Contracted Porphyrins

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meso-Aryl Subporphyrins**

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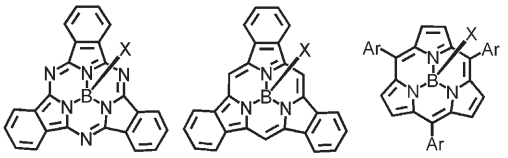
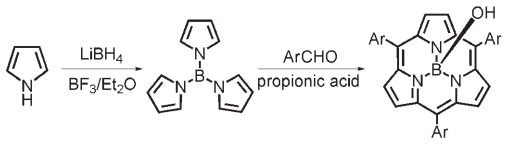
Porphyrins, especially tetraphenylporphyrins (TPPs), have been intensively studied and used in various fields.[1] In recent years, larger congeners of porphyrins, known as expanded porphyrins,[2] have been of interest because of a variety of unique properties. However, although ring-contracted boron-stabilized azaporphyrins, that is, subphthalocyanines, are known (**1**),[1b] ring-contracted congeners were unknown until the recent synthesis of the boron-containing tribenzosubporphyrin **2** by Osuka et al.[3,4] More recently Latos-Grażyński



et al. reported the first synthesis of what they named *meso*-aryl subpyriporphyrin, which has a boron-free structure.[5] These subporphyrin analogues, however, have aromatic moieties at the periphery or are modified by pyridine rings, which would have a strong effect on the electronic structure of the parent subporphyrin skeleton. Thus, the advent of boron-containing *meso*-aryl subporphyrins **3** with three pyrrole rings has long been awaited for investigation of the inherent properties of the subporphyrin core per se. We report herein the first such *meso*-aryl subporphyrins consisting of three pyrrole and three aryl rings, that is, triphenyl-, tritolyl-, and tripyridylsubporphyrins.

meso-Phenylsubporphyrin **3a** was synthesized by a method based on utilizing tripyrrolylborane **4**[6] as a template for the Adler reaction (Scheme 1). Tripyrrolylborane (0.1 g) was dissolved in propionic acid (35 mL) and the solution added dropwise to a refluxing solution of benzaldehyde (ca. 0.1M) in propionic acid (35 mL)[7] over 1 h. After addition, the solution was further heated to reflux for 2 h. The solvent was removed, and the residue purified by column chromatography on silica gel and alumina and TLC with $CHCl_3$/methanol as



Scheme 1. Synthetic route to various boron-containing *meso*-aryl subporphyrins.

eluent, and size-exclusion HPLC with $CHCl_3$. The TLC analysis indicated a moderate yield of about 15%, but pure *meso*-phenylsubporphyrin **3a** was obtained only in about 5% yield because of several tedious column-chromatography stages. *meso*-Tolylsubporphyrin **3b** and *meso*-pyridylsubporphyrin **3c** were similarly synthesized by using *p*-tolualdehyde and 4-pyridinecarboxaldehyde, respectively, instead of benzaldehyde.

In the ^{1}H NMR spectrum of **3a**, signals for six pyrrolic β protons and protons at *ortho*, *meta*, and *para* positions of the phenyl group were observed at $\delta = 8.12$, 8.05–8.07, 7.67–7.72, and 7.58–7.62 ppm (in $CDCl_3$), respectively. The axial OH proton was detected at high field (−2.65 ppm), plausibly because of the ring-current effect of 14π-electron aromaticity. The ^{1}H NMR spectra of **3b** and **3c** could be reasonably assigned in a similar manner.[8] The ^{13}C NMR spectra were also satisfactory and signals were assigned by performing ^{13}C-^{1}H COSY experiments (see the Supporting Information). For all subporphyrins, the ESI-TOF mass spectra of the molecular ion peaks matched with the theoretical isotopic distribution (see the Supporting Information). The high-resolution ESI-TOF mass analysis of **3a**–**c** also gave closely matched molecular ion peaks with *m*/*z* 470.1820 for **3a** (calcd for $[M-OH]^+$: *m*/*z* 470.1829), 512.2289 for **3b** (calcd for $[M-OH]^+$: 512.2298) and 491.1786 for **3c** (calcd for $[M+H]^+$: 491.1792). All *meso*-aryl subporphyrins are yellow in solution and highly soluble in many common organic solvents including methanol, ethanol, diethyl ether, hexane, ethyl acetate, acetic acid, chloroform, THF, dioxane, DMF, and benzene.

Figure 1 shows the electronic absorption, magnetic circular dichroism (MCD), and theoretical UV/Vis spectra of *meso*-phenylsubporphyrin **3a** and the Zn complex of tpp ([Zn(tpp)]) as a reference. The Q band appears at around 440–510 nm, and the very intense Soret band (one order of magnitude more intense than the Q band) at 340–400 nm. The blue shift of the Soret band by approximately 50 nm relative to that of [Zn(tpp)] reflects the contracted π-conjugated system. The absorption coefficient of the Soret band of **3a** is about one fourth of that of [Zn(tpp)]. A similar tendency is seen for azaporphyrin congeners, that is, compared with

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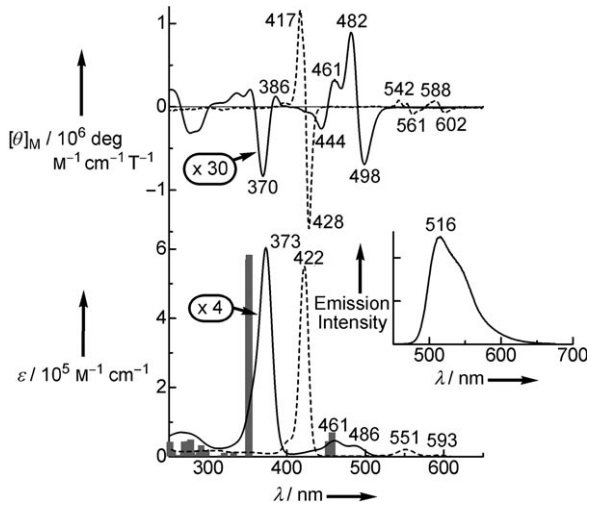

Figure 1. MCD (top) and electronic absorption spectra (bottom) of **3a** (solid lines) and [Zn(tpp)] (dashed lines) in $CHCl_3$ and calculated (TD-DFT) absorption bands (gray bars). The inset shows fluorescence emission of **3a** (in $CHCl_3$). Excitation was at 360 nm.

phthalocyanines (Pc), the absorption intensity of subphthalocyanine (subPc) **1** is much lower.[9] The MCD spectrum indicates that this compound has characteristics of porphyrins. Reflecting the large angular momentum in the Q-band region, the Q band is much more intense than that expected from the weak Q absorption band. In addition, the observed Faraday *A* terms in the Q-band region strongly suggest that the excited states are degenerate.[10] However, the Soret MCD is peculiar and unique in that the negative envelope alone is much larger than the positive envelope.[11] The MCD intensity of **3a** is also much smaller than that of [Zn(tpp)].

Figure 2 shows the spectra of *meso*-pyridylsubporphyrin **3c** and *meso*-phenylsubporphyrin **3a** with similar absorption-spectroscopic patterns. However, the weaker Q(0–0) band suggests that the energy difference between the HOMO and HOMO−1 (ΔHOMO) in **3c** is smaller than in **3a**. The most

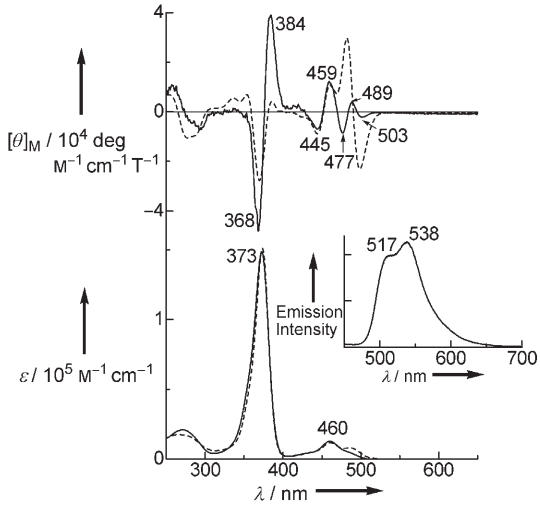

Figure 2. MCD (top) and electronic absorption spectra (bottom) of **3a** (dashed lines) and **3c** (solid lines) in $CHCl_3$. The inset shows fluorescence emission of **3c** (in $CHCl_3$). Excitation was at 360 nm.

prominent difference from [Zn(tpp)] and **3a** is seen in the MCD spectrum (Figures 1 and 2). The MCD pattern in the Q and Soret band regions is minus-to-plus and plus-to-minus, respectively, in ascending energy. These patterns are unknown in hitherto reported porphyrins. According to Michl's perimeter model,[12] this kind of pattern appears in the bands of forbidden and allowed characters, respectively, of 12-membered planar polyenes. In the case of the Soret MCD of **3a** (Figure 1), a clear *A* term is not seen. However, it appears that it is essentially a negative Faraday *A* term since the MCD trough (370 nm) is located at a shorter wavelength than the Soret absorption peak (373 nm). The large difference in Soret MCD between **3a** and **3c** suggests that the electronic structures of subporphyrins are more sensitive to *meso*-aryl substituents than those of *meso*-aryl porphyrins.

As shown in the inset of Figures 1 and 2, all subporphyrins exhibit green fluorescence, and the quantum yields Φ_F of the so-called S1 emission were determined to be 0.10–0.12 in benzene by the use of 9,10-diphenylanthracene as calibrant ($\Phi_F = 0.85$).[13] These values are much larger than that of [Zn(tpp)] in benzene ($\Phi_F = 0.03$).[14] The Stokes shifts of **3a–c** of about 30 nm (30, 33, and 30 nm, respectively) suggest that triaryl subporphyrins have more flexible structures than [Zn(tpp)] (Stokes shift of ca. 8 nm[15]).

Cyclic and differential-pulse voltammetry was carried out for all subporphyrins. The first oxidation and reduction potentials of **3a** were recorded at about 0.77 and −1.85 V versus the ferrocene/ferrocenium couple, while those of **3b** lie at 0.55 and −2.02 V, respectively. The potential difference of the subporphyrins (2.57–2.62 V) is larger than that of *meso*-phenylporphyrins (ca. 2.25 ± 0.15 V),[16] in accordance with the smaller π conjugation and the appearance of the absorption spectra at shorter wavelength. For some reason, *meso*-pyridylsubporphyrin (**3c**) exhibited only a reduction wave at −1.80 V under the experimental conditions.

Geometry optimization was performed for compounds **3** using DFT calculations (for optimized structures, see the Supporting Information). Transition energy and oscillator strength were calculated by the TD-DFT method. These calculations were all based on the B3LYP functional within Gaussian 03 with 6-31G* basis sets. Obtained MOs and energy diagram of **3a** and **3c** are shown in Figure 3. The absorption spectra can be explained by the so-called four-orbital model, as for normal porphyrins.[1a] According to the results of TD-DFT calculations, the Q bands are mainly derived from HOMO→LUMO and HOMO→LUMO+1 transitions, while the Soret bands are mainly derived from HOMO−1→LUMO and HOMO−1→LUMO+1 transitions, which suggests that the spectra of subporphyrins can be interpreted like those of normal porphyrins. The LUMO is theoretically doubly degenerate, and the two HOMOs can be regarded as being accidentally degenerate. The ΔHOMO and ΔLUMO values for **3a** were calculated to be 0.348 and 0.063 V, respectively, while those for **3c** were 0.211 and 0.065 V, respectively, in support of the experimental fact that the Q(0–0) band of the latter is weaker than that of the former.[12] It was also revealed that the HOMO, LUMO, and LUMO + 1 of these subporphyrins have larger coefficients in the phenyl and pyridyl moieties than those of TPPs, that is, the

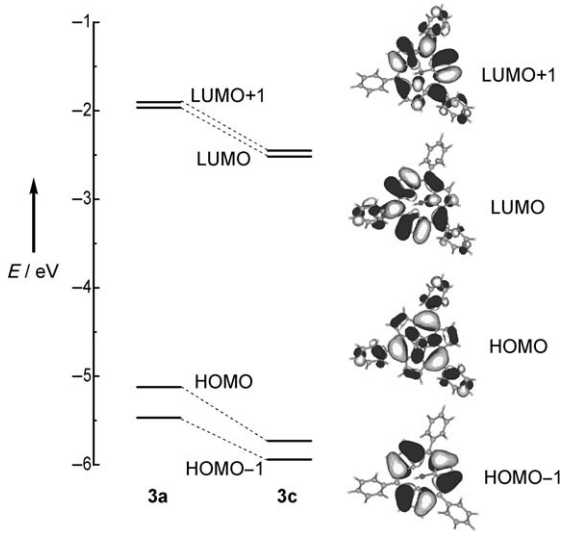

Figure 3. Frontier MOs and energy levels of **3a** and **3c**.

meso-aryl substituents make significant contributions to the electronic structure of subporphyrins. This is, however, not surprising, since the HOMO and LUMO of phenyl or pyridyl groups are closer to those of subporphyrins than to those of *meso*-phenylporphyrins (note that the subporphyrin skeleton is smaller than the porphyrin skeleton).

In conclusion, we have reported the synthesis of novel *meso*-aryl subporphyrins and some of their spectroscopic properties, which were interpreted on the basis of MO calculations. The subporphyrins were synthesized by using tripyrrolylborane as a template for the Adler reaction. They show electronic absorption and MCD spectra characteristic of porphyrins, and these were interpreted by the so-called four-orbital model used for porphyrins and phthalocyanines. However, the MCD pattern was clearly different from those of porphyrins reported to date. Reflecting the smaller conjugated system, the potential difference between the first oxidation and reduction was larger (ca. 2.6 V) than for conventional porphyrins (ca. 2.25 V).

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