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Unraveling the Reactivity of Semiconducting Chiral Carbon Nanotubes through Finite-Length Models Based on Clar Sextet Theory

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Finite-length models of chiral semiconducting carbon nanotubes based on Clar sextet theory allowed carrying out accurate calculations, performed by application of gradient-corrected density functional theory, on the energetic of sidewall reactions. In particular, we analyzed the addition of atomic fluorine and carbene (CH_2) to (6,4) and (6,5) nanotubes, finding excellent convergence of reaction energies with respect to the model length and good agreement with literature data. Our study demonstrates the importance of using models of carbon nanotubes based on chemical considerations to evaluate consistently the electronic and reactive properties of the sidewall.

I. Introduction

In the past few years, the properties of carbon nanotubes (CNTs) have been deeply investigated¹ in view of their potential use in several applications of nanotechnology or in nanostructured devices.² One of the most interesting aspects of both basic and applied research on CNTs concerns their functionalization with external agents.³ Covalent functionalization of CNTs has been successfully applied in several cases,⁴ allowing for example the selective separation of CNTs of different chiralities on the basis of specific reactivities.⁵

Concurrently to experimental studies, theoretical investigation techniques have also been applied with success, in recent years, to the study of CNTs functionalization.⁶ In particular, methods based on density functional theory (DFT) have been widely applied to the study of the chemistry of CNTs. However, the peculiarities of materials based on CNTs pose significant problems to their computational modeling and to the comparison of computed properties with the experiments.⁷ A particularly critical issue is represented by the definition of proper models for the CNTs, which should ideally be constituted by a small number of atoms and, at the same time, be able to provide a quantitative agreement with the experimental data. This problem is especially evident in the simulation of CNT properties related to the details of their electronic structure, as in the case of reactivity.

A convenient approach to the modeling of CNTs is based on the use of finite-length models, as it has been recently demonstrated by previous work.⁸ It has also been shown that finite-length models of CNTs should be carefully constructed to obtain suitable representatives of their real (quasi-one-dimensional) counterparts.⁹ Indeed, the complex electronic features of the hexagonal carbon atom network are properly described by a correct representation of the π -conjugation pattern and aromatic properties of the sidewall, analogously to the case of polycyclic aromatic hydrocarbons.¹⁰ These problems have been recently addressed by several research groups, which suggested the use of Clar sextet theory¹¹ to study the electronic properties of CNTs.^{12,13} In previous work, we applied finite-length models based on Clar sextet theory to investigations on

the electronic properties of zigzag, armchair, and chiral CNTs and graphene nanoribbons.^{14,15} Notably, application of models defined in terms of finite-length Clar clusters (FLCCs)¹⁴ resulted in a consistent assessment of their electronic properties, calculated at the DFT level, and in remarkable computational advantages.¹⁶

In this paper we analyze the possibility of performing DFT calculations on FLCC models to unravel the reactivity of (6,5) and (6,4) CNTs toward different functionalization agents. Namely, addition of fluorine atom and carbene (CH_2) was taken into account. Addition of fluorine to CNTs was first reported in 1998¹⁷ and is nowadays considered one of the most effective ways both for sidewall functionalization¹⁸ and for obtaining suitable precursors for further functionalization reactions.¹⁹ Due to the interest in such reaction, fluorination of the sidewall was also considered in recent theoretical works,^{9,20–23} most of which, however, took into account only zigzag or armchair CNTs. Addition of carbenes is another effective route to sidewall functionalization and was also investigated in both experimental²⁴ and theoretical^{9,25–27} works. However, theoretical calculations concerning addition reactions to the sidewall of chiral CNTs have been only scarcely considered, due to the aforementioned difficulties in modeling efficiently nanotubes of any stereochemistry. Moreover, the two reactions at the sidewall involving fluorine and CH_2 , respectively, differ in the topology of the addition. Hence, these two examples constitute ideal cases to benchmark the performance of our approach. Although in the present study we focus on purely energetic factors, our approach can in principle be extended to the analysis of mechanistic aspects involved in addition reactions, such as transition-state calculations.

The case of the (6,5) and (6,4) chiralities analyzed here can be considered as representative of the more general case of semiconducting chiral CNTs with different values of the parameter $R = \text{mod}(n-m, 3)$ ($R = 1$ and $R = 2$ for the (6,5) and (6,4) CNTs, respectively), which accounts for the conducting behavior of CNTs. Our results confirm the possibility of using CNT models based on FLCCs to describe correctly the electronic properties of semiconducting chiral CNTs and, consequently, their reactivity.

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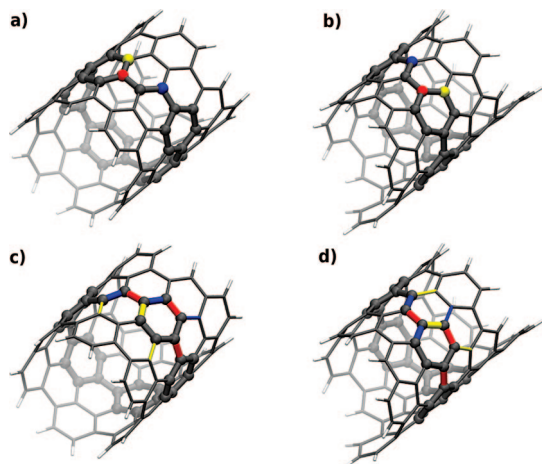


Figure 1. FLCC CNT models (three unit cells shown) and adsorption sites for the interaction with F and CH₂: (a) F@ (6,5); (b) F@ (6,4); (c) CH₂@ (6,5); (d) CH₂@ (6,4). Atoms in ball-and-sticks highlight the Clar unit cell. In panels c and d, same colors correspond to equivalent sites for the infinite nanotubes.

II. Computational Details

Initial geometries for finite-length models of (6,4) and (6,5) CNTs were taken from ref 14. For the evaluation of binding energies, on-top and bridging adsorption sites for fluorine and CH₂, respectively, were taken into account, as shown in Figure 1. Such coordination modes lead to the most stable chemisorbed adducts on zigzag and armchair CNTs, as suggested by previous work.^{9,20–27} All calculations were performed by applying the hybrid B3LYP²⁷ functional as implemented in the Gaussian03 program package.²⁹ Energies and optimized geometries of all systems were evaluated with the 3-21G basis set. Frequency calculations performed on optimized structures of representative systems yielded only positive values (see Supporting Information), thus confirming the nature of optimized geometries as local energy minima.

Calculations on adducts were performed in the spin-unrestricted formalism for the addition of fluorine, by assigning the doublet state to the wave function and in the spin-restricted formalism for the addition of CH₂. Calculations on reagents were carried out by assigning the doublet state to fluorine and the triplet state to CH₂, similarly to previous work,²⁵ and singlet states to all CNT models. All systems were considered as neutral species.

Binding energies were evaluated as

$$BE = E_{(F,CH_2)@CNT} - (E_{CNT} + E_{(F,CH_2)}) \quad (1)$$

where $E_{(F,CH_2)@CNT}$ is the energy of the system after reaction with F or CH₂, respectively, E_{CNT} is the energy of the isolated CNT, and $E_{(F,CH_2)}$ is the energy of isolated F or CH₂ species, respectively. Binding energies were corrected for the basis set superposition error (BSSE) through application of the counterpoise formalism.³⁰

We also checked the effect of a larger basis set on reaction energies. To this end, calibration calculations for the reaction of fluorine and CH₂ on selected sites of the (6,5) CNT were performed by evaluating energies with the 6-311G(d) basis set of species optimized with the 3-21G basis (see Supporting Information). Although the 6-311G(d) basis set is known to yield a better representation of the electronic structure and energetic of π -conjugated systems than smaller bases,³¹ the basic aspects of the discussion are substantially unchanged. Indeed, with both basis sets we found similar convergence of reaction energies

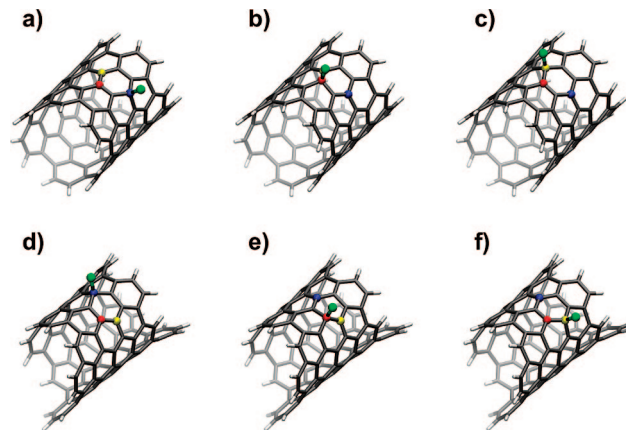


Figure 2. Optimized geometries for structures resulting from the addition of fluorine to FLCC models of (6,5) (a–c) and (6,4) (d–f) CNTs constituted by three Clar cells. Adsorption sites are color-coded as in Figure 1. Fluorine atoms are highlighted in green.

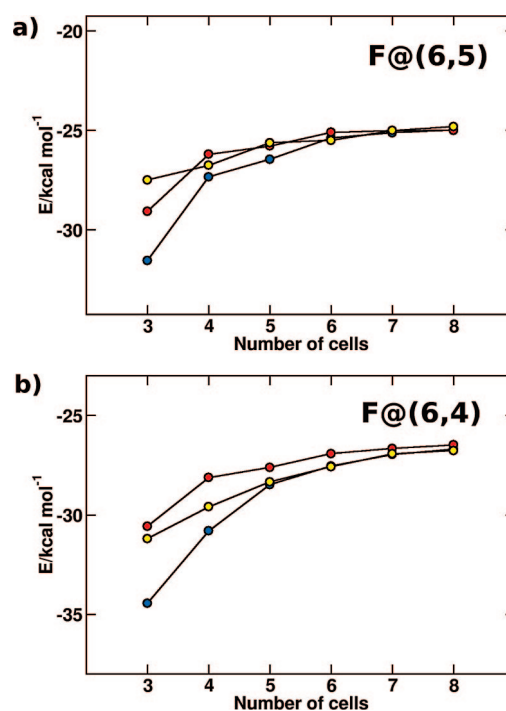


Figure 3. Binding energies for the addition of F to FLCC models of (6,5) and (6,4) CNTs: (a) F@ (6,5); (b) F@ (6,4). Colors code different reaction sites according to the scheme in Figure 1.

with the cluster length, thus supporting the validity of the proposed models. Calculations were performed at the Nano-Cluster computing facility, INSTM, Italy.

III. Results and Discussion

In an ideal (infinite) CNT, all carbon atoms are equivalent. Accordingly, the interaction energy for a single atom chemisorbed on top of a carbon atom of a finite-length model of CNTs should converge to a unique value with the model length, depending only on the theoretical level used in calculations.

Optimized geometries of fluorinated systems, for models constituted of three Clar cells, are shown in Figure 2. In Figure 3 the computed binding energy of fluorine to the sites of Figure 1 and its dependence on the FLCC model size is plotted. Indeed, very short-sized FLCC models exhibit a strong dependence of fluorination energy on the adsorption site considered. This evidences the different bonding situation for the coordinating

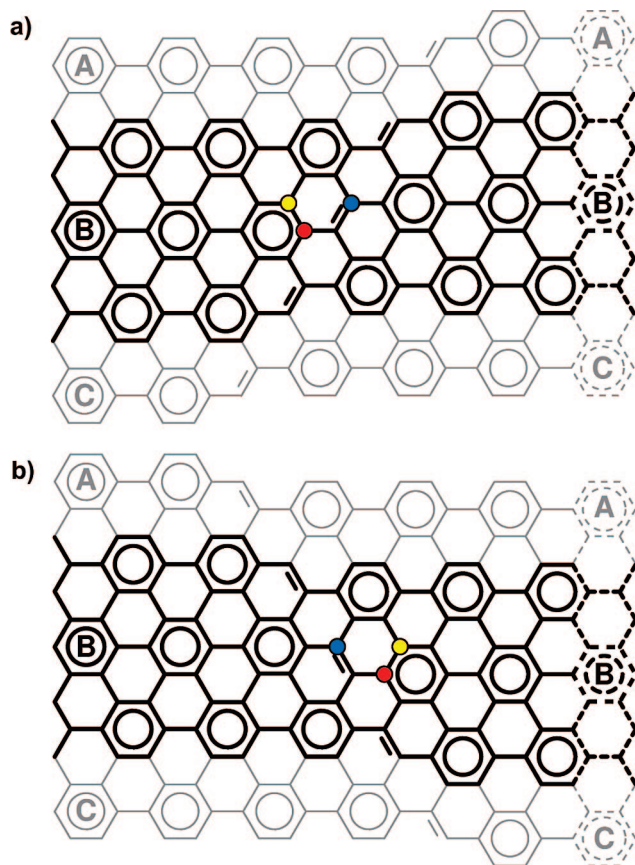


Figure 4. Planar schemes and Clar representation of reaction sites for the addition of fluorine to (a) (6,5) and (b) (6,4) CNTs.

site (belonging to rings with benzenoid or double bond character) induced by edge effects and also indicates that the electronic structure of short FLCCs matches the valence-bond (VB) representation provided by Clar's theory,¹⁴ as shown in Figure 4. As expected, double bond sites (sites colored in blue in Figures 1–4) are more reactive toward fluorination than benzenoid sites (sites in red in Figures 1–4). However, for longer FLCC models fluorine binding energies converge to the value of 25 kcal mol⁻¹ for (6,5) CNTs and 27 kcal mol⁻¹ for (6,4) CNTs, respectively, within a deviation of less than 1 kcal mol⁻¹ for models constituted with 6 Clar unit cells (see Figure 3). The (6,4) CNT is slightly more reactive than the (6,5) CNT due to a more favorable orientation of C–C bonds.⁷ Nonetheless, the convergence behavior is similar for both chiralities considered.

Hence, our results indicate the fluorination of both the (6,5) and (6,4) CNTs as energetically favorable, with a reactivity similar to that of a semiconducting (10,0) CNT²¹ and lower than that of a metallic (5,5) CNT,⁹ in line with the experiments.⁵ Although a larger basis set provides fluorination energies around 10 kcal mol⁻¹ larger than with the 3-21G basis (see Supporting Information), we should note that our study focuses on the convergence of binding energies with the model size at a given theoretical level.

In the case of reaction with the CH₂ species, ideal infinite (*n,m*) CNTs exhibit three intrinsically distinct adsorption sites, depending on the orientation of the C–C bond involved in the chemisorption with respect to the CNT axis.

Optimized structures of CH₂@(CNT) adducts, for models constituted of three Clar cells, are shown in Figure 5, whereas Figure 6 shows the computed reaction energies of CH₂ to the sites of Figure 1 and their dependence from the FLCC model size. Analogously to the case of fluorination, the reaction energy

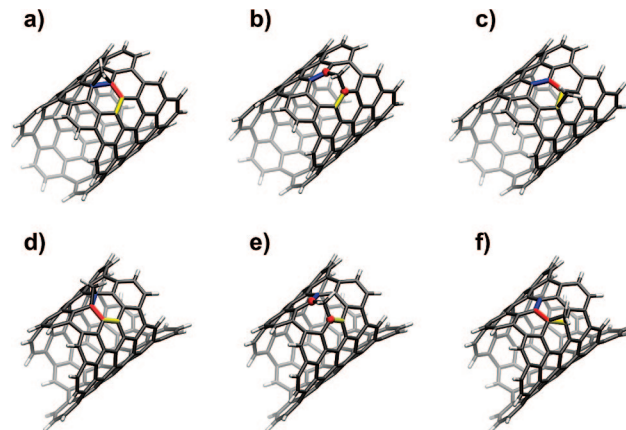


Figure 5. Optimized geometries for structures resulting from the addition of CH₂ to FLCC models of (6,5) (a–c) and (6,4) (d–f) CNTs constituted by three Clar cells. Adsorption sites are color-coded as in Figure 1.

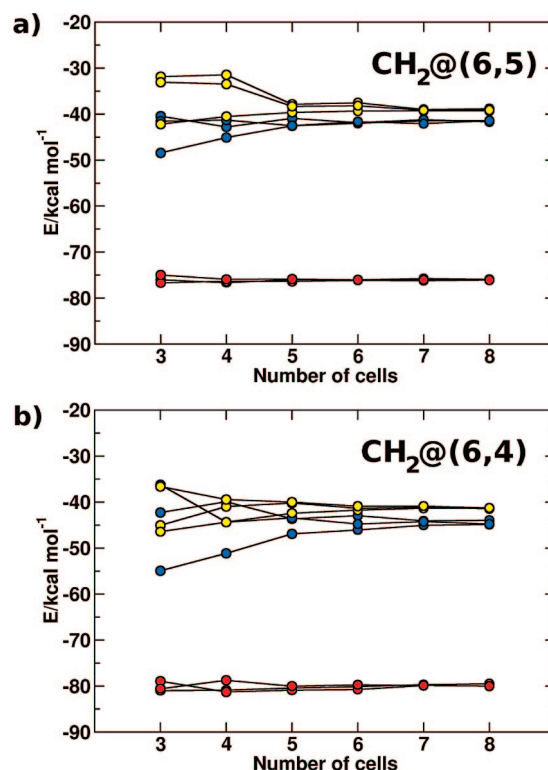


Figure 6. Binding energies for the addition of CH₂ to FLCC models of (6,4) and (6,5) CNTs: (a) CH₂@(6,5); (b) CH₂@(6,4). Colors code different reaction sites according to the scheme in Figure 1.

for CH₂ addition for short-sized models depends strongly on the adsorption site considered. This arises from both the intrinsic differences mentioned above, to be ascribed to the C–C orientation, and from the different electronic situation, as described by the Clar representation of the CNT model (see Figure 7). However, binding energies for CH₂ converge very quickly with respect to the model length for both (6,5) and (6,4) CNTs. Namely, in both cases binding energies converge to three distinct values (39, 41, and 76 kcal mol⁻¹ for (6,5) CNTs and 41, 44, and 80 kcal mol⁻¹ for (6,4) CNTs, respectively), reflecting the different nature of the C–C adsorption sites.

For reaction toward CH₂, convergence is achieved within less than 2 kcal mol⁻¹ for FLCC models constituted of 5 unit cells. In agreement with previous studies,^{7,9,25} reaction of CH₂ on C–C bonds with orientation close to the nanotubes axis results in

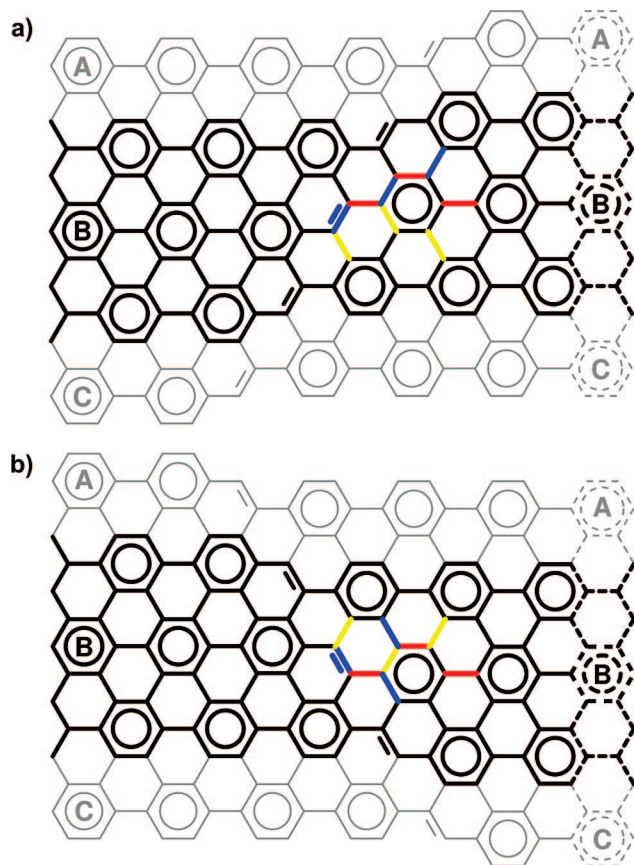


Figure 7. Planar schemes and Clar representation of reaction sites for the addition of CH_2 to (a) (6,5) and (b) (6,4) CNTs.

cycloaddition adducts (sites in blue and in yellow in Figures 5–7), whereas reaction on C–C bonds with a larger mechanical strain (sites in red in Figures 5–7) leads to the sidewall opening (see Figure 5b,e) and, consequently, to larger addition energies. The computed binding energies result for sidewall-opening reactions is only 10 kcal mol^{-1} lower than those obtained by Bettinger for a metallic (5,5) nanotube.⁹ Therefore, the difference between reaction energies for distinct sites of the same nanotube can be larger than the difference between reaction energies for analogous sites of different nanotubes with a comparable diameter. This points to the relevance of local effects in determining binding energies for reactions which do not alter consistently the overall π -electron system of the pristine nanotube, as previously observed.^{16,26,27}

The convergence of reaction energies with the model length reflects the fact that, with an increase in the cluster size, different VB representations of the sidewall become energetically similar and tend to mix up together. Therefore, the local electronic properties of sites which differ in the VB representation of the sidewall, but are topologically equivalent in the infinite nanotube, tend to converge with the model length. The analogy between FLCC models and the VB representation of the sidewall guarantees the consistency of the electronic properties of CNT clusters with those of ideal (infinite) systems and ensures fast convergence to the asymptotic value.

It is worth noting that binding energies for addition of CH_2 converge much better with the model length with respect to the case of fluorine atom. This can be ascribed to the drastic change in the electronic structure induced by the adsorption of a fluorine atom, which leads to a spin-doublet state for the chemisorbed adduct. The situation is depicted in Figure 8, which shows plots for the difference between highest-occupied mo-

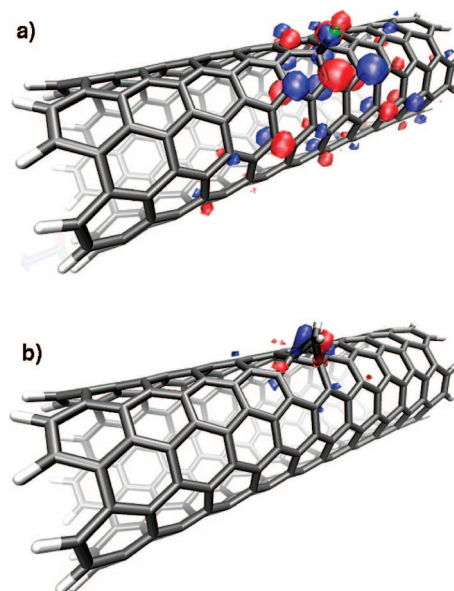


Figure 8. Plots of the difference between highest occupied molecular orbital (HOMO) isosurfaces ($0.02 \text{ e}\text{\AA}^3$) of the FLCC model (7 Clar cells) for the (6,5) CNT before and after functionalization with (a) fluorine and (b) CH_2 .

lecular orbital (HOMO) isosurfaces of the FLCC model for the (6,5) CNT before and after functionalization with fluorine (see Figure 2b) and CH_2 (see Figure 5b), respectively. As shown in Figure 8a, chemisorption of fluorine leads to dramatic changes in the electronic density of frontier orbitals. Inversely, chemisorption of CH_2 (see Figure 8b) induces more local effects, leaving the electronic structure of the pristine nanotube substantially unaltered. In terms of VB representations, the bonding pattern of the pristine FLCC model is strongly affected by fluorine adsorption which, consequently, changes the overall aromatic properties, as already pointed out by Bettinger.⁹ Inversely, reaction of CH_2 on a C–C bond at the sidewall induces practically only local modifications, due to the formation of new carbon–carbon bonds which do not affect remarkably the bonding situation at the sidewall.²⁶ Hence, reaction energies for CH_2 are expected to depend more on local effects and, consequently, are less affected by the size of finite-length models.

IV. Conclusions

In summary, FLCC models allow one to describe quantitatively the reactivity of semiconducting chiral CNTs, as evidenced in the cases of reaction of fluorine and CH_2 with (6,5) and (6,4) CNTs. However, the chemical considerations behind the definition of the computational models allow one to conclude that the FLCC approach can in principle be applied to other reactions at the sidewall and to different chiralities. Our results indicate both reactions as thermodynamically feasible, with addition energies typically lower with respect to the case of metallic CNTs of similar diameter, in agreement with previous calculations. Most notably, much larger binding energies are observed for addition of CH_2 to sites where the reaction leads to sidewall opening. Therefore, the locality of the addition is a crucial factor in determining the overall reaction energy. The information obtained by theoretical calculations can be used to design experimental processes for selective functionalization of CNTs and to engineer their electronic properties.

It is worth mentioning that calculations on FLCC models of chiral CNTs are computationally much less demanding with

respect to the use of periodic or finite-length models based on the periodically translated unit cell. Work is in progress to extend the applicability of the FLCC approach to other cases of interest in the study of functionalized carbon nanotubes.

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Supporting Information Available: Comparison between results obtained with the 3-21G and 6-311G(d) basis sets, binding energies for all reactions discussed in the text, optimized geometries of selected structures in .xyz format, and normal mode frequencies for selected structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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