### SUPPORTING INFORMATION

# Substituent effects in a series of 1,7-C<sub>60</sub>(R<sub>F</sub>)<sub>2</sub> compounds (R<sub>F</sub> = CF<sub>3</sub>, C<sub>2</sub>F<sub>5</sub>, *n*-C<sub>3</sub>F<sub>7</sub>, *i*-C<sub>3</sub>F<sub>7</sub>, *n*-C<sub>4</sub>F<sub>9</sub>, *s*-C<sub>4</sub>F<sub>9</sub>, *n*-C<sub>8</sub>F<sub>17</sub>): Electron affinities, reduction potentials, and *E*(LUMO) values are not always correlated

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## Table of Contents

page

Experimental details
Preparation of and spectroscopic data for $1,7-C_{60}(CF_3)_2$
Preparation of and spectroscopic data for $1,7-C_{60}(C_2F_5)_2$
Preparation of and spectroscopic data for $1,7-C_{60}(n-C_3F_7)_2$
Preparation of and spectroscopic data for $1,7-C_{60}(i-C_3F_7)_2$
Preparation of and spectroscopic data for $1,7-C_{60}(n-C_4F_9)_2$
Preparation of and spectroscopic data for 1,7-C <sub>60</sub> (s-C <sub>4</sub> F <sub>9</sub> ) <sub>2</sub>
Preparation of and spectroscopic data for $1,7-C_{60}(n-C_8F_{17})_2$
Peak maxima and apparent peak maxima in UV-Vis spectra of $1,7-C_{60}(R_F)_2$ compounds S16
Solubilities of $1,7-C_{60}(R_F)_2$ compounds in toluene
$E_{1/2}$ values of 1,7-C <sub>60</sub> (R <sub>F</sub> ) <sub>2</sub> compounds in dichloromethane and benzonitrile
Graphs of electron affinity vs. $E_{1/2}(0/-)$ values
Absolute values of experimental and DFT-predicted EA, $E_{1/2}(0/-)$ , and $\Delta E_{solv}$
Information about the X-ray crystallographic study of $1,7-C_{60}(n-C_3F_7)_2 \cdot CDCl_3$ S22
X-ray determined C(cage)–C(R <sub>F</sub> ) distances for $C_{60}(C_2F_5)_n$ and $C_{60}(i-C_3F_7)_n$ compounds S27
Absolute values of parameters cited in the Background section of the article

#### **Experimental Details**

**Solvents and Reagents.** The solvents toluene (Fisher Scientific; HPLC grade), *n*-heptane (Fisher Scientific; HPLC grade), and 2-propanol (Fisher Scientific; ACS grade) were used as received. Dichloromethane (Fisher Scientific; ACS grade), 1,2-dichlorobenzene (*o*-DCB; Acros Organics; ACS grade), and benzonitrile (Sigma-Aldrich; ACS grade) used for electrochemical measurements were distilled from CaH<sub>2</sub> under a purified dinitrogen atmosphere. The compounds  $C_{60}$  (99.9%, Term-USA),  $R_{FI}$  ( $R_{F} = CF_3$ ,  $C_2F_5$ , *n*- $C_3F_7$ , *i*- $C_3F_7$ , *n*- $C_4F_9$ , *s*- $C_4F_9$ , and *n*- $C_8F_{17}$  (SynQuest Labs), and Cu powder (Fisher Scientific; electrolytic grade) were used as received. The solvent CDCl<sub>3</sub> (Cambridge Isotope) was treated with 4 Å molecular sieves and distilled.

**Instruments.** HPLC analysis and separation was accomplished using Shimadzu HPLC instrumentation (CBM-20A control module, SPD-20A UV-detector set to 300 nm detection, LC-6AD pump, manual injector valve) equipped with a 20-mm I.D. × 250 mm preparative Cosmosil Buckyprep column (Nacalai Tesque, Inc.). APCI mass spectra were recorded using a 2000 Finnigan LCQ-DUO mass spectrometer (CH<sub>3</sub>CN carrier solvent, 0.3 mL·min<sup>-1</sup> flow rate); the PFAF samples were injected as toluene solutions in toluene. UV-Vis spectra were recorded using a Varian Cary-500 UV-Vis spectrophotometer with a resolution of 1 nm. Fluorine-19 NMR spectra were recorded using a Varian INOVA 400 spectrometer operating at 376.477 MHz (C<sub>6</sub>F<sub>6</sub> internal standard,  $\delta$  –164.9).

**Preparation of individual**  $C_{60}(R_F)_2$  **compounds. 1,7-** $C_{60}(CF_3)_2$ **.** This compound was prepared as described in the literature: I. V. Kuvychko, J. B. Whitaker, B. W. Larson, R. S. Raguindin, K. J. Suhr, S. H. Strauss, and O. V. Boltalina, *J. Fluorine Chem.* **2011**, *132*, 679. This reference also contains a detailed description of the GTGS reactor (see below) developed for the synthesis of 1,7-C<sub>60</sub>(CF<sub>3</sub>)<sub>2</sub> compounds. The <sup>19</sup>F NMR spectrum of 1,7-C<sub>60</sub>(CF<sub>3</sub>)<sub>2</sub> consists of a single resonance at  $\delta$  –72.3 and is shown on the next page. The APCI mass spectrum and UV-Vis spectrum are also shown on the next page.



Large cylindrical Gradient-Temperature Gas-Solid (GTGS) reactor used for the solution perfluoroalkylation of C<sub>60</sub>.



Fluorine-19 NMR spectrum of  $1,7-C_{60}(CF_3)_2$  (singlet at  $\delta$  -72.3).



UV-Vis spectra of 1,7-C<sub>60</sub>(CF<sub>3</sub>)<sub>2</sub> solution in toluene (different plots correspond to progressive dilutions).

**1,7-C**<sub>60</sub>(**C**<sub>2</sub>**F**<sub>5</sub>)<sub>2</sub>. A finely ground sample of C<sub>60</sub> (216.0 mg) was mixed with 3.241 g of copper powder and loaded into a small-scale GTGS reactor equipped with a 10 mm thick spacer.<sup>1</sup> The reactor was put under dynamic vacuum and heated to  $T_{\text{hot plate}} = 500 \text{ °C}$  ( $T_{\text{hz}} = 430 \text{ °C}$ ); then 15.0 torr of C<sub>2</sub>F<sub>5</sub>I was added. The additional portions of C<sub>2</sub>F<sub>5</sub>I were added twice when the pressure dropped below 12 torr. After 16 hours the reactor was cooled down and the product was washed off with toluene; the toluene extract was filtered and separated using HPLC: the peak labelled F3 in the HPLC trace below was assigned to 1,7-C<sub>60</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>2</sub> based on the spectroscopic data, which are also shown below. The total yield of 1,7-C<sub>60</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>2</sub> was ca. 1–2%.



HPLC separation of  $1,7-C_{60}(C_2F_5)_2$  from the crude product mixture (100% toluene eluent at 16 mL min<sup>-1</sup>).



UV-Vis spectra of  $1,7-C_{60}(C_2F_5)_2$  solution in toluene (different plots correspond to progressive dilutions).



Fluorine-19 NMR spectrum of  $1,7-C_{60}(C_2F_5)_2$  (the singlet at  $\delta$  –81.4 corresponds to the isochronous CF<sub>3</sub> groups).



Expansion of the  $CF_2$  region of the <sup>19</sup>F NMR spectrum of 1,7- $C_{60}(C_2F_5)_2$  (top) and a spin simulation of the AA'BB' pattern (bottom). The spin simulation was performed using the software SpinNMR software.

**1,7-C**<sub>60</sub>(*n*-C<sub>3</sub>**F**<sub>7</sub>)<sub>2</sub>. A sample of C<sub>60</sub> (92.0 mg), copper powder (502 mg), 150  $\mu$ L of *n*-C<sub>3</sub>**F**<sub>7</sub>I (8 equiv. based on C<sub>60</sub>), and 130 mL of *o*-DCB were loaded into the GTGS reactor. The resulted reaction mixture was vigorously agitated to ensure a complete dissolution of the C<sub>60</sub>, degassed using a freeze-pump-thaw technique (two cycles were performed), and placed into a vertically-oriented tube furnace with only the Teflon valve resting outside. The reactor was heated at 190 °C for 72 h; then the reaction mixture was cooled down and evaporated to dryness using a rotary evaporator equipped with a rotary-vane vacuum pump. The resulting material was dissolved in a minimal amount of a mixture of 70% toluene and 30% 2-propanol (by volume), filtered, and separated using HPLC, as shown below. Two separatory stages were required to achieve 98+ mol% purity, as shown below. The yield of the purified compound was ca. 15%. Spectroscopic data are shown below and on the next page.



HPLC separation of  $1,7-C_{60}(n-C_3F_7)_2$  from the crude reaction mixture (the left trace corresponds to the first stage and the right trace to the second stage of the separation).



Negative-ion APCI mass spectrum of a purified sample of  $1,7-C_{60}(n-C_3F_7)_2$ .



UV-Vis spectra of  $1,7-C_{60}(n-C_3F_7)_2$  solution in toluene (different plots correspond to progressive dilutions).



Fluorine-19 NMR spectrum of  $1,7-C_{60}(n-C_3F_7)_2$ .

**1,7-C**<sub>60</sub>(*i*-C<sub>3</sub>**F**<sub>7</sub>)<sub>2</sub>. A sample of fullerene extract (200.4 mg), copper powder (8.413 g), 860  $\mu$ L of *i*-C<sub>3</sub>**F**<sub>7</sub>I (24 equiv. based on C<sub>60</sub>, assuming 90 wt% of C<sub>60</sub> in the fullerene extract) and 130 mL of *o*-DCB were loaded into the GTGS reactor. The resulted reaction mixture was vigorously agitated to ensure a complete dissolution of the fullerene extract, degassed using a freeze-pump-thaw technique (two cycles were performed), and placed into a vertically-oriented tube furnace with only the Teflon valve resting outside. The reactor was heated at 180 °C for 24 h; then the reaction mixture was cooled down and evaporated to dryness using a rotary evaporator equipped with a rotary vane vacuum pump. The resulting material was dissolved in a minimal amount of toluene, filtered, and separated using HPLC, as shown below. Two separatory stages were required to achieve 98+ mol% purity, as shown below. The yield of the purified material was ca. 10% based on C<sub>60</sub>. Spectroscopic data are shown below and on the next page.



HPLC separation of  $1,7-C_{60}(i-C_3F_7)_2$  from the crude reaction mixture (the left trace corresponds to the first stage and the right trace to the second stage). Fraction F1-4 was assigned to  $1,7-C_{60}(i-C_3F_7)_2$  based on spectroscopic data.



Negative-ion APCI mass spectrum of a purified sample of  $1,7-C_{60}(i-C_3F_7)_2$ .



UV-Vis spectra of  $1,7-C_{60}(i-C_3F_7)_2$  solution in toluene (different plots correspond to progressive dilutions).



Fluorine-19 NMR spectrum of  $1,7-C_{60}(i-C_3F_7)_2$ .

**1,7-C**<sub>60</sub>(*n*-C<sub>4</sub>**F**<sub>9</sub>)<sub>2</sub>. A sample of C<sub>60</sub> (117.4 mg), copper powder (650 mg), 160  $\mu$ L of *n*-C<sub>4</sub>F<sub>9</sub>I (6 equiv. relative to C<sub>60</sub>) and 130 mL of *o*-DCB were loaded into the GTGS reactor. The resulted reaction mixture was vigorously agitated to ensure a complete dissolution of the fullerene extract, degassed using a freeze-pump-thaw technique (two cycles were performed), and placed into a vertically-oriented tube furnace with only the Teflon valve resting outside. The reactor was heated at 190 °C for 13 h; then the reaction mixture was cooled down and evaporated to dryness using a rotary evaporator equipped with a rotary vane vacuum pump. The resulting material was dissolved in a minimal amount of toluene, filtered, and separated using HPLC, as shown below. Two separatory stages were required to achieve 98+ mol% purity, as shown below. The yield of the purified compound was ca. 10% based on C<sub>60</sub>. Spectroscopic data are shown below and on the next page.



HPLC separation of  $1,7-C_{60}(n-C_4F_9)_2$  from the crude reaction mixture (the left trace corresponds to the first stage and the right trace to the second stage). Fraction F1-5 was assigned to  $1,7-C_{60}(n-C_4F_9)_2$  based on spectroscopic data.



Negative-ion APCI mass spectrum of a purified sample of  $1,7-C_{60}(n-C_4F_9)_2$ .



UV-Vis spectra of  $1,7-C_{60}(n-C_4F_9)_2$  solution in toluene (different plots correspond to progressive dilutions).



Fluorine-19 NMR spectrum of  $1,7-C_{60}(n-C_4F_9)_2$ .

**1,7-C**<sub>60</sub>(*s*-C<sub>4</sub>**F**<sub>9</sub>)<sub>2</sub>. A sample of C<sub>60</sub> (53.5 mg), copper powder (850 mg), 100  $\mu$ L of *s*-C<sub>4</sub>F<sub>9</sub>I (8 equiv. based on C<sub>60</sub>) and 50 mL of *o*-DCB were loaded into the GTGS reactor The resulted reaction mixture was vigorously agitated to ensure a complete dissolution of the fullerene extract, degassed using a freeze-pump-thaw technique (two cycles were performed), and placed into a vertically-oriented tube furnace with only the Teflon valve resting outside. The reactor was heated at 190 °C for 7 h; then the reaction mixture was cooled down and evaporated to dryness using a rotary evaporator equipped with a rotary vane vacuum pump. The resulting material was dissolved in a minimal amount of toluene, filtered, and separated using HPLC, as shown below. Two separatory stages were required to achieve 98+ mol% purity, as shown below. The yield of the purified compound was ca. 20% based on C<sub>60</sub>. Spectroscopic data are shown below and on the next page.



HPLC separation of  $1,7-C_{60}(s-C_4F_9)_2$  from the crude reaction mixture (the left trace corresponds to the first stage and the right trace to the second stage).



Negative-ion APCI mass spectrum of a purified sample of  $1,7-C_{60}(s-C_4F_9)_2$ .



UV-Vis spectra of  $1,7-C_{60}(s-C_4F_9)_2$  solution in toluene (different plots correspond to progressive dilutions).



Fluorine-19 NMR spectrum of 1,7-C<sub>60</sub>(s-C<sub>4</sub>F<sub>9</sub>)<sub>2</sub>.

**1,7-C**<sub>60</sub>(*n*-C<sub>8</sub>F<sub>17</sub>)<sub>2</sub>. A sample of C<sub>60</sub> (113.5 mg), copper powder (980 mg), 256 µL of 1-C<sub>8</sub>F<sub>17</sub>I (6 equiv. based on C<sub>60</sub>) and 130 mL of *o*-DCB were loaded into the GTGS reactor. The resulted reaction mixture was vigorously agitated to ensure a complete dissolution of the fullerene extract, degassed using a freeze-pump-thaw technique (two cycles were performed), and placed into a vertically-oriented tube furnace with only the Teflon valve resting outside. The reactor was heated at 190 °C for 19 h; then the reaction mixture was cooled down and evaporated to dryness using a rotary evaporator equipped with a rotary vane vacuum pump. The resulting material was dissolved in a minimal amount of toluene, filtered, and separated using HPLC, as shown below. Two separatory stages were required to achieve 98+ mol% purity, as shown below. The molar of the purified compound was ca. 13% based on C<sub>60</sub>. Spectroscopic data are shown below and on the next page.



HPLC purification of  $1,7-C_{60}(n-C_8F_{17})_2$  from the crude reaction mixture (the left HPLC trace corresponds to the first stage and the right trace to the second stage).



Negative-ion APCI mass spectrum of a purified sample of  $1,7-C_{60}(n-C_8F_{17})_2$ .



UV-Vis spectra of  $1,7-C_{60}(n-C_8F_{17})_2$  solution in toluene (different plots correspond to progressive dilutions).



Fluorine-19 NMR spectrum of  $1,7-C_{60}(n-C_8F_{17})_2$ .

The following is a list of the peak maxima and apparent peak maxima (nm) in the UV-Vis spectra of the seven  $1,7-C_{60}(R_F)_2$  compounds studied in this work. Below the list is a graphical representation of these data.

$\mathbf{R}_{\mathrm{F}} =$						
CF <sub>3</sub>	$C_2F_5$	$n-C_3F_7$	<i>i</i> -C <sub>3</sub> F <sub>7</sub>	$n-C_4F_9$	<i>s</i> -C <sub>4</sub> F <sub>9</sub>	$n-C_8F_{17}$
328	327	329	328	328	327	328
445	448	447	445	447	445	447
529	535	532	475	532	476	536
565	561	565	534	570	534	568
602	601	602	565	598	567	599
633	630	631	604	632	603	627
662	657	659	628	659	629	660
693	692	692	691	692	691	692



UV-Vis peaks or apparent peaks for 1,7-C<sub>60</sub>(R<sub>F</sub>)<sub>2</sub> compounds

Comparison of the positions of the UV-Vis bands for the seven  $1,7-C_{60}(R_F)_2$  compounds studied in this work dissolved in toluene. The uncertainties for actual peak maxima are  $\pm 2$  nm; for apparent peaks that appear as shoulders in the spectra the uncertainties shown are  $\pm 10$  nm. The data for each peak maximum or appraent peak maximum are offset on the horizontal axis for clarity.

The solubilities of HPLC-purified samples of the seven  $1,7-C_{60}(CF_3)_2$  compounds studied in this work in HPLC-grade toluene are listed below. They were determined as follows. Saturated solutions containing excess solid compound were prepared and allowed to equilibrate for several days to ensure full saturation. Precisely measured aliquots of the filtered solutions were transfered to tared vials, after which all traces of toluene were removed under vacuum, first at 70 °C for 24 h and then at 110 °C for an additional 24 h. The vials containing the dry samples were weighed to determine the solubilities. The samples were then redissolved in CDCl<sub>3</sub>, an aliquot of  $1,4-C_6H_4(CF_3)_2$  was added, and both <sup>1</sup>H and <sup>19</sup>F NMR spectra were recorded. The <sup>19</sup>F NMR spectra confirmed that no decomposition of the samples had occured during the drying process, and a comparison of the integrated intensities in both spectra for each compound demonstrated that the amount of residual toluene (which would have contributed to the mass of the sample and hence would have affected the solubility calculation) was << 1 wt%.

compound	solubility, mg m $L^{-1}$	$10^{-3}$ × solubility, mM
$1,7-C_{60}(CF_3)_2$	2.4	2.8
$1,7-C_{60}(C_2F_5)_2$	6.0	6.3
$1,7-C_{60}(n-C_3F_7)_2$	4.4	4.2
$1,7-C_{60}(i-C_{3}F_{7})_{2}$	1.5	1.4
$1,7-C_{60}(n-C_4F_9)_2$	2.7	2.3
$1,7-C_{60}(s-C_4F_9)_2$	8.6	7.4
$1,7-C_{60}(n-C_8F_{17})_2$	4.4	2.8

Solubilities of 1,7-C<sub>60</sub>( $R_F$ )<sub>2</sub> compounds in toluene at 24(1) °C. The relative uncertainties for each measurement are less than or equal to  $\pm 3\%$ 



Solubilities of  $1,7-C_{60}(R_F)_2$  compounds in toluene at 24(1) °C. Uncertainties shown are  $\pm 3\%$ .

Cyclic voltammograms and square-wave voltammograms were recorded in dichloromethane, benzonitrile, and in 1,2-dichlorobenzene (*o*-DCB) for the seven 1,7-C<sub>60</sub>(R<sub>F</sub>)<sub>2</sub> compounds studied in this work. The electrolyte was 0.1 M N(*n*-Bu)<sub>4</sub><sup>+</sup>BF<sub>4</sub><sup>-</sup>. All measurements were performed with a scan rate of 100 mV/sec. The  $E_{1/2}$  values for the 0/–, –/2–, 2–/3–, and 3–/4– electrochemical processes listed in the tables below were determined using both ferrocene and decamethylferrocene as internal standards (CVs were recorded both before and after the addition of the ferrocenes), and are shown vs. the  $E_{1/2}$  value for the first reduction of C<sub>60</sub> under the same conditions.

d		$E_{1/2}$ values in dichlo	promethane, V vs C <sub>60</sub>	0/-
compound	0/-	-/2-	2-/3-	3-/4-
C <sub>60</sub>	0.00	-0.40	-0.85	—
$1,7-C_{60}(CF_3)_2$	0.15 <sup>a</sup>	-0.30	$(-0.80)^{b}$	(-1.25) <sup>b</sup>
$1,7-C_{60}(C_2F_5)_2$	$(0.17)^{b}$	$(-0.24)^{b}$	$(-0.78)^{b}$	(-1.26) <sup>b</sup>
$1,7-C_{60}(n-C_3F_7)_2$	0.13	-0.28	(-0.82)	—
$1,7-C_{60}(i-C_3F_7)_2$	0.14	-0.29	-0.82	—
$1,7-C_{60}(n-C_4F_9)_2$	0.11	-0.31	-0.84	(-1.30) <sup>b</sup>
$1,7-C_{60}(s-C_4F_9)_2$	0.14	-0.29	(-0.83) <sup>b</sup>	—
$1,7-C_{60}(n-C_8F_{17})_2$	0.15	(-0.27) <sup>b</sup>	$(-0.81)^{b}$	—

<sup>a</sup> Average of 4 measurements (estimated standard deviation = 0.004 V).

<sup>b</sup> Potentials in parentheses are from square-wave voltammetry.

compound	$E_{1/2}$ values in benzonitrile, V vs ${ m C_{60}}^{0/-}$				
	0/—	—/2—	2-/3-	3-/4-	
C <sub>60</sub>	0.00	-0.41			
$1,7-C_{60}(CF_3)_2$	0.13	-0.32	—		
$1,7-C_{60}(C_2F_5)_2$	0.13	-0.31	—		
$1,7-C_{60}(n-C_3F_7)_2$	0.13	-0.30	—		
$1,7-C_{60}(i-C_3F_7)_2$	0.10	-0.36	—		
$1,7-C_{60}(n-C_4F_9)_2$	0.14	-0.30	—		
$1,7-C_{60}(s-C_4F_9)_2$	0.10	-0.36	—		
$1,7-C_{60}(n-C_8F_{17})_2$	0.13	-0.34	—		

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Compound	Relative $E_{1/2}$ [V] vs $C_{60}^{0/-}$ in <i>o</i> -DCB			
	0/-	-/2	2-/3-	3–/4–
C <sub>60</sub>	0.00	-0.39	0.85	-1.31
$1,7-C_{60}(CF_3)_2$	0.13	-0.28	-0.81	-1.26
$1,7-C_{60}(C_2F_5)_2$	0.13	-0.30	-0.82	-1.29
$1,7-C_{60}(n-C_3F_7)_2$	0.13	-0.29	-0.82	(-1.29)
$1,7-C_{60}(i-C_3F_7)_2$	0.13	-0.31	-0.83	(-1.31)
$1,7-C_{60}(n-C_4F_9)_2$	0.13	-0.30	-0.83	-1.30
$1,7-C_{60}(s-C_4F_9)_2$	0.11	-0.32	(-0.85)	(-1.33)
$1,7-C_{60}(n-C_8F_{17})_2$	0.12	-0.30	-0.82	-1.28



Graphs of electron affinity vs.  $E_{1/2}(0/-)$  values for three sets of data from the literature and from this work. Ruoff et al. = R. S. Ruoff, K. M. Kadish, P. Boulas, and E. C. M. Chen, *J. Phys. Chem.*, 1995, **99**, 8843. Djurovich et al. = P. I. Djurovich, E. I. Mayo, S. R. Forrest, and M. E. Thompson, *Org. Electronics*, 2009, **10**, 515. Popov et al. = A. A. Popov, I. E. Kareev, N. B. Shustova, E. B. Stukalin, S. F. Lebedkin, K. Seppelt, S. H. Strauss, O. V. Boltalina, and L. Dunsch, *J. Am. Chem. Soc.*, 2007, **129**, 11551.

compound	EA, eV		$E_{1/2}(0/-)$ , V vs. $C_{60}^{0/-}$		$\Delta E$ solv, eV	
	exp.	DFT	exp.	DFT	DFT	
C <sub>60</sub>	2.685(8) <sup>b</sup>	2.642	0.00(1)	0.000	-1.083	
1,7-C <sub>60</sub> (CF <sub>3</sub> ) <sub>2</sub>	2.920(8)	2.767	0.13(1)	0.067	-1.026	
$1,7-C_{60}(C_2F_5)_2$	2.950(8)	2.793	0.13(1)	0.071	-1.004	
$1,7-C_{60}(i-C_3F_7)_2$	2.950(8)	2.803	0.13(1)	0.066	-0.989	
$1,7-C_{60}(n-C_3F_7)_2$	2.970(10)	2.808	0.13(1)	0.068	-0.986	
$1,7-C_{60}(s-C_4F_9)_2$	2.960(10)	2.823	0.11(1)	0.062	-0.964	
$1,7-C_{60}(n-C_4F_9)_2$	2.985(8)	2.826	0.13(1)	0.072	-0.971	
$1,7-C_{60}(n-C_8F_{17})_2$	3.010(8)	2.842	0.12(1)	0.069	-0.952	

Absolute values of experimental and DFT-computed EA,  $E_{1/2}(0/-)$ , and  $\Delta E_{solv}^{a}$ 

<sup>a</sup> All values from this work unless otherwise noted. The numbers in parentheses represent the experimental uncertainties. Note that the values listed in Table 1 of the main article are relative to the absolute values for  $1,7-C_{60}(CF_3)_2$ , not for  $C_{60}$ . The  $E_{1/2}(0/-)$  values listed in this table were measured in *o*-DCB. <sup>b</sup> This value is from X. B. Wang, H. K. Woo, and L. S. Wang, L. S. *J. Chem. Phys.*, 2005, **123**, 051106/1.

Information about the X-ray crystallographic study of 1,7-C<sub>60</sub>(*n*-C<sub>3</sub>F<sub>7</sub>)<sub>2</sub>·CDCl<sub>3</sub> (The references in this section are listed at the end of this section)

The  $1,7-C_{60}(n-C_3F_7)_2$  compound was crystallized by a slow evaporation of the CDCl<sub>3</sub> solution to form crystals of  $1,7-C_{60}(n-C_3F_7)_2$ ·CDCl<sub>3</sub> suitable for X-ray crystallography. Synchrotron radiation was employed for the data set collection due to the small size of the crystal (yellow needle,  $0.082 \times 0.054 \times 0.021$  mm, orthorhombic, *Pnma*, a = 9.9798(5) Å, b =6.4442(10) Å, c = 24.1424(14) Å, ChemMatCARS Sector 15-B at the Advanced Photon Source at Argonne National Laboratory, 100 K, diamond (111) crystal monochromator,  $\lambda = 0.41328$  Å). Other experimental and refinement parameters are available in the .cif file included in the Electronic Supporting Information for this article. Several types of disorder that have been encountered in other X-ray structures of fullerene  $(R_F)_n$  compounds also complicated the refinement of this structure: disorder of R<sub>F</sub> chains; fullerene-cage-orientation disorder; and disorder of the solvent molecule.

The refinement of fullerene structures with only a few substituents on the cage can be very challenging due to cage-orientation disorder. This was true for  $1,7-C_{60}(n-C_3F_7)_2$ ·CDCl<sub>3</sub>. The figure below (left) shows the major orientation of the molecule, which was refined anisotropically (see also the figure on the next page). In the case of the minor orientation (0.19 occupancy), the fullerene cage was refined isotropically. Cage-orientation disorder has been observed for the X-ray structures of underivatized fullerenes or derivatives with a low number of substituents. For example, fullerene-cage disorder was observed in  $1,7-C_{60}(i-C_3F_7)_2$  $C_{60}(CH_2Si(CH_3)_3)_2$ ,<sup>2</sup>  $C_{60}(C_6H_4OCH_3)(C_{11}H_{16}NSi)$ ,<sup>3</sup>  $Sc_3N@C_{80}(C_7H_7)_2$ ,<sup>4</sup>  $La_2@C_{78}(C_{10}H_{14})$ ,<sup>5</sup>  $Y@C_{82}(C_{10}H_{14})$ , <sup>6</sup> La@C<sub>72</sub>(C<sub>10</sub>H<sub>14</sub>), <sup>7</sup> and Ce<sub>2</sub>@C<sub>80</sub>(C<sub>2</sub>H<sub>4</sub>N(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>), <sup>8</sup> all of which have only two substituents or one cycloadduct per fullerene cage.



Rotational disorder within  $R_F$  chains is commonly observed in crystal structures of perfluoralkyl derivatives in general compounds and can require the application of modeling procedures.<sup>9</sup> The figure above (right) shows the disorder in the unique *n*-C<sub>3</sub>F<sub>7</sub> group in the structure of 1,7-C<sub>60</sub>(*n*-C<sub>3</sub>F<sub>7</sub>)<sub>2</sub>·CDCl<sub>3</sub>. In addition, one of the Cl atoms in the solvent molecule CDCl<sub>3</sub> is disordered (not shown), with two major positions have 0.86 and 0.14 occupancies. All three types of disorder led to a relatively high *R*<sub>1</sub> value of 0.0895 (*I* > 2 $\sigma$ (*I*)) and *wR*<sub>2</sub> value of 0.295. Although interatomic distances and angles cannot be discussed in detail, the location of the two *n*-C<sub>3</sub>F<sub>7</sub> substituents is not in doubt.

Taking into account the cage-orientation and  $R_F$  disorders, the structure of  $1,7-C_{60}(n-C_3F_7)_2$  has  $C_s$  symmetry, with the two symmetry-related  $n-C_3F_7$  groups attached to *para* positions of one of the twenty  $C_{60}$  hexagons, as shown in the drawings below (50% probability ellipsoids).



Note that the relative orientation of the two n-C<sub>3</sub>F<sub>7</sub> groups is *cisoid* rather than *transoid*. DFT calculations on C<sub>2</sub>F<sub>5</sub> derivatives of fullerenes have shown that the three possible relative orientations (there are two *cisoid* orientations) are equienergetic to within 3 kJ mol<sup>-1</sup>,<sup>10</sup> and therefore these orientations can easily be determined by crystal packing forces. In fact, all three relative orientations, shown below, have been observed in two structures with isolated *para*-C<sub>6</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>2</sub> hexagons, 1,7,16,36,46,49-C<sub>60</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>6</sub> and 1,6,11,18,24,27,32,35-C<sub>60</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>8</sub>.<sup>11</sup>



In the DFT calculations that we carried out on the  $1,7-C_{60}(R_F)_2$  derivatives in this work, the transoid relative orientation, which is always the lowest in energy, was employed. Two examples are shown below, for  $1,7-C_{60}(n-C_3F_7)_2$  and for  $1,7-C_{60}(n-C_8F_{17})_2$ .



Despite the several types of disorder in this structure, useful information about the solid-state packing in the structure of  $1,7-C_{60}(n-C_3F_7)_2$ ·CDCl<sub>3</sub> can be determined. The drawing below, on the left, is a packing diagram. The F atoms are small spheres and the Cl atoms are large spheres. All of the dotted lines involve Cl···F or, a few, Cl···C contacts. It looks as though the CDCl<sub>3</sub> molecules are involved in some sort of halogen–halogen bonding with the F atoms of the *n*-C<sub>3</sub>F<sub>7</sub> groups. It also looks like rows of fullerene molecules are "insulated" from adjacent rows by the *n*-C<sub>3</sub>F<sub>7</sub> groups.



With the caveat that defining the "centroid" of a substituted fullerene is a little arbitrary, a cage centroid ( $\Theta$ ) was defined, allowing  $\Theta \cdots \Theta$  distances for neighboring molecules to be determined. The drawing above, on the right, shows the centroids with nearly the same orientation as the packing plot (but slightly rotated). The short  $\Theta \cdots \Theta$  distances (solid lines) range from 9.98 to 10.15 Å (cf. C<sub>60</sub> at 100 K,<sup>12</sup> which is CCP with 12 equal  $\Theta \cdots \Theta$  distances of 9.94 Å). The long  $\Theta \cdots \Theta$  distances in 1,7-C<sub>60</sub>(*n*-C<sub>3</sub>F<sub>7</sub>)<sub>2</sub>·CDCl<sub>3</sub> are 14.6 (× 2) and 16.0 (× 2) Å. Note that the centroids in 1,7-C<sub>60</sub>(*n*-C<sub>3</sub>F<sub>7</sub>)<sub>2</sub>·CDCl<sub>3</sub> form a pseudo-HCP lattice with 8 short and 4 long distances (the "hexagonal" layer of seven centroids is vertical in the drawing above instead of horizontal).

References for the X-ray section of this ESI (the previous 4 pages)

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Absolute values of parameters cited in the Background section of the article

From the Background: Hammett  $\sigma_p$  values for CF<sub>3</sub>, C<sub>2</sub>F<sub>5</sub>, *i*-C<sub>3</sub>F<sub>7</sub>, *n*-C<sub>3</sub>F<sub>7</sub>, and *n*-C<sub>4</sub>F<sub>9</sub> only range from 0.48 (*n*-C<sub>3</sub>F<sub>7</sub>) to 0.54 (CF<sub>3</sub>), whereas  $\sigma_p$  values for a list of hundreds of neutral substituents range from -0.70 to 1.35.<sup>2</sup>

The actual values are: 0.54 for CF<sub>3</sub>, 0.53 for C<sub>2</sub>F<sub>5</sub>, 0.53 for *i*-C<sub>3</sub>F<sub>7</sub>, 0.48 for *n*-C<sub>3</sub>F<sub>7</sub>, and 0.52 for *n*-C<sub>4</sub>F<sub>9</sub>.

Ref 2: C. Hansch, A. Leo, and R. W. Taft, Chem. Rev., 1991, 91, 165.

From the Background: The  $E_{1/2}(0/-)$  value for *trans*-C<sub>2</sub>(CF<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>2</sub> is 60 mV more positive than for C<sub>2</sub>(CF<sub>3</sub>)<sub>4</sub>, suggesting that for these two olefins the C<sub>2</sub>F<sub>5</sub> group *is* more electron withdrawing than the CF<sub>3</sub> group.<sup>33</sup>

The actual values from Ref. 33 are -0.61 V vs. SCE for  $C_2(CF_3)_4$  and -0.55 V vs. SCE for *trans*- $C_2(CF_3)_2(C_2F_5)_2$  (0.1 M NEt<sub>4</sub>ClO<sub>4</sub> in acetonitrile).

Ref 33: C. Corvaja, G. Farnia, G. Formenton, W. Navarrini, G. Sandonà, and V. Tortelli, *J. Phys. Chem.*, 1994, **98**, 2307.

From the Background: In contrast, the  $E_{1/2}(0/-)$  values for 7,24-C<sub>70</sub>(R<sub>F</sub>)<sub>2</sub>, with R<sub>F</sub> = CF<sub>3</sub> or C<sub>2</sub>F<sub>5</sub>, only differed by 10 mV, which is within the uncertainty of the measurements, suggesting that C<sub>2</sub>F<sub>5</sub> *is not* more electron withdrawing than CF<sub>3</sub>, at least not for a large substrate like C<sub>70</sub>.<sup>34</sup>

The actual values from Ref. 34 are 0.28 V for 7,24- $C_{70}(CF_3)_2$  and 0.27 V for 7,24- $C_{70}(C_2F_5)_2$  (both vs.  $C_{70}^{0/-}$ ; 0.1 M N(*n*-Bu)<sub>4</sub>BF<sub>4</sub> in dichloromethane). For comparison, the  $E_{1/2}$  (0/–) value for  $C_{70}$  is 0.48 V vs. Fe(Cp\*)<sub>2</sub><sup>+/0</sup> in the same solvent with the same electrolyte.

Ref 34: A. A. Popov, N. B. Shustova, O. V. Boltalina, S. H. Strauss, and L. Dunsch, *ChemPhysChem*, 2008, **9**, 431.

From the Background: Furthermore, the cathodic peak potentials (note: not reversible  $E_{1/2}$  values) for three p-C<sub>6</sub>H<sub>4</sub>(CN)(R<sub>F</sub>) derivatives were the same to within ±10 mV for R<sub>F</sub> = n-C<sub>4</sub>F<sub>9</sub>, n-C<sub>6</sub>F<sub>13</sub>, and n-C<sub>8</sub>F<sub>17</sub>, suggesting no difference in electron-withdrawing ability for these R<sub>F</sub> groups.<sup>35</sup>

The actual values of the  $E_p$  potentials are -1.57 V for  $R_F = n-C_4F_9$ , -1.57 V for  $R_F = n-C_6F_{13}$ , and -1.58 V for  $R_F = n-C_8F_{17}$  (all vs. SCE; 0.1 M N(*n*-Bu)<sub>4</sub>BF<sub>4</sub> in dimethylformamide).

Ref 35: C. Combellas, F. Kanoufi, and A. Thiébault, J. Phys. Chem. B, 2003, 107, 10894.

From the Background: In addition, two other electrochemical studies of  $R_F$ -substituted perylene diimides found negligible differences in  $E_{1/2}(0/-)$  values when comparing  $CF_3$  vs.  $n-C_8F_{17}^{36}$  or when comparing  $n-C_4F_9$  vs.  $n-C_8F_{17}^{37}$ 

The actual values are shown below (all vs.  $Fe(Cp)_2^{+/0}$ ; 0.05 or 0.1 M N(*n*-Bu)\_4PF<sub>6</sub> in CH<sub>2</sub>Cl<sub>2</sub>).



Ref 36: Z. Yuan, J. Li, Y. Xiao, Z. Li, and X. Qian, J. Org. Chem., 2010, 75, 3007.
Ref 37: Y. Li, C. Li, W. Yue, W. Jiang, R. Kopecek, J. Qu, and Z. Wang, Org. Lett., 2010, 12, 2374.

From the Background: Consistent with this lack of an electronic difference for different  $R_F$  groups, a series of Ir(acac)(CO)<sub>2</sub>( $R_F$ )I complexes with  $R_F = CF_3$ ,  $C_2F_5$ , *i*- $C_3F_7$ , *n*- $C_3F_7$ , and *s*- $C_4F_9^{38}$  and a series of CpMo(CO)<sub>3</sub>( $R_F$ ) complexes with  $R_F = CF_3$ ,  $C_2F_5$ , and *n*- $C_3F_7^{39}$  each had the same average v(CO) value to within ±2 or ±1 cm<sup>-1</sup>, respectively.

The actual values are shown below:

trans-Ir(acac)(CO) <sub>2</sub> (CF <sub>3</sub> )Cl	v(CO) (CH <sub>2</sub> Cl <sub>2</sub> ): 2150, 2106 cm <sup>-1</sup> ; ave. 2128 cm <sup>-1</sup>
<i>trans</i> -Ir(acac)(CO) <sub>2</sub> (C <sub>2</sub> F <sub>5</sub> )Cl	v(CO) (CH <sub>2</sub> Cl <sub>2</sub> ): 2148, 2105 cm <sup>-1</sup> ; ave. 2127 cm <sup>-1</sup>
trans-Ir(acac)(CO) <sub>2</sub> ( $n$ -C <sub>3</sub> F <sub>7</sub> )C	Cl $v(CO)$ (CH <sub>2</sub> Cl <sub>2</sub> ): 2145, 2103 cm <sup>-1</sup> ; ave. 2124 cm <sup>-1</sup>
trans-Ir(acac)(CO) <sub>2</sub> (i-C <sub>3</sub> F <sub>7</sub> )C	<sup>cl</sup> $v(CO)$ (CH <sub>2</sub> Cl <sub>2</sub> ): 2149, 2104 cm <sup>-1</sup> ; ave. 2127 cm <sup>-1</sup>
trans-Ir(acac)(CO) <sub>2</sub> (s-C <sub>4</sub> F <sub>9</sub> )C	Cl $v(CO)$ (CH <sub>2</sub> Cl <sub>2</sub> ): 2147, 2104 cm <sup>-1</sup> ; ave. 2126 cm <sup>-1</sup>
CpMo(CO) <sub>3</sub> (CF <sub>3</sub> )	v(CO) (hexane): 2040, 1963, 1948 cm <sup>-1</sup> ; ave. 1984 cm <sup>-1</sup>
$CpMo(CO)_3(C_2F_5)$	v(CO) (hexane): 2040, 1966, 1944 cm <sup>-1</sup> ; ave. 1983 cm <sup>-1</sup>
$CpMo(CO)_3(n-C_3F_7)$	v(CO) (hexane): 2040, 1966, 1943 cm <sup>-1</sup> ; ave. 1983 cm <sup>-1</sup>

Ref 38: H. Huang, N. R. Hurubeanu, C. J. Bourgeois, S.-M. Cheah, J. Yuan, A. L. Rheingold, and R. P. Hughes, *Can. J. Chem.*, 2009, 87, 151.
Ref 39: H. Huang, R. P. Hughes, and A. L. Rheingold, *Organometallics*, 2010, 29, 1948.

From the Background: The DFT-predicted ionization energies of a series of  $BF_3(R_F)^-$  anions show that the CF<sub>3</sub> anion (relative ionization energy = 0 eV) is *harder* to oxidize than the C<sub>2</sub>F<sub>5</sub> (-0.058 eV), *n*-C<sub>3</sub>F<sub>7</sub> (-0.119 eV), or *n*-C<sub>4</sub>F<sub>9</sub> (-0.085 eV) anions (note also that this is not a monotonic trend).<sup>40</sup>

The actual values are 4.635 eV for BF<sub>3</sub>(CF<sub>3</sub>)<sup>-</sup>, 4.577 eV for BF<sub>3</sub>(C<sub>2</sub>F<sub>5</sub>)<sup>-</sup>, 4.516 eV for BF<sub>3</sub>(n-C<sub>3</sub>F<sub>7</sub>)<sup>-</sup>, and 4.550 eV for BF<sub>3</sub>(n-C<sub>4</sub>F<sub>9</sub>)<sup>-</sup> (B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) level of theory).

Ref 40: M. Ue, T. Fujii, Z.-B. Zhou, M. Takeda, and S. Kinoshita, *Solid State Ionics*, 2006, **177**, 323.

From the Background: The CCSD(T)-predicted relative ionization energies of a series of neutral  $R_FI$  compounds are 0, -0.020, and -0.118 eV for  $CF_3I$ ,  $C_2F_5I$ , and n- $C_3F_7I$ , respectively.<sup>41</sup> However, the CCSD(T)-predicted relative electron affinities for these three  $R_FI$  compounds showed the opposite trend, 0, 0.165, and 0.062 eV for  $CF_3I$ ,  $C_2F_5I$ , and n- $C_3F_7I$ , respectively.<sup>41</sup>

The actual values are shown below:

IP + ZPVE, eV	EA + ZPVE, eV
10.522	1.216
10.502	1.381
10.420	1.278
	IP + ZPVE, eV 10.522 10.502 10.420

Ref 41: L. Cheng, Z. Shen, J. Lu, H. Gao, and Z. Lü, Chem. Phys. Lett., 2005, 416, 160.