Transient Spectroscopic Properties of Endohedral Metallofullerenes, La@C_{82} and La_2@C_{80}

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Properties of the excited states of endohedral metallofullerenes (La@C_{82} and La_2@C_{80}) have been investigated by time-resolved absorption spectroscopy. Transient absorption bands of La@C_{82} showed two decay-components, which were attributed to excited states of different spin multiplicity. The properties of photoexcited states of La_2@C_{80} are also reported.

Physical and chemical properties of endohedral metallofullerenes have attracted much attention, since purified macroscopic samples were first isolated.[1] Although the photo-luminescence spectra of erbium-containing metallofullerenes have been reported,[2,3] no transient absorption spectrum has been reported for any endohedral metallofullerenes. In the present study, we have observed the transient absorption spectra of La@C_{82} and La_2@C_{80} for the first time by a nanosecond laser flash photolysis in the visible and near-infrared regions.

La@C_{82} and La_2@C_{80} were prepared according to methods described in the literature.[4,5] The steady-state absorption spectra of La@C_{82} and La_2@C_{80} in 1,2,4-trichlorobenzene are shown in Figure 1. The absorption bands of La@C_{82} at 1410, 1000 and 640 nm are characteristic of the C_{82} cage in which the lanthanide metal is encapsulated.[6] Since it has been reported that the change of central metal does not affect the positions of absorption maxima,[6] the electronic transitions take place on C_{82}^{3-}. In other word, the charge-transfer transition from C_{82}^{3-} to central La^{3+} must have either higher transition energy or lower transition moment. Since the ground state of La@C_{82} is a doublet (D_0),[4b,7–9] the first excited state is the doublet state (D_1) as shown in Figure 2. Density functional calculations at the B3LYP//ROHF level[10] predicted that the longest transition band from D_0 to D_1 is at 1360 nm; this is in good agreement with the observed band at 1410 nm (Figure 1).

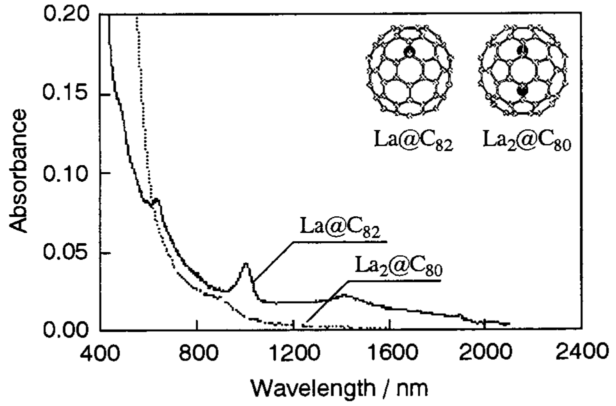

Figure 1. Steady-state absorption spectra of La@C_{82} and La_2@C_{80}. Inset: Optimized stractures of La@C_{82} and La_2@C_{80}.

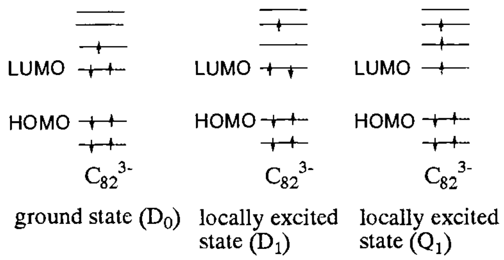

Figure 2. Orbital diagrams of La@C_{82} at the ground and excited states.

The absorption spectrum of La_2@C_{80} shows a broad band at 900 nm and a relatively sharp shoulder at 400–450 nm, which are characteristic bands of endohedral dimetallofullerenes.[6]

The transient absorption spectrum obtained by the irradiation of La@C_{82} with a nanosecond laser pulse at 355 nm is shown in Figure 3. Immediately after laser irradiation, the transient absorption spectrum shows a sharp band at 780 nm with broad bands around 1500 and 840 nm. The broad band around 1500 nm extends to longer wavelengths, but observation in the region longer than 1600 nm was difficult due to intense absorption of the solvent and low sensitivity of the present detector system in the region. As shown in the inset of Figure 3, transient absorption bands decayed according to two components. The fast decay-component refers to the component decaying within 200–300 ns after the laser irradiation and the slow decay-component is the latter decay part. By applying the first-order decay function, the decay rate of the fast component was estimated to be 1.2×10^7 s^{-1}, which corresponds to 83 ns decay lifetime. At 500 ns after laser irradiation (Figure 3), the absorption spectrum shows an absorption band at 780 nm with depletion around 1000 and 620 nm, which accords well with the peak positions of the ground state absorption spectrum (Figure 1). From the long time scale measurements, the decay rate of the slow component was evaluated to be 3.4×10^5 s^{-1}, i.e., 2.9 μs decay lifetime. The slow decay-component is due to the lowest excited state of La@C_{82}, since further spectral change was not observed in the transient spectrum. Because of relatively long lifetime of the slow decay-component, the excited state is expected to have a different spin-multiplicity from the ground state, i. e., excited quartet state (Q_1) is expected for the lowest excited state (Figure 2). As for the fast decay-component, the

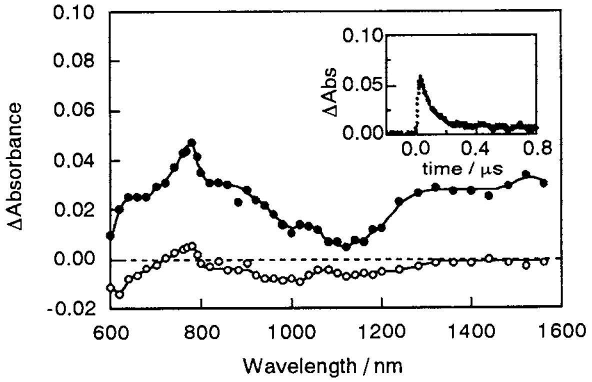

Figure 3. Transient absorption spectra at 50 ns (closed circle) and 500 ns (open circle) of La@C_{82} in 1,2,4-trichlorobenzene by 355 nm-laser irradiation. Inset: Time profile at 780 nm.

excited doublet state (D_1) is expected, since spin multiplicity of the ground-state of La@C_{82} is doublet (D_0) (Figure 2).[7] It should be stressed that these identifications are tentative; further work should be carried out.

It is interesting to note that both decay components were accelerated in the presence of oxygen. The decay rate of the fast component was 1.5×10^7 s^{-1} in the oxygen-saturated solution, indicating that the bimolecular rate constant for quenching with oxygen is 3×10^8 dm^3 mol^{-1} s^{-1}.[11] The slow decay-component was completely quenched. The quenching results from energy transfer and/or electron transfer with oxygen, indicating high reactivities of the excited states of La@C_{82}.

The transient spectrum of La_2@C_{80} also shows two step decay. Immediately after laser irradiation, weak and broad transient absorption bands were observed around 1400, 1020, 840, and 640 nm (Figure 4). The decay rate of the first component was ~7×10^6 s^{-1}, corresponding to ca. 150 ns lifetime. As for the slow decay-component, the lifetime was estimated to be ~40 μs from the long time-scale measurement. Since La_2@C_{80} is a closed shell molecule,[5] the observed transient bands on the microsecond time scale are attributed to the triplet-triplet transitions. These weak bands may be caused by the low intersystem quantum yield from the singlet excited state to the triplet state. On cooling the solution to –30 °C, the intensity and decay lifetime were not increased. Thus, the movement of internal La ions does not affect the excited state properties much. It is interesting that the decay rates of the fast and slow components were also accelerated in the presence of oxygen, indicating the high reactivities of the excited states of La_2@C_{80}.

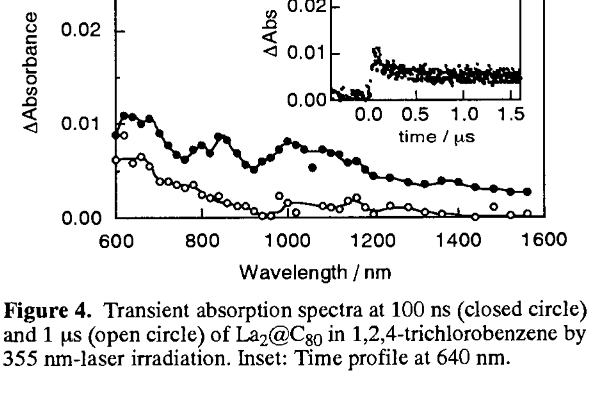

Figure 4. Transient absorption spectra at 100 ns (closed circle) and 1 μs (open circle) of La_2@C_{80} in 1,2,4-trichlorobenzene by 355 nm-laser irradiation. Inset: Time profile at 640 nm.

In summary, we report the first observations of the transient spectra of endohedral metallofullerenes on the nanosecond time scale. A further study is in progress for other endohedral metallofullerenes.

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Dedicated to Professor C. S. Foote at UCLA on the occasion of his 65th birthday.