THE JOURNAL OF PHYSICAL CHEMISTRY A LETTERS

2005, *109,* 9709−9711
Published on Web 10/11/2005

Poly(trifluoromethyl)fullerene Radical Anions. An ESR/Vis−NIR Spectroelectrochemical Study of $C_{60}F_{2,4}$ and $C_{60}(CF_3)_{2,10}$

Alexey A. Popov,[*,†,‡] Ján Tarábek,[†] Ivan E. Kareev,[§,||] Sergey F. Lebedkin,[§]
Steven H. Strauss,[*,⊥] Olga V. Boltalina,[*,⊥] and Lothar Dunsch[*,†]

Chemistry Department, Moscow State University, Moscow 119992, Russia, Department of Electrochemistry and Conducting Polymers, Leibniz Institute for Solid State and Materials Research Dresden, Helmholtzstrasse 20, Dresden D01069, Germany, Forschungszentrum Karlsruhe, Institute for Nanotechnology, Karlsruhe 76021 Germany, Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka 142432, Russia, and Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523, U.S.A.

Received: September 5, 2005; In Final Form: September 19, 2005

Cyclic voltammograms are reported for $C_{60}(CF_3)_n$ derivatives for the first time. The compounds studied were 1,9-$C_{60}(CF_3)_2$ and 3 isomers of $C_{60}(CF_3)_{10}$, including the structurally characterized derivative 1,3,7,10,14,17,23,28,31,40-$C_{60}(CF_3)_{10}$ ($C_{60}(CF_3)_{10}$-3). The compound 1,9-$C_{60}(CF_3)_2$ exhibited 3 reversible reductions; $C_{60}(CF_3)_{10}$-3 exhibited 2 reversible reductions; the other 2 isomers of $C_{60}(CF_3)_{10}$ each exhibited 1 reversible reduction. ESR and near-IR spectroelectrochemical experiments were performed to characterize some of the $C_{60}(CF_3)_n^-$ and $C_{60}(CF_3)_n^{2-}$ species generated by cyclic voltammetry. The ESR spectrum of the $C_{60}(CF_3)_{10}$-3^- radical anion consisted of an envelope of 25 lines centered at $g = 2.0032$ (the apparent a value is ca. 0.5 G), evidence of coupling between the unpaired electron and a significant number of the CF_3 fluorine atoms. The most significant finding is that this radical anion has a half-life in solution at 25 °C of about 7 min.

Optical and electrochemical properties are of particular interest for fullerene derivatives because of their application in energy storage and photovoltaic devices.[1] The voltammetric behavior of fullerenes[2] and fullerene derivatives[3] in various solvents has been described. Most C_{60} and C_{70} derivatives with electrochemically inactive substituents have lower reduction potentials than the parent fullerene, which results from the reinforcing factors of (i) fullerene π-system saturation and (ii) substituent electron-donating effects.

Derivatives with reduction potentials higher than the parent fullerene, such as $C_{60}(CN)_2$,[4] some methanofullerenes,[5] $C_{70}Ph_n$,[6] and $C_{60}F_n$,[7−10] are less common, but demonstrate that fullerene π-system saturation can be more than offset by a sufficient number of strongly electron withdrawing groups. The most striking example is the $C_{60}F_{48}{}^{0/-}$ couple, the potential for which is 1.38 V more positive than the $C_{60}{}^{0/-}$ couple.[7,10] However, most fluorofullerenes[11] exhibit irreversible one-electron reductions, presumably due to facile fluorine atom or fluoride ion loss from $C_{60,70}F_n^-$ ions in solution,[7,10,12] and this severely limits their practical use as electron acceptors in a variety of devices.

Poly(perfluoroalkyl)fullerenes (PPFs) may prove more practical for device applications. They are highly soluble in organic solvents, and some are stable up to 480 °C.[13,14] The limited data reported so far indicate that they are resistant to hydrolysis.[15] We report here the first electrochemical data for this growing class of compounds,[16] including spectroelectrochemical (SE) results that show that some PPFs form radical anions in solution at 25 °C with half-lives longer than 7 min.

Details about the cyclic voltammetry (CV) and electron spin resonance (ESR)/vis−near(N)IR SE experiments are in the Supporting Information. Reduction potentials for C_{60}, $C_{60}F_2$,[17] $C_{60}F_4$,[18] 1,9-$C_{60}(CF_3)_2$,[19] three isomers of $C_{60}(CF_3)_{10}$,[14] and other relevant compounds[7,9,10] are listed in Table 1 ($C_{60}F_2$ and $C_{60}F_4$ were purified to 90+% purity by a new[20] two-dimensional high-performance liquid chromatography procedure). Selected CV curves are shown in Figure 1.

Like C_{60}, $C_{60}(CF_3)_2$ has three accessible reversible reductions. The first is positively shifted by 0.11 V relative to C_{60}. The compounds $C_{60}(CF_3)_{10}$-1 and $C_{60}(CF_3)_{10}$-2 each exhibited one reversible reduction, at 0.44 and 0.32 V vs $C_{60}{}^{0/-}$, respectively, and $C_{60}(CF_3)_{10}$-3, the structure of which is known,[14] exhibited two reversible reductions at 0.17 and −0.44 V vs $C_{60}{}^{0/-}$. Interestingly, the 0.61 V difference between the first and second $E_{1/2}$ values for $C_{60}(CF_3)_{10}$-3 is 50% larger than the differences for C_{60}, $C_{60}(CF_3)_2$, and even $C_{60}F_{48}$, 0.42(2) V. Nevertheless, shifts in $E_{1/2}$ values relative to C_{60} for successive reductions are attenuated for PPFs (e.g., $E_{1/2}(C_{60}(CF_3)_{10}\text{-}3) - E_{1/2}(C_{60})$ is 0.17 V for the first reduction and −0.04 V for the second; the three $\Delta E_{1/2}$ values for $C_{60}(CF_3)_2$ vs C_{60} are 0.11, 0.10, and 0.01 V).

When $C_{60}(CF_3)_{10}$-3 was reduced at a fixed potential of 0.0 or −0.1 V vs $C_{60}{}^{0/-}$, the ESR signal for the radical anion shown in Figure 2 was observed. The 25 lines ($a = 0.5{-}0.6$ G) are presumably due to hyperfine coupling between the unpaired electron with all or a subset of the 30 F atoms.[21] The decay of the open-circuit ESR signal for $C_{60}(CF_3)_{10}$-3^- shows that the

---

[†] Moscow State University.
[‡] Leibniz Institute for Solid State and Materials Research Dresden.
[§] Institute for Nanotechnology.
[||] Russian Academy of Sciences.
[⊥] Colorado State University.

10.1021/jp0550006 CCC: $30.25

TABLE 1: Cyclic Voltammetric Data[a] for Poly(trifluoromethyl)[60]fullerenes and Fluoro[60]fullerenes

compd	scan rate V s^{-1}	electrolyte (conc, M)	$E_{1/2}$ or E_{pc} V vs $C_{60}{}^{0/-}$	ΔE_p mV	$E_{1/2}$ or E_{pc} V vs $C_{60}{}^{0/-}$	ΔE_p mV	$E_{1/2}$ or E_{pc} V vs $C_{60}{}^{0/-}$	ΔE_p mV	ref
C_{60}	0.02	$TBA^+PF_6^-$ (0.1)	0.00	nr	−0.44	nr	nr		9
C_{60}	0.02	$TBA^+BF_4^-$ (0.1)	0.00	69	−0.40	64	−0.84	64	this work
$C_{60}(CF_3)_2$	0.02	$TBA^+BF_4^-$ (0.1)	0.11	64	−0.30	59	−0.83	99	this work
$C_{60}(CF_3)_{10}$-1[b]	0.02	$TBA^+BF_4^-$ (0.1)	0.44	80					this work
$C_{60}(CF_3)_{10}$-2[b]	0.02	$TBA^+BF_4^-$ (0.1)	0.32	92					this work
$C_{60}(CF_3)_{10}$-3[b]	0.01	$TBA^+BF_4^-$ (0.1)	0.17	110	−0.44	110			this work
$C_{60}F_2$	0.02	$TBA^+BF_4^-$ (0.1)	0.04 (E_{pc})						this work
$C_{60}F_4$	0.02	$TBA^+BF_4^-$ (0.1)	0.08 (E_{pc})						this work
$C_{60}F_{18}$	5.00	$TBA^+PF_6^-$ (0.05)	0.26 (E_{pc})						10
$C_{60}F_{36}$[c]	0.02	$TBA^+PF_6^-$ (0.1)	0.80 (E_{pc})						9
$C_{60}F_{36}$[d]	1.00	$TBA^+PF_6^-$ (0.05)	0.71	92	0.18 (E_{pc})				10
$C_{60}F_{48}$	0.20	$TBA^+PF_6^-$ (0.08)	1.38	66	1.03 (E_{pc})				7
$C_{60}F_{48}$	1.00	$TBA^+PF_6^-$ (0.05)	1.37	170	0.93	150			10

[a] Anhydrous dichloromethane; all potentials relative to the $C_{60}{}^{0/-}$ couple; $Fe(Cp)_2{}^{+/0}$, $Fe(Cp^*)_2{}^{+/0}$, or 9,10-Ph_2-anthracene$^{0/-}$ internal standard; $TBA^+ = N(n\text{-}Bu)_4{}^+$; nr = not reported. [b] Different C_1 isomers. [c] Mixture of ≥80% C_3 isomer and ≤20% T isomer. [d] C_3 isomer.

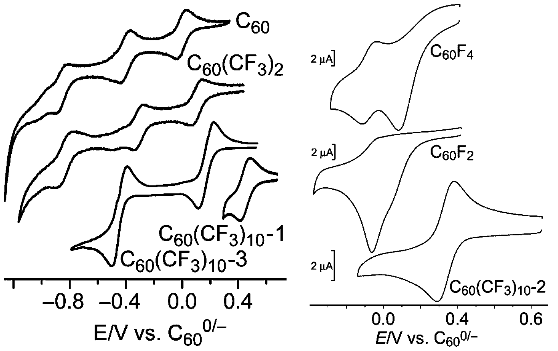

Figure 1. Cyclic voltammograms (scan rate 0.02 V/s except as noted, 0.1 M $TBABF_4/CH_2Cl_2$ solutions). Left: C_{60}, $C_{60}(CF_3)_2$, $C_{60}(CF_3)_{10}$-1, and $C_{60}(CF_3)_{10}$-3 (0.01 V/s). Right: $C_{60}F_2$, $C_{60}F_4$, and $C_{60}(CF_3)_{10}$-2.

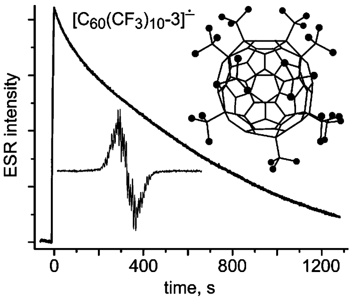

Figure 2. ESR spectrum ($g = 2.0032$; $a \approx 0.5$ G) and the decay in ESR signal intensity for $C_{60}(CF_3)_{10}$-3. For the decay experiment, the radical was generated by stepping the potential to 0.00 V vs $C_{60}{}^{0/-}$ for 10 s at $t = 0$, then opening the circuit. The ESR spectrum shown is the average of 400 scans recorded at a potential of −0.1 V vs $C_{60}{}^{0/-}$ for 1 h.

half-life of this radical anion in CH_2Cl_2 at 25 °C is more than 7 min. A half-life of 5 min was recorded for $C_{60}(CF_3)_{10}$-2^-. This can be compared to the half-life of the $C_{60}F_{18}{}^-$ radical anion, ca. 0.25 s in PhCN,[22] *which is more than 3 orders of magnitude shorter*. The fact that PPF radical anions can have lifetimes of *minutes* is a significant finding as far as the incorporation of such acceptors into photovoltaic devices with long operational lifetimes is concerned. It is now apparent that PPFs, which can be better acceptors than C_{60} by up to 0.44 V with only 10 perfluoroalkyl groups, are far superior to fluorofullerenes for device applications as well as for fundamental photophysical experiments involving one-electron reductions.

Vis−NIR spectra (not shown) were recorded during cyclic voltammograms of $C_{60}(CF_3)_2$ and $C_{60}(CF_3)_{10}$-3. The $C_{60}(CF_3)_2{}^-$ radical anion has bands at 932 and 1516 nm and a featureless ESR signal at $g = 2.0016$, while the $C_{60}(CF_3)_2{}^{2-}$ dianion has bands at 880 and 1336 nm and no ESR signal. The $C_{60}(CF_3)_{10}$-3^- radical anion has bands at 565 and 828 nm.

The compounds $C_{60}F_2$ and $C_{60}F_4$ exhibited CVs with irreversible reductions characteristic of more highly substituted fluorofullerenes. At a scan rate of 0.02 V/s, the cathodic peak in each case is accompanied by an additional cathodically shifted peak which appeared to be reversible in most experiments. Similar patterns were observed at all scan rates probed (≤5 V/s) except that the intensities of the cathodically shifted peaks varied with scan rate. NIR spectra for $C_{60}F_2$ and $C_{60}F_4$ recorded at potentials more negative than 0 V vs $C_{60}{}^{0/-}$ exhibited a band characteristic of the $C_{60}{}^-$ radical anion at 1080 nm.[23] An absorption at 940 nm, characteristic of the $C_{60}{}^{2-}$ dianion,[23] was observed at more negative potentials. The data indicate that both $C_{60}F_2$ and $C_{60}F_4$ undergo an ECE sequence of reactions involving the cleavage of one or more C−F bonds, behavior that is entirely analogous to electrochemical defluorinations observed for the more highly fluorinated fullerenes such as $C_{60}F_{18}$, $C_{60}F_{36}$, and others.[7,10,12]

We are continuing to study the spectroelectrochemical behavior of other $C_{60,70}(CF_3)_n$ derivatives, especially those with $2 \leq n \leq 10$. We are using calculations at the density functional theory (DFT) level to understand the shift in the first reduction potential from 0.44 to 0.32 to 0.17 V vs $C_{60}{}^{0/-}$ for the three isomers of $C_{60}(CF_3)_{10}$ and the hyperfine coupling between the unpaired electron in the $C_{60}(CF_3)_{10}$-3^- radical anion and the CF_3 fluorine atoms.

Acknowledgment. We thank the Volkswagen Stiftung (I-77/855) and the U.S. NSF, Dr. I. V. Goldt for experimental assistance, and Prof. M. Kappes for his generous support.

Supporting Information Available: Details of the spectroelectrochemical experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Nierengarten, J.-F. *New J. Chem.* **2004**, *28*, 1177−1191. Hoppe, H.; Sariciftci, N. S. *J. Mater. Res.* **2004**, *19*, 1924−1945. Segura, J. L.; Martin, N.; Guldi, D. M. *Chem. Soc. Rev.* **2005**, *34*, 31−47.

(2) Xie, Q.; Perez-Cordero, E.; Echegoyen, L. *J. Am. Chem. Soc.* **1992**, *114*, 3978. Guldi, D. M.; Prato, M. *Acc. Chem. Res.* **2000**, *33*, 695.

(3) Echegoyen, L.; Herranz, M. A. In *Fullerenes: From Synthesis to Optoelectronic Properties*; Guldi, D. M., Martin, N., Eds.; Kluwer Academic: Dordrecht, The Netherlands, 2002. Yanilkin, V. V.; Gubskaya, V. P.; Morozov, V. I.; Nastapova, N. V.; Zverev, V. V.; Berdnikov, E. A.; Nuretdinov, I. A. *Russ. J. Electrochem.* **2003**, *39*, 1147−1165.

(4) Keshavzarz, K. M.; Knight, B.; Srdanov, G.; Wudl, F. *J. Am. Chem. Soc.* **1995**, *117*, 11371−11372.

(5) Deng, F.; Wang, G.-W.; Zhang, T.-H.; Jiao, L.-J.; Chen, S. *Chem. Commun.* **2004**, 1118−1119.

(6) Avent, A. G.; Birkett, P. R.; Carano, M.; Darwish, A. D.; Kroto, H. W.; Lopez, J. O.; Paolucci, D.; Roffia, S.; Taylor, R.; Wachter, N.; Walton, D. R. M.; Zerbetto, F. *J. Chem. Soc. Perkin Trans. 2* **2001**, 140−145.

(7) Zhou, F.; Van Berkel, G. J.; Donovan, B. T. *J. Am. Chem. Soc.* **1994**, *116*, 5485−5486.

(8) Okino, F.; Yajima, S.; Suganuma, S.; Mitsumoto, R.; Seki, K.; Touhara, H. *Synth. Met.* **1995**, *70*, 1447−1448. Matsuo, Y.; Nakajima, T. *Electrochim. Acta* **1996**, *41*, 15−19. Liu, N.; Touhara, H.; Morio, Y.; Komichi, D.; Okino, F.; Kawasaki, S. *J. Electrochem.* Soc. **1996**, *143*, L214−L217. Liu, N.; Touhara, H.; Okino, F.; Kawasaki, S.; Nakacho, Y. *J. Electrochem. Soc.* **1996**, *143*, 2267−2272. Claves, D.; Giraudet, J.; Hamwi, A.; Benoit, R. *J. Phys. Chem. B* **2001**, *105*, 1739−1742.

(9) Liu, N.; Morio, Y.; Okino, F.; Touhara, H.; Boltalina, O. V.; Pavlovich, V. K. *Synth. Met.* **1997**, *86*, 2289−2290.

(10) Paolucci, D.; Paolucci, F.; Marcaccio, M.; Carano, M.; Taylor, R. *Chem. Phys. Lett.* **2004**, *400*, 389−393.

(11) Boltalina, O. V.; Strauss, S. H. In *Dekker Encyclopedia of Nanoscience and Nanotechnology*; Schwarz, J. A., Contescu, C. I., Putyera, K., Eds.; Marcel Dekker: New York, 2004; pp 1175−1190.

(12) Touhara, H. *Denki Kagaku* **1998**, *66*, 368−375. Hamwi, A. *J. Phys. Chem. Solids* **1996**, *57*, 677−688.

(13) Goryunkov, A. A.; Kuvychko, I. V.; Ioffe, I. N.; Dick, D. L.; Sidorov, L. N.; Strauss, S. H.; Boltalina, O. V. *J. Fluorine Chem.* **2003**, *124*, 61−64.

(14) Kareev, I. E.; Kuvychko, I. V.; Lebedkin, S. F.; Miller, S. M.; Anderson, O. P.; Seppelt, K.; Strauss, S. H.; Boltalina, O. V. *J. Am. Chem. Soc.* **2005**, *127*, 8362−8375.

(15) Fagan, P. J.; Krusic, P. J.; McEwen, C. N.; Lazar, J.; Parker, D. H.; Herron, N.; Wasserman, E. *Science* **1993**, *262*, 404−407.

(16) See Supporting Information for a complete list of references.

(17) Boltalina, O. V.; Lukonin, A. Y.; Street, J. M.; Taylor, R. *Chem. Commun.* **2000**, 1601−1602.

(18) Boltalina, O. V.; Darwish, A. D.; Street, J. M.; Taylor, R.; Wei, X.-W. *J. Chem. Soc. Perkin Trans. 2* **2002**, 251−256.

(19) Avent, A. G.; Boltalina, O. V.; Goryunkov, A.; Darwish, A. D.; Markov, V. Y.; Taylor, R. *Fullerenes, Nanotubes, Carbon Nanostruct.* **2002**, *10*, 235−241.

(20) Kareev, I. E.; Quinones, G. S.; Kuvychko, I. V.; Ioffe, I. N.; Goldt, I. V.; Lebedkin, S. F.; Seppelt, K.; Strauss, S. H.; Boltalina, O. V. *J. Am. Chem. Soc.* **2005**, *127*, 11497−11504.

(21) The ESR multiplet is complex and has not been fully analyzed. However, other organic radicals with multiple CF_3 groups also exhibit multiplets with intensities that are quite different from the expected binomial expansion, an effect that has been attributed to unresolved second-order splitting of the hyperfine components and to the rotational dynamics of the CF_3 groups. See Corvaja, C.; Farnia, G. Formenton, G.; Navarrini, W.; Sandona, G.; Tortelli, V. *J. Phys. Chem.* **1994**, *98*, 2307−2313, and references therein.

(22) Ohkubo, K.; Taylor, R.; Boltalina, O. V.; Fukuzumi, S. *Chem. Commun.* **2002**, 1952−1953.

(23) Rapta, R.; Bartl, A.; Gromov, A.; Stasko, A.; Dunsch, L. *Chem. Phys. Chem.* **2002**, 351−356. Reed, C. A.; Bolskar, R. D. *Chem. Rev.* **2000**, *100*, 1075−1120.