Structural Studies of Sc Metallofullerenes by High-resolution Ion Mobility Measurements

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Endohedral metallofullerenes have been extensively studied over the past decade because of their unique structural and electronic properties.1 Scandum metallofullerenes are especially interesting because they can contain more than two metal atoms (Scn@Cm) which form metal clusters.2,3 Furthermore, a Sc nitride metallofullerene, ScN@C80 has been synthesized recently.4 The structures of these metallofullerenes have been studied so far by ultrahigh vacuum scanning tunnel microscopy (UHV-STM),5 electron spectroscopy,6 and X-ray diffraction.7 However, these measurements require a large amount (~mg) of purified (>99.9%) samples, which are not always available. It is thus necessary to develop new methods to study the stability and the structures of these novel carbon nanomaterials.

Gas-phase ion mobility measurements have been applied to various species, such as clusters,8−10 fullerene-related materials,11 and polypeptides.12 This method has some favorable features in comparison with STM, NMR, and X-ray measurements. High sensitivity and high selectivity originating from ion mass detection allow us to use only a small amount of mixtures of metallofullerenes. Furthermore, high-speed (~ms) gas-phase detection can provide us structural information on intermediate species. Here we present the first successful high-resolution ion mobility measurements on Scn@Cm (n = 1−3, m = 74−90). The results show that all of the metallofullerenes have endohedral structures and that, for some, the carbon cages shrink when exposed to high desorption/ionization laser fluence.

The Sc metallofullerene samples are prepared by a large-scale DC discharge apparatus using Sc graphite composite rods as anodes (Sc 1.6 at %, Toyotamso Inc.). A discharge current of 500 A is employed along with a He buffer gas at 40 Torr.13 The metallofullerenes are extracted from the soot by C8H4. The high-resolution ion-mobility apparatus has been described in detail previously.13 The apparatus consists of a source region coupled directly to a 63 cm long drift tube. The metallofullerenes extracts are drop-coated onto a copper rod and then desorbed/ionized by a focused pulsed excimer laser (XeCl 308 nm). The resulting ions are introduced into the drift tube, which contains helium buffer gas at 500 Torr and has a drift voltage of 10 kV. After traveling through the drift tube, the ions are mass analyzed by a quadrupole mass spectrometer (Extrel Inc.). Drift-time distributions are recorded with a multichannel analyzer (Tennecals/Nucleus Inc. MCLS-II).

Figure 1 shows drift time distributions for positive ions of empty fullerences and metallofullerenes obtained from solvent extractable C82 and Scn@C82 (n = 1−3). The ions of C82 and Scn@C82 show a single peak, and the drift time is exactly the same as those of previous measurements on C82− from other fullerence samples and from well annealed C82 clusters.10,14 These results are consistent with the endohedral structures determined by X-ray diffraction.15 However, two structural isomers of Sc@C82 (I, II) existing in the sample15 are not resolved because as in most cage-isomers they have almost the same ion mobilities. On the other hand, the dimetallofullerene Scn@C82 (n = 1−3) shows two distinct peaks. The main peak with larger drift time corresponds to the peaks measured for C82− and Scn@C82. The other peak has a substantially smaller drift time, which suggests that it has a smaller cage size. The trimetallofullerene Scn@C82 shows only one peak which appears to correspond to the Scn@C82− peak with the shorter drift time. The high-resolution ion mobility measurements enable us to detect these two structures for the first time.

Figure 1. High-resolution ion mobility distributions of C82+ and Scn@C82+ (n = 1−3) produced from laser desorption/ionization of solvent extractable fullerences. Scn@C82+ shows two distinct peaks (details see text).

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Figure 2. Inverse mobility dependences of Sc@C\textsubscript{8n} (n = 1~3) on cage sizes (n = 74~90): (a) Sc@C\textsubscript{84} vs C\textsubscript{84}, (b) Sc\textsubscript{2}@C\textsubscript{8n} vs C\textsubscript{8n}, (c) Sc\textsubscript{3}@C\textsubscript{8n} vs C\textsubscript{8n}. All Sc@C\textsubscript{8n} have inverse mobilities identical to those of C\textsubscript{8n}. Smaller inverse mobilities of Sc\textsubscript{2}@C\textsubscript{8n} as well as those of Sc\textsubscript{3}@C\textsubscript{8n} are almost the same as those of C\textsubscript{8n−2}, suggesting (Sc\textsubscript{2}C\textsubscript{2})@C\textsubscript{8n−2} and (Sc\textsubscript{2}C\textsubscript{2})@C\textsubscript{8n−2} structures.

Figure 2 shows the inverse mobilities of mono-, di-, and triscandium fullerences plotted as a function of cage size. The inverse mobilities are proportional to the cross sections for collisions between the fullerences and the He buffer gas. The larger dimetallofullerenes, Sc\textsubscript{2}@C\textsubscript{8n}, have inverse mobilities identical to those of C\textsubscript{8n−2}. The relative intensity of Sc\textsubscript{2}@C\textsubscript{8n−2} is 0.41 at Sc\textsubscript{2}@C\textsubscript{82} and increases to 0.88 and 1.0 at Sc\textsubscript{2}@C\textsubscript{74} and Sc\textsubscript{2}@C\textsubscript{90}; (a) Sc@C\textsubscript{8n}, (b) middle, and (c) high laser fluence. The shorter drift time peak becomes prominent as the laser fluence increases.

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Supporting Information Available: A mass spectrum of Sc metallofullerenes (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Figure 3. Drift time distribution of Sc\textsubscript{2}@C\textsubscript{82} produced under (a) low, (b) middle, and (c) high laser fluence. The shorter drift time peak becomes prominent as the laser fluence increases.