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Realistic nanostructures from first-principles: fluxional handles to control the conductance of carbon nanotubes[1]

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We have combined large-scale, $\Gamma-$point electronic-structure calculations and the maximally-localized Wannier functions approach to calculate efficiently and with full first-principles accuracy the electronic structure and the quantum conductance of complex systems containing thousands of atoms. This approach is applied to study covalent functionalizations in metallic single-wall carbon nanotubes. We find that for most covalent ligands (from hydrogens to aryl moieties) the electronic structure around the Fermi energy is much less dependent on the chemical nature of the ligands than on the sp^3 functionalization pattern disrupting the conjugation network. These covalent functionalizations are more stable when paired with saturating hydrogens. Even when paired, they still act as strong scattering centers that degrade the conductance of the tubes already at low degrees of coverage. Instead, we find that cycloadditions of carbenes or nitrenes can preserve metallicity to an unusually high degree, whenever bond cleavage between two sidewall carbon atoms is induced. This process restores the original sp^2 hybridization for the sidewall carbons and preserves, even in the presence of significant distortions, the original "transparency" of the π manifold. The chirality and curvature of the nanotube and the chemistry of the addends determine this bond cleavage and in turn the transport properties. Remarkably, a well-defined range of diameters can be found for which certain addends - such as dicyanocarbene - exhibit a bistable switchable state, where the opening or closing of the bond, and thus the opening and closing of the conduction channels, could be directed with chemical, electrochemical or optical means. This discovery opens the way to novel and promising routes to control and modulate nanotube conductance, with applications ranging from sensors to memories to opto- and nano-electronics.

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