Smooth and Jump-like Metal-Dielectric Transitions in Single-Walled Carbon Nanotubes under Functionalization

Stas M. Avdoshenko,[†,]* Ilya N. Ioffe,[‡,§,]* and Lev N. Sidorov[§]

[†]Institute for Materials Science and Max Bergmann Center of Biomaterials, Dresden University of Technology, D-01062 Dresden, Germany, [‡]Humboldt Universität zu Berlin, Institut für Chemie, Brook-Taylor-Str.2, D-12489 Berlin, Germany, and [§]Chemistry Department, Moscow State University, Leninskie Gory, 119992 Moscow, Russia

ABSTRACT We examine at the DFT level of theory the topology of side wall functionalization of the (5,5)metallic single-wall carbon nanotube (CNT) with carbenes ($>CX_2$) and its effect on electronic properties of the system. It is demonstrated that specific substructures/topology known to stabilize functionalized fullerene molecules can play the same role in CNTs, as well. Upon deepening of functionalization, "uniformity" of addition motives and related continuous changes in properties transform into regular addition patterns with isolated aromatic islands on the nanotube backbone that give rise to jump-like changes in electronic structure.

T he coming several years may see a new major step toward implementation of molecular circuits. Presently, many expectations are associated with carbon nanostructures. Their unique electronic properties and availability of any desirable dimensionality—from discrete fullerene and graphene flakes through 1D carbon nanotubes (CNTs) to large 2D graphene sheets and 3D graphite—are expected to fulfill the breadth of needs of nanoscale technology rather than a graphene showing promising properties for further electronics.[1−4] Especially versatile are carbon nanotubes with their topology (*i.e.*, chirality) dependent electronic structure.

It is well-known that CNTs are either metallic or semiconducting materials according to their chirality type.[5,6] Moreover, experiment and theory agree on the sensitivity of their electronic properties to mechanical deformations[7,8] or exposure to chemically active atmosphere.[9−11] This makes technological applicability of CNTs even more diverse. Formally speaking, they may cover almost all needs in the chips industry: the metallic CNTs may serve as circuit interconnects[12] and semiconductor CNTs as FET interfaces. An important task arising in this respect is to develop reliable techniques of stable chemical functionalization of CNTs, in order to achieve even fur-

ther flexibility *via* fine-tuning of electronic properties through the effects of addends. To date, studies of polyfunctionalized CNTs (PFCNTs) are mostly limited to the theoretical realm,[13−19] which is due to the complexity of experimentally obtainable mixtures.

An obvious intuitive idea corroborated by these theoretical results is that functionalization of CNTs provides means of band structure engineering. Unfortunately, most of the said theoretical studies deal with poorly justified addition motives that are not supported by any kinetic or thermodynamic arguments. In the present paper, we suggest a model of sequential functionalization of CNTs based on energetic criteria and involving our knowledge of derivatization of fullerenes. Changes in the band structure as incurred by progressive attachment of addends are traced. Additionally, we show how the regular patterns of (quasi)planar isolated aromatic fragments, which are known in halogenated fullerenes such as $C_{60}F_{20}$,[20] $C_{60}F_{36}$,[21] and $C_{60}Cl_{30}$[22] and expected in deeply functionalized CNTs, provide stable structures with properties of quantum dot array.

RESULTS AND DISCUSSION

Object Choice. Recent practice of the silicon-based FET technology already scratches the 20 nm level, so any alternative CNT-based devices must be of further smaller size to become competitive. This miniaturization trend will ultimately shift both physical and chemical properties of the respective short CNT segments toward those of discrete fullerene molecules rather than 1D periodic material. Functionalization of such mini-CNTs will be, accordingly, describable not as quasi-uniform and stochastic but as driven by certain thermodynamic
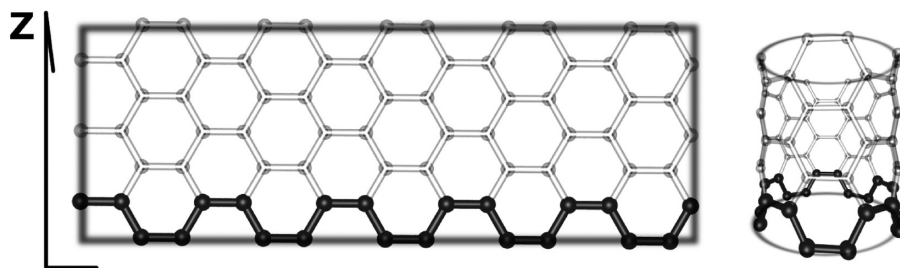
Figure 1. Two-dimensional projection of the supercell of the (5,5)CNT used in periodical calculations with a smaller unit cell highlighted.

and kinetic factors in some regular way. One could expect, for example, that at some point stable isolated aromatic motifs may emerge, similar to those observed in $C_{60}F_{20}$, $C_{60}F_{36}$, $C_{60}Cl_{30}$, as well as higher fullerene derivatives.[23] The already quasi-discrete electronic spectra of such structures will be a function of the type and particular arrangements of addends.[24,25]

For our study, we selected carbene addends that may be of special interest according to some recent reports.[26,27] They demonstrate quite a flexibility in switching between closed cyclopropane and open bridging conformations that are characterized by sufficiently different electronic properties.[27] As a backbone, we consider the (5,5)CNT as the smallest and simplest metallic tube among those not overstrained sterically. By functionalizing this metallic nanotube sensitive to addend attachment, it is theoretically possible to cover a wide range of band gaps starting from the zero gap in the pristine CNT.

While the fullerene derivatives are usually presented as Schlegel diagrams, their 2D projections,[28] we will use 2D unfoldings for nanotube segments, as shown in Figure 1. In this figure, a supercell of the (5,5)CNT used for periodic calculations is shown, and a unit cell is highlighted with black. The choice of the supercell will be discussed in more detail below.

Distance of Correlation in Polyaddition to a Nanotube. In polyfunctionalized CNTs, like in many classes of fullerene derivatives, one could expect rich isomerism. Hence, the primary task while studying functionalization is to rationalize the most probable pathways favored thermodynamically or kinetically. Apparently, at a certain distance, which may be called "distance of correlation", two addends will lose any appreciable mutual influence. Therefore, a question arises, whether addition of two (or more) groups within this distance can be more favorable than their independent addition at larger distances. In the case of a positive answer, one may expect "condensation" of addends around the primarily formed first addition centers. In the opposite case, one can initially expect independent addition to the sites spaced by the said distance of correlation or larger and further slower population of the nanotube segments thus delimited by the first addends following several competitive pathways. The difficulties of the experimentalists in achieving regular addition patterns[18,30] may be indicative of this latter scenario.

Indeed, our calculations for CF_2 addends confirm that distant addition of the two groups is much more favorable. In Figure 2, we provide an energy map for various relative locations of two addends. First of all, one can see a drastic difference between the two different types of the nanotube C−C bonds. Addition to the
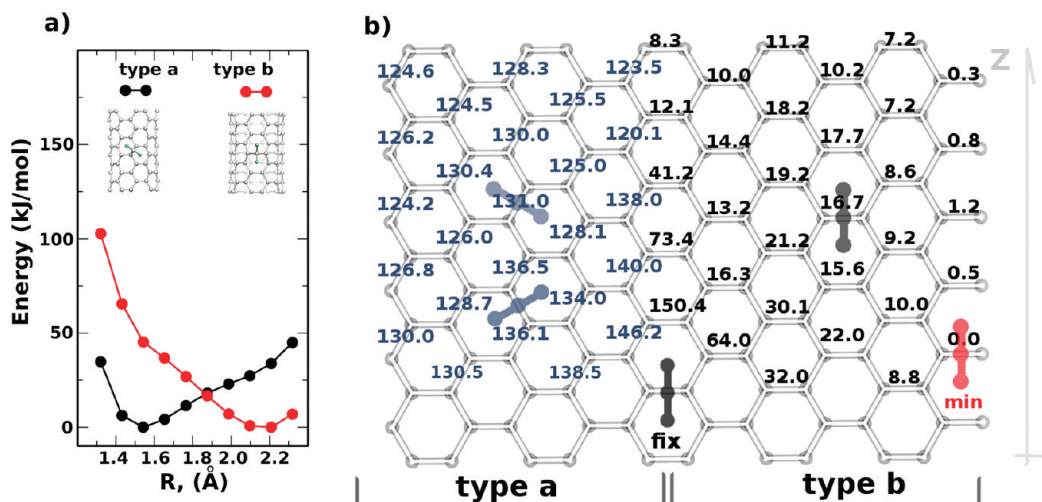

Figure 2. (a) Potential energy profile for stretching of CF_2-functionalized bonds of types "a" and "b". (b) Relative energy (kJ/mol) map for various positions of the second attached group with respect to the fixed first one. The results for the second subclass of type a bonds are almost identical and are omitted for the reasons of clarity.

bonds perpendicular to the nanotube axis (type b) appears to be *ca.* 120 kJ/mol more favorable than addition to those with nonzero longitudinal projection (type a). This clearly reflects much higher strains in the most curved perpendicular cross section of the nanotube. Thus, initial stages of CF_2 addition can involve only the perpendicular bonds of the (5,5)CNT in question and, more generally, the bonds with the least projection on the nanotube axis in the other chirality types of CNTs. Additional consequence of stronger steric strains in the perpendicular direction is open bridging conformations of the "type a" CF_2 addends at least as far as their number remains low. In addition to preservation of the sp^2 conjugation,[29] this bond opening in the nanotube backbone results in favorable decrease of its local effective curvature. On the contrary, addends of "type b" tend to form closed cyclopropane conformations. Interestingly, the respective potential energy minima turn out to be much more pronounced than that previously reported for $C_{60}CF_2$[26,27] (see Figure 2a). Thus, open and closed conformations in the CF_2-functionalized (5,5)CNT are much less flexible, and one cannot expect any dynamic open−close equilibrium. However, as will be demonstrated below, close attachment of two CF_2 addends may sometimes result in a shift of the potential energy minimum from open to closed geometry.

Second, the most energetically favorable is addition of the second group at the very opposite side of the nanotube wall with respect to the first one. Addition on the same side (*i.e.*, along a generatrix of a nanotube cylinder) remains considerably less stable until the spacing between the two groups reaches 4−5 hexagons, which naturaly defines the distance of correlation in question. Thus, contrary to fullerenes where more thermodynamically preferable is compact addition and, accordingly, maximal preservation of the original π-system, (5,5)CNT prefers remote distribution of steric defects to their concentration. Remote and uncorrelated initial addition of the first addends and availability of multiple isoenergetic positions leave space only for some general ideas about the most probable addition subpatterns. That is why predefined geometries proposed in some theoretical studies[14,17] may be a bit too speculative, and the respective band structure calculations may be an oversimplification because of possible loss of translational symmetry in real-life systems. Such calculations could be sensible only in the case of weaker dependence of the band structure on particular addition motifs than on the average addition density. Therefore, there directly emerges a task of investigating the said dependence.

Effect of Addition Motifs on the Band Structure. The calculations of the band structure were based on a supercell shown in Figure 1. Though the length of the said cell equals only three hexagons, which is less than the above determined distance of correlation, consideration of less dense initial addition based on larger, say,

5-hexagon, supercells does not reveal appreciable band distortions.

Initially, we considered more thermodynamically preferable addition patterns with CF_2 addends attached to the type b bonds of Figure 2. The examples of unit cells of such systems are given in Figure 3. As one can see, in all cases, the addends form open conformations thus reducing connectivity of the π-system but without withdrawal of CNT atoms from it. As a result, sometimes the band gap even does not emerge, that is, the system remains metallic; in other cases, the gap develops but stays within 0.5 eV. Interestingly, there is no clear correlation between the width of the gap and the number of addends: in particular, addition density of one CF_2 group per supercell provides a semiconducting system, while with 2−3 groups, it is again essentially metallic.

For comparison, we considered some mixed addition patterns that are less energetically preferable but still acceptable from the kinetic point of view. Some examples of such patterns with both type a and type b addition involved are shown in Figure 4. Here we see some manifestations of interactions of the adjacent groups. Whereas the type a groups always form closed cyclopropane conformations, type b addends are now not necessarily open. Their conformation depends on the particular system and even may not correlate with the local surrounding of the group. The band gap values for these mixed addition patterns are generally larger than in the pure type b case and may exceed 1.0 eV even with three addends per supercell. Again, they do not depend monotonously on the addition density, but the general trend of their broadening seems quite clear.

The somewhat oscillating results of Figure 4 are difficult to explain quantitatively. On a qualitative level, there is interplay of two effects: π-electron density polarization by the electron-withdrawing CF_2 groups and changes in π-system topology due to their addition. The polarizing effect is likely to act toward broadening of the band gap while the topological consequences are less straightforward. It is not surprising that very few addends may create an appreciable band gap in a metallic tube since the pristine tubes themselves divide into metallic and semiconducting due to topological reasons. However, we see that in many cases the band gaps and the shape of the frontier bands do not change too much for the type a + type b patterns with the same number of addends per supercell.

Thus, two possible cases can be distinguished in initial stages of functionalization of a metallic (5,5)CNT with CF_2 groups. The thermodynamically preferable type b addition will generally provide metallic tubes, though not without exclusions. The stochastic type a + type b addition results in semiconducting structures, with variable band gaps depending on the addition density but not in a monotonous way. It is an impor-
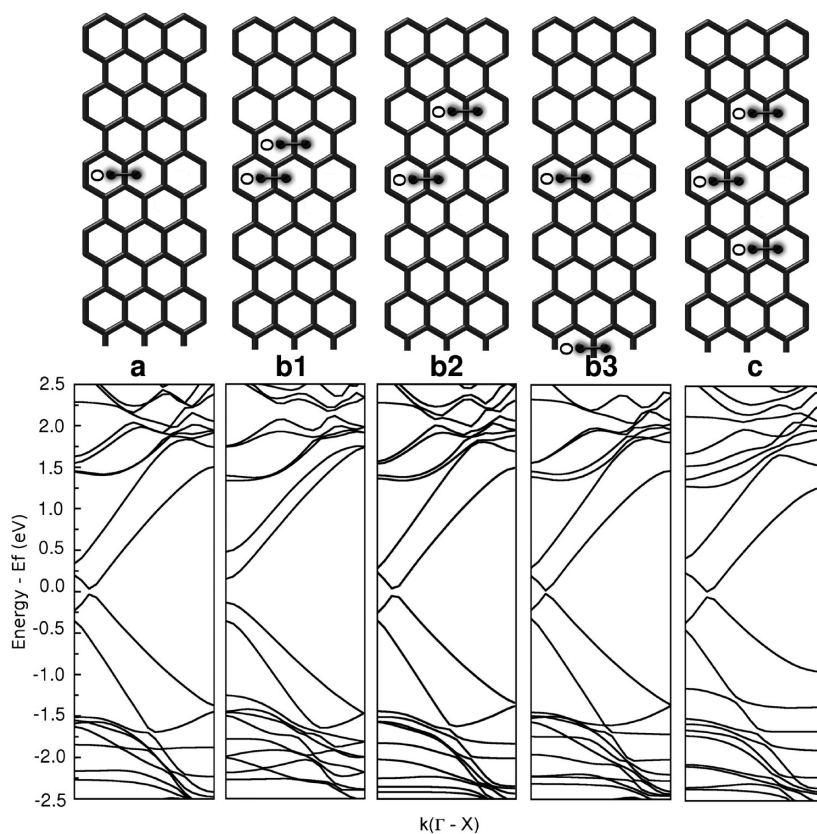
Figure 3. Band structure for some exemplary regular >CF₂ addition motifs of (5,5)CNT with only stable type of addition type b. Only for the strongly stressed structure b1, the theoretical band gap is ~0.45 eV; the other type b structures demonstrate a metallic character. O denotes an *open* conformation of a cage bond.
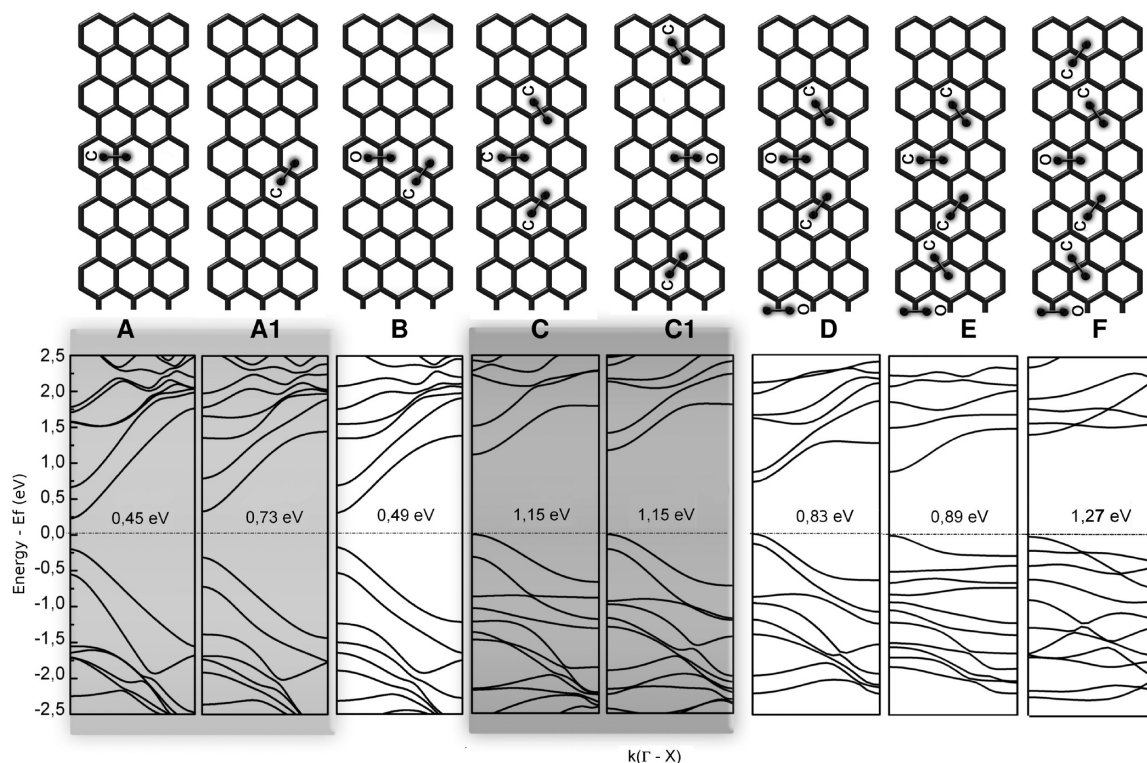

Figure 4. Band structure for some exemplary regular >CF₂ addition motifs of (5,5)CNT. For small gap materials, effective Fermi level is taken as $E_f = (E_c - E_v)/2$; otherwise $E_f = E_v$. Behaviors of such fashion can also nicely explain conductance escalation in work.[30] C and O denote *closed* and *open* conformations, respectively.
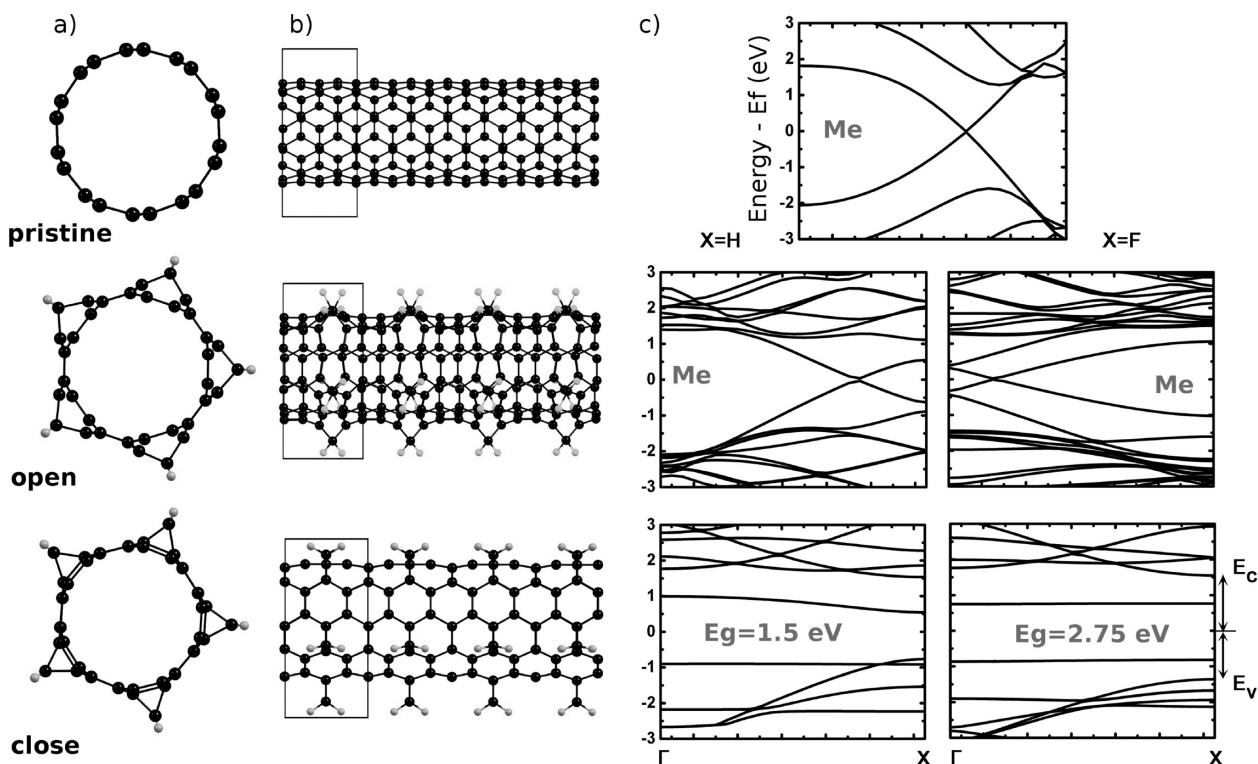
Figure 5. Calculated band structure for $(5,5)_3(CX_2)_3$ (X = H,F) structures for open and closed bridge bond cases (see text for details). (a) *XY* projection of the structure; (b) *ZY* projection of the structure; (c) band structures, where Me denotes *metallic* phases.

tant challenge for the experimentalists to find out which addition motifs are synthetically accessible. In this respect, quite helpful may be the above-discussed considerable difference in addition energy between the type a and type b groups: presence of both types of addends must result in a much broader spectrum of detachment energy.

In ref 31, we reported the first successful analysis of functionalized nanotubes by means of MALDI mass spectrometry. The development of this work was hampered by poor reproducibility of the major peaks in the mass spectra; nevertheless, the nanotube origins of the signals were doubtless. In view of the above, there may be a need in MALDI experiments for precise control of the energy density in the laser spot in order to control and study various degrees of fragmentation *via* detachment of addends.

Band Structure in Case of Specific Regular Patterns. Chemistry of simple fullerene derivatives provides numerous examples of formation of benzenoid or other aromatic substructures isolated by addends. The examples include $C_{60}F_{18}$, $C_{60}F_{36}$, and $C_{60}Cl_{30}$; especially interesting is the latter one, where the aromatic stabilization energy proves to be large enough to compensate multiple unfavorable close contacts of the bulky chlorine addends. Therefore, formation of similar aromatic substructures in polyfunctionalized nanotubes may be the case when addition is governed thermodynamically.

Some relevant examples for (5,5)CNT regularly functionalized with CF_2 and CH_2 addends are shown in Fig-

ure 5. In cluster calculations, these addition motifs are *ca.* 140 kJ/mol more stable than the structures with the same addition density (5 groups per supercell) from Figure 4. The stable conformation of the addends is open, but we also considered the closed cyclopropane conformation found to lie 30 kJ/mol higher (the lengths of the cyclopropane C—C bonds were taken to be 1.62 Å as in the closed $C_{60}CCl_2$ molecule[26]).

Similarly to most of the structures of Figure 4, the open conformation of the regular structure of Figure 5 retains its metallic properties both with CF_2 and CH_2 addends. However, closure of the cyclopropane rings cuts the π-system of the nanotube into disjointed belts of benzenoid rings and drastically changes the picture. We observe formation of (almost) flat frontier bands separated by a gap equal (CH_2) or higher than the HOMO—LUMO gap in C_{60}. With the donor CH_2 groups, the screening of the conjugated fragments is somewhat imperfect, which results in finite, though very high, effective masses while the electron-withdrawing CF_2 addends lead to formation of two perfect deep levels.

This drastic change of electronic structure due to transformation of open CF_2 bridges into cyclopropane fragments deserves serious attention in the light of the findings of previous work,[26,27] where it was demonstrated that the analogous conformational change in $C_{60}CF_2$ may be easily effected by charging or application of the electric field. One can hypothesize that gradual charging of the discussed nanotube systems may initiate a chain of conforma-

tional transitions through partial or equilibrium to complete closure of CX_2 groups with associated changes in conductivity. This may provide a uniquely flexible molecular switching system, provided, however, that regular patterns of addends are achievable synthetically.

CONCLUSIONS

The present study has demonstrated that functionalization of metallic (5,5)CNTs by CF species or similar nature groups may not only lead to smooth metal-dielectric transition with the increasing degree of attachment but also yield such remarkable systems where transitions of electric properties might be controlled electrically. Nowadays, however, the commonly synthetically available nanotubes are usually of larger diameter than the (5,5)CNT. For those larger tubes, one could expect certain deviations from the findings of the present work. In particular, steric effects of gradual decrease of the tube curvature (*i.e.*, of approach to the graphene limit) may favor closed conformations of the CX_2 addends even in the case of type a addition. Thus, each addend will have a destructive effect on the π-conjugated system of a nanotube, which, in its turn, may bring about different regiochemical principles of multiple CX_2 attachment. Therefore, functionalization of larger CNTs deserves further theoretical studies purported, in particular, to find the range of nanotube sizes where the herein described behavior of the (5,5)CNT will be paralleled. Such studies can follow the strategy of the present work, that is, going from regiochemistry and energetic of addition to band structures. Of special interest may also be those "intermediate" nanotube diameters where open and closed conformations of CX_2 groups will be in a sort of equilibrium like in $C_{60}CF_2$. There is also a strong need for experimental studies of the CX_2-modified nanotubes to verify the theoretical findings of the present work. Most importantly, this is the question of regioselectivity in functionalization, which, as we demonstrate, may be of definitive importance with regard to further aspects of direct practical significance, such as band structure. Furthermore, it would be very desirable to find diverse regimes of carbene attachment in order to have a choice between more chaotic and more regular (*e.g.*, thermodynamic) structures.

METHODS

The present study is based on the Kohn–Sham[32] DFT widely known to be a fast and relatively inexpensive technique for investigation of the large-scale systems. With GGA (or better) exchange-correlation functionals, it usually demonstrates good agreement between experiment and theory for both molecular and periodic fullerene systems.[33−36] The electronic properties of the periodic systems were calculated with the use of the CRYSTAL06 package[37] and molecular calculations using the PRIRODA code[38] with the PBE[39] exchange-correlation functional.

For a typical periodic task in the case of pristine and regularly functionalized CNTs, the numbers of k-points were chosen to achieve 10^{-6} au Fermi energy convergence. Generally, it required about 2−4 k-points. Smaller 3-21G atomic basis set was used for the full periodic optimizations since no significant changes in geometry and electronic properties were observed with more accurate 6-31G and 6-31G* basis sets (does not change drastically a geometry or an electronic property). All molecular calculations were performed at the DFT|PBE|TZ2p[39,40] level of theory with optimization tolerance of 10^{-5} au.

As an additional test of the quality of the periodic calculations with their smaller basis sets, for verification, we performed molecular calculations for the supercells selected. We found that deviations in geometric parameters were always within 0.005 Å, and those of the HOMO−LUMO gaps were within only 0.05 eV.

REFERENCES AND NOTES

1. Iijima, S.; Ichihashi, T. Single-Shell Carbon Nanotubes of 1-nm Diameter. *Nature* **1993**, *363*, 603–605.
2. Dekker, C. Carbon Nanotubes as Molecular Quantum Wires. *Phys. Today* **1999**, *52*, 22–28.
3. Novoselov, K. Graphene: Mind the Gap. *Nat. Mater.* **2007**, *6*, 720.
4. Ponomarenko, L. A.; Schedin, F.; Katsnelson, M. I.; Yang, R.; Hill, E. W.; Novoselov, K. S.; Geim, A. K. Chaotic Dirac Billiard in Graphene Quantum Dots. *Science* **2008**, 356–358.
5. Dresselhaus, M. S.; Dresselhaus, G.; Eklund, E. P. *Science of Fullerenes and Carbon Nanotubes*; Academic Press: New York, 1996.
6. Charlier, J.-C.; Blase, X.; Roche, S. Electronic and Transport Properties of Nanotubes. *Rev. Mod. Phys.* **2007**, *79*, 677–732.
7. Park, C. J.; Kim, Y. H.; Chang, K. J. Band-Gap Modification by Radial Deformation in Carbon Nanotubes. *Phys. Rev. B* **1999**, *60*, 10656–10659.
8. Chan, B.; Lakatos, G. V.; Peng, S.; Cho, K. First-Principles Study of Band-Gap Change in Deformed Nanotubes. *Appl. Phys. Lett.* **2005**, *87*, 173109.
9. Picozzi, S.; Santucci, S.; Lozzi, L.; Valentini, L.; Delley, B. Ozone Adsorption on Carbon Nanotubes: The Role of Stone-Wales Defects. *J. Chem. Phys.* **2004**, *120*, 7147–52.
10. Li, Y.; Zhou, Z.; Zhao, J. Transformation from Chemisorption to Physisorption with Tube Diameter and Gas Concentration: Computational Studies on NH_3 Adsorption in BN Nanotubes. *J. Chem. Phys.* **2007**, *127*, 184705.
11. Okazaki, T.; Okubo, S.; Nakanishi, T.; Joung, S.-K.; Saito, T.; Otani, M.; Okada, S.; Bandow, S.; Iijima, S. Optical Band Gap Modification of Single-Walled Carbon Nanotubes by Encapsulated Fullerenes. *J. Am. Chem. Soc.* **2008**, *130*, 4122–4128.
12. Raychowdhury, A.; Roy, K. Modeling of Metallic Carbon-Nanotube Interconnects for Circuit Simulations and a Comparison with Cu Interconnects for Scaled Technologies. *Comput.-Aided Des. Integr. Circuits Syst.* **2006**, *25*, 58–65.
13. Bettinger, H. F.; Kudin, K. N.; Scuseria, G. E. Thermochemistry of Fluorinated Single Wall Carbon Nanotubes. *J. Am. Chem. Soc.* **2001**, *123*, 12849–12856.

14. Zhao, J.; Chen, Z.; Zhou, Z.; Park, H.; Schleyer, P. R.; Lu, J. P. Engineering the Electronic Structure of Single-Walled Carbon Nanotubes by Chemical Functionalization. *Chem. Phys. Chem.* **2005**, *6*, 598–601.

15. Lee, Y.-S.; Nardelli, M. B.; Marzari, N. Band Structure and Quantum Conductance of Nanostructures from Maximally Localized Wannier Functions: The Case of Functionalized Carbon Nanotubes. *Phys. Rev. Lett.* **2005**, *95*, 76804.

16. Pan, H.; Feng, Y. P.; Lin, J. Y. *Ab Initio* Study of F- and Cl-Functionalized Single Wall Carbon Nanotubes. *J. Phys.: Condens. Mater.* **2006**, *18*, 5175–5184.

17. Ranjan, N.; Seifert, G. Transport Properties of Functionalized Carbon Nanotubes: Density-Functional Green's Function Calculations. *Phys. Rev. B* **2006**, *73*, 153408.

18. Park, H.; Zhao, J.; Lu, J.-P. Effects of Sidewall Functionalization on Conducting Properties of Single Wall Carbon Nanotubes. *Nano Lett.* **2006**, *6*, 916–919.

19. Lim, S.-H.; Ji, W.; Lin, J. First-Principles Study of Carbon Nanotubes with Bamboo-Shape and Pentagon−Pentagon Fusion Defects. *J. Nanosci. Nanotechnol.* **2008**, *8*, 309–313.

20. Boltalina, O. V.; Markov, V. Yu.; Troshin, P. A.; Darwish, A. D.; Street, J. M.; Taylor, R. $C_{60}F_{20}$: "Saturnen", an Extraordinary Squashed Fullerene. *Angew. Chem., Int. Ed.* **2001**, *40*, 787–789.

21. Jenkins, S.; Heggie, M. I.; Taylor, R. Aromaticity of [60]-Fullerene Derivatives ($C_{60} X_n$, X = H, F; n = 18, 36) Constrained To Have Planar Hexagonal Rings. *J. Chem. Soc., Perkin Trans. 2* **2000**, 2415–2419.

22. Troshin, P. A.; Lyubovskaya, R. N.; Ioffe, I. N.; Shustova, N. B.; Kemnitz, E.; Troyanov, S. I. Synthesis and Structure of the Highly Chlorinated [60]Fullerene $C_{60}Cl_{30}$ with Drum-Shaped Carbon Cage. *Angew. Chem., Int. Ed.* **2005**, *44*, 234–237.

23. Kareev, I. E.; Kuvychko, I. V.; Shustova, N. B.; Lebedkin, S. F.; Bubnov, V. P.; Anderson, O. P.; Popov, A. A.; Boltalina, O. V.; Strauss, S. H. C_1-(C84-C_2(11))$(CF_3)_{12}$: Trifluoromethylation Yields Structural Proof of a Minor C_{84} Cage and Reveals a Principle of Higher Fullerene Reactivity. *Angew. Chem., Int. Ed.* **2008**, *47*, 6204–6207.

24. Ioffe, I. N.; Avdoshenko, S. M.; Boltalina, O. V.; Sidorov, L. N.; Berndt, K.; Weber, J. M.; Kappes., M. M. Photoelectron Spectroscopy and Quantum Chemical Studies of $C_{60}F_{34}^{2-}$. *Int. J. Mass Spectrom.* **2005**, *243*, 223–237.

25. Popov, A. A.; Kareev, I. E.; Shustova, N. B.; Stukalin, E. B.; Lebedkin, S. F.; Seppelt, K.; Strauss, S. H.; Boltalina, O. V.; Dunsch, L. Electrochemical, Spectroscopic, and DFT Study of $C_{60}(CF_3)_n$ Frontier Orbitals (n = 2−18): The Link between Double Bonds in Pentagons and Reduction Potentials. *J. Am. Chem. Soc.* **2007**, 11551–11568.

26. Pimenova, A. S.; Kozlov, A. A.; Goryunkov, A. A.; Markov, V.Yu.; Khavrel, P. A.; Avdoshenko, S. M.; Vorobiev, V. A.; Ioffe, I. N.; Sakharov, S. G.; Troyanov, S. I.; *et al.* Preparation and Structures of [6,6]-Open[60]Fullerenes: $C_{60}(CF_2)$ and $C_{60}(CF_2)_2$. *Dalton Trans.* **2007**, 5322–5328.

27. Pimenova, A. S.; Kozlov, A. A.; Goryunkov, A. A.; Markov, V. Yu.; Khavrel, P. A.; Avdoshenko, S. M.; Ioffe, I. N.; Sakharov, S. G.; Troyanov, S. I.; Sidorov, L. N. Synthesis and Characterization of Difluoromethylene-HOMO[60]Fullerene, $C_{60}CF_2$. *Chem. Commun.* **2007**, 374–376.

28. Glukhovtsev, M. N.; Pross, A.; Schlegel, H. B.; Bach, R. D.; Radom, L. Gas-Phase Identity S_N2 Reactions of Halide Anions and Methyl Halides with Retention of Configuration. *J. Am. Chem. Soc.* **1996**, *118*, 11258–11264.

29. Dubois, S. M. M.; Lopez-Bezanilla, A.; Cresti, A.; Triozon, F.; Biel, B.; Charlier, J.-C.; Roche, S. Quantum Transport in Graphene Nanoribbons: Effects of Edge Reconstruction and Chemical Reactivity. *ACS Nano* **2010**, *4*, 1971–1976.

30. Cabana, J.; Martel, R. Probing the Reversibility of Sidewall Functionalization Using Carbon Nanotube Transistors. *J. Am. Chem. Soc.* **2007**, *129*, 2244–2245.

31. Avdoshenko, S. M.; Ioffe, I. N.; Kozlov, A. A.; Markov, V. Yu.; Nikolaev, E. N.; Sidorov, L. N. Novel Possibilities in the Study of Isolated Carbon Nanotubes. *Rapid Commun. Mass Spectrom.* **2008**, *22*, 1372–1376.

32. Kohn, W.; Sham, L. J. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.* **1965**, *140*, 5890–5906.

33. Blase, X.; Benedict, L. X.; Shirley, E. L.; Louie, S. G. Hybridization Effects and Metallicity in Small Radius Carbon Nanotubes. *Phys. Rev. Lett.* **1994**, *72*, 1878–1881.

34. Reich, S.; Thomsen, C.; Ordejon, P. Electronic Band Structure of Isolated and Bundled Carbon Nanotubes. *Phys. Rev. B* **2002**, *65*, 155411.

35. Wang, Y.-B.; Lin, Z. Supramolecular Interactions between Fullerenes and Porphyrins. *J. Am. Chem. Soc.* **2003**, *125*, 6072–6083.

36. Zhou, Z.; Zhao, J.; Schleyer, P. R.; Chen, Z. Insertion of C_{50} into Single-Walled Carbon Nanotubes: Selectivity in Interwall Spacing and C_{50} Isomers. *J. Comput. Chem.* **2008**, *29*, 781–787.

37. Dovesi, R.; Saunders, V. R.; Roetti, R.; Orlando, R.; Zicovich-Wilson, C. M.; Pascale, F.; Civalleri, B.; Doll, K.; Harrison, N. M. *et al. CRYSTAL06 User's Manual*; University of Torino: Torino, Italy, 2006.

38. Laikov, D. N. Fast Evaluation of Density Functional Exchange-Correlation Terms Using the Expansion of the Electron Density in Auxiliary Basis Sets. *Chem. Phys. Lett.* **1997**, *281*, 151–156.

39. Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

40. Laikov, D. N. A New Class of Atomic Basis Functions for Accurate Electronic Structure Calculations of Molecules. *Chem. Phys. Lett.* **2005**, *416*, 116–120.