A supramolecular photosynthetic triad of slipped cofacial porphyrin dimer, ferrocene, and fullerene†

**Hiromichi Nakagawa, Kazuya Ogawa, Akiharu Satake and Yoshiaki Kobuke***

A supramolecular triad consisting of self-assembled imidazolyl–zinc–porphyrin dimer, ferrocene, and fullerene was successfully constructed, resulting in long-lived charge separated species after efficient photoinduced electron transfer and charge shift reactions.

In relation to the photoinduced multistep electron transfer (ET) in natural photosynthetic reaction centers (RC), many models have been synthesized to help understand the natural system and as a means of developing the solar energy conversion systems.[1–3] In these studies, interest has been focused on extending the lifetime of the charge-separated state to facilitate the succeeding multistep ET reactions. Gust[2] and Imahori[3] have independently developed initial charge separation (CS) models by combining the central porphyrin unit with carotene and ferrocene (Fc) as donors, and fullerene (C_{60}) as an acceptor. In these studies, the excellent features of C_{60} were crucial for obtaining the long-lived CS state with high quantum yields. The small reorganization energy of C_{60} contributed to accelerating the forward ET while decelerating the back ET at the same time. In addition, the charges are separated over a long distance as a result of multistep ET. The combined effects make the system favourable for the generation of the long-lived CS state.

The difficulty exists in the synthesis of complex molecular systems performing the multistep ET by using two or more chromophores. Incorporation of a special pair into these ET systems accompanies an inherent difficulty. During the study of photosynthetic mimicry, we have developed a slipped cofacial imidazolyl–zinc–porphyrin dimer [$(ZnP)_2$] as a special pair mimic.[4] The dimer is exceptionally stable with a stability constant of more than 10^{11} M^{-1}, and dissociated, on the other hand, into the respective monomer units by the addition of coordinating solvents, and thus facilitates structural reorganization simply by evaporating the solvent. Therefore, the self-assembled porphyrin dimer has been a source of facile syntheses of complicated porphyrin systems such as one-dimensional porphyrin arrays,[5] and macrocyclic porphyrin arrays.[6] If two kinds of imidazolyl–zinc–porphyrin are used as unit components, a heterodimeric porphyrin system is obtained under coordination equilibrium conditions. In this communication, we report the supramolecular synthesis of a triad system consisting of a slipped cofacial zinc–porphyrin dimer, Fc as

an electron donor and C_{60} as an electron acceptor, and its photophysical measurements.

Scheme 1 shows the synthetic strategy of the target compound of Fc–$(ZnP)_2$–C_{60} triad **3** and the structure of reference
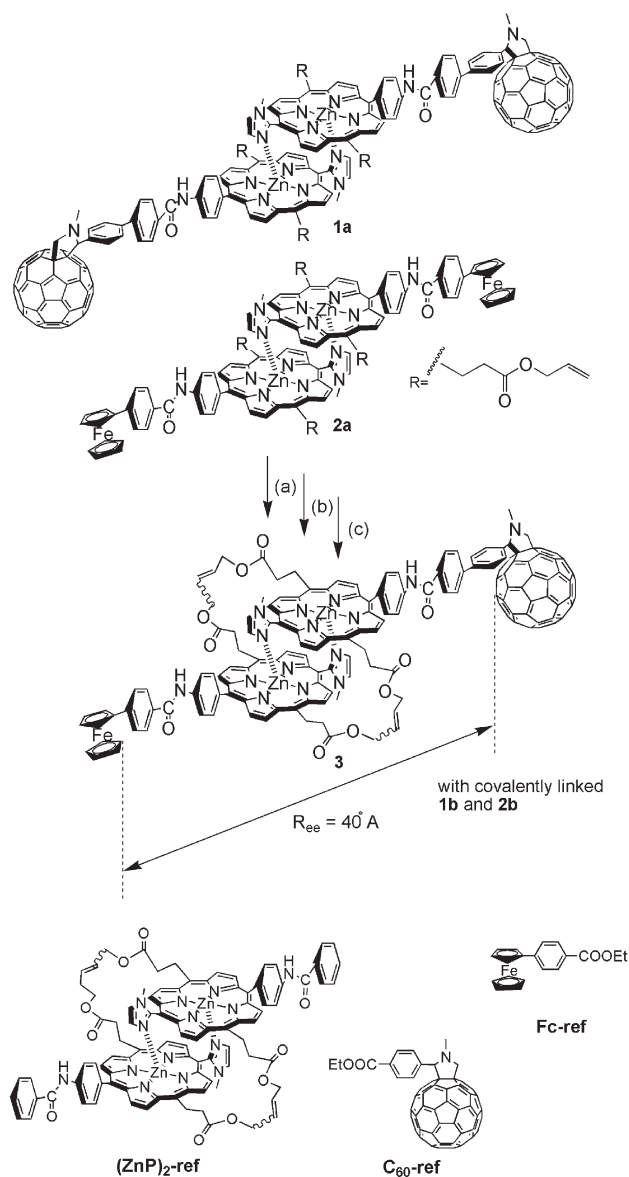

Scheme 1 Construction of ferrocene-slipped cofacial porphyrin dimer–fullerene triad **3** by using supramolecular methodology and the structure of the reference compounds used in this study. (a) Reorganization process. (b) Ring-closing metathesis reaction. (c) GPC separation.

School of Materials Science, Nara Institute of Science and Technology, 8916-5 Takayama-cho, Ikoma, Nara, 630-0101, Japan.
E-mail: kobuke@ms.naist.jp
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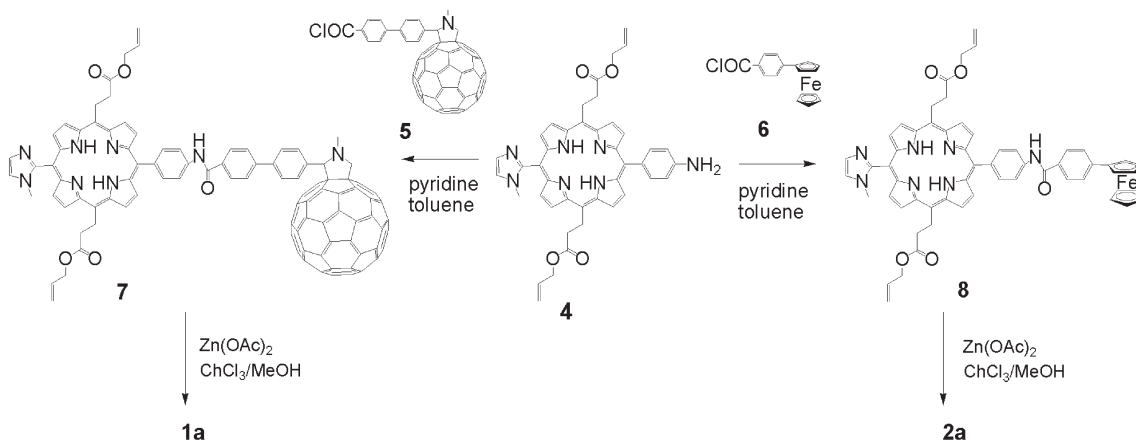
Scheme 2 Syntheses of C_{60}–$(ZnP)_2$–C_{60} **1a** and Fc–$(ZnP)_2$–Fc **2a** from 4-aminophenylporphyrin **4**.

compounds used in this study. To obtain the triad system incorporating the special pair, we employed Fc- and C_{60}-linked imidazolyl–zinc–porphyrin as the building blocks. Thus, two porphyrin dimers **1a** and **2a** were prepared. Both porphyrins are appended with *meso*-allyloxycarbonylethyl substituents to fix covalently the dimeric structure after complementary coordination.[7] Biphenylamidophenyl and phenylamidophenyl groups were used as the spacer between dimer and C_{60}, and dimer and Fc, respectively, to separate the ion pair over a long distance of 40 Å. Free base porphyrin **7** was prepared from 4-aminophenyl-porphyrin **4** and C_{60}-biphenyl acid chloride **5** (Scheme 2), which was synthesized by 1,3-dipolar cycloaddition[8] of C_{60}, *N*-methylglycine and 4-formyl-4′-biphenylcarboxylic acid in toluene followed by chlorination with $SOCl_2$. Dimer **1a** was obtained spontaneously on inserting Zn(II) into a free base **7**. Ferrocene–zinc–porphyrin dimer **2a** was prepared by a similar way to **1a** from 4-carboxyphenylferrocene and **4** in 50% yield (two steps). Triad **3** was prepared finally by the reorganization procedure, namely equivalent amounts of **1a** and **2a** were dissolved in pyridine to dissociate into the respective monomeric species, and then the solvent was evaporated to reorganize in a mixture of heterodimer Fc–$(ZnP)_2$–C_{60}, along with homodimers **1a** and **2a**. These three complementary dimer pairs were covalently fixed by ring-closing metathesis reaction (RCM) between the facing *meso*-allyl substituents.[7] Fig. 1 shows an analytical GPC chart of the mixture after the metathesis reaction. Three peaks corresponding to **2b**, **3**, and **1b** are observed. Since the eluted order does not agree
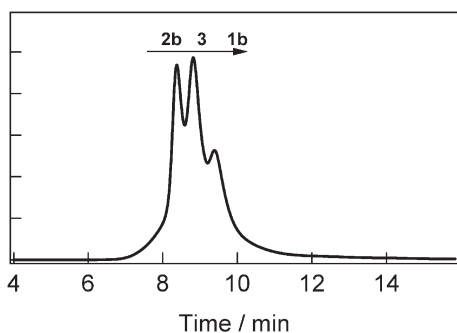
with the order of their molecular weights, some interactions between C_{60} and polystyrene gel are suggested. The desired heterodimer **3** was isolated by recycling preparative GPC along with covalently linked homodimers **1b** and **2b** in 40, 22 and 21% yields, respectively. Because the yields agreed with those expected statistically, the reorganization proceeded randomly between Fc- and C_{60}-porphyrins. All these products were characterized by ^{1}H NMR, MALDI-TOF mass, UV visible absorption, and fluorescence spectra.

The UV visible absorption spectrum of **3** in benzonitrile was a superposition of the spectra of the components, **$(ZnP)_2$-ref**, **C_{60}-ref** and **Fc-ref**, indicating no significant electronic interaction among the three chromophores in the ground state (Fig. 2a). The Soret band of the porphyrin moiety split into two bands due to strong exciton interaction between the two porphyrins brought into the
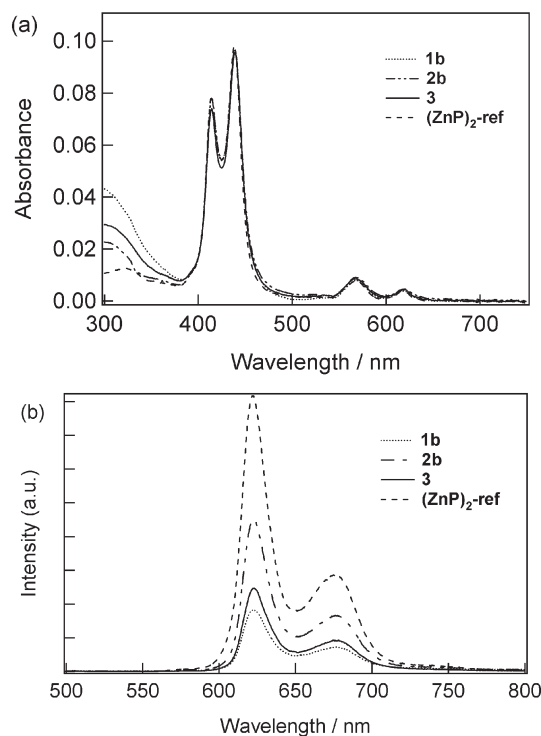

Fig. 1 An analytical GPC chart of reaction mixture after the ring-closing metathesis reaction. Inset: purified **3**.

Fig. 2 Steady-state (a) absorption and (b) fluorescence spectra of **1b**, **2b**, **3**, and **$(ZnP)_2$-ref** in benzonitrile, $\lambda_{EX} = 439$ nm.

complementary coordination of imidazolyl to zinc.[4] The UV visible absorption spectra of **1b** and **2b** were also superpositions of the spectra of the components, **(ZnP)$_2$-ref**, **C$_{60}$-ref** and **Fc-ref**, respectively. The steady-state fluorescence of **1b**, **2b**, and **3** was compared to **(ZnP)$_2$-ref** used as a reference. The relative fluorescence intensities decrease to 0.3 for **3**, 0.22 for **1b**, and 0.55 for **2b** as shown in Fig. 2b. The fluorescence lifetime of **3** measured in benzonitrile at 624 nm was 430 ps, which was much shorter than that of **(ZnP)$_2$-ref** (τ = 2000 ps), suggesting efficient photoinduced ET or energy transfer from the excited singlet state. The fluorescence lifetimes of **1b** and **2b** were 270 ps and 1200 ps, respectively. Thus, the additional quenching rate by introducing two C$_{60}$'s and ferrocenes is obtained as 3.2×10^9 s^{-1} ($1/\tau_{\mathbf{1b}}-1/\tau_{\mathbf{(ZnP)2\text{-}ref}}$) for **1b** and 3.3×10^8 s^{-1} ($1/\tau_{\mathbf{2b}}-1/\tau_{\mathbf{(ZnP)2\text{-}ref}}$) for **2b**, indicating that C$_{60}$ quenches the excited singlet energy approximately 10 times faster than ferrocene. In the singlet excited energy quenching of **3**, therefore, contribution of the fullerene part is more dominant than that of the ferrocene part. It is noted that **1b** has two fullerenes and the additional quenching rate must be estimated almost double as compared with that of **3** (1.8×10^9 s^{-1} ($1/\tau_{\mathbf{3}}-1/\tau_{\mathbf{(ZnP)2\text{-}ref}}$). The above kinetics suggest that the first photophysical process in heterodimer **3** after photoexcitation will be charge separation from ^{1}(ZnP)$_2^*$ to C$_{60}$ to generate the first CS state of Fc–(ZnP)$_2^{\cdot+}$–C$_{60}^{\cdot-}$ followed by the second process of charge shift by the ET from Fc to (ZnP)$_2^{\cdot+}$ to form the final CS state of Fc$^+$–(ZnP)$_2$–C$_{60}^{\cdot-}$. The time-resolved transient absorption measurements now in progress will finally identify the multistep ET processes of **3**. A long-lived CS state over 100 μs was observed and the details will be reported soon with complete analyses of various steps.

We successfully synthesized imidazolyl–zinc–porphyrin heterodimer **3** having Fc and C$_{60}$ from the corresponding homodimers through a simple reorganization process followed by covalent fixation *via* the ring-closing metathesis reaction. The efficient and multistep electron transfer was suggested for **3** from steady-state and time-resolved fluorescence measurements.

Notes and references

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