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REALISTIC EFFICIENCY LIMITS FOR SINGLET FISSION SILICON SOLAR CELLS

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Benjamin Daiber, Koen van der Hoven, Moritz H. Futscher, and Bruno Ehrler, "Realistic Efficiency Limits for Singlet Fission Silicon Solar Cells", *in Preparation* (2020)

Singlet fission is a carrier multiplication mechanism that could make silicon solar cells much more efficient. We calculated the efficiency potential of three technologically relevant singlet fission-silicon solar cell implementations. We assume realistic but optimistic parameters for a singlet fission material and we investigate the effect of singlet energy and entropic gain as well as relevant loss mechanisms. If the transfer of triplet excitons occurs via charge transfer, where the triplet exciton is dissociated at the interface, the maximum efficiency is 34.6% at a singlet energy of 1.85 eV. The viable range of singlet fission materials is large, many materials with singlet energies from 1.3 eV to 3 eV can improve on the silicon solar cell efficiency. For the Dexter-type triplet energy transfer the maximum efficiency is 32.9% with an optimal singlet energy of 2.15 eV, enhancing the silicon efficiency is only possible with singlet fission materials that have triplet energies larger than the silicon band gap. For Förster Resonant Energy Transfer (FRET), the triplet excitons are first transferred into an emitter, e.g. a quantum dot, which can then undergo FRET into silicon. For this transfer route the maximum efficiency is 28.7%

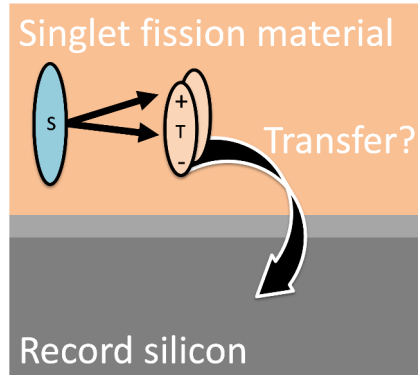


Figure 3.1: Schematics of the simulated singlet fission and transfer process.

at 2.33 eV which is lower than the previous two because of additional parasitic absorption and transfer losses into the quantum dots. We show that the efficiency gain from singlet fission is larger the more efficient the silicon base cell is, which stands in contrast to tandem perovskite-silicon solar cells.

3.1 INTRODUCTION

Solar cells are the most important cornerstone of transitioning the world's energy production from a fossil-based system to a CO₂ neutral future. The main solar cell technology in use today is based on silicon. Silicon solar cells have shown large improvements in efficiencies and cost, the technology is mature and highly optimized. However, the record efficiency of silicon solar cells has improved only slightly from ~ 24% to 26.7% in the past 20 years [87] because it gets harder and harder to improve the already highly optimized cell structure and material quality. Including Auger recombination in the thermodynamic detailed-balance limit of solar cell efficiency leads to a theoretical maximum efficiency of silicon solar cells of 29.4% [130]. The efficiency of the record silicon solar

cell is 26.7% [41], which is a remarkable 91% of the theoretical maximum. New approaches are needed to improve the efficiency further. In this paper we calculate the realistic efficiency potential of singlet fission-silicon solar cells with three different geometries and transfer mechanisms, each with distinct advantages and challenges. These results can inform the practical application and search for new singlet fission materials.

Silicon has a fairly low bandgap energy (1.12 eV), above which photons are absorbed. A large fraction of the photons of the solar spectrum have a higher energy and will lose their excess energy to thermalization losses. These high-energy photons can be converted into electricity more efficiently if they are split into multiple photons or excitations with an energy above the silicon bandgap. If such downconversion can be applied to silicon, we can build on the vast knowledge of silicon solar cells without the need for large changes in silicon solar cell architecture.

Singlet fission is an example of a downconversion process that can potentially increase the efficiency of silicon solar cells by using the solar spectrum more efficiently. High-energy photons are absorbed in the singlet fission material and form a spin-0 singlet exciton. In certain organic materials like poly-acenes and perylene diimides (PDIs) this singlet exciton will split into two spin-triplet excitons of roughly half the energy of the singlet exciton [118]. For an efficient implementation, this singlet fission layer would be placed on top of a silicon solar cell, absorb all the high-energy light, convert each photon into two triplet excitons, and transfer their energy or charge into the silicon solar cell. The absorption-coefficients of organic materials are high at the energies of the molecular transitions [61]. Singlet fission can also be a very efficient process with efficiencies close to 200% in pentacene [140], meaning each singlet generates two triplet excitons. The main bottleneck for the singlet fission-sensitized silicon solar cells is the transfer of excitons from the absorber layer into silicon.

Here we simulate how efficient a singlet fission-silicon solar cell could be given realistic materials and device parameters. We find that the broadband absorption of typical singlet fission materials needs to be improved, for example by sensitization schemes. The most efficient implementation based on a record-efficiency silicon solar cell would be the charge transfer

from triplet excitons into silicon with the highest efficiency of 34.6%. This efficiency maximum is reached at a surprisingly low singlet exciton energy of 1.85 eV with a realistic entropic gain of 100 meV. The simplest triplet transfer implementation, Dexter transfer, could also achieve high efficiency (32.9%) but puts a stronger constraint on the singlet energy. FRET shows the lowest efficiency potential of 28.7% because of additional loss channels. Finally, we compare the behavior to perovskite-silicon tandem solar cells and find that singlet fission shows the largest efficiency improvements for efficient silicon base cells, while tandem solar cells show a larger efficiency improvement for less efficient silicon base cells.

3.2 METHODS

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 [33]. 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. [23] 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 [130]. 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 [130]. Unless otherwise stated we use the record 26.7% interdigitated back contact silicon solar cell from Kaneka [41] as a base silicon cell.

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 [140]. 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% [121]. Each absorbed photon in our model leads to 1.9 triplet excitons at half the singlet exciton energy.

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 PDIs (endoergic *and* efficient singlet fission [25]) and 200 meV in tetracene [62]. 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 [62], and other materials could be engineered or selected for a high entropic gain by optimizing the singlet and triplet delocalization and crystal structure.

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.

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 3.1, adjusted from the general recombination equation [23, 89].

$$J_{\text{Rad0}} = q \frac{2\pi}{c^2 h^3} \int_{E_{\text{Si}}}^{\infty} \frac{E_n^2}{\exp(E_n - (E_{\text{Si}} - E_{\text{Triplet}})) - 1} dE_n \quad (3.1)$$

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:

$$f_E(E, T) = 2\sqrt{\frac{E}{\pi}} \left(\frac{1}{kT}\right)^{\frac{3}{2}} \exp\left(-\frac{E}{2kT}\right)$$

We then integrate over all energies above ΔE , the difference of silicon bandgap and triplet energy. This gives us the probability of excitons that have enough energy to overcome ΔE 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 $\Delta E \rightarrow 0$.

$$P_{\text{Dexter}} = \frac{\int_{\Delta E}^{\infty} f_E(E, 300\text{K}) dE}{\int_0^{\infty} f_E(E, 300\text{K}) dE}$$

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, this which allows for a very small Stokes shift [136].

3.3 RESULTS

3.3.1 Absorption in the singlet fission material

The absorption of any downshifting material should be large so that the maximum number of incoming photons can be absorbed and undergo the downshifting mechanism to multiply carriers and increase the photocurrent. Singlet fission takes place in organic molecules with a relatively large singlet-triplet exciton energy splitting, thus with a large exchange energy. Often these molecules are conjugated molecules. The absorption of these organic molecules is considered to be strong because the absorption coefficient is relatively high compared to other semiconductors [61]. However, this is only the case at the absorption peaks at the specific energies of the pi-orbital transitions, leading to a narrow absorption spectrum if compared to the band-to-band absorption of most inorganic semiconductors. Since the solar spectrum is broadband and reaches from energies of ca. 0.3 eV (4000 nm) to 4 eV (310 nm), the fraction of absorbed

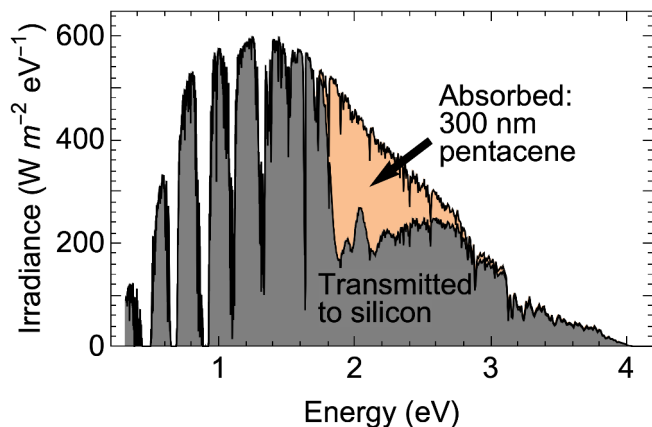


Figure 3.2: AM1.5 Spectrum split into the light absorbed in a 300 nm thick pentacene layer and light that is transmitted through the pentacene layer to the bottom silicon solar cell. Even a thick 300 nm pentacene layer only absorbs 32 % of the light with an energy above the singlet energy.

light of most singlet fission materials is very low. To illustrate this point we show the absorbed solar irradiance in a thin pentacene layer of 300 nm (Figure 3.2). Thicknesses below 300 nm are typical for films used in singlet fission solar cells [28, 76]. This thickness is also the order of the triplet exciton diffusion length in polycrystalline pentacene of (40 – 80) nm and single crystal pentacene (350 – 800) nm [98]. Figure 3.2 shows that only 32 % of the power above the singlet energy is absorbed. 67 % of the light above the singlet exciton energy is transmitted and is lost to the singlet fission process. Instead, the light is absorbed in the silicon solar cell below the singlet fission absorber, where it adds current but does not benefit from carrier multiplication. Even for a film thickness of 1000 nm, around three times the single-crystal triplet diffusion length, we still lose 34 % of the solar power above the pentacene singlet exciton energy.

The small fraction of absorbed photons from the solar spectrum in typical singlet fission materials like pentacene and tetracene directly translates into a smaller photocurrent gain. To illustrate this point, we

have calculated the theoretical maximum solar cell efficiency for a system that is ideal, where the only loss mechanism is incomplete absorption. We perform a detailed balance type calculation, with the tetracene and pentacene absorption spectra but otherwise 200 % efficient singlet fission, no non-radiative recombination except Auger recombination in silicon, and no parasitic absorption. In case of pentacene there is a voltage penalty since the triplet energy is smaller than the silicon bandgap. The recombination of charge carriers in the dark (J_0) does not happen across the silicon bandgap but instead across a smaller gap equivalent to the triplet energy, since this is the smallest energy difference where recombination can occur. The larger recombination due to the smaller energy gap in turn leads to a reduced voltage. Figure 3.3 shows the efficiency of a tetracene-silicon and pentacene-silicon solar cell as a function of tetracene or pentacene thickness, including the limits for an ideal absorber with the respective absorption onsets (horizontal lines in Figure 3.3). The dashed horizontal line shows the silicon-Auger limit, the solid lines represent the efficiency limits of tetracene and pentacene if they were ideal absorbers, which is also the limit for large thicknesses. We use energy at which tetracene and pentacene start to absorb as the absorption onset of the ideal absorber, which explains the discrepancies with the singlet exciton energies. In this ideal case even a very thin tetracene layer increases the current, but the efficiency gain keeps rising for layer thicknesses well above the polycrystalline triplet diffusion length of ~ 600 nm [2]. A pentacene layer however would have to be at least 950 nm thick to improve on the silicon Auger limit, which is many times the diffusion length of triplets in polycrystalline pentacene [98].

Below we assess the influence of different loss factors on the efficiency potential of singlet fission-silicon solar cells. Because of the poor broadband absorption, we treat the absorption of our theoretical materials as ideal in the following, absorbing all light above the singlet energy. This broadband absorption could be achieved by using a sensitizing layer, as in a recent study where perovskite quantum dots were used as a broadband absorber, then the excitons are transferred into a singlet fission material where they can undergo singlet fission [73]. This additional layer makes use of the efficient band-to-band absorption, with the penalty of a certain

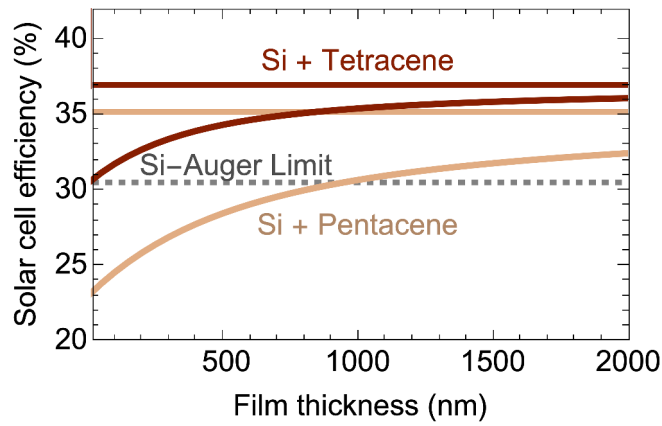


Figure 3.3: Detailed balance limit with the Auger recombination of silicon taken into account (dashed gray line) for an AM1.5 spectrum. The efficiency limit of a singlet fission-silicon cell based on this silicon base cell with tetracene and pentacene layers of different thicknesses, tetracene in red and pentacene in orange with an ideal absorber case of the respective materials as horizontal lines. The singlet energy/absorption onset is 1.7 eV for pentacene and 2.3 eV for tetracene. Triplet energies are 0.86 eV for pentacene and 1.25 eV for tetracene. The singlet fission efficiency is set to 2 and no additional loss channels are assumed.

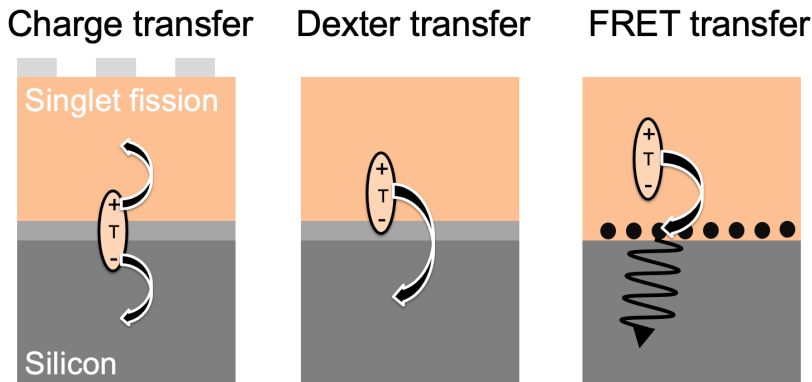


Figure 3.4: Schematics of the three transfer schemes discussed in this paper. *Charge transfer* includes the disassociation of the triplet exciton at the interface and subsequent transfer of both electron and hole independently. *Dexter transfer* entails the transfer of the energy of the triplet exciton into silicon by concurrently transferring electron and hole. *FRET transfer* consists of the transfer of the triplet exciton energy into a quantum dot with subsequent transfer of the energy from quantum dot into silicon via FRET.

transfer loss from the sensitizer to the singlet fission material. Since this first sensitizing study already reports a singlet exciton transfer efficiency of 80% and additional gains are likely possible, we do not explicitly take this transfer step loss into account in the following calculations.

3.3.2 Different Transfer Mechanisms

In the following we calculated the efficiency for three distinct transfer schemes, charge transfer, Dexter transfer and FRET. We use the record silicon solar cell with an efficiency of 26.7% [41] as a base cell into which additional current from singlet fission is injected. We explore the influence of different loss mechanisms and the difference between the transfer schemes, depicted in Figure 3.4.

3.3.2.1 Charge transfer

Triplet excitons can be transferred into a silicon solar cell by charge transfer. In this transfer mechanism, the triplet exciton is dissociated into electron and hole at the interface between singlet fission material and silicon. C_{60} and other fullerenes are often used as an electron acceptor for singlet fission materials and can efficiently dissociate the triplet excitons [17, 91]. Here we assume that the electron is transferred into silicon and the hole has to travel through the singlet fission material to an additional set of contacts on top of the singlet fission layer. The holes from the photocurrent generated in silicon need to transfer through the singlet fission material as well. The additional contacts and the long diffusion through the singlet fission layer will lead to additional losses. A variation of this transfer scheme is to use silicon top contacts to accept the singlet fission holes by adding an additional electron blocking layer around the contacts, in between the singlet fission layer and the metal of the contacts. If the hole mobility of a singlet fission material is high this buried contact could eliminate the need for additional top contacts which would reduce parasitic absorption losses. In our model we assume a doubled series resistance and a 3 % parasitic absorption loss from the additional top contacts. Further we assume 95 % efficient triplet generation and a 95 % efficient triplet disassociation leading to an overall triplet yield of 1.805 per absorbed photon. We discuss the requirements for the hole mobilities in the singlet fission material below.

An important element of modeling the charge transfer is the voltage penalty that applies if the triplet energy is smaller than the silicon bandgap. The radiative recombination will then occur between the smallest energy gap of the cell, which in this case is between the HOMO of the singlet fission material and the silicon conduction band. We assume ideal alignment of the LUMO of the singlet fission material and the silicon conduction band. By the smaller effective bandgap the dark recombination current increases which leads to a voltage penalty for triplet energies smaller than the silicon bandgap. In Figure 3.5 we plot the solar cell efficiency of the charge transfer-singlet fission-silicon solar cell as a function of the singlet energy of the singlet fission material. The singlet energy is

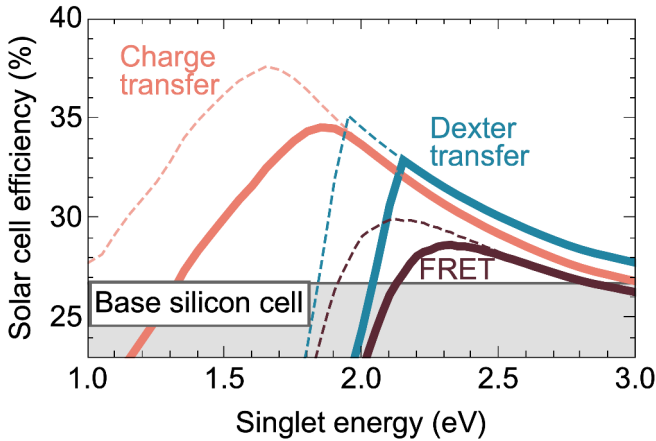


Figure 3.5: Solar cell efficiency of charge transfer, Dexter energy transfer, and FRET as a function of the singlet energy of a theoretical singlet fission material. The horizontal grey line is the record silicon solar cell that forms the bottom cell for the simulated singlet fission solar cells with the different transfer schemes. Thick lines assume a 100 meV entropy gain, dashed lines assume an optimistic 300 meV entropy gain. We show the charge transfer (orange), Dexter transfer (blue) and FRET (red) efficiencies. The most efficient transfer mechanism is the Charge transfer, which also shows the widest possible range of potential singlet fission materials.

also the absorption onset of our ideal absorber. The triplet energy is half of the singlet energy, plus an entropic gain term. The entropic gain can dramatically increase the efficiency of a singlet fission-solar cell as shown by the dashed lines in Figure 3.5.

OPTIMAL ENERGY Naively, the maximum singlet fission-silicon solar cell efficiency could be expected at a singlet exciton energy of 2.2 eV, twice the silicon bandgap of 1.1 eV. However, this is not the case as seen in Figure 3.5. The optimum singlet energy depends both on the transfer scheme and the entropic gain that is assumed. The charge transfer model shows the maximum solar cell efficiency of 34.6% at a singlet exciton energy of 1.85 eV at 100 meV entropy gain, considerably lower than twice

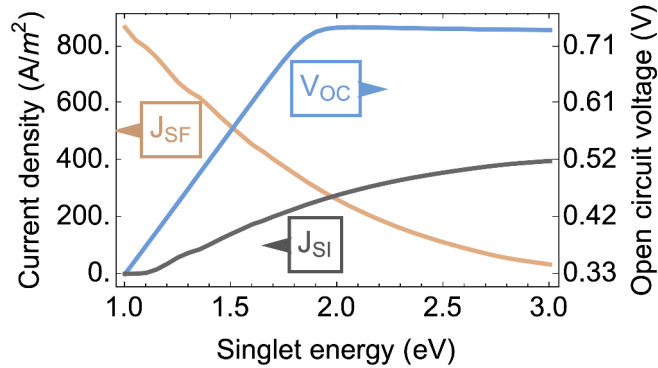


Figure 3.6: Different parts of the charge transfer solar cell efficiency for different singlet energies. We can see that the voltage penalty decreases the V_{OC} below a singlet energy of 1.8 eV. J_{SF} increases with lower singlet energy, since more absorbed photons can be converted in the singlet fission process. The current generated in silicon decreases.

the silicon bandgap. To explain this behavior, we show the three most important quantities for the singlet fission-silicon solar cell efficiency: the short circuit current from the singlet fission layer (J_{SF}), the silicon cell (J_{Si}), and the silicon solar cell open-circuit voltage (V_{OC}), in Figure 3.6 with the same x-axis of singlet energy as in Figure 5. J_{SF} continuously increases with lower singlet energy thanks to an increased number of absorbed photons that can create two triplet excitons. At the same time J_{Si} decreases, but not as quickly since every photon absorbed by the silicon cell generates at most one electron-hole pair. The voltage penalty, as seen in the decreasing V_{oc} with decreasing singlet energy appears slightly below twice the silicon bandgap because of the entropic gain. Initially, the increase in photocurrent compensates the drop in voltage so that the efficiency optimum is in a regime where the solar cell suffers voltage penalty. The penalty only starts to reduce the efficiency at below 1.85 eV. The fill factor also decreases, similarly to V_{oc} , albeit not as strongly. We omit the fill factor from Figure 3.6 for clarity.

3.3.2.2 Influence of Entropy

The entropic gain discussed earlier also leads to an increased efficiency and lower optimal singlet energy. Figure 3.5 shows the absolute efficiency gain plotted for 100 meV entropic gain and 300 meV entropic gain. We only consider the entropic gain during the singlet fission process in the singlet fission material. Since there is also a certain density of states in silicon it is conceivable that an increased number of available states inside silicon could also lead to an additional entropy gain. Since the a change in entropy during the process will lead to a gain in Gibbs free energy, G via $\Delta G = -T\Delta S$ with the temperature T and the change in entropy ΔS . The increased Gibbs free energy could therefore increase ($\Delta G < 0$) or decrease ($\Delta G > 0$) the transfer efficiency. The change in entropy can be calculated with the formula $\Delta S = k_B (\ln \Omega_S - \ln \Omega_T)$ by counting the states in silicon Ω_S , and the available states of the free triplet exciton Ω_T .

We will now perform a rough calculation for the entropy gain for the transfer between tetracene and silicon. The number of states of a triplet excitons in tetracene has been calculated by Kolomeiskiy et al. [62] by calculating the number of molecules within the Dexter radius of (10 – 20) Å. The number of molecules accessible for a triplet exciton is 19 for a Dexter radius of 10 Å, 37 for a radius of 15 Å and 61 for a dexter radius of 20 Å.

We can estimate the number of states in silicon by integrating square-root dependence of the density of states (units: $\frac{1}{\text{cm}^3 \text{eV}}$) from the conduction band edge to 150 meV above the band edge. We use 130 meV since this is the difference in energy between the tetracene triplet exciton and silicon. Different effective masses for electrons and holes in silicon are taken into account, and the integral is split into two with integration boundaries for electron and hole from the bandedge to 75 meV above. This calculation leads to a density of states of 0.12 nm^{-3} . In silicon the exciton size is much larger than the Dexter radius since the dielectric constant is large (~ 11) which leads to a large Wannier exciton of around 9 nm radius. This leads to a large number of states available within the sphere occupied by the Wannier exciton in silicon, namely 448. This change in the number of available states would lead to an additional en-

entropy gain of 76 meV if the triplet state in tetracene has a Dexter radius of 10 Å, 59 meV for a Dexter radius of 15 Å, and 46 meV for a Dexter radius of 20 Å.

The additional entropy term could be beneficial to the transfer efficiency and potentially the solar cell efficiency. We calculated the entropy gain by using exciton radii which is presumably only realistic for a direct Dexter exciton transfer. Other transfer mechanisms might behave differently and our naive assumptions might not hold.

In Figure 3.5 we can see that a higher entropy term would extend the possible singlet fission materials to lower singlet energies, as low as 1.65 eV at 300 meV entropy gain, where the efficiency is calculated to be 37.6%. We therefore conclude that it would be hugely beneficial if we could control and increase the entropy gain to increase the singlet fission-silicon solar cell efficiency. Also, most synthetic efforts towards new singlet fission molecules aim for singlet energies above 2 eV. However, our results show that low-bandgap singlet fission materials are potentially even more interesting, since the peak of increased solar cell efficiency is very broad thanks to the charge transfer and the entropy gain.

3.3.2.3 *Space Charge limited current*

Since the charge transfer scheme involves transport of holes from the singlet fission material and silicon through tetracene, the low mobility of organic singlet fission materials like tetracene will make charge extraction inefficient. This will be especially problematic since organic semiconductors have poor broadband absorption as described earlier, which necessitates thick singlet fission absorber layers. To estimate the necessary hole mobilities and the resulting maximum thicknesses for any singlet fission-layer, we model the system using the Mott-Gurney law of space charge limited current. This model assumes that the contacts are not introducing any additional barriers, that the holes are not transported via traps or that the cell operates above the trap filling voltage. The space-charge limited current then becomes

$$J(V) = \frac{9}{8} \epsilon \mu \frac{V^2}{L^3}$$

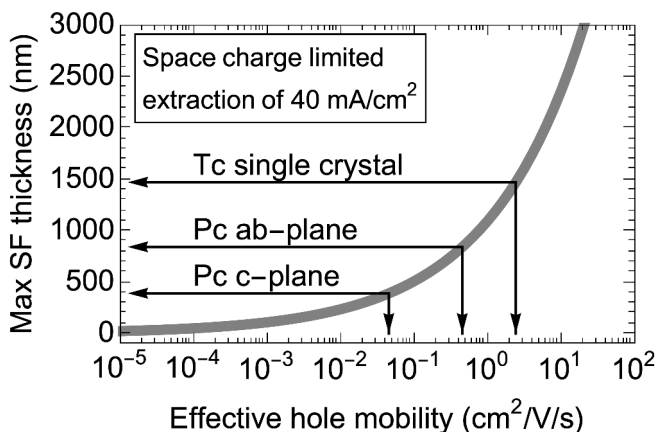


Figure 3.7: Maximum singlet fission layer thickness as a function of effective hole mobility. We assume a voltage drop of 0.36 eV and an extracted current of 40 mA/cm².

with ϵ the singlet fission-material permittivity, μ the hole mobility, and L the layer thickness. We assume that we have to extract a typical current from the silicon cell of 40 mA/cm² through the singlet fission layer and that half of the silicon voltage drops over the singlet fission layer, set to $V = 0.36$ V. With these assumptions we can solve for the thickness as a function of mobility as shown in Figure 3.7. We show three characteristic singlet fission materials, a best-case scenario of single crystal tetracene with a mobility of 2.4 cm²/Vs [107] would allow for a maximum layer thickness of ~ 1500 nm, which would lead to an ideal efficiency of 36% (Figure 3.3). The mobility in polyacenes is typically anisotropic [45], requiring aligned growth of the singlet fission material for optimal performance. For pentacene the mobilities in two different crystal axes have a value of 0.45 cm²/Vs in the ab-plane and a 10 times lower mobility in the c-plane direction [45]. In real devices, the transport would most likely occur in the low-mobility c-plane since that is the preferred growth direction on silicon [122, 123], which would limit the singlet fission layer thickness to 400 nm.

Since there is a long history of research towards high-mobility organic materials for organic transistors [90] that has yet to overcome mobilities above $20 \text{ cm}^2/\text{Vs}$ this is most likely a hard problem to solve with molecular engineering. However, if we use a sensitizer to efficiently absorb the light, we could design a much thinner singlet fission layer combined with a thick absorber layer that also has a high mobility (e.g. a metal halide perovskite), which in turn puts lower requirements on the necessary hole mobility in the organic layer. Another strategy is the use of a bulk heterojunction, used in organic solar cells to overcome low mobilities by mixing the donor and acceptor phases resulting in much shorter transport distances for example with a bulk heterojunction between the singlet fission material and a hole extraction material such as PEDOT:PSS. Since there are already strategies of functionalizing organic molecules with TIPS groups such as TIPS-tetracene and TIPS-pentacene, a solution of singlet fission material and hole extraction layer that could be spin-coated is feasible. Similarly, a very thin singlet fission dye on a mesoporous substrate, as is used in dye-sensitized solar cells, could also overcome the absorption length problem.

As mentioned above, another route would be to add buried contacts on top of silicon but below the singlet fission layer that collects holes from both silicon and the singlet fission material. If the lateral distance to a contact would be smaller than the film thickness, this geometry would also allow for shorter hole transport distances. The lateral mobility in organic crystals can also be higher than the vertical mobility. However, the metal fingers used to collect charges on top of standard silicon solar cells would be unsuitable for this scheme since they are usually several millimeters apart. Metal grids with a pitch of $1 \mu\text{m}$ have been shown [59] and could be combined with a singlet fission charge transfer solar cell. In case of a degraded singlet fission layer, the direct collection of silicon holes at the silicon surface is also beneficial since the silicon solar cell continues to be operational with an inactive, then transparent singlet fission layer [55]. Despite the attractive efficiency potential, charge transfer from triplet excitons into silicon has been attempted but not yet experimentally shown to occur with high transfer efficiencies [76].

3.3.2.4 Dexter transfer

Dexter energy transfer directly transfers the whole triplet exciton energy at once, by concurrently transferring the electron and hole into the silicon. Since triplet excitons are dark states, FRET or photon emission cannot occur directly, and Dexter transfer is the only accessible energy transfer mechanism. For efficient Dexter transfer the wavefunction overlap between the triplet excited state on a singlet fission molecule and the accepting material has to be large. In upconversion systems it has been shown that the triplet exciton states can be populated from electrons and holes occupying bands in inorganic semiconductors. A recent example is the sensitization of the rubrene triplet states by a lead halide perovskite film [86]. These examples show the potential for large wavefunction overlap between the excitonic states and the band-like states.

The first demonstration of Dexter transfer from triplet excitons, generated by singlet fission, into an inorganic semiconductor was from tetracene into PbS quantum dots [129] and from pentacene into PbSe quantum dots [125]. After a long search, triplet transfer from tetracene into silicon has finally been demonstrated in a recent set of experimental studies [20, 29], even though there is no conclusive evidence that the transfer mechanism was indeed Dexter transfer.

In our model we assume efficient transfer if the triplet energy is sufficient, meaning larger than the silicon bandgap. If the triplet energy is smaller than the silicon bandgap then we assume that the thermal energy can add to the total energy and allow the transfer. We implemented this by a higher-energy population of triplets following the Maxwell-Boltzmann distribution. At room temperature the energy of 25 meV is small compared to the exciton energy, so the efficiency for Dexter transfer still falls dramatically if the triplet energy is too small, as can be seen in Figure 3.5 by the steep decrease of efficiency at lower singlet energies. In practice the Dexter transfer solar cell would be very simple, just a single organic layer on top of a suitably prepared silicon solar cell. We assume no parasitic additional absorption since there are no additional extraction or disassociation layers, and as above, a quantum yield of 1.805 for the

singlet fission process, assuming an efficiency of 95 % for both the triplet generation and triplet transfer.

In comparison to charge transfer, Dexter transfer shows a higher efficiency for high singlet energies above 2.1 eV since the parasitic absorption is absent (Figure 3.5). The thick line in Figure 3.5 is calculated with an entropic gain of 100 meV, the dashed line assumes a 300 meV entropic gain. The additional entropic gain extends the possible singlet energies further to down to lower values for potential singlet fission materials, but shows the same abrupt decrease if the triplet energy is smaller than the silicon bandgap. We can see that the possible efficiencies are lower than in the charge transfer case, with a maximum of 32.9 % at 2.15 eV if 100 meV entropy gain is assumed and 35.1 % at 1.95 eV for 300 meV entropy gain. This transfer scheme, however, might be easier to realize than the charge transfer or FRET (see below) since there is no need for an additional top contacts or quantum dot layer.

For the practical implementation one needs to consider the silicon passivation. Efficient silicon solar cells are typically covered with a layer of thick SiO_2 or Si_3N_4 which acts both as a passivation layer and as an anti-reflection coating. For all transfer schemes the contact between the organic material and silicon needs to be close, thus one needs to remove the coating. While the low-index organic material would have some anti-reflection effect, the full performance would likely need to be restored by an additional anti-reflection layer on top of the organic layer. Also, the silicon layer would need to be passivated electronically. While some ultrathin layers have been developed (1.2 nm of SiO_2 [38], 7 nm of Al_2O_3 [50], 15 nm of HfO_2 [147]), they may still be too thick to transmit triplet excitons. In that case, ideally, the singlet fission material would directly act as the passivation layer on silicon, for example by covalently attaching a singlet fission molecule on the silicon surface [19].

3.3.2.5 Förster resonant energy transfer

Förster Resonant Energy Transfer (FRET) is the dominating transfer for singlet excitons in organic semiconductors. However, since triplet exciton states are dark states, they cannot undergo FRET directly. It is, however,

possible to transfer the excitons into an emissive material, for example quantum dots that have a large spin-orbit coupling so that triplet excitons can be converted into emissive excitons in these quantum dots. Then the exciton could be transferred into silicon via FRET. The main factor determining the efficiency of FRET between these quantum dots and the silicon acceptor is the very short Förster radius (distance at which transfer efficiency is 50 %), which means that the quantum dots have to be very close (1 nm) to the silicon surface [126]. The reason for the short Förster radius is the small overlap integral between the quantum dot emission at the silicon band-edge (1.2 eV) and the weak absorption cross section of silicon, an indirect-bandgap semiconductor. In an earlier work we have extended the FRET model that describes energy transfer between two dipoles to a more appropriate dipole-3D acceptor model, with a tunable energy PbS QD as the emitter and a slab of silicon as the acceptor. The distance dependence changes from a $\frac{1}{r^6}$ dependence of the dipole-dipole model to a $\frac{1}{r^3}$ dependence, making the transfer efficient for longer distances. The Förster radius in the 3D acceptor model for suitable quantum dots of 1.2 eV emission is 1.4 nm. In this work we place the dots directly at the interface, at a distance of 1 nm. The resulting transfer efficiency then depends on the wavelength of the emission since the overlap integral of the quantum dot PL and absorption changes. The PL emission wavelength is matched to the triplet energy of the singlet fission material plus the entropic gain described earlier. Thus, we assume no energetic losses from the triplet energy transfer into the quantum dot. We assume no Stokes shift. The Stokes shift in PbS QDs originates in the polydispersity of the ensemble [136], in our case the QDs can be very dilute and presumably monodisperse, leading to a small or no Stokes shift.

The triplet diffusion length can be short in this scheme since the QDs could be intermixed into the singlet fission layer. The transfer efficiency of triplets into the quantum dots is an additional loss channel and is assumed to be 90 % efficient, a realistic number for small singlet fission-QD distances [129], leading to an overall quantum yield of 1.71. In Figure 3.5 we show the efficiency as a function of singlet energy. The FRET curve follows the same general trend as the other transfer mechanisms, albeit

with lower efficiency of 28 % in the 100 meV entropy gain case, because of additional parasitic absorption, additional transfer losses and quickly decreasing FRET transfer efficiency at lower quantum dot emission energies. Additional entropy gains of 300 meV lead to a maximum efficiency of 30 % at a singlet energy of 2.1 eV, extending the singlet exciton energies with an efficiency gain to lower singlet energies, just as with the other two transfer mechanisms. In a realistic cell, this transfer scheme might be the easiest to manufacture, since it could be applied to any silicon solar cell with a thin passivation layer. However, for thick passivation layers that are currently the standard in silicon solar cells (for example a 80 nm Si_3N_4 passivation and antireflection layer) the FRET efficiency would effectively be zero and one would have to rely on the photon emission and absorption by the quantum dots, which necessitates new ways of directing the light downwards toward silicon. We calculate the efficiency potential of such a “photon multiplier” scheme elsewhere [34].

3.3.3 Influence of the underlying silicon solar cell

The transfer efficiencies that have been discussed so far have been calculated with a record silicon solar cell of 26.7 % efficiency [41]. This is, however, not what is currently available commercially, so how does the performance change if the base cell is less efficient?

To explore the efficiency potential on a broad range of silicon base cells we used the same diode model as above but now with recombination constants and resistance values that fit the IV curves for these less efficient silicon solar cells. This approach is based on work of Futscher et al. [33, 34]. The models for different silicon solar cells allow us to run the same calculations as before and observe the change with silicon cell efficiency. Figure 3.8 shows the results, with the optimal singlet energy for each transfer scheme and an entropy gain of 100 meV and other parameters as described above. As a comparison we have also included the results of an earlier calculation of an optimistic case for a perovskite-silicon two terminal tandem solar cell [34]. In this optimistic tandem cell the perovskite top cell is as optimized in terms of non-radiative recombination

and resistances as the current silicon record cell. We can see that the improvement in singlet fission-silicon solar cell efficiency is larger for more efficient base cells. This is in stark contrast to the behavior of the perovskite tandem cell, where the efficiency improvement decreases with more efficient base cells. The main reason for this difference is that we do not have to change the base cell at all. The energetics and voltage matching stays the same, we simply inject additional current. Thus, to first order, the efficiency is increased by a certain percentage of the silicon efficiency, which leads to higher absolute efficiency gains for more efficient silicon cells. In the tandem solar cell, both cells have to be electrically connected and the electrical properties of the full cell are limited by each of the subcells, so it is easy to degrade the highly optimized record silicon solar cells. Therefore, the largest relative gains in efficiency with singlet fission can be found in already efficient base cells, where they are otherwise most difficult to achieve and most valuable.

3.4 CONCLUSION

Singlet fission can lead to large absolute efficiency gains for silicon solar cells. While the best silicon solar cells are now very difficult to improve, with sub-percent level improvements celebrated as great successes, singlet fission can potentially increase the efficiency of a record silicon solar cell from 26.7% to 37.6%. Such a huge efficiency improvement could be reached with charge transfer from the triplet state into silicon when all processes work well: The singlet fission material absorbs all light above its bandgap, the efficiency of singlet fission is 95%, the triplet transfer is 95% efficient, the entropic gain during singlet fission is 300 meV and the additional resistance and optical losses in the silicon cell are small (doubled series resistance and 3% parasitic absorption). With the exception of charge transfer from the triplet state into silicon, each of these quantities has been demonstrated individually, but the combination will still be a significant challenge to achieve. Yet, even somewhat less optimistic assumptions can lead to massive efficiency gains. We have shown that all