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Spectral Management for Quantum Solar Energy Harvesting
Changing the Colour of the Sun

A thesis submitted in fulfilment of the requirements for admission to the degree of

Doctor of Philosophy
by
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THE UNIVERSITY OF SYDNEY

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Abstract

Projects worldwide for the study, manufacture and deployment of man-made solar energy conversion systems are justified on many grounds: environmental, economic, geopolitical, and societal. Collectively, these justifications provide a dynamic and compelling backdrop for the continuing narrative of solar energy.

Quantum solar energy harvesters form a significant sub-set of the solar energy field. The ‘quantum’ refers to the necessarily quantum mechanical description of the mode by which energy is extracted: in these devices, absorbed photons cause the excitation of charge carriers across a band gap, an arrangement from which useful energy extraction can occur. Solar cells, of course, fit squarely into this category.

The energy conversion efficiency of a solar cell is determined both by the design of the cell and by the properties of the incident sunlight. Thus, in addition to the many and varied works aimed at improving solar cells directly, are those directed towards favourably altering the spectrum of sunlight incident on the cell, prior to its interaction with the cell itself. So-called spectral management is distinct from, but closely related to, solar cells.

In this thesis, I document a largely experimental study of two spectral management techniques. The first of these, luminescent concentration, aims to downshift the energy and concentrate the flux of incident solar photons within a cheaply-produced luminophore-doped waveguide. The result is two-part: better conversion efficiency of the narrow-band higher-intensity photon flux, and reduced material requirements for the solar cell portion of the device. Luminescence concentration has been an active research area for some decades but is yet to result in a commercially-successful design. Systemic problems associated with luminescence concentrators are reported. This motivates the introduction of a novel arrangement for the light absorbing centers aimed at ameliorating at least one such problem, lossy emission biasing by inherited photon anisotropy. We present the first experimentally-realised implementation of the design. The eventual commercial success of the technology depends on many factors not examined in this work, but it is clear that most concentrator designs can benefit from the use of the presented dephasing absorber scheme.

Photons with energy less than the solar cell band gap cannot be harvested by conventional cells. This represents typically the most significant efficiency loss mechanism for so-called second generation thin-film cells. The latter portion of this thesis concerns the study of triplet-triplet annihilation upconversion (TTA-UC), a means by which such sub-band gap photon losses can be reduced.

In standard TTA-UC systems, two identical molecular chromophores (‘sensitisers’) absorb sub-band gap photons, then transfer this energy to a second species (the ‘emitter’) which undergoes TTA to combine these energies and re-radiate a higher-energy photon back into the solar cell. Since TTA-UC is a bimolecular process, the output is quadratically-dependent on the excitation intensity at low light levels. Thus one of the challenges in implementing TTA-UC
schemes for solar cell enhancement is obtaining a sufficiently bright UC response under illumination by unconcentrated sunlight. We have pursued several scheme for tethering the TTA-UC sensitiser to nanostructured solids in a bid to increase the chromophore concentration, without inducing the formation of lossy aggregate sites. Kinetic studies of these materials using pulsed laser excitation are presented, with kinetic modelling used in analysis of the sensitiser and emitter components. The results suggest the formation of heterogeneous structures dependent on the chromophore structure, binding mechanism and scaffold material.

In addition to temporally-resolved measurements, two additional TTA-UC characterisation experiments were carried out, this time under continuous wave (cw) sun-like excitation. The first, solar cell enhancement, has been previously reported, and was used here to measure the enhancement of a hydrogen-passivated amorphous silicon solar cell by a solid-tethered upconverter. Modest gains in short-circuit current were found compared to a similar isotropic liquid upconverter. The second cw characterisation technique, termed the action spectrum, is a novel method of measuring upconversion efficiency without the involvement of a solar cell. Two TTA-UC systems were studied, and the results were corroborated using previous rate measurements. The action spectrum is fast and simple to collect, and is a promising addition to the stable of upconversion characterisation methods.
Declaration of Originality

I declare that all work reported herein is of my own doing, except where explicitly stated otherwise. Portions of the work that have been published are stated as such. No portion of this thesis has been submitted for any other degree or academic qualification at this or any other university or institution.

Rowan William MacQueen
August 28, 2014
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Finally, to my partner Belle: thankyou for coming with me, I can’t wait for the next part!
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Introduction

1.1 Spectral Management for Solar Cells

The power conversion efficiency of single-junction quantum energy collectors under solar irradiation is limited by a mismatch between the sharp edge given by the band gap and the broad energy distribution of sunlight. Quantum solar energy collectors — henceforth, solar cells — do work with absorbed light by separating photo-generated charge carriers over a band gap (henceforth we refer exclusively to single-junction solar cells unless otherwise noted).\(^1\) The exact nature and definition of a solar cell’s band gap is device- and discipline-dependent, but for the purposes of this discussion the band gap is simply an energy, \(E_g\), that sets the threshold for photon absorption. Absorbed photons generate current, which the cell outputs at a voltage proportional to the band gap. Photons with energy \(< E_g\) cannot be collected for energy conversion as they have insufficient energy to separate charge across the band gap; we will refer to this as sub-band gap transparency, since the cell is effectively transparent to these photons. On the other hand, photons with energy \(> E_g\) are absorbed, but the portion of their energy that exceeds \(E_g\) will typically be lost to thermalisation — the emission of phonons as the charge carriers cool rapidly to the vicinity of the band gap.\(^2\) Clearly then, the band gap is one of the most strongly defining characteristics of a solar cell.\(^*\)

From this discussion it should be apparent that only photons with energies on par with \(E_g\) can be collected without significant energy loss due to thermalisation or sub-band gap transparency. The solar cell quandary then, and the source of the ‘mismatch’ assertion at the start of this section, is the very broad range of photon energies contained in the solar spectrum. The sun, a black body emitter, radiates photons into an effective continuum of energies over a broad swathe of the electromagnetic spectrum, as given by Planck’s law. How then can a solar cell efficiently convert this broadband incident radiation to useful energy? Under the regime of a

\(^*\)The power output of the cell, which is the ultimate measure of interest in discussions of cell efficiency, is given by the product of the current and voltage measured at the maximum power point. See, for example, [Würfel, 2009] for a more thorough description.\(^3\)
single-junction solar cell and an unmodified incident solar spectrum, there is no ideal answer: decreasing $E_g$ lets the solar cell absorb more of the incident spectrum and produce more current, but output at a lower voltage and with increasing energy loss to thermalisation. Increasing $E_g$ means the cell becomes transparent to a greater proportion of the incident photons, so although the output voltage increases the current drops. This trading-off between voltage and current means changing the band gap energy in either direction involves compromise.

The problem of the mismatch and its limiting effect on solar cell efficiency was famously quantified by Shockley and Queisser in their 1961 paper, *Detailed Balance Limit of Efficiency of p-n Junction Solar Cells*, in which they derived the limiting (i.e. thermodynamically ideal) power conversion efficiency for a range of band gap energies exposed to simulated solar radiation. This relationship has became widely known as the Shockley-Queisser (S-Q) limit. The peak limiting efficiency calculated by S-Q was 30%, for a band gap energy of 1.1 eV, which has since been revised to 33.7% at 1.34 eV using the updated AM1.5G spectrum. The portion of absorbed photon energy not converted to work is lost to a range of mechanisms, but largely to sub-band gap transmission and carrier thermalisation, the severity of losses to both stemming from the breadth of the solar spectrum.

Efforts to redress this limitation in solar cell efficiency come from two directions:

1. **Change the absorber**
   Changing the way in which the energy collector operates can, in principle, make the energy conversion process more compatible with broadband solar radiation. The S-Q limit is predicated upon absorption by a single-junction solar cell, with the inherent mechanisms of carrier thermalisation and sub-band gap transparency. One way around this is to stack multiple junctions together, each absorbing a different energy component of the incident spectrum. This raises the limiting efficiency to 63.2% for a stack of three junctions, for instance. Indeed, the conversion efficiencies realised by real-world crystalline multi-junction cells is verging on 50%, well in excess of the S-Q limit. The drawback of multi-junction cells is that they require rarefied conditions to work in a cost-effective manner: the junctions need to be current-matched, so the cell performance is very sensitive to changes in the incident spectrum. They’re also more expensive per-area to produce than typical single-junction cells. This leaves them well-suited for large-scale installations utilising solar concentration in sites with carefully selected insolation, but not for small-scale highly distributed generation.

A number of recent efforts to ‘change the absorber’ in order to raise the S-Q limit can be grouped under the banner of third-generation photovoltaics. This is a broad research area motivated in part by the high material costs of crystalline single- and multi-junction cells. Third-generation approaches accordingly adopt techniques and materials from second-generation thin-film cells, themselves intended as a cheaper approach to first-generation crystalline cells. Third-generation designs try to engineer around the main efficiency sinks
in single-junction cells without engendering prohibitively expensive current- or lattice-matching. For instance, the hot carrier solar cell program aims to produce a cell in which thermalisation is restricted by a phononic band gap to the extent that charge carriers can be extracted at energies significantly greater than that of the band gap.\textsuperscript{2} A comprehensive discussion of third-generation concepts can be found in [Green, 2006].

2. Change the sunlight

Instead of changing the structure of the light absorber, we can instead alter the energy distribution of incident radiation to make conversion by existing solar cells more efficient. It is important to realise that the ‘impaired’ efficiency set by the S-Q limit is not in itself a fundamental limit for the conversion efficiency of single-junction solar cells. Rather, any calculation of limiting efficiency requires the assumption of an incident solar spectrum. To state an obvious but nonetheless important point, the extent of the mismatch between the spectral continuity of sunlight and band gap discontinuity depends, clearly, on the spectrum. Shockley and Queisser used a modified 6000 K blackbody spectrum as their model for incident radiation,\textsuperscript{4} while similar contemporary efforts often use the AM1.5G spectrum.\textsuperscript{6} And indeed these both represent device-relevant spectra of sunlight attenuated by transmission through and scattered by a column of atmospheric gases. But the efficiency limits they spawn in calculations of limiting efficiency apply only to cases where the modelled incident spectrum is accurate. If we can change the distribution of photon energies that make up the incident sunlight, we can change the limiting efficiency of the exposed device. This idea is at the heart of solar cell spectral management, or changing the colour of the sun. In short, if we can use efficient processes to modify sunlight to have a clustering of photon energies on the peak of a solar cell’s conversion efficiency, we stand to gain substantial improvements in the limiting efficiency.

The dividing line between the two approaches above is far less sharp than it might appear, and many processes discussed in the coming sections could plausibly be claimed by both camps. The main distinguishing factor in that case is that spectral management techniques are aimed at augmenting the efficiency of existing single-junction solar cells, whereas absorber-based approaches are concerned more with making new types of cells.

1.2 Limiting Efficiencies

If the distribution of photon energies in sunlight can be modified favourably prior to charge carrier extraction by a solar cell, the limiting efficiency can be raised. Table 1.1 summarises the three general forms of spectral management and, where relevant, the improved limiting efficiency they confer to single-junction cells. The following sections detail each form along with current efforts in the field. A plot of the enhanced limiting efficiency for each technique is shown in Figure 1.1.
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<td>$1, E &gt; nE_g$</td>
<td>$n, E \approx E_g$</td>
<td>40% at 1.0 eV$^{11}$</td>
</tr>
<tr>
<td>Downshifting</td>
<td>$1, E &gt; E_g$</td>
<td>$1, E \approx E_g$</td>
<td>33.7% at 1.34 eV$^5$</td>
</tr>
<tr>
<td>Upconversion</td>
<td>$n, E_g &gt; E &gt; E_g/n$</td>
<td>$1, E \approx E_g$</td>
<td>50% at 2.0 eV$^{12}$</td>
</tr>
</tbody>
</table>

Table 1.1: Different modes of spectral management applicable to solar cells, and the general scheme of incident photons to generated charge carriers for each. The augmented efficiencies available to a single-junction solar cell by each method are also listed for AM1.5G incident radiation. Note that the limiting efficiency calculations are sensitive to details like the energy level structure of the light absorber and the refractive index, so the exact limits are prone to shifting for different variations of each scheme. Nonetheless, the substantial improvements available through spectral management are apparent. The inclusion here of downshifting, which does not improve limiting efficiency over the single-junction limit, is justified in-text.

Figure 1.1: The enhanced limiting efficiencies of single-junction solar cells under AM1.5G illumination using upconversion and downconversion, plotted with respect to band gap energy. Plots were generated by Dr Murad Tayebjee and used with permission.
1.2.1 Downconversion

Downconversion primarily addresses thermalisation losses in solar cells. Energy from one high-energy photon absorbed in a downconverting system can be split into two or more smaller units of energy, each \( > E_g \), in order to generate more charge carrier pairs per photon.\(^{13}\) Various radiative and non-radiative implementations of downconversion are currently under investigation. I include non-radiative downconversion schemes under the umbrella of spectral management because although they do not result in re-emission of an altered incident spectrum, they are very much in the spirit of spectral management because they alter the incident energy composition prior to charge carrier extraction from the solar cell.\(^{9}\) On the radiative front, Bryce Richards has reviewed a number of potential downconversion methods that use inorganic lattices doped with rare earth phosphors for coupling to crystalline silicon solar cells.\(^{14}\) The downconverted emission here comes from sensitised \( f \rightarrow f \) transitions within lanthanide centers. Richards noted the challenge of finding a workable material: the phosphor combination must have downconverted emission of \( > 1.1 \text{eV} \) (the silicon band gap) under solar irradiation, and a downconversion yield great enough to overcome the optical losses introduced by the downconverting layer.\(^{14}\) Radiative downconversion with organic materials is perhaps even harder, as no schemes have yet been reported, for reasons discussed below.

Non-radiative downconversion schemes are those that do not convert the lower-energy states generated by downconversion back into photons before injecting into the solar cell. This is a more forgiving process than radiative downconversion because the emissive characteristics of the lower-energy states are unimportant, as long as charge injection is fast compared to the state’s natural lifetime. Within inorganic systems, impact ionisation\(^{15}\) (II) and multiple exciton generation\(^{16}\) (MEG) are both vehicles for downconversion. II is the time-reversal of Auger recombination, generating two pairs of charge carriers low in the conduction band from one hot carrier. II is active in bulk semiconductors, and has long been known to make a small contribution to the output current of crystalline silicon solar cells illuminated in the ultraviolet.\(^{15}\) On the other hand, MEG is prevalent in semiconductor quantum dots.\(^{17}\) Beard and coworkers have argued that there are important differences between the photophysical mechanisms of II and MEG. They state that MEG should have superior downconversion yields compared to II because of the confining effect of the quantum dot, and its influence on momentum conservation, carrier cooling rates, and Auger recombination.\(^{17}\) An ongoing challenge for MEG schemes is to have the multiply-generated excitons inject before they can recombine.\(^{18}\)

Downconversion in organic materials is generally referred to as singlet fission (SF), in which an optically excited singlet state fissions into two triplet states of approximately half the singlet energy.\(^{19}\) Triplet states in organic molecules have notoriously poor room-temperature phosphorescence quantum yields, particularly at lower energies as required of fission.\(^{20}\) This presumably

\(^{9}\)As noted earlier, the line between absorber- and spectrum-based approaches to lifting the S-Q limit is far from sharp.
Figure 1.2: A comparison of the spectrally-resolved external quantum efficiency of a hydrogen-passivated amorphous silicon solar cell (a-Si:H, measured by Dr Dennis Cheng and used with permission), a CdTe cell at room temperature (data adapted from [Rugescu, 2010]) and an ideal solar cell with arbitrary \( E_g \), as would be used in calculating the limiting efficiency for that band gap. Downshifting incident photons from the blue to the orange region of the spectrum would have a large effect on both of the real cells here, and none on the ideal. So while downshifting has no impact on the limiting efficiency of a cell, it can play a very useful role in enhancing real devices.

explains why no radiative downconversion schemes using organic materials have been reported. Instead, organic downconverters rely on charge injection from the triplet excited state. Proof-of-principle singlet fission schemes have already been reported for organic and hybrid organic-inorganic solar cells, although currently the device efficiencies are low. The exact mechanisms at play during the singlet fission process is still a topic of some debate.

Although downconversion is gaining traction as a method of circumventing the Shockley-Queisser limit, we will have no major dealings with the topic in this thesis. However, it is worth remembering that many of the mechanisms governing upconversion — which we will deal with, in some detail — are of immediate relevance to the study of downconversion. After all, the two processes are intimately linked, particularly in organic solids.

1.2.2 Downshifting and luminescence concentration

Not all efforts in spectral management go towards lifting the limiting efficiency of solar cells. In contrast to downconversion, downshifting typically refers to the one-to-one conversion of a higher energy photon into a lower energy photon by, for instance, Stokes-shifted fluorescence. Thus while downconversion is a head-on attempt to defeat thermalisation losses, downshifting
CHAPTER 1. INTRODUCTION

incident photons concedes some degree of thermalisation loss but aims to improve the conversion efficiency of the remaining photon energy. The wavelength-resolved external quantum efficiency (EQE(λ)) of a solar cell is a measure of the cell’s short-circuit current output (I_Sc) for a given incident flux of monochromatic light wavelength λ; an EQE of unity means every incident photon is converted to current. In simulations of ideal cells EQE(λ) is unity everywhere above the band gap and zero below it. But in many real solar cells the EQE is contorted, with some regions above the band gap showing EQEs of considerably less than unity. For example, see Figure 1.2. We can relate this in part to the changing absorption characteristics of different wavelengths incident upon a cell.* For one, many cells are patterned with anti-reflection (AR) coatings to decrease the otherwise sizeable reflection losses.† AR coatings are optimised for a certain wavelength range, and wavelengths outside of this will experience higher reflection losses and a correspondingly poorer EQE. Within the cell, the absorption coefficient is wavelength-dependent. Inorganic cells have an absorption coefficient that is dependent on the bandstructure but is generally larger at shorter wavelengths, so bluer light is absorbed at a shallower depth.‡ The absorption coefficient of organic cells resembles that of the constituent chromophores, which can exhibit multiply-peaked vibronic structures along with regions of very low absorption. Absorption too shallow or too deep within a cell can result in poor separation of the charge carriers and thus a poor EQE. So, while these mechanisms of EQE degradation are irrelevant to the modelling of ideal solar cells (and thus have no impact on limiting efficiencies), they can have a large effect on the performance of real cells. Downshifting the incident spectrum means a solar cell can be optimised for a smaller range of incident wavelengths, yielding improved conversion efficiency.

Downshifting layers benefit solar cells with a poor EQE at shorter wavelengths. A luminescent downshifting slab placed atop and optically coupled to a solar cell can absorb short wavelengths associated with a poor EQE and re-radiate longer wavelengths more favourably absorbed in the cell. Re-radiated photons incident on the cell from the slab can be absorbed directly; others are trapped in the slab by waveguiding or escape through a different slab surface, depending on their angle of incidence at the slab-air boundary. Bryce Richards has published extensively on this topic: with Shalav on the potential of polymers as downconverting and downshifting media;§ on the enhancement of silicon solar cells by passive luminescence conversion;¶ with McIntosh on the simulation of downshifting in CdS and CdTe solar cells;‖ and most recently in 2009 with Klampaftis and coworkers in a comprehensive review of current efforts in the area.¶ Many reports of downshifting layers enhancing cell efficiency can be found in the literature, particularly in the case of CdTe cells, where parasitic absorption by the CdS buffer layer sets in from the green region of the spectrum.¶ For example, Li and coworkers recently reported a 6–10% improvement in the short circuit current density of a CdTe cell using an organic downshifting layer.¶Applied to dye-sensitised solar cells, Hosseini and coworkers have reported a sizeable improvement in the spectral response of a dye-sensitised solar cell using an

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* A more comprehensive discussion of short-wavelength loss mechanisms, beyond the scope of this work, is given in [Klampaftis, 2009].
† A more comprehensive discussion of short-wavelength loss mechanisms, beyond the scope of this work, is given in [Klampaftis, 2009].
‡ A more comprehensive discussion of short-wavelength loss mechanisms, beyond the scope of this work, is given in [Klampaftis, 2009].
integrated downshifting layer.\textsuperscript{31}

I now introduce an extension of the downshifting slab concept that results in concentration of the downshifted radiation: the luminescent solar concentrator (LSC). As for downshifting layers, an LSC in its simplest form is a luminescent slab that absorbs and downshifts certain wavelengths of incident radiation.\textsuperscript{32} The difference compared to a downshifter is in the absorbing area of the cell, \( A_{\text{cell}} \), compared to that of the slab, \( A_{\text{slab}} \). In a downshifting slab setup \( A_{\text{cell}} = A_{\text{slab}} \), but in an LSC \( A_{\text{slab}} > A_{\text{cell}} \). Without preempts too much of Part I of this thesis, where we meet the LSC in full, downshifted light can propagate through the slab in waveguide modes so the LSC can concentrate downshifted light onto an optically-coupled solar cell.\textsuperscript{*} The severity of problems that sap the efficiency gains from downconverting slab systems are enhanced in LSCs commensurate with the mismatch of \( A_{\text{slab}} \) and \( A_{\text{cell}} \), so producing LSCs that produce non-trivial (i.e. worth-doing) improvements in cell performance is a challenging task. We begin a discussion of these issues in Chapter 2.

1.2.3 Upconversion

Upconversion (UC) is the last component of spectral management to be introduced. UC is a general term for a material emitting higher energy light than it absorbs (\( \hbar \nu_{\text{em}} > \hbar \nu_{\text{abs}} \), where \( h \) is Planck’s constant and \( \nu_{\text{abs}} \) and \( \nu_{\text{em}} \) are the frequencies of the absorbed and emitted photons, respectively). Solar cells and upconverters are a tantalising proposition; mounted behind a solar cell, an upconverter could absorb photons transmitted through the cell, upconvert them, and re-radiate energy at shorter wavelengths back into the cell. By sensitising the cell to sub-band gap photons, UC can, in principle, claw back some of the photon losses otherwise inherent to single-junction solar cells.\textsuperscript{33}

There are a number of ways by which photon UC can be brought about, some more suited to solar cells than others. I discuss some of the mechanisms below, mindful of the intended application.

**Thermal upconversion**

Hot-band excitation of fluorescent dyes with small Stokes shifts can yield upconverted emission, with energy extracted from the thermal bath making up the shortfall. This has been termed anti-Stokes fluorescence, and is the basis of fluorescence cooling experiments\textsuperscript{34,35}. Semiconductor light-emitting diodes (LEDs) have long been known to extract energy from the thermal bath (akin to Peltier cooling) when the applied voltage is below \( E_g/q \).\textsuperscript{36} Recently, Santhanam et al.\textsuperscript{*}

\textsuperscript{*}As an aside, I have spent time explaining the benefits of downshifting partly as a motivation for the introduction of the LSC. This is the inverse of the usual approach to the topic, which goes along the lines of problems with light concentration by geometric optics (mirrors, lenses etc.) motivating the development of LSCs, adding improved spectral matching as an incidental benefit of the nonimaging concentration process. The gains in current density widely reported for downshifting slabs combined with the low concentration factors obtained thus far in LSCs convince me that downshifting will be at least as important as concentration in producing economically competitive energy generators using LSCs.
demonstrated an extreme example of this behaviour, in which thermal UC was found to enable the energy efficiency of an LED to apparently exceed unity when operated at very low power.\textsuperscript{37} Since the light emitting process actively cools the host material, thermal UC is applicable to cooling applications. As Clark suggests, it could be applied as a non-intrusive temperature sensor, since the thermal distribution of the emitting material is closely linked to the intensity of emitted light.\textsuperscript{35} Applications for thermal UC in solar cells do exist,\textsuperscript{38} but as solar cells operate at near-room temperatures the limit of any possible efficiency enhancement is small. On the other hand, operating a solar cell at high temperature in order to raise the available thermal energy to a non-trivial fraction of the band gap and improve the thermal UC yield is likely to backfire due to massively increased carrier recombination rates.\textsuperscript{39} We therefore turn our attention to other forms of UC.

Second-harmonic generation

Upconversion by second-harmonic generation (SHG) or, more generally, parametric processes, occurs by the frequency summation of light waves co-propagating within a material lacking a center of inversion. Efficient SHG requires the use of very large electric fields, unfeasible under solar illumination. Tellingly, the authors of the first paper to report SHG commented that it was the development of pulsed ruby optical masers (i.e. lasers) that allowed them to explore this phenomenon.\textsuperscript{40} Clearly, SHG cannot produce useful UC of the sub-band gap solar spectrum under incoherent solar illumination.

Sequential photon absorption in rare earths

Several photon UC mechanisms in trivalent rare earth ions have been known for some decades; a good overview of the subject is by Joubert.\textsuperscript{41} The energy pooling required for upconversion happens in these materials by excited state absorption by single ions, sequential energy transfer from excited donor ions, or some combination of the two processes. Upconverted emission is generally from transitions between levels of the \textit{4f} electron shell.\textsuperscript{42} Trupke, Green and Würfel have calculated the limiting efficiency of a solar cell coupled to an ideal version of such an upconverter.\textsuperscript{43} Rare earth upconverters have been applied to solar cell enhancement, as reported by de Wild and coworkers.\textsuperscript{44} One of the challenges appears to be getting the upconverter to operate effectively under device-relevant illumination conditions.\textsuperscript{12}

Triplet-triplet annihilation upconversion

An overview of the triplet-triplet annihilation upconversion (TTA-UC) mechanism and a brief history of its study is presented below.

Two molecular excited states in close proximity can form an encounter complex, combining their energies to excite one of the molecules further up in the manifold while the other participant returns to the ground state. Presupposing a standard arrangement of energy levels, as for an
Figure 1.3: Triplet-triplet annihilation upconversion (TTA-UC). Triplet sensitisers are photo-excited (A), undergo efficient intersystem crossing (B), and Dexter exchange with emitter molecules (C). Two triplet-excited emitters can collide and undergo TTA (D), dropping one emitter to the ground state and promoting the other to its first excited singlet state. Subsequent fluorescence out of $S_1$ (E) has been upconverted with respect to the excitation.
alternant polyaromatic hydrocarbon, the usual outcome of this would be for the doubly-excited species to rapidly decay back to the energy of the first excited state, effectively annihilating one of the starting excited states - assuming the existence of a rapid decay pathway. And indeed, in the singlet manifold, vibrational relaxation from $S_{n>1}$ back to $S_1$ is typically very fast. This accords with Kasha’s rule, which says that the emission spectrum of a molecule will generally be independent of the excitation wavelength due to this fast relaxation.\textsuperscript{45}

But if the two colliding species are in a triplet excited state and the energy levels are right, spin statistics gives a 1 in 9 chance of the encounter complex dissociating to yield one partner in $S_1$ and the other in $S_0$, such that $2T_1 \rightarrow S_0 + S_1$.\textsuperscript{46} Now, if the molecules are highly fluorescent, there is every chance that the annihilation results in fluorescence from the $S_1$ state of the colliding species. If we can optically prepare the interacting triplet states using energies below that of the emitted photon, we have an upconversion method. Indeed, this is the basis of TTA-UC.

Studies of TTA in organic materials have been carried out for a number of decades; for example, in the early 1960s Sternlicht and coworkers, reporting on the observation of delayed fluorescence in organic crystals, proposed that TTA was the responsible mechanism as triplets trapped in crystal defects hopped between trap sites, eventually meeting and annihilating.\textsuperscript{47} At the same time Parker reported so-called P-type (for Pyrene-type) delayed fluorescence when the TTA-generated singlet emission was at higher energy than the excitation source.\textsuperscript{48,49} To generate this upconverted emission a relatively low-energy triplet sensitiser is required. This species absorbs light of a lower energy than the emitter fluorescence, crosses to a triplet state, then transfers this triplet excitation to the emitter. A diagram of the TTA-UC process is shown in Figure 1.3.

TTA is also of great relevance to OLED performance because statistically, $3/4$ of the injected charge carrier-formed excitons are triplet-excited. TTA is typically a loss process in OLEDs, and occurs at high current densities by both the collisional mechanism advanced here and by resonant dipole coupling to $T_1 \rightarrow T_n$ transitions.\textsuperscript{50}

The Baluschev group has been active in proposing and testing mechanisms for the description of upconversion in organic materials. In 2003 the group published on upconversion from a polyfluorene film doped with a metallated porphyrin triplet sensitiser.\textsuperscript{51} The incorporation of the sensitiser greatly improved the upconversion response of the material at low light intensities compared to two-photon absorption, which suggested that the sensitiser facilitated a very different upconversion mechanism. The authors proposed two mechanisms for the observed effect, while noting that the current experiments were insufficient to definitively prove one over the other. The first mechanism was sequential photon absorption, presumably enabled by intersystem crossing to a long-lived triplet state in the sensitiser, followed by population of the radiative singlet state of the emitter and upconverted emission. The second proposed method was TTA in the sensitiser followed by singlet energy transfer from the doubly-excited sensitiser to the radiative emitter singlet. In the currently understood model of TTA-UC, the first triplet state of the emitter is populated by quenching of the triplet-excited sensitiser; TTA within the emitter
then generates the radiative first excited singlet state, and upconverted emission follows. This mechanism was seemingly not in contention as an explanation of TTA-UC in solid materials at this point.

In 2005, the Baluschev group reported an upconverter based on a new poly(ladder-type pentaphenylene) using the same metallated porphyrin sensitizer as before. Compared to the old system, the new upconverter had a 5 times greater upconversion yield, which was attributed to reduced reabsorption of the upconverted emission. The stability of the polymer upconverters did not rate a mention until later that year, when the group reported that an end-capped poly(pentaphenylene) emitter exhibited improved (but still poor) stability under pumping compared to the previous two polymers. Output degradation in these solid systems was attributed to pump heating leading to accelerated phase-separation of the blended components and reduced polymer fluorescence yield, and the activity of residual oxygen trapped within the matrix during preparation.

At this stage the upconversion mechanism of triplet-sensitizer polymitters was still awaiting clarification. To this end, in 2005 Laquai and coworkers argued in favour of a different mechanism of triplet-sensitized photon upconversion – the TTA-UC process as we have come to understand it today. The key piece of evidence from their experiments in support of this mechanism was that the upconversion effect was enhanced by an order of magnitude and the sensitizer phosphorescence quenched upon the inclusion of anthracene in the polymer host. Anthracene has a triplet level below that of the sensitizer and therefore facilitates the quenching of sensitizer triplets and subsequent TTA-UC.

In the same year, the Castellano group supported the same interpretation of the upconversion mechanism. In reporting a green-to-blue upconverter consisting of a ruthenium-based triplet sensitizer and anthracene (later diphenylanthracene) emitter dissolved in a mixture of organic solvents, the authors attributed upconversion to sensitizer triplet quenching followed by TTA of the triplet-excited emitters. The authors reported the generation of upconverted emission for a large range of sensitizer and emitter concentrations; to speculate, perhaps the liquid sample environment and the insensitivity of the upconversion mechanism to changes in dye concentration and emitter structure made it clear that the quenching-then-TTA model was a more plausible description than those proposed by the Baluschev group in 2003 that relied on inter-molecular energy transfer from short-lived highly excited singlet states.

The year 2007 saw another dispute regarding the TTA-UC mechanism. The Baluschev group published the testing of two polymitter-host upconverters, one with the emitter triplet energy level 0.05 eV greater than that of the metalloporphyrin sensitizer, and the other about the same energy below. The higher-energy triplet emitter produced a low yield of upconverted emission with a lifetime close to that of the sensitizer triplet and a sensitizer concentration dependence that favoured a higher doping level. The authors argued that this upconversion was generated by TTA in the sensitizer followed by singlet energy transfer to the emitter (one of the mechanisms they had put forward in 2003). By comparison, the lower-energy emitter gave a 23-fold higher
output of upconverted emission with a lifetime echoing the emitter triplet state and peak output at a lower doping level. The proposed mechanism for this upconverter was the currently-accepted model of TTA-UC, as put forward in 2005. The explication and acceptance of this mechanism in solids is a recent event. For instance, Steer disputed the explanation given in the Baluschev group’s 2007 paper. In a reply to the paper, he argued that given the solid host material, the heavy doping of metalloporphyrin sensitisers and the predilection of many metalloporphyrins to aggregate, even in low-concentration solutions, the authors were incorrect in neglecting to consider the effects of aggregation and coaggregation in their description of the upconversion mechanism. Steer argued that a better description would include the effects of hetero-TTA between triplet-excited sensitisers and emitters, and allow for triplet-triplet excitation of the sensitisir followed by back-intersystem crossing and singlet energy transfer to the radiative emitter state. In a sign of growing convergence within the field to the currently understood mechanism of solid TTA-UC, the Baluschev group’s subsequent response to Steer had them advocating against some of the mechanisms previously put forward as possible explanations of the effect. In short, they argued that while aggregates are certainly of great importance to TTA-UC, they are almost entirely detrimental to the UC yield, and so aggregate-enabled forms of TTA and energy transfer cannot be the agents responsible for the observed phenomena. As evidence of this, they cited the greatly superior UC yields of liquid upconverters compared to solids, and the increasing internal UC quantum yields in systems with lower sensitiser concentrations. But the bulk of the response can be encapsulated in the argument that the sensitisir triplet lifetime is greatly shortened in the proximity of emitter, which is known to quench the state quite effectively. Therefore the rate of any hetero-TTA process, which requires sensitisir triplets in proximity to emitter, must be vanishingly small compared to the rate at which the emitter triplet state is populated. The Baluschev group also argue that Steer’s account of multiply-excited triplet sensitisers reproduces known models of sequential photon absorption in rare earth ions, which would be inoperational at the relatively low excitation densities used in their work.

1.3 Light Falling on Organic Chromophores

TTA-UC uses organic chromophores as the photon-absorbing and emitting centers. Compared to the rare earth upconverters described previously, organic chromophores tend to have broader, more strongly absorbing bands, and absorb in the visible to near-infrared region of the spectrum. This makes TTA-UC more suited to coupling with thin-film solar cells that have larger band gaps than first-generation crystalline cells. Chapters 4-6 of this thesis are devoted to the study of TTA-UC, specifically its kinetic description and modelling, its implementation in solid media, and its characterisation under low-intensity excitation. In the meantime, this section introduces a formal definition of organic chromophores, and a rate model for their de-excitation by various
processes relevant to the studies at hand.

A chromophore is a colored center within a material. Organic chromophores are associated with characteristic structural moieties, often regions of conjugated double and single bonds that promote the spreading of electron density into molecular orbitals. Colouration stems from the absorption and emission of characteristic wavelengths of visible light by these centers, corresponding to electronic transitions between occupied and unoccupied molecular orbitals. In crystalline semiconductors, light absorption promotes charge-carrier pairs into highly delocalised bands; but in a system of organic chromophores, excitation is typically localised spatially to within the confines of a few molecules. This conception of a chromophore as a highly localised center for energy exchange between organic material and the electromagnetic spectrum is central to the molecular picture of light-matter interaction, and to many of the processes discussed in this thesis.

Molecules under illumination by sunlight will become excited at a rate $k_\phi$ given by

$$ k_\phi = \int \sigma(\lambda) \rho(\lambda) \, d\lambda, $$

where $\sigma(\lambda)$ is the absorption cross-section of the molecule (units of area·nm$^{-1}$) and $\rho(\lambda)$ is the flux of solar radiation incident on the absorber (units of photons·area$^{-1}$·nm$^{-1}$). Typical values are on the order of a few excitations per second for AM1.5G radiation. The objective of all optoelectronic applications, including spectral management, is to direct the electronic energy of excited absorbers into useful modes. So we need to consider the various ways in which electronically excited molecules can relax back to the ground state, which we begin to do in the following section.

### 1.3.1 Rate description of electronic relaxation

A quantum mechanical treatment of organic chromophores interacting with light will be given in Chapter 2. In this portion of the thesis we are better served by a bigger picture view of the various pathways an excited molecule can take back to the ground state, and the ways in which we can influence pathway selection.

To that end, let us assume a mechanism for photoexcitation and a general energy level structure for the molecule (for example, that of a closed-shell alternant polycyclic aromatic hydrocarbon) and focus on a rate model for the processes by which the molecule can undergo electronic relaxation. Relaxation is governed by transition rates between coupled states. As an example, $k_{ij}^X$ is the rate, in inverse seconds, at which state $i$ depopulates into a manifold of coupled states $j$, mediated by coupling process $X$. But of more relevance is the total rate with which state $i$ depopulates via $X$,
\[ k_i^X = \sum_{\text{All } j \text{ coupled by } X} k_{ij}^X, \]  

or the total relaxation rate of state \( i \),

\[ k_i = \sum_{\text{All } X} k_i^X. \]  

The state of the molecule is described by its position on a Jablonski diagram, as shown in Figure 1.4. The lifetime of state \( i \) is given by \((k_i)^{-1}\); the destination state upon relaxation is determined by the competing coupling rates from the initial state to all accessible states. The probability of relaxing by one particular process \( X \), given here by the quantum yield \( \phi_i^X \), is

\[ \phi_i^X = \frac{k_i^X}{k_i}. \]  

To simplify the discussion of electronic relaxation processes we introduce a simple heuristic of relaxation by ‘structural’ and ‘environmental’ processes. The ‘structural’ part of the heuristic embodies all the intrinsic pathways by which the excited molecule can relax back to the ground state; that is, all processes with rates that are fairly insensitive to the molecule's surroundings. The ‘environmental’ part then embodies extrinsic relaxation processes — those that depend strongly on systems external to the molecule, such as other nearby molecules. The molecule will relax under the influence of both sets of processes. The purpose of the heuristic is to distinguish between elements of a molecule’s relaxation behaviour that are susceptible to influences in the chemical environment (and can in principle be manipulated), and elements that are intrinsic to the chemical structure. In the following section we will use this distinction to examine some of the relaxation processes relevant to the work in this thesis. It is my intention that the following section act as a reference source for terms used later in the thesis without explanation. For the forthcoming discussion of mechanisms assume each starts with a closed-shell molecule having just been excited by photon absorption into a vibrationally-excited mode of the first excited singlet state. Two electrons with opposite spins are duly located, one apiece, in the HOMO and LUMO of the excited molecule.

### 1.3.2 Intrinsic relaxation

A Jablonski diagram representing the mechanisms discussed in this section is provided in Figure 1.4.

**Fluorescence** is a spontaneous spin-allowed electronic relaxation of the molecule, corre-
Figure 1.4: Jablonski diagram showing some of the intrinsic relaxation processes available to a molecule optically excited to the $S_1$ state (process A). These are, relaxation to the bottom of $S_1$ followed by: internal conversion then nonradiative decay (B), fluorescence (C), intersystem crossing to (D) and from (E) the $T_1$ state, and phosphorescence from $T_1$ (F)
sponding to the return of the higher-energy electron back to the HOMO with the emission of one photon. Fluorescence occurs by coupling of the transition moment to resonant modes of the photon field.\textsuperscript{*} The emission rate depends on the transition’s oscillator strength and the density of photon modes. Oscillator strength $f_{ij}$, for a transition $i \rightarrow j$, is defined by comparison to a classical single-electron oscillator, and sets the rate with which the transition absorbs and emits radiation. The absorption cross-section and oscillator strength of a transition are related by the following:\textsuperscript{60}

$$f_{ij} = \frac{2\epsilon_0 mc}{\pi e^2} \sigma_0$$

where $f_{ij}$ and $\sigma_0$ have been integrated over the frequency range of the band, and $\epsilon_0$, $m$ and $c$ are the standard physical constants. This relation says that an increased absorption cross-section will result in an increased fluorescence rate, which hints at the linked nature of photon absorption and emission. All other relaxation processes being unchanged, a larger fluorescence rate increases the fluorescence quantum yield of the state as per Equation 1.4. Fluorescence is typically a rather slow process compared to nonradiative decay between closely-spaced vibrational levels (covered below), and so the emission quantum yield from vibrationally excited states is usually vanishingly small. Only once the molecule has relaxed back to the bottom of the excited state where there are no readily accessible lower energy vibrational modes does spontaneous emission have a good chance of taking place. This is the origin of Kasha’s rule.\textsuperscript{45}

**Intersystem crossing** occurs as a molecule moves between the singlet and triplet potential energy surfaces. This process is spin-forbidden: the electron in the LUMO is of opposite spin to the remaining occupant of the HOMO, and flipping the spin of either electron is forbidden by the conservation of angular momentum. So by that measure intersystem crossing should have a negligible quantum yield. But the effect can come to dominate relaxation if sufficiently strong spin-orbit coupling (SOC) is introduced. In SOC a spinning body moving in an orbit experiences coupling of the angular momentum inherent in its orbital motion, and that in its spinning, leading to distortion of the spin angular momentum vector. SOC manifests widely in physical systems, including orbiting planets, atoms and nuclei. In the current context SOC refers particularly to coupling of the orbital angular momentum with the spin angular momentum of its occupying electron. The coupling is generally weak for light nuclei and so most organic compounds do not cross to the triplet state with high yield. But heavy nuclei (e.g. Pd, Pt, or a heavy halogen) in close proximity to the electron can massively enhance SOC through the heavy atom effect, heavily distorting the spin vector and break the spin-forbidden symmetry.\textsuperscript{61} Spin flipping is then encouraged by an energy drop upon entering the triplet state equal to twice the exchange integral. The long triplet lifetime of many organic materials comes about because of the singlet ground-state; the spin-paired electrons in the HOMO and LUMO are forbidden from

\textsuperscript{*} A more comprehensive treatment of this process using the Fermi golden rule is given in Chapter 2.
recombining in the HOMO by the Pauli exclusion principle (the two electrons have identical spins so cannot occupy the same orbital). Eventual relaxation comes by ISC back to the singlet manifold, photon emission (phosphorescence) or by internal conversion.

I have listed ISC as a structurally-determined relaxation process mindful of the metalloporphyrins used to sensitise TTA-UC systems presented later in this thesis. In these triplet sensitiser the metal is structurally incorporated into the chromophore, hence structurally-determined ISC. But ISC via the heavy atom effect can also be induced ‘environmentally’, by dissolving an otherwise unmetallated organic chromophore in a ‘heavy solvent’, containing for example one or more heavy halogen atoms.\textsuperscript{62}

\textbf{Nonradiative decay} (NRD) is a blanket term for the many ways in which an excited molecule may dissipate vibrational or rotational energy and move lower in mode. For instance, a vibrationally hot molecule can dissipate energy by buffeting with surrounding solvent molecules, heating the local environment. Coupling between closely-spaced energy levels is strong, consistent with the energy gap law whereby coupling strength decreases exponentially with increasing energy gap.\textsuperscript{63} Hence nonradiative decay within a single electronic surface is often very fast.

Upon reaching the minimum of the excited electronic potential energy surface, the molecule may fluoresce, as described above, or undergo \textit{internal conversion} (IC) to the ground-state electronic surface by nonadiabatic vibronic coupling. In doing so, electronic and vibrational modes are coupled in violation of the Born-Oppenheimer approximation, which posits electrons moving independently of nuclear vibrations. Systems experiencing vibronic coupling can transfer energy from an electronically excited but vibrationally relaxed state (the bottom of the \(S_1\) energy surface) to a highly vibrationally excited mode on the ground state electronic surface (i.e. high in the \(S_0\) well). This coupling is strongest in the vicinity of conical intersections, which are regions of strong Born-Oppenheimer breakdown that link adjacent electronic potential energy surfaces at a given set of molecular coordinates. In regular alternant PAHs, IC followed by NRD is the dominant form of relaxation for electronic states \(S_{n>1} \rightarrow S_1\), since the energy gap between the electronic energy surfaces decreases with increasing \(n\). Again, this is consistent with Kasha’s rule.

Organic solar cells, spectral management systems and LEDs, in general, try to collect or exploit the energy present in the \(S_0 - S_1\) energy gap of an electronically excited molecule. IC of the excited molecule back to the \(S_0\) surface will always compete against this. Beating IC by a sufficiently large margin to ensure a good yield from the chosen relaxation mechanism is a necessary challenge of most organic optoelectronic devices.

\subsection*{1.3.3 Extrinsic relaxation}

Other molecules in proximity to the excited species can open new channels for relaxation:

\textbf{Resonance energy transfer} (RET) is a through-space resonant coupling of two transition dipoles on neighbouring chromophores, termed the donor and acceptor.\textsuperscript{64} The donor is the ini-
CHAPTER 1. INTRODUCTION

RESONANCE ENERGY TRANSFER

1DONOR *
3DONOR* 1ACCEPTOR 
1ACCEPTOR 
S0
LUMO
HOMO
HOMO - 1
LUMO + 1
S1
S1
S0
A
B
1DONOR 3ACCEPTOR *

Figures 1.5: Two application-relevant relaxation processes available to an excited molecule in proximity to other interacting systems. Resonance energy transfer occurs when an ensemble of radiative relaxation modes on the donor (A) couple resonantly to like modes on a nearby acceptor (B). Dexter exchange (note the change to an orbital diagram here) has two systems in close proximity exchange electrons through orbital overlap. The overall effect is a transfer of the excitation energy and the spin state to the acceptor. In this example, a triplet excited state has been transferred from the donor to the acceptor.
tially excited species, and its electronic relaxation back to the ground state occurs in conjunction with excitation of a resonant transition in the acceptor. Electronic energy thus flows from the donor to acceptor. A Jablonski diagram representation of RET is provided in Figure 1.5.

Although the outcome is similar, RET is a separate process to energy transfer via uncorrelated spontaneous emission from the donor followed by absorption by the acceptor. A separate rate governs relaxation of the donor by the RET channel, therefore RET competes with spontaneous emission and the other available relaxation processes. Broadly, three components go into determining the RET activity: the oscillator strengths of the donor and acceptor, since stronger oscillators should couple more strongly; the degree of energetic resonance, since more highly resonant transitions will couple better; and the spacing and orientation of the two transition dipoles, as dipole-dipole coupling is distance- and orientation-dependent. From a review of the topic by Scholes, the RET rate from the bottom of $S_1$, given here by $k^\text{RET}_{S_1}$, is

$$
k^\text{RET}_{S_1} = \frac{1}{\tau_D} \frac{9000 (\ln 10) \kappa^2 \phi_D J}{128\pi^6 N_A n^4 R^6}.
$$

(1.6)

Grouping the above terms into the three components described above, the oscillator strength of the donor enters via $\phi_D$ and $\tau_D$, the donor fluorescence quantum yield and lifetime. The acceptor oscillator strength enters along with the degree of resonance in $J$, the overlap integral between the donor fluorescence and the acceptor absorption spectrum (recall the link between absorption cross section and oscillator strength). $N_A$ is Avogadro’s number. The refractive index of the host is $n$. The physical positioning of the coupled dipoles enters with $R$ and $\kappa$, the center-to-center distance between the coupled pair and the orientation factor. $\kappa$ accounts for the effect that the relative geometry of the two dipoles has on the coupling,

$$
\kappa = \cos(\phi_{DA}) - 3 \cos(\phi_D) \cdot \cos(\phi_A),
$$

(1.7)

where $\cos(\phi_{DA})$ is the angle formed between the transition dipole vectors laid center-to-center, and $\cos(\phi_D)$ and $\cos(\phi_A)$ are the angles between the transition dipoles and a line joining the two centers. Thus the alignment of two coupling dipoles can influence their exchange of energy through RET, a notion that we will see again in Chapter 2. The $R^{-6}$ term in Equation 1.6 means that RET is a fairly short-ranged process, typically degrading to a negligible rate for distances on the order of 10 nm in RET-active systems.

RET is pervasive in both natural and artificial organic optoelectronic systems. In the present work, we use RET to improve the light harvesting capabilities of anisotropic dyes within an LSC. A more application-specific introduction to the process will be presented in Chapter 2.

Electron exchange as a process for energy transfer was elucidated by Dexter in 1953. The aim of his work was to better understand sensitised luminescence in crystalline solids, but
CHAPTER 1. INTRODUCTION

the findings are widely applicable to interacting chromophores, organic and inorganic alike. The following explanation of electron exchange is drawn from the 1953 paper.\textsuperscript{66}

Dexter’s examination of energy transfer by electron exchange starts from a general description of coupling based on the interaction matrix element containing a Coulomb term and an exchange term. The Coulomb term accounts for the electrostatic interaction of the donor electrons with those of the acceptor, and can be Taylor expanded to yield the familiar dipole-dipole interaction, dipole-quadrupole interaction, and so on. The exchange term, on the other hand, represents the spatial overlap of the donor and acceptor charge clouds. For a well-separated donor and acceptor the exchange term is negligible, and transfer depends only on the Coulomb term. If the coupled transition is dipole-allowed this can result in RET, as described above. But if the transition is dipole- and quadrupole-forbidden, the Coulomb term is rendered negligible. The exchange term may come to dominate the interaction if the donor and acceptor are in very close proximity such that their charge clouds overlap. Energy transfer in this case is carried out by the exchange of two electrons, one from each interacting center, into an energetically available orbital of the other. An upshot of exchange-driven energy transfer is that the spin restrictions change compared to transfer by Coulomb interaction. The spin states of the two interacting molecules can be exchanged, along with their electrons, since the electron spins are unaffected by exchange. For example, this means that the spin-forbidden interaction $^3D^* + 1A \rightarrow 1D + ^3A^*$ is allowed by exchange. The only caveat is that the new spin states formed are not forbidden by the Pauli principle (in this example, $^1D$ and $^3A^*$ are both spin-allowed states). A cartoon of the Dexter exchange process is provided in Figure 1.5.

Dexter exchange is a key process in TTA-UC systems, as will become apparent in Chapter 4. The close proximity required for the exchange interaction means that the donor and acceptor form an encounter complex. This has significant implications for the design of TTA-UC materials.

\textbf{Aggregation} of organic molecules can have profound effects on the energy level structure and relaxation processes of a molecule.\textsuperscript{67} Molecules will tend towards aggregated states under the influence of increasing concentration or reducing solubility, with molecular structure and temperature playing a large role in the onset and extent of the process. For instance, a 1936 letter by Jelly, future eponym of the J-type aggregate (below), reports the preparation of fluorescent aggregates by, among other methods, rapid dilution of a dye solution using a poor solvent, and sudden chilling of a dye solution.\textsuperscript{68} The proximity of molecules within an aggregate leads to strong coupling of the transition dipoles, which can distort and split the absorption and emission bands; the orientation of the aggregated molecules determines the nature of the split bands and the relaxation behaviour. For example, J-type aggregates have a predominantly head-to-tail arrangement of coupled transitions, which adds oscillator strength for the lower-energy aggregate band that manifests as red-shifted fluorescence with narrowed linewidth.\textsuperscript{69} H-type (for ‘hypsochromic’) aggregates have parallel transitions located side-by-side, show more complicated blue-shifted absorption structures, and are typically less fluorescent than the unaggregated
species.\textsuperscript{70,71} Highly fluorescent H-aggregates have on occasion been reported, however.\textsuperscript{72}

Clearly, molecular aggregates are a research topic unto themselves and far exceed the bounds of the simple heuristic of structure+environment set out earlier in this section. Without pre-empting too much of the forthcoming content, aggregation will always play some part (typically deleterious) in the molecular systems described in this work, which involve high concentrations of aggregation-prone molecules. These cases will be discussed as they arise.

Other relaxation mechanisms mediated by extrinsic factors that are not directly relevant to the work in this thesis (although some applications are apparent) include electron injection, stimulated emission, and optical mode engineering.

1.4 Thesis Overview

This thesis documents my examination of two forms of spectral management — photon up-conversion by triplet-triplet annihilation, and luminescence concentration — carried out using organic chromophores. Both techniques attempt to shift the density of incident solar photons into closer proximity to the band gap of a solar cell (luminescence concentration compresses the light spatially as well); the application of both techniques is to improve the energy output of a solar cell compared to its output under illumination by unmodified sunlight. Solar cell performance, then, is an important metric of the success or failure of these techniques. Chapter 6, for example, documents the enhancement to the short-circuit current of a thin-film solar cell by the inclusion of an upconverter module.

But given that solar cells are complex devices in their own right, measuring the coupled device, formed by a solar cell working in optical concert with a spectral management system, can cloud the understanding of the spectral management system. To wit, in our study of the luminescent solar concentrator, we leave the device integration to later works and focus instead on understanding the mechanisms at play using simpler photoluminescence detection. Likewise, following the solar cell enhancement experiment in Chapter 6, the next study in Chapter 7 dispenses with the solar cell entirely and opts for direct measurement of the upconverter photoluminescence. In one sense this is a retrograde step, but as we will see, simplifying the system enables a new and clearer analysis of the upconverter.

The first portion of this thesis deals with the LSC, and the latter with TTA-UC systems under a range of measurement conditions. The mode of investigation is predominantly experimental, with modelling of the results used to infer the mechanisms of interest. Experimental techniques and modelling are presented prior to the results, discussion and analysis. Hyperlinks to cited articles and to referenced sections, equations and so on are provided in the digital version of this thesis.*

\*Numbers following each entry in the bibliography indicate the page numbers at which it is cited. These are hyperlinks, allowing the reader to quickly transition back and forth between the main text and the bibliography.
Part I

Polarisation-switching Luminescent Solar Concentrator
Overview

In Section 1.2.2 the LSC was introduced as a downshifting slab that also concentrates light onto a receiving solar cell. The potential of the device springs from both these aspects: as we have seen, downshifting incident radiation can improve the output of a solar cell by better matching incident radiation to the peak of the cell’s EQE, while concentrating the downshifted radiation reduces the area of cell needed to collect a given photon flux. Both attributes can potentially reduce the cost per unit power output of a solar cell.

This chapter dives deeper into a description of LSCs, examining the operation and sources of inefficiency, and recent research efforts in the field. We will pay particular attention to the role played by interaction anisotropy (IA) in the behaviour of these deceptively simple devices. IA refers to the general understanding that the interaction of light with organic chromophores depends on the spatial orientation and symmetry of the interacting chromophore and the polarisation of light. Until recently IA was a relatively neglected aspect of LSCs, but as we will see it can have important implications for the design of efficient systems.

This chapter begins with a discussion of the origins of IA and its generalisation to ensemble behaviour, in Section 2.1. In doing so we establish the terms and arguments used throughout Section 2.3, in which the detailed operation of the LSC is presented, with particular focus on the effects of IA and current efforts to improve this and other aspects of the device. Finally in Section 2.6 the findings from throughout the chapter are summarised as a motivation for Chapter 3, in which we document the design and testing of a proof-of-concept LSC specifically engineered to address losses by IA in LSCs.

### 2.1 Interaction Anisotropy

#### 2.1.1 Origin

A Fermi golden rule treatment for light interacting with an electronic transition of a molecule begins with the general rate expression:
CHAPTER 2. OVERVIEW

\[ k_{ij} = \frac{\omega}{2\pi} \langle j | \nabla | i \rangle \rho_j \]  

(2.1)

where \( k_{ij} \) is the transition rate from state \( i \) to an ensemble of states \( j \), \( \rho_j \) is the density of receiving states, and \( \nabla \) is the coupling term. A full derivation of the rates of photon absorption and emission by a molecule is given in Appendix B. In brief, we derive the derivative form of the emission rate by calculating the coupling of polarisation with the electronic transition for all interacting polarisation vectors, defined with respect to the electronic transition by the azimuthal angle \( \phi \) and the zenith angle \( \theta \). \( \rho_j \) is found by considering the density of accessible photon modes in a virtual cavity surrounding the emitter. The expansion of the coupling term is truncated at the dipole level, which is justified by the small size of the molecule compared to the wavelength of the interacting light. In emission, the electric field in the cavity is that of a single photon, and can be derived from the formula for irradiance. Combining the coupling term with the density of states and integrating over the isotropic azimuthal angle gives the following rate for light emission:

\[ dk_\theta = \frac{\omega^3}{2\hbar c^3 \epsilon_0} |\langle j | \hat{\mu} | i \rangle|^2 \cos^3 (\theta) d\theta, \]  

(2.2)

where \( \omega \) is the angular frequency of the transition, and \( \hat{\mu} \) is the dipole operator. Clearly, the emission rate is maximum at \( \theta = 0 \), when the polarisation vector is parallel with the transition dipole. This is the origin of emission anisotropy in molecules.

Time inversion results in the phase conjugation of electric fields, so photon absorption and emission should be closely related. Indeed, a similar treatment of absorption from an isotropic broadband radiation field gives an absorption rate of

\[ dk_\theta = \frac{2\pi^2}{\hbar^2 \epsilon_0} \frac{dN}{d\omega} \frac{h\omega}{V} |\langle j | \hat{\mu} | i \rangle|^2 \cos^3 (\theta) d\theta \]  

(2.3)

where \( dN/d\omega \) is the density of receiving states on the molecule. Polarisation is orthogonal to the propagation vector, so Equation 2.2 reproduces the familiar dipole radiation profile, as expected. But the same profile exists in absorption. We can therefore consider the dipole radiation profile more generally as an ‘interaction profile’, mapping \((E \cdot \mu)^2\) for both absorption and emission. By way of example, consider a single stationary molecule exposed to an isotropic broadband photon flux. If excited state rotation of the transition dipole is negligible, symmetry of interaction means photon modes which couple more strongly to the photon field will feature more prominently in both absorption and emission by the dye. The opposite scenario of a single photon mode propagating through an isotropic ensemble of the same dye yields the same behaviour: dyes in the ensemble oriented to absorb most readily from the mode are the ones best positioned to emit back into it. It is this symmetry that can lead to problems for an LSC. To be clear, this is not a completely general statement, since it is predicated on the interacting
species having minimal excited state rotation of the transition dipole moment vector. But a sufficiently large number of fluorescent dyes fit this description to make the discussion of IA relevant to a great many LSC designs.

2.1.2 Ensemble treatment

In this section I outline the formalism for dealing with ensemble-level anisotropic interactions between molecules and photons.

Until now we have treated the transition dipole as an abstract 3-vector. But of course it has a physical origin, in the movement of electrons in molecular orbitals interacting with resonant photon fields. Determining the electronic transition density that underlies the formulation of a transition dipole moment is a difficult task and beyond the scope of this thesis. But as a general guide, an axis linking regions of change in the electron density of the ground-state and electronically-excited molecule is indicative of the transition dipole vector. This linking of physical and electronic structure means IA can be used as a method of exchanging information back and forth between polarised light and the physical orientation of molecules.

In an ensemble of isotropically oriented absorbers, linearly polarised light will preferentially excite molecules that are physically oriented to maximise Equation 2.3. An isotropic ensemble excited with linearly polarised light should therefore contain a distribution of excited molecules with orientations that cluster around the polarisation of the excitation source. Excited molecules will radiate light in an envelope that reflects their own orientation, as given by Equation 2.2. So by the same token, any light emission from an anisotropic excited ensemble should have polarisation clustered around that of the excitation source. Anisotropy $r$ is a term used to quantify the extent of this clustering in experiments using a linearly polarised excitation source:

$$r = \frac{I_\parallel - I_\perp}{I_\parallel + 2I_\perp}. \quad (2.4)$$

Here, $I_\parallel$ and $I_\perp$ represent the intensity of light signals collected coaxially with the excitation beam with parallel and perpendicular polarisations. Samples with high anisotropy will emit light with pronounced grouping of the polarisation (propagation) vectors in directions parallel (perpendicular) to the transition dipole orientation. Samples with zero anisotropy will emit isotropically. Anisotropy experiments can be used to infer physical and electronic properties of the excited species by measuring the decay of $r$ away from the limiting (i.e. maximum possible) anisotropy. There are many possible mechanisms for anisotropy decay, some of which we examine shortly. First, though, comes a discussion of what constitutes limiting anisotropy.

2.1.3 Limiting anisotropy

Given the expression for anisotropy in Equation 2.4, what value of $r$ represents an excited population with limiting anisotropy? A visual guide to the process is shown in Figure 2.1.
To calculate $r_0$, the limiting anisotropy, consider the extent to which molecular absorbers can discriminate between orthogonal polarisations. The coupling strength is given by $(\mathbf{E} \cdot \mu)^2$, and so a single photon mode with arbitrary polarisation given by $\gamma = 0$ will excite an isotropically-oriented population of absorbing transition dipoles with probability $\propto \cos^2(\gamma)$ (the additional cosine power in Equation 2.3 for photon absorption comes from coupling to all accessible photon modes. In treating absorption from only one mode, the additional power falls away). The polarisation of the excitation pulse, along $\gamma = 0$, defines the axis from which anisotropy is measured.

The orange envelope in Figure 2.1 shows the $\cos^2(\gamma)$ distribution of molecules excited by the incident beam, assuming no saturation or dephasing. The probe beam in an anisotropy experiment arrives at the sample collinear with the excitation beam. Again, the beam interacts according to $(\mathbf{E} \cdot \mu)^2$, but this time with the excited ensemble only. The interaction envelopes for parallel and perpendicular probe polarisations with respect to $\gamma$ are $\cos^2(\gamma)$ and $\sin^2(\gamma)$, respectively. These represent the greatest and the least interaction of the probe with the excited ensemble.

The measured probe signals are given by the overlap of the interaction profile with the excited ensemble:
\[ I_{\parallel} \propto \int_{-\pi/2}^{\pi/2} d\gamma \cos^2(\gamma) \cdot \cos^2(\gamma) \]

and

\[ I_{\perp} \propto \int_{-\pi/2}^{\pi/2} d\gamma \cos^2(\gamma) \cdot \sin^2(\gamma) . \]

Note that in order for anisotropy to be accurately determined the constant of proportionality must be the same for \( I_{\parallel} \) and \( I_{\perp} \). Integrating both equations and evaluating the limits gives \( I_{\parallel} \propto 3\pi/8 \) and \( I_{\perp} \propto \pi/8 \). Substituting these terms into Equation 2.4 yields the widely-reported limiting anisotropy value of 0.4, for a population excited by a linearly-polarised beam.\(^{75}\)

### 2.2 Mechanisms of Anisotropy Decay

In this section I list the main sources of anisotropy decay, focusing in particular on the method employed later in a proof-of-concept LSC.

Time-resolved anisotropy experiments measure changes in \( r \) following pulsed excitation. In most circumstances an excited population with limiting anisotropy is a transient phenomenon, and \( r \) will begin to decay immediately after excitation. Any process that causes an effective rotation of the excited transition dipole without relaxing to the ground state deforms the initially-excited \( \cos^2(\gamma) \) distribution and reduces the anisotropy. Mechanisms for this decay can be physical or electronic.

The excited chromophore can rotate, under Brownian motion or by an excitation-induced conformation change. Both effects reduce anisotropy, the extent depending on the degree and rate of rotation. The decay rate due to Brownian motion is indicative of the hydrodynamic bulk of the chromophore and the viscosity of the host material; smaller molecules in less viscous solvents will rotate more rapidly, leading to faster anisotropy decay.\(^{76}\) Energy transfer will also lead to anisotropy decay. Non-correlated photon transfer and RET both lead rapidly to an isotropic population, since with each energy transfer step the alignment of the excited ensemble moves stochastically away from the initial clustering. In solid materials with negligible absorber rotation, anisotropy decay can be used to infer the rate of exciton hopping.\(^{77,78}\) High-concentration solutions will show anisotropy decay due to electronic and physical mechanisms, which complicates the analysis.\(^{79}\) Anisotropy decay times are often of the order 100 ps for viscous solvents or highly doped solids, so a good understanding of the instrument response function is important to most anisotropy experiments.\(^{80}\)

For reasons that will be made clear in Section 2.3, it is important that an LSC have mechanisms to dispense with anisotropy induced by sunlight absorption. We have chosen to make use of electronic dephasing in a high-symmetry chromophore to accomplish this. I explain the
2.2.1 Dephasing in high-symmetry chromophores

Metallated porphyrins have a $D_{4h}$ symmetric structure, which means they have a doubly degenerate $S_1$ state. This gives them an unusual response to electronic excitation that can be harnessed as a mechanism for reducing anisotropy. In short, the degenerate excited state is subject to dynamic Jahn-Teller distortion, which leads to rapid re-orientation of the excited transition dipole and, thus, a very rapid reduction in anisotropy. To explain the effect I draw heavily upon a model system presented by Longuet-Higgins. The following description is taken from source, with some additional commentary on the less-clear steps of the derivation added.

**Dynamic Jahn-Teller effect**

The model presented by Longuet-Higgins is of a single electron that moves on a circular ring. The electron position is given by $\theta$, measured from some fixed axis. The ring itself can undergo doubly degenerate in-plane elliptical deformations with normal coordinates $x$ and $y$ (representing the movement of the ring away from its equilibrium position). Defining the deformable ring in polar coordinates,

$$x + iy = re^{i\phi}. \quad (2.7)$$

The magnitude of the deformation is thus equal to $r$, and the direction of the major axis is given by $\frac{1}{2}\phi$. The schematic in Figure 2.2 demonstrates why this is the case.

In the absence of coupling between the electronic and vibrational motions, the wave function of the system is given by
The vibrational component \( \psi (x, y) \) satisfies the wave equation for an isotropic two-dimensional harmonic oscillator. Skipping over some of the reference paper, in which a general wave equation is presented and re-cast in units of \( r \) and \( \phi \), we arrive at the solutions to the wave equation:

\[
\psi_{nm} (r, \phi) = \rho_{n|m|} (r) e^{im\phi}, \quad E_{nm} = n, \tag{2.9}
\]

where \( n = 1, 2, \ldots, m = n-1, n-3, \ldots, -n+1, \rho_{n|m|} \) is the radial vibrational wavefunction, and \( m \) is the vibrational angular momentum quantum number. At this point in the derivation there are wave functions for the vibrational and the electronic components of the system, but they are uncoupled.

A general expression for the coupling energy \( H' \) is derived by considering the symmetry of the elliptical deformation of the ring. The coupling energy must remain constant with a \( \pi \) rotation of \( \theta \), the electron position on the ring, since on an ellipse these points will be equi-distant from the origin. The coupling must therefore be even with \( \phi = 2 \), the angle the electron makes with the semi-major axis. This gives a general coupling formula of

\[
H' = V (r, \theta - \phi/2) \tag{2.10}
\]

where \( V \) is a function that is even with \( \theta - \phi/2 \). Consider that the simple trigonometric functions \( \sin(\theta - \phi/2) \) and \( \cos(\theta - \phi/2) \) do not satisfy the symmetry requirements of the elliptical system. The next-simplest function which \textit{does} is \( \cos[2(\theta - \phi/2)] \). Using this and higher-order cosine functions which also show the appropriate symmetry, the function \( V \) can be expanded as

\[
V = V_2 (r) \cos[2(\theta - \phi/2)] + V_4 (r) \cos[4(\theta - \phi/2)] + \ldots, \tag{2.11}
\]

where the indices on \( V \) denote the expansion term. Uneven terms lead to non-symmetric behaviour and have been excluded, as per the discussion above. Continuity requires that \( V_2 \) is of order \( r \) at \( r = 0 \). Retaining only the first term for the simple model, the coupling becomes

\[
H' = 2kr \cos(2\theta - \phi) = kr \left( e^{i(2\theta - \phi)} + e^{-i(2\theta - \phi)} \right). \tag{2.12}
\]

The Euler notation for counter-propagating waves has been used in the final expression, and \( k \) is a positive constant, not important in the model system.

Having determined an expression for the coupling, we now examine the total (electronic plus vibrational) wave function. Equation 2.9 provides an expression for the uncoupled vibrational wave function \( \psi_{nm} \). Now, incorporating the electronic wave function yields
\[ \Psi^j_{nm} = \psi_{nm} e^{ij\theta} \]
\[ = \rho_{n|m|} e^{im\phi} e^{ij\theta} \]
\[ = \rho_{n|m|} e^{i(m\phi+j\theta)}, \quad (2.13) \]

with the matrix elements

\[ \langle \Psi^j_{nm} | H' | \Psi^{j'}_{n'm'} \rangle. \quad (2.14) \]

Recall that bra-ket notation is short-hand, and assumes integration over all space. Therefore, any terms generated from evaluating the above expression that contain functions such as \( \cos(\theta) \) and \( \sin(\theta) \) that will integrate to zero, likewise equal zero. Only expressions that set the phase of these trigonometric terms to zero will be non-vanishing. In the above expression, substituting in Equation 2.12 and taking the complex conjugate of the bra gives

\[ \langle \Psi^j_{nm} | H' | \Psi^{j'}_{n'm'} \rangle = \int A \left( e^{-i(m\phi+j\theta)} \left\{ e^{i(2\theta-\phi)} + e^{-i(2\theta-\phi)} \right\} e^{i(m\phi+j\theta)} \right) d\theta, \quad (2.15) \]

where the terms that give no contribution to the phase have been collected in \( A \). Grouping \( \theta \) and \( \phi \) terms together and setting the sum to zero gives the conditions under which a non-zero integral is obtained. Physically, these conditions designate states that are allowed to couple. Grouping terms here gives non-vanishing matrix elements for two sets of conditions:

\[ j' = j + 2, \quad m' = m - 1 \]
\[ \text{and} \]
\[ j' = j - 2, \quad m' = m + 1 \quad (2.16) \]

The two interacting states belong to the same electronic state only if \( |j| = |j'| \), so clearly interaction only occurs when \( |j| = 1 \). This corresponds to the two degenerate electronic states \( e^{i\theta} \) and \( e^{-i\theta} \).

At this point we deviate slightly from the work of Longuet-Higgins. Treating the coupling as a perturbation to the Hamiltonian such that

\[ H = H_0 + H', \quad (2.17) \]

where \( H' \) is the coupling strength derived in Equation 2.12, and treating only the interacting states as per Equation 2.16, we arrive at:
CHAPTER 2. OVERVIEW

Figure 2.3: Conical intersection formed by two offset parabolas (half the well is drawn). Movement around the base of the well, on the path indicated, is barrierless and thus very fast. A π rotation of ϕ constitutes a π/2 rotation of the model structure, and a π/2 rotation of the electronic transition dipole.

\[ \langle j_{nm}| H'| j'_{n'm'} \rangle = \left( \begin{array}{cc} \omega r^2 & 0 \\ 0 & \omega r^2 \end{array} \right) + \left( \begin{array}{cc} 0 & kre^{-i\phi} \\ kre^{+i\phi} & 0 \end{array} \right) \]

\[ = \left( \begin{array}{cc} \omega r^2 & kre^{-i\phi} \\ kre^{+i\phi} & \omega r^2 \end{array} \right). \]  

Obtaining the eigenvalues \( \epsilon \) by subtracting \( \epsilon \) off the diagonal terms and setting the determinant to zero yields

\[ (\omega r^2 - \epsilon)^2 - k^2 r^2 = 0 \]

\[ \epsilon = \omega r^2 \pm kr \]  

(2.19)

Geometrically this corresponds to a pair of offset parabolas, characteristic of conical intersections, as drawn in Figure 2.3. We can now solve the eigenvalue problem

\[ \left[ \left( \begin{array}{cc} \omega r^2 & kre^{-i\phi} \\ kre^{+i\phi} & \omega r^2 \end{array} \right) - \epsilon I_2 \right] \left( \begin{array}{c} c_1 \\ c_2 \end{array} \right) = 0, \]  

(2.20)

where \( I_2 \) is the 2 × 2 identity matrix, resulting in the solution,
\[ c_1 = \pm c_2 e^{-i\phi}. \] (2.21)

Physically, this means that the coupled states are degenerate in energy and offset in vibrational coordinate.

This is a simple model system but it successfully encapsulates the dephasing behaviour of real systems with doubly degenerate excited electronic states. As the wave function orbits around the conical intersection under the effects of solvent buffeting and thermally-activated symmetry breaking, as per Figure 2.3, the polarisation of the excited transition will rotate in a corresponding fashion. De-excitation of the electronic state by the usual channels can then occur out of any polarisation states sampled by the molecule. In an ensemble this random sampling will therefore manifest as a rapid drop in the anisotropy of the system. Indeed, measurements of the electronic anisotropy of a silicon naphthalocyanine molecule by Ferro and Jonas have shown the anisotropy to decay within 200 fs of excitation\textsuperscript{83}.

Recall that the objective in presenting this model was to understand the mechanism by which anisotropy can decay in an excited \( D_{4h} \) symmetric molecule. In contrast to the other decay mechanisms presented earlier in this section, electronic dephasing is intrinsic to the molecular structure and not dependent on intermolecular energy transfer or physical rotation of the chromophore. It is also demonstrably very rapid. This makes electronic dephasing an ideal mechanism for ridding an absorbing ensemble of anisotropy. We make full use of this attribute is the following chapter.

### 2.3 Anisotropy and the LSC

We now turn our attention to LSCs, but it should soon be clear that the previous discussion of anisotropy is of great relevance to the device. A flowchart of the simplified LSC process is given in Figure 2.4. Throughout this chapter the description of LSC operation loosely follows the sequence shown. In Section 2.3.1 the external and internal quantum efficiency is introduced and advocated as a more useful metric of LSC performance than power conversion efficiency, motivating the aim of maximising quantum efficiency and ignoring power conversion efficiency. In Section 2.3.2 the notion of the LSC as a mode-switching device is discussed, an idea central to the relationship between anisotropy and LSCs. Sections 2.3.3–2.3.6 describe LSC light absorption, light emission and escape cone biasing, reabsorption, and multiple-dye systems. Finally, we discuss homeotropic dye alignment and its role in maximising the mode-switching efficacy of the LSC. Other concerns that important to LSCs but not addressed in this work are given in Section 2.5.
Figure 2.4: Simplified flowchart of the LSC process showing the main paths of photon loss. Additional sources of complexity such as daisy-chaining dyes, substrate scattering and Fresnel losses have been omitted for clarity.
2.3.1 Efficiency

The primary function of luminescent concentration has long been cast as reducing the generating cost of solar cells by replacing solar cell with a less-expensive LSC.\textsuperscript{32,84–86} But, as solar prices continue to drop,\textsuperscript{87} it seems increasingly likely that other properties of LSCs — optically uniform faces with tunable colour; robust protection for the attached solar cell — will feature equally in their eventual marketability. Other applications for LSCs have also been touted, such as energy-harvesting polarisers\textsuperscript{88,89} and indoor lighting.\textsuperscript{90} LSCs are commonly constructed using flat planar waveguides, although the concept is applicable to other waveguide geometries.\textsuperscript{91,92}

Despite its base simplicity, many possible additions to the basic LSC design (optical, photophysical and otherwise) make the concise formulation of a general device efficiency a non-trivial task. Without pre-empting too much of the forthcoming discussion, if we assume that substrate absorption and scattering is negligible, and that any non-radiative intermolecular energy transfer pathways operate with unity quantum yield, we can formulate a simple expression for $\eta_{\text{LSC}}$, the external quantum efficiency of an LSC:

$$\eta_{LSC} = \eta_{\text{col.}} \left[ \phi_l \eta_{\text{trap}} \right]^n$$

where $\eta_{\text{col.}}$ is the fraction of incident photons absorbed by the LSC, $\phi_l$ is the luminescence quantum yield of the emitting chromophore, $\eta_{\text{trap}}$ is the average fraction of emitted photons entering waveguide modes, and $n$ is the average number of times a waveguided photon is reabsorbed.

The source of each term will be explained in the following sections. The geometric ratio $G$ of an LSC is given by $G = A_{\text{slab}} / A_{\text{cell}}$, where the two terms denote the areas of the sunlight absorbing surface and the attached solar cells, respectively. The concentration factor $C$ of an LSC represents the effective number of suns worth of photon flux brought to bear on the attached solar cells:

$$C = G \eta_{LSC} .$$

It pays to be cautious when discussing the performance of an LSC. The performance of solar cells is typically summarised as a power efficiency $\frac{P_{\text{out}}}{P_{\text{in}}} \times 100\%$, or the output power of the solar cell at the maximum power point divided by the power of solar radiation incident on the collector surface. But as per the discussion of downshifting in Chapter 1, solar cells illuminated by a quasi-monochromatic output are no longer under standard illumination conditions, and have a potentially much greater power efficiency. Simply, the energy loss due to thermalisation has occurred prior to the solar cell, during cooling and downhill energy transfer from the absorbing chromophore. So discussing the power conversion efficiency of an LSC does not always make sense, because only in concert with an attached solar cell will the figure be meaningful. It is instead better to frame the discussion of LSC performance in terms of the EQE, which for the
LSC is given in the spectrally resolved and integrated form by

\[ \text{EQE}(\lambda) = \frac{A_{\text{cell}} \rho_{\text{col}}(\lambda)}{A_{\text{slab}} \rho_{\text{inc}}(\lambda)} \quad \text{and} \]
\[ \text{EQE} = \frac{A_{\text{cell}} \int \rho_{\text{col}}(\lambda) d\lambda}{A_{\text{slab}} \int \rho_{\text{inc}}(\lambda) d\lambda} \quad (2.25) \]

where \( \rho_{\text{inc}}(\lambda) \) and \( \rho_{\text{col}}(\lambda) \) is the photon flux incident on the slab and arriving at the outcoupling surface, respectively. The integrated value depends on the choice of the \( \lambda \) integral limits, but wavelengths that are lower-energy than \( E_g \) of the intended solar cell would typically be excluded. By maximising EQE rather than power conversion efficiency, thermalisation loss, which is an integral part of the LSC design, has no ill effect. Instead, focus is cast towards improving photon absorption and concentration.

2.3.2 From outcoupling to waveguide modes

A simple LSC is depicted in Figure 2.5. At its heart, the LSC has two functions: downshifting incident radiation, and concentrating the re-radiated energy. The former function occurs by way of the Stokes shift of the luminescent absorber, and it can be extended further by chaining together several dyes to form an energy cascade. This process is discussed in Section 2.3.3. Here we discuss the mechanism of light concentrating and its relationship with anisotropy. This begins with a discussion of total internal reflection.

The light concentrating function is by way of a sharp refractive index step between the external ‘cladding’ of the LSC (which we assume here is air) and the slab material. Snell’s law

\[ n_{\text{air}} \sin \theta_{\text{air}} = n_s \sin \theta_s , \quad (2.26) \]

where \( n_s \) is the refractive index of the slab and \( \theta \) gives the angle of incidence on either side of the interface, predicts the refraction of light when crossing a boundary with a discontinuous change in refractive index. Sunlight incident on an LSC interface can arrive with \( \theta_{\text{air}} \) ranging from zero to \( \pi/2 \); as long as \( \theta_s > \theta_{\text{air}} \) Equation 2.26 produces real values for the angle the refracted beam makes when entering the slab. The limiting angle of incidence, \( \pi/2 \), gives rise to the critical angle \( \theta_c \):

\[ \theta_c = \arcsin \left( \frac{n_{\text{air}}}{n_s} \right) . \quad (2.27) \]

The critical angle is so-called because Snell’s law breaks down when considering a light beam incident on the boundary from within the slab with angle of incidence exceeding \( \theta_c \). The
Figure 2.5: Operation of a basic slab-shaped LSC. The orange material represents the large waveguide surfaces. The light emitting centers in an organic LSC are luminescent dyes, which are here dispersed within the waveguide. The dyes absorb light entering through the sunlight-facing surface (blue arrow). Excited centers emit downshifted light, a portion of which is lost to outcoupling through escape cones (the lower escape cone is depicted along with the critical angle, $\theta_c$). The remainder of the downshifted light is confined in waveguide modes and propagates though the slab. Reabsorption through resonant interaction with other dyes drives nonradiative decay and escape cone loss, and limits the maximum achievable concentration. Finally, waveguided photons that reach a narrow edge can be coupled into an attached solar cell, generating photocurrent. Additions to this basic design include the use of multiple dye species, air-gap mirrors, scattering layers, alternative cell placement, and selectively-reflective filters.
predicted refraction of the beam crossing the boundary becomes complex. In fact, this is the
source of waveguiding: the incident beam does not exit the medium, but rather reflects from
the boundary at the angle of incidence and continues propagating within the slab. Such photon
modes are referred to as ‘waveguide modes’, since their propagation is guided and constrained
by the higher-index material. Modes that connect the inside of the slab with the air are referred
to here as ‘outcoupling modes’, since light in these modes can couple between the slab and the
air (‘incoupling modes’ is an equally valid name). All photon transport between the air and the
sunlight-facing portion of the slab is necessarily via outcoupling modes.

Selection of one mode-type over the other is dependent on \( \theta_c \): downshifted photons incident
on the interface at \( \theta > \theta_c \) are waveguided, those incident at \( \theta < \theta_c \) are outcoupled in so-
called escape cones. A successful LSC therefore takes photons from outcoupling modes and
re-radiates them, with reduced energy, into waveguide modes at a higher photon density. This
mode-swapping is the crucial function of an LSC. An efficient LSC will strongly absorb from
outcoupling modes, and re-radiate with a high probability into waveguide modes. Recall that
the likelihood of photon emission is greatest orthogonal to a dye’s transition dipole. As per the
discussion of IA in Section 2.1 of this chapter, the physical orientation of a dye is intimately
linked with its spatial emission properties. The efficacy of mode switching in the LSC is therefore
tied to the physical orientation of the interacting dyes.

2.3.3 Absorption from outcoupling modes

We have seen in the previous section that, at its heart, the LSC is designed to transfer photons
from outcoupling to waveguide modes, thereby concentrating the photon flux. In the following,
we examine the first part of this process: absorption from outcoupling modes.

External photons incident on the light-absorbing surface of an LSC are subjected to Fresnel
reflection off the waveguide surface. Higher refractive index waveguides will experience greater
reflection losses, which counterweighs any improvement in waveguide coupling through the
decreased critical angle. Solar cells commonly make use of anti-reflection coatings to mitigate
Fresnel losses, but the LSC is reliant on a sharp refractive index boundary and optically smooth
surfaces to sustain waveguiding so cannot benefit from the same treatment.

Given the broadband nature of the solar spectrum, many of the photons incident on the
device will not be absorbed by the embedded chromophores. The \( \eta_{col.} \) term from Equation
2.22 gives the fraction of photons incident on the collector surface that are absorbed. The fundamental \( S_0 \rightarrow S_1 \) transition of the absorber defines an energy threshold much like the band
gap of a single-junction solar cell, below which no photon absorption occurs. The selection of
this energy gap depends on the application. For solar cell enhancement, the emission spectrum
should be matched to the peak EQE of the attached solar cell. For daylighting purposes, the
colour index of the emission is paramount. No matter the application, the choice of threshold is
constrained by the availability of highly luminescent species that emit at the chosen wavelength.
Absorbing dyes must couple strongly to outcoupling modes so that incident radiation can be absorbed over a short path length. In the absence of mechanisms for energy transfer or anisotropy decay following excitation this can lead to problematic escape cone biasing, as discussed below.

2.3.4 Downshifted emission and escape cone biasing

The luminescence quantum yield $\phi_l$ determines the probability that an excited dye returns to the ground state by photon emission. As per the discussion in Chapter 1, $\phi_l$ is determined by competing decay rates. Many organic dyes in transparent host materials have $\phi_l$ approaching unity, which has been one of the main drivers of their widespread use in LSCs. High $\phi_l$ is a prerequisite of an efficient LSC, particularly if reabsorption is significant.

The dipole interaction profile derived earlier in this chapter means that the physical orientation of a dye affects its likelihood of emitting into local photon modes. And we have just now seen that the deciding factor in whether a photon, emitted in the LSC, enters an outcoupling or a waveguide mode is the angle of incidence on the waveguide surface. So it is clear that the orientation of emitting dyes will affect the efficacy of mode switching by the LSC.

This effect can be quantified by calculating the fraction of emitted light that is confined in waveguide modes, $f$, for given emitting dipole orientations. We do this by integrating over the portion of the emission envelope that lies outside of the escape cones and normalising by the full solid angle integral. The angle $\theta$ is measured from the interface normal and $\phi$ is the angle of rotation about the normal.

Isotropic emitters

For an isotropically-aligned distribution of emitting transition dipoles,

$$f_{iso} = 2 \times \frac{1}{4\pi} \int_0^{2\pi} d\phi \int_{\theta_c}^{\pi/2} \sin(\theta) d\theta,$$

(2.28)

where the factor of 2 reflects the symmetry of the integral and $1/4\pi$ is to normalise by the full solid angle integral. Integration over $\phi$ produces a factor of $2\pi$ such that

$$f_{iso} = \int_{\theta_c}^{\pi/2} \sin(\theta) d\theta,$$

(2.29)

$$\cos(\theta_c),$$

(2.30)

and

$$f_{iso} \approx 0.75\text{ for } n_s = 1.5.$$

$$\sqrt{n_s^2 - 1}.$$
homeotropic alignment

Transition dipoles oriented orthogonal to the substrate plane are in homeotropic alignment. The \((E \cdot \mu)^2\) portion of the coupling expression means emission is generated according to a \(\sin^2(\theta)\) distribution. The trapping fraction is therefore given by

\[
f(\theta) = \frac{\int_0^{2\pi} d\phi \int_0^{\pi/2} \sin^2(\theta) \cdot \sin(\theta) d\theta}{\int_0^{2\pi} d\phi \int_0^{\pi/2} \sin^2(\theta) \cdot \sin(\theta) d\theta} = \frac{\cos(3\theta) - 9 \cos(\theta) |_{0}^{\pi/2}}{\cos(3\theta) - 9 \cos(\theta) |_{0}^{\pi/2}} = -\frac{1}{8} [\cos(3\theta_c) - 9 \cos(\theta_c)] .
\]

(2.32)

Using the triple-angle formula \(\cos(3\theta) = 4 \cos^3(\theta) - 3 \cos(\theta)\) and substituting Equation 2.27 gives

\[
f(\theta) = \frac{3}{2} \sqrt{1 - \frac{1}{n_s^2}} \left(1 - \frac{1}{n_s^2}\right)^{3/2},
\]

(2.35)

and \(f(\theta) = 0.91\) for the same substrate.

Homogeneous alignment

Molecules oriented parallel to the plane of the waveguide are in homogeneous alignment. The following equation for trapping fraction is from Mulder and coworkers, who devised a general formula for trapping fraction as a function of dipole orientation,\(^{94}\)

\[
f(\theta) = \sqrt{1 - \frac{1}{n_s^2}} \left(1 + \frac{1}{2n_s^2} \left[1 - \frac{3}{2} \sin^2(\theta)\right]\right).
\]

(2.36)

Homogeneous alignment has \(\theta = \pi/2\), giving \(f(\parallel) = 0.66\) for the \(n_s = 1.5\) substrate. As a check on the veracity of the derived values of \(f(\parallel)\) and \(f(\perp)\), we note that \((2f(\perp) + f(\parallel))/3 \approx 0.75\), as predicted for isotropic molecules equally distributed among the three spatial axes.

Escape cone biasing

In an isotropic ensemble of dyes, those dyes with the transition dipole in near-homogeneous alignment couple most strongly to outcoupling modes. Sunlight incident through the outcoupling modes will preferentially pick out these dyes for excitation, inducing an anisotropic population of excited dyes in roughly homogeneous alignment. By the relations given above for trapping
fractions, this anisotropic population has an increased probability of emitting out the escape cones. This effect is known as escape cone biasing, and has been detected in real devices and reproduced in simulations.\textsuperscript{95–98} Escape cone biasing impairs the efficiency with which the LSC performs mode-swapping.

To reduce deleterious biasing, the absorption-induced anisotropy needs to be dissipated prior to downshifted emission. All of the decay mechanisms given in 2.2 are potentially available to LSCs for this purpose. As the orientation of excited dipoles becomes increasingly isotropic, the trapping fraction increases. It should be apparent however that the best waveguide coupling can be obtained with homeotropic aligned transition dipoles. In this case the LSC requires a mechanism to re-enter a highly anisotropic state prior to downshifted emission. We present such a mechanism in Section 2.4.

\subsection*{2.3.5 Reabsorption}

We have already discussed the problem of emission into escape cones, and biasing of this loss route by absorption from outcoupling modes. Once emitted into waveguide modes, however, confined photons are still subject to mode disruption and loss through reabsorption. Reabsorption occurs through the overlap of absorption and emission bands in dyes, and has long been recognised as one of the primary limitations to achieving efficient LSCs.\textsuperscript{99,100} Indeed, reabsorption is a severe limitation on the level of concentration ultimately obtainable in a device.\textsuperscript{101} The effect is so pronounced in LSCs because of the large mismatch between the path lengths of absorbed and emitted photons. Incident photons must be absorbed over a short distance, since the concentrator must be thin to achieve a worthwhile concentration effect. A relatively high optical density of absorber is therefore required. On the other hand, photons emitted into waveguide modes must travel long distances - perhaps tens of centimeters - before outcoupling at a narrow periphery. Even a very small absorption coefficient can lead to strong attenuation over such distances, as determined by the Beer-Lambert law:

\[
I(z) = I_0 \exp(-\alpha z),
\]  

where \(I\) is the intensity of a light beam, \(z\) is the path length through the LSC, and \(\alpha\) is the absorption coefficient. Single-chromophore LSCs using fluorescent dyes will likely always be adversely affected by reabsorption, with the extent of the effect depending on the degree of reabsorption.

As seen in Figure 2.4, reabsorption is not in itself a loss mechanism. Rather, it recycles photons back to the start of the LSC process, where they can again undergo escape cone loss, nonradiative decay, or re-emission with a randomised path.

The general approach to reducing reabsorption is to reduce the optical density seen by light in waveguide modes, which by the Beer-Lambert law will increase the average path length traveled between reabsorption events. This can be achieved by increasing the Stokes shift of the
emitting species. For example, leveraging their work in phosphorescent materials for organic light emitting diodes, Baldo and coworkers were the first to report the use of a phosphorescent dye as the terminal emitter in an LSC, which showed negligible levels of reabsorption. As described in Chapter 1, phosphorescence occurs by the radiative relaxation of a triplet-excited molecule. Some mixing with the singlet state $S_1$ via spin-orbit coupling is required for photon emission, so it is not true that in such a system, absorption from $S_0$ to $T_1$ is strictly forbidden and thus optically transparent. Rather, it is the comparatively long lifetime of the triplet state combined with comparatively weak spin-orbit coupling that yields phosphorescence with negligible reabsorption back to $T_1$. One of the problems in attempting to utilise phosphorescence is the lack of high quantum yield phosphorescent emitters. For Baldo’s work, the authors state a phosphorescence quantum yield of 0.5 (an earlier paper gives a value of 0.7), which is a significant blow to the obtainable concentrator efficiency. Excited triplet states are also quenched by oxygen, which represents an additional challenge in device manufacturing.

Another method of reducing the optical density for waveguide modes is to lower the concentration of the emitting species, which has much the same effect optically as increasing the Stokes shift. As discussed in the next section, multiple dyes linked energetically lets us decouple the optimisation of absorption and emission, allowing the concentration of the terminal emitter to be decreased. But the efficiency of exciton transport to the terminal species will impose a lower limit on this concentration, below which reduced reabsorption loss will be traded off against increasingly poor energy transfer to the emitting species. Finding an optimal solution here will likely involve careful balancing of the energy transfer rate to the emitter, the emitter Stokes shift, and the substrate dimensions.

Perhaps the most exciting concept for reducing reabsorption loss is that of resonance-shifting, as reported by Giebink and coworkers. Resonance-shifting uses the principles of microcavity optics to couple photoluminescence from a sub-wavelength thickness emissive layer into a bulk waveguide through the evanescent component of light emitted by the layer. The emitted light is drawn into the waveguide at a well-defined angle, and reflects from the bottom surface to return to the emissive layer a short distance from the generation point. Careful design of the thickness of the emissive layer means that the resonance conditions governing coupling between the emissive layer and the waveguide can be altered so that the guided light no longer couples strongly to the emissive layer and thus does not return to the heavily reabsorbing portion of the device. Work on this system appears to be in the proof-of-concept device stage and no reports of fully-implemented LSC devices have yet appeared. Indeed, it remains to be seen if an emissive layer structure can be found that provides resonance shifting across a macroscopic-sized substrate without too many repetitions of lossy return resonance conditions. But the potential of resonance-shifting seems very high.

Given the very different function of a resonance-shifting LSC, we will exclude them from the following discussion. But many of the following topics, particularly improving spectral coverage, are still relevant to the technique.
2.3.6 Multiple-dye systems

For the mode-swapping function of an LSC to operate efficiently, the LSC needs to strongly absorb from outcoupling modes, and not reabsorb from waveguide modes. To the extent that it is allowed by the second law of thermodynamics, an LSC should be a one-way device — photons arrive in outcoupling modes, are absorbed, emitted into waveguide modes, and left alone to propagate to a receiving solar cell; the entropy generated during exciton cooling compensates thermodynamically for the decreased étende.\textsuperscript{105} An ideal device would absorb all post-Fresnel loss incident photons with energies equal to or greater than the $S_0 \rightarrow S_1$ origin of the terminal emitter species, increasing $\eta_{col}$ to the greatest possible value. In simple single-dye LSCs, this is typically not possible. Further, in such a system the efficacy of each of the stages in the LSC processes (absorption, emission, waveguiding) are inter-dependent, since they all depend on the same dye chromophore. In general, one process may not be optimised without compromising another. For example, increasing the fluorescent dye concentration of an LSC means that a greater proportion of incident radiation will be absorbed, but the reabsorption of waveguided light is also increased. Likewise, structuring the orientation of the bright transition to improve coupling to waveguide modes will diminish the interaction with outcoupling modes, which reduces optical density and the absorbed flux.

Decoupling the light absorbing and light emitting roles by the inclusion of multiple linked chromophores allows the LSC mechanisms to be optimised with reduced interference from each other, and also improves the spectral coverage of the LSC.\textsuperscript{84,106,107} Linking together chromophores of different energies using a resonance energy transfer-mediated energy ladder is primarily a way of improving the spectral response, covering the spectrum with the absorption maxima of a range of linked chromophores. Many researchers have reported improved device efficiency upon adding additional chromophore species to a device.\textsuperscript{108,109} But linking chromophores also represents a decoupling of absorption and emission, which gives greater freedom to optimise each aspect of the LSC process. Shifting the majority of light absorption away from the terminal (lowest energy) species lets us optimise it entirely for efficient emission and low reabsorption. If excitation of the terminal emitter comes largely through resonance energy transfer, it can be made uncoupled (as much as possible) to outcoupling modes and the concentration lowered to reduce reabsorption. Baldo and coworkers have reported improved LSC performances using such a process.\textsuperscript{84} Decoupling roles cannot wholly circumvent the reabsorption problem, since the terminal emitting species will still reabsorb to some degree, but it lowers the demand for an ideally-performing dye. In addition, linking chromophores in an energy ladder leads to the decay of absorption anisotropy, as outlined in Section 2.2.

\textsuperscript{105}The requirement for the terminally-emitted photon to propagate without reabsorption means the LSC is transparent to a small portion of the solar spectrum that would otherwise impinge freely on a cell operating under normal sunlight. Hence, this light is effectively unavailable to solar cells attached to the LSC. However, this loss is counterbalanced by the ability to spectrally match the attached cell to the LSC emission spectrum, red-shifting the cell’s EQE peak compared to a device optimised for broadband illumination.
2.4 Sensitising Homeotropic Aligned Dyes

In the discussion of escape cone biasing, anisotropy was induced in an otherwise isotropic population of dyes by the absorption of photons incident through outcoupling modes. This led to the unwanted result of escape cone biasing, which increased emission into outcoupling modes. A system that sheds the absorption-induced anisotropy can operate with improved emission coupling to waveguide modes. But the best possible coupling to waveguide modes can be obtained by mechanically orienting the emitting transition dipoles in a homeotropic configuration. In this case, a second highly anisotropic state must be induced prior to emission, but this time with the alignment direction set by the mechanical orientation of the emitting dyes. The challenges for an LSC using homeotropic dyes are therefore

1. **Absorbing effectively**
   Aligning transition dipoles orthogonal to the substrate plane minimises their interaction with outcoupling modes, for the same reason it maximises their coupling to waveguide modes. The absorption coefficient for incident photons is therefore reduced.*

2. **Generating an anisotropic emitting state**
   A homeotropic LSC needs the emitting state to be highly anisotropic but with a $\pi/2$ rotation of the clustering direction from the absorption-induced anisotropic state, from parallel to perpendicular to the substrate (assuming a separate absorbing species). Thus the LSC needs some mechanism of anisotropy decay and energy transfer that can produce a fast $\pi/2$ polarisation rotation to the emitting state.

3. **Mechanically inducing homeotropic alignment**
   The LSC must be engineered to create robust homeotropic alignment of the emitting dye.

4. **Keeping reabsorption down**
   Dyes in a homeotropic configuration are optimally positioned to re-absorb waveguided light. Compared to isotropic dye at the same concentration, a simple geometrical analysis shows that the homeotropic system has a 3 times greater absorption coefficient for emitted light.† So the challenges presented by reabsorption are actually increased in a

---

*Note that this ignores the possibility of higher excited states absorbing from transition dipoles at different orientations on the molecule. While this is a real phenomenon, it is of little significance here: firstly because $S_2$ of many organic molecules is already into the ultraviolet where the incident photon flux plummets, and secondly because the maximum concentration of the homeotropic species will typically be limited by reabsorption, so it cannot be used as the primary absorber (see point 4).

†Consider that in an isotropic dye population, the orientation of transition dipoles is evenly distributed among the x, y, and z spatial axes. A emitted photon will find that about one-third of the neighbouring dyes it encounters will, roughly, share the same alignment axis as the emitting dye, and will be liable to reabsorb the photon. Two-thirds of the dyes encountered will be approximately orthogonal. In a homeotropic system, every dye shares the alignment of the emitter and is liable to reabsorb, so the absorption coefficient for photons emitted by the system is three times greater.
homeotropic system, the reduction in escape cone losses notwithstanding. The trivial answer to increasing sunlight absorption (item 1) is to increase the absorber concentration; but this is immediately ruled out by the reabsorption problem.

Homeotropic dye alignment for LSCs is an emerging topic in the field, having been proposed by Debije in 2008. In 2010 Mulder and coworkers published a study of homeotropic dye alignment in LSCs, where alignment was induced by polymerisable liquid crystal. Concurrently, we published work on an LSC where homeotropic alignment was reversibly induced by applying an electric field across a dye-doped liquid crystal layer. In both works, homeotropic alignment led to improved coupling to waveguide modes and a reduction in escape cone losses, in good agreement with theoretical predictions. In the same year Debije reported an LSC-type window with switchable dye alignment that could swap between stronger- and weaker-absorbing states by adjusting a voltage. Window transmission in the homeotropic state increased due to weaker dye absorption from outcoupling modes, but waveguide coupling was improved markedly. In 2013 the same group reported an improved version of this device, replacing the original dye with rigid dimer and trimer units that were better aligned by the host. This greatly improved the window’s contrast ratio.

Thus at this stage, much of the research effort in homeotropic-dye LSCs has been directed towards improving the dye alignment. The other challenges listed above have received considerably less attention. We have begun to address these in recently-published work. Using a $D_{4h}$ symmetric absorber and dichroic* emitter aligned in a homeotropic host liquid crystal, we address items 1 and 2 in the above list by the intrinsic electronic dephasing of the absorber and resonance energy transfer to the emitter. This work is detailed in Chapter 3.

### 2.5 Problems Not Discussed

In writing this chapter I have necessarily presented only a subset of the problems facing LSCs and the solutions propounded. For example, I have skipped over the not inconsiderable challenge of developing materials that are of high optical quality, compatible with organic dyes, and photostable over many years of exposure to ambient conditions. For instance, a recent paper by Geoff Smith highlights the unexpected nuance of long-term photodegradation mechanisms in dye-doped polymer. I have also skipped over selectively reflective coatings, secondary edge concentrators, and (discounting the brief discussion of resonance-shifting) manipulation

*The term ‘dichroic’ is used here with the somewhat colloquial optoelectronics usage in mind, which signifies a chromophore that exhibits a large absorption contrast for polarisations parallel and perpendicular to the molecular axis, as in [Wolarz, 1992]. $C_{2v}$ symmetric chromophores like perylene bisdiimides are good examples of ‘dichroic’ dyes.
of interacting photon modes through photonics. More information on each of these topics can be found in the given references, and in the references therein.

Likewise I have discussed the actual application of LSCs only in passing. The basic objective of the process – solar energy collection – is clear enough, but many implementation schemes are possible. For example, LSCs are good candidates for solar energy harvesting windows, since incident radiation not absorbed in the waveguide passes through in the manner of an ordinary window, and the collecting surface is visually uniform. This application represents a good opportunity for building-integrated photovoltaics. In non-window uses non-absorbed radiation is wasted, so a low-band gap solar cell or a heat collector can be mounted behind the LSC – although this partially impairs the function of optical concentration. The LSC-enhancing mechanisms described in this chapter are useful regardless of the exact LSC architecture chosen.

As something of an aside, I have developed an LSC raytrace program that fully accounts for photon polarisation and anisotropic interactions. As the direction of my research moved away from producing fully-fledged LSCs the simulator went largely unused. However, I have included a write-up of the work along with a literature review of LSC simulations in Appendix C, for the interested.

2.6 Conclusion

I have presented the LSC as a device that, at its core, harvests photons from outcoupling modes and re-emits them, at lower frequency, into waveguide modes. To the extent that is allowed by the second law of thermodynamics, this should be a one-way process in an efficient device. The anisotropic interaction of the absorbing and emitting centers with the photon field becomes an important consideration in this, because the reversibility of absorption and emission by an excited transition dipole are at odds with this being an efficient one-way process, as seen with lossy escape cone biasing. But emission anisotropy also presents the opportunity to maximise waveguide coupling through the use of homeotropic aligned transition dipoles.

To be sure, not all luminophores used in LSCs experience appreciably anisotropic interactions with light. Those that do not are not subjected to interaction anisotropy and need not address escape cone biasing. But they also cannot benefit from improved waveguide coupling due to alignment.

In practice, of course, no single approach to improving LSC performance used in isolation is likely to yield a commercially-relevant device. This includes the implementation of homeotropic-aligned dyes. The way towards high concentration factors involves synergistic implementation of several strategies - for instance, inducing homeotropic alignment of the terminal dye in a device employing daisy-chaining to improve spectral coverage. The implementation of solutions must be balanced by the real-world arbiter of device cost per unit power output, adjusting for any value-adding aspects such as aesthetic appeal.
Chapter 3

Experiment and Results

3.1 Rotating the Polarisation Vector

In Section 2.4 of the previous chapter I listed the attributes required of an LSC using homeotropic-aligned dyes — briefly, these were effective absorption of incident light, an anisotropic emitting state, robust dye alignment, and reabsorption within tolerable limits. Following on from the work on homeotropic-aligned dyes in 2010,\textsuperscript{110} we wanted to study a method of sensitising such aligned dyes to photons incident along the collector surface normal.

Our approach to this problem ended up also solving escape cone biasing by normal-incident radiation. In many respects this is the opposite of the sensitisation problem, where we try to couple a favourably-aligned dye ensemble to unfavourably-directed photon modes. Homeotropic-aligned dipoles are orthogonal to the polarisation vector of normal-incidence photons and so they cannot absorb effectively. The problem can best be expressed as the need to rotate the polarisation vector between incident and emitted photons. Let $\mathbf{E}_{\text{inc}}$ denote the polarisation vector of normally-incident light, which lies in the plane of the substrate. $\mathbf{E}_{\text{ideal}}$ is the polarisation vector of light emitted from a homeotropic aligned emitter, which stands normal to the substrate plane. The two polarisation vectors are orthogonal, and so somewhere between a photon being incident on the LSC and an excited chromophore emitting within the substrate, the polarisation has to be rotated. In the case of normal incidence a $\pi/2$ rotation is required to yield maximum waveguide coupling. For light incident on the waveguide at slanted angles the required rotation is less.

Cast in this terminology the problems of escape cone biasing and homeotropic dye sensitisation are clearly related. An isotropic ensemble of single transition dyes will not, on average, rotate the polarisation vector between incident and emitted light, and so the emitted light will have an increased chance of coupling to lossy modes. Incorporating a mechanism to carry out this rotation should decrease this loss. In the limit of rotation to an effectively homeotropic-aligned emitter population, our initial problem - sensitising homeotropic emitters - is recovered.
CHAPTER 3. EXPERIMENT AND RESULTS

Figure 3.1: The use of dephasing and RET to sensitize homeotropic-aligned emitters to normal incidence solar radiation. 1. Absorption of normal incidence light by the $D_{4h}$ sensitizer, causing excitation of one electronic transition dipole. 2. Decoherence of the excitation across the sensitizer chromophore leads to excitation of the orthogonal transition dipole. 3. Rapid RET from the second transition dipole to the homeotropic-aligned emitter dye results in emitter fluorescence, with a high probability of the photon coupling to a waveguide mode.

Clearly then, the problem becomes how to accomplish rotation of the polarisation vector. In their work on LSCs using homeotropic-aligned dyes, Baldo and coworkers opted to use a physical light diffuser to bend incident light into more heavily slanted modes. This duly diminishes the anisotropy generated by absorption, but photons entering the waveguide are necessarily still within the escape cone, so a complete $\pi/2$ rotation is impossible using external optics alone. Adding an external diffuser also increases the complexity of the LSC and Fresnel reflection losses. We propose a different method, making use of electronic dephasing in high-symmetry chromophores followed by resonance energy transfer.

3.2 Experiment introduction

We have begun to address anisotropy in LSCs in a body of work centered on the process of absorption and electronic dephasing in a $D_{4h}$ chromophore, followed by RET to a second dichroic highly fluorescent chromophore; a process we refer to as ‘polarisation switching’. With the two dyes aligned in a homeotropc-dye LSC, such a system could absorb effectively from outcoupling modes and emit with maximal waveguide coupling. Anisotropy induced by absorbing incident photons is dissipated by electronic dephasing, as described in Section 2.2.1, which improves the RET rate to the second chromophore by increasing $\kappa^2$ in Equation 1.6. A schematic of the process is shown in Figure 3.1.

We tested a proof-of-concept LSC incorporating this scheme using polarisation-resolved mea-
surements of photoluminescence generated under broadband excitation by incoherent light at normal incidence to the substrate. The metric of success is the extent to which adding a $D_{4h}$ absorber improves the mode-swapping of photons at normal incidence to a homeotropic-aligned emitter.

Sample preparation is given in Section 3.3, Section 3.4 contains the setup of the optical experiments, and the results are presented in Section 3.5. This body of work has recently been published:


so the following account draws heavily from that paper, but with more extensive details and discussion.

3.3 Sample Preparation

3.3.1 Homeotropic-aligned liquid crystal host

Polarisation switching will benefit LSCs that lack any form of alignment control, simply by reducing escape cone biasing and shifting the alignment of the emitting population towards true isotropy. Nonetheless, we use the mechanism in this work specifically to improve light absorption in LSCs using homeotropic-aligned emitter dyes, which have reduced absorption from outcoupling modes due to their orientation. We use the common guest-host liquid crystal technique to induce dye alignment. In guest-host systems, dyes that are geometrically comparable to the liquid crystal host take on the orientation of the host director. In these systems then, inducing dye alignment is a question of inducing alignment in the liquid crystal host.

Liquid crystal can be aligned in a Fréedericksz transition, where the alignment directors in randomly-oriented domains cooperatively align throughout a bulk volume under the influence of an externally-applied electric field. We have utilised this effect in work towards an LSC that was published in 2010, in which a dye-doped liquid crystal host was induced into homeotropic alignment by application of an electric field across two sandwiching electrodes. Applying a potential over the threshold value resulted in a visible phase change in the liquid crystal layer, and changes to the fluorescence output of the LSC consistent with the dye becoming homeotropic aligned. But this work was hampered by occasional shorting between the electrodes, colouration introduced by the indium tin oxide-coated glass electrodes, and problematic electrode contacting.

So I elected in this more recent work to instead use a surface coating to induce alignment in the guest-host system. Structured surfaces have long been known to influence the alignment director of contacting liquid crystal. For example, rubbed polyimide layers induce homogeneous alignment in the rubbing direction; this is widely exploited in the construction
of twisted nematic liquid crystal displays.\textsuperscript{123–127} To induce homeotropic alignment I used a method that appears to be in routine use by several research groups, whereby the liquid crystal 5CB (4-cyano-4’-pentylbiphenyl) is aligned by a glass substrate silanated by the surfactant DMOAP (N,N-dimethyl-N-octadecyl-3-aminopropyltrimethoxysilyl-chloride).\textsuperscript{128–130} 5CB has a room-temperature nematic phase.\textsuperscript{130} Compared to alignment by an applied electric field the surfactant method yields more robust devices better suited to reproducible measurements.

### 3.3.2 Selection of guest dyes

Candidate dye pairs for demonstrating polarisation switching must meet a number of requirements. Of primary importance is their chromophore symmetry and their absorption-emission properties. The absorber – the higher-energy dye – should be of at least $D_{3h}$ symmetry to allow fast electronic dephasing; the emitter should be highly dichroic such that dephasing is forbidden and the emitting transition dipole moment is along the alignment axis of the molecule. The overlap integral in the RET rate (Equation 1.6) requires that the absorber emission spectrum has good overlap with the emitter absorption spectrum. In this implementation of the scheme within an aligned-dye LSC the dyes must also be soluble in the aligning host and amenable to alignment.

After some searching I settled on beta-substituted octaethyl porphyrin (OEP) as the absorber. Singh and coworkers report that OEP has a planar macrocycle, giving the chromophore
suitable $D_{4h}$ symmetry. For the emitter I chose rhodamine 800, which is resonant with OEP emission and has a largely linear structure. Both are very soluble in 5CB. The absorption and emission spectra of the two dyes are shown in Figure 3.2.

Testing for resonance energy transfer

The spectra of OEP and R800 indicate that they are probably a good RET couple. Nonetheless, several checks were carried out for confirmation. An absorption spectrum of the two dyes together in a 9:1 v/v mixture of dichloromethane and methanol could be re-composed accurately by a suitably weighted sum of the individual absorption spectra, which indicated that ground-state interaction between the two species was not significant.

One of the predictions of RET is lifetime shortening of the donor. If uncorrelated photon emission and absorption is the main energy transfer process, OEP lifetime should be unaffected by the addition of R800. But if the RET rate is competitive against OEP fluorescence, the lifetime should shorten as R800 concentration is increased. This kind of interaction can be quantified by the Stern-Volmer (SV) relationship:

$$\frac{\tau_0}{\tau(q)} = 1 + \kappa_q \tau_0 [\text{R800}]$$

Figure 3.3: Results from the OEP Stern-Volmer quenching experiment. Lifetimes were measured by single-photon counting; fitting yields the indicated quenching rate constant.

\[ k_Q = (7.4 \pm 0.4) \times 10^{10} \text{s}^{-1} \text{M}^{-1} \]
constant, and [R800] is the R800 concentration. To carry out the SV experiment we measured the fluorescence lifetime of a 0.4 mM solution of OEP as a function of R800 concentration in a single-photon counting experiment. Photoexcitation was by the 405 nm output of an OPA (TOPAS) pumped by a 1 kHz regeneratively amplified Ti:Sapphire laser (Clark). OEP fluorescence was detected in a photomultiplier tube after passing through a double monochromator set to 625 nm. No R800 fluorescence was detected at this wavelength. The high optical density of the sample meant we used front-face excitation-detection geometry, which complicates accurate lifetime measurements but not on the nanosecond timescale relevant to this experiment. OEP lifetime was measured for R800 concentrations ranging from zero to 4 mM.

Results of the Stern-Volmer experiment are shown in Figure 3.3. OEP lifetime was 10.7 ns in the pure solution, and decreased with the addition of R800. Fluorescence transients were fit with a single exponential decay, and \( \tau(q)/\tau_0 \) was plotted against [R800] and fit with a linear model (least-squares regression analysis, fit constrained to a y-intercept of 1.0) to give a quenching rate constant \( k_q = (7.4 \pm 0.4) \times 10^{10} \text{M}^{-1} \text{s}^{-1} \). Error was calculated from the 2\( \sigma \) value of the slope of the fit; the scatter in the data points is ascribed in part to the volatility of the solvent mixture affecting the sample concentration. The quenching rate constant is well in excess of diffusion rates detected for similar molecules in solution (\( \sim 10^{10} \)), which indicates, alongside the other evidence given, that RET between the two species occurs in sufficient yield to demonstrate polarisation switching.

### 3.3.3 Assembled device

LSC devices were assembled by first preparing the surfactant-treated glass substrates. Clear glass microscope slides were cleaned with methanol, sonication in a detergent solution, rinsing with water (Millipore water was used throughout), then 30 seconds in a nitrogen plasma cleaner. A 1:2 v/v solution of DMOAP in methanol was diluted with water to give a 1 v% DMOAP concentration. Cleaned slides were placed in this solution for 5 minutes, then rinsed with water and analytic-grade isopropanol and baked at 110°C for 2 hours to allow cross-linking. The treated slides were rendered hydrophobic.

Three mixtures were prepared in 5CB: pure OEP (5 mM), pure R800 (60 mM), and a mixture of the two (5 mM OEP, 60 mM R800). Samples were prepared by transferring a suitable aliquot of stock solution to a 1 mL sample vial and evaporating the solvent; this allowed transfer of sub-milligram quantities with reproducible accuracy. 250 \( \mu \)L of 5CB was added to each sample vial once dried. Vials were sealed and heated to 40°C on a hot plate with gentle agitation; dye dissolution was rapid.

LSCs were prepared by dispersing 38 \( \mu \)m glass spacer spheres over a DMOAP-treated glass slides and gently clamping another over the top using rubber-lipped bulldog clips. A 50 \( \mu \)L drop of the 5CB mixture was deposited in the middle of a clean Petri dish, then the dish, the drop and an assembled slide pair were warmed with a heat gun. A narrow edge of the slide was
Figure 3.4: Depiction of the homeotropic-aligned 5CB LSC environment and the excited dye ensemble, the blue slab represents one of the glass planes comprising the sandwich structure of the LSC.
placed in the drop and the mixture was drawn inside by capillary action. Approximately half
the structure was filled by the droplet; all experiments were performed probing filled regions of
the device.

3.4 Optical Setup and Coordinate System

The objective of polarisation switching is ultimately to improve the coupling of incident radia-
tion to homeotropic-aligned emitters. In order to test this I constructed a simple optical setup
for excitation at normal incidence with controlled polarisation, and polarisation-resolved fluo-
rescence measurements. The excitation source was a 1 kW xenon arc lamp (Oriel) with integrated
collimating optics, and fluorescence detection was by a fixed-grating linear array spectrometer
(Ocean Optics). Polarisation control was by split-prism polarisers and a broadband half-wave
plate. These perform optimally at normal incidence, so back-reflections were aligned over a
long path length to help ensure that this was the case. During measurements the polarisers
were locked in a fixed orientation and polarisation was rotated using the half-wave plate, this
avoided beam-steering within the polarisers that could lead to spurious changes in detected light.
Accordingly results are presented below as a function of the ‘effective’ polarisation axis of the
detector; this reflects that polarisation discrimination on the detector arm was by the rotatable
half-wave plate and a fixed polariser which behaved identically to rotating a single polariser but
without beam-steering.

There are two versions of the setup, both shown in Figure 3.5. The functions of each are
described below, followed by the coordinate conventions used and the results.

3.4.1 Setup 1: OEP alignment in homeotropic 5CB

Setup 1, an on-axis configuration, was used to test OEP alignment in 5CB. This was an im-
portant check because some disc-like molecules adopt a columnar liquid crystal configuration,
which would have them align in the plane of the substrate and impair the polarisation switching
mechanism.\textsuperscript{132} OEP alignment was inferred by exciting the OEP-5CB sample at normal inci-
dence with a fixed linear polarisation, and measuring on-axis OEP fluorescence intensity as a
function of detector polarisation, as shown in Figure 3.5. We calculated the expected response
for isotropic, homeotropic and homogeneous alignment of the OEP macrocycle, as discussed in
Section 3.5.1.

3.4.2 Setup 2: Polarisation switching

Setup 2 is an off-axis configuration used to demonstrate the polarisation switching mechanism by
comparing the fluorescence response of R800 excited by direct absorption, and by dephasing and
RET. Samples were excited at normal incidence by the unpolarised lamp beam; the partially-
closed iris and long focal length lens produced a small beam half-angle at the sample (\(\approx 1^\circ\))
**Figure 3.5: Setup 1:** for the detection of OEP alignment in homeotropic 5CB by on-axis polarised fluorescence measurements. Collimated, isotropically polarised white light is produced by a high-powered xenon arc lamp (a), passed through a blue short-pass filter (b), two split-prism polarisers with identical polarisation axes (2 × c), and focused (f = 5 cm) (d) into the OEP-5CB sample. Fluorescence is collected from the sample (e) by a collimating lens (f = 2.5 cm) (f), passed through a red long-pass filter (g), a rotatable broadband half-wave plate (h), a linear polariser (i) and imaged (f = 5 cm) (j) into a spectrometer (k).

**Setup 2:** for the off-axis detection of polarisation rotation in a two-dye homeotropic 5CB LSC. The output of the arc lamp (A) passes through a removable blue short-pass filter (B), an iris (C), and a focusing lens (f = 20 cm) (D) to excite the LSC sample (E) near a narrow edge. Fluorescence is collected by a collimating lens (f = 2.5 cm) (F), passed through a broadband half-wave plate (G) and a split-prism polariser (H), and imaged (f = 5 cm) (I) into the spectrometer (J).
which meant that the excitation source was, to a good approximation, fully $p$-polarised. As depicted in Figure 3.5, samples were illuminated with the lamp spot a few millimeters from the narrow edge facing the collimating lens of the detection arm. Fluorescence intensity was measured orthogonal to the excitation beam as a function of the detector polariser angle. The position of the sample plane along the detector axis was adjustable with a translation stage, the chosen position maximised detected fluorescence without generating excessive lamp scatter and without introducing severe reabsorption, recognisable by an apparent red-shifting of the emission spectrum. Reabsorption leads to depolarisation and thus diminished discernment of polarisation switching, hence the concern with its minimisation.

Excitation of the pure R800 sample was by direct absorption of the unfiltered lamp, which provided a baseline response for R800 in homeotropic 5CB excited at normal incidence. For the OEP-R800 sample the lamp output was spectrally filtered so as to selectively excite OEP via the Soret band, such that excitation of the R800 was predominantly by RET.
3.4.3 Coordinate system

The general coordinate system for both setups is shown in Figure 3.6. The angles \( \theta \) and \( \phi \) are the colatitude and longitude of the emitting transition dipole moment, respectively. \( \phi \) is measured from the excitation polarisation vector in setup 1 and from the detection axis in setup 2. The effective polarisation axis of the detector is \( \alpha_1 \) in setup 1, measured with respect to the excitation polarisation, and \( \alpha_2 \) in setup 2, measured from the substrate plane. For modelling the expected results we introduce \( p_{\text{exc}} \) and \( p_{\text{det}}^{\alpha} \), the relative probabilities of excitation and fluorescence detection. \( p_{\text{exc}} \) is unchanging for constant excitation conditions, while \( p_{\text{det}}^{\alpha} \) is a function of the detector polarisation axis, which is rotated incrementally to collect a data series. \( I(\phi) \) is the measured fluorescence intensity at polarisation \( \phi \), thus \( I(\phi) \) depends on \( p_{\text{exc}} \) and \( p_{\text{det}}^{\alpha} \).

\[ I(\phi) = I_\parallel, \quad I(\phi) = I_\perp \]

With \( \alpha_1 = 0 \) and \( \alpha_2 = \pi/2 \), respectively. The experimentally determined quantity is \( I(\phi)/I_\parallel \) for \( \alpha \approx (-\pi/2 \rightarrow \pi/2) \). Of most interest are the points \( I_\perp/I_\parallel \), since these represent the limiting cases of possible polarisation switching. In fitting the results from setup 2 we account for imperfect alignment of R800 in the host by the ensemble weight factor \( \chi(\theta) \).

3.5 Results and Discussion

3.5.1 OEP alignment in 5CB

The OEP-5CB device measured with setup 1 (on-axis detection) produced a distribution of points \( I(\alpha)/I_\parallel \) that were symmetric with \( \pi \) rotations of the detector axis and well-fitted by a baseline-shifted \( \cos^2(\alpha) \) function (plot shown in Appendix D). The \( I_\perp/I_\parallel \) value was \( \approx 0.85 \).

OEP with the macrocycle aligned in-plane, as expected for columnar structures, produces uniform excitation in \( \phi \) (i.e. \( p_{\text{exc}} \) is independent of \( \phi \)) since dephasing of excited transition dipoles can energise dipoles equally at all values of \( \phi \). For the same reason \( p_{\text{det}}^{\alpha_1} \) is uniform for all \( \phi \). Homogeneous OEP is therefore expected to yield \( I_\perp/I_\parallel = 1 \).

If the OEP macrocycle aligns normal to the substrate plane in the homeotropic host, the fluorescence should show some dependence on \( \alpha \), since dephasing cannot excite transitions evenly throughout all polarisation envelopes of the detector in the on-axis detection arrangement. Thus, \( p_{\text{exc}} \propto \cos^2(\phi) \) and \( p_{\text{det}}^{\alpha_1} \propto \cos^2(\alpha - \phi) \). We calculate the expected ratio of \( I_\perp/I_\parallel \) by integrating over the excited population and the detector polarisation envelope for both values of \( \alpha \):

\[ \frac{I_\perp}{I_\parallel} \propto \frac{\int_0^{2\pi} d\phi \cos^2(\phi) \cdot \sin^2(\phi)}{\int_0^{2\pi} d\phi \cos^2(\phi) \cdot \cos^2(\phi)}. \]  \( (3.2) \)

Evaluating the integrals leads to \( I_\perp/I_\parallel = 0.33 \). A similar derivation for the case of isotropically-aligned OEP leads to \( I_\perp/I_\parallel = 0.77 \) (Appendix D). The experimental value is slightly in excess

\[ *I \text{ have simplified } p_{\text{det}}^{\alpha_1} \text{ in the limit of parallel and perpendicular detection: } \int_0^{2\pi} d\phi \cos^2(\alpha - \phi) = \int_0^{2\pi} d\phi \cos^2(\phi) \text{ when } \alpha - \phi = 0, \text{ and } \int_0^{2\pi} d\phi \cos^2(\alpha - \phi) = \int_0^{2\pi} d\phi \sin^2(\phi) \text{ when } \alpha - \phi = \pi/2. \]
Figure 3.7: $I(\alpha)/I_\parallel$ for R800 in homeotropic 5CB for direct absorptive excitation (black circles) and excitation by OEP RET (red squares). The lines are predicted values for two ensemble weight functions, $\chi(\theta) = 0.7 + \cos^2(\theta)$ (dashed lines) and $\chi(\theta) = 0.25 + \cos^2(\theta)$ (solid lines) of this, which suggests that the porphyrins were not well-aligned by the 5CB host. This is not particularly surprising given the different geometric forms of the guest and host. Nonetheless, the fact that OEP fluorescence was detectable and still somewhat polarisation-dependent meant that the OEP was still able to participate in polarisation switching.

3.5.2 Polarisation-switching LSC

The $I(\alpha)/I_\parallel$ data for the R800 and OEP+R800 devices measured using setup 2 (off-axis detection) are shown in Figure 3.7. The circles are for direct absorptive excitation of the R800 sample. The peak in $I(\alpha)/I_\parallel$ for direct excitation defines $\alpha = 0$, since we know that $p$-polarised light most readily excites R800 molecules with the transition dipole moment in the plane of the substrate. In spite of the aligned liquid crystal host, it is reasonable to suppose that some portion of the R800 is not well-aligned by the material, especially at the high concentration used. Fluorescence from the directly excited sample is diminished at $\alpha = \pm \pi/2$ such that $I_\perp/I_\parallel \approx 0.67$, which is consistent with there being a large population of homeotropic-aligned R800 that has poor absorption of normal incidence light.

The red, square points in Figure 3.7 are for RET excitation of R800 in the OEP+R800 sample. Of immediate note is the $\pi/2$ offset in the peak of $I(\alpha)/I_\parallel$ compared to direct excitation. Also notable is the greatly increased value of $I_\perp/I_\parallel \approx 1.85$. We interpret this to mean that polarisation switching has led to the excitation of a large sub-population of R800
that is homeotropic-aligned in the 5CB host and unable to effectively absorb normal incidence radiation.

To further strengthen this conclusion, we model these results using the variables defined in Section 3.4.3. The two excitation mechanisms have different \( p_{\text{exc}} \), while the functional form of \( p_{\text{det}}^\alpha \) is unchanging. For direct excitation of R800, \( p_{\text{exc}}^{\text{dir}} \propto \sin^2(\theta) \) and isotropic in \( \phi \). On the other hand, we assume that RET excitation from the dephased OEP is isotropic with \( \alpha \) and \( \phi \), thus \( p_{\text{exc}}^{\text{RET}} \propto 1 \).

The detection probability depends on both \( \theta \) and \( \phi \), such that \( p_{\text{det}}^\alpha \propto \sin^2(\phi) \sin^2(\theta - \alpha) \). In the limits of detection parallel and perpendicular to the substrate plane, \( p_{\text{det}}^\parallel \propto \sin^2(\phi) \sin^2(\theta) \) and \( p_{\text{det}}^\perp \propto \sin^2(\phi) \cos^2(\theta) \).

The detected intensity depends on \( p_{\text{exc}} \), \( p_{\text{det}}^\alpha \) and \( \chi(\theta) \), the ensemble weight function. The modelled peak value is therefore

\[
\frac{I^\perp}{I^\parallel} = \frac{\int_0^{2\pi} \int_0^{2\pi} \sin(\theta) \chi(\theta) p_{\text{exc}} p_{\text{em}}^\perp d\theta d\phi}{\int_0^{2\pi} \int_0^{2\pi} \sin(\theta) \chi(\theta) p_{\text{exc}} p_{\text{em}}^\parallel d\theta d\phi}.
\]

If we assume that the R800 is isotropically oriented, the weight function \( \chi(\theta) \) plays no role in the above expression and direct excitation of R800 results in a ratio of 0.5 (Appendix D). But the observed ratio is 0.67, which we can reproduce by introducing \( \chi(\theta) = 0.7 + \cos^2(\theta) \). A fit to \( I^\perp/I^\parallel \) for direct excitation using this \( \chi(\theta) \) is drawn as the black dashed line in Figure 3.7. This result in itself is support for there being partial homeotropic alignment of R800 within the sample. But more compelling evidence comes from fitting to \( I^\perp/I^\parallel \) for RET-excited R800, neglecting \( p_{\text{exc}} \) due to the isotropic excitation of R800. Now, the ratio predicted by Equation 3.3 for an isotropically-oriented R800 population is 1 (again, a derivation is in Appendix D). But the observed ratio \( I^\perp/I^\parallel \) is closer to 2, which suggests there is more R800 aligned orthogonal to the substrate than would be expected of an isotropic population. Indeed, we can reproduce this result using the weight function \( \chi(\theta) = 0.25 + \cos^2(\theta) \); the fit is shown by the solid red line in Figure 3.7. This weight function differs the one used to reproduce the direct-excitation result, possibly because the real distribution of R800 alignments within the 5CB is more complicated than our chosen function of \( \theta \). Nonetheless, the modelling supports our conclusion that the abundance of fluorescence polarised in the direction of \( \alpha = \pi/2 \) is due to a large homeotropic-aligned population of R800 which is missed by direct excitation at normal incidence, but becomes excited by dephasing and RET from the porphyrin absorber. This constitutes a convincing demonstration of polarisation switching.
3.6 Conclusion and Further Work

Recall from Chapter 2 that the objective of homeotropic emitter alignment in an LSC was to improve the coupling of downshifted emission into waveguide modes. This is one of the two core requirements of an effective LSC, the other being to transfer, with good quantum efficiency, photons incident via outcoupling modes into these waveguide-coupling emitters. One of the challenges of using homeotropic emitters is that they no longer couple well to externally incident light, and the coupling strength diminishes as alignment improves and angle of incidence decreases. Consequently an LSC using homeotropic-aligned dyes risks suffering from poor sunlight absorption.

Polarisation switching solves this by sensitising homeotropic-aligned emitter dyes to normal incidence light by incorporating a $D_{4h}$ symmetric absorber which can resonantly couple to the emitter by RET. Electronic dephasing in the absorber dissipates absorption-induced anisotropy and leads to excitation of transition dipoles favourably oriented to undergo efficient RET to a nearby aligned emitter. In this way, the polarisation of p-polarised light at normal incidence is rotated by $\pi/2$ upon emission into the waveguide. The work described in this chapter is the first demonstration of this mechanism in an aligned-dye LSC structure.

Less stringent variants of the polarisation rotation scheme just outlined can certainly still yield favourable results in LSCs. For instance, a non-dephasing absorber will still go some way towards dissipating absorption-induced anisotropy, simply by adding an additional stochastic step between photon absorption and terminal emission. Absorber dephasing will likely become more important as the emitter concentration is lowered and the alignment is improved, since both moves are more likely to yield absorber sites where the initially excited transition dipole has poor $\kappa^2$ values with the few nearby RET receivers.

This chapter propounds polarisation switching by comparing ratios of polarisation-resolved fluorescence for R800 excitation by direct uncorrelated photon absorption and by RET. An obvious extension of this is to use raw fluorescence intensity to directly measure changes in LSC performance from switching between excitation mechanisms. But doing so entails a much more complex experiment to reliably untangle real effects from all other possible causes of intensity variation. Raw fluorescence intensity is sensitive to the optical quality of the LSC, the beam position on the sample, the absorbed photon flux, and reabsorption. On the other hand, the intensity ratio is sensitive to these properties only so far as they lead to fluorescence depolarisation, which can be limited by having only a very small region of optically dense material between the spot and the collimating lens. Nonetheless, we are confident on the basis of this result that polarisation switching will appreciably improve the performance of homeotropic-dye LSCs.
Part II

Upconversion with nanostructured sensitiser supports
Chapter 4

Introduction and Preparations

Triplet-triplet annihilation upconversion (TTA-UC) can be used to sensitisie solar cells to sub-band gap photons and raise the limiting efficiency. A brief recount of the history of TTA-UC studies and a description of the underlying photophysical mechanisms was provided in Chapter 1, Section 1.2.3. In this and the following chapter I document efforts to produce and characterise upconverters based on solid materials, in a bid to unlock systems with higher upconversion yields.

We start the current chapter by introducing a simple kinetic model for the fate of triplet excited states in TTA-UC systems under continuous-wave excitation. This description arises naturally from the bimolecular nature of TTA, and serves as the motivation for efforts to produce upconverters based on solid materials. We go on to review current work in the field of solid-state upconverters. Finally, the preparation of solid upconverter materials using nanostructured scaffolds is presented. The implementation of the techniques and materials presented in this chapter is the subject of Chapter 5.

4.1 Steady-state TTA-UC Rate Model

To recap briefly, in TTA-UC a triplet sensitiser absorbs low-energy light, crosses to the triplet manifold, and is quenched by a singlet ground-state emitter with the exchange of singlet and triplet character. Two such triplet-excited emitters can form an encounter complex and undergo TTA, promoting one chromophore to an excited singlet state from which it emits upconverted fluorescence. The generation of upconverted light by TTA in the steady state is therefore governed by the general rate equation for the emitter triplet population:

\[
\frac{d[^3E^*]}{dt} = k_\phi[^1S] - k_1[^3E^*] - k_2[^3E^*]^2 = 0
\]  

(4.1)

where \(k_\phi\) is the sensitisier excitation rate constant, \[^1S\] is the ground-state sensitisier concentration, \(k_1\) and \(k_2\) are the first- and second-order emitter decay rate constants, and \[^3E^*\] is
Figure 4.1: Upconversion response curve (solid line) and efficiency (dotted line) as a function of the excitation metric $\Sigma$ for a model TTA-UC system. The dashed line delineates the onset of the linear regime, where the efficiency becomes independent of excitation conditions.

the concentration of triplet-excited emitter. It is assumed within the model that intersystem crossing and sensitizer-emitter triplet energy transfer both occur with unit efficiency.

The bright emitter singlet state, responsible for upconverted emission, is generated through bimolecular collisions between triplet-excited emitters at a rate governed by $k_{e1}$. Generating efficient upconversion is therefore a matter of suppressing and enhancing the first- and second-order emitter triplet decay channels, respectively.

Measuring $[^3E^*]$ directly is possible using transient absorption, or by numerical simulation of photoluminescence data. But the more application-relevant quantity is the intensity of upconverted emission, $I_{UC}$. The bimolecular nature of TTA means that $I_{UC} \propto [^1E^*] \propto [^3E^*]^2$. A typical upconversion intensity response plots $I_{UC}$ against some analogue of $k_{\phi[1S]}$, which we define here as the excitation metric, $\Sigma$. The plot can be derived by considering the changing response of a model TTA-UC system as $\Sigma$ is increased. At low emitter triplet concentrations, triplet decay in the system from Equation 4.1 is dominated by the $k_{e1}[^3E^*]$ term, thus:

$$\frac{d[^3E^*]}{dt} \approx k_{\phi[1S]} - k_{e1}[^3E^*] = 0$$

$$[^3E^*] \propto \frac{k_{\phi[1S]}}{k_{e1}}$$

$$\therefore I_{UC} \propto \frac{k_{\phi[1S]}^2}{(k_{e1})^2} = \left(\frac{\Sigma}{k_{e1}^2}\right)^2.$$  \hspace{1cm} (4.2)

Hence in the low-$\Sigma$ regime, the upconversion intensity is quadratically dependent on $\Sigma$ and the yield is initially low. But as $\Sigma$ increases, and with it the emitter triplet concentration,
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$k_2[^3E^*]^2$ comes to dominate Equation 4.1, and now:

$$\frac{d[^3E^*]}{dt} \approx k_\phi[^1S ] - k_2[^3E^*]^2 = 0$$

$$[^3E^*] \propto \sqrt{\frac{k_\phi[^1S ]}{k_2}}$$

$$\therefore I_{UC}^{high\Sigma} \propto \frac{k_\phi[^1S ]}{k_2} = \frac{\Sigma}{k_2},$$ (4.3)

and so the upconversion intensity response gradually straightens to become linear with $\Sigma$.

The derivative of the response curve, $dI_{UC}/dk_\phi$, is proportional to the upconversion efficiency, $\phi_{UC}$. Thus the upconversion efficiency becomes formally independent of the excitation intensity only in the linear response region. We can therefore predict the response and efficiency curves shown in Figure 4.1, where the dashed line marks the transition between the quadratic and linear regions.

This characteristic behaviour underlies many of the challenges at the heart of upconversion studies and applications. To upconvert efficiently, a system must achieve $\Sigma$ capable of invoking a linear response. In experiments it is often the case that the $k_\phi$ component of $\Sigma$ can be increased with a dial on the light source, but in solar energy applications it is limited by the local insolation. A thorough treatment for calculating the threshold power needed to reach the efficient linear response region for a given system has been presented by Monguzzi and coworkers.134 Through similar reasoning to the work above they define an intensity threshold, $I_{th}$, where the conditions are such that $k_1[^3E^*] = k_2[^3E^*]^2$. In the following passages I discuss ways in which this threshold can be lowered to an application-relevant level by tailoring the chemical and optical design of upconverters.

4.2 Wanted: Linear Response at Low Flux! (with caveats)

Equations 4.2 and 4.3 demonstrate the components that must underlie efficient upconversion, namely, the excitation rate and sensitiser concentration. Not coincidentally, these constitute the excitation metric $\Sigma$. The rate constants governing emitter relaxation from the triplet state are determined by the structure and microenvironment of the emitter. The only dynamic determinant of the response regime is therefore the emitter triplet concentration, $[^3E^*]$. Both components of $\Sigma$ contribute to the growth of this term: $k_\phi$ is the rate at which each sensitiser can produce emitter triplets, and $[^1S ]$ is the concentration of these producing centers.

A simple directive for improving upconverter performance can thus be given: increase $k_\phi$, and increase $[^1S ]$. This creates two complementary objectives that can be pursued in parallel. My work has been directed towards the latter, so this portion of the thesis deals mainly with increasing $[^1S ]$. But I summarise current efforts towards improving $k_\phi$ below.


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4.2.1 Increased excitation rate

Recall from Chapter 1 that $k_{\phi}$ is given by the integral of solar flux over the absorption cross-section (Equation 1.1). Thus, there are two complementary approaches to improving the excitation rate. The first, solar concentration, locally boosts the solar fluence. Solar concentration applied to TTA-UC systems has been studied within our own research group by designing micro-optical cavities that reflect and focus incident light into the upconverter, locally raising the photon fluence.\(^\text{135}\) Full solar concentration using macroscopic optics and solar tracking would certainly result in a very large improvement to $k_{\phi}$ but this approach is economically unrealistic, especially given that TTA-UC operates in an energy range that best complements cheap second-generation solar cells.

Micro-optical cavities are instead a compromise, cheaply produced and effective enough without solar tracking to be a viable addition to upconverters coupled to inexpensive solar cells. A related approach is to use plasmonic phenomena to increase the local amplitude of the photon electric field, enhancing the effective photon intensity.\(^\text{136}\) We note that the introduction of plasmonic centers must be handled carefully, since nonradiative decay rates can also be plasmonically enhanced.\(^\text{137}\)

Another approach to improve $k_{\phi}$ is to modify the absorption cross-section of the sensitiser to allow a better match with the incident spectrum. This can be done by modifying the sensitiser structure, or using multiple absorbing chromophores. In the former category, our research group has reported improved upconversion under sunlight conditions from a modified metalloporphyrin sensitiser. Nitro-amine addition to two adjacent sites on a quinoxaline group of a palladium tetrakisquinoxalino porphyrin led to a flatter and broader Q-band (the low-energy absorption feature common to porphyrins) to give an enhanced $k_{\phi}$ (this dye, Q\(_4\)PdPNA, is utilised in Chapter 6).\(^\text{138}\) Of the second method, the Baluschev group has reported that multiple up-conversion sensitisers can be additively combined to yield an upconversion response across a broader range of the solar spectrum, likewise leading to an improved excitation rate.\(^\text{139}\)

4.2.2 Increased sensitiser concentration

Complementary to increasing $k_{\phi}$, increasing the concentration of sensitiser chromophores improves the subsequent concentration of emitter triplets, with one important caveat. The simple rate model introduced at the start of this chapter (Equation 4.1) and used to motivate this objective assumes that the sensitisation portion of the TTA-UC process occurs with unit efficiency. In other words:

$$\text{[1S*]} \xrightarrow{\text{ISC}} [3S^*] \xrightarrow{\text{Dexter}} [3E^*]. \quad (4.4)$$

In current optimised liquid-based upconverters this is a good pair of assumptions. The first,
intersystem crossing to the sensitiser triplet, has been routinely measured and found to occur with efficiency on the order of 99.9% for metalloporphyrins with heavy central atoms.\textsuperscript{140,141} The second step, triplet energy transfer to the emitter, occurs with near-quantitative yield if \( k_Q[1E] \) is much greater than the intrinsic decay rate of the sensitiser triplet, to return to the Stern-Volmer quenching rate constant first described in Chapter 3. This has been found to be the case in liquid upconverters employing high emitter concentrations.\textsuperscript{134,141} But we note with emphasis that the best-performing liquid upconverters we have produced in our lab have sensitiser concentrations well below the solubility limit.\textsuperscript{142} This experience seems to be in accord with reports from other groups, although typically no rationale is provided for chosen sensitiser concentrations.\textsuperscript{134,139}

We expect that the primary reason increasing the sensitiser concentration fails to improve the upconversion yield is because the second assumption in Equation 4.4 becomes suspect. In other words, it is no longer accurate to assume that sensitiser triplets are deactivated overwhelmingly by Dexter exchange with ground-state emitters. For example, triplet-excited sensitisers in close proximity are prone to the same triplet-triplet annihilation mechanisms as emitters, but with the usual result being the loss of one triplet state.

A modified steady-state expression for emitter triplet concentration incorporating lossy sensitiser mechanisms is derived in Appendix E. In short, we derive the model by assuming efficient intersystem crossing but with additional loss channels for the triplet-excited sensitiser. Grouping terms leads to the expression

\[
\frac{d[3E^*]}{dt} = k_\phi[1S] - k_{loss}'[3S^*] - k_1[3E^*] - k_2[3E^*]^2,
\] (4.5)

where \( k_{loss}' \) is the pseudo-first order rate constant for lossy decay of the sensitiser triplet. The revised response curve is now dependent on the severity of the \( k_{loss}'[3S^*] \) term and the order of the lossy responses. As sensitiser concentration grows, the likelihood of aggregation between chromophores increases. In the limit of heavy aggregation the rate model description is rendered defunct, because it implicitly assumes homogeneity of microenvironments. At this point we would expect severe triplet losses in the sensitiser and an effectively non-functioning upconverter.

The objective of increasing sensitiser concentration is to lower the fluence required to reach the efficient linear response region. But as we have seen, sensitiser losses already constrain the concentration even in the comparatively low concentration systems current under study. So satisfying this objective is as much a matter of suppressing these sensitiser loss channels as it is introducing sensitiser at the required concentration. The development of high-sensitiser concentration upconverters therefore has two distinct requirements:

1. **Create a dense sensitiser material** that can generate a high concentration of triplet states, and
2. **Suppress sensitiser-sensitiser interactions** to retain the behaviour of isolated chromophores.

At this time, liquid-based upconverters have achieved by far the best reported TTA-UC performance.\textsuperscript{138,143} But the two aims above make it apparent that liquid systems have relatively little room for improvement when it comes to boosting the concentration side of the excitation metric. The typical solubility of large organic chromophores means liquids cannot generally support high sensitiser concentrations, and the lack of morphology control in the liquid phase means lossy sensitiser-sensitiser interactions are likely to occur. Thus we are motivated to develop mixed-morphology upconverting materials.

A brief overview of other works in this field and the associated difficulties with sensitiser losses is given in the following section.

### 4.3 Recent Work in Solid Upconverters

Migrating upconversion systems to the solid state is an increasingly popular objective. Most reported work seems to be motivated more by the processing convenience offered by solid materials than by an explicit drive to higher upconversion efficiency. Thus, the implied aim of these works is to reproduce in the solid phase the comparatively much greater performance currently found in liquid upconverters. Nonetheless, at this stage of development the two aims are functionally identical. One substantial difficulty in moving to solid upconverters is the loss of molecular diffusion, which in liquid systems gives the interacting species a method of coming together and — just as importantly — separating again. The various responses to this issue of diffusion are a convenient sorting criteria for current work in the field. Many of the references given below were found in a thorough review of the field by Simon and Weder, published in 2012.\textsuperscript{144}

#### 4.3.1 Optically inert hosts

One of the more successful types of solid upconverter reported to date makes use of an optically inert rubbery polymer matrix as a host for standard upconverting chromophore pairs, as reported by the Castellano group.\textsuperscript{145} It is thought that the soft host allows a limited degree of molecular diffusion, thus to some extent the material behaves like a liquid upconverter in a very viscous solution. Dye concentrations reported are akin to those used in liquid systems, and sample preparation is by drop-casting at room temperature.\textsuperscript{145} A study by the same group of the temperature dependence of upconversion in the rubbery host showed that upconversion virtually ceased below the glass transition temperature, which accords with the ascribed mechanism.\textsuperscript{146} More recently the group has studied the Stern-Volmer quenching behaviour in rubbery films through the careful preparation of samples at a range of emitter concentrations.\textsuperscript{147}

Given the apparent cessation of upconversion below the glass transition temperature of rubbery matrices, it is somewhat surprising that other groups have found measurable upcon-
verted emission from standard dopant pairs encapsulated in rigid glassy polymers. For example, Merkel and Dinnocenzo doped PMMA with the common upconversion combination of platinum octaethylporphyrin sensitisier (PtOEP, \(\sim 0.5\) wt\%) and diphenylanthracene emitter (DPA, \(\sim 10\) wt\%). The comparatively high emitter loading was found to facilitate energy migration by exciton hopping, supplanting molecular diffusion in the rigid host. Films in this study were fabricated by doctor-blading at room temperature. A recent report from Simon and Weder extended this concept by compression-molding similar blends of dyes at high temperature followed by rapid cooling, with the intention of producing a more homogeneous distribution of dyes within the polymer by preventing phase separation. Even after these careful preparations however, they found that the output of upconverted light was greatest for a comparatively low sensitiser concentration of 0.05 wt\%. This suggested sensitiser aggregation opening lossy triplet decay channels.

4.3.2 Optically functional hosts

The use of inert polymer hosts for upconverting materials is appealing from a device integration perspective. But the upconversion performance is restricted by the energy transfer radii of participating chromophores, which are typically much smaller than those enabled by molecular diffusion in liquid microenvironments. One solution is to encase the sensitiser directly within the emitter, using the emitter as a mechanical scaffold and avoiding the limitations imposed by a non-interacting matrix. This approach has obvious parallels to organic LEDs (OLEDs), which must provide for effective energy transport throughout the active layer.

Indeed, several groups have reported upconverters consisting of standard triplet sensitisers doped at low concentration into common OLED polyemitters (photophysically-active polymers). In 2003 Laquai and coworkers doped poly(phenylene-vinylene) (PhPPV) with PtOEP in order to observe phosphorescence from the polyemitter, the metalloporphyrin acting as an efficient triplet generator and circumventing the low ISC yield of the polymer. Sample preparation was by spin-coating. They noted that a fraction of the PtOEP phosphorescence remained unquenched by the PhPPV, and ascribed this to aggregation that became more pronounced at higher dye loadings. As an aside to the main study they observed delayed fluorescence from the PhPPV that was attributed to TTA-UC within the material. This forms perhaps the earliest report of solid-state upconversion in the current batch of studies.

Later that same year the Baluschev group reported upconversion from a spin-coated polyfluorene film doped with 3 wt\% PdOEP sensitiser. The early portion of that group’s subsequent studies into upconversion using polyemitters, and their elucidation of the mechanisms at play, have already been presented in Chapter 1 by way of an introduction to upconversion.

More recently, the Keivanidis group has investigated the role of sensitiser aggregation in polyfluorene emitter films doped with PtOEP and spin-cast at room temperature. They found that aggregation sets in at 2-3 wt\% PtOEP and that the sensitisers are implicated in lossy
quenching of emitter singlets via RET. In 2011 the group published work exploring a different upconversion mechanism whereby TTA in the sensitizer was followed by energy transfer to a polymethine which was energetically incapable of receiving the sensitizer triplet. This work differs from the majority of TTA-UC studies in that sensitizer aggregation was a sought-after effect; accordingly, a high wt% of PtOEP was used.

In 2013 Jankus et al. reported an upconverter using the conventional mechanism based on a commercially-available OLED polymer, Super Yellow (a PPV derivative), doped with 4 wt% palladium (meso-tetraphenyl-tetrabenzoporphyrin) (TPBPdP). Films were drop-cast at a raised temperature. They found that sensitizer aggregates severely degraded the upconversion performance, consuming somewhere in the range of 76 to 99% of triplet excitons prior to transfer to the emitter. We note that 4 wt% sensitizer concentration is quite high compared to the best-performing concentrations in other reports, and that the large sensitizer macrocycle looks particularly prone aggregation.

Karpicz et al. have recently reported the upconversion behaviour of neat films of DPA doped with PtOEP. Sensitizer phosphorescence was quenched more rapidly at low PtOEP concentrations, which suggested domain formation. Triplet diffusion out of the sensitizer domains was slow (on the order of tens of ns) and thermally activated, as expected for disordered trappy media. Atypically, no TTA was detected in the photoexcited sensitizers during this slow triplet migration to the emitter domain. This can likely be ascribed in part to the film morphology, but also to the low excitation power used.

Recognising that energy migration is typically much faster in crystalline rather than amorphous materials, Monguzzi and coworkers have produced crystals of DPA doped with PtOEP. The idea is that triplets injected into the DPA crystal can delocalise rapidly and find an annihilation partner with high probability. Unfortunately they found that phase-separation of the two components led to poor energy transfer between the sensitizer and emitter, crippling the efficiency. Further efforts with tailored co-crystallising species seems warranted, although Simon and Weder note the great difficulty of the task.

### Encapsulated liquids

A recent approach to the creation of solid upconverters avoids the pitfalls of mobility-impeding solids by encapsulating liquid systems in microscopic particles, creating effectively solid materials that retain the favourable properties of fluidic upconverters. The Monguzzi group embedded PtOEP and DPA in 16 nm diameter polymeric nanoparticles, which could be used to create solid films of dispersed high-efficiency upconverting units. Their report stresses the general applicability of the approach to different chromophore pairs and photonic applications.

In a similar approach Li and coworkers created water-soluble upconverting nanoparticles by loading PdOEP and DPA into silica nanoparticles. Their work addresses the potentially large role that TTA-UC can play in biological imaging, which is currently hindered by the toxicity
and poor water solubility of standard upconverting chromophore pairs. These concerns are neatly addressed by nanoparticle encapsulation. Upconversion in biological imaging is appealing because upconverted emission is fully distinguishable from the auto-fluorescence, which is Stokes shifted from the excitation wavelength. Excitation can also be delivered through the near-IR biological window while retaining the use of visible-wavelength photodetectors.\textsuperscript{157}

An important consideration regarding the application of encapsulated liquid upconverters to solar energy collection is that ultimately the systems are subject to the same limitations as bulk liquid upconverters. That is, the encapsulated dyes are still subject to the solubility limit, and efforts to increase the concentration to obtain a corresponding increase in upconversion efficiency are likely to meet with the same problems of dye aggregation and efficiency loss. So while encapsulated liquids can solve half the problem — the poor mobility in solids — they seem unlikely to provide for higher sensitisier concentrations without invoking the same lossy processes found in high sensitisier concentration bulk liquid systems.

4.3.4 Summary

From the above review of the literature, it seems apparent that film formation methods that rely on the statistical distribution of sensitisers are incapable of raising the sensitisier concentration above current levels without incurring crippling triplet losses in regions of aggregated sensitisiser. The tendency for metalloporphyrin sensitisers to aggregate seemingly overcomes the aggregation-impeding measures available to researchers, such as casting conditions and kinetic trapping — although we note a lack of reported efforts to modify sensitisier dye structures to prevent aggregation in the solid state. We have directed our efforts in this field towards producing materials where the sensitisers are chemically tethered to nanostructured solids. The idea is that aggregation is mechanically impeded by attachment to the surface, while the high surface area of the nanostructured solid allows a high density of binding sites and thus a high sensitisier concentration. In addition, upon assembly into an upconverter the emitter material is excluded from the volume of the solid, which confines photophysical activity to interstitial sites and further raises the triplet concentration.

We note a related work by Morandeira and coworkers where PdOEP and DPA were absorbed onto a mesoporous zirconium oxide surface to yield an upconverting solid.\textsuperscript{158} However, if tethering the sensitisier impedes the mobility and self-interactions as intended, the triplet diffusion necessary to sustain efficient upconversion is then entirely dependent on the emitter. Thus in our approach to solid sensitisers we attempt to maximise the mobility of emitter triplets, and do not tether the emitter along with the sensitisier.
4.4 Solid Sensitiser Preparations

In order to investigate TTA-UC with solid supports, several variations of solid-tethered sensitisers have been developed and studied as proof-of-principle experiments. The remainder of this chapter contains the design rationale and preparation of each studied system. Experimental results and analysis are then presented in Chapter 5.

4.4.1 Mesoporous zirconia scaffold

The carboxylate form of the carboxylic acid moiety binds spontaneously to TiO$_2$ (titania) in a bi-dentate configuration.$^{159}$ This is an ideal mechanism for the straight-forward binding of carboxylate-functionalised chromophores to a solid surface. The dye-sensitised solar cell (DSC) community makes widespread use of this process in preparing dye-functionalised working electrodes on mesoporous titania substrates.$^{160}$ Our requirement of a high surface loading of isolated sensitisers is actually very similar to DSCs, so we can exploit this body of knowledge. The one important difference between the two applications involves electron injection. DSCs need fast electron injection from the photoexcited dye into the conduction band of the binding surface to produce photocurrent,$^{161}$ whereas charge injection from tethered upconversion sensitisers is obviously something to be avoided. So, in adopting the coordination chemistry of DSCs for our first iteration of tethered sensitisers, we substituted TiO$_2$ (band gap 3.2 eV)$^{162}$ for the higher-band gap analogue ZrO$_2$ (band gap 5.5 eV)$^{163}$ thereby suppressing electron injection.

**Preparation**

\[
\text{TCPPdP} + \text{ZrO}_{2(s)} \xrightarrow{\text{EtOH, NaOH}} \text{ZrO}_2^{-}\cdot\text{TCPPdP}^{-}_{(s)} + H^\text{+}
\]

Work with zirconia involved the use of a green-absorbing upconversion metalloporphyrin, meso-tetra(4-carboxyphenyl) palladium porphyrin (TCPPdP), as sensitiser. TCPPdP has four possible linking groups and is commercially available (Sigma-Aldrich). Although not suited to solar cell enhancement, such green-to-blue upconverters have possible synergy with water splitting systems.

To prepare the material, a concentrated dye solution was made up in alkaline ethanol and the absorbance was measured. A known quantity of mesoporous zirconia (Sigma-Aldrich) was added to the solution, then the vessel was sealed and left for 24 hr in the dark at room temperature. The contents of the reaction vessel were then separated by centrifugation. The isolated solid was washed copiously and dried under vacuum, then sealed and stored in the dark until use. Dye loading was determined by measuring the absorbance of the combined supernatant and washes, back-calculating for the starting concentration.

We found that the high refractive index of zirconia combined with the mesoporous (i.e. highly irregular) structure made the material highly scattering. Incident light would be multiply scattered by the solid to the point where much of the intercalated dye was effectively hidden from
interaction – no light could penetrate the material enough to probe it. A vivid demonstration of this came about for one zirconia sample which had absorbed virtually all the dye in a dye bath. The bath colour had changed from a deep opaque red to colourless and transparent, but the zirconia, although occupying a much smaller volume than the bath, had changed in colour only from white to a very pale pink. The majority of the dye had thus been absorbed in optically-inaccessible sites. This has obvious problems for the intended application, so after some preliminary measurements on the dye-coated material we sought other scaffolding materials for tethering dyes.

Alumina is one such candidate, as is silica. Both materials are discussed below.

### 4.4.2 Sintered alumina substrates

In collaboration with Dr Andrew Nattestad (University of Wollongong) sintered alumina substrates for the tethering carboxylate-functionalised sensitiser dyes were prepared. Dye binding to alumina is through the same coordination mechanism as zirconia and titania. The band gap is 8.8 eV,\(^{164}\) so electron injection is unlikely to take place.*

**Preparation**

\[
Q_xPdPCOOH + Al_2O_3(s) \xrightarrow{\text{DMF}} Al_2O_3 - Q_xPdPCOO^- + H^+ \]

Porous sintered alumina substrates were prepared by Dr Nattestad. Al\(_2\)O\(_3\) paste (2 g Leeco 0.3 \(\mu\)m particles, 2 mL Alfa Aesar colloidal alumina + 1 mL ethanol) was blade-cast onto a clean glass slide, then annealed in air at 500\(^\circ\)C for 30 minutes. The resulting substrate was approximately 5 \(\mu\)m thick, and appeared largely transparent in air with a slightly translucent sheen. Alumina has a refractive index of \(~1.77\) in the visible range, so the non-scattering appearance suggested that a very smooth and homogeneous alumina layer had been formed. Observations of the films with a scanning electron microscope confirmed this (micrograph shown in Appendix F).

Dyed substrates were prepared by immersing an alumina slide in a dye bath. The dye loading obtained was found to depend most heavily on the dye bath concentration and the binding time. Achieving high enough bath concentration to enable high dye loading on the substrate was difficult; we had the most success using DMF and immersion times on the order of days. Slides were washed copiously and immersed in neat DMF post-treatment to remove any unbound dye, then dried under vacuum. Concentration in the alumina layer was determined by measuring absorbance across the layer with an untreated alumina slide as control.

The substrate approach to a solid sensitiser is appealing from an integrated device perspective, but ironically it made deaerating the devices in the lab setting much more difficult.

*More formally, electron injection from the conduction band will not occur when \(E_0 - E_{CB} \ll E_0 - E_{LUMO}\), where \(E_{CB}\), \(E_{LUMO}\) and \(E_0\) are the energies of the conduction band, the chromophore LUMO, and the vacuum, respectively.
than for powdered solids. Powdered solids can be loaded into a vacuum cuvette and, subject to some precautions, evacuated like a regular liquid sample. But the alumina substrates required the use of a vacuum chamber. Probing sensitiser phosphorescence could be carried out in the sample chamber of a cryostat, while anything with a liquid emitter required use of the half-cuvette, a custom-built vacuum cuvette with an adjustable cavity depth and the ability to mount substrates.\textsuperscript{165}

4.4.3 Peptide coupling to silanized silica

Index-matching the solid sensitiser with the surrounding material prevents scattering of the excitation light, which hindered the performance of zirconia. Silica is closely matched with toluene (1.47 vs 1.49, respectively) and is readily available in many nanostructured forms, so we elected to produce tethered dyes on silica surfaces. The carboxylic acid moiety will not coordinate with silica directly, so we elected to tether dyes to nonporous silica nanospheres using a two-step process of silanization followed by peptide coupling. Two batches of nonporous silica nanospheres were purchased: 20 nm spheres (SkySpring Nano) and 80 nm spheres (NanoAmor). In practice we observed no consistent differences between the two varieties, and the following procedures apply to both.

Silanization

The two-step procedure for preparing tethered-dye silica nanoparticles involved first silanizing the nanoparticle surface with an amine-terminated organic compound, the amine acting as the linking group in the second peptide coupling step. Silanization was by aminopropyltrimethoxysilane (APTMS) and later the ethoxy equivalent, aminopropyltriethoxysilane (APTES). The basic reaction is carried out by immersing silica in an anhydrous solution of the surfactant, which binds to the oxide surface through formation of a siloxane bond. However, Zhu and coworkers note many possible hydrogen bonds, electrostatic interactions and hydrolysis reactions that can occur in the aminosilane-oxide surface system, particularly with a primary amine present.\textsuperscript{166} By chemically and physically hindering the formation of siloxane bonds, these side-processes lead to sub-optimal surface coatings.\textsuperscript{166} Useful silanization of the surface is therefore a matter of carrying out the reaction under the right reaction conditions.

Unfortunately, the right reaction conditions may not be readily apparent from a survey of the literature. Many permutations of the basic reaction scheme can be found, with variations in aminosilane concentration, reaction time, reaction temperature, washing procedure, and annealing conditions being common. Several studies have attempted to bring some clarity to the procedure. For example, a 2006 report by Howarter and Youngblood addressed apparent confusion over the effects of concentration, temperature and reaction time on the film-forming behaviour of APTES in dry toluene. The authors identified basic film morphologies obtainable by varying the studied parameters.\textsuperscript{167}
In 2008 Chauhan and coworkers studied the mechanism by which APTMS forms multi-layers and its dependency on concentration and reaction time. In so doing, they identified a set of reaction parameters that should lead to uniform monolayer formation, based on observations of the film thickness ($2 \times 10^{-3} \text{ v/v APTMS in dry toluene, 30 min immersion, room temperature}$). We used these conditions in preparing our first batch of silanized silica nanoparticles.

The references given above are for aminosilane growth on bulk surfaces. Using dispersed nanoparticles required that we depart from the prescribed procedures. For example, it is common to aggressively pre-treat silica substrates with piranha solution prior to aminosilane functionalisation, to remove organic residues and maximise the surface density of hydroxyl groups. In one experiment I treated our commercially-sourced silica nanoparticles with an acidic piranha solution (3:1 v/v conc. H$_2$SO$_4$ and H$_2$O$_2$), followed by exhaustive washing and spinning. However, upon drying a translucent gel had formed, and it appeared that the treatment had destroyed some crucial component of the nanostructure. I therefore abandoned further attempts to aggressively pre-treat the silica nanoparticles.

Common techniques for the determination of film quality like water contact angle, ellipsometry, and atomic force microscopy were not amenable to our use of nanoparticles, and the nanoscaled surface morphology meant the results obtained on bulk surfaces were not necessarily the same as those obtained with the nanoparticles for a given set of conditions. This led to us eventually abandoning our aim of creating a neat aminosilane monolayer on the silica spheres in favour of a less surface-specific multilayer approach, as described later in this section.

In carrying out the ATPMS reaction, anhydrous toluene (dried over molecular sieves) with the specified aminosilane concentration was added to several hundred milligrams of oven-dried nanoparticles in a plastic centrifuge vial. Note that the silica nanoparticles are readily dispersed into the air and should be handled accordingly. I modified the literature procedure slightly to account for using nanoparticles: dry nitrogen gas was bubbled into the reaction vessel to agitate the particles and impede aggregation, and the post-reaction washing was carried out with centrifugation of the solid. After immersion for 60 minutes and washing with dried toluene, the particles were dried in air at 120°C for 30 minutes, then sealed in the vessel. Where possible the silanized particles were used immediately in the next reaction, or else they were stored in an airtight container.

**Peptide coupling of sensitiser dyes**

$$Q_x\text{PdPCOOH} \xrightarrow{\text{HBTU, DIPEA, DCM}} Q_x\text{PdPCOO-L},$$

where $L = \text{coupling reagent leaving group};$

$$Q_x\text{PdPCOO-L} + \text{SiO}_2-R-NH_2(s) \xrightarrow{\text{DCM}} Q_x\text{PdPCOO-NH-R-SiO}_2(s) + \text{HL}$$

The second step in dye tethering involved the covalent attachment of a suitably functionalised sensitiser dye to the primary amine-coated nanoparticles. Again, we used the carboxylic acid moiety owing to the availability of several such dyes in the porphyrin library of our coworkers.
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The straight reaction of carboxylic acid with an amine leads to the amine becoming protonated and poor yields of the amide product. A good leaving group is required to drive the reaction forward. I elected to activate the acid using a peptide coupling reagent, rather than generating the acyl chloride species. The reaction took place under standard peptide coupling conditions: the coupling reagent HBTU* and the sterically-hindered based DIPEA† were added to a concentrated DCM solution of the sensitizer dye in a molar ratio of approximately 1:1.2:4, dye to coupling reagent to base. This solution was added to a vessel containing a known mass of aminated silica nanoparticles, which was then sealed.

The reaction vessel was placed on the housing of a large continuously-operated rotary backing pump, which provided gentle heating and mechanical agitation of the silica nanoparticles. The vessels were stationed on the housing in the dark for at least 24 hours. Use of the coupling reagent meant that the reaction was likely completed much sooner than this but, given the low material throughput of the experiment, optimisation of the reaction time was not a priority.

Material preparation

After this time the entirety of the reaction vessel contents, solid and liquid, were transferred to centrifuge vials and spun, then the supernatant was collected and retained. Additional washing by DCM followed by mechanical re-dispersal and centrifugation was carried out, retaining all supernatant, until a colourless supernatant was obtained. No further colouration of the supernatant was observed after sonication of the solid (allowing the dispersed particles to re-settle), which suggested strong binding. Complete collection of the unattached dye is critical to determining the dye loading on the particles, so the washing procedure should be carried out carefully.

Supernatant from all washes was combined and evaporated, then the dried material was de-dissolved in a known volume of toluene with prolonged sonication to ensure complete dissolution. A known portion of the toluene was collected, centrifuged, and the concentration of dye in the supernatant was determined by absorbance measurements. The total amount of dye in the wash (i.e. not bound) was back-calculated from this result; the difference between this and the dye added at the start of the reaction was thus tethered on the silica. The mass and density of the treated nanoparticles was known, so a calculation of surface loading and concentration could then be carried out.

The now-coloured silica nanoparticles were dried in a desiccator, sealed, then stored in darkness. Upconverters were made by combining the dyed nanoparticles with an emitter — a concentrated solution of rubrene, for example — and grinding the mixture in an agate mortar and pestle to encourage good mixing. O₂ was removed by freeze-pump-thawing the upconverter in a vacuum cuvette, as described below.

*N,N,N\textsuperscript{\prime},N\textsuperscript{\prime}-Tetramethyl-\textalpha-(1H-benzotriazol-1-yl)uronium hexafluorophosphate
†N,N-diisopropylethylamine
Several iterations of silica-tethered sensitisers were developed as new dyes became available and the binding technique was refined. We soon wanted to increase the loading of sensitiser. The referenced reports earlier in this section, on which the silanization procedure was based, are for bulk silica surfaces. Thinking that the nanostructured silica might have sterically hindered the aminosilane binding and led to a sub-monolayer coating in the allotted time, we turned again to the silanization conditions to try to increase the density of binding sites. Multilayer formation occurs readily with increased aminosilane concentration and/or reaction time.\(^{167,168}\) So we abandoned attempts to generate a neat monolayer, and instead opted to grow a thick multilayer with the hope that this would make the growth less sensitive to the microscopic conditions of the silica surface. Dye attachment to these newer surfaces was carried out in the same manner.

### 4.4.4 Direct binding of ethoxysilane-porphyrin to silica

\[
\text{APTES}_{2/3} \text{TPPdP} + \text{SiO}_2(s) \xrightarrow{1/1 \text{v/v DCM:DMF}} \text{APTES}_{2/3} \text{TPPdP - SiO}_2(s)
\]

As discussed in the previous section, the two-step functionalisation of silica nanospheres was complicated by the uncertain configuration of the aminosilane surfacing coating. In light of this we developed a sensitiser dye that allowed single-step functionalisation, by incorporating triethoxysilane (TES) groups directly into the structure of a metalloporphyrin. Combining the dye and silica then allowed direct binding between the two. Now, rather than having to characterise the pre-treated solid surface prior to dye attachment, routine characterisation of the synthesised dye during its work-up was also characterisation of the film-forming groups, which aided understanding of the dye layer assembly.

The tetraphenyl palladium porphyrin (TPPdP) chromophore was used as the sensitiser in the test compound due to its straightforward synthesis. The synthesis of APTES TPPdP is given in Appendix G. The TES groups on the final raw product make separation and purification challenging, which possibly limits the applicability of this route. Due to these difficulties, a statistical mixture consisting predominantly of bis- and tris-propyl TES palladium TPP was generated and no further separations were carried out. Instead, this solid was dissolved in a 1:1 \(v/v\) mixture of dried DCM and DMF, and added evenly to four plastic centrifuge vials, each containing a progressively larger mass of oven-dried (110°C, 24 hr) 20 nm silica nanoparticles. The filled vessels were sealed and left to stand overnight at room temperature. Each vessel was then centrifuged, the supernatant collected, the solid washed with the same mixture of dry DCM and DMF, and re-dispersed by mechanical shaking. The centrifuge-wash-redisperse process was repeated a further seven times per sample, until colourless wash was obtained.

The wash solutions were combined to give four samples, corresponding to the remnants of dye left unbound in each reaction vessel. The absorbance of each wash solution was measured and used to back-calculate the mass of sensitiser dye left in solution and consequently, the dye absorbed onto the silica surfaces. The four wash solutions had identical absorption spectra,
with the absorption bands broadened and slightly red-shifted compared to the free monomer, indicating dimerisation of the porphyrin. Hence the majority of TES-functionalised PdTPP had become bound on the silica without saturating the binding sites, and the dye concentration on the surface scaled with the mass of silica added to the vessel. The dye-coated nanoparticles were dried in an oven at 120°C then stored in sealed vials in the dark until use. Upconverter preparation was as for the two-step functionalised silica, above.

4.4.5 Quantifying tethered dye concentration

To express the concentration of dye in the tethered solids we use the density of the nanoparticle support, supplied by the manufacturer, and the weight percent of incorporate dye, which we calculate ourselves by the method provided earlier. We can then calculate the amount of dye contained within the volume filled by nanoparticles, which we refer to as the total volume concentration and express in moles litre$^{-1}$. A truer measure of dye concentration is that given by the interstitial concentration, which accounts for volume excluded by the nanoparticle itself, but is of course much harder to accurately calculate. The nanoparticle packing determines the interstitial volume, and is sensitive to the sample preparation and history. Thus we use the total volume concentration as a rough indicator of the dye loading, mindful of the fact that on a microscopic scale there are many factors affecting the local dye density.

4.5 Sample Preparation and Laser Measurements

4.5.1 Deaeration by freeze-pump-thaw cycles

The electronic ground-state of molecular oxygen has a triplet configuration of electron spins with a $T_0$–$S_1$ energy gap of 0.97 eV. This makes it an effective quencher of triplet-excited chromophores in TTA-UC systems by the reaction $[^3O_2] + [^3M^*] \rightarrow [^1O_2] + [^1M]$, where $[^3M^*]$ represents a triplet-excited molecule. So O$_2$ must be removed from these systems to avoid exacerbating the first-order triplet decay of sensitisers and emitters alike. Equally motivating is the reactivity of singlet-excited O$_2$ towards organic compounds, which is harnessed in photodynamic therapy, but in upconversion leads only to the rapid degradation of chromophores. This reactivity typically renders TTA-UC systems inoperable within minutes of operation with exposure to ambient atmosphere.

We use the freeze-pump-thaw technique to remove atmospheric gases from liquid-containing upconverter samples. Essentially this involves removing gases from a vessel by dynamic pumping, but with the addition of a freezing step to mitigate solvent evaporation. The sample is placed within a vacuum cuvette, which consists of a 1 cm quartz cuvette, a glass bulb, and an adaptor that connects to a vacuum line, all built onto a contiguous glass vessel that is sealable with a valve or tap on the adaptor. The liquid component is poured into the glass bulb, and the cuvette is sealed. The bulb is immersed in liquid nitrogen to freeze the liquid, then the valve is opened
and the vessel evacuated through a vacuum line attached to the adaptor. The vapour pressure of the frozen liquid is negligible, so no solvent loss occurs here as long as the bulb contents remain frozen.

After \(~30\) s pumping, the valve is re-sealed and the bulb contents warmed back to room temperature. A PC case fan blowing onto the bulb can speed this step up. Gasses trapped within the frozen matrix are released back into the glass vessel upon warming. A portion of the solvent inevitably evaporates at this stage to provide a solvent atmosphere in the sealed vessel equal to the vapor pressure, but the volume is small so this is an insignificant quantity, particularly with a lower vapor pressure solvent like toluene. The freeze-pump-thaw process is repeated twice more.

One important aspect of the process is the base pressure obtained through pumping. We typically use a rotary-backed diffusion pump for the second and third repetitions, when the total gas load under pumping has been greatly reduced, and reach base pressures of \(< 8 \times 10^{-4}\) mbar. Assuming the distribution of remnant air in the solvent and the vessel is equal after three cycles, this means an \(O_2\) content of \(< 0.16\) ppm and a corresponding \(O_2\) quenching rate that makes a negligible contribution to triplet deactivation.

Upconverters using granular solid sensitisers, such as the materials used in this work, can generally be deaerated in the same way, but opening the valve to apply the vacuum should be done slowly to avoid drawing solids up into the vacuum line. If accidently dispersed up the line, the solid can easily interfere with sealing the cuvette valve, which causes sub-par deaeration and poor upconverter performance and longevity. With repeated re-evacuation of a sensitisier sample, like in a Stern-Volmer experiment, the solid tends to change from an evenly-dispersed powder into clumps with patchy coverage on the cuvette face. This can be avoided to some extent by having the solid as dry as possible before pumping.

All-solid upconverter samples can be degassed simply by pumping within a vacuum chamber to a suitable base pressure. To prepare our all-solid sample we placed the coated slide within the sample chamber of a cryostat (Oxford Instruments), which has windows allowing optical access to the sample position. The sample was dynamically pumped by a rotary-backed diffusion pump throughout measurements.

### 4.5.2 Kinetics experiments

Kinetic analysis of an upconverter provides information about the rates of energy buildup, transfer and loss in each component of the system. To collect kinetic data, time-resolved photoluminescence is recorded as the excitation source is deactivated and the excited state population decays towards zero. Pulsed lasers have excellent temporal and energy control, and are an ideal excitation source for this experiment.
CHAPTER 4. INTRODUCTION AND PREPARATIONS

Figure 4.2: Pulsed excitation kinetics experiment. High-intensity 780 nm laser pulses are generated in a regeneratively amplified Ti:Sapphire laser (a) and directed to a tuneable optical parametric amplifier (b), generating pulses that are resonant with the sensitiser Q-band. The light is focused onto the deaerated sample (c), exciting the system. A pair of lenses collimates then focuses emitted light into a monochromator (d) with an attached intensified charge-coupled device (CCD) array (e). Temporal control and camera readout takes place via the camera control unit (f), which contains a programmable timing generator. Control and readout is by PC (g).
Excitation source

The majority of kinetic experiments presented in this body of work were carried out using the 1 kHz regeneratively-amplified Ti:Sapphire laser (Clark MXR) first introduced in Section ref3Vsection. The laser has a pulse duration of 150 fs. This system pumped an optical parametric amplifier (Light Conversion) which produces laser pulses with the similar temporal properties to the pump pulse but with tunable wavelength. During maintenance of this system we used a nanosecond pulsed YAG laser (Infinity) coupled to an optical parametric oscillator (Euroscan). Both systems had sufficiently short pulses to easily resolve triplet kinetics over the timescale of interest. The second system operated at a lower repetition rate of 10-20 Hz so higher-energy pulses were used to retain practical acquisition times.

Detection

Sample luminescence in both instances was spectrally and temporally resolved by an intensified gated CCD array detector (Pi-Max) attached to a tunable spectrometer (Acton). The camera’s intensifier enabled electronic control over the detection timing, and excellent detection of weak signals. The intensifier consists of a photocathode, a microchannel plate (MCP) and a phosphor screen, which is coupled to the CCD itself by a fiber optic bundle. The CCD is Peltier-cooled to $-20^\circ$C to reduce dark current.

The photocathode turns incident photons into a spray of free electrons using the photoelectric effect. A controllable bias voltage on the photocathode directs these photoelectrons into the MCP, which produces secondary electron cascades that exit the MCP and are accelerated into the phosphor screen. The CCD reads this signal, which is significantly amplified compared to the incident signal. Since the MCP amplifies within microchannels, the amplified signal is spatially-constrained and reflects the position of the incident photon on the photocathode, so the system retains spectral resolution of the amplified signal. Temporal resolution is achieved by rapid switching of the photocathode bias, because photoelectrons will only enter the MCP when the bias is more negative than the MCP entrance.

Timing electronics in the camera controller detect a synchronisation pulse from the laser, count off a user-defined ‘gate delay’, then switch on the positive photocathode bias (‘open the gate’) for a duration specified by the ‘gate width’. During this period light striking the photocathode is intensified and a spectrum corresponding to the specified delay after excitation is collected. A two-dimensional data set with axes of emission wavelength and delay time is built up by collecting spectra with a progressively increasing gate delay, with the delay increment typically equal to the gate width. This is a tremendously flexible method of data collection and allows a user to resolve kinetic processes with lifetimes from hundreds of nanoseconds up to milliseconds in duration. Temporal resolution in the system is roughly 10 ns, limited by the switching electronics and the speed with which the photocathode changes potential.
Data processing

The 2D data from pulsed-excitation kinetics experiments is useful for identifying spectral components that behave with different time constants. In the absence of such phenomena however, we are more interested in the overall kinetics of the excited system, represented by all spectral components in the 2D data. Hence in processing this data we integrate each spectrum over the wavelength range of the emission bands of interest, and present these integrals as a function of the gate delay. These 1D ‘transients’ are thus a compact record of the kinetic behaviour of the emitting species.

4.5.3 Spot size measurement

The emissive response of an upconverter to incident light resonant with the sensitizer varies with the square of photon flux at low light levels. The reasons for and implications of this response were given in Section 4.1. Naturally this also has implications for the measurement of upconversion kinetics. In order to accurately compare the kinetics of upconverting samples they should be studied under the same fluence, in which case we can say that samples were measured under the same excitation conditions. The components affecting fluence, which has dimensions...
of photons \cdot \text{area}^{-1} \cdot \text{time}^{-1}, are the photon rate of the excitation light source, and the spot size this source makes on the sample. The photon rate of a monochromatic source can be easily determined using a calibrated power meter and a simple calculation (rate = (P \lambda)/(hc)$, where $P$ is the beam power, $\lambda$ the wavelength, and $h$ and $c$ the usual physical constants). Measuring spot size, on the other hand, is less simple.

In this work, we measured spot size using a technique developed by Dr Murad Tayebjee, and illustrated in Figure 4.3. After the completion of sample measurements, we remove the sample and in its place mount a flat scatterer, consisting of millimeter-grid graph paper attached to a rigid scattering medium, such as a business card or beam block, with a portion of the grid removed where the spot itself hits. The grid should have easily resolved markings surrounding the spot to allow good spatial resolution. The beam should fall on this scatterer exactly as it did on the emissive material of the sample, so a sensible placement of posts and references is important.

We photograph the spot on the scatterer, ensuring that the beam intensity is low enough to not saturate the camera sensor but sufficiently high to give good contrast with the background. Adjusting the room lighting to provide diffuse illumination of the photographed area can be useful in obtaining a good digital image. The image is manipulated using software prepared by Dr Tayebjee using the MATLAB compiler. First, four corners of a square are defined on the image, with the user providing the side length of the square by reading from the grid (hence the need for well-resolved grid points). The software then flattens the image contained within these points, and the user selects a smaller area to export as a 2D intensity plot with true spatial axes. Spot size is calculated by plotting the 2D data, subtracting the background, then re-plotting the spot with zero intensity set to some boundary that defines the spot edge. Determining this edge requires an assumption about the intensity profile of the spot, which thankfully the image can help inform. For a Gaussian beam profile, we re-plot the image such that the spot edge is at 86.5% of the background-subtracted peak intensity. The contained area then represents the portion $(1 - e^{-2})I_{\text{peak}}$ of the beam, where $I_{\text{peak}}$ is the peak intensity, which means the spot diameter is equal to that of the Gaussian beam. The area of the spot is calculated by fitting, with spatial dimensions taken from the plot axes.

As well as quantifying the excitation conditions, we will see later in this thesis that measuring the spot size is an important part of comparing the experimental excitation conditions with excitation by the solar spectrum.

4.6 Pulsed-excitation Kinetic Model

A substantial portion of the work undertaken in this project involved measuring and modelling triplet kinetics in mixtures of organic chromophores. Of particular relevance to our work in upconversion is the behaviour of triplet excitons at densities sufficient for the emergence of significant second-order kinetics — indeed, two-exciton collisions underpin the TTA-UC process.
In analysing results I have used the kinetic model described by Cheng and Schmidt in a 2010 paper, which was successfully applied to the modelling of liquid-phase upconverters.\textsuperscript{141} The model builds on work by Bachilo and Weisman, who determined triplet quantum yields from the measurement of delayed fluorescence arising from TTA.\textsuperscript{173} The following derivation was taken from their 2000 paper, and is presented with some additional commentary. Much like the steady-state model from the beginning of this chapter, the model here begins with a differential rate law describing a population of triplet-excited species, $[^3M^*]$, but this time with no excitation term.

$$\frac{d[^3M^*]}{dt} = -k_1[^3M^*] - k_2[^3M^*]^2.$$ \hfill (4.6)

As before, $k_1$ and $k_2$ are the rate constants for first- and second-order decay, respectively. Solving this yields the time-dependent relation

$$\frac{[^3M^*]_t}{[^3M^*]_0} = \frac{1 - \beta}{\exp(k_1 t) - \beta},$$ \hfill (4.7)

where $\beta = \alpha/(k_1 + \alpha)$ and $\alpha = k_2[^3M^*]_0$. $\beta$ is a dimensionless parameter equal to the initial fraction of decay that occurs through the second-order channel. In accordance with our understanding of TTA, we see that the second-order character of the decay can be enhanced by any combination of increasing $k_2$, increasing the triplet concentration, or decreasing $k_1$. In the absence of second-order decay $\beta$ is zero and the model reverts to a single-exponential decay, as expected of non-annihilating chromophores.

To be clear, the mixed-order kinetics model is general, and can and will be applied to the study of both sensitisier and emitter triplet kinetics, since both are susceptible to mixed-order decay. For the study of phosphorescence, we can directly model the normalised background-subtracted transients. For delayed fluorescence, the photoluminescence is due to the pool of singlet-excited emitters, which is generated by emitter TTA and thus depends on the square of the emitter triplet concentration. We therefore model the normalised, background-subtracted square root of the raw delayed fluorescence transient.

The fitting parameters in the mixed-order kinetics model are $k_1$ and $\alpha$. We have found that two-parameter fits performed ‘blindly’ (with no guiding by any approximately-known values) can reach a situation where several parameter pairs, sometimes with dramatically different values, give equally good fits to the data. Noisy or truncated data is especially prone to this. To reduce instances of undetermined parameters in our work we fit, where possible, global parameters for a given material, such that one parameter controls the fit to several transients and so becomes better constrained. Transients collected under constant excitation conditions, like in a Stern-Volmer experiment, are fitted with a global value of $\alpha$ since $k_2[^3M^*]_0$ should
remain constant. Transients collected with unchanging first-order decay conditions, like in a power response experiment, are similarly fit with a constant $k_1$.

It is convenient to define $f_1$ and $f_2$, the proportion of triplets that undergo first- and second-order decay, respectively. Again, the derivation of the following is in the 2010 paper by Cheng et al.$^{141}$

\[
\begin{align*}
    f_1 &= \frac{\beta - 1}{\beta} \ln 1 - \beta, \text{ and} \\
    f_2 &= 1 - f_1.
\end{align*}
\]

(4.8) (4.9)

These two variables are a concise measure of our requirements for a good upconverter. In an efficient system we want sensitisers with no second-order decay ($f_1$ maximised), and emitters with heavily second-order decay ($f_1$ minimised).

4.7 Solid-sensitiser Experiments

The forthcoming chapter is a direct continuation of this work. The techniques and materials just described are put to work to determine the behaviour of triplet-excited species under pulsed laser excitation.*

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*Where possible, the digital version of this thesis has hyperlinks between the reference tables to the relevant preparation and measurement sections.
## Results and Discussion

### 5.1 Introduction

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**Table 5.1**: List of experiments conducted on mixed-morphology upconverters. ‘N.R.’ denotes a null result, when insufficient signal was detected to reliably report a result. Solar cell enhancement results are reported in Chapter 5.

Table 5.1 contains a list of experiments performed using the solid sensitiser materials prepared as per the previous chapter. The experiments are listed on the basis of solid support, sensitiser, emitter, and experiment type. Results are presented throughout this chapter as a series of
vignettes, followed by a summary of measured rates and concluding remarks. Each write-up begins with a schematic of the studied system and the sensitizer absorption and emitter fluorescence spectra.

5.2 TCPPdP on ZrO$_2$

5.2.1 Stern-Volmer quenching experiment

Tetracarboxyphenyl Pd-porphyrin (TCPPdP) sensitizer in alkaline ethanol was tethered on zirconia to a total-volume concentration of 0.2 M, as per the procedure in Section 4.4.1. As discussed in Chapter 4, TCPPdP is a green absorbing sensitizer so is not of use for solar cell enhancement, but is a good candidate for water-splitting enhancement experiments. Despite the remarkably high concentration obtained in the solid, heavy scattering by the solid support meant the material appeared only lightly coloured. We carried out a Stern-Volmer experiment to measure the phosphorescence lifetime $\tau$ of the tethered dye as a function of perylene concentration in toluene. This was our first test of emitter quenching in the presence of a solid interface, the main question being: does the sensitizer remained accessible to the emitter once clustered on an interface? The Stern-Volmer formalism presented earlier in Equation 3.1 is a good framework with which to find the answer. In this first experiment we measured the sensitizer phosphorescence and the emitter delayed fluorescence kinetics as a function of the perylene emitter concentration.

The zirconia-toluene mixtures were degassed using the freeze-pump-thaw technique before each measurement. Pulsed laser excitation at 522 nm generated photoluminescence that was collected using the spectrally-resolved luminescence setup described in Chapter 4. The acquisition parameters were set such that the most intense signal was safely below the saturation threshold of the camera, then left unchanged to facilitate direct comparison of the transient intensities as a proxy for upconversion quantum yield. The first measurement was of the solid sensitizer in neat toluene, then an aliquot of perylene stock solution was added and the lifetimes of the two emission processes were measured. Two further pairs of measurements were made after adding
additional toluene to the cuvette to dilute the emitter. At the outset of the experiment the plan was to increase the perylene concentration from the first sample, but the 2D data from the first sample showed signs of excimer emission which prompted the use of lower concentrations from that point on, to give a better indication of diffusion-driven quenching.

Phosphorescence

Sensitiser phosphorescence is generated by spontaneous radiative decay from the first triplet state:

\[ ^3S^* \rightarrow ^1S + h\nu , \]

where \( \nu \) is the frequency of the emitted photon. Phosphorescence transients were background-subtracted, normalised, and fit using the mixed-order kinetics model from Section 4.6. \( \alpha \) was set as a global coordinate, since the excitation conditions were constant. The sample in neat toluene returned a lifetime \( \tau_0 \) of 392 \( \mu s \) from the fit. As a check on the model a single exponential decay was fit to the tail of the transient, where fast decay processes had presumably ceased; this gave a lifetime of 391 \( \pm 8 \mu s \), in excellent agreement with the model. We had measured the phosphorescence decay of the dry (in vacuum) dye-coated solid prior to this experiment, and the lifetime was 60 \( \pm 3 \mu s \) for similar excitation conditions to the wet measurement. Suspension
in liquid thus seemed to increase the triplet lifetime of the solid quite dramatically, possibly due to the solvent spacing out interacting dyes.

The perylene-quenched phosphorescence transients revealed lifetime shortening as a result of triplet energy transfer to the emitter. The Stern-Volmer quenching rate constant was $k_Q = (6.3 \pm 0.1) \times 10^8 \text{M}^{-1} \text{s}^{-1}$ (2σ error) at room temperature, as shown in Figure 5.1. This value is almost an order of magnitude lower than that reported by Singh-Rachford for a free solution of a porphyrin sensitiser and perylene in benzene ($4.08 \times 10^9 \text{M}^{-1} \text{s}^{-1}$); the difference is likely due to the stationary sensitiser used here, and the physical occlusion of volume by the solid zirconia substrate.

**Delayed fluorescence**

Delayed fluorescence is generated by TTA between two triplet-excited emitters, followed by spontaneous radiative decay of the singlet-excited annihilation partner:

\[
^{3}E^* + ^{3}E^* \xrightarrow{\text{TTA}} ^{1}E^* + ^{1}E \\
^{1}E^* \rightarrow ^{1}E + h \nu ,
\]
where \( \nu \) is the frequency of the delayed fluorescence. Delayed fluorescence transients collected during the Stern-Volmer experiment were baseline-subtracted, square-rooted, normalised, then fit with the mixed-kinetics model and plotted in Figure 5.2. There was a barely-detectable rise in the transients following excitation, with noise obscuring any trend in the rise time with emitter concentration. The rise time was sufficiently short to allow fitting with the kinetic model, which assumes by its formulation that emitter excitation has ceased entirely before the decay begins. In later delayed fluorescence experiments with higher emitter concentrations, the breakdown of this assumption forces us to use numerical fitting to the data.

The low emitter concentration results in comparatively poor signal to noise in the transients and a low fraction of emitter triplets annihilating via the second-order channel, as indicated in the inset of Figure 5.2. Of course, the strong scattering of pump light by the zirconia scaffold also makes a contribution to the apparently poor performance. Nonetheless the low emitter concentration offers one advantage here, in that we can obtain an accurate measure of the first-order emitter decay rate constant, since this term dominates the measured decay. A global optimisation of \( k_1^e \) across the four delayed fluorescence transients gives 56700 s\(^{-1}\). Measurements of the perylene triplet \( k_1 \) in isotropic liquid upconverters made by Dr Cheng have \( k_1 \approx 1700 \) s\(^{-1}\), so the rate constant measured here is substantially greater than anticipated. There are several possible explanations for this: the high sensitiser concentration means back-transfer of the emitter triplet to the sensitiser is more entropically favoured, along with RET from the emitter singlet state, despite the small overlap integral. The solid material itself may also cause quenching of the emitter through surface states.

### 5.2.2 Power-dependence of kinetics

Second-order decay processes can be identified in kinetic studies by a non-linear dependence on the pulse energy in the unsaturated regime. To better understand the decay processes at work in the TCPPdP-zirconia plus perylene system we measured the power-dependence of the phosphorescence and upconverted fluorescence kinetics of the final sample from the Stern-Volmer experiment (5.2.1, \([\text{Perylene}] = 0.15 \text{ mM}\)). The pulse energy of the 522 nm laser was varied by neutral density filters, from 0.05-2.3 \( \mu \text{J} \), and the two sets of kinetics were collected at each pulse energy by driving the spectrograph grating between wavelength positions. The optical setup was otherwise unchanged between measurements. In addition to measuring the kinetics themselves, the total photoluminescence intensity at each pulse energy was found by integrating over the unnormalised background-subtracted transients.

**Phosphorescence**

Phosphorescence transients were very similar (once normalised) across the measured range of pulse energies, as shown in Figure 5.3. The relative stability of \( \beta \) with power indicates that the rapid component of the transient decay is unchanging, which suggests that second-order decay
Figure 5.3: Phosphorescence (top) and delayed fluorescence (bottom) transients of the ZrO$_2$-tethered TCPPdP plus 0.15 mM perylene system. Transients have been normalised and offset by 10 µs to help viewing. The insets show $\beta$ values for both populations, and the integrated yield of the unnormalised transients. The yields of both components roll off to a sub-linear response with increasing pulse energy; the dashed lines indicate the approximate expected intensity progression *sans* this effect. The $\beta$ values appear to be randomly distributed within a narrow range, and do not exhibit a discernable trend.
in the sensitiser is not the dominant decay pathway at the studied excitation and quenching conditions. The near-unity $f_1$ value for modest perylene concentrations found earlier supports this finding. The total phosphorescence intensity increases sub-linearly with pulse energy, as seen in the inset of Figure 5.3. This could indicate either the onset of saturation in the bright sensitiser regions (those that emit appreciably at low pulse energies), or, that the emitter quenching improves with increasing pulse energy. The second explanation would be implausible in a liquid system with a homogeneous dye distribution, but is conceivable in a tethered solid. For instance, one could imagine a material where the most strongly absorbing sites were J-aggregates, where emitter access was impaired by the bulk of the aggregated dyes. With increasing pulse energy there could come progressive excitation of less-aggregated sensitisers that are more easily quenched, thus explaining the sub-linear phosphorescence intensity with pulse energy. The delayed fluorescence results are required to distinguish between these two explanations.

\textbf{Delayed fluorescence}

Delayed fluorescence transients and the corresponding $\beta$ and intensity values collected at each pulse energy are shown in the second panel of Figure 5.3. A global fit of $k^e_1$ gives 60000 s$^{-1}$, which agrees well with, and reinforces, the result obtained earlier in the Stern-Volmer experiment (5.2.1). Unlike in that experiment, however, the delayed fluorescence $\beta$ does not trend in any expected way. In 5.2.1 we saw that adding perylene increased the proportion of emitter triplet decay via the second-order channel, which makes sense in an ideal system. But, in the current experiment, $\beta$ varies seemingly at random with pulse energy, much like for the phosphorescence. According to the accepted mechanism of TTA-UC, increasing a low emitter concentration and increasing a low pulse energy should both increase the second-order decay fraction of the emitter. The fact that in this system the former process does but the latter does not points to the sensitiser material as the culprit, since adding emitter at a constant pulse energy does not alter the efficiency with which the sensitiser produces quenchable triplets, only the rate at which those triplets are quenched. We therefore focus the explanation of these observations on the zirconia-bound sensitiser.

The two explanations advanced above for the sub-linear growth in phosphorescence intensity were the saturation of bright centers or improved emitter quenching. We can discount the latter because the total delayed fluorescence intensity also appears saturated, and the transients do not show an improving $\beta$ as we would expect from a greater concentration of emitter triplets enabled by improved quenching. A final piece of evidence for bright sensitiser saturation is that the delayed fluorescence intensity grows as roughly the square root of the phosphorescence. The question, then, is what causes this saturation? We propose that some component of the apparent saturation is due to the highly scattering zirconia substrate — since excitation pulses cannot penetrate far into the material, there is a limited supply of sensitiser on the excited edge of the material that may become optically excited with each pulse. At higher pulse energies, that layer
may become saturated. But the arrangement of sensitisers on the solid material is also likely to play a role in the sub-linear response, especially given the high concentration. Apportioning the result to one or the other is not possible on the basis of this data.

5.2.3 Conclusion

The zirconia-tethered sensitiser seemingly has a long-lived triplet state that is well-quenched by perylene. But the actual intensity data shows that the availability of quenchable triplets from the sensitiser is severely constrained, at least in detectable portions of the material, since the supply saturates even at the low pulse energies used in this experiment. The majority of absorbing sites seem to remove energy from the system without ever reaching a long-lived state, and thus do not register in our photoluminescence experiments. Heavy aggregation is the likely candidate, although the heavy scattering probably plays some role too.

In light of this we turned to alumina- and silica-tethered sensitisers, and using more controllable binding chemistry through single moieties. The alumina substrates were low-scattering due to the smooth deposited layers. But the required apparatus for mounting and deaerating the substrates along with a liquid emitter restricted the range of experiments we were able to perform, and thus the only alumina substrate result reported here is for solar cell enhancement, discussed in Chapter 6.

On the other hand, silica can be fairly well index-matched with toluene, which prevents the heavy scattering problem, the two-step peptide coupling reaction described in Chapter 4 offers potentially greater control over the conformation of binding dyes, and the granular nanoparticles were compatible with our vacuum cuvettes. Hence silica-tethered sensitisers soon became the focus of the solid sensitiser studies.

5.3 Q$_3$PdP on SiO$_2$

Trisquinoxalino PdP carboxylic acid (Q$_3$PdPCOOH) was made available by our synthetic collaborators during our work with TCPPdP on zirconia. Q$_3$PdPCOOH is a redder-absorbing
dye than TCPPdP and a stepping-stone towards the synthesis of tetrakisquinoxalino PdP carboxylic acid \((Q_4\text{PdPCOOH})\), which was the target compound for studying solar cell enhancement with tethered sensitisers. Hence we began the study of silica-tethered dyes using the available intermediate compound.

\(Q_3\text{PdP}\) was bound to 20 nm silica nanospheres using the two-step functionalisation process from Section 4.4.3, giving a total-volume concentration of 1.5 mM. After leaving the reaction for 24 hr approximately 10% of the dye remained unbound to the silica, which indicated that the binding sites had most likely been fully occupied despite the loading being well under our estimates for the achievable surface binding density. An absorption spectrum of the unattached dyes retained the features expected of isolated molecules, so dye-dye association (e.g. dimerisation) can be ruled out as an explanation for the incomplete binding. The low binding density motivated us to try to increase the density of aminosilane groups on the silica, and later, to incorporate the linking group into the sensitiser itself, leading to the one-step functionalisation process. The results described in this section were all obtained with the 1.5 mM material.

### 5.3.1 Stern-Volmer quenching

The time-resolved phosphorescence decay of the deaerated porphyrin-coated silica was recorded for a range of rubrene emitter concentrations using the gated spectrograph setup. The coated nanospheres were suspended in toluene then added to a vacuum cuvette, and deoxygenated by three freeze-pump-thaw cycles. Phosphorescence transients were recorded after exciting the sensitisers in the \(Q\)-band. A Stern-Volmer quenching experiment was carried out by adding known quantities of a rubrene stock-solution and re-degassing the cuvette. The new concentration of rubrene was inferred from the volume of solvent in the cuvette after sealing the tap, which accounted for any solvent evaporation during degassing. Five rubrene concentrations were measured, from zero up to 5.7 mM.

**Phosphorescence**

Phosphorescence decay transients were fit using the mixed-order kinetics model from Section 4.6. The \(\alpha\) value was obtained from a fit to the decay transient in neat toluene and retained throughout. The remainder of the transients were then well-fit using \(k_1^s\). The phosphorescence transients and their fits are shown in the top panel of Figure 5.4, and the bottom panel shows the lifetime shortening ratio and \(f_1\) values of the sensitiser decay. The sensitiser triplet lifetime, \(\tau_0\), was 81.3 \(\mu\)s in neat toluene. The data series \(\tau_0/\tau\) was fit with a linear model constrained to a \(y\)-intercept of 1. Using the Stern-Volmer relation we obtained \(k_Q = (2.18 \pm 0.03) \times 10^8 \text{M}^{-1} \text{s}^{-1}\) (2\(\sigma\) error). An analogous experiment by Dr Cheng on the quenching of untethered \(Q_4\text{PdP}\) by rubrene in toluene found \(k_Q\) of 3.1 \(\times 10^8\) M\(^{-1}\) s\(^{-1}\).\(^{141}\) The slightly reduced quenching rate found here with the tethered species is in contrast to the greatly reduced rate constant found for perylene in the zirconia solid. We suppose that the microscopic structure of the solid material
Figure 5.4: A. Phosphorescence transients of silica-tethered Q$_3$PdP recorded for a range of emitter concentrations with constant excitation conditions. Fitting is with the kinetic model from Section 4.6 using a constant $\alpha$; the unquenched phosphorescence lifetime is 81.5 $\mu$s. The different start times are a result of the different time increments used for each transient. B. Lifetime shortening and the proportion of decay via the first-order channel for the same data series. As the emitter concentration grows a greater fraction of triplet decay becomes first-order, reflecting the increasing emitter quenching rate. The inset shows the sensitizer phosphorescence spectrum.
Turning to the $f_1$ values in Figure 5.4, at low concentrations the sensitisier material is strongly affected by what the kinetic model conveys as second-order kinetics, which would suggest undesirable two-exciton annihilation taking place within the excited sensitisier. Lacking any exotic ordering of the energy levels, sensitisier TTA results in the loss of one triplet exciton as the $S_n$ excited sensitisier decays rapidly back to $S_1$ and re-crosses to the triplet manifold. I couch this explanation carefully because while the function representing the kinetic model fits the data, the meaning assigned to the parameters may yet be misdirected. We expand on this line of thought at the conclusion of this chapter. Nonetheless, it is clear that $f_1$ asymptotically approaches unity as the rubrene concentration increases, and the apparently second-order decay component becomes small. Adding emitter to the system introduces a new first-order decay channel for the sensitisier, which in a useful upconverter should become the dominant decay channel at a practical emitter concentration. In other words, triplets should migrate to the emitter before they can be lost within the sensitisier, whatever the loss mechanism. In both this system and the zirconia-tethered TCPPdP previously described, this appears to be possible for at least some portion of the material, which is a promising result for solid-tethered sensitisers.

**Delayed fluorescence**

Delayed fluorescence kinetics were measured for each non-zero emitter concentration during the Stern-Volmer experiment by driving the spectrograph grating to the peak of the emitter fluorescence. All other optical components, and the excitation conditions, were unchanged between the two sets of measurements. The integrated delayed fluorescence transients are shown in Figure 5.5.

The transients have a clear rise-time, which indicates a slow build-up of triplet-excited emitters. The rise-time decreases for higher emitter concentrations in accordance with the Stern-Volmer behaviour documented in Section 5.3.1. The non-zero rise time complicates fitting of the usual kinetic model, which assumes instantaneous excitation of the emitting material. One option to deal with this is to fit the model starting later in the transient, when transfer from the sensitisier is effectively complete. But this sacrifices data points and risks missing the faster second-order decay component, particularly at low emitter concentrations where transfer is slow. Instead, we fit these transients numerically by tracking the generation and decay of sensitisier and emitter triplets over time based on the kinetic rates, which were the fitting parameters. At time zero ($t_0$), the populations of triplet-excited sensitisier, $[^3S^*]$, and emitter, $[^3E^*]$, were 1 and 0, respectively. The concentrations evolved in the following way: for each time increment $t_i \rightarrow t_{i+1}$,
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[Rubrene] (mM)
0.16
0.34
3.28
5.71
normalised (intensity)
0.5
time (μs)
1 10 100
10
100
1000

Figure 5.5: Delayed fluorescence transients of silica-tethered Q$_3$PdP for four rubrene concentrations. Fits were by a numerical model of triplet transfer and mixed-kinetics decay, which could better account for the non-instantaneous triplet build-up particularly at lower rubrene concentrations. Arrows indicate the temporal intensity peak for each concentration. We suspect that sample 2 (upright triangles) was contaminated by oxygen due to the trend-defying short lifetime; this transient was fitted independently of the others.

$$\left\langle \text{Rubrene}\right\rangle_{i+1} = \left\langle \text{Rubrene}\right\rangle_i (1 - k^{s}_{1} \Delta t) \quad \text{and}$$

$$\left\langle \text{E}^{*}\right\rangle_{i+1} = \left\langle \text{E}^{*}\right\rangle_i + \Delta \left\langle \text{Rubrene}\right\rangle - (\left\langle \text{E}^{*}\right\rangle_i k^{e}_{1} + \left\langle \text{E}^{*}\right\rangle_i^2 k^{e}_{2}) \Delta t, \quad \text{(5.2)}$$

where $\Delta t = t_{i+1} - t_{i}$, $\Delta \left\langle \text{Rubrene}\right\rangle = \left\langle \text{Rubrene}\right\rangle_i - \left\langle \text{Rubrene}\right\rangle_{i+1}$, and $k^{m}_x$ is the $x$th-order triplet decay rate of species $m$ ($e = \text{emitter}, s = \text{sensitiser}$). The modelled quantity is the emitter triplet concentration, scaled as necessary, so we take the square root of the delayed fluorescence transient prior to fitting. We fit $k^{e}_1$ globally, since the decay should be independent of emitter concentration, and use $k^{s}_1$ from the Stern-Volmer results. The remaining free parameters are then the effective TTA rate ($k^{e}_2$) and a scale factor, which accounts for the data accumulation period and optical collection efficiency. We obtained good fits to the data using a global value of $k^{e}_1$ with the exception of one intermediate concentration (0.34 mM rubrene). We suspect this sample was contaminated by oxygen, since the first-order decay rate was much greater than anticipated, and we discounted it in the global fitting of $k^{e}_1$. The fitted transients are shown in Figure 5.5.

From this data we obtained $k^{e}_1$ of 15600 s$^{-1}$. This is approximately double the rate recorded for rubrene in a very similar upconverter using a solubilised sensitiser (i.e. with no solid interface present). Recall the likewise-accelerated first-order decay of the perylene triplet in the
zirconia experiments, where the decay rate was increased by roughly 33 times. This finding is evidence that accelerated emitter triplet decay might be a general symptom of using solid-tethered sensitisers, with the difference in rate enhancement between the two experiments possibly due to some combination of dye loading, emitter species and solid material. Unfortunately any shortening of the emitter triplet lifetime hampers the upconversion efficiency and raises the threshold fluence required to obtain a linear response, so is in direct opposition to our efforts. We do not have enough data at this point to say whether this is a general side-effect of using tethered sensitisers, or something unique to our choice of dyes or scaffold materials. Further experiments are needed.

### 5.3.2 Delayed fluorescence power response

The power response of an upconverter is characteristic of the bimolecular nature of the process. Recall that the aim of increasing the sensitiser concentration was to increase the excitation metric, such that the photon fluence required to transition from an inefficient quadratic response to an efficient linear response could be reduced.

We studied the delayed fluorescence power response of the final sample from the Stern-Volmer experiment, above (Q₃PdP on silica, [rubrene] = 5.7 mM). Without changing the optical setup, we altered the pulse energy using a continuously-variable neutral density filter wheel (Thorlabs NDC-50C-2M) and recorded 100 single-gate acquisitions of the entire delayed fluorescence decay for each energy. Beam power was measured using a calibrated photodiode. This style of data

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**Figure 5.6:** Upconversion power response of silica-tethered Q₃PdP with 5.7 mM rubrene in toluene under pulsed 650 nm excitation.
acquisition does not allow kinetic analysis of the decay but is a rapid way of obtaining the power response.

Data processing consisted of integrating the collected spectra over the rubrene emission band (keeping well away from pump beam scatter), subtracting the dark background, and plotting the logarithm of the integrated fluorescence intensity against that of pulse energy per cm$^2$. The result is shown in Figure 5.6. Fitting a linear model to the data yields a slope of $1.30 \pm 0.05$, contrary to expectations of a slope of 2 trending to 1. In carrying out other power-response experiments we found that the response slope is very sensitive to pump light leaking into the detector, which could certainly explain this in-between response slope as the sum of a quadratic upconversion response and a linear scatter component. But before performing this experiment we had already found that optical filters could not always provide sufficiently high absorbance to fully block the pump source from detection. Hence our use of the spectrograph here, which disperses the incident signal according to wavelength and duly makes simple the identification of spurious pump light in the signal. We are therefore confident that stray pump light is not responsible for the observed slope.

Instead, we propose that the intermediate slope is due to sample heterogeneity. The phosphorescence transients collected during the Stern-Volmer experiment indicate that the sensitizers undergo triplet decay with a range of first-order decay rates. It is reasonable to suspect that these heterogeneous sites therefore also experience different emitter quenching rates, and have various surface loadings. Some portions of the material could therefore generate efficient linear-response upconversion at low pulse energies, while others will upconvert poorly, giving rise to an intermediate response trend. Consider three possible types of sites, arranged from lowest to highest sensitiser loading:

- **Isolated sites**: Those with a sparse arrangement of isolated tethered sensitizers behaving much like a low-concentration solution system. The response trend is quadratic to linear ($2 \to 1$).

- **Bright sites**: Those with a good loading of yet-isolated sensitizers, optimally configured to produce bright upconversion at low pump energies. The response is linear from the outset. If such sites are relatively scarce this response would quickly saturate, resulting in a response that dips from linear to sub-linear with pulse energy ($1 \to <1$). Such sites could explain the power response of the zirconia-tethered system, where the upconversion response did saturate.

- **Aggregate sites**: Regions of heavy sensitiser loading with significant aggregate effects. Photon absorption is by aggregate ensembles and sensitiser triplets are lost to trap sites inaccessible to the emitter (no UC response).

The excitation beam samples all absorbing environments, so the detected response and its trend with energy is a combination of these various environments. We do not have enough
data to be able to prove this model, but we propose it as a heuristic for understanding how a seemingly constant intermediate slope could be obtained across a wide range of pulse energies. Presumably at a sufficiently high energy the various sites would all produce a linear response, but we cannot estimate at what energy this might happen.

5.3.3 Checking for lossy back-transfer

Although phosphorescence quenching was found to be functioning as expected, the upconversion performance of the silica-tethered Q$_3$PdP sensitiser plus rubrene system was unimpressive. One of the possible reasons had already been identified as the increased emitter $k_e$. In this experiment, we looked to back-transfer from the bright emitter singlet state as another possible explanation.

One of the loss mechanisms identified in solid-phase upconverters is energy transfer from the singlet-excited emitter back to the sensitiser, typically by resonance energy transfer but also possible through uncorrelated photon emission and reabsorption.\(^\text{151}\) Although the photon energy can be partially recycled by proceeding back through sensitiser intersystem crossing, triplet energy transfer and TTA, there are considerable quantum yield and energy losses involved. Heavily concentrated condensed phase systems, where the chromophores are fixed in close proximity, seem especially likely to suffer back-transfer losses. The likelihood of emitter-sensitiser singlet back-transfer can be inferred from the absorption and emission spectra of the system, as per the RET mechanism described in Chapter 1; greater overlap of the emitter fluorescence spectrum with the sensitiser absorption means a higher likelihood of back-transfer loss through RET. This serves as one of the motivations for the widespread use of metalloporphyrin sensitisers, which typically possess a largely transparent absorption window between the Q-band and Soret band (the strong short-wavelength absorption feature) into which emitter singlet states may fluoresce unimpeded by sensitiser quenching.

One of the common effects of changing the microenvironment of a chromophores is shifting or distorting the absorption bands due to the changing steric and electronic interactions. We wanted to see if the absorption window of the Q$_3$PdP sensitiser had been shifted by tethering, causing it to interfere with rubrene fluorescence. A direct measurement of the dye absorbance would be the simplest indicator, but the solid material made this a difficult task. Transmission measurements were impossible, even in very thin cuvettes, due to the high dye concentration and the scattering arising from the imperfect index-matching between the silica and toluene. I had begun work on a process for measuring the scattering spectrum of solids using an integrating sphere, but it was not yet completed. So we opted instead to perform a direct measurement of the emitter singlet lifetime in unobstructed solution, and in the vicinity of the solid sensitiser. Any lossy back-transfer from the emitter singlet should then manifest as a shortening of the emission lifetime.

We prepared a sample of silica-tethered Q$_3$PdP in a 7.3 mM solution of rubrene in toluene un-
Figure 5.7: Fluorescence lifetime of a 7.3 mM rubrene solution measured in clear toluene and in compacted solid sensitiser banked against the cuvette face. The residual is plotted below. Allowing for timing jitter, there is no clear difference between the transients. This suggests that deactivation of the emitter singlet by quenching to the sensitiser is an insignificant source of efficiency loss.
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In a time-correlated single photon counting setup using the Ti:Sapphire laser and OPA as a 490 nm pulsed excitation source, we measured the fluorescence lifetime of the emitter in the clear solution, and in solution containing silica-bound sensitiser banked up against the illuminated cuvette face. The cuvette was translated vertically to select the excitation area, and no other changes to the excitation conditions were made between measurements. Fluorescence detection was by a double monochromator and photomultiplier tube.

The fluorescence signal was more intense by about an order of magnitude in the clear solution, so we adjusted the pump beam energy as necessary to keep the acquisition rate within the single photon counting regime. Despite the intensity difference, the two fluorescence decay transients both returned lifetimes of approximately 11 ns when fit with a single exponential decay. The residual of the normalised pair yields no systematic differences, as shown in Figure 5.7. So the solid sensitiser did not seem to induce lifetime shortening of the rubrene singlet, and the absorption window is presumably intact in the silica-bound species. The intensity difference between the clear and solid regions of the solution is likely due to the shorter path length of the excitation source into the solid, and the correspondingly smaller number of excited rubrene molecules.

A competing hypothesis – bimodal emitter quenching – cannot be completely ruled out by this measurement. In this hypothesis, rubrene near the silica particles is quenched effectively instantaneously, while more distant rubrene radiates with an unaffected rate. Our understanding of the RET process, however, makes this implausible, since lifetime shortening due to back-transfer should vary continuously with rubrene proximity to the solid, and this should manifest in a detectable lifetime shortening. Other possible interactions based on electron exchange or charge transfer are short-ranged enough that most of the photoexcited rubrenes should be unaffected by such processes, and as such would cause only a small change in fluorescence intensity. It is thus with some confidence that we ascribe the loss of intensity to the changed optical arrangement of the sample, rather than a bimodal quenching process.

5.3.4 Conclusion

Compared to the zirconia-tethered dye system, we have a better understanding of the morphology of this material. The silica scaffold itself is much better quantified by the manufacturer, and we have confirmed the manufacturer’s claims regarding particle size and shape as best we can using electron microscopy (as shown in the following section). Heavy scattering is no longer an issue with index-matching by toluene so it can be discounted as an explanation of any unexpected behaviours. We are also more confident in there being at least some non-aggregated

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*Positioning the bulky vacuum cuvette inside the TCSPC setup was impractical, so this measurement was made with an oxygen-containing sample. But there is no clear mechanism by which oxygen would interfere directly with the back-transfer of energy from singlet-excited emitter to the sensitiser. Of course, sensitiser excitation would lead to intersystem crossing, then triplet oxygen generation, but meanwhile the back-transfer would manifest as emitter lifetime shortening near the solid material. So we expect that the presence of oxygen in this measurement had no bearing on the result.
bound dyes because of the use of a single binding moiety per molecule and the dyes being bound at a much lower concentration.

The Stern-Volmer experiment with rubrene mimics the results of the zirconia system and appears to show that near-unit efficiency emitter quenching is achievable, since the phosphorescence lifetime decreases significantly with emitter concentration, as expected. But in zirconia, the power response study showed that something in that finding was misleading, because although we appeared to be quenching almost all sensitizer triplets the upconversion generated by the system falls away sub-linearly, which suggests that most absorbing sites do not participate in energy transfer to the emitter. In studying the power response of the silica-tethered $Q_3$PdP we found a quite different result: a slope of 1.30, seemingly constant with pulse energy. The good news from this is that the net upconversion response is not saturated, at least at the pulse energies studied. But as we suggested in that section, the intermediate slope is probably the sum of the responses of different sites throughout a heterogeneous sensitizer medium.

This site-averaging means we cannot extract much useful information from the response experiment. To wit, the response could be due largely to linearly-responding sites, in which case we would have almost achieved our objective of a low-fluence linear upconversion response. Or, the response could be due to rapidly-saturating bright sites with a strengthening contribution from aggregates, in which case the material is a poor upconverter and a long way from our goal. In other words there are many site combinations from which an intermediate slope could be composed. Clearly a quantifiable measure of the actual light output is required to fully interpret the findings here. This forms the subject of Chapter 6.

### 5.4 $Q_4$PdP on SiO$_2$

A short way into our study of silica-tethered $Q_3$PdPCOOH, our collaborators completed the synthesis of the tetrakis equivalent, $Q_4$PdPCOOH. We set about preparing dye-coated silica nanospheres using the same method as the last set of particles, again achieving a total-volume concentration of about 1.5 mM. Rather than repeating the previous measurements of triplet...
kinetics in toluene for this material we first used it in a solar cell enhancement experiment, which is described in the following chapter. This section of the current chapter instead describes a standalone experiment where we measured the triplet kinetics of the silica-tethered sensitiser combined with rubrene in a dried solid sample.

5.4.1 Triplet kinetics in a solvent-free configuration

As discussed in Chapter 4, one of the approaches to retaining triplet mobility in a solid upconverter is to have triplets diffuse in a crystalline solid emitter. Monguzzi and coworkers found that this approach was hindered by the tendency of the two chromophore species to phase separate during crystallisation. Our motivation for tethering sensitiser dyes to nanostructured solids is primarily to impede sensitiser crystallisation, which is one component of the phase separation behaviour that hindered the Monguzzi group’s approach. Thus we were interested to see what kind of upconverter was formed from a dried mixture of silica-tethered sensitiser and solubilised emitter, and if performance-killing phase separation was impeded in any way. To be clear, the presence of the silica host means the two dyes are unlikely to co-crystallize, but perhaps it is sufficient to have the emitter crystallised and the sensitiser molecules isolated.

In darkness, 34 mg of dry rubrene, 15 mg of the Q4PdP-coated silica and 10 drops of toluene were combined in an agate mortar and pestle and ground until the liquid was homogeneous in appearance. This liquid was drop-cast onto an indium tin oxide (ITO)-coated glass tile at room temperature using a glass pipette, and left to evaporate. We used the ITO substrate to increase conductivity across the sample, so we could obtain scanning electron microscope (SEM) micrographs without excessive substrate charging. Micrographs of the coated tile surface were recorded using a Zeiss Ultra SEM with an N2 charge compensator, which blows a gentle stream of N2 gas across the probed region to remove surface charge from low-conductivity samples. Triplet kinetics were studied using the pulsed-excitation kinetics setup, with the sample mounted in a cryostat chamber under dynamic vacuum at 8 \times 10^{-4} \text{ mbar}. The sample was excited at 670 nm, resonant with the sensitiser Q-band peak.

The micrographs are shown in Figure 5.8. The morphology is clearly heterogeneous on all length scales studied. The solid consists of clumps of nanoparticles dispersed among and on top of larger rubrene crystals.

Phosphorescence

To judge the quenching effects of solid rubrene, a control sample consisting of only the dried dye-coated silica was prepared in a vacuum cuvette and studied under the same excitation conditions at three pump energies. Transients were well-fit by the mixed-kinetics model; a global optimisation of \( k_s^1 \) gave a sensitiser triplet lifetime of 150 \( \mu \text{s} \). The transients appear very similar by eye, but for a small but noticeable increase in the steepness of the initial decay with pulse energy. Unlike the zirconia-tethered sensitiser, here the fitting reveals a trend of an
Figure 5.8: SEM micrographs of dried silica-tethered Q₄PdPCOOH with rubrene prepared by drop-casting from toluene at room temperature. Scale bars are drawn for each micrograph, and the red boxes indicate the magnification change between micrographs. Blurring is due to charge accumulation on the low-conductivity materials.
Figure 5.9: Normalised phosphorescence transients of dried evacuated Q₄PdPCOOH on silica nanospheres for three pulse energies. The transients are offset by 100 μs to aid viewing. The upper and lower insets show β for each transient, and the phosphorescence spectrum in vacuo, respectively. The triplet lifetime of the dried material is 150 μs.
increasing $\beta$ value with pump energy, indicating greater participation in apparent second-order decay at higher excitation energies. The transients, fits and $\beta$ values are shown in Figure 5.9. Out of interest, an identical measurement but with the solid material suspended in toluene gave a triplet lifetime of 45 $\mu$s, which is the opposite trend to that observed in zirconia, where immersion in toluene led to a sizeable improvement in sensitiser triplet lifetime. This may relate to the very different concentrations and surface binding functionality of the two.

Turning our attention back to the sample containing silica-tethered dye and dried rubrene, we first examine the phosphorescence decay under the same excitation conditions as the sensitiser-only control to gauge the effect of solid rubrene. The integrated transient shows strongly bimodal behaviour, consisting of a very rapid drop in intensity followed by a lingering tail. As such, it is poorly fit by the kinetic model. A double exponential decay with lifetimes 1 and 11 $\mu$s fits well, but an explanation of the mechanisms responsible for the two lifetimes is not necessarily apparent from such a model.

Instead, the transient can be recomposed quite well by a weighted sum of two mixed-order kinetics transients:

$$f(t) = \frac{1}{A + B} \left[ A \left( \frac{1 - \beta^q}{\exp(k_1^q t) - \beta^q} \right) + B \left( \frac{1 - \beta^{uq}}{\exp(k_1^{uq} t) - \beta^{uq}} \right) \right],$$

(5.3)

where $\beta^q = \frac{\alpha}{k_1^q + \alpha}$, $\beta^{uq} = \frac{\alpha}{k_1^{uq} + \alpha}$, and $A$ and $B$ are scale factors. The $\alpha$ value is fixed to that of the phosphorescence decay of the pure-sensitiser sample (200 nJ transient in Figure 5.9), and $k_1$ and the relative amplitudes are the fitting parameters. The ‘$q$’ and ‘$uq$’ superscripts denote the quenched and unquenched portions of the material, respectively.

Equation 5.3 was fit to the solid rubrene-quenched phosphorescence transient using least-squares analysis. For the slower-decaying notionally unquenched region, the model returns $k_1^{uq} = 43000 \text{ s}^{-1}$, or about six times the rate constant of the neat sensitiser material, and a $\beta^{uq}$ value of 0.63. This represents portions of the material that are poorly quenched by the rubrene solid and behave mostly like the free solid sensitiser. The second, faster, component has $k_1^q = 937000 \text{ s}^{-1}$ and $\beta = 0.07$, and twice the relative amplitude of the slower component. This second transient represents a second, faster-decaying component of the sensitiser phosphorescence, presumably related to efficient quenching by the solid rubrene. The transient and fit of Equation 5.3 are shown in Figure 5.10.

As in the Stern-Volmer experiments reported earlier, a drop in $\beta$ corresponds to an increasing fraction of sensitiser triplet decay via first-order processes, in this case due to fast emitter quenching. In all, this commingled fit points to a highly heterogeneous system, which is unsurprising given the micrographs in Figure 5.8. On the other hand, it is surprising that the fits suggest a good portion of the photoexcited sensitisers are effectively quenched by solid rubrene.
In practice, of course, there are likely to be many site variations in quenching and intrinsic decay rates, but expanding the fit to incorporate this presumption saps the fit of explanatory power.

**Delayed fluorescence**

A study of the delayed fluorescence kinetics further supports the notion of a heterogeneous sample. Upconversion transients measured at three excitation energies are all strongly second-order and appear indistinguishable. Unlike the liquid emitter system from Section 5.3, there is no detectable rise-time in the delayed fluorescence signal, which points to triplet transport via non-Brownian diffusion. Fitting $\sqrt{[^3E^*](t)/[^3E^*](0)}$ with the mixed kinetics model using a global $k_1^*$ value gives $\alpha$ and $\beta$ values that do not trend detectably with excitation energy. The strongly second-order decay means $k_1^*$ is only weakly determined, as it has little effect on the decay fit over the measured time. Rather, the second-order decay rate in alpha (recall that $\alpha = k_2[^3M^*]$) is the dominant term in the fit. Ryasnyanskiy and coworkers report a 100 $\mu$s triplet lifetime in rubrene crystals ($k_1^* = 10000$ s$^{-1}$);\textsuperscript{175} using this value as a global parameter yields $\beta$ of 0.99 for the three transients. A representative transient recorded at 200 nJ/pulse is plotted in Figure 5.10 alongside the quenched phosphorescence decay.

The strongly second-order transients, and the invariance of their decay parameters with power, point to saturation of the upconverting portions of the solid material. Given the morphology, it seems likely that only a small fraction of excited sensitisers are in close enough
proximity to rubrene crystals to undergo immediate energy transfer to the emitter. The mobility of sensitiser triplets is a key factor in how big of an impact this has on the upconversion efficiency. The surprisingly large fraction of phosphorescence that is rendered short-lived by the addition of rubrene crystals suggests that there is some degree of excited state mobility in the sensitiser material; temperature-dependent studies of the phosphorescence quenching would be a good verification of this behaviour. But the apparently saturated upconversion response implies that energy from many of the quenched sensitisers ends up in ‘dark’ sites which do not generate upconversion, perhaps due to accelerated first-order triplet decay in small or defect-ridden crystals. Optically-gated photoluminescence or transient absorption measurements are most likely required to further test this idea. Another proposal, discussed below, is that the phosphorescent sensitiser sites represent just a sub-set of the total absorbing sites, hence their being quenched leads to an over-expectation of the yield of generated upconversion.

Within the rubrene crystals that do upconvert, the kinetic data suggests that triplets are decaying predominantly by TTA, which is a good outcome. Our transients do not allow a good measure of \( k_e^1 \), but on the basis of the limited evidence gathered here, solid rubrene may well be a good upconversion emitter, if the problem of apparently dark quenching sites can be overcome. Further evidence for the existence of these sites comes from the power response of the material, shown as the inset of Figure 5.10. By integrating over the first 59 µs of each transient, subtracting the equivalent integrated background and normalising by the number of acquisitions per time increment, we obtain an effective upconversion response for the excitation energy. The response is clearly sub-linear at the highest energy used, so the absorbing sites that are spatially positioned to transfer energy to emissive rubrene sites are most likely few in number. This result, the bimodal quenching, and the SEM micrographs all suggest that unsurprisingly, the triplet kinetics of this dry system are heavily dependent on the morphology. Further work on this system should then be largely concerned with morphology control, to re-iterate a recurring theme in the study of solid-state upconverters. It also remains to be seen what role singlet fission in solid rubrene will play in solid-phase TTA-UC.\(^{176}\)

5.4.2 Conclusion

Again, with this material, we see a disconnect between sensitiser quenching results and the delayed fluorescence output. The former suggests that energy is being effectively channeled to the emitters, while the latter suggests that the majority of absorbing sites play no role in generating delayed fluorescence. In the above section we proposed that sensitiser triplets were surprisingly mobile but many of the quenching sites were non-emissive. A competing hypothesis, equally consistent with the above observations (and more generally consistent with the results for liquid-phase emitters), is that our photoluminescence experiments only ever detect a small sub-population of sensitisers which produce long-lived triplet states, that phosphoresce and are emitter-quenchable. The majority of sensitisers in this hypothesis are permanently dark –
they do not produce phosphorescence, nor are they emitter-quenchable, and they are effectively invisible to our experiments on the nanosecond timescale. Thus in this and earlier experiments the few bright sensitiser sites are quickly saturated, causing the fall-off in phosphorescence and delayed fluorescence outputs. To better test this dour hypothesis we need to carry out transient absorption measurements, to test for non-emissive states in the material; optically-gated measurements, to check for fast relaxation processes; and measurements where the true emission intensity is more easily quantified.

These uncertainties notwithstanding, for such a primitively-prepared material the results are rather encouraging. Upconversion from the excited material was visually apparent, so alongside the results of the kinetics experiments we can be confident that at least some portion of this material exhibits an upconversion response worthy of further study. The SEM micrographs revealed several regions of large rubrene crystals with small groupings of silica nanoparticles nested atop them. Further studies should aim to maximise the occurrence of these style of sites, perhaps by using a two-step film preparation method.

5.5 APTES$\text{$_{2/3}$TPPdP}$ on SiO$_2$

In parallel with our studies of peptide-coupled sensitisers on silica, we sought a means of bypassing the structural uncertainties introduced by the aminosilane treatment of silica in the two-step procedure. Equally, we wanted to see if direct dye binding could achieve higher dye concentration than had thus far been achieved. Hence the development of the APTES-functionalised TPPdP sensitiser, and the one-step preparation described in Section 4.4.4.

One benefit of the simplified binding scheme was the ability to control the dye loading simply by changing the mass of silica nanoparticles added to a dye bath. This allowed us to create samples with variable binding densities that were otherwise identical. Using this system we were therefore able to study trends with sensitiser concentration as well as excitation energy and emitter concentration. In this work we studied four tethered TPPdP sensitiser samples with total-volume concentrations ranging evenly from 0.28 to 2.2 mM, corresponding to 0.5–4.0 wt%
dye on silica. Given that we have four sensitiser samples rather than one, the work in this section is presented differently. First we study the phosphorescence kinetics and their variation with both pulse energy and dye loading, then we look at the delayed fluorescence kinetics and power response.

### 5.5.1 Sensitiser kinetics: effect of dye concentration and pulse energy

Solid sensitiser material was dispersed in neat toluene, transferred to a vacuum cuvette and deaerated using the standard procedure. Excitation was at 525 nm, resonant with the sensitiser Q-band. Temporally-resolved phosphorescence transients were collected using the pulsed excitation kinetics setup, described in section 4.2. The excitation source for this series of experiments was the pulsed nanosecond laser and OPO. The much lower repetition rate of this system necessitated the use of higher pulse energies than the femtosecond laser to obtain workable acquisition times. Kinetics were measured for each of the four samples at a range of excitation energies, which were varied using neutral density filters that could be inserted and removed without altering the laser spot size.

Transients collected with changing pulse energy and dye concentration are shown in Figure 5.11. Normalised background-subtracted transients were fit with the mixed-kinetics model, with transients for the same dye concentration grouped and globally fit for $k_1^*$, leaving alpha as the free parameter. Visually the transients are all quite similar, but fitting reveals clear, if puzzling, trends. The fitting parameters are plotted in Figure 5.12. The first unexpected result is that the first-order decay rate is lower for nanoparticles with a higher dye loading, whereas we would expect that a more concentrated system should lead to more aggregate-induced quenching and a greater decay rate. The second unexpected result is that $\beta$, the fraction of triplets initially undergoing second-order decay, drops with increasing pulse energy contrary to our expectations. We venture an explanation for these counterintuitive behaviours on the basis of the dye binding mechanism. In the two-step functionalised silica nanoparticles process, we used sensitiser dyes containing a single carboxylic acid moiety to rule out the formation of strongly-bound dye multilayers through interactions of the unbound carboxylic acid groups. Multilayers impede emitter access and increase the likelihood of sensitiser aggregate formation, so are something we want to avoid. Unfortunately we were unable to implement the single-binding-moiety precaution in the single-step APTES-dye process, because separating the raw synthesised product into the mono-, bis-, tris- and tetrakis-APTES species was simply too lossy. Instead we were forced to apply a statistical mixture consisting largely of the bis- and tris-APTES TPPdP to the silica nanospheres. Although we were careful to keep the binding reaction dry throughout by using distilled solvents and sealed reaction vessels, given these unexpected trends in kinetic parameters we suspect that a portion of the bound dye has become incorporated into aggregated dye structures on the silica surface, probably facilitated by the anchoring groups. Interacting chromophores with a predominantly J-type configuration have an increased long-wavelength oscillator strength.
Figure 5.11: Representative power- and concentration-dependent phosphorescence transients of APTES$_{2/3}$TPPdP tethered to silica nanoparticles in deaerated toluene (top and bottom panels, respectively). Fitting was carried out using the mixed-order kinetics model with $k_i^*$ fixed for each dye concentration. The inset shows the phosphorescence spectrum of the sensitiser in-situ.
Figure 5.12: Trend in $\beta$ with excitation energy and loading of APTES$_{2/3}$TPPdP on silica, the dashed lines are a guide for the eye. In the kinetic model, $\beta$ relates to apparent second-order annihilation, and typically increases with pulse energy. The opposite trend observed here suggests that a strongly-excited region of the material with fast triplet relaxation is becoming saturated at higher pulse energies, leading to an apparent reduction in second-order decay. The trend with dye loading is less clear: the drop in $\beta$ between the highest and next-highest loading is apparent, but then there is little distinguishing the lower three loadings from each other. The inset shows $k_1'$ for each material.
compared to the free dye, so these regions will preferentially absorb long-wavelength incident radiation and then rapidly dissipate that energy from the absorbing aggregate.

The trend in $\beta$ can therefore be explained as the saturation of these aggregate sites at higher pulse energies, leading to the excitation of longer-lived more weakly-absorbing centers and a reduction in decay by what the kinetic model ascribes to the second-order channel. The ‘backwards’ trend in $k_1^s$ suggests that these bound aggregate structures are initially formed more favourably than isolated surface-bound dyes. Thus with a large amount of silica in the dye bath, aggregate sites are the main form in which dye binds to the material. With a lesser quantity of silica, the aggregate sites grow to the point of being unfavourable for further binding before the dye bath is depleted, and so the remained dye binds in the isolated form. The proportion of isolated to aggregated dye therefore increases at higher dye loadings, resulting in the apparently increased triplet lifetime.

5.5.2 Sensitiser quenching, delayed fluorescence kinetics, power response

Having studied the triplet kinetics in the isolated sensitiser, we added a perylene solution in toluene to the most concentrated solid sample to study sensitiser quenching and delayed fluorescence. In a vacuum cuvette, 2.5 mL of a 10 mM perylene stock solution was added to 35 mg of 4 wt% APTES-TPPdP on silica suspended in 0.4 mL neat toluene. A magnetic stirrer bar was also added to the cuvette. The sample was deaerated by the standard procedure, and phosphorescence then delayed fluorescence transients were collected using the pulsed excitation kinetics setup. Excitation conditions were unchanged from the previous experiment (section 5.5.1) allowing retention of kinetic parameters in the analysis of results. Transients were collected with the stirrer off, which left the solid material compacted at the base of the cuvette, and with it on, which dispersed the solid throughout the liquid, creating an opaque solution.

Phosphorescence

For the unstirred sample, the sensitiser triplets decay through a bimodal process similar to that seen in the all-solid upconverter in Section 5.4. As before, the transient is well-fit by Equation 5.3, the weighted sum of a slow-decaying mixed kinetics transient (that of the tethered sensitiser in neat toluene) and a new faster-decaying component, representing emitter quenching. This faster component decays with a rate 432000 s$^{-1}$, or about 106 times the first-order decay rate of the slower transient. Stirring the sample further increased the sensitiser decay rate on the order of 200 times, to the point where good temporal resolution of the decay became impossible. Stirring disperses the solid evenly throughout the solution and presumably gives the emitter much greater access to the tethered sensitiser, which can explain the truncated decay. We suppose that the physical migration of excited sensitisers out of the region of the sample that is imaged due to the mechanical agitation cannot be responsible for the apparent lifetime shortening, since the decay is on the order of nanoseconds, during which the nanoparticles would be effectively stationary.
Figure 5.13: **A**: Phosphorescence decay of 4 wt% APTES-TPPdP on silica in neat toluene, and in an 8.6 mM perylene solution with and without magnetic stirring. Fits are using the mixed kinetics model with a constant alpha value. The stirrer lifted particles from their resting compacted state and created an even distribution of suspended nanoparticles throughout the liquid. Clearly the quenching is greatly improved by stirring, to the point where accurate resolution of the decay kinetics became impossible using our setup. The dashed line is a guide to the eye. **B**: Fitted delayed fluorescence transient for the unstirred perylene-nanoparticle mixture. Delayed fluorescence was rendered practically undetectable by stirring.
The fitted decay transients are presented in the top panel of Figure 5.13. Unfortunately equipment failures left us unable to conduct a full Stern-Volmer experiment on this material, or any quenching studies of the other lower-concentration particles. The one pair of data points obtained lead to quenching rate constants of $4.8 \times 10^7$ and $9.4 \times 10^9 \text{M}^{-1} \text{s}^{-1}$ for the unstirred and stirred samples respectively, with unquantifiable uncertainty. We cannot base too much on these values, other than to note the first value is an order of magnitude lower than that measured in the zirconia-tethered dye experiment (Section 5.2), while the latter suggests that perylene access is greatly improved by dispersing the nanoparticles into solution.

**Delayed fluorescence**

Despite the excellent quenching rate, delayed fluorescence from the stirred sample was too weak to be temporally resolved. This is likely due to the sensitisier solid being so well dispersed that emitter triplets are created at low concentration over a greater depth into the cuvette, leading to a low probability of excited emitters finding annihilation partners. The unstirred sample generated much brighter emission, presumably absorbing incident light over a shorter path length and creating emitter triplets more strongly confined to interstitial sites in the solid material. The obtained transient and fit are shown in the bottom panel of Figure 5.13. The transient has a detectable rise-time, so again we used a numerical model to fit the decay, as described in section 5.3.1. The decay is strongly second-order and $k_1^e$ is thus only weakly determined by the fit, so we cannot use this transient as evidence for or against emitter triplet lifetime shortening with solid sensitisers. For example, the value of $250 \text{s}^{-1}$ reported by Parker and Joyce for a low-concentration perylene solution yields a good fit, but so do much higher rates. In fitting we therefore fixed $k_1^e$ to the value of $1700 \text{s}^{-1}$, as measured in-house by Dr Cheng for perylene at a similar concentration to this experiment.

**Power response**

We carried out an upconversion power response study on the 8.7 mM perylene plus 4 wt% APTES-TPPdP silica sample. Much like in section 5.3.2, pulse energy was controlled by neutral density filters and the entire delayed fluorescence transient was recorded in one acquisition by the spectrograph. Results are shown in Figure 5.14. Although the data shows some systematic offsets from the trend, probably due to site-dependent variation in the transmissivity of the somewhat damaged neutral density filters used, a transition between a slope of 2 and 1 is clearly visible. The two response slopes meet at a pulse energy of approximately $1.66 \mu\text{J}$. The spot size in this experiment was recorded and modelled as per the process from section 4.5.3. The spot is 0.11 mm$^2$, which gives an excitation density of 1.5 mJ cm$^{-2}$ (0.4 photons A$^2$) at the transition point. Translating this to an effective solar concentration factor requires knowledge of the sensitisier excitation rate under laser- and solar-excited conditions, which we do not have. In later work (Chapter 6) we study the system under continuous wave excitation, which considerably
CHAPTER 5. RESULTS AND DISCUSSION

Figure 5.14: Upconversion power response for deaerated 4 wt% APTES-TPPdP on SiO$_2$ with 8.6 mM perylene in toluene, showing the change from a quadratic to a linear response with increasing pulse energy. The intersection of the two regions is at roughly 1.66 uJ/pulse, which corresponds to 1.5 mJ cm$^{-2}$ or 0.4 photons s$^{-1}$ A$^{-2}$. The two solid lines are a guide for the eye showing the indicated slopes.

simplifies this calculation. Nonetheless, the response here is unlike that of the zirconia-tethered system and the dry silica plus rubrene system, since the emitter response is unsaturated under the studied conditions, and also unlike the Q$_3$PdP on silica, which had an unchanging response slope of 1.3. The supply of triplets to the emitter thus seems less constrained than in the former two systems, and the microenvironments less varied than in the latter. The apparent simplicity of the delayed fluorescence power response is surprising given the counter-intuitive behaviour of the phosphorescence. But whether or not this renders the APTES-TPPdP system a better upconverter than a peptide-coupled equivalent is at this point an open question that we must pursue with quantifiable yield experiments.

5.5.3 Triplet lifetime in tethered and free sensitisers

The purpose of tethering sensitisers to nanostructured materials is to enable high surface loadings while isolating the chromophores from each other, leaving sensitiser triplets to survive longer and giving them a greater chance of collection by the emitter. In light of this aim, we compared the phosphorescence decay times of tethered and untethered TPPdP sensitiser at equivalent total volume concentrations in neat toluene using the pulsed-excitation kinetics setup. We used the 4 wt% APTES-TPPdP on silica sample, which has a total volume concentration of 2 mM. The phosphorescence kinetics of this material have already been reported in
Figure 5.15: Phosphorescence decay for 4 wt% silica-tethered and free (dissolved) TPPdP at the same total volume concentration of 2 mM. The transients are fit using the mixed-order kinetics model from Section 4.6. \( \beta \) values are 0.95 and 0.86 for the untethered and tethered dyes, respectively.

section 5.5.1; to create a comparable untethered sample we prepared a 2 mM solution in toluene of tetrakis-di(turtbutylphenyl) palladium porphyrin, which has the same chromophore as the APTES-anchored TPPdP but with tertiary butyl groups added to improve solubility and dissuade aggregation – thus, this was a generous comparison. The solid dissolved readily under ambient conditions. The toluene sample was deaerated in a vacuum cuvette using the standard procedure and the phosphorescence decay was measured. Excitation conditions at 525 nm (power and spot size) were equivalent to those used in measurement of the tethered sample.

The first-order decay rate of the 4 wt% tethered solid was globally-fit in Experiment 5.5.1 to give 4080 s\(^{-1}\). The rate in the untethered sample is significantly greater, at 381000 s\(^{-1}\). Thus the triplet lifetime is apparently increased by almost two orders of magnitude by attachment of the chromophore to silica nanoparticles. The tethered transient is also somewhat less second-order in character, with a \( \beta \) value of 0.86 compared to 0.95 for the untethered. This finding suggests that our approach is potentially useful in extending the achievable sensitiser concentrations at which efficient upconversion may be performed. But, given the findings presented in this chapter, it is currently unknown whether the measured photoluminescence decays truly represent the entire sensitiser population, or if portions remain dark and invisible to the photoluminescence kinetics experiments. This result should therefore be regarded with caution until we can conduct measurements with greater temporal resolution.
5.5.4 Conclusion

The sensitiser kinetics of APTES-TPPdP on silica are the least intuitive of the systems studied in this work, while the delayed fluorescence response accords most closely with our prior expectations. The backwards trends in $\beta$ and $k_1^+$ with pulse energy hint at the competing growth of aggregated and non-aggregated dye structures, as does the bimodal quenched phosphorescence transient. And yet, the delayed fluorescence is strongly second-order, and responds to pulse energy with the characteristic transition from a quadratic and linear response, in stark contrast to the other materials studied here. This suggests that despite the sensitiser aggregation, there are still enough sites supplying triplets to the emitter that saturation is not an issue. The higher pulse energies used in this work make this an especially significant comparison with the other materials, which saturated with the lower-energy pulses from the femtosecond laser.

The reactivity of the APTES moiety makes the sensitiser from this study a difficult synthetic target. This, and the inability to effectively separate the differently-substituted products, works against certainty of binding, which was the original motivation for producing this compound. Nonetheless, with revisions to the binding chemistry the one-step approach is worth further study. As with the other systems here, the sensitiser material needs to be checked for dark sites — those proposed sites that absorb energy but remain invisible to photoluminescence measurements — and measured in a quantified yield experiment. To use the system for solar cell enhancement the binding moiety must be reproduced on a redder-absorbing sensitiser.

5.6 Summary of Tethered-Sensitiser Results

The work presented in this chapter forms the beginning of our kinetics study of solid sensitisers for TTA-UC. Moving away from fully liquid systems presents challenges in the material and optical design of systems, but more than anything in the analysis of kinetic data. We have retained use of the mixed kinetics model that has presided over the successful explication of liquid upconverters, and used it to extract and compare rates of triplet decay in both components of the upconverting systems. A summary of these results is presented in Table 5.2.

The kinetic model itself helps to qualify its own shortcomings. Lacking multiple sets of rates for different microenvironments, faster decay processes in the sensitiser become classed as second-order decay, whereas power studies strongly suggest that these decay pathways are often not truly due to bimolecular interactions. But until we can better understand the distribution of microenvironments, or more tightly control their distribution through improved dye coupling and steric effects, adding terms to the kinetic models serves only to dilute its explanatory power. Indeed, one of the difficulties in explaining these highly heterogeneous materials is the rapid multiplication of possible hypotheses. Our retention of a relatively simple model, even if flawed, is a net gain in our trying to understand these materials.

Regardless of the model’s applicability, raw results tell us much of significance. In all sys-
### Table 5.2: Summary of results for the solid-sensitiser kinetics experiments. ‘n.d.’ denotes a non-determined quantity due to loose fitting of the kinetic model.
tems, the availability of triplets from the sensitiser material is a key concern. The Stern-Volmer relationship between sensitiser lifetime and emitter concentration holds in all instances studied here, which superficially implies that the sensitiser’s role has been carried out successfully. But measurements of the total phosphorescence and delayed fluorescence intensities point to a different outcome, where the supply of triplets can become constrained and the response duly saturated (as in the zirconia system). One possible implication of this is that our photoluminescence experiments are measuring only a sub-set of the sensitisers, while others remain invisible to our measurements on the nanosecond timescale. This is something we will need to study and verify using optical gating methods, which operate with temporal resolution far greater than the gated spectrograph allows us. In any case the emphasis of further work clearly needs to be on the sensitiser material, and understanding the fate of excited states over all relevant timescales. Ghiggino and Steer make frequent use of zinc tetraphenyl porphyrin to monitor homo-TTA by the generation of fluorescence from an unusually bright $S_2$ state.\textsuperscript{178} Incorporating this into one of the tethering schemes could be useful as an indicator of lossy sensitiser TTA.
Part III

Measuring upconversion under sun-like conditions
Chapter 6

Solar Cell Enhancement by Upconversion

In the last chapter we studied the kinetic behaviour of upconverters under pulsed excitation. Such measurements are ideal for quantifying the rates of energy transfer within an upconverter, and thereby inferring the efficacy of mechanisms that affect the performance of the upconversion system. For instance, we know from the simple relations derived in Section 4.1 that having a smaller first-order emitter decay rate $k_1$ will increase the upconversion yield, all other aspects of the system being equal. But at the same time, deriving a device-relevant upconversion yield from kinetic data is difficult. The main issue is that the different excitation regimes — short, high-intensity laser pulses compared to continuous low-intensity incoherent excitation by sunlight — are not easily translatable due to the nonlinear response of the upconversion yield to fluence.

The TTA efficiency $\phi_{TTA}$ under pulsed excitation can be determined using a method developed by Cheng, Schmidt and coworkers. The upconverter is excited first via the sensitiser, then via the emitter, without altering the imaging conditions. For both excitation modes, a single-gate spectrum of the emitter fluorescence is collected, with the gate delay and width set to ensure complete collection of the emission. The two spectra are normalised by the relevant pulse fluence, then $\phi_{UC}$ is calculated from twice the ratio of the delayed to the prompt intensity. For the comparison to be valid, both excitation wavelengths must produce comparable singlet emitter generation profiles, so that reabsorption of the generated fluorescence attenuates both signals equally. Thus the optical pathlength of the laser pulse for generating delayed fluorescence should be the square of the pulse for prompt fluorescence, since in the delayed fluorescence route triplets must annihilate to produce the singlet state. In liquid systems the concentration of both components can be controlled to yield suitable generation profiles.

The comparative yields technique was used to great effect by the authors in disproving the existence of a spin-statistics dictated 11.1% limit to $\phi_{TTA}$, a topic of some controversy at the time ($\phi_{UC} = \phi_{TTA} \phi_{PL}$, where $\phi_{PL}$ is the fluorescence quantum yield of the emitter singlet). However, the requirement of comparable generation profiles makes it difficult to implement reliably with solid upconverter materials, which do not allow such straight-forward
control of the chromophore concentration and can show wavelength-dependent optical effects, such as scattering, which have non-trivial solutions to their effects on pulse propagation. And in any case, this method is no help in translating yields measured under pulsed excitation to those expected with much weaker continuous-wave excitation. In short, kinetics measurements are ideally suited to quantifying rates and the limiting performance of upconverters. Studying the performance under device-relevant conditions can be better achieved using continuous-wave excitation and simpler but better quantified detection methods. This is the topic of the section at hand.

6.1 Measuring Solar Cell Enhancement

Notwithstanding the role that TTA-UC has to play in biological imaging and, perhaps, OLEDs, solar cell enhancement is often the primary focus of research efforts in this field. As discussed in Chapter 1, sub-band gap photon transparency is the main contributor to the poor limiting efficiency of higher-band gap solar cells, including all second-generation thin-film cells. The absorption range of typical TTA-UC systems and their potential to achieve useful low-light performance make them well-suited to tackling this efficiency shortfall. Accurately quantifying the improvements afforded to solar cells by TTA-UC systems is therefore a compelling research objective.

Several properties of upconverters under low-intensity excitation make this a complicated adventure — primarily, the nonlinear response and, currently at least, the low upconversion efficiency and the correspondingly small effect of upconversion on the cell output. A solar cell enhancement experiment that addresses these challenges grew out of a collaboration in 2010 between the Schmidt group and Prof. Klaus Lips of Helmholtz-Zentrum Berlin (HZB). The eventual working setup was due to work done by Lips, Schmidt, Füeckel, Cheng, and myself. In the following work I outline the rationale behind the measurement procedure, then present the experimental setup, modelling of the upconversion enhancement, and finally a solar cell enhancement result using a nanostructured upconverter. Results from this experiment have appeared in several publications thus far.\textsuperscript{135,138,165,179–182}. In the following work we assume an upconverter-solar cell couple consisting of the upconverter mounted behind the sun-facing surface of a bifacial solar cell.

6.1.1 The problem with upconverter substitution

In this section I briefly canvass some possible enhancement experiments and their failings, as a way of foreshadowing the necessary elements of the eventual working experiment.

A simple approach to measuring solar cell enhancement would seemingly be to make two measurements of the cell efficiency under broadband illumination, one with and one without the upconverter mounted behind the cell. The difference in efficiencies would then be ascribed
to upconversion. But this approach is insensitive to the other optical effects that accompany upconverter attachment to the solar cell, and so any change in the efficiency cannot credibly be attributed only to the upconversion effect. For example, many solar cell designs implement a scattering layer on the rear surface of the device to increase the path length of photons within the active layer. Attaching an index-matched upconverter will change the performance of such a layer. Similarly, back-fluorescence may be generated by the upconverter responding to transmitted light. Each such effect will change the cell efficiency, and must be controlled for in a simple substitution experiment. Under low-intensity, low-efficiency device-relevant conditions these errant effects can alter cell performance to an extent comparable to the actual upconversion mechanism. Reliably untangling the ‘real’ effect from these screening effects is not practical with such a simple experiment.

A contrived style of substitution measurement is possible where excitation of the cell is by fully sub-band gap photons, such that the cell-plus-upconverter generates a response while the unamended cell elicits none whatsoever. But the result in this case is trivial, as it simply confirms that the upconverter does indeed produce blueshifted emission. Two cell-plus-upconverter couples built identically but for one upconverter being non-functional could, in principle, control for the interplay of optical effects above the cell’s band gap and make clear the efficiency contribution from upconversion. But the dummy upconverter needs to retain all the same optical properties as the real system — absorption features, emitter fluorescence quantum yield, and so on — without actually generating upconversion. Creating such a system would be a non-trivial task. Simply oxygenating an upconverter is not sufficient, as the singlet oxygen generated can damage chromophores and alter the back-fluorescence.

6.1.2 Spectrally-resolved cell response: overview

In the solar cell enhancement experiment, the upconverter’s contribution to the cell performance is revealed by spectrally-resolved excitation of the couple. The wavelength-dependent short-circuit current density, $J_{SC}(\lambda)$, is measured while the solar cell face of the couple is illuminated by a tunable incoherent quasi-monochromatic beam of wavelength $\lambda$, called the probe beam. The probe beam is mechanically chopped and $J_{SC}(\lambda)$ is phase-locked to the chopper reference signal. Scanning the probe beam across the visible spectrum while collecting $J_{SC}(\lambda)$, then normalising $J_{SC}(\lambda)$ by the probe beam flux at $\lambda$, allows calculation of the spectrally-resolved external quantum efficiency of the cell-upconverter couple, EQE(\lambda). This corresponds to the likelihood of an incident photon of wavelength $\lambda$ generating current under short-circuit conditions.

Efficiency biasing with the pump beam

For a linearly-responding upconverter, this would be the end of the story. Wavelengths transmitted by the solar cell and resonant with the sensitisers would produce a bump in the EQE
spectrum indicative of the extent of the upconversion effect. The appearance of sensitizer absorption features in the enhanced EQE spectrum, accounting for distortion by the cell transmission spectrum, would confirm that the measured improvements to $J_{SC}$ were, in fact, due to the upconverter and not some other optical effect.

But this is not the case: exposed to the low-intensity probe beam, the triplet concentration in a real upconverter is low enough that the upconverter is essentially inoperational, making very little long-wavelength imprint on the EQE spectrum. To invoke a greater upconversion response, a second light beam is introduced to the experiment: the pump beam, which is resonant with the sensitizer in the upconversion region and typically much more intense than the probe beam. The pump beam, which is not optically chopped, produces a constant background population of triplet-excited species in the upconverter, which improves the likelihood of emitters excited by the probe beam finding annihilation partners. Thus the pump beam positively biases the upconversion efficiency by increasing the excitation metric of the probed system.

The pump beam wavelength is typically at the extreme red edge of the solar cell response curve, but the high intensity of the pump beam compared the probe means it can still make a comparatively large contribution to $J_{SC}$ by direct absorption at the cell active layer, as well as by emission generated from the pumped upconverter. Therefore under biased conditions, $J_{SC}$ consists of a large continuous term with a periodic component superimposed:

$$J_{SC}(\lambda, t) = J_{bSC}^b + A(t) J_{pSC}^p(\lambda),$$  \hspace{1cm} (6.1)

where $A(t)$ is a square wave of amplitude 1 and frequency determined by the chopper wheel, mapping the changing state (on/off) of the probe beam. In the experiment, the $J_{SC}(\lambda, t)$ signal is digitally phase-locked to the chopper reference signal, isolating the time-varying component as the magnitude $R$ of a vector sweeping phase-space with the frequency of the chopper wheel. Thus the acquisition program records only the response due to the probe signal, while the pump beam biases the upconverter efficiency such that the weak probe produces a measurable response.

The extent of the pump beam biasing is quantified by the sensitizer excitation rate due to the pump biasing, $k_{b\phi}$, which is calculated as per Equation 1.1. Comparison to the excitation rate under the AM1.5G solar spectrum, $k_{s\phi}^s$, gives the solar concentration factor:

$$f_c = k_{b\phi}^b / k_{s\phi}^s.$$  \hspace{1cm} (6.2)

Thus the EQE of the couple can be measured for a range of effective sunlight conditions by varying the intensity of the pump beam.
Baseline measurement

To effectively bias the probed area of the upconverter, the spot of the focused pump beam on the upconverter must wholly encompass that of the probe during measurement of EQE(\(\lambda\)). Thus the pump and probe beams are made to propagate collinearly before focusing through the cell and into the upconverter, with the beam diameters controlling the relative width of the focused spots. Measurement of the biased system is thus with the pump and probe beams aligned.

In order to properly gauge the effect of TTA-UC on \(J_{SC}\), we require a baseline measurement of the EQE spectrum with a non-operational upconverter, denoted EQE\(_0\). Deactivating the pump beam switches off the biasing effect and allows the measurement of just that. Under excitation by the probe beam alone, the upconverter has a negligible efficiency and makes no significant long-wavelength contribution to \(J_{SC}(\lambda)\).

Disabling the pump beam reduces the \(J_{bSC}\) term in Equation 6.1 to zero. Formally this should have no effect on the time-varying component of \(J_{SC}(\lambda,t)\). But in practice the internal quantum efficiency (IQE), which is the efficiency with which the solar cell extracts photo-generated charge carriers, can depend on the current density through trap filling. This is especially true of second-generation cell designs, which by virtue of their amorphous layers typically have an abundance of trap-generating interfaces and impurities. Thus deactivating the pump beam in an enhancement experiment significantly reduces the current density in the cell, leading to a drop in the IQE and a skewed measurement of EQE\(_0\).

So instead, EQE\(_0\) is measured after slightly mis-aligning the pump and probe beam spots on the upconverter surface, such that the two beams illuminate adjacent regions of the upconverter while still passing through the active layer of the cell. Now, the cell receives the same incident flux from the pump beam, but the probe beam spot is outside of that of the pump on the upconverter. The upconverter is duly rendered inoperational in the probed region. The mis-alignment is performed by rotating a fine-adjustment control on an optics mount, allowing good reproducibility. Crucially, this method means that the sample remains untouched between measurements of the baseline and the biased EQE spectra, so the two may be compared directly to deduce the enhancement due to upconversion. There is an assumption of sufficient lateral carrier mobility within the cell.

6.1.3 Spectrally-resolved cell response: experimental setup

The experimental setup is shown in Figure 6.1. The output of a xenon arc lamp (Oriel) passes through a monochromator (Spectral Products) and chopper wheel, forming the probe beam. The 670 nm output of a diode laser forms the pump beam. The two beams are combined in a polarising beam splitter cube then co-focused onto the solar cell-upconverter couple. The pump intensity is controlled by polarising optics placed prior to the beam splitter cube; by rotating the pump polarisation in a half-wave plate, the fraction of pump light reflected in the cube is controlled. The probe beam is unpolarised, so approximately 50% of the beam is transmitted.
Figure 6.1: Solar cell enhancement experimental setup. The diverging output of a high-powered xenon arc lamp (1) passes through a long-pass filter (2), is collimated, then coupled into a CM-110 monochromator (3). The quasi-monochromatic probe beam passes through a chopper wheel (4) and a high-transmittance beamsplitter such that a small portion of the beam reaches a reference photodiode (5). The pump beam is generated by a diode laser (6) and passes through a linear polariser (7) and a half-wave plate (8). The pump and probe beams are combined in a polarising beam-splitter (9) and are focused onto the solar cell-upconverter couple (10). The probe beam width prior to focusing is greater than that of the pump beam such that the focused probe spot size is smaller than the pump. Upconverted light is re-radiated into the solar cell, increasing $J_{SC}$.
through the cube.

The solar cell is back-contacted by a custom-built sample holder, and front-contacting is by a flexible copper finger that presses against the cell close to the illuminated spot. The upconversion sample is degassed within a vacuum cuvette, which is then pressed against the rear of the cell substrate and optically contacted along the probe beam path using index-matching immersion oil. Beam misalignment is by manual rotation of the fine adjustment knob on an optics mount, the aligned and misaligned positions are marked during setup to allow good reproducibility of the positions.

The EQE measurements are made under short-circuit conditions. The cell’s output current is passed through a current amplifier (Stanford Research Systems), which converts the weak current signal to a voltage that is read by a digital acquisition device (National Instruments). The LabView control and acquisition program on the lab PC reads the input voltage and performs the digital phase-locking. The quantity of interest is the spectrally-resolved EQE ratio, which is found by measuring several (typically 3) aligned and misaligned EQEs, averaging, then calculating the ratio.

Following the measurements, the pump beam power and spot size are recorded to allow calculation of the solar concentration factor.

### 6.2 Dual Propagating Beams Model

The EQE ratio can be fit using a one-dimensional model of a bulk upconverter solution developed by Prof Schmidt in 2012.\(^\text{165}\) I present the model now, with additional explanatory comments, so that modifications I have made can be introduced later within the proper context.

In order to model upconversion within the sample, the attenuation of the excitation source with propagation further into the cuvette and its effect on the sensitiser excitation rate is modelled using the Beer-Lambert law. Since excitation is continuous the generation and decay of triplets is balanced. We assume the low-efficiency quadratic response regime, so emitter decay is dominated by the first-order decay term. At any depth \(z\) into the cuvette the steady-state condition is therefore

\[
k_\phi N_s = k_1 N_t ,
\]

where \(k_\phi\) is the sensitiser excitation rate, \(N_s\) the sensitiser concentration, \(k_1\) the emitter first-order decay rate and \(N_t\) the emitter triplet concentration. As in the steady-state model introduced in Chapter 4, this expression assumes fast and efficient intersystem crossing in the sensitiser and unit efficiency sensitiser quenching by the emitter, as well as negligible diffusion of excited chromophores over macroscopic distances.

Given our assumption of the quadratic response region, the upconverted emission generated
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at $z$ is of the form

$$\text{UC}(z) \propto \frac{k_\phi(z)^2 N_s^2}{k_1^2}. \quad (6.4)$$

Having $N_s$ independent of $z$ assumes no saturation of the sensitizer, which is reasonable under the assumed low-intensity conditions. During measurement $k_\phi$ depends on both the bias (subscript $b$) and the probe ($p$) beams such that $k_\phi = k_{\phi_b} + k_{\phi_p}$. Henceforth, all $k_\phi$ terms are for the excitation rate at the front face of the cuvette, i.e. where $z = 0$. The expression for $\text{UC}(z)$ given above can be expanded to explicitly include both components of the excitation rate:

$$\text{UC}(z) = \frac{N_s^2}{k_1^2} \left[ k_{\phi_b} \exp(-\alpha_b^* z) + k_{\phi_p} \exp(-\alpha_p^* z) \right]^2, \quad (6.5)$$

where $\alpha_b^*$ and $\alpha_p^*$ are the sensitizer absorption coefficients for the bias and probe beams, respectively; here it is assumed that the sensitizer alone contributes to optical density within the upconverter at the modelled wavelengths. This expression shows how the intensity of both beams will decay independently, depending on the relevant absorption coefficients, as they propagate into the cuvette. The excitation rate is smaller at greater depths, reflecting the reduced light intensity.

Integrating this expression over $z$ with limits of $(0, \infty)$ gives the cumulative upconversion output, if we assume no depth-dependent outcoupling losses such as reabsorption (this assumption may seem surprising, and it will be addressed shortly):

$$\int_0^\infty \text{d}z \frac{\text{UC}(z)}{N_s^2} \propto \frac{k_{\phi_b}^2}{2\alpha_b} + \frac{k_{\phi_p}^2}{2\alpha_p} + \frac{2k_{\phi_b}k_{\phi_p}}{\alpha_b + \alpha_p}. \quad (6.6)$$

Note that the $k_1$ term has been incorporated into the implied constant of proportionality. The above expression can be simplified into more experimentally-relevant quantities using the following two sets of relations:

$$k_{\phi_b} = I_b \sigma_b, \quad k_{\phi_p} = I_p \sigma_p, \quad (6.7)$$

and

$$N_s = \frac{\alpha_b}{\sigma_b} = \frac{\alpha_p}{\sigma_p}, \quad (6.8)$$
where $I$ is beam intensity (dimensions of photons per area per time) and $\sigma$ is the absorption cross-section. Using these simplifications, the new expression for upconversion output duly becomes:

$$UC \propto N_s \left( \frac{I_b^2 \sigma_b}{2} + \frac{I_p^2 \sigma_p}{2} + \frac{2I_b I_p \sigma_b \sigma_p}{\sigma_b + \sigma_p} \right). \quad (6.9)$$

Note that $I_b$ and $I_p$ are the photon fluxes of the bias and probe beams incident on the upconverter after transmission through the solar cell, whereas in the original publication the transmissivity of the solar cell to the probe, $T_p$, was formally included.\textsuperscript{165} At this point we have a model for the total output of upconverted light generated in response to the pump and probe beams. Recall, however, that phase-locking makes the experimental measurement sensitive only to the probe beam, which actually measures what is effectively the derivative of the upconverter response with respect to $I_p$. The response measured in the FoM experiment is therefore

$$\frac{dUC}{dI_p} \propto N_s \left( I_p \sigma_p + \frac{2I_b \sigma_b \sigma_p}{\sigma_b + \sigma_p} \right). \quad (6.10)$$

Since the bias beam is much brighter than the probe, the $I_p \sigma_p$ term can be ignored. It is now possible to model the upconverter-cell couple’s EQE curve as

$$\text{EQE}_{UC} = \text{EQE}_0 + \text{const.} \times \frac{\sigma_b \sigma_p}{\sigma_b + \sigma_p}, \quad (6.11)$$

where $\text{EQE}_0$ is the EQE curve measured with the upconverter deactivated by beam misalignment, and the EQE, cell transmittance and cross-sections are all wavelength-dependent quantities. The EQE ratio, used to determine the proportional increase in EQE resulting from upconversion, is given by

$$\frac{\text{EQE}_{UC}}{\text{EQE}_0} = 1 + \text{const.} \times \frac{1}{\text{EQE}_0} \frac{\sigma_b \sigma_p}{\sigma_b + \sigma_p}, \quad (6.12)$$

The constant in the expression is the single free parameter used to fit to the measured EQE ratio. In published works so far, fitting is typically very good, signifying that this model has captured the essential behaviour of a biased upconverter. Thus, the assumption of no reabsorption appears vindicated, despite the high emitter concentration and the low Stokes shift of the emitter. The likely explanation is a combination of the high extinction coefficient
of the sensitisers used in studies thus far, and the quadratic upconversion response to triplet concentration. The former means that the medium is more optically dense at the sensitisier absorption peak than around the emitter fluorescence wavelengths, and the latter means that the upconversion generation profile is even further truncated. Thus it is possible to imagine this model no longer accurately fitting the EQE ratio for high pump intensity experiments or for a very efficient system with a linear response to emitter concentration, but so far no such occurrences have been observed.

6.2.1 Figure of Merit for solar cell enhancement

The EQE ratio in itself is a reportable result. But the extent of the performance increase afforded the cell is not clear from the ratio alone, since a large increase in the ratio may be starting from a vanishingly small EQE. A better-quantified measure of the performance enhancement is found by using the concentration factor $f_c$ to calculate $\Delta J_{SC}^{UC}$, the increase in short circuit current density resulting from the upconverter for a given pump condition:

$$\Delta J_{SC}^{UC} = e \int \Delta EQE^{UC}(\lambda) f_c \rho(\lambda) \, d\lambda,$$

(6.13)

where $\Delta EQE^{UC}$ is the difference between the EQE curves measured with the active and inactive upconverter, i.e. with the pump and probe beams aligned and misaligned, respectively. But it should be apparent that $\Delta J_{SC}^{UC}$ can be increased almost indefinitely by increasing $k_{\phi p}$, i.e., using a brighter pump beam. So a fair measure of the cell enhancement from upconversion needs to account for this. This motivated the introduction of a Figure of Merit (FoM) for the performance of a solar cell-upconverter couple. The FoM is found by dividing $\Delta J_{SC}^{UC}$ by $f_c^2$, returning units of mA cm$^{-2}$ sun$^{-2}$. In this way the increase in current density from upconversion is characterised independently of the pump conditions used, for measurements taken at low intensity conditions (in the quadratic response region). This makes the FoM very useful as a unit of comparison.

6.3 Results

In this section I report on the enhancement of a hydrogen-passivated amorphous silicon (a-Si:H) solar cell using the nanostructured upconverters introduced in Chapter 4. The solar cell was fabricated by collaborators at the Helmholtz-Zentrum Berlin. In the formal depiction of solar cell enhancement by upconversion, the upconverter absorbs light with energy below that of a sharply-defined band gap. But in this experiment the band gap is less defined, owing to the presence of defect states with energies comparable to that of the band gap. Hence when discussing the enhancement of such solar cells the upconversion mission is better stated as re-emitting absorbed energy at a wavelength where the EQE is significantly improved compared to the incident wavelength, whether or not the incident wavelength is strictly sub-band gap.
If the sensitiser-resonant and upconverted wavelengths have similar EQEs within the solar cell, no real gain can come from upconversion: light absorbed directly from the probe beam will generate current with the same likelihood as upconverted emission, the EQE spectrum will be unaffected by the pump beam, and the EQE ratio will therefore be unity at all points. Hence the experiment will record no enhancement by the upconverter. For this reason, the green-to-blue upconverters (TCPPdP and APTES$_3$TPPdP sensitisers) are not testable for solar cells with band gaps less than $\sim 2.5$ eV. The a-Si:H cells used in this work have a band gap of $\sim 1.7$ eV (with a degree of flexibility during fabrication), so these systems have not been tested for solar cell enhancement. On the other hand, the Q$_3$PdP, Q$_4$PdP, and Q$_4$PdPNA sensitisers are all potentially compatible upconversion sensitisers.

Of the systems with results reported in Chapter 5, only the wet Q$_3$PdP on silica (1.5 mM) plus rubrene (10 mM) upconverter was tested for enhancement of the a-Si:H cell. No enhancement to $J_{SC}$ could be reliably detected, which was attributed to the fairly low EQE contrast between the sensitiser peak excitation wavelength (650 nm) and rubrene peak emission wavelength. A 650 nm diode laser was used as the pump source.

The closely-related system of Q$_4$PdP on silica (1.5 mM) plus rubrene toluene solution (10 mM) was also measured, and did produce a measurable enhancement to the a-Si:H cell using a 670 nm diode laser pump, the redder peak absorption lending the experiment an improved EQE contrast. This result has recently been published in refereed conference proceedings. The solar cell enhancement was measured with four pump powers, with $f_c$ ranging from 7.5 to 13.4 suns. The measured EQE ratio and fitted model ratio are shown in Figure 6.2 for $f_c = 9.3$ suns.
Compared to isotropic liquid systems, the nanostructured material produced a noisier EQE ratio, possibly due to inhomogeneity in the solid, leading to heightened sensitivity to the exact pump/probe overlap. Lacking the ability to perform accurate measurements of the solid-tethered dye’s absorption parameters, the simulated EQE ratio was generated using the absorption cross-section of the free dye. Hence some of the deviation evident in the blue wing of the fitted ratio might be due to changes in the sensitiser absorption features brought about by tethering to silica.

Using the fitted ratio produced an FoM of $5.0 \times 10^{-5}$ mA cm$^{-2}$ sun$^{-2}$. Measurements by Dr Cheng of a similar a-Si:H cell coupled to an isotropic liquid upconverter with a $Q_4PdP$ concentration of 0.3 mM and 5 mM rubrene emitter achieved an FoM of $2.8 \times 10^{-5}$ mA cm$^{-2}$ sun$^{-2}$. While the different concentrations mean these results are not directly comparable, it is known from other works (including the report in Section 5.5.3) that increasing the sensitiser concentration much beyond the range used in the isotropic system leads to decreased upconversion yields. The roughly doubled increase in FoM with the increased sensitiser concentration is therefore a sign that, under the right circumstances, the nanostructured sensitiser can yield improved solar cell enhancement and thus, presumably, improved upconversion yields. The magnitude of the increase is lower than anticipated for full participation of the tethered sensitisers, but given the complicated results for the similar material presented in Chapter 5 it seems likely that the solid system is currently far from optimised.

### 6.3.1 Increased tethered-sensitiser loading

A cautionary finding, in addition to the result above, is that increasing the sensitiser loading in the tethered-sensitiser materials greatly diminished the upconversion response (by visual observation) and led to unmeasurably low solar cell enhancement, despite the good EQE contrast. The 1.5 mM $Q_4PdP$ on silica material was one of the earliest batches of tethered sensitiser generated in this work, and the unexpectedly low concentration prompted an immediate move towards a thicker aminosilane layer and higher sensitiser loading. This move was successful, and led to silica-tethered carboxylic acid derivatives of $Q_4PdP$ and $Q_4PdPNA$ with approximately double the concentration of the material successfully measured here. The upconversion response of both these materials was visually weak when prepared in the standard fashion with rubrene emitter solution, and neither material produced a measurable enhancement to the solar cell EQE. Alumina substrate-tethered $Q_4PdPNA$ prepared with a rubrene solution in the half-cuvette, as described in Section 4.4.2, likewise produced unmeasurable solar cell enhancement for a range of total-volume concentrations starting at several millimolar.
6.4 Discussion and Conclusion

Silica-tethered Q₄PdP with 1.5 mM total volume concentration produced an appreciable gain in the FoM over an earlier isotropic liquid system. This concentration is well in excess of the optimum range used in isotropic liquid systems and yet the upconversion yield is improved quite significantly. In particular, this result was obtained in spite of the doubled first-order emitter decay rate of the Q₃PdP system identified in Chapter 5, which we assume applies equally to the very similar Q₄PdP system.

However, the loss of an appreciable upconversion yield at the higher dye loadings tested means that sensitiser tethering has possibly forestalled, but certainly not solved the problem of providing a high-concentration sensitiser environment without inducing overbearing loss mechanisms. One of the possible explanations is that in allowing a higher density of binding sites, the tethered sensitisers are more likely to become positioned in lossy aggregated configurations on the surface. Changing the aminosilane deposition target from a monolayer to a thick multilayer may also have increased the mean volume sampled by the tethered sensitisers, granting more opportunities to self-interact. If this were the case, however, it is unclear how this surface functionalisation method could produce yet more concentrated films without inducing similarly lossy interaction modes.

In Chapter 5, I emphasised the need to carry out simpler yield experiments to better relate kinetics data to upconversion output under device-relevant conditions. The solar cell enhancement experiment described in this chapter is one such example, albeit somewhat restricted in applicability by the need for an EQE contrast in the coupled solar cell. Now, the shoe is on the other foot. Lacking kinetics data for the two concentrations of Q₄PdP-silica sensitiser, for example, we cannot offer a firm explanation of the drop in upconversion yield upon changing the aminosilane film and doubling the sensitiser loading, whether the responsible mechanism is sensitiser self-interaction, a reduced emitter triplet lifetime, or something else again. Further kinetic studies in parallel with enhancement experiments are required.

6.5 Possible Changes to the Setup

This concludes the reporting of solar cell enhancement results. However, a significant portion of work conducted on the experiment was concerned with the design of the experiment itself. To this end, I briefly discuss several aspects of the as-reported solar cell enhancement experiment which will be targeted for improvement in ongoing development.

Non-uniform biasing

The pump beam spot size must be known to calculate \( k_{\phi p} \), the sensitiser excitation rate under experimental conditions. Implicit in calculating \( k_{\phi p} \) is the assumption that the probed area is uniformly illuminated by the pump. But the pump beam profile is never truly uniform,
particularly when tightly focused. Thus the probe spot should be significantly smaller than the pump, so the non-uniformity in the pump is not severe over the probed area. Generally the larger the disparity in the pump and probe spot sizes, the better the uniformity of the biased region, but this comes with the price of a lower achievable concentration factor and a poorer signal to noise ratio, and a greater required physical misalignment that risks local changes in the IQE bias.

The impacts of non-uniform biasing is variation in the concentration factor across the probed area, which leads to diminished certainty in the FoM. As described in the next chapter, an incoherent pump beam can achieve a uniform biased region more easily than a laser, as long as the system can operate sufficiently well at the comparatively low pump intensity.

**Polarisation**

In the version of the setup described in this chapter, the pump and probe beams are made collinear by combining them in a polarising beam splitter cube. In order for both beams to outcouple from the same face of the beam splitter they need orthogonal polarisations, since one beam transmits through the slanted dielectric layer in the middle of the cube while the other reflects. Hence the probe beam is testing a system biased by the orthogonal linear polarisation.

Beam polarisation is of crucial concern in two-beam ultrafast pump-probe experiments, being the basis of anisotropy measurements. But in TTA-UC experiments this is of less concern, for a number of reasons. Primarily, the electronic dephasing inherent to $D_{4h}$ chromophores described in Chapter 2 means that anisotropy induced by the pump beam will dissipate effectively instantaneously. On top of this, random oscillations in the position of the molecule over the long timescales used in TTA-UC experiments mean another mode by which anisotropy will dissipate, at least in wet systems.

Nonetheless it is possible to imagine a TTA-UC system where the orthogonal polarisations of the collinear pump and probe beams might be of concern. For example, for an aligned sensitizer in which full electronic dephasing is impaired (such as a $C_{2v}$-symmetric metalloporphyrin) embedded in a solid emitter matrix, it is plausible that triplet excitons could retain some degree of anisotropy upon transfer to the emitter. Once there, the annihilation parameters may differ depending on the relative orientation of the interacting triplet excitons.

Clearly, actually bringing about a situation where orthogonal pump and probe polarisations are problematic would be a complicated task, but investigating such a material could be instructive in helping to design better solid upconverters. In any case, the use of non-polarising beam splitters or non-collinear pump and a probe beams are both possible methods of achieving non-orthogonal polarisations.
Broadband pumping

Biasing the solar cell-upconverter couple with a broadband incoherent light source better mimics the conditions experienced under solar irradiation, and may give a better indication of how the device will perform in a real installation. In particular, a cell bathed in bright, broadband light should experience improved trap filling, and may show improved resolution for the excitation of very weakly absorbing features (e.g. the extreme red edge of the sensitizer absorption). But the large current density produced by biasing the cell to a workable concentration factor with white light (much of it resonant with the solar cell active layer) may impair detection of the comparatively small component generated by the monochromatic probe. Suitable baseline filtering in the current amplifier may ameliorate this problem however.

The modified experimental setup reported in Chapter 6 has some potential for testing solar cell enhancement with broadband pumping, and will be implemented as such in future works.
Chapter 7

Upconverter Action Spectrum

7.1 Limitations of the FoM Experiment

The solar cell enhancement experiment described in Chapter 6 has been used very successfully to characterise the performance enhancement granted to thin-film solar cells as a result of an attached TTA-UC module (for example, see the references at the beginning of that chapter). But although certain properties of the upconverter can be inferred from the results of this experiment, measuring solar cell enhancement is, in some respects, a roundabout way of studying upconverters directly.

To explain, if the aim of the enhancement experiment is re-cast to be purely about the study of upconverters, with the solar cell acting simply as a photodetector, the geometry of the solar cell-upconverter couple makes the analysis and comparison of data unusually complicated. In standard photoluminescence experiments the photodetector and the excitation source do not interact, except for perhaps a scatter component that can be easily subtracted. But in an upconverter-focused recasting of the enhancement experiment, the probe beam passes through the photodetector before reaching the sample, so the recorded photocurrent is the sum of currents generated by direct excitation and by fluorescence from the upconversion unit. The probe is also attenuated by transmission through the cell so the second signal, which is the one of interest, is collected with a reduced signal to noise ratio.

In addition to the unusual optical structure, the detected signal depends upon many properties of the cell itself. Most pressing is the EQE contrast mentioned in Chapter 6, but also the optical transmission and photostability of the cell can alter the measured current for an upconverter unit with unchanging performance. In short, the results obtained in the enhancement experiment depend on both components of the solar cell-upconverter couple, whether or not the experimentalist wishes it were so. For example, in experiments carried out by Dr Cheng the FoM for solar cell enhancement could be improved without changing the composition of the upconversion unit, but by changing the cell design to increase the transmission of light resonant
with the sensitiser (manuscript in preparation).

This interdependence of components is well and good (indeed, required) for the solar cell enhancement study — since the objective is to measure the enhancement of a specific solar cell by a specific upconverter — but it complicates a study interested only in the upconverter performance, and makes difficult the comparison of different upconverters sans influence from the solar cell. This restriction in the enhancement experiment led to the creation of a similar experiment, in which the solar cell is removed and photoluminescence from the excited upconverter is measured as in a regular photoluminescence experiment. This chapter details the evolving design of this experiment, the modifications in modelling and analysis compared to the enhancement experiment, and some results from the system.

7.2 Upconverter Action Spectrum

As stated in the introduction, a simple modification to the solar cell enhancement experiment yields what we term the upconverter action spectrum experiment. The solar cell is removed, and instead the upconverter fluorescence is measured using a conventional photodetector arrangement. The necessarily high optical density of upconverting samples makes the use of front-face fluorescence detection geometry preferable to the standard 90° arrangement of many fluorometers. Thus, the new detection arm of the experiment is arranged to view the illuminated face of the sample, while avoiding specular reflections of the excitation source.

As in the enhancement experiment, excitation is by the pump and probe beams, which now focus directly onto the upconverter. As before, the pump beam biases the upconverter efficiency by creating a background population of triplet-excited emitters. Now — much like in a normal fluorescence excitation experiment — the probe beam is scanned over the absorption range of the sensitiser and emitter, while the emitter fluorescence response is recorded. The action spectrum therefore shows the intensity of emitter fluorescence generated by excitation of the sensitiser and the emitter under the bias conditions set by the pump beam.

The action spectrum method has a number of benefits compared to the solar cell enhancement experiment. Primarily, removing the solar cell from the upconverter allows for the direct comparison of prompt fluorescence and delayed fluorescence, generated by excitation of the emitter and the sensitiser, respectively. This is exceedingly useful for determining the qualitative and quantitative efficiency of the upconversion mechanism, since the prompt fluorescence acts as a reference for the optical collection efficiency of the experiment. This will be discussed further throughout the chapter.

Another advantage of the action spectrum compared to the solar cell enhancement experiment is that of acquisition time. A deactivated-upconverter baseline measurement is still required for the upconverter portion of the spectrum, to eliminate pump-independent signals due to probe scattering and remnant white light in the probe beam. But no pump-probe misalignment is required to obtain the baseline measurement, as long as the dynamic range of the detector
CHAPTER 7. UPCONVERTER ACTION SPECTRUM

Figure 7.1: The action spectrum experimental setup. A laser-driven xenon lamp (1) generates a broadband incoherent beam which is UV-filtered, collimated, telescoped, then split in a polarising beam splitter cube (2) to create the pump and probe beams. The pump is telescoped and attenuated with a variable neutral density filter wheel (3), then directed through a chromatic filter (4) and into a second beam splitter cube (5). The probe beam passes through a chopper wheel (6), a monochromator (7), then 4% of the beam is split into a reference photodiode (8) while the remainder enters the second beam splitter. The re-combined pump and probe beams are focused into the upconverter sample (9). Emitter fluorescence is imaged into a second monochromator (10) with an attached PMT (11).

is sufficient to maintain a linear response over the full range of the measured signal.* Rather, the baseline is recorded with the pump beam blocked, then the same baseline is applicable to all the collected spectra in that data series. Compare this situation to the solar cell enhancement experiment, where the pump and probe beams must be misaligned to record a background for every pump energy measured.

7.2.1 Setup

The original design of the action spectrum experiment closely mimicked that of the solar cell enhancement experiment, but for the removal of the solar cell and the addition of the photoluminescence detection arm. In the current setup, depicted in Figure 7.1, the design of the experiment has been extensively revised. The light source is a high-intensity laser-driven xenon lamp (Energetiq EQ1500), which now generates both the pump and probe beams. The laser-driven lamp has greater plasma density and stability compared to a standard electrode-driven lamp.

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*This is easily testable, and if necessary the photoluminescence signal can be optically attenuated prior to detection.
arc lamp design, which gives the lamp improved brightness and beam stability.

Off-axis replicated parabolic mirrors are used throughout the setup to minimise wavelength-dependent changes in the pump-probe overlap and general beam alignment. The lamp output is highly diverging with numerical aperture of 0.5, so is collimated by the first optic at a large beam diameter. Hence the beam is directed through a telescope arrangement to halve the beam diameter prior to splitting within a polarising beam splitter cube.

The two beams constitute the pump and probe. The pump is telescoped a further time, and a variable neutral density filter wheel is situated at the telescope focus. The beam is then directed through a long-pass filter (imparting the pump spectrum) and towards a second beam splitter cube. Meanwhile, the probe beam is focused through a chopper wheel and into a monochromator at $f/4$, then re-collimated and directed into the second beam splitter. The pump and probe beams are thus recombined with the probe beam diameter twice that of the pump. A final off-axis parabolic mirror focuses the two collinear beams into the upconverter sample. The distance between the optic and the sample changes the spot size of the beams, which gives a degree of control over the pump intensity in addition to the variable filter on the pump beam. The relative beam diameters ensures that the probe beam is always focused within the pump.

The optical setup allows imaging of the incoherent lamp plasma onto the sample surface. Thus, uniform-intensity incoherent pump biasing can be obtained by beam expansion, yielding a uniform pump spot in the probed area, and a correspondingly lower solar concentration factor. Because the pump beam is incoherent, the polarising optics approach to beam attenuation is more difficult to implement without introducing beam-steering, which defeats the purpose of the improved beam stability. Instead, the pump intensity is controlled by a variable neutral density filter wheel situated in the focal plane of the pump beam telescope. The net effect of the new light source and achromatic optics is greatly improved beam stability and signal-to-noise ratio. This allows accurate measurement of the upconversion response at and below device-relevant excitation conditions.

**Detection arm changes**

As well as changes to the beam generation optics, the design of the detection arm went through several iterations during the development of this experiment. The first version of the experiment was slated as a 2D experiment, where the full emitter fluorescence spectrum is collected for each probe wavelength. By doing this we hoped to monitor any changes in the emitter fluorescence spectrum that would signify sample degradation, hot band excitation, and relative intensity shifts that would signal increased reabsorption of upconversion generated deeper within the sample. But several iterations of this 2D experiment, first using a USB spectrometer then a more sophisticated spectrograph plus CCD array detector, failed on such bases as slow readout, response hysteresis, and non-linear responses.
Hence, the current action spectrum experiment reported herein instead uses *quasi*-monochromatic detection based on a detection monochromator coupled to a photomultiplier tube (PMT). It was found that, compared to the attempted 2D setups, such an arrangement achieved a greater dynamic range, could acquire data more quickly, and integrated more easily into the phase-locked detection setup carried over from the solar cell enhancement experiment. To wit, the PMT output takes the place of the solar cell current, and is amplified then fed to the LabView acquisition program *via* the DAQ. The recorded signal is again phase-locked to the probe beam chopper wheel frequency. To be sure, 2D detection is a desirable feature to have, but the simpler 1D system has sufficient merit to carry the first working version of the experiment.

All work reported in this chapter was carried out using the incoherent pump beam version of the setup, with 1D fluorescence detection by the PMT.

### 7.2.2 Data collection

Preparing for the measurement of an action spectrum involves evacuating the upconverter sample using standard techniques, setting the detector monochromator to the peak emission wavelength of the emitter, and setting suitable pump conditions (spectrum and intensity) by adjusting the chromatic and neutral density filtering of the pump beam. A full action spectrum is then recorded by scanning the probe wavelength over the absorption bands of the sensitiser and emitter. Repeated scans with changing pump intensity allow measurement of the upconversion response to changing bias conditions.

Secondary measurements necessary for quantitative analysis of the data include measurement of the pump spot size, spectrum and power, and measurement of the probe beam power at each step of the action spectrum scan. The pump spectrum is recorded using a USB spectrometer (Ocean Optics), then the power is measured using a calibrated silicon photodiode and power meter (Newport 918D-SL-OD3, 2936-C), set to the flux-averaged center wavelength of the pump spectrum to minimise the effect of wavelength-dependent photodiode responsivity. The spot size is measured as described in Section 4.5.3.

These measurements are typically made after collection of the action spectra. The pump spot size, pump spectrum, and the sensitiser absorption cross-section are required to calculate the front-surface sensitiser excitation rate $k_{\phi_b}$ for each pump power, which leads to the calculation of $f_c$. A simple addition to the standard calculation is made to account for the broadband pump spectrum, whereby the pump beam spectrum, power, and spot size are first used to calculate $\rho_b(\lambda)$, the calibrated spectrally-resolved pump beam photon flux, which then enters Equation 1.1 to calculate $k_{\phi_b}$, as normal.

Once more, $f_c$ is then calculated as $k_{\phi_b}/k_{\phi_{sun}}$. Prior to analysis, action spectra are normalised by the probe beam photon flux recorded at the sample position.
7.3 Analysis of Action Spectra

The various methods by which action spectra may be analysed are presented below.

7.3.1 Qualitative: Response peak height

The simplest action spectrum study is to measure the height of the spectrum in the sensitiser absorption region for a range of pump biases, and compare this to the height of the directly-excited emitter response. Clearly, a larger relative upconversion peak implies greater upconversion efficiency. Multiple samples with the same emitter concentration can be compared to gain a relative indication of the upconversion efficiency, the direct emitter response acting as an internal standard to which the upconversion response can be reliably compared (for a given bias) even with sample replacement, setup changes, and so on. The growth in the sensitiser response band with pump intensity likewise can be used to indicate the relative power response of each system.

As in the enhancement experiment, growth in the probe beam response with pump intensity is proportional to the derivative of the response curve, so at low light levels the growth of the upconversion portion of the action spectrum should be linear with pump energy, directly reflecting the efficiency. Any flattening-out of this growth at higher pump energies signifies the onset of the linear-response regime.

7.3.2 Quantitative: Modified dual beams model

The action spectrum measures emitter fluorescence generated by upconversion and by direct excitation of the emitter. The source of the technique’s usefulness is being able to compare the response from both generation pathways and infer the efficiency of the upconversion route compared to emitter fluorescence. Comparison of the gross peak heights, as discussed in the previous section, is sufficient to infer relative efficiency between similar samples and bias conditions. But in order to obtain an absolute measure of the upconversion efficiency, optical modelling of the sample is required.

In order to do this the dual beams model introduced in Chapter 6 is modified to reproduce both generation methods on a comparable basis. The constants of proportionality are removed and instead both generation methods are modelled without implicit proportionalities. In addition, reabsorption is incorporated into both generation systems, which is crucial for accurately reproducing the direct excitation portion of the spectrum.

Upconversion portion of the action spectrum

This derivation begins much like that of the dual beams model from Chapter 6, but retains strict equality throughout and takes account of the effect of optical density on the response measured by the system.
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Starting from the expression for the generation of emitter triplets within a volume element at a depth \( z \) within the sample, we assume the low-efficiency regime in which most triplets decay through the first-order channel:

\[
k_\phi(z)N_s = k_1N_t(z)
\]

\[
\therefore N_t(z) = \frac{k_\phi(z)N_s}{k_1}, \tag{7.1}
\]

where \( N_s \) is the sensitiser concentration and \( N_t(z) \) the depth-dependent triplet-excited emitter concentration.

The intensity of the upconversion response generated per volume element, \( I_{UC}(z)/dz \), depends on the population of singlet-excited emitters, which itself is determined by the square of the local triplet concentration and the second-order rate constant:

\[
dI_{UC}(z) = 0.5k_2N_t^2(z)\eta_c dz. \tag{7.2}
\]

The factor of 0.5 accounts for the 2 to 1 annihilation of triplets to singlets, and \( \eta_c \) is the likelihood that emitter TTA yields the singlet-excited state. Combining these two expressions gives

\[
I_{UC}(z) = k_2N_t^2(z)\frac{N_s^2\eta_c}{2k_1^2} dz, \tag{7.3}
\]

which is the in-situ intensity of upconversion generated at depth \( z \). To convert this to the measured quantity, we need to consider the sources of excitation, and the attenuation of light reaching depth \( z \) and returning to the cuvette surface.

As in the previous dual-beams model, the excitation rate has contributions from both the probe beam and the bias beam. The excitation rate at \( z \) depends on the attenuation of both beams on their path to that depth, while in a new addition to this model, the intensity of the returned light also depends on reabsorption:

\[
I_{UC}(z) = k_2N_t^2(z)\frac{N_s^2\eta_c}{2k_1^2} \frac{\left[ k_\phi_b(0)\exp(-\alpha_b^p z) + k_\phi_b(0)\exp(-\alpha_b^s z)\right]^2}{\exp(-\alpha_p^l z)} dz, \tag{7.4}
\]

where \( \alpha_b^p \) and \( \alpha_b^s \) are the absorption coefficients of the probe and bias beams in the medium. Although the data reported in this chapter was collected using relatively broadband incoherent pumping, we retain the use of a single bias beam \( \alpha \) value for simplicity. As long as the pump beam is still strongly resonant with the sensitiser Q-band, the beam attenuation is akin to that of a single-wavelength beam and this treatment suffices. The pump beam spectrum can be
modified using optical filters to satisfy this condition.

The term \( \alpha_{pl}^e \) is the emitter absorption coefficient at the detection wavelength. This accounts for the reabsorption of emitter fluorescence on the path back towards the detector. The single term here belies a more complex wavelength-dependent transmission of fluorescence through the emitter medium, but because the detector is viewing only a narrow bandwidth of the fluorescence spectrum the approximation is good. No factor is included here to account for possible absorption by the sensitizer, which is acceptable in the case of a sensitizer with an absorption window well-matched to the emitter fluorescence spectrum. We also assume that reabsorbed fluorescence is not re-emitted into detectable paths, which considering the refractive index mismatch of the cuvette-air interface should be true in at least 75% of cases.

Integrating Equation 7.4 over \( z \) gives the upconversion intensity emitted from the cuvette surface:

\[
I_{UC} = \frac{k_2 N_s^2 \eta_c}{2k_1^2} \int_0^\infty dz \, k_{\phi b}^2 \exp[-z(2\alpha_b^s + \alpha_{pl}^e)] + k_{\phi p}^2 \exp[-z(2\alpha_p^s + \alpha_{pl}^e)] + 2k_{\phi b} k_{\phi p} \exp[-z(\alpha_b^s + \alpha_p^s + \alpha_{pl}^e)],
\]  

(7.5)

where \( k_{\phi} = k_{\phi}(0) \), truncated for convenience. Evaluating the integral produces

\[
I_{UC} = \frac{k_2 N_s^2 \eta_c}{2k_1^2} \left[ \frac{k_{\phi b}^2}{2\alpha_b^s + \alpha_{pl}^e} + \frac{k_{\phi p}^2}{2\alpha_p^s + \alpha_{pl}^e} + \frac{2k_{\phi b} k_{\phi p}}{\alpha_b^s + \alpha_p^s + \alpha_{pl}^e} \right].
\]  

(7.6)

Before simplifying this expression, we recognize that much like in the solar cell enhancement experiment, the detected signal is that which is generated by the probe beam. The first term in Equation 7.6 has no dependence on the probe beam, and can thus be ignored. The second term can also be ignored because it depends only upon the probe beam, which produces a very weak upconversion response. Only the third term, where the probe and bias beams both contribute, is relevant to the experiment.

The remaining term is simplified gradually using the following set of expressions:

*For instances of emitter fluorescence being attenuated by more than reabsorption, the optical density of the medium would be used instead of that of the emitter alone.
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\[ k_{\phi_b} = \sigma_b I_b, \quad k_{\phi_p} = \sigma_p I_p \]  
(7.7)

\[ \alpha_b = \sigma_b N_s, \quad \alpha_p = \sigma_p N_s \]  
(7.8)

\[ N_{t_0} = \frac{k_{\phi_b} N_s}{k_1}, \]  
(7.9)

and

\[ f_{2_0} = \frac{k_2 N_{t_0}}{k_1}. \]  
(7.10)

where \( N_{t_0} \) and \( f_{2_0} \) are at the front of the cuvette. Applying Equation 7.7 to the simplified form of Equation 7.6 gives

\[ I_{UC} = \frac{k_2 N_s^2 \eta_c}{k_1} \left[ \frac{I_b \sigma_b I_p \sigma_p}{\alpha_b^s + \alpha_p^s + \alpha_{pl}^s} \right], \]  
(7.11)

then taking the derivative with respect to \( I_p \) to recreate the effect of phase-locking measurement to the probe beam, and employing Equations 7.7 and 7.8, gives

\[ \frac{dI_{UC}}{dI_p} = \frac{k_2 N_s \eta_s}{k_1} \left[ \frac{k_0 \alpha_p^s}{\alpha_b^s + \alpha_p^s + \alpha_{pl}^s} \right]. \]  
(7.12)

Finally, making use of 7.9 then 7.10:

\[ \frac{dI_{UC}}{dI_p} = f_{2_0} \eta_c \left[ \frac{\alpha_p^s}{\alpha_b^s + \alpha_p^s + \alpha_{pl}^s} \right], \]  
(7.13)

\[ = \phi_{TTA} \left[ \frac{\alpha_p^s}{\alpha_b^s + \alpha_p^s + \alpha_{pl}^s} \right], \]  
(7.14)

where \( \phi_{TTA} \) is the TTA yield of singlet states at the cuvette surface, the ultimate variable of interest.

Direct excitation portion of the action spectrum

Equation 7.14 alone is insufficient to determine \( \phi_{TTA} \) from an action spectrum, since the experiment scaling factor is undetermined. The direct emitter excitation region of the action spectrum provides the necessary reference. This response is linear and independent of the bias beam, which simplifies the model of the response.

Prompt fluorescence generated per volume element at depth \( z \), \( I_f/dz \) will reach the cuvette
surface with intensity

\[
dI_f = N_e \left[ k_{\phi_p} \exp(-\alpha_p^e z) \exp(-\alpha_p^s z) \exp(-\alpha_p^{el} z) \right] dz \tag{7.15}
\]

\[
= N_e \left[ k_{\phi_p} \exp(-z(\alpha_p^e + \alpha_p^s + \alpha_p^{el})) \right] dz \tag{7.16}
\]

where \( N_e \) is the emitter concentration, and \( \alpha_p^s \) is the absorption coefficient of the probe due to the sensitiser, which often has strong absorption features in the blue portion of the spectrum. Once again, the model of reabsorption used here is a simplification, but justified by the narrow detection bandwidth and the sensitiser absorption window. Integrating over \( z \) gives

\[
I_f = \frac{N_e k_{\phi_p}}{\alpha_p^e + \alpha_p^s + \alpha_p^{el}}. \tag{7.17}
\]

Applying Equations 7.8 then 7.7 gives

\[
I_f = \frac{I_p \alpha_p^e}{\alpha_p^e + \alpha_p^s + \alpha_p^{el}}, \tag{7.18}
\]

which yields the derivative with respect to probe intensity,

\[
\frac{dI_f}{dI_p} = \frac{\alpha_p^e}{\alpha_p^e + \alpha_p^s + \alpha_p^{el}}. \tag{7.19}
\]

Thus we obtain a model for the prompt component of the action spectrum.

**Fitting function**

The fitting function is produced by combining the upconversion and prompt fluorescence portions of the model (Equations 7.14 and 7.19, respectively). Two free parameters are used in fitting the just-derived model to action spectra: \( \phi_{TTA} \), and a scale factor, \( A \). In generating the model, only the absorption cross-section and concentration are required. More complex optical systems will likely require greater complexity, but at least in this simple case of a bulk liquid upconverter there is a pleasing scarcity of parameters. The completed model is thus:

\[
f(\lambda) = A \left[ \frac{\alpha_p^e(\lambda)}{\alpha_p^e(\lambda) + \alpha_p^s(\lambda) + \alpha_p^{el}} + \phi_{TTA} \frac{\alpha_p^s(\lambda)}{\alpha_p^s(\lambda) + \alpha_p^s(\lambda) + \alpha_p^{el}} \right], \tag{7.20}
\]
7.3.3 Internal vs external referencing

The just-derived model can be used to determine $\phi_{TTA}$. But the actual yield of light generated through TTA-UC is given by $\phi_{TTA} \cdot \phi_{PL}$, where $\phi_{PL}$ is the fluorescence quantum yield of the emitter. Determining this quantity requires a step outside of internal referencing, and a measure of either $\phi_{PL}$ or the real photon yield from the excited sample.

The emitter $\phi_{PL}$ can be located in the literature, although most reported measurements are for much lower concentrations than those used in TTA-UC systems. Alternatively, the yield may be measured directly using a photoluminescence quantum yield technique such as that of Rohwer and Martin. The procedure for carrying out this measurement is given in Appendix H.

Another approach to determining the absolute photon yield of the sample is agnostic in its approach to mechanisms and formalism. The real photon yield of the measured system can be determined directly, by calibrating the detector response of the action spectrum experiment against a known photon flux. By replacing the action spectrum sample with an identically-positioned Lambertian scatterer, then scanning the probe beam over the detection wavelength, the detector voltage measured in the experiment can be equated to an actual photon flux (the probe beam flux at the sample position is measured as part of the routine experiment). Comparison of the detection window to the sample emission spectrum gives a scaling factor that accounts for fluorescence wavelengths outside of the detection window. Then, the measured voltage can be scaled, converted to photon flux, and compared to the incident flux of the probe beam to yield the actual EQE of the system — the real proportion of incident photons that cause the emission of sample fluorescence from the cuvette face.

Of course, there are a host of assumptions that accompany such a determination of the EQE, and the attractive simplicity of internally-referenced intensity comparisons is lost. Crucially, the technique for swapping between the sample and the scatterer must be sufficiently robust that the flux calibration remains accurate throughout the experiment. But if this can be made so, the scatterer-calibrated technique is a valuable link between the internal photochemical behaviour revealed by the basic action spectrum and the absolute photon yield from the sample, which is ultimately of equal relevance for device applications.

7.4 Action Spectrum of an Isotropic Liquid Upconverter

In this section, an internally-referenced action spectrum experiment performed on a real system is described. The sample preparation and the full gamut of measurements required for a fully-quantified measure of $\phi_{TTA}$ are given. Finally, results and their analysis using the internally-referenced dual beams model from Section 7.3 are presented.
7.4.1 Sample preparation and measurement

A liquid upconverter was prepared by dissolving Q$_4$PdPNA (0.58 mM) and rubrene (11 mM) in toluene. The structures and spectra of both species are shown in Figure 7.2. The solution was degassed using the freeze-pump-thaw method then permanently sealed inside a 2 mm path-length glass-stemmed quartz cuvette with half the cuvette volume filled by 100 µm-diameter silver-coated glass spheres. The spheres are a simple method of obtaining an approximate optical cavity effect as they pack together with upconverting solution in the interstitial sites. As reported in a 2012 publication, their use caused an approximate doubling of the cell enhancement figure of merit. The optical cavity effect allows double-passing of excitation light that would otherwise propagate deep into the bulk solution, while also increasing the fraction of generated photoluminescence that is returned to the front of the upconverter.

Action spectra measurements

Two sets of action spectra, one for each portion of the sealed sample, were measured under identical pumping conditions. The lamp output was long-pass filtered to remove ultraviolet wavelengths, and an IR absorber attenuated wavelengths beyond 800 nm. The pump arm was directed into a 610 nm long-pass filter, which generated a broadband pump beam resonant with the sensitiser Q-band. The probe beam was chopped at 532 Hz.

The detection monochromator was set to an emission wavelength of 555 nm and the incident light was band-pass filtered to reduce scatter. The monochromator slit width and the PMT sensitivity were adjusted so that the most intense signal measured (full pump intensity, direct emitter excitation at 475 nm) was well within the linear response range of the detector. The PMT output was amplified using low-noise mode without additional electronic filtering, then the amplifier output was read by the DAQ.

The upconverting portion of the action spectrum (600-780 nm), defined by the absorption
range of the sensitiser Q-band, was recorded for a range of pump powers by varying the neutral density filter wheel. Then the full scan range (400-780 nm) was recorded twice, for maximum and zero pump intensity, allowing a fit using the dual beams model and calibration of the Q-band scans. The current amplifier scale was changed between the two series to allow the larger signal generated by direct emitter excitation to sit within the voltage read limit of the DAQ. But since identical biasing conditions were used for the highest-intensity Q-band scan and the pump-on full wavelength range scan, the two scales were easily corrected for when processing.

**Additional measurements**

Following data measurements for both regions of the sealed upconverter sample came the others necessary for a quantitative analysis of the data. As described in Section 7.2.2, the pump spectrum, spot size, and power were measured at the sample position; the power measurement was repeated for each filter setting. Finally, the probe beam spectrum at the sample position was measured for the full scan range using the same calibrated photodiode and power meter. The extinction spectrum of both chromophores was known from previous experiments.
Full action spectrum recorded at a solar concentration factor of 3.2. Fitting is by the modified dual beams model. The Q-band region is scaled up by a factor of 52. $\phi_{TTA}$ extracted from this fit is 0.035. The lamp filtering conditions cause the signal to noise ratio to sharply decline at the edges of the scan, which partly explains the deviations there. The signal spike at 550 nm is due to scatter of the probe beam into the detector; this portion of the data was ignored during fitting.

$\phi_{TTA}$ plotted with respect to the solar concentration factor. The red line is a linear fit to the data, the inset shows the progression on a linear scale. The dashed lines indicate the expected $\phi_{TTA}$ value under standard solar illumination.

**Figure 7.4:** Action spectrum results for the Q$_4$PdPNA plus rubrene upconverter
7.4.2 Results

Clear solution

To calculate $\phi_{TTA}$, both direct and upconversion portions of the action spectrum must be collected under identical conditions. As long as the direct-excitation portion of the action spectrum is demonstrably independent of the pump beam intensity, it is sufficient to measure just one full range action spectrum at a known pump bias, then measure for that same bias and then all others of interest only over the upconversion region. The $\phi_{TTA}$ value for each pump bias can then be inferred by comparison to the full-wavelength range scan result. This proved to be the case for this system, so Equation 7.20 was fitted to the full range action spectrum to yield $\phi_{TTA}$ for full pump power, then the progression of the Q-band response with changing solar concentration factor allowed the calculation of $\phi_{TTA}$ for the other pumping conditions.

Figure 7.3 shows the action spectra series collected over the sensitiser Q-band for a range of solar concentration factors. The impressive sensitivity of the experiment is evident in the definition of the spectra, despite their collection at such low concentration factors. Spectra were fully reproducible throughout the experiment, demonstrating good light-source and sample stability.

The full-wavelength range scan is shown in Figure 7.4a, fitted using Equation 7.20. The good agreement between the data and fit suggests that the modified dual beams model has successfully captured the main components of the system. The fit extracts a $\phi_{TTA}$ value of 0.035 under the measured $f_c$ of 3.2 suns.

Scaling the result for $\phi_{TTA}$ obtained from fitting to the full wavelength scan by the relative integral over the higher-resolution Q-band scans from Figure 7.3, the progression of $\phi_{TTA}$ with concentration factor was obtained. This is shown in Figure 7.4b. A linear fit to this data series returns the relation $\phi_{TTA} = \text{slope} \times f_c$. The slope obtained is $(1.09 \pm 0.01) \times 10^{-2}$, hence the estimated $\phi_{TTA}$ value of this system under one-sun illumination is $1.09(1)\%$.

Ag bead microcavities

Analogously to the clear solution result, the full wavelength range scan and the fit of Equation 7.20 are shown in Figure 7.5a. Compared to the previous result, the enhancement seems to be significantly increased by the silver-coated beads. The fitted model returns a $\phi_{TTA}$ value of 0.13 at 3.2 suns, an improvement of approximately 3.7 times and roughly double the enhancement reported in the solar cell enhancement experiment. This may relate to the use of broadband pumping in this experiment compared to the 670 nm laser diode pump of the earlier work. The broadband pump beam has a much greater spread of wavelengths, which will be absorbed less strongly than the peak-resonant 670 nm beam and consequently experience longer path lengths through the solution. The double-passing cavity effect may therefore produce a greater return of otherwise-lost pump light in the broadband pump experiment.
(a) Fitted action spectrum for the silver bead microcavity upconverter measured at $f_c$ of 3.2 suns. The Q-band inset is zoomed in by 14 times compared to the full spectrum. The microcavity causes a significant enhancement to the measured upconversion yield, due to the optimised double-passing of sensitizer-resonant light. $\phi_{TTA}$ is 0.13 at 3.2 suns, a factor of 3.7 times greater than the bulk liquid system.

(b) $\phi_{TTA}$ plotted with respect to $f_c$. The inset shows the plot on a linear scale. The highest-intensity point, fitted as shown in the figure above, is well above the trend extrapolated from the lower-intensity points, for an unknown reason.

Figure 7.5: Action spectrum results for the silver-coated bead microcavity upconverter
However, an anomaly is found upon examination of the Q-band action spectrum response, so we cannot say for certain the exact extent to which the silver beads increase the output. Upon plotting the integral of each Q-band response against $f_c$, we find that all the points except that of the highest-intensity pump, used in determining $\phi_{TTA}$, fall nicely onto a straight line. The highest $f_c$ point deviates clearly from this trend, showing a higher-than-predicted response in three repeated measurements.

The model fit to this data point is good, so the $\phi_{TTA}$ value returned is not in dispute. Scaling this value by the relative integral over the Q-band scans returns the $\phi_{TTA}$ values with respect to $f_c$ shown in Figure 7.5b. Ignoring the apparently anomalous point, a linear model fit to the remaining lower-intensity points has a slope of 0.0261(3), leading to a one-sun $\phi_{TTA}$ prediction of 2.6%, much closer to the doubling in efficiency found in the enhancement experiment. The trend including the highest-intensity point has a slope of 0.041, but is poorly fit to the data.

The discrepancy of the highest-intensity point is puzzling. For one, the good fit between the model and the data suggest that trivial errors such as a baseline offset or a bad flux normalisation are not to blame. The series of pumping conditions used was identical for these and the clear solution measurements, so error in the calculated $f_c$ value of the point should have produced anomalies in both data sets, which is not the case. The anomalous point was measured in triplicate to check sample stability: once before, once during and once after measuring the remainder of the points, and the results coincide each time.

### 7.4.3 Discussion

The action spectrum and accompanying optical modelling have been shown to be a rapid technique for the determination of triplet-triplet annihilation yields in upconverters under device-relevant conditions. To check the veracity of the values returned, a calculation of the expected yield in the clear-solution system was carried out using Equations 7.9 and 7.10, and $\phi_{TTA} = f_2 \eta_c$. From the experiment, $k_\phi = 21.8 \text{s}^{-1}$ (corresponding to $f_c = 3.2$), and $N_s = 5.8 \times 10^{-4} \text{M}$. The remaining rates and coefficients were taken from reports for a similar upconverter in [Auckett, 2009] and [Cheng, 2010]: $k_1 = 9000 \text{s}^{-1}$, $k_2 = 1 \times 10^8 \text{M}^{-1} \text{s}^{-1}$, and $\eta_c = 0.6$. This returns a predicted $\phi_{TTA}$ value of 0.012 at 3.2 suns, which is in excellent agreement with the value extracted from fitting to the action spectrum. It is worthwhile noting the considerable effort expended on determining these parameters, without which the theoretical prediction of $\phi_{TTA}$ for this system would be impossible.

The optical cavity effect introduced by the silver-coated microbeads breaks the assumptions underlying the simple theoretical calculation. Nonetheless, the agreement between the augmentation effect of the beads measured in this experiment and the earlier solar cell enhancement experiment is reassuring, notwithstanding the anomalous high-intensity point that is yet to be explained.

The dual-beams optical model advanced in Section 7.3.2 makes several simplifying assump-
tions regarding reabsorption and the attenuation of the spectrally-broad incoherent pump beam. Nonetheless, the good match between the experimental data and the model suggest they have not severely impacted the model’s accuracy. Certain changes to the experiment may yet diminish the model’s effectiveness, such as if the pump bandwidth is further increased or shifted significantly off-resonance with sensitiser absorption bands, or if 2D fluorescence detection is reintroduced such that the single-wavelength reabsorption approximation becomes insufficient, or likewise if a sensitiser that significantly absorbs emitter fluorescence is used. The model could, however, be made amenable to such situations with only a handful of changes.

7.4.4 Note on the action spectra of solid materials

Along with the problems with solar cell enhancement as a method of upconverter study, another motivation for developing the action spectrum experiment was to measure the actual upconversion yields of solid-tethered upconverters. As discussed in Chapter 5, kinetics data from pulsed laser experiments cannot be easily used to infer actual photon yields under device-relevant conditions. An experiment such as the action spectrum, free of the requirements of an EQE contrast and so on, is ideal for doing so.

Unfortunately, the solid systems available during work on the action spectrum setup produced upconversion responses so weak as to be unmeasurable, in spite of the excellent low-intensity measurements already made using the laser-driven lamp and achromatic optics. In particular, we attempted unsuccessfully to measure upconversion from the four APTES\textsubscript{3,4}TPPdP on silica systems described in Chapter 5, thus indicating the extensive performance gap between these materials and the liquid upconverters thus far studied without issue. The Q\textsubscript{4}PdP-silica material responsible for the successful solar cell enhancement measurement was depleted, but will be measured once replaced.

7.5 Action Spectrum using External Calibration

In the final portion of this chapter, we turn to the externally-calibrated yield experiment to study the optical properties of the upcoverter. The externally-calibrated measurement is sensitive to the emitter fluorescence quantum yield and outcoupling efficiency, which the action spectrum itself is blind to, since measurement is always made relative to the emitter fluorescence. External referencing can thus be used in conjunction with the regular action spectrum to determine the source of low upconverter performance and the target for device improvement, whether it be poor upconversion efficiency (revealed by the action spectrum), poor optical engineering (revealed by external referencing), or both.


7.5.1 Sample preparation and measurement

The same sealed upconverter from Section 7.4 was used. Both the clear solution and the silver-coated bead regions were studied in separate measurements.

Action spectra measurements

The detector slit width and PMT amplification were adjusted such that a linear response was obtained at the maximum signal level, corresponding to full pump intensity and direct emitter excitation at 475 nm. The detection wavelength, pump spectrum and so on were identical to the action spectrum experiment in Section 7.4. As in the previous experiment, action spectra over the Q-band region then the full wavelength range were measured for a range of pump energies, and with the pump fully deactivated to allow backgrounding.

Additional measurements

Following the data measurements, the system response was calibrated. A thin white card was placed over the sample cuvette and the probe beam was filtered with a 5% transmission neutral density filter. Without changing any other aspect of the setup, the probe beam was scanned with 1 nm increments over the detection window.

After calibration, the usual action spectrum quantification measurements were carried out. The pump beam spectrum, spot size and powers were measured, along with the sample emission spectrum. Then the probe beam spectrum was recorded over the full scan range with the usual 5 nm wavelength increment, and again over the calibration region with 1 nm increments with the 5% transmission neutral density filter re-inserted. In this way the incident flux during the calibration measurement was determined.

7.5.2 Results

The flux calibration is a way to tie a voltage measurement in the detection apparatus to the real photon flux generated at the sample. Hence, the peak phase-locked $r$-value of the detector measured during scattering calibration, normalised by the incident probe beam flux, was equated to the incident photon flux recorded at that wavelength, assuming ideal Lambertian scattering by the white card. This constant $\gamma$ was $2.18 \times 10^{13}$ photons V$^{-1}$.

The unitless scale factor $\chi$, accounting for wavelengths of the sample fluorescence spectrum that are outside of the detection window, was calculated as the ratio of the integral over the normalised sample emission spectrum to the integral over the normalised detector response. This yielded $\chi = 6.75$. To calculate the so-called ‘raw’ EQE (photons in/photons out) of the upconverter, action spectra were normalised by the incident flux, then multiplied by $\gamma\chi$.

Externally-calibrated action spectra for the Q-band portion of the data are shown in Figure 7.6a, with the progression and linear model fitting shown in Figure 7.6b. All points lie approxi-
CHAPTER 7. UPCONVERTER ACTION SPECTRUM

(a) Raw EQEs for the Q-band portion of both samples.

(b) Progression in peak Q-band EQEs with concentration factor

Figure 7.6: Q-band results for the externally-calibrated action spectrum experiment
CHAPTER 7. UPCONVERTER ACTION SPECTRUM

Figure 7.7: Raw EQEs for the direct emitter excitation portion of the externally-calibrated action spectrum. The longest-wavelength point of the red trace is raised due to probe scatter.

approximately along the linear fit, which has an intercept of zero within error. Using the slope of the fit leads to predicted raw EQEs at \( f_c = 1 \) of 0.29% and 0.84% for the clear solution and silver beads samples, respectively. Thus the cavity effect of the beads seems to enhances the upconversion output approximately 2.9 times, or about half-way between the two enhancement factors found in the internally-calibrated experiments.

The direct emitter excitation portions of the action spectra were invariant with pump power, indicating no significant participation of triplet channels in the decay of the directly-excited emitters. The raw EQEs are shown in Figure 7.7. Discounting the scattering contribution, the EQEs peak at 0.25 and 0.42 for the clear and silver bead systems, respectively. The relative enhancement due to the beads is thus a factor of 1.68, or approximately the square root of 2.9. This suggests that the optical cavity effect of the beads increase the concentration of directly-excited emitters and sensitisers to a comparable extent, and the quadratic dependence of TTA-UC results in the larger apparent enhancement of the upconversion response.

7.5.3 Discussion

A discussion of what exactly the raw EQE signifies, and how it relates to the \( \phi_{TTA} \) value of the internally-referenced experiment, is warranted. The raw EQE shows the actual yield of photons emitted from the sample surface, relative to the incident photon flux. The measurement is blind to the mechanisms by which the photon yield is diminished. On the other hand, the internally-referenced action spectrum indicates the real photochemical behaviour of the upconverter with \( \phi_{TTA} \), while itself being blind to the actual yield of photons emitted from the sample. In short, the internally-referenced measurement shows what upconversion yield is achievable for the given
upconverter chemistry, and the externally-referenced measurement shows what yield is actually achieved, given the chemistry and the optical setup.

Scaling the raw EQEs to account for the estimated losses from non-outcoupling emission brings the peak raw EQEs into agreement with measured $\phi_{TTA}$ values. Based on the work on LSCs documented in Chapters 2 and 3 of this thesis, we can estimate that in the clear liquid system approximately 25% of fluorescence photons leave the upconverter through the front escape cone, while the rest are emitted into waveguide modes in the higher-index solution/cuvette and do not escape. Hence the raw EQEs from the clear solution should be multiplied by 4 to estimate the real photon yield. For the direct emitter excitation, this gives a peak EQE of unity, while the upconversion component reaches an ‘optimised’ EQE of 0.012 at $f_c = 1$, in good agreement with the $\phi_{TTA}$ value measured in the internally-referenced experiment.

Predicting the achievable optimised EQE for the silver beads system is less straightforward, because the optical cavity interferes with the otherwise-simple estimate of the fraction of non-outcoupled fluorescence. But a prediction is possible by scaling the peak of the prompt fluorescence EQE to unity, then scaling the Q-band response by the same. Doing so gives a Q-band peak EQE of 0.020 at $f_c = 1$, slightly less than that predicted from the internally-referenced measurements.

The veracity of the externally-calibrated measurement depends heavily on the care with which the scatter calibration is carried out. In particular, small misalignments between the sample and the scattering layer can have a large effect on the calibration. Consequently the yields obtained in this portion of the work are to be considered less reliable than those found using internal referencing, which by design is insensitive to changes in the optical setup. In future iterations of the scattering-calibration experiment, we will make use of an integrating sphere to curtail the acute sensitivity to sample positioning and alignment.

7.6 Conclusions

The action spectrum experiment was brought about by a simple modification to the solar cell enhancement experiment. This new measurement technique circumvents the problems associated with measuring upconverter performance by way of solar cell enhancement. The improved version of the dual excitation beams optical model developed herein allows quantification of the upconversion yield measured with respect to the emitter fluorescence quantum yield. The unconditional comparison of all varieties of upconverters under precisely-determined excitation conditions enabled by this development is a significant step forward in the characterisation of these systems.

The externally-referenced variant of the action spectrum experiment quantifies the actual photon flux emitted from the sample surface. This variant is agnostic towards the actual photo-chemical processes happening within the sample and instead treats the upconverter as a black box. The photon yield indicates the effectiveness of both the fluorescence generation mechanisms
and the outcoupling efficiency. Taken in concert with the internally-referenced variant, in which the first aspect is determined, external referencing reveals the extent to which optical engineering of the system can improve the photon outcoupling and thus, the apparent upconversion efficiency of the system.
Epilogue

Throughout this thesis I have avoided discussing the extensive reasons justifying the need for an urgent acceleration of solar energy research and development. That is not to say that I disagree with the reasons at all, rather I wanted to avoid preaching to the choir. In any case, it is heartening to witness an accelerating worldwide growth in the capacity of installed solar energy.

The contribution towards this effort documented in this thesis concerns the enhancement of solar cell conversion efficiency by modifying the spectrum of sunlight, prior to its absorption within the solar cell, a practice termed ‘spectral management’. Within this field, the particular approach pursued here makes use of molecular chromophores as the light-absorbing and emitting centers. The first topic introduced was luminescence concentration, a process combining photon downshifting and waveguiding that has been seemingly poised on the cusp of commercially-realisable designs for several decades now. The simple premise of the device masks a web of inter-related mechanisms that makes mastering all aspects of the device a significant undertaking. The focus of our work on luminescent concentrators was on the roles that dye alignment and photoluminescence anisotropy play in determining the device efficiency. The anisotropy dephasing-energy transfer mechanism proposed is broadly applicable to luminescent concentrators, and can hopefully play some role in an eventual commercial design. Further work on this system will involve ultrafast studies of the donor electronic dephasing and energy transfer in model dimers, and extending the functionality onto larger energy transfer series.

The remainder of the thesis was concerned with the study and development of TTA-UC materials, photophysics and characterisation experiments. TTA-UC for solar cell enhancement is a much newer research field than luminescent concentrators. Even though we likely do not have four decades to produce a commercial system, the future of the technology looks bright. We began to develop solid-tethered TTA-UC sensitisers on the basis that an upconverter that is efficient at low light intensities needs a high sensitizer concentration, which liquid systems generally forbid through solubility limits and aggregation. Kinetic studies of these materials produced a mass of results that point towards sample heterogeneity and multiple interdependent
variables. These findings emphasise the analysis challenges created by removing the statistical
averaging effect of unimpeded Brownian motion. Further work must produce materials with
lower heterogeneity if photoluminescence kinetics modelling is to play a lead role in quantifying
the system behaviour.

But within the work there are results that nonetheless bode well for solid upconverters. In
particular, upconversion in doped solid rubrene crystals seems to be very efficient on a local
scale, and begs for further study. Improved film preparation techniques may yield more uniform
samples and hence a simpler analysis task. Temperature-dependent studies will qualify the
exciton mobility in the sensitised system. It remains to be seen the extent to which singlet
fission in solid rubrene will impact TTA-UC yields, and whether the solid rubrene domain size
can be optimised to favour one process or the other.

A primary question arising from the solid-tethered sensitisers work is whether or not the
photoluminescence recorded in our experiments represents the entirety of the material, or just
an unusually bright subset. Answering this question is a necessary component of explaining
the lacklustre upconversion yields of some of the solid-tethered materials, despite the seemingly
efficient transfer of energy to the emitter. Ultrafast pump-probe studies of the solid-tethered
sensitisers are an obvious next step in attacking this problem: the much-improved temporal
resolution being key to tracking the behaviour of excited states shortly after photoexcitation. If
heavily-aggregated sites truly do play a significant role in the material, this should be detectable
in photoluminescence measurements as a fast decay tapering off to the slow decay detected in this
work, or in transient absorption as long-lived sensitisers states not producing photoluminescence.

Following the kinetics experiments, we reported the first measurement of solar cell enhance-
ment using a solid-tethered TTA-UC system. The extent of the enhancement was comparable to
early experiments using liquid upconverters and is hence not particularly remarkable. But given
that these materials were produced as an initial ‘shot in the dark’, the detection of any enhance-
ment is nonetheless encouraging. Further work in solar cell enhancement will occur in two parts:
improving the upconverter material, and improving the solar cell’s match to the upconverter
absorption and emission properties. Of course, the real objective in the solar cell optimisation
must be to produce a device that makes the best possible use of the available upconverter, while
itself performing as well as possible under solar illumination.

The final work reported in this thesis was the development and testing of a new variety of
upconversion experiment, aimed at measuring the upconversion efficiency under sun-like condi-
tions without interference by a solar cell. The so-called action spectrum experiment turns out to
be rather successful at this, and the TTA yields of two liquid upconverters were measured, with
the results being corroborated by other data. Ongoing work with this system will characterise a
broad range of upconverters, and hone the setup to make maximum use of the stability granted
by the laser-driven lamp and achromatic optics.

It is early days for the action spectrum experiment, for TTA-UC studies, and for spectral
management in general, and it is a safe bet that the best results are ahead of us.
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dynamics of multiple exciton harvesting in the cdsezno system: Electron injection versus


Abbreviations

A table of abbreviations and terms used commonly throughout the thesis is provided for the reader overleaf.
### Table A.1: Abbreviations and units used commonly throughout the thesis

<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_g$</td>
<td>Band gap energy</td>
</tr>
<tr>
<td>AM1.5G</td>
<td>Air Mass 1.5 Global reference solar spectrum</td>
</tr>
<tr>
<td>EQE($\lambda$)</td>
<td>Spectrally-resolved external quantum efficiency</td>
</tr>
<tr>
<td>LSC</td>
<td>Luminescent solar concentrator</td>
</tr>
<tr>
<td>UC</td>
<td>Upconversion</td>
</tr>
<tr>
<td>TTA-UC</td>
<td>Triplet-triplet annihilation upconversion</td>
</tr>
<tr>
<td>ISC</td>
<td>Intersystem crossing</td>
</tr>
<tr>
<td>Sensitiser</td>
<td>Low-energy photon absorber in a TTA-UC system</td>
</tr>
<tr>
<td>Emitter</td>
<td>High-energy photon emitter in a TTA-UC system</td>
</tr>
<tr>
<td>$k_\phi$</td>
<td>Excitation rate of an absorbing chromophore</td>
</tr>
<tr>
<td>$\sigma(\lambda)$</td>
<td>Absorption cross-section of a chromophore</td>
</tr>
<tr>
<td>$\rho(\lambda)$</td>
<td>Photon flux per wavelength increment</td>
</tr>
<tr>
<td>RET</td>
<td>Resonance energy transfer</td>
</tr>
<tr>
<td>IA</td>
<td>Interaction anisotropy</td>
</tr>
<tr>
<td>$E$</td>
<td>Electric field vector</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Transition anisotropy</td>
</tr>
<tr>
<td>$r$</td>
<td>Anisotropy (unitless metric)</td>
</tr>
<tr>
<td>$\theta_c$</td>
<td>Critical angle for waveguiding</td>
</tr>
<tr>
<td>$\Phi_{PL}$</td>
<td>Luminescence quantum yield</td>
</tr>
<tr>
<td>$I(z)$</td>
<td>Intensity of a light beam at depth $z$</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Coefficient of absorption</td>
</tr>
<tr>
<td>$k_Q$</td>
<td>Rate constant of quenching</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Luminescence lifetime</td>
</tr>
<tr>
<td>$3E^*$</td>
<td>Triplet-excited emitter molecule</td>
</tr>
<tr>
<td>$\Sigma$</td>
<td>Excitation metric</td>
</tr>
<tr>
<td>$\Phi_{UC}$</td>
<td>Upconversion quantum efficiency</td>
</tr>
<tr>
<td>TCPPdP</td>
<td>Tetracarboxyphenyl palladium porphyrin</td>
</tr>
<tr>
<td>Q$_3$PdPCOOH</td>
<td>Tris-quinoxalino carboxylic acid palladium porphyrin</td>
</tr>
<tr>
<td>Q$_4$PdPCOOH</td>
<td>Tetrakis-quinoxalino carboxylic acid palladium porphyrin</td>
</tr>
<tr>
<td>$k_1$</td>
<td>First-order decay rate constant</td>
</tr>
<tr>
<td>$k_2$</td>
<td>Second-order decay rate constant</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Second-order metric of the TTA-UC process</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Initial fraction of triplets that decay through the second-order channel</td>
</tr>
<tr>
<td>$f_1$</td>
<td>Total proportion of triplets decaying through the first-order channel</td>
</tr>
<tr>
<td>$f_2$</td>
<td>Total proportion of triplets decaying through the second-order channel</td>
</tr>
<tr>
<td>$J_{SC}(\lambda)$</td>
<td>Wavelength-dependent short-circuit current density</td>
</tr>
<tr>
<td>$f_c$</td>
<td>Solar concentration factor</td>
</tr>
<tr>
<td>FoM</td>
<td>Figure of Merit for solar cell enhancement by upconversion</td>
</tr>
</tbody>
</table>
Appendix B

Dipole absorption and emission rates

Fermi golden rule derivation of transition rates

Dipole emission

The following is based on work by Prof Tim Schmidt that was presented in a similar form in my 2009 Honours thesis. The proof is presented here to show the derivation of the anisotropic interaction terms in Chapter 2. I have modified the approach to treat the photon purely in terms of its populating a mode of the electric field that manifests as the polarisation vector, rather than a propagation vector. The difference is largely semantic but this new approach seems the more realistic of the two, since it is really the electric field interacting with the molecule.

Beginning with Fermi’s golden rule, we derive the emission profile of an electronic dipole:

$$k_{ij} = \frac{\omega}{2\pi} \langle j | \mathcal{V} | i \rangle \rho_j$$

where $k_{ij}$ is the emission rate from excited state $i$ to an ensemble of states $j$, $\rho_j$ is the density of receiving states, and $\mathcal{V}$ is the general coupling expression. First, we can calculate $\rho_j$ by considering emission into cavity modes. A cavity with side length $L$ is placed around the emitter, with the emitter transition dipole at the origin and polarised along $+z$ (the cavity volume is arbitrary, as it eventually cancels from the derivation). The photon energy associated with a mode with wavelength $\lambda$ and principle quantum number $n$ is given by

$$E = \frac{2\pi hc}{\lambda} = \frac{2\pi hcn}{2L}.$$  

Rearranging this equation gives
APPENDIX B. DIPOLE ABSORPTION AND EMISSION RATES

\[ n = \frac{2LE}{2\pi hc} \]  

and taking the derivative yields

\[ dn = \frac{2L}{2\pi hc} dE. \]

The density of states \( \rho_j \) is expressed as \( dN \ dE \), and is found by performing an infinitesimal rotation of the polarisation vector within the cavity. The angles \( \theta \) and \( \phi \) are the zenith and azimuthal angles of the polarisation vector, respectively. Thus

\[ dN = n^2 \cos \theta dn \ d\theta d\phi. \]  

Substituting the re-arranged density of states expressions for \( n \) and \( dn \) gives

\[ dN = \frac{E^2 L^2}{\pi^2 h^2 c^2} \frac{L}{\pi hc} \cos \theta dE d\theta d\phi. \]  

Combining terms \( (L^3 = V) \) and dividing by \( dE \),

\[ \frac{dN}{dE} = \frac{E^2 V}{\pi^3 h^3 c^3} \cos(\theta) d\theta d\phi, \]

gives the density of accessible receiving states \( \rho_j \) (a second set of states orthogonal to the first represents the opposite polarisation, which is orthogonal and non-interacting with the transition).

The interaction term in equation .1 for photon emission is for coupling of the transition to the photon (electric) field. In describing this interaction we use the dipole approximation, which means we do not use anything beyond the dipole term in the multipole expansion of the electric field interaction. The interaction term is therefore

\[ |\langle j|\mathbf{V}|i \rangle|^2 = |\mathbf{E}(t) \cdot |\langle j|\hat{\mu}|i \rangle||^2, \]  

where \( \hat{\mu} \) is the dipole moment operator. The electric field due to a photon can be derived from the irradiance formula:
\[ I = \frac{1}{2} \epsilon_0 c |E_0|^2. \] (10)

Irradiance \( I \) has units of power per area. Dividing irradiance by \( c \) (units of distance per time) yields energy per volume. The energy of a single photon is \( \hbar \omega \) where \( \omega \) is the angular frequency. If \( N \) is the number of photons in the mode, \( I/c \) gives the following:

\[ \frac{N \hbar \omega}{V} = \frac{1}{2} \epsilon_0 |E_0|^2. \] (11)

For \( N = 1 \) this expression can be re-arranged to give the electric field due to a single photon, expressed as a time-dependent variable:

\[ E(t) = \sqrt{\frac{2 \hbar \omega}{\epsilon_0 V}} \cos(\omega t). \] (12)

Applying the rotating wave approximation to the above expression has the effect of averaging over \( \cos(\omega t) \). Applying this to the interaction term gives a simple dot product:

\[ \langle \langle E(t) \cdot |j|\hat{\mu}|i| \rangle \rangle^2 = \frac{\hbar \omega}{2 \epsilon_0 V} |\langle j|\hat{\mu}|i| \rangle^2 \cos^2(\theta). \] (13)

Combining this with the density of states gives the emission rate derivative with respect to the two angles:

\[ dk_{\theta, \phi} = \frac{2\pi}{h} \frac{V E^2}{\pi^2 \hbar^3 c^3 2 \epsilon_0 V} |\langle j|\hat{\mu}|i| \rangle^2 \cos^3(\theta) d\theta d\phi \] (14)

\[ = \frac{\omega^3}{h\pi^2 c^3 \epsilon_0} |\langle j|\hat{\mu}|i| \rangle^2 \cos^3(\theta) d\theta d\phi. \] (15)

We integrate over the variable \( \phi \) from \((0 \rightarrow \pi/2)\), because emission is into the all-positive octant of the cavity (the mode numbers are only defined for positive values). Therefore

\[ dk_{\theta} = \frac{\omega^3}{2h\pi c^3 \epsilon_0} |\langle j|\hat{\mu}|i| \rangle^2 \cos^3(\theta) d\theta. \] (16)

This is the emission rate from state \( i \) into the ensemble represented by state \( j \). The emission rate is greatest for \( \cos^2(\theta) = 0 \), which corresponds to emitted light with polarisation parallel to the alignment of the transition dipole. Intuitively this is a satisfying result, because photon modes which couple most strongly to the transition should be the most rapidly populated.
APPENDIX B. DIPOLE ABSORPTION AND EMISSION RATES

The derived result can be checked against the Einstein A coefficient for spontaneous emission, \( A_{ij} \), by integrating equation \( .16 \) over all allowed values of \( \theta \):

\[
k_{ij} = \frac{\omega^3}{2\hbar \pi c^3 \epsilon_0} |\langle j | \hat{\mu} | i \rangle |^2 \int_0^{\pi/2} \cos^3(\theta) d\theta
\]

\[
= \frac{\omega^3}{3\hbar \pi c^3 \epsilon_0} |\langle j | \hat{\mu} | i \rangle |^2
\]

\[
= A_{ij}.
\]

\[ (\text{.17}) \]

\[ (\text{.18}) \]

\[ (\text{.19}) \]

**Dipole absorption**

The rate of photon absorption is found in a similar manner, but the rate depends upon the properties of the photon field. We assume a modally isotropic photon field with constant spectral intensity across the absorbing band. The density of states is

\[
\rho_j = \frac{dN}{\hbar d\omega}.
\]

\[ (\text{.20}) \]

The simplified interaction term is unchanged from the previous section,

\[
\langle |E(t) \cdot | \langle j | \hat{\mu} | i \rangle |^2 \rangle = \frac{\hbar \omega}{2\epsilon_0 V} |\langle j | \hat{\mu} | i \rangle |^2 \cos^2(\theta),
\]

\[ (\text{.21}) \]

and we can again form the rate in differential form:

\[
dk_{\theta \phi} = \frac{2\pi}{\hbar} \frac{\hbar \omega}{2\epsilon_0 V} |\langle j | \hat{\mu} | i \rangle |^2 \frac{dN}{\hbar d\omega} \cos^3(\theta) d\theta d\phi
\]

\[ (\text{.22}) \]

\[
= \frac{\pi}{\hbar^2 \epsilon_0} dN \hbar \omega V d\omega |\langle j | \hat{\mu} | i \rangle |^2 \cos^3(\theta) d\theta d\phi
\]

\[ (\text{.23}) \]

\[
dk_{\theta} = \frac{2\pi^2}{\hbar^2 \epsilon_0} \frac{dN \hbar \omega}{V d\omega} |\langle j | \hat{\mu} | i \rangle |^2 \cos^3(\theta) d\theta.
\]

\[ (\text{.24}) \]

Again, the rate depends on the overlap of the photon field with the transition dipole, and is greatest when the overlap is complete. We can again compare the integrated rate with the Einstein absorption coefficient \( B_{ij} \). First it is necessary to re-express the absorption rate in terms of the radiation energy density \( \rho_\omega \), which has units of energy per volume per angular frequency. Equation \( .24 \) was arranged so that this corresponds to the second term, excluding a factor of \( 4\pi \) which accounts for the full unit sphere solid angle. The integrated rate is therefore
\[ k_{ji} = \frac{\pi}{2\hbar^2 \varepsilon_0} \rho_\omega |\langle j | \hat{\mu} | i \rangle|^2 \int_0^{\pi/2} \cos^2(\theta) \, d\theta \]  

\[ = \frac{\pi}{3\hbar^2 \varepsilon_0} \rho_\omega |\langle j | \hat{\mu} | i \rangle|^2 \]  

\[ = \rho_\omega B_{ji}. \]
Appendix C

LSC simulation

LSCs are particularly well-suited to simulation by ray tracing. Typical LSCs are topologically simple, materially uniform bulk devices. Simple analytically-solvable optical effects — which are easy to code — are therefore good descriptions of the behaviour of light within the object. At the same time, deterministic solutions to the overall device behaviour are difficult to obtain without stringent approximations. Under uniform illumination, any one volume element of an LSC is illuminated by every other, with each contributing differently to the net photon flux through the volume element based on proximity to the element and to the illuminated surface. Reabsorption within each element makes all such flux contribution interdependent. Adding anisotropy to absorption and emission further increases the complexity, as each flux exchange then also depends on polarisation.

Sahin and Ilan recently published an analytic study of an LSC using radiative transport theory. The authors note that statistical (i.e. ray tracing) simulation is easier to code and is more easily adapted to many-dimensional problems, whereas the deterministic approach is computationally more efficient and is commonly used to study real-world problems. Their model is two-dimensional (no LSC depth) and does not include polarisation effects, which is telling of the difficulty of achieving a full deterministic simulation.

Statistical and thermodynamic modelling have both been used to better understand LSCs since early in the original wave of research. In 1980 Yablonovitch published what seems to have been the first thermodynamic model of an LSC. The model required that the incident light intensity be uniform across the depth of the waveguide slab, which is quite a restrictive approximation as it puts a low upper limit on the absorbance of the slab. More recently Barnham and Chatten have further developed the thermodynamic approach, using a detailed balance model to successfully describe the operation of a quantum dot-based LSC.

Statistical LSC simulations have been much more widely reported. In 1981 Olson and coworkers used a random walk formalism to study the reabsorption problem in single-dye LSCs. Incidentally, their conclusion that radiationless electronic excited state transport to bright, lower-
Coordinate system used in the LSC simulation, and the vector and angle conventions of the simulated photons.

Energy trap states could substantially avoid the reabsorption problem precedes a large body of work attempting to implement precisely that. In 1983 Carrascosa and coworkers carried out Monte Carlo simulations of the performance of several LSCs under direct and diffuse insolation conditions, although they did not include polarisation. In the same year Sansregret et al. published a study that found a good match between Monte Carlo simulation of the emission profile of an active waveguide (LSC) and the working device, reproducing the reabsorption shift which occurs as the excitation source is moved further from the emission point. After a slump in the number of publications through the late 1980s, research into LSCs again started to grow, and with it, the use of Monte Carlo device simulations. These newer simulations have shown steadily increasing complexity in the modelled interactions between light and dye.

**Attribution, coordinates, variables, vectors**

I have progressively developed code for a Monte Carlo LSC simulation over the course of my Honours and postgraduate study. The original ray trace algorithm, in C, was written by my supervisor Prof. Schmidt. I have since added a number of features: the explicit treatment of polarisation and dipole alignment, true dipolar absorption and emission envelopes, the absorption of errant incident light by edge-mounted solar cells, the capacity to simulate imperfect substrate materials, birefringent host materials, and in partnership with Honours student Nate Davis, the ability to quickly search large parameter spaces using a Markov Chain Monte Carlo process.

The simulated LSC is situated on a Cartesian grid in 3-space. The illuminated face sits in
APPENDIX C. LSC SIMULATION

<table>
<thead>
<tr>
<th>VARIABLE</th>
<th>DEFINITION</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E(p, q, r) )</td>
<td>Polarisation</td>
</tr>
<tr>
<td>( k(a, b, c) )</td>
<td>Propagation vector</td>
</tr>
<tr>
<td>( \Gamma(p, q, r) )</td>
<td>Dipole orientation</td>
</tr>
<tr>
<td>( \phi'_v )</td>
<td>Zenith angle of ( v ) in local frame</td>
</tr>
<tr>
<td>( \theta'_v )</td>
<td>Azimuthal angle of ( v ) in local frame</td>
</tr>
<tr>
<td>( \phi_v )</td>
<td>Zenith angle of ( v ) in global frame</td>
</tr>
<tr>
<td>( \theta_v )</td>
<td>Azimuthal angle of ( v ) in global frame</td>
</tr>
</tbody>
</table>

Variables used in the LSC ray tracer. Vector \( v \) is a generic stand-in for vectors \( E, k, \Gamma \).

...the \((x, y)\) plane at \( z = 0\), and the waveguide depth extends into \(-z\). Solar cells are attached with perfect index matching to the four narrow edges in the \((x, z)\) and \((y, z)\) planes. The coordinate and angle conventions are as-depicted. The main variables used in the simulation are tabulated.

The interaction of three vectors in Cartesian 3-space is at the heart of the simulation. These are photon polarisation \( E(p, q, r) \), photon propagation \( k(a, b, c) \), and dipole orientation \( \Gamma(x_d, y_d, z_d) \). Giving these vectors primacy throughout the simulation ensures systematic modelling of essential effects like anisotropy. \( E \) and \( k \) are always orthogonal, as required of light. \( E \) and \( \Gamma \) interact according to the dipole interaction profile, which governs both photon absorption and emission. In the current iteration of the simulator the dipole wholly defines the dye orientation, which requires two assumptions: that there is no excited-state conformation change or dephasing, and that absorption across the entire simulated energy range is by the same orientation of dipole. The first assumption is reasonable for so-called ‘linear’ dyes with a high dichroic ratio, which are widely used in aligned-dye LSCs, and the second assumption does not affect the propagation and reabsorption of downshifted photons, which is the primary difficulty in LSCs and the primary concern of the simulation.

Vector interactions in local reference frames

This section describes the vector generation and interactions that are at the heart of the simulation, and the method for calculating their interaction in local frames and rotating to the global coordinate system. The full simulation procedure is given below.

The simulator generates and tracks single photons sequentially, binning the outcome for each incident photon for later analysis. For each new photon incident on the LSC, the program generates a zenith angle \( \phi_k \), measured from the \( z \) axis, an azimuthal angle \( \theta_k \), formed between the projection of \( k \) in the \((x, y)\) plane and \(+x\), and a wavelength \( \lambda \). The distribution of these variables is chosen to reflect the simulated sunlight conditions. A transformation to Cartesian coordinates using \( a = \cos \theta_k \sin \phi_k \), \( b = \sin \theta_k \sin \phi_k \) and \( c = \cos \phi_k \) yields \( k \), the propagation...
vector in the global frame. The coordinates of first strike on the substrate are then chosen.*

Next the program finds $\mathbf{E}'$, the polarisation vector defined in a local coordinate system where $\mathbf{k}$ forms the local $z$ axis. This makes it simple to ensure that the polarisation vector is orthogonal to the propagation vector while ensuring full sampling of all possible polarisations. Modelling incident sunlight with no preferred polarisation, a randomly-selected angle $\theta'$ [0 : $2\pi$] is chosen to define $\mathbf{E}'$ using the coordinate transformations $a' = \cos\theta'$, $b' = \sin\theta'$ and $c' = 0$.

Transformation from the local to the global frame occurs by vector rotation. $\mathbf{E}'$ is rotated into the global frame by angle $\phi_k$ about a rotation axis formed by $\mathbf{k} \times \hat{z}$. The rotation axis needs to be normal to the plane formed by the start and end vectors, and the dot product is a reliable way of ensuring this is the case. Rather than rotation matrices, the program uses quaternion rotations to swap vectors between local and global frames.

The program now has a photon of known wavelength with the position, propagation vector and polarisation defined in the global frame. $\phi_E$ defines the zenith angle of the polarisation vector. The next vector interaction comes when the photon is absorbed within the LSC. Now the program must determine $\mathbf{r}$, the orientation of the absorbing dipole. Once again we make use of a local coordinate system. Primacy is given to the polarisation such that $\mathbf{E}$ defines the local $z$ axis. Two angles determine $\mathbf{r}'$: $\phi'$ is sampled from a $\cos^2(\phi')$ distribution, and $\theta'$ is selected randomly from a uniform distribution [0 : $2\pi$]. $\mathbf{r}'$ is calculated by transforming from local spherical polar to local Cartesian coordinates using the standard relations, as above. Now, $\mathbf{r}$ is calculated by rotating $\mathbf{r}'$ by $\phi_E$ about the axis $\mathbf{E} \times \hat{z}$. The zenith angle of $\mathbf{r}$ is defined as $\phi_r$.

The final vector interaction occurs upon light emission by the dipole. This time, $\mathbf{r}$ defines $z$ in the local frame. $\phi'$ is picked from a $\cos^3(\phi')$ distribution, the additional power of $\cos(\phi')$ compared to absorption reflecting the density of accessible photon modes. $\theta'$ is selected as before from [0 : $2\pi$]. Coordinate transformation to Cartesian form gives $\mathbf{r}'$. $\mathbf{k}'$ is found by adding $\pi/2$ to $\phi'$ and similarly transforming. Rotation of both local vectors into the global frame is by the angle $\phi_r$ about the axis $\mathbf{r} \times \hat{z}$.

**Program sequence**

Based on the flowchart shown, the following steps take place in the simulator:

1. Generate an incident photon. $\mathbf{E}$ and $\mathbf{k}$, the polarisation and propagation vectors in Cartesian space, are chosen based on the sunlight conditions under consideration. The photon wavelength $\lambda_{inc}$ is chosen by interpolating a random number onto the probability distribution function of the AM1.5G spectrum in units of photon flux.

2. The net absorptivity of the LSC at $\lambda$ is calculated from each absorbing component of

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*Fresnel reflection of the incident light are not simulated because the focus of the simulator is on device trends rather than absolute efficiency. But they are easily incorporated using the propagation and polarisation vectors and stochastically testing for reflection using calculated reflection coefficients.
APPENDIX C. LSC SIMULATION

1. Generate new photon \((k, E, \lambda, x, y)\)
2. Pick path length. Absorbed within LSC bounds?
   - Yes
   - No
3. Update position, pick absorbing species
4. Pick decay pathway
   - RET
   - NR decay
   - Fluorescence
5. Pick dye orientation \((\bar{I})\)
6. Generate new photon \((\tilde{k}, \tilde{E}, \lambda)\)
7. Pick path length. Still within LSC bounds?
   - Yes
   - No
8. Exited narrow edge?
   - Yes
   - No

Flowchart depicting the main stages of the LSC simulator
the LSC, i.e. \( \alpha = \alpha_{\text{dye}1} + \alpha_{\text{dye}2} + \ldots \). The incident photon path length is calculated by \(-\log(\text{ran}/\alpha)\), where ‘ran’ is a random number between 0 and 1. If the path length is greater than the substrate thickness, accounting for refraction into the substrate at non-normal incidence, the photon is discarded and the simulation restarts. The program is fully capable of simulating absorption by the substrate material, to do so an extra term, \( \alpha_{\text{substrate}} \), would be added to the above formula. This has not currently been implemented.

The program is able to detect direct excitation of the edge-mounted solar cells by incident photons - if the photon leaves the substrate through a narrow periphery and is above the solar cell band gap, it is included as current.

3. The absorbing species is chosen based on the contributions to \( \alpha \). Substrate absorptivity would be included here, and its selection as the absorbing species would cause an automatic break and generation of a new incident photon.

4. The fate of the new excited state is chosen based on the fluorescence quantum yield \( \Phi_f \) and, for multi-dye systems, the relevant RET probability. Non-radiative decay (if ran > \( \Phi_f \)) sends the program back to photon generation, and RET triggers a re-calculation of the excitation state outcome, for the new acceptor species.

5. Once it has been established that a new photon will be generated, the orientation of the emitting species is determined. This saves the program from unnecessarily calculating the orientation of absorbers which end up nonradiatively decaying. If no RET occurred, the emitting dipole is determined by the incident photon properties. With RET, we make an approximation and assume that the emitting dipole is now randomly oriented. This assumption will at some point be updated so we can better model phenomena such as polarisation dephasing by exciton hopping (anisotropy decay by reabsorption already occurs as expected).

6. The new photon’s polarisation, propagation vector and wavelength are determined

7. A new path length is calculated

8. The program tests if the photon still resides within the substrate. If so, reabsorption has occurred and the program returns to step 3, carrying with it the polarisation and propagation vector. Otherwise the program tests whether the photon has left through an escape cone, in which case the photon is lost, or through a narrow edge, in which case current is added to the solar cell.

Each generated incident photon increments a counter by one, and the program repeats until the counter reaches the predetermined limit (typically on the order of \(10^6\) photons), logging all relevant data such as current collected, escape cone losses, number of reabsorptions, and the spectral composition of each of these sets. Wider-ranging simulations can easily be carried out
by having the program progressively index parameters such as dye concentration, RET efficiency, or substrate length. More sophisticated methods of determining parameter progression can also be built-in. For instance, as part of his 2012 Honours project, Nathaniel Davis modified a copy of the simulator to carry out Markov chain Monte Carlo routines, whereby the program would stochastically migrate through parameter space and map out optimised parameter sets based on a user-defined figure of merit.
LSC additional data and modelling

OEP alignment in 5CB

Result of the polarised excitation fluorescence experiment for determining the alignment of OEP in the liquid crystal host 5CB.

The result of the polarised fluorescence excitation measurement of the 5CB-OEP system, as described in Chapter 2 Section 3.5, is shown in the figure. The data most resembles the prediction for isotropic OEP alignment in the 5CB host.
Model for direct excitation of R800 at normal incidence

A derivation of the intensity ratios used in analysing the results of the aligned-dye OEP-R800 LSC, as per Chapter 3 Section 3.5.2.

\[ I_\perp \propto \int_0^{2\pi} \sin^3(\phi) \, d\phi \int_0^\pi \sin^3(\theta) \cos^2(\theta) \, d\theta. \]  

The integral over \( \phi \) cancels with the same term in \( I_\parallel \) when we calculate \( I_\perp / I_\parallel \), so we exclude it from here onwards.

\[ I_\perp \propto \int_0^\pi \sin^3(\theta) \cos^2(\theta) \, d\theta \]  
\[ = \frac{1}{30} \left[ \cos^3(\theta) (3 \cos(2\theta) - 7) \right]_0^\pi \]  
\[ = \frac{4}{15}. \]  

\[ I_\parallel \propto \int_0^{2\pi} \sin^2(\phi) \, d\phi \int_0^\pi \sin^5(\theta) \, d\theta. \]  

As above, the integral over \( \phi \) is ignored due to impending cancellation.

\[ I_\parallel \propto \left[ -\frac{5}{8} \cos(\theta) + \frac{5}{48} \cos(3\theta) - \frac{1}{80} \cos(5\theta) \right]_0^\pi \]  
\[ = \frac{16}{15}. \]  

In calculating \( I_\perp / I_\parallel \) we multiply \( I_\perp \) by 2 to account for the second orthogonal axis. Therefore,
for isotropically oriented R800 excited at normal incidence.

Excitation via RET from the dephasing porphyrin absorber removes dependence on the $P_{\text{exc}}$ term used above; we retain the same expressions for $P_{\text{em}}$ and $P_{\text{em}}^\parallel$. Again we ignore the terms dependent on $\phi$, as they cancel in the final step. Now,

\[
I_\perp = \frac{8}{16} = 0.5
\]

(10)

(11)

for isotropically oriented R800 excited at normal incidence.

Excitation via RET from the dephasing porphyrin absorber removes dependence on the $P_{\text{exc}}$ term used above; we retain the same expressions for $P_{\text{em}}$ and $P_{\text{em}}^\parallel$. Again we ignore the terms dependent on $\phi$, as they cancel in the final step. Now,

\[
I_\perp \propto \int_0^{\pi} \sin(\theta) \cos^2(\theta) d\theta
\]

(12)

\[
= \left[ \frac{-1}{3} \cos^3(\theta) \right]_0^\pi
\]

(13)

\[
= \frac{2}{3}
\]

(14)

\[
I_\parallel \propto \int_0^{\pi} \sin^3(\theta) d\theta
\]

(15)

\[
= \left[ \frac{1}{12} (\cos(3\theta) - 9 \cos(\theta)) \right]_0^\pi
\]

(16)

\[
= \frac{4}{5}
\]

(17)

Finally,

\[
\frac{I_\perp}{I_\parallel} = 2 \times \frac{2/3}{4/3}
\]

(18)

\[
= 1
\]

(19)

That is, RET-excited isotropically oriented R800 should show no dependence on detector polarisation angle.
Derivation of lossy upconversion rate model

Modifying the simple rate model in Equation 4.1 to include additional loss channels in the sensitiser. The modelled system is in equilibrium.

The sensitiser singlet excited state is governed by

\[
\frac{d[^1S^*]}{dt} = k_\phi[^1S] - 1 \kappa_{\text{loss}}[^1S^*] - k_{\text{ISC}},
\]

where \( \kappa'_{\text{loss}} \) is the pseudo-first order rate constant for undesirable singlet loss and \( k_{\text{ISC}} \) is the intersystem crossing rate. We assume that ISC remains dominant even in the lossy system, which is valid for a system of largely non-interacting chromophores given the extremely fast rate in applicable systems. In systems with high levels of aggregation this approximation will become null, but so will the remainder of the derivation, which implicitly assumes that chromophores can be treated as isolated systems in a homogeneous system. Neglecting this possibility for now, because the system is at equilibrium (the derivative is equal to zero) we can now say that

\[
k_\phi[^1S] = k_{\text{ISC}}.
\]

The triplet-excited sensitiser concentration is governed by

\[
\frac{d[^3S^*]}{dt} = k_{\text{ISC}} - 3 \kappa'_{\text{loss}}[^3S^*] - \kappa_Q[^1E] = k_\phi[^1S] - 3 \kappa_{\text{loss}}[^3S^*] - \kappa_Q[^1E],
\]

where, analogously, \( \kappa'_{\text{loss}} \) is the pseudo-first order rate constant for undesirable loss from the sensitiser triplet state (retaining generality; the loss processes could be mixed first- and second-order). \( \kappa_Q \) is the Stern-Volmer quenching rate constant of the sensitiser-emitter system and we
have made use of relation 2. At equilibrium we therefore have

\[ \kappa_Q[1^E] = k_\phi[1^S] - 3 \kappa_{\text{loss}}[^3S^*]. \] (5)

Finally, we consider the emitter triplet concentration:

\[ \frac{d[^3E^*]}{dt} = \kappa_Q[1^E] - \kappa_1[^3E^*] - \kappa_2[^3E^*]^2. \] (6)

Using equation 5, we end with

\[ \frac{d[^3E^*]}{dt} = k_\phi[1^S] - 3 \kappa_{\text{loss}}[^3S^*] - \kappa_1[^3E^*] - \kappa_2[^3E^*]^2, \] (7)

as given in the main text.
SEM micrograph of alumina substrate

The SEM micrographs were obtained during training by Dr Pat Trimby from the Australian Center for Microscopy and Microanalysis.
APTES-TPPdP synthesis

The following synthesis was carried out by Dr. Josh Peterson:

A solution of 52.0 mg (0.058 mmol) 5,10,15,20-tetrakis(phenyl-4-carboxylic acid)porphyrin (TCPdP) in ~ 3 mL of dry N,N-dimethylformamide was added under dry nitrogen atmosphere to 6.6 mL of thionyl chloride at room temperature. The mixture was heated to reflux for at least 2 hours then removed from heat and thionyl chloride was removed by distillation. The reaction mixture was then transferred in dry dichloromethane (10 mL) to a mixture of triethylamine (0.613 g, 6.06 mmol) and 3-aminopropyltriethoxysilane (0.755 g, 3.41 mmol) and stirred overnight at room temperature. The crude mixture was then precipitated into dry pentane in plastic falcon tubes (2 mL reaction mixture to 40 mL pentane) and centrifuged at 4000 rpm for 5 minutes to afford a sticky red solid. The solid was redissolved in dichloromethane and precipitated into pentane three times and then dried under a stream of dry nitrogen. The product was a red solid that was estimated by NMR to be a mixture of isomers containing approximately 2.6 triethoxysilane ligands per porphyrin core with an estimated molecular weight of 1452.68 g/mol. The product was stored in plastic tubes under nitrogen.
Appendix H

Absolute quantum yield measurement

The internally-referenced upconversion action spectrum measures with respect to the emitter fluorescence quantum yield. Thus an absolute measure of the quantum yield is in some circumstances desirable. The following experiment is near-finished at the time of writing, and we include it here for interest.

Setup

I used the method published by Rohwer and Martin in 2005 for measuring absolute photoluminescence quantum efficiency. The luminescent sample is mounted at one port of an integrating sphere, and excited by diffuse light scattering within the sphere. The excited sample radiates light which is similarly scattered within the sphere. Two calibrated photodiodes mounted at measurement ports on the sphere detect the power change in the excitation and emission sources. Calibration measurements account for the wavelength-dependent sphere attenuation and detector responses. Rohwer and Martin have used the technique to measure the quantum yields of solutions and solids with a large range of optical densities. This diffuse light measurement technique is far more amenable to measuring the unusually dense upconverter materials than comparative yields techniques, which require low optical densities and negligible scattering, or complicated corrections for the inner-filter effect.

A thorough description of the experimental setup is given in Rohwer and Martin’s paper. The two photodiodes, A and B, respectively measure excitation power and emission power. In our version of the experiment, which is very similar, a 5.3 inch diameter 4-port integrating sphere (Labsphere) is positioned such that the monochromated output of a xenon lamp is directed into the 1 inch equatorial port. The beam is focused to a point at the entrance with a short focal length lens, and just within the sphere entrance we mount a plastic centrifuge tube with a white-out coated tip. This scatters the excitation light entering the sphere, which helps to achieve isotropic light within the sphere after the first wall strike. Rohwer and Martin use a teflon diffuser element mounted at the beam entrance to achieve the same effect. The sample, in a
transparent NMR tube, intrudes several millimeters into the sphere at the opposite equatorial port. During measurement, photodiode B views the third equatorial port, positioned 90° around the equator from the other two. The diode is long-pass filtered to render it opaque to the chosen excitation wavelength, but visible to some portion of the sample emission. Photodiode A is placed on the final port, positioned on the north pole of the sphere. A short- or band-pass filter blocks sample emission from this diode.

The quantum yield measurement itself is very simple. Both detectors have their dark background subtracted. Photodiode A and the monochromator are set to the excitation wavelength (detector B wavelength is arbitrary but must be known). Power at A and B is denoted $P_{\text{ex}}$ and $P_{\text{em}}$, respectively, the subscripts denoting their excitation and emission roles. The powers are monitored as the sample blank is replaced with the emissive sample ($P_{\text{ex}}^s$ and $P_{\text{em}}^s$), then swapped back ($P_{\text{ex}}^b$ and $P_{\text{em}}^b$). Temporal signal averaging can be employed to better resolve the drop and rise of signals from A and B respectively, which are caused by absorption of the excitation light and emission from the sample. These measured quantities require correcting, which presents the more challenging component of the experiment. As long as photodiode A is opaque to the sample emission, only four additional measurements are required:

1. **Power meter multiplier for detector B.** Photodiodes output current, and cannot spectrally resolve absorbed light. In a calibrated photodiode system, the user tells the power meter the incident wavelength ($\lambda_0$). The power meter, assuming monochromatic light of that wavelength, then uses the stored multiplier value for $\lambda_0$, $M(\lambda_0)$, to calculate power from the measured current. Clearly this power is incorrect if the incident light is polychromatic, or if the user selects the wrong wavelength. This quantum yield method corrects for detector sensitivity to obtain a true power. As suggested by Rohwer and Martin, the multiplier spectrum was measured by exposing photodiode B to an unchanging incoherent light source and scanning $\lambda_0$. Only relative values are required so the exact units and scale are unimportant. Once obtained, this data can be used across multiple experiments.

2. **The power spectrum of the excitation beam** at the sphere entrance, $P_{\text{beam}}(\lambda)$. Measure this using photodiode B and scanning $\lambda_0$ with the mono output.

3. **The sphere efficiency** $E(\lambda)$, which is the ratio of excitation power measured at the detector position to that measured at the sphere input. It is important that $E(\lambda)$ is measured with the sphere in exactly the same configuration as for the quantum yield measurement, since this factor accounts for attenuation and light leakage brought about by the sphere surface and everything positioned at the ports. We only need to know $E(\lambda)$ for detector B, so this can be calculated partly from the previous measurement. Once the sphere has been set up with all detectors, filters and the sample blank in position, scan $\lambda_0$ and the mono output. The ratio of power measured here to power measured in the
previous step gives $E(\lambda)$.

4. **The sample emission spectrum.** Once a reliable measurement of the power changes with sample replacement have been made, re-insert the emissive sample and measure instead the spectrum of the light measured by photodiode B. This can be done by removing the photodiode without disturbing the filter and coupling the light into a spectrometer. This spectrum is used to correct the power reading of detector B, accounting for the broadband emission spectrum and any leakage of the excitation light.

To calculate the quantum yield, first we need to know the power absorbed by the sample. This is given by

$$P_{\text{abs}} = P_{\text{beam}}(\lambda_{\text{ex}}) \frac{P_{\text{ex}}^{b} - P_{\text{ex}}^{s}}{P_{\text{ex}}^{b}} ,$$

where $\lambda_{\text{ex}}$ is the excitation wavelength and the superscript denotes blank-inserted ($P_{\text{ex}}^{b}$) and sample-inserted ($P_{\text{ex}}^{s}$) measurements of the power at detector A.

Then we can start to account for the broadband illumination of detector B, and correct it to obtain a true power measurement. Rohwer and Martin define the emission spectrum as $\int cP(\lambda)\,d\lambda$ where $c$ is an unknown constant. They define a calibration factor $S(\lambda_0)$, where $\lambda_0$ is the user-defined measurement wavelength of photodiode B,

$$S(\lambda_0) = \int cP(\lambda)\,d\lambda / \int \frac{M(\lambda_0)}{M(\lambda)}E(\lambda)cP(\lambda)\,d\lambda .$$

The emission power, at detector B, is then corrected using the following relation:

$$P_{\text{em}} = S(\lambda_0) \left[ P_{\text{em}}^{s} - P_{\text{em}}^{b} \frac{P_{\text{ex}}^{s}}{P_{\text{ex}}^{b}} \right] .$$

The fraction in this expression accounts for the drop in excitation power upon insertion of the sample. Once the corrected values $P_{\text{ex}}$ and $P_{\text{em}}$ have been obtained, radiant efficiency can be calculated by $\text{RE} = P_{\text{em}}/P_{\text{ex}}$ and the quantum yield by

$$QE = \frac{\bar{\lambda}}{\lambda_{\text{ex}}} \text{RE}$$

where $\bar{\lambda}$ is the central emission wavelength of the sample as determined on an energy scale.
Appendix I

List of Published Works
## Journal Articles

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<th>Main Contribution</th>
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## Conference Proceedings

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## Patents

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<tr>
<td>Rowan W. MacQueen, Tim F. Schulze, and Timothy Schmidt. Photon Upconverter. AU20139000279</td>
<td>Experimental work, patent drafting</td>
</tr>
<tr>
<td>Rowan W. MacQueen and Timothy Schmidt. Luminescent Solar Concentrator and Method for Making the Same. WO Patent 2,011,127,530</td>
<td>Experimental work, patent drafting</td>
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