

Crystal field effect on pentacene charge-transfer excitons

Piotr Petelenz, Mateusz Snamina

The K. Gumiński Department of Theoretical Chemistry
Jagiellonian University, Ingardena 3, 30-060 Kraków, Poland
E-mail: petelenz@chemia.uj.edu.pl

A dimer is the simplest model on which the mechanism of singlet exciton fission in crystalline pentacene may be studied. One of the relevant issues is the role of charge transfer (CT) states in this process. Conclusions in this regard critically depend on the energy gap between the triplet pair state (tt) and the CT configurations (ac and ca) of the model dimer [1], which is inevitably affected by the polarizable crystalline environment. The dimer eigenstates are strongly influenced by the value of the splitting between the dimer CT configurations of opposite polarities (ac and ca). According to *ab initio* calculations [1], it amounts to 0.8 eV, contrary to our estimate of 0.23 eV, based on the self-consistent microelectrostatic scheme [2]. This inspired us to use instead the new Self Consistent Charge Field approach (SCCF, [3]) that harnesses routine quantum chemistry software to do the requisite calculations, automatically including molecular polarization and taking full advantage of large basis sets. With the 6-311++G** basis, it yields the ac - ca splitting of 0.65 eV as, close enough to the best *ab initio* value [1].

Then we applied the same method to a ten-molecule cluster containing the original model dimer as its core; the interaction with more distant molecules forming the rest of the crystal was treated in the ZINDO approximation [2]. The results indicate that the large ac - ca gap predicted for the dimer is almost totally obliterated (to the level of 0.025 eV) in the crystalline environment.

This unexpected effect is a consequence of the fact that in the crystal the intra-dimer charge-quadrupole (CQ) interaction, mediating the ac - ca splitting, is counterbalanced by similar interactions with the surrounding molecules. For the higher-energetic CT configuration (ca) of the dimer, the CQ term is negative and concurs with polarization to yield a large red shift, bringing this state into close neighborhood of the lower ac configuration, for which, in contrast, the two terms compensate each other.

[1] T. Zeng, R. Hoffmann, N. Ananth, J. Am. Chem. Soc. **136**, 5755–5764 (2014).

[2] E. V. Tsiper, Z. G. Soos, Phys. Rev. B **64**, 195124 (2001).

[3] M. Snamina, P. Petelenz, Self Consistent Charge Field method for charge-transfer excitons (accompanying abstract).