

Evaluation of Transient Absorption Spectra of N, N, N', N'- Tetra - (*p*-methylphenyl) - 4, 4'- diamino - 1, 1'- diphenyl Ether (TPDAE) for Electron Transfer from TPDAE to Fullerenes (C₆₀/ C₇₀) by Laser Flash Photolysis

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Abstract: Photoinduced electron transfer processes between fullerenes (C₆₀/ C₇₀) and N, N, N', N'- tetra - (*p*-methylphenyl) - 4, 4'- diamino - 1, 1'- diphenyl ether (TPDAE) have been studied by nanosecond laser flash photolysis. Quantum yields and rate constants of electron transfer from TPDAE to excited triplet state of fullerenes (C₆₀/ C₇₀) in benzonitrile have been evaluated by observing the transient absorption bands in the near-IR region where the excited triplet state, radical anion of fullerenes (C₆₀/ C₇₀) and radical cations of TPDAE appear.

Keywords: Photoinduced electron transfer, fullerenes (C₆₀/ C₇₀), transient absorption bands.

Fullerenes C₆₀ and C₇₀ have high electron affinity (2.6 - 2.8 eV) and readily form anions on electrochemical reduction¹, which were famous as electron acceptor in photo-excitation because of symmetrical shape, large size, and properties of its π -electron system². After observation of molecular ferromagnetism³ in the tetrakis (dimethylamino) ethylene salt of C₆₀ as well as the occurrence of ultra-fast photoinduced electron transfer within the dimethyl aniline - C₆₀ complex⁴, prompted us to investigate the photoinduced electron transfer processes of fullerenes for understanding of general features of electron transfer mechanisms with title aromatic amines.

On the other hand, triarylamine derivatives have been received great attention as a novel class of functional materials⁵, which were one of the strong electron donors and an important class of compounds because they have unique optical property, both fluorescence and phosphorescence. They can form stable ammonium radical cations and can be built blocks for high-spin poly-radical⁶ and conductor as well as the hole-transport layer in electro-luminescent device⁷. Title aromatic amine, N, N, N', N'- tetra - (*p*-methylphenyl) - 4, 4'- diamino-1, 1'- diphenyl ether (TPDAE) have already been used for thermal recording material containing triarylamine derivatives⁸.

On this basis, we report herein the photoinduced electron transfer processes between fullerenes C₆₀ and C₇₀ and TPDAE (**Scheme 1**) by laser flash photolysis. Furthermore,

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quantum yields and rate constants of electron transfer from TPDAE to excited triplet state of fullerenes C_{60} and C_{70} in Ar-saturated benzonitrile have been evaluated by observing the transient absorption band in the near-IR region where the excited triplet state radical anion of fullerenes C_{60} and C_{70} and radical cation of TPDAE appear. Evaluated rate constants are listed in **Table 1**. The constant value refers to the quantum yield of electron transfer (Φ_{et}^T) via ${}^3C_{60}^*$.⁹

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

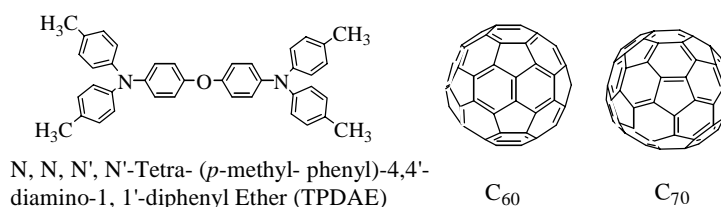
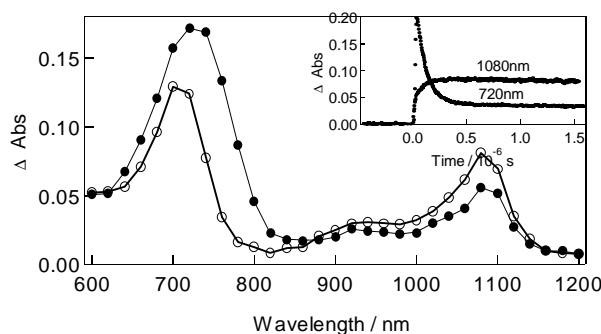


Figure 1 shows the transient absorption spectra in the near – IR region obtained by the laser flash photolysis of C_{60} with 532 nm in the presence of TPDAE in Ar-saturated benzonitrile. The transient absorption band at 720 nm is attributed to the triplet-triplet (T-T) absorption of ${}^3C_{60}^*$. With the decay of ${}^3C_{60}^*$, a new absorption band appears at 1080 nm with a shoulder at 920 nm, which is assigned to the absorption of $C_{60}^{\cdot -}$. In the visible region, the transient bands that appeared immediately after the laser pulse are attributed to ${}^3C_{60}^*$, while the absorption band remaining at 700 nm can be assigned to the TPDAE radical cation (TPDAE^{•+}).

Figure 1 Transient absorption spectra obtained by 532 nm laser light photolysis of C_{60} (0.1 mmol) in the presence of TPDAE (2.0 mmol) in Ar-saturated benzonitrile. Inset: time profile at 720 nm and 1080 nm.



The observed time profiles of the absorption bands are shown in the inset of **Figure 1**. The decay of ${}^3C_{60}^*$ at 720 nm, with the decay of ${}^3C_{60}^*$, the absorption intensity of $C_{60}^{\cdot -}$ at 1080 nm increases, the decay of ${}^3C_{60}^*$ and the appearance of $C_{60}^{\cdot -}$ is produced via ${}^3C_{60}^*$ by accepting an electron from TPDAE.

With 532 nm laser excitation of C_{70} in Ar-saturated benzonitrile (**Figure 2**), the

main absorption at 980 nm and the strong one at 700 nm due to ${}^3\text{C}_{70}^*$ were quenched by the addition of TPDAE, concomitantly with appearance of the absorption band of $\text{C}_{70}^{\cdot-}$ at 1380 nm. As shown in the inseted time profile of **Figure 2**, 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 ${}^3\text{C}_{70}^*$.

Figure 2 Nanosecond transient absorption of C_{70} (0.1 mmol) in the presence of TPDAE (1.0 mmol) benzonitrile at 0.1 μs (closed circle) and 1 μs (open circle) after 532 nm laser excitation. Inset: absorption time profiles at 1380 nm, 980 nm and 700 nm.

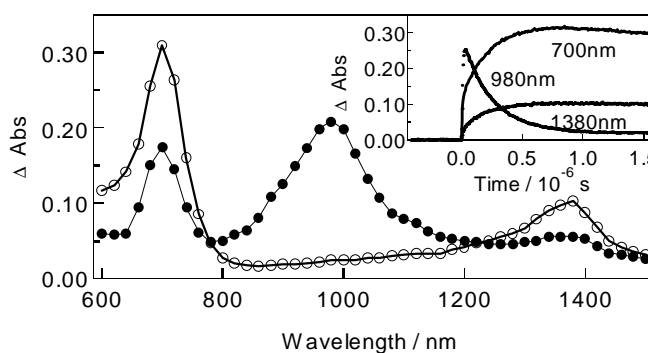
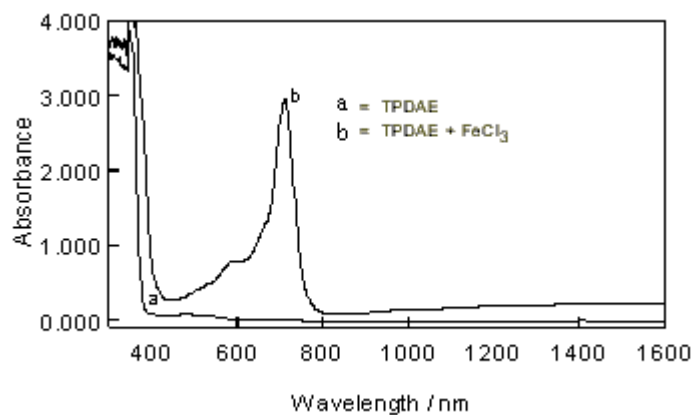


Table I. Rate constants and quantum yields for electron transfer in BN.

Fullerene/ PTADE	$k_q/\text{M}^{-1}\text{S}^{-1}$	$\Phi_{\text{et}}^{\text{T}}$	$k_{\text{et}}/\text{M}^{-1}\text{S}^{-1}$	$k_{\text{bet}}/\text{M}^{-1}\text{S}^{-1}$
$\text{C}_{60}/\text{PTADE}$	1.7×10^9	0.56	6.5×10^8	2.2×10^9
$\text{C}_{70}/\text{PTADE}$	3.32×10^9	0.78	2.6×10^9	3.82×10^{10}

$$K_{\text{et}} = k_q \cdot \Phi_{\text{et}}^{\text{T}}$$

Figure 3 Absorption spectra of the TPDAE radical cations in dichloromethane



It is well know that the chemical oxidation of small aromatics by Lewis acids as the

oxidant to generate the corresponding radical cations⁶. In order to understand TPDAE radical cation in details, we examined the occurrence of TPDAE radical cations. The absorption spectra of oxidized TPDAE in dichloromethane were measured by stepwise addition of FeCl₃. **Figure 3** shows the optical absorption spectra of TPDAE. **Figure 3a** shows the steady-state absorption spectra of TPDAE in dichloromethane, which did not exhibit any absorption bands in the near – IR region, with addition of FeCl₃, new absorption band appeared as shown in **Figure 3b**.

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