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$C_{74}F_{38}$: An Exohedral Derivative of a Small-Bandgap Fullerene with D_3 Symmetry**

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Toluene-soluble fullerenes with large HOMO–LUMO energy gaps (e.g., C_{60}, C_{70}) have been intensely studied.[1] In contrast, toluene-insoluble fullerenes with HOMO–LUMO gaps less than 0.5 eV have not been extensively studied due to their low solubility and air sensitivity. An important example of the latter is C_{74}, which may have a HOMO–LUMO gap as small as 0.05 eV.[2–4] We present here the isolation and characterization of a single regioisomer (pair of enantiomers) of the $C_{74}F_{38}$ fullerene derivative with D_3 symmetry (denoted D_3-$C_{74}F_{38}$), the first exohedral derivative of C_{74}.

Pure samples of the small-bandgap (SBG) fullerene C_{74} were reported for the first time in 1998.[2] Diener and Alford at TDA processed solutions containing the stable C_{74}^{2-} ion by anaerobic HPLC, then reoxidized the C_{74}^{2-}-enriched fraction to yield solid C_{74}.[2] Up until that point, the insolubility of empty (i.e., metal-free) C_{74}, which may be a consequence of the small HOMO–LUMO gap,[2] had prevented the exploration of its exohedral derivative chemistry. However, there were indications that some fluoro[74]fullerenes might be prepared. The gas-phase difluoro monoanion $C_{74}F_2^-$ was observed in 1994 by Knudsen-cell mass spectrometry.[5] Significantly, the C–F bonds in $C_{74}F_2^-$ appeared to be stronger than the C–F bonds in $C_{60}F_2^-$ and $C_{70}F_2^-$.[6] In addition, it was recently shown that a specific set of Knudsen-cell conditions led to the generation of $C_{74}F_{38}^+$ as the dominant gas-phase [74]fullerene species.[7] Highly fluorinated [60]fullerenes are well known to be stable and to have higher volatilities and solubilities than the parent fullerene C_{60}.[8,9] With this in mind,

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we began to investigate the selective fluorination of enriched samples of C_{74} and herein report our initial results.

The high-temperature solid-state reaction of C_{74} and K_2PtF_6 followed by sublimation and HPLC purification resulted in the isolation of milligram amounts of $C_{74}F_{38}$ with $>90\%$ compositional purity. This compound, the first isolable exohedral derivative of any SBG fullerene, is stable in air even when dissolved in common organic solvents and has been characterized by electron-ionization (EI) mass spectrometry, FTIR, and ^{19}F NMR spectroscopy.

The 20 eV EI mass spectrum of purified $C_{74}F_{38}$ is shown in Figure 1 along with an FTIR spectrum of a KBr pellet of $C_{74}F_{38}$. The relatively simple $\tilde{\nu}$(CF) region, dominated by one intense band (1142 cm^{-1}), and the absence of intense bands in the 500–800 cm^{-1} region are reminiscent of the IR spectrum of $C_{60}F_{36}$[10] but not of the spectra of $C_{60}F_{18}$[11] and $C_{60}F_{48}$,[12] both of which exhibit many intense bands in the $\tilde{\nu}$(CF) and 500–800 cm^{-1} regions.

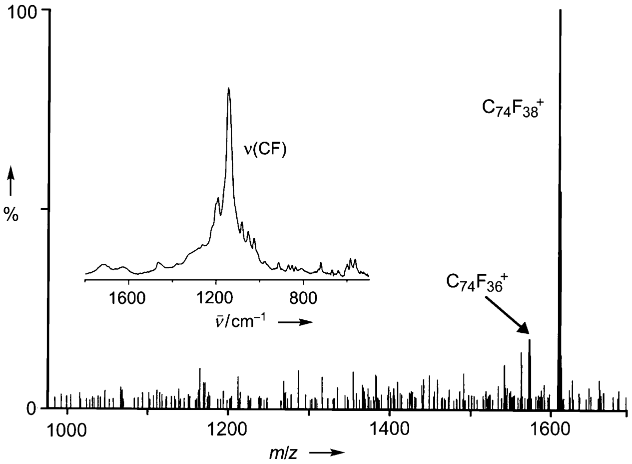

Figure 1. Electron-ionization mass spectrum of HPLC-purified $C_{74}F_{38}$ ($U_e = 20$ eV) showing very little fragmentation of the parent ion $C_{74}F_{38}^+$. Inset: FTIR spectrum of a KBr pellet of the same batch of $C_{74}F_{38}$.

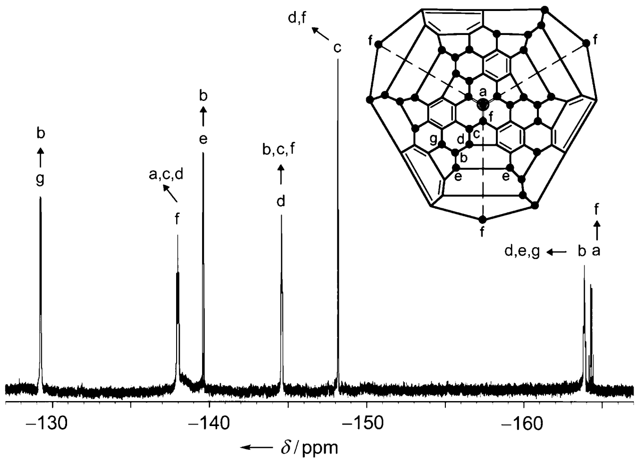

Figure 2. ^{19}F NMR spectrum of HPLC-purified $C_{74}F_{38}$ (376.5 MHz, CD_2Cl_2, 25 °C). The solid isolated from an aliquot of this sample was used to collect the FTIR and mass spectra shown in Figure 1. The relative integrated intensities of the signals labeled a–g are, respectively, 2:6:6:6:6:6:6. The arrows indicate the correlations observed in the 2D spectrum shown in Figure 3. The Schlegel-like diagram is a view down the C_3 axis of the proposed D_3 structure of $C_{74}F_{38}$. The spectral assignments are based on chemical shifts, integrated intensities, ^{19}F–^{19}F coupling constants, and the 2D spectrum. The solid black circles represent fluorine-bearing carbon atoms. The two fluorine-bearing carbon atoms on the C_3 axis (a) are superimposed, and one is depicted as an open circle connected by dashed lines to the three f carbon atoms at the periphery.

The 1D and 2D ^{19}F NMR spectra of $C_{74}F_{38}$ are shown in Figures 2 and 3. The 2:6:6:6:6:6:6 intensity pattern (signals a–g, respectively) for the 38 F atoms requires D_3, C_{3h}, or D_{3h} point symmetry, with two F atoms situated on the C_3 axis. The ^{19}F signal for these F atoms (a) is split by three equivalent F atoms into a 1:3:3:1 quartet with $J_{FF} = 32.4$ Hz. The other signals are complex multiplets, some of which exhibit unresolved ^{19}F–^{19}F couplings. The range of δ values (−129 to −164 ppm) is the same as observed for C_{3v}-$C_{60}F_{18}$,[11] T- and C_3-$C_{60}F_{36}$,[10] and D_3- and S_6-$C_{60}F_{48}$.[13] The network of correlations in the 2D COSY spectrum of $C_{74}F_{38}$ confirms that all seven signals belong to the same molecular species and suggests that each sp^3 C atom is adjacent to at least one other sp^3 C atom, as in $C_{60}F_{18}$, $C_{60}F_{36}$, and $C_{60}F_{48}$.

To propose a structure for what appears to be a single isomer of $C_{74}F_{38}$, it was first necessary to consider the structure of the C_{74} cage. There is only one isomer of C_{74} that obeys the isolated-pentagon rule (IPR), and it has long been assumed (but never experimentally verified) that empty

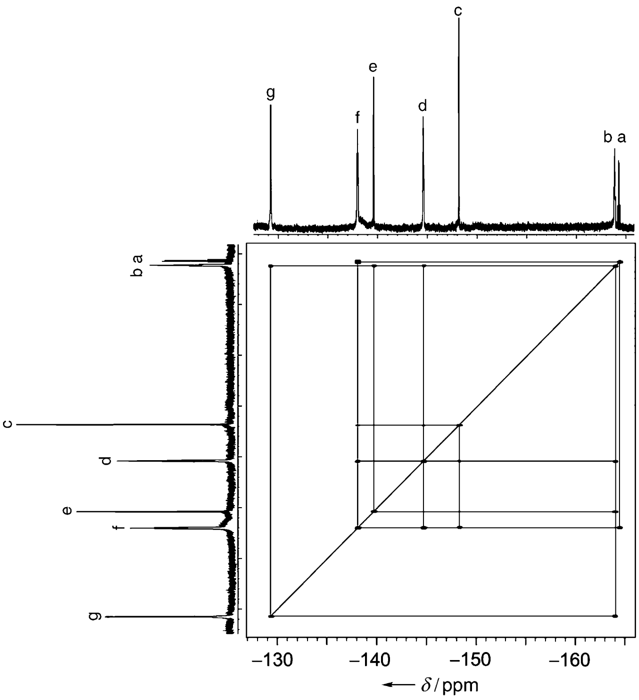

Figure 3. 2D COSY ^{19}F NMR spectrum of HPLC-purified $C_{74}F_{38}$ (376.5 MHz, CD_2Cl_2, 25 °C). The signals labeled a–g are assigned to the corresponding fluorine atoms in the Schlegel-like diagram in Figure 2. The assignments of resonances e and g, which cannot be distinguished by the COSY correlations, are based on chemical shift similarities with structurally characterized fluoro-[60]fullerenes.

(i.e., metal-free) C_{74} has the IPR-D_{3h} structure.[14–16] This assumption is consistent with the nearly isoenergetic singlet and triplet ground states (i.e., small bandgap) predicted for IPR-D_{3h}-C_{74}.[2–4,14–17] We have calculated, for the first time, the relative energies of IPR-D_{3h}-C_{74} and the nine other isomers of C_{74} that have C_{3h}, D_3, or D_{3h} symmetry. The most stable of these, a D_3 isomer with three pentalene fragments, was found to be nearly 400 kJ mol^{-1} less stable than IPR-D_{3h}-C_{74}. We conclude that the carbon core of $C_{74}F_{38}$ is, as previously assumed, IPR-D_{3h}-C_{74}.

Our proposed structure of $C_{74}F_{38}$ is depicted in the Schlegel-like diagram in Figure 2 and will be referred to as **1**. This D_3 isomer was proposed when $C_{74}F_{38}^+$ was observed by Knudsen-cell mass spectrometry[7] by analogy with T-$C_{60}F_{36}$, which is believed to be especially stable because it contains four stabilizing isolated benzenoid (SIB) rings.[10] Structure **1** contains six SIB rings, the maximum number possible for any derivative of IPR-D_{3h}-C_{74}. It is the only possible isomer of $C_{74}F_{38}$ that is consistent with the NMR data and that has six SIB rings. The proposed contiguous pattern of adjacent fluorine-bearing C atoms in **1** is a structural feature common to $C_{60}F_{18}$, $C_{60}F_{36}$, and $C_{60}F_{48}$, and therefore may be a feature common to many fluorofullerenes prepared at high temperatures, regardless of cage size. There is an additional similarity between **1** and T-$C_{60}F_{36}$: each pentagon in both structures has three F atoms.[10] The similarities suggest that fluorinated derivatives of higher fullerenes with compositions and structures that lead to the maximum possible number of SIB rings, a contiguous pattern of sp^3 C atoms, and three F atoms per pentagon should be considered as worthwhile synthetic targets.

Structure **1** is supported by DFT calculations. In addition to **1**, other possible isomers of $C_{74}F_{38}$ were considered that were consistent with the NMR data. All were found to be less stable than **1** by ≥ 200 kJ mol^{-1}. To explore the possibility that **1** might represent a kinetic product and not the most stable isomer, we also investigated isomers that are not consistent with the ^{19}F NMR pattern. Given the enormous number of possible isomers, some restrictions were necessary. All possible C_{3v} and C_3 isomers were considered, some of which contain three SIB rings. We also considered a number of lower-symmetry four- or five-SIB-ring isomers that were formed by moving one or both of the F atoms, labelled (a) in Figure 2, which are attached to the two unique triple-hexagon junctions (THJs) of IPR-D_{3h}-C_{74}. These lower-symmetry isomers were chosen taking into account the theoretical results on C_{76} hydrogenation, which demonstrated that addition to THJs was energetically unfavorable relative to the usual junction of two hexagons and one pentagon.[18] However, in that work the two isomers of $C_{76}H_{18}$ considered both had one SIB ring. Therefore, it may be that an isomerization involving loss of an SIB is more destabilizing than one involving attachment of an atom to a THJ. All of the alternative isomers we considered were less stable than **1** by ≥ 120 kJ mol^{-1}.

In summary, the high-temperature fluorination of purified C_{74} by K_2PtF_6 afforded milligram quantities IPR-D_3-$C_{74}F_{38}$, the first isolable exohedral derivative of any small-bandgap fullerene and the first structurally characterized fluorinated higher fullerene. The excellent isomeric purity and high compositional purity are especially noteworthy. In addition, the IPR-D_{3h} structure of C_{74} now has direct experimental support as well as additional theoretical support from the first DFT study of alternative cage structures. Finally, our results suggest that selective fluorination should be explored as a general procedure for solubilizing and stabilizing other nonextractable and/or reactive carbon clusters, including endohedral molecules, that represent the bulk of fullerene soots.

Experimental Section

Arc-generated fullerenes were sublimed out of the soot at 750 °C and 10^{-3} Torr. Under an argon atmosphere, the sublimate was collected and washed with o-dichlorobenzene at 100 °C and 40 Torr using a Soxhlet extractor until the washings were colorless. The remaining C_{74}-enriched solid residue was washed with hexane and dried under vacuum.

In a typical preparation, the C_{74}-enriched solid (32 mg, 0.036 mmol based on C_{74}) was ground with K_2PtF_6 (459 mg, 1.19 mmol) in a nitrogen-filled glove box. The mixture was heated under dynamic vacuum at 500 °C for 8 h in the sealed end of a long glass reactor, as previously described for other solid-state fullerene fluorinations.[19] The volatile products, which had condensed in a broad zone near the 25 °C end of the reactor, were collected as two approximately equal-length fractions. EI mass spectrometry (EI-MS) revealed that the fraction that was closer to the reactor hot zone consisted mainly of $C_{74}F_{38}$. This fraction was processed by HPLC (10 × 250 mm Cosmosil Buckyprep column; 5 mL toluene min^{-1}, UV detector, 300 nm). A typical chromatogram (Figure 4) clearly illustrates that selective fluorination is possible when many sets of reaction conditions are pre-screened with only a few Knudsen-cell experiments.[7] The most intense HPLC peak, with a retention time of 2.92 min, was shown by EI-MS to contain $C_{74}F_{38}$ with $> 90\%$ compositional purity ($\leq 10\%$ may be due to the presence of $C_{74}F_{36}$).The yield of $C_{74}F_{38}$ was as high as 3 mg in some batches.

Geometry optimizations for a large set of possible isomers were carried out at the AM1 level of theory. The most stable structures were reoptimized by DFT using the program PRIRODA, the TZ2P basis set[20] and the PBE exchange-correlation functional.[21] Since

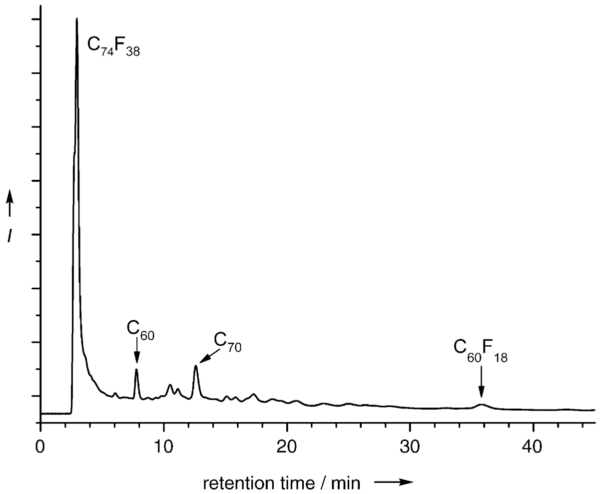

Figure 4. HPLC trace of the hot-zone crude sublimate from a reaction of C_{74} and K_2PtF_6 (10 × 250 mm Cosmosil Buckyprep, 5 mL toluene/min, UV detector, 310 nm). The intense peak at 2.92 min is due to $C_{74}F_{38}$. I = relative intensity.

AM1 calculations are known to underestimate the stabilizing effects of SIB rings in fullerene derivatives,[22] only DFT-derived relative energies have been considered in this paper.

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