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Metal-Centered Photoinduced Electron Transfer Reduction of a Gold(III) Porphyrin Cation Linked with a Zinc Porphyrin to Produce a Long-Lived Charge-Separated State in Nonpolar Solvents

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One of the most fundamental steps in photosynthesis and light-to-chemical energy conversion is photoinduced charge separation in the photosynthetic reaction center.¹ Toward this end, a number of electron donor–acceptor (D–A) linked systems have been designed and the photodynamics has been examined to mimic photosynthetic charge separation.^{2–9} Photoinduced electron-transfer reactions of D–A have been examined mostly in polar solvents to stabilize the charge-separated (CS) states.^{2–9} The longest lifetime of the CS state of donor–acceptor linked dyad systems (310 μ s at 278 K) was reported for a zinc imidazoporphyrin–C₆₀ dyad (ZnImP–C₆₀) with a short linkage in a polar solvent such as benzonitrile.^{8,9} In nonpolar solvents, the CS state of donor–acceptor linked systems becomes higher in energy than the triplet excited state of the donor or acceptor moiety when charge recombination results in formation of the triplet excited-state rather than the ground state.⁶ However, the protein environment surrounding the photosynthetic reaction center is rather nonpolar with a low dielectric constant (ϵ) of ca. 2.¹⁰ There have so far been no donor–acceptor linked systems which show long-lived CS states in nonpolar solvents.

We report herein the photoinduced electron-transfer dynamics of an electron donor–acceptor linked system containing Au(III) and Zn(II) porphyrins (ZnPQ–AuPQ⁺PF₆[–] in Figure 1)¹¹ which exhibits an unprecedented long-lived CS state with the lifetime of 10 μ s in a nonpolar solvent such as cyclohexane ($\epsilon = 2.02$). The introduction of quinoxaline annelation to the gold porphyrin results in a lowering of the CS state energy to less than that of the porphyrin triplet excited state even in nonpolar solvents.

A ZnPQ reference compound shows a fluorescence band at 623 and 678 nm.^{11b} The fluorescence emission of ZnPQ–AuPQ⁺ is quenched 20-fold compared to emission from the ZnPQ reference (see Supporting Information, Figure S1). Intramolecular electron transfer from the singlet excited state of ZnPQ (¹ZnPQ*) to AuPQ⁺ to produce the CS state is the most likely mechanism for fluorescence quenching in ZnPQ–AuPQ⁺ judging from the free energy change of photoinduced electron transfer (vide infra).

The CS energy in toluene is determined as 1.11 eV from the one-electron oxidation potential of the ZnPQ moiety ($E^0_{\text{ox}} = 0.81$ V vs SCE) and the one-electron reduction potential of the AuPQ⁺ moiety ($E^0_{\text{red}} = -0.30$ V vs SCE) in ZnPQ–AuPQ⁺ (see Supporting Information, Figure S2).¹² The CS energy in toluene is smaller than the value (1.21 eV) obtained from the one-electron redox

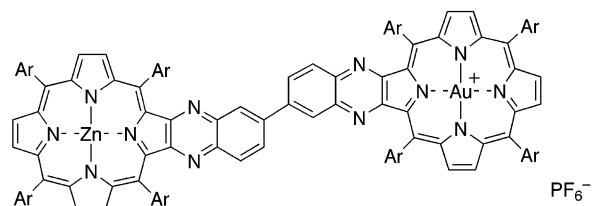


Figure 1. Structure of ZnPQ–AuPQ⁺PF₆[–] dyad (Ar = 3,5-Bu₂C₆H₃).

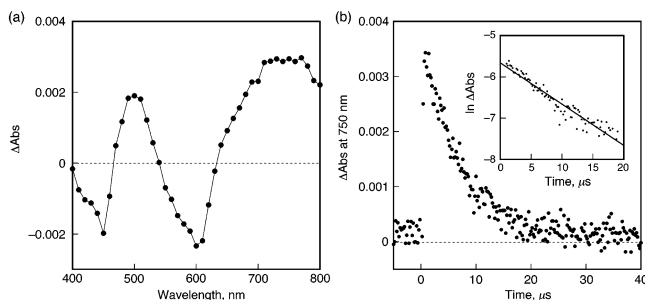


Figure 2. (a) Transient absorption spectrum of ZnPQ–AuPQ⁺ (1.0×10^{-4} M) in deaerated cyclohexane at 298 K taken 1.4 μ s after laser excitation at 440 nm. (b) The decay profile at 750 nm. Inset: First-order plot.

potentials in a much more polar solvent (PhCN, see Figure S3). Such a smaller CS energy in toluene than the value in PhCN results from the less negative E^0_{red} values in toluene as compared with that in PhCN (–0.40 V) and this is due to the smaller solvation of the AuPQ⁺ moieties in toluene. On the other hand, the E^0_{ox} value of the ZnPQ moiety is virtually the same in PhCN (0.81 V). Thus, in contrast to the case of neutral donor–acceptor dyads, the CS energy of ZnPQ–AuPQ⁺ becomes smaller in a less polar solvent. The CS energy is lower in energy than both the triplet excited states of ZnPQ (1.32 eV) and AuPQ⁺ (1.64 eV).¹³ The free energy change of photoinduced electron transfer (ΔG^0_{ET}) from the singlet excited state of the ZnPQ to the AuPQ⁺ moiety in toluene is determined as –0.93 eV from the CS energy and the excitation energy ($S_1 = 2.04$ eV)^{11b} of the ZnPQ moiety. Since the excitation energy is rather insensitive to solvent polarity, the ΔG^0_{ET} value also becomes more negative in a less polar solvent.

Time-resolved transient absorption spectra of ZnPQ–AuPQ⁺ were measured by nanosecond laser photolysis in toluene and cyclohexane. A transient absorption spectrum observed at 1.4 μ s after the laser pulse excitation of a cyclohexane solution of ZnPQ–AuPQ⁺ is shown in Figure 2a. The transient absorption bands at 650–800 nm are assigned to the charge-separated state (ZnPQ^{•+}–

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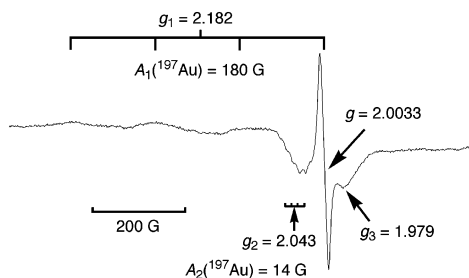


Figure 3. ESR spectrum observed under photoirradiation of a toluene solution of ZnPQ–AuPQ⁺ at 143 K.

AuPQ) by comparison with the thin-layer UV–visible spectra of ZnPQ⁺ and AuPQ (Figure S4) produced by the electrochemical oxidation of ZnPQ and reduction of AuPQ⁺, respectively. Thus, photoinduced electron transfer from the singlet excited state of the ZnPQ (¹ZnPQ*) to the AuPQ⁺ moiety occurs to produce the CS state,¹⁴ ZnPQ*–AuPQ, in competition with the intersystem crossing to ³ZnPQ*. The CS state detected in Figure 2a decays via back electron transfer (BET) to the ground-state rather than to the triplet excited state. The BET rate was determined from the disappearance of the absorption band at 750 nm due to ZnPQ⁺ in ZnPQ*–AuPQ (Figure 2b). The decay of the absorption band obeys first-order kinetics (see inset of Figure 2b). The k_{BET} value in cyclohexane is determined as $1.0 \times 10^5 \text{ s}^{-1}$ which corresponds to the lifetime of 10 μs . Similarly the CS lifetime in toluene was determined as 9.1 μs . In contrast, no CS state was observed in PhCN; instead only the triplet–triplet absorption due to the ³ZnPQ* was observed (Figure S5).

Such a relatively long-lived ZnPQ*–AuPQ in toluene enabled detection of the CS state produced by the photoinduced electron transfer with measurements of the ESR spectrum under photoirradiation of the compound. The resulting spectrum of the photoirradiated dyad ZnPQ–AuPQ⁺ in toluene at 143 K is shown in Figure 3. The broad signal is clearly assigned to the Au^{II} species, since the hyperfine interaction with ¹⁹⁷Au ($I = 3/2$, $A_1 = 180 \text{ G}$, $A_2 = 14 \text{ G}$) is observed with the g factors of $g_1 = 2.182$, $g_2 = 2.043$ and $g_3 = 1.979$.¹⁵ The large anisotropic hyperfine coupling (hfc) constants, being comparable to the hfc value of Au^{II} ion, indicate clearly that the site of electron transfer is the Au metal rather than the porphyrin ligand.¹⁶ The sharp isotropic ESR signal at $g = 2.0033$ corresponds to the radical cation of ZnPQ. These assignments were confirmed by the ESR spectra of ZnPQ⁺ and Au^{III}PQ produced independently via chemical oxidation of ZnPQ–Au^{III}PQ⁺ with Ru(bpy)₃³⁺ (bpy = 2,2′-bipyridine) and via chemical reduction with tetramethylsemiquinone radical anion, respectively (Figure S6). The positive shift of the E_{red}^0 value of Au^{III}PQ⁺ in toluene as compared with the E_{red}^0 value in PhCN (vide supra) results from the metal-centered reduction of Au^{III}PQ⁺, whereas the small change in the E_{ox}^0 value of ZnPQ results from the ligand-centered oxidation, since the change in solvation may be much larger in the former case.

In summary, we have successfully attained a long-lived CS state in nonpolar solvents using the ZnPQ–AuPQ⁺ dyad. In general the smaller the reorganization energy of electron transfer, the slower the back electron transfer becomes in the Marcus inverted region.¹⁷ Thus, the long CS lifetime may result from a small reorganization energy for the *metal-centered* electron transfer of AuPQ⁺ in nonpolar solvents due to the small change in solvation upon the electron transfer as compared with that in polar solvents. In contrast,

the absence of an observable CS state in the polar solvent PhCN is attributed to the much slower photoinduced electron transfer due to the large reorganization energy as compared with that in nonpolar solvents, allowing an efficient intersystem crossing process in the ZnPQ–AuPQ⁺ dyad to produce the triplet excited state ³ZnPQ*–AuPQ⁺ (Figure S5).

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Supporting Information Available: Fluorescence spectra, CV data, spectroelectrochemical data of ZnPQ–AuPQ⁺, the transient absorption spectra in PhCN, and ESR spectra of ZnPQ*–AuPQ⁺ and ZnPQ–AuPQ (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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