Isolation and structure
determination of missing
fullerenes Gd@C_{74}(CF_3)_n
through in situ
trifluoromethylation

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Our trifluoromethyl functionalization method enables the dissolution and isolation of missing metallofullerenes of Gd@C_{74}(CF_3)_n. After multi-stage high-performance liquid chromatography purification, Gd@C_{74}(CF_3)_3 and two regioisomers of Gd@C_{74}(CF_3) are isolated. X-ray crystallographic analysis reveals that all of the isolated metallofullerenes react with CF_3 groups on pentagons of the D_{3h}-symmetry C_{74} cages. Highest occupied molecular orbital-lowest unoccupied molecular orbital gaps of these trifluoromethylated derivatives, estimated by absorption spectra, are in the range 0.71–1.06 eV, consistent with density functional calculations.

1. Introduction

Endohedral metallofullerenes M@C_{2m} (M = rare earth metal), encapsulating metal atoms in the internal space of spherical carbon structures, have attracted much attention due to their unique properties [1,2]. Of these, gadolinium-encapsulated metallofullerenes have been widely investigated for biomedical applications [3–8]. With such high magnetic moments, Gd@C_{2m} are of interest as novel magnetic resonance imaging (MRI) contrast agents [3–6]. The fully enclosing carbon cage completely prevents...
leaching of the Gd atoms, resulting in lower toxicity than commercially available metal chelate reagents such as Gd-DTPA. However, only M@C_{2m} type metallofullerenes have been used for these applications. Although a lot of small-cage endohedral metallofullerenes M@C_{2m} (2m = 60, 70, 72 and 74) are obtained in as-synthesized carbon soot, there are few examples of successful isolation [9–15]. These metallofullerenes, so-called missing (or small highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gap) metallofullerenes, are highly reactive and tend to form insoluble polymerized solids in raw soot.

Recently, we developed an in situ trifluoromethylation method for the extraction and purification of these missing metallofullerenes [16–19]. CF_{3} groups [20–23], furnished by the thermal pyrolysis of polytetrafluoroethylene (PTFE), were introduced to the outer cages of fullerenes and stabilized reactive missing metallofullerenes during the production simultaneously. A series of yttrium- and lanthanum-encapsulated missing metallofullerenes were isolated by this technique. However structural determination still remains an important open question for fullerene science. We herein report the isolation of CF_{3}-functionalized Gd@C_{74} and structural determination by single-crystal X-ray diffraction.

2. Method

2.1. Synthesis and purification of Gd@C_{74}(CF_{3}) (I), Gd@C_{74}(CF_{3}) (II) and Gd@C_{74}(CF_{3})_{3}

Trifluoromethylated Gd-metallofullerenes were synthesized by the modified arc-discharge method. A cross-sectional view of the DC arc-discharge chamber is illustrated in electronic supplementary material, figure S1, where PTFE rods (40 g) are placed near the discharge area. A graphite rod (100 g) impregnated with Gd (La) (0.8 mol%, Toyo Tanso Co. Ltd) was used as the anode. A pure graphite rod (Toyo Tanso Co. Ltd) was used as the cathode. Arc discharge was performed at a DC current of 500 A in a flowing He atmosphere with a pressure of 7–9 kPa. During arc discharge, because of the high temperature around the arc zone, PTFE was decomposed and evaporated to produce CF_{3} radicals. Normally, 50–70 g of raw soot was obtained per discharge. Gd-metallofullerenes and empty fullerenes were extracted from the raw soot with o-xylene.

2.2. Separation of trifluoromethylated Gd-metallofullerenes from empty fullerenes by TiCl_{4}

To a 500 ml CS_{2} solution of the crude mixture, ca 5 ml of TiCl_{4} was added. Metallofullerenes were reacted immediately and insoluble complexes were precipitated out [24–26]. After mixing for 5 min, the precipitate was collected on PTFE membrane filter and washed with 10–20 ml of CS_{2} to separate from the fullerenes in solution. Deionized water was passed through the filter to decompose the complexes of metallofullerene/TiCl_{4}, and then washed with acetone to eliminate extra water. Finally, CS_{2} was passed through the filter to collect the desired metallofullerenes as a solution.

2.3. Multi-stage high-performance liquid chromatography purification of Gd-metallofullerenes

High-performance liquid chromatography (HPLC) purification was conducted using a JAI (Japan Analytical Industry Co.) recycling preparative HPLC LC-9104HS. Three isomers of Gd@C_{74}(CF_{3})_{n} were isolated from the mixture by the multi-stage HPLC method. Two kinds of columns were used alternatively with toluene eluent for the isolation, i.e. Buckyprep column (20 mm diameter × 250 mm, Nacalai Tesque Inc.) and Buckyprep-M column (20 mm diameter × 250 mm, Nacalai Tesque Inc.). The initial (first-stage) HPLC purification was performed with Buckyprep-M. Gd@C_{74}(CF_{3})_{3} was obtained in fraction A and Gd@C_{74}(CF_{3}) (I) and (II) were obtained in fraction B. The overall separation scheme and the HPLC chromatograms are shown in electronic supplementary material, figures S2–S10.

2.4. X-ray crystal structure analysis

Single crystals of Gd@C_{74}(CF_{3}) (I) and (II) and Gd@C_{74}(CF_{3})_{3} were obtained by co-crystallization with Ni(OEP) (OEP = octaethylporphyrin) from solution. The single-crystal X-ray diffraction data were collected at SPring-8 BL02B1 [27]. The crystal structures were determined using SIR [28] and SHELX [29]. The crystallographic data are summarized in electronic supplementary material, table S1, and crystallographic information files (CIF). A theoretical $D_{3h}$-symmetry C_{74} rigid-body molecule was used in modelling of the Gd@C_{74}(CF_{3})_{n} molecules showing severe orientation disorder. Although the
Gd@C_{74}(CF_3)_n molecules have chiral structures, the space groups of the crystals are centrosymmetric. Therefore, each crystal contains the same number of the chiral isomers. The anisotropic atomic displacement parameters of carbon atoms on disordered C_{74} cages of Gd@C_{74}(CF_3) (I) and (II) were determined by using two parameters of translation and libration motions of the rigid-body molecules \[30,31\]. The CIF deposition numbers at the Cambridge Crystallographic Data Centre (CCDC) are 1824999 for Gd@C_{74}(CF_3) (I), 1825000 for Gd@C_{74}(CF_3) (II) and 1825001 for Gd@C_{74}(CF_3)_3.

2.5. Density functional calculations

Density functional (DFT) calculations were performed under the local spin density approximation, as implemented in the AIMPRO code \[32–34\]. Relativistic pseudopotentials were included via the Hartwigsen–Goedecker–Hütter scheme \[35\]. For C/Gd/F, a basis set containing 38/90/28 independent Gaussian-based functions was used \[36\]. Calculations were fully spin polarized with spin relaxation. Periodic boundary conditions at the gamma point were used, with cell size large enough to avoid interaction between neighbouring fullerenes. A system-dependent plane wave energy cutoff of 300 Ha (Ha: Hartree energy) was applied with a non-zero electron temperature of \(kT = 0.04\) eV for electronic level occupation. Atomic positions were geometrically optimized until the maximum atomic position change in a given iteration dropped below 10^{-6} \(a_0\) (\(a_0\): Bohr radius). The method has been previously successfully applied to study Gd-metallofullerenes \[19\] and is discussed in more detail in another article \[37\].

3. Results

The purity of the three metallofullerenes obtained by multi-stage HPLC preparation was confirmed by matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectroscopy (figure 1). The mass spectra of the isolated samples show strong isolated peaks of Gd@C_{74}(CF_3) (I and II) and Gd@C_{74}(CF_3)_3, respectively, confirming that these species are highly purified through the multi-stage HPLC separation. Figure 1a–c indicates a peak corresponding to the presence of Gd@C_{74}, attributed to the parent fullerene dissociated by laser-induced fragmentation. Close inspection reveals that this peak is enhanced in the positive-ion mass spectra. The preferential detection of Gd@C_{74} in the positive-ion spectra results from the elimination of the electron-withdrawing CF_3 group. After the dissociation of the CF_3 moieties the remaining Gd@C_{74} tends to lose electrons and be detected as a cation \[16–19\]. Figure 2a shows the molecular arrangement of the monoclinic crystal consisting of Gd@C_{74}(CF_3) (I) and NiI(OEP) in a ratio of 1:1. The crystal also contains toluene and chloroform solvent molecules. The disordered Gd@C_{74}(CF_3) (I) molecule on the crystallographic mirror plane was modelled by a Gd atom occupying four (two independent) positions and a C_{74}(CF_3) (I) molecule with six (three independent) orientations (electronic supplementary material, figure S11). The complicated disorder can be represented by an overlap of Gd@C_{74}(CF_3) (I) molecules with an ordered structure shown in figure 2d with different orientations.
Figure 2d shows a feasible molecular structure of Gd@C74(CF3) (I) derived from the X-ray crystal structure analysis. A CF3 group is attached to a carbon atom on a pentagon of the D3h-symmetry C74 cage. The D3h-symmetry C74 cage has six independent carbon atoms on pentagons, which are labelled as C1–C6 in the figure. The structural model with a CF3 group attached to the C1 atom gave the best reliable factor in the X-ray crystal structure analysis of Gd@C74(CF3) (I). The Gd atom locates near the carbon atom labelled as C10 in figure 2b. The C10 atom is the third nearest to the C1 atom with the CF3 group attached. Interestingly, the C1 and C10 atoms are equivalent in the D3h-symmetry C74 cage with the mirror symmetry. The metal atoms of Gd@C60(CF3)5 (I) and (II), La@C60(CF3)5 (I) and La@C70(CF3)3 also locate near a carbon atom which is the third nearest to a carbon atom with a CF3 group attached [17,19]. The interatomic distance between the Gd and C10 distance is 2.20 Å in Gd@C74(CF3) (I), which is slightly shorter than Gd-C distances of 2.35 and 2.38 Å in Gd@C60(CF3)5 (I) and (II), respectively [19]. On the other hand, it is slightly longer than a Gd-C distance of 2.08 Å in Gd@C2v(9)-C82 [38].

The molecular arrangement and lattice constants of the Gd@C74(CF3) (II) crystal are similar to those of the Gd@C74(CF3) (I) crystal (figure 2b). Solvent molecules in the Gd@C74(CF3) (II) crystal are toluene and carbon disulfide, which are different from those (toluene and chloroform) in the Gd@C74(CF3) (I) crystal. The disordered Gd@C74(CF3) (II) molecule on the crystallographic mirror plane was modelled by a Gd atom occupying seven (four independent) positions and a C74(CF3) (II) molecule with two (independent) orientations (electronic supplementary material, figure S12). Site occupancies for the major Gd position and the major C74(CF3) orientation are 0.63 and 0.74, respectively. Figure 2f shows a feasible molecular structure of Gd@C74(CF3)3 consisting of the Gd atom at the major position and...
the C74(CF3)3 with the major orientation. Three CF3 groups of Gd@C74(CF3)3 are attached to carbon atoms on three pentagons of the D3h-symmetry C74 cage. One of the three carbon atoms with CF3 groups attached (C2) is the same as the carbon atom with the CF3 group attached in Gd@C74(CF3) (II) shown in figure 2e. The Gd position in Gd@C74(CF3)3 is also similar to that in Gd@C74(CF3) (II). The Gd−C3′ distance is 2.34 Å in Gd@C74(CF3)3, which is slightly longer than that of 2.27 Å in Gd@C74(CF3) (II).

Visible–near-infrared (Vis-NIR) spectra of isolated Gd@C74(CF3) (I and II) and Gd@C74(CF3)3 are shown in figure 3. The quite different spectra of two mono-substituted Gd@C74(CF3) species show that the two derivatives are isomers having different substituent group positions. HOMO–LUMO gaps of metallolfullerenes and their derivatives can be roughly estimated from the onset in absorption spectra. Gd@C74(CF3) (I), Gd@C74(CF3) (II) and Gd@C74(CF3)3 have the onset at 1330, 1750 and 1170 nm (figure 2), corresponding to HOMO–LUMO gap of 0.93, 0.71 and 1.06 eV, respectively. The estimated gaps of Gd@C74(CF3)n (n = 1, 3) are approximately close to HOMO–LUMO gaps of Y@C74(CF3)n (n = 1, 3), reported in our previous work [16]. In addition, the absorption spectra of Gd@C74(CF3) (I, II) are also similar to those of two isomers of La@C74(C6H3Cl2) [11]. The analogy between these Vis-NIR spectra suggests that the HOMO, LUMO and their neighbouring orbits of M@C74 are dominated by features of the cage, irrespective of functional groups as well as encapsulated species.

Density functional calculations were performed to obtain more detailed information on the trifluoromethyl derivatives. On the basis of the structures obtained by X-ray crystal structure analysis, we carried out geometry optimizations and energy calculations on isolated pristine and functionalized Gd@C74. Aside from small bond length changes attributable to the exchange correlation functional used, the molecular structures from X-ray analysis were confirmed as stable. Figure 4 shows optimized structures and molecular orbital energy levels. Gd@C74 is an open-shell system in agreement with the discussion above, with HOMO energy of −4.41 eV and LUMO energy of −4.23 eV, confirming that Gd@C74 has a very small HOMO–LUMO gap. The states lie higher in the gap than for the subsequent CF3 functionalized species, in agreement with the experimental observation of a prevalence of positively charged species in the mass spectra. Once functionalized with CF3 the calculated HOMO−LUMO gaps are significantly increased, with gaps for Gd@C74(CF3) (I), Gd@C74(CF3) (II) and Gd@C74(CF3)3 of 0.92, 0.71 and 1.00 eV, respectively, consistent with those estimated from the absorption onsets. It is clear that the energy gap is enlarged considerably upon exohedral trifluoromethylation, and all three species have closed-shell configurations confirming the demonstrated stability of odd-number CF3 additions. All three have fully unpaired Gd f-states, which are a pre-requisite for biomedical applications such as MRI contrast agents [3–6].

4. Discussion

The present trifluoromethylation method provides only mono- and tri-substituted derivatives [16–18]. One of the possible reasons for the selectivity is that it has an open-shell structure. Valence electrons...
are transferred from Gd to the cage, resulting in a charge distribution of Gd$^{3+}$@C$_{74}^3$ [10]. Addition of odd-number CF$_3$ groups to the carbon cage may result in a closed-shell configuration, which is more stable than an open-shell configuration of non-substituted Gd@C$_{74}$. A similar trend has been observed in the case of previous yttrium- and lanthan-encapsulated metallofullerenes [16].

It is interesting also to examine the binding energy of CF$_3$ groups to the Gd@C$_{74}$ cage. Considering the reaction

$$n_2^1\text{(CF}_3\text{)}_2 + \text{Gd@C}_{74} \rightarrow \text{Gd@C}_{74}(\text{CF}_3)_n,$$

we obtain a CF$_3$ binding energy for the two $n = 1$ isomers of 6.26 and 7.73 kcal mol$^{-1}$, respectively. These are close to each other, explaining the presence of both isomers (i.e. there is no single CF$_3$ functionalized isomer with significantly higher thermodynamic stability than any other). At the same time, the binding energy is considerably lower than for Gd@C$_{60}$ [19], which averages at 10.35 kcal mol$^{-1}$ per CF$_3$ group for Gd@C$_{60}$(CF$_3$)$_5$. In the case of the Gd@C$_{74}$ $n = 3$ isomer the average binding energy per CF$_3$ groups drops even further to 5.78 kcal mol$^{-1}$ (i.e. the two new CF$_3$ groups are each bound by only 4.81 kcal mol$^{-1}$), and it is reasonable to assume from this that subsequent pairwise CF$_3$ addition will be even less stable, presumably explaining the absence of stable $n = 5$ addition species.

5. Conclusion

In conclusion, the fullerene derivatives Gd@C$_{74}$(CF$_3$)$_1$ (I), Gd@C$_{74}$(CF$_3$)$_2$ (II) and Gd@C$_{74}$(CF$_3$)$_3$ were isolated by in situ trifluoromethylation followed by multi-stage HPLC purification. Their chemical structures were determined by X-ray crystal structure analysis and all of Gd@C$_{74}$ isomers have D$_{3h}$-symmetry cages. CF$_3$ groups are attached to carbon atoms on pentagons of fullerene cages. Formation of closed-shell systems and HOMO–LUMO gap widening of Gd@C$_{74}$ by the one- or three-fold addition of CF$_3$ group were confirmed by Vis-NIR spectra measurement and computational modelling.

Data accessibility. The crystal structures are freely available from the Cambridge Crystallographic Data Centre (CCDC) with CIF numbers 1824999 for Gd@C$_{74}$(CF$_3$)$_1$ (I), 1825000 for Gd@C$_{74}$(CF$_3$)$_2$ (II) and 1825001 for Gd@C$_{74}$(CF$_3$)$_3$. All DFT calculated structures (in xyz format) discussed in this article are provided in the electronic supplementary material associated with this article.

Authors’ contributions. H.S. conceived the study, A.N., H.O., K.I., M.N. performed the synthesis, isolation and MALDI-TOF, S.A. performed the synchrotron studies, J.R. and C.E. performed the density functional calculations. All authors discussed results, helped edit the manuscript and gave final approval for publication.

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