

# meso-Hydroxysubporphyrins: A Cyclic Trimeric Assembly and a Stable meso-Oxy Radical\*\*

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**Abstract:** Treatment of meso-chlorosubporphyrin with potassium hydroxide in DMSO followed by aqueous work up and recrystallization gave a cyclic trimer consisting of meso-hydroxysubporphyrin units linked between the central boron atoms and meso-hydroxy groups. Solutions of this trimer are nonfluorescent, but become fluorescent when exposed to acid or base, since hydrolytic cleavage of the axial B–O bonds generates the meso-hydroxysubporphyrin monomer or its oxyanion. Ring cleavage of the trimer was also effected by reaction with phenylmagnesium bromide to produce meso-hydroxy-B-phenyl subporphyrin, which can be quantitatively oxidized with PbO<sub>2</sub> to furnish a subporphyrin meso-oxy radical as a remarkably stable species as a result of spin delocalization over almost the entire molecule.

The exploration of stable radicals<sup>[1a]</sup> has been one of the central topics in organic radical chemistry in light of their diverse applications such as in organic synthesis,<sup>[1b]</sup> polymer chemistry,<sup>[1c]</sup> magnetic materials,<sup>[1d]</sup> organic batteries,<sup>[1e]</sup> quantum information science,<sup>[1f]</sup> and bioimaging.<sup>[1g]</sup> Stabilization of organic radicals is usually achieved through effective steric protection and/or extensive spin delocalization.

Oxophlorin and meso-hydroxyporphyrin, a tautomeric pair that plays an important role in the catabolism of heme moieties, have been known to be easily and reversibly oxidized to the corresponding radical, a porphyrin meso-oxy radical.<sup>[2]</sup> This radical has been demonstrated to be stable enough for electrochemical investigations and crystallo-

graphic analysis when stabilized by coordinating solvents (typically pyridine), but forms a C(15)–C(15′)-linked dimer when such coordinating solvents are not present.<sup>[2b,c]</sup> The stability of this porphyrin meso-oxy radical was improved somewhat by the rational installation of a bulky *tert*-butyl group at the 15-position, but even with such steric protection, 30% degradation occurred after two weeks in solution.<sup>[3]</sup> Recently, [26]hexaphyrins have emerged as effective porphyrinic platforms for radical stabilization because of their large conjugated electronic networks that favorably accommodate spin delocalization, as seen for their fairly stable meso-oxy radicals.<sup>[4]</sup>

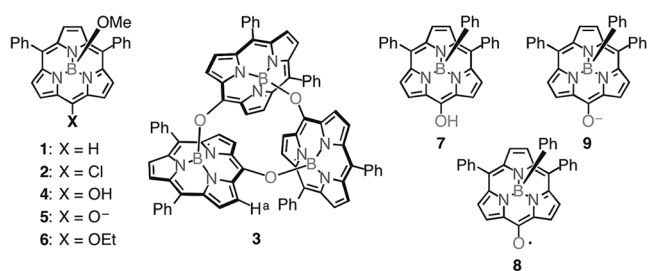
Since the first synthesis of tribenzosubporphyrins in 2006,<sup>[5a]</sup> the potential of subporphyrins, ring-contracted cousins of the porphyrin, has been increasingly recognized as a result of their attractive chemical, optical, and electrochemical properties.<sup>[5]</sup> In most cases so far, subporphyrins have been explored as functional pigments and their optical properties have been effectively controlled by taking advantage of the large influence that the meso substituents exert on the electronic network of subporphyrin. Herein we report the synthesis and characterization of meso-hydroxysubporphyrins, which have the ability to form a self-assembled trimer through an axial ligand exchange reaction with the meso-hydroxy group, and can also stabilize a meso-oxy radical species to such a remarkable extent that it can be manipulated like a usual closed-shell organic molecule in the presence of air and moisture.

meso-Chlorosubporphyrin **2** (Scheme 1) was prepared by chlorination of meso-free subporphyrin **1** with *N*-chlorosuccinimide in 87% yield.<sup>[6]</sup> Subporphyrin **1** can now be prepared

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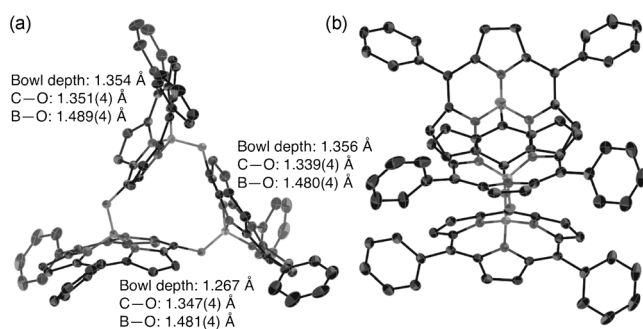


**Scheme 1.** Subporphyrins studied herein.

in an improved yield of 17% by modification of an existing procedure that originally gave **1** in 9.7% yield from 5,15-diphenyltripyrane (for details see the Supporting Information).<sup>[7]</sup> By following recently developed  $S_NAr$  methods,<sup>[6]</sup> subporphyrin **2** was treated with an excess of potassium hydroxide in dimethyl sulfoxide (DMSO) at 50 °C for 12 h.

Surprisingly, the reaction furnished cyclic trimer **3** as a yellow solid in 94 % yield after usual aqueous work up and recrystallization. During the work up procedure, the organic layer initially displayed fluorescence, but the fluorescence was visibly diminished following removal of the solvent under reduced pressure, thus indicating that the cyclic trimer forms preferentially at high concentration. High-resolution atmospheric-pressure-chemical-ionization time-of-flight (HR-APCI-TOF) mass spectrometry exhibited a signal for the parent cation of **3** at  $m/z = 1228.4213$  (calcd 1228.4191 for  $[3]^+$ ;  $[C_{81}H_{48}^{11}B_3N_9O_3]^+$ ). The  $^1H$  NMR spectrum of **3** shows a sharp and simple spectrum that is consistent with its symmetric structure. A doublet observed at  $\delta = 6.60$  ppm, which is related to the pyrrolic  $\beta$ -protons ( $H^a$ , see Scheme 1), is considerably high-field shifted compared with previously observed values for pyrrolic  $\beta$ -proton resonances of monomeric subporphyrins (ca.  $\delta = 7.7$ – $8.3$  ppm). This effect is most likely due to the shielding effects of the diatropic ring currents residing on adjacent subporphyrin units.

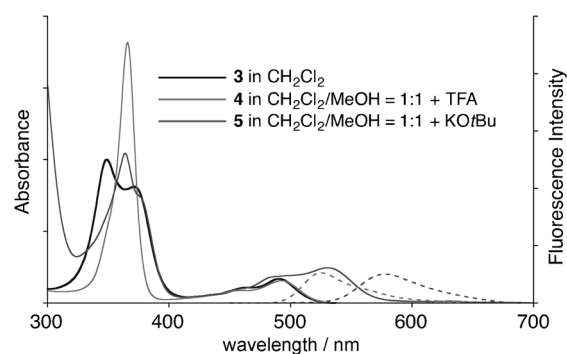
X-Ray crystallographic analysis has revealed that the structure of **3** is indeed a self-assembled molecular triangle, in which the meso-hydroxy groups are bonded to the central boron atoms of adjacent subporphyrins (Figure 1). In **3**, the



**Figure 1.** X-ray crystal structures of **3**: a) side view and b) top view. Thermal ellipsoids are set at the 50 % probability level. All hydrogen atoms and solvent molecules are omitted for clarity.

bowl depths<sup>[8]</sup> of the constituent subporphyrin units are 1.267, 1.354, and 1.356 Å, which are in line with values previously reported for subporphyrins. Compared with the reference subporphyrin **6**, which shows a B–O bond distance of 1.439 Å and a C–O bond distance of 1.367 Å,<sup>[9]</sup> subporphyrin trimer **3** shows distinctly longer B–O bonds (1.480(4), 1.481(4), and 1.489(4) Å) and shorter C–O bonds (1.339(4), 1.347(4), and 1.351(4) Å), thus indicating a slight meso-oxosubphlorin bond character. This type of cyclic trimer was reported for  $\beta$ -hydroxymetalloporphyrins,<sup>[10]</sup> while meso-hydroxyporphyrins gave dimeric complexes.<sup>[11]</sup> The angle between the axial ligand on boron and the meso substituent (i.e.  $\angle O-B-C$ ) in subporphyrin is approximately 120°, which is ideal for the formation of a cyclic trimer.<sup>[12]</sup>

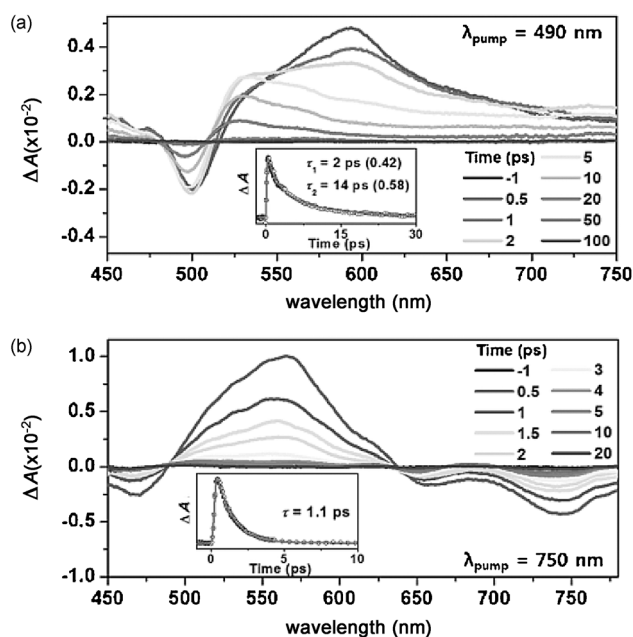
The UV/Vis absorption spectrum of **3** (Figure 2) displays a split Soret-like band with maxima at 349 and 371 nm and a Q-like band at 490 nm. The split Soret-like band suggests that strong exciton coupling exists between the neighboring subporphyrin units, since the average interchromophoric



**Figure 2.** UV/Vis absorption (solid) and emission (dashed) spectra of **3** (in  $CH_2Cl_2$ ), **4**, and **5** (in  $CH_2Cl_2/MeOH = 1:1$  + TFA or base for **4** and **5**).

separation distance of 7 Å is adequate for through-space excitonic interaction. Interestingly, spectroscopic solutions of trimer **3** were practically nonfluorescent ( $\Phi_f < 10^{-3}$ ) in aprotic solvents such as  $CH_2Cl_2$ ,  $CHCl_3$ , acetone, toluene, acetonitrile, and DMF (changing the polarity of the medium has no effect), but became fluorescent upon the addition of protic solvents such as methanol. The dropwise addition of trifluoroacetic acid (TFA) or potassium *tert*-butoxide to a solution of cyclic trimer **3** in  $CH_2Cl_2/MeOH = 1:1$  (Figure 2) results in the absorption profile undergoing a distinct spectral transformation. In the case of the dropwise addition of TFA, the gradual disappearance of the initial spectral profile containing a split Soret-like band at 349 nm coincides with the gradual appearance of a simple nonsplit Soret-like band at 366 nm. In the case of the dropwise addition of a dilute solution of KO $t$ Bu, the initial spectral profile of the cyclic trimer is gradually replaced with a profile containing a Soret-like band at 364 nm which has a pronounced shoulder. These spectral transformations have been ascribed to the gradual turnover of subporphyrin monomer **4** or the corresponding anion **5**, respectively. Namely, methanol serves to monomerize **3** through an axial ligand exchange reaction, with the rate of the process being enhanced under acidic or basic conditions. This has been confirmed by  $^1H$  NMR experiments of **3** conducted in  $CDCl_3/CD_3OD$  (see Figure S3-6 in the Supporting Information).

Femtosecond transient absorption (TA) measurements were carried out to probe the excited-state dynamics of **3** (Figure 3a). The TA spectra of trimer **3** showed a characteristic broad excited-state absorption (ESA) signal at wavelengths longer than 515 nm.<sup>[13]</sup> However, the TA spectra of **3** rapidly decayed with time components of 2 and 14 ps. Such a fast TA decay feature of **3** was in sharp contrast to that of monomer **4**, which exhibited typical TA spectral features of subporphyrins and a lifetime of 2.3 ns (see Figure S6-4 in the Supporting Information). Although the detailed mechanism of the accelerated decay in **3** remains unclear, we suspect that the cyclic system assumes a structural nature and bond character reminiscent of oxosubphlorin, which may facilitate the accelerated decay. The transient absorption anisotropy measurement of **3** revealed a depolarization with a time component of 0.7 ps (see Figure S6-5 in the Supporting Information), which allowed us to estimate an exciton



**Figure 3.** Transient absorption spectra and decay profiles of **3** (a) and **8** (b) in toluene. TA decay profiles of **3** and **8** were obtained by monitoring at 490 and 750 nm, respectively.

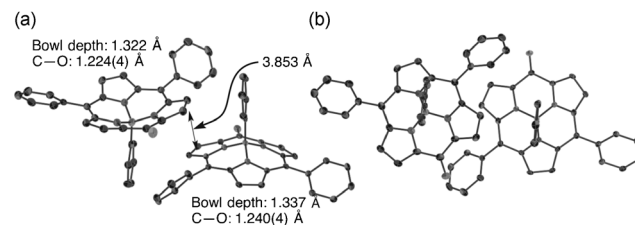
hopping time of 2.1 ps on the basis of regular polygon model for cyclic molecular arrays [see Eq. (1)].<sup>[14]</sup> These significantly different excited-state dynamics of trimer **3** and monomer **4** rationalize the sharp contrast in their fluorescence features, and suggest a potential for subporphyrin-based sensing systems.

$$\tau_{\text{dep}} = \frac{\tau_{\text{hop}}}{4 \left[ 1 - \cos^2 \left( \frac{2\pi}{N} \right) \right]} \quad (1)$$

In the next step, we examined the reactions of **3** with phenylmagnesium bromide as an alternative approach for effecting ring cleavage.<sup>[15]</sup> Namely, a solution of **3** in 1,4-dioxane was treated with phenylmagnesium bromide in THF to give meso-hydroxy-B-phenylsubporphyrin **7** in 54% yield. It is noteworthy that the reaction of **3** with phenylmagnesium bromide in THF without dioxane gave B-phenyl-meso-triphenylsubporphyrin exclusively, thus indicating that the Grignard reagent attacked both the central boron and carbonyl-like meso-hydroxy carbon atoms. Therefore, the addition of dioxane is important in modulating the reactivity of phenylmagnesium bromide toward **3**. Intriguingly, subporphyrin **7** was gradually oxidized in solution under air to give subporphyrin meso-oxy radical **8**. The <sup>1</sup>H NMR spectrum of **7** in CDCl<sub>3</sub> was silent, probably because of a small presence of the radical species **8**, but became sharp upon addition of one drop of hydrazine monohydrate to the solution (see the Supporting Information).<sup>[16]</sup> Oxy radical **8** was quantitatively obtained by oxidation of **7** with PbO<sub>2</sub>. HR-APCI-TOF mass spectrometry indicated a signal of the parent cation of **8** at *m/z* = 486.1776 (calcd 486.1778 for [**8**]<sup>+</sup>; [C<sub>33</sub>H<sub>21</sub><sup>11</sup>BN<sub>3</sub>O]<sup>+</sup>). Despite a smaller porphyrin-like 14π electronic network,

subporphyrin oxy radical **8** is exceptionally stable toward air and moisture, thereby allowing its manipulation like normal closed-shell organic molecules. Radical **8** did not show any change in the solid state and was stable in solutions under open air at room temperature for up to one month or longer.

Fortunately, we obtained single crystals of **8** and confirmed its structure. As shown in Figure 4, **8** is a relatively rare



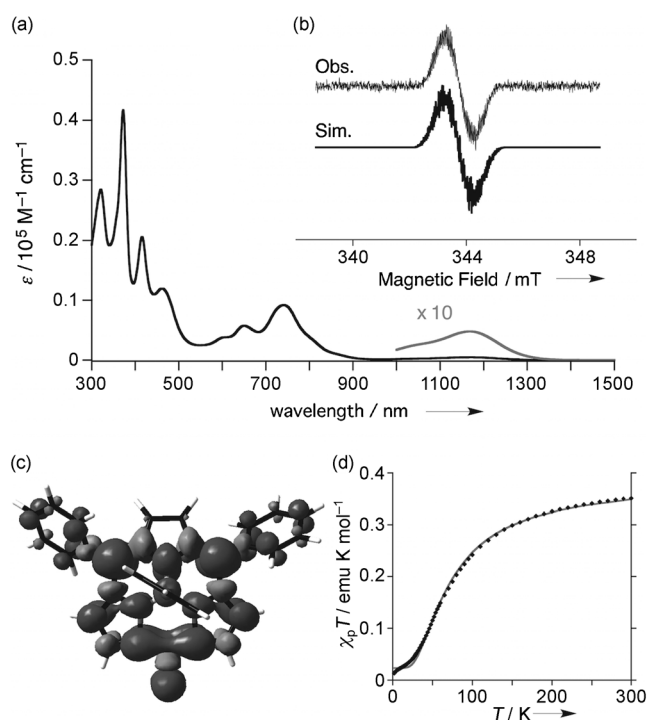
**Figure 4.** X-ray crystal structures of **8**: a) side view, b) top view. Two independent molecules are shown. Thermal ellipsoids are set at the 50% probability level. All hydrogen atoms and solvent molecules are omitted for clarity.

bowl-shaped curved radical<sup>[17]</sup> with two independent molecules paired with their convex surfaces aligned in a complementary off-set head to head fashion. The C–O bond lengths are 1.224(4) and 1.240(4) Å, being considerably shorter than that of meso-ethoxysubporphyrin **6** (1.367 Å), thus indicating a substantial double-bond character of the C–O bond. This partial double-bond character is further supported by the characteristic carbonyl-like IR absorption band at 1591 cm<sup>−1</sup> (calcd: 1660 cm<sup>−1</sup>, see Figure S6-3 in the Supporting Information). The bowl depths were 1.322 and 1.337 Å, which are in the range of those of usual subporphyrins. The pairing of the two molecules in the unit cell of **8** is aided by mutual CH/π interactions between the β-hydrogen atom and axial phenyl group, which results in partial π stacking with a shortest separation between the β-carbon atoms of 3.853 Å.

Subporphyrin **8** is NMR silent as a result of its radical character and exhibits an ill-defined absorption spectrum without a sharp Soret-like band or Q-like band. Instead, a weak and broad band is observed around 1200 nm that is characteristic of radical porphyrinoid species (Figure 5a). On the basis of the absorption edge at around 1400 nm, the excitation energy of the S<sub>1</sub> state has been estimated to be approximately 0.89 eV. Oxy radical **8** was quantitatively reduced with hydrazine monohydrate to give meso-oxy anion **9** (conjugate base of **7**), as confirmed by <sup>1</sup>H NMR and UV/Vis measurements (see the Supporting Information). The radical character of **8** is also evident from its excited-state dynamics. The TA spectra of **8** decayed rapidly with a time constant of 1.1 ps (Figure 3b). Since radical species show ultrafast relaxation process by the greater density of states,<sup>[4]</sup> such an extremely short excited-state lifetime of **8** is consistent with its radical character.

The electronic-spin structure of **8** was examined by ESR spectroscopy in a degassed 2-methyltetrahydrofuran solution at room temperature. The ESR spectrum of **8** showed a signal (*g* = 2.0039) with hyperfine couplings, which has been simulated as shown in Figure 5b. Simulation of the spectra shows





**Figure 5.** a) UV/Vis absorption spectrum of **8**, b) the ESR spectrum observed at room temperature and corresponding simulated spectra, c) spin density distribution calculated at the UB3LYP/6-311G(d) level (isovalue: 0.001; the molecular geometry was optimized from the X-ray crystal structure), and d) temperature-dependent magnetic susceptibility in the solid state [dots: observed, solid: calculated; see also Eq. (2)].

the spin is coupled with the  $\beta$ -protons and even with the protons on the meso-phenyl groups (see Figure S4-1 in the Supporting Information). Density functional theory (DFT) calculations<sup>[18]</sup> of **8** at the UB3LYP/6-311G(d) level also revealed extensive delocalization of spin density over the subporphyrin  $14\pi$  electronic system and even over the meso-phenyl substituents (Figure 5c). This efficient delocalization should play a crucial role for the stabilization of the radical in addition to the steric effect of meso- and axial-phenyl groups, which probably prevent dimerization at the meso-carbon atoms. Time-dependent DFT (TD-DFT) calculation of **8** at UB3LYP/6-311G(d) indicates the lowest energy absorption band is assigned to the HOMO-SOMO excitation (at 1239 nm, oscillator strength:  $f=0.005$ ) and the successive absorption band is ascribed to SOMO-LUMO excitation (at 624 nm,  $f=0.068$ ), which is consistent with the observed spectrum (see Figure S10-3 in the Supporting Information).

The electrochemical properties of **8** were evaluated by cyclic voltammetry (CV) in  $\text{CH}_2\text{Cl}_2$  containing 0.1M  $n\text{Bu}_4\text{NPF}_6$  as a supporting electrolyte versus the ferrocene/ferrocenium cation (see Figure S9 in the Supporting Information). Fairly reversible one-electron oxidation and reduction waves were observed at 0.34 V and  $-0.51$  V, respectively, in line with its stable radical character possessing a SOMO orbital. The excitation energy gap to the S1 state can be estimated to be 0.85 eV on the basis of these values. The magnetic character of **8** in the solid state was also examined

by temperature-dependent magnetic susceptibility measurements (SQUID). The Bleaney–Bowers singlet-triplet model was employed to reproduce the observed  $\chi T$  plot with fitted parameters  $f_1=0.979$ ,  $f_2=0.0311$ , and  $J_1/k_B=-64.2$  K [see Figure 5d and Eq. (2)]. This analysis indicated a relatively strong antiferromagnetic interaction, which can be interpreted in terms of intermolecular  $\pi$ - $\pi$  interactions that are feasible because of its spin-delocalizing nature.

$$\chi T = f_1 \frac{N_A g^2 \mu_B^2}{k_B} \frac{1}{3 + \exp\left(-\frac{2J_1}{k_B T}\right)} + f_2 \frac{N_A g^2 \mu_B^2}{2k_B} \quad (2)$$

In summary, meso-hydroxysubporphyrin was efficiently synthesized from meso-chlorosubporphyrin by an  $\text{S}_\text{N}\text{Ar}$  reaction with KOH. The resulting meso-hydroxysubporphyrin underwent self-assembly to give a subporphyrin-based cyclic trimer linked at the axial sites of the central boron atoms and the meso-hydroxy groups. Solutions of this trimer are nonfluorescent, but become fluorescent when monomerized to meso-hydroxysubporphyrin upon treatment with methanol. The reaction of the cyclic trimer with phenylmagnesium bromide gave a meso-hydroxy-B-phenylsubporphyrin, which was quantitatively oxidized with  $\text{PbO}_2$  to give a subporphyrin meso-oxy radical. This radical is remarkably stable under ambient conditions, thus allowing its manipulation like a normal closed-shell organic molecule. The stability of this radical has been ascribed to effective delocalization of the spin over almost the entirety of the subporphyrin electronic network. Finding applications for this very stable subporphyrin meso-oxy radical in materials chemistry is a topic worthy of further investigation.

**Keywords:** boron · porphyrinoids · radicals · self-assembly · subporphyrin

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