Singlet Exciton Fission in Organic Semiconductors

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Photovoltaics made of silicon are the most widely deployed in the world today. Despite rapid reductions in cost over the past decade, the efficiencies of the best silicon cells have not improved by more than 2% in the last twenty years. This is largely because silicon PV have been well optimized and is close to the Shockley-Queisser limit on efficiency ^[1], that applies to all single-junction solar cells, and is 29% for an ideal silicon cell (bandgap 1.1 eV). The main loss is such devices is thermalization, i.e. high-energy photons in the solar spectrum produce one electron-hole pair just as the absorption of lower-energy photons does, but the energy of photons in excess of the bandgap is lost as heat as the carriers relax to the band edges.

Singlet exciton fission is a carrier multiplication process in organic semiconductors (OSCs)^[2]. Within OCSs the absorption of a photon leads to the formation of a bound electron-hole pair, an exciton. The photogenerated exciton is in a spin-0 singlet configuration. However, these systems also posses a lower-energy spin-1 triplet exciton state and under the right conditions the initially photogenerated singlet exciton can convert to a pair of triplet excitons, a process termed singlet fission, Figure 1.

In this talk I will outline the basic physics of singlet fission. I will present results from ultrafast spectroscopy studies that elucidate that quantum mechanical dynamics ^[3-4] of this process, demonstrating how it is driven by the strong coupling of electronic and vibrational degrees of freedom which lead to the formation of mixed electronic state and allow the fission to occur with unity efficiency on the timescale of a few hundred fs. I will also discuss the transfer of the triplet excitons formed vis fission to inorganic nanocrystals ^[5] and how novel organic-inorganic nanostructures could be used to create a new generation of photovoltaics that can overcome thermalisation losses and could break through the Shockley-Queisser limit.



Figure 1. SF in an exothermic system followed by triplet transfer to QDs and photon emission

References:

[1] Shockley, W. & Queisser, H. J. Detailed Balance Limit of Efficiency of p-n Junction Solar Cells. Journal of Applied Physics 32, (1961).

[2] Wilson et al., Singlet Exciton Fission in Polycrystalline Pentacene: From Photophysics toward Devices. Accounts of Chemical Research, 46, 1330, (2013), 10.1021/ar300345h.

[3] Musser et al., Evidence for conical intersection dynamics mediating ultrafast singlet exciton fission, Nature Physics, (2015), 10.1038/nphys3241

[4] Bakulin et al., "Real-Time Observation of Multiexcitonic States and Ultrafast Singlet Fission Using Coherent 2D Electronic Spectroscopy", Nature Chemistry, doi:10.1038/nchem.2371.

[5] Tabachnyk et al., Resonant energy transfer of triplet excitons from pentacene to PbSe nanocrystals. Nature Materials, 13, 1033-1038, (2014), 10.1038/nmat4093