University of Louisville
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Literature Seminar

When: November 20, 2023
Time: 3:00 p.m.
Location: CBLL-16

Singlet Fission: Progress and Pathways

Abstract:

Singlet Fission (SF) is a photophysical reaction in which a singlet excited state upon collision with a neighboring singlet ground state produces two triplet states. The SF process was known and studied since 1965, and its interest in research has been undergone resurgence due to its application in photovoltaic devices. For successful application of the SF process in solar cells the electronic coupling between initial S_1S_0 and final ^{1}(TT) state has to be significantly large which also depends upon the overlaps of the frontier orbitals corresponding to the chromophore molecules. The molecules with conjugated π bonds, e.g., the members of the acene series, anthracene, tetracene, pentacene etc. are the commonly developed chromophores for optoelectronic applications. The electronic coupling in these types of molecules can be limited due to the orthogonal π and π* overlaps which leads to large symmetry cancellation of SF couplings. The electronic coupling in these types of molecules can be enhanced by the presence of nonbonding orbitals of different symmetries. Secondly, the SF process may occur in different types of dimers of these types of molecules, e.g., for pentacene, where the pentacene monomers may be spatially separated or covalently connected. In such type of dimers, Intramolecular SF is an important process as well as its reverse process, Triplet-triplet Annihilation (TTA). The SF and TTA couplings and their rates depend upon the relative position of pentacene monomers in the dimer molecules. The intramolecular triplet pair generated from intramolecular SF also needs to be separated into intermolecular triplet pair for successful application in photovoltaic devices. Recently, Pyrazino[2,3-g] quinoxaline-1,4,6,9-tetraoxide was designed as the smallest intramolecular SF chromophore which undergoes fastest SF with a 16 fs time scale. Subsequently the generated intramolecular triplet pair upon collision with a neighboring ground state chromophore separates into two intermolecular triplet pairs with an ~80% probability. So, ultimately the SF is an important aspect of chemistry research from both theoretical and experimental viewpoints and it also proposes great diversity in different aspects of practical applications.

References:

1) Yang et al; Enhancing Singlet Fission Coupling with Nonbonding Orbitals; *Journal of Chemical Theory and Computation* 2022 *18* (2), 1017-1029
2) Lin et al ; First Principle Prediction of Intramolecular Singlet Fission and Triplet Triplet Annihilation Rates; *Journal of Chemical Theory and Computation* 2019 *15* (4), 2246-2253
3) Pradhan et al ; Triplet Separation after the Fastest Intramolecular Singlet Fission in the Smallest Chromophore; *Journal of Chemical Theory and Computation* 2023 *19* (7), 2092-2101