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Photoinduced Intramolecular Electron Transfer of Carbazole Trimer-[60]Fullerene Studied by Laser Flash Photolysis Techniques

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Photoinduced intramolecular events of newly synthesized bis(carbazole trimer)-C₆₀ adducts have been studied by laser flash photolysis techniques in polar and nonpolar solvents. For bis(*tert*-butyl-substituted carbazole trimer)-C₆₀ adduct, charge separation takes place via the excited singlet state of the C₆₀ moiety in polar solvents as revealed by the combination of the C₆₀-fluorescence quenching and transient absorptions of the radical ion pair. On the other hand, for bis(nonsubstituted carbazole trimer)-C₆₀ adduct, although charge separation takes place, the charge recombination is fast because of the lower electron-donor ability.

Introduction

Photoinduced intramolecular electron-transfer processes in donor–acceptor systems are of considerable interest and importance from the aspects of light-energy conversion in relation to the photosynthetic reaction.¹ Fullerenes, which possess a unique three-dimensional π -electron system, have been well known as excellent electron acceptors.² Since the functionalization of fullerenes have been developed, a variety of C₆₀ adducts covalently linked with donor moieties have been synthesized, and their photophysical properties, especially the photoinduced electron transfer, have been clarified.³ The efficient charge separation (CS) and slow charge recombination (CR) were accomplished by using C₆₀ as electron acceptor due to its small reorganization energy.⁴ The efficiencies and rates of the electron-transfer processes in the donor–C₆₀ dyads depend on the energy of CS state for the donor–C₆₀ pair, the distances and orientations between the donor and C₆₀ moieties, and the type of linkages connecting them.⁵ As electron donors, olefins, aromatic amines, porphyrins, phthalocyanines, ruthenium complexes, ferrocenes, tetrathiafulvalenes, and oligothiophenes have been employed for the preparation of fullerene-based dyads and triads.⁶ Among the amine–C₆₀ dyads, various triphenylamine–C₆₀ dyads and *N,N*-dimethylaniline–C₆₀ dyads have been synthesized with changing the linkages, and their photophysical properties have been extensively investigated extensively.⁷

Carbazole, known as a component of photoconductive poly(*N*-vinylcarbazole) (PVCz), is also one of the typical aromatic amines and good electron donors.⁸ While the intermolecular photoinduced electron transfer between carbazole derivatives and fullerenes has been well investigated,⁹ there have been only a few examples of the intramolecular photoinduced electron transfer of carbazole-linked C₆₀ dyads. The *N*-ethylcarbazole–C₆₀ (EtCz–C₆₀) prepared by Prato reaction generated the CS

state with a lifetime of 300 ns in *N,N*-dimethylformamide (DMF).¹⁰ Recently, we have successfully prepared C₆₀ adduct (MCz–C₆₀) bearing a monocarbazole moiety by using Bingel reaction (MCz denotes monocarbazole).¹¹ However, the photoinduced electron transfer via the excited states of C₆₀ was not evidently detected in MCz–C₆₀. One of the reasons for the failure to observe the photoinduced electron transfer is the lack of the electron-donating ability of the carbazole moiety in MCz–C₆₀. Therefore, we were prompted to utilize trimeric carbazole moieties with more electron-donating ability than the single carbazole systems in MCz–C₆₀.¹² The larger π -conjugated system in carbazole trimer enables the delocalization of positive charge in the CS state, leading to the slow CR process. Recently, it has been reported that multiple donor attachments to C₆₀ improve the photoinduced electron-transfer characters.¹³ Thus, in the present study, we have synthesized two novel C₆₀ adducts, TCz–C₆₀ and *t*TCz–C₆₀, bearing dual carbazole trimer moieties attached to the cyclopropane ring symmetrically (TCz and *t*TCz denote carbazole trimer and *t*-butyl-substituted carbazole trimer, respectively). The *t*-butyl groups in *t*TCz–C₆₀ are expected to further enhance the electron-donating ability. Herein, we disclose the photophysical properties of TCz–C₆₀ and *t*TCz–C₆₀, mainly focusing on their CS and CR processes.

Results and Discussion

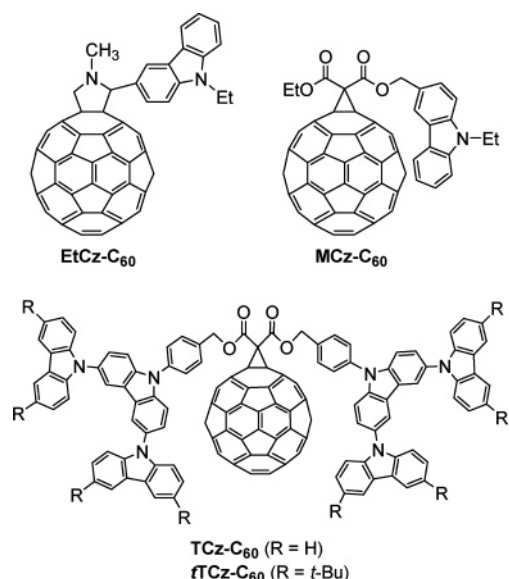
Synthesis of Materials. Scheme 1 depicts the synthetic sequence of bis(carbazole trimer)–C₆₀ adducts, TCz–C₆₀ (**5a**) and *t*TCz–C₆₀ (**5b**). The synthetic procedure was described in detail in Supporting Information. The palladium-catalyzed coupling reactions of carbazole trimers, TCz (**1a**)^{14a} and *t*TCz (**1b**),^{14b} with *p*-bromobenzaldehyde gave aldehydes **2a** and **2b**.¹⁵ The NaBH₄-reduction, followed by the reaction with malonyl dichloride, afforded malonate esters TCzME (**4a**) and *t*TCzME (**4b**). The Bingel reaction of C₆₀ with TCzME and *t*TCzME provided TCz–C₆₀ and *t*TCz–C₆₀ in moderate yields. Both TCz–C₆₀¹³ and *t*TCz–C₆₀ were characterized by ¹H and ¹³C NMR, atmospheric pressure chemical ionization (APCI)-mass, and UV/vis spectroscopies as summarized in Experimental Section.

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Photoinduced Intramolecular Events. Figure 1 shows the steady-state absorption spectra of *t*TCz-C₆₀, *t*TCz, and C₆₀C(COOEt)₂ in CH₂Cl₂. The spectral features of *t*TCz-C₆₀ in the visible range showing absorption bands at 695 and 430 nm are characteristic of the fullerene entity as demonstrated in C₆₀C(COOEt)₂ (bis(ethoxycarbonyl)methano-[60]fullerene). The absorption bands in the UV range (<400 nm) correspond to both fullerene and *t*TCz entities. Appreciable increase of the absorbance of *t*TCz-C₆₀ was observed in the 450–500 nm region compared with the component, suggesting slight interaction between *t*TCz and C₆₀ moieties in their ground states. Similar spectra were obtained in other solvents. TCz-C₆₀ showed almost the same spectra as *t*TCz-C₆₀.

The photoinduced intramolecular events of TCz-C₆₀ and *t*TCz-C₆₀ were investigated, first, by the steady-state fluorescence spectra. Figure 2 depicts the spectra of *t*TCz-C₆₀ in toluene (TN) and DMF. The fluorescence spectrum of *t*TCz-

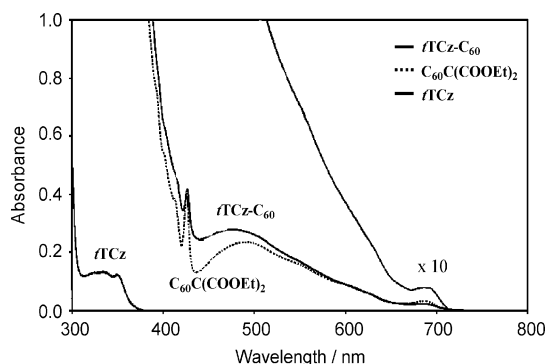


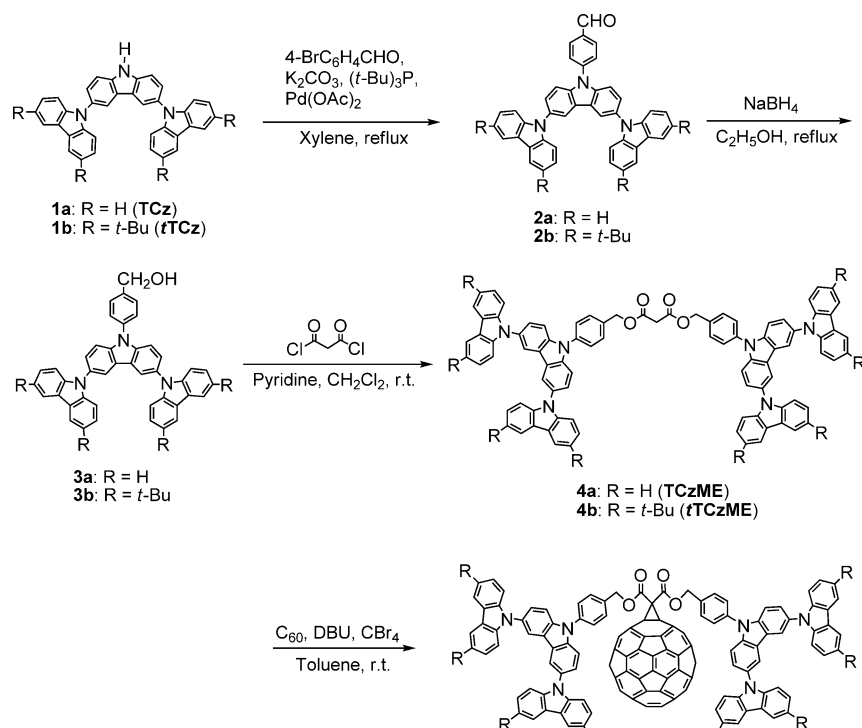
Figure 1. Steady-state absorption spectra of *t*TCz-C₆₀, *t*TCz, and C₆₀C(COOEt)₂ (0.1 mM) in CH₂Cl₂.

C₆₀ observed with visible light excitation in TN is similar to those of typical C₆₀ monoadducts such as C₆₀C(COOEt)₂; the fluorescence of the C₆₀ moiety is hardly quenched by the appended *t*TCz moiety. In polar DMF, however, efficient C₆₀-fluorescence quenching was observed. Such observations suggest efficient quenching of the singlet state of the C₆₀ moiety (¹C₆₀^{*}) by the appended carbazole trimer entities in only polar solvents. Similar results were obtained for TCz-C₆₀; the fluorescence of C₆₀ moiety is almost quenched in DMF. With UV-light excitation, fluorescence spectra were almost the same as those with visible-light excitation, because UV light predominantly excites the C₆₀ moiety with a small fraction of the TCz or *t*TCz moiety; even if the TCz or *t*TCz moiety is excited, the energy transfer to the C₆₀ moiety efficiently takes place.

By using the streakscope as a detector, the fluorescence spectra were observed by applying the 400 nm laser light in the time range 0–2 ns as shown in Supporting Information (Figure S1). Although significant quenching of the ¹C₆₀^{*} moiety was observed in DMF, a fluorescence peak was found near 700 nm.

Fluorescence lifetime measurements of TCz-C₆₀ and *t*TCz-C₆₀ track the above considerations in a more quantitative way, giving kinetic data of the charge-separation processes. As shown

SCHEME 1: Synthetic Routes of Bis(carbazole Trimer)-C₆₀ Adducts, *t*TCz-C₆₀ and TCz-C₆₀



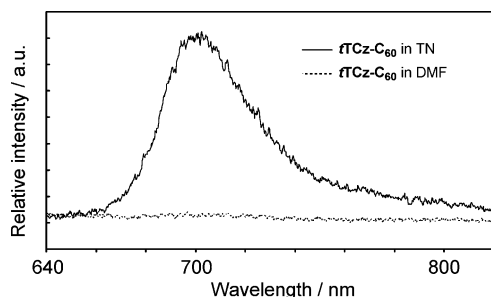


Figure 2. Steady-state fluorescence spectra of *tTCz-C*₆₀ (0.1 mM) in TN and DMF; $\lambda_{\text{ex}} = 430$ nm.

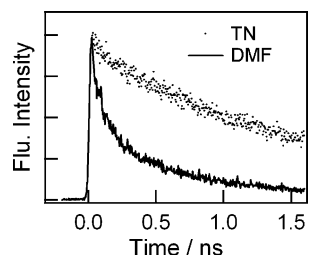


Figure 3. Time profiles of ¹C₆₀* emission at 700 nm of *tTCz-C*₆₀ in TN and DMF; $\lambda_{\text{ex}} = 400$ nm.

TABLE 1: Free-Energy Changes for CS Process ($-\Delta G_{\text{CS}}$), Fluorescence Lifetimes (τ_f), and Rates (k_{CS}) and Quantum Yields (Φ_{CS}) of CS Process of *tTCz-C*₆₀ and *TCz-C*₆₀ via ¹C₆₀* in Toluene and DMF

compound	solvent	$-\Delta G_{\text{CS}}/\text{eV}$	τ_f/ps (fraction%)	$k_{\text{CS}}/\text{s}^{-1}$	Φ_{CS}
<i>tTCz-C</i> ₆₀	DMF	0.30	110 (58%) 720 (42%)	7.80×10^9 6.88×10^8	0.91 0.50
	toluene	-0.22	1400 (100%)		
<i>TCz-C</i> ₆₀	DMF	0.10	190 (75%) 950 (25%)	4.56×10^9 3.52×10^8	0.86 0.33
	toluene	-0.43	1400 (100%)		

in Figure 3, fluorescence time-profile of *tTCz-C*₆₀ in toluene revealed a monoexponential decay of the ¹C₆₀* moiety with a lifetime of 1400 ps (τ_f), which is similar to the lifetime of C₆₀ reference (τ_{f0}). On the other hand, the fluorescence decay in DMF was clearly not monoexponential, which can be attributed to the presence of more conformations of the *tTCz* moiety with respect to the C₆₀ unit. The time profiles of *tTCz-C*₆₀ could be approximately fitted to biexponential decays, where the major short lifetimes were found to be 110 ps in DMF. For *TCz-C*₆₀, the major short lifetime in DMF was found to be 190 ps. These findings support an efficient deactivation of the ¹C₆₀* moiety by the attached carbazole trimer moieties in polar solvents. In general, energy transfer and electron transfer can be thought as an origin of fluorescence deactivation, but the charge separation is predominant in this case, because the energy level of the ¹C₆₀* moiety is lower than that of carbazole trimer unit. Thus, by using the short lifetimes of *tTCz-C*₆₀ and *TCz-C*₆₀ and the lifetime of C₆₀ reference, the rates (k_{CS}) and quantum yields (Φ_{CS}) for the CS processes were evaluated from the following equations:¹⁶

$$k_{\text{CS}} = (1/\tau_f) - (1/\tau_{f0}) \quad (1)$$

$$\Phi_{\text{CS}} = k_{\text{CS}}/(1/\tau_f) \quad (2)$$

The k_{CS} (Φ_{CS}) values of *tTCz-C*₆₀ were evaluated as 7.80×10^9 s⁻¹ (0.91) in DMF. Less efficient CS process was observed for the *TCz-C*₆₀ adduct as listed in Table 1.

The CS process via the ¹C₆₀* was supported from the viewpoint of thermodynamics of electron-transfer processes. The

cyclic voltammogram of the *tTCz-C*₆₀ in benzonitrile (PhCN), which gave sharper peaks than DMF due to higher solubility, recorded the first reduction potential (E_{red}) of the C₆₀ moiety at -950 mV versus Fc/Fc⁺, while the first oxidation potential (E_{ox}) of the *tTCz* was located at 580 mV versus Fc/Fc⁺. The potential difference between the first E_{ox} and E_{red} was found to be 1.53 eV. The E_{ox} of the donor moieties in *TCz-C*₆₀ was located at 780 mV versus Fc/Fc⁺, which is 200 mV higher than that of *tTCz-C*₆₀, reflecting the lower donor ability of the TCz moiety compared with *tTCz* moiety. On the basis of the first E_{ox} of the carbazole trimer moiety, the first E_{red} of the C₆₀ moiety and a solvent correction term (ΔG_{S}), the driving forces for the CR process ($-\Delta G_{\text{CR}}$) and the CS process ($-\Delta G_{\text{CS}}$) via ¹C₆₀* were calculated from the Rehm–Weller equation as follows:¹⁷

$$-\Delta G_{\text{CR}} = e(E_{\text{ox}} - E_{\text{red}}) + \Delta G_{\text{S}} \quad (3)$$

$$-\Delta G_{\text{CS}} = \Delta E_{00} - (-\Delta G_{\text{CR}}) \quad (4)$$

ΔE_{00} is the energy of the 0-0 transition (1.75 eV for ¹C₆₀*), and ΔG_{S} was calculated by the following equation:¹⁷

$$-\Delta G_{\text{S}} = -(e^2/(4\pi\epsilon_0))[(1/(2R_+) + 1/(2R_-) - 1/R_{\text{CC}})/\epsilon_{\text{S}} - (1/(2R_+) + 1/(2R_-))/\epsilon_{\text{R}}] \quad (5)$$

where R_+ and R_- are radii of the radical cation (6.0 Å) and radical anion (4.2 Å), respectively, as evaluated from the molecular orbital (MO) calculations; R_{CC} is the center–center distance between C₆₀ and donor (ca. 12 Å), which were evaluated from the optimized structure in the next paragraph; ϵ_{R} and ϵ_{S} refer to solvent dielectric constants for electrochemistry and photophysical measurements, respectively. The $-\Delta G_{\text{CS}}$ values in DMF were evaluated as 0.30 and 0.10 eV for *tTCz-C*₆₀ and *TCz-C*₆₀, respectively. These values suggest exothermic CS process via the ¹C₆₀* moiety to form the radical ion pairs in polar solvents whereas endothermic in toluene.

Moreover, the CS process from the carbazole trimer unit to the ¹C₆₀* moiety to form the radical ion pair (*TCz*^{•+}–C₆₀^{•-}) was supported by MO calculation studies. On the basis of the density functional method at the B3LYP/3-21G* level after optimizing the structure,¹⁸ the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) of *TCz-C*₆₀ were obtained as shown in Figure 4. In the optimized structure, two carbazole trimers cover the spherical C₆₀ moiety as open wings of a bird, although two carbazole trimers are not completely symmetric. In each carbazole trimer, three carbazoles are not at equal position to C₆₀; that is, one terminal carbazole unit of the carbazole trimer is closer to the C₆₀ moiety, whereas another is far from the C₆₀ moiety. Although the two terminal carbazole units in each carbazole trimer are not coplanar with respect to the central carbazole unit, the HOMO and HOMO-1, which are almost degenerated, spread over the right and left three carbazole units, respectively. Thus, in the one-electron oxidation state of *TCz-C*₆₀ the radical cation delocalized over the three carbazoles. The R_{CC} was evaluated as an averaged distance from the center of C₆₀ to the center of three nitrogen atoms in carbazole trimer to be 11.8 Å. A similar optimized structure was obtained for *tTCz-C*₆₀ with $R_{\text{CC}} = 12.0$ Å (Supporting Information, Figure S2).

The majority of the electron distribution of the LUMO is located on the C₆₀ moiety; therefore, the charge-separated state was presumed as a radical cation localized on the carbazole trimer unit and a radical anion localized on the C₆₀ moiety

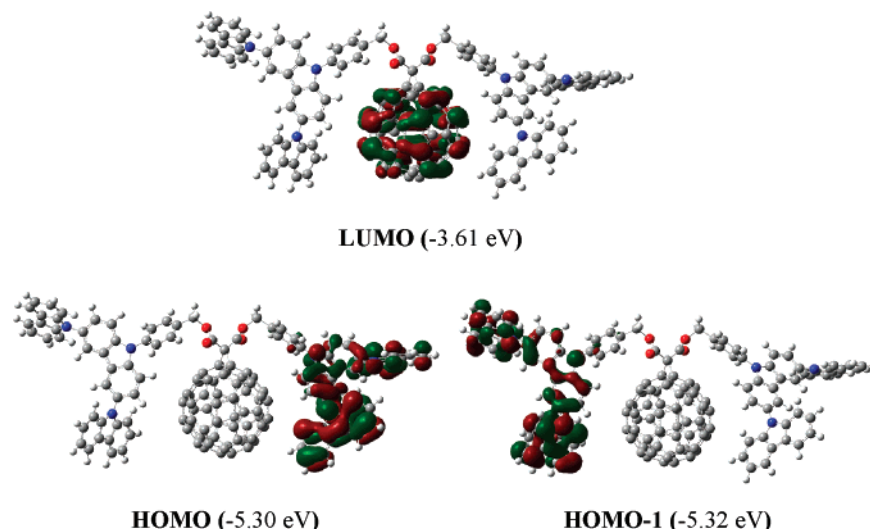


Figure 4. Optimized structure calculated by MO method (C, gray; O, red; N, blue; and H, white) and the HOMO, HOMO-1, and LUMO of TCz-C₆₀ obtained with DFT (B3LYP/3-21G*) method.

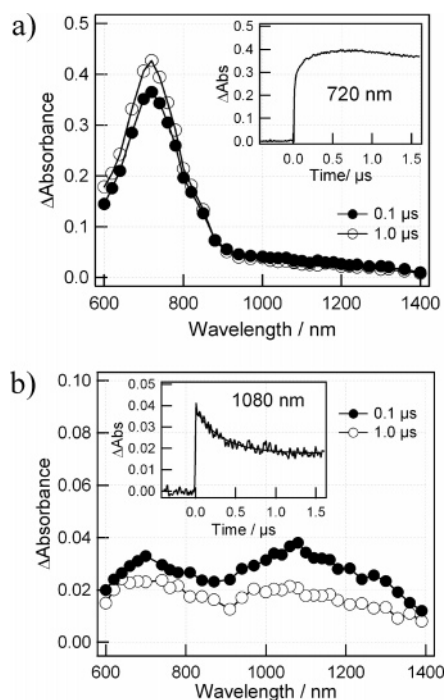


Figure 5. Nanosecond transient spectra obtained by 355 nm laser light of *t*TCz-C₆₀ adduct (0.13 mM); (a) in Ar-saturated toluene and (b) in Ar-saturated DMF. Inset: time profiles.

(TCz^{•+}-C₆₀^{•-}). Similar results were obtained for *t*TCz-C₆₀, predicting *t*TCz^{•+}-C₆₀^{•-} (Supporting Information, Figure S2).

In the case of TCz-C₆₀, the orbital energy of the LUMO was found to be -3.61 eV, while the orbital energies of the HOMO and HOMO-1 were found to be -5.30 and -5.32 eV, respectively. Thus, the average value of the calculated HOMO-LUMO gap is 1.70 eV, which is quite similar to the electrochemically obtained HOMO-LUMO gap (1.73 eV).

The nanosecond transient spectra of *t*TCz-C₆₀ were obtained by 355 nm laser light, which excites mainly the C₆₀ moiety with small fraction of *t*TCz moiety as evaluated from the steady-state absorption spectrum. In toluene (Figure 5a), the absorption spectra exhibited only the absorption peak at 700 nm, which is attributed to the triplet state of C₆₀ (³C₆₀^{*}).^{19,20} In DMF (Figure 5b), a decisive evidence for the CS from the carbazole trimer to the C₆₀ was observed from the transient spectra, which

TABLE 2: Free-Energy Changes for CR ($-\Delta G_{\text{CR}}$), Rates of CR (k_{CR}), and Lifetimes of Radical Ion Pairs (τ_{RIP}) of *t*TCz-C₆₀ and TCz-C₆₀ in Toluene and DMF

compounds	solvent	$-\Delta G_{\text{CR}}/\text{eV}$	$k_{\text{CR}}/\text{s}^{-1}$	$\tau_{\text{RIP}}/\text{ns}$
<i>t</i> TCz-C ₆₀	DMF	1.45	3.3×10^6	300
	toluene	1.97	-	-
TCz-C ₆₀	DMF	1.65	5.0×10^7	20
	toluene	2.17	-	-

exhibited absorption bands of the radical ion pairs in the near-IR region; that is, the peak at 1020 nm is characteristic of the C₆₀^{•-} moiety,²¹ and the broad absorptions with a maximum at 1080 nm are most likely to be assigned to the *t*TCz^{•+} moiety. This assignment was confirmed by the observed absorption spectra by mixing *t*TCz-C₆₀ with FeCl₃, which exhibited new peak around 1100 nm and weak broad band appeared in the 1200–1400 nm region as a result of one-electron oxidation of the *t*TCz moiety, giving *t*TCz^{•+} (Supporting Information, Figure S3). The time profiles of *t*TCz^{•+} and C₆₀^{•-} were curve-fitted by a single-exponential and gave similar decay rate constant from which the rate constant of the CR process (k_{CR}) of *t*TCz^{•+}-C₆₀^{•-} in DMF was evaluated as $3.3 \times 10^6 \text{ s}^{-1}$. From the value of k_{CR} , the lifetime of the radical ion pairs *t*TCz^{•+}-C₆₀^{•-} (τ_{RIP}) was evaluated as 300 ns (Table 2).

For TCz-C₆₀, the transient spectra in DMF exhibited the absorption peaks of the ³C₆₀^{*}, C₆₀^{•-}, and TCz^{•+} moieties with 355 nm laser excitation as shown in Figure 6. The absorption intensity of the ³C₆₀^{*} moiety of TCz-C₆₀ was remarkably higher than that of *t*TCz-C₆₀, which reflects the lower electron-donor ability of TCz compared with that of *t*TCz. From the initial decay at 1080 nm, the k_{CR} value in DMF was evaluated as $5.0 \times 10^7 \text{ s}^{-1}$, which gave the τ_{RIP} of TCz^{•+}-C₆₀^{•-} to be 20 ns.

The solvent effects can be interpreted by the relative energy level of the RIP with respect to ³C₆₀^{*}. As shown in the energy diagram in Figure 7, in highly polar solvents such as DMF the energy level of *t*TCz^{•+}-C₆₀^{•-} (1.45 eV) is lower than that of ³C₆₀^{*} (1.50 eV); therefore, the CR process takes place going to the ground state, which belongs to the inverted region of the Marcus parabola,²² because of the small reorganization energy of the fullerene derivatives, usually ca. 0.6 eV.⁴

Appreciable different behavior between *t*TCz^{•+}-C₆₀^{•-} and TCz^{•+}-C₆₀^{•-} can be explained by the same concept (Figure 7) because of 200 mV difference in the first E_{ox} . In the case of

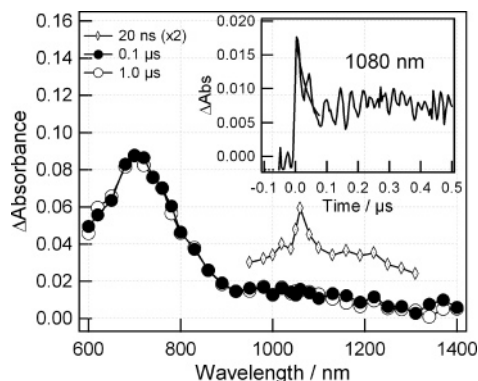


Figure 6. Nanosecond transient spectra obtained by 355 nm laser light of TCz-C_{60} (0.13 mM) in Ar-saturated DMF. Inset: time profile.

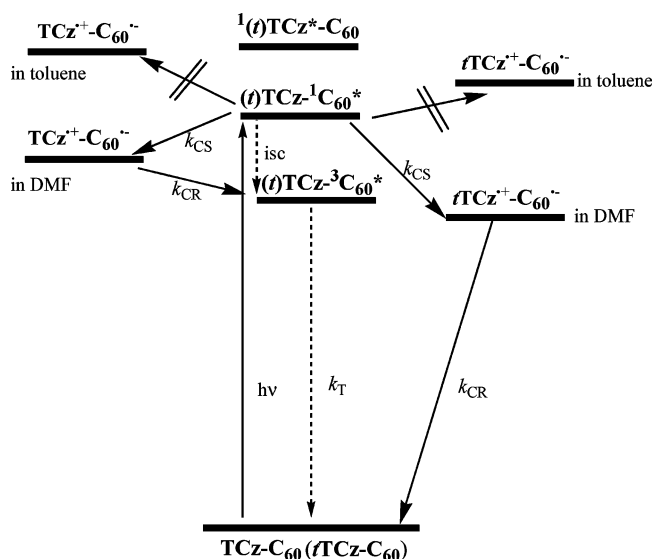


Figure 7. Energy diagram for photoinduced processes of $t\text{TCz-C}_{60}$ and TCz-C_{60} .

$\text{TCz}^{+\bullet}-\text{C}_{60}^{\bullet-}$, because the energy level of $\text{TCz}^{+\bullet}-\text{C}_{60}^{\bullet-}$ (1.65 eV in DMF) is higher than that of the $^3\text{C}_{60}^{\bullet*}$ moiety, the CR process going to the $^3\text{C}_{60}^{\bullet*}$ moiety quickly takes place in the normal region of the Marcus parabola.²²

Conclusions

Photoinduced intramolecular charge-separation process of newly synthesized bis(carbazole trimer)- C_{60} adducts has been studied by laser flash photolysis techniques in polar and nonpolar solvents. As summarized in energy diagrams illustrated in Figure 7, for bis(*tert*-butyl-substituted carbazole trimer)- C_{60} , charge separation takes place via the excited singlet state of the C_{60} -moiety in highly polar solvents such as DMF as revealed by the combination of the C_{60} -fluorescence quenching and transient absorptions of the radical ion pair. On the other hand, for bis-(nonsubstituted carbazole trimer)- C_{60} , although charge separation takes place in DMF, the charge recombination is fast because of the lower electron-donor ability of the nonsubstituted carbazole trimer. In addition to the substituents on the carbazole trimer, the solvent polarity also drastically controlled the charge-separation process and charge-recombination process.

Experimental Section

Materials. *Synthesis of TCz-C_{60} .*¹⁴ 1,8-Diazabicyclo[5.4.0]-undec-7-ene (DBU) (93 mg, 0.61 mmol) was added to a mixture

of C_{60} (147 mg, 0.20 mmol), TCzME (260 mg, 0.20 mmol), and CBr_4 (135 mg, 0.41 mmol) in toluene (200 mL) at room temperature, and the mixture was stirred for 7 h under a nitrogen atmosphere. The crude material was filtered through a short column (silica gel), eluting first with hexane to remove unreacted C_{60} and then with toluene/hexane (1:1), to give monoadduct **5a**. This fraction was further purified by GPC (solvent; CHCl_3) to give **5a** (65 mg, 15.9%). ^1H NMR (CDCl_3 , 500 MHz): δ 8.24 (s, 4H), 8.13 (d, J = 8.0 Hz, 8H), 7.85 (d, J = 8.5 Hz, 4H), 7.77 (d, J = 8.0 Hz, 4H), 7.61 (d, J = 9.0 Hz, 4H), 7.54 (dd, J = 8.8 Hz, 4H), 7.37–7.34 (m, 16H), 7.28–7.24 (m, 8H), 5.71 (s, 4H). ^{13}C NMR (CDCl_3 , 125 MHz): δ 163.5, 145.2, 145.1, 144.9, 144.8, 144.7, 144.6, 144.5, 144.4, 143.7, 143.0, 142.9, 142.8, 142.0, 141.6, 141.5, 140.9, 140.2, 138.9, 137.8, 134.4, 131.1, 130.6, 128.3, 127.2, 126.2, 125.9, 124.1, 123.1, 120.3, 119.7, 111.2, 109.6, 71.2, 68.3, 51.5. APCI-MS: m/z 1992 (M^+).

Synthesis of $t\text{TCz-C}_{60}$. DBU (113 mg, 0.74 mmol) was added to a mixture of C_{60} (178 mg, 0.25 mmol), $t\text{TCzME}$ (426 mg, 0.25 mmol), and CBr_4 (164 mg, 0.49 mmol) in hexane (300 mL) at room temperature, and the mixture was stirred for 8 h under a nitrogen atmosphere. The crude material was filtered through a short column (silica gel), eluting first with toluene to remove unreacted C_{60} and then with toluene/hexane (1:1), to give monoadduct **5b**. This fraction was further purified by GPC (solvent; CHCl_3) to give **5b** (131 mg, 21.8%). ^1H NMR (CDCl_3 , 500 MHz): δ 8.23 (s, 4H), 8.15 (s, 8H), 7.87 (d, J = 8.5 Hz, 4H), 7.79 (d, J = 8.0 Hz, 4H), 7.61 (d, J = 9.0 Hz, 4H), 7.56 (dd, J = 9.0 Hz, 4H), 7.43 (dd, J = 8.5 Hz, 8H), 7.31 (d, J = 8.5 Hz, 8H), 5.74 (s, 4H), 1.45 (s, 72H). ^{13}C NMR (CDCl_3 , 125 MHz): δ 163.5, 145.2, 145.0, 144.9, 144.7, 144.6, 144.5, 144.3, 143.7, 143.0, 142.9, 142.8, 142.6, 142.0, 141.6, 140.9, 140.0, 139.9, 138.9, 137.9, 134.3, 131.0, 127.2, 125.9, 124.1, 123.6, 123.1, 119.3, 116.2, 111.0, 109.1, 71.2, 68.3, 51.5, 34.7, 32.0.

Instruments. Electrochemical redox potential values were measured by the cyclic voltammetry (CV) technique by applying a Hokuto HAB-151 potentiostat/galvanostat with a function generator. A platinum disk electrode was used as the working electrode with a platinum wire and an Ag/Ag^+ electrode serving as the counter and reference electrodes, respectively. All measurements were carried out in PhCN solvent containing (*n*-Bu) $_4\text{N}^+\text{PF}_6^-$ (0.1 M) as a supporting electrolyte in a scan rate of 0.2 V s^{-1} .

Steady-state absorption spectra were measured with JASCO UV/vis/near-IR spectrophotometer and a HITACHI U-3210 spectrophotometer. Steady-state fluorescence spectra were collected on a Shimadzu RF-5300 PC spectrofluorophotometer equipped with a photomultiplier tube having high sensitivity in the 700–800 nm region and a HITACHI F-4500 spectrophotometer. Fluorescence lifetimes were measured by a single-photon counting method using a second harmonic generation (SHG, 400 nm) of a Ti:sapphire laser (Spectra-Physics, Tsunami 3950-L2S, 1.5 ps fwhm) and a streakscope (Hamamatsu Photonics) equipped with a polychromator as an excitation source and a detector, respectively.²³ Nanosecond transient absorption measurements in the near-IR region were carried out by laser flash photolysis using an excitation light source of Nd:YAG laser (Spectra-Physics and Quanta-Ray GCR-130, 6 ns fwhm). Monitoring lights from a pulsed Xe-lamp were detected via Ge-avalanche photodiode module.²⁴ Prior to the measurement, the sample solution in a quartz cell (1.0×1.0 cm) was deaerated by bubbling argon gas for a period of 20 min.

Supporting Information Available: Synthetic details, fluorescence spectra measured by streak-scope, MO calculation data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) (a) Connolly, J. S.; Bolton, J. R. In *Photoinduced Electron Transfer*; Fox, M. A.; Chanon, M., Eds.; Elsevier: Amsterdam, 1988. (b) Mataga, N.; Miyasaka, H. In *Electron Transfer*; Jortner, J.; Bixon, M., Eds.; John Wiley & Sons: New York, 1999; Part 2, pp 431–496. (c) Balzani, V., Ed. *Electron Transfer in Chemistry*; Wiley-VCH: Weinheim, 2001; Vols. I–V.
- (2) (a) Guldi, D. M.; Kamat, P. V. In *Fullerenes, Chemistry, Physics and Technology*; Kadish, K. M.; Ruoff, R. S., Eds.; Wiley-Interscience: New York, 2000; pp. 225. (b) Fujitsuka, M.; Ito, O. *Photochemistry of Fullerenes*. In *Handbook of Photochemistry and Photobiology*; H. S. Nalwa, Ed.; American Scientific Publisher: New York, 2003; Vol. 2, Chapter 2, pp 111–145.
- (3) (a) Imahori, H.; Sakata, Y. *Adv. Mater.* **1997**, *9*, 537. (b) Guldi, D. M.; Prato, M. *Acc. Chem. Res.* **2000**, *33*, 695. (c) Otsubo, T.; Aso, Y.; Takimiya, K. *J. Mater. Chem.* **2002**, *12*, 2565. (d) Segura, J. L.; Martin, N.; Guldi, D. M. *Chem. Soc. Rev.* **2005**, *34*, 31. (e) Martin, N. *Chem. Commun.* **2006**, 2093–2104.
- (4) (a) Imahori, H.; Hagiwara, K.; Akiyama, T.; Akoi, M.; Taniguchi, S.; Okada, T.; Shirakawa, M.; Sakata, Y. *Chem. Phys. Lett.* **1996**, *263*, 545. (b) Tkachenko, N. V.; Rantala, L.; Tauber, A. Y.; Helaja, J.; Hynninen, P. H.; Lemmetyinen, H. *J. Am. Chem. Soc.* **1999**, *121*, 9378. (c) Fukuzumi, S.; Guldi, D. M. In *Electron Transfer in Chemistry*; Balzani, V., Ed.; Wiley-VCH: Weinheim, 2001; Vol. 2, pp 270–337.
- (5) (a) Verhoeven, J. W.; van Ramesdonk, H. J.; Groeneveld, M. M.; Benniston, A. C.; Harriman, A. *ChemPhysChem* **2005**, *6*, 2251. (b) Verhoeven, J. W. *J. Photochem. Photobiol. C* **2006**, *7*, 40.
- (6) Maggini, M.; Guldi, D. M. In *Molecular and Supramolecular Photochemistry*; Ramamurthy, V.; Schanze, K. S., Eds.; Marcel Dekker Inc.: New York, 2001; Vol. 7, pp 149–196.
- (7) (a) Williams, R. M.; Zwier, J. M.; Verhoeven, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 4093. (b) Williams, R. M.; Koeberg, M.; Lawson, J. M.; An, Y.-Z.; Rubin, Y.; Paddon-Row, M. N.; Verhoeven, J. W. *J. Org. Chem.* **1996**, *61*, 5055. (c) Thomas, K. G.; Biju, V.; George, M. V.; Guldi, D. M.; Kamat, P. V. *J. Phys. Chem. A* **1998**, *102*, 5341. (d) Thomas, K. G.; Biju, V.; Guldi, D. M.; Kamat, P. V.; George, M. V. *J. Phys. Chem. A* **1999**, *103*, 10755. (e) Komamine, S.; Fujitsuka, M.; Ito, O.; Moriwaki, K.; Miyata, T.; Ohno, T. *J. Phys. Chem. A* **2000**, *104*, 11497.
- (8) (a) Wang, Y. *Nature* **1992**, *356*, 585. (b) Wang, Y.; Suna, A. *J. Phys. Chem. B* **1997**, *101*, 5627.
- (9) (a) Watanabe, A.; Ito, O. *J. Chem. Soc., Chem. Commun.* **1994**, 1285. (b) Sauvé, G.; Dimitrijević, N. M.; Kamat, P. V. *J. Phys. Chem.* **1995**, *99*, 1199. (c) Itaya, A.; Suzuki, I.; Tsuboi, Y.; Miyasaka, H. *J. Phys. Chem. B* **1997**, *101*, 5118. (d) Yahata, Y.; Sasaki, Y.; Fujitsuka, M.; Ito, O. *J. Photosci.* **1999**, *6*, 117. (e) Fujitsuka, M.; Yahata, Y.; Watanabe, A.; Ito, O. *Polymer* **2000**, *41*, 2807. (f) T. Midorikawa, T.; Araki, Y.; Fujitsuka, M.; Ito, O. *J. Nanosci. Nanotechnol.* **2007**, *7*, 1419.
- (10) Zeng, H.-P.; Wang, T.; Sandanayaka, A. S. D.; Araki, Y.; Ito, O. *J. Phys. Chem. A* **2005**, *109*, 4713.
- (11) Nakamura, Y.; Suzuki, M.; Imai, Y.; Nishimura, J. *Org. Lett.* **2004**, *6*, 2797.
- (12) Nakamura, Y.; Konno, T.; Watanabe, S.; Suzuki, M.; Yoshihara, T.; Tobita, S.; Nishimura, J. *Chem. Lett.* **2007**, *36*, 264.
- (13) (a) Sandanayaka, A. S. D.; Ikeshita, K.; Rajkumar, G. A.; Furusho, Y.; Araki, Y.; Takata, T.; Ito, O. *J. Phys. Chem. A* **2005**, *109*, 8088. (b) El-Khouly, M. E.; Hasegawa, J.; Momotake, A.; Sasaki, M.; Araki, Y.; Ito, O.; Arai, T. *J. Porphyrins Phthalocyanines* **2006**, *10*, 1380.
- (14) (a) Kimoto, A.; Cho, J.-S.; Higuchi, M.; Yamamoto, K. *Macromolecules* **2004**, *37*, 5531. (b) McClenaghan, N. D.; Passalacqua, R.; Loiseau, F.; Campagna, S.; Verheyde, B.; Hameurlaine, A.; Dehaen, W. *J. Am. Chem. Soc.* **2003**, *125*, 5356.
- (15) Loiseau, F.; Campagna, S.; Hameurlaine, A.; Dehaen, W. *J. Am. Chem. Soc.* **2005**, *127*, 11352.
- (16) (a) *Principles of Fluorescence Spectroscopy*, 2nd edition; Lakowicz, J. R., Ed.; Kluwer Academic: New York, 1999. (b) D' Souza, F.; Deviprasad, G. R.; El-Khouly, M. E.; Fujitsuka, M.; Ito, O. *J. Am. Chem. Soc.* **2001**, *123*, 5277.
- (17) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.
- (18) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision B-04; Gaussian, Inc.: Pittsburgh, PA, 2003.
- (19) (a) Ito, O.; Sasaki, Y.; Yoshikawa, Y.; Watanabe, A. *J. Phys. Chem.* **1995**, *99*, 9838. (b) Ito, O. *Res. Chem. Intermed.* **1997**, *23*, 389.
- (20) (a) Arbogast, J. W.; Foote, C. S.; Kao, M. *J. Am. Chem. Soc.* **1992**, *114*, 2277. (b) Steren, C. A.; von Willigen, H.; Biczók, L.; Gupta, N.; Linschitz, H. *J. Phys. Chem.* **1996**, *100*, 8920.
- (21) *Electronic Absorption Spectra of Radical Ions*; Shida, T., Ed.; Elsevier Science Publishing Company: Amsterdam, The Netherlands, 1988; p 212.
- (22) (a) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265. (b) Marcus, R. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1111.
- (23) (a) Sandanayaka, A. S. D.; Matsukawa, K.; Ishi-i, T.; Mataka, S.; Araki, Y.; Ito, O. *J. Phys. Chem. B* **2004**, *108*, 19995. (b) Sandanayaka, A. S. D.; Sasabe, H.; Araki, Y.; Furusho, Y.; Ito, O.; Takata, T. *J. Phys. Chem. A* **2004**, *108*, 5145.
- (24) (a) Fujitsuka, M.; Ito, O.; Yamashiro, T.; Aso, Y.; Otsubo, T. *J. Phys. Chem. A* **2000**, *104*, 4876. (b) Yamazaki, M.; Araki, Y.; Fujitsuka, M.; Ito, O. *J. Phys. Chem. A* **2001**, *105*, 8615. (c) Nakamura, T.; Kanato, H.; Araki, Y.; Ito, O.; Takimiya, K.; Otsubo, T.; Aso, Y. *J. Phys. Chem. A* **2006**, *110*, 3471.