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Effects of Trimethylpyridine Addition on forward and backward Electron Transfer between Triplet States of C_{60}/C_{70} and 2-Naphthols

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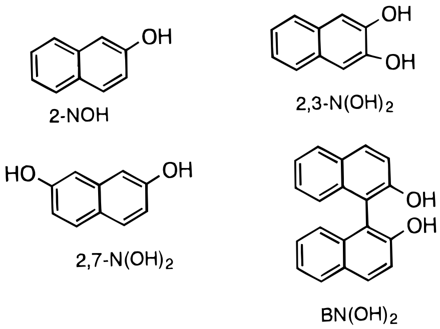
Photoinduced electron-transfer processes between C_{60}/C_{70} and 2-naphthols have been studied by nanosecond laser flash photolysis. Quantum yields (Φ_{et}^{T}) and rate constants (k_{et}) of electron transfer from naphthols to the excited triplet states of C_{60} and C_{70} have been determined by observing the transient absorption bands in the wide wavelength (UV−vis/NIR regions), where the naphthoxy radicals, triplet states, and anion radicals of fullerenes appear. Both Φ_{et}^{T} and k_{et} were increased by the addition of trimethylpyridine (Py), indicating that Py promotes the electron-donor ability of naphthols. The $C_{60}^{\bullet-}/C_{70}^{\bullet-}$ decay with second-order kinetics in the absence of Py, suggesting charge recombination of free ion radicals. In the presence of Py, on the other hand, the initial decays of $C_{60}^{\bullet-}/C_{70}^{\bullet-}$ obey first-order kinetics, suggesting that back electron transfer takes place within the ion radicals bridged via Py.

Introduction

Fullerenes acts as electron acceptors without any electron-withdrawing functional group.[1] It is well-known that the electron-accepting abilities of C_{60} and C_{70} in the ground state are further increased by photoexcitation of the fullerenes with visible light.[2−7] Thus, photoinduced electron transfer processes of fullerenes are an important subject, as good models for charge-separation systems. Time-resolved measurements have led to better understanding of general features of electron-transfer mechanisms. So far, various kinds of electron donors, including aromatic amines, afford usually reversible electron-transfer systems for fullerenes.[2−7]

In the case of phenols and naphthols with low electron-donor ability, it has been reported by Linschitz and co-workers that photoinduced electron transfer to C_{60} takes place only when pyridines are added to polar solution;[8] this phenomenon was shown to be coupled electron−proton transfer by Linschitz et al.[8]

In our previous paper about naphthylamine and binaphthylamine, we reported that the electron-transfer efficiencies to the triplet states of C_{60} and C_{70} ($^3C_{60}$* and $^3C_{70}$*, respectively) from perpendicular binaphthylamine are significantly different from those of planar naphthylamine suggesting some kind of steric effect on the electron-transfer process.[9] In the present study, we measured the transient absorption spectra for the systems C_{60}/C_{70} with 2-naphthol, dihydroxy-naphthalenes, and 1,1-bi-2-naphthol (Scheme 1) over wide wavelength regions and time scales to reveal the various aspects controlling electron-transfer processes in the presence and absence of pyridine. Especially, pronounced effects of pyridine addition have been found on the backward electron-transfer processes in addition to the acceleration of the forward electron-transfer rates.



Experimental Section

C_{60} and C_{70} were obtained in a purity of 99.9% and 99.5%, respectively, from Texas Fullerenes Corp. Commercially available 1,1′-bi-2-naphthol ($BN(OH)_2$) (Aldrich Co. Ltd.) was used as received. Optically active $BN(OH)_2$ was used to try to obtain the optically active adduct between C_{60}/C_{70} and $BN(OH)_2$ under various conditions. 2-Naphthol (2-NOH) and dihydroxynaphthalenes ($N(OH)_2$) of the highest grade were used. Trimethylpyridine (Py), benzonitrile and benzene were of the highest grade commercially available.

C_{60}/C_{70} was selectively excited by 532 nm light from a Nd:YAG laser (Quanta-Ray; 6 ns fwhm) with 7 mJ pulse energy. For the transient absorption spectra in the short time scale (<10 μs), a Si−PIN photodiode (300−600 nm) and Ge-APD (600−1400 nm) were used as detectors to monitor the transmitted light from a pulsed Xe-lamp (150 W).[10a] For longer time scale (>10 μs), an InGaAs detector was used to monitor the light from a continuous Xe-lamp.[10b] The solution of C_{60} (or C_{70}) and naphthols was deaerated by Ar bubbling for 15 min before measurements.

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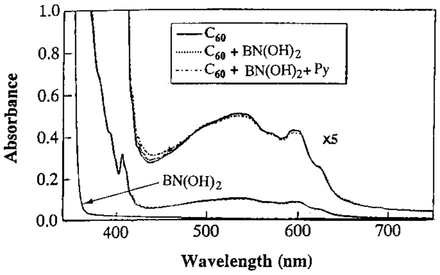


Figure 1. Steady-state absorption in the UV−vis region C_{60} (0.1 mM), $BN(OH)_2$ (4 mM), and their mixture in the presence of Py (0.5 M) in benzonitrile.

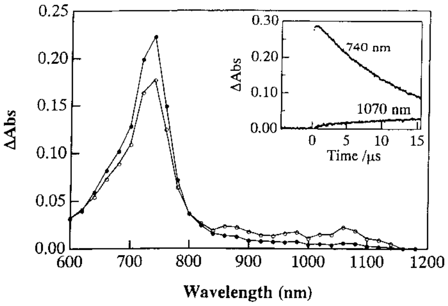


Figure 2. Transient absorption spectra obtained by 532 nm laser photolysis of C_{60} (0.1 mM) in the presence of $BN(OH)_2$ (20 mM) in Ar-saturated benzonitrile. Inset: time profiles. (●) 1 μs and (○) 10 μs.

The steady-state UV−vis absorption spectra were measured with a JASCO/V-570 spectrophotometer. The circular dichroism (CD) spectra were measured on a JASCO/I0015 spectropolarimeter. Steady-state photolysis was carried out with a Xe-Hg lamp (150 W); the wavelength region of light was selected by cut-off filters. All experiments were carried out at 23 °C.

Results and Discussion

Steady-State UV−vis Spectra. As Biczok et al. pointed out, the absorption spectra of naphthols in the UV region were changed considerably on addition of Py, indicating the interaction between naphthols and Py.[8b] The vis absorption spectra of C_{60} and $BN(OH)_2$ in the longer wavelength region are shown in Figure 1. In the absence or presence of Py, appreciable change was not observed between the absorption spectrum of the mixed system and the synthesized spectrum. Also, no spectral change was observed for other naphthols and C_{60} systems nor for C_{70} on addition of naphthols in the absence or presence of Py. These observations indicate that ground-state interaction between C_{60}/C_{70} and naphthols is negligibly small regardless of the presence of Py.

Photoinduced Electron Transfer. Laser flash photolysis of C_{60} with 532 nm light in the presence of $BN(OH)_2$ (20 mM) in deaerated benzonitrile produced the transient absorption spectra in the vis/NIR region as shown in Figure 2. The transient absorption band at 740 nm is attributed to the triplet−triplet (T−T) absorption of $^3C_{60}^*$.[11−13] With the slight decay of $^3C_{60}^*$, a new weak absorption band appears at 1070 nm with a shoulder at 900 nm, which are assigned to the absorption of $C_{60}^{\bullet-}$.[14] From the time profiles (inset of Figure 2), the decay of $^3C_{60}^*$ at 740 nm and the rise of $C_{60}^{\bullet-}$ at 1070 nm observed on addition of relatively high concentration of $BN(OH)_2$ (20 mM) seem to be almost mirror images. These observations clearly indicate that the electron transfer occurs from $BN(OH)_2$ to $^3C_{60}^*$ (eq 1), in which naphthols are written as NOH. For C_{70} in the absence of Py, a similar slow electron-transfer process was confirmed from NOH's to $^3C_{70}^*$ (980 nm)[15] yielding $C_{70}^{\bullet-}$ (1380 nm).[16]

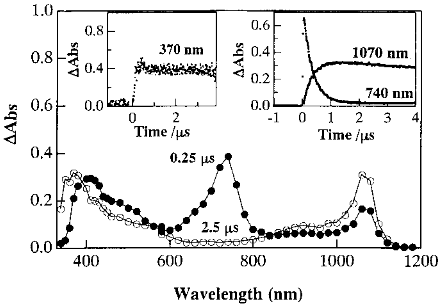


Figure 3. Transient absorption spectra obtained by 532 nm laser photolysis of C_{60} (0.1 mM) in the presence of $BN(OH)_2$ (3 mM) and Py (0.5 M) in Ar-saturated benzonitrile. Inset: time profiles.

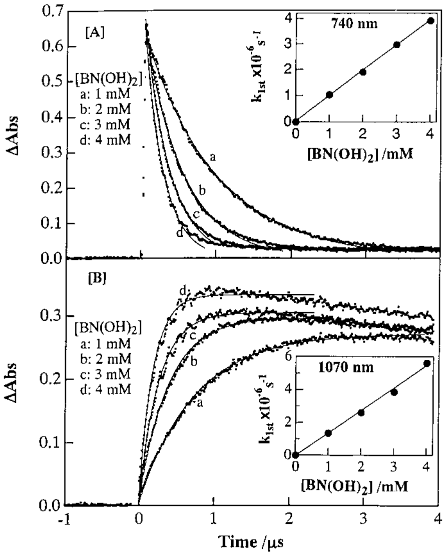


Figure 4. (A) Decay profiles of $^3C_{60}^*$ at 740 nm with changing $BN(OH)_2$. Inset: pseudo-first-order plot. (B) Rise profiles of $C_{60}^{\bullet-}$ at 1070 nm with changing $[BN(OH)_2]$. Inset: pseudo-first-order plot in the presence of Py (0.5 M) in Ar-saturated benzonitrile.

$$^3C_{60}^*/^3C_{70}^* + NOH \xrightarrow[\Phi_{et}^{T}]{k_{et}} C_{60}^{\bullet-}/C_{70}^{\bullet-} + NOH^{\bullet+} \qquad (1)$$

With 532 nm laser-light excitation of C_{60} in the presence of $BN(OH)_2$ and Py (Figure 3), the absorption of $^3C_{60}^*$ at 740 nm was quickly quenched, concomitantly with appearance of the absorption band of $C_{60}^{\bullet-}$ at 1070 nm. As shown in the inserted time-profile of Figure 3, the absorption intensity at 1070 nm begins to rise immediately after the laser pulse, corresponding to the quick decay of $^3C_{60}^*$. It is revealed that Py accelerates the electron-transfer rate from $BN(OH)_2$ to $^3C_{60}^*$ very much; i.e., donor abilities of naphthols are increased in the presence of Py as shown by Biczok et al.[8b]

The decay rates of $^3C_{60}^*$ increase with $[BN(OH)_2]$ in the presence of Py as shown in Figure 4A. Each decay curve of $^3C_{60}^*$ in the presence of $BN(OH)_2$ was fitted with a single exponential (k_{1st}). The second-order rate constant (k_q) was obtained from the linear dependence of k_{1st} on $[BN(OH)_2]$ as shown in the inset of Figure 4A. The obtained k_q values are listed in Table 1.

The rates of $C_{60}^{\bullet-}$ rise increase with $[BN(OH)_2]$ in benzonitrile as shown in Figure 4B. Each rise curve was fitted with a single exponential, yielding k_{1st} without taking the slow decay of $C_{60}^{\bullet-}$ into consideration. The second-order rate constant k_A (where subscript A represents $C_{60}^{\bullet-}$) was obtained by plotting k_{1st} vs $[BN(OH)_2]$ (Figure 4B). The obtained k_A values are in

TABLE 1: Quenching Rate Constants (k_q), Quantum Yields (Φ_{et}^T), Electron-Transfer Rate Constants (k_{et}), Second-order Back-Electron-Transfer Rate Constants (k_{bet}^{2nd}), and First-order Back Electron-transfer Rate Constant (k_{bet}^{1st}) in Benzonitrile[a]

fullerene/ NOH/Py	k_q/ $M^{-1} s^{-1}$ [b]	Φ_{et}^T	k_{et}/ $M^{-1} s^{-1}$ [c]	k_{bet}^{2nd}/ $M^{-1} s^{-1}$ [d]	k_{bet}^{1st}/ s^{-1}
C_{60}/2-NOH	1.4×10^6	0.20	2.8×10^5	1.7×10^9	
C_{60}/2-NOH/Py	7.2×10^8	1.00	7.2×10^8	1.6×10^9	3.4×10^4
C_{60}/2,3-N(OH)$_2$	1.5×10^6	0.23	3.5×10^5	2.2×10^{10}	
C_{60}/2,3-N(OH)$_2$/Py	1.5×10^9	1.00	1.5×10^9	1.8×10^{10}	3.2×10^4
C_{60}/2,7-N(OH)$_2$	9.9×10^5	0.23	1.3×10^5	2.2×10^9	
C_{60}/2,7-N(OH)$_2$/Py	1.1×10^9	1.00	1.1×10^9	1.5×10^9	2.9×10^4
C_{60}/BN(OH)$_2$	2.0×10^6	0.13	2.8×10^5	2.1×10^9	
C_{60}/BN(OH)$_2$/Py	9.7×10^8	0.68	6.6×10^8	2.3×10^9	1.2×10^4
C_{70}/2-NOH	7.1×10^5	0.26	1.8×10^5	2.6×10^9	
C_{70}/2-NOH/Py	8.4×10^8	1.00	8.4×10^8	2.6×10^9	4.3×10^4
C_{70}/2,3-N(OH)$_2$	2.9×10^6	0.49	1.4×10^5	1.6×10^{10}	
C_{70}/2,3-N(OH)$_2$/Py	1.2×10^9	1.00	1.2×10^9	5.2×10^{10}	9.8×10^4
C_{70}/2,7-N(OH)$_2$	9.8×10^6	0.32	3.1×10^5	3.2×10^9	
C_{70}/2,7-N(OH)$_2$/Py	1.0×10^9	1.00	1.0×10^9	7.9×10^9	2.6×10^4
C_{70}/BN(OH)$_2$	8.5×10^5	0.23	1.9×10^5	2.3×10^9	
C_{70}/BN(OH)$_2$/Py	1.2×10^9	0.60	7.2×10^8	5.0×10^9	1.2×10^4

[a] Each value conatins estimation error of ±5%. [a] The k_q values were evaluated from the decay of ${}^3C_{60}^*/{}^3C_{70}^*$. [b] $k_{et} = k_q \Phi_{et}^T$, [c] $\epsilon_A = 12000$ M^{-1} cm^{-1} at 1070 nm for $C_{60}^{\bullet-}$,[14b] and $\epsilon_A = 4000$ M^{-1} cm^{-1} at 1380 nm for $C_{70}^{\bullet-}$.[16] $\epsilon_T = 16100$ M^{-1} cm^{-1} at 740 nm for ${}^3C_{60}^*$,[4a] and $\epsilon_T = 6500$ M^{-1} cm^{-1} at 980 nm for ${}^3C_{70}^*$.[13,16]

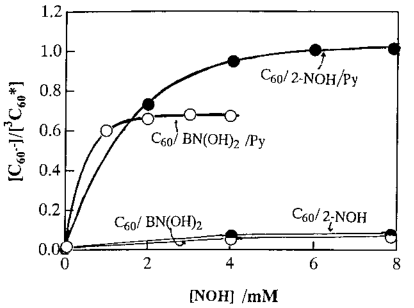


Figure 5. Dependence of $[C_{60}^{\bullet-}]/[{}^3C_{60}^*]$ on [BN(OH)$_2$] and [2-NOH] in the absence and presence of Py (0.5 M) in Ar-saturated benzonitrile.

good agreement with the corresponding k_q values within the experimental errors.

The efficiency of electron transfer via ${}^3C_{60}^*$ or ${}^3C_{70}^*$ can be estimated by the quantity $[C_{60}^{\bullet-}]/[{}^3C_{60}^*]$ (or $[C_{70}^{\bullet-}]/[{}^3C_{70}^*]$) as evaluated by the maximal and initial absorbances and reported ϵ_A and ϵ_T, which refer to molar extinction coefficients of $C_{60}^{\bullet-}$ or $C_{70}^{\bullet-}$ and ${}^3C_{60}^*$ or ${}^3C_{60}^*$, respectively.[4,11-16] In Figure 5, the ratios of $[C_{60}^{\bullet-}]/[{}^3C_{60}^*]$ are plotted against [BN(OH)$_2$] or [2-NOH] in the presence and absence of Py in benzonitrile. The efficiencies increase with [BN(OH)$_2$] or [2-NOH] reaching a plateau, from which the quantum yield (Φ_{et}^T) for electron transfer via ${}^3C_{60}^*$ was estimated (Table 1). The Φ_{et}^T values for C_{70} were obtained similarly. In the absence of Py, $[C_{60}^{\bullet-}]/[{}^3C_{60}^*]$ and $[C_{70}^{\bullet-}]/[{}^3C_{70}^*]$ reach plateaus at higher concentrations of NOH's, more than 20 mM; the Φ_{et}^T values are less than 0.23 for C_{60} and 0.26 for C_{70}. In the presence of Py, the Φ_{et}^T values increase by a factor of ca. 5. For both C_{60} and C_{70}, the Φ_{et}^T values of BN(OH)$_2$ are lower than those of 2-NOH by a factor of ca. 0.6, which is particularly interesting in regard to molecular structure of donors. A possible explanation of this observation is that the approach of perpendicular BN(OH)$_2$ to almost spherical fullerenes is hindered, while planar 2-NOH easily contacts the fullerene molecules in the excited states.[9] In the absence of Py, the Φ_{et}^T value for C_{60}/BN(OH)$_2$ is lower than that for C_{60}/2-NOH. The Φ_{et}^T values for C_{70}/N(OH)$_2$'s are higher than those for C_{70}/2-NOH and C_{70}/BN(OH)$_2$. As for difference in the acceptor abilities between C_{60} and C_{70}, the Φ_{et}^T values of C_{70} are slightly higher than those of C_{60} for both BN(OH)$_2$ and 2-NOH in the absence of Py, suggesting that C_{70} is a slightly stronger acceptor than C_{60}.

The rate constant for electron transfer (k_{et}) can be evaluated from the relation, $k_{et} = \Phi_{et}^T k_q$.[8b,17] In the presence of Py, the k_{et} values increase by a factor of ca. 1000 compared with those in the absence of Py. The k_{et} values in the presence of Py (Table 1) are slightly smaller than the diffusion controlled limit ($k_{diff} = 5.6 \times 10^9$ M^{-1} s^{-1} in benzonitrile).[18] In the absence of Py, the k_{et} values for all the naphthol donors are similar ((1.4−3.5) × 10^5 M^{-1} s^{-1}). In the presence of Py, on the other hand, the k_{et} values for BN(OH)$_2$ and 2-NOH ((7−8) × 10^8 M^{-1} s^{-1})) are smaller compared with those for N(OH)$_2$'s ((1.0−1.5) × 10^9 M^{-1} s^{-1}). This further supports that N(OH)$_2$'s become stronger electron donors than 2-NOH and BN(OH)$_2$ in the presence of Py.

From these observations, three types of description by equations are possible for the interaction between NOH's and Py in the neutral and ion radical states, as described below. Equation 2 considers the interaction with NOH and Py to be weak, leaving the proton of NOH still near the O-atom. Equation 3 represents a strong interaction between the proton of NOH and the N-atom of Py, moving the proton to the Py side. Equation 4 shows a weak interaction before electron transfer, but strong interaction after electron transfer.

$$ {}^3C_{60}^*/{}^3C_{70}^* + NOH{-}Py \xrightarrow[\Phi_{et}^T]{k_{et}} C_{60}^{\bullet-}/C_{70}^{\bullet-} + NOH^{\bullet+}{-}Py \tag{2} $$

$$ {}^3C_{60}^*/{}^3C_{70}^* + NO^{-}{-}PyH^{+} \xrightarrow[\Phi_{et}^T]{k_{et}} C_{60}^{\bullet-}/C_{70}^{\bullet-} + NO^{\bullet}{-}PyH^{+} \tag{3} $$

$$ {}^3C_{60}^*/{}^3C_{70}^* + NOH{-}Py \xrightarrow[\Phi_{et}^T]{k_{et}} C_{60}^{\bullet-}/C_{70}^{\bullet-} + NO^{\bullet}{-}PyH^{+} \tag{4} $$

Since the characteristic absorption due to NO^- did not appear on mixing NOH with Py, the strong interaction like $NO^-{-}PyH^+$ (equation 3) is not necessary to take into consideration. As shown in Figure 3, the transient spectra in the shorter wavelength region (300−400 nm) display new absorption bands at 350 and 390 nm due to the naphthoxy radical interacting with Py like as BN(OH)(O$^\bullet$)−PyH$^+$,[8b,19] along with the decay of ${}^3C_{60}^*$ in this region. In the case of 2-NOH in the presence of Py, a sharp absorption peak appeared at 350 nm after the decay of ${}^3C_{60}^*$, which is assigned to 2-NO$^\bullet$−PyH$^+$.[8b,19] Thus, eq 4 seems to be more appropriate representations than equation 2.

From the Rehm−Weller relation, free energy of electron transfer ($\Delta G°$) for the systems with $k_{et} = (1.1-3.5) \times 10^5$ M^{-1} s^{-1} can be estimated to be ca. 10 kcal/mol.[20] On addition of Py, the k_{et} values increase up to (0.66−1.5) × 10^9 M^{-1} s^{-1}, suggesting that $\Delta G°$ becomes more negative than −10 kcal/mol.[21] This indicates that the oxidation potentials of NOH's are decreased by 20 kcal/mol on addition of Py, which is in agreement with the observation by Biczok et al.[8b] This suggests that Py attracts proton from NOH's, resulting in the increase in the electron-donating ability of NOH−Py.

The contribution of the singlet states of C_{60}/C_{70} (${}^1C_{60}^*/{}^1C_{70}^*$) to $C_{60}^{\bullet-}/C_{70}^{\bullet-}$ formation need not to be considered, because the rise of $C_{60}^{\bullet-}$ is slow, as shown in the inserts of Figures 2 and 3.

Solvent Effect on Photoinduced Electron Transfer. In a less polar solvent such as a mixture of benzene and benzonitrile

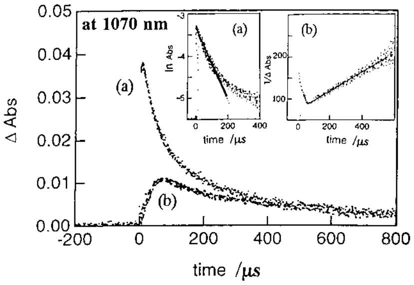


Figure 6. Decay profiles over long time scale of $C_{60}^{\bullet-}$ in the presence of equimolar $BN(OH)_2^{\bullet+}$ in benzonitrile; (a) in presence of Py (0.5 M) and (b) in absence of Py. Inset: (a) First-order plot in the presence of Py and (b) second-order plot in the absence of Py.

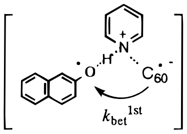
(1:1 in volume), the transient absorption spectra for C_{60}/NOH's/Py or C_{70}/NOH's/Py are similar to those in neat benzonitrile. The Φ_{et}^{T} values and k_{et} values are similar to the corresponding values in benzonitrile. In the absence of Py, on the other hand, the decays of $^3C_{60}^*$/$^3C_{70}^*$ and rises of $C_{60}^{\bullet-}$/$C_{70}^{\bullet-}$ are too slow to observed clearly, suggesting that the k_{et} values are far less than those in benzonitrile. This is reasonable on the basis of the Rehm−Weller curve,[20] in which the k_{et} values for fullerenes/NOH's/Py with sufficiently negative $\Delta G°$ are less sensitive toward a decrease in solvent polarity than those for fullerenes/NOH's with positive $\Delta G°$.[21]

In nonpolar solvents, such as benzene, neither the rise of $C_{60}^{\bullet-}$/$C_{70}^{\bullet-}$ nor the decay of $^3C_{60}^*$/$^3C_{70}^*$ was observed on the addition of $BN(OH)_2$ or 2-NOH, even in the presence of Py, indicating that electron transfer via $^3C_{60}^*$/$^3C_{70}^*$ does not occur.

Back Electron Transfer. Figure 6 shows the time profiles of $C_{60}^{\bullet-}$ on the long-time scale; $C_{60}^{\bullet-}$ begins to decay slowly after reaching each maximal concentration at 10−80 μs. This decay can be attributed mainly to the back electron transfer from $C_{60}^{\bullet-}$ to $BN(OH)^{\bullet+}$, because extra reactions such as an adduct formation were not observed by repeated 532 nm laser irradiation of C_{60}/C_{70} in solutions containing $BN(OH)_2$/2-NOH and Py. The back electron-transfer rate constants (k_{bet}^{2nd}) were evaluated from the decay time profiles of $C_{60}^{\bullet-}$/$C_{70}^{\bullet-}$, which obey second-order kinetics in the absence of Py. From the slope of the second-order plot in the inset of Figure 6, the k_{bet}^{2nd}/ϵ_A value was evaluated. The k_{bet}^{2nd} values were evaluated by substituting the reported ϵ_A values as listed in Table 1. In benzonitrile, the k_{bet}^{2nd} values are close to the diffusion controlled limit ($k_{diff} = 5.6 \times 10^9$ M^{-1} s^{-1} in benzonitrile),[18] which also supports that the solvated ion-radicals encounter after moving freely in the polar solution in the absence of Py (equation 5).

$$[\mathrm{NOH}]^{\bullet+}_{\mathrm{solvated}} + [\mathrm{C_{60}}]^{\bullet-}_{\mathrm{solvated}} \xrightarrow{k_{bet}^{2nd}} \mathrm{NOH} + \mathrm{C_{60}} \quad (5)$$

In the presence of Py, an interesting observation is that the initial part of the decay of $C_{60}^{\bullet-}$/$C_{70}^{\bullet-}$ obeys first-order kinetics, whereas the latter part seems to obey second-order kinetics (Figure 6). This suggests that the initial stage of back electron transfer takes place within the ion pairs.[7] Although benzonitrile is polar enough to solvate the ion radicals, Py plays a role to connect $C_{60}^{\bullet-}$/$C_{70}^{\bullet-}$ with $NOH^{\bullet+}$ as schematically illustrated below:



$$\xrightarrow{k_{\mathrm{diss}}} [\mathrm{NOH}]^{\bullet+}_{\mathrm{solvated}} + [\mathrm{C_{60}}]^{\bullet-}_{\mathrm{solvated}} + \mathrm{Py} \quad (6)$$

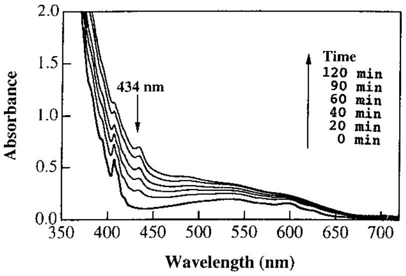


Figure 7. Steady-state photolysis in the UV−vis region of deaerated benzonitrile solution containing C_{60} (0.2 mM) and BN(OH)2 (3 mM) with light of l > 330 nm in the presence of Py (0.5 M).

In the latter stage, this type of complex may dissociate in to the free ion radicals; thus, the later part of the decay is consistent with the second-order back electron transfer in the absence of Py (see the k_{bet}^{2nd} values in Table 1). Comparing the k_{bet}^{1st} values of $BN(OH)_2$ with those of 2-NOH and $N(OH)_2$, the former is smaller than those of the latter (Table 1). This supports the conclusion that the ion pairs produced from fullerenes/$BN(OH)_2$/Py are looser than those of others due to the perpendicular two OH groups.

In the case of 2,3-$N(OH)_2$, the k_{bet}^{2nd} values are larger than k_{diff} for both C_{60} and C_{70} in the presence and absence of Py, which suggests that $C_{60}^{\bullet-}$ and $C_{70}^{\bullet-}$ are interacting with (2,3-$N(OH)_2)^{\bullet+}$ or more precisely with (2,3-$N(O^-)O^\bullet$−$(PyH^+)_2$). This type of interaction is characteristic to vicinal diol (2,3-$N(OH)_2$), but not distant diol (2,7-$N(OH)_2$) and perpendicular diol (BN-$(OH)_2$).

Steady-State Photolysis. When C_{60} was selectively excited with $\lambda > 400$ nm in the presence of $BN(OH)_2$ and Py (0.5 M) in deaerated benzonitrile, no spectral change was observed in steady-state UV/vis spectra. $BN(OH)_2^{\bullet+}$ (or $BN(O^-)O^\bullet$−$(PyH^+)_2$) produced by electron transfer via $^3C_{60}^*$ may return to $BN(OH)_2$ by back electron transfer with equimolar $C_{60}^{\bullet-}$. On the other hand, when short wavelength light ($\lambda > 330$ nm) was used to excite both C_{60} and $BN(OH)_2$, a spectral change was observed as shown in the steady-state UV−vis spectra (Figure 7). An increase in the absorbance at 434 nm clearly suggests a C_{60}-adduct formation.[22,23] In order to disclose the adduct structure, the CD spectra were measured after 90 min irradiation of a deaerated benzonitrile solution of C_{60} and an optically active $BN(OH)_2$ in the presence and absence of Py. However, no-CD signal was observed, which suggests that the adduct does not include an optically active $BN(OH)_2$ moiety. Probably, the adduct is H_2C_{60}. The structure analysis of the adduct by mass spectra was complicated, because of low yield. These findings indicate the importance of the direct irradiation of $BN(OH)_2$, from which H-atoms are generated followed by the addition to C_{60}. Surprisingly, no adduct formation was observed for C_{70} even by the direct irradiation of NOH's.

Conclusions

The efficiencies and rate constants of photoinduced electron transfer from 2-NOH, $N(OH)_2$'s and $BN(OH)_2$ to the excited triplet states of fullerenes were greatly increased on addition of Py. In both the presence and absence of Py, the Φ_{et}^{T} values were decreased on going from planar 2-NOH and $N(OH)_2$ to perpendicular $BN(OH)_2$. Addition of Py affects the mechanism of back electron transfer, suggesting that Py (or PyH^+) plays a role of bridging $C_{60}^{\bullet-}$/$C_{70}^{\bullet-}$ with $NOH^{\bullet+}$ (or $NO^\bullet$−PyH^+).

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References and Notes

(1) (a) Allemand, P. M.; Koch, A.; Wudl, F.; Rubin, Y.; Diederich, F.; Alvarez, M. M.; S. J. Anz, S. J.; Whetten, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 1050. (c) Dubois, D.; Kadish, K. M.; Flanagan, S.; Haufler, R. E.; Chibante, L. P. F.; Wilson, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 4364. (b) Hwang, K. C.; Mauzerall, D. *Nature* **1993**, *361*, 138.

(2) (a) Sension, R. J.; Szarka, A. Z.; Smith, G. R.; Hochstrasser, R. M. *Chem.* Phys. Lett. **1991**, *185*, 179. (b) Sension, R. J.; Phillips, C. M.; Szarka, A. Z.; Romanow, W. J.; Macghie, A. R.; McCauley, J. P.; Smith, A. B., III, Jr.; Hochstrasser, R. M. *J. Phys. Chem.* **1991**, *95*, 6075.

(3) (a) Arbogast, J. W.; Darmanyan, A. P.; Foote, C. S.; Robin, Y.; Diederich, F. N.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Phys. Chem.* **1991**, *95*, 11. (b) Arbogast, J. W.; Foote, C. S.; Kao, M. *J. Am. Chem. Soc.* **1992**, *114*, 2277. (c) Nonell, S.; Arbogast, J. W.; Foote, C. S. *J. Phys. Chem.* **1992**, *96*, 4169.

(4) (a) Biczok, L.; Linschitz, H.;. Walter, R. I. *Chem. Phys. Lett* **1992**, *195*, 339. (b) Steren, C. A.; van Willigen, H.; Biczok, L.; Gupta, N.; Linschitz, H. *J. Phys.* Chem. **1996**, *100*, 8920.

(5) (a) Palit, D. K.; Ghosh, H. N.; Pal, H.; Sapre, A. V.; Mittal, J. P.; Seshadri, R.; Rao, C. N. R. *Chem. Phys. Lett.* **1992**, *198*, 113. (b) Ghosh, H.; Pal, H.; Sapre, A. V.; Mittal, J. P. *J. Am. Chem. Soc.* **1993,** *115*, 11722.

(6) (a) Guldi, D. M.; Hungerbuhler, H.; Janata, E.; Asmus, K.-D.*J. Chem. Soc.*, Chem. Commun. **1993**, 84. (b) Guldi, D. M.; Hungerbuhler, H.; Janata, E.; Asmus, K.-D. *J. Phys. Chem. A*, **1993**, *97*, 11258. (c) Guldi, D. M.; Hungerbuhler, H.; Asmus, K.-D. *J. Phys. Chem.* **1995**, *99*, 13487. (d) Guldi, D. M.; Hungerbuhler, H.; Asmus, K.-D. *J. Phys. Chem.* **1995**, 99, 9380. (e) Guldi, D. M.; Asmus, K.-D. *J. Phys. Chem. A* **1997**, *101*, 1472. (f) Guldi, D. M.; Hungerbuhler, H.; Asmus, K.-D. *J. Phys. Chem. A* **1997**, *101*, 1783.

(7) (a) Ito, O.; Sasaki, Y.; Ysohikawa, Y.; Watanabe, A. *J. Phys. Chem*. **1995**, *99*, 9838. (b) Sasaki, Y.; Fujitsuka, M.; Watanabe, A.; Ito, O. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 4275.

(8) (a) Biczo'k, L.; Linschitz, H. *J. Phys. Chem*. **1995**, *99*, 1843. (b) Biczo'k, L.; Gupta, N.; Linschitz, H. *J. Am. Chem. Soc*. **1997**, *119*, 12601. (c) Gupta, N.; Linschitz, H., Biczo'k, L. *Fullerene Sci. Technol.* **1997**, *5*, 343.

(9) El-Kemary, M.; Fujitsuka, M.; Ito, O. *J. Phys. Chem*. A. **1999**, *103*, 1329.

(10) (a) Watanabe, A.; Ito, O. *J. Phys. Chem*. **1994**, *98*, 7736. (b) Konishi, T.; Sasaki, Y.; Fujitsuka, M.; Toba, Y.; Moriyama, H.; Ito, O. *J. Chem. Soc., Perkin Trans. 2* **1999**, 551.

(11) Kajii, Y.; Nakagawa, T.; Suzuki, S.; Achiba, Y.; Obi, K.; Shibuya, K. *Chem. Phys. Lett.* **1991**, *181*, 100.

(12) Ebbesen, T.; Tanigaki, K.; Kuroshima, S. *Chem. Phys. Lett.* **1991**, *181*, 501.

(13) Dimitrijevic, N. M.; Kamat, P. V. *J. Phys. Chem.* **1992**, *96*, 4811.

(14) (a) Kato, T.; Kodama, T.; Shida, T.; Nakagawa, T.; Matsui, Y.; Suzuki, S.; Shiromaru, H.; Yamauchi, K.; Achiba, Y. *Chem. Phys. Lett.* **1991**, *180*, 446. (b) Heath, G. A.; McGray, J. E.; Martin, R. *J. Chem. Soc., Chem. Commun.* **1992**, 1272.

(15) (a) Fraelich, R. M.; Weisman, R. B. *J. Phys. Chem.* **1993**, *97*, 11145. (b) Etheridge, H. T.; Weisman, R. B. *J. Phys. Chem.* **1995**, *99*, 278.2

(16) (a) Lawson, D. R.; Feldheim, D. L., Foss, C. A.; Dorhout, P. K.; Elliott, C. M.: Martin, C. R.; Parkinson, B. *J. Phys. Chem.* **1992**, *96*, 7175. (b) Hase, H.; Miyataka, Y. *Chem. Phys. Lett.* **1993**, *215*, 141. (c) Alam, M. M.; Watanabe, A.; Ito, O. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1833.

(17) Alam, M. M.; Watanabe, A.; Ito, O. *J. Photochem. Photobiol. A* **1997**, *104*, 59.

(18) Murov, S. L.; Carmichael, I.; Hig, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker: New York, 1993.

(19) Das, P. K.; Encinas, M. V.; Steenken, S.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 4166.

(20) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

(21) Luo, C.; Fujitsuka, M.; Huang, C.-H.; O. Ito, *J. Phys. Chem. A* **1998**, *102*, 8716.

(22) Lu, Q.; Schuster, D. I.; Wilson, S. R. *J. Org. Chem.* **1996**, *61*, 4764.

(23) Nakamura, Y.; Taki, M.; Tobita, S.; Shizuka, H.; Yokoi, H.; Ishiguro, K.; Sawaki, Y.; Nishimura, J. *J. Chem. Soc., Perkin Trans. 2* **1999**, 127.