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Cycloaddition Functionalizations to Preserve or Control the Conductance of Carbon Nanotubes

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We identify a class of covalent functionalizations that preserve or control the conductance of single-walled metallic carbon nanotubes. [2+1] cycloadditions can induce bond cleaving between adjacent sidewall carbons, recovering in the process the sp^2 hybridization and the ideal conductance of the pristine tubes. This is radically at variance with the damage permanently induced by other common ligands, where a single covalent bond is formed with a sidewall carbon. Chirality, curvature, and chemistry determine bond cleaving, and in turn the electrical transport properties of a functionalized tube. A well-defined range of diameters can be found for which certain addends exhibit a bistable state, where the opening or closing of the sidewall bond, accompanied by a switch in the conductance, could be directed with chemical, optical, or thermal means.

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Chemical functionalizations of carbon nanotubes (CNTs) are the subject of intensive research [1,2] and could offer new and promising avenues to process and assemble tubes, add sensing capabilities, or tune their electronic properties (e.g., doping levels, Schottky barriers, work functions, and electron-phonon couplings). However, the benefits of functionalizations are compromised by the damage to the conduction channels that follows sp^3 rehybridization of the sidewall carbons [3,4], as evidenced by absorption spectra and electrical transport measurements [5–7]. We report here on a class of cycloaddition functionalizations that preserve instead the remarkable transport properties of metallic CNTs. In addition, we identify a subclass of addends that display a reversible valence tautomerism that can directly control the conductance.

We focus here on [2+1] cycloaddition reactions, where the addition of a carbene or a nitrene group saturates a double bond between two carbon atoms, forming a cyclopropane-like three-membered ring. Such functionalizations have been reported extensively in the literature [8–10]. All our calculations are performed using density-functional theory in the Perdew-Burke-Ernzerhof generalized-gradient approximation (PBE-GGA) [11], ultrasoft pseudopotentials [12], a plane-wave basis set with a cutoff of 30 Ry for the wave functions and 240 Ry for the charge density, as implemented in QUANTUM-ESPRESSO [13].

We examine first the simplest members in this class of addends, CH_2 and NH. Figures 1(a) and 1(b) show the two inequivalent choices available on a (5, 5) metallic CNT; for convenience, we label these as "S" (skewed) and "O" (orthogonal), reminiscent of the relative positions of the sidewall carbons with respect to the tube axis. Our simulation cells include $12n$ carbons for a given (n, n) CNT, plus one functional group. We use a 1×1×4 Monkhorst-Pack mesh (including Γ) for structural optimizations, and a 1×1×8 mesh for single-point energy calculations, with a cold smearing of 0.03 Ry [14].

First, and for (n, n) metallic tubes, we highlight how strongly the reaction energies of these functionalizations depend on the curvature of the nanotubes and on their attachment sites S and O. We plot in Fig. 2(a) the reaction energies ΔE_{CNT} (defined as $\Delta E_{\mathrm{CNT}} = E_{\mathrm{CNT\text{-}func}} - E_{\mathrm{CNT}} - E_{\mathrm{func}}$, func $= CH_2$ or NH), taking as a zero reference the same reaction on graphene. The reaction energies have a well-defined linear dependence on curvature, clearly demonstrating the higher reactivity of smaller-diameter tubes. The O site is always more stable, and significantly so for all diameters considered; at room temperature all small-diameter armchair CNTs strongly favor the O configuration. The energy difference between the O and the S form of the (5, 5) CNT is 1.24 eV, in good agreement with other plane-wave and localized basis calculations (1.24 eV [15] and 1.4 eV [16], respectively).

Second, we find that the C_1-C_6 distance for the O form [d_{16} in Fig. 1(c)] is much larger than the usual C-C distance (1.54 Å in diamond and 1.42 Å in graphite), a clear indication that the sidewall bond is broken [15–18]. We observe bond cleaving up to the (12, 12) CNT [Fig. 2(b)];

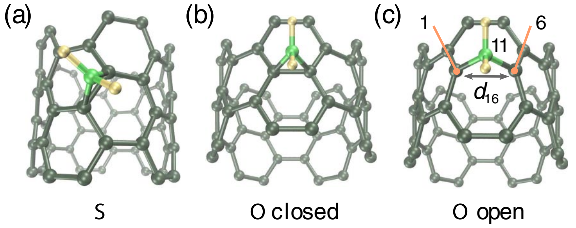

FIG. 1 (color online). The three different configurations for a functional group on an armchair nanotube are shown [CH_2 on a (5, 5) CNT]: (a) skewed S, (b) orthogonal O with an intact ("closed") sidewall bond, and (c) orthogonal O with a broken ("open") sidewall bond.

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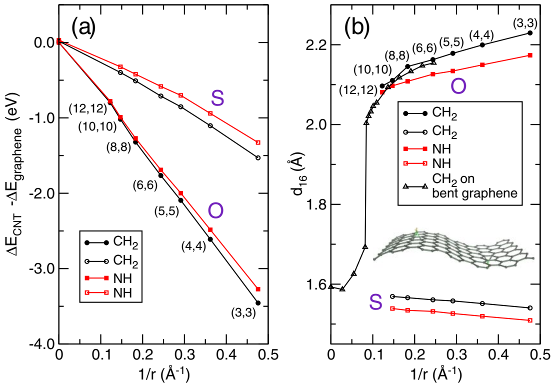

FIG. 2 (color online). (a) Energy change ΔE_{CNT} upon functionalization as a function of curvature, for (n, n) armchair CNTs—the zero reference is for graphene. (b) Sidewall equilibrium bond distance C_1-C_6 (d_{16}) for (n, n) CNTs and for a bent graphene sheet, functionalized at the stable O site. The sidewall bond is broken in all the (n, n) CNTs considered. Continuous bending of a graphene sheet shows that a well-defined transition from the closed to the open form takes place as the curvature increases.

on the other hand, in graphene the bond is intact. We estimate the critical diameter that separates the two regimes by bending a graphene sheet [Fig. 2(b)]: such a model closely reproduces the nanotube results, and a sharp transition from the bond-intact to the bond-broken form takes place around a diameter of 2.4 nm, i.e., an (18, 18) tube, for CH_2 functionalizations.

Broken or intact sidewall bonds play a fundamental role in the electronic transport properties of a metallic CNT. We show this in Fig. 3, where the Landauer conductance is calculated for a (5, 5) CNT functionalized with dichlorocarbene (CCl_2) (first reported experimentally in 1998 [8]), using an approach recently introduced by us that allows one to accurately treat realistic nanostructures with thousands of atoms [4]. For this diameter the sidewall bond is broken, and the scattering by a single CCl_2 group is found to be remarkably weak, with the conductance approaching its ideal value. Even after adding 30 groups on the central 43 nm segment of an infinite nanotube the conductance is reduced by only 25%. This is in sharp contrast with the case of a hydrogenated tube, where the conductance drops drastically when functionalized with a comparable number of ligands. This distinction is easily rationalized: Hydrogen and other single-bond covalent ligands induce sp^3 hybridization in C_1 and C_6, which act as very strong scatterers [4] (such dramatic decrease in the conductance has also been confirmed experimentally [7]). On the other hand, after bond cleavage, C_1 and C_6 recover an sp^2 bonding environment [Fig. 1(c)], with three covalent bonds to their nearest neighbors, allowing for the p_z orbitals of C_1 and C_6 to contribute again to the graphitic π manifold (as confirmed by inspection of the maximally localized Wannier functions [19]). As a result, conductance approaches again that of a pristine CNT, highlighting the promise of cycloadditions in *preserving* the conductance of metallic CNTs.

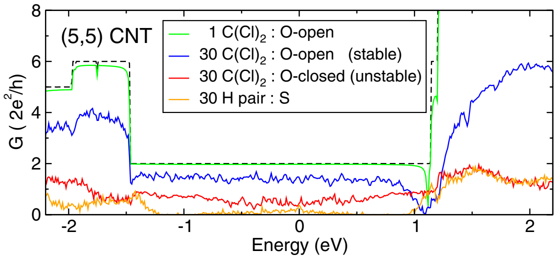

FIG. 3 (color online). Quantum conductance for a (5, 5) CNT functionalized with one CCl_2 group, with 30 CCl_2 groups, and with 30 hydrogen pairs [dashed line: pristine (5, 5) CNT]. A CCl_2 addend will choose the O-open configuration, while hydrogens prefer to pair in the S configuration; the results correspond to these stable choices. The conductance for the energetically unstable O-closed configuration is also plotted. The 30 functional groups are arranged randomly on the central 43-nm segment of an otherwise infinite tube; the conductance is then averaged over 10 different configurations.

In principle, around the critical diameter shown in Fig. 2(b), a functional group could be found that displays as stable states on the same tube both the open and the closed configuration. If this is the case, interconversion between the two valence tautomers would have a direct effect on the conductance. We illustrate this paradigm with the dichlorocarbene example of Fig. 3; if we force the tube in its closed configuration, with all the sidewall bonds frozen in their ideal pristine-tube geometry, conductance decreases by a factor of 2 or 3 with respect to the case of the relaxed tube [20]. The configuration where the sidewall bonds are intact is not stable for this case, but, depending on the chemistry of the addends and the diameter considered, optimal ligands could be found for which a double-well stability is present.

In order to identify the factors that determine stability in the open or closed form, we first screen several addends on small molecules. We find that the bridged 1, 6-*X*-[10] annulene [inset of Fig. 4(a)] is an excellent molecular homologue of a functionalized CNT [17]. It is well known that the substitutional group *X* dictates the preference for the annulene (henceforth labeled as **1o**) or for its valence tautomer, a bisnorcaradiene derivative (**1c**), corresponding to the open and closed configurations of a functionalized CNT [22–27]. Similar tautomerization between an open (**2o**) and a closed (**2c**) form takes place in a pyrene derivative [28] [inset of Fig. 4(b)]. We thus tested on these molecules the substitutional groups $X = CH_2$, NH, SiH_2, $C(NO_2)_2$, $C(CN)_2$, $C(CCH)_2$, $C(CH_3)_2$, $C(COOH)_2$, CCl_2, $C(NH_2)_2$, C_6H_4O [29], and $C_{13}H_8$ [29]. To assess the accuracy of our PBE-GGA approach, we compare in Table I our results for d_{16} in **1** with those obtained from experiments or other theoretical methods [second order Møller-Plesset perturbation theory (MP2) [34] and Becke three parameter Lee-Yang-Parr hybrid functional (B3LYP) [35]], finding excellent agreement. Hydrogen and halogens have been reported to stabilize **1o** both experimentally

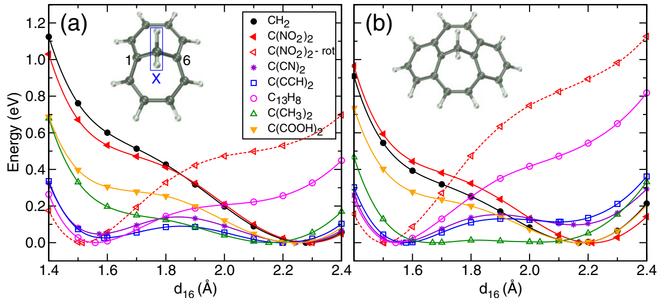

FIG. 4 (color online). Potential energy surface as a function of d_{16} for select cases of (a) **1** and (b) **2**. C(CN)$_2$ (star) and C(CCH)$_2$ (open square) show a double-well minimum in both **1** and **2**. C(NO$_2$)$_2$-rot (open left-pointing triangle) indicates the unstable conformation where the two NO$_2$ groups are rotated from their equilibrium position (solid left-pointing triangle) by 90°.

and theoretically [22,23,31]. Cyano group favors **1c** experimentally (the possibility of coexistence with **1o** is discussed) [24], and two minima have been actually predicted theoretically [31,33]. We show the potential energy profile of select groups in Fig. 4. All carbenes stabilizing the closed form in both **1** and **2** share a common feature: partially occupied p orbitals parallel to the in-plane [the plane of C$_1$-C$_{11}$-C$_6$ in Fig. 1(c)] p_σ orbital of the bridgehead C$_{11}$ atom [36]. This conclusion is strongly supported by examining the energy minimum conformation for $X =$ C(NO$_2$)$_2$. At equilibrium, the two oxygen atoms in the NO$_2$ group lie on a line parallel to the C$_1$-C$_6$ bond, and the open form is stable (solid left-pointing triangle in Fig. 4). The sidewall bond will switch from open to closed upon rotation of the two NO$_2$ groups by 90°, thereby placing the p orbitals of the nitrogens parallel to the p_σ orbital of C$_{11}$ (open left-pointing triangle in Fig. 4). Among all the substituents tested, SiH$_2$, C(CCH)$_2$, and C(CN)$_2$ show most clearly the presence of two minima; we study here $X =$ C(CN)$_2$ since both **1c** [24] and a C$_{60}$ derivative [37] have already been synthesized.

TABLE I. Experimental and theoretical d_{16} of **1**. Note that the calculations assume isolated molecules at 0 K, while experimental data are obtained from crystalline systems at finite temperature. Theory predicts two stable minima for $X =$ C(CN)$_2$. The long d_{16} of $X =$ C(CH$_3$)$_2$ indicates that the potential energy surface would be very flat, which is also predicted in Fig. 4, especially for **2**.

X	Expt.	MP2	B3LYP	This work
CH$_2$	2.235^{a}	2.251^{f}	2.279^{g}	2.278
CF$_2$	2.269^{b}	2.268^{f}	2.296^{f}	2.300
C(CN)$_2$	1.542^{c}	1.599, 2.237^{f}	1.558, 2.253^{h}	1.572, 2.245
C(CH$_3$)$_2$	1.836^{d}	2.156^{f}	2.168^{f}	2.151
NH	(open)^{e}		2.237^{g}	2.239

[a]Ref. [22] [b]Ref. [23] [c]Ref. [24] [d]Ref. [25] [e]Ref. [30] [f]Ref. [31]
[g]Ref. [32] [h]Ref. [33]

We explored, therefore, the potential energy landscape for armchair CNTs functionalized with C(CN)$_2$. The results shown in Fig. 5 reflect closely those found in the molecular homologues. A unique minimum in the open form is located in small-diameter tubes, as is generally the case in these [2+1] cycloadditions. As the diameter is increased, the signature of the closed minimum starts to appear, first as an inflection point [(5, 5) CNT], then as a local minimum for the (10, 10) CNT ($\phi = 1.36$ nm, as in **1c**), and finally as a global minimum for the (12, 12) CNT ($\phi = 1.63$ nm, as in **2c**). As discussed before, the conductance is controlled by the bonding and hybridization of the sidewall carbons. We compare in Fig. 6 the two stable open and closed forms for the (10, 10) CNT functionalized with C(CN)$_2$. The scattering induced by a single group is negligible, especially in the open form, and the conductance around the Fermi energy is extremely close to its ideal value [Fig. 6(a)]. As the number of functional groups is increased, the difference between the two minima becomes rapidly apparent [Fig. 6(b)].

Two conclusions can be drawn: First, even with a large number of functional groups, the conductance remains high whenever cycloadditions break the sidewall bond. Second, a subclass of substituents can be found [e.g., C(CN)$_2$] that stabilizes two tautomeric forms on the same tube, separately displaying high and low conductance. Several mechanisms, including photochemical, electrochemical, and thermal, could then direct interconversion between the two tautomeric forms. Photochemical and electrochemical interconversion rely on the fact that the energy levels of the frontier orbitals are affected by d_{16}, depending on their symmetries and charge distributions [31,36] (e.g., the bond weakens as a filled orbital that has bonding character along C$_1$-C$_6$ is emptied). Both photochemical excitations or electrochemical reduction or oxidation can populate or depopulate those frontier orbitals that favor the open or closed form; as a result, they would modulate the bond distance, and ultimately the conductance. As a proof of principle, time-dependent density functional calculations in **2** for $X =$ C(CN)$_2$ show that the first singlet excitation (S_1) drives the system from the

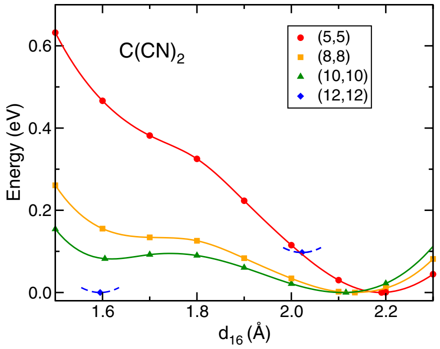

FIG. 5 (color online). Potential energy surface for (n, n) CNTs functionalized with C(CN)$_2$. Both (10, 10) and (12, 12) CNTs display a double-well minimum.

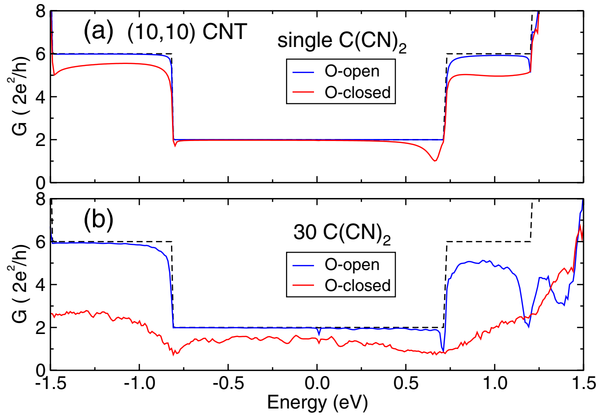

FIG. 6 (color online). Quantum conductance for a (10, 10) CNT functionalized with $C(CN)_2$, in the O-open and O-closed stable configurations [dashed line: pristine (10, 10) CNT]. (a) Single group. (b) 30 functional groups arranged randomly on the central 32-nm segment of an infinite tube; the conductance is then averaged over 10 different configurations.

open to the closed form [38]. A similar conclusion is drawn from experimental observations in **2o** for $X = CH_2$, where this open form is stable in the ground state while the closed **2c** is presumed to be stable in the S_1 energy surface [28]. Temperature also plays an important role, and ^{13}C NMR spectroscopy and x-ray data have captured the temperature-dependent equilibrium: a higher temperature stabilizes **1o** for $X = C(CN)(CH_3)$, while destabilizing it for $X = C(CH_3)_2$ [26,27].

In conclusion, our calculations predict that (i) cycloaddition functionalizations on narrow-diameter nanotubes can recover, as a consequence of bond cleaving, the conductance of the original pristine tubes, allowing for organic chemistry approaches to manipulation, assembly, and doping that preserve the remarkable electronic properties of these materials, and that (ii) a subclass of addends, exemplified in this work by dicyanocarbene, exhibits fluxional behavior that could be controlled with optical or electrochemical means. Such conductance control, if realized, could have practical applications in nano- and optoelectronics, chemical sensing, and imaging.

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