

Selectivity of Reaction Pathway for Formation of Divalent sp^3 Defects in Carbon Nanotubes

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Organic color centers (OCCs) created on the sidewalls of single-wall carbon nanotubes (SWCNTs) through the covalent functionalization show structure-selective near-infrared photoluminescence. OCCs have attracted much attention due to their potential applications such as bio-imaging, bio-sensing, and single-photon emission. In this work, we carry out density functional theory (DFT) calculations to study the divalent OCCs on (6,5) CNTs. One finds that there are three binding configurations of divalent OCCs, designated as $o+$, $o++$, and $o-$, each of which shows distinct structural, electronic, and optical properties. Computed emission spectra following the Kasha's rule by adopting the independent orbital approximations (IOAs) show redshift and bright emission peaks of the divalent OCCs compared to the pristine CNT. We also explore cycloaddition reaction pathways leading to the formation of OCCs by the climbing image nudged elastic band (CI-NEB) method and ab initio molecular dynamics (AIMD). It is found that the reaction pathways of three divalent OCCs are similar with slight differences in barrier heights. This study illustrates the tunability of CNT emission by modification of binding sites and contributes to the thermodynamic and kinetic control of divalent OCCs using temperature.

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