

Excited state dynamics of BODIPY-based acceptor-donor-acceptor systems: a combined experimental and computational study

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Donor-bridge-acceptor systems based on boron dipyrromethene (BODIPY) are attractive candidates for bio-imaging and sensing applications because of their sensitivity to temperature, micro-viscosity and solvent polarity. The optimization of the properties of such molecular sensors requires a detailed knowledge of the relation between the structure and the photophysical behavior in different environments. In this work we have investigated the excited-state dynamics of three acceptor-donor-acceptor molecules based on benzodithiophene and BODIPY in solvents of different polarities using a combination of ultrafast spectroscopy and DFT-based electronic structure calculations. Transient absorption spectra show that upon photoexcitation an initial excited species with an induced absorption band in the near-infrared regime is formed independent of the solvent polarity. The subsequent photophysical processes strongly depend on the solvent polarity. In non-polar toluene this initial excited state undergoes a structural relaxation leading to a delocalized state with partial charge transfer character, while in the more polar THF a fully charge separated state is formed. The results clearly show how factors such as donor-acceptor distance and restricted rotational motion by steric hindrance can be used to tune the excited state photophysics to optimize such systems for specific applications.