Singlet Exciton Fission: Using Organic Semiconductors to Break the Shockley–Queisser Limit

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Singlet exciton fission is a carrier multiplication process in organic semiconductors, which allows for the generation of two electron-hole pairs for each photon absorbed. First discovered in the late 1960s, the area has witnessed an explosion of interest within the last 5 years, with demonstrations that singlet fission can occur on sub 100fs timescales, with 200% yield and can be used to build photovoltaics with external quantum efficiencies above 100% percent. The grand challenge of the field is to use singlet fission to enhance the efficiency of conventional inorganic solar cells, such as silicon, and break the Shockley–Queisser limit on the efficiency of single junction photovoltaics. Achieving this goal will require a greatly broadened effort than at present, with collaboration between synthetic chemistry, spectroscopy, theory, material science, organic and inorganic semiconductor device physics and engineering. This review critically assesses the current state of the field, highlighting the key results and identifying the crucial challenges ahead. In doing so, we seek to open the area to new expertise and ideas, which will in turn further both fundamental science and device applications.

1. Introduction

As the world transitions to a more sustainable economy, renewable energy sources are set to play an increasing role in electricity generation. Photovoltaics (PV), which convert sunlight into electrical current, are one of the most promising technologies in this area. Although invented in the 1950s, it has only been in the past decade that PV has begun to make an impact in large scale energy generation. At the end of 2014, a total of 180GW of PVs had been deployed with a year on year growth of 70% in 2013. It is predicted that total PV deployment could reach 6000GW by 2050[1,2]. This wide scale deployment has been driven by increasing demand for renewables, advances in technology and rapid reduction in the price of PV modules. For instance, the price of Si modules has fallen by a factor of ten in the past decade, with prices predicted to drop further. This drastic price reduction means that the module will make up a falling share of the total cost of the PV installation, with the balance of system (BOS) cost, which refers to all the other components that are required for a PV installation, taking up a greater cost[2]. Thus, to further lower the total cost of PV generated electricity two things will be needed. One is a reduction in BOS costs. The other is an increase in the efficiency of PV modules, as this increases electricity generation for the same BOS costs[2].

The efficiency of PV modules has been rising steadily for the past few years, as they approach the performance of the best lab cells. But there are fundamental thermodynamic limits, beyond which these devices cannot be pushed via conventional methods. An illustrative case is that of Si based PV devices. The best lab cells give a power conversation efficiency (PCE), the total efficiency with which solar irradiation in converted to electricity, of 25.5%. There is not much scope for further improvements in PCE, as evidenced by the fact that the PCE of the best Si devices have improved by less than 2% in the last twenty years. This is because Si PVs, like all single junction PV cells developed to date suffers from a fundamental energy loss mechanism, *thermalisation*.

Semiconductors have a fixed bandgap. If the energy of an incident photon is above the bandgap the photon can be absorbed to generate an electron-hole pair. But the absorption of a high-energy photon generates one electron-hole pair just as the absorption of a low-energy photon does. The extra energy of photons above the bandgap is lost via thermalisation. This is the dominant loss in solar cells as shown in Figure 1, leading to the so-called Shockley–Queisser limit on efficiency[3], which is 29% for an idea silicon cell (E_g 1.1eV).

Several strategies to overcome thermalisation losses are being studied. These include multi-junction PVs[2,4,5] and multiple exciton generation (MEG)[6-8]. Multi-junction PVs are the most mature of these technologies, with efficiencies above 45%, but suffer from high costs, which has so far limited their

wide scale deployment[4,5]. MEG in semiconductor nanocrystals has been widely explored over the past decade but for the current generation of materials the yield of this process is not high enough[6,8]. An analogous process to MEG, called singlet exciton fission (SF), occurs in organic semiconductors and shows great promise to beat thermalisation losses in PVs[9].

This review critically assesses the current state of SF, introducing the basic concepts and proposed mechanisms of SF. Various device architecture which seeks to use SF are discussed and evaluated and the challenges that need to be overcome into order to enable SF to break the Shockley–Queisser limit are highlighted.

2. The Basics of Singlet Exciton Fission (SF)

SF refers to the spin-allowed conversion of one spin singlet exciton to two spin triplet excitons on two neighbouring chromophores[9]. In conjugated organic materials, the absorption of a photon leads to the formation of a singlet exciton (S_n), see Figure 2a. If the energy of this singlet state $E(S_n)$ is greater than twice the energy of the lowest-lying triplet state (T_1), i.e. ($E(S_n) > 2E(T_1)$), then spin-allowed fission of the singlet to form two triplets ($S_n \rightarrow 2T_1$) can occur rapidly. For instance, in pentacene and many of its derivatives, triplet excitons are formed on sub 100fs timescales[10,11], with unity efficiency[12]. If on the other hand, there is a small barrier to fission, i.e. ($E(S_1) < 2E(T_1)$), fission can occur via thermal activation on slower time scales. An example of such a system is Tetracene, where triplets form on a 30-120ps timescale[13].

In 1970 Johnson and Merrifield put forward a kinetic model to explain the SF process[14],

$$S_0 + S \rightarrow TT \rightarrow T + T \qquad\qquad 1$$

Where: S is a excited singlet state, S_0 is the ground state, T is the molecular triplet state and $T+T$ is a pair of fully independent T states. TT corresponds to a doubly excited pair of spin-correlated triplets, forming an overall spin singlet. The TT state, often referred to as the multiexciton state, is considered a dark state that cannot be optically populated from the ground state, but serves as an intermediate to the formation of free independent triplets T+T. For an overview of the Merrifield model, materials criteria, as well as a history of the field, the reader is directed to a comprehensive review by Michl et.al.[9]

For SF to be efficient it needs to outcompete other photophysical process, such as radiative and non-radiative recombination to the ground state and charge and energy transfer at heterojunctions (See

Figure 2a). The rate of singlet fission is thus extremely important. Within the frame work described above, it is the coupling between S and TT that controls the rate of fission[9,11], an issue that will be explored further in the next section. In the ideal case, singlet fission proceeds on ps or sub-ps time scales and results in the formation of two independent molecular triplet excitons (T+T) for each photon absorbed.

3. Thermodynamic considerations for SF PV

If we seek to use SF to boost the efficiency of PV devices, we need to take into account several thermodynamics considerations. Unlike MEG in semiconductor nanocrystals, SF produces two triplets for each photon absorbed by the material (in the ideal case). The two triplets produced have an energy equivalent to roughly half the Eg of the material. This means that compared to a material with the same Eg that did not undergo fission, the SF material can at best produce half the open circuit voltage (V_{OC}), but double the photocurrent (J_{SC}). There is thus no net gain in power conversion efficiency (PCE) if a singlet fission material is used on its own in a PV device[15-18].

To realise a gain in PCE a SF material must be combined with a low Eg semiconductor material (LGS)[15,16]. Ideally the LGS has a Eg half that of the SF material. As illustrated in figure 1b, high energy photons are absorbed in the SF material to generate two triplet excitons. Low energy photons pass through the SF layer and are absorbed in the LGS, generating one exciton/electron-hole pair. In such a case, the V_{OC} of the system is set by the LSG, but now above twice the Eg of the LGS (i.e. when the SF material starts absorbing), two excitons are generated instead of one. This allows for thermalisation losses to be partly overcome and increases the PCE. Calculations suggest that for an ideal silicon solar (Eg 1.1eV) SF could improve the PCE from 29% to 35%[9,15].

4. Mechanism of SF

The mechanism of singlet fission has been the most hotly debated topic in the field in recent years, with the bulk of literature dedicated to this discussion. Here we touch upon this topic only briefly, to give the reader an overview of the area and provide a background for the topics to follow. Several in-depth reviews of the different proposed mechanisms are available for the interested reader[13,19-25].

In common with the model of Johnson and Merrifield (see above) the S and TT states, and the interplay between them, have been the focus of theoretical models attempting to describe singlet fission. While it is generally accepted that the coupling between *S* and the TT state controls the dynamics of the

fission, the nature of the coupling and the electronic and structural properties controlling it have been the subject of much debate. Crucial to obtaining the correct coupling is not only the electronic structure of the individual chromophores, but also the way they are arranged next to each other.

In the simplest description, the so-called direct mechanism[19], it is only the direct coupling between S_0S and TT, $V = \langle S_1S_0 | \hat{H} | TT \rangle$, that determines the rate of fission, see figure 3a. Alternatively, in the 'in-direct/mediated' mechanism, using higher-order perturbation theory the mixing of S_0S and TT with virtual states, which are charge-transfer (CT) in nature, are considered in determining the rate of fission[19,24]. We note that in many of the widely studied singlet fission systems, such as the polyacenes, the photogenerated singlet exciton may already have significant CT character, with as much as 50% CT character for S_1 in pentacene[26]. There is some debate over the energies of the charge-transfer states and whether they participate as actual intermediates in the SF process, or as virtual states that mediate effective coupling of S and TT via a type of 'super-exchange'[24]. In the limiting case, the CT states may act not as virtual states helping to mix S_0S and TT, but real intermediates[27], i.e. S_0S is converted to CT via electron transfer and then CT is converted to TT via back electron transfer. Through the efforts of several group[11,13,15,19-21,23,24,26,27], much progress has been made is modelling the electronic states involved in fission and the coupling between them. There is a growing consensus that the virtual mediated-mechanism with a varying degree of CT contribution allows for a good description of the observed experimental results.

However, most models till date have been limited to a static picture of fission, dealing only with coupling between S_0S and TT, and provide limited mechanistic insight into the extremely rapid (<100 fs) dynamics of singlet fission observed in common materials – a time scale on which the Born-Oppenheimer approximation breaks down. Strong electron-phonon coupling is one of the ubiquitous feature of molecular materials and hence molecular vibrations can strongly effect electronic coupling. This mixed 'vibronic' coupling is thought to play a key role in many ultrafast process in molecular systems such as photosynthesis[28] and charge separation at organic heterojunctions[29,30]. Some recent theoretical work has also begun to evaluate the influence of molecular motion in modulating the coupling between S and TT[31,32], and recent ultrafast spectroscopy results suggest that vibronic dynamics play a dominant role in mixing S and TT states and driving the transformation between them[33,34]. Further experiments and refinements of current theoretical models to take into account the role of vibronic coupling will no doubt provide a much more complete picture of SF. This in turn should allow for precise design rules to drive the synthesis of the next generation of SF materials.

5. Detecting and Quantifying SF

A crucial aspect of studying SF is to know when it is occurring and with what efficiency. This turns out to be rather a complicated task due to the 'dark' nature of triplet excitons, i.e. they no not emit light due to the spin-forbidden nature of the transition to the ground state, and the fact that triplets can also be formed via Intersystem crossing (ISC), mediated by either hyper-fine or spin-orbit interactions[35]. As described in the model of Johnson and Merrifield[14], SF preferentially populates certain spin sub-levels of the triplet states, as opposed to ISC which gives rise a thermalized spin population. This can give rise to quantum beats in the delayed fluorescence of the sample, which arise from the recombination of triplets for reform the emissive singlet state, see Figure 4a. However, despite extensive efforts, quantum beats have only been observed in tetracene till date[36,37]. In the most efficient systems, such as pentacene, fission in exothermic and the triplet excitons formed cannot regenerate the emissive singlet exciton. Thus, these materials do not show any delayed fluorescence.

The preferential population of triplet sub-levels can also be detected via electron paramagnetic resonance (EPR). This provides a powerful way to not only to assess whether SF is occurring, but also elucidate the underlying spin-dynamics and two recent studies using EPR have discovered the formation of spin-2 quintet states in these systems[38,39]. This represents the first time that high spin states have been detected in organic semiconductors and it is certain that EPR spectroscopy will play an increasing role in SF studies.

Magnetic field effects provide another way of detecting SF, by modifying the number of TT states which can couple to S_1 and thus modifying the equilibrium between singlets and triplets[40]. The effect of this modulation can be detected via changes in prompt and delayed fluorescence and photocurrent[15,18,41]. However, these changes can be small, on the order of a few percent, and their absence is not conclusive proof that fission is not occurring[42]. It is worth nothing that neither magnetic field effects, nor quantum beats or EPR can provide an estimate of the yield of fission.

In recent years, time resolved optical spectroscopy has been the tool of choice to study and attempt to quantify singlet fission. Time resolved photoluminescence has been used to study the rate of decay of singlets[13,43]. The drawback of this technique is that it cannot confirm the presence of 'dark' triplet excitons. In this respect, ultrafast transient absorption spectroscopy has emerged as the leading technique to study fission. It provides both high time-resolution (sub 10fs) and the ability to detect the optical absorption associated with triplets being excited from the lowest excited state to the higher lying excited states, i.e. the $T_1 \text{->} T_n$ transitions, see Figure 4c. However, organic molecules often have congested spectra with overlapping signatures from singlets, charges, thermal artifacts, and electro-

absorption features[12]. This can make identifying triplets challenging. Triplet sensitisation and oxygen quenching of triplets can help to overcome these problems[44]. But quantifying the yield of triplets in the solid state remains a key challenge. Recently, other techniques such as time-resolved Raman[33,45] (see Figure 4d), photo-emission[46,47] (see Figure 4b) and 2D electronic photon echo spectroscopies[34] have been used to study SF. Each of these techniques provide unique information about the SF process, but also suffer from problems of congested spectra and quantifying triplet yields. Thus, there is no magic bullet for the experimental study of SF. A combination of experimental methods is needed to study rates, quantify yields and ultimately to try and understand the underlying mechanism of fission.

6. SF Materials

As improved models for SF are developed, new and more detailed design rules are being put forward to enable efficient SF in chromophores. Below we briefly summarise the current state of knowledge. More detailed discussions can be found in the references cited.

a. **Electronic Structure**: Chromophores with a range of electronic structures can undergo SF (see ref X for an complete discussion), but the most important criteria is that $E(S) > 2E(T_1)$, where S is a singlet state that can sustain fission[11]. This allow for rapid SF that can outcompete other process as discussed above. A significant CT character in the excited state also appears to be beneficial for SF[19,24,26].

b. **Chromophore Packing:** The coupling between S and TT can be extremely sensitive to the packing of chromophores. For instance, edge on packing is normally highly detrimental for SF, while a slip-stacked packing provides the optimal configuration in many materials[19]. Figure 3b-d shows different crystal packing motifs for pentacene derivatives that undergo SF. However, an important point to consider is that molecular motion can dynamically change the orientation of chromophores, especially after photoexcitation[23,32]. An example is the case a pentacene dimers in which the individual chromophores dramatically change their mutual orientation, allowing quantitative SF, even though their ground state orientation is highly unfavorable for SF[48]. An understanding of molecular orientations in the excited state is thus key to understanding SF.

While the above-mentioned criteria are crucial for efficient SF, they are not sufficient if one wishes to build efficient SF based PV devices. For this several other criteria need to be met.

c. **High absorption coefficients:** Strong absorption, with absorption coefficients above 10^5 are needed in the next generation of materials, to reduce device thickness and mitigate problems with triplet diffusion (see below).

d. **Bandgap (E_g) and Energy Levels:** As discussed above, SF materials need to be paired with a complimentary low Eg material, ideally half the Eg of the SF material. In practice, this entails designing SF materials which are twice the Eg of semiconductors widely used in PV devices today. This includes silicon (1.1eV), but also CdTe (1.5eV) and CIGS (1-1.7eV). Ideally, the energy levels of these SF materials would be such as to form type 1 heterojunctions with the low Eg semiconductors, to allow energy but not charge transfer to the low badgap semiconductor.

e. **Long triplet lifetime and diffusions lengths:** To harvest SF generated triplets efficiently it is crucial that the triplet have sufficiently long life times and diffusion lengths, such that they can reach an appropriate heterojunction where they can be harvested. The conditions that enable long-triplet diffusion lengths are reasonably well understood, although more remains to be done in the area[35]. Bulk-heterojunction type morphologies can reduce the need for long diffusion lengths, but they create challenges related to triplet-charge annihilation in devices where triplets are dissociated[15].

f. **Stability:** In the long run, any SF based PV technology will need to have an operational lifetime of at least 5-10 years. Photostability of organic chromophores has long been as issue and has created huge challenges, for instance in the field of organic photovoltaics[49]. Till date, there have been no systematic attempts to study the stability of SF based chromophores and their degradation mechanisms, although many of the current generation of SF molecules are known to be rather unstable. The example of organic light emitting diodes (OLEDs), now a major commercial technology with operating lifetimes in excess of 100000 hours[50], shows what can be achieved with concentrated effort and gives some room for optimism that stable SF systems can be achieved. But this will require a large scale interdisciplinary effort and the challenge should not be underestimated.

For many decades, attempts to study and utilise SF were hampered by the small range of materials that showed the phenomena. Most studies focussed on just a few molecular crystals, such as anthracene and tetracene. However, the surge in interest in SF over the past 5 years has led to a dramatic increase in the number of chromophores known to undergo SF, with newly synthesised materials being added to the list all the time. It has been suggested that several polyacenes/polyacene dimers[11,51-53], PDIs[32,54,55], terrylenes/TDIs[27,56] and CT-polymers[57] undergo efficient fission. Some of these molecules fulfil many of the above criteria, but none can fulfil all of them. Thus, the quest for the ideal SF

chromophore continues and one can be optimistic that such molecules will be realised in the coming years.

7. Harvesting Triplets in Photovoltaics Devices

The idea of using SF to boost the efficiency of PV devices was first proposed by Dexter in 1979[58]. In his pioneering paper, Dexter suggested coating a silicon solar cell with a layer of tetracene, which could harvest higher energy photons to generate triplet excitons which could then be transferred into silicon cell. As we will discuss below, realising this seemingly simple scheme has proven to be extremely challenging.

An important fact to consider in a SF enhanced PV device is the voltage losses associated with converting an absorbed photon into charges in the external circuit, $V_{Loss} = E_g - V_{OC}$. The lowest loss occurs in GaAs PV devices, <380mV. Below we will consider these losses for each potential SF device architecture and evaluate their potential benefits and drawbacks.

a) All Organic Devices – SF OPV

The field of OPVs has made great progress in the last decade with efficiencies rising steadily[49]. The best single junction cells now give PCE above 11%[59] and the best triplet junction cells PCE above 13%[49]. While external quantum efficiencies of the best devices are above 80%, V_{Loss} continues to be large, about 600mV[60]. These higher losses are caused by the energetic offsets needed between donor and acceptor to dissociate excitons, disorder and non-radiative recombination[61].

OPVs are the first devices in which SF chromophores have been used. Most devices consist of acenes, such as pentacene or tetracene, as donors with C_{60} as an acceptor (see Figure 1a), although other acceptors have also been used[15,62]. An important milestone was reached by Baldo and co-workers with the demonstration of a pentacene/C_{60} device with an EQE > 100%[18]. Such devices were further optimised to give EQEs of 130%[63], Figure 5b.

Two major challenges present themselves when trying to integrate SF chromophores into OPV systems. Firstly, there are no high performance OPV materials with Eg close to 1eV, that could act as the LGS to be paired with the SF material. Taking a higher Eg material would mean that the potential gain in PCE is reduced sharply. The second challenge involves dissociating the triplet excitons at a heterojunction with the LGS. Most efficient OPV systems have used fullerenes as acceptor molecules and only recently have successful non-fullerene acceptors been demonstrated[59]. New materials are thus

needed to tackle these two challenges, allowing either efficient acceptors with Eg close to 1eV to be combined with SF donors, or efficient donors with Eg close to 1eV to be combined with efficient SF acceptors.

It must be noted however, that SF based OPVs are not likely to break the Shockley–Queisser limit in the near future, given the low starting point for PCE. A 20% increase in PCE for such system would only represent a 2% increase in total PCE. Also, in comparison to many inorganic PVs, multi-junction OPVs can be fabricated relatively easily and could offer a simpler route from a materials perspective as different donors can be combined with the same acceptor (such as a fullerene) in different sub-cells[64].

b) SF based Dye Sensitised Solar Cells (DSSCs)

DSSCs, first demonstrate in 1991, consist of monolayer of a molecular dye attached to mesoporous oxide scaffold (normally TiO_2) into which the dye injects electrons[65]. The holes left behind after electron transfer to the oxide are shuttled to the electrode by a hole transporting layer (either a liquid electrolyte or a solid state transporter such as Spiro-MeOTAD). As shown in Figure 5c, the idea of using SF in DSSCs is based on having two dyes instead of one, with one, the SF dye, being twice the bandgap of the other[9]. The SF dyes would then inject two electrons into the oxide per high energy photons and the low energy dye one electron per low energy photon. Although at first glance this appears to be a simple concept, a closer examination reveals numerous challenges and drawbacks of this approach. The SF dye would have to form a monolayer on the oxide surface with a packing that allows the correct coupling to enable fission. So far no such systems have been developed. This problem could be overcome by using SF based dimers[52]. Another problem relates to the fact that triplets in such systems would not be free to diffuse away from each other before charge separation. Following electron injection from one triplet into the oxide, a hole would be left on that molecule. The second triplet generated via fission would sit on a molecule next to it, or in the case of a dimer on the same molecule and could rapidly be lost via triplet-charge annihilation.

It must also be noted that while the EQE of DSSCs is above 80% for the best cells, V_{Loss} is very high, and the best liquid based DSSCs give a PCE below 12% (solid states cells give lower PCE)[66]. DSSC PCEs have also not improved significantly in almost two decades, suggesting that fundamental barriers exist in such systems. This would suggest that DSSCs are not the ideal architecture to try and utilise SF.

c) Hybrid Organic/Quantum Dot Devices

Organic/quantum dot PV devices have very similar architectures to donor-acceptor OPVs (see Figure 1d). In most cases the quantum dot acts as an electron acceptor and the organic the donor. SF is more amenable to be used in such systems, as unlike organics, low Eg quantum dots can be readily synthesised. These provide the LGS to be combined with the SF material. The first demonstration of hybrid SF-Organic/Quantum dots cells was made in 2012[16] and a handful of studies have now explored the area in more detail[17,62,67]. Internal quantum efficiencies of 170% have been demonstrated for a TIPS-Pentacene/PbSe systems[68], suggesting that triplets can be effectively dissociated at these hybrid heterojunctions. However, like OPVs the overall PCE of quantum dot PVs is still low, around 11%[6]. This is because they suffer from high V_{Loss}, thought to be related to trap states in the quantum dots and poor charge transport[6]. Thus, will promising candidates for the use of SF, these systems will not reach their full potential until the large V_{Loss} in quantum dot systems is eliminated.

d) Combining SF with conventional inorganic photovoltaics

Inorganic PVs based on Si are the dominant PV technology today, while thin films alternative such as CIGS and CdTe are also seeing increasing commercial deployment. They all show high efficiencies, with the best lab cells giving PCEs of 25.5%, 21.7% and 21.5% for Si, CIGS and CdTe respectively. Yet all these devices are fundamentally limited by thermalisation as discussed previously. Using SF to improve the PCE of these cells is thus a very interesting area to explore. This can in principal be achieved in two ways, using charge transfer or energy transfer, as illustrated in Figure 5e.

In the first approach, triplets generated via fission are dissociated at a heterojunction formed between the SF material and the inorganic semiconductor[67]. Electrons and holes then flow through the organic and inorganic and are collected at electrodes. The challenge of this approach is to form a high-quality heterojunction between the organic and inorganic, minimising energy losses, from band offsets and also from recombination across the interface. There have been few studies exploring heterojunctions between organic semiconductors and bulk inorganic semiconductors, and thus little is known about the obstacles to be overcome. It is likely that careful control of this interface will be required to passivate surface defects on the inorganic, which could otherwise lead to increased recombination.

An alternative approach, is to try and transfer the energy of the triplet excitons generated via fission into the bulk inorganic semiconductors, where charge generation and collection are already optimised. In this approach, no charge flows through the SF layer and both holes and electrons are collected via the inorganic. This is essentially the approach suggested by Dexter in his pioneering paper[58]. The main problem is that triplets do not possess a significant dipole moment (return to the ground state is spin

forbidden) and thus cannot undergo energy transfer via the Coulomb interactions, i.e. FRET[35]. Instead, much shorter range exchange interactions allow triplets to move. This is referred to as Dexter energy transfer[35].

Recently, it was shown for the first time that triplets can be transferred from organic to inorganic quantum dots via Dexter Transfer. Experiments on pentacene/PbSe and tetracene/PbS systems showed that this transfer could be close to 100% efficient if the ligands on the quantum dot surface were sufficiently short[69,70]. Although these studies were for inorganic quantum dots, efforts are underway to see if the same effect can be achieved with bulk inorganic semiconductors. One study found no evidence for energy transfer from tetracene to Si[71], but further work is needed to fully explore triplet energy transfer to bulk inorganic semiconductors and numerous challenges related to device architectures, interfaces and surface treatments will need to be overcome.

An alternate strategy, is to use quantum dots as an intermediary between the organic SF material and bulk inorganic semiconductors. When triplets are injected into quantum dots the spin-1 dark state is converted into bright states, due to spin mixing in the quantum dot, leading to photo emission[69,70]. This opens the door to an all-optical method of utilising the triplet excitons generated via SF, effectively converting a carrier multiplication process into a photon multiplication process. The basic scheme of such a device, which we label a "Singlet Fission Photon-Multiplier" is shown in Figure 5f and consists of a thin film of a SF material of appropriate band gap and triplet energy doped with a small amount of inorganic quantum dots. The device function as follows: light absorption creates singlet excitons (1) that rapidly undergo SF to form two triplet excitons (2). The triplets then diffuse and undergo efficient triplet transfer into the quantum dots (3). The electron-hole pairs in the quantum dots can then recombine radiatively, leading to the emission of two low-energy photons for each high-energy photon absorbed (4). The emitted photons are then absorbed in a conventional solar cell onto which the photon multiplier is coated or laminated. If such a photon-multiplier film could be developed, it would have clear advantages over other methods to harness SF, such as being a passive optical film that could be easily integrated into existing PV module designs, with no requirement for interfacing with the inorganic semiconductor and no extra cost or complexity associated with electrodes, charge transport layers or external circuits. Such films could also be tuned to work with silicon, CIGS, CdTe or perovskites PVs. Thus, all optical schemes such as the "Singlet Fission Photon-Multiplier" offer a very promising strategy for harnessing SF and breaking the Shockley–Queisser limit.

Outlook

The field of singlet fission research has generated many exciting results over the past few years that have shed light on the fundamental quantum mechanics and structure-function relationships governing the process. The challenge for the community is now to build on this and use these insights to develop not just new materials, but new ways to harness the process of singlet fission to improve photovoltaics. While theory, spectroscopy and synthetic chemistry have led the way so far, going forwards much greater input will be needed from device physics, materials science and engineering. This promises to be a very exciting time, with these new inputs not only brining us closer to device applications but also feeding back into fundamental science. The recent development of all optical methods to couple singlet fission to inorganic photovoltaics, eg Singlet Fission Photon-Multiplier, suggest that singlet fission enhanced inorganic photovoltaics could be realised in the near term and provide a real boost to the photovoltaics technology.

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Figures
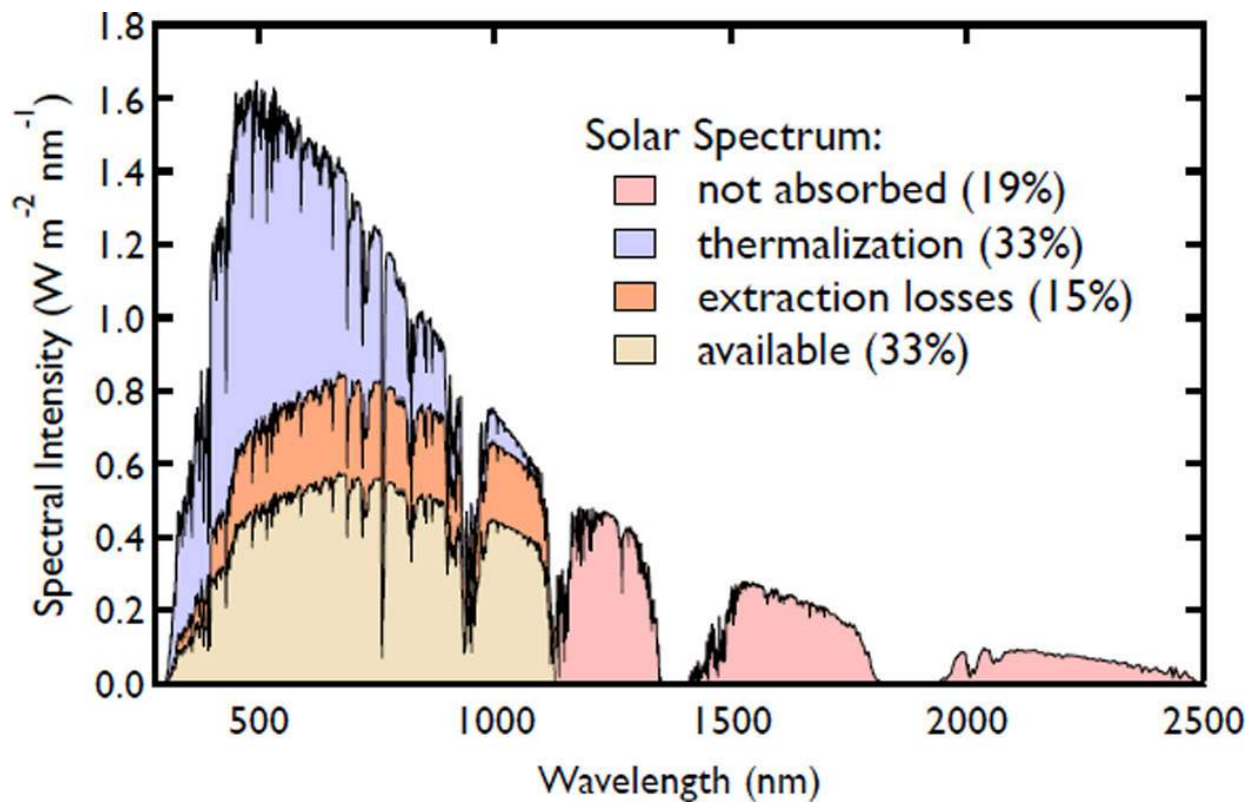
Figure 1: Losses in an ideal silicon cell leading to the Shockley–Queisser limit.
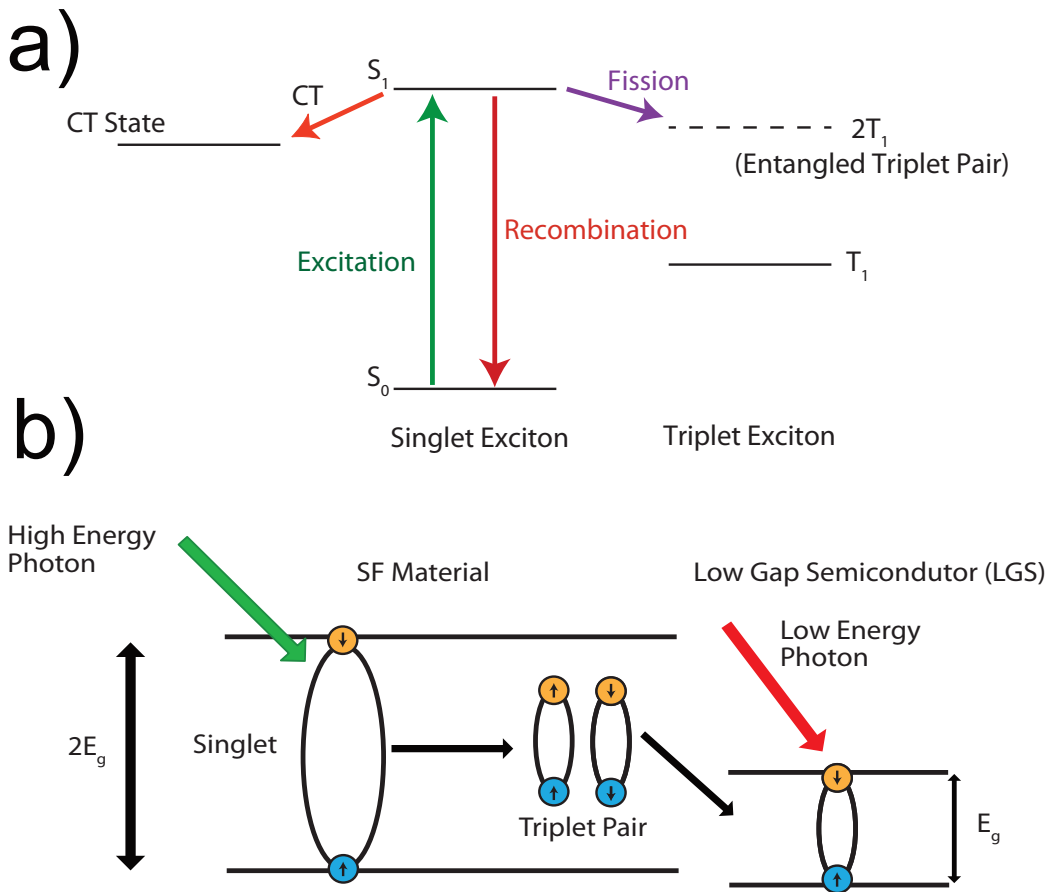
Figure 2: (a) Jabolowski diagram showing singlet exciton fission process. The absorption of a photon in a conjugated organic semiconductor (green) leads to the formation of a singlet exciton, S_1. The singlet and then undergo SF to form a pair of triplet excitons $2T_1$ (purple). Competing loss channels can include CT from the singlet state at a donor-acceptor interface or recombination of the singlet back to the ground state. **(b)** Scheme for improving PV efficiency of a Low Gap Semiconductor (LGS) using SF. The SF material with bandgap $2E_g$ absorbs high energy photons, forming singlet excitons, which then undergo SF to two triplet excitons. The SF material is combined with a LGS with bandgap E_g, which absorbs low energy photons to generate one electron hole pair. The combined system generates 2 electron-hole pairs for high energy photons, while the voltage is still determined by the LGS.
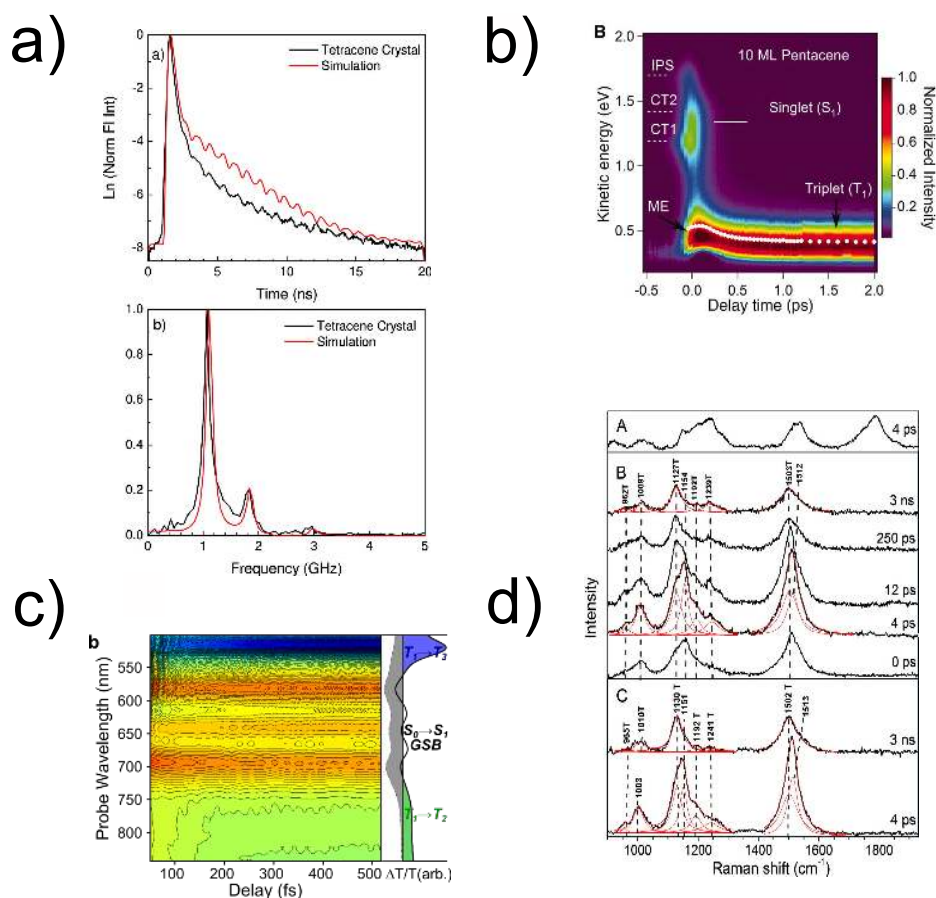
Figure 3: (a) Quantum beats in the delayed fluorescence of Tetracene, which arise from the recombination of entangled triplet pair states. The frequency of the beats is connected to the zero field splitting energy between the spin sub-levels of the triplets. Taken from Burdett et al, J. Am. Chem. Soc. 2012, 134, 8597−8607

(b) Time-Resolved 2 Photon Photoelectron Spectroscopy (TR2PPES) measurements show ultrafast formation of low energy features, assigned to triplet excitons, in thin films of pentacene upon photoexcitation. Taken from Chan et al, Science, Vol. 334 no. 6062 pp. 1541-1545

(c) Ultrafast transient optical absorption spectra of TIPS-pentacene thin films show a rapid conversion of singlet excitons to triplet excitons. Taken from Musser et al, Nature Physics, 11, 352–357 (2015).

(d) Time-resolved resonance raman signatures of SF in a zeaxanthin aggregate. Taken from Wang C and Tauber MJ, J Am Chem Soc 2010, 132(13988-13991)
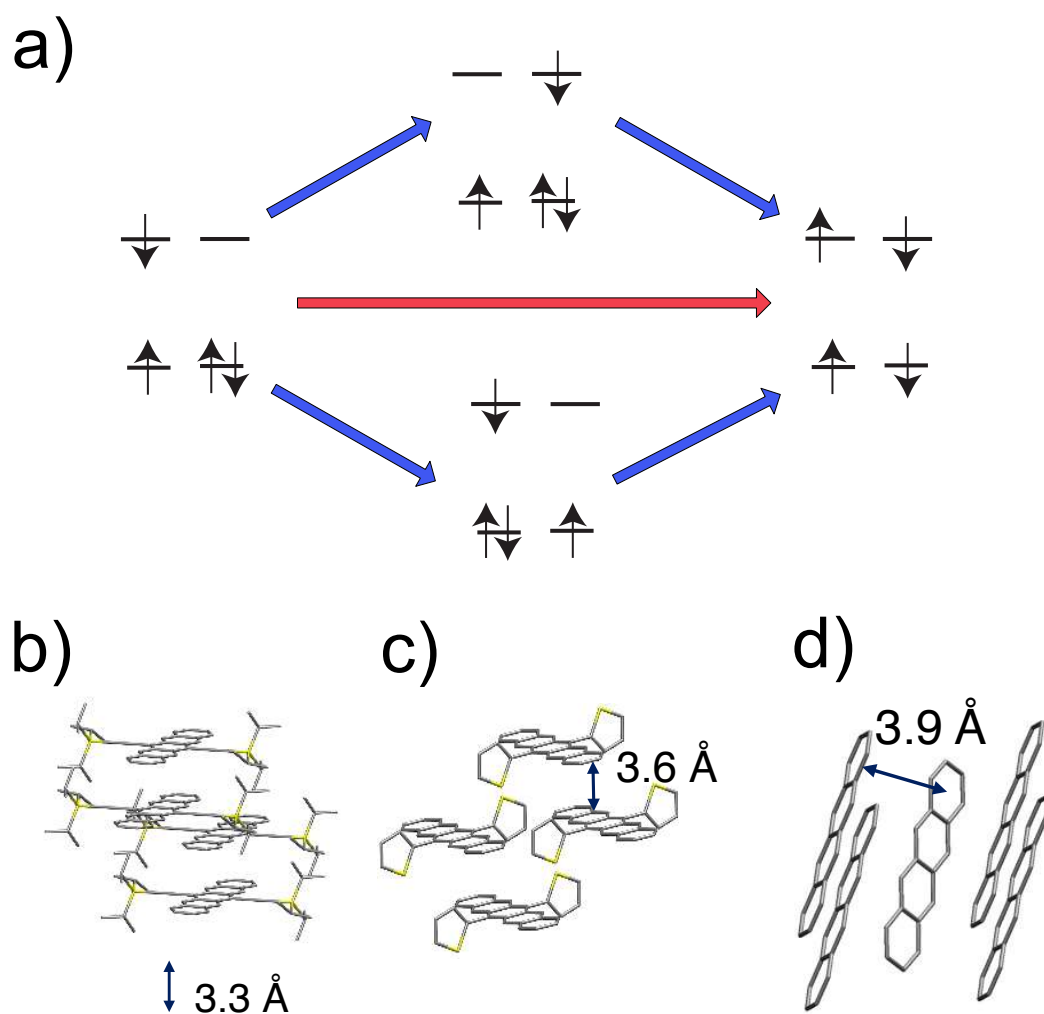
Figure 4: (a) Model of direct (red) and mediated (blue) pathways for SF. <mark>Figure made by authors.</mark>

Crystal packing motifs for **(a)** 6,13-bis(triisopropyl-silylethynyl) pentacene (TIPS-P), **(b)** 6,13-di (2′-thienyl)pentacene (DTP) and **(c)** tetracene. The molecules pack in 2D π-stack, Slip stacked and Herringbone configurations respectively. <mark>Figure taken/adapted from Yost et. al, Nature Chemistry, 6, 492–497 (2014).</mark>
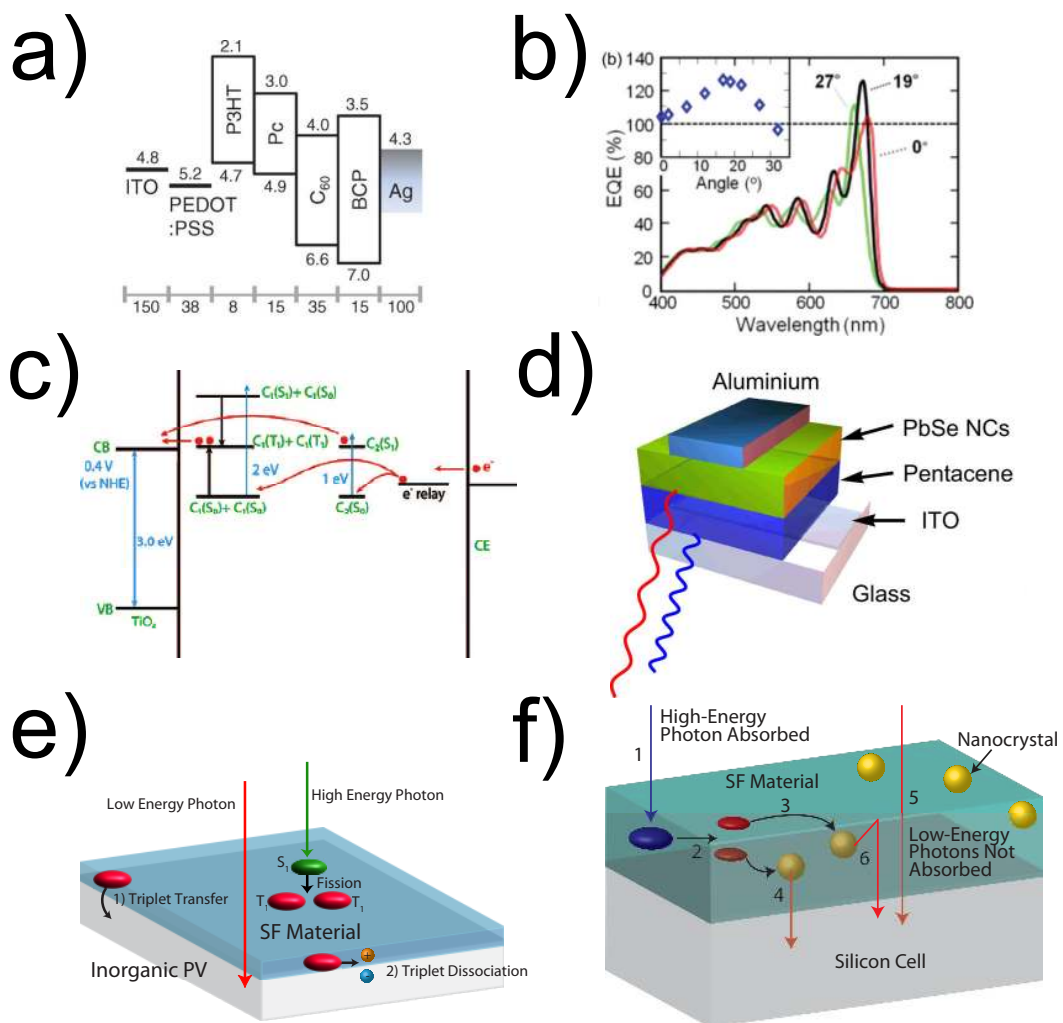
Figure 5: (a) Energy levels of a SF based OPV, using pentacene (as SF material) and C_{60} 0as donor and acceptor respectively. Taken from Congreve et al, Science 340 (6130), 334, 2013

(b) These cells have been shown to give external quantum efficiencies above 100%, but do not offer any net increase in power conversion efficiency via the use of SF. Taken from Applied Physics Letters 103, 263302 (2013)

(c) Concept of a SF based dye sensitised solar cell (DSSC), which utilises two dyes, one low bandgap dye (the LGS) and the other a high bandgap SF dye to try and overcome the SQ limit. Taken from Smith et al, Chem. Rev. 2010, 110, 6891–6936

(d) Cartoon of a SF-nanocrystal PV device. Here, PbSe nanocrystals serve as the LGS combined with a higher bandgap SF material, pentacene.

(e) Cartoon of a SF enhanced inorganic PV device. Here the inorganic PV serves as the LGS and could be silicon, CIGS, CdTe or a perovskite based device. The triplet excitons generated via SF are either **(1)** dissociated via charge transfer or **(2)** transferred directly into the inorganic via energy transfer.

(f) Cartoon of a Singlet Fission Photon-Multiplier. Here, light absorption creates singlet excitons (1) that rapidly undergo SF to form two triplet excitons (2). The triplets then diffuse and undergo efficient triplet transfer into the quantum dots (3). The electron-hole pairs in the quantum dots can then recombine radiatively, leading to the emission of two low-energy photons for each high-energy photon absorbed (4). The emitted photons are then absorbed in a conventional solar cell onto which the photon multiplier is coated or laminated.