Account / Revue

Photoinduced electron-transfer and magnetic field effects on the dynamics of the radical pair in a C_{60} cluster–phenothiazine system

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Abstract

Photoinduced electron-transfer and magnetic field effects in clusters of C_{60} derivative ($C_{60}N^+$)–methylphenothiazine (**MePH**) system were investigated. Clusters of $C_{60}N^+$ were prepared by solving in THF–H_2O mixed solvent. Diameters of the clusters were estimated to be ca. 100 nm by using of dynamic light scattering and AFM measurements. Transient absorption spectra of the clusters of $C_{60}N^+$–**MePH** system following laser excitation at 355 nm indicate that photoinduced intermolecular electron-transfer from the triplet excited state of phenothiazine (PH) to C_{60} cluster occur. The yield of the escaped radical of PH increased with increase of magnetic field. The magnetic field effects suggest the generation of triplet radical pair. *To cite this article: H. Yonemura et al., C. R. Chimie 9 (2006).*
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Résumé

Le transfert photo-induit des électrons et les effets de champ magnétique dans le système clusters de C_{60} dérivés ($C_{60}N^+$)–méthylphénothiazine (**MePH**) ont été étudiés. Les clusters de $C_{60}N^+$ ont été préparés par dissolution dans le solvant mixte THF–H_2O. Le diamètre des clusters a été estimé, par mesure de diffusion dynamique de la lumière et AFM, comme étant de l'ordre de 100 nm. Les spectres d'absorption transitoire du système clusters de $C_{60}N^+$–**MePH** obtenus par excitation laser à 355 nm indiquent que le transfert intermoléculaire photo-induit des électrons s'effectue depuis l'état triplet excité de la phénothiazine (PH) vers le cluster C_{60}. Le rendement de formation du radical de la phénothiazine augmente avec le champ magnétique. Les effets de champ magnétique suggèrent la génération d'une paire radicalaire triplet. *Pour citer cet article : H. Yonemura et al., C. R. Chimie 9 (2006).*
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1. Introduction

Recently, photochemical and photoelectrochemical properties of fullerene (C_{60}) have been widely studied [1]. Photoinduced electron-transfer reactions of donor-C_{60} linked molecules have been also reported [1–7]. In a series of donor-C_{60} linked systems, some of the compounds show novel properties, which accelerate photoinduced charge separation and decelerate charge recombination [3–5]. Those properties have been explained by the remarkably small reorganization energy in their electron-transfer reactions. The porphyrin-C_{60} linked compounds, where the porphyrin moieties act as both donors and sensitizers, have been extensively studied [3–5].

It has been reported that C_{60} and its derivatives formed optically transparent microscopic clusters in mixed solvents [8,9]. The clustering behavior of C_{60} is mainly associated with the strong three-dimensional hydrophobic interactions between the C_{60} units. Photoinduced electron-transfer and photoelectrochemical reactions using the C_{60} clusters have been extensively reported because of the interesting properties of C_{60} clusters [8,9].

Magnetic field effects (MFEs) on the reaction kinetics or yields of photochemical reactions in the condensed phase have been studied [10–13]. The MFEs have been powerful for verifying the mechanism of photochemical reactions. Previously, we have obtained photogenerated triplet biradicals of donor–acceptor linked compounds, and found that the lifetimes of the biradicals are remarkably extended in the presence of magnetic fields up to 1 T with electromagnet [14–20].

High MFEs on the dynamics of radical pairs or biradicals generated by photochemical reactions have been extensively investigated to establish the measurement of MFEs under high magnetic fields above 1 T [12,13,21–29]. The reverse phenomena in the MFEs have been reported in some radical pairs or biradicals. The reverse phenomena of the MFEs on the lifetime, in the linked biradicals, have been observed only in high magnetic fields above 1 T [23–28].

As to the MFEs in donor-C_{60} linked systems, C_{60} has interesting properties. First, C_{60} has no magnetic nuclei based on hydrogen, and thus there are little hyperfine interactions due to the C_{60} radical contributing to the MFEs. Second, C_{60} is a highly symmetric molecule, and therefore anisotropic Zeeman interaction, due to the C_{60} radical, is very small. Third, the g-value

($g = 1.9982$) [30] of C_{60} is smaller than that of the donor radical such as phenothiazine cation radical ($g = 2.0052$) [31]. Therefore, the difference of g-values between the donor and C_{60} is expected to be large. On the basis of the three points, the MFEs in various donor-C_{60} linked compounds are expected to provide useful information for studying the spin chemistry of C_{60}. From these considerations, we recently examined photoinduced electron-transfer reactions and MFEs on the photogenerated biradicals in phenothiazine (Ph)-C_{60} linked compounds and found the MFEs on the triplet biradicals which were photogenerated from intramolecluar electron-transfer reactions from the Ph to the triplet excited state of C_{60} ($^3C_{60}^*$) in benzonitrile [16–18]. In addition, we have also investigated the MFEs on the photogenerated biradical in a zinc-tetraphenylporphyrin (ZnP)-C_{60} linked compound. The MFEs verified that the triplet biradicals were generated by the intramolecular electron-transfer from the triplet excited state of ZnP to C_{60} and/or from ZnP to $^3C_{60}^*$ in benzonitrile. Especially, the reverse phenomena in the MFEs occurring around 0.1 T have been found in benzonitrile [19]. Similar reverse phenomena were observed in Ph-C_{60} linked compounds [17,18]. These unique phenomena may be explained by the contribution of the anisotropic Zeeman interaction to the spin-lattice relaxation (SLR) of the biradical.

The MFEs on the decay of the radical pair between a C_{60} cluster anion and a pyrene cation have been observed in a micellar system [29]. However, the MFEs on the photoinduced electron-transfer reactions using the C_{60} cluster in mixed solvents have been studied yet. In the present paper, we have examined photoinduced electron-transfer reaction and MFEs on the dynamics of radical pair generated by the intermolecular electron-transfer reaction between C_{60} cluster and methyl phenothiazine (**MePH**).

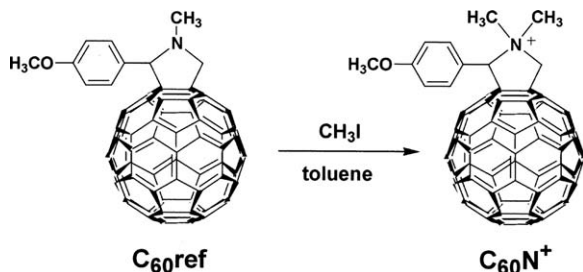$C_{60}N^+$ **MePH**
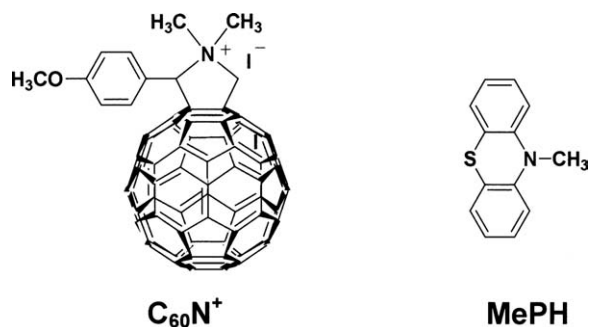
2. Experimental

Synthetic procedure of a C_{60} derivative containing a positive charge ($C_{60}N^+$) was prepared according to the previous paper [32] and is shown in Scheme 1. The structure of $C_{60}N^+$ was confirmed by ^{1}H-NMR and MALDI-TOF MS spectra and elemental analysis.

^{1}H-NMR, steady-state absorption, and transient absorption spectra, and MFEs were measured according to the previous papers [16–19]. Methylphenothiazine (**MePH**) (Wako, extra pure), THF (Dojindo, spectrosol), and DMSO (Dojindo, spectrosol) were used as received.

Clusters of $C_{60}N^+$ were prepared by solving in THF–H_2O mixed solvent. $C_{60}N^+$ forms optically transparent clusters by the following procedure. First, the suspension of $C_{60}N^+$ and **MePH** were sonicated in THF for 15 min. Next, H_2O was injected into the suspension by a syringe. After sonication for 15 min, the suspension became optically transparent mixed solvent (THF/H_2O = 2:1) solution. The diameter of $C_{60}N^+$ clusters were measured using AFM. The THF–H_2O mixed solution of $C_{60}N^+$ or both $C_{60}N^+$ and **MePH** was dropped on freshly cleaved mica.

After drying at ambient temperature, the AFM images of $C_{60}N^+$ clusters were recorded in tapping mode using a Nanoscope IIIa (Digital Instrument).

For laser photolysis experiments, a THF–H_2O mixed solution of $C_{60}N^+$ (0.1 mM), **MePH** (1 mM), or $C_{60}N^+$ (0.1 mM) and **MePH** (1 mM) in a cylindrical quartz cell (3.5 cm optical path length) with a water jacket was deoxygenated by passing argon streams. The cell was placed in the gap of an electromagnet and was irradiated by the 532- or 355-nm laser light of a Nd–YAG laser (Continuum Surelite I-10, pulse width 4–6 ns). The transient signals from a photomultiplier (R928 Hamamatsu Photonics Co., Ltd.) with a wide band preamplifier (NF Electronic Instruments BX-31) were recorded by a digital storage oscilloscope (Tektronix TDS350P). The signals were analyzed by a microcomputer.

3. Results and discussion

3.1. Characteristic of the $C_{60}N^+$ clusters

The absorption spectrum of $C_{60}N^+$ in DMSO is shown in Fig. 1a. The spectrum in the region of 400-800 nm is essentially identical with 6,6-closed mono-functionalized C_{60} derivative [1]. On the contrast, the absorption spectrum of $C_{60}N^+$ in THF/H_2O (2:1) mixed solvent (Fig. 1b) was different from that in Fig. 1a. The absorption bands in the 400–800 nm region in the mixed solvent were broadened and became featureless as comparison with that in DMSO (Fig. 1a). The results suggested the formation of cluster of $C_{60}N^+$ occurred in the THF/H_2O mixed solvent. In addition, the absorption spectrum of $C_{60}N^+$ (0.1 mM) and **MePH** (1 mM) in THF/H_2O (2:1) mixed solvent was similar to that in Fig. 1b. The result indicated similar formation of cluster of $C_{60}N^+$ occurred in the addition of **MePH**.
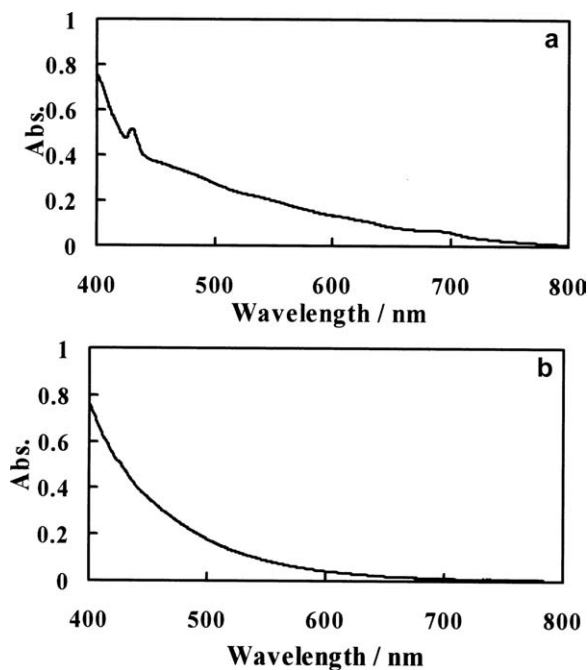

Fig. 1. Absorption spectra of (**a**) $C_{60}N^+$ (0.1 mM) in DMSO and (**b**) $C_{60}N^+$ (0.1 mM) in THF/H_2O (2:1) mixed solvent at room temperature.

Scheme 1.

The formations of clusters of $C_{60}N^+$ were examined by AFM measurement. From the AFM image (Fig. 2), the diameters of the clusters of $C_{60}N^+$ were estimated to be ca. 100 nm. In the case of $C_{60}N^+$ (0.1 mM) and **MePH** (1 mM) in THF/H$_2$O (2:1) mixed solvent, similar AFM image was observed. The estimated diameters by AFM are similar to those estimated by using of dynamic light scattering (DLS) measurement. On the basis of the absorption spectra, AFM, and DLS, the formations of clusters of $C_{60}N^+$ were confirmed in the THF/H$_2$O (2:1) mixed solution of only $C_{60}N^+$ or $C_{60}N^+$ and **MePH**.

When the DMSO solution of $C_{60}N^+$ was dropped on freshly cleaved mica, the formation of clusters (ca.100 nm) as shown in Fig. 2 was not observed. The result is in agreement with that in the absorption spectrum (Fig. 1a).

3.2. Photoinduced electron transfer in $C_{60}N^+$ clusters–MePH system

Transient absorption spectra of the $C_{60}N^+$ clusters–MePH system were measured following laser excitation at 532 or 355 nm in THF/H$_2$O (2:1) mixed solvent at 298 K. At first, we attempted to measure transient absorption spectrum by the second harmonic light (532 nm). However, no significant transient absorption was observed in nanosecond time-region.

Next, we attempted to measure transient absorption spectra of $C_{60}N^+$ clusters–**MePH** system in the THF/H$_2$O (2:1) mixed solvent by the third harmonic light (355 nm). The significant transient absorption spectra were clearly observed as shown in Fig. 3a. The
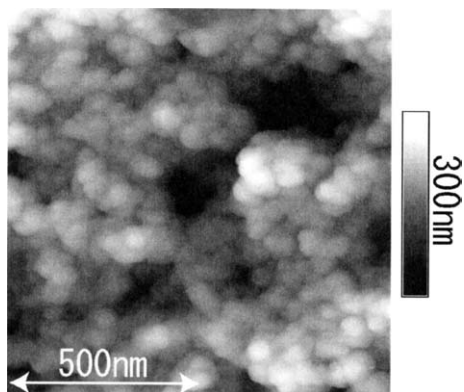

Fig. 2. A AFM image of $C_{60}N^+$ cluster obtained from $C_{60}N^+$ (0.1 mM) in THF/H$_2$O (2:1) mixed solvent on a mica surface.
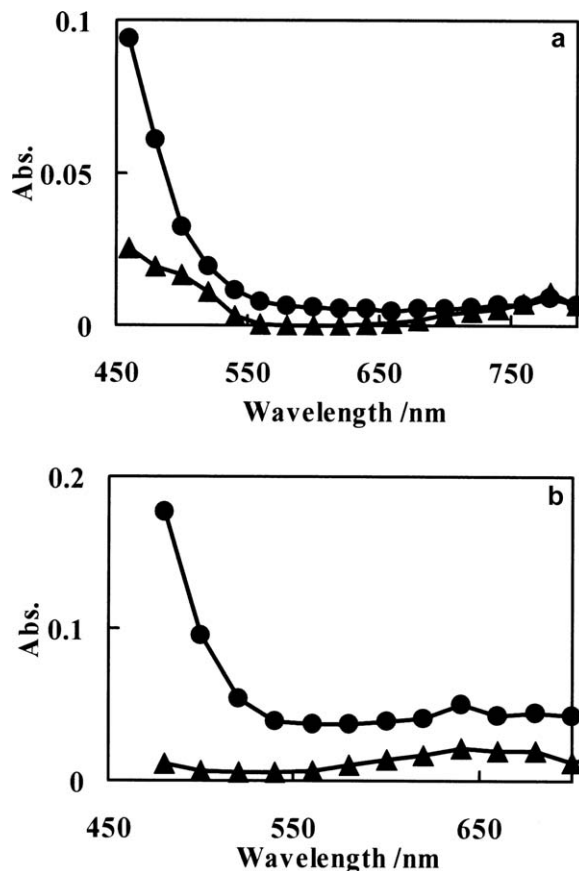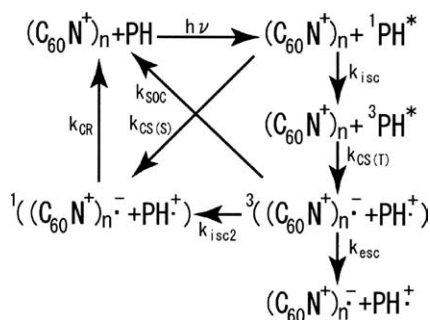

Fig. 3. Transient absorption spectra of (a) $C_{60}N^+$ (0.1 mM)–**MePH** (1 mM) at 1 (●) and 8 (▲) µs and (b) **MePH** (1 mM) at 1 (●) and 10 (▲) µs in THF/H$_2$O (2:1) mixed solvent at 298 K.

broad absorption band in the 450–800-nm region was observed at 1 µs after laser excitation. As a reference system, the transient absorption spectra of **MePH** in the THF/H$_2$O (2:1) mixed solvent were measured at the same experimental condition. The broad absorption band in the 450–800 nm region was also observed at 1 µs after laser excitation (Fig. 3b). The broad band is assignable to the T_1–T_n absorption of the PH moiety. The result indicates that the triplet excited state of PH (^{3}PH*) was generated by laser excitation. The broad band was similar to that at 1 µs in Fig. 3a. Therefore, the broad absorption band around 450 nm at 1 µs in Fig. 3a is mainly ascribed to the T_1–T_n absorption of the PH moiety in **MePH**.

At 8 µs after laser excitation, the broad absorption decayed and then the shoulder band around 520 nm due to phenothiazine cation radical (PH$^{\bullet+}$) and the absorption bands (λ_{max}, 780 nm) above 650 nm due to

Scheme 2.

C_{60} anion radical ($C_{60}^{\bullet-}$) appeared in Fig. 3a. As another reference system, the transient absorption spectrum of only $C_{60}N^+$ cluster in the THF/H$_2$O (2:1) mixed solvent was measured at the same experimental condition. However, no significant transient absorption was observed in nanosecond time-region. On the basis of these observations, the photoinduced intermolecular electron-transfer process ($k_{CS(T)}$) from $^3PH^*$ to $C_{60}N^+$ cluster, $(C_{60}N^+)_n$ occurred as shown in Scheme 2.

3.3. Magnetic field effects on the dynamics of radical pair in $C_{60}N^+$ clusters–MePH system

MFEs on the dynamics of radical pair in $C_{60}N^+$ clusters–MePH system were examined in THF/H$_2$O (2:1) mixed solvent. MFEs on the decay profiles of the transient absorption at 520 nm due to $PH^{\bullet+}$ were shown in Fig. 4. The decay was retarded in the presence of magnetic field. In addition, the absorbance at 10 μs after laser excitation increased with the increase of magnetic field. The result indicated that the yield of the
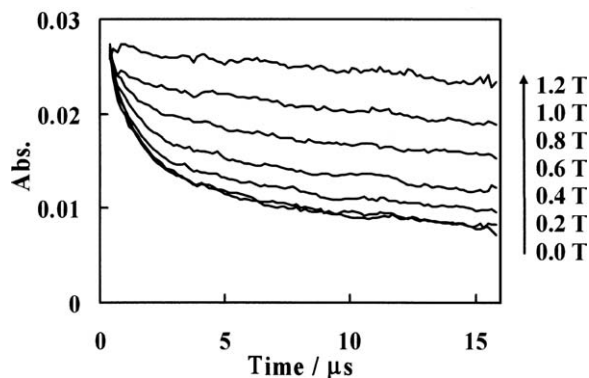

Fig. 4. MFEs on the decay profiles of the transient absorption at 520 nm upon laser excitation of $C_{60}N^+$ (0.1 mM)–MePH (1 mM) in THF/H$_2$O (2:1) mixed solvent at 298 K.

escaped $PH^{\bullet+}$ increased with the increase of magnetic field. Therefore, the magnetic field effects on the decay profile were clearly observed.

The magnitudes of the MFEs were evaluated by the following equation; Δ = Abs(H T)/Abs(0 T), where Abs(H T) and Abs(0 T) represent the absorbance at 10 μs at 520 nm in the presence (H T) and the absence of magnetic field. The Δ-values increased with the increase of magnetic field. The Δ-value became 2.7 at 1.2 T as shown in Fig. 5.

As a reference system of MFEs, we have examined the MFEs on the decay profiles of the transient absorption at 520 nm in the case of the nonlinked system; C_{60}ref and MePH in benzonitrile [33]. In the homogeneous solution, the absorption band due to $^3C_{60}^*$ in C_{60}ref was observed around 680 nm and the absorption due to $PH^{\bullet+}$ at 520 nm initially rose and then decayed in the transient absorption spectra following laser excitation at 532 nm. The decay at 680 nm corresponded well with the rise at 520 nm. The results indicated that the triplet radical pairs were generated by photoinduced intermolecular electron-transfer from PH to $^3C_{60}^*$. However, no MFEs on the decay profile at 520 nm due to $PH^{\bullet+}$ were observed. The result is ascribed to fast diffusion of the radicals in homogeneous solution. Therefore, the observation of MFEs in the $C_{60}N^+$ clusters–MePH system are most likely ascribed to the cage effect due to the incorporation of MePH into the $C_{60}N^+$ cluster.

The MFEs in $C_{60}N^+$ clusters–MePH system are explained by radical-pair mechanism between $C_{60}N^+$
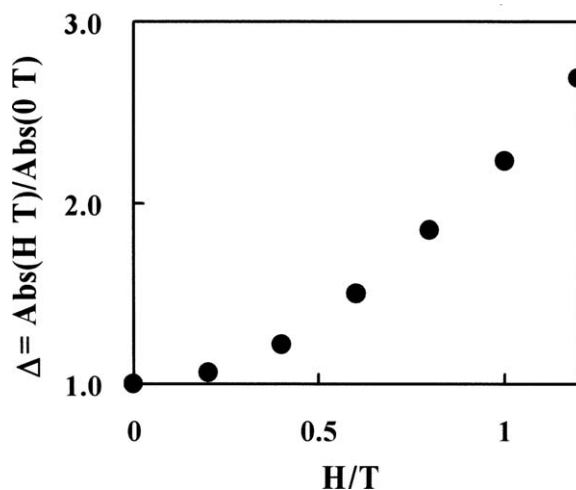

Fig. 5. MFEs on Δ = Abs(H T)/Abs(0 T) in $C_{60}N^+$ (0.1 mM)–MePH (1 mM) in THF/H$_2$O (2:1) mixed solvent.

cluster, $(C_{60}N^+)_n$, and MePH, as shown in Scheme 2. **MePH** is mainly photoexcited by the 355-nm laser light, because of the excess amount of **MePH** as comparison with $C_{60}N^+$. The singlet excited state of PH (^{1}PH*) is generated by the laser excitation. The intersystem-crossing process (k_{isc}) occurs and ^{3}PH* is generated. The intermolecular electron-transfer process ($k_{CS(T)}$) from ^{3}PH* to $C_{60}N^+$ cluster, $(C_{60}N^+)_n$, occurs and generates triplet radical pair, $^3((C_{60}N^+)_n^{\bullet-} + PH^{\bullet+})$. The triplet radical pair disappears partly via spin-orbit coupling (SOC)-induced intersystem-crossing process (k_{SOC}) to the ground state. The process (k_{SOC}) is independent of magnetic field. The triplet radical pair decayed to ground state via singlet radical pair, $^1((C_{60}N^{\bullet+})_n^{\bullet-} + PH^{\bullet+})$. The intersystem-crossing process (k_{isc2}) for the radical pair, but not reverse electron-transfer process (k_{CR}) from the singlet radical pair to the ground state, becomes a rate-determining step for the radical pair to decay via reverse electron-transfer reaction. The intersystem-crossing process (k_{isc2}) is influenced by magnetic field. In the absence of magnetic field, the three sublevels of triplet radical pair are degenerate. In the presence of magnetic field, Zeeman splitting of triplet sublevels occurs. As a consequence of Zeeman splitting, the intersystem-crossing process (k_{isc2}) is retarded in the presence of magnetic field. As a result, the escape process (k_{esc}) from the triplet radical pair increased with the increase of magnetic field and the yield of the escaped PH$^{\cdot+}$ increased with increase of magnetic field. In the presence of magnetic field, the intersystem-crossing process (k_{isc2}) is controlled by the spin-lattice relaxation from triplet sublevels. Thus the MFEs are explained in terms of spin-lattice relaxation mechanism [10–13].

In the donor-C_{60} linked compounds such as Ph–C_{60} [16–18] and ZnP–C_{60} [19] linked compounds, the decay rate constant of biradical decreases steeply in lower magnetic fields (< 0.1–0.2 T), and then gradually increases and finally becomes almost constant in higher magnetic fields (0.1–$0.2 \leq H \leq 1$ T). The MFEs on the decay of the radical pair between a C_{60} cluster anion and a pyrene cation have been also reported in a micellar system [29]. In that case, decay rates of the radicals increased with increasing the magnetic field, and MFEs above 2 T were ascribed to the SLR mechanism due to anisotropic Zeeman interaction. The present MFEs are different from those reported previously in the donor-C_{60} linked compounds or the micellar C_{60} cluster–

pyrene system. Therefore, the MFEs in the present study are most likely ascribed to the nanoclusters of $C_{60}N^+$.

4. Conclusion

A Fullerene derivative containing a positive charge (a monopyrrolidinium salt) ($C_{60}N^+$) formed optically transparent clusters (diameter of ca. 100 nm) in THF/H_2O mixed solvent from the results of the absorption spectra and AFM images, and dynamic light scattering. Transient absorption spectra of $(C_{60}N^+)_n$–MePH system following laser excitation at 355 nm indicated that the photoinduced intermolecular electron-transfer from triplet excited state of PH to $C_{60}N^+$ cluster $(C_{60}N^+)_n$ occurred and the yield of the escaped PH$^{\bullet+}$ increased with increase of the magnetic field. The MFEs are explained by radical pair mechanism and are most likely ascribed to the nanoclusters of $(C_{60}N^+)_n$. The present study provides useful information for designing the nanostructures using donor-C_{60} systems for the development of novel molecular spin systems. Further investigations on the $C_{60}N^+$ cluster-other donor (such as porphyrin) systems and quantitative analysis of the MFEs are now in progress.

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