doi:10.1246/cl.2010.439
Published on the web March 31, 2010

Editor's Choice

meso-Trifluoromethyl-substituted Subporphyrin from Ring-splitting Reaction of *meso*-Trifluoromethyl-substituted [32]Heptaphyrin(1.1.1.1.1.1.1)

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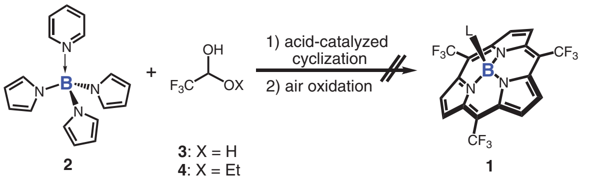
meso-Trifluoromethyl-substituted subporphyrin was obtained through an extrusion reaction from *meso*-trifluoromethyl-substituted heptaphyrin(1.1.1.1.1.1.1) upon combined metallation of Cu(II) and B(III) ions. The subporphyrin exhibited the most blue-shifted Soret-like absorption band among those ever prepared.

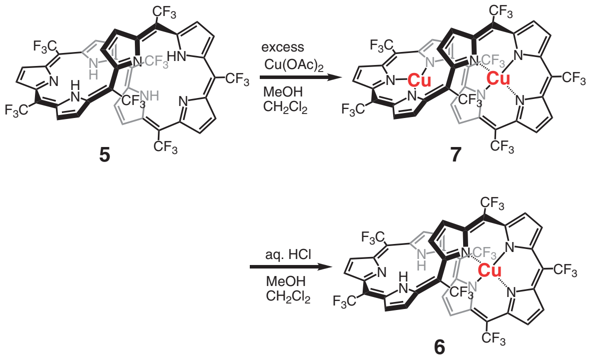
Boron(III) subporphyrin, a genuine ring-contracted porphyrin, has emerged as a promising functional molecule in light of a curved 14π-aromatic network, robust chemical stability, intense green fluorescence, and highly tunable electronic properties.[1] The chemistry of subporphyrin was initiated by our first synthesis in 2006[2] and has been actively advanced in recent years along with the development of various differently substituted subporphyrins.[3–5] In spite of these extensive efforts, a serious problem lies in a limited synthetic access to this class of molecules. Usually acid-catalyzed condensation reactions have been used for the preparation of *meso*-aryl-substituted subporphyrins,[5] and such reactions have been quite ineffective in production of *meso*-alkyl-substituted congeners to date. Quite recently, we explored an indirect synthetic route to *meso*-alkyl-substituted subporphyrins via desulfurization of *meso*-thienyl-substituted subporphyrins.[6] In this paper, we report the synthesis of *meso*-trifluoromethyl-substituted subporphyrin **1**, on the basis of extrusion reaction from a mono-Cu(II) complex of *meso*-trifluoromethyl-substituted [32]heptaphyrin(1.1.1.1.1.1.1) **5** upon treatment with BBr_3.

Initially, we attempted the synthesis of **1** by following reported synthetic protocols of *meso*-aryl-substituted subporphyrins;[5a] i) treatment of pyridine-tri-*N*-pyrrolylborane (**2**)[5g] and 2,2,2-trifluoroacetoaldehyde hydrate **3** or **4** with trifluoroacetic acid (TFA) at room temperature followed by neutralization with pyridine and refluxing, or ii) the Adler condensation of **2** and **3** with chloroacetic acid under air. Neither protocol produced subporphyrin **1**. We also attempted the condensation of **2** and **4** with methanesulfonic acid without success (Scheme 1).

We then changed our synthetic strategy to a possible splitting reaction of expanded porphyrins. This idea came from recent findings that expanded porphyrins sometimes undergo unique skeletal rearrangements upon metallation or heating,[7,8] which are probably aided by transannular π-electron interactions. A remarkable example is the quantitative splitting reaction of a bis-Cu(II) complex of [36]octaphyrin into two molecules of Cu(II) porphyrins upon heating.[8] A similar splitting reaction was triggered upon the treatment of mono-Cu(II) complex of *meso*-pentafluorophenyl [32]heptaphyrin with BBr_3 in the presence of EtN(*i*-Pr)$_2$ to produce B(III) *meso*-pentafluorophenyl subporphyrin.[9] It was thus thought that similar subporphyrin-extrusion from *meso*-trifluoromethyl [32]heptaphyrin **5** may occur upon suitable metallation, since **5** is known to take a figure-eight conformation,[10] being suitable for the transannular interaction at the hinge-position.



Scheme 1. Attempted acid-catalyzed condensation reactions for **1**.



Scheme 2. Synthesis of **6** from **5** via **7**.

Since the selective Cu(II)-metallation of **5** turned out to be difficult, we prepared mono-Cu(II) complex **6** via selective demetallation of bis-Cu(II) complex **7** (Scheme 2). Bis-Cu(II) [32]heptaphyrin complex **7** was quantitatively prepared by treatment of **5** with an excess amount of $Cu(OAc)_2$ in a mixture of CH_2Cl_2 and methanol at room temperature. High-resolution electrospray-ionization mass spectrometry (HR-ESI-MS) showed the parent ion peak of **7** at m/z 1140.9589 ($[M]^+$); Calcd for $C_{42}H_{14}N_7Cu_2F_{21}$, 1140.9561. Single-crystal X-ray diffraction analysis showed the preliminary structure of **7**, where two Cu(II) ions are coordinated by tripyrrolic and tetrapyrrolic segments of a figure-eight heptaphyrin macrocycle (SI).[15] One Cu(II) ion was believed to be bound within a unique T-shape coordination environment.[11] In the next step, selective mono-demetallation of fragile three-coordinated Cu(II) ion was effected by treatment of **7** with 1 M HCl in CH_2Cl_2 and MeOH to furnish mono-Cu(II) complex **6** in 97% yield. The parent ion peak of **6** was detected at m/z 1081.0518 ($[M + H]^+$); Calcd for $C_{42}H_{17}N_7CuF_{21}$, 1081.0500. The structure of **6** was unambiguously determined by single-crystal X-ray diffraction to be a figure-eight conformation (Figure 1),[12] in which the hemiporphyrin-like pocket accommodated Cu(II) ion in a distorted square-planar coordination and the tripyrrolic moiety was empty.

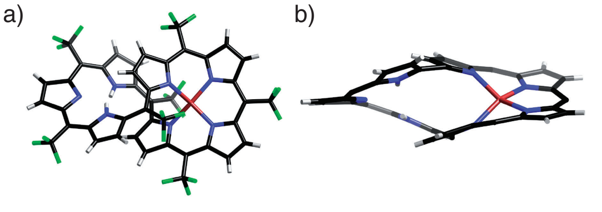
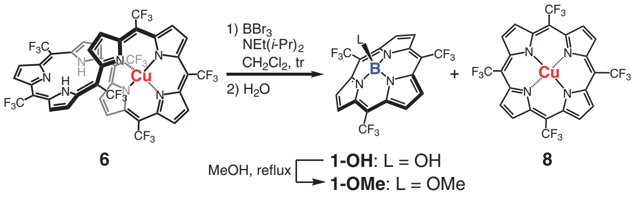


Figure 1. Crystal structure of **6**: a) top view and b) side view. In side view, *meso*-trifluoromethyl substituents are omitted for clarity.



Scheme 3. Ring-splitting reaction of **6** to afford **1** and **8**.

B(III) metallation induced splitting reaction was examined by treating **6** with BBr_3 under various conditions. In CH_2Cl_2, the complex **6** was stirred in the presence of 100 equiv BBr_3 and 150 equiv EtN(*i*-Pr)$_2$ at room temperature for 24 h. This simple procedure produced B(III)–subporphyrin **1-OH** and Cu(II)–porphyrin **8** in 6% and 18% yields, respectively. The formation of **1-OH** and **8** was reproducible and after extensive optimization experiments we found that slower, dropwise addition of a dilute solution of BBr_3 in CH_2Cl_2 improved the yields of **1-OH** and **8** up to 12% and 28%, respectively (Scheme 3). HR-ESI-MS and NMR measurements were performed after the axial hydroxy ligand was quantitatively exchanged to a methoxy ligand to give **1-OMe** by refluxing in MeOH. The parent ion peak of **1-OMe** was detected at m/z 446.0488 ($[M - OMe]^+$); Calcd for $C_{18}H_6BF_9N_3$, 446.0508. The ^{1}H NMR spectrum of **1-OMe** displayed a singlet at 8.48 ppm due to the peripheral pyrrolic β-protons and a singlet at 0.55 ppm due to the axial methoxy protons, and the ^{11}B NMR spectrum showed a signal at -16.2 ppm, in line with its distinct diatropic ring current. The UV–vis absorption spectrum of **1-OH** exhibited a Soret band at 341 nm with shoulders at 327 nm and Q bands at 412, 446, and 473 nm (Figure 2a). It is worthy to note that the Soret band of **1-OH** is the most blue-shifted among the subporphyrins so far reported. In addition, the Q(0,0) band is most intense among the observed Q bands as an unprecedented case. These unique optical properties may be ascribed to the nonconjugated and strong electron-withdrawing trifluoromethyl group.[13] The fluorescence spectrum of **1-OH** is similar to the mirror image of the Q bands, exhibiting the most intense (0,0) band at 482 nm (Figure 2b), while the fluorescenece quantum yield is quite small, only $\Phi_F = 0.013$, considerably smaller than that of *meso*-phenyl subporphyrin ($\Phi_F = 0.14$).

DFT (B3LYP/6-31G(d)) optimized structure of **1-OH** shows a bowl-depth of 1.42 Å within the normal range of *meso*-aryl subporphyrins (Figure 3).[14] More importantly, the calculated moleculer orbital diagram of **1-OH** indicates that the a_1 moleculer orbital, which is normally HOMO in subporphyrins with large coefficients at the *meso*-positions, is drastically stabilized to become HOMO$-$1 by the electron-withdrawing effect of the *meso*-trifluoromethyl substituents. This is a first example of the subporphyrin with the reversed HOMO and HOMO$-$1, compared to known subporphyrins (Figure 4).

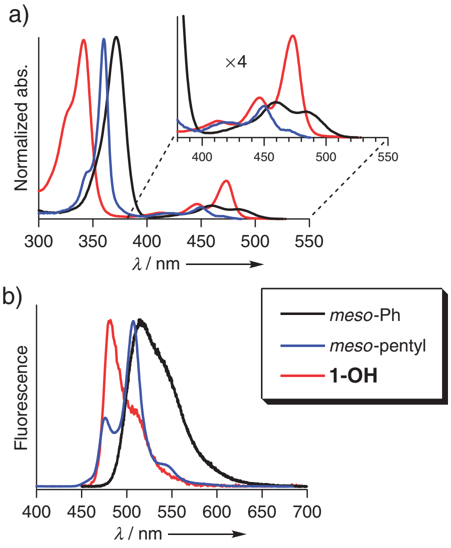


Figure 2. (a) UV–vis absorption and (b) fluorescence spectra of **1-OH** (red), compared to those of *meso*-phenyl subporphyrin (black) and *meso*-pentyl subporphyrin (blue).

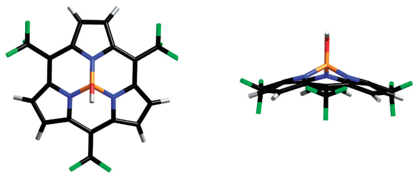


Figure 3. DFT optimized structure of **1-OH** calculated at B3LYP/6-31G(d) level.

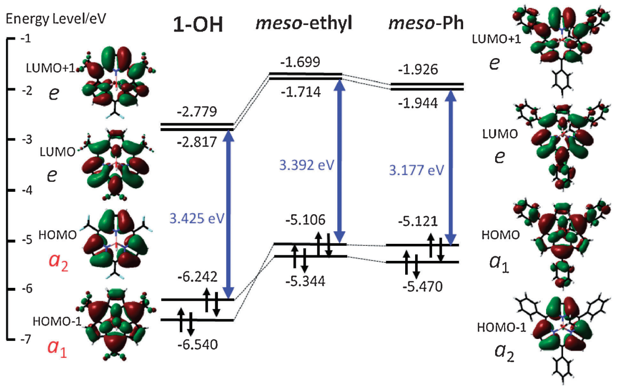


Figure 4. DFT moleculer orbital diagram of **1-OH**, *meso*-ethyl subporphyrin and *meso*-phenyl subporphyrin calculated at B3LYP/6-31G(d) level.

The other extruded product was Cu(II) *meso*-tetrakis(trifluoromethyl)-substituted porphyrin **8**. The conformation of *meso*-tetrakis(perfluoroalkyl)porphyrin and their metal complexes have been often discussed.[10,13] While the crystal structure of **8** has been elusive, we have confirmed a severely ruffled structure for **8** by preliminary crystal structural analysis (SI),[15] which is consistent with its characteristic absorption spectrum.[10]

In summary, we isolated *meso*-trifluoromethyl-substituted B(III) subporphyrin **1** from the ring-splitting reaction of the corresponding [32]heptaphyrin. Subporphyrin **1** displayed the most blue-shifted Soret band at 341 nm among subporphyrins yet prepared.

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12 Crystallographic data for **6**: $C_{42}H_{16}N_7F_{21}Cu$, $M_r = 1081.16$, monoclinic, space group $P2_1/n$ (No. 14), $a = 12.3747(15)$, $b = 11.8954(15)$, $c = 26.732(3)\,Å$, $\beta = 102.318(2)°$, $V = 3844.5(8)\,Å^3$, $\rho_{calcd} = 1.868\,g\,cm^{-3}$, $Z = 4$, $R_1 = 0.0371$ $[I > 2.0\sigma(I)]$, $R_w = 0.1038$ (all data), GOF = 1.033. Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-763253. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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