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# Photoinduced Electron Transfer between C<sub>60</sub>/C<sub>70</sub> and Zinc Tetraphenylporphyrin in Polar Solvents

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Photoinduced electron transfer between C<sub>60</sub>/C<sub>70</sub> and zinc tetraphenylporphyrin (ZnTPP) in a polar solvent has been investigated with a nanosecond laser photolysis method by observing the transient absorption bands in the near-IR region. The transient absorption bands of the C<sub>60</sub>/C<sub>70</sub> radical anion (C<sub>60</sub><sup>•−</sup>/C<sub>70</sub><sup>•−</sup>) in the near-IR region gave evidence of electron transfer for the system ZnTPP and C<sub>60</sub>/C<sub>70</sub>. In ZnTPP solution where C<sub>60</sub> and C<sub>70</sub> were photoexcited predominantly, electron transfer takes place from the ground state of ZnTPP to the triplet states of C<sub>60</sub>/C<sub>70</sub> (<sup>3</sup>C<sub>60</sub><sup>\*</sup>/<sup>3</sup>C<sub>70</sub><sup>\*</sup>). In the concentrated ZnTPP solution where ZnTPP was predominantly photoexcited, the triplet state of ZnTPP donates the electron to the ground state of C<sub>60</sub>/C<sub>70</sub>, producing C<sub>60</sub><sup>•−</sup>/C<sub>70</sub><sup>•−</sup>. The efficiency of electron transfer via the <sup>3</sup>C<sub>60</sub><sup>\*</sup>/<sup>3</sup>C<sub>70</sub><sup>\*</sup> route is higher than that via <sup>3</sup>ZnTPP<sup>\*</sup>.

## Introduction

Both fullerenes and porphyrins are well-known as unique compounds in photochemical and photophysical views.<sup>1,2</sup> When they are mixed, promotion of photoinduced electric conductivity has been reported.<sup>3</sup> To disclose the mechanism of the photoinduced electron-transfer reactions, photochemical techniques such as laser flash photolysis are useful.<sup>4–6</sup> When fullerenes were mixed with high concentrated electron donors, forming the charge-transfer complexes in the ground state, electron transfer takes place via the exciplexes.<sup>4</sup> When electron donors were connected with fullerenes by the covalent bonds with appropriate length, electron transfer occurs via the excited singlet route.<sup>5</sup> In dilute polar solution systems, C<sub>60</sub><sup>•−</sup> and C<sub>70</sub><sup>•−</sup> were usually produced via their triplet states (<sup>3</sup>C<sub>60</sub><sup>\*</sup> and <sup>3</sup>C<sub>70</sub><sup>\*</sup>), which abstract the electron from the electron donors.<sup>6</sup>

For porphyrins in nonpolar solvent, it is reported that energy transfer predominantly occurs from triplet states of porphyrins to C<sub>60</sub>/C<sub>70</sub>, from which the energy levels of the lowest <sup>3</sup>C<sub>60</sub><sup>\*</sup>/<sup>3</sup>C<sub>70</sub><sup>\*</sup> were evaluated; the lowest triplet energy level of zinc tetraphenylporphyrin (ZnTPP) is slightly higher than those of <sup>3</sup>C<sub>60</sub><sup>\*</sup>/<sup>3</sup>C<sub>70</sub><sup>\*</sup>.<sup>7</sup> On the other hand, it is also reported that a stacked film of porphyrin and C<sub>60</sub> acts as a highly effective solar cell, suggesting photoinduced electron transfer between them.<sup>8</sup> However, no clear evidence of the photoinduced electron transfer has been reported yet between porphyrin and C<sub>60</sub>/C<sub>70</sub> in solution. The evidence of electron transfer can be given by the direct observation of the ion radicals. For such highly conjugated molecules such as C<sub>60</sub> and C<sub>70</sub>, the transient absorption bands such as C<sub>60</sub><sup>•−</sup>/C<sub>70</sub><sup>•−</sup> are expected to appear in the near-IR region.<sup>9,10</sup> In the present paper, we elucidate the photoinduced electron-transfer mechanism between ZnTPP and C<sub>60</sub>/C<sub>70</sub> and disclose that both ZnTPP and C<sub>60</sub>/C<sub>70</sub> play important roles in the excited states in electron transfer. In addition, the effect of the central metals such as Cu and Ni including H<sub>2</sub> is investigated. It is also interesting to compare the mechanism and efficiency of the photoinduced electron transfer between phthalocyanine with <sup>3</sup>C<sub>60</sub><sup>\*</sup> and <sup>3</sup>C<sub>70</sub><sup>\*</sup> as reported in our previous paper.<sup>11</sup>

## Experimental Section

C<sub>60</sub> and C<sub>70</sub> were obtained from Texas Fullerenes Corp. in a purity higher than 99%. Commercially available zinc tetraphenylporphyrin (ZnTPP) was used after repeated recrystallization. The solutions of C<sub>60</sub>/C<sub>70</sub> and ZnTPP were deaerated with Ar bubbling before measurements.

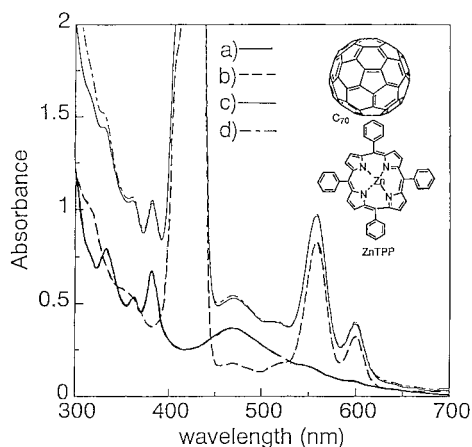
C<sub>60</sub>/C<sub>70</sub> and ZnTPP were excited by a Nd:YAG laser (6 ns fwhm; 10 mJ laser power) with 532 nm light at a constant power of 7 mJ. The transient absorption spectra in the visible and near-IR regions were observed by the laser-flash photolysis apparatus with a pulsed xenon flash lamp as a monitor light, which was passed through a rectangular quartz reaction cell (1 cm) and monochromator. As a detector in the visible and near-IR regions, a Ge avalanche photodiode module (Hamamatsu, C5331-PL) was employed.<sup>12</sup> The steady-state UV–visible absorption spectra were measured with a JASCO V-570 spectrophotometer. All experiments were carried out at 23 °C.

## Results and Discussion

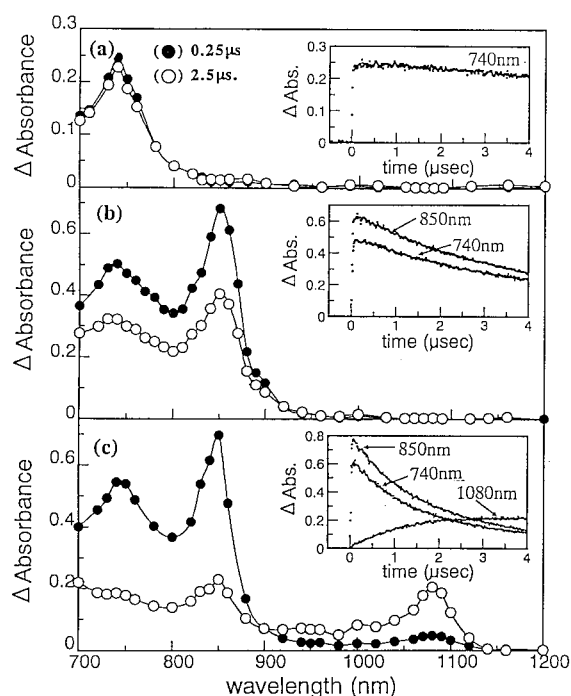
**Steady-State UV and Visible Spectra.** The steady-state UV–visible spectra of C<sub>70</sub> and ZnTPP are shown in Figure 1. The absorption spectrum of the mixture was identical with the superposition of the absorption of the components, suggesting no appreciable interaction in the ground state in benzonitrile under the dilute concentration range used for laser flash photolysis in this study. Both compounds have considerable absorption intensity in the wavelength region at 532 nm, which was used as the excitation wavelength. The molar extinction coefficient (ε) of C<sub>60</sub> at 532 nm was twice that of ZnTPP. Thus, we can control the excitation molecules by their concentrations.

Similarly, the UV–visible spectra of C<sub>60</sub> and ZnTPP show no appreciable change in the visible region between the mixture spectrum and synthesized spectrum. Although a slight change was observed in the UV region between them, the change might be small, taking their high ε values in this region. The ε values at 532 nm were almost same for C<sub>70</sub> and ZnTPP.

**Transient Absorption Spectra.** Figure 2a shows the transient absorption spectra of C<sub>60</sub> observed by the 532 nm

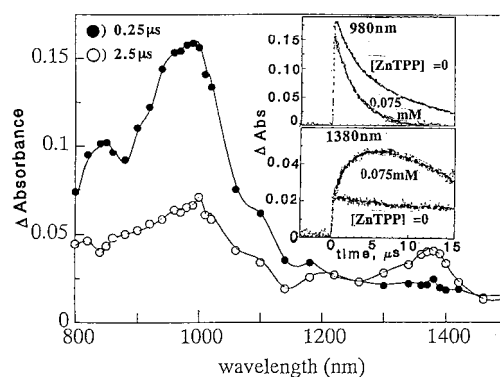


**Figure 1.** Steady-state absorption spectra in the UV and visible region in benzonitrile: (a)  $C_{70}$  (0.05 mM); (b) ZnTPP (0.05 mM); (c) mixture of  $C_{70}$  (0.05 mM) and ZnTPP (0.05 mM); (d) synthesized spectrum of curves a + b overlapping with curve c.



**Figure 2.** Transient absorption spectra obtained by 532 nm laser photolysis: (a)  $C_{60}$  (0.2 mM), (b) ZnTPP (0.2 mM), and (c)  $C_{60}$  (0.2 mM) in the presence of ZnTPP (0.2 mM) in deaerated benzonitrile. The inset shows time profiles.

excitation in deaerated benzonitrile. The transient absorption band at 740 nm was assigned to  ${}^3C_{60}^*$ ,<sup>13</sup> which decays slowly for 4  $\mu$ s in the absence of  $O_2$ . The maximum concentration of  ${}^3C_{60}^*$  ( $[{}^3C_{60}^*]_{\max}$ ) produced by a laser pulse was calculated from the maximal absorbance to be 0.02 mM by using the reported  $\epsilon = 16\,100\text{ cm}^{-1}\text{ M}^{-1}$ .<sup>13</sup> By the laser excitation of ZnTPP in deaerated benzonitrile, the transient absorption bands (Figure 2b) appeared at 850 and 750 nm, which were attributed to  ${}^3\text{ZnTPP}^*$ ,<sup>14</sup> whose maximum concentration ( $[{}^3\text{ZnTPP}^*]_{\max}$ ) was also calculated as 0.09 mM ( $\epsilon = 8500\text{ cm}^{-1}\text{ M}^{-1}$ ).<sup>14</sup> By the excitation of the mixture solution of  $C_{60}$  (0.2 mM) and ZnTPP (0.2 mM) (Figure 2c), an extra transient absorption band appeared at 1080 nm, which can be ascribed to  $C_{60}^{\bullet-}$  ( $[C_{60}^{\bullet-}]_{\max} = 0.02\text{ mM}$ ).<sup>9</sup> Since the 850 nm band decays, showing a mirror image with respect to the rise of  $C_{60}^{\bullet-}$ ,  ${}^3\text{ZnTPP}^*$  may contribute to the formation of  $C_{60}^{\bullet-}$ . Since absorption bands of  $\text{ZnTPP}^{\bullet+}$  are expected to appear at 500–650 nm,<sup>15</sup>  $\text{ZnTPP}^{\bullet+}$  was not



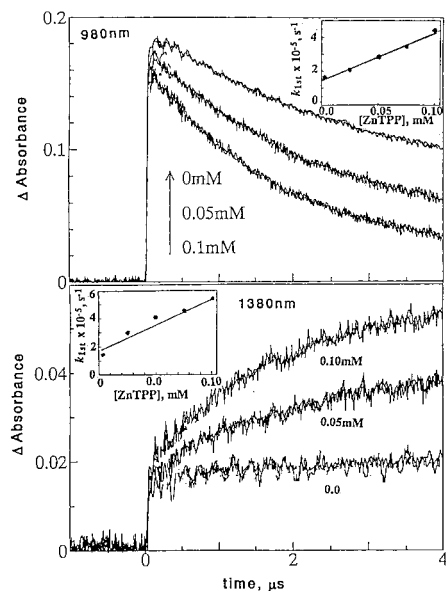
**Figure 3.** Transient absorption spectra obtained by 532 nm laser photolysis of  $C_{70}$  (0.25 mM) in the presence of ZnTPP (0.075 mM) in deaerated benzonitrile. The inset shows time profiles at (a) 980 nm and (b) 1380 nm.

confirmed by Figure 2. The contribution of  ${}^3C_{60}^*$  to the  $C_{60}^{\bullet-}$  formation is not clear because the transient absorption band of  ${}^3C_{60}^*$  at 750 nm was overlapped with that of  ${}^3\text{ZnTPP}^*$ . Since the intensity of the 740 nm band ( ${}^3C_{60}^* + {}^3\text{ZnTPP}^*$ ) relative to that of the 850 nm band ( ${}^3\text{ZnTPP}^*$ ) in Figure 2c is rather similar to that of  ${}^3\text{ZnTPP}^*$  (Figure 2b),  ${}^3C_{60}^*$  may decay quickly, suggesting the contribution of  ${}^3C_{60}^*$  to the formation of  $C_{60}^{\bullet-}$ .

In the case of  $C_{70}$ , it would be expected that the contribution of  ${}^3C_{70}^*$  becomes clear, since the transient absorption band of  ${}^3C_{70}^*$  appears in a longer wavelength region than that of  ${}^3\text{ZnTPP}^*$ .<sup>16</sup> Under the condition of  $[C_{70}]$  (0.25 mM) >  $[\text{ZnTPP}]$  (0.075 mM) in polar benzonitrile, the transient absorption spectra obtained by the 532 nm laser light exposure are shown in Figure 3. The new absorption bands at 980 nm was attributed to  ${}^3C_{70}^*$ <sup>16</sup> and weak absorption at 850 nm to  ${}^3\text{ZnTPP}^*$ .<sup>14</sup> The initial concentrations of the triplet states were calculated to be 0.02 mM for  ${}^3C_{70}^*$  and 0.007 mM for  ${}^3\text{ZnTPP}^*$  by using the reported  $\epsilon$  values.<sup>14,16</sup> Thus, the contribution of  ${}^3\text{ZnTPP}^*$  to electron transfer may be negligibly small.

With the decay of  ${}^3C_{70}^*$ , a new absorption appears at 1380 nm, which was ascribed to  $C_{70}^{\bullet-}$ .<sup>10</sup> The concentration of  $C_{70}^{\bullet-}$  at 2.5  $\mu$ s ( $[{}^3C_{70}^*]_{\max}$ ) was also calculated to be about 0.013 mM using the reported  $\epsilon_A$  value after correction of the absorption tail of  ${}^3C_{70}^*$  at 1380 nm.<sup>10</sup> The time profiles for the decay of  ${}^3C_{70}^*$  are shown in Figure 4; under the constant  $C_{70}$  concentration, the decay rates of  ${}^3C_{70}^*$  increase with the ZnTPP concentration. Assuming a pseudo-first order relation under the condition of  $[\text{ZnTPP}]$  (>0.05 mM) >  $[{}^3C_{70}^*]_{\max}$  (ca. 0.02 mM), the second-order rate constant for the quenching of  ${}^3C_{70}^*$  by ZnTPP, which is denoted as  $k_T^{\text{obs}}$ , was evaluated. The rise rates of  $C_{70}^{\bullet-}$  also increase with  $[\text{ZnTPP}]$  as shown in Figure 4. By the curve-fitting of these rise curves with a single exponential, the first-order rate constants were evaluated. From the pseudo-first-order plot, the second-order rate constant for the rise of  $C_{70}^{\bullet-}$  by ZnTPP ( $k_A^{\text{obs}}$ ) was obtained. Since  $k_A^{\text{obs}}$  is in agreement with  $k_T^{\text{obs}}$  within experimental and estimation errors, the  $k_A^{\text{obs}}$  value is listed in Table 1. Under similar conditions ( $[\text{ZnTPP}] > [{}^3C_{60}^*]_{\max}$ ), the  $k_A^{\text{obs}}$  value for  ${}^3C_{60}^*$  was evaluated (Table 1).

The quantity  $[C_{70}^{\bullet-}]_{\max}/[{}^3C_{70}^*]_{\max}$ , which is the efficiency of  $C_{70}^{\bullet-}$  formation via  ${}^3C_{70}^*$  by electron transfer, can be evaluated because both quantities were observable in the near-IR region. When  $[C_{70}^{\bullet-}]_{\max}/[{}^3C_{70}^*]_{\max}$  is plotted against  $[\text{ZnTPP}]$ ,  $[C_{70}^{\bullet-}]_{\max}/[{}^3C_{70}^*]_{\max}$  increases with  $[\text{ZnTPP}]$  as shown in Figure 5. Usually,  $[C_{70}^{\bullet-}]_{\max}/[{}^3C_{70}^*]_{\max}$  shows a saturation curve with respect to  $[\text{ZnTPP}]$ , yielding the quantum yield  $\Phi_{\text{et}}$  for  $C_{70}^{\bullet-}$  formation via  ${}^3C_{70}^*$ .<sup>17</sup>



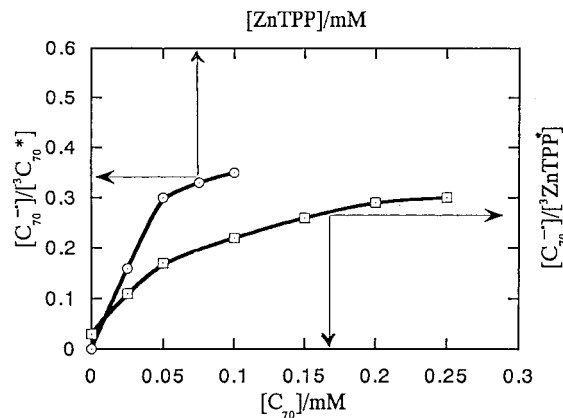
**Figure 4.** Decay profiles of  $[^3\text{C}_{70}^*]$  at 980 nm and rise profiles of  $[\text{C}_{70}^{\bullet-}]$  at 1380 nm with changing  $[\text{ZnTPP}]$  (mM). The inset shows pseudo-first-order plots.

From Figure 5,  $\Phi_{\text{et}}$  via  $^3\text{C}_{70}^*$  is evaluated to be about 0.35 for  $^3\text{C}_{70}^*/\text{ZnTPP}$ . This implies that 35% of  $^3\text{C}_{70}^*$  is converted to  $\text{C}_{70}^{\bullet-}$ , while 65% of  $^3\text{C}_{70}^*$  is deactivated without forming  $\text{C}_{70}^{\bullet-}$ . Therefore, the mechanism of the electron-transfer process is as shown in Scheme 1. The electron-transfer rate constant ( $k_{\text{et}}$ ) via  $^3\text{C}_{70}^*$  was calculated by the relation of  $\Phi_{\text{et}}k_{\text{A}}^{\text{obs}} (=7.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1})$ , which is in accord with that calculated by  $\Phi_{\text{et}}k_{\text{T}}^{\text{obs}}$  to be  $9.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>17</sup> The  $\Phi_{\text{et}}$  and  $k_{\text{et}}$  values are listed in Table 1. The remaining part ( $1 - \Phi_{\text{et}}$ ) can be attributed to the deactivation processes of  $^3\text{C}_{70}^*$  by excess ZnTPP such as energy-transfer, charge-transfer, and collisional quenching processes.

The contribution of  $^3\text{C}_{70}^*$  to  $\text{C}_{70}^{\bullet-}$  formation was also confirmed, since  $\text{C}_{70}^{\bullet-}$  formation was suppressed almost completely on addition of  $\text{O}_2$  into solution.<sup>17b,c</sup> This implies that  $\text{O}_2$  (about 1 mM in  $\text{O}_2$ -saturated solution in benzonitrile)<sup>18</sup> quenches  $^3\text{C}_{70}^*$  more quickly than ZnTPP (0.1 mM) does because both rate constants are ca.  $1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ .

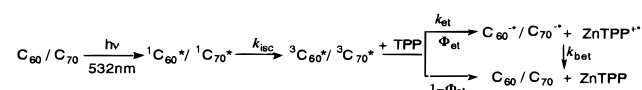
In the case of electron transfer from ZnTPP to  $^3\text{C}_{60}^*$ , the  $\Phi_{\text{et}}$  value was approximately evaluated because of overlap of the absorption of  $^3\text{C}_{60}^*$  with  $^3\text{ZnTPP}^*$  as shown in Figure 2. Separation of  $^3\text{C}_{60}^*$  with  $^3\text{ZnTPP}^*$  at the 740 nm band was performed using the reported  $\epsilon$  values.<sup>14</sup> For electron transfer from CuTPP to  $^3\text{C}_{60}^*$ , the  $\Phi_{\text{et}}$  and  $k_{\text{et}}$  values were evaluated, since the absorption bands of  $^3\text{CuTPP}^*$  did not disturb the decay of  $^3\text{C}_{60}^*$  and appearance of  $\text{C}_{60}^{\bullet-}$  (Table 1). For NiTPP, the quenching of  $^3\text{C}_{60}^*/\text{C}_{70}^*$  took place predominantly without the appearance of  $\text{C}_{60}^{\bullet-}/\text{C}_{70}^{\bullet-}$ .

The free-energy change of the electron-transfer process from ZnTPP to  $^3\text{C}_{70}^*/^3\text{C}_{60}^*$  ( $\Delta G_0$  via  $^3\text{C}_{70}^*/^3\text{C}_{60}^*$ ) was calculated to be  $-48 \pm 5 \text{ kJ/mol}$  from the Rehm–Weller relation,<sup>19</sup> employing the lowest triplet energies of  $^3\text{C}_{70}^*/^3\text{C}_{60}^*$  ( $T_1 = 1.50 \text{ eV}$ ),<sup>20</sup> reduction potentials of  $\text{C}_{70}/\text{C}_{60}$  ( $E_{\text{red}} = -0.50 \text{ V vs SCE}$ ),<sup>21</sup> oxidation potential of ZnTPP ( $E_{\text{ox}} = 0.71 \text{ V vs SCE}$ ),<sup>22</sup> and Coulomb energy = 0.06 eV in benzonitrile.<sup>6b</sup> The  $\Delta G_0$  (via  $^3\text{C}_{70}^*/^3\text{C}_{60}^*$ ) value is far negative, suggesting that  $k_{\text{et}}$  via  $^3\text{C}_{70}^*/^3\text{C}_{60}^*$  should be close to the diffusion-controlled limit ( $k_{\text{dif}}$ ). In the case of  $^3\text{C}_{70}^*/^3\text{C}_{60}^*$ , however, the reported  $k_{\text{et}}$  values for  $\text{C}_{60}/\text{C}_{70}$  are usually less than  $k_{\text{dif}}$  by a factor of  $1/5$ .<sup>6,17</sup> Thus, the estimated  $k_{\text{et}}$  values of ca.  $10^9 \text{ M}^{-1} \text{ s}^{-1}$  for ZnTPP may be reasonable. In Table 1,  $k_{\text{et}}$  for CuTPP is small because of the



**Figure 5.** Dependence of  $[\text{C}_{70}^{\bullet-}]/[^3\text{C}_{70}^*]$  on  $[\text{ZnTPP}]$  for  $[\text{C}_{70}] > [\text{ZnTPP}]$ , and  $[\text{C}_{70}^{\bullet-}]/[^3\text{ZnTPP}^*]$  on  $[\text{C}_{70}]$  for  $[\text{ZnTPP}] > [\text{C}_{70}]$ .

#### SCHEME 1



low  $\Phi_{\text{et}}$ , which may be ascribed to the higher oxidation potential of CuTPP ( $E_{\text{ox}} = 0.90 \text{ V vs SCE}$ ).<sup>22</sup> The  $\Phi_{\text{et}}$  via  $^3\text{C}_{70}^*$  is similar to that via  $^3\text{C}_{60}^*$  with respect to ZnTPP; these  $\Phi_{\text{et}}$  values for ZnTPP are smaller than those for zinc phthalocyanine (ZnPc) by a factor of ca.  $1/2$ .<sup>11</sup> This is caused by the low oxidation potential of ZnPc ( $E_{\text{ox}} = 0.4 \text{ V vs SCE}$ ).<sup>11</sup>

After reaching maximal concentration,  $\text{C}_{70}^{\bullet-}$  begins decaying (inserted time profile at 1380 nm in Figure 3). The decay obeys second-order kinetics in benzonitrile, yielding a slope of  $k_{\text{bet}}/\epsilon_{\text{A}} = 9.5 \times 10^5 \text{ s}^{-1} \text{ cm}$ , where  $k_{\text{bet}}$  refers to the back electron-transfer rate constant. By substitution of the reported  $\epsilon_{\text{A}}$ ,<sup>10</sup>  $k_{\text{bet}}$  was evaluated to be  $3.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , which is close to the diffusion-controlled limit in benzonitrile ( $4.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ). Second-order kinetics suggests that the back electron transfer takes place between the free ion radicals.<sup>23</sup> On the other hand, although a small amount of  $\text{C}_{70}^{\bullet-}/\text{C}_{60}^{\bullet-}$  was formed [ $\Phi_{\text{et}}(^3\text{C}_{70}^*/^3\text{C}_{60}^*) < 0.05$ ] in benzene,  $\text{C}_{70}^{\bullet-}/\text{C}_{60}^{\bullet-}$  decayed quickly within  $1.5 \mu\text{s}$  obeying first-order kinetics [ $k_{\text{1st}} = (5-8) \times 10^6 \text{ s}^{-1}$ ], indicating that the back electron transfer takes place within the ion pair of the ion radicals.<sup>23</sup>

Under the conditions of excess in ZnTPP (0.4 mM) compared with  $\text{C}_{70}$  (0.1 mM), the transient absorption spectra are shown in Figure 6, where the absorption band of  $^3\text{ZnTPP}^*$  at 850 nm appears accompanying a shoulder at 760 nm. In addition, the weak absorption band of  $^3\text{C}_{70}^*$  appears at 980 nm. From the initial absorption intensities,  $[\text{ZnTPP}^*]_{\text{max}} = 0.07 \text{ mM}$  and  $[\text{C}_{70}^*]_{\text{max}} = 0.008 \text{ mM}$ . With the decays of these triplet states, the absorption of  $\text{C}_{70}^{\bullet-}$  appears at 1380 nm up to  $[\text{C}_{70}^{\bullet-}]_{\text{max}} = 0.01 \text{ mM}$ , which is a higher concentration than initial  $[\text{C}_{70}^*]$ . Thus, it is certain that the electron transfer forming  $\text{C}_{70}^{\bullet-}$  takes place via  $^3\text{ZnTPP}^*$ . The weak absorption of  $^3\text{C}_{70}^*$  decays quite quickly, indicating that some amount of  $\text{C}_{70}^{\bullet-}$  is produced via  $^3\text{C}_{70}^*$  as shown in Scheme 1. By use of  $\Phi_{\text{et}}(^3\text{C}_{70}^*) = 0.35$ , about a half of  $\text{C}_{70}^{\bullet-}$  is formed via  $^3\text{C}_{70}^*$ .

The time profiles are shown in Figure 7. The decay rate of  $^3\text{ZnTPP}^*$  was increased by the addition of  $\text{C}_{70}$ , indicating that electron transfer takes place from  $^3\text{ZnTPP}^*$  to  $\text{C}_{70}$  in the ground state (Scheme 2). This supports the proposed mechanism by Hwang and Mauzerall in their study of vectorial electron transfer in a lipid bilayer.<sup>8a,b</sup> The triplet route was also confirmed by the depression of  $\text{C}_{70}^{\bullet-}$  formation in the presence of  $\text{O}_2$ .<sup>17b,c</sup> With an increase in  $[\text{C}_{70}]$  from 0.025 to 0.2 mM, the first-order



TABLE 1: Electron-Transfer Rate Constants for Electron Transfer and Quantum Yields in Benzonitrile

reaction	$k_A^{\text{obs}}$ ( $\text{M}^{-1} \text{s}^{-1}$ ) <sup>a</sup>	$\Phi_{\text{et}}$	$k_{\text{et}}$ ( $\text{M}^{-1} \text{s}^{-1}$ ) <sup>b</sup>
$^3\text{C}_{70}^* + \text{ZnTPP} \rightarrow \text{C}_{70}^{\bullet-} + \text{ZnTPP}^{*+}$	$2.2 \times 10^9$	0.35	$7.7 \times 10^8$
$^3\text{C}_{60}^* + \text{ZnTPP} \rightarrow \text{C}_{60}^{\bullet-} + \text{ZnTPP}^{*+}$	$4.3 \times 10^9$	0.26	$1.1 \times 10^9$
$^3\text{C}_{60}^* + \text{CuTPP} \rightarrow \text{C}_{60}^{\bullet-} + \text{CuTPP}^{*+}$	$2.1 \times 10^9$	0.13	$2.7 \times 10^8$
$^3\text{ZnTPP}^* + \text{C}_{70} \rightarrow \text{ZnTPP}^{*+} + \text{C}_{70}^{\bullet-}$	$4.7 \times 10^9$	$0.30^c$ (0.15) <sup>d</sup>	$7.0 \times 10^8$ <sup>d</sup>
$^3\text{ZnTPP}^* + \text{C}_{60} \rightarrow \text{ZnTPP}^{*+} + \text{C}_{60}^{\bullet-}$	$4.0 \times 10^9$	$0.24^c$ (0.12) <sup>d</sup>	$4.8 \times 10^8$ <sup>d</sup>
$^3\text{H}_2\text{TPP}^* + \text{C}_{60} \rightarrow \text{H}_2\text{TPP}^{*+} + \text{C}_{60}^{\bullet-}$	$1.1 \times 10^9$	$0.26^c$ (0.13) <sup>d</sup>	$1.4 \times 10^8$ <sup>d</sup>

<sup>a</sup>  $k_A^{\text{obs}}$  refers to the second-order rate constant for the rise of  $\text{C}_{60}^{\bullet-}/\text{C}_{70}^{\bullet-}$ . <sup>b</sup>  $k_{\text{et}}$  refers to the electron-transfer rate constant evaluated from the relation of  $k_{\text{et}} = \Phi_{\text{et}} k_A^{\text{obs}}$ . <sup>c</sup> Observed  $\Phi_{\text{et}}$  was evaluated on the basis of  $[\text{C}_{60}^{\bullet-}/\text{C}_{70}^{\bullet-}]_{\text{max}}/[\text{ZnTPP}^*]_{\text{max}}$  or  $[\text{C}_{60}^{\bullet-}]_{\text{max}}/[\text{H}_2\text{TPP}^*]_{\text{max}}$ , which contains both  $\Phi_{\text{et}}$  via  $^3\text{ZnTPP}^*$  and  $\Phi_{\text{et}}$  via  $^3\text{C}_{60}^*/^3\text{C}_{70}^*$ . <sup>d</sup> The  $\Phi_{\text{et}}$  values in parentheses are corrected ones, and  $k_{\text{et}}$  values were calculated using corrected  $\Phi_{\text{et}}$ .

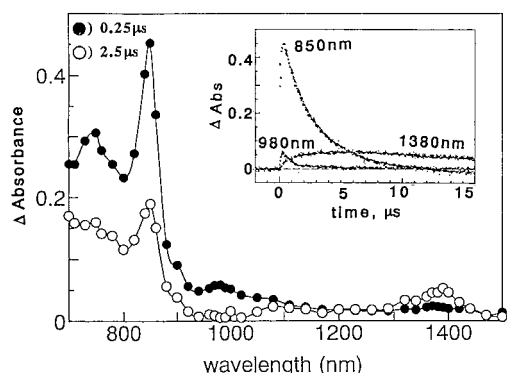


Figure 6. Transient absorption spectra obtained by 532 nm laser photolysis of ZnTPP (0.4 mM) in the presence of  $\text{C}_{70}$  (0.1 mM) in deaerated benzonitrile. The inset shows time profiles.

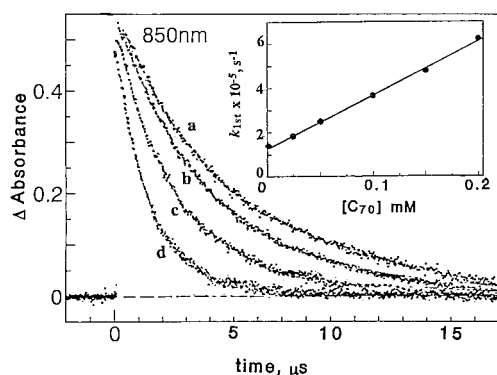


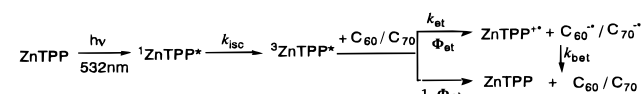
Figure 7. Decay profiles of  $^3\text{ZnTPP}^*$  at 850 nm with change of  $[\text{C}_{70}]$ : (a) 0.05, (b) 0.1, (c) 0.15, and (d) 0.20 mM. The inset shows a pseudo-first-order plot.

rate constants evaluated from the decay of  $^3\text{ZnTPP}^*$  increase. From the pseudo-first-order relationship, the rate constant for the quenching of  $^3\text{ZnTPP}^*$  by  $\text{C}_{70}$  ( $k_{\text{T}}^{\text{obs}}$ ) was evaluated to be  $2.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . Similarly, from the dependence of the rise rate of  $\text{C}_{70}^{\bullet-}$  on the concentration of  $\text{C}_{70}$ , the second-order rate constant ( $k_A^{\text{obs}}$ ) was evaluated. The rate constants for  $^3\text{ZnTPP}^*/\text{C}_{60}$  and  $^3\text{H}_2\text{TPP}^*/\text{C}_{60}$  were evaluated with the same method (Table 1).

The efficiency of  $\text{C}_{70}^{\bullet-}$  formation via  $^3\text{ZnTPP}^*$  is plotted against  $[\text{C}_{70}]$  (Figure 5). The quantum yield of  $\text{C}_{70}^{\bullet-}$  formation via  $^3\text{ZnTPP}^*$ ,  $\Phi_{\text{et}}$ , was estimated. By correction of  $\text{C}_{70}^{\bullet-}$  formation via  $^3\text{ZnTPP}^*$ , a half value can be attributed to  $\Phi_{\text{et}}$  (via  $^3\text{ZnTPP}^*$ ). Thus, the rate constant of electron transfer forming  $\text{C}_{70}^{\bullet-}$  via  $^3\text{ZnTPP}^*$ , which is denoted as  $k_{\text{et}}$  (via  $^3\text{ZnTPP}^*$ ), was calculated as summarized in Table 1, which is slightly smaller than that of  $k_{\text{et}}$  (via  $^3\text{C}_{70}^*$ ).

The  $\Delta G_0$  (via  $^3\text{ZnTPP}^*$ ) for the electron-transfer process from  $^3\text{ZnTPP}^*$  to  $\text{C}_{70}/\text{C}_{60}$  was calculated to be  $-53 \pm 2 \text{ kJ/mol}$  from the Rehm–Weller relation<sup>19</sup> by employing the lowest triplet

## SCHEME 2



energy  $T_1(^3\text{ZnTPP}^*) = 1.59 \text{ eV}$ <sup>24</sup> and  $E_{\text{ox}}$  of ZnTPP (0.71 V vs SCE).<sup>22</sup> The estimated  $\Delta G_0$  (via  $^3\text{ZnTPP}^*$ ) is far negative, suggesting that  $k_{\text{et}}(^3\text{ZnTPP}^* + \text{C}_{70}/\text{C}_{60})$  should be close to  $k_{\text{dif}}$ ; in the case of  $\text{C}_{70}/\text{C}_{60}$ , ca.  $10^9 \text{ M}^{-1} \text{ s}^{-1}$  is reasonable. In Table 1, the values of  $\Phi_{\text{et}}$  via  $^3\text{ZnTPP}^*$  are about half of  $\Phi_{\text{et}}$  via  $^3\text{C}_{60}^*/^3\text{C}_{70}^*$  (Scheme 1). Nevertheless,  $\Delta G_0$  (via  $^3\text{ZnTPP}^*$ ) is less negative than  $\Delta G_0$  (via  $^3\text{C}_{60}^*/^3\text{C}_{70}^*$ ), which may be caused by the Marcus inverted region.<sup>25</sup> The small  $k_{\text{et}}$  for  $^3\text{H}_2\text{TPP}^*/\text{C}_{60}$  compared with  $^3\text{ZnTPP}^*/\text{C}_{60}$  may come from the higher oxidation potential of  $\text{H}_2\text{TPP}$  [ $E_{\text{ox}} = 0.95 \text{ V}$  vs SCE]<sup>22</sup> than  $E_{\text{ox}}$  for ZnTPP by 0.2 V, since the triplet energy of  $\text{H}_2\text{TPP}$  is the same as that of ZnTPP.<sup>22</sup>

The back electron transfer was also followed by the decay of  $\text{C}_{70}^{\bullet-}$  after reaching the maximum. From the second-order plot yielding  $k_{\text{bet}}/\epsilon_A$  ( $1.5 \times 10^6 \text{ s}^{-1} \text{ cm}^{-1}$  for  $\text{C}_{70}$ ),  $k_{\text{bet}}$  was evaluated to be  $6.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . The  $k_{\text{bet}}$  should be almost the same irrespective of the formation routes of the ion radicals, which is proved in this study within the experimental errors.

## Concluding Remarks

The photoinduced electron transfer takes place in a mixture of  $\text{C}_{60}/\text{C}_{70}$  and ZnTPP via their lowest triplet states in polar solvent. The direction of electron transfer depends on their concentrations. Under the condition of  $[\text{C}_{60}/\text{C}_{70}] > [\text{ZnTPP}]$ ,  $^3\text{C}_{60}^*/^3\text{C}_{70}^*$  abstracts the electron from ZnTPP. On the other hand, under the condition of  $[\text{ZnTPP}] > [\text{C}_{60}/\text{C}_{70}]$ ,  $^3\text{ZnTPP}^*$  donates its electron to  $\text{C}_{60}/\text{C}_{70}$ , in addition to the  $^3\text{C}_{60}^*/^3\text{C}_{70}^*$  route. The former has a higher efficiency of  $\text{C}_{60}^{\bullet-}/\text{C}_{70}^{\bullet-}$  formation than the latter. Since fullerenes and ZnTPP have intense absorptions in the wide UV–visible region, these combined systems can be used as efficient solar-energy conversion systems.

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