Ultrafast dynamics of singlet fission in tips- tetracene nanoparticles

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Singlet fission is the spin allowed conversion of a photo-generated singlet exciton into two triplet excitons in organic semiconductors which helps in bypassing thermodynamic limitations of single-junction photovoltaic cells and increases their power conversion efficiency. In recent years, singlet fission has been extensively studied in acenes such as pentacene, tetracene, anthracene and their derivatives such as diphenyltetracene (DPT), 6,13-bis(triisopropylsilylethynyl) pentacene (TIPS- pentacene), TIPS- tetracene and so on. It is currently an accepted notion that the photo physical dynamics of crystalline organic materials differ from that of more amorphous forms such as nano-aggregates[1,2].

In this study, we focus on the ultrafast dynamics of nanoparticles of TIPS- tetracene, tens of nanometers in size. Stern *et al.*[3] has previously shown that triplet formation dynamics of TIPS-tetracene in solution is based on an indirect mechanism involving the formation of triplet intermediate states (TT). A recent study[4] on singlet fission in films of TIPS- tetracene investigates the influence of morphology on the rate and mechanism of triplet formation. Interestingly, the nanoparticles in the current study exhibit crystalline morphology at their core, but also an amorphous exterior (Figure 1), which is quite unique to study singlet fission in. We find that the early time dynamics are highly dependent on pump-energy, suggesting that the pathway for singlet fission in these nanoparticles are strongly influenced by the initial sub-100 fs relaxation away from the Frank-Condon point. Singlet excitons that are produced in the nanoparticles give rise to TT states that are converted to free triplets in tens of nanoseconds (Figure 2). The long lived nature of the triplets formed is promising for transfer of charges to an inorganic layer of appropriate bandgap in a solar cell. We present outcomes from various steady-state and transient spectroscopic measurements along with structural analysis of the nanoparticles. Our results demonstrate that these nano- aggregates are a versatile and highly tunable platform to study singlet fission.

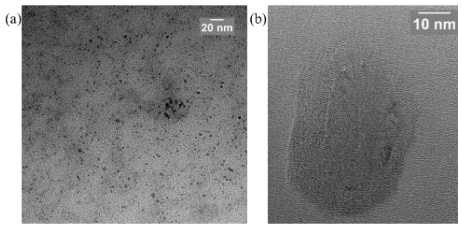

Figure 1. Transmission electron microscopy images of TIPS- tetracene nanoparticles (a) one day post-synthesis, and (b) 75 days post- synthesis. All figures are calibrated to the scale bar shown in the index.

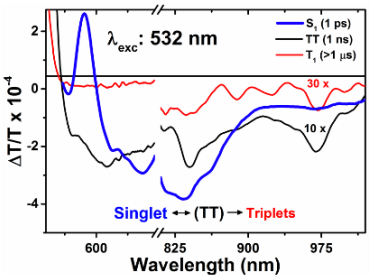

Figure 2. Transient absorption spectra of singlets (blue), TT states (black) and free triplets (red) when excited with a pump energy of 532 nm. Time delays associated with individual spectra are shown in legend.

References

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[3.] H. L. Stern *et al.*, *Proc. Nat. Acad. Sci.*, **112** (25): 7657-7661 (2015).
[4.] H. L. Stern *et al.*, Article in review.

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