Solvent Tuning of Photochemistry upon Excited-State Symmetry Breaking

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Excited-state symmetry breaking (ESSB) is a photophysical phenomenon that underlies fundamentally unstable nature of multipolar excitons in presence of high fluctuating electric fields.[1] Upon photoexcitation of quadrupolar/octupolar molecules, that are essentially two/three oppositely oriented dipolar charge-transfer arms, the initially prepared symmetric and delocalized excited state quickly asymmetrizes and can collapse onto a single arm. This behavior is caused by femtosecond to picosecond motions of surrounding solvent molecules.[1-3] Extent of ESSB can be fine-tuned by various parameters of solvent or solute itself.[4-5] At the same time, in non-polar media, the multipole pertains its symmetric and delocalized character for the entire excited-state lifetime.

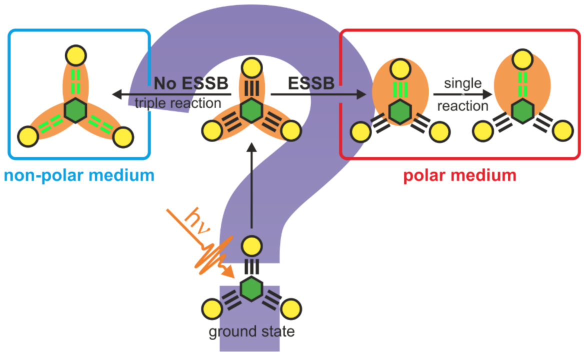

Figure 1. (De)Coherence and (de)localization vs. functional (a)symmetry dilemma.

Several interesting photochemical questions emerge. How can symmetry breaking affect the ensuing intramolecular photochemistry? If excited state is so different in polar versus non-polar media, can different photoproducts be obtained by changing the solvent appropriately (Figure 1)? Since a symmetric excited state represents a coherent delocalized exciton, whereas the localized exciton is the one that underwent decoherence, it is a broad question of functional symmetry/asymmetry of coherent excited states. Can ESSB work as a switch between coherent and incoherent modalities? Here, using an array of femtosecond broadband techniques, we provide an answer to these questions from the perspective of a class of multipolar charge-transfer molecules.[6]

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