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Excitation Energy Dependence of Photoinduced Processes in Pentathiophene−Perylene Bisimide Dyads with a Flexible Linker

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In the present paper, photoinduced processes in the dyad molecules of pentathiophene (5T) and perylene-3,4:9,10-bis(dicarboximide) (PDI) with a flexible alkyl linker (propyl or hexyl) were investigated by using femtosecond laser flash spectroscopy in various solvents. Since absorption of 5T covers the wavelength region where absorption of PDI has minima and fluorescence of 5T overlaps with absorption of PDI, combination of 5T and PDI is favorable to achieve light energy harvesting as well as efficient electron transfer. When the sample was excited at the PDI moiety of the dyad, charge separation occurred almost quantitatively even in nonpolar solvent as well as in polar solvents. When the 5T moiety of the dyad was excited, efficient energy transfer to the PDI moiety from which charge separation occurred was confirmed, indicating that 5T acts as an antenna of the charge separation system, like a photosynthesis system of a plant. On the basis of Förster and Marcus theories and the estimated energy and electron-transfer rates, it was indicated that these dyads tend to take a folded structure in all solvents investigated.

Introduction

The reaction center of a natural photosynthesis system is surrounded by the light harvesting systems, in which chromophores such as carotenoids and chlorophylls are organized in order to absorb solar light ranging from UV to near-IR regions efficiently and to transfer absorbed photon energy to the central reaction center.[1,2] This system facilitates light energy conversion even in deep sea. Thus, the combination of chromophores, which allows funneling of a wide range of photon energies to the electron-transfer (ET) system, seems to be important also in the realization of efficient artificial photosynthesis systems composed of organic donors and acceptors linked by an adequate bridge.

Recently, perylene-3,4:9,10-bis(dicarboximide) (PDI) has been employed in various supramolecular systems with efficient ET functionality because of its excellent photophysical properties such as the high fluorescence quantum yield, the large absorption band at around 550 nm, the high reduction power in its excited state, and the high stability under photoirradiation.[3−8] The ability to form nanometer-size aggregates is also an interesting property of PDI.[4b,d−h,j,5b,c,h−m,o] For the artificial photosynthesis system using PDI as an electron acceptor, the combination with other chromophores, of which absorption covers a spectral range where PDI has minima, that is, 300−480 nm, will be useful because such a combination will enhance photon energy harvesting in a wide wavelength region like that of the natural light harvesting system. For such a purpose, oligomers of conjugated polymers will be candidates for the partner of PDI because of the large extinction coefficient in the above-mentioned region and the high donor-ability. From these reasons, oligo *p*-phenylenevinylenes and oligothiophenes seem to be good electron donors for PDI.[7,8]

In the present paper, we synthesized dyad molecules of pentathiophene and PDI (Figure 1) because the combination of these chromophores seems to attain the above purpose. These chromophores were linked by an alkyl (propyl or hexyl) linker. The dyads were expected to take various conformations, such as folded and stretched forms, because of the flexible linkers. The photoinduced processes such as charge separation (CS) and recombination (CR) and energy transfer (ENT) were investigated by using transient absorption spectroscopy mainly. The photoinduced process depending on the excitation wavelength was an important subject to be cleared in this study, from which the function as an antenna for the artificial photosynthesis systems became clear. Furthermore, from a set of the CS and ENT rate constants, conformation of these dyads in solution was discussed.

Experimental Section

Materials. 4′,3‴-Dihexyl-(2,2′:5′,2″:5″,2‴:5‴,2⁗)pentathiophene (5T) and *N*-(2′-ethylhexyl)-1,7-di(3′,5′-di-*t*-butylphenoxy)perylene-3,4-dicarboxyanhydride-9,10-dicarboxyimide (PMI) were synthesized as described in refs 4e and 9.

Synthesis of 5-(3-chrolopropyl)-4′,3‴-dihexyl-(2,2′:5′,2″:5″,2‴:5‴,2⁗)pentathiophene ($5T-C_3-Cl$). A quantity of 200 mg (345 *μ*mol) of 5T and 50 *μ*L of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) were dissolved in 3 mL of THF. The reaction mixture was cooled in an acetone bath with dry ice, and *n*-BuLi in toluene solution was added dropwise into the THF solution slowly. The reaction mixture was stirred for 30 min at 0 °C. The flask was cooled in the acetone bath with dry ice again, and 500 mg (317 *μ*mol) of 1-bromo-3-chloropropane was added to the reaction mixture and stirred for 5 h at room temperature. The crude product was extracted with CH_2Cl_2 and water and purified by column chromatography (hexane/CH_2Cl_2 (1/9)). The yield of $5T-C_3-Cl$ (92.9 mg) was 41%. ^1H NMR ($CDCl_3$): δ 6.73−7.28 (m, 8H); 3.60 (t, $J = 6.21$ Hz, 2 H); 3.00 (t, $J = 7.29$ Hz, 2H); 2.76 (t, $J = 6.75$ Hz, 4H); 2.14 (dd, $J = 6.75$ Hz, 2H); 1.68 (m, 2H); 1.32 (m, 12H); 0.90 ppm (t, $J = 6.75$ Hz, 6H). FAB-MS: 656 (656.2, calcd).

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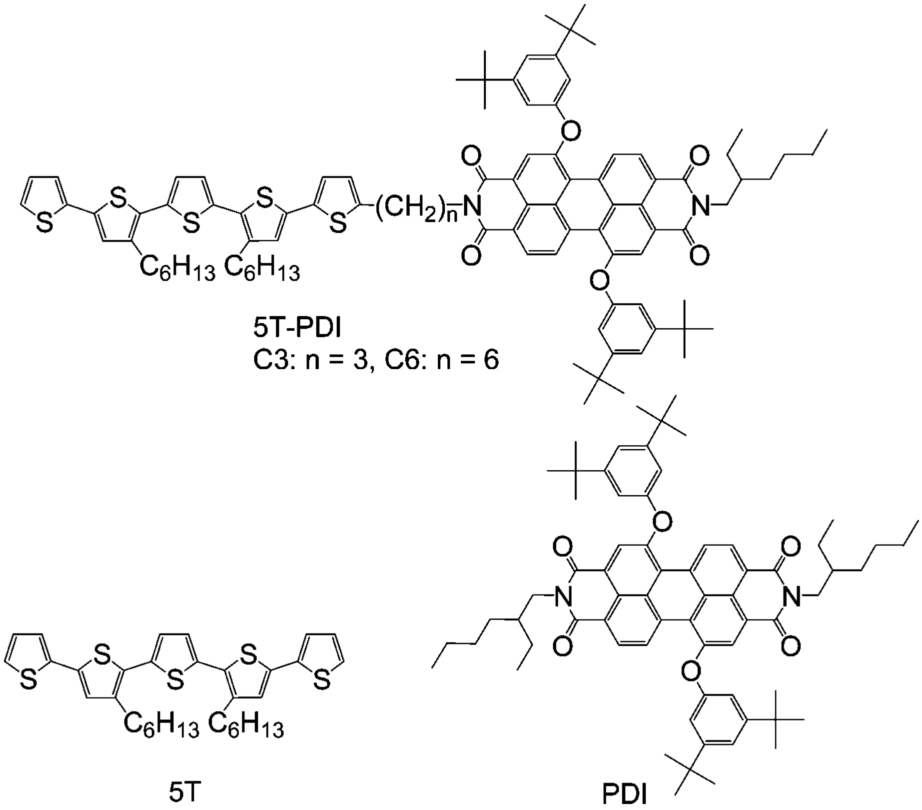

Figure 1. The structures of 5T−PDI dyads and reference compounds.

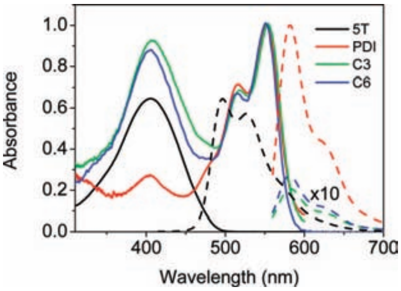

Figure 2. Absorption (solid lines) and fluorescence spectra (broken line) of 5T, PDI, C3, and C6 in benzonitrile. Concentration for absorption measurements: 2.2×10^{-5} M.

Synthesis of *N*-(2′-ethylhexyl)-*N*′-H-1,7-di(3′,5′-di-*t*-butylphenoxy)perylene bisimide (PDI(NH)). Quantities of 26.6 mg (33.2 μmol) of PMI and 110 mg (1.83 mmol) of urea were added into 3.3 mL of DMF under Ar atmosphere. The reaction mixture was refluxed and stirred overnight. The crude product was extracted with $CHCl_3$ and water and washed with NH_4Cl and with brine. Further purification was not performed. The yield of crude PDI(NH) (20.0 mg) was 76%. FAB-MS: 800 (798.4, calcd).

Synthesis of C3. Quantities of 200 mg (304 μmol) of $5T{-}C_3{-}Cl$, 40.0 mg (43.9 μmol) of PDI(NH), and 16.3 mg (150 μmol) of K_2CO_3 were dissolved in 5 mL of DMF and stirred for 3.5 h at 100 °C. The crude product was extracted with CH_2Cl_2 and water and purified by column chromatography. The yield of C3 (26.9 mg) was 40%. ^1H NMR (CD_2Cl_2): δ 9.50 (dd, $J = 8.37$ Hz, 2H); 8.40 (dd, $J = 8.37$ Hz, 2H); 8.11 (s, 1H); 8.11 (s, 1H); 6.56−7.30 (m, 9H); 4.18 (t, $J = 4.32$ Hz, 2H); 3.81 (m, 2H); 2.86 (t, $J = 7.29$ Hz, 2H); 2.64 (t, $J = 7.83$ Hz, 2H); 2.53 (t, $J = 7.97$ Hz, 2H); 2.10 (t, $J = 6.75$ Hz, 2H); 1.72 (b, 1H); 1.26 (m, 60 H); 0.77 ppm (m, 12H). FAB-MS: 1533 (1530.7, calcd).

Synthesis of 5-(6-bromohexyl)-4′,3‴-dihexyl-(2,2′:5′,2″:5″,2‴:5‴,2⁗)pentathiophene ($5T{-}C_6{-}Br$). A quantity of 840 mg (1.45 mmol) of 5T and 0.2 mL of TMEDA were dissolved in 10 mL of THF. The reaction mixture was cooled in an acetone bath with dry ice, and 0.95 mL of *n*-BuLi in toluene solution was added dropwise into the THF solution slowly. The reaction mixture was stirred for 30 min at 0 °C. The flask was cooled in the acetone bath with dry ice again, and 1 mL of 1,6-dibromohexane was added to the reaction mixture and stirred for 5 h at room temperature. The crude product was extracted with CH_2Cl_2 and water and purified by column chromatography (hexane/CH_2Cl_2 (1/9)). The yield of $5T{-}C_6{-}Br$ (77.5 mg) was 7.2%. FAB-MS: 744 (742.2, calcd).

Synthesis of C6. Quantities of 88.5 mg (119 μmol) of $5T{-}C_6{-}Br$, 87.7 mg (96.3 μmol) of PDI(NH), and 16.6 mg (120 μmol) of K_2CO_3 were dissolved in 5 mL of DMF and stirred for 3.5 h at 100 °C. The crude product was extracted with CH_2Cl_2 and water and purified by column chromatography (hexane/CH_3Cl (1/1)) and GPC. The yield of C6 (34.3 mg) was 23%. ^1H NMR (CD_2Cl_2): δ 9.62 (dd, $J = 8.10$ Hz, 2H); 8.52 (m, 2H); 8.22 (m, 2H); 6.66−7.38 (m, 9H); 4.10 (m, 2H); 4.02 (m, 2H); 2.76 (m, 6H); 1.87 (b, 1H); 1.33 (m, 68H); 0.87 ppm (m, 12H). FAB-MS: 1574 (1572.7, calcd).

Apparatus. Details of the subpicosecond transient absorption spectra measurements are described in the previous papers. In the present experiment, the sample was excited with a 550 or 400 nm laser pulse.[10] The typical concentration for the transient absorption spectroscopy was 0.1 mM.

The steady-state absorption and fluorescence spectra were measured using a Shimadzu UV-3100PC and a Hitachi 850, respectively.

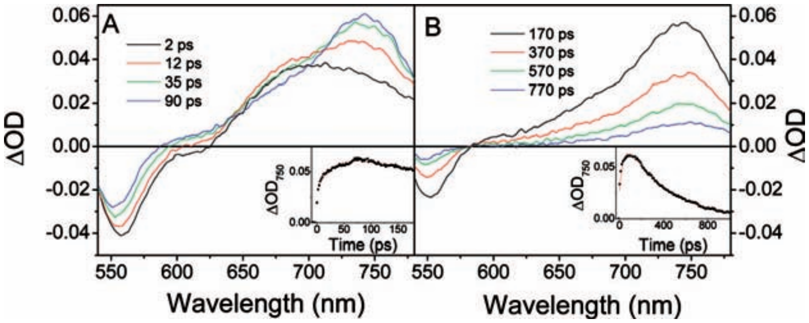

Figure 3. Transient absorption spectra of C3 in toluene during the laser flash photolysis using a 550 nm laser pulse at 2−90 (A) and 170−770 ps (B) after the excitation. Inset: Absorption−time profiles at 750 nm.

TABLE 1: The Rate Constants and Quantum Yields of CS and CR in C3 and C6 Obtained by 550 nm Laser Excitation

	C3			C6		
solvent	k_{CS}/s^{-1}	Φ_{CS}	k_{CR}/s^{-1}	k_{CS}/s^{-1}	Φ_{CS}	k_{CR}/s^{-1}
benzonitrile	2.1×10^{11}	1.0	2.2×10^{10}	9.1×10^{10}	1.0	5.7×10^{8}
anisole	5.8×10^{10}	1.0	7.1×10^{9}	1.1×10^{10}	0.98	2.4×10^{8}
toluene	2.1×10^{10}	0.99	2.7×10^{9}	6.1×10^{9}	0.97	1.4×10^{8}

Results and Discussion

Absorption and Fluorescence Spectra. Figure 2 shows absorption spectra of the dyads as well as their components, that is, 5T and PDI. C6 in benzonitrile shows absorption peaks at 552, 515, and 403 nm. The two former peaks can be attributed to PDI and the last one to 5T from the comparison with the spectra of the components. The absorption spectrum of C6 coincides with the sum spectrum of PDI and 5T, indicating the absence of the interaction in the ground state. In the case of C3, absorption peaks appeared at 555, 518, and 406 nm, which are slightly red shifted compared with C6 and the components, that is, PDI and 5T. Furthermore, C3 exhibits a slight increase in absorbance in the 400−500 nm region when compared with C6. These slight spectral changes indicate weak interaction between PDI and 5T in C3, although the interaction between chromophores can be regarded as a minor one because it is reported that strong charge-transfer interaction induces a red shift of the absorption band of PDI as large as 174 nm.[4b] The existence of a weak interaction between two chromophores coincides with the results of the theoretical calculation indicated in a later section. From the absorption spectra of the present dyads, we can exclude the formation of aggregates of PDI, which reduces the relative intensity of the $v = 0$ band compared to the $v = 1$ of PDI.[4d−h]

It is reported that PDI shows fluorescence at 581 nm, of which the quantum yield is almost unity.[3] When C3 and C6 dyads were excited at 550 nm, where the PDI moiety solely has absorption, the fluorescence intensity of PDI dramatically decreased in all solvents investigated. For example, the fluorescence quantum yield of C3 in benzonitrile was estimated to be 0.02, which is 1/48 of that of PDI. Because the S_1 state energy level of PDI is lower than that of 5T, ENT from PDI to 5T cannot occur in the dyad when the PDI moiety is excited. Thus, it is indicated that CS from 5T to singlet-excited PDI occurred in these dyads.

When the dyads were excited at 400 nm, which also excites the 5T moiety, fluorescence attributable to 5T was not confirmed in all solvents, although the reference compound, 5T, showed fluorescence at 496 nm with a 0.33 quantum yield.[11] This finding indicates that a photoinduced process such as ENT and/or CS occurred from the singlet-excited 5T moiety of the dyad. Because the fluorescence spectrum of 5T and the absorption spectrum of PDI were overlapped substantially as indicated in Figure 2, ENT is expected in C3 and C6 dyads when the 5T moiety of the dyads is excited.

Driving Force for ET. The driving force for ET, ΔG, can be estimated from eq 1

$$\Delta G = E_{OX} - E_{RED} - E_{00} - C \tag{1}$$

where E_{OX} and E_{RED} are the oxidation potential of 5T (0.98 V vs NHE)[12] and the reduction potential of PDI (−0.70 V),[4h] respectively. E_{00} is the excitation energy. C is the Coulombic term depending on the solvent polarity and donor−acceptor distance and tends to become negligibly small when distance becomes larger and in polar solvents. As for the distance between two chromophores, we will discuss this in the later sections. By assuming a negligibly small C, ΔG for ET from 5T to singlet-excited PDI was estimated to be −0.57 eV in polar solvents by using E_{00} = 2.25 eV for PDI, suggesting that ET from 5T to singlet-excited PDI is a possible photoinduced process. On the other hand, the E_{00} of 5T is 2.50 eV, from which ΔG for ET from singlet-excited 5T to PDI was estimated to be −0.82 eV, indicating that ET from excited 5T to PDI is also an energetically favorable process while ENT to PDI is also possible for singlet-excited 5T. In order to clarify the photoinduced processes in the dyads, transient absorption measurements were carried out as indicated in the next section.

Photoinduced Processes from the Singlet-Excited PDI. In the present study, photoinduced processes of the dyads were investigated by changing the excitation wavelength and solvent in the laser flash photolysis experiments. As a solvent, toluene, anisole, and benzonitrile were employed because by using these solvents, the solvent-polarity effect on the photoinduced process in the dyads can be investigated. By using a 550 nm laser pulse, the PDI of the dyads can be excited selectively. Figure 3 shows transient absorption spectra of C3 in toluene at 2−770 ps after the excitation pulse during the laser flash photolysis using a 550 nm pulse. Immediately after the laser excitation of C3 in toluene, absorption due to the singlet-excited state of PDI was observed at 700 nm as well as ground-state bleaching at 560 nm (Supporting Information, Figure S1).[4] The absence of the absorption of 5T in the singlet-excited state indicates that the PDI was selectively excited. With the delay time, the

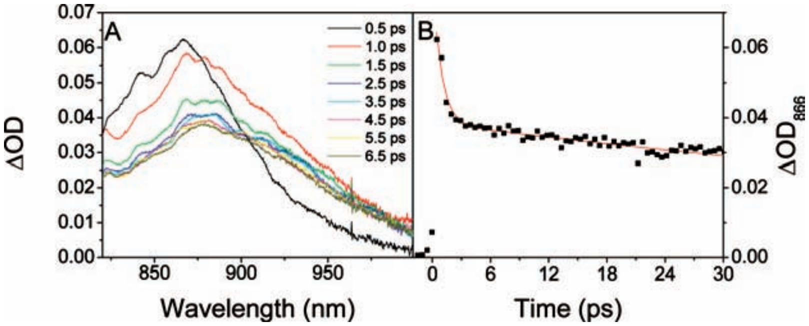

Figure 4. (A) Transient absorption spectra of C3 excited at 400 nm in toluene. (B) Time profile at 866 nm.

TABLE 2: Rate Constants of ENT in C3 and C6 Obtained by a 400 nm Laser Excitation

	$k_{\mathrm{ENT}}/\mathrm{s}^{-1}$	
solvent	C3	C6
benzonitrile	1.4×10^{12}	9.8×10^{11}
anisole	1.6×10^{12}	9.0×10^{11}
toluene	1.3×10^{12}	1.0×10^{12}

spectral feature due to the singlet-exited PDI, that is, bleaching at 560 nm and a peak at 700 nm, became obscure, and an absorption peak at 750 nm due to $\mathrm{PDI}^{\bullet-}$ became clear.[4] The generation of $\mathrm{PDI}^{\bullet-}$ with a decay of $^1\mathrm{PDI}^*$ indicates CS from 5T to the $^1\mathrm{PDI}^*$. It should be pointed out that the radical cation of 5T is reported to show absorption peaks at 720 and 1270 nm.[13] The former peak should be overlapped with the absorption band of $\mathrm{PDI}^{\bullet-}$, while the latter one is out of the present measurable range. As indicated in the inset figure of Figure 3A, the absorption band due to $\mathrm{PDI}^{\bullet-}$ showed gradual growth, and $\mathrm{PDI}^{\bullet-}$ showed maximal concentration at about 90 ps. By fitting the single exponential function, the growth rate of $\mathrm{PDI}^{\bullet-}$ was estimated to be $2.1 \times 10^{10}\ \mathrm{s}^{-1}$. Because the CS process via $^1\mathrm{PDI}^*$ occurred as a competitive process of the deactivation of $^1\mathrm{PDI}^*$ including radiative, internal conversion and intersystem crossing, the CS rate (k_{CS}) could be estimated by subtracting the deactivation rate from the apparent growth rate (k_{obs}) of the CS state as indicated in eq 2

$$k_{\mathrm{CS}} = k_{\mathrm{obs}} - k_{\mathrm{d,PDI}} \tag{2}$$

where $k_{\mathrm{d,PDI}}$ is the deactivation rate of $^1\mathrm{PDI}^*$, which can be estimated as a reciprocal of the fluorescence lifetime of PDI without the donor moiety. The CS rate of C3 in toluene was estimated to be $2.1 \times 10^{10}\ \mathrm{s}^{-1}$. In addition, the quantum yield of CS can be estimated by using eq 3

$$\Phi_{\mathrm{CS}} = k_{\mathrm{CS}}/(k_{\mathrm{CS}} + k_{\mathrm{d,PDI}}) \tag{3}$$

The Φ_{CS} value was estimated to be 0.99, indicating efficient CS.

As seen in Figure 3B, the absorption band of $\mathrm{PDI}^{\bullet-}$ decreased gradually due to the CR process. Because no transient species was observed after the decay of the CS state, the CR process generated the ground-state molecule. The CR generating the ground-state dyad is also supported by the isosbestic point observed at 580 nm with zero absorption. The rate constant for CR (k_{CR}) was estimated to be $2.7 \times 10^9\ \mathrm{s}^{-1}$, equivalent to 370 ps of the lifetime by applying the single exponential function to the absorption−time profile indicated in the inset of Figure 3B.

In benzonitrile and anisole, CS from the $^1\mathrm{PDI}^*$ of C3 was confirmed by observing the absorption band of $\mathrm{PDI}^{\bullet-}$ at 750 nm (Supporting Information). The rate constants for CS and CR processes were estimated by a similar manner, as summarized in Table 1. It can be pointed out that both the CS and CR rate constants became faster with an increase in the solvent polarity.

In addition, the CS and CR processes in C6 were also investigated by using the laser flash photolysis using the 550 nm pulse (Supporting Information). Generation of the CS state was confirmed in three solvents, that is, benzonitrile, anisole, and toluene. The estimated rate constants were also indicated in Table 1. It is clear that both the CS and CR rate constants of C6 were slower than that of C3 in each solvent. This finding indicates that the long distance of the hexyl linker in C6 decelerated both the CS and CR rates. The longest CS state lifetime of C6 was 7.1 ns, which was observed in toluene.

Photoinduced Processes from the Singlet-Excited 5T. Transient absorption spectra obtained by excitation of C3 in toluene with a 400 nm laser pulse are shown in Figure 4A. As indicated previously, 5T of the dyad was also excited by the 400 nm laser pulse. The formation of the singlet-excited state of 5T is confirmed by the appearance of the 866 nm band immediately after the laser pulse excitation (Supporting Information, Figure S6).[14] The absorption band of $^1\mathrm{5T}^*$ decayed within 1 ps after the excitation, and an absorption band with a peak at 880 nm, which can be attributed to $^1\mathrm{PDI}^*$, was observed. Decay of $^1\mathrm{5T}^*$ and appearance of $^1\mathrm{PDI}^*$ can be attributed to the singlet ENT from $^1\mathrm{T}^*$ to PDI. The absence of the formation of a radical ion pair, which should show a peak at around 750 nm, on the time scale of the decrease of $^1\mathrm{5T}^*$ indicates that CS is not included in the deactivation process of $^1\mathrm{5T}^*$ of the dyad. The absence of CS can be attributed to the larger driving force of the CS, which places the process in the Marcus inverted region, as well as sufficient overlap of the absorption of PDI and the fluorescence of 5T, which enhances ENT. The rate constant of ENT (k_{ENT}) was estimated from the decay rate of $^1\mathrm{5T}^*$ to be $1.3 \times 10^{12}\ \mathrm{s}^{-1}$ (Figure 4B). Similar ENT processes were observed in other solvents, that is, anisole and benzonitrile. The rate constants of ENT are summarized in Table 2. It is clear that the ENT rate constants were almost identical in these solvents, as expected for ENT, while a large solvent effect was expected for the CS rate. It is interesting to note that the identical ENT rate independent of the solvent polarity indicates that the average distance between the two chromophores is also identical in these solvents. Furthermore, a quite fast ENT rate indicates almost quantitative ENT from 5T to PDI, which explains almost no fluorescence from 5T in the dyad when 5T is excited, as indicated in the previous sections. These findings indicate effective light energy harvesting to PDI from

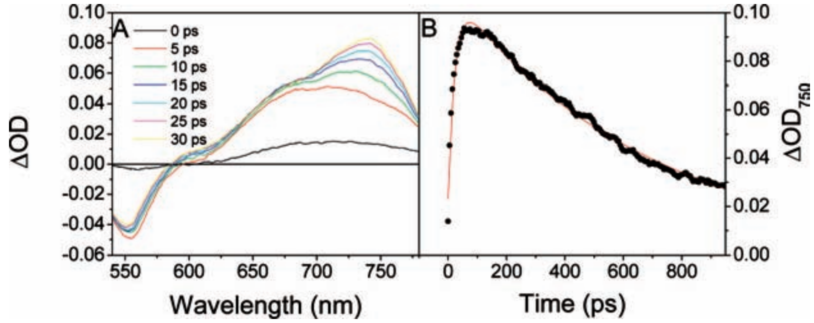

Figure 5. (A) Transient absorption spectra of C3 excited at 400 nm in toluene. (B) Time profile at 750 nm.

5T, which absorbs photons in the wavelength region where absorbance of PDI is weak.

The ENT processes in C6 were also confirmed in all solvents, and the rate did not depend on the solvent (Table 2). The ENT rate constants of C6 are slower than those of C3 in each solvent. The slower ENT rate of C6 than that of C3 can be attributed to the longer distance between two chromophores of C6 than C3. According to Förster theory governing singlet ENT, the ENT rate is largely dependent on the distance between the energy donor and acceptor, while the observed difference in the ENT rate between C3 and C6 seems to be small. This finding will indicate some information on the conformation of the dyads, as discussed in the following section.

Figure 5 shows transient absorption spectra of C3 in toluene in the visible region during the laser flash photolysis using a 400 nm laser pulse. As pointed out before, $^15T^*$ generated immediately after the laser excitation donates its singlet energy to PDI. The ENT process is confirmed as the initial rise of $^1PDI^*$ within 1 ps after the laser excitation, which agrees with the initial decay of $^15T^*$. The absence of an absorption band due to a radical ion pair indicates that the decay of $^15T^*$ is due to ENT process. After ENT, CS from 5T to $^1PDI^*$ becomes possible, as in the case when $^1PDI^*$ was generated directly by the 550 nm laser excitation. Actually, generation of $PDI^{\bullet -}$ was confirmed at 750 nm with 3.2×10^{10} s^{-1} as the rate constant. The generated radical ion pair decreased with 1.8×10^9 s^{-1} as the rate constant. The observed CS and CR rates are essentially the same as those obtained by 550 nm laser excitation. The rate constants for the CS and CR processes of the dyads by 400 nm laser excitation in various solvents were summarized in Table S1 in the Supporting Information. The estimated rates in each solvent were essentially the same as those obtained by the 550 nm laser excitation. This fact indicates that the same photoinduced processes occurred after the generation of the singlet-excited state of PDI, independent of the excitation wavelength. The photoinduced processes observed by 550 and 400 nm laser pulse excitation are summarized in Figure 6.

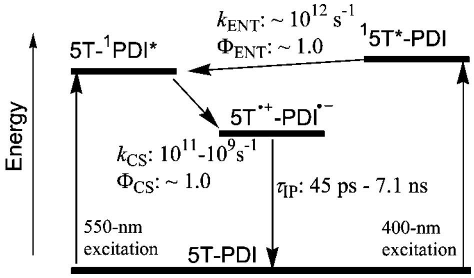

Figure 6. The photoinduced processes observed by 550 and 400 nm laser pulse excitation. Φ_{ENT} and τ_{IP} are the quantum yield of ENT and the lifetime of the ion pair, respectively.

Conformation of the Dyads during the Photoinduced Process. In the present study, 5T and PDI are connected with the flexible linker, alkyl chain. Thus, various conformations will be possible, such as folded and stretched conformations. By using theoretical modeling of the dyad molecules, the distance between two chromophores can be estimated. In the present study, the center-to-center distance (d_{cc}) between two chromophores of the dyads in the stretched and folded conformations was estimated by using MM calculation (Supporting Information, Figure S7),[15] in which stretched and folded structures given as initial structures were energetically minimized because stretched and folded structures can be regarded as two extreme structures of the various conformations. In the folded form, the d_{cc} values of C3 and C6 were estimated to be 4.8 and 5.3 Å, respectively. On the other hand, the respective d_{cc} values in the stretched form were 16.0 and 22.3 Å. Thus, C6 tends to take longer d_{cc} values both in the folded and stretched conformations, although the difference in the folded structure is small.

From the laser flash photolysis study, it was revealed that both the CS and ENT rates of C6 are slower than those of C3. On the basis of the estimated rate constants, information on the conformation of these dyads can be obtained. According to the Förster theory for the ENT process, the rate (k_{ENT}) can be expressed as eq 4[16]

$$k_{ENT} = \tau_{5T}{}^{-1}(R_0/r)^6 \tag{4}$$

where τ_{5T} is fluorescence lifetime of 5T. R_0 and r are Förster distance and the distance between donor and acceptor, respectively. Furthermore, R_0 (Å) can be determined from eq 5

$$R_0{}^6 = 8.79 \times 10^{23} \cdot \kappa^2 \cdot n^{-4} \cdot Q_D \cdot J(\lambda) \tag{5}$$

where κ is the geometrical factor, n is the refractive index of medium, Q_D is the quantum yield of donor fluorescence, and $J(\lambda)$ is the overlap integral calculated from the acceptor absorption spectrum and the fluorescence spectrum of the donor, with the total intensity normalized to unity. For the present dyads, $J(\lambda)$ was calculated to be 2.14×10^{15} M^{-1} cm^{-1} nm^4. From eq 5, R_0 values for the folded and stretched forms were estimated to be 48 and 61 Å, respectively, by employing $\kappa^2 =$ 1 and 4. The ENT rate varies significantly when r is comparable to R_0. The r values of the stretched form are close to R_0 values, and the difference is large between C3 and C6 when compared to that of the folded form. The ratio of the theoretically estimated ENT rates of C3 and C6 using eqs 4 and 5 was 1.8 for the folded conformer, while that of the stretched conformer was

7.2. Since the experimentally determined ratio, 1.3−1.8, was close to that for the folded conformer, C3 and C6 are considered to be taking the folded conformation.

According to the Marcus theory for ET, the rate (k_{ET}) can be expressed as eq 6[17]

$$k_{ET} = k_0 \exp(-\beta(r - r_0)) \qquad (6)$$

where β is a factor depending on the ET media or the linker nature and r_0 is the distance for van der Waals contact. By assuming that β and r_0 are 1.2 Å^{-1} and 3.5 Å, respectively, the ratios of the CS rates of C3 and C6 are estimated to be 3.3 and 1.9×10^3 for the folded and stretched conformations, respectively. Since the ratios of the CS rates of C3 and C6 are estimated to be 2.3, 5.3, and 3.4 in benzonitrile, anisole, and toluene, respectively, the folded conformation explains well the difference in the CS rate constants of C3 and C6. Therefore, comparison between theoretical and experimental rates for ENT and CS indicates that the dyad tends to take a folded structure in all solvents examined in the present study. The folded structure seems to be adequate because the absorption spectrum of C3 showed slight interaction between two chromophores. In the case of C6, the longer linker allows a larger freedom for conformation than that for C3, which weakens the interaction between chromophores.

In the present paper, we showed that the photon energy absorbed by 5T is transferred to PDI by efficient energy transfer to generate singlet-excited PDI, from which CS occurred, indicating photon energy funneling. Such energy funneling to PDI has been reported by some researchers. Wasielewski et al. reported that energy transfer from the energy donor directly attached to the N position of PDI occurred within 1 ps.[4c,j] Such fast energy transfer can be attributed to a very short distance between the energy donor and acceptor. On the other hand, Würthner and co-workers reported that energy transfer from pyrene attached to PDI bay positions via alkyl ester linkage occurred with 0.12 ns as the time constant. From the energy-transfer rate, they estimated the distance between the energy donor and acceptor to be 8.6 Å based on the Förster theory.[5e] They also observed that energy transfer from naphthalimide linked at the bay position to PDI occurred within ∼50 ps.[5n] In the present case, the energy-transfer rate from 5T to PDI is ∼1 ps, even though the 5T and PDI are linked by a propyl or hexyl chain. The fast energy transfer can be attributed to the folded structure, as indicated above.

Conclusion

In the present paper, we investigated photoinduced processes in the dyad molecules of 5T and PDI, in which the absorption of 5T covers the wavelength region where absorption of PDI has minima. When the sample was excited at the PDI moiety of the dyad, CS occurred almost quantitatively, even in nonpolar solvent as well as polar solvents. When the 5T moiety of the dyad was excited, efficient ENT to the PDI moiety, from which CS occurred, was confirmed, indicating that 5T acts as an antenna of the ET system. From the evaluated CS and ENT rate constants, it was indicated that these dyads tend to take a folded structure.

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Supporting Information Available: Transient absorption spectra of reference compounds, C3 and C6, energy-minimized structures, and CS and CR rate constants obtained by laser flash photolysis using 400 nm laser excitation. This material is available free of charge via the Internet at http://pubs.acs.org.

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