Supporting Information for:
Realistic Efficiency Limits for Singlet-Fission Silicon Solar Cells

Benjamin Daiber¹, Koen van den Hoven¹, Moritz H. Futscher¹, and Bruno Ehrler¹*

¹AMOLF, Center for Nanophotonics, Science Park 102,1098XG Amsterdam

E-mail: ehrler@amolf.nl

S1 Absorption Model

The absorption in the singlet fission layer is modeled using the Lambert-Beer law. Upon absorption of a photon a singlet exciton is formed which can undergo the singlet fission process. Singlet fission takes place with a certain efficiency up to 200% which is reached in pentacene.¹ We set this efficiency in our model to 190%, to account for inefficiencies in different singlet fission materials. TIPS-Tetracene for example has a singlet fission efficiency of 180%.² Each absorbed photon in our model leads to 1.9 triplet excitons at half the singlet exciton energy.

S2 Detailed Balance Silicon Solar Cell Model

We model the singlet fission-silicon solar cell by calculating the absorption and exciton generation in the singlet fission layer, the resulting triplet excitons are then transferred into a silicon solar cell model assuming three different transfer mechanisms. The injection of these additional charge carriers in the silicon solar cell changes the short circuit current,
open circuit voltage and fill factor in a nontrivial manner, depending on the transfer mechanism. We therefore start with the description of a silicon solar cell current-voltage curve and then add the singlet fission current to the generated current in the silicon solar cell.

The silicon solar cell current-voltage curve is calculated with a diode master equation following previous work. The radiative recombination current calculated with the absorbed photons that have to be equal to the emitted photons of a black body at room temperature, following the detailed-balance argument. The non-radiative recombination is modeled following De Vos et al. and adjusted for the charge transfer case as described below. Shockley-Read-Hall (SRH) and Auger recombination are described with a diode equation with an ideality factor of 1 for SRH and $\frac{3}{2}$ for Auger recombination. The SHR recombination prefactor is a fitting parameter for each solar cell. The Auger recombination is modeled using an Auger coefficient that is dependent on the temperature and the intrinsic charge carrier density. Unless otherwise stated we use the record 26.7% interdigitated back contact silicon solar cell from Kaneka as a base silicon cell.

S4 Transfer Schemes

We consider three different schemes of harvesting the energy of the triplet excitons for the silicon solar cell. The transfer of charges from triplet excitons into silicon, where the exciton is dissociated at the interface, the transfer of energy where the whole triplet energy is transferred into silicon, or the transfer of the triplet exciton energy into an intermediate emitter which then transfers the energy into silicon by FRET.

S3.1 Charge Transfer

Modeling charge transfer requires adjusting the recombination current if the triplet exciton energy is smaller than the silicon bandgap. This approach assumes that we can change the absolute energy position of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) such that the LUMO aligns with the
valence band of silicon. If $E_{\text{Triplet}} < E_{\text{Silicon}}$ the recombination current is higher and the recombination gap is smaller by the difference of the bandgap and triplet energy, as seen in equation (1) adjusted from the general recombination equation:

$$J_{\text{rad}} = \frac{2\pi}{c^2 k^3} \int_{E_{\text{Si}}}^{\infty} \exp \left( \frac{E_n - (E_{\text{Si}} - E_{\text{Triplet}})}{kT} \right) - 1 dE_n$$

Figure S1: Fill Factor of the solar cell with charge transfer mechanism, as in Figure 3b with 100 meV entropy gain and the same parameters. The Fill Factor starts to decrease below 2 eV Singlet energy, like the open circuit voltage.

S3.2 Dexter Transfer

The Dexter transfer model assumes that the energy transfer is possible if the triplet energy with entropy gains is larger than the silicon bandgap, assuming a perfect absolute energy alignment of the singlet fission material HOMO and LUMO and silicon valence and conduction band energy respectively. If the triplet energy is smaller than the silicon bandgap, then the transfer could still be thermally activated. Since the triplet excitons have a certain temperature and do not interact, we use the Maxwell-Boltzmann distribution in energy for an ideal gas for the probability density of triplet excitons:

$$f_E (E, T) = 2\sqrt{\frac{E}{\pi kT}} \left( \frac{1}{kT} \right)^{\frac{3}{2}} \exp \left( -\frac{E}{2kT} \right)$$
We then integrate over all energies above $\Delta E$, the difference of silicon bandgap and triplet energy. This gives us the probability of excitons that have enough energy to overcome $\Delta E$ due to the energy distribution at room temperature. We normalize by the integral over all energies to get a probability. For all $\Delta E < 0$ the triplet energy is larger than silicon bandgap and the probability is 1, which also follows from the limit $\Delta E \to 0$.

$$P_{Dexter} = \frac{\int_{\Delta E}^{\infty} f_E(E, 300K) \, dE}{\int_{0}^{\infty} f_E(E, 300K) \, dE}$$

S3.3 FRET Transfer

FRET transfer is modeled by using a previously published model for FRET transfer efficiency from a quantum dot to a bulk silicon acceptor. The distance between donor (quantum dot) and acceptor (bulk silicon) is set to 1 nm. The quantum dot has an emission energy of the singlet fission triplet energy including entropy gains and a FWHM of 0.2 eV. This assumes that there is no Stokes shift. This is optimistic but since there is only a very dilute layer of quantum dots necessary and we assume that the quantum dots will be monodisperse, which allows for a very small Stokes shift.\(^8\)

S4 Entropy Gain

However, the energy of the triplet excitons is not necessarily half of the singlet exciton energy. In some materials like pentacene it is less than half the energy, while in others like tetracene two triplet excitons can actually carry more energy than the singlet exciton energy. This surprising observation seems to violate thermodynamics, since the two triplet excitons originate from one singlet exciton. The relevant measure here is the free energy that includes the enthalpy (which we commonly refer to as energy) but also an entropy term. This entropy term allows for the free energy to increase during a reaction (one singlet to two triplet excitons) if the gain in the number of states and therefore the entropy gain is significant. The gain in free energy from the entropy term can be up to 220 meV in Perylene diimides (PDIs) (endoergic and efficient singlet fission\(^9\)) and 200 meV in
We therefore include an entropic gain of 100 meV during singlet fission in the realistic case and an entropic gain of 300 meV as an optimistic case. The entropic gain stems from the fact that the singlet state has a lower entropy than the two triplet excitons. The number of states that the delocalized singlet state can occupy is lower compared to the two localized triplets, who can reside on many different combinations of molecules, thus the number of states and entropy is larger. In tetracene this entropic gain is the driving force for singlet fission, and other materials could be engineered or selected for a high entropic gain by optimizing the singlet and triplet delocalization and crystal structure.

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