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A Linear Multiporphyrinic [2]-Rotaxane via Amide Bond Formation

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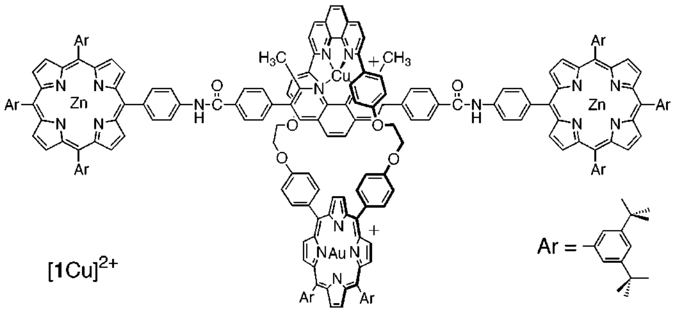
ABSTRACT


[**1**Cu]$^{2+}$

A linear multiporphyrinic [2]-rotaxane has been synthesized using the transition metal-templating method for threading a gold(III)-incorporating macrocycle onto a rodlike, phenanthroline-derived chelate bearing carboxylate end groups. Stoppering has been performed by reacting the resulting prerotaxane with the amino derivative of a zinc tetraarylporphyrin under EDC−HOBt activation. A 34% yield has been realized for this one-pot, double amide bond formation.

Rotaxanes have become very accessible compounds thanks to the many efficient template syntheses that have been discovered in the past decade.[1] Interest in these compounds has switched from synthetic exercise to the development of functional molecular systems that take advantage of the mechanical bond between the ring and the dumbbell components.[2] In particular, rotaxanes based on porphyrins (as stoppers and as elements of the macrocycle) have shown remarkable photochemical properties.[3] The molecules developed in our group are usually synthesized using transition metal-controlled threading of the macrocycle onto a stringlike fragment prior to in situ generation of the porphyrin stoppers.[4] Both organic precursors incorporate a 2,9-diphenyl-1,10-phenanthroline chelate, to enforce a tetrahedral coordination sphere on the metal center. As a result of the

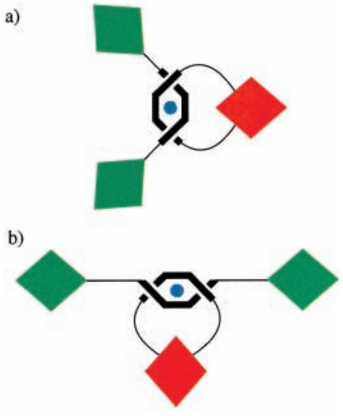


Figure 1. Schematic representations of copper(I) complexes of [2]-rotaxanes based on oblique (a) and linear (b) Zn(II) (green diamonds) bisporphyrin dumbbells and incorporating a gold(III) (red diamond) porphyrin in the ring. The bold lines represent the coordinating sites and the blue disk is a Cu^I atom.

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[1] For recent references, see: (a) Rowan, A. E.; Aarts, P. P. M.; Koutstaal, K. W. M. *Chem. Commun.* **1998**, 611. (b) Kolchinski, A. G.; Alcock, N. W.; Roesner, R. A.; Busch, D. H. *Chem. Commun.* **1998**, 1437. (c) Loeb, S. J.; Wisner, J. A. *Chem. Commun.* **1998**, 2757. (d) Hübner, G. M.; Gläser, J.; Seel, C.; Vögtle, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 383. (e) Tuncel, D.; Steinke, J. H. G. *Chem. Commun.* **1999**, 1509. (f) Chichak, K.; Walsh, M. C.; Branda, N. R.; *Chem. Commun.* **2000**, 847. (g) Buston, J. E. H.; Young, J. R.; Anderson, H. L. *Chem. Commun.* **2000**, 905.

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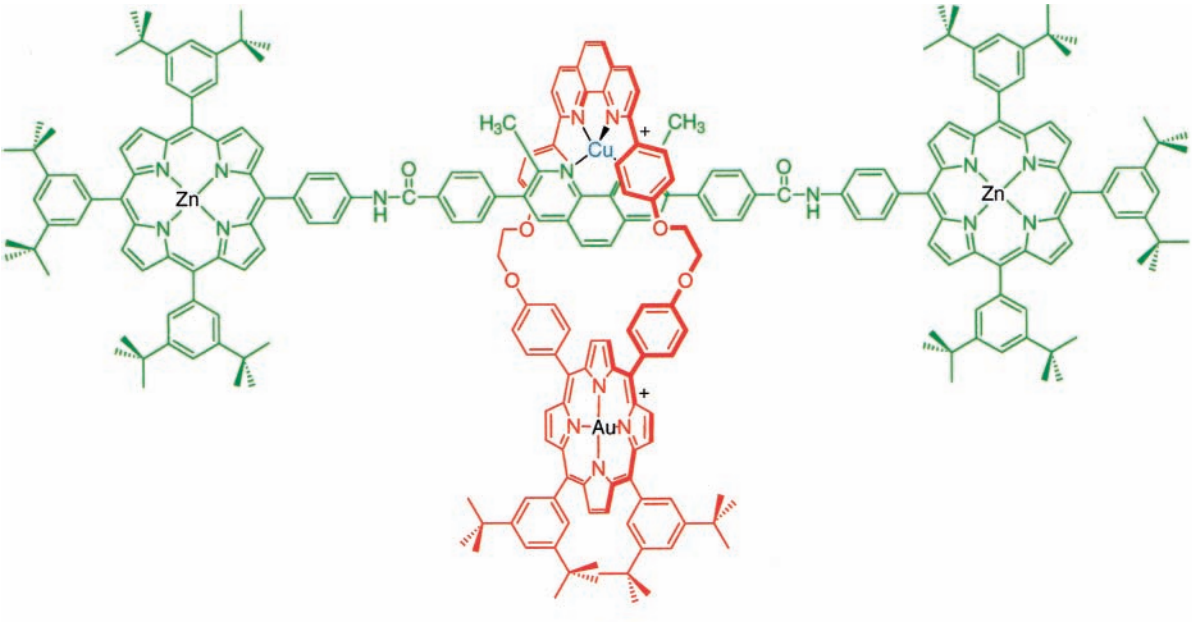

$[\mathbf{1}Cu]^{2+}$

Figure 2. Chemical structure of the copper(I) complex $[\mathbf{1}Cu]^{2+}$ of [2]-rotaxane $\mathbf{1}^{+}$.

2,9-disubstitution of the phenanthroline nuclei, the porphyrin stoppers display oblique orientations with respect to each other, as shown schematically in Figure 1a. This geometrical property was essential in the design of reaction center mimics.[5]

In this Letter, we report on the synthesis of a zinc(II) porphyrin-stoppered [2]-rotaxane built from a linear thread component in order to maximize the distance between the stoppers and a gold(III) porphyrin-incorporating macrocycle, as shown schematically in Figure 1b.

The structural formula of the Cu^{I} complex $[\mathbf{1}Cu]^{2+}$ of [2]-rotaxane $\mathbf{1}^{+}$ of this study is depicted in Figure 2. This molecule was designed according to the following features: (i) The linear arrangement of the porphyrin termini is achieved by connecting them through a sequence of spacers to the positions 3 and 8 of the threading phenanthroline chelate. (ii) 2,9-Dimethyl substitution of the same chelate allows one to strictly control the coordination geometry of the metal template (Cu^{I}). (iii) Amide bonds were chosen as connections between the phenylene spacers attached respectively to the porphyrin stoppers and to the central chelating piece of the molecular thread for the rigidity imparted by their partial double bond character.

Synthetic routes to the key intermediates phenanthroline **8** and porphyrin **11** are shown in Figures 3 and 4, respectively. Macrocycle **12**PF_6 (Figure 4) was prepared as

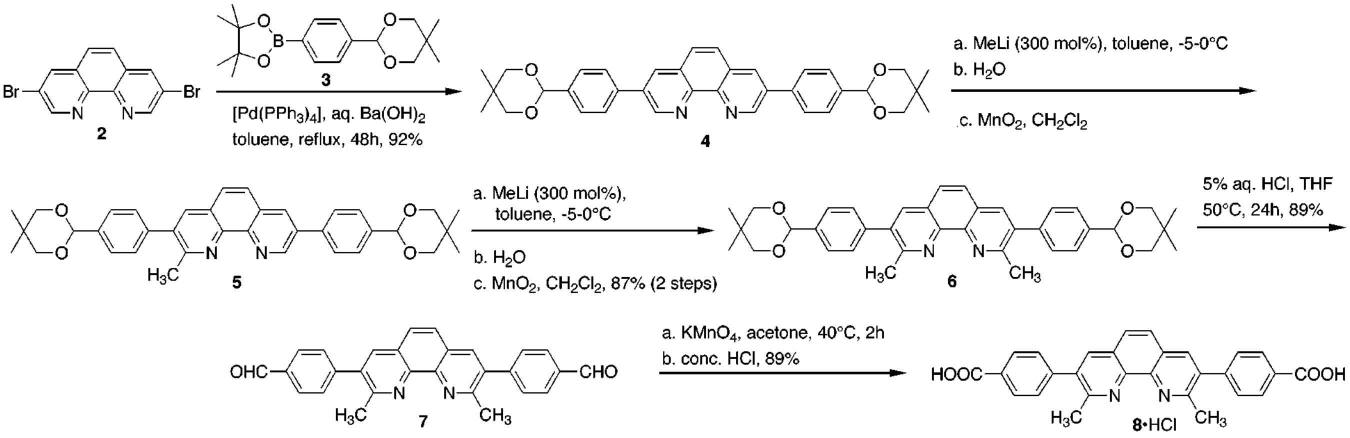

Figure 3. Synthesis of the rod component **8**·HCl.

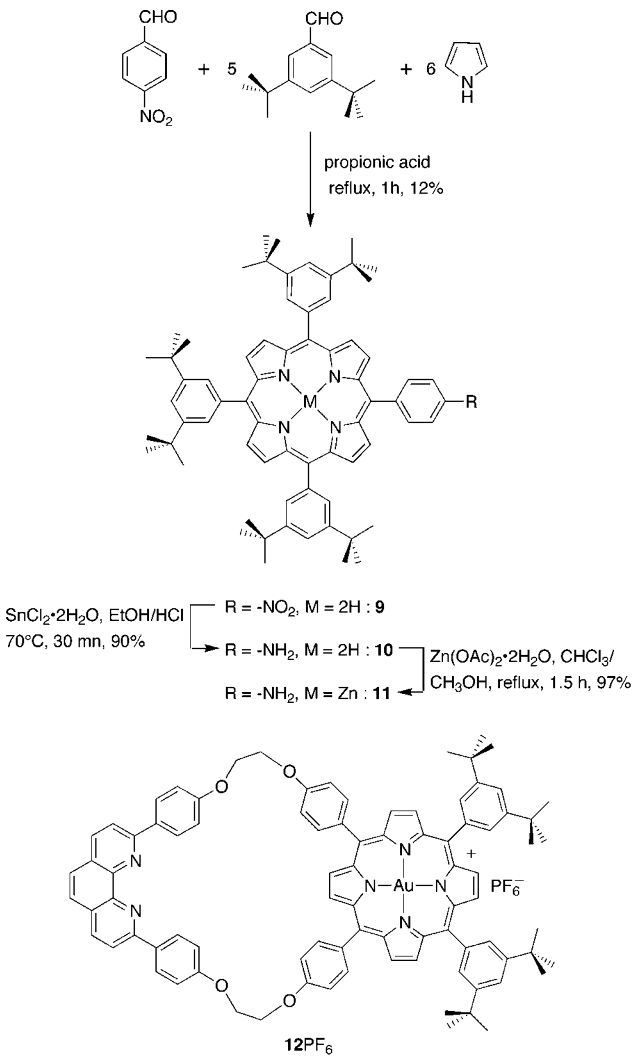

Figure 4. The porphyrin intermediates of [2]-rotaxane $\mathbf{1}^+$.

described in ref 4. Phenanthroline **8** was synthesized as follows. Double Suzuki cross-coupling of 3,8-dibromo-1,10-phenanthroline **2**[6] with *p*-(5,5-dimethyl-1,3-dioxan-2-yl)-phenylpinacylborate **3**[7] ([Pd(PPh$_3$)$_4$], toluene, reflux) using Ba(OH)$_2$ as a base to minimize the competitive deboronation reaction[8] afforded **4** in 92% yield. Dimethylation leading to

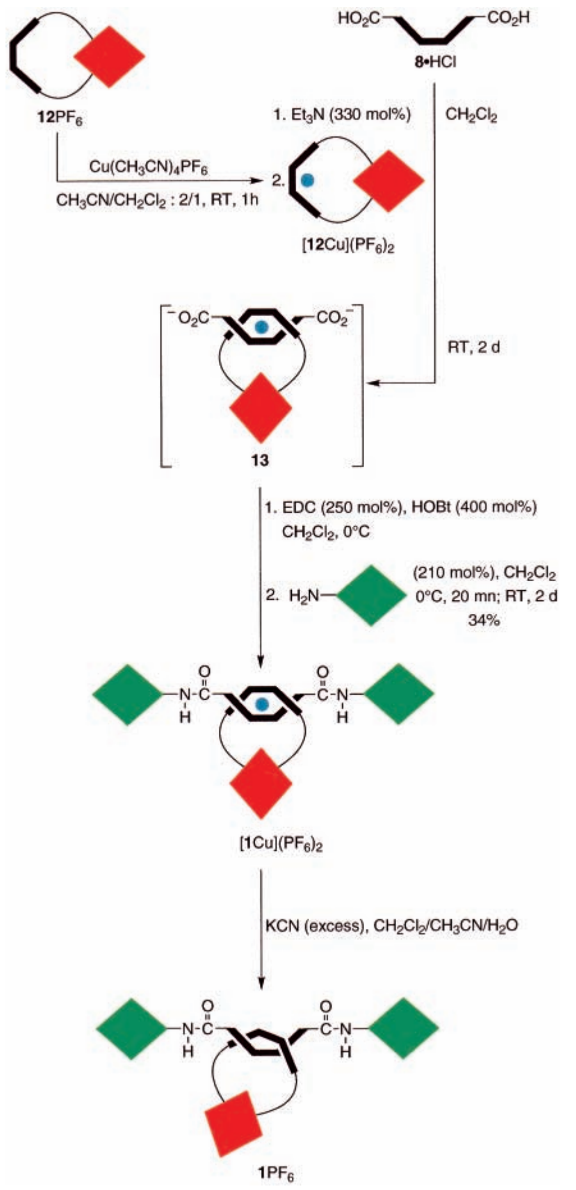

Figure 5. Copper(I)-templated strategy and synthetic steps for the preparation of [2]-rotaxane $\mathbf{1}^+$, using schematic representations for the different compounds (see legend of Figure 1 for the key).

6 was carried out in a stepwise manner.[9] Addition at 0 °C of a 3-fold excess of MeLi to **4** followed by hydrolysis and MnO$_2$ oxidation provided the monomethylated phenanthroline derivative **5**, which was treated similarly, affording, after purification, the disubstituted compound **6** in 87% overall yield. HCl cleavage of the acetal groups produced dialdehyde **7** in 89% yield. The target diacid **8** was obtained in 89% yield as the hydrochloride salt by KMnO$_4$ oxidation in acetone followed by HCl precipitation. 5,10,15-Tris(3,5-di-*tert*-butylphenyl)-20-(4-nitrophenyl)porphyrin **9** was prepared

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by following the method of Adler and Longo,[10] by reaction of 4-nitrobenzaldehyde, 3,5-di-*tert*-butylbenzaldehyde,[11] and pyrrole in refluxing propionic acid, and isolated in 12% yield after chromatography. Reduction of **9** with $SnCl_2$ in the presence of HCl in EtOH at 70 °C afforded the aminoporphyrin derivative **10** in 90% yield. Its zinc complex (**11**) was obtained in 97% yield by reaction with $Zn(OAc)_2 \cdot 2H_2O$ in refluxing $CHCl_3$/MeOH.

Figure 5 shows the strategy for rotaxane construction and the synthetic route that has been followed to prepare [2]-rotaxane **1**PF_6. Effective copper(I)-templated threading to form prerotaxane **13** was observed only upon reaction of the dicarboxylate form of **8**, generated by treating **8**·HCl with Et_3N (330 mol %), with the copper complex of macrocycle **12**PF_6, prepared by reaction of **12**PF_6 with $Cu(CH_3CN)_4PF_6$ in stoichiometric amounts. The stoppering reaction was performed by coupling zinc aminoporphyrin **11** with in situ activated prerotaxane **13**. 1-Hydroxybenzotriazole (HOBt)[12] and 1-ethyl-3-(3-dimethylamino)propylcarbodiimide (EDC)[13] were used as mild coupling reagents for the formation of the activated ester. Accordingly, to a solution of **13** at 0 °C were sequentially added EDC (250 mol %), HOBt (400 mol %), and zinc aminoporphyrin **11** (210 mol %). After 2 days at room temperature, anion exchange with KPF_6, and chromatographic purification, copper(I)-complexed [2]-rotaxane [**1**Cu]$(PF_6)_2$ was obtained in 34% yield. The true rotaxane species **1**PF_6 was obtained by reaction of the Cu^I complex with excess of KCN.

Photoinduced electron-transfer properties of [2]-rotaxane **1**$^+$, its copper complex **1**Cu^+, and those of related compounds are under investigation and will be reported in due course.

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