Photophysical and Photochemical Properties of The La@C_{82} Anion

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Properties of the excited states of the La@C_{82} anion have been investigated by laser flash photolysis measuring the fluorescence and absorption spectra. Transient absorption bands in the visible and near-IR region observed by the laser excitation of the La@C_{82} anion were attributed to the excited triplet, which showed high electron-donor ability to viologen dication, yielding La@C_{82} and viologen radical cation, establishing a reversible photoelectron transfer cycle.

Much attentions have been focused on the physical and chemical properties of endohedral metallofullerenes, encapsulating atoms inside hollow fullerene cages.[1] In the case of La@C_{82},[2,3] we previously reported that the anion form $[La@C_{82}]^-$ having closed shell electronic structure becomes quite stable with moisture and O_2 compared with neutral La@C_{82} having open shell structure.[4] Furthermore, although the photophysical and photochemical properties have been reported for neutral endohedral metallofullerenes,[5] any research on the excited-state properties of the endohedral metallofullerene anions has not been reported yet. In the present study, we have observed for the first time the steady-state fluorescence spectrum and transient absorption spectra of the La@C_{82} anion by a nanosecond laser flash photolysis apparatus with a photodiode detector in the visible/near-infrared region.

$[La@C_{82}]^-$ was prepared by electrochemical method according to the method in the literature.[4] The steady-state absorption spectrum of $[La@C_{82}]^-$ is shown in Figure 1 with that of La@C_{82} in *o*-dichlorobenzene. In the absorption spectrum of $[La@C_{82}]^-$, the sharp absorption bands appeared at 930 and 580 nm and the broad band appeared around 1400 nm, replacing the peaks of La@C_{82} at 1410, 1000, and 640 nm bands.[3] Theoretical calculations of $[La@C_{82}]^-$ after optimizing the geometry with hybrid density functional theory at the B3LYP level predicted that the transitions from the HOMO to the LUMO and LUMO+1 are at 1340 and 890 nm, respectively (Figure 2) at the TD-B3LYP level for vertical excitation.[6]

The steady-state emission spectrum of $[La@C_{82}]^-$ in 1,2,4-trichlorobenzene (TCB) at room temperature is shown in Figure 3, which was measured by using an argon-ion laser as an excitation source focusing the emission from the sample on to a monochromator equipped with an InGaAs-PIN photodiode.[7] From the theoretical calculation on $[La@C_{82}]^-$ (Figure 2), the transition from the LUMO+1 to the HOMO can be considered to participate the emission band around 1000 nm and probably 1250 nm. The transition from the LUMO to the HOMO may be considered to appear as a minor emission around 1400–1600 nm.

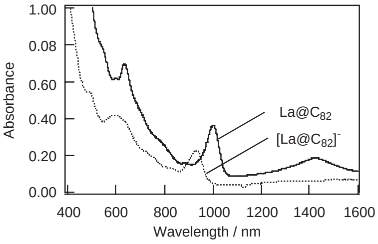


Figure 1. Steady-state absorption spectra of La@C_{82} and $[La@C_{82}]^-$ in *o*-dichlorobenzene.

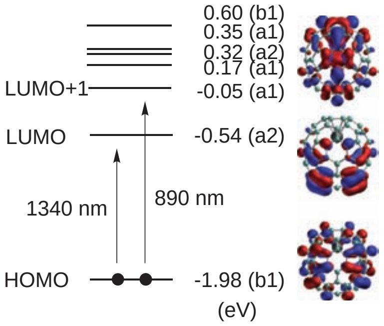


Figure 2. Orbital diagram of $[La@C_{82}]^-$.

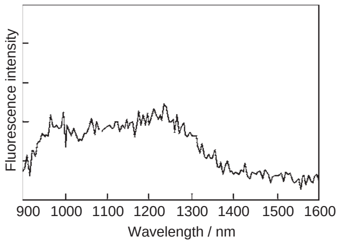


Figure 3. Steady-state fluorescence spectrum of $[La@C_{82}]^-$ in TCB; $\lambda_{ex} = 488$ nm.

The transient absorption spectrum obtained by the irradiation of $[La@C_{82}]^-$ with the nanosecond laser light at 532 nm with pulse width of 6 ns is shown in Figure 4a, in which spectra in the visible region (400–600 nm) and the near-infrared region (600–1600 nm) were monitored with a Si-PIN photodiode and a Ge-avalanche photodiode, respectively.[8] The transient band appeared in the wide region of 600–1600 nm, although the transient absorption band seems to extend to the longer wavelength region than 1600 nm. The main peak appeared at 700 nm, which is similar to the main band at 790 nm of La@C_{82}, although the longer band in the region of 1300–1550 nm of neutral La@C_{82}

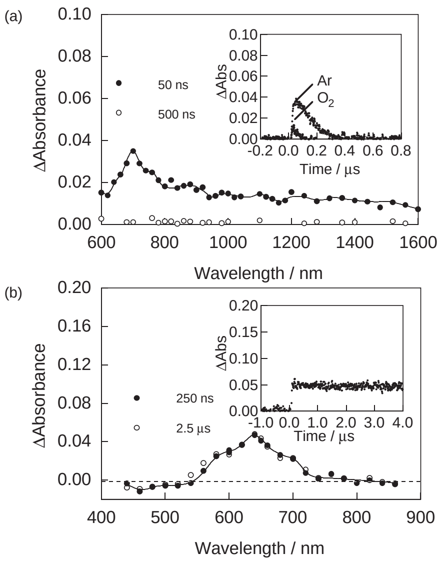
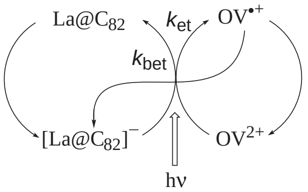


Figure 4. (a) Transient absorption spectra at 50 and 500 ns obtained by irradiation of $[La@C_{82}]^-$ with laser light (532 nm) in deaerated TCB. Inset: Time profiles at 700 nm. (b) Transient absorption spectra at 100 ns obtained by irradiation of $[La@C_{82}]^-$ with laser light (355 nm) in the presence of OV^{2+} (10 mM) in TCB. Insert: Absorption-time profile at 640 nm in Ar-saturate solution.



Scheme 1.

decreased much in $[La@C_{82}]^-$. The transient absorption spectrum of $[La@C_{82}]^-$ rather resembles the triplet state of C_{82} reported previously, in which the main peak was observed at 750 nm.[7] Thus, the transient absorption spectrum of $[La@C_{82}]^-$ in Figure 4a can be attributed to the triplet state of $[La@C_{82}]^-$. The longer wavelength transient bands may correspond to the many LUMO+N ($N \geq 2$) orbitals with similar energies as shown in the MO energies in Figure 2.

The time profile of $[La@C_{82}]^-$ at 700 nm is shown in inset of Figure 4a. The decay rate of $[La@C_{82}]^-$ in Ar-saturated solution was evaluated to be $9.3 \times 10^6\,s^{-1}$, which corresponds to the lifetime of 110 ns. This lifetime was similar to that of $La@C_{82}$, while compared with the triplet state of C_{82}, the decay rate of $[La@C_{82}]^-$ was quite faster. This finding suggests that the lifetime of the excited triplet state of $[La@C_{82}]^-$ is strongly affected by the heavy La ion inside the C_{82} cage, and is similar to the excited state of $La@C_{82}$.

On addition of O_2, the decay rate increased as shown in inset of Figure 4a, supporting the assignment of the triplet state of $[La@C_{82}]^-$. The second-order rate constant for the quenching by O_2 was evaluated to be $2.1 \times 10^9\,M^{-1}\,s^{-1}$. It is difficult to attribute this rate constant to the energy transfer from the triplet state of $[La@C_{82}]^-$ to O_2, since the near-infrared absorption (Figure 1) and fluorescence (Figure 3) suggest quite low triplet energy level. Since appreciable decrease in the initial intensity of the 700 nm band was observed in the presence of O_2, some oxidation reactions including electron transfer may take place between the excited triplet state $[La@C_{82}]^-$ and O_2.

By the laser excitation of $[La@C_{82}]^-$ in the presence of octylviologen dication (OV^{2+}), which is an electron acceptor soluble in organic solvents, the transient band of the radical cation ($OV^{\bullet +}$) appeared at 640 nm (Figure 4b), indicating the electron transfer from the triplet state of $[La@C_{82}]^-$. The rise of $OV^{\bullet +}$ at 640 nm seems to be very fast (<ca. 100 ns), because of the overlap with the quick rise and decay of the triplet state of $[La@C_{82}]^-$ to which the absorption of the generated $La@C_{82}$ may also overlap. The observation of the specific bands of $La@C_{82}$ at 640 and 1000 nm was difficult owing to the overlap with $OV^{\bullet +}$ and depletion of $[La@C_{82}]^-$, respectively. Using the rise rate $10^7\,s^{-1}$ evaluated from time profile, the second-order rate constant can be evaluated to be $1 \times 10^9\,M^{-1}\,s^{-1}$, which is reasonable rate constant for intermolecular electron-transfer process. Thus, it was confirmed that electron transfer takes place from the triplet state of $[La@C_{82}]^-$ to OV^{2+}, generating $OV^{\bullet +}$. Then, the produced $OV^{\bullet +}$ begins to decay slowly within several hundred μs. The decay time profile obeys second-order kinetics, from which the back electron-transfer rate constant was evaluated to be $4.9 \times 10^9\,M^{-1}\,s^{-1}$, by employing the reported molar extinction coefficient of $OV^{\bullet +}$ at 640 nm.[9] This indicates that the photoinduced electron-transfer cycle in Scheme 1 is established. By continuous light irradiation, the accumulation of $OV^{\bullet +}$ at 640 nm and consumption of $[La@C_{82}]^-$ were not observed with steady-state absorption measurements, indicating that this photoinduced electron-transfer cycle is reversible.

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References and Notes

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