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## Investigation of molecular dimers in $\alpha$ -PTCDA by *ab initio* methods: Binding energies, gas-to-crystal shift, and self-trapped excitons

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Time-dependent density functional theory (TD-DFT), Hartree-Fock, second-order Møller-Plesset perturbation theory (MP2), and configuration interaction of singly excited states (CIS) are applied to crystalline PTCDA (3,4,9,10-perylene tetracarboxylic dianhydride). The systems investigated include single molecules in an optimized rectangular shape, and molecules and molecular dimers compatible with the experimental geometry in the crystalline  $\alpha$ -phase. Total energy calculations for pairs of adjacent molecules result in a microscopic estimate for the intermolecular binding energy in the solid. The electronic transition energies are calculated with TD-DFT techniques and CIS. From a detailed comparison between the molecular excitations of a single molecule and different molecular dimers in the crystal, a large fraction of the gas-to-crystal shift can be assigned to the redshift of the HOMO-LUMO excitation energy induced by the neighboring molecules in the crystal. The molecular dimers are generalized to deformed molecules, resulting in model geometries for self-trapped excitons with long radiative lifetimes related to the small transition dipole moment associated to intermolecular charge transfer (CT) transitions. The part of the Stokes shift resulting from internal deformations is obtained from TD-DFT calculations, and the self-trapping along the intermolecular distance is determined from a combination of an MP2-based intermolecular van der Waals potential with CIS for the CT transitions. After a careful elimination of the energy offsets related to the applied methods and to the lack of the complete crystalline surroundings, the calculated transition energies for the deformed dimers can be used for assigning the long-living components of the photoluminescence spectra to pairs of oppositely charged molecules and to excimer states. For the crystalline ground state, we deduce a CT transition energy of 2.14 eV along the stacking direction, significantly below previous theoretical estimates.

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