An Extremely Small Reorganization Energy of Electron Transfer in Porphyrin−Fullerene Dyad

**Hiroshi Imahori,* Nikolai V. Tkachenko,*,† Visa Vehmanen,† Koichi Tamaki,‡
Helge Lemmetyinen,† Yoshiteru Sakata,‡ and Shunichi Fukuzumi***

Department of Material and Life Science, Graduate School of Engineering, Osaka University, CREST, Japan Science and Technology Corporation, Suita, Osaka 565-0871, Japan, The Institute of Materials Chemistry, Tampere University of Technology, P.O. Box 541, FIN-33101 Tampere, Finland, and The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihoga-oka, Ibaraki, Osaka 567-0047, Japan

Received: September 12, 2000; In Final Form: December 18, 2000

Both charge-transfer absorption and emission have been observed in porphyrin-linked fullerene where the C_{60} moiety is closely located on the porphyrin plane. Electron-transfer parameters including reorganization energies, free energy changes, and electronic coupling matrix elements were determined by analyzing the charge-transfer absorption and emission in benzene. The reorganization energy is estimated as 0.23 ± 0.11 eV, which is the smallest value among inter- and intramolecular donor−acceptor systems ever reported and is comparable to the smallest ones for the primary charge separation in the photosynthetic reaction center. The results clearly show that fullerenes combined with porphyrins are potential components for constructing artificial photosynthetic systems.

Introduction

Photosynthesis is a natural energy-conversion system that converts solar energy to chemical energy. The primary electron transfer (ET) processes of photosynthesis are characterized by an extremely small reorganization energy ($\lambda = \sim 0.2$ eV).[1,2] This is essential in order to achieve the ultrafast forward ET and to retard the energy-wasting back ET (BET), which is highly exergonic ($-\Delta G^0{}_{\mathrm{BET}} = 1.1$ eV) and thereby deeply in the Marcus inverted region.[1,2] The photoexcitation leads to the production of the long-lived, charge-separated state with almost 100% efficiency across the transmembrane protein.[1] The reactants involved in the natural photosynthesis are chromophores (i.e., chlorophylls) holding highly delocalized π electron orbitals and are incorporated into the essentially nonpolar protein backbone, which leads to a small λ.[1]

There has been a widespread interest in synthesis of systems capable of mimicking the behavior of natural photosynthesis and thus providing artificial photosynthesis.[3−5] The Marcus inverted region is now well established, both in rigidly linked molecules[6] and in radical ion pair systems produced by intermolecular photoinduced ET.[7] However, the smallest λ values so far reported (∼0.5 eV)[3−10] are still significantly larger than the λ value for the natural photosynthetic system.[1] Since the Marcus equation for reorganization energy predicts that reorganization energy becomes smaller upon decreasing the donor−acceptor separation distance,[2] a small reorganization energy may be obtained when electron donor and acceptor molecules are covalently linked with a short bridge to place the donor moiety in the vicinity of the acceptor moiety. In such a case, one can expect to observe formation of an emitting charge-transfer (CT) state. The CT emissions have proven to be the key to accurate determination of ET parameters,[11] such as vibrational (λ_v) and solvent (λ_s) reorganization energies, driving force ($-\Delta G^0{}_{\mathrm{ET}}$), and electronic coupling matrix element (V), in intermolecular donor−acceptor systems.[7a,12] Although intramolecular CT emissions have been extensively studied,[13] there have so far been only a few reports on CT absorption or emission that was analyzed to give ET parameters in the intramolecular systems. In addition, relatively large λ values (>0.5 eV) have been reported for the linked donor−acceptor systems.[14]

Here we report the first experimental determination of the λ value for the CT emission of a porphyrin−fullerene dyad covalently linked with a short bridge, **ZnP−O34−C$_{60}$** (Figure 1). The reference compounds (**ZnP−O34** and **C$_{60}$−REF**) and other types of porphyrin-linked fullerenes, **ZnP−P34−C$_{60}$**, **ZnP−P23−C$_{60}$**, and **ZnP−M34−C$_{60}$**, used in this study are also shown in Figure 1.[15] The remarkably small reorganization energy (0.23 ± 0.11 eV) is deduced from the CT emission spectra of **ZnP−O34−C$_{60}$**, providing valuable information for the construction of artificial photosynthetic systems.

Experimental Section

Materials. Porphyrin-linked C_{60} (**ZnP−O34−C$_{60}$**, **ZnP−M34−C$_{60}$**, **ZnP−P23−C$_{60}$**, and **ZnP−P34−C$_{60}$**)[15] was obtained by the Diels−Alder reaction of the corresponding porphyrin *o*-quinodimethane produced from the dibromide in situ and C_{60}, followed by treatment with zinc acetate in $CHCl_3$. Porphyrin reference compounds (**ZnP−O34**, **ZnP−M34**, **ZnP−P23**, and **ZnP−P34**) were prepared by the coupling reaction of the corresponding aminoporphyrin and benzoic acid, followed by treatment with zinc acetate in $CHCl_3$, respectively.[15] **C$_{60}$−REF**[15] was synthesized from the corresponding dibromide and C_{60} by the same method as that described for porphyrin-linked fullerenes.

Structures of all new compounds were confirmed by spectroscopic analysis including ^{1}H-, ^{13}C-, and 2D-COSY NMR, IR, and FAB mass spectra.[15] Tetrahexylammonium perchlorate

---

* Corresponding authors. E-mail: imahori@ap.chem.eng.osaka-u.ac.jp; tkatchen@cc.tut.fi; fukuzumi@ap.chem.eng.osaka-u.ac.jp.

† Tampere University of Technology.

‡ The Institute of Scientific and Industrial Research, Osaka University.

10.1021/jp003207n CCC: $20.00

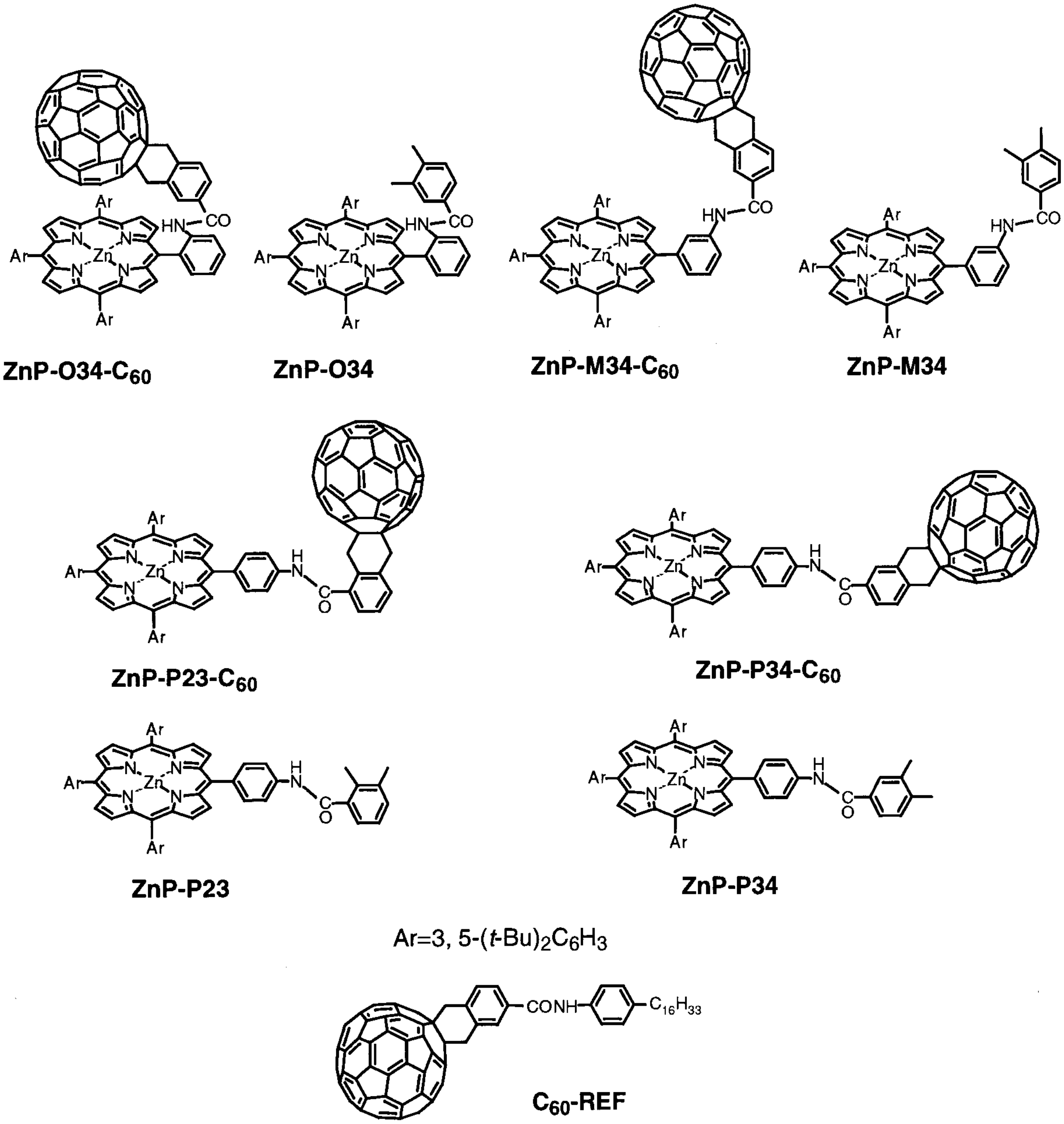

Figure 1. Molecular structures of model compounds.

(Hex_4NClO_4) was used as a supporting electrolyte for the electrochemical measurements. Hex_4NClO_4 was prepared from tetrahexylammonium bromide (Tokyo Kasei Organic Chemicals) and sodium perchlorate monohydrate (Wako Chemicals). Benzene and benzonitrile were purchased from Wako Pure Chemical Ind., Ltd., and purified by successive distillation over calcium hydride.

Spectral Measurements. To deduce the CT spectra, the difference spectra were measured under calibrated conditions on a Shimadzu UV-3100PC spectrophotometer. In a typical procedure, the spectrum of a benzene solution of **ZnP−O34−C_{60}** was first measured against a reference solution of the same solvent by using a matched pair of 10-mm quartz cuvettes. Next, the solution of the same concentration of **ZnP−O34** and **C_{60}−REF** was run against the same solvent using the same matched pair of 10-mm quartz cuvettes. It was confirmed that the sum of separately measured spectra of **ZnP−O34** and **C_{60}−REF** was the same as the spectrum of the solution containing the same concentration of both **ZnP−O34** and **C_{60}−REF**. The second spectrum was subtracted from that obtained in the first run to afford the CT spectrum. All transfers were effected with glass pipets to obviate contamination from trace metal impurities. In control experiments using a benzene solution of **ZnP−O34−C_{60}** or a mixed solution of the same concentration of **ZnP−O34** and **C_{60}−REF**, it was confirmed that no thermal or photochemical reaction occurred during the time required for the spectral measurements.

Steady-state fluorescence spectra were recorded using a Fluorolog 3 fluorimeter (SPEX Inc.). The emission was detected using a cooled, IR-sensitive photomultiplier (Hamamatsu R2658). The emission spectra were corrected using the correction function supplied by the manufacturer after subtracting the photomultiplier dark counts signal. The air-saturated samples were excited at 440 nm, slits were 3 nm for both excitation and emission monochromators, and the accumulation time was 5 s. These showed emission spectra, similar to those under the deaerated conditions. The concentrations were 10^{-6}~10^{-4} M for all the optical measurements.

Electrochemical Measurements. The cyclic voltammetry (CV) measurements were performed on a BAS 50W electro-

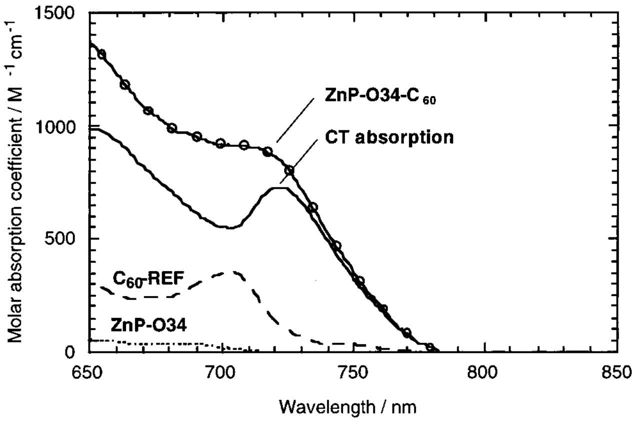

Figure 2. Absorption spectra of **ZnP−O34−C$_{60}$** (solid line with circles), **ZnP−O34** (dotted line), and **C$_{60}$−REF** (dashed line) in benzene and CT absorption of **ZnP−O34−C$_{60}$** in benzene (solid line). The contribution of absorption from the porphyrin and the C$_{60}$ has been subtracted to obtain the CT absorption.

chemical analyzer in deaerated benzene solution containing 1.2 M Hex$_4$NClO$_4$ as a supporting electrolyte at 40 °C (10 mV s^{-1}). The glassy carbon working electrode was polished with BAS polishing alumina suspension and rinsed with acetone before use. The counter electrode was a platinum wire. The measured potentials were recorded with respect to an Ag/AgCl (saturated KCl) reference electrode.

Fitting Procedure of the Emission Spectra. The emission spectra were converted from the wavelength to the energy domain, $I(\nu) = I(\lambda)\lambda^2$, where $\nu = c/\lambda$. A nonlinear curve-fitting algorithm utilizing mean least squares evaluation criterion was used to fit the spectra in the frequency domain to eq 2 taking into account only the four first summands, $j = 0, 1, 2, 3$ (see Results and Discussion).

Results and Discussion

We have earlier reported the synthesis, structures, and photophysical properties of porphyrin-linked fullerenes, in which a phenyl group has been employed to link the electron acceptor (C$_{60}$) to the porphyrin moiety.[15] Such a linkage with a phenyl group enabled a systematic variation of the linkage in the ortho-, meta-, and para-position of the phenyl group to afford **ZnP−O34−C$_{60}$**, **ZnP−M34−C$_{60}$**, **ZnP−P23−C$_{60}$**, and **ZnP−P34−C$_{60}$**, respectively, as shown in Figure 1.[15] The time-resolved transient absorption and fluorescence lifetime measurements revealed the formation of zinc porphyrin radical cation (ZnP$^{•+}$) and C$_{60}$ radical anion (C$_{60}$$^{•-}$) in nonpolar solvents as well as in polar solvents, regardless of the specific position of the linkage, indicating that the extent of CT is complete even in nonpolar solvents.[15−22] The reference compounds (**ZnP−O34**, **ZnP−M34**, **ZnP−P23**, **ZnP−P34**, and **C$_{60}$−REF**) were also made to determine the photophysical properties of the porphyrin and C$_{60}$ moieties (Figure 1).[15] From the ^{1}H NMR spectra, absorption spectra, and molecular mechanics calculations of **ZnP−O34−C$_{60}$**, the C$_{60}$ moiety is folded onto the porphyrin plane, leading to a van der Waals contact between the C$_{60}$ and two *tert*-butyl groups at meta-positions of the meso-phenyl groups (center-to-center distance (R_{cc}) = 7.6 Å, edge-to-edge distance (R_{ee}) = 3.2 Å).[15] This is in sharp contrast with other isomers, where the porphyrin and the C$_{60}$ were separated by a considerable distance [R_{cc} = 18.6 Å (**ZnP−P34−C$_{60}$**), R_{cc} = 14.4 Å (**ZnP−M34−C$_{60}$**), R_{cc} = 12.5 Å (**ZnP−P23−C$_{60}$**)].[15]

Figure 2 shows the enlarged absorption spectra (650−850 nm) of **ZnP−O34−C$_{60}$** and the reference compounds (**ZnP−O34** and **C$_{60}$−REF**) in benzene.[15] A broad and weak band is seen around 650−800 nm in **ZnP−O34−C$_{60}$**, as compared to **ZnP−O34** and **C$_{60}$−REF** (λ_{max} = 703 nm). The CT spectrum (λ_{max} = 721 nm) from **ZnP−O34−C$_{60}$** in benzene has been obtained by subtracting of the spectra of **ZnP−O34** and **C$_{60}$−REF** from that of **ZnP−O34−C$_{60}$** (see Experimental Section). In benzonitrile the CT band (λ_{max} = 724 nm) of **ZnP−O34−C$_{60}$** is broad and slightly red-shifted by 3 nm, relative to that in benzene. In contrast to the case of **ZnP−O34−C$_{60}$**, no CT absorption band was observed for **ZnP−P34−C$_{60}$**, **ZnP−M34−C$_{60}$**, and **ZnP−P23−C$_{60}$** in benzene as shown in Figure 3 for **ZnP−P34−C$_{60}$**. Furthermore, benzene solutions of **ZnP−O34** and **C$_{60}$−REF** show UV−visible spectra that are simply the superposition of the spectra of the two individual chromophores. This indicates that the close contact between the porphyrin plane and the C$_{60}$ moiety achieved only for **ZnP−O34−C$_{60}$**[23] (Figure 1) is essential for the observation of the CT spectrum.

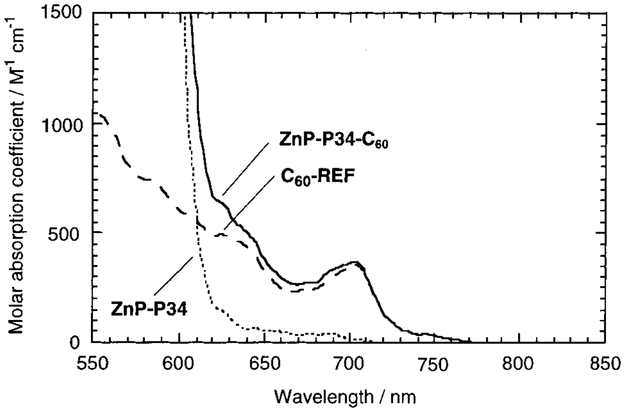

Figure 3. Absorption spectra of **ZnP−P34−C$_{60}$** (solid line), **ZnP−P34** (dotted line), and **C$_{60}$−REF** (dashed line) in benzene.

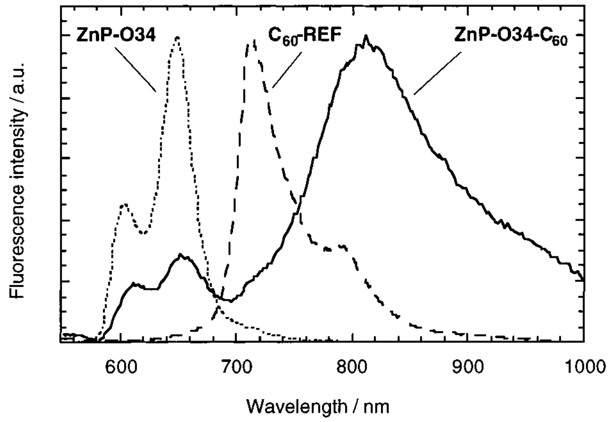

Figure 4. Fluorescence spectra of **ZnP−O34−C$_{60}$** (solid line, λ_{ex} = 440 nm), **ZnP−O34** (dotted line, λ_{ex} = 425 nm), and **C$_{60}$−REF** (dashed line, λ_{ex} = 370 nm) in benzene. The spectra are normalized for comparison.

Figure 4 displays emission spectra of **ZnP−O34−C$_{60}$**, **ZnP−O34**, and **C$_{60}$−REF** in benzene. The reference compounds (**ZnP−O34** and **C$_{60}$−REF**) exhibit fluorescence with typical peaks as zinc *meso*-tetraphenylporphyrins (λ_{max} = 605, 648 nm)[15] and monoadducts of C$_{60}$ (λ_{max} = 713, 787 nm),[15] respectively. In contrast, **ZnP−O34−C$_{60}$** shows relatively strong CT emission (λ_{max} = 810 nm) that extends into the near-infrared region,[24] in addition to weak emission from the porphyrin at 612 and 652 nm.[25] Emission from the C$_{60}$ moiety is negligible. The CT emission in benzonitrile becomes broader and weaker (see the Supporting Information, Figure S1), which is charac-

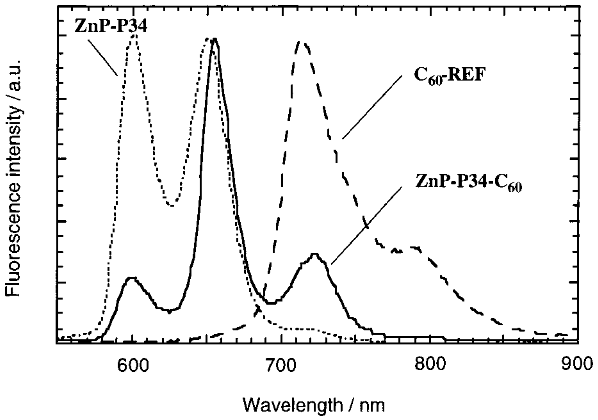

Figure 5. Fluorescence spectra of **ZnP−P34−C$_{60}$** (solid line, λ_{ex} = 425 nm), **ZnP−P34** (dotted line, λ_{ex} = 425 nm), and **C$_{60}$−REF** (dashed line, λ_{ex} = 370 nm) in benzene. The spectra are normalized for comparison.

teristic of CT emission in donor−acceptor systems.[26] It is interesting to note that there was no CT emission in the solution containing a mixture of the same concentrations of the reference compounds (**ZnP−O34** and **C$_{60}$−REF**). As it was the case of the CT absorption, no CT emission was observed for **ZnP−P34−C$_{60}$**, **ZnP−M34−C$_{60}$**, or **ZnP−P23−C$_{60}$** in benzene, as shown in Figure 5 for **ZnP−P34−C$_{60}$**. This also indicates that the close disposition and the resulting relatively strong interaction between the porphyrin and C$_{60}$ moieties[23] are required for the observation of the CT emission as well as the CT absorption.[10f]

It should be noted here that even in polar solvents such as benzonitrile the CT emission for **ZnP−O34−C$_{60}$** can be detected, whereas the conventional donor−acceptor systems typically exhibit CT emission in only nonpolar and moderately polar solvents.[7a,11−14,27] The small Stokes shift of the CT emission (**ZnP−O34−C$_{60}$**: 1530 cm^{-1}) in benzene supports the rigid framework of C$_{60}$ in both the excited and the ground states. The energy difference nearly equals 2λ,[11,13e] resulting in $\lambda = 0.10 \pm 0.02$ eV for **ZnP−O34−C$_{60}$**. This value is much smaller than the vibrational reorganization energy (0.3 eV)[28] estimated using the CT absorption of C$_{60}$ in pure diethylaniline (550 nm)[29a] and the CT emission of C$_{60}$ in methylcyclohexane containing 0.1 M diethylaniline (740 nm).[29b−e] The total reorganization energy is quite consistent with the small vibrational reorganization energy (0.06 eV for C$_{60}$) obtained from theoretical calculation.[30] The small Stokes and Raman shifts reported in the photoexcitation and reduction of fullerenes support the rigid structure of C$_{60}$, where the vibrational reorganization energy is small.[31]

According to the semiclassical Marcus theory, the ET rate constant (k_{et}) is expressed by eq 1:[32]

$$k_{et} = \sum_{j=0}^{\infty}\left[\exp\left(-\frac{\lambda_v}{h\nu_v}\right)\right]\left(\frac{\lambda_v}{h\nu_v}\right)^j\left(\frac{V^2}{j!}\right)\left(\frac{4\pi^3}{h^2\lambda_s k_B T}\right)^{1/2} \exp\left[-\frac{(jh\nu_v + \Delta G^0_{BET} + \lambda_s)^2}{4\lambda_s k_B T}\right] \quad (1)$$

High-frequency ($h\nu \gg k_BT$) skeletal vibrations of the donor and acceptor are represented by a single "average mode" (the v mode), with a fixed frequency, ν_v, and vibrational reorganization energy, λ_v, which is associated with changes in the nuclear positions of the species undergoing ET. Low-frequency ($h\nu \ll k_BT$) motions associated with the solvent reorientation are given by a solvent reorganization energy, λ_s. Each summand in eq 1 represents the ET rate for a single contribution to the total ET rate from a $j \leftarrow 0$ nonradiative vibronic transition. Overall, the ET rate constant is proportional to a square of the electronic coupling matrix element, V^2, which is assumed to be small or moderate to fulfill the conditions of a nonadiabatic process.

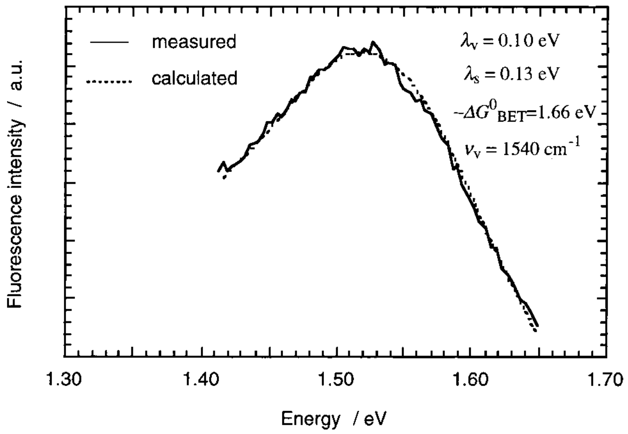

Figure 6. CT emission spectrum of **ZnP−O34−C$_{60}$** in benzene. The contribution of emission from the excited singlet states of the porphyrin and the C$_{60}$ has been subtracted. The fit of the curve based on the Marcus model (eq 2) is shown by the dotted line (see text for the best fit BET parameters).

It is well-established that there is a close relationship between thermal ET and radiative CT spectra.[11] The intensity of emission (photons per molecule per unit time per unit spectral energy) is given by eq 2, which is similar to the expression for the ET rate, eq 1:

$$I(\nu) = \left[n\left(\frac{n^2+2}{3}\right)^2\right]\left(\frac{16\pi^2\tilde{\nu}_f^3}{3}\right) \times \sum_{j=0}^{\infty}\left[\exp\left(-\frac{\lambda_v}{h\nu_v}\right)\right]\left(\frac{\lambda_v}{h\nu_v}\right)^j\left(\frac{M^2}{j!}\right)\left(\frac{4\pi^3}{h^2\lambda_s k_B T}\right)^{1/2} \exp\left[-\frac{(jh\nu_v + \Delta G^0_{BET} + \lambda_s + h\nu_f)^2}{4\lambda_s k_B T}\right] \quad (2)$$

Here n is the refractive index of the solvent, M is the magnitude of the electronic transition moment (dipole length form), ν_f is the frequency, and $h\nu_f$ is the energy of the emitted photon. In a simple model, M is related to the electronic coupling matrix element (V), the energy of maximum emission intensity [$(h\nu_f)_{max}$], and the static dipole moment of the ion pair state (μ_{cp}), as shown in eq 3:[33,34]

$$M = \frac{V\mu_{cp}}{(h\nu_f)_{max}} \quad (3)$$

Thus, an analysis of the CT emission spectra of **ZnP−O34−C$_{60}$** according to eq 2 would provide an independent method for evaluating the ET parameters of eq 1. It is important to note that the value of M^2 has an effect on intensity of the emission only, but the shape of the spectrum and position of its maximum are independent of M^2 (i.e., V^2) and totally determined by four parameters, namely λ_v, λ_s, $-\Delta G^0_{BET}$, and ν_v. The CT emission spectrum from **ZnP−O34−C$_{60}$** in benzene has been fitted using the Marcus model to determine the BET parameters as shown in Figure 6 (see Experimental Section).[12,14,35] The best fit values of **ZnP−O34−C$_{60}$** for λ_v, λ_s, $-\Delta G^0_{BET}$, ν_v in benzene are 0.10 eV, 0.13 eV, 1.66 eV, 1540 cm^{-1}, respectively, with experimental accuracies of ±0.01 eV for λ_s and $-\Delta G^0_{BET}$, and ±0.1 eV for λ_v and ν_v.[36] Since the ratio $\lambda_v/h\nu_v$ is less than unity, a few first summands in eq 2 determine the shape of the emission band, and the contribution of the transitions to higher vibrational modes is negligible. Therefore, the sum can be limited by $j = 3$ for a successful least-squares fitting.

The one-electron oxidation potential (E^0_{ox}) of the ZnP moiety of **ZnP−O34−C$_{60}$** in benzene containing 1.2 M Hex$_4$NClO$_4$ was determined as 1.01 V (vs Ag/AgCl (saturated KCl) (see Experimental Section).[37] The one-electron reduction potential (E^0_{red}) of the C$_{60}$ moiety of **ZnP−O34−C$_{60}$** in benzene containing 1.2 M Hex$_4$NClO$_4$ was also determined as −0.38 V (vs Ag/AgCl (saturated KCl)).[38] From the E^0_{ox} and E^0_{red} values one can determine the free energy change of BET from the C$_{60}$ to the ZnP moiety of **ZnP−O34−C$_{60}$** ($-\Delta G^0_{BET}$) in benzene as 1.39 eV. This value is smaller than the $-\Delta G^0_{BET}$ value (1.66 eV) evaluated on the basis of the CT emission spectrum of **ZnP−O34−C$_{60}$** (vide supra). Such a difference may be mainly attributed to the presence of the high concentration of an electrolyte (1.2 M Hex$_4$NClO$_4$) required for the cyclic voltammetric measurements in benzene, which results in a decrease in the free energy change of BET as compared to that in the absence of an electrolyte.[39] In fact, the $-\Delta G^0_{BET}$ value of **ZnP−P23−C$_{60}$** in benzene was reported to be 1.73 eV on the basis of the energetic equilibrium between **ZnP$^{•+}$−P23−C$_{60}^{•-}$** and **ZnP−P23−^{1}C$_{60}$***.[15] The Coulombic stabilization of **ZnP$^{•+}$−O34−C$_{60}^{•-}$** may be larger than that of **ZnP$^{•+}$−P23−C$_{60}^{•-}$** in benzene, since the separation distance between the porphyrin and the C$_{60}$ in **ZnP−O34−C$_{60}$** (R_{cc} = 7.6 Å) is smaller than that in **ZnP−P23−C$_{60}$** (R_{cc} = 12.5 Å). This justifies the somewhat smaller $-\Delta G^0_{BET}$ value of **ZnP−O34−C$_{60}$** (1.66 eV), as compared to that of **ZnP−P23−C$_{60}$** (1.73 eV).

It is also possible to estimate the electronic coupling matrix element V from CT absorption (eq 4)[40]

$$V = \frac{2.06 \times 10^{-2}}{R_{cc}}(\epsilon_{max}\nu_{max}\Delta\nu_{1/2})^{1/2} \qquad (4)$$

where ϵ_{max} and ν_{max} represent the molar extinction coefficient (M^{-1} cm^{-1}) and the energy (cm^{-1}) of the CT absorption, respectively, and $\Delta\nu_{1/2}$ is the bandwidth at half-maximum (cm^{-1}). From the CT absorption in benzene, one can deduce the following parameters for **ZnP−O34−C$_{60}$**: ϵ_{max} = 745 M^{-1} cm^{-1}, ν_{max} = 13 900 cm^{-1}, $\Delta\nu_{1/2}$ = 940 cm^{-1}. Given the above data, the V value of **ZnP−O34−C$_{60}$** is also calculated as 270 cm^{-1}.[41] This V value is significantly larger than typical values for the solvent-separated (SSRIP) radical-ion pair (∼12 cm^{-1}),[7a] indicating that the radical ion-pair of **ZnP$^{•+-}$O34−C$_{60}^{•-}$** is in close contact to form contact radical-ion pair (CRIP), which generally exhibits almost 2 orders of magnitude larger V value (∼750 cm^{-1}).[7a] In general, the solvent reorganization energy for BET in the CRIP produced by an intermolecular photoinduced ET (∼0.5 eV) is much smaller than that for the SSRIP, since reduced interpenetration of outer shell solvent molecules around the radical ions in the CRIP, in addition to no extra solvent molecules between the radical ions, results in the smaller solvent reorganization energies as compared to those for the SSRIP (∼1.6 eV).[7a]

The small total reorganization energy ($\lambda = \lambda_v + \lambda_s$) determined for BET in the radical ion-pair of **ZnP$^{•+}$−O34−C$_{60}^{•-}$** (0.23 ± 0.11 eV) is consistent with the value (0.10 ± 0.02 eV) obtained from the Stokes shift between the CT absorption and emission.[42,43] The λ value is much smaller than those reported previously for porphyrin−quinone (0.5−1.8 eV)[8] and bisporphyrin-linked systems (0.5−1.5 eV).[9] In addition, the experimental value is small, as compared to the calculated values in donor−C$_{60}$ linked systems (i.e., λ = 0.67 eV and R_{cc} = 9 Å in toluene for the aniline−C$_{60}$ system[28] and λ = 1.11 eV and R_{cc} = 20.4 Å in benzonitrile for the porphyrin−C$_{60}$ system[18b]) and the experimental values in intermolecular ET systems involving fullerenes [λ = 0.60 eV in dichloromethane for one-electron oxidation of C$_{76}$ and C$_{78}$ by arene radical cations[10b] and λ = 0.64 eV in benzonitrile/benzene (1:7 v/v) for electron exchange between *t*-BuC$_{60}^{-}$ and *t*-BuC$_{60}^{•}$ [10c]].

More important, the λ value is comparable to the smallest ones (0.22 ± 0.16 eV) in the photosynthetic reaction center where the primary charge separation takes place from the excited state of the special pair to the active-branch pheophytin via a two-step sequential mechanism or a one-step superexchange mechanism.[1] The small λ value in **ZnP−O34−C$_{60}$** may be ascribed to the large π systems in which an electron and a hole are delocalized over a three-dimensional framework of the porphyrin and the C$_{60}$, respectively.[5,10a,b,e,f,16b,17f] Other important conditions to achieve the small λ value are the short linkage between the porphyrin and the C$_{60}$ in **ZnP−O34−C$_{60}$** and the use of a nonpolar solvent (benzene).

In conclusion, the reorganization energy of ET in porphyrin-linked fullerene has been determined by analyzing the CT emission in benzene. The experimental value (0.23 ± 0.11 eV) is the smallest value among inter- and intramolecular donor−acceptor systems ever reported and is comparable to the smallest ones for the primary charge separation in a photosynthetic reaction center. Thus, an intramolecular charge separation system consisting of porphyrins and fullerenes can mimic efficient photosynthetic charge separation without the special surrounding environment (i.e., protein matrix).

Acknowledgment. This work was supported by Grant-in-Aids for COE Research and Scientific Research on Priority Area of Electrochemistry of Ordered Interfaces and Creation of Delocalized Electronic Systems from Ministry of Education, Science, Sports and Culture, Japan, and the National Program on Material and Structure Research, Academy of Finland. H.I. thanks the Sumitomo Foundation for financial support.

Supporting Information Available: Fluorescence spectrum of **ZnP−O34−C$_{60}$** in benzonitrile (Figure S1). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Woodbury, N. W.; Allen, J. P. In *Anoxygenic Photosynthetic Bacteria*; Blankenship, R. E., Madigan, M. T., Bauer, C. E., Eds.; Kluwer Academic Publishers: Dordecht, 1995; Chapter 24, pp 527−557. (b) Moser, C. C.; Keske, J. M.; Warncke, K.; Farid, R. S.; Dutton, P. L. *Nature* **1992**, *355*, 796. (c) Moser, C. C.; Keske, J. M.; Warncke, K.; Farid, R. S.; Dutton, P. L. In *The Photosynthetic Reaction Center*; Deisenhofer, J., Norris, J. R., Eds.; Academic Press: San Diego, 1993; Vol. 2, Chapter 1, pp 1−22. (d) Iwaki, M.; Kumazaki, S.; Yoshihara, K.; Erabi, T.; Itoh, S. *J. Phys. Chem.* **1996**, *100*, 10802.

(2) (a) Marcus, R. A. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1111. (b) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265.

(3) (a) Meyer, T. J. *Acc. Chem. Res.* **1989**, *22*, 163. (b) Bard, A. J.; Fox, M. A. *Acc. Chem. Res.* **1995**, *28*, 141. (c) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435. (d) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **1993**, *26*, 198. (e) 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.

(4) (a) Chambron, J.-C.; Chardon-Noblat, S.; Harriman, A.; Heitz, V.; Sauvage, J.-P. *Pure Appl. Chem.* **1993**, *65*, 2343. (b) Paddon-Row, M. N. *Acc. Chem. Res.* **1994**, *27*, 18. (c) Kurreck, H.; Huber, M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 849. (d) Balzani, V.; Juris, A.; Venturi, M.;

Campagna, S.; Serroni, S. *Chem. Rev.* **1996**, *96*, 759. (e) Osuka, A.; Mataga, N.; Okada, T. *Pure Appl. Chem.* **1997**, *69*, 797. (f) Blanco, M.-J.; Jiménez, M. C.; Chambron, J.-C.; Heitz, V.; Linke, M.; Sauvage, J.-P. *Chem. Soc. Rev.* **1999**, *28*, 293. (g) Verhoeven, J. W. In *Electron Transfer*; Jortner, J., Bixon, M., Eds.; John Wiley & Sons: New York, 1999; Part 1, pp 603−644.

(5) (a) Imahori, H.; Sakata, Y. *Eur. J. Org. Chem.* **1999**, 2445. (b) Guldi, D. M. *Chem. Commun.* **2000**, 321.

(6) (a) Miller, J. R.; Calcaterra, L. T.; Closs, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 3047. (b) Closs, G. L.; Miller, J. R. *Science* **1988**, *240*, 440. (c) Wasielewski, M. R.; Niemczyk, M. P.; Svec, W. A.; Pewitt, E. B. *J. Am. Chem. Soc.* **1985**, *107*, 1080.

(7) (a) Gould, I. R.; Farid, S. *Acc. Chem. Res.* **1996**, *29*, 522. (b) Mataga, N.; Kanda, Y.; Okada, T. *J. Phys. Chem.* **1986**, *90*, 3880. (c) Mataga, N.; Miyasaka, H. In *Electron Transfer*; Jortner, J., Bixon, M., Eds.; John Wiley & Sons: New York, 1999; Part 2, pp 431−496.

(8) (a) Harrison, R. J.; Pearce, B.; Beddard, G. S.; Cowan, J. A.; Sanders, J. K. M. *Chem. Phys.* **1987**, *116*, 429. (b) Asahi, T.; Ohkohchi, M.; Matsusaka, R.; Mataga, N.; Zhang, R. P.; Osuka, A.; Maruyama, K. *J. Am. Chem. Soc.* **1993**, *115*, 5665. (c) Khundkar, L. R.; Perry, J. W.; Hanson, J. E.; Dervan, P. B. *J. Am. Chem. Soc.* **1994**, *116*, 9700. (d) Heitele, H.; Pöllinger, F.; Häberle, T.; Michel-Beyerle, M. E.; Staab, H. A. *J. Phys. Chem.* **1994**, *98*, 7402. (e) Macpherson, A. N.; Liddell, P. A.; Lin, S.; Noss, L.; Seely, G. R.; DeGraziano, J. M.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Am. Chem. Soc.* **1995**, *117*, 7202. (f) Häberle, T.; Hirsch, J.; Pöllinger, F.; Heitele, H.; Michel-Beyerle, M. E.; Ander, C.; Döhling, A.; Krieger, C.; Rückemann, A.; Staab, H. A. *J. Phys. Chem.* **1996**, *100*, 18269. (g) Tsue, H.; Imahori, H.; Kaneda, T.; Tanaka, Y.; Okada, T.; Tamaki, K.; Sakata, Y. *J. Am. Chem. Soc.* **2000**, *122*, 2279.

(9) (a) Harriman, A.; Heitz, V.; Sauvage, J.-P. *J. Phys. Chem.* **1993**, *97*, 5940. (b) DeGraziano, J. M.; Liddell, P. A.; Leggett, L.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Phys. Chem.* **1994**, *98*, 1758. (c) DeGraziano, J. M.; Macpherson, A. N.; Liddell, P. A.; Noss, L.; Sumida, J. P.; Seely, G. R.; Lewis, J. E.; Moore, A. L.; Moore, T. A.; Gust, D. *New J. Chem.* **1996**, *20*, 839. (d) Osuka, A.; Noya, G.; Taniguchi, S.; Okada, T.; Nishimura, Y.; Yamazaki, I.; Mataga, N. *Chem. Eur. J.* **2000**, *6*, 33.

(10) (a) Imahori, H.; Hagiwara, K.; Akiyama, T.; Aoki, M.; Taniguchi, S.; Okada, T.; Shirakawa, M.; Sakata, Y. *Chem. Phys. Lett.* **1996**, *263*, 545. (b) Guldi, D. M.; Asmus, K.-D. *J. Am. Chem. Soc.* **1997**, *119*, 5744. (c) Fukuzumi, S.; Nakanishi, I.; Suenobu, T.; Kadish, K. M. *J. Am. Chem. Soc.* **1999**, *121*, 3468. (d) Williams, R. M.; Koeberg, M.; Lawson, J. M.; An, Y.-Z.; Rubin, Y.; Paddon-Row, M. N.; Verhoeven, J. W. *J. Org. Chem.* **1996**, *61*, 5055. (e) Imahori, H.; Tamaki, K.; Yamada, H.; Yamada, K.; Sakata, Y.; Nishimura, Y.; Yamazaki, I.; Fujitsuka, M.; Ito, O. *Carbon* **2000**, *38*, 1599. (f) Tkachenko, N. V.; Guenther, C.; Imahori, H.; Tamaki, K.; Sakata, Y.; Fukuzumi, S.; Lemmetyinen, H. *Chem. Phys. Lett.* **2000**, *326*, 344.

(11) Marcus, R. A. *J. Phys. Chem.* **1989**, *93*, 3078.

(12) Gould, I. R.; Young, R. H.; Moody, R. E.; Farid, S. *J. Phys. Chem.* **1991**, *95*, 2068.

(13) (a) Chandross, E. A.; Thomas, H. T. *Chem. Phys. Lett.* **1971**, *9*, 393. (b) Pasman, P.; Verhoeven, J. W.; de Boer, T. J. *Chem. Phys. Lett.* **1978**, *59*, 381. (c) Okada, T.; Karaki, I.; Matsuzawa, E.; Mataga, N.; Sakata, Y.; Misumi, S. *J. Phys. Chem.* **1981**, *85*, 3957. (d) Pasman, P.; Mes, G. F.; Koper, N. W.; Verhoeven, J. W. *J. Am. Chem. Soc.* **1985**, *107*, 5839. (e) Oevering, H.; Paddon-Row, M. N.; Heppener, M.; Oliver, A. M.; Cotsaris, E.; Verhoeven, J. W.; Hush, N. S. *J. Am. Chem. Soc.* **1987**, *109*, 3258. (f) Heitele, H.; Finckh, P.; Michel-Beyerle, M. E. *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 619. (g) Wasielewski, M. R.; Minsek, D. W.; Niemczyk, M. P.; Svec, W. A.; Yang, N. C. *J. Am. Chem. Soc.* **1990**, *112*, 2823. (h) Gust, D.; Moore, T. A.; Luttrull, D. K.; Seely, G. R.; Bittersmann, E.; Bensasson, R. V.; Rougée, M.; Land, E. J.; De Schryver, F. C.; Van der Auweraer, M. *Photochem. Photobiol.* **1990**, *51*, 419. (i) Kamioka, K.; Cormier, R. A.; Lutton, T. W.; Connolly, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 4414.

(14) (a) Zeng, Y.; Zimmt, M. B. *J. Phys. Chem.* **1992**, *96*, 8395. (b) Wynne, K.; LeCours, S. M.; Galli, C.; Therien, M. J.; Hochstrasser, R. M. *J. Am. Chem. Soc.* **1995**, *117*, 3749. (c) Claude, J. P.; Williams, D. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 9782.

(15) Imahori, H.; Hagiwara, K.; Aoki, M.; Akiyama, T.; Taniguchi, S.; Okada, T.; Shirakawa, M.; Sakata, Y. *J. Am. Chem. Soc.* **1996**, *118*, 11771.

(16) (a) Martín, N.; Sánchez, L.; Illescas, B.; Pérez, I. *Chem. Rev.* **1998**, *98*, 2527. (b) Imahori, H.; Sakata, Y. *Adv. Mater.* **1997**, *9*, 537. (c) Prato, M. *J. Mater. Chem.* **1997**, *7*, 1097. (d) Diederich, F.; Gómez-López, M. *Chem. Soc. Rev.* **1999**, *28*, 263. (e) Sun, Y.-P.; Riggs, J. E.; Guo, Z.; Rollins, H. W. In *Optical and Electronic Properties of Fullerenes and Fullerene-Based Materials*; Shinar, J., Vardeny, Z. V., Kafafi, Z. H., Eds.; Marcel Dekker: New York, 2000; pp 43−81. (f) Guldi, D. M.; Kamat, P. V. In *Fullerenes*; Kadish, K. M., Ruoff, R. S., Eds.; John Wiley & Sons: New York, 2000; pp 225−281.

(17) (a) Liddell, P. A.; Sumida, J. P.; Macpherson, A. N.; Noss, L.; Seely, G. R.; Clark, K. N.; Moore, A. L.; Moore, T. A.; Gust, D. *Photochem. Photobiol.* **1994**, *60*, 537. (b) Kuciauskas, D.; Lin, S.; Seely, G. R.; Moore, A. L.; Moore, T. A.; Gust, D.; Drovetskaya, T.; Reed, C. A.; Boyd, P. D. W. *J. Phys. Chem.* **1996**, *100*, 15926. (c) Liddell, P. A.; Kuciauskas, D.; Sumida, J. P.; Nash, B.; Nguyen, D.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Am. Chem. Soc.* **1997**, *119*, 1400. (d) Carbonera, D.; Valentin, M. D.; Corvaja, C.; Agostini, G.; Giacometti, G.; Liddell, P. A.; Kuciauskas, D.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Am. Chem. Soc.* **1998**, *120*, 4398. (e) Kuciauskas, D.; Liddell, P. A.; Lin, S.; Johnson, T. E.; Weghorn, S. J.; Lindsey, J. S.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Am. Chem. Soc.* **1999**, *121*, 8604. (f) Kuciauskas, D.; Liddell, P. A.; Lin, S.; Stone, S. G.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Phys. Chem. B* **2000**, *104*, 4307.

(18) (a) Baran, P. S.; Monaco, R. R.; Khan, A. U.; Schuster, D. I.; Wilson, S. R. *J. Am. Chem. Soc.* **1997**, *119*, 8363. (b) Bell, T. D. M.; Smith, T. A.; Ghiggino, K. P.; Ranasinghe, M. G.; Shephard, M. J.; Paddon-Row: M. N. *Chem. Phys. Lett.* **1997**, *268*, 223. (c) Schuster, D. I.; Cheng, P.; Wilson, S. R.; Prokhorenko, V.; Katterle, M.; Holzwarth, A. R.; Braslavsky, S. E.; Klihm, G.; Williams, R. M.; Luo, C. *J. Am. Chem. Soc.* **1999**, *121*, 11599.

(19) (a) Guldi, D. M.; Luo, C.; Prato, M.; Dietel, E.; Hirsch, A. *Chem. Commun.* **2000**, 373. (b) Guldi, D. M.; Luo, C.; Da Ros, T.; Prato, M.; Dietel, E.; Hirsch, A. *Chem. Commun.* **2000**, 375. (c) Armaroli, N.; Diederlich, F.; Echegoyen, L.; Habicher, T.; Flamigni, L.; Marconi, G.; Nierengarten, J.-F. *New. J. Chem.* **1999**, 77. (d) Da Ros, T.; Prato, M.; Guldi, D. M.; Alessio, E.; Ruzzi, M.; Pasimeni, L. *Chem. Commun.* **1999**, 635. (e) Tkachenko, N. V.; Rantala, L.; Tauber, A. Y.; Helaja, J.; Hynninen, P. H.; Lemmetyinen, H. *J. Am. Chem. Soc.* **1999**, *121*, 9378. (f) Armaroli, N.; Marconi, G.; Echegoyen, L.; Bourgeois, J.-P.; Diederlich, F. *Chem. Eur. J.* **2000**, *6*, 1629.

(20) (a) Imahori, H.; Hagiwara, K.; Akiyama, T.; Taniguchi, S.; Okada, T.; Sakata, Y. *Chem. Lett.* **1995**, 265. (b) Imahori, H.; Sakata, Y. *Chem. Lett.* **1996**, 199. (c) Sakata, Y.; Imahori, H.; Tsue, H.; Higashida, S.; Akiyama, T.; Yoshizawa, E.; Aoki, M.; Yamada, K.; Hagiwara, K.; Taniguchi, S.; Okada, T. *Pure Appl. Chem.* **1997**, *69*, 1951. (d) Tamaki, K.; Imahori, H.; Nishimura, Y.; Yamazaki, I.; Shimomura, A.; Okada, T.; Sakata, Y. *Chem. Lett.* **1999**, 227. (e) Imahori, H.; Ozawa, S.; Ushida, K.; Takahashi, M.; Azuma, T.; Ajavakom, A.; Akiyama, T.; Hasegawa, M.; Taniguchi, S.; Okada, T.; Sakata, Y. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 485. (f) Yamada, K.; Imahori, H.; Nishimura, Y.; Yamazaki, I.; Sakata, Y. *Chem. Lett.* **1999**, 895. (g) Imahori, H.; El-Khouly, M. E.; Fujitsuka, M.; Ito, O.; Sakata, Y.; Fukuzumi, S. *J. Phys. Chem. A* **2001**, *105*, 325.

(21) (a) Imahori, H.; Yamada, K.; Hasegawa, M.; Taniguchi, S.; Okada, T.; Sakata, Y. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2626. (b) Higashida, S.; Imahori, H.; Kaneda, T.; Sakata, Y. *Chem. Lett.* **1998**, 605. (c) Tamaki, K.; Imahori, H.; Nishimura, Y.; Yamazaki, I.; Sakata, Y. *Chem. Commun.* **1999**, 625. (d) Imahori, H.; Yamada, H.; Ozawa, S.; Ushida, K.; Sakata, Y. *Chem. Commun.* **1999**, 1165. (e) Fujitsuka, M.; Ito, O.; Imahori, H.; Yamada, K.; Yamada, H.; Sakata, Y. *Chem. Lett.* **1999**, 721. (f) Imahori, H.; Yamada, H.; Nishimura, Y.; Yamazaki, I.; Sakata, Y. *J. Phys. Chem. B* **2000**, *104*, 2099. (g) Luo, C.; Guldi, D. M.; Imahori, H.; Tamaki, K.; Sakata, Y. *J. Am. Chem. Soc.* **2000**, *122*, 6535. (h) Imahori, H.; Norieda, H.; Yamada, H.; Nishimura, Y.; Yamazaki, I.; Sakata, Y.; Fukuzumi, S. *J. Am. Chem. Soc.* **2001**, *123*, 100.

(22) It is well-established that in polar solvents porphyrin-C_{60} linked systems yield the charge-separated state via photoinduced ET.[16] Some of them are reported to produce the charge-separated state even in nonpolar solvents.[10a,15,16b,17f,18c,19a,20g]

(23) It is known that porphyrin and fullerene make remarkably close contact in the solid state: (a) Boyd, P. D. W.; Hodgson, M. C.; Rickard, C. E. F.; Oliver, A. G.; Chaker, L.; Brothers, P. J.; Bolskar, R. D.; Tham, F. S.; Reed. C. A. *J. Am. Chem. Soc.* **1999**, *121*, 10487. (b) Olmstead, M. M.; Costa, D. A.; Maitra, K.; Noll, B. C.; Phillips, S. L.; Van Calcar, P. M.; Balch, A. L. *J. Am. Chem. Soc.* **1999**, *121*, 7090.

(24) Recently CT absorption and emission of porphyrin-linked C_{60}[19f] and CT emission of chlorin-linked C_{60}[19e] in toluene have been reported, respectively.

(25) The fluorescence lifetime of **ZnP−O34−C_{60}** in benzene was reported to be 81 ps at 610 nm, which is much shorter than that of **ZnP−O34** (2.0 ns).[15] This rules out the possibility that the emitting species is due to the porphyrin-only impurity.

(26) (a) Beens, H.; Weller, A. In *Organic Molecular Photophysics*; Birks, J. B., Ed.; Wiley: New York, 1975; Vol. 2, Chapter 4. (b) Mataga, N.: Ottolenghi, M. In *Molecular Association*; Foster, R., Ed.; Academic Press: New York, 1979; Vol. 2, p 1.

(27) There are several reports on CT emission of donor−acceptor linked compounds in polar solvents.[4g,13b,d]

(28) Williams, R. M.; Zwier, J. M.; Verhoeven, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 4093.

(29) (a) Wang, Y.; Cheng, L.-T. *J. Phys. Chem.* **1992**, *96*, 1530. (b) Wang, Y. *J. Phys. Chem.* **1992**, *96*, 764. (c) Seshadri, R.; Rao, C. N. R.; Pal, H.; Mukherjee, T.; Mittal, J. P. *Chem. Phys. Lett.* **1993**, *205*, 395. (d) Sun, Y.-P.; Bunker, C. E.; Ma, B. *J. Am. Chem. Soc.* **1994**, *116*, 9692. (e) Rath, M. C.; Pal, H.; Mukherjee, T. *J. Phys. Chem. A* **1999**, *103*, 4993.

(30) Larsson, S.; Klimkãns, A.; Rodriguez-Monge, L.; Duškesas, G. *J. Mol. Struct.* **1998**, *425*, 155.

(31) McGlashen, M. L.; Blackwood, M. E., Jr.; Spiro, T. G. *J. Am. Chem. Soc.* **1993**, *115*, 2074.

(32) (a) Hopfield, J. J. *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*, 3640. (b) Van Duyne, R. P.; Fischer, S. F. *Chem. Phys.* **1974**, *5*, 183. (c) Ulstrup, J.; Jortner, J. *J. Chem. Phys.* **1975**, *63*, 4358. (d) Siders, P.; Marcus, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 741, 748. (e) Marcus, R. A. *J. Chem. Phys.* **1984**, *81*, 4494.

(33) Knoester, J.; Mukamel, S. *Phys. Rev. A* **1989**, *40*, 7065.

(34) Cannon, R. D. *Electron Transfer Reactions*; Butterworths: Boston, 1980; Section 8.3.

(35) The emission in polar solvents such as benzonitrile was too weak to be analyzed accurately according to eq 2.

(36) The estimation of the standard deviations does not take into account the possible inaccuracy of the spectrum correction.

(37) For the reported E^0_{ox} values of ZnP in benzene, see: Geng, L.; Ewing, A. G. G.; Jernigan, J. C.; Murray, R. W. *Anal. Chem.* **1986**, *58*, 852.

(38) For the reported E^0_{red} values of C_{60} in various solvents, see: Dubois, D.; Moninot, G.; Kutner, W.; Jones, M. T.; Kadish, K. M. *J. Phys. Chem.* **1992**, *96*, 7137.

(39) The $-\Delta G^0_{\mathrm{BET}}$ value determined from the redox potentials includes the effects of high concentrations of electrolytes in benzene, whereas the $-\Delta G^0_{\mathrm{BET}}$ value derived from the CT emission includes the electrostatic interaction in the absence of electrolytes. Both effects may result in a decrease in the $-\Delta G^0_{\mathrm{BET}}$ value.

(40) Barbara, P. F.; Meyer, T. J.; Ratner, M. A. *J. Phys. Chem.* **1996**, *100*, 13148.

(41) Owing to a large uncertainty in estimating the quantum yield for the CT emission in the near-infrared region, the *V* value was determined only from the CT absorption data. Oliver, A. M.; Paddon-Row, M. N.; Kroon, J.; Verhoeven, J. W. *Chem. Phys. Lett.* **1992**, *191*, 371.

(42) The reorganization energy derived from the Stokes shift is known to be slightly smaller than the actual value; see: Mertz, E. L.; Tikhomirov, V. A.; Krishtalik, L. I. *J. Phys. Chem. A* **1997**, *101*, 3433.

(43) A small λ value can also be obtained from the k_{ET} (1.0×10^{10} s^{-1}),[15] V (270 cm^{-1}), and $-\Delta G^0_{\mathrm{ET}}$ (0.42 eV)[15] values using Marcus equation[2] as 0.11 eV.