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Multiporphyrin [2]-rotaxanes and [3]-catenates via copper(I)-templated synthesis

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Summary – Condensation of dipyrrylmethane units onto a copper(I) complex, in which a diphenylphenanthroline ligand bearing aldehyde functions is threaded into a phenanthroline-containing macrocycle, afforded a copper(I)-complexed bis-porphyrin-stoppered [2]-rotaxane or a bis-porphyrin-bridged [3]-catenate, depending on whether a second, aromatic aldehyde was added to the reaction mixture or not. The isolated yields were 18 and 5% respectively. In a separate experiment, a macrocyclic compound identical to the central ring of the [3]-catenate (46-membered ring) has also been synthesized in 28% yield.

rotaxane / catenate / porphyrin / template synthesis

Introduction

Multiporphyrin systems are especially promising in relation to photoinduced electron transfer and mimicking of the photosynthetic reaction center (RC) function [1]. A large body of dimeric, trimeric, and so on, covalently linked arrays of porphyrins in cofacial or oblique arrangements have been synthesized in order to imitate the relative arrangement of the chlorophyll-like chromophores in the bacterial RC [2]. For example, several porphyrin cofacial dimers [3] have been designed as models of the so-called special pair of bacteriochlorophylls, which is the primary electron donor [4].

Recently, porphyrin units have been incorporated in topologically complex molecules, such as rotaxanes [5] and catenanes [6]. In particular, copper(I)-complexed rotaxanes turned out to be remarkably useful in the study of interporphyrin electron-transfer process [7] (Zn(II) porphyrin as donor in the excited state, and Au(III) porphyrin as acceptor) aimed at simulating the primary charge separation step occurring between the special pair (donor) and the bacteriopheophytin (acceptor) in the bacterial RC [8].

In order to generalize the results obtained on our first porphyrin-stoppered [2]-rotaxane, we investigated on the possibility of using porphyrin formation reactions for making symmetrical [2]-rotaxanes and [3]-catenates in one-pot syntheses.

Results

Rotaxanes are molecules in which a molecular dumbbell is threaded into a macrocycle, the stoppers being bulky enough to prevent unthreading of the acyclic fragment from the macrocycle (fig 1). Since the late sixties, different strategies were developed for the synthesis of such molecules *eg* statistical [9] or directed [10]. The procedure that we have developed for making rotaxanes relies on the template effect of copper(I), which was previously used for the synthesis of catenanes [11]. A generalization of this strategy is schematically represented in figure 2, route (i); both porphyrin stoppers are assembled in a single step. The structural formulae of the different reactants and precursors are depicted in figure 3. According to a procedure derived from the methodology recently reported by Lindsey *et al* [12], the porphyrins are formed by condensation of dipyrrylmethane **4** on bis-aldehyde **2** bridged by a 2,9-diphenyl-1,10-phenanthroline spacer and threaded into macrocycle **1**. Both species are held together by coordination of copper(I). The terminal aldehyde is a substituted benzaldehyde **3**. We reasoned that if the prerotaxane bis-aldehyde $\mathbf{5}^+$ was condensed with dipyrrylmethane **4** only, then a bis-copper(I) [3]-catenate could be obtained, as indicated in figure 2, route (ii), in spite of expected strain in the central cycle to be constructed (46-membered conjugated ring).

The compounds synthesized in this study are represented in figures 4 and 5.

To a pale-yellow solution of macrocycle **1** [11] in dichloromethane was added a colorless solution of $Cu(CH_3CN)_4PF_6$ [13] in acetonitrile, producing a color change of the solution to bright-orange. This indicated coordination of Cu(I) to the phenanthroline chelate of **1**. A slurry of dialdehyde **2** [14] in dichloromethane was then added to the reaction mixture and the color of the solution turned dark-red, indicating that the diphenylphenanthroline (dpp)-like fragment **2** had

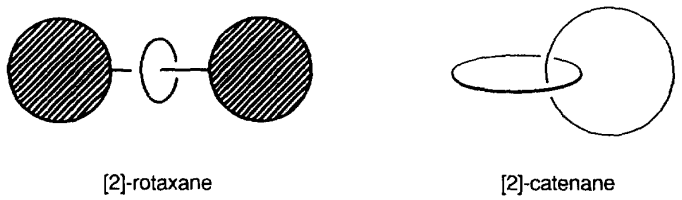


Fig 1. Schematic views of a [2]-rotaxane and a [2]-catenane.

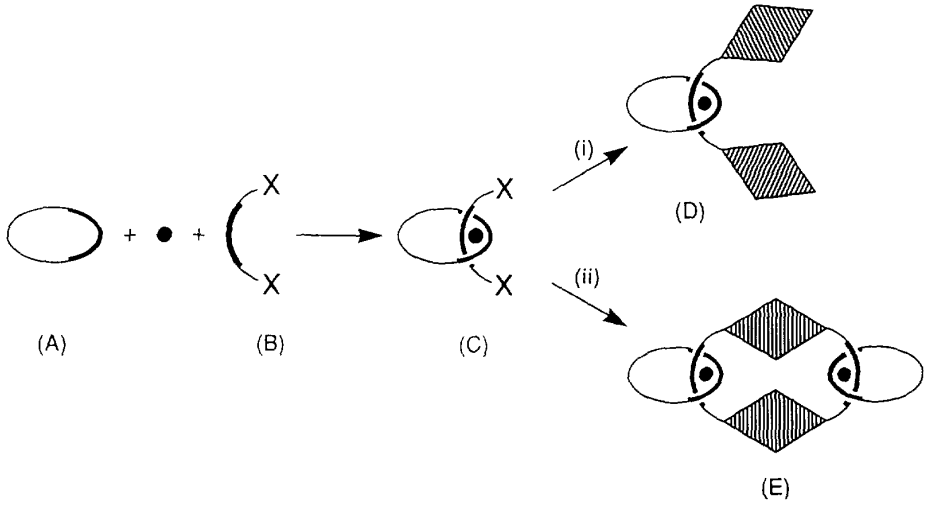


Fig 2. Principle of synthesis of bis-porphyrin-stoppered [2]-rotaxanes and bis-porphyrin-bridged [3]-catenates. The macrocycle (A) incorporating a coordinating fragment (thick line) interacts with a metal center (black circle) and a symmetrical open-chain chelate (B) bearing precursor functions X to form the threaded intermediate (C). The porphyrin rings are constructed, affording either the transition metal-complexed [2]-rotaxane (D) or the transition metal-complexed [3]-catenate (E).

threaded into macrocycle **1** by coordination to copper(I), affording $\mathbf{5}^+$ (PF_6^-). This intermediate complex was obtained quantitatively and was characterized by proton NMR spectroscopy. The aromatic region of the spectrum of the crude complex is shown in figure 6a. As discussed below, protons 5 and 6 of the macrocycle-incorporated phenanthroline turned out to be precious probes for evidencing porphyrin-based rotaxane and catenate structures. These protons shift to lower field when the ligands are entwined around copper(I) [15]. For example, in the case of the catenate made up with two interlocked macrocycles **1**, protons 5 and 6, which are equivalent, shift from 7.79 ppm in the free macrocycle to 8.28 ppm in the catenate [11]. In threaded complexes [16], protons 5 and 6 of the threaded phenanthroline are less shielded than those of the macrocycle-included phenanthroline. Therefore it is reasonable to attribute the singlet at 8.35 ppm to the protons 5 and 6 of the threaded bis-aldehyde **2** (7.89 ppm in the free ligand) and the other singlet at 7.91 ppm to their homologues in macrocycle **1** (7.79 in the free macrocycle) (fig 6a).

One-pot synthesis of a Cu(I)-complexed [2]-rotaxane, $\mathbf{6}^+$ *(*PF_6^-*)*

Following strategy (i), prerotaxane $\mathbf{5}^+$ (PF_6^-) was reacted with 3,5-di-*tert*-butylbenzaldehyde **3** [14] and 3,3′-diethyl-4,4′-dimethyl-2,2′-methylene-bis-1*H*-pyrrole **4** [17] in presence of trifluoroacetic acid. After equilibration to the porphyrinogen species, the reaction mixture was treated with *p*-chloranil. Copper(I)-complexed [2]-rotaxane $\mathbf{6}^+$ (PF_6^-) was isolated in 18% yield (*ie* above 40% yield per single porphyrin formation) by chromatography. As expected, the reaction also produced amounts of **7** (fig 4). The structure of rotaxane $\mathbf{6}^+$ (PF_6^-) was demonstrated by electrospray mass spectrometry (ES-MS) and proton NMR spectroscopy. The mass spectrum shows the molecular peak corresponding to the ion $\mathbf{6}^+$ at m/z = 2 291.42 and the peaks corresponding to the doubly and triply charged ions $M^+ + H^+/2$ and $M^+ + 2H^+/3$ at m/z = 1 146.46 and 764.29 respectively. Since anchoring of porphyrins onto diphenylphenanthroline shifts the signal of protons 5 and 6 downfield, the singlet at 8.57 ppm in $\mathbf{6}^+$ is likely to originate from the dumbbell phenanthroline

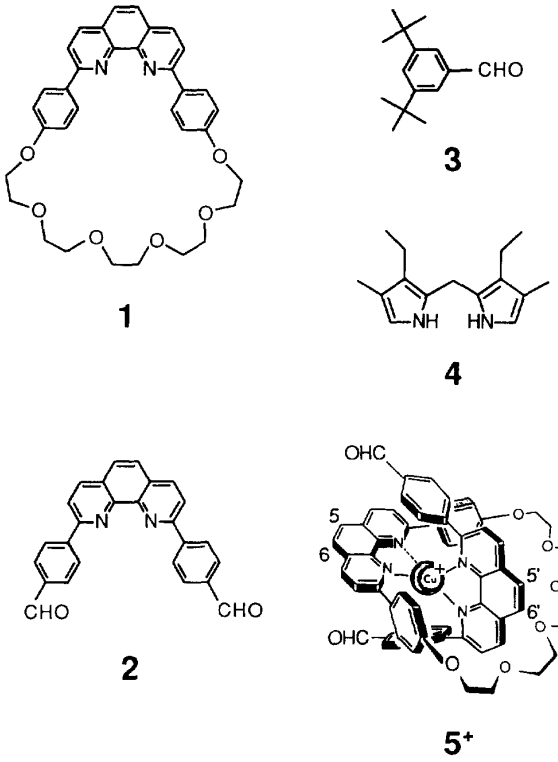


Fig 3. Structural formulae of the organic precursors, and the threaded, macrocyclic copper(I) complex $\mathbf{5}^+$, precursor to both the [2]-rotaxane and the [3]-catenate.

($\Delta\delta$ = 8.57-8.35 = 0.22 ppm). The remaining singlet at 7.54 ppm arises from protons 5 and 6 of macrocycle-included phenanthroline. These protons are thus shifted upfield by 7.54-7.91 = −0.37 ppm when compared to their homologues in the threaded precursor $\mathbf{5}^+$ (fig 6b). This is certainly due to the fact that they now lie in the highly shielding field of the porphyrin substituents [5] (see fig 4).

One-pot synthesis of a Cu(I)-complexed [3]-catenate $\mathbf{8}^{2+}$ $(PF_6^-)_2$

Following strategy (ii) in figure 2, precatenate $\mathbf{5}^{2+}$ $(PF_6^-)_2$ was then reacted with only dipyrrylmethane **4** in the presence of trifluoroacetic acid. Oxidation of the porphyrinogen species with *p*-chloranil followed by workup and repeated chromatographic purification of the product afforded Cu(I)-complexed [3]-catenate $\mathbf{8}^{2+}$ $(PF_6^-)_2$ in nearly 5% yield. The compound was characterized by ES-MS and proton NMR spectroscopy. The ES-MS spectrum shows only the peak calculated for $M^{2+}/2$ at m/z = 1 486.85. This is sufficient to ascertain that $\mathbf{8}^{2+}$ is a [3]-catenate and not a higher order catenate. The proton NMR spectrum was interpreted using a 2D ROESY experiment. It shows two well-separated singlets which can be assigned to protons 5 and 6 of each type of phenanthroline : the signal at 8.56 ppm is likely to be due to the phenanthroline included in the central bis-porphyrin macrocycle, by comparison with the signal observed for the dumbbell phenanthroline in

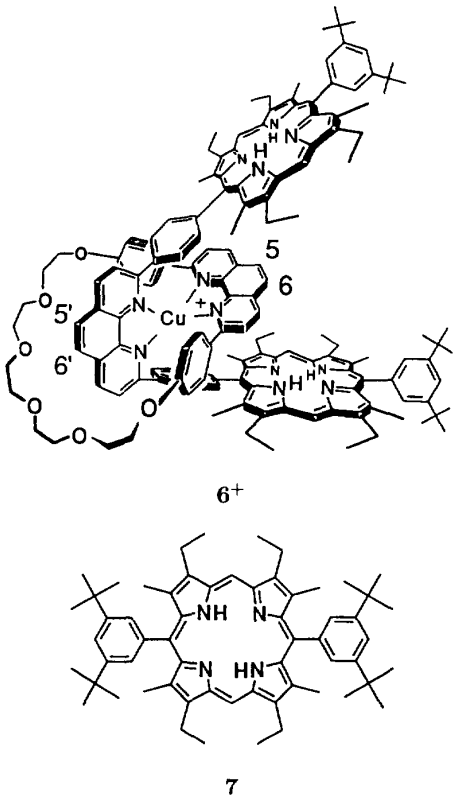
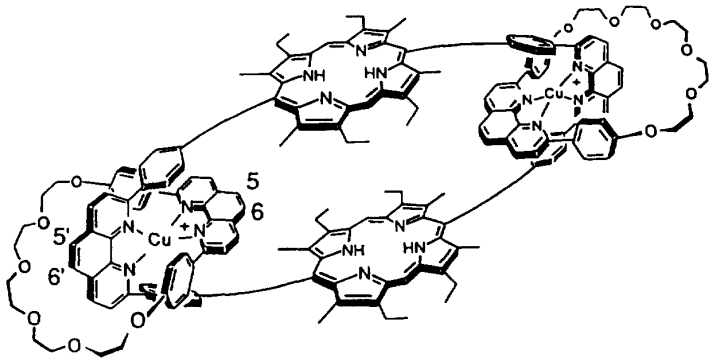


Fig 4. Representation of bis-porphyrin-stoppered copper(I)-complexed [2]-rotaxane $\mathbf{6}^+$ together with by-product **7**.

[2]-rotaxane $\mathbf{6}^+$ (8.57 ppm). Thus, the singlet at 7.31 ppm can be assigned to protons 5 and 6 of the phenanthroline included in the smallest, peripheral cycle **1** (fig 6c). The protons are more strongly shielded than their homologues in $\mathbf{6}^+$, from which a signal arises at 7.54 ppm. Compared to precatenate $\mathbf{5}^+$, the shift is now 7.31-7.91 = −0.60 ppm. This may be easily rationalized by the fact that in [3]-catenate $\mathbf{3}^{2+}$, the porphyrins belonging to the inner, largest macrocycle, are compelled to be closer to one another than in [2]-rotaxane $\mathbf{6}^+$, thus sandwiching more efficiently the phenanthrolines of the outer, smallest rings. In addition, these large aromatic intercalated units seem to shield the porphyrin meso (10.12) and NH (−2.82 ppm) protons which have moved upfield by comparison with their homologues in monomeric model compound **7** (10.28 and −2.37 ppm respectively).

Preparation of a bis-porphyrin-containing macrocycle **9**

The ring identical to the inner bis-porphyrin-containing macrocycle of [3]-catenate $\mathbf{8}^{2+}$ was synthesized by reaction of dialdehyde **2** with dipyrrylmethane **4** in the presence of trifluoroacetic acid, followed by oxidation with *p*-chloranil. After usual workup and chromatographic separation, macrocycle **9** was obtained in 28% yield. It was characterized by ES-MS and proton NMR spectroscopy (*vide infra*). The mass spectrum showed three peaks corresponding to $M + H^+$, $M + 2H^+/2$ and



8^{2+}

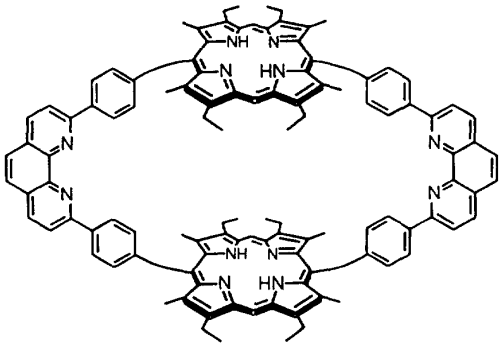


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Fig 5. Representation of bis-porphyrin-bridged copper(I)-complexed [3]-catenate 8^{2+} and bis-porphyrin-bridged macrocycle **9**.

M + $3H^+$/3 at m/z = 1 613.8, 807.8 and 528.6 respectively. The product was sparingly soluble in chlorofom. Fortunately, its proton NMR spectrum could be run in CF_3CO_2D with chloroform as internal standard.

Discussion

Face-to-face bis-porphyrins : comparison with other face-to-face dimeric porphyrins

Many face-to-face dimeric porphyrins have been described in the literature [18]. In several cases, the resulting molecule has a macrocyclic superstructure [19]. In a few instances, however, the latter was generated by porphyrin formation [20], rather than by cyclizing porphyrin-containing building blocks. The yields are generally very low, *ie ca* 5%. By contrast, the 28% yield for the obtention of macrocycle **9** is remarkable. In this 46-membered ring, and in [3]-catenate 8^{2+}, the porphyrin rings are forced to be more or less parallel to each other, whereas in [2]-rotaxane 6^{2+}, the same porphyrin nuclei are likely to adopt an oblique orientation. Indeed, as shown by X-ray single crystal analysis [21], the angle between the two porphyrin planes is very close to the theoretical value of 60°. Thus, it is expected that in macrocycle **9** as well as in [3]-catenate 8^{2+}, either bending of the phenyl bridging groups or porphyrin ruffling takes place. The deformation of the porphyrin skeleton in response to strain can be detected, for example, by the red shift of the Q bands [22]. In fact, the visible spectra of Cu(I)-[2]-rotaxane 6^+ and Cu(I)-[3]-catenate 8^{2+} are very similar, the Q bands pointing at 507, 540, 573 and 624-625 nm in CH_2Cl_2. These wavelengths are also those of the maxima recorded for model porphyrin **7** (507, 540, 573 and 626 nm). In contrast, the Q bands of free macrocycle **9** are red shifted by *ca* 4 nm, since they appear at 511, 545, 577 and 629 nm. This shift is small. However, it may indicate that the porphyrin backbones are distorted from planarity. Surprisingly, no distortion of the porphyrin rings could be detected by UV-vis spectroscopy in Cu^+-[3]-catenate 8^{2+}. It is clear that the problem of porphyrin distortion will be best addressed by a crystal structure analysis.

A remarkable property of several face-to-face porphyrin dimers is the possibility that an electronic interaction between the two tetrapyrrolic macrocycles is established, leading to a red shift of the Q bands, *together with a blue shift of the Soret band* [23]. Since the latter appears at 411 nm in **9** (*vs* 409 nm for model compound **7**), there is no interaction (exciton coupling) between the two porphyrins in **9**.

Other syntheses of [3]-catenates via copper(I)-templated methods

So far, [3]-catenates have been synthesized in the laboratory using two different methodologies. The first

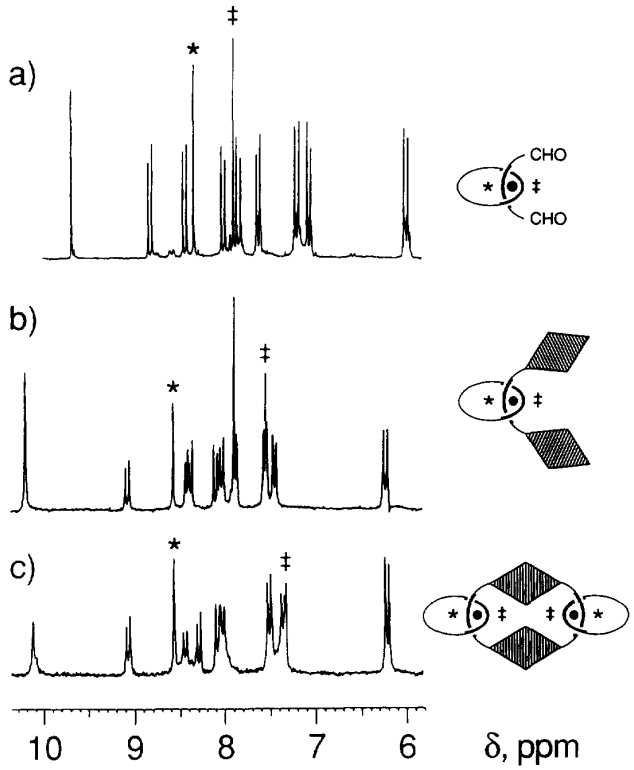

Fig 6. Proton NMR spectra (200 MHz), aromatic region of (a) crude 5^+, (b) rotaxane 6^+ and (c) catenate 8^{2+}. Protons 5, 6 (see fig 3-5) belonging to the macrocycle **1** are marked with ‡ and protons 5, 6 belonging to the phenanthroline threaded into macrocycle **1** are marked with an asterisk.

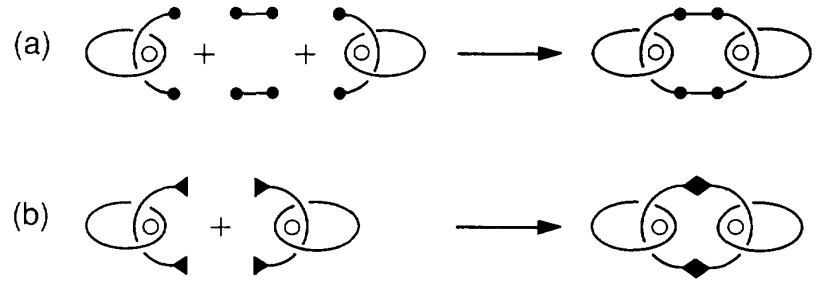

Fig 7. Strategies for the template synthesis of [3]-catenates. The transition metal disposes the two coordinating fragments (thread and macrocycle) perpendicular each other, leading to a precatenate. (a) The [3]-catenate is obtained by bridging two precatenate species with a third component. (b) The [3]-catenate is obtained by cyclodimerization of the precatenate precursor.

method developed involved a direct extension of the strategy used for the synthesis of [2]-catenates (fig 7a). If the linking fragment (represented as a dumbbell in fig 7a) used in the cyclization step is too short to allow intramolecular ring formation, dimerization leads to a [3]-catenate. The best yield, 6%, was obtained with trioxyethylene glycol fragments as bridging units [24]. It must be stressed that these reactions involve *eight* reaction centers; this might account for the low yields observed.

The second method of synthesis of [3]-catenates used an acetylenic oxidative coupling reaction, forming rigid, rod-like, diacetylenic bridging units [25]. This method is much more efficient than the first. It corresponds to a cyclo-dimerization involving four reacting centers only (fig 7b), in contrast to the former. As a matter of fact, [3]-catenates synthesized following this route were obtained in high yield, *ca* 23%. Besides [3]-catenate, formation of higher-order catenates (up to the octamer) was revealed by ES-MS analysis of fractions isolated by chromatography of the crude reaction mixture [26]. In the case of porphyrin-bridged catenates, no higher-order species could be isolated besides [3]-catenate 8^{2+}.

Conclusion

Copper(I)-complexed [2]-rotaxanes and [3]-catenates can be prepared in one-pot reactions from a com-

mon precursor. Remarkably, these reactions involve porphyrin condensation from β-substituted dipyrrylmethane in acidic conditions. Thus, porphyrin formation plays the role of the "locking" reaction in the case of rotaxane synthesis and the "topologically fixing step" in the case of catenate synthesis. As a result, porphyrins act as stoppers in the former case and as bridging units in the latter.

Experimental section

Unless otherwise stated, all the reactions were performed at a vacuum/argon line using Schlenk glassware and techniques. Dichloromethane was distilled from P_2O_5 prior to use. Dialdehyde **2** [14], macrocycle **1** [11], 3,5-di-*tert*-butyl-benzaldehyde **3** [14], and 3,3′-diethyl-4,4′-dimethyl-2,2′-methylene-bis-1*H*-pyrrole **4** [17] were prepared following literature procedures. NMR spectra were run at 200 MHz using a Bruker WP 200 SY spectrometer. ES-MS spectra were obtained from a VG BIO Q apparatus.

Preparation of $\mathbf{5}^+(PF_6^-) = Cu(\mathbf{1}, \mathbf{2})^+(PF_6^-)$

To a pale-yellow solution of macrocycle **1** (0.100 g, 1.765×10^{-4} mol) in CH_2Cl_2 (10 mL) was added a solution of $Cu(CH_3CN)_4^+PF_6^-$ (0.0643 g, 1.726×10^{-4} mol) in CH_3CN (5 mL) via canula. The resulting orange-red solution was stirred for 25 min. Thereupon, a slurry of dialdehyde **2** (0.0685 g, 1.763×10^{-4} mol) in CH_2Cl_2 (10 mL) was added via canula. The flask initially containing **2** was rinsed twice with CH_2Cl_2 (5 mL). The dark-red reaction mixture was stirred for 2.5 h. The solvents were evaported *in vacuo*. The resulting solid was redissolved in CH_2Cl_2, washed with water. The two layers were carefully separated, the solvent was evaporated with a rotary evaporator and the remaining solid vacuum-dried. As shown by TLC (SiO_2, 10% MeOH in CH_2Cl_2) the product was obtained quantitatively. Therefore it was used without purification.

^{1}H NMR (CD_2Cl_2) : 9.68 (s, 2H); 8.82 (d, 2H, J = 8.3 Hz); 8.44 (d, 2H, J = 8.4 Hz); 8.35 (s, 2H); 8.02 (d, 2H, J = 8.4 Hz); 7.91 (s, 2H); 7.85 (d, 2H, J = 8.4 Hz); 7.64 (d, 4H, J = 8.2 Hz); 7.22 (d, 4H, J = 8.7 Hz); 7.09 (d, 4H, J = 8.4 Hz); 6.03 (d, 4H, J = 8.7 Hz); 3.84 (s, 4H); 3.76-3.54 (m, 16H).

Preparation of $\mathbf{6}^+(PF_6^-)$

To a solution of $\mathbf{5}^+(PF_6^-)$ (0.491×10^{-4} mol) and 3,5-di-*tert*-butylbenzaldehyde **3** (0.0861 g, 3.95×10^{-4} mol) in CH_2Cl_2 (14 mL) was added via canula a solution of **4** (0.113 g, 4.91×10^{-4} mol) in CH_2Cl_2 (20 mL). The flask containing the dipyrrylmethane was rinsed with CH_2Cl_2 (20 mL). Then 5 drops of CF_3SO_2H were introduced and the reaction mixture stirred overnight at room temperature. Then, to the red-orange solution was added *p*-chloranil (0.7265 g, 29.5×10^{-4} mol) and the reaction mixture was refluxed for 2 h. The resulting brown-orange solution was transferred into a separatory funnel and shaked with a 10% aq. Na_2CO_3 solution (30 mL). The organic layer was washed twice with water, then concentrated to a volume of 50 mL, and finally treated with a 6.5% aq KPF_6 solution (30 mL) overnight. The organic solution was washed again twice with water and evaporated with a rotary evaporator. The desired product was isolated by column chromatography : SiO_2, 0.8% MeOH in CH_2Cl_2, then Al_2O_3, 20% hexane in CH_2Cl_2. Yield : 0.0215 g (18%).

ES-MS for $(C_{150}H_{162}N_{12}O_6)$ $CuPF_6$: m/z, found : 2 291.42, 1 146.16, 764.29. Calc : 2 292.55 (M^+), 1 146.78 ($M^+ + H^+/2$), 764.86 ($M^+ + 2H^+/3$).

^{1}H NMR (CD_2Cl_2) : 10.19 (s, 4H), 9.07 (d, 2H, J = 8.5 Hz); 8.57 (s, 2H); 8.41 (d, 2H, J = 8.3 Hz); 8.39 (d, 2H, J = 8.3 Hz); 8.11 (d, 2H, J = 8.2 Hz); 8.03 (d, 4H, J = 8.1 Hz); 7.90 (d, 4H, J = 1.8 Hz); 7.87 (d, 2H, J = 1.7 Hz); 7.55 (d, 4H, J = 8.5 Hz); 7.54 (s, 2H); 7.44 (d, 4H, J = 8.0 Hz); 6.24 (d, 4H, J = 8.6 Hz); 4.01 (q, 8H); 3.92 (s, 4H); 3.91 (q, 8H); 3.77 (t, 8H); 3.57 (t, 8H); 2.48 (s, 12 H); 1.81 (s, 12H); 1.77 (t, 12H); 1.70 (t, 12H); 1.51 (s, 36H); −2.59 (d, 4H).

UV-vis (CH_2Cl_2) : 321, 410, 507, 540, 573, 625 nm.

Preparation of $\mathbf{8}^{2+}(PF_6^-)_2$

To a solution of $\mathbf{5}^+(PF_6^-)$ (0.500 g, 4.296×10^{-4} mol) and **4** (0.2485 g, 10.8×10^{-4} mol) in CH_2Cl_2 (200 mL) were added **5** drops of CF_3CO_2H. The reaction mixture was stirred overnight at room temperature. Then *p*-chloranil (0.9642 g, 39.2×10^{-4} mol) was added and the reaction mixture heated to reflux for 1.5 h. It was subsequently treated with a 10% aq Na_2CO_3 solution, and then washed with water. The organic layer was concentrated to 100 mL and treated overnight with a 6.5% aq KPF_6 solution (100 mL). The organic layer was washed again twice with water and evaporated with a rotary evaporator. The desired product was isolated by column chromatography : SiO_2, 1.6% MeOH in CH_2Cl_2, then Al_2O_3, 0.5-0.55% MeOH in CH_2Cl_2.

Yield : 0.0325 g (4.8%).

ES-MS for $(C_{180}H_{168}N_{16}O_{12})$ $Cu_2P_2F_{12}$: m/z, found : 1 436.85. Calc : 1 437.26 ($M^{2+}/2$).

^{1}H NMR (CD_2Cl_2) : 10.12 (s, 4H); 9.06 (d, 4H, J = 8.4 Hz); 8.56 (s, 4H); 8.44 (d, 4H, J = 8.6 Hz); 8.29 (d, 4H, J = 8.3 Hz); 8.08 (d, 4H, J = 8.4 Hz); 8.03 (d, 8H, J = 8.1 Hz); 7.50 (d, 8H, J = 8.4 Hz); 7.35 (d, 8H, J = 8.1 Hz); 7.31 (s, 4H); 6.21 (d, 8H, J = 8.5 Hz); 3.92 (s, 8H); 3.86 (m, 16H); 3.76 (m, 16H); 3.57 (m, 16H); 1.79 (s, 24H); 1.66 (t, 24H); −2.82 (s, 4H).

UV-vis (CH_2Cl_2) : 318, 411, 507, 541, 573, 625 nm.

Preparation of macrocycle **9**

To a degassed solution containing dialdehyde **2** (0.215 g, 5.5×10^{-4} mol) and **4** (0.256 g, 1.11×10^{-3} mol) in CH_2Cl_2 (500 mL), was added 4 drops of trifluoroacetic acid. The mixture protected from light was stirred at room temperature for 19 h. *p*-Chloranil (1.35 g, 54.9×10^{-4} mol) was then added and the resulting solution heated to reflux for 1.5 h. After cooling, the crude mixture was neutralized with a 10% sodium carbonate solution. The organic phase was washed 3 times with water and evaporated to dryness. The crude product was purified by column chromatography. After elimination of chloranil on an alumina column (eluent : CH_2Cl_2/hexane = 80/20), chloroform was used as eluent to afford 110 mg of crude **9** (28%). The best solvent for **9** is $CHCl_3$ but even then the solubility did not exceed 10^{-5} mol L^{-1}. Two other chromatographies on a silica-gel column with $CHCl_3$ as eluent were done to afford 20 mg pure compound.

ES-MS for $C_{112}H_{100}N_{12}$: m/z, found : 1 613.8; 807.8; 538.6. Calcd : 1 613.8 ($M + H^+$), 807.4 ($M + 2H^+/2$); 538.6 ($M + 3H^+/3$).

^{1}H NMR : (200 MHz, CF_3COOD + 2 drops $CDCl_3$) : 10.26 (s, 4H); 9.30 (d, 4H, J = 8.5 Hz); 8.98 (d, 4H, J = 8.5 Hz); 8.76 (d, 8H, J = 8.4 Hz); 8.54 (s, 4H); 7.78 (d, wide, 8H); 3.66 (q, 16H); 2.36 (s, 24H); 1.04 (t, 24H, J = 7.5 Hz).

Acknowledgments

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