

Transient Absorption Spectral Characterization of Electron Transfer between Fullerenes (C_{60}/C_{70}) and N, N, N', N' -Tetra(p -methylphenyl)-4,4'-diamino-1,1'-diphenyl Sulphide (TPDAS)

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In search of new systems with a photoexcited redox pair which exhibits a strong and stable photoinduced absorption band to understand the photophysical and photochemical properties of electron transfer between fullerenes (C_{60}/C_{70}) and organic donor [N, N, N', N' -tetra(p -methylphenyl)-4,4'-diamino-1,1'-diphenyl sulphide (TPDAS)], we studied characteristic absorption spectra in the near-IR region obtained from 532 nm nanosecond laser flash photolysis of a mixture of the fullerenes (C_{60}/C_{70}) and TPDAS in polar solvents. When fullerenes (C_{60}/C_{70}) were photoexcited, the rise of the radical anion of fullerenes (C_{60}/C_{70}) with the rapid decay of their excited triplet states were observed in benzonitrile. It can be deduced that the electron transfer reaction does take place from TPDAS to excited triplet state of fullerenes (C_{60}/C_{70}). The rate constants (k_{et}) and quantum yields (Φ_{et}) of this process have been also evaluated.

Keywords photoinduced electron transfer, N, N, N', N' -tetra(p -methylphenyl)-4,4'-diamino-1,1'-diphenyl sulphide [TPDAS], fullerenes (C_{60}/C_{70})

One of the most important aims of photochemistry is the design and construction of molecular devices for energy conversion and information processing. The photoactive molecular devices are based on the photoinduced electron transfer between donor-acceptor type organic compounds and acceptor molecules such as fullerenes (C_{60}/C_{70}) which have high electron affinity (2.6—2.8 eV) and readily form anions in electrochemical reduction.¹ Fullerenes (C_{60}/C_{70}) have been widely used as good electron acceptors because of their symmetrical shape,

large size, characteristic of their π -electron system,² and molecular ferromagnetism³ in the tetrakis-bis-dimethyl-aminoethylene salt of C_{60} as well as the occurrence of ultra-fast photoinduced electron transfer within the dimethyl aniline- C_{60} complex.⁴ The possibility of employing fullerenes and functionalized fullerenes for photoelectrochemical and photovoltaic cells has already been demonstrated.⁵

On the other hand, N, N, N', N' -tetra(p -methylphenyl)-4,4'-diamino-1,1'-diphenyl sulphide (TPDAS) with fairly high LUMO levels (3.408 eV by HF/3-21G calculations) is of interest and significance for developing photo- and electro-active amorphous molecular materials, which consist of π -electron systems and have glass-transition temperature higher than room temperature, for use in electronic devices.⁶ TPDAS also has unique optical property, both in fluorescence and phosphorescence, and significantly improves the device durability in organic light-emitting diodes by doping both hole transport and emitter layers.⁷

The present study explored new systems with a photoexcited redox pair which exhibits a strong and stable photoinduced absorption band to study the photophysical and photochemical properties of electron transfer between fullerenes (C_{60}/C_{70}) and organic donor [N, N, N', N' -tetra(p -methylphenyl)-4,4'-diamino-1,1'-diphenyl sulphide (TPDAS)] (Scheme 1). When fullerenes (C_{60}/C_{70}) are photoexcited, the electron transfer from TPDAS to photo-excited fullerenes (C_{60}/C_{70}) has been investigated by laser photolysis with observation of the transient ab-

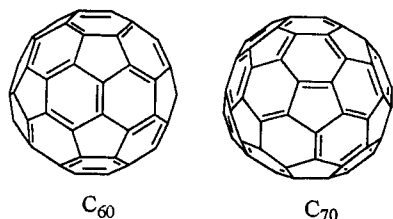
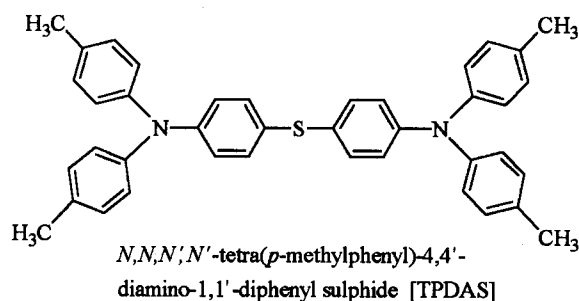
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sorption bands in benzonitrile. The rise of the radical anion of fullerenes (C_{60}/C_{70}) with the rapid decay of their excited triplet state is observed. The rate constant (k_{et}) and quantum yield (Φ_{et}) of electron transfer of the TPDAS are smaller than those of the corresponding triphenylamine (TPA).⁸

Scheme 1 Molecular structures of C_{60} , C_{70} and TPDAS



Experimental

Instruments and reagents

C_{60} and C_{70} were obtained in a purity of 99.9% and 99.5% respectively from Tokyo Kasei Kogyo Co. TPDAS was prepared by the method described in the literature.^{6,9} Benzonitrile of high performance liquid chromatograph (HPLC) and spectrophotometric grade was used as solvents.

C_{60} (or C_{70}) and TPDAS were dissolved in benzonitrile, and the sample solutions were then deaerated by bubbling with argon gas prior to measurements. To examine the effect of O_2 , oxygen-saturated solution was prepared by O_2 bubbling.

The solution of C_{60}/C_{70} and TPDAS was selectively excited by a Nd:YAG laser (spectra-physics, Quanta-Ray, GCR-130, FWMH, 6 ns) with 7 mJ power. For the transient absorption spectra in the near-IR and visible region, a Ge avalanche photodiode (Hamamatsu photowice, B2834) was used as a detector for monitoring light from a

pulsed Xe-lamp. A Si-PIN photodiode (Hamamatsu photonics, S1722-02) was used as a detector to monitor the transmitted light from a pulsed Xe lamp (150 W) passing through a rectangular quartz reaction cell (1 cm) and monochromator. Steady-state photolysis was carried out with a Xe-Hg lamp (150 W) and steady-state UV/vis absorption spectra were measured with a JASCO/V-570 spectrophotometer. The sample contained in a 10 mm quartz cell was deaerated with Argon bubbling before measurements and all experiments were carried out at 22 °C.

Results and discussion

Steady-state UV/vis spectra

Steady-state UV/vis spectra of C_{60} , TPDAS, and a mixture of C_{60} (or C_{70}) with TPDAS in benzonitrile were recorded between 380 nm and 750 nm as shown in Fig. 1.

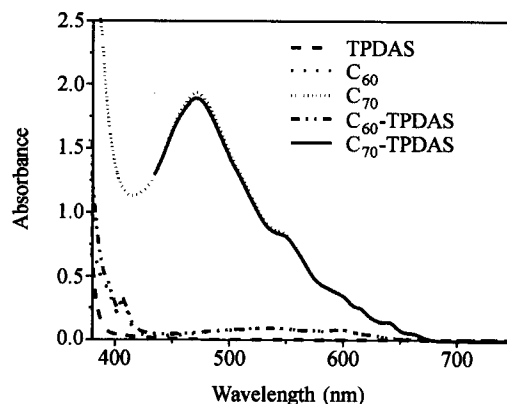


Fig. 1 Steady-state absorption spectra of TPDAS (1.0 mmol/L), C_{60} (0.1 mmol/L), C_{70} (0.1 mmol/L) and their mixture in Ar-saturated benzonitrile.

The absorption spectrum of a mixture of C_{60} (0.1 mmol/L) (or C_{70}) and TPDAS (1.0 mmol/L) in benzonitrile in Fig. 1 is a superimposition of that of the corresponding components. This fact suggests that in the mixture of C_{60} (or C_{70}) and TPDAS there is no apparent interaction in the ground state under the condition of concentration range employed in the laser photolysis experiments. On laser photolysis at 532 nm, only C_{60} (or C_{70}) is excited, while TPDAS remains in unexcited state at this wavelength, suggested by the absence of absorption band

of this wavelength.

Photoinduced electron transfer

Fig. 2 shows the transient absorption spectra in the Vis/NIR region obtained by the laser flash photolysis of C_{60} (0.1 mmol/L) with 532 nm light in the presence of TPDAS (1.0 mmol/L) in deaerated benzonitrile. The transient absorption band at 780 nm appeared immediately after the nanosecond laser pulse. The 780 nm band was assigned to the excited triplet state absorption of C_{60} (${}^3C_{60}^*$).¹⁰ With the decay of ${}^3C_{60}^*$, a new absorption band appeared at 1100 nm, which was assigned to the absorption band of $C_{60}^{\cdot-}$.¹¹ In the visible region, the transient bands that appeared immediately after the laser pulse were attributed to ${}^3C_{60}^*$. The observed time profiles of the absorption bands are shown in the inset of Fig. 2. The decay of ${}^3C_{60}^*$ at 780 nm, which did not show appreciable decay over a few microseconds without TPDAS, was accelerated in the presence of TPDAS. In the case of TPDAS, the new absorption band appearing at 860 nm with shoulder at 820 nm may be assigned to the absorption band of radical cations of TPDAS.

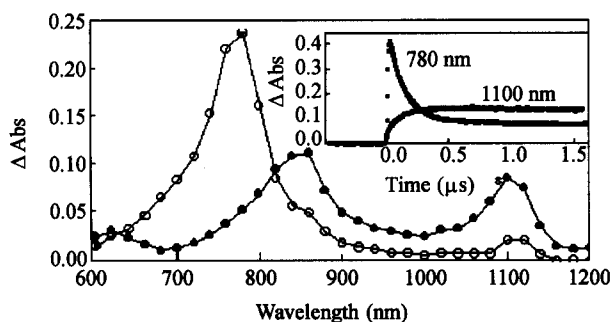


Fig. 2 Transient absorption spectra obtained by 532 nm laser light photolysis of C_{60} (0.1 mmol/L) in the presence of TPDAS (2.0 mmol/L) in the Ar-saturated benzonitrile at 0.1 μ s (●) and 1 μ s (○). Inset: time profile at 780 nm and 1100 nm.

With the decay of ${}^3C_{60}^*$ at 780 nm, the absorption intensity of $C_{60}^{\cdot-}$ at 1100 nm increases, reaching a maximum at about 1.0–10 μ s. The decay of ${}^3C_{60}^*$ and the appearance of $C_{60}^{\cdot-}$ are produced via ${}^3C_{60}^*$ by accepting an electron from TPDAS, indicating that electron transfer takes place via ${}^3C_{60}^*$.¹² By use of the molar absorption coefficient (ϵ_T) of ${}^3C_{60}^*$ at 720 nm ($16000 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$),¹³ the initial maximum concentration of ${}^3C_{60}^*$ ($[{}^3C_{60}^*]_{\text{max}}$) produced by a laser pulse was calculated.

The maximum concentration of $C_{60}^{\cdot-}$ ($[C_{60}^{\cdot-}]_{\text{max}}$) at 1 μ s was also determined using the reported molar extinction coefficients (ϵ_A) of $C_{60}^{\cdot-}$ in benzonitril ($12000 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$) at 1070 nm.¹³

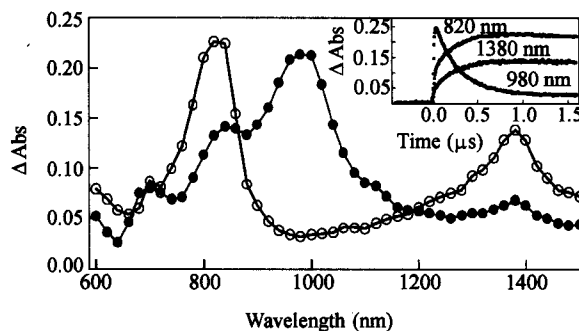


Fig. 3 Transient absorption spectra obtained by 532 nm laser photolysis of C_{70} (0.1 mmol/L) in the presence of TPDAS (1.0 mmol/L) in Ar-saturated benzonitrile at 0.1 μ s (●) and 1 μ s (○). Inset shows time profiles at 820 nm, 980 nm and 1380 nm.

In the similar case, transient absorption spectra for C_{70} (0.1 mmol/L) with TPDAS (1.0 mmol/L) in Ar-saturated benzonitrile obtained by the exposure of the 532 nm laser excitation are shown in Fig. 3. Immediately after the laser pulse, the absorption band of ${}^3C_{70}^*$ appears at 980 nm.¹⁴ The main absorption at 980 nm was quenched by the addition of TPDAS and the absorption band of $C_{70}^{\cdot-}$ appeared at 1380 nm instead.¹⁵ The strong one at 820 nm can be assigned to the TPDAS cation radical. As shown in the inserted time profile of Fig. 3, the absorption intensity at 1380 nm begins to rise immediately after the laser pulse followed by a slow rise, which corresponds to the decay of ${}^3C_{70}^*$. $[{}^3C_{70}^*]_{\text{max}}$ and $[C_{70}^{\cdot-}]_{\text{max}}$ were calculated using the reported ϵ_T value ($6500 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$ at 980 nm)¹¹ and ϵ_A value ($4000 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$ at 1370 nm).¹⁵

The effect of TPDAS concentration on the time profiles for the decay of ${}^3C_{60}^*$ is shown in Fig. 4. It is apparent that the decay rate of ${}^3C_{60}^*$ increases with [TPDAS] increasing. Each decay curve of ${}^3C_{60}^*$ in the presence of TPDAS was fitted with a single exponential, while weak nondecaying absorption may be attributed to TPDAS radical cations, which did not affect the kinetic analysis. The second-order rate constant (k_q) was ob-

tained from the linear dependence of k_{obs} on $[\text{TPDAS}]$ as shown in the inset of Fig. 4. The obtained k_{q} values are summarised in Table 1.

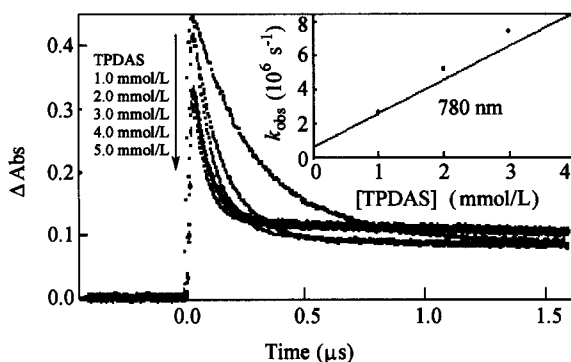


Fig. 4 Decay profiles of ${}^1\text{C}_{60}^*$ at 780 nm with changing $[\text{TPDAS}]$. Inset shows pseudo-first-order plot in Ar-saturated benzonitrile.

The rates of $\text{C}_{60}^{\cdot-}$ rise increase with $[\text{TPDAS}]$ in benzonitrile as shown in Fig. 5. Each rise curve was fitted with single exponential, yielding k_{obs} without taking the decay of $\text{C}_{60}^{\cdot-}$ into consideration. The second-order rate constant k_{q} was obtained by plotting k_{obs} vs. $[\text{TPDAS}]$ (Fig. 5).

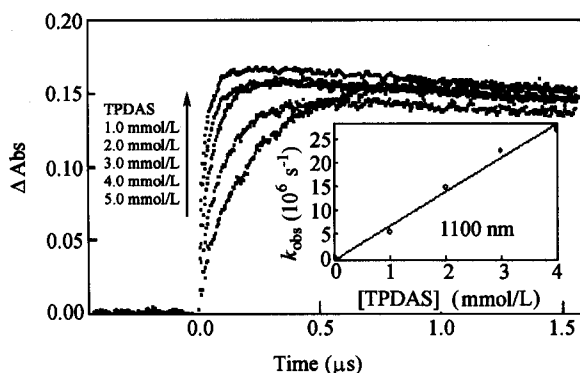


Fig. 5 Rise profiles of $\text{C}_{60}^{\cdot-}$ at 1100 nm with changing $[\text{TPDAS}]$. Inset shows pseudo-first-order plot in Ar-saturated benzonitrile.

Absorption spectra of radical cation of TPDAE

It is well known that the chemical oxidation of small aromatics by Lewis acids as the oxidant generates the corresponding radical cations.¹⁶ In order to examine the occurrence of TPDAS radical cations, absorption spectra of oxidized TPDAS in Ar-saturated dichloromethane was measured by stepwise addition of FeCl_3 . The new absorption band appeared after addition of two equivalents of FeCl_3 as shown in Fig. 6. The new absorption maximum at 820 nm is similar in position to that of radical cation of TPDAS. Fig. 6 shows the optical absorption spectra of TPDAS.

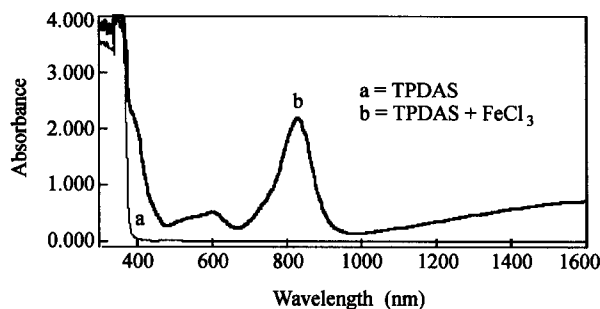


Fig. 6 Absorption spectra of radical cation of TPDAS in Ar-saturated dichloromethane.

Quantum yields and electron transfer rates

The efficiency of electron transfer via ${}^1\text{C}_{60}^*$ can be estimated by the quantity $[\text{C}_{60}^{\cdot-}]/[{}^1\text{C}_{60}^*]$ as evaluated by the maximal and initial absorbance. The ratios of $[\text{C}_{60}^{\cdot-}]_{\text{max}}/[\text{C}_{60}^{\cdot-}]_{\text{max}}$ are plotted against the concentration of $[\text{TPDAS}]$ in benzonitrile. The efficiencies increase and stepwisely reach a plateau, from which the quantum yield (Φ_{et}) for electron transfer to the triplet state was estimated. In Table 1, the k_{q} value can be calculated from the dependence of first-order decay rate of ${}^1\text{C}_{60}^*$ on the concentration of TPDAS. The constant value refers to the quantum yield of electron transfer (Φ_{et}) via

Table 1 Rate constants and quantum yield for electron transfer in benzonitrile

Fullerene/TPDAS	k_{q} ($\text{mol}^{-1}\cdot\text{L}\cdot\text{s}^{-1}$)	$\Phi_{\text{et}}^{\text{T}}$	k_{et} ($\text{mol}^{-1}\cdot\text{L}\cdot\text{s}^{-1}$) ^a	k_{bet} ($\text{mol}^{-1}\cdot\text{L}\cdot\text{s}^{-1}$)
$\text{C}_{60}/\text{TPDAS}$	1.98×10^9	0.82	1.64×10^9	4.4×10^9
$\text{C}_{70}/\text{TPDAS}$	3.83×10^9	1.0	3.83×10^9	3.3×10^{10}

^a $k_{\text{et}} = k_{\text{q}} \cdot \Phi_{\text{et}}^{\text{T}}$

$^3C_{60}^*$. The k_{et} value can be obtained from the following equation, $k_{et} = k_q \times \Phi_{et}$. The evaluated Φ_{et} and k_{et} value are summarized in Table 1, in which the Φ_{et} values for the reactions via $^1C_{70}^*$ were also evaluated similarly. In the case of TPDAS, the k_q and k_{et} values based on TPDAS concentration are listed. The Φ_{et} values are usually less than unity, which may indicate that some deactivation processes of the triplet excited states compete with the electron transfer processes.

In order to confirm the electron transfer mechanism via $^1C_{60}^*/^1C_{70}^*$, oxygen was added to the solution of C_{60} /TPDAS. In oxygen-saturated solution, the $C_{60}^{\cdot-}$ formation was suppressed (Fig. 7). The decay of $^1C_{60}^*$ was accelerated on addition of oxygen to C_{60} (0.1 mmol/L)/TPDAS (1.0 mmol/L) solution (Fig. 8), indicating that $^1C_{60}^*$ was quenched by oxygen due to energy transfer from $^1C_{60}^*$ to oxygen, suppressing the electron transfer reaction between $^1C_{60}^*$ and TPDAS. Although the amount of $C_{60}^{\cdot-}$ formation was suppressed by adding oxygen to solution, the decay rate of $C_{60}^{\cdot-}$ was not affected by the oxygen concentration, indicating that the reaction between $C_{60}^{\cdot-}$ and oxygen does not take place. This finding also suggests that the photoinduced electron transfer between C_{60} and TPDAS takes place via $^1C_{60}^*/^1C_{70}^*$.¹⁵

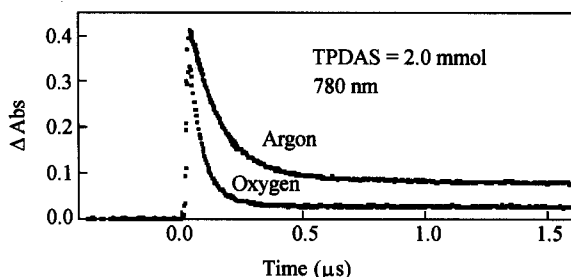


Fig. 7 Time profiles of absorbance obtained by 532 nm laser photolysis of C_{60} (0.1 mmol/L) in the presence of TPDAS (2.0 mmol/L) in argon-saturated benzonitrile and oxygen-saturated benzonitrile at 780 nm.

Back electron transfer

Figs. 9 and 10 show the time profiles of $C_{60}^{\cdot-}$ and $C_{70}^{\cdot-}$ on the long-time scale. It is clear that the anion radicals begin to decay slowly after reaching each maximum. This can be attributed mainly to the back electron transfer from $C_{60}^{\cdot-}/C_{70}^{\cdot-}$ to TPDAS, because extra re-

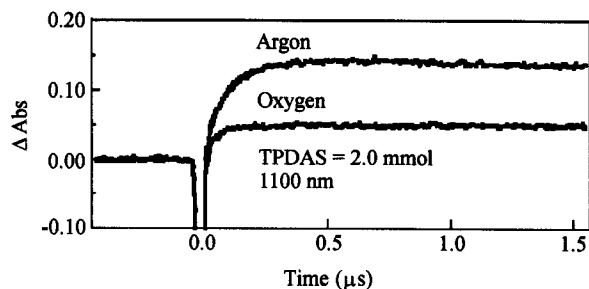


Fig. 8 Time profiles of absorbance obtained by 532 nm laser photolysis of C_{60} (0.1 mmol/L) in the presence of TPDAS (2.0 mmol/L) in argon-saturated benzonitrile and oxygen-saturated benzonitrile at 1100 nm.

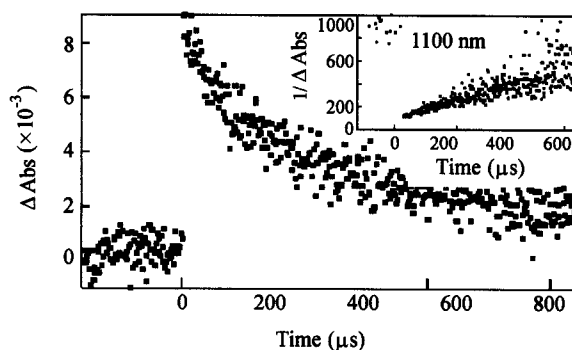


Fig. 9 Decay profiles over long time scale of $C_{60}^{\cdot-}$ in the presence of [TPDAS] in Ar-saturated benzonitrile. Inset shows second-order plot.

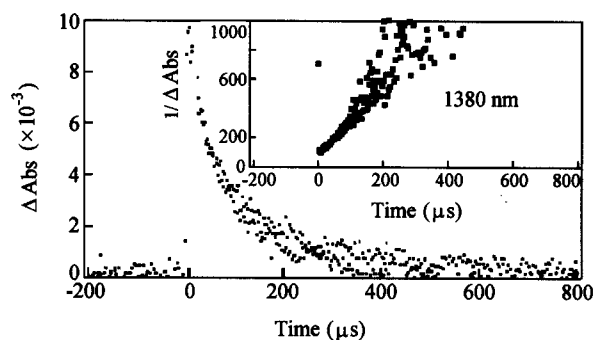


Fig. 10 Decay profiles over long time scale of $C_{70}^{\cdot-}$ in the presence of [TPDAS] in Ar-saturated benzonitrile. Inset shows second-order plot.

actions such as adduct formation were not observed in the steady-state absorption spectra after irradiation of C_{60}/C_{70} with 532 nm light in the presence of TPDAS. The decay time profiles obey second-order kinetics. From the slope of the second-order plot in the inset of Figs. 9 and 10, the back electron transfer rate constants (k_{bet}) were evaluat-

ed as listed in Table 1. On the other hand, the second-order plots are slightly bent, suggesting that ion radicals are not always freely solvated; the back electron transfer may occur within a solvent-separated ion pair in benzonitrile.

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