

Porphyrinoids

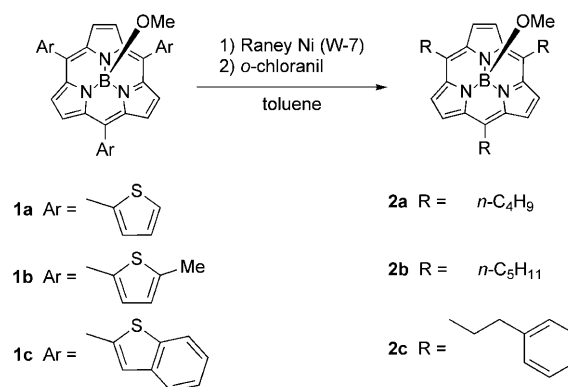
Meso-Trialkyl-Substituted Subporphyrins**

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In recent years, subporphyrins, which are ring-contracted porphyrins, have emerged as promising functional molecules because of their attractive features, including bowl-shaped structures, 14π -electronic aromatic systems, porphyrinlike spectral characteristics, intense fluorescence, and supramolecular chemistry based on axial chelation of the boron atom.^[1–3] Notably, the free rotation of meso-aryl substituents of subporphyrins leads to the large electronic effects that give rise to highly perturbed optical properties, as demonstrated by oligo-1,4-phenyleneethynylene and 4-aminophenyl substituted subporphyrins.^[4] Despite this progress, the chemistry of subporphyrins still remains in its infancy and an effective synthetic entry into novel subporphyrins is highly desirable. Considering the important roles that meso-alkyl-substituted porphyrins have played in the development of porphyrin chemistry since the first porphyrin synthesis in 1935,^[5] it is desirable to study the chemistry of meso-trialkyl-substituted subporphyrins, but the synthesis of this class of molecules has not been reported to date. Herein, we report the first synthesis of meso-trialkyl-substituted subporphyrins.

We initially applied our synthetic protocol for meso-triaryl-substituted subporphyrin^[1c] to the synthesis of meso-trialkyl-substituted subporphyrins. Pyridine-tri-*N*-pyrrolylborane was condensed with 1-pentanol under various reaction conditions by changing reaction parameters such as solvent, temperature, molar ratio, and any possible additives. Unfortunately, the desired meso-tributyl subporphyrin was not detected. These negative results led us to explore an indirect

route that involved the synthesis of meso-thienyl subporphyrins, and subsequent reductive desulfurization with Raney nickel. Thus, subporphyrins **1a** and **1b** were prepared by using our protocol in 1.7 and 3.7% yield, respectively (Scheme 1).



Scheme 1. Synthesis of meso-trialkylsubporphyrins **2a–c**.

The higher yield of **1b** may be ascribed to the absence of the free α -thienyl position, since free α -thiophenes are prone to oxidative degradation. It is noteworthy that these compounds are the first examples of subporphyrins that bear five-membered aromatic heterocycles. Single-crystal X-ray diffraction analysis revealed the bowl-shaped structure of **1b** (Figure 1), in which the dihedral angles^[6] of the meso-thienyl

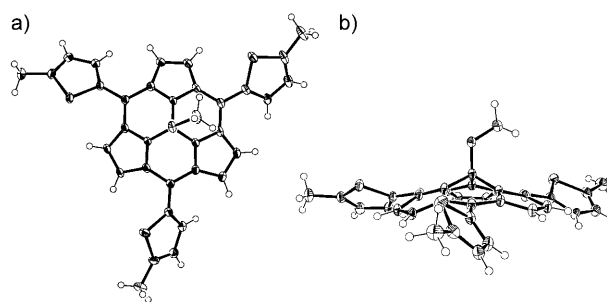


Figure 1. X-ray crystal structure of subporphyrin **1b** (thermal ellipsoids are set at the 50% probability level).

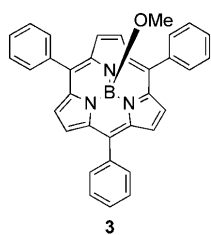
substituents are all small (31.7 , 35.6 , and 48.2°), thus allowing the strong electronic conjugation of these substituents with the subporphyrin core. These dihedral angles are slightly smaller than those of meso-triphenyl subporphyrin **3** (38.3 , 45.7 , and 48.1°), which reflect the compact size of the meso-thienyl substituents.

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The UV/Vis absorption spectra of **1a** and **1b** exhibit broadened Soret-like bands at 394 and 400 nm, respectively, which are red-shifted by 21 and 27 nm from that of **3** at 373 nm (Figure 2 and the Supporting Information). The Q-like band of **1b** was observed as a considerably broadened band at 534 nm. The fluorescence of

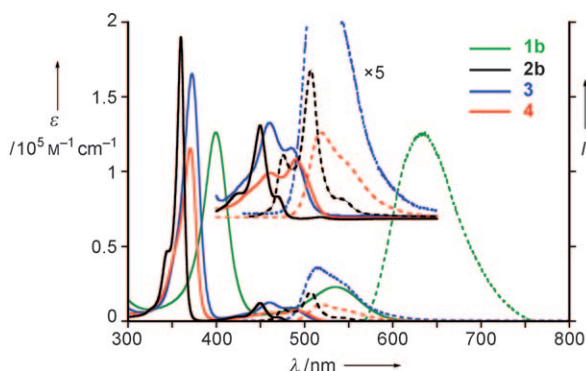


Figure 2. UV/Vis absorption (solid lines) and fluorescence (dashed lines) spectra of subporphyrins **1b**, **2b**, **3**, and **4** in CH_2Cl_2 .

1b was observed at 632 nm with a fluorescence quantum yield $\Phi_F = 0.45$. To the best of our knowledge, the Φ_F value of **1b** is the highest reported to date for simple porphyrinoid systems without charge-transfer interactions. These spectral data indicate large electronic influences of the meso-thienyl substituents on the subporphyrin core, and the large Stokes shift (Table S1 in the Supporting Information) suggests a large structural change in the excited state. The fluorescence lifetime of **1b** measured by the time-correlated single photon counting method (TCSPC) was 5.6 ns, which is approximately twice that of **3** (2.4 ns; Figure 3 and the Supporting Information). Furthermore, the natural radiative rate constants calculated from Φ_F and τ_F using the relationship

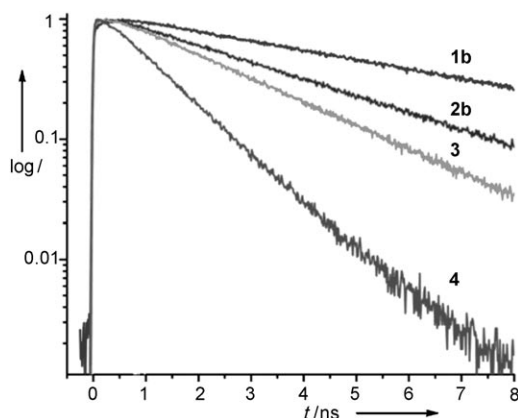


Figure 3. Fluorescence decay profiles of subporphyrins **1b**, **2b**, **3**, and **4** in CH_2Cl_2 obtained by the TCSPC method ($\lambda_{\text{ex}} = 420$ nm; the decays are collected at the respective fluorescence maxima).

($k_r = 1/\tau_0$; $\tau_0 = \tau_F/\Phi_F$) were $5.4 \times 10^7 \text{ s}^{-1}$ and $8.0 \times 10^7 \text{ s}^{-1}$ for **3** and **1b**, respectively. The natural radiative rate of a molecule has often been related to the radiative size of a chromophore.^[4a] Thus, the larger radiative rate of **1b** than **3** is attributed to the relatively facile rotation of the thienyl groups around the subporphyrin core. This rotation facilitates larger electronic interactions between the meso substituents and the core.

We then examined the reductive desulfurization of meso-thienyl-substituted subporphyrins. A solution of **1b** in toluene was treated with W-7 Raney Nickel^[7] at 40 °C for 30 min, and TLC analysis confirmed the consumption of **1b**. Comparison of the ^1H and ^{11}B NMR spectra of the reaction mixture with those of meso-triaryl-substituted counterparts indicated the formation of meso-tripentylsubporphyrin **1b**, along with several over-reduced products (see the Supporting Information).^[1c,8] Since these reduction products were difficult to separate, the reaction mixture was oxidized with *o*-chloranil to give a simpler mixture, from which **2b** was isolated in 50 % yield. In the same manner, meso-tributylsubporphyrins **2a** was obtained in 48 % yield.

By following essentially the same procedures, meso-tris(2-benzo[b]thienyl)-subporphyrin **1c** was prepared in 0.9 % yield from the reaction of 2-formyl-benzothiophene with pyridine-*N*-tripyrrolylborane. Compound **1c** was converted to meso-tris(2-phenylethyl)subporphyrin **2c** in 43 % yield.

The high-resolution ESI mass spectrum of **2b** shows an intense borenium cation peak at m/z 452.3232 (calcd for $\text{C}_{30}\text{H}_{39}\text{N}_3\text{B}_1 = 452.3237$ [**2b**-OMe] $^+$). The ^1H NMR spectrum of **2b** shows a singlet at $\delta = 8.06$ ppm for the six β -pyrrolic protons, a set of five signals at $\delta = 3.92$, 2.30, 1.72, 1.53, and 0.97 ppm for the protons in meso-pentyl substituents, and a singlet at $\delta = 0.75$ ppm for the axial B methoxy protons. The chemical shift of the β -pyrrolic proton signal of **2b** is shifted upfield from that of **3** ($\delta = 8.12$ ppm)^[1c] because of the absence of the local anisotropic ring current effect of the meso-phenyl substituent. The signal for the boron atom in the ^{11}B NMR spectra was observed at $\delta = -15.0$ ppm, which is similar to that of **3** at $\delta = -15.3$ ppm.

Subporphyrins **2a–c** are quite soluble in organic solvents including methanol and hexane, thus making their crystallization rather difficult. Therefore, in order to obtain single crystals suitable for X-ray diffraction, we examined many groups for the axial ligand of **2b**. Fortunately, we found that suitable crystals could be obtained by slow recrystallization of an ether solution of 3,5-dinitrobenzyl-subporphyrin DN-**2b** that was prepared by heating a toluene solution of **2b** at reflux in the presence of 3,5-dinitrobenzylalcohol. The crystal structure of DN-**2b** displays a bowl-shaped C_3 -symmetric structure with a bowl depth of 1.37 Å, which is the distance from the boron atom to the mean plane of the six peripheral β -carbon atoms (Figure 4). The bond distances of three B–N and B–O bonds are 1.48, 1.49, 1.49, and 1.46 Å, respectively.

The UV/Vis absorption spectrum of **2b** in CH_2Cl_2 exhibits Soret-like bands at 360 nm with a shoulder at 344 nm, and Q-like bands at 450 and 472 nm, which are both blue-shifted and more intense than those of **3** (Figure 2). Importantly, the comparison of the optical data of **2b** and **3** reveals a substantial electronic conjugation of the meso-phenyl

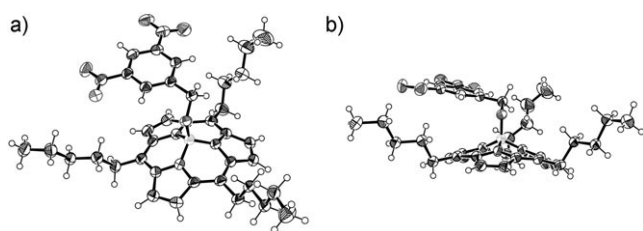


Figure 4. Crystal structure of subporphyrin DN-**2b** (thermal ellipsoids are set at the 50% probability level).

groups to the subporphyrin core in **3**; in contrast, this conjugation is only marginal for porphyrins. It is noteworthy that the absorption spectrum of **2b** indicates clear vibronic structures, which are reminiscent of the absorption features of typical porphyrins, for the Soret-like band as well as the Q-like bands. The steady-state fluorescence spectrum of **2b** also exhibits a vibronic structure with peaks at 476 and 507 nm, which are a mirror image of the Q-like band spectrum. The small Stokes shift value (489 cm^{-1}) reflects the rigid structure of subporphyrin core in **2b**, because the radiative part of the chromophore is limited to the core alone. The fluorescence quantum yield of **2b** was also determined to be small (0.07). The fluorescence lifetime of **2b** was measured to be 3.2 ns, and the natural radiative rate constant was calculated to be $2.2 \times 10^7\text{ s}^{-1}$. The larger radiative rates of **1b** and **3** with respect to that of **2b** (Table S1 in the Supporting Information) confirm that the intrinsic photophysical properties of subporphyrins are remarkably influenced by conjugated interactions with meso-aryl substituents. In addition, the larger Stokes shifts (Table S1 in the Supporting Information) for the meso-aryl subporphyrins are due mainly to the different dihedral angles between the core and the aryl groups in the ground and excited states. Thus, the enhanced fluorescence properties of **3** ($\Phi_F = 0.13$) and meso-trithienyl subporphyrins (**1a**, $\Phi_F = 0.35$; **1b**, $\Phi_F = 0.45$; **1c**, $\Phi_F = 0.47$) are considered to arise from the effective electronic interactions with the meso-aryl substituents.

The oxidation and reduction potentials of subporphyrins were measured by cyclic voltammetry. In CH_2Cl_2 solution, **3** exhibited the first oxidation and reduction potentials at 0.82 and -1.84 V , respectively (Figure 5), while **1b** exhibited two reversible oxidation potentials at 0.45 and 0.84 V , and a reduction potential at -1.71 V . Accordingly, the electrochemical HOMO–LUMO (HOMO = highest occupied molecular orbital, LUMO = lowest unoccupied molecular orbital) gap of **1b** was only 2.16 eV, which was considerably lower than that of **3** (2.67 eV). This value is approximately consistent with MO calculations at the B3LYP/6-31G* level (Figure S9 in the Supporting Information). On the other hand, the subporphyrin **2b** exhibited the reversible oxidation process at 0.77 V , but the reduction was outside the potential window. Thus, the measurements were carried out in acetonitrile, in which oxidation and reduction potentials of 0.78 and -1.82 V (**3**) and 0.77 and -2.16 V (**2b**) were recorded (Figures S7 and S8 in the Supporting Information).

Finally, we examined the chemical transformations at the benzylic positions of the meso-alkyl-substituents in **2b**. Treat-

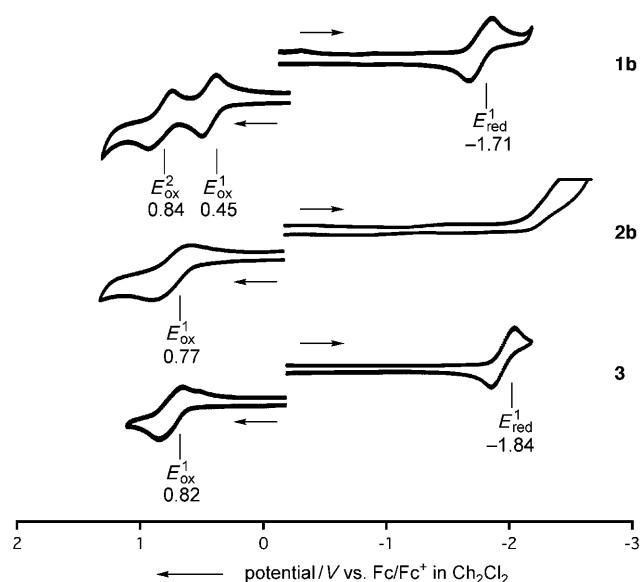
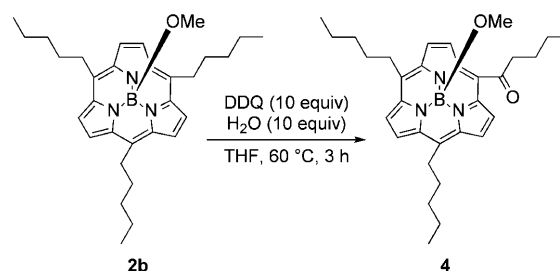


Figure 5. Cyclic voltammograms of subporphyrins **1b**, **2b**, and **3**. Fc/Fc^+ = ferrocene/ferrocenium.

ment of **2b** with ten equivalents of 2,3-dichloro-5,6-dicyano-benzoquinone (DDQ) in the presence of water in THF at 60°C ^[9] afforded meso-valeryl subporphyrin **4** in 24% yield (Scheme 2). The high-resolution ESI mass spectrum of **4**



Scheme 2. Synthesis of meso-valeryl subporphyrin **4**.

revealed an intense borenium cation peak at $m/z\ 466.3024$ (calcd for $\text{C}_{30}\text{H}_{37}\text{N}_3\text{O}_1\text{B}_1 = 466.3029$ [**4-OMe**] $^+$). The ^1H NMR spectrum reflects the C_s symmetry of **4** and shows the three β -proton signals as a singlet at $\delta = 8.45\text{ ppm}$ and as a pair of doublets at $\delta = 8.11$ and 8.08 ppm , and a set of signals for the valeryl group at $\delta = 3.84$, 2.08 , 1.64 , and 1.08 ppm . The ^{11}B NMR spectrum of **4** exhibits a peak at $\delta = -14.9\text{ ppm}$. The absorption spectrum of **4** shows a Soret-like band at 371 nm and Q-like bands at 461 and 490 nm . Both the absorption bands are red-shifted and are less intense than those of **2b**. The fluorescence spectrum of **4** exhibits a broad band at 519 nm ($\Phi_F = 0.04$) with $\tau_F = 1.1\text{ ns}$. The small fluorescence quantum yield may originate from charge-transfer-type interactions because of the electron-withdrawing nature of the carbonyl group, or mixing of its $n\pi^*$ character. The oxidation and reduction potentials of **4** are positively shifted to 1.11 and -1.54 V , respectively (Table S2 in the Supporting Information). Hence, it may be concluded that the simple

modification at the benzylic position led to large changes in the optical properties of subporphyrin.

In summary, the first synthetic route to meso-trialkylsubporphyrins proceeds by desulfurization of meso-trithienylsubporphyrins, which are attractive molecules that exhibit strongly perturbed absorption and fluorescence spectra induced by large electronic interactions with meso-thienyl substituents. Meso-alkylsubporphyrins are very important in understanding the electronic systems of subporphyrins as they show the optical and electrochemical properties of the unmodified subporphyrin macrocycle. Furthermore, oxidation at the benzylic position of the meso-alkyl substituent has been used to prepare a valeryl-substituted subporphyrin that exhibits highly perturbed optical and electrochemical properties. This work provides a firm basis for the exploration of functional subporphyrins, which is currently under investigation.

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