

Cost-Efficient Modeling of Polymorph- and Coformer-dependent Solid-state Photoluminescence

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Electronic excitations occur ubiquitously in nature. Prominent examples include photosynthesis and vision, which are of fundamental importance to human life. In particular, the photoluminescence (PL) of solid-state materials has a wide range of potential applications, including solar cells and fluorescent sensors. Solid-state PL has recently gained much research attention with the discovery of many novel materials with unique PL properties. Examples of such novel PL properties include compositional tunability, mechanical-force and heat responses. The cases of polymorph- and coformer-dependent PL is particularly interesting, as subtle changes in the intermolecular interactions within the crystal lattice can sometimes induce significant shifts in the PL wavelengths among different polymorphs or cocrystals. Herein, we present our recent theoretical modeling of polymorph- and coformer-dependent PL via a novel and cost-efficient computational method. Our method employs a combination of molecular and periodic-boundary calculations based on ground-state density-functional theory to account for intermolecular interactions, which play a subtle, yet critical, role in rendering the aforementioned PL properties. For the facile calculation of first-singlet excitation energies, our method incorporates the Virial Exciton Model [1,2], thereby bypassing the costly and complicated excited-state methods. Previously, our method had been successful in modeling pressure-dependent PL (a.k.a. piezochromism) in molecular solids [3]. In this work, our method again achieved overall success in replicating the experimental-reported PL shifts among our investigated sets of polymorphs and cocrystals, displaying excellent transferability. Valuable theoretical insights into the origin of the aforementioned PL properties are also gained through our results.

References:

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