Materials Science & Engineering Doctoral Defense

Theoretical Characterization of Zinc Phthalocyanine and Porphyrin Analogs for Organic Solar Cell Absorption

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abstract

The absorption spectra of metal-centered phthalocyanines (MPc's) have been investigated since the early 1960's. With improved experimental techniques to characterize this class of molecules the band assignments have advanced. The characterization remains difficult with historic disagreements. A new push for characterization came with a wave of interest in using these molecules for absorption/donor molecules in organic photovoltaics. The use of zinc phthalocyanine (ZnPc) became of particular interest, in addition to novel research being done for azaporphyrin analogs of ZnPc.

A theoretical approach is taken to research the excited states of these molecules using time-dependent density functional theory (TDDFT). Most theoretical results for the first excited state in ZnPc are in only limited agreement with experiment (errors near 0.1 eV or higher). This research investigates ZnPc and 10 additional porphyrin analogs. Excited-state properties are predicted for 8 of these molecules using ab initio computational methods and symmetry breaking for accurate time-dependent self-consistent optimization. Franck–Condon analysis is used to predict the Q-band absorption spectra for all 8 of these molecules. This is the first time that Franck–Condon analysis has been reported in absolute units for any of these molecules. The first excited-state energy for ZnPc is found to be the closest to experiment thus far using a range-separated meta-GGA hybrid functional. The theoretical results are used to find a trend in the novel design of new porphyrin analog molecules.

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