Metallofullerenes

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Isolation and Structure Determination of a Missing Endohedral Fullerene La@C_{70} through In Situ Trifluoromethylation

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Abstract: *D_{5h}-symmetric fullerene C_{70} (D_{5h}-C_{70}) is one of the most abundant members of the fullerene family. One long-standing mystery in the field of fullerene chemistry is whether D_{5h}-C_{70} is capable of accommodating a rare-earth metal atom to form an endohedral metallofullerene M@D_{5h}-C_{70}, which would be expected to show novel electronic properties. The molecular structure of La@C_{70} remains unresolved since its discovery three decades ago because of its extremely high instability under ambient conditions and insolubility in organic solvents. Herein, we report the single-crystal X-ray structure of La@$C_{70}(CF_3)_3$, which was obtained through in situ exohedral functionalization by means of trifluoromethylation. The X-ray crystallographic study reveals that La@$C_{70}(CF_3)_3$ is the first example of an endohedral rare-earth fullerene based on D_{5h}-C_{70}. The dramatically enhanced stability of La@$C_{70}(CF_3)_3$ compared to La@C_{70} can be ascribed to trifluoromethylation-induced bandgap enlargement.*

One fascinating property of fullerene is its ability to accommodate atoms, ions, or clusters in its inner space to form a core–shell structured complex, that is, the so-called endohedral fullerenes X_m@C_{2n}.[1] Since its discovery in 1985,[2] a variety of different types of endohedral fullerenes, such as mono-metallofullerene,[3] di-metallofullerene,[4] and cluster-fullerene,[5] have been studied extensively. In fact, the number of endohedral fullerenes that have been isolated experimentally is even larger than that of the isolated empty fullerenes. As a large class of fullerene derivatives, the endohedral fullerenes have versatile and tunable electronic, optical, and magnetic properties, which are correlated with the nature of the encapsulated species.[1,6]

Among the many known endohedral fullerenes, C_{60}- and C_{70}-based mono-metallofullerenes (M@C_{60} and M@C_{70}) are of particular interest because of their (theoretically predicted) exotic electronic properties.[1,7] Smalley and co-workers observed signals attributable to La@C_{60} and La@C_{70} in the laser vaporization TOF mass spectra of $LaCl_3$-impregnated graphite rods several days after the discovery of C_{60} in 1985.[2,8] The macroscopic production of M@C_{60} and M@C_{70} was subsequently achieved by the high-temperature laser ablation method in 1991.[3] Unfortunately, however, M@C_{60} and M@C_{70} were found to be insoluble in organic solvents normally suitable for fullerenes and fullerene derivatives. Since then, the extraction and purification of M@C_{60} and M@C_{70} have posed a major challenge. Although some progress has been made during the past decades,[9] the molecular structures of M@C_{60} and M@C_{70} remain unknown to date. We were also interested to determine whether or not M@C_{60} and M@C_{70} adopt the conventional I_h-symmetric C_{60} (I_h-C_{60}) and D_{5h}-symmetric C_{70} (D_{5h}-C_{70}) fullerene cages, respectively.

Recently, we reported an in situ functionalization method for the extraction and purification of the so-called missing small-bandgap metallofullerenes including M@C_{60} and M@C_{70}.[10] We found that M@C_{60} and M@C_{70} are stabilized greatly by exohedral functionalization with trifluoromethyl groups. This finding prompted us to investigate the structures (thus far unreported) and properties of the small-bandgap metallofullerenes. Herein, we report the first experimental determination of the molecular and crystal structures of La@C_{70} since it was first detected by laser vaporization mass spectrometry three decades ago. The metallofullerene La@C_{70} is stabilized by attachment of trifluoromethyl groups and its structure is determined by means of single-crystal synchrotron X-ray diffraction (XRD).

The metallofullerene La@C_{70} was trifluoromethylated in situ by using a modified arc-discharge method as reported previously.[10] Polytetrafluoroethylene (PTFE) was used as a source for the CF_3 groups. Without using PTFE, the intact La@C_{70} can also be found in the soot in a high yield. However, in this case, La@C_{70} would form insoluble polymers in the raw soot because of its small bandgap. By placing PTFE rods near the arc zone in the chamber, La@C_{70} is efficiently captured and stabilized by CF_3 groups during the growth.[10] After the extraction and purification process (see the Supporting Information for details), we have obtained two isomers of La@$C_{70}(CF_3)_3$ (denoted isomers **1a** and **1b**). In this study, the structure of La@$C_{70}(CF_3)_3$ (**1a**) is determined by single-crystal X-ray diffraction.

Isomer **1a** of La@$C_{70}(CF_3)_3$ is soluble in solvents typically employed for fullerenes and fullerene derivatives, such as CS_2, toluene, and *o*-xylene. Figure 1 shows the mass spectrum and the UV/Vis/near-IR absorption spectrum of the purified La@$C_{70}(CF_3)_3$ isomer **1a**. The experimentally detected isotopic distribution pattern in the mass spectrum is consistent with the corresponding simulated one (Figure 1a). The absorption spectrum (Figure 1b) of isomer **1a** of La@C_{70}-$(CF_3)_3$ shows two distinct bands at $\lambda = 576$ and 671 nm and weak bands between $\lambda = 820$ and 1080 nm. There is no obvious absorption band beyond 1200 nm, indicating that

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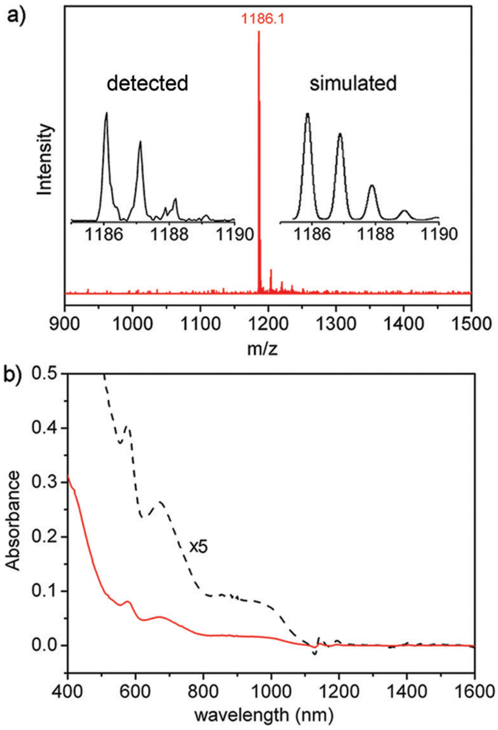

Figure 1. a) Matrix-assisted laser desorption/ionization TOF mass spectrum (negative-ion mode) of isomer **1a** of La@$C_{70}(CF_3)_3$. Sulfur (S_8) was used as the matrix for the measurement. The signal at *m*/*z* 1186.1 corresponds to La@$C_{70}(CF_3)_3$. Insets: the experimentally detected (left) and the simulated (right) isotopic distribution patterns. b) UV/Vis/near-IR absorption spectrum of isomer **1a** of La@$C_{70}(CF_3)_3$ in CS_2. The dotted line is a fivefold magnification of the original spectrum.

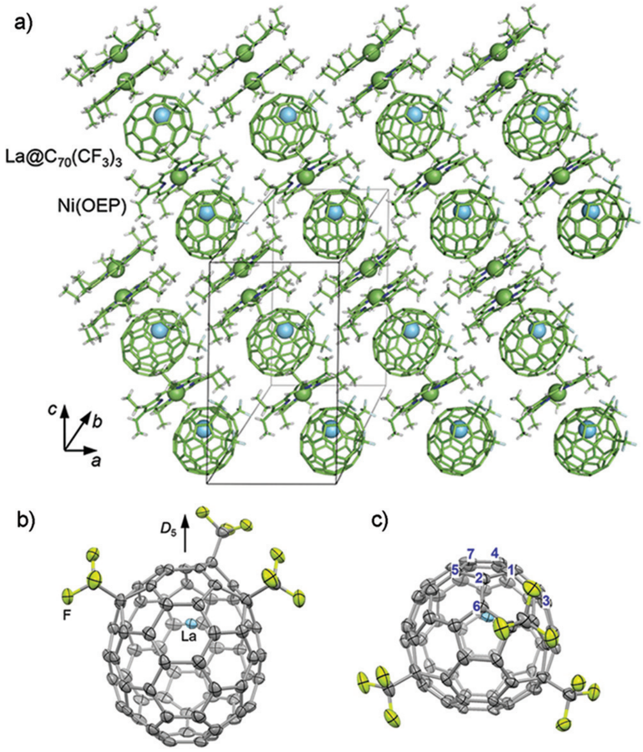

Figure 2. X-ray structure of the cocrystal of **1a**–[Ni(OEP)]. a) The molecular arrangement along the *ac* plane in the crystal (space group = $P\bar{1}$). The solid lines indicate the triclinic unit cell. b, c) The refined structure of **1a**, with thermal ellipsoids set at 50% probability, viewed b) perpendicular to and c) along the D_5 axis of the C_{70} cage. In (c), carbon atoms adjacent to the endohedral La atom position are labeled in order as 1–7 from the first to the seventh nearest.

the metallofullerene has a large HOMO–LUMO gap (HOMO = highest occupied molecular orbital, LUMO = lowest unoccupied molecular orbital) of about 1.0 eV.

A single crystal of isomer **1a** of La@$C_{70}(CF_3)_3$ was obtained by cocrystallization with [Ni(OEP)] (OEP = octaethylporphyrin). Figure 2a shows the molecular arrangement in the crystal at 100 K, which consists of isomer **1a** of La@$C_{70}(CF_3)_3$ and [Ni(OEP)] in a ratio of 2:3 without any solvent molecules. The coordination structure, where two [Ni(OEP)] molecules sandwich one molecule of **1a**, suppresses the orientational disorder of **1a** sufficiently so that structure determination is possible (see the Supporting Information for details).[11] Two different views of the refined structure of one independent **1a** molecule are shown in Figure 2b and c. The carbon cage in **1a** is found to be that of the conventional D_{5h}-C_{70}. It should also be noted that isomer **1a** of La@$C_{70}(CF_3)_3$ has a chiral structure. The centrosymmetric crystal with a space group of $P\bar{1}$ is racemic and thus it contains two chiral isomers with the same number of molecules.

In the refined structure of **1a**, three CF_3 groups are attached to carbon atoms of pentagons on the fullerene (Figure 2b and c). The three pentagons with CF_3 groups are located at one side of the long axis of the C_{70} cage. One CF_3 group is attached to one of the five carbon atoms nearest to the long axis with D_5 symmetry. The remaining two CF_3 groups are attached to two of the ten carbon atoms at the third carbon site away from the line of the axis. The endohedral La atom is also on the same side of the C_{70} long axis where the three CF_3 groups are attached. The La atom is located beneath a C–C bond between two carbon atoms on a pentagon, which are labeled as carbons 1 and 2 in Figure 2c. The distances between the La atom and the selected seven carbon atoms labeled as 1–7 in Figure 2c are listed in Table 1. The La–C distances are comparable to that for La@C_{2v}-C_{82}.[12]

The molecular structure determined by the present X-ray diffraction study suggests that an interaction may exist between the endohedral La atom and the exohedral CF_3 groups. For endohedral metallofullerenes with high-symmetry carbon cages such as I_h-C_{60}, I_h-C_{80}, and D_{5h}-C_{80}, the endohedral metal atoms often occupy multiple equivalent positions.[13] In contrast, metal atoms in low-symmetry carbon cages, such as C_{2v}-C_{82} and C_s-C_{82}, occupy typically only one position.[11–12] The localization of the La atom at a specific position in D_{5h}-C_{70} (Figure 2b and c) can be achieved by lowering the symmetry by attachment of CF_3 groups. The positional relationship between the La atom and the CF_3 groups, in which they gather at only one side of the long axis of the C_{70} cage, would be a result of an electrostatic interaction between the cationic La atom and the electron-attractive CF_3 groups. The La atom is located near the two carbon atoms (labeled as 1 and 2 in Figure 2c) that are the second and third nearest neighbors of the carbon atom (with a CF_3 group attached) which is closest to the D_5 axis. A similar

Table 1: Measured and calculated La–C distances in isomer **1a** of La@C_{70}(CF_3)$_3$ for the seven carbon atoms labeled as 1–7 in Figure 2c.[a]

Carbon No.	XRD Distance [Å]	Calculated Distance [Å]
1	2.488(6)	2.50
2	2.494(6)	2.50
3	2.556(6)	2.56
4	2.621(6)	2.65
5	2.639(6)	2.65
6	2.679(6)	2.66
7	2.746(6)	2.78

[a] See the Experimental Section for details of the calculations.

relationship can be detected for the Sc positions of $Sc_3N@D_{5h}$-$C_{80}(CF_3)_{18}$ and $Sc_3N@I_h$-$C_{80}(CF_3)_{14}$.[14]

To understand the stability of the trifluoromethylated metallofullerene La@C_{70}(CF_3)$_3$, we have performed density functional theory (DFT) calculations. In the case of the pristine La@C_{70}, the La atom transfers formally three electrons to the C_{70} cage. Accordingly, the La@C_{70} molecule has an open-shell structure. The DFT-optimized structure and the calculated molecular orbital energy levels for La@C_{70} are shown in Figure 3. The spin-up and spin-down energy gaps for La@C_{70} are 0.42 and 0.16 eV, respectively. The open-shell structure and the small energy gaps induce a kinetic instability within the La@C_{70} molecule. As a consequence, La@C_{70} tends to react with other highly reactive species in raw soot and form insoluble products.

Geometric optimization and electronic-structure calculations on isomer **1a** of La@C_{70}(CF_3)$_3$ were carried out based on the X-ray structure. The DFT-optimized structure of isomer **1a** is shown in Figure 3b. The position of the La atom in the DFT-optimized structure corresponds well with that detected by means of X-ray diffraction. As shown in Table 1, the DFT-calculated La–C distances are very close to those derived from XRD analysis. From the molecular orbital energy levels for isomer **1a** of La@C_{70}(CF_3)$_3$ (Figure 3c), we can expect that the HOMO–LUMO gap increases to 1.00 eV upon trifluoromethylation. The closed-shell structure and the enlarged HOMO–LUMO gap are responsible for the enhanced stability of La@C_{70}(CF_3)$_3$ as compared with pristine La@C_{70}. Besides isomer **1a** of La@C_{70}(CF_3)$_3$, we have also performed DFT calculations on some other isomers of La@C_{70}(CF_3)$_3$. It was found that isomer **1a** is the most thermodynamically stable of these isomers.

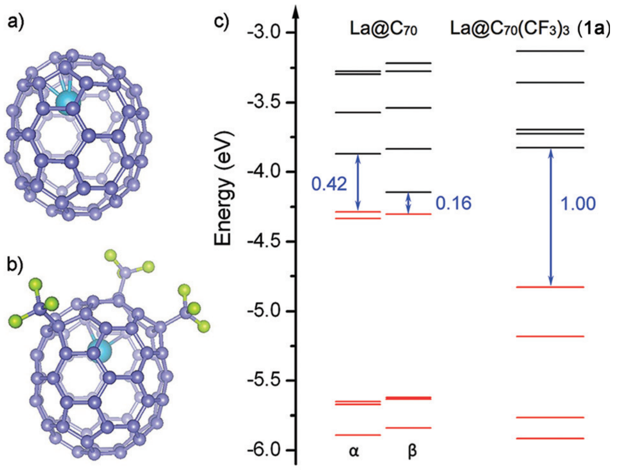

Figure 3. DFT-optimized molecular structures of a) La@C_{70} and b) isomer **1a** of La@C_{70}(CF_3)$_3$. c) The calculated molecular orbital energy levels for La@C_{70} (left) and isomer **1a** of La@C_{70}(CF_3)$_3$ (right). The occupied molecular orbitals are given in red, the unoccupied molecular orbitals are given in black. Energy gaps are expressed in eV.

Table 2: DFT-calculated relative energies (RE) and HOMO–LUMO gaps (H–L) for the five isomers of La@C_{70}(CF_3) and isomer **1a** of La@C_{70}(CF_3)$_3$.

Compound	La@C_{70}(CF_3)					La@C_{70}(CF_3)$_3$
Isomer	**2a**	**2b**	**2c**	**2d**	**2e**	**1a**
RE [kJ mol^{-1}]	8.67	7.35	0.00	28.99	57.20	–
H–L gap [eV]	0.30	0.34	0.37	0.39	0.23	1.00

Interestingly, to stabilize the open-shell-structured La@C_{70}, an odd number of CF_3 groups is required to form a closed-shell structure, which is similar to the cases of Y@C_{82}[15] and K@C_{70}.[16] In this work, no monosubstituted derivative (La@C_{70}(CF_3)) was observed experimentally, with only trisubstituted derivatives being obtained. To explain this observation, we performed DFT calculations on La@C_{70}(CF_3). In the case of La@D_{5h}-C_{70}, there are five addition sites for mono-trifluoromethylation (Figure S7 in the Supporting Information). The calculated relative energies and HOMO–LUMO gaps for the five isomers of La@C_{70}(CF_3) are listed in Table 2. The third isomer (**2c**) is the most stable in energy, and it has a HOMO–LUMO gap of 0.37 eV. The HOMO–LUMO gaps for the other four isomers are in the range of 0.23–0.39 eV. It is obvious that all of these five isomers have much smaller HOMO–LUMO gaps than isomer **1a** of La@C_{70}(CF_3)$_3$. The fact that La@C_{70}(CF_3) was missing in our experiments could thus be ascribed to its small HOMO–LUMO gap and low kinetic stability. We have examined the stability of bis-trifluoromethylated derivatives that are intermediates of isomer **1a** of La@C_{70}(CF_3)$_3$ (Figure S9) by DFT calculations. All of the bis-trifluoromethyl derivatives have small HOMO–LUMO gaps (0.43–0.57 eV).

In summary, the molecular structure of La@C_{70} has been determined for the first time by means of in situ trifluoromethylation and an X-ray crystallographic study. The carbon cage in isomer **1a** of La@C_{70}(CF_3)$_3$ is found to be the same as that of the conventional D_{5h}-C_{70}. The endohedral La atom and the three CF_3 substituents in **1a** are located on the same side of the C_{70} long axis. DFT calculations demonstrate that the stability of the La@C_{70} derivative is dependent on the number and addition pattern of the CF_3 functional groups. La@C_{70} is stabilized greatly as a consequence of trifluoromethylation-induced bandgap enlargement. This experimental technique not only allows structure determination of unexplored small-bandgap fullerenes and metallofullerenes but also provides a means to discover new endohedral fullerenes.

Experimental Section

Synthesis and purification: Direct-current arc discharge was performed to produce the metallofullerenes.[10] The metallofullerenes in raw soot were extracted with *ortho*-xylene by sonication. Then La@C_{70}(CF_3)$_3$ isomers **1a** and **1b** were isolated from the extract by using the $TiCl_4$-based method we developed[17] and multi-stage HPLC. The details of the extraction and purification process are described in the Supporting Information.

X-ray crystallographic study: A saturated toluene solution of isomer **1a** of $La@C_{70}(CF_3)_3$ and a saturated chloroform solution of [Ni(OEP)] were mixed in an attempt to grow single crystals. After slow evaporation of about 10 μL of the mixture solution at 80 °C, a cocrystal of **1a**–[Ni(OEP)] with a crystal size of 0.05 mm was obtained. The X-ray diffraction data for the structure analysis was collected at 100 K using a large cylindrical image plate camera at SPring-8 BL02B1 (Hyogo, Japan). The crystal has a triclinic unit cell with $a = 14.918$ Å, $b = 24.594$ Å, $c = 25.455$ Å, $\alpha = 68.166°$, $\beta = 89.087°$, $\gamma = 76.691°$, $V = 8411$ Å^3. 31422 independent Bragg reflections ($|F| > 3\sigma$, $d > 0.6$ Å, $\Sigma\sigma_I/\Sigma I = 0.08$) were used in the structure analysis. The initial structure model was derived by a direct method using SIR.[18] The structure refinement and modification were performed by using SHELX[19] and ENIGMA.[20] The reliability factor of the final structure model is $R1 = 0.0781$ ($|F| > 3\sigma$, $d > 0.6$ Å). The results are summarized in Table S1 and the crystal information file (CIF) is available from the Cambridge Crystallographic Data Centre (CCDC). CCDC 1055712 (**1a**–[Ni(OEP)]) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Computational details: Geometry optimization and electronic structure calculations on metallofullerenes were performed using the PBEPBE[21] functional in the Gaussian 09[22] software package. The 6-31g(d)[23] basis set was employed for C and F atoms. The effective core potential ECP28MWB[24] developed by the Stuttgart/Cologne group and corresponding optimized valence basis set were used for the La atom. Vibrational frequency calculations were performed on the same level to confirm that the optimized structures correspond to real minima on the potential energy surface.

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