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Transition Metal Templated Formation of [2]- and [3]-Rotaxanes with Porphyrins as Stoppers[†]

Jean-Claude Chambron, Valérie Heitz, and Jean-Pierre Sauvage*

Contribution from the Laboratoire de Chimie Organo-Minérale, UA 422 au CNRS, Faculté de Chimie, Université Louis Pasteur, 67000 Strasbourg, France

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Abstract: The transition metal-directed threading of a molecular fragment containing a central chelate and an end-attached gold(III) porphyrin into a presynthesized coordinating ring affords a general precursor to rotaxane-type structures. After threading, construction of the second porphyrin acting as an efficient stopper affords a copper(I)-complexed [2]-rotaxane as well as a novel compartmental [3]-rotaxane. The latter compound consists of a three-porphyrin-containing molecular fragment threaded through two 30-membered rings. Quantitative demetalation of the copper(I)-complexed [2]-rotaxane affords a free-ligand [2]-rotaxane. The two porphyrins are bulky enough to inhibit any process leading to separate fragments, the cycle and the thread. ^{1}H NMR spectroscopy demonstrates that upon decomplexation the [2]-rotaxane undergoes profound conformation changes. Recomplexation using zinc(II) regenerates an entwined and compact structure similar to that of the copper(I)-complexed [2]-rotaxane obtained in the template reaction.

Introduction

Strictly speaking, the molecular graph of a [2]-rotaxane is planar since the factors which keep the ring and the dumbbell threaded inside the cycle together are solely related to chemical bond distances and angles. It is sufficient to imagine the compression of the two stoppers borne by the ends of the acyclic fragment so as to allow the blocking groups to pass through the ring and thus to obtain a cycle and a linear fragment. Both entities are now clearly separated from one another and obviously lead to a topologically trivial system (planar molecular graph). The same result is obtained by stretching the chemical bonds of the cycle and thus expanding it until the unthreading process can take place. The only [2]-rotaxane with a nonplanar graph (*i.e.* for which it is compulsory for its figure to have crossings once represented in a plane) consists of a cycle threaded by an infinite straight line. In that case, the system would be topologically identical to a catenane for which one of the rings would be infinitely large (see Chart I).

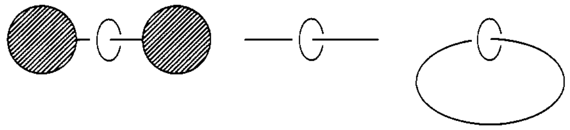
Catenanes and rotaxanes have been associated for decades although the topologically very different nature of both systems has only been clearly stated in a limited number of discussions.[1-5]

The first mention of synthetic rotaxanes appeared in 1967.[5] It was based on statistical threading of an immobilized cycle by decane-1,10-diol followed by capping using a trityl ether bulky group. Another system using statistical threading led to rotaxanes in relatively high yield.[6] A directed synthesis was also reported in 1969 by Schill and Zollenkopf.[7]

The most useful procedures for making rotaxanes preparatively are based on template effects. Numerous examples take advantage of the capability of a cyclodextrin to be threaded by an end-functionalized polymethylene chain prior to attaching various bulky blocking groups at the two ends of the string. Transition metal complexes have been used as stoppers,[8,9] leading to cyclodextrin-containing rotaxanes in good yield. More recently, cyclodextrins have also been used as components of various rotaxanes.[10-14] Apart from cyclodextrin, an electron-deficient tetracationic macrocycle has been extensively used in a template synthesis of rotaxanes and catenanes by Stoddart *et al.* This approach, based on aromatic stacks formed between electron-rich and electron-deficient nuclei, leading to threading of a presynthesized cycle, afforded a broad series of promising rotaxanes.[15-17]

In order to make rotaxanes usable as parts of molecular devices and with the purpose of studying long-range electron-transfer processes within large molecular systems of well-controlled geometries, the introduction of photo- and electroactive com-

Chart I[a]



(a) (b) (c)

[a] (a) A classical rotaxane; (b) a rotaxane with an infinitely long thread; (c) a catenane. Note that b and c have nonplanar molecular graphs.

[†] Dedicated to Professor Raymond Weiss on the occasion of his 65th birthday.

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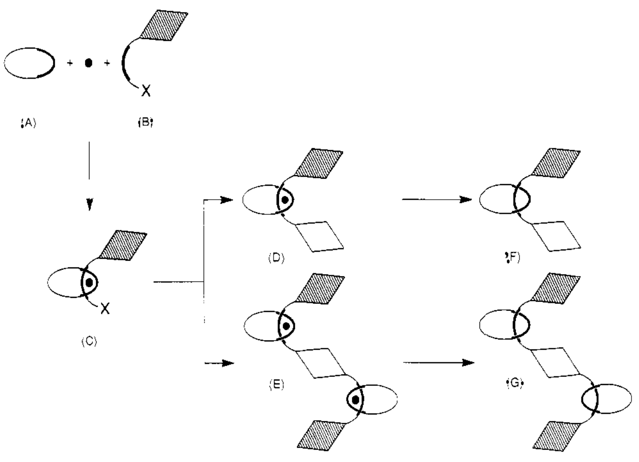
Scheme I[a]



[a] The macrocycle (A) incorporating a coordinating fragment (thick line) interacts with a metal center (black circle) and an asymmetrical open chain chelate (B) bearing one porphyrin and a precursor function X which is small enough to pass through the ring; after the threaded intermediate C is formed, the additional porphyrin ring is constructed, affording the transition metal-complexed rotaxanes D and E. Demetalation leads to the free-ligand rotaxanes F and G from D and E, respectively.

ponents seemed to be a valuable extension. In particular, the stoppers having to be bulky groups, it was envisioned that porphyrins would constitute interesting components able (i) to act as blocking groups, (ii) to respond to photonic excitation by electron transfer or abstraction, and (iii) to behave as electron donor or acceptor groups in their ground state.

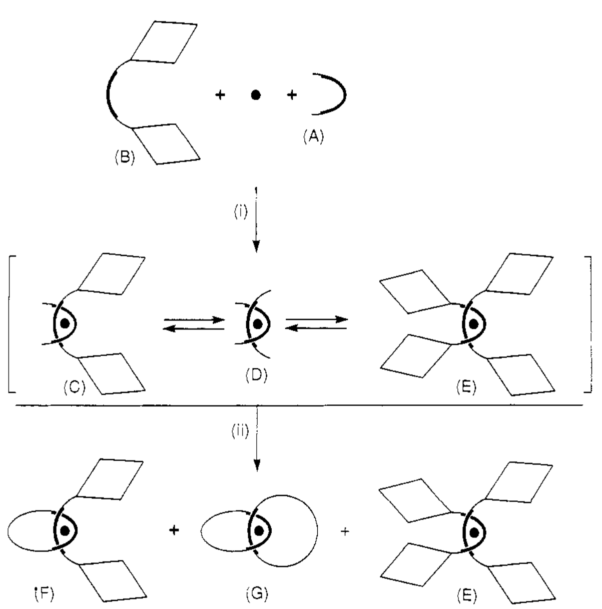
We would now like to describe the synthesis of [2]-rotaxanes (consisting of one ring and one thread) and [3]-rotaxanes (two rings and one thread) by template synthesis using copper(I) as the gathering metal and rigidly held porphyrins as stoppers. A preliminary account of this work was recently reported.[18] Another example of a porphyrin-stoppered rotaxane was also recently described by Stoddart and co-workers.[19] The strategy used in the present work is related to that utilized for making various catenanes and knots.[4,20] A similar approach has also been applied by others for preparing a rotaxane with two trityl ether bulky groups.[21]

Results and Discussion

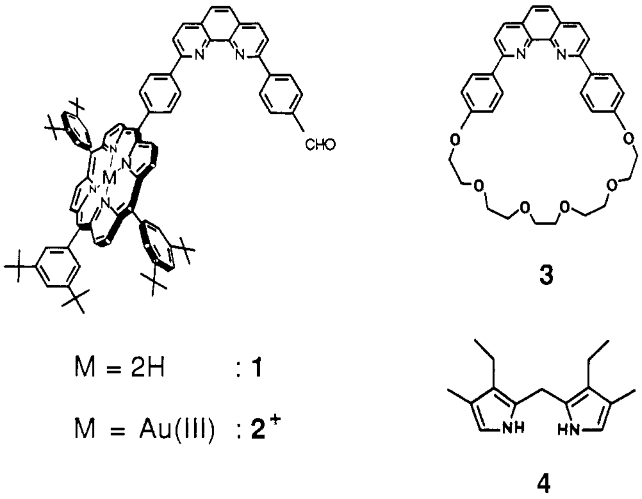
1. Principle Results. The templated strategy using the gathering and orienting effect of transition metals has been abundantly used for entwining and interlacing molecular strings with subsequent formation of catenanes of various complexity and trefoil knots.[4,20] The present approach utilizes a derived principle, the main difference with the strategies developed previously being that the topologically-fixing step is now the construction of a big stopper (porphyrin) instead of a cyclization reaction. In Scheme I are indicated the two possible strategies leading either to a [2]-rotaxane or to a [3]-rotaxane.

A priori, two possibilities exist for making a rotaxane using a transition metal template synthesis. Either the ring can be constructed around the dumbbell (Scheme II) or the blocking groups can be anchored to the end-functionalized string once the latter has been threaded inside a presynthesized cycle (Scheme I). In fact, working along the strategy described in Scheme II, if kinetically labile bis-chelate complexes of the type of those we generally work with are to be used (*i.e.* $Cu(dpp)_2^+$ derivatives, where dpp is 2,9-diphenyl-1,10-phenanthroline), only intermediate C will unambiguously afford the desired rotaxane.

Scheme II[a]



[a] The alternative templated route to rotaxanes. In the complexation step (i), a statistical mixture of bis-chelate complexes should be obtained from A, B, and the metal out of which the heteroleptic system C only (formed in 50% yield besides D and E) can afford the desired rotaxane F after the cyclization step (ii). If the intermediate complexes C, D, and E are labile, the statistical mixture will be obtained regardless of the order of addition of the three components A, B, and the metal.



M = 2H : **1**

M = Au(III) : $\mathbf{2}^+$

3

4

Figure 1.

2. Synthesis of Rotaxane Transition Metal Complexes. By following the strategy described in Scheme I, the ideal precursor corresponding to B is a nonsymmetrical dpp derivative attached to both a porphyrin and an aromatic aldehyde. The macrocycle A of Scheme I can obviously be the dpp-incorporating 30-membered ring used previously for making catenates and catenands.[22] As shown by handling of CPK molecular models, it is sufficiently small to prevent release of the phenanthroline-bridged bis-porphyrin dumbbell. The starting materials are represented in Figure 1. Trivalent gold was selected for two reasons: (i) it forms very stable porphyrin complexes and will thus not be lost during the synthesis of the second porphyrin nucleus,[23] (ii) due to its strong electropositive character, it confers

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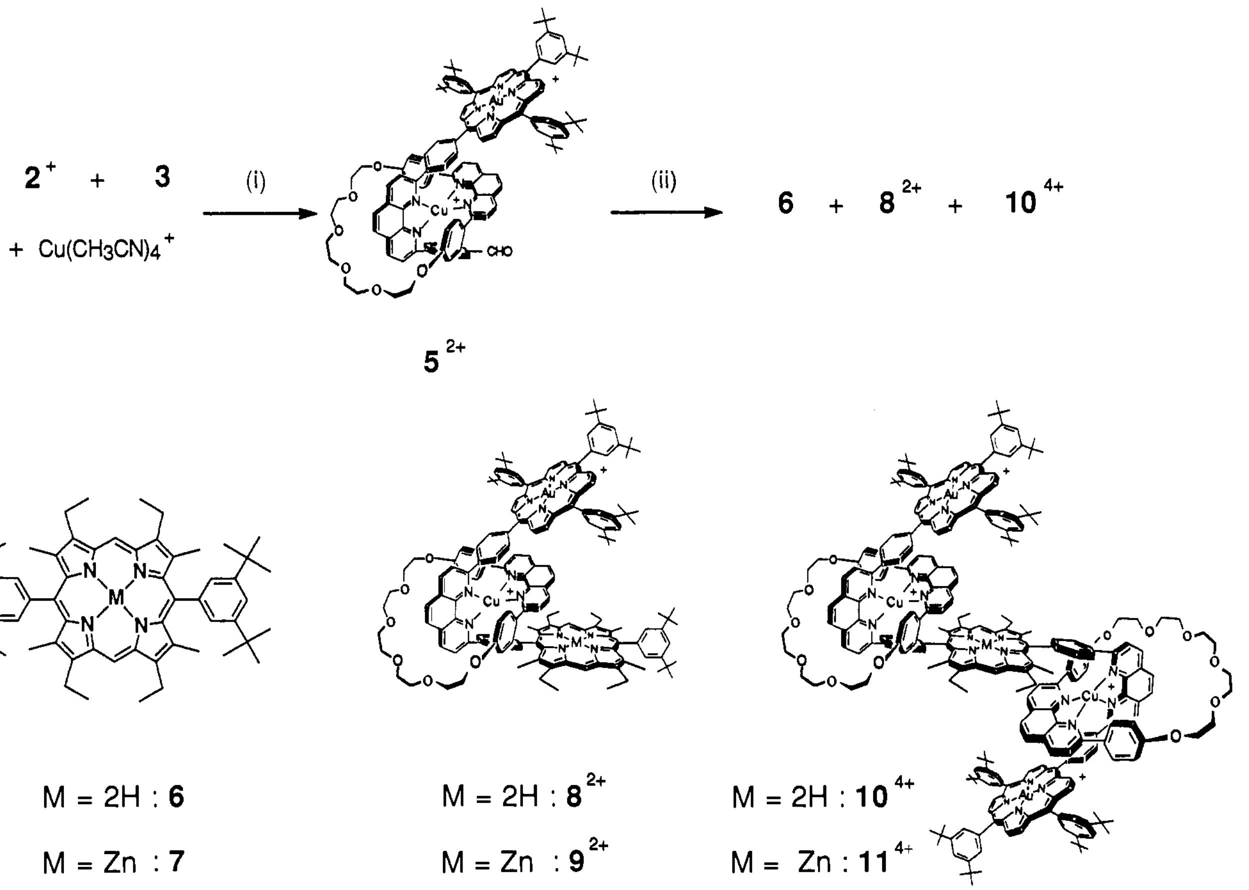

Figure 2. Synthesis of the various [2]- and [3]-rotaxanes: (i) CH_2Cl_2/CH_3CN, room temperature; (ii) di-*tert*-butyl-3,5-benzaldehyde, (diethyl-3,3′-dimethyl-4,4′-dipyrryl-2,2′)methane, CF_3CO_2H, CH_2Cl_2, room temperature, then chloranil, CH_2Cl_2, reflux.

to the aromatic porphyrin ring to which it is complexed a remarkable electron-accepting ability with a resulting very accessible reduction potential.[24] This latter property has recently been taken advantage of to build multi-porphyrin systems able to undergo fast photoinduced electron transfer leading to gold(III) porphyrin radicals as transient species.[25,26]

Compounds **1** and **3** were made according to literature procedures.[22,27] The mono-porphyrin **1** was metalated with $KAuCl_4$ (2.5 equiv) in refluxing CH_3COOH, with 4 equiv of CH_3COONa, to afford the gold(III) porphyrin $\mathbf{2}^+$ in 95% yield after column chromatography. The reactions leading to the transition metal-complexed [2]- and [3]-rotaxanes $\mathbf{8}^{2+}$ and $\mathbf{10}^{4+}$, respectively, are indicated in Figure 2. Importantly, the synthesis of the second porphyrin had to be compatible with the existence of the threaded pre-rotaxane intermediate C of Scheme I or $\mathbf{5}^{2+}$ of Figure 2. A mild reaction had thus to be selected, for which no demetalation of the copper(I) complex $\mathbf{5}^{2+}$ was expected to take place. Since Rothemund–Adler[28] synthesis provides too stringent a set of conditions for copper(I) bis-chelate complexes to survive the reaction quantitatively, we investigated a milder procedure recently developed by Lindsey and co-workers.[29] The condensation reaction of the dipyrrylmethane **4**[30] was used in the presence of CF_3COOH in CH_2Cl_2 at room temperature. In preliminary work, we checked by UV–visible spectroscopy that $Cu(dap)_2^+$ (dap = 2,9-dianisyl-1,10-phenanthroline), an acyclic model compound[31] of $\mathbf{5}^{2+}$, could survive these experimental conditions. The sequence of reactions leading to the preparation of the rotaxanes $\mathbf{8}^{2+}$ and $\mathbf{10}^{4+}$ is as follows (Figure 2): Pre-rotaxane $\mathbf{5}^{2+}$ was first formed. Macrocycle **3** was complexed with Cu(I) by reaction with $Cu(CH_3CN)_4BF_4$ in CH_3CN/CH_2Cl_2 solution. Then the gold porphyrin $\mathbf{2}^+(BF_4^-)$ was added. Noteworthy, although $Cu(dpp)_2^+$-type complexes are notoriously highly colored,[32] the presence of the gold(III) porphyrin made any color change in the course of the formation reaction of $\mathbf{5}^{2+}$ virtually undetectable. Thin-layer chromatography and NMR spectroscopy showed that complex $\mathbf{5}^{2+}$ had formed quantitatively. It was used in the next step, without further purification: $\mathbf{5}^{2+}(BF_4^-)_2$, di-*tert*-butyl-3,5-benzaldehyde, and (diethyl-3,3′-dimethyl-4,4′-dipyrryl-2,2′)methane in molar ratio 1:4:40 were mixed and stirred in dichloromethane in the presence of trifluoroacetic acid (3:1) for 17 h. Subsequently, a large excess of chloranil (30:1) was added in order to oxidize the intermediate porphyrinogen and the reaction mixture was heated to reflux for 1.5 h. After workup and chromatographic separations, three porphyrins were isolated: etioporphyrin **6**, the desired copper(I) [2]-rotaxane $\mathbf{8}^{2+}$, and the compartmental bis-copper(I) [3]-rotaxane $\mathbf{10}^{4+}$. The rotaxanes were isolated as their PF_6^- salts in 25% and 32% yields, respectively. All three compounds contained a free-base etioporphyrin and could be readily metalated with $Zn(OAc)_2 \cdot 2H_2O$ to afford **7**, $\mathbf{9}^{2+}$, and $\mathbf{11}^{4+}$, respectively. The rotaxanes which were synthesized in this way are complexed copper(I) rotaxanes. The two constituent parts, a ring (mac-

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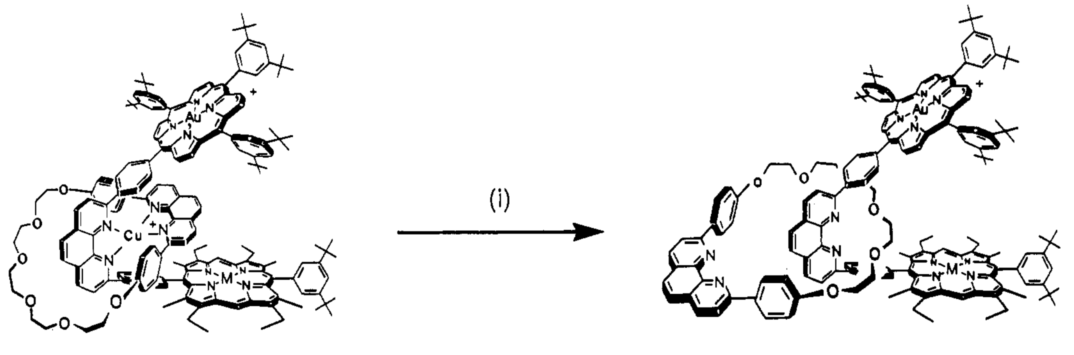

M = Zn : $\mathbf{9}^{2+}$

M = Zn : $\mathbf{12}^{+}$

M = 2H : $\mathbf{13}^{+}$

M = Cu : $\mathbf{14}^{+}$

Figure 3. Decomplexation reaction of the Cu(I)-complexed [2]-rotaxane $\mathbf{9}^{2+}(PF_6^-)_2$ leading to the free-ligand [2]-rotaxane $\mathbf{12}^{+}(PF_6^-)$: (i) KCN, $CH_3CN/CH_2Cl_2/H_2O$.

rocycle 3) and the dumbbell (the phenanthroline-bridged bis-porphyrin), are held together by coordination to copper(I). Upon removal of copper(I), the two rotaxane subunits would loose any chemical bonding, yet they would be forced to be held together by some kind of "mechanical" link. Linking is provided only by steric crowding of the porphyrin moieties, preventing unthreading of the bis-porphyrin from macrocycle 3.

3. Preparation of the Copper-Free [2]-Rotaxane. Copper(I)-free [2]-rotaxane $\mathbf{12}^{+}(PF_6^-)$ was obtained by treatment of $\mathbf{9}^{2+}(PF_6^-)_2$ with excess KCN (see Figure 3). Care had to be taken to avoid both large excess of KCN and too long reaction times, which were responsible for some decomposition as shown by TLC and UV–visible spectroscopy.

Copper-free [2]-rotaxane $\mathbf{12}^{+}(PF_6^-)$ was purified by chromatography and was shown to contain traces of the starting material as indicated by electrospray mass spectroscopy (ES-MS). It should be noted that direct demetalation of $\mathbf{8}^{2+}(PF_6^-)_2$ (*i.e.*, the rotaxane complex containing a free-base porphyrin) led to contamination of the free-base porphyrin with copper, affording a mixture of free-base porphyrin [2]-rotaxane $\mathbf{13}^{+}$ and copper(II) porphyrin [2]-rotaxane $\mathbf{14}^{+}$. On the contrary, by first metalating the porphyrin site of $\mathbf{8}^{2+}$ with zinc, no metal exchange was observed. In our case, Zn(II) turned out to be an excellent protective group for the etioporphyrin moiety in addition to the interesting photochemical properties which it induces for that same metalloporphyrin.[25,26,33]

The fact that demetalation of Cu^+-complexed rotaxane $\mathbf{9}^{2+}(PF_6^-)_2$ afforded a single product and the absence of release of the bis-porphyrin by macrocycle 3 is proof that the compound we have synthesized is a true rotaxane. It should be noted that this compound contains two "mechanically" linked species, one of them, the bis-porphyrin fragment, having not been synthesized as a free species. This seems at first glance paradoxical, but this is one of the appealing features of rotaxanes.

4. Metalation of Free Rotaxanes. One of the special features of the rotaxanes presently described is that their coordination sites comprise two dpp-type chelates, both of which being incorporated in different subunits, *i.e.* the ring and the dumbbell thread. The compounds thus contain a coordinating tetradentate site well suited for tetrahedral geometries. Given the fact that these rotaxanes are also used to study photoinduced electron transfer between the zinc(II) and the gold(III) porphyrins,[33] it is of interest to be able to modify the redox parameters of the spacer used between the donor (zinc(II) porphyrin) and the acceptor (gold(III) porphyrin). In particular, it is important to control the electronic properties of the species lying in between the two porphyrins. Clearly, this should be effectively done by introducing different metal centers in the tetrahedral site and by varying their oxidation states.

Zn^{2+} was selected because its geometrical requirements are approximately those of Cu^+, but its higher charge will alter more the π-accepting ability of the complexed phenanthrolines. Thus metal-free [2]-rotaxane $\mathbf{12}^{+}(PF_6^-)$ was reacted with $Zn(OAc)_2{\cdot}2H_2O$, and after chromatographic purification, the zinc(II) [2]-rotaxane ($\mathbf{15}^{3+}(PF_6^-)_3$) was obtained in 35% yield. As shown by ES-MS, this material contained traces of copper rotaxane $\mathbf{9}^{2+}(PF_6^-)_2$ and free rotaxane $\mathbf{12}^{+}(PF_6^-)$ which could not be removed by chromatography.

5. Study of [2]-Rotaxanes $\mathbf{8}^{2+}$, $\mathbf{9}^{2+}$, $\mathbf{12}^{+}$, and $\mathbf{15}^{3+}$ and [3]-Rotaxanes $\mathbf{10}^{4+}$ and $\mathbf{11}^{4+}$ by ^1H NMR Spectroscopy. All the rotaxanes could be characterized by ^1H NMR spectroscopy. Assignments of the signals, whenever possible, were made by comparison with the related bis-porphyrin compounds.[23,25] In this section, we will comment in detail only on the spectra of copper(I) [2]-rotaxane $\mathbf{9}^{2+}(PF_6^-)_2$ and metal-free [2]-rotaxane $\mathbf{12}^{+}(PF_6^-)$. The spectrum of the zinc(II) [2]-rotaxane $\mathbf{15}^{3+}(PF_6^-)_3$ is nearly superimposable with that of the copper(I) one ($\mathbf{9}^{2+}(PF_6^-)_2$), showing that replacement of Cu^+ with Zn^{2+} does not affect very much the geometry of the system. Similarly, the spectra of the compartmental [3]-rotaxanes $\mathbf{10}^{4+}(PF_6^-)_4$ and $\mathbf{11}^{4+}(PF_6^-)_4$ are also very similar to those of the [2]-rotaxanes $\mathbf{8}^{2+}(PF_6^-)_2$ and $\mathbf{9}^{2+}(PF_6^-)_2$, respectively, at least for the protons these molecules share in common. Due to the higher symmetry of the compartmental [3]-rotaxanes, their spectra are simpler than those of the corresponding [2]-rotaxanes. It was shown in the past[31] that the structure of entwined $Cu(dpp)_2^+$-type complexes could be probed by ^1H NMR spectroscopy. In particular, the shielding of the phenyl protons of a dpp chelate by the ring current of the other dpp chelate was a proof of the tight entwining of the ligands around copper. The ^1H NMR spectrum of copper(I) [2]-rotaxane $\mathbf{9}^{2+}$ shown in Figure 4 is in agreement with the structure drawn in Figure 2. (See also Figure 5 for proton numbering). Because of the symmetry plane contained by the bis-porphyrin chelate, the protons of the macrocycle are pairwise related. Those of the phenanthroline bridging the porphyrins are not because the two different porphyrins destroy the intrinsic symmetry of 1,10-phenanthroline. Entwining of the two dpp nuclei around copper is proven by the shielding of all meta protons,

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[33] Chambron, J.-C.; Harriman, A.; Heitz, V.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1993**, *115*, 6109–6114.

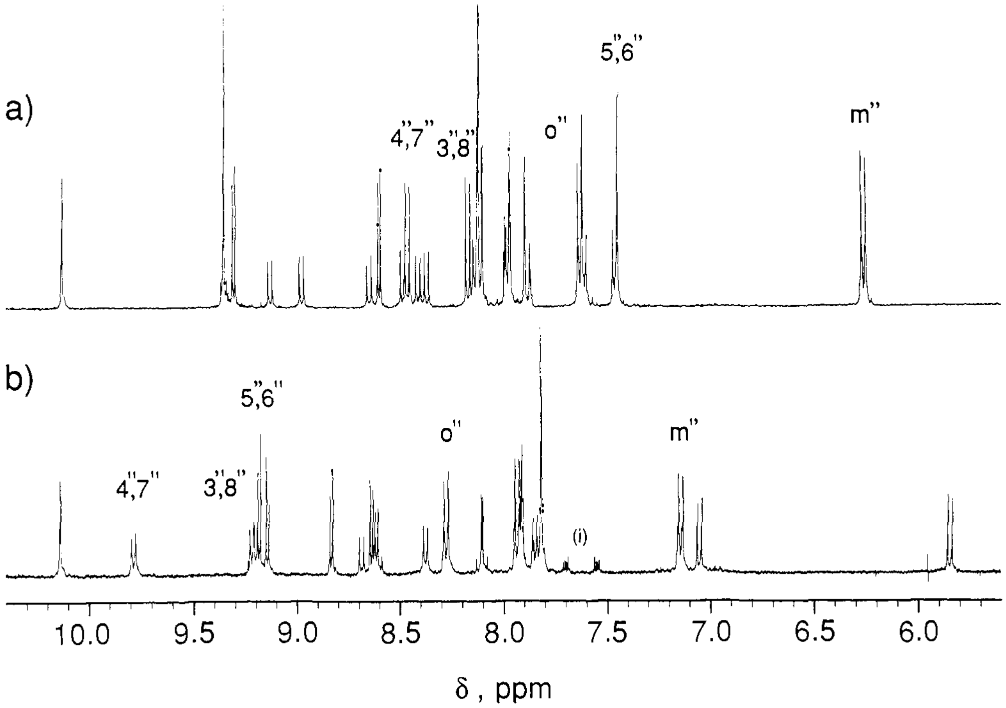

Figure 4. 400-MHz ^{1}H NMR spectra (CD_2Cl_2): (a) Cu(I) [2]-rotaxane 9^{2+}; (b) free [2]-rotaxane 12^+. Very significant downfield shifts (up to 1.7 ppm) tend to indicate substantial molecular rearrangement with, in particular, gliding of the ring and removal of the phenanthroline belonging to the cycle from the shielding cleft provided by the two porphyrins. (i) is a solvent impurity.

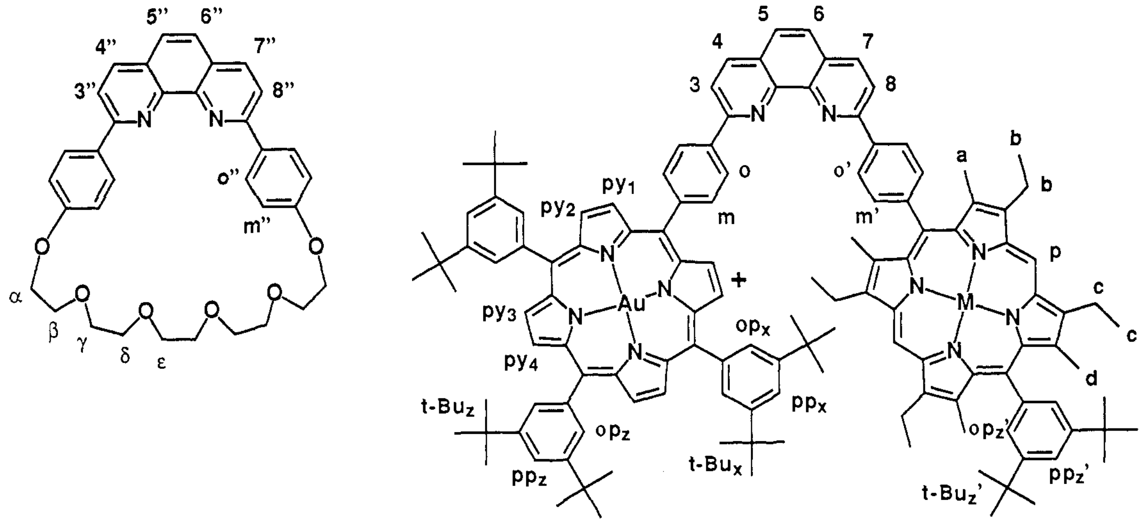

Figure 5. Proton labeling of the different subunits of the rotaxanes discussed in this work.

especially those of the macrocycle. Protons 5″ and 6″ of this macrocycle show a strong shielding when compared to their analogues in the bis-porphyrin (5 and 6), owing to the fact that they lie between two highly shielding porphyrins. The pyrrolic protons py_1 and py_2 show clearly differentiated doublets because they experience differently the shielding of the phenanthroline nucleus of the macrocycle. The same explanation stands for the clear splitting of the signals originating from protons of the alkyl chains of the etioporphyrins: chemical shifts decrease in the order $CH_{3d} > CH_{3a}$, $CH_{2c} > CH_{2b}$, and $CH_{3c} > CH_{3b}$.

The spectrum of the free [2]-rotaxane 12^+ shows differences when compared to that of the copper(I)-bound [2]-rotaxane 9^{2+} (see Figure 4). In particular protons of the phenanthroline nucleus belonging to the macrocycle are strongly deshielded now ($\Delta\delta$ = +1.74, +0.66, and +0.89 ppm for 5″ and 6″, o″, and m″, respectively). This indicates that the phenanthroline of the macrocycle does no longer sit between the two porphyrin nuclei. Very probably, the dpp part of the macrocycle now lies outside the cleft formed by the two porphyrins.

Conclusion

In this paper, we have shown how the template strategy which had been developed for the synthesis of catenates could be extended to the synthesis of metallorotaxanes. Provided chelating units are incorporated in the complementary parts of the complex molecule to be synthesized, a transition metal ion (*i.e.*, Cu^+) can be used to gather and orient these fragments prior to the reaction leading to the desired product. This "locking" reaction is a cyclization reaction in the case of catenate syntheses, and for the preparation of metallorotaxanes, it is the formation of the second porphyrin. The use of Lindsey's procedure turned out to be determining. Furthermore and unexpectedly, this reaction afforded a good yield of compartmental [3]-rotaxane beside the desired [2]-rotaxane. Compartmental [3]-rotaxanes are promising species as far as multistep long-range electron transfer is concerned and as components of photochemical molecular devices.

We have shown that the template metal could be selectively removed from the metallorotaxane, exactly in the same way as copper(I) catenates were demetalated. Demetalation of a metallo-

[2]-rotaxane leads to a species in which a molecular ring is entrapped by the bulky end groups of the molecular dumbbell (phenanthroline-bridged bis-porphyrin) through which it is threaded.

^{1}H NMR studies have shown that the metal-free [2]-rotaxane has a structure different from that of the metalated [2]-rotaxane. The macrocycle has a different orientation relative to the bis-porphyrin thread, its dpp part sitting outside the cavity formed by the two porphyrins.

Finally we have shown that the metal-free [2]-rotaxane made could be remetalated at the bis-dpp tetracoordinate site which had been used for its template synthesis. The reaction can be performed with Zn^{2+} for example.

Experimental Section

Macrocycle **3**,[22] porphyrin **1**,[27] dipyrrylmethane **4**,[30] and di-*tert*-butyl-3,5-benzaldehyde[27] were prepared according to literature procedures. Except for the preparations of $\mathbf{2}^+(BF_4^-)$, $\mathbf{12}^+(PF_6^-)$, and **7**, all reactions were performed under argon. Proton numbering for ^{1}H NMR assignments is given in Figure 5.

$\mathbf{2}^+(\mathbf{BF_4^-})$. Porphyrin **1**, 0.307 g (0.25 mmol), was dissolved in 100 mL of glacial acetic acid. Potassium tetrachloroaurate, 0.236 g (0.62 mmol), and sodium acetate, 0.079 g (0.99 mmol), were added to the green solution. The course of the reaction was followed by TLC (SiO_2, 6% MeOH in CH_2Cl_2) and by UV–visible spectroscopy. After 2 days, the deep red reaction mixture was evaporated to dryness. The residue was taken up in CH_2Cl_2 (100 mL) and neutralized with 10% Na_2CO_3 (100 mL). The organic phase was subsequently treated with saturated $NaBF_4$ (2 × 50 mL), washed with water (100 mL), dried over $MgSO_4$, and evaporated to dryness. The crude product was purified by column chromatography (60 g of SiO_2, 1% MeOH in CH_2Cl_2), which afforded 0.360 g of $\mathbf{2}^+(BF_4^-)$(95% yield) as a red-orange solid, mp 114 °C (dec): ^{1}H NMR (200 MHz, CD_2Cl_2) δ 10.07 (s, 1H, H_{HCO}), 9.50 (d, 2H, H_{py1}), 9.40 (d, 2H, H_{py_2}), 9.39 (s, 4H, H_{py_3}, H_{py_4}), 8.97 (d, 2H, H_o), 8.86 (d, 2H, $H_{o'}$), 8.57 (d, 1H, H_4), 8.53 (d, 2H, H_m), 8.52 (d, 1H, H_3), 8.41 (d, 1H, H_7), 8. 25 (d, 1H, H_8), 8.11 (d, 6H, H_{op_x}, H_{op_z}), 8.07 (d, 2H, $H_{m'}$), 8.00 (two t, 3H, H_{pp_x}, H_{pp_z}), 7.95 (d, 1H, H_5), 7.87 (d, 1H, H_6), 1.56 (s, 54H, $H_{t\text{-}Bu_x}$, $H_{t\text{-}Bu_z}$); FAB-MS, for $C_{87}H_{86}AuBF_4N_6O$, found *m/z* 1427.5, calcd *m/z* 1427.7 (M^+).

$\mathbf{5}^{2+}(\mathbf{BF_4^-})_2$. The preparation was performed under argon. To a solution of macrocycle **3** (0.057 g, 0.10 mmol) in CH_2Cl_2 (4.5 mL) was added *via canula* a solution of $Cu(CH_3CN)_4BF_4$ (0.0315 g, 0.10 mmol) in CH_3CN (3 mL). The red-orange reaction mixture was stirred for 15 min, then treated with gold porphyrin $\mathbf{2}^+(BF_4^-)$, 0.151 g (0.10 mmol), in CH_2Cl_2 (4 mL). The dark-red reaction mixture was stirred overnight. TLC showed that the reaction had proceeded quantitatively. The solvents were evaporated and the residue was taken up in CH_2Cl_2 (50 mL) and washed with water (2 × 20 mL). The organic phase was evaporated to dryness, and the red-orange solid residue was used in the subsequent reaction without further purification. $\mathbf{5}^{2+}(BF_4^-)_2$: ^{1}H NMR (200 MHz, CD_2Cl_2) δ 9.59 (s, 1H, H_{HCO}), 9.35 (s, 4H, H_{py_3} + H_{py_4}), 9.27 (d, 2H, *J* = 5.2 Hz, H_{py_2}), 9.09 (d, 1 H, *J* = 8.4 Hz, H_4); 8.76 (d, 2H, *J* = 5.2 Hz, H_{py_1}); 8.73 (d, 1H, *J* = 8.1 Hz, H_7), 8.62 (d, 1H, *J* = 8.9 Hz, H_3), 8.46 (d, 2H, *J* = 8.3 Hz, $H_{4'',7''}$), 8.45 (d, 1H, *J* = 8.4 Hz, H_8), 8.39 (d, 1H, *J* = 8.2 Hz, H_5), 8.31 (d, 1H, *J* = 8.8 Hz, H_6), 8.10 (d, 4H, *J* = 1.8 Hz, H_{op_x}), 8.08 (d, 2H, *J* = 1.8 Hz, H_{op_z}), 8.03 (t, 2H, *J* = 1.8 Hz, H_{pp_x}), 8.02 (d, 2H, *J* = 8.3 Hz, $H_{3'',8''}$), 7.98 (d, 2H, *J* = 9.0 Hz, H_o), 7.98 (t, 1H, *J* = 1.8 Hz, H_{pp_z}), 7.77 (s, 2H, $H_{5'',6''}$), 7.76 (d, 2H, *J* = 7.9 Hz, $H_{o'}$), 7.52 (d, 4H, *J* = 8.7 Hz, $H_{o''}$), 7.47 (d, 2H, *J* = 9.0 Hz, H_m), 6.93 (d, 2H, *J* = 8.1 Hz, $H_{m'}$), 6.17 (d, 4H, *J* = 8.7 Hz, $H_{m''}$), 3.91 (s, 4H, H_ϵ), 3.79 (m, 4H, H_δ), 3.69 (m, 8H, H_β, H_γ), 3.60 (m, 4H, H_α), 1.59 (s, 36H, $H_{t\text{-}Bu_x}$), 1.54 (s, 18H, $H_{t\text{-}Bu_z}$), FAB-MS, for $C_{121}H_{120}AuB_2CuF_8N_8O_7$, found m/z 2144.0, 2057.0, 1028.9, 1427.0, 628.9, calcd *m/z* 2144.7 ($M^{2+}BF_4^-$), 2057.9 ($M^{2+} + e^-$), 1427.7 ($\mathbf{2}^+$), 1028.9 (M^{2+}), 629.1 ($3Cu^+$).

6, $\mathbf{8}^{2+}(\mathbf{PF_6^-})_2$, and $\mathbf{10}^{4+}(\mathbf{PF_6^-})_4$. $\mathbf{5}^{2+}(BF_4^-)_2$ (0.10 mmol), di-*tert*-butyl-3,5-benzaldehyde (0.091 g, 0.42 mmol), and (diethyl-3,3′-dimethyl-4,4′-dipyrryl-2,2′)methane (0.250 g, 1.08 mmol) were dissolved in CH_2Cl_2 (45 mL). Trifluoroacetic acid (0.25 mL, 0.3 mmol) was then added, and the reaction mixture was stirred at room temperature for 17 h. Chloranil (0.744 g, 2.97 mmol) was added, and the reaction mixture refluxed for 1.5 h. After cooling, the crude reaction mixture was neutralized with 10% sodium carbonate (20 mL). The resulting organic phase (100 mL) was washed twice with water, treated overnight with 6.5% KPF_6 (50 mL), washed again with water (3 × 40 mL), and evaporated to dryness. The residue (1.215 g) was subjected to column chromatography (170 g of SiO_2, CH_2Cl_2/hexane = 50/50). After elimination of excess of chloranil, elution with 0.5% MeOH in CH_2Cl_2 afforded crude **6** (0.213 g). Elution with 1.2% MeOH in CH_2Cl_2 afforded crude $\mathbf{8}^{2+}(PF_6^-)_2$, and elution with 2–3.5% MeOH in CH_2Cl_2 afforded crude $\mathbf{10}^{4+}(PF_6^-)_4$ (0.097 g). $\mathbf{8}^{2+}(PF_6^-)_2$ was further purified by column chromatography (42 g of SiO_2, CH_2Cl_2/hexane = 50/50). Elution with 0.13–0.15% MeOH in CH_2Cl_2 afforded $\mathbf{8}^2(PF_6^-)_2$ (0.073 g, 25%). Small amounts of a compound which is the result of the complexation of the free-base porphyrin of $\mathbf{8}^{2+}(PF_6^-)_2$ by Cu^{2+} (as shown by FAB-MS) were detected in the last fractions and were thus discarded. $\mathbf{10}^{4+}(PF_6^-)_4$ was further purified by column chromatography (42 g of SiO_2, CH_2Cl_2/hexane = 50/50). Elution with 0.55% MeOH in CH_2Cl_2 afforded $\mathbf{10}^4(PF_6^-)_4$ (0.081 g, 32%). **6** was further purified by column chromatography (106 g of SiO_2, CH_2Cl_2/hexane = 50/50). Elution with 80% CH_2Cl_2 in hexane and 15% MeOH in CH_2Cl_2 afforded 0.101 g of pure **6**. Additional amounts were recovered after further chromatography. Total yield of **6** was 0.116 g. **6** (purple solid): ^{1}H NMR (200 MHz, CD_2Cl_2) δ 10.28 (s, 2H, H_p); 7.95 (d, 4H, *J* = 1.8 Hz, H_{op}), 7.88 (t, 2H, *J* = 1.8 Hz, H_{pp}), 4.07 (q, 8H, *J* = 7.6 Hz, $(CH_2)_b$), 2.52 (s, 12H, $(CH_3)_a$), 1.82 (t, *J* = 7.6 Hz, 12H, $(CH_3)_b$), 1.54 (s, 36H, $H_{t\text{-}Bu}$); FAB-MS, for $C_{60}H_{78}N_4$, found *m/z* 855.6, calcd *m/z* 855.3 (M^+). $\mathbf{8}^{2+}(PF_6^-)_2$ (red solid): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 10.19 (s, 2H, H_p), 9.34 (d, *J* = 5.2 Hz, 4H, H_{py_3} + H_{py_4}), 9.28 (d, *J* = 5.2 Hz, 2H, H_{py_2}), 9.13 (d, *J* = 1.8 Hz, 1H, H_4), 8.98 (d, *J* = 8.3 Hz, 1H, H_3), 8.65 (d, *J* = 8.9 Hz, 1H, H_7), 8.57 (d, *J* = 5.0 Hz, 2H, H_{py_1}), 8.49 (d, *J* = 8.9 Hz, 1H, H_8), 8.43 (d, *J* = 8.3 Hz, 2H, $H_{4'',7''}$), 8.41 (d, *J* = 8.5 Hz, 1H, H_5), 8.36 (d, *J* = 8.3 Hz, 1H, H_6), 8.15 (two d, *J* = 8.2 Hz, 4H, $H_{3'',8''}$, H_o), 8.10 (d, *J* = 1.8 Hz, 4H, H_{op_x}), 8.09 (d, *J* = 1.8 Hz, 2H, H_{op_z}), 7.99 (t, *J* = 1.8 Hz, 1H, H_{pp_z}), 7.98 (d, *J* = 7.9 Hz, 2H, $H_{o'}$), 7.96 (t, *J* = 1.8 Hz, 2H, H_{pp_x}), 7.90 (d, 2H, $H_{op_{z'}}$), 7.89 (t, 1H, $H_{pp_{z'}}$), 7.61 (d, *J* = 8.7 Hz, 4H, $H_{o''}$), 7.60 (d, 2H, H_m), 7.46 (d, *J* = 8.2 Hz, 2H, $H_{m'}$), 7.43 (s, 2H, $H_{5'',6''}$), 6.26 (d, *J* = 8.7 Hz, 4H, $H_{m''}$), 4.00 (q, *J* = 7.8 Hz, 4H, $(CH_2)_c$), 3.95 (s, 4H, H_ϵ), 3.87 (q, *J* = 7.4 Hz, 4H, $(CH_2)_b$), 3.80 (t, *J* = 4.3, 5.4 Hz, 4H, H_δ), 3.77 (t, *J* = 4.7 Hz, 4H, H_γ), 3.64 (t, *J* = 5.5, 4.4 Hz, 4H, H_β), 3.59 (m, 4H, H_α), 2.97 (s, 6H, $(CH_3)_d$), 1.85 (s, 6H, $(CH_3)_a$), 1.75 (t, *J* = 7.4 Hz, 6H, $(CH_3)_c$), 1.65 (t, *J* = 8.0 Hz, 6H, $(CH_3)_b$), 1.55 (s, 18H, $H_{t\text{-}Bu_z}$), 1.53 (s, 36H, $H_{t\text{-}Bu_x}$), 1.52 (s, 18H, $H_{t\text{-}Bu_{x'}}$), −2.60 (s, br, 2H, NH); ES-MS, for $C_{166}H_{176}AuCuF_{12}N_{12}P_2O_6$, found *m/z* 2841.8, 1348.4, 899.0, calcd *m/z* 2840.8 ($M^{2+}PF_6^-$), 1347.9 ($M^{2+}/2$), 898.9 ($[M^{2+} + H^+]/3$); UV–vis (CH_3CN) [λ, nm (ϵ, mol L^{-1} cm^{-1})] 243 (73 500 sh), 308 (50 400), 413 (382 000), 507 (19 700), 523 (19 200), 623 (1700), 649 (800, sh). $\mathbf{10}^{4+}(PF_6^-)_4$: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.99 (s, 2H, H_p), 9.34 (d, *J* = 1.1 Hz, 8H, H_{py_3} + H_{py_4}), 9.29 (d, *J* = 5.2 Hz, 4H, H_{py_2}), 9.11 (d, *J* = 8.5 Hz, 2H, H_4), 8.95 (d, *J* = 8.4 Hz, 2H, H_3), 8.64 (d, *J* = 9.0 Hz, 2H, H_7), 8.60 (d, *J* = 5.2 Hz, 4H, H_{py_1}), 8.46 (d, *J* = 9.0 Hz, 2H, H_8), 8.43 (d, *J* = 8.2 Hz, 4H, $H_{4'',7''}$), 8.37 (d, *J* = 8.3 Hz, 2H, H_5), 8.34 (d, *J* = 8.2 Hz, 2H, H_6), 8.14 (d, *J* = 8.2 Hz, 4H, $H_{3'',8''}$), 8.10 (d, *J* = 1.8 Hz, 8H, H_{op_x}), 8.08 (d, *J* = 1.8 Hz, 4H, H_{op_z}), 8.08 (d, *J* = 9 Hz, 4H, H_o), 7.97 (t, *J* = 1.8 Hz, 4H, H_{pp_x}), 7.96 (d, *J* = 8.7 Hz, 4H, $H_{o'}$), 7.95 (t, *J* = 1.7 Hz, 2H, H_{pp_z}), 7.60 (d, *J* = 8.6 Hz, 8H, $H_{o''}$), 7.55 (d, *J* = 8.1 Hz, 4H, H_m), 7.43 (d, *J* = 8.2 Hz, 4H, $H_{m'}$), 7.40 (s, 4H, $H_{5'',6''}$), 6.24 (d, *J* = 8.7 Hz, 8H, $H_{m''}$), 3.93 (s, 8H, H_ϵ), 3.79 (q, *J* = 4.5 Hz, 8H, $(CH_2)_{b+c}$), 3.75 (t, *J* = 5.3 Hz, 8H, H_δ), 3.63 (t, *J* = 5.3 Hz, 16H, $H_{\gamma+\beta}$), 3.59 (m, 8H, H_α), 1.74 (s, 12H, $(CH_3)_{a+d}$), 1.54 (s, 36H, $H_{t\text{-}Bu_z}$), 1.51 (s, 72H, $H_{t\text{-}Bu_x}$) (The triplet corresponding to $(CH_3)_{b+c}$ (12H) is hidden by the large singlets of $H_{t\text{-}Bu_x}$ and $H_{t\text{-}Bu_{x'}}$.); ES-MS, for $C_{272}H_{274}Au_2Cu_2F_{24}N_{20}O_{12}P_4$, found *m/z* 1133.9, calcd *m/z* 1134.1 ($M^{4+}/4$).

$\mathbf{9}^{2+}(\mathbf{PF_6^-})_2$. $\mathbf{8}^{2+}(PF_6^-)_2$ (0.066 g, 22 μmol) was dissolved in CH_2Cl_2 (15 mL). The red-orange solution was heated to reflux. $Zn(OAc)_2{\cdot}2H_2O$ (0.010 g, 45 μmol) in MeOH (5 mL) was added dropwise to the reaction mixture. The course of the reaction was followed by TLC and UV–visible spectroscopy. After 1.5 h of reflux, the reaction mixture had turned deep red. The solvents were removed *in vacuo*. The residue was taken up in CH_2Cl_2 (50 mL) and washed with 5% sodium carbonate (30 mL), then water (30 mL). The organic phase was concentrated to 50 mL and stirred overnight with 6.5% KPF_6 (25 mL). It was washed further with water, carefully isolated, and evaporated to dryness, leaving 0.11 g of crude product. All subsequent handling of the product was done by minimizing exposure to light as much as possible. The crude product was purified by column chromatography (50 g of alumina, CH_2Cl_2/hexane = 50/50). The fractions (200 mL) were monitored by TLC (alumina, 4% MeOH in CH_2Cl_2) and UV–visible spectroscopy. Those which did not show maxima at 534 and 573 nm with a constant OD ratio of 2.6 and a smooth OD decrease above 580 nm were discarded, although TLC analysis had shown they were quite acceptable. Elution with 0.16–0.27% MeOH in CH_2Cl_2 afforded a product which was further purified by chromatography (7.7 g of SiO_2, CH_2Cl_2/hexane = 50/50) to remove the impurities of very low polarity brought by the solvents. After washing of the column with CH_2Cl_2, the product was recovered by eluting with 1–2% MeOH in CH_2Cl_2. Solvents used in the latter column were of analytical grade. The purified product was handled in glassware which had been rinsed with high-quality solvents only. The amount of purified product was 0.036 g. Several chromatographic separations of the fractions which had been discarded earlier afforded an additional amount of 0.0084 g of pure product. The total yield of **9**$^{2+}(PF_6^-)_2$ was 0.0444 g (66%). Of course the yield of the metalation reaction was much higher, but we needed a spectroscopically pure product for photophysical studies. Subsequent studies indicated that it was indeed the case since the fluorescence decay of the compound could not be distinguished from the instrument response.[33] **9**$^{2+}(PF_6^-)_2$ is a cherry-red solid: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 10.12 (s, 2 H, H_p), 9.35 (d, J = 0.91 Hz, 4H, H_{py_3}, H_{py_4}), 9.30 (d, J = 5.2 Hz, 2H, H_{py_2}), 9.13 (d, J = 8.4 Hz, 1H, H_4), 8.97 (d, J = 8.4 Hz, 1H, H_3), 8.65 (d, J = 9.0 Hz, 1H, H_7), 8.60 (d, J = 5.2 Hz, 2H, H_{py_1}), 8.48 (d, J = 9.9 Hz, 1H, H_8), 8.46 (d, J = 8.3 Hz, 2H, $H_{4'',7''}$), 8.40 (d, J = 8.4 Hz, 1H, H_5), 8.36 (d, J = 8.3 Hz , 1H, H_6), 8.16 (d, J = 8.2 Hz, 2H, $H_{3'',8''}$), 8.13 (d, J = 8.6 Hz, 2H, H_o); 8.11 (d, J = 1.8 Hz, 4H, H_{op_x}), 8.09 (d, J = 1.8 Hz, 2H, H_{op_z}), 7.98 (t, J = 1.8 Hz, 1H, H_{pp_z}), 7.97 (d, J = 7.0 Hz, 2H, $H_{o'}$), 7.96 (t, J = 1.8 Hz, 2H, H_{pp_x}), 7.89 (t, J = 1.8 Hz, 2H, $H_{op_{z'}}$), 7.86 (t, J = 1.9 Hz, 1H, $H_{pp_{z'}}$), 7.62 (t, J = 8.6 Hz, 4H, $H_{o''}$), 7.60 (d, J = 7.4 Hz, 2H, H_m), 7.45 (d, J = 8.4 Hz, 2H, $H_{m'}$), 7.44 (s, 2H, $H_{5'',6''}$), 6.25 (d, J = 8.7 Hz, 4H, $H_{m''}$), 3.99 (q, J = 7.6 Hz, 4H, $(CH_2)_c$), 3.94 (s, 4H, H_ϵ), 3.84 (q, J = 7.6 Hz, 4H, $(CH_2)_b$), 3.80 (t, J = 5 Hz, 4H, H_δ), 3.77 (t, J = 4.8 Hz, 4H, H_γ), 3.64 (t, J = 5 Hz, 4H, H_β), 3.58 (m, 4H, H_α), 2.44 (s, 6H, $(CH_3)_d$), 1.80 (s, 6H, $(CH_3)_a$), 1.75 (t, J = 7.5 Hz, 6H, $(CH_3)_c$, 1.65 (t, J = 7.5 Hz, 6H, $(CH_3)_b$), 1.55 (s, 18H, $H_{t\text{-}Bu_z}$), 1.53 (s, 36H, $H_{t\text{-}Bu_x}$), 1.51 (s, 18H, $H_{t\text{-}Bu_{z'}}$), FAB-MS, for $C_{166}H_{174}AuCuF_{12}N_{12}O_6P_2Zn$, found m/z 2903.3, 2758.0, 2127.7, 1379.4, 629, calcd m/z 2903.7 ($M^{2+}PF_6^-$), 2759.2 ($M^{2+} + e^-$), 2128.9 (threaded fragment), 1379.6 ($M^{2+} + 2e^-$), 630.2 ($3Cu^+$); UV–vis (CH_3CN) [λ, nm (ϵ, mol L^{-1} cm^{-1})] 244 (90 700 sh), 320 (68 600), 413 (678 000), 538 (32 000), 573 (9600).

11^{4+}**$(PF_6^-)_4$.** **10**$^{4+}(PF_6^-)_4$ (0.073 g, 14.3 μmol) was dissolved in CH_2Cl_2 (15 mL). The resulting solution was heated to reflux. $Zn(OAc)_2 \cdot 2H_2O$ (0.0065 g, 29.6 μmol) in MeOH (6 mL) was added dropwise to the reaction mixture. The course of the reaction was followed by UV–visible spectroscopy. After 2 hours heating, more zinc acetate (0.0057 g, 25.9 μmol) was added, and reflux was continued for 1.5 h. The solvents were evaporated off. The residue was taken up in CH_2Cl_2 and washed with 5% Na_2CO_3 (40 mL). The organic phase was washed with water, and the solvents were evaporated off. The residue was dissolved in CH_2Cl_2 (10 mL) and treated overnight with 6.5% KPF_6 (10 mL). The two phases were separated, and the organic phase was washed with water. The solvents were evaporated off, and the residue was dried *in vacuo*. It was purified by column chromatography (alumina, CH_2Cl_2/hexane = 50/50). Elution with 0.2% MeOH in CH_2Cl_2 afforded pure **11**$^{4+}(PF_6^-)_4$: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.99 (s, 2H, H_p), 9.34 (d, 8H, H_{py_3}, H_{py_4}), 9.29 (d, J = 4.6 Hz, 4H, H_{py_2}), 9.12 (d, J = 8.4 Hz, 2H, H_4), 8.95 (d, J = 7.4 Hz, 2H, H_3), 8.65 (d, J = 8.9 Hz, 2H, H_7), 8.61 (d, J = 4.6 Hz, 4H, H_{py_1}), 8.47 (d, J = 9.9 Hz, 2H, H_8), 8.43 (d, J = 8.2 Hz, 4H, $H_{4'',7''}$), 8.37 (d, J = 8.4 Hz, 2H, H_5), 8.35 (d, J = 7.4 Hz, 2H, H_6), 8.14 (d, J = 8.3 Hz, 4H, $H_{3'',8''}$), 8.10 (d, 8H, H_{op_x}), 8.08 (d, 4H, H_{op_z}), 7.98 (t, 2H, H_{pp_z}), 7.97 (d, 4H, $H_{o'}$), 7.95 (br s, 4H, H_{pp_x}), 7.60 (d, J = 8.6 Hz, 8H, $H_{o''}$), 7.55 (d, J = 8.4 Hz, 4H, H_m), 7.43 (d, J = 7.9 Hz, 4H, $H_{m'}$), 7.40 (s, 4H, $H_{5'',6''}$), 6.24 (d, J = 8.7 Hz, 8H, $H_{m''}$), 3.93 (s, 8H, H_ϵ), 3.79 (q, 8H, $(CH_2)_{b+c}$), 3.75 (m, 16H, $H_{\gamma+\delta}$), 3.65 (m, 8H, H_β), 3.57 (m, 8H, H_α), 1.74 (s, 12 H, $(CH_3)_{a+d}$), 1.55 (s, 36H, $H_{t\text{-}Bu_z}$), 1.54 (s, 72H, $H_{t\text{-}Bu_x}$) (H_o (4H) is hidden by H_{op_x} and H_{op_z}; $(CH_3)_{b+c}$ (12H) is hidden by the large singlets of $H_{t\text{-}Bu_x}$ and $H_{t\text{-}Bu_z}$).

12^{+}**(PF_6^-).** **9**$^{2+}(PF_6^-)_2$ (0.011 g, 3.61 μmol) and potassium cyanide (0.0055 g, 84.4 μmol) were dissolved in a mixture of CH_3CN (7 mL), CH_2Cl_2 (1.2 mL), and H_2O (1 mL). The reaction mixture was stirred for 2 h and checked by TLC. Potassium cyanide (0.0026 g, 40 μmol) in H_2O (0.8 mL) was added, and stirring was continued for 2 h. The reaction mixture was diluted with CH_2Cl_2, and the organic phase was washed with water to remove excess KCN. The solvents were evaporated, and the residue was dissolved in CH_2Cl_2 (15 mL). The solution was stirred overnight with 6.5% KPF_6 (15 mL). The organic phase was isolated, washed three times with H_2O, and evaporated to dryness. The product was purified by column chromatography (7 g of alumina, CH_2Cl_2/hexane = 50/50). Elution with CH_2Cl_2 afforded pure **12**$^{+}(PF_6^-)$, 0.0081 g (79%): ^{1}H NMR (400 MHz, CD_2Cl_2), δ 10.14 (s, 2H, H_p), 9.78 (d, J = 8.2 Hz, 2H, $H_{4'',7''}$), 9.22 (d, J = 8.1 Hz, 2H, $H_{3'',8''}$), 9.18 (d, J = 5.2 Hz, 2H, H_{py_3}), 9.14 (d, J = 5.2 Hz, 2H, H_{py_4}), 8.83 (d, J = 5.2 Hz, 2H, H_{py_2}), 8.69 (d, J = 8.5 Hz, 1H, H_4), 8.64 (d, J = 5.2 Hz, 2H, H_{py_1}), 8.61 (AB, J = 8.4 Hz, 2H, $H_{3,8}$), 8.37 (d, J = 8.4 Hz, 2H, H_o), 8.28 (d, J = 8.7 Hz, 4H, $H_{o''}$), 8.10 (AB, J = 8.9 Hz, 2H, $H_{5,6}$), 7.94 (d, J = 1.8 Hz, 2H, H_{op_z}), 7.92 (t, J = 1.8 Hz, 2H, H_{pp_x}), 7.91 (d, J = 1.8 Hz, 2H, $H_{op_{z'}}$), 7.86 (t, J = 1.8 Hz, 1H, $H_{pp_{z'}}$), 7.83 (d, J = 8.1 Hz, 2H, $H_{o'}$), 7.82 (d, J = 1.8 Hz, 4H, H_{op_x}), 7.14 (d, J = 8.8 Hz, 4H, $H_{m''}$), 7.05 (d, J = 8.3 Hz, 2H, H_m), 5.85 (d, J = 8.3 Hz, 2H, $H_{m'}$), 4.04 (q, J = 6 Hz, 4H, $(CH_2)_c$), 3.84 (m, 12H, $(CH_2)_b$, H_γ, H_δ), 3.61 (m, 12H, H_α, H_β, H_ϵ), 2.46 (s, 6H, $(CH_3)_d$), 2.02 (s, 6H, $(CH_3)_a$), 1.79 (t, J = 7.6 Hz, 6H, $(CH_3)_c$), 1.68 (t, J = 7.5 Hz, 6H, $(CH_3)_b$), 1.50 (s, 18 H, $H_{t\text{-}Bu_z}$), 1.47 (s, 36H, $H_{t\text{-}Bu_x}$), 1.46 (s, 18H, $H_{t\text{-}Bu_{z'}}$) (According to the integrals, the peaks of the following protons are hidden by other peaks, H_7(1) and H_{pp_z}(1) (region H_{op_z}, H_{pp_x}, and $H_{op_{z'}}$), and $H_{5'',6''}$(2) (H_{py3}).); ES-MS, for $C_{166}H_{174}AuF_6N_{12}O_6PZn$, found m/z 2698.9, 1379.7, 1348.2, 934.9, 913.8, 899.4, 878.1, calcd m/z 2695.6 (M^+), 1348.3 ($MH^{2+}/2$), 899.2 ($MH^{3+}/3$) (The peak at m/z 1379.7 could be identified as arising from **9**$^{2+}/2$, but this compound is a trace impurity, since it could not be detected either by ^{1}H NMR or by TLC.); UV–vis (CH_3CN) [λ, nm (ϵ, mol L^{-1} cm^{-1})] 240 (68 900), 276 (69 700), 330 (54 400), 413 (423 700), 538 (21 900), 573 (6500).

15^{3+}**$(PF_6^-)_3$.** **12**$^{+}(PF_6^-)$ (0.0077 g, 2.71 μmol) was dissolved in CH_2Cl_2 (9 mL). The solution was heated to reflux, and $Zn(OAc)_2 \cdot 2H_2O$ (0.0029 g, 13.2 μmol) in MeOH (3 mL) was added to the reaction mixture. Reflux was continued for 1.3 h. The solvents were evaporated off, and the residue was retaken in CH_2Cl_2 (10 mL). The solution was washed with water, stirred overnight with 6.5% KPF_6 (10 mL), washed again with H_2O, and evaporated to dryness. The crude product was purified twice by column chromatography (alumina, hexane/CH_2Cl_2 = 50/50). Elution with 0.2% MeOH in CH_2Cl_2 afforded **15**$^{3+}(PF_6^-)_3$ (0.003 g, 35%): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 10.10 (s, 2H, H_p), 9.34 (d, J = 1.2 Hz, 4H, $H_{py_3+py_4}$), 9.29 (d, J = 5.2 Hz, 2H, H_{py_2}), 9.12 (d, J = 8.4 Hz, 1H, H_4), 8.96 (d, J = 8.4 Hz, 1H, H_3), 8.65 (d, J = 9.0 Hz, 1H, H_7), 8.58 (d, J = 5.2 Hz, 2H, H_{py_1}), 8.47 (d, J = 9.0 Hz, 1H, H_8), 8.44 (d, J = 8.3 Hz, 2H, $H_{4'',7''}$), 8.40 (d, J = 8.3 Hz, 1H, H_5), 8.35 (d, J = 8.3 Hz, 1H, H_6), 8.15 (d, J = 8.3 Hz, 2H, $H_{3'',8''}$), 8.12 (d, J = 8.3 Hz, 2H, H_o), 8.10 (d, J = 1.8 Hz, 4H, H_{op_x}), 8.08 (d, J = 1.8 Hz, 2H, H_{op_z}), 7.98 (t, J = 1.8 Hz, 1H, H_{pp_z}), 7.96 (d, J = 8 Hz, 2H, $H_{o'}$), 7.96 (d, J = 1.8 Hz, 2H, H_{pp_x}), 7.87 (d, J = 1.8 Hz, 2H, $H_{op_{z'}}$), 7.85 (t, J = 1.7 Hz, 1H, $H_{pp_{z'}}$), 7.61 (d, J = 8.6 Hz, 4H, $H_{o''}$), 7.60 (d, J = 7 Hz, 2H, H_m), 7.44 (d, J = 8.2 Hz, 2H, $H_{m'}$), 7.43 (s, 2H, $H_{5'',6''}$), 6.25 (d, J = 8.7 Hz, 4H, $H_{m''}$), 3.98 (q, J = 7.3 Hz, 4H, $(CH_2)_c$), 3.94 (s, 4H, H_ϵ), 3.83 (q, J = 7.5 Hz, 4H, $(CH_2)_b$), 3.80 (t, J = 4.1–5.6 Hz, 4H, H_γ), 3.76 (t, J = 4.9 Hz, 4H, H_δ), 3.64 (t, J = 5 Hz, 4H, H_β), 3.58 (m, 4H, H_α), 2.43 (s, 6H, $(CH_3)_d$), 1.79 (s, 6H, $(CH_3)_a$), 1.73 (t, J = 7.6 Hz, 6H, $(CH_3)_c$), 1.64 (t, J = 7.4 Hz, 6H, $(CH_3)_b$), 1.54 (s, 18H, $H_{t\text{-}Bu_z}$), 1.52 (s, 36H, $H_{t\text{-}Bu_x}$), 1.50 (s, 18H, $H_{t\text{-}Bu_{z'}}$); ES-MS, for $C_{166}H_{174}AuF_{18}N_{12}O_6P_3Zn_2$, found m/z 1379.1, 1347.4, 920.1, 899.2, 878.2, calcd m/z 920.3 ($M^{3+}/3$). The peaks at 1379.1 on the one hand, 1347.4 and 899.2 on the other hand, could be identified as arising from compounds **9**$^{2+}$ and **12**$^{+}$, respectively, as trace impurities, since they could be detected neither by ^{1}H NMR nor by TLC.

7. **6** (0.040 g, 51 μmol) was dissolved in CH_2Cl_2 (36 mL). The solution was heated to reflux. $Zn(OAc)_2 \cdot 2H_2O$ (0.030 g, 138 μmol) in MeOH (14 mL) was added dropwise to the reaction mixture, and refluxing was continued for 3 h. The reaction mixture was evaporated to dryness, redissolved in CH_2Cl_2, and treated with 5% Na_2CO_3 (40 mL). The organic phase was washed with water and evaporated to dryness. The crude product was purified by column chromatography (15 g of alumina, hexane). Elution with 30% CH_2Cl_2 in hexane afforded pure **7**: ^{1}H NMR (200 MHz, CD_2Cl_2) δ 10.23 (s, 2H, H_p), 7.93 (d, J = 1.8 Hz, 4H, H_{op}), 7.86 (t, J = 1.8 Hz, 2H, H_{pp}), 4.04 (q, J = 7.5 Hz, 8H, $(CH_2)_b$), 2.47 (s, 12H, $(CH_3)_a$), 1.79 (t, J = 7.5 Hz, 12H, $(CH_3)_b$), 1.52 (s, 36H, $H_{t\text{-}Bu}$); FAB-MS, for $C_{60}H_{76}N_4Zn$, found m/z 918 (M + H^+), calcd m/z 917; UV–vis (dmf) [λ, nm (ϵ, mol L^{-1} cm^{-1})] 418 (336 000), 546 (17 900), 580 (4600).

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