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EELS and ^{13}C NMR Characterization of Pure $Ti_2@C_{80}$ Metallofullerene

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The novel molecular and electronic structures and solid-state properties associated with endohedral metallofullerenes[1] have attracted worldwide attention. The metallofullerenes isolated so far are centered on groups 2[2,3] and 3[4−6] and rare earth metal atoms,[1,7] among which C_{80}-based metallofullerenes are especially interesting. For example, $La_2@C_{80}$ possesses an intriguing dynamical property in that the two La atoms exhibit a unique internal motion inside the cage at room temperature.[8] Sc_3N present in $Sc_3N@C_{80}$ has a wheel-like motion within the C_{80} cage.[9] Also, $Sc_2@C_{80}$ (I_h) might be one of the best candidates in endo-fullerene materials for superconductivity.[10] Recently, Sueki et al.[11,12] observed in trace quantities the existence of metallofullerenes containing Zr, Hf, and Nb. However, no other transition metal atoms have so far been incorporated inside the fullerenes. Here, we report the first synthesis, isolation, electron energy loss spectroscopy (EELS) and ^{13}C NMR characterization of Ti-metallofullerenes.

Titanium endohedral metallofullerenes were produced by DC arc discharge. Ti/C composite rods (size: 15 mm × 15 mm × 300 mm; 0.8 atom % of Ti; Toyo Tanso Co.) were vaporized at 500 °C under 50 Torr flowing He conditions. The soot was collected under anaerobic conditions and extracted by CS_2. The multistage high performance liquid chromatography (HPLC) isolation was performed on a 5PYE column (Nacalai Cosmosil, 25 × 250 mm) and then on a Buckyclutcher column (Regis, 20 × 300 mm) with toluene eluent. Laser-desorption time-of-flight (LD TOF) mass spectral analyses (Shimadzu MALDI-4) indicated the presence of a series of dititanium metallofullerenes, $Ti_2@C_{2n}$ ($2n = 80, 84$), in the CS_2 extract. 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 in the present experiment were reduced as much as possible so as not to disrupt the fullerene structures. The high-resolution ^{13}C NMR measurements were performed on a JEOL JNM-500 spectrometer at 500 MHz (CS_2 solution, $Cr(acac)_3$ relaxant, acetone-d_6 lock at 25 °C).

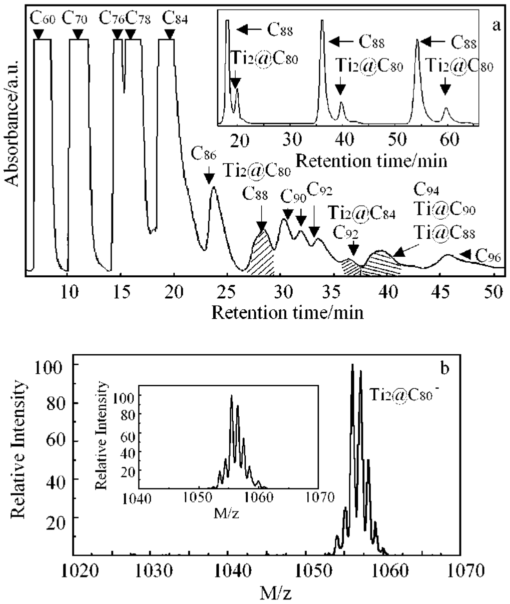

Figure 1. (a) Two-stage HPLC separation scheme of $Ti_2@C_{80}$: the first stage with a 5PYE column and the second stage (inset) with a Buckyclutcher column; (b) experimental (negative ion) and simulated theoretical (inset) mass spectra of $Ti_2@C_{80}$.

Figure 1a shows a typical HPLC chromatogram of a CS_2 extract. The $Ti_2@C_{80}$ fraction is overlapped with that of C_{88} in the first stage but can finally be separated from C_{88} through a recycling HPLC in the second stage (cf. inset of Figure 1a). Figure 1b shows the experimental and simulated theoretical mass spectra of $Ti_2@C_{80}$. The experimental and theoretical ^{13}C isotope distributions of $Ti_2@C_{80}$ agree well with each other, indicating the complete isolation of this species. The UV−vis−NIR absorption spectrum of $Ti_2@C_{80}$ shows several characteristic features at 499, 554, 614, 720, and 850 nm with an onset around 1400 nm as seen in Figure 2a. Interestingly, the current absorption spectrum of $Ti_2@C_{80}$ resembles none of the $M_2@C_{80}$ (M = La,[8] Ce,[13,14] Pr,[14] Hf,[12] Sc[10]) spectra thus far reported. This strongly suggests that the geometrical and electronic structures of $Ti_2@C_{80}$ are different from those of the $M_2@C_{80}$ metallofullerenes.

The EELS analysis as shown in Figure 2b also confirms the chemical composition of $Ti_2@C_{80}$ in addition to the mass spectral analysis presented above. The two peaks observed at 465.4 and 460.0 eV correspond to the Ti L_{23}-edge.[15] The experimental atomic Ti/C ratio based on the EELS analysis is 2.5 ± 0.4%, which agrees with the theoretical composition of $Ti_2@C_{80}$ (2.5%). The abundance ratios of $Ti_2@C_{80}$, $Ti_2@C_{84}$, $Ti@C_{88}$, and $Ti@C_{90}$ relative to C_{60} are 0.8, 0.4, 0.2, and 0.1%, respectively. The current arc synthesis conditions particularly favor the formation of $Ti_2@C_{80}$.

EELS has been known as an excellent method for investigating the valency of endohedral metallofullerenes.[16] The EELS spectra of $Ti_2@C_{80}$ together with those of TiO_2, Ti_2O_3, TiO, and TiC

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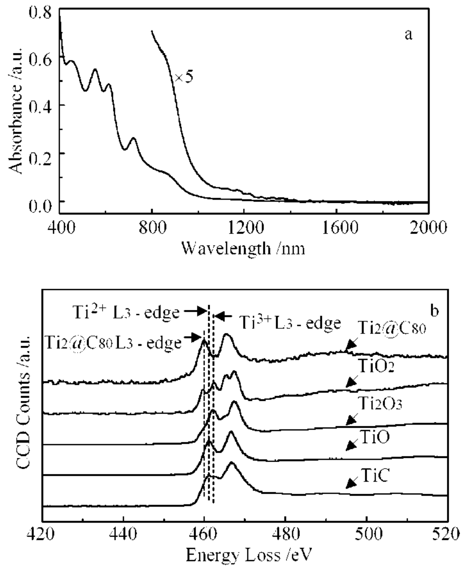

Figure 2. (a) UV−vis−NIR absorption spectrum of $Ti_2@C_{80}$ in CS_2 solution; (b) The Ti L_{23}-edge EELS spectra of $Ti_2@C_{80}$ together with those of TiO_2, Ti_2O_3, TiO, and TiC for reference.

were measured under a similar experimental condition (see Figure 2b). The observed peak positions of TiO_2 and $Ti_2@C_{80}$ in the Ti L_{23}-edge EELS differ substantially with each other, indicating that the Ti atoms within $Ti_2@C_{80}$ are not in a +4 oxidation state. Furthermore, in reference to Ti^{3+} (Ti_2O_3) and Ti^{2+} (TiO and TiC), the L_3-edge of $Ti_2@C_{80}$ is shifted to the even lower energy by 2.3 and 1.4 eV, respectively, suggesting that the valence state of Ti within $Ti_2@C_{80}$ is lower than +2. This is obviously different from the lanthanide-metallofullerenes with a similar composition, such as $La_2@C_{80}$ or $Ce_2@C_{80}$, in which the encapsulated metal atoms are definitively in a trivalent state.[8,13,14] Therefore, the result distinguished the electronic properties for transition metallofullerenes from those for the lanthanide ones.

The ^{13}C NMR spectrum of $Ti_2@C_{80}$ in CS_2 solution presents eight lines, three of which have full, four at half, and one at one-third intensities (see Figure 3). This NMR pattern can be attributed to a mixture of two $Ti_2@C_{80}$ isomers in an abundance ratio of 3:1 with D_{5h} (marked with circles) and I_h (labeled by asterisks) symmetric C_{80} cages, respectively.[17] Since the full intensity line of I_h-C_{80} can usually be found in the range 138−145 ppm and the line with one-third intensity in 130−138 ppm,[9,18] the two lines at 138.95 and 130.46 ppm are ascribed to I_h-C_{80}, whereas the remaining six lines are due to D_{5h}-C_{80}.

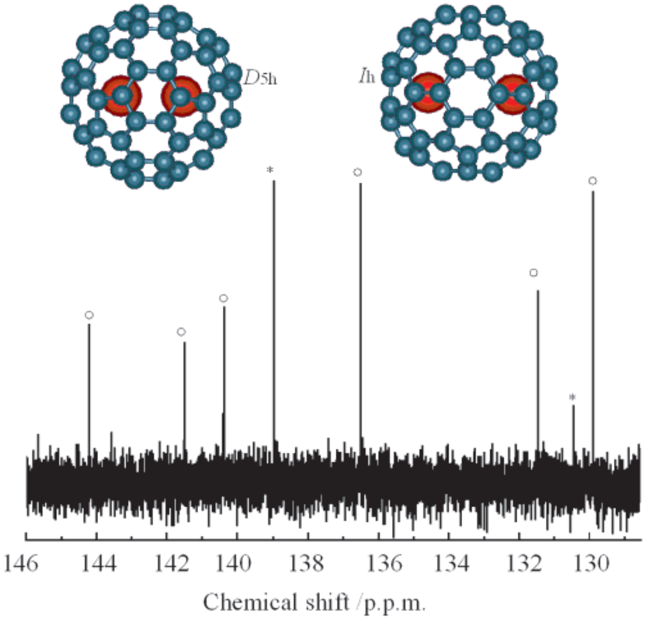

Figure 3. ^{13}C NMR spectrum and structures of two $Ti_2@C_{80}$ isomers.

Because the two cages are very similar in shape (see Figure 3), the separation of the two $Ti_2@C_{80}$ isomers is extremely difficult. The I_h-C_{80} cage can be generated by dissecting D_{5h}-C_{80} into two equal hemispheres from the σ_h mirror plane and rotating clockwise one hemisphere by 36° against the other around the C_5 axis. A rotation by further 36° can recover D_{5h}-C_{80} from I_h-C_{80}. Therefore, the overall cage shapes, the bond lengths/angles, and the cage diameters are very similar to each other, so that the interactions between the metallofullerenes and HPLC column for the two isomers are almost identical (see Figure 3).

The C_{80} fullerene has seven structural isomers satisfying isolated pentagon rule (IPR) with symmetry of D_2, D_{5d}, C_{2v}, $C_{2v'}$, D_3, D_{5h}, and I_h.[17] Only three isomers, however, have been experimentally observed, two of which are empty fullerenes with D_2[19] and D_{5d}[20] symmetry and one endohedral metallofullerene with I_h[8,9] symmetry. The present $Ti_2@C_{80}$ metallofullerene is the first production and experimental observation of D_{5h}-C_{80}.

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Supporting Information Available: UV−vis−NIR absorption spectra and HPLC retention times of $Ti_2@C_{80}$ and $La_2@C_{80}$, and structures of two $Ti_2@C_{80}$ isomers (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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