the free-base porphyrin was examined in a nanosecond flash-photolysis experiment ($\lambda_{exc} = 532$ nm). This revealed a lifetime of 2 µs and a yield of 0.6, calculated on the basis of the photons absorbed by the PH_2 unit. The calculated yield allows us to establish that the PH_2^+-[Ir]-PAu^- state, formed by a two-step mechanism from the excited-state singlet of the free base, is essentially deactivated through the triplet state. The presence of this low-lying triplet state clearly facilitates charge recombination. It is expected that longer-lived charge-separated states can be obtained with other metalated porphyrins that do not display such low-lying triplet states.

The present system utilizes an iridium(III) complex as electron relay and central core. This species is particularly well suited to the construction of multicomponent assemblies that can undergo charge separation, as demonstrated, in particular, by the behavior of the triad PH_2-[Ir]-PAu. The fully charge-separated state is formed with a quantum efficiency of 0.5, and recombination is 50 times slower than in the corresponding diad PH_2-[Ir].

Experimental Section

Cyclic voltammetry was carried out in MeCN solution with Bu_4NPF_6 as supporting electrolyte, a Pt working electrode, a Pt counterelectrode, and a saturated calomel electrode (SCE) as reference. The typical sweep rate was 200 mV s^{-1}, and the window used was from -1.4 to $+1.3$ V. All waves were irreversible. Absorption spectra were recorded with a Perkin-Elmer Lambda 9 spectrophotometer. Uncorrected emission spectra were detected by a Spex Fluorolog II spectrofluorimeter, equipped with a phosphorimeter accessory (1934 D). The time-resolved luminescence apparatus was based on an Nd:YAG laser (35 ps FHWM = full width at half maximum) and a Streak Camera. The standard iterative reconvolution procedure with the laser profile was used to measure emission lifetimes shorter than 90 ps. Transient absorbance in the picosecond range was measured with a pump and probe system based on the same laser and an OMA detector. Time zero for these experiments was set at the end of the laser pulse, calibrated by a 3,3′-diethyloxadicorbocyanine iodide (DODCI, $C_{23}H_{23}N_2O_2I$) solution in methanol,[11] and decay analysis was performed after the end of the laser pulse. Under these conditions deconvolution of the signal with the laser profile was unnecessary. For excitation at 598 nm, the second harmonic (532 nm) was Raman-shifted by a cell containing perdeuterated cyclohexane. The PH_2 triplet yields and lifetimes were determined by a laser flash photolysis apparatus with a Nd:YAG laser (20 ns pulse). Triplet yields were measured in oxygen-free solutions with the models PAu and PH_2 as reference, only the photons absorbed by the examined unit were taken into account, and calculations were performed on the basis of the molar absorption coefficients. The error for quantum yield determinations was 20 % and that for lifetime determinations 10 %, unless otherwise specified. Further details on the experimental setup, solvents, sample preparation and experimental procedures can be found elsewhere.[5, 11, 12].

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A Hermaphrodite Molecule: Quantitative Copper(I)-Directed Formation of a Doubly Threaded Assembly from a Ring Attached to a String**

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Whereas catenanes, rotaxanes, and knots were regarded as laboratory curiosities only 15 years ago,[1] they are now relatively common molecules[2, 3] with a fast growing number of uses regarding electron transfer,[4] polymers,[5] and controlled molecular motions. The last-mentioned field of research is particularly active and has recently produced

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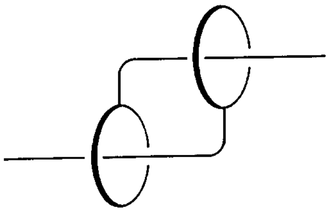
several examples of so-called molecular machines and motors.[6] To extend the number of working parts of future machines, topologies other than simple catenanes and rotaxanes are needed. In particular, one-dimensional molecular assemblies that can undergo stretching and contraction under the action of an external signal might contain the doubly threaded topology represented in Scheme 1.



Scheme 1. A molecular assembly with a doubly threaded topology.

Such a doubly threaded topology was recently obtained by Stoddart et al. in the solid state by dimerization of a self-complementary monomer, whereas in solution single-threading processes led to the formation of various pseudo-oligomeric rotaxane topologies.[7, 8] We now report that, by using copper(I) as a gathering and threading center, it is possible to generate the doubly threaded species shown schematically in Figure 1, both in solution and in the solid state. In such a dinuclear dimer each organic unit is a self-complementary monomer of a chelating ring attached to a coordinating stick. Due to the structural features of the ring-and-stick ligand **1**,[9] the complexation reaction that affords the doubly threaded copper(I) complex $\mathbf{2}^{2+}$ can be regarded as a double plugging-in process between the female (ring) and the male (coordinating stick) components; thus, the organic ligand has a hermaphroditic character.

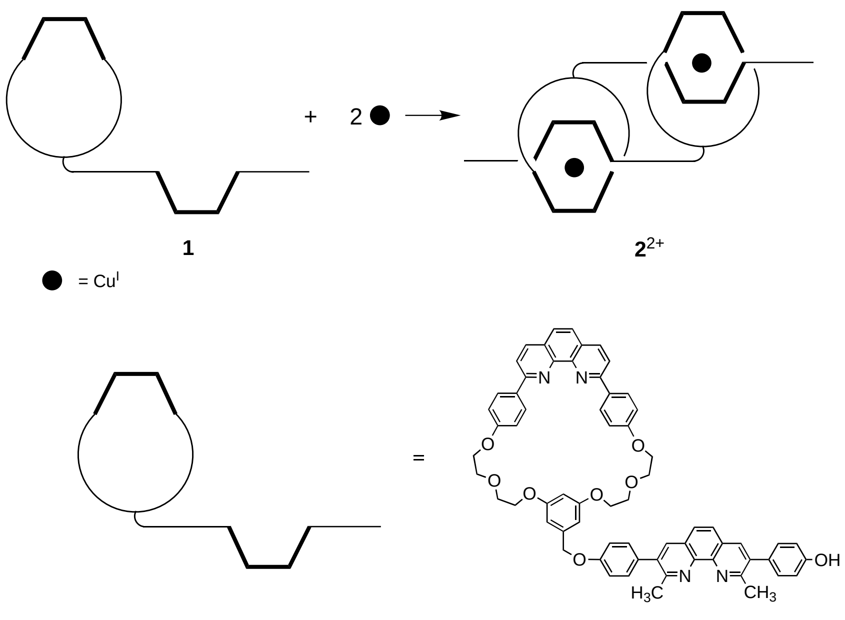


Figure 1. Schematic representation of the double-threading process induced by Cu^I (black dots) between two hermaphrodite ligands, each containing a chelating ring and a coordinating stick (the bidentate 1,10-phenanthroline units are represented by bold lines) and chemical structure of the ligand **1**.

The CPK model strongly suggested that **1** was not able to form an intramolecular tail-biting complex. The rigid rod consisting of 3,8-diaryl-1,10-phenanthroline is too stiff and connected to the ring by too short a linker for **1** to fold up so as to allow a self-threading process, comparable to what was observed in previously reported organic systems.[10] In fact, the dimerization shown in Figure 1 occurred quantitatively in solution when **1** was treated with a stoichiometric amount of $[Cu(CH_3CN)_4]PF_6$ in CH_3CN/CH_2Cl_2 at room temperature. Interestingly, ^1H NMR studies and thin-layer chromatography clearly showed that the initial kinetic mixture of copper(I) complexes obtained immediately after addition of the copper(I) salt to **1** re-equilibrates. The various cyclic or linear oligomers initially present in the reaction mixture besides $\mathbf{2}^{2+}$ are spontaneously converted to the thermodynamically more stable dimer $\mathbf{2}^{2+}$ in quantitative yield over a period of 48 h at room temperature.[11] The pronounced upfield shift observed for the aromatic protons H_o and H_m (Figure 2) and the various interfragment interactions revealed by 2D-ROESY NMR experiments (e.g., between CH_3 and H_o, H_m and $H_{o''}$, H_m and $H_{m'}$, $-OCH_2-$ and $H_{4'}$, H_m and $H_{m'}$) are clear evidence for the threading of the rigid linear stick of one ligand through the macrocycle of the other. The dimeric nature of $\mathbf{2}^{2+}$ was unambiguously supported by high-resolution mass spectrometry (ESI-MS). The spectrum of the single product obtained is that expected for $\mathbf{2}^{2+}$: it not only contains the molecular ion peak at m/z 2310.3 (calcd 2310.3), but also displays an intense, well-resolved peak at m/z 1082.7 (calcd for $M/2$: 1082.7) characteristic of a doubly charged species.

The dimer $\mathbf{2}^{2+}$ was isolated as deep red crystals of its PF_6^- salt. X-ray quality crystals were grown from acetone/diethyl ether by diffusion. The molecular structure of the dinuclear dimer $\mathbf{2}^{2+}$, which possesses only a single C_2 axis, is shown in Figure 3.[12] The complex contains two identical symmetry-related subunits, each consisting of one macrocycle, one linear 3,8-diaryl-1,10-phenanthroline rod, and one copper ion. The most striking feature of the structure is its linear extended arrangement, which results in a distance between the two terminal phenolic oxygen atoms of 36.3 Å. The two copper atoms are 18.3 Å apart and occupy similar environments. The coordination tetrahedron around each copper atom appears to be distorted, with two wide angles, one opening towards the outside of the molecule (N1-Cu-N3 125.6°) and the other towards the second copper ion of the complex (N2-Cu-N4 137.3°). The N−Cu distances range from 2.035 to 2.076 Å and are thus close to the values found in copper(I) complexes of related ligands.[13]

In conclusion, a new transition metal directed assembly and double-threading process has been shown to take place quantitatively in solution. Interestingly, the two threaded sticks are disposed antiparallel to one another, opening the door to

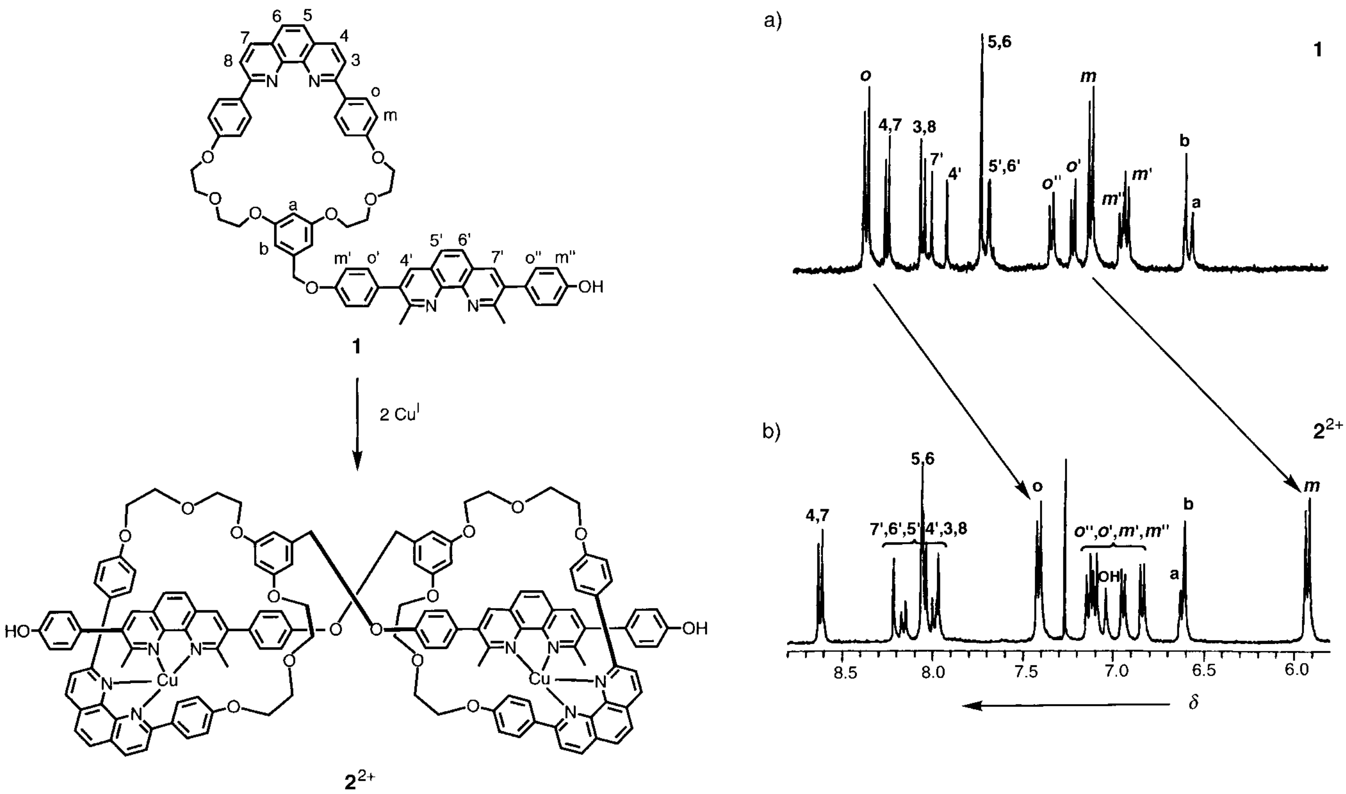


Figure 2. ^{1}H NMR spectra (400 MHz) of a) the free ligand **1** (in CD_2Cl_2/CD_3CN) and b) the doubly threaded dinuclear copper(I) dimer **2**$^{2+}$ (in CD_2Cl_2).

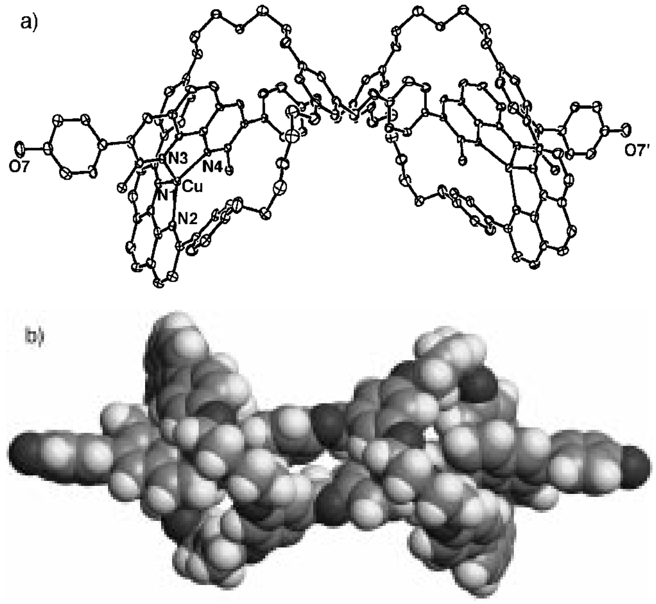


Figure 3. Crystal structure of the dicopper(I) dimer **2**$^{2+}$. a) ORTEP plot showing the numbering scheme adopted. b) Space-filling representation; the C_2 axis is shown perpendicular to the plane.

new one-dimensional multicomponent molecular systems and devices.

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[9] The synthesis of **1** will be reported elsewhere. **1**: ^{1}H NMR (400 MHz, CD_2Cl_2;see Figure 2 for assignments): $\delta = 2.77$ and 2.82 (2s, 6H, CH_3), 3.97 (m, 8H, $H_{\gamma,\delta}$), 4.20 (m, 4H, H_β), 4.36 (m, 4H, H_α), 5.05 (s, 2H, $ArOCH_2Ar$), 6.63 (brs, 1H, H_a), 6.67 (brs, 2H, H_b), 6.98 (d, $J = 8.6$ Hz, 2H, $H_{m'}$), 7.01 (d, $J = 8.3$ Hz, 2H, $H_{m''}$), 7.19 (d, $J = 8.8$ Hz, 4H, H_m), 7.28 (d, $J = 8.5$ Hz, 2H, $H_{o'}$), 7.40 (d, $J = 8.3$ Hz, 2H, $H_{o''}$),

7.75 (s, 1H, $H_{5'}$), 7.76 (s, 1H, $H_{6'}$), 7.80 (s, 2H, $H_{5,6}$), 7.99 (s, 1H, $H_{4'}$), 8.07 (s, 1H, $H_{7'}$), 8.12 (d, $J = 8.3$ Hz, 2H, $H_{3,8}$), 8.31 (d, $J = 8.3$ Hz, 2H, $H_{4,7}$), 8.43 (d, $J = 8.8$ Hz, 4H, H_o); FAB-MS: m/z calcd for $C_{65}H_{55}N_4O_8^+$: 1019.4; found: 1019.5.

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[11] $\mathbf{2}^{2+}$: ^1H NMR (400 MHz, CD_2Cl_2/CD_3CN): $\delta = 2.00$ and 2.09 (2s, 12H, CH_3), 3.35–3.89 (m, 32H, $H_{\alpha,\beta,\delta,\gamma}$), 4.96 (s, 4H, $ArOCH_2Ar$), 5.94 (d, $J = 8.6$ Hz, 8H, H_m), 6.62 (d, $J = 2.2$ Hz, 4H, H_b), 6.65 (t, $J = 2.2$ Hz, 2H, H_a), 6.85 (d, $J = 8.8$ Hz, 4H, $H_{m''}$), 6.96 and 7.12 (2d, $J = 8.2$ Hz, 8H, $H_{m'}$, $H_{o'}$), 7.06 (s, 2H, OH), 7.15 (d, $J = 8.5$ Hz, 4H, $H_{o''}$), 7.43 (d, $J = 8.6$ Hz, 8H, H_o), 7.99 (s, 2H, $H_{4'}$), 8.01 and 8.18 (2d, $J = 8.6$ Hz, 4H, $H_{5'}$, $H_{6'}$), 8.06 (d, $J = 8.5$ Hz, 4H, $H_{3,8}$), 8.09 (s, 4H, $H_{5,6}$), 8.18 (d, $J = 8.6$ Hz, 2H, $H_{5'}$), 8.24 (s, 2H, $H_{7'}$), 8.64 (d, $J = 8.3$ Hz, 4H, $H_{4,7}$); ESI-MS: m/z calcd for $Cu_2C_{130}H_{108}N_8O_{16}PF_6^+$: 2310.3; found: 2310.3; $M/2$ calcd for $Cu_2C_{130}H_{108}N_8O_{16}^{2+}$: 1082.7; found: 1082.7.

[12] X-ray crystallography for $\mathbf{2}^{2+}$. Deep red single crystals of $\mathbf{2}^{2+} \cdot 2PF_6^- \cdot 2CH_3OH$ were obtained as described above. $C_{67}H_{61}O_{10}N_4PF_6Cu$, $M_r = 1290.76$, monoclinic, $a = 25.543(1)$, $b = 20.870(1)$, $c = 27.869(1)$ Å, $\beta = 116.96(2)°$, $V = 13242(2)$ Å^3, space group $C2/c$, $Z = 4$, $\rho_{calcd} = 1.295$ g cm^{-3}, $\mu = 4.296$ mm^{-1}. Data were collected at −100 °C on a Nonius Kappa CCD diffractometer by using the standard data-collection procedures ($2.5 < \theta < 30°$) and graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) on a crystal of dimensions $0.30 \times 0.30 \times 0.20$ mm^3. 21423 data collected; 7329 with $I > 3\sigma(I)$. The structure was solved by direct methods. The diffraction power of the crystals was very poor, and the data of four samples were collected with the same results. It was therefore not possible to fully resolve the disorder of one of the PF_6^- ions and to locate all solvent molecules, even by refining on F^2 and using all data with $I > 2\sigma(I)$. Nevertheless, the core of the molecule is correct and refines normally. Final results: $R = 0.142$, $Rw = 0.193$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-135902. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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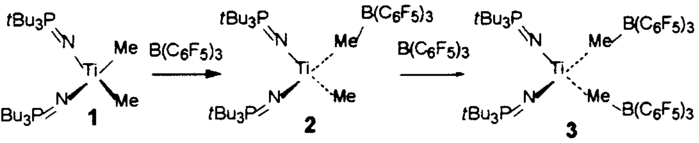
Synthesis and Structure of the Dicationic Bisborate Adduct $[(tBu_3PN)_2Ti\{\mu\text{-}MeB(C_6F_5)_3\}_2]$**

Frédéric Guérin and Douglas W. Stephan*

Complexes of nitrogen-based ligands have been the focus of much attention in the quest for new olefin polymerization catalysts. For example, Brookhart and co-workers[1–4] and Gibson and co-workers [5, 6] have recently reported unprecedented Fe- and Cr-based polymerization catalysts containing Schiff-base ligands, while McConville and co-workers[7, 8] observed living olefin polymerization using a Ti–amide catalyst. Recently, we described titanium compounds containing phosphanimide ligands of the form $[CpTi(NPR_3)Me_2]$ (R = tBu, iPr, Cy; Cp = C_5H_5) and $[(tBu_3PN)_2TiMe_2]$ (**1**).[9, 10] These species are catalyst precursors for olefin polymerization, and in fact **1** is highly active under both laboratory screening (1 atm, 25 °C) and commercially relevant (103 bar, 160 °C) polymerization conditions. The interaction of the precursors with Lewis acid activators is of fundamental importance. Marks,[11–15] Jordan,[16–18] and Bochmann[19] and their groups have elucidated the interaction of metallocenes with Lewis acid activators. The analogous chemistry of non-metallocene catalysts with Lewis acids has drawn lesser attention. Herein, we describe reactions of **1** with the Lewis acid $B(C_6F_5)_3$. In the reaction with excess borane $B(C_6F_5)_3$, a bis-borate zwitterionic species is obtained.

We have previously described the stoichiometric reaction of **1** with $B(C_6F_5)_3$ which generates the zwitterionic species $[(tBu_3PN)_2TiMe(\mu\text{-}Me)B(C_6F_5)_3]$ (**2**) (Scheme 1).[9] This isolated species is an active catalyst for ethylene polymerization.[9] While single-component catalysts are of interest, in situ generation of catalysts by the combination of precursor complex and co-catalyst is a more common practice. In the generation of **2** in situ for ethylene polymerization experiments, we noted that the order of addition of the reagents had a dramatic effect on the activity. Initially, **2** was generated by adding **1** to a solution of $B(C_6F_5)_3$ at 25 °C under an ethylene atmosphere. This led to poor activity and thus to only a small amount of polyethylene (PE; < 50 g of PE per mmol per hour). In contrast, addition of $B(C_6F_5)_3$ to a solution of **1** gave significantly increased catalyst activity[20] (265 g PE mmol^{-1} h^{-1}).



Scheme 1. Generation of **2** and **3** through reaction of **1** with $B(C_6F_5)_3$.

In probing these observations, we examined the reaction of **1** in the presence of excess $B(C_6F_5)_3$ in CH_2Cl_2 under an N_2 atmosphere. Upon addition of **1**, a yellow crystalline product **3** was formed immediately, which was isolated in 95 % yield. ^1H, ^{13}C, ^{19}F, ^{11}B, and ^{31}P NMR spectroscopic data confirmed the presence of the B and Ti moieties. The observation of a distinct ^{31}P chemical shift indicated that this new product **3** was not the 1:1 zwitterionic species **2**. Moreover, the presence of a single, temperature-invariant, Ti–methyl environment suggested the formation of a bis-$B(C_6F_5)_3$ adduct.

Crystals of $\mathbf{3} \cdot 2CH_2Cl_2$ were isolated from CH_2Cl_2. A crystallographic study[21] confirmed that $[(tBu_3PN)_2Ti\{\mu\text{-}MeB(C_6F_5)_3\}_2]$ (**3**), an unprecedented di-zwitterionic species, sits on a position with crystallographically imposed twofold symmetry (Figure 1). The pseudo-tetrahedral coordination sphere about Ti comprises the nitrogen atoms of the

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