

Theoretical Study of fluorination of fullerenes and carbon nanotubes

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In recent years, there has been a significant interest in fluorine derivatives of C₆₀. They are promising synthons as enhanced acceptors in donor-acceptors diads, due to their specific characteristics (good solubility, high reactivity towards nucleophiles and enhanced dienophilicity of the unsubstituted part of the cage, resulting from electron withdrawal by fluorine atoms).^[1]

We present a systematic study of addition patterns occurring upon fluorination of C₆₀, from C₆₀ to C₆₀F₆₀, using the program SACHA^[2]. This increments the number of fluorine addends, tests all available addition sites within a given cut-off radius, and selects the most energetically stable structure for further addition on the basis of full AM1 optimisations for every isomer. The lowest energy structures are optimised using HF/3-21G.

A number of distinct addition patterns are predicted (octahedral, *S*, *T*, and mixed *ST*), leading both to experimentally observed C₆₀F_n isomers (notably n=18,20,36,48), as well as to isomers not previously described in the literature (notably n=30,36,48). Lowest energy F₂ addition always occurs at the shortest available C-C bond.

The main addition routes are also analysed for C₆₀F_{2n} isomers, using *ab initio* global and local aromaticity calculations. For this, magnetisability and NICS calculations have been carried out at HF/3-21G level of theory. We show the possibility of using NICS to predict the next preferential addition site, leading to the above-described addition routes.

Fluorination of carbon nanotubes shows distinct behavioural differences depending on the fluorination temperature. Below 200-250°C fluorination is semi-ionic, above this temperature the bonding is covalent leading to a maximum C₂F coverage. We study fluorination of curved graphene surfaces using large hydrogen terminated clusters. Density functional calculations using AIMPRO are used to determine preferential binding sites for F₂ and migration barriers. It is found that nearest neighbour F₂ bonding leads to asymmetric C-F bonds and this is proposed as the source of the semi-ionic behaviour. F is found to migrate over nanotube surfaces with a migration barrier of 1.2eV, suggesting that the observed change in behaviour corresponds to the temperature at which fluorine becomes mobile on the nanotube surface. We also examine the effect of water on the binding and migration of F on nanotube surfaces.

Using a range of theoretical techniques we examine high fluorine coverage on armchair and zig-zag nanotubes, and propose a mechanism for experimental STM observed fluorine “banding” around the tube axis based on concurrent axial line growth.
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[1] R. Taylor *Chem. Eur. J.* 7, 4074-4083 (2001).

[2] C. P. Ewels, G. Van Lier, M. Amat, in preparation (2004).