Fullerenes

Trifluoromethylated Endohedral Metallofullerenes: Synthesis and Characterization of Y@C$_{82}$(CF$_3$)$_5$**

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In contrast to the exohedral modification of empty fullerenes, which has been well-establshed, the development of regioselective reaction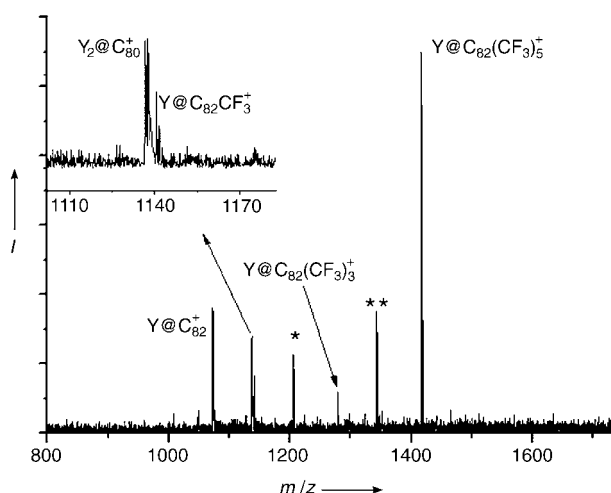s for endohedral metallofullerenes (EMFs) is still in its infancy. This is because of the following factors: 1) their limited availability to most synthetic chemists, 2) their difficult purification to homogeneity from fullerene soots, 3) the difficulty in characterizing EMFs (many EMFs are paramagnetic, thus precluding routine NMR spectroscopic characterization), and 4) the paucity of theoretical studies on hypothetical chemically modified EMFs that would guide synthetic chemists to investigate productive but not immediately apparent reaction schemes.

The cycloaddition of disilacyclopropane to La@C$_{82}$ was the first chemical modification of an EMF and was reported in 1995.[1] Several other research groups also reported cycloadducts of EMFs,[2,3] but unambiguous structural characterization has only been achieved in one study.[4] More recently, water-soluble EMFs, such as the cycloadduct Gd@C$_{60}$-(C(COOH)$_2$)$_{10}$ reported by Bolskar et al.,[5] have been prepared to explore their potential use as magnetic resonance imaging (MRI) contrast agents.[5,6] Also Shinohara et al. used fluorous biphase techniques to prepare La@C$_{82}$(C$_8$F$_{17}$)$_2$.[7] However, until now La@C$_{82}$(C$_8$F$_{17}$)$_2$ was the only reported exohedral derivative of an EMF with atomic substituents, such as H, F, Cl, or Br, or with organic substituents (R) having only R–C$_{EMF}$ single bonds.

Herein, we applied our recently developed chemical derivatization of the rare, unstable, small-band-gap fullerene C$_{74}$[8] to a rare (but stable) EMF. The reaction of interest, the first trifluoromethylation of an EMF, was carried out on crude EMF material and was followed by exhaustive chromatographic separation and characterization of the purified isolated products. This approach ensures that no EMF (mg or sub-mg quantities) is wasted during purification of the starting material or during synthetic investigations. In addition, many underivatized EMFs have low solubilities and tend to oxidize and/or polymerize in air during their separation and purification from crude EMF-containing soots.[9] Therefore, a derivatized EMF may not only be more soluble than the parent EMF, it may also be more stable, further aiding the laborious but necessary purification by chromatography (compare unstable C$_{74}$[10] with stable C$_{74}$F$_{38}$[8]).
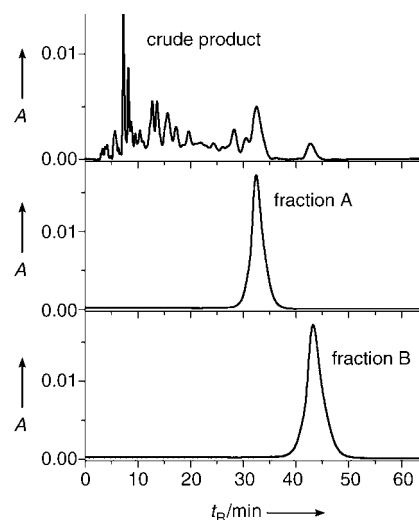
Despite our extensive experience with regioselective fluorination reactions of fullerenes,[11,12] we chose to study EMF trifluoromethylation because CF$_3$ derivatives are less prone to hydrolysis than fluorofullerenes and are more soluble in common organic solvents.[13–15] Figure 1 shows the MALDI mass spectrum of the crude product of the high-temperature reaction between the Y@C$_{82}$-enriched EMF starting material and silver(I) trifluoroacetate (AgCF$_3$CO$_2$). In addition to the main product, Y@C$_{82}$(CF$_3$)$_5$, ions corresponding to Y$_2$@C$_{80}$ derivatives with one and three CF$_3$ groups were observed. It is interesting to note that no EMF derivative with more than five CF$_3$ groups was formed, since similar high-temperature reactions of AgCF$_3$CO$_2$ and empty fullerenes yielded C$_{60/70}$(CF$_3$)$_n$ products where n as high as 22.[13,14,16] Figures 2 and 3 show the subsequent multiple-stage, two-column HPLC separation that afforded two isomers of Y@C$_{82}$(CF$_3$)$_5$. The FTIR and MALDI mass spectra of isomer **II** are shown in Figure 4.

The addition of an odd number of CF$_3$ groups to paramagnetic Y@C$_{82}$ rendered the two isomers of Y@C$_{82}$-

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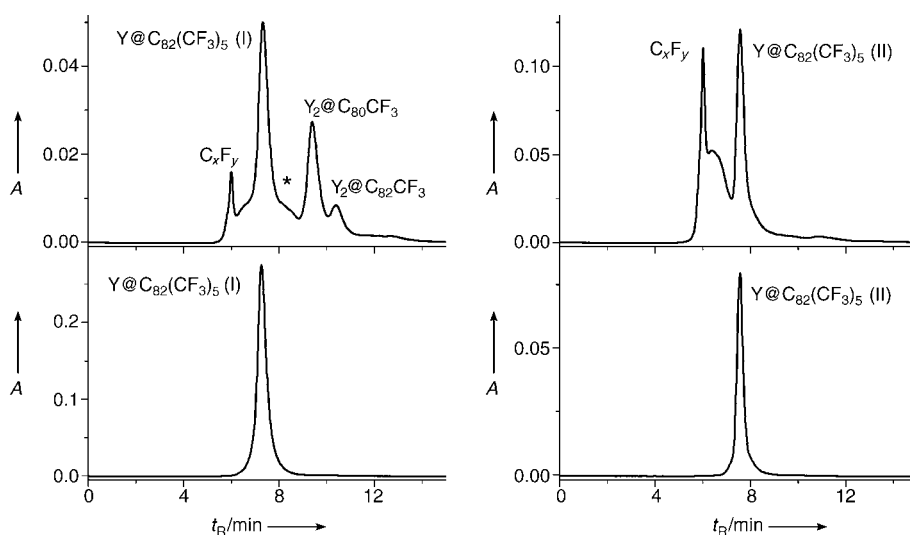Chemistry Department
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Figure 1. Positive-ion S_8-MALDI mass spectrum of the crude reaction product. Signals marked with one or two asterisks are assigned to $Y_2@C_{80}(CF_3)^+$ and $Y_2@C_{80}(CF_3)_3{}^+$, respectively. The inset shows the expanded mass range 1100–1170 Da (note the characteristic isotope distributions for the mono- and dimetallic EMF species $Y@C_{82}$ and $Y_2@C_{80}$). Matrix S_8 suppresses fragmentation and enhances the yields of molecular ions.

Figure 2. HPLC traces (Cosmosil Buckyprep column) of the crude reaction product (a) as well as isolated fractions A (b) and B (c).

$(CF_3)_5$ diamagnetic, thus allowing 1D and 2D ^{19}F NMR spectroscopic analysis to be used for structure elucidation. Previously reported EMF cycloaddition products retained the paramagnetic nature of the parent EMFs, and routine NMR spectroscopic characterization was not possible.[17] Both isomers of $Y@C_{82}(CF_3)_5$ exhibited a ^{19}F NMR spectrum with five resonances having a 1:1:1:1:1 intensity pattern. The δ values for isomer **II** ranged from $\delta = -53$ to -69 ppm, which is similar to the δ values for $C_{60}(CF_3)_{2/4/6}$ (which ranged from $\delta = -66$ to -72 ppm).[13] Figure 5 shows the 2D COSY ^{19}F NMR spectrum of isomer **II** and the labeling of resonances a–e. The topology of the 2D spectrum, the simple 1:3:3:1 splitting of resonances d and e, and the similar J_{FF} values for all of the resonances of both isomers (12–14 Hz) indicate that 1) the distances between pairs of J-coupled CF_3 groups are similar and 2) the d-a-c-b-e groups are located on a chain of 1,3- or 1,4-$C_6(CF_3)_2$ hexagons on the surface of the C_{82} cage. The second conclusion is based on the fact that the J_{FF} values for resonances d and e of 13.8(3) and 11.9(3) Hz, respectively, for isomer **I** and 13.6(3) and 12.7(3) Hz, respectively, for isomer **II** are virtually the same as the J_{FF} values for the end-of-chain CF_3 groups in C_1-$C_{60}(CF_3)_4$ and C_1-$C_{60}(CF_3)_6$, which ranged from 12.3(3) to 14.5(3) Hz.[13] DFT calculations have shown that 1,2-additions of CF_3 groups in those two trifluoromethylated [60]fullerenes, as well as in $C_{60}(CF_3)_2$, do not lead to stable structures.[13] Instead, 1,4-additions, which led to the occasional 1,3 arrangement of CF_3 groups in the


Figure 3. HPLC traces (Buckyclutcher column) of fraction A (top left), purified sample of $Y@C_{82}(CF_3)_5$ isomer **I** (bottom left), fraction B (top right), and purified sample of $Y@C_{82}(CF_3)_5$ isomer **II** (bottom right). The signal marked with an asterisk in the upper left trace corresponds to $Y@C_{82}(CF_3)_3$.
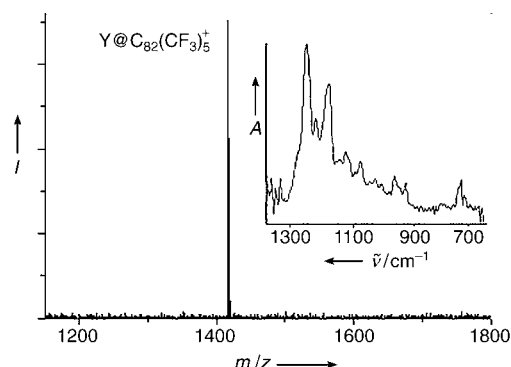
Figure 4. Positive-ion S_8-MALDI mass spectrum of HPLC-purified $Y@C_{82}(CF_3)_5$ isomer **II**. The inset shows the ATR–FTIR spectrum of $Y@C_{82}(CF_3)_5$ isomer **II**.
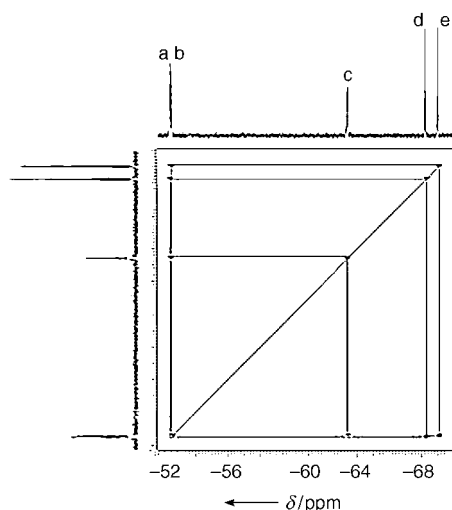
Figure 5. 376.5 MHz 1D and 2D COSY ^{19}F NMR spectra of Y@C$_{82}$-(CF$_3$)$_5$ isomer **II** in [D$_6$]benzene.

interior of a chain of C$_6$(CF$_3$)$_2$ edge-sharing hexagons, led to the most stable structures.[13]

New DFT calculations[18] of structures, relative energies, and chemical shifts for a large group of Y@C$_{82}$(CF$_3$)$_5$ isomers support this interpretation of the NMR spectroscopic data for isomers **I** and **II** of Y@C$_{82}$(CF$_3$)$_5$. For simplicity, we chose the C_{2v} isomer of Y@C$_{82}$ as the basis for our calculations because this particular cage structure has been proven for the related compounds Sc@C$_{82}$ and La@C$_{82}$.[9] For isomers with a chain of four 1,4-C$_6$(CF$_3$)$_2$ hexagons, the first, third, and fifth CF$_3$ groups were found to have a staggered conformation with respect to the C−C bonds of the carbon cage which forces the two remaining CF$_3$ groups to exhibit eclipsed conformations because of F···F steric repulsions. The calculated differences between the δ values for the ^{19}F atoms for these two types of conformations were found to be in good agreement with the experimentally observed values irrespective of the position of the 1,4-C$_6$(CF$_3$)$_2$ hexagons on the C_{2v}-C$_{82}$ cage. On the contrary, steric interactions in 1,2-C$_6$(CF$_3$)$_2$ or 1,3-C$_6$(CF$_3$)$_2$ hexagons forced all of the CF$_3$ groups to exhibit similar conformations (all staggered or all nearly staggered, respectively) and, as a result, the δ values of the ^{19}F atoms were nearly the same.

The structures of 56 1,4 isomers of Y@C$_{82}$(CF$_3$)$_5$ in which the 1,4-C$_6$(CF$_3$)$_2$ edge-sharing hexagons had various arrangements and locations on the C_{2v}-Y@C$_{82}$ cage were computationally studied. The two almost isoenergetic structures shown in Figure 6a and b were calculated to be approximately 14 kJ mol^{-1} more stable than the third isomer (Figure 6c) and at least 50 kJ mol^{-1} more stable than the other 53 isomers.

We propose that isomers **I** and **II** of Y@C$_{82}$(CF$_3$)$_5$ have 1,4 chain structures similar to those shown in Figure 6. Significantly, the two structures in Figure 6 are also predicted to be more than 100 kJ mol^{-1} more stable than the hypothetical structures with a closed loop of 1,4-additions that would result in the formation of an isolated, six-electron, aromatic cyclopentadienyl (Cp) ring, such as those observed in Tl(C$_{60}$Ph$_5$)[19] and related organometallic compounds that contain Cp-like C$_{60}$R$_5^-$ ligands.[20] Although such a structure might be the most stable isomer for a hypothetical EMF M@C$_{82}$(CF$_3$)$_5$ in which the metal atom can donate only one electron to the C$_{82}$ cage, the calculated lowest energy structures shown in Figure 6 are apparently the most stable isomers when the metal atom donates three electrons to the cage.

In summary, we have 1) demonstrated an efficient method for the exohedral derivatization of the EMF Y@C$_{82}$, 2) isolated and characterized two diamagnetic stable isomers of Y@C$_{82}$(CF$_3$)$_5$, 3) used a combination of 2D ^{19}F NMR spectroscopic analysis and DFT calculations to elucidate the most probable type of CF$_3$ addition pattern of these isomers, and 4) isolated and characterized by mass-spectrometric analysis Y@C$_{82}$(CF$_3$)$_n$ ($n = 1, 3$) and Y$_2$@C$_{80}$(CF$_3$). Further studies on other EMFs will show if particular compositions and addition patterns depend on the nature of the encapsulated metal atom(s).

Experimental Section

EMF-containing soot was prepared by burning composite graphite electrodes with metallic yttrium in an arc-discharge reactor. The
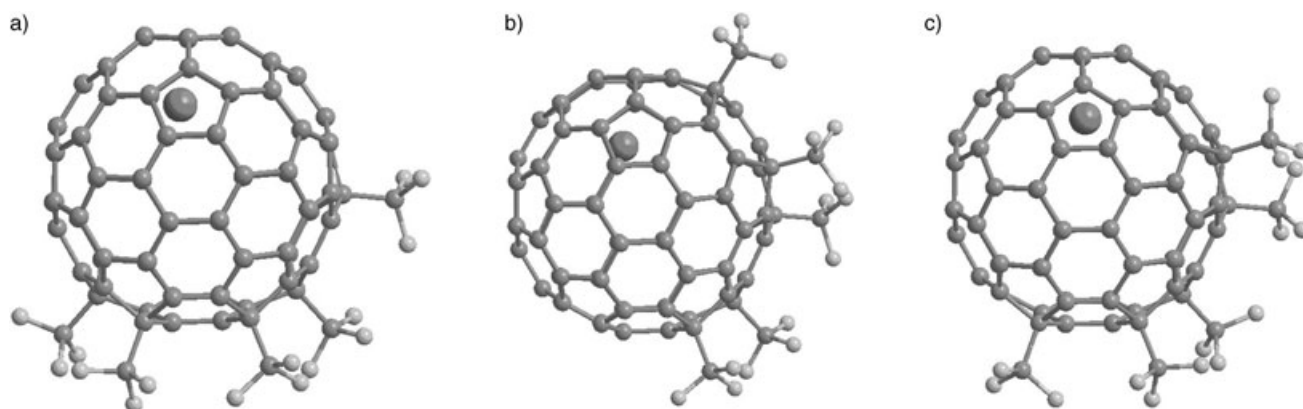
Figure 6. Three low-energy structures of Y@C$_{82}$(CF$_3$)$_5$ chains of 1,4-C$_6$(CF$_3$)$_2$ edge-sharing hexagons calculated at the DFT level of theory. Structures (a) and (b) were found to be 14 kJ mol^{-1} more stable than structure (c) and at least 50 kJ mol^{-1} more stable than the other 53 calculated isomers (see text).

EMFs $Y_m@C_{2n}$ were extracted in a two-stage procedure under an atmosphere of argon (using *ortho*-dichlorobenzene followed by *N,N*-dimethylformamide (DMF), both heated to reflux),[21,22] which resulted in an extract enriched in $Y@C_{82}$, as evidenced by mass-spectrometric analysis.[21] The isomeric composition of the EMFs in DMF extract is not known. However, ESR analysis of the *ortho*-dichlorobenzene extract of the same soot showed the presence of two main isomers of $Y@C_{82}$ in an approximate 3:1 ratio, which agreed with literature data on $Y@C_{82}$-containing soots.[23–25]

In a typical synthetic experiment, $Y@C_{82}$-enriched extract (100 mg) was thoroughly mixed with $AgCF_3CO_2$ (Aldrich, 500 mg). The reaction mixture was placed in a quartz rector under dynamic vacuum (10^{-6} Torr) and heated to 400°C (at 40°C min^{-1}) for 10 h. An IR spectrum of the cooled product mixture showed that no $AgCF_3CO_2$ remained. Increasing the $AgCF_3CO_2$/EMF extract ratio above 25:1 did not yield products with more than five CF_3 groups per cage. A MALDI mass spectrum of the crude product mixture (MALDI Voyager-DE PRO Biospectrometry Workstation, Applied Biosystems, USA, with 0.5 ns radiation pulses at 3 Hz from a 337 nm N_2 laser) and HPLC analysis (HP-1050, Hewlett Packard Co.) showed that the main product was $Y@C_{82}(CF_3)_5$. The following two-stage HPLC purification procedure was used: 1) Cosmosil Buckyprep column (20 mm i.d. × 250 mm, Nacalai Tesque Inc., 9 mL injections, 18 mL min^{-1} flow rate, toluene eluent) for separation of the two major $Y_m@C_{80/82}(CF_3)_n$-containing fractions A (28 min) and B (38 min; cf. C_{60}: 8.8 min); 2) Regis Buckyclutcher column (20 mm i.d. × 250 mm, Regis Chemical Co., 1.2 mL injections, 12 mL min^{-1} flow rate, toluene eluent) for isolation of the pure compounds from fraction A: $Y@C_{82}(CF_3)_5$ (isomer **I**, 6.2 min), $Y@C_{82}(CF_3)_3$ (6.8 min), $Y_2@C_{80}(CF_3)$ (8 min), $Y@C_{82}(CF_3)$; 9.8 min); and from fraction B: $Y@C_{82}(CF_3)_5$ (isomer **II**; 6.8 min; Figure 3). The 99% purity of $Y@C_{82}(CF_3)_5$ (isomers **I** and **II**) was determined by HPLC and MALDI-MS analysis. The main IR bands were (ReactIR-1000 ATR-FTIR, Applied Systems Inc., 4 cm^{-1} resolution): isomer **I**, $\tilde{v} = 1248$(s), 1223(m), 1179(s), 733(w), and 675(w) cm^{-1}; isomer **II**, $\tilde{v} = 1256$(s), 1225(m), 1181(s), and 720(w) cm^{-1}. ^{19}F NMR spectra (376.5 MHz, C_6D_6, 25°C, J_{FF} values ±0.3 Hz) showed five equal-intensity resonances for isomer **I** ($\delta = -52.8$ (sept, $J = 12.4$ Hz, 1F, a), -53.1 (sept, $J = 11.3$ Hz, 1F, b), -63.6 (sept, $J = 12.0$ Hz, 1F, c), -66.9 (quint, $J = 13.8$ Hz, 1F, d), -69.1 ppm (quint, $J = 11.9$ Hz, 1F, e)) and for isomer **II** ($\delta = -52.8$ (2 × sept, $J = 12.8$ Hz, 2F, a, b), -63.5 (m, $J \approx 12$ Hz, 1F, c), -68.3 (quint, $J = 13.6$ Hz, 1F, d), -69.1 ppm (quint, $J = 12.7$ Hz, 1F, e)).

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