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Quantitative formation of a tetraporphyrin [2]catenane *via* copper and zinc coordination

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A [2]catenane is formed quantitatively by mixing substituted 1,10-phenanthroline-based chelates with copper(I) acting as central template, the ring-forming reaction being based on 1the coordination of pyridinic bidentate ligands onto the zinc atoms of the four porphyrins surrounding the core of the molecule.

The ring-closing reactions used for making catenanes have mostly been restricted to the formation of strong covalent bonds[1] from the catenane precursor or, more recently, to that of dynamic covalent bonds, thus driving the system to its thermodynamic equilibrium.[2] An alternative strategy consists of forming the catenane from various coordinating fragments and transition metals, which after allowing the appropriate interactions between the ligands and the metals to take place, affords an interlocking structure.[3] If the coordination chemistry step is done under thermodynamic control, the yield of catenane is usually quantitative. In order for the system to find its way to the most stable structure, substitutionally labile metals have to be used in conjunction with suitable ligands. The first example of such a catenane was described by Fujita and co-workers in 1994.[3a] It is based on palladium(II)–pyridinic nitrogen bonds, which are labile and allow thermodynamic control. By combining copper(I)–1,10-phenanthroline interactions and palladium(II)–pyridine interactions, several catenanes assembled *via* coordination chemistry have been made, which demonstrates the power of this approach based on associating two distinct coordination bonds.[3b–h]

We would now like to report that when the copper(I)-based strategy is used in cooperation with the coordination bond formed between a pyridyl group and the central zinc(II) atom of a porphyrin, a [2]catenane is also obtained quantitatively. The principle is depicted in Scheme 1.

The chemical structures of the various organic components **1** and **3**, and of the intermediate and final complexes $\mathbf{2}^+$ and $\mathbf{4}^+$, respectively, are represented in Scheme 2.

In a typical experiment, a CH_3CN solution of $Cu(CH_3CN)_4 \cdot PF_6$ (5.1 mg; 0.014 mmol) was added at r.t. to a CH_2Cl_2 solution of **1** (50.2 mg; 0.023 mmol). After stirring of the mixture for 3 h, solvent evaporation and work-up, $[\mathbf{2}^+][PF_6^-]$ was obtained quantitatively (53 mg) as a purple solid. This compound was reacted with two equivalents of **3**[4] at r.t. in CH_2Cl_2 for three hours. After pumping off the solvent, catenane $\mathbf{4}^+$ was isolated pure as its PF_6^- salt in quantitative yield.[5] $\mathbf{4}^+$ was characterized by ^{1}H NMR and ES-MS.

Upon coordination of the pyridinic fragments of **3** to the Zn porphyrin motifs of $\mathbf{2}^+$, very strong upfield shifts are observed. In particular, $H_{m'}$ is in the shielding region of the Zn porphyrin nuclei, its resonance signal appearing at 4.4 ppm (8.9 ppm in free **3**). The most characteristic ^{1}H NMR signals are shown in Fig. 1 for **3**, $\mathbf{2}^+$ and $\mathbf{4}^+$.

In order to check whether $\mathbf{4}^+$ is obtained as a kinetic product in the sequence of reactions presented in Scheme 1a) or if it is formed under thermodynamic control, two types of experiments were carried out:

(i) $\mathbf{4} \cdot (PF_6)$ (10 mg) was dissolved in 0.4 mL of CD_2Cl_2 and the composition of the solution was monitored by ^{1}H NMR as a function of time. Within 15 h at r.t., new peaks were formed, which correspond to the presence of the asymmetric catenane $\mathbf{5}^+$. The mixture contains approximately 80% of $\mathbf{4}^+$ and 20% of $\mathbf{5}^+$. Even after two weeks, the same ratio of $\mathbf{4}^+$ and $\mathbf{5}^+$ was measured. This observation tends to indicate that the equilibrium between the various possible catenanes depicted in Scheme 1b) has been reached.

(ii) $Cu(CH_3CN)_4 \cdot PF_6$ in CH_3CN was added to a CH_2Cl_2 solution of **1** and **3** (Cu^I : **1** : **3**, 1 : 2 : 2). After one day at r.t. with stirring, ^{1}H NMR shows that the same mixture as that obtained in experiment (i) has been formed, with exactly the same relative proportions of $\mathbf{4}^+$ and $\mathbf{5}^+$ (approximately 80% : 20%, respectively).

From experiments (i) and (ii), it is clear that $\mathbf{4}^+$ is the most stable product, formed under thermodynamic control, but contaminated by a significant amount of $\mathbf{5}^+$. The putative catenane $\mathbf{6}^+$ could not be detected.

The greater stability of $\mathbf{4}^+$ *versus* $\mathbf{5}^+$ and $\mathbf{6}^+$ can be relatively easily explained by considering the pyridyl–Zn interaction. The magnitude of the interaction is mostly determined by the basicity of the donor ligand and the Lewis acidity of the Zn atom. The more basic the ligand and the more acidic the central zinc atom, the stronger the interaction. Coordination of **1** to the central copper(I) atom in $\mathbf{2}^+$ increases the Zn acidity and thus favours formation of $\mathbf{4}^+$ over that of $\mathbf{5}^+$ or $\mathbf{6}^+$. In these two latter compounds, two and four pyridinic groups, respectively would be made less basic than in free **3**. This effect is detrimental to the formation of $\mathbf{5}^+$ and even explains the absence of $\mathbf{6}^+$ in experiments (i) and (ii).

In the diversity of compounds formed by mixing **1**, **3**, and Cu^+, Cu(I) has therefore a dual role:

It acts as a template which gathers and orients 2,9-diphenyl-1,10-phenanthroline incorporating compounds.

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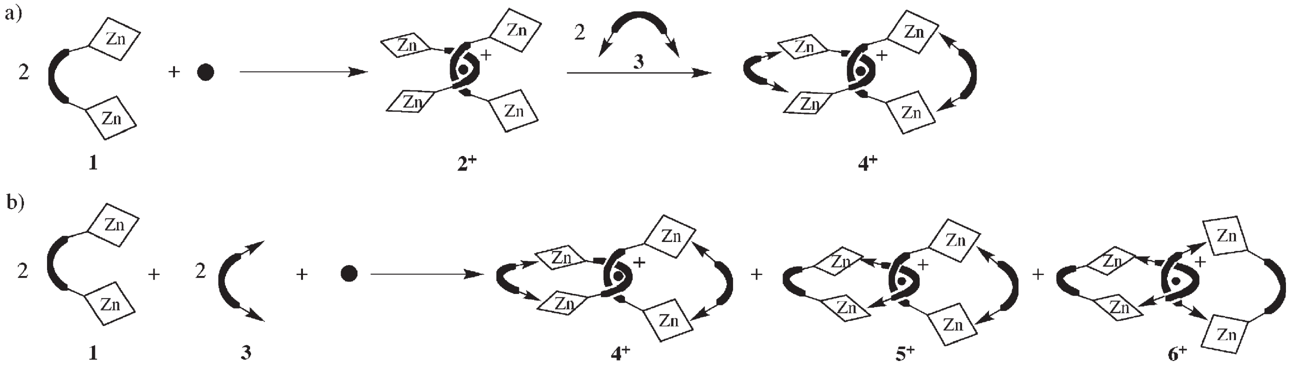
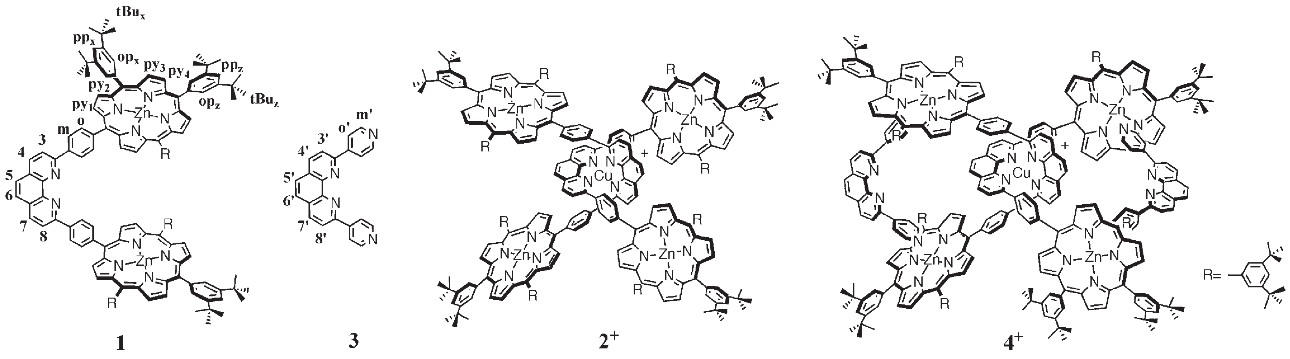


Scheme 1 (a) Stepwise formation of a [2]catenane using coordination bonds only. The diamonds represent Zn-complexed porphyrins, the black dot is a copper(I) atom and the arcs (thick lines) symbolise bidentate chelates of the 2,9-diphenyl-1,10-phenanthroline family. The second step leading to the catenane $\mathbf{4}^+$ involves ligand **3** whose two exotopic arrows symbolise 4-pyridyl nuclei. (b) the same [2]catenane $\mathbf{4}^+$ is expected to be obtained by mixing the various components in a statistical order provided ligand exchange is fast enough to allow thermodynamic control. Formation of asymmetric catenane $\mathbf{5}^+$ and symmetrical catenane $\mathbf{6}^+$ cannot, *a priori*, be excluded.



Scheme 2

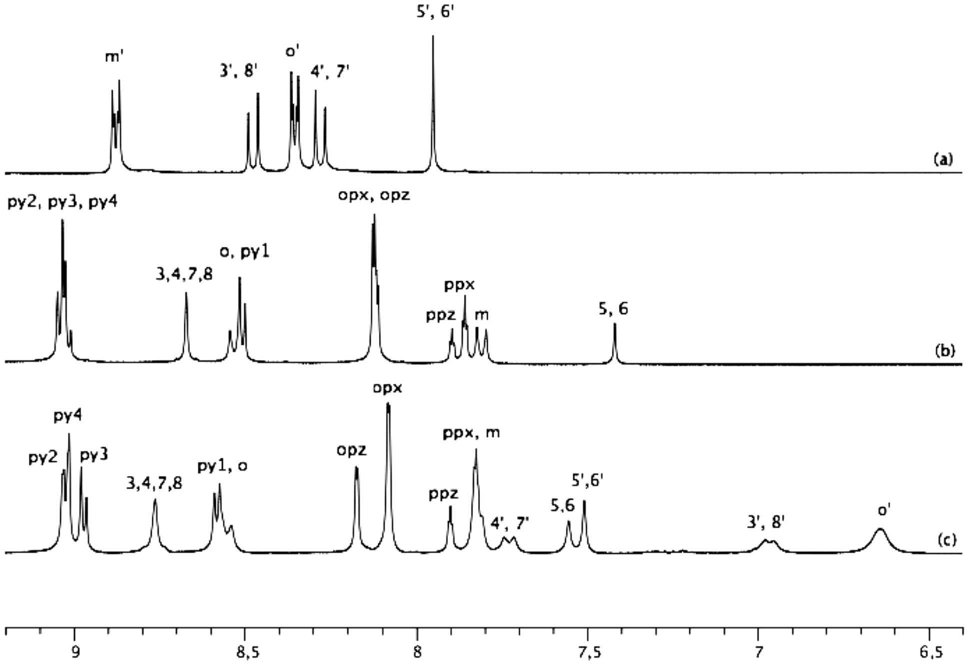


Fig. 1 Partial ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C) spectra of (a) **3**, (b) $\mathbf{2}^+$, (c) $\mathbf{4}^+$.

It has an electronic effect on the pyridine and porphyrin groups thus amplifying the formation of $\mathbf{4}^+$ at the expense of $\mathbf{5}^+$ and $\mathbf{6}^+$.

In conclusion, the interplay between the very strong copper(I)-1,10-phenanthroline interaction and the weaker Zn–pyridyl bond allows to prepare in high yield new catenanes with four peripheral Zn porphyrins surrounding the central copper(I) complex core. In addition, the two vacant coordination sites provided by the laterally disposed 1,10-phenanthroline nuclei opens the gate to more complex catenanes.

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4 The synthesis of compound **3** will be described in a forthcoming publication.

5 Compound $\mathbf{2}^+$: ^{1}H NMR (CD_2Cl_2, 300 MHz, 298 K) δ 9.05 (d, 8 H, ^{3}J = 4.7 Hz, py_2), 9.03 (d, 8 H, ^3J = 4.8 Hz, py_4), 9.02 (d, 8 H, ^3J = 4.7 Hz, py_3), 8.68 (bs, 8 H, 3, 8 + 4, 7), 8.54 (d, 8 H, ^3J = 8.7 Hz, o), 8.52 (d, 8 H, ^3J = 4.8 Hz, py_1), 8.13 (m, 24 H, op_z + op_x), 7.90 (t, 4 H, ^4J = 1.7 Hz, pp_z), 7.86 (t, 8 H, ^4J = 1.7 Hz, pp_x), 7.82 (d, 8 H, ^3J = 8.1 Hz, m), 7.43 (s, 4 H, 5, 6), 1.57 (s, 72 H, $t\mathrm{Bu}_z$), 1.54 (s, 144 H, $t\mathrm{Bu}_x$) ppm; ES/MS *m*/*z* 4475.56 ($\mathbf{2}^+$) calcd. 4474.97 for $C_{296}H_{312}N_{20}CuZn_4$; UV-vis (toluene): λ_{max} (logε) = 428 (6.07), 552 (4.79), 594 (4.60) nm. Compound **3**: ^{1}H NMR (CD_2Cl_2, 300 MHz, 298 K) δ 8.87 (d, 4 H, ^3J = 6.2 Hz, m′), 8.47 (d, 2 H, ^3J = 8.5 Hz, 3′, 8′), 8.35 (d, 4 H, ^3J = 6.2 Hz, o′), 8.26 (d, 2 H, ^3J = 8.5 Hz, 4′, 7′), 7.94 (s, 2 H, 5′, 6′) ppm; ES/MS *m*/*z* 335.13 ($\mathbf{3} + H^+$) calcd. 335.39 for $C_{22}H_{14}N_4 + H^+$. Compound $\mathbf{4}^+$: ^{1}H NMR (CD_2Cl_2, 300 MHz, 298 K) δ 9.03 (d, 8 H, ^3J = 4.7 Hz, py_2), 9.01 (d, 8 H, ^3J = 4.8 Hz, py_4), 8.98 (d, 8 H, ^3J = 4.7 Hz, py_3), 8.76 (bs, 8 H, 3, 8 + 4, 7), 8.58 (d, 8 H, ^3J = 4.7 Hz, py_1), 8.56 (d, 8 H, ^3J = 8.7 Hz, o), 8.17 (d, 8 H, ^4J = 1.6 Hz, op_z), 8.08 (d, 16 H, ^4J = 1.6 Hz, op_x), 7.90 (t, 4 H, ^4J = 1.7 Hz, pp_z), 7.83 (m, 16 H, ^3J = 1.7 Hz, pp_x + m), 7.73 (bd, 4 H, ^3J = 8.2 Hz, 4′, 7′), 7.55 (s, 4 H, 5, 6), 7.50 (s, 4 H, 5′, 6′), 6.96 (bd, 4 H, ^3J = 7.6 Hz, 3′, 8′), 6.65 (bs, 8 H, o′), 4.40 (vbs, 8 H, m′), 1.60 (s, 72 H, $t\mathrm{Bu}_z$), 1.50 (s, 144 H, $t\mathrm{Bu}_x$) ppm; ES/MS *m*/*z* 2572.20 ($(\mathbf{4}^+ + H^+)/2$) calcd. 5144.74 for $C_{340}H_{340}N_{28}CuZn_4 + H^+$; UV-vis (toluene): λ_{max} (logε) = 430 (6.07), 561 (4.79), 606 (4.60) nm.