Divalent Defects from Pyrrolidine and 3-Pyrroline Bounded to (6,5) Carbon Nanotubes and Their Effect on Emission: DFT Insights

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The emission properties of a single-walled carbon nanotube (SWCNT) can be significantly enhanced by creating the sp^3-hybridized defect at the tube's lattice via covalent attachment of a small number of organic molecules to the surface of SWCNTs. The energy and optical intensity of the defect-associated optically active state strongly depends on the defect configuration – a way of molecule attachment with respect to the tube's axis. In our studies, we utilize Density Functional Theory (DFT) and Time-Dependent DFT (TD-DFT) to investigate the ground and excited state properties of the (6,5) SWCNT with the defect introduced by attachment of pyrrolidine and 3-pyrroline molecules. We compare the divalent defects, when a molecule is bound to more than one carbon atom in the SWCNT, with their monovalent counterparts. Our calculations reveal a noticeable distortion of the sp^2-hybridized C-C bond in the nanotube where both carbons are involved in binding with the molecule. This distortion is the largest for the molecule alignment nearly normal to the nanotube axis featuring the C-C elongation up to 1.7 Å. In contrast, all conformations of the monovalent defect exhibit typical sp^3-hybridized C-C bond lengths in the nanotube of 1.5-1.6 Å. Despite these strong distortions in the bonds of the nanotube, the divalent defect configurations result in the optically active lowest energy transition, significantly redshifted with respect to the main E_{11} optical band of the pristine SWCNT. This redshift is more significant than those of monovalent defects. Obtained insights into optical and structural properties of SWCNTs with chemical defects are important for potential applications of SWCNT as single photon emitters in the near-infrared range.