

Synthesis, Spectroscopic and Electrochemical Characterization, and DFT Study of Seventeen $C_{70}(CF_3)_n$ Derivatives ($n=2, 4, 6, 8, 10, 12$)

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Abstract: Eight new $C_{70}(CF_3)_n$ derivatives ($n=2, 6, 10, 12$) have been synthesized and characterized by UV/Vis and ^{19}F NMR spectroscopy, cyclic voltammetry, and quantum chemical calculations at the DFT level of theory. Nine previously known derivatives of $C_{70}(CF_3)_n$ with $n=2-12$ were also studied by cyclic voltammetry (and seven of them by UV/Vis spectroscopy for the first time). Most of the 17 com-

pounds exhibited two or three reversible reductions at scan rates from 20 mVs^{-1} up to 5.0 Vs^{-1} . In general, reduction potentials for the $0/-$ couple are shifted anodically relative to the $C_{70}^{0/-}$ couple. However, the $0/-$ $E_{1/2}$ values for a given composition are

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strongly dependent on the addition pattern of the CF_3 groups. The data show that the addition pattern is as important, if not more important in some cases, than the number of substituents, n , in determining $E_{1/2}$ values. An analysis of the DFT-predicted LUMOs indicates that addition patterns that have non-terminal double bonds in pentagons result in derivatives that are strong electron acceptors.

Introduction

Prior to this work, the reactions of fullerene C_{70} with i) $Ag(CF_3CO_2)$ at 320°C followed by sublimation at $420-540^\circ\text{C}$ and ii) CF_3I at $390-470^\circ\text{C}$ had resulted in the isolation of 16 $C_{70}(CF_3)_n$ derivatives with well-defined addition patterns ($n=2-18$).^[1-11] X-ray structures are known for 12 of the 16 compounds, and the structures of four others were previously determined by ^{19}F NMR spectroscopy.^[1-11] However, little is known about their optical and electrochemical properties, information that would need to be known before one or more of these compounds could be used in the fabrication of high-performance photovoltaic energy-conversion and -storage devices.^[12-14]

In this paper we report the isolation and characterization of eight additional $C_{70}(CF_3)_n$ derivatives with $n=2, 6, 10,$ and 12 , including four new isomers of $C_{70}(CF_3)_{10}$ and two new isomers of $C_{70}(CF_3)_{12}$. The addition patterns for the new compounds have been narrowed down to a most-probable structure in each case by a combination of ^{19}F NMR and UV/Vis data and DFT calculations. A total of 17 $C_{70}(CF_3)_n$ derivatives with $n=2-12$ are now available, and all of them were studied by UV/Vis spectroscopy, DFT calculations, and cyclic voltammetry in this work (the UV/Vis spectra of two $C_{70}(CF_3)_6$ isomers were previously reported^[2] and are not included in this paper). The electrochemical results reveal up to three reversible reductions for each compound and, sig-

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nificantly, demonstrate that $E_{1/2}$ values for a given reduction step for isomers of a given $C_{70}(CF_3)_n$ composition can vary by up to 0.45 V. We also report the isolation, characterization, and electrochemical behavior of an isomer of $C_5-C_{70}(CF_3)_4O$.

Results and Discussion

The 17 $C_{70}(CF_3)_n$ derivatives studied in this investigation are listed, along with their abbreviations, in Table 1 (IUPAC lowest locants^[15] are also listed, including those for addition patterns that are tentative at this time).^[1–9,16,17] A Schlegel diagram showing the IUPAC numbering for C_{70} ^[15] and a structural diagram identifying the five types of cage carbon atoms for this fullerene are both shown in Figure 1. The new compounds are 70-2-2, 70-6-2, 70-10-2, -3, -4, and -5, and 70-12-3 and -4, and represent a near doubling of the number of known $C_{70}(CF_3)_n$ derivatives with $n=2–12$. ¹⁹F NMR chemical shifts and J_{FF} values for all 17 compounds are listed in Table 2. Six structurally-characterized $C_{70}(CF_3)_n$ derivatives with $n=14, 16$, and 18 are also known,^[10,11] but they were not included in this study.

Improved synthesis of 70-10-1 and 70-8-1: In 2005 we reported that the reaction of C_{70} and CF_3I at 470 °C in a flow reactor resulted in a 27% yield of 70-10-1 (based on converted C_{70} ; this single isomer constituted about 40 mol% of all $C_{70}(CF_3)_n$ compounds in the crude reaction product).^[5] The synthesis involved a high-temperature reactor referred to as re-

actor 1 (see Experimental Section for details). We now report that a 55% yield of 70-10-1 (based on converted C_{70}) can be obtained at 520 °C using reactor 1, as shown in Figure 2 and Table 3. Figure 2 also demonstrates that significant amounts of $C_{70}(CF_3)_{12,14}$ isomers are formed at 470 °C along with the major product $C_{70}(CF_3)_{10}$, but no observable amount of the composition $C_{70}(CF_3)_8$ was formed. In addition, decreasing the temperature to 420 °C resulted in increasing amounts of $C_{70}(CF_3)_n$ compounds with $n=12–20$, as shown in Figure S1 in Supporting Information). The compounds 70-12-1 and 70-12-2, which have been structurally characterized by X-ray diffraction, were previously prepared in this way at 420–450 °C.^[6,8]

Significant improvements in both the yield and selectivity of 70-10-1 were achieved by changing the reactor design and reaction conditions. The hot-zone of reactor 2 was 40 cm long instead of only 5 cm for reactor 1. Furthermore, the flow rate of CF_3I used with reactor 2 was half the rate used with reactor 1. Both of these changes increased the residence time of $C_{70}(CF_3)_n$ compounds in the hot zone. The data in Table 3 show that these changes resulted in a yield of $C_{70}(CF_3)_n$ isomers with $n=10$ and 12 up to 68 mol% (based on converted C_{70}) and a yield of 70-10-1 up to 89 mol% (based on all $C_{70}(CF_3)_n$ products present ($T_{rxn}=530$ °C).

The seemingly counterintuitive result that higher temperatures result in lower values of n can be explained as follows. Compounds with low values of n are less volatile than those with higher values of n . Therefore, compounds with lower values of n will rapidly sublime out of the hot zone

Table 1. $C_{70}(CF_3)_n$ derivatives ($n=2–12$).^[a]

Compound	Addition pattern	Abbr.	X-ray ref.	UV/Vis ref.	¹⁹ F NMR ref.	DFT rel. energy [kJ mol ⁻¹] ^[b]	DFT LUMO energy [eV] ^[c,d]	DFT HOMO–LUMO gap [eV] ^[c]
7,24- $C_{70}(CF_3)_2$	C_1 - <i>para</i> (<i>p</i>)	70-2-1		tw	[1], tw	0.0 ^[1]	–4.697	1.372
8,23- $C_{70}(CF_3)_2$ ^[e]	C_5 - <i>p</i>	70-2-2		tw	tw	5.1 ^[1]	–4.533	1.232
7,24,44,47- $C_{70}(CF_3)_4$	C_1 - <i>pmp</i>	70-4-1		tw	[1], tw	1.0 ^[f] , [1]	–4.648	1.334
1,4,11,19,31,41- $C_{70}(CF_3)_6$	C_2 - <i>p</i> ⁵	70-6-1		[2]	[1], tw	0.0 ^[1,2]	–4.731	1.333
1,4,11,23,31,44- $C_{70}(CF_3)_6$ ^[e]	C_1 - <i>p</i> ³ , <i>p</i>	70-6-2 ^[g]		tw	tw	9.3 ^[2]	–4.758	1.304
1,4,10,19,25,41- $C_{70}(CF_3)_6$	C_1 - <i>p</i> ³ <i>mp</i>	70-6-3	[2]	[2]	tw	12.6, ^[1] 12.3 ^[2]	–4.639	1.560
1,4,11,19,31,41,51,64- $C_{70}(CF_3)_8$	C_5 - <i>p</i> ⁷	70-8-1	[3]	tw	[1], tw	0.0 ^[1]	–4.555	1.707
1,4,11,19,31,41,51,60- $C_{70}(CF_3)_8$	C_2 - <i>p</i> ⁷	70-8-2		tw	[1], tw	6.0 ^[1]	–4.829	1.263
1,4,10,19,25,41,49,60,66,69- $C_{70}(CF_3)_{10}$	C_1 - <i>p</i> ⁷ <i>mp</i>	70-10-1	[4]	tw	[5], tw	0.0 ^[1]	–4.351	2.071
1,4,11,19,31,41,49,60,66,69- $C_{70}(CF_3)_{10}$	C_2 - <i>p</i> ⁹	70-10-2		tw	tw	12.3 ^[1]	–4.536	1.823
1,4,11,19,26,31,41,48,60,69- $C_{70}(CF_3)_{10}$	C_1 - <i>p</i> ⁷ , <i>p</i>	70-10-3		tw	tw	27.5 ^[c]	–4.588	1.679
1,4,10,19,23,25,44,49,66,69- $C_{70}(CF_3)_{10}$ ^[e]	C_1 - <i>p</i> ² <i>mpmp</i> , <i>p</i> ²	70-10-4		tw	tw	19.5 ^[c]	–4.599	1.628
1,4,11,19,24,31,41,51,61,64- $C_{70}(CF_3)_{10}$ ^[e]	C_1 - <i>p</i> ⁸ , <i>i</i>	70-10-5		tw	tw	14.3 ^[c]	–4.813	1.370
1,4,10,19,25,32,41,49,54,60,66,69- $C_{70}(CF_3)_{12}$	C_1 - <i>p</i> ⁷ <i>mp</i> , <i>p</i> -1	70-12-1	[6, 7]	tw	tw	0.0 ^[c] , [7]	–4.664	1.700
1,4,10,14,19,25,35,41,49,60,66,69- $C_{70}(CF_3)_{12}$	C_1 - <i>p</i> ⁷ <i>mp</i> , <i>p</i> -2	70-12-2	[7, 8]	tw	[9]	1.0, ^[c] 2.5 ^[7]	–4.676	1.671
1,4,8,11,18,23,31,35,51,58,61,64- $C_{70}(CF_3)_{12}$	C_1 - <i>p</i> ⁷ <i>mp</i> , <i>p</i> -3	70-12-3		tw	tw	3.9, ^[c] 3.7 ^[7]	–4.777	1.634
1,4,8,11,23,31,38,51,55,58,61,64- $C_{70}(CF_3)_{12}$	C_1 - <i>p</i> ⁷ <i>mp</i> , <i>p</i> -4	70-12-4		tw	tw	3.9, ^[c] 2.5 ^[7]	–4.774	1.687

[a] Abbreviations: tw, this work; *p*, *para*; *m*, *meta*; *i*, an isolated CF_3 group. [b] DFT-predicted energies relative to the lowest-energy isomer for each composition. These energies are for the lowest energy set of conformations of the CF_3 groups found for each isomer. [c] This work. The DFT-predicted E - (LUMO) value and HOMO–LUMO gap for C_{70} are –4.315 and 1.702 eV, respectively. [d] DFT-predicted LUMO energies relative to the LUMO energy of C_{70} . [e] This addition pattern is not certain and must be considered tentative. It is the lowest energy possibility consistent with the data discussed in the text. [f] The lowest-energy isomer of $C_{70}(CF_3)_4$ is the as-yet unknown C_5 -*p*³ isomer with CF_3 groups on three edge-sharing **bb** hexagons (see ref. [1]). [g] An isomer of $C_{70}(CF_3)_6$ was reported as “isomer II” in ref. [2], but nothing was reported about its structure or ¹⁹F NMR spectrum; it may or may not be the same as 70-6-2.

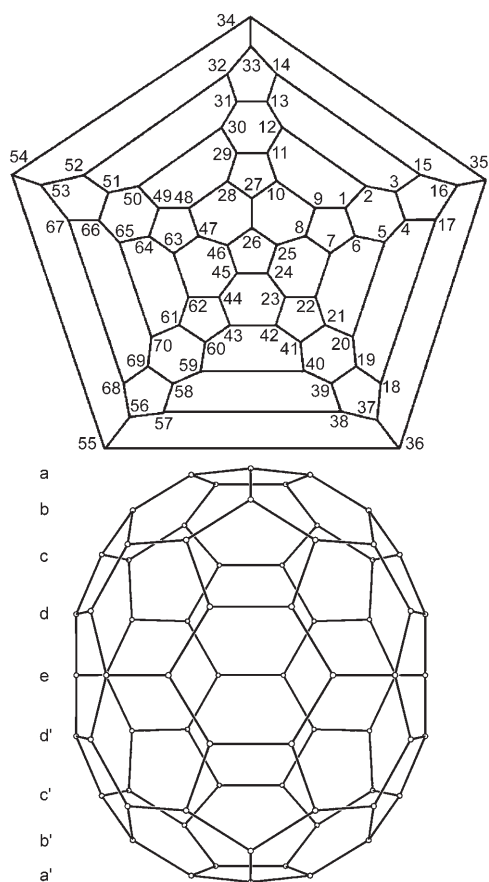


Figure 1. Schlegel diagram showing the IUPAC numbering of C₇₀ (top) and a drawing of the structure of C₇₀ indicating the five different types of cage carbon atoms (bottom).

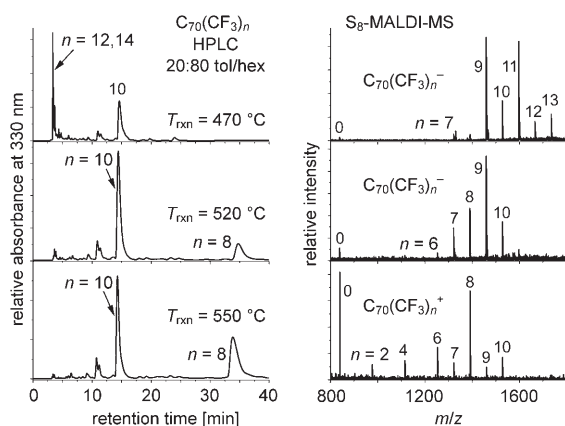


Figure 2. HPLC traces (left) and S₈-MALDI mass spectra (right) of the crude C₇₀(CF₃)_n products obtained from the reactions of C₇₀ and CF₃I at 470 °C (top), 520 °C (middle), and 550 °C (bottom). Note that negative-ion detection is shown in the mass spectra for the 470 and 520 °C reaction products and that positive-ion detection is shown for the 550 °C reaction products.

only at high temperatures. At lower temperatures, their residence time in the hot zone is increased to the point that they are converted to compounds with higher values of *n*.

The HPLC traces in Figure 2 show that progressively more C₇₀(CF₃)₈ isomers were formed when the temperature of reactor 1 was increased from 470 to 520 to 550 °C (the HPLC peak for 70-8-2, at 52 min, is not shown in Figure 2). The integrated areas of the HPLC peaks labelled *n*=8 and 10 in the 550 °C trace in Figure 3 are approximately 50:50. Since

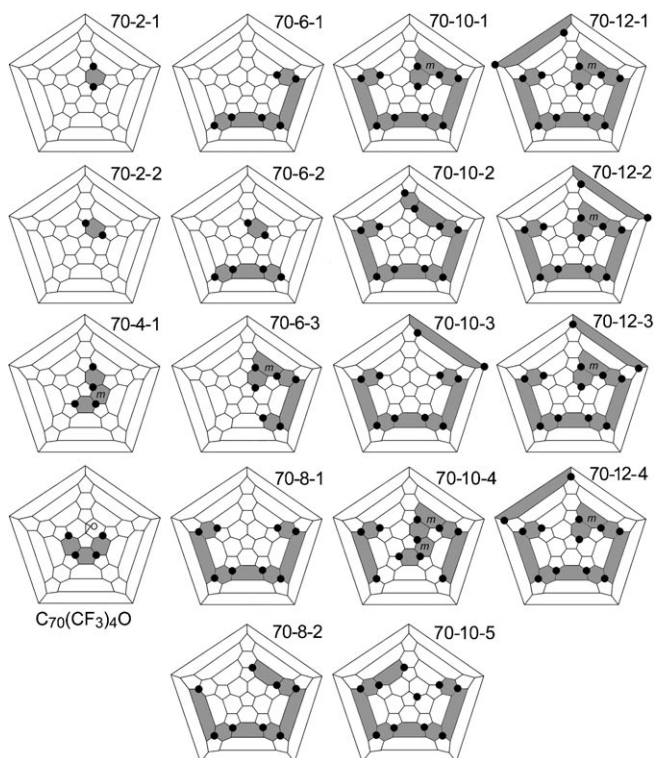


Figure 3. Schlegel diagrams of the 17 C₇₀(CF₃)_n compounds studied by cyclic voltammetry in this work. The black circles are the cage carbon atoms to which the CF₃ groups are attached. The isolated *p*-C₆(CF₃)₂ hexagons and the ribbons of edge-sharing *m*- and *p*-C₆(CF₃)₂ hexagons are highlighted, and the *m*-C₆(CF₃)₂ hexagons are indicated with the letter *m*. The compounds 70-12-3 and 70-12-4 are the first examples of an *n*=2–12 C₇₀(CF₃)_n derivatives with a C₅(CF₃)₂ pentagon. The compound 70-10-5 is the first example of any fullerene(CF₃)_n derivative with an isolated CF₃ group. The diagrams do not depict the lowest locants relative to a fixed numbering scheme. See Table 1 for a list of IUPAC lowest locants.

these peaks correspond to pure 70-8-1 and 70-10-1, and since their combined HPLC intensities are 73 % of the total for all isomers of C₇₀(CF₃)_{8,10}, the highest-yield synthesis of 70-8-1 to date, about 22 % based on the amount of C₇₀ starting material, is the 550 °C synthesis using reactor 1.

Note that no observable amount of 70-8-1 was prepared at 530 °C when reactor 2 was used (see Table 3). In this case, the much longer hot zone increased the residence time so much that even a temperature above 520 °C was insufficient to remove 70-8-1 from the hot zone before it was converted to compounds with higher *n* values.

Synthesis and characterization of new compounds: We have isolated three new compounds from the reaction of C₇₀ with

Table 2. ¹⁹F NMR data for C₇₀(CF₃)_n compounds (n = 2–12).^[a]

70-2-1 q: {68.9, 70.0 (12.4 Hz)}	70-2-2 s: 71.8	70-4-1, C ₁ -pmp as/qq: 67.0, 67.7 q: 68.2 (13.9 Hz), 70.4 (11.6 Hz)	70-6-1, C ₂ -p ⁵ as/qq: 63.4, 63.8 q: 67.9 (16.0 Hz)	70-6-3, C ₁ -p ³ mp as/qq: 61.4, 63.1, 65.1, 65.4 q: 68.1 (17.3 Hz), 72.1 (10.4 Hz)
70-6-2, C ₁ -p ³ .p as/qq: 66.4, 67.4 q: 68.7 (14.7 Hz), {69.8, 70.1 (11.7 Hz)}, 71.3 (16.5 Hz)		70-8-1, C ₅ -p ⁷ as/qq: 61.9, 62.0, 62.3 q: 66.4 (16.1 Hz)	70-8-2, C ₂ -p ⁷ as/qq: 61.8, 62.4, 63.6 q: 69.2 (11.3 Hz)	
70-10-1, C ₁ -p ⁷ mp as/qq: 60.9, 62.9, 63.3 × 2, 63.6 × 2, 64.9, 65.5 q: 67.6 (15.9 Hz), 70.7 (10.3 Hz)		70-10-2, C ₂ -p ⁹ as/qq: 63.6, 63.7, 63.9, 65.2 q: 70.7 (15.0 Hz)	70-10-3, C ₁ -p ⁷ .p as/qq: 63.2, 63.4, 63.8, 64.7, 65.1, 65.8 q: 68.4 (16.6 Hz), 68.7 (16.6 Hz), {72.7, 72.8 (12.4)}	
70-10-4, C ₁ -p ² mpmp.p ² as/qq: 61.4, 63.5, 64.4, 64.5, 67.0, 67.6 q: 69.2 (14.9 Hz), 70.4 (11.4 Hz), 72.5 (11.4 Hz), 72.9 (9.7 Hz)		70-10-5, C ₁ -p ⁹ .i as/qq: 63.3 × 3, 63.8, 64.1, 64.6, 64.9 q: 68.5 (15.5 Hz), 71.9 (10.4 Hz) s: 74.3		
70-12-1, C ₁ -p ⁷ mp.p as/qq: 62.4, 62.7, 62.9, 63.4, 64.7, 65.2, 65.7, 66.1 q: 69.1 (16.9 Hz), 72.0 (9.8 Hz), {72.6, 72.7 (12.4 Hz)}		70-12-2, C ₁ -p ⁷ mp.p as/qq: 62.6, 63.1, 63.4, 63.7, 64.0, 64.9, 66.4 q: 69.6 (15.8 Hz), 72.1 (10.2 Hz), {72.6, 72.8 (12.0 Hz)}		
70-12-3, C ₁ -p ⁷ mp.p um: 56.7 as/qq: 61.8, 62.3, 62.5, 63.4, 64.3, 66.0, 68.2, 68.8 q: 68.8 (13.7 Hz), 71.3 (13.4 Hz), 72.1 (9.7 Hz)		70-12-4, C ₁ -p ⁷ mp.p um: 56.2 as/qq: 62.9, 63.2, 63.7, 63.8, 65.0, 65.8, 68.8, 69.1 q: 68.8 (13.8 Hz), 69.4 (16.1 Hz), 72.0 (10.0 Hz)		

[a] All data from this work; 376.5 MHz, CDCl₃, C₆F₆ int. std. (δ –164.9), 24 °C. Abbreviations: *p*, *para*; *m*, *meta*; *i*, isolated CF₃ group; *s*, singlet; *q*, quartet; *as/qq*, apparent septet or quartet of quartets; *um*, broad unresolved multiplet. The values listed are –δ values; ⁷J_{FF} values are shown in parentheses (the precision to which the coupling constants are known is ca. ±0.3 Hz); pairs of quartets enclosed in braces are assigned to CF₃ groups coupled to one another because they are on an isolated *p*-C₆(CF₃)₂ hexagon. Some NMR spectra in [D₆]benzene were previously reported, but the CDCl₃ data are listed here to provide a complete set of chemical shift data for all 17 compounds in a common NMR solvent (the coupling constants are essentially the same in both solvents).

Table 3. Effects of reaction conditions on C₇₀ + excess CF₃I reaction.^[a]

Mass of C ₇₀ [mg]	Reaction temp. [°C]	Reaction time [min]	Mass of C ₇₀ (CF ₃) _n [mg] ^[b]	<i>n</i> value	Yield [mol %] ^[c]
24	470	60	35	10, 12, 14	73 (27% ^[d])
26	520	120	35	8, 10	67 (55% ^[d])
31	520	120	44	8, 10	81 (55% ^[d])
50	550	180	41	8, 10	47
55	550	240	51	8, 10	59
30 ^[a]	530	90	38	10, 12	68 (80% ^[d])
20 ^[a]	530	90	20	10, 12	54 (89% ^[d])

[a] The first five rows refer to syntheses carried out using reactor 1; the last two rows refer to syntheses carried out using reactor 2 (see Experimental Section for details). [b] The total mass of C₇₀(CF₃)_n isolated (after removal of I₂ and, in some cases, a negligible amount of C₇₀). [c] The mol % of C₇₀(CF₃)_n isolated based the amount of C₇₀ used (moles of C₇₀(CF₃)_n were calculated using the weighted-average molar mass based on HPLC integrated peak intensities of the C₇₀(CF₃)_n components in the isolated product). [d] Values in parentheses are the mol % of C₇₀(CF₃)₁₀ in the isolated product.

AgCF₃CO₂ at 320 °C, 70-2-2, 70-6-2, and C_s-C₇₀(CF₃)₄O. Details about their isolation and purification are given in the Supporting Information. The improved C₇₀/CF₃I reactions performed with reactor 2 resulted in narrower ranges of compositions than with reactor 1 in addition to higher yields. Scaling up the reactions to as high as 0.1 g of C₇₀ resulted in product mixtures in sufficient amounts so that previously-unknown, low-abundance isomers of C₇₀(CF₃)_{10,12} were isolated and characterized. Four new isomers of C₇₀(CF₃)₁₀ and two new isomers of C₇₀(CF₃)₁₂ are reported in this work (see Table 1).

Electronic absorption (UV/Vis) spectra of all new compounds and all but two of the previously known compounds in the common solvent dichloromethane are collected in the Supporting Information (Figure S2).

New C₇₀(X)_n addition patterns: The combination of ¹⁹F NMR spectroscopy, electronic absorption spectroscopy, and DFT has proven to be almost as valuable as X-ray crystallography for determining the structures (i.e., the addition patterns) of fullerene(CF₃)_n compounds. (At this writing there are 26 published X-ray structures (fullerene = C₆₀, C₇₀,

C₇₄, C₇₈) plus 23 other compounds the addition patterns of which were determined by spectroscopy combined with DFT-predicted relative energies and HOMO-LUMO gaps; see Supporting Information in ref. [28] for a complete list of references.) Studies in the past few years have repeatedly demonstrated that i) CF₃ groups in fullerene(CF₃)_n derivatives are generally arranged on *p*-C₆(CF₃)₂ hexagons and/or ribbons and/or loops of edge-sharing *m*- and/or *p*-C₆(CF₃)₂ hexagons (the shared edges are C(sp²)-C(sp³) bonds);^[1-11,18-22] ii) CF₃ groups on contiguous cage carbon atoms are rare for *n*=2-12 (only one example out of 38 well-characterized compounds before this work;^[23] this example is also the only case of three CF₃ groups sharing the same hexagon for *n*=2-12—note that all fullerenes have precisely 12 pentagons); iii) two CF₃ groups sharing the same pentagon (i.e., a 1,3-C₅(CF₃)₂ pentagon) are rare for *n*=2-12 derivatives (only two examples^[5,22] out of 38 well-characterized compounds); iv) terminal CF₃ groups, and CF₃ groups on isolated C₆(CF₃)₂ hexagons, have always been found to be *para* to their nearest-neighbor CF₃ group, never *meta* (but see below); v) stable exohedral fullerene(X)_n derivatives with substituents on triple-hexagon junctions and *without* endohedral atoms are unknown for *n* < 38 (the only known example for C₇₀ is C₇₀F₃₈^[24]); vi) J_{FF} coupling between CF₃ groups is only observed for proximate CF₃ groups on the same hexagon or pentagon;^[1,5,9,25-27] vii) the ⁶J_{FF} and ⁷J_{FF} values for *m*-C₆(CF₃)₂ and *p*-C₆(CF₃)₂ hexagons, respectively, depend upon the F...F distance between the CF₃ groups and on the F-C...C-F torsion angle (shorter distances and larger torsion angles lead to larger J_{FF} values);^[1,9,27] and viii) ¹⁹F NMR -δ values for the CF₃ multiplets are less than 60 ppm only when the corresponding CF₃ groups are eclipsed or nearly eclipsed.^[5,9,25]

The number and types of ¹⁹F NMR multiplets can reveal the symmetry and type of addition pattern, if not the exact addition pattern, for a fullerene(CF₃)_n compound.^[1,5,9,22,23,25,26] The types of multiplets range from singlets,^[9] quartets (for terminal CF₃ groups), quartets of quartets (for non-terminal CF₃ groups in a ribbon or loop; these can appear as unresolved multiplets or as apparent septets), and quartets of quartets of quartets (for CF₃ groups with three nearest neighbor CF₃ groups; these can appear as unresolved multiplets^[5,22] or apparent dectets^[23]). In the absence of an X-ray structure, the number and types of ¹⁹F NMR multiplets, “general observations” i)-viii) cited above, DFT-predicted relative energies of isomers with a given *n* value, and a comparison of DFT-predicted HOMO-LUMO gaps with UV/Vis spectra have been used,^[9] and will be used in this paper, to narrow the number of possible addition patterns for a given composition as much as possible, usually to one “most probable” structure.

The certain, most-probable, or tentative addition patterns for the *n*=2-12 C₇₀(CF₃)_n compounds are shown as Schlegel diagrams in Figure 3. The compounds 70-6-3, 70-8-1, 70-10-1, 70-12-1, and 70-12-2 were previously characterized by X-ray crystallography (see Table 1) and the addition patterns of 70-2-1, 70-4-1, 70-6-1, and 70-8-2 were determined by

spectroscopy and DFT in a previous study.^[1] The new compounds in Figure 3 were assigned an addition pattern by comparison of their ¹⁹F NMR spectra and DFT-predicted relative energies and HOMO-LUMO gaps to known structures.

The ¹⁹F NMR spectra of 70-2-1 and 70-4-1 were first reported in 2003 and 2004, respectively, but their addition patterns were not correctly determined (the proposed structures included CF₃ groups on contiguous cage carbon atoms).^[16,17] It is now virtually certain that 70-2-1, which must have C₁ symmetry if the CF₃ groups are not on contiguous cage carbon atoms because its ¹⁹F NMR spectrum exhibits two quartets, has a *p*-C₆(CF₃)₂ pattern with one of the CF₃ groups bonded to a type **a** cage carbon atom (see Figure 1 for a type key).^[1] It is also virtually certain that 70-4-1 has the *pmp* ribbon structure shown in Figure 3.^[1] The spectrum of 70-2-1 demonstrates that a terminal CF₃ group on a *p*-C₆(CF₃)₂ hexagon spanning type **a** and type **c** cage carbon atoms (an “**ac** hexagon”) can have a ⁷J_{FF} value of 11.0 ± 1.5 Hz (cf. ⁷J_{FF} values of 10.4, 10.3, 12.4, and 12.0 Hz for the terminal CF₃ group on a type **a** carbon atom in 70-6-3, 70-10-1, 70-12-1, and 70-12-2, respectively). However, when the CF₃ group on a type **c** carbon atom in an **ac** hexagon is the terminal CF₃ group, as in 70-4-1, the ⁷J_{FF} value can be as large as 13.9 Hz. The spectrum of 70-4-1 further demonstrates that a terminal CF₃ group on a **bb** hexagon can have a ⁷J_{FF} value of 11.9 Hz.

The proposed addition pattern of 70-2-2 cannot be determined using its ¹⁹F NMR spectrum. The observed singlet indicates C_s or C₂ symmetry (no C₇₀ derivative can have C_i symmetry) but does not indicate whether the two CF₃ groups are on contiguous cage carbon atoms (violating general observation ii), on a *p*-C₆(CF₃)₂ hexagon (the most likely possibility), on a 1,3-C₅(CF₃)₂ pentagon (violating general observation iii), or on non-adjacent carbon atoms from different hexagons (i.e., two isolated CF₃ groups). The latter possibility is unlikely because the lowest-energy isomer of C₇₀(CF₃)₂ with two isolated CF₃ groups is more than 60 kJ mol⁻¹ higher than the most stable isomer of this composition, which is 70-2-1. The three possible symmetric *p*-C₆(CF₃)₂ hexagon addition patterns are shown in Figure 4 along with their DFT-predicted relative energies.^[1] The isomer 1,11-C₇₀(CF₃)₂ can be ruled out as the correct structure for 70-2-2 since our DFT calculations show that its HOMO-LUMO gap is 0.89 eV, much too small to account for the UV/Vis spectrum of 70-2-2 even if the systematic underestimation of HOMO-LUMO gaps by DFT^[28] is taken into account. The isomer 1,4-C₇₀(CF₃)₂ can be ruled out because the UV/Vis spectrum of 70-2-2 is significantly different than that of 1,4-C₇₀Ph₂ (see Figure S2, Supporting Information).^[29] Therefore, based on all of the evidence, we tentatively propose that 70-2-2 has the C_s symmetry structure with CF₃ groups on a **bb** hexagon.

The addition pattern of 70-6-2 can be narrowed down to one of a number of C₁-*p*³,*p* addition patterns, three of which are shown in Figure 4 along with their DFT-predicted relative energies. The pair of CF₃ groups that are coupled to

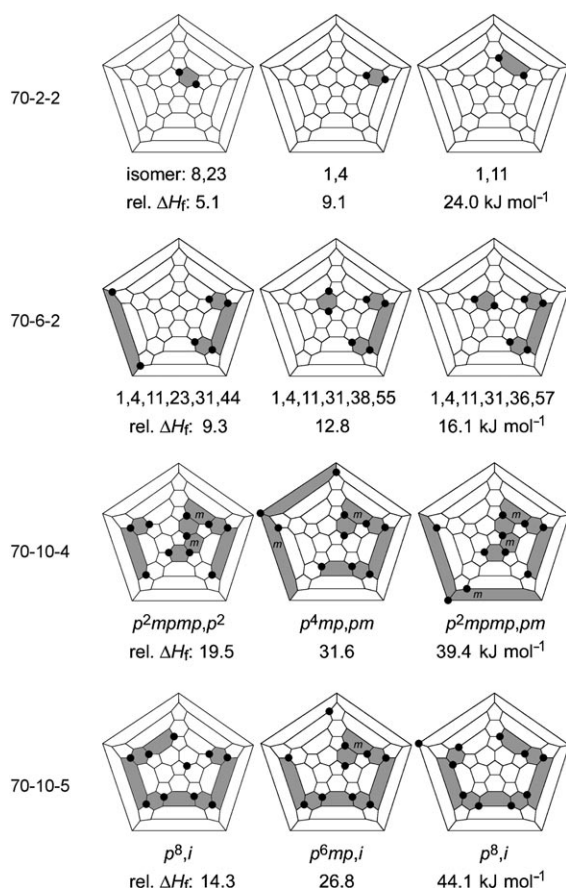


Figure 4. Schlegel diagrams of some of the possible addition patterns of the new compounds 70-2-2, 70-6-2, 70-10-4, and 70-10-5. The latter compound is the first fullerene(CF₃)_n derivative with an isolated CF₃ group (i.e., one that does not share a pentagon or hexagon with another CF₃ group). For each of these four compounds, the diagram on the left is considered the most likely addition pattern.

one another by 11.7 Hz indicates that they are on an isolated **ac**, **bb**, or **dd** hexagon. The ribbon of four C₆(CF₃)₂ hexagons is almost certainly a *p*³ ribbon on the equator with the terminal CF₃ groups on **dd'** hexagons because their ⁷J_{FF} values are 14.7 and 16.5 Hz. These values all but rule out the possibility of a *pmp* ribbon on one of the polar regions of C₇₀ (as in 70-4-1). They also rule out the alternate *pmp* ribbon **acdd'**. Furthermore, structures having a *p*³ equatorial ribbon **ddd'd'**, with terminal CF₃ groups on a **dd** hexagon and a **d'd'** hexagon, can be ruled out as follows. The C₂-*p*⁷ compound 70-8-2 has terminal CF₃ groups on two **dd** hexagons and exhibits a ⁷J_{FF} value of only 11.3 Hz for the terminal quartets. On the other hand, the C_s-*p*⁷ compound 70-8-1 has its terminal CF₃ groups on **dd'** hexagons and exhibits a ⁷J_{FF} value of 16.1 Hz for the terminal quartet (cf. ⁷J_{FF} values of 16.0, 17.3, 15.9, 16.9, and 15.8 Hz for the terminal **dd'** quartets in the spectra of 70-6-1, 70-6-3, 70-10-1, 70-12-1, and 70-12-2, respectively). Therefore, a terminal **dd'** quartet exhibits a ⁷J_{FF} value of 16.0 ± 1.3 Hz, and the compound 70-6-2 has two of them (there is one case we will propose later for which the ⁷J_{FF} value for a *distorted* terminal **dd'** hexagon

is 13.4 Hz). The three shown in Figure 4 are the lowest energy structures with either an isolated **ac**, **bb**, or **dd** hexagon. We tentatively propose that the structure with an isolated **bb** hexagon in Figure 4 is the likely structure for 70-6-2 because it is the most stable, but this assignment is subject to change as new data appear and as the thermodynamics and kinetics of the high temperature addition of CF₃ radicals to fullerenes are better understood. In any event, all of the aforementioned possible *p*³,*p* addition patterns are unprecedented for C₇₀(X)₆ derivatives. Note that the relative energy of the proposed addition pattern for 70-6-2 is lower by 3.0 kJ mol⁻¹ than the DFT-predicted energy of the known structure of 70-6-3^[2] (the most stable isomer of this composition is 70-6-1^[1,2]).

The compound 70-10-2, with only one quartet in its NMR spectrum, has a single ribbon and either C₂ or C_s symmetry. Its terminal ⁷J_{FF} value is 15.0 Hz, so it is almost certainly the C₂-symmetry structure shown in Figure 3, which happens to be the most stable C₇₀(CF₃)₁₀ isomer (12.3 kJ mol⁻¹) after 70-10-1 (0.0 kJ mol⁻¹).^[1] This addition pattern has been found for the decakis(peroxo) derivative C₂-C₇₀(*t*BuOO)₁₀ reported by Gan and co-workers,^[30] which, like the C₇₀(CF₃)_n derivatives, was prepared by the sequential addition of ten free radicals to C₇₀ (albeit at 25 °C^[30] instead of at 530 °C).

The ¹⁹F NMR spectra of 70-10-3 and 70-10-4 demonstrate that they each have C₁ symmetry and four terminal CF₃ groups. In 70-10-3, two of the CF₃ groups are on an isolated **ac**, **bb**, or **dd** hexagon (⁷J_{FF} = 12.4 Hz) as shown in Figure 5.

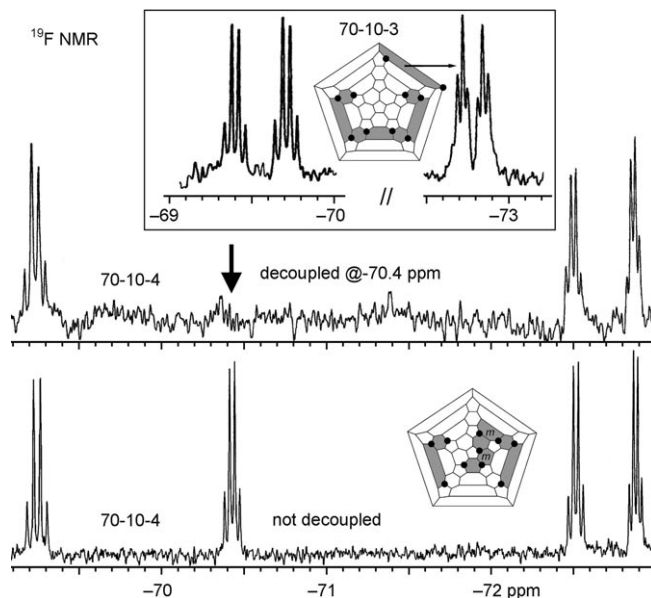


Figure 5. Fluorine-19 NMR spectra (376.5 MHz, CDCl₃, 25 °C, C₆F₆ int. std. (δ -164.5)) of 70-10-3 (inset; no decoupling) and 70-10-4 (with and without homonuclear decoupling at δ -70.4 ppm). The chemical shift axes are to scale in all three spectra. The second-order nature of the two “quartets” at δ -72.7 and -72.8 in the spectrum of 70-10-3 indicates that this compound has an isolated *p*-C₆(CF₃)₂ hexagon. The decoupling experiment for 70-10-4 indicates that this compound does not have an isolated *p*-C₆(CF₃)₂ hexagon.

Both the **bb** and **dd** options can be ruled out since the remaining ribbon of eight CF₃ groups, with independent ⁷J_{FF} values of 16.6 Hz, must be an equatorial ribbon identical to the one in 70-8-1. Therefore, there is only one possible *p*⁷.*p* addition pattern that fits the NMR data for 70-10-3, and it is shown as a Schlegel diagram in Figures 3 and 5. In 70-10-4, the decoupling experiment shown in Figure 5 proves that the two quartets with ⁷J_{FF} = 11.4 Hz are not due to an isolated hexagon, leaving the possibilities that the two ribbons have either five and five CF₃ groups, six and four CF₃ groups, or seven and three CF₃ groups. In searching for possible addition patterns that fit the NMR data, we imposed general observations i)–viii) and the untested requirement that the relative energy of the most-probable addition pattern for 70-10-4 would be within 40 kJ mol⁻¹ of 70-10-1. Within the confines of these restrictions, the only isomer that fits the NMR data was the “7+3” isomer shown in Figures 3 and 5. However, there are at least two other isomers that qualitatively fit the NMR data, and they are shown in Figure 4 along with their DFT relative energies. All three of these possible 7+3 addition patterns are unprecedented for C₇₀(X)₁₀ derivatives. Other 5+5, 6+4, 7+3, and 8+2 addition patterns are shown as Schlegel diagrams in the Supporting Information along with their DFT-predicted energies (Figures S3–S6).

The arbitrary limit of 40 kJ mol⁻¹ was chosen as follows. We recently reported the X-ray structure of a C₁ isomer of C₆₀(CF₃)₁₂,^[22] made with CF₃I at high temperature, that is 39 kJ mol⁻¹ higher in energy (using the same DFT code and functional^[22]) than the S₆ isomer of this composition,^[9,18] the X-ray structure of which has also been reported.^[18] This represents the least thermodynamically stable fullerene(CF₃)_n derivative isolated to date (i.e., the highest energy isomer of a given fullerene(CF₃)_n composition). Before C₁-C₆₀(CF₃)₁₂ was reported, the highest energy isomer that had been isolated was C₅-C₆₀(CF₃)₆,^[23] which was predicted to be only 14.4 kJ mol⁻¹ higher in energy than the C₁ isomer.^[31] All other well-characterized fullerene(CF₃)_n isomers, including all 16 previously reported C₇₀(CF₃)_n derivatives, had been found to be either the most stable isomer or within 10 kJ mol⁻¹ of the most stable isomer. It is possible that a mixture of products similar to a thermodynamic mixture of products is obtained when sufficiently high temperatures are used in fullerene/CF₃I reactions (but this has not yet been demonstrated). If this is true, it is sensible that isomers as far from equilibrium as 40 kJ mol⁻¹ are only now being reported, because only when large-scale (i.e., 0.1 g of C₇₀) reactions are carried out, as in this work, can low-abundance isomers be collected in sufficient quantities for detailed physicochemical characterization. For example, using the relative energies of 0.0, 27.5, and 19.5 kJ mol⁻¹ for 70-10-1, 70-10-3, and 70-10-4, respectively, the 530 °C equilibrium molar ratios 70-10-3/70-10-1 and 70-10-4/70-10-1 are 0.016 and 0.054, respectively.

We have examined more than 400 isomers of C₇₀(CF₃)₁₀ with 5+5, 6+4, 7+3, 8+2, and 9+1 addition patterns. The most stable of these are listed in Figures S3–S7 (see Sup-

porting Information). Some of them are within 15 kJ mol⁻¹ of 70-10-1 but do not fit the NMR spectra of any derivative we have isolated. Until more is known about the dependence of fullerene(CF₃)_n product distributions on a variety of thermodynamic and kinetic factors, proposed addition patterns based on an arbitrary relative-energy limit such as 40 kJ mol⁻¹ must be considered tentative.

With one exception, all previous ribbons of edge-sharing *m*- and/or *p*-C₆(CF₃)₂ hexagons in fullerene(CF₃)_n derivatives have an even number of CF₃ groups in the ribbon. The exception is the proposed structure of C₅-(C₇₆-T_d)(CF₃)₁₂, which has a *p*⁹ loop of nine CF₃ groups and a *p*² ribbon of three CF₃ groups.^[9] Although it is uncertain at this time whether 70-10-4 has ribbons of 3, 4, 5, 6, and/or 7 CF₃ groups, it is certain that the fifth isomer of C₇₀(CF₃)₁₀, 70-10-5, has a ribbon of nine CF₃ groups and an isolated CF₃ group (this is first example of an isolated CF₃ group in a fullerene(CF₃)_n compound. The singlet at δ -74.3 in this asymmetric compound demonstrates that one CF₃ group does not share its pentagon or two hexagons with any of the other nine CF₃ groups, and the two quartets strongly suggest a *p*⁸ ribbon on the equator of C₇₀, starting with a **dd'** hexagon (⁷J_{FF} = 15.5 Hz) and ending with a **dd** hexagon (⁷J_{FF} = 10.4 Hz).

While this manuscript was in preparation, the X-ray structures of seven isomers of C₇₀(C₂F₅)₁₀ were published.^[32] One isomer exhibited the 70-10-1 addition pattern, but the other six addition patterns were unique. They included two *pmp.p²pm* isomers, a *p⁴pm.p* isomer, and a *pmp.p².p.i* isomer. Based on our NMR data, none of these unprecedented addition patterns are possible addition patterns for 70-10-2, -3, -4, or -5, but they do show that C₇₀(R_i)_n addition patterns with *pm* ribbons or with isolated R_i groups can be stable enough to be isolated.

The two C₁ isomers of C₇₀(CF₃)₁₂ that have been structurally characterized, 70-12-1 and 70-12-2,^[6–8] are the most stable and the second most stable isomers of this composition, respectively (relative energies 0.0 and 1.0 kJ mol⁻¹, respectively (this work); our values are slightly different than those published by Troyanov and co-workers^[7]). The ¹⁹F NMR spectra of these compounds exhibit four quartets and eight quartets of quartets (some of which are not fully resolved). The four quartets, indicating that there are four terminal CF₃ groups, are consistent with the X-ray structures of these derivatives (see Table 1). For example, the two quartets assigned to the isolated *p*-C₆(CF₃)₂ hexagon in 70-12-2, which is an **ac** hexagon, have, as required, the same ⁷J_{FF} value, 12.0(3) Hz. The quartet assigned to the terminal CF₃ group on a type **a** carbon atom (at the **ac** hexagon end of the *p⁷mp* ribbon) has a typical ⁷J_{FF} value of 10.2(3) Hz, and the quartet assigned to the terminal CF₃ group on the end-of-ribbon **dd'** hexagon has a typical ⁷J_{FF} value of 15.8(3) Hz. (The ⁷J_{FF} values for the terminal CF₃ groups on the *p⁷mp* ribbon in 70-10-1 are 10.3(2) and 15.9(2) Hz.) Significantly, there are no multiplets with -δ values lower than 60, and this indicates that there are no CF₃ groups that are eclipsed or nearly eclipsed with respect to the fullerene

cage.^[9,33] This too is consistent with the X-ray structures of these compounds.

The two new isomers of $C_{70}(CF_3)_{12}$, 70-12-3 and 70-12-4, have ^{19}F NMR spectra that are significantly different than those of 70-12-1 and 70-12-2 but are entirely consistent with the proposed addition patterns shown in Figure 3 as well as with the DFT-optimized geometries for these isomers. In addition, they are among the most stable isomers of the composition $C_{70}(CF_3)_{12}$ (the DFT-predicted lowest-energy conformations for these addition patterns are both only 3.9 kJ mol^{-1} above the energy of 70-12-1). They are the first examples of $C_{70}(CF_3)_n$ compounds with $n=12$ and with two CF_3 groups on the same pentagon, yet they are only $3\text{--}4 \text{ kJ mol}^{-1}$ less stable than the alternative $p^7mp.p$ addition patterns of 70-12-1 and 70-12-2 that have only one CF_3 per pentagon. There are only three quartets in each NMR spectrum, with J_{FF} values of 13.7, 13.4, and 9.7 Hz for 70-12-3 and 13.8, 16.1, and 10.0 Hz for 70-12-4. Both spectra have one unresolved multiplet with a $-\delta$ value below 60, indicating that both compounds contain exactly one CF_3 group that is eclipsed or nearly eclipsed. Figure 6 shows fragments of their structures in the region of the eclipsed CF_3 groups. It can be seen that the eclipsed group in 70-12-3, which is on a terminal dd' hexagon, should significantly affect the coupling constant for the quartet assigned to its dd' hexagon neighbor. It was on this basis that the assignments of the

otherwise similar addition patterns of 70-12-3 and 70-12-4 were made.

Common and uncommon addition pattern motifs for $C_{70}(CF_3)_n$ compounds: The mechanism(s) by which multiple CF_3 radicals add to fullerenes at $300\text{--}600^\circ\text{C}$ are not known at this time, and any attempt to rationalize observed addition patterns with either kinetic or thermodynamic arguments (as we did above when discussing the 40 kJ mol^{-1} energy limit for viable structures), must be greeted with a dose of skepticism and therefore must be considered tentative. In this paragraph and the next, we will not argue whether or not a particular $C_{70}(CF_3)_n$ compound is a literal precursor to a $C_{70}(CF_3)_{n+2}$ product *without* rearrangement of the original n CF_3 groups on the surface of the fullerene. However, it is useful to note the structural similarities among the 17 compounds in this study in order to highlight, for future workers in this field, particularly common motifs that are ribbons of edge-sharing $C_6(CF_3)_2$ hexagons. Interestingly, the pmp pattern of 70-4-1 is not part of the addition pattern of any of the other compounds except possibly for 70-10-4. In this regard, it is important to note that 70-4-1 is not the only isomer of this composition present in product mixtures, nor is it the most abundant isomer of $C_{70}(CF_3)_4$. It is simply the isomer that can be purified to 95 mol% purity, and characterized, at this time.

A ribbon of edge-sharing dd' and dd' $p\text{-}C_6(CF_3)_2$ hexagons on the equator of C_{70} is a very common addition-pattern motif. It is part of the proposed addition patterns of 70-6-2, 70-10-3, and 70-10-5, it is the entire proposed addition pattern of 70-6-1, 70-8-2, and 70-10-2, and it is known from X-ray crystallography to be the addition pattern of 70-8-1.^[3] An equator-to-pole p^xmp ribbon of edge-sharing $C_6(CF_3)_2$ hexagons is another common motif. It is present in 70-6-3 ($x=3$), 70-10-1, 70-12-1, and 70-12-2 ($x=7$) and is proposed to be present in 70-12-3 and 70-12-4 ($x=7$). The p^7mp ribbon is also present in some of the six structurally-characterized $C_{70}(CF_3)_n$ derivatives with $n=14$.^[10,11]

Reduction potentials and E -(LUMO) values: Representative cyclic voltammograms for eight of the 17 $C_{70}(CF_3)_n$ derivatives are shown in Figure 7. The $E_{1/2}$ values for reversible

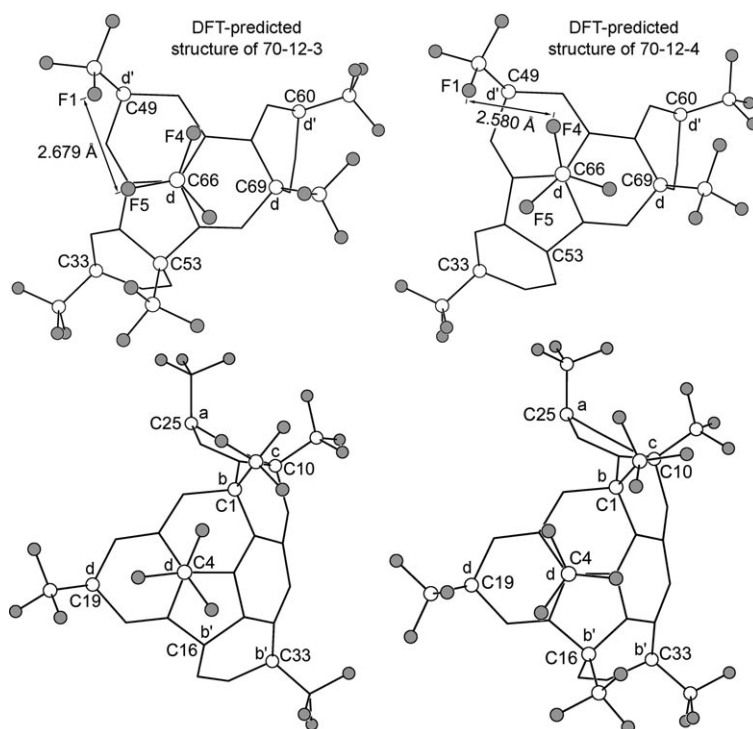


Figure 6. Fragments of the DFT-optimized structures of 70-12-3 and 70-12-4. The CF_3 groups on C66 and C25 define the beginning and the end, respectively, of the p^7mp ribbon of edge-sharing $C_6(CF_3)_2$ hexagons in both $C_1\text{-}p^7mp.p$ compounds. The drawings show the predictions that i) the CF_3 group on C66 is eclipsed in 70-12-3 ($\delta = -56.7$) and lengthens the $F\cdots F$ distance between the CF_3 groups on C66 and C49 relative to the analogous distance in 70-12-4 and ii) the CF_3 group on C4 is eclipsed in 70-12-4 ($\delta = -56.7$) but, since C4 is not on a terminal $p\text{-}C_6(CF_3)_2$ hexagon, it does not affect the terminal $F\cdots F$ distances or coupling constants for the two terminal ac hexagons relative to the respective distances and coupling constants for 70-12-3.

reductions (i.e., quasi-reversible waves with $\Delta E_p = 90$ mV for a scan speed of 20 mV s^{-1} and $\Delta E_p = 150$ mV for scan speeds greater than or equal to 0.5 V s^{-1}) are listed in Table 4 for all 17 C₇₀(CF₃)_n compounds studied. The com-

Table 4. Reversible $E_{1/2}$ values for C₇₀(CF₃)_n Derivatives ($n = 2-12$).^[a]

Compound	Relative $E_{1/2}$ [V] vs C ₇₀ ^{0/-} {V vs Fe(Cp*) ₂ ⁺⁰ }		
	0/- couple	-/2- couple	2-/3- couple
C ₇₀	0.00 [-0.48]	-0.40 [-0.88]	-0.80 [-1.28]
70-2-1	0.28	-0.14	-0.71
70-2-2	0.12	-0.26	-0.74
70-4-1	0.21	-0.18	-0.77
70-6-1	0.30	-0.14	-0.57 ^[b]
70-6-2	0.34	-0.13	-0.48
70-6-3	0.17	-0.27	irreversible
70-8-1	0.04	-0.41	-1.04 ^[c]
70-8-2	0.31	-0.21	-1.28 ^[e]
70-10-1	-0.11 ^[d]	-0.66	irreversible
70-10-2	-0.01	-0.50	irreversible
70-10-3	0.04	-0.41	irreversible
70-10-4	0.08	-0.48	-0.86 ^[e]
70-10-5	0.28	-0.21	-1.11 ^[e]
70-12-1	0.09	-0.46	-0.91 ^[c]
70-12-2	0.07	-0.47	-0.98 ^[b]
70-12-3	0.26	-0.37	-0.90 ^[e]
70-12-4	0.25	-0.41	-0.90 ^[f]

[a] All data from this work. Reversible wave observed at 20 mV s^{-1} unless otherwise noted. Electrolyte = $0.10 \text{ M N}(\text{nBu})_4\text{BF}_4$ in dichloromethane; Fe(Cp*)₂⁺⁰ internal standard ($E_{1/2} = -0.48 \text{ V}$ vs. C₇₀^{0/-}). The values shown in braces are $E_{1/2}$ values vs Fe(Cp*)₂⁺⁰. In general, the $E_{1/2}$ values were reproducible to ± 10 mV. [b] Scan rate = 3.5 V s^{-1} . [c] Scan rate = 2.0 V s^{-1} . [d] Irreversible first reduction; the value shown is the cathodic peak potential. [e] Scan rate = 500 mV s^{-1} . [f] This value is only approximately known.

pound 70-10-1 is unusual in that only the 2nd reduction appears to be electrochemically reversible. It will be discussed in detail later. Thirteen of the remaining 16 compounds exhibited three reversible reductions (in addition to 70-10-1, the other exceptions were 70-6-3, 70-10-2, and 70-10-3, which only exhibited reversible 1st and 2nd reductions).

There are four studies in the literature in which the effect of addition pattern on $E_{1/2}$ values was reported for two or more isomers of a given C₇₀(X)_n composition. These are listed in Table 5.^[34-37] In three of the studies, the largest $\Delta E_{1/2}$ range reported was 0.05 V. The largest previously reported $\Delta E_{1/2}$ range for the first reduction of C₇₀(X)_n compounds (i.e., the range of 0/- $\Delta E_{1/2}$ values) is 0.15 V for three isomers of C₇₀(Bn)₂.^[34] In contrast, the smallest 0/- $\Delta E_{1/2}$ range for isomers of a given C₇₀(CF₃)_n composition we are reporting here is 0.16 V for the two isomers of C₇₀(CF₃)₂. The largest range for any reduction step for any of the sets of C₇₀(CF₃)_n isomers is 0.45 V for the -/2- $E_{1/2}$ values of the five isomers of C₇₀(CF₃)₁₀. There is a general tendency for $\Delta E_{1/2}$ ranges to decrease from the first to the second to the third reversible reduction for isomers of a given value of n , but there are a few exceptions to this trend.

We recently reported an electrochemical, spectroscopic, and DFT study of 18 C₆₀(CF₃)_n derivatives with $n = 2-12$.^[28]

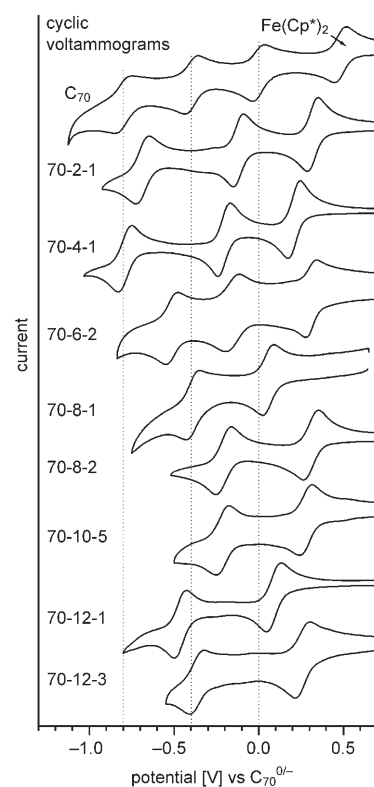


Figure 7. Representative cyclic voltammograms (CVs) for C₇₀(CF₃)_n derivatives (dichloromethane, $0.1 \text{ M TBA}^+\text{BF}_4^-$, glassy carbon or Pt working electrode, 20 mV s^{-1} scan rate, Fe(Cp)₂ or Fe(Cp*)₂ internal standard added immediately after the CV was recorded). Reversible third reduction potentials for some of the compounds could only be determined at higher scan rates ($0.5-3.5 \text{ V}$; not shown). The CV of a mixture of C₇₀ and Fe(Cp*)₂ is shown at the top.

Table 5. Ranges of $E_{1/2}$ values for C₇₀(X)_n isomers.^[a]

composition	no. of isomers	$\Delta E_{1/2}$ [V]		
		0/- couple	-/2- couple	2-/3- couple
C ₇₀ (Bn) ₂ ^[b]	3	0.15	0.10	0.00
C ₇₀ H ₂ ^[c]	2	0.01	0.04	0.03
C ₇₀ (c-ONCR) ₂ ^[d]	3	ca. 0	ca. 0	ca. 0
C ₇₀ (COOCH ₂ -COOMe) ₂ ^[e]	3	0.04	0.02	0.05
C ₇₀ (CF ₃) ₂	2	0.16	0.12	0.03
C ₇₀ (CF ₃) ₆	3	0.17	0.14	0.09 ^[f]
C ₇₀ (CF ₃) ₈	2	0.27	0.20	0.24
C ₇₀ (CF ₃) ₁₀	5	0.35 ^[g]	0.45	0.25 ^[f]
C ₇₀ (CF ₃) ₁₂	4	0.19	0.10	0.08
C ₆₀ (CF ₃) ₆ ^h	2	0.33	0.25	0.09
C ₆₀ (CF ₃) ₈ ^h	5	0.39	0.35	0.40
C ₆₀ (CF ₃) ₁₀ ^h	6	0.50	0.40	0.20
C ₆₀ (CF ₃) ₁₂ ^h	2	0.49		

[a] Reversible couples only unless otherwise noted. The error on $E_{1/2}$ values was generally ± 10 mV. All values for C₇₀(CF₃)_n compounds from this work [b] Ref. [34]. [c] Ref. [37]. [d] Ref. [36]. [e] Ref. [35]. [f] Two isomers only. [g] The hypothetical $E_{1/2}$ value used for 70-10-1 for this calculation was -0.07 V ; omitting 70-10-1 changes this $\Delta E_{1/2}$ value from 0.35 V for five isomers to 0.29 V for four isomers. [h] Ref. [28].

Ranges of $E_{1/2}$ values up to 0.50 V for a given composition were found, and these are also listed in Table 5. Prior to that study, the largest variation in $E_{1/2}$ values reported for isomers of a given $C_{60}(X)_n$ composition was 0.16 V for seven isomers of $C_{60}(C(CO_2Et)_2)_3$.^[38]

The electrochemical data show that altering the addition pattern for $C_{70}(X)_n$ isomers can affect $E_{1/2}$ values to a greater extent than was previously known, at least when X is large enough so that 1,4-additions are favored over 1,2-additions. Even seemingly subtle changes in addition pattern have a large effect for $C_{70}(CF_3)_n$ derivatives. For example, moving one CF_3 group from one end of the C_5-p^7 ribbon in 70-8-1 to the other end, generating the C_2-p^7 addition pattern of 70-8-2, raises the first reduction potential by 0.27 V, and moving one CF_3 group by only two cage carbon atoms on its own pentagon would change 70-10-1 into 70-10-5, raising the second reduction potential by 0.45 V.

The only previous study in which a series of $C_{70}(X)_n$ compounds with the same substituent X but with different values of n was studied by electrochemical techniques is for X=Ph and $n=2, 4, 6, 8,$ and 10 (one isomer each).^[39] The $E_{1/2}$ values for the first and second reductions are shown graphically in Figure 8 along with the corresponding $E_{1/2}$ values for the 17 $C_{70}(CF_3)_n$ compounds studied in this work. The lines connecting the data points represent structural relationships, as defined above. Although the authors of the X=Ph paper stated in that paper,^[39] and in others,^[29,40] that their isomer of $C_{70}Ph_6$ was the C_5-p^5 isomer, it has been recently shown that it is much more likely that the isomer they studied was in fact the C_2-p^5 isomer of $C_{70}Ph_6$ (i.e., the isomer with the same addition pattern as 70-6-1).^[1] On the other hand, there is no doubt that $C_{70}Ph_8$,^[39] like the structurally characterized compound $C_{70}Me_8$,^[41] has the same addition pattern as 70-8-1.^[3] The 70-6-1 and 70-8-1 addition patterns are the only two addition patterns that the $C_{70}(CF_3)_n$ and $C_{70}Ph_n$ sets of compounds have in common.

The solvent used in the X=Ph study was tetrahydrofuran, as opposed to dichloromethane in this study, but that difference does not preclude comparisons of the two sets of results because all potentials in Figure 8 are referenced to the $C_{70}^{0/-}$ potential in the solvent used for the respective $C_{70}(X)_n$ $E_{1/2}$ measurements. The data in Figure 8 show that $E_{1/2}$ values increase significantly when the substituent X is changed from Ph to CF_3 for a constant addition pattern, by 0.42 V for the first reduction and 0.51 V for the second reduction for the 70-6-1 addition pattern, and by 0.60 V for the first reduction and 0.61 V for the second reduction for the 70-8-1 addition pattern. Another way of appreciating the difference, using the 70-6-1 addition pattern as an example, is to note that adding six Ph groups to C_{70} to form $C_2-p^5-C_{70}Ph_6$ lowers the $0/-$ $E_{1/2}$ value by 0.12 V but adding six CF_3 groups to C_{70} to form 70-6-1 raises the $0/-$ $E_{1/2}$ value by 0.30 V.

The $0/-$ and $-/2-$ $E_{1/2}$ values for the X=Ph compounds both show the same trend, a monotonic decrease with increasing n . The authors of the X=Ph study concluded that the trend is “the result of a competition between the elec-

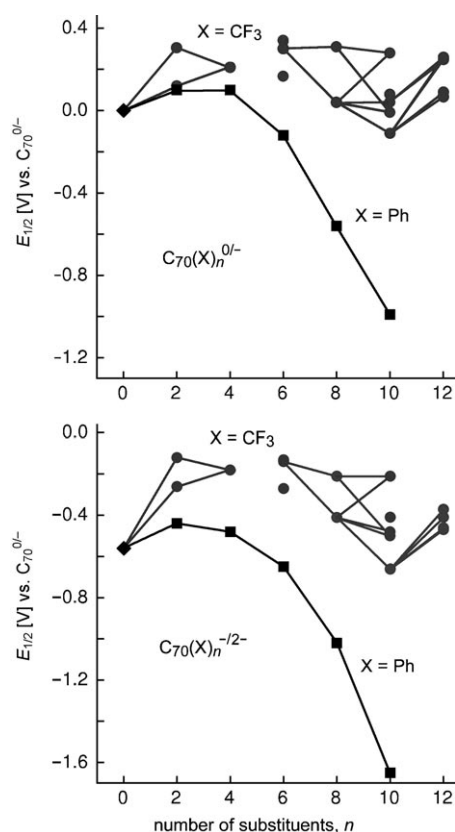


Figure 8. First (top) and second (bottom) reduction potentials vs. n , the number of X groups in $C_{70}(X)_n$ (circles, X= CF_3 (dichloromethane, this work); squares, X=Ph (tetrahydrofuran, ref. [39])). The lines connecting data points indicate structural, not mechanistic, relationships (i.e., the structures of compounds represented by connected points are related by the addition or removal of two X groups with no other changes to the addition patterns). For the $C_{70}(CF_3)_n$ compounds, the isomers are (top to bottom): 70-2-1 and 70-2-2; 70-6-2, 70-6-1, and 70-6-3; 70-8-2 and 70-8-1; 70-10-5, 70-10-4, 70-10-3, 70-10-2, and 70-10-1; 70-12-3, 70-12-4, 70-12-1, and 70-12-2. This order is the same for both plots except that the points for 70-10-3 and 70-10-4 are reversed in the plot of second reduction potentials vs. n .

tron-withdrawing effect exerted by the phenyl groups and the destabilization of redox orbitals deriving from the saturation of double bonds [in C_{70}].^[39] The observation that, in general, fullerene(X) $_n$ reduction potentials decrease as n increases has been made by many investigators and is perhaps the most widely known paradigm in fullerene electrochemistry.^[42-45] Nevertheless, it is now apparent that if one uses substituents that are strongly electron withdrawing, like CF_3 groups, this paradigm has little or no predictive value. We will return to this point below.

Figure 9 displays DFT-predicted $E(\text{HOMO})$ and $E(\text{LUMO})$ values for 30 $C_{70}(X)_n$ derivatives with the 70-2-1, 70-4-1, and 70-6-1 addition patterns (X= CH_3 , Ph, H, NH_2 , CH_2F , CHF_2 , CF_3 , F, NO_2 , and CN). Interestingly, for all three addition patterns the $E(\text{HOMO})$ and $E(\text{LUMO})$ values for the X=Ph compounds are higher, not lower, than the corresponding orbital energies for the X=H compound. Thus, a phenyl group does not appear to be a stronger elec-

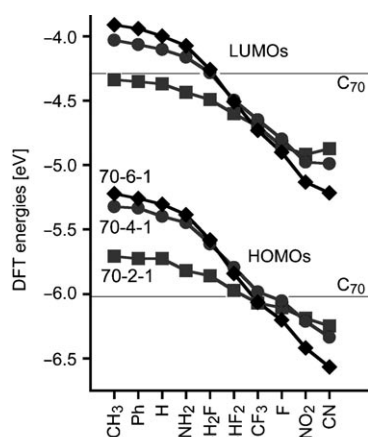


Figure 9. DFT-predicted $E(\text{HOMO})$ and $E(\text{LUMO})$ values for each of ten $\text{C}_{70}(\text{X})_n$ compounds with the 70-2-1, 70-4-1, and 70-6-1 addition patterns. The horizontal lines at -6.018 and -4.315 eV represent the DFT-predicted $E(\text{HOMO})$ and $E(\text{LUMO})$ values, respectively, for C_{70} .

tron-withdrawing group than a hydrogen atom, at least not for fullerene(X)_n derivatives with certain addition patterns (this could be a combination of electronic and steric effects). It is unfortunate that $E_{1/2}$ values for the compounds $\text{C}_s\text{-}p^7\text{-C}_{70}(\text{CH}_3)_8$ ^[41] and $\text{C}_s\text{-}p^7\text{-C}_{70}\text{H}_8$ ^[46] are not available in the literature in order to compare their $E_{1/2}$ values to those of $\text{C}_s\text{-}p^7\text{-C}_{70}\text{Ph}_8$.

The plots in Figure 9 also reveal an interesting finding about 70-2-1, 70-4-1, and 70-6-1. For these three compounds, the $\text{X} = \text{CF}_3$ points nearly coincide, suggesting that the electron-withdrawing effect of a pair of CF_3 groups just compensates for the saturation of an additional double bond (but note that all three of these $E(\text{LUMO})$ values are significantly lower than $E(\text{LUMO})$ for C_{70}). The near-coincidence of the three $E(\text{LUMO})$ data points should result in similar $0/- E_{1/2}$ values for these three compounds, with the potential for 70-6-1 slightly more positive than the potential for 70-2-1, which in turn should be slightly more positive than the potential for 70-4-1. Table 4 shows that the three $E_{1/2}$ values in question are 0.30, 0.28, and 0.21 V, respectively, relative to $\text{C}_{70}^{0/-}$. However, for a different choice of addition patterns, a substituent to the right or left of CF_3 in Figure 9 might represent the “crossover” substituent. Further DFT calculations and $E_{1/2}$ values for a wider range of $\text{C}_{70}(\text{X})_n$ compounds, when they become available, will make such an analysis possible.

Plots of the $E(\text{LUMO})$ values for the 70-6-1 addition pattern versus various sets of group electronegativities^[47–49] are shown in Figure S8 (see Supporting Information). They clearly demonstrate that the effect of a particular substituent on shifting $E(\text{LUMO})$ up or down is not merely a function of the substituent’s ability to withdraw electrons from the C_{70} cage. The anomalous $E(\text{LUMO})$ values for the cyano derivatives shown in Figure 9 are a case in point. The group electronegativity of CN is about the same as CF_3 ,^[47,48] but the LUMO for the cyano analogue of 70-6-1 is stabilized by about 0.5 eV relative to the LUMO for 70-6-1 itself.

Most importantly, the $\text{C}_{70}(\text{CF}_3)_n$ electrochemical results demonstrate conclusively that there is no simple correlation between adding more substituents and the direction of change in $E_{1/2}$ values. It depends on the addition patterns of the compounds in question. Ignoring structural relationships, one can find virtually all possible trends imaginable for the 17 $\text{C}_{70}(\text{CF}_3)_n$ data points in each plot in Figure 8. For example, there is a steady decrease in $0/- E_{1/2}$ with increasing n from 70-2-2 to 70-4-1 to 70-6-3 to 70-8-1 to 70-10-1 and another steady decrease from 70-6-2 to 70-8-2 to 70-10-5 to 70-12-1, but there is also a steady increase in $0/- E_{1/2}$ from 70-2-2 to 70-4-1 to 70-8-2 and another steady increase from 70-8-1 to 70-10-4 to 70-12-3. In addition, there is a series of compounds with increasing n values that have, to within ± 5 mV, a constant $0/- E_{1/2}$ value, from 70-2-1 to 70-6-1 to 70-8-2 to 70-10-5 to 70-12-1. Finally, there is a series of compounds with alternating lower and higher $0/- E_{1/2}$ values as a function of n , from 70-2-1 to 70-4-1 to 70-6-2 to 70-8-1 to 70-10-5 to 70-12-2. Whether $E_{1/2}$ increases, decreases, or remains the same when the degree of saturation of C_{70} increases from composition $\text{C}_{70}(\text{CF}_3)_n$ to composition $\text{C}_{70}(\text{CF}_3)_{n+2}$ depends on the ways that those substituents are distributed on the surface of [70]fullerene, not on the number of substituents. For each value of n from 2 to 10, there is at least one $\text{C}_{70}(\text{CF}_3)_n$ isomer that has a higher potential, and one isomer that has a lower potential, than at least one of the isomers that results when n is increased (by any value up to $n=12$). This may be found to be true as well for $\text{C}_{70}(\text{X})_n$ compounds with substituents other than CF_3 once multiple isomers of them become available.

In the recent electrochemical study of 18 $\text{C}_{60}(\text{CF}_3)_n$ derivatives, it was discovered that the $0/- E_{1/2}$ values were a linear function of the corresponding DFT-predicted $E(\text{LUMO})$ values (this plot is reproduced in the Supporting Information as Figure S9).^[28] The correlation coefficient for this plot was 0.98, and the average deviation of the linear least-squares calculated $E_{1/2}$ values from the experimental $E_{1/2}$ values was ± 20 mV.^[28] Linear $0/- E_{1/2}$ values vs. $E(\text{LUMO})$ plots have also been previously reported in three electrochemical studies of fullerene cycloadducts.^[50–52] However, a plot of experimental $0/- E_{1/2}$ values vs. $E(\text{LUMO})$ for the $\text{C}_{70}(\text{CF}_3)_n$ derivatives we have described in this paper was not a single straight line. Instead, an approximately linear plot was observed for each value of n with three or more isomers, and these plots were approximately parallel but were not co-linear, as shown in Figure 10. It is not clear at this time why the individual plots in Figure 10 are not co-linear, and this aspect of the electrochemical behavior of $\text{C}_{70}(\text{CF}_3)_n$ compounds will continue to be investigated in our labs.

Two of the most important results of the recent CV/DFT study of $\text{C}_{60}(\text{CF}_3)_n$ derivatives were that i) the energy of the LUMO was related to the degree of delocalization of the LUMO, an expected result, and ii) the LUMO itself was located on a fragment of the remaining pi system that included non-terminal double bonds in pentagons (nt-DBIPs), a quite unexpected result.^[28] An nt-DBIP is defined as a short

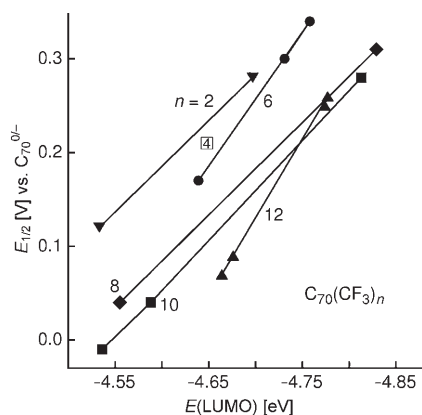


Figure 10. Fifteen first reduction potentials ($0/- E_{1/2}$ values) vs. DFT-predicted LUMO energies. The limits of the x and y axes span 0.36 V and 0.36 eV, respectively. The $E_{1/2}$ value for the first reduction of 70-10-1 was omitted because this redox process is irreversible, and the $E_{1/2}$ value for 70-4-1 was omitted because this is the only isomer of $C_{70}(CF_3)_4$ that was studied.

pent-hex junction that has two $C(sp^2)$ nearest neighbors. Different addition patterns result in different numbers of nt-DBIPs, and when the LUMO fragments associated with different nt-DBIPs in the same derivative overlap, $E(LUMO)$ is especially low and, consequently, the experimental $E_{1/2}$ value was relatively high.^[28] This is the basis for understanding how the addition pattern of a fullerene(X)_n derivative determines the electron acceptor properties of the molecule. It is ironic that DBIPs, which are destabilizing as far as the total energy of a fullerene derivative is concerned,^[53,54] are exactly what is needed to lower the energy of its LUMO and increase its electron affinity. However, DBIPs are necessary but not sufficient. Many fullerene(CF_3)_n compounds have terminal DBIPs (t-DBIPs), which have only one $C(sp^2)$ nearest neighbor, and these are generally among the shortest C–C bonds in the cage.^[4,5] Nevertheless, none of the LUMOs we have examined for $C_{60}(CF_3)_n$ and $C_{70}(CF_3)_n$ derivatives are associated with t-DBIPs.^[28] Only nt-DBIPs generated low-energy π^* fragments that were incorporated into the LUMO.

The correspondence between the shape of $C_{70}(CF_3)_n$ LUMOs, $E(LUMO)$ values, and $E_{1/2}$ values is more complex than for $C_{60}(CF_3)_n$ derivatives. Nevertheless, it appears that the LUMOs for $C_{70}(CF_3)_n$ compounds, in general, are also “anchored” to non-terminal double bonds in pentagons (nt-DBIP). Note that two compounds with no nt-DBIPs, 70-10-1 and 70-10-2, have negative first reduction potentials relative to $C_{70}^{0/-}$. The analysis for one pair of isomers, 70-8-1 and 70-8-2, is straightforward and will be presented here. Much of this analysis depends on the interpretation of cage C–C distances predicted with the PBE functional, which is used extensively in our work, and we have recently validated this functional by comparing predicted cage C–C distances with those available from the most precise fullerene(CF_3)_n X-ray structures.^[28]

Fragments of the DFT-predicted structures of 70-8-1 and 70-8-2 are shown in Figure 11 along with the LUMOs for

these two molecules. The blue (+) and green (–) lobes of the LUMOs of the derivatives are very similar to the LUMOs of the planar aromatic hydrocarbons acenaphthalene for 70-8-1 and naphthalene (i.e., linear tetracene) for 70-8-2.^[55,56] The LUMO drawings in Figure 11 show that the 70-8-2 LUMO is more extensively delocalized than the 70-8-1 LUMO, and we propose that this is the reason that $E_{1/2}$ for 70-8-2 is more than 0.25 V more positive than $E_{1/2}$ for 70-8-1.

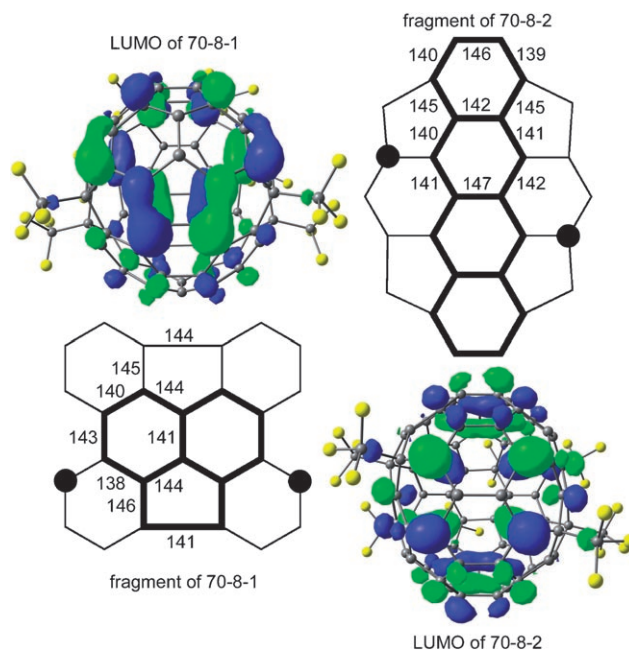


Figure 11. Fragments of the DFT-predicted structures and the DFT-predicted LUMOs for 70-8-1 and 70-8-2. The numbers in the structure fragments are cage C–C distances in pm (the black circles indicate the cage C atoms to which the CF_3 groups are attached).

The electrochemical behavior of 70-10-1 was significantly different than that of the other 16 $C_{70}(CF_3)_n$ derivatives, as shown in Figure 12. The first reduction was not electrochemically reversible at any scan rate, from 10 mVs^{-1} to 50 Vs^{-1} . The i versus E pattern observed at 20 mVs^{-1} was virtually unchanged up to 2 Vs^{-1} . The re-oxidation peak was shifted about 0.5–0.6 V from the position expected for a reversible process. From 2 Vs^{-1} to the highest scan rate investigated, an apparently normal re-oxidation peak was observed. Relative to the anodic current for the reduction peak, the current for the new peak increased with increasing scan rate, as also shown in Figure 12.

The position of the irreversible re-oxidation peak exhibited a significant scan-rate dependence, from about 0.4 V at 20 mVs^{-1} to 0.6 V at 20 Vs^{-1} . It also depended on the potential at which the CV was reversed. For example, at 2 Vs^{-1} it was observed at 0.57, 0.61, and 0.64 V when the potential was reversed at –0.40, –0.90, and –1.4 V, respectively. Extending the potential range to more negative potentials also resulted in a significant current increase for the irreversible

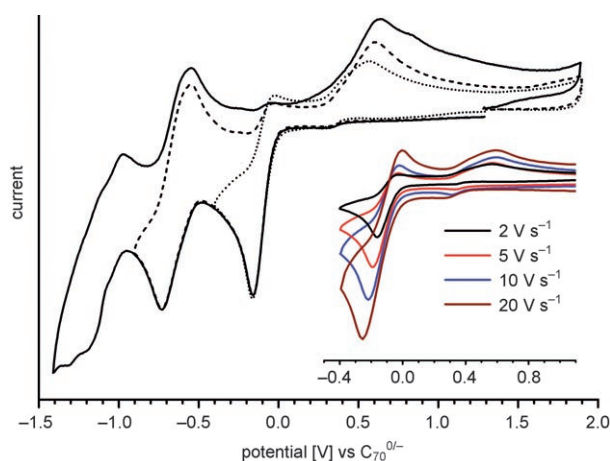


Figure 12. Cyclic voltammograms (CVs) of 70-10-1 (dichloromethane, 0.1 M TBA⁺BF₄⁻, Pt wire working electrode, 20 mV s⁻¹ scan rate, Fe(Cp)₂ or Fe(Cp*)₂ internal standard added immediately after the CV was recorded). The inset shows CVs recorded at different scan rates.

re-oxidation at 0.6 V. In addition, multiple cycling at 0.5 V s⁻¹ revealed that the first reduction of 70-10-1, although *electrochemically* irreversible, was *chemically* reversible. The reduction current recorded for multiple cycles remained the same as long as the potential limits included both the reduction and the re-oxidation peaks. We do not know what product forms during the irreversible first reduction, but apparently 70-10-1 is regenerated during the irreversible re-oxidation. The increase in re-oxidation current with more negative reverse potentials can be attributed to the longer time available for the reduced species to undergo the chemical transformation.

The second reduction of “70-10-1” (i.e., the unknown species that is formed reversibly when 70-10-1 was reduced by one electron) was electrochemically reversible at all scan rates. A third reduction wave of “70-10-1” was observed at scan rates in excess of 2 V s⁻¹, but it was not electrochemically reversible even for a scan rate of 20 V s⁻¹. In ongoing experiments, we are attempting to isolate and characterize the product, possibly a dimer, formed by the first reduction of 70-10-1.

C₅-C₇₀(CF₃)₄O: On the basis of the similarity of the ¹⁹F NMR spectra for this compound and for the structurally-characterized compound C₅-C₆₀(CF₃)₄O,^[23] we believe that C₅-C₇₀(CF₃)₄O also has a skew-pentagonal pyramid (SPP) addition pattern.^[23,30,57] This assignment is also supported by the striking similarity of the UV/Vis spectra of C₇₀(CF₃)₄O and the compound C₇₀(tBuOO)₆, reported by Gan and co-workers (which has been shown to have an SPP addition pattern),^[30] as shown in Figure S10 (see Supporting Information). Cyclic voltammograms of C₅-C₇₀(CF₃)₄O are shown in Figure S11 (the 0/- E_{1/2} values for C₆₀ and C₇₀ differ by only 10 mV). In contrast to the majority of C₇₀(CF₃)_n derivatives, C₅-C₇₀(CF₃)₄O exhibited an irreversible first reduction (E_p = 0.06 V). There was no re-oxidation peak for the first reduction, but a new feature appeared at much more positive po-

tentials. The new feature was absent if the first cycle began in the anodic range, as shown in the inset in Figure S11, and it appeared to be reversible (E_{1/2} = 1.22 V). The identity of the new species has not yet been ascertained.

The second and the third reductions of “C₇₀(CF₃)₄O” appeared to be reversible (E_{1/2} = -0.33 and -0.67 V, respectively, vs. C₇₀^{0/-}). Similar behavior was observed for C₅-C₆₀(CF₃)₄O: it also exhibited an irreversible first reduction (i.e., the double peak at -0.05/-0.12 V vs. C₇₀^{0/-}) and a new reversible peak (E_{1/2} = 1.23 V vs. C₇₀^{0/-}). The second and the third reductions of “C₆₀(CF₃)₄O” were observed at -0.47 and -0.89 V, respectively. The peak potential for the first reduction can be compared with the 0/- E_{1/2} value of C₅-C₆₀(CF₃)₆, -0.07 V vs C₆₀^{0/-} (this compound also has the skew-pentagonal pyramid structure^[23]). The two isostructural compounds are both reduced at about 0 V. These data are discussed further in the Supporting Information.^[58,59]

Conclusion

The ranges of electrochemical potentials for isomers of C₇₀(CF₃)_n derivatives can vary by up to 0.45 V depending on the particular addition pattern of the isomer. Changes in E_{1/2} values this large can result by changing the position of only one CF₃ group for isomers of C₇₀(CF₃)₁₀. This parallels the behavior recently published for C₆₀(CF₃)_n derivatives and demonstrates that the electronic tunability of the C₇₀ cage in C₇₀(X)_n derivatives is much more extensive than previously observed, even with a given substituent X and a given value of n. The addition pattern is as important, if not more important in many cases, than the number of substituents, n, in determining E_{1/2} values of exohedral fullerene derivatives. An initial analysis of C₇₀(CF₃)₈ isomers indicates that addition patterns that lead to non-terminal double bonds in pentagons and extensive LUMO delocalization result in derivatives that are strong electron acceptors, a conclusion that is similar to that recently reported for C₆₀(CF₃)_n derivatives.^[62]

Experimental Section

Reagents, solvents, and C₇₀(CF₃)_n derivatives: The reagents and solvents CF₃I (Apollo Scientific), C₇₀ (Term USA), ferrocene ([Fe(Cp)₂], Fluka) and decamethylferrocene ([Fe(Cp*)₂], Fluka), CDCl₃ (Cambridge Scientific), hexafluorobenzene (Sigma-Aldrich), and hexane, heptane and toluene for HPLC purifications (HPLC grade, Sigma-Aldrich) were used as received. The following solvent and supporting electrolyte for cyclic voltammetry were purified as indicated: dichloromethane (Fluka, puriss. grade; stored in a nitrogen-filled glovebox over 4 Å molecular sieves (Merck)); tetrabutylammonium tetrafluoroborate (N(nBu)₄BF₄, Fluka puriss. grade, stored in the glovebox after drying under vacuum at 70 °C for 24 h). The following C₇₀(CF₃)_n derivatives were prepared as previously described: 70-2-1, 70-4-1, and 70-6-1;^[1] 70-6-3;^[1,2] C₆₀(CF₃)₄O.^[23]

Improved synthesis of C₇-p⁷-C₇₀(CF₃)₈ (70-8-1) and C₂-p⁷-C₇₀(CF₃)₈ (70-8-2): Finely ground C₇₀ (55 mg, 0.065 mmol) was placed in a 0.8 cm I.D. Pyrex tube connected to a gas handling system at one end and a mineral-oil bubbler at the other. The portion of the tube containing C₇₀ was placed in a 5 cm long tube furnace (reactor 1). After purging the sample with argon, it was heated to 550 °C and treated with 12 scem of gaseous

CF₃I (ca. 0.05 mmol min⁻¹) for four hours (**CAUTION**: CF₃I decomposes in air above 300 °C and produces toxic HF, COF₂, and I₂; handle only in a well-ventilated fume hood). Orange-brown C₇₀(CF₃)_{8,10} compounds and purple I₂ condensed inside the tube approximately 1 cm outside of both ends of the furnace (i.e., in the cold zones). The two isomers of C₇₀(CF₃)₈ were purified by HPLC as follows (20 mm I.D. × 250 mm Cosmosil Buckyprep column, Nacalai Tesque, Inc.; 330 nm UV detector; 18 mL min⁻¹ eluent flow rate): in the first stage, 1.8 mL injections were eluted with toluene; in the second stage, 1.8 mL-injections of each fraction were eluted with 20:80 toluene/hexane (the retention times were 32 min for 70-8-1 and 52 min for 70-8-2).

Synthesis and purification of C_{1-p}^{7mp,p}-C₇₀(CF₃)₁₂₋₁ (70-12-1) and C_{1-p}^{7mp,p}-C₇₀(CF₃)₁₂₋₂ (70-12-2): These compounds were prepared in two reactions at 420 and 450 °C using reactor 1 as described in the previous paragraph. Figure S1 (Supporting Information) shows the MALDI mass spectra of the crude reaction products. The two compounds were isolated and purified by HPLC as described above using heptane instead of 20:80 toluene/hexane (the retention times were 4.0 min for 70-12-1 and 4.5 min for 70-12-2).

Improved synthesis of C_{1-p}^{7mp}-C₇₀(CF₃)₁₀ (70-10-1): Finely ground C₇₀ (see Table 3 for amounts used) was placed in a 0.7 cm I.D. fused-silica tube connected to a gas handling system as above. The portion of the tube containing C₇₀ was placed in a 40 cm long tube furnace (reactor 2). After purging the sample with argon, it was heated to 530 °C and treated with 6 sccm of gaseous CF₃I (ca. 0.025 mmol min⁻¹) for 90 min. Orange-brown C₇₀(CF₃)_{10,12} compounds and purple I₂ condensed in the cold zones. The ¹⁹F NMR spectrum of the crude product showed that 70-10-1 constituted 89 mol % of the C₇₀(CF₃)_{10,12} compounds present (only negligible amounts of other C₇₀(CF₃)_n compositions were detected). The compound 70-10-1 was isolated and purified by HPLC as follows (10 mm I.D. × 250 mm Cosmosil Buckyprep column, Nacalai Tesque, Inc.; 300 nm UV detector; 5 mL min⁻¹ eluent flow rate): in the first stage, 1.5 mL injections were eluted with toluene; in the second stage, the 3.6–3.9 min fraction from the first stage was eluted with 60:40 toluene/heptane to separate 70-10-1 from impurities of C₇₀(CF₃)₈ and C₇₀(CF₃)₁₂. The ¹⁹F NMR spectrum showed that 70-10-1 prepared by this procedure is 98 % pure.

Synthesis and purification of new isomers of C₇₀(CF₃)_{10,12}: Several batches of crude products from the improved synthesis of 70-10-1 were combined and processed by HPLC as described in the previous paragraph. A third stage of purification using heptane resulted in the isolation of (retention times shown in parentheses) 70-12-3 (6.3 min), 70-12-4 (7.3 min), 70-10-3 (18.0 min), 70-10-4 (20.0 min), 70-10-5 (22.0 min), and 70-10-2 (24.0 min). The compounds 70-12-3, 70-12-4, and 70-10-3 were obtained in 90+ % compositional and isomeric purity. Fractions containing 70-10-2, -4, and -5, which have HPLC peaks that partially overlap, were processed again using heptane as the eluent to yield each compound in ca. 95–98 % compositional and isomeric purity.

Physicochemical measurements: Cyclic voltammetry experiments were carried out in a purified-dinitrogen-filled glovebox (water and oxygen content below 1 ppm) in a one-compartment electrochemical cell. The electrolyte solution was 0.1 M N(nBu)₄BF₄ in dichloromethane. The working electrodes were either glassy-carbon, a platinum wire, or a platinum wire terminated with a platinum plate (0.04 cm²). A platinum wire loop and a silver wire served as the counter and reference electrodes, respectively. The potentials were measured relative to the Fe(Cp)₂⁺⁰ or Fe(Cp*)₂⁺⁰ potential (i.e., either Fe(Cp)₂ or Fe(Cp*)₂ was added as an internal standard and the CV was re-recorded). The experiments were controlled by an EG&G 263 or 273 A potentiostat/galvanostat. Electronic absorption spectra of dichloromethane solutions of the C₇₀(CF₃)_n compounds (n = 2–12) were recorded using either a Shimadzu 3100 or a Varian Cary 500 spectrophotometer. The absorption spectra of C₇₀(CF₃)₂O and all C₇₀(CF₃)_n compounds studied in this work except for 70-6-1 and 70-6-3, which have been published,^[2] are collected in the Supporting Information. Matrix-assisted laser-desorption/ionization time-of-flight (MALDI-TOF) mass spectra were recorded using a Voyager-DE PRO Workstation (Applied Biosystems). Sulfur was used as the matrix material. It was mixed with the sample in toluene or toluene-hexane im-

mediately prior to deposition on the target. Nitrogen laser pulses of 337 nm wavelength, 0.5 ns duration, and 3 Hz frequency were used to desorb the species into the gas phase. The negative or positive ions formed were detected in reflectron mode. Atmospheric-pressure chemical-ionization (APCI) mass spectra were recorded using a ThermQuest Finnigan LCQ-DUO spectrometer. Fluorine-19 NMR spectra were recorded using a Bruker INOVA-400 spectrometer operating at 376.48 MHz (CDCl₃ solutions, 25 °C, C₆F₆ internal standard (δ = -164.9)).

Quantum chemical calculations: Geometry optimization of all structures was done in vacuo with the use of the PBE functional^[60] and the TZ2P-quality basis set implemented in PRIRODA package,^[61] as previously described.^[9,28] Evaluation of Coulomb and exchange-correlation terms was accelerated by expansion of the electron density in an auxiliary basis set.^[61] The molecular geometry optimization using this methodology typically took two or three days with one Opteron CPU (in contrast, molecular geometry optimization with hybrid functionals such as B3LYP typically took weeks).

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- [62] **Note added in proof:** The X-ray structures of 70-10-2 and 70-10-5 have now been determined. They confirm the addition patterns proposed in this paper and will be published in the near future. Another isomer, 70-10-6, has been isolated and its structure has already been published (*Acta Crystallogr. Sect. E* **2007**, *63*, 4073). The $0l^-E_{1/2}$ value for 70-10-6 is -0.03 V vs C₇₀^{0/-}.

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