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Optical properties of perfluorotetracene (PFT) crystal polymorphs and Perfluoropentacene (PFP) co-crystals

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The family of perfluorinated acenes is gaining popularity among organic materials for optoelectronics. Since the electronic and optical properties of molecular solids are crucially dependent on their packing motifs, it is crucial to consider crystalline phases in the simulations to understand the structure-property relationships of these materials, especially regarding electronic correlations and excitations. Here, we investigate from first principles by means of density functional theory and many-body perturbation theory the electronic structure and the optical excitations of two crystal polymorphs of perfluorotetracene, considering for comparison tetracene and the corresponding isolated molecules. In addiction to that the triclinic pentacene:perfluoropentacene co-crystal is including in our study. This way, we can assess the effects of fluorination as well as of the crystal periodicity. In the polymorphs crystals we find that the absorption spectra are only mildly influenced by the packing motif. However, our analysis gives insight into the exciton binding energies as well as the spatial distribution of the excitons. We inspect not only the first excitations but also the higher-energy ones, thus providing an all-around understanding of the optical excitations in these materials. Interesting in the case of molecule co-crystal, we demonstrate that the nature of optical excitations cannot be reproduced by a molecular cluster model where the first excitation is unambiguously polarized along the short molecular axis.