Primary charge-recombination in an artificial photosynthetic reaction center

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Photoinduced primary charge-separation and charge-recombination are characterized by a combination of time-resolved optical and EPR measurements of a fullerene–porphyrin-linked triad that undergoes fast, stepwise charge-separation processes. The electronic coupling for the energy-wasting charge recombination is evaluated from the singlet-triplet electronic energy gap in the short-lived, primary charge-separated state. The electronic coupling is found to be smaller by ~40% than that for the primary charge-separation. This inhibition of the electronic interaction for the charge-recombination to excited triplet state largely results from a symmetry-broken electronic structure modulated by configuration interaction between \( \langle b_{1u} b_{3g} \rangle \) and \( \langle a_u b_{3g} \rangle \) electronic states of the free-base porphyrin.

Electronic coupling | long-range electron transfer | molecular orbital symmetry

To construct nanoscale devices or molecular wires that efficiently convert photon energies to chemical potentials, extensive studies have produced photoinduced, long-distance electron transfer reactions centers (12). From Marcus theory (13–20), the ET rate constant \( k_{ET} \) is described in the weak coupling regime as

\[
k_{ET} = \frac{2\pi}{\hbar} |V|^2 \text{FCWDS},
\]

where \( \hbar \) is Planck’s constant divided by \( 2\pi \) and \( V \), the electronic coupling matrix element, represents the electronic tunneling interaction between D and A. FCWDS denotes Franck–Condon weighted density states parameterized by the reorganization energy \( \Lambda \) and the driving force \( -\Delta G \) for the ET reaction. The FCWDS term is given by \( \left( 4\pi k_b T \right)^{-1/2} \exp[-(\Delta G + \lambda)^2/4k_b T] \) where \( k_b \) is the Boltzmann constant and \( T \) is the temperature. Although for several long-range ET systems, \( V \) has been interpreted in terms of a superexchange coupling model (21) that bridges the redox sites (22–28), much remains to be resolved regarding the tunneling mechanism (29–34). In addition, characterization of \( V \) will be useful for designing molecular electronic devices (35).

Key to efficient photoinduced CS is prevention of the energy-wasting charge recombination (CR) characterized in part by \( \Delta G \). Although \( V \) and \( \Lambda \) have been investigated for various ET steps by experimentally measuring \( k_{ET} \) systems in such as D2–D1–A triad (7, 9, 36) and protein complexes (24, 25, 34), primary CR, \( \text{D}_2\text{D}_1^{+} \text{A}^- \rightarrow \text{D}_2\text{D}_1^{-} \text{A}^- \), has escaped elucidation, especially in the efficient stepwise CS systems because the CR kinetics is hidden by subsequent CS processes, \( \text{D}_2\text{D}_1^{+} \text{A}^- \rightarrow \text{D}_2^- \text{D}_1^- \text{A}^- \). In the photosynthetic reaction center protein of "Rhodobacter sphaeroides," which contains as cofactors a special pair (P), two bacteriopheophytins \( \text{H}_A \text{H}_B \), and two quinones \( \text{Q}_A \text{Q}_B \), the CR kinetics of the primary CS state of \( \text{P}^+\text{H}_A \text{Q}_A \) cannot be observed, because \( \text{H}_A^* \rightarrow \text{Q}_A \) forward ET (~200 ps) is much faster than the primary CR (10–20 ns, which has been reported for \( \text{Q}_A \)-depleted complex) in the CS state (37).

Here, a method to characterize \( V (V_{CR}) \) is presented for the primary CR (as shown by a red dotted arrow in Fig. 2) in a linked triad, \( \text{ZnP–H}_2\text{P–C}_6\text{O} \) (8, 9), in which the zinc tetrathiaporphyrin \( \text{ZnP} \), free-base tetrathiaporphyrin \( \text{H}_2\text{P} \), and fullerene \( \text{C}_6\text{O} \) moieties \( \text{N}(\text{methyl-2-phenyl-3,4-fulleropyrrolidine}) \) are rigidly linked by amide spacers (Fig. L4). The means of characterizing the \( V_{CR} \) is based on a method of time-resolved EPR (TREPR) involving the phenomenon of chemically induced dynamic electron polarization (32, 38–40). In part, chemically induced dynamic electron polarization depends on the connection between the singlet–triplet \( (S\rightarrow T) \) electronic energy splitting (exchange coupling; \( 2J = E_S - E_T \) in CS state) and \( V_{CR} \). The parameter \( 2J \) is governed by the spin-selective interaction (41) of \( V_{CR} \) in accordance with Marcus theory (32, 40, 42–46). Fig. 2 illustrates the potential surfaces of the photoexcited states and the primary CS state with respect to reaction coordinate \( \langle X \rangle \) by using \( \lambda \) and the excited-state energies of \( \text{H}_2\text{P} \) and the CS-state energies reported for the fullerene–porphyrin-linked system (9).

In Fig. 2, the triplet CS state of \( \text{ZnP–H}_2\text{P}^+ \text{C}_6\text{O}^- \) interacts the most with the nearly first excited triplet \( (T_1) \) state (red potential) around \( X = 1 \) populated by a thermal equilibrium distribution as shown by a Gaussian function \( P(X) \). This interaction \( (V_{CR}) \) results in an energetic stabilization in the triplet CS state. Stabilization also occurs in the singlet CS state by interaction with the excited singlet \( (S_1) \) state (blue potential in Fig. 2). These energy shifts, determined by the \( V_{CR} \)S, result in the \( E_S - E_T \) difference \( (2J) \) for the primary CS state (42, 43). The \( 2J \) parameters have been investigated for the \( \text{P}^+\text{H}_A \) state in the \( \text{Q}_A \)-depleted natural photosynthetic reaction centers through measurements of the magnetic field dependence of the reaction yield (47, 48). By using the \( 2J \) parameter, \( V_{CR} = 1 - \text{cm}^{-1} \) has been estimated for the primary CR in \( \text{P}^+\text{H}_A \), whereas \( V_{CS} \sim 30 \text{ cm}^{-1} \) has recently been characterized for the primary CS \( (\text{P}^+\text{H}_A^+ \rightarrow \text{P}^+\text{H}_A^-) \), implying that the primary CR is significantly retarded with respect to the primary CS process.

Often TREPR signals are characterized by enhanced microwave absorptions and emissions arising from non-Boltzmann populations among the energy levels of the electron spins. These non-Boltzmann EPR signals are referred to as electron spin

Abbreviations: A, acceptor; D, donor; CR, charge recombination; CS, charge separation; \( \text{ZnP} \), zinc tetrathiaporphyrin; \( \text{H}_2\text{P} \), free-base tetrathiaporphyrin; \( \text{C}_6\text{O} \), fullerene; ESP, electron spin polarization; ET, electron transfer; FCWDS, Franck–Condon weighted density states; LUMO, lowest unoccupied molecular orbital; TREPR, time-resolved EPR.

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polarization (ESP) and in our case are explained by singlet-initiated, sequential ET in which the ESP developed in the first CS state, ZnP–H2P–C60, is “memorized” by the second CS state, ZnP*–H2P–C60 (49, 50). During the secondary CS process (kCS2) in Fig. 2, both the sign and the magnitude of the 2J1 of the initial radical pair is “recorded into” the EPR spectrum of the secondary radical-pair CS state, making possible the characterization of the VCR1 of the triad.

To obtain the value of 2J1, the ESP revealed by TREPR is analyzed on the basis of a sequential ET model. In the analysis, the value of kCS2 (the rate of which is much faster than the response of the TREPR spectrometer) is needed. To provide the missing rate information, time-resolved fluorescence and transient absorption data were analyzed, determining the primary and secondary CS rate constants, kCS1 and kCS2.

We report herein that the VCR1 for ZnP–H2P–C60, is ZnP–H2P–C60 (red arrow in Fig. 2) is somewhat smaller than that of VCS1 for the primary CS process, ZnP–H2P–C60 → ZnP–H2P–C60 (green arrow in Fig. 2), showing that the primary CR is partially inhibited by a reduced electronic interaction.

Materials and Methods

Chemicals. The synthesis of ZnP–H2P–C60 is described in ref. 8. Benzonitrile (PhCN) was used as received (Aldrich, 99+% anhydrous). The sample solution (5 × 10−4 M) of ZnP–H2P–C60 was deaerated on a vacuum line (pressure ≈ 10−5 torr (1 torr = 133 Pa)) for the TREPR measurements. Suprasil quartz was used for the EPR sample tube (Wilmsd, Buena, NY; i.d. = 1 mm).

Time-Resolved Fluorescence Spectroscopy. The picosecond time-resolved fluorescence was measured with light excitation by the second harmonic (400 nm) of a Ti:sapphire laser (Tsunami 3950-L2S, full width at half maximum 1.5 ps, Spectra-Physics) with a streak scope (C4334-01, Hamamatsu Photonics, Hamamatsu City, Japan). The fluorescence of ZnP–H2P–C60 was monitored at 650 nm at room temperature.

TREPR. The X-band TREPR measurements were carried out by using a magnet and console (Varian E-112) equipped with a microwave bridge (ER 041MR, Bruker, Billerica, MA) in which a microwave preamplifier was added to enhance the time resolution (∼25 ns) and signal sensitivity (51). Light excitations were performed by using the second harmonic (532 nm) of a Nd:YAG laser (Spectra-Physics, Quanta-Ray GCR-4, full width at half maximum ∼5 ns). Time traces of the EPR signals were stored on a digital oscilloscope (Waverunner LT322, LeCroy, Chestnut Ridge, NY). Data analysis was performed by using MATLAB R12 software (Version 6.0, Mathworks, Natick, MA) on a personal computer (500X, Gateway, Irvine, CA).

Molecular Orbital Calculations. A semiempirical PM3 calculation was performed by using the MOPAC 2000 C in the CS CHEM 3D ULTRA (Version 6.0, CambridgeSoft, Cambridge, MA). Density functional theory molecular orbital calculations were performed with GAUSSIAN-98W (Version 5.4, Rev. A9) (67). Geometry optimizations were carried out with unrestricted Becke’s hybrid functional including the Lee–Yang–Parr correlation function (UB3LYP) with the 3-21G(d) basis set.

Experimental Results

Sequential CS Processes. Fig. 3A shows the fluorescence decay profile of ZnP–H2P–C60 in PhCN. This profile was fitted by a single-exponential decay. The fluorescence lifetime (1.6 ns) in the triad is much shorter than the Sn state lifetime (∼10 ns) of H2P. Fig. 3B shows time profiles of the transient absorptions obtained by the 532-nm laser (full width at half maximum ∼18 ps) irradiation (8). The initial decays (lifetime, 60 ps) in Fig. 3B are assigned to the Sn ← S0 transition in the ZnP moiety, which is deactivated by an intramolecular S1 excitation energy transfer from 1ZnP* to H2P in the triad. In Fig. 3B, the transient
E signal is attributed to ZnP/H11001 absorption of the secondary CS state (ZnP\textsuperscript{g}) competing processes, the primary CS and the 1H2P\* absorption decay in the H\textsubscript{2}P moiety. The primary CS state, ZnP\textsuperscript{g}–H2P–C\textsubscript{60} (0.3 \mu s) after the laser irradiation in PhCN. (8) Time profile of the signal at 324.65 mT indicated by the arrow (bottom) in A with microwave power = 1 mW. In A and B, blue, red, and green lines were calculated by the sequential ET polarization model by using the 2J parameters shown in B, giving rise to 2J\textsubscript{g} = 0.12 mT for the primary CS state. Absorption decay (after 200 ps) at 505 nm resembles the fluorescence decay in Fig. 3A and is thereby assigned to the S\textsubscript{1} absorption decay in the H\textsubscript{2}P moiety.

The differential absorption spectrum (data not shown) obtained at 50 ns (8) is explained by the superposition of the absorption of the secondary CS state (ZnP\textsuperscript{g}–H2P–C\textsubscript{60}) and of the T\textsubscript{g} \leftrightarrow T\textsubscript{1} transition of the C\textsubscript{60} component of ZnP–H2P–C\textsubscript{60} (9). The total quantum yield (\Phi\text{total}) of the secondary CS state is reported to be 0.4 (8). A significant amount of the ZnP–H2P–C\textsubscript{60} exciton energy transfer (k\text{SS2} = 3.2 \times 10\textsuperscript{4} s\textsuperscript{-1}) followed by the rapid intersystem crossing (k\text{ISC} = 5.6 \times 10\textsuperscript{5} s\textsuperscript{-1}) of the C\textsubscript{60} moiety (8). The 650-nm rise in Fig. 3B is thereby attributed to the superposition of increases in ZnP\textsuperscript{g}–H\textsubscript{2}P–C\textsubscript{60} (by the sequential CS processes) and in C\textsubscript{60} (by the intersystem crossing following the 1\textsuperscript{H}2P\* → C\textsubscript{60} excitation energy transfer). The 1.6-nm fluorescence lifetime in Fig. 3A is attributed to the 1\textsuperscript{H}2P\* deactivation by two competing processes, the primary CS and the 1\textsuperscript{H}2P\* → C\textsubscript{60} excitation energy transfer. The three time traces in Figs. 3 and 4 and \Phi\text{total} = 0.4 were simultaneously reproduced as shown by black lines in Fig. 4B by solving the coupled time-differential equations for populations in 1\textsuperscript{ZnP}–H2P–C\textsubscript{60}, ZnP–H2P–C\textsubscript{60}–ZnP, ZnP–H2P–C\textsubscript{60}, ZnP–H2P–C\textsubscript{60}–ZnP, ZnP–H2P–C\textsubscript{60}–ZnP–H2P–C\textsubscript{60}, and ZnP–H2P–C\textsubscript{60} (see Supporting Text and Figs. 6 and 7, which are published as supporting information on the PNAS web site). The CS rate parameters were determined as k\text{CS1} = 3.0 \times 10\textsuperscript{8} s\textsuperscript{-1} and k\text{CS2} = 1.5 \times 10\textsuperscript{9} s\textsuperscript{-1}.

Sequential ET Spin Polarization. Fig. 4A shows the TREPR spectrum (black line) observed 0.3 \mu s after the 532-nm laser irradiation of the triad in PhCN at room temperature (T = 294 K). Microwave emission (E) was observed at the lower field (around g = 2.0027, indicated by an arrow at the bottom of Fig. 4A). This signal is attributed to ZnP\textsuperscript{+} (52). Microwave absorption (A) is detected at the higher field region (around g = 2.0004) assigned to the C\textsubscript{60} part (11). Therefore, the EPR spectrum is attributed to the secondary CS state. As has been reported for the sequential CS systems in the photosynthetic reaction centers, this emission/absorption (E/A) pattern in Fig. 4A is explained by the ESP originating from the primary CS state (50). Fig. 4B is a time profile (black line) of the TREPR signal that was observed at the center resonance position (g = 2.0027) of ZnP\textsuperscript{+}.

No microwave power \(B_1\) dependences were observed in the time traces in Fig. 4 for 0.5 < \(B_1\) < 5 mW. The decay of the E-signal is therefore explained by spin-lattice relaxation to a thermal equilibrium (A) that ultimately decays to zero by means of the CR of the secondary CS state.

**Quantitative Analysis of ESP.** For analysis of the ESP, the stochastic-Liouville equations were described by the Laplace transform \(\rho_i(s)\) of the density matrix \(\rho_i(t)\) for the S, T\textsubscript{+}, T\textsubscript{0}, and T\textsubscript{−} electron spin wavefunctions of the primary \(k = 1\) and secondary \(k = 2\) CS states (38, 39).

\[
\begin{align*}
\dot{\rho}_1 (s) &= -\frac{i}{\hbar} [\hat{H}_1, \rho_1 (s)] - k_{\text{CS1}} \rho_1 (s), \\
\dot{\rho}_2 (s) &= -\frac{i}{\hbar} [\hat{H}_2, \rho_2 (s)] + k_{\text{CS2}} \rho_1 (s) - k_{\text{CR2}} \rho_2 (s) - R \rho_2 (s),
\end{align*}
\]

where \(n = 1\) and \(R\) represent the CR and the spin-relaxation in the secondary CS state. The CR and the spin-relaxation are negligible in Eq. 2 because \(k_{\text{CS2}}\) is much faster than these processes. The spin Hamiltonians \(\hat{H}_k\) are composed of the Zeeman, the hyperfine, the dipolar \((D_k)\), and the 2J \((2J_k)\) interactions, as

\[
\begin{align*}
\hat{H}_k &= \beta B_0 [g_{\text{CS}0}(\Omega) \hat{S}_{\text{CS}0} + g_D \hat{S}_{\text{D}}] + \sum_m A_{\text{CS}m} \hat{S}_{\text{CS}m} \\
&+ \sum_n A_{\text{D}n} \hat{S}_{\text{D}n} + (S_{\text{CS}0} + S_{\text{D}}) \hat{D}_k (\Omega) (S_{\text{CS}0} + S_{\text{D}}) \\
&- 2J_k (1/2 + S_{\text{CS}0} + S_{\text{D}}),
\end{align*}
\]

where \(S\) and \(I\) are the electron and nuclear spin operators, respectively. The parameters \(g(\Omega)\) and \(D(\Omega)\) denote the g-tensor and the dipolar \((D)\)-tensor that depend on the molecular orientation \(\Omega\) with respect to the magnetic field \(B_0\). Subscripts \(P_1\) and \(P_2\) represent H2P\textsuperscript{+} and ZnP\textsuperscript{+}, respectively. Because the two-peak signal in the absorptive region in Fig. 4A represents the anisotropic Zeeman interaction of the C\textsubscript{60} moiety, an \(\Omega\)-dependent g-factor was considered in C\textsubscript{60}. For H2P\textsuperscript{+} and ZnP\textsuperscript{+}, the g-factors were set to be isotropic. Anisotropic terms of the hyperfine couplings are negligible in A\textsubscript{6}. The dipolar axis systems were defined by the polar angles \(\theta_k\) and \(\phi_k\) with respect to the \(z\) and \(x\) principal axes, respectively, of the g-tensor \((g_x, g_y, g_z)\) of C\textsubscript{60}. By solving Eqs. 2 and 3, assuming \(k_{\text{CS1}} = 1.5 \times 10^7\) s\textsuperscript{-1} as described above, time-dependent EPR spectra were computed as illustrated in Fig. 4. Details of the TREPR analysis based on Eqs. 2–4 are described in Supporting Text. The EPR parameters are listed in Table 1 for the simulations of Fig. 4.

It is noteworthy that both the spectrum (at \(t = 0.3 \mu s\)) and the time profile are reproduced with a common set of parameters (in Table 1) by using the same analysis procedure. This good agreement (red lines in Fig. 4) was accomplished only when a \(D_2\) of \(-0.046 (\pm 0.001)\) mT was used for the secondary CS state. Based on \(D_2 = -0.046\) mT, the distance between the two spins is calculated to be \(r_2 = 39\) Å by using the point-dipole approximation for the dipolar interaction. This distance is consistent with the center-to-center distance (39 Å) between the C\textsubscript{60} and ZnP moieties estimated by a semiempirical PM3 molecular orbital calculation (Fig. 5A). The magnitude of the sequential ET

**Fig. 4.** Sequential ET spin polarization of ZnP–H2P–C\textsubscript{60}. (A) TREPR spectrum of the secondary CS state, ZnP\textsuperscript{+}–H2P–C\textsubscript{60}, at 0.3 \mu s after the laser irradiation in PhCN. (B) Time profile of the signal at 324.65 mT indicated by the arrow (bottom) in A with microwave power = 1 mW. In A and B, blue, red, and green lines were calculated by the sequential ET polarization model by using the 2J parameters shown in B, giving rise to 2J\textsubscript{g} = 0.12 mT for the primary CS state.
polarization is quite sensitive to the $2J_1$ values in the primary CS state, as seen in the calculated curves for the different $2J_1$ in Fig. 4B. This sensitivity supports the validity of quantifying the $2J_1$ value in the short-lived (lifetime $\approx 650$ ps) primary CS state.

**Analyses of Electronic Coupling Matrix Elements**

**Primary CS and CR Rates in the Triad and Dyad.** In the event that intramolecular contributions to the ET reorganization energy are present, a high-frequency intramolecular vibrational mode with a frequency of $v$ has been considered for the FCWDS of Eq. 1 as follows (20):

$$FCWDS = \sum_j \frac{FC_j}{\sqrt{4\pi\lambda JyTB}} \exp \left\{ -\left( \frac{(\lambda_s + \Delta G + jv\nu^2)}{4\lambda JyTB} \right) \right\},$$

where $FC_j = \exp(-\lambda_s/jv\nu)(\lambda_s/jv\nu)(j/2)!$ is the Franck–Condon factor. The parameters $\lambda_s$ and $\lambda_j$ denote the solvent reorganization energy and the intramolecular reorganization energy, respectively. From charge-transfer emission spectra of a porphyrin-C$_{60}$ dyad with the donor–acceptor in close proximity, $\lambda_j = 0.05$ eV (1 eV $= 1.602 \times 10^{-19}$ J) and $v = 0.14$ eV were determined for the CR to the ground state (53). For the porphyrin–C$_{60}$ dyad systems in Fig. 1B, the total reorganization energy ($\lambda = \lambda_j + \lambda_s$) is reported to be 0.66 eV in PhCN (9), leading to $\lambda_s = 0.61$ eV. The ET distances between H$_2$P and C$_{60}$ in the triad are the same as the ET distances in the dyads (18). Also, the fluorescence lifetime (which is governed in part by the primary CS rate) in Fig. 3A is the same as the fluorescence lifetime (1.6 ns) reported on a H$_2$P–C$_{60}$ dyad with the identical –CONH– spacer (54), indicating no difference in reorganization energies between the triad and the dyad concerning 1H$_2$P$^+$–C$_{60} \rightarrow$ H$_2$P$^+$–C$_{60}^\cdot$. Thus, $\lambda_s = 0.61$ eV is assumed for the primary CS and the primary CR processes in the triad. In the case of the primary CS (in Fig. 2), $V_{CSI} = 2.6$ cm$^{-1}$ is obtained from $\lambda_{CSI} = 3.0 \times 10^8$ s$^{-1}$ by using the reorganization parameters above and $-\Delta G_{CSI} = 0.30$ eV in Eqs. 1 and 5 (9). For the ZnP–C$_{60}$ dyad in PhCN, the reported CS rate constant (5.5 $\times 10^8$ s$^{-1}$) for ZnP$^+–$C$_{60} \rightarrow$ ZnP$^+–$C$_{60}^\cdot$ ($-\Delta G_{CSI} = 0.37$ eV) (9) was calculated by using $V_{CSI} = 2.4$ cm$^{-1}$ and the same reorganization parameters as described above. The decay rate constant for the return of ZnP$^+–$C$_{60}^\cdot$ to the ground state was measured to be $1.3 \times 10^6$ s$^{-1}$ in the absence of an external magnetic field (9). The lifetime of the CS state is significantly longer than the singlet–triplet mixing time, which is estimated from hyperfine coupling constants to be $<10^{-5}$ s in ZnP$^+–$C$_{60}$. Also, no triplet CR deactivation occurs in the radical pairs. Under these circumstances, deactivation of the CS state is inhibited by the singlet–triplet mixing and is four times slower than the actual radical pair’s CR time occurring through the singlet state (55). Therefore, the singlet CR rate constant of $5.2 \times 10^6$ s$^{-1}$ is applicable for ZnP$^+–$C$_{60} \rightarrow$ ZnP$^+–$C$_{60}^\cdot$ ($-\Delta G_{CR} = 1.38$ eV). This rate constant was calculated by using $V_{CR} = 2.6$ cm$^{-1}$, $\lambda_s = 0.61$ eV, and $\lambda_j = 0.05$ eV. Almost identical $V$ values are obtained for the above three ET rate constants by setting $\lambda_j = 0.61$ eV.

With this value of 0.61 eV for $\lambda_s$, a smaller value of $V_{CS} = 1.7$ cm$^{-1}$ (Table 2) reproduces the reported CS rate constant $1.5 \times 10^8$ s$^{-1}$ for the T$_1$ state, i.e., for ZnP$^+–$C$_{60} \rightarrow$ ZnP$^+–$C$_{60}^\cdot$ where $-\Delta G_{CS} = 0.12$ eV (9). From the similarity in lineshapes between the electron detachment spectra reported for transitions of C$_{60}$$^\cdot$ $\rightarrow$ 1C$_{60}$ + e$^-$ and for C$_{60}$$^\cdot$ $\rightarrow$ 3C$_{60}$ + e$^-$ (56), $\lambda_j = 0.05$ eV is also used for the ET in ZnP$^+–$C$_{60}$. Regarding the CS state, H$_2$P$^+$–C$_{60}^\cdot$ in the dyad, the deactivation rate constant of $2.2 \times 10^6$ s$^{-1}$ was attributed to CR to 3H$_3$P$^\cdot$ (9). We have performed density functional theory calculations of the T$_1$ state and of the cation radical of the H$_2$P moiety and found $\lambda_j = 0.12$ eV for the reaction of H$_2$P$^+$ $\rightarrow$ 3H$_3$P$^\cdot$ (57). From the CR rate constant ($2.2 \times 10^7$ s$^{-1}$) (8), $V_{CR} = 1.6$ cm$^{-1}$ was found by using

<table>
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<tr>
<th>g-Tensor components*</th>
<th>g-Values (isotropic)*</th>
<th>Spin–spin dipolar couplings ($D$, mT)</th>
<th>Dipolar tensor orientations</th>
<th>Exchange couplings ($J$, mT)</th>
<th>Spin-lattice relaxation times per $\mu$s</th>
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<td>$g_{C_{60}}$</td>
<td>$g_{H_2P}$</td>
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<td>$J_1 = +0.12$</td>
<td>$T_{1,C_{60}} = 0.90$</td>
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<td>$g_{ZnP}$</td>
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<td>$J_2 = +0.45$</td>
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<td>$g_{C_{60}}$</td>
<td>$g_{ZnP}$</td>
<td>$\theta_2 = 41^\circ (\pm 2)^\circ$</td>
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*The $g$ components were set to hold a relation of $g_x > g_y > g_z$, which is reported for N-methylfulleropyrrolidine anion radical. Three lines from a nitrogen HF-coupling constant ($\lambda_n = 0.022$ mT) also were taken into account with Lorentzian peak-functions (65).

$\lambda_{CSI}$ is also used for the ET in ZnP$^+–$C$_{60}$. (9) was calculated with $V_{CS} = 2.6$ cm$^{-1}$, $\lambda_s = 0.61$ eV, and $\lambda_j = 0.05$ eV. Almost identical $V$ values are obtained for the above three ET rate constants by setting $\lambda_j = 0.61$ eV.

With this value of 0.61 eV for $\lambda_s$, a smaller value of $V_{CS} = 1.7$ cm$^{-1}$ (Table 2) reproduces the reported CS rate constant $1.5 \times 10^8$ s$^{-1}$ for the T$_1$ state, i.e., for ZnP$^+–$C$_{60} \rightarrow$ ZnP$^+–$C$_{60}^\cdot$ where $-\Delta G_{CS} = 0.12$ eV (9). From the similarity in lineshapes between the electron detachment spectra reported for transitions of C$_{60}$$^\cdot$ $\rightarrow$ 1C$_{60}$ + e$^-$ and for C$_{60}$$^\cdot$ $\rightarrow$ 3C$_{60}$ + e$^-$ (56), $\lambda_j = 0.05$ eV is also used for the ET in ZnP$^+–$C$_{60}$. Regarding the CS state, H$_2$P$^+$–C$_{60}^\cdot$ in the dyad, the deactivation rate constant of $2.2 \times 10^6$ s$^{-1}$ was attributed to CR to 3H$_3$P$^\cdot$ (9). We have performed density functional theory calculations of the T$_1$ state and of the cation radical of the H$_2$P moiety and found $\lambda_j = 0.12$ eV for the reaction of H$_2$P$^+$ $\rightarrow$ 3H$_3$P$^\cdot$ (57). From the CR rate constant ($2.2 \times 10^7$ s$^{-1}$) (8), $V_{CR} = 1.6$ cm$^{-1}$ was found by using

![Fig. 5. Electronic couplings for primary ET processes and connection to molecular orbital symmetry. (A) Molecular structure of ZnP–H$_2$P–C$_{60}$ triad obtained by the PM3 molecular orbital calculation. Electronic couplings are shown for the primary charge-separation ($V_{CSI} = 2.6$ cm$^{-1}$) from the excited singlet H$_2$P and the CR ($V_{CR} = 1.6$ cm$^{-1}$) to the excited triplet H$_2$P. (B and C) The basis-type singly occupied molecular orbitals of the cation radical (B) and the T$_1$ state of the H$_2$P (C) obtained by the molecular orbital calculation (UB3LYP/3–21G*) is also shown in C, indicating the transitions between H$_2$P$^+$ and H$_2$P$^\cdot$ are partially inhibited on the CR due to the symmetry breaking in H$_2$P$^\cdot$.](https://www.pnas.org/cgi/doi/10.1073/pnas.0504598102) Kobori et al.
Table 2. Electronic couplings (V) for CS and CR processes in the fullerene–porphyrin–linked triad and dyads in benzonitrile

<table>
<thead>
<tr>
<th>ET process</th>
<th></th>
<th>V/cm²</th>
<th>Data source</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnP-^1H2P^<em>-C60 → ZnP-^1H2P</em>-^1C60</td>
<td>2.6 †</td>
<td>kCS1 = 3.0 × 10⁸ s⁻¹</td>
<td></td>
</tr>
<tr>
<td>ZnP-^1H2P^<em>-^1C60 → ZnP-^1H2P</em>-^1C60</td>
<td>2.4 †</td>
<td>kCR = 5.5 × 10⁴ s⁻¹</td>
<td></td>
</tr>
<tr>
<td>ZnP-^1H2P^<em>-^1C60 → ZnP-^1H2P</em>-C60 (S₀)</td>
<td>2.6 †</td>
<td>kCR = 5.2 × 10⁶ s⁻¹</td>
<td></td>
</tr>
<tr>
<td>ZnP-^1H2P^<em>-C60 → ZnP-^1H2P</em>-^1C60</td>
<td>1.7 †</td>
<td>kCS = 1.5 × 10⁸ s⁻¹</td>
<td></td>
</tr>
<tr>
<td>H2P-^1H2P^<em>-^1H2P</em>-^1C60</td>
<td>1.6 †</td>
<td>kCR = 2.2 × 10⁴ s⁻¹</td>
<td></td>
</tr>
<tr>
<td>ZnP-H2P^<em>-C60 → ZnP-H2P</em>-^1C60</td>
<td>1.6 †</td>
<td>2J1 = +0.12 mT</td>
<td></td>
</tr>
</tbody>
</table>

† Determined by Eq. 1.
‡ Determined by Eq. 6.
§ Obtained in this study.
¶ From ref. 9.

−ΔGCR = 0.19 eV (9). This VCR value operating through the triplet state is also smaller than the V values operating through the singlet spin multiplicities as shown in Table 2.

Exchange Coupling for Primary CS State in the Triad. According to the charge–transfer interaction (40) in the CS states, the singlet–triplet energy gap 2J is expressed as

\[ 2J = \sum_{i,j} \int_{-\infty}^{\infty} \Delta e(X)_i P(X)dX, \]

where \( \Delta e(X)_i \) is the singlet–triplet energy splitting at X created by ith CR state and is dependent on VCR as 2Δe(X)_i = ECS(X) - ECR(X) + [(ECS(X) - ECR(X))]² + 4FCrVCR² around X = 1 when the Δe(X)_i is produced by H^1H2P* (see Supporting Text and Fig. 8, which is published as supporting information on the PNAS website). ECS and ECR denote potential energies in the CS and the CR states in Fig. 2 as determined by −ΔGCR, λS, and λV. The population distribution shown in Fig. 2 is given by P(X) = (λS/2πkT)³exp[-λS(X - 1)/2kBT]. The driving force −ΔGCR is defined by −ΔGCR(S or T) = Eox - Ered = E(S or T), where Eox, Ered, and E(S or T) are the oxidation potential, the reduction potential, and the excited singlet or triplet state energy of the ith CR state, respectively. The numerical integration of Δe(X)_i with respect to X provides an adequate computation of the 2J value averaged by P(X) in liquid solution. We have considered nine CR states of the S₀, S₁(H₂P), S₂(H₂P), T₁(H₂P), T₂(H₂P), S₁(C₆₀), S₂(C₆₀), T₁(C₆₀), and T₂(C₆₀) to simulate the 2J value (see Supporting Text). Because VCR = 2.6 cm⁻¹ obtained through the singlet spin multiplicity in Table 2, VCR,SO = VCR,S₁(H₂P) = VCR,S₂(H₂P) = 2.6 cm⁻¹ was set for the CR to the S₀, S₁, and S₂ states in H₂P, respectively. Also, VCR,S₁(C₆₀) = VCR,S₂(C₆₀) = 2.4 cm⁻¹ was considered from Table 2. Then 2J1 = +0.12 mT was fitted by using a single parameter of VCR,T for the CR to the triplet manifolds, assuming VCR,T = VCR,SO for H₂P and C₆₀. A λVH2P = 0.12 eV (for H₂P−^1H2P* → ^1H2P*) was used while a λV = 0.05 eV was used for the other CS states as described above. From the previous section, a λS of 0.61 eV was applied. As a result, VCR,TL = 1.6 cm⁻¹ was determined for the primary CR of ZnP−H₂P*−^1C₆₀ → ZnP−^1H₂P*−C₆₀ (Table 2).

Discussion and Conclusions

We have shown here that, even though the primary CR kinetics is not observable in the triad (because kCS₂ = 2.2 × 10⁹ s⁻¹ is two orders of magnitude larger than kCR₂ = 2.2 × 10⁹ s⁻¹ reported for the dyad), the VCR₁ can be characterized through the quantitative detection of the ESP memorized from the primary CS state.

The determined value of VCR,TL = 1.6 cm⁻¹ for the triad is in agreement with VCR = 1.6 cm⁻¹ for the corresponding H₂P−C₆₀ dyad as seen in Table 2. We also found that the determined VCR,TL is insensitive to possible errors in the λ parameters used in the fitting procedure. For example, when the value 0.50 eV instead of 0.61 eV was used for λS in Eq. 6, VCR,TL = 1.6 cm⁻¹ was obtained again, denoting quite small errors (less than ±0.1 cm⁻¹) in determining VCR.

Molecular Orbital Effect on Electronic Coupling. To clarify the relation VCS > VCR for the primary CS and CR processes as shown in Fig. 5A, we rationalize why the energy-wasting back ET is inhibited by the electronic interaction between H₂P and C₆₀. According to the bridge-mediated, superexchange mechanism, V is controlled by the electronic properties of D, A, and the spacer (B) linking D and A (21). In the case of the CS from 1D*, VCS is approximated as VCS = VDB⁺VBA/ΔEB, (28) where VDB⁺ and VBA denote the electronic couplings for transitions of 1D* → B ↔ D⁺ → B⁻ and B⁻ ↔ A ↔ B−, respectively. ΔEB represents the vertical energy difference between the lowest unoccupied molecular orbitals (LUMOs) of B and D. Similarly, in the case of the CR to 1D*, VCR,T = VDB⁺VBA/ΔEB, where ΔEB is the vertical energy gap between the LUMOs of B and A. From the superexchange model, two different factors can contribute to the difference between VCS and VCR,T: (i) the orbital energy difference between ΔEB and ΔEB, and (ii) the electronic coupling difference between VDB⁺ and VDB⁻. The relation of VCS > VCR has often been explained by a relation of ΔEB < ΔEB because the donor’s LUMO is located at higher energy (by 0.3 eV in the present H₂P–C₆₀ system) than the acceptor’s LUMO. However, as shown in Table 2, VCR = 2.6 cm⁻¹ obtained for CR to the ground state (ZnP−^1H₂P* → ZnP−C₆₀) is almost the same as VCS. This result indicates that the difference between ΔEB and ΔEB is not so large as to contribute to the ≈40% difference in the V in Fig. 5. At the −PhCO− bridge moiety in the spacer linking the porphyrin skeleton to C₆₀ (Fig. 1), the bridge’s LUMO level is approximated to be 2.4 eV higher than that of C₆₀ from the electron affinity of acetophenone (electron affinity = 0.34 eV) and of C₆₀ (electron affinity = 2.7 eV). The vertical energy gap for B− ↔ A− is thus estimated to be ΔEB = 3.1 eV when we assume the reorganization energy of 0.7 eV for PhCN, whereas ΔEB = 2.8 eV is estimated from the ΔEB and ΔCS = −0.3 eV for the CS process. This energy difference between ΔEB and ΔEB can contribute to only an ≈10% decrease in the VCR, and is consistent with VCS ≈ VCR throughout the singlet manifold. Therefore, the second factor is invoked to explain the 40% reduction in V in the triplet CR, namely, the T₁ electronic state alters the interaction in VDB⁻.

Fig. 5B shows the singly occupied molecular orbital of the cation radical of the H₂P moiety obtained by using density functional theory. The electronic structure exhibits the 3B₁g-type orbital (using the D₃h point group of the porphyrin skeleton in H₂P) and is in good agreement with the previous experimental studies in free-base tetraphenylporphyrins (58). In the T₁ state (Fig. 5C), a symmetry-broken electronic structure was obtained in the b₁u-type orbital, which is also one of the singly occupied molecular orbitals in the T₁ state (59). This orbital modulation is explained by the configuration interaction between the (1b₁a, b₃a) and the (1b₃a, b₃a) orbitals as discussed in the triplet studies on the free-base porphyrins (60, 61). This difference in electronic structure (between B and C in Fig. 5) will inhibit the transition for 1D* → T₁ because of the forbidden transition between the orthogonal (b₁a, a₃) orbitals.

Concerning the S₀ state in H₂P, based on the absorption band intensities for the Q₁ and Q₂ vibronic states compared with the B band intensity (54, 62), the electronic configuration is dominated by the (1b₁a, b₃a) configuration resulting from the configuration interaction between the (1b₁a, b₃a) and (1a₃a, b₃a) orbitals (61, 63). The larger VCS value follows because the orbital overlap is more symmetrical in VDB⁺. If we assume the electronic wavefunction
to be a 50%/50% mixing of the $3(b_{1u}, b_{3g})$ and $3(a_u, b_g)$ configurations in $^{3}H_2P^*$ (60), then $3D^* \approx 0.7 \times (b_{1u}, b_{3g}) + 0.7 \times (a_u, b_g)$, $4D_{ub}^*$ is 25% smaller than $4D_{ub}^*$ when $4D^* \approx 0.92 \times (b_{1u}, b_{3g}) - 0.46 \times (a_u, b_g)$ (Supporting Text) and $D^* \approx V_{1b}$ are considered. Adding the 10% contribution in the value difference that arises from the $\Delta E$ effect, an $\approx 35\%$ decrease in $V$ is expected in total for the primary CR to $^{3}H_2P^*$. This result is sufficiently compatible with the 38% decrease in the electronic coupling as shown in Fig. 5.

In $C_60$, the symmetry breaking occurs through the dynamic Jahn–Teller effect in the $T_1$ state (64). This effect was confirmed by the temperature dependence of the TREPR spectra of the $C_{60}^-$ moiety in the triad and is consistent with the smaller $V$ value for the CS from the $ZnP–3C^*$ in Table 2. We will report details of the dynamic Jahn–Teller effect elsewhere.

Conclusions. We have detailed a procedure for determining the electronic coupling for primary CR, a procedure that works even when the CR kinetics of the primary CS state cannot be observed. Accordingly, we have characterized the electronic couplings for the primary ET processes in the photoinduced CS system of $ZnP–H_2P–C_{60}$ by stepwise ET rates and by the $2J_2$ of the primary CS state. A 38% smaller $V$ has been found for the primary CR than for the primary CS and has been explained primarily by a loss in electronic-structure symmetry induced by state mixing in the excited triplet states. These findings demonstrate the importance of the excited-state electronic character in donor and acceptor complexes for designing molecular wires.

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