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Lower trifluoromethyl[70]fullerene derivatives: novel structural data and an survey of electronic properties

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ABSTRACT

We revisit a series of trifluoromethylated $C_{70}(CF_3)_n$ compounds with $n = 2–12$ to provide a comprehensive comparative characterization thereof by means of a combination of physico-chemical methods. X-ray diffraction studies, including first structural determinations of the major isomers of $C_{70}(CF_3)_2$, $C_{70}(CF_3)_4$, and the third most abundant isomer of $C_{70}(CF_3)_8$ as co-crystals with octaethylporphyrin Ni(II), produce accurate CF_3 group rotation angles and intergroup F···F distances that enable more reliable ^{19}F NMR signal assignment based on the through-space J_{FF} spin-spin coupling relation to the F···F distances. Cyclic voltammetry measurements were performed in a potential range that covers oxidation on the one end and reduction to tri- or tetraanionic states on the other. It was demonstrated that the CF_3 addition patterns have marked effects on the redox potentials. A consistent set of the experimental HOMO energy values of the $C_{70}(CF_3)_n$ molecules is reported for the first time in complement to the LUMO data, and the both sets of results were found to demonstrate good correlation with quantum-chemical DFT predictions. Most of the compounds exhibit electrochemically reversible one-electron reductions up to trianionic (sometimes even tetraanionic) state, a notable exception being $C_{70}(CF_3)_{10}$ with irreversibility of its very first reduction. Bulk electrolysis of $C_{70}(CF_3)_{12}$ at its 4-th reduction potential identifies CF_3 detachment as the most likely cause of the observed irreversible processes yielding $C_{70}(CF_3)_{11}^-$ anions as was identified by means of MALDI MS.

1. Introduction

Perfluoroalkylated fullerenes constitute the broadest family of fullerene derivatives in terms of compositional and isomeric diversity [1–4]. This diversity makes possible to pick a compound with the desired optical and electronic properties [5–10] and chemical behavior [11–20], and thus to select optimal building blocks for novel functional materials. High thermal and electrochemical stability, processability in both gas and solution phase, tunable band gaps (1.5–2.5 eV), and low lying LUMO levels (from −3.6 to −4.1 eV) suggest promise of perfluoroalkylfullerenes as molecular switches [9,10] and molecular semiconductors with electron conductivity for luminescent and photovoltaic applications [21–25].

Most accessible and best studied perfluoroalkylfullerenes are trifluoromethylated C_{60} and C_{70}. These fullerene derivatives provide attractive libraries of compounds for studying structure-property relationships within a broad range of the degree of derivatization. Remarkably, trifluoromethylation of the most affordable C_{60} fullerene gives, despite its higher symmetry, drastically more complex isomeric mixtures than those with C_{70}. For example, no less than 27 isomers of $C_{60}(CF_3)_{10}$ have been identified, of which 13 have been structurally characterized [4], compared to only 7 known isomers of $C_{70}(CF_3)_{10}$ [1]. Thus, the diversity of $C_{70}(CF_3)_n$ compounds with $n = 2–20$ is advantageously less extensive while still highly representative. Yet $C_{70}(CF_3)_n$ isomers with $n = 2–12$ previously demonstrated less accurate correlation between the first reduction potentials and the DFT LUMO energies [6], than the analogous $C_{60}(CF_3)_n$ compounds [4,5], and the cause of that difference remained unclear.

In order to revisit and rationalize the discrepancies reported for the $C_{70}(CF_3)_n$ molecules, we kept expanding and refining our set of

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data on trifluoromethylated fullerenes. Conveniently, the $C_{70}(CF_3)_n$ compounds in question are available via well-developed and straightforward synthetic and separation protocols [3,26,27]. Additional motivation was due to the lack of direct structural data on some of the key CF_3 derivatives of C_{70} despite a considerable overall progress in XRD characterization of the $C_{70}(CF_3)_n$ compounds. In particular, the structure of such relatively simple molecules as the major isomers of $C_{70}(CF_3)_4$ and $C_{70}(CF_3)_6$ was previously suggested only on the basis of ^{19}F NMR data and quantum chemical calculations [3,6,26].

Here we report the first X-ray crystallography data for the co-crystals of octaethylporphyrin nickel(II) Ni(OEP) with the major isomers of $C_{70}(CF_3)_2$ and $C_{70}(CF_3)_4$ (**2-I** and **4-I**) as with the third most abundant C_1-p^5mp-$C_{70}(CF_3)_8$ isomer (**8-IV**, Fig. 1, right). Those new data not only provide ultimate verification of the previous structural suggestions but also facilitate more reliable assignment of the ^{19}F NMR data [3,26]. We further present electrochemical behaviour of the whole range of lower trifluoromethylfullerenes $C_{70}(CF_3)_n$ with $n = 2–12$ studied by means of cyclic voltammetry. The ten compounds studied are presented in Fig. 1 (left) as Schlegel diagrams that depict the positions of CF_3 groups on the fullerene cage. Compared to previously reported electrochemical data [6], our measurements span a wider range of potentials to encompass tetraanionic states on the one end and first oxidation peaks on the other. Thus, a consistent set of HOMO energy values is reported for the first time in addition to the LUMO levels, and the both sets of data were found to demonstrate fairly good linear correlation with the DFT values.

2. Experimental

2.1. Materials and Methods

All reagents were obtained from commercial suppliers and used without further purification. Solvents were dried by the usual methods and distilled before use. The lowest-locant nomenclature for poly(trifluoromethyl)fullerenes is given according to the IUPAC recommendations [28].

2.2. Synthetic procedures

Synthesis of highly trifluoromethylated [70]fullerenes. The mixture of highly trifluoromethylated [70]fullerenes, $C_{70}(CF_3)_n$, $n = 12–20$, was prepared at the first stage. An excess of CF_3I (P&M-Invest, 98%; ca. 1 mL) was condensed under cooling by liquid nitrogen to a glass tube with fullerene C_{70} (Fullerene-center, 99.8%, 25 mg). Then the tube was sealed and heated in a gradient furnace at 385 °C for 24 h. Two major isomers of $C_{70}(CF_3)_{12}$ were isolated from the prepared mixture by means of HPLC separation (Cosmosil Buckyprep 10 mm I.D. × 25 cm, hexane, 4.6 mL min^{-1}). The retention times are given for Cosmosil Buckyprep 4.6 mm I.D. × 25 cm, hexane, 1 mL min^{-1}; yields were estimated according to integration of HPLC traces.

12-I: ***C_1-p^7mp,p*-1-$C_{70}(CF_3)_{12}$, 1,4,10,19,25,32,41,49,54,60,66,69-$C_{70}(CF_3)_{12}$.** Yield 6%. t_R 5.3 min. UV/VIS (hexane), λ_{max}: 312, 344, 354, 398, 426, 494 nm. MALDI-TOF MS, m/z (%): 1612.2 (8) [$C_{70}(CF_3)_{11}^{-*}$ metastable, {M_1–CF_3}$^{-*}$], 1667.9 (100) [$C_{70}(CF_3)_{12}^-$, M_1^-], 1805.9 (2) [$C_{70}(CF_3)_{14}^-$, M_2^-]. ^{19}F NMR (376 MHz, toluene-d_8, 25 °C, C_6F_6), δ_F: −59.60 (*m*, 9F, $3CF_3$), −60.59 (*m*, 3F, CF_3), −60.90 (*m*, 3F, CF_3), −61.72 (*m*, 6F, CF_3), −62.70 (*m*, 6F, CF_3), −63.29 (*m*, 3F, CF_3), −65.80 (*q*, *J* = 14.9 Hz, 3F, CF_3), −68.72 (*q*, *J* = 9.2 Hz, 3F, CF_3), −69.35 (*q*, *J* = 11.4 Hz, 3F, CF_3), −69.51 (*q*, *J* = 11.4 Hz, 3F, CF_3).

12-II: ***C_1-p^7mp,p*-2-$C_{70}(CF_3)_{12}$, 1,4,10,14,19,25,35,41,49,60,66,69-$C_{70}(CF_3)_{12}$.** Yield 4%. t_R 5.9 min. UV/VIS (hexane), λ_{max}: 312, 358, 396, 420, 476, 530 nm. MALDI-TOF MS, m/z (%):1598.9 (2) [$C_{70}(CF_3)_{11}^-$, {M_1–CF_3}$^-$], 1612.2 (18) [$C_{70}(CF_3)_{11}^{-*}$ metastable, {M_1-CF_3}$^{-*}$], 1667.9 (100) [$C_{70}(CF_3)_{12}^-$, M_1^-], 1684.9 (2) [$C_{70}(CF_3)_{12}OH^-$, M_2^-], 1805.9 (2) [$C_{70}(CF_3)_{14}^-$, M_3^-], 1943.9 (2) [$C_{70}(CF_3)_{16}^-$, M_4^-]. ^{19}F NMR (376 MHz, toluene-d_8, 25 °C, C_6F_6), δ_F: −58.51 (*m*, 3F, CF_3), −59.23 (*m*, 3F, CF_3), −59.72 (*m*, 3F, CF_3), −60.54 (*m*, 3F, CF_3), −61.42 (*m*, 6F, CF_3), −62.70 (*m*, 6F, CF_3), −65.67 (*q*, *J* = 16.0 Hz, 3F, CF_3), −68.63 (*q*, *J* = 10.3 Hz, 3F, CF_3), −69.40 (*q*, *J* = 10.0 Hz, 3F, CF_3), −69.48 (*q*, *J* = 10.0 Hz, 3F, CF_3).

Synthesis of lower trifluoromethylated [70]fullerenes. At the second stage the transalkylation reaction was performed. The obtained mixture of highly trifluoromethylated fullerenes $C_{70}(CF_3)_n$, $n = 12–20$, (40 mg) and pristine fullerene C_{70} (15 mg) were mixed and heated in sealed glass ampoule at 450 °C for 40 h.

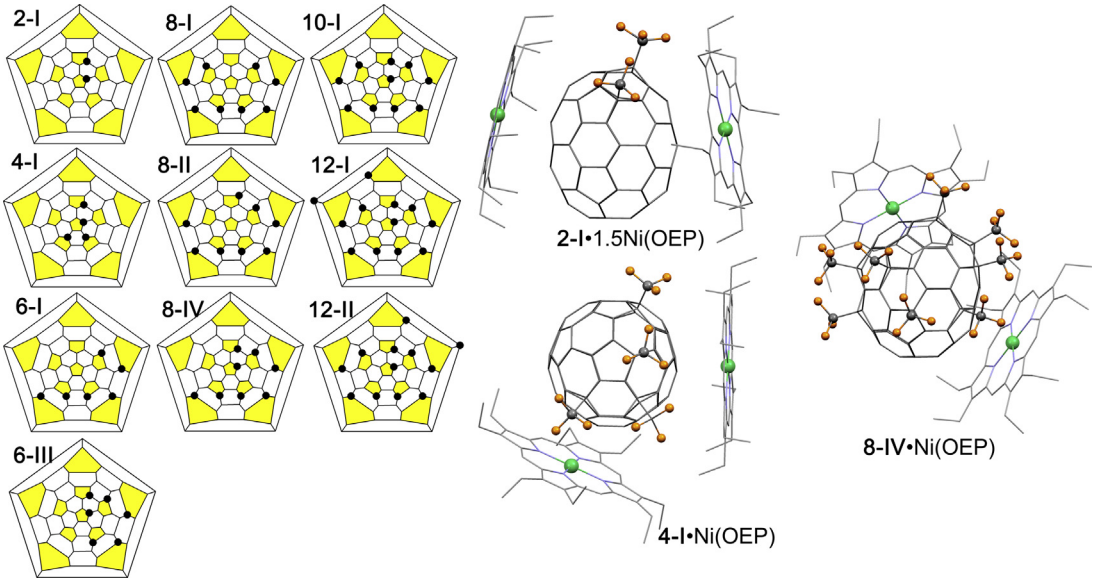

Fig. 1. Schlegel diagrams of $C_{70}(CF_3)_n$, $n = 2–12$ (left) and X-ray structures of the co-crystals of **2-I**, **4-I**, and **8-IV** with Ni(OEP) (right; only the major molecular orientation is shown for **2-I** and **4-I**, hydrogen atoms and solvent molecules are omitted for clarity).