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Production, Isolation, and EELS Characterization of Ti$_2$@C$_{84}$ Dititanium Metallofullerenes

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Three isomers of Ti$_2$@C$_{84}$ metallofullerenes, Ti$_2$@C$_{84}$ (I,II,III), have been isolated by the so-called multistage high-performance liquid chromatography (HPLC) method and characterized by laser-desorption time-of-flight mass spectrometry (LD-TOF MS), UV−vis−NIR absorption, and electron energy loss spectroscopy (EELS). Both the HPLC elution behaviors and UV−vis−NIR absorption spectra of these isomers are different from those of the other M$_2$@C$_{84}$ type metallofullerenes of groups 2 and 3 and lanthanide metal atoms. The results indicate that the Ti$_2$@C$_{84}$ isomers possess unique electronic structures, which are substantiated by EELS analyses on the valence state of Ti atoms within these metallofullerenes.

1. Introduction

Endohedral metallofullerenes have so far attracted particular interest because of their novel geometrical and electronic properties together with their inherent charge-transfer nature from metal atoms to fullerenes.[1] It has been revealed by synchrotron X-ray diffraction,[2] ^{13}C NMR spectroscopy,[3] and ultrahigh vacuum scanning tunneling microscopy (UHV−STM)[4] that within metallofullerenes the metal atoms have indeed been encapsulated inside the carbon cages. Electron spin resonance (ESR),[5] synchrotron ultraviolet photoelectron spectroscopy (UPS),[6] as well as theoretical calculations[7] have revealed that substantial intrafullerene electron transfers are occurring from the encaged metal atoms to carbon cages. The structure has been viewed as a positively charged metal core surrounded by a negatively charged carbon cage, that is, the so-called superatom character. Studies directed toward applications of endohedral metallofullerenes have achieved salient progresses in new therapeutic radiopharmaceuticals[8] as well as in conventional diagnostic radiology such as MRI contrast and X-ray imaging agents.[9−10]

However, investigations on metallofullerenes have so far been centered on rare earth endohedrals.[1] Little concern has been given to the metallofullerenes involving main transition-metal atoms (d-block elements) except for those of group 3 (Sc, Y).[11−12] Recently, we have reported the first production, isolation, EELS, and ^{13}C NMR characterization of Ti$_2$@C$_{80}$.[13] It was concluded that the geometrical and electronic structures of Ti$_2$@C$_{80}$ are different from those of the other M$_2$@C$_{80}$ (M = Sc, La, Ce, Pr, and Hf) metallofullerenes. Surprisingly, the monometallofullerenes such as M@C$_{82}$ and M@C$_{84}$, which are the most abundant (solvent-extractable) lanthanide and groups 2 and 3 atoms containing fullerenes,[1] have not yet been observed for titanium metallofullerenes in solvent extracts. Instead, Ti$_2$@C$_{80}$ is the most abundant Ti-fullerene extracted.[13] Ti$_2$@C$_{84}$ was also found in the extract but has not been reported yet.

Here, we present in detail the first isolation and spectroscopic characterization of Ti$_2$@C$_{84}$. Three isomers of Ti$_2$@C$_{84}$ have

been isolated through the multistage HPLC separation and characterized by laser-desorption time-of-flight mass spectrometry (LD TOF MS), UV−vis−NIR absorption, and electron energy loss spectroscopy (EELS). The HPLC elution behaviors are discussed in terms of cage geometry. The valence state of titanium atom within Ti$_2$@C$_{84}$ is proposed on the basis of analyses of UV−vis−NIR absorption spectra and EELS measurements. A probable rationale is presented for the observed difference in favored fullerene cages between the current group 4 Ti-metallofullerenes and lanthanides, groups 2 and 3 metallofullerenes.

2. Experimental Section

Various titanium metallofullerenes were produced through the dc arc discharge method.[1] Details of synthesis and extraction were reported in the previous paper.[13] Briefly, the isolation of three isomers of Ti$_2$@C$_{84}$ was achieved through the so-called multistage HPLC separation process on two complementary columns. In the first stage, a 5PYE column (Nacalai Cosmosil, 20 × 250 mm) was used to remove the abundant empty fullerenes (C$_{60}$−C$_{86}$) from the fraction containing Ti$_2$@C$_{84}$. In the second stage, a recycling HPLC separation on a Bucky-clutcher column (Regis, 21 × 500 mm) was employed to completely isolate the Ti$_2$@C$_{84}$ isomers.

Laser-desorption time-of-flight mass spectrometry (LD-TOF MS) measurement was performed on a MALDI-4 reflectron mass spectrometer (Shimadzu/Kratos). UV−vis−NIR absorption spectra were recorded on a UV-3100 PC UV−vis−NIR Scanning Spectrophotometer (Shimadzu) in CS$_2$ solution at room temperature. EELS spectra were obtained with a transmission electron microscope (JEOL 2010F) equipped with an electron energy loss spectrometer (Gatan, GIF). The beam density and the acquisition time were reduced as much as possible in order not to damage structures of the Ti-metallofullerenes.

3. Results and Discussion

3.1. HPLC Separation and Isolation. Figure 1 shows the two-stage HPLC separation processes. As shown in Figure 1a, the Ti$_2$@C$_{84}$ fractions are overlapped with those of empty C$_{92}$ and C$_{94}$ fullerenes in the first stage. Figure 1b and 1c shows

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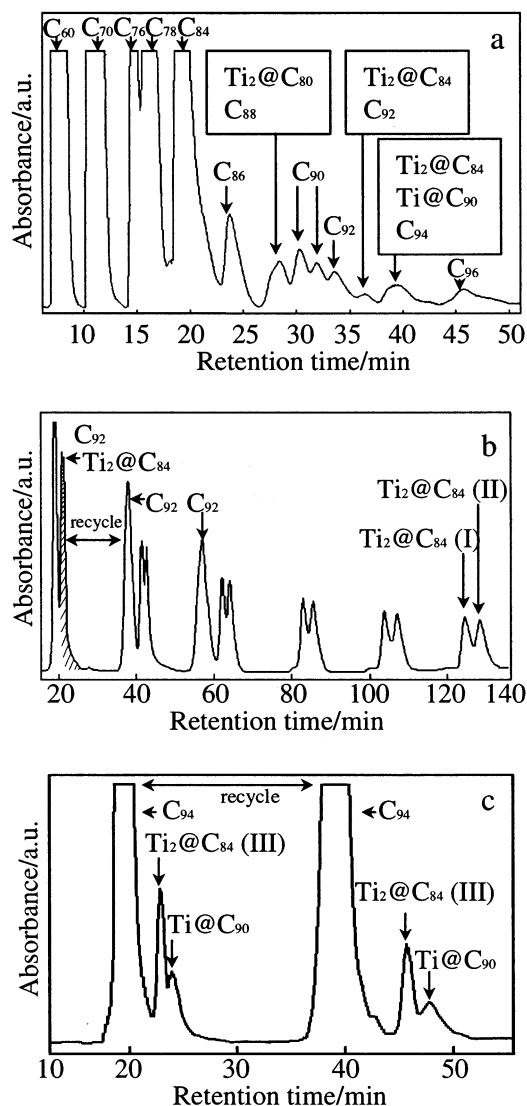   [†] Nagoya University.
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Figure 1. Two-stage HPLC separation scheme of $Ti_2@C_{84}$ isomers: (a) The first stage with a 5PYE column; (b) and (c) the second stage with a Buckyclutcher column.

Figure 2. (a) Experimental (negative ion) and simulated theoretical (inset) mass spectra of $Ti_2@C_{84}$ (I); (b) EELS spectra of $Ti_2@C_{84}$ (I) and $Ti@C_{90}$ containing the C K-edge and Ti L-edge. The Ti L-edge spectra magnified after background subtraction are superimposed.

the recycling HPLC isolation chromatograms of $Ti_2@C_{84}$ isomers on the Buckyclutcher column in the second stage. As seen in Figure 1b, isomers I and II of $Ti_2@C_{84}$ are overlapped with each other in the first cycle but can finally be well separated after five cycles with almost the same abundance. The third isomer was isolated from the fraction containing C_{94} and $Ti@C_{90}$ (cf. Figure 1c). On the basis of HPLC analysis, the abundance ratio of $Ti_2@C_{84}$ (isomers I–III) relative to C_{60} is ~0.6%, which is much less than those (1 ~ 5%) of the corresponding metallofullerenes $M_2@C_{84}$ encapsulating, for example, group 3 metal atoms.

The HPLC elution behaviors of the three isomers of $Ti_2@C_{84}$ are quite different from those of the other C_{84} based metallofullerenes such as $Sc_2@C_{84}$,[14] $Dy_2@C_{84}$,[15] and $Er_2@C_{84}$.[16] For example, on the 5PYE column under similar HPLC conditions, the fractions of $Ti_2@C_{84}$ isomers were overlapped with those of C_{92} and C_{94}, whereas the fractions of three isomers (I, II, and III) of $Sc_2@C_{84}$ and $Dy_2@C_{84}$ were overlapped with those of C_{88}, C_{90}, and C_{92}, respectively; the only $Er_2@C_{84}$ isomer is similar to $Dy_2@C_{84}$ (I).[14–16] Since the HPLC retention time of metallofullerene depends strongly on the molecular geometry of the cage and the number of electrons transferred from the encaged metal atoms to fullerenes,[15] the difference in HPLC
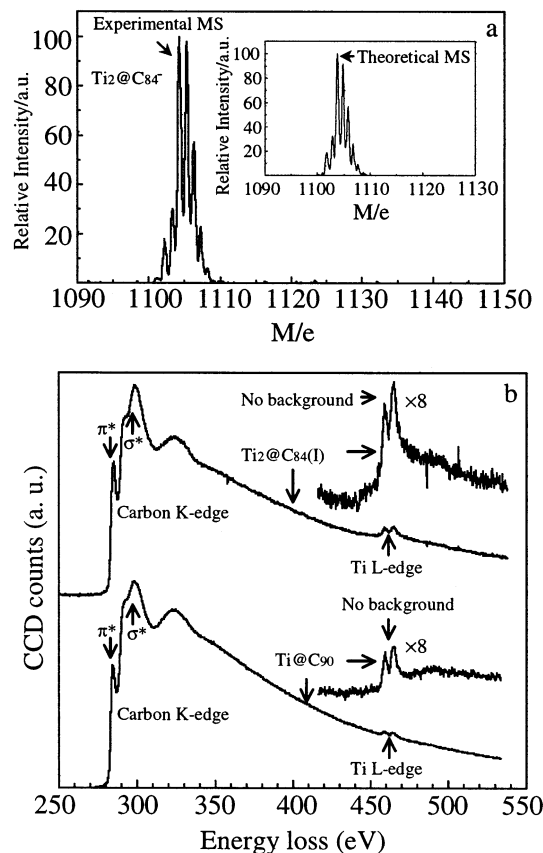
elution behavior mentioned above suggests that the geometrical and electronic structures of $Ti_2@C_{84}$ isomers are different from those of the other $M_2@C_{84}$ metallofullerenes (M = Y, Sc, Er, and Dy).

3.2. LD-TOF MS and EELS Characterization of $Ti_2@C_{84}$. Figure 2a shows the experimental and simulated theoretical (cf. inset) mass spectra of the isolated $Ti_2@C_{84}$ (I). Negative ion mass spectrum was chosen for comparison. The experimental isotope distribution of $Ti_2@C_{84}$ is in good agreement with the theoretical one, indicating the complete isolation of this species.

The EELS analysis also confirms the chemical composition of $Ti_2@C_{84}$ in addition to the mass spectral identification. An EELS spectrum of higher monometallofullerene, $Ti@C_{90}$, is also presented in Figure 2b for comparison. The EELS spectra of $Ti_2@C_{84}$ isomers (I, II, III) have similar spectroscopic features which involve both the carbon K and Ti L absorption edges. Two sharp peaks located at 459.6 and 465 eV correspond to the Ti $L_{2,3}$ (2p) edge.[17] A fine structure of the carbon K (1s) absorption edge starting at 285 eV shares the common features with the other metallofullerenes:[18] a sharp π^* peak and humps in a σ^* peak with a shoulder around 292 eV. Using appropriate cross sections and after background subtraction, normalization of both the edges gives the Ti/C atomic ratio of 2.7 ± 0.3% for the dimetallofullerene $Ti_2@C_{84}$ and 1.7 ± 0.5% for the monometallofullerene $Ti@C_{90}$ (see insets in Figure 2b). These are consistent with the expected theoretical compositions of $Ti_2@C_{84}$ (2.38%) and $Ti@C_{90}$ (1.11%).

Surprisingly, the monometallofullerenes of $M@C_{82}$ and $M@C_{84}$ types, which are the most abundant and well-studied soluble metallofullerenes involving lanthanide elements and groups 2 and 3 metal atoms, are not observed for the present
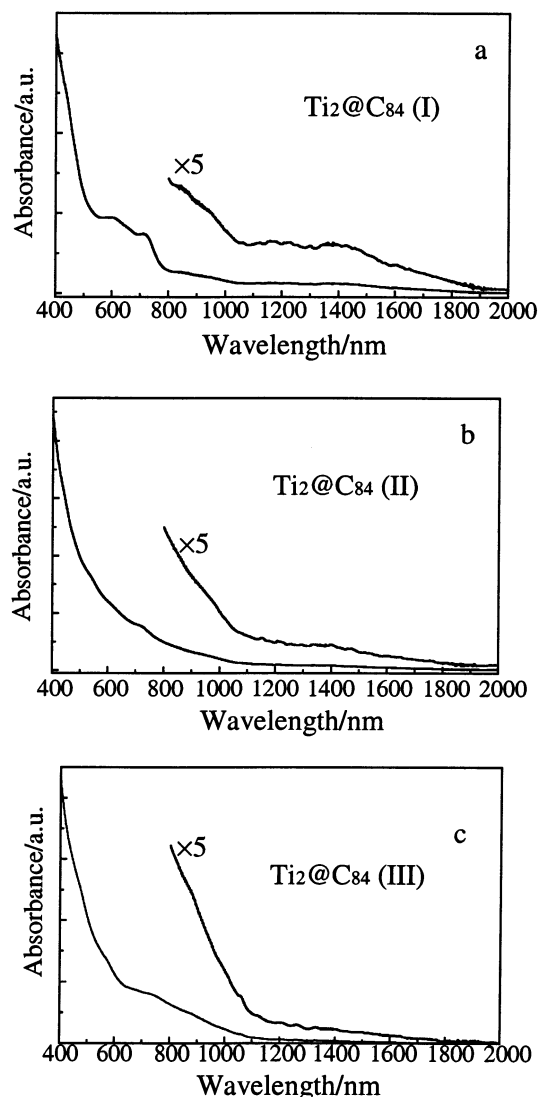
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Figure 3. UV−vis−NIR absorption spectra of Ti$_2$@C$_{84}$ in CS$_2$ solution: (a) Isomer I; (b) Isomer II; (c) Isomer III.

Figure 4. Ti L-edge EELS spectra of Ti$_2$@C$_{84}$ (isomers I and II) together with those of TiO$_2$, Ti$_2$O$_3$, TiO, and TiC for reference.

Ti-metallofullerenes in the solvent extract. Instead, Ti$_2$@C$_{80}$ is the most abundant extractable titanium endohedral fullerene, which is followed by the three isomers of Ti$_2$@C$_{84}$ in abundance. Ti@C$_{82}$ and Ti@C$_{84}$ have not been observed. Similar observations have been reported for group 4 hafnium and zirconium metallofullerenes.[11,12,19] In lanthanide and groups 2 and 3 metallofullerenes, the most abundant species are in general M@C$_{82}$ and M@C$_{84}$ followed by M$_2$@C$_{84}$, and M$_2$@C$_{80}$ is the least abundant metallofullerenes except for La$_2$@C$_{80}$.[1]

In general, the amount of intrafullerene electron transfer contributes greatly to the stability of endohedral fullerenes,[1] which plays crucial roles in the growth mechanism of metallofullerenes. In this context, it is highly necessary to study the valence state (valency) of the Ti atoms in Ti-metallofullerenes with respect to those of, for example, lanthanide metallofullerenes.

3.3. UV−Vis−NIR Absorption Spectra. The UV−vis−NIR absorption spectra of Ti$_2$@C$_{84}$ isomers (I−III) are shown in Figure 3. Three broad absorption peaks around 600, 712, and 850 nm were observed for isomer I (cf. Figure 3a), whereas isomers II and III are almost featureless (see Figure 3b and 3c). The absorption onsets of isomers I, II, and III are around 1900, 1800, and 1800 nm, respectively, indicating these titanium metallofullerenes possess small HOMO−LUMO gaps. None of
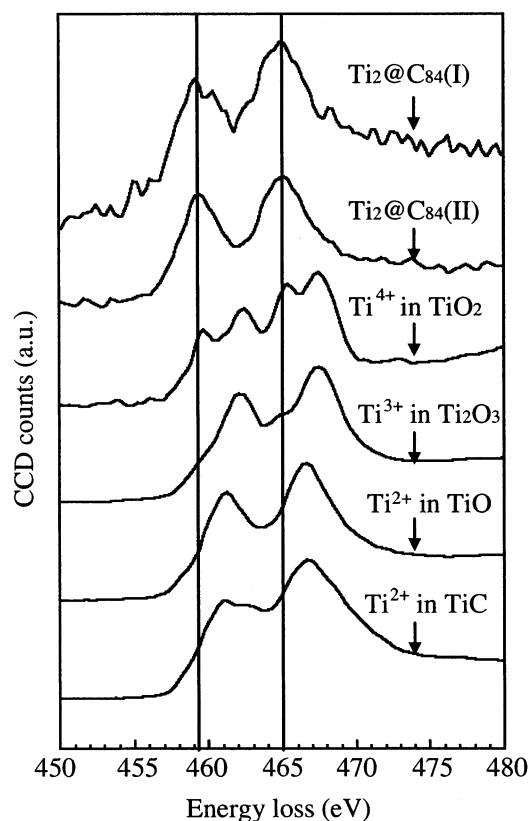
the absorption spectra of M$_2$@C$_{84}$ metallofullerenes with divalent (M = Sc)[14] or trivalent (M = Dy, Er)[15−16] metal atoms encaged match those of the present Ti$_2$@C$_{84}$ metallofullerenes. Since UV−vis absorption spectra of a metallofullerene are governed by the electronic structure of its cage, the geometrical and electronic structures of Ti$_2$@C$_{84}$ isomers are, therefore, different from those of the other M$_2$@C$_{84}$ (M = Y, Sc, Dy, and Er).

3.4. Valence State of Titanium within Ti$_2$@C$_{84}$. EELS is a powerful and efficient technique for investigating the electronic structure of metallofullerene.[18,20] The EELS L$_{23}$ edge of 3d transition metals is governed by the dipole-allowed transition of 2p electrons to unoccupied 3d states (L$_2$: 2p$_{1/2}$ → 3d$_{3/2}$, L$_3$: 2p$_{3/2}$ → 3d$_{5/2}$) and generally reflects the valence state of the transition-metal atoms. In the Ti compounds, the energy position of the L$_3$ or L$_2$ peak varies with the amount of charge transfer from Ti to its adjacent ligands.[17] A detailed analysis of Ti L edge for Ti-metallofullerenes, therefore, gives a measure for the amount of charge transfer from Ti to the fullerene cage.

Figure 4 shows the experimentally obtained Ti EELS L edge spectra of Ti$_2$@C$_{84}$ (I and II) together with those of TiO$_2$, Ti$_2$O$_3$, TiO, and TiC as reference. The observed spectra of TiO$_2$ and Ti$_2$@C$_{84}$ differ substantially from each other, indicating that the Ti atoms within Ti$_2$@C$_{84}$ are not in +4 oxidation state. The Ti L edge peak positions in the reference spectra shift toward the higher energy region with the increased charge transfer (L$_3$ edge from ∼461 eV for Ti^{2+} to ∼463 eV for Ti^{4+}). Therefore, the peak position of ∼459.4 eV for Ti$_2$@C$_{84}$ indeed suggests that the valence state of Ti within the metallofullerenes is even less than +2. This is substantially different from the other metallofullerenes having the C$_{84}$ cage such as Dy$_2$@C$_{84}$[15] and Er$_2$@C$_{84}$,[16] in which the encapsulated metal atoms are definitively in a trivalent state, and Sc$_2$@C$_{84}$,[14] in which Sc is in a divalent state.[21] This is also supported by the HPLC elution

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behaviors and UV–vis–NIR absorptions of the $Ti_2@C_{84}$ isomers discussed above. This presents the major reason for the observed difference in formation pattern between the Ti-metallofullerenes and the lanthanides, groups 2 and 3 metallofullerenes.

4. Conclusions

Three isomers of $Ti_2@C_{84}$,$Ti_2@C_{84}$ (I,II,III), have been isolated and spectroscopically characterized. The formation pattern of titanium metallofullerenes is different from those of rare earth and group 2 metallofullerenes. Compared with the other C_{84} based metallofullerenes, $M_2@C_{84}$ (M = Sc, Dy, and Er) reported ealier, $Ti_2@C_{84}$ isomers are unique in HPLC elution behaviors, UV–vis–NIR absorptions, and valency. EELS analyses show that the valence state of Ti within $Ti_2@C_{84}$ is less than +2. This novel valence state of Ti atom within the metallofullerenes is responsible for all the differences described above.

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