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A 1,10-Phenanthroline-Containing Ring Connected to a Porphyrin by a Rigid Aromatic Spacer and Its Copper-Complexed Pseudorotaxane

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A condensation reaction involving a free base tetraarylporphyrin-2,3-dione, a macrocyclic compound containing a 1,10-phenanthroline-5,6-dione and a 1,2,4,5-tetraminobenzene as a linker affords the corresponding conjugate in good yield. The porphyrin ring and the phenanthroline fragment of the other ring are connected in such a way that mutual rotation between these two groups is prohibited. Metallation of the porphyrinic site affords the corresponding zinc complex. By reacting this zinc porphyrin with copper(I), followed by the addition of the bidentate chelate 2,9-bis(*p*-anisyl)-1,10-phenanthroline, the threading reaction leading to the corresponding pseudorotaxane takes place quantitatively.

Porphyrins have been incorporated in rotaxanes and catenanes as electro- and photoactive components, mostly in relation to models of the photosynthetic reaction centre, to host–guest chemistry or to dynamic systems able to undergo large amplitude motions.[1] Our group has been particularly interested in energy and electron transfer studies within such rotaxanes or catenanes.[2] The porphyrin nucleus can be used as a stopper (for rotaxanes), either attached to or part of the ring.[3] Till now, limited geometrical control could be achieved as the mutual orientation between the porphyrin and the ring was not controlled, especially when the porphyrin fragment was appended to the cyclic component(s) of the rotaxane or the catenane. To have strict geometrical control over the system, it is necessary to connect the porphyrin and the ring by a rigid spacer, for which free rotation is not allowed. In the present report, we would like to describe the synthesis of such a conjugate consisting of a 30-membered ring built from 2,9-diaryl-1,10-phenanthroline and a free-base porphyrin or a zinc-complexed porphyrin. The spacer between these two components is a rigid aromatic nucleus. In addition, to demonstrate that the rigidly held porphyrin-macrocycle conjugates prepared can be used as components of interlocking structure, we have assembled a pseudorotaxane using the copper(I)-based strategy already applied in other related reactions.[2,3] The threaded species obtained by mixing the Zn-containing porphyrin-ring conjugate, copper(I) and a coordinating fragment of the 1,10-phenanthroline family, is indeed obtained in quantitative yield.

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The synthetic strategy relies on porphyrin α-dione **1** similar to that used by Crossley and coworkers for making di- and multiporphyrins as well as electrodeficient porphyrins with quinoxaline groups at their periphery.[4] The other important fragment, namely the macrocycle containing phenanthroline dione **2**, was prepared in our group in the frame of another project dealing with multirotaxanes.[5] Phenanthroline–porphyrin conjugates with back-to-back connection were described recently by other groups but in these examples, the 1,10-phenanthroline part was not contained within the macrocycle.[6]

Starting diones **1** and **2**, as well as the condensation reaction leading to porphyrin conjugates **4** and **5**, are represented in Figure 1.

The synthesis of porphyrin α-dione **1** proceeds from the copper(II) complex of *meso*-tetra(3′,5′-di-*tert*-butylphenyl)-porphyrin, which was first reacted with $LiNO_3$ in AcOH/Ac_2O to afford the corresponding β-nitro copper(II) porphyrin in high yield (90%) as described by Callot.[7] Then, adapted from Burn's methodology,[8] this porphyrin was demetallated with H_2SO_4 and the NO_2 function was reduced to an NH_2 group by $SnCl_2$ and HCl in CH_2Cl_2. The subsequent oxidation reaction leading to **1** was carried out by using Dess–Martin periodinane. The analytical and spectroscopic properties of the compound obtained are similar to those of the literature.[8] Compound **1** was obtained from the starting copper(II) porphyrin in four steps (nitration, demetallation, reduction and oxidation) with an overall yield of approximately 40%.

The coupling reaction between **1** and **2**[5] was performed by a stepwise condensation using 1,2,4,5-benzenetetramine.[6] Porphyrin α-dione **1** and benzenetetramine tetrahydrochloride **3** (1.2 equiv.) were dissolved in freshly distilled pyridine, and the reaction mixture was kept in the

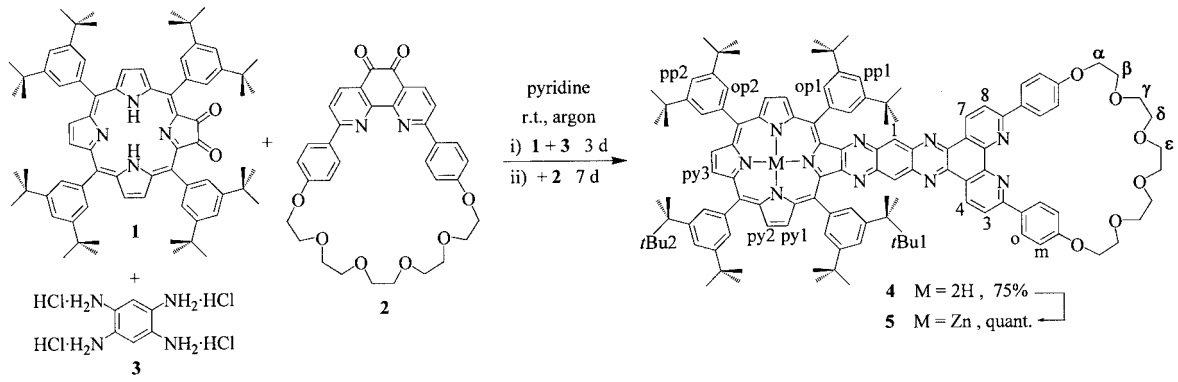

Figure 1. Stepwise condensation of the two diones with the bridging spacer.

dark. After gentle stirring at room temperature under an atmosphere of argon for 3 d, macrocycle **2** (1.5 equiv.) was added, and the reaction was prolonged under the same reaction conditions for an additional week. After workup and chromatographic purification (silica gel, CH_2Cl_2 with increasing amounts of CH_3OH – up to 0.3% – as eluent), **4** was obtained as a violet solid in 75% yield. It was fully characterised by ^1H NMR spectroscopy and high resolution (HR) ESMS.

Metallation of the porphyrinic site of **4** was selectively carried out by the addition of $Zn(OAc)_2$ (5 equiv., dissolved in CH_3OH) to a solution of **4** in CH_2Cl_2 heated at reflux.[6] Further treatment with an EDTA solution to remove Zn^{II} from the phenanthroline chelate allowed **5** to be obtained quantitatively from **4**.

The ^1H NMR spectra are in accordance with the structures of the compounds (Figure 2). As expected from the formation of the bridge at the back of the phenanthroline, protons 1 and 4,7 are strongly shifted upfield. Owing to the C_{2v} symmetry of the molecule, protons *t*Bu1 differ from protons *t*Bu2, which gives rise to two sets of signals. For the same reason, proton py3 is assigned to a characteristic singlet at δ = 8.76 ppm.

Compounds **4** and **5** are well adapted to the synthesis of more elaborate catenanes and rotaxanes. As an example, pseudorotaxane **7**·PF_6 was prepared quantitatively from the various corresponding organic fragments, **5** and **6**, in the presence of copper(I), acting as a gathering and threading centre. As represented in Figure 3, **6** is a 2,9-disubstituted 1,10-phenanthroline that is able to form very stable four-coordinate complexes with copper(I) once associated to another bidentate chelate of the 1,10-phenanthroline family. As expected, the reaction proceeded very cleanly: stoichiometric amounts of **5** and $[Cu(CH_3CN)_4](PF_6)$ were first mixed in dichloromethane to afford the desired copper(I) complex. Subsequently, a stoichiometric quantity of **6** was added, which led to desired pseudorotaxane **7** quantitatively after workup. Compound **7**·PF_6 is a deep purple solid, which was characterised by ^1H NMR (COSY-ROESY) and electronic spectroscopy and HRESMS.

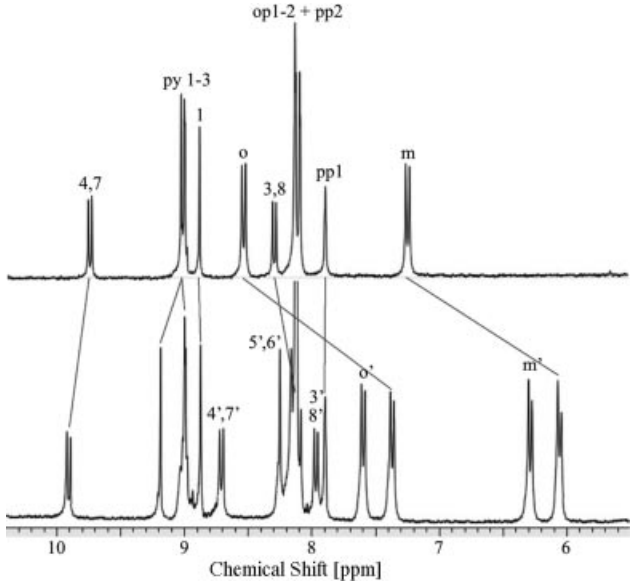

Figure 2. ^1H NMR spectra (aromatic region) of compounds **5** and **7**·PF_6 in CD_2Cl_2.

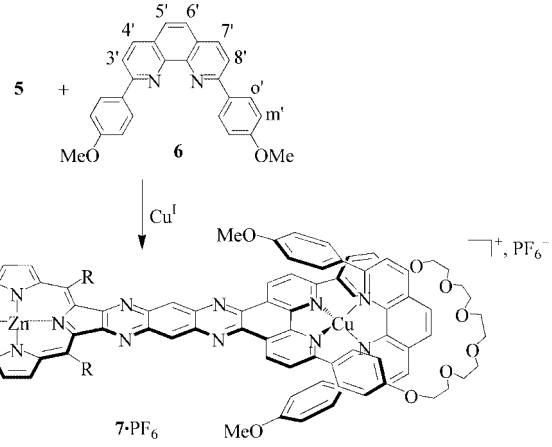

Figure 3. The threading reaction affording pseudorotaxane **7**.

To estimate the electronic coupling between the various aromatic fragments of **5** and **7** (the 1,10-phenanthroline chelate and the zinc-containing porphyrin), electronic absorption and emission measurements were performed. The absorption and emission spectra of the two compounds are represented in Figure 4.

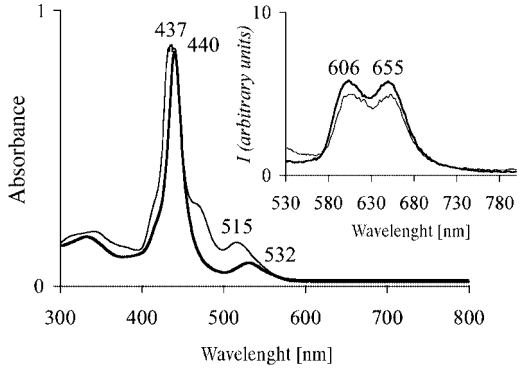

Figure 4. Normalised absorption and emission spectra (inset) of an optically matched solution of **5** (thin) and **7**·PF_6 (bold) (excitation at 438 nm) at 298 K in dichloromethane.

Interestingly, the Soret band for the two porphyrin-containing compounds is bathochromically shifted relative to that of the classical tetraaryl porphyrins.[9] Whereas a normal Soret band is typically observed around 420 nm for Zn porphyrins of this series, the present compounds show a Soret band in the range 435–440 nm. In addition, significant broadening is observed, which is a clear indication that the aromatic system is perturbed by the presence of the tetraazaanthracene nucleus at the periphery of the porphyrin, as already observed by Flamigni and coworkers.[10] The observed broadening is likely to be due to the loss of symmetry of the porphyrin aromatic system by introducing a tetraazaanthracene fragment at its rim. A contribution of a hypothetical 1,10-phenanthroline-porphyrin electronic coupling cannot be excluded.

Whereas the absorption spectra of **5** and **7** are significantly different from that of a normal zinc(II) tetraarylporphyrin, their emission spectra have emission maxima at similar values (**5** and **7**; λ = 606, 655 nm). The tetraazaanthracene phenanthroline aromatic fragment at the back of the porphyrin has therefore little influence on the energy level of the lowest excited state of the porphyrin ring. This is quite surprising considering that in related tetraazaanthracene-substituted porphyrins studied by Flamigni and coworkers,[10] the excited state was stabilised by 0.2 eV. Nevertheless, in **5** and **7**, the emission intensity decreases dramatically and the quantum yield of the emission relative to that of zinc(II) 5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrin is only 0.3%. Further photophysical studies will be performed to understand these results.

In conclusion, a new conjugate consisting of a porphyrin and a coordinating ring was prepared in a few steps from sophisticated organic fragments, with a relatively good overall yield. The zinc-complexed porphyrinic system was further utilised to prepare a novel pseudorotaxane by taking advantage of the template effect of copper(I). The conjugate itself, either containing a free base or a zinc porphyrin, is rigid, which allows strict control over the geometry of the system and over that of the pseudorotaxane prepared. The same will hold true for future, more complex rotaxanes and catenanes containing **4** and **5**.

Experimental Section

General: Nuclear Magnetic Resonance (NMR) spectra were acquired with a Bruker AM300 spectrometer operating at 300.17 MHz. The spectra were referenced internally to residual proton-solvent reference. High resolution electrospray mass spectra (HRESMS) were recorded with a VG BOIQ triple quadrupole spectrometer by the Service de Spectrométrie de Masse (ISIS, Strasbourg). All anhydrous solvents were prepared by distillation under an atmosphere of argon with the use of the appropriate drying agents. All commercial chemicals were at the best commercially available grade and used without further purification. Thin layer chromatography was carried out with precoated polymeric sheets of silica gel (Macheray-Nagel, POLYGRAM, SIL G/UV_{254}) and preparative column chromatography was carried out by using silica gel (Merck Kiesegel, silica gel 60, 0.063–0.200 mm).

Compound 4: Avoiding light exposure, porphyrin tetraone **1** (50 mg, 4.58×10^{-5} mol) and benzene tetramine tetrahydrochloride **3** (15.7 mg, 5.53×10^{-5} mol, 1.2 equiv.) were dissolved in freshly distilled pyridine (25 mL), and the mixture was stirred at room temperature under an atmosphere of argon. After 2 d, macrocyclic dione **2** (41 mg, 6.87×10^{-5} mol, 1.5 equiv.) was added under a stream of argon, and the solution was reacted for another week under the same conditions. After removal of the solvent, the product was extracted with CH_2Cl_2 (50 mL) and water (50 mL). The organic layers were separated, washed with water (2×50 mL) and the solvents evaporated to dryness. The crude product (154 mg) was subjected to column chromatography (110 g of silica, prepared in CH_2Cl_2, gradient elution from CH_2Cl_2/MeOH 0 to 0.3%) to give compound **4** as a purple solid (60 mg, 75%). ^{1}H NMR (300 MHz, CD_2Cl_2, COSY-ROESY, 25 °C): δ = 9.75 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, $H_{4,7}$), 9.10 (d, $^3J_{H,H}$ = 4.9 Hz, 2 H, H_{py1}), 9.03 (d, $^3J_{H,H}$ = 4.9 Hz, 2 H, H_{py2}), 8.95 (s, 2 H, H_{py3}), 8.76 (s, 2 H, H_1), 8.56 (m, $^3J_{H,H}$ = 8.8 Hz, 4 H, H_o), 8.31 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H, $H_{3,8}$), 8.12–8.05 (m, 10 H, H_{op1}, H_{op2}, H_{pp2}), 7.86 (t, $^4J_{H,H}$ = 1.8 Hz, 2 H, H_{pp1}), 7.28 (m, $^3J_{H,H}$ = 8.9 Hz, 4 H, H_m), 4.39 (t, $^3J_{H,H}$ = 5.9 Hz, 4 H, H_α), 3.88 (t, $^3J_{H,H}$ = 5.9 Hz, 4 H, H_β), 3.76–3.64 (m, 12 H, H_γ, H_δ, H_ε), 1.57 (s, 36 H, H_{tBu2}), 1.54 (s, 36 H, H_{tBu1}), –2.35 (br. s, 2 H, H_{NH}) ppm. UV/Vis (CH_2Cl_2): λ (logε) = 434 (5.54) nm. HRESMS: calcd. for $C_{166}H_{127}N_{10}O_6$ and for 1/2[$C_{166}H_{127}N_{10}O_6$]$_2$ [**4** + H]$^+$ and [**4** + H]$_2^{2+}$ 1756.9967; found 1757.0025.

Compound 5: A solution of $Zn(OAc)_2$ (34 mg, 1.55×10^{-4} mol, ca. 5 equiv.) in MeOH (7 mL) was added to a boiling solution of compound **4** (50 mg, 2.85×10^{-5} mol) in CH_2Cl_2 (25 mL), and the mixture was heated at reflux for 6 h. After removal of the solvents, the product was extracted with CH_2Cl_2 (50 mL) and water (2×50 mL). The organic layers were separated, and the volume of the solution was reduced to approximately 30 mL. A solution of [EDTA]Na_4 (0.1 M, pH ca. 4–5, 10 mL) was added, and the mixture was stirred for 24 h. The organic layers were then extracted with CH_2Cl_2 (80 mL), separated, washed with saturated Na_2CO_3 (50 mL), brine (50 mL) and water (100 mL) and the solvents evaporated to dryness to give quantitatively compound **5** (51 mg). ^{1}H NMR (300 MHz, CD_2Cl_2, COSY-ROESY, 25 °C): δ = 9.69 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, $H_{4,7}$), 8.98 (s, 2 H, H_{py3}), 8.97–8.94 (2d, $^3J_{H,H}$ = 4.8 Hz, 4 H, H_{py1}, H_{py2}), 8.85 (s, 2 H, H_1), 8.48 (m, $^3J_{H,H}$ = 8.8 Hz, 4 H, H_o), 8.24 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H, $H_{3,8}$), 8.11–8.04 (m, 10 H, H_{op1}, H_{op2}, H_{pp2}), 7.85 (t, $^4J_{H,H}$ = 1.8 Hz, 2 H, H_{pp1}), 7.18 (m, $^3J_{H,H}$ = 8.8 Hz, 4 H, H_m), 4.26 (t, $^3J_{H,H}$ = 5.9 Hz, 4 H, H_α), 3.73 (t, $^3J_{H,H}$ = 5.9 Hz, 4 H, H_β), 3.62–3.51 (m, 12 H, H_γ, H_δ, H_ε), 1.57 (s, 36 H, H_{tBu2}), 1.55 (s, 36 H, H_{tBu1}) ppm. UV/Vis (CH_2Cl_2): λ (logε) = 437 (5.47), 515 (4.66) nm. HRESMS: calcd. for $C_{116}H_{124}N_{10}O_6Zn$ [**5** – e]$^+$

1818.9017; found 1818.8987 and calcd. for $C_{116}H_{125}N_{10}O_6Zn$ [**5** + H]$^+$ 1819.9095; found 1819.9013.

Compound 7·PF$_6$: A solution of $[Cu(MeCN)_4](PF_6)$ (3.6 mg, 9.34×10^{-6} mol) in MeCN (5 mL) was added by cannula to a degassed solution of **4** (17.0 mg, 9.34×10^{-6} mol) in CH_2Cl_2 (5 mL), and the mixture was stirred under an atmosphere of argon for 30 min. A degassed solution of dianisyl phenanthroline **6** (3.67 mg, 9.34×10^{-6} mol) in CH_2Cl_2 (5 mL) was then also added by cannula. After stirring for 2 h, the solution was extracted with CH_2Cl_2 (50 mL) and water (50 mL); the organic layers were separated, dried with $MgSO_4$ and evaporated to give pure rotaxane **7** as its PF_6 salt (22 mg, 97%). ^{1}H NMR (300 MHz, CD_2Cl_2, COSY-ROESY, 25 °C): δ = 9.88 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, $H_{4,7}$), 9.16 (s, 2 H, H_{py3}), 8.97–8.98 (2d, $^3J_{H,H}$ = 4.6 Hz, 4 H, H_{py1}, H_{py2}), 8.86 (s, 2 H, H_1), 8.68 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, $H_{4',7'}$), 8.22 (s, 2 H, $H_{5',6'}$), 8.13 (t, $^4J_{H,H}$ = 1.8 Hz, 2 H, H_{pp2}), 8.13 (t, $^4J_{H,H}$ = 1.7 Hz, 2 H, H_{pp1}), 8.06 (m, 10 H, $H_{3,8}$, H_{op1}, H_{op2}), 7.94 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, $H_{3',8'}$), 7.87 (t, $^4J_{H,H}$ = 1.7 Hz, 2 H, H_{pp1}), 7.57 (m, $^3J_{H,H}$ = 8.6 Hz, 4 H, $H_{o'}$), 7.35 (m, $^3J_{H,H}$ = 8.6 Hz, 4 H, H_o), 6.27 (m, $^3J_{H,H}$ = 8.6 Hz, 4 H, $H_{m'}$), 6.04 (m, $^3J_{H,H}$ = 8.6 Hz, 4 H, H_m), 3.85 (s, 4 H, H_ε), 3.79–3.55 (3m, 16 H, H_δ, H_γ, H_β, H_α), 3.26 (s, 6 H, H_{OMe}), 1.60 (s, 36 H, H_{tBu2}), 1.55 (s, 36 H, H_{tBu1}) ppm. UV/Vis (CH_2Cl_2): λ (logε) = 440 (5.55), 532 (4.55) nm. HRESMS: calcd. for $C_{142}H_{144}N_{12}O_8CuZn$ 2274.9843; found 2274.9647.

Acknowledgments

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