Project title: Ultrafast electronic processes in molecular crystals

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Current state of the art

Molecular crystals show rich exciton dynamics, including intersystem crossing, charge transfer, bimolecular annihilation and singlet fission [1]. The latter process, in particular, has recently attracted intense research as it holds promise to improve the efficiency of organic solar cells [2, 3]. In this process, a singlet exciton generated by absorption of a photon splits into two triplet excitons. Despite current research, the detailed evolution of the process is still unclear. In particular, the role and nature of a triplet pair state as an intermediate are yet to be clarified.

Research goals and working program

This issue will be addressed in the present project by means of ultrafast transient absorption spectroscopy of organic crystals. By varying the polarisation of the pump and probe pulses relative to the crystal axis, the transition dipoles associated with the different states and species will be imaged in time. It should be possible to identify these states from their spectra and an accurate knowledge of the orientation of the transition dipoles.

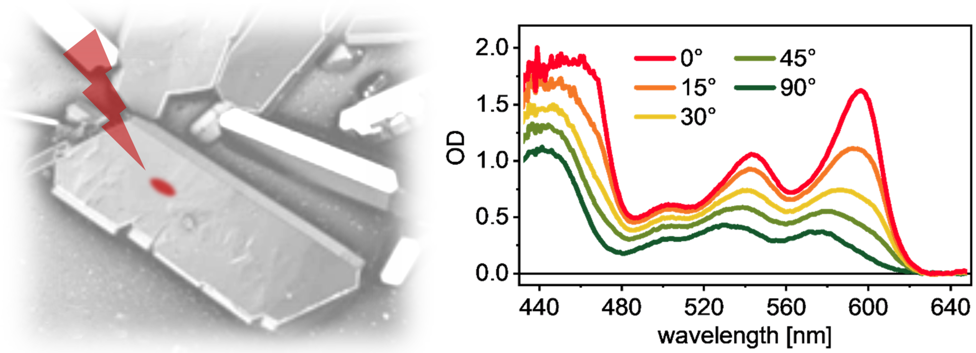

Figure 1: Left: Organic molecular microcrystals of a perylene bisimide dye grown from solution. Right: Polarisation resolved absorption spectrum of the crystal showing two Davydov components and revealing the orientation of the associated transition dipoles.

The key lies in performing the transient absorption measurements on microcrystals, see Figure 1. They are rather easy to prepare and they have a thickness of some ten nanometers to about one micrometer. These thicknesses are well suited for absorption measurements and pump-probe experiments in transmission. This is demonstrated in Figure 1 for stationary absorption spectra of microcrystals made of a perylene bisimide dye. The polarisation dependence points to two Davydov components and reveals the orientation of the associated transition dipoles.

Transient absorption spectra will be recorded by means of a home built pump-probe microscope featuring a non-collinear optical parametric amplifier to generate sub-30 fs excitation pulses. Using an achromatic half-wave plate and a rotational mount for the microcrystals allow the pump polarisation and the optical axes in the sample plane to be adjusted freely. With the help of a microtome, we can cut the crystals along almost any crystal plane. In this way three dimensional mapping of the transition dipoles is possible. Together with the spectral signatures of the transiently populated states, this information should allow for an identification of these states. The observed kinetics will be analysed using rate models in order to reveal the mechanisms responsible for the different relaxation steps [4].

The analysis of the experiments will be supported by advanced ab-initio simulations which will be conducted by our collaboration partner Oliver Kühn and his coworkers.

[1] H. C. Wolf and M. Schwoerer, *Organic Molecular Solids*, Wiley-VCH, 2007.

[2] J. J. Burdett and C. J. Bardeen, *Quantum beats in crystalline tetracene delayed fluorescence due to triplet pair coherences produced by direct singlet fission*, J. Am. Chem. Soc. **134**, 8597 (2012).

[3] E. A. Wolf and I. Biaggio, *Geminate exciton fusion fluorescence as a probe of triplet exciton transport after singlet fission*, Phys. Rev. B **103**, L201201 (2021).

[4] S. Wolter, K. M. Westphal, M. Hempel, F. Würthner, O. Kühn and S. Lochbrunner, *Low temperature exciton dynamics and structural changes in perylene bisimide aggregates*, J. Phys. B: At. Mol. Opt. Phys. **50**, 184005 (2017).