Can CF$_3$-functionalized La@C$_{60}$ be isolated experimentally and become superconducting?

Jie Guan and David Tománek

Physics and Astronomy Department, Michigan State University, East Lansing, Michigan 48824, USA
E-mail: tomanek@pa.msu.edu

Abstract

Superconducting behavior even under harsh ambient conditions is expected to occur in La@C$_{60}$ if it could be isolated from the primary metallofullerene soot when functionalized by CF$_3$ radicals. We use *ab initio* density functional theory calculations to compare the stability and electronic structure of C$_{60}$ and the La@C$_{60}$ endohedral metallofullerene to their counterparts functionalized by CF$_3$. We found that CF$_3$ radicals favor binding to C$_{60}$ and La@C$_{60}$, and have identified the most stable isomers. Structures with an even number $m$ of radicals are energetically preferred for C$_{60}$ and structures with odd $m$ for La@C$_{60}$ due to the extra charge on the fullerene. This is consistent with a wide HOMO-LUMO gap in La@C$_{60}$(CF$_3$)$_m$ with odd $m$, causing extra stabilization in the closed-shell electronic configuration. CF$_3$ radicals are both stabilizing agents and molecular separators in a metallic crystal, which could increase the critical temperature for superconductivity.

Keywords

metallofullerene, La@C$_{60}$, *ab initio*, electronic structure

The discovery of the C$_{60}$ fullerene$^1$ with a hollow cage structure immediately triggered the question, whether the space inside could be filled by other atoms. This question has been answered affirmatively shortly afterwards by successfully encapsulating metal atoms including Li, Na, K, Rb, Sr, Ba, Sc, La, Tc and U inside M@C$_{2n}$ endohedral fullerenes, also called metallofullerenes.$^2$–$^{13}$

A major reason for the current interest in metallofullerenes such as La@C$_{60}$ is the possibility to observe superconductivity in solid C$_{60}$ that is doped endohedrally rather than exohedrally by 3 electrons.$^{14}$ A molecular crystal formed of isolated and recrystallized La@C$_{60}$ molecules would be electronically related to M$_3$C$_{60}$ with M representing alkali atoms. In M$_3$C$_{60}$ crystals, superconductivity with $T_c \lesssim 40$ K has been observed and explained by electron-phonon coupling that is modulated by the lattice constant.$^{15,16}$ The same behavior is expected to occur in the isoelectronic La@C$_{60}$ crystal. Unlike alkali-based C$_{60}$ superconductors, La@C$_{60}$ crystals will be stable under ambient or even harsh conditions.

In spite of the fact that fullerene cages of different size favor encapsulation of metal atoms energetically,$^3$,$^5$,$^{13,17,18}$ most of the resulting complexes are highly reactive due to their open-shell configuration and form insoluble polymerized solids.$^{19}$ Only M@C$_{2n}$ metallofullerenes with large cages$^5$ ($2n \gtrsim 74$) have been successfully isolated from the raw soot, with M@C$_{82}$ dominating. It has been difficult to extract the most abundant M@C$_{60}$ and M@C$_{70}$ metallofullerenes due to their insolubility in regular fullerene solvents$^{13,20,21}$ such as toluene and CS$_2$. Even though several metallofullerenes...
with cages as small as \( C_{60} \) have been extracted by solvents such as pyridine and aniline,\textsuperscript{21–24} it has become a large challenge to separate the \( M@C_{60} \) fraction, since pyridine and aniline solvents are not suitable for high-performance liquid chromatography (HPLC).\textsuperscript{20} Only recently, \( \text{La} @ \text{C}_{70} \) and \( \text{Y} @ \text{C}_{2n} \) with \( 2n \geq 60 \), functionalized by \( \text{CF}_3 \) radicals, have been separated using toluene and \( \text{CS}_2 \) as solvents.\textsuperscript{19,25} In this new strategy, the function of trifluoromethyl radicals was to further separate the metallofullerene cages and to chemically stabilize their unstable open-shell electronic configuration.\textsuperscript{26} Isolation and crystallization of the more interesting \( \text{La} @ \text{C}_{60} \) molecules is currently being attempted.\textsuperscript{14}

In view of the possibility to obtain superconducting behavior in crystalline \( \text{La} @ \text{C}_{60} \) even under harsh ambient conditions, we provide theoretical support for the experimental effort to solubilize the \( \text{La} @ \text{C}_{60} \) endohedral metallofullerene from the primary soot. We made use of \textit{ab initio} density functional theory calculations to compare the stability and electronic structure of the bare \( C_{60} \) fullerene and \( \text{La} @ \text{C}_{60} \) to their counterparts functionalized by \( m \) \( \text{CF}_3 \) radicals. We found that several \( \text{CF}_3 \) radicals can form stable bonds to \( C_{60} \) and \( \text{La} @ \text{C}_{60} \), and have identified the most stable structural isomers for \( m \leq 5 \). Generally, structures with an even \( m \) are energetically preferred for \( C_{60} \) and structures with an odd \( m \) for \( \text{La} @ \text{C}_{60} \) due to the extra 3 electrons donated by the encapsulated La. This is consistent with our finding that a wide HOMO-LUMO gap opens in \( \text{La} @ \text{C}_{60} \left( \text{CF}_3 \right)_m \) molecules with an odd \( m \) value, causing extra stabilization in the closed-shell electronic configuration. The two-fold function of \( \text{CF}_3 \) radicals as stabilizing agents and molecular separators may help in isolating specific molecules from the primary soot. If \( \text{La} @ \text{C}_{60} \left( \text{CF}_3 \right)_m \) could be solubilized and recrystallized, endohedral instead of exohedral doping by three electrons per \( C_{60} \) and use of stabilizing \( \text{CF}_3 \) radicals as spacers may lead to superconductivity with a relatively high \( T_c \) achieved by increasing the lattice constant of the molecular crystal.\textsuperscript{15,16} We should note that the range of favorable lattice constants is limited, since their increase beyond a critical value changes doped \( C_{60} \) from a metal to a Mott-Hubbard insulator.\textsuperscript{27,28} Even more appealing than changing the lattice constant appears the possibility to remove \( \text{CF}_3 \) radicals after obtaining \( \text{La} @ \text{C}_{60} \left( \text{CF}_3 \right)_m \) in solution and subsequently recrystallize \( \text{La} @ \text{C}_{60} \). Stability even under harsh ambient conditions is expected due to the absence of alkali atoms filling interstitial sites in known \( M_{3}C_{60} \) superconductors. Moreover, the possibility to encapsulate different elemental species provides an additional handle on tuning \( T_c \) of \( M@C_{60} \) superconductors.\textsuperscript{29}

![Figure 1: (Color online) Ball-and-stick models of the optimized structure of the most stable isomers of \( \text{La} @ \text{C}_{60} \left( \text{CF}_3 \right)_m \) molecules with (a) \( m = 0 \), (b) \( m = 1 \), (c) \( m = 2 \), (d) \( m = 3 \), (e) \( m = 4 \), (f) \( m = 5 \).](image)

**Results**

We have used density functional theory (DFT) with the Perdew-Burke-Ernzerhof (PBE)\textsuperscript{30} exchange-correlation functional to determine the equilibrium geometry of \( \text{La} @ \text{C}_{60} \) and \( \text{La} @ \text{C}_{60} \left( \text{CF}_3 \right)_m \) molecules for \( m \leq 5 \). For a given number \( m \) of attached \( \text{CF}_3 \) radicals, we optimized many different regioisomers, as specified in the Supporting Information, and displayed the most stable structures in Figure 1. Figure 1(a) displays the bare \( C_{60} \) molecule containing a La atom in its equilibrium off-center configuration. As seen in Figure 1(b), \( \text{CF}_3 \) radicals prefer to attach on-top of C atoms in the \( C_{60} \) cage. Whereas the adsorption of a single \( \text{CF}_3 \) radical on the bare \( C_{60} \) cage in a
ΔEt(m) = Etot(m)−Etot(m−1)−1/2Etot((CF3)2)
The lower ΔEt(m) the more stable for m
m = 3 is the best

La@C60(CF3)m
Stable
Unstable

ΔEt(m) = Etot(m)−Etot(m−1)−1/2Etot((CF3)2)
The lower ΔEt(m) the more stable for m
m = 3 is the best

Figure 2: (Color online) Energy change ΔEt(m) associated with attaching an extra trifluoromethyl radical to the most stable La@C60(CF3)m–1 isomer. Negative values denote stable structures and ΔEt(0) is set to zero. ΔEt(m) values for the most stable isomers are shown by the larger symbols and are connected by the solid green line to guide the eye.

The structural paradigm changes when increasing the number of CF3 radicals attached to La@C60 to m = 4. Among the 10 regioisomers presented in Figure S3 of the Supporting Information, the most stable structure, shown in Figure 1(e), contains two pairs of CF3 radicals in para-arrangement on hexagonal rings that are separated by half the circumference of the C60 molecule. Another arrangement, with all CF3 radicals in para arrangement on adjacent hexagonal rings, is energetically the second-best isomer, with its energy only 0.051 eV higher than the most stable structure. The most stable isomer has a C2v symmetry and the second-best isomer only a mirror symmetry.

The structural paradigm for La@C60(CF3)m regioisomers with m = 5 CF3 radicals is similar to the m = 4 case. The most stable of ten regioisomers, presented in Figure S4 of the Supporting Information and displayed in Figure 1(f), contains 4 CF3 radicals in para arrangement on three adjacent hexagonal rings. The last radical is separated by 4 neighbor distances from the closest CF3 radical. It is also possible to arrange all five CF3 radicals in para positions on four adjacent hexagonal rings, but this highly symmetric regioisomer is less stable by 0.9 eV than the most stable structure.

To find out the preferential number of CF3 radicals attached to the La@C60 molecule, we calculated the energy change ΔEt(m) associated with attaching an extra trifluoromethyl radical to the most stable La@C60(CF3)m–1 isomer and display our results in Figure 2. We defined ΔEt(m) by

\[
\Delta E^t(m) = E_{tot}\,(m) - E_{tot}\,(m-1) - \frac{1}{2}E_{tot}(C_2F_6).
\] (1)
\( E_{\text{tot}}^{\text{min}}(m) \) denotes the total energy of the most stable \( \text{La@C}_{60}\left(\text{CF}_3\right)_m \) isomer. A negative value of \( \Delta E_t^{(m)} \) indicates an exothermic reaction for adsorbing an extra \( \text{CF}_3 \) radical that had been initially formed by dissociating a hexafluoroethane molecule. \( \Delta E_t^{(0)} \) for the bare metallofullerene has been set to zero.

According to our results in Figure 2, it is always possible to find a structural arrangement of \( \text{CF}_3 \) radicals that would further stabilize the \( \text{La@C}_{60} \) structure. We find structures with odd number of radicals to be relatively more stable, with \( m = 3 \) providing the optimum stabilization with \( \Delta E_t^{(3)} = -0.44 \) eV. In comparison, the stability gain \( \Delta E_t^{(4)} = -0.11 \) eV upon adsorbing four radicals is much smaller. Equally interesting as the optimum regioisomer is the range of \( \Delta E_t^{(m)} \) values for a given \( m \), which is as wide as 3 eV. We should not neglect the fact that functionalization by \( \text{CF}_3 \) radicals within the raw soot may not always yield the most stable isomers.

The even-odd alternation in the \( \Delta E_t^{(m)} \) values for the most stable isomers, with odd values referring to higher stability, has been found previously for \( \text{CF}_3 \)-functionalized \( \text{La@C}_{70} \) and \( \text{Y@C}_{70} \) molecules.\(^{19,25}\) The even-odd alternation is also found in \( \text{CF}_3 \)-functionalized fullerenes, which, however, display an energetic preference for an even number of \( \text{CF}_3 \) radicals.\(^{31,32}\) The preference of fullerenes for an even number of \( \text{CF}_3 \) radicals can be explained easily. Attaching an even number of radicals to nominal double-bonds in the fullerene cage converts the \( C \) atoms in the double-bond from an \( sp^2 \) to an \( sp^3 \) configuration, leaving no radical behind. Consequently, an odd number of \( \text{CF}_3 \) radicals will leave at least one \( C \) radical behind, lowering the stability of the structure.

As we will discuss next, an \( \text{La} \) atom – upon its encapsulation – transfers 3 electrons to the \( \text{C}_{60} \) shell, whereas the charge transfer caused by attached \( \text{CF}_3 \) radicals is significantly smaller. The odd number of electrons added to the shell modifies its electronic structure, resulting in an energetic preference for an odd instead of an even number \( m \) of \( \text{CF}_3 \) radicals attached to \( \text{C}_{60} \).

Electronically, there is no difference if the negative charge of the \( \text{C}^{3-}_{60} \) shell stems from encapsulated \( \text{La} \) in a hypothetical \( \text{La@C}_{60} \) or from 3 alkali atoms that are interstitial in the \( \text{M}_3\text{C}_{60} \) crystal. The electronic structure of the corresponding molecular crystal will be determined by the narrow band formed of the partly occupied LUMO of the \( \text{C}_{60} \) molecules. Except for a dynamical Jahn-Teller effect, the system should be metallic and superconducting, with \( T_c \) depending in the same way on the lattice constant as in the equivalent \( \text{M}_3\text{C}_{60} \) molecular crystal.\(^{16}\) The present understanding of the origin of superconductivity in alkali-based \( \text{M}_3\text{C}_{60} \) solids is discussed in the Supporting Information.

Plausibilizing the difference between the functionalization of a bare \( \text{C}_{60} \) fullerene and the \( \text{La@C}_{60} \) metallofullerene requires understanding the charge redistribution introduced by the encapsulated \( \text{La} \) atom in \( \text{C}_{60} \). We discuss this charge redistribution in detail in the Supporting Information, in particular in Figure S1. The essence of our findings is consistent with the Bader charge analysis\(^{33–36}\) of the bare \( \text{C}_{60} \) molecule and all metallofullerenes depicted in Figure 1. Independent of the presence and number \( m \) of attached \( \text{CF}_3 \) radicals, we found a net transfer of \( \approx 1.8 \) electrons from the encapsulated \( \text{La} \) atom to the \( \text{C}_{60} \) cage. Restating this finding in a different way, the net charge of the \( \text{La} \) atom was not affected by the presence of \( \text{CF}_3 \) radicals carrying a net Bader charge \( Q \approx -0.1 e \), which was transferred locally from the \( \text{C}_{60} \) cage alone. In view of the ambiguity to assign a delocalized charge to particular atoms, we may assume that the charge transfer from the \( \text{La} \) atom to the cage is likely underestimated by the Bader analysis. Comparing to similar systems, where a Bader analysis has been performed,\(^{37,38}\) we found the enclosed \( \text{La} \) to be most likely in the 3+ oxidation state, with the \( \text{C}_{60} \) cage carrying extra 3 electrons.

The net electron transfer from the encapsulated \( \text{La} \) atom to the surrounding cage is also the cause of the off-center displacement of \( \text{La} \) by \( \approx 1.2 \) Å. In DFT-PBE, this symmetry-lowering displacement is associated with an energy gain of \( \approx 3.3 \) eV. This stabilization energy can be simply explained by the electrostatic polarization energy gain caused by a point charge.
Figure 3: (Color online) Structural and energetic change caused by hydrogen atom adsorption on (a) a C_{60} (top panel) and La@C_{60} (middle panel), and (b,c) on C_{60}CF_{3} (top panels) and La@C_{60}CF_{3} (middle panels). The CF_{3} radical and the H atom are adsorbed on the same hexagonal ring, occupying (b) para (or third-neighbor) positions or (c) ortho (or first-neighbor) positions. The bottom panels contain the corresponding Schlegel diagrams of C_{60} with the hydrogen sites indicated by the blue and the CF_{3} sites by the red dots. \( \Delta E^H \) denotes the energy change due to hydrogenation, with H_{2} as the hydrogen source and negative values denoting an exothermic process.
moving off-center inside a spherical metallic shell, as discussed previously for other metallofullerenes.\cite{39,40} Using $+3e$ as the net charge of the enclosed La and 3.5 Å as the radius of the C$_{60}$ shell, we estimated in this way an energy gain of 1.7 eV, the same order of magnitude as the value obtained in the DFT calculation.

If the reason for altering the energetic preference from an even to an odd number of attached CF$_3$ radicals is leaving or not leaving a C radical behind, then a single chemisorbed H atom chemisorbed on the same double-bond as a lone CF$_3$ radical may reverse this preference. To investigate this possibility, we studied the structural and energetic changes associated with the chemisorption of a hydrogen atom on bare and CF$_3$-functionalized fullerenes and metallofullerenes and present our results in Figure 3.

We defined the energy change $\Delta E^H$ associated with attaching a single H atom to a bare of CF$_3$-functionalized fullerene C$_{60}$ or metallofullerene La@C$_{60}$, denoted by R, by

$$\Delta E^H = E_{\text{tot}}(H/R) - E_{\text{tot}}(R) - \frac{1}{2}E_{\text{tot}}(H_2). \quad (2)$$

A negative value of $\Delta E^H$ indicates that the adsorption of an H atom, which had initially been formed by dissociating an H$_2$ molecule, is exothermic.

The top row in Figure 3 describes different ways of chemically functionalizing a C$_{60}$ cage. The positive value of $\Delta E^H$ in the top panel of Figure 3(a) indicates that hydrogen prefers not to adsorb on the bare C$_{60}$ cage, as discussed previously for carbon nanotubes and fullerenes.\cite{41,42} This behavior changes in presence of an adsorbed CF$_3$ radical, which modifies the electronic structure of the cage. Noting that adsorption of an isolated H atom or an isolated CF$_3$ radical on the cage are both exothermic processes, it is remarkable that the co-adsorption of CF$_3$ and H turns strongly exothermic, as seen in the top panels of Figs. 3(b) and 3(c). As anticipated above and seen in the top panel of Figure 3(c), the largest energy gain occurs when the adsorbates attach to the same double-bond on the cage, in ortho arrangement on the same hexagonal ring, changing the configuration of the adjacent C atoms from $sp^2$ to $sp^3$ and leaving no C radical behind. Somewhat less favorable is co-adsorption in a para arrangement on the same hexagon, shown in the top panel of Figure 3(b). The adsorption sites and the differences in local bonding mentioned above are best discussed using the Schlegel diagrams in the bottom panels of Figure 3.

The energetics of chemical functionalization changes completely when a La atom becomes enclosed in the C$_{60}$ cage. Since the adsorption of an isolated H atom or an isolated CF$_3$ radical become exothermic processes on La@C$_{60}$, it is not surprising that all values of $\Delta E^H$ are negative, as seen in the second row of Figure 3. This means, in other words, that hydrogenation of La@C$_{60}$(CF$_3$)$_m$ is always exothermic, irrespective of the presence of CF$_3$ radicals on the surface. Unlike in the top row, the three values of $\Delta E^H$ in the second row are much more similar: adsorbing an extra CF$_3$ radical next to a pre-adsorbed H atom lowers the energy by $\approx 0.1$ eV in the para configuration and raises it by $\approx 0.2$ eV in the ortho configuration. We note the small energetic preference for the para configuration in this case, which is reminiscent of the most stable regioisomer of La@C$_{60}$(CF$_3$)$_2$ shown in Figure 1(c).

The change in behavior can be attributed to the 3 electrons donated to the C$_{60}$ cage from the encapsulated La atom. Each of these extra electrons can be partly transferred to the electronegative CF$_3$ radical and participate in bonding, leaving no C radical behind. This is the reason behind our finding in Figure 2 that La@C$_{60}$(CF$_3$)$_m$ is most stable for $m = 3$.

As suggested by the above results, electronic structure plays the key role in determining both the stability and reactivity of fullerenes and (functionalized) metallofullerenes. The electronic eigenstates of the optimized bare C$_{60}$ molecule and of the La@C$_{60}$(CF$_3$)$_m$ molecules with $0 \leq m \leq 5$, depicted in Figure 1, are presented in Figure 4. The energy eigenvalues are the Kohn-Sham energies of our DFT-PBE calculations, which are known to underestimate the HOMO-LUMO gap.
As seen in Figure 4(a), the calculated gap between the fivefold degenerate \( h_u \) HOMO and the threefold degenerate \( t_{1u} \) LUMO of the highly symmetric \( C_{60} \) molecule is \( \approx 1.6 \) eV wide, slightly lower than the observed value\(^{43} \) of \( 1.9 \) eV. The calculated electronic spectrum of \( \text{La@C}_{60} \) is shown in Figure 4(b). As expected, the off-center displacement of the La atom reduces the symmetry and the degeneracy of electronic states. For the sake of simple comparison, we highlighted the occupied \( h_u \) state of \( C_{60} \) and the corresponding occupied eigenstates in \( \text{La@C}_{60} \) by the orange-bounded rectangle. As seen in Figure 4(b), the symmetry lowering due to the off-center displacement of La splits the \( h_u \) state of \( C_{60} \) into three closely-spaced states, two of which are doubly degenerate. More interesting is the behavior of the initially unfilled \( t_{1u} \) state in the \( C_{60} \) molecule, which splits into two states, as highlighted by the red-bounded rectangle in Figs. 4(a) and 4(b). The lower of these states in \( \text{La@C}_{60} \) is doubly degenerate and acquires 3 extra electrons from the enclosed La atom. Consequently, this partly occupied state defines the Fermi level and provides a metallic character for the \( \text{La@C}_{60} \) molecule. The significant fundamental band gap is responsible for the high stability and low reactivity of the \( C_{60} \) molecule, whereas a vanishing band gap renders \( \text{La@C}_{60} \) highly reactive. To better understand the effect of the encapsulated La atom on the electronic structure of the \( \text{La@C}_{60} \) molecule, we discuss the frontier states near the Fermi level of \( C_{60} \) and \( \text{La@C}_{60} \) molecules in the Supporting Information.

For \( \text{La@C}_{60}(\text{CF}_3)_m \) metallofullerenes functionalized with \( m \geq 1 \) \( \text{CF}_3 \) radicals, the eigenstates undergo a complex change and can no longer be simply compared to those of the bare \( C_{60} \) molecule. Comparing our results in Figs. 4(b-g), we find zero fundamental band gap in molecules with an even number \( m \) of \( \text{CF}_3 \) radicals and a nonzero band gap if \( m \) is odd. This finding suggests that \( \text{La@C}_{60} \) molecules with an odd number of \( \text{CF}_3 \) radicals should be more stable, in accord with our previous findings based on total energy calculations. Among \( \text{La@C}_{60}(\text{CF}_3)_m \) molecules, we found the largest HOMO-LUMO gap \( E_g \approx 1.0 \) eV for \( m = 5 \), followed by \( E_g \approx 0.7 \) eV for \( m = 3 \) and a very small value \( E_g \approx 0.1 \) eV for \( m = 1 \). Consequently, we expect metallofullerenes with \( m = 3 \) and \( m = 5 \) \( \text{CF}_3 \) radicals to be most abundant and easiest to separate from the primary soot, as also suggested by preliminary experimental data.\(^{14} \) Metallofullerenes with an even number of \( \text{CF}_3 \) radicals have unpaired electrons at the Fermi level, which makes these molecules more reactive and less stable.

All molecules discussed above will be further stabilized when crystallizing in a lattice. We performed corresponding calculations and found that, same as \( C_{60} \) molecules, the metallofullerenes prefer the close-packed fcc lattice, and also found no indication of dimerization in the lattice. One issue that is typ-
ically neglected when judging the stability of crystalline lattices using single-molecule description is the effect of the long-range dipole-dipole interaction. To judge the importance of this effect, we performed DFT-PBE calculations for selected fullerene and metallofullerene lattices. Even though the PBE exchange-correlation functional does not describe the van der Waals interaction accurately, such calculations still provide an adequate description of the charge redistribution and dipole-dipole interaction. $C_{60}$ molecules, carrying no dipole moment, crystallize preferably in an fcc lattice with a nearest-neighbor distance of 10.83 Å, gaining energetically $\approx 0.06$ eV per molecule. According to our Bader charge analysis, La@$C_{60}$ metallofullerenes carry a dipole moment $p = 3.3$ D and crystallize in an fcc lattice with a slightly reduced nearest-neighbor distance of 10.72 Å, gaining $\approx 0.10$ eV per molecule. The stabilization of the La@$C_{60}$ lattice with respect to crystalline $C_{60}$ lattice, however small, benefits to a large degree from the long-range dipole-dipole interaction, since an fcc lattice of $p = 3.3$ D point dipoles should be stabilized by a comparable energy of $\approx 0.06$ eV/molecule. We have furthermore found that functionalization of the La@$C_{60}$ metallofullerene by CF$_3$ radicals increases the molecular dipole moment, but also increases the nearest-neighbor distance. In the fcc lattice of La@$C_{60}$CF$_3$ molecules with a dipole moment $p \approx 12.4$ D, the nearest-neighbor distance increases to 11.72 Å and the stabilization in the lattice changes to $\approx 0.09$ eV/molecule. Similarly, in the fcc lattice of the most stable La@$C_{60}$(CF$_3$)$_2$ molecules with a dipole moment $p \approx 18.9$ D, the nearest-neighbor distance changes to 11.68 Å and the stabilization in the lattice changes to $\approx 0.10$ eV/molecule. The above DFT-PBE values of the lattice stabilization energy in CF$_3$-functionalized metallofullerenes are one order of magnitude smaller than estimates based on the interaction of point dipoles. Our overall finding is that long-range dipole-dipole interaction is of secondary importance for these lattices.

Conclusions

In summary, exploring the possibility to obtain superconducting behavior in crystalline La@$C_{60}$ even under harsh ambient conditions, we provided theoretical support for the experimental effort to solubilize the La@$C_{60}$ endohedral metallofullerene from the primary soot. We used $ab$ $initio$ density functional theory calculations to compare the stability and electronic structure of the bare $C_{60}$ fullerene and La@$C_{60}$ to their counterparts functionalized by $m$ CF$_3$ radicals. We found that several CF$_3$ radicals can form stable bonds to $C_{60}$ and La@$C_{60}$ and structures with an odd $m$ for La@$C_{60}$ due to the extra 3 electrons donated by the encapsulated La. This is consistent with our finding that a wide HOMO-LUMO gap opens in La@$C_{60}$(CF$_3$)$_m$ molecules with an odd $m$ value, causing extra stabilization in the closed-shell electronic configuration. We also addressed the possibility of a single hydrogen atom adsorbing at a C radical site in La@$C_{60}$(CF$_3$)$_m$, which would further stabilize the open-shell configuration for odd $m$ values and reduce the even/odd alternation in stability. We found that the two-fold function of CF$_3$ radicals as stabilizing agents and molecular separators may help in isolating specific molecules from the primary soot. If La@$C_{60}$(CF$_3$)$_m$ could be solubilized and recrystallized, endohedral instead of exohedral doping by three electrons per $C_{60}$ and use of stabilizing CF$_3$ radicals as spacers may lead to superconductivity with a relatively high $T_c$ achieved by optimizing the lattice constant of the molecular crystal. Stability even under harsh ambient conditions should then be expected due to the absence of alkali atoms filling the interstitial sites in known M$_3$C$_{60}$ superconductors.

Computational Techniques

We utilized $ab$ $initio$ density functional theory (DFT) as implemented in the VASP code$^{44–46}$ to optimize the structure of $C_{60}$ and
La@C_{60}(CF_3)_m functionalized with 0 ≤ m ≤ 5 CF_3 radicals and obtained the total energy as well as the electronic structure for these systems. We used projector-augmented-wave (PAW) pseudopotentials and the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional. All isolated structures have been represented using periodic boundary conditions and separated by a 12 Å thick vacuum region, so that no band dispersion could be detected. We used 500 eV as the electronic kinetic energy cutoff for the plane-wave basis and a total energy difference between subsequent iterations below 10^{-5} eV as the criterion for reaching self-consistency. All geometries have been optimized using the conjugate-gradient method until none of the residual Hellmann-Feynman forces exceeded 10^{-2} eV/Å.

**Supporting Information Available**

The following files are available free of charge. Additional information is provided regarding the origin of superconductivity in alkali-based M_3C_{60} solids, charge distribution in the frontier states of pristine C_{60} and La@C_{60} molecules, and the equilibrium structure and stability of different La@C_{60}(CF_3)_m regioisomers.

**Author Information**

**Corresponding Author**

*E-mail: tomanek@pa.msu.edu*

**Notes**

The authors declare no competing financial interest.

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Supporting Information for:
Can CF$_3$-functionalized La@C$_{60}$ be isolated experimentally and become superconducting?

Jie Guan and David Tománek*

Physics and Astronomy Department, Michigan State University, East Lansing, Michigan 48824, USA
E-mail: tomanek@pa.msu.edu

Figure S1: Partial charge distribution $\rho_{vc}$ of (a) the threefold degenerate $t_{1u}$ LUMO of C$_{60}$, (b) the fivefold degenerate $h_u$ HOMO of C$_{60}$, and (c) the partly occupied doubly degenerate state of La@C$_{60}$ at the Fermi level. The isosurface value of $\rho_{vc}$ plotted is 0.003 e/Å$^3$.

Origin of superconductivity in alkali-based M$_3$C$_{60}$ solids

After a long scientific discussion following the observation of superconductivity in K$_3$C$_{60}$ and other alkali-based M$_3$C$_{60}$ intercalation compounds, the following interpretation of this phenomenon has emerged and is now accepted by the scientific community. (i) Alkali-based M$_3$C$_{60}$ solids are superconductors described well by the BCS theory. The electron-phonon coupling results from a dynamical Jahn-Teller effect on individual C$_{60}$ cages, made possible by retardation, and is confirmed by the isotope effect observed when substituting pure $^{12}$C$_{60}$ by pure $^{13}$C$_{60}$ fullerenes. (ii) The dominating role of the intercalated alkali atoms is to partly fill the $t_{1u}$ LUMO of C$_{60}$ that broadens to a narrow band in the M$_3$C$_{60}$ molecular solid. (iii) Changes in $T_c$ are well described by the changing electron-phonon coupling constant $\lambda = VN(E_F)$ in the McMillan equation. Since the on-ball Bardeen-Pines interaction $V$ does not change, $\lambda$ is proportional to the electronic density of states at the Fermi level $N(E_F)$, which is roughly inversely proportional to the width of the $t_{1u}$-derived band. Substituting intercalated K atoms by heavier alkali atoms M leads to an increase of the C$_{60}$−C$_{60}$ separation, thus reducing the width of the $t_{1u}$ band and consequently increasing the electron-phonon coupling constant $\lambda$. We should note that the range of lattice constants allowing superconductivity is limited. Changing the lattice constant changes the inter-ball hopping integral $t$, while not affecting the on-ball Coulomb integral $U$. The $U/t$ ratio increases with increasing lattice constant and, beyond a critical value, changes doped C$_{60}$ from a metal to a Mott-Hubbard insulator$^{1,2}$.

Frontier states in C$_{60}$ and La@C$_{60}$ molecules

To better understand the effect of the encapsulated La atom on the electronic structure of the La@C$_{60}$ molecule, we calculated the partial charge density of the LUMO and the HOMO of C$_{60}$ as well as that of the partly degenerate
Figure S2: Ten different La@C$_{60}$(CF$_3$)$_2$ isomers functionalized with 2 CF$_3$ radicals. The subfigures display the following isomers: (a) 2(1), (b) 2(2), (c) 2(3), (d) 2(4), (e) 2(5), (f) 2(6), (g) 2(7), (h) 2(8), (i) 2(9), (j) 2(10). The top panels show the ball-and-stick models of the structures, followed by the DFT-PBE relative total energy values $\Delta E$ with respect to the most stable isomer. The bottom panels show the Schlegel diagrams of functionalized C$_{60}$ molecules, with the trifluoromethyl sites indicated by the red dots.

level of La@C$_{60}$ at the Fermi level. The corresponding results are presented in Figure S1. As mentioned in the main manuscript, there is an $\approx$1.6 eV wide gap between the threefold degenerate $t_{1u}$ LUMO and the fivefold degenerate $h_u$ HOMO of the pristine C$_{60}$ molecule. In La@C$_{60}$, on the other hand, the partly occupied, doubly degenerate state at $E_F$, which originally belonged to the threefold degenerate LUMO of C$_{60}$, defines the Fermi level and provides this molecule with a "metallic" character.

The partial charge densities of the LUMO state in Figure S1(a) and the HOMO of C$_{60}$ in Figure S1(b) show that both states are mainly associated with the $p_\perp$ orbitals of C atoms and are equally distributed across all atoms of the pristine fullerene molecule. The partial charge density of the partly occupied state at the Fermi level of the endohedrally doped La@C$_{60}$ molecule, shown in Figure S1(c), resembles that of the $t_{1u}$ LUMO of C$_{60}$. It consists mostly of $p_\perp$ orbitals of C atoms, with only a small contribution from the enclosed La atom, consistent with our claim that the main role of La is to transfer extra electrons to the $\pi$ electron network on the C$_{60}$ cage. We note that the charge in the HOMO/LUMO level of La@C$_{60}$ is not distributed evenly across the C$_{60}$ cage. This finding agrees with our Bader charge analysis and is particularly noticeable in Figure S1(c). It can be explained by the positively charged La atom gaining energetically from an off-center displacement, caused by the image-charge interaction, which skews the electron distribution...
on the cage towards the encapsulated La atom. Very similar changes occur in the $t_{1u}$-derived state of C$_{60}$ that acquires a net charge from nearby exohedral alkali atoms M in the superconducting M$_3$C$_{60}$ solid.

**Equilibrium structure and stability of different La@C$_{60}$(CF$_3$)$_m$ isomers**

As mentioned in the main manuscript, the endohedral fullerene La@C$_{60}$ can be functionalized by CF$_3$ radicals that attach on-top of C atoms and can be arranged in different ways across the C$_{60}$ cage. To identify the most stable La@C$_{60}$(CF$_3$)$_m$ geometry, we compared the total energies of different regioisomers containing $m$ trifluoromethyl radicals. Our results for $m = 2, 3, 4$ and 5 are shown in Figures S2, S3, S4 and S5, respectively. Each isomer is identified as $m(i)$, where $m$ denotes the number of CF$_3$ radicals and $i$ is the assigned isomer number.

Our results for 10 different arrangement of $m = 2$ CF$_3$ radicals adsorbed on the C$_{60}$ cage are shown in Figure S2. For each regioisomer, we display the optimum geometry, the corresponding Schlegel diagram and relative energy with respect to the most stable isomer. Our results indicate that CF$_3$ radicals in the most stable $m = 2$ regioisomer are in the para (third neighbor) positions on a single hexagon on the C$_{60}$ surface and the molecule has a C$_{2v}$ symmetry. Other arrangements penalized energetically up to $\lesssim$1 eV, with the least stable arrangement containing CF$_3$ radicals in adjacent sites. Comparing the relative energies, we found that CF$_3$ radicals prefer to be close, but not too close on the C$_{60}$ surface.

As seen in Figure S3, a very similar picture emerges for $m = 3$ CF$_3$ radicals adsorbed on La@C$_{60}$. Comparing the structure of six different isomers in ball-and-stick models as well as Schlegel diagrams, we found that the most stable isomer, shown in Figure S3(a), contains all CF$_3$ radicals in para (third neighbor) positions on adjacent hexagonal rings on the C$_{60}$ surface, resulting in a mirror symmetry. The second most stable isomer, shown in Figure S3(f), contains CF$_3$ radicals separated by 5 neighbor distances, is only $\approx$0.1 eV less stable and has a C$_3$ symmetry. Even though nearest-neighbor arrangements of CF$_3$ radicals were not considered, other structural candidates incurred an energy penalty of up to $\lesssim$1.3 eV with respect to the most stable isomer.

The structural paradigm changes for $m = 4$ CF$_3$ radicals adsorbed on the La@C$_{60}$ metallofullerene. Among the 10 regioisomers displayed in Figure S4, the most stable structure, shown in Figure S4(a), contains two pairs of CF$_3$ radicals in para-arrangement on hexagonal rings that are separated by half the circumference of the C$_{60}$ molecule. The arrangement in Figure S4(e), with all $m = 4$ CF$_3$ radicals in para arrangement on adjacent hexagonal rings, is energetically the second-best isomer, with its energy only 0.051 eV higher than the most stable structure. The most stable isomer has a C$_{2v}$ symmetry and the second most stable isomer only a mirror symmetry.

The structural paradigm for La@C$_{60}$(CF$_3$)$_m$ regioisomers with $m = 5$ CF$_3$ radicals is similar to the $m = 4$ case. Ten regioisomers are presented in Figure S5. The most stable of them, shown in Figure S5(a), contains 4 CF$_3$ radicals in para arrangement on three adjacent hexagonal rings. The last radical is separated by 4 neighbor distances from the closest CF$_3$ radical. It is also possible to arrange all five CF$_3$ radicals in para positions on four adjacent hexagonal rings. As seen in Figure S5(b), this highly symmetric regioisomer is less stable by $\lesssim$0.9 eV than the most stable structure.

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Figure S3: Six different La@C₆₀(CF₃)₃ isomers functionalized with 3 CF₃ radicals. The subfigures display the following isomers: (a) 3(1), (b) 3(2), (c) 3(3), (d) 3(4), (e) 3(5), (f) 3(6). The top panels show the ball-and-stick models of the structures, followed by the DFT-PBE relative total energy values $\Delta E$ with respect to the most stable isomer. The bottom panels show the Schlegel diagrams of functionalized C₆₀ molecules, with the trifluoromethyl sites indicated by the red dots.
Figure S4: Ten different La@C_{60}(CF_3)_4 isomers functionalized with 4 CF_3 radicals. The subfigures display the following isomers: (a) 4(1), (b) 4(2), (c) 4(3), (d) 4(4), (e) 4(5), (f) 4(6), (g) 4(7), (h) 4(8), (i) 4(9), (j) 4(10). The top panels show the ball-and-stick models of the structures, followed by the DFT-PBE relative total energy values ΔE with respect to the most stable isomer. The bottom panels show the Schlegel diagrams of functionalized C_{60} molecules, with the trifluoromethyl sites indicated by the red dots.
Figure S5: Ten different La@C$_{60}$(CF$_3$)$_5$ isomers functionalized with 5 CF$_3$ radicals. (a) 5(1), (b) 5(2), (c) 5(3), (d) 5(4), (e) 5(5), (f) 5(6), (g) 5(7), (h) 5(8), (i) 5(9), (j) 5(10). The top panels show the ball-and-stick models of the structures, followed by the DFT-PBE relative total energy values $\Delta E$ with respect to the most stable isomer. The bottom panels show the Schlegel diagrams of functionalized C$_{60}$ molecules, with the trifluoromethyl sites indicated by the red dots.