Supporting Information

Chemical tailoring of fullerene acceptors: synthesis, structures and electrochemical properties of perfluoroisopropylfullerenes

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Experimental Section

Reagent and solvents

The reagents and solvents *i*-C_3F_7I (Apollo Scientific, 98% and SynQuest, 97%), C_{60} and C_{70} (Term USA), hexafluorobenzene (Sigma-Aldrich), heptane and toluene for HPLC purification (Sigma-Aldrich), chloroform-*d* (Chembridge Isotopes) were used as received.

Synthesis of $C_{60}(i\text{-}C_3F_7)_n$ and $C_{70}(i\text{-}C_3F_7)_n$ derivatives

Three methods of preparation of $C_{60}(i\text{-}C_3F_7)_n$ and $C_{70}(i\text{-}C_3F_7)_n$ derivatives were performed in this work which include reactions under UV-vis radiation, in the continuous flow apparatus, and in glass sealed ampules.

In a typical UV-vis experiments, a finely ground C_{60} or C_{70} (5–30 mg, 0.007–0.042 or 0.006–0.036 mmol), *i*-C_3F_7I (0.5 ml, 6.2 mmol), and toluene (0.5 ml) or hexafluorobenzene (0.5 ml) were placed in the thin glass tube (i.d. = 5 mm). The tubes with the samples were exposed under UV-vis radiation at room temperature during 21 h or 7 days.

In the reactions, which were performed in the heated quartz tube, C_{60} (or C_{70}) (50−100 mg, 0.069–0.139 mmol (0.060−0.119 mmol)) was mixed with fine copper powder (500 mg, 7.87 mmol). Nitrogen gas was bubbled through the liquid perfluoroalkylating agent (*i*-C_3F_7I) which was delivered to the hot reaction zone (320–500 °C) by N_2 gas flow. The reaction time was varied from 2 to 9 hours.

The syntheses in the sealed glass ampules were carried out at 290–416 °C during 24 h in which 20−50 mg (0.028−0.069 mmol) of C_{60} and 1 ml (12.4 mmol) *i*-C_3F_7I were used (Table S1).

The preparation of $C_{60}(n\text{-}C_3F_7)_n$ and $C_{70}(n\text{-}C_3F_7)_n$ compounds was performed in a continuous flow apparatus and sealed glass ampules. In typical experiment in continuous flow apparatus, 50–100 mg (0.069–0.139 mmol) of C_{60} and 100 mg of C_{70} (0.119 mmol) were used. *n*-C_3F_7I was delivered in the hot reaction zone (350–380 °C) using the same procedure as in case of *i*-C_3F_7I. The reaction time was varied from 7 to13 hours. Details of the experiments are given in the Table S1.

Isolation of $C_{60}(i\text{-}C_3F_7)_n$, $C_{70}(i\text{-}C_3F_7)_n$, and $C_{60}(i\text{-}C_3F_7)_n(CF_3)_m$ derivatives

$C_{60}(i\text{-}C_3F_7)_n$ products was purified by HPLC (10 mm i.d. × 250 mm long Cosmosil Buckyprep column (Nacalai Tesque, Inc.), 300 nm UV detector). First separation of the $C_{60}(i\text{-}C_3F_7)_n$

crude samples obtained in sealed glass ampule (290 °C) was done in toluene as an eluent at 5 mL min^{-1} flow rate. Three different fractions 2.9 min (**I**), 3.6 min (**II**), 5.6 min (**III)**, and 6.3 min (**IV**) were isolated. Subsequent purification of **III** and **IV** fractions using 100% toluene as an eluent at 5 mL min^{-1} flow rate resulted in the isolation of pure $C_{60}(i\text{-}C_3F_7)_2$ (5 min) and $C_{60}(i\text{-}C_3F_7)(CF_3)$ (5.8 min) compounds. The mixture of 10:90 (v:v) toluene/heptanes was used as eluent to perform the further purification of **I** and **II** fractions. As a result, three pure fractions (retention times shown in parenthesis) such as $C_{60}(i\text{-}C_3F_7)_4$ (8.5 min), $C_{60}(i\text{-}C_3F_7)_4$ (11.2 min), and **60-4-5** (11.8 min) were isolated from fractions **I** and **II**. The rest of the fractions **I** and **II** were finally purified in 100 % heptane (at 5 mL min^{-1} flow rate) to yield the following pure isomers: $C_{60}(i\text{-}C_3F_7)_6$ (3.4 min), **60-6-9** (4.5 min), $C_{60}(i\text{-}C_3F_7)_6$ (5.0 min), **60-6-5** (5.8 min**)**, $C_{60}(i\text{-}C_3F_7)_4$ (13.7 min from 8.5 min using10:90 toluene/heptane as an eluent**)**, **60-4-4** (17.3 min**)**, $C_{60}(i\text{-}C_3F_7)_4$ (21.5 min**)**, and **60-4-5** (23 min**)**.

Two isomers of $C_{60}(i\text{-}C_3F_7)_2(CF_3)_2$ were isolated from the sample which was obtained in flow continuous apparatus at 320 °C. First purification was performed in 100% toluene at 5 mL min^{-1} flow rate with following isolation of 3.5 min fraction. On the second step, toluene/heptane (60:40 (v:v)) mixture was used as an eluent which allowed us to isolate two isomers at 5.7 min and 7.0 min.

From the crude $C_{70}(i\text{-}C_3F_7)_n$ mixture, the fraction with retention time 6.8 min was isolated using 100% toluene as an eluent at 5 mL min^{-1} flow rate. The is fraction was then processed using (50:50)(v:v) dichloromethane/heptanes eluent, at 5 mL min^{-1} flow rate, which resulted in the isolation of **70-2-1** (13.5min) and **70-2-**2 (14.5min). The **70-4-2**, **70-4-3**, and **70-4-4** isomers were isolated from the fraction eluted at 2.8–3.3 min using toluene as an eluent (5 mL min^{-1} flow rate). Subsequent purification of **70-4-2** and **70-4-3** compounds were performed in 20:80 (v:v) toluene/heptane at 5 mL min^{-1} flow rate, and the retention times of pure isomers were 22 and 14.5 min, respectively. The **70-4-4** isomer was finally purified in 10:90 (v:v) toluene/heptane mixture, in which **70-4-4** was eluted at 20.5 min.

X-ray Crystallography.

C_s-$C_{60}(i\text{-}C_3F_7)_2$ (60-2-1). X-ray diffraction data from crystals of C_s-$C_{60}(i\text{-}C_3F_7)_2$·were collected at 150 K on a D8 goniostat equipped with a Bruker APEXII CCD detector at Beamline 11.3.1 at the Advanced Light Source (Lawrence Berkeley National Laboratory) using synchrotron radiation tuned to λ = 0.7749 Å. A series of 3-s data frames measured at 0.2° increments of ω were collected to calculate a unit cell. For data collection frames were measured for a duration of 3-s at 0.3° intervals of ω with a maximum 2θ value of ~60°. Two C_{60} cage orientations in C_s-$C_{60}(i\text{-}C_3F_7)_2$ structure were found. The main component of C_{60} sphere was located after several cycles of the refinement. The minor one was treated as a rigid group with the same geometry as a major one. These orientations have been indentified with fractional occupancies 83% and 17%. The minor component is related to the major one by a mirror plane which contains two C1−C201 and C1A−C201A bonds. Notably, this symmetry operation does not move the C1−C2−C2A−C1A−C9A−C9 hexagon with attached i-C_3F_7 groups. The displacement parameters of the overlapping atoms in both cages were constrained to be equal.

C_2-$C_{60}(i\text{-}C_3F_7)_4$ (60-4-4) and C_1-$C_{60}(i\text{-}C_3F_7)_4$ (60-4-5). X-ray diffraction data from crystals of C_2-$C_{60}(i\text{-}C_3F_7)_4$ and C_1-$C_{60}(i\text{-}C_3F_7)_4$ (grown by slow evaporation from saturated toluene and benzene solution, respectively) were recorded on a Bruker Kappa APEX II CCD diffractometer employing Mo Kα radiation (graphite monochromator). The rotational disorder of two i-C_3F_7 groups in **60-4-4** structures was successfully modeled. The site-occupancy factors of the two modeled orientations for the i-C_3F_7 groups in **60-4-4** structure attached to the C28 and C31 were 89/11% and 58/42%, respectively.

In **60-4-5** structure, the site occupancy factors for the four disordered i-C_3F_7 groups which attach to C1, C7, C36, and C39 cage carbon atoms are 88/12%, 81/19%, 85/15%, and 89/11%, respectively. In addition, the two C_{60} cage orientations have been identified with fractional occupancies 86% /14%.

C_1-$C_{60}(C_3F_7)_6$ (60-6-9). The crystals of C_1-$C_{60}(C_3F_7)_6$ compound were grown by slow evaporation of the saturated heptanes/toluene solution. The diffraction-quality single crystal was mounted in paratone oil on a glass fiber rod glued to a small copper wire. X-ray diffraction data were collected at ChemMatCARS (CARS = Consortium for Advanced Radiation Sources) sector 15-B at the Advanced Photon Source (Argonne National Laboratory). The data set was collected at 100 K using a diamond (111) crystal monochromator at a wavelength of 0.4428 Å. Data were recorded using a Bruker CCD (charge-coupled device) detector. Absorption and other corrections were applied by using SADABS.[1] The site-occupancy factors of the two modeled orientations for the one disordered i-C_3F_7 group were 86% and 0.14%.

The all structures were solved by using direct methods and refined (on F^2, using all data) by a full-matrix, weighted least squares process. All carbon and fluorine atoms were refined by using anisotropic atomic displacement parameters. Standard Bruker control and integration software (APEX II) was employed, and Bruker SHELXTL[2] software was used for structure solution, refinement, and graphics. Selected details related to the crystallographic experiments are listed in Table S3.

Spectroscopic Characterization.

Atmospheric-pressure chemical-ionization (APCI) and atmospheric pressure photo-ionization (APPI) mass spectra were recorded using a ThermQuest Finnagan LCQ-DUO spectrometer (acetonitrile eluent, 0.3 $mL\cdot min^{-1}$ flow rate) and Agilent Technologies Model 6210 TOF with APPI spectrometer. In latter case, flow injection was done using acetonitrile which contained 1% toluene. Samples for ^{19}F NMR spectroscopy were chloroform-*d* solutions containing a small amount of hexafluorobenzene as an internal standard (δ = –164.9). Spectra were recorded using a Varian INOVA-unity 400 spectrometer operating at 367.45 MHz.

Cyclic voltammetry was carried out in a glove box (water and oxygen content bellow 1 ppm) in one compartment electrochemical cell. The electrolyte solution was 0.1 M $N(n\text{-}Bu)_4BF_4$ ($TBABF_4$) in *o*-dichlorobenzene. Platinum wire, platinum wire loop and a silver wire served as working, counter, and pseudo-reference electrodes, respectively. The potentials were measured as referred to the $Fe(Cp)_2^{+/0}$ or $Fe(Cp^*)_2^{+/0}$ couple, i.e., $Fe(Cp)_2$ was added as the internal standard at the end of the voltammetric measurements which were controlled by PAR 273 potentiostat/galvanostat.

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[1] Sheldrick, G. M. SADABS – *A program for area detector absorption corrections* 2004.

[2] Sheldrick, G. M. *Acta Crystallographica Section A* **2008**, *64*, 112.

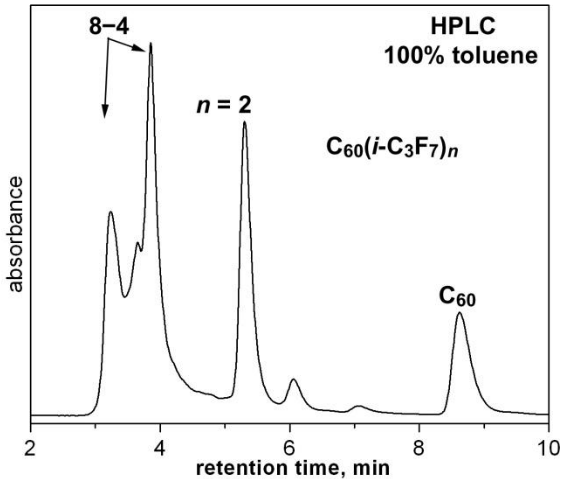

Figure S1. HPLC trace of the crude $C_{60}(i\text{-}C_3F_7)_n$ (n = 2–8) product obtained in the sealed glass ampule at 290 °C for 24 h.

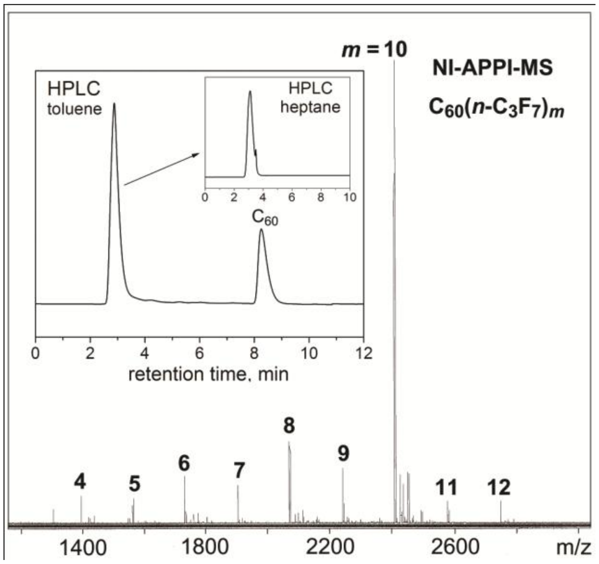

Figure S2. HPLC trace of the crude $C_{60}(n\text{-}C_3F_7)_m$ (m = 4–12) product obtained in the sealed glass ampule at 290 °C for 24 h.

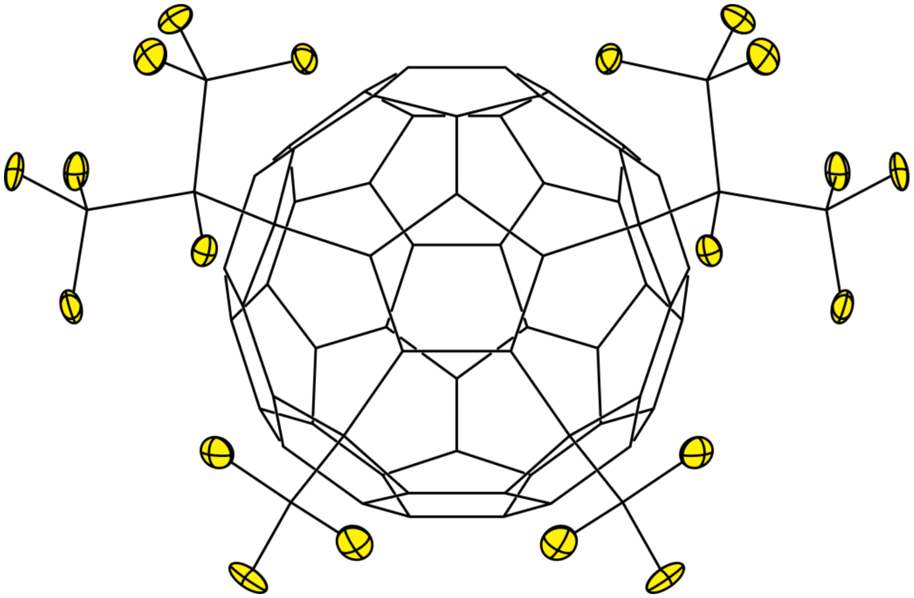

Figure S3. X-ray crystal structure of $C_{60}(i\text{-}C_3F_7)_2(CF_3)_2$ (**60-4-3**) (50% anisotropic probability ellipsoids for all atoms).

Table S1. Reaction conditions and products of C_{60} and C_{70} perfluoroalkylation using i-C_3F_7I.

Fullerene, mg	$n(i\text{-}C_3F_7I)/n(\text{fullerene})$	Reactor type/T_{rxn}, °C	Reaction time	Solvent/or catalyst	MS data on $C_{60}(i\text{-}C_3F_7)_k(CF_3)_m$		
					k	k_{max}	m
C_{60}							
30	68	UV/25	21 h	C_6F_6	4–10	6	–
5	507	UV/25	48 h	C_6H_6	8–10	8	–

10	152	UV/25	7 days	C_6F_6	4–12	10	–
10	152	UV/ 25	7 days	C_6F_6/Cu	4–12	6	–
40	63	Amp./290	24 h	Cu	1–8	6	1
50	31	Amp./316	24 h	Cu	1–6	2	1
20	38	Amp./319	24 h	–	1–6	2	{1;1}
20	38	Amp./390	24 h	Cu	no product		
100	excess	Flow/320	4 h	Cu	6,8	6	
100	excess	Flow/380	9 h	Cu	6–12	10	10–12
50	excess	Flow/480	5 h	Cu	6–10	6	8–10
60	excess	Flow/500	2–4 h	Cu	no product		
C_{70}							
100	excess	Flow/320	10.5 h	Cu	8–10	10	–
34	30	Amp./180	24 h	Cu/o-DCB	2–6	4	–
23	53	Amp./416	24 h	Cu	no product		
5	592	UV/ 25	48 h	C_6F_6	10–12	10	–

Table S2. Reaction conditions and products of C_{60} and C_{70} perfluoroalkylation using n-C_3F_7I.

Fullerene, mg	n(n-C_3F_7I)/ n(fullerene)	Reactor type/T_{rxn}, °C	Reaction time	Solvent/or catalyst	MS data $C_{60}(n\text{-}C_3F_7)_k(CF_3)_m$		
					k	k_{max}	m
			C_{60}				
21	84	Amp./290	24 h	Cu	6–12	10	–
50	excess	Flow/350	7 h	Cu	8–12	10	–
100	excess	Flow/380	7 h	Cu	8–12	10	–
			C_{70}				
100	excess	Flow/380	13 h	Cu	4–12	10	–

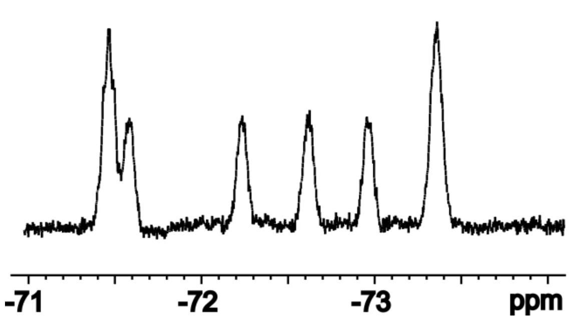

Figure S4. ^{19}F NMR of $C_{60}(i\text{-}C_3F_7)_4$ (r.t. 13.7 min) in chloroform-*d*, 376.5 MHz.

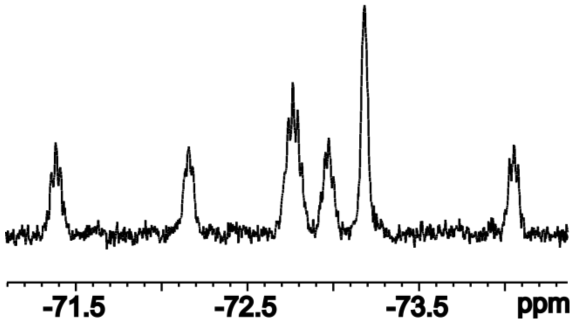

Figure S5. ^{19}F NMR of $C_{60}(i\text{-}C_3F_7)_4$ (r.t. 21.5 min) in chloroform-*d*, 376.5 MHz.

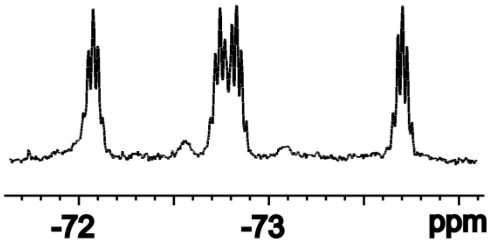

Figure S6. ^{19}F NMR of **60-6-5** in chloroform-*d*, 376.5 MHz.

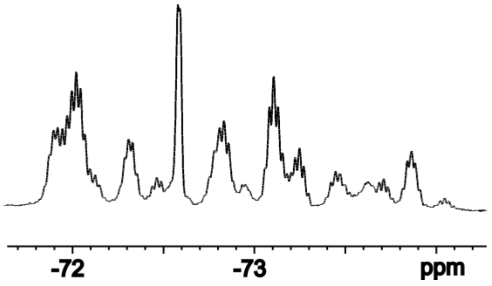

Figure S7. ^{19}F NMR of **60-6-9** in chloroform-*d*, 376.5 MHz.

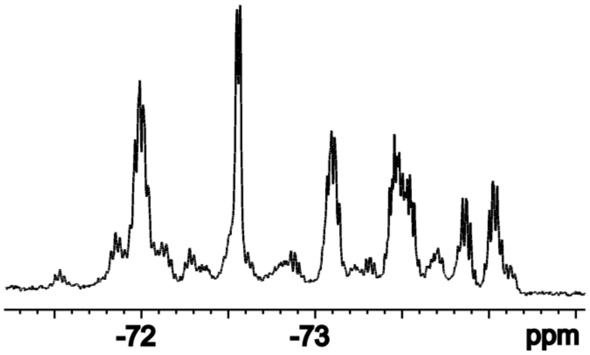

Figure S8. ^{19}F NMR of $C_{60}(i\text{-}C_3F_7)_6$ (r.t. 5.0 min) in chloroform-*d*, 376.5 MHz.

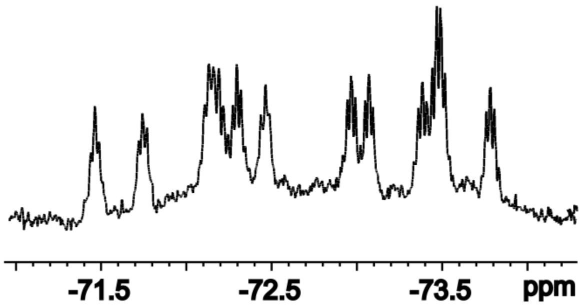

Figure S9. ^{19}F NMR of $C_{60}(i\text{-}C_3F_7)_6$ **60-6-8** (r.t. 3.4 min) in chloroform-*d*, 376.5 MHz.

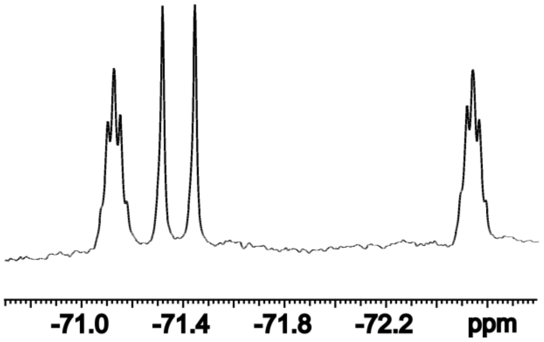

Figure S10. ^{19}F NMR of $C_{60}(i\text{-}C_3F_7)(CF_3)$ in chloroform-*d*, 376.5 MHz.

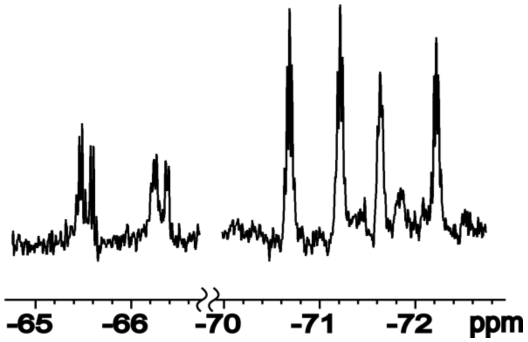

Figure S11. ^{19}F NMR of $C_{60}(i\text{-}C_3F_7)_2(CF_3)_2$ (r.t. 5.7 min) in chloroform-*d*, 376.5 MHz.

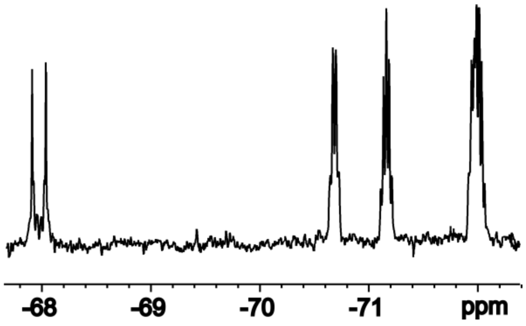

Figure S12. ^{19}F NMR of $C_{60}(i\text{-}C_3F_7)_2(CF_3)_2$ (r.t. 7.0 min) in chloroform-*d*, 376.5 MHz.

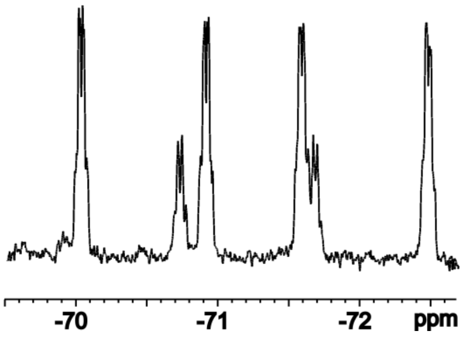

Figure S13. ^{19}F NMR of 6.8min fraction from 100% toluene containing **70-2-1** (four main peaks) and **70-2-2** (two smaller peaks) in chloroform-*d*, 376.5 MHz.

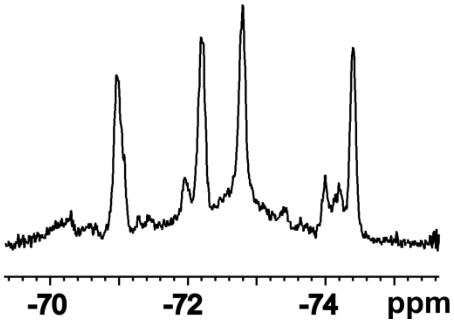

Figure S14. ^{19}F NMR of **70-4-2** in chloroform-*d*, 376.5 MHz.

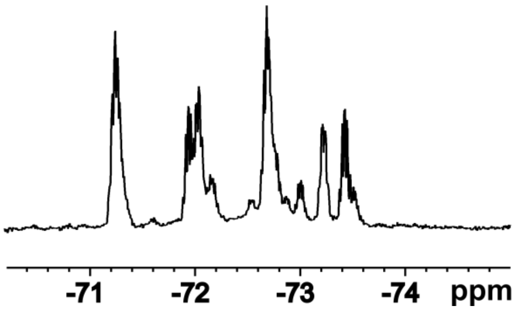

Figure S15. ^{19}F NMR of **70-4-3** in chloroform-*d*, 376.5 MHz.

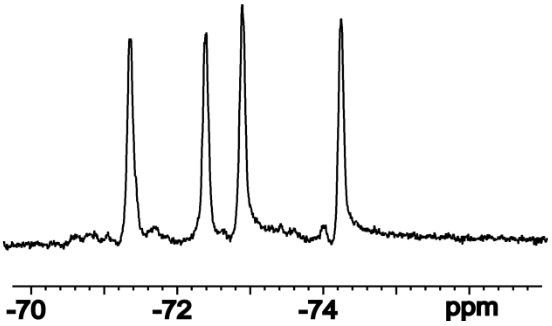

Figure S16. ^{19}F NMR of **70-4-4** in chloroform-*d*, 376.5 MHz.

Table S3. Crystal data and structure refinement for $C_{60}(i\text{-}C_3F_7)_2$, C_2-$C_{60}(i\text{-}C_3F_7)_4{\cdot}0.5C_7H_8$, C_1-$C_{60}(i\text{-}C_3F_7)_4{\cdot}C_6H_6$, and C_1-$C_{60}(i\text{-}C_3F_7)_6$.

	$C_{60}(i\text{-}C_3F_7)_2$	$C_{60}(i\text{-}C_3F_7)_4{\cdot}0.5C_7H_8$	$C_{60}(i\text{-}C_3F_7)_4{\cdot}C_6H_6$	$C_{60}(i\text{-}C_3F_7)_6$
molecular formula	$C_{66}F_{14}$	$C_{75.5}H_4F_{28}$	$C_{78}H_6F_{28}$	$C_{78}F_{42}$
formula weight	1058.66	1442.79	1474.83	1734.78
crystal system	orthorhombic	monoclinic	triclinic	triclinic
space group	$Pnma$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
Z	4	4	2	2
color of crystals	red-brown	red	brown	brown
unit cell dimensions				
a, Å	19.622(4)	22.645(4)	10.0294(4)	10.2212(6)
b, Å	17.836(3)	10.1528(17)	12.1981(5)	13.6183(8)
c, Å	10.009(2)	23.011(4)	23.011(4)	21.99z 33(9)
α, °	90	90	75.600(2)	80.248(2)
β, °	90	115.435(8)	81.858(2)	87.129(2)
γ, °	90	90	75.199(2)	71.128(2)
temperature, K	150(2)	100(2)	100(2)	100(2)
final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0399$ $wR_2 = 0.115$	$R_1 = 0.0643$ $wR_2 = 0.1759$	$R_1 = 0.0671$ $wR_2 = 0.2005$	$R_1 = 0.0598$ wR2 = 0.1625
goodness-of-fit on F^2	1.024	1.058	1.008	1.046

Table S4. PBE/TZ2P computed LUMO and EA (all eV) for $C_{60,70}(R_f)_n$ derivatives (R_f = i-C_3F_7 and CF_3).

	LUMO			EA		
	i-C_3F_7	CF_3	$\Delta(CF_3 - i\text{-}C_3F_7)$	i-C_3F_7	CF_3	$\Delta(i\text{-}C_3F_7 - CF_3)$
C_{60}	–4.379			2.924		
60-2-1	–4.589	–4.592	–0.004	3.195	3.162	0.033
60-4-3	–4.837	–4.792	0.045	3.442		
60-4-4	–4.786	–4.804	–0.018	3.433	3.381	0.051
60-4-5	–4.680	–4.706	–0.026	3.346	3.307	0.039
60-6-3	–4.830	–4.858	–0.027	3.538	3.476	0.062
60-6-5	–4.735	–4.792	–0.057	3.454	3.422	0.032
60-6-8	–4.900	–4.937	–0.037	3.577	3.548	0.029
60-6-9	–4.752	–4.798	–0.047	3.470	3.428	0.041
60-8-11	–5.187	–5.212	–0.024	3.939	3.854	0.085
C_{70}	–4.315			2.942		
70-2-1	–4.708	–4.697	0.011	3.376	3.333	0.043
70-4-2	–4.952	–4.957	–0.005	3.657	3.605	0.052
70-4-3	–4.764	–4.770	–0.006	3.475	3.424	0.051
70-4-4	–4.896	–4.894	0.002	3.621	3.563	0.058
70-4-5	–4.865	–4.872	–0.008	3.577	3.526	0.050
70-4-6	–4.806	–4.804	0.003	3.531	3.471	0.059

Note that ΔLUMO is computed as LUMO(CF_3) – LUMO(i-C_3F_7); while

ΔEA is computed as EA(i-C_3F_7) – EA(CF_3);

this way, positive value for both ΔLUMO and ΔEA indicate that i-C_3F_7 derivative is stronger electron acceptor than corresponding CF_3-derivative. Not however that in most cases ΔLUMO and ΔEA have opposite signs.

Table S5. Notations of isomers used in the work. IUPAC numbering for the isomers with the known addition patterns.

Introduction: In this paper we continue using the isomer notation system that we introduced in our paper on the electrochemical studies of seventeen $C_{60}(CF_3)_n$ compounds.

For example: isomer three of $C_{60}(CF_3)_{10}$ will be denoted as **60-10-3.**

This number determines a unique addition pattern. If a compound with the same addition pattern but different substituents becomes known, it is assigned the same notation **60-10-3**. When it is necessary to denote a type of addend, the notation can be given as follows: **60-10-3-C_4F_9.**

The number of an isomer is arbitrary and it follows in general the publication time.

The notations of the isomers mentioned in this work can be found in the following references:

60-4-1, 60-4-2, 60-6-1, 60-6-2, 60-8-1 through **60-8-5**	Popov, et al. *JACS* **2007**, *129*, 11551.
60-6-6, 60-6-7, 60-8-6 through **60-8-10**	Shustova, et. al., *JFC* **2010**, in press
70-2-1, 70-2-2, 70-4-1, 70-4-1	Popov, et al. *Chem. Eur. J.*

The proper IUPAC numbering is provided below for the isomers with the addition patterns determined in this work and in ref. (Mutig, et al., JFC, 2009, *130*, 241-247).

Table S5. Notations of isomers used in the work, and IUPAC numbering for the isomers with the known addition patterns.

IUPAC	abbreviations
1,7-C_s-C_{60}(iso)$_2$	**60-2-1**
1,7,36,39-C_1-C_{60}(iso)$_4$	**60-4-5**
1,7,28,31-C_2-C_{60}(iso)$_4$	**60-4-4**
1,7,16,30,36,47-C_3-C_{60}(iso)$_6$	**60-6-5**
1,7,16,36,45,57-C_1-C_{60}(iso)$_6$	**60-6-8**
1,7,16,36,43,46-C_1-C_{60}(iso)$_6$	**60-6-9**
1,7,11,24-C_s-C_{60}(iso)$_2$(CF_3)$_2$	**60-4-3**
1,7,16,36,46,49-C_1-C_{60}(iso)$_6$	**60-6-3**
1,7,14,31,36,39,45,57-C_1-C_{60}(iso)$_8$	**60-8-11**
7,17,24,36-C_s-C_{70}(iso)$_4$	**70-4-2**
7,14,24,35-C_1-C_{70}(iso)$_4$	**70-4-3**
7,24,36,57-C_2-C_{70}(iso)$_4$	**70-4-4**

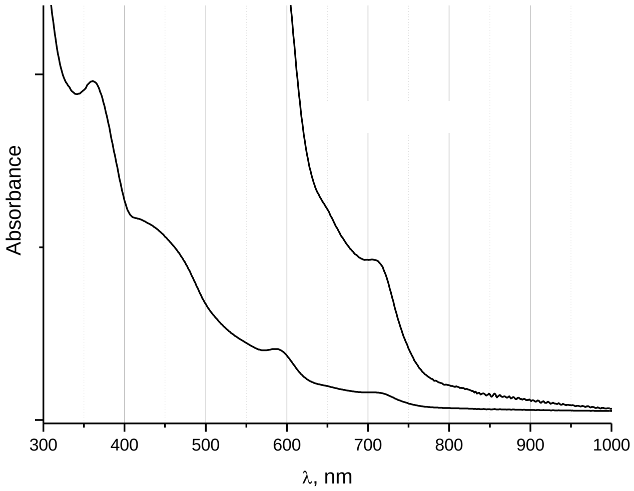

Figure S17. UV-vis spectrum of toluene solution of **70-2-1** compound.

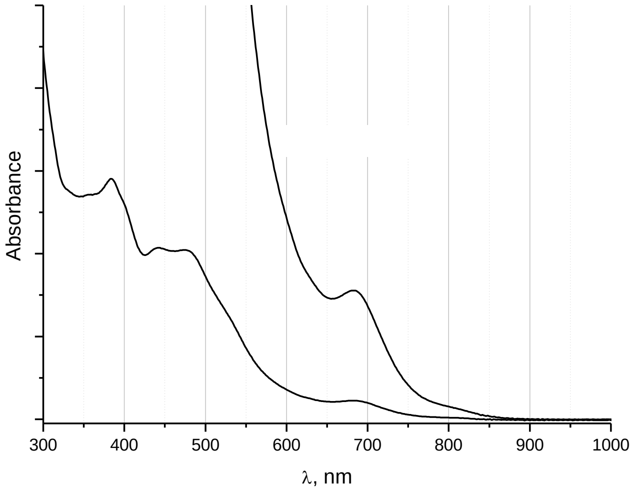

Figure S18. UV-vis spectrum of toluene solution of **70-2-2** compound.

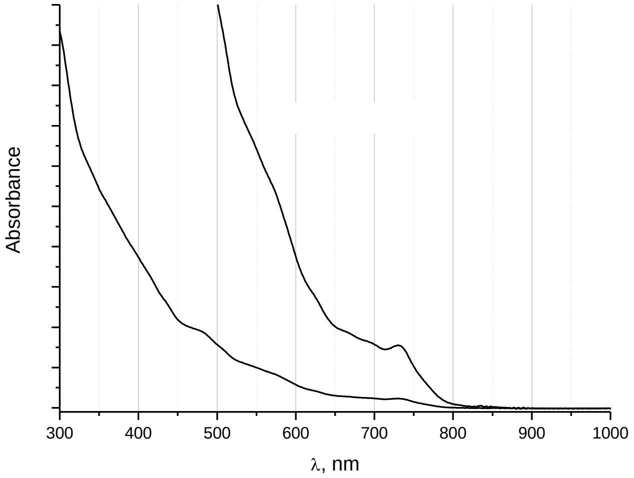

Figure S19. UV-vis spectrum of toluene solution of **70-4-4** compound.

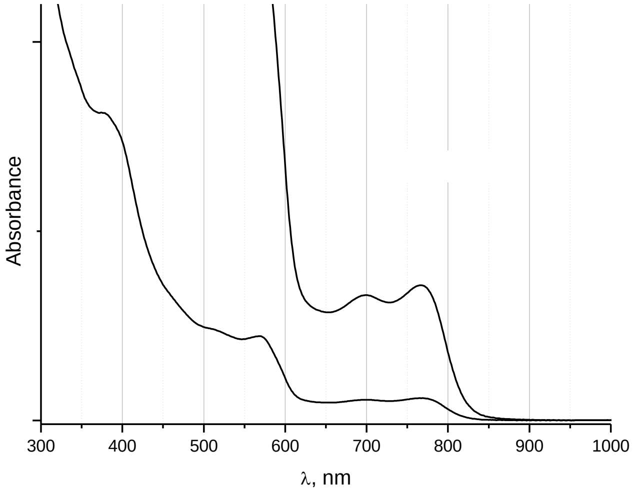

Figure S20. UV-vis spectrum of toluene solution of $C_{70}(i\text{-}C_3F_7)_4$ compound (22.7 min, 10:90 (v:v) toluene:heptane).

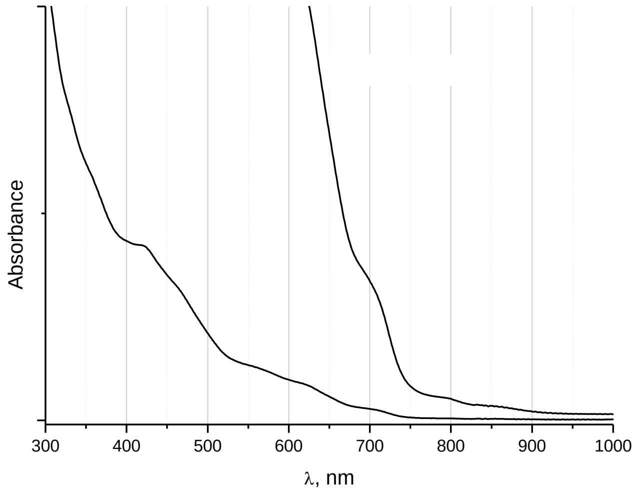

Figure S21. UV-vis spectrum of toluene solution of **70-4-3** compound.

Additional references on the fullerene OPVs and crystal disorder modeling.

OPVs:

Ross, R. B.; Cardona, C. M.; Swain, F. B.; Guldi, D. M.; Sankaranarayanan, S. G.; Van Keuren, E.; Holloway, B. C.; Drees, M. *Adv. Functional Mater.* **2009**, *19*, 2332-2337.
Delgado, J. L.; Bouit, P. A.; Filippone, S.; Herranz, M. A.; Martin, N. *Chem. Commun.*, *46*, 4853-4865.
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Ross, R. B.; Cardona, C. M.; Guldi, D. M.; Sankaranarayanan, S. G.; Reese, M. O.; Kopidakis, N.; Peet, J.; Walker, B.; Bazan, G. C.; Van Keuren, E.; Holloway, B. C.; Drees, M. *Nature Mater.* **2009**, *8*, 208-212.

Crystal disorder modeling:

Deya, A.; Metrangolo, P.; Pilati, T.; Resnati, G.; Terraneo, G.; Wlassics, I. *J. Fluorine Chem.* **2009**, *130*, 816-823