Complete rearrangement of a multi-porphyrinic rotaxane by metallation–demetallation of the central coordination site

Myriam Linke, Jean-Claude Chambron, Valérie Heitz, Jean-Pierre Sauvage* and Vincent Semetey

Laboratoire de Chimie Organo-Minérale, UMR 7513 du CNRS, Université Louis Pasteur, Institut Le Bel, 4, rue Blaise Pascal, 67000 Strasbourg, France. E-mail: sauvage@chimie.u-strasbg.fr

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A new multiporphyrinic [2]rotaxane has been made in which a gold(III) porphyrin is part of the ring; rotation of the string-like fragment within the ring between two diametrically opposed positions is triggered by metallation–demetallation of the central coordination site.

In relation to molecular switches,[1] machines and motors,[2,3] it is of special interest to be able to control at will, amongst other properties, the shape of multicomponent molecular systems. The triggering signal, responsible for the rearrangement of the compound can be photochemical,[4] electrochemical[5] or chemical.[6] Catenanes and rotaxanes are ideally suited for undergoing large amplitude motions under the action of an external stimulus.[7,8]

In the present work, we show that complexing or decomplexing an appropriate metal in a coordination site can bring to close proximity, or spread a long distance apart, given porphyrinic components of the system. The principle is depicted in Fig. 1.

The compound made and studied is a [2]rotaxane in which the string-like fragment bears two zinc(II) porphyrins as blocking groups. The ring through which the string is threaded incorporates a gold(III) porphyrin. It should be noted that these metalloporphyrins are key components of multichromophoric systems undergoing photoinduced electron transfer and proposed as models of given fragments of the photosynthetic reaction centre.[9]

The organic compounds used as intermediates in the synthesis of the [2]rotaxane are represented in Fig. 2. The tetraaryl porphyrin **1** was prepared in 6% yield using pyrrole and a 1 : 1 mixture of the appropriate aldehydes ($\text{CF}_3\text{CO}_2\text{H}$, in CH_2Cl_2 followed by chloranil treatment[10]). After metallation (KAuCl_4) to afford **2** (76%), demethylation (BBr_3) furnished **3** in almost quantitative yield. **5** was obtained by reacting **4**[11] with 2-bromoethanol (K_2CO_3, refluxing DMF) and it was converted to **6** (tosyl chloride, NEt_3, CH_2Cl_2) and subsequently to **7** (NaI, acetone; 30% yield from **4**). Macrocycle **11** was prepared from **3** and **7** (Cs_2CO_3 in DMF, 55 °C; 31% yield). Rotaxane **14** was synthesized following a strategy previously developed in our group for making porphyrin-stoppered rotaxanes.[9] An equimolar mixture of **8**, **11** and Cu(MeCN)_4^+ led quantitatively to prerotaxane **12** (not drawn) in which the open chain fragment **8** has been threaded through the ring **11** thanks to the gathering effect of copper(I). The terminal porphyrinic blocking groups of **13** were built from **9**, **10** and **12** ($\text{CF}_3\text{CO}_2\text{H}$ in CH_2Cl_2; chloranil). **14**† was obtained after metallation $[\text{Zn(OAc)}_2]$ in 13% yield from **8**.

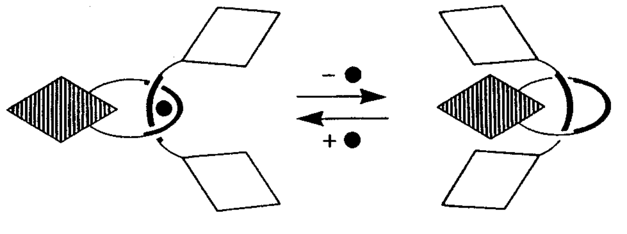

Fig. 1 Control of the mutual arrangement between the gold porphyrin (PAu^+ incorporated in the ring, black diamond) and the zinc porphyrins (PZn end-function of the dumbell, white diamond) by complexation/decomplexation of a metal centre (black circle) within/from the central coordination site. (a) The chemical structure of the two organic constitutive fragments of the rotaxane (ring and thread) is such that, in the complex, the gold porphyrin is remote from the two zinc porphyrins. (b) After removal of the central metal, weak forces may favour an attractive interaction between PAu^+ and the PZn nuclei, leading to a situation in which PAu^+ is pinched between the two PZn units. The interconversion between the situations [(a) and (b)] implies a half-turn rotation of the threaded fragment (axle) within the ring (wheel), the latter being artificially considered as fixed. This motion is reminiscent of the process taking place in the rotary motor of ATP-synthase.[3b]

The conformation of **14** is indeed similar to what the drawing of Fig. 3 suggests. In particular, NOE effects measured on $\text{H}_{5,6}$ and H_{py} demonstrate unambiguously that a close proximity

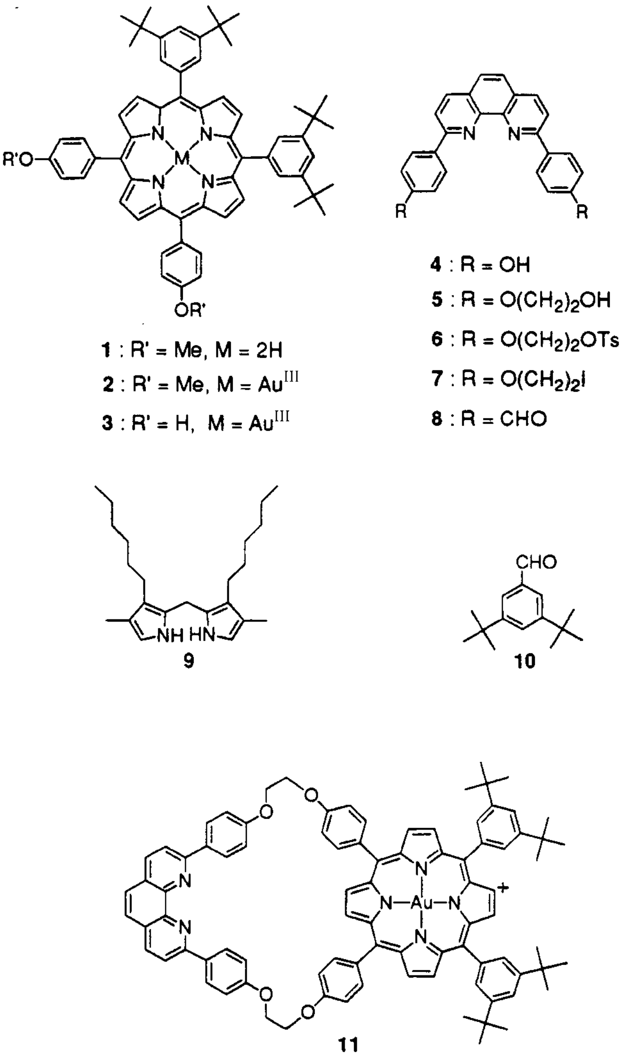

Fig. 2 Intermediates used in the synthesis of the [2]rotaxane.

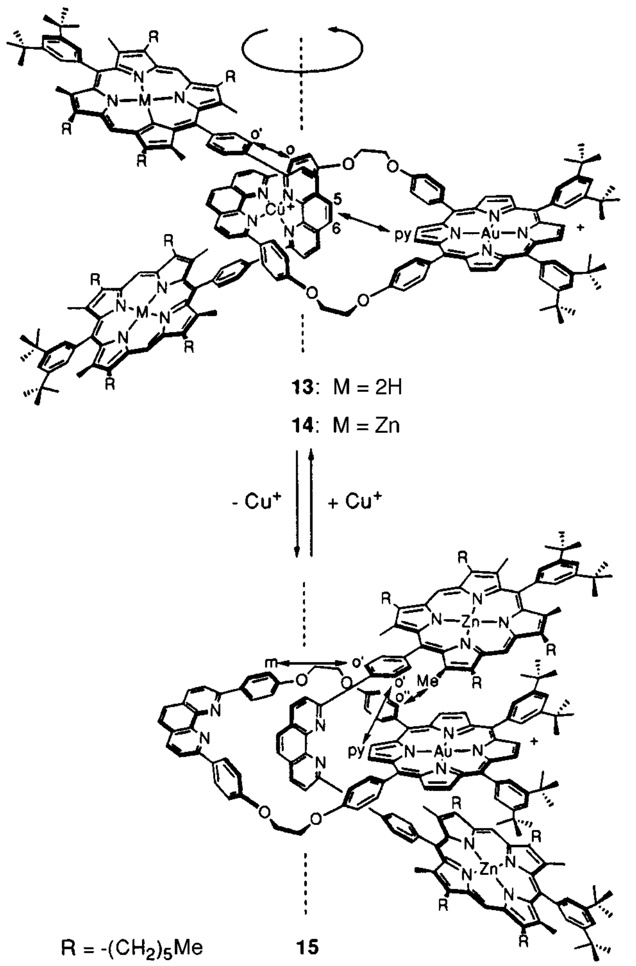

Fig. 3 Metallation–demetallation of the rotaxane induces a complete changeover of the molecule. The most important proton connectivities, as determined by 2D ^{1}H NMR, are indicated by double arrows.

exists between the rear of the 1,10-phenanthroline nucleus belonging to the dumbbell-like fragment and the endocyclic part of the ring-embedded porphyrin. As indicated in Fig. 3, demetallation of **14** affords **15**,† this compound displaying a profoundly modified geometry as compared to **14**. In particular, NOE effects show close proximity between H_m and $H_{o'}$ as well as between H_{py} and $H_{o'}$ and between $H_{o''}$ and H_{Me}, which indicates that the geometry of the molecule is roughly as depicted in Fig. 3.

Space-filling models suggest that within the demetallated rotaxane **15**, free rotation of the ‘axle’ within the ring can take place. The driving force for bringing PAu$^+$ between the PZn units, playing the role of two jaws, is certainly related to the extremely different and complementary electronic properties of PAu$^+$ (electron acceptor) and PZn (electron donor). Very approximate geometrical features can be estimated from the models. Of particular interest are the centre-to-centre (Au···Zn) and the edge-to-edge distances between PAu$^+$ and PZn. The estimated centre-to-centre separation is *ca.* 19 and *ca.* 7 Å for **14** and **15** respectively. The edge-to-edge distance, which is more relevant to electron transfer, is *ca.* 12 and *ca.* 5 Å for **14** and **15**, although it should be kept in mind that **15** is certainly very flexible, with difficult to estimate interatomic distances. Interestingly, the interconversion between **14** and **15**, although leading to dramatic geometrical changes, is quantitative and reversible. This changeover process can be triggered by other metals such as Ag$^+$ and Li$^+$.

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Notes and references

† *Selected data*: **14**: δ_H(CD_2Cl_2, 400 MHz) 10.13 (s, 4H), 9.60 (d, 2H), 9.47 (d, 2H), 9.43 (s, 2H), 9.30 (s, 2H), 8.90 (d, 2H), 8.52 (d, 2H), 8.42 (d, 4H), 8.31 (d, 2H), 8.17 (d, 4H), 8.13 (d, 4H), 8.04 (t, 2H), 7.98 (s, 2H), 7.97 (d, 2H), 7.89 (d, 4H), 7.86 (t, 2H), 7.78 (d, 4H), 7.75 (s, 2H), 7.62 (d, 4H), 7.54 (d, 4H), 6.63 (d, 4H), 4.95 (m, 4H), 4.41 (m, 4H), 3.95 (t, 8H), 3.81 (t, 8H), 2.44 (s, 12H), 2.17 (t, 8H), 2.06 (t, 8H), 1.84 (s, 12H), ≈ 1.68 (m, 16H), 1.60 (s, 36H), 1.51 (s, 36H), ≈ 1.50 (m, 16H), ≈ 1.40 (m, 16H), 0.87 (t, 12H), 0.83 (t, 12H); *m/z* (FAB) 3783.6 (M$^+$); λ(CH_2Cl_2)/nm 415, 538, 574.

15: δ_H(CD_2Cl_2, 400 MHz) 10.07 (s, 4H), 9.56 (d, 2H), 9.39 (d, 2H), 9.36 (s, 2H), 9.15 (d, 4H), 8.80 (s, 2H), 8.57 (d, 2H), 8.46 (d, 2H), 8.26 (d, 4H), 8.21 (d, 4H), 8.18 (d, 4H), 8.11 (d, 2H), 8.09 (d, 4H), 8.00 (t, 2H), 7.99 (d, 2H), 7.91 (d, 4H), 7.90 (s, 2H), 7.85 (d, 4H), 7.82 (t, 2H), 7.46 (s, 2H), 7.39 (d, 4H), 4.82 (m, 4H), 4.43 (m, 4H), 3.91 (t, 8H), 3.70 (t, 8H), 2.40 (s, 12H), 2.27 (s, 12H), 2.12 (t, 8H), 1.93 (t, 8H), 1.68 (t, 8H), 1.55 (s, 36H), 1.47 (s, 36H), ≈ 1.40 (m, 16H), ≈ 1.35 (m, 8H), ≈ 1.25 (m, 8H), ≈ 1.20 (m, 8H), 0.85 (t, 12H), 0.72 (t, 12H); *m/z* (FAB) 3720.6 (M$^+$); λ(CH_2Cl_2)/nm 413, 538, 574.

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