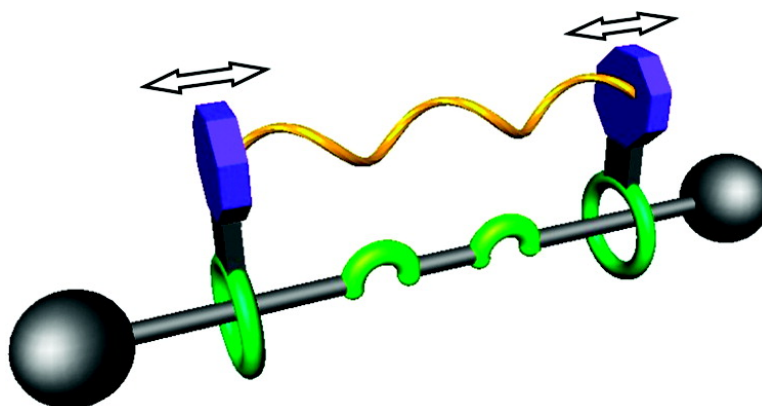Communication

A [3]Rotaxane with Two Porphyrinic Plates Acting as an Adaptable Receptor

Julien Frey, Christian Tock, Jean-Paul Collin, Valrie Heitz, and Jean-Pierre Sauvage

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 3 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

A [3]Rotaxane with Two Porphyrinic Plates Acting as an Adaptable Receptor

Julien Frey, Christian Tock, Jean-Paul Collin,* Valérie Heitz,* and Jean-Pierre Sauvage*

Laboratoire de Chimie Ogano-Minérale, LC3 UMR 7177 du CNRS, Université Louis Pasteur, Institut de Chimie, 4 rue Blaise Pascal, 67070 Strasbourg Cedex, France

Received December 12, 2007; E-mail: sauvage@chimie.u-strasbg.fr; jpcollin@chimie.u-strasbg.fr; heitz@chimie.u-strasbg.fr

Catenanes and rotaxanes occupy a key position in the field of chemical topology[1] as well as that of artificial molecular machines and motors,[2] although non-interlocking systems have also led to spectacular results in this latter field.[3] By contrast, catenanes and rotaxanes have not been much used in host−guest chemistry. Rare examples are those of luminescent anion binders[4] or systems related to biomolecules.[5] We would now like to report that a bis-porphyrinic [3]rotaxane behaves as an efficient receptor toward guests of the type py-Z-py (py: 4-pyridyl; Z: spacer). Moreover, the ability of the two rings to glide freely along the axis onto which they are threaded allows the distance between the binding sites borne by the rings to be varied over a wide range, thus allowing guests of very different lengths to be complexed between these two sites. The principle of the recognition process and of the ability of the receptor to adapt to the guest is represented in Scheme 1. As shown in Figure 1, porphyrin nuclei are rigidly attached to the mobile rings of the rotaxane receptor. Our group as well as others have already described several porphyrin-incorporating catenanes or rotaxanes,[6] mostly in relation to electron and energy transfer. In the field of host−guest chemistry, whereas porphyrin-based catenanes and rotaxanes have not been explored as yet, a myriad of bis-porphyrins have been elaborated and studied as ditopic receptors.[7]

The copper complex $2^{2+} = Cu_2(1)^{2+}$ was obtained as the ultimate precursor to **1**, before the demetalation reaction (KCN) affording **1**. Rotaxane 2^{2+} was obtained following the copper(I)-templated strategy already used in numerous syntheses in our group for making various catenanes rotaxanes.

The complete synthesis of 2^{2+} is extremely complex and requires many individual chemical steps. It will be described in a separate publication. The chemical structure of the free [3]rotaxane **1** used in the present study is represented in Figure 1. Each ring of the [3]rotaxane contains a 2,9-diaryl-1,10-phenanthroline coordinating fragment. The back of the 1,10-phenanthroline nucleus (positions 5 and 6) has been modified in order to perform a condensation reaction leading to the attachment of a porphyrin in a rigid fashion.

The synthesis of the constitutive rings of **1** and 2^{2+} has recently been reported.[8] The core of the axis contains a 3,8-di(4-pyridyl)-4,7-phenanthroline motif, providing the axis with two rigidly connected bidentate chelates of the 2,2′-bipyridine family. This fragment has been used in the past to prepare various multinuclear transition metal complexes,[9] including a [4]pseudorotaxane complexed to four copper(I) atoms.[10] The X-ray structure of an iridium-(III) complex[11] of the coordinating central core indicates that the distance between the two complexed metal centers should be around 8−8.5 Å, in agreement with CPK models.

In order to verify that **1** can accommodate substrates of markedly different geometries, coordination of the two bis-pyridyl compounds **3** and **4** was studied. The substrate **3** is obviously geometrically very different from **4** since, in the latter substrate, the pyridyl groups are directly connected to one another via their 4 positions (Figure 2).

Scheme 1 [a]
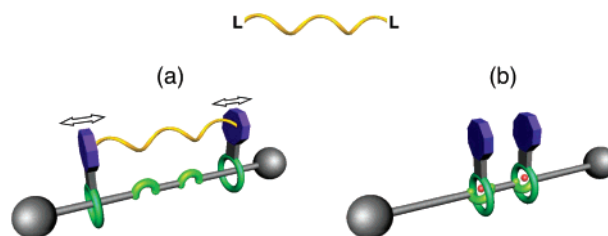
[a] (a) Principle of the adaptable [3]rotaxane receptor. The two rings threaded by the rotaxane axis are rigidly attached to a Zn-porphyrin (blue moieties); they can glide along the axis so as to allow the receptor to adjust the Zn−Zn distance and thus to fit the dimensions of the L−L ditopic substrate. L is an organic fragment able to coordinate the Zn atom of the porphyrins. (b) Schematic representation of a dicopper(I) rotaxane complex, in which the porphyrin−porphyrin distance is roughly imposed by the geometry of the central dinucleating unit (represented by a double half of a circle symbol).

The stability constants of the complexes [**1·3**], [**1·4**], [**2·3**]$^{2+}$, and [**2·4**]$^{2+}$ were determined by UV−vis spectroscopic measurements (see Supporting Information). The Soret band of the Zn-porphyrins is an excellent probe to monitor the complexation reaction between host **1** or 2^{2+} and both guests. The spectroscopic characteristics of **1** are as follows: $\lambda_{max}(\log \epsilon) = 437$ nm (5.70) (Soret band), 518 nm (4.84), and 672 nm (4.23) (Q bands). By adding gradual amounts of the bis-pyridyl substrate **3** or **4** to a toluene solution of **1**, a significant bathochromic shift of the Soret band was observed as well as a small hyperchromic effect, in accordance with previous observations.[12] Clear isosbestic points were observed in the titration, which is an indication that one complex species only is obtained. In addition, the stoichiometry is obviously that of a 1 to 1 complex since a plateau is observed for the absorbance of the mixture obtained by adding **3** or **4** to **1** beyond a ratio of 1 to 1.2. The stability constants for the complexes corresponding to the following equilibrium have been determined:

$$H + G \rightleftharpoons [H\bullet G] \qquad K_{assn} = \frac{[H\bullet G]}{[H] \times [G]}$$
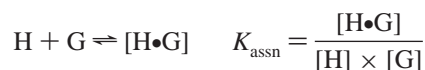
$$H: \textbf{1} \text{ or } \textbf{2}^{2+} \text{ and } G: \textbf{3} \text{ or } \textbf{4}$$

Their values are as follows: $\log K_{assn}[\textbf{1·3}] = 7.5 \pm 0.2$ and $\log K_{assn}[\textbf{1·4}] = 6.0 \pm 0.2$, which reflect both the adaptability of the [3]rotaxane host **1** and the respective basicities of guests **3** and **4**.

The corresponding complexes of the copper(I)-complexed receptor 2^{2+} could be obtained quantitatively either by adding a stoichiometric amount of the given di-pyridyl substrate (**3** or **4**) to 2^{2+} or by first preparing the copper-free complex [**1·3**] or [**1·4**] and, subsequently, adding 2 equiv of a copper(I) salt to the solution. **1** can obviously adjust its geometry to the complexed guest. As testified by the very similar binding constants for [**2·3**]$^{2+}$ and [**2·4**]$^{2+}$ ($\log K_{assn} = 6.8 \pm 0.2$ for both complexes) the copper(I)-complexed rotaxane 2^{2+} is also adaptable. The long aromatic spacers
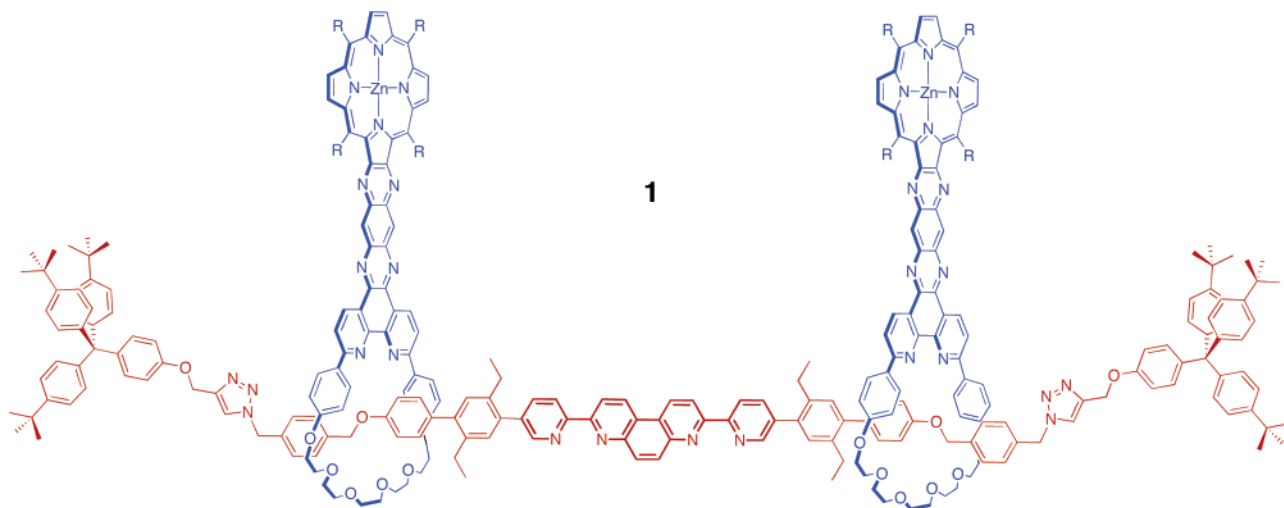
Figure 1. Chemical structures of the free rotaxane **1** where R groups represent 3,5-di-*tert*-butylphenyl substituents.
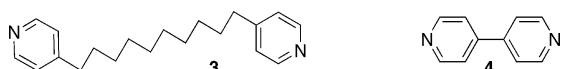

Figure 2. Two bis-pyridyl substrates **3** and **4**.

between the porphyrin nuclei and the rings can easily be distorted. Indeed, coordination of **3** to the two zinc porphyrins of $\mathbf{2}^{2+}$ has to induce pronounced distortions of the receptor itself. Indeed, if the conformation of $\mathbf{2}^{2+}$ was frozen in the most stable one, as obtained by simulation, it would be virtually impossible to insert the substrate in between the two porphyrinic plates.

In conclusion, the two-porphyrin [3]rotaxane **1** represents the first example of an adaptable receptor based on interlocking or threaded compounds. The center-to-center distance between the two porphyrinic plates can vary substantially, roughly from 10 to 80 Å. The order of magnitude of the binding constants (about 10^{6}–10^{7} M^{-1}) underlines a cooperative effect between both porphyrins of the two receptor rotaxanes **1** and $\mathbf{2}^{2+}$. This strong association imposes that one guest binds (either **3** or **4**) to one host, the demetalated rotaxane **1** being a slightly better host for guest substrates due to the greater adaptability of its bis-porphyrinic receptor.

Supporting Information Available: Analytical data of compounds **1** and $\mathbf{2}^{2+}$ and spectroscopic titration studies. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Dietrich-Buchecker, C.; Sauvage, J.-P. *Chem. Rev.* **1987**, *87*, 795–810. (b) Amabilino, D. B.; Stoddart, J. F. *Chem. Rev.* **1995**, *95*, 2725–2828. (c) Vögtle, F.; Dünnwald, T.; Schmidt, T. *Acc. Chem. Res.* **1996**, *29*, 451–460. (d) Dietrich-Buchecker, C.; Sauvage, J.-P. *Catenanes, Rotaxanes and Knots. A Journey Through the World of Molecular Topology*; Wiley-VCH: Weinheim, Germany, 1999. (e) Fujita, M. *Acc. Chem. Res.* **1999**, *32*, 53–61.

(2) (a) Sauvage, J.-P. *Acc. Chem. Res.* **1998**, *31*, 611–619. (b) Stoddart, J. F. *Acc. Chem. Res.* **2001**, *34*. (c) Harada, A. *Acc. Chem. Res.* **2001**, *34*, 456–464. (d) Balzani, V.; Venturi, M.; Credi, A. *Molecular Devices and Machines. A journey into the Nano World*; Wiley-VCH: Weinheim, Germany, 2003. (e) Kay, E. R.; Leigh, D. A.; Zerbetto, F. *Angew. Chem., Int. Ed.* **2007**, *46*, 72–191.

(3) (a) Feringa, B. L. *Molecular Switches*; Wiley-VCH: Weinheim, Germany, 2001 and references therein. (b) Muraoka, T.; Kinbara, K.; Aida, T. *Nature* **2006**, *440*, 512–515.

(4) Beer, P.; Sambrook, M. R.; Curiel, D. *Chem. Commun.* **2006**, 2105–2117.

(5) (a) Smukste, I.; Smithrud, D. B. *J. Org. Chem.* **2003**, *68*, 2547–2558. (b) Lam, R. T. S.; Belenguer, A.; Roberts, S. L.; Naumann, C.; Jarrosson, T.; Otto, S.; Sanders, J. K. M. *Science* **2005**, *308*, 667–669. (c) Wenz, G.; Han, B.-H.; Müller, A. *Chem. Rev.* **2006**, *106*, 782–817.

(6) (a) Chambron, J.-C.; Heitz, V.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1993**, *115*, 12378–12384. (b) Gunter, M. J.; Johnston, M. R. *J. Chem. Soc., Chem. Commun.* **1994**, 829–830. (c) Amabilino, D. B.; Sauvage, J.-P. *New J. Chem.* **1998**, 395–409. (d) Linke, M.; Fujita, N.; Chambron, J.-C.; Heitz, V.; Sauvage, J.-P. *New J. Chem.* **2001**, *25*, 790–796. (e) Schuster, D. I.; Li, K.; Guldi, D. M.; Ramey, J. *Org. Lett.* **2004**, *6*, 1919–1922. (f) Flamini, L.; Heitz, V.; Sauvage, J.-P. In *Non-Covalent Multi-porphyrin Assemblies: Synthesis and Properties*; Enzo, A., Ed.; Structure and Bonding; Springer: Berlin, New York, 2006; Vol. 121, pp 217–261.

(7) (a) Sanders, J. K. M. In Atwood, J. L.; Davies, J. E. D.; MacNicol, D. D.; Vögtle, F. *Comprehensive Supramolecular Chemistry*; Pergamon: Oxford, United Kingdom, 1996; Vol. 9, pp 131–164. (b) Satake, A.; Kobuke, Y. *Tetrahedron* **2005**, *61*, 13–41 and references therein.

(8) Frey, J.; Dobbs, W.; Heitz, V.; Sauvage, J.-P. *Eur. J. Inorg. Chem.* **2007**, 2416–2419.

(9) (a) Sleiman, H.; Baxter, P. N. W.; Lehn, J.-M.; Airola, K.; Rissanen, K. *Inorg. Chem.* **1997**, *36*, 4734–4742. (b) Baxter, P. N. W.; Khoury, R. G.; Lehn, J.-M.; Baum, G.; Fenske, D. *Chem.—Eur. J.* **2000**, *6*, 4140–4148.

(10) Collin, J.-P.; Frey, J.; Heitz, V.; Sakelleriou, E.; Sauvage, J.-P.; Tock, C. *New J. Chem.* **2006**, *30*, 1386–1389.

(11) Auffrant, A.; Barbieri, A.; Barigelletti, F.; Lacour, J.; Mobian, P.; Collin, J.-P.; Sauvage, J.-P.; Ventura, B. *Inorg. Chem.* **2007**, *46*, 6911–6919.

(12) Nappa, M.; Valentine, J. S. *J. Am. Chem. Soc.* **1978**, *100*, 5075–5080.

JA7110493