

Metal-Assisted Formation of an Extremely Long-Lived Charge-Separated State in a Porphyrin–Flavin Dyad

Takahiko Kojima,¹ Ryosuke Kobayashi,¹ Tomoya Ishizuka,¹ Shinya Yamakawa,¹ Hiroaki Kotani,¹ Tatsuaki Nakanishi,² Kei Ohkubo,² and Shunichi Fukuzumi^{2,3}

¹Department of Chemistry, University of Tsukuba, 1-1-1 Tennoudai, Tsukuba, Ibaraki 305-8571, ²Department of Material and Life Science, Osaka University, and ALCA, JST, Suita, Osaka 565-0871, Japan, ³Department of Bioinspired Science, Ewha Womans University, Seoul 120-750, Korea.

A long-lived charge-separated (CS) state formed by photoinduced electron transfer (ET) is indispensable to convert absorbed light energy into other energies as observed in photosynthesis, solar cells, photocatalysts for material production.¹ Porphyrins have been linked to various kinds of electron acceptors including fullerenes and quinones to provide donor-acceptor dyads forming CS states upon photo-excitation.^{1,2} Recently, oxidized forms of flavin derivatives have been demonstrated to act as electron acceptors in photoinduced ET to afford long-lived CS states due to their small reorganization energy (λ) in ET reactions.³ Herein, we synthesized a porphyrin–flavin-linked dyad and its zinc and palladium complexes (MPor–Fl, **1-M**, M = 2H, Zn, Pd; Figure 1) and investigated their photodynamics of intramolecular photoinduced ET to form long-lived CS states.

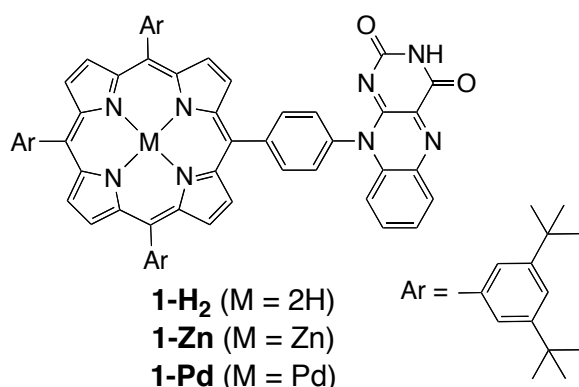


Figure 1. Structures of porphyrin-flavin dyads.

The pigments of **1-M** were bridged by a phenyl ring at the *para* position of one of the *meso*-phenyl groups of the porphyrin and at the 10-*N* position of the flavin framework. A target free-base porphyrin–flavin linked dyad, **1-H₂**, and the palladium complex, **1-Pd**, were prepared from the corresponding *p*-nitrophenylporphyrin derivatives *via* a four-step synthesis that are general synthetic route for flavin derivatives. The Zn(II) insertion was made straightforward by the reaction of **1-H₂** with Zn(OAc)₂ in a CH₂Cl₂/CH₃OH mixed solvent to give **1-Zn**. Spectroscopic measurements and theoretical calculations suggested that the HOMO and the LUMO resided on the porphyrin and the flavin moieties, respectively, and there was no interaction between them at the ground state. In addition, UV-Vis and CV titrations on **1-Pd** with Sc(OTf)₃ demonstrated that **1-Pd** could accept two Sc³⁺ ions at the flavin moiety with binding constants of $K_1 = 1.0 \times 10^5 \text{ M}^{-1}$ and $K_2 = 1.8 \times 10^3 \text{ M}^{-1}$, respectively (Figure 2). The binding of Sc(OTf)₃ to a flavin has been reported previously.⁴

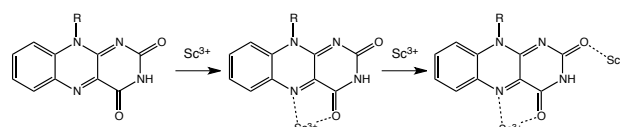


Figure 2. Plausible binding manners of Sc³⁺ ions to the flavin skeleton.

Femtosecond laser flash photolysis clarified that **1-M** underwent four photodynamic pathways by changing the metal center of the porphyrin moiety and a binding Sc³⁺ ion. In **1-H₂**, photoinduced ET reaction occurred to produce the CS state (H₂Por^{•+}–Fl^{•–}) and back ET to form ³[H₂Por]^{•+}–Fl with the rate constants of $1.2 \times 10^{10} \text{ s}^{-1}$ and $1.2 \times 10^9 \text{ s}^{-1}$, respectively. **1-Zn** experienced photoinduced ET to afford the CS state and back ET to give the ground state with the rate constants of 1.6×10^{11} and $6.5 \times 10^{10} \text{ s}^{-1}$, respectively. As for **1-Pd**, photoinduced ET reaction occurred to form a CS state, PdPor^{•+}–Fl^{•–}, showing the lifetime of 20 ps in PhCN. In the Sc(OTf)₃-containing PhCN solution of **1-Pd**, photoexcitation of the Sc³⁺-bound complex, **1-Pd**·Sc³⁺, allowed us to observe photoinduced ET in a triplet excited state of the complex, ³[PdPor]^{•+}–Fl·Sc³⁺, to form a triplet CS state (³[PdPor^{•+}–Fl^{•–}·2Sc³⁺]) exhibiting a remarkably long lifetime of $\tau = 110 \text{ ms}$ ($k_{\text{BET}} = 9.1 \text{ s}^{-1}$). This remarkable elongation of the lifetime for the CS state may result from the triplet spin-multiplicity of the CS state and the second Sc³⁺-binding to the Fl^{•–} moiety in the CS state. As results of the second Sc³⁺ ion binding, the CS state may be more stabilized and thus the rate constant of the charge-recombination (CR) reaction should decrease by the effect of decrease in the driving force. Moreover, since the Sc³⁺-binding at the CS state significantly increases the reorganization energy (λ) of the CR process, the CR process can be significantly retarded.

In conclusion, we have prepared novel porphyrin-flavin dyads and have succeeded in the control of the energy levels of the CS states and the triplet excited states of the dyads by insertion of a metal center to the porphyrin moiety or addition of a strong Lewis acid bound to the flavin moiety. This manipulation allowed us to observe extremely long-lived CS state as can be seen at the reaction center in PS II. The photochemical and reductive activation of flavin coenzymes in dyads should be useful for the development of photofunctional molecules as electron mediators in electron-transfer cascades to utilize electron(s) delivered from electron donors.

Reference

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