

Photoinduced Charge Separation of the Covalently Linked Fullerene–Triphenylamine–Fullerene Triad. Effect of Dual Fullerenes on Lifetimes of Charge-Separated States

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Photoinduced intramolecular events of the newly synthesized fullerene–triphenylamine–fullerene (C_{60} –TPA– C_{60}) triad, in which the TPA entity was substituted with an electron-donating CH_3O -group to increase electron-donating ability, were investigated in relation to a C_{60} –TPA dyad. The molecular orbital calculations showed that the radical cation is located on the TPA entity, whereas the radical anion is located on two C_{60} entities in the radical ion pair. The fluorescence intensity of the singlet excited state of C_{60} was efficiently quenched by the attached TPA moiety in polar solvents. The quenching pathway involves a charge-separation process from the TPA to the singlet excited state C_{60} . The lifetimes of the radical ion-pairs for C_{60} –TPA– C_{60} evaluated from nanosecond transient absorption measurements were found to be 600 and 454 ns in benzonitrile and dimethylformamide, respectively. These lifetimes of radical ion-pairs of C_{60} –TPA– C_{60} are longer than those of the C_{60} –TPA dyad, which reflects the effect of the second C_{60} moiety in stabilizing the radical ion-pairs.

Photoinduced intramolecular electron transfer of donor–acceptor systems is the most elementary and ubiquitous of all photochemical reactions, and it plays a crucial role in many essential photophysical processes.^{1,2} Functionalization of fullerene (C_{60}) with electron-donating moieties has drawn considerable attention as building blocks to construct artificial light energy harvesting systems and also to develop molecular electronic devices.^{3,4} Among the electron-donors, aromatic amines are the most fundamental donors used in optoelectronic materials owing to their low oxidation potential and good film-forming properties.⁵

To date, various C_{60} –amine dyads with different linkages have been synthesized, and their photophysical properties have been investigated.⁶ In our continuous efforts to explore the intramolecular events of C_{60} –aromatic amine connected systems, we have reported the photoinduced processes of the covalently linked C_{60} –triphenylamine dyads with the H- and CH_3 -groups,⁷ in which we have shown that there is efficient charge separation in these systems by employing the time-resolved and nanosecond transient techniques. It is notable that the charge recombination of such systems occurs quickly to the ground state, from which the lifetimes of the radical ion-pairs (RIPs) can be evaluated in the range of a few nanoseconds.

In order to reveal the effect of the second fullerene to the C_{60} –donor dyads, related triads consisting of two C_{60} units co-

valently linked with different electron-donor compounds have been investigated, e.g., porphyrins, phthalocyanines, π -conjugated oligomers, tetrathiafulvalenes (TTFs), substituted polyfluorene, etc.⁸ The presence of two C_{60} units could contribute to establish well-ordered solid phases, which is a crucial factor in the field of optoelectronic devices research.^{8c} In this manuscript, we designed a new molecular C_{60} –TPA– C_{60} triad **1** (Fig. 1), in which the TPA moiety is bounded by two C_{60} units, aiming to use it as a constituent of the electronic devices. Here, the CH_3O -group on triphenylamine was expected to increase the electron-donating ability compared to our previous CH_3 -substituted C_{60} –TPA dyad.^{7d} Both picosecond fluorescence and nanosecond transient absorption spectral studies were performed in order to characterize the electron-transfer species in polar solvents and to explore the mechanistic details of the light-induced electron-transfer reactions. Finally, by comparing to the C_{60} –TPA dyad **2**, the effect of the second C_{60} moiety for prolonging the lifetimes of the charge-separated state was clarified in this study.

Results and Discussion

Synthesis and Characterization. The most straightforward preparation of C_{60} –TPA– C_{60} **1** and C_{60} –TPA **2** can be envisaged to proceed through a reaction sequence of the following steps, i.e., the Ullmann,⁹ Vilsmeier,¹⁰ Prato's 1,3-dipolar cycloaddition¹¹ reactions depicted in Scheme 1. Every

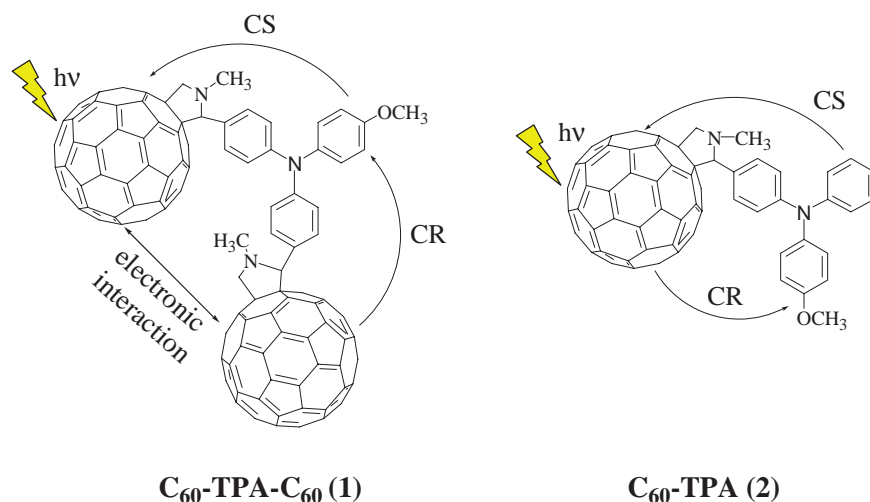
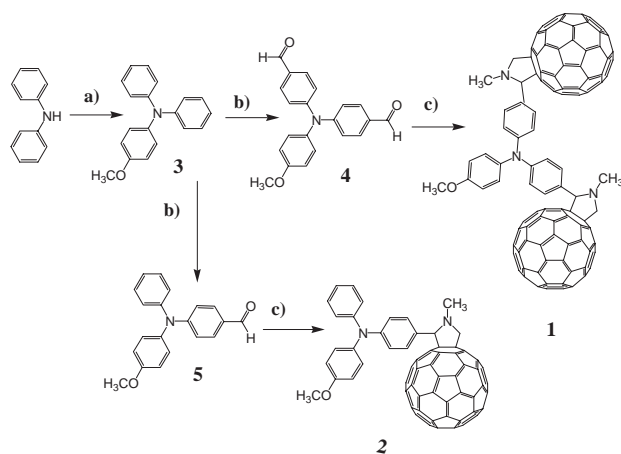


Fig. 1. Molecular structures and expected photoinduced processes: CS; charge separation, CR; charge recombination. In the present study, TPA refers as to CH₃O-substituted triphenylamine otherwise cited.



Scheme 1. Synthesis of compounds **1** and **2**; a) 4-iodoanisole, K₂CO₃, Cu, 18-crown-6, *o*-dichlorobenzene (DCB), 180, 48 h, 86.0% yield, b) POCl₃, DMF, *o*-dichloroethane, reflux, 36.7% yield for **4** and 73.0% yield for **5**, and c) sarcosine, fullerene, reflux, 10.0% yield for **1**, 29.0% yield for **2**.

step of the reaction sequence proceeded smoothly and efficiently to give a good or moderate yield of the product. Diphenylamine was coupled with 4-iodoanisole under Ullmann condition to give 4-methoxytriphenylamine (**3**, abbreviated as TPA) in 86.0% yield followed by Vilsmeier formylation with a large excess of POCl₃/DMF to produce diformylated TPA **4**. The functionalization of C₆₀ was based on azomethine 1,3-dipolar cycloaddition. Treatment of C₆₀ in toluene with dialdehyde **4** and sarcosine or methylglycine afforded dyad **1** in 10.0% yield. Although C₆₀-TPA-C₆₀ **1** should be obtained as a stereoisomeric mixture due to the formation of two asymmetric centers in two-fold cycloaddition reaction, high resolution ¹H NMR spectrum (400 MHz) of C₆₀-TPA-C₆₀ **1** showed that one of the two stereoisomers is predominant.

Analogously, monoaldehyde **5** was obtained in 73.0% yield by the Vilsmeier reaction under normal stoichiometry of POCl₃/DMF (up to 3.0 equivalents), and subsequent 1,3-

dipolar cycloaddition of the azomethine ylide afforded C₆₀-TPA **2** in 29.0% yield.

The structure and purity of the new compounds were confirmed by ¹H NMR, ¹³C NMR, and IR spectroscopies, MALDI-TOF mass spectrometry, and elemental analysis (see experimental section). The ¹H NMR spectra of **1** and **2** are consistent with the proposed structures, and ¹³C NMR spectra showed characteristic aliphatic carbon peaks: seven resonance lines for **1** and four resonance lines for **2**. The complex pattern of ¹³C NMR signals between 114.82–158.68 ppm was assigned to the aromatic carbons and also the resonance peaks of C₆₀. These patterns of signals are unambiguously diagnostic for the proposed structures of **1** and **2**. The MALDI-TOF-MS provided a direct evidence for the structures of **1** and **2** by a singly charged molecular ion peak at *m/z* = 1826.71 and 1051.14, respectively.

Photophysical Studies. The absorption spectra of C₆₀-TPA-C₆₀ **1** and C₆₀-TPA **2** are shown in Fig. 2. In the UV-vis region, the absorption spectra exhibited the characteristic peaks of a 1-methyl-3,4-fullero-2,3,4,5-tetrahydropyrrol (abbreviated as fulleropyrrolidine) below 350 nm in addition to 432 and 704 nm. The TPA moiety showed an absorption in the UV region with a maximum at 298 nm. The UV-vis spectrum is a superimposition on the sum of the two fulleropyrrolidine units and the TPA moiety, indicating that there is no significant ground-state electronic interaction between the components. Spectral features observed in *o*-dichlorobenzene (DCB) and benzonitrile (BN) were the same as in toluene.

Photoinduced intramolecular events of both compounds were investigated by using steady-state fluorescence spectroscopy on exciting the C₆₀ moiety (λ_{ex} = 400 nm). In toluene, the intensity of the ¹C₆₀* moiety of C₆₀-TPA-C₆₀ at 710 nm was found to be almost the same as that obtained for the fulleropyrrolidine reference.^{3,4,12} The spectral shape is insensitive to solvent changes, whereas the fluorescence properties are found to be sensitive to solvent polarity. Changing the solvent from toluene to DCB gave rise to significant quenching of the excited singlet state of the C₆₀ moiety (¹C₆₀*) compared to that in toluene. These observations suggest efficient quench-

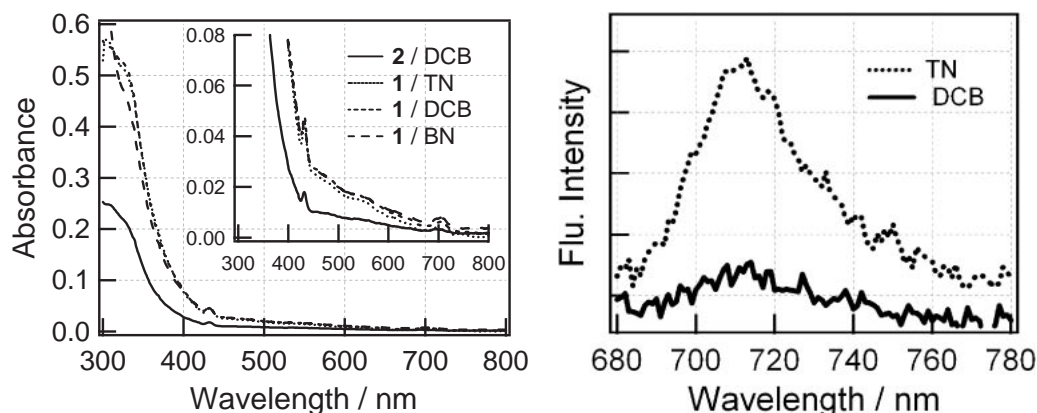


Fig. 2. Steady-state absorption of C_{60} -TPA- C_{60} **1** and C_{60} -TPA **2** (left) and fluorescence spectra (right) of C_{60} -TPA- C_{60} in toluene (TN), and *o*-dichlorobenzene (DCB); $\lambda_{\text{ex}} = 400$ nm. Concentrations are kept at 1×10^{-6} mol dm $^{-3}$.

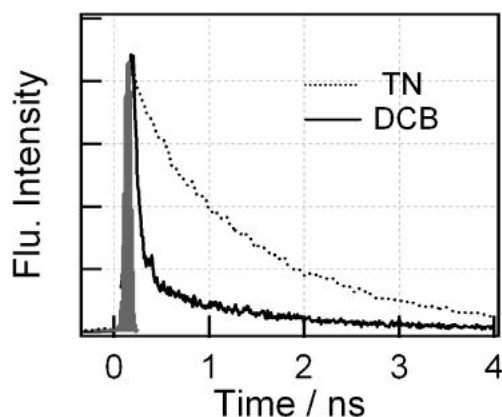


Fig. 3. Time profiles of $^1C_{60}^*$ -fluorescence at 710 nm of C_{60} -TPA- C_{60} **1** in toluene (TN) and DCB; $\lambda_{\text{ex}} = 400$ nm.

ing of the $^1C_{60}^*$ moiety by the appended TPA moiety in the polar solvents. The fluorescence quenching of the $^1C_{60}^*$ moiety became more prominent with an increase in the solvent polarity, providing evidence for intramolecular electron transfer in polar solvents.⁶ Similar behavior was observed for C_{60} -TPA. By using a streak-scope as a detector, time-resolved fluorescence spectra were observed by irradiating with a 400-nm laser for 0–2 ns, which afforded similar fluorescence spectra to those of the steady-state fluorescence spectra, supporting the reliability of the both fluorescence measurements.

The fluorescence lifetime measurements (Fig. 3) track the above considerations in a more quantitative way, giving kinetic data of the charge-separation processes in polar solvents. In toluene, the time-profiles of the $^1C_{60}^*$ of C_{60} -TPA- C_{60} and C_{60} -TPA exhibited a single-exponential decay with a lifetime of 1400 ps, which is almost the same as the fulleropyrrolidine reference,¹² suggesting no fluorescence quenching of the $^1C_{60}^*$ unit by the TPA moiety. The time-profile of C_{60} -TPA- C_{60} in DCB could be satisfactorily fitted by a bi-exponential decay: one has a short lifetime of 92 ps (80%) which reflects the actual intramolecular deactivation of the $^1C_{60}^*$ moiety, and the other has a longer lifetime, which resembles that of the C_{60} reference. In BN and dimethylformamide (DMF), the decays of $^1C_{60}^*$ were too fast to be detected using our instrument (ca. 20 ps). The fluorescence time-profiles of C_{60} -TPA show a

similar decay as C_{60} -TPA- C_{60} , where the fluorescence lifetime of the major component was evaluated to be 107 ps (90%). Based on the short lifetimes of the major components, the rate (k_{CS}) and quantum yield (Φ_{CS}) for the charge-separation process in DCB were determined to be 9.9×10^9 s $^{-1}$ and 0.94 for C_{60} -TPA- C_{60} and 8.6×10^9 s $^{-1}$ and 0.93 for C_{60} -TPA, respectively. In more polar solvents, such as BN and DMF, higher values for k_{CS} and Φ_{CS} were obtained, as listed in Table 1.

Electrochemical Studies. The charge-separation process via $^1C_{60}^*$ was supported from the viewpoint of thermodynamics of electron-transfer processes. The cyclic voltammogram of C_{60} -TPA- C_{60} in DCB showed the first reduction potential (E_{red}) of the C_{60} moiety at -930 mV vs. Ag/AgCl, and the corresponding first oxidation potential (E_{ox}) of the TPA moiety was located at 610 mV vs. Ag/AgCl. The potential difference between the first oxidation of the TPA moiety and the first reduction of the C_{60} moiety was found to be 1.54 V. Compared to the redox values of C_{60} -TPA, the first oxidation (618 mV vs. Ag/AgCl) and reduction (-930 mV vs. Ag/AgCl) potentials of C_{60} -TPA- C_{60} were slightly change (ca. 10 mV), suggesting appreciable interaction between the two fullerene moieties of C_{60} -TPA- C_{60} . Based on the first oxidation potential of the TPA moiety, the first reduction potential of the C_{60} moiety and a solvent correction term (ΔG_{S}), the thermodynamic driving forces for charge-recombination process ($-\Delta G_{\text{CR}}$) and the intramolecular charge-separation ($-\Delta G_{\text{CS}}$) via the $^1C_{60}^*$ moiety calculated from the Rehm–Weller equation are listed in Table 1.¹³ These values suggest an exothermic charge-separation process via the $^1C_{60}^*$ moiety to form the RIPs in polar solvents, whereas endothermic in toluene. The $-\Delta G_{\text{CS}}$ values of C_{60} -TPA- C_{60} were found to be 0.28, 0.43, and 0.48 eV in DCB, BN, and DMF, respectively, which are slightly more negative than the corresponding values of C_{60} -TPA.

Molecular Orbital Calculations. Moreover, the charge-separation process from the TPA unit to the $^1C_{60}^*$ moiety forming the RIPs was supported by studying the molecular geometries and electronic structures of C_{60} -TPA- C_{60} and C_{60} -TPA on the basis of molecular orbital calculation using density functional method (DFT) at B3LYP/3-21G level.¹⁴ From the optimized structure of C_{60} -TPA- C_{60} , shown in Fig. 4, the center-to-center distance (R_{CC}) between the C_{60}

Table 1. Free-Energy Changes ($-\Delta G_{\text{CR}}$ and $-\Delta G_{\text{CS}}$) via $^1\text{C}_{60}^*$, Initial-Quick Fluorescence Lifetimes of $^1\text{C}_{60}^*$ (τ_f), Rates (k_{CS}) and Quantum Yields (Φ_{CS}) of Charge-Separation via $^1\text{C}_{60}^*$, Rates of Charge-Recombination (k_{CR}) and Lifetimes of Radical Ion-Pairs (τ_{RIP}) of $\text{C}_{60}\text{-TPA}^{\bullet+}\text{-C}_{60}^{\bullet-}$ and $\text{C}_{60}^{\bullet-}\text{-TPA}^{\bullet+}$

Compound	Solvent	$-\Delta G_{\text{CR}}^{\text{a)}}$ /eV	$-\Delta G_{\text{CS}}^{\text{a)}}$ /eV	τ_f /ps	$k_{\text{CS}}^{\text{b)}}$ /s ⁻¹	$\Phi_{\text{CS}}^{\text{b)}}$	k_{CR} /s ⁻¹	τ_{RIP} /ns
C ₆₀ -TPA-C ₆₀	TN	1.92	-0.17	1400	—	—	—	—
	DCB	1.59	0.28	93	9.9×10^9	0.94	2.5×10^7	40
	BN	1.32	0.43	<20	$>5 \times 10^{10}$	>0.99	1.6×10^6	600
	DMF	1.27	0.48	<20	$>5 \times 10^{10}$	>0.99	2.2×10^6	450
C ₆₀ -TPA	TN	2.03	-0.28	1390	—	—	—	—
	DCB	1.59	0.26	107	8.6×10^9	0.93	2.5×10^7	40
	BN	1.32	0.43	<20	$>5 \times 10^{10}$	>0.99	2.1×10^6	480
	DMF	1.31	0.44	<20	$>5 \times 10^{10}$	>0.99	2.7×10^6	360

a) The driving forces for ΔG_{CR} and ΔG_{CS} were calculated by equations; $-\Delta G_{\text{CR}} = e(E_{\text{ox}} - E_{\text{red}}) + \Delta G_{\text{S}}$ and $-\Delta G_{\text{CS}} = \Delta E_{00} - (-\Delta G_{\text{CR}})$, where ΔE_{00} is the energy of the 0-0 transition (1.75 eV for $^1\text{C}_{60}^*$). ΔG_{S} refers to the static energy, which was calculated by $-\Delta G_{\text{S}} = -(e^2/(4\pi\epsilon_0))[(1/(2R_+) + 1/(2R_-) - (1/R_{\text{CC}})/\epsilon_{\text{S}} - (1/(2R_+) + 1/(2R_-))/\epsilon_{\text{R}})]$, where R_+ and R_- are radii of the radical cation (0.37 nm) and radical anion (0.42 nm), respectively; R_{CC} is the center-center distance between C₆₀ and TPA (1.2 nm), which were evaluated from optimized structure. ϵ_{R} and ϵ_{S} refer to solvent dielectric constants for electrochemistry and photophysical measurements, respectively.

b) The k_{CS} and Φ_{CS} via $^1\text{C}_{60}^*$ were calculated from the relation; $k_{\text{CS}} = (1/\tau_f) - (1/\tau_{\text{f0}})$ and $\Phi_{\text{CS}} = k_{\text{CS}}/(1/\tau_f)_{\text{sample}}$, in which τ_{f0} is the lifetime of C₆₀ reference (1400 ps).

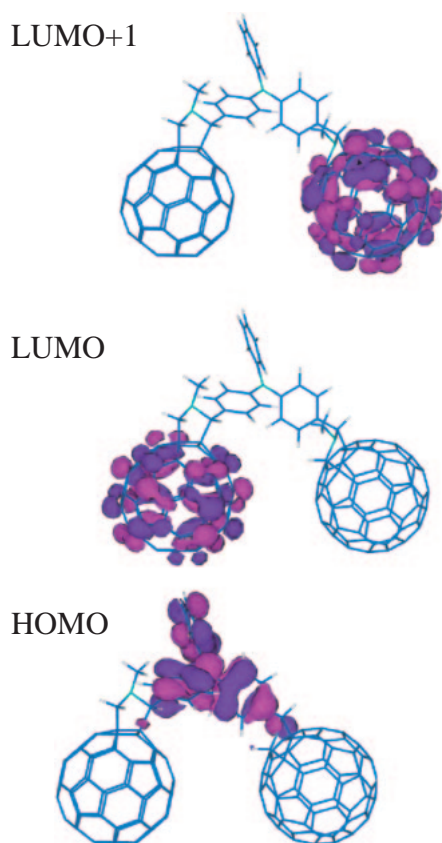


Fig. 4. Optimized structure and the HOMO, LUMO, and LUMO+1 of C₆₀-TPA-C₆₀ calculated by ab initio molecular orbital method at B3LYP/3-21G level.

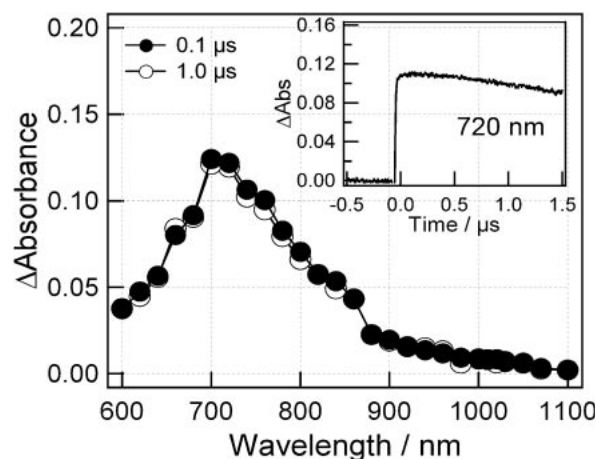


Fig. 5. Transient absorption spectra of C₆₀-TPA-C₆₀ **1** obtained by irradiating 532 nm laser light in Ar-saturated toluene.

and TPA moieties was estimated to be 1.2 nm. The electron distribution of the highest occupied molecular orbital (HOMO) was found to be entirely located on the TPA entity, whereas the electron distribution of the lowest unoccupied molecular orbital (LUMO and LUMO+1) was found to be entirely located on the C₆₀ spheroids. This suggests the charge-separated state as $\text{C}_{60}^{\bullet-}\text{-TPA}^{\bullet+}\text{-C}_{60}$ or $\text{C}_{60}\text{-TPA}^{\bullet+}\text{-C}_{60}^{\bullet-}$.

Transient Absorption Studies. Conclusive evidence about the charge separation from the TPA unit to the $^1\text{C}_{60}^*$ moiety was obtained from the nanosecond transient absorption measurements by irradiating at 532 nm with 6 ns laser pulses, which selectively excited the C₆₀ moiety. In toluene, the transient spectra of C₆₀-TPA-C₆₀ (Fig. 5) exhibited absorption peak at 700 nm corresponding to the excited triplet state of the C₆₀ moiety ($^3\text{C}_{60}^*$), which is almost identical to that

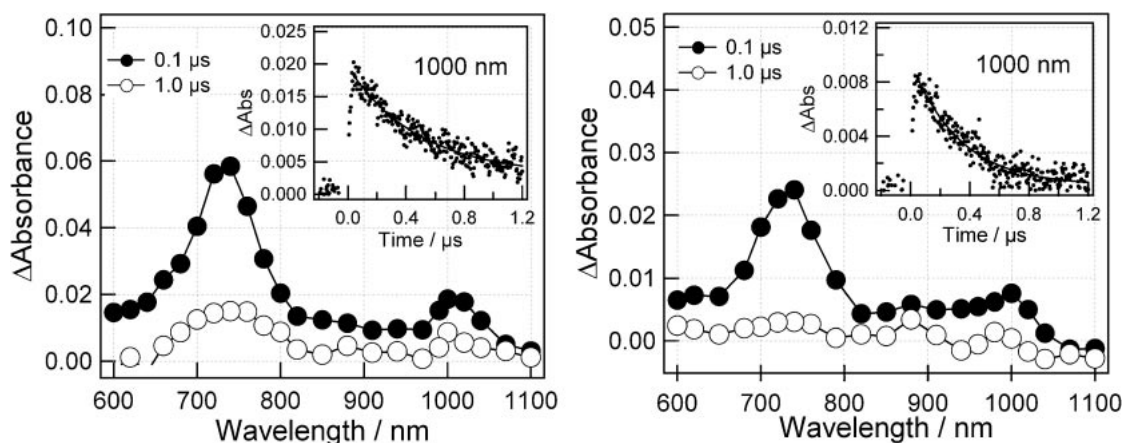


Fig. 6. Transient absorption spectra of C_{60} -TPA- C_{60} obtained by 532 nm laser light in Ar-saturated BN (left) and DMF (right).

of the excited triplet state of fulleropyrrolidine reference; the slow decay at 700 nm in inset of Fig. 5 also supports this assignment. The absence of the characteristic peaks of the RIPs indicates no electron transfer, which is in good agreement with the no-emission decay and with the positive ΔG_{CR} value in toluene. Therefore, the $^3C_{60}^*$ moiety is generated via intersystem crossing (isc) from the $^1C_{60}^*$ moiety.

In DCB, although the transient absorption spectra of C_{60} -TPA- C_{60} (see Supporting Information, Fig. S1) are almost the same as those in toluene, the absorption intensity of the $^3C_{60}^*$ moiety is considerably lower than that in toluene, indicating the presence of competitive path along with intersystem crossing (isc) via $^1C_{60}^*$. In addition, a weak absorption band was observed at 1000 nm. The time-profile at 1000 nm showed the quick decay ($2.5 \times 10^7 s^{-1}$), followed by a slow decay ($\approx 10^5 s^{-1}$). The slow decay part was ascribed to the absorption tail of $^3C_{60}^*$, whereas the quick decay part can be assigned to the radical anion of the C_{60} moiety ($C_{60}^{\bullet-}$),^{3,4,15–17} since formation of RIPs via intramolecular charge-separation process via $^1C_{60}^*$ was evidenced by the efficient quenching of $^1C_{60}^*$ -fluorescence. The quick decay of the $C_{60}^{\bullet-}$ moiety may be related to the relatively higher energy of the charge-separated state compared to the energy level of the $^3C_{60}^*$ moiety, which promotes the charge-recombination process to the $^3C_{60}^*$ moiety, in addition to the ground state.

As shown in Fig. 6, quite different spectra and time profiles were observed for C_{60} -TPA- C_{60} in highly polar solvents, such as BN and DMF, compared to those in toluene and DCB. The narrow band in the near-IR region at 1000 nm served as a diagnostic probe for identification of the $C_{60}^{\bullet-}$ moiety,^{3,4,15–17} and the absorption band in the vis region at 740 nm was assigned to the radical cation of the TPA moiety, which overlaps with the $^3C_{60}^*$ moiety.

The characteristic band of the $C_{60}^{\bullet-}$ moiety in the near-IR region was employed as reliable probe to determine the rate constant of the charge recombination, k_{CR} , because the $C_{60}^{\bullet-}$ band at 1000 nm does not overlap the bands of other species. The time profiles (insets) were well-fitted by a single-exponential function. The k_{CR} values of C_{60} -TPA- C_{60} were evaluated to be $1.6 \times 10^6 s^{-1}$ (BN) and $2.2 \times 10^6 s^{-1}$ (DMF), from which the lifetimes of the radical ion-pairs (τ_{RIP}) were evaluated as 600 and 450 ns, respectively. For C_{60} -TPA, the k_{CR} values were evaluated to be $2.1 \times 10^6 s^{-1}$ (BN) and $2.7 \times$

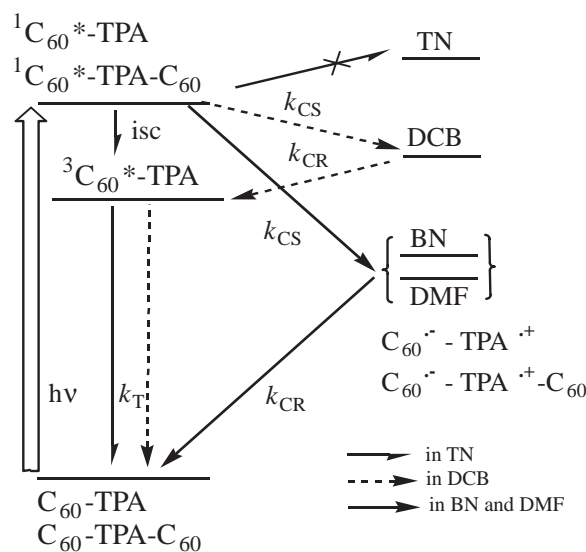


Fig. 7. Energy diagram of C_{60} -TPA- C_{60} and C_{60} -TPA in the studied solvents.

$10^6 s^{-1}$ (DMF), and the τ_{RIP} values were 480 and 360 ns, respectively. The τ_{RIP} values of C_{60} -TPA- C_{60} are longer than those of C_{60} -TPA. Since the energy levels of the charge-separated states of C_{60} -TPA- C_{60} and C_{60} -TPA are almost similar, the slightly longer τ_{RIP} values of C_{60} -TPA- C_{60} may reflect an effect of the second C_{60} moiety on stabilizing the RIPs due to electronic interaction between the two C_{60} moieties.

Furthermore, the τ_{RIP} values of C_{60} -TPA- C_{60} and C_{60} -TPA are much longer than those reported for C_{60} -tetrathiafulvalene (TTF)- C_{60} and C_{60} -substituted-polyfluorene- C_{60} triads, revealing the role of the TPA moiety in stabilizing the charge-separated states, due to of geometric and electronic reasons.^{8a,d} As for the substituent effect on triphenylamine donors, the τ_{RIP} values with CH_3O -group are apparently longer than the reported amine- C_{60} dyads with the H- and CH_3 -groups;^{7d} this may be due to the effect of the CH_3O -group on increasing the electron-donating character of the triphenylamine moiety.

Energy Diagram. Figure 7 illustrates energy level diagrams summarizing the observed photoinduced intramolecular events of C_{60} -TPA- C_{60} and C_{60} -TPA. In toluene, the $^1C_{60}^*$

moiety decayed without forming the RIPs, where the charge-separation is thermodynamically unfavorable. The ¹C₆₀^{*} moiety relaxes to the ³C₆₀^{*} moiety by an intersystem crossing process. Finally, the ³C₆₀^{*} decays to the ground state. In polar solvents, fluorescence quenching takes place through electron transfer from the TPA entity to the covalently bonded ¹C₆₀^{*} moiety, which was confirmed by observing the characteristic bands of C₆₀^{•-} and TPA^{•+} with nanosecond transient technique. The charge-recombination of the charge-separated states may direct to the ground state in BN and DMF, whereas in DCB, charge-recombination may produce mainly the ³C₆₀^{*} moiety in addition to the ground state. The longer lifetimes of the radical ion-pairs (τ_{RIP}) in BN compared to that in DMF suggest that the charge-recombination process with a highly negative ΔG_{CR} (ca. -1.30 eV) belongs to the Marcus inverted region,¹⁸ because the reorganization energy of the C₆₀-donor dyads has been reported to be as small as 0.6 eV.¹⁵

Conclusion

The photophysical events of a C₆₀-triphenylamine-C₆₀ triad were studied by using time-resolved emission and nanosecond transient techniques. From the collected data, presence of the second fullerene unit seems to afford a stabilizing electronic or structural effect on the photo-generated ion radical pair. In line with the enhanced stabilization of the charge-separated state, higher quantum yields of charge separation were also found in the triad system. This clearly points to cooperative effects evolving from the two fullerene moieties. Despite the simplicity of studied compounds, the photo-generated charge-separated states possess a significant stability, suggesting their potential to be photosynthetic models.

Experimental

Reagents and Instruments. All chemicals were purchased as reagent grade and used without further purification. All solvents employed for the photophysical studies were purchased from Aldrich and used as received. All reactions were performed using dry glassware under nitrogen atmosphere. Analytical TLC was carried out on Merck 60 F254 silica gel plates, and column chromatography was performed using Merck 60 silica gel (230–400 mesh). Melting points were determined on an Electrothermal IA 9000 series melting point apparatus and are uncorrected. NMR spectra were recorded on a Varian Mercury-400 (400 MHz) spectrometer with the TMS peak as a reference. IR spectra were recorded on a Nicolet 550 FT infrared spectrometer and measured as KBr pellets. UV-vis spectra were recorded on a JASCO V-550 spectrometer. MALDI-TOF-MS spectra were recorded with an Applied Biosystems Voyager-DE-STR. Elemental analyses were performed with a Perkin-Elmer 2400 analyzer.

UV-vis spectral measurements were carried out on a JASCO model V570 DS spectrophotometer. Steady-state fluorescence spectra were measured on a Shimadzu RF-5300 PC spectrofluorophotometer equipped with a photomultiplier tube having high sensitivity in the 700–800 nm region. Molecular orbital calculations were performed by using density functional B3LYP/3-21G method with the Gaussian 98 package.¹⁴ Cyclic voltammetry was performed on a BAS CV-50 W electrochemical analyzer in deaerated DCB solution containing tetrabutylammonium perchlorate as a supporting electrolyte at 298 K. The glassy carbon working electrode was polished with BAS polishing alumina suspension and

rinsed with acetone before use. The counter electrode was a platinum wire. The measured potentials were recorded with respect to an Ag/AgCl (saturated KCl) reference electrode.

Lifetime measurements were performed by using a single-photon counting method with a second harmonic generation (SHG, 400 nm) of a Ti:sapphire laser (Spectra-Physics, Tsunami 3950-L2S, 1.5 ps fwhm) and a streak scope (Hamamatsu Photonics) equipped with a polychromator (Action Research, SpectraPro 150) as an excitation source and a detector, respectively. Lifetimes were evaluated with software attached to the equipment. The nanosecond transient absorption measurements in the near-IR region were measured by means of laser-flash photolysis; 532 nm light from a Nd:YAG laser (Spectra-Physics and Quanta-Ray GCR-130, 6 ns fwhm) was used as an excitation source. For transient absorption spectra in the near-IR region (600–1100 nm), monitoring light from a pulsed Xe-lamp was detected with a Ge-avalanche photodiode module (Hamamatsu Photonics).¹⁹ All of the samples in a quartz cell (1 × 1 cm) were deaerated by nitrogen bubbling through the solution for 20 min.

Synthetic Details. 4-Methoxytriphenylamine (3): To a solution of 4-iodoanisole (4.15 g, 17.7 mmol) in *o*-dichlorobenzene (20 mL) were added copper powder (1.50 g, 23.6 mmol), K₂CO₃ (6.55 g, 54.4 mmol), 18-crown-6 (0.31 g, 1.17 mmol), diphenylamine (2.00 g, 11.8 mmol). After refluxing for 48 h, the reaction mixture was cooled to room temperature and filtered off. The solvent was evaporated from the filtrate, and the residue was washed with ethanol and recrystallized from ethanol to give compound **3** (1.43 g, 86.0%) as a brown solid. Mp 108–109 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.18 (m, 4H), 7.05 (d, *J* = 4.4 Hz, 2H), 7.01 (d, *J* = 4.8 Hz, 4H), 6.92 (m, 2H), 6.82 (d, *J* = 4.4 Hz, 2H), 3.78 (s, 3H); IR (KBr): ν = 1036, 1238, 1506, 1585 cm⁻¹; Anal. Calcd for C₁₉H₁₇NO: C, 82.88; H, 6.22; N, 5.09%. Found: C, 82.87; H, 6.25; N, 5.12%.

4-Methoxy-4',4''-diformyltriphenylamine (4): To a solution of DMF (1.41 mL, 18.2 mmol) in 1,2-dichloroethane (20 mL) was added compound **3** (0.50 g, 1.81 mmol), and carefully poured POCl₃ (1.69 mL, 18.2 mmol). The mixture was refluxed for 6 h, then cooled to room temperature, and poured into saturated aqueous sodium acetate solution (50 mL). The product was extracted with dichloromethane (3 × 50 mL) and the extract was dried over MgSO₄. The solvent was then evaporated. The residue was chromatographed on silica gel with dichloromethane to give compound **4** (0.22 g, 36.7%) in a yellow solid. Mp 92–95 °C; ¹H NMR (400 MHz, CDCl₃): δ 9.86 (s, 2H), 7.72 (d, *J* = 4.8 Hz, 4H), 7.15 (d, *J* = 4.8 Hz, 4H), 7.10 (d, *J* = 4.4 Hz, 2H), 6.92 (d, *J* = 4.4 Hz, 2H), 3.83 (s, 3H); IR (KBr): ν = 1032, 1161, 1246, 1504, 1587, 1693, 2731, 2833 cm⁻¹; Anal. Calcd for C₂₁H₁₇NO₃: C, 76.12; H, 5.17; N, 4.23%. Found: C, 76.09; H, 5.20; N, 4.20%.

N-4-Methoxyphenyl-N,N-bis[4-(1-methyl-3,4,4,5-tetrahydropyrrol-2-yl)phenyl]amine (1): Compound **4** (50 mg, 0.15 mmol) and sarcosine (33 mg, 0.37 mmol) were added to a solution of fullerene (0.22 g, 0.30 mmol) in chlorobenzene (30 mL). The reaction mixture was refluxed for 18 h, and then filtered. The solvent was evaporated from the filtrate and the residue was subjected to chromatography on silica gel with toluene to give compound **1** (27 mg, 10.0%) in a black solid. Mp > 410 °C (dec.); ¹H NMR (400 MHz, CS₂): δ 7.56 (br, 4H), 6.95 (d, *J* = 4.4 Hz, 4H), 6.91 (d, *J* = 4.8 Hz, 2H), 6.74 (d, *J* = 4.4 Hz, 2H), 4.94 (d, *J* = 5.6 Hz, 2H), 4.86 (s, 2H), 4.24 (d, *J* = 5.6 Hz, 2H), 3.77 (s, 3H), 2.84 (s, 6H); ¹³C NMR (CS₂): δ 156.55, 156.37, 154.00, 153.60, 153.52, 147.98, 147.42, 146.90, 146.61, 146.49, 146.43, 146.36, 146.32, 146.25, 146.08, 145.93, 145.77, 145.65, 145.55,

145.44, 145.42, 145.31, 145.29, 144.87, 144.83, 144.54, 143.32, 143.19, 142.86, 142.79, 142.76, 142.41, 142.34, 142.28, 142.25, 142.19, 141.97, 141.84, 141.79, 141.78, 140.40, 140.33, 140.18, 139.98, 139.45, 136.92, 136.78, 136.03, 135.96, 130.48, 127.50, 125.81, 115.17, 83.36, 70.35, 69.16, 55.52, 50.00, 30.89, 30.63. IR (KBr): $\nu = 1032, 1178, 1240, 1504 \text{ cm}^{-1}$; UV-vis (toluene): $\lambda_{\text{max}} = 323, 432, 705 \text{ nm}$; MS (MALDI-TOF); m/z for $\text{C}_{145}\text{H}_{27}\text{N}_3\text{O}$ Calcd 1826.79. Found 1826.71; Anal. Calcd: C, 95.33; H, 1.49; N, 2.30%. Found: C, 95.29; H, 1.50; N, 2.34%.

4-Methoxy-4'-formyltriphenylamine (5): To a solution of DMF (0.60 mL, 7.63 mmol) in 1,2-dichloroethane (20 mL) was added compound **3** (0.70 g, 2.54 mmol), and carefully poured POCl_3 (0.71 mL, 7.63 mmol). The mixture was refluxed for 4 h, then cooled to room temperature, and poured into a saturated aqueous sodium acetate solution (50 mL). The product was extracted with dichloromethane ($3 \times 50 \text{ mL}$), and the extract was dried over MgSO_4 . The solvent was evaporated. The residue was chromatographed on silica gel with dichloromethane/hexane (3:1) to give compound **5** (0.56 g, 73.0%) in a yellow solid. Mp 88–90 °C; ^1H NMR (400 MHz, CDCl_3): δ 9.74 (s, 1H), 7.64 (d, $J = 4.8 \text{ Hz}$, 2H), 7.31 (m, 2H), 7.14 (d, $J = 4.8 \text{ Hz}$, 2H), 7.10 (m, 3H), 6.93 (d, $J = 4.8 \text{ Hz}$, 2H), 6.88 (d, $J = 4.4 \text{ Hz}$, 2H), 3.80 (s, 3H); IR (KBr): $\nu = 1034, 1161, 1244, 1506, 1585, 1689, 2733, 2835 \text{ cm}^{-1}$; Anal. Calcd for $\text{C}_{20}\text{H}_{17}\text{NO}_2$: C, 79.19; H, 5.65; N, 4.62%. Found: C, 79.23; H, 5.64; N, 4.64%.

N-4-Methoxyphenyl-N-[4-(1-methyl-3,4-fullero-2,3,4,5-tetrahydropyrrol-2-yl)phenyl]-N-phenylamine (2): Compound **5** (0.10 g, 0.33 mmol) and sarcosine (88 mg, 1.00 mmol) were added to a solution of fullerene (0.26 g, 0.36 mmol) in toluene (110 mL). The reaction mixture was refluxed for 18 h, and then filtered. The solvent was evaporated from the filtrate, and the residue chromatographed on silica gel with toluene/hexane (2:1) to give compound **2** (0.10 g, 29.0%) in a black solid. Mp > 410 °C (dec.); ^1H NMR (400 MHz, CDCl_3): δ 7.57 (br, 2H), 7.17 (m, 2H), 7.03–6.95 (m, 5H), 6.91 (d, $J = 4.8 \text{ Hz}$, 2H), 6.80 (d, $J = 4.4 \text{ Hz}$, 2H), 4.96 (d, $J = 5.6 \text{ Hz}$, 1H), 4.87 (s, 1H), 4.24 (d, $J = 5.6 \text{ Hz}$, 1H), 3.78 (s, 3H), 2.84 (s, 3H); ^{13}C NMR (CDCl_3): δ 158.68, 156.24, 154.18, 153.86, 153.67, 148.34, 147.95, 147.41, 147.02, 146.57, 146.40, 146.32, 146.05, 145.67, 145.41, 144.76, 144.50, 143.10, 142.80, 142.68, 142.39, 142.27, 142.14, 141.71, 140.59, 140.27, 138.48, 136.82, 135.97, 130.10, 129.27, 127.42, 123.36, 122.49, 122.33, 114.91, 83.39, 55.71, 40.47, 30.11; IR (KBr): $\nu = 1038, 1178, 1242, 1504 \text{ cm}^{-1}$; UV-vis (toluene): $\lambda_{\text{max}} = 311, 430 \text{ nm}$; MS (MALDI-TOF); m/z for $\text{C}_{82}\text{H}_{22}\text{N}_2\text{O}$ Calcd: 1051.09. Found 1051.14; Anal. Calcd: C, 93.70; H, 2.11; N, 2.67%. Found: C, 93.67; H, 2.14; N, 2.71%.

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Supporting Information

Transient absorption spectra of C_{60} -TPA- C_{60} in Ar-saturated DCB. This material is available free of charge on the Web at <http://www.csj.jp/journals/bsj/>.

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