

Photophysical Properties and Photoinduced Electron Transfer between [60]Fullerene-Containing Cyclic Sulphoxide [C₆₀-C₆H₈SO] and Tetrathiafulvalene (TTF) by Laser Flash Photolysis

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Photoinduced electron transfer (PET) processes between C₆₀-C₆H₈SO and Tetrathiafulvalene (TTF) have been studied by nanosecond laser photolysis. Quantum yields (Φ_{et}) and rate constants of electron transfer (k_{et}) from TTF to excited triplet state of [60] fullerene-containing cyclic sulphoxide in benzonitrile (BN) have been evaluated by observing the transient absorption bands in the NIR region. With the decay of excited triplet state of [60] fullerene-containing cyclic sulphoxide, the rise of radical anion of [60] fullerene-containing cyclic sulphoxide is observed.

Keywords laser flash photolysis, [60] fullerene-containing cyclic sulphoxide, tetrathiafulvalene

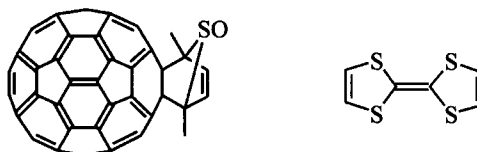
Introduction

Electron transfer chemistry has been a topic intensively studied in biological and artificial systems. [60]Fullerene-containing electroactive donor-acceptor dyads have become current focus of research in the field of efficient conversion of solar energy to usable forms of energy.¹⁻⁴ Such efficient conversion is a consequence of the remarkable acceptor properties of [60]fullerenes, as appeared in cyclic voltammetry experiments, where six reversible one-electron reduction waves can be observed,⁵⁻⁷ in alkali-metal intercalated complexes, which demonstrate superconductivity,⁸⁻¹³ and in charge transfer salts, which show ferromagnetic properties.¹⁴ Furthermore, very inter-

estingly, [60]fullerene is a great partner for light-induced electron transfer processes, holding strong promise for the fabrication of photovoltaic devices.^{15,16}

Numbers of [60] fullerene-donor dyads have been designed and prepared.¹⁷⁻²⁰ However, most of the [60]fullerene derivatives have lower electronegativities than the [60]fullerene itself, and only a few of them exhibit better reduction potentials than the parent systems. Therefore, it is still a desirable goal to improve the electron affinity of [60]fullerene-containing electroactive. For this reason, we designed and synthesized a novel structure in which the [60]fullerene cage is covalently attached to a cyclic sulphoxide¹⁷ exhibiting better reduction potentials than the parent [60]fullerene and allowing to address the attachment of the first electron in the reduction process either to [60]fullerene cage or to the cyclic sulphoxide moiety (Scheme 1).

Scheme 1 Molecular structures of C₆₀-C₆H₈SO and TTF



Photophysical and photochemical properties of [60]fullerene and its derivatives have attracted much attention recently.²¹⁻²⁴ In the present work we have observed

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the transient absorption spectra of [60] fullerene-containing cyclic sulphoxide for the first time by a nanosecond laser flash photolysis in the visible and near-infrared regions. The characterization of the charge transfer complex of [60] fullerene-containing cyclic sulphoxide with tetrathiafulvalene (TTF) is also reported as shown in Scheme 1. The rate constant of electron transfer from TTF to excited triplet state of [60] fullerene cage or to the cyclic sulphoxide moiety in the benzonitrile has also been evaluated by observing the transient absorbance bands in the near-IR region where the excited triplet state and radical anion of [60] fullerene cage appear.

Experimental

Instruments and reagents

C_{60} - C_6H_8SO was prepared by the method described in the literature.¹⁷ TTF was obtained from Tokyo Kasei Kogyo Co.. Benzonitrile was of high performance liquid chromatographic (HPLC) and spectrophotometric grade, respectively.

C_{60} - C_6H_8SO and TTF were dissolved in benzonitrile, and the sample solutions were then deaerated by bubbling with argon gas before measurements. O_2 -saturated solution was produced by O_2 bubbling when the effect of O_2 was to be investigated.

Transient absorption spectra were observed by the laser flash photolysis in the visible/NIR regions. C_{60} was excited with the SHG (532 nm) light of a Nd:YAG laser (Quanta-Ray; 6 ns fwhm). For time-scale measurements shorter than 10 μs , a Si-PIN photodiode module (400–600 nm) and a Ge-APD module (600–1600 nm) were employed as detectors for monitoring the light from a pulsed Xe-lamp. For time-scale measurements longer than 10 μs , an InGaAs-PIN photodiode was used as a detector for monitoring light from a continuous Xe-lamp (150 W). The sample solutions were deaerated by bubbling with argon gas before measurements. All the measurements were carried out at 23 °C.

Results and discussion

Steady-state UV-vis spectra

We will describe briefly the steady-state absorption

spectra of [60] fullerene-containing cyclic sulphoxide in benzonitrile and toluene, that were recorded between 400 and 800 nm as shown in Fig. 1.

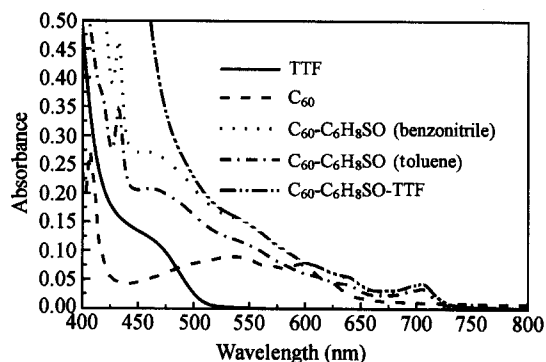


Fig. 1 Steady-state absorption spectra of C_{60} - C_6H_8SO (0.1 mmol/L) in the UV/vis in benzonitrile and toluene, a mixture of C_{60} - C_6H_8SO and TTF, TTF (2.0 mmol/L) and C_{60} (0.1 mmol/L) in benzonitrile

The absorption spectrum of a mixture of C_{60} - C_6H_8SO and TTF in benzonitrile, as shown in Fig. 1 is a superimposition of that of the components. This suggests that, for a mixture of C_{60} - C_6H_8SO and TTF, there is no apparent interaction between them in the concentration region employed in the laser photolysis experiments. On laser photolysis at 532 nm, only C_{60} - C_6H_8SO is excited, and no absorption of TTF appears at this wavelength.

With the laser-light excitation of [60] fullerene-containing cyclic sulphoxide in toluene, transient absorption bands appear at 740, 840 nm and at around 880 and 1000 nm with broad bands, which can be attributed to excited states of different spin multiplicity as shown in Fig. 2.

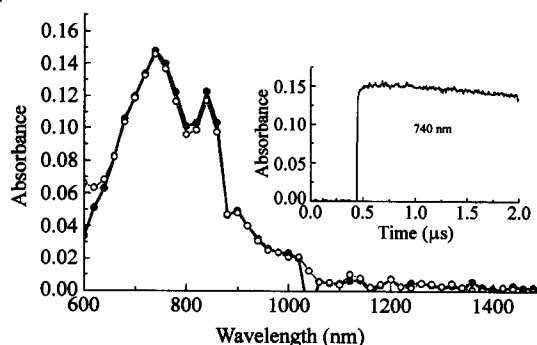


Fig. 2 Nanosecond time-resolved absorption spectra obtained by 532 nm laser photolysis of [60] fullerene-containing cyclic sulphoxide (0.1 mmol/L) in argon-saturated toluene. Inset Shows time-profile at 740 nm.

These absorption bands can be ascribed to the excited triplet state of [60]fullerene-containing cyclic sulphoxide, because the absorption can be efficiently quenched in the presence of oxygen, an excited triplet state energy acceptor.

From absorption-time profiles at 740 and 840 nm, and time profile as shown in the inset of Fig. 2, the decay rate constants of [60] fullerene-containing cyclic sulphoxide are estimated to be $6.05 \times 10^4 \text{ s}^{-1}$ and $7.63 \times 10^4 \text{ s}^{-1}$, respectively, which correspond to 16 μs and 13 μs of the triplet excited state lifetimes. The lifetime of excited triplet state is shorter than that of [60]fullerene (55 μs). Such short lifetimes of excited triplet states of [60]fullerene-containing cyclic sulphoxide result from vibrations of the bonds connecting cyclic sulphoxide which may efficiently quench the excited triplet states by means of the radiation process.

In the polar solvent such as benzonitrile, the transient absorption bands appear at 720–760, 840 nm and at around 880 and 1000 nm with broad bands, as shown in Fig. 3.

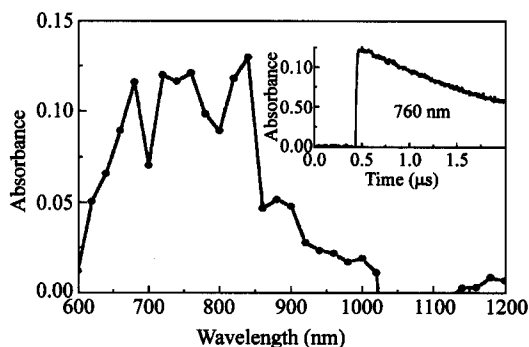


Fig. 3 Nanosecond time-resolved absorption spectra obtained by 532 nm laser photolysis of [60]fullerene-containing cyclic sulphoxide (0.1 mmol/L) in argon-saturated benzonitrile. Inset Shows time-profiles at 740 nm.

From the time profile shown in the inset of Fig. 3, the decay rate constants of [60]fullerene-containing cyclic sulphoxide are estimated to be $4.7 \times 10^5 \text{ s}^{-1}$ and $5.46 \times 10^5 \text{ s}^{-1}$ which correspond to 2.1 μs and 1.8 μs of lifetimes of the excited triplet states, respectively. The lifetime of excited triplet state of [60] fullerene-containing cyclic sulphoxide in benzonitrile is much shorter than that in toluene. This finding agrees with that deactivation of [60]fullerene-containing cyclic sulphoxide by intermolecular and/or intramolecular triplet-triplet (T-T) annihilation

under the present experimental conditions. The efficient quench of the excited triplet state of [60]fullerene-containing cyclic sulphoxide may be due to the formation of the excited charge-transfer complex under the present experimental conditions.

Photoinduced electron transfer

Fig. 4 shows the transient absorption spectra in the visible and near-IR region obtained by the laser flash photolysis of $\text{C}_{60}\text{-C}_6\text{H}_8\text{SO}$ with 532 nm light in the presence of TTF (2.0 mmol) in deaerated benzonitrile. The transient absorption band at 760 nm can be attributed to the excited triplet state of $\text{C}_{60}\text{-C}_6\text{H}_8\text{SO}$. With the decay of excited triplet state of $\text{C}_{60}\text{-C}_6\text{H}_8\text{SO}$, a new absorption band can be seen at 1020 nm with a shoulder at 960 nm, which is assigned to the absorption of radical anion of $\text{C}_{60}\text{-C}_6\text{H}_8\text{SO}$ in the visible region. The absorption band of radical cation of TTF fails to appear in the near-IR.

The observed time profiles of the absorption bands are shown in Fig. 4. The decay of excited triplet state of $\text{C}_{60}\text{-C}_6\text{H}_8\text{SO}$ at 760 nm is accelerated in the presence of TTF (2.0 mmol). With the decay of excited triplet state of $\text{C}_{60}\text{-C}_6\text{H}_8\text{SO}$, the absorption intensity of radical anion of $\text{C}_{60}\text{-C}_6\text{H}_8\text{SO}$ at 1020 nm increases, reaching a maximum at about 0.5–1.0 μs . The decay of excited triplet state of $\text{C}_{60}\text{-C}_6\text{H}_8\text{SO}$ and the appearance of radical anion of $\text{C}_{60}\text{-C}_6\text{H}_8\text{SO}$ provide evidence for the electron-transfer process in which radical anion of $\text{C}_{60}\text{-C}_6\text{H}_8\text{SO}$ is produced via the acceptance of an electron from TTF by excited triplet state of $\text{C}_{60}\text{-C}_6\text{H}_8\text{SO}$.

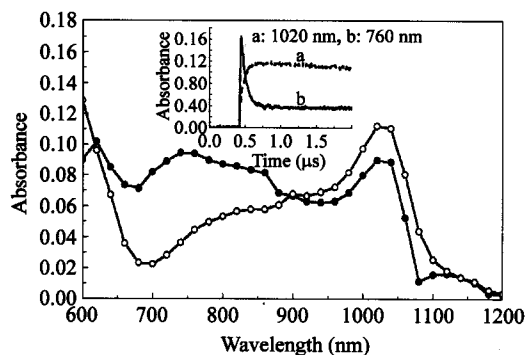


Fig. 4 Nanosecond time-resolved absorption spectra obtained by 532 nm laser photolysis of $\text{C}_{60}\text{-C}_6\text{H}_8\text{SO}$ (0.1 mmol/L) in the presence of TTF (2.0 mmol/L) in argon-saturated Benzonitrile. Inset shows time profiles.

The contribution of excited triplet state of [60]fullerene-containing cyclic sulphoxide to photoinduced electron transfer is further confirmed by the O_2 effect on the yields of radical anion of $C_{60}-C_6H_8SO$. The maximal concentration of radical anion of $C_{60}-C_6H_8SO$ is considerably suppressed on addition of O_2 to the solution as shown in Fig. 5.

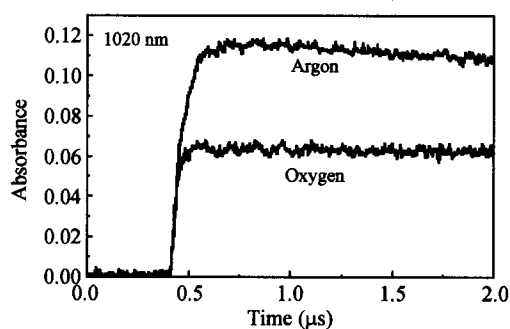


Fig. 5 Time profiles of absorbance obtained by 532 nm laser photolysis of $C_{60}-C_6H_8SO$ (0.1 mmol/L) in the presence of TTF (2.0 mmol/L) in argon-saturated and oxygen-saturated benzonitrile at 1020 nm.

The decay of excited triplet state of [60]fullerene-containing cyclic sulphoxide is accelerated on addition of O_2 as shown in Fig. 6 indicating that the excited triplet state of [60]fullerene-containing cyclic sulphoxide is quenched by O_2 because of the energy transfer from the excited triplet state of [60]fullerene-containing cyclic sulphoxide to O_2 . As a result, the generation of radical

anion of [60]fullerene-containing cyclic sulphoxide is suppressed. The ratio of the excited triplet state of [60]fullerene-containing cyclic sulphoxide consumed by the two processes is determined by $K_{et}[C_{60}-C_6H_8SO]/K_{O_2}[O_2]$. At $[C_{60}-C_6H_8SO] = 0.1$ mmol the maximal absorbance of radical anion of $C_{60}-C_6H_8SO$ in argon-saturated solution decreases to about one-second in air-saturated solution ($[O_2] = 0.3$ mmol/L in benzonitrile).²⁵

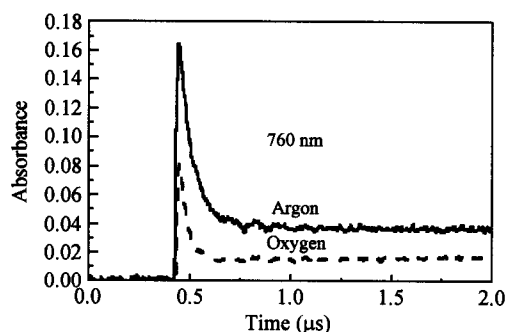
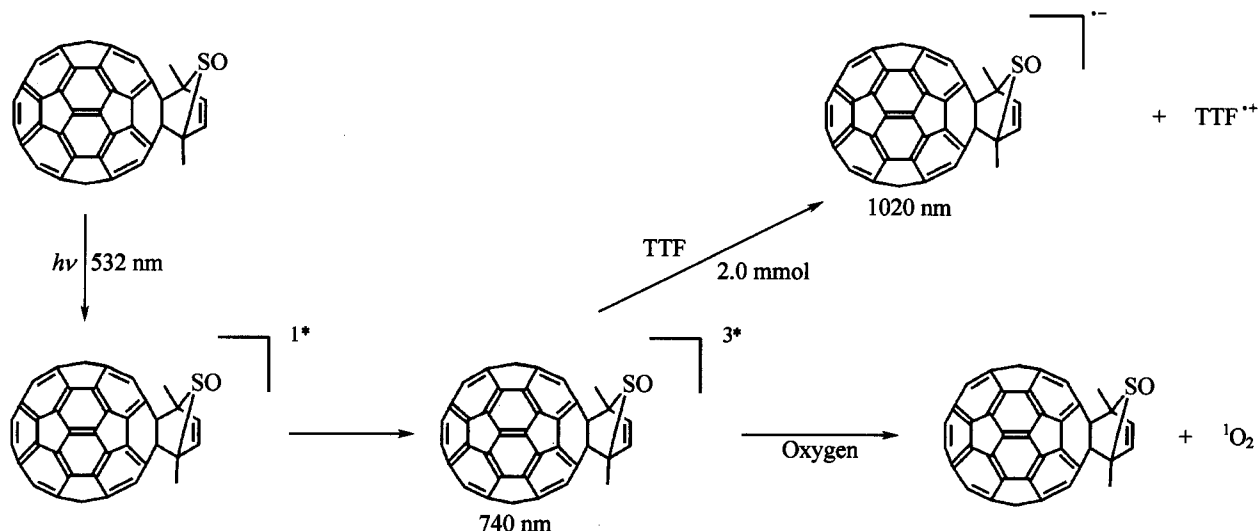


Fig. 6 Time profiles of absorbance obtained by 532 nm laser photolysis of $C_{60}-C_6H_8SO$ (0.1 mmol/L) in the presence of TTF (2.0 mmol/L) in argon-saturated and oxygen-saturated benzonitrile at 760 nm.

The rise and decay curves of radical anion of $C_{60}-C_6H_8SO$ in deaerated and O_2 -saturated solution are shown in Figs. 5 and 6. With an increase in the O_2 concentration, the yield of anion radical of C_{60} decreases, about one-second of the radical anion of $C_{60}-C_6H_8SO$ disappears in O_2 -saturated solution. These also confirm that

Scheme 2 Photoinduced electron transfer of [60]fullerene-containing cyclic sulphoxide



anion radical of $C_{60}-C_6H_8SO$ is formed via excited triplet state of $C_{60}-C_6H_8SO$, about one-second of the anion radical of $C_{60}-C_6H_8SO$ may be produced via the excited singlet state of $C_{60}-C_6H_8SO$.

Back electron transfer

After reaching maximal concentration, the absorbance of radical anion of $C_{60}-C_6H_8SO$ begins to decay as shown in Fig. 7. The decay time profile of radical anion of $C_{60}-C_6H_8SO$ observed on the longer time-scale obeys second-order kinetics in benzonitrile (inset of Fig. 7), indicating that the radical anion of $C_{60}-C_6H_8SO$ and radical cation of TTF are recombined after being solvated as free ions or as a solvent separated ion pair.

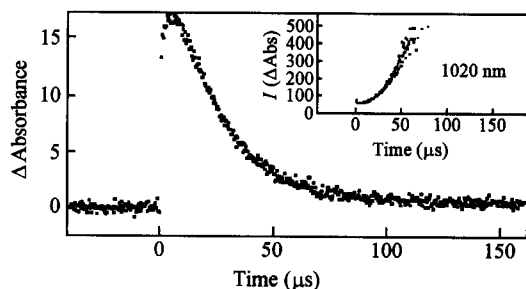


Fig. 7 Decay profiles over long time-scale of radical anion of $C_{60}-C_6H_8SO$ (0.1 mmol/L) in argon-saturated benzonitrile at 1020 nm. Insert shows a second-order plot.

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