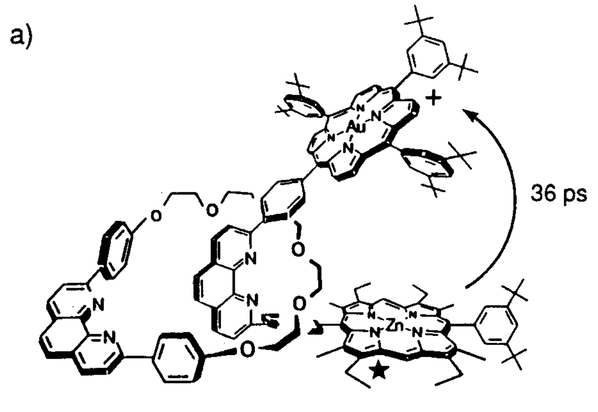


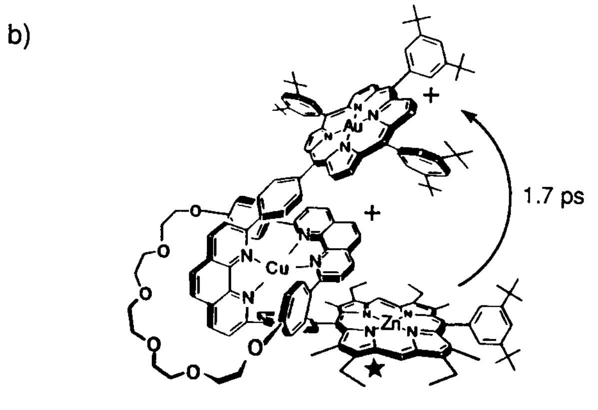
Figure 6. A rotaxane in motion (**7**) based on the redox-state dependence of the stereoelectronic requirements of a transition metal (Cu: ● $\mathrm{Cu^{I}}$, ○ $\mathrm{Cu^{II}}$).[11] The axle incorporates a bidentate and a terdentate chelating site. The macrocycle coordinates $\mathrm{Cu^{I}}$ together with the bidentate site of the linear component in a tetrahedral fashion. Electrochemical oxidation of $\mathrm{Cu^{I}}$ to $\mathrm{Cu^{II}}$ triggers the transfer of the $\mathrm{Cu^{II}}$-complexed ring to the terdentate chelate of the thread.

oxidation of Cu^I to Cu^{II} triggers a modification of the coordination sphere of the copper atom, which results in the transfer of the copper(II)-complexed ring to the terpy site of the string. This translation motion is slow (ca. 1–2 h) but complete under the experimental conditions used (CH_3CN, room temperature). The reversal to the starting state is initiated by reduction of Cu^{II} to Cu^I and is somewhat faster (minutes) than the forward motion. The presence of the stoppers, that is, the rotaxane structure, is essential: when the string has open ends, motions of the ring along the string are accompanied by partial dethreading.

The use of porphyrins as rotaxane stoppers is obvious since porphyrins are both voluminous (good stoppers) and electro- and photoactive.[12] Our interest in photosynthesis has prompted us to make porphyrin-containing rotaxanes as models of precise fragments of the photosynthetic reaction centre.[13] The two representative examples in Figure 7 undergo fast photoinduced intramolecular electron transfer between the zinc(II) porphyrin (singlet excited state) and the gold(III) porphyrin (which is an electron acceptor in its ground state). Interestingly, the electron transfer rate can be, to a large extent, governed by the nature of the central metal or by demetalation of the central coordination site.[14] In the case of the uncomplexed rotaxane **8**, photoinduced electron transfer from the zinc to the gold porphyrin took place in 36 ps, whereas for the Cu^I-complexed rotaxane **9**, the same event was accelerated by a factor of ≈20. The rate enhancement was explained in terms of a superexchange mechanism, involving the virtual electronic states of the central copper(I) complex fragment.



8



9

Figure 7. a) A rotaxane containing zinc(II) porphyrin and gold(III) porphyrin as stoppers, **8**.[13, 14] Photoinduced electron transfer takes place between the Zn porphyrin component in its singlet excited state (*) and the Au porphyrin component in its ground state. b) The same rotaxane complexing a Cu^I cation with the chelate fragments incorporated in the dumbbell and the macrocyclic components (**9**). The rate of electron transfer was found to be increased by a factor of 20 by comparison with **8**.

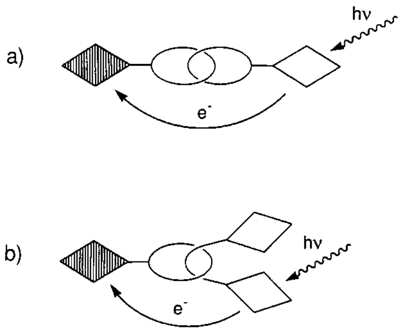
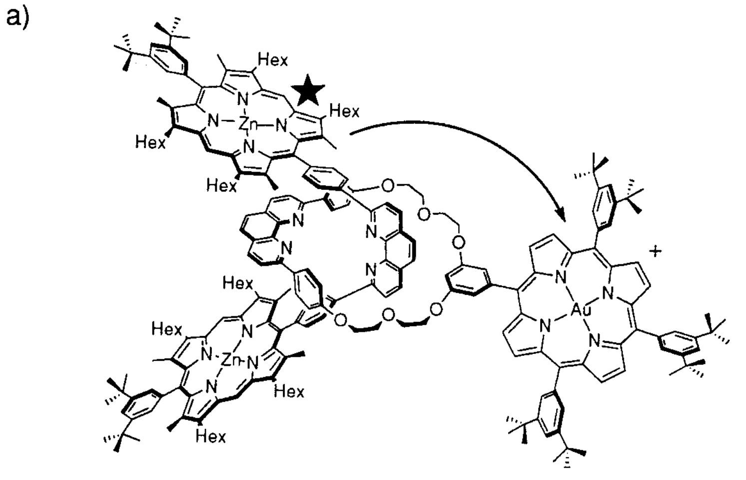


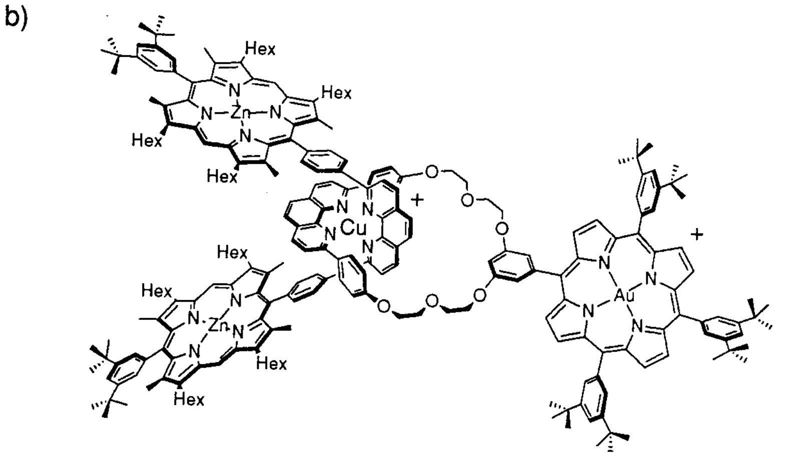
Figure 8. Donor–acceptor multiporphyrin conjugates. The donor porphyrin (empty diamond) and the acceptor porphyrin (hatched diamond) are mechanically linked in either a) catenane or b) rotaxane structure. The arrows show the direction of photoinduced electron transfer.

In the previous examples (rotaxanes **6**, **8**, **9**) photoinduced electron transfer takes place between covalently linked photo- and electroactive components. In order to make impossible electron transfer involving a bond sequence, catenane[15] and rotaxane[16] systems in which the donor and acceptor components are maintained in the same molecule by mechanical bonds only seem to be ideal targets (Figure 8). In particular, this problem was addressed with rotaxane **10,** composed of a) a macrocycle incorporating a dpp chelate and bearing a pendent gold(III) porphyrin, and b) a dumbbell component containing the same dpp chelate and stoppered by two identical bulky zinc(II) porphyrins (Figure 9). It was obtained by demetallation of the copper(I)-complexed rotaxane (**11**). Structural studies in solution suggested that demetallation leading to the template-free rotaxane induced the translation motion of the dumbbell component towards the gold(III) porphyrin of the macrocycle. Preliminary photophysical studies showed that the fluorescence of the zinc porphyrins was strongly quenched in both cases; with respect to the uncomplexed rotaxane, this clearly indicated that electron transfer from the zinc porphyrin (singlet excited state) to the gold(III) porphyrin component occurred. Therefore electron transfer between mechanically bound species has been achieved in this molecule.

In summary, the rotaxane framework can be used with advantage for making molecules in which *controlled* motions occur: translational motions of a molecular ring threaded onto a molecular rod, through-bond or through-space electron transfer from donor to acceptor electroactive components. These molecular or electronic motions are driven either by a redox process (by electrochemical means, for example) or by



10



11

Figure 9. a) Through-space electron transfer (represented by an arrow) in [2]rotaxane **10** from a Zn porphyrin stopper in its singlet excited state (*) to Au porphyrin covalently attached to the macrocycle. b) The same rotaxane complexing a Cu^I cation **11**.

a photochemical event (triggered by light). The rotaxane structure comes into play in different manners: a) stabilizing heteroleptic transition metal complexes (two differently substituted dpp fragments or a dpp and a terpy unit around a copper centre) which could not be obtained otherwise because of fast ligand exchange (scrambling), if the coordinating fragments were independent and free to diffuse in solution; b) allowing nondissociative, large-amplitude motions (translation of a ring threaded onto a rod); c) providing mechanical bonds for studying through-space intramolecular electron- or energy-transfer processes.

Acknowledgements: We warmly thank Jean-Paul Collin, Christiane Dietrich-Buchecker, Pablo Gaviña, Valérie Heitz, and Myriam Linke for their skilful contributions to the work described in this article.

Received: January 9, 1998 [C957]

[1] a) G. Schill, *Catenanes, Rotaxanes and Knots*, Academic Press, New York, **1971**; b) C. O. Dietrich-Buchecker, J.-P. Sauvage, *Chem. Rev.* **1987**, *87*, 795–810; c) C. O. Dietrich-Buchecker, J.-P. Sauvage, *Bioorganic Chemistry Frontiers* **1991**, *2*, 195–248; d) H. W. Gibson, M. C. Bheda, P. T. Engen, *Progr. Polym. Sci.* **1994**, *19*, 843; e) D. B. Amabilino, J. F. Stoddart, *Chem. Rev.* **1995**, *95*, 2725–2828; f) R. Jäger, F. Vögtle, *Angew. Chem.* **1997**, *109*, 966–980; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 930–944.

[2] a) H. L. Frisch, E. Wasserman, *J. Am. Chem. Soc.* **1961**, *83*, 3789–3795; b) V. I. Sokolov, *Russ. Chem. Rev. (Engl. Transl.)* **1972**, *41*, 452–463.

[3] A. Lüttringhaus, F. Cramer, H. Prinzbach, F. M. Henglein, *Liebigs Ann. Chem.* **1958**, *613*, 185–198.

[4] a) H. Ogino, *J. Am. Chem. Soc.* **1981**, *103*, 1303–1304; b) H. Ogino, K. Ohata, *Inorg. Chem.* **1984**, *23*, 3312–3316.

[5] a) G. Schill, H. Zollenkopf, *Liebigs Ann. Chem.* **1969**, *721*, 53–74; b) G. Schill, R. Henschel, *Liebigs Ann. Chem.* **1970**, *731*, 113–119; c) G. Schill, C. Zürcher, W. Vetter, *Chem. Ber.* **1973**, *106*, 228–235.

[6] a) I. T. Harrison, S. Harrison, *J. Am. Chem. Soc.* **1967**, *89*, 5723–5724; b) I. T. Harrison, *J. Chem. Soc. Chem. Commun.* **1972**, 231–232; c) I. T. Harrison, *J. Chem. Soc. Perkin Trans. I* **1974**, 301–304.

[7] a) K. Yamanari, Y. Shimura, *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2283–2289; b) R. Isnin, A. E. Kaifer, *J. Am. Chem. Soc.* **1991**, *113*, 8188–8190; c) R. S. Wylie, D. H. Macartney, *J. Am. Chem. Soc.* **1992**, *114*, 3136–3138; d) D. J. Cárdenas, P. Gaviña, J.-P. Sauvage, *Chem. Commun.* **1996**, 1915–1916; e) D. J. Cárdenas, P. Gaviña, J.-P. Sauvage, *J. Am. Chem. Soc.* **1997**, *119*, 2656–2664.

[8] R. Ballardini, V. Balzani, M. T. Gandolfi, L. Prodi, M. Venturi, D. Philp, H. G. Ricketts, J. F. Stoddart, *Angew. Chem.* **1993**, *105*, 1362–1364; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1301–1303.

[9] R. A. Bissell, E. Córdova, A. E. Kaifer, J. F. Stoddart, *Nature* **1994**, *369*, 133–137.

[10] F. Diederich, C. Dietrich-Buchecker, J.-F. Nierengarten, J.-P. Sauvage, *J. Chem. Soc. Chem. Commun.* **1995**, 781–782.

[11] a) P. Gaviña, J.-P. Sauvage, *Tetrahedron Lett.* **1997**, *38*, 3521–3524; b) J.-P. Collin, P. Gaviña, J.-P. Sauvage, *New J. Chem.* **1997**, *21*, 525–528.

[12] a) P. R. Ashton, M. R. Johnston, J. F. Stoddart, M. S. Tolley, J. W. Wheeler, *J. Chem. Soc. Chem. Commun.* **1992**, 1128–1131; b) F. Vögtle, F. Ahuis, S. Baumann, J. L. Sessler, *Liebigs Ann.* **1996**, 921–926.

[13] a) J.-C. Chambron, V. Heitz, J.-P. Sauvage, *J. Chem. Soc. Chem. Commun.* **1992**, 1131–1133, b) J.-C. Chambron, V. Heitz, J.-P. Sauvage, *J. Am. Chem. Soc.* **1993**, *115*, 12378–12384; c) J.-C. Chambron, S. Chardon-Noblat, A. Harriman, V. Heitz, J.-P. Sauvage, *Pure Appl. Chem.* **1993**, *65*, 2343–2349.

[14] a) J.-C. Chambron, A. Harriman, V. Heitz, J.-P. Sauvage, *J. Am. Chem. Soc.* **1993**, *115*, 6109–6114; b) J.-C. Chambron, A. Harriman, V. Heitz, J.-P. Sauvage, *J. Am. Chem. Soc.* **1993**, *115*, 7419–7425.

[15] a) D. B. Amabilino, J.-P. Sauvage, *Chem. Commun.* **1996**, 2441–2442; b) D. B. Amabilino, J.-P. Sauvage, *New J. Chem.* **1998**, *22*, 395–409.

[16] M. Linke, J.-C. Chambron, V. Heitz, J.-P. Sauvage, *J. Am. Chem. Soc.* **1997**, *119*, 11329–11330.