

Project Title: Simulation of dynamics and nonlinear spectroscopy of novel polycyclic heteroaromatic compounds in gas-phase, solution and thin films for application in photoconversion through Singlet Fission

Research Project: Singlet fission (SF), a process by which a photoexcited bright state in organic chromophores splits into a pair of free triplets (T). The phenomenon, mediated by a dark “triplet-pair” state (TT) in which the two triplets are correlated into an overall spin-zero configuration, has the potential to overcome thermalization losses by generating two electron-hole pairs per single high-energy photon absorbed, as it renders conceivable single-junction devices beyond the Shockley-Queisser limit in terms of power conversion efficiency.

The quest for SF eligible materials is very challenging as the materials have to fulfill a number of non-trivial (and sometimes contradicting) conditions. Beside thermodynamical conditions such as the energy matching of singlet and triplet pair ($ES \geq 2ET$), another fundamental requirement is a sufficiently strong coupling between chromophores in order to assure SF dominates over competing processes. Thus, packing in crystals is of utmost importance for allowing strong electronic coupling. Lately, intramolecular SF (iSF), reported for covalently linked SF chromophores and for conjugated polymers has attracted attention. Conjugated polymers exhibit a unique electronic structure where the lowest-lying excited state (ES), which shares the same symmetry as the ground state (denoted A_g), can be equivalently described as a pair of triplets bound into an spin-zero state, suggesting intramolecular (TT) states.

A huge advantage of iSF chromophores is that the necessary interchromophore coupling is encompassed within a single molecule. This eliminates the need for tenuous crystal engineering as it is much easier to incorporate desired electronic properties in molecules and polymers. However, the simple architecture comes at a cost. One of the limiting properties of iSF materials is the rapid annihilation of the triplet pair (<1 ns) precluding the formation of free triplets. This can be ameliorated by incorporation into films. In the last couple of years SF has been documented in thin films of small poly-heteroaromatic chromophores designed to favor ultrafast (sub-ps) intramolecular (TT) formation. The preclusion of polymer engineering, together with the commercial availability and/or straightforward synthesis/functionalization, makes such compounds very appealing for industrial applications. While it is hypothesized that incorporation in thin films opens an ultrafast (ps) intra-to-intermolecular (TT) formation pathway which competes with internal conversion in the monomers, fundamental understanding of the mechanism is lacking.

The aim of the project is to disentangle some of the unsolved aspects governing the ultrafast molecular mechanism of SF in small poly-heteroaromatic chromophores and their aggregates by means of theoretical modeling. Specifically, it will be investigated what is the role of intermediate dark states, such as low lying charge transfer and doubly excited states, in the (TT) formation and how they facilitate the generation of free triplets in thin films. This will be realized by spectroscopy simulations – transient absorption and two-dimensional electronic spectroscopy – from first principles based on short-time multidimensional quantum dynamics driven by Hamiltonians parametrized with multi-reference methods, thereby explicitly taking into account solvent effects by means of hybrid Quantum Mechanics / Molecular Mechanics protocol.

The research will be conducted on benzodithiophene-monothiophene-1,1-dioxide (BTDO1) and benzodipyrrolidone (BDPP) that excel in terms of photostability and extinction coefficients while exhibiting triplet energies comparable to those of the SF archetype acenes.

Activity plan:

1. Multireference electronic structure calculations will be performed in gas-phase at the RASSCF/RASPT2 level for BTDO1, BDPP and derivatives with electron-donating and -withdrawing functional groups with full- π active spaces to obtain a reference for the valence manifold. These calculations will be used to benchmark reduced- π active spaces.
2. The effect of the solvent polarity on the electronic structure of the parent and functionalized BTDO1 and BDPP will be studied with a hybrid QM/MM scheme with explicit solvent.
3. Multi-dimensional LVC Hamiltonians will be parametrized for BTDO1, BDPP and for one functionalized derivative thereof in gas-phase and in solvent. Necessary quantities, such as intra- and inter-state vibronic couplings will be obtained at the RASSCF/RASPT2 level. The effect of the solvent polarity will be considered by re-parametrizing the LVC Hamiltonian for different solvent arrangements.
4. The LVC Hamiltonian will be coupled to the MCTDH protocol to simulate the ultrafast dynamics in gas-phase and in solvent
5. UV/Vis transient spectroscopy simulations will be performed on top of the quantum dynamics. Using a crystal structure of either BTDO1 or BDPP the model Hamiltonian for a single molecule will be extended to a unit cell to study the formation of triplet-pair states localized on different units in an aggregate. The Hamiltonian will be used to simulate quantum dynamics and transient spectroscopy in the aggregate.