# Effect of the silicon substrate on singlet and triplet exciton binding energy in crystalline tetracene

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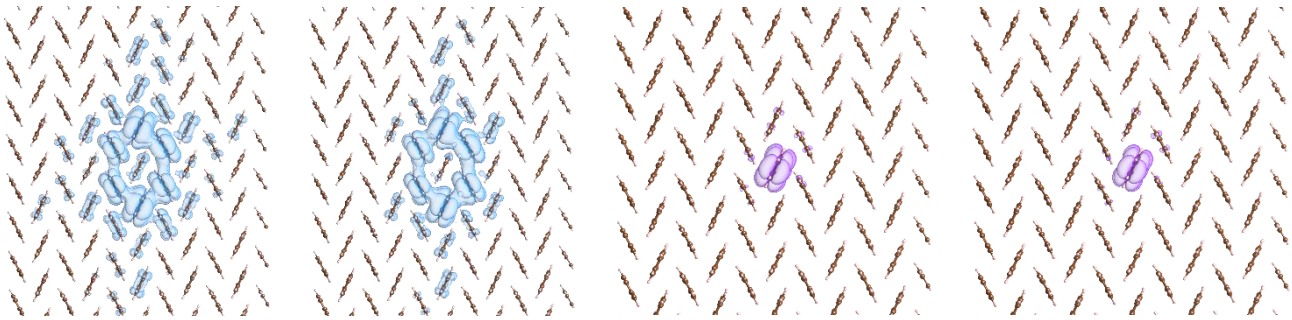
Although singlet fission (SF) in organic crystals has been first observed back in 1965 [1], it draws more and more attention nowadays due to its possible applications in photovoltaic devices. The main feature of this effect is an efficient down-conversion of one singlet excited state into two triplet excitons which can in turn be converted into two pairs of charge carriers [2]. Many proposals for the photovoltaic devices based on the SF effect consider hybrid inorganic-organic semiconductor heterostructures, for instance, tetracene (Tc) and silicon (Si) [3, 4]. The aim of this work is to estimate the effect of the substrate on the exciton binding energies and its implications for the SF effect. Our methodology is based on the many-body perturbation theory in the GW approximation and the Bethe-Salpeter equation. The electron-hole correlation function, shown in Fig. 1, indicates that the singlet exciton is more delocalized compared to the triplet exciton, as is expected. For the singlet, most of the electron density is located on the first nearest neighbours, while for the triplet the electron and hole are located on the same molecule. Hence, the lowest singlet state has a charge transfer exciton character, and the lowest triplet exciton has a Frenkel exciton character. For the suspended tetracene layer, the probability to find an electron on the same molecule with a hole is higher due to larger exciton binding energy (compare Fig. 1 a and b). The contact with Si substrate increases the charge transfer character by reducing the binding energy that is caused by the screening effects.



a) b) c) d)

Fig. 1 Electron-hole correlation function for the lowest singlet (a, b) and triplet (c, d) exciton states. The data in a) and c) are for the suspended Tc layer, and b) and d) are for Tc on the Si substrate.

[1] S. Singh et al., *J. Chem. Phys.*, **42**, 330 (1965)

[2] A. Rao and R. H. Friend, *Nat. Rev. Mat.*, **2**, 17063 (2017)

[3] R. W. MacQueen et al., *Mater. Horiz.*, **5**, 1065 (2018).

[4] M. Einzinger et al., *Nature*, **571**, 90 (2019)