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Energy transfer and electron transfer of photoexcited 5,6-open-azaC_{60} and 6,6-closed-azaC_{60} in the presence of retinyl polyenes: hydrogen-bonding effect

Mariko Yamazaki[a], Mamoru Fujitsuka[a], Osamu Ito[a,*], Atsushi Ikeda[b], Chie Fukuhara[b], Masaru Kawaguchi[b], Seiji Shinkai[b]

[a] Institute for Chemical Reaction Science, Tohoku University, Katahira, Aoba-ku, Sendai 980-8577, Japan
[b] Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Fukuoka 812-8581, Japan

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Abstract

Photoinduced energy transfer and electron transfer processes via the triplet state of 5,6-open-azaC_{60} (**2**) were compared with those of 6,6-closed-azaC_{60} (**3**) on the basis of kinetic data obtained by means of the transient absorption spectra. In nonpolar solvents such as toluene, energy transfer predominantly took place from the triplet states of **2** ($^{T}\mathbf{2}^*$) and **3** ($^{T}\mathbf{3}^*$) to retinol and β-carotene. The rate constant for energy transfer (k_{ent}) from $^{T}\mathbf{2}^*$ to retinol was significant different from that of $^{T}\mathbf{3}^*$. Furthermore, on the addition of methanol, the k_{ent} value of $^{T}\mathbf{2}^*$ for retinol was decreased, while no change was observed for that of $^{T}\mathbf{3}^*$. These findings suggest that retinol is connected with $^{T}\mathbf{2}^*$ via the hydrogen-bond, but not with $^{T}\mathbf{3}^*$. The decrease of the k_{ent} value of $^{T}\mathbf{2}^*$ by the addition of methanol suggests that retinol was replaced with methanol. In polar solvents such as benzonitrile, electron transfer took place from $^{T}\mathbf{2}^*/^{T}\mathbf{3}^*$; however, the difference in the electron transfer rate between $^{T}\mathbf{2}^*$ and $^{T}\mathbf{3}^*$ was not observed for retinol. This finding implies that the hydrogen-bond between $^{T}\mathbf{2}^*$ and retinol was not formed in benzonitrile, since retinol was strongly solvated by the solvent molecules. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Energy transfer; Electron transfer; Fullerenes; Hydrogen-bond

1. Introduction

Photophysical and photochemical properties of the pristine fullerenes C_{60} (**1**) have been intensively studied in this decade. It has been proved that the pristine fullerenes can be used as both photosensitizers and photoinduced electron transfer reagents [1–7]. In addition to the pristine fullerenes, the modifications of fullerenes with functional groups extend the wide variety of applications to material and life sciences [8–13]. In the previous papers [14,15], we showed that retinol and β-carotene are good electron donors in addition to the good energy acceptor for triplet excited C_{60}. It was also revealed that competition of energy transfer with electron transfer depends clearly on the solvent polarity.

In the preceding studies, 5,6-open-azaC_{60} (**2**) and 6,6-closed-azaC_{60} (**3**) were prepared [16–18]; it was found that alcohols such as methanol interact with the ground state of **2** via a hydrogen-bonding interaction (Fig. 1), but not with the ground state of **3**. Furthermore, the hydrogen-bonding interaction led the significant changes in the steady-state absorption spectra and the cyclic voltammogram of **2**. In the present paper, we studied how the hydrogen-bonding interaction with the excited state of **2** affects on the rates and efficiencies of energy and electron transfer.

2. Experimental

2.1. Materials

C_{60} (**1**; purity = 99.5%) was obtained from Term USA. 5,6-open-azaC_{60} (**2**) and 6,6-closed-azaC_{60} (**3**) were prepared as described in the previous papers [16–18]. Retinyl polyene, β-carotene, and triphenyl amine were purchased from Aldrich. Solvents used were the best grade available commercially.

2.2. Apparatus

Transient absorption spectra in the near-IR region were measured using a Ge-APD detector to monitor the light from

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* Corresponding author. Tel.: +81-22-217-5608; fax: +81-22-217-5610.
E-mail address: ito@icrs.tohoku.ac.jp (O. Ito).

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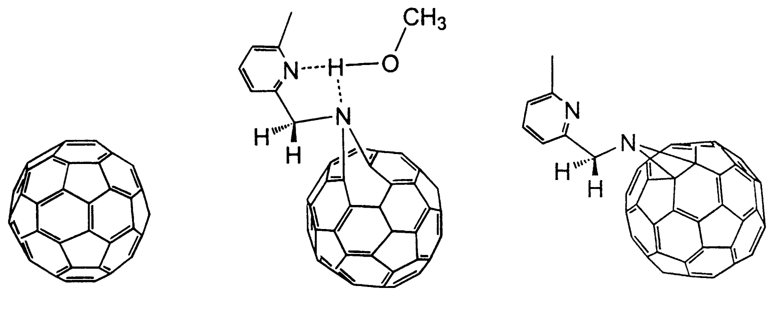


1 **2** **3**

Fig. 1. Molecular structures of C_{60} (**1**), 5,6-open-aza-C_{60} (**2**) and 6,6-closed aza-C_{60} (**3**). Hydrogen-bond with alcohols is possible with **2**, but not with **3** [18].

pulsed Xe-lamp (150 W) after the excitation with light at 532 nm from a Nd:YAG laser (6 ns fwhm). For spectra in the visible region, a photomultiplier tube and a Si-PIN photodiode were used as the detector of the continuous Xe-monitor light (150 W) and pulsed Xe-light, respectively.

Time-resolved fluorescence spectra were measured by a single-photon counting method using SHG (410 nm) of a Ti:sapphire laser (Spectra Physics, Tsunami 3950-L2s, 1.5 ps fwhm) and a streak-scope (Hamamatsu Photonics, C4334-01) equipped with a polychromator.

Steady-state absorption and fluorescence spectra in Vis/near-IR region were measured with a JASCO V-570DS spectrophotometer and a Shimadzu RF-5300 PC spectrofluorophotometer, respectively, at room temperature.

All samples in a quartz cell (1 cm × 1 cm) were deaerated by bubbling with Ar through the solution for 10 min for both steady and transient measurements.

3. Results and discussion

3.1. Steady-state absorption spectra

UV/Visible spectra of **2** and **3** in toluene are shown in Fig. 2, in which absorption bands were observed at 410 nm and in 500–600 nm, in addition to 340 nm band. On the addition of methanol (16 mM), the absorption intensity of **2** increased in the shorter wavelength region than 650 nm, while appreciable change was not observed for **3**.

3.2. Steady-state and time-resolved fluorescence measurements

Steady-state fluorescence spectra of **2** and **3** are shown in Fig. 3. The fluorescence peaks in 700–800 nm region may be corresponding to the absorption band in 500–650 nm. In the case of **2**, the fluorescence peak around 740 nm in toluene increased on the addition of methanol (16 mM), while such change was not observed for **3**.

The lifetimes of fluorescence (τ_F) were evaluated as shown in inserted time-profiles in Fig. 3. Each decay time-profile was fitted with a single exponential, yielding $\tau_F = 1.0$ ns for **2**, which is slightly shorter than that of **1** ($\tau_F = 1.3$ ns) [19–21]. The τ_F of **2** becomes shorter in the presence of methanol ($\tau_F = 0.8$ ns). Considering that the hydrogen-bonding interaction between the ground state of **2** and methanol affects the ground state properties of **2** [18], this finding indicates that **2** interacts with methanol in the singlet excited state via the hydrogen-bond.

3.3. Transient absorption spectra in toluene

The transient absorption spectra observed by the ns-laser photolysis of **2** in toluene are shown in Fig. 4. The transient absorption band at 760 nm can be attributed to the triplet state of **2** (^{T}**2***), because of the similarity of the triplet–triplet

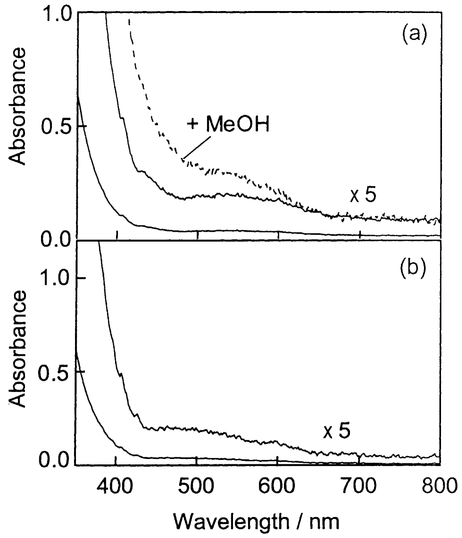


Fig. 2. Steady-state absorption spectra of (a) **2** (0.02 mM) in the absence (solid line) and presence (dashed line) of methanol (16 mM) in toluene and (b) **3** (0.06 mM) in toluene; in (b), spectrum in the presence of methanol (16 mM) is identical with that in the absence of methanol.

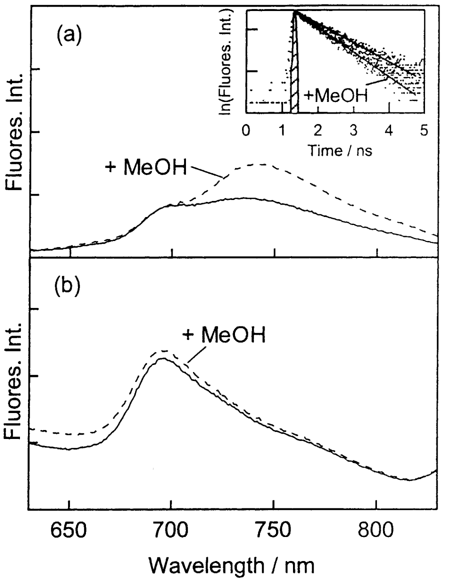


Fig. 3. Steady-state fluorescence spectra of (a) **2** (0.02 mM) and (b) **3** (0.06 mM) in the absence (solid line) and presence (dashed line) of methanol (16 mM) in toluene. Inset: ln(fluorescence intensity) vs. time at 750 nm in the absence and presence of methanol (16 mM).

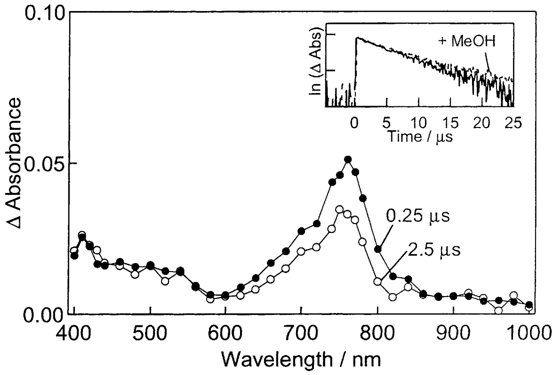


Fig. 4. Transient absorption spectra observed by the excitation of **2** (0.04 mM) with 532 nm-laser light in deaerated toluene. Inset: decay time-profiles at 760 nm in the absence (solid line) and presence (dashed line) of methanol (16 mM).

bands to the other fullerene derivatives [22,23]. For **3**, similar transient spectra were also observed, showing the main peak at 760 nm, which can be attributed to the triplet state of **3** ($^{T}\mathbf{3}^{*}$). The decay behavior of $^{T}\mathbf{2}^{*}$ and $^{T}\mathbf{3}^{*}$ obey a single exponential in dilute solution, yielding the lifetimes of the triplet states (τ_T) as listed in Table 1. On the addition of methanol (16 mM), appreciable shift of the absorption peak of $^{T}\mathbf{2}^{*}$ was not observed, while the decay rate was slightly slowed down in the presence of methanol (Table 1). No addition effect of methanol on the decay rate was observed for $^{T}\mathbf{3}^{*}$. These findings indicate that **2** also interacts with methanol in the triplet excited state via the hydrogen-bond, which is the same as the singlet excited state. The τ_T value is more sensitive to the hydrogen-bond than the peak and shape of the triplet–triplet absorption band.

As for the methanofullerene derivatives, it has been reported that 5,6-open fulleroid is converted photochemically into 6,6-closed methanofullerene by irradiation using an Ar ion laser [24]. However, in this work, the photochemical conversion from 5,6-open isomer (**2**) to 6,6-closed isomer (**3**) was not observed by repeated photoirradiation of a Nd:YAG laser (532 nm), because the steady-state absorption spectra were unchanged before and after the transient absorption measurements.

3.4. Energy transfer in toluene

Fig. 5(a) shows the transient absorption spectra obtained by the excitation of **2** with 532 nm-laser light in the presence of *all-trans*-retinol in toluene. Retinol is a kind of alcohol; therefore, there is a possibility that the hydrogen-bond is formed between **2** and retinol. However, the hydrogen-bonding interaction between the ground state of **2** and retinol was scarcely observed in the steady-state absorption spectra. This result implies that the hydrogen-bond is scarcely formed between the ground state of **2** and retinol. The transient absorption band of $^{T}\mathbf{2}^{*}$ decayed quickly with concomitant rise of the absorption at 420 nm, which can be attributed to the triplet state of retinol (^{T}retinol*) [25,26]. No evidence for electron transfer was found in nonpolar toluene, since the absorption band of the cation radical of retinol (retinol$^{\bullet+}$) was not found around 600 nm [27–29] at all. Thus, it is revealed that energy transfer from $^{T}\mathbf{2}^{*}$ to retinol takes place predominantly in toluene. Similar

Table 1
Fluorescence lifetimes (τ_F), and lifetimes (τ_T), energy levels (E_T) and molar extinction coefficients (ε_T) of the triplet states of **2** and **3**

Fullerene	Solvent[a]	τ_F (s)	τ_T (s)	E_T (eV)[b]	ε_T ($M^{-1}\,cm^{-1}$)[c]
2	Tol	1.0×10^{-9}	7.0×10^{-6}	1.50	2.45×10^{4}
	Tol + MeOH[d]	0.8×10^{-9}	8.7×10^{-6}	–	–
3	Tol	–	8.9×10^{-6}	1.52	2.3×10^{4}
	Tol + MeOH[d]	–	8.8×10^{-6}	–	–

[a] Tol: toluene; MeOH: methanol.

[b] From the Sandros equation for the k_{ent}^{2nd} values in the case of retinol [32].

[c] The ε_T values of $^{T}\mathbf{2}^{*}$ and $^{T}\mathbf{3}^{*}$ were determined by the comparison with that of retinol ($\varepsilon_T = 5.75 \times 10^{4}\,M^{-1}\,cm^{-1}$) [25,26].

[d] [MeOH] = 16 mM.

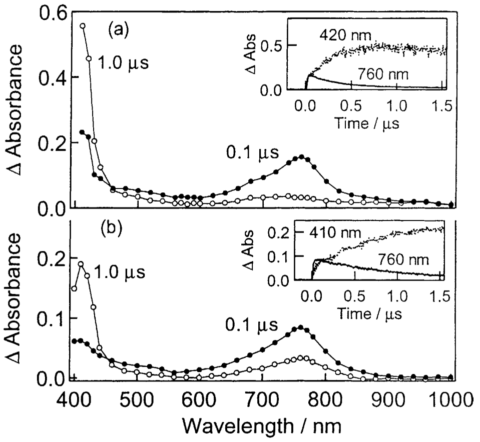


Fig. 5. Transient absorption spectra observed by the excitation of (a) **2** (0.12 mM) and (b) **3** (0.05 mM) with 532 nm-laser light in the presence of retinol ((a) 2.8 mM and (b) 2.1 mM) in deaerated toluene. Inset: Absorption time-profiles for the decays of the triplet states of (a) **2** and (b) **3**, and the rise of the triplet state of retinol.

Table 2
Rate constants (k_{ent}^{2nd}) for energy transfer

Acceptor	Fullerene	Solvent[a]	k_{ent}^{2nd} ($M^{-1}\,s^{-1}$)[b]
Retinol	**2**	Tol	(1.5×10^9)[c]
		Tol + MeOH[d]	3.9×10^8
	3	Tol	4.8×10^8
		Tol + MeOH[d]	5.4×10^8
β-Carotene	**2**	Tol	4.6×10^9
		Tol + MeOH[d]	5.7×10^9
	3	Tol	6.5×10^9
		Tol + MeOH[d]	7.2×10^9
Retinoic acid	**2**	BN	1.6×10^9
	3	BN	1.6×10^9

[a] BN: benzonitrile.

[b] Since the Φ_{ent} values are in unity in these cases, the relation of $k_q^T = k_{ent}^{2nd}$ was employed.

[c] $k_{ent}^{1st} = 1.0 \times 10^7\ s^{-1}$. At low concentration region of retinol, energy transfer can be treated as the bimolecular reaction, $k_{ent}^{2nd} = k_h$.

[d] [MeOH] = 16 mM.

transient absorption spectra and the time-profiles were also observed for $^{T}\mathbf{3}^{*}$ as shown in Fig. 5(b).

These findings indicate that the lowest energies of the triplet states (E_T) of **2** and **3** are higher than that of retinol ($E_T = 1.45$ eV) [30], but probably similar to that of **1** ($E_T = 1.51$ eV) [31]. Transient absorption measurements were carried out not only for retinol, but also for β-carotene and *all-trans*-retinoic acid. Energy transfer from $^{T}\mathbf{2}^{*}/^{T}\mathbf{3}^{*}$ to β-carotene ($E_T = 0.90$ eV) [30] was also predominantly observed in toluene. β-Carotene does not have the OH substituent; it is impossible to form the hydrogen-bond with **2**. Thus, β-carotene can be adopted as a standard compound of energy transfer. In the case of retinoic acid ($E_T = 1.28$ eV) [30], only energy transfer was observed even in polar benzonitrile, in which retinol and β-carotene have shown the photoinduced electron transfer to $^{T}\mathbf{1}^{*}$ [14,15].

Each decay of $^{T}\mathbf{2}^{*}/^{T}\mathbf{3}^{*}$ in the presence of retinyl polyenes obeys first-order kinetics under the conditions of $[^{T}\mathbf{2}^{*}]/[^{T}\mathbf{3}^{*}] \ll$ [retinyl polyenes], yielding the first-order rate constants (k_{obs}). The relation of k_{obs} vs. [retinol] for $^{T}\mathbf{2}^{*}$ shows a curvature as shown in Fig. 6(a) (solid line), while the k_{obs} values for $^{T}\mathbf{3}^{*}$–retinol and $^{T}\mathbf{2}^{*}/^{T}\mathbf{3}^{*}$–β-carotene increase linear with [retinyl polyenes] (Fig. 6(b), solid line). From these results, it is expected that the hydrogen-bond between $^{T}\mathbf{2}^{*}$ and retinol may be formed, which influences energy transfer kinetics. In other words, the hydrogen-bond does not exist for $^{T}\mathbf{3}^{*}$–retinol and $^{T}\mathbf{2}^{*}/^{T}\mathbf{3}^{*}$–β-carotene.

To confirm the hydrogen-bonding effect on energy transfer, methanol (16 mM) was added as a hydrogen-bond competitor. On the addition of methanol, the k_{obs} value for $^{T}\mathbf{2}^{*}$ decreased drastically as shown in Fig. 6(a) (dotted line), but no effect on that of $^{T}\mathbf{3}^{*}$ (Fig. 6(b), dotted line). For β-carotene, the k_{obs} values of both $^{T}\mathbf{2}^{*}$ and $^{T}\mathbf{3}^{*}$ were not appreciably changed on addition of methanol, indicating that the observed methanol-addition effect on the k_{obs} value for $^{T}\mathbf{2}^{*}$–retinol is not caused by the solvent polarity change. These findings support the hydrogen-bond formation between $^{T}\mathbf{2}^{*}$ and retinol.

In the absence of the hydrogen-bond system, to which $^{T}\mathbf{3}^{*}$–retinol and $^{T}\mathbf{2}^{*}/^{T}\mathbf{3}^{*}$–β-carotene belong, the bimolecular quenching rate constants (k_q^T) were evaluated from the pseudo-first-order plots as summarized in Table 2. Usually,

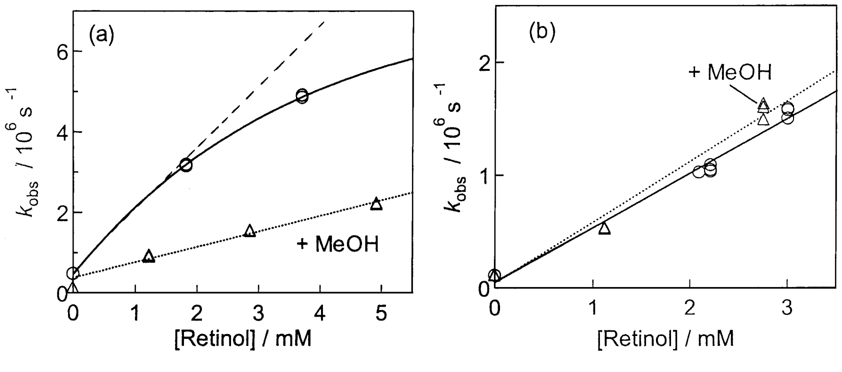
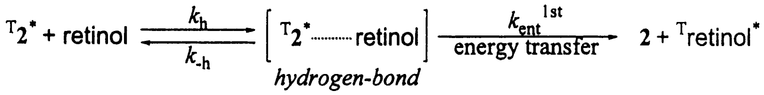


Fig. 6. Pseudo-first-order plots for (a) **2** and (b) **3** for the decay of 760 nm with the increase of the concentration of retinol in the absence and presence of methanol (16 mM) in deaerated toluene.



Scheme 1.

since it is safely assumed that the quantum yield of energy transfer is unity, these $k_q{}^{T}$ values can be put equal to the second-order rate constants for energy transfer ($k_{ent}{}^{2nd}$).

However, when energy transfer occurs via the hydrogen-bond formation, to which $^{T}\mathbf{2}^{*}$–retinol belongs, the reaction should be treated as Scheme 1.

Thus, it is unsuitable for $^{T}\mathbf{2}^{*}$–retinol to treat as the bimolecular reaction as the above. From Scheme 1, the relation between k_{obs} and [retinol] is derived (Eq. (1)).

$$\frac{1}{k_{obs}} = \frac{1}{k_{ent}{}^{1st}} + \frac{1}{Kk_{ent}{}^{1st}[\text{retinol}]} \tag{1}$$

On applying Eq. (1), the $k_{ent}{}^{1st}$ value is evaluated from the plot of $1/k_{obs}$ vs. 1/[retinol] to be $1.0 \times 10^{7}\,\mathrm{s^{-1}}$, and the K ($=k_h/k_{-h}$) value is also evaluated to be $253\,\mathrm{M^{-1}}$. At low concentration region of retinol, since the formation of the hydrogen-bond (k_h) is the rate-determining step, energy transfer can be treated as the bimolecular reaction; therefore the relation of $k_h = k_{ent}{}^{2nd}$ is applied to the $^{T}\mathbf{2}^{*}$–retinol system. From the slope in the low concentration region of retinol showing linearity in Fig. 6(a) (dashed line), the $k_{ent}{}^{2nd}$ value can be obtained to be $1.5 \times 10^{9}\,\mathrm{M^{-1}\,s^{-1}}$, which is larger than that of $^{T}\mathbf{3}^{*}$ ($4.8 \times 10^{8}\,\mathrm{M^{-1}\,s^{-1}}$) by 2.5-fold, while for β-carotene, the $k_{ent}{}^{2nd}$ values of $^{T}\mathbf{2}^{*}$ ($4.6 \times 10^{9}\,\mathrm{M^{-1}\,s^{-1}}$) and $^{T}\mathbf{3}^{*}$ ($6.5 \times 10^{9}\,\mathrm{M^{-1}\,s^{-1}}$) are almost equal. It is predicted that the $k_{ent}{}^{2nd}$ value in the presence of the hydrogen-bond is larger than that in the absence; accordingly the difference in the $k_{ent}{}^{2nd}$ value between $^{T}\mathbf{2}^{*}$ and $^{T}\mathbf{3}^{*}$ is a reasonable result.

As listed in Table 2, on the addition of methanol, the $k_{ent}{}^{2nd}$ value of $^{T}\mathbf{2}^{*}$–retinol ($3.9 \times 10^{8}\,\mathrm{M^{-1}\,s^{-1}}$) decreases to one-third of that in the absence of methanol, and becomes almost equal to that of $^{T}\mathbf{3}^{*}$–retinol ($5.4 \times 10^{8}\,\mathrm{M^{-1}\,s^{-1}}$). These results suggest that the hydrogen-bond between $^{T}\mathbf{2}^{*}$ and retinol is hindered by methanol. It has been reported that the interaction of **2** with alcohol is significantly influenced by the steric bulkiness in the guest compounds [18]; therefore, **2** is considered to form the hydrogen-bond more favorable with methanol than retinol. Consequently, retinol may be replaced by methanol as shown in Scheme 2. On this view, in the presence of methanol, energy transfer for $^{T}\mathbf{2}^{*}$–retinol can be regarded as the bimolecular reaction similar to $^{T}\mathbf{3}^{*}$–retinol.

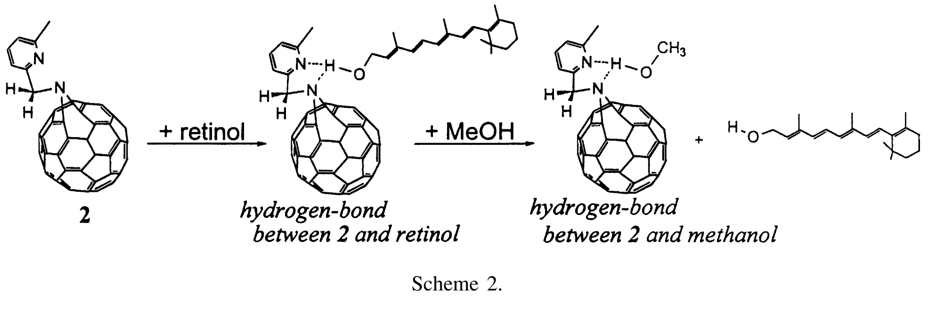
In the case of retinoic acid, although the hydrogen-bond with $^{T}\mathbf{2}^{*}$ would be anticipated, no difference in the $k_{ent}{}^{2nd}$ value between $^{T}\mathbf{2}^{*}$ and $^{T}\mathbf{3}^{*}$ was observed in benzonitrile. Since benzonitrile is a highly polar solvent, retinoic acid may be solvated by benzonitrile molecules; as a result, the hydrogen-bond formation becomes difficult for $^{T}\mathbf{2}^{*}$ and retinoic acid.

Using these $k_{ent}{}^{2nd}$ values for retinol, the E_T values of $^{T}\mathbf{2}^{*}$ and $^{T}\mathbf{3}^{*}$ were estimated to be 1.50 and 1.52 eV, respectively, from the Sandros equation [32]. The E_T value of $^{T}\mathbf{2}^{*}$ is slightly lower than that of $^{T}\mathbf{3}^{*}$. The same tendency was reported for the other open-aza fulleroid and closed-aza fullerene in the literature [33].

The molar extinction coefficients (ε_T) of the triplet–triplet transitions of $^{T}\mathbf{2}^{*}$ and $^{T}\mathbf{3}^{*}$ were also evaluated on the comparison with the observed absorbance of retinol and the reported ε_T for ^{T}retinol* [25,26] as listed in Table 1.

3.5. Electron transfer in benzonitrile

The transient absorption spectra obtained by the 532 nm-laser excitation of **3** in the presence of triphenyl amine (TPA), which is a typical electron donor in benzonitrile, are shown in Fig. 7. With the decay of $^{T}\mathbf{3}^{*}$ at 760 nm, the new absorption bands appeared at 1060 and 670 nm. The new absorption band at 1060 nm is ascribed to the anion radical of **3** ($\mathbf{3}^{\bullet-}$) from the similarity to those of the other fullerene derivatives [22,34]. And the absorption band at 670 nm is ascribed to the cation radical of TPA ($\mathrm{TPA}^{\bullet+}$) [35]. These findings indicate that electron transfer takes place from TPA to $^{T}\mathbf{3}^{*}$, producing $\mathbf{3}^{\bullet-}$ and $\mathrm{TPA}^{\bullet+}$. For $^{T}\mathbf{2}^{*}$–TPA, similar transient spectra and time-profiles were observed. For electron transfer, TPA is adopted as a standard compound, since TPA cannot form the hydrogen-bond with **2**.



2

hydrogen-bond between 2 and retinol

hydrogen-bond between 2 and methanol

Scheme 2.

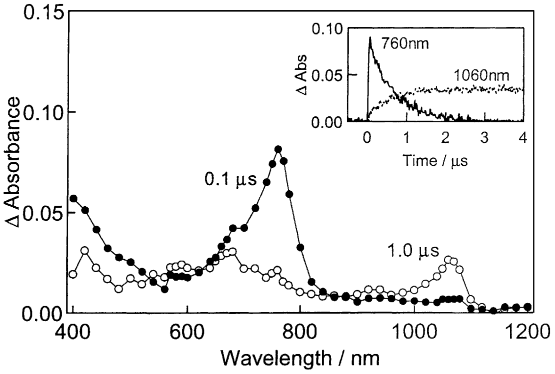


Fig. 7. Transient absorption spectra observed by the excitation of **3** (0.1 mM) with 532 nm-laser light in the presence of TPA (1.1 mM) in deaerated benzonitrile. Inset: Absorption time-profiles for the decay of the triplet state of **3** at 760 nm and the rise of the radical anion of **3** at 1060 nm.

The decay rates of $^{T}\mathbf{2}^{*}$ increase linearly with the concentration of TPA as well as $^{T}\mathbf{3}^{*}$. The rate constant ($k_q{}^{T}$) evaluated from the decay of $^{T}\mathbf{3}^{*}$ is almost identical with the rise of $3^{\bullet -}$ as shown in the inserted time-profiles in Fig. 7. The $k_q{}^{T}$ values for electron transfer systems are listed in Table 3, in which the $k_q{}^{T}$ value for $^{T}\mathbf{2}^{*}$–TPA is almost same as that for $^{T}\mathbf{3}^{*}$–TPA in benzonitrile. This finding implies that there are no appreciable differences between $^{T}\mathbf{2}^{*}$ and $^{T}\mathbf{3}^{*}$ in the electron transfer properties.

In the case of retinol, the transient absorption spectral changes observed in benzonitrile are shown in Fig. 8. The sharp band at 610 nm and weak band at 940 nm observed after the decays of $^{T}\mathbf{2}^{*}$ and $^{T}\mathbf{3}^{*}$ were attributed to retinol$^{\bullet +}$. The absorption bands at 1060 nm were attributed to $\mathbf{2}^{\bullet -}$ and $\mathbf{3}^{\bullet -}$. In addition to these absorption bands due to the ion radicals, new absorption band showing rise was observed at 420 nm, which was already attributed to ^{T}retinol* as shown in Fig. 5, indicating that energy transfer takes place even in polar solvents simultaneously with electron transfer.

If $^{T}\mathbf{2}^{*}$ is connected with retinol via the hydrogen-bond in benzonitrile, the relation of k_{obs} vs. [retinol] should show a curvature as observed in toluene. However, as for benzonitrile, the k_{obs} values for $^{T}\mathbf{2}^{*}$ showed a good linear correlation with [retinol] as well as $^{T}\mathbf{3}^{*}$; therefore, it is presumed that the hydrogen-bond between $^{T}\mathbf{2}^{*}$ and retinol is not formed in benzonitrile. On this postulate, since electron and energy transfer for $^{T}\mathbf{2}^{*}$–retinol may be treated as the bimolecular reaction, which is the same as $^{T}\mathbf{3}^{*}$–retinol, the $k_q{}^{T}$ value was evaluated from the pseudo-first-order plot. Furthermore, for such systems, it is necessary to evaluate the quantum yields for electron transfer (Φ_{elt}) via the triplet states of fullerenes. The Φ_{elt} values were calculated from the ratios of the maximal concentrations of retinol$^{\bullet +}$ to the initial concentrations of the triplet states of fullerenes at sufficiently high concentrations of the electron donors. On employing the ε_T values of $^{T}\mathbf{2}^{*}$ and $^{T}\mathbf{3}^{*}$ in Table 1 and the reported ε_C value for retinol$^{\bullet +}$ [25–27], the Φ_{elt} values were evaluated as listed in Table 3. Comparing the Φ_{elt} and k_{elt} values of $^{T}\mathbf{2}^{*}$ with those of $^{T}\mathbf{3}^{*}$, there are no appreciable differences, which is the same result as TPA.

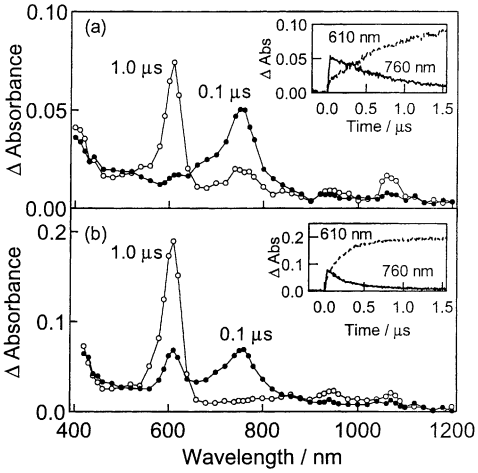


Fig. 8. Transient absorption spectra observed by the excitation of (a) **2** (0.05 mM) and (b) **3** (0.12 mM) with 532 nm-laser light in the presence of retinol ((a) 1.2 mM and (b) 6.2 mM) in deaerated benzonitrile. Inset: Absorption time-profiles for the decays of the triplet states of (a) **2** and (b) **3**, and the rise of the radical cation of retinol at 610 nm.

The quantum yields for energy transfer (Φ_{ent}) via the triplet states of fullerenes can be evaluated similarly from [^{T}retinol*]/[$^{T}\mathbf{2}^{*}$] and [^{T}retinol*]/[$^{T}\mathbf{3}^{*}$] on the basis of reported ε_T value for ^{T}retinol*. As for energy transfer, no appreciable difference in the Φ_{ent} and k_{ent} values between

Table 3
Rate constants and quantum yields for electron transfer and energy transfer in benzonitrile

Donor	Fullerene	Solvent	$k_q{}^{T}$ (M^{-1} s^{-1})	Φ_{elt}	k_{elt} (M^{-1} s^{-1})^{a}	Φ_{ent}	k_{ent} (M^{-1} s^{-1})^{b}	k_{belt} (M^{-1} s^{-1})
Retinol	**2**	BN	6.0×10^{8}	0.30	1.8×10^{8}	0.29	1.7×10^{8}	2.6×10^{10}
		BN + MeOH^{c}	7.8×10^{8}	0.39	3.0×10^{8}	0.27	2.1×10^{8}	–
	3	BN	5.2×10^{8}	0.46	2.4×10^{8}	0.34	1.8×10^{8}	2.1×10^{10}
		BN + MeOH^{c}	4.3×10^{8}	0.46	2.0×10^{8}	0.34	1.5×10^{8}	–
TPA	**2**	BN	1.3×10^{9}	0.71	9.0×10^{8}	–	–	2.2×10^{10}
	3	BN	1.4×10^{9}	0.93	1.3×10^{9}	–	–	1.7×10^{10}

[a] The k_{elt} values evaluated from the relation of $k_{elt} = \Phi_{elt} k_q{}^{T}$.
[b] The k_{ent} values evaluated from the relation of $k_{elt} = \Phi_{elt} k_q{}^{T}$.
[c] [MeOH] = 16 mM.

^{T}**2*** and ^{T}**3*** is observed, which is the same result as β-carotene. These findings indicate that the hydrogen-bond is not formed between ^{T}**2*** and retinol in benzonitrile. For this reason, the solvation by benzonitrile molecules must be considered as observed in the ^{T}**2***–retinoic acid system. Besides, the sums of Φ_{elt} and Φ_{ent} are less than unity, which implies that other deactivation processes such as exciplex formation and collisional deactivation of ^{T}**2*** and ^{T}**3*** are present. In such case, it is difficult to evaluate the effect of the hydrogen-bonding interactions on electron and energy transfer exactly. Although electron and energy transfer were observed in the presence of methanol, considerable changes were not obtained for ^{T}**2***–retinol as well as ^{T}**3***–retinol. It is clear that the hydrogen-bond formation is hard for methanol in polar solvent; therefore, methanol does not influence both ^{T}**2***–retinol and ^{T}**3***–retinol.

For TPA system, the Φ_{elt} values were calculated similarly from the ratios of [TPA$^{\bullet+}$]/[^{T}**2***] and [TPA$^{\bullet+}$]/[^{T}**3***] on employing the reported ε_{C} value for TPA$^{\bullet+}$ [32]. As the Φ_{elt} values are not unity, some deactivation processes of ^{T}**2*** and ^{T}**3*** may also exist for TPA similar to retinol.

Furthermore, the Φ_{elt} values of ^{T}**3*** are slightly higher than those of ^{T}**2*** in both retinol and TPA systems as listed in Table 3. Since the reduction potential of **3** is slightly more positive than that of **2** [18], reduction of **3** is easier than that of **2**; therefore, electron transfer occurred more efficiency in the ^{T}**3***–donor systems.

3.6. Back electron transfer in benzonitrile

After reaching maximum absorbance, the absorption intensities of the ion radicals begin decaying in the long time-scale measurements (Fig. 9). In the case of TPA$^{\bullet+}$ (Fig. 9(a)), the second-order plot (reciprocal of absorbance vs. time) gives a straight line, indicating that TPA$^{\bullet+}$ decays with second-order kinetics, which may indicate that back electron transfer (k_{belt}) takes place between the free radical ions; i.e., from **2**$^{\bullet-}$ and **3**$^{\bullet-}$ to TPA$^{\bullet+}$. The slopes of the second-order decay plots give $k_{\mathrm{belt}}/\varepsilon_{\mathrm{C}}$, where ε_{C} is molar extinction coefficient of TPA$^{\bullet+}$ at 670 nm. The k_{belt} values are close to the diffusion controlled limit as listed in the last column of Table 3.

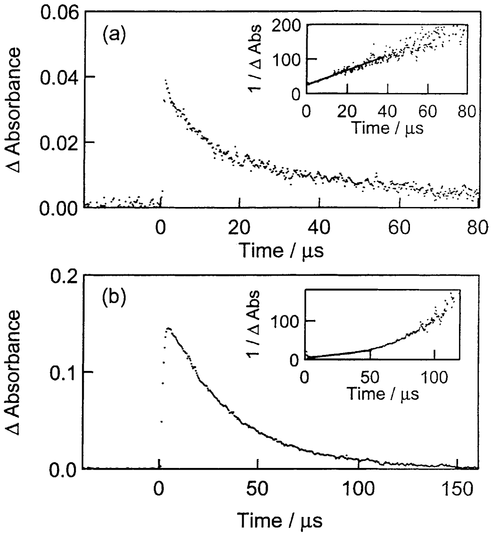


Fig. 9. Decay time-profiles in long time-scale in benzonitrile (a) at 670 nm for **2** and TPA and (b) at 610 nm for **2** and retinol. Inset: Second-order plots.

For retinol, a whole decay of retinol$^{\bullet+}$ does not obey second-order kinetics in the long time-scale measurements; from the initial linear part, the k_{belt} values close to the diffusion controlled limit were evaluated as listed in Table 3. In the latter part, the decay rate of retinol$^{\bullet+}$ seems to be accelerated, suggesting that the intramolecular reactions of retinol$^{\bullet+}$ such as cyclization take place.

4. Conclusion

The hydrogen-bonding interaction of the excited state of **2** with methanol has been confirmed by the fluorescence and T–T absorption measurements. In nonpolar toluene, an appreciable decrease in the energy transfer rate from ^{T}**2*** to retinol was observed on the addition of methanol, but not for ^{T}**3***, which indicates the hydrogen-bonding interaction between ^{T}**2*** and retinol. In electron transfer rate constant in polar benzonitrile, such a clear tendency was not observed, since retinol may be strongly solvated by benzonitrile molecules, and the deactivation processes of ^{T}**2*** and ^{T}**3*** other than electron transfer are present.

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