

# Light Activated Formation of Emissive Carbon Nanotubes: Role of Spin Multiplicity of Transition State

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Single-wall carbon nanotubes (SWCNTs) with local covalent functionalization have shown intriguing photophysical properties, making them well suited to applications such as room-temperature single-photon emission and high contrast bio-imaging. Photochemical reaction is an effective route to achieve aryl functionalization of SWCNTs with enhanced photoluminescence and improved quantum properties. In general, such a reaction requires that a pair of chemical species (e.g. aryl + H) of aromatic compounds tie up two electrons from the  $\pi$ -electron system of the nanotube, leading to the attachment in close proximity at the same carbon ring. This reaction may result in several isomeric products. To address this challenge and to better understand the reaction mechanism, we calculate the minimum energy reaction pathway and transition state of the functionalization using climbing image nudged elastic band (CI-NEB) method. Interestingly, both reactant and product exhibit singlet ground-state electronic configurations. However, one finds the change of spin multiplicity for transition state structures and intermediates along certain reaction pathways. This work explores correlation between (a) spin multiplicity of the pathway, (b) transition state energy, and (c) geometry of the product. Our results show that *ortho* aryl-H products are generated through singlet pathways, whereas *para* aryl-H products are generated through triplet pathways. In addition, we determine the contribution of each distinct aryl-H configuration to the overall emission of functionalized CNTs by exploring the relationship between chemical configurations and electronic structures. We also compute excited-state dissipative dynamics for six distinct aryl-H products through on-the-fly nonadiabatic couplings using reduced density matrix theory in the Redfield formalism. This work reveals the fundamental mechanism of nanotube functionalization and allows interpretation of excited state dynamics at an atomistic level.

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