Extracting Solar Energy from Singlet Fission Materials

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Singlet Fission is a process wherein a highly excited spin-singlet exciton divides its energy to form a pair of spin-correlated triplet excitations. We report ultrafast transient absorption and electronic sum frequency generation experiments that establish structure-function relationships that allow triplet exciton formation and extraction from perylene diimide thin films.

A primary loss mechanism that impacts the performance of silicon photovoltaics is the thermalization of charge carriers produced by photons with energy in excess of silicon's bandgap. An appealing strategy to negate these losses is to coat silicon with materials that capture high energy photons and use their energy to undergo singlet exciton fission (SF), a process that generates a pair of spin-triplet excitons from a single photoexcitation (Fig. 1). Here, we report on ultrafast transient absorption measurements performed on perylene diimide (PDI) thin films. PDI monomers possess the correct energetic alignment of singlet and triplet energies to undergo SF, however excitonic interactions between neighboring molecules in the solid state can strongly impact the energetic driving force for this process. By systematically altering functional groups placed at the PDI core's imide positions, we can shift the preferred packing structure of these materials and their level of excitonic coupling. We find that subtle shifts in PDI intermolecular structure, particularly along the long axis of the PDI core, have a substantial impact on SF rates and yield. We also report electronic sum frequency generation (ESFG) measurements carried out on thin films of small molecule organic semiconductors. While PDI triplet excitons possess an energy sufficient to resonantly transfer to silicon, band bending of either the PDI or silicon density of states near their interface can strongly impact this process. As an even order technique, ESFG can probe the PDI density of states at the silicon interface. However, this requires isolating the portion of the emitted ESFG signal that originates from the buried interface. As such, we have built an interference model that accounts for ESFG emitted by each interface in a sample and have used this to describe ESFG spectra of copper phthalocyanine (CuPc) thin films deposited on SiO_2 (Fig. 2).[1] Work is underway to extend this approach to time-resolved measurements that examine excited state dynamics at the PDI:silicon interface.

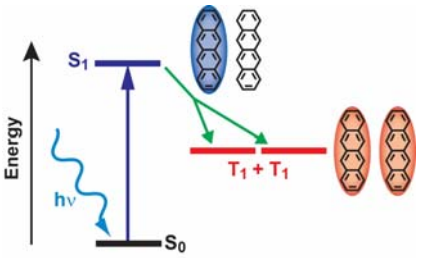

Figure 1: SF materials can prepare two electrons from a single photon by generating triplet pairs.

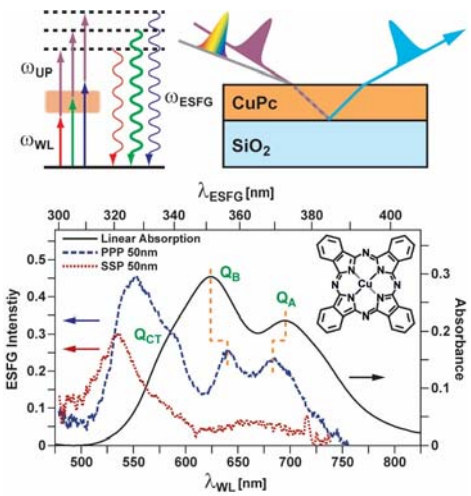

Figure 2: Comparison of ESFG and absorption spectra of a 50 nm CuPc film (structure inset).

[1] R. Pandey *et al.*, *J. Phys. Chem. Lett.* (2016) **DOI:**10.1021/acs.jpclett.6b00178.