Symmetry, disorder and the excited-state dynamics of multipolar conjugated molecules.

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Abstract

There is presently an intense interest in multipolar conjugated molecules for various applications, such as two-photon induced polymerization, organic photovoltaics and OLEDs. Although these molecules have not permanent dipole moment, their fluorescence exhibits a strong solvent dependence, pointing to a dipolar character of the emissive state. This was explained in terms of an excited-state symmetry breaking (ESSB),[1] i.e., by the localisation, at least partial, of the excitation on a single donor-acceptor branch of the molecule. Some of our efforts to visualize this phenomenon in real time using various ultrafast spectroscopic techniques will be presented.[2,3] Our results reveal the crucial role of the environment in this process. The conditions required for ESSB to be operative as well as its chemical relevance will also be discussed.[4]

Most of these molecules exhibit significant torsional flexibility in the electronic ground state but not in the excited state because of conjugation. This leads to an inhomogeneous broadening of their electronic absorption band and allows for the selective excitation of sub-populations with different geometries. Recent results on the effect of torsional disorder on ESSB,[5] and on the possibility to tune the excited-state properties of conjugated dyes, e.g., their intersystem crossing dynamics, using different excitation wavelengths[6] will be presented.

References:

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