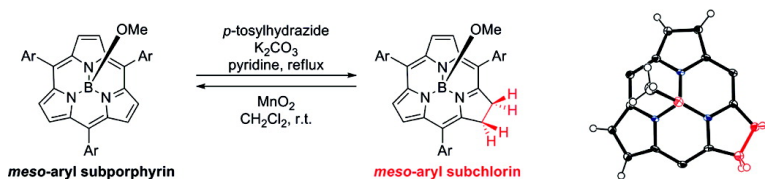


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## Synthesis and Characterization of *meso*-Aryl-Substituted Subchlorins

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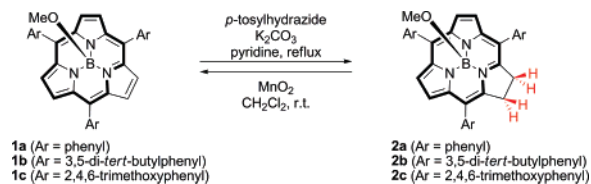
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Subporphyrin, a genuine ring-contracted porphyrin, had been elusive until our synthesis of a tribenzosubporphine in 2006,<sup>1</sup> despite its relatively simple structure.<sup>2</sup> Shortly later, synthetic protocols of *meso*-aryl-substituted subporphyrins were independently reported by Kobayashi et al.<sup>3a,c</sup> and us.<sup>3b</sup> This burgeoning chemistry of subporphyrin contrasts sharply with the chemistry of subphthalocyanines,<sup>4</sup> which has been continuously studied since the discovery by Meller and Ossko in 1972.<sup>4a</sup> Subporphyrins are bowl-shaped macrocycles bearing 14 $\pi$ -electron aromatic circuits, serving as an important benchmark molecule for understanding the electronic property of C<sub>3</sub> symmetric porphyrinoids. Actually, the preservation of porphyrin-like electronic properties in subporphyrins has been confirmed by their absorption spectra that contain a sharp Soret-like band and Q-like bands as well as the bright green fluorescence.

Chlorin,  $\beta,\beta$ -reduced porphyrin, is one of the most important chromophores in nature and displays characteristic optical properties, which are significantly altered from those of porphyrin, such as a weakened Soret band, red-shifted and intensified Q-bands,<sup>5</sup> and enhanced fluorescence. These features are ideal for photosynthetic functions. These spectral characteristics of chlorins have been understood in terms of symmetry lowering from porphyrins, since such symmetry lowering has a significant influence on the electronic properties of porphyrinoids according to Gouterman's four orbital theory.<sup>6</sup> It is then an intriguing question whether the similar symmetry lowering from subporphyrin (C<sub>3v</sub>) to subchlorin (C<sub>s</sub>) effects the similar spectral change from porphyrin to chlorin. Subchlorin can be characterized as a conjugated 14 $\pi$ -electronic network that is essentially the same as subporphyrin **1** as shown in Scheme 1. In this context, subchlorin, a ring-contracted congener of chlorin, will be another important benchmark macrocycle. Herein we wish to report the first synthesis and characterization of *meso*-aryl-substituted subchlorins.

*meso*-Aryl subporphyrins were prepared by treatment of pyridine–tri-*N*-pyrrolylborane and aryl aldehydes with trifluoroacetic acid at 0 °C for 1 h followed by refluxing in 1,2-dichlorobenzene under aerobic conditions.<sup>3b</sup> This synthesis is reliable but suffers from tedious separation of subporphyrin products. This difficulty comes from low yields of subporphyrins and more seriously from severely overlapping side products. Typically, in the synthesis of *meso*-phenyl subporphyrin **1a**, a reddish orange band always elutes closely with a yellow band of **1a**. This side product was isolated after repeated separations over silica gel columns, which turned out to be subchlorin **2a**. The high-resolution electrospray ionization mass measurement revealed an intense borenium cation peak at  $m/z = 472.2000$  (calcd for C<sub>33</sub>H<sub>23</sub>N<sub>3</sub>B = 472.1985 [**2a**-OMe]<sup>+</sup>). The <sup>1</sup>H NMR spectrum of **2a** in CDCl<sub>3</sub> at room temperature displays a couple of doublets at 7.82 and 7.45 ppm with  $J = 4.6$  Hz along with two sets of signals due to the *meso*-phenyl protons. The four

**Scheme 1.** Interconversion between Subporphyrins **1** and Subchlorins **2**



methylene  $\beta$ -protons resonate differently at 4.17, 4.13, 3.52, and 3.48 ppm as pseudo-double doublets each coupled with  $J = 16.9$  and 14.2 Hz at room temperature but coalesce into a pair of doublets at 4.14 and 3.53 ppm ( $J = 11.0$  Hz) at 50 °C (Supporting Information, SI). This result reveals that the reduced macrocycle of **2a** is nonsymmetric at room temperature but becomes symmetric at high temperature due to dynamic averaging. A singlet signal due to the axial methoxy protons appears at 1.51 ppm and the central boron peak appears at  $-12.2$  ppm in <sup>11</sup>B NMR, both indicating a diatropic ring current of **2a**, which is slightly weaker than that of **1a**. Consistent with this interpretation, NICS values at the center defined by 15 carbon atoms of the cores of **1a** and **2a** are calculated to be  $-19.0$  and  $-15.6$  ppm, respectively.

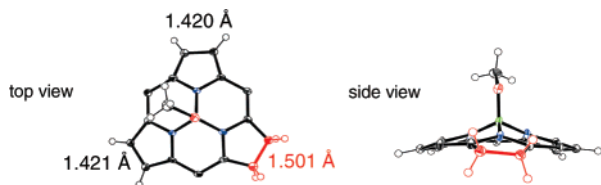
The bowl-like structure of subchlorin **2b** was unambiguously determined by X-ray diffraction analysis as shown in Figure 1. The bond length of the  $\beta$ – $\beta$  single bond is 1.501(16) Å, which is distinctly longer than the  $\beta$ – $\beta$  double bonds (1.420(16) and 1.421(17) Å), whereas the bond-length alternation of the conjugated 14 $\pi$ -system is quite small (SI), indicating a delocalized nature of the conjugated aromatic network. The bowl-depth of the macrocycle, defined by the distance from the boron atom to the mean plane of the peripheral six  $\beta$ -carbons, is 1.26 Å, which is slightly shorter than that of **1b** (1.33 Å).

We then examined the hydrogenation of **1a** to establish a rational synthetic route to subchlorins and found that treatment of **1a** with *p*-tosylhydrazide under basic conditions<sup>7</sup> provided **2a** in 34% yield, which was in turn oxidized with activated MnO<sub>2</sub> to regenerate **1a** almost quantitatively. On the basis of this finding, our subporphyrin synthesis was considerably improved by oxidizing a roughly separated mixture of subporphyrin and subchlorin with activated MnO<sub>2</sub>. This procedure facilitated the separation of subporphyrin, and the yield of **1a** was improved from 3.8% to 6.3%, similarly to the Adler porphyrin synthesis.<sup>8</sup>

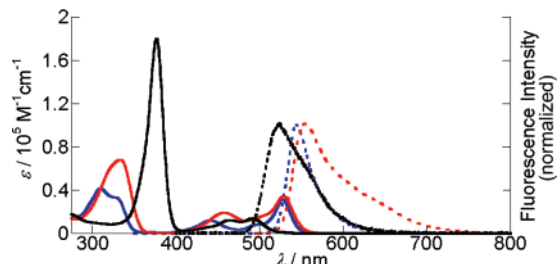
Subporphyrin **1b** shows a sharp Soret-like band at 377 nm and Q-like bands at 464 and 492 nm, whereas **2b** exhibits a less intense and blue-shifted Soret-like band at 333 nm and intensified and red-shifted Q-like bands at 458 and 529 nm (Figure 2). Such changes from subporphyrin to subchlorin are quite similar to those from porphyrin to chlorin.<sup>6</sup> Subchlorin **2b** shows the fluorescence at 552 nm that tails characteristically over 700 nm. The tailing feature suggests effective vibronic coupling of the fluorescence process with the relevant molecular vibrations. The fluorescence quantum

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**Figure 1.** X-ray crystal structure and selected bond lengths of **2b**. *meso*-Aryl groups are omitted for clarity. See SI for detail.



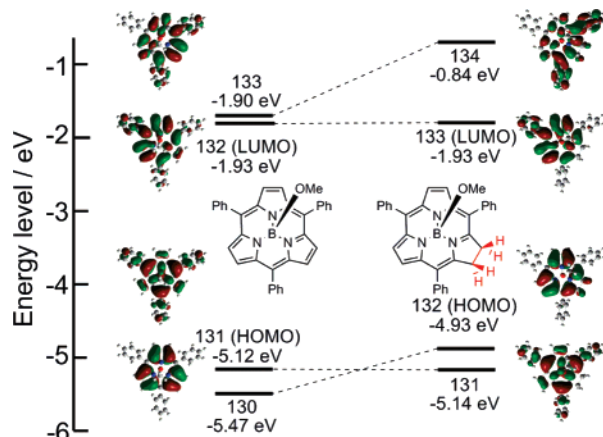
**Figure 2.** Absorption (solid) and fluorescence (dashed) spectra of **1b** (black), **2b** (red), and **2c** (blue) in  $\text{CH}_2\text{Cl}_2$ .

yield ( $\Phi_F$ ) is 0.09 and the fluorescence lifetime ( $\tau_F$ ) is 2.83 ns. Subporphyrin **1b** exhibits the fluorescence at 524 nm with  $\tau_F = 2.01$  ns and  $\Phi_F = 0.11$ . The decay of the lowest triplet excited-state of **1b** and **2b** in  $\text{CH}_2\text{Cl}_2$  has been found to obey a single-exponential function with  $\tau = 38 \mu\text{s}$  and  $\tau = 111 \mu\text{s}$ , respectively. The changes in the optical properties from **1b** to **2b** are reminiscent of those from porphyrins to chlorins.

In our recent publication,<sup>3b</sup> we revealed large substituent effects on the electronic properties of *meso*-aryl-substituted subporphyrins. Such effects stem from free rotation of sterically unhindered substituents. We thus prepared subchlorin **2c** to examine the *meso*-aryl-substituent effects. Free rotation of *meso*-(2,4,6-trimethoxyphenyl) substituents is prohibited in **2c** at room temperature, judging from its  $^1\text{H}$  NMR spectrum that displays two different signals for the *o*-methoxy protons and the two meta protons of the aryl substituents. The Soret-like band of **2c** was observed at 311 nm with a shoulder at 326 nm and the fluorescence was observed at 544 nm with  $\Phi_F = 0.11$  as a much sharper spectrum as compared with those of **2a** and **2b** (SI and Figure 2). This is presumably due to decreased interactions with the *meso*-aryl substituents, hence suggesting the importance of the *meso*-aryl substituents for vibronic coupling.

MO calculations on **1a** and **2a** were performed at the B3LYP/6-31G\* level with the Gaussian 03 package.<sup>9</sup> The molecular orbitals of **1a** are quite similar to those of porphyrins, involving  $a_{2u}$ -like HOMO and  $a_{1u}$ -like HOMO-1, and a couple of degenerate  $e_g$ -like orbitals (LUMO and LUMO+1) (Figure 3). Since molecular orbitals which have large coefficients at the reduced  $\beta$ -positions of subchlorins are drastically destabilized, the  $a_{1u}$ -like orbital becomes HOMO, and LUMO+1 is raised in **2a**. As a consequence, the degeneracy of LUMOs is largely lifted, and the HOMO-LUMO gap is reduced as compared with **1a**. This orbital diagram nicely explains the intensified and red-shifted Q-like bands of subchlorins.

The electrochemical data are also in line with the calculated orbital diagram. Cyclic voltammetry performed in acetonitrile revealed that **1a** exhibits the first one-electron oxidation and reduction waves at 0.78 and  $-1.82$  V, while **2a** exhibits the corresponding waves at 0.42 and  $-1.83$  V, all as reversible waves



**Figure 3.** Molecular orbital diagrams of **1a** (left) and **2a** (right) calculated at the B3LYP/6-31G\* level.

versus the ferrocene/ferrocenium ion couple. Namely, **2a** undergoes the first oxidation at low potential in comparison to **1a** but the first reduction potentials are similar for **1a** and **2a**. Electrochemical HOMO-LUMO gaps are 2.60 eV for **1a** and 2.25 eV for **2a**, which are similar to the optical HOMO-LUMO gaps, 2.52 eV for **1a** and 2.35 eV for **2a**.<sup>10</sup>

In summary, *meso*-aryl subchlorins **2** were first isolated in our synthesis of subporphyrins as a byproduct and were more efficiently prepared by the reduction of subporphyrins **1** with *p*-tosylhydrazide. Subporphyrin-to-subchlorin structural change is accompanied by large optical and electrochemical changes that are quite similar to those observed for porphyrin-to-chlorin change. Importantly, the optical and electrochemical properties of subchlorins are well understood by Gouterman's four orbital theory.

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**Supporting Information Available:** Complete ref 9; detailed experimental data for subchlorins. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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