Organic-Quantum Dot Hybrid Interfaces and their Role in Photon Fission/Fusion Applications

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Abstract

Solar energy is rapidly becoming a more important aspect in today's energy systems and solar cells are playing a major role in this shift. However, to further boost the efficiency of conventional solar cells fundamental thermodynamic limits must be overcome. Photon fission and photon fusion, also known as photon down conversion and photon upconversion, are gaining increasing attention as a means to improve solar energy harvesting in solar cells by overcoming thermalization and transmission losses, respectively. Important developments in these fields include the use of organic-inorganic hybrid materials that can leverage the advantages of each material. In this review we look at the development of organic-quantum dot (QD) hybrid materials and their use as components of photon fission and fusion systems. We put a particular focus on the triplet energy transfer across these organic-inorganic hybrid interfaces and how this understanding has been developed. In the later part of the review we focus on the recent examples of these hybrid materials as crucial components in solar energy harvesting applications based on triplet-triplet annihilation photon upconversion or singlet-fission-based photon multiplication. By highlighting the most relevant discoveries towards understanding and designing organic-QD hybrid interfaces for photon fission and fusion applications we establish a starting point for researchers to continue moving this research field forward towards practical applications.

Introduction

Semiconductor materials play a central role in today's society, with applications in electronics, optoelectronics and sensing, to name a few.[1] To date, inorganic semiconducting material have played the major role in commercial applications, however both organic and inorganic semiconducting material each have their own benefits and drawbacks when it comes to stability, tunability, processability and cost.[1,2] Furthermore, organic and inorganic materials have differences in their physical properties such as exciton nature (*e.g.* exciton binding strength), spin properties, mobilities etc[1–3] By combining organic and inorganic semiconductors to form hybrid materials the material properties can be tuned and optimized over a wider range. Constructing these hybrid materials on the nanoscale have proven particularly powerful.[4] A crucial part of these nanocomposites are the organic-inorganic interfaces, control of which can dictate and fine tune the physical properties. It is therefore important that these interfaces be controlled and understood to design optimal materials.

In this review we cover the recent progress in using organic-inorganic hybrid materials for enhanced solar energy harvesting, with the main focus on energy transfer across the organic-inorganic interface and its role in photon upconversion (photon fusion) and photon multiplication (photon fission). We will detail the role of each component, and the crucial organic-inorganic interface in particular. We start by a brief introduction to organic semiconductors and semiconducting nanocrystals (quantum dots, QDs), these sections only aim to highlight the key differences between these two classes of materials. For a deeper treatment of organic semiconductor and quantum dot physics, the reader is referred to books addressing these topics comprehensively (see for example the books by Köhler and Bässler[2], Agranovich[3] or Pope and Swenburg[5] regarding organic semiconductors and the book by Klimov[6] on nanocrystal quantum dots. These sections are followed by an overview of how these hybrid materials can be prepared. The rest of the review takes on a chronological summary of the advances from polymer-QD photovoltaics to the more recent progress in photon modulation through photon upconversion and multiplication. By highlighting the most relevant discoveries towards understanding and designing organic-inorganic hybrid interfaces in materials for photon modulation applications and pointing out remaining key challenges we hope to establish a starting point for researchers to continue moving this research field forward towards practical applications.

Organic Semiconductors

Most conjugated organic molecules can be considered as organic semiconductors and the energy separation between the frontier orbitals (the Highest occupied molecular orbital, HOMO, and lowest unoccupied molecular orbital, LUMO) parallels the optical bandgap in inorganic semiconductors.[2] Following the Pauli exclusion principle, the ground state of most organic molecules have paired spin-0 electron configurations. Further, in most organic molecules spin-orbit coupling is low, leading to inefficient interconversion between spin states.[2] Consequently, photon absorption by an organic semiconductor then leads to a spin-0 singlet excited state, and conversion to a triplet spin-1 state usually proceeds through intersystem crossing (ISC).[2,7] As radiative decay from an excited triplet state to the singlet ground state is also extremely inefficient, triplet states are often referred to as dark states. In many organic materials, and in acenes in particular, the energy difference between the first excited singlet and first triplet state can be large, even exceeding 1 eV.[2]

Singlet Fission and Triplet-Triplet Annihilation

Singlet fission (SF) and triplet-triplet annihilation (TTA) are two related processes that can occur between two organic semiconducting molecules. As seen in Figure 1 (b) and (c) they are in fact the reverse of each other:[8,9] where SF proceeds from a singlet excited state to form two triplet excited states,[10–20] one on each molecule and TTA fuses two triplet excitons on two molecules to form one excited singlet state.[21–30] By changing the relative energy of the singlet and triplet states through materials design one can change which process dominates.[31,32] For SF the energy alignment should ideally fulfil the energy conservation criteria shown in Figure 1 (b) indicating that twice the triplet energy is less than the singlet energy,[10,11,13–2012] and for TTA the energetic criteria is the reverse, *i.e.* twice the triplet energy should exceed the singlet energy, Figure 1 (c).[21–30]

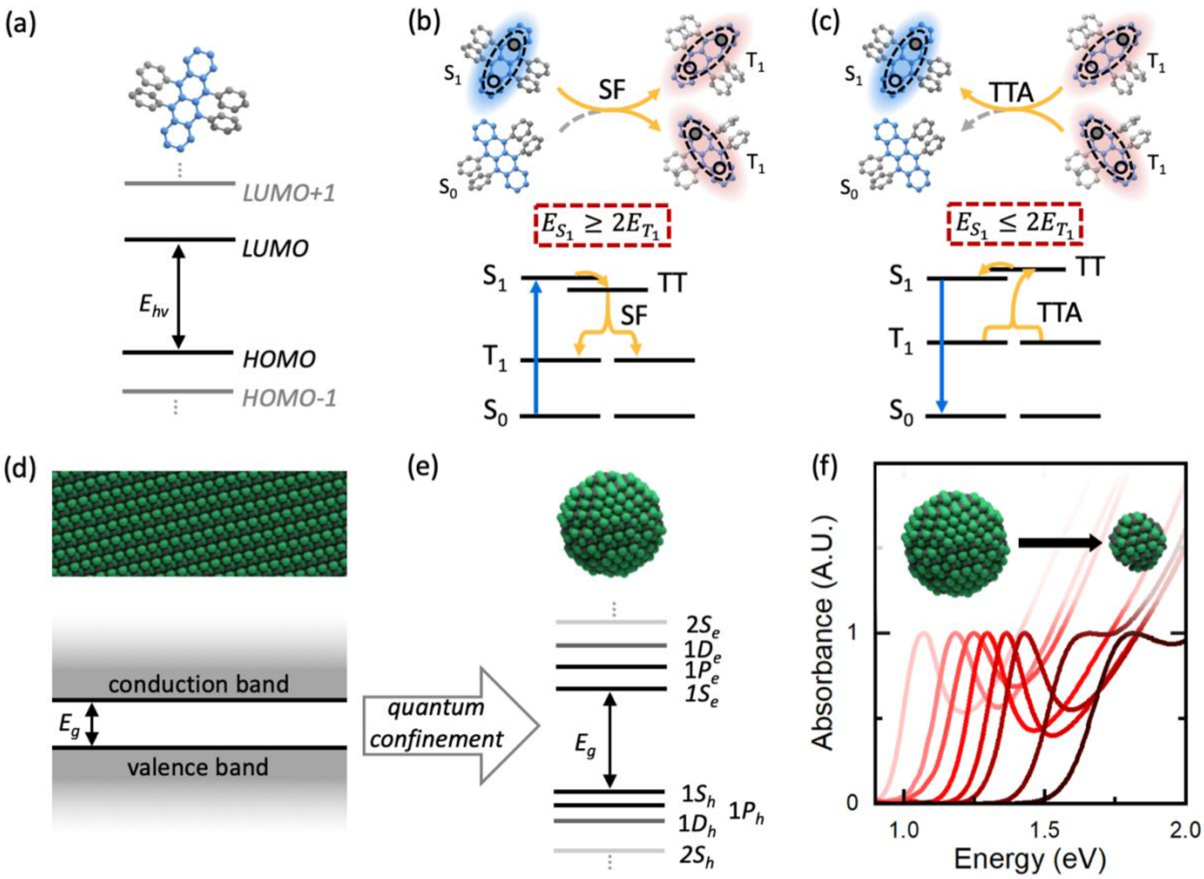


Figure 1.Schematic illustration of the energy levels in an organic semiconductor (a) and the energy level description of singlet fission (b) and triplet-triplet annihilation (c). Illustration of the energy levels for a bulk inorganic semiconductor (d) and quantum dot (QD) (e) with the band gap E_g. (f) Change in excitonic absorption in PbS QDs as a function of QD size, illustrative of the quantum confinement effect.

Besides the energetic considerations mentioned above, there are more specific requirements of orbital overlap and molecular coupling determining the rate and efficiency of these two processes. The understanding of these processes has improved considerably over the last decade with the help from advanced experimental techniques, such as ultrafast optical spectroscopy,[8,12,33–43]electron spin resonance,[44–48] as well as computational and theoretical studies.[14,42,49,50]For example, it has been shown that singlet fission proceeds from the singlet (S_1) state *via* an intermediate triplet pair state (TT) which later can break up to free triplet states (T_1).[16–18,40,51] For a detailed discussion on the TT state the reader is directed to the recent reviews by , Musser and Clark,[16] Miyata et al.[17] and Sanders *et al*.[18] TT formation, and in some cases also T_1 formation, can be ultrafast, on the order of 100's fs.[52,53] There are fewer fundamental studies using ultrafast spectroscopy of the TTA process compared to SF, perhaps due to the fact that, out of these ultrafast process, SF can be probed directly after excitation, whereas for TTA the triplets are typically formed *via* intersystem crossing with TTA occurring at a later timescale. As a consequence of the delayed bi-molecular nature of the TTA event the yield of TTA is excitation intensity dependent. The kinetic origin of this dependence has been discussed in detail by the groups of Castellano and Meinardi.[54,55]

Besides conventional optical spectroscopy, magnetic field dependent measurements, as pioneered by Merrifield and co-workers in the 60s,[56–58] has found extensive use to gain fundamental understanding of both TTA and SF.[56–59] Detailed reviews of recent advances has been summarized for both singlet fission[10–20] and triplet-triplet annihilation,[21–30]and will be beyond the scope of this review. Instead, we will focus on the application of these processes to modulate photons in photon upconversion and multiplication. In these applications the SF or TTA in the organic material is used to split or fuse photon energies, respectively. The role of the inorganic material, which will be discussed in more detail in the next paragraphs, is to efficiently convert between photons and triplet states.

Quantum Dots

Colloidal semiconductor nanocrystals, or quantum dots (QDs), are nanometre sized crystals prepared and suspended in solution.[60–62] Shrinking a bulk material to the nanoscale leads to a particle whose size is smaller than the exciton Bohr radius, with significant implications on the electronic and optical properties of the materials.[63] These size effects are often referred to as quantum confinement effects, and lead to size tuneable optical properties and discrete energy levels. In Figure 1 (d) and (e) the difference in electronic structure of a bulk material and the corresponding quantum confined material is shown and in Figure 1 (f) the size dependent absorption of a QD is illustrated.

Over the last decades the synthesis of colloidal QDs has gained considerable attention and much effort has been devoted to carefully control the size and shape of the QDs.[62,64]Thanks to this intensive work it is now relatively simple to synthesize QDs of different sizes and composition, hence there is a large library of materials with absorption properties spanning the UV, Visible, NIR and IR spectral regions. QD are therefore extensively studied as the absorbing or emitting species in many kinds of optoelectronic devices.[62,64–72]

Compared to organic semiconductors, QDs do not have clearly defined spin-states and the bright−dark state splitting in QDs is much smaller than kT at room temperature, resulting in efficient interconversion and emission with no losses due to dark spin states.[73,74] QDs have therefore also gained considerable attention as spin-converters in applications such as photon upconversion, photon multiplication and spin memories.[4,75,76]

Configurations of The Hybrid Materials

In order to fabricate a functional hybrid material that serves certain applications, the organic semiconductors and QDs must be combined in a way that allows efficient energy transfer between each other.[27,29,77,78] To achieve efficient transfer, three major aspects should be considered when constructing the hybrid material: (1) the distance between the two components should be sufficiently short to maximize the energy transfer rate and hence the probability of such events to occur.[79–81] (2) The configuration should form a sufficiently large interfacial / contact area between the two components in order to create a sufficient number of sites per volume for energy transfer[82,83] (3) The material must be chosen so that the energetic alignment of the two materials are compatible with the desired energy or electron transfer process.[84,85] Other aspects such as the chemical compatibility, mixing ratio and stability should also be considered when designing the structure of the hybrid materials.

To date, most of the reported hybrid materials based on organic semiconductor and QDs can be categorized into three configurations as described in Figure 2. The advantages and limitations of each will be discussed in this review.

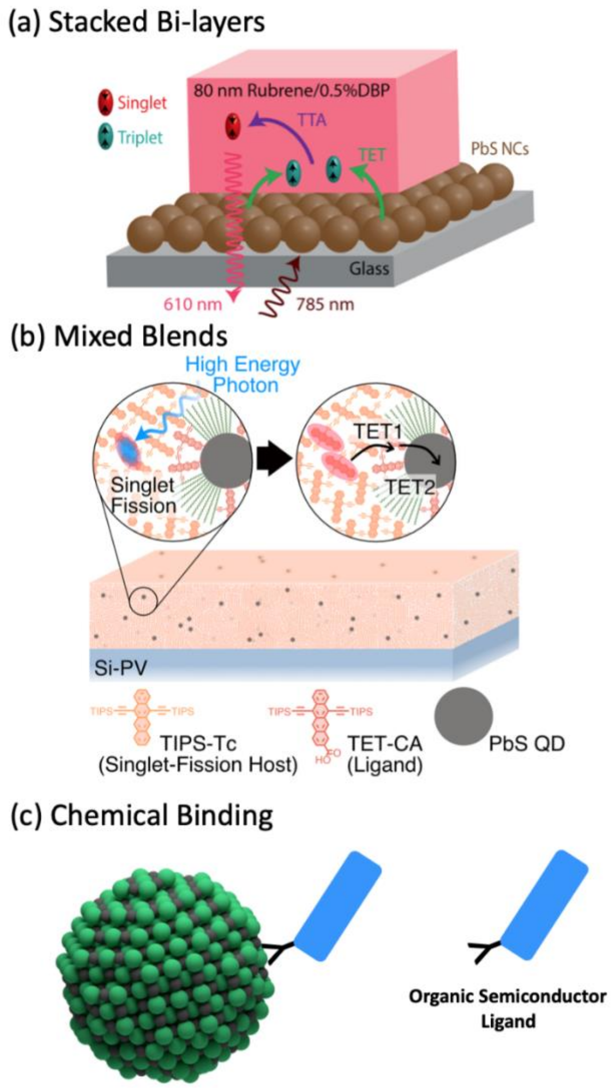


Figure 2. (a). Examples from literature of organic-inorganic mixing approaches. (a) the bilayer approach, reprinted with permission from Nienhaus et al., ACS Nano 2017, 11 (8), 7848, ref [45]. Copyright 2017 American Chemical Society (b) the mixed blend approach, reprinted with permission from Allardice et al., arXiv:2009.05764, Ref [52] (c) the chemically binding approach.

Stacked Bi-Layers

The stacked bi-layer configuration, seen in Figure 2(a), is normally fabricated by sequential deposition of the materials onto a substrate to form two layers that are in close contact. [80,86–88] It is a relatively simple structure to achieve and is very suitable for materials that are incompatible for mixing, for example due to problems such as a great solubility difference in particular solvents. Solubility issues can indeed be a common problem for colloidal QDs and organic semiconductors mixtures.[89–95] With the stacked layer structure, one material, for example the QDs can be deposited first with solution-based methods such as spin-coating. The organic semiconductor with lower solubility (such as many poly-acenes) can then be deposited on the top of the QD layer by other methods such as thermal evaporation.

In stacked bi-layers the energy transfer events are expected to occur at the interfaces between the two materials. The actual distance between the two materials is mainly determined by the ligand length of the QDs, which can be modified by solution-based ligand exchange prior to QD deposition, or solid-state ligand exchange of deposited QDs before the deposition of the organic layer. Bi-layered structures have been widely used in studies of both down-conversion and up-conversion employing organic semiconductors and QDs.[80,86–88,96]

The stacked bi-layer configuration provides a convenient way to study energy transfer mechanisms in the hybrid materials, however it has several limitations that inhibit the system to work efficiently. One issue is that energy transfer can only occur at the interfaces between the two layers. Excitons generated in the bulk of the film need to move to the interfaces before transfer to the other layer, which implies that the diffusion length of the excitons will limit the transfer efficiency.[97,98]Even though some singlet fission materials can demonstrate diffusion lengths on the order of 100s of nm, many materials have much shorter triplet diffusion lengths.[97,98] By reducing the film thickness below that of the diffusion length of the donor material, these limits can be partially relieved. However, a thinner film also decreases the optical density of the film and consequently fewer absorbed photons, which in some applications can be detrimental for performance.[98] Another issue that has to be considered for the bi-layer structure is that as the distance between the two materials is determined by the ligands of the QDs, however, reducing the ligand length to improve transfer also inevitably shortens the distance between the QDs themselves. A smaller QD-QD separation often leads to stronger QD-QD coupling and hence a significant quench in the photoluminescence quantum yield of the QDs.[99,100], for applications that employ QDs as the photon emitter, this quenching can be extremely detrimental.

Mixed Blends

Mixed blends are suitable for materials that have good compatibility with each other and are ready for mixing, for example, when both the organic semiconductors and QDs have high solubility in a common solvent, Figure 2(c). Mixed blends are therefore highly flexible structures and hybrid material with mixing ratios best suited for the current application can often be made.

The hybrid materials formed by mixed blending provide several advantages in terms of enhancing energy transfer between the two components. For instance, it can provide a much higher contact interfacial area compared to that of the stacked layer configuration, as one material is directly blended into the bulk of the other.[101] With efficient mixing the average distance that an exciton has to travel before it finds a site available for energy transfer can be greatly reduced. Furthermore, although the distance (for energy transfer) between the two materials is also determined by the ligand length of the QDs, mixed blend configurations can avoid the problem of unwanted QD-QD coupling as they can be uniformly distributed into the organic semiconductor matrix.[92–95]

The biggest problem of the mixed blend configuration is the pre-requisite of material compatibility, which does not usually come naturally for QDs and most organic semiconductors, and hence limit the selection of materials for the hybrid. Extra effort is required to modify the molecular structure of the organic semiconductor or the surface of the QDs in order to improve the compatibility[92–95,102–104] As described in the next section this incompatibility has led to intense research efforts to engineer the ligand shell of the QDs to achieve better compatibility with the mixing partner, both for optoelectronic and bio-compatible applications.[105–107] However, it is still a great challenge to successfully disperse QDs into organic semiconductor matrixes in the solid state without significant aggregation between the two components.[93–95,102–104] So far most studies have required a combination of the mixed blend approach and the chemically binding strategy (as described in the section below) to yield materials with compatible surface energies.[92–95,102–104] These surface energy matching requirements are relaxed in the solution state and efficient photon up- and down-conversion in mixed solution blends have been achieved. [21–23,25–30]

Chemical Binding

Apart from putting the organic semiconductors and QDs into physical contact within the hybrid, the two materials can also be chemically bound together to achieve the short distance desired for energy transfer, Figure 2(d).[108–110] To achieve chemical bonding, the organic semiconductor is often first functionalized with an anchor group normally used in the aliphatic capping ligands of QDs, such as carboxylic acids, phosphates and thiols[27,29,77,78,108,109,111–115] The functionalized molecules can then be used to replace the native ligands on the QDs through a ligand exchange process, hence creating a hybrid material that involves direct chemical bonding between the two components. Chemically binding the two components is likely the approach that can achieve the closest distance between the organic semiconductors and the QDs, while it also fully utilizes the large surface-to-volume-ratio of QDs to create a large interfacial contact area. With chemically attached functional ligands very efficient energy transfer has been reported.[77,109]

Chemically attached organic semiconductors on QDs have been investigated in many studies on photon up- and down-conversion.[28,108–110,116] As SF and TTA are involved in these photon conversion systems, a relatively high concentration of the organic semiconductor molecules is required. High concentrations can be achieved by either increasing the organic semiconductor ligand density on the QDs,[117,118] or putting the QD-ligand complex into another matrix that contains concentrated SF or TTA molecules.[28,108–110,116] The latter strategy is basically a combination of the chemical binding and the mixed blend approach. The combined approach has been demonstrated to be very efficient for up-conversion in solution,[108,109,112,119] while we have also recently demonstrated its first example in SF based down-conversion.[116] It has been shown that in such structures the organic semiconductor ligand attached on the QD serve as a mediator and greatly enhance the energy transfer rate and efficiency.[108,109]

The main challenge with the chemical binding approach is to preserve the desired physical properties of the materials such as energetics and high photoluminescence quantum yield when they are subjected to the modifications of functionalization and ligand exchange. Nevertheless, the reported studies have demonstrated very promising results and it is likely chemical binding organic semiconductors to QDs will continue being a significant approach for hybrid materials in photon conversion applications.

Towards Triplet Exciton Transfer in QD-Organic Hybrid Materials

In this and the following sections we look at the long history of devices utilising energy transfer at the hybrid organic semiconductor and inorganic quantum dot interface. We highlight their use in a variety of optoelectronic applications; from photovoltaics, singlet fission sensitised photovoltaics, to the more recent use in photon modulation applications. Critical to the understanding of the research into hybrid devices, we expand on the relationship between the energy tunability of the QDs and energy level matching with organic semiconductors.

Polymer-Quantum Dot Photovoltaics

The combination of many parallel fields of research intermingling has led to the proposal of both singlet-fission photon-multiplier and triplet-triplet annihilation upconversion, devices. The progression to this point takes root in the QD/organic PV field, as one of the initial inorganic QD and organic semiconductor hybrid structures. For the best part of two decades, QDs were investigated for use in hybrid PV devices with organic semiconductors. Over this period of time the field saw many milestones, from the first demonstration of charge separation at the interface of organic polymers and CdSe QDs, to full photovoltaic devices with ~3 % power conversion efficiency in 2010.[120,121] As illustrated by Figure 3 (a), key lessons from this research were that the ‘type-2 heterojunction’ between QD and organic could result in ultrafast charge transfer and charge separation, as well as the use of hybrid structures in general for optoelectronic applications.[122]

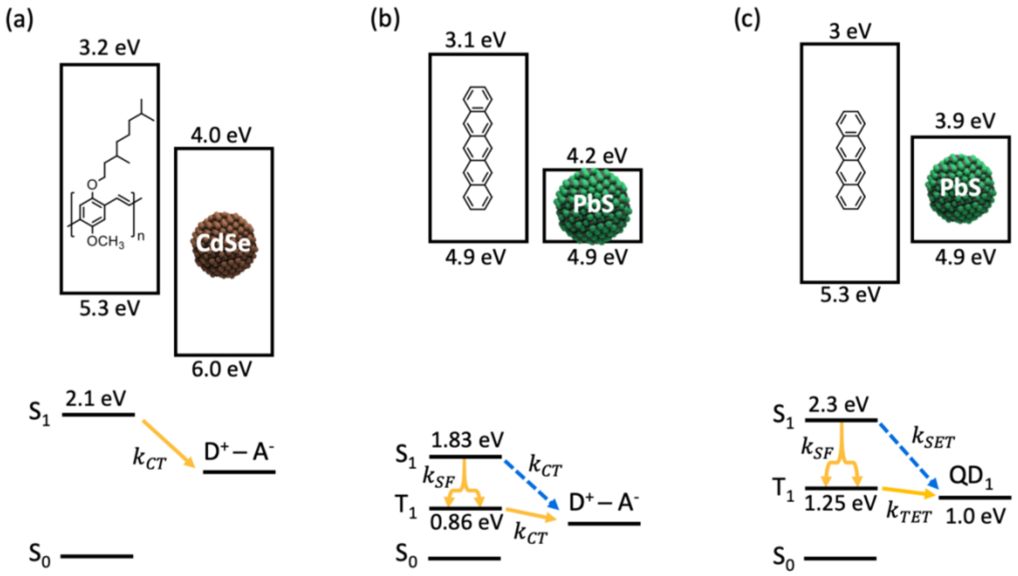


Figure 3. Schematic of the relevant energy levels at organic-inorganic interfaces. The HOMO and LUMO energy levels (top) and corresponding Jablonski energy diagrams (bottom) for a variety of hybrid structures. a) Organic polymer-QD photovoltaic device. b) Singlet fission sensitised QD photovoltaic device. c) Singlet-fission photon multiplier device.

Meanwhile, there were developments in using singlet fission in 'fullerene' based devices. The demonstration of triplet exciton charge separation in pentacene/fullerene type-2 heterojunctions, was an influential discovery.[123] Crucially, it showed the enhanced quantum efficiency in a photodetector was possible with the use of singlet fission in pentacene, an exothermic singlet fission material. This singlet fission device was one of the first successful application-relevant uses for a singlet fission material. The work called attention to the use of external magnetic fields to identify the contribution of singlet fission generated triplets to overall performance in devices. It was followed by renewed interest in singlet fission and lead to spectroscopic identification of the triplet transfer dynamics, showing that singlet fission was occurring rapidly within 200 fs after photoexcitation.[52,124]

Singlet Fission Sensitized Photovoltaics

Parallel to the developments of polymer-QD photovoltaics was the influential development of singlet-fission sensitised infrared QD solar cells.[125] This type-2 heterojunction demonstrated the first combination of an organic singlet fission material and inorganic QDs, Figure 3 (b). The key development achieved by this structure is the charge dissociation of triplet excitons generated by singlet fission at the QD/organic interface.

Many different combinations of organic singlet fission triplet donors and acceptors of both organic molecules and inorganic QDs were tested in these early reports of charge transfer.[126,127] The dependence of the triplet exciton dissociation on the alignment of energy levels in the two materials was extensively mapped.[128] This research climaxed with the development of singlet fission based organic photovoltaic devices with external quantum efficiency greater than 100%.[129] This measure of how many charges are captured per incident photon, is typically limited to 100 %. Notable efficient utilisation of a singlet fission material for charge multiplication allowed the researchers to achieve an efficiency above this limit, cementing the value of singlet fission for improving solar energy harvesting. However, these devices have a considerable limitation, this particular use of singlet fission materials as part of the active material allowed a doubling of the extracted photocurrent but at half the voltage. These competing effects result in little to no, net improvement in power conversion efficiency with respect to a traditional organic single junction cell. In fact, often the overall power conversion efficiency has been significantly lower than the traditional cells as the materials and morphology can be optimised without the need to satisfy the additional requirements of singlet fission and triplet migration.

Electron injection from singlet fission generated triplets into inorganic semiconductors in singlet fission dye sensitized solar cells (DSSC) and perovskite films have also been pursued.[130–132]

Diphenylisobensofurane, TIPS-tetracene and TIPS-pentacene DSSCs have all been investigated, but there has been difficulties achieving efficient charge injection from the singlet fission generated triplets.[132–136] As the singlet fission chromophores are directly anchored to the semiconductor surface one challenge has been the competition between direct electron injection from the singlet state *versus* singlet fission.[132–136] Often an insulating layer between the electrode and singlet fission materials has been used to slow down the direct injection from the singlet, albeit often with a reduction of the triplet injection rate as well.[132–134] Another issue has been the reduction of the singlet fission rate as the adsorbed dyes are not as ideally packed as in the crystalline or solid state.[135]

Triplet Energy Transfer across QD-Organic Interfaces

The next step along our technological road map is the harvesting of entire triplet excitons, rather than charge separation of an electron and hole. Triplet energy transfer across QD-organic interfaces has attracted considerable attention with applications spanning optoelectronic devices such as solar cells and photon modulation, spin memories to photocatalysis and synthetic chemistry.[4,28,76,110,137]

Triplet Transfer to Inorganic QDs

The transfer of triplet excitons, generated by singlet fission, to inorganic QDs was first demonstrated in bi-layers structures.[86,87] Critical to this triplet exciton transfer is the alignment of the QD energy levels relative to the electronic level within the organic molecules. As illustrated by Figure 3 (c), to inhibit singlet exciton dissociation, a type-1 heterojunction was employed. Additionally, the energy of the QD bandgap needed not to be greater than the triplet exciton energy. The key benefit of this triplet exciton transfer, over charge separation, was that the triplet exciton once inside the QD resulted in excited state emission identical to the pure QD photoluminescence. This was attributed to the high spin-orbit coupling within the QD allowing for the usually spin-forbidden triplet state to become emissive.[86,87,138] Other than the significant milestone of showing harvesting of triplet excitons, these studies identified Dexter transfer as the likely transfer mechanism for triplet excitons between the organic molecule and QD, as illustrated in Figure 4 (a). The key indicator of this being that the transfer efficiencies had exponential dependence on the donor-acceptor separation, as determined by the length of the aliphatic ligands surrounding the QD. With short enough ligands, the triplet transfer efficiency increased towards unity.[86,87] However, the synthesised QDs with long aliphatic oleic acid ligands showed little transfer, highlighting the need for engineering of the QD ligand shell. This particular method for controlling triplet transfer rates has the drawback that QD films with shorter ligands typically suffer from reduced photoluminescence quantum efficiency due to aggregation assisted interdot transfer and trapping, as discussed above. These studies also employed the effect of external magnetic fields applied to the devices to confirm the dominance of triplet exciton transfer over singlet transfer.[86,87] As illustrated by Figure 4 (b), they observed a shift in the equilibrium between singlet excitons on the organic and QD excitons with the application of a ~0.5 T magnetic field. The shift in equilibrium was identified by an increase in fluorescence from the organic at high fields, as expected for material undergoing singlet fission. In contrast, the photoluminescence from the QD followed a corresponding reduction, consistent with a state populated by the triplet excitons generated by singlet fission.[86,87]

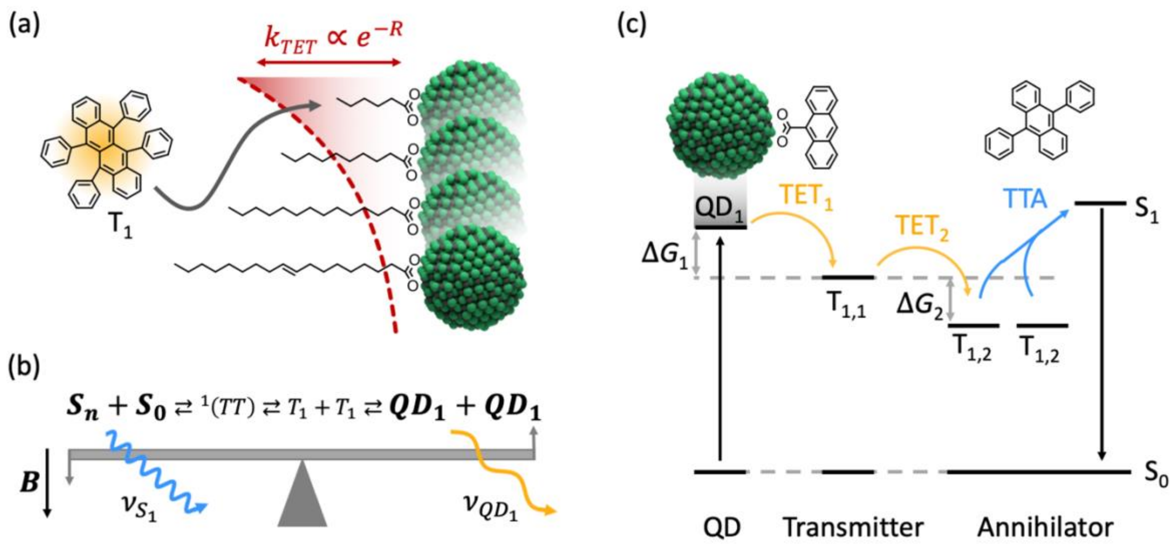


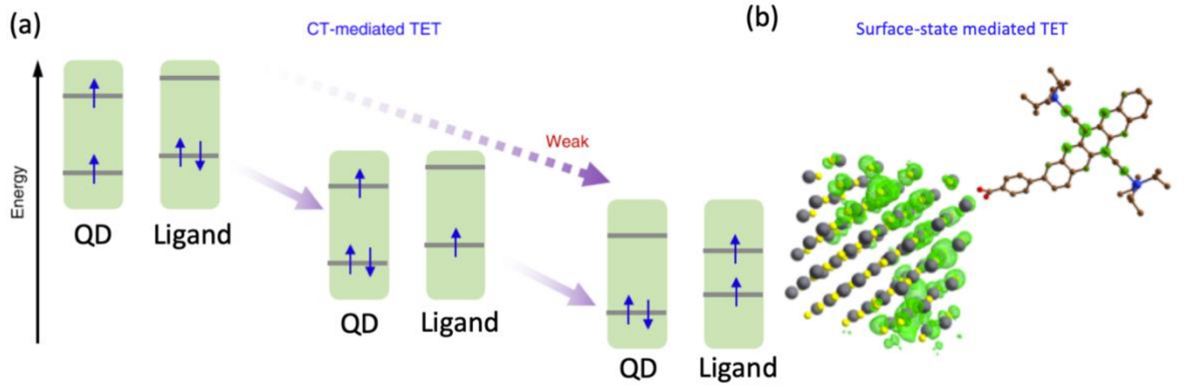
Figure 4. Triplet exciton transfer at the hybrid organic-inorganic QD interface. a) Illustration of the triplet exciton transfer at the hybrid organic-inorganic QD interface, mediate by the Dexter transfer mechanism. b) Visual analogy of the equilibrium between singlet excitons on the organic and excitons on the QD. Application of a ~0.5 T external magnetic field shifts the equilibrium towards the singlet exciton population (singlet heavy). This shift in population is reflected in the photoluminescence from these states. c) Schematic of the triplet-triplet annihilation upconversion process. After the absorption of a low energy photon by the QD, the resultant exciton undergoes triplet energy transfer (TET) to the triplet exciton state on the transmitter ligand. The triplet exciton then undergoes a second transfer to the triplet state of the annihilator material. Finally, a high energy photon is emitted from the annihilator material, after the annihilation of a pair of triplet excitons form a singlet exciton.

Triplet Transfer from Inorganic QDs

Following the above work, three separate studies, Huang *et al.*, Wu *et al.*, and Mongin *et al.* investigated the possibility of transferring triplets in reverse, from QD to the triplet state of an organic molecule.[88,108,109] By adjusting the materials so that the QD exciton was higher in energy than the organic's triplet exciton, they demonstrated that such a process is possible and further illustrated the use of the generated triplet excitons for triplet-triplet annihilation photon upconversion in both the solution phase and solid state. Huang *et al.* reported that after photoexcitation of the QD, a delayed fluorescence from organic rubrene molecules was identified and well described by triplet bi-molecular decay regenerating the singlet exciton. The researchers additionally introduced a novel strategy involving the use of an electronically active triplet 'transmitter' ligand attached to the surface of the QDs, as opposed to the usual high bandgap aliphatic ligands.[108,109] This strategy relied on the rapid exciton transfer from the CdSe QD to the transmitter ligand, followed by a secondary transfer step to the 9,10-diphenylanthracene in solution surrounding the QD (Figures 2 (d) and 4 (c)). Though the upconversion efficiency was relatively low, ~0.01 %, the developments described in these reports inspired a significant amount of future work. Many studies have since then employed the ligand mediator to realise efficient triplet transfer, [77,82,112,114,139–143] and triplet transfer has now also been observed for other materials than the initial CdSe,PbS and PbSe QDs including: perovskite nanocrystals and films,[84,144–150] CdS QDs and other chalcogenide core-shell QDs,[77,139,140,151] as well as from Si nanoparticles.[143]

Further investigations have showed that the diffusion mediated transfer follows a Stern-Volmer like quenching dependence on the concentration of the accepter molecules. Also the bi-molecular transfer rate is heavily dependent on the amount of excess energy between QD exciton and organic triplet exciton energy.[152] Marcus theory is pointed to as an appropriate theoretical framework to understand the role of this driving energy in the transfer process, with recent experiments supporting this assignment.[110,141,153] The use of phenyl spacer units between the triplet transmitter chromophore and the QD core showed that the triplet transfer from QDs to organics also follows an exponential dependence on the separation between donor and acceptor, assigned as Dexter transfer.[79,119] Recently, it was shown that this exponential dependence stopped if the triplet energy of the phenyl spacer was in resonance with the QD. A stepwise hopping mechanism, where the triplet exciton transfers first to the phenyl spacer and then to the anthracene core, was proposed to explain this observation.[81] Using a bilayer approach of PbS QDs and rubrene Nienhaus *et al.* investigated the distance dependence of triplet transfer by varying the chain length of the alkyl ligands.[80] In these systems no transmitter ligand was used, however at large distances the triplet transfer was found to follow a distance dependence in line with Dexter energy transfer. However, the increased dielectric constant, for more tightly packed QDs with shorter ligands, results in little gain in transfer rate for ligands shorter than a six carbon chain.[80]

The triplet transmitter ligands are usually attached to the QDs post synthesis by solution ligand exchange. This ligand exchange has been shown to introduce additional states other than the QD exciton and organic triplet state, possibly leading to a delayed stepwise triplet transfer.[84,153–155] The role that these states play in the transfer is, however, still under debate. The two pictures suggest either a surface bound intermediate state, or a stepwise charge transfer mediated mechanism with initial hole transfer to the ligand followed by electron transfer, without the involvement of any surface states, Figure 5.[77,84,154–156]



$$QD^{*} + L \rightarrow QD^{-} + L^{+} \rightarrow QD + L_{T}^{*}$$

$$QD^{*} + L \rightarrow \mathrm{QD}_{Surface-State}^{*} + L \rightarrow QD + L_{T}^{*}$$

Figure 5. Two different mechanism explaining stepwise triplet transfer in organic-inorganic hybrid systems.(a) charge transfer mediated triplet transfer can occur when the ligand (L) HOMO and LUMO levels are favourable for hole or electron transfer. Adapted from Luo et al., Nature Commun. 2020, 11, 28, Ref.[88]. (b) Illustration of a surface bound spin-triplet state from constrained DFT calculations as a possible intermediate in triplet transfer from the quantum dot (QD) to the ligand (L). Reprinted (adapted) with permission from Bender et al., J. Am. Chem. Soc. 2018, 140, 7543-7553. Copyright 2018 American Chemical Society, Ref. [94].

Generalised Photon Modulation

Based on the developed understanding of triplet transfer across organic-inorganic hybrid interfaces as discussed in the two sections above, a general scheme for ‘photon modulation’ can be constructed to describe photon multiplication (photon fission) or photon upconversion (photon fusion), the choice of which is determined by the energetic alignment, Figure 6. We emphasize that the interconversion between one high energy and two low energy photons is determined by the relative Gibbs free energy of the QD exciton, triplet transmitter, and triplet and singlet states of the ‘triplet modulator’. In this scheme the QD acts as a spin-mixing component, allowing the conversion between photons and exciton states. The energy flow across the interface is tuned with the transmitter ligand. Triplet excitons can additionally transfer between the transmitter state and the triplet state of the triplet modulator. The triplet modulator is a generalisation of the singlet fission or triplet-triplet annihilation materials, which performs predominantly one of these processes based on the Gibbs driving energy between the singlet exciton and two triplet excitons. Choice of materials dictates the direction photon modulation occurs.

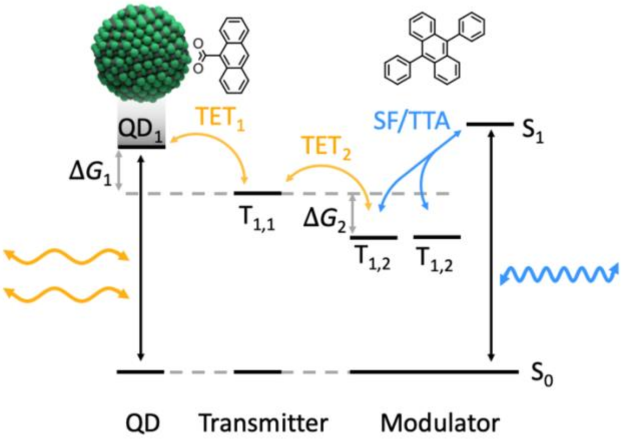


Figure 6. Schematic of a generalised photo modulator. Interconversion between one high energy and two low energy photons is mediated by the QD, triplet transmitter, and triplet modulator.

Developing singlet-fission based photon multipliers will rely on understanding how to efficiently harvest triplet excitons from an organic singlet fission molecule by a QD. While, triplet-triplet annihilation upconversion builds on the developed knowledge base for the triplet transfer from the QD to organic molecules. With the intrinsic relation between the photon multiplication and photon upconversion applications, however, lessons learnt when studying one can often be translated to the other.

Singlet Fission Based Photon Multiplication

A singlet fission photon multiplier (SF-PM) device offers a mechanism to break the thermodynamic limit of single junction photovoltaics by overcoming the thermalisation losses.[10,13,157]Thermalisation losses arise from high energy photons that excite the semiconductor well above the band gap, resulting in heat loss as the hot exciton cools to the band edge.[157,158] A singlet fission material that absorbs the high energy photons from the solar spectrum and undergoes singlet fission to generate two triplets per absorbed photon could overcome thermalisation,losses as most of the photon energy would be conserved by generating twice the charge carriers.[10,13,157,159,160] SF-PM is one of the most promising methods to harness the singlet fission process.[160] The absorption of high-energy photons in a thin SF-PM layer on top of a Si-PV, results in a photoexcited singlet exciton which subsequently undergoes rapid and efficient singlet fission to form two triplet excitons, Figure 7 (a).[13,116,160] Triplet generation is followed by efficient harvesting of the triplet excitons by a homogeneous dispersion of quantum dots within the singlet fission material. After transfer to the QDs, the excitons then recombine radiatively. Thereby, for every high-energy photon absorbed by the SF-PM, a pair of low energy photons is emitted that can then be captured in a conventional silicon photovoltaic.

The low bandgap quantum dots can absorb photons across a wide range of photon energies and so they are maintained at a low density within the SF-PM to minimise absorption. Other than this parasitic absorption by the QDs, mid-energy photons pass through SF-PM and are absorbed by the Si-PV. The absorbed photons by the Si-PV are then converted to electricity.

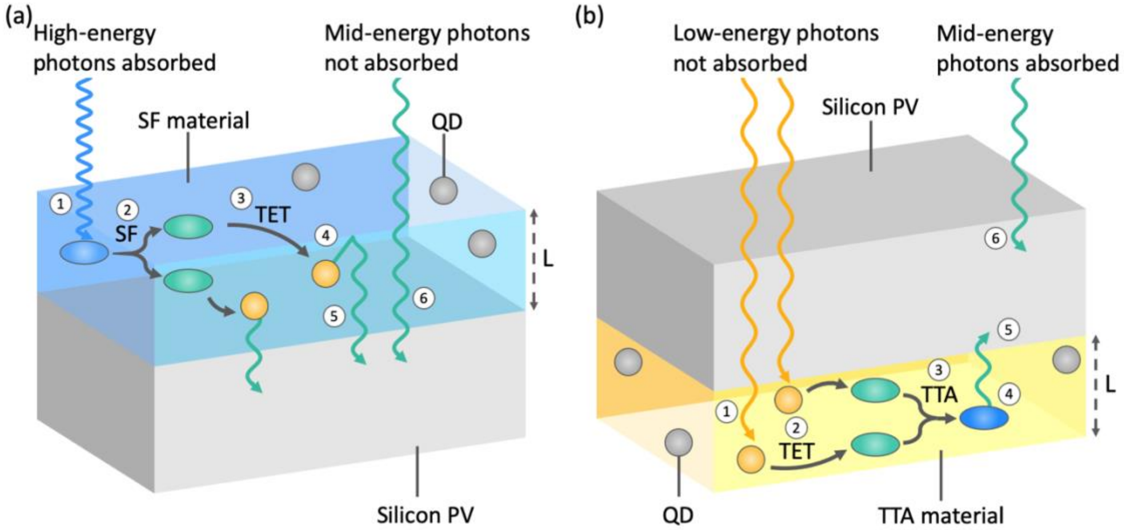


Figure 7. Schematic of SF-PM and TTA-UC films. ***a)*** *Bulk SF-PM system, with illustration showing the operation separated into constituent steps. 1) Absorption of high-energy photon in the SF host material. 2) Singlet fission process. 3) Triplet exciton transfer to the QDs distributed within the SF host. 4) Emission of low energy photons from QDs and (5) optical coupling where a significant fraction of the emitted photons are absorbed by the conventional Si-PV. 6) Mid energy photos pass through SF-PM and are absorbed by the Si-PV.* ***b)*** *Bulk TTA-UC system, with illustration showing the operation separated into constituent steps. 1) Low energy photon not absorbed by the Si-PV and are absorbed in the TTA host material. 2) Triplet exciton transfer from the QDs, distributed within the TTA host. 3) Triplet-triplet annihilation in the TTA host. 4) Emission of mid energy photons from TTA material. 5) Optical coupling where a significant fraction of the emitted photons are absorbed by the conventional PV device. 6) Mid energy photos absorbed by the Si-PV as usual. SF-PM illustration adapted from the schematic proposed by Rao and Friend.*[27]

The efficiency of a SF-PM ($\eta_{SF-PM}(\lambda)$), as a function of the absorbed photon's wavelength, can be separated into its constituent parts,[87]

$$\eta_{SF-PM}(\lambda) = \big(\alpha_{QD}(\lambda) + \alpha_{SF}(\lambda)\eta_{SF}\eta_{TET}\big)\eta_{QD}\eta_{OC}\ . \tag{1}$$

Here, η_{SF} is the efficiency of the triplet generation in the per photon absorbed in the singlet fission material, ideally 200 %. η_{TET} is the fraction of generated triplets that transfer to the quantum dot. η_{QD} is the photoluminescent quantum efficiency of the quantum dots. η_{OC} is the optical coupling factor, the fraction of photons emitted by the QD that are absorbed by the underlying PV cell. $\alpha_{QD}(\lambda)$ and $\alpha_{SF}(\lambda)$ are the fraction of the absorbed photons which are absorbed by the quantum dots and singlet fission material respectively. Equation (1) shows that for a SF photon multiplier to achieve high efficiencies each step in the process needs to be understood and optimised. An important factor in the operation of this device is the optical bandgap of the QD. The optical bandgap of the QD must be larger than the bandgap of silicon (Eg = 1.1 eV), such that its photoluminescence can be absorbed by the Si-PV.[161]

In a recent report the potential benefits of the SF-PM were investigated and it was found that incorporation with the best Si-PV devices, currently with a power conversion efficiency of 26.7%, could be improved to 32.5%.[160] This value refers to 'optimistic' system parameters and a power conversion efficiency of 29.0 % is considered more achievable. This second calculation relates to what the authors refer to as a 'realistic' SF-PM, defined as follows; there is less than 5% parasitic absorption by the QDs, there is negligible self-absorption by the QDs (i.e. re-absorption of photons emitted by the QDs before the photon reaches the solar cell), the singlet fission yield is 200 %, the product of $\eta_{TET}\eta_{QD}\eta_{OC}$ is greater than 85%, and the singlet fission process results in entropic gain of 100 meV. Additionally, the authors calculate the photon escape cone for QD emission as less than 10%, based on a singlet fission material with a refraction index of 1.7. This reasonable refractive index results in $\eta_{OC} > 90$ % and can be improved by dielectric nanostructures. As a result, the optical coupling factor in Equation (1) is often omitted. These calculations suggest that an efficient SF-PM device could result in as much as a 22 % relative improvement of the underlying Si-PV.[160]

Recently, we experimentally demonstrated an SF-PM in solution, and investigated some of the intrinsic limitations.[116] Our system consisted of the highly soluble singlet fission material 5,12-bis((triisopropylsilyl)ethynyltetracene (TIPS-Tc), PbS QDs with a band gap of 1.05 eV and 6,11-bis((triisopropylsilyl)ethynyl)tetracene-2-carboxylic acid (TET-CA) as transmitter ligand. This system had a singlet fission yield of 135% and quantitative triplet transfer to the PbS QD. The limiting factor was the intrinsically low QD photoluminescence quantum yield of the PbS QDs at 14.6%. However, the PLQE was improved to 18.2% when exciting the singlet fission material. The enhancement corresponds to an exciton multiplication and triplet transfer efficiency ($\eta_{SF}\eta_{TET}$) of 125%. Importantly, this was achieved with a low enough QD concentration to allow for minimal (<5%) parasitic absorption of the QD.[116]

We later translated our solution work to the solid state, achieving a bulk organic-inorganic hybrid material with well dispersed QDs and efficient singlet fission. Due to the closer packing in the solid state the singlet fission yield was improved to 190% while the quantitative triplet transfer was maintained. Efficient triplet transfer was possible due to the transmitter ligand both mediating triplet transfer, and directing the QDs to a well dispersed composition. Without the transmitter ligand QDs aggregated severely. These findings have widespread implications for other optoelectronic applications requiring morphological tuning of organic-inorganic nanocomposites.[92]

The QDs used in the studies above had a too low band gap for incorporation with a Si-PV. We therefore followed up with a study investigating the effect of QD band gap energy on the triplet transfer and photon multiplication efficiency.[153] This work highlighted the need of an energetic driving force of about 0.1 eV for efficient transfer from the ligand to the QD. A smaller energy offset leads to an equilibrium of QD-ligand states resulting in reduced QD photoluminescence. For a QD with photoluminescence above 1.1 eV (band gap of Silicon) we conclude that singlet fission material with energies around 1.4 eV will be necessary.[153]

It is important to compare the SF-PM system to the alternative approach to incorporating singlet fission materials with Si-PVs, namely the direct sensitization of the PV by the singlet fission material.[159,162,163] Here the triplets are also transferred across an organic-inorganic interface, but directly to the PV without the detour of photon emission. The singlet-fission sensitised silicon PVs is a recent advancement that also has significant potential as a means to break the Shockley-Queisser limit.[159,162,163] A recent report demonstrated the transfer of triplet excitons to a silicon photovoltaic, after generation by singlet fission in tetracene. Such a process has long been predicted as a means to increase power conversion efficiencies.[159] However, these bi-layer, tetracene/silicon, structures are limited by the use of elaborate interlayers, necessary for achieving high PV performance. Such an approach, while promising, requires a change in cell design and thus has the added challenge of integration into existing PV manufacturing systems. Furthermore, the organic layers are thin, typically limited to <100 nm by the triplet diffusion length, resulting in <20 % photon absorption.[163] This limits the thickness of the singlet fission sensitizer and the related efficiency gains.

Triplet-Triplet Annihilation based Photon Upconversion

The triplet-triplet annihilation upconverter (TTA-UC) device offers a mechanism to break the thermodynamic limit of single junction photovoltaics by overcoming sub-bandgap absorption losses.[28,30,157,164,165] As illustrated by Figure 7 (b), the absorption of mid to high energy photons by the conventional Si-PV continues as usual. However, low energy photons not absorbed by the silicon, pass straight through and are absorbed by a homogeneous dispersion of quantum dots within the triplet annihilator material.[21–30] Photoexcitation of the QD is followed by triplet exciton transfer to the organic material, where pairs of triplet excitons annihilate to form singlet excitons. The mid-energy photons from the organic's fluorescence are then optically coupled into the Si-PV. With this arrangement, it is imperative that the QD bandgap is less than that of silicon (1.1 eV). The organics' fluorescence is ideally greater than this, so that silicon can absorb the emitted photons. With these factors accounted for, the efficiency of a TTA-UC per absorbed photon can be separated into its constituent parts,[28]

$$\eta_{TTA-UC} = \eta_{ISC}\eta_{TET}\eta_{TTA}\eta_{FL}\eta_{OC} \ .$$

(2)

Here, η_{ISC} is the intersystem crossing efficiency from the photoexcited singlet state to a triplet state in the sensitizer. η_{TET} is the triplet transfer efficiency from inorganic QD to organic triplet annihilator, which in the case of a triplet mediator ligand involves two triplet energy transfer steps, first transfer from QD to ligand followed by transfer from ligand to annihilator. η_{TTA} is the quantum efficiency of triplet-triplet annihilation to the singlet state in the organic. η_{FL} is the fluorescence quantum efficiency from the organic's singlet state. η_{OC} is the optical coupling factor, the fraction of photons emitted by the QD that are absorbed by the underlying PV cell. The efficiency of η_{TTA} is limited to 50 %, due to the requirement of two triplets to create one singlet exciton.[166,167] The refractive index of the organic components of the TTA-UC, will be very similar to that of the SF-PM. Therefore, the optical coupling factor will be greater than 90 % and is often omitted.

The TTA-UC system has many similar constraints as the SF-PM system. The aggregation of QDs within the organic host must be low. It is ideal if the system is of bulk form, so that it is optically dense enough. The QD's parasitic and self-absorption must be kept to a minimum as to not interfere with the upconversion fluorescence. Finally, they share a need for readily achievable manufacturing conditions, which can be easily incorporated into existing Si-PV fabrication. The TTA-UC system has the additional constraints that the triplet-triplet annihilation should be efficient under solar fluence. If these conditions can be meet then there is the possibility of reaching the predicted thermodynamic limit of ~40 % power conversion efficiency when coupled with PV cell.[28] An 18 % relative improvement is on par with that offered by the SF-PM device. Ultimately these two systems could be combined, SF-PM on top and TTA-UC below a conventional Si-PV, and a ~35 % relative improvement in power conversion efficiency could be achieved.[168] This improvement would be technologically, economically and environmentally significant on a global scale.

To achieve efficient TTA-UC systems relevant for solar energy harvesting there are some key challenges that must be overcome. First, it is intrinsically difficult to upconvert low energy NIR light below the band gap of silicon as the number of suitable materials with low lying triplets and efficient light emission from the singlet state are limited. Not surprising the majority and most efficient of the TTA-UC examples has therefore been of converting low energy visible light to blue photons.[24,108,109,165,166,169] However, there is a significant advantage of using QDs as the triplet sensitizer, as the facile synthesis and size tuneable optical properties makes them more feasible to design for NIR absorption, compared to all organic sensitizers which require multistep organic synthesis.[170] Wu *et al.* used a bilayer structure of NIR absorbing PbS QDs and organic rubrene annihilator to demonstrate a solid state TTA-UC capable of converting >1μm photons to 612 nm orange photons with about 1% efficiency.[88] To overcome inefficient emission from rubrene dibenzotetraphenylperiflanthene (DBP) was used as a singlet harvester and emitter. Using a bilayer approach, much like the first demonstration of triplet transfer from singlet fission molecules to QDs,[86,87] no transmitter ligand was necessary. For use in solar harvesting this system is still limited by the low absorption in the bilayer structure. Wu *et al.* later improved the system by adding a back reflector to improve light harvesting.[96]

Recently, there has been two reports of QD sensitizers absorbing at or below the band gap of Si leading to visible upconverted emission, Figure 8.[171,172] One advantage of using such low energy triplets is that triplet quenching by oxygen does not occur, in fact oxygen can then mediate triplet transfer.[172,173] In the first example 5,11-bis((triethylsilyl)ethynyl)anthra[2,3-b:6,7-b']dithiophene (TES-ADT) was used as the annihilator. It was concluded that TES-ADT likely also bound dynamically to the PbS surface to some extent, functioning as both mediator ligand and annihilator.[171] The second study used violanthrone-79 (V79) as the low triplet energy annihilator.[172] In fact, since the V79 triplet energy lies below that of molecular oxygen it was found that oxygen enhanced the upconverted emission by facilitating triplet transfer from the QD to the annihilator.[172,173] In regards of the challenge of using low energy photons it might be more reasonable to consider TTA-UC enhancing other types of photovoltaic devices, such as dye-sensitized or amorphous silicon solar cells with larger band gaps.[174–183] Solar driven photocatalysis could also benefit from improved solar harvesting by TTA-UC.[184–186]

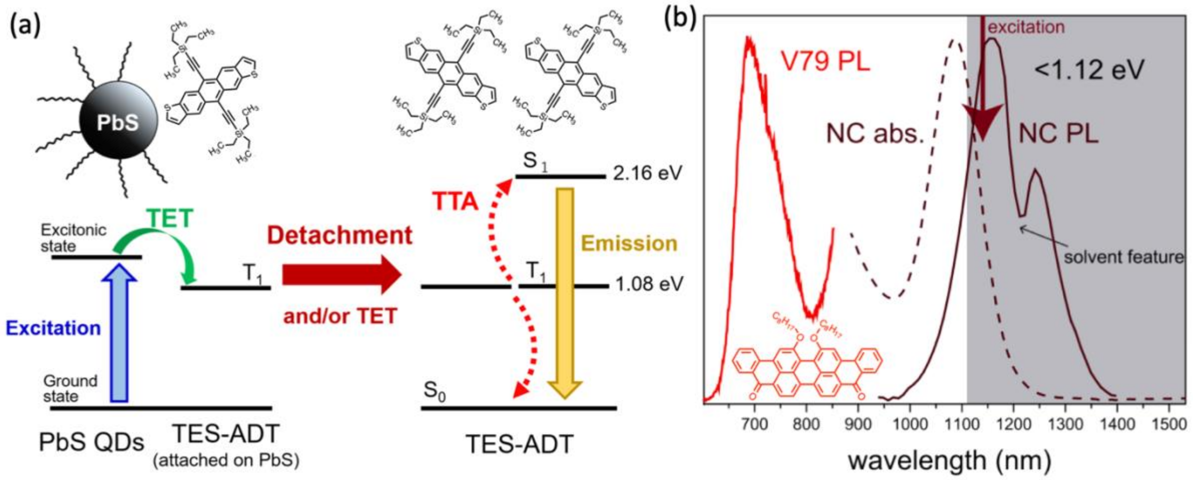


Figure 8. Examples of triplet-triplet annihilation photon upconversion of photons at or below the bandgap of silicon realised by using quantum dot (QD) triplet sensitizers. (a)Energy diagram describing the upconversion process with 5,11-bis((triethylsilyl)ethynyl)anthra[2,3-b:6,7-b']dithiophene (TES-ADT) as both the mediator and annihilator molecule and PbS QDs as triplet sensitizer. Adapted from Ref. [107] Nishimura, et al., Chem. Sci. 2019, 10, 4750-4760 - Published by The Royal Society of Chemistry. (b) Upconverted emission of the annihilator Violanthrone-79 (V79) and absorption and emission spectra of the triplet sensitizer PbS QDs, with the low energy acceptor V79 molecular oxygen functioned as a triplet mediator shuttle between the oleic acid capped PbS QDs and V79 molecule. Adapted from Ref [108] Gholizadeh et al. (2020) Nature Photonics, 14, 558-590 .

A second challenge for enhanced solar energy harvesting through TTA-UC is, just as for SF-PM systems, to develop suitable solid state structures with sufficient light harvesting, with limited self-absorption and minimal aggregation induced quenching.[24] We argue based on our experience from solid SF-PM systems that the transmitter ligand can play a dual role in that by properly matching the ligand with the annihilator host material well dispersed QDs and reduced quenching can be achieved.[92] What remains then is to obtain a highly emissive TTA material in solid state. Since many TTA materials also can undergo SF in the aggregated or crystalline state it can be a significant challenge to maintain high emission efficiencies in the solid state. A possible approach is to dope the TTA material with singlet acceptors with high emission quantum yields.[75,88,187]

Effect of QD quality and surface states

We have summarized the results from many studies showing that efficient triplet energy transfer is feasible between organic semiconductors and inorganic QDs. However, the overall photon conversion efficiencies of the hybrid systems reported need to be further improved in order to be feasible in commercial applications.

One of the main problems from the material chemistry point of view is to preserve the quality of the materials when they are mixed into a hybrid. For example, the PLQE of QDs depends on many factors, including particle size, purification methods, passivation and the number of dangling bonds exposed on the QD surface.[153,188–193] A significant amount of work has been done to achieve high PLQEs of the standalone QDs.[62,64,71,72] However it is still questionable whether these methods are fully transferable when the QDs are combined with organic semiconductors, and if the effects are preserved. For example, in the case of singlet fission based photon multiplication, we observed a significant drop in the PLQE of QDs when they were bonded with the organic semiconductor ligands.[116,153] It is possible that new surface defect states are formed on the QDs during the ligand attachment process, especially when it involves the displacement of original ligands that are chemically bonded to the QD surface. The dynamic equilibrium between the surface ligands and ligands in solution, as well as the QDs sensitivity to the surrounding solvents changing when introducing organic semiconductors, can possibly lead to more dynamically defective sites on the QDs.[194–196]

The effect of the well-developed halide and core-shell passivation methods for QDs to the energy transfer efficiency in the hybrids is also not fully understood. There are some reports of core-shell structures aiding triplet transfer from QDs to attached organic semiconductors by reducing surface trapping.[77,119,139] However, a thick insulating shell also increases the tunnelling barrier and therefore reduces the transfer efficiency. [77,119,139] A careful balance of both QD design and ligand structure must therefore be found to allow fast and efficient triplet transfer while reducing trap states and unproductive pathways. This will call for the modifications of the chemical processes from that suitable to standalone materials to that compatible for both materials in the hybrid in order to achieve high performance. The effect to the material quality needs to be taken into consideration when selecting of QDs, organic semiconductors, functional groups, device morphology and process methods.

Conclusions

In the drive towards achieving efficient photon fission and photon fusion materials, composite materials leveraging the advantages of inorganic nanomaterials and organic semiconductors have become commonplace. In these systems the inorganic nanomaterial acts a means of efficiently converting between photons and excitons and the organic semiconductor performs the fusion or fission of the excitons. Herein we have summarized the evolution of these composites from QD-organic PV materials to the more recent use in triplet-triplet annihilation photon upconversion and singlet-fission-based photon multiplication. Even though crucial achievements, such as the photon upconversion of light below the bandgap of silicon, have recently been demonstrated there are many more steps left to take towards commercial applications in solar energy harvesting. These steps relate to both the separate materials, like the development and understanding of new annihilator and singlet fission materials with improved efficiencies and suitable energy levels, as well as to the improved understanding of the nanocomposites as a whole. In particular the development of solid-state nanocomposites with retained efficiencies is an essential target. Towards these goals continuously broadening the materials scope will be inevitable and highly desirable, and we envision an increase of nanocomposites using organic semiconductors beyond the acene family and the continued introduction of new nanomaterials and perhaps also 2D materials. To end we want to reiterate the remarkable development of these hybrid nanocomposites over the last few years which should act as a further motivation to taking the last steps towards commercial applications.

Data Availability

No data has been produced for the preparation of this review.

Acknowledgments

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