

# Synthesis and Properties of Boron(III)-Coordinated Subbacteriochlorins

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Supporting Information

**ABSTRACT:** Subbacteriochlorins, which were prepared via hydrogenation of subporphyrins with Raney nickel, are modestly aromatic due to  $14\pi$ -diazaannulenic circuit and exhibit characteristic blue-shifted Soret-like bands, intensified fluorescence spectra, and high oxidation potentials.

Doubly reduced porphyrins such as bacteriochlorins and isobacteriochlorins play vital roles in natural systems. Bacteriochlorophylls are photosynthetic pigments which had been used before the emergence of chlorophylls and are still around in purple bacteria and other anaerobic or microaerobic bacteria.<sup>1</sup> Sirohydrochlorin, having an isobacteriochlorin framework, serves as a redox enzyme and a biosynthetic intermediate of vitamin  $B_{12}$ .<sup>2</sup> These macrocycles retain  $18\pi$ -conjugated circuits, while displaying attenuated Soret bands and low-energy lying and intensified Q-bands as compared with porphyrins because of changes in the molecular orbital diagrams. Various synthetic bacteriochlorin models have been explored to understand and examine their unique optical and electronic properties.<sup>3</sup>

In recent years, subporphyrin has emerged as a genuine ringcontracted porphyrin that bears a  $14\pi$ -electronic circuit lying on a curved bowl-shaped conformation.<sup>4,5</sup> While sharing some attributes with porphyrins, meso-aryl-substituted subporphyrins exhibit extremely substituent-dependent optical properties due to effective conjugative interactions of the subporphyrin core with meso-aryl substituents, which arise from their small rotational barriers.<sup>6</sup> Subchlorins, singly reduced subporphyrins, were recently prepared by reduction of subporphyrins with *p*-tosylhydrazide under basic conditions.<sup>7</sup> Optical and electrochemical properties of subchlorins change from those of subporphyrins in an analogous manner to the changes from porphyrins to chlorins. As shown in Chart 1, while subporphyrins 1 and subchlorins 2 share [14]azaannulene circuits and are aromatic, subbacteriochlorins 3 have a rare [13]diazaannulene circuit, in which the  $14\pi$ -electronic conjugation is kept through the lone-pair electrons of the nitrogen atom.<sup>8</sup>

Here we report the first synthesis of subbacteriochlorins. Raney nickel was found effective for hydrogenation of *meso*-substituted subporphyrins 1a-c to furnish *meso*-aryl-substituted subbacteriochlorins 3a-c in 47, 21, and 39% yields, respectively. The reduction of 1a and 1b was conducted in THF at 60 °C, while 1c was reduced at 40 °C to suppress the degradation of 3c.

Chart 1. Subporphyrin 1 and 4, Subchlorin 2, and Subbacteriochlorin 3;  $14\pi$ -Electronic Circuits Are Indicated in Red Bold Lines



meso-Alkyl-substituted subbacteriochlorin 3d was prepared in 16% yield by the reduction of meso-(2-thienyl)-substituted subporphyrin 4, since subporphyrin 1d was formed from 4 under these reduction conditions.<sup>9,10</sup> Here it is worthy to note that any further reduction over subbacteriochlorin has not been detected for all the cases, and quick separation over a silica gel column is critical for the isolation of pure subbacteriochlorins due to their feasibility toward oxidation. The high-resolution electrospray ionization mass measurement revealed intense borenium cation peaks at m/z 474.2140 (calcd for C<sub>33</sub>H<sub>25</sub>B<sub>1</sub>N<sub>3</sub> = 474.2142 [3a - $OMe]^+$ ), m/z 678.1766 (calcd for  $C_{36}H_{22}B_1N_3F_9 = 678.1764$  $[3b - OMe]^+$ ), m/z 564.2464 (calcd for  $C_{36}H_{31}B_1N_3O_3 =$ 564.2459  $[3c - OMe]^+$ ), and a cationic parent peak as a B-axial hydroxy derivative at m/z 431.3094 (calcd for C<sub>27</sub>H<sub>38</sub>B<sub>1</sub>N<sub>3</sub>O<sub>1</sub> = 431.3107  $[3d-OH]^+$ ). The <sup>1</sup>H NMR spectrum of 3a in CDCl<sub>3</sub> exhibits a singlet at 6.87 ppm due to the  $\beta$ -pyrrolic protons and four signals at 3.68, 3.41, 3.21, and 3.12 ppm due to the saturated methylene  $\beta$ -protons that correlate to each other. The B-axial methoxy protons resonate at 2.34 ppm, which is slightly

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Figure 1. X-ray crystal structure of 3a-OEt. Thermal ellipsoids represent 50% probability. Solvent molecules are omitted for clarity.



Figure 2. UV-vis absorption (solid lines) and fluorescence (dashed lines) spectra of 1a, 2a, and 3a in  $CH_2Cl_2$ .

downfield shifted from those of 1a (0.82 ppm) and 2a (1.51 ppm), and the central boron resonates at -8.0 ppm that is also downfield shifted from those of 1a (-15.3 ppm) and 2a (-12.2 ppm). These data indicate distinct aromaticity of 3a, which is modest as compared with those of 1a and 2a. In line with this trend, the nuclear independent chemical shifts (NICS) value of 3a has been calculated at B3LYP/6-311G(d) level using the Gaussian 09 package<sup>11</sup> to be -10.9 ppm, which is again smaller than those of 1a (-18.9 ppm) and 2a (-14.9 ppm).

Slow recrystallization from a mixture of acetonitrile and heptane provided nice crystals of **3a-OEt** that was easily prepared by heating **3a** in the presence of ethanol. Single-crystal X-ray diffraction analysis revealed that **3a-OEt** has a nonsymmetric structure with two  $\beta - \beta$  single bonds of 1.486(5) and 1.511(5) Å and a  $\beta = \beta$  double bond of 1.425(5) Å and a bowl-depth of 1.26 Å<sup>12</sup> (Figure 1).

Figure 2 shows the absorption and emission spectra of 1a, 2a, and 3a. The absorption spectrum of subchlorin 2a is characterized by an attenuated and blue-shifted Soret-like band as well as intensified and red-shifted Q-like bands as compared to those of

subporphyrin 1a.<sup>7</sup> Subbacteriochlorin 3a exhibits even smaller and double-peaked Soret-like bands at 301 and 336 nm and Q-like bands at 393, 412, 472, and 498 nm. Importantly, the fluorescence of 3a is remarkably intensified ( $\Phi_F = 0.42$ ) at 550 nm, which is distinctly red-shifted from 1a (520 nm,  $\Phi_F =$ 0.13) or slightly blue-shifted from 2a (556 nm,  $\Phi_F = 0.07$ ). These spectral changes are reminiscent of those from chlorins to isobacteriochlorins rather than to bacteriochlorins.<sup>13</sup> Notable substituent effects are observed for the Soret bands of subbacteriochlorins; the similar double-peaked Soret band is observed for 3c, a single-peaked Soret band is observed for 3b, and a much sharper Soret band is observed for 3d due to the absence of conjugative electronic interaction with *meso*-substituent, while the substituent effects are marginal for the fluorescence spectra (Figure S4, Supporting Information [SI]).

To quantitatively analyze the energy relaxation dynamics of 3a in the S<sub>1</sub> state, the radiative and nonradiative decay rates have been determined using the fluorescence quantum yield and the S<sub>1</sub> fluorescence lifetime (Table S2, SI). Since the nonradiative decay rates of subporphyrin and subchlorin are nearly 10 times faster than their radiative decay rates presumably due to an efficient intersystem crossing process,<sup>6a,7</sup> the overall S<sub>1</sub> fluorescence lifetimes of these molecules are mainly determined by the nonradiative decay rates. In the case of 3a, however, the nonradiative decay rate  $(9.8 \times 10^7 \text{ s}^{-1})$  was similar to the radiative decay rate  $(6.6 \times 10^7 \text{ s}^{-1})$  probably by decreasing the intersystem-crossing rate, which leads to an increased fluorescence quantum yield. On the other hand, the nonradiative decay rates of 1a and 2a were estimated to be  $4.4 \times 10^8$  s<sup>-1</sup> and  $3.2 \times$  $10^8$  s<sup>-1</sup>, respectively. The reason for slower intersystem crossing in 3a is probably a lowered energy level of its triplet state which can lead to an increased energy gap between the singlet and triplet states as compared to those of subporphyrins and subchlorins. Further support for this conjecture comes from a triplet state lifetime of  $3a(30 \mu s)$  that is shorter than those of  $1a(60 \mu s)$ and 2a (100  $\mu$ s), which have been determined by nanosecond time-resolved transient absorption spectra (Figure S9, SI). These data are consistent with a decrease in the fluorescence quantum yield in the order of 3a > 1a > 2a.

The molecular structures and MO diagrams were optimized at B3LYP/6-311G(d) level using the Gaussian 09 package (Figure 3).<sup>11</sup> The molecular orbitals of subporphyrin 1a are similar to those of porphyrin in terms of a2u-like HOMO, a1u-like HOMO-1, and a couple of degenerate eg-like LUMO and LUMO+1. Subchlorin 2a possesses destabilized a<sub>1u</sub>-like HOMO and largely destabilized LUMO+1 along with HOMO-1 and LUMO that are lying at energy levels similar to those of 1a. Upon another  $\beta$ -hydrogenation, the LUMO and LUMO+1 of **3a** are stabilized and destabilized, respectively, to become LUMO+1 and LUMO, and HOMO are further destabilized. This MO diagram can explain two-peaked Soret band features of 3a and 3c on the basis of Gouterman's four orbital model.<sup>14</sup> In 3b, the electron-withdrawing 4-trifluoromethylphenyl substituents considerably stabilize LUMO+1, hence making the energy gap between LUMO and LUMO+1 small, which causes a singlepeaked Soret-like band.

The electrochemical properties of 3a-d were studied by the cyclic voltammetry in CH<sub>3</sub>CN containing 0.10 M Bu<sub>4</sub>NPF<sub>6</sub> as a supporting electrolyte (Figure S5, SI). Subbacteriochlorins 3a-d exhibit irreversible reduction waves with peak positions at -2.53, -2.33, -2.53, and -2.82 V, respectively, and quasi-reversible oxidation waves at 0.00 and 0.57 V, and 0.06 and 0.63 V,



**Figure 3.** MO diagrams of **1a**, **2a**, and **3a** calculated with Gaussian 09 package.<sup>11</sup> (All energy levels were calculated at the B3LYP/6-311G(d) level. And each MO was visualized with cubegen program.)

-0.05 and 0.43 V, and -0.18 and 0.35 V, respectively. Characteristically high oxidation potentials of subbacteriochlorins are in accord with their easily oxidizable propensity with molecular oxygen.

Finally, **3a** was found to be smoothly and selectively oxidized to **2a** with  $Ag_2O$  in 86% yield. Therefore, the initial reduction of subporphyrin to subbacteriochlorin followed by oxidation with  $Ag_2O$  constitutes a novel synthetic route to subchlorins that is superior to our previous direct route of the reduction of **1** with *p*-tosylhydrazide.<sup>7</sup> Actually, subchlorin **2a** was prepared in 74% from **1a** via the two-step route involving the Raney nickel reduction and the  $Ag_2O$  oxidation without isolation of unstable **3a**.

In summary, subbacteriochlorins were synthesized by the hydrogenation of subporphyrins with Raney nickel. Despite double  $\beta$ -hydrogenation, subbacteriochlorins are modestly aromatic owing to the 14 $\pi$ -electronic circuit that involves the lone pair electrons of the nitrogen atom and exhibit characteristic blue-shifted Soret-like bands, red-shifted Q-like bands, enhanced fluorescence, and high oxidation potentials. Incorporation of this interesting porphyrinic chromophore into novel functional molecular systems is now actively pursued in our laboratories.

## ASSOCIATED CONTENT

**Supporting Information.** Preparation and analytical data for samples, crystallographic data for **3a-OEt** (CIF), cyclic voltammograms, calculated molecular orbitals, and time-resolved fluorescence decays and nanosecond time-resolved transient absorption decays. Complete ref 11. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Spectroscopic data of 3d; see Figure S4 of SI. At the present time, we isolated almost pure 3d but failed its complete purification.

(11) For the full Gaussian citation, see SI.

(12) Crystallographic data for **3a-OEt**:  $2(C_{35}H_{30}B_1N_3O_1) \cdot C_2H_3N_1$ , M = 1079.91, monoclinic, space group  $P_{2_1}$  (no. 4), a = 12.251(4) Å, b = 18.924(6) Å, c = 13.226(5) Å,  $\beta = 115.098(12)^\circ$ , V = 2776.9(16) Å<sup>3</sup>, T = 123 K,  $\rho_{calcd} = 1.292$  gcm<sup>-3</sup>, Z = 2,  $R_1 = 0.0631$  ( $I > 2\sigma(I)$ ),  $R_w = 0.1840$  (all data), GOF = 1.016. CCDC-806996.

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