Prospects for harvesting sub-bandgap photons by harnessing triplet-triplet annihilation in organic molecules

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Photovoltaic solar energy conversion devices waste a major part of the incident energy, due to the requirement of a gap in the continuum of electronic states in the light-harvesting material, acting as an absorption threshold. For photon energies higher than this bandgap, the excess energy is converted into heat by thermalization of excited charge carriers, while light with sub-bandgap energies cannot be harvested at all.

These effects dominate the fundamental losses of single-threshold photovoltaic (PV) devices, and restrain their conversion efficiency to 34 % under the AM1.5G spectrum, or about 30 % under a model 6000 K spectrum.

While power conversion losses in low-bandgap materials such as germanium or crystalline silicon (c-Si) are dominated by thermalization, transmission of sub-bandgap light is dominant for bandgaps of greater than 1.3 eV, that is, for most thin-film photovoltaic absorber materials and for all known oxide-based electrode materials of interest to photoelectrochemical energy storage Even solar cells made from c-Si sacrifice a considerable part of the solar spectrum by transmission.

Sub-bandgap losses can be remedied by the application of photonic upconversion, whereby transmitted light is converted to light of higher energy, which can then be harvested by the cell and contribute to current generation. Based on detailed balance considerations it has been shown that upconversion can boost the maximum energy conversion efficiency to about 43 % under one sun for a solar cell with a bandgap of 1.76 eV, and >50$ % under solar concentration Crystalline silicon cells could still reach about 38 %, although the potential gain is smaller than for the high-bandgap devices.

An active field of research is the exploitation of *triplet-triplet-annihilation* in organic chromophores to achieve upconversion (TTA-UC). TTA-UC exploits the longevity of molecular triplet states. However, as the longevity diminishes with energy, TTA-UC is most readily applied to solar cells with bandgaps above about 1.5 eV. This talk will summarize the state-of-the-art in TTA-UC and its application to solar energy conversion.

We have prepared various solar cells with upconverting compositions placed in optical contact behind them. These cells are then subject to EQE measurement, continuously pumped under known conditions. With the pump-photons aligned with the probe photons on the upconvertor, the upconvertor is activated. A slight misalignment causes deactivation, and in this way, the EQE can be measured under both conditions. The ratio of the two thus-generated EQE curves is plotted in the figure. Immediately clear is the imprint of the molecular absorption spectrum on the EQE ratio, confirming the effect. Plotted as solid lines in the figure is a model for the expected EQE ratio with just one adjustable parameter – the height. All other parameters are derived from measured spectra.

In order to compare the performance of TTA-enhanced thin-film solar cells, we have developed a figure of merit, whereby the increase in short circuit current density due to the upconvertor, ΔJ_{sc} is evaluated under one-sun conditions. These are plotted below. At present, we are approaching the 10^{-3} mA/cm^2 “barrier”, though an improvement of more than an order of magnitude is needed under on sun conditions.

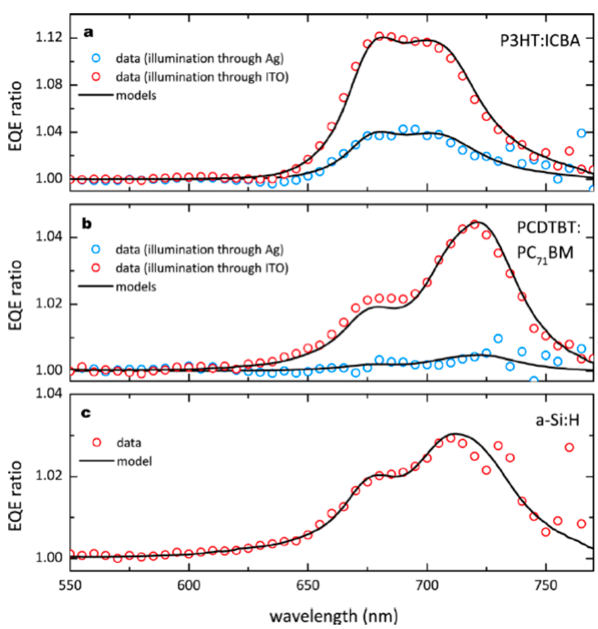
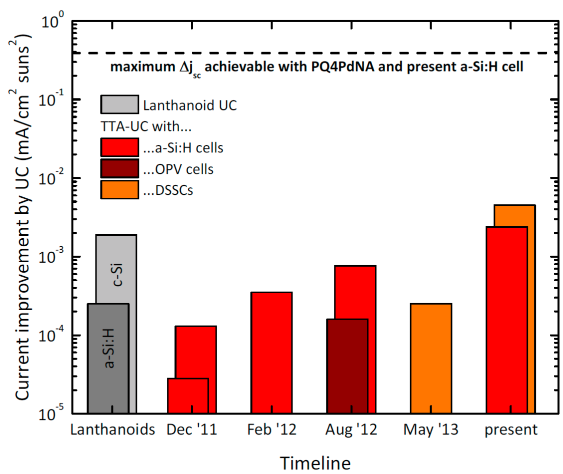


Figure: (left) The ratio of EQE curves measured with the upconvertor operative and inoperative. The absorption peak of the sensitizer molecule is evident in the relative efficiency increase. (below) The evolution of our Figure of Merit over time.



How to improve the performance under low pumping conditions shall be the focus of the second part of my talk, where I will outline our planned research over the coming 12 months.