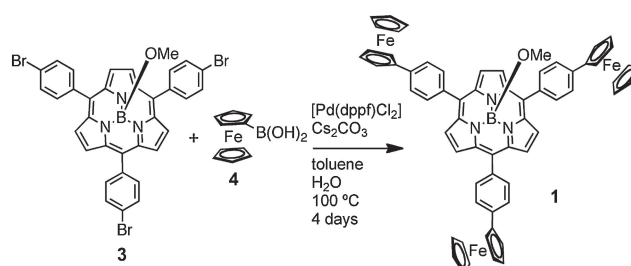# Ferrocene-appended Subporphyrins

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meso-Tris(4-ferrocenylphenyl)subporphyrin **1** and *meso*-triferrocenylsubporphyrin **2** were prepared. The structure of **2** was confirmed by X-ray analysis. Both molecules exhibit substantially red-shifted absorption spectra and almost complete fluorescence quenching, due to the influence of the electron-donating ferrocene substituents. Subporphyrin **1** exhibits a nonsplit oxidation wave for the oxidation of the ferrocene moieties, while subporphyrin **2** exhibits a split reversible oxidation wave with $\Delta E = 168\,\mathrm{mV}$ to indicate effective electronic communication.

Scheme 1. Synthesis of **1**.

Figure 1. UV–vis absorption spectra of **1**, **2**, and parent subporphyrin **5** in CH_2Cl_2.

Since the first report on tribenzosubporphines in 2006,[1] subporphyrins have been actively studied as promising functional molecules in light of a bowl-shaped 14π-aromatic network, robust chemical stability, intense green fluorescence, and highly tunable electronic properties.[2–5] Stepwise hydrogenation has been used to prepare subchlorins and subbacteriochlorins, which exhibit substantial changes in their electronic properties that are analogous to those from porphyrins to chlorins[6a] and bacteriochlorins.[6b] Different from the usual porphyrins, *meso*-aryl substituents of subporphyrins have smaller rotational barriers and have large substituent effects on the electronic properties of subporphyrins.[5] Interesting examples are *meso*-(4-aminophenyl)-substituted subporphyrins that exhibit systematic changes in Soret bands depending upon the number of 4-aminophenyl substituents[5c] and *meso*-oligo[4-(phenylethynyl)phenyl]-substituted subporphyrins that exhibit intensity-enhanced Soret bands.[5b] These unique features have continuously encouraged the exploration of novel functionalized subporphyrins.[7]

Ferrocene has been often employed in various functional molecules due to its facile and reversible one-electron oxidation property. For example, ferrocene-appended porphyrins have been extensively explored as photosynthetic reaction center models to achieve long-lived charge-separated states[8,9] and as molecular-based information storage systems that can undergo multistep electron-transfer reactions.[10,11] Among these, directly *meso*-ferrocenyl-appended porphyrins are particularly interesting because of long-range electronic interaction between ferrocene subunits through a conjugated porphyrin backbone.[12–15] In these systems, the dihedral angle between the ferrocene and the porphyrin plane has been identified as a key factor controlling electronic communication.

In this paper, we report the synthesis of ferrocene-appended subporphyrins **1** and **2**. *meso*-Tris(4-ferrocenylphenyl)subporphyrin **1** was prepared by the Suzuki–Miyaura coupling of *meso*-tris(4-bromophenyl)subporphyrin **3**[2b] with ferrocenylboronic acid (**4**) in 30% yield (Scheme 1). High-resolution electrospray time-of-flight (HR-ESI-TOF) mass spectrum revealed the molecular ion peak of **1** at m/z 1053.1915 (calcd for $C_{64}H_{48}$-$BOFe_3N_3$, 1053.1949 $[M]^+$). The ^1H NMR spectrum of **1** in
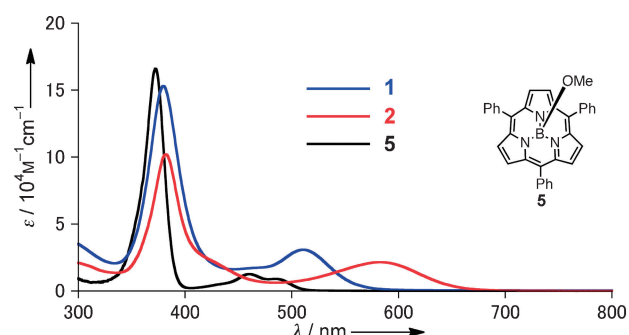
CDCl$_3$ indicates a singlet signal at 8.21 ppm due to the pyrrolic β-protons, a pair of doublet signals at 8.03 and 7.81 ppm due to the phenylene protons, two signals at 4.82 and 4.44 ppm due to the ferrocene protons at the attached side and a signal at 4.19 ppm due to the ferrocene protons at the intact side. The ^{11}B NMR spectrum of **1** exhibits a singlet at -15.1 ppm, which is slightly low-field shifted as compared with that of *meso*-triphenylsubporphyrin **5** (-15.3 ppm). The absorption spectrum of **1** shows the Soret band at 380 nm and Q-band at 510 nm, respectively, which are both considerably red-shifted from the corresponding bands of **5** at 373, 461, and 484 nm (Figure 1).

In the next step, we examined the synthesis of directly *meso*-ferrocene-linked subporphyrin. Following our synthetic protocol,[2] pyridine-*N*-tripyrrolylborane (**6**) and ferrocenecarboxaldehyde **7** were condensed with the aid of trifluoroacetic acid to give a complicated reaction mixture, from which subporphyrin **2** was isolated in 0.6% yield after repeated chromatographic separations over size-exclusion column and silica gel column (Scheme 2). In this synthesis, the final oxidation process with quinone oxidants should be avoided, since the ferrocene parts are quite fragile toward such oxidants. The HR-ESI-TOF mass spectrum of **2** revealed the molecule-related ion peak at m/z 794.0822 (calcd for $C_{45}H_{33}BFe_3N_3$, 794.0821 $[M - OMe]^+$). The ^1H NMR spectrum of **2** exhibits a singlet due to the pyrrolic β-protons at 8.27 ppm, two triplets due to the substituted
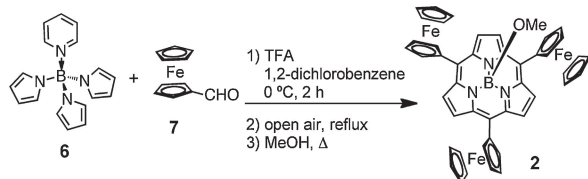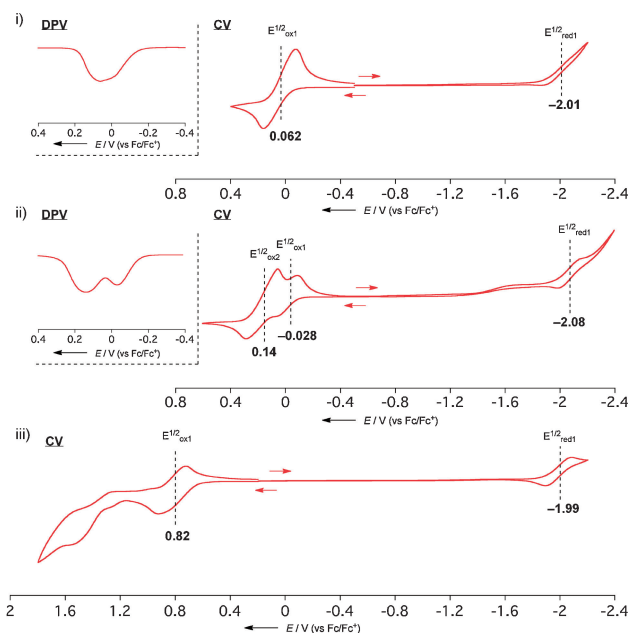
Scheme 2. Synthesis of **2**.
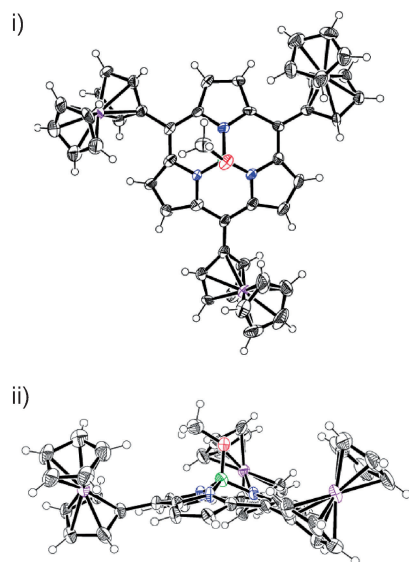
Figure 2. X-ray crystal structure of **2**. i) Top view; ii) side view. Thermal ellipsoids were scaled to 50% probability. Solvent molecules are omitted for clarity.

Figure 3. Cyclic voltammograms of i) **1**, ii) **2**, and iii) **5** measured in CH_2Cl_2 with 0.1 M Bu_4NPF_6 as electrolyte (potentials vs. ferrocene/ferrocenium ion pair, reference electrode: Ag/AgClO₄, working electrode: platinum electrode, counter electrode: platinum wire electrode, scan rate: 0.05 V s⁻¹). Inset shows DPV results of oxidation waves in i) and ii).

ferrocene protons at 5.30 and 4.66 ppm, and a singlet due to the unsubstituted ferrocene protons at 4.36 ppm in accord with its C_3 symmetric structure. These spectral features indicate a free rotation of the *meso*-ferrocenyl substituents at room temperature, which do not change even at −80 °C in toluene-d_8. The ¹¹B NMR spectrum of **2** exhibits a singlet at −14.3 ppm.

The structure of **2** was confirmed by single crystal X-ray diffraction analysis (Figure 2).[16] The dihedral angles between the ferrocene moieties and subporphyrin plane defined by neighboring C_α–C_{meso}–C_α atoms are 41.4, 37.6, and 36.7°, which are slightly smaller than those of *meso*-tetraferrocenylporphyrin (ca. 44°).[17] The bowl-depth defined by the distance between the central boron atom and the mean plane of six β-carbons is 1.26 Å, and the mean Fe–Fe distance is 9.93 Å. Subporphyrin **2** shows a broader and more red-shifted absorption spectrum with the Soret band at 382 nm and Q-band at 583 nm (Figure 1). The red shift of the Q-band of **2** is quite large, due to the strong electron-donating ability of the directly attached *meso*-ferrocenyl groups. Fluorescence emissions of **1** and **2** are both completely quenched, probably because of the efficient intramolecular electron transfer.[18]

The electrochemical potentials of **1** and **2** were measured by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in CH_2Cl_2 (Figure 3). Subporphyrin **5** shows reversible oxidation and reduction waves at 0.82 and −1.99 V. Characteristically, subporphyrins **1** and **2** exhibited oxidation waves due

to the appended ferrocenes at higher potentials than the oxidation of a subporphyrin unit, while the reduction potentials of the subporphyrin were observed at −2.01 and −2.08 V, respectively, which are not so much changed from that of **5**. While the first oxidation potential of the ferrocene moiety in **1** was observed as a nonsplit, quasi-single wave at 0.062 V, the corresponding potential of **2** was observed as a split wave at −0.028 and 0.14 V with $\Delta E = 168$ mV.[19] This split wave has been interpreted as an indication of the effective electronic communication among the appended ferrocene units. Under similar conditions, 5,10,15,20-tetraferrocenylporphyrin[12] and 5,10-diferrocenyl-15,20-diphenylporphyrin[13b] showed split waves both with $\Delta E = 90$ mV. The nonsplit oxidation wave of **1** thus can be interpreted in terms of smaller electronic interaction among the attached ferrocene moieties. A similar nonsplit oxidation wave was also reported for the corresponding 5,10,15,20-tetrakis(4-ferrocenylphenyl)-substituted porphyrin.[20] Therefore, it may be concluded that the electronic communication between *meso*-ferrocene substituents is slightly larger than that of porphyrin. On the basis of these electrochemical data along with the optical data, the driving force values (ΔG_{ET}) for the intramolecular electron transfer from the appended ferrocene to the S_1-state of the subporphyrin have been estimated to be −0.52 and −0.35 eV for **1** and **2**.[21] These large negative driving forces support the belief that the almost complete fluorescence quenching of **1** and **2** arises from efficient intramolecular electron transfer judging from the previous examples.[8,22]

In summary, the ferrocene-appended subporphyrins **1** and **2** were prepared, both of which showed red-shifted absorption spectra and strong fluorescence quenching. Subporphyrin **2**

displayed split first oxidation potential with $\Delta E = 168\,\text{mV}$, indicating effective electronic communication, while subporphyrin **1** exhibited the corresponding nonsplit wave. Further photophysical studies of these molecules are underway.

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$$\Delta G_{ET} = -\Delta E(S_1) + E_{ox} - E_{red} - \frac{1}{4\pi\varepsilon_0} \cdot \frac{e}{\varepsilon_s r}$$

where ε_s is static dielectric constant and r is the center to center distance between subporphyrin and ferrocene (10.11 Å for **1** and 5.89 Å for **2**). E_{ox} and E_{red} were given in Fiugre 3. $\Delta E(S_1)$ was calculated from the peak positions of lowest energy bands to be 2.43 eV for **1** and 2.13 eV for **2**.

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