Comparative study of photoluminescence of single and ensembles of cis-polyacetylene semiconductor materials

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Semiconducting conjugated polymers (CPs) have shown great potential in organic solar cells and organic field-effect transistors (OFETs) due to their tunable electronic and optical properties. Photoluminescence (PL) is one of the key observables in experimental characterizations of optoelectronic materials, including CPs. In this study, two different models of *cis*-polyacetylene (single cis-PA oligomer and ensemble of cis-PA) are used to explain the mechanism of PL of the CPs. The photo-induced excited state dynamics are computed using a combination of the ab initio electronic structure and time-dependent density matrix methodology [1]. We explore the phonon-induced relaxation of the excited states. Here, the dissipative Redfield equation is used with the nonadiabatic couplings as parameters. The simulated results for both models show that the relaxation rate of the electron is found to be faster than the relaxation rate of the hole. The dissipative excited-state dynamics are combined with radiative recombination channels to predict the PL spectrum. The simulation results reveal similarities and differences in the absorption and emission spectra for single and multiple oligomers[2]. The main result of the single oligomer is that the computed PL spectrum demonstrates two mechanisms of light emission originating from (i) the inter-band transitions, corresponding to the same range of transition energies as the absorption spectrum and (ii) intra-band transitions which are not available in the absorption spectra.[2,3] This work compares spectroscopic signatures of single cis-PA oligomer versus ensemble of such oligomers. Formation of an ensemble results in noticeable changes in transitions energies and intensities of transitions for both absorption and emission spectra. As the excited state charge density changes over time, ensembles of cis-PA demonstrate processes of charge density localization and delocalization. These results can be used for improving organic semiconductor materials for photovoltaic and LED (light emission diode) applications.

References

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