Electron Transfer between Mechanically Linked Porphyrins in a [2]Rotaxane

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Charge separation is a key process of natural photosynthesis,[1,2] and many synthetic systems have been proposed as functional mimics of the photosynthetic reaction center based on transition metal complexes,[3−5] organic chromophores,[6,7] or porphyrins.[8−12] An interesting question is related to the intimate mechanism of electron transfer (ET), with the now classical distinction between "through-bond" and "through-space" ET steps.[13−15] If connection between the various electron donors (D) and acceptors (A) have almost exclusively been realized using covalent bonds, a few examples of so-called "self-assembled" systems, mostly based on hydrogen-bonding but also on ionic interactions (salt-bridge-mediated systems), have recently been proposed.[16−19] In order to suppress any classical bond and, in particular, to make impossible the recognition of an electron transfer pathway involving a bond sequence, we designed multicomponent systems in which D and A are maintained in the same molecule by *mechanical* (or topological) *bonds only*[20−22] (Figure 1).

We now report the synthesis of a [2]rotaxane (Figure 1a) whose ring is attached to a pendent porphyrin (A) and whose stoppering groups are electron donor porphyrins (D). Preliminary luminescence measurements show that ET between D (singlet excited state) and A is likely to take place and is a fast process (<1 ns).
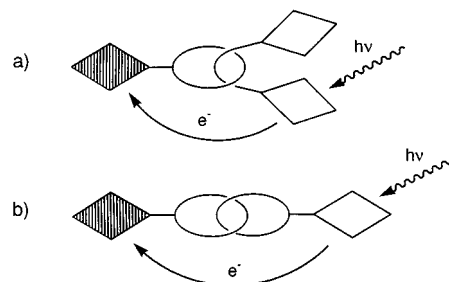

Figure 1. Donor−acceptor multiporphyrin conjugates. The donor porphyrin (white diamond) and the acceptor porphyrin (hatched diamond) are mechanically linked in either rotaxane (a) or catenane structure (b).
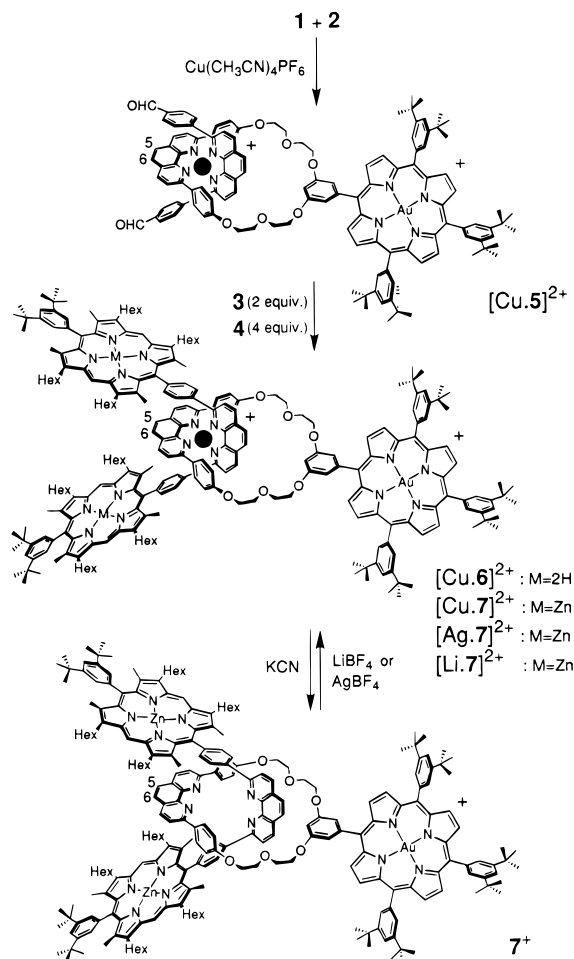

Figure 2. Sequence of reactions leading to [2]rotaxane **7**⁺ and the various metal-complexed [2]rotaxanes [M·**7**]²⁺. The black disk is Cu⁺ in [Cu·**6**]²⁺ and in [Cu·**7**]²⁺, Ag⁺ in [Ag·**7**]²⁺, and Li⁺ in [Li·**7**]⁺. Also indicated are protons 5 and 6 of the phenanthroline nucleus incorporated into the macrocycle.

Rotaxane **7**⁺ (Figure 2) is composed of the following two components: a macrocycle incorporating a 2,9-diphenyl-1,10-phenanthroline (dpp) chelate and bearing a pendent gold(III) porphyrin, and a dumbbell-shaped molecular thread incorporating the same dpp chelate and stoppered by two identical bulky zinc(II) porphyrins. It was synthesized by using an approach derived from the transition metal template strategy developed for making catenanes, rotaxanes, and knots in our laboratory.[22−24] The precursors are shown in Chart 1.

(1) Deisenhofer, J.; Epp, O.; Miki, K.; Huber, R.; Michel, H. *J. Mol. Biol.* **1984**, *180*, 385−398.
(2) Allen, J. P.; Feher, G.; Yeates, T. O.; Komiya, H.; Rees, D. C. *Proc. Natl. Acad. Sci. U.S.A.* **1987**, *84*, 5730−5734.
(3) Meyer, T. J. *Acc. Chem. Res.* **1989**, *22*, 163−170.
(4) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Ellis Horwood: London, 1991.
(5) Sauvage, J.-P.; Collin, J.-P.; Chambron, J.-C.; Guillerez, S.; Coudret, C.; Balzani, V.; Barigelletti, F.; De Cola, L.; Flamigni, L. *Chem. Rev.* **1994**, *94*, 993−1019.
(6) Oevering, H.; Verhoeven, J. W.; Paddon-Row, M. N.; Warman, J. M. *Tetrahedron* **1989**, *45*, 4751−4766.
(7) Miller, J. R.; Calcaterra, L. T.; Closs, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 3047−3049.
(8) Gust, D.; Moore, T. A. *Topics Curr. Chem.* **1991**, *159*, 103−151.
(9) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435−461.
(10) Chambron, J.-C.; Harriman, A.; Heitz, V.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1993**, *115*, 6109−6114.
(11) Harriman, A.; Odobel, F.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1995**, *117*, 9461−9472.
(12) Harriman, A.; Sauvage, J.-P. *Chem. Soc. Rev.* **1996**, *25*, 41−48.
(13) Winkler, J. R.; Gray, H. B. *Chem. Rev.* **1992**, *92*, 369−379.
(14) Guarr, T.; McLendon, G. *Coord. Chem. Rev.* **1985**, *68*, 1−52.
(15) Casimiro, D. R.; Wong, L.-L.; Colon, J. L.; Zewert, T. E.; Richards, J. H.; Chang, I.-J.; Winkler, J. R.; Gray, H. B. *J. Am. Chem. Soc.* **1993**, *115*, 1485−1489.
(16) Sessler, J. L.; Wang, B.; Harriman, A. *J. Am. Chem. Soc.* **1993**, *115*, 10418−10419.
(17) Tecilla, P.; Dixon, R. P.; Slobodkin, G.; Alavi, D. S.; Waldeck, D. H.; Hamilton, A. D. *J. Am. Chem. Soc.* **1990**, *112*, 9408−9410.
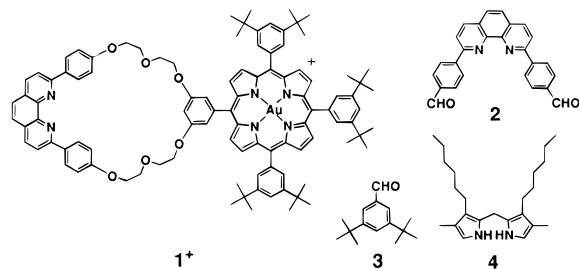(18) Kuroda, Y.; Kawashima, A.; Hayashi, Y.; Ogoshi, H. *J. Am. Chem. Soc.* **1997**, *119*, 4929−4933.
(19) Roberts, J. A.; Kirby, J. P.; Nocera, D. G. *J. Am. Chem. Soc.* **1995**, *117*, 8051−8052.
(20) Walba, D. M. *Tetrahedron* **1985**, *41*, 3161−3212.
(21) Amabilino, D.; Sauvage, J.-P. *Chem.Commun.* **1996**, 2441−2442.
(22) Chambron, J.-C.; Dietrich-Buchecker, C. O.; Sauvage, J.-P. *Comprehensive Supramolecular Chemistry*; Pergamon: Oxford, 1996; Vol. 9, pp 43−83.
(23) Dietrich-Buchecker, C. O.; Sauvage, J.-P. *Bioorg. Chem. Front.* **1991**, *2*, 195−248.
(24) Chambron, J.-C.; Heitz, V.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1993**, *115*, 12378−12384.

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Chart 1

Macrocycle **1**$^+$,[21] dialdehyde **2**,[25] and Cu(CH$_3$CN)$_4$PF$_6$ were mixed in CH$_2$Cl$_2$/CH$_3$CN, forming prerotaxane [Cu·**5**]$^{2+}$ quantitatively. This complex was subsequently reacted with 2 equiv of aldehyde **3**[26] and 4 equiv of dipyrrylmethane **4**[27−30] in dichloromethane acidified with CF$_3$COOH[31] (Figure 2). After the reaction was stirred overnight, oxidation of the porphyrinogen intermediates with chloranil and chromatographic separation provided copper(I)-complexed [2]rotaxane [Cu·**6**]$^{2+}$ 17% isolated yield. This corresponds to an average yield of single porphyrin formation of 41%, since two porphyrins are formed simultaneously in the same molecule. The free-base porphyrins were metalated with zinc(II) by reaction of [2]rotaxane [Cu·**6**]$^{2+}$ with Zn(OAc)$_2$·2H$_2$O in a refluxing mixture of CHCl$_3$ and CH$_3$-OH, and copper(I)-complexed [2]rotaxane [Cu·**7**]$^{2+}$ was obtained in 82% yield after chromatography. The template cation was finally removed, by treatment of [Cu·**7**]$^{2+}$ with KCN in CH$_3$CN/CH$_2$Cl$_2$/H$_2$O mixtures. The reaction proved sluggish and did not go farther than 35%. It was thus necessary to separate the rotaxane liberated (i.e., **7**$^+$) using chromatography and to subject the starting material left to fresh KCN/CH$_3$CN/CH$_2$Cl$_2$/H$_2$O mixtures. This process allowed finally to free all the complexed [2]rotaxane [Cu·**7**]$^{2+}$ from Cu(I). No macrocycle unthreading was observed, proving the very rotaxane nature of **7**$^+$.

In both compounds, complexed [Cu·**7**]$^{2+}$ and metal-free **7**$^+$ [2]rotaxanes, the two porphyrinic stoppers of the dumbbell sandwich the phenanthroline subunit belonging to the macrocycle. This is clearly established by ^{1}H NMR spectroscopy. A 0.4 ppm upfield shift of protons 5 and 6 of this subunit in [Cu·**7**]$^{2+}$ is induced as compared to prerotaxane [Cu·**5**]$^{2+}$. For [2]rotaxane **7**$^+$, the shielding is even stronger: the chemical shift difference is as large as 3 ppm! This suggests that following the demetalation process the dumbbell component has moved toward the gold(III) porphyrin of the macrocycle, allowing the zinc(II) porphyrins to clamp more tightly the phenanthrolinic subunit of the macrocycle.

A rich coordination chemistry could be developed at the bis-dpp tetrahedral site left by the metal template. [2]Rotaxane **7**$^+$ could be metalated with monocations Li$^+$ and Ag$^+$.[32] The insertion of Ag$^+$ (using AgBF$_4$ in CH$_3$CN/CH$_2$Cl$_2$) afforded [Ag·**7**]$^{2+}$ cleanly and quantitatively. The reaction with LiBF$_4$ in CH$_2$Cl$_2$/MeOH produced [Li·**7**]$^{2+}$ which was not purified by chromatography, due to its expected poor stability. Nevertheless, the purity of [Li·**7**]$^{2+}$ could be estimated to 90% by ^{1}H NMR.

All four rotaxanes described in this paper involve two zinc-(II) porphyrins, which are good electron donors in their singlet excited state, and a gold(III) porphyrin, which is the partner of choice for its electron-accepting properties.[33] Remarkably, the components incorporating these chromophores and electrophores are either connected by metal−ligand bonds (when M = Cu$^+$, Ag$^+$, Li$^+$) or not connected chemically, although held together by a mechanical link. We had observed earlier by transient absorption spectroscopy electron transfer from a zinc porphyrin connected to a gold(III) porphyrin by a dpp spacer. As expected from thermodynamic data, energy transfer could experimentally be ruled out unambiguously.[34] In addition, the rate of electron transfer was strongly enhanced by coordination of the spacer to copper(I).[10]

The [2]rotaxanes described here now allow for the study of electron transfer through metal−ligand bonds (in [M·**7**]$^{2+}$ where M = Cu$^+$, Ag$^+$ or Li$^+$) or through space (in **7**$^+$). Preliminary results were obtained from steady state luminescence measurements. For all compounds, strong quenching of the luminescence of the zinc porphyrin components is observed. The quenching mechanism in [Li·**7**]$^{2+}$ is likely to be ET, whereas for [Cu·**7**]$^{2+}$ and [Ag·**7**]$^{2+}$ the mechanism is less straightforward, since the central complex fragments could more or less participate in the quenching processes. For free rotaxane **7**$^+$, which involves only zinc(II) and gold(III) porphyrins as electron transfer partners, the situation is not as ambiguous as for the other compounds, owing to the lack of any additional electroactive component. The fluorescence of the zinc porphyrin subunits of [2]rotaxane **7**$^+$ is decreased by 87%. As supported by previous studies,[10,34] this strong quenching is very likely to be due to electron transfer from a zinc porphyrin stopper in its singlet excited state to the gold porphyrin cation attached to the ring. The electron transfer rate can be roughly estimated from the present steady state luminescence measurements and the known singlet excited state lifetime of 5,15-bis[3,5-bis(1,1-dimethylethyl)phenyl]-2,8,12,18-tetrahexyl-3,7,13,17-tetramethyl-21H,23H-porphine,[35] according to eq 1:

$$k_{ET} = (1/\tau_0)(I_0/I - 1) \qquad (1)$$

In this equation, I is the emission intensity of the [2]rotaxane and I_0 is that of the reference porphyrin. With $\tau_0 = 1.94$ ns, the value found for k_{ET} is 3.5×10^9 s^{-1}, which is much slower than the rate observed for the bis-porphyrin conjugate where the zinc and the gold porphyrins are connected by a dpp spacer.[34] This is consistent with the lack of any chemical bond between the zinc(II) and the gold(III) porphyrins in [2]rotaxane **7**$^+$. Transient absorption spectroscopy studies are underway and will be reported in due course.

Supporting Information Available: Spectral data and characterization for **7**$^+$ (5 pages). See any current masthead page for ordering and Internet access instructions.

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(25) Note: dialdehyde **2** was obtained in 47% yield by reaction of 1,10-phenanthroline (1 equiv) with the *p*-lithio-derivative of benzaldehyde neopentylacetal (2.5 equiv) in THF, hydrolysis, and MnO$_2$ oxidation of the intermediate.
(26) Chardon-Noblat, S.; Sauvage, J.-P. *Tetrahedron* **1991**, *47*, 5123−5132.
(27) Kleinspehn, G. G. *J. Am. Chem. Soc.* **1955**, *77*, 1546−1548.
(28) Chang, C. K. *J. Am. Chem. Soc.* **1977**, *99*, 2819−2822.
(29) Bastida de Almeida, J. A. P.; Kenner, G. W.; Rimmer, J.; Smith, K. M. *Tetrahedron* **1976**, *32*, 1793−1799.
(30) Young, R.; Chang, C. K. *J. Am. Chem. Soc.* **1985**, *107*, 898−909.
(31) Lindsey, J. S.; Schreiman, I. C.; Hsu, H. C.; Kearney, P. C.; Marguerettaz, A. M. *J .Org. Chem.* **1987**, *52*, 827−836.
(32) Dietrich-Buchecker, C.; Sauvage, J.-P.; Kern, J.-M. *J. Am. Chem. Soc.* **1989**, *111*, 7791−7800.
(33) Heitz, V.; Chardon-Noblat, S.; Sauvage, J.-P. *Tetrahedron Lett.* **1991**, *32*, 197−198.
(34) Brun, A. M.; Harriman, A.; Heitz, V.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1991**, *113*, 8657−8663.
(35) Chambron, J.-C.; Oberlé, J.; Rullière, C.; Sauvage, J.-P.; Solladié, N. Unpublished results.