Properties of Photoexcited States of C_{180}, a Triangle Trimer of C_{60}

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Photophysical properties of C_{180} "*cis*-2/*cis*-2/*cis*-2", a triangle triad of C_{60}, were investigated by various methods including a transient absorption spectroscopy. Fluorescence and triplet absorption spectra were similar to those of C_{120} (C_{60} dimer) and other 1,2-adducts of C_{60}. On the other hand, short fluorescence lifetime and small quantum yield for the intersystem crossing process indicate that the photophysical properties of C_{180} are affected by the non-radiative process in the singlet excited state.

Fullerenes form their polymers and oligomers under various conditions.[1] Studies on well-defined oligomers give fruitful information on the properties of fullerene polymers. Nowadays, photophysical and photochemical properties of fullerene dimers have been investigated by several groups.[2–6] On the other hand, there is no report on the photoexcitation and relaxation processes of larger oligomers, such as C_{180}. In the present paper, we report the first study on the photoexcited states of C_{180} "*cis*-2/*cis*-2/*cis*-2", a triangle trimer of C_{60}.

C_{180} (Inset of Figure 1) was synthesized by the method reported previously.[7] Identification of the sample was carried out using APCI mass spectroscopy, IR, and STM observation.[7,8] Purity of the sample was ca. 95%. In the present paper, all the experiments were carried out employing *o*-dichlorobenzene (DCB) as a solvent, since other conventional organic solvents for fullerenes such as toluene and benzonitrile did not show sufficient solubility for the spectroscopic measurements of C_{180}.

An absorption spectrum of C_{180} showed peaks at 700 and 329 nm with a shoulder around 433 nm (Figure 1). The absorption band at 700 nm is a characteristic band for 1,2-adducts of fullerene (C_{60}R):[9] Similar absorption bands were confirmed in the spectrum of C_{120} (C_{60}-dimer).[2,3] These findings indicate that electronic interaction between the C_{60}-moieties of C_{180} is small in the ground state.

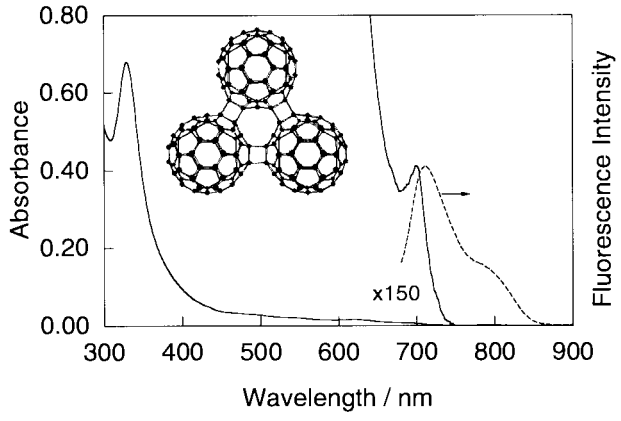

Figure 1. Absorption and fluorescence spectra of C_{180} in DCB. Inset: Molecular structure of C_{180} "*cis*-2/*cis*-2/*cis*-2".

A fluorescence spectrum showed a peak at 710 nm as shown in Figure 1, indicating that the energy level of the lowest singlet excited state (Es) of C_{180} is almost the same as C_{60}, C_{60}R and C_{120} (Table 1). Stokes shift was 200 cm^{-1}, which is larger than those of C_{60} and C_{60}R (120–140 cm^{-1}),[9] suggesting that structural relaxation of C_{180} in the singlet excited state is larger than C_{60} and C_{60}R. The quantum yield for the fluorescence (Φ_F) was estimated to be 5.5×10^{-4}, which is an intermediate value of C_{60} and C_{120} (C_{60}-dimer). The larger Φ_F value than C_{60} can be explained by the reduction of symmetry of the C_{60}-moiety. On the other hand, increase in vibration-mode will reduce the Φ_F value of C_{180} than C_{120}. The increase of the non-radiative processes of C_{180} accords with a shorter fluorescence lifetime of C_{180} (τ_F = 0.9 ns) than other fullerene compounds (Table 1).

Table 1. Photophysical properties of C_{60}, C_{60}R, C_{120}, and C_{180}

	C_{60}	C_{60}R[a]	C_{120}[b]	C_{180}
singlet				
Es / eV	1.7	1.7–1.8	1.7	1.7
τ_F / ns	1.2	1.2–1.3	1.6	0.9
Φ_F	3.2×10^{-4}	$(1.0–1.2)\times10^{-3}$	7.9×10^{-4}	5.5×10^{-4}
triplet				
λ_{TT} / nm	750	680–700	700	700
ε_T[c]	1.6×10^{4}	$(1.4–1.6)\times10^{4}$	1.4×10^{4}	2.7×10^{3}
τ_T / μs	55	24–29	23	24
Φ_{isc}	1.0	0.88–0.95	0.7±0.1	0.74±0.1

[a]From ref 9. [b]From ref 3. [c]In mol^{-1} cm^{-1}.

Upon nanosecond laser irradiation (355 nm, 6 ns fwhm), C_{180} showed transient absorption bands (λ_{TT}) at 700 and < 400 nm accompanying shoulders around 1000 and 560 nm (Figure 2). The transient absorption spectrum was always measured with a fresh sample, in order to avoid degradation of C_{180}.[7] The absorption bands are assigned to the triplet excited state of C_{180} ($^3C_{180}$*), since the absorption bands were quenched in the presence of oxygen, a triplet energy quencher. The decay lifetime (τ_T) of $^3C_{180}$* was estimated to be 24 μs (Inset of Figure 2), which is a similar value to those of C_{60}R and C_{120} (Table 1).[3,9] In Figure 2, a transient absorption spectrum of C_{120} is also shown. The spectrum of C_{180} showed slight broadening and increase in absorption intensity around 1000 nm compared to C_{120}. These findings will indicate slight interaction between C_{60}-moieties of $^3C_{180}$*.

As mentioned above, the triplet absorption bands were quenched in the presence of oxygen with 1.2×10^9 dm^3 mol^{-1} s^{-1} of the rate constant. The quenching of the absorption band

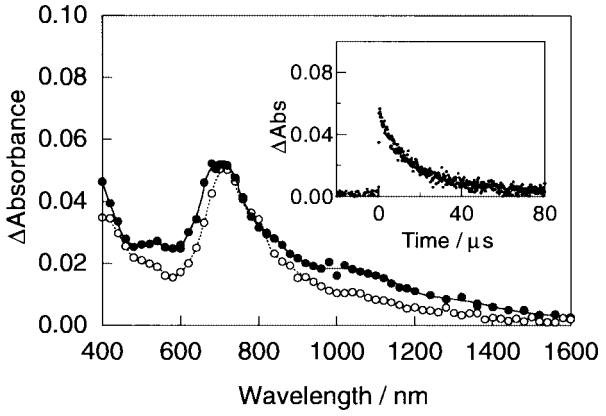

Figure 2. Transient absorption spectrum of C_{180} in DCB at 100 ns after the laser irradiation (355 nm). Dot line indicates a transient absorption spectrum of C_{120}. Inset: Absoption-time profile of C_{180} at 700 nm.

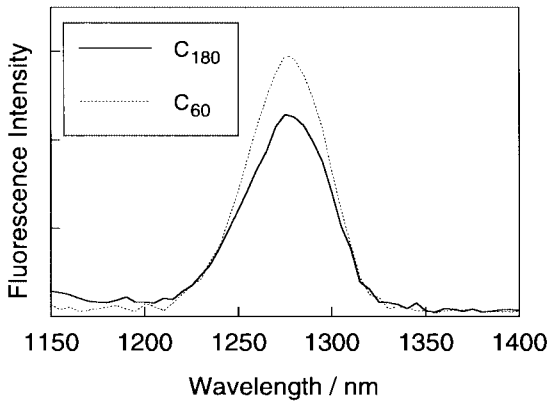

Figure 3. Fluorescence spectra of singlet oxygen generated via C_{180} and C_{60} by excitation at 488 nm. Absorbance of C_{60} and C_{180} was matched at the excitation wavelength.

can be attributed to the energy transfer process, which yields singlet oxygen ($^1O_2$*). The generation of $^1O_2$* was confirmed by observation of a fluorescence band of $^1O_2$* in the near-IR region (Figure 3), indicating that the energy level of $^3C_{180}$* is higher than $^1O_2$*. In Figure 3, the fluorescence of $^1O_2$* via the triplet excited C_{60} ($^3C_{60}$*) was also shown. Intensity of the fluorescence band of $^1O_2$* via $^3C_{180}$* is ca. 3/4 of that via $^3C_{60}$*, even though the absorbance of C_{180} was matched with C_{60} at the excitation wavelength (488 nm). This finding indicates that the quantum yield for the intersystem crossing process (Φ_{isc}) of C_{180} is smaller than that of C_{60}. By employing the Φ_{isc} value of C_{60} as a standard (1.0),[10] the Φ_{isc} value of C_{180} was estimated to be 0.74 ± 0.1, which is smaller than those of C_{60} and C_{60}R. The smaller Φ_{isc} value of C_{180} accords with the increase in the non-radiative process in the singlet excited state.

By employing the relative actinometry, an extinction coefficient of the triplet excited state (ε_T) of C_{180} was estimated to be 2.7×10^3 mol^{-1} cm^{-1} at 700 nm. The estimated value is smaller than other fullerene derivatives as listed in Table 1. The smaller ε_T value of C_{180} explains the fact that the transient absorption band of C_{180} is smaller than that of C_{60} even though the absorbance of C_{180} was matched with C_{60}. It has been reported by Ma et al. that C_{60}-polymer showed barely detectable triplet-state absorption.[2] Thus, excited state properties of C_{180} seem to be intermediate one of C_{60}R and C_{60}-polymer.

In conclusion, the excited properties of C_{180} such as λ_{TT} and τ_T values are similar to those of C_{60}R and C_{120}, while other excited state properties of C_{180} are affected by the non-radiative processes, which result in shorter fluorescence lifetime and small Φ_{isc} value. These aspects of C_{180} seem to become more evident in the photochemical processes, such as electron transfer. The studies are in progress.

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