

Photoinduced Electron Transfer between N, N, N', N' -Tetra- $(p$ -methylphenyl)-4, 4'-diamino-1, 1'-diphenyl Ether (TPDAE) and Fullerenes (C_{60}/C_{70}) by Laser Flash Photolysis

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The photoinduced electron-transfer reaction of N, N, N', N' -tetra- $(p$ -methylphenyl)-4, 4'-diamino-1, 1'-diphenyl ether (TPDAE) and fullerenes (C_{60}/C_{70}) by nanosecond laser flash photolysis occurred in benzonitrile. Transient absorption spectral measurements were carried out during 532 nm laser flash photolysis of a mixture of the fullerenes (C_{60}/C_{70}) and TPDAE. The electron transfer from the TPDAE to excited triplet state of the fullerenes (C_{60}/C_{70}) quantum yields and rate constants of electron transfer from TPDAE to excited triplet state of fullerenes (C_{60}/C_{70}) 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 (C_{60}/C_{70}) and radical cations of TPDAE are expected to appear.

Keywords photoinduced electron-transfer, N, N, N', N' -tetra- $(p$ -methylphenyl)-4, 4'-diamino-1, 1'-diphenyl ether (TPDAE), fullerenes (C_{60}/C_{70})

Introduction

Photoinduced electron transfer (PET) is one of the most interesting features of donor-acceptor systems for the design and the construction of artificial molecular devices for energy conversion and information processing which have a number of potentially intriguing applications, including sensitization of their photoconductivity and photovoltaic phenomena. The photoactive devices is based on the photoinduced electron transfer between donor type organic compounds and acceptor molecules, such as

fullerenes (C_{60}/C_{70}) which have high electron affinity (2.6—2.8 eV) and can readily form anions on electrochemical reduction.¹ Fullerenes are well known as an electron acceptor in photoexcitation because of its symmetrical shape, large size and properties of its π -electron system,² after observation of 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

Polyarylamines, a novel class of functional materials⁵, which have received much attention, is one of strong electron donors and an important class of compounds because they have unique optical properties, such as fluorescence and phosphorescence. Furthermore, polyarylamines can form stable aminium radical cations and can be used as building blocks for high-spin polyradical⁶ and conductor as well as the hole-transport layer in electroluminescent device.⁷ The title aromatic amine, N, N, N', N' -tetra- $(p$ -methyl-phenyl)-4, 4'-diamino-1, 1'-diphenyl ether (TPDAE) has already been used for thermal recording material.⁸

In our study, intermolecular photoinduced electron transfer in mixtures of fullerenes (C_{60}/C_{70}) and TPDAE is studied in benzonitrile, and photoinduced absorption spectroscopy is used to show that the photoexcitation of fullerenes (C_{60}/C_{70}) generates the corresponding triplet state which is quenched in an electron reduction reaction by TPDAE. It has attracted wide interest in many differ-

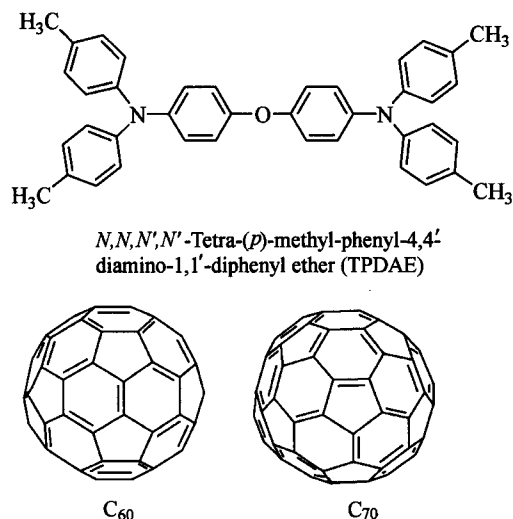
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ent scientific fields. We report herein the photoinduced electron transfer processes between fullerenes (C_{60}/C_{70}) and N,N,N',N' -tetra-(*p*-methylphenyl)-4,4'-diamino-1,1'-diphenyl ether (TPDAE) (Scheme 1) by laser flash photolysis. Transient absorptions were observed in near-infrared regions. Quantum yields and rate constants of electron transfer from TPDAE to excited triplet state of fullerenes (C_{60}/C_{70}) in Ar-saturated benzonitrile have also been evaluated.

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



Experimental

Instruments and reagents

C_{60} and C_{70} were obtained from Texas Fullerenes Corp with purity of 99.9% and 99.5%, respectively. TPDAE was prepared by the method described in the literature.⁹ Benzonitrile used as solvents was of high performance liquid chromatographic (HPLC) and spectrophotometric grade, respectively.

C_{60} (or C_{70}) and TPDAE were dissolved in benzonitrile and the sample solutions were deaerated by bubbling with argon gas before measurement. Oxygen-saturated solution was produced by oxygen bubbling when the effect of oxygen was under investigation.

The mixture solution of C_{60}/C_{70} and TPDAE was selectively excited by a Nd:YAG laser (spectra-physics, Quanta-Ray, GCR-130, FWMH, 6 ns) at 532 nm with a laser power of 7 mJ per pulse. For the transient absorption spectra in the near-IR and visible region, a Ge ava-

lanche 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 transient 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 were deaerated with Argon bubbling before measurements. All experiments were carried out at 22 °C.

Results and discussion

Steady-state UV/Vis spectra

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

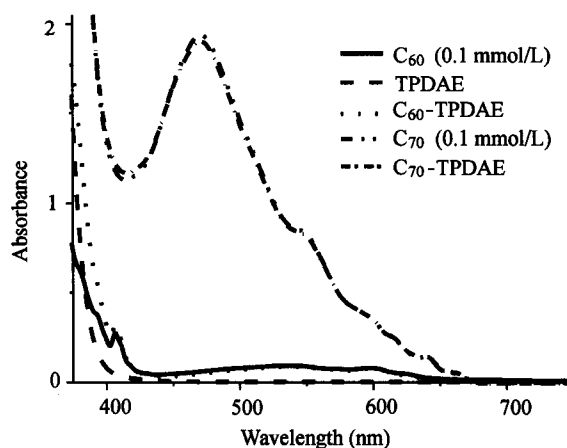


Fig. 1 Steady-state absorption spectra of TPDAE (1.0 mmol/L), C_{60} (0.1 mmol/L), C_{70} (0.1 mmol/L) and their mixture in Ar-saturated benzonitrile.

The absorption spectrum of a mixture of C_{60} (0.1 mmol/L) (or C_{70}) and TPDAE (1.0 mmol/L) in benzonitrile in Fig. 1 is a superimposition of the components, suggesting that the mixture of C_{60} (or C_{70}) and TPDAE does not have apparent interaction in the ground state under the present concentration condition region employed in the laser photolysis experiments. On laser photolysis at 532 nm, only C_{60}/C_{70} is excited, for lack of absorption of

TPDAE at 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 TPDAE (1.0 mmol/L) in deaerated benzonitrile. The transient absorption band at 720 nm appeared immediately after the nanosecond laser pulse. The 720 nm band is assigned to the excited triplet state absorption of C_{60} (${}^3C_{60}^*$).¹⁰ 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 band of $C_{60}^{\cdot-}$.¹¹ In the visible region, the transient bands that appeared immediately after the laser pulse are 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 720 nm, which did not show appreciable decay over a few microseconds without TPDAE, was accelerated in the presence of TPDAE.

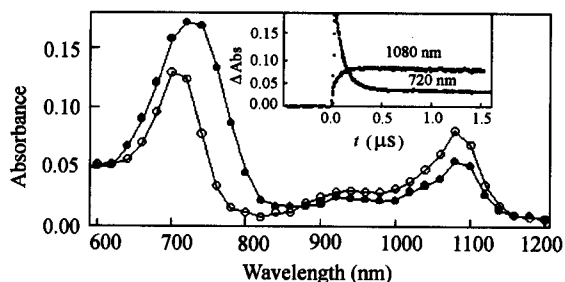


Fig. 2 Transient absorption spectra obtained by 532 nm laser light photolysis of C_{60} (0.1 mmol/L) in the presence of TPDAE (2.0 mmol/L) in Ar-saturated benzo nitrile at 0.1 μ s (\bullet) and 1 μ s (\circ). Inset: time profile at 720 nm and 1080 nm.

With the decay of ${}^3C_{60}^*$, the absorption intensity of $C_{60}^{\cdot-}$ at 1080 nm increases, reaching a maximum at about 0.1–1.0 μ s. The decay of ${}^3C_{60}^*$ and the appearance of $C_{60}^{\cdot-}$ are produced via ${}^3C_{60}^*$ by accepting an electron from TPDAE, 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 ($16000 \text{ mol} \cdot \text{L}^{-1}$)¹³ the initial maximum concentration of ${}^3C_{60}^*$ ($[{}^3C_{60}^*]_{\text{max}}$) produced by a laser pulse is calculated. The maximum concentration of $C_{60}^{\cdot-}$ ($[C_{60}^{\cdot-}]_{\text{max}}$) at 1 μ s was also de-

termined using the reported molar extinction coefficients (ϵ_A) of $C_{60}^{\cdot-}$ in benzonitrile ($12000 \text{ mol} \cdot \text{L}^{-1}$) at 1070 nm.¹³

Similarly, the transient absorption spectra for C_{70} (0.1 mmol/L) with TPDAE (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 ${}^3C_{70}^*$ appeared at 980 nm instead of 1380 nm for $C_{70}^{\cdot-}$.¹⁴ The main absorption at 980 nm was quenched by the addition of TPDAE. The strong one at 700 nm can be assigned to the TPDAE 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 ($6500 \text{ mol} \cdot \text{L}^{-1}$ at 980 nm)¹¹ and ϵ_A value ($4000 \text{ mol} \cdot \text{L}^{-1}$ at 1379 nm).¹⁵

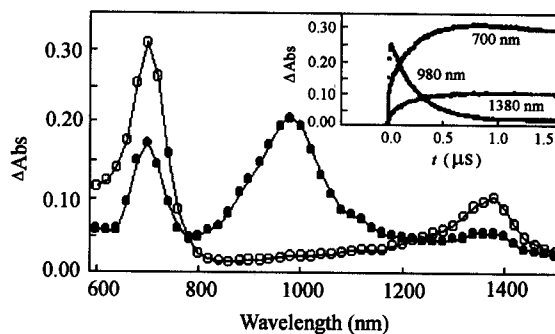


Fig. 3 Transient absorption spectra obtained by 532 nm laser photolysis of C_{70} (0.1 mmol/L) in the presence of TPDAE (1.0 mmol/L) in Ar-saturated benzonitrile at 0.1 μ s (\bullet) and 1 μ s (\circ). Inset shows time profiles at 700 nm, 980 nm and 1380 nm.

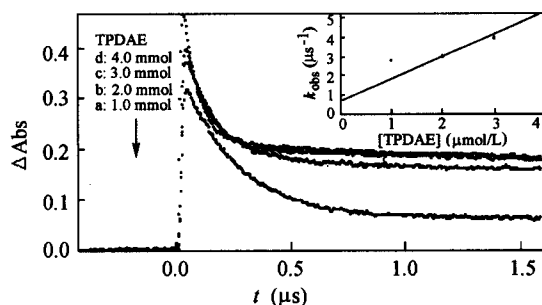
The effect of TPDAE concentration on the time profiles for the decay of ${}^3C_{60}^*$ is shown in Fig. 4. It is apparent that the decay rate of ${}^3C_{60}^*$ increases with $[TPDAE]$. Each decay curve of ${}^3C_{60}^*$ in the presence of TPDAE is fitted with a single exponential, while weak nondecaying absorption can be attributed to TPDAE radical cations, which do not affect the kinetic analysis. The second-order rate constant (k_q) is obtained from the linear dependence of k_{obs} on $[TPDAE]$ as shown in the inset of Fig. 4. The obtained k_q values are also listed in Table 1.

The rising rates of $C_{60}^{\cdot-}$ increase with $[TPDAE]$ in

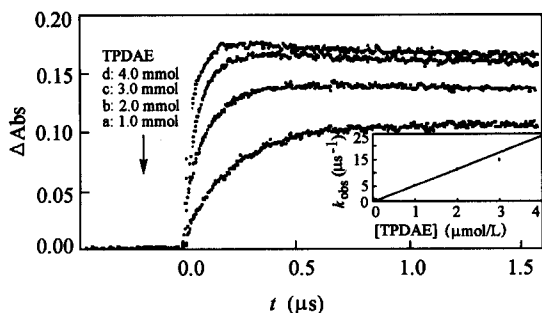
Table 1 Rate constants and quantum yields for electron transfer in BN

Fullerene/ TPDAX	k_q (mol ⁻¹ · L·s ⁻¹)	Φ_{et}^T	k_{et} (mol ⁻¹ · L·s ⁻¹)	k_{bet} (mol ⁻¹ · L·s ⁻¹)
C ₆₀ /TPDAE	1.7×10^9	0.56	6.5×10^8	2.2×10^9
C ₇₀ /TPDAE	3.32×10^9	0.78	2.6×10^9	3.82×10^{10}

$$k_{et} = k_q \cdot \Phi_{et}^T$$

**Fig. 4** Decay profiles of ${}^3C_{60}^*$ at 720 nm with changing TPDAE, Inset shows pseudo-first-order plot in Ar-saturated benzonitrile.

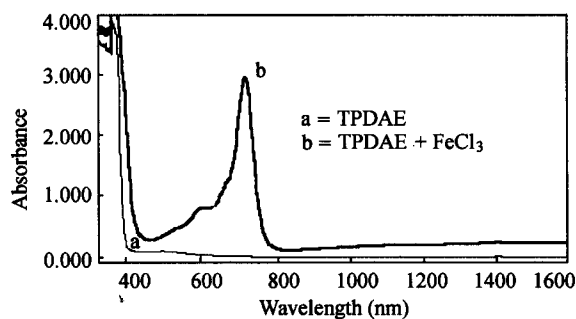
benzonitrile as shown in Fig. 5. Each rise curve was fitted with single exponential, yields k_{obs} without taking the decay of $C_{60}^{\cdot-}$ into consideration. The second-order rate constant k_q was obtained by plotting k_{obs} vs. $[TPDAE]$ (Fig. 5).

**Fig. 5** Rise profiles of $C_{60}^{\cdot-}$ at 1080 nm with changing TPDAE, Inset shows pseudo-first-order plot in Ar-saturated benzonitrile.

Absorption spectra of radical cation of TPDAE

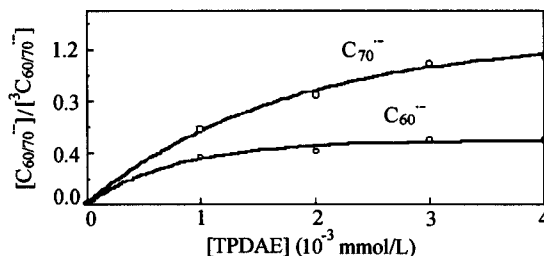
It is well known that the chemical oxidation of small aromatics by Lewis acids as the oxidant can generate corresponding radical cations.¹⁶ In order to examine the occurrence of TPDAE radical cations, absorption spectra of

oxidized TPDAE in Ar-saturated dichloromethane were measured by stepwise addition of $FeCl_3$. The new absorption band appeared, as shown in Fig. 6 after addition of two equivalents of $FeCl_3$. The new absorption maximum at 700 nm is assigned to cation similar to that of radical cation of TPDAE. Fig. 6 shows the optical absorption spectra of radical TPDAE.

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

Quantum yields and electron transfer rates

The efficiency of electron transfer via ${}^3C_{60}^*$ or ${}^3C_{70}^*$ can be estimated by the quantity $[C_{60}^{\cdot-}]/[{}^3C_{60}^*]$ or $[C_{70}^{\cdot-}]/[{}^3C_{70}^*]$ as evaluated by the maximal and initial absorbance. The ratios of $[C_{60}^{\cdot-}]_{max}/[{}^3C_{60}^*]_{max}$ and $[C_{70}^{\cdot-}]_{max}/[{}^3C_{70}^*]_{max}$ in benzonitrile are plotted against the concentration of $[TPDAE]$ as shown in Fig. 7. The efficiencies increase at the beginning, then reach a plateau, from which the quantum yield (Φ_{et}^T) for electron transfer to the triplet state is estimated. In Table 1, the k_q can be calculated from the dependence of first-order decay rate of ${}^3C_{60}^*$ on the concentration of TPDAE. The constant value refers to the quantum yield of electron transfer (Φ_{et}^T) via ${}^3C_{60}^*$. The k_{et} can be obtained from

**Fig. 7** Dependence of $[C_{60}^{\cdot-}]/[{}^3C_{60}^*]$ and $[C_{70}^{\cdot-}]/[{}^3C_{70}^*]$ on $[TPDAE]$ in Ar-saturated benzonitrile.

the following equation, $k_{et} = k_q \times \Phi_{et}^T$. The evaluated Φ_{et}^T and k_{et} are summarized in Table 1. The Φ_{et}^T values for the reactions via ${}^3C_{70}^*$ are also evaluated in a similar way. In the case of TPDAE, the k_q and k_{et} values based on TPDAE concentration are also listed. The Φ_{et}^T values are usually less than unity, indicating that some deactivation processes of the excited triplet states are competitive to the electron transfer processes.

In order to confirm the electron transfer via ${}^3C_{60}^*/{}^3C_{70}^*$, oxygen was added to the solution of $C_{60}/TPDAE$. In oxygen-saturated solution, the $C_{60}^{\cdot-}$ formation was suppressed (Fig. 8). The decay of ${}^3C_{60}^*$ was accelerated on addition of oxygen to C_{60} (0.1 mmol/L)/TPDAE (2.0 mmol/L) solution (Fig. 9), indicating that ${}^3C_{60}^*$ was quenched by oxygen due to energy transfer from ${}^3C_{60}^*$ to oxygen, resulting in the suppression of the electron transfer reaction between ${}^3C_{60}^*$ and TPDAE. Although the $C_{60}^{\cdot-}$ formation was suppressed by adding oxygen to solution, the decay rate of $C_{60}^{\cdot-}$ was not affected by the oxygen concentration, which indicates 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 TPDAE takes place via ${}^3C_{60}^*/{}^3C_{70}^*$.

Back electron transfer

Figs. 10 and 11 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 maximum. This can be attributed mainly to the back electron transfer from $C_{60}^{\cdot-}/C_{70}^{\cdot-}$ to TPDAE, because extra reactions 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 TPDAE. The decay time profiles obey second-order kinetics. From the slope of the second-order plot as shown in the inset of Fig. 10, the back electron transfer rate constants (k_{bet}) were evaluated as listed in Table 1. On the other hand, the second-order plots are slightly bent, suggesting that ion radicals are not

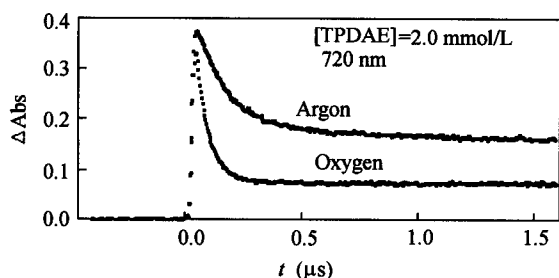


Fig. 8 Time profiles of absorbance obtained by 532 nm laser photolysis of C_{60} (0.1 mmol/L) in the presence of TPDAE (2.0 mmol/L) in argon-saturated benzonitrile and oxygen-saturated benzonitrile at 720 nm.

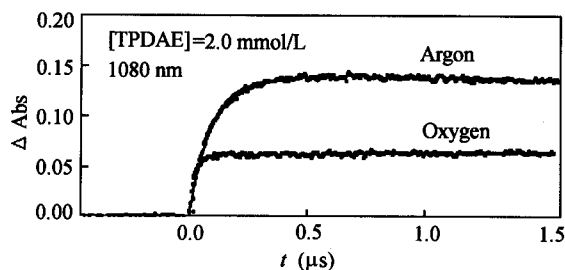


Fig. 9 Time profiles of absorbance obtained by 532 nm laser photolysis of C_{60} (0.1 mmol/L) in the presence of TPDAE (2.0 mmol/L) in argon-saturated benzonitrile and oxygen-saturated benzonitrile at 1080 nm.

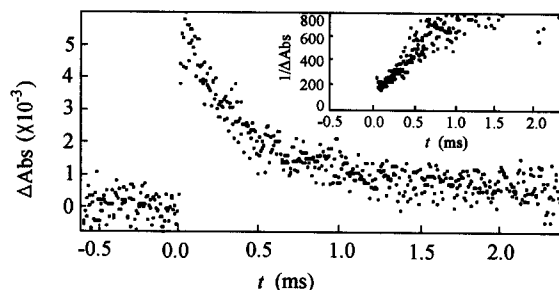


Fig. 10 Decay profiles over long time scale of $C_{60}^{\cdot-}$ in the presence of TPDAE in Ar-saturated benzonitrile. Inset shows second-order plot.

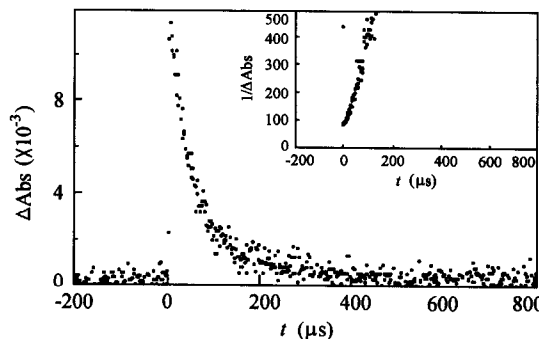


Fig. 11 Decay profiles over long time scale of $C_{70}^{\cdot-}$ in the presence of TPDAE in Ar-saturated benzonitrile. Inset shows second-order plot.

always freely solvated and the back electron transfer may occur within a solvent-separated ion pair in benzonitrile.

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