Structures and structure-related electronic properties of new $C_{60}(CF_3)_{10}$ isomers

Eric V. Bukovsky,^a Bryon W. Larson,^a Tyler T. Clikeman,^a Yu-Sheng Chen,^b

Alexey A. Popov,^{c,*} Olga V. Boltalina,^{c,*} and Steven H. Strauss^{c,*}

^a Department of Chemistry, Colorado State University, Fort Collins, CO 80523 (USA)

^b ChemMatCARS University of Chicago, Advanced Photon Source, Argonne, IL 60439 (USA)

^c Leibniz Institute for Solid State and Materials Research, Dresden 01069 (Germany)

Email addresses: ebukovsky@gmail.com; bwlarson@gmail.com; yschen@cars.uchicago.edu;
a.popov@ifw-dresden.de; olga.boltalina@colostate.edu; steven.strauss@colostate.edu

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Corresponding Author:

Professor Steven H. Strauss, Department of Chemistry, Colorado State University,
Fort Collins, CO 80523 USA, 970-227-0976 (phone), 970-491-1801 (fax),
steven.strauss@colostate.edu

Abstract

The largest collection of well-characterized homoleptic fullerene derivatives $C_{60}(X)_n$ is for $X = CF_3$ and $n = 2-18$. The largest subset of these with a given composition is the set of 27 isomers of $C_{60}(CF_3)_{10}$. The X-ray structures of five of them were reported previously. In this paper we report the X-ray structures of, and extensive DFT calculations on, eight additional $C_{60}(CF_3)_{10}$ isomers and the electrochemical reduction potentials of eight of the (now) 13 structurally-characterized isomers. The connections between their molecular structures (i.e., their addition patterns), the positions, extents of delocalization, and relative energies of their DFT-predicted LUMOs, and their first reduction potentials are compared and contrasted with each other and with the previously reported isomers. It is shown that addition patterns that produce the greatest number of non-terminal double bonds in fullerene pentagons are the best electron acceptors and tend to exhibit relatively small HOMO-LUMO gaps. A detailed analysis of the nearest-neighbor packing patterns in the 13 X-ray structures reveals significant differences in the number of nearest neighbor fullerene molecules and differences in the ranges of fullerene centroid...centroid distances even when the number of nearest neighbors is constant. Nevertheless, ten solvent-free structures exhibit nearly equally-efficient lattice packing arrays as far as crystal density is concerned. When the addition pattern results in two sterically-accessible $C(sp^2)_6$ hexagons on the fullerene surface, a one-dimensional chain of electronically-coupled nearest-neighbor $C_{60}(CF_3)_{10}$ molecules is formed.

1. Introduction

One of the most important properties of the hollow nanospheroidal molecules known as fullerenes is that they are excellent electron acceptors, as evidenced by their gas-phase electron affinities (EAs; e.g., 2.689(8), 2.77(1), and 2.98(1) eV for C_{60} [1], C_{70} [2], and $C_{76}-D_2(1)$ [3], respectively), and by their ability to undergo up to six reversible one-electron reductions in solution [4, 5]. It is therefore no surprise that fullerenes have been extensively studied as electron acceptors for energy storage, photovoltaic energy conversion, and other molecular electronic applications [6-8]. Ever since the discovery of fullerenes [9] and their availability in macroscopic quantities [10], chemists have prepared and studied fluorofullerenes (FFs) with the expectation that they would be even stronger electron acceptors [11-14]. Although FFs do have EAs in excess of 4 eV (e.g., 4.06(30) eV for $C_{60}F_{48}$ [15]), their usefulness in electronic devices is limited because they readily undergo reductive defluorination in condensed phases [16-20] and because at least some of them are unstable towards hydrolysis [21].

Complex mixtures of C_{60} derivatives with multiple electron-withdrawing perfluoroalkyl (R_F) groups were first prepared by Fagan, Krusic, et al. in 1993 [22]. Although the mixtures were not separated into individual compounds, the authors clearly demonstrated that $C_{60}(R_F)_n$ derivatives do not hydrolyze in contact with water and can be heated to at least 270 °C without decomposition. Since that time, hundreds of well-characterized, HPLC-purified compounds collectively known as perfluoroalkylfullerenes (PFAFs) have been reported, with fullerenes from C_{60} to C_{90} , with heterofullerenes and endohedral metallofullerenes, and with straight-chain and branched R_F groups from CF_3 to C_8F_{17} [23, 24]. PFAFs are now one of the largest classes of fullerene derivatives. For example, consider just one fullerene, C_{60} , and one type of R_F group, CF_3 . There are more than 60 well-characterized $C_{60}(CF_3)_n$ compounds, with even n values from 2 to 18 (there are multiple isomers known for all n values except $n = 2$) [24, 25]. Some PFAFs are stable at temperatures exceeding 350 °C, most are significantly stronger electron acceptors than

their respective parent fullerene, and many have been shown to have one-electron-reduced radical anions that are stable indefinitely in solutions of organic solvents at 25 °C [24].

The abbreviations we use to denote specific $C_{60}(CF_3)_n$ derivatives consist of three numbers. As an example, the two known isomers of $C_{60}(CF_3)_6$ are denoted 60-6-1 and 60-6-2. The first number indicates that the compound is a derivative of C_{60} ; the second number specifies the number of CF_3 groups (even numbers from 2 to 18); the third number is an arbitrary number denoting a particular isomer of that composition, that is to say, a particular addition pattern. In 2007 we published a spectroscopic, electrochemical, and DFT study of the 18 $C_{60}(CF_3)_n$ derivatives shown in Figure S-1 (Supporting Information) [26], including six isomers with the composition $C_{60}(CF_3)_{10}$, abbreviated 60-10-1 through 60-10-6 [26, 27]. The X-ray structures of 60-10-2 through 60-10-6 have been reported [26-30]. Although the addition pattern of 60-10-1 had not been verified by X-ray crystallography before this work, a combination of through-space Fermi-contact J_{FF} values in its ^{19}F NMR spectrum and DFT calculations allowed its most-likely molecular structure to be predicted [26] (note that all fullerene(CF_3) $_n$ compounds exhibit ^{19}F NMR through-space J_{FF} couplings for CF_3 groups that share the same hexagon or pentagon [26, 27, 31-36]).

In the course of the Ph.D. dissertation research of one of us [37], 21 additional isomers of $C_{60}(CF_3)_{10}$ were isolated. Crystals suitable for single-crystal X-ray diffraction have now been grown for seven of the new isomers, abbreviated 60-10-7, and 60-10-9 through 60-10-14, as well as for 60-10-1. In this work we report the X-ray structures of these eight isomers and a comparison of them with the structures of the five previously reported isomers. We also compare and contrast their DFT-predicted relative energies, the shapes and energies of their frontier molecular orbitals, and the electrochemically-determined first reduction potentials for eight of the 13 isomers.

2. Results and Discussion

2.1. Thirteen isomers of $C_{60}(CF_3)_{10}$

Crystal data, refinement parameters, and CCDC deposition numbers for the eight new X-ray structures are listed in Table 1. The structurally-characterized isomers of $C_{60}(CF_3)_{10}$ now number 13. Table 2 lists their abbreviations, addition patterns, point-group symmetries, IUPAC lowest locants, cyclic-voltammetric $E_{1/2}(0/-)$ values, and DFT-predicted relative energies and $E(\text{LUMO})$ values [26-30, 37, 38]. Five compounds either did not have an electrochemically quasi-reversible first reduction (60-10-12) or a sufficient amount of compound was not available for a cyclic voltammetric experiment (60-10-4, 60-10-7, 60-10-9, and 60-10-11), and for these compounds $E_{1/2}(0/-)$ values are not reported. Table 3 lists the crystal densities, idealized lattice packings, numbers of nearest neighbor fullerene molecules, and fullerene centroid...centroid ($\odot \cdots \odot$) distances for the 10 solvent-free X-ray structures. Schlegel diagrams for all 13 isomers are shown in Fig. 1. A plot of $E_{1/2}(0/-)$ vs. DFT-predicted $E(\text{LUMO})$ for eight of the isomers is shown in Fig. 2, which also shows how various arrangements of five independent $p\text{-}C_6(CF_3)_2$ hexagons on the surface of C_{60} can lead to $C_{60}(CF_3)_{10}$ addition pattern with ribbons of edge-sharing p - and $m\text{-}C_6(CF_3)_2$ hexagons and 1,3- $C_5(CF_3)_2$ pentagons.

2.2. Addition pattern guidelines for $C_{60}(CF_3)_n$ derivatives ($n \leq 12$).

With only a few exceptions, the addition patterns of $C_{60}(CF_3)_n$ derivatives with $n \leq 12$ were historically found to follow three guidelines [24, 26, 27], not only for the 18 compounds shown in Fig. S-1 [26] but also for two additional isomers of $C_{60}(CF_3)_4$ [29, 39]. The first guideline is that the CF_3 groups are arranged on one or more *para* (p) $C_6(CF_3)_2$ hexagons and/or on one or more ribbons or loops of edge-sharing *meta*- (m -) and/or $p\text{-}C_6(CF_3)_2$ hexagons (each shared edge is a cage $C(\text{sp}^3)\text{--}C(\text{sp}^2)$ bond). The *para-meta-para* (pmp) ribbon region in 60-4-1 is shown in Fig. S-2. The compound 60-6-1 has a p^3mp ribbon, and 60-8-2, 60-8-3, and 60-8-5 each have a

Table 1

Crystal data, refinement parameters, and CCDC deposition numbers for the X-ray structures of $C_{60}(CF_3)_{10}$ isomers 60-10-1, 60-10-7, and 60-10-9 through 60-10-14.

compound abbreviation	60-10-1 ^a	60-10-7 ^a	60-10-9 ^a	60-10-10 ^a	60-10-11·CDCl ₃ ^b	60-10-12 ^a	60-10-13 ^a	60-10-14·CHCl ₃ ^b
crystal system	triclinic	monoclinic	triclinic	monoclinic	triclinic	monoclinic	orthorhombic	triclinic
space group, <i>Z</i>	$P\bar{1}$, 4	$P2_1/c$, 4	$P\bar{1}$, 2	$C2/c$, 8	$P2_1/c$, 4	$P2_1/n$, 4	$P2_12_12_1$, 4	$P\bar{1}$, 2
<i>a</i> , Å	12.2718(6)	20.5157(8)	12.1441(6)	46.403(6)	12.253(1)	17.794(1)	11.521(1)	11.532(1)
<i>b</i> , Å	20.270(1)	12.1614(5)	12.3855(7)	12.115(2)	24.771(3)	13.1545(8)	19.77(2)	12.088(1)
<i>c</i> , Å	21.071(1)	20.1763(8)	17.3822(9)	17.249(3)	17.001(2)	20.108(1)	20.524(2)	19.854(2)
α , deg	113.470(1)	90	93.614(3)	90	90	90	90	72.791(4)
β , deg	101.524(1)	114.3613(8)	96.249(3)	104.164(7)	106.035(3)	102.099(2)	90	74.569(5)
γ , deg	90.041(1)	90	114.298(2)	90	90	90	90	85.305(5)
<i>V</i> , Å ³	4692.2(4)	4585.8(3)	2351.9(2)	9402(2)	4959.2(8)	4602.0(5)	4676.5(7)	2548.3(4)
ρ_{calc} g cm ⁻³	1.997	2.043	1.992	1.993	2.051	2.036	2.004	1.994
<i>T</i> , K	100(2)	100(2)	120(2)	120(2)	100(2)	100(2)	120(2)	120(2)
$R(F)$ ($I > 2\sigma(I)$) ^c	0.0567	0.0523	0.0520	0.0458	0.0716	0.0445	0.0644	0.0628
$wR(F^2)$ [all data] ^c	0.1420	0.1535	0.1556	0.1436	0.2217	0.1123	0.1651	0.2285
GOF	1.002	1.029	1.036	1.057	0.985	1.017	0.975	0.975
CCDC deposition number	1442897	1442898	1442900	1442901	1442902	1442903	1443790	1442899

^a The formula and formula weight for $C_{60}(CF_3)_{10}$ isomers 60-10-1, 60-10-7, 60-10-9, 60-10-10, 60-10-12, and 60-10-13 are $C_{70}F_{30}$ and 1410.70 g mol⁻¹, respectively. ^b The formulas for 60-10-11·CDCl₃ and 60-10-14·CHCl₃ are $C_{71}DF_{30}Cl_3$ and $C_{71}HF_{30}Cl_3$, respectively; their formula weights are 1531.08 and 1530.08 g mol⁻¹, respectively. ^c $R(F) = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$; $wR(F^2) = (\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2])^{1/2}$.

Table 2
Structurally Characterized C₆₀(CF₃)₁₀ Isomers.^a

abbreviation ^b	addition-pattern ^c	IUPAC lowest locants ^d	synthesis and isolation Ref.	X-ray Ref.	$E_{1/2}(0/-)$, vs. C ₆₀ ^{0/-} ^d	DFT predictions ^e	
						rel. energy, kJ mol ⁻¹	$E(\text{LUMO})$, eV
60-10-1	$C_1\text{-}p^3mpmp,p$	1,6,11,16,18,24,27,36,41,57	[27]	this work	0.65	9.22	-5.129
60-10-2	$C_1\text{-}p^3mpmpmp$	1,6,11,16,18,24,27,36,54,60	[27]	[28, 29]	0.38	0.06	-4.894
60-10-3	$C_1\text{-}pmp^3mpmp$	1,3,7,10,14,17,23,28,31,40	[27]	[27]	0.16	4.56	-4.754
60-10-4	$C_2\text{-}(p^3m^2\text{-loop})^2$	1,6,12,15,18,23,25,41,45,57	[26]	[30]	—	7.60	-4.529
60-10-5	$C_1\text{-}pmpmpmpmp$	1,6,11,16,18,26,36,41,44,57	[26]	[26]	0.12	1.25	-4.638
60-10-6	$C_1\text{-}p^3mp,pmp$	1,6,11,18,24,27,33,51,54,60	[26]	[38]	0.41	0.00	-4.922
60-10-7	$C_1\text{-}pmpmpmp,p$	1,6,11,16,18,28,31,36,42,56	[37]	this work	—	10.10	-4.816
60-10-9	$C_1\text{-}pmpmpmp,p$	1,6,11,16,18,28,31,36,44,58	[37]	this work	—	17.36	-4.829
60-10-10	$C_1\text{-}p^3mpmp,p$	1,6,11,16,18,24,27,36,50,60	[37]	this work	—	20.55	-4.924
60-10-11	$C_1\text{-}p^3mp,p,p$	1,6,11,14,18,24,27,31,53,56	[37]	this work	—	29.60	-5.090
60-10-12	$C_1\text{-}pmp^3mp,p$	1,3,7,10,14,17,28,31,43,55	[37]	this work	0.37	15.41	-4.867
60-10-13	$C_1\text{-}pmpmpmp,p$	1,6,11,16,18,25,36,45,54,60	[37]	this work	0.42	18.46	-4.938
60-10-14	$C_1\text{-}p^3mp,pmp$	1,6,11,18,24,27,34,50,52,55	[37]	this work	0.47	16.03	-4.983

^a All results from this work except as otherwise noted. A hypothetical addition pattern denoted 60-10-8 was discussed in Ref [24]. ^b The numbers 60 and 10 in the compound abbreviations refer to the fullerene (C₆₀) and number of CF₃ groups, respectively. The third number is an arbitrary index denoting the specific isomer. ^c The addition pattern abbreviations refer to the ribbons, loops, and/or isolated edge-sharing *meta*- (*m*) and *para*-C₆(CF₃)₂ (*p*) hexagons (each shared edge is a C(sp³)–C(sp²) bond) and also indicate the point-group symmetry. ^d The $E_{1/2}(0/-)$ potentials were measured in 1,2-C₆H₄Cl₂ containing 0.1 M N(*n*-Bu)₄PF₆ and Fe(Cp)₂ as an internal standard ($E_{1/2}(\text{Fe}(\text{Cp})_2^{+/0}) = 1.08$ V vs. C₆₀^{0/-}). ^e The DFT predicted results are from Refs. [37] and [40] except for 60-10-7 through 60-10-13, which are from this work.

Table 3Structural results for solvent-free X-ray structures of $C_{60}(CF_3)_{10}$ isomers.^a

compound abbreviation	60-10-1	60-10-2 ^b	60-10-3 ^c	60-10-4 ^d	60-10-6 ^e	60-10-7	60-10-9	60-10-10	60-10-12	60-10-13
data collection temp., K	100(2)	100(2)	173(2)	100(1)	100(2)	100(2)	120(2)	120(2)	100(2)	120(2)
ρ_{calc} , g cm ⁻³	1.997	2.033	2.040	2.072	2.054	2.043	1.992	1.993	2.036	2.004
idealized lattice packing ^f	NCP	CCP	HCP	HCP	NCP	HCP	HCP	HCP	CCP	NCP
number of nearest neighbors	13	12	12	12	14	12	12	12	12	13
$\odot \cdots \odot$ distances, Å	10.05– 14.56	9.95– 14.52	10.17– 14.17	9.93– 12.59	10.95– 14.47	10.86– 12.97	9.70– 13.74	10.07– 14.35	10.20– 13.96	10.13– 14.41
mean $\odot \cdots \odot$ distance, Å	12.57	11.87	11.90	11.81	12.26	11.85	12.01	12.12	11.97	12.63
median $\odot \cdots \odot$ distance, Å	12.31	11.97	12.03	12.09	11.87	11.87	12.14	12.12	11.95	11.88

^a All results from this work unless otherwise noted; $\odot$ = fullerene centroid. ^b Ref. [29]. ^c Ref. [27]. ^d Ref. [30]. ^e Ref. [38]. ^f HCP = hexagonal close packed; CCP = cubic close packed; NCP = not close packed.

Fig. 1. Schlegel diagrams for the 13 structurally-characterized isomers of $C_{60}(CF_3)_{10}$. The black circles indicate the cage C atoms to which the CF_3 groups are attached. The ribbons and loops of edge-sharing p - and m - $C_6(CF_3)_2$ hexagons and isolated p - $C_6(CF_3)_2$ hexagons are highlighted in yellow; the m - $C_6(CF_3)_2$ hexagons are indicated with the letter m . The bonds highlighted in red are *non-terminal* double-bonds-in-pentagons (*nt*-DBIPs). The X-ray structures of 60-10-1, 60-10-7, and 60-10-9 through 60-10-14 are reported for the first time in this work. A hypothetical addition pattern denoted 60-10-8 (not shown) was discussed in Ref. [24].

Fig. 2. First reduction potentials ($E_{1/2}(0/-)$ values) measured in 1,2-dichlorobenzene (*o*-DCB) for eight $C_{60}(\text{CF}_3)_{10}$ isomers vs. their DFT-predicted LUMO energies ($E(\text{LUMO})$ values). The data are listed in Table 1. The Schlegel diagrams for 60-10-2 (upper left) and 60-10-12 (lower right) show how the arrangement of five $p\text{-C}_6(\text{CF}_3)_2$ hexagons (highlighted in yellow) on the surface of C_{60} can lead to $C_{60}(\text{CF}_3)_{10}$ addition pattern with ribbons of edge-sharing p - and $m\text{-C}_6(\text{CF}_3)_2$ hexagons and 1,3- $\text{C}_5(\text{CF}_3)_2$ pentagons.

p^3mp ribbon plus a different isolated p - $C_{60}(CF_3)_2$ hexagon, so their addition patterns are denoted p^3mp,p . The first three isomers of $C_{60}(CF_3)_{10}$ have the addition patterns p^3mpmp,p (60-10-1), $p^3mpmpmp$ (60-10-2), and pmp^3mpmp (60-10-3). The second guideline is that there is only one CF_3 group per pentagon, undoubtedly for steric reasons. The only exceptions are 60-10-3 and 60-12-2. The third guideline is that CF_3 groups do not occupy adjacent cage $C(sp^3)$ atoms, also undoubtedly for steric reasons, and the only exceptions are 60-6-2 and 60-12-3.

There are millions of possible isomers of $C_{60}(CF_3)_{10}$, but only a limited number that have DFT-predicted relative energies ≤ 30 kJ mol $^{-1}$ (the DFT-predicted highest energy of the 13 structurally-characterized isomers, 60-10-11, is 29.60 kJ mol $^{-1}$). The Supporting Information in ref. [26] lists 36 $C_{60}(CF_3)_{10}$ low-energy isomers based on ribbons or loops of edge-sharing p - and m - $C_6(CF_3)_2$ hexagons (i.e., based on the $C_{60}(CF_3)_n$ guidelines discussed above for $n \leq 12$).

There are only three possible single-ribbon addition patterns with five edge-sharing p - and m - $C_6(CF_3)_2$ hexagons and no 1,3- $C_5(CF_3)_2$ pentagons. The compounds 60-10-2 ($p^3mpmpmp$) and 60-10-5 ($pmpmpmpmp$) are two of these, and they are within 1.25 kJ mol $^{-1}$ of the lowest-energy isomer, which is the p^3mp,pmp isomer 60-10-6. The third is a different $pmpmpmpmp$ isomer, yet to be isolated and identified, with a relative energy of 8.01 kJ mol $^{-1}$ [26]. There is only one possible single-ribbon isomer that includes a 1,3- $C_5(CF_3)_2$ pentagon that forms an isolated fulvene-like portion of the fullerene π system, and that is the pmp^3mpmp isomer 60-10-3. No single-ribbon isomers with p^4 addition-pattern fragments are possible for C_{60} , because four consecutive edge-sharing p - $C_6(CF_3)_2$ hexagons on C_{60} produces a p^4 loop like the ones that are part of the addition patterns of 60-6-2 and 60-12-3, not a p^4 ribbon. (Note that higher-fullerene CF_3 derivatives *can* have p^n ribbons with $n \geq 4$; some examples are p^7mp - $C_{70}(CF_3)_{10}$ [41], p^9 -($C_{78}-C_{2v}(2)$)(CF_3) $_{10}$ [33], p^5,p^5 -($C_{78}-D_{3h}(1)$)(CF_3) $_{10}$ [33], p^{11} -($C_{78}-D_{3h}(5)$)(CF_3) $_{12}$ [42], and p^6,p^2,p -($C_{84}-C_{2v}(11)$)(CF_3) $_{12}$ [43].)

There are eleven "8+2" addition patterns among the DFT-predicted low-energy isomers, either p^3mpmp,p pmp^3mp,p , or $pmpmpmp,p$, and six of them are now known with certainty: 60-

10-1, 60-10-7, 60-10-9, 60-10-10, 60-10-12, and 60-10-13. There is one other p^3mpmp,p isomer that is possible (21.01 kJ mol⁻¹, very similar to 60-10-10) and four other possible $pmpmpmp,p$ isomers (10.05, 16.67, 18.71, and 18.78 kJ mol⁻¹) yet to be isolated and identified [26].

There are seventeen "6+4" addition patterns among the DFT-predicted low-energy isomers [26], and only two of them, the p^3mp,pmp isomers 60-10-6 and 60-10-14, have been verified by X-ray crystallography. As of this writing none of the following C₆₀(CF₃)₁₀ addition patterns have been confirmed crystallographically: p^3mp,p^3 ; $pmpmp,pmp$; $pmpmp,p^3$; SPP, pmp ; and SPP, p^3 (the SPP addition-pattern fragment is the one exhibited by 60-6-2 [29] (see Fig. S-1)).

The highest energy addition pattern among the 13 structurally-characterized C₆₀(CF₃)₁₀ isomers is the $pmpmp,p,p$ "6+2+2" isomer 60-10-11 (29.60 kJ mol⁻¹). Although its structure does follow the addition-pattern guidelines, it was not listed in the Supporting Information for Ref. [26]. Interestingly, there is an as-yet-unknown p^3mp,p,p isomer predicted to have a relative energy of only 14.08 kJ mol⁻¹ [26]. It is possible that some of the yet-to-be identified isomers referred to above are among the 14 additional new isomers of C₆₀(CF₃)₁₀ that have been isolated [37] but have not yet been characterized by X-ray crystallography.

Note that many of the 13 C₆₀(CF₃)₁₀ structures have ribbons or parts of ribbons in common. The most obvious is that 60-10-3 and 60-10-12 both have a pmp^3mp ribbon. Isomers 60-10-5, 60-10-7, 60-10-9, and 60-10-13 all have a $pmpmpmp$ ribbon. Eight isomers have a p^3mp ribbon (60-10-1, 60-10-2, 60-10-3, 60-10-6, 60-10-10, 60-10-11, 60-10-12, and 60-10-14), and four of these have a p^3mpmp ribbon (60-10-1, 60-10-2, 60-10-3, and 60-10-10).

2.3. The molecular structures of 60-10-1, 60-10-7, and 60-10-9 through 60-10-14.

A thermal ellipsoid plot of the structure of 60-10-12 is shown in Fig. 3. Thermal ellipsoid plots for the other seven C₆₀(CF₃)₁₀ isomers reported in this work are shown in Figs. S-3 and S-4. There are two independent asymmetric C₆₀(CF₃)₁₀ molecules in the structure of 60-10-1. The

Fig. 3. Drawings of the X-ray structures of C_{60} (lower left; Ref. [44]) and 60-10-12, including a 50% probability thermal ellipsoid plot (top left; F atoms highlighted in yellow). Portions of the 60-10-12 structure on the right show F...F distances between proximal CF_3 groups and the conformations of the CF_3 groups attached to C1 and C10. The smallest C–C–C–F torsion angles for these two CF_3 groups are 12.1° (i.e., significantly eclipsed) and 58.8° (i.e., staggered), respectively. The orientation of the 60-10-12 cage (middle left, CF_3 groups not shown) is not the same as the orientation in the thermal ellipsoid plot.

asymmetric unit in each of the structures of 60-10-7 and 60-10-9 through 60-10-14 is a single asymmetric $C_{60}(CF_3)_{10}$ molecule, with 90 unique cage C–C bonds, plus a solvent molecule in the cases of 60-10-11 and 60-10-14. All eight structures contain an equal number of both $C_{60}(CF_3)_{10}$ enantiomers, and none of the eight structures exhibits molecular disorder (i.e., the enantiomers are not randomly superimposed on a given site in any of the structures). In addition, none of the CF_3 groups in any of the structures is disordered (i.e., none exhibits multiple conformations due to rotations about their respective $F_3C-C(\text{cage})$ single bonds). The C–F distances and F–C–F angles in the CF_3 groups are normal (e.g., 1.301(3)–1.336(2) Å and 106.1(2)–108.7(2)°, respectively, in 60-10-9), as are the $F_3C-C(\text{cage})$ distances (e.g., 1.539(3)–1.553(3) Å in 60-10-9).

In compounds such as *m*- and *p*- $C_6H_4(CF_3)_2$ the $F_3C-C(sp^2)$ bonds lie in the same plane as the aromatic C_6 hexagon. This is not the case for the *m*- and *p*- $C_6(CF_3)_2$ hexagons in $C_{60}(CF_3)_n$ compounds due to the curvature of the fullerene cage. For example, in 60-10-7 the angles between the $F_3C-C(sp^3)$ bonds and the least-squares plane of the four $C(sp^2)$ atoms in the isolated $C_6(CF_3)_2$ hexagon are $154 \pm 1^\circ$.

In general, the CF_3 groups in the structures of 60-10-7 and 60-10-9 through 60-10-14 are staggered with respect to their three underlying cage $C(sp^3)-C(sp^2)$ bonds. Two exceptions are the pair of CF_3 groups on the 1,3- $C_5(CF_3)_2$ pentagon in 60-10-12, as shown in Fig. 2. The proximity of CF_3 groups on the 1,3- $C_5(CF_3)_2$ pentagons in 60-10-12, 60-10-3, and 60-12-2 and the *m*- and *p*- $C_6(CF_3)_2$ hexagons in all $C_{60}(CF_3)_n$ derivatives results in $F\cdots F$ contacts ≤ 2.9 Å over the shared hexagons or pentagons, and these contacts in turn result in through-space Fermi contact $^{6,7}J_{FF}$ nuclear spin-spin couplings observed in their ^{19}F NMR spectra [24, 27, 33, 37, 40, 45]. The instantaneous $^{6,7}J_{FF}$ values range from 70–180 Hz, but only time-averaged 8–20 Hz splittings are observed for fullerene(CF_3) $_n$ derivatives due to rapid rotation of the CF_3 groups on the NMR timescale. When rotational averaging does not occur, as in *p*- $C_6(i-C_3F_7)_2$ hexagons in the compounds $C_2-C_{60}((i-C_3F_7)_4$ [46] and $C_3-C_{60}((i-C_3F_7)_6$ [47], the $^7J_{FF}$ values observed for

the $(\text{CF}_3)_2\text{C}-\text{F}\cdots\text{F}-\text{C}(\text{CF}_3)_2$ interactions of 2.61 and 2.66 Å, respectively, were found to be 172 and 160 Hz, respectively [24].

The curvature of C_{60} also requires that its $\text{C}(\text{sp}^2)$ atoms cannot be coplanar with their three nearest neighbors. Each C_{60} vertex is common to two hexagons and one pentagon [48, 49], unlike the rigorously planar $\text{C}(\text{sp}^2)$ atoms in graphite, which are at the junction of three hexagons (the interior angles for the cage $\text{C}(\text{sp}^2)$ atoms in $\text{C}_{60}(\text{CF}_3)_n$ structures are $109 \pm 1^\circ$ for their pentagons and $120 \pm 2^\circ$ for their hexagons). The distortion from planarity introduces significant non-planar strain energy into C_{60} , believed to be ca. $33 \text{ kJ mol}^{-1} \text{ C-atom}^{-1}$ [50]. The exohedral derivatization of fullerenes is driven, in large measure, by the relief of this strain as substituents (such as CF_3 groups) are added to some cage C atoms, changing their hybridization from nominally $\text{C}(\text{sp}^2)$ to $\text{C}(\text{sp}^3)$ [51].

The degree to which fullerene cage atoms are non-planar can be defined by a vector through each cage C atom that makes equal angles, φ , to its three nearest neighbors [49]. A pyramidalization figure of merit, θ , is defined as $\theta = \varphi - 90^\circ$ (i.e., for an ideal planar $\text{C}(\text{sp}^2)$ atom $\theta = 0^\circ$ (i.e., $90^\circ - 90^\circ$) and for an ideal $\text{C}(\text{sp}^3)$ atom $\theta = 19.5^\circ$ (i.e., $109.5^\circ - 90^\circ$)) [52]. The value of θ for the cage C atoms in DFT-optimized icosahedral C_{60} is 11.64° ; for the X-ray structure of C_{60} discussed above the values of θ ranged from 11.4 to 11.9° [44].

The distortion of the C_{60} cage from icosahedral symmetry caused by the addition of 10 CF_3 groups can be seen in Fig. 2 for 60-10-12. The 10 cage $\text{C}(\text{sp}^3)$ atoms are clearly more pyramidal than the 50 remaining cage $\text{C}(\text{sp}^2)$ atoms. Their θ angles range from 22.0 to 23.5° . Since fullerenes and their derivatives are *closed* carbon cages, the average θ angle for all 60 cage atoms must be essentially constant regardless of the degree of derivatization. As a consequence, most of the remaining cage $\text{C}(\text{sp}^2)$ atoms in fullerene derivatives must be less pyramidal than in C_{60} itself. In 60-10-12, the average θ angle for the 50 remaining $\text{C}(\text{sp}^2)$ atoms is 9.4° (they range from 5.1 to 12.4°). Therefore, the addition of substituents to C_{60} makes some cage atoms more pyramidal because they have become sp^3 hybridized, and makes the remaining $\text{C}(\text{sp}^2)$ atoms, on

average, less pyramidal, both of which are stabilizing changes with respect to the non-planar strain in underivatized C_{60} . The ranges and average values of the $C(sp^3)$ and $C(sp^2)$ θ angles for all $C_{60}(CF_3)_{10}$ isomers are essentially the same.

2.4. *The presence of double bonds in pentagons.*

The 90 cage $C(sp^2)$ – $C(sp^2)$ bonds in DFT-optimized C_{60} are divided into 30 short hexagon–hexagon edges (1.399 Å) and 60 long pentagon–hexagon edges (1.453 Å) [26]. This was verified in the aforementioned ordered and precise X-ray structure of underivatized C_{60} , which is in a co-crystal with a platinum porphyrin [44]. In that structure the C_{60} molecule is on a general position, making all 90 C–C bonds unique, allowing the small variations in their distances due to packing forces to be observed. Fig. 4 shows that these bonds are indeed divided into 30 short ones, 1.379(3)–1.396(3) Å, all of which are hex–hex edges, and 60 long ones, 1.440(3)–1.461(3) Å, all of which are pent–hex edges. The hex–hex and pent–hex edges are usually referred to as "double" and "single" bonds, respectively, although this is an oversimplification because all 90 $C(sp^2)$ – $C(sp^2)$ bonds are conjugated with one another and therefore they all have some degree of double-bond character. The short bond/long bond discontinuity in C_{60} and theoretical results on $C_{60}X_n$ derivatives [53, 54] have led to the oft-quoted "rule" that double bonds in pentagons (DBIPs) in fullerene derivatives are destabilizing, presumably because of angle strain [49].

The most precise $C_{60}(CF_3)_{10}$ X-ray structures are of 60-10-2 [28], 60-10-3 [27], 60-10-7, and 60-10-9 (the average cage C–C standard error is ± 0.0016 Å for 60-10-2 and 60-10-7 and ± 0.003 Å for 60-10-3 and 60-10-9). A plot of the 90 DFT-predicted vs. X-ray cage C–C distances in the structure of 60-10-9 is also shown in Fig. 4. They span a range from 1.346(3) Å for the shortest $C(sp^2)$ – $C(sp^2)$ bond to 1.553(3) Å for the longest $C(sp^2)$ – $C(sp^3)$ bond. The nearly-continuous range of $C(sp^2)$ – $C(sp^2)$ distances, from 1.346(3) to 1.474 (3) Å in 59 increments that average

Fig. 4. X-ray vs. DFT cage C–C distances in the $C_{60}(CF_3)_{10}$ isomer 60-10-9 (top) and the 90 cage C–C distances determined by X-ray crystallography in the C_{60} molecule in $C_{60}\cdot Pt(OEP)\cdot 2C_6H_6$ (Ref. [44]; OEP = the dianion of octaethylporphyrin). The error bars for the X-ray distances in both plots are $\pm 3\sigma$. In both structures the fullerene molecule is on a general position and therefore all 90 cage C–C bonds are unique.

0.002 Å, blurs the distinction between "single" and "double" bonds in fullerene derivatives with multiple substituents (similar plots for 60-10-2, 60-10-3, and 60-10-7 are shown in Fig. S-5). These plots also show how well the DFT code we use reliably duplicates the observed cage C–C bond distances in the X-ray structure at the $\pm 3\sigma$ level of precision.

Although most of the shorter cage C–C bonds in the $C_{60}(CF_3)_{10}$ X-ray structures are the 20 remaining $C(sp^2)$ – $C(sp^2)$ hex–hex edges, five of the shortest cage C–C bonds are pent–hex edges, as shown in Fig. 5 (similar plots for 60-10-2 and 60-10-7 are shown in Fig. S-6). This is because a short pent–hex edge, with significant double-bond character, is always formed when substituents are added to the *para* positions of a C_{60} hexagon, and five p - $C_6(CF_3)_2$ hexagons are distributed on the surface of C_{60} in all 13 of the $C_{60}(CF_3)_{10}$ isomers except 60-10-4 (the two loops in 60-10-4 are not made with five p - $C_6(CF_3)_2$ hexagons). The five short pent–hex bonds are of two types, those with only one $C(sp^2)$ nearest neighbor (i.e., terminal double bonds in pentagons (*t*-DBIPs)) and those with two $C(sp^2)$ nearest neighbors (i.e., non-terminal double bonds in pentagons (*nt*-DBIPs)). The *nt*-DBIPs are highlighted in red in the Schlegel diagrams in Fig. 1 and elsewhere in this paper. Not counting 60-10-4, the fewest *nt*-DBIPs in a $C_{60}(CF_3)_{10}$ isomer is one, in 60-10-5, which therefore has four *t*-DBIPs. The greatest number of *nt*-DBIPs is four, in 60-10-11, which therefore has only one *t*-DBIP. The unusual isomer 60-10-4 actually has six DBIPs, two *nt*-DBIPs and four *t*-DBIPs.

The Schlegel diagram for 60-10-9 in Fig. 5 is annotated with the 60 remaining cage $C(sp^2)$ – $C(sp^2)$ bond distances in pm ($\pm 3\sigma$ is less than ± 1 pm). The longest of the five DBIPs in 60-10-9, one of the two *nt*-DBIPs, is 137(1) pm (i.e., 1.367(3) Å). All of the other 35 pent–hex $C(sp^2)$ – $C(sp^2)$ distances in 60-10-9 are longer than 141(1) pm, and all of the 20 hex–hex $C(sp^2)$ – $C(sp^2)$ distances are 140(1) pm or shorter.

Fig. 5. Top: Schlegel diagram for the $C_{60}(CF_3)_{10}$ isomer 60-10-9 annotated with the cage $C(sp^2)$ – $C(sp^2)$ bond distances in pm ($\pm 3\sigma$ is less than ± 1 pm). The *nt*-DBIPs are highlighted in red. Bottom: Plot of the 11 shortest $C(sp^2)$ – $C(sp^2)$ bonds in 60-10-9 (the error bars shown are $\pm 3\sigma$).

Fig. 6. Schlegel diagrams, DFT-predicted LUMOs, and $E_{1/2}(0/-)$ values for the $C_{60}(CF_3)_{10}$ isomers 60-10-1, 60-10-2, and 60-10-3. The bonds highlighted in red are nt -DBIPs. The blue (+) and green (-) circles in the middle Schlegel diagrams represent the exohedral lobes of the p- π atomic orbitals for cage C atoms scaled approximately to their contribution to the LUMO.

2.5. The electronic significance of double bonds in pentagons.

In 2007 we reported that the number and positions of *nt*-DBIPs in $C_{60}(CF_3)_n$ derivatives, and by inference in other $C_{60}(X)_n$ derivatives, are correlated with the positions, extents of delocalization, and relative energies of their LUMOs, and hence with their $E_{1/2}(0/-)$ values [26]. Fig. 6 shows this effect in an unambiguous and dramatic way. The DFT-predicted LUMOs of 60-10-1, 60-10-2, and 60-10-3 all include large contributions from their *nt*-DBIP carbon atoms [26]. In all three cases, the two *nt*-DBIPs associated with the p^3 portion of their addition-pattern form a fulvene-like fragment of the π system. The fulvene fragment in 60-10-3 is isolated from the rest of the π system, and the LUMO is essentially confined to this fragment. In 60-10-2, the fulvene fragment is not isolated from the rest of the π system, and the LUMO is delocalized over several $C(sp^2)$ atoms on adjacent hexagons. As a result, 60-10-2 has a lower DFT-predicted LUMO energy than 60-10-3 and is 0.22 V easier to reduce than 60-10-3. The compound 60-10-1 has a third *nt*-DBIP, and its position relative to the fulvene-like fragment leads to a much more delocalized LUMO than in 60-10-2 or 60-10-3. The significant difference in LUMO delocalization results in 60-10-1 being 0.27 V easier to reduce than 60-10-2 and 0.49 V easier to reduce than 60-10-3.

Three of the 18 $C_{60}(CF_3)_n$ compounds previously studied by cyclic voltammetry were found to be *harder to reduce* than C_{60} itself, namely 60-6-2, 60-12-1, and 60-12-3 [26]. At the time this was a very surprising result. Even with 12 strong electron-withdrawing CF_3 substituents, 60-12-1 was found to be 0.17 V harder to reduce than underivatized C_{60} . Significantly, as shown by their Schlegel diagrams in Fig. S-1, they have no *nt*-DBIPs (i.e., 60-6-2 has three *t*-DBIPs and no *nt*-DBIPs, and 60-12-1 and 60-12-3 have six *t*-DBIPs and no *nt*-DBIPs). For the first time it became clear that the addition pattern is as important as, if not more important than, the number of substituents or the electronic properties of the substituents in fullerene derivatives [26].

The range of $E_{1/2}(0/-)$ values listed in Table 2 and plotted against their respective $E(\text{LUMO})$ values in Fig. 2 is 0.53 V. The range of values for $C_{60}(CF_3)_6$, $C_{60}(CF_3)_8$, and $C_{60}(CF_3)_{12}$ isomers

reported in ref [26] are 0.33, 0.39, and 0.48 V, respectively. These large variations in first reduction potentials far exceed the ranges for any other set of $C_{60}(X)_n$ isomers. The next largest $E_{1/2}(0/-)$ ranges reported in the literature are 0.14 and 0.16 V for eight isomers of $C_{60}(c\text{-CH}_2\text{N(R)CH}_2)_2$ [55] and seven isomers of $C_{60}(\text{C}(\text{CO}_2\text{Et})_2)_3$ [56], respectively.

The structural, electrochemical, and DFT characterization of the seven new $C_{60}(\text{CF}_3)_{10}$ isomers reported in this work (i.e., 60-10-7 and 60-10-9 through 60-10-14) has allowed us to further explore the connections between addition patterns, *nt*-DBIPs, LUMO energies, and $E_{1/2}(0/-)$ reduction potentials, that is, the links between the molecular and electronic structures of $C_{60}(\text{CF}_3)_{10}$ isomers. Several points about the plot in Fig. 2 are noteworthy. The two lowest $E_{1/2}(0/-)$ values are for 60-10-5 and 60-10-3, and both isomers have a single-ribbon addition pattern. Furthermore, the $E_{1/2}(0/-)$ value for 60-10-5, an isomer with only one *nt*-DBIP, is lower than for 60-10-3, which has two *nt*-DBIPs. In contrast, the four highest $E_{1/2}(0/-)$ values are for 60-10-6, 60-10-13, 60-10-14, and 60-10-1, and all of them have either a two-ribbon addition pattern (60-10-6 and 60-10-14) or a ribbon plus an isolated *p*- $\text{C}_6(\text{CF}_3)_2$ hexagon (60-10-1 and 60-10-13). Three of these four high-potential isomers have three *nt*-DBIPs. The isomer 60-10-13 has only two *nt*-DBIPs, but as discussed below these two *nt*-DBIPs are in close proximity and lead to an extensively delocalized LUMO with a relatively low energy.

Three new examples of the connections between the number and positions of *nt*-DBIPs and the positions, extents of delocalization, and energies of $C_{60}(\text{CF}_3)_{10}$ LUMOs are shown in Fig. 7. The two LUMO-Schlegel diagrams on the left show that the consequence of the isolated *p*- $\text{C}_6(\text{CF}_3)_2$ hexagon in 60-10-12 is to give this isomer a third *nt*-DBIP to go along with the two contained in the isolated fulvene fragment. The isomer 60-10-3 has only the two isolated-fulvene *nt*-DBIPs. For these reasons, the 60-10-12 LUMO is much more extensively delocalized than the 60-10-3 LUMO, and as a result 60-10-12 is 0.21 V easier to reduce than 60-10-3. The two isomers 60-10-6 and 60-10-14 have very similar *p*³*mp*,*pmp* addition patterns that involve the same

Fig. 7. Schlegel diagrams with *nt*-DBIPs highlighted in red, LUMO-Schlegel diagrams, and representations of the LUMOs for six of the thirteen structurally characterized $\text{C}_{60}(\text{CF}_3)_{10}$ isomers. The blue (+) and green (-) circles in the LUMO-Schlegel diagrams represent the exohedral lobes of the $p-\pi$ atomic orbitals for cage C atoms scaled approximately to their contributions to the LUMO.

eight C₆₀ hexagons. Nevertheless, the two LUMO-Schlegel diagrams in the middle of Figure 7 demonstrate that the *nt*-DBIP formed by the *pmp* ribbon in 60-10-14 is closer to, and is more extensively delocalized with, the other two *nt*-DBIPs in its LUMO than is the case in 60-10-6. As a result, 60-10-14 is easier to reduce than 60-10-6, albeit in this case by only 0.06 V. Finally, the *pmpmpmpmp* and *pmpmpmp,p* addition patterns of 60-10-5 and 60-10-13 are very similar, having the positions of eight of their 10 CF₃ groups in common. However, 60-10-5 has only one *nt*-DBIP. The presence of two *nt*-DBIPs in 60-10-13, and their close proximity, results in a very delocalized LUMO relative to 60-10-5, as shown by the two LUMO-Schlegel diagrams on the right in Fig. 7. The seemingly minor change in the addition pattern results in a major change in the LUMO and makes 60-10-13 significantly easier to reduce, by 0.3 V, than 60-10-5.

One final link between the molecular and electronic structures of C₆₀(CF₃)₁₀ isomers that is not yet fully understood is the correlation between the HOMO-LUMO gap (i.e., the absolute value of $E(\text{HOMO}) - E(\text{LUMO})$) and the number of *nt*-DBIPs, which is shown in Fig. S-7. Although the ranges of HOMO-LUMO gaps overlap, there is a clear trend. Isomers with more *nt*-DBIPs tend to have smaller HOMO-LUMO gaps. This may be a general result for C₆₀(CF₃)_{*n*} isomers, not only for isomers with *n* = 10, and this correlation will be investigated in more detail in a future study.

2.6. Solid-State Packing of C₆₀(CF₃)₁₀ Isomers

It is widely believed that the number of electronically coupled nearest neighbor fullerene derivative electron acceptors and their three-dimensional arrangement are among the key factors that determine charge transport properties in the fullerene domains in Type II heterojunction solar cells (see Ref. [57] and references therein). Accordingly, the determination of the number of nearest neighbor fullerene derivatives is important, and it depends on the choice of the maximum relevant fullerene centroid...centroid (⊙...⊙) distance beyond which fullerene–fullerene electronic coupling is probably negligible.

Before discussing the solid-state packing of the 10 solvent-free $C_{60}(CF_3)_{10}$ structures, it is instructive to review the solid-state packing of the solvent-free X-ray structures of two C_{60} derivatives with only a single cycloadduct substituent and therefore with only two cage $C(sp^3)$ atoms, 1,9- $C_{60}(cyclo-CF_2(2-C_6F_4))$ (hereinafter known as the faux-hawk fullerene, or FHF) [57] and phenyl- C_{61} -butyric acid methyl ester (hereinafter known as PCBM) [58], both of which are shown in Figure S-8 (note that the two cage $C(sp^3)$ atoms are adjacent to one another). The substituents in these two derivatives have nearly the same number of non-hydrogen atoms, 13 for FHF and 14 for PCBM, but the FHF substituent is clearly more compact. There are only seven nearest-neighbor fullerene molecules in crystalline solvent-free PCBM, with $\odot \cdots \odot$ distances of 9.95–10.28 Å (the mean and median distances are 10.17 and 10.24 Å, respectively). On the other hand, there are 10 nearest neighbors in the structure of FHF, with $\odot \cdots \odot$ distances of 9.74–10.34 Å (the mean and median distances are 10.09 and 10.05 Å, respectively). The result is that the 1.885 g cm⁻³ density of crystalline solvent-free FHF is 15.6% higher than the 1.631 g cm⁻³ density of crystalline solvent-free PCBM even though the molar masses of the two compounds, 918.67 g mol⁻¹ for FHF and 910.83 g mol⁻¹ for PCBM, differ by only 1.1%. This comparison shows that fullerene derivatives that appear to be sterically similar can have very different packing patterns in the solid state (and presumably in thin films as well), including the number of closely-approaching nearest neighbors.

After the seven closest nearest neighbors in the structure of PCBM, the two next shortest $\odot \cdots \odot$ distances are 11.61 and 13.23 Å. On what basis was the 11.61 Å molecule excluded as an electronically-relevant nearest neighbor? The criterion used in Ref. [57] is as follows. The 11.61 Å distance was considered to be too long for effective electronic coupling because the closest $C_{cage} \cdots C_{cage}$ distance between these two PCBM molecules is 5.03 Å. In contrast, the closest $C_{cage} \cdots C_{cage}$ distances for PCBM molecules with $\odot \cdots \odot$ separations of 10.28 and 10.24 Å are 3.23 and 3.32 Å, respectively, approximately the same as the 3.35 Å interplanar separation in graphite [59]. For FHF, the closest $C(cage) \cdots C(cage)$ distance between two molecules with a

separation of 10.34 Å is 3.38 Å, and the next closest $\odot\cdots\odot$ distances are 14.00 Å. Finally, note that one of the $\odot\cdots\odot$ separations in FHF, 9.74 Å, is actually shorter than the $\odot\cdots\odot$ distance of 9.94 Å in the cubic close-packed structure of pure crystalline C_{60} [60].

The isomers of $C_{60}(CF_3)_{10}$ are composed of 100 non-hydrogen atoms, and as such would not be expected to have multiple short $\odot\cdots\odot$ separations as in C_{60} , FHF, and PCBM. Nevertheless, the distances listed in Table 3 show that the X-ray structures of 10 of the 13 isomers have one or two distances shorter than 10.4 Å (only 60-10-6 and 60-10-7 do not), and five of them have a $\odot\cdots\odot$ separation shorter than 9.94 Å. If we consider only the solvent-free $C_{60}(CF_3)_{10}$ structures (i.e., excluding 60-10-5, 60-10-11, and 60-10-14), some surprising observations can be made. The $\odot\cdots\odot$ distances for these 10 structures are shown graphically in Figure 8. Seven of these 10 structures have distorted close-packed packing patterns, with 12 nearest neighbors if $\odot\cdots\odot$ separations out to 14.6 Å are included. This distance corresponds to a pair of $C_{60}(CF_3)_{10}$ molecules with a CF_3 group on each molecule oriented along the $\odot\cdots\odot$ vector and with intermolecular $F\cdots F$ distances of ca. 3 Å. For these seven structures, the ranges of the 12 $\odot\cdots\odot$ distances are very different, almost by a factor of two. The narrowest range, 2.67 Å is for 60-10-4 (from 9.93 to 12.59 Å); the widest range, 4.57 Å, is for 60-10-2 (from 9.95 to 14.52 Å). The mean $\odot\cdots\odot$ distances vary from 11.81 Å for 60-10-4 to 12.12 Å for 60-10-10, an increase of 2.6%, and a corresponding decrease in the crystal density of 3.8%, from 2.072 g cm⁻³ for 60-10-4 to 1.993 g cm⁻³ for 60-10-10. It is remarkable that the very different ranges and distributions of $\odot\cdots\odot$ distances lead to mean $\odot\cdots\odot$ distances and crystal densities that only vary by a few percent. Equally surprising are the differences in the structures of 60-10-4 and 60-10-6. Their shortest $\odot\cdots\odot$ distances differ by 1.02 Å (9.93 Å for 60-10-4 and 10.95 Å for 60-10-6) and their longest $\odot\cdots\odot$ distances differ by 1.88 Å (12.59 Å for 60-10-4 and 14.47 Å for 60-10-6), yet their crystal densities differ by less than 1%. This is because 60-10-6 has 14 nearest neighbors instead of only 12. Significantly, the distribution of CF_3 groups in the 10 isomers with solvent-

Fig. 8. The fullerene centroid...centroid ($\odot \cdots \odot$) distances in the X-ray structures of ten solvent-free isomers of $C_{60}(CF_3)_{10}$. The shortest and longest $\odot \cdots \odot$ distances are highlighted as black circles. The numbers 2 and 4 next to some of the data points indicated that two or four identical $\odot \cdots \odot$ distances, respectively, are exhibited by that structure. The numbers at the top of the figure indicate the number of nearest neighbors for each fullerene molecule in each structure. The packing of molecules in the structures of 60-10-3, 60-10-4, 60-10-7, 60-10-9, 60-10-10, and 60-10-12 are distorted cubic or hexagonal close-packed arrays.

free structures are very different. For example, the CF_3 groups in 60-10-4 are essentially confined to one hemisphere of C_{60} whereas the CF_3 groups in 60-10-6 are distributed over the entire surface of C_{60} (there are four $\text{C}(\text{sp}^2)_6$ hexagons in 60-10-4 that are only bonded to other cage $\text{C}(\text{sp}^2)$ atoms but none in 60-10-6).

Fig. 9 shows the distorted hexagonal close-packed (HCP) arrays of fullerene centroids in the X-ray structures of 60-10-9 and 60-10-10, two structures that have the same crystal density and nearly the same mean $\odot \cdots \odot$ distance. However, their HCP arrays are organized very differently. The rigorously planar arrays of nearest neighbor centroids exhibit longer $\odot \cdots \odot$ distances in 60-10-9 (12.14–13.31 Å) than in 60-10-10 (10.07–12.12 Å), and the perpendicular interplanar spacings are shorter in 60-10-9 (7.89 and 9.27 Å) than in 60-10-10 (11.18 and 11.31 Å).

There is an important difference in the ways that 60-10-9 and 60-10-10 molecules approach one another in their respective lattices. A pair of 60-10-9 molecules whose centroids are in parallel planes separated by 7.89 Å exhibit the shortest $\odot \cdots \odot$ distance in that structure, 9.70 Å. Those two molecules are shown in Fig. 10. They are sufficiently close together that a pair of hexagons, one of each molecule, are π - π stacked with a perpendicular separation of 3.24 Å, a distance even shorter than the interplanar separation in graphite. This occurs because the closest CF_3 groups on each molecule do not lie along the $\odot \cdots \odot$ vector. Instead, they interdigitate with intermolecular $\text{F} \cdots \text{F}$ distances no shorter than the sum of van der Waals distances for two F atoms, ca. 3 Å. However, this is the only pair of molecules in the structure of 60-10-9 with a $\odot \cdots \odot$ distance considered to be important for effective electronic coupling (i.e., shorter than 10.4 Å). This is because the hexagons that interact in this way in 60-10-9 are symmetry related. For this reason, pairs of 60-10-9 molecules in a solid-state array would be electronically coupled, but delocalized coupling throughout the array is not likely.

Fig. 9. The distorted hexagonal close-packed arrays of fullerene centroids ($\odot$) in the solvent-free X-ray structures of 60-10-9 and 60-10-10. The $\odot \cdots \odot$ distances shown are rounded off to the nearest 0.01 Å.

Fig. 10. Drawings of the X-ray structure of 60-10-9 (all atoms shown as points or spheres of arbitrary size; F atoms highlighted in yellow). The drawing on the right shows the two molecules of 60-10-9 with the shortest fullerene centroid $\cdots$ centroid distance (9.70 Å; centroids shown as small spheres). The dashed lines indicate the vectors connecting the 12 centroids that surround the bottom molecule in the drawing on the right. The drawings on the left are two orientations of portions of two molecules in the X-ray structure of 60-10-9, the centroids of which are separated by 9.70 Å. The distance between the least-squares planes of the rigorously parallel fullerene hexagons highlighted with their C(sp²) atoms shown as hollow spheres is 3.24 Å. The dashed lines indicate intermolecular F $\cdots$ F van der Waals contacts of ca. 3 Å.

In contrast, the structure of 60-10-10 has $C(sp^2)_6$ hexagons that are sterically-accessible so that π - π interactions with two nearest neighbors with $\odot \cdots \odot$ distances of 10.07 Å can occur. The result is that a one-dimensional chain of electronically-coupled nearest-neighbor $C_{60}(CF_3)_{10}$ molecules is formed, as shown in Fig. 11.

3. Conclusions

X-ray structures, reduction potentials, and DFT calculations reported in this work more than double the published results showing correlations between the molecular and electronic structures of isomers of C_{60} derivatives with 10 very strong electron-withdrawing groups. Addition patterns that lead to multiple *nt*-DBIPs, and especially with *nt*-DBIPs in close proximity, have extensively delocalized and low-energy LUMOs and are the best electron acceptors. In addition, the number of *nt*-DBIPs vs. *t*-DBIPs appears to affect the HOMO–LUMO gap, with isomers having the greatest number of *nt*-DBIPs exhibiting the smallest gap.

The subtle ways that the multiple CF_3 groups on each $C_{60}(CF_3)_{10}$ interlock with one or more CF_3 groups on each neighboring molecule leads to different numbers of nearest neighbor fullerene molecules in the solvent-free structures (either 12, 13, or 14), and to differences in the ranges of fullerene centroid $\cdots$ centroid distances even when the number of nearest neighbors is constant. Nevertheless, all of the solvent-free structures exhibit nearly equally-efficient packing arrays as far as crystal density is concerned. When there are two sterically-accessible hexagons, a one-dimensional chain of electronically-coupled nearest-neighbor $C_{60}(CF_3)_{10}$ molecules can result from parallel hexagon–hexagon graphite-like π - π interactions. By studying the connections between the molecular and electronic structures and the packing patterns of $C_{60}(CF_3)_{10}$ isomers, it may now be possible to design fullerene derivatives with *fewer than* 10 CF_3 groups that are strong electron acceptors *and* have many short $\odot \cdots \odot$ distances necessary for good three-dimensional electron mobility in the solid state.

Fig. 11. Drawing of the X-ray structure of $C_{60}(CF_3)_{10}$ isomer 60-10-10, showing the one-dimensional chain of electronically-coupled molecules with centroid...centroid ($\odot \cdots \odot$) distances of 10.07 Å (the four centroids shown are in the plane of the page). The $\odot \cdots \odot \cdots \odot$ angle is 117.4°. The 60-10-10 Schlegel diagram shows the sterically-accessible hexagons that most closely approach one another on neighboring molecules highlighted in blue. The two $C(sp^2)$ atoms that are common to the pair of adjacent blue hexagons most closely approach the least-squares plane of the third blue hexagon. The orientation of these hexagons on neighboring molecules is shown in Fig. S-9.

4. Experimental Section

4.1. Materials

All solvents were reagent grade and were dried using standard procedures. The electrolyte $\text{N}(n\text{-Bu})_4^+\text{PF}_6^-$ was recrystallized from ethyl acetate after azeotropic distillation to remove traces of H_2O . The $\text{C}_{60}(\text{CF}_3)_{10}$ isomers studied in this work were prepared as previously described [37]. Single crystals of 60-10-1 and 60-10-7 through 60-10-13 were grown from saturated toluene, dichloromethane, chloroform, or chloroform- d solutions by slow evaporation.

4.2. Cyclic voltammetry

Cyclic voltammetry measurements were carried out in a purified dinitrogen-filled glovebox using a PAR 263 potentiostat/galvanostat with ca. 1 mM solutions of $\text{C}_{60}(\text{CF}_3)_{10}$ isomer dissolved in *o*-dichlorobenzene containing 0.1 M $\text{N}(n\text{-Bu})_4\text{PF}_6$. A single-compartment cell was fitted with 0.2 mm diameter Pt wire working and counter electrodes and an Ag wire quasi-reference electrode. Ferrocene was added as an internal standard after first recording several voltammograms at different scan rates. The CVs are shown in Figure S-12.

4.3. DFT calculations

All structures were optimized at the PBE/TZ2P level using the Priroda code [61, 62].

4.4. X-ray crystallography

Single crystals of 60-10-9, 60-10-10, 60-10-12, 60-10-13, and 60-10-14 were mounted on Mylar loops using paratone oil. Diffraction data were collected using a Bruker Kappa APEX 2 CCD diffractometer equipped with a sealed X-ray tube (Mo K_α radiation; $\lambda = 0.71073 \text{ \AA}$) and a graphite monochromator at 120(2) K for 60-10-9, 60-10-10, and 60-10-13 and at 100(2) K for 60-10-12 and 60-10-14. Data reduction was performed with the Bruker APEX 2 suite of software [63]. Absorption and other corrections were applied using SADABS [64] except for the twinned

structure 60-10-13, for which TWINABS [65] was used. The structures were solved using with SHELXTL [63] or OLEX 2 GUI version 1.2.5 software [66], operating SHELXS [67] or SHELXT [68], respectively, and refinements were carried out using SHELXL [69]. Non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and refined using a riding model. All figures were generated with SHELXTL XP software. See the crystallographic information files (CIFs) for additional information about structure refinement for each isomer.

Single crystals of 60-10-1, 60-10-7, and 60-10-11 were mounted on glass fiber filaments using paratone oil. Diffraction data were collected at 100(2) K using synchrotron radiation ($\lambda = 0.41328 \text{ \AA}$ for 60-10-1 and 60-10-7; $\lambda = 0.49594 \text{ \AA}$ for 60-10-11) at the Advanced Photon Source ChemMatCARS Sector 15 beamline, a diamond (111) monochromator, a Bruker D8 goniometer, and a Bruker CCD detector controlled by Bruker APEX 2 software [63]. Data reduction, solution, refinement, and the preparation of figures were performed following same procedures described above. See the crystallographic information files (CIFs) for additional information about structure refinement for each isomer.

Crystallographic data (excluding structure factors) for all eight structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC 1142897 and 1142898 (for 60-10-1 and 60-10-7, respectively), 1142900–1142903 (for 60-10-9 through 60-10-12, respectively), 1443790 (for 60-10-13), and 1142899 (for 60-10-14). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk.

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