Fundamental and applied chemistry of fullerene$(CF_3)_n$ compounds

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The observation that fullerenes and their derivatives are powerful electron acceptors has attracted considerable attention because of the potential application of these compounds to problems in energy storage and photovoltaic energy conversion. One of our goals in fullerene science and technology is to prepare and study series of fullerene$(X)_n$ derivatives with as wide a range of electron accepting properties as possible. Only in this way can we completely understand how different X groups, different values of n (for a given X), and different addition patterns (for a given X and n) affect the frontier orbitals of those derivatives, the orbitals that are directly involved in electrochemical and photoelectrochemical processes.

The X-ray structures of more than 25 hollow fullerene$(CF_3)_n$ compounds (n = 2–18) have appeared since mid-2005, and the addition patterns of more than 20 others have been deduced by spectroscopy, other physicochemical methods, and DFT calculations. This wealth of information makes fullerene$(CF_3)_n$ derivatives the largest class of well-characterized fullerene$(X)_n$ compounds. No other substituent X that forms one 2c-2e$^-$ bond with one cage C atom is reported to form even half as many well-characterized derivatives.

The addition patterns of fullerene$(CF_3)_n$ derivatives prepared at or above 400°C, which are controlled predominantly but not exclusively by thermodynamic considerations, will be analyzed in light of recent computational results. In addition, we will present an analysis of new physicochemical and computational results for 21 $C_{60}(CF_3)_n$ derivatives and new computational results for more than 70 other $C_{60}(X)_n$ compounds with similar addition patterns, results that bear directly on the nature of the frontier orbitals of these potentially important molecules.