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C_{60} as Photosensitizing Electron-Transfer Mediator for Ion-Pair Charge-Transfer Complexes between Borate Anions and Methyl Viologen Dication

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Photochemical reactions between the excited triplet state of C_{60} and the ion-pair charge-transfer complex which consists of electron-acceptor cation (methyl viologen (MV^{2+})) and electron-donor anion (organo borates ($^{-}BPh_3R$, where R = Ph or Bu)) have been investigated by both steady-state and laser-flash photolysis. By photoirradiation of C_{60} in the presence of $MV^{2+}(^{-}BPh_3R)_2$ in organic solvents, the amount of $MV^{+\bullet}$ increases with irradiation time, and persists for a long time even in the dark. From the laser-flash photolysis, it is found that electron transfer proceeds via $^3C_{60}^*$ from $^{-}BPh_3R$ in the complex, yielding $^{\bullet}BPh_3R$ and $C_{60}^{-\bullet}$. Although generated $C_{60}^{-\bullet}$ does not decay in the absence of MV^{2+} because of the rapid dissociation of $^{\bullet}BPh_3R$, in the presence of MV^{2+}, $C_{60}^{-\bullet}$ decays quickly by transferring an electron to MV^{2+} yielding $MV^{+\bullet}$. Thus, it is proved that C_{60} acts as a photosensitizer for pumping up an electron from $^{-}BPh_3R$ as well as an electron mediator to MV^{2+}. In these systems, $MV^{+\bullet}$ persists even in air-saturated solution for more than an hour, suggesting that the electron transfer from $MV^{+\bullet}$ to O_2 is retarded.

Introduction

Because of the high π-electron densities on the round molecules, fullerenes have unique reactivities[1] and properties such as electric conductivity,[2] superconductivity,[3] ferromagnetism,[4] and photoconductivity.[5] Fullerenes act the role of an effective visible-light photosensitizer. Recently, we have reported an efficient photoinduced electron transfer between C_{60} and organo borates ($^{-}BPh_3R$, where R = Ph, Bu) in polar solvents, yielding persistent anion radical of C_{60} ($C_{60}^{-\bullet}$) and C_{60} adduct anion (RC_{60}^{-}).[6] The $^{-}BPh_3R$ derivatives are known as good electron donors depressing the back electron transfer, because the boranyl radical ($^{\bullet}BPh_3R$) produced after electron donation easily dissociates into BPh_3 and $R^{\bullet}$ (yielding mainly R−R) with poor electron-accepting abilities.[7,9]

It was also reported that $^{-}BPh_3R$ is used as an effective alkyl radical source for photoinduced radical alkylation and radical polymerization.[7−9,10(a−e)] Photosensitized electron-transfer reactions of onium borate compounds containing both electron-accepting radical generator and electron-donating radical generator within the same ion pair lead to the effective photoinitiated radical polymerization of vinyl monomers such as acrylates.[10(f,g),11] An onium borate compounds containing stable cation such as $MV^{2+}(^{-}BPh_3R)_2$ would be expected to possess high-efficiency for photoinduced charge separation.

In the present paper, we report that electron transfer between $^{-}BPh_3R$ and MV^{2+} is effectively induced by photoexcitation of C_{60}. Methyl viologen cation radical ($MV^{+\bullet}$) accumulates with the photoirradiation and persists even in aerated organic solvents. By observing the transient absorption in the near-IR region, the electron-transfer mechanism was examined. Electron transfer from $^{-}BPh_3R$ to MV^{2+} proceeds efficiently through the sensitization and electron mediation by C_{60}.

Experimental Section

Materials. Tetrabutylammonium triphenylbutylborate ($^{-}BPh_3Bu$ ($^{+}NBu_4$)) and tetrabutylammonium tetraphenylborate ($^{-}BPh_4$ ($^{+}NBu_4$)) were prepared by the method described in the literature.[12] Methyl viologen chloride ($MV^{2+}(Cl^{-})_2$) was obtained from Tokyo Chemical Industries Co., Ltd. Methyl viologen bis(tetraphenylborate) ($MV^{2+}(^{-}BPh_4)_2$) was prepared as described in a previous report.[13] Methyl viologen bis(triphenylbutylborate) ($MV^{2+}(^{-}BPh_3Bu)_2$) was prepared from $MV^{2+}(Cl^{-})_2$ and $^{-}BPh_3Bu$ ($^{+}NBu_4$) in 80% yield (as MV^{2+} recovery): A methanol solution (50 mL) of $MV^{2+}(Cl^{-})_2$ (0.3 mmol) was added to $^{-}BPh_3Bu$ ($^{+}NBu_4$) (1.8 mmol) in methanol (450 mL) under stirring. While the reaction mixture was stored in the dark at room temperature for 3 days, red needlelike crystals were deposited. The crystals were washed vigorously by methanol and then dried in vacuo. Anal. Calcd. for $C_{56}H_{62}N_2B_2$: C, 85.7; H, 7.96; N, 3.57. Found: C, 85.6; H, 8.06; N, 3.60.

C_{60} was obtained from Texas Fullerenes Corp. in a purity of 99.9%. Extra-pure grade benzonitrile (BN), *o*-dichlorobenzene (DCB), and THF were used as solvent.

Steady-State Photolysis and Measurements. All of the steady-state photolysis studies were performed with visible light from a Xe−Hg arc lamp (150 W) equipped with a cutoff filter ($\lambda > 580$ nm) in order to excite C_{60} selectively. The UV/visible absorption spectra were measured with a JASCO V-570 spectrophotometer before and after photoirradiation of the solution. To make air-saturated solution, air was kept in contact with the solution during experiments. All experiments were carried out at 20 °C.

Laser-Flash Photolysis. Transient absorption spectra and the absorption−time profiles of transient species were measured by the selective excitation of C_{60} with 610 nm laser light from an OPO laser (HOYA continuum Surelite OPO, 6 ns fwhm, and 21 mJ/pulse). For the transient absorption spectra in the near-IR region, an InGaAs-PIN photodiode (Hamamatsu Pho-

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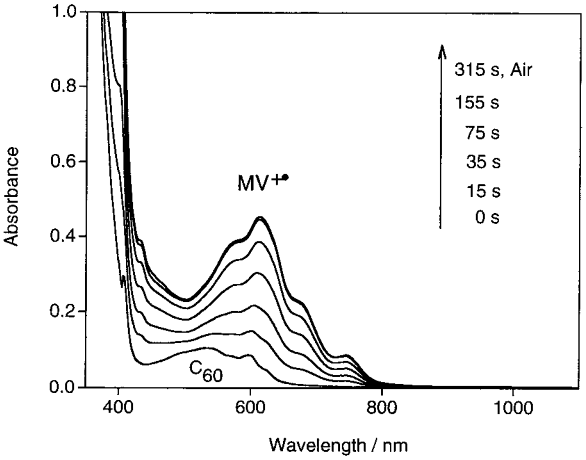


Figure 1. Absorption spectral changes observed during photoirradiation of C_{60} (0.1 mM) in the presence of $MV^{2+}(^-BPh_3Bu)_2$ (0.05 mM) in BN; optical path length = 1.0 cm.

tonics C5125−10) was employed as a detector for a probe light from a steady 150 W Xe-lamp equipped with cutoff filters to avoid the further photolysis. A sample solution in a rectangular quartz reaction cell was deaerated by Ar gas bubbling for 25 min before the experiment.

Results and Discussion

Steady-State Photolysis of C_{60} in the Presence of $MV^{2+}(^-BPh_3R)_2$. MV^{2+} $(Cl^-)_2$ and $^-BPh_3R$ $(^+NBu_4)$ (R = Ph, Bu) showed absorption bands in a wavelength region shorter than 325 nm in solvent; however, $MV^{2+}(^-BPh_3R)_2$ exhibited absorption in the visible region (<530 nm), which can be attributed to a charge-transfer (CT) interaction between MV^{2+} and $^-BPh_3R$. $MV^{2+}(^-BPh_3R)_2$ is considered to be an ion-pair CT complex.[13,14] An absorption of mixed solution of C_{60} and $MV^{2+}(^-BPh_3R)_2$ is almost identical to the summation spectrum of each compound, indicating no interaction between C_{60} and $MV^{2+}(^-BPh_3R)_2$ in the ground state.

By the steady photoirradiation of C_{60} with light longer than 580 nm in the presence of $MV^{2+}(^-BPh_3Bu)_2$ in deaerated benzonitrile (BN), a new absorption band appeared at 605 nm with a shoulder at 400 nm (Figure 1), which can be attributed to $MV^{+\bullet}$.[15] For $C_{60}/MV^{2+}(^-BPh_4)_2$, a similar spectral change was observed. It is clear that $MV^{+\bullet}$ is not generated by direct light illumination to $MV^{2+}(^-BPh_3R)_2$, because of negligible light absorption of $MV^{2+}(^-BPh_3R)_2$ at the longer wavelength (>580 nm). In the case of photoillumination of C_{60} with $^-BPh_3R$ $(^+NBu_4)$, generation of $C_{60}^{\bullet -}$ was observed at 1075 nm, because the back electron transfer from $C_{60}^{\bullet -}$ to $^\bullet BPh_3R$ is hindered by the rapid dissociation of $^\bullet BPh_3R$.[6] In the presence of $MV^{2+}(^-BPh_3R)_2$, however, the absorption band due to $C_{60}^{\bullet -}$ did not appear, indicating that $C_{60}^{\bullet -}$ is not persistent in the $C_{60}/MV^{2+}(^-BPh_3R)_2$ system.[16] This observation suggests that $C_{60}^{\bullet -}$ formed by accepting an electron from $^-BPh_3R$ via photoinduced electron transfer is consumed completely by donating an electron to MV^{2+}. This may imply that C_{60} acts as a photosensitizer as well as an electron mediator, successively transferring an electron from $^-BPh_3R$ to MV^{2+} as a whole.

Figure 2 shows the absorption time profiles of $MV^{+\bullet}$ during and after steady photoirradiation. In the deaerated $C_{60}/MV^{2+}(^-BPh_3Bu)_2$ or $C_{60}/MV^{2+}(^-BPh_4)_2$ system, $MV^{+\bullet}$ concentration exhibited a saturation at 300 s (Figure 2a and b). In the aerated solutions, a very slight buildup of $MV^{+\bullet}$ was observed for $C_{60}/MV^{2+}(^-BPh_3Bu)_2$ (Figure 2c); the rise of $MV^{+\bullet}$ was negligibly low for $C_{60}/MV^{2+}(^-BPh_4)_2$ (Figure 2d). It suggests that the $MV^{+\bullet}$ formation takes place via $^3C_{60}^*$, which is easily quenched by O_2 as well as $^-BPh_3R$.[17] The contribution of excited singlet state of C_{60} $(^1C_{60}^*)$ to the $MV^{+\bullet}$ formation should be quite low, because of the fast intersystem crossing rate from $^1C_{60}^*$ to $^3C_{60}^*$ under the low concentration of $MV^{2+}(^-BPh_3R)_2$.

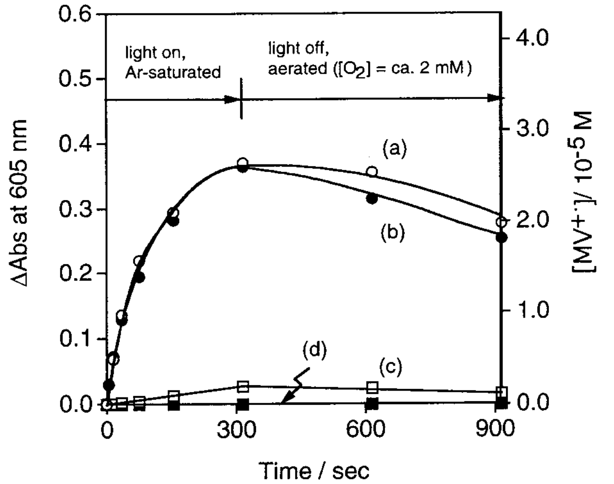


Figure 2. Absorption−time profiles during and after steady photoirradiation of C_{60} (0.1 mM) in the presence of (a) $MV^{2+}(^-BPh_3Bu)_2$ and (b) $MV^{2+}(^-BPh_4)_2$, in Ar-saturated BN, and (c) $MV^{2+}(^-BPh_3Bu)_2$ and (d) $MV^{2+}(^-BPh_4)_2$ in aerated BN; $[MV^{2+}(^-BPh_3R)_2]$ = 0.05 mM and optical path length = 1.0 cm.

When the light was turned off after generating the maximal concentration of $MV^{+\bullet}$ in the deaerated $C_{60}/MV^{2+}(^-BPh_3R)_2$ solution, the concentration of $MV^{+\bullet}$ remained for a long time. Furthermore, when air was introduced into the $MV^{+\bullet}$ solution, $MV^{+\bullet}$ was quenched very slowly (Figure 2). $MV^{+\bullet}$ persisted for over an hour even under shaking with air, in which the O_2 concentration (ca. 2 mM) is far excess to the amount of $MV^{+\bullet}$ by a factor of ca. 100. It was reported that $MV^{+\bullet}$ is rapidly consumed by electron transfer to O_2 dissolving in solvents.[18] However, the present observation indicates that the persistent $MV^{+\bullet}$ is protected from O_2 oxidation by some mechanisms in these reaction systems. This stabilization mechanism is hard to explain. It seems that $MV^{+\bullet}$ is not stabilized by $C_{60}^{-\bullet}$, but by $^-BPh_3R$ for some mechanisms such as a steric encumbrance, since persistent $MV^{+\bullet}$ is also formed via direct illumination to IPCT-band of $MV^{2+}(^-BPh_3R)_2$.

When $[C_{60}] \ll [MV^{2+}(^-BPh_3R)_2]$ (Figure 3), the maximal concentration of $MV^{+\bullet}$ was higher than $[C_{60}]$ by factors of 3−4, suggesting that C_{60} acts as a photocatalyst during irradiation (Figure 3). At the latter periods of irradiation, some differences in the rise rate and final concentrations of $MV^{+\bullet}$ were observed between $MV^{2+}(^-BPh_3Bu)_2$ and $MV^{2+}(^-BPh_4)_2$. The findings may be attributed to slight differences in the reactivities between $^-BPh_3Bu$ and $^-BPh_4$. On the other hand, at the initial phase of the photocatalytic cycle the difference was not observed (Figure 2).

The internal light-shielding effect due to absorption of $MV^{+\bullet}$ will suppress this photocatalytic cycle.

Laser-Flash Photolysis of C_{60} and $MV^{2+}(^-BPh_3R)_2$. Figure 4 shows the transient absorption spectra obtained by 610 nm laser excitation of C_{60} in the presence of $MV^{2+}(^-BPh_3Bu)_2$ in Ar-saturated BN. The transient absorption band at 740 nm appearing immediately after laser exposure is attributed to $^3C_{60}^*$.[20] With the decay of $^3C_{60}^*$, a new absorption band appeared at 600 nm, which can be attributed to $MV^{+\bullet}$. The weak absorption at 1070 nm is attributable to $C_{60}^{-\bullet}$.[20] Because the decay rate of $^3C_{60}^*$ in the presence of $MV^{2+}(^-BPh_3Bu)_2$ is

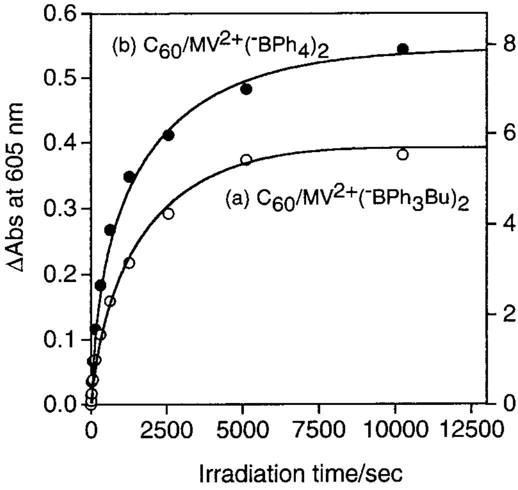


Figure 3. Absorption−time profiles during steady photoirradiation on C_{60} (0.02 mM) in the presence of $MV^{2+}(^{-}BPh_3R)_2$ (0.2 mM): (a) $MV^{2+}(^{-}BPh_3Bu)_2$ and (b) $MV^{2+}(^{-}BPh_4)_2$ in deaerated BN (optical path length = 0.5 cm).

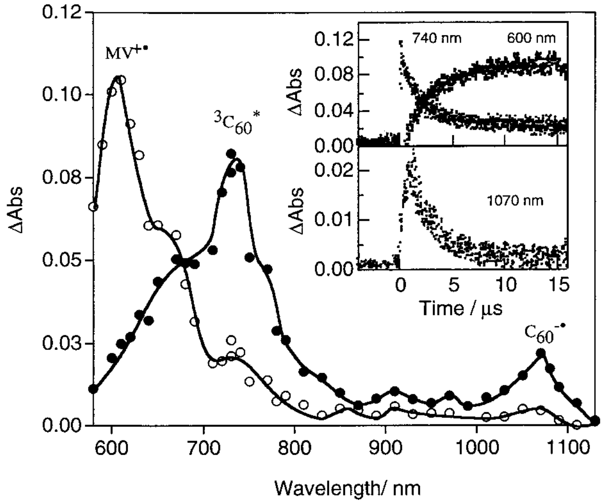


Figure 4. Transient absorption spectra obtained by 610 nm laser flash photolysis of C_{60} (0.1 mM) in the presence of $MV^{2+}(^{-}BPh_3Bu)_2$ (0.2 mM) in Ar-saturated BN. ● (1 μs), ○ (10 μs). Inset: time profiles.

similar to that with $^{-}BPh_3Bu$ ($^{+}NBu_4$) at the same concentration, electron transfer takes place from $^{-}BPh_3Bu$ to $^3C_{60}{}^*$, yielding $C_{60}^{-\bullet}$. Generated $C_{60}^{-\bullet}$ from $MV^{2+}(^{-}BPh_3Bu)_2$ decayed quickly, which indicates fast electron transfer from $C_{60}^{-\bullet}$ to MV^{2+}, yielding $MV^{+\bullet}$. From comparison of the decay curve of $C_{60}^{-\bullet}$ with that of $^{-}BPh_3Bu$ ($^{+}NBu_4$), the rate constant for electron transfer from $C_{60}^{-\bullet}$ to MV^{2+} was evaluated to be 2.8×10^9 M^{-1} s^{-1} (in BN). The decay rate of $C_{60}^{-\bullet}$ is too fast to observe the initial concentration of $C_{60}^{-\bullet}$ immediately after laser flash in Figure 4.

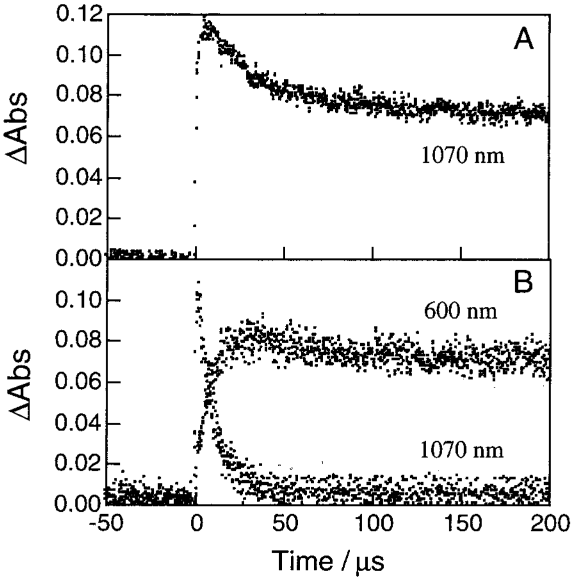
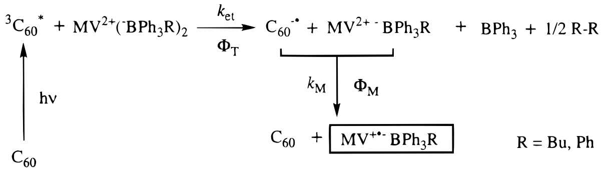


Figure 5. Time absorption profiles of $C_{60}^{-\bullet}$ after laser photolysis of C_{60} (0.1 mM) (A) in the presence of $^{-}BPh_3Bu$ ($^{+}NBu_4$) (2.0 mM) and (B) further addition of $MV^{2+}(^{-}BPh_3Bu)_2$ (0.05 mM) in Ar-saturated THF/DCB (1:1).

SCHEME 1



To confirm the electron transfer from $C_{60}^{-\bullet}$ to MV^{2+}, the stepwise experiments were designed as shown in Figure 5A. It is shown that persistent $C_{60}^{-\bullet}$ was at first produced via electron transfer from $^{-}BPh_3Bu$ ($^{+}NBu_4$) in THF/DCB mixed solvent (1:1). $^{-}BPh_3R$ ($^{+}NBu_4$) was denoted as donating anion (DA) in this study, because only the anion site has electron-donating ability. In this time region, the decay rate of $C_{60}^{-\bullet}$ generated from $^{-}BPh_3Bu$ ($^{+}NBu_4$) is quite slow. However, by addition of $MV^{2+}(^{-}BPh_3Bu)_2$ to the $C_{60}/^{-}BPh_3Bu$ ($^{+}NBu_4$) solution, the decay rate of $C_{60}^{-\bullet}$ increased with generating $MV^{+\bullet}$ (Figure 5B). The decay curve of $C_{60}^{-\bullet}$ is a mirror image of the rise curve of $MV^{+\bullet}$, indicating electron transfer from $C_{60}^{-\bullet}$ to MV^{2+}. From the decay curve of $C_{60}^{-\bullet}$ and the rise curve of $MV^{+\bullet}$, the rate constant for electron transfer from $C_{60}^{-\bullet}$ to MV^{2+} was evaluated as 2.0×10^9 M^{-1} s^{-1} (in THF/DCB). This electron transfer process is slightly suppressed by the low solvent polarity.

From these observations, the major photoreaction process for $C_{60}/MV^{2+}(^{-}BPh_3Bu)_2$ can be illustrated in Scheme 1. The photoreaction between C_{60} and $MV^{2+}(^{-}BPh_3Bu)_2$ is initiated by the reductive quenching of $^3C_{60}{}^*$, and followed by extraelectron transfer between $C_{60}^{-\bullet}$ and MV^{2+}, yielding $MV^{+\bullet}$ and C_{60}. The coupling reaction[6] between $C_{60}^{-\bullet}$ and $Bu^\bullet$ is completely hindered by fast electron transfer between $C_{60}^{-\bullet}$ and MV^{2+}, which can be deduced by the high yield of $MV^{+\bullet}$ ($\Phi_{MV^{+\bullet}} = 1.0$, which is described in a later section).

In the case of $MV^{2+}(^{-}BPh_4)_2$ and C_{60} in BN, weak absorption bands were observed at 980 and 1070 nm in addition to $MV^{+\bullet}$ at 600 nm as shown in Figure 6. These weak bands at 980 and 1070 nm are attributed to $C_{60}^{+\bullet}$ and $C_{60}^{-\bullet}$, respectively. The formation of $C_{60}^{+\bullet}$ may indicate that direct electron transfer from $^3C_{60}{}^*$ to MV^{2+} occurs, which may appear due to a slower electron-transfer rate from $^{-}BPh_4$ to $^3C_{60}{}^*$ than that of $C_{60}/MV^{2+}(^{-}BPh_3Bu)_2$. The rise of $MV^{+\bullet}$ at 600 nm may include $MV^{+\bullet}$ formed via both the reductive and oxidative quenching of $^3C_{60}{}^*$ by $^{-}BPh_4$ and MV^{2+}, respectively. The decay of $C_{60}^{+\bullet}$ may be due to electron transfer from $^{-}BPh_4$. The rate constant was evaluated to be 5.1×10^8 M^{-1} s^{-1}. After donating an electron, $^{-}BPh_4$ rapidly dissociates into BPh_3 and Ph−Ph (biphenyl);[9c] thus, $MV^{+\bullet}$ produced by this route is also persistent. The high quantum yield for $MV^{+\bullet}$ formation from $C_{60}/MV^{2+}(^{-}BPh_4)_2$ ($\Phi_{MV^{+\bullet}} = 1.0$, which is described in a later section) supports this reaction scheme.

To confirm the reactivity for the direct electron-transfer process from $^3C_{60}{}^*$ to MV^{2+}, the transient spectra were

TABLE 1: Rate Constants and Quantum Yields for Electron Transfer Processes

quencher	type[a]	solvent	k_q (M^{-1} s^{-1})	Φ_T[b]	k_{et} (M^{-1} s^{-1})	$\Phi_{MV^{+\bullet}}$
$MV^{2+}(^-BPh_3Bu)_2$	IPCT	BN	2.4×10^9	(1.0)	2.4×10^9	1.0
$MV^{2+}(^-BPh_3Bu)_2$	IPCT	THF/DCB	2.0×10^9	(0.52)	1.0×10^9	0.52[d]
$MV^{2+}(^-BPh_4)_2$	IPCT	BN	1.8×10^8	(1.0)	1.8×10^8	1.0
$MV^{2+}(^-PF_6)_2$	AC	BN	1.6×10^7	(0.15)	2.4×10^6	0.15
$^-BPh_3Bu$ ($^+NBu_4$)[c]	DA	BN	1.4×10^9	1.0	1.4×10^9	
$^-BPh_3Bu$ ($^+NBu_4$)	DA	THF/DCB	2.0×10^9	1.0	2.0×10^9	
$^-BPh_3Bu$ ($^+NBu_4$)[c]	DA	DCB	4.2×10^8	1.0	1.4×10^9	
$^-BPh_4$ ($^+NBu_4$)[c]	DA	BN	3.5×10^7	0.88	3.1×10^7	
$^-BPh_4$ ($^+NBu_4$)[c]	DA	DCB	2.8×10^7	0.75	2.1×10^7	

[a] Types of quenchers; IPCT (ion pair charge transfer), AC (accepting cation), and DA (donating anion). [b] Φ_T in parentheses is evaluated on assuming $\Phi_M = 1.0$ [c] From ref 6. [d] The maximal $\Phi_{MV^{+\bullet}}$ cannot be performed because of low solubility to THF/DCB. *Pseudo-first-order plots of $MV^{2+}(^-BPh_4)_2$ and $MV^{2+}(PF_6^-)_2$ could not be performed because of poor solubility to THF/DCB.

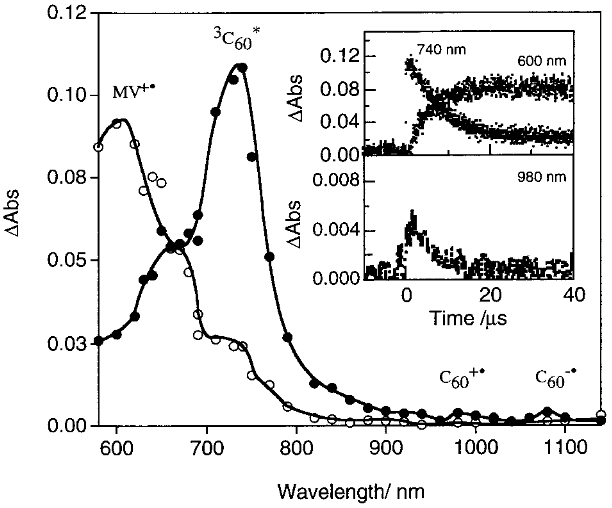


Figure 6. Transient absorption spectra obtained by 610 nm laser flash photolysis of C_{60} (0.1 mM) in the presence of $MV^{2+}(^-BPh_4)_2$ (0.5 mM) in Ar-saturated BN. ● (2.5 μs), ○ (25 μs). Inset: time profiles.

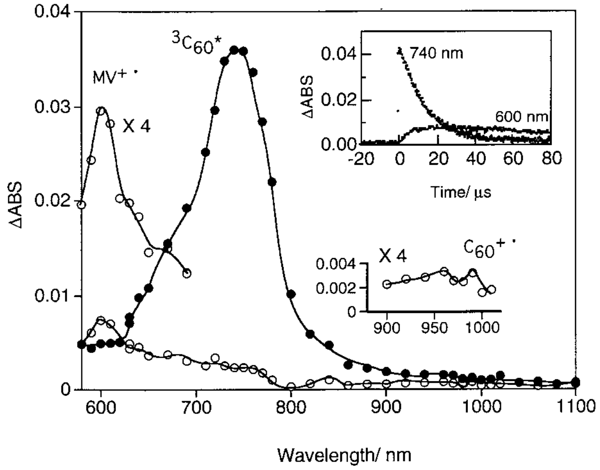


Figure 7. Transient absorption spectrum obtained by 610 nm laser flash photolysis of C_{60} (0.1 mM) in the presence of $MV^{2+}(^-PF_6)_2$ (0.5 mM) in Ar-saturated BN. ● (5 μs), ○ (50 μs). Inset: time profiles.

measured by 610-nm laser exposure of C_{60} in the presence of $MV^{2+}(^-PF_6)_2$ in BN (Figure 7). The decay of $^3C_{60}$* was slightly accelerated and a weak rise of $MV^{+\bullet}$ at 600 nm was observed. Because the electron-transfer rate from $^-PF_6$ to $^3C_{60}$* is anticipated to be extremely slow, direct electron transfer from $^3C_{60}$* to MV^{2+} takes place yielding $MV^{+\bullet}$ and $C_{60}^{+\bullet}$. $MV^{2+}(^-PF_6)_2$, in which only the cation site has electron-accepting ability, was denoted as accepting cation (AC) in this study. The efficiency and rate constant for electron transfer between $^3C_{60}$* and MV^{2+} is small ($\Phi_{MV^{+\bullet}} = 0.15$, $k_{et} = 2.4 \times 10^6$ M^{-1} s^{-1}).

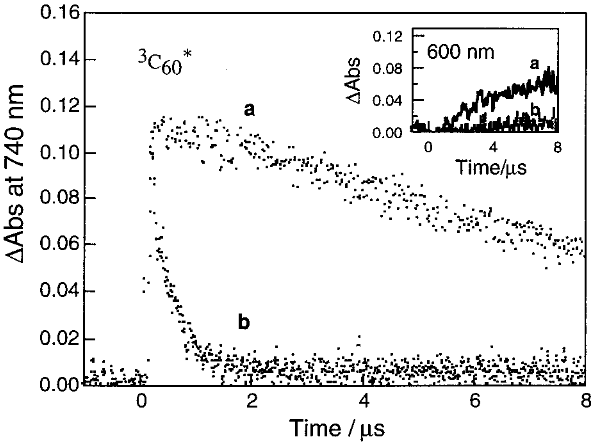
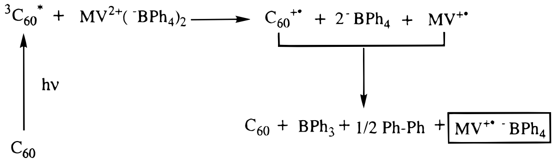


Figure 8. The time−absorption profile of $^3C_{60}$* and $MV^{+\bullet}$ obtained by laser exposure to C_{60} in the presence of $MV^{2+}(^-BPh_3Bu)_2$ in (a) Ar-saturated BN and (b) aerated BN. [C_{60}] = 0.1 mM and [$MV^{2+}(^-BPh_3Bu)_2$] = 0.2 mM.

SCHEME 2



In our previous study,[6] we have revealed the high quantum yield (0.88) for $C_{60}^{-\bullet}$ formation by the illumination of the C_{60}/$^-BPh_4$($^+NBu_4$) system despite a relatively small rate constant for electron transfer ($k_{et} = 3.1 \times 10^7$ $M^{-1}S^{-1}$ in BN). From these findings, we can deduce that the electron transfer between $^3C_{60}$* and $^-BPh_4$ (reductive quenching) is the major reaction path (Scheme 1). The rate for electron transfer between $^3C_{60}$* and $^-BPh_4$ may be enhanced by IPCT interaction to overcome competing MV^{2+}. In the case of oxidative quenching of $^3C_{60}$* by MV^{2+}, $MV^{+\bullet}$ also becomes persistent because the back electron transfer from $MV^{+\bullet}$ to $C_{60}^{+\bullet}$ is suppressed by electron transfer from $^-BPh_4$ to $C_{60}^{+\bullet}$, yielding fast dissociative $^\bullet BPh_4$ (Scheme 2).

In an aerated solution of C_{60}/$MV^{2+}(^-BPh_3Bu)_2$, $^3C_{60}$* was rapidly quenched by O_2 (Figure 8), which results in a prominent decrease in $MV^{+\bullet}$ formation (Figure 8 inset), because O_2 decreases the yield of $C_{60}^{-\bullet}$. This is caused by energy transfer from $^3C_{60}$* to O_2, which competes with electron transfer from $^-BPh_3Bu$ to $^3C_{60}$*. Under the condition of [O_2] ≫ [$MV^{2+}(^-BPh_3Bu)_2$], the quenching of $^3C_{60}$* by O_2 became predominant, suppressing the formation of $C_{60}^{-\bullet}$. This is the reason why $MV^{+\bullet}$ was not accumulated by the steady photolysis in the presence of O_2 (Figure 2). Because the rate for electron transfer between $C_{60}^{-\bullet}$ and MV^{2+} is very fast, $C_{60}^{-\bullet}$ may be almost quantitatively consumed by MV^{2+}, but not by competing O_2.

On the other hand, when O_2 was introduced into reaction solution after the $MV^{+\bullet}$ formation, $MV^{+\bullet}$ was persistent as shown in Figure 2; this clearly suggests that electron transfer from $MV^{+\bullet}$ to O_2 is suppressed, which may be related to the structural environment of $MV^{+\bullet}$ in the ion pairs in solution.

From the laser-flash experiments, the decay curve of $^3C_{60}$* obeys first-order kinetics in the presence of an excess amount of $MV^{2+}(^-BPh_3R)_2$ with respect to [$^3C_{60}$*]. The second-order rate-constants (k_q) were obtained by plotting the first-order rate constants with [$MV^{2+}(^-BPh_3R)_2$]. The quantum yield of the $MV^{+\bullet}$ formation via $^3C_{60}$* ($\Phi_{MV}{}^{+\bullet}$) was estimated from the time profiles as shown in Figure 4. From comparison of the maximum concentration of $^3C_{60}$* and $MV^{+\bullet}$ after laser flash,[17,19,20] the $\Phi_{MV}{}^{+\bullet}$ was evaluated to be 1.0 in BN. The $\Phi_{MV}{}^{+\bullet}$ is defined as multiplying two quantum yields; one is the quantum yield for electron transfer from $^-BPh_3R$ to $^3C_{60}$* (Φ_T), another is that from $C_{60}^{-\bullet}$ to MV^{2+} (Φ_M). Since the total quantum yield ($\Phi_{MV}{}^{+\bullet}$) is 1.0, Φ_T and Φ_M must be 1.0. The Φ_M value also can be evaluated to be about 1.0 from Figure 6. The rate constant for electron transfer between $^3C_{60}$* and $MV^{2+}(^-BPh_3R)_2$ (k_{et}) can be evaluated by the relation, $k_{et} = \Phi_T k_q$. Thus, k_q can be put equal to k_{et} as summarized in Table 1. Since the Φ_M values are close to unity, Φ_T can be put equal to $\Phi_{MV}{}^{+\bullet}$.

For $MV^{2+}(^-BPh_3Bu)_2$, the k_{et} values in polar solvent (BN) are larger than the corresponding values in less polar solvent (THF/DCB). This suggests that the donor ability of $^-BPh_3Bu$ in loose ion pair with MV^{2+} is more reactive than that in the contact ion pair. Since the difference in the k_M and Φ_M values between contact ion pair and loose ion pair is not experimentally prominent, the difference seems to be not large. The k_{et} value between $^3C_{60}$* and $MV^{2+}(^-BPh_3Bu)_2$ is larger than that of $MV^{2+}(^-BPh_4)$, which is the same tendency with k_{et} of borate anions (DA). Since $^-BPh_3Bu$ ($^+NBu_4$) is more reactive to $^3C_{60}$* than $MV^{2+}(^-PF_6)_2$ by a factor of 100 (in Table 1), it should be concluded that $^3C_{60}$* is quenched by $^-BPh_3Bu$ rather than MV^{2+}.

By comparison of Φ_T ($= \Phi_{MV}{}^{+\bullet}$) and k_{et} for $^-BPh_4$ ($^+NBu_4$) with those for $MV^{2+}(^-PF_6)_2$, the partition of electron transfer from $^3C_{60}$* to MV^{2+} for $MV^{2+}(^-BPh_4)$ is presumed to be very small.

Concluding Remark

Photoinduced electron transfer between C_{60} and MV^{2+}-$(^-BPh_3R)_2$ occurs mainly from $^-BPh_3R$ to $^3C_{60}$*, yielding $C_{60}^{-\bullet}$ and $^\bullet BPh_3R$. Since the back electron transfer is suppressed, the quantitative formation of $MV^{+\bullet}$ is realized through the intermediary of C_{60}. C_{60} is a good photocatalyst because its ion radicals have long half-lives and high yields of extraelectron transfer. This photocatalytic cycle is continued until suppression by the internal light shielding effect of $MV^{+\bullet}$. We found that $^-BPh_3Bu$ and $^-BPh_4$ are efficient electron donors of MV^{2+}, yielding persistent $MV^{+\bullet}$ with a high efficiency. We revealed that C_{60} is an effective sensitizer which can act as a good electron mediator to construct the photosensitization reaction.

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