Unraveling the Photodynamics of Donor-Acceptor Co-Crystals with Ultrafast Transient Absorption Spectroscopy and Ab Initio Molecular Dynamics

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Unraveling the photodynamics of molecular crystalline materials poses many challenges for spectroscopy due to broad and overlapping spectral features arising from many states and pathways. This leads researchers to make many assumptions about the dynamics of a system in choosing an appropriate kinetic fitting model. On the theoretical side, electronic structure methods are either prohibitively expensive or underdeveloped for computing the excited state structure of molecular materials, especially states that exhibit charge transfer. Researchers must therefore perform calculations of excited electronic states using truncated models of molecular materials. Here we present a joint experimental-theoretical approach to bridging the gap between the photodynamics of a molecular material and its constituent molecules. We focus our efforts on quantifying the timescales and mechanisms of photoexcitation in donor-acceptor co-crystals vs. donor-acceptor dimers where the lowest-lying excited state is characterized by charge transfer from the donor to the acceptor. Specifically, we investigate crystals formed from 4-(1-naphthylvinyl) pyridine (Npe) and 1,2,4,5-tetracyanobenzene (TCNB), which have been used as 1D waveguides in next-generation optoelectronic devices. We employ ultrafast UV pump, UV-Vis probe transient absorption spectroscopy to unravel the time-resolved spectroscopic signatures of the photodynamics in both the crystalline material and donor-acceptor dimers in solution. We perform electronic structure and excited state dynamics calculations of the dimers to inform kinetic fitting models and assign the spectral features. The photodynamics of the crystal vs. dimer systems are strikingly similar, enabling unprecedented insights into the formation and evolution of charge transfer excitons in the crystalline systems. Furthermore, we perform parallel analyses of the kinetic fits based on three physically-feasible models, finding that a branched decay model is most likely and involves intersystem crossing occurs within ~900 ps. Finally, we outline the differences in the spectroscopy and dynamics of the material vs. dimer, emphasizing the strengths and limitations of the model.