Phenylated Acene Derivatives as Candidates for Intermolecular Singlet Fission

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Singlet fission (SF), a spin-conserving process where one singlet exciton is converted into two triplet excitons, may improve the efficiency of organic photovoltaics. Only a few materials have been experimentally observed to undergo intermolecular SF, most of which are acenes and their derivatives. Using many-body perturbation theory in the GW approximation and the Bethe−Salpeter equation, we systematically investigate the electronic and excitonic properties of tetracene, pentacene, and their phenylated derivatives in the gas phase and solid state. Their potential for SF is evaluated with respect to the thermodynamic driving force and the singlet exciton charge-transfer character. In both the gas phase and solid state, pentacene and its derivatives are more promising than tetracene analogues. Within a family of molecules containing the same acene backbone, increasing the number of phenyl side groups is detrimental for the SF driving force in the gas phase. However, in the solid state, the SF driving force and the exciton character are modulated by intermolecular interactions present within different packing arrangements. Molecules with a higher number of phenyl side groups often form crystals with less cofacial interactions between the acene backbones. These crystals are found to exhibit a higher SF driving force and a higher degree of singlet exciton charge-transfer character. In particular, 5,7,12,14-tetraphenylpentacene, 1,4,6,8,11,13-hexaphenylpentacene, and 1,2,3,4,6,8,9,10,11,13- decaphenylpentacene emerge as promising candidates for intermolecular SF in the solid state.