

## Synthesis, structure, and chemistry of the fullerene-based fluorocarbons

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Fullerene-based fluorocarbons, namely polyfluorinated fullerenes and polyperfluoroalkylated fullerenes, are among the most extensively studied polyfunctionalized fullerenes. The synthetic methodology that involves reaction of  $\text{CF}_3\text{I}$  and  $\text{CF}_3\text{COOAg}$  with  $\text{C}_{60}$  and  $\text{C}_{70}$  fullerenes makes possible to prepare and isolate  $\text{C}_{60}(\text{CF}_3)_n$  and  $\text{C}_{70}(\text{CF}_3)_n$  compounds with  $n = 2-20$ . X-ray diffraction studies of these compounds have already resulted in structural determination of  $\text{C}_{60}(\text{CF}_3)_n$  molecules with  $n = 16$  (3 isomers) and 18, as well as  $\text{C}_{70}(\text{CF}_3)_m$  molecules with  $m = 6, 8, 12$  (2 isomers), 14 (4 isomers), 16, and 18. The theoretical calculations have demonstrated that the experimentally obtained isomers are among the most energetically preferable structures, though the absence of many other anticipated isomers in the synthetic mixtures indicates to importance of kinetic factors.

Recently, a new method of preparation of  $\text{CF}_2$ -derivatized fullerenes has been developed, aimed to expand the available range of fullerene-based fluorocarbons. The synthetic methodology comprises thermal decarboxylation of  $\text{CF}_2\text{ClCOONa}$  and cycloaddition of  $:\text{CF}_2$  carbene thus formed to the fullerene cage. Apart from typical products of [2+1]-cycloaddition to the fullerene cage,  $\text{CF}_2$ -derivatives represent a unique example of [6,6]-open cycloaddition as confirmed by  $^{13}\text{C}$  NMR analysis and quantum chemical calculations. The resulting combinations of electron-withdrawing  $\text{CF}_2$  groups with all- $sp^2$  fullerene cage provide improved acceptor properties of the molecules.

Enhanced electron-withdrawing properties, chemical stability against nucleophilic substitution and high solubility in the common organic solvents makes  $\text{CF}_3$ - and  $\text{CF}_2$ -derivatives of fullerenes promising building blocks for light-harvesting systems. Development of such photovoltaic devices requires further functionalization of the fluorinated or fluoroalkylated fullerene molecule with some organic donor systems. One of the most versatile and widespread methods of such functionalization is Bingel reaction with stabilized  $\alpha$ -halocarbanions. Bingel reaction between diethyl bromomalonate and  $\text{C}_{60}(\text{CF}_2)$  in presence of bases has been found to yield a library of products dominated by two isomeric  $\text{C}_{60}(\text{CF}_2)[\text{C}(\text{CO}_2\text{Et})]$  monoadducts. On the contrary, analogous reaction involving  $p^7mp\text{-C}_{70}(\text{CF}_3)_{10}$  leads to the single isomer of  $\text{C}_{70}(\text{CF}_3)_{10}[\text{C}(\text{CO}_2\text{Et})_2]$ . XRD study of the latter compound demonstrates that cycloaddition occurs at the unoccupied pole of the  $p^7mp\text{-C}_{70}(\text{CF}_3)_{10}$  molecule. This unexpected selectivity is shown to have both thermodynamics and kinetic origins.