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Crystalline functionalized endohedral C₆₀ metallofullerides

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Endohedral metallofullerenes have been extensively studied since the first experimental observation of La@C₆₀ in a laser-vaporized supersonic beam in 1985. However, most of these studies have focused on metallofullerenes larger than C₆₀ such as (metal)@C₈₂, and there are no reported purified C₆₀-based monomeric metallofullerenes, except for [Li@C₆₀]⁺(SbCl₆)⁻ salt. Pure (metal)@C₆₀ compounds have not been obtained because of their extremely high chemical reactivity. One route to their stabilization is through chemical functionalization. Here we report the isolation, structural determination and electromagnetic properties of functionalized crystalline C₆₀-based metallofullerenes Gd@C₆₀(CF₃)₅ and La@C₆₀(CF₃)₅. Synchrotron X-ray single-crystal diffraction reveals that La and Gd atoms are indeed encapsulated in the I_h-C₆₀ fullerene. The HOMO-LUMO gaps of Gd@C₆₀ and La@C₆₀ are significantly widened by an order of magnitude with addition of CF₃ groups. Magnetic measurements show the presence of a weak antiferromagnetic coupling in Gd@C₆₀(CF₃)₃ crystals at low temperatures.

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C₆₀ fullerene is the most abundant member of the so-called fullerene family^{1–4}. However, monomeric C₆₀-based endohedral metallofullerenes (i.e., fullerenes with metal atom(s) encapsulated), referred to hereafter as M@C₆₀, have not been obtained in macroscopic and pure form to date. Most previous studies on metallofullerenes reported during the past 25 years have focused on higher fullerenes than C₆₀ such as C₈₀, C₈₂, and C₈₄², even though the presence of M@C₆₀ has been confirmed by mass spectrometry of supersonic cluster beams in the gas phase³ as well as laser-vaporized processed soot⁴. Theoretical calculations also suggested the stability and possible structure of M@C₆₀^{5–7}. An exception is [Li@C₆₀]⁺(SbCl₆)[–] salt, which was produced by Li-ion bombardment with C₆₀ onto a target plate in vacuum^{8, 9}. Neutral Li⁺@C₆₀[–] radicals have been obtained by the electrochemical reduction of cationic Li⁺@C₆₀; however, Li@C₆₀ oligomerizes¹⁰ and has a dimerized form in the crystal¹¹.

The inability to extract and purify M@C₆₀ is due to their very small highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) gaps predicted, which lead to high chemical reactivity toward surrounding soot, air, moisture, and various organic solvents. There have been, however, several attempts^{12–15} to try and extract and purify M@C₆₀ by, for example, vacuum sublimation from soot followed by liquid chromatographic separation^{13, 14}. Unfortunately, none of these efforts led to the final macroscopic preparation of pure and isolated M@C₆₀. For this reason, M@C₆₀ are often referred to as the missing metallofullerenes^{2, 16, 17}.

One of the main reasons for the long-standing interest in M@C₆₀ is due to their expected novel electronic and magnetic behavior at low temperatures such as superconductivity, because the electronic band structures near the Fermi levels of M³⁺@C₆₀^{3–} solids resemble those of superconducting alkali-doped C₆₀ fullerenes such as (K₃)³⁺C₆₀^{3–}¹⁸. If this is the case, the presence of heavy atoms like lanthanoid elements inside C₆₀ might enhance the superconducting transition temperatures¹⁹. One way to stabilize such species and open the HOMO-LUMO gap is through chemical functionalization. Here we report the macroscopic preparation of purified (>99.9%) trifluoromethylated Gd@C₆₀ and La@C₆₀, stable as Gd@C₆₀(CF₃)_{3,5} and La@C₆₀(CF₃)_{3,5}, respectively, and their structural determination, and electronic and magnetic properties.

Results

Enhanced stabilization of Gd@C₆₀ and La@C₆₀. To stabilize Gd@C₆₀ and La@C₆₀, we have employed in situ trifluoromethylation during the arc-discharge synthesis of the metallofullerenes developed in the present laboratory (see Supplementary Discussion 1 and Supplementary Figure 1)^{11, 19}. For example, the in situ trifluoromethylation of Gd@C₆₀ generates Gd@C₆₀(CF₃)_{*n*} (*n* = 1–6) together with other sizes of trifluoromethylated Gd-metallofullerenes, Gd@C_{2*m*}(CF₃)_{*n*} (2*m* ≥ 70) (see Supplementary Figures 2 and 3 for La). The high-temperature arc-discharge induces evaporation of polytetrafluoroethylene (PTFE) placed near the arc zone to produce CF₃ radicals¹¹. We found trifluoromethyl-derivatized metallofullerenes, Gd@C₆₀(CF₃)_{*n*} and La@C₆₀(CF₃)_{*n*} (*n* = 3, 5), were formed efficiently. Trifluoromethyl derivatives of Gd@C₆₀ and La@C₆₀ are totally soluble and stable in toluene and carbon disulfide, which enabled us to perform high-performance liquid chromatography (HPLC) purification and thus subsequent characterization. As discussed in later sections, the stability of these trifluoromethyl derivatives, Gd@C₆₀(CF₃)_{3,5} and La@C₆₀(CF₃)_{3,5}, can be attributed to their closed-shell electronic structures, leading to wider HOMO-LUMO gaps than those of pristine Gd@C₆₀ and La@C₆₀, respectively. With the current separation/

isolation protocol (see Supplementary Figure 4), one may, for example, obtain ca. 1.0–2.0 mg of purified (>99.9%) Gd@C₆₀(CF₃)₅ within 24 h from the initial *o*-xylene extraction of the soot containing Gd@C_{2*m*}(CF₃)_{*n*} obtained by 10 arc-discharge syntheses (see Supplementary Figures 5–8). The absorption onsets of the ultraviolet-visible-near-infrared (UV-Vis-NIR) absorption spectra of CS₂ solution of Gd@C₆₀(CF₃)₅ and La@C₆₀(CF₃)₅ suggest the presence of enlarged HOMO-LUMO gaps of ca. 1.2 eV approaching that of C₆₀ (1.6 eV) (see Supplementary Figure 9). Interestingly, Gd@C₆₀(CF₃) and Gd@C₆₀(CF₃)₂ have not been solvent-extracted because of their much smaller HOMO-LUMO gaps even though mass spectrometric analysis indicates the presence of these metallofullerenes in raw soot.

Because of the very high reactivity of M@C₆₀, it has not been self-evident that the metal is encapsulated in the conventional truncated icosahedral I_h-C₆₀. The C₆₀ might have a so-called non-isolated pentagon rule (non-IPR) structure^{20, 21}, where two (or three) pentagons are fused with each other, since non-IPR fullerenes have frequently been observed in metallofullerenes during the past decade². To answer this question, the molecular and crystal structures of Gd@C₆₀(CF₃)₅ (structural isomers I and II) and La@C₆₀(CF₃)₅ (I) have been determined by synchrotron radiation single-crystal X-ray diffraction (XRD) at SPring-8 (see Supplementary Tables 1–5).

Synchrotron single-crystal XRD measurements. The X-ray results clearly show that the C₆₀ cage structures of Gd@C₆₀(CF₃)₅ (I, II) and La@C₆₀(CF₃)₅ (I) are very similar to that of the conventional empty C₆₀(I_h). The five CF₃ groups of isomer I are attached to carbon atoms numbered as 6, 9, 12, 15, and 53 in a Schlegel diagram shown in Fig. 1a. In isomer II the five CF₃ groups are attached to carbon atoms numbered as 6, 9, 12, 15, and 36. In both isomers, four of the five CF₃ groups are attached to carbon atoms 6, 9, 12, and 15 bonded to carbon atoms 5, 1, 2, and 3 on a pentagon. Figure 1b–e shows the molecular structures of Gd@C₆₀(CF₃)₅(I) and (II), respectively. Very interestingly, the remaining CF₃ group is attached not to carbon atom 18 but to carbon atom 53 (isomer I) or 36 (isomer II) located far from the 1-2-3-4-5 pentagon. This asymmetric attachment of five CF₃ groups results in C₁ symmetry. If the fifth CF₃ group had been attached to carbon atom 18, neighbouring carbon atom 4 on the pentagon, the molecule would have had five-fold symmetry. Instead of the fifth CF₃ group, a Gd (La) atom inside the C₆₀ cage is located near carbon atoms 18 and 4. The distances between the Gd atom and carbon atoms 18 and 4 are ~2.38 Å in both isomers (see Supplementary Tables 2–5).

The selective location of the Gd (La) atom is explained in terms of the elongation of C–C bond lengths by the attachment of CF₃ groups. The conventional C₆₀(I_h) molecule consists of two kinds of C–C bonds: short 6:6 bonds fusing two hexagons with a bond length of 1.39 Å and longer 6:5 bonds fusing a hexagon and a pentagon with a bond length of 1.45 Å. As expected, the C–C bonds around the carbon atoms with CF₃ groups attached (6, 9, 12, 15, and either 53 or 36) have *sp*³ character, resulting in the elongation of the bonds. The 6:6 bond lengths between 6-5, 9-1, 12-2, and 15-3 carbon atoms are ~1.51 Å in both of the isomers (see Supplementary Tables 2 and 5). The 6:6 bond lengths between 18 and 4 atoms (~1.46 Å) are also longer than the normal 6:6 bond length (1.39 Å). This suggests that the Gd is interacting with the *p*_z-orbitals of atoms 18 and 4, resulting in the breaking of the *π*-bond and elongation of the bond length. At the same time, there is a general attraction for the Gd toward the area of the C₆₀ surface that has been functionalized, hence this location beneath two carbon atoms rather than staying at the center of the neighboring hexagon.

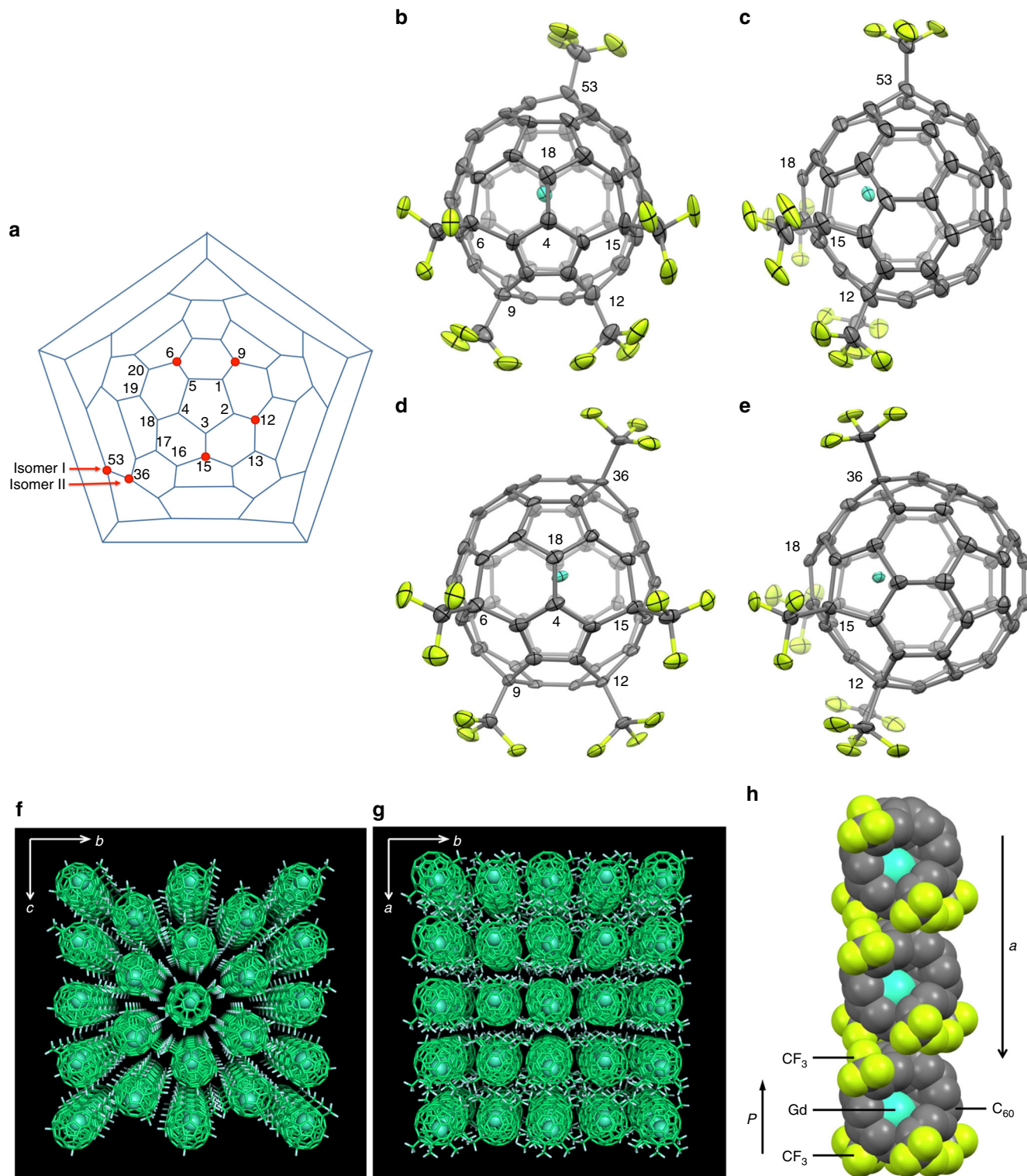


Fig. 1 $\text{Gd}@C_{60}(\text{CF}_3)_5$ (I) and (II). **a** Schlegel diagram of C_{60} . CF_3 groups attached to $\text{Gd}@C_{60}(\text{CF}_3)_5$ (I) and (II) are shown as red circles. **b, c** Molecular structure of $\text{Gd}@C_{60}(\text{CF}_3)_5$ (I). **d, e** Molecular structure of $\text{Gd}@C_{60}(\text{CF}_3)_5$ (II). Front views facing the bond between carbon atoms 4 and 18 (**b, d**) and side views (**c, e**) are shown. The thermal ellipsoids in (**b–e**) are drawn at 50% probability level. **f, g** Molecular packing in the $\text{Gd}@C_{60}(\text{CF}_3)_5$ (I) crystal viewed along the *a*- and *c*-axis, respectively. Pseudo-hexagonal close-packed layers in the *bc*-plane are stacked along the *a*-axis. **h** Steric and electrostatic stacking of the $\text{Gd}@C_{60}(\text{CF}_3)_5$ (I) molecules with an electric dipole moment (*P*) along the *a*-axis, which form a close-packed array

$\text{Gd}@C_{60}(\text{CF}_3)_5$ (I) and $\text{La}@C_{60}(\text{CF}_3)_5$ (I) form pure crystals that contain neither solvent nor ligand molecules. Figure 1f, g shows the molecular packing of the $\text{Gd}@C_{60}(\text{CF}_3)_5$ (I) crystal. The centrosymmetric crystal with a space group of $P2_1/c$ contains

two chiral isomers of $\text{Gd}@C_{60}(\text{CF}_3)_5$ (I) with the same number of molecules. Most of the endohedral metallofullerene crystals so far reported contain either solvent or ligand molecules². $\text{Gd}@C_{60}(\text{CF}_3)_5$ (II) has been obtained only as a co-crystal with Ni

(OEP) (OEP: octaethylporphyrin). The crystals of $\text{Gd@C}_{60}(\text{CF}_3)_5$ (I) and $\text{La@C}_{60}(\text{CF}_3)_5$ (I) are the first example of pure crystals of M@C_{60} derivative. The crystal structure determined possesses a pseudo-hexagonal close-packed layer of the molecules in the *bc*-plane (Fig. 1f) and stacking of the layers along the *a*-axis (Fig. 1g). The stacking of the molecules is caused by inter-molecular steric and electrostatic interactions. The molecule has an electric dipole moment (*P*) because of the electron-withdrawing CF_3 groups asymmetrically attached to the C_{60} cage and the presence of the off-centered Gd (La) atom inside. The stacking of the turtle-like molecules with an electric dipole moment can provide an electrostatically stable close-packed allay along the *a*-axis as shown in Fig. 1h (see Supplementary Figures 10–11). The detailed crystallographic data are summarized in Supplementary Tables 1–6.

We then carried out ^{19}F -nuclear magnetic resonance (NMR) measurements of $\text{La@C}_{60}(\text{CF}_3)_n$ (see Supplementary Discussion 3 and Supplementary Figure 14). The spectra of the two $\text{La@C}_{60}(\text{CF}_3)_5$ isomers consist of five equal-intensity peaks, which are four quartets (or multiplets) due to the through-space coupling of the four grouped CF_3 units and the other singlet due to fifth more isolated CF_3 unit^{22, 23}. In contrast, the ^{19}F -NMR spectrum of $\text{La@C}_{60}(\text{CF}_3)_3$ only showed a singlet peak at -75.5 ppm because the three trifluoromethyl groups are geometrically equivalent, indicating C_3 symmetry of $\text{La@C}_{60}(\text{CF}_3)_3$.

Discussion

To obtain information on the growth mechanism, structure and electronic properties of $\text{Gd@C}_{60}(\text{CF}_3)_5$, we perform spin unrestricted density functional calculations under the local spin density approximation^{24–26}, applying relativistic pseudopotentials²⁷. Wavefunctions are constructed from 38/90/28 independent Gaussian-based functions for C/Gd/F, respectively, up to $l = 3$ angular momentum, with an electron temperature of $k_{\text{B}}T = 0.04$ eV for level occupation and 300 Ha cut-off plane-waves for the charge density. To explore the addition pathways for CF_3 functionalization of $\text{Gd@C}_{60}(\text{CF}_3)_n$, $n = 0-5$, we assume that CF_3 adds to the most thermodynamically favored site and is then immobile, which is justified by a calculated high surface migration barrier of CF_3 ($n = 1$) of 59 kcal mol⁻¹. Taking the most stable *n*th isomer as a starting point for $n + 1$ stepwise addition allows us to reduce the number of isomers considered to a manageable several hundreds. Where two stable isomers are closer in energy than 2.3 kcal/mol of each other, we have used both as starting points for subsequent addition, allowing us to trace bifurcations in the addition pathway.

The Gd atom in Gd@C_{60} is initially covalently bound beneath hexagon (3-4-15-16-17-18) with 2.41 Å Gd–C bond lengths. The most stable CF_3 addition pathway involves sequential addition to back bonds of the 1-2-3-4-5 pentagon, i.e., addition at sites 6, 9, 12, and 15 in that order shown in top line of Fig. 2a. Instead of completing the pentagon at site 18, which is excluded due to the presence of Gd below this last pentagon back bond with ~ 2.35 Å Gd–C bond lengths, the fifth CF_3 group adds behind the neighboring pentagon at sites 53 (isomer I) or 36 (isomer II). Adding a sixth CF_3 group is endothermic compared to $\frac{1}{2}(\text{CF}_3)_2$, confirming that $n = 5$ is the end point in the addition sequence in agreement with the experimental observation. Interestingly, isomer II matches a $\text{La@C}_{60}(\text{CF}_3)_5$ structure proposed previously⁷, but the intermediate $n = 4$ structure proposed there is different to the structure we find here and can only be linked to $n = 3$ and 5 with additional surface CF_3 migration.

After $n = 1$ addition at site 6 there is a second stable isomer for $n = 2$, where Gd maintains its hexagonal site and CF_3 adds to site 36 (lower line of Fig. 2a). The pathway then bifurcates once again, the energetically favored route continuing the 9, 12, 15 addition

sequence to isomer II. However, an alternative $n = 3$ addition at site 13 results instead in a C_3 symmetry $\text{Gd@C}_{60}(\text{CF}_3)_3$ isomer. Further CF_3 addition to this is endothermic, showing this to be a third stable end point in the addition sequence. This mapping process thus shows remarkable agreement with the current X-ray and ^{19}F -NMR experimental results, successfully predicting the three observed $\text{Gd@C}_{60}(\text{CF}_3)_n$ species, i.e., $\text{Gd@C}_{60}(\text{CF}_3)_5$ (I), $\text{Gd@C}_{60}(\text{CF}_3)_5$ (II) and $\text{Gd@C}_{60}(\text{CF}_3)_3$.

These three stable isomers have multiplicity 7/2, associated with the Gd atom. They are closed-shell systems (unlike many of the less-stable isomers), restoring the gap between HOMO and LUMO to $\sim 2/3$ that of C_{60} (Fig. 2b) with the largest gap for $\text{Gd@C}_{60}(\text{CF}_3)_3$. The unpaired Gd *f*-states are deep lying with the HOMO and LUMO localized primarily over the fullerene cage with minor CF_3 character (Fig. 2c). Gd plays an interesting dual role when selecting CF_3 addition sites, acting as donor and localizing surface charge, while also affecting surface chemistry through strong hybridization with the carbon 2*p* states. This suggests different addition sequences are likely for non-covalently bound endohedral +3 oxidation species. As seen above, the agreement between the X-ray and the theoretical results for the presence of the stable isomers of $\text{Gd@C}_{60}(\text{CF}_3)_{3,5}$ strongly suggests that CF_3 groups are sequentially added to Gd@C_{60} during the arc-discharge synthesis. The energy levels, HOMO-LUMO and spin-up and -down charge density for $\text{Gd@C}_{60}(\text{CF}_3)_3$ and $\text{Gd@C}_{60}(\text{CF}_3)_5$ (I,II) are shown in Supplementary Figures 15 and 16, respectively.

Literature calculations for $\text{M@C}_{60}(\text{CF}_3)_3$ using comparable methods give a calculated HOMO-LUMO gap of 0.81 eV for $\text{Y@C}_{60}(\text{CF}_3)_3$ ¹⁶, and ~ 0.7 eV for $\text{La@C}_{60}(\text{CF}_3)_3$ ⁷, at first sight in discrepancy with our significantly larger calculated gap for $\text{Gd@C}_{60}(\text{CF}_3)_3$ of 1.4 eV. This is because the literature calculations consider a $\text{M@C}_{60}(\text{CF}_3)_3$ isomer with the CF_3 groups arranged around a shared pentagon. Our calculated HOMO-LUMO gap for this $\text{Gd@C}_{60}(\text{CF}_3)_3$ isomer is indeed 0.78 eV, close to these values. However, we do not predict this structure to be stable in isolation but simply an intermediate structure en-route to the formation of isomer I and isomer II $\text{Gd@C}_{60}(\text{CF}_3)_5$ structures. The $\text{Gd@C}_{60}(\text{CF}_3)_3$ isomer we predict to be a stable end point is instead the C_3 symmetry isomer shown in Fig. 2, with CF_3 groups arranged symmetrically around a central hexagon. This arrangement of CF_3 groups gives the much wider calculated HOMO-LUMO gap of 1.4 eV.

The magnetic properties of $\text{Gd@C}_{60}(\text{CF}_3)_3$ metallofullerene was investigated by SQUID measurements (see Supplementary Discussion 5). The HOMO-LUMO gap of $\text{Gd@C}_{60}(\text{CF}_3)_3$ (1.4 eV) is larger than that of $\text{Gd@C}_{60}(\text{CF}_3)_5$ (1.2 eV) suitable for solvent extraction and HPLC isolation. Magnetization curves of solid $\text{Gd@C}_{60}(\text{CF}_3)_3$ indicate no hysteresis as shown in Fig. 3, where the ordinate is normalized by experimentally determined saturation magnetization M_s of 41 108 emu · G mol⁻¹. Except for the magnetization curve at 2 K, other data points are on the same curvature trace. When magnetic moments thermally fluctuate without strong interaction between the magnetic moments, magnetization curves are fitted by the following Brillouin function $B_J(x)$

$$M = M_s B_J(x) \quad (1)$$

$$M_s = NgJ\mu_B \quad (2)$$

$$B_J(x) = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J} \coth\left(\frac{1}{2J}x\right) \quad (3)$$

$$x = \frac{gJ\mu_B H}{k_{\text{B}}T} \quad (4)$$

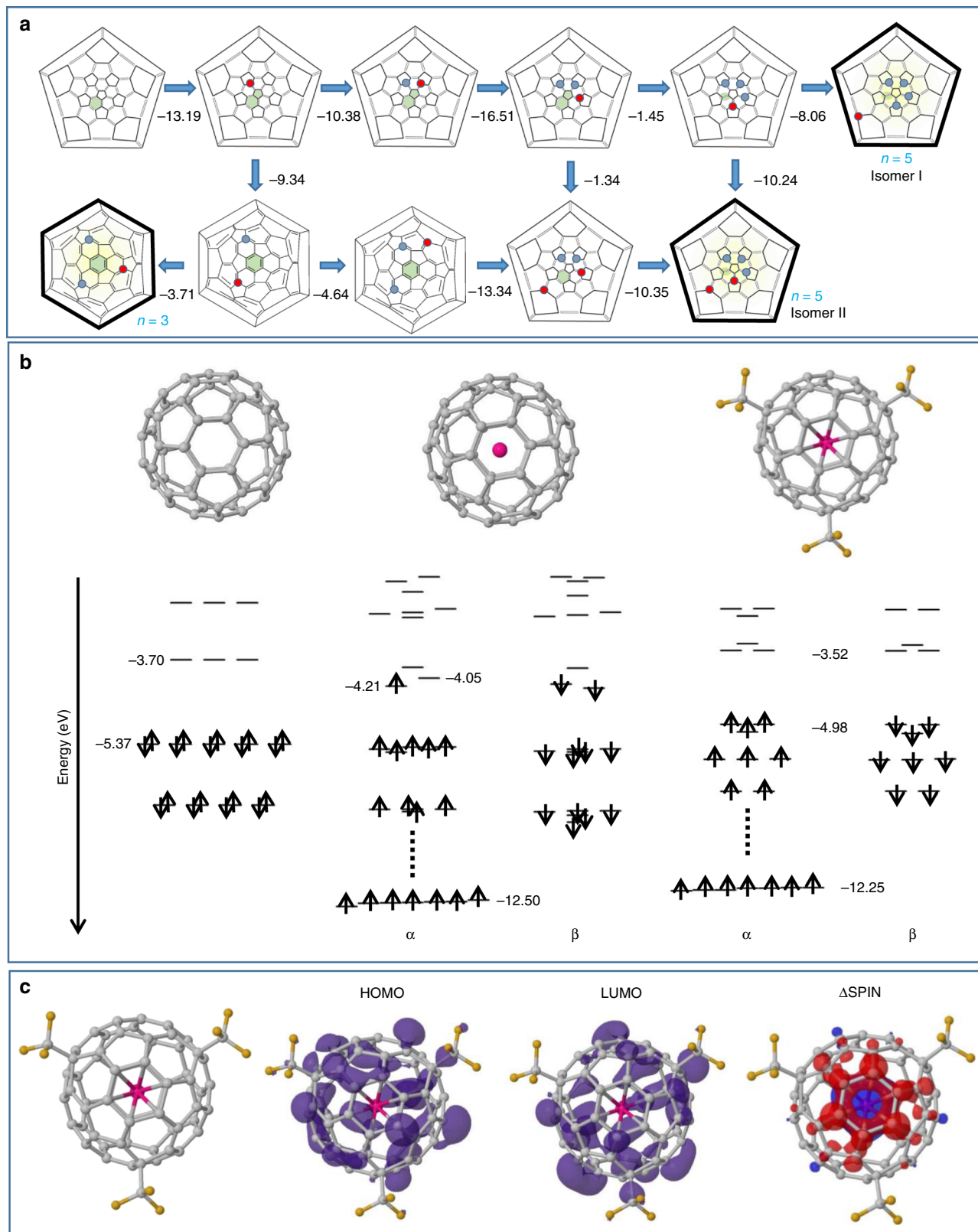


Fig. 2 Calculated functionalization sequences and electronic properties of $\text{Gd@C}_{60}(\text{CF}_3)_n$. **a** Calculated preferential addition sequences for CF_3 to Gd@C_{60} . Previous addition sites marked in blue, new addition site in red. Pink shading indicates location of the encapsulated Gd atom. Numbers indicate energy release in kcal mol^{-1} according to the reaction $\text{Gd@C}_{60}(\text{CF}_3)_{n-1} + \frac{1}{2} (\text{CF}_3)_2 \rightarrow \text{Gd@C}_{60}(\text{CF}_3)_n$. All pathways are shown where isomers are within $2.3 \text{ kcal mol}^{-1}$ of the most stable. Fullerenes where next addition is endothermic have black outlines and represent stable end points of a reaction pathway. **b** Calculated Kohn-Sham eigenvalues (eV) for (left) C_{60} , (center) Gd@C_{60} , and (right) $\text{Gd@C}_{60}(\text{CF}_3)_3$, showing CF_3 functionalization results in a closed-shell system, reopening the HOMO-LUMO gap to nearly that of C_{60} . **c** Spatial distribution of calculated Kohn-Sham eigenstates showing highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) and their neighboring states around the Fermi level for the most stable $\text{Gd@C}_{60}(\text{CF}_3)_5(\text{I})$ isomer. The states are delocalized across the fullerene cage with very limited CF_3 character

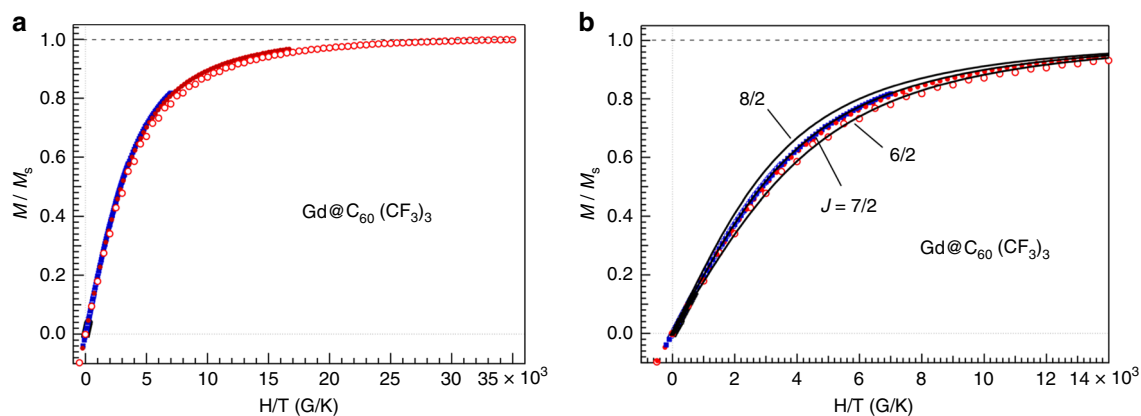


Fig. 3 Normalized magnetization curves of $\text{Gd@C}_{60}(\text{CF}_3)_3$. **a** Whole trace of magnetization taken at 273, 100, 20, 10, 4.2, and 2 K, and **b** is an expansion around the origin of abscissa. M_s value determined experimentally is $41108 \text{ emu} \cdot \text{G mol}^{-1}$. Solid lines are the calculated magnetization curves using Brillouin function with $J = 8/2, 7/2$, and $6/2$. Red open circles are for the data taken at 2 K. Only this data set did not fit with the same curvature

where N is the spin concentration, g the g -factor, J the total quantum number, μ_B the Bohr magneton, and k_B the Boltzmann constant. From the curve fitting, we found that the total quantum number $J = 7/2$ is needed to explain the experimental results by setting $g = 2$. This gives an effective magnetic moment $\mu_{\text{eff}} (= g\sqrt{J(J+1)}\mu_B)$ of $7.94 \mu_B$ per $\text{Gd@C}_{60}(\text{CF}_3)_3$ molecule. This experimental analysis supports a trivalent Gd^{3+} state by transferring three electrons to the C_{60} cage ($\text{Gd}^{3+}@\text{C}_{60}^{3-}$) and these electrons are then used to make chemical bonds with three CF_3 on C_{60} . Mulliken charge analysis shows that most of the transferred charge is indeed spread around the C_{60} cage beneath the CF_3 groups, on the central pentagon, and on the neighbors of the Gd. The magnetic moment is thus essentially located on the encaged Gd^{3+} ion ($4f^7, J = 7/2$ with orbital quantum number $L = 0$, i.e., Gd^{3+} has spin $7 \mu_B$) in agreement with the theoretical result shown in Fig. 2b. According to the previous studies on $\text{M}^{3+}@\text{C}_{82}^{3-}$ ($M = \text{Gd, Dy, Ho, Er}$) metallofullerenes^{28–32}, the magnetic moments observed are significantly small compared to the expected moments of free M^{3+} ions.

This reduction of the magnetic moments was theoretically explained by antiferromagnetic coupling between the trivalent endohedral metals and free spins on the carbon cage³³. In the present Gd (La)-encapsulating C_{60} fullerenes, since free spins on C_{60} are very small by forming the chemical bonds with CF_3 on the cage, this guarantees an almost ideal magnetic moment of Gd^{3+} ion. Theoretically, a trace counter-spin can be seen localized on the C_{60} cage between the Gd and CF_3 groups at 0 K (Fig. 2c), presumably too weak to be detectable by SQUID but partially responsible for the weak antiferromagnetic coupling observed at low temperature. This was also confirmed by the analysis of temperature dependence of molar magnetic susceptibility as explained in Supplementary Discussion 5.

To further investigate the electronic structures of $\text{Gd@C}_{60}(\text{CF}_3)_5$ (I,II), we also performed electron spin resonance (ESR) measurements in CS_2 frozen solution (see Supplementary Discussion 6 and Supplementary Table 7). The spectra recorded by an X-band continuous wave ESR spectrometer at 4 K and by a W-band at 20 K are shown in the upper and lower panels of Fig. 4, respectively, where the observed spectra with fine structure in red are compared with simulated ones in blue^{34, 35}. The parameters shown in Supplementary Table 7 were determined so that both of the observed spectra by the X- and W-band measurements should simultaneously be reproduced by the simulation. In both cases the spin quantum number of $S = 7/2$ was obtained, consistent with the theoretical and magnetic

measurement results described above. The zero-field splitting parameters, $D = 0.162 \text{ cm}^{-1}$ and $D = 0.193 \text{ cm}^{-1}$, were obtained for $\text{Gd@C}_{60}(\text{CF}_3)_5$ (I) and $\text{Gd@C}_{60}(\text{CF}_3)_5$ (II), respectively, comparable to those for $S = 7/2$ states of Gd@C_{82} ³⁴ and Eu@C_{82} ³⁵. The lift of the x and y degeneracy of $E = 0.012 \text{ cm}^{-1}$ for $\text{Gd@C}_{60}(\text{CF}_3)_5$ (II), which is bigger than that ($E = 0.000 \text{ cm}^{-1}$) of $\text{Gd@C}_{60}(\text{CF}_3)_5$ (I), suggests that the position of the Gd^{3+} ions in the two isomers differs slightly, since the E parameters originate basically in the spin-orbit coupling of the Gd^{3+} ions. Our calculations indeed indicate that the Gd^{3+} ion of isomer (I) lies more symmetrically beneath the C–C bond (so more symmetrically with respect to the four CF_3 groups around the pentagon) than that of isomer (II). The observed ESR parameters are summarized in Supplementary Table 7.

In summary, the missing metallofullerenes, Gd@C_{60} and La@C_{60} , in the trifluoromethylated forms of $\text{Gd@C}_{60}(\text{CF}_3)_{3,5}$ and $\text{La@C}_{60}(\text{CF}_3)_5$, have been obtained in pure bulk forms. In situ trifluoromethylation widens the HOMO-LUMO gaps of Gd@C_{60} and La@C_{60} , enabling isolation of the metallofullerenes and the subsequent single-crystal synchrotron XRD. The crystals exhibit a pseudo-hexagonal close-packed layer of molecules in the bc -plane and stacking of the layers along the a -axis (a turtle-like stacked structure). The temperature dependence of the magnetic susceptibility of $\text{Gd@C}_{60}(\text{CF}_3)_3$ is well fitted by the Curie-Weiss law. The magnetic moment is located on the encaged Gd^{3+} ion ($4f^7, J = 7/2$ with orbital quantum number $L = 0$), with very small magnetic moment on the cage in agreement with the theoretical results. The intact forms of Gd@C_{60} and La@C_{60} might exhibit superconductivity as the electronic structures resemble those of superconducting alkali-doped C_{60} fullerenes. The preparation and isolation of intact Gd@C_{60} fullerene is now underway in the present laboratory.

Methods

Synthesis, purification, and crystallization. A cross-sectional view of the DC arc-discharge chamber is illustrated in Supplementary Figure 1, where PTFE rods (40 g) are placed near the discharge area. Graphite rods (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.

Extraction and separation. The rapid separation of the metallofullerenes from empty fullerenes was carried out by the TiCl_4 Lewis acid method developed in the

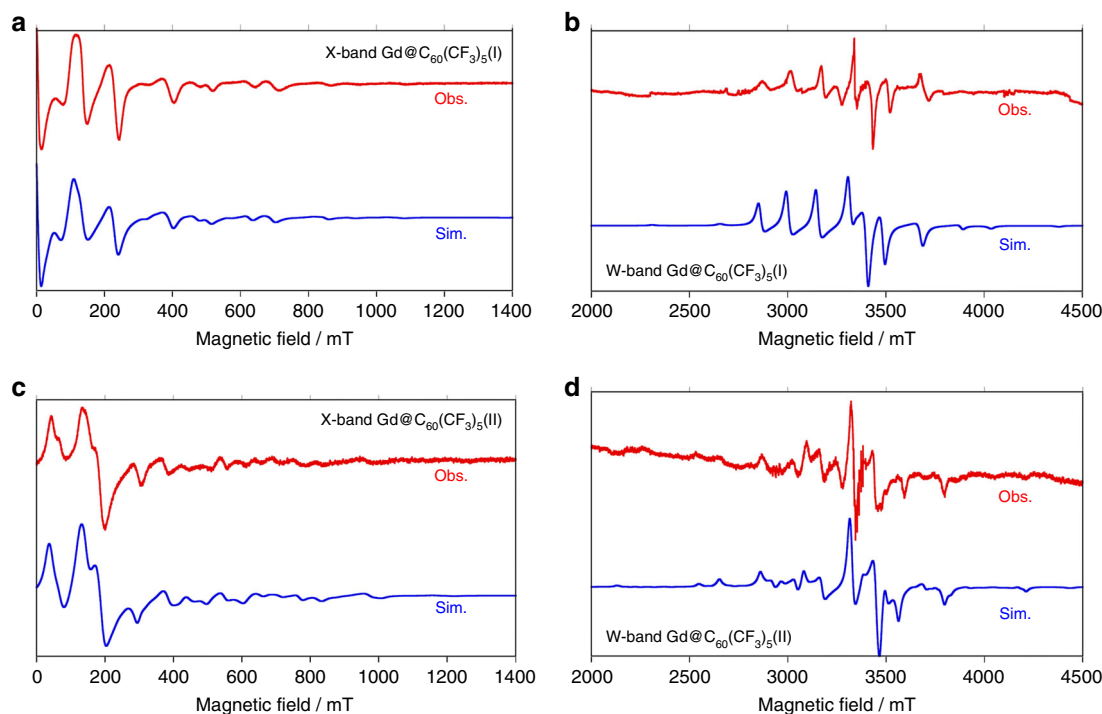


Fig. 4 Confirmation of ESR parameters for $\text{Gd@C}_{60}(\text{CF}_3)_5(\text{I})$ and $\text{Gd@C}_{60}(\text{CF}_3)_5(\text{II})$. **a, c** ESR spectra (red lines) of $\text{Gd@C}_{60}(\text{CF}_3)_5(\text{I})$ and $\text{Gd@C}_{60}(\text{CF}_3)_5(\text{II})$ recorded by X-band (9 GHz) spectrometer in CS_2 at 4 K, **b, d** W-band (90 GHz) spectrometer in CS_2 at 20 K. ESR parameters were determined so that both observed spectra in **a-d** should be simultaneously reproduced by simulation (blue lines)

present laboratory. To a 500 mL CS_2 solution of the crude mixture of Gd-fullerenes and empty fullerenes, ca. 5 mL of TiCl_4 was added. Metallofullerenes were reacted immediately and insoluble complexes were precipitated out. After mixing for 5 min, the precipitate was collected on a PTFE membrane filter and washed with 10–20 mL of CS_2 to separate from the empty fullerenes solution. Deionized water was passed through the filter to decompose the complex of metallofullerene/ TiCl_4 , and then washed with acetone to eliminate extra water. Finally, CS_2 was passed through the filter to collect desired Gd-metallofullerenes as a solution as shown in Supplementary Figure 2 (equivalent for La in Supplementary Figure 3).

Multi-stage HPLC purification. HPLC purification was conducted by using a JAI (Japan Analytical Industry Co. LTD.) recycling preparative HPLC LC-9104HS. The overall separation and isolation scheme of $\text{Gd@C}_{60}(\text{CF}_3)_n$ is shown in Supplementary Figure 4. For the identification of metallofullerenes, mass spectrometric analysis was performed on Shimadzu MALDI-TOF-MS Spectrometer. Vis/NIR absorption spectra of metallofullerenes in CS_2 were recorded by a Jasco V-570 spectrophotometer. Three isomers of $\text{Gd@C}_{60}(\text{CF}_3)_n$ were isolated from the mixture by the multi-stage HPLC method developed in the present laboratory. Two kinds of columns were used alternatively with toluene eluent for the isolation, i.e., Buckyprep column (20 mm diameter \times 250 mm, Nacalai Tesque Inc.) and Buckyprep-M column (20 mm diameter \times 250 mm, Nacalai Tesque Inc.). The initial (the first stage) HPLC purification was performed with Buckyprep-M. $\text{Gd@C}_{60}(\text{CF}_3)_n$ ($n = 3, 5$) was obtained in fraction 1. The HPLC chromatograms are shown in Supplementary Figure 5 (equivalent for La in Supplementary Figure 6). Identification and isolation of the metallofullerenes were checked by MALDI mass spectroscopy as shown in Supplementary Figures 7 and 8. UV-Vis-NIR absorption spectra of the metallofullerenes exhibit characteristic features and also provide an estimate on their HOMO-LUMO gaps judging from the absorption onsets. The spectral features between Gd- and La-metallofullerenes are almost the same with each isomer as shown in Supplementary Figure 9.

Synchrotron single-crystal X-ray structure analysis. Single-crystal XRD measurements of $\text{Gd@C}_{60}(\text{CF}_3)_5(\text{I})$, $\text{La@C}_{60}(\text{CF}_3)_5(\text{I})$, $\text{Gd@C}_{60}(\text{CF}_3)_5(\text{II})$, and $\text{Gd@C}_{60}(\text{CF}_3)_3$ were performed at SPring-8 BL02B1. The crystallographic data and various bond lengths for $\text{Gd@C}_{60}(\text{CF}_3)_5(\text{I,II})$, $\text{Gd@C}_{60}(\text{CF}_3)_3$, and $\text{La@C}_{60}(\text{CF}_3)_5(\text{I})$ are summarized in Supplementary Tables 1–6. The crystal structures for $\text{Gd@C}_{60}(\text{CF}_3)_5(\text{I})$, $\text{La@C}_{60}(\text{CF}_3)_5(\text{I})$, and $\text{Gd@C}_{60}(\text{CF}_3)_5(\text{II})$ are shown in Supplementary Figures 10–12, respectively. The charge density surface of $\text{Gd@C}_{60}(\text{CF}_3)_3$ is shown in Supplementary Figure 13.

$\text{Gd@C}_{60}(\text{CF}_3)_5(\text{I})$ and $\text{La@C}_{60}(\text{CF}_3)_5(\text{I})$: Single crystals of $\text{Gd@C}_{60}(\text{CF}_3)_5(\text{I})$ and $\text{La@C}_{60}(\text{CF}_3)_5(\text{I})$ were obtained from CS_2 solution by vapor diffusion.

Results of the XRD measurement are summarized in Supplementary Table 1.

The crystal structures were determined by using *SIR* and *SHELX* with good reliable factors. $\text{Gd@C}_{60}(\text{CF}_3)_5(\text{I})$ and $\text{La@C}_{60}(\text{CF}_3)_5(\text{I})$ have similar crystal structures. The centrosymmetric monoclinic crystals consist of the same number of two chiral isomers of the molecule. The unit cell contains two right-handed isomers and two left-handed isomers as shown in Supplementary Figures 10a and 11a. An independent molecule in the asymmetric unit has a disordered structure in which two chiral isomers overlap with the ratios of 0.8 and 0.2 as shown in Supplementary Figures 10b and 11b. In all, 95 C–C, 15 C–F, and 4 C–Gd (La) bond lengths of the major part of the disordered $\text{Gd@C}_{60}(\text{CF}_3)_5(\text{I})$ and $\text{La@C}_{60}(\text{CF}_3)_5(\text{I})$ are listed in Supplementary Tables 2 and 3, respectively. A total of 30 short 6:6 bonds fusing two hexagons and 60 long 6:5 bonds fusing a hexagon and a pentagon on the C_{60} cage are separately shown. The CIF deposition numbers at the Cambridge Crystallographic Data Centre (CCDC) are 1587428 for $\text{Gd@C}_{60}(\text{CF}_3)_5(\text{I})$ and 1587430 for $\text{La@C}_{60}(\text{CF}_3)_5(\text{I})$.

$\text{Gd@C}_{60}(\text{CF}_3)_5(\text{II})$: Single crystals of $\text{Gd@C}_{60}(\text{CF}_3)_5(\text{II})$ were obtained from CS_2 solution as co-crystals with Ni(OEP) by vapor diffusion. Results of the XRD measurement are summarized in Supplementary Table 4. The crystal structure was determined by using *SIR* and *SHELX* with a good reliable factor. The centrosymmetric triclinic crystals consist of the same number of two chiral isomers of $\text{Gd@C}_{60}(\text{CF}_3)_5(\text{II})$. The unit cell contains a right-handed isomer, a left-handed isomer, three Ni(OEP), and half toluene molecules as shown in Supplementary Figure 12a. An independent molecule in the asymmetric unit has a disordered structure in which two chiral isomers overlap with the ratios of 0.8 and 0.2 as shown in Supplementary Figure 12b. In all, 95 C–C, 15 C–F, and 4 C–Gd bond lengths of the major part of the disordered $\text{Gd@C}_{60}(\text{CF}_3)_5(\text{II})$ are listed in Supplementary Table 5. A total of 30 short 6:6 bonds fusing two hexagons and 60 long 6:5 bonds fusing a hexagon and a pentagon on the C_{60} cage are separately shown. The CIF deposition number at CCDC is 1587429.

$\text{Gd@C}_{60}(\text{CF}_3)_3$: Single crystals of $\text{Gd@C}_{60}(\text{CF}_3)_3$ were obtained from CS_2 solution by vapor diffusion. Results of the XRD measurement were summarized in Supplementary Table 6. The tetragonal unit cell can contain 16 $\text{Gd@C}_{60}(\text{CF}_3)_3$ molecules. An expected molecular arrangement was obtained by charge flipping using *Superflip* and maximum entropy method using *ENIGMA* as shown in Supplementary Figure 13. The figure shows an electron charge density surface obtained by maximum entropy method. A structure model with 16 double uniform shells of Gd@C_{60} located at $(1/4 \pm 1/8, 1/4 \pm 1/8, 0)$, $(-1/4 \pm 1/8, -1/4 \pm 1/8, 0)$, $(1/4 \pm 1/8, -1/4 \pm 1/8, 1/2)$, and $(-1/4 \pm 1/8, 1/4 \pm 1/8, 1/2)$ was used in the analysis. Detailed structure of $\text{Gd@C}_{60}(\text{CF}_3)_3$ could not be determined due to a severe orientation disorder and lack of resolution. We also attempted to obtain co-crystals of $\text{Gd@C}_{60}(\text{CF}_3)_3$ with Ni(OEP); however, that have not been obtained.

19F-NMR measurements. NMR spectra were recorded on a JEOL ECS-400 spectrometer; chemical shifts for ^{19}F -NMR (376 MHz, $\text{CDCl}_3/\text{CS}_2$) are expressed in parts per million (ppm) relative to C_6F_6 ($\delta = -164.9$ ppm). Data are reported as follows: chemical shift; multiplicity (s = singlet, q = quartet, m = multiplet); coupling constant (Hz); and integration. $\text{La}@C_{60}(\text{CF}_3)_3$: $\delta -75.5$ (s, 9F). $\text{La}@C_{60}(\text{CF}_3)_5$ (I): $\delta -79.4$ (s, 3F), -76.0 (q, $J = 10$ Hz, 3F), -74.9 (q, $J = 12$ Hz, 3F), -67.4 (m, 3F), and -66.9 (m, 3F). $\text{La}@C_{60}(\text{CF}_3)_5$ (II): $\delta -78.9$ (s, 3F), -78.0 (q, $J = 12$ Hz, 3F), -73.6 (q, $J = 10$ Hz, 3F), -68.3 (m, 3F), and -67.3 (m, 3F).

SQUID magnetic measurement. Sample dissolved in CS_2 was transferred into quartz tube and the solution was vaporized under argon flow. Then the sample in quartz tube was evacuated by using turbo molecular pump at 260°C for 12 h and vacuum sealed. By this heat treatment, weight of $\text{Gd}@C_{60}(\text{CF}_3)_3$ sample was decreased by ~65% (finally 0.71 mg of sample was loaded in the quartz tube), while no such weight change was observed for $\text{La}@C_{60}(\text{CF}_3)_5$ one. Former finding suggests that the CS_2 molecules were incorporated in a $\text{Gd}@C_{60}(\text{CF}_3)_3$ solid, forming $\text{Gd}@C_{60}(\text{CF}_3)_3(\text{CS}_2)_{6,4}$ just after vaporizing CS_2 in Ar flow, and such incorporated CS_2 molecules have been completely removed by heating at 260°C in vacuo. On the other hand, from the latter fact, $\text{La}@C_{60}(\text{CF}_3)_5$ solid did not incorporate any CS_2 molecule. That is, all SQUID measurements were carried out by using solution free samples. As described in the Discussion, magnetic behavior can be explained as an intramolecular feature and the interaction between the molecules is very small. Therefore, even if the sample incorporates some CS_2 molecules, these molecules do not affect the present results.

ESR measurements. The X- and W-band ESR measurements were performed using a Bruker E500 and a E680 spectrometer, respectively. The temperature was controlled by helium flow cryostat (Oxford Instruments model ITC500). The X-band ESR spectra were measured at 4.0 K, and W-band ESR spectra were measured at 20 K. The spectral simulation were performed by using MATLAB software package with EasySpin toolbox. The observed ESR parameters are shown in Supplementary Table 7.

Data availability. Structural data are available in Supplementary Information. All additional data such as calculated xyz structures are available from the authors on request. The X-ray crystallographic coordinates for structures reported in this study have been deposited at the CCDC, under deposition numbers 1587428–1587430. These data can be obtained free of charge from The CCDC via www.ccdc.cam.ac.uk/data_request/cif.

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Author contributions

H.S. led the entire project and contributed to the experimental work, including synthetic apparatus design of the present metallofullerenes. A.N., M.N., H.N., K.I., and Z.W. contributed to the synthesis, purification, and crystal growth of the materials. H.O. and A.N. contributed to ^{19}F -NMR measurement. K.F., T.Y., and T.K. contributed to the ESR measurement. S.B. contributed to the SQUID magnetic measurement. S.A. contributed to the synchrotron X-ray diffraction measurement at SPring-8 and the data analyses. J.R.

and C.E. contributed to the theoretical part of the work. H.S., T.K., S.B., S.A., H.O., and C.E. wrote the paper.

Additional information

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Competing interests: The authors declare no competing interests.

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