

Theoretical study of CNTs functionalized by fluorine and chlorine

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Functionalization of carbon nanotubes (CNTs) via chemical attachment of atoms, molecules or molecular groups has attracted much attention, as it offers a prospective approach towards modification of the electronic, chemical, optical and mechanic properties of CNTs. Besides, CNTs can be used as starting material for bulk synthesis of graphene nanoribbons (GNRs), another promising system for nanoelectronics, by means of axial unzipping [1]. To date, studies of polyfunctionalized CNTs are mostly limited to the theoretical realm, which is due to the complexity of experimentally obtainable mixtures. Unfortunately, most of the said theoretical studies consider addition motives that are not supported by any kinetic or thermodynamic arguments.

The present quantum chemical study follows the sequential functionalization approach based on energetic criteria, as suggested by the authors of [2]. It is aimed at determining the most preferable arrangement of fluorine and chlorine atoms chemisorbed on a CNT's backbone. The choice of fluorine as functionalizing addend is motivated by high stability of carbon-fluorine bonds, which makes fluorinated CNTs a reliable test case for future experimental verification of the theoretical results. Chlorine addends are more interesting with regard to unzipping CNTs into GNRs analogously to the theoretical suggestions made in [3] for hydrogenated CNTs. Chlorine addends may be even more efficient as promoters of unzipping due to lower C-Cl bond energy, which facilitates the necessary sigmatropic rearrangements. Model systems considered in this work are based on the (6,6) and (12,0) CNTs. Quantum chemical calculations were performed at the DFT level of theory using the PRIRODA package (PBE exchange correlation functional, TZ2P basis set) [4].

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