Photoelectron Spectroscopy of  $C_{60}F_n^-$  and  $C_{60}F_m^{2-}$  (n = 17, 33, 35, 43, 45, 47; m = 34, 46) in the Gas Phase and the Generation and Characterization of  $C_1$ - $C_{60}F_{47}^-$  and  $D_2$ - $C_{60}F_{44}$  in Solution

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Received: October 11, 2009; Revised Manuscript Received: December 9, 2009

A photoelectron spectroscopy investigation of the fluorofullerene anions  $C_{60}F_n^-$  (n = 17, 33, 35, 43, 45, 47) and the doubly charged anions  $C_{60}F_{34}^{2-}$  and  $C_{60}F_{46}^{2-}$  is reported. The first electron affinities for the corresponding neutral molecules,  $C_{60}F_n$ , were directly measured and were found to increase as n increased, reaching the extremely high value of  $5.66 \pm 0.10$  eV for  $C_{60}F_{47}$ . Density functional calculations suggest that the experimentally observed species  $C_{60}F_{17}^-$ ,  $C_{60}F_{35}^-$ , and  $C_{60}F_{47}^-$  were each formed by reductive defluorination of the parent fluorofullerene,  $C_{3\nu}$ - $C_{60}F_{18}$ ,  $C_{60}F_{36}$  (a mixture of isomers), and  $D_3$ - $C_{60}F_{48}$ , respectively, without rearrangement of the remaining fluorine atoms. The DFT-predicted stability of  $C_{60}F_{47}^-$  was verified by its generation by chemical reduction from  $D_3$ - $C_{60}F_{48}$  in chloroform solution at 25 °C and its characterization by mass spectrometry and <sup>19</sup>F NMR spectroscopy. Further reductive defluorination of  $C_{60}F_{47}^-$  in solution resulted in the selective generation of a new fluorofullerene,  $D_2$ - $C_{60}F_{44}$ , which was also characterized by mass spectrometry and <sup>19</sup>F NMR spectroscopy.

### Introduction

Ever since the discovery of fullerenes, extensive experimental and theoretical studies have been devoted to the preparation and characterization of fluorofullerenes (FFs), which were originally proposed as potential lubricants and strong oxidizers.<sup>1-3</sup> Possible applications of these fullerene derivatives have been extended to components of (i) cathode materials for lithium batteries,<sup>4,5</sup> (ii) materials with tunable optical gaps,<sup>6</sup> and (iii) light-harvesting materials.<sup>7</sup> FFs can be readily prepared as *mixtures* of isomers with a range of compositions  $C_{60}F_n$ , where n is one or more even integers from 38 to 46, by using sufficiently strong fluorinating agents such as F2, XeF2, or highvalent transition metal fluorides.8,9 However, the selective synthesis of specific compounds (i.e., one or only a few isomers of a single composition) with well-defined structures remains much more difficult to achieve. Only three FFs, C<sub>60</sub>F<sub>18</sub>, C<sub>60</sub>F<sub>36</sub>, and  $C_{60}F_{48}$ , can be prepared in synthetically useful quantities (i.e.,  $\geq 0.5$  g) and purity. Two of them are formed as single isomers,  $C_{3\nu}$ -C<sub>60</sub>F<sub>18</sub><sup>10</sup> and  $D_3$ -C<sub>60</sub>F<sub>48</sub>;<sup>11</sup> bulk C<sub>60</sub>F<sub>36</sub> has been found to contain two major isomers,  $C_3$ - $C_{60}F_{36}$  and  $C_1$ - $C_{60}F_{36}$ , and the minor isomer T- $C_{60}F_{36}$ .<sup>12</sup>

One of the most interesting properties of FFs is their ability to accept electrons, which makes them ideal model systems to study charge-transfer and/or electron-capture phenomena. A number of FF dianions, and even long-lived trianions, have been produced via charge transfer in collisions of singly charged FF anions with neutral atoms or molecules.13 In general, the electron affinities (EA) of  $C_{60}F_n$  derivatives are expected to be higher than that of  $C_{60}$  and to increase as *n* increases because of the inductive electron-withdrawing effect of the F atoms (despite the fact that the fullerene  $\pi$  system becomes smaller as n increases).<sup>14</sup> So far, this has only been experimentally verified for a handful of  $C_{60}F_n$  species, all of which have an even numbers of F atoms:  $EA(C_{60}F_2) = 2.74(7) \text{ eV}$  (by gas-phase ion-molecule equilibria),<sup>15</sup> EA( $C_{60}F_{44}$ ) = EA( $C_{60}F_{46}$ ) = 4.06(25) eV (by Fourier transform mass spectrometry (FTMS); the sample was probably a mixture of isomers of both compositions),<sup>16</sup> and EA( $C_{60}F_{48}$ ) = 4.06(30) eV (also by FTMS).<sup>17</sup> In addition, electrochemical studies have shown that the wellcharacterized FFs studied to date (n = 2, 4, 18, 36, 48) are easier to reduce in solution than the parent fullerene, although precisely determined reversible reduction potentials have been difficult to measure because of the rapid and irreversible loss of F atoms from electrochemically generated FF- radical anions.<sup>18–21</sup> Nevertheless, approximate  $E_{1/2}$  values or cathodic peak potentials were found to increase as *n* increased. However, note that some isomers of  $C_{60}(CF_3)_6$  and  $C_{60}(CF_3)_{12}$  have more negative reduction potentials than  $C_{60}$  (although most  $C_{60}(CF_3)_n$ 

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derivatives have more positive  $E_{1/2}$  values than  $C_{60}$ ),<sup>22</sup> so it is conceivable that some  $C_{60}F_n$  isomers yet to be studied may be more difficult to reduce than  $C_{60}$ .

In the gas phase, both experimental<sup>15</sup> and theoretical studies<sup>23</sup> suggest that  $C_{60}F_n$  species with odd values of n should have higher EAs than the corresponding closed shell species with even values of n + 1. This has also been predicted theoretically, but not verified experimentally, for perfluorinated polycyclic aromatic hydrocarbons: the DFT-predicted EAs for C14F10 (perfluoroanthracene) and  $1-C_{14}F_9$  are  $1.84^{24}$  and 3.14 eV,<sup>25</sup> respectively. EAs of  $C_{60}F_n$  species have proven to be difficult to measure experimentally. Various experimental techniques, such as surface thermal ionization, electron ionization, and laser desorption, have been employed to produce singly charged  $C_{60}F_n^{-}$  anions in the gas phase.<sup>2,17,15</sup> Recently, electrospray ionization (ESI) has been used to generate both fullerene  $\bar{}$  and  $C_{60}F_n^{-}$  anions.<sup>18,26–30</sup> Using ESI, we have obtained vibrationally resolved photoelectron spectroscopy (PES) spectra of  $C_{60}^{-.30,31}$ Kappes and co-workers have carried out PES studies of higher fullerene dianions.<sup>32,33</sup> We have developed a low-temperature PES technique which couples an ESI source with a temperaturecontrolled ion trap.<sup>34</sup> Using low-temperature PES, we have carried out a series of studies including both singly and doubly charged fullerene and fullerene oxide anions.31,35-38 Detailed electronic structure information and vibrationally resolved PES spectra were obtained at low temperatures, yielding precise adiabatic detachment energies (ADEs) of the anions (which correspond to the first or second EAs of the corresponding neutral species). Ioffe et al. reported the first ESI-PES study of the dianions  $C_{60}F_{34}^{2-}$  and  $C_{60}F_{46}^{2-}$  and estimated the second EAs for the corresponding neutral species to be 2.4(1) and 3.2(1) eV, respectively.<sup>29</sup> However, no PES spectra of singly charged FF<sup>-</sup> anions have been reported, probably because the corresponding neutral molecules have such high electron binding energies.

Here we present a joint PES and theoretical study of a number of gas-phase  $C_{60}F_n^-$  anions with odd numbers of F atoms (n =17, 33, 35, 43, 45, and 47) and two gas-phase FF dianions,  $C_{60}F_{34}^{2-}$  and  $C_{60}F_{46}^{2-}$ , which were produced by ESI of solutions of  $C_{3v}$ - $C_{60}F_{18}$ , a mixture of isomers of  $C_{60}F_{36}$ , or  $D_3$ - $C_{60}F_{48}$ . The combined gas-phase and theoretical study of the ionic and neutral species also led to (i) the successful generation and characterization of the remarkably stable  $C_{60}F_{47}^-$  anion in chloroform solution at 25 °C and (ii) the observation of its slow transformation to the new FF  $D_2$ - $C_{60}F_{44}$ .

# **Experimental and Theoretical Methods**

Materials. The compound  $C_{3\nu}$ -C<sub>60</sub>F<sub>18</sub> was prepared from C<sub>60</sub> (Term USA; 99.5%) and K<sub>2</sub>PtF<sub>6</sub> as previously described.<sup>10,39</sup> APCI mass spectrometry, <sup>19</sup>F NMR spectroscopy, and HPLC analysis showed that the product contained 90+%  $C_{3v}$ -C<sub>60</sub>F<sub>18</sub> and small amounts of other FFs. The compound  $C_{60}F_{36}$  was prepared from C<sub>60</sub> and MnF<sub>3</sub> (Apollo Scientific) as previously described.<sup>40</sup> The APCI mass spectrum of the product showed that the only composition present was  $C_{60}F_{36}$  (99+%). The <sup>19</sup>F NMR spectrum showed the presence of the three known isomers,  $C_3$ - $C_{60}F_{36}$  (70%),  $C_1$ - $C_{60}F_{36}$  (25%), and T- $C_{60}F_{36}$  (5%). The compound  $D_3$ -C<sub>60</sub>F<sub>48</sub> was prepared by heating C<sub>60</sub> with F<sub>2</sub> gas at 330 °C for 24 h in a quartz flow reactor as previously described.<sup>12,41</sup> The one-electron reducing agent 1,1',3,3'-tetrakis(2-methyl-2-nonyl)ferrocene (DEC) was prepared from ferrocene (Sigma-Aldrich) and 2-chloro-2-methylnonane as previously described.42

Low-Temperature Photoelectron Spectroscopy. The PES experiments were performed with a low-temperature apparatus that couples an ESI source and a temperature-controlled ion trap to a magnetic-bottle time-of-flight photoelectron spectrometer.34 Fresh spray solutions were prepared by adding an organic electron donor compound (either tetramethylphenylenediamine or tetrakis(dimethyamino)ethylene) to  $10^{-3}$  M stock solutions of each FF sample dissolved in a mixture of o-dichlorobenzene and acetonitrile as previously described.<sup>20,22</sup> The anions produced by the ESI source were guided by RF-only devices into the 3-D ion trap. The trap was attached to the cold head of a cryostat, which consists of a closed-cycle helium refrigerator and a feedback heating system that allows the temperature to be controlled from 10 to 350 K. In this work the trap was operated at either 12 or 20 K. The ions from the ESI source were trapped and collisionally cooled for 0.1 s by ca. 0.1 mTorr 80/20 He/H<sub>2</sub> background gas before being pulsed out into the extraction zone of the time-of-flight mass spectrometer.

During each PES experiment, anions of interest were mass selected and decelerated before being intercepted by a detachment laser beam in the interaction zone of a magnetic-bottle photoelectron analyzer. Spectra of the C<sub>60</sub>F<sub>17</sub><sup>-</sup> monoanion and the  $C_{60}F_{34}^{2-}$  and  $C_{60}F_{46}^{2-}$  dianions were obtained at both 266 and 193 nm (4.661 and 6.424 eV, respectively). Spectra of the more highly fluorinated  $C_{60}F_n^-$  monoanions (n = 33, 35, 43, 45, and 47) were only measured at 193 nm. Photoelectrons were collected with high efficiency by the magnetic bottle and analyzed in a 5.2 m long electron flight tube. Photoelectron timeof-flight spectra were collected and converted into kinetic energy spectra, which were calibrated using the known spectra of I<sup>-</sup> and  $ClO_2^{-}$ . Electron binding energy spectra were obtained by subtracting the kinetic energy spectra from the detachment photon energies. The energy resolution ( $\Delta E/E$ ) was estimated to be 2% (i.e., 20 meV for 1 eV electrons).

NMR Spectroscopy and ESI Mass Spectrometry. Fluorine-19 NMR spectra of chloroform-*d* solutions were recorded at 25 °C using a Varian INOVA-unity 400 spectrometer operating at 376.5 MHz. In some measurements, a small amount of hexafluorobenzene was added as an internal standard ( $\delta$ -164.9). ESI mass spectra were recorded using a ThermQuest Finnagan LCQ-DUO spectrometer. Chloroform-*d* was used as the solvent.

**Theoretical Calculations.** DFT calculations were performed using the GGA PBE density functional<sup>43</sup> and the original TZ2Pquality basis set with {6,3,2}/(11s,6p,2d) contraction schemes implemented in the PRIRODA package.<sup>44</sup> The code used expansion of the electron density in an auxiliary basis set to accelerate evaluation of Coulomb and exchange-correlation terms.<sup>45</sup> Single-point energy calculations at the B3LYP/6-311G\* level and optimization of the structures at AM1 level were performed using PC GAMESS/Firefly package.<sup>46</sup> Analysis of the electron localization function (ELF) was performed using TopMoD,<sup>47</sup> and ELFs and spin density distributions were visualized with Molekel 4.3.<sup>48</sup>

## **Results and Discussion**

**Photoelectron Spectra.** Our home-built ESI source did not produce sufficiently strong signals for FF anions by direct spray of solutions of the FF precursors unless an organic electron donor compound was added. With a donor compound added, the most abundant ESI-generated anions were singly charged species formed by removal of an odd number of F atoms from the parent monoanion and doubly charged dianions formed by removal of two F atoms from the parent dianion. These included



**Figure 1.** Low-temperature (12 K) photoelectron spectra of  $C_{60}F_{17}^{-}$  at (a) 266 nm (4.661 eV), and (b) 193 nm (6.424 eV). Note that the low-binding-energy features below 4 eV are assigned to two photon processes (i.e., either detachment of fragments from ground-state  $C_{60}F_{17}^{-}$  or photoexcitation of  $C_{60}F_{17}^{-}$  and subsequent photodetachment from the excited-state anion).

 $C_{60}F_{17}^{-}$  (from a solution of  $C_{3v}$ - $C_{60}F_{18}$ ),  $C_{60}F_{33}^{-}$ ,  $C_{60}F_{35}^{-}$ , and  $C_{60}F_{34}^{2-}$  (from a solution of the three  $C_{60}F_{36}$  isomers), and  $C_{60}F_{43}^{-}$ ,  $C_{60}F_{45}^{-}$ ,  $C_{60}F_{47}^{-}$ , and  $C_{60}F_{46}^{2-}$  (from a solution of  $D_3$ - $C_{60}F_{48}$ ). The observed compositions are consistent with previous reports<sup>18,28,29,49</sup> and are related to the greater stability of closed-shell FF<sup>-</sup> anions with an odd number of F atoms and closed-shell FF<sup>2-</sup> dianions with an even number of F atoms relative to homologous open-shell anions.<sup>23</sup> We had previously shown, but only qualitatively, that EA( $C_{60}F$ ) > EA( $C_{60}F_2$ ).<sup>15</sup> However, before this work there were no quantitative EA measurements for FFs with odd numbers of F atoms.

Figure 1 shows the 12 K PES spectra of  $C_{60}F_{17}^{-}$  at 266 and 193 nm. Relatively weak and broad features between 2.3 and 4.2 eV were observed at both wavelengths. We found that the relative intensities of these features depended on the square of the photon flux, suggesting that they arise from two-photon processes, either photodetachment from anionic fragments of the parent anion (after fragmentation by the first photon) or from excited states of the parent anion (following excitation by the first photon). A strong and sharp transition (X) was observed at 4.285 eV in the 266 nm spectrum as well as in the 193 nm spectrum, which defines the ADE of  $C_{60}F_{17}^{-}$  (or the EA of neutral  $C_{60}F_{17}$ ). In the 193 nm spectrum, a second band (A) was observed with a sharp transition at 5.71 eV, which represents an excitation energy of 1.42 eV above the ground state. Vibrational structures are resolved for the X band at both wavelengths.

Only 193 nm spectra could be recorded for  $C_{60}F_n^-$  with  $n \ge$  33 due to their high electron binding energies. Figure 2 shows the 12 K spectra of  $C_{60}F_{33}^-$  and  $C_{60}F_{35}^-$ . For  $C_{60}F_{33}^-$ , a sharp transition at 4.92 eV is well resolved, which defines the ADE of  $C_{60}F_{33}^-$ . A shoulder is partially resolved in the threshold region for  $C_{60}F_{35}^-$ , yielding an ADE of 4.98 eV. A very weak and broad feature is discernible between 3.5 and 4.5 eV in the spectrum of  $C_{60}F_{33}^-$  (see Figure 2a), most likely due to multiphoton processes as described above for  $C_{60}F_{17}^-$ . The 193 nm PES spectra of  $C_{60}F_{43}^-$ ,  $C_{60}F_{45}^-$ , and  $C_{60}F_{47}^-$  are shown in Figure 3. Only a broad band was observed in each case. Since no vibrational structures were resolved for these species, their ADEs were estimated by drawing a straight line along the rising edge of the peak and then adding the instrumental resolution to the intersection with the binding energy axis.



Figure 2. Low-temperature (12 K) photoelectron spectra at 193 nm of (a)  $C_{60}F_{33}^{-}$  and (b)  $C_{60}F_{35}^{-}$ .



Figure 3. Low-temperature (12 K) photoelectron spectra at 193 nm of (a)  $C_{60}F_{43}^{-}$ , (b)  $C_{60}F_{45}^{-}$ , and (c)  $C_{60}F_{47}^{-}$ .

The experimental ADEs of the  $FF^-$  monoanions with n =17, 33, 35, 43, 45, and 47, which correspond to the EAs of the corresponding neutral species, are listed in Table 1. Figure 4 is a plot of these EA values vs n and also includes EA values for species with n = 0 (i.e., C<sub>60</sub>),<sup>30,31</sup> 2,<sup>15</sup> 44,<sup>16</sup> 46,<sup>16</sup> and 48.<sup>17</sup> There is now no doubt that  $C_{60}F_n$  species with odd *n* values are *much* stronger electron acceptors than homologous species with one more or one fewer F atom. For example, the differences  $EA(C_{60}F_{n-1}) - EA(C_{60}F_n)$  are 1.49(27), 1.56(27), and 1.60(32) eV for n = 44, 46, and 48, respectively. Whereas the largest previously known difference  $EA(C_{60}F_n) - EA(C_{60})$  was 1.38(30) eV for n = 48, it is now 2.98(10) eV for n = 47, more than a factor of 2 larger. There is a reasonably good linear correlation between  $EA(C_{60}F_n)$  and *n* for n = 17, 33, 35, 43, 45, and 47(see Figure 4; the slope and y-axis intercept are 0.048(3) and 3.40(13) eV, respectively). If one extrapolates back to n = 1, the value of  $EA(C_{60}F)$  predicted by the linear fit is 3.45(13) eV, which is 0.77(13) eV higher than the experimental value

TABLE 1: Experimental Adiabatic Detachment Energies (ADEs) and Repulsive Coulomb Barriers (RCBs) for  $C_{60}^{-}$ ,  $C_{60}F_n^{-}$ , and  $C_{60}F_n^{2-}$  Species<sup>*a*</sup>

species	ADE, <sup>b</sup> eV	RCB, <sup>c</sup> eV
C <sub>60</sub> -	$2.683(8)^d$	
$C_{60}F_{17}^{-}$	4.285(10)	
$C_{60}F_{33}^{-}$	4.92(5)	
$C_{60}F_{35}^{-}$	4.98(5)	
$C_{60}F_{43}^{-}$	5.55(10)	
$C_{60}F_{45}^{-}$	5.62(10)	
$C_{60}F_{47}^{-}$	5.66(10)	
$C_{60}F_{34}^{2-}$	$2.50(5) [2.4(1)]^{e}$	1.4(1)
$C_{60}F_{46}{}^{2-}$	$3.33(10) [3.2(1)]^e$	1.0(1)

<sup>*a*</sup> All values from this work unless otherwise noted. The numbers in parentheses represent the experimental uncertainties. <sup>*b*</sup> The ADEs for the monoanions correspond to the EAs for the corresponding neutral species; the ADEs for the dianions correspond to the second EAs for the corresponding neutral species. <sup>*c*</sup> Estimated from PES spectral cutoffs. <sup>*d*</sup> This value is from ref 31. <sup>*e*</sup> The values in square brackets are from ref 29.



**Figure 4.** Experimental and DFT-predicted gas-phase electron affinities (EAs) for  $C_{60}F_n$  species. The values for n = 44 and 46 were determined in a single experiment using a mixture of isomers of these two compositions and was reported in ref 16. The values for n = 0 (i.e., for  $C_{60}$ ), 2, and 48 are from refs 31, 15, and 17, respectively. The linear least-squares fit to the experimental data for n = 17, 33, 35, 43, 45, and 47 has a slope, *y*-axis intercept, and  $R^2$  value of 0.048(3), 3.40(13), and 0.980, respectively. The letters **a**, **e**, **g**, and **j** indicate particular isomers and are discussed in the text.

of EA(C<sub>60</sub>) and 0.67(15) eV higher than the experimental value of EA(C<sub>60</sub> $F_2$ ).

To our knowledge, the EAs for  $C_{60}F_{43}$ ,  $C_{60}F_{45}$ , and  $C_{60}F_{47}$ , at 5.55(10), 5.62(10), and 5.66(10) eV, respectively, are the highest experimental gas-phase electron affinities reported for organic molecular species. For comparison, the experimental EA for the trifluoroacetyl radical (CF<sub>3</sub>COO) is 4.20(27) eV.<sup>50</sup> The term "superhalogen" has been used<sup>51,52</sup> to describe molecular species with EAs higher than 3.613 eV, the electron affinity of a Cl atom.<sup>53</sup> Superhalogens with the highest experimental EAs include PtF<sub>6</sub> (7.00(35) eV)<sup>54</sup> and LaCl<sub>4</sub> (7.03(10) eV).<sup>55</sup> The data in Figure 4 suggest that all FFs with  $n \ge 33$ , possibly including  $C_{60}F_{34}$  and  $C_{60}F_{36}$ , can be classified as superhalogens. Other fluorocarbons with DFT-predicted LUMO energies comparable to that of  $C_3$ - $C_{60}F_{36}$  (-5.363 eV) include particular



**Figure 5.** Low-temperature (20 K) photoelectron spectra of  $C_{60}F_{34}^{2-}$  at (a) 266 nm and (b) 193 nm.



Figure 6. Low-temperature (12 K) photoelectron spectra of  $C_{60}F_{46}^{2-}$  at (a) 266 nm and (b) 193 nm.

isomers of  $C_{60}(CF_3)_8$  and  $C_{60}(CF_3)_{10}$ ,<sup>22</sup> and these superhalogen candidates should have their electron affinities measured in the near future.

We were also able to measure the PES spectra of the dianions  $C_{60}F_{34}^{2-}$  and  $C_{60}F_{46}^{2-}$ . The spectra are shown in Figures 5 and 6, respectively. The 266 nm PES spectra of these two dianions were reported previously.<sup>29</sup> The new low-temperature spectra are better resolved, with discernible vibrational structure. In the case of  $C_{60}F_{34}^{2-}$ , a more precise ADE was observed: 2.50(5) eV (cf. the previously reported value of 2.4(1) eV<sup>29</sup>). In the case of  $C_{60}F_{46}^{2-}$ , an equally precise ADE was observed: 3.33(10) eV (cf. the previously reported value of 3.2(1) eV<sup>29</sup>). The 266 nm spectra display clear cutoffs, relative to the respective 193 nm spectra, at high binding energies (ca. 3.2 eV for  $C_{60}F_{46}^{2-}$ ) and ca. 3.6 eV for  $C_{60}F_{46}^{2-}$ ). These are due to repulsive Coulomb barriers (RCB) that are universally present in multiply charged anions.<sup>56–58</sup> On the basis of the cutoffs, we estimate RCBs of 1.4(1) and 1.0(1) eV for  $C_{60}F_{46}^{2-}$  and  $C_{60}F_{46}^{2-}$ , respectively.

**Theoretical Studies.** Schlegel diagrams for the parent FFs  $C_{3\nu}$ - $C_{60}F_{18}$ ,  $C_3$ - $C_{60}F_{36}$ , and  $D_3$ - $C_{60}F_{48}$  are shown in Figures 7, 8, and 9, respectively. The various types of fluorine atoms in each Schlegel diagram are denoted  $F_a$ ,  $F_b$ ,  $F_c$ , etc. and are attached to the fullerene cage at positions denoted  $C_a$ ,  $C_b$ ,  $C_c$ , etc., respectively. Calculations were performed for  $C_{60}F_{17}^{0/-}$ ,  $C_{60}F_{35}^{0/-}$ , and  $C_{60}F_{47}^{0/-}$  species that correspond to the removal of an F atom from the parent FF without rearrangement of the remaining F atoms. This restriction was



**Figure 7.** Schlegel diagram of  $C_{3v}$ - $C_{60}F_{18}$  (top). The black circles indicate the cage C atoms to which the F atoms are attached. The letters indicate the different types of C–F bonds. The drawings at the bottom are the spin density of the **a**- $C_{60}F_{17}$  radical computed at the B3LYP/6-311G\*//PBE/ TZ2P level with an isovalue of 0.005 au (left) and the ELF of the **a**- $C_{60}F_{17}$  anion with an isovalue of 0.72 (color codes: yellow, disynaptic V(C,C) basins; dark green, disynaptic V(C,F) and monosynaptic V(F) basins; light green, core C(C) basins; red, monosynaptic valence V(C) basins) (right).

necessary because unconstrained global minimum searches that allowed for rearrangement would have been computationally prohibitive. In the discussion that follows, the neutral species formed by removal of an  $F_a$  atom from  $C_3$ - $C_{60}F_{36}$  is denoted  $\mathbf{a}$ - $C_{60}F_{35}$ , the anionic species formed by removal of an  $F_g$  atom from  $D_3$ - $C_{60}F_{48}^-$  is denoted  $\mathbf{g}$ - $C_{60}F_{47}^-$ , and so on. Table 2 lists the PBE/TZ2P relative energies of various isomers of  $C_{60}F_{17}^-$ ,  $C_{60}F_{35}^-$ , and  $C_{60}F_{47}^-$ . Their ADEs, which correspond to the EAs for the isostructural neutral species, are also listed. Several isomers were also calculated at the B3LYP/6-311G\*//PBE/TZ2P level. The PBE EA for  $C_{60}F$  was found to be 3.699 eV.

The most stable isomers for each monoanionic composition are those in which removal of the F atom resulted in the formation of an extended conjugated fragment. Electron delocalization in these fragments can be visualized as the spatial distribution of the electron localization function (ELF)<sup>59,60</sup> for the anion or, alternatively, as the spin density distribution in the corresponding neutral radical. For  $C_{60}F_{17}^{-}$ , there is only one isomer with extended delocalization,  $\mathbf{a}$ - $\mathbf{C}_{60}\mathbf{F}_{17}^{-}$ , and it is at least 0.6 eV more stable than the other possible isomers. On this basis, we propose that  $\mathbf{a} - \mathbf{C}_{60} \mathbf{F}_{17}^{-1}$ is the structure of the observed  $C_{60}F_{17}^{-}$  anion. This assignment is consistent with reactions that resulted in the substitution of one or more  $F_a$  atoms in  $C_{3v}$ -C<sub>60</sub> $F_{18}$  by, for example, aryl groups.<sup>61</sup> The PBE/TZ2P-predicted EA for  $\mathbf{a}$ -C<sub>60</sub>F<sub>17</sub>, 4.268 eV, is very close to the experimental value of  $4.285 \pm 0.010$  eV and is at least 0.127 eV higher than the predicted values for the other  $C_{60}F_{17}$  isomers that can be derived from  $C_{3\nu}$ -C<sub>60</sub>F<sub>18</sub> without rearrangement. This excellent agreement further supports the assignment of  $\mathbf{a}$ -C<sub>60</sub>F<sub>17</sub><sup>-</sup> as the observed monoanion at m/z 1043.

Figure 7 also shows the spin density for  $\mathbf{a}$ -C<sub>60</sub>F<sub>17</sub> and the ELF for  $\mathbf{a}$ -C<sub>60</sub>F<sub>17</sub><sup>-</sup>. A typical ELF pattern for a fullerene includes only core carbon monosynaptic basins, C(C), and valence disynaptic C-C basins (V(C,C)). At an ELF isovalue of 0.72, which was used to visualize the ELFs in this work, the V(C,C)basins do not overlap in the parent fullerenes  $C_{3\nu}$ -C<sub>60</sub>F<sub>18</sub>,  $C_3$ - $C_{60}F_{36}$ , and  $D_3$ - $C_{60}F_{48}$ . In **a**- $C_{60}F_{17}^-$ , however, increased delocalization is evident in the spatial extension of the ELF V(C,C) basins in the region around C<sub>a</sub>, including their overlap in some regions. Moreover, when the overlap of V(C,C) basins is strong, separate monosynaptic valence carbon basins (V(C)) emerge. (Note that monosynaptic valence basins are usually associated with lone pairs of electrons.) In particular, Ca in the anion  $\mathbf{a}$ - $\mathbf{C}_{60}\mathbf{F}_{17}^{-}$  has a V(C) basin, highlighted in red in Figure 7, with a population of 0.48 e<sup>-</sup>. Two other V(C) basins in  $\mathbf{a}$ -C<sub>60</sub>F<sub>17</sub><sup>-</sup>, which are also highlighted in red, have populations of 0.25 e<sup>-</sup>. These features parallel the spin density distribution in  $\mathbf{a}$ -C<sub>60</sub>F<sub>17</sub>: the largest spin populations are found for those carbon atoms that exhibit the strongest overlap of V(C,C) basins or have monosynaptic V(C) basins in  $\mathbf{a}$ -C<sub>60</sub>F<sub>17</sub><sup>-</sup>.

Two low-energy  $C_{60}F_{35}^{-}$  anions,  $\mathbf{a}$ - $C_{60}F_{35}^{-}$  and  $\mathbf{j}$ - $C_{60}F_{35}^{-}$ , can be derived from  $C_3$ - $C_{60}F_{36}$  without rearrangement. The predicted EAs of the corresponding neutral radicals, 4.879 and 4.907 eV, respectively, are in good agreement with the experimental value of 4.98  $\pm$  0.05 eV, although two higher-energy isomers,  $\mathbf{e}$ - $C_{60}F_{35}^{-}$  and  $\mathbf{i}$ - $C_{60}F_{35}^{-}$ , also have ADEs that are close to the experimental value. We propose that both  $\mathbf{a}$ - $C_{60}F_{35}^{-}$  and  $\mathbf{j}$ - $C_{60}F_{35}^{-}$  can be formed from  $C_3$ - $C_{60}F_{36}$  in our experiments. This is consistent with the lack of sharply resolved vibrational structure in the PES spectrum of  $C_{60}F_{35}^{-}$  shown in Figure 2b. Alternatively, the broad nature of the 4.9–5.6 eV band in that



**Figure 8.** Schlegel diagram of  $C_3$ - $C_{60}F_{36}$  (top). The black circles indicate the cage C atoms to which the F atoms are attached. The letters indicate the different types of C-F bonds. The drawings below the Schlegel diagram on the left are the spin densities of the **a**- $C_{60}F_{35}$  and **j**- $C_{60}F_{35}$  radicals computed at the B3LYP/6-311G\*//PBE/TZ2P level with isovalues of 0.005 au. The drawings below the Schlegel diagram on the right are the ELFs of the **a**- $C_{60}F_{35}^-$  and **j**- $C_{60}F_{35}^-$ 

spectrum may be due to the fact that the sample of  $C_{60}F_{36}$  we used contained 25%  $C_1$ - $C_{60}F_{36}$  in addition to 70%  $C_3$ - $C_{60}F_{36}$ .

core C(C) basins; red, monosynaptic valence V(C) basins).

Figure 8 shows the ELFs for  $\mathbf{a}$ -C<sub>60</sub>F<sub>35</sub><sup>-</sup> and  $\mathbf{j}$ -C<sub>60</sub>F<sub>35</sub><sup>-</sup> and the spin density distributions for  $\mathbf{a}$ -C<sub>60</sub>F<sub>35</sub> and  $\mathbf{j}$ -C<sub>60</sub>F<sub>35</sub>. In  $\mathbf{a}$ -C<sub>60</sub>F<sub>35</sub><sup>-</sup>, a V(C) basin with a population of 0.41 e<sup>-</sup>, highlighted in red, is found for the C<sub>a</sub> atom of the conjugated C<sub>5</sub><sup>-</sup> *trans,trans*-pentadienide fragment, and the same atom has the largest spin population in  $\mathbf{a}$ -C<sub>60</sub>F<sub>35</sub>. Although V(C) basins are not evident for the terminal atoms of the C<sub>5</sub><sup>-</sup> fragment, significant extension of V(C,C) can be seen in the large spin populations of these cage C atoms in  $\mathbf{a}$ -C<sub>60</sub>F<sub>35</sub>. In contrast, no monosynaptic V(C) basins are evident in  $\mathbf{j}$ -C<sub>60</sub>F<sub>35</sub><sup>-</sup>, which nevertheless has a delocalized benzyl-like fragment that can be readily seen in the spin density distribution of  $\mathbf{j}$ -C<sub>60</sub>F<sub>35</sub> in Figure 8 (note that the largest spin population is for C<sub>j</sub>, which also exhibits the largest extension of the V(C,C) basins in the  $\mathbf{j}$ -C<sub>60</sub>F<sub>35</sub><sup>-</sup> anion).

Due to the high degree of saturation of  $D_3$ -C<sub>60</sub>F<sub>48</sub>, the maximum delocalization in any C<sub>60</sub>F<sub>47</sub><sup>-</sup> anion formed without rearrangement is limited to C<sub>3</sub><sup>-</sup> allyl-like fragments. Two low-energy C<sub>60</sub>F<sub>47</sub><sup>-</sup> anions with such fragments are **e**-C<sub>60</sub>F<sub>47</sub><sup>-</sup> and **g**-C<sub>60</sub>F<sub>47</sub><sup>-</sup>. Their predicted ADEs, 5.433 and 5.503 eV, respectively, are close to the experimental value of 5.66  $\pm$  0.10 eV.



Figure 9. Drawing showing half of the structure of DFT-optimized  $D_3$ -C<sub>60</sub>F<sub>48</sub> (top). The yellow circles are F atoms and are attached to cage  $C(sp^3)$  atoms. The six  $C(sp^2)$  atoms shown as large red circles, which form three of the six remaining C=C  $\pi$  bonds in  $D_3$ -C<sub>60</sub>F<sub>48</sub>, are pyramidalized toward the center of the fullerene instead of away from it. This is shown by the red lines, which are vectors that make equal angles (either 96.6° or 97.8°) with the three cage C–C bonds of each  $C(sp^2)$  atom. The Schlegel diagram of  $D_3$ - $C_{60}F_{48}$  (middle). The black circles indicate the cage C atoms to which the F atoms are attached. The letters indicate the different types of C-F bonds. The drawings at the bottom are the spin density of the  $g-C_{60}F_{47}$  radical computed at the B3LYP/6-311G\*//PBE/TZ2P level with an isovalue of 0.005 au (left) and the ELF of the  $g-C_{60}F_{47}^{-}$  anion with an isovalue of 0.72 (color codes: yellow, disynaptic V(C,C) basins; dark green, disynaptic V(C,F) and monosynaptic V(F) basins; light green, core C(C) basins; red, monosynaptic valence V(C) basins) (right).

Only one other isomer of  $C_{60}F_{47}^{-}$ ,  $\mathbf{d}$ - $C_{60}F_{47}^{-}$ , which is ca. 0.25 eV higher in energy, has a higher DFT-predicted ADE (5.564 eV). It does not have a delocalized negative charge. On the basis of these results, we propose that both  $\mathbf{e}$ - $C_{60}F_{47}^{-}$  and  $\mathbf{g}$ - $C_{60}F_{47}^{-}$  may be formed from  $D_3$ - $C_{60}F_{48}$  in our experiments.

The ELFs for  $\mathbf{e}$ -C<sub>60</sub>F<sub>47</sub><sup>-</sup> and  $\mathbf{g}$ -C<sub>60</sub>F<sub>47</sub><sup>-</sup> and the spin density distributions for  $\mathbf{e}$ -C<sub>60</sub>F<sub>47</sub> and  $\mathbf{g}$ -C<sub>60</sub>F<sub>47</sub> are very similar. Those for  $\mathbf{g}$ -C<sub>60</sub>F<sub>47</sub><sup>-</sup> and  $\mathbf{g}$ -C<sub>60</sub>F<sub>47</sub> are shown in Figure 9. The allyl-like fragment in  $\mathbf{g}$ -C<sub>60</sub>F<sub>47</sub> is readily evident in the spin density drawing and does not warrant further discussion. The "red" V(C) basin on C<sub>g</sub> in  $\mathbf{g}$ -C<sub>60</sub>F<sub>47</sub><sup>-</sup>, which has a population of 0.98 e<sup>-</sup>, is highly unusual in that it is located *inside* the fullerene cage, not outside the cage like the V(C) basins in  $\mathbf{a}$ -C<sub>60</sub>F<sub>17</sub><sup>-</sup> and  $\mathbf{a}$ -C<sub>60</sub>F<sub>48</sub><sup>-11</sup> the 12 remaining C(sp<sup>2</sup>) atoms form concave regions on the outer surface of the otherwise convex cage, as also shown in Figure 9. This is also true for the C<sub>g</sub> region of

TABLE 2: DFT-Predicted Relative Energies and Adiabatic Detachment Energies (ADEs) of Isomers of  $C_{60}F_n^-$  Derived from  $C_{3v}$ - $C_{60}F_{18}$ ,  $C_3$ - $C_{60}F_{36}$ , and  $D_3$ - $C_{60}F_{48}$  (n = 17, 35, and 47)

composition	isomer <sup>a</sup>	relative energy, <sup>b</sup> eV	ADE, eV
$C_{60}F_{17}^{-}$	а	0.000 [0.000]	4.268 [4.080]
	с	0.615	
	d	0.739	
	b	0.947	
	expt		4.285(10)
$C_{60}F_{35}^{-}$	а	0.000 [0.010]	4.879 [4.760]
	j	0.041 [0.000]	4.907 [4.785]
	i	0.227	4.963
	с	0.321	4.781
	f	0.329	4.888
	e	0.471	4.912
	d	0.528	4.757
	h	0.648	4.821
	g	0.678	4.799
	k	0.825	4.795
	1	0.890	4.813
	b	1.020	4.596
	expt		4.98(5)
$C_{60}F_{47}^{-}$	g	0.000 [0.000]	5.503 [5.460]
	e	0.042 [0.037]	5.433 [5.391]
	d	0.286	5.564
	а	0.455	5.175
	с	0.559	5.226
	h	0.592	5.480
	f	1.200	5.043
	b	1.537	5.007
	expt		5.66(10)

<sup>*a*</sup> These isomer labels correspond to the Schlegel diagrams in Figures 7, 8, and 9. <sup>*b*</sup> Calculated at the PBE/TZ2P level except for values in square brackets, which were calculated at the B3LYP/ 6-311G\*//PBE/TZ2P level. The ADEs correspond to the EAs of the corresponding neutral species.

the cage in the DFT-optimized structure of  $\mathbf{g}$ - $\mathbf{C}_{60}\mathbf{F}_{47}^-$  (see Figure S-1 in Supporting Information), and for this reason the "lone pair" of electrons in  $\mathbf{g}$ - $\mathbf{C}_{60}\mathbf{F}_{47}^-$  appears to be located inside the cage. This discovery suggested that if  $\mathbf{C}_{60}\mathbf{F}_{47}^-$  could be generated in solution from  $D_3$ - $\mathbf{C}_{60}\mathbf{F}_{48}$ , it might be stable enough to characterize, even at 25 °C, not only because the gas-phase species has such a high ADE but also because the negative charge would be effectively shielded from attack by electrophiles. In the remainder of this paper, we present our initial results on condensed-phase  $\mathbf{C}_{60}\mathbf{F}_{47}^-$ , the first condensed-phase fluorofullerene anion to be characterized by <sup>19</sup>F NMR spectroscopy, and its slow transformation to the new FF  $D_2$ - $\mathbf{C}_{60}\mathbf{F}_{44}$ .

**Reductive Defluorination of**  $C_{60}F_{48}$  **in Solution.** The chemical reduction of  $D_3$ - $C_{60}F_{48}$  by iodide ion and by ferrocene (Fe(Cp)<sub>2</sub>) was reported in 1994.<sup>18</sup> A flow injection reaction of the FF and an excess of I<sup>-</sup> in dichloromethane that was analyzed by ESI-MS within 20 s showed that the principal anionic product was the radical  $C_{60}F_{48}^-$ . A similar reaction with a 3-fold excess of Fe(Cp)<sub>2</sub> led to a major peak corresponding to  $C_{60}F_{47}^-$  and a minor peak corresponding to  $C_{60}F_{45}^-$  in the ESI mass spectrum. With a 4-fold excess of decamethylferrocene (Fe(Cp\*)<sub>2</sub>), the dianions  $C_{60}F_{46}^{2-}$  and  $C_{60}F_{44}^{2-}$  were observed in the mass spectrum.<sup>18</sup>

Inspired by our gas-phase PES experiments with  $D_3$ -C<sub>60</sub>F<sub>48</sub> and the DFT prediction of an endohedral lone pair of electrons in **g**-C<sub>60</sub>F<sub>47</sub><sup>-</sup>, we performed a series of experiments involving the chemical reduction of C<sub>60</sub>F<sub>48</sub> with a modified ferrocene, 1,1',3,3'-tetrakis(2-methyl-2-nonyl)ferrocene (DEC), that has a Fe(Cp')<sub>2</sub><sup>+/0</sup> E<sub>1/2</sub> value midway between those of Fe(Cp)<sub>2</sub><sup>+/0</sup> and



**Figure 10.** Fluorine-19 NMR spectra (376.5 MHz, CDCl<sub>3</sub>, C<sub>6</sub>F<sub>6</sub> external standard ( $\delta$  -164.9)) and NI-ESI mass spectra spectra of sample A ( $D_3$ -C<sub>60</sub>F<sub>48</sub>), sample B (sample A plus DEC after 5 min and up to several hours), and sample C (sample B after 24 h and up to a week; DEC = 1,1',3,3'-tetra(2-methyl-2-nonyl)ferrocene).

 $(Fe(Cp^*)_2^{+/0})$  (in addition, DEC<sup>+</sup> salts are soluble even in low dielectric constant solvents).<sup>42</sup> We carried out these reactions in chloroform-*d* at 25 °C, both in the presence and the absence of air, and monitored the products by both <sup>19</sup>F NMR spectroscopy and ESI mass spectrometry over time.

When a colorless CDCl<sub>3</sub> solution of  $D_3$ -C<sub>60</sub>F<sub>48</sub> was mixed with a bright orange CDCl<sub>3</sub> solution of DEC, a brown solution was formed immediately (note that the color of the DEC<sup>+</sup> cation is bright green<sup>42</sup>). No precipitate was observed, even after many hours. The <sup>19</sup>F NMR and ESI mass spectra of  $D_3$ -C<sub>60</sub>F<sub>48</sub> starting material (sample A) and the brown reaction mixture (sample B) are shown in Figure 10. The starting material exhibited the known eight-line NMR spectrum for  $D_3$ -C<sub>60</sub>F<sub>48</sub><sup>62</sup> and a mass spectrum with a dominant peak at m/z 1632 due to the molecular ion C<sub>60</sub>F<sub>48</sub><sup>-</sup>. The NMR and mass spectra of sample B, taken within 30 min, were consistent with one or more  $C_{60}F_{47}^{-}$  species  $(m/z \ 1613)$ . Careful integration of the resonances allowed us to identify 47 equal-intensity peaks, several of which overlap one another. These spectra did not change substantially for several hours. A 2D-COSY <sup>19</sup>F NMR spectrum, shown in Figure S-2 (Supporting Information), revealed that at least 40 of the resonances are internally correlated, suggesting that sample B contains a single  $C_1$ - $C_{60}F_{47}^-$  isomer. However, we cannot rule out the possibility that sample B contains more than one  $C_1$ - $C_{60}F_{47}^{-}$  isomer with very similar NMR spectra. The reaction of  $D_3$ -C<sub>60</sub>F<sub>48</sub> with DEC was repeated several times with different reagent ratios, and every time the NMR and mass spectra were identical to those for sample B shown in Figure 10. The remarkable stability of the isomer (or isomers) of  $C_{60}F_{47}^{-}$  in sample B will be investigated further in an ongoing study. It may be possible to isolate it as a crystalline salt and determine its structure and other physicochemical properties.

After 24 h, sample B had become bright green in color, the NMR spectrum exhibited 11 equal intensity resonances (three of which are nearly isochronous), and the mass spectrum exhibited a single peak (with appropriate isotopomeric peaks) for  $C_{60}F_{44}^{-}$  at m/z 1556. These spectra are shown



**Figure 11.** Schlegel diagrams of  $D_3$ -C<sub>60</sub>F<sub>48</sub> (top) and the proposed isomer of  $D_2$ -C<sub>60</sub>F<sub>44</sub> (second from top) and the DFT-optimized structure of  $D_2$ -C<sub>60</sub>F<sub>44</sub> (third from top). The C=C  $\pi$  bonds that are common to both molecules are indicated with arrows in the Schlegel diagrams. The two points centered in the C<sub>6</sub>F<sub>6</sub> hexagons define the molecular  $C_3$  axis in  $D_3$ -C<sub>60</sub>F<sub>48</sub>. The eight C=C bonds in  $D_2$ -C<sub>60</sub>F<sub>44</sub> (bottom; 376.5 MHz, CDCl<sub>3</sub>, C<sub>6</sub>F<sub>6</sub> external standard ( $\delta$  –164.9)). The correlations shown were determined by a 2D-COSY experiment (see Figure S-3 for the 2D-COSY spectrum).

in Figure 10 (sample C) and were unchanged even after 1 week. When the green solution was filtered through a short column of silica gel, the green component(s) were retained and a colorless solution eluted. This solution, sample D (not shown), had the same 11-line NMR spectrum and the same single peak at m/z 1556 in the mass spectrum as sample C. Since the mass spectrum of sample C did not contain a peak at m/z 778, and because the fluorofullerene component of sample C was not retained on silica gel, the 24 h reaction product is almost certainly not a diamagnetic C<sub>60</sub>F<sub>44</sub><sup>2–</sup> dianion. Therefore, we propose that the colorless 24 h reaction product is a single isomer of a new fluorofullerene, C<sub>60</sub>F<sub>44</sub>, with 11 unique types of F atoms.

**Proposed Structure of C**<sub>60</sub>**F**<sub>44</sub>. We optimized the molecular structures and determined the relative energies of all 75 closed-shell  $D_2$ ,  $C_{2\nu}$ , and  $C_{2h}$  isomers of C<sub>60</sub>F<sub>44</sub> that are consistent with the 11-line <sup>19</sup>F NMR spectrum at the AM1 level of theory. The most stable isomers were further optimized at the PBE/TZ2P level. The  $D_2$  symmetry structure shown in Figure 11, which

we will refer to as  $D_2$ -C<sub>60</sub>F<sub>44</sub>, was found to be 95.0 kJ mol<sup>-1</sup> more stable than the second most stable structure. We propose that the isomer of C<sub>60</sub>F<sub>44</sub> we have generated is  $D_2$ -C<sub>60</sub>F<sub>44</sub>. This structure is consistent with the 2D-COSY <sup>19</sup>F NMR correlations also shown in Figure 11 (the 2D spectrum itself is shown in Figure S-3). However, as commonly observed for other FFs,<sup>62,63</sup> all possible correlations between neighboring F atoms could not be identified, preventing an unambiguous structural assignment at this time.

The eight C=C  $\pi$  bonds in  $D_2$ -C<sub>60</sub>F<sub>44</sub> are isolated from one another, as are the six C=C  $\pi$  bonds in  $D_3$ -C<sub>60</sub>F<sub>48</sub>. The lowestenergy isomer of C<sub>60</sub>F<sub>44</sub> with conjugated diene moieties that is consistent with the NMR spectrum for sample C is 135 kJ mol<sup>-1</sup> less stable than  $D_2$ -C<sub>60</sub>F<sub>44</sub>. Comparison of the Schlegel diagram for  $D_2$ -C<sub>60</sub>F<sub>44</sub> with a suitably oriented Schlegel diagram for  $D_3$ -C<sub>60</sub>F<sub>48</sub>, both of which are shown in Figure 11, shows that these two FFs have only two C=C bonds in common. Whereas all six of the C=C bonds in  $D_3$ -C<sub>60</sub>F<sub>48</sub> are on pentagon/hexagon (5/6) edges, four of the C=C bonds in  $D_2$ -C<sub>60</sub>F<sub>44</sub> are 5/6 edges and four are 6/6 edges.

The mechanism or mechanisms by which  $C_1$ - $C_{60}F_{47}$  in sample B is converted into  $D_2$ -C<sub>60</sub>F<sub>44</sub> are unknown at this time. A recent theoretical study by Avdoshenko et al. has shown that F atom rearrangements in fluorofullerenes may be facilitated by interactions with electron donor molecules.<sup>64</sup> In addition, it has been shown experimentally that  $C_1$ - $C_{60}F_{36}$  dissolved in CDCl<sub>3</sub> is slowly converted into the more stable isomer  $C_3$ - $C_{60}F_{36}$ (this may be due to the presence of oxygen and/or a trace amount of water in the solution).<sup>65</sup> The reaction of  $D_3$ -C<sub>60</sub>F<sub>48</sub> and other FFs with one-electron reducing agents such as DEC has become a new synthetic and mechanistic investigation in our lab, and future experiments will focus on the characterization of neutral and charged FF intermediates and the determination of their structures. For this reason, we will not speculate on possible mechanisms or possible intermediates in this report other than to point out that it is not possible to produce  $D_2$ -C<sub>60</sub>F<sub>44</sub> from  $D_3$ -C<sub>60</sub>F<sub>48</sub> (or to produce any other isomer of C<sub>60</sub>F<sub>44</sub> that is consistent with the 11-line NMR spectrum from  $D_3$ -C<sub>60</sub>F<sub>48</sub>) without the rearrangement of some C-F bonds. However, the fact that F atom rearrangements are necessary does not require that the observed product must be the thermodynamically most stable isomer. Therefore, our structural assignment for the new isomer of  $C_{60}F_{44}$ , which is based on its DFT-predicted relative energy, is tentative. Whatever the mechanism or mechanisms, the remarkable selectivity of the reductive-defluorination process reported here was not expected and may very well prove useful synthetically in the search for new fullerene derivatives with as wide a range of properties as possible.

### **Summary and Conclusions**

The EAs of a series of fluorofullerenes  $C_{60}F_n$  (n = 17, 33, 35, 43, 45, and 47) were directly measured by low-temperature PES as ADEs of the corresponding anions, revealing a monotonic increase in EA as *n* increases. Notably, the EAs are significantly higher than for the even-*n* homologue with one more or one fewer F atom. Theoretical calculations suggest likely structures for the experimentally observed anions  $C_{60}F_{17}^{-}$ ,  $C_{60}F_{35}^{-}$ , and  $C_{60}F_{47}^{-}$ . The most stable structures for these anions are those in which the charge can be delocalized over an extended conjugated fragment. The good agreement between the DFT-predicted ADEs for the proposed structures of these anions can be reliably used to design FF molecules with particular EAs for particular applications. Low-temperature PES spectra for the

dianions  $C_{60}F_{34}^{2-}$  and  $C_{60}F_{46}^{2-}$  were also recorded, leading to precise ADEs as well as RCBs. The reaction of  $C_{60}F_{48}$  with the tetraalkylated ferrocene DEC in CDCl<sub>3</sub> solution at room temperature produced the remarkably stable anion  $C_1$ - $C_{60}F_{47}^{-}$ , which is predicted by DFT calculations to have the excess charge located on the inside surface of the fullerene cage rather than on the outside suface. This anion is slowly (hours) converted to an unprecedented FF compound,  $D_2$ - $C_{60}F_{44}$ , which was characterized by 1D and 2D <sup>19</sup>F NMR spectroscopy. The unexpected selectivity of this reductive defluorination should be explored in a more general sense in the search for new FFs with desired electronic properties.

Acknowledgment. The PES work was supported by the U.S. Department of Energy (DOE), Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences and Biosciences, and in part by the U.S. National Science Foundation (CHE-0749496), and was performed at the EMSL, a national scientific user facility sponsored by DOE's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory, which is operated for DOE by Battelle. M.F.Z. thanks the National Natural Science Foundation of China (Grant No. 20528303) and National Basic Research Program of China (2007CB815203) for partial support of the work. A.A.P. thanks Lothar Dunsch for his encouragement and support, the Alexander von Humboldt Foundation for financial support, the Research Computing Center of the Moscow State University for computer time at the supercomputer Chebyshev SKIF-MGU, and Ulrike Nitzsche for assistance with computational resources in IFW Dresden. I.V.K., O.V.B., and S.H.S. acknowledge the support of the U.S. National Science Foundation (CHE-0707223). O.V.B. thanks the Alexander von Humboldt Foundation for a Freidrich Bessel Award (2003) and an AvH Research Award (2009).

**Supporting Information Available:** Drawing of the DFToptimized structure of  $D_2$ -C<sub>60</sub>F<sub>47</sub><sup>-</sup> and 2D <sup>19</sup>F NMR spectra of solutions containing C<sub>60</sub>F<sub>47</sub><sup>-</sup> and  $D_2$ -C<sub>60</sub>F<sub>44</sub>. This material is available free of charge via the Internet at http:// pubs.acs.org.

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JP9097364