PERKIN 2

# Persistent $C_{60}$ anion-radical formation *via* photoinduced electron transfer from tetraphenylborate and triphenylbutylborate

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Photochemical reactions between photo-excited $C_{60}$ and borates ($^{-}BPh_4$ and $^{-}BPh_3Bu$) have been investigated by steady-state photolysis and laser flash photolysis. On steady-state photolysis of $C_{60}$ in the presence of the borates in polar solvents, the absorption of $C_{60}^{-\bullet}$ increases with irradiation time, suggesting that irreversible photoinduced electron-transfer occurs. By the measurements of the transient absorption spectra, it is indicated that electron transfer takes place from the borate anions to $^{3}C_{60}^{*}$, yielding $C_{60}^{-\bullet}$ and $^{\bullet}BPh_3R$ (R = Ph or Bu), in which the latter dissociates into $Ph_3B$ and $R^{\bullet}$, yielding biphenyl (or octane). Electron-donor ability of $^{-}BPh_3Bu$ is higher than that of $^{-}BPh_4$, while the steady-state photolysis to a $C_{60}$/borate system shows an opposite tendency. The addition reaction of $C_{60}^{-\bullet}$ with $Bu^{\bullet}$ yielding $BuC_{60}^{-}$ is more efficient than that with $Ph^{\bullet}$ producing $PhC_{60}^{-}$. The rate constant of electron-transfer *via* the triplet state of $C_{60}$ increases with solvent polarity.

## Introduction

Fullerenes have unique properties and photoreactivities[1] caused by the highly dense π-electron clouds in the round molecules. When they are chemically treated with some electron-donors and acceptors, new properties such as superconductivity,[2] ferromagnetism[3] and photoconductivity are induced.[4] Metal doped fullerenes are usually produced under rather drastic conditions, such as at the solid/solid and/or at the solid/gas interface. Recently, Moriyama *et al.* found that tetraphenyl borates ($M^{+-}BPh_4$) reacted with $C_{60}$ in solution producing the single crystal of $M^{+}C_{60}^{-\bullet}$, which showed high electric conductivity.[5]

Tetraphenylborate and triphenylalkylborates ($^{-}BPh_3R$; R = Ph, alkyl) are good electron-donors. It was reported that triphenylalkylborates generate efficiently free alkyl radical ($R^{\bullet}$) after one electron donation under light illumination.[6] Thus, one of the characteristics of triphenyl alkylborates is to act as a photo-radical alkylation reagent[7] and an initiator of photo-radical polymerization.[8] Another characteristic is to obscure back electron transfer, producing persistent reduction forms of the acceptors.[9] The chemistry of $^{-}BPh_4$ has been studied intensely by means of electrochemical and photochemical techniques.[10,11] The electrochemical oxidation of $^{-}BPh_4$ leads to the formation of biphenyl as a major product *via* intramolecular dimerization. Its reaction mechanism was proposed for two-electron transfer.[10] The direct excitation of $^{-}BPh_4$ by UV-irradiation results in the formation of biphenyl and phenyl derivatives *via* intramolecular rearrangements.[11] However, for the photo-sensitized oxidation of $^{-}BPh_4$, the reaction mechanism is not clear.

Usually, $C_{60}^{-\bullet}$ formed *via* photo-induced electron-transfer returns quickly to $C_{60}$ by back electron-transfer; *i.e.*, $C_{60}^{-\bullet}$ formed *via* $^{1}C_{60}^{*}$ with aromatic amine returns to $C_{60}$ within 100 ps in non-polar solvents.[12] In the case of the $^{3}C_{60}^{*}$-route, $C_{60}^{-\bullet}$ persists for *ca.* 100 μs in polar solvents.[13]

In the present paper, we found that electron-transfer is induced by photo-excitation of $C_{60}$ in the presence of these borates in polar solvents. Persistent $C_{60}^{-\bullet}$ was observed after the photo-irradiation. By the transient absorption measurements, the electron-transfer mechanism was examined. The rate for the formation of $C_{60}^{-\bullet}$ may depend on the structure of the borates and on the solvent polarity. The alkyl/phenyl radicals ($R^{\bullet}$) are generated after these borates have been oxidized by photo-excited $C_{60}$. Coupling reactions between $C_{60}^{-\bullet}$ and $R^{\bullet}$ producing $RC_{60}^{-}$ were observed. It was also confirmed that further R-adducts form during the steady photo-irradiation.

## Results and discussion

### Steady-state photolysis of $C_{60}$ and borates in solution

With the photo-irradiation of $C_{60}$ in the presence of $^{-}BPh_4$ in deaerated benzonitrile (BN), new absorption bands appeared in the region of 900–1100 nm, which can be attributed to $C_{60}^{-\bullet}$ (Fig. 1A).[14] This indicates that the photoinduced electron-transfer reaction from $^{-}BPh_4$ to $C_{60}$ occurs, and that back electron-transfer is almost hindered. The maximal concentration of $C_{60}^{-\bullet}$ achieved during 300–1200 s was calculated to be *ca.* 0.1 mmol $dm^{-3}$, which is half that of fed $C_{60}$ under excess $^{-}BPh_4$. In the aerated solution, on the other hand, no spectral changing of the reaction solution was observed, suggesting that the precursor of the $C_{60}^{-\bullet}$-formation reaction may involve $^{3}C_{60}^{*}$, which may be easily quenched by $O_2$.[15]

In the reported spectrum of $C_{60}^{-\bullet}$, the absorbance ratio of 930 nm to 1075 nm ($A_{930nm}/A_{1075nm}$) is *ca.* 0.25.[16] For the spectrum after irradiation, $A_{930nm}/A_{1075nm}$ is *ca.* 0.5, indicating that other species which show broad absorption at *ca.* 940 nm may be formed. The species showing the absorption bands in the longer wavelength region up to 940 nm may be attributable to the ionic and/or radical species of pristine $C_{60}$ or $C_{60}$-derivatives.[17] By introduction of air to the irradiated solution, the absorption spectra were changed (Fig. 1B). The sharp peak at 1075 nm of $C_{60}^{-\bullet}$ disappeared, while the broad band at 940 nm persisted, indicating that the latter species are less reactive toward $O_2$ than $C_{60}^{-\bullet}$. Because addition of trifluoroacetic acid

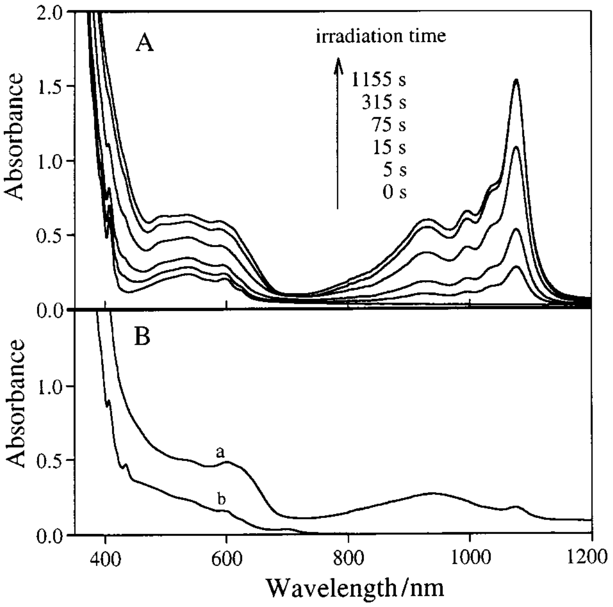


**Fig. 1** Absorption spectra of $C_{60}$ (0.2 mmol $dm^{-3}$) and $Bu_4NBPh_4$ (1.0 mmol $dm^{-3}$) in Ar-saturated benzonitrile (cell length = 1.0 cm). (A) After photolysis and (B) (a) on introduction of air after irradiation (1155 s), (b) on addition of trifluoroacetic acid (10 mmol $dm^{-3}$) to solution (a).

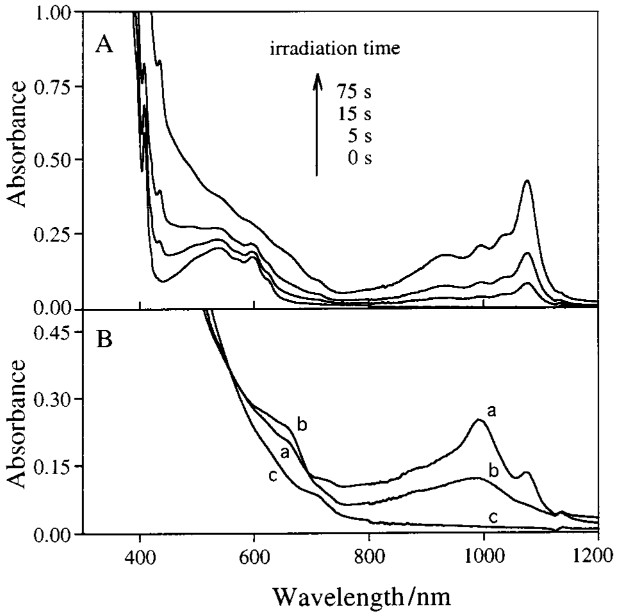


**Fig. 2** Absorption spectra of $C_{60}$ (0.2 mmol $dm^{-3}$) and $Bu_4NBPh_3Bu$ (1.0 mmol $dm^{-3}$) in Ar-saturated benzonitrile (cell length = 1.0 cm). (A) After photolysis and (B) (a) after irradiation for 315 s, (b) on introduction of air after irradiation (315 s), (c) on addition of trifluoroacetic acid (10 mmol $dm^{-3}$) to solution (b).

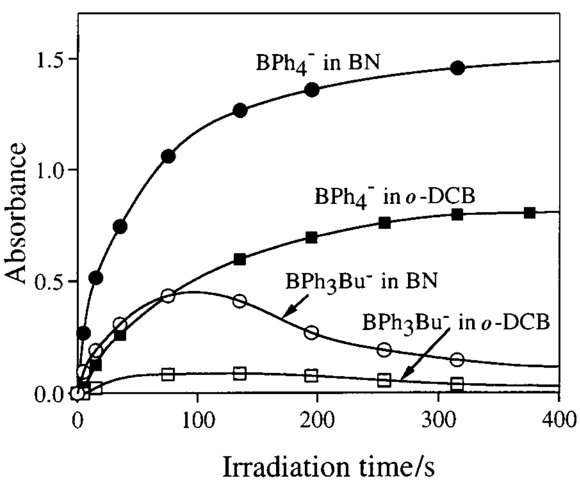


**Fig. 3** Generation of $C_{60}^{-\bullet}$ during irradiation of $C_{60}$ in Ar-saturated solutions (0.2 mmol $dm^{-3}$) and borates (1.0 mmol $dm^{-3}$).

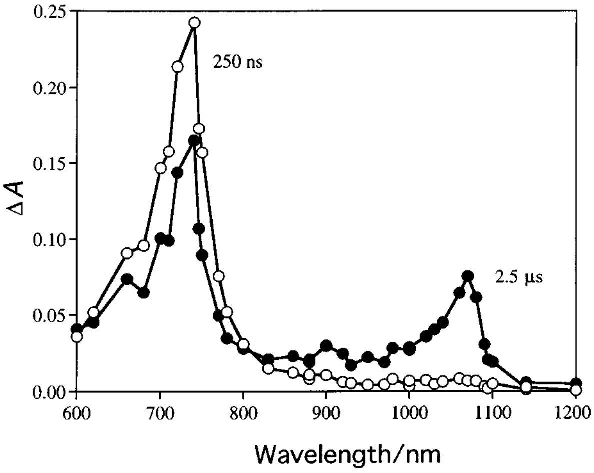


**Fig. 4** Transient absorption spectra obtained by laser flash photolysis of $C_{60}$ (0.2 mmol $dm^{-3}$) in the presence of $Bu_4NBPh_4$ (1.0 mmol $dm^{-3}$) after laser excitation at 532 nm in benzonitrile.

(10 mmol $dm^{-3}$) leads to the disappearance of the broad band at 940 nm, this may be attributed to absorption of $C_{60}$ anionic-species, $RC_{60}^-$, which is reported to have a broad absorption band with an absorption peak at about 990 nm.[17]

With the steady-state photolysis of $C_{60}$ in the presence of $^-BPh_3Bu$ in the same manner, the $C_{60}^{-\bullet}$ absorption bands appeared in the region of 900–1100 nm (Fig. 2A), while the absorption intensity of $C_{60}^{-\bullet}$ is relatively low compared with the $C_{60}/^-BPh_4$ system. The maximal concentration of $C_{60}^{-\bullet}$ achieved during 75 s was calculated to be *ca.* 0.03 mmol $dm^{-3}$, which is one sixth that of fed $C_{60}$ under excess $^-BPh_3Bu$. This indicates that $C_{60}^{-\bullet}$ under the photolysis system of $C_{60}/^-BPh_3Bu$ is unstable. By further prolonged irradiation (Fig. 2Ba), the absorption peak of $C_{60}^{-\bullet}$ at 1075 nm decreased without the appearance of a 990 nm band. By introduction of air (Fig. 2Bb), the relatively sharp 990 nm band and $C_{60}^{-\bullet}$ band disappeared, leaving the broad band at 990 nm, which is closely similar to the reported absorption spectrum of $RC_{60}^-$.[17,18] The broad band finally disappeared on addition of acid. Thus, the sharp band at 990 nm may be attributed to a $C_{60}$-anion radical species such as $Bu_2C_{60}^{-\bullet}$ and the broad band to a $C_{60}$-anionic species such as $BuC_{60}^-$.[17,18]

The build-up curves of $C_{60}^{-\bullet}$ during photo-irradiation of $C_{60}$ and borates in deaerated BN and *o*-dichlorobenzene (DCB) are shown in Fig. 3. The $C_{60}/^-BPh_4$ system exhibits a saturation of $C_{60}^{-\bullet}$-formation at *ca.* 300 s. By further irradiation (more than *ca.* 1000 s), the peak of $C_{60}^{-\bullet}$ began to decrease very slightly, while the peaks at *ca.* 930 nm and at *ca.* 600 nm kept increasing (Fig. 1A), suggesting that these bands can be attributed to anionic species formed from $C_{60}^{-\bullet}$. On the other hand, the photolysis of $C_{60}/^-BPh_3Bu$ system results in a relatively fast saturation of $C_{60}^{-\bullet}$ at *ca.* 100 s. By further irradiation (*ca.* 300 s), the absorption peak intensity of $C_{60}^{-\bullet}$ begins to decrease, and a new sharp band at 990 nm appears with the broad band (Fig. 2B).

In less polar solvents such as DCB, the increase rate of $C_{60}^{-\bullet}$ was slower than that in highly polar BN by a factor of over two for $C_{60}/^-BPh_4$, suggesting that the polar solvent favors persistent $C_{60}^{-\bullet}$-formation. For $C_{60}/^-BPh_3Bu$ in DCB, although an increase–decrease curve similar to that in BN was observed, the maximal concentration of $C_{60}^{-\bullet}$ was as low as *ca.* 0.2.

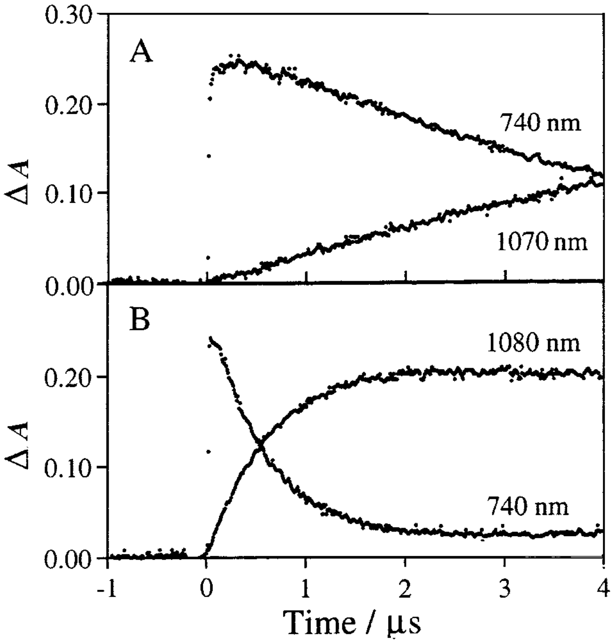


**Fig. 5** Absorption–time profiles obtained by laser flash photolysis of $C_{60}$ (0.2 mmol $dm^{-3}$) in the presence of (A) $Bu_4NBPh_4$ (1.0 mmol $dm^{-3}$) and (B) $Bu_4NBPh_3Bu$ (1.0 mmol $dm^{-3}$) after laser excitation at 532 nm in benzonitrile.

### Laser-flash photolysis

From the findings above, it is presumed that the formation of $C_{60}^{-\bullet}$ is stimulated by the excitation of $C_{60}$ to $^3C_{60}^*$ in the presence of borates. Further details of the mechanism can be disclosed by the measurements of the transient absorption bands. Fig. 4 shows the transient absorption spectra in the near-IR region obtained by the 532 nm laser photolysis of $C_{60}$ (0.2 mmol $dm^{-3}$) in the presence of $^-BPh_4$ (1.0 mmol $dm^{-3}$) in deaerated BN. The transient absorption band at 740 nm appearing immediately after nano-second laser exposure is attributed to the absorption band of $^3C_{60}^*$.[19] With the decay of $^3C_{60}^*$, new absorption bands appeared in the region of 1000–1100 nm, which can be attributed to $C_{60}^{-\bullet}$.[11,13] Similar transient absorption spectra of $^3C_{60}^*$ and $C_{60}^{-\bullet}$ were observed by the 532 nm laser photolysis of $C_{60}$ (0.2 mmol $dm^{-3}$) in the presence of $^-BPh_3Bu$ (1.0 mmol $dm^{-3}$) in BN solution and in DCB solution.

The decay and rise curves of $^3C_{60}^*$ and $C_{60}^{-\bullet}$ are shown in Fig. 5. The decay curve of $^3C_{60}^*$ is almost the mirror image of the rise curve of $C_{60}^{-\bullet}$, confirming that $C_{60}^{-\bullet}$ is produced *via* $^3C_{60}^*$, as shown in Scheme 1. Electron-transfer route *via* $^1C_{60}^*$ was not considered because of the large intersystem crossing rate constant of $C_{60}$ ($k_{isc} = 10^9\ s^{-1}$).[20]

$$C_{60} \xrightarrow[532\text{ nm}]{h\nu} {}^1C_{60}^* \xrightarrow{k_{isc}} {}^3C_{60}^* \xrightarrow[k_{et}\,\Phi_{et}]{+\,^-BPh_3R} C_{60}^{-\bullet} + {}^{\bullet}BPh_3R$$

(R = Bu or Ph)

**Scheme 1**

Both the decay and rise curves obey first-order kinetics in the presence of excess borates with respect to $[^3C_{60}^*]$. The first-order rate constants ($k_{1st}^{obs}$) were evaluated from the decay of $^3C_{60}^*$ and rise of $C_{60}^{-\bullet}$. Since the concentration of borate is the same in Fig. 5, it is apparent that the $k_{1st}^{obs}$ value of $C_{60}/^-BPh_4$ is smaller than that of $^-BPh_3Bu$ in BN. In DCB, quite slow decay of $^3C_{60}^*$ and rise of $C_{60}^{-\bullet}$ were observed, indicating small $k_{1st}^{obs}$ values.

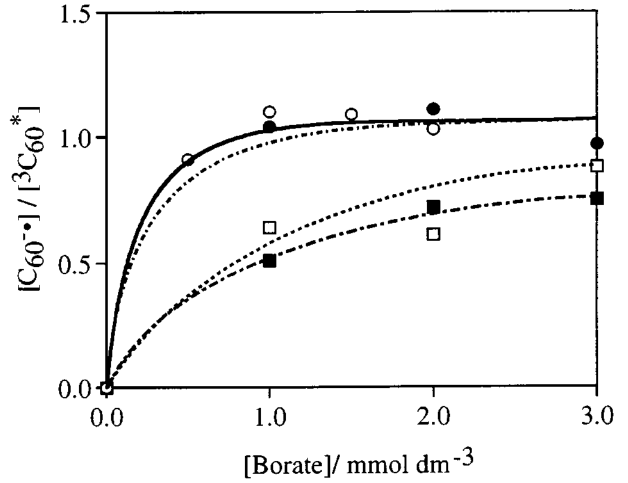


**Fig. 6** Dependence of $[C_{60}^{-\bullet}]/[^3C_{60}^*]$ on concentration of borates: $Bu_4NBPh_4$ in BN (□), $Bu_4NBPh_4$ in DCB (■), $Bu_4NBPh_3Bu$ in BN (○), $Bu_4NBPh_3Bu$ in DCB (●).

**Table 1** Rate constants and quantum yields for electron-transfer[a]

| Donor | Solvent | $k_{2nd}^{obs}$/ $dm^3\ mol^{-1}\ s^{-1}$ | $\Phi_{et}$ | $k_{et}$/ $dm^3\ mol^{-1}\ s^{-1}$ |
|---|---|---|---|---|
| $^-BPh_3Bu$ | BN | $1.4 \times 10^9$ | 1.00 | $1.4 \times 10^9$ |
| | DCB | $4.2 \times 10^8$ | 1.00 | $4.2 \times 10^8$ |
| $^-BPh_4$ | BN | $3.5 \times 10^7$ | 0.88 | $3.1 \times 10^7$ |
| | DCB | $2.8 \times 10^7$ | 0.75 | $2.1 \times 10^7$ |

[a] Each value contains an estimation error of ±5%.

### Efficiency and rate constants of electron-transfer

The efficiency of electron-transfer *via* $^3C_{60}^*$ can be evaluated by the ratio of $[C_{60}^{-\bullet}]_{max}$ to $[^3C_{60}^*]_{int}$, which were calculated from the observed absorbance and reported molar extinction coefficients as shown in Fig. 6.[13,15,19] Each curve shows a tendency to saturate at high concentration of borates. From the saturated ratio ($[C_{60}^{-\bullet}]_{max}/[^3C_{60}^*]_{int}$), the quantum yield($\Phi_{et}$) of electron-transfer *via* $^3C_{60}^*$ can be evaluated.

The $\Phi_{et}$ values are listed in Table 1; $^-BPh_3Bu$ shows higher $\Phi_{et}$ values than $^-BPh_4$. Solvent polarity effect on the $\Phi_{et}$ values is not so large in this range. For the reaction systems of $C_{60}/^-BPh_4$ with $\Phi_{et}$ less than 1, the deactivation processes of $^3C_{60}^*$ without electron-transfer may exist; the charge-transfer interaction and energy-transfer are candidates for such deactivation processes.

The rate constants for electron-transfer can be evaluated by the following relation, $k_{et} = \Phi_{et}k_{2nd}^{obs}$,[21] where $k_{2nd}^{obs}$ refers to the second-order rate constant for electron-transfer, obtained by plotting the $k_{1st}^{obs}$ values with [borate]. The $k_{et}$ values thus obtained are listed in Table 1. The $k_{et}$ value for $^3C_{60}^*/^-BPh_3Bu$ in BN is the highest just below the diffusion controlled limit ($k_{diff}$ = *ca.* $5 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$ in BN);[22] usually, the $k_{et}$ values of fullerenes are smaller than $k_{diff}$ by a factor of *ca.* 0.5. In the DCB, the $k_{et}$ value of $^-BPh_3Bu$ is smaller than that in BN, suggesting that the polar solvent accelerates the electron-transfer reaction. In BN, the $k_{et}$ values of $^-BPh_4$ are smaller than those of $^-BPh_3Bu$ by factors of more than 0.1.

From the evaluated $k_{et}$ values, it is presumed that the electron-transfer process of $^3C_{60}^*/^-BPh_4$ is considerably endothermic, while that of the $^3C_{60}^*/^-BPh_3Bu$ system is exothermic in BN. However, the free-energies for electron-transfer ($\Delta G^\circ$), which were calculated using the oxidation potentials of borates (+0.84 V for $^-BPh_3Bu$ and +0.87 V for $^-BPh_4$ *vs.* SCE in acetonitrile),[10c] reduction potential of $C_{60}$ (−1.51 V *vs.* SCE)[23] and the lowest triplet energy of $C_{60}$ (1.56 eV),[24] are −6.8 and −6.1 kcal $mol^{-1}$ for $^-BPh_3Bu$ and $^-BPh_4$, respectively.[25] They are very low, predicting the $k_{et}$ values to be close to $k_{diff}$. The finding that the evaluated $k_{et}$ of the $^3C_{60}^*/^-BPh_3Bu$ system in BN is close to $k_{diff}$ is in agreement with this prediction. On the other hand, the $k_{et}$ values of $^3C_{60}^*/^-BPh_4$ are less than $k_{diff}$,

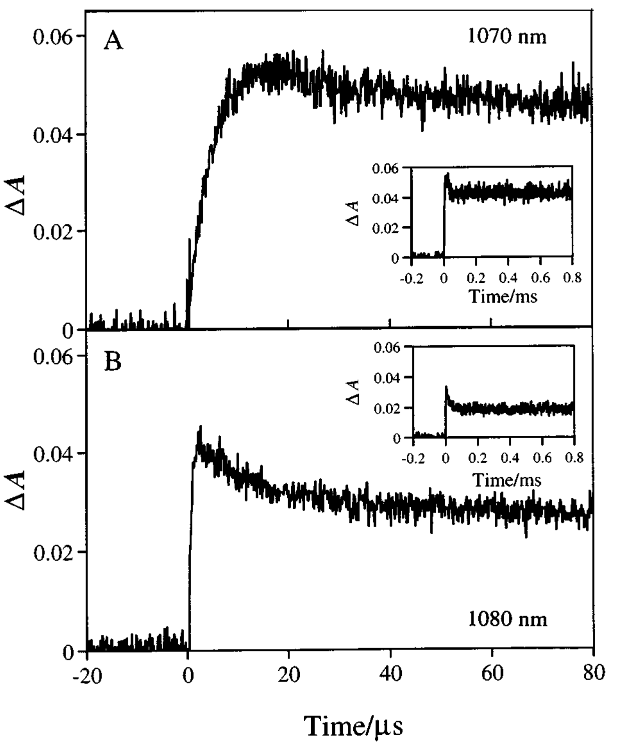


**Fig. 7** Long absorption–time profiles of $C_{60}^{-\bullet}$ up to 80 μs obtained by laser flash photolysis of Ar-saturated benzonitrile solution of $C_{60}$ (0.2 mmol $dm^{-3}$) containing (A) $Bu_4NBPh_4$ (1.0 mmol $dm^{-3}$) and (B) $Bu_4NBPh_3Bu$ (1.0 mmol $dm^{-3}$). Insert: Absorption–time profiles of $C_{60}^{-\bullet}$ up to 800 μs.

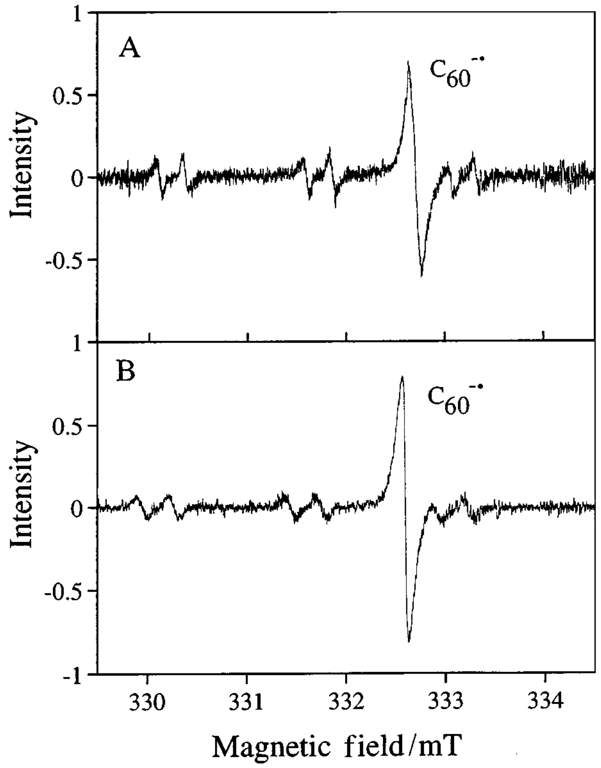


**Fig. 8** EPR spectra of $C_{60}^{-\bullet}$ and trapped $R^\bullet$ in DCB. (A) $C_{60}$/$Bu_4NBPh_4$/PBN (9.517 GHz) and (B) $C_{60}$/$Bu_4NBPh_3Bu$/PBN (9.511 GHz). [Borate] = 5.0 mmol $dm^{-3}$, $[C_{60}]$ = 1.0 mmol $dm^{-3}$, [PBN] = 10 mmol $dm^{-3}$. Field modulation = 0.025 mT (100 kHz).

which may indicate that some factors, such as steric effect, may be affecting this phenomenon.

The order of $\Phi_{et}$ and $k_{et}$ ($^-BPh_3Bu > {}^-BPh_4$) is opposite to that of persistent $C_{60}^{-\bullet}$, as seen in Fig. 3 ($^-BPh_3Bu < {}^-BPh_4$) in both solvents. The amount of persistent $C_{60}^{-\bullet}$ may be related with successive reactions after the photoinduced electron-transfer.

## Reaction of $C_{60}^{-\bullet}$ on a longer time scale

The time profiles of $C_{60}^{-\bullet}$ in a longer time scale up to 80 μs are shown in Fig. 7 (in BN). The slower rise–time profile of $^-BPh_4$ than that of $^-BPh_3Bu$ corresponds to the rise curves in Fig. 5. Usually, the photoproduced $C_{60}^{-\bullet}$ should disappear completely after reaching maxima in this time scale by back electron-transfer from $C_{60}^{-\bullet}$ to the cation radicals of the donors. For both of the $C_{60}$/$^-BPh_4$ and $C_{60}$/$^-BPh_3Bu$ systems, however, slow decays of $C_{60}^{-\bullet}$ were observed after reaching maxima at 5 and 1 μs, respectively. The similar rise and decay time–profiles were observed in DCB. These findings indicate that the back electron-transfer reaction was partly prohibited by successive fast decomposition of boranyl radical, $^\bullet BPh_4$ and $^\bullet BPh_3Bu$ (Scheme 1). It is reported that $^\bullet BPh_3Bu$ dissociates into $BPh_3$ and $Bu^\bullet$ within the femto-second time scale.[8] From the decay behavior of $C_{60}^{-\bullet}$, $^\bullet BPh_4$ seems to dissociate into $BPh_3$ and $Ph^\bullet$ within a similar time scale. Another possible route of the initial decay of $C_{60}^{-\bullet}$ after reaching a maximum may be attributed to back electron-transfer to $Bu^\bullet$ and $Ph^\bullet$. The remaining concentration of $C_{60}^{-\bullet}$ can be related to the concentration of $Bu^\bullet$ ($Ph^\bullet$) changing by radical coupling reaction to octane (biphenyl) competitively with back-electron-transfer.

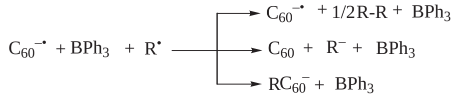
## $C_{60}$-adduct formation

The EPR-spectra of $C_{60}$/borate with spin-trap reagent (α-phenyl-*N*-*tert*-butylnitrone: PBN) in DCB after light-irradiation are shown in Fig. 8. Both of the systems show the EPR signal of $C_{60}^{-\bullet}$ and $R^\bullet$ trapped by PBN, which shows triple-doublet signals (R = Ph: $g = 2.006$, $a_N = 1.49$ mT, $a_H = 0.263$ mT; R = Bu: $g = 2.006$, $a_N = 1.50$ mT, $a_H = 0.326$ mT).[6c,26] From these facts, the proposed decomposition mechanism of $^\bullet BPh_3R$ is reasonably supported.

From the spectral changes by steady-state photolysis (Figs. 1A and 2A) observed after further prolonged light-irradiation, it was found that the $C_{60}^{-\bullet}$ was consumed by addition reaction of $Ph^\bullet$ or $Bu^\bullet$ to $C_{60}^{-\bullet}$ forming the $C_{60}$-adduct anion, $PhC_{60}^{-\bullet}$ and $BuC_{60}^{-\bullet}$. Thus, the decay of Fig. 7 may also include such addition reactions. We confirmed the formation of $C_{60}$-adducts ($C_{60}PhH$, $C_{60}Ph_2$, $C_{60}BuH$, $C_{60}Bu_3H_3$) and triphenylboron ($BPh_3$) by means of matrix assisted laser desorption ionization time-of-flight mass spectroscopic analysis on the reaction solution after photolysis.

In the μs-order time scale, the initial decay of $C_{60}^{-\bullet}$ under photolysis of $C_{60}$/$^-BPh_3Bu$ was faster than that of $C_{60}$/$^-BPh_4$. Usually, it can be presumed that $Ph^\bullet$ with σ-radical character is more reactive than $Bu^\bullet$.[27] Thus, it is deduced that the concentration of $Ph^\bullet$ becomes low by the various reactions, mainly including radical coupling reaction. These observed different reactivities between $Bu^\bullet$ and $Ph^\bullet$ may be related with the concentrations of the both free radicals.

In Fig. 7, the amount of remaining $[C_{60}^{-\bullet}]$ for $C_{60}$/$^-BPh_4$ is higher than that of $C_{60}$/$^-BPh_3Bu$ at 800 μs (Fig. 7, insert), which is the same trend as that of persistent $C_{60}^{-\bullet}$ seen in Fig. 3. The amount of $C_{60}^{-\bullet}$ remaining for a long time (up to *ca.* 1 ms) may be due to the fraction of radical coupling. Biphenyl formation may be faster than octane formation by the electric and steric factors in addition to the difference in the decomposition mechanism of borates such as intramolecular biphenyl formation. These reactions are summarized in Scheme 2.



(broad band at 940 nm(R=Ph), 990 nm(R=Bu) )

**Scheme 2**

The species showing sharp absorption at 990 nm is formed by further photo-irradiation to $C_{60}$ and $^{-}BPh_3Bu$ in BN (Fig. 2B). As one of the possibilities, $Bu_2C_{60}^{-\bullet}$ may be formed by the further addition reaction of $Bu^{\bullet}$ to $BuC_{60}^{-}$ as shown in Scheme 3.

$$C_{60}^{-\bullet} \xrightarrow{+\,Bu^{\bullet}} BuC_{60}^{-} \xrightarrow{+\,Bu^{\bullet}} Bu_2C_{60}^{-\bullet}$$

(sharp band at 990 nm)

**Scheme 3**

In the case of $C_{60}$/$^{-}BPh_4$, the sharp band due to $Ph_2C_{60}^{-\bullet}$ was not observed as seen in Fig. 1B, indicating that the steady concentration of $Ph^{\bullet}$ is quite low.

## Conclusions

The mechanism for the persistent $C_{60}^{-\bullet}$ formation can be revealed by nano-second laser flash photolysis observing transient absorption spectra in the visible/near-IR region. After photoinduced electron-transfer from borates to $^{3}C_{60}^{*}$, back electron-transfer from $C_{60}^{-\bullet}$ to the boranyl radicals is suppressed, since the boranyl radicals immediately dissociate generating the free radicals ($Bu^{\bullet}$ and $Ph^{\bullet}$), which further change into non-electron accepting materials ($Bu^{-}$, $Ph^{-}$, octane and biphenyl). By the selective quenching of the persistent $C_{60}^{-\bullet}$ by $O_2$, formation of $RC_{60}^{-}$ can be confirmed; alkylation by free-radical occurs with $C_{60}^{-\bullet}$. It is also confirmed that $R_2C_{60}^{-\bullet}$ is formed by the further alkylation to $RC_{60}^{-}$. The different reactivities between $^{-}BPh_4$ and $^{-}BPh_3Bu$ can be interpreted by the different reactivities of the free radicals, in which the steady concentration of $Bu^{\bullet}$ is enough to react with $C_{60}^{-\bullet}$, while concentration of $Ph^{\bullet}$ is low preserving high concentration of $C_{60}^{-\bullet}$.

## Experimental

### Materials

$C_{60}$ was obtained from Texas Fullerenes Corp. in a purity of 99.9%. Tetrabutylammonium tetraphenylborate ($Bu_4NBPh_4$) and tetrabutylammonium triphenylbutylborate ($Bu_4NBPh_3Bu$) were prepared by the method described in the literature.[10c] HPLC-grade benzonitrile (BN) and extra-pure grade *o*-dichlorobenzene (DCB) were used as solvents. The solution of $C_{60}$ and borates was deaerated with Ar-bubbling before photochemical reactions and measurements.

### Laser-flash photolysis study

The transient absorption and the decay–rise time profiles were measured by the nano-second laser flash photolysis method. The apparatus details were described elsewhere.[13] The $C_{60}$ solution was excited by 532 nm light from a Nd:YAG laser (6 ns fwhm) with 22 mJ pulse power. For the transient absorption spectra in the near-IR region, a Ge-APD detector was employed to monitor the transmitted light from a pulsed Xe-flash lamp, which passed through a rectangular quartz reaction cell (1 cm) and a monochromator. The long-time decay–rise time profiles were measured by an InGaAs-PIN photodiode module using a probe light from steady 150W Xe-lamp equipped with R-66 cut-off filter to avoid the photolysis by the monitor light.

### Steady-state photolysis

All the photolysis studies were performed with visible light from a Xe-Hg lamp (150 W) equipped with V-B46 band-pass blue filter ($350\ \text{nm} < \lambda_{ex} < 600\ \text{nm}$: selective excitation of $C_{60}$). All experiments were carried out at 20 °C.

The steady-state UV/visible/near-IR absorption spectra were measured with a JASCO/V-570 spectrophotometer before and after photo-irradiation of solution.

The EPR spectra were measured with a Varian E-4 EPR spectrometer system after irradiation to DCB solution.

The time-of-flight mass spectra were measured with a Bruker REFLEX III-T MALDI-TOF-MS (linear-mode). The reaction solutions (in DCB, $[C_{60}] = 1.0\ \text{mmol dm}^{-3}$, $[^{-}BPh_3R] = 5.0\ \text{mmol dm}^{-3}$) were irradiated for *ca.* 4 hours until the $C_{60}$ absorption disappeared and fully changed to the $C_{60}$-adducts one. After irradiation, the solutions were mixed with 9-nitroanthracene as a matrix compound.

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## References

1 (*a*) H. Imahori and Y. Sakata, *Adv. Mater.*, 1997, **9**, 537; (*b*) M. Prato, *J. Mater. Chem.*, 1997, **7**, 1097 and references cited therein.

2 (*a*) A. F. Hebard, M. J. Rosseinsky, R. C. Haddon, D. W. Murphy, S. H. Glarum, T. T. M. Palstra, A. P. Ramirez and A. R. Kortan, *Nature*, 1991, **350**, 600; (*b*) K. Tanigaki, T. W. Ebbesen, J. Sato, J. Mizuki, J. S. Tsai, Y. Kubo and S. Kuroshima, *Nature*, 1991, **352**, 222.

3 (*a*) P.-K. Allemand, K. C. Khemani, A. Koch, F. Eudl, K. Holczer, S. Donovan, G. Gruner and J. D. Thompson, *Science*, 1991, **253**, 301; (*b*) K. Tanaka, A. A. Zakhidov, K. Yoshizawa, K. Okahara, T. Yamabe, K. Yasuki, K. Kikuchi, S. Sizuki, I. Ikemoto and Y. Achiba, *Phys. Lett. A*, 1992, **164**, 354; (*c*) V. Buntar, F. M. Sauerzopf and H. W. Weber, *Aust. J. Phys.*, 1997, **50**, 329; (*d*) S. Hino, K. Umishima, K. Iwasaki, K. Tanaka, T. Sato, T. Yamabe, K. Yoshizawa and K. Okahara, *J. Phys. Chem. A*, 1997, **101**, 4346; (*e*) K. Pokhodnia, J. Demsar, A. Omerzu, D. Mihailovic and H. Kuzmany, *Synth. Methods*, 1977, **85**, 1749.

4 (*a*) Y. Wang, *Nature*, 1992, **356**, 585; (*b*) K. Yoshino, H. Y. Xiao, K. Nuro, S. Kiyomatsu, S. Morita, A. A. Zakihdov, T. Noguchi and T. Ohnishi, *Jpn. J. Appl. Phys.*, 1993, **32**, L357; (*c*) Y. Wang, R. West and C.-H. Yuan, *J. Am. Chem. Soc.*, 1993, **115**, 3844; (*d*) R. G. Kepler and P. A. Cahill, *Appl. Phys. Lett.*, 1993, **63**, 1552; (*e*) B. Kraabel, D. McBranch, N. S. Sariciftci, D. Moses and A. J. Heeger, *Phys. Rev. B*, 1994, **50**, 18543.

5 H. Moriyama, H. Kobayashi, A. Kobayashi and T. Watanabe, *Chem. Phys. Lett.*, 1995, **238**, 116.

6 (*a*) S. T. Murphy, C. Zou, J. B. Miers, R. M. Ballew, D. D. Dlott and G. B. Schuster, *J. Phys. Chem.*, 1993, **97**, 13152.

7 (*a*) J. Y. Lan and G. B. Schuster, *J. Am. Chem. Soc.*, 1985, **107**, 6710; (*b*) J. Y. Lan and G. B. Schuster, *Tetrahedron Lett.*, 1986, **27**, 4261.

8 (*a*) S. Chatterjee, P. D. Davis, P. Gottschalk, M. E. Kurtz, B. Sauerwein, X. Yang and G. B. Schuster, *J. Am. Chem. Soc.*, 1990, **112**, 6329; (*b*) S. Hasson, A. Sarker, M. A. Rodger and D. C. Neckers, *J. Am. Chem. Soc.*, 1995, **117**, 11369; (*c*) Y. Toba, Y. Usui, M. M. Alam and O. Ito, *Macromolecules*, 1998, **31**, 6022; (*d*) Y. Toba, M. Yasuike and Y. Usui, *J. Photoscience*, 1998, **5**, 63.

9 T. Konishi, Y. Toba and Y. Usui, submitted to *Chem. Commun.*

10 (*a*) D. H. Geske, *J. Phys. Chem.*, 1959, **63**, 1062; (*b*) D. H. Geske, *J. Phys. Chem.*, 1962, **66**, 1743; (*c*) E. E. Bancroft, H. N. Blount and E. G. Janzen, *J. Am. Chem. Soc.*, 1979, **101**, 3692; (*d*) J. H. Morris, H. J. Gysling and D. Reed, *Chem. Rev.*, 1985, **85**, 51.

11 (*a*) J. L. R. Williams, J. C. Doty, P. J. Grisdale, R. Searle, T. H. Regan, G. P. Happ and D. P. Maier, *J. Am. Chem. Soc.*, **89**, 1967; (*b*) G. C. Calhoun and G. B. Schuster, *J. Org. Chem.*, 1984, **49**, 1925; (*c*) J. D. Wilkey and G. B. Schuster, *J. Org. Chem.*, 1987, **52**, 2117.

12 R. Sension, A. Z. Szarka, G. R. Smith and R. M. Hochstrasser, *Chem. Phys. Lett.*, 1991, **185**, 179.

13 O. Ito, Y. Sasaki, Y. Yoshikawa and A. Watanabe, *J. Phys. Chem.*, 1995, **99**, 9838.

14 G. A. Heath, J. E. McGrady and R. L. Martin, *J. Chem. Soc., Chem. Commun.*, **1992**, 1272.

15 M. M. Alam, A. Watanabe and O. Ito, *J. Photochem. Photobiol. A: Chem.*, 1997, **104**, 59.

16 (*a*) D. F. Lawson, D. L. Felheim, C. A. Foss, P. K. Dorhout, C. M. Elliot, C. R. Martin and R. S. Armstrong, *J. Electrochem.*, 1992, **139**, L68; (*b*) R. D. Bolskar, S. H. Gallagher, R. S. Armstrong, P. A. Lay and C. A. Reed, *Chem. Phys. Lett.*, 1993, **205**, 405.

17 (*a*) S. Fukuzumi, T. Suenobu, S. Kawamura, A. Ishida and F. Mikami, *Chem. Commun.*, 1997, 291; (*b*) S. Fukuzumi, I. Nakanishi, J. Maruta, T. Yorisue, T. Suenobu, S. Itoh, R. Arakawa and K. M. Kadish, *J. Am. Chem. Soc.*, 1998, **120**, 6673; (*c*) S. Fukuzumi, T. Suenobu, M. Patz, T. Hirasaka, S. Itoh, M. Fujitsuka and O. Ito, *J. Am. Chem. Soc.*, 1998, **120**, 8060.

18 C. Luo, M. Fujitsuka, A. Watanabe, O. Ito, L. Gan, Y. Huang and C.-H. Huang, *J. Chem. Soc.*, *Faraday Trans.*, 1998, **94**, 527.

19 (*a*) R. J. Sension, C. M. Phillips, A. Z. Szarka, W. J. Romanow, A. R. Macghie, J. P. McCauley, A. B. Smith, III, Jr. and R. M. Hochstrasser, *J. Phys. Chem.*, 1991, **95**, 6075; (*b*) N. M. Dimitrijievic and P. V. Kamat, *J. Phys. Chem.*, 1992, **96**, 4811; (*c*) M. A. Greaney and S. M. Gorun, *J. Phys. Chem.*, 1991, **95**, 7142; (*d*) Z. Gasyna, L. Andrews and P. N. Schatz, *J. Phys. Chem.*, 1992, **96**, 1525.

20 (*a*) D. K. Palit, H. N. Ghosh, H. Pal, A. V. Sapre, J. P. Mittal, R. Seshadri and C. N. R. Rao, *Chem. Phys. Lett.*, 1992, **198**, 113; (*b*) A. Watanabe, O. Ito, H. Saito, M. Watanabe and M. Koishi, *J. Chem. Soc.*, *Chem. Commun.*, 1996, 117.

21 C. A. Steren, H. von Willigen, L. Biczok, N. Gupta and H. Linschitz, *J. Phys. Chem.*, 1996, **100**, 8920.

22 M. Fujitsuka, A. Watanabe, O. Ito, K. Yamamoto and H. Funasaka, *J. Phys. Chem.*, 1997, **101**, 4840.

23 (*a*) P. M. Allemand, A. Koch, F. Wudl, Y. Rubin, F. Diederich, M. M. Alvarez, S. J. Anz and R. L. Whetten, *J. Am. Chem. Soc.*, 1991, **113**, 1050; (*b*) D. Dubois, K. M. Kadish, S. Flanagan, R. E. Haufler, L. P. F. Chibante and L. J. Wilson, *J. Am. Chem. Soc.*, 1991, **113**, 4364.

24 R. R. Hung and J. J. Grabowski, *J. Phys. Chem.*, 1991, **95**, 6073.

25 D. Rehm and A. Weller, *Isr. J. Chem.*, 1970, **8**, 259.

26 (*a*) E. G. Janzen and B. J. Blackburn, *J. Am. Chem. Soc.*, 1968, **90**, 5909; (*b*) E. G. Janzen and C. A. Evans, *J. Am. Chem. Soc.*, 1975, **97**, 205; (*c*) A. J. Bard, J. C. Gilbert and R. D. Goodin, *J. Am. Chem. Soc.*, 1974, **96**, 620; (*d*) N. Nishimura, T. Nakamura, Y. Sueishi and S. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1994, **67**, 165.

27 O. Ito, R. Omori and M. Matsuda, *J. Am. Chem. Soc.*, 1982, **104**, 3934.

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