Porphyrinoid Interconversion

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Extrusion of Boron(III) Subporphyrin from *meso*-Heptakis(pentafluorophenyl)[32]heptaphyrin upon Cooperative Cu^{II} and B^{III} Metalation**

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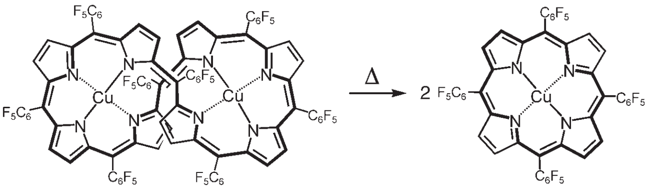
In recent years, there has been a surge in the discovery of chemical transformations that interconnect different porphyrinic macrocycles.[1] Recent representative examples include a transannular skeletal rearrangement of a diketo octaphyrin(1.1.1.0.1.1.1.0) to a spirodicorrole upon metalation with Ni^{II} ion,[2] a porphyrin-to-corrole ring contraction upon metalation with $[Re_2(CO)_{10}]$,[3] a spontaneous corrole-to-porphyrin ring expansion,[4] a corrole-to-hemiporphycene ring expansion in the reaction with carbon tetraiodide,[5] and double pyrrolic rearrangement of *meso*-aryl-substituted hexaphyrin to doubly N-confused hexaphyrin upon treatment with Cu^{I} ion.[6] Additionally, we reported the thermal splitting reaction of a bis-copper(II) octaphyrin into two copper(II) porphyrins, a novel topological process that proceeds quantitatively with perfect material balance in a metathesis fashion (Scheme 1).[7]



Scheme 1. Splitting reaction of bis-copper(II) octaphyrin.

These results strongly suggest that some porphyrinic macrocycles are not robust but susceptible to drastic skeletal rearrangements under suitable conditions. Here we report the extrusion reaction of boron(III) *meso*-tris(pentafluorophenyl)subporphyrin from *meso*-heptakis(pentafluorophenyl)[32]heptaphyrin(1.1.1.1.1.1.1) (**1**) upon cooperative metalation of Cu^{II} and B^{III} ions as a novel metathesis-type transformation.

Until our first synthesis of tribenzosubporphines in 2006,[8,9] subporphyrin was a long-sought but elusive ring-contracted porphyrin analogue despite its simple structure and important position in porphyrin chemistry. This is in sharp contrast to subphthalocyanines, which have been extensively studied since the first report by Meller and Ossko in 1972.[10] The difference can be ascribed largely to a particular synthetic difficulty of subporphyrins. While subphthalocyanines can be prepared in more than 50 % yield in favorable cases, syntheses of subporphyrin require harsh reaction conditions and tedious separation. The synthesis of tribenzosubporphines was accomplished at most in 1.4 % yield, and *meso*-aryl-substituted subporphyrins were synthesized also in low yields (< 6 %).[11] Boron(III) *meso*-tris(pentafluorophenyl)subporphyrin (**2**) is an important ring-contracted porphyrin to complete the series of *meso*-pentafluorophenyl-substituted porphyrinoids including expanded porphyrins,[12] but it has been elusive, as the previous protocols of subporphyrin synthesis were not applicable to this particular macrocycle.

Heptaphyrin **1** adopts a distorted figure-of-eight structure consisting of a semiporphyrin-like tetrapyrrolic segment and a tripyrrolic segment.[13] In both sites, the pyrrolic nitrogen atoms all point inwards, a favorable orientation for metal coordination. It occurred to us that the simultaneous metalation of **1** with a divalent metal ion at the semiporphyrin-like pocket and B^{III} ion at the tripyrrolic pocket might trigger a splitting reaction into a metalloporphyrin and a boron(III) subporphyrin in a similar manner to the splitting reaction of bis-copper(II) octaphyrin into two copper(II) porphyrins (Scheme 2).

Thus, we examined the metalation of **1** at the semiporphyrin-like pocket by treating **1** with a solution of $Zn(OAc)_2 \cdot 2H_2O$ in methanol at room temperature which provided **1-Zn** in quantitative yield. Complex **1-Zn** shows the parent ion peak at *m*/*z* 1767.0182 (calcd for $C_{77}H_{16}F_{35}N_7Zn$ $[M]^+$: *m*/*z* 1767.0194) in its high-resolution electrospray ionization (HR-ESI) mass spectrum, and it exhibits a simple ^1H NMR spectrum that reveals its C_2-symmetric structure in solution (Supporting Information).

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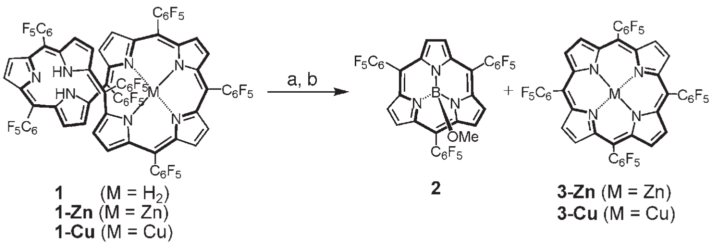
Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.



Scheme 2. Extrusion reaction of **1-Zn** and **1-Cu**: a) BBr_3 (100 equiv), EtN(*i*Pr)$_2$ (150 equiv), CH_2Cl_2, room temperature, 24 h, and then aqueous $NaHCO_3$; b) MeOH, reflux, 3 h.

The structure of **1-Zn** was confirmed by single-crystal X-ray diffraction analysis (Figure 1), which shows that the Zn^{II} ion is coordinated at the tetrapyrrolic segment in a distorted square-planar fashion.[14a] Note that Zn^{II} metalation of **1** led to complete suppression of N-fusion reactions,[13] which are rather facile in the free-base heptaphyrin **1**. Next, we attempted metalation of **1-Zn** with B^{III} using BBr_3 or BCl_3 under various conditions, which, however, gave a complicated mixture containing **1**, a Zn^{II}-B^{III} bis-metalated complex (< 6 %), and subporphyrin **2** (< 1 %). Formation of Zn^{II}-porphyrin **3-Zn** was not detected. The Zn^{II}-B^{III} bis-metalated complex easily decomposed without forming **2** or **3-Zn** upon heating it at reflux in CH_2Cl_2.

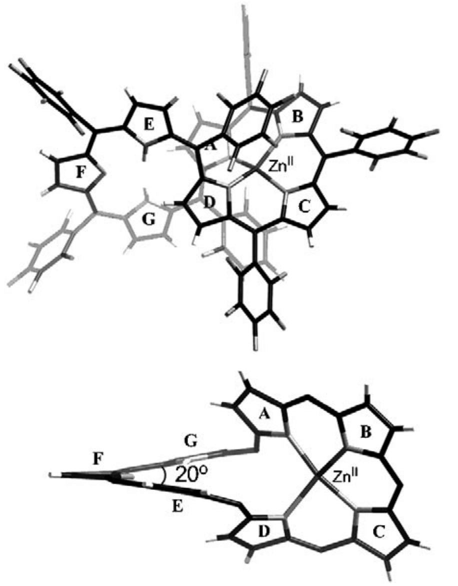


Figure 1. X-ray crystal structure of **1-Zn**: top view (upper) and side view (lower, with pentafluorophenyl substituents omitted for clarity).

Then, we changed the substrate to the copper(II) complex **1-Cu**, which was prepared in quantitative yield by metalation of **1** with Cu(OAc)$_2$. Complex **1-Cu** shows the parent ion peak at *m*/*z* 1766.0218 (calcd for $C_{77}H_{16}F_{35}N_7Cu$ [*M*]$^+$: *m*/*z* 1766.0199) in its HR-ESI mass spectrum. The valence state of the Cu(II) ion was confirmed by magnetic susceptibility analysis of **1-Cu** (Supporting Information). The structure of **1-Cu** was determined by X-ray diffraction analysis to be similar to that of **1-Zn**, where the Cu^{II} ion is bound to the tetrapyrrolic segment with overall molecular symmetry close to C_2 (Figure 2).[14b] The complex **1-Cu** was treated with a source of boron(III) such as BBr_3 or BCl_3, and the presence of a product with blue-green fluorescence in the reaction mixture was noted. This product was separated in yields of 1–10 % through a silica gel column by monitoring its fluorescence. To our delight, this product turned out to be subporphryin **2**. The preparation of **2** was reproducible, and after many experiments an improved yield of 36 % was obtained under optimized reaction conditions (BBr_3 (100 equiv), EtN(*i*Pr)$_2$ (150 equiv), CH_2Cl_2; stirring at room temperature for 24 h), along with Cu^{II}-porphyrin **3-Cu** in 13 % yield. In the reaction, the Cu^{II}-B^{III} bis-metalated complex was not detected. This extrusion reaction is initiated by the simple treatment of **1-Cu** with BBr_3 in the presence of an appropriate base without particular thermal activation.

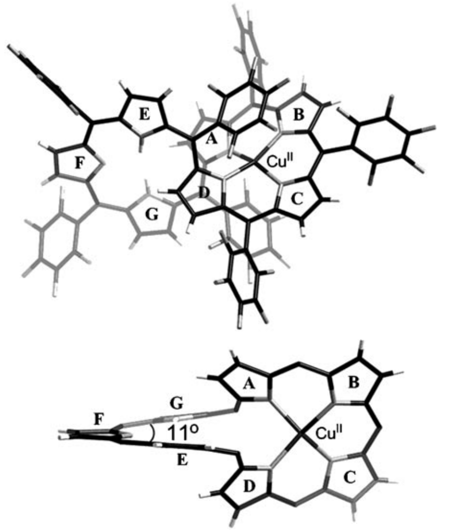


Figure 2. X-ray crystal structure of **1-Cu**: top view (upper) and side view (lower, with pentafluorophenyl substituents omitted for clarity.

Subporphyrin **2** shows the parent ion peak at *m*/*z* 794.0480 (calcd for $C_{34}H_9F_{15}N_3BONa$ [*M* + Na]$^+$: *m*/*z* 794.0497) in its HR-ESI mass spectrum. Single-crystal X-ray diffraction analysis of **2** revealed a bowl-like triangular structure with a bowl depth of 1.37 Å (Figure 3).[14c,15] The *meso*-pentafluorophenyl substituents of **2** are tilted by 61–79° relative to the

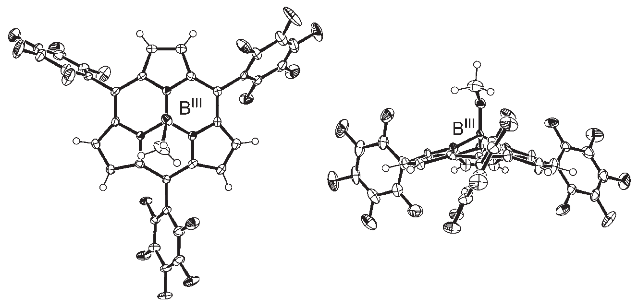


Figure 3. X-ray crystal structure of **2**: top view (left) and side view (right). Thermal ellipsoids are shown at the 50 % probability level.

subporphyrin framework (compared with 38–56° for *ortho*-free *meso*-aryl-substituted subporphyrins). Importantly, ^{19}F NMR spectroscopy revealed an inhibited rotation of the *meso*-pentafluorophenyl substituents of **2** even at 413 K in solution (Supporting Information).

As the first example of a subporphyrin bearing rotationally frozen electron-withdrawing *meso* substituents, **2** displays optical properties that are different to those of other *meso*-aryl-substituted subporphyrins. The absorption spectrum of **2** features an intense Soret-like band at 359 nm that is the most blue-shifted among the *meso*-aryl subporphyrins reported to date, and three Q-like bands at 422 (shoulder), 449, and 470 nm. Its fluorescence spectrum exhibits distinct bands at 487 and 517 nm (Figure 4) with a quantum yield of 12 %.[16] Thus, the Stokes shift of **2** is about 700 cm^{-1}, which is the smallest among the reported *meso*-aryl subporphyrins (1200–2900 cm^{-1}).[11] The fluorescence of **2** involves single-exponential decay with a lifetime of 2.34 ns.

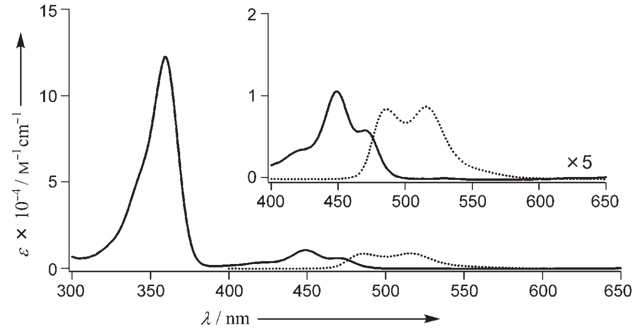


Figure 4. UV/Vis absorption (——) and fluorescence (λ_{exc} = 359 nm, •••••) spectra of **2** in CH_2Cl_2.

Besides its synthetic merit, the extrusion of **2** from **1-Cu** is mechanistically interesting, as it can be regarded as a formal metathesis that involves two double-bond cleavages and two double-bond formations.[1,7] A marked difference in the reactivity of **1-Zn** and **1-Cu** is also notable, suggesting a crucial role of Cu^{II} ion in the extrusion reaction. The detailed reaction mechanism is not clear at the present stage, however, a subtle structural difference between **1-Cu** and **1-Zn** may be important as the tilting angle of the pyrrole rings E and G is slightly but distinctly smaller in **1-Cu** (11°) than in **1-Zn** (20°) (Figures 1 and 2). The smaller tilting angle between the pyrrole rings that cyclize to form a subporphyrin macrocycle might be favorable for the extrusion reaction. Alternatively, the Cu^{II} ion may serve as an important electronic factor in helping the extrusion reaction.

In summary, we have described the extrusion of subporphyrin from [32]heptaphyrin **1** upon cooperative metalation with Cu^{II} and B^{III} ions which demonstrates a wider applicability of transannular formal metathesis-type transformation of expanded porphyrins to produce even a ring-contracted porphyrin. Further study on the extrusion reaction is underway to explore its scope and limitation as well as its mechanistic details.

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[14] a) Crystallographic data for **1-Zn**: $C_{89}H_{47}F_{35}N_7O_3Zn$, M_w = 1992.71, triclinic, space group $P\bar{1}$ (No.2), a = 15,716(6), b = 15.898(4), c = 18.477(5) Å, α = 105.143(11), β = 100.739(13), γ = 107.991(12)°, V = 4055(2) Å^3, ρ_{calcd} = 1.632 g cm^{-3}, Z = 2, R_1 = 0.0563 [$I > 2.0\sigma(I)$], R_w = 0.1317 (all data), GOF = 0.802 [$I > 2.0\sigma(I)$]. b) Crystallographic data for **1-Cu**: $C_{176}H_{32}F_{70}N_{14}O_5Cu_2$, M_w = 3879.24, monoclinic, space group $C2/c$ (No.15), a = 42.784(5), b = 11.319(5), c = 33.927(5) Å, β = 99.353(5)°, V = 16211(8) Å^3, ρ_{calcd} = 1.589 g cm^{-3}, Z = 4, R_1 = 0.0749 [$I > 2.0\sigma(I)$], R_w = 0.2343 (all data), GOF = 1.049 [$I > 2.0\sigma(I)$]. c) Crystallographic data for **2**: $C_{34}H_9BF_{15}N_3O_{2.62}$, M_w = 797.25, orthorhombic, space group $Pbcn$ (No.60), a = 25.096(3), b = 18.170(2), c = 14.3348(18) Å, V = 6536.6(14) Å^3, ρ_{calcd} = 1.620 g cm^{-3}, Z = 8, R_1 = 0.0989 [$I > 2.0\sigma(I)$], R_w = 0.2615 (all data), GOF = 1.105 [$I > 2.0\sigma(I)$]. CCDC-643985 (**1-Zn**), 648936 (**1-Cu**), and 648937 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[15] The bowl depth is defined as the distance from the mean plane of six β-peripheral carbon atoms to the boron atom.

[16] The quantum yield was determined by using *meso*-phenyl subporphyrin as the standard (Ref. [11b]).