

Influence of the crystal packing in singlet fission: one step beyond the gas phase approximation

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Singlet fission (SF), a multiexciton generation process, has been proposed as an alternative to boost the efficiency of current solar cells since in principle two pairs of charge carriers can be generated per single absorbed photon. In this process, two singlet-coupled triplets (1TT) are formed from a photoexcited chromophore combined with a neighbour in the ground state (S_1S_0). The probability of SF to occur in any system can be related to the electronic coupling between these two states.

Theoretical modelling of SF is often done by employing a gas-phase dimer model, the minimal system where SF can occur.[1,2] This model has shown its utility to study this process, but it does not always cover all the physics and the effect of the surrounding atoms has to be included in such cases. Here, we study the effect of the crystal packing on (1) the charge transfer-mediated electronic couplings between the S_1S_0 and 1TT states calculated with a non-orthogonal configuration interaction approach and (2) the excited state character of different arrangements within the crystal structure. Since in reality the process takes place in the crystalline solid phase, knowing how the coupling gets affected by the crystal environment becomes crucial.

We focus our attention on tetracene and 1,3-diphenylisobenzofurane (DPBF), two chromophores known to exhibit SF. DPBF is of particular interest since it crystallizes in two different polymorphs with one of them exhibiting a much higher SF efficiency than the other one. Besides the influence on the couplings, we also offer an insight on how the excited state character of identified dimers and trimers is altered by the presence of the environment by means of an excited state analysis. Our study aims to explore how the excited state analysis can be used to unravel differences between the excited state character in the two polymorphs, and explain their rather different SF yields.[3]

[1] L. E. Aguilar Suarez, R. K. Kathir, E. Siagri, R. W. A. Havenith, S. Faraji, *Adv. Quantum Chem.* 79, 263-287 (2019)

[2] L. E. Aguilar Suarez, M. F. S. J. Menger, S. Faraji, *Mol. Phys.* 118, e1769870 (2020)

[3] L. E. Aguilar Suarez, C. de Graaf, S. Faraji. *Phys. Chem. Chem. Phys.* **under revision**