Photoinduced Electron Transfer Competitive with Energy Transfer of the Excited Triplet State of [60]Fullerene to Ferrocene Derivatives Revealed by Combination of Transient Absorption and Thermal Lens Measurements

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Received: December 9, 2004; In Final Form: February 12, 2005

The quenching processes of the exited triplet state of fullerene ($^3C_{60}^*$) by ferrocene (Fc) derivatives have been observed by the transient absorption spectroscopy and thermal lens methods. Although $^3C_{60}^*$ was efficiently quenched by Fc in the rate close to the diffusion controlled limit, the quantum yields (Φ_{et}) for the generation of the radical anion of C_{60} ($C_{60}^{\bullet -}$) via $^3C_{60}^*$ were quite low even in polar solvents; nevertheless, the free-energy changes (ΔG_{et}) of electron transfer from Fc to $^3C_{60}^*$ are sufficiently negative. In benzonitrile (BN), the Φ_{et} value for unsubstitued Fc was less than 0.1. The thermal lens method indicates that energy transfer from $^3C_{60}^*$ to Fc takes place efficiently, suggesting that the excited triplet energy level of Fc was lower than that of $^3C_{60}^*$. Therefore, energy transfer from $^3C_{60}^*$ to ferrocene decreases the electron-transfer process from ferrocene to $^3C_{60}^*$. To increase the participation of electron transfer, introduction of electron-donor substituents to Fc ($\Phi_{et} = 0.46$ for decamethylferrocene in BN) and an increase in solvent polarity ($\Phi_{et} = 0.58$ in BN:DMF (1:2) for decamethylferrocene) were effective.

Introduction

Photoexcited fullerenes act as good electron acceptors in the presence of electron donors such as amines and tetrathiafluvalenes;[1−3] in the mixture systems, electron transfer takes place via the excited triplet states of C_{60} ($^3C_{60}^*$) and C_{70} ($^3C_{70}^*$) under the appropriate concentrations of donors.[4−7] High quantum yields for electron transfer via $^3C_{60}^*$ and $^3C_{70}^*$ have been reported in polar solvents such as benzonitrile (BN).[8,9] For donors with relatively low triplet energy levels such as retinol,[10] carotenol,[11] porphyrins,[12] phthalocyanine,[13] and oligothiophenes,[14] electron transfer takes place competitively with energy transfer via $^3C_{60}^*$ and $^3C_{70}^*$. In highly concentrated donor solutions, electron transfer takes place via the excited singlet states of C_{60} ($^1C_{60}^*$) and C_{70} ($^1C_{70}^*$); in such cases, electron transfer takes place competitively with intersystem crossing process.[15−18]

In the dyad systems of C_{60} with covalently connected electron donors, the charge separation efficiently takes place via the $^1C_{60}^*$ moieties.[1−3] As electron donors, amines,[19] carotenyls,[20] porphyrinds,[21] tetrathiafulvalenes,[22] oligothiophenes,[23] retinyl,[24] and azulene[25] have been studied. Among them, ferrocene (Fc) derivatives have been frequently employed as various C_{60}−Fc dyads, because of the very low oxidation potential, expecting high electron-donor ability.[26−28] Recently, Fc derivatives were also used as a hole-shifting reagent in the triad of ferrocene−porphyrin−C_{60}, resulting in long-lived charge-separated state between the cation of Fc and the radical anion of C_{60} after the photoexcitation of the porphyrin.[29] To increase the utilization of Fc derivatives as good electron donors in the mixture systems, dyads systems, and triad systems, it is important to reveal the photochemical properties of Fc with respect to C_{60}. In the present work, we investigated the photoinduced electron transfer and excited energy transfer between $^3C_{60}^*$ and Fc derivatives by observing the transient absorption spectra and the thermal lens (TL) method.[30−32] Structures of the Fc derivatives employed in this study are shown in Figure 1 with C_{60}.

Experimental Section

Materials. C_{60} (>99.9%) was purchased from Texas Fullerene Corp. Fc, [(Dimethylamino)methyl]ferrocene (Me$_2$NCH$_2$Fc), (*p*-aminophenyl)ferrocene (H$_2$NPhFc), aminoferrocene (H$_2$NFc), and decamethylferrocene (Me$_{10}$Fc) were used as ferrocene derivatives (Figure 1). Fc and Me$_{10}$Fc were purchased from Aldrich, Me$_2$CH$_2$Fc and Me$_2$NCH$_2$Fc were from Tokyo Kasei, and NH$_2$PhFc was kindly presented by Imahori and Fukuzumi.[29] Solvents used in the present study were all the best grade of the commercially available reagents.

Measurements. Square wave volumetric measurements were carried out with a potentiostat (BAS CV50W) and a cell equipped with platinum working electrode, an Ag/Ag$^+$ reference electrode and a platinum counter electrode. All electrochemical measurements were performed in BN or BN:DMF mixed solution containing 0.10 M of *tetra-n*-butylammonium hexafluorophosphate (Nacalai Tesque) at room temperature. The redox potentials were corrected against the ferrocene/ferrocenium (Fc/Fc$^+$) couple.

The nanosecond transient absorption spectra were measured by using 532 nm laser light (SHG) of a Nd:YAG laser (Spectra-Physics, Quanta-Ray GCR-130, fwhm 6 ns) as an excitation source. A pulsed xenon flash lamp was used as a probe light. A Ge-APD module (Hamamatsu Photonics, B2834) attached to a monochromator (Ritsu MC-10N) was employed as a detector of transient absorption spectra in the visible and near-IR regions (600−1200 nm).[7,9−14]

The thermal lens (TL) method described in the literature was employed, in which 532 nm (SHG) laser light of a Nd:YAG

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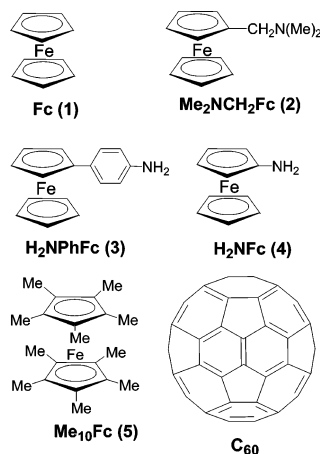
Figure 1. Ferrocene derivatives and C_{60}.

laser (Continnm Surlite II-10, fwhm 6 ns) was used as an excitation source. In the case of the energy transfer system from the lowest triplet state of C_{60} to β-carotene, 600 nm laser light from an OPO laser light (Continuum Surelite OPO, fwhm 6 ns) was used for the selective excitation of C_{60}. The excitation beam was focused inside a sample cell by a lens ($f = 20$ cm). Fundamental laser light at 1064 nm of LD-pumped continuous Nd:YAG laser (Spectra-Physics, TDS-10-v-106C) used as a probe beam, which was parallel to the excitation beam, was focused by another lens ($f = 20$ cm).[30−32] The probe beam through a pinhole was monitored by InGaAS−PIN detector (Hamamatsu Photonics, C5125−10).

All the measurements were carried out in 1 cm optical cell after bubbling with Ar-gas for 15 min at ambient temperature.

Results and Discussion

Electrochemical Properties and Free-Energy Changes. The redox potentials of Fc derivatives were measured by square wave voltammetry in BN and BN:DMF mixed solvents systems. The order of oxidation potentials (E_{ox}) is Fc $\approx$ Me$_2$NCH$_2$Fc $<$ H$_2$-NPhFc $<$ H$_2$NFc $<$ Me$_{10}$Fc in BN:DMF mixed solvents, whereas the E_{ox} of Me$_2$NCH$_2$Fc became postive compared with that of Fc in BN, probably due to considerable solvent effect. In general, the E_{ox} values of the Fc derivatives tend to shift negative with the introduction of electron-donating substituents.

From the E_{ox} values of the Fc derivatives, the electron-donor abilities increase in the order of Me$_{10}$Fc $>$ H$_2$NFc $>$ H$_2$NPhFc $>$ Me$_2$NCH$_2$Fc $\approx$ Fc in BN-DMF mixed solvents. From these E_{ox} values, the free-energy changes for the electron-transfer process (ΔG_{et}) were calculated using Weller's equation (1):[33]

$$-\Delta G_{et} = \Delta E_{0-0} - E_{ox} + E_{red} \qquad (1)$$

where E_{red} and ΔE_{0-0} refer to the energy of the reduction potential and lowest excited triplet state of C_{60} ($^3C_{60}^*$), respectively. These ΔG_{et} values for Fc and $^3C_{60}^*$ systems are all sufficiently negative to generate the radical ions in BN and BN:DMF mixtures as listed in Table 1.

Transient Absorption Spectra. Figure 2 shows the transient absorption spectra in the visible and near-IR regions obtained by nanosecond laser flash photolysis of C_{60} (0.1 mM) with 532 nm laser light in the presence of Fc (1 mM) in Ar-saturated BN. The transient absorption band at 750 nm is attributed to the triplet−triplet absorption of $^3C_{60}^*$.[4,5,15a] Rapid decay of $^3C_{60}^*$ was observed, whereas the only weak absorption of $C_{60}^{\bullet-}$ was observed at 1080 nm.[34] From the time profile for the decay of $^3C_{60}^*$, the second-order quenching rate-constant (k_q) of $^3C_{60}^*$

TABLE 1: Rate Constant (k_q) for Quenching of $^3C_{60}^*$ and Quantum Yield (Φ_{et}), Rate Constant (k_{et}) and Free-Energy Changes (ΔG_{et}) for Electron Transfer via $^3C_{60}^*$

system	k_q/M^{-1} s^{-1}	Φ_{et}	k_{et}/M^{-1} s^{-1}	ΔG_{et}/eV
C_{60}/Fc/BN	4.6×10^9	0.06	2.8×10^8	−0.70
C_{60}/Fc/BN:DMF(2:1)	5.3×10^9	0.09	4.8×10^8	−0.73
C_{60}/Fc/BN:DMF(1:1)	5.5×10^9	0.11	6.1×10^8	−0.77
C_{60}/Fc/BN:DMF(1:2)	5.9×10^9	0.13	7.7×10^8	−0.78
C_{60}/Me$_2$NCH$_2$Fc/BN	4.6×10^9	0.09	4.1×10^8	−0.52
C_{60}/Me$_2$NCH$_2$Fc/BN:DMF(2:1)	5.3×10^9	0.10	5.3×10^8	−0.74
C_{60}/Me$_2$NCH$_2$Fc/BN:DMF(1:1)	4.9×10^9	0.16	7.8×10^8	−0.78
C_{60}/Me$_2$NCH$_2$Fc/BN:DMF(1:2)	4.6×10^9	0.17	7.8×10^8	−0.80
C_{60}/H$_2$NPhFc/BN	5.3×10^9	0.12	6.4×10^8	−0.79
C_{60}/H$_2$NPhFc/BN:DMF(2:1)	4.8×10^9	0.30	1.4×10^9	−0.83
C_{60}/H$_2$NPhFc/BN:DMF(1:1)	4.4×10^9	0.34	1.5×10^9	−0.86
C_{60}/H$_2$NFc/BN	4.5×10^9	0.32	1.4×10^9	−1.08
C_{60}/H$_2$NFc/BN:DMF(2:1)	5.9×10^9	0.43	2.5×10^9	−1.14
C_{60}/H$_2$NFc/BN:DMF(1:1)	6.6×10^9	0.48	3.2×10^9	−1.17
C_{60}/H$_2$NFc/BN:DMF(1:2)	5.5×10^9	0.51	2.8×10^9	−1.20
C_{60}/Me$_{10}$Fc/BN	5.5×10^9	0.46	2.5×10^9	−1.23
C_{60}/Me$_{10}$Fc BN:DMF(2:1)	6.2×10^9	0.47	2.9×10^9	−1.25
C_{60}/Me$_{10}$Fc/BN:DMF(1:1)	5.9×10^9	0.55	3.2×10^9	−1.27
C_{60}/Me$_{10}$Fc/BN:DMF(1:2)	6.3×10^9	0.58	3.7×10^9	−1.28
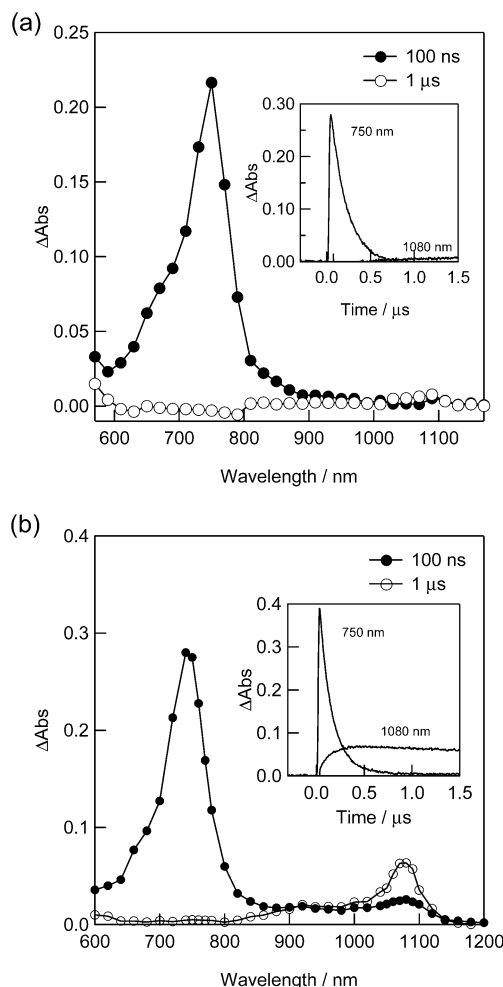
Figure 2. Transient absorption spectra of (a) C_{60} (0.1 mM) and Fc (1.0 mM) and (b) C_{60} (0.1 mM) and Me$_{10}$Fc (1.0 mM) observed by selective excitation of C_{60} with 532 nm laser light in Ar-saturated BN. Inset: time profiles of 750 and 1080 nm.

by Fc was evaluated to be 4.6×10^9 M^{-1} s^{-1} from the pseudo-first-order relation. This value is close to a diffusion controlled limit in BN ($k_{diff} = 5.2 \times 10^9$ M^{-1} s^{-1}).[35] The k_q values for Fc were increased slightly with the fraction of DMF in BN. For other Fc derivatives, the k_q values are listed in Table 1.

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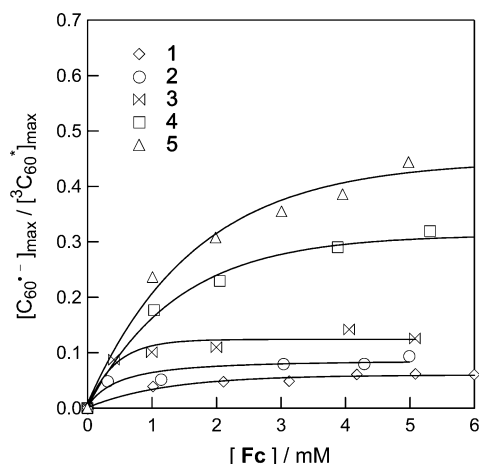
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Figure 3. Plots of $[C_{60}{}^{\bullet-}]_{max}/[{}^3C_{60}{}^*]_{max}$ vs concentration of Fc derivatives [Fc] in Ar-saturated BN. Compound numbers refer to Figure 1.

In transient absorption spectra of C_{60} in the presence of Me_{10}-Fc (Figure 2b), the prominent rise of the absorption band of $C_{60}{}^{\bullet-}$ was observed at 1080 nm with the decay of ${}^3C_{60}{}^*$, indicating that appreciable electron transfer takes place. From the decay of ${}^3C_{60}{}^*$ and rise of $C_{60}{}^{\bullet-}$, the k_q value of ${}^3C_{60}{}^*$ by $Me_{10}Fc$ was evaluated to be 5.5×10^9 M^{-1} s^{-1} in BN, which is 20% larger than that of Fc in BN. The k_q value for $Me_{10}Fc$ increased by ca. 20% with an increase of the fraction of DMF in the BN:DMF mixed solution. These small changes in the k_q values are reasonable, because these rates are quite close to a diffusion-controlled limit.

The ratios of $[C_{60}{}^{\bullet-}]_{max}/[{}^3C_{60}{}^*]_{max}$ can be evaluated from the observed transient absorption intensities by employing the reported extinction coefficients of $C_{60}{}^{\bullet-}$ and ${}^3C_{60}{}^*$.[8,34] As shown in Figure 3, the ratios increase with the concentrations of Fc reaching to a maximal value, which can be attributed to the quantum yield (Φ_{et}) of electron transfer from Fc via ${}^3C_{60}{}^*$, as listed in Table 1. In the same solvent, the Φ_{et} values increase with the electron-donor ability of the Fc derivatives; i.e., in BN, the Φ_{et} value for $Me_{10}Fc$ is larger than that of Fc by a factor of 8. In BN:DMF (1:2), the Φ_{et} value for $Me_{10}Fc$ is larger than that of Fc by a factor of 4.5.

The electron-transfer rate constant (k_{et}) via ${}^3C_{60}{}^*$ can be evaluated by the following relation (eq 2):[8,9]

$$k_{et} = k_q \Phi_{et} \quad (2)$$

The k_{et} values are also listed in Table 1. In the case of Fc, the k_{et} values decreased compared with the k_q values by factors of ca. 0.1, whereas for $Me_{10}Fc$, the factors increase up to 0.46–0.59. With an increase in the solvent polarity, the k_{et} values increase by factors of 1.3–2.0. Thus, it was revealed that although the donor ability of unsubstituted Fc is quite low, the Φ_{et} values and the k_{et} values could be appreciably increased by the efforts to increase the donor ability and solvent ability.

Comparison with Other Systems. For electron donors such as aromatic amines or carbazole, the k_q, Φ_{et}, and k_{et} values from ${}^3C_{60}{}^*$ are reported in the literature.[8-14] The k_q values for the Fc derivatives are almost the same as the reported value for the aromatic amines, when ΔG_{ET} values are sufficiently negative.[4a,36] On the other hand, the Φ_{et} and k_{et} values for the Fc derivatives are quite small compared with those for aromatic amines. An example is shown for the Φ_{et} values in Figure 4, in which the very small Φ_{et} values for the Fc derivatives are prominently shown compared with those for aromatic amines. These findings
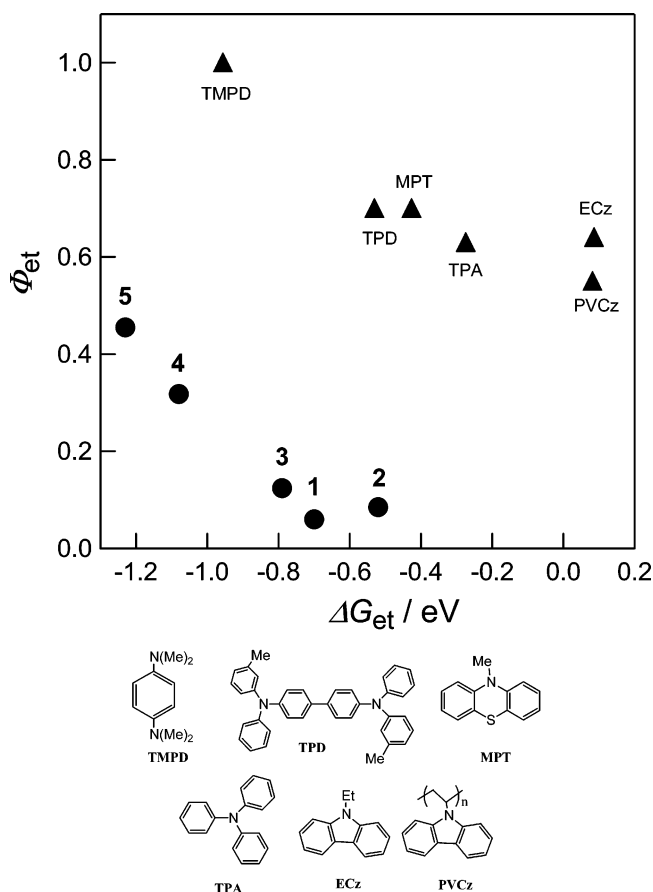

Figure 4. Comparison of quantum yields (Φ_{et}) of Fc derivatives with various amines in Ar-saturated BN.

suggest the presence of the quenching process of ${}^3C_{60}{}^*$ other than electron transfer. As a candidate of such a process, energy transfer from ${}^3C_{60}{}^*$ to Fc can be considered; however, the triplet energy of Fc was reported to be 1.7 eV,[37] which is higher than that of ${}^3C_{60}{}^*$ (1.56 eV). Therefore, it is necessary to reinvestigate the triplet energy of Fc by the reliable methods such as thermal lens method.[32]

Thermal Lens Measurements. The thermal lens method (TL) measured in the microsecond time region is one of the appropriate methods to reveal the radiationless process via the triplet states of molecules excited directly by light or by indirectly by energy transfer.[32] The inset of Figure 5 shows the time profiles of the probe light intensity after the photoexcitation of C_{60} in toluene in the presence of β-carotene, as an example to reveal the validity for the evaluation of the triplet energy by the TL method. Because the TL experiments were carried out in nonpolar solvents such as toluene, cyclohexane, octane and dodecane, no electron transfer between C_{60} and β-carotene was expected.[32] Therefore, the mixture system of C_{60} (0.1 mM) and β-carotene (1.0 mM) in nonpolar solvents can be thought as predominant energy-transfer system. For such systems in which energy-transfer process is predominant, the ratio of the pure slow decrease ($U_{slow}{}^{TL}$) to the total decrease ($U_{total}{}^{TL} = U_{fast}{}^{TL} + U_{slow}{}^{TL}$) can be expressed by eq 3.[32-34]

$$U_{slow}{}^{TL}/U_{total}{}^{TL} = \Phi_{ISC}E_T{}'\Phi_{en}(1 - \Phi_p{}')/(h\nu_{ex} - \Phi_{ISC}E_T{}'\Phi_{en}\Phi_p{}') \quad (3)$$

In eq 3, Φ_{ISC} refers to quantum yield of the intersystem-crossing (ISC) process of C_{60}; $h\nu_{ex}$ refers to light energy to excite C_{60}; $E_T{}'$ and $\Phi_p{}'$ refer to the triplet energy and phosphorescence
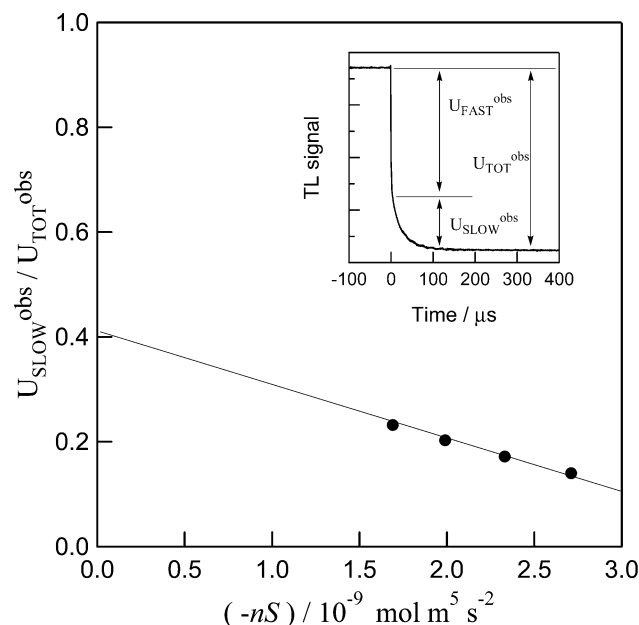
Figure 5. Plot of eq 4 for the TL signals of the energy-transfer system from $^3C_{60}$* to β-carotene in Ar-saturated nonpolar solvents (toluene, cyclohexane, octane, and dodecane). Inset: time profile of a typical TL signal by the excitation of C_{60} (0.1 mM) by 600 nm laser light in the presence of β-carotene (1.0 mM) in Ar-saturated toluene.

quantum yield of the energy acceptor (β-carotene), respectively; Φ_{en} refers to the quantum yield for triplet energy transfer. For the probe light of the TL experiments, continuous Nd:YAG laser light at 1064 nm was employed at appropriately low intensity to avoid the two-photon excitation of C_{60}. Because the molar extinction coefficients of $^3C_{60}$* and $^3\beta$-carotene* at 1064 nm are negligibly small, the contribution of transient absorption on the TL signal was practically negligible.

$U_{slow}^{TL}/U_{total}^{TL}$ can be related to the observed ratio, $U_{fast}^{obs}/U_{total}^{obs}$, in which the fast decrease (U_{fast}^{obs}) of the light intensity is due to the combination of the population lens and thermal lens effects, whereas the slow decrease (U_{slow}^{obs}) is attributed to the radiationless-relaxation process of $^3\beta$-carotene* generated by energy transfer from $^3C_{60}$*,[38,39] in addition to physical constants ($D\Delta n_{PL}/Sn$) as in eq 4. D is constant determined by

$$U_{fast}^{obs}/U_{total}^{obs} = U_{slow}^{TL}/U_{total}^{TL} + D\Delta n_{PL}/Sn \qquad (4)$$

the experimental setup; Δn_{PL} refers to absorption band shape parameter, which is constant with changing solvent; $S = (dn/dT)/\rho C_p$ (n = reflective index, T = absolute temperature, ρ = density, and C_p = specific heat of solvent). Under our experimental conditions, the variations of Δn_{PL} in the different solvents were small enough to be ignored, because 1064 nm was used as a monitor wavelength, which is quite far from the main absorption band of $^3C_{60}$* and $^3\beta$-carotene* in every solvents.[32] Therefore, from the plots of $U_{fast}^{obs}/U_{total}^{obs}$ vs $(Sn)^{-1}$ with changing solvents (Figure 5), the intercept gave the right term of eq 3. By employing $\Phi_{ISC} = 0.98$, $h\nu_{ex} = 1.34$ eV (600 nm), and $E_T = 1.51$ eV for C_{60}, we evaluated the E_T' value of β-carotene to be 0.93 eV, which is in good agreement with the reported value (0.91 eV).[40] This proves the reliability of the E_T' value evaluated by the energy-transfer systems employing this method.

The system of C_{60} (0.1 mM) and Fc (1 mM) in nonpolar solvents might be thought of as predominantly an energy-transfer system, because no rise of $C_{60}^{•-}$ was observed in nonpolar
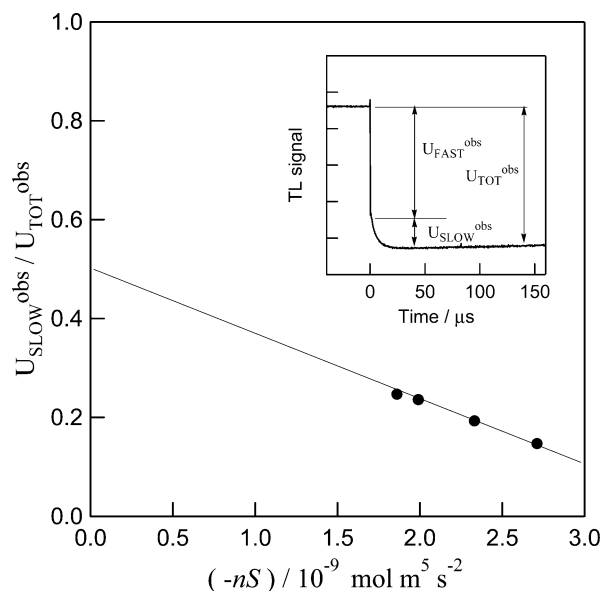

Figure 6. Plot of eq 4 for the TL signals of the energy-transfer system from $^3C_{60}$* to Rc in Ar-saturated nonpolar solvents (toluene, cyclohexane, octane, and dodecane). Inset: Time profile of a typical TL signal by the excitation of C_{60} (0.1 mM) by 532 nm laser light in the presence of Fc (1.0 mM) in Ar-saturated cyclohexane.
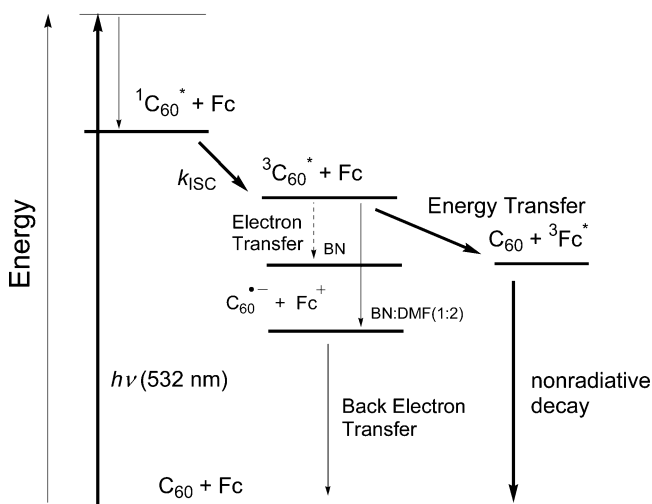

Figure 7. Energy diagram and major processes in C_{60} and Fc mixture system after light excitation of C_{60} in polar solvents.

solvents. For the systems in which the energy-transfer process is predominant, we can use eqs 3 and 4. The observed TL signal by the selective excitation of C_{60} in the presence of Fc in cyclohexane is shown in the inset of Figure 6. From the plot of the observed TL signals in various nonpolar solvents (eq 4), the E_T' value for Fc was evaluated to be 1.16 eV by employing $\Phi_p' = 0$ and $\Phi_{en} = 0.998$. Then, this E_T' value for Fc is quite lower than that reported one in the literature (1.7 eV).[37]

Energy Diagrams. On combining our new result (triplet energy of Fc = 1.16 eV) with the reported values for C_{60}, we can illustrate the energy diagram for the C_{60} and Fc system, as shown in Figure 7. When C_{60} is excited to the upper excited singlet state with 532 or 600 nm laser light, fast internal relaxation takes place going down to the lowest excited singlet state ($^1C_{60}$*), from which the ISC process takes place, generating the lowest excited triplet state ($^3C_{60}$*) within the nanosecond laser pulse. In nonpolar solvents, the triplet energy of $^3C_{60}$* predominantly transfers to the triplet state of the Fc derivatives. In polar solvents, a small fraction of electron transfer takes place

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competitively with the predominant energy transfer. The quantum yields of electron transfer were increased by the increases of the electron-donor ability of the Fc derivatives and solvent polarity.

Supporting Information Available: Description of thermal lens measurements, a figure of the thermal lens signal profile, and a figure of the contribution of PL in the TL signal of $^3C_{60}*$ in solution. This material is available free of charge via the Internet at http://pubs.acs.org.

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(38) Under our experimental conditions ([β-carotene] = 1.0 mM), the energy-transfer process was finished within 1 μs after 600 nm laser light irradiation, because the energy-transfer process from $^3C_{60}$* to β-carotene

takes place in the diffusion-controlled rate.[20] Therefore, the slow components of the TL singals in Figures 5 and 6 correspond to the thermal decay of $^3\beta$-carotene* and ^{3}Fc*, respectively.

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