Dyads and Triads Containing Perylenetetracarboxylic Diimide and Porphyrin: Efficient Photoinduced Electron Transfer Elicited via Both Excited Singlet States

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Received: October 22, 2004; In Final Form: December 12, 2004

Synthesis, characterizations, and photophysical properties of new photoactive dyads and triads containing perylenetetracarboxylic diimide (PIm) and porphyrin (free-base porphyrin (H₂P) and zinc porphyrin (ZnP)), in which both entities were connected with a short ether bond, were examined with the aim of using these systems for molecular photonics. The porphyrin(P)-PIm systems absorbed strongly across the visible region, which greatly matched the solar spectrum. The geometric and electronic structures of the dyads and triads were probed using density function theory method at the B3LYP/3-21G level. It was revealed that the majority of the highest-occupied molecular orbital was located on the porphyrin entity, while the lowest-unoccupied molecular orbitals were entirely on the PIm entity. The excited-state electron-transfer processes were monitored by both steady-state and time-resolved emission as well as transient-absorption techniques in polar solvent benzonitrile. Upon excitation of the P (H₂P and ZnP) moieties, efficient fluorescence quenching of the P moiety was observed, suggesting that the main quenching paths involved charge separation from the excited singlet porphyrin (¹P*) to the PIm moiety. Upon excitation of the PIm moiety, fluorescence quenching of the ¹PIm* moiety was also observed. The nanosecond transience of spectra in near-IR region revealed the charge separation process from the P moieties to the PIm moiety via their excited singlet states. The lifetimes of the charge-separated states were evaluated to be 7-14 ns, depending on the solvent polarity. Photosensitized electron mediation systems were also revealed in the presence of methyl viologen and sacrificial electron donor.

Introduction

Recently, developing renewable energy sources has stimulated tremendous interest in construction of light energy conversion systems.^{1–8} Development of molecular photoelectronic devices requires the creation of molecular arrays that undergo electrontransfer processes after photoexcitation with light of specific wavelengths. For this purpose, several organic compounds have been applied to construct solar cells. Among them, perylenetetracarboxylic diimide (PIm) dyes seem to be ideal for lightbased applications due to their excellent photophysical properties. The PIm dyes have strong absorption with high molar absorption coefficients ($\epsilon \approx 58\ 000\ M^{-1}\ cm^{-1}$ at 490 nm in CHCl₃), a long fluorescence lifetime, near unity fluorescence quantum yields, and very high photostability.9,10 Although many perylenetetracarboxylic diimide derivatives have poor solubility in common organic solvents, their solubility can be considerably enhanced by the introduction of bulky substituents.

To date, many redox active chromophores were involved in these donor–acceptor systems based on the PIm derivatives.^{11–28} Incorporating PIm within molecular donor–acceptor systems, in which PIm acts as an electron acceptor linked with appropriate photosensitizers and/or electron donors, is a viable route to design photovoltaics and molecular electronics.^{11–28} Among

counterpart donors, porphyrin analogues (P = ZnP and H₂P) displayed many attractive photophysical and chemical features.^{29,30} Porphyrins contain an extensively conjugated π system with high electron donor ability, and such a delocalized π system is suitable for efficient electron-transfer processes.

To the best of our knowledge, there are fewer examples of connected systems prepared from porphyrin and PIm, revealing their unique photophysical and photochemical properties. Wasielewski's group prepared a molecular optical switch comprised of a PIm dye attached to two free base porphyrins via short *N*-phenyl linkers.²⁰ Excitation of the PIm and porphyrin moieties resulted in electron transfer from porphyrin to the PIm, showing that the PIm unit participated as an electron acceptor with the porphyrin as a donor in their excited singlet states. Another series of porphyrin (H₂P, ZnP, and MgP)–PIm systems were reported by Lindsey, Holten, Bocian, et al. using a longer linker in an attempt to suppress electron-transfer quenching while maintaining energy transfer.^{21,22,24,25}

In the present paper, we report the synthesis, characterizations, and photophysical properties of new photoactive dyads and triads of porphyrin—PIm systems that would be applied to improve the light absorption efficiency and achieve the efficient charge-separation states for appropriately long times.

Results and Discussion

Synthesis. 5-(4-Hyroxyphenyl)-10,15,20-tris-(3',4',5'-trimethoxyphenyl)- porphyrin (H₂P) as shown in Scheme 1 was

10.1021/jp045163e CCC: \$30.25 © 2005 American Chemical Society Published on Web 01/28/2005

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H₂P M= 2H $Zn(AcO)_2$ ZnP M= Zn $CHCl_3$, reflux

SCHEME 2: Synthesis of H₂P-PIm and ZnP-PIm



SCHEME 3: Structures of H₂P-PIm-H₂P and ZnP-PIm-ZnP



conveniently synthesized in 10% yield from the acid-catalyzed condensation of 3,4,5-trimethoxy benzaldehyde and 4-hydroxybenzaldehyde with pyrrole at an appropriate portion.³¹ Anhydrous potassium carbonate mediated the condensation of H₂P with N,N'-dioctyl-1-bromoperylene-3,4:9,10-tetracarboxylic-bis-(imide) to afford the dyad H₂P-PIm (Scheme 2). The triad $H_2P-PIm-H_2P$ (Scheme 3) was prepared by the same method with N,N'-dioctyl-1,7-dibromoperylene-3,4:9,10-tetracarboxylicbis(imide) as starting PIm. Preparations of all Zn(II)-porphyrined samples were carried out by treatments of porphyrin-containing samples with Zn(OAc)₂. SMP-PIm and DMP-PIm as shown in Scheme 4 were also prepared as reference compounds in the same way. All the new compounds were characterized by ¹H NMR, ¹³C NMR, matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra, and FT-IR spectra (see Experimental Section).

Optimized Molecular Structures. To gain insights into the intramolecular interactions and the electronic structure, computational studies have been performed by using density functional theory (DFT) methods at the B3LYP/3-21G level. For this aim, both the dyads and triads were fully optimized to a



Figure 1. Optimized structure and the HOMO and LUMO of H_2P -PIm obtained by DFT at the ab initio B3LYP/3-21G level.

SCHEME 4: Structure of SMP-PIm and DMP-PIm



stationary point of the Born–Openheimer potential-energy surface. For H₂P–PIm, the H₂P plane and PIm plane were almost in the same plane. The distance between the center of H₂P and the center of the PIm (R_{CC}) was estimated to be 8.3 Å. The highest-occupied molecular orbital (HOMO) and lowest-unoccupied molecular orbital (LUMO) for H₂P–PIm obtained by using the B3LYP/3-21G method were shown in Figure 1. The electron distribution of the HOMO was found to be entirely located on the H₂P entity, while the electron distribution of the LUMO was found to be entirely located on the PIm, suggesting the hole (radical cation) and electron (radical anion) distribution in the charge-separated state, respectively. In the case of ZnP– PIm, the R_{CC} value was found to be 9.3 Å, and the HOMO and LUMO were calculated (Supporting Information, Figure S1).

A similar picture can be summarized for $H_2P-PIm-H_2P$ and ZnP-PIm-ZnP triads, where the porphyrin plane and PIm plane were almost perpendicular. The estimated R_{CC} between the centers of H_2P and PIm was found to be 8.3 Å, while the distance between the centers of ZnP and PIm was found to be 9.3 Å. The HOMO and LUMO were also calculated as shown in Figure 2, in which the HOMO located on the two porphyrin rings, while the LUMO located on the PIm moiety.

Redox Potentials and Free-Energy Changes. The determination of the redox potential in the donor-acceptor systems



Figure 2. Optimized structure and the HOMO and LUMO of H_2P -PIm- H_2P obtained by density function method at ab initio B3LYP/ 3-21G level.

TABLE 1: Half-Wave Potentials ($E_{1/2}$ vs SCE) for Porphyrin–PIm Compounds, Detected by CV (scan rate 50mV/s) in *o*-Dichlorobenzene Solutions (0.1 M *n*-Bu₄N⁺PF₆⁻ as Supporting Electrolyte) at Room Temperature

	oxidation p	red	reductio n potential s/V			
	H ₂ P/ZnP		PIm		H ₂ P/ZnP	
compounds	$E_{\text{ox}(1)}$	$E_{\text{ox}(2)}$	$E_{red(1)}$	Ered(2)	$E_{red(1)}$	Ered(2)
H ₂ P	+1.06				-1.31	-1.62
H ₂ P-PIm	+1.06		-0.67	-0.86	-1.29	-1.58
H ₂ P-PIm-H ₂ P	+1.07		-0.67	-0.87	-1.30	-1.60
ZnP	+0.85	+1.08			-1.62	-1.90
ZnP-PIm	+0.86	+1.09	-0.67	-0.86	-1.63	-1.90
ZnP-PIm-ZnP	+0.86	+1.09	-0.67	-0.87	-1.63	-1.90
SMP-PIm			-0.66	-0.86		
DMP-PIm			-0.68	-0.86		

is important to evaluate the energy of electron-transfer reactions. We have performed a systematic study to evaluate the redox behavior of the dyads and triads using the cyclic voltammetry (CV) technique by sweeping an applied voltage to the compound in solution with a suitable electrolyte. The oxidation potentials (E_{OX}) for donor moieties and reduction potentials (E_{RED}) for acceptor moieties were evaluated as summarized in Table 1. A comparison between the E_{OX} potentials of the H₂P-PIm and ZnP-PIm dyads with those of the H2P and ZnP recorded under similar conditions was revealed to be almost the same, suggesting the absence of ground-state interactions between the H₂P (and ZnP) and the PIm moieties. Similar electrochemical behaviors were observed for the triads (H₂P-PIm-H₂P and ZnP-PIm-ZnP). These results collectively suggested the absence of weak interactions between the different entities of the triads.

The free-energy changes for charge separation $(-\Delta G_{CS})$ and charge recombination $(-\Delta G_{CR})$ can be calculated based on the electrochemical data by Rehm–Weller (eqs $1-2)^{32}$

$$-\Delta G_{\rm CR} = E_{\rm ox} - E_{\rm red} + \Delta G_{\rm S} \tag{1}$$

$$-\Delta G_{\rm CS} = \Delta E_{0-0} - (-\Delta G_{\rm CR}) \tag{2}$$

where ΔE_{0-0} refers to the energy of the 0–0 transition energy gap between the lowest excited state and the ground state of P and PIm depending on the excitation wavelength and ΔG_s refers to the solvation energy that can be calculated according to eq 3^{32}

$$-\Delta G_{\rm S} = (e^2/(4\pi\epsilon_0))[(1/(2R_+) + 1/(2R_-) - 1/R_{\rm D-R})/\epsilon_{\rm S} - (1/(2R_+) + 1/(2R_-))/\epsilon_{\rm R}] (3)$$

where R_+ refers to the radii of the radical cation of P and R_- refers to the radii of the radical anion of PIm (Figure 1), e, ϵ_0 , ϵ_s , and ϵ_R refer to elementary charge, vacuum permittivity, and static permittivities of the solvents used for rate measurements and redox potential measurements, respectively. In benzonitrile, the charge-separated state of ZnP*+-PIm*- located at 1.53 eV above the ground state, 0.56 eV lower than the first excited singlet state of ZnP and 0.85 eV lower than the first excited state of PIm (Table 2). In general, the charge-separation process via the excited singlet state of the porphyrin (¹P*) and perylene (¹PIm*) was exothermic and favorable in benzonitrile.

UV-Vis Spectral Studies. UV-vis spectroscopy is a simple method for determining the presence of ground-state interactions between the moieties in the connected systems. Steady-state absorption spectra of H₂P-PIm and ZnP-PIm in CHCl₃ were shown in Figure 3, together with the absorption bands of the components. An obvious feature can be observed that the PIm moiety absorbed strongly in the region between the porphyrin Soret and Q bands of the ZnP moiety. The absorption spectra of H₂P-PIm and H₂P-PIm-H₂P showed superposition features of their components, which indicated no evidence for strong electronic interactions among the component chromophores in the ground state. In Figure 4, absorption bands of H₂P-PIm-H₂P and ZnP-PIm-ZnP were shown together with their components. These spectra also indicated the absence of interaction between the components. These results were consistent with the conclusion drawn from the electrochemistry data.

On addition of tetrakis(dimethylamino)ethylene (TDAE), which is well-known as a strong reducing organic reagent, the color of the solution containing SMP–PIm changed, and the new absorption bands appeared in the 700–1000-nm region as shown in Figure 5. The absorption bands at 720, 800, 850, and 950 nm were attributed to PIm^{•-}.³³ On further addition of octyl viologen dication (OV²⁺), the absorption bands of PIm^{•-} disappeared, and new absorption bands with a peak at 600 nm appeared, indicating the generation of the radical cation of octyl viologen (OV^{•+}) by the electron transfer from PIm^{•-}.

Fluorescence Studies. The photoexcited states of PIm, H₂P, H₂P-PIm, and H₂P-PIm-H₂P were investigated by steadystate fluorescence measurements (Figure 6). The measurements of Figure 6a were carried out at an excitation wavelength of 490 nm, where the PIm was exclusively excited. The fluorescence intensity of the PIm moiety at 540 nm decreased in H₂P-PIm and H₂P-PIm-H₂P in toluene and benzonitrile compared with that of PIm,³⁴ suggesting that energy transfer and charge separation took place via ¹PIm* and formed ¹H₂P*-PIm $({}^{1}H_{2}P^{*}-PIm-H_{2}P)$ and $H_{2}P^{\bullet+}-PIm^{\bullet-}$ $(H_{2}P^{\bullet+}-PIm^{\bullet-}-H_{2}P$ or $H_2P-PIm^{\bullet-}-H_2P^{\bullet+}$), which can be supported by negative $\Delta G_{\rm CS}$ values. The quenching of fluorescence intensity of H₂P-PIm-H₂P was more efficient compared with that of H₂P-PIm. For ZnP-PIm and ZnP-PIm-ZnP, the similar tendency was observed. These findings suggested that two H₂P (or ZnP) moieties were cooperating to enhance energy migration.

TABLE 2: Free-Energy Changes for Charge Separation $(\Delta G_{\rm CS})$ and Charge Recombination $(\Delta G_{\rm CR})$ of P⁺⁺ – PIm⁺⁻ in Toluene and Benzonitrile^{*a*}

		$-\Delta$		
	solvent	via ¹ P*	via ¹ PIm*	$-\Delta G_{\rm CR}/{\rm V}$
H ₂ P–PIm	BN	0.17	0.65	1.73
	toluene	-0.08	0.40	1.98
$H_2P-PIm-H_2P$	BN	0.16	0.64	1.74
	toluene	-0.09	0.39	1.99
ZnP-PIm	BN	0.56	0.85	1.53
	toluene	0.10	0.39	1.99
ZnP-PIm-ZnP	BN	0.56	0.85	1.53
	toluene	0.10	0.39	1.99

 $^aE_{0-0}$ for $^1\text{PIm}*$ is 2.38 eV, for $^1\text{H}_2\text{P}*$ 1.90 eV, and for $^1\text{ZnP}*$ 2.08 eV.

When the H₂P moiety of H₂P–PIm and H₂P–PIm–H₂P was excited at 420 nm, the fluorescence intensity of them at 653 nm decreased much more compared with that of reference compound H₂P in benzonitrile (Figure 6b),^{35,36} suggesting that charge separation took place via ¹H₂P* and formed H₂P*+– PIm*- (or H₂P*+–PIm*-–H₂P). Efficient fluorescence quenching of H₂P–PIm–H₂P more than H₂P–PIm was also observed. For ZnP–PIm and ZnP–PIm–ZnP, the similar tendency was observed as well.

Time-resolved emission and nanosecond transient absorption studies were performed for both the dyad and triad systems to follow the kinetics of photoinduced processes.

Time-Resolved Fluorescence Studies. The time-resolved fluorescence measurements of PIm, H₂P–PIm, and H₂P–PIm–H₂P shown in Figure 7 were consistent with those of the steady-state fluorescence measurements. Figure 7 showed the fluorescence decay profiles of the H₂P in benzonitrile (λ_{ex} = 400 nm) where the PIm moiety was exclusively excited. The fluorescence time profiles of SMP–PIm, H₂P–PIm, and H₂P–PIm–H₂P at 540 nm exhibited single-exponential decays with the lifetimes (τ_f) of 5.0, 0.17, and 0.61 ns, respectively. Similarly, the fluorescence lifetimes of the H₂P moiety at 650 nm of H_2P -PIm and H_2P -PIm- H_2P were evaluated from the single exponential decays as listed in Tables 3 and 4. On the other hand, the fluorescence lifetimes of the ZnP moiety at 600 nm of ZnP-PIm and ZnP-PIm-ZnP showed dual exponential decays. The lifetimes were also listed in Tables 3 and 4.

Attaching the PIm moiety to H_2P or ZnP introduced a new quenching pathway to reduce the lifetimes of the ¹PIm*, ¹ZnP*, or¹H₂P* in toluene and benzonitrile, which was in agreement with the steady-state results. This quenching was due to the photoinduced charge separation between excited singlet states of porphyrins and PIm to yield charge-separated states (P*+-PIm*- and P*+-PIm*--P).

The rate constant for fluorescence quenching can be calculated from eq 4

$$k_{\rm q} = (1/\tau_{\rm f})_{\rm sample} - (1/\tau_{\rm f})_{\rm reference} \tag{4}$$

where $(\tau_f)_{\text{sample}}$ is the lifetime of the ¹PIm*, ¹ZnP*, or¹H₂P in the dyads and triads, while $(\tau_f)_{\text{reference}}$ refers to the lifetime of reference samples. The k_q values were calculated out in the range of $1.6 \times 10^9 - 1.7 \times 10^{10}$ in toluene and benzonitrile. In Table 3, the k_q values via ¹H₂P* were larger than those via ¹PIm* both in H₂P–PIm and H₂P–PIm–H₂P. The k_q values via ¹H₂P* were also larger than those via ¹ZnP. For ZnP–PIm–ZnP, the k_q values via ¹PIm* were quite large. The quantum yields of the charge-separated states were calculated according to eq 5

$$\Phi_{q} = k_{q}(\tau_{f})_{\text{sample}} \tag{5}$$

The Φ_q values were larger than 0.90 for all processes. In the case of fluorescence lifetimes of the ¹PIM* moiety, the k_q and Φ_q values included both the energy transfer (k_{EN} and Φ_{EN}) and charge separation (k_{CS} and Φ_{CS}), respectively. While in the case of fluorescence lifetimes of the ¹H₂P* and ¹ZnP* moiety, the k_q and Φ_q values corresponded to k_{CS} and Φ_{CS} , respectively. Even if energy transfer took place in toluene, the Φ_{CS} values



Figure 3. The absorption spectra of H_2P -PIm, ZnP–Pim, and reference compounds H_2P , ZnP, and SMP–PIm in chloroform at the fixed concentration of 1 μ M at room temperature. The dotted lines are fluorescence spectra of H_2P , ZnP, and SMP–PIm in chloroform at room temperature obtained upon exciting the porphyrin unit at Soret band and exciting PIm at 490 nm. All spectra are normalized to the same amplitude in their corresponding panels.



Figure 4. The absorption spectra of $H_2P-PIm-H_2P$, ZnP-PIm-ZnP, and reference compounds H_2P , ZnP, and DMP-PIm in chloroform at the fixed concentration of 1 μ M at room temperature. The dotted lines are fluorescence spectra of H_2P , ZnP, and DMP-PIm in chloroform at room temperature are obtained upon exciting the porphyrin unit at Soret band and exciting PIm at 490 nm. All spectra are normalized to the same amplitude in their corresponding panels.



Figure 5. (Solid lines) Absorption spectra of SMP–PIm (7 × 10⁻³ mM) in benzonitrile in the presence of TDAE (0.0–0.2 mM). (Dotted lines) Further addition of octyl viologen (OV²⁺, 0.4 mM) in the presence of TDAE (0.2 mM) and SMP–PIm (7 × 10⁻³ mM) in deaerated benzonitrile.

in benzonitrile became predominant, taking into consideration the more negative ΔG_{CS} values in benzonitrile than those in toluene.

Transient Absorption Measurements. The nanosecond transient absorption spectra of P-PIm and P-PIm-P were observed in Ar-saturated toluene by applying 532-nm laser light excitation. In the case of H₂P-PIm, both H₂P and PIm were photoexcited. Whereas the 532-nm laser light exclusively excited the PIm moiety in the case of ZnP-PIm (Figure 8). The transient absorption spectra revealed sharp absorption bands at 720, 800, 850-860, and 920-940 nm with fast rise and decay. These absorption peaks can be ascribed to PIm^{•-}. In some transient spectra, absorption peaks at 720 and 800 nm were hidden within the emission of H₂P-PIm and ZnP-PIm in this region. The rapid rise indicated that the charge-separation process took place from ZnP to ¹PIm*. In the case of H₂P-PIm, charge separation took place in both directions: from H₂P to ¹PIm* and from ${}^{1}\text{H}_{2}\text{P}^{*}$ to PIm due to sufficiently negative ΔG_{CS} values in both processes (Table 2).

The lifetimes of the charge-separated states were evaluated from the decay of the PIm^{•-} moiety at 820–1020 nm. The decays of P^{•+}–PIm^{•-} can be attributed to the recombination to the ground state. The lifetime of the charge-separated states were calculated in the range of 7–14 ns in benzonitrile as listed in Tables 3 and 4.

In benzonitrile, similar transient absorption spectra were observed as shown in Figure 9, in which the 700-nm bands were unclearly observed because of stronger emission or scattering of the light in this region.

Steady-State Photolysis in the Presence of External Electron Donors and Electron Acceptors. The formation of the charge-separated state of the investigated systems was further confirmed in deoxygenated solutions under irradiation upon adding methyl viologen (MV2+) or octyl viologen (OV2+) as an external sacrificial electron acceptor and 1-benzyl-1,4dihydronicotinamide (BNAH) as an external electron donor.37 A comparison between the one-electron reduction potential of the PIm unit (-0.67 vs SCF) in H_2P -PIm and MV^{2+} (-0.45 V vs SCF) indicated that an electron transfer from PIm^{•-} to MV²⁺ was exothermic by 0.22 eV. Also, on addition of an external electron donor, benzyldihydro nicotinamide (BNAH) $(E_{\text{ox}} = 0.57 \text{ V vs SCF})$, the hole shift from H₂P⁺ in H₂P-PIm to BNAH was expected to be exothermic by 0.49 eV. Under these conditions, once the charge-separation state was obtained upon photoirradiation of P-PIm and P-PIm-P, the oxidation of BNAH and reduction of MV²⁺ were expected to take place simultaneously (Scheme 5). The process was experimentally confirmed by photolysis of the H₂P-PIm/ MV²⁺-BNAH system with monochromatized light of 423 nm in Ar-saturated DMF/H₂O (95:5, v/v) solution. The steady-state photolyhfsis of the dyad produced a progressive increase in the characteristic absorption band of MV⁺ ($\lambda_{max} = 605$ and 398 nm) and a progressive decrease in the absorption band of BNAH at 347 nm according to the time of the irradiations as shown in Figure 10. By contrast, no reaction occurred in the





Figure 6. Steady-state fluorescence spectra (a) (i) PIm, (ii) H₂P-Pim, and (iii) H₂P-PIm-H₂P obtained by 490-nm excitation laser light. (b) (i) H₂P, (ii) H₂P-Pim, and (iii) H₂P-PIm-H₂P obtained by 420-nm excitation laser light. The concentrations of compounds were maintained at 5.0 \times 10⁻⁶ M in benzonitrile.



Figure 7. Fluorescence decay profiles of (a) SMP-PIm, (b) H₂P–Pim, and (c) H₂P–PIm–H₂P in benzonitrile. $\lambda_{ex} = 400$ nm. The concentrations were maintained at 0.05 mM.

dark or in the absence of H₂P-PIm under photoirradiation. From the H₂P-PIm-H₂P/MV²⁺/BNAH system and corresponding

zinc analogue systems, the same steady-state photolysis results were also obtained (see Supporting Information).

The electron-mediating process was confirmed by applying 532-nm laser excitation of ZnP-PIm (0.05 mM) in the presence of OV²⁺ (4 mM) in Ar-saturated benzonitrile, as shown in the transient absorption spectra and time profiles in Figure 11. The presence of $OV^{\bullet+}$ was observed at 1.0 μ s by building up of absorption around 620 nm and paralleling a disappearance of PIm^{•-} at 840 and 920 nm.

These observations indicated that, in the presence of MV^{2+} , laser irradiation of PIm induced electron transfer from ZnP to ¹PIm*. The produced PIm^{•-} successively donated its excess electron to MV^{2+} yielding MV^{+} as indicated by the very fast disappearance of PIm^{•-} that we could not record due to the instrument limitation. Here it is worth mentioning that the slow rise of MV²⁺ might also arise from the intermolecular interaction between MV²⁺ and the excited triplet states of porphyrins. In

TABLE 3: Photophysical Properties of Porphyrin–Perylene Systems via ¹H₂P^{*}, ¹ZnP^{*}, and ¹PIm^{*a} in Tolune where $\lambda_{ex} = 420$ nm

	excited state	$ au_{ m f}/ m ns$	k_q^b/s^{-1}	$\Phi_{\mathfrak{q}}{}^b$	$k_{\rm CR}/{ m s}^{-1}$ ($ au_{\rm CS}/{ m ns}$)
H ₂ P-PIm	${}^{1}\text{H}_{2}\text{P}^{*}$	0.31(31%) 2.20(69%)	$2.7 \times 10^9 (9.5 \times 10^7)^c$	$0.83 (0.15)^c$	8.4×10^{7}
	¹ PIm*	0.24(52%) 3.10(48%)	$3.6 \times 10^9 (9.5 \times 10^7)^c$	$0.87 (0.15)^c$	(12)
$H_2P-PIm-H_2P$	${}^{1}H_{2}P^{*}$	0.32(33%) 2.10(67%)	$2.6 \times 10^9 (9.5 \times 10^7)^c$	$0.83 (0.15)^c$	1.5×10^{8}
	¹ PIm*	0.06(100%)	1.6×10^{10}	0.97	(11)
ZnP-PIm	¹ ZnP*	0.20(52%) 2.45(48%)	$4.5 \times 10^9 (3.1 \times 10^8)^c$	$0.91 (0.39)^c$	9.6×10^{7}
	¹ PIm*	0.22(71%) 3.14(29%)	$4.1 \times 10^9 (4.7 \times 10^8)^c$	$0.88 (0.49)^c$	(14)
ZnP-PIm-ZnP	¹ ZnP*	0.12(61%) 1.42(39%)	$7.9 \times 10^9 (1.2 \times 10^9)^c$	$0.94 (0.70)^c$	1.4×10^{8}
	¹ PIm*	0.14(100%)	6.7×10^{9}	0.93	(11)

^a $\tau_{\rm f}$ values for H₂P, ZnP, and SMP–PIm are 13.6, 2.1, and 5.0, respectively. ^b Calculated from the fast component. ^c Calculated from the average values of both fast and slow components.

TABLE 4:	Photophysical Pro	perties of Porph	nvrin-Pervlene S	vstems via ¹ H ₂ P*,	¹ ZnP*, and	¹ PIm ^{*a} in Benzonitrile
					,	

	excited state	$ au_{ m f}/ m ns$	$k_{\mathrm{q}}{}^{b}/\mathrm{s}^{-1}$	$\Phi_{\mathfrak{q}}{}^b$	$k_{\rm CR}/{ m s}^{-1}$ ($ au_{\rm CS}/{ m ns}$)
H ₂ P-PIm	${}^{1}\text{H}_{2}\text{P}*$	0.06 (100%)	1.7×10^{10}	0.99	1.5×10^{8}
	¹ PIm*	0.17 (100%)	5.7×10^{9}	0.97	(7)
$H_2P-PIm-H_2P$	${}^{1}H_{2}P^{*}$	0.06 (100%)	1.7×10^{10}	99	2.0×10^{8}
	¹ PIm*	0.61 (100%)	1.6×10^{9}	0.99	(5)
ZnP-PIm	¹ ZnP*	0.21 (66%) 2.51 (33%)	$4.2 \times 10^9 (2.8 \ 10^9)^c$	$0.90 (0.60)^{c}$	1.5×10^{8}
	¹ PIm*	0.18 (44%) 3.14 (56%)	$5.4 \times 10^9 (2.3 \ 10^9)^c$	0.96 (0.42) ^c	(7)
ZnP-PIm-ZnP	¹ ZnP*	0.12 (100%)	6.7×10^{9}	0.94	1.4×10^{8}
	¹ PIm*	0.08 (100%)	1.2×10^{10}	0.98	(7)

a τ_f values for H₂P, ZnP, and SMP–PIm are 13.6, 2.1, and 5.0, respectively. ^b Calculated from the fast component. ^c Calculated from the average values of both fast and slow components.



Figure 8. Transient absorption spectra obtained by 532 nm laser photolysis of (a) H_2P-PIm , (b) $H_2P-PIm-H_2P$, (c) ZnP-Pim, and (d) ZnP-PIm-ZnP (0.1 mM) in Ar-saturated toluene.



Figure 9. Transient absorption spectra obtained by 532 nm laser photolysis of (a) H_2P-PIm , (b) $H_2P-PIm-H_2P$, (c) ZnP-Pim, and (d) ZnP-PIm-ZnP (0.1 mM) in Ar-saturated benzonitrile.

SCHEME 5: Summarization of the Whole Photosensitized Electron-Mediation/Hole-Shift Processes within the Dyad of H_2P -Pim



this case, PIm acted as an electron mediator in addition to a photosensitizing electron acceptor. The whole photosensitized electron-mediating/ hole-shift processes were summarized in Scheme 5.

Conclusions

In conclusion, we demonstrated here the synthesis and the photoinduced electron-transfer process of new photoactive dyads and triads containing porphyrin (H₂P and ZnP), as an electron donor, and perylenetetracarboxylic diimide (PIm), as an electron acceptor. Thermodynamically, the electron transfer process from porphyrin to perylene in their excited singlet states was exothermic and favorable in benzonitrile. The steady-state, time-resolved emission and transfer mainly from the porphyrin to perylene entities in the polar solvent by observing the anion radical of the perylene moiety. The formation of the CS state was evidenced by the formation of MV^{•+} in the presence of BNAH as illustrated by the energy diagram shown in Figure 12. Further studies on photophysics of the dyads and triads and



Figure 10. (a) Absorption spectral changes observed in the steady-state photolysis with monochromatized light ($\lambda = 423$ nm) of H₂P–PIm (1.0 × 10⁻⁶ M) in the presence of BNAH (4.0 × 10⁻⁴ M) and MV²⁺ (8.0 × 10⁻⁴ M) in an Ar-saturated DMF/H₂O (95:5, v/v) solution. (b) Differences in spectral changes between after and before steady-state photolysis (the inset shows the absorption band at 605 nm with a multiple of 10).



Figure 11. Transient absorption spectra obtained by 532-nm laser photolysis of ZnP-PIm in the (a) absence and (b) presence of OV^{2+} (0.3 mM) in Ar-saturated benzonitrile.



Figure 12. Energy-level diagrams of ZnP-PIm systems by applying excitation laser light in the presence of MV^{2+} and BNAH.

their application as photoactive materials in photovoltaic devices is currently underway.

Experimental Section

General. Reagents were purchased reagent grade from Acros or Aldrich Corporation and were utilized as received unless indicated otherwise. N,N'-Dioctyl-1-bromoperylene-3,4:9,10-tetracarboxylic bisimide,³⁸ N,N'-dioctyl-1,7-dibromoperylene-3,4:9,10-tetracarboxylic bisimide,³⁸ H₂P,³¹ ZnP,³¹ and DMP–PIm³¹ were prepared as described in the literature. TDAE was commercially available. Octyl viologen (OV²⁺) pechlorate

was prepared from commercially available octyl viologen bromide. All solvents were purified using standard procedures. Evaporation and concentration in vacuo were done at water aspirator pressure, and compounds were dried at 10^{-2} Torr. Column chromatography (CC): SiO₂ (160–200 meshes). TLC glass plates coated with SiO₂ F₂₅₄ were visualized by UV light.

Instrumental Techniques. All spectroscopic data were collected at room temperature. UV–vis spectra were measured on a Hitachi U-3010 spectrometer. FT-IR spectra were recorded as KBr pellets on a Perkin-Elmer System 2000 spectrometer. ¹H NMR (400-MHz) and ¹³C NMR spectra were recorded on a Bruker ARX400 spectrometer. The solvent signal was used as an internal reference for both ¹H and ¹³C NMR spectra. MALDI-TOF mass spectrometric measurements were performed on Bruker Biflex β MALDI-TOF.

Cyclic voltammetry (CV) was performed on a CHI voltammetric analyzer (BAS 100w, Bioanalytical Systems) at room temperature with a three-electrode configuration in o-dichlorobenzene solution containing a supporting electrolyte. A glassy carbon (Ø3 mm) disk served as the working electrode; a platinum foil and a SCE were the counter and the reference electrodes, respectively. Both the counter and the reference electrodes were directly immersed in the electrolyte solution. The surface of the working electrode was polished with commercial alumina (No. 1C, Alpha Micropolish, Aldrich; particle size 1.0 µm) prior to use. Tetra-n-butylammonium hexafluorophosphate (>99%, Fluka) was recrystallized twice from ethanol and dried in a vacuum at 100 °C overnight prior to use and was employed as the supporting electrolyte (0.1 M). Solutions were stirred and deaerated by bubbling nitrogen for about 10 min prior to each voltammetric measurement. The scan rate was 50 mV s⁻¹ unless otherwise specified.

The time-resolved fluorescence spectra were measured by a single-photon-counting method using a second harmonic generation (SHG, 410 nm) of Ti:sapphire laser (Spectra-Physics, Tsunami 3950-L2S, 1.5 ps full width at half maximum (fwhm)) and a streak-scope (Hamamatsu Photonics, C43334-01) equipped with a polychromator (Action Research, SpectraPro 150) as an excitation source and a detector, respectively. Lifetimes were evaluated with software attached to the equipments.

The nanosecond transient absorption measurements were carried out using SHG (532 nm) of a Nd:YAG laser (Spectra-Physics and Quanta-Ray GCR-130, 6 ns fwhm) as an excitation source. For transient absorption spectra in the near-IR region (600–1200 nm), monitoring light from a pulsed Xe lamp was detected with a Ge-APD (Hamamatsu Photonics, B2834). All

samples in a quartz cell $(1 \times 1 \text{ cm})$ were deaerated by bubbling Ar through the solution for 15 min.

Steady-State Photolysis. A square quartz cell (10 mm inside diameter) containing a deaerated DMF-water (95:5, v/v) solution of H₂P-PIm (1.0 × 10⁻⁶ M), MV²⁺ (8.0 × 10⁻⁴ M), and BNAH (4.0 × 10⁻⁴ M) was irradiated with monochromatized light of $\lambda = 423$ nm from a 150-W metal halogen lamp through a filter. The light intensity was determined as 2.3 mW/cm². The photochemical reactions were monitored by measuring the absorption spectra at different irradiation times.

H₂P-PIm. N,N'-Dioctyl-1-bromoperylene-3,4:9,10-tetracarboxylic bisimide (70 mg, 0.1 mmol) in 40 mL of dry toluene containing K₂CO₃ (2 equiv) and 18-crown-6 (2 equiv) was stirred under N₂ for 20 min, and subsequently H₂P (100 mg, 1.1 equiv) was added. The mixture was heated to 100 °C and continuously stirred for 3 h until the reaction finished from the detection of TLC. When the solvent was evaporated under reduced pressure, the resulting mixture was loaded to a column chromatography to afford 90 mg of pure target product $H_2P-PIm (R_f = 0.78, CHCl_3/CH_3COOC_2H_5, 10:1, yield 60\%)$ eluted by chloroform. ¹H NMR (CDCl₃): 9.75 (d, 1H, J = 8.3Hz), 9.02 (d, 2H, J = 4.7 Hz), 8.98 (s, 4H), 8.97 (d, 2H, J =4.7 Hz), 8.79 (d, 1H, J = 8.3 Hz), 8.71 (s, 1H), 8.70 (d, 1H, J = 8.1 Hz), 8.67 (s, 2H), 8.61 (d, 1H, J = 8.1 Hz), 8.32 (d, 2H, J = 8.5 Hz), 7.59 (d, 2H, J = 8.5 Hz), 7.49 (s, 6H), 4.23 (m, 4H), 4.19 (s, 9H), 3.98 (s, 18H), 1.81 (m, 4H), 1.26-1.48 (m, 20H), 0.88 (t, 3H, J = 7.0 Hz), 0.86 (t, 3H, J = 7.0 Hz). ¹³C NMR (CDCl₃): 163.4, 163.2, 162.7, 155.5, 154.8, 151.5, 139.2, 138.0, 137.5, 136.4, 134.2, 134.1, 133.5, 131.9, 130.7, 129.8, 128.9, 128.6, 128.5, 126.7, 125.8, 125.1, 124.4, 124.0, 123.5, 123.1, 122.7, 122.4, 120.2, 118.6, 117.6, 113.0, 113.0, 61.3, 56.4, 40.9, 31.8, 29.7, 29.4, 29.3, 28.2, 27.2, 22.6, 14.1. MALDI-TOF: 1512.9. FT-IR (KBr, *v*(cm⁻¹)): 3455, 2926, 2853, 1696, 1658, 1593, 1500, 1465, 1407, 1352, 1236, 1206, 1169, 1127, 1008, 975, 925, 854, 805, 730.

H₂P-PIm-H₂P. N,N'-Dioctyl-1,7-dibromoperylene-3,4:9,10tetracarboxylic diimide (39 mg, 0.05 mmol) in 40 mL of dry toluene containing K₂CO₃ (2 equiv) and 18-crown-6 (2 equiv) was stirred under N_2 for 20 min and subsequently H_2P (100 mg, 2.2 equiv) was added. The mixture was heated to 100 °C and continuously stirred until the reaction finished from the detection of TLC. When the solvent was evaporated under reduced pressure, the resulting mixture was loaded to a column chromatography to afford 78 mg of pure target product $H_2P-PIm-H_2P$ ($R_f = 0.70$, CHCl₃/CH₃COOC₂H₅, 10:1, yield 65%) eluted by chloroform. ¹H NMR (CDCl₃): 9.93 (d, 2H, J = 8.3 Hz), 9.01 (d, 4H, J = 4.0 Hz), 8.98 (m, 8H), 8.89 (d, 2H, J = 8.3 Hz), 8.80 (s, 2H), 8.32 (d, 4H, J = 8.3 Hz), 7.61 (d, 4H, J = 8.3 Hz), 7.48 (s, 12H), 4.30 (m, 4H), 4.19 (s, 18H),3.98 (s, 36H), 1.86 (m, 4H), 1.52 (m, 4H), 1.26–1.43 (m, 20H), 0.88 (t, 6H, J = 6.6 Hz). ¹³C NMR (CDCl₃): 163.4, 163.1, 155.3, 154.9, 151.5, 139.0, 138.0, 137.5, 136.4, 133.5, 131.5, 130.7, 129.6, 129.3, 128.0, 125.6, 124.9, 124.7, 124.4, 122.7, 120.2, 118.7, 117.6, 117.4, 113.0, 112.9, 61.3, 56.4, 40.9, 31.8, 29.7, 29.4, 29.3, 28.2, 27.3, 14.1. MALDI-TOF: 2411.7 (M + H⁺), 2434.6 (M + Na⁺), 2451.6 (M + K⁺). FT-IR (KBr, $\nu(cm^{-1})$): 3472, 2929, 2154, 1698, 1659, 1593, 1580, 1499, 1464, 1407, 1356, 1235, 1128, 1105, 1007, 973, 924, 855, 801, 732.

All the Zn(II)—porphyrin samples were synthesized as follows and converted almost completely. To a saturated solution of dehydrated zinc acetate in methanol was added a solution of porphyrin-containing samples in chloroform and refluxed for about 30 min. After cooling, the reaction mixture was washed with saturated sodium bicarbonate aqueous solution and water successively and dried over anhydrous sodium sulfate, and then the solvent was removed under reduced pressure. Column chromatography on silica gel with chloroform as an eluent afforded the corresponding Zn(II)-porphyrin containing targets.

ZnP–Pim. ($R_f = 0.68$, CHCl₃/CH₃COOC₂H₅, 10:1.) ¹H NMR (CDCl₃): 9.52 (d, 1H, J = 8.2 Hz), 9.10 (d, 2H, J = 4.5Hz), 9.08 (m, 6H), 8.60 (s, 1H), 8.44 (s, 2H), 8.30–8.36 (m, 4H), 7.91 (br, 1H), 7.57 (d, 2H, J = 7.8 Hz), 7.45 (s, 6H), 4.18 (s, 9H), 4.16 (br, 2H), 3.92 (s, 18H), 3.66 (m, 2H), 1.76 (m, 2H), 1.27–1.45 (m, 22H), 0.84–0.89 (m, 6H). MALDI-TOF MS: 1574.6. FT-IR (KBr, ν (cm⁻¹)): 2926, 2853, 1696, 1658, 15937, 1497, 1458, 1406, 1346, 1237, 1204, 1165, 1126, 1001, 940, 808, 722.

ZnP–PIm–ZnP. ($R_f = 0.48$, CHCl₃/CH₃COOC₂H₅, 10:1.) ¹H NMR (CDCl₃): 9.64 (br, 2H), 9.05–9.11 (m, 16H), 8.65 (s, 2H), 8.30 (4H), 7.80 (2H), 7.46–7.59 (m, 16H), 4.15 (s, 18H), 3.92 (s, 36H), 3.65 (m, 4H), 1.1–1.4 (m, 24H), 0.87 (t, 6H, J = 6.7 Hz). MALDI-TOF MS: 2533.9. FT-IR (KBr, ν (cm⁻¹)): 2929, 2853, 1697, 1659, 1591, 1497, 1460,1406, 13476, 1237, 1165, 1126, 1073, 1001, 941, 799, 722.

Reference compounds SMP–PIm and DMP–PIm³¹ were prepared according to the general method described for the synthesis of compound H₂P–PIm except that *p*-methyl phenol was used as the starting materials instead of H₂P.

SMP-**Pim.** ¹H NMR (CDCl₃): 9.43 (d, 1H, J = 8.3 Hz), 8.44-8.58 (m, 5H), 8.16 (s, 1H), 7.27 (d, 2H, J = 9.6 Hz), 7.06 (d, 2H, J = 9.6 Hz), 4.12 (m, 4H), 2.42 (s, 3H), 1.72 (m, 4H), 1.28-1.50 (m, 20H), 0.87 (t, 6H, J = 7.2 Hz). MALDI-TOF MS: 720.6. FT-IR (KBr, ν (cm⁻¹)): 2926, 2854, 1695 (s), 1657 (s), 1594 (s), 1505, 1407, 1343 (s), 1260 (s), 1201, 808, 747.

Acknowledgment. This work was supported by the Major State Basic Research Development Program and the National Natural Science Foundation of China (20151002, 50372070). This research was partially supported by a Grant-in-Aid for the COE Project, Giant Molecules and Complex Systems, 2002. This work was also supported by a Grant-in-Aid for Scientific Research on Priory Area (417) from the Ministry of Education, Culture, Sports, Science, and Technology of the Japanese Government.

Supporting Information Available: Optimized structure and HOMO and LUMO of ZnP–PIm and absorption spectral changes observed in the steady-state photolysis of ZnP–PIm, H_2P –PIm– H_2P , and ZnP–PIm–ZnP in the presence of BNAH and MV^{2+} in an Ar-saturated solution. This material is available free of charge via the Internet at http://pubs.acs.org.

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