



High-temperature and photochemical syntheses of C₆₀ and C₇₀ fullerene derivatives with linear perfluoroalkyl chains

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Dedicated to Russell P. Hughes on the occasion of his receiving the ACS Award for Creative Work in Fluorine Chemistry.

ABSTRACT

New experimental results on perfluoroalkylation of C₆₀ and C₇₀ with the use of R_fI (R_f = CF₃, C₂F₅, *n*-C₃F₇, *n*-C₄F₉, and *n*-C₆F₁₃), along with a critical overview of the existing synthetic methods, are presented. For the selected new fullerene (R_f)_n compounds we report spectroscopic, electrochemical and structural data, including improved crystallographic data for the isomers of C₇₀(C₂F₅)₁₀ and C₆₀(C₂F₅)₁₀, and the first X-ray structural data for the dodecasubstituted perfluoroethylated C₇₀ fullerene, C₇₀(C₂F₅)₁₂, which possesses unprecedented addition pattern.

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1. Introduction

Our interest in extending the family of fullerene(R_f)_n compounds beyond trifluoromethylfullerenes (TMFs), which we have been studying in the past few years [1,2], is driven by several factors. For various practical applications, these compounds potentially may be used as materials with strong electron accepting properties. We have recently proven that fullerene (CF₃)_n compounds exhibit a wide range of E_{1/2} values (in the case of C₆₀(CF₃)_n it spans over a 750 mV range), and most TMFs are better

electron acceptors than the parent fullerenes [2,3]. Similarly strong electron accepting properties can also be predicted for other fullerene (R_f)_n derivatives, since electron-withdrawing character of the longer-chain R_f radicals is very close to or higher than that of CF₃. Furthermore, we discovered that redox properties are linked to the addition patterns of fullerene(CF₃)_n derivatives, so that within one composition, e.g. for C₆₀(CF₃)₁₀ isomers, E_{1/2} values can vary by more than 500 mV. Such remarkable variability in redox properties, in combination with their superb thermal stability, good solubility in various organic solvents, stability in air and upon exposure to moisture or aggressive chemical environment, makes this new class of compounds excellent candidates for practical applications in electronic devices and for energy conversion.

From the fundamental point of view, TMFs have already provided an unprecedented wealth of information on the fullerene

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addition patterns, not only for C₆₀ and C₇₀ [2,3] but also for higher fullerenes, [4,5] and endo hedral metallofullerenes [6,7]. Due to the ease with which fullerene(CF₃)_n can form well-ordered single crystals by simple solvent evaporation, several dozen X-ray-determined structures are known by now [1–4,8–22]. Even when TMFs do not form suitable crystals for crystallography, ¹⁹F NMR spectroscopy coupled with DFT calculations serves as a very valuable tool for structural elucidations [4,8]. Besides, NMR studies, including dynamic or VT experiments may help to study conformations of R_f chains; J_{F-F} coupling constant- and chemical shift analysis contributes new knowledge to the field of fluorine magnetic resonance [4,8].

Before starting exploration of PFAFs other than TMFs, we hypothesized that replacing CF₃ groups with larger R_f addends could lead to variations in the addition patterns of the corresponding fullerene derivatives. By varying gradually the size and the structure of R_f radicals (while keeping the composition of the PFAF constant) one could get insights into the effect of the R_f sterics on the fullerene addition patterns. Indeed, our first results on the X-ray structures of C₆₀(C₂F₅)₆ [23] and C₆₀(i-C₃F₇)₆ [24] revealed new fullerene addition patterns, that were not seen in C₆₀(CF₃)₆ structures, and later reports for several X-ray structures of C_{60/70}(C₂F₅)_n or C₇₀(C₃F₇)_n isomers provided further examples of new structures [25–28]. A closely related question that will be addressed in this work concerns determination of the highest possible degree of addition for various R_fs. On the one hand, it is easy to predict that the larger the R_f chain, the fewer substituents will attach to the fullerene cage, with TMFs having the largest number of substituents per cage. On the other hand, it is not clear if the length of the linear chain R_f radicals will be affecting considerably maximal compositions for the series of PFAFs with R_fs > C₂F₅, since the bulkiness of the CF₂ moiety which is directly attached to the cage C atom is the same for various R_fs. It is also worthwhile examining if for the PFAFs with maximal substitution degrees one might expect formation of fewer geometric isomers and hence higher selectivity, especially under high-temperature conditions. Finally, findings on the fundamental aspects of reactions of perfluoro alkyl radicals with fullerenes may aid better understanding of one of the most common types of derivatizations in fullerene chemistry, namely radical addition reactions.

In this paper, we report extensive experimental studies of the fullerene perfluoroalkylation reactions involving linear-chain R_f radicals, and their products. These studies involved synthesis, isolation, spectroscopic characterization, structural studies, and electrochemical measurements for the selected compounds.

2. Results and discussion

2.1. Synthesis, characterization, and isolation

Table 1 summarizes the reaction conditions and compositions of the perfluoroalkylated C₆₀ products obtained in this study and in the literature. In general, perfluoroalkylation of fullerenes is not a selective process: in most cases products represent complex mixtures of compounds which vary not only in molecular composition but also in the addition patterns within a given composition. Therefore, common analytical methods such as elemental chemical analysis, IR spectroscopy or mass spectrometry are not sufficient for characterization of the composition of PFAFs when used alone or in their combinations. In this work, crude reaction products have been characterized systematically by an array of the spectroscopic methods such as MALDI/APCI/APPI/EI mass spectrometry, NMR (¹⁹F) spectroscopy and HPLC, the latter with the use of several eluents of varying polarity. As we have demonstrated recently in the study on chlorofullerenes [29], only a combination of the above methods of analysis will provide most reliable information on the composition of the products of polyadditions to fullerenes. Yet, as we show in this study, for some products, especially for highly substituted PFAFs, these methods were not sufficient either, since (i) capabilities of the used chromatographic technique reached their limits in separations and (ii) due to complexity of the ¹⁹F NMR spectral features of PFAFs it became difficult (if not impossible) to get reliable information on the isomeric compositions. In more favorable cases, ¹⁹F NMR spectroscopy was successfully used for isolated fractions to determine the number of isomers or to identify the dominant isomer in the product and to determine its symmetry. Many PFAF compounds were isolated as pure isomers in this work, this was proven by ¹⁹F NMR, HPLC and mass spectrometry, and these samples were also characterized by UV-vis and Raman spectroscopy, cyclic voltammetry, and by X-ray crystallography, when good-quality single crystals were obtained. We report such data below and in the supporting information, along with the detailed description of the separation procedures by HPLC. Such a detailed approach to characterization allows one to unambiguously identify these compounds in future studies of PFAFs when larger amounts of the samples are available and new approaches to their purifications are developed.

2.1.1. Perfluoroethylation of C₆₀

Fagan and co-workers were the first to report the synthesis of fullerene(C₂F₅)_n with the use of either C₂F₅I (in hexafluorobenzene

Table 1
Perfluoroalkylating agents, reaction conditions, and products of C₆₀ perfluoroalkylation.

R _f in R _f I	T _{rxn} , °C	t, h	Reactor/solvent/promoter	MS data on C ₆₀ (R _f) _n		Refs.
				n	n _{max}	
C ₂ F ₅	200	24	SA/C ₆ F ₆	10–16	14	[30]
	320	4	FT/Cu	10–14	12	This work
	380–440	40–70	SA	6–10	8	[25]
	400	2–4	FT/Cu	6–10	8	This work
	420–440	40–70	SA	8–10	8	[25]
	430	2–4	FT/Cu	4–8	6	[23]
	460	2–4	FT/Cu	2	2	This work
n-C ₃ F ₇	500	2–4	FT/Cu	2–8 (CF ₃)	8 (CF ₃)	This work
	290	24	SA	4–12	10	This work
	350	7	FT/Cu	10–12	10	This work
n-C ₄ F ₉	380	6	FT/Cu	8–10	10	This work
	350	4	FT/Cu	8–10	10	This work
n-C ₆ F ₁₃	200	24	SA/1,2,4-C ₆ H ₃ Cl ₃	6–12	10	[30,34]
	340	5.5	FT/Cu	8–10	10	This work
n-C ₁₂ F ₂₅	200	24	SA	6–12	10	[34]

SA – sealed ampule reactor; FT – flow tube reactor; n_{max} – most abundant n in C₆₀(R_f)_n.

at 200 °C) or $C_2F_5-C(O)O-O(C)C-C_2F_5$ (in Freon 113 at 25 °C under UV light) [30]. In the latter case, the species with 9–16 C_2F_5 groups per cage were detected in the product by electron capture mass spectrometry; no attempts to isolate pure compounds from the crude mixture were mentioned. Our earlier work revealed that performing a reaction of C_{60} with C_2F_5I in a flow-tube reactor at 400–430 °C resulted in the formation of a dark-brown product containing $C_{60}(C_2F_5)_n$ derivatives, of which two compounds, $C_{60}(C_2F_5)_6$ and $C_{60}(C_2F_5)_8$ were successfully isolated from the crude product by HPLC and studied by X-ray crystallography [23]. It is noteworthy, the latter compound was shown to have an addition pattern similar to some of the isomers of $C_{60}(CF_3)_8$ [3], while the former has a new type of addition pattern that has not been seen for TMFs. These two examples manifested that C_2F_5 radical being the closest homologue of CF_3 may not have as profound effect on the addition patterns in $C_{60}(C_2F_5)_n$ due to sterics as originally expected.

We have now studied this reaction in more detail. Gradual change of the reaction temperature from 320 to 500 °C resulted in significant changes in the product distribution, as shown in Fig. 1. In line with the results reported by us earlier for fullerene trifluoromethylation [1,31], the n value in $C_{60}(C_2F_5)_n$ decreases gradually as the temperature increases. For example, at 320 °C the highest $n(C_2F_5) = 14$ (not shown) at 400 °C $n_{max} = 10$, at 430 °C $n_{max} = 8$ and at 460 °C $n_{max} = 2$ (Table 1 and Fig. 1).

At 440 °C, a new type of molecular species containing both CF_3 and C_2F_5 groups attached to the same fullerene cage, were identified in the mass spectra (Fig. S1-1c, d). Since these species have not been observed in the mass spectra of the $C_{60}(C_2F_5)_n$ products obtained at lower temperatures, it is reasonable to assume that these mixed perfluoroethyl-trifluoromethylated derivatives were not formed in the mass spectrometer as a result of fragmentation, but they rather formed during the reaction in the flow-tube reactor at higher temperature. This conclusion was further supported by ^{19}F NMR data for some isolated fractions from the products prepared at 440 °C, which showed resonances in the ($-\delta$) 65–70 region – a typical range for $F(CF_3)$ signals in trifluoromethylated fullerenes – along with the peaks in the ($-\delta$) 79–80 due to $F(CF_3)$ from C_2F_5 . This result indicates that thermal fragmentation of the $C_2F_5^*$ radicals becomes appreciable at temperatures above 430 °C and relative content of CF_3 -containing species increases.

Remarkably, further increase of the reaction temperature to 460 °C yielded almost no perfluoroethylated products, while a trifluoromethylated derivative with $n(CF_3) = 2$ and a mixed bisadduct $C_{60}(CF_3)(C_2F_5)$ became the most abundant species (Fig. 1). The HPLC trace of the 460 °C-reaction product recorded with the use of toluene as an eluent shows an exceptional complexity of the product mixture, despite a relatively narrow compositional distribution of the products, which is demonstrated by MALDI mass spectrometry data in Fig. 1. This implies that multiple isomers of $C_{60}(CF_3)_n(C_2F_5)_m$, where $n = 0-4$ and $m = 0-3$ are formed in the reaction under these conditions.

Finally, raising the temperature to 500 °C yielded almost exclusively trifluoromethylated products with $n(CF_3) = 2-6$ (Fig. 1).

From the products of the 400- and 430 °C-reactions, we were able to isolate several isomers of $C_{60}(C_2F_5)_8$ and $C_{60}(C_2F_5)_6$ (detail on pp. S2–S4 in SI). They were characterized by MALDI, Raman, UV–vis, and ^{19}F NMR spectroscopies and, when possible, by X-ray crystallography (Figs. S1–S3 in SI). In Fig. 2, the spectroscopic data for two isomers of $C_{60}(C_2F_5)_6$ are presented. Using these two compounds as examples we demonstrate that ^{19}F NMR spectra provide unique spectroscopic fingerprints for PFAFs which can and should be used for the unambiguous identification and purity characterization of the isolated PFAF isomers. The UV–vis spectra are commonly used by fullerene chemists as a tool to distinguish between the fullerene isomers or derivatives with various addition

patterns. For some isomers of PFAFs UV–vis spectra exhibit several characteristic bands, e.g. one of the isomers of $C_{60}(C_2F_5)_8$ (**60-8-3-C₂F₅**) has a virtually identical UV–vis spectrum with that of an isomer of $C_{60}(CF_3)_8$, (**60-8-3**). For the latter, its addition pattern was determined using ^{19}F NMR spectroscopy and DFT calculations [3], while for the former compound, the single-crystal X-ray data obtained in this work confirmed that they have the same additions patterns. There are other cases when UV–vis spectra do not have sufficiently resolved fine structure to use them for identification, we therefore conclude that use of ^{19}F NMR is a preferable, more reliable and more sensitive method for PFAFs.

For preparation of mixtures of $C_{60}(C_2F_5)_n$ the authors [25] used the technique described by Fagan et al. [30], i.e. heating a sealed glass ampule with C_{60} and C_2F_5I . Interestingly, a comparison of the HPLC traces of the crude products obtained in this work in the flow-tube reactor and those from ref. [25] shows similarity in the distribution of the products despite differences in the conditions of the synthetic procedures (Fig. S4-3 in SI). Furthermore, several fractions, for which X-ray crystallographic data are available from both ref. [25] and from this work, were proven to be the same isomers, e.g., one isomer of $C_{60}(C_2F_5)_{10}$ and three isomers of $C_{60}(C_2F_5)_8$ (see details on the structures below). Unfortunately, no ^{19}F NMR or UV–vis data were reported for the fractions studied in Ref. [25] except for the X-ray crystallography and mass spectrometry data, which did not allow us to examine if it is true also for other compounds from these mixtures for which the X-ray data were not obtained.

2.1.2. Perfluoroethylation of C_{70}

Previously, a highly selective, high-yield synthesis of a single isomer of $C_{70}(CF_3)_{10}$ was achieved under specific set of reaction conditions while using CF_3I as a trifluoromethylating agent [2]. Predominant formation of the single isomer of $C_{70}(CF_3)_8$ was also reported (though with very moderate yield) when different set of conditions, including a different trifluoromethylating agent (CF_3COOAg) was applied [32]. We hypothesized that it could also be possible to develop techniques for selective preparation of $C_{70}(C_2F_5)_n$ compounds by carefully tuning reaction parameters.

Prior reports on the synthesis of perfluoroethylated C_{70} derivatives, however, provided no evidence for high selectivity in these reactions. In the first study, Fagan and co-workers obtained $C_{70}(C_2F_5)_n$ ($n = 10-16$) derivatives using $C_2F_5-C(O)O-O(O)C-C_2F_5$ as a perfluoroethylating agent (in Freon-113 at 25 °C) [30]. In the second study, reactions between C_{70} and C_2F_5I in the sealed glass ampules (180–360 °C) were used to produce $C_{70}(C_2F_5)_n$ ($n = 8-12$) compounds; in all cases complex mixtures with multiple isomers were formed [26,27].

Flow-tube reactions of C_{70} with C_2F_5I were studied in this work at 320–460 °C (Fig. 3, data for 460 °C not shown). The use of temperatures lower than 300 °C or higher than 460 °C yielded very little product. The range of $C_{70}(C_2F_5)_n$ compositions obtained at 320–430 °C was unexpectedly narrow – mostly $C_{70}(C_2F_5)_n$ with $n = 10$ and 12 were formed. The trend of decreasing n with the increase in temperature was similar to the one observed previously for the trifluoromethyl derivatives of C_{60} and C_{70} [1,32], although the range of the compositions was much more narrow than for TMFs. Carrying reactions at 300 or 320 °C gave $C_{70}(C_2F_5)_{12}$ as the dominant composition; the reaction at 430 °C produced $C_{70}(C_2F_5)_{10}$ as the main product (Fig. 3). We observed that relative content of one isomer of $C_{70}(C_2F_5)_{10}$ with retention time 5.8 min (20:80 (v:v) toluene/heptane eluent at 5 ml/min flow rate) gradually increased with the reaction temperature and reached its maximal content in the product formed at 430 °C (Fig. S4-4 in SI). This isomer was isolated and characterized spectroscopically and by X-ray crystallography (see below and Fig. S4-10 in SI).

From the crude reaction products obtained at 400 °C, we were also able to isolate and characterize three minor components,

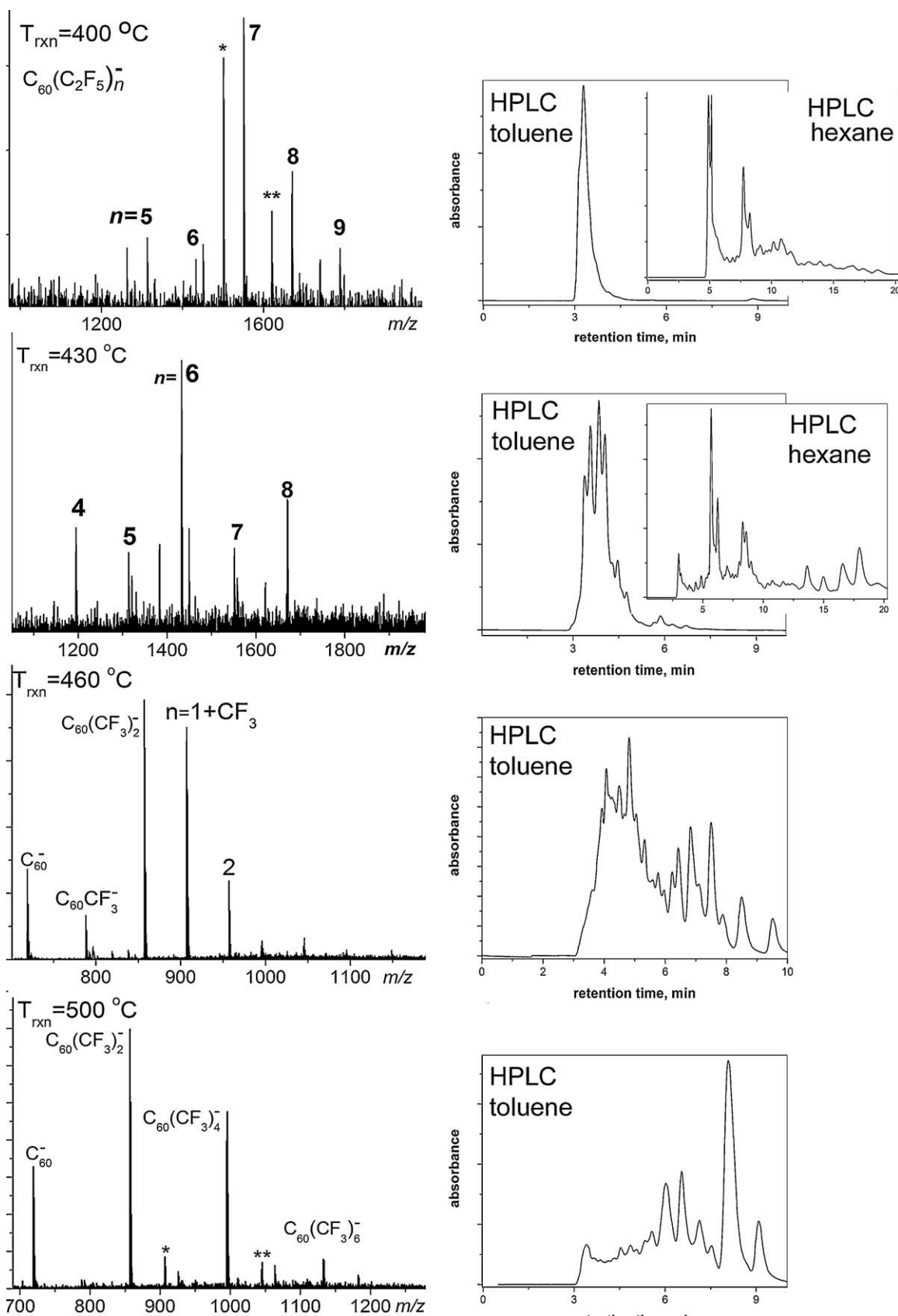


Fig. 1. MALDI mass spectra and HPLC traces of the crude products obtained in C_{60}/C_2F_5I flow-tube reactions at 400, 430, 460, and 500 °C.

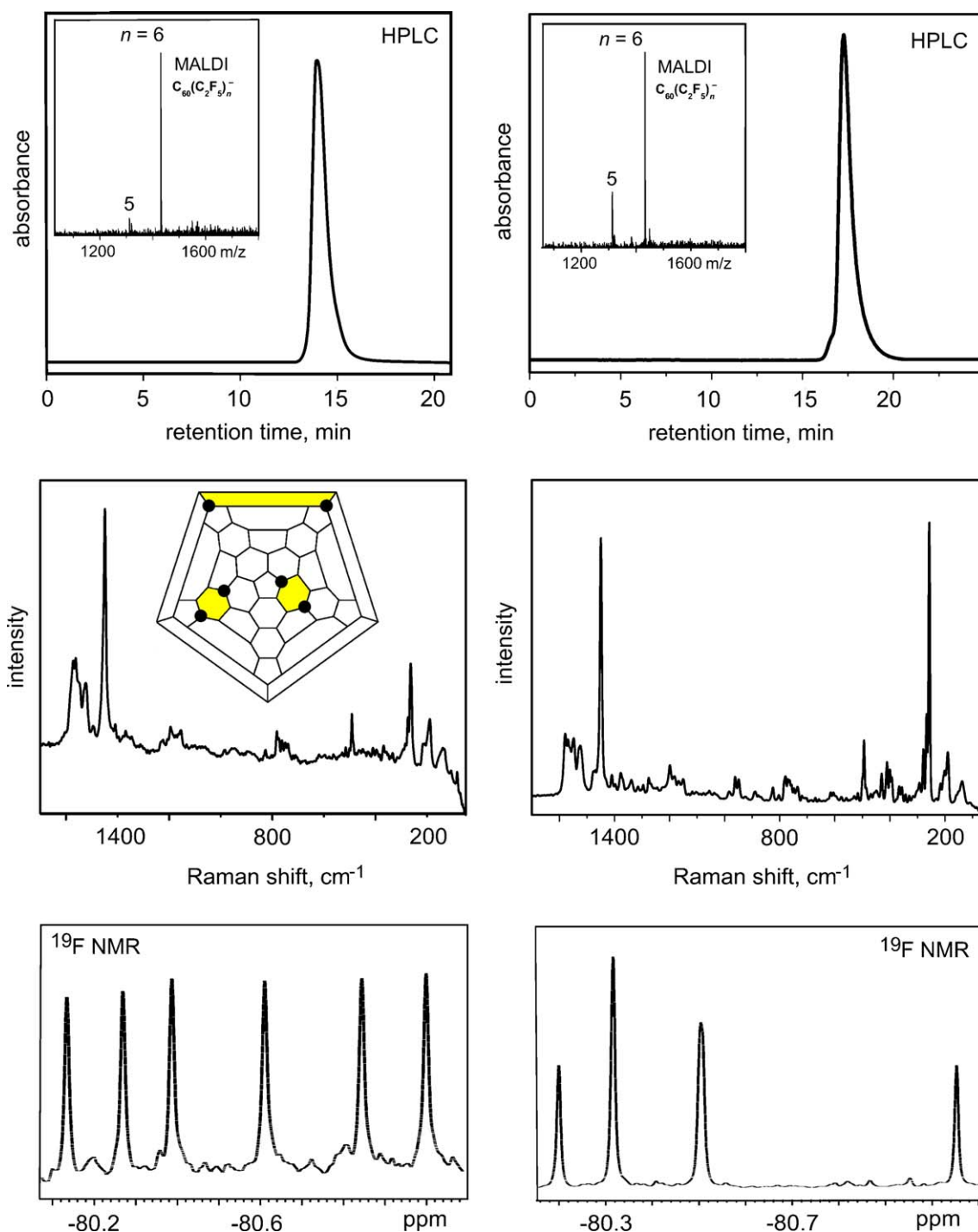


Fig. 2. HPLC traces, NI-MALDI mass spectra (insets), Raman and ^{19}F NMR spectra (only CF_3 region is shown) of two $\text{C}_{60}(\text{C}_2\text{F}_5)_6$ isomers. Schlegel diagram is shown for **60-6-3- C_2F_5** isomer (left) which structure was determined by X-ray crystallography [23]. The addition pattern of $\text{C}_{60}(\text{C}_2\text{F}_5)_6$ isomer (right) is unknown.

$\text{C}_{70}(\text{C}_2\text{F}_5)_2$ (one isomer) and $\text{C}_{70}(\text{C}_2\text{F}_5)_4$ (two isomers) (Figs. S4-8 and S4-9 in SI). The $\text{C}_{70}(\text{C}_2\text{F}_5)_2$ isomer was studied earlier [33]. The ^{19}F NMR spectrum of $\text{C}_{70}(\text{C}_2\text{F}_5)_4$ -I has four narrow resonances at ($-\delta$) 79.68, 80.05, 80.30, and 80.52 due to fluorine atoms of the four magnetically inequivalent CF_3 groups and a group of peaks in the ($-\delta$) 110–120 region due to $\text{F}(\text{CF}_2)$ atoms (Fig. S4-8). This ^{19}F NMR spectrum is reminiscent of the spectra of some other non-symmetric fullerene(C_2F_5) $_n$ compounds; e.g., the structurally characterized *p,p,p*- $\text{C}_{60}(\text{C}_2\text{F}_5)_6$ has six sharp resonances (6 CF_3 groups) in the ($-\delta$) 78–82 region [23].

We then attempted to produce larger amounts of the $\text{C}_{70}(\text{C}_2\text{F}_5)_4$ and other compounds with low degree of substitution by increasing the reaction temperature. However, further increase in temperature to 460 °C did not result in the shift towards the species with lower n values, as was expected based on the analogy with trifluoromethylation process. Instead, a drastic drop in the yield was observed and partial fragmentation of C_2F_5 caused by high temperature led to the generation of CF_3 radicals followed by the formation of the fullerene(CF_3) $_n$ derivatives (n ranging between 4 and 10).

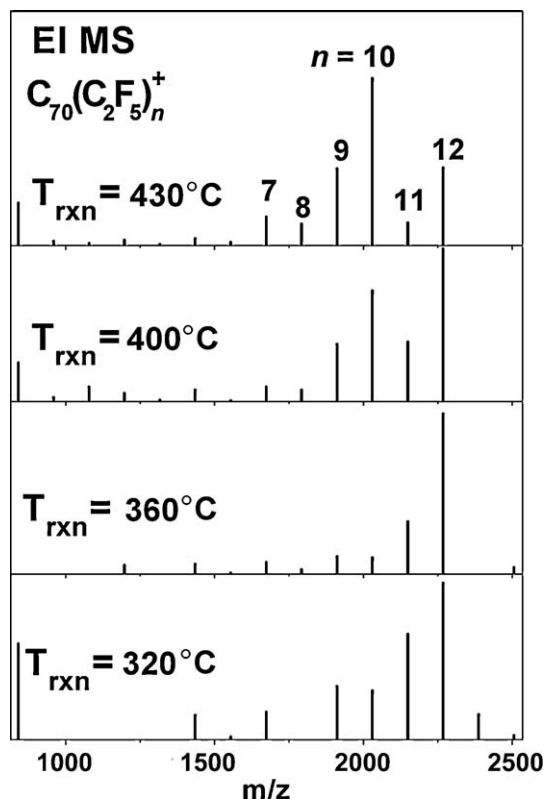


Fig. 3. EI mass spectra of the crude products obtained in the C_{70}/C_2F_5I flow-tube reactions at 320–430 °C.

Perfluoroethylation in the sealed glass ampule at 400 °C resulted in the crude product which mostly contained $C_{70}(C_2F_5)_{10}$ as shown in Fig. 4. Up to 95% ion intensity in the NI-APPI mass spectrum was due to $C_{70}(C_2F_5)_{10}$ suggesting highly selective process. However, analysis of the ^{19}F NMR spectrum and HPLC trace (recorded in 20:80 (v:v)-toluene/heptanes eluent) has proven that multiple isomers were present in the product. When

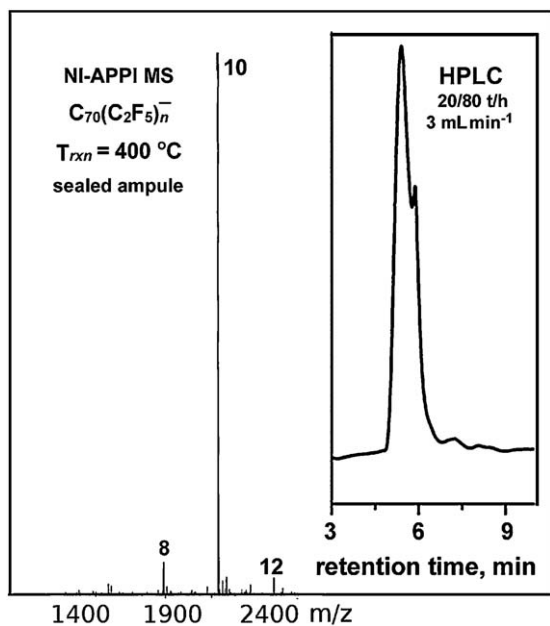


Fig. 4. NI-APPI mass spectrum and HPLC trace (20:80 (v:v) toluene/heptane eluent) of the $C_{70}(C_2F_5)_n$ ($n = 8-12$) products prepared at 400 °C in a sealed glass ampule for 24 h.

we added copper powder as a promoter, the reaction yielded products with $n(C_2F_5) = 10$ and 12, the latter being more abundant composition. HPLC analysis of the crude products from both reactions performed in toluene and then in pure heptane showed us that the main products elute at very short retention times, which made further chromatographic processing unproductive. Such a situation made it impossible for us to isolate and characterize main products of these reactions. A similar result was obtained by Troyanov and co-workers for the sealed-ampule synthesis of $C_{70}(C_2F_5)_{10}$ at 350, 360, and 400 °C [26,27]. Though several minor isomers of $C_{70}(C_2F_5)_{8,10}$ were isolated and characterized by X-ray crystallography [26], the most abundant $C_{70}(C_2F_5)_{10}$ isomers (2.7–3.25 min retention time) were not characterized at all.

We have also explored the possibility of exhaustive perfluoroethylation of C_{70} . To achieve maximum degree of addition, the crude product, $C_{70}(C_2F_5)_{10-12}$ obtained in 400 °C-reaction was treated again with C_2F_5I at 300 °C for 4 h in the flow tube. The composition has not practically changed after such treatment (Fig. S4-5 in SI). In contrast, similar experiments performed with $C_{70}(CF_3)_{10}$ (>90% single isomer) at 300 °C in the flow tube resulted in its partial conversion into $C_{70}(CF_3)_{12-16}$. This approach can be elaborated further to achieve even higher degree of substitution and a higher conversion of $C_{70}(CF_3)_{10}$. Our experiments with crude trifluoromethylated products of C_{60} performed under similar conditions yielded even deeper trifluoromethylation than in case of C_{70} , i.e., mass spectral data indicated the presence of $C_{60}(CF_3)_n$ ($n = 14-23$, Fig. 5). We also note that a high degree of trifluoromethylation can be achieved in the UV-initiated reactions of C_{60} with CF_3I in C_6F_6 at room temperature (Fig. S4-6 in SI). When a crude trifluoromethylated $C_{60}(CF_3)_n$ ($n = 8-12$) product dissolved in C_6F_6 was irradiated with UV light for 24 h at room temperature, a significantly smaller shift in composition was observed, i.e., the maximum addition of 16 CF_3 groups was achieved (Fig. 5).

These data demonstrate that the difference in size between CF_3 and C_2F_5 radicals plays a more important role for the highly substituted derivatives: it appears that formation of the stable compounds with more than 14 C_2F_5 groups to C_{70} is unfavorable under the conditions studied in this work. It is feasible that the higher steric strain in $C_{70}(C_2F_5)_{n>12}$ can result in the lower thermal stability, which may explain that Fagan et al. who prepared $C_{70}(C_2F_5)_n$ at room temperature, were able to achieve the addition of as many C_2F_5 groups as 16 [30].

2.1.3. Preparation of $C_{2n}(R_f)_n$ with $R_f = C_3F_7$, C_4F_9 , and C_6F_{13}

Fagan et al. [30] reported that the reaction between C_{60} and perfluorohexyl iodide in 1,2,4-trichlorobenzene at 200 °C led to the formation of the compound with ten C_6F_{13} groups as a major component in the reaction mixture. Furthermore, even for longer chain R_f radicals such as $C_{12}F_{25}$ this composition was dominant [30,34]. Fig. 6 presents the EI mass spectra of the products obtained in this work using reactions of C_{60} with R_fI , where $R_f = n-C_3F_7$, $n-C_4F_9$, and $n-C_6F_{13}$. All reactions were performed at 320 or 350 °C in a flow tube in the presence of copper powder (Table 1). Notably, all three products have very similar compositional distributions, i.e. $C_{60}(R_f)_{10}$ is the predominant species (Fig. 6). A very similar result was obtained for the reaction between C_{60} and $n-C_3F_7I$ (290 °C, 24 h) in the sealed ampule.

When C_{70} (mixed with Cu powder) and $n-C_3F_7I$ were reacted at 350–380 °C for 7 h in the flow tube, the product with predominant composition $C_{70}(n-C_3F_7)_{10}$ was obtained. Use of lower temperature and longer time of the reaction between C_{70} and $n-C_3F_7I$ in a sealed-ampule procedure by the authors [28] yielded a mixture of $C_{70}(n-C_3F_7)_n$ ($n = 2-10$) with $n = 8$ being the dominant composition. All these results clearly indicate that $n = 10$ is the highest substitution degree in fullerene $(R_f)_n$ with $R_f > C_3F_7$.

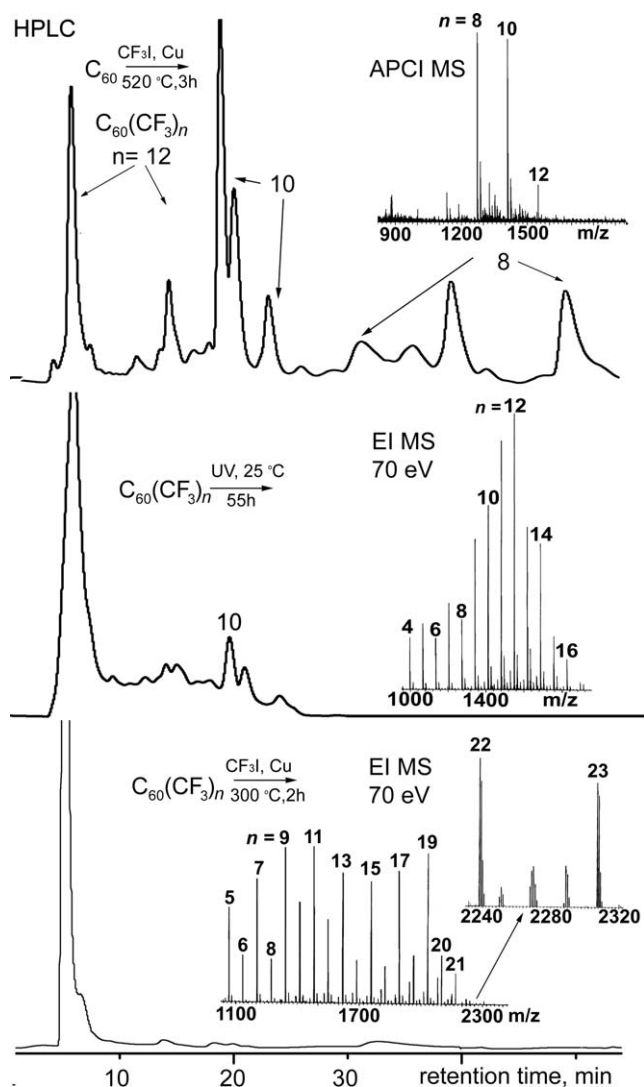


Fig. 5. (Top) HPLC trace and APCI mass spectrum of the product of C_{60}/CF_3I reaction ($520\text{ }^\circ\text{C}$, 3 h); (middle) HPLC trace and EI mass spectrum (70 eV) of the product of trifluoromethylation of $C_{60}(CF_3)_n$ ($n = 8\text{--}12$) under UV irradiation at room temperature; (bottom) HPLC trace and EI mass spectrum (70 eV) of the product of $C_{60}(CF_3)_n$ ($n = 8\text{--}12$) trifluoromethylation at $300\text{ }^\circ\text{C}$ in a hot tube.

As expected, PFAFs with $R_f > C_2F_5$ are much harder to separate than their perfluoroethyl- and TMF analogues. The tendency of decreasing retention times as the size of R_f increases (for a given composition) has been noted by us earlier [33] and observed in the present study. For example, under similar HPLC conditions, $C_{70}(n-C_3F_7)_{10}$ isomers elute at 2.7–3.5 min whereas retention times of $C_{70}(C_2F_5)_{10}$ are 2.7–7.0 min [26,28]. In the case of $C_{70}(n-C_3F_7)_8$ and $C_{70}(C_2F_5)_8$ isomers, the respective ranges of retention times are 3.5–13 and 7–42 min in pure heptane, respectively [27,28]. This situation makes the use of the HPLC method in the current configuration (Cosmosil Buckyprep column and heptane as the weak solvent) very challenging. We found that under these conditions it is practically impossible to achieve separation of the isomers of fullerene(R_f) $_{n>10}$ for $R_f > C_2F_5$.

Physical properties of fullerene(R_f) $_n$ R_f are markedly different from those of trifluoromethyl derivatives. First, their solubility in hexane or toluene is significantly lower, while solubility in perfluorinated solvents is very high, especially, in case of fullerene(C_6F_{13}) $_n$. Secondly, the volatility is lower than that of TMFs. We also observed melting of the crude $C_{60}(CF_3)_n$ ($n = 8\text{--}10$) mixtures at $400\text{ }^\circ\text{C}$ and melting of $C_{60}(C_2F_5)_n$ mixtures at $290\text{ }^\circ\text{C}$,

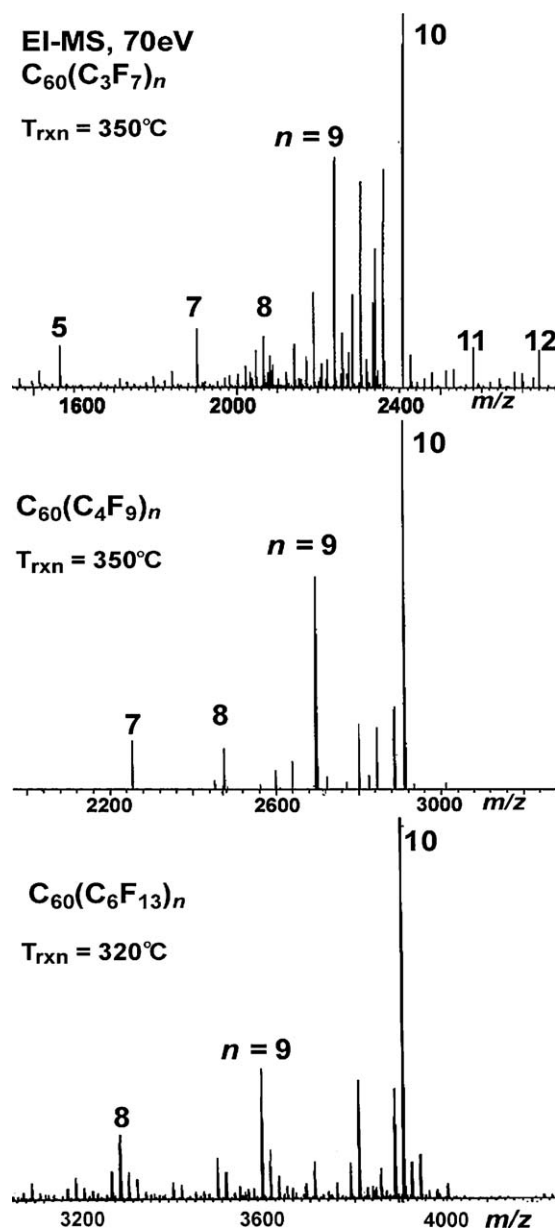


Fig. 6. EI mass spectra of the products obtained in the reactions of C_{60} and $n-C_3F_7I$ at $350\text{ }^\circ\text{C}$ for 7 h (top), $n-C_4F_9I$ at $350\text{ }^\circ\text{C}$ for 4 h (middle), and $n-C_6F_{13}I$ at $350\text{ }^\circ\text{C}$ for 5.5 h (bottom).

which has not been reported for other polyadducts of fullerenes, to the best of our knowledge. Such versatility in the properties of PFAFs expands the options for processing of these potentially important electron acceptor materials in future applications.

2.2. On selectivity of perfluoroalkylation reactions

A selective one-step preparation of a single-isomer of any PFAF could not be achieved under any conditions examined. It was possible, however, in several cases to prepare products with one predominant composition. In particular, a high compositional purity for fullerene(R_f) $_{10}$ was obtained in the reaction of C_{70} and C_2F_5I and in reactions between C_{60} and R_fI ($R_f = n-C_3F_7$, $n-C_4F_9$, and $n-C_6F_{13}$). However, in all these cases subsequent HPLC and ^{19}F NMR analysis demonstrated the presence of many isomers. In our experience, trifluoromethylations of C_{60} , C_{70} , and higher fullerenes are also not selective reactions, except for one case, when a single

isomer of $C_{1-C_{70}}(CF_3)_{10}$ was prepared with high yield and high isomeric purity using a long-flow-tube reactor [2]. In 2006, it was reported that a reaction of C_{60} and CF_3I in a sealed ampule at $440\text{ }^\circ\text{C}$ yielded $S_6-C_{60}(CF_3)_{12}$ with high compositional and isomeric purity [9]. This result was very different from the reaction at $440\text{ }^\circ\text{C}$ in the long flow-tube that we reported earlier [4]. The latter reaction yielded a mixture of products $C_{60}(CF_3)_n$ with $n = 10\text{--}14$. Among many different isomers with composition $C_{60}(CF_3)_{12}$ isolated from this mixture (at least five were identified by ^{19}F NMR spectroscopy), it was also $S_6-C_{60}(CF_3)_{12}$, which was identified both by X-ray crystallography and ^{19}F NMR spectroscopy [4]. This isomer was not nearly a dominant product in the crude. Though the conditions of the experiments were clearly different (e.g., pressure of CF_3I in the sealed ampule was 5 bar [9], while in a flow tube it was 1 bar) such a drastic difference in the relative abundances of the products was puzzling. In addition, conclusions by the authors [9] on the remarkable compositional and isomeric purity were only based on the X-ray crystallography performed for a single crystal, which is not a reliable method for characterization of the purity of the bulk samples of fullerene derivatives [29]. Therefore, we repeated the reaction described in [9]. Conditions of the synthesis were reproduced as close as possible to the procedure described in ref. [9], and then crude products were carefully analyzed by ^{19}F NMR spectroscopy, HPLC, and APCI mass spectrometry methods. While mass spectrometry data may provide only qualitative data on the molecular composition, ^{19}F NMR spectroscopy allows one to estimate quantitatively the content of a specific $C_{60}(CF_3)_n$ isomer in the product mixture, provided that its peaks do not overlap with those of the other compounds. In order to have representative data for the whole bulk crude product we made sure that the crude solid sample was homogenized, and then 1–2 mg of the solid was completely dissolved in $CDCl_3$, its ^{19}F NMR spectrum is shown in Fig. 7. Estimation of the relative content of $S_6-C_{60}(CF_3)_{12}$ was relatively easy since due to high symmetry it has a very characteristic 2-line spectrum ($-\delta$ 66.1(m, CF_3) and 67.3(m, CF_3)), each peak represents resonances from 6 CF_3 groups (right inset in Fig. 7 shows the ^{19}F NMR spectrum of a purified sample of $S_6-C_{60}(CF_3)_{12}$). Because of the high symmetry, its presence seems indeed very striking in the ^{19}F NMR spectrum of the crude sample; however, according to the peaks integration, $S_6-C_{60}(CF_3)_{12}$ constitutes ca. 20% of total intensity. We then repeated this synthesis four more times keeping the same temperature, time, amounts of the reagents as in ref. [9], and varying the size or geometry (or both) of the glass ampule, and the rate of heating of reaction mixture that are also important parameters but were not specifically described in ref. [9]. In all four new experiments, the result was very similar to our first reaction, and again – very different from the results reported in Ref. [9]. The typical HPLC traces of the crude products obtained with toluene or heptane as eluents are given in Fig. 7, along with its NI-APCI mass spectrum. The latter shows the presence of the species with 10, 12, 14, and even 16 CF_3 groups. The HPLC trace recorded with heptane as an eluent clearly demonstrates the presence of multiple products – in full agreement with the ^{19}F NMR results described above (Fig. 7). We cannot ascribe these significant differences with the results described in [9] to any particular reason at this time. Results of our several experiments in the sealed ampules at $440\text{ }^\circ\text{C}$ for 48 h consistently showed that this reaction yields a mixture of $C_{60}(CF_3)_n$, where $n = 12\text{--}16$. The $S_6-C_{60}(CF_3)_{12}$ isomer is present in this mixture in the amounts of at most 20–25% of the overall mixture of trifluoromethylated products. In contrast to the reported earlier extremely low solubility of $S_6-C_{60}(CF_3)_{12}$ in organic solvents [9], we were able to perform its purification using HPLC method with toluene and heptane as eluents and also record its ^{19}F NMR spectra both in $CDCl_3$ and C_6D_6 [4]. We also observed that dry crystals of the purified $S_6-C_{60}(CF_3)_{12}$ re-dissolve

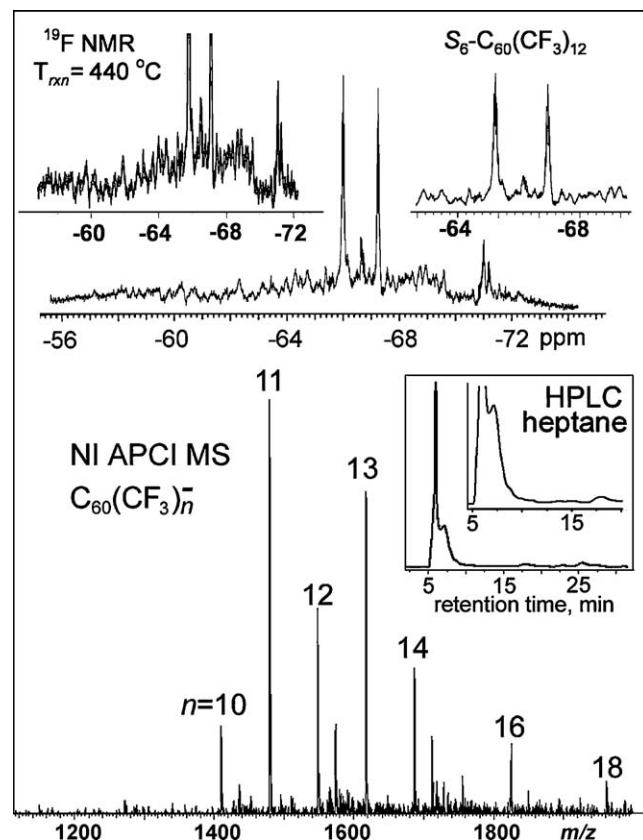


Fig. 7. (Top) ^{19}F NMR spectrum of the $C_{60}(CF_3)_n$ product obtained at $440\text{ }^\circ\text{C}$ for 48 h in a sealed ampule (the inset on the left is an expansion). The inset on the right shows ^{19}F NMR spectrum of the purified $S_6-C_{60}(CF_3)_{12}$ (bottom) NI-APCI MS of the same product and (inset) its HPLC trace (100% heptane, 3 mL min^{-1} flow rate).

in organic solutions at a much slower rate than before its purification and crystallization, but it is a common feature for many other purified fullerene(CF_3) $_n$ compounds that we have worked with. After an ^{19}F NMR solution spectrum of $S_6-C_{60}(CF_3)_{12}$ was published [4], the authors [9] partially addressed controversy about solubility and provided more detail on the synthetic procedure: “the selective formation of $C_{60}(CF_3)_{12}$ (S_6 isomer) was observed *in some cases* (italicized by us) in the hot zone when clogging of the narrow middle section of the ampoule with crystalline iodine effectively blocked supply of gaseous CF_3I for further trifluoromethylation” [13]. This remark helps one to realize that the necessary condition for selectivity of the reaction is “clogging” of the reaction vessel, otherwise applying the right temperature, reagent amounts and time of reaction in the sealed glass tube *will not result in the selective synthesis*, as was demonstrated in our experiments. Clogging of the ampule can hardly be controlled or easily reproduced; therefore, more experimental work is needed to develop (if possible) a fully reproducible method for the selective preparation of a highly symmetric $S_6-C_{60}(CF_3)_{12}$ in practically significant amounts.

2.3. Electrochemical studies

Preliminary electrochemical studies of some isolated perfluoroethylated C_{60} and C_{70} compounds have been done in this work. Presently, it is not possible to carry out a comprehensive study of electrochemical properties of fullerene(C_2F_5) $_n$ compounds that would be parallel in depth and quality to our earlier study of fullerene(CF_3) $_n$ compounds [2,3]. Most fullerene(C_2F_5) $_n$ compounds for which molecular structures are known were available to us either in insufficient quantities or low purity (or both) due to

low selectivity of the synthetic procedures and challenging chromatographic separations. Therefore, the goal here was to determine if it would be worthwhile to direct future efforts into studies of electrochemical properties of PFAFs. We first examined if our suggestion that PFAFs with the same addition pattern but different R_f groups would have similar redox properties. We recently demonstrated that it is the case for 7,24- $C_{70}(CF_3)_2$ and 7,24- $C_{70}(C_2F_5)_2$: their $E_{1/2}$ values were measured as 0.26 and 0.28 V vs. $C_{70}^{0/-}$, respectively [33]. In this study, the first peak potentials for two isomers of $C_{60}(C_2F_5)_{10}$, which presumably have the same addition patterns as those of two of $C_{60}(CF_3)_{10}$ isomers (**60-10-6** and **60-10-1**) were estimated as 0.44 and 0.68 V *cf.* $E_{1/2}(\mathbf{60-10-6}) = 0.33$ V and $E_{1/2}(\mathbf{60-10-1}) = 0.57$ V vs. C_{60} [3]. Electrochemical study was done for the mixture of isomers of $C_{70}(C_2F_5)_{10}$, from which one of the isomers, **70-10-8-C₂F₅**, was characterized by single-crystal X-ray diffraction (see below). While it is not possible yet to assign the observed peaks to the isomers with definitive structures, it is clear that at least one of the $C_{70}(C_2F_5)_{10}$ isomers has its first reduction potential 0.60 V more positive than $C_{60}^{0/-}$ and $C_{70}^{0/-}$. For comparison, DFT calculated LUMO energy of the isomer **70-10-8-C₂F₅**, -4.947 eV, is 0.63 eV lower than the value for C_{70} (-4.315 eV). Preliminary cyclic voltammetry measurements for two isomers of $C_{60}(C_2F_5)_6$ ($E_{1/2} = 0.28$ and 0.43 V) and an isomer of $C_{60}(C_2F_5)_8$ ($E_{1/2} = 0.34$ V) indicate that this class of PFAFs may provide as rich collection of new acceptor materials with variable redox properties as TMFs.

2.4. Structural studies

Many dozens of TMFs have been carefully studied by X-ray crystallography [1–3]. In many cases, predictions of the most probable addition patterns for trifluoromethylated derivatives were based on the analysis of the ^{19}F NMR spectra and DFT calculations. In all cases reported to date, these predictions were proven to be correct by the subsequent X-ray crystallography [1–3].

Structural characterization of perfluoroalkylated fullerenes with $R_f = C_mF_{2m+1}$ substituents where $m > 1$ represents a more challenging task. Three main factors contribute to this. First, a smaller compositional range of fullerene(R_f) $_n$ ($n < 12$) than TMFs can be subjected to isolation and purification using currently developed HPLC procedures. Consequently, fewer highly substituted compounds can be available in the pure form for structural studies. For example, as noted above, none of the crude mixtures of fullerene(R_f) $_n$ with $n-R_f = C_4F_9$ or C_6F_{13} could be separated into pure compounds, only four out of dozens compounds in the crude $C_{70}(n-C_3F_7)_n$ were characterized, while $C_{60/70}(C_2F_5)_n$ compounds with $n \geq 12$ were found practically inseparable. Even for $C_{70}(C_2F_5)_n$ with $n = 8, 10$ only a few minor isomers were isolated from crude mixtures, while the most abundant isomers were inseparable, leaving a large gap in our knowledge and understanding of the most favorable addition patterns for these PFAFs. The only class of PFAFs (not counting TMFs) which has been satisfactorily studied to date is $C_{60}(C_2F_5)_n$ with $n = 6, 8,$ and 10 (Fig. 8).

The second problem is higher complexity of the ^{19}F NMR spectra of PFAFs than those of TMFs. Their interpretation and particularly obtaining structural information is far more difficult, therefore one cannot rely on the NMR as a complement to X-ray crystallography for structural determinations. For instance, for $C_{60}(C_2F_5)_{6,8}$ compounds, a typical ^{19}F NMR spectrum contains a group of narrow resonances assigned to the CF_3 groups at $(-\delta)$ 78–82, and a group of complex peaks in the CF_2 region at $(-\delta)$ 112–116 [23]. The ^{19}F NMR method remains very useful and sensitive for evaluation of the purity of PFAFs or determination of molecular symmetry, but it cannot provide compelling information on the addition patterns at this time. As the PFAFs include larger and

larger R_f radicals they become more and more challenging for computational studies as well. Finally, even if one succeeds in growing suitable for crystallography single crystals, more complications arise in solving their structures due to challenging modeling of rotational disorder of long perfluoroalkyl chains [35]. We conclude that at present the most complete set of structural data for PFAFs is that of $C_{60}(C_2F_5)_{6,8,10}$. For all other PFAFs, only fragmentary information is available, which does not allow one to discuss in-depth or make conclusions about preferred structures for a given R_f . Below we will discuss available structural data on PFAFs from the literature and present new data on the X-ray structures for several PFAFs.

2.4.1. Addition patterns in $C_{60}(C_2F_5)_n$

These PFAFs are formed predominantly with n values of 8–12, both in the flow-tube and sealed ampule syntheses. We analyzed the HPLC traces of crude products from both syntheses and determined that relative isomeric distributions are very close (Fig. S4-3). Several X-ray structures of $C_{60}(C_2F_5)_8$ and $C_{60}(C_2F_5)_6$ have been determined previously [23,25]. In this work we determined addition patterns for three isomers of $C_{60}(C_2F_5)_8$ (**60-8-1-C₂F₅**, **60-8-3-C₂F₅**, and **60-8-7-C₂F₅**) and one isomer of $C_{60}(C_2F_5)_{10}$ (**60-10-6-C₂F₅**) using X-ray crystallography. The X-ray structure for the latter compound is determined more accurately than previously published in ref. [25]. The Schlegel diagrams of the $C_{60}(C_2F_5)_8$ and $C_{60}(C_2F_5)_6$ isomers with the known structures are presented in Fig. 8 and Table S3. The compounds **60-8-1-C₂F₅**, **60-8-3-C₂F₅**, and **60-10-6-C₂F₅** have the same addition patterns as their TMF counterparts [3]. The isomer **60-8-1-C₂F₅** is the first example of the fullerene (C_2F_5) $_n$ in which all eight C_2F_5 groups form a single *pmpmpmp* ribbon; earlier we published the X-ray structure of **60-8-6-C₂F₅** with the *pmppp* ribbon containing 6 C_2F_5 groups (which constitutes the addition pattern of isomer **60-6-1** [3]) and a pair of C_2F_5 groups on an isolated hexagon. The formation of these isomers as abundant products (as well as **60-8-3-C₂F₅**, **60-8-8-C₂F₅**, **60-8-9-C₂F₅**, and **60-8-10-C₂F₅**) demonstrates that the steric strain introduced in these structures due to larger size of C_2F_5 groups than CF_3 does not affect significantly the distribution of the most favorable addition patterns; even additions of C_2F_5 groups in *meta* positions appear in these structures. It is therefore not surprising that one of the isomers of $C_{60}(C_2F_5)_{10}$, **60-10-6-C₂F₅**, has the same addition pattern as a trifluoromethylated derivative, **60-10-6** [3], its ten addends are arranged in *pmp*- and *pmppp*-ribbons. The second isomer of $C_{60}(C_2F_5)_{10}$, **60-10-7-C₂F₅**, which crystal structure was determined in ref. [25] has a pair of C_2F_5 groups on the isolated *p*- $C_6(CF_3)_2$ hexagon and a *pmpmpmp*-ribbon, the latter is also a pattern of **60-8-4** [3]. As shown in Fig. 9, **60-10-7-C₂F₅** addition pattern can be obtained from **60-8-4** by the addition of two C_2F_5 groups (two red dots) to the 42 and 56 carbon atoms which form an isolated *p*- $C_6(CF_3)_2$ hexagon.

2.4.2. X-ray structure of $C_{60}(C_2F_5)_{10}$

Table 2 shows the experimental data on the X-ray structure of the isomer of $C_{60}(C_2F_5)_{10}$ (**60-10-6-C₂F₅**). It repeats the addition pattern reported earlier for **60-10-6** [3,25]. At present, X-ray crystal structures are known only for two isomers of $C_{60}(C_2F_5)_{10}$, and the crystal lattices of both isomers do not contain solvent molecules [25]. In Fig. 9, the distances for the closest neighbors in three different layers of both isomers are shown. Each $C_{60}(C_2F_5)_{10}$ molecule has six nearest neighbors in the same layer, three ones in the layer above, and three molecules in the layer below. Therefore, the stacking of the *ABCABC* packed layers of $C_{60}(C_2F_5)_{10}$ molecules in the crystals of both isomers can be considered as distorted cubic close packing (*ccp*). In contrast, molecules of **60-10-6** form a distorted hexagonal close packing (*hcp*) despite the absence of the solvent in the crystal lattice and the identical addition pattern to

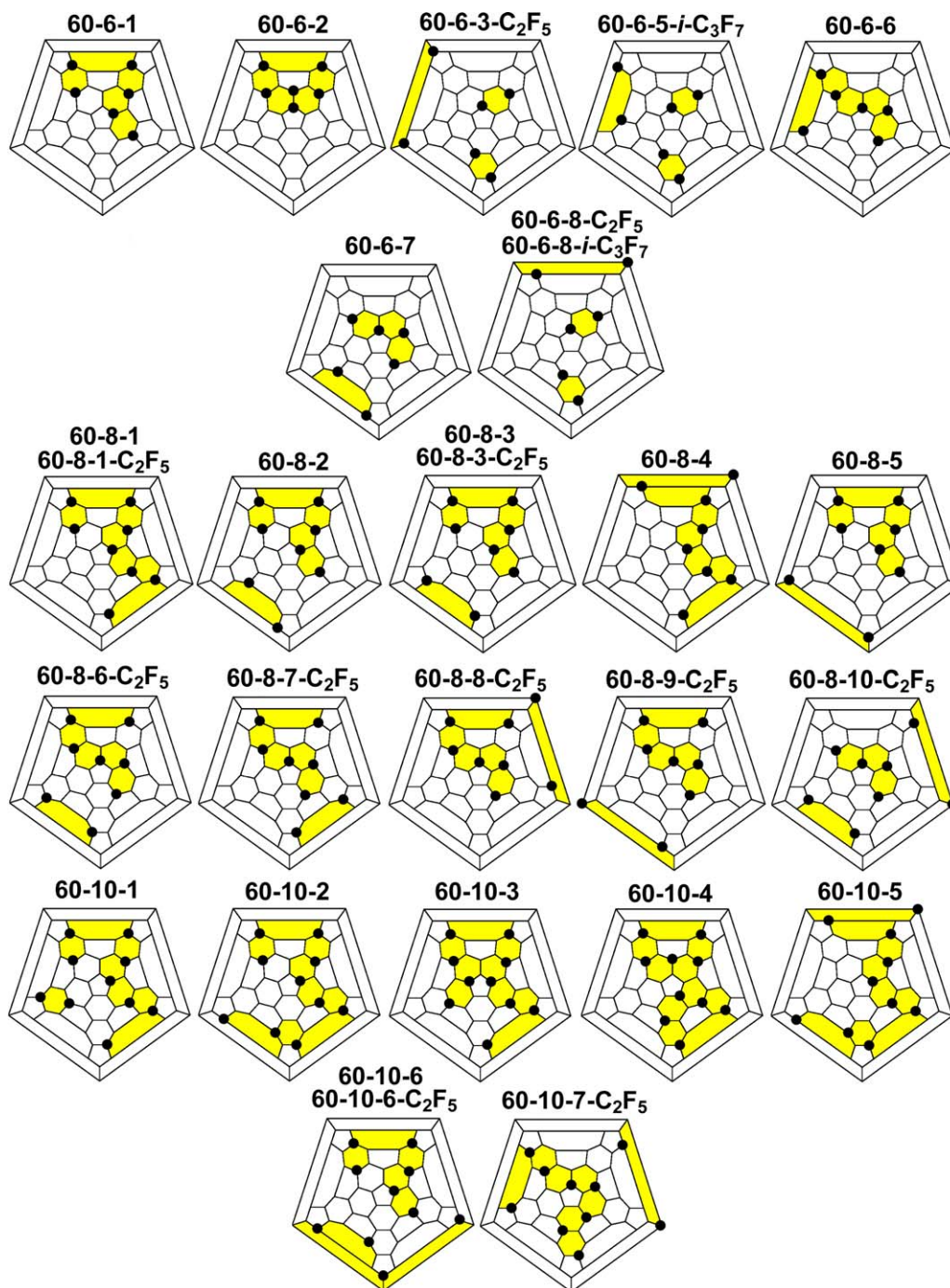


Fig. 8. Schlegel diagrams of isomers of $C_{60}(CF_3)_{6/8/10}$, $C_{60}(C_2F_5)_{6/8/10}$ and $C_{60}(i-C_3F_7)_{6/8}$ with the known structures (X-ray crystallography or ^{19}F NMR spectroscopy). Black dots represent the addition site of R_f group. Yellow-filled hexagons represent hexagons with added R_f groups.

that of **60-10-6- C_2F_5** . As shown in Fig. S4-13, one $C_{60}(CF_3)_{10}$ molecule has six neighbors in the same layer, three ones in the layer above and three molecules in the layer below. Other known isomers of $C_{60}(CF_3)_{10}$ (**60-10-3** (Fig. S4-17) [1] and **60-10-4** (Fig. S4-18)) with the crystal lattice without solvent molecules form a distorted *ccp*.

2.4.3. Addition patterns in $C_{70}(C_2F_5)_n$

In contrast to the $C_{60}(C_2F_5)_n$ crude products, from which it was possible to isolate and characterize almost all main components, both in this work and earlier [23,25], the most abundant products in the crude $C_{70}(C_2F_5)_n$ mixtures have not been isolated despite our attempts. Recent reports by Tamm and co-workers described

synthesis of $C_{70}(C_2F_5)_n$ in the sealed ampule [26,27]. The HPLC separation of the crude resulted in the identification of at least 17 different fractions as various $C_{70}(C_2F_5)_{10}$ isomers, several minor components were successfully isolated and studied by X-ray method [26], while the most dominant products contained in the fraction eluting 2–9 min in pure hexane were not characterized at all. Therefore, it remains unknown how many isomers of $C_{70}(C_2F_5)_{10}$ constitute the most abundant fraction and what addition patterns are favored under the reported experimental conditions. The Schlegel diagrams of the nine isomers of $C_{70}(C_2F_5)_{10}$ determined by X-ray analysis are shown in Table S1. Some $C_{70}(C_2F_5)_n$ compounds have the same addition pattern as $C_{70}(CF_3)_n$ derivatives. For example, in the structures of **70-10-1-**

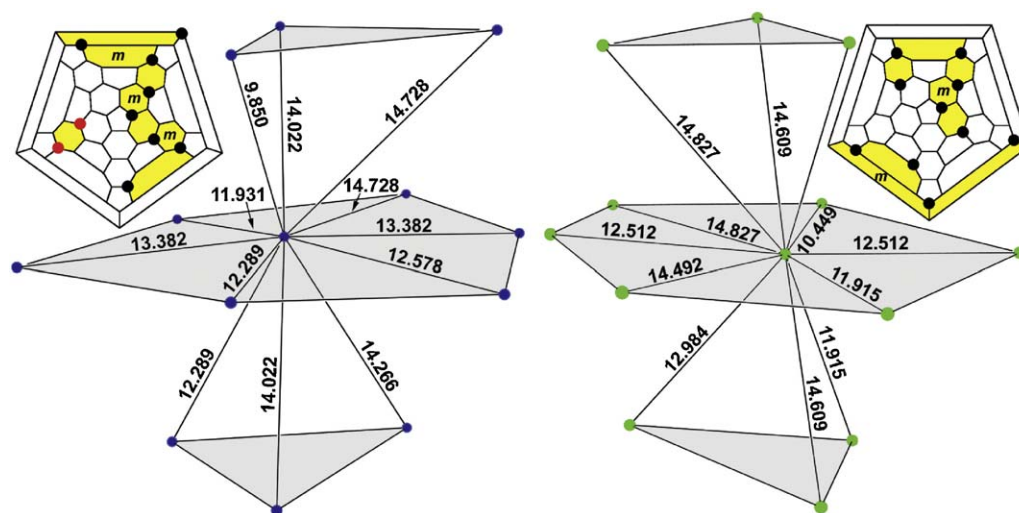


Fig. 9. Schlegel diagrams and packing of **60-10-7-C₂F₅** (left) and **60-10-6-C₂F₅** (right) isomers. On the Schlegel diagram of **60-10-7-C₂F₅** black dots represent the addition pattern of **60-8-4** isomer as a sub-pattern. For both isomers, each $C_{60}(C_2F_5)_{10}$ molecule is surrounded by six molecules in one layer and by three ones in the top and bottom layers which leads to formation of the distorted cubic close packing. The distances between neighboring molecules are shown. The blue and green dots represent centroids of $C_{60}(C_2F_5)_{10}$ molecules. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of the article.)

Table 2

Crystallographic data and structure refinement parameters for **70-12-5-C₂F₅**, **70-10-8-C₂F₅**, and **60-10-6-C₂F₅**.

	$C_{70}(C_2F_5)_{12}$	$C_{70}(C_2F_5)_{10}$	$C_{60}(C_2F_5)_{10}$
Molecular formula	$C_{94}F_{60}$	$C_{90}F_{50}$	$C_{80}F_{50}$
Formula weight	2268.94	2030.90	1910.80
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
Z	4	4	4
Color of crystal	Red	Brown	Brown
Unit cell dimensions			
<i>a</i> , Å	14.3871(11)	19.5072(6)	17.9226(7)
<i>b</i> , Å	22.2798(16)	16.3789(4)	16.7522(6)
<i>c</i> , Å	23.3969(16)	20.8066(6)	20.3122(9)
α , °	90	90	90
β , °	103.890(2)	98.356(2)	98.988(1)
γ , °	90	90	90
Temperature, K	120(2)	100(2)	100(2)
Final <i>R</i> indices	$R_1 = 0.0499$	$R_1 = 0.0665$	$R_1 = 0.0667$
$[I > 2\sigma(I)]$	$wR_2 = 0.1410$	$wR_2 = 0.1943$	$wR_2 = 0.2141$
Goodness-of-fit on F^2	1.019	1.032	1.048

C₂F₅ and **70-8-1-C₂F₅** addends have the same locations as in TMs **70-10-1** and **70-8-1**, respectively. In addition, several isomers of $C_{70}(C_2F_5)_8$ and $C_{70}(C_2F_5)_{10}$ contain addition patterns of **70-6-2** and **70-4-1** as sub-patterns.

Interestingly, similarities in the addition patterns of perfluoroethyl- and trifluoromethylated compounds were also recently demonstrated for the $C_{78}(2)$ fullerene [36]. The difference between $p^5,p,p-C_{78}(C_2F_5)_{10}$ [36] and $p^9-C_{78}(CF_3)_{10}$ [8] was found only in the position of two C_2F_5 groups. The latter compound forms one long p^9 ribbon, while in the former compound this ribbon is broken into a shorter ribbon p^7 and two isolated *para*- $C_6(C_2F_5)_2$ hexagons.

In this work, we have obtained significantly improved data for crystal structure of an isomer of $C_{70}(C_2F_5)_{12}$, (**70-12-5-C₂F₅**), which are described below.

2.4.4. X-ray structure of $C_{70}(C_2F_5)_{10}$

The crystals of **70-10-8-C₂F₅** (Fig. 10) have a tendency to grow as non-merohedral twins from various solvents. The first data set was collected on a Bruker Kappa APEX II CCD diffractometer at

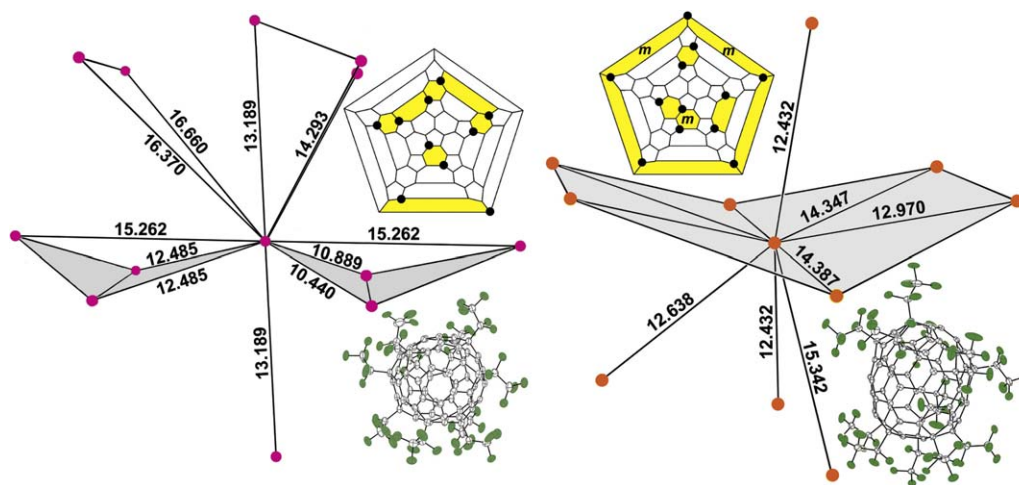


Fig. 10. Crystal packing diagrams of **70-10-8-C₂F₅** (left) and **70-12-5-C₂F₅** (right) isomers. The distances between centroids of the neighboring molecule cages are shown. The pink and orange dots are the centroids of $C_{70}(C_2F_5)_{10}$ and $C_{70}(C_2F_5)_{12}$ molecules, respectively. The insets show the respective Schlegel diagrams and X-ray crystal structures (50% probability ellipsoids). (For interpretation of the references to color in this figure caption, the reader is referred to the web version of the article.)

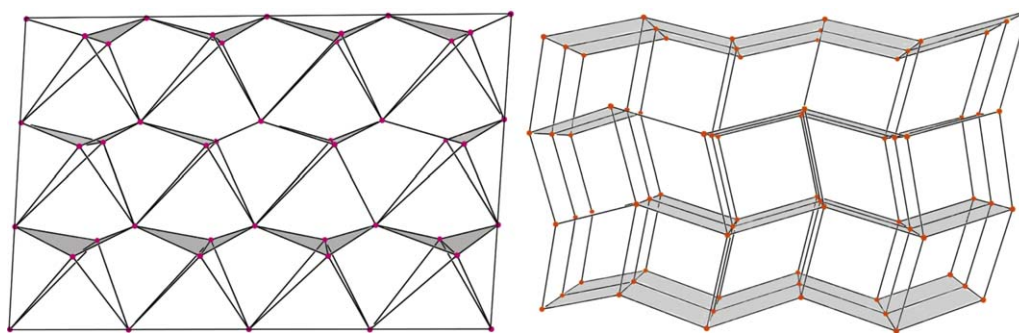


Fig. 11. Crystal packing diagrams for **70-10-8-C₂F₅** (left) and **70-12-5-C₂F₅** (right) isomers. $C_{70}(C_2F_5)_{10}$ (left) and $C_{70}(C_2F_5)_{12}$ (right) molecules form puckered layers. The pink and orange dots are the centroids of $C_{70}(C_2F_5)_{10}$ and $C_{70}(C_2F_5)_{12}$ molecules, respectively. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of the article.)

100 K. Our original structural model, which did not take into account twinning, was of very low quality, and close to the result reported for the same compound (which also crystallized in the same space group) by Troyanov and co-workers (Table S4) [25]. After detailed analysis of our data, two twin domains were assigned, and final refinement against twinned data resulted in the significant improvement of our original model (Table S4).

The second data set for these crystals was collected at Advanced Light Source, Berkeley National Laboratory using synchrotron radiation which allowed us to use a smaller (0.031 mm × 0.041 mm × 0.103 mm) and better quality non-twinned single crystal. Final structural information is presented in Table 2.

The molecule of **70-10-8-C₂F₅** has one p^5 -ribbon and four C_2F_5 groups attached to two isolated $para$ - $C_6(C_2F_5)_2$ hexagons. Thus, six C_2F_5 groups form a ribbon on the equator and the four of them attach to the reactive sites on the two poles of C_{70} molecule. This addition pattern also contains p^3, p subpattern of **70-6-2**.

There are no solvent molecules in the crystal lattice of C_2 - p^5, p, p - $C_{70}(C_2F_5)_{10}$ structure. $C_{70}(C_2F_5)_{10}$ molecules form complex puckered layers as shown in Fig. 11. The distance between two mean planes of the closest layers is 13.79 Å, and in one layer the neighboring molecules are arranged at 10.440, 10.889, and 12.485 Å from each other as shown in Fig. 10. The analysis of the four $C_{70}(C_2F_5)_{10}$ crystal structures without solvent in the lattice showed that fullerene molecules in **70-10-9-C₂F₅**, **70-10-11-C₂F₅**, **70-10-13-C₂F₅**, and **70-10-15-C₂F₅** isomers [26,27] (Table S1 and Figs. S4-14, S4-15, S4-12, and S4-16, respectively) form layers as in the case of **70-10-8-C₂F₅** structure (Fig. 11). In addition, the stacking of the ABAB packed layers of $C_{70}(C_2F_5)_{10}$ molecules in the **70-10-11-C₂F₅** isomer [26] can be considered as distorted *hcp* (Fig. S4-15).

2.4.5. X-ray structure of $C_{70}(C_2F_5)_{12}$

In the first experimentally determined molecular structure of C_{70} with 12 C_2F_5 addends (**70-12-5-C₂F₅**; IUPAC: 1,4,23,25,27,31,38,44,47,51,55,68) substituents form a unique addition pattern

that contains four C_2F_5 groups on the two isolated $para$ - $C_6(C_2F_5)_2$ hexagons, three C_2F_5 groups form a pm ribbon, and five groups form a mp^3m loop which can be considered as a part of a common skew pentagonal pyramid (SPP) addition pattern, in this case an isolated butadiene moiety is formed (Fig. 10). In Table 3, the comparison of the C–C distances in the central pentagon of SPP fragment for four perfluoroalkylated derivatives, which have this motif, is given. Each type of the following C–C bonds has similar values of C–C distances in all four structures, at $\pm 3\sigma$ level of confidence: **a, d** (double bonds) and **e, f** (single bonds). At the same time, **b** and **c** C–C bonds are the same in $C_{60}(C_2F_5)_4O$ [31] and $C_{60}(CF_3)_4O$ [31] structures (at $\pm 3\sigma$ level of confidence) but significantly different from **70-12-5-C₂F₅** and **60-10-4**. Remarkably, the structure of **70-12-5-C₂F₅** does not have any kind of disorder, in contrast to **70-10-8-C₂F₅** in which four C_2F_5 groups are disordered due to the rotation of either CF_3 or both CF_3 and CF_2 parts around C–C bond in the perfluoroethyl group. The presence of rotational disorder was frequently observed in PFAFs [26–28]. The comparison of addition patterns for the known isomers of $C_{70}(C_2F_5)_{10}$ [26,27] with the $C_{70}(C_2F_5)_{12}$ isomer shows that the latter cannot be obtained by simple addition of two C_2F_5 groups to any of the reported $C_{70}(C_2F_5)_{10}$ isomers.

There are no solvent molecules in the crystal lattice of $C_{70}(C_2F_5)_{12}$ molecule. As shown in Fig. 11, $C_{70}(C_2F_5)_{12}$ molecules form puckered layers. The closest F–F distance between $C_{70}(C_2F_5)_{12}$ molecules is 2.571(3) Å. The distance between two mean planes is 11.47 Å which is close to the value observed in the molecular packing of $C_{70}(C_2F_5)_{10}$ (see above). One $C_{70}(C_2F_5)_{12}$ molecule inside the layer is surrounded by six others, and the distances between the neighboring molecules are 12.970, 14.347, and 14.387 Å as shown in Fig. 10.

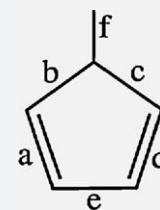
2.4.6. Addition patterns in $C_{70}(n-C_3F_7)_n$

As mentioned above, the main components in the $C_{60(70)}(n-C_3F_7)_n$ reaction mixtures prepared in our work were not separable

Table 3

X-ray C–C bond distances in the cyclopentadiene pentagon in the structures of **70-12-5-C₂F₅**, $C_{60}(C_2F_5)_4O$, $C_{60}(CF_3)_4O$ and **60-10-4**.

Bond type, Å	$C_{70}(C_2F_5)_{12}$ this work	$C_{60}(C_2F_5)_4O$ [31]	$C_{60}(CF_3)_4O$ [31]	$C_{60}(CF_3)_{10}$ [3]
a	1.354(4)	1.358(7)	1.342(5)	1.347(3)
b	1.542(4)	1.481(7)	1.482(5)	1.534(3)
c	1.545(3)	1.476(4)	1.481(5)	1.530(3)
d	1.343(4)	1.361(7)	1.353(5)	1.344(3)
e	1.479(4)	1.496(7)	1.480(5)	1.481(3)
f	1.506(4)	1.511(7)	1.488(6)	1.508(3)



by existing HPLC procedures. Out of at least two dozens of different components revealed by the HPLC analysis of the crude $C_{70}(n-C_3F_7)_n$ product, only four minor fractions which contained $C_{70}(n-C_3F_7)_8$ isomers were characterized by X-ray crystallography by others [28]. The addition patterns of all four $C_{70}(n-C_3F_7)_8$ isomers repeat those of $C_{70}(C_2F_5)_8$ compounds (Table S3).

3. Conclusions

In this work we have developed several high-temperature synthetic procedures for the preparation of air- and thermally stable PFAFs with linear perfluoroalkyl chains. These reactions occur at high temperatures and with good-to-quantitative fullerene conversion. Systematic studies of the effect of reaction conditions (temperature, time, effect of metal promoter, etc.) on the product composition allowed us to find specific conditions for preparation of the products with a narrow composition. For example, we developed procedures for several $C_{60(70)}/R_fI$ ($R_f = C_3F_7, C_4F_9, \text{ and } C_6F_{13}$) systems in which fullerene(R_f)₁₀ was the major component in the reaction mixture. We have demonstrated that isomers of fullerene(R_f)_{m>10} are practically inseparable by HPLC method while using Cosmosil Buckyprep column and pure heptane as an eluent because of the general tendency for longer- R_f chain derivatives to have shorter retention times in comparison with trifluoromethylated analogs. Furthermore, our own results and literature data [25] indicate that even in the case of fullerene(R_f)₁₀ isomers, only a small fraction of isomers is subject to HPLC purifications, leaving the most abundant isomers yet to be isolated and characterized in the future, when appropriate separation techniques are found. In the present work, $C_{70}(C_2F_5)_{12}$, the first C_{70} -based PFAF other than CF_3 with $n(R_f) > 10$ was isolated using fractional crystallization. Determination of its X-ray structure revealed an unprecedented addition pattern, which is not a product of subsequent R_f addition to any of the known isomers of $C_{70}(C_2F_5)_{10}$. PFAFs with a low number of addends (e.g., $C_{70}(C_2F_5)_4$ or $C_{70}(C_2F_5)_2$) which are usually well separable were only found as the minor products in the reaction mixtures. Presently, no synthetic methods exist that afford PFAFs with low substitution degree.

We showed that the maximum degree of addition for trifluoromethylated derivatives was 22–23 CF_3 groups per cage; in contrast, perfluoroethylation (both for C_{60} and C_{70}) results in the maximal addition of 14 groups, while for larger R_f s the highest addition value was 10. For C_{60}/C_2F_5I system we were able to perform the most complete characterization of the isolated compounds using MALDI, Raman, UV–vis, ^{19}F NMR spectroscopies, and X-ray crystallography. We demonstrated the value of ^{19}F NMR spectroscopy for unambiguous identification of the isolated pure isomers with long linear chains, even though obtaining structural information from ^{19}F NMR remains an unsolved challenge.

Based on the results of the present work, two routes for the future development of long-chain perfluoroalkyl fullerene chemistry can be proposed. The first direction is the search for new methods or optimization of the known synthetic techniques for preparation of the compounds with a low degree of substitution. These compounds can be easily separated by existing HPLC methods and can potentially become important alternatives for trifluoromethylated derivatives including their use for further derivatizations. Another direction is the exploration of the new separation techniques which would allow one to isolate highly substituted perfluoroalkyl fullerenes, which are easy to prepare in high yields as mixtures but difficult to purify with the currently used chromatographic approach.

Finally, our electrochemical data for the selected PFAFs demonstrate that they exhibit strong electron accepting properties, reversible reductions in solution, their redox properties vary with the addition patterns, which indicates that they have potential to develop into a new and promising class of organic electron acceptor materials.

4. Experimental

4.1. Reagents and solvents

The reagents and solvents CF_3I (Apollo Scientific, 98%), C_2F_5I (Sigma–Aldrich, 97%), $n-C_3F_7I$ (Sigma–Aldrich, 98%), $n-C_4F_9I$ (Sigma–Aldrich, 98%), $n-C_6F_{13}I$ (Sigma–Aldrich, 99%), C_{60} (Term USA), C_{70} (Term USA), Cu powder (Sigma–Aldrich, ~40 mesh, 99.5%) chloroform-*d* and toluene-*d*⁸ (Cambridge Isotopes), hexafluorobenzene (Sigma–Aldrich), and heptane or toluene for HPLC purification (Sigma–Aldrich) were used as received. 1,2-dichlorobenzene (Sigma–Aldrich, ACS grade) was distilled over CaH_2 under dry N_2 and stored in the glovebox. Tetrabutylammonium tetrafluoroborate ($N(n-Bu)_4BF_4$) (Fluka puriss. grade) was stored in the glove box after drying under vacuum at 70 °C for 24 h.

4.2. Synthesis

4.2.1. Photochemical reactions

In a typical UV–vis experiment, a finely ground C_{60} (50 mg, 0.007 mmol) and hexafluorobenzene (0.5 mL) were placed in the thin glass ampule (I.D. = 5 mm). After condensation of CF_3I (1.5 mL, 6.2 mmol), the glass ampule was sealed. The tubes with the samples were exposed under UV radiation at room temperature during 48 h or 7 days.

4.2.2. Reactions in a hot-flow tube

$C_{60}(C_2F_5)_n$: In a typical reaction, a finely ground C_{60} (20–50 mg, 0.028–0.069 mmol) mixed with Cu powder (500 mg) 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 C_{60} was placed in a 5 cm long tube furnace. After purging the apparatus with argon, the C_{60} sample was heated to 400, 430, 460 or 500 °C and treated with gaseous C_2F_5I (~0.2 L/h) for several hours as listed in Table 1.

$C_{60}(C_nF_{2n+1})_n$, $n = 1, 3, 4, 6$ and $C_{70}(C_nF_{2n+1})_n$, $n = 2, 3, 4$: In a typical experiment, finely ground $C_{60}(C_{70})$ (100 mg, 0.139 (0.119) mmol) was placed in a 0.8-cm I.D. quartz tube connected to a gas handling system at one end and a mineral-oil bubbler at the other (Table 1). The portion of the tube containing $C_{60}(C_{70})$ was placed in a 40-cm long tube furnace. The perfluoroalkylating agents which were used in this work have a wide range of the boiling temperatures. Therefore, to perform the perfluoroalkylation reactions at high temperatures, several different methods of R_fI introduction to the system were used. CF_3I and C_2F_5I were introduced directly from the gas cylinders at room temperature. In the reaction between $C_{60}(C_{70})$ and $n-C_3F_7I$ (b.p. = 40 °C) or $i-C_3F_7I$ (b.p. = 39 °C), nitrogen was used as a carrier gas and bubbled through liquid C_3F_7I at room temperature. In case of C_4F_9I (b.p. = 67 °C) and $C_6F_{13}I$ (b.p. = 117 °C), nitrogen was bubbled through perfluoroalkylating agents at 65 °C and 113 °C, respectively.

After purging the apparatus with argon or flow of perfluoroalkylating agent, C_{60} (or C_{70}) was heated to 320–500 °C. [CAUTION: Perfluoroalkylating agents decompose in air above 300 °C and produce toxic HF, COF_2 , and I_2 ; handle only in a well-ventilated fume hood]. Orange-brown products and purple I_2 condensed inside the tube (in the cold zones). After the reaction, the obtained product (together with iodine) was washed from the tube using hexane (or toluene) followed by evaporation of the solvent and iodine at room temperature.

Two reactions of $C_{60}(C_{70})$ with CF_3I were performed at 500 °C during 2 and 12 h, while other parameters such as the length of the quartz tube, flow rate of CF_3I , amount of the C_{60} were the same. Two nearly identical HPLC traces of the products from both experiments, shown in Fig. S4–1 in the Supporting Information. To

examine reproducibility of C_{60}/CF_3I reactions (520 °C, 3 h), two experiments were performed, HPLC results are shown in Fig. S4-2.

4.2.3. Reactions in sealed ampoules

In a typical experiment, finely ground $C_{60}(C_{70})$ was placed in a glass ampule, the ampule was evacuated, R_fI was then added, and the ampule was sealed. In some cases, fine copper powder was added as a promoter. The reactions were carried out at 320–550 °C during 24–48 h (Table 1). After the reaction, formed iodine and an excess of the unreacted perfluoroalkylating agent were removed under vacuum. In the reactions between C_{60} and CF_3I , the conditions (amounts of the reagents, time and temperature) described in [9] were followed as precisely as possible. The reaction between C_{60} (20 mg, 0.028 mmol) and excess of $n-C_3F_7I$ was carried out in a sealed-ampule at 290 °C for 24 h (Table 1).

4.3. Isolation and purification

Isolation and purification of $C_{60}(C_2F_5)_n$ ($n = 6, 8, \text{ and } 10$) compounds were performed by HPLC method using Cosmosil Buckyprep column (Nacalai Tesque Inc., 10 mm i.d. \times 250 mm) at 300 nm UV detection; the detailed procedures are described in the SI (pp.S2–S4 in SI). $C_{70}(C_2F_5)_2$ was isolated and characterized as described earlier [33]. Two isomers of $C_{70}(C_2F_5)_4$ were isolated from the high-temperature flow tube reaction product and purified in 20:80 toluene/heptane eluent at 5 mL min^{-1} ($C_{70}(C_2F_5)_4$ -I) and 60:40 (v:v) toluene/heptane eluent at 5 mL min^{-1} ($C_{70}(C_2F_5)_4$ -II), and their retention times were 24.6 and 12.8 min, respectively. The $C_{70}(C_2F_5)_{10}$ isomer (**70-10-8- C_2F_5**) eluted at 5.8 min was isolated and purified from 400- to 430 °C-product using 20:80 (v:v) toluene/heptane mixture as an eluent.

4.4. X-ray crystallography

Crystals of $C_{70}(C_2F_5)_{12}$ were grown by slow evaporation from saturated perfluoroheptane solution. A diffraction-quality single crystal (0.175 mm \times 0.192 mm \times 0.215 mm) was mounted in paratone oil on a glass fiber glued to a small copper pin. The data set was collected at 120 K using a diamond (1 1 1) crystal monochromator, a wavelength of 0.41328 Å, and a Bruker CCD detector at ChemMatCARS Sector 15-B at the Advanced Photon Source at Argonne National Laboratory (CARS = Center for Advanced Radiation Sources).

Single crystals of $C_{70}(C_2F_5)_{10}$ (0.031 mm \times 0.041 mm \times 0.103 mm) were grown from saturated heptane solution. The crystals were mounted in paratone oil on a MiTeGen 10 μm loop. The data set was collected at 100 K using a silicon (1 1 1) crystal monochromator on a D8 goniostat equipped with a Bruker APEXII CCD detector at Beamline 11.3.1 at the Advanced Light Source at Lawrence Berkeley National Laboratory using synchrotron radiation tuned to $\lambda = 0.7749$ Å.

For $C_{60}(C_2F_5)_{10}$ crystals (0.250 mm \times 0.130 mm \times 0.050 mm), measurements were performed on a Bruker SMART diffractometer (Mo-K α , $\lambda = 0.71073$ Å; graphite monochromator; $T = 100(2)$ K).

For all structures, absorption and other corrections were applied using SADABS [37]. The structures were solved using direct methods and refined (on F^2 , using all data) by a full-matrix, weighted least squares process. Standard Bruker control and integration software (APEX II) was employed, and Bruker SHELXTL[38] software was used for structure solution, refinement, and graphics.

4.5. Spectroscopic measurements

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 immediately 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 were detected in reflectron mode. ^{19}F NMR spectra were recorded using a Bruker INOVA-400 spectrometer operating at 376.48 MHz (C_6F_6 was used as an internal standard) ($\delta = -164.9$). Negative-ion atmospheric-pressure chemical-ionization (NI-APCI) mass spectra were recorded using a Thermo Quest Finnigan LCQ-DUO spectrometer. An Agilent Technologies Model 6210 TOF spectrometer was used to record negative-ion atmospheric-pressure-photo-ionization (NI-APPI) mass spectra. Electronic absorption spectra of hexane or perfluorohexane solutions of the $C_{60}(C_2F_5)_n$ solutions were recorded using Varian Cary 500 Scan UV-Vis-NIR spectrophotometer. Cyclic voltammetry experiments were carried out in the inert atmosphere in the glove box (water and oxygen content below 1 ppm) in a single-compartment electrochemical cell. The electrolyte solution was 0.1 M $N(n\text{-Bu})_4\text{BF}_4$ in *o*-dichlorobenzene. The working electrode was a platinum wire (0.5 mm diameter). A platinum wire (0.5 mm diameter) and a silver wire (0.5 mm diameter, Alfa Aesar Premion, 99.99%) served as the counter electrode and quasi-reference electrode, respectively. The potentials were measured relative to $\text{Fe}(\text{Cp}^*)_2^{+/0}$ and $\text{Fe}(\text{Cp})_2^{+/0}$ potentials. The experiments were controlled by a PAR 263 potentiostat/galvanostat.

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Appendix A. Abbreviations used in the manuscript

APCI	atmospheric-pressure chemical-ionization
APPI	atmospheric-pressure photoionization
MALDI-TOF	Matrix-assisted laser-desorption-ionization time-of-flight
EI	electron ionization
HPLC	high performance liquid chromatography
PFAF	perfluoroalkylfullerene
TMF	trifluoromethylfullerene

The following notation for the isomers of PFAFs with the known structures was adopted.

It was first introduced in Ref. [3] and then used throughout all our publications on PFAFs. New addition patterns which are unambiguously determined (X-ray crystallography or ^{19}F NMR) are assigned a consecutive number for a given composition of PFAF.

For example, the ninth isomer of $C_{60}(C_2F_5)_8$ will be denoted as **60-8-9- C_2F_5** . First number **60** is carbon cage, second number (**8**) is

number of R_f groups, third number (9) is isomer number or type of addition pattern, and, lastly, type of R_f (C₂F₅) is given. If two PFAF molecules with the same number of R_f groups have the same addition pattern they will have the same isomer number.

Appendix B. Supplementary information

Crystallographic data for **60-10-6-C₂F₅**, **70-10-8-C₂F₅** and **70-12-5-C₂F₅** have been deposited with the Cambridge Crystallographic Data Centre (deposition CCDC numbers, 773356, 773326 and 773325, respectively). 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, e-mail: deposit@ccdc.cam.ac.uk.

Appendix C. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jfluchem.2010.08.001](https://doi.org/10.1016/j.jfluchem.2010.08.001).

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