Photoexcited State Properties of C_{60} Encapsulated in a Water-Soluble Calixarene

Shafiqul D.-M. Islam, Mamoru Fujitsuka, Osamu Ito,* Atsushi Ikeda,† Tsukasa Hatano,† and Seiji Shinkai†
Institute for Chemical Reaction Science, Tohoku University, Katahira, Aoba-ku, Sendai 980-8577
†*Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Fukuoka 812-8581*

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Properties of the excited states of C_{60} incorporated into a cationic homooxacalix[3]arene (C_{60}/calixarene) in water have been investigated and compared with bare C_{60} in benzene. A new transient absorption band which appeared at about 545 nm was attributed to triplet-triplet (T-T) absorption band of C_{60}/calixarene. The λ_{max} of the T-T transition shifts to the shorter wavelength compared with that of bare C_{60} in benzene and the decay rate increases very much.

Much attentions have been focused to discover new photophysical and photochemical properties of the fullurene derivatives. One promising approach is to establish the water soluble fullerenes for the application to biological systems. For this purpose, incorporation of C_{60} into water-soluble super-structures[1,2] such as γ-cyclodextrin was reported.[3] The other approach demands functionalization of the fullerene core with hydrophilic ligands.[4,5] Recently, it has been reported that the water-soluble C_{60}-containing calixarene (C_{60}/calixarene, Inset in Figure 1) was prepared and that it has activity for DNA cleavage under the photoillumination.[6] In the present study, we report on the first observation of T-T absorption spectra of C_{60}/calixarene in addition to emission spectra and on its reaction with molecular oxygen and electron donor.

Figure 1 shows the steady-state absorption spectrum of C_{60}/calixarene in water, which shows two absorption maxima in UV and visible region at 340 nm and around 448 nm. They showed blue shift compared with bare C_{60} in benzene, which suggests comparatively stronger interaction between C_{60} and calixarene.

The fluorescence spectrum of C_{60}/calixarene is shown in Figure 2. The marked blue shift of the fluorescence maxima of C_{60}/calixarene (maxima at 531 nm) was observed as compared with that of bare C_{60} in benzene (700 nm). Such blue shift of

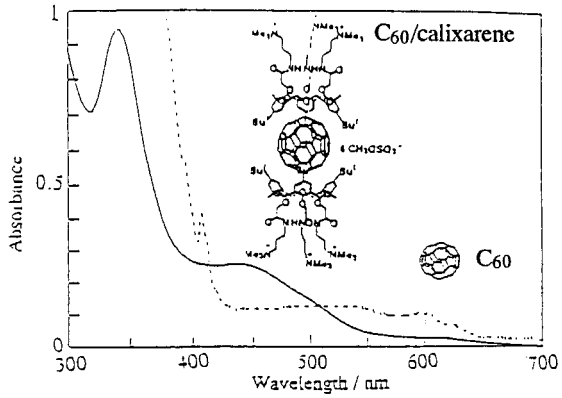

Figure 1. Steady-state absorption spectra of C_{60}/calixarene (0.1 mM) in aqueous solution and bare C_{60} in benzene.

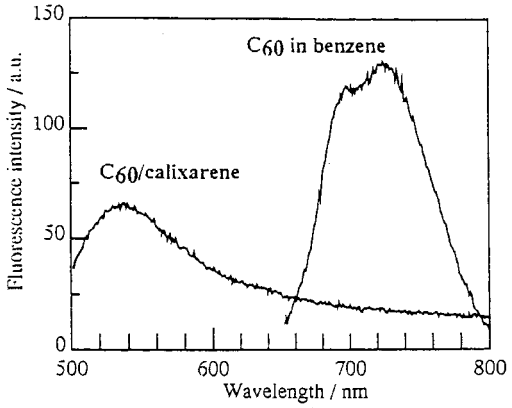

Figure 2. Steady-state fluorescence spectra of C_{60} /calixarene (0.1 mM) in aqueous solution and bare C_{60} in benzene.

the fluorescence maximum resembles with the tendency of the blue shift for the fluorescence of C_{60} incorporated in polymers.[7-9]

The transient absorption spectrum at 200 ps observed by 532 nm pico-second laser pulse excitation of 0.1 mM C_{60}/calixarene in deaerated water is shown in Figure 3. The growth of the absorption band at 545 nm due to the triplet excited state of C_{60}/calixarene was observed after the decay of the singlet excited state of C_{60}/calixarene (Insert in Figure 3). From the rise, the intersystem crossing rate from the singlet excited state to the triplet state of C_{60}/calixarene in water was evaluated to be 9.0×10^8 s^{-1}, which is similar to that of bare C_{60} in benzene.[10]

Nanosecond flash photolysis was also employed to confirm the transient absorption changes due to the triplet state of C_{60}/calixarene. Laser pulse excitation of a solution of C_{60}/calixarene at 355 nm resulted in the same transient absorption that displayed a maximum at around 545 nm (Figure 4). The tran-

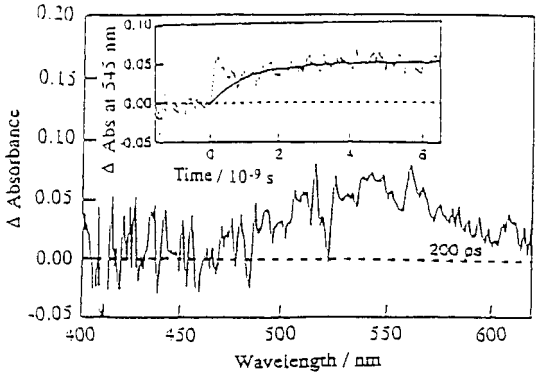

Figure 3. Transient absorption spectrum observed at 200 ps following picosecond laser (532 nm) photolysis of C_{60}/calixarene (0.1 mM) in deaerated water. Insert: Rise time profile at 545 nm.

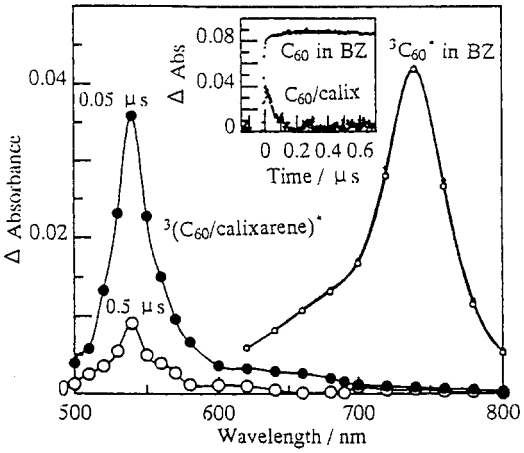

Figure 4. Transient absorption spectra observed by nanosecond laser (355 nm) photolysis of C_{60}/calixarene (0.1 mM) in water and C_{60} in benzene. Insert: Decay plots of the triplets of C_{60}/calixarene and C_{60} in benzene.

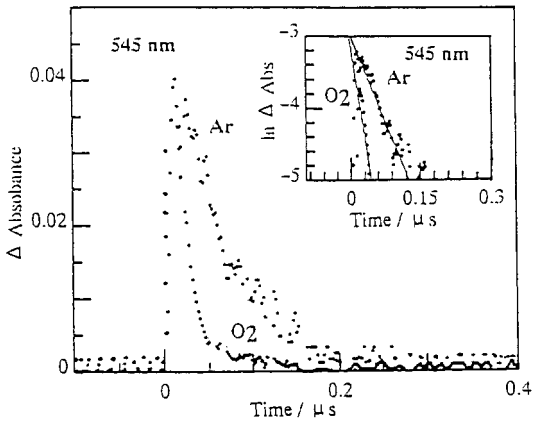

Figure 5. Decay plots at 545 nm for C_{60}/calixarene in Ar-saturated and O_2-saturated solutions. Insert: First-order plots.

sient absorption band observed by nanosecond laser pulse resembles the one detected in the picosecond experiment. For inclusion complex of C_{60} into calix[8]arene in solid state, the transient absorption band due to T-T transition was reported to appear at 780 nm;[11] however, the structure of the inclusion complex may be quite different from C_{60}/calixarene in water. The T-T absorption band of C_{60}/calixarene in water was also blue shifted compared to that of C_{60}/γ-cyclodextrin in water. This may be caused by the differences in the interactions between C_{60} and calixarene with π-systems from that between C_{60} and γ-cyclodextrin without π-systems.

The transient absorption band of the triplet state of C_{60}/calixarene in water at 545 nm decayed very fast as shown in Figure 5, from which the lifetime ($\tau_T = 1/k_{1st}$) was evaluated to be about 50 ns. This value is quite shorter than those for other water-soluble C_{60}. The short lifetime may be influenced by the strong interaction of C_{60} with the surrounding calixarene, although the ion radical absorption due to electron transfer from C_{60} to calixarene was not observed in the near-IR region.

In the presence of well-known triplet quenchers such as O_2, the transient absorption band at 545 nm was effectively quenched obeying first-order kinetics (Insert in Figure 5), which again supports that the transient absorption band at 545 nm is due to the T-T absorption band of C_{60}/calixarene. From this decay rate, the triplet-quenching rate constant (k_{O2}) was evaluated to be 3.0×10^9 M^{-1} s^{-1}, which is very close to the k_{diff} value in water. This k_{O2} value is similar to that of bare C_{60} in benzene. For O_2-quenching reaction in water, either energy transfer or electron transfer reaction can be considered. In the presence of *p*-anisidine, the quenching rate constant due to electron transfer from *p*-anisidine to the triplet state of C_{60}/calixarene was also evaluated to be 8.0×10^8 M^{-1} s^{-1}. This rate constant is similar to that of bare C_{60} in polar solvents such as benzonitrile.[12]

In summary, the transient absorption band due to the triplet state of C_{60}/calixarene was found in visible region at 545 nm, which shifted to the shorter wavelength compared to bare C_{60} in benzene. Further studies on photophysical and photochemical properties of C_{60}/calixarene are in progress, which need ps/fs laser flash photolysis experiments.

References and Notes

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