Endohedrally Metal-Doped Heterofullerenes: $La@C_{81}N$ and $La_2@C_{79}N$

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The first evidence of the gas-phase formation of endohedrally La-doped azafullerene ions $La@C_{81}N^+$ and $La_2@C_{79}N^+$ was obtained by the fast atom bombardment mass (FABMS) fragmentation of the adducts, $La@C_{82}(NCH_2Ph)$ and $La_2@C_{80}(NCH_2Ph)$.

Much interest is currently directed toward the variation of the chemical and physical properties of fullerenes to extend the applications. For this purpose, there are two interesting methods: encapsulation of metal atoms inside the carbon cages (endohedral metallofullerenes) and substitution of one or more cage carbons by heteroatoms (heterofullerenes). As the examples of endohedral doping, lanthanide fullerenes such as $La@C_{82}$ and $La_2@C_{80}$ have been most extensively investigated, these having significantly different electronic properties[1,2] and reactivities[3] (compared with empty fullerenes) owing to electron transfer from metals to fullerene cages, unlike the encapsulation of noble gas atoms.[4] Considerable progress has been also made for substitutional doping. Most interesting is the recent efficient formation of azafullerene ions such as $C_{59}N^+$ and $C_{69}N^+$.[5-7] Since the resultant $C_{59}N$ and $C_{69}N$ radicals are highly reactive, only the dimers or derivatives have been isolated and their properties have been characterized.[5,8] It is an interesting challenge to prepare a new class of fullerene molecules whose properties are enhanced by a combination of endohedral and substitutional doping.

We now report the first evidence of the formation of La-doped azafullerene ions $La@C_{81}N^+$ and $La_2@C_{79}N^+$. We have found that these ions are efficiently formed by fast atom bombardment mass (FABMS) fragmentation of the adducts afforded from chromatographic separation (Buckyprep column; toluene as eluent) of the reaction mixture of benzyl azide with $La@C_{82}$ and $La_2@C_{80}$ at 170 °C.

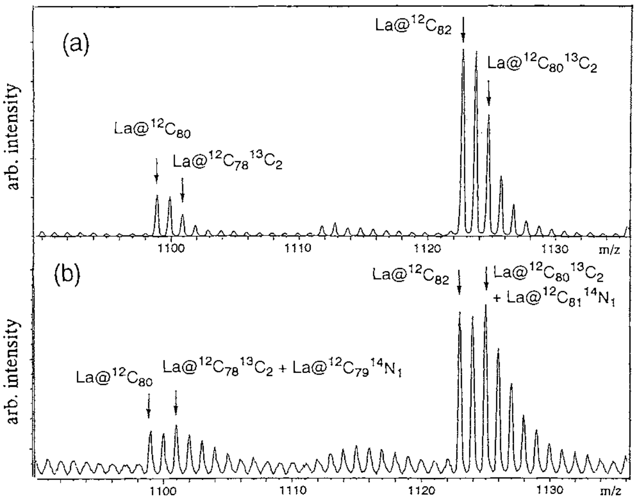

Figure 1. FABMS fragmentation spectra (from 1090 to 1135 amu) of (a) $La@C_{82}$ and (b) $La@C_{82}(NCH_2Ph)$.

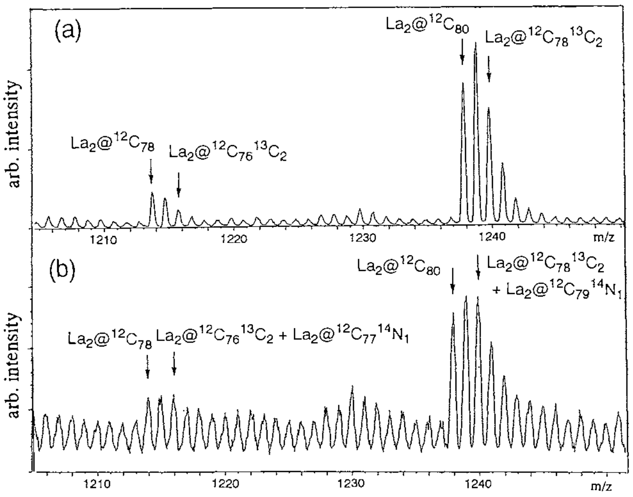

Figure 2. FABMS fragmentation spectra (from 1205 to 1250 amu) of (a) $La_2@C_{80}$ and (b) $La_2@C_{80}(NCH_2Ph)$.

The FABMS spectrum of $La@C_{82}$ itself is shown in Figure 1a which has a parent peak at m/z = 1123. As Figure 1b shows, the FABMS fragmentation of the adduct $(La@C_{82}(NCH2Ph))$[9] of $La@C_{82}$ and benzyl azide provides an increased peak at m/z = 1125. A high-resolution measurement of the peak at m/z = 1124.9071 agrees with the theoretical value of 1124.9094 for $La@C_{81}N^+$. Information of ^{13}C abundance in mass peaks is useful.[5] The increased signal at mass 1125 in Figure 1b is composed of a signal from $La@^{12}C_{80}{}^{13}C_2{}^+$ and a signal from $La@^{12}C_{81}{}^{14}N_1{}^+$. Based on the isotope distribution, the relative ratio of $La@C_{82}^+$ and $La@C_{81}N^+$ was calculated as 1: 0.6, the intensity of $La@C_{81}N^+$ increasing in the desired mass region. The formation of $La@C_{81}N^+$ is also reflected in the "shrink-wrap" fragmentation pattern with a peak at m/z = 1101 in Figure 1b due to the loss of a C_2 unit (m/z = 24). Although successive loss of C_2 units is observed for C_{60},[10] there is a marked difference in the shrink-wrapping between $C_{59}N^+$ and $La@C_{81}N^+$. Whereas $C_{59}N^+$ first loses exclusively a CN unit

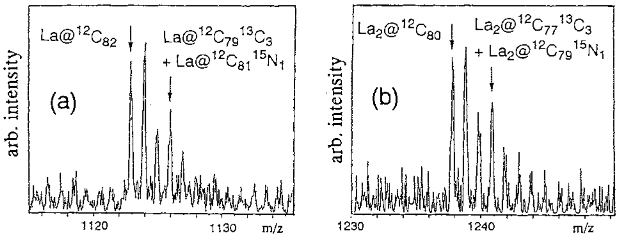

Figure 3. FABMS fragmentation spectra (a) $La@C_{82}(^{15}NCH_2Ph)$ from 1115 to 1135 amu and (b) $La_2@C_{80}(^{15}NCH_2Ph)$ from 1230 to 1250 amu.

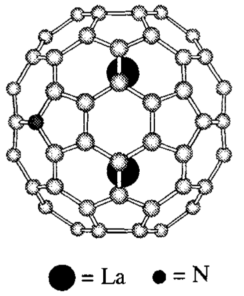

Figure 4. The optimized structure of $La_2@C_{79}N$.

and then C_2 units,[5] $La@C_{81}N^+$ loses C_2 units (down to $La@C_{75}N^+$). This difference is ascribed to the variation of the bond strengths due to La-doping. Shrink-wrapping is a high energy process (>40 eV) that can make all exohedrally bound groups removed first.[10b] Therefore, it is unlikely that the peaks at 1125 and 1101 are due to exohedral metallofullerene derivatives such as dihydro-metallofullerenes. As Figure 2 shows, $La_2@C_{79}N^+$ is formed by the FABMS fragmentation of the adduct $(La_2@C_{80}(NCH_2Ph)$[9] of $La_2@C_{80}$ and benzyl azide and the relative ratio of $La_2@C_{80}^+$ and $La_2@C_{79}N^+$ is 1: 0.65, as in the case of $La@C_{82}$.

To further confirm the formation of $La@C_{81}N^+$ and $La_2@C_{79}N^+$, we prepared a 99% ^{15}N-labeled benzyl azide ($PhCH_2{}^{15}NNN$). Figures 3a and 3b show the FABMS fragmentation spectra of the adducts of the ^{15}N-labeled benzyl azide with $La@C_{82}$ and $La_2@C_{80}$, respectively. Like the unlabeled cases in Figures1b and 2b, the intense fragmentation signals are due to $La@^{12}C_{79}{}^{13}C_3^+$ and $La@^{12}C_{81}{}^{15}N_1^+$ for m/z = 1126, and $La_2@^{12}C_{77}{}^{13}C_3^+$ and $La_2@^{12}C_{79}{}^{15}N^+$ for m/z = 1241, respectively.

$La_2@C_{79}N^+$ and $La@C_{81}N^+$ are isoelectronic with $La_2@C_{80}$ and $La@C_{82}$, respectively. Ab initio calculations[11] of $La_2@C_{79}N^+$ show that almost all three valence electrons are transferred from each La ($5d^16s^2$) to the LUMO, LUMO + 1, and LUMO + 2 of the azafullerene cage, as in $La_2@C_{80}$.[12] Consequently, $La_2@C_{79}N^+$ has a closed shell electronic structure. Acceptance of an electron leads to the $La_2@C_{79}N$ radical. However, it is noteworthy that the electron is not distributed on the cage surface but localized on each La with a spin density of 0.5; two La atoms serve as a spin-absorbent. The most stable optimized structure of $La_2@C_{79}N$ is shown in Figure 4, which has C_s symmetry. The La - La distance of 3.585 Å is shorter than those of 3.655 and 3.622 Å for $La_2@C_{80}$[12] and $La_2@C_{79}N^+$, respectively, as a result of the acceptance of an electron into the La - La bonding orbital and the decreased positive charge on La. In $La_2@C_{79}N$ the nitrogen atom occupies the position which is 4.518 Å away from each La. On the other hand, three electrons are transferred in $La@C_{81}N^+$ from La to the LUMO and LUMO + 1 of the azafullerene cage, as in $La@C_{82}$.[13] However, the singly occupied LUMO + 1 level is filled up in $La@C_{81}N$ by accepting an electron. Therefore, the cage atoms in both $La_2@C_{79}N$ and $La@C_{81}N$ have no significant radical character. This is in sharp contrast with the high spin localization onto the carbons near nitrogen in $C_{59}N$ and $C_{69}N$ which leads to facile dimerization and abstraction.[5,8]

On the basis of the unique stability and properties, we are currently working on the synthesis and isolation of $La@C_{81}N$ and $La_2@C_{79}N$ in macroscopic amounts to develop a new class of cage molecules promising for material applications.

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