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

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Supporting Information

ABSTRACT: Two new porphycenes functionalized with ferrocenyl pendants have been synthesized and characterized spectroscopically and structurally. The porphycene-based emission in porphycene-ferrocene dyads was switched on and off by the reversible control of the ferrocenyl pendant redox states. Transient absorption spectroscopy with a femtosecond laser-pulsed technique has successfully detected the picosecond charge-separated excited state of the dyad upon Q-band excitation of the porphycene ring.

P orphycene,^{1,2} a constitutional isomer of porphyrin, has a rectangular 18π-electron system of the tetrapyrrolic macrocycle and shows intriguing aspects from basic science to applications, including catalysis,³ hydrogen-atom-transfer dynamics,⁴ coordination chemistry,⁵ photodynamic therapy,⁶ small-molecule binding,⁷ and materials chemistry.⁸ Relative to the porphyrins, the porphycenes show red-shifted Q bands with larger intensity, which is ascribed to the symmetry reduction of the tetrapyrrolic framework. In order to tune the physicochemical properties of the porphycene and to develop porphycene-based advanced functions, the choice of substituents on the periphery of the porphycene ring is crucial. The modification of pyrrole β positions has been extensively studied.^{2,9} In contrast, meso-position modification, in which ethylenic carbon atoms in porphycene are relatively inert for activation, is limited.¹⁰

In this work, we have successfully introduced a redox-active ferrocenyl (Fc) group at the 9 position of 2,7,12,17-tetra-*n*-propylporphycene (H₂TPrPc, **1-OH**) as the first example of porphycene bearing a functional coordination motif at the porphycene periphery through covalent attachment. Among the meso-modified porphycenes, a 9-hydroxy-substituted derivative of **1-OH**,¹¹ which is obtained by reacting 9-acetoxy-2,7,12,17-tetra-*n*-propylporphycene (**1-OAc**)¹² with sodium methoxide in dry tetrahydrofuran (THF),^{11a} is useful as a synthetic precursor for tagging functional pendants selectively at the 9 position of the porphycene ring. In this Communication, two new porphycene–ferrocene dyads, **2** and **3**, are reported with their redox and photoluminescent properties. Electrochemical control of the porphycene-based red emission has been achieved. Also, the

charge-separated (CS) excited state of the dyad has been successfully characterized by femtosecond-pulsed transient absorption spectroscopy. Despite numerous studies on ferrocene-appended porphyrins,¹³ porphycene has been decorated only through axial binding to the metal center.¹⁴

Compounds 2 and 3 were synthesized by reacting 1-OH with ferrocenyl acid chlorides FcC(O)Cl and $FcCH_2C(O)Cl$, respectively, in dry N,N'-dimethylformamide $-CH_2Cl_2$ in the presence of 4-(dimethylamino)phenol. After column chromatography and recrystallization, compounds 2 and 3 were obtained as deep-purple solids in 23 and 34% yield, respectively, and were fully characterized by spectroscopic means and electrospray ionization time-of-flight mass spectrometry.¹⁵

The molecular structure of **3** was determined by single-crystal X-ray diffraction analysis and is shown in Figure 1. The



Figure 1. Molecular structure of $3 \cdot CH_2Cl_2$ at 100 K (50% probability level): (a) top view; (b) side view.

introduction of the Fc pendant to the 9 position of the porphycene ring was unambiguously identified (Figure 1a), and the iron atoms are separated from the center of the porphycene ring by 10.5 Å. The porphycene ring is almost planar (Figure 1b).

Cyclic voltammetry (CV) profiles of **2** and **3**, along with those of reference compounds **1-OAc** and PhOC(O)Fc, in 0.1 M n-

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 Bu_4NPF_6 -CH₂Cl₂ are depicted in Figure 2. Compound 1-OAc underwent two successive reductions ($E_{1/2}$ = -1.22 and -0.86 V



Figure 2. CV profiles (0.1 M *n*-Bu₄NPF₆-CH₂Cl₂; $\nu = 100$ mV s⁻¹) of (a) **1-OAc**, (b) PhOC(O)Fc, (c) **2**, and (d) **3**. Concentration of the compounds = 1.0 mM. Working electrode = glassy carbon. Counter electrode = platinum coil. Reference electrode = Ag/AgCl.

vs Ag/AgCl) and one oxidation ($E_{1/2} = +1.03$ V), all of which are ascribed to porphycene-based processes¹¹ (Figure 2a). The PhOC(O)Fc compound showed (Figure 2b) a one-electron oxidation wave at $E_{1/2} = +0.79$ V. Compound 2 showed a CV profile that is ascribed to two distinct redox centers, Fc and porphycene, with redox potentials almost identical with those of the corresponding monomers (Figure 2c), indicating negligible electronic communication between the two centers in the ground state. For 3 (Figure 2d), the Fc-based wave was significantly shifted to the negative side ($E_{1/2} = +0.55$ V vs +0.81 V for 2) as a result of a decreasing inductive effect of CO upon insertion of a methylene spacer.

UV–vis spectroelectrochemistry (0.1 M n-Bu₄NPF₆– CH₂Cl₂) was studied for 3 to confirm the assignment of the two oxidation processes in CV.¹⁵ In the first oxidation process, only a minimal spectral change was observed because of the occurrence of an oxidation at the Fc site. In the second oxidation process, a substantial spectral change was then observed with clean isosbestic points at 660, 540, 400, and 390 nm to give a spectrum similar to that of a monocationic radical of H₂TPrPc,¹⁶ confirming that the second oxidation takes place at the porphycene ring.

Free-base porphycenes are emissive in red upon UV- and visible-light excitation. As shown in Figure 3, compound 1-OAc is emissive at 645 nm with a shoulder at 700 nm at 298 K. However, the emissions from 2 and 3 are considerably weak, suggesting that the attachment of the Fc pendant is responsible for quenching of the porphycene-based emission in an intramolecular fashion. Observation of the porphycene-based emission of 1-OAc in the presence of 1 equiv of ferrocene ruled out an intermolecular quenching mechanism. Emission quantum yields (toluene, 298 K, $\lambda_{ex} = 370$ nm) were determined to be 2.2 and 1.1% for 2 and 3, respectively, relative to 28% for 1-OAc.

The porphycene-based emission from the dyads was switched on and off by changing the oxidation level of the Fc pendant.¹⁷ Figure 4 shows emission spectral changes of 2 and 3 upon electrochemical oxidation of the Fc pendant to Fc⁺. When the potential was applied at +0.90 V to convert 2 to the cationic radical 2⁺, the initial tiny emission (650 nm) was continuously increased (Figure 4a). The identical behavior was also obtained for 3 (Figure 4b). These observations indicate that the quenching



Figure 3. Emission spectra (CH₂Cl₂, 298 K) of (a) **1-OAc**, (b) **1-OAc** + ferrocene (1:1 mixture), (c) **2**, and (d) **3**. λ_{ex} = 563 nm (absorbance = 0.1). Inset: Pictures showing CH₂Cl₂ solutions of parts a–d upon UV excitation.



Figure 4. Luminescence recovery upon one-electron oxidation of the ferrocenyl pendant for (a) **2** and (b) **3** in CH₂Cl₂ containing *n*-Bu₄NPF₆ (0.1 M). Top: Luminescence spectra. $\lambda_{ex} = 563$ nm. Bottom: CV profiles and electrode potentials applied. Optical path length = 0.5 mm. Working electrode = platinum mesh. Counter electrode = platinum rod. Reference electrode = Ag/AgCl. *T* = 298 K.

ability of the neutral Fc pendant is reduced when it is oxidized to Fc^+ . The on/off behavior in emission was reversible. For neutral dyads, Fc behaves as an efficient electron donor to the Fc-localized excited state, allowing quenching of the porphycene-localized emission to be observed. In contrast, the cationic Fc⁺ pendant prepared electrochemically is no more efficient as an electron donor, thereby allowing the intensity of the porphycene-based emission to be increased.

Femtosecond-pulsed transient absorption spectroscopy was successfully used to study the excited-state property of 3.¹⁴ Transient absorption spectra of 3 in THF with excitation at 620 nm (4 μ J pulse⁻¹) are presented in Figure 5a. After excitation of 0.4 ps, a broad absorption band was observed in the near-IR region (850–950 nm), which was assigned to the formation of a singlet excited state of the porphycene ring.¹⁴ This absorption band subsequently decayed continuously until 20.4 ps to give a distinct spectrum with new peaks at 850 and 750 nm due to the porphycene radical anion,¹⁸ which suggested the formation of a CS state as a result of intramolecular electron transfer from Fc to porphycene in the excited state. An absorption band of Fc⁺ (~800 nm), however, was not detected because of its comparatively smaller intensity ($\varepsilon \sim 10^3$ M⁻¹ cm⁻¹).¹⁹ Curve



Figure 5. (a) Transient absorption spectra of 3 in THF (298 K) upon laser flash photolysis with a 620 nm femtosecond pulse for excitation. (b) Curve fitting of the time course of Δ OD at 750 nm.

fitting of the observed profiles for the rise and decay of the peak intensity at 750 nm gave rate constants of $1.0 \times 10^{11} \text{ s}^{-1}$ for evolution and $2.2 \times 10^{10} \text{ s}^{-1}$ for decay of the porphycene radical anion.

In conclusion, we have synthesized and characterized two new covalently linked porphycene–ferrocene dyads, which are the first examples of free-base porphycenes tagging transition-metal coordination groups at the periphery of the porphycene ring. In $\rm CH_2Cl_2$, the porphycene-based emission from the dyads was switched on and off by the reversible control of the ferrocenyl pendant redox states. The result described herein can be extended to the fabrication of new porphycene-based advanced materials such as redox-triggered luminescent probes and molecular switches.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.5b02078.

Experimental details (PDF) X-ray crystallographic data of **3** in CIF format (CIF)

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Notes

The authors declare no competing financial interest.

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