Defect Associated Emission in Carbon Nanotubes

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Recent focus on optical properties of single walled carbon nanotubes (SWCNTs) have been re-emerged due to possible improvements of their emission efficiency by means of covalently functionalization. However, the photophysical nature of the defect-associated low energy transitions is still under debates in the quest to precisely control their brightness and energy alignment via chemical modifications of functional groups. The main open question is to what degree the interplay between a chemical composition and a binding conformation of functional groups governs the energy and optical intensity of defect-associated transitions is SWCNTs.

We perform quantum chemistry studies to explain the energy dependence of emission features (E_{11}^*) introduced via functionalization of several SWCNT by aryl bromides and chlorides at different conformations and in various solvent media. We use analytical gradient time-dependent density functional theory (TDDFT) allowing for optimization of the excited state and calculations of the reorganization energy that is found to be from 10 meV to 100 meV depending on the defect position. Our calculations reveal that the predominant effects on emission properties is a result of functionalization configuration at the nanotube surface, while modifications of binding groups and impact of a polar solvent have much less pronounced impacts. Such a dominant role of the defect confirmation is rationalized by exciton extent on the pristine regions of the SWCNT around the sp^3-defect introduced by the functional group, rather than on the functional group itself.

Predicted energies of optical transitions, however, are significantly blue-shifted compared to those measured in experiments, due to artificial confinement of finite-length models and methodology errors. We found that confinement and methodology errors cannot be corrected by a simple constant-energy shift, since confinement errors depend on the degree of exciton localization. Herein, we present a method that corrects for confinement and methodology errors independently, extrapolating energies of infinite-length SWCNTs from TDDFT calculations. Corrected emission energies calculated for four different SWCNTs, functionalized by aryl groups, are in remarkable agreement with experiment, suggesting the value of this straightforward method towards predicting and interpreting the optical features of functionalized SWCNTs. Obtained insights into the mechanisms that are responsible for changes in the lowest energy excitonic band originated from the chemical functionalization make envisioned applications of SWCNTs in optoelectronics, single photon sources, sensing, and imaging technologies more feasible.