Singlet Fission in Conjugated Oligomer Systems

Oliver Lin — Literature Seminar — November 18, 2020

The inspiration of the working mechanisms in current organic light emitting diode (OLED) technology can be tracked back to the 1963, when Kepler *et al*. discovered organic small molecules' delay fluorescence via triplet-triplet annihilation, in which long-lived triplet excitons are "fused" into a singlet and fluoresce at a high quantum yield.[1] The reverse process, reported in 1965 and coined as singlet fission later in the 2010s,[2–4] is currently bringing another revolution in organic optoelectronic by breaking conventional one-photon-to-one-electron conversion in photovoltaics, also known as the Shockley-Queisser limit. By splitting one high-energy singlet in half to two triplet excitons and thus two electron charges by organic chromophores, such multiexciton generation (MEG) process reserves most of the photon energy and is considered one of the major strategies for future solar energy harvesting. With the fruitful studies of ultrafast optical spectroscopy and theoretical simulation in the past two decades, the field has obtained enough science to depict the details of the process and starts to show successfully results in extending the knowledge to various chromophores. Beyond single, small molecules, this talk will make a stride to discuss how singlet fission process manifests in oligomer systems, or covalently bound chromophores, and peak into what the field has learned from them in both aspects of fundamental understandings and implications to real-world applications.

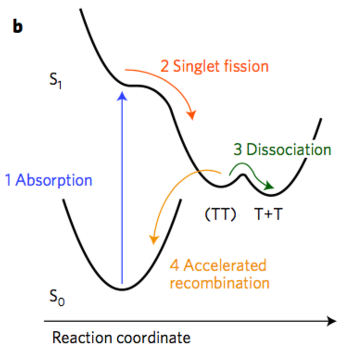

Figure 1. Energetic and pathway scheme of singlet fission.

Singlet fission process has been found in various polycyclic aromatic hydrocarbons (PAH), as long as their first excited triplet state (T_1) energy is about half of the first singlet excited state (S_1) energy.[5] Yet, tetracene and pentacene, despite of the similarity in chemical structures and in high triplet yield, as the first few PAH molecules being first studied in the 1960's, were found to manifest singlet fission process very differently, e.g. rate of fission, k_{fis}, of tetracene is about 4 magnitude lower than that of pentacene (0.0091 ps^{-1} v.s. 12.5 ps^{-1}).[6] Theoreticians battled to generalize this bizarre phenomenon with every detail throughout the reaction. In experiments, time-resolved 2-photon photoemission spectroscopy (tr-2PPE) generated an concise, observable explanation that is coherent with theories and presented the reaction to be Equation (1). [7]

$$[S_1 \Leftrightarrow ME] \rightleftharpoons ME' \rightleftharpoons T_1 + T_1 \qquad (1)$$

The process upon light absorption starts with a superposition state of S_1 and ME (multi-exciton, or charge transfer, CT, state) such that when that quantum coherence is lost, ME relaxes to correlated ME’ state and then uncorrelated T1 states at two chromophores at ultrafast time scale (~100fs). It turned out the different kinetics between tetracene and pentacene is resulted from the driving force (ΔG) of the actual “fission” step, (Step 2 in Figure 1): endothermic (+150meV) for tetracene vs. exothermic (-110meV) for pentacene. By not only characterizing the ME’ state conclusively but also solidifying the energetics of the reaction being the energy difference between S1 and twice the T1 state, the authors developed a general guideline to evaluate fission kinetics of this crucial step for future novel materials.

While this exact working mechanism was being figured out, engineers at MIT demonstrated the first singlet-fission photovoltaic cell in 2013. An 109% external quantum efficiency (EQE) was measured at 650-700nm region, the overall device power conversion efficiency (PCE) was only 1.8 ± 0.1%.[8] The major of limit for higher PCE in this device was due to severe carrier recombination at repeatedly thermal-deposited thin film acceptor interfaces. To alleviate the short range of carrier transportation of organic molecules, the field of organic photovoltaics has paved the way: by using semiconducting polymers, or covalently bound chromophores, in bulk heterojunction (BHJ) device configuration. Since singlet fission beyond single, small molecular systems is still nebulous, the field has to start from scratch and centers around how extended chromophores motifs influence, for example, the ME’→ T1 transition as well as the triplet excitons decay pathways, kinetics, and energy transfer mechanisms.

In this talk, two cases of study in singlet fission oligomers are discussed, including perylene oligomers and phenylene-bridged bipentacene, their structures shown in Fig. 2. Korovina *et al.* reported prolonged triplet exciton lifetime as the perylene monomer number (n = 1-4) increases, which agrees with the observations in tetracene oligomer systems.[9,10] The authors further presented two interesting manifestations of singlet fission in only the longer oligomers (n=3, 4). The spatial separation of two triplet exciton wavefuctions at two ends of oligomers facilitated the dissociation process. Furthermore, the endothermic torsion distortion away from more stable planar conformation at the alkyne bond locked in the wavefunction separation, which greatly reduced the triplet-triplet recombination or annihilation rates. The study demonstrated that, though perylene molecule exhibits endothermic fission process, by extending the chromophore numbers and locking in the uncorrelated T1 states, it is still possible to modify the rather intrinsic property from chromophore building blocks and control the behavior of triplet excitons. The second case of precise control of the distance between two chromophores, pentacene in this case, by phenylene linkers (n= 0-2) showed that as n number increased,

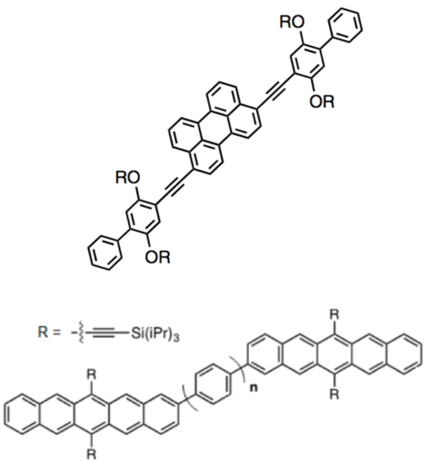

Figure 2. Molecular structures of two sets of simple yet representative oligoners for studies of singlet fission in extended conjugation systems.

dissociation rate (ME'→ T1) increased and yet singlet fission process was slowed down (longer ME ⇌ ME' lifetime).[11] And the later result further helped scientists to resolve the spin-flip process using time-resolved electron spin resonance (ESR) experiment and showed experimentally for the first time that quintet states unambiguously participate in singlet fission proess.[12] As a result, by a tiny step of extending small molecules to oligomers, the scientists were not only able to support the potential of singlet-fission-active BHJ solar cell but also gain more insight into the fundamental mechanisms of triplet excitons in organic systems.

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