

Supporting Information

Covalently-Attached Porphycene–Ferrocene Dyads: Synthesis, Redox-Switched Emission, and Observation of the Charge-Separated State

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Experimental Section

Materials. All chemical reagents and solvents used in this study were obtained from commercial sources and used as received unless otherwise stated. Spectroscopic-grade toluene, acetonitrile, and dichloromethane used for UV–vis and emission spectroscopy and transient absorption spectroscopy were purchased from Dojin and Kishida Chemical Co. Ltd, Japan. Anhydrous dichloromethane used for the synthesis of **2** and **3** was obtained by stirring for 24 h in the presence of CaH₂ under an N₂ atmosphere and distilled prior to the synthetic reactions. 9-Hydroxy-2,7,12,17-tetra-*n*-propylporphycene (**1-OH**) was prepared according to the literature method.^{1,2}

Physical Measurements. UV–vis absorption spectra were obtained on a Hitachi U-3310 spectrophotometer. Fourier transform infrared (FT-IR) spectra were recorded with KBr method on a JASCO FT/IR-460 Plus spectrometer. ¹H NMR spectra were obtained on a Bruker AVANCE 500 FT-NMR spectrometer in CDCl₃ using tetramethylsilane as an internal reference. Electrospray ionization time-of-flight mass spectrometry (ESI-TOF-MS) was carried out with a JEOL JMS-T100CS. Elemental analysis was conducted at the Service Center of Elemental Analysis of Organic Compounds at Kyushu University.

Cyclic voltammograms (CVs) were recorded with an ALS 630c instrument (Bioanalytical Systems) using a three-electrode cell consisting of glassy carbon ($\phi = 3.0$ mm), Pt coil, and Ag/AgCl as working,

counter, and reference electrodes, respectively. Dichloromethane and TBAPF₆ (0.1 M) were used as a solvent and a supporting electrolyte, respectively. The preparation of the electrolyte solutions containing the desired compounds (1 mM) and cyclic voltammetry were carried out in an N₂-filled glove box at room temperature. Under the present conditions, the half-wave potential ($E_{1/2}$) of ferrocene/ferricinium (Fc/Fc⁺) couple was obtained at +0.48 V vs. Ag/AgCl.

Spectroelectrochemistry was carried out under the N₂ atmosphere with a Jasco V-670KS spectrophotometer equipped with an ALS 630c instrument. An optically-transparent thin-layer electrode cell (optical path length, 0.5 mm) equipped with Pt mesh, Pt wire, and Ag/AgCl as working, counter, and reference electrodes, respectively, was used. Dichloromethane and TBAPF₆ (0.1 M) were used as a solvent and a supporting electrolyte, respectively. Sample solutions were degassed by N₂ bubbling prior to the measurements.

Fluorescence Measurements. Fluorescence was recorded on a Hitachi FL4500 spectrometer. Steady-state fluorescent spectra for **2** and **3** were measured in CH₂Cl₂ at room temperature. The relative fluorescence quantum yield (Φ_f) values of **2** and **3** were measured using compound **1-OAc** as the standard. To measure Φ_f , degassed solutions of **2** and **3** in toluene were prepared and the concentration was adjusted so that the absorbance of the solution at 370 nm would be between 0.05 and 0.10. The excitation was performed at 370 nm. under the conditions studied, the fluorescent intensity showed a linear relationship with the concentration. The Φ_f values were obtained by eq. 1.

$$\Phi_f = (I / I_0) \cdot \Phi_{f0} \quad (\text{eq. 1})$$

where, I and I_0 stand for fluorescent intensities of the samples and the standard, respectively, and Φ_{f0} stands for the fluorescent quantum yield of the standard obtained by the absolute method.³

Single-Crystal X-Ray Diffraction Study. Single crystals of **3**•CH₂Cl₂ suitable for X-ray diffraction study were obtained from CH₂Cl₂/*n*-hexane at room temperature. Reflection data were collected at 223 K on a Bruker SMART APEX CCD detector with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) and a fine-focus sealed tube generator. The data frames were integrated using SAINT⁴ and merged to give a unique data set for the structure determination. Empirical absorption corrections by SADABS⁵ were carried out. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares methods using the SHELX suite of programs.⁶ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located at calculated positions and included in the structure factor calculation but were not refined. The two inner hydrogen atoms were assumed to ride on the four nitrogen atoms as half occupancy. CCDC-1055937 contains the supplementary crystallographic data of **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; fax (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk or via the http://www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of 2. Compound FcCOOH (176 mg, 0.77 mmol) was placed in a two-necked round-bottom flask (200 mL) with a stir bar and dissolved in anhydrous CH₂Cl₂ (100 mL) under an N₂ atmosphere.

Oxalyl dichloride (10.5 mL) was added to the solution, and the mixture was allowed to stir for 24 h at room temperature. The excess amount of oxalyl dichloride and the solvent were removed under reduced pressure. Compound **1-OH** (19 mg, 0.038 mmol) and 4-(*N,N*-dimethylamino)pyridine (100 mg, 0.82 mmol) were combined to the residue and the mixture was dissolved in anhydrous DMF (20 mL). The purple solution was allowed to stir for 30 min at room temperature. After the excess amount of FcCOCl was quenched by water, the product, **2**, was extracted with CH₂Cl₂. The organic layer was dried over anhydrous Na₂SO₄ overnight. After filtration, the solution was concentrated under reduced pressure. The residue was purified with column chromatography of silica gel with CH₂Cl₂ as an eluent. Yield: 5.9 mg (23%). Anal. Calcd for C₄₃H₄₆FeN₄O₂: C, 73.08; H, 6.56; N, 7.93. Found: C, 72.87; H, 6.59; N, 7.91. ¹H NMR (500 MHz, 298 K, CDCl₃) δ 9.75 (d, 1H, *J* = 11 Hz, *meso*-CH), 9.70 (d, 1H, *J* = 11 Hz, *meso*-CH), 9.58 (s, 1H, *meso*-CH), 9.33 (s, 1H, β-CH), 9.30 (s, 3H, β-CH) 5.40 (t, 2H, *J* = 2 Hz, Fc-CH), 4.75 (t, 2H, *J* = 2 Hz, Fc-CH), 4.70 (s, 5H, Fc-CH), 4.03 (m, 6H, CH₂CH₂CH₃), 3.82 (t, 2H, *J* = 7.5 Hz, CH₂CH₂CH₃), 3.70 (s, 1H, NH), 3.30 (s, 1H, NH), 2.43 (m, 6H, CH₂CH₂CH₃), 2.30 (m, 2H, CH₂CH₂CH₃), 1.35 (m, 9H, CH₂CH₂CH₃), 1.16 (t, 3H, *J* = 7.5 Hz, CH₂CH₂CH₃). UV-vis (CH₂Cl₂, 298 K) λ_{max}/nm (log(ε/M⁻¹ cm⁻¹)) 373 (5.19), 562 (4.48), 603 (4.55), 632 (4.53). ESI-TOF-MS (CH₂Cl₂/CH₃OH) *m/z* 707 ([M + H]⁺). IR (KBr, cm⁻¹) 1729 (C=O).

Synthesis of 3. To an anhydrous CH₂Cl₂ solution (15 mL) of FcCH₂COOH (74 mg, 0.30 mmol) was added oxalyl dichloride (0.5 mL) under N₂ atmosphere, and the solution was allowed to stir for 2 h at room temperature. The excess amount of oxalyl dichloride and the solvent were removed under reduced pressure to give crude FcCH₂COCl which was dissolved in anhydrous DMF (8 mL). The solution was added dropwise to an anhydrous DMF solution (8 mL) containing **1-OH** (10 mg, 0.020 mmol) and 4-(*N,N*-dimethylamino)pyridine (40 mg, 0.32 mmol). The reaction mixture was stirred for 30 min at room temperature. After the excess amount of FcCH₂COCl was quenched by water, compound **3** was extracted with CH₂Cl₂. The organic layer was dried over anhydrous Na₂SO₄ overnight. The product was concentrated under reduced pressure. The residue was purified by size-exclusion chromatography using chloroform as an eluent. The purple band was collected, evaporated, and the residue recrystallized from CH₂Cl₂/*n*-hexane. Yield: 5.0 mg (34%). Anal. Calcd for C₄₄H₄₈FeN₄O₂•CH₂Cl₂: C, 67.09; H, 6.26; N, 6.95. Found: C, 66.79; H, 6.16; N, 7.09. ¹H NMR (500 MHz, 298 K, CDCl₃) δ 9.74 (d, 1H, *J* = 11 Hz, *meso*-CH), 9.69 (d, 1H, *J* = 11 Hz, *meso*-CH), 9.40 (s, 1H, *meso*-CH), 9.31 (s, 1H, β-CH), 9.30 (s, 1H, β-CH), 9.26 (s, 2H, β-CH), 4.65 (t, 2H, *J* = 2 Hz, Fc-CH), 4.38 (s, 5H, Fc-CH), 4.34 (t, 2H, *J* = 2 Hz, Fc-CH), 4.21 (s, 2H, FcCH₂COOPc), 4.00 (m, 4H, CH₂CH₂CH₃), 3.95 (t, 2H, *J* = 7.5 Hz, CH₂CH₂CH₃), 3.84 (t, 2H, *J* = 7.5 Hz, CH₂CH₂CH₃), 3.69 (s, 1H, NH), 3.22 (s, 1H, NH), 2.42 (m, 8H, CH₂CH₂CH₃), 1.35 (m, 12H, CH₂CH₂CH₃). UV-vis (CH₂Cl₂, 298 K) λ_{max}/nm (log(ε/M⁻¹ cm⁻¹)) 372 (5.14), 562 (4.44), 603 (4.49), 632 (4.48). ESI-TOF-MS (CH₂Cl₂/CH₃OH) *m/z* 721 ([M + H]⁺). IR (KBr, cm⁻¹) 1759 (C=O).

Electrochemical Control of Fluorescence Properties. Absorbance of **2** and **3** in CH₂Cl₂ containing 0.1 M TBAPF₆ were adjusted to be 0.1 at 563 nm so that the photoluminescence intensity could be directly compared. Spectroelectrochemistry was performed in an optically transparent cell (optical pass length = 0.5 mm) equipped with a Pt mesh working, a Pt wire counter and an Ag/AgCl reference electrodes.

Femtosecond Transient Absorption Spectroscopy. The femtosecond transient absorption spectra of **3** in THF were measured by the pump and probe method using a regeneratively amplified titanium sapphire laser pumped by a Nd:YLF laser.⁷ The second harmonic oscillation (400 nm, 4 $\mu\text{J pulse}^{-1}$) of the output of the regeneratively amplified titanium sapphire laser was used as the excitation pulse. The excitation pulse at 620 nm was generated by an optical parametric amplifier. Probe and reference lights were directed to a sample cell with 1.0 mm of optical path length and detected with a CCD detector equipped with a polychromator.

References:

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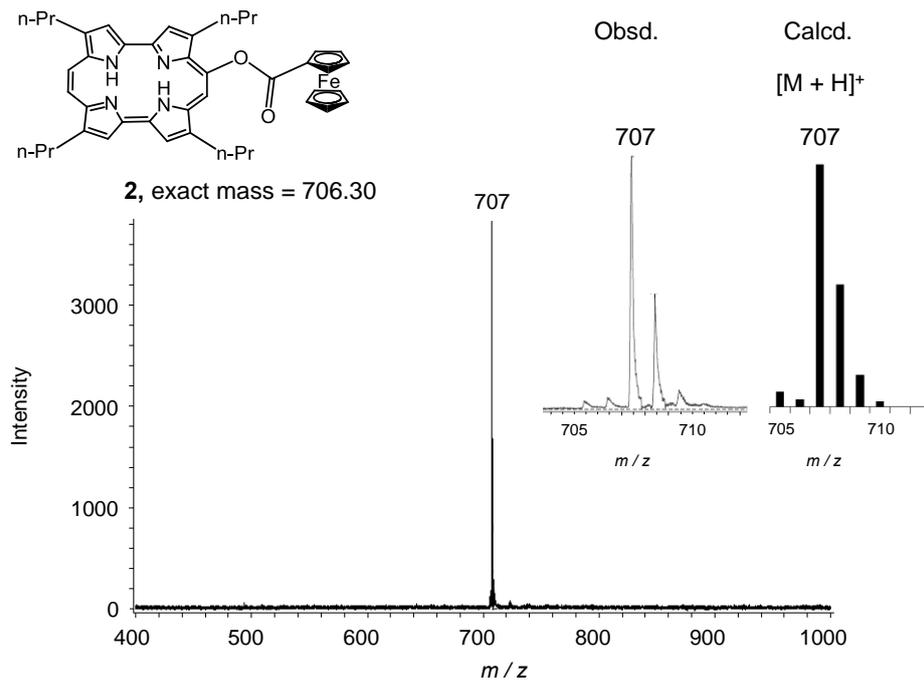


Figure S1. ESI-TOF-MS of **2** ($\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH} = 1:1$, v/v). Inset: observed (left) and calculated (right) isotope patterns ($[M + H]^+$) are also shown.

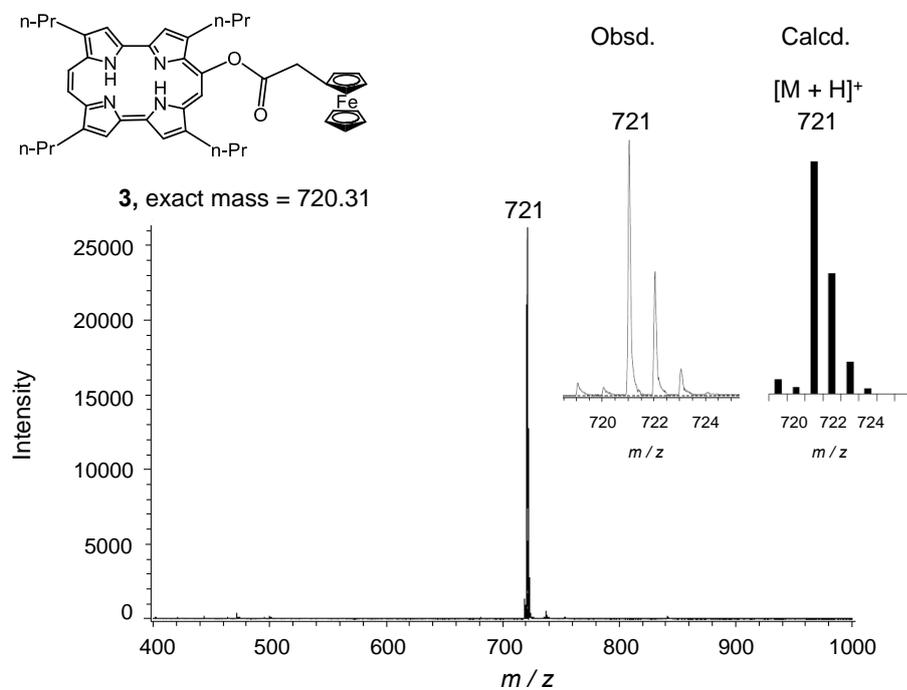


Figure S2. ESI-TOF-MS of **3** ($\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH} = 1:1$, v/v). Inset: observed (left) and calculated (right) isotope patterns ($[M + H]^+$) are also shown.

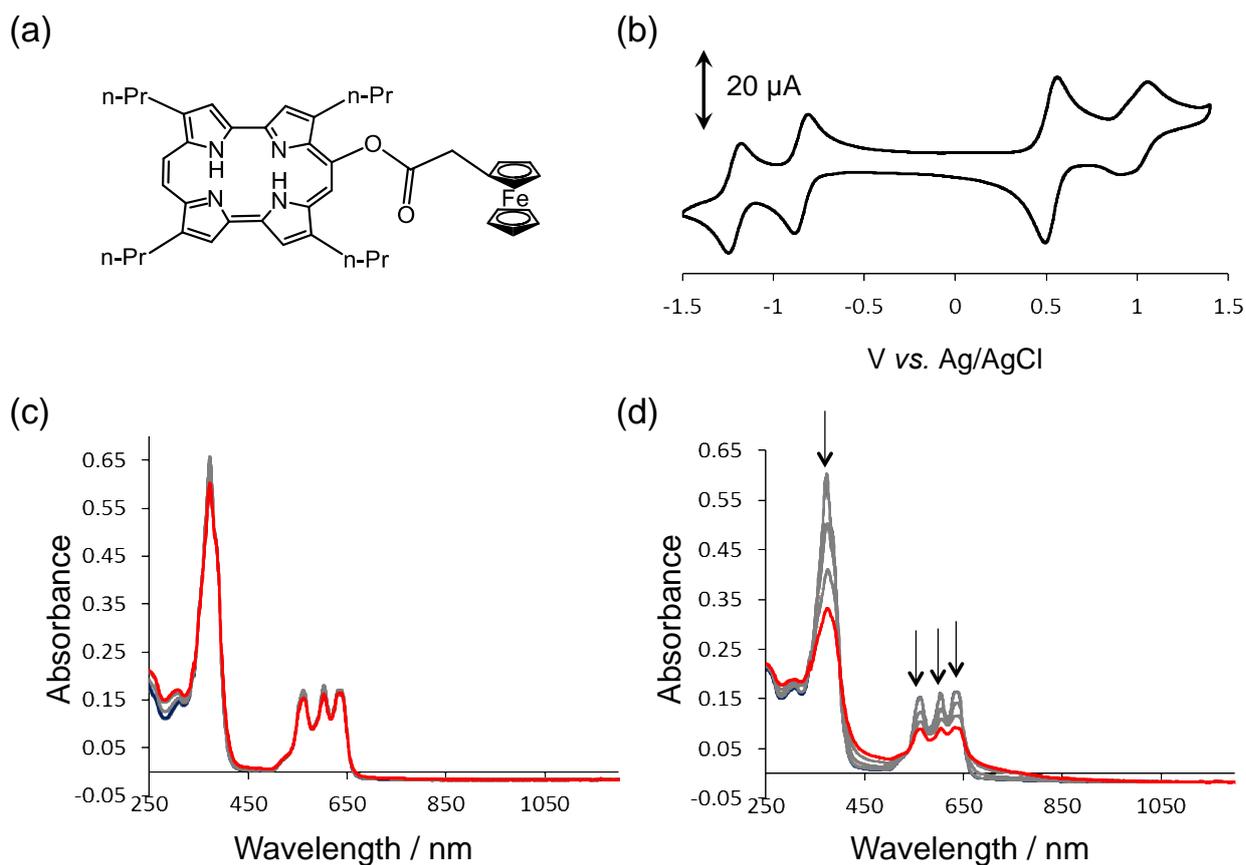


Figure S3. Electrochemistry and spectroelectrochemistry of **3** in 0.1 M *n*-Bu₄NPF₆-CH₂Cl₂ at 25°C. (a) Chemical structure of **3**. (b) Cyclic voltammogram of **3** (1.0 mM). Scan rate = 100 mV s⁻¹. Working electrode = Pt disc (ϕ = 3.0 mm). Counter electrode = Pt coil. Reference electrode = Ag/AgCl. (c) Absorption spectral change during the first oxidation process. Applied potential: +0.40 (gray) to +0.85 V (red). Working electrode = Pt disc. Counter electrode = Pt coil. Reference electrode = Ag/AgCl. (d) Absorption spectral change during the second oxidation process. Applied potential: +0.85 (gray) to +1.20 V (red). The same electrode configuration as (c) is employed. For panels (c) and (d), baseline correction has not been made.