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Long-Lived Charge-Separated State Produced by Photoinduced Electron Transfer in a Zinc Imidazoporphyrin-C_{60} Dyad

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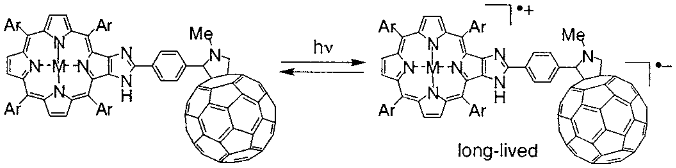
ABSTRACT



Photoexcitation of a zinc imidazoporphyrin-fullerene dyad with a short linkage results in formation of the charge-separated state by photoinduced electron transfer. The charge-separated state has a lifetime of 310 μs in benzonitrile at 278 K, which is the longest lifetime in solution ever reported for electron donor–acceptor-linked dyads.

As porphyrins and fullerenes have rich redox properties in both the ground and excited states, porphyrin-fullerene dyads linked with an appropriate spacer have been frequently utilized as important components for the design of novel artificial photosynthetic systems.[1−3] In porphyrin-fullerene dyads, only a small reorganization energy is required for the electron-transfer reactions due to the minimal change in the structure and solvation upon electron transfer.[2] According to the Marcus theory of electron transfer,[4] the smaller the reorganization energy, the faster the forward photoinduced electron transfer, but the back electron transfer becomes slower when the driving force for back electron transfer is larger than the reorganization energy of electron transfer. The lifetimes of charge-separated (CS) states are highly

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(1) (a) Gust, D.; Moore, T. A. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, CA, 2000; Vol. 8, pp 153−190. (b) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **2001**, *34*, 40.

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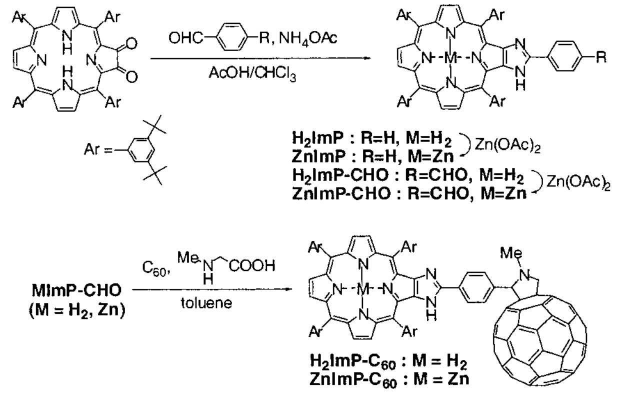
Scheme 1



sensitive to the energy of the CS state, the type of linkage between the donor and acceptor molecules, and also the solvent. Extensive efforts have been made to achieve a long-lived CS state by tuning these factors. The longest lifetime of the CS state in a donor−acceptor-linked dyad reported so far in solution is 110 μs for a zinc chlorin-C_{60} dyad at 298 K.[5]

We report herein that a zinc imidazoporphyrin-C_{60} dyad (ZnImP−C_{60}) with a short linkage has the longest lifetime of the CS state ever reported for donor−acceptor-linked dyads in solution. The decay mechanism of the CS state was elucidated by examining the photodynamics of ZnImP−C_{60} with the use of picosecond and nanosecond laser flash photolysis.

ZnImP−C_{60} was synthesized as shown in Scheme 1. The 2-aryl-1*H*-imidazo[4,5-*b*]porphyrins, H_2ImP and H_2ImP−CHO, were prepared in good yield by the condensation of porphyrin-2,3-dione with the corresponding arylaldehyde in the presence of excess NH_4OAc in a refluxing 1:1 mixture of AcOH−$CHCl_3$ for 2 h.[6] Treatment of H_2ImP and H_2ImP−CHO with zinc acetate gave ZnImP and ZnImP−CHO, respectively. H_2ImP−CHO and ZnImP−CHO were then converted to the dyads, H_2ImP−C_{60} and ZnImP−C_{60}, by treatment with C_{60} and *N*-methylglycine in 75 and 46% yields, respectively. The ^{1}H NMR spectra of the dyads revealed the presence of only a single species in solution.[7]

The absorption spectrum of ZnImP−C_{60} in benzonitrile (PhCN) is a reasonable superposition of the spectra of the component chromophores making up the molecule. Thus, there is no significant electronic interaction between the individual chromophores in their ground-state configuration. The cyclic voltammogram of ZnImP−C_{60} in deaerated PhCN containing 0.10 M Bu_4NPF_6 at 298 K consists of two one-electron reduction processes of C_{60} in the dyad (−0.58 and −0.98 V vs SCE), a one-electron reduction process of ZnImP (−1.38 V), and a single one-electron oxidation process of ZnImP (0.76 V). These redox potentials are virtually the same as those of the reference compounds (Table 1). This also indicates that there is no significant interaction between the ZnImP and C_{60} units in the dyads.

Table 1. One-Electron Redox Potentials and Energy Levels of the CS State in PhCN

compound	E^0 vs SCE, V ImP/ImP$^{\bullet+}$	$C_{60}/C_{60}^{\bullet-}$	energy level of CS state, eV
ZnImP−C_{60}	0.76	−0.58	1.34
ZnImP	0.76		
H_2ImP−C_{60}	0.97	−0.57	1.54
H_2ImP	0.98		

Table 2. Fluorescence Lifetimes and Rate Constants of Photoinduced Electron Transfer, Back Electron Transfer, and Triplet Decay in ZnImP−C_{60} and H_2ImP−C_{60} in PhCN at 298 K

compound	fluorescence lifetime, ns	k_{ET}, s^{-1}	k_{BET}, s^{-1}	k_T, s^{-1}
ZnImP−C_{60}	0.059	1.6×10^{10}	3.9×10^3	
ZnImP	2.0			1.1×10^3
H_2ImP−C_{60}	0.21	4.7×10^9		6.0×10^3
H_2ImP	10.0			2.4×10^3

The photoexcitation of a deaerated PhCN solution containing ZnImP−C_{60} with 434 nm monochromatized light results in fluorescence with the emission maximum at 606 nm. The emission intensity is much smaller than that of the reference compound ZnImP. This indicates that the singlet excited state of ZnImP is quenched efficiently by C_{60}. The fluorescence decay was monitored at 615 nm relating to the emission of the ZnImP unit (Table 2).[8] The fluorescence lifetime of the unlinked ZnImP (τ = 2.0 ns) was significantly reduced in the ZnImP−C_{60} dyad (τ = 59 ps) due to electron transfer from the singlet excited state of ZnImP (^{1}ZnImP*) to C_{60}. The rate constant of electron transfer (k_{ET}) from ^{1}ZnImP* to C_{60} was determined from the difference between reciprocal lifetimes of ZnImP−C_{60} and unlinked ZnImP to be 1.6×10^{10} s^{-1}. Similarly, the k_{ET} value of H_2ImP−C_{60} was determined to be 4.7×10^9 s^{-1}. The free energy change of photoinduced electron transfer (ΔG^0_{ET}) from the ^{1}ZnImP*

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(7) ZnImP−C_{60} was obtained in 46% yield (21 mg): UV−vis (PhCN, nm (ϵ, M^{-1} cm^{-1})) 434 (2.9×10^6), 557 (1.6×10^4), 598 (9.8×10^3); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.07−8.98 (m, 6H), 8.49 (s, 1H), 8.14 (t, *J* = 1.8 Hz, 1H), 8.12−8.09 (m, 6H), 8.06 (t, *J* = 1.8 Hz, 1H), 8.01 (t, *J* = 1.8 Hz, 1H), 7.84 (t, *J* = 1.8 Hz, 1H), 7.79−7.77 (m, 6H), 4.85 (s, 1H), 4.78 (d, *J* = 7.9 Hz, 1H), 4.07 (d, *J* = 7.9 Hz, 1H), 2.80 (s, 3H), 1.52−1.45 (m, 72H); MALDI-TOF MS *m/z* 2018 (M^+). H_2ImP−C_{60} was obtained in 75% (37 mg) yield: UV−vis (PhCN, nm (ϵ, M^{-1} cm^{-1})) 425 (2.1×10^6), 521 (1.6×10^4), 555 (8.2×10^3), 590 (6.0×10^3), 650 (2.9×10^3); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.01−8.94 (m, 4H), 8.86−8.82 (m, 2H), 8.31 (s, 1H), 8.15−8.08 (m, 7H), 8.06 (t, *J* = 1.8 Hz, 1H), 8.02 (t, *J* = 1.8 Hz, 1H), 7.83 (t, *J* = 1.8 Hz, 1H), 7.80−7.74 (m, 6H), 4.89 (s, 1H), 4.87 (d, *J* = 9.8 Hz, 1H), 4.16 (d, *J* = 9.8 Hz, 1H), 2.82 (s, 3H), 1.56−1.45 (m, 72H), −2.81 (s, 2H); MALDI-TOF MS *m/z* 1955 (M+).

(8) Time-resolved fluorescence spectra were measured by a single-photon counting method using a second harmonic generation (SHG, 400 nm) of a Ti:sapphire laser as an excitation source.

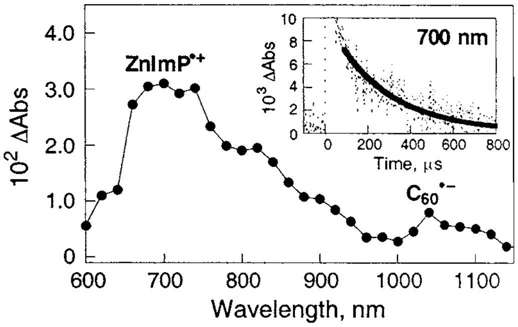


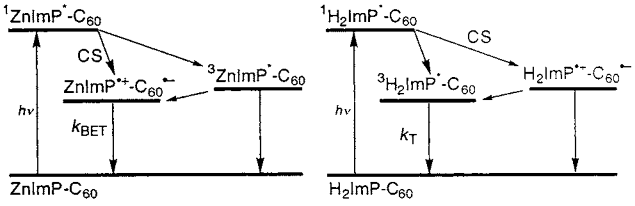
Figure 1. Transient absorption spectrum of ZnImP−C_{60} (1.0 × 10^{-5} M) in deaerated PhCN at 298 K taken 1.0 μs after laser excitation at 532 nm. Inset: Time profile at 700 nm.

unit to the C_{60} unit in PhCN was determined to be −0.72 eV from the one-electron oxidation potential and the excitation energy (S_1 = 2.06 eV) of the ZnImP unit and the one-electron reduction potential of the C_{60} unit in ZnImP−C_{60}.

The occurrence of photoinduced electron transfer was confirmed by picosecond transient absorption spectra.[9] A deaerated PhCN solution containing ZnImP−C_{60} gave rise upon a 560 nm laser pulse to a transient absorption maximum at 470 nm due to the ^{1}ZnImP*. The decay rate constant was determined to be 1.4×10^{10} s^{-1}, which agrees with the value determined from the fluorescence lifetime measurements. The decay of absorbance at 470 nm due to ^{1}ZnImP* is accompanied by an increase in the absorbances between 650 and 900 nm due to $ZnImP^{\bullet+}$. This indicates that electron transfer from ^{1}ZnImP* to C_{60} occurs to form the CS state, $ZnImP^{\bullet+}$−$C_{60}^{\bullet-}$.[10]

The CS state was also detected as the transient absorption spectrum obtained upon nanosecond laser pulse excitation (532 nm) of a deaerated PhCN solution of ZnImP−C_{60} as shown in Figure 1.[11] The absorption band at 1040 nm is a clear attribute of the monofunctionalized fullerene radical anion.[12] The absorption bands in the 600−1000 nm region in Figure 1 agree with those of ZnImP π-radical cation produced by the electrochemical oxidation of ZnImP at an applied potential of 0.94 V (vs SCE); see Supporting Information S1. Thus, the transient absorption spectrum in Figure 1 indicates formation of the CS state ($ZnImP^{\bullet+}$−$C_{60}^{\bullet-}$). The CS state (1.34 eV) is lower in energy than the triplet excited state of both C_{60} (1.50 eV)[12] and ZnImP (1.36 eV)[13] as shown in Scheme 2.

Scheme 2



In contrast to the case of ZnImP−C_{60}, no CS state was detected by the nanosecond transient absorption measurements of H_2ImP−C_{60} in PhCN. Only the triplet−triplet absorption spectrum due to $^3H_2$ImP*−C_{60} was detected because the CS state is higher in energy than the triplet excited state of H_2ImP (1.37 eV),[13] as shown in Scheme 2. The triplet decay rate constant (k_T) is listed in Table 2 together with those of reference compounds.

The CS state detected in Figure 1 decays by back electron transfer (BET) to the ground state, obeying first-order kinetics (inset of Figure 1). Disappearance of absorption bands at 700 and 1040 nm due to $ZnImP^{\bullet+}$ and $C_{60}^{\bullet-}$ in the CS state afforded the same BET rate constant (k_{BET}); see S2. The k_{BET} value was determined to be 3.9×10^3 s^{-1} (the lifetime is 260 μs) at 298 K (Table 1). At 278 K, the lifetime of the CS state was determined to be 310 μs. This is the longest lifetime in solution ever reported for intramolecular charge recombination in donor−acceptor dyad systems involving one-step electron transfer.[1−3,14] The energy of the CS state, the type of linkage of the dyad, and also the solvent are certainly better optimized as compared with previously reported dyad systems to achieve such a long lifetime of the CS state.

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Supporting Information Available: Spectra of $ZnImP^{\bullet+}$ produced by electrochemical oxidation of ZnImP (S1) and time profiles of transient absorptions at 700 and 1000 nm (S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Picosecond laser flash photolysis experiments were carried out with 560 nm laser pulses from a vis-OPO (Clark-MXR) apparatus pumped by an Er-doped fiber laser (Clark-MXR CPA-2001 plus, 1 kHz, 150 fs).

(10) Photoexcitation of C_{60} is negligible as compared with that of ZnImP. The exciplex may also be formed, leading to the CS state. See: Kesti, T. J.; Tkachenko, N. V.; Vehmanen, V.; Yamada, H.; Imahori, H.; Fukuzumi, S.; Lemmetyinen, H. *J. Am. Chem. Soc.* **2002**, *124*, 8067.

(11) Nanosecond transient absorption measurements were carried out using a Nd:YAG laser at 532 nm with the power of 30 mJ as an excitation source.

(12) Guldi, D. M.; Kamat, P. V. In *Fullerenes, Chemistry, Physics, and Technology*; Kadish, K. M., Ruoff, R. S., Eds.; Wiley-Interscience: New York, 2000, pp 225−281.

(13) Triplet excitation energies were determined by the phosphorescence spectrum of ZnImP and H_2ImP in 2-methyltetrahydrofuran at 77 K.

(14) For a tetrad system involving multistep electron transfer, a lifetime of 380 ms has been achieved. See: Imahori, H.; Guldi, D. M.; Tamaki, K.; Yoshida, Y.; Luo, C.; Sakata, Y.; Fukuzumi, S. *J. Am. Chem. Soc.* **2001**, *123*, 6617.