

Effect of Crystal Packing on the Excitonic Properties of Rubrene Polymorphs

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Singlet fission (SF), the conversion of one singlet exciton into two triplet excitons, may lead to the realization of high efficiency organic photovoltaics by generating two carriers from one photon. Recently, SF has been observed in molecular crystals of rubrene. While the orthorhombic form of rubrene is most often observed under ambient conditions, metastable monoclinic and triclinic polymorphs are known. Here, dispersion-inclusive density functional theory (DFT) is used to investigate the relative stability of all three phases. Many-body perturbation theory is then employed to study the effect of crystal structure on the electronic and excitonic properties. Band structures are calculated within the GW approximation and optical properties are calculated by solving the Bethe-Salpeter equation (BSE). We find that crystal packing significantly affects the electronic and excitonic properties of rubrene. Based on our calculations, the triclinic and especially the monoclinic forms of rubrene are expected to exhibit higher SF efficiencies than the orthorhombic form.