VIP Fullerenes Very Important Paper

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Missing Small-Bandgap Metallofullerenes: Their Isolation and Electronic Properties**

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In contrast to the extensively studied empty C_{60} and C_{70} fullerenes, the extraction of the corresponding endohedral metallofullerenes M@C_{60} and M@C_{70} (e.g., M = Sc, Y, La, Ce, or Gd) (Figure 1a) has been a long-standing challenge ever since the experimental discovery in 1985[1] and the first macroscopic production in 1991[2] of metallofullerenes. It has been well-known[3] that M@C_{60} and M@C_{70} are insoluble in common fullerene solvents such as toluene and carbon disulfide, although the yields of M@C_{60} and M@C_{70} in raw soot are fairly high according to mass spectrometric analysis. Besides M@C_{60} and M@C_{70}, there are a large number of other insoluble, the so-called small-bandgap (or small HOMO–LUMO gap) metallofullerenes such as M@C_{72} and M@C_{74}. These metallofullerenes are highly reactive because of their open-shell electronic configurations or small bandgaps, and they tend to form insoluble polymerized solids in raw soot.[4]

The highly reactive small-bandgap metallofullerenes can be stabilized either by electrochemical reduction or chemical functionalization. Diener and Alford reported that insoluble polymerized Gd metallofullerenes can be reduced into soluble closed-shell anions by an electrochemical method.[4] Exohedral derivatization is another way to stabilize small-bandgap fullerenes and metallofullerenes. For example, C_{74} can be extracted through exohedral fluorination or trifluoromethylation.[5] Similarly, insoluble metallofullerenes La@C_{2n} ($2n$ = 72, 74, and 80) become soluble in organic solvents after functionalization with dichlorophenyl groups.[6] However, the most interesting La@C_{60} and La@C_{70} fullerenes are still unavailable.

Arc discharge is the most commonly used technique for the production of metallofullerenes, which is typically performed with a metal/graphite composite rod in a helium atmosphere.[3a,7] It is convenient to introduce additional gaseous or solid reagents into the arc-discharge chamber to produce new types of fullerenes or metallofullerenes.[8] For instance, trifluoromethyl derivatives of C_{60} were produced using polytetrafluoroethene (PTFE) as a source for functional groups during arc discharge.[8e] Here we demonstrate an arc-discharge method for producing derivatives of small-bandgap metallofullerenes using PTFE. As shown schematically in Figure 1b, PTFE is placed near the area where arc discharge occurs. Because of the high-temperature of the arc zone, PTFE is evaporated together with the metal/graphite rod during arc discharge. As a consequence, a series of trifluoromethyl derivatives of insoluble metallofullerenes M@C_{2n}-$(CF_3)_m$ (e.g., $2n$ = 60, 70, 72, or 74) are formed effectively. Surprisingly, these derivatives, including those of M@C_{60} and M@C_{70}, are totally soluble and stable in such organic solvents as toluene and carbon disulfide, which is important for further purification and characterization.

This arc-discharge method can be applied for various metals. Similar results have been obtained in the present laboratory for metals such as yttrium, gadolinium, or dyspro-

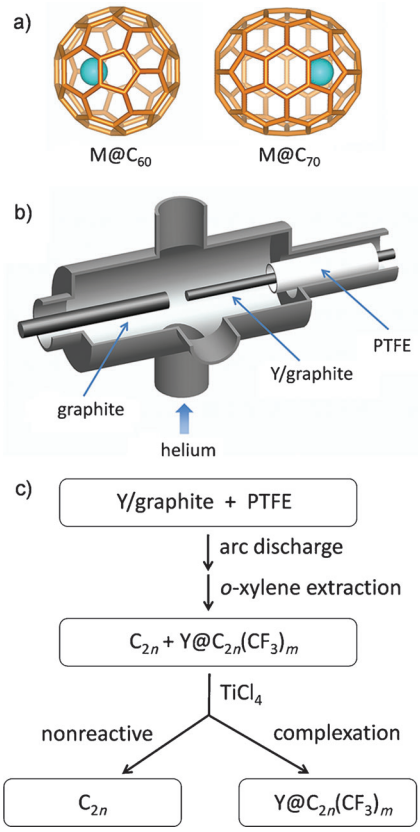

Figure 1. a) Molecular structural models for missing metallofullerenes M@C_{60} and M@C_{70}. b) The arc-discharge apparatus. c) Production, extraction, and purification process for Y metallofullerenes functionalized with trifluoromethyl groups.

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sium. The experimental procedure for the preparation and extraction of yttrium metallofullerenes is described in Figure 1c. After arc discharge with a Y/graphite rod and PTFE in helium, the soot was extracted with *o*-xylene. Then, laser desorption time-of-flight (LD-TOF) mass measurement was carried out for the extract. Signals from both the empty fullerenes C_{2n} (e.g., $2n = 60$, 70, 76, 78, 82, or 84) and yttrium metallofullerenes $Y@C_{2n}$ (e.g., $2n = 60$, 70, 72, or 74) can be seen in the mass spectrum (Figure 2a). The observed $Y@C_{2n}$

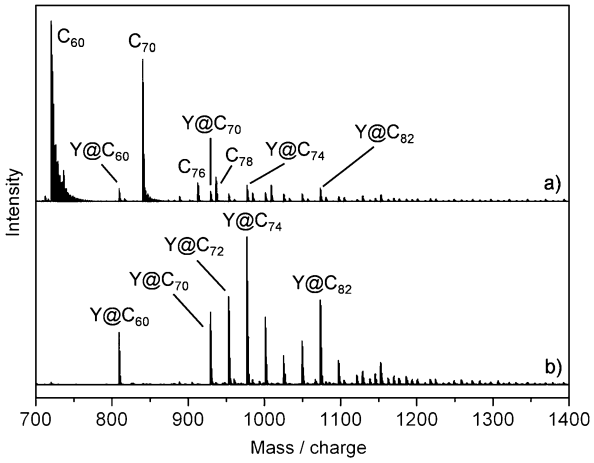

Figure 2. LD-TOF mass spectra (positive-ion mode) for a) *o*-xylene extract and b) separated derivatives of Y metallofullerenes with $TiCl_4$ treatment.

ions are actually fragments of $Y@C_{2n}(CF_3)_m$. Because of the laser-induced fragmentation at the time of desorption/ionization, no peaks from the parent molecules $Y@C_{2n}(CF_3)_m$ are observed (evidence for the parent molecules will be shown below). It is well-known that only $M@C_{82}$ among various mono-metallofullerenes $M@C_{2n}$ (M = trivalent metals, $2n \geq 60$) can be readily extracted in the case of the conventional arc discharge.[2] In contrast, herein, derivatives of the missing insoluble metallofullerenes are dissolved readily in organic solvents.

After the extraction with *o*-xylene, derivatives of $Y@C_{2n}$ were separated from the empty fullerenes with the $TiCl_4$-based method that we have reported previously.[9] We found that metallofullerenes form complexes with $TiCl_4$ in organic solvents, whereas empty fullerenes do not. The selective reactivity of $TiCl_4$ with metallofullerenes can be used for the separation/purification of metallofullerenes. Here, we demonstrate that the $TiCl_4$-based method is equally effective for the separation of trifluoromethyl derivatives of $Y@C_{2n}$. The spectrum in Figure 2b corresponds to the metallofullerenes separated with $TiCl_4$. It is clear that empty fullerenes have been well removed and the $Y@C_{2n}$ (e.g., $2n = 60$, 70, 72, or 74) species dominate the spectrum. We have previously found that the reactivity of metallofullerenes/fullerenes toward $TiCl_4$ is dependent on their first oxidation potentials. The threshold of the oxidation potential for complexation with $TiCl_4$ is determined to be 0.62–0.72 V versus Fc/Fc^+ (Fc = ferrocene).[9b] The present successful separation of trifluoromethylated $Y@C_{2n}$ from empty fullerenes implies that these derivatives have first oxidation potentials lower than the threshold value. It should be pointed out that this separation step with $TiCl_4$ greatly simplifies the subsequent HPLC purification process. As the retention time on HPLC columns for some of the $Y@C_{2n}$ derivatives is quite close to that of C_{60}/C_{70}, the purification would be difficult if there is a large amount of C_{60}/C_{70} present in the extract.

Multistage HPLC purification was then performed on the mixture of trifluoromethylated $Y@C_{2n}$, and a number of purified derivatives were obtained (the HPLC profile is shown in Figure S1 in the Supporting Information). Figure 3a

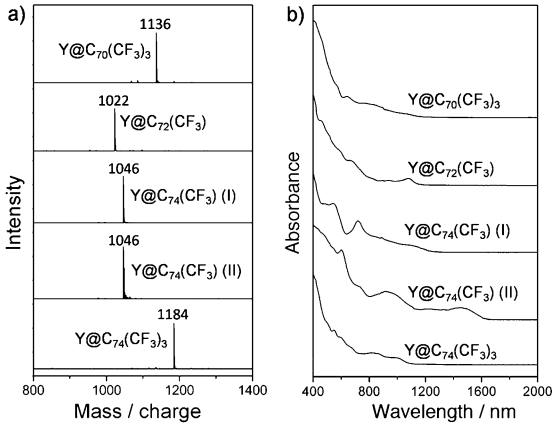

Figure 3. a) MALDI-TOF mass spectra (positive-ion mode) and b) UV/Vis/NIR absorption spectra in carbon disulfide for the isolated samples of $Y@C_{70}(CF_3)_3$, $Y@C_{72}(CF_3)$, $Y@C_{74}(CF_3)$ (I), $Y@C_{74}(CF_3)$ (II), and $Y@C_{74}(CF_3)_3$. Sulfur (S_8) was used as a matrix for the mass spectrometric measurements.

shows the matrix-assisted laser desorption time-of-flight (MALDI-TOF) mass spectra for the isolated $Y@C_{70}(CF_3)_3$, $Y@C_{72}(CF_3)$, $Y@C_{74}(CF_3)$ (isomer I and II) and $Y@C_{74}(CF_3)_3$ (LD-TOF mass spectra for these derivatives are shown in Figure S2 in Supporting Information). According to the mass spectra, $Y@C_{2n}$ ($2n = 70$, 72, 74) is functionalized with either one or three trifluoromethyl groups. The number of substituents on $Y@C_{2n}$ metallofullerenes is different from the trifluoromethyl derivatives of C_{60} fullerene and the trimetallic nitride template (TNT) metallofullerenes (e.g. $Sc_3N@C_{80}$). In general, even-number $-CF_3$ groups are attached to C_{60} and $Sc_3N@C_{80}$,[10] as there is no unpaired electron on the fullerene cages of C_{60} and $Sc_3N@C_{80}$. For $Y@C_{2n}$ ($2n = 70$, 72, 74) metallofullerenes, the yttrium atom donates three electrons to the carbon cage, forming an open-shell electronic configuration. Addition of odd-number $-CF_3$ groups to the carbon cage may result in a closed-shell structure, which is similar to the case of trifluoromethylated $Y@C_{82}$.[11] As a result, the highly reactive metallofullerenes can be stabilized by trifluoromethyl derivatization, and thus can be dissolved in normal organic solvents.

UV/Vis/NIR spectroscopic studies on the trifluoromethylated metallofullerenes provide some insights into their electronic structures. The HOMO–LUMO gaps of metallofullerenes can be roughly estimated from the onsets in the

absorption spectra, that is, a gap (eV) of about 1240/onset (nm). $Y@C_{70}(CF_3)_3$, $Y@C_{72}(CF_3)$, $Y@C_{74}(CF_3)$ (I), $Y@C_{74}(CF_3)$ (II), and $Y@C_{74}(CF_3)_3$ have the onsets at 1400, 1245, 1330, 1668, and 1335 nm (Figure 3b), corresponding to HOMO–LUMO gaps of 0.89, 1.00, 0.93, 0.74, and 0.93 eV, respectively. These derivatives have moderate HOMO–LUMO gaps as compared with other soluble and stable metallofullerenes,[12] indicating that the derivatives are more stable than their pristine counterparts $Y@C_{2n}$.

Density functional theory (DFT) calculations were performed to obtain more detailed information on the electronic structures of the trifluoromethyl derivatives. We found that the absorption spectra of $Y@C_{74}(CF_3)$ (I) and (II) are very similar to those two isomers of $La@C_{74}(C_6H_3Cl_2)$ reported previously.[6d] It is highly probable that $Y@C_{74}(CF_3)$ will have the same cage structure (C_{74}-D_{3h}) as well as the same addition site as $La@C_{74}(C_6H_3Cl_2)$. On the basis of the analogous structures, we carried out geometry optimizations and energy calculations on pristine and functionalized $Y@C_{74}$. Figure 4

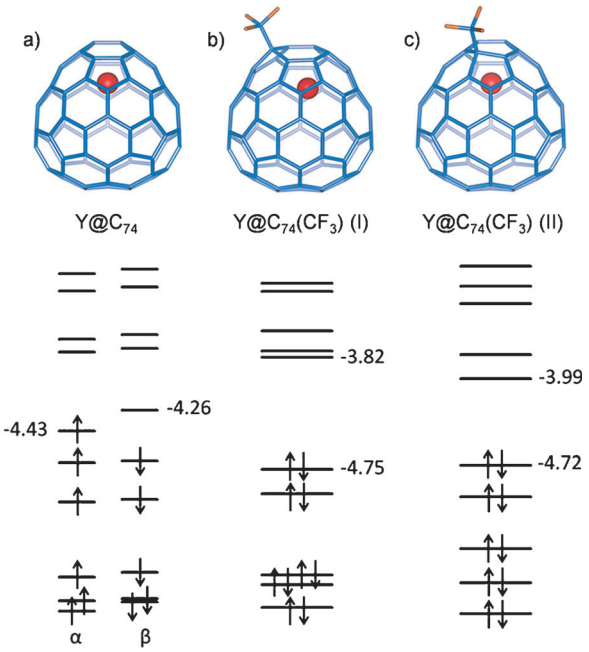

Figure 4. DFT-optimized structures and the calculated molecular orbital energy levels (in eV) for a) $Y@C_{74}$, b) $Y@C_{74}(CF_3)$ (I), and c) $Y@C_{74}(CF_3)$ (II). The addition sites are different for the two isomers of $Y@C_{74}(CF_3)$. The calculations were performed using the PBEPBE functional[13] with the Gaussian 09 program package.[14] The 6-31 G(d) basis set was used for the C and F atoms, and LanL2DZ basis set[15] with a relativistic effective core potential was employed for the Y atoms.

depicts the optimized structures and molecular orbital energy levels. For $Y@C_{74}$ with an open-shell structure, the energy of the highest occupied alpha orbital is −4.43 eV, and the energy of the lowest unoccupied beta orbital is −4.26 eV, suggesting a very small energy gap. In contrast, both $Y@C_{74}(CF_3)$ (I) and (II) have closed-shell configurations, and the HOMO–LUMO gaps are 0.93 and 0.73 eV, respectively. The calculated HOMO–LUMO gaps for the derivatives are consistent with those estimated from the absorption onsets. It is clear that the energy gap is enlarged considerably upon exohedral trifluoromethylation.

Herein, a derivative of $Y@C_{70}$ has been isolated for the first time. For a better understanding of its stability, DFT calculations were carried out on $Y@C_{70}$ and $Y@C_{70}(CF_3)_m$. As shown in Figure 5a, $Y@C_{70}$ has an open-shell configuration

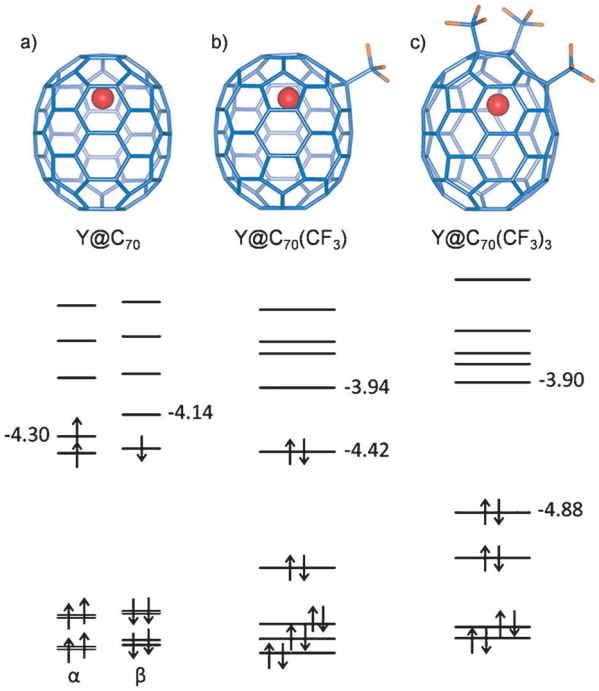

Figure 5. DFT-optimized structures and the calculated molecular orbital energy levels (in eV) for a) pristine $Y@C_{70}$, b) $Y@C_{70}(CF_3)$, and c) $Y@C_{70}(CF_3)_3$. For the $Y@C_{70}(CF_3)_3$ molecule, one of the addition sites is the same as that in $Y@C_{70}(CF_3)$; the other two addition sites are at the top of the cage.

and a very small energy gap, indicating a high chemical instability. There are five structural isomers for $Y@C_{70}(CF_3)$. DFT calculations reveal that the HOMO–LUMO gaps of these five isomers are in the range of 0.26–0.48 eV. The isomer having a HOMO–LUMO gap of 0.48 eV is shown in Figure 5b. For $Y@C_{70}$ derivatives with three -CF_3 substituents, there are a large number of isomers. We have examined some of the isomers and found that one isomer has a HOMO–LUMO gap of 0.98 eV (Figure 5c), which is close to the estimated gap for the experimentally isolated $Y@C_{70}(CF_3)_3$. The LUMO level of $Y@C_{70}(CF_3)_3$ (−3.90 eV) is very close to that of $Y@C_{70}(CF_3)$ (−3.94 eV). On the other hand, the HOMO level of $Y@C_{70}(CF_3)_3$ (−4.88 eV) is much lower than that of $Y@C_{70}(CF_3)$ (−4.42 eV), indicating a higher stability for $Y@C_{70}(CF_3)_3$. The differences in the HOMO level and the chemical stability may account for the easy accessibility of $Y@C_{70}(CF_3)_3$ rather than $Y@C_{70}(CF_3)$ as observed in our experiments. On the basis of these theoretical results, the stability of the trifluoromethyl derivatives of $Y@C_{2n}$ can be attributed to their closed-shell configurations and the enlarged HOMO–LUMO gaps.

Theoretical studies were also conducted for the trifluoromethyl derivatives of $Y@C_{60}$. As mentioned above, the derivatives of $Y@C_{60}$ have been observed in the *o*-xylene extract, even though a purified derivative of $Y@C_{60}$ has not been obtained yet. Similarly to the case of $Y@C_{70}$ derivatives, DFT calculations (Figure S3 in Supporting Information) reveal a wide bandgap opening for $Y@C_{60}$ upon trifluoromethyl derivatization. $Y@C_{60}(CF_3)_3$ has a HOMO–LUMO gap (0.81 eV) comparable with those of trifluoromethylated $Y@C_{70}$ and $Y@C_{74}$. Thus, it is possible to obtain $Y@C_{60}$ fullerene functionalized with three -CF_3 groups experimentally.

In summary, we have demonstrated an arc-discharge method for the production of trifluoromethyl derivatives of (otherwise insoluble) small-bandgap metallofullerenes. These metallofullerenes are stabilized with exohedral functional groups. They are soluble and stable in common organic solvents. A number of trifluoromethylated metallofullerenes have been purified with $TiCl_4$ and HPLC. Detailed research on the structures and electronic properties of the metallofullerenes is in progress. This study provides a powerful strategy for the extraction and purification of missing unconventional metallofullerenes, and it will open unprecedented opportunities for chemistry and materials science of metallofullerenes.

Experimental Section

Trifluoromethyl derivatives of yttrium metallofullerenes were prepared with a direct current arc-discharge method. A yttrium/graphite composite rod (100 g, 0.8 mol% of yttrium) and a pure graphite rod were used as anode and cathode, respectively. PTFE (10 g) was placed near the arc zone. Arc discharge was performed at a current of 500 A in a flowing He atmosphere with a pressure of 7.5–8.5 kPa. Typically, 28–33 g raw soot was obtained. The raw soot was rinsed in *o*-xylene to extract fullerenes and metallofullerenes. The weight of the extracted mixture of fullerenes and metallofullerenes is about 1.2–1.4 g. $TiCl_4$ (0.5 mL) was added into a CS_2 solution (250 mL) of the extracted fullerenes and metallofullerenes. Derivatives of yttrium metallofullerenes reacted with $TiCl_4$ and precipitated from the solution, while empty fullerenes were nonreactive and remained intact in the solution. After shaking for 3 minutes, the mixture was filtered with a PTFE membrane filter. The precipitate was washed first with deionized water to decompose the complex of metallofullerene/$TiCl_4$, followed by acetone to eliminate residual water. Finally, the metallofullerene solids on the PTFE filter were dissolved in CS_2. In this process, the derivatives of yttrium metallofullerenes were separated effectively from empty fullerenes. After multistage HPLC purification, about 1 mg $Y@C_{74}(CF_3)$ (I) and 1 mg $Y@C_{74}(CF_3)$ (II) were obtained. The amounts of purified $Y@C_{70}(CF_3)_3$, $Y@C_{72}(CF_3)$, and $Y@C_{74}(CF_3)_3$ are less than 1 mg.

Mass spectrometric analysis was performed on a Shimadzu Biotech MALDI-MS spectrometer. UV/Vis/NIR absorption spectra of metallofullerenes in CS_2 were acquired on a Jasco V-570 spectrophotometer.

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