Mapping exciton localization in linear TDBC aggregates by two-dimensional electronic spectroscopy

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Exciton dephasing and relaxation is observed by two-dimensional electronic spectroscopy (2DES) in linear aggregates of TDBC molecules. Combining global analysis with quantum mechanical simulations, we distinguish dephasing from exciton relaxation and quantify the dynamics of exciton localization on specific low energy segments.

TDBC, which is sodium salt of 1,18-diethyl-3,38-bis~4-sulfobutyl-5,58,6,68-tetrachloro-benzimidazolo carbocyanine, forms linear aggregates in aqueous solution, giving rise to the formation of quasi one-dimensional excitons with a delocalization length of about 15 units at room temperature and a strong intermolecular coupling of $2V \approx 2500$ cm^{-1} [1]. In order to resolve the details of exciton relaxation, we apply two-dimensional electronic spectroscopy (2DES) using ultrabroadband visible pulses in a partially collinear geometry. The high time resolution of the setup allows us to characterize population dynamics by tracing the temporal evolution of off-diagonal spectral contributions to the 2DES spectra (Fig.1). By combining global analysis techniques [2] with quantum mechanical simulations [3], we distinguish the dynamics of stimulated emission and ground state bleach which allows us to trace exciton localization on specific low energy sites on the chain with reduced coupling to adjacent segments.

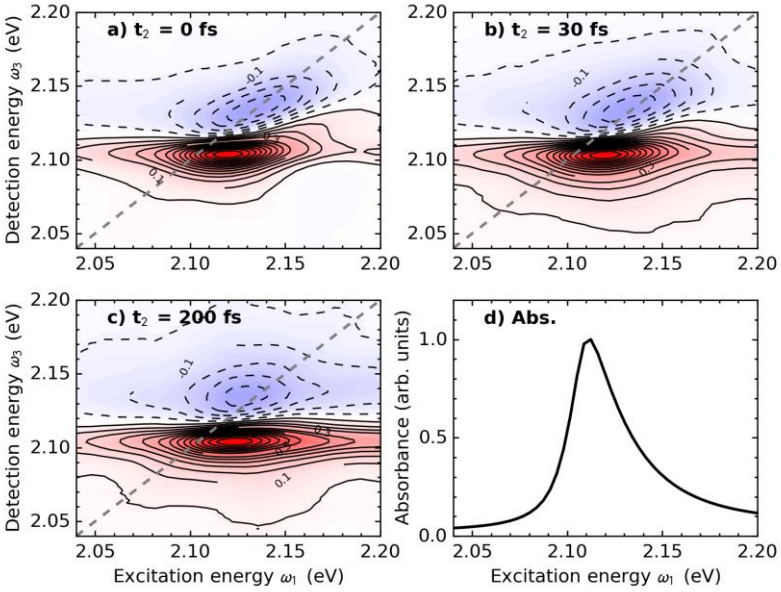

Fig.1 (a)-(c) Two-dimensional electronic spectra of TDBC aggregates in water at room temperature at different waiting times t_2, as indicated. In panel d) the corresponding ground state absorption spectrum is shown.

[1] M. van Burgel et al., J. Chem. Phys. **102**(1), 20-33 (1995).
[2] M. Maiuri et al., J. Chem. Phys. **142**(21), 212433 (2015)
[3] I. Stiopkin et al., J. Phys. Chem. B **110**, 20032-20037 (2006)