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Photoinduced Electron Transfer from Phthalocyanines to Fullerenes (C$_{60}$ and C$_{70}$)

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Photoinduced electron transfer between fullerenes (C$_{60}$ and C$_{70}$) and phthalocyanines such as tetra-*tert*-butylphthalocyanine (H$_2$TBPc) and its zinc derivative (ZnTBPc) in solution has been investigated with nanosecond laser photolysis method by observing the transient absorption bands in the visible/near-IR regions. By the predominant excitation of fullerenes with 532 nm laser light, slow rises of the transient absorption bands of phthalocyanine cation radicals and fullerene anion radicals were observed instead of the decays of the excited triplet states of fullerenes (^{T}C$_{60}$* and ^{T}C$_{70}$*) in polar solvents. Electron-transfer from the phthalocyanines to ^{T}C$_{60}$* or ^{T}C$_{70}$* was confirmed. The quantum yield of the electron transfer via ^{T}C$_{70}$* is higher than that via ^{T}C$_{60}$*; ZnTBPc acts as stronger electron donor than H$_2$TBPc. In nonpolar solvent, energy transfer from ^{T}C$_{60}$* (and ^{T}C$_{70}$*) to the phthalocyanines occurs predominantly as confirmed by the consecutive appearance of the triplet states of the phthalocyanines.

Introduction

Fullerenes such as C$_{60}$ and C$_{70}$ were known to accelerate the photoinduced electric conductivity when they are added into some molecules such as phthalocyanines and porphyrins.[1−8] In solutions and polymer films, the mechanisms of the photoinduced electron-transfer reactions of fullerenes have been investigated by photochemical techniques such as laser flash photolysis.[9−19] In the mixture system of C$_{60}$ (or C$_{70}$) with electron donors in polar solvents, C$_{60}$$^{•−}$ and C$_{70}$$^{•−}$ were usually produced via their triplet states (^{T}C$_{60}$* and ^{T}C$_{70}$*) which abstract the electron from the electron donors such as aromatic amines when the concentrations of electron donors are appropriately dilute.[20−22] For the C$_{60}$ compounds connected with chromophores by the covalent bonds, photoinduced electron transfer takes place via the singlet state of the chromophores.[17−21]

In nonpolar solvent, when C$_{60}$ and C$_{70}$ were photoexcited in the presence of chromophores with low lying triplet state, it is reported that energy transfer occurs from the triplet states of C$_{60}$ (or C$_{70}$) to the chromophores.[9] From these findings, the lowest energies of ^{T}C$_{60}$* and ^{T}C$_{70}$* were evaluated.[9] In polar solvents, on the other hand, it would be anticipated that photoinduced electron transfer takes place between ^{T}C$_{60}$* (or ^{T}C$_{70}$*) and the chromophores such as phthalocyanines and porphyrins. But it is difficult to confirm the electron transfer only from the acceleration of the decay rates of ^{T}C$_{60}$* and ^{T}C$_{70}$*. Thus, it is necessary to obtain the direct evidence for electron transfer by observing formations of the anion radicals of C$_{60}$/C$_{70}$ (C$_{60}$$^{•−}$/C$_{70}$$^{•−}$), which are observable in the near-IR region.[10,11,28−34]

In the present report, phthalocyanines in solutions have been investigated with nanosecond laser photolysis method by observing the transient absorption bands in the visible/near-IR regions. As phthalocyanines, we employed tetra-*tert*-butylphthalocyanine (H$_2$TBPc) and zinc derivative (ZnTBPc) as shown in Scheme 1, because of their high solubility in the solvents such as benzonitrile and benzene which dissolve also C$_{60}$ and C$_{70}$ in considerable amount. It is noticeable that 532 nm laser light is absorbed by C$_{60}$ and C$_{70}$, but not by H$_2$TBPc and

SCHEME 1

M=H$_2$; H$_2$TBPc, M=Zn; ZnTBPc
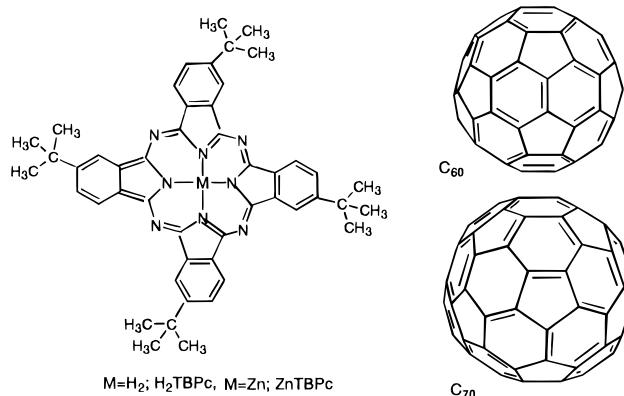
ZnTBPc. Thus, we can expect to disclose the roles of the excited states of C$_{60}$ and C$_{70}$ in electron transfer.

## Experimental Section

C$_{60}$ and C$_{70}$ were obtained from Texas Fullerenes Corp. in a purity of 99.9% and 99%, respectively. Zinc tetra-*tert*-butylphthalocyanine (ZnTBPc) was prepared according to the method described elsewhere and purified through silica gel column using diethyl ether as eluent.[35] An elemental analysis of C$_{36}$H$_{24}$N$_8$Zn was as follows: Anal. Calcd: C, 68.19; H, 3.81; N, 17.67; Zn, 10.33. Found: C, 68.11; H, 4.13; N, 17.30; Zn, 10.46. Purity of commercially available tetra-*tert*-butylphthalocyanine (H$_2$TBPc) was checked with TLC and found to be high purity. The solution of C$_{60}$ (or C$_{70}$) and ZnTBPc (or H$_2$TBPc) was deaerated with Ar bubbling before measurements.

C$_{60}$ and C$_{70}$ were selectively excited by 532 nm light from a Nd:YAG laser (6 ns fwhm) with 7 mJ power. For the transient absorption spectra in the visible region, a photomultiplier tube was used as a detector for the continuous Xe-monitor light (150 W). In the near-IR region, a Ge-APD detector was employed to monitor the transmitted light from a pulsed xenon-flash lamp (150 W), which was passed through a rectangular quartz reaction cell (1 cm) and monochromator.[36,37] The steady-state UV/vis absorption spectra were measured with a JASCO/V-570 spectrophotometer. All experiments were carried out at 23 °C.
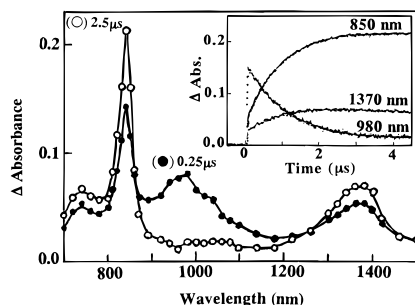
[†] Tohoku University.
[‡] Miyagi National College of Technology.
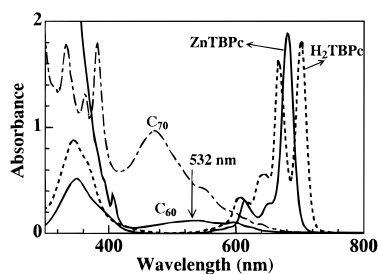
Figure 1. Steady-state absorption spectra in the UV and visible region in benzonitrile: C_{60} (0.25 mM), C_{70} (0.3 mM), H_2TBPc (0.05 mM), and ZnTBPc (0.05 mM) in 2 mm cell.

Figure 2. Transient absorption spectra obtained by 532 nm laser photolysis of C_{70} (0.3 mM) in the presence of ZnTBPc (0.2 mM) in benzonitrile. Insert: time profiles.

Results and Discussion

Steady-State UV and Visible Spectra. The steady-state UV and visible spectra of C_{60}, C_{70}, H_2TBPc, and ZnTBPc in benzonitrile are shown in Figure 1. Since both ZnTBPc and H_2TBPc have not appreciable absorption intensity at 532 nm, C_{60} and C_{70} were predominantly excited by 532 nm laser light. The spectrum of the mixture of C_{60} (or C_{70}) with ZnTBPc (or H_2TBPc) is similar to the synthesized one, suggesting that appreciable charge transfer interaction does not exist in the ground state under the concentration range (0.05−0.3 mM), where the laser experiments were performed. In benzene, similar spectra were obtained.

Transient absorption spectra obtained by the 532 nm laser light exposure on C_{70} in the presence of ZnTBPc in benzonitrile are shown in Figure 2. The absorption band appearing at 980 nm immediately after the laser exposure was attributed to $^{T}C_{70}*$.[38−41] With the decay of the absorption band of $^{T}C_{70}*$, new absorption bands appeared at 850 and 1370 nm, which are assigned to ZnTBPc[42,43] and $C_{70}^{\bullet-}$,[28−34] respectively. Since the weak absorption band at 750 nm tends to increase with time, this band is also attributed to ZnTBPc[42,43]

The time profiles (inset in Figure 2) show that ZnTBPc (850 nm) and $C_{70}^{\bullet-}$ (1370 nm) begin to rise with the decay of $^{T}C_{70}*$ (980 nm). The initial fast rise of $C_{70}^{\bullet-}$ may be ascribed to the absorption tail of $^{T}C_{70}*$. Incomplete decay of $^{T}C_{70}*$ after 5 μs may be due to the absorption tail of $C_{70}^{\bullet-}$. The initial concentration of $^{T}C_{70}*$ was calculated to be 0.025 mM by using the reported ϵ value (6500 M^{-1} cm^{-1} at 980 nm).[31,44] The maximal concentration of $C_{70}^{\bullet-}$ at 2.5 μs was also calculated to be about 0.019 mM after subtraction the absorption tail using $\epsilon = 4000$ M^{-1} cm^{-1} at 1370 nm.[32]

Similar transient absorption spectra were obtained by the 532 nm laser light exposure on C_{60} in the presence of ZnTBPc in benzonitrile (Figure 3). The absorption band appeared at 750 nm was attributed to $^{T}C_{60}*$.[45−48] With the decay of $^{T}C_{60}*$, the absorption bands appeared at 850 and 1070 nm, which are assigned to ZnTBPc and $C_{60}^{\bullet-}$, respectively.[10,11,28−31] Inset in Figure 3 shows the time profiles, in which ZnTBPc and
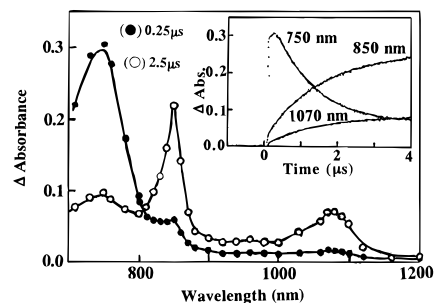
Figure 3. Transient absorption spectra obtained by 532 nm laser photolysis of C_{60} (0.3 mM) in the presence of ZnTBPc (0.2 mM) in benzonitrile. Insert: time profiles.
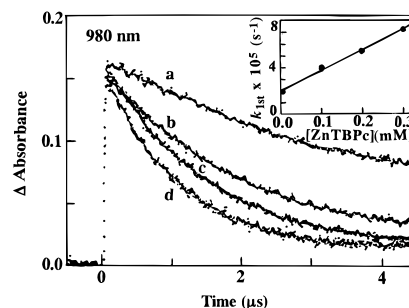
Figure 4. Decay profiles of [$^{T}C_{70}*$] at 980 nm with changing [ZnTBPc]: (a) 0, (b) 0.1, (c) 0.2, and (d) 0.3 mM. Insert: pseudo-first-order plot.

$C_{60}^{\bullet-}$ increase with the decay of $^{T}C_{60}*$. The absorption intensity at 750 nm did not decay completely, because the absorption due to ZnTBPc may be overlapping. The rise curves of $C_{60}^{\bullet-}$ and ZnTBPc seem to be mirror image of the decay curve of $^{T}C_{60}*$, indicating that both ZnTBPc and $C_{60}^{\bullet-}$ are produced from $^{T}C_{60}*$. The initial concentration of $^{T}C_{60}*$ was 0.016 mM ($\epsilon = 16\,000$ M^{-1} cm^{-1} at 750 nm).[48] The maximal concentration of $C_{60}^{\bullet-}$ at 4 μs was 0.008 mM ($\epsilon = 12\,000$ M^{-1} cm^{-1} at 1070 nm).[31,49]

The decay rate of $^{T}C_{70}*$ increases with an increase in the concentration of ZnTBPc as shown in Figure 4. Each decay curve obeys first-order kinetics, showing the linear line in the plot of ln(Absorbance) vs time; the slope of the plot is the first-order rate constant (k_{first}). The decay kinetic may satisfy the pseudo-first-order condition, since [ZnTBPc] > [$^{T}C_{70}*$]. The k_{first} values increase with [ZnTBPc] as shown in the inset of Figure 4; this slope yields the second-order rate constant which is denoted as k_{second}^{T}. The k_{second}^{T} values are summarized in Table 1 for C_{60} and C_{70} as triplet sensitizers and ZnTBPc and H_2TBPc as electron donors in benzonitrile and benzene.

The rise rates of $C_{60}^{\bullet-}$ increase with the concentration of ZnTBPc in benzonitrile as shown in Figure 5. Immediately after the laser pulse, each absorption intensity increases from absorbance = 0 at time = 0, which denies the contribution of the fast electron-transfer process from the singlet state. Each rise curve was fitted with a single exponential, yielding k_{first}. The k_{first} is plotted with [ZnTBPc] as shown in insert of Figure 5, in which the slope gives the second-order rate constant, k_{second}^{A}. Table 1 includes the k_{second}^{A} values which are in agreement with the corresponding k_{second}^{T} values within the experimental and estimation errors.

By the 532 nm laser exposure of C_{60} in the presence of ZnTBPc in nonpolar benzene, the transient absorption band of $^{T}C_{60}*$ was observed at 750 nm, but the absorption bands due to ZnTBPc and $C_{60}^{\bullet-}$ were not observed in the near-IR region (Figure 6). The negative absorbance in the shorter wavelength region than 750 nm may be due to the depletion of ZnTBPc.

TABLE 1: Rate Constants and Quantum Yields for Electron Transfer and Energy Transfer[a]

fullerene	donor	solvent	k_{second}^T $(M^{-1} s^{-1})$	k_{second}^A $(M^{-1} s^{-1})$	Φ_{elt}	Φ_{ent}	k_{elt} $(M^{-1} s^{-1})$	k_{ent} $(M^{-1} s^{-1})$
C_{60}	ZnTBPc	BN	1.6×10^9	2.2×10^9	0.50	0.50	8.0×10^8	8.0×10^8
		BZ	2.1×10^9	b	0.00	1.00	b	2.1×10^9
	H_2TBPc	BN	3.0×10^9	3.2×10^9	0.18	0.82	5.4×10^8	2.5×10^9
		BZ	2.8×10^9	b	0.00	1.00	b	2.8×10^9
C_{70}	ZnTBPc	BN	1.7×10^9	1.7×10^9	0.75	0.25	1.3×10^9	4.0×10^8
		BZ	1.8×10^9	b	0.00	1.00	b	1.8×10^9
	H_2TBPc	BN	3.5×10^9	3.6×10^9	0.20	0.80	7.0×10^8	2.8×10^8
		BZ	1.8×10^9	b	0.00	1.00	b	1.8×10^8

[a] Abbreviations are as follows: k_{second}^T, observed second-order rate constant for decay of $^TC_{60}*$ and $^TC_{70}*$; k_{second}^A; observed second-order rate constant for rise of $C_{60}^{\bullet-}$ and $C_{70}^{\bullet-}$; Φ_{elt}, quantum yield for electron transfer; Φ_{ent}, quantum yield of energy transfer obtained by $(1-\Phi_{elt})$; k_{elt}, rate constant for electron transfer from $^TC_{60}*$ and $^TC_{70}*$ ($=\Phi_{elt} k_{second}^T$); and k_{ent}, rate constant for energy transfer from $^TC_{60}*$ and $^TC_{70}*$ ($=\Phi_{ent} k_{second}^T$). BN, benzonitrile and BZ, benzene. [b] Anion radicals were not observed.
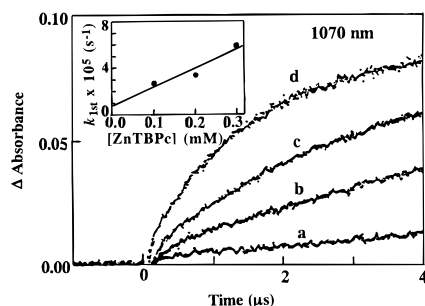
Figure 5. Rise profiles of $[C_{60}^{\bullet-}]$ at 1070 nm with changing [ZnTBPc]: (a) 0, (b) 0.1, (c) 0.2, and (d) 0.3 mM. Insert: pseudo-first-order plot.

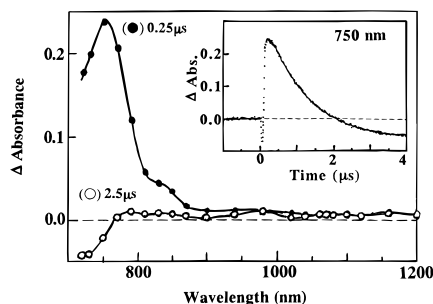**Figure 6.** Transient absorption spectra obtained by 532 nm laser photolysis of C_{60} (0.3 mM) in the presence of ZnTBPc (0.3 mM) in benzene. Insert: time profile at 750 nm.

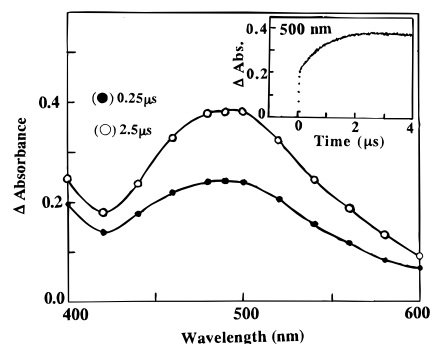**Figure 7.** Transient absorption spectra obtained by 532 nm laser photolysis of C_{60} (0.3 mM) in the presence of ZnTBPc (0.3 mM) in benzene. Insert: time profile at 500 nm.

Since the decay of $^TC_{60}*$ was accelerated on addition of ZnTBPc, the reactions other than electron transfer may take place. In the visible region, the transient absorption band appeared at 500 nm with the decay of $^TC_{60}*$ (Figure 7). The new absorption band at 500 nm was ascribed to $^TZnTBPc*$.[50,51] The fast rise of the absorption intensity at 500 nm was attributed to the absorption band of $^TC_{60}*$ having considerable absorption intensity in this region. Contribution of the direct excitation

SCHEME 2
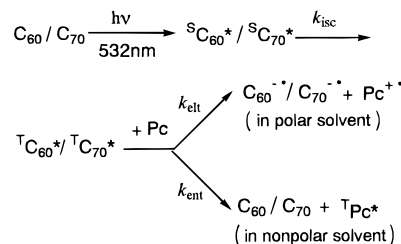
of ZnTBPc to the formation of $^TZnTBPc*$ is small; the initial absorbance of 0.02 due to $^TZnTBPc*$ was observed by the 532 nm excitation of 0.3 mM of ZnTBP in the absence of C_{60}. In the case of H_2TBPc in benzene, the transient absorption bands due to $^TH_2$TBPc* were observed in the region of 1100−1200 nm in addition to 480 nm.[50,52]

From these findings, the observed reactions are illustrated as Scheme 2, in which ZnTBPc and H_2TBPc are abbreviated as Pc. In benzene, energy transfer from $^TC_{60}*$ (and $^TC_{70}*$) to ZnTBPc (and H_2TBPc) takes place without electron transfer. In the literature, electron transfer from aromatic amines to $^SC_{60}*$ was observed in benzene only when the aromatic amines were high concentration; forward electron transfer takes place within ca. 10 ps and the back electron-transfer finishes within ca. 100 ps.[10,15,16] In our case, since the concentrations of ZnTBPc and H_2TBPc were low, electron transfer via $^SC_{60}*$ would not be anticipated.

The contribution of $^TC_{60}*$ (or $^TC_{70}*$) to electron transfer was confirmed, since the formation of $C_{60}^{\bullet-}$ (or $C_{70}^{\bullet-}$) was suppressed almost completely on addition of O_2 into benzonitrile solution containing ZnTBPc. This implies that $^SC_{60}*$ (or $^SC_{70}*$) changes to $^TC_{60}*$ (or $^TC_{70}*$) by intersystem crossing before $^SC_{60}*$ (or $^SC_{70}*$) accepts an electron from ZnTBPc. Since the intersystem-crossing rate constant from $^SC_{60}*$ (or $^SC_{70}*$) to $^TC_{60}*$ (or $^TC_{70}*$) is as fast as ca. 1×10^9 s^{-1}, maximum concentration of ZnTBPc (0.3 mM) cannot compete with the intersystem crossing, even if the diffusion controlled limit (ca. 5×10^9 M^{-1} s^{-1}) is expected for the electron-transfer rate constant between $^SC_{60}*$ (or $^SC_{70}*$) and ZnTBPc. $^TC_{60}*$ (or $^TC_{70}*$) thus formed is quenched efficiently by O_2 (ca. 5 mM in O_2-saturated solution), interrupting electron transfer from ZnTBPc (0.3 mM).

The efficiency for the formation of $C_{60}^{\bullet-}$ (or $C_{70}^{\bullet-}$) via $^TC_{60}*$ (or $^TC_{70}*$) by electron transfer can be evaluated by quantity of $[C_{60}^{\bullet-}]/[^TC_{60}*]$ (or $[C_{70}^{\bullet-}]/[^TC_{70}*]$) on substituting the observed absorption intensities and the reported ϵ values. This is one of the merits to observe the transient absorption spectra in the near-IR region. On plotting $[C_{70}^{\bullet-}]/[^TC_{70}*]$ against [ZnTBPc], $[C_{70}^{\bullet-}]/[^TC_{70}*]$ increases with [Pc's] as shown in Figure 8, usually $[C_{70}^{\bullet-}]/[^TC_{70}*]$ shows a saturation with respect to [Pc's], yielding the quantum yield $\Phi_{elt}(^TC_{70}*)$.[53,54] They are also listed
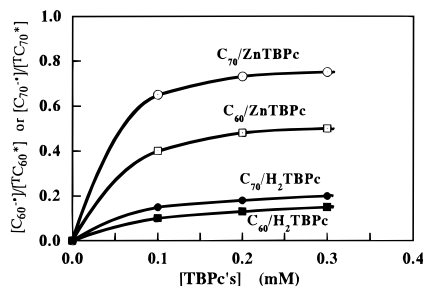
Figure 8. Dependence of $[C_{60}^{\bullet-}]/[^TC_{60}^*]$ and $[C_{70}^{\bullet-}]/[^TC_{70}^*]$ on [ZnTBPc] and [H$_2$TBPc] in benzonitrile.
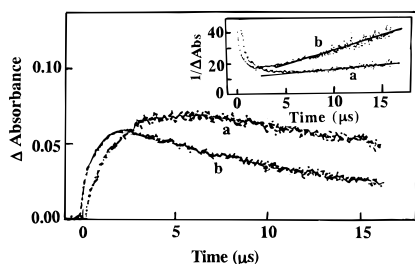
Figure 9. Decay profiles of $C_{60}^{\bullet-}$ and $C_{70}^{\bullet-}$ in benzonitrile. Insert: second-order plot.

in Table 1; Φ_{elt}^T values are less than unity even in benzonitrile. This indicates that some other reactions take place competitively with the electron-transfer reaction. In the case of C$_{70}$–ZnTBPc, a weak absorption band appearing at 500 nm was observed even in benzonitrile, indicating that energy transfer from $^TC_{70}^*$ to ZnTBPc occurred with the same time of electron transfer. For ZnTBPc, Φ_{elt}^T for C$_{70}$ is higher than that for C$_{60}$. Compared with H$_2$TBPc, Φ_{elt}^T for ZnTBPc is high for both C$_{60}$ and C$_{70}$.

From Scheme 2, the electron-transfer rate constant via $^TC_{60}^*$ (or $^TC_{70}^*$) k_{elt} was calculated by the relation $k_{elt} = \Phi_{elt}^T k_{second}^T$ (or $\Phi_{elt}^T k_{second}^A$).[53-55] On the other hand, the energy transfer rate constant via $^TC_{60}^*$ (or $^TC_{70}^*$) k_{ent} was calculated by the relation $k_{ent} = (1-\Phi_{elt}^T) k_{second}^T$ or $[(1-\Phi_{elt}^T) k_{second}^A]$. They are listed in Table 1. The k_{elt} values of C$_{70}$ are greater than those of C$_{60}$ both for ZnTBPc and H$_2$TBPc. The k_{elt} values of ZnTBPc are greater than those of H$_2$TBPc. These trends are almost in accord with Φ_{elt}^T.

The k_{ent} values in benzonitrile are smaller than those in benzene, which is mainly controlled by $(1 - \Phi_{elt}^T)$, because the observed k_{second}^T values are similar in both solvents. This implies that even in polar medium, free-energy change (ΔG_o) for electron transfer is only slightly more negative than that of energy transfer.

ΔG_o's of electron transfer from ZnTBPc to $^TC_{60}^*$ and $^TC_{70}^*$ were calculated to be -18.4 and -17.7 kcal M^{-1}, respectively, from the Rehm–Weller relation[56] by employing the reported lowest triplet energies (T_1) of $^TC_{60}^*/^TC_{70}^*$,[9,14,57] reduction potentials (E_{red}) of $^TC_{60}^*/^TC_{70}^*$,[58-61] and the oxidation potential (E_{ox})[62] of ZnTBPc and Coulombic energy (0.085 eV in benzonitrile). The negative values of ΔG_o predict that k_{elt} values are close to diffusion controlled limit in benzonitrile. The estimated k_{elt} values are smaller than the diffusion controlled limit by a factor of $^1/_4$–$^1/_6$. Such small k_{elt} values are in accord with the reported tendency for electron transfer of fullerenes.[63]

After reaching maximum concentration, $C_{70}^{\bullet-}$ and ZnTBPc$^{\bullet+}$ in benzonitrile begin to decay slowly (Figure 9) with obeying second-order kinetics. From the slope of the second-order plots, k_{second}/ϵ_A was evaluated (ϵ_A denotes molar extinction coefficients of $C_{60}^{\bullet-}$ and $C_{70}^{\bullet-}$).[31,32,49] The k_{second} can be attributed to the back electron-transfer rate constants (k_{bet}), which were evaluated by employing the reported ϵ_A values as listed in Table 2. The

TABLE 2: Rate Constants for Back-Electron Transfer in Benzonitrile[a]

fullerene	donor	k_{bet}/ϵ_A (cm s^{-1})	k_{bet} (M^{-1} s^{-1})
C$_{60}$	ZnTBPc	5.6×10^5	6.7×10^9
	H$_2$TBPc	3.0×10^5	3.6×10^9
C$_{70}$	ZnTBPc	1.8×10^6	7.2×10^9
	H$_2$TBPc	8.5×10^5	3.4×10^9

[a] $\epsilon_A = 12\,000$ M^{-1} cm^{-1} at 1070 nm for $C_{60}^{\bullet-}$ [31] and $\epsilon_A = 4000$ M^{-1} cm^{-1} at 1370 nm for $C_{70}^{\bullet-}$.[32]
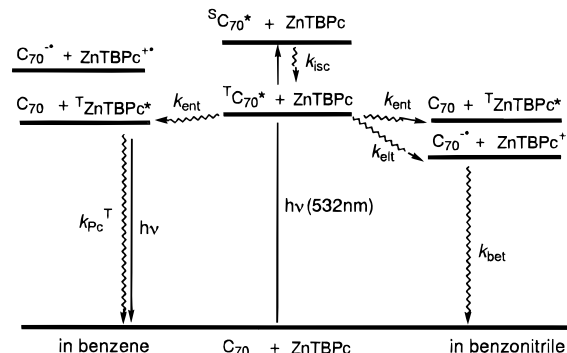
Figure 10. Schematic illustration of energy diagram for C$_{70}$/ZnTBPc. The rates of radiative and nonradiative decay of $^TPc^*$ are represented as k_{Pc}^T.

values of k_{bet} are close to the diffusion controlled limit. The values of k_{bet} for both H$_2$TBPc$^{\bullet+}$/$C_{60}^{\bullet-}$ and H$_2$TBPc$^{\bullet+}$/$C_{70}^{\bullet-}$ are slightly slower than those for ZnTBPc$^{\bullet+}$/$C_{60}^{\bullet-}$ and ZnTBPc$^{\bullet+}$/$C_{70}^{\bullet-}$. Although the efficiencies of electron transfer from H$_2$TBPc to C$_{60}$ (and C$_{70}$) are lower than those of ZnTBPc, the lifetimes of the ion radicals of H$_2$TBPc/C$_{60}$ and H$_2$TBPc/C$_{70}$ are longer than those of ZnTBPc/C$_{60}$ and ZnTBPc/C$_{60}$.

Conclusion

Photoinduced electron transfer via $^TC_{60}^*$ and $^TC_{70}^*$ from ZnTBPc and H$_2$TBPc was confirmed by observing the transient absorption spectra of their ion radicals in near-IR region. The energy diagram is schematically illustrated as shown in Figure 10 for ZnTBPc/C$_{70}$. In polar solvent, the ion radicals [$C_{70}^{\bullet-}$ and ZnTBPc$^{\bullet+}$] are stabilized by solvation; the energy level of the ion radicals is lower than that of $^TZnTBPc^*$, while the ion radicals in benzene may be upper level than the $^TZnTBPc^*$. The medium effects may be important to perform efficient photoinduced electron transfer in these system.

For ZnTBPc/C$_{60}$, the energy level of the ion radicals is similar to that of $^TZnTBPc^*$. In the case of H$_2$TBPc, energy transfer occurs in preference to electron transfer even in polar solvent.

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