

A Rotaxane with Two Rigidly held Porphyrins as Stoppers

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A rotaxane with two rigidly held porphyrins as stoppers is synthesized by a copper(I)-based template strategy.

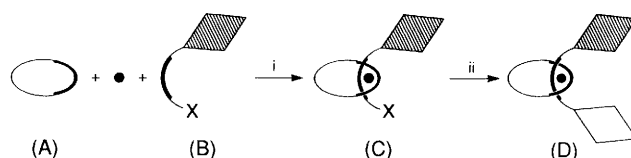
Although rotaxanes are topologically much less interesting than catenanes and knots owing to the planarity of their molecular graph,^{1,2} they have been the subject of intense interest for decades. In fact, the chemical nature of rotaxanes is close to that of catenanes in that two non-covalently linked components are forced to stay together as long as no chemical bond is cleaved. In the past, organic rotaxanes have been prepared by statistical threading³⁻⁴ or by following a directed route.⁵ The bulky groups used were triphenyl (or aryl) methyl. Another approach utilises cyclodextrins threaded by a molecular string both ends of which are linked to voluminous transition metal complexes preventing unthreading.⁶ The most recent syntheses are based on template effects induced by electron donor-acceptor stacks⁷ or transition metals.⁸ The latter approach is derived from the strategy we have developed for making catenanes and knots.²

Till now, the two end-functions (stoppers) used had no other role than preventing the acyclic ribbon from being threaded out from the cycle. The use of electro- and/or photo-active species is a promising extension, allowing preparation of multicomponent molecular systems displaying novel electronic and photochemical properties. We now report the synthesis of such a rotaxane assembled *via* the copper(I) templated approach and bearing two different porphyrins as chemical stoppers. The principle of the strategy is indicated in Scheme 1.

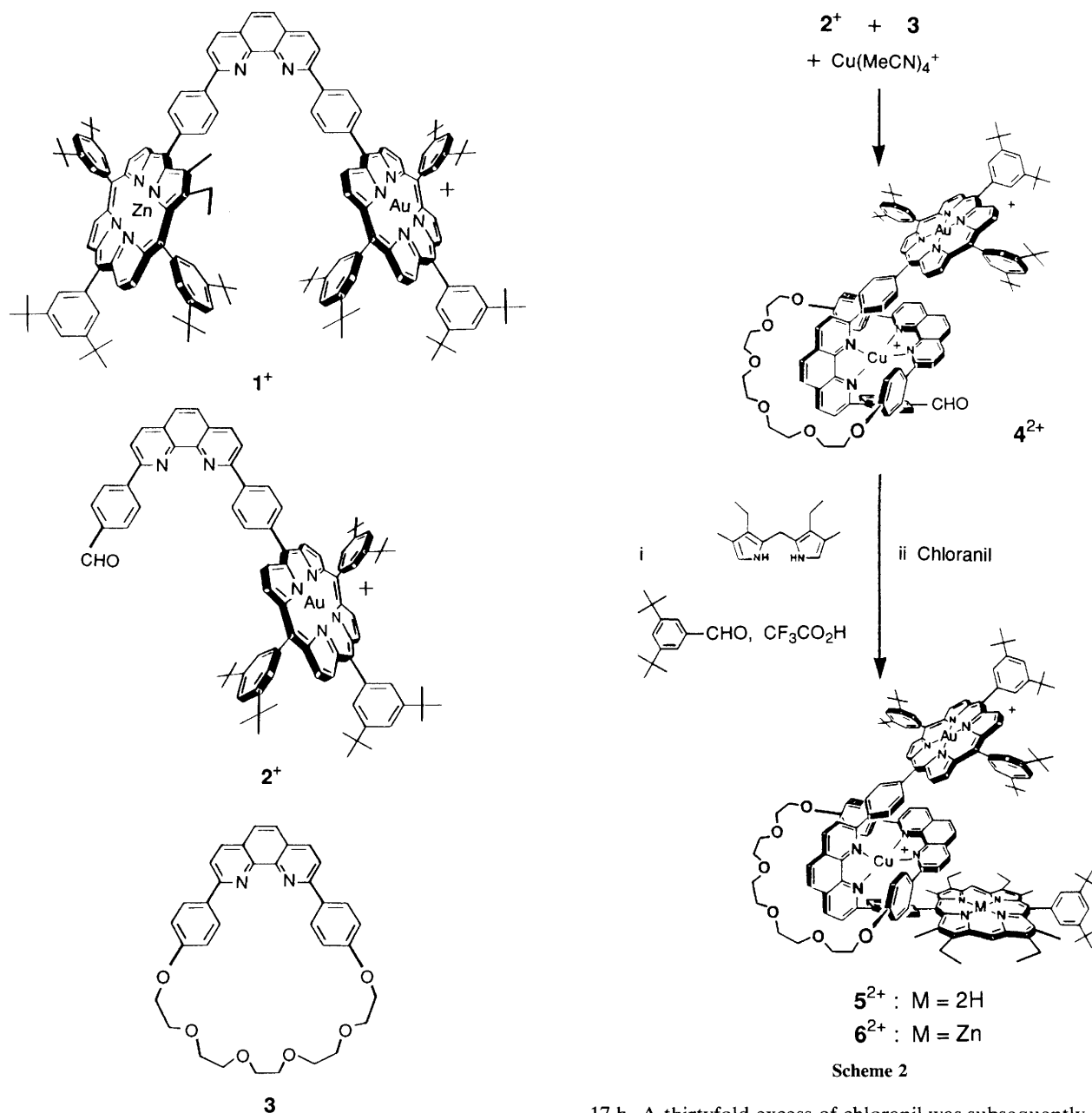
Rigid bis-porphyrins with a 2,9-diphenyl-1,10-phenanthroline spacer have recently been prepared as models of photosynthesis.⁹ The most representative example is **1**⁺. It consists of zinc(II)- and gold(III)-containing porphyrins

arranged in oblique fashion. Photoinduced intramolecular electron transfer between the zinc(II) and the gold(III) porphyrins within **1**⁺ or its cluster assembled on copper(I) have been shown to occur¹⁰ within picoseconds, with the possible contribution of a 'superexchange' mechanism involving aromatic parts located between the porphyrin nuclei. The bis-porphyrin rotaxane **6**²⁺ represents a modular system in which the electronic properties of the groups or of the medium through which the electron is supposed to travel can be tuned at will by demetallating the tetrahedral site or recomplexing it by a selected metal.

The various compounds made and the reactions leading to the rotaxane **6**²⁺ are shown in Scheme 2. Stoichiometric amounts of **2**⁺·BF₄^{-12,13} and Cu(MeCN)₄⁺·BF₄⁻ were mixed



Scheme 1 i, The macrocycle (A) incorporating a coordinating fragment (thick line) interacts with a metal centre (black circle) and an asymmetrical open chain chelate (B) bearing *one* porphyrin and a precursor function X to form the threaded intermediate (C); ii, the second porphyrin ring is then constructed affording the transition metal complex-rotaxane (D)



in MeCN-CH₂Cl₂ (1:3) at room temperature under argon, leading to quantitative formation of **4** as a deep-red solid.†

Formation of the second porphyrin was carried out using Lindsey's method.¹⁴ 3,5-Di-*tert*-butylbenzaldehyde¹⁵ (0.8 mmol), 3,3'-diethyl-4,4'-dimethyl-di-2-pyrromethane¹⁶ (1 mmol) and **4²⁺**·2BF₄⁻ (0.1 mmol) were mixed in degassed CH₂Cl₂ at room temperature under argon. After addition of a threefold excess of CF₃CO₂H, the mixture was stirred for

† Characterization of the new compounds: **4²⁺**·2BF₄⁻ ¹H NMR (200 MHz, CD₂Cl₂): δ 9.59 (1H, s); 9.35 (4H, s); 9.27 (2H, d); 9.09 (1H, d); 8.76 (2H, d); 8.73 (1H, d); 8.62 (1H, d); 8.46 (2H, d); 8.45 (1H, d); 8.39 (1H, d); 8.31 (1H, d); 8.10 (4H, d); 8.08 (2H, d); 8.03 (2H, t); 8.02 (2H, d); 7.98 (2H, d); 7.98 (1H, t); 7.77 (2H, s); 7.76 (2H, d); 7.52 (4H, d); 7.47 (2H, d); 6.93 (2H, d); 6.17 (4H, d); 3.91 (4H, s); 3.79 (4H, m); 3.69 (8H, m); 3.60 (4H, m); 1.59 (36H, s); 1.54 (18H, s).

5²⁺·2PF₆⁻ ¹H NMR (400 MHz, CD₂Cl₂): 10.19 (2H, s); 9.34 (2H, d); 9.33 (2H, d); 9.28 (2H, d); 9.13 (1H, d); 8.98 (1H, d); 8.65 (1H, d); 8.57 (2H, d); 8.49 (1H, d); 8.43 (2H, d); 8.41 (1H, d); 8.36 (1H, d); 8.15 (4H, d); 8.10 (4H, d); 8.09 (2H, d); 7.99 (1H, d); 7.98 (2H, d); 7.96 (2H, d); 7.90 (2H, d); 7.89 (1H, t); 7.61 (4H, d); 7.60 (2H, d); 7.46 (2H, d); 7.43 (2H, s); 6.26 (4H, d); 4.00 (4H, q); 3.95 (4H, s);

17 h. A thirtyfold excess of chloranil was subsequently added and the deep red-orange solution was refluxed for 1.5 h. After work-up, anion exchange (PF₆⁻) and several chromatographic separations (silica; 0.2–2% MeOH in CH₂Cl₂), a 25% yield of

3.87 (4H, q); 3.80 (4H, t); 3.77 (4H, t); 3.64 (4H, t); 3.59 (4H, m); 2.47 (6H, s); 1.85 (6H, s); 1.75 (6H, t); 1.65 (6H, t); 1.55 (18H, s); 1.53 (36H, s); 1.52 (18H, s); -2.60 (2H, br s). ES-MS: molecular weight calc. for [**5²⁺**, 2PF₆⁻] = 2985.75; characteristic ions found (*m/z*): [**5²⁺**] = 1348.4 (calc.: 1347.9); [**5²⁺** + H⁺] = 897.5 (calc.: 898.9). UV-VIS (MeCN) λ_{max}/nm, ε/mol l⁻¹ cm⁻¹: 243 (73500 sh), 308 (50400), 413 (382000), 507 (19700), 523 (19200), 623 (1700), 649 (800 sh).

6²⁺·2PF₆⁻ ¹H NMR (400 MHz, CD₂Cl₂): δ 10.12 (2H, s); 9.35 (4H, d); 9.30 (2H, d); 9.13 (1H, d); 8.97 (1H, d); 8.65 (1H, d); 8.60 (2H, d); 8.48 (1H, d); 8.46 (2H, d); 8.40 (1H, d); 8.36 (1H, d); 8.16 (2H, d); 8.13 (2H, d); 8.11 (4H, d); 8.09 (2H, d); 7.98 (1H, t); 7.98 (2H, d); 7.96 (2H, d); 7.89 (2H, d); 7.86 (1H, t); 7.62 (4H, d); 7.60 (2H, d); 7.45 (2H, d); 7.44 (2H, s); 6.25 (4H, d); 3.99 (4H, q); 3.94 (4H, s); 3.84 (4H, q); 3.80 (4H, t); 3.77 (4H, t); 3.64 (4H, t); 3.58 (4H, m); 2.44 (6H, s); 1.80 (6H, s); 1.75 (6H, t); 1.65 (6H, t); 1.55 (18H, s); 1.53 (36H, s); 1.51 (18H, s). FAB-MS (NBA matrix): molecular weight calculated for [**6²⁺**, 2PF₆⁻] = 3049.12, characteristic ion found (*m/z*): [**6²⁺**] = 2757.7 (calc. 2759.2). UV-VIS (MeCN) λ_{max}/nm, ε/mol l⁻¹ cm⁻¹: 244 (90700 sh); 320 (68600); 413 (678000); 538 (32000); 573 (9600).

$5^{2+} \cdot 2PF_6^-$ (73 mg) was obtained.† Besides the desired compound $5^{2+} \cdot 2PF_6^-$, substantial amounts (~0.1 g) of the expected monoporphyrin 5,15-di(3',5'-di-*tert*-butylphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin were formed and isolated.

Assuming that the gold(III) porphyrin is inert towards demetallation, 5^{2+} contains two potentially tunable coordination sites. The porphyrin ring was indeed quantitatively metallated using zinc(II) acetate (CH_2Cl_2 -MeOH 3:1; reflux for 1.5 h under argon). Compound $6^{2+} \cdot PF_6^-$ was obtained as a cherry-red crystalline solid after column chromatography (alumina; 0.3-0.5% MeOH in CH_2Cl_2).†

The tetrahedrally coordinated copper(I) centre should easily be removed (CN^- for instance) and replaced by an appropriate metal.² Selective and controlled binding of metals at either coordination site will be possible thanks to the very different complexing properties of a porphyrin (square planar, five- or six-coordinate; oxidation states >2) or the neutral coordination site provided by two entwined 2,9-diphenyl-1,10-phenanthroline chelates (pseudotetrahedral; low oxidation states).

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- 11 Note that compounds 5^{2+} and 6^{2+} are not 'free' rotaxanes, as long as Cu^I has not been removed. Recent work showed that the 'free' rotaxane is indeed stable and does not undergo an unthreading process under normal conditions.
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