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INTRODUCTION

This chapter will introduce the basics of solar cell physics, organic semiconductors and singlet fission, which will help in the understanding of the following chapters. We will also quickly introduce the need for solar cell efficiency gains and provide the context of solar cells in the green energy transition.

1.1 SOLAR CELLS AND THE GREEN ENERGY TRANSITION

Manmade global warming is a key challenge in the next 20 years. We have to reduce the emission of greenhouse gasses drastically if we want to avoid the devastating effects of global warming. The Intergovernmental Panel on Climate Change says in its fifth assessment report that we have to reduce the amount of greenhouse gasses starting immediately if we want to limit global warming below 2°C [102]. Electrical power generation is currently a large emitter of greenhouse gasses, so a climate neutral alternative to fossil power plants is urgently needed. Solar cells are one such technology for green energy generation, promising because of their scalability and low cost [72]. In many places in the world it is now cheaper to install new solar cells than to *run* existing coal power plants [67]. Compared to nuclear power the lower capital cost, construction time, and the lack of nuclear waste is an advantage. Wind energy is another green energy source that is complementary to the installation of solar cells since the wind and sun are often active in different parts of the day, increasing the availability of electricity in the grid. However, wind power is not easily scalable, the cheaper on-shore wind parks often lead to citizen complaints and a slow roll out, and off-shore wind turbines are three

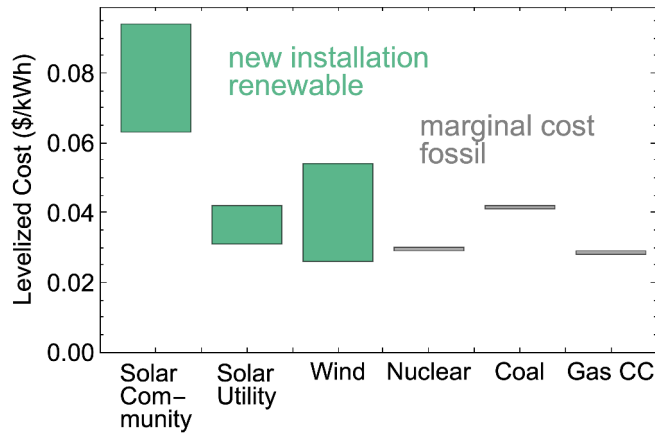


Figure 1.1: Select LCOE's taken from Lazard LCOE 14.0 [67]. Solar on the utility scale and wind power is now competitive with the marginal cost of running and maintaining fossil fuel power plants.

times more expensive to construct, operate and maintain [132]. Cost is the driving force in the energy market, any technology that is scalable and has a lower cost than the existing power plants will dominate over time. A good metric to compare the cost of energy generation between different technologies is the levelized cost of energy (LCOE), which takes the sum of all cost over the power plant lifetime into account. The investment bank Lazard has released a study of LCOE for 2020, a selection of costs are reproduced in Figure 1.1. The gray bars in Figure 1.1 are the marginal costs for keeping paid-off power plants running, which is, amazingly, in the same price region as installing a new wind or solar cell power plant.

If current technology is already so competitive, where is the need for new solar cell materials and designs? First, we have to accelerate growth, current installation speeds are not fast enough to meet expected future demand even with constant 30% year-over-year growth until 2030 [46]. We will need a large overcapacity to electrify our economy. The transportation sector is currently transformed by the advent of the electric vehicle, but other fields like heating and cooling are also expected to increase electric energy consumption dramatically. Especially heating

during winter in the global north will need vast amounts of electricity, which will require us to install much more solar cell capacity. Unfortunately the increased demand falls in a time with lower average irradiance levels. An overcapacity plus some storage will also allow us to alleviate the problem of intermittent irradiation during the day and night cycle and between winter and summer. Hydrogen is also discussed as a fuel for heating, aviation, trucks and shipping. Currently hydrogen is generated by splitting natural gas into CO₂ and hydrogen, so-called grey hydrogen. We will need large amounts of cheap electricity to replace this process with electrolysis.

The costs of silicon solar cells have fallen dramatically already, but since silicon solar cell generation is energy intensive, there is a lower cost limit, although it is unclear where exactly it is [72]. The energy payback time for silicon solar cells is currently around 1 year [92]. The main way of reducing the cost of electricity generated by solar cells is the increase of solar cell efficiency. Installation, land and upkeep are fixed costs and are always expensive, so even a free solar cell would only cut costs by around 50% [92]. These fixed costs do not increase for higher efficiency solar cells, which makes efficiency gains the main goal for much of the solar cell manufacturers nowadays.

However, silicon solar cells are already very efficient. The theoretical maximum for silicon solar cell efficiency that can ever be achieved is 29.4%, the so-called Auger limited detailed-balance limit [130]. The currently reported record silicon solar cell has an efficiency of 26.7% (90%(!) of the theoretical maximum), achieved with concerted efforts over the last 40 years [40]. It is clear that additional gains will be even harder to achieve, and additional efficiency gains with novel solar cell concepts are needed. One of these novel concepts is the singlet fission-silicon solar cell. In this concept high-energy light is absorbed in a separate layer that can then split the energy and inject it into a conventional solar cell like silicon. This concept has the potential for cheap manufacturing, since the underlying solar cell would remain largely untouched. In the following we will discuss how a conventional solar cell works, the principles behind organic semiconductors and singlet fission, and the challenges that arise

when combining organic and inorganic semiconductors to increase solar cell efficiencies.

1.2 INORGANIC SEMICONDUCTORS AND SOLAR CELLS

SEMICONDUCTORS Semiconductors are the building blocks for all solar cells, that allows us to extract the energy of light as usable electrical energy. When a photon hits a semiconductor it can generate an electron-hole pair, which can then be extracted with extraction layers and metallic contacts to drive an electrical load. Each semiconductor has a bandgap, which is the energy difference between the electron in the conduction band and the hole in the valence band. If the incoming photon has an energy smaller than the bandgap it will not be absorbed and can therefore not be used to generate power. In case of a photon energy with an energy larger than the bandgap energy the photon will be absorbed, but the excess energy will be lost as heat. Both of these loss mechanisms are fundamental when using a single bandgap, because the bandgap energy is very well defined but the solar spectrum is very broad, there are always photons that will not be used efficiently. This concept is visualized with the real solar spectrum and the silicon bandgap in Figure 1.2.

EFFICIENCY LIMIT A practical question is which semiconductor we should select to have the most efficient solar cell. This question has been answered by a detailed-balance calculation using a standardized input spectrum of the sun [115]. The optimal bandgap is between 1.1 eV and 1.5 eV, which is fortunate since there are many known materials that have this bandgap. Silicon is one of them, with a bandgap of 1.1 eV it has a high theoretical maximum efficiency above 31 %.

SILICON Most of the installed solar cells in the world are silicon solar cells [92], all aspects have been optimized for performance. This includes surface passivation, which prevents electrons and holes from recombining at the surface. The surface also usually has a micrometer-scale pyramidal

texture which decreases reflection losses and leads to higher currents. The surface with pyramids will look matte, as compared to bare silicon wafers that reflect visible light and look metallic to the eye. On top of the pyramidal structure a thin passivation layer is applied. This binds the dangling hydrogen atoms at the interface of silicon which are recombination centers. Often this passivation layer also acts as an additional antireflection coating, as in the case of silicon-nitride layers, which is the origin of the blue hue of many silicon solar cells. There are also effective ways of separating electron and hole by doping silicon with impurities.

One route for a new generation of solar cells is to keep all the aforementioned knowledge and technology for efficient silicon solar cells and use new materials as an add-on to increase efficiency.

Silicon is an indirect semiconductor, which means that a photon alone is not enough to form an electron hole pair across the bandgap, a phonon is also needed for the transition. Phonons are quasiparticles of the modes of vibrations in a crystal and their momentum is needed to absorb a photon in an indirect bandgap semiconductor. For solar cells this additional requirement is detrimental, it leads to lower light absorption coefficients which requires the silicon layer to be thick. To absorb 90% of the light incident on earth (AM1.5) the silicon layer needs to be at 50 μm thick, in the absence of any additional light trapping scheme [139].

EXCITONS IN SILICON Upon absorption of a photon, an electron-hole pair is created that is very close in space. Electron and hole are Coulombically bound in a state called the exciton. In inorganic semiconductors like silicon this state is of little importance since the binding energy is small and electron and hole are readily separated. The binding energy is inversely proportional to the dielectric constant. The high dielectric constant of silicon is 11.7 leading to a binding energy of 14.7 meV [58], smaller than $k_{\text{B}}T = 25$ meV, the thermal energy of a particle at room temperature. In other materials the exciton binding energy is much larger than $k_{\text{B}}T$, as we will see in the next section about organic semiconductors. This leads to very different behaviors of the semiconductor, including the main topic of the thesis, singlet fission.

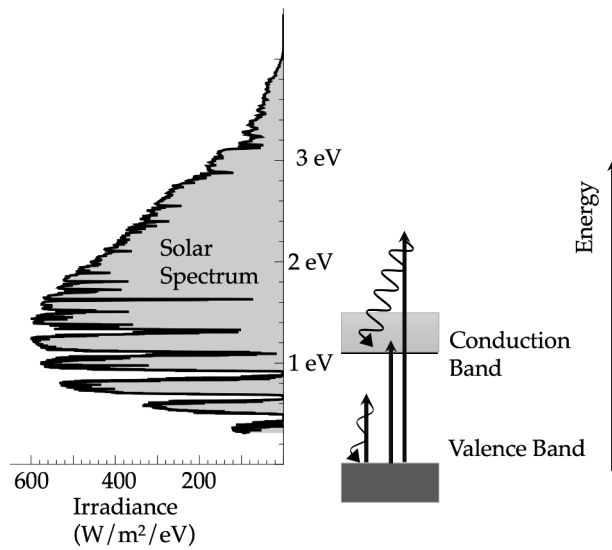


Figure 1.2: Solar spectrum and valence and conduction band of silicon. Photons with an energy smaller than the bandgap will not be absorbed, photons with a larger energy than the bandgap will be absorbed, but the additional energy will be lost through thermalization.

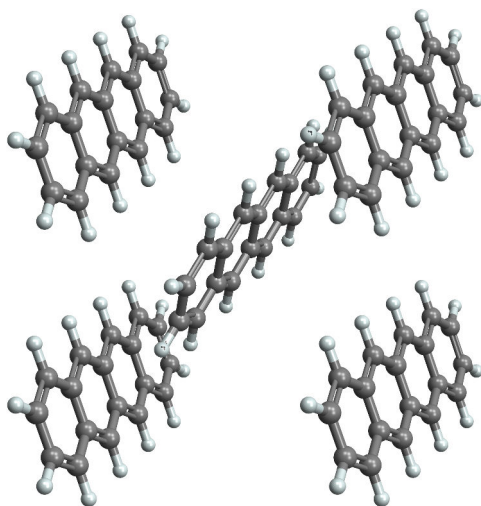


Figure 1.3: Molecular crystal of tetracene, an organic semiconductor consisting of four benzene rings that exhibits efficient singlet fission and is the focus of this thesis.

1.3 ORGANIC SEMICONDUCTORS

Organic semiconductors consist of covalently bound carbon and hydrogen atoms, that form amorphous molecular films, polymers and molecular crystals. They usually have a larger bandgap of (2 – 3) eV [60], which means they absorb light in the visible and appear colorful to the human eye. In the following we will shortly introduce the optoelectronic behavior of molecular crystals, starting with a single molecule.

WAVEFUNCTIONS IN ORGANIC MATERIALS Each molecule has a so-called molecular wavefunction, which describes the volume that an electron occupies. These volumes are also called orbitals, each with different energies corresponding to their distance from the positively charged nucleus. There are different kinds of orbitals depending on their angular momentum quantum number. In carbon there are p-orbitals and s-orbitals, filled with electrons in the lowest possible energy state. Two close carbon atoms will lead to a hybridization of the orbitals called sp-

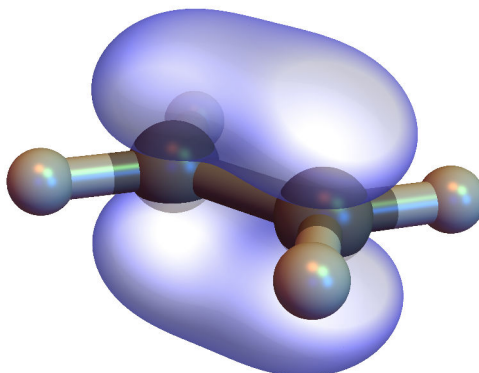


Figure 1.4: Wavefunctions (blue) of the π -bond in ethene. Hydrogen atoms are grey, carbon atoms are black. Modified, based on work of Günther Gsaller “Some examples of molecular orbitals” CC BY 3.0

Orbital, two electrons in such orbitals can form a bond, the strong σ -bond. If two electrons in p-orbitals overlap they form a more delocalized and weaker π -bond, the base for all organic semiconductors. Figure 1.4 shows the π -bond orbitals for ethene, a simple organic molecule.

HOMO AND LUMO We shall now discuss the energy levels of the electrons in these new bonds. The wavefunctions of the two electrons in a bond can interfere either constructively, leading to a state with so called bonding-character which leads to a new state with lower energy, or destructively, with so-called anti-bonding character and a higher energy level. This energy split is depicted in Figure 1.5, the anti-bonding orbitals are denoted with a star. This energy difference is very important, since we can excite an electron across it. Just like in inorganic semiconductors where the excitation happens across the bandgap, in organic semiconductors we excite an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) by absorbing a photon of the appropriate energy. The difference in energy is determined by the exchange integral of the two electron orbitals. The exchange integral can be expressed as the interaction of the positive nucleus

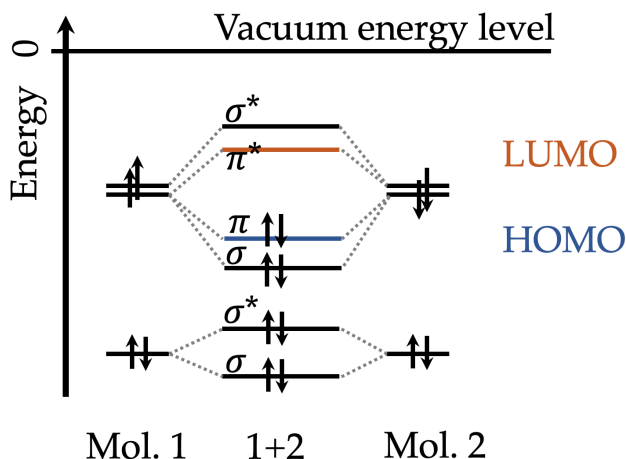


Figure 1.5: Electronic structure of ethene. Bonds form from single molecule orbitals. HOMO and LUMO are orbitals with an energy difference in the UV, larger organic molecules have lower HOMO-LUMO gaps with absorption in the visible spectrum of light. All electrons are in the ground state.

and the overlap of the two electrons centered around two different atoms. Luckily, for many organic semiconductors the energy difference between HOMO and LUMO is a couple eV, the same as photons in visible light, making them attractive for solar cell applications.

EXCITONS An exciton is a multi-electron state of a molecule, taking all electrons into account. In our previous case where we excited an electron from the HOMO to the LUMO we also have to take into account all the interactions between electrons and the smaller probabilities that an electron occupies higher lying orbitals. The main contribution to the state will still be from one electron in the HOMO and one in the LUMO, so it is common to omit all other states and depict that as an excited state exciton, called S_1 or singlet exciton. However, it is important stress that the singlet exciton is a multi electron state and has a different, smaller, energy than the HOMO-LUMO energy difference. The difference between

ground and excited singlet state, called the optical bandgap, is indeed the actual energy that a photon needs to have to excite the molecule, which can be slightly different from the HOMO-LUMO gap, also called the electrical bandgap, that we described before.

The *singlet* exciton state refers to the exciton spin state, described by the spin wavefunctions of all electrons. If we have two electrons with two spin states, called up and down and a total spin of 1, we can arrange the electrons in four states, three triplet states $(|\uparrow\uparrow\rangle, \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle), |\downarrow\downarrow\rangle)$ and one singlet state $(\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle))$. The difference in energy between the triplet and singlet states is the exchange energy, twice the exchange integral between the two electrons. If the wavefunction overlap is large between the spin-up and down electrons in the HOMO and LUMO for example, the exchange energy will be large and the triplet exciton will be at a much lower energy than the singlet exciton.

The triplet exciton cannot be accessed optically, we cannot directly photoexcite from the ground state singlet exciton to the triplet exciton, absent a spin flip or spin mixing from heavy atoms that lead to intersystem crossing between the singlet and triplet exciton states. This, however, also means that triplet excitons cannot be directly converted to light when they relax back to their ground state, the triplet exciton is therefore called a *dark state*. A welcome side-effect of a dark state is that the fast optical relaxation pathway is not available, which leads to a long lifetime of triplet exciton states in the μs range, allowing for more time to extract or convert energy of a triplet state.

1.4 SINGLET FISSION

Singlet fission is the process of converting an excited singlet exciton state into two triplet excitons with about half the energy each. Since two triplet excitons together have spin 0, just as the singlet exciton, this is a spin-allowed process, and can be both fast and efficient. Since singlet fission is an effective way of splitting the higher energy of singlet excitons in organic semiconductors, it can be used to increase the efficiency of a

single junction solar cell. In this scheme, we absorb high-energy photons in the organic semiconductor, singlet fission generates two triplet excitons that we then have to inject into a lower-bandgap semiconductor where the electrical energy can be extracted. Effectively we then created a solar cell with two bandgaps with a higher detailed-balance efficiency limit of 42 % [22], but with potentially only one material needing to be optimized for charge extraction.

The simplest way of depicting the singlet fission process is shown in Equation 1.1 and Figure 1.6. An excited singlet exciton in an organic material can be converted readily, on a subpicosecond time scale [119], into a correlated triplet pair (TT) that is overall still a spin-singlet state. If the coupling energy of the (TT) state is not too large then over time the TT state can lose spin-coherence and diffuse into two independent triplet exciton states, usually on two different molecules. This process is also spin allowed, since the two spins of the free triplets also add up to zero, but may, over time, lose spin coherence.



The two free triplet excitons can then diffuse in the organic semiconductor and have to be transferred into another semiconductor or disassociated into free electrons and holes.

We can also monitor the density of singlet excitons over time and will find that the quenching of the singlet state, and with it the photoluminescence is related to the singlet fission efficiency. Certain singlet fission materials like tetracene also allow for the backwards process, where two triplets recombine to form a singlet exciton which can then decay radiatively, called triplet-triplet annihilation (TTA). We can detect TTA as delayed photoluminescence. This delayed photoluminescence can be used to monitor the triplet population, and any quenching or transfer mechanisms will be visible as a reduced delayed photoluminescence intensity.

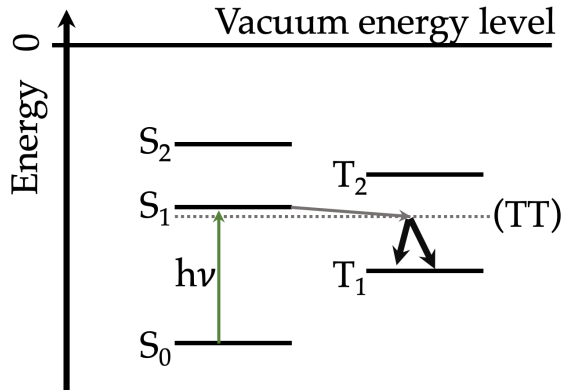


Figure 1.6: States involved in the singlet fission process, as described in Equation 1.1

SINGLET FISSION SOLAR CELLS The main unresolved problem in the realization of the singlet fission solar cell is about how the energy of the triplet excitons can be used to generate electricity.

Since the triplet exciton is a dark state, singlet fission cannot be used as a spectral downshifting layer that converts blue to red light. However, triplet excitons can be transferred into inorganic quantum dots like PbS which can emit light of the energy of the triplet excitons [21]. The quantum dots used for this purpose consist of heavy atoms that provide a large spin-orbit coupling, leading to spin mixing so the spin quantum number is no longer a good quantum number. Quantum dot emission and absorption can be tuned by changing their size, which is on the order of few nanometers, by exploiting the quantum confinement effect. Tuning the energy to accept the triplet excitons of many different singlet fission materials makes quantum dots very versatile.

Another example for the successful application of a singlet fission solar cell is the disassociation of triplet excitons in pentacene at a PbS quantum dot interface [28].

Attempts at disassociating the triplet exciton at disassociating the triplet exciton with an electron accepting layer of C₆₀ fullerenes have also been reported and may also be viable, if the efficiencies are increased [76].

The most elegant solution would be the direct transfer of triplet excitons into a bulk semiconductor like silicon, which has recently been shown to occur when deploying a thin HfO_xN_y interlayer between tetracene and silicon [29].

UPCONVERSION SYSTEMS The reverse process of singlet fission, triplet-triplet annihilation, should also be mentioned as it is a closely related process that can offer insights and tools useful for singlet fission solar cells. The upconversion layer absorbs low-energy photons, generates triplets via intersystem crossing and their energy is then transferred into an annihilator where two triplet excitons are combined to emit a high energy photon towards a solar cell [36], or in biological tissue to activate medicine with blue light [106].

Recently, direct transfer of a triplet exciton has been reported between a lead-halide perovskite and rubrene [86] which is relevant for singlet fission solar cells as it is the inverse process and shows that transfer of a band-like semiconductor excitation into a triplet state of an organic semiconductor is possible.

1.5 RESEARCH QUESTIONS AND OUTLINE

The main goal of this work was to realize a singlet fission solar cell by facilitating and investigating the transfer of triplet excitons at a semiconductor interface.

How can we transfer triplet excitons over longer distances if they are dark states? Is it possible to exploit FRET transfer from quantum dots to silicon for that purpose and achieve high transfer efficiencies?

We investigate the FRET efficiency from quantum dots into silicon in Chapter 2.

Since there are many different triplet transfer processes available, what are the challenges of realizing each of them, and if efficient triplet transfer is achieved, what is the effect of the transfer mechanism on the singlet fission-silicon solar cell efficiency? Can we, and should we search for different singlet fission materials with different singlet exciton energies?

We calculate the solar cell efficiencies for three transfer schemes in Chapter 3

If transfer of triplet excitons is the goal, can we use optical measurements to detect it, rather than building a complete solar cell? What are the limits of detection for triplet exciton transfer and how can we eliminate other influences of sample to sample variation and other quenching pathways to isolate the signal of triplet transfer?

We describe a new method of combining optical and height measurements of tetracene islands on silicon samples to detect triplet quenching in Chapter 4.

What kind of interlayer between tetracene and silicon can enable the transfer of triplet excitons, and what influence does the orientation of the triplet molecules have on transfer efficiency? How can we be sure to detect triplet transfer, and can we quantify the transfer efficiency?

We show a solar cell with triplet transfer in Chapter 5 and quantify the triplet transfer efficiency using a singlet fission model to describe delayed photoluminescence decay data.