Computational studies of the structural, electronic, and optical properties of single-walled carbon nanotubes functionalized by DNA and diazonium salts

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Given that structural aspects such as chirality and diameter govern the electronic, optical, and chemical properties of single-walled carbon nanotubes (SWNTs), it would be advantageous to develop methods to solubilize and separate SWNTs as well as manipulate the electronic structure in order to obtain desirable photophysical and photochemical properties. Chemical functionalization of SWNTs is one such method that not only aids with post synthesis separation and identification, it also provides a way to fine tune the electronic and optical properties of SWNTs. We present our findings from molecular mechanical (MM) computations on the morphology and structural stability of non-covalent, π-bonded, single-stranded DNA (ssDNA) functionalized semiconducting (SC) SWNTs[1]. In addition, we discuss results from our time-dependent density functional (TD-DFT) studies on the electronic structure and optical properties of SC-SWNTs functionalized by covalent and non-covalently attached diazonium salts[2]. Results of our MM computations demonstrate a distinct relationship between SWNT chirality and ssDNA base binding preference for the ssDNA-SWNT hybrids. Our results also indicate a preferred wrapping angle of the ssDNA with respect to SWNT chirality. Both of these characteristics are useful in the identification of SWNTs. All ssNDA-SWNT hybrids in our MM study yield very stable structures with binding energies well above room-temperature thermal fluctuations, suggesting application not only to SWNT dispersion, but a wide range of nanoscale devices such as biosensors and drug delivery systems. Our TD-DFT calculations on SWNTs functionalized with diazonium salts indicate small insignificant shifts in the optical spectra for the physisorbed hybrids compared those of pristine (optically dark) SWNTs and are attributed to the π–π nature of the aryl-SWNT interaction. Conversely, the covalently functionalized hybrids show a significant red-shift and brightening of the lowest exciton suggesting that the photoluminescent efficiency of SWNTs may be controlled through selective covalent chemical functionalization, a highly desired feature particularly for photovoltaic applications.

1. M. L. Mayo, Z. Chen, and S. V. Kilina, *J. Phys Chem. Lett.* **3**, 2790 (2012).
2. J. Ramirez, M. L. Mayo, S. Kilina, and S. Tretiak, *Chem. Phys*, *in press*, http://dx.doi.org/10.1016/j.chemphys.2012.10.010 (2012).