Bimolecular Triplet-Triplet Annihilation Upconversion for Photovoltaics

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Abstract

Organic upconversion of photons through triplet energy exchange between two or more molecules (OUC) has been investigated through transient absorption and fluorescence spectroscopy, kinetic rate modelling and morphological analysis of thin films. An OUC system, consisting of one sensitising molecule (PQ₄Pd) and an emitting molecule (rubrene), was first studied to explore the possibility of modelling the entire OUC process with a kinetic rate model. Transient absorption spectroscopy allowed for the intermediate steps of OUC to be directly observed and fitted, producing rate constants for each step in the process. This complete model was then optimised against fluorescence measurements from a system containing PtTPBP (sensitiser) and perylene (emitter) to calculate rate constants for that system from a single fluorescence type experiment, as opposed to several orthogonal Stern-Volmer type experiments.

The possibility of fabricating a thin film OUC has been investigated through microscopy, fluorescence spectroscopy and a simple Monte-Carlo model. Using a system of PtOEP (sensitiser) and DPA (emitter), it was shown that the maximal efficiency of a thin film containing these molecules suspended in a PMMA matrix is found when the matrix is between 80 and 85 weight% of the total mixture. It was shown that on short timescales (a few seconds to a few minutes), atmospheric oxygen does not adversely affect thin film upconverters of this type as local oxygen is extremely rapidly quenched (less than a μs) and fresh oxygen is not able to diffuse back into the matrix at a rate that is competitive to OUC. It was shown that the degree of intermixing of active materials is of absolute importance in this fabrication, and a novel optical technique for measuring this intermixing in air was developed, some preliminary results are included.
Declaration

The research presented in this dissertation was conducted at the Blackett Laboratory in the Imperial College London Department of Physics between October 2010 and August 2014. This dissertation is the work of the author alone, and includes nothing which is the outcome of work done in collaboration, except where specifically indicated to the contrary. None of the work presented in this dissertation has been submitted to any other University or Institution for any other qualification. This dissertation contains approximately 40,000 words, 85 figures and 5 tables.

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Roland Bryn Piper
01-09-2014
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<td>AM1.5</td>
<td>Air Mass 1.5 reference spectrum</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge-Coupled Device</td>
</tr>
<tr>
<td>DET</td>
<td>Dexter Energy Transfer</td>
</tr>
<tr>
<td>E&lt;sub&gt;g&lt;/sub&gt;</td>
<td>Band Gap in eV</td>
</tr>
<tr>
<td>EM</td>
<td>Electro-Magnetic</td>
</tr>
<tr>
<td>EQE</td>
<td>External Quantum Efficiency</td>
</tr>
<tr>
<td>ET</td>
<td>Energy Transfer</td>
</tr>
<tr>
<td>FRET</td>
<td>Forster Resonant Energy Transfer</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>IBSC</td>
<td>Intermediate-Band Solar Cell</td>
</tr>
<tr>
<td>iCCD</td>
<td>intensified Charge-Coupled Device</td>
</tr>
<tr>
<td>IEEE</td>
<td>Institute of Electrical and Electronics Engineers</td>
</tr>
<tr>
<td>ISC</td>
<td>Inter-System Crossing</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium Tin Oxide</td>
</tr>
<tr>
<td>k&lt;sub&gt;NR&lt;/sub&gt;</td>
<td>Rate constant of non radiative decay</td>
</tr>
<tr>
<td>k&lt;sub&gt;p&lt;/sub&gt;</td>
<td>Rate constant of phosphorescence</td>
</tr>
<tr>
<td>k&lt;sub&gt;phi&lt;/sub&gt;</td>
<td>Rate constant of absorption</td>
</tr>
<tr>
<td>k&lt;sub&gt;TET&lt;/sub&gt;</td>
<td>Rate constant of triplet energy transfer</td>
</tr>
<tr>
<td>k&lt;sub&gt;TTA&lt;/sub&gt;</td>
<td>Rate constant of triplet-triplet annihilation</td>
</tr>
<tr>
<td>KRM</td>
<td>Kinetic Rate Model</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
</tr>
<tr>
<td>MCM</td>
<td>Monte-Carlo Model</td>
</tr>
<tr>
<td>NIR</td>
<td>Near infra-red</td>
</tr>
<tr>
<td>OLED</td>
<td>Organic Light Emitting Diode</td>
</tr>
<tr>
<td>OSC</td>
<td>Organic Solar Cell</td>
</tr>
<tr>
<td>OUC</td>
<td>Organic Upconversion</td>
</tr>
<tr>
<td>PC</td>
<td>Personal Computer</td>
</tr>
<tr>
<td>PCI</td>
<td>Peripheral Component Interconnect</td>
</tr>
<tr>
<td>PCMCIA</td>
<td>Personal Computer Memory Card</td>
</tr>
<tr>
<td>RE</td>
<td>Rare Earth</td>
</tr>
<tr>
<td>Si-CCD</td>
<td>Silicon Charge-Coupled Device</td>
</tr>
<tr>
<td>SV</td>
<td>Stern-Volmer</td>
</tr>
<tr>
<td>T&lt;sub&gt;g&lt;/sub&gt;</td>
<td>Glass transition temperature</td>
</tr>
<tr>
<td>TAS</td>
<td>Transient Absorption Spectroscopy</td>
</tr>
<tr>
<td>TET</td>
<td>Triplet Energy Transfer</td>
</tr>
<tr>
<td>TTA</td>
<td>Triplet-Triplet Annihilation</td>
</tr>
<tr>
<td>UC</td>
<td>Upconversion</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra-violet</td>
</tr>
<tr>
<td>UV/VIS</td>
<td>Ultraviolet/Visible spectroscopy</td>
</tr>
<tr>
<td>VIS</td>
<td>Visible</td>
</tr>
<tr>
<td>weight%</td>
<td>Percentage of a mixture by weight</td>
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### Materials and Chemicals

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<tr>
<th>Abbreviation</th>
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<tbody>
<tr>
<td>AN</td>
<td>Anthracene</td>
</tr>
<tr>
<td>a-Si</td>
<td>amorphous Silicon</td>
</tr>
<tr>
<td>BODIPY</td>
<td>boron-dipyrromethene</td>
</tr>
<tr>
<td>BPEA</td>
<td>9,10-bis(phenylethynyl)anthracene</td>
</tr>
<tr>
<td>BPEN</td>
<td>9,10-bis(phenylethynyl) napthacene</td>
</tr>
<tr>
<td>DPA</td>
<td>9,10-dihenylanthracene</td>
</tr>
<tr>
<td>DPBF</td>
<td>1,3-diphenylisobenzofuran</td>
</tr>
<tr>
<td>Er</td>
<td>Erbium</td>
</tr>
<tr>
<td>IPA</td>
<td>Isopropyl alcohol</td>
</tr>
<tr>
<td>IR820</td>
<td>2-{2-[2-Chloro-3-[[1,3-dihydro-1,1-dimethyl-3-(4-sulfobutyl)-2H-benzol[2,3-ylidene]-ethylidene]-1-cyclohexen-1-yl]-ethenyl]-1,1-dimethyl-3-(4-sulfobutyl)-1H-benzo[e]indolium hydroxide inner salt</td>
</tr>
<tr>
<td>P3HT</td>
<td>Poly(3-hexylthiophene)</td>
</tr>
<tr>
<td>PCBM</td>
<td>Phenyl-C61-butyric acid methyl ester</td>
</tr>
<tr>
<td>PdPh₄TPB</td>
<td>meso-tetraphenyl-octamethoxide-tetranaphtho[2,3]porphyrin</td>
</tr>
<tr>
<td>PdTAP</td>
<td>tetrakis-5,10,15,20-(p-methoxycarbonylphenyl)tetaanthra[2,3,-b,g,l,q]porphyrin</td>
</tr>
<tr>
<td>PMMA</td>
<td>Poly(methyl methacrylate)</td>
</tr>
<tr>
<td>PQ₄Pd</td>
<td>Palladium (II) tetrakisquinoxalinoporphyrin</td>
</tr>
<tr>
<td>PtOEP</td>
<td>Platinum (II) octaethyl-porphyrin</td>
</tr>
<tr>
<td>PtTPBP</td>
<td>Platinum (II) tetraphenyltetrabenzoporphyrin</td>
</tr>
<tr>
<td>Yb</td>
<td>Ytterbium</td>
</tr>
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Chapter 1

Introduction

This chapter introduces the structure of this document, and briefly describes the fundamental principles of photovoltaic technology and the inherent limits to photovoltaic efficiency. It subsequently explains how various designs, including upconversion, can address the fundamental losses inherent in photovoltaic devices. Finally, some other potential applications for organic upconversion are introduced.

Cartoon of the benefit upconversion can have for solar cells. Photons with wavelength shorter than the dashed black vertical can be absorbed by a solar cell, the rest cannot.
1.1 General background

From the first development of high quality glasses: lenses, optics and optical effects have driven the development of technology through the modification of light and how we perceive it. The research in this thesis investigates the process of photon upconversion, which increases the energy of photons in a beam of light. This process can be mediated in organic molecules by triplet excitations which are spatially confined to these molecules. Upconversion was first observed to occur in the optical frequency range in rare earth (RE) glasses in 1961. This observation followed the development of optical masers, which allowed generation of sufficiently intense beams of light that an excited site in a crystal could absorb a second photon before that excitation relaxed. It wasn’t until much more recently that upconversion could be observed at sufficiently low, and non-coherent, intensities that might make it applicable for photovoltaic applications, where it could increase the fundamental limiting efficiency of a solar cell from almost 29.4% to 48%.

1.2 Photovoltaics

The function of a photovoltaic (PV) device is to generate voltage from photons, a phenomenon which is used, for example, for light sensors and for generating electrical power from solar radiation. The sun generates photons with a spectrum similar to that of a black body radiator. It produces an irradiance of approximately $1000 \, \text{Wm}^{-2}$, calculated for a surface positioned at sea level that is perpendicular to the emitted rays. Integrated over the sun-facing side of the earth, this is enormously in excess of global energy consumption. Photovoltaic power generation has, therefore, a significant role to play in the reduction of global dependence on fossil fuels and atmospheric carbon generation. The following sections briefly review both the fundamental science of photovoltaic devices and the state-of-the-art of efficiency improvement techniques.

The first generation of solar cells were made of crystalline silicon. These remain the simplest design of cell: a single heterojunction between an n-doped semiconductor and a p-doped semiconductor. Incident light excites an electron from the valence band of the junction to the conduction band, this charge then travels, though a combination of random drift and induced diffusion through the space charge zone into the n-doped side, while the associated hole drifts into the p-doped side. The induced diffusion is a process driven by the bending of the band energy levels at the interface, creating a charge imbalance. A schematic of this process is shown in figure 1.1 and is the basic process which all other inorganic PV devices exploit. This type of cell remains the most commercially exploited, accounting
for 90% of production in 2013. The continued dominance of this type of technology, in the face of newer designs, is in large part due to the economic cost of developing manufacturing centres for the new technologies, and due to the huge successes of the silicon manufacturing industry in reducing their costs.

Figure 1.1: Schematic of a p-n junction solar cell.

The theoretical limit of efficiency for a single one of these cells was originally calculated as around 30%, but has recently been revised down to 29.4%. The record reported efficiency for a monocrystalline silicon PV cell as of April 2014 is 25.6%.

In order to improve the commercial appeal (and hence uptake) of PV systems, the cost per Watt of energy generated must be reduced. There are a number of research avenues which may eventually be able to reduce this ratio, including the use of highly absorbent thin films and various methods of improving efficiency to increase the power output of the cells. Some of these are discussed in section 1.2.1, including concentrator systems, multi-junction devices, intermediate bandgap cells and hot carrier devices.

1.2.1 Reducing cost per Watt

Clearly a reduction in the cost per Watt ratio can either be achieved by reducing cost, or increasing efficiency. The most effective way of improving the $/W ratio is to combine techniques, such as using solar concentrators in combination with more expensive, high efficiency multi-junction cells.

Techniques for reducing cost

One of the largest costs associated with first generation PV cells is that of raw material. This has been addressed by the development of highly absorbent thin film cells. These cells
do not require a thick substrate and should hence cost less. However, the continued development of efficient and cheap processing techniques has not yet reached the point where these cells can compete with the existing large manufacturing centres of first generation cells. It is often assumed that once sufficiently efficient and long-lived PV cells are developed, economies of scale will bring down the cost of producing them. However, the scarcity of some of the materials required (such as indium or gallium arsenide) to make these high efficiency cells means that cost can increase with demand rather than fall.

The development of organic solar cells (OSCs), based on conjugated carbon chains and rings, has been encouraged partly because these cells do not rely on such large quantities of valuable metals. However, the transparent conducting layers required for these cells still mostly use indium tin oxide (ITO), another costly material, so much research is being done to try to find replacements. Up until 1991, these cells were generally found to be much less efficient than their silicon counterparts. In 1991 Grätzel and O'Regan developed a ‘dye sensitized’ cell which used an organic dye (a trimeric ruthenium complex) bound to a colloidal solution of titanium dioxide (TiO$_2$) to produce 7.5 $\pm$ 0.4% light to electric energy yield in AM1.5 simulated sunlight. The record efficiency for a dye sensitized cell as of July 2013 is 11.9 $\pm$ 0.4%. The development of OSCs using entirely organic active layers has also progressed significantly. The most commonly used research design of OSC involves blending organic donor materials, such as Poly (3-Hexylthiophene) (P3HT), and acceptor materials such as [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) in order to create a bulk heterojunction cell. The current record efficiency for a polymer solar cell is 10.7 $\pm$ 0.3%.

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Techniques for improving efficiency

To improve efficiency, energy losses must be reduced. Hirst and Ekins-Daukes (2011) analytically examined the fundamental energy losses associated with an ideal single junction PV device. Their paper shows that all of the energy from solar radiation incident on a PV cell can be accounted for through five processes. These are listed below.

1. A Carnot factor, associated with the loss from conversion of thermal energy to entropy free work.
2. A Boltzmann loss due to carrier thermalisation and the mismatch between emission and absorption angles.
3. Re-emission from the device, which was found to be a small loss.
4. Failed, or inefficient, absorption.
5. Thermalisation of above band gap ($E_g$) photons

The most significant energy losses are: failed absorption of below band gap photons and the thermalisation of above band gap photons. An illustration showing the proportion of incident photon energy that each of these losses accounts for and the fraction of solar irradiance which can be extracted for a certain bandgap cell is given in figure 1.2.

Real PV devices suffer from losses additional to those described in the above paper. Minimizing each of these losses is the goal of much research in PV and has driven the development of most so called ‘third generation’ devices. Some of these losses are shown schematically in figure 1.3.

Process A shows thermalisation, where the absorbed photon has energy in excess of the band gap of the material and this energy is rapidly lost as the excitation relaxes to the valence band of the material (equivalent to process 1 in the previous list). When combined with the loss of energy from photons with sub band gap energy (equivalent of process 4, above), these losses can limit efficiency to around 44%. Process B shows the loss associated with the potential difference across the p/n heterojunction and processes C, C’, show the drop from contact voltage loss. The fourth process shown (D and D’) is that of recombination, which occurs when an electron and hole recombine radiatively before the free charge can be extracted at the electrodes.

Techniques for improving efficiency may be categorised under two general headings: increasing the amount of energy absorbed by the cell; and reducing the loss of this energy as
it is extracted from the cell. We will first discuss increasing the amount of energy absorbed by the cell. There are three ways of doing this: concentration of sunlight; light trapping; or by designing a cell which can absorb a wide range of wavelengths. Light concentration can be effectively exploited through the use of mirrors or lenses, both of which require the use of sun tracking motors to be effective and do not work in diffuse light conditions. This has the effect of increasing the number of electrons excited to the conduction band of the material, filling charge traps and thereby improving both charge transport and efficiency of
the cell. The maximum concentration of sunlight which can be achieved on Earth is 46,200 suns. For example, under 92 times concentration, a single junction silicon cell can reach $27.6 \pm 1.0\%$.

Light trapping uses physical structures such as plasmonic particles or arrays, textured surfaces and back-reflectors to increase the path length of light within the cell. It is also possible to alter the band gap of a cell in such a way that it is sensitive to a wider range of photon wavelengths. Unfortunately, while it is possible to absorb many more photons by lowering the band gap of a solar cell, the energy of each photon would be mostly lost as heat into the device as generated charges thermalise, as shown on the left hand edge of figure 1.2. Some designs which incorporate broadening the effective solar spectrum and exploit concentration effects are described below.

**Device designs**

There are a number of device designs which have been developed in order to increase the efficiency of solar power conversion. These can be grouped into techniques for matching the device to the sun’s spectrum, and matching the sun’s spectrum to the devices. Firstly, attempts to match the properties of the cell to the sun’s spectrum are discussed:

- **Tandem/Multi-junction Cells** - A tandem cell is designed to reduce losses through thermalisation, and losses associated with being unable to absorb from the whole solar spectrum. This is achieved by stacking independent cells which have different band gaps, with the highest band gap at the surface. Ideally, each layer is transparent to wavelengths of light below its band gap so more of the spectrum is harvested and the amount of energy lost in thermalisation is reduced significantly. Each cell is connected in series. Which means that unless each subcell is current-matched to each adjacent subcell, there will be a build up of charges at the interface between those subcells, reducing the output current of the collected subcells.

- **Mechanical stack** - A mechanical stack separates the individual cells, removing the requirement for current matching but introducing optical losses and increasing the cost of fabrication by increasing the amount of substrate required to make the device. For an infinite stack of independently operating inorganic cells the conversion efficiency approaches $86.8\%$. Figure 1.4 shows a schematic of a multi-junction cell alongside a mechanical stack.

- **Concentrator Cells** - Concentrator cells follow the same basic design principles of the various other cells described in this section but include carefully designed light-guiding structures above the absorption area. The concentration of light also leads to
massive heating, so complex heat extraction systems are required. These can be used to form part of a combined heat and power system. These cells are very expensive but also very efficient. The record module, based on a triple-junction design, achieved 35.9 ± 1.8% efficiency.\(^{26}\)

Secondly: the three ways of matching the existing solar spectrum to a PV device are up-conversion, downshifting and quantum cutting (also referred to as singlet fission). Photon upconversion is a process whereby the energy of one stream of photons is combined to produce another, less intense, stream of photons. Each new photon has higher energy than each incident photon. This is the opposite of Stokes shift (a decrease in re-radiated energy) which is observed in most materials, and is sometimes referred to as anti-Stokes shift. There are three commonly used methods to achieve photon upconversion: molecular upconversion through triplet-triplet annihilation, sequential absorption in rare earth materials, and sum-frequency generation. Each of these will be described briefly in the following chapter but this thesis is primarily concerned with triplet-triplet annihilation, organic upconversion (OUC). Downshifting works by shifting photons with wavelengths too short to be efficiently absorbed into a region where the cell does absorb strongly.\(^{27}\) Quantum cutting achieves the same effect, but also increases the number of carriers that can generated by each high energy photon. Figure 1.5 shows a schematic of how these concepts work.

**Figure 1.4:** Sketches of a multi junction (left) and a prism-split mechanical stack (right) solar cell.

### Applying upconversion to photovoltaics

Considering a ‘perfect’ upconverting system, with no energy losses, that can upconvert all photons below the band gap of the cell into usable photons, Trupke (2002) calculated
a maximum efficiency enhancement of 48%.\footnote{7} This calculation was based on the detailed balance model that is often applied to solar devices, i.e. it is assumed that no non-radiative losses occur at any point in the process. This has the additional effect of shifting the optimal band gap of the cell to around 2.0 eV. This band gap is higher than that of silicon, but is close to that which is found in many organic solar cell devices, making these cells the obvious choice for upconversion enhancement implementation. However, we must also consider the practical aspects of implementing such a device. The first hurdle is that of incident photons. We take the standard reference solar spectrum AM1.5 global, and consider a cell with the ‘optimal upconversion’ band gap of 2.0 eV. We can then calculate how many photons with energy between 2.0 and 1.0 eV (in a situation with no losses, each photon must have at least this much energy to upconvert to 2.0 eV) will arrive per second per square meter. In this case it is $2.99 \times 10^{21}$. In order to upconvert, the energy of two of these photons must interact. We assume that this energy will be trapped for some time, and will be able to move, either diffusively or through hopping or other transport. If we use the relation in equation (1.1), where lifetime $\times$ rate of arrival represents the number of potential excitations in a unit time and the square of transport length is analogous to the cross-section of each excitation, we find the minimum combination of lifetime and transport length to have the energy of two photons in the same place at the same time, when confined to a surface.

$$\text{Rate of coincidence} = \text{Lifetime} \times \text{Rate of arrival} \times \text{transport length}^2$$ \hspace{1cm} (1.1)

Figure 1.6 shows this sample space. We see that lifetimes of the order of tens of microseconds and transport lengths on the order of a few nm are required. Taking this simple construction one step further, we can calculate this same value for an existing solar cell, amorphous silicon (bandgap of 1.7 eV), and we find that the constraints are very similar: any generated trapped energy must survive for at least tens of $\mu$s if it is nearly immobile,
or be able to move at least 10 nm if it is short lived. Ideally it would be a combination of the two. Monguzzi et al. (2008)\(^\text{28}\) found that the diffusive range of a molecular upconverter is up to 200 nm, depending on concentration, temperature and solvent. In chapter 5 we will see that excitations in a molecular system can have lifetimes ranging from a few tens of µs up to nearly a millisecond.

![Figure 1.6: Contour plot of arrival rate of two photons at the same space in a hypothetical symmetrical upconverter which could upconvert from 1.0 to 2.0 eV.](image)

Both rare earth upconversion and organic upconversion (OUC) have been successfully integrated in solar cells. For example, de Wild et al. (2010)\(^\text{29}\) found that they could improve the external quantum efficiency (EQE) of their amorphous silicon (a-Si) cell by 0.03% at 980 nm by using a rare earth phosphor, though only when excited by a 28 mW laser. Richards and Shalav (2007)\(^\text{30}\) found an absolute EQE enhancement of their cell of up to 3.4% over the absorption range of their phosphor when excited with a 6 mW laser. For their system, this is equivalent to approximately 1000 suns. The current record for solar cell enhancement with rare-earth upconversion comes from Goldschmidt et al. 2014,\(^\text{31}\) who enhanced their crystalline silicon solar cell with a mono-crystalline upconverter. They achieved a 17.0±3.0 mAcm\(^{-2}\) increase in short circuit current density on top of the 33.4 mAcm\(^{-2}\) of the bare solar cell. Cheng et al. (2012)\(^\text{32}\) found that their OUC sample could produce a relative increase in the EQE of an a-Si cell by up to 1% at light intensity equivalent to 24 suns. Subsequently, that research group found that they could double this enhancement with the addition of a back reflector.\(^\text{33}\)

As will be clear by now, it is not trivial to compare upconverter efficiencies. Particularly
between different groups, who generally report different metrics. It would, of course, be most helpful to be able to report a standardised metric for each experiment. However, there exists no agreed-upon metric and publications do not, as a rule, provide enough information for their results to be compared on a case by case basis. The various attempts to introduce a comparison metric for upconverter performance are detailed in section 2.3.

**A molecular Intermediate-band Solar Cell (IBSC)**

One other design which increases the limit of external quantum efficiency is that of the intermediate band gap solar cell (IBSC). This cell requires that two photons be absorbed before charge is extracted, the same requirement as upconversion. Van Roosmalen\(^\text{34}\) discusses using two dyes within a dye sensitized solar cell to produce an IBSC. However, the mechanism involved in this type of upconversion is quite distinct from that of TTA and will not be discussed further. Ekins-Daukes and Schmidt (2008)\(^\text{35}\) present an approach which includes TTA within an IBSC design. In their scheme, the OUC process occurs as detailed in chapter 2. However, rather than allowing the final singlet excitation to fluoresce, its energy is extracted through an electrical contact, quenching the upconverted fluorescence. This difference is shown schematically in figure 1.7.

![Figure 1.7](image_url)

**Figure 1.7:** Schematic of the difference between the classic OUC scheme and a molecular intermediate band cell design working on the same principle. The singlet excitation on the emitter molecule is either A) extracted to a metal contact, or B) fluoresces to produce upconversion.

The biggest, and most obvious, difference between an OUC system and an IBSC is that in the IBSC case charge must actually be extracted within the cell, from the \(S_1\) state of the emitter. As this, or at least a similar, process is already achieved in dye sensitized cells it is clearly not impossible. The much tougher challenge to overcome is the regeneration of the emitters ground state. In OUC, the excitation relaxes and fluoresces, leaving the emitter neutral and relaxed. In the IBSC, the emitter will become positively charged as it may lose
an electron every time it is excited. Again, this process is similar to that which occurs in
dye sensitised cells, but remains a significant challenge as the regeneration step has not yet
been extensively investigated for this type of device.

Two separate cases are discussed by Ekins-Daukes and Schmidt in their 2008 paper; a sym-
matic case (where one sensitising molecule is used) and an anti-symmetric case where two
sensitizing molecules are used to pump the emitter into its $S_1$ state. In the first case, the
IBSC can only absorb photons from one region of spectrum, and in the second the absorp-
tion of photons may be achieved by either molecule. Providing that these sensitiser have
sufficiently different absorption spectra, the effective absorption range of the system almost
doubles. The calculated limiting efficiencies for each of these cases are 40.6% and 49%
respectively for ideally constructed devices. The anti-symmetric case is inherently more ef-
ficient as it is able to harvest light from more of the solar spectrum, though it would also be
more difficult to realise practically as the behaviour at least one more molecule needs to be
included and understood. In their calculations, the highest efficiency for a symmetric IBSC
(40.6%) was found to be for a theoretical molecule with a bandgap of around 2 eV. Rubrene,
a fluorescent molecule often used in OUC research, has a singlet bandgap of approximately
2.3 eV, close to this ideal. In fact, according to their calculations, an IBSC extracting charge
from rubrene would operate at an efficiency of around 39% at one sun.

1.3 Other applications for upconversion

There are several potential uses for upconversion other than photovoltaics, and many of the
results in this thesis can be applied to those too. Very brief descriptions of some potential
uses are outlined below.

1.3.1 Ultra-fast spectroscopy

Upconversion through sum-frequency generation (SFG) has been used as a spectroscopic
technique to provide ultrafast time resolution for spectroscopic and luminescence experimen-
tation for many years. The principle of this is that luminescence generated in a sample
by a laser pulse is mixed in a non-linear crystal with light from another, much shorter, laser
pulse. This second pulse can be delayed by a very small time increments (typically by
slightly extending the path length of this pulse). The luminescence of the sample decays
many times slower than the pump pulse, so over many repetitions the pump pulse can be
shifted across the entire duration of the luminescence signal. The optical gating effect as
a result of this convolution means that signal is only recorded when both the pump pulse and the luminescence signal are co-incident on the crystal. Upconversion of this kind can provide luminescence gating time resolution comparable to the laser pulse width. Unlike the other uses of upconversion in this section, OUC is particularly inappropriate for optical gating, as it is much less efficient than SFG/SHG at laser intensities. For comparison, SFG can convert up to 90% of incident photons at high intensities, whereas OUC is reported to convert a maximum of around 60% of incident photons.

1.3.2 Medical

As will be explained in chapter 2, OUC generates singlet oxygen. This can be used in some cancer treatments, such as photo-dynamic therapy (PDT), where cytotoxic (singlet) oxygen is formed from local, dissolved, oxygen in the body. This oxygen attacks nearby cells, so accurate targeting of this treatment is vital, and the generation of singlet O₂ only where it is needed is essential. Skin and flesh are poor transmitters of the high energy light required to form singlet oxygen conventionally. So longer wavelength light is ideal for deeper tissue transmission. Chatterjee and Yong (2008) used PEI/NaYF₄:Yb³⁺,Er³⁺ nanoparticles to achieve 80% annihilation of cancerous cells in lab conditions. The energetic process for PDT (figure 1.8) is identical to the first step in our TTA-UC scheme, figure 2.4. The obvious requirement for efficient PDT excitation is that the triplet generated by the sensitising molecule has sufficient energy to encourage transfer to the oxygen molecule. This is almost always the case for attempting TTA-UC at optical frequencies (see section 2.5), so much of the molecular expertise already developed in this field is potentially of use.

\[
\begin{align*}
S_1 & \xrightarrow{\text{ISC}} T_1 \\
\text{h}_\nu & \\
S_0 & \xrightarrow{\text{TET}} S_1 \quad \text{Sensitiser} \\
& \quad \text{O}_2
\end{align*}
\]

**Figure 1.8:** Schematic of the formation of singlet oxygen via molecular TET for PDT.

Wang and Liu (2011) showed that it is also possible to load drugs onto an upconverting nanoparticle, which can penetrate into cells. When activated by low energy light, the
upconversion process produces light of the correct wavelength to release these drugs into target cells.

1.3.3 Imaging and display

Upconverted fluorescence imaging is used extensively in the medical world, even for use in vivo. Again, most of this research uses RE nanoparticles, though OUC could also perform similarly well. Upconversion is rarely, if ever, observed in biological tissue at non-dangerous light intensities. This means that using upconverted fluorescence as the imaging source removes any problems with tissue auto-fluorescence which occurs much more readily in nature. To use this method, the upconverting material is injected into an animal or set of cells. Upon excitation by IR laser light, the material exhibits upconverted fluorescence, and is easily imaged using short pass filters. If the material has been functionalised to attach to particular structures or proteins it stays attached to those structures, providing information on the condition of the areas that it is present in.

The use of upconversion for displays has also been investigated. Miteva et al. showed that an NIR laser (at ≈20 mWcm$^{-2}$) could excite their OUC materials sufficiently to produce a clearly visible image on a rubbery polymer screen. This image could be refreshed at up to 12kHz, easily fast enough for high quality video. They also demonstrate that the choice of emitter molecule allows for many colours to be emitted. It is thus possible to imagine the production of an almost entirely transparent, full colour, emissive screen with no electrical connections.

Though not completely identical to OUC for PV, upconversion is also used in some LED designs. In OLEDs, organic molecules are electrically pumped into their excited states and allowed to fluoresce. Normally OLED research groups see triplet excitations as losses, as they allow for phosphorescence as an alternative to the desired fluorescence and emit in a spectral region that is not what is normally desired. However, it has been shown that triplets generated in this way may also be induced to undergo TTA and fluoresce. This property means that the device may be operated at a lower voltage, increasing its lifetime, though using TTA of course requires at least double the current and intrinsically reduces the efficiency of the device.

1.3.4 Light activated actuators

One recent novel example of an upconversion application is in the actuation of polymers. Jiang et al. (2013) used an OUC pairing of PtTPBP and 9,10-bis(diphenylphosphoryl)
anthracene (BDPPA) to form a phototrigger of a photodeformable cross-linked liquid-crystal polymer. The OUC materials were incorporated into a rubbery polyurethane film, which also contained azotolane. This film was observed to physically bend towards the excitation light source as the azotolane has a \textit{trans-dis} photoisomerisation which leads to an alignment change. On a macro scale, this change is sufficient to physically deform the films. The authors proposed that this technology has potential use in novel biological applications, citing the low thermal heating involved in actuation and the excellent tissue penetration of the excitation light.

1.4 Structure of document

This thesis documents the investigation of two-photon molecular upconversion. Following this introductory chapter, which describes the fundamentals of solar power and how upconversion can be an asset to that technology, the specifics of upconversion are detailed in chapter 2. Chapter 3 details the theory and modelling work undertaken in the course of this research. Specifically, information from time-dependant experimental spectroscopy is first used to inform the construction of a kinetic rate model (KRM). This model builds on a steady state model, first published in 2009.\textsuperscript{46} Chapter 4 details the experimental techniques that were used heavily throughout this work, including the construction of an automated fluorescence experiment. Chapter 5 then reports upon the spectrographic data used in construction of the KRM and shows how the KRM allowed for the fitting of experimental data and prediction of important rate constants. Knowing that if this technology is to be used in a commercial setting, it must be easily fabricated, we then went on to investigate how a solid-state upconverter based on this system would perform, further background and results are presented in chapter 6. A Monte-Carlo particle model (MCM, chapter 3) was used to help explain why intimate intermixing of components, and hence materials processing, is absolutely vital for a solid state upconverter to function. In the final part of chapter 6, an introduction is made to a technique for measuring the degree of intermixing in a system such as this: micro-absorption imaging. A concluding chapter follows, which also presents several leads on new interesting research questions for this field.
Chapter 2

Upconversion Review

This chapter reviews the fundamental principles of both inorganic and organic upconversion and briefly addresses how each process differs. It goes on to discuss organic upconversion in detail, from singlet and triplet states through energy transfer steps to efficiency metrics and how to compare between organic and inorganic upconversion.

It then discusses the considerations which must be made when choosing molecular pairs for organic upconversion, both for sensitisers and emitters. Finally it discusses the importance of removing ground state oxygen from organic upconverting systems.

Photograph of OUC from a PQ₄Pd/rubrene blend excited with a He-Ne laser.
2.1 Inorganic upconversion

Sequential absorption of photons leading to upconversion was first experimentally observed by Kaiser and Garrett (1961). In this process one photon is absorbed, which excites an ion or molecule. Before this excitation can relax, a second photon is absorbed by the same site. From the second excited state, a single photon can be emitted which has higher energy than the two input photons. Clearly, if the lifetime of the initial excited state is short (as it is in most materials), the arrival rate of photons must be extremely rapid, requiring photon flux densities of around $1 \times 10^{24}$ photon m$^{-2}$s$^{-1}$.

2.1.1 Rare earth upconversion

Photon upconversion of this type is most often observed in rare earth (RE) materials, typically nanocrystals containing lanthanides and other transition metal ions. Lanthanides are elements whose electron orbitals are filled up to the 4$f$ level. There are, in fact, three mechanisms that can lead to rare earth upconversion: (1) resonant, or (2) phonon assisted energy transfer (ET), and (3) ground state absorption (GSA) followed by excited state absorption (ESA). These mechanisms are shown in figure 2.1. The energy transfer mechanisms (numbers 1 and 2) require two ion sites, and can both be considered as energy transfer up-conversion (ETU). For a PV application, where all wavelengths of light are present, there is little practical difference between them, though when calculating rates and efficiencies the flux of each wavelength must be considered in case 2. GSA/ESA requires only one ion site. However, as shown in chapter 1, trapping the excitation on one site will not allow for efficient upconversion as only very few photons will be coincident on that spot within a short period, at low photon flux. The heavier lanthanides then have a partially filled 4$f$ shell which provides the ions of these metals with a large number of possible electronic configurations, and hence optical transitions. These absorptions are spread across the NIR, visible (VIS) and ultra-violet (UV) ranges of the visible spectrum. Many rare earth upconverters make use of erbium and ytterbium ions ($Er^{3+}$ and $Yb^{3+}$ respectively).

Rare earth upconversion is often limited by the relatively small absorption cross section of the material, though it has been shown to produce a reasonable upconverted output power of 0.47 mW when excited by 1.27 Wcm$^{-2}$, 980 nm laser. This significant upconverted luminescence can be explained by the fact that the low absorption cross section is a consequence of the fact that the electronic transitions being targeted are ‘forbidden’ in quantum mechanics. This means that the reverse process is also ‘forbidden’ so each excited state has a long lifetime, typically on the order of milliseconds.
Figure 2.1: Sketch of the energy transfer mechanisms involved in rare earth upconversion. Either resonant or phonon assisted energy transfer, and ground state absorption (GSA) followed by excited state absorption (ESA). The ET mechanisms require two ion sites, whereas GSA/ESA requires only one.

2.1.2 Sum-frequency generation

An entirely optical method of upconversion is sum-frequency generation. In this scheme, photons are never absorbed. Rather, the non-linear dielectric coefficient of the upconverting crystal causes the photons to combine. The first example of upconversion through sum-frequency generation (SFG) was in 1961 when Franken et al. generated 347.1 nm light by passing a 694.2 nm laser through a quartz crystal. This is a special case of SFG where the angular frequency of each input photon is equal to exactly half of the angular frequency of the output photon, i.e. $\omega_1 = \omega_2 = \frac{1}{2}\omega_3$. This is also known as second harmonic generation (SHG). For the SFG process to proceed with reasonable efficiency the phase of each photon should also be well matched. This is relatively simple to achieve in SHG as all photons come from one laser source. More generally, this condition can be achieved in SFG with two light sources but it is more difficult. Then, for SHG we require that two photons interact with the same oscillator, at the same time, with the same angular frequency and phase. As pointed out in chapter 1, without any sort of mobility or significant lifetime, the chance of coincidence of photon energy is minute under low photon flux. Therefore any application of SFG/SHG requires carefully designed optics and very high coherent photon flux, typically laser intensities in the order of kWcm$^{-2}$ and MWcm$^{-2}$ and spectral power densities in the order of 10Wnm$^{-1}$, which is entirely inappropriate for photovoltaics.
2.2 Organic upconversion (OUC) through triplet-triplet annihilation

Organic upconversion (OUC) is a less direct method of achieving an anti-Stokes shift than those mentioned previously. Like rare earth upconversion, this method exploits long-lived excited states to achieve upconversion. In OUC these long-lived states are triplets, which typically survive for several tens of $\mu$s, as opposed to singlet states which typically only survive for tens of ns.\(^{57}\) This extended lifetime relaxes the requirement for two photons to be in the same place at precisely the same time. Molecules can also be chosen such that two or more sensitising molecules can populate a single emitting molecule, broadening the spectral range of the technique.\(^{58}\) These triplets are able to undergo a triplet-triplet annihilation (TTA), also known as triplet fusion,\(^{44}\) process to excite an emitting molecule into a singlet state which can then fluoresce promptly.\(^{59}\)

2.2.1 Singlets, triplets and intersystem crossing

Electrons are fermions, so an individual electron has a spin angular momentum quantum number (S) of $S = \frac{1}{2}$, this can be either a spin ‘up’ or ‘down’. If we consider the two highest energy electrons in a molecule as a pair, they are allowed to form either a singlet (where the spatial part of their combined wavefunction is symmetric) or a triplet (where the spatial part of the combined wavefunction is anti-symmetric).\(^{60}\) For a singlet state, the total angular momentum must be $S = 0$, and the electrons must have opposite spin. If $S = 1$, there are three ways to orient these paired electron spins so that state is denoted a triplet. These arrangements are shown in figure 2.2. A quintet state has $S = 2$ and can only form when four unpaired electrons possess the same spin.

Hund’s rule states that the electronic configuration that leads to greatest stability also has greatest spin. Accordingly, this means that every orbital in a subshell is singly occupied with one electron before any one orbital is doubly occupied, and that all electrons in singly occupied orbitals have the same spin. For our purposes, this means that atomic, or molecular, orbitals of equal energy will be filled first by electrons with parallel spin before starting to pair electrons into the same orbitals. Having parallel spins makes the spin part of the wavefunction symmetric, but the total wavefunction for the electrons must be anti-symmetric since they must obey the Pauli exclusion principle. This means that the space part of the wavefunction must be anti-symmetric. An anti-symmetric space wavefunction for the two electrons implies a larger average distance between them than a symmetric function of the same type. The probability of finding an electron at some point is the square of its
Figure 2.2: Sketch of the spin configuration of a singlet, left, and the three triplet configurations, right.

wavefunction, and from a simple functional point of view, the square of an anti-symmetric function must go to zero at the origin. In general then, the two electrons are more likely to be further apart than if they had a symmetric space wavefunction. If the electrons are on the average further apart, then there will be less shielding of the nucleus by the ground state electron(s), and the excited state electron will therefore be more exposed to the nucleus. This implies that it will be more tightly bound and of lower energy. This simple argument is illustrated in figure 2.3.

Figure 2.3: Sketches of symmetric and anti-symmetric spatial wavefunctions. In the symmetric case, when the spatial part of the wavefunction is squared to find the expectation value, the two electrons are expected to be close to the origin. However, in the anti-symmetric case, the expectation value must be zero at the center as the function changes sign. This forces the expectation value to move further from the origin.
Spin must normally be conserved, and a photon has no spin, so photons can only strongly couple to transitions up and down either the singlet or triplet channels. Spin-orbit coupling increases the splitting of energy levels in the molecule. Increased overlap between the energy level of the highest energy triplet state and the singlet state facilitates a spin flip and allows a singlet to become a triplet and vice-versa. This increased overlap proceeds in proportion to the number of protons that the electron can ‘see’, i.e. the size of the relevant nucleus. This process of a single ‘forbidden’ spin flip is referred to as intersystem crossing (ISC).

2.2.2 Organic upconversion scheme

Several groups including Baluschev et al. (2008),5 and Auckett et al. (2009),46 have proposed an energetic scheme of TTA wherein a sensitising molecule is excited to its \( S_1 \) (singlet) state, which undergoes rapid ISC to its \( T_1 \) (triplet) state. Along with the trivial depopulation channels for these states (both radiative and non-radiative decay) the triplet excitation can be transferred directly to the triplet state of an emitter molecule, referred to as triplet energy transfer (TET). When two emitter molecules in their \( T_1 \) states interact, they form encounter complexes of singlet, triplet, or quintet multiplicity in the ratio 1:3:5.61 If the singlet complex is formed, it may decay radiatively. This scheme is shown in figure 2.4. This figure is a slightly modified Jablonski diagram,62 where molecular electronic energy levels are represented by horizontal lines, and triplet energies are offset slightly sideways to differentiate them. In this figure, \( S_0 \) and \( S_1 \) represent ground state and excited singlets and \( T_1 \) represents the first excited triplet state. Monguzzi et al. (2008)28 demonstrated that the energy transfer step in figure 2.4 can be treated as a Dexter energy transfer plus a diffusive term by performing a temperature-dependent analysis of transient upconverted photolu-
minescence. Auckett et al. developed a steady state model to describe the entire process, which has been the theoretical basis for several papers from that group since then. The groups of Baluschev and Castellano (among others) subscribe to this scheme as well. However, in general each group has only shown evidence of the input and output from the process and inferred the internal mechanisms involved. A paper based on work in chapter 5 (included in Appendix A) provides direct evidence that the intermediate TET step also proceeds according to this scheme, Piper et al. (2014).

It is clear that there are several steps to achieving upconversion in this way, and each of these has an associated energy loss. These losses, and their importance, are discussed later in this section. It has been argued from a spin-statistical starting point that the maximum efficiency of the key TTA process should be 11%. However, as explained at the end of this section, the fundamental limit is not so easy to determine. This method is the most efficient upconversion pathway for organic systems yet discovered and has been shown to function at around 60% efficiency, well above 11%.

Energy transfers

While the ISC process occurs in the sensitising molecule, the mechanisms which control triplet energy transfer (TET) and triplet-triplet annihilation (TTA) must inherently involve the transfer of energy between molecules and therefore requires a more complex conversion mechanism.

Between molecules, even those containing heavy metal atoms, interaction and exchange of electrons must conserve spin. Two kinds of radiationless energy transfer are often considered. The first of these is Förster energy transfer, also known as Fluorescent Resonant Energy Transfer (FRET). In this theory, energy transfer is mediated through long-range dipole-dipole interaction between molecules. Efficient FRET requires that there is a spectral overlap in the emission spectrum of the donating molecule and the absorption spectrum of the receiving molecule, and that the molecules are reasonably close to each other as the transfer efficiency also depends on a factor of \( r^{-6} \). As it is desired that the energy transfers involved in OUC do not have much or any spectral overlap, FRET is not considered a significant contributor to the process of OUC. However, in the case of hetero-annihilation (see section 3.1.1), it is possible that the singlet levels of the two molecules are sufficiently close to one another that a FRET type transfer can occur, which is equivalent to the loss of a sensitiser triplet to the system.

The second type of energy transfer considered herein is Dexter energy transfer, or ‘exchange type’. This kind of transfer relies on the overlap of the electronic wave functions of the
donor and acceptor molecules. The rate constant $k_{ET}$ for Dexter type transfer decreases exponentially with increased distance, and decays even more rapidly than that of FRET. This decay can be represented by equation (2.1). This formalism, also known as the Perrin approximation, simply means that if two molecules are within their Dexter radius, $R_{D0}$, an exchange will happen instantaneously and if they are beyond that radius there will never be an exchange. The Dexter radius can also be described as the radius at which energy transfer occurs at the same rate as the decay of the sensitizer in absence of emitter molecules.

$$k_{ET} = \begin{cases} 0 & \text{for } R > R_{D0} \\ \infty & \text{for } R < R_{D0} \end{cases}$$  \hspace{1cm} (2.1)

Unlike FRET, Dexter ET does not require an additional spin flip for each for triplet energy transfer. This is because it is a correlated electron transfer. Effectively meaning that as an excited electron is passed from the donor to the acceptor, a ground state electron is passed back and each retains its spin. A sketch of FRET and Dexter ET, showing why FRET is not an effective triplet exchange mechanism, can be seen in figure 2.5.

![Sketch of triplet energy transfer](image)

**Figure 2.5:** Sketch of the triplet energy transfers possible under Dexter and FRET formalisms. FRET requires two spin flips (ISC), whereas Dexter ET does not.

A typical Dexter radius is on the order of 0.1 - 0.2 nm. Monguzzi et al. calculated the Dexter radius of the sensitiser/emitter pair PtOEP and DPA as 26.5 Å. This is much larger.
than the ‘expected’ value. The authors rationalised this value as being due to the excellent match between sensitizer and emitter energy levels increasing the transfer probability and hence effective range. This conclusion follows from the form of the Dexter rate equation,\textsuperscript{68} which as mentioned above depends on both the overlap of electronic wavefunctions and spectral overlap.

**Energy losses**

There are several inherent energy losses inherent to the OUC process. These are shown in figure 2.6. First, there must be an energy drop when crossing from $S_1$ to $T_1$ (ISC), or back-transfer could occur and the triplet state would not be stable. A less stable, shorter lived, mixed state would then form. This is $\Delta E_1$ on figure 2.6. Second, there must also be an energy drop (though this can also be a gain in specific circumstances\textsuperscript{63}) to drive TET from the sensitizer triplet to the emitter triplet, $\Delta E_2$. The last required energy loss is that which is lost when the sum of the energy of the two triplets ($E_{\text{Triplet}}$) is greater than the single singlet state, $\Delta E_3$. If $E_{\text{Triplet}} \times 2 \neq E_{S_1\rightarrow S_0}$ then the emitter singlet will not form and there can be no upconverted emission. This means that the highest possible energy of an upconverted photon is not $E_{\text{out}} = 2 \times (E_{\text{in}})$, rather it is $E_{\text{out}} = 2 \times E_{\text{in}} - \Delta E_1 - \Delta E_2 - \Delta E_3$.

\[ \text{Figure 2.6: Sketch of the fundamental losses implied by the TTA-UC scheme. } \Delta E_1 \text{ is a required loss to form a stable triplet state, } \Delta E_2 \text{ is a loss required to drive TET and } \Delta E_3 \text{ is a loss required to populate the emitter singlet state.} \]

In addition to these fundamental losses, any terrestrial system based on this scheme will also be exposed to atmospheric oxygen. The consequences of this are discussed in section 2.5.
Spin statistical arguments\textsuperscript{70} suggest that the fundamental efficiency limit of triplet mediated upconversion is 11.1\%. When two emitter molecules in their triplet state come together, singlet, triplet and quintet spin multiplicities are formed. Assigning equal probability to the formation of each of these states, a singlet state will be formed once in nine collisions, triplets in three of nine collisions and quintets in the remaining five of nine. This gives a maximum of one upconverted photon out for 18 photons in, or 11.1\%.

However, it has been shown that the triplet and quintet encounter complexes do not necessarily quench the combined energies of the interacting triplet states.\textsuperscript{3,61} This is the case for molecules where the second excited triplet state is higher in energy than twice the energy of each contributing triplet i.e. the encounter complex would require additional energy (thermal or entropic) to form the second excited triplet state. This is true in the case of rubrene.\textsuperscript{71} This compound has also been shown to undergo TTA when electrically pumped, to function as an organic light emitting diode (OLED).\textsuperscript{72} The TTA emission here was found to significantly exceed the spin-statistical limit.

The possibility of breaking this spin limit is explained through consideration of the decay pathways available to triplet and quintets when they interact. The quintet state is unable to undergo a spin-allowed, radiationless, transition to a lower state. There is therefore a reasonable probability that the encounter complex will dissociate back into triplet states. This would preserve the excitation energy for another collision. A triplet encounter complex could convert to a state where one moiety is in the $T_2$ state and the other returns to the ground state, provided that this is not energetically forbidden. The $T_2$ state could then decay into the $T_1$ state which would have the net effect of quenching the energy of one of the original triplets. This would allow for the maximum TTA yield to be 40\%. However, this limit can also be broken; if the $T_2$ state of the emitter is many times $k_BT$ higher than twice the energy of $T_1$ then the triplet encounter complex will behave in the same way as the quintet and preserve its energy through unsuccessful collisions. This removes all spin-based efficiency limits and allows a 100\% TTA yield to be considered, but only if the emitters quintet and $T_2$ states are thermally inaccessible i.e. the only option for relaxation is fluorescence. This explanation is shown diagrammatically in figure 2.7.
Figure 2.7: Diagrams of excited state combination possibilities for two excited triplets. a) two excited triplets (*T) may form singlet (1[^*]), triplet (3[^*]) or quintet (5[^*]) encounter complexes. Only one of these may fluoresce (singlet) so \( \eta_{conv} \) is limited to 11%. b) the quintet channel is now energetically inaccessible, and the triplet encounter complex is understood to no longer relax both excited molecules, and regenerates one triplet. \( \eta_{conv} \) is now 40%. c) both quintet and triplet encounter complexes are energetically inaccessible, so the only option is fluorescence and here \( \eta_{conv} \) may exceed 40%.

2.3 Upconversion efficiency metrics

This thesis deals almost exclusively with molecular upconversion, but it has been important to introduce the other methods of upconversion so that their relative strengths, weaknesses, and uses could be discussed. In order to make a comparison between these methods we must have a standard figure of merit to compare them on. The definition of such a figure has not yet been settled upon by the various communities, and groups understandably often use whichever figure of merit, or efficiency rating makes their result look best. The most
straightforward figure would seem to be to simply count the number of upconverted photons being emitted, and divide that by the number of photons that are absorbed. However, this leaves a maximum attainable efficiency of 50%, so many groups multiply their result by 2 so that the maximum efficiency remains 100% i.e. equation (2.2). From here on we will only consider this ‘100%’ definition.

\[ \eta = 2 \times \frac{\text{upconverted photons}}{\text{absorbed photons}} \] (2.2)

Upconversion quantum yield can be calculated from photoluminescence (PL) experiments using equation (2.3),\textsuperscript{73,74} where \( \Phi, A, I \) and \( \eta \) symbolise quantum yield, absorbance, PL intensity and refractive index of a sample (\( \text{sam} \)) and reference material (\( \text{ref} \)) respectively. Providing that measurements of the sample and reference are made using the same equipment, there is no need to account for detector quantum yield, providing the detector behaves linearly in that regime of illumination.

\[ \Phi_{\text{sam}} = 2 \Phi_{\text{ref}} \left( \frac{A_{\text{ref}}}{A_{\text{sam}}} \right) \left( \frac{I_{\text{sam}}}{I_{\text{ref}}} \right) \left( \frac{\eta_{\text{sam}}}{\eta_{\text{ref}}} \right)^2 \] (2.3)

This is insufficient to compare results between groups and techniques, as it does not take into account the spectral response of the material system. Spectral dependence is not of critical importance in situations where the upconversion process is laser driven, but is vital when the system is intended for solar cell efficiency enhancement, which was discussed in section 1.2. In order to account for the spectral dependence of upconversion, Fischer et al. (2010)\textsuperscript{75} define spectral optical UC efficiency, \( \eta_{\text{UC,spectral}}(\lambda_{\text{inc}}, \lambda_{\text{UC}}, I) \), as shown in equation (2.4) where \( \lambda_{\text{inc}} \) is the wavelength of incident photons, \( \lambda_{\text{UC}} \) is the wavelength of upconverted photons and \( I \) is the irradiance of photons. They then integrate this over the wavelength of upconverted photons, equation (2.5), and normalise against irradiance: equation (2.6). This normalised upconversion efficiency, \( \bar{\eta}_{\text{UC}} \), has units of cm\(^2\)W\(^{-1}\). Equation (2.3) includes terms describing the absorption properties of the system, so the following equations can be considered as ‘external’, and so account for incomplete absorption. Corresponding equations can be constructed to only take into account internal processes, by omitting the absorption terms in equation (2.3), and assuming 100% absorption of photons. This distinction is particularly important in rare-earth upconversion, where external efficiency is limited by the relatively low absorbance of the upconverting material. For OUC this condition is relaxed as the molecules are chosen to be strongly absorbing.

\[ \eta_{\text{UC,spectral}}(\lambda_{\text{inc}}, \lambda_{\text{UC}}, I) = \frac{\Phi_{\text{UC}}(\lambda_{\text{UC}}, I)}{\Phi_{\text{inc}}(\lambda_{\text{inc}}, I)} \] (2.4)
This value is independent of upconverted and incident wavelengths and the absorption bandwidth of the upconverting material. A further development of this unit provides normalised upconversion efficiency per sun, $\eta_{UC}^\circ$, equation (2.7), where $F^\circ_\lambda$ is the spectral radiative emittance of the upconverted light flux and is integrated over the absorption region of the upconverter.

$$
\eta_{UC}^\circ(\lambda_{inc}, I) = \eta_{UC}(\lambda_{inc}, I) I
$$

In the case of upconversion for solar cell efficiency enhancement, see section 1.2, Schulze et al. (2012) have applied a figure of merit to compare real-world advantages of experimental upconverting systems. This value calculates the total short circuit current density increase of solar cells due to upconversion, equation (2.8), where $e$ is the elementary charge, $f_c$ a concentration factor (number of suns), $\rho_\circ$ is the AM1.5 solar flux in photons area$^{-1}$wavelength$^{-1}$ and $\Delta\text{EQE}^{UC}$ is the difference of EQE measurements with, and without, active upconverter. $\Delta J_{SC}^{UC}$ has units of mAcm$^{-2}$.

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

This equation can be further extended to consider the relative effectiveness of upconverting schemes at any solar concentration, by normalising for the square of solar concentration. This gives a figure $\zeta$ with units of mAcm$^{-2} \circ^{-2}$, where $\circ^{-2}$ denotes ‘per sun squared’. Schulze et al. (2012) make a comparison between a rare earth upconverter and the upconverter used in that reference molecular system, using this metric. It was found that the best case molecular system out-performed the rare earth device by $\zeta = 4.9 \times 10^{-4}$mAcm$^{-2} \circ^{-2}$ to $\zeta = 1.7 \times 10^{-4}$mAcm$^{-2} \circ^{-2}$. Schulze also points out that to be of commercial interest, this value still needs to be improved by more than three orders of magnitude. The most recent record which has been calculated to conform to this metric is $\zeta = 6.8 \times 10^{-4}$mAcm$^{-2} \circ^{-2}$, held by Fischer et al. (2014). Though Goldschmidt et al. (2014) claim higher efficiencies, they have not provided enough information to convert their result into this metric so comparison, again, becomes difficult.


2.4 Choice of molecules for OUC

Every process involved in OUC depends on the electronic, optical and chemical properties of the compounds used. The following sections discuss the most important factors in choosing which molecules to use, and introduce those used during the experimental phase of this research.

2.4.1 Sensitisers

There are four desirable properties that sensitising molecules should possess. Firstly, they must strongly absorb in the desired region of the EM spectrum. Upconversion efficiency increases with this cross section. This is partly because the concentration of sensitiser required to absorb a given proportion of incident light is reduced as cross section increases. Therefore a higher concentration of emitter molecules may be used without increasing non-radiative losses. The exact position of the lowest absorption band can be tuned to some degree by changing the conjugation length of the molecule. A longer section of conjugated $\pi$ orbitals allows absorption of lower energy light. Secondly, they must undergo efficient ISC to produce triplets. Thirdly, this new triplet level must have a sufficiently long half-life while minimizing the energy lost from the ISC process. Fourthly, the triplet level must be slightly more energetic than that of the emitter triplet, to facilitate TET.

Generally we find that the metalated macrocycle family of molecules fit these properties well. In literature, commonly used sensitizing molecules include platinum, palladium, zinc and copper octaethylporphyrins, Ru(II)diimine and iridium phenylpyridine-metal-to-ligand charge transfer complexes, a selection of these are displayed in 2.1. The ISC process is strongly enhanced in these metallated molecules by spin-orbit coupling to their central heavy metal atoms, and is complete within 2 picoseconds of excitation.\(^3\) This rapid crossing leads to an ISC efficiency which approaches unity.\(^{77}\) Molecules employed as sensitisers in OUC typically require complex synthesis pathways, which are not discussed here. For an indication of some of these see Yakutkin \textit{et al.} (2008)\(^{78}\) and Cheng \textit{et al.} (2009).\(^{79}\)

The development of new sensitizers continues to be an active area of research, for example in the boron dipyrrromethene (BODIPY) class of fluorophores.\(^{80}\) Yakutki \textit{et al.} (2008)\(^{78}\) report the synthesis of a tetraanthrkaporphyrin complex (PdTAP), which shows upconversion in solution with rubrene from 790 nm to 570 nm at low excitation intensity, 250 mW cm\(^{-2}\). To date, this is the furthest into the IR end of the electromagnetic spectrum that has been reached in a TTA system and was achieved through increased $\pi$-conjugation in the sensitizing molecule, reducing the HOMO/LUMO gap.
Table 2.1: A selection of popular emitters and sensitisers, with the maximum upconversion energy step that can be achieved by using these molecules, in eV.

<table>
<thead>
<tr>
<th>Sensitisers</th>
<th>Emitters</th>
<th>PtOEP &amp; 5,83,86,88-90</th>
<th>PdPh4TPB &amp; 5,87</th>
<th>PtTPB &amp; 45,80-82</th>
<th>PQ4P &amp; 32,61,65</th>
<th>PdTAP &amp; 78,82</th>
</tr>
</thead>
<tbody>
<tr>
<td>AN &amp; 90-93</td>
<td></td>
<td>0.12</td>
<td>0.13</td>
<td>0.21</td>
<td>0.23</td>
<td>0.33</td>
</tr>
<tr>
<td>DPA &amp; 83,84,88,89</td>
<td>0.08</td>
<td>0.08</td>
<td>0.16</td>
<td>0.19</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td>Perylene &amp; 42,81</td>
<td>0.07</td>
<td>0.07</td>
<td>0.15</td>
<td>0.18</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>bis(tetracene) &amp; 18,72,74</td>
<td>0.04</td>
<td>0.04</td>
<td>0.13</td>
<td>0.15</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>BPEA &amp; 84,87</td>
<td>0.01</td>
<td>0.02</td>
<td>0.10</td>
<td>0.12</td>
<td>0.22</td>
<td></td>
</tr>
<tr>
<td>Rubrene &amp; 32,42,58,61,65</td>
<td>-0.02</td>
<td>-0.02</td>
<td>0.06</td>
<td>0.09</td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td>BPEN &amp; 5,82</td>
<td>-0.13</td>
<td>-0.13</td>
<td>-0.05</td>
<td>-0.02</td>
<td>0.07</td>
<td></td>
</tr>
</tbody>
</table>

2.4.2 Emitters

The requirements for emitter molecules are more relaxed than those for sensitising molecules. They are that: the energy of the triplet level is slightly greater than half of the energy of the singlet transition; the molecule exhibits very efficient fluorescence and; the triplet level is slightly below that of whichever sensitising molecule(s) this emitter is being paired with.

Frequently referenced molecules used as emitters include: rubrene,63,58,61,82 perylene,63,83,84 bis(tetracene),18,9,10 - diphenylanthracene (DPA),84-86 9,10 - bis(phenylethynyl)anthracene (BPEA)82,84,87 and 9,10 - bis(phenylethynyl) napthacene (BPEN).5,82

Table 2.1 contains a selection of sensitiser/emitter pairs which can be found in literature. The values in the middle of the table correspond to the energy gain, in eV, for photons processed by that pair. A negative value here shows that the emitted photon would in fact be lower in energy than the absorbed photons, so more straightforward processes would dominate, and no upconversion would occur.

2.5 Oxygen scavenging

To perform TTA-UC at optical frequencies, the sensitiser triplet level must always be higher in energy than that of ground state oxygen. If we assume that the lower bound for an optical wavelength is 700 nm, or 1.77 eV, and assume we can use an imaginary upconverter with no energy losses, i.e. the absolute minimum triplet energy required to allow for TTA without involving an entropy driven process, then the required energy of each photon to
produce this would be 0.89 eV. This is lower than the energy gap between triplet and singlet oxygen, 0.98 eV. Ideally then, there could be a suitable optical sensitizer which did not excite ground state oxygen with its triplets. Unfortunately as discussed in section 2.2.2, there are several losses that are unavoidable. This means that for optical frequency upconversion, ground state oxygen will always be a scavenger of triplets, and will form singlet oxygen. Figures 2.8a and 2.8b show this schematically.

![Energy level diagrams showing oxygen scavenging of triplet energy. a) The ideal case where no energy loss is required to drive ISC, a sensitizer might exist that could produce visible upconversion (1.77 eV emission). b) A more realistic case, where the triplet level of the sensitizer is sufficient to generate singlet oxygen. In this case the triplet is scavenged before it could be transferred to the emitting molecule.](image)

The singlet form of O$_2$ is also highly reactive, and known to attack the molecules often used in OUC, destroying the function of the system entirely. The exact reaction that occurs of course depends on the structure of the molecules in question. However, often the reaction takes place over one of the many aromatic benzene rings that bulk out these structures, forming an endoperoxide. This breaks up conjugation and completely alters the energy levels of the molecule. It is therefore essential for high TTA yield and long chemical lifetime to remove as much oxygen as possible from the mixture under investigation. Various methods have been reported as being used for the de-oxygenation of TTA mixtures.

Of course, in a real device there could be some encapsulation or sacrificial component to mitigate and slow the incursion of molecular oxygen. In an experimental setting, however, we must be aware of the effect oxygen can have on a triplet based upconverter.
Chapter 3

Theory and Modelling

This chapter answers two research questions: ‘how can a rate model be used to predict the behaviour of OUC, and to predict and define the key parameters and rate constants of the process¿ and ‘how can a descriptive model be useful in gaining deep intuitive understanding of complex behaviour in rigid media¿. As such, it is concerned with the development and implementation of the two significant models used in this research to describe and investigate the molecular upconversion process. These are a Kinetic Rate Model (KRM), based on the equations of Auckett et al. (J. Phys. Conf. Ser 2009 185) that is primarily used to understand triplet dynamics in solutions (see chapter 4 and appendix A) and a Monte-Carlo particle model (MCM) which uses a simple decision tree to determine what might happen in a two dimensional layer of a bi-molecular upconverting system.

The equations which make up the KRM are discussed, as are the developments we have made to the equations as found in literature. The programmatic structure of the KRM is presented along with how it can be included in an optimisation routine. This model is also validated in both the steady state and transient cases. The decision tree for the MCM is shown, and its use is illustrated.

Successive images of the MCM model allowing molecules to interdiffuse.
3.1 Kinetic Rate Model (KRM)

Auckett et al. (2009)\textsuperscript{46} developed a rate model which quantifies the schematic shown in figure 3.1. This allowed that group to experimentally determine key variables which affect the efficiency of upconversion in a given system. Their equations are transcribed below equations (3.1) and (3.2). Table 3.1 shows the definitions for the various symbols used in these rate equations. Each important term is described in detail in section 3.1.1.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.1.png}
\caption{Jablonski diagram showing every step of OUC.}
\end{figure}

\begin{equation}
\frac{d[X_T]}{dt} = k_\phi[X_G] - k_{TET}[X_T][Y_G] - k_p[X_T] - k_{TTA}(2[X_T]^2 + [X_T][Y_T]) = -\frac{d[X_G]}{dt} \tag{3.1}
\end{equation}

\begin{equation}
\frac{d[Y_T]}{dt} = k_{TET}[Y_G][X_T] - k_{NR}[Y_T] - k_{TTA}(2[Y_T]^2 + [X_T][Y_T]) = -\frac{d[Y_G]}{dt} \tag{3.2}
\end{equation}

\begin{table}[h]
\centering
\begin{tabular}{|c|c|}
\hline
[ ... ] & Concentration of \ \\
\hline
X & Sensitiser molecule \ \\
\hline
Y & Emitter molecule \ \\
\hline
G & Ground state \ \\
\hline
T & Triplet excitation \ \\
\hline
\end{tabular}
\begin{tabular}{c|c|}
& (rate of) Absorption \ \\
\hline
k_\phi & (rate of) Phosphorescence \ \\
\hline
k_p & (rate of) Triplet energy transfer \ \\
\hline
k_{TET} & (rate of) Triplet-triplet annihilation \ \\
\hline
k_{TTA} & (rate of) Non radiative decay \ \\
\hline
\end{tabular}
\caption{Summary of symbols used in equations (3.1) and (3.2). These terms are individually discussed in section 3.1.1.}
\end{table}

Equation (3.1) describes the rate of generation of sensitizer triplet states. It assumes 100% ISC from sensitizer $S_1$ to $T_1$ which, as discussed in reference\textsuperscript{77}, is not unreasonable. Hence
there is no $k_{ISC}$ term. If ISC is not 100% efficient then that loss would be included as part of the non-radiative losses in the system ($k_{nr}$). The only positive term in equation (3.1) is the generation of $X_T$ states through photo-absorption, $k_\phi$. The other terms represent losses to this population. The critical term here is the second one, which represents the generation of $Y_T$ states. For efficient upconversion, all losses other than this should be minimised. This term is then the only positive one in equation (3.2), which describes the depopulation pathways for $Y_T$. It is within equation (3.2) that the rate term for TTA between $Y_T$ molecules is found, which is the term which governs the upconverted fluorescence of the entire system.

The concentrations of emitter and sensitiser molecules are clearly vital to the efficiency of TTA. However, there is a limit to the maximum concentration of these molecules in solution. As observed by Baluschev et al. (2008), when using sufficiently high concentrations of molecules, above 5% of total concentration in their study, non-radiative decay becomes a large loss mechanism and upconversion efficiency drops rapidly. This is due to nearest neighbour coupling and aggregation effects. Thus relative concentration becomes the variable to maximise, with the implication that sensitizing molecules with high absorption coefficients are desirable.

Auckett et al. (2009) found that there is a regime of high photon flux and low losses in this rate model that suggests that the dependence of the number of output photons on the number of incident photons is linear. This conjecture is contrary to previously held belief that there is always a quadratic dependence between the two, but experimental evidence has since found for the existence of a linear regime. Figure 3.2, created using the KRM, finds the same result as that found by Auckett et al. (2009) and Kim et al. (2014). There are two regimes, with different dependencies on photon input. In the region where $k_{NR}$ is large compared to the other rates the dependence is quadratic, i.e. there is a gradient of 2 on a log-log plot. In the regime where $k_{NR}$ is not as significant, the gradient of this dependence changes to one. In this situation, where $k_{nr} \approx 0$, non radiative losses are entirely extinguished so that every emitter triplet always survives to undergo TTA and eventually produces an upconverted photon. In figure 3.2 we also see that there is a high photon flux regime (for every $k_{NR}$) where the system is entirely saturated, and no more upconverted photons are emitted regardless of how much the input flux is increased, there are no more ground state sensitiser molecules to excite. Having a higher $k_{NR}$ here reduces the absolute maximum output flux attainable by the system.

The is also some experimental evidence for this change gradient, though as it is impractical to realise $k_{nr} = 0$, a completely linear slope has not been observed. Rather, Yakutkin et al. (2008) observed that this slope was 1.65 for their system. In order to approach a slope of unity, a sensitiser with high absorbance must be used in low concentration to maximize
the concentration of emitter molecules without encouraging phonon interactions. A system with a linear dependence between the rate of photons absorbed and the rate of upconvertes emission can be considered to be ‘full’. Every emitter site that can be filled with a triplet excitation is filled, so any further input of triplets will immediately complete the OUC process.

![Plot of rate of upconverted photon emission with rate of input photons, $k_\varphi$, for several values of $k_{nr}$.](image)

**Figure 3.2:** Plot of rate of upconverted photon emission with rate of input photons, $k_\varphi$, for several values of $k_{nr}$.

The change of efficiency from quadratic to linear dependence on power followed by a saturation correlates with that which is observed in rare earth upconversion, where the efficiency increases linearly in a low-pump regime and rolls over to sublinear and saturates under high pumping conditions.\(^\text{101}\)

These rate equations were the starting point for our development of this kinetic model. A table containing the default values for the input variables can be found below, table 3.2, there are the values used in each simulation unless otherwise stated. The ways in which we modified those two equations and our justifications for doing so are discussed in section 3.1.3, and can also found in Piper et al. (2014).\(^\text{65}\)
Table 3.2: Default values for variables used in KRM unless otherwise stated elsewhere.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
<th>Variable</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>[X]</td>
<td>$1.16 \times 10^{-4}$ M</td>
<td>$k_{TET}$</td>
<td>$3.33 \times 10^8$ s$^{-1}$</td>
</tr>
<tr>
<td>[Y]</td>
<td>$2.30 \times 10^{-3}$ M</td>
<td>$k_{TTA}$</td>
<td>$1.00 \times 10^8$ s$^{-1}$</td>
</tr>
<tr>
<td>$k_\phi$</td>
<td>$10$ s$^{-1}$</td>
<td>$k_{NR}$</td>
<td>$9.00 \times 10^3$ s$^{-1}$</td>
</tr>
<tr>
<td>$k_p$</td>
<td>$2.50 \times 10^4$ s$^{-1}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.1.1 Rate equation terms

Absorption - $k_\phi$

$k_\phi$ is the first rate constant in these equations. It describes the rate at which photons enter the system. Without a non-zero $k_\phi$ the process would never start. It relates simply to the absorption of light of a particular wavelength by a molecule. Molecules are able to interact with light because there are discrete energy steps associated with their physical properties. These are classified as rotational, vibrational and electronic transitions and are generally found in the microwave, infra-red and visible regions of the electromagnetic spectrum. Obviously, in this thesis we are mostly concerned with electronic transitions as they are of the correct frequency to interact with visible light.

Intersystem Crossing (ISC) - $k_{ISC}$

It is ISC that generates triplets for the upconversion process. An efficient, fast, rate of ISC is essential. Without a rapid ISC channel a large proportion of absorbed energy would be lost as fluorescence. ISC was discussed in section 2.2.1 and is always assumed to be 100% in our models. This assumption is know to be valid for sensitisers with heavy metal centers, for example the rate of fluorescence from tetra PQ$_4$Pd is several orders of magnitude slower than that of ISC, such that all fluorescence from this molecule is complete within 12 ps of excitation.

Sensitiser phosphorescence - $k_p$

$k_p$ relates to the rate of phosphorescent decay of triplets in the sensitiser molecule. It will depend only on the sensitiser molecule itself and can be measured through standard transient photoluminescence/phosphorescence experiments. Discussed in section 4.2.
**Triplet Energy Transfer (TET) - \( k_{\text{TET}} \)**

\( k_{\text{TET}} \) relates to the rate at which energy is transferred from a sensitiser triplet to an emitter triplet. This can be measured through either measuring how phosphorescence decay varies with the presence of a triplet energy quencher (say, the emitter) or through directly observing the average triplet lifetime of a sensitiser molecule through transient absorption spectroscopy (TAS). Stern-Volmer analytics can then be applied to derive the value. Both approaches have been used when investigating a porphyrin/rubrene mixture. The techniques agreed to within 2% of each other.\(^3,6^5\) The energy transfer process which takes place here is a combination of Dexter ET and diffusive processes, see section 2.2.2. As such this rate constant will vary with the ability of molecules, or charges, in the sample to diffuse. As such it will, at the very least, vary with temperature, viscosity and crystallinity (when solid).

**Non-Radiative Decays - \( k_{\text{NR}} \)**

\( k_{\text{NR}} \) is the rate constant associated with the non-radiative decay of triplet energy from the emitter molecule in this system. This rate should only depend on the physical properties of the molecule, and the refractive index of the environment that the molecule is in. It is not affected by experimental variables except at high concentrations, where aggregation and phonon effects become significant.

**Triplet-triplet Annihilation (TTA) - \( k_{\text{TTA}} \)**

This rate can be split into three distinct values, because it occurs for self annihilation of triplets in both the sensitiser and emitter molecules and for annihilation of triplets between them. Each rate will vary with temperature, viscosity and crystallinity (when solid) because, again, diffusion is vital. These rates will also vary with the Dexter parameter.

**Homoannihilation**

For homo annihilation of emitter triplets, providing that the \( S_1 \) energy level is at a useful position, the result is a doubly excited encounter complex. This complex has a 1 in 9 chance of producing a singlet excitation which can fluoresce, see discussion of spin statistics in TTA in 2.2.3. In an unsuccessful event, the initial triplets are not necessarily quenched\(^3\) and the energy is not always lost. In the case of homoannihilation between two sensitiser
molecules, as shown in figure 3.3, it is possible that either the \( S_1 \) or \( S_2 \) state of one sensitisier is populated. If \( S_1 \) is directly populated, ISC will transfer that energy to the triplet state, losing the energy of one of the initial triplets. If \( S_2 \) is populated, internal conversion will rapidly reduce the excitation to the \( S_1 \) state which will then undergo ISC to \( T_1 \) as above. In either case, the energy of one triplet is lost. This can be a significant loss in systems which have highly concentrated regions of sensitisers.

Figure 3.3: Schematic of homoannihilation between sensitisier molecules. Each sensitisier starts with a \( T_1 \) excitation which undergoes TTA. Either \( S_1 \) (solid lines) or \( S_2 \) (dotted lines) on either sensitisier can then be populated.

**Heteroannihilation**

Heteroannihilation, necessarily between a sensitisier and emitter and shown in figure 3.4, exhibits similar behaviour to the homoannihilation example above. As there is an asymmetry in the energy levels it is possible that both \( S_1 \) states will be accessible to any generated singlet. However, if the singlet forms on the molecule with higher lying \( S_1 \) it can immediately transfer through a FRET type transfer to the lower lying molecule. If the \( S_1 \) levels of each molecule are closely matched then FRET will be very likely. As discussed in section 2.2.2, the efficiency of FRET depends on spectral overlap and proximity (and is proportional to \( r^{-6} \)). As the TTA process itself requires molecular proximity to proceed, the requirement for proximity between sensitisier and emitter is already met.
Figure 3.4: Schematic of homo annihilation between a sensitiser and an emitter molecule. Each molecule starts with a triplet excitation which annihilates. A singlet excitation may form on either molecule. If it forms on the sensitiser, on the left, that energy is lost non-radiatively. If it forms on the emitter molecule, on the right, that energy can either fluoresce, or be transferred to the sensitiser by a FRET type transfer.

### Fluorescence - Sensitiser or emitter

Fluorescence occurs when a promoted electron relaxes back to its valence band in a spin-allowed transition, this process typically occurs on nanosecond timescales. In molecular upconversion, fluorescence from a sensitiser is to be avoided without exception. If $k_{TET}$ is close to or less than the combined rates of fluorescence and phosphorescence from the sensitiser then a large proportion of absorbed energy will be immediately released and lost. Emitter fluorescence yield is, of course, absolutely critical.

### 3.1.2 Model scheme

We construct the KRM by considering each molecular state (sensitiser and emitter, singlet and triplet) individually and writing equations describing how the concentration of each state can be increased and decreased by every process. The first of these we consider is sensitiser singlets, the concentration of which is primarily increased by absorbing photons. We then consider two loss mechanisms to this population: fluorescence and ISC. The next state, sensitiser triplets, is populated only by the ISC process and is depopulated through phosphorescence, triplet energy transfer and homoannihilation between sensitiser triplets. This homoannihilation partially regenerates sensitiser singlet states, and is a partial loss. TET then populates the third state, emitter triplets. This population is reduced through
non-radiative decays and TTA. This final TTA step is that which generates the final states: emitter singlets. This last population is reduced only though fluorescence as we incorporate other losses into a slowing of that rate. Figure 3.5 shows a scheme of this construction, and section 3.1.4 discusses the programmatic structure of the model.

![Figure 3.5: Schematic of our construction for describing molecular upconversion, from sensitiser absorption to fluorescent emission from emitter molecules.](image)

### 3.1.3 Derivation of rate equations

**One sensitiser, one emitter**

We start from the construction described above, and first consider the simplest molecular upconverting system: one sensitising species and one emitting species. From figure 3.5 we can construct rate equations describing the flow of energy through this system. Firstly the generation and depopulation of sensitiser singlets, where $X_s$ is the number of singlet excited sensitiser molecules:

$$\frac{dX_s}{dt} = \text{photons absorbed} - \text{number of fluorescent emissions} - \text{number of ISC events} \quad (3.3)$$

The ISC term in the above equation generates triplet excitations on sensitiser molecules, which can be depopulated through phosphorescence and TET exchange:
\[ \frac{dX}{dt} = \text{number of ISC events} - \text{number of phosphorescent emissions} - \text{number of TET exchange events} \quad (3.4) \]

If we then let \( Y \) represent the number of triplet excited emitter molecules, we can write a third equation:

\[ \frac{dY}{dt} = \text{number of TET exchange events} - \text{number of non-radiative decays} - \text{number of TTA events} \quad (3.5) \]

Each energy transfer or loss process occurs at a rate which is proportional to the number of molecules in each state. In practice this means that the magnitude of each process can be calculated by a rate constant multiplied by the concentration of the relevant excited state. We now assume 100% ISC so that \([X_s] = [X_t]\). If we also let: the rate constant of photon absorption = \( k_\phi \); the rate constant of phosphorescent decay = \( k_p \); the rate constant of triplet energy transfer = \( k_{TET} \); the rate constant of non radiative decay = \( k_{nr} \); and the rate constant of triplet-triplet annihilation = \( k_{TTA} \), then equations (3.4) and (3.5) can be written as follows.

\[ \frac{dX_{\text{triplet}}}{dt} = k_\phi[X_{\text{groundstate}}] - k_p[X_{\text{triplet}}] - k_{TET}[X_{\text{triplet}}][Y_{\text{groundstate}}] \quad (3.6) \]

\[ \frac{dY_{\text{triplet}}}{dt} = k_{TET}[X_{\text{triplet}}][Y_{\text{groundstate}}] - k_{nr}[Y_{\text{triplet}}] - k_{TTA}2[Y_{\text{triplet}}]^2 \quad (3.7) \]

The final term in equation (3.7), \( 2 \times k_{TTA}[Y_{\text{triplet}}]^2 \), includes a factor of two. Intuitively, this can be explained because two molecules are involved in each collision so two triplet excitations are relaxed each time this occurs. This prefactor makes no significant difference to the this model (as it only modifies how the rate constant is interpreted), but is included for completeness. A more rigorous explanation follows.

Equation (3.8) shows three processes, only the third of which requires the presence of two separate entities to proceed.

\[ 2A \rightarrow 2A' \text{(rate}_1) \]
\[ 2B' \rightarrow 2B' \text{(rate}_2) \]
\[ C + D \rightarrow C' + D' \text{(rate}_3) \quad (3.8) \]
For a rate equation such as $xX + yY \rightarrow zZ + qQ$, the rates can be written as:

$$-\frac{1}{x} \frac{d[X]}{dt} = -\frac{1}{y} \frac{d[Y]}{dt} = \frac{1}{z} \frac{d[Z]}{dt} = \frac{1}{q} \frac{d[Q]}{dt} \quad (3.9)$$

Relating this to equations (3.8), we can say that:

$$\text{rate}_1 = -\frac{1}{2} \frac{d[A]}{dt} = -\frac{1}{2} \frac{d[A']}{dt} \quad (3.10)$$

$$\text{rate}_3 = -\frac{d[A]}{dt} = \frac{d[A']}{dt} \quad (3.11)$$

Therefore $2\text{rate}_1 = \text{rate}_3$, meaning that the rate of reaction between two entities is twice that of self interaction.

Using these simplifications modifies the original diagram to that shown in figure 3.6. By setting each equation to zero, it is possible to find steady state solutions for the system analytically, provided that there is a constant input of photons. This formulation was initially proposed by J. Auckett et al. in 2009, and has been introduced previously.

![Figure 3.6](image.png)

**Figure 3.6:** Schematic of model described by the simplified equations (3.6) and (3.7).

At this point, it is prudent to mention that so far we have ignored self annihilation between sensitiser molecules and triplet-triplet annihilation between an emitter triplet and a sensitiser triplet. To include this, we split the original $k_{TTA}$ terms into $k_{TTA}^{XY}$, $k_{TTA}^{YY}$, and $k_{TTA}^{XX}$. This allows for the potential differences in annihilation rates between two emitter molecules, two sensitiser molecules and that between a sensitiser and an emitter. We also remove a factor of two from the homoannihilation of sensitiser triplets term to make it $k_{TTA}[X_T]^2$. This is because since Auckett’s paper in 2009, upconversion efficiency has been proven to not be limited to 11%. As discussed in section 2.2.3 an ‘unsuccessful’ annihilation event between
two sensitiser molecules does not necessarily depopulate both triplet levels: one sensitiser will be excited to a singlet state and undergo ISC once more, leaving one triplet state sensitisier and one ground state sensitiser. Accounting for these processes, and abbreviating groundstate to ‘G’ triplet to ‘T’, modifies the equations as follows.

\[
\frac{d[X_T]}{dt} = k_\phi[X_G] - k_p[X_T] - k_{TET}[X_T][Y_G] - k_{XY}^{TTA}[X_T][Y_T] - k_{XX}^{TTA}[X_T]^2 = \frac{-d[X_G]}{dt} \quad (3.12)
\]

\[
\frac{d[Y_T]}{dt} = k_{TET}[X_T][Y_G] - k_{NR}[Y_T] - k_{XY}^{TTA}[X_T][Y_T] - 2k_{XX}^{TTA}[Y_T]^2 = \frac{-d[Y_G]}{dt} \quad (3.13)
\]

Within the range of input intensities and rate constants used by Auckett et al. (2009) there is no significant difference between the results produced by their equations ((3.6) and (3.7)) and our modified versions ((3.12) and (3.13)). In fact, the ordinary differential equation (ODE) solver we used becomes unstable before reaching such an extreme condition that a significant difference can be observed. Figure 3.7 shows an example of this, the triangles show how the KRM preforms with the original equations and the solid lines show how it performs with the modified versions. The data points are almost identical.

![Figure 3.7](image-url)

**Figure 3.7:** Comparison of time dependence of triplet excitations following laser pulse, as calculated with the original equations (triangles) and with modified versions (solid curves).

Experimental studies in literature have calculated the rate constants in these equations. For example by using steady-state and transient techniques such as delayed fluorescence or phosphorescence measurements. In those experiments, the triplet concentrations must be
back-calculated based on the framework of these equations. We can now use the concentration information produced by the KRM to model experiments in the reverse manner, as shown at the end of section 5.2. In chapter 5 we will use transient absorption spectroscopy to measure the triplet concentrations directly, as described in chapter 4.

**One sensitiser, two emitters**

In 2013, Cao et al. found that adding a second emitter to the standard pairing of sensitiser and emitter increased the TTA QY of their system from 9.5% to 19.2%. The interplay of this system is significantly more complex than that of the one emitter system described above. Again, we let: X=sensitizer; Y=emitter one; Z=emitter two; T=triplet state; G=ground state; t=time. Equation (3.14) shows the minor changes made to the depopulation channel available to sensitisers in a two emitter system. Here there is a possibility of TET to both Y and Z emitter molecules from X. TTA in both [X/Y] and [X/Z] complexes are also possible, so are included as explained in the above section.

\[
\frac{d[X_T]}{dt} = k_{\phi}[X_G] - k_p[X_T] - k_{TETxy}[X_T][Y_G] - k_{TETxz}[X_T][Z_G] - k_{TTAxy}[X_T][Y_T] - k_{TTAxz}[X_T][Z_T] - k_{TTAxz}2[X_T]^2 = \frac{-d[X_G]}{dt} \quad (3.14)
\]

The following equations, (3.15) & (3.16) show that there are now two triplet generation terms for each emitter. The usual TET from the sensitiser, and the possibility of transfer from the other emitter. Each of these extra transfers is of course also a loss term in the opposing equation. The other major difference is the inclusion of a \(k_{TTAyz}\) term in each equation, with a prefactor of 2. This prefactor is justified in the same manner as that for \(k_{TTA}[Y_{triplet}]\) in equation (3.7).

\[
\frac{d[Y_T]}{dt} = k_{TETxy}[X_T][Y_G] + k_{TETzy}[Z_T][Y_G] - k_{TETyz}[Y_T][Z_G] - k_{NRy}[Y_T] - k_{TTAxy}2[Y_T]^2 - k_{TTAxy}[X_T][Y_T] - k_{TTAyz}4[Y_T][Z_T] = \frac{-d[Y_G]}{dt} \quad (3.15)
\]

\[
\frac{d[Z_T]}{dt} = k_{TETxz}[X_T][Z_G] + k_{TETyz}[Y_T][Z_G] - k_{TETzy}[Z_T][Y_G] - k_{NRz}[Z_T] - k_{TTAxx}2[Z_T]^2 - k_{TTAxx}[X_T][Z_T] - k_{TTAyz}4[Y_T][Z_T] = \frac{-d[Z_G]}{dt} \quad (3.16)
\]
Table 3.3: Table of Matlab’s ODE solvers, and the time they took to solve the KRM for the standard conditions specified in table 3.2. Details of the methods used in each solver can be found in Matlab documentation.

<table>
<thead>
<tr>
<th>Name of solver</th>
<th>Method</th>
<th>Time to find solution (seconds)</th>
<th>Short pulse (50 ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ode45</td>
<td>Runge-Kutta</td>
<td>32.0014</td>
<td>31.9166</td>
</tr>
<tr>
<td>ode23</td>
<td>Runge-Kutta</td>
<td>31.9129</td>
<td>Unphysical result</td>
</tr>
<tr>
<td>ode113</td>
<td>Adams</td>
<td>31.8135</td>
<td>Unphysical result</td>
</tr>
<tr>
<td>ode15s</td>
<td>NDFs (BDFs)</td>
<td>32.1499</td>
<td>Unphysical result</td>
</tr>
<tr>
<td>ode23s</td>
<td>Rosenbrock</td>
<td>32.3230</td>
<td>Unphysical result</td>
</tr>
<tr>
<td>ode23t</td>
<td>Trapezoidal rule</td>
<td>31.9904</td>
<td>Unphysical result</td>
</tr>
<tr>
<td>ode23tb</td>
<td>TR-BDF2</td>
<td>32.0425</td>
<td>Unphysical result</td>
</tr>
<tr>
<td>ode15i</td>
<td>BDFs</td>
<td>Did not finish</td>
<td>Did not finish</td>
</tr>
</tbody>
</table>

3.1.4 Programmatic structure of KRM

From the rate equations described above, our kinetic rate model (KRM) was designed to solve the differential equations numerically for a succession of time steps. The core of a model of this kind is a robust ODE solver. Matlab has a number of built in ODE solvers. With some experimentation, the ODE45 solver was found to be a good compromise between speed and stability for this problem. This can be seen in table 3.3 where we see that for a short pulse, ode45 is not actually the fastest solver but that it is the only one to produce a physically realistic result at short pulse widths.

The first step the program takes is to read in the options and variables relating to the kind of light pulse that will be incident on the modelled solution. Various controls were developed, including constant illumination and laser pulses simulated as short Gaussian distributions. Using the absorption coefficient of the molecule in question, the number of sensitisier molecules that are excited by this pulse, or continuous light, are calculated and used as the initial value for [X<sub>T</sub>]. The rate constants, as defined in section 3.1.1, are then given values and the linked equations are solved. At each time step, the concentrations of X<sub>T</sub> and Y<sub>T</sub> are recorded, and a check is in place to make sure that the value of [X<sub>S</sub>]+[X<sub>T</sub>]=[X], and that the corresponding relation holds true for [Y]. A relative tolerance limit was applied, such that the difference between [X<sub>S</sub>]+[X<sub>T</sub>] and [X] was not more than 0.1% of [X].
Once replication of experimental data was achieved, a version of the Matlab optimisation toolbox was used to take this model one step further, to predict rate constants rather than just model them. Given a target function, in this case the minimisation of any difference between an experimental result (e.g. TAS (examples in section 5.1.2, or PL (section 5.1.1) and the output of the model (equation (3.17)), the optimiser runs the model sequentially while changing the input variables according to a search algorithm. If a change in a particular variable improves the match between experiment and model, that is kept and expanded upon until some minimum is found.

\[
\text{Minimisation value} = \sqrt{\left( \sum_x \left[ \text{Normalised experimental fit}_x - \text{KRM fit}_x \right] \right)^2} \quad (3.17)
\]

The search algorithm used was generally a pattern search, which does not require the gradient of the search surface to be found, making each iteration computationally more simple. This algorithm simply varies each variable sequentially by some amount. When there is no further improvement from this variation, the variation step is reduced until the required accuracy, or maximum number of iterative steps is reached. As there are potentially very many variables to optimise for (13 different rate constants, two initial concentrations and laser power), there are a large number of local minima that the optimisation routine can find. To avoid getting stuck in a local minimum, these variables are generally constrained to realistic values, such as those close to ones published in literature for similar systems. In addition, each optimisation was also run with different starting conditions to help find global maxima. Figure 3.8 shows the programmatic flow for the optimiser routine. This technique was used successfully to predict the difference in rates between PQ$_4$Pd/rubrene and PtTPBP/perylene mixtures. This result can be found in chapter 5.

### 3.2 KRM validation

#### 3.2.1 Steady-state solutions

The first test of this KRM was to replicate the results of Auckett et al. (2009)\textsuperscript{46} in the steady state. We simply use identical rate constants, apply a continuous light source for a moderate period, take the last solution from a particular run and so arrive at the steady state solution for those parameters. We found that our two models agreed very well. Figure 3.2 showed one plot from Auckett et al. (2009) reproduced closely with the KRM. Figure 3.9
Figure 3.8: Programmatic flow for optimisation routine to compare KRM to experimental data. First the excitation source is modelled (as steady-state, a short pulse, or an instantaneous population of sensitisier triplets), then the initial rate constants are read in and the usual ode solver script runs (rounded box). This output is converted to the equivalent of an experiment and compared with that experiment. The optimisation tool then chooses one of the rate constants to vary and does so, it then re-runs the ode solver and compares the new output to the same experiment. In this way it slowly converges onto a minimum difference between model and experiment.

shows another example from that paper, again reproduced with the KRM. In this case, the quantum efficiency of an upconverting system (defined as the percentage of triplet pairs which survive to undergo TTA and leave an emitter in its S₁ state) is shown to vary with the rate of incident photons and the magnitude of \( k_{NR} \). It shows that when \( k_{NR} \) is low and \( k_\phi \) is sufficiently high, the QE of the system can approach 100%. As mentioned in section 3.1, the predictions of this model have been experimentally verified in literature.

After we modified the equations to account for new understanding, described in section 3.1.3, these validation trials were also undertaken using the new versions of the key equations. As mentioned in that section, the solver broke down before a regime where our modified equations showed a significant deviation from Auckett’s results. The ODE45 routine mentioned above usually uses a variable step size, but this had to be constrained in order to produce physical solutions at high irradiance and other extremes such as high, or low, concentrations. Figure 3.10 shows how an constrained variable step can lead to a meaningless result, an example of a simulation run which succeeded has already been shown in figure 3.7.
Figure 3.9: (a) Figure 3a) from Auckett et al. (2009) showing how quantum efficiency varies with $k_\phi$ and $k_{NR}$ for a set of other rate constants (defined in that paper). Reproduced with permission of IOP Science. (b) Reproduction of this figure using the KRM. The two plots are almost identical, showing that the KRM reproduces Auckett’s results very well.

Figure 3.10: Example of a failed KRM simulation resulting from an unconstrained time-step, an example of a simulation run which succeeded has already been shown in figure 3.7.

With the steady state solutions of this model verified, we proceeded to investigate the steady state solutions produced from our equations which consider two emitter species, Y and Z. In this case, we chose a laser power regime where solutions are relatively quickly found (in our case, finding a solution within 30 seconds was considered reasonable) and varied the relative concentration of emitters Y and Z, keeping the total concentration of emitter the same.

Figure 3.11 shows the total number of quanta emitted by a three component system such as this for a standard set of rate constants, while varying the proportion of emitter Y and Z in such a way that the total concentration of emitter molecules does not change. In this case, emitter Y and emitter Z are identical: they have the same rate constants. That the total amounts of phosphorescence (red line), and upconversion (blue line) remain the same.
shows that the rate equations derived here are indeed consistent.

![Figure 3.11: Total emitter light as a function of concentration of two identical emitters, Y and Z. The two non radiative terms are divided by a factor of ten because at the simulated irradiance levels, they dominate these processes completely.](image)

We expect that the result at 0% and 100% will be the same, the interesting behaviour is found in-between. The non radiative decay of energy from each emitter varies linearly with the relative concentration of its source, but fluorescence from each molecule increases with the square of the proportion of its excited triplet states. If there was no synergistic term, then there would be a minimum in fluorescence at 50%, the addition of the Y/Z synergistic annihilation term compensates identically for the reduction in fluorescence from each Y and Z at every proportion. We will see in chapter 5 that in practice (with different emitters) this synergistic term significantly overcompensates for the reduction in fluorescence from each individual species, leading to an overall increase in efficiency for the system.

### 3.2.2 Transient solutions

It is possible to model transient behaviour in this system with two methods. First, we can define a laser pulse with Gaussian type curve and convert that to the corresponding $k_\phi$ required, or in use by whichever experiment. The second method is to calculate the number of molecules that will be excited by a laser pulse using the Beer-Lambert law (equation (3.18)) and assuming that the sample is infinitely thin, that sample is uniform, that the
laser pulse is infinitely short and that laser profile is uniform. These assumptions allow for a fairly trivial calculation of initial triplet concentration: the total number of photons can be calculated from pulse energy and wavelength, the fraction of these photons that will be absorbed comes from the Beer-Lambert law, and these values (at the energies used here) can be multiplied to give a reasonable estimate for the number of triplet excitations that will be generated by a given laser pulse. For short, intense, pulses the second method works much better with the KRM. This is because in order to produce a stable solution, the step size in the solver must be many times smaller than the pulse width of the laser. While it is possible to do this, it forces the model to run much more slowly. Figure 3.12 shows the transition from a continuous wave type pulse to a modelled pulse on only 100 ns. Trying to reduce the pulse width below this value results in the meaningless curves shown in figure 3.10.

![Graphs showing the transition from a continuous wave type pulse to a modelled pulse on only 100 ns.](image)

**Figure 3.12:** Examples of KRM output with varying laser pulse width: a) quasi continuous wave, b) 50 µs pulse, and c) 100 ns pulse.

With a stable transient solver completed, it becomes possible to compare experimental data to modelled results. A transient absorption spectroscopy (TAS) experiment takes a constant irradiance probe beam through a sample, which provides a measure of steady state absorbance for the sample. This absorbance is measured with a photodetector. The sample is then pulsed with relatively high intensity laser light, whichexcites a particular transition. As molecules are excited by the laser, the effective concentration of ground-state molecules is reduced, hence increasing the amount of probe light which gets through and decreasing the optical density of the solution for a time. The particular TAS experiment that was used in preparation of this thesis is fully described in chapter 4. Absorbance is calculated through the relation below, where $A$ is absorbance, $I_0$ is the intensity of the light source and $I$ is the intensity of light after it has passed through the sample. This is related to the concentration of molecules through the Beer-Lambert law, equation (3.18). Where $l$ is the path length through the sample in cm, $c$ is concentration of a species in moles and $\epsilon$ is the molar extinction coefficient at a certain wavelength, in $\text{M}^{-1}\text{cm}^{-1}$.
\[ A = \log_{10} \left( \frac{I_0}{I} \right) \]  
\[ A = c \times l \times \epsilon \]  

By taking steady state UV/VIS absorption spectra of each molecule in isolation it is possible to calculate the molar extinction coefficients for each molecule. This allows the experimentally observed variable, change in optical density (absorbance), to be related directly to the concentration of molecules. Providing that there is an absorption peak of either molecule which does not overlap with one from the other molecule it is possible to calculate what proportion of the post-pulse change in optical density is due to excitations in each molecule. If there is some overlap, then a deconvolution must be performed by investigating two probe wavelengths. For example, let two chemicals A and B have UV/VIS spectra as shown in Figure 3.13 (which is not based on an experiment). From this plot we can see that any absorbance between 600 and 700 nm is due to chemical B, and that absorbances between 200 and 550 nm are due to the presence of both species. The contribution to this absorbance of each species is simply the ratio of each species’ absorbance at each wavelength.

![Figure 3.13: An example UV/VIS spectrum.](image)

If we consider the concentrations shown on the graph legend and choose a particular path length, the absorbance values can be converted to the molar absorption coefficient spectrum for each molecule using the relation shown in equation (3.19). The reverse calculation, relating concentration of a mixture to its UV/VIS spectrum, is equally simple. Using the transient spectra collected while performing TAS experiments, as will be discussed in chapter 5, the absorption coefficient of triplet species can be calculated in the same manner. This value can then be multiplied with the output of the KRM to calculate the expected experimental TAS result from a particular set of conditions, see section 5.1.5.\(^{65}\)
3.3 Monte-Carlo particle Model (MCM)

In order to visualise the process of molecular diffusion often considered vital in molecular upconversion systems, and to illustrate how removing that diffusion affects the efficiency of the process, a simple Monte-Carlo box model (MCM) was constructed. In this model, a 2D grid with periodic boundaries is populated by molecules, then each of these is allowed to move, and interact with other molecules. This model was never intended to become a ‘full platform’ for the description of thin film upconverters so the third dimension was not included. Adding a height dimension would also mean that computation time would be proportional the the cube of the number of vertices, rather than the square, making the model unwieldy. That said, the third dimension shouldn’t actually influence the behaviour of this model greatly. Only by introducing a vertical distribution of charge, and as we assume elsewhere that each thin film is infinitely thin, this isn’t expected to be a significant effect.

3.3.1 Decision Tree

The molecules in this 2D grid are able to hop into empty spaces, with some probability, or stay still. At some point during the simulation, points on the grid are selected to be ‘excited’ by a photon. If the photon coincides with a sensitiser molecule then there is some probability that this molecule will be excited. We assume instant ISC so the triplet property of the molecule is activated. These triplet molecules will either decay by phosphorescence, or have their energy transferred to a sensitiser molecule that is within range. As discussed in section 2.2.2, we use the Perrin approximation of Dexter transfer and say that if (within some assumed Dexter radius) there is a suitable emitter for the excitation to be transferred to then it will immediately take that opportunity. If there is more than one spot available then the destination molecule is randomly selected. From this point, the emitter triplet can undergo TTA if there is another emitter triplet within range. Each iteration (time) step, every molecule and every charge is queried and allowed to do be involved in any of the interactions described in the model. The full set of decisions is shown graphically in Figure 3.14. The probabilities of each decision are used as inputs for the model. The movement probability is related to the equivalent of viscosity in the system. It was often chosen to be around 33%. The decay probability of each charge was chosen to be similar to that which relates to the phosphorescence probability of a real triplet on a sensitiser. The charge transfer probability was chosen to be the same magnitude as a typical TET rate (approx. $1 \times 10^8 \text{M}^{-1}\text{s}^{-1}$).
Figure 3.14: Flow diagram showing the decision tree presented to each vertex in the 2D grid. The final box, resolve collisions, is the step where TTA, TET and UC events occur and are counted.

3.4 MCM: Illustrations and limitations

3.4.1 Validation of behaviours

Although this model is much less easy to validate by comparison to experiment than the KRM, checks are required to show that it behaves in a physical way, as intended. There are three important checks to make: that the hopping method of molecular transport shows realistic diffusion characteristics; that no molecules, and hence excited states, are lost; and that every ‘photon’ packet absorbed by the system can be accounted for at the end of a run, be that through fluorescence, phosphorescence or non-radiative decay.
Validation of diffusive behaviour and conservation of mass

We demonstrate that this model displays behaviour analogous to diffusive transport by taking two different arrangements of blocks of particles, red (sensitiser) and green (emitter), and allowing them to move over time. Figure 3.15 shows the time evolution of particle position when one type of particle is entirely encased in a block of the other. The behaviour exhibited here demonstrates that particles are moving and intermixing properly. Note that there is no movement of red particles until there is space for it to break out of the shell of green particles.

![Figure 3.15: Snapshot images of Monte-Carlo box at increasing time.](image)

Figure 3.16 shows an example where there are two separate blocks of 100 particles which are allowed to intermingle. The top four images show the distribution of these particles, and the lower two line graphs plot the total number of particles in each quadrant. In this example, the distance that each particle is allowed to move is reduced from that in the previous example. In this case, each block of particles begins in only one quadrant of the grid. As time progresses we expect, and observe, that the amount of both sensitiser and emitter particles in each quadrant tends towards the average density of 25 red and 25 green particles per quadrant. By summing the values of the coloured lines at each timestep we can also show that despite many movements, no mass is lost and every particle is accounted for at the end.

Conservation of charge and quanta

The next two quantities to conserve are charge and quanta. Energy is input into this system in quantised packets, analogous to photons. Once we allow energy into this simple model, we can keep track of where it is by counting each sensitiser triplet that is formed, and each decay event that occurs, keeping track of phosphorescence, non-radiative decay and TTA fluorescence (multiplying this emission by two). If the sum of all decay events equals the number of absorbed photons after a run then the model conserves ‘photon’ packets. This is, indeed, the case.
This model enables the role of diffusion to be elucidated in thin films and poorly mixed systems. Hence the importance of intermixing and morphology in solid films. This is shown in chapter 6. However, the crude nature of this model means that in its present state it would be impractical to try to model ‘real-life’ solutions or films. The calculations simply take too long, and adding a third dimension would increase this processing time enormously.

The transfer constants used for this model were roughly based on the processes that were being modelled (TTA, TET, etc), but was never intended to be used to make predictions. The model is limited to describing behaviours in a visual, and less abstract, manner than the KRM. It was intended to give some natural understanding of the processes involved through simplification.
Chapter 4

Experimental Methods

This chapter is concerned with general experimental practices applied throughout this research. Starting with sample preparation and storage, and moving on to increasingly less intuitive experimental procedures. The methodology for preparing solutions is first explained, followed by a discussion of the preparation of thin films from these solutions. Wire bar coating, spin coating and drop casting are all briefly discussed. The principles of photoluminescence spectroscopy, insofar as they are relevant to this investigation, are mentioned. The equipment used to carry out such experiments is also presented. These experimental principles are expanded upon as the design for an automated experiment (Fluorescence (Upconversion) Robot, FUR) is detailed. Equipment, control and data handling software for this experiment are all discussed as each was developed specifically for this project. The final experiment detailed here is transient absorption spectroscopy (TAS). Again, both the general principles, and specifics relevant to OUC are discussed.
4.1 Experimental considerations

As shown in chapter 2, the concentrations of each active molecule (and their ratio) are critical variables in OUC investigations. As such, an accurate and repeatable set of experimental methods are required. Additionally, the presence of atmospheric oxygen is known to have an effect on the upconversion process, so must reliably be excluded, or controlled.

Software was specifically written for this project in order to control experiments and to automatically record all pertinent information into structures designed to interface with Matlab, which was also used as an analysis program.

4.1.1 Materials

During the experimental phase of this research, three sensitising molecules were used: Palladium (II) tetrakisquinoxalinoporphyrin (PQ$_4$Pd), platinum (II) tetraphenyletetrabenzoporphyrin (PtTPBP) and Pt (II) octaethylporphyrin (PtOEP). These compounds have Q-band absorptions at 670 nm, 635 nm and 532 nm respectively. The Q-band of a molecule refers to the lowest possible excitation of a molecule, i.e. excitation of an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The structures of these molecules are displayed in Figure 4.1.

![Figure 4.1: Structures of a) Palladium (II) tetrakisquinoxalinoporphyrin (PQ$_4$Pd), b) Platinum (II) tetraphenyletetrabenzoporphyrin (PtTPBP) and c) Platinum (II) octaethylporphyrin (PtOEP).](image)

The PQ$_4$Pd was synthesised at the University of Sydney, and the other two porphyrins were purchased from Frontier Scientific and used without further purification. The PQ$_4$Pd, also used by Cheng et al. in several papers, has a molecular extinction coefficient exceeding 10$^5$ M$^{-1}$cm$^{-1}$ in the Q-band. This means that at concentrations as low as 10$^{-4}$M, 90% of 670 nm photos are absorbed within 1 mm of solution. This Q-band absorption co-
efficient is much larger than the equivalent absorption coefficients for the other porphyrins used herein.

Additionally, four emitting molecules were used, the structures of which are shown in figure 4.2. These are rubrene, perylene, anthracene (AN) and 9,10-diphenylanthracene (DPA). Each emitter was purchased from Sigma-Aldrich and used without further purification.

![Structures of Rubrene, Perylene, Anthracene and 9,10-diphenylanthracene.](image)

**Figure 4.2:** Structures of a) Rubrene, b) Perylene, c) Anthracene and d) 9,10-diphenylanthracene.

Where used, poly(methyl methacrylate) (PMMA) was of 150,000 MW, and used as purchased from Sigma-Aldrich. In almost every case, the solvent of choice was toluene, due to its high transparency, the good solubility of each material used in this solvent and the low Stokes shift that it induces in similar molecules. Additionally, toluene has a lower toxicity than many other commonly used solvents. When used in the nitrogen glovebox, degassed dry toluene was used as purchased, again from Sigma-Aldrich. Degassing and drying was also done by Sigma-Aldrich themselves before our use.

Once prepared, the concentrations of each solution as tested were also experimentally determined through Ultraviolet-Visible spectroscopy (UV-VIS). Absorption spectra were collected using either a Shimadzu UV-2600 or a Shimadzu UV-1601 spectrometer. Table 4.1 shows the levels (in units of eV) of $S_1$ and $T_1$ for each of the main molecules studied in this research.

### 4.1.2 Preparation of solutions

The various research groups looking into OUC use different methods to exclude oxygen from their experiments. For example, Singh-Rachford et al. (2009) pass dry helium through their mixtures for 1 hour. Helium is an alternative to dry nitrogen when degassing, both gasses displace other gasses in the solution but as helium is less soluble it displaces more gas faster. In the above paper the authors do not report an estimate of the remaining amount of oxygen, but observe that the lifetime of the sensitizer emission in absence of
Table 4.1: Table of $T_1$ and $S_1$ levels in eV for each molecule studied in this research

<table>
<thead>
<tr>
<th>Sensitisers</th>
<th>$T_1$ (eV)</th>
<th>$S_1$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PQ$\text{Pd}^{63}$</td>
<td>1.46</td>
<td>1.85</td>
</tr>
<tr>
<td>PtTPBP$^{81}$</td>
<td>1.61</td>
<td>1.95</td>
</tr>
<tr>
<td>PtOEP$^{83}$</td>
<td>1.92</td>
<td>2.33</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Emitters</th>
<th>$T_1$ (eV)</th>
<th>$S_1$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rubrene$^3$</td>
<td>1.14</td>
<td>2.34</td>
</tr>
<tr>
<td>Perylene$^{81}$</td>
<td>1.53</td>
<td>2.75</td>
</tr>
<tr>
<td>DPA$^{107}$</td>
<td>1.80</td>
<td>2.85</td>
</tr>
<tr>
<td>Anthracene$^{108}$</td>
<td>1.83</td>
<td>3.1</td>
</tr>
</tbody>
</table>

an emitter increased after deoxygenation from a few microseconds to 27 µs, indicating a vastly reduced amount of triplet energy being quenched. Cheng et al. prefer to prepare their solutions in atmospheric conditions and subsequently deaerate them through several freeze-pump-thaw cycles.$^{32,61,63}$ This is where the sample is frozen (to halt solvent evaporation), placed under high vacuum ($1 \times 10^{-5}$ mbar), and thawed. This cycle is then repeated. Cheng et al. also do not estimate how much oxygen remains after this process. Other groups, including Yakutkin et al.$^{78}$ and Baluschev et al.$^5$ prepare and seal their solutions in nitrogen filled gloveboxes. Yakutkin et al. (2008)$^{78}$ reported that at 0.1 ppm glovebox oxygen content, the mixture remained active for more than 60 days, and an increase to 5-10 ppm meant that the molecules started to degrade almost immediately, the extent of this degradation was not quantified.

We chose to make use of the passive method of oxygen removal using a nitrogen glovebox. Our glovebox was consistently maintained at lower than 0.1 ppm O$_2$ and 2.3 ppm H$_2$O. For comparison, atmospheric oxygen contains on average 209,460 ppm.$^{110}$ There was no indication that this remaining oxygen affected any result in experimental chapters 5 and 6. In order to maximise the efficacy of this method, samples of single molecular species were weighed in air, transferred to the glovebox through an antechamber and only dissolved on the inside of the glovebox using degassed solvent. The antechamber procedure was to slightly loosen the lids of each sample vial, slowly evacuate the chamber to its minimum pressure, hold it there for 15 minutes and then refill slowly with dry nitrogen. At least three cycles of this purging process were applied to each solid (powder) sample. Once dissolved, each solution was stored in the glovebox. When removing samples from this storage location, they were placed in a 1 mm quartz cuvette (Hellma 100-QS) which was stoppered and wrapped in Parafilm tape. Of course, this will not stop oxygen ingress, only slow it down. As a result, every experiment was performed as rapidly as possible once each sample had been removed from the glovebox. The efficacy of this passive oxygen removal
process is demonstrated in section 5.1.3. The result presented there shows that there was not a significant effect from oxygen ingress when using this experimental procedure.

4.1.3 Thin films

Three techniques were used to fabricate thin film samples during this research: blade coating, spin coating and drop casting. For each of these, CORNING soda lime glass slides were cut to size using a score/break method. Before use they were each rinsed with isopropanol (IPA), placed in a sonic bath (Fischer-Scientific), also in IPA, for 10 minutes and dried with dry nitrogen. Initially, thin film samples were also prepared in a nitrogen glovebox using the methods outlined in section 4.1.2. Figure 4.3 shows sketches of how the three coating methods work. In each case it is possible to heat the substrate to drive solvent off more rapidly, forcing a less energetically stable morphology to form. As shown in section 6.2.2 it was found that it was also acceptable to prepare these films in atmosphere for some experiments.

![Figure 4.3: Schematic of (a) wire bar coating, (b) spin coating and (c) drop casting.](image)

**Figure 4.3:** Schematic of (a) wire bar coating, (b) spin coating and (c) drop casting.

Wire bar coating

In the wire bar coating process, a metal bar wrapped in metal wire of specific gauge with calibrated pitch and width is dragged across a substrate at a constant height and rate. The thickness of film produced by this method is controlled by the amount of solution held in between the the coils of wire, the concentration of the solution used to make the film, the specific bar used, the temperature of the support plate and the speed at which the bar is drawn across the substrate. Films cast with this method generally have sufficient time to self
organise and reach an equilibrium morphology as, without heating, solvent is only slowly driven off. This method is necessarily slower than drop casting, and uses much larger substrates than both drop casting and spin coating. Various bars with close wound wires were tried before finding that a close wound wire width of 0.15 mm (that should produce a wet surface coating of around 12 µm) produced films that were sufficiently optically dense to be of interest while being sufficient transparent to allow for experimentation at the concentrations used. Results from the few samples fabricated with wire bar coating in this research can be seen in section 6.2.1, where we find that increasing the weight% of polymer in a film increases the upconverted fluorescence emitted by that sample. The machine used to fabricate these films was an RK-K202.

Spin coating

In contrast to the wire bar coating method, a spin coater rapidly rotates the substrate upon which a volume of material has been deposited. From the initial droplet, material is flung away from the centre of rotation and coats the substrate. A coater can commonly be programmed for acceleration ramp, top speed and duration. Fast acceleration produces an even coating across the substrate, with few streaks, and reduces film thickness. Aside from the usual concentration term, top speed and duration of spin are the major determinants of eventual film thickness.111 Fabricating films in this way can lead to production of morphologies that are not in equilibrium as solvent will evaporate before the components can re-orient themselves. This means that film morphology may not be stable to heat, time or light, but such morphologies may well have a higher degree of intermixing than if they had time to reach equilibrium. Very good control of thickness can be achieved with this method, but of these three techniques, it is the most wasteful in terms of material. It also takes much longer to prepare large numbers of samples than drop casting, below. The results from spin coated films can be found in section 6.2.3, where we see a difference in the kinetics of upconverted fluorescence between a solid and liquid sample. The spin coater used to fabricate this was an MBraun MB-SC-200, within a nitrogen atmosphere.

Drop casting

Drop casting is by far the simplest method of fabrication for organic films. At its simplest, a drop of solution containing the materials under investigation is placed onto a clean slide and solvent is allowed to evaporate. As this procedure is, of course, carried out in a fume hood or other area with rapid air flow, it can lead to rapid, and/or uneven drying rates which adversely affect film uniformity. To prevent this, and to encourage formation of films
with stable morphology, a glass cover was placed over the sample as it dried. It was found that the addition of a small amount of solvent in the same container slowed drying further and lead to the formation of higher quality films. Each film was dried for at least 30 minutes in the dark. This darkness condition was to minimise degredation of the active materials in the films. This is discussed further in section 5.1.1.

The eventual thickness of these films depended most strongly on the weight % of polymer added and would vary from around 300 nm to around 1.5 µm (as measured with a VEECO / SLOAN DEKTAK 3). However, physical thickness is not particularly relevant in a discussion of efficiency. The key variable is optical thickness, which was controlled by using the same amount of active material in each sample. It was further accounted for by measuring the absorbance of each sample before experimentation and correcting for the small variations found (typically no more than a few hundredths of an OD).

### 4.2 Photoluminescence spectroscopy

Photoluminescence (PL) of both upconverted light (delayed fluorescence) and phosphorescence measurements were collected in two ways, either spectrally resolved through the use of a spectrograph and charge coupled device (CCD) or imaged directly onto a CCD through the use of appropriate filters, see the following section. The CCD system used in these experiments was a QIClick. Figure 4.4 shows a schematic of a typical PL system used for this research.

**Figure 4.4:** Schematic of a typical fluorescence/PL experiment.

Samples were excited with either a *Melles GRIOT 05-LHP-111* He-Ne laser (635 nm) or *Thor Labs LDC205C* laser driver as appropriate to the excitation wavelength required. This driver connected to a *TCLDM9* laser diode mount along with a *TED200c* temperature controller. A *DJ532* diode-pumped solid state laser diode was employed to produce (535 nm) laser light. Laser power was measured with a *Newport Optical Power Meter*. Samples were back-illuminated with these lasers so that minimal laser scatter would be collected by the optics.
4.3 Fluorescence (Upconversion) Robot - FUR

In order to explore even a small region of the sample space described by the materials and processing techniques available here, a robot was designed and constructed to automate the measurement process, for example figure 6.7 alone required 45 individual sample measurements. Figure 4.5 shows a schematic. In this design, the sample holder from figure 4.4 is replaced with a wheel which holds up to 10 film samples, filters are mounted on another wheel and a rotating shutter is placed in front of the diode laser. Filters were used so that a spectrograph would not be required. This increased the total signal recorded by the QIClick (by spectrally integrating phosphorescence and upconverted fluorescence), and simplified the collection of data. It is only appropriate to use filters in this way when the spectroscopic properties of the samples under investigation are taken into account. In this investigation only mixtures of PtOEP/DPA were examined using this setup.

![Schematic of the FUR robot](image)

**Figure 4.5:** Schematic of the FUR robot used mainly for work described in chapter 6.

This automated experiment was controlled with an Arduino UNO micro-controller, using the LabView Arduino libraries. Figure 4.6 shows photos of the various components of the experiment. Two of the three motors used had to be able to accurately rotate in small increments so were chosen as ROB-09238 stepper motors, driven by a 5V power supply and a EadyDriver ROB-10267 stepper motor driver. These have a step angle of 1.8°, suitable for both the 10 sample holder wheel and the filter wheel. The third motor, for the laser shutter, was only required to repeatedly rotate 180°, so a different model of motor, with larger angle steps, was used to improve repeatability over many full rotations. This was a 28BYJ-48 motor in combination with a ULN2003 driver board. The sample wheel could be positioned within a vacuum chamber, but it was found that this was not required as our thin film samples did not show the same oxygen quenched behaviour as our solutions. The reasons for this can be found in section 6.2.2.
The spectral filters were purchased from *Thor Labs* and were: FEL0600 - Longpass Filter, Cut-On Wavelength 600 nm; FES0550 - Shortpass Filter, Cut-Off Wavelength 550 nm; NF533-17 - Notch Filter, centre wavelength = 533 nm, FWHM = 17 nm. The absorbances of the filters used for these experiments are shown in figure 4.7, the noise towards short wavelengths on the red curve is due to the combination of lower light output and increasing optical density reducing the signal to noise ratio of the experiment.
Figure 4.7: UV-Vis absorption spectra of filters used to differentiate between laser reflection/scatter, upconverted fluorescence and phosphorescence. Notch filter (‘NF533-17’, centred on 533 nm) in green, short pass in blue (‘FES0550’, cut-off at 550 nm) and long pass in red (‘FEL0600’, cut-off at 600 nm).

Optical density, or absorbance, can be calculated with equation (4.1). Where $OD_\lambda$, $I_0$ and $I_1$ are optical density, light intensity before interaction with a sample and light intensity after passing through a sample (transmittance).

$$OD_\lambda = \log_{10} \left( \frac{I_1}{I_0} \right)$$  \hspace{1cm} (4.1)

Figure 4.8a overlays the relevant filter data from figure 4.7 with the scaled phosphorescence spectrum of PtOEP. In this arrangement the combined optical density at 533 nm, the laser excitation wavelength, is nearly 8. Therefore only 1 in $1 \times 10^8$ photons of this wavelength will get through to the detector. Figure 4.8b does the same with the fluorescence spectrum of DPA. The overlap between the filter cut-off and upconverted fluorescence at wavelengths longer than 500 nm means that this arrangement captures 97.1% of the upconverted fluorescence, this factor is used in results section 6.2.4.
Figure 4.8: (a) Comparison of PtOEP phosphorescence with the set of optical filters used to differentiate it from DPA fluorescence. (b) Comparison of DPA fluorescence with the set of optical filters used to differentiate it from PtOEP phosphorescence.

Data acquisition and handling

The QIClick CCD camera used for these experiments has a number of LabView libraries available from the QI website to allow for bespoke control and acquisition systems. Although these libraries, or Virtual Instruments (VIs), are only officially supported up to LabView version 8.6, they were effectively implemented within LabView 2012 for this work. LabView is also capable of controlling stepper motors, in this work this was done, through an Arduino Uno microcontroller. This is also supported in recent versions of LabView, and allows very simple control programs to be written to activate the various motors.

Figure 4.9 shows a screenshot of the acquisition VI used to collect the automated data. The top control box in this VI includes controls for determining the number of acquisitions to take per trace, the exposure time for each acquisition, control over various camera functions (in the figure, normalised gain is selected), the sample number or designation and what kind of filter is in front of the CCD. The values from these boxes are determined by the VI one level up, which also controls the stepper motors, shown in figure 4.10. These values then go on to inform the name of the data file that is generated. This file is manipulated in LabView to produce a binary ‘.m’ file so that it can be immediately dropped into Matlab and analysed. These variables also inform and populate Matlab variable names and values so that batch processing of many trials is simplified. The two main figures in the VI show the most recently acquired image from the CCD, and a plot showing the summed intensity of each image over time.
The bottom box contains another stop control, which terminates the VI at the end of the current acquisition, readouts showing the value of the brightest pixel, the exposure actually used by the camera, region of interest settings and a progress meter that also counts any ‘bad frames’. The only output from this model of CCD camera is via IEEE 1394 ‘firewire’ cable. When initially being developed, a PCMCIA card was required to communicate with the development laptop. This card led to errors which caused some image acquisitions to fail. A work around was developed that detected these failures, ‘bad frames’, and discarded them so that the experiment could continue. Once a permanent desktop PC with a PCI firewire card was installed, this communication problem was resolved, but the error handling segments of the code were useful in handling other problems that arose during development. The value of the brightest pixel is a valuable piece of information as with it, it is possible to see when the CCD moves into a saturation regime, and stops behaving
linearly. Using this information it was possible to modify the exposure time of the CCD so that linear behaviour could be maintained at a great range of laser intensities. The main results from experiments using this equipment can be found in chapter 6.

4.3.1 Intensified CCD (iCCD) experiments

In addition to the CCD camera mentioned above, some experiments were conducted using intensified CCD (iCCD) equipment. Two devices were used, a Princeton Instruments PI-MAX2 and an Andor iStar. Each of these devices operates on the same principle, low photon count signals are amplified with a multichannel plate (MCP) to produce a large number of electrons. These electrons eventually hit a phosphor screen, which emits more light, so the signal can be detected by a high quality CCD. An MCP is a piece of insulating material riddled with parallel tubes, micro channels. Each photon which enters the plate will necessarily hit the side of one of these tubes. If a high voltage is maintained across the plate, each photon collision will lead to the emission of several electrons on the other side of the tube wall. These electrons can then cascade through the entire plate producing very large signal gain. The extra benefit of a system such as this is that the voltage across the MCP can be turned on and off extremely rapidly and with great temporal precision. The MCP then becomes an electrically driven optical shutter. These kinds of iCCD devices are therefore able to take time-resolved spectra (if attached to a spectrograph) with a gate width of as little as a few nanoseconds. This gate width and delay can be controlled with great precision. Results of experiments using this equipment can be found in section 6.2.4.

4.4 Transient absorption spectroscopy (TAS)

Most published investigations into upconversion processes use time resolved fluorescent spectroscopy to measure the delayed luminescence associated with the upconversion. However some studies, for example by Singh-Rachford et al. (2009 and 2010),\textsuperscript{81,113} use transient absorption spectroscopy (TAS) to study organic upconversion. This technique is particularly interesting as it allows for the investigation of the intermediate steps of the upconversion scheme, by directly observing the population of molecular triplet states.

In a TAS experiment white light is filtered to produce a variable probe beam, which sets up a steady-state absorption in the sample. This is measured by a photodetector. The sample is then excited by a pump pulse, often provided by a laser. The wavelength of this pump has been chosen to excite a particular optical transition in the sample. This pulse increases
the population of a particular set of excited states, leading to a bleach (reduction in optical density) with the same spectral characteristics as the steady state absorbance of the excited molecule. The wavelength of the probe beam determines which transitions are monitored. It is often chosen so that it investigates a single particular transition. Additional ‘induced absorptions’ (increases in optical density) are observed if the pump pulse causes an increase in the population of an excited state that allows additional optical transitions to take place at the wavelength of the probe beam. These induced absorptions come from excited states which have been made available by the pump pulse. This idea is illustrated in figure 4.11.

Figure 4.11: Schematic of a TAS experiment. Top left: a probe beam at 670 nm is absorbed by the $S_0 \rightarrow S_1$ transition of the sample molecule, which can then populate the $T_1$ state. Top right: a probe beam of 530 nm is not absorbed by this molecule. Bottom left: after a pump excitation which populated the $T_1$ state of this molecule, the 670 nm beam now passes through the molecule (a bleach). Bottom right: With the probing beam now set to 530 nm, the $T_1 \rightarrow T_2$ transition can be optically excited (an induced absorption).

TAS can be used in two modes of operation: either to observe the decay (or recovery) in signal after a pump pulse, or to look at the spectrum of an excited state by picking a point in time after excitation and scanning the probe beam across the spectral region of interest. Figure 4.12 shows a schematic of the system used in this research. The laser used was a Photon Technology International GL-301 dye laser pumped by a Photon Technology International GL-3300 nitrogen gas laser. The pump laser was run at 4 Hz, and its pulses were directed into the sample through an optical fibre. The probe source was a Bentham IL1 - Illuminator,
powered by a stabilised Bentham 605 power supply. This broad spectrum light was first passed through a monochromator, then through the sample under investigation, and finally through a second monochromator before being recorded by a photodetector. This double monochromation scheme was put in place to reduce scatter from the laser pulses and to reduce second order diffraction from the first grating. The signal from the photodetector was passed through an analogue amplifier before being input to an oscilloscope (Tektronics TBS1042). The equipment was controlled by a purpose built LabView program which also accumulated the data.

Figure 4.12: Schematic of the TAS equipment used in this research, excluding optical elements.

Figure 4.13 shows some sample spectra of the probe beam, after being passed through both monochromators, but not through a sample. These spectra were recorded with an Ocean Optics USB2000+ spectrometer. There are two features of note: firstly, each spectrum has an average full-width half-max (FWHM) of 23 nm with a standard deviation from this mean of 1.8 nm. This large spectral width is a consequence of opening the slits on the monochromators to allow sufficient light through to give signal on the oscilloscope. The unfortunate side effect of this is that the probe beam is spectrally almost as wide as the absorbance peaks of the molecules under investigation, meaning that there will always be some overlap of absorbance and probe wavelengths. The maximum of each curve does, however, correspond well to the wavelength setting of the monochromators.

The second feature that is significant is the best functional range of the lamp, which is limited to between 500 and 650 nm. Beyond this range, the probe intensity falls to less than half of its maximum. The practical effect of this in TAS experiments is to increase the level of noise in a transient measurement. As a TAS measurement is concerned with a change in optical density, the critical determinant of signal is the amount of probe light getting through to the detector, which is in turn determined by the amount of light being emitted by the probe and the proportion of that which is absorbed by the sample. This can be seen very clearly in figure 5.4 where an otherwise very flat signal decays to noise beyond approximately 530 nm. A combination of much higher absorption from the sample and lower lamp power reduces the signal dramatically at shorter wavelengths. Two steps were
employed in order to increase the signal to noise ratio in these measurements. First, each transient measurement was made once with the probe beam blocked (B-trace) and once with the probe beam exposed (A-trace). Then each of these measurements were repeated 500 times and averaged. The last step is to mathematically subtract the B-trace from the A-trace, removing systematic errors introduced by laser scatter reaching the detector.

Figure 4.13: Output of halogen lamp used for TAS probe after being passed through both monochromators at various wavelengths. The three small peaks observed at the shortest wavelengths (325, 350 and 375 nm) are the second order diffractions of the three longest wavelengths (650, 700 and 750 nm). They are considered to be much to small to have any effect on the experiment.

As the pump laser requires dyes to produce light of various wavelengths, a characterisation of the available dyes and their relative outputs was undertaken. Figure 4.14 shows the result of this. As discussed in chapter 1, the sensitising molecules used most regularly in this research were PQ4Pd, PtTPBP and PtOEP. These have peak Q-band absorptions at 670 nm, 614 nm and 533 nm respectively. The dyes used to produce light closest to those peaks were:

1. 5-imino-5H-benzo[a]phenoxazin-9-amine monoperchlorate (Cresyl Violet 670, CV-670).
2. 2-[2-[4-(dimethylamino)phenyl]ethenyl]-6-methyl-4H-pyran-4-ylidene-propanedinitrile (DCM).
3. 7-(ethylamino)-4-(trifluoromethyl)-2H-1-benzopyran-2-one (Coumarin 500, C-500).
Each of these was purchased from *Exciton* and used without further purification. While the peak output from these dyes does not sit exactly on the absorption peaks of the molecules under investigation, those absorbances are sufficiently broad for the relevant molecules to strongly absorb this light. The power of each laser pulse was measured before and after experiments with a *Coherent FieldMax* power meter and was typically around 10 $\mu$Jcm$^{-2}$.

![Image of TAS pump laser spectra](image)

*Figure 4.14*: TAS pump laser spectra, imaged through neutral density filters.
Chapter 5

Solution based Upconversion

This chapter discusses experiments conducted in the liquid phase. Primarily these concern two chemical partnerships: PQ₄Pd/rubrene and PtTPBP/perylene. Firstly, the PQ₄Pd/rubrene system is characterised and our transient absorption spectroscopy experiment is tested. We then present the first direct observation of triplet energy transfer from sensitiser to emitter species, and fit the resulting transient curve with the KRM. The KRM is then included into a global optimiser and used to characterise the PtTPBP/perylene system. Finally, enhanced upconversion is observed in a system containing PtOEP AN and DPA. This behaviour is replicated with the KRM and a mechanism is proposed. Lastly, work on a singlet oxygen mediated upconverting scheme is presented.

Photograph of OUC from a PtOEP/DPA mixture, excited with a 535 nm diode laser.
5.1 Characterisation of PQ$_4$Pd and rubrene system

In order to gain some experience and familiarity with the preparation, processing and experimentation described in the previous chapter, basic characterisation of the well studied PQ$_4$Pd/rubrene system was carried out. This was then extended into new experiments which showed the first observation of TET from a sensitiser to an emitter molecule.

5.1.1 Stability to light and oxygen

We have already discussed the importance of excluding molecular oxygen from standard OUC systems from an energetic and chemical perspective in chapter 2. In the case of rubrene, it readily oxidises to rubrene endoperoxide under light and in the presence of oxygen,\textsuperscript{114} figure 5.1 shows this simple reaction.

![Figure 5.1: Reaction of molecular oxygen with rubrene, under illumination.](image)

In order to demonstrate the dramatic effect this chemical change has on the OUC materials in solution when laser light is applied, a functional (but not degassed) upconverting mixture of PQ$_4$Pd and rubrene was exposed to 670 nm laser radiation for 20 minutes. At this wavelength, only the PQ$_4$Pd should absorb the radiation. Figure 5.2 shows the visible change in the major frequency of light emitted over twenty minutes. UV/VIS absorption spectra were also taken before and after this exposure and are shown in figures 5.3a and 5.3b. While the absorption due to the emitter molecule is entirely lost, the signal from the porphyrin remains essentially unchanged. Although the porphyrin did not decay noticeably during this very short trial, it is not immune to oxygen attack. As the singlet oxygen is generated in proximity to either the sensitiser or emitter molecule, the reaction is likely to take place rapidly. We know from transient spectroscopy that the triplet excitation on sensitising molecules rapidly transfers to emitters, suggesting that while emitter species are present, most of the singlet oxygen will be generated in proximity to those emitters.
Figure 5.2: Photographs of a solution of PQ$_4$Pd and rubrene under atmospheric conditions and excited by a 635 nm He-Ne laser.

Figure 5.3: (a) UV/VIS spectra of rubrene [4 mM] and PQ$_4$Pd [0.1 mM] and, (b) UV/VIS spectra of PQ$_4$Pd rubrene mixture before and after 20 minutes of laser illumination (5 mW at 635 nm) in ambient conditions.

5.1.2 Transient Absorption Spectroscopy

Using the TAS experiment as described in chapter 4, we investigated the behaviour of both PQ$_4$Pd and rubrene in isolation. As we are only investigating energy transfer from PQ$_4$Pd to rubrene and not the other way around, the first experiment was to take a transient spectrum of neat degassed rubrene when being pumped at the peak absorption frequency of the Q-band of PQ$_4$Pd, 670 nm. The outcome of this experiment is shown below in figure 5.4. It is clear that there is no transient signal in the range 520 to 700 nm produced by excitation of neat rubrene pumped at this wavelength. Note though, the dramatically increased noise level as the probe beam moves towards shorter wavelengths. This is due to the fall-off of output from the probe lamp, as shown in figure 4.13. In comparison, and partly to show that the sample was not degraded or contaminated, figure 5.5 shows the same rubrene sample under excitation from 530 nm pulses. Here we can see two distinct
features, a dramatic bleach at 530 nm showing depopulation of the groundstate, and a moderate induced absorption between 570 nm and 590 nm. This induced absorption is due to the generation of meso-stable excited states which are able to absorb light from the probe beam.

Figure 5.4: Transient spectrum of pristine degassed rubrene under 670 nm excitation at 5, 6, 7 and 8 µs.

Figure 5.5: Transient spectrum and decay traces from pristine degassed rubrene under 530 nm excitation. a) Transient spectrum at 5, 25, 50 and 80 µs after laser excitation. b) Decay traces for the largest induced absorption (at 580 nm) and bleach (at 530 nm).

Figure 5.6 shows the TAS spectrum of neat degassed PQ₄Pd when pumped at 660 nm. There are two clear features: a narrow bleach at 660 nm (ground state bleaching); and a broad induced absorption between 530 and 600 nm ascribed to the first singlet state generated by ISC. The lifetime of each of these corresponding curves is around 60 µs.
Figure 5.6: Transient spectrum and decay traces from pristine degassed PQ₄Pd under 670 nm excitation. a) Transient spectrum at 5, 25, 50 and 80 µs after laser excitation. b) Decay traces for the largest induced absorption (at 550 nm) and bleach (at 670 nm).

5.1.3 Calculation of $k_{TET}$: Stern-Volmer

As discussed in chapter 4, the standard method used in this thesis to exclude atmospheric oxygen from solutions was to prepare each solution in an oxygen free glovebox, from de-oxygenated solvent. In order to experimentally verify that this passive process was excluding a sufficient and repeatable amount of oxygen, and to gain some familiarity with the TAS experiment detailed in chapter 4, an experiment was designed so that a standard Stern-Volmer (SV) relationship could be applied. An SV relationship describes the effect of a change in concentration of one species on the rate of a reaction. In this case, we vary the concentration of emitter, rubrene, while keeping the concentration of sensitiser, PQ₄Pd, the same. The SV relation, equation (5.1), also allows us to extract the rate of triplet energy transfer, $k_{TET}$.

$$\frac{1}{\tau} = k_{TET} \times [Emitter] + \frac{1}{\tau_0} \quad (5.1)$$

Figure 5.7a shows single exponential decays ($y = a \times e^{-b} + c$) fitted, with a Matlab routine, to normalised TAS data from these experiments. Normalising this plot means that what would have been a bleach and recovery appears as a decay. It is clear from this plot that the lifetime of sensitiser triplets decreases with an increase in concentration of emitter, as expected. Figure 5.7b shows an SV plot extracted from the lifetimes of the curves in figure 5.7a. The value of $k_{TET}$ extracted from this curve with equation (5.1) is $3.4 \times 10^8$.
\[ M^{-1}s^{-1} \pm 3 \times 10^3 \]. The value which has been reported in literature is \( 3.1 \times 10^8 M^{-1}s^{-1} \). This close agreement, and excellent fit, shows that the oxygen exclusion procedures used herein are sufficiently rigorous and repeatable.

\[ \text{Rubrene} = 0.00 \text{ mM} \]
\[ \text{Rubrene} = 0.15 \text{ mM} \]
\[ \text{Rubrene} = 0.30 \text{ mM} \]
\[ \text{Rubrene} = 1.20 \text{ mM} \]

\( 0 \to 3 \times 10^3 \times 10^3 \). The value reported in \( \text{Rubrene} \) was \( 3.1 \times 10^8 M^{-1}s^{-1} \).

\[ k_+TET \] and has a value of \( 3.4 \times 10^8 M^{-1}s^{-1} \pm 3 \times 10^3 \). The value reported in \( ^{61} \) was \( 3.1 \times 10^8 M^{-1}s^{-1} \).

\[ 5.1.4 \text{ Kinetic model and fitting} \]

As part of the validation of the kinetic rate model described in chapter 3 we used data from Cheng et al. (2010)\(^3\) to check the quality of fit that the KRM is capable of producing. In that paper, the authors use rubrene and PQ\(_4\)Pd to show that the efficiency of TTA is well beyond the statistical limit of of 11\%. They provide the equation, and values, for a fit to the normalised decay of rubrene triplets that was experimentally observed. To produce our curve, the known rate constants for this pair of molecules\(^46\) were used as the inputs for the KRM. The details of the laser pulse used in that paper were used to calculate the number of triplets generated when the pulse hit the sample in the experiment, and the curve was normalised to that value. From these starting points, the model produced values of \( [Y_T] \) with increasing time. These were simply normalised using \( [Y_T]_{t=0} \) to provide a direct comparison with the published data.

Figure 5.8 shows the outcome of this trial. There is a slight divergence at long time scales, but there is otherwise an excellent fit to the data. This is strong evidence that the model describes OUC, in this region of concentration and illumination intensity, extremely
well. There is no observable difference between using Auckett’s equations (equations (3.1) and (3.2)), or our extended versions (equations (3.12) and (3.13)) in this case.

![Graph](#source)

**Figure 5.8:** Comparison of model output, stars, with a fit to experimental data from Cheng et al. (2010).³

### 5.1.5 Direct observation of TET from sensitiser to emitter

One of the advantages of TAS, as has been mentioned before, is that it can probe the intermediate states of the OUC process. This is shown in the paper which makes up Appendix A.⁶⁵ In this paper, we take a mixture of 0.1 mM PQ₄Pd and 2 mM rubrene, pump at the ground state of PQ₄Pd (660 nm, where rubrene does not absorb) and probe at the rubrene ground state (535 nm).

Pumping PQ₄Pd at its ground state absorption peak (λ = 660 nm) forms a long lived triplet state on that species, figure 5.7. This excited state also has a characteristic absorption spectrum, shown in figure 5.9. Here it can be seen that, along with the expected bleach of the PQ₄Pd ground state, there is a broad transient absorption feature induced between 530-600 nm, which we attribute to optical excitation up the triplet channel of the porphyrin. This absorption feature, specific to PQ₄Pd, overlaps the ground state absorption of the rubrene emitter, also shown in figure 5.9. The overlap between the excited sensitiser’s induced absorbance and the ground state emitter’s absorbance spectrum has important implications when considering the TAS spectra of these species when mixed.
Figure 5.9: Top: transient absorption spectrum of PQ$_4$Pd when excited at $S_0$ (660 nm), 3 µs after pump excitation. Inset indicates relevant optical transitions: a bleach at 660 nm due to a reduction in population of ground state PQ$_4$Pd, and an induced absorption due to the increased population of PQ$_4$Pd triplet states. Bottom: absorption spectrum of ground state rubrene. Reproduced from Piper et al. (2014).
The solid line in figure 5.10 shows the result produced by the KRM, when initialised with known experimental parameters and the published rate constants for this system. The value of $\Delta OD$ was calculated from equation 5.2: where $TS_{abs}$ is the contribution of one triplet excited sensitiser molecule to the induced absorption and $GE_{abs}$ is the contribution of one molecule to the ground state absorbance of our emitter, or its molar extinction coefficient. The result is then normalised against the value at time $t = 0$. The rise time of the induced absorbance is taken to be instantaneous, as the ISC process is complete within a few tens of picoseconds. The rate of the subsequent decay is primarily determined by two terms in equation (3.12): $k_p[X_T]$ and $k_{TET}[X_T][Y_G]$. As $[X_T]$ is always small, the $k_{XX}[X_T]^2$ term has little impact. After the delayed bleach builds, it decays at some rate, determined by terms in equation (3.13): at high $[Y_T]$, the $2k_{YY}[Y_T]^2$ term is dominant, and at longer time scales the $k_{NR}[Y_T]$ term takes over.

\[ \Delta OD = [X_T] \times TS_{abs} - [Y_T] \times GE_{abs} \]  

(5.2)

We attribute the initial induced absorption seen in figure 5.10 to the previously observed optical triplet excitation of the sensitisier, shown in figure 5.9. The decay of this induced absorption proceeds at a rate comparable to the regeneration of the sensitisier ground state,
as indicated in figure 5.7b. The delayed bleach in the rubrene ground state that follows
this induced absorption then directly shows the process of triplet energy transfer from
sensitiser to emitter molecules. It is clear that at each stage of the curve our rate model
fits the experimental data well, showing that each regime is described by the model in
a physically consistent way. The principal source of uncertainty in this calculation is the
value of $GE_{abs}$. The probe beam produces much lower intensity at shorter wavelengths,
from which $GE_{abs}$ is derived. A more accurate measurement of $GE_{abs}$ would not alter the
dynamics of the decay curve, it would simply scale the normalised $\Delta$ OD axis.

5.2 Global optimiser and fitting parameters for another system

To explore and demonstrate the power and possibilities of this KRM, the global optimisation
toolbox in Matlab was used to investigate the rate constants of another OUC pairing. This
fitting process is explained in chapter 3.

5.2.1 PtTPBP/Perylene

For this demonstration, we chose to examine another well known OUC paring: PtTPBP
and perylene. To use the global optimiser, a target transient curve is required. In this
case, it is provided by fitting a double exponential ($y = a \times e^{-b} + c \times e^{-d} + e$) to experi-
mental data from a fluorescence experiment involving 0.12 mM of PtTPBP and 0.83 mM of
perylene. Time resolved spectra were recorded with an intensified CCD, and integrated to
produce a transient fluorescence curve. The fluorescent signal relating to OUC from pery-
lene molecules in a mixture of PtTPBP and perylene can be related to the concentration of
perylene triplets by equation (5.3), and vice-versa.

$$\text{Upconverted fluorescence} = k_{TTA}[\text{Emitter}_{\text{triplet}}]^2$$

(5.3)

Figure 5.11a shows the values of the minimisation function that were found when the opti-
miser was run from the starting condition of the same rate constants as PQ$_4$Pd and rubrene,
which are known from literature. With each iteration the value of minimisation function
approaches 0, though the most significant advances occur within the first 30 iterations. If
the optimiser is left to continue indefinitely, after an extra 1000 iterations the ‘best func-
tion value’ does not decrease by more than 0.1. Figure 5.11b shows the experimental fit in
red, the KRM result using the PQ$_4$Pd/rubrene rates in green and the KRM result after 30
iterations in blue.
Figure 5.11: (a) Plot showing the reduction in value of minimisation function over 30 iterations. (b) A double-exponential fit to experimental data, red, the initial KRM output, green, and the optimised KRM output after 30 iterations, blue.

We find that in order to achieve this excellent fit, only $k_p$ and $k_{TET}$ have to be changed. The change in $k_p$ is a 33% increase, which is of the order of the known difference in phosphorescent lifetime between PQ$_4$Pd and PtTPBP triplets,$^{115}$ and the change in $k_{TET}$ is a 40% increase which is explained by a better relative match in triplet energy levels between PtTPBP and perylene. A sensitivity analysis showed that each other rate constant varied by less than 1% for this fit. Showing that for this experiment, at least, the other rate constants did not have a significant effect on the result. Running this experiment in a more efficient (higher) power regime (where emitter triplet decay is dominated by TTA rather than non-radiative decay) would make the TTA rate constant much more important, and hence more visible in the plot and sensitivity analysis.

The physical reason for the increase in magnitude of $k_{TET}$ can be seen in figure 5.12 where we show that the triplet level of PQ$_4$Pd is within 0.32 eV of rubrene (78.1%) whereas that of PtTPBP is within 0.08 eV (95%) of that of perylene.

5.3 Two emitter systems

As discussed in chapter 3, there is some evidence that adding a second emitting molecule increases the efficiency of upconversion in solution. We tested this proposition by modifying the key rate equations as shown in section 3.1.3 and attempting to recreate the results of Cao et al. (2013).$^{92}$ In that paper, PtOEP is combined with three emitters (DPA, DPBF and
AN) in various mixtures. Cao et al. found that, despite the fluorescence yield of DPBF exceeding that of DPA (96% to 87%), a mixture of both produces more upconverted fluorescence per molecule than the same concentration of either molecule individually. In reproducing these results, we varied the relative concentration of DPA and AN (fluorescent yield 27%) in combination with the same sensitiser, PtOEP. The diode laser fluorescent experiment, detailed in chapter 4, was used in combination with a spectrograph/intensified CCD to collect spectra at various laser powers. The relevant spectral bands were then integrated to give a single value for each mixture percentage and illumination intensity. Figure 5.13 shows the result of this experiment. We see that the fluorescent signal at 0% AN (100% DPA) is slightly higher than that at 100% AN, as expected due to their differing fluorescent yields. However, in every case, and particularly as incident power increases, this difference is dwarfed by the increase found when the emitters are mixed. We chose to use AN in our experiments, despite its low fluorescence yield, as this result was the most surprising of the Cao et al. paper and as such was most interesting to try to replicate.

To explain the observation of a clear hump at 50% mixture of AN and DPA, we return to the KRM. As shown in section 3.2.1, it is possible to examine the output of a three component, two emitter OUC system by looking at the final result from the KRM. Figure 5.14 shows three examples of a two emitter system: (a) where $k_{TET}$ for emitter Z is ten times smaller; (b) where $k_{TTA}$ for emitter Z is ten times smaller and; (c) where the term governing heteroannihilation between emitters is twice as large as homoannihilation for each emitter. In (a), there is no significant difference in fluorescent output in any combination, only a small decrease at 100% ‘poor’ emitter (low $k_{TET}$). We might expect figure 5.13 to resemble 5.14b as the vastly lower fluorescent yield of AN compared to DPA can be considered a correspondent loss to upconversion QY. However, the plot that most resembles our experimental result is figure 5.14c. This provides some indication that the hypothesis published by Cao et al. 2013, that there is a synergistic effect which increases the relative efficiency
Figure 5.13: Plot showing total upconverted light from mixture of PtOEP and DPA/AN.

We will go one step further here, and propose that the origin of this synergistic effect comes from an energy gap mismatch. TTA is the reverse process of singlet fission, which is not observed in two molecule systems. Figure 5.15 shows why this is: the $S_1$ level of emitter Y is lower than that of emitter Z, so if a singlet forms on emitter Z there is an energy cost to split that excitation into two triplets. If we regard singlet fission as a loss pathway for the TTA process, and reduce that by introducing a second emitter species then, it is obvious that there will be an enhancement of the efficiency, hence rate, of TTA between distinct species. In October 2014 Schmidt et al. published a different description of this same argument, but approached it from a perspective of rate constants. They essentially argue that an undesirably low TTA rate in one molecule can be more than ameliorated if that molecule possesses a superior TET rate to the other. This is equivalent to the argument presented above.
Figure 5.14: KRM comparison of three ‘two emitter’ systems with (a) $k_{TETxy} = 10 \times k_{TETxz}$ (b) $k_{TTAyy} = 10 \times k_{TTAzz}$ and (c) $k_{TTAyz} = 2 \times k_{TTAyy} = 2 \times k_{TTAzz}$. The y-axes represent the proportion of total energy that is relaxed by way of phosphorescence, fluorescence and non-radiative decay from each of the various molecules. The fluorescence curves can be considered as related to PLQY.
Figure 5.15: Energy scheme for synergistic TTA emission from two emitter system. (a) A singlet has formed on emitter Z. From here it may either undergo a FRET type transfer (providing it is physically close to emitter Y), fluoresce, or undergo singlet fission to produce a triplet on each of Y and Z. (b) A singlet has formed on emitter Y, the energy gap $E_{\text{gap}}$ prevents FRET and singlet fission, so the only option is to fluoresce.
5.4 Singlet Oxygen Mediated Upconversion (SOMUC)

As has been discussed in chapters 1 and 3, atmospheric oxygen has significant detrimental effect on the efficiency of molecular oxygen. However, it can also be used as a mediating agent, as has been demonstrated by Fückel et al. (2011),\textsuperscript{19} (Appendix B). The process here is an extended version of the scheme outlined in chapter 3. Figure 5.16 (reproduced from the above paper) shows that there are now two triplet energy transfer steps. The first relaxes the sensitizer triplet, and excites the oxygen into its singlet state. The second is the reverse of this and relaxes the oxygen to excite the triplet level in the emitter molecule. This paper shows that this process not only works under atmospheric oxygen, but that it works much better when oxygen is being circulated through the cuvette.

![Figure 5.16: Schematic of Singlet Oxygen Mediated Upconversion. Inset a) shows potential TTA between two triplet excited emitter molecules, b) shows potential for direct population of emitter singlet states through energy transfer from singlet oxygen. Figure reproduced from 19.](image)

We performed TAS experiments on this system, and showed that there was no transient signal from the absorbing material used for the experiments (IR820) under either ambient or oxygen-free conditions. Figures 5.17 and 5.18 show examples of these experiments. In figure 5.17 it is shown that a degassed mixture of IR820 and V79, at the concentrations used in Fückel et al. (2011) (1.7×10\textsuperscript{-3}M and 2.4×10\textsuperscript{-3}M respectively), do not produce a transient signal when pumped and probed at 820 nm. This wavelength is the absorption peak of IR820 and should show dramatic bleaching after being pumped unless the excitations
generated by the laser pulse relax on a time scale shorter than a few $\mu s$. Two power levels are shown here, which are similar to those used earlier in this chapter to produce clear transients in similarly strongly absorbing materials.

![Graph showing transient absorption](image)

**Figure 5.17:** Result of transient absorption experiment showing that no triplets are observed when a degassed mixture of IR820 and V79 is pumped and probed at 820 nm.

Additionally, figure 5.18 shows that a pristine degassed sample of IR820 ($1.7 \times 10^{-3}$M), when pumped and probed at its absorption peak of 820 nm, still produces no transient signal. This means that the lack of signal in figure 5.17 is really due to no triplets being formed, they are not simply being quenched at a rate faster than $\mu s$. The very short-lived sharp drop in OD on the red curve is a common artefact in measurements taken with this equipment, and is due to light leaking from the laser pulse into the detector. The samples used were of course checked for absorption and emission behaviour which matched that in published literature.

While these negative results do not appear in full in the published paper, they did guide our investigation and helped to show that oxygen was not only essential for TET in this system, but also that the ISC efficiency of IR820 is negligible without molecular oxygen, due to a paramagnetic effect. Under degassed conditions, the IR820 did not produce sufficient triplet density to be recorded. Conversely, when under atmospheric conditions, any triplets generated were scavenged by molecular oxygen too quickly for a measurable population of triplet excited IR820 to build up.
Figure 5.18: Result of transient absorption experiment showing that no triplets are observed when a pristine sample of degassed IR820 is pumped and probed at 820 nm.
Chapter 6

Thin Film Upconversion

This chapter answers the research question ‘What physical factors control the efficiency of OUC from thin films, and how can those factors be influenced and measured through material science?’. It starts with a short review of available literature in this area, and makes an argument for the benefits of creating a thin film upconverter. The first results we obtained in this area are then presented and explained with the help of the Monte-Carlo Model (MCM). The subsequent section exposes the kinetics of upconverted fluorescence in solid and liquid states, modelled with the MCM. We show that while diffusion is indeed slowed or stopped entirely in a thin film, the OUC process may proceed even faster than in solution if a very well intermixed film is created. We then discuss the progress made towards optimising the fabrication conditions for a maximally efficient upconverter, showing that crystallinity and morphology are critical determinants of output. The next section details development and initial testing of a novel optical technique for investigating the degree of intermixing in an OUC film. This technique can produce SIMS-like information on intermixing, at some significant cost to accuracy, in air and with relatively cheap optical elements. It therefore allows for cheaper and faster acquisition of 2-dimensional film blend information that any other currently available technique. The final section in this chapter reports on an attempt to improve upconversion efficiency with plasmonic structures.

Cross-polarised micrograph of a film containing PtOEP, DPA and polystyrene.
6.1 Organic upconversion in thin films

Recently, there has been increased interest in the area of fabricating thin films of organic upconverters. This has mostly been encouraged by the requirement for simple fabrication of practical and long-lived upconverters for real devices. Sensitizer/emitter solutions are reported to have lifetimes of approximately 60 days in an inert atmosphere. This reduces to a few hours if left in air and under light. Keeping samples in the dark reduces the production of singlet oxygen and increases lifetime significantly. The realization of an efficient thin film upconverter would necessarily provide good encapsulation and protection from oxygen and water, which would immediately increase the lifetime of the chemicals used in such a device. However, for practical use in a commercial device, this active lifetime must be further increased by more than an order of magnitude. Shulze and Schmidt (2014) showed that in a well-sealed system, light degrades each sensitiser and emitter species equally. They also extrapolated their results under multiple sun concentration to one sun and showed that their system would survive at above 90% of maximum for more than a year without any further modification.

A brief history of the history of this field follows.

Islangulov et al. (2007) found some evidence of TTA luminescence when their drop cast and annealed film (of PdOEP and DPA embedded in an ethyleneoxide/epichlorohydrin copolymer) was at room temperature, but report none below the glass transition temperature ($T_g$) of the film. The term ‘glass transition’ refers to the temperature at which cross-linking occurs in polymers, i.e. the temperature at which there is insufficient thermal energy to prevent the formation of inter-chain bonds. Below this temperature, reptation of polymers and diffusion of molecules is considered to halt entirely. Therefore, these authors attribute the reduction in upconverted fluorescence below the $T_g$ of the host matrix to a reduction and halt of translational mobility of the active molecules. The authors also observe ‘clear signs of DPA phase separation’ in their films, though they add that they do not believe that this affected their result. No quantitative estimate of upconversion efficiency was reported in this paper.

Baluschev et al. (2007) proposed two energetic pathways for film based upconversion: the OUC scheme discussed at length in chapter 3, and through sequential absorption on a sensitising molecule, followed by FRET to an emitter and subsequent fluorescence. They found some evidence that upconversion could proceed by this second route but, unsurprisingly, it was much less efficient. This is consistent with the energy level and rate models presented in section 2.2.2 and chapter 3. A functional upconverting film display, powered by a rapidly moving laser beam, was demonstrated by Miteva in 2008. In this paper it
is suggested that highly viscous matrices possess a sufficiently high rate of diffusion that upconversion can proceed at moderate efficiency while remaining solid enough to be encapsulated. Monguzzi et al. (2009) showed that a film of PtTPBP and BEPA embedded in a cellulose acetate host matrix produced upconverted fluorescence at low excitation intensity, in the range of 1 mWcm$^{-2}$, a huge improvement from Baluschev et al.’s 5 kWcm$^{-2}$. Evidence presented later in this chapter suggests that the success of Monguzzi’s display, and the reduction in upconverted fluorescence observed by Islangulov et al. (2007) may owe as much to morphology as it does the diffusive properties of the host matrices. As will be further explained in section 6.2, the relative immobility of active molecules and excitation in thin films requires that they be well mixed for the required energy transfers to have any chance of occurring.

The above studies have focussed on molecules dispersed within polymer matrices. Some research groups are also investigating the possibility of polymer-based upconverters. For example Laquai et al. (2005) doped a spirobifluorene-anthracence copolymer with PtOEP and, unsurprisingly, the authors observed more upconverted fluorescence signal from this combination than from an anthracene free spirofluorene polymer. Unfortunately, they do not calculate the yield of this system, or enough information to apply the metrics introduced in section 2.3.

6.1.1 Concentration for efficiency

In chapter 3 it was shown that the concentrations of sensitiser and emitter molecules are absolutely key in determining the efficiency of an OUC system. It is also understood that it is important to optimise the ratio between sensitiser and emitter molecules, while keeping the concentration of sensitisers high enough to be able to absorb enough light. If we ignore losses due to extra phonon relaxation modes, nearest neighbour coupling, homo-annihilation between sensitiser molecules and hetero-annihilation between emitters and sensitisers, we can construct a simple argument showing that thin film OUC satisfies the requirement for high efficiency.

If we consider a droplet of active OUC molecules in solution, with a volume of say 5 µl and moderate total concentration of molecules of 0.5 mM. There are $1.6 \times 10^{16}$ molecules in that drop. If we drop cast this solution, it might form a disc of around 1 cm radius, with a height of a few hundred nanometers, say 250 nm. On average in the solution one molecule is found per volume with radius of 15 nm, in the cast film, this has reduced to just under 2 nm. Simplistically, one could argue that this nearly tenfold reduction in molecular separation would lead to a 1000 fold increase in concentration and a commensurate increase
in TTA efficiency, as defined by Auckett et al. (2009),\textsuperscript{46} equation (6.1).

\[ \epsilon = 2 \times \frac{k_{TTA}[\text{Emitter}_{\text{triplet}}]^2}{k_{\Phi}[\text{Sensitiser}_{\text{ground state}}]} \]  

Unfortunately, as demonstrated by several groups, it is not so simple to fabricate a solid state OUC device. Most groups attribute this to the nature of the triplet transfer process. As it is a combination of both Dexter transfer and mass diffusion, removing all mass diffusion cripples the process. However, Monguzzi et al. (2008)\textsuperscript{28} calculated that for PtOEP and DPA in solution, the diffusion length on a triplet excitation in toluene at room temperature is around 200 nm, and that the Dexter radius of the PtOEP/DPA pairing is 1.2 nm. That is to say, if two molecules are within 1.2 nm of each other, TET or TTA will occur. In a solid, there will be no diffusion, but if we follow the example calculation above, we find that the average molecular separation in a thin film will be on the order of nanometers. This suggests that if an appropriate morphology can be created, there will be no requirement for diffusive transport.

### 6.1.2 Temperature dependence

Monguzzi et al. (2008)\textsuperscript{28} found that the upconversion quantum yield of a solution of PtOEP and DPA in 1,1,1-trichloroethane varied with temperature. Below the freezing point of the mixture, 77 K, they were able to model the TET step as purely Dexter transfer driven. At 300 K, the TET process became much more efficient, even at low DPA concentration. Dexter transfer is temperature independent, so the authors proposed that the additional phosphorescence quenching must be due to a diffusive process. The Einstein relation for describing diffusion of spherical particles through a liquid was used in conjunction with the viscosity of the solvent and an estimate of the effective molecular radius of the molecules\textsuperscript{121} to calculate diffusion coefficients for the PtOEP and DTA. When this diffusive term was included with the Dexter transfer term, their model again described the observed results well.

Islangulov et al. (2007)\textsuperscript{120} and Singh-Rachford et al. (2009)\textsuperscript{109} both found that the upconversion efficiency of films of polymer blend of PdOEP and DPA depends strongly on the temperature of the film, such that when cooled below the glass transition all upconversion was reported to be completely suppressed. This provides evidence that efficient TTA requires the diffusion of the excited molecules, rather than a pure quantum mechanical charge transfer. Upconversion intensity was found to increase with temperature, reversibly, up to 400 K. Above this temperature, upconversion was suppressed and did not occur.
when the temperature was reduced, suggesting thermal decomposition of the materials. This degradation theory is supported by a complete lack of hysteresis on heating/cooling cycles below 380 K. Fluorescence was integrated over 500 ns, though the authors note that the start time of this integration was varied such that the integral was obtained from the maximum intensity reached for each temperature, as this occurred at varying time delays after laser excitation. This variation in onset of maximum fluorescence suggests that more molecular diffusion was indeed occurring, but the authors do not elaborate on their findings in this regard. Section 6.2.3 contains further evidence of this kinetic difference between fluid upconverters and their rigid counterparts.

These studies suggest that both TET from sensitiser to emitter and TTA between two emitter molecules follow the same ET mechanism. The apparent dependence of TTA efficiency on molecular mobility provides an explanation for the low efficiency reported in thin film OUC devices and the general dependence of TTA on temperature.

6.2 Thin film results

A significant amount of effort has been put into developing an understanding of thin film based OUC. Some progress has already been made in addition to that introduced in section 6.1, for example Lissau et al. (2011)\textsuperscript{89} attached porphyrins to nanostructured ZrO\textsubscript{2} films and observed low excitation power upconversion. This method is not considered here, but shares many of the same considerations as the approach we take. Rather, we attempted the same methods as discussed in section 6.1: fabricating OUC films in polymer matrices.

6.2.1 Addition of polymer to thin films

Our first attempts at fabricating a thin film OUC were to simply drop cast a mixture of PtTPBP and perylene onto a prepared slide and measure the light emitted after excitation at the PtTPBP absorption peak. Using an experimental set up similar to that in section 4.2, a laser excited the sample and emission was collected after being passed through a spectrograph. We found no evidence of upconversion from these samples. Following the leads of Islangulov et al. (2007)\textsuperscript{120} and Singh-Rachford et al. (2009),\textsuperscript{109} we next tried to embed our active molecules in a polymer matrix, in our case PMMA. Figure 6.1 shows our first observed indication that increasing polymer concentration has an effect on the efficiency of thin film OUC, acquired with a PIMax iCCD during a visit to the University of Sydney. These films of PtTPBP and perylene, concentrations 0.09 mM and 8 mM respectively, were
wire bar coated in the dark, in air, and measured under vacuum. From them we clearly see that as we increase the weight% PMMA in the films from 3% to nearly 9% PMMA, upconverted fluorescence begins to be observed. The magnitude of this fluorescence more than doubles as the weight% is doubled from 4.8% to 8.9%.

Figure 6.1: Initial results showing dramatically increased upconversion fluorescence from films containing progressively higher weight percentages of electrically and optically inert polymer.

The result is not immediately intuitive, as one might expect the addition of a polymer to pad the spaces between active molecules, increasing the average distance between active sites, and reducing the chance of upconversion taking place. However, the addition of PMMA also breaks up crystals within the film, increasing the number of grain boundaries from which upconversion can take place. We can apply the MCM to this problem to get some feeling for why this is the case. Consider two situations of intermixed sensitiser and emitter, in each case no diffusion takes place. The difference is that each case has vastly different crystal grain size. Figure 6.2 shows this example. In each subfigure the molecules are under constant illumination and charges are allowed to interact over a distance of up to 10 vertices. In each case, upconversion is only observed to occur close to the boundary of each grain. Figure 6.2a recorded 1781 upconversion events, whereas in figure 6.2b recorded 3532 events. Clearly, the more grain boundaries there are, the more upconversion events may occur. This increase is directly proportional to the ‘active area’ around each boundary.
6.2.2 Oxygen sensitivity, and lack thereof

Sections 1.3.2, 2.5 and 5.1.1 have all mentioned how important it is to reliably remove atmospheric oxygen from an OUC system, as it is a triplet energy quencher and also physically destroys the active molecules. However, while investigating OUC film behaviours, it was noticed that the behaviour of these films was indistinguishable, whether their PL emissions were recorded from inside an evacuated cryostat or in air.

Simon and Weder (2012), among others, have report observing the a slow build up of upconverted fluorescence from liquid OUC samples (taking place over the order of seconds). In that paper, the authors attribute this build up to a combination of the build up of triplet emitter states and the depopulation of any oxygen in the sample. In figure 6.3 we see a kinetic trace from a liquid sample of PtOEP and DPA in toluene which has not
been degassed. The shutter was lifted from the excitation laser at time $t = 0$. Initially, there is no fluorescence, only phosphorescence from PtOEP. Then both phosphorescence and upconverted fluorescence signals show a linear increase from $6.5 \text{ ms}$ to $10 \text{ ms}$, with fluorescence beginning to dominate at around $8 \text{ ms}$. This linear section of the curves is due to the depletion of atmospheric oxygen. Atmospheric oxygen is a quencher for both PtOEP and DPA triplets, so it should be expected that oxygen would quench PtOEP phosphorescence as well. This is also shown in the figure as the linear regime for both phosphorescence and upconverted fluorescence starts and end at the same time. The phosphorescence signal then stabilises, while the upconverted fluorescence signal continues to build. The shape of the second feature is related to the build up of emitter triplets. As shown in section 5.2, equation (5.3), the rate of fluorescence is dependant on the square of the concentration of emitter triplets, and figure 3.12a shows this same build up as modelled by the KRM (in absence of a quencher which is depleted over time).

![Figure 6.3: Kinetics of delayed OUC fluorescence from atmospheric sample under CW illumination.](image)

When the same experiment was performed on thin film samples, not only was no build up of any kind seen in phosphorescence or fluorescence, there was also no difference in output from either an atmospheric or evacuated cryostat. We propose that this is because of the dramatically reduced active volume of the samples. The experimental cuvette used for solutions was $1 \text{ mm}$ thick, and the thin films had an average thickness of a few $100s$ of $\text{nm}$. In this reduced volume, there is commensurately less oxygen to remove. We therefore suspect that any build up of fluorescence occurred on a time scale shorter than we could measure.
This finding was very helpful in speeding up the measurement of thin films, as we no-longer had to pump down a cryostat before measuring each sample. It should be mentioned, however, that the lifetime of each sample was dramatically decreased if it was measured in air rather than a vacuum (from a few hours under excitation to a few minutes). Therefore all samples were kept in the dark, and measurements were carried out as rapidly as possible once samples had been mounted onto the sample wheel. Uttiva et al. (2012)\textsuperscript{114} showed that while rubrene oxidises rapidly under atmospheric conditions, when crystalline the reaction slows dramatically. This supports our assertion that once all the local oxygen has been reacted with and formed endoperoxides, atmospheric oxygen will take a relatively long time to re-enter a film.

### 6.2.3 Kinetic changes from liquid to solid

Another key piece of evidence that thin film TTA could be efficient is that there is a significant difference in the shape of the upconverted fluorescence curve produced by a mixture depending on its physical state, as illustrated by figure 6.4. In this experiment, the rise time of delayed fluorescence from a PtTPBP and perylene system is examined in either a solution or doped into a thin film of PMMA, spin cast in a nitrogen atmosphere. The concentrations of PtTPBP and perylene used here were again 0.09 mM and 8 mM respectively, the weight percentage of PMMA in the film was 8.9%.

The liquid sample shows a significant rise time before the upconverted fluorescence hits its peak. In the case of this film however, this fluorescence peak immediately starts decaying. We can again use the MCM to illustrate why this is the case.

The accepted energy transfer method involved in TTA-UC is Dexter energy transfer.\textsuperscript{28} This formalism states that within a certain radius, energy transfer to an available state will occur instantaneously and that beyond that radius it will never happen. The MCM is built on this assumption. If we take a randomly dispersed mixture of sensitiser and emitter vertices, excite some proportion of the sensitiser vertices (to simulate a laser pulse) and vary the maximum distance that a molecule may move per time step ($r_{\text{Diff}}$) we arrive at the result in figure 6.5a. This is analogous to a temperature (or viscosity) variation as molecules are able to move faster when we set the diffusion range higher. We find that there is a significant rise time in each case. We also see that as $r_{\text{Diff}}$ increases, even over a very small range, the rate of build up of emitter triplets increases significantly. We can also see that at $r_{\text{Diff}} = 0$, there should be no build up. This is indeed the case, only emitters close to the excited sensitisers are excited, effectively instantaneously, and then undergo TTA or non radiative decay accordingly. Figure 6.5b shows what happens if we then reduce the average
starting distance between molecules in this same ‘frozen’ situation. Here, we see that as we approach the allowed TET range (in this case just one vertex, as opposed to the 10 in section 6.2.1) the number of emitters which are successfully excited rises exponentially. This supports the assertion that the quality of intermixing of active components in a film is vital.

Figure 6.4: Comparison of normalised fluorescent kinetics of a solution (squares) and a PMMA film (circles) containing the same mixture and concentrations of active molecules.

Figure 6.5: MCM results showing (a) change in rise time of emitter triplets with diffusion length ($r_{Diff}$) and (b) change in number of emitter triplets generated in frozen matrix, buffered with empty space. Solid lines in each case are single exponential fits to this data.
6.2.4 Upconverted fluorescence and crystallinity

Section 6.2.1 showed that crystallinity is critical to solid OUC performance. Figure 6.6 contains cross-polarised micrographs of a mixture of PtOEP and DPA in increasing amounts of PMMA. Crystallite formation is dramatically arrested with the addition of polymer. In figure 6.6a, containing 2% PMMA by weight, the entire cross-polarised micrograph is full of crystallites, figure 6.6b (5 weight% PMMA) displays only a very faint regions of crystallinity and figure 6.6c (10 weight% PMMA) shows an entirely amorphous film.

![Micrographs of drop cast PtOEP and DPA mixed with increasing weight% of PMMA.](image)

**Figure 6.6**: Micrographs of drop cast PtOEP and DPA mixed with increasing weight% of PMMA. (a) 2 weight% PMMA, (b) 5 weight% PMMA and (c) 10 weight% PMMA.

Figure 6.7 shows a full investigation of the trend indicated in figure 6.2.1, by increasing weight% polymer until the trend stops. In this figure, each blue point corresponds to the average fluorescence collected from at least nine films, meaning that 45 fluorescence measurements were taken to produce this plot, clearly this would have been much more tedious without the FUR experiment. One confounding effect of increasing polymer weight% is that the amount of active material in the same volume decreases significantly. This of course leads to a decrease in the absolute signal collected from each sample. Because of this, the points in red have been corrected for the number of photons actually absorbed by each film, by measuring the UV/VIS spectrum of each film and scaling the blue values. The error bars on this figure are one standard deviation from the average measurement. The most significant errors come at high weight% PMMA for the corrected values of upconverted fluorescence. This uncertainty comes from the UV/VIS absorption measurements of these very weakly absorbing films. Both sets of points show the same trend, that upconverted fluorescence continues to increase well above 80 weight% PMMA. Once we account for the reduced absorption from using more dilute samples, we see that the actual maximum lies between 80 and 95 weight%, and drops off rapidly above 95 weight%. This impressive new result has since been superseded by a group who have managed to combine a liquid-like diffusion speed with thin film fabrication by means of an organogel structure, so is
unlikely to be published elsewhere.

Figure 6.7: Normalised upconversion fluorescence from drop cast thin films of PtOEP and DPA in a PMMA matrix, varying the weight% of PMMA.

Of course, PMMA is not the only polymer available for use as a matrix for thin films. Polystyrene and polycarbonate were also investigated in the course of this research. Unfortunately, neither of these polymers showed any sign of upconverted fluorescence at any weight%. Figure 6.8 shows cross polarised micrographs of each of these polymers at the same weight% to indicate how much change to morphology the choice of polymer can make. From our earlier experiments and simulations with the MCM we would expect that polycarbonate would be the best performing polymer as it has the lowest amount of crystalline regions at this relatively low weight%. However, it is only PMMA that shows upconverting behaviour, this is because the active molecules are not miscible in the polycarbonate, it forms large crystallites even at 99 weight%.

The control of morphology of thin films is the subject of a large field in materials science, and many of the same considerations apply here. Temperature, solvent, drying time, surface treatments and exposure to light can all affect the morphology of these films. The scope of this research did not allow for a thorough investigation of the effects each of these, and other, experimental controls have on our thin film OUC. As such, every film was cast in as similar a manner as was possible.

Clearly, intermixing of active materials is critical to the performance of a thin film upconverter of this kind and as such we need some method to quantify that degree of intermixing.
The high weight% regime where these thin film OUC devices work best is entirely amorphous, so the cross-polarised microscopy used in figure 6.6, above, was not useful. While Secondary-Ion Mass Spectroscopy (SIMS) could determine the intermixing of these films very accurately, it is an expensive and time consuming technique. A novel optical technique was devised in order to investigate the morphology, and intermixing, of these films. This cheap and rapid ‘micro-absorption imaging’ technique is the subject of the next section.

6.3 Micro-absorption Imaging

Following the conjecture that an efficiently upconverting thin film must be well mixed in some ratio, a rapid, cheap and reliable method for determining the degree of mixing within a thin film was developed, called micro-absorption imaging. The schematic for the original experimental apparatus is shown below, in figure 6.9. It was modified from an existing micro-QE (quantum efficiency) experiment, so is not a optimal configuration for this design. A second experiment was designed to improve the effectiveness of this equipment, but full testing and characterisation of this system was outside the scope of this project. The operating principle of micro-absorption imaging is simple: light of specific wavelengths is preferentially absorbed by particular molecules, so illuminating a sample with light of those wavelengths reveals where these molecules are physically present in such a film. An example of how a result from this type of experiment should be handled is shown in the following few paragraphs.

In each design we must start by obtaining the absorption spectrum for each material under investigation. These spectra should be taken from films as close as possible to those that will be investigated so as to minimise error from shifts in absorption due to crystal packing and
other thin film effects. From these data we determine the most appropriate wavelengths to investigate. In this example we chose 400 nm, 500 nm and 600 nm. We then say 500 nm is a point where neither molecule absorbs, 600 nm is a point where only the sensitiser absorbs, and 400 nm is where both molecules absorb, in accordance with some known ratio.

With this information we then take images of a clean slide, or a clean section of the slide that the material has been deposited on, at each of the key wavelengths. This allows us to check that we do not saturate the detector, and gives the profile of light incident on the mirror/detector. We then choose a section of film to investigate, and take further images at each wavelength. Ideally, the image taken at 500 nm will show where structures and defects in the film block light in a way that is not related to the absorption of molecules. We can use this information to correct for these effects in the other images. The image at 600 nm should now only be darkened by absorption from the sensitiser molecule, and the one at 400 nm will have a contribution from both sensitiser and emitter molecules.

Finally, we can combine the information gathered so far to produce a map showing the relative population of each molecule throughout the film. We start by calculating the concentration of sensitiser molecules per pixel in the film, $A = \epsilon c l$, where $\epsilon$ can be measured with UV/VIS, $l$ can be estimated, or measured and $A = -\log_{10} \left( \frac{l}{L} \right)$ as usual. Knowing this concentration, we can say that at 400 nm $A_{Total} = l(c_{sensitiser} \epsilon_{sensitiser} + c_{emitter} \epsilon_{emitter})$ at each pixel. It is then simple to calculate $c_{emitter}$ for each pixel and work out the mixing ratio at each point.
Initial tests with this technique were promising but, as mentioned above, full development of this technique was outside the scope of this project. Figure 6.10 shows examples of images of a PtTPBP and perylene doped PMMA film. These images were taken with the first experimental system, and illustrate the difference in morphology that can be achieved by simply varying the weight% of polymer in the blend. In the image on the left, 3% PMMA, there is clear differentiation between regions of PtTPBP and perylene. When the weight fraction of PMMA is increased to 9%, as it is on the right, we see that the signal from PtTPBP is much better spread throughout the film, implying more intimate mixing of the components. With further development, it should be possible to greatly improve the resolution and sensitivity of this technique.

![Figure 6.10: Early example of the micro-absorption technique, showing the difference in PtOEP distribution throughout two films that only differ in weight% of polymer blended in.](image)

**6.4 Plasmonic enhancement**

The KRM used throughout this thesis has only one generation term, \( k_\phi \), and it has been understood for many years that the efficiency of molecular upconversion increases quadratically with a linear increase in excitation intensity, until nonradiative losses become negligible and the relationship becomes linear,\(^{46}\) as shown in chapter 3. It is therefore of great importance that the amount of light absorbed by any molecular upconverter is maximised. Two approaches to increasing this intensity, through structural manipulation have been attempted during the course of this research: plasmonic enhancement plasmonic enhancement through fabrication of nano-scale arrays of particles; and grating-waveguide structures fabricated from alternating layers of materials with different refractive indices. The grating-waveguide enhancement research was only started in the research part of this work, so that is included in section 7.2. The plasmonic enhancement work, however, did progress to an experimental stage, so is included here.

Light absorption enhancement through plasmonic effects has already been developed as a
means of improving solar cell efficiencies.\textsuperscript{124} In the case of simple absorption enhancement, plasmonic nanostructures allow resonant oscillating electric fields to be established when under illumination. These fields effectively increase the absorption cross section of the material in close proximity to the plasmonic structure. This situation would be perfect for both rare earth and OUC upconverters as it would allow more light to get into the upconversion process faster. A drawback of a plasmonic approach to enhancing light absorption directly for PV is that the resonances are naturally narrow band phenomena,\textsuperscript{125} and as such would only enhance a small fraction of solar radiation. For OUC, we can target the Q-band absorption peak of a sensitising porphyrin. This resonance has a bandwidth of a few 10s of nanometers, effectively mitigating the drawback of narrow band enhancement, providing that plasmonic absorption is well tuned to the Q-band absorption of the porphyrin.

Two samples of nanoparticles were fabricated through e-beam lithography by the plasmonics group at Imperial College London. These structures were designed by Dr. Vincenzo Giannini, and fabricated by Dr. Tyler Roschuk. In total, 9 arrays of square gold islands were designed with varying pitch widths (distance between each square). Of these, one was destroyed during the fabrication process. The absorption spectra of the successfully fabricated arrays, as measured with a Bruker FTIR, are shown in figure 6.11. Where it can be seen that the variation in pitch width altered the peak of absorption/scattering as was hoped, towards the peak absorption of PtTPBP (635 nm).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{absorption_spectra.png}
\caption{Absorption spectra of plasmonic structures designed to enhance absorption of PtTPBP. The noise at short wavelength is an unfortunate artefact of the FTIR reaching its limit of operation.}
\end{figure}

Unfortunately no effect, either enhancement or quenching of upconversion efficiency was found from these samples when they were examined using the iCCD equipment used elsewhere during the course of this project. This can be seen in figure 6.12. Here, we coated the substrate with a layer of immersion oil containing our active mixture and sandwiched it
between two glass slides, spaced apart by beads of 100 µm diameter to control for thickness. We then excited at 635 nm with a dye laser, use a short pass filter to cut out all phosphorescence and image using the iCCD without a spectrograph. A basic microscope arrangement allowed the plane of the film to be imaged. Equal areas of pixels comprising arrays 8 to 5, as numbered above, and one where no array was present, were then integrated over at each time step. These curves were the normalised to compensate for the lower transmission of light through the metal arrays. We hoped to see a difference in the relative rate of decay of as a faster rate (with a more significant second order term) would indicate a higher concentration of triplets, i.e. an enhanced OUC over a particular array. Every curve investigated showed the same decay characteristics, to within error on each fit.

![Figure 6.12: Decay of emitter triplet concentration over plasmonic arrays. Arrays 8 to 5, with spectra as numbered in figure 6.11, are shown. These decays are normalised to the peak emitter triplet concentration after laser excitation and share the same decay constant, showing no effect from the plasmonic substrate.](image)

The layers used to coat this substrate were simply too thick for any plasmonic effect to be distinguishable from the bulk film (plasmonic enhancements can only take effect within a few tens of nm of the structure). It was also found to be impossible to clean the surfaces of these arrays without destroying them. Figure 6.13 shows an SEM micrograph of one plasmonic array after cleaning was attempted, it is clear that the square edges have been rounded off, and that much of the array is still covered with material. Towards the bottom right of the image, a section where the metal has peeled of from the glass substrate can be seen.
Figure 6.13: SEM micrograph of one plasmonic array after coating, experiment and attempted cleaning.
Chapter 7

Conclusions and Outlook

This chapter first summarises the conclusions of the main body of work undertaken in the course of this research. It subsequently discusses where the future of this research may lie now that this project is complete.

Photograph of a thin film OUC (green excitation to blue emission from PtOEP and DPA), imaged through a short pass filter.
7.1 Conclusions

This thesis has presented and expanded upon the present state of understanding of organic upconversion, both in solutions and thin films. Chapter 1 reviewed the basic physics and principles of photovoltaic devices and explained how upconversion can be of benefit to enhance their efficiency. It also introduced some other potential applications for OUC technology. Chapter 2 went on to review the history of the field of OUC and provide some context for the new theory developed during the course of chapter 3. This third chapter detailed the development of the KRM, from the principles that lead to the development of the first steady-state model which inspired the KRM, through to validation of both the steady state and dynamic regimes of the KRM. This model was then further expanded to include the possibility of having two distinct emitter molecules, and the equations used to model this were justified. The MCM was also introduced in this chapter and was shown to behave in a physical manner. Chapter 4 went into detail on the experimental methods used and developed in and for the experimental chapters that followed. This included materials characterisation through optical spectroscopy, coating methods, and the construction and coding of the automated fluorescence robot used in chapter 6.

The main experimental conclusion from chapter 3 and chapter 5 (regarding the KRM) is that we have developed a model for molecular upconversion that is valid at all times following laser excitation, as well as under steady state illumination. We know this because when left to run for a significant period under continuous illumination, the KRM results fit those found in literature, and we directly observed an induced absorption from sensitiser triplets, followed by a delayed bleach in emitter ground states. This can even be seen to occur in a single figure (figure 5.10). Despite the complexity of this result, we showed that the KRM models each section of this curve very well. This result is also the first direct evidence of triplet energy transfer from a sensitiser to an emitter. These conclusions are further summarised in the work that we published in early 2014,\textsuperscript{65} a copy of this paper is included in Appendix A. Additionally, we showed that the introduction of a second emitter molecule to the standard OUC pairing does indeed increase the efficiency of upconversion, and that our model can be adapted to include this effect. We also provided a possible explanation for its origin.

Chapter 6 was mostly concerned with developing methods for thin film upconverters from a materials science perspective. In this chapter we showed that the addition of electrically and optically inert polymer increases the upconversion yield of a thin film OUC, and that this is due in large part to the breaking up of crystal grains. We demonstrated that there is an optimal blend of sensitiser:emitter:host polymer that produces the most efficient upconversion,
though there may also be a different blend which will produce more upconverted light due to the lower absorbance of more dilute films. Work in this chapter also showed that thin film OUC is not significantly affected by atmospheric oxygen. Though this resilience is dependent on the thickness of the film under investigation, and the viable lifetime of the film is reduced significantly when experimented upon in air. From this work we conclude that it is entirely possible to fabricate an efficient thin film upconverter based on triplet-triplet annihilation. Our model of particles in a box, the MCM, was used to support the conjecture that a well mixed system will not be limited by the difficulties imposed by lack of mass transport through molecular diffusion, and the final part of this chapter presented a design for a cheap and relatively easy way to calculate the degree of intermixing in an OUC thin film.

7.2 Outlook

Now that this work is complete, we will briefly discuss some interesting avenues for further investigation that we have discovered during this research. The work relating to the use of multiple emitters, presented in chapters 3 and 5, provides a good foundation for the further study of the multiple emitter effect and may well be a route to higher efficiency OUC in general. Unfortunately, there was not sufficient experimental time available in this project to fully investigate the physics behind the observed increase in emitted fluorescence. It would also be very interesting to see how the two emitter enhancement effect behaves in a thin film environment. It may be that the addition of another emitter molecule helps to break up crystallinity, reducing the optimal weight% of polymer for the blend.

The grating-waveguide structures fabricated from alternating layers of materials with different refractive indices that were mentioned in chapter 6 provide a very interesting route to enhancing upconversion efficiency in thin films by increasing local density of states in the required wavelength regime and reducing that of the phosphorescent channel. The motivator of this piece of work was Dr J. C. Goldschmidt from Fraunhofer ISE in Germany. Dr N.J. Ekins-Daukes and I collaborated with Dr Goldschmidt and his students Barbara Herter and Clarissa Hofmann to design structures which are analogous to those already employed by that group. Calculations made by that team show that a structure of material with alternating refractive indices can be designed to enhance the irradiance received within the structure. The transition enhancement factors for the relevant wavelengths (absorption, phosphorescence and fluorescence from both emitter and sensitiser) were also calculated.

From this information we were able to calculate the effect that this structure would have on an embedded upconverting system. We found that such a structure could provide an aver-
age enhancement of 1.2 times the unstructured phosphorescence, 1.6 times the energy loss through non radiative decay and a 4.5 times increase in upconverted fluorescence. These values depend heavily on irradiance, and fractional increase in upconverted fluorescence will be maximised when irradiance is low, as it will increase with the square of the optical enhancement factor until irradiance levels rise significantly.

A second approach has also been modelled. Using a vertical, interleaved, Bragg stack such as the one used in reference\textsuperscript{127} should allow absorption to be enhanced while minimising phosphorescence in the region of the upconverter. Simulations of one of these stacks show that this kind of enhancement is also an interesting route to higher efficiency upconverters. This work was taken on by Clarissa Hofmann, at the Fraunhofer ISE, and some preliminary results were presented at the SPIE Photonics Europe meeting in April 2014.\textsuperscript{128}

Combining the work in chapter 6 with the side projects mentioned in above is a promising route to high efficiency solid OUC devices, though much more investigation will be needed in both the irradiance enhancement and materials science fields to exploit this combination.

Finally, the micro-absorption imaging technique developed in chapter 6 is an exciting development and its design could be improved upon to provide really detailed information on the degree of intermixing in these thin films in a cheap and fast manner.
Bibliography


Appendix A

Kinetic insight into bimolecular upconversion: experiment and simulation

Introduction

Upconversion is a process in which two low energy photons are absorbed to allow one higher energy photon to be emitted. Two distinct sequential absorption processes requiring relatively low excitation intensity, a few 10 s of mW, have been demonstrated in rare-earth glasses\textsuperscript{12} and molecular solutions.\textsuperscript{13} One demonstrated application for upconversion is enhancement of solar cell efficiency. In high band-gap solar cells, the single largest energy loss is the lack or incomplete absorption of photons with energy below the cells’ band gap.\textsuperscript{4} Upconversion addresses this loss, and has the potential to raise the fundamental power conversion efficiency limit of a single junction solar cell from 33% to 47.6%.\textsuperscript{7} Enhanced power conversion efficiency has been experimentally realised through both rare-earth\textsuperscript{4} and molecular\textsuperscript{9} upconversion, where low energy photons that reach the rear of a solar cell are re-radiated at a higher energy, sufficient for the solar cell to absorb.

The molecular upconversion energy step ladder is shown in Fig. 1. This method of upconverting light is particularly well suited for upconversion of the visible and near-IR wavelengths ($\gamma_1 < 700$ nm). This is because sensitising dyes exhibit strong absorption in this region, providing a good way to get energy into the system. Metallated porphyrin molecules are often employed in this role. The excitation crosses rapidly into the triplet state ($T_1$), typically within a few picoseconds and with an inter-system crossing (ISC) efficiency close to unity. Providing that the triplet energy level of a paired fluorescent, emitting, molecule is close to that of the sensitisier’s, and that there is an excess of emitter in the mixture, the sensitisier triplet is rapidly transferred to a triplet state in an emitter molecule via Dexter energy transfer,\textsuperscript{10} also known as triplet energy transfer (TET). When two triplet-excited emitter molecules interact, they can undergo a triplet–triplet annihilation (TTA) process whereby the excited singlet level of one emitter is populated and the other emitter relaxes to its ground state. This triplet–triplet annihilation process has been found to be highly efficient and while the TTA process does obey spin-selection rules, the efficiency of that process is not limited by those rules.\textsuperscript{11}

The steady state and kinetic properties of many of these emitter/sensitisier pairs have been thoroughly investigated in previous articles, for example Murakami \textit{et al.}\textsuperscript{12} recently used delayed fluorescence measurements to examine the kinetics of the final output of an upconverting system and Deng \textit{et al.}\textsuperscript{13} analyse transient absorption measurements in the same way.

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**Fig. 1** Triplet–triplet annihilation upconversion schematic. Each sensitisier molecule is excited by a photon, $\gamma_1$, the excitation undergoes fast intersystem crossing (ISC) to transition into a triplet state. Triplet energy transfer (TET) the occurs between each sensitisier and an emitter. Two triplet-excited emitter molecules interact and their excitations undergo triplet–triplet annihilation (TTA). This relaxes one emitter back to its ground state and excites the other to it’s $S_1$ state, which can then fluoresce, $\gamma_2$. 

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Further information on fluorescent emitters and frequently used sensitisers can be found in (ref. 14–18).

## 2 Model

The rate model for photochemical upconversion, proposed by Auckett et al.,\textsuperscript{14} describes the dynamics of the system in terms of the rate of change of concentration of sensitiser triplets and emitter triplets. It is based on empirically determined rates of energy transfer throughout the upconversion scheme. That paper is limited to describing the steady-state conditions of an upconverting system. With our approach we are able to consider the build-up and stabilisation times as well, demonstrated here by using our equations to model a pulsed experiment for the first time.

For efficient upconversion, the rate constants, \( k_i \) associated with the Dexter energy transfer step \( (k_{\text{Dex}}) \) and the final annihilation step \( (k_{\text{AT}}) \) must be much faster than the associated loss mechanisms. Namely phosphorescence, \( k_p \), and non-radiative decay, \( k_{\text{NR}} \). In the model presented in this paper the two governing equations have been adapted from Auckett’s work. These modified equations are presented below as eqn (1) and (2), where: \([\cdot]\) denotes concentration; \(X\) a sensitiser species; \(Y\) an emitter species; \(G\) and \(T\) ground and triplet states respectively; \( k_b \) the flux of photons capable of exciting the sensitiser; \( k_p \) the rate of phosphorescence; \( k_{\text{NR}} \) the rate of non-radiative decay; \( k_{\text{ET}} \) the rate of triplet energy transfer and \( k_{\text{AT}} \) the rate of triplet annihilation.

\[
\frac{d[X]}{dt} = k_b[X_G] - k_p[X_T] - k_{\text{ET}}[X_T][Y_G] - k_{\text{AT}}[X_T][Y_T]
\]

\[
\frac{d[Y]}{dt} = k_{\text{ET}}[X_T][Y_G] - k_{\text{NR}}[Y_T] - k_{\text{AT}}[X_T][Y_T]
\]

We make two changes to the equations reported in (ref. 19). We split the original \( k_{\text{AT}} \) terms into \( k_{\text{AT}}^{\text{X}} \) and \( k_{\text{AT}}^{\text{Y}} \) to allow for the potential differences in annihilation rates between two emitter molecules, two sensitiser molecules and that between a sensitiser and an emitter. We also remove a factor of two from the homoaannihilation of sensitiser triplets term to make it \( k_{\text{AT}}^{\text{X}}[X_T]^2 \). This reflects new understanding on recombination dynamics of these triplets: an unsuccessful annihilation event between two sensitiser molecules that does not necessarily depopulate both triplet levels. One sensitiser will be excited to a singlet state and undergo ISC once more, leaving one triplet state sensitiser and one ground state sensitiser.\textsuperscript{11} In our experimental section we find that these changes make very little difference to the output of our model in this experimental regime. These changes only become significant at impractically high irradiance levels, and impossibly high concentrations. We make them only to provide the most correct description of the molecular dynamics possible with our current understanding.

Previous studies have used experimental techniques to calculate these rate constants, for example using steady-state and transient techniques such as delayed fluorescence or phosphorescence measurements.\textsuperscript{11} In these experiments, the triplet concentrations must be back-calculated based on the framework of eqn (1) and (2), whereas in this paper we use transient absorption spectroscopy to measure the triplet concentrations directly, as presented in the following sections.

The time-dependant rate model that was developed for this work solves the rate eqn (1) and (2) numerically. This is done by using the ODE45 library in Matlab, which employs a Runge-Kutta order 4 method\textsuperscript{20} to solve eqn (1) and (2) at dynamically varying discrete time intervals (1–10 ns). This provides a time-dependent description of the population of triplet states on emitter and sensitiser molecules within the upconversion system. By choosing a constant \( k_b \) and taking the values of \([X_T]\) and \([Y_T]\) at long times, i.e. once \( \frac{d[X_T]}{dt} = \frac{d[Y_T]}{dt} = 0 \), our model reproduces the steady-state results presented in the original model.\textsuperscript{19} If we then include experimentally determined rate constants of a particular molecular system in the calculations, it is possible to predict or replicate steady state experimental results. Setting \( k_b = 0 \) and starting the simulation with a non-zero \([X_T]\) to simulate the effect of an excitation pulse allows even pulsed laser experiments to be modelled. The value of \([X_T]\) is calculated by determining the number of molecules that would be excited by a laser pulse, we assume that ISC efficiency is 100% so this number is equal to the initial value of \([X_T]\).

## 3 Experimental details

By choosing the active upconverting molecules under investigation to be the same as those in the above study,\textsuperscript{11} it is possible to validate our model in relation to previously published data. Palladium(ii) tetrakisquinoxalinoporphyrin (PQ4Pd) is the absorbing (sensitising) species and rubrene the emitter species. The structures of these molecules and the relevant optical transitions are shown in Fig. 2.

The PQ4Pd was synthesised at the University of Sydney.\textsuperscript{21} The rubrene was purchased from Sigma-Aldrich, and was used without further purification. Following dissolution in toluene to the required concentration, each solution was purged of oxygen by being left open in a nitrogen glovebox overnight. The reliability of this passive process is demonstrated here by experimentally determining the value of \( k_{\text{ET}} \) for this system and comparing it to published data.\textsuperscript{14} We derive \( k_{\text{ET}} \) through transient absorption spectroscopy. This is achieved by varying the concentration of rubrene in a PQ4Pd/rubrene sample and observing the recovery time of the ground state of the porphyrin after laser excitation. The Stern–Volmer eqn (3) is then used to extract the rate constant, as shown in Fig. 3, where we find that there is a 2% difference between our result and that which has been published previously.

\[
\frac{1}{\tau} = k_{\text{ET}}[\text{rubrene}] + \frac{1}{\tau_0}
\]
Transient Absorption Spectroscopy (TAS) is a pump-probe technique that allows for direct observation of excited state yields and dynamics, making it possible to understand the energy flow through a molecular upconversion system. In our experiments pump pulses were produced by a Photon Technology International GL-301 dye laser, pumped with a Photon Technology International GL-3300 Nitrogen laser source. These pulses had a pulse width of 2 ns at a repetition rate of 4 Hz. The output from a Xe lamp was passed through a monochromator to provide the probe beam. Samples were sealed in a 1 mm quartz cuvette and placed at the conjunction of the probe beam and pump pulses.

4 Results

A plot of the reduction in population of emitter triplets per laser illumination from a selection of pulse energies is given in Cheng et al. (2010).\textsuperscript{11} In this paper, the authors provide the equations used to fit their data. Our rate model lends itself to the straightforward reproduction of this experiment. So we first validate our model by comparing it’s result to that which has been published, as shown in Fig. 4. This figure clearly has an excellent fit between the two curves, which diverge slightly only at relatively long time scales.

Pumping PQ4Pd at its ground state absorption peak ($\lambda = 660$ nm) forms a long lived triplet state on that species. This excited state also has a characteristic absorption spectrum, shown in Fig. 5. Here it can be seen that, along with the expected bleach of the PQ4Pd ground state, there is a broad absorption feature induced between 530 and 600 nm, which we attribute to optical excitation up the triplet channel of the molecule.
porphyrin. This PQ4Pd specific absorption feature overlaps the ground state absorption of the rubrene emitter, also shown in Fig. 5. The overlap between the excited sensitiser's induced absorbance and the ground state emitters absorbance spectrum has important implications when considering the TAS spectra of these species when mixed.

From Fig. 3 we see that sensitiser triplet lifetime decreases as higher concentrations of emitter molecules are incorporated into the system. This is because a triplet quenching pathway is introduced by the emitter. The decrease in lifetime does not, in itself, provide direct evidence of TET. To provide that we must probe at the ground state absorption of the rubrene itself, while the pump remains at 660 nm. Fig. 6 shows the result of this experiment: a mixture of [0.1 mM] PQ4Pd and [2 mM] rubrene in toluene was pumped at 660 nm, where rubrene does not absorb, and the probe wavelength was chosen as 535 nm, corresponding to the \( \lambda_{\text{max}} \) of ground state rubrene.

We attribute the initial induced absorption seen in Fig. 6 to the previously observed optical triplet excitation of the sensitiser, shown in Fig. 5. The decay of this induced absorption proceeds at a rate comparable to the regeneration of the sensitiser ground state, as indicated in Fig. 3. The delayed bleach in the rubrene ground state that follows this induced absorption then directly shows the process of triplet energy transfer from sensitiser to emitter molecules.

The solid line in Fig. 6 shows the result of running our model with known experimental parameters and the published rate constants for this system as inputs.\(^9\) The value of \( \Delta \text{OD} \) was calculated from eqn (4): where \( \text{TS}_{\text{abs}} \) is the contribution of one triplet excited sensitiser molecule to the induced absorption and \( \text{GE}_{\text{abs}} \) is the contribution of one molecule to the ground state absorbance of our emitter, or its molar extinction coefficient. These values are then normalised. The rise time of the induced absorbance is taken to be instantaneous, as the ISC process is complete within a few 10 s of ps. The rate of the subsequent decay is primarily determined by two terms in eqn (1): \( k_{\text{f}}[X_T] \) and \( k_{\text{TET}}[X_T][Y_{T0}] \). As \([X_T]\) is always small, the \( k_{\text{TET}}[X_T]^2 \) term has little impact. After the delayed bleach builds, it then decays at some rate, determined by terms in eqn (2): at high \([Y_{T0}]\), the \( 2k_{\text{ISC}}[Y_{T0}]^2 \) term is dominant, and at longer times the \( k_{\text{ISC}}[Y_T] \) term takes over.

\[
\Delta \text{OD} = [X_T] \times \text{TS}_{\text{abs}} - [Y_T] \times \text{GE}_{\text{abs}} \tag{4}
\]

It is clear that at each stage of the curve our rate model fits the experimental data well, showing that each regime is described by the model in a physically consistent way. The principal source of uncertainty in this calculation is the value of \( \text{GE}_{\text{abs}} \). The probe beam produces much lower intensity at shorter wavelengths, from which \( \text{GE}_{\text{abs}} \) is derived. A more accurate measurement of \( \text{GE}_{\text{abs}} \) would not alter the dynamics of the decay curve, it would simply scale the normalised \( \Delta \text{OD} \) axis.

5 Conclusions

We have modified established rate equations and solved them to produce a time-dependent rate model for a bimolecular upconversion system. Our model reproduces experimental data from both steady state modelling results,\(^{11} \) and delayed fluorescence experiments.\(^3\) We have also used Transient Absorption Spectroscopy (TAS) to directly observe triplet energy transfer between sensitiser (PQ4Pd) and emitter (rubrene) molecules in this system. We find that an initial induced absorption due to sensitiser triplets decays into the characteristic delayed bleach on the emitter ground state on the expected time scale, providing direct evidence of triplet energy transfer between the molecules. Additionally, our rate model produces a physically consistent reproduction of this TAS result, confirming that these rate equations are sufficient to describe the dynamics of molecular upconversion in solution.

Acknowledgements

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Appendix B

Singlet Oxygen Mediated
Photochemical Upconversion of NIR Light

Singlet Oxygen Mediated Photochemical Upconversion of NIR Light


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ABSTRACT: We report photochemical upconversion (UC) of near-infrared (NIR) light to the visible spectrum mediated by molecular oxygen. Thereby, we address two of the main challenges in the field of photochemical UC, (i) UC of photons above 800 nm and (ii) utilization of molecular oxygen, which is necessarily excluded in conventional photochemical UC systems. In the employed system, singlet oxygen is generated upon photoexcitation of the sensitizer molecules and then acts as an energy transmitter for the UC process. The excitation energy of two singlet oxygen molecules is subsequently harvested by emitter molecules, which in turn gives rise to delayed fluorescence of the emitter species. We discuss strategies for improvement of the currently achieved efficiencies of ≤0.01% to produce excited singlet states in the emitter molecules.

SECTION: Kinetics, Spectroscopy

Singlet oxygen is a common reactive oxygen species that is formed as a byproduct of many photosensitized processes. Due to its high reactivity, singlet oxygen irreversibly damages a range of unsaturated organic compounds. The transition of dioxygen is typically induced by quenching of a triplet excited state of an organic molecule. Biological systems have evolved ways of handling singlet oxygen, such as sequestration by carotenoids that protect the sensitive pigments in the photosynthetic reaction center of plants. However, artificial organic systems, for example, light-harvesting applications such as organic photovoltaics and dye-sensitized photochemical upconversion (UC), are currently not as sophisticated as their biological counterparts and are more susceptible to damage by singlet oxygen.

Photochemical UC is a rapidly expanding field because of its envisaged and already-implemented applications in light-harvesting and light-emitting devices due to its incoherent nature. Two of the major challenges in the field are (i) to overcome the rapid quenching of the employed triplet states by molecular oxygen, which drastically diminishes the UC efficiency, and (ii) UC of near-infrared (NIR) light to the visible spectrum, which could be applied in medicine and biology because tissues are transparent for NIR radiation. Herein, we report singlet oxygen mediated upconversion (SOMUC) of NIR light to the visible spectrum, thereby addressing the aforementioned issues. SOMUC employs singlet oxygen as an energy transmitter, thus relying on the presence of molecular oxygen. Singlet oxygen is generated upon photoexcitation of a sensitizer species with an absorption maximum at 830 nm, well outside of the visible region. While the process is currently unoptimized, we demonstrate its proof-of-principle and suggest several possibilities for significant improvements in UC efficiency in the future.

As depicted in Figure 1, after the initial photosensitization step to generate singlet oxygen, the excitation energy of singlet oxygen is transferred to emitter (E) molecules in the ground state. SOMUC can now proceed in two different ways. In the first pathway (Figure 1a), two triplet excited emitter molecules can undergo triplet-triplet annihilation (TTA), resulting in a singlet excited emitter molecule and upconverted fluorescence. Second, it is known that singlet oxygen can induce luminescence in some molecules through singlet oxygen sensitized delayed fluorescence (SOSDF), a phenomenon first documented by Kurtz and later explained by Ogryzlo and Pearson as well as Abbott et al. In this case, one emitter molecule accumulates the electronic energy of two equivalents of singlet oxygen in a stepwise fashion, as displayed in Figure 1b. Because this process requires a distinctive structure of the molecular energy levels, a relatively limited number of emitter molecules are known to undergo SOSDF. Note that both mechanisms give rise to a delayed fluorescence signal. In contrast, conventional photochemical UC proceeds by direct triplet energy transfer (TET) from the sensitizer to the emitter species.

It should be noted that oxygen in its triplet ground state facilitates the mixing between singlet and triplet states of organic chromophores due to an exchange interaction between the paramagnetic and the organic molecule. By lending singlet character to triplet states, the probability of spin-forbidden transitions is enhanced, increasing the rates of phosphorescence and intersystem crossing. Furthermore, when such a coupling manifests in two different molecules, triplet energy transfer is enhanced due to the gain of Förster character from the...
two respective singlet states, effectively increasing the transfer radius. Indeed, Monguzzi et al. have recently pointed out that even small amounts of oxygen can enhance TET rates by orders of magnitude.\(^{13}\)

To experimentally establish SOMUC, we have employed the cyanine dye IR820 as the sensitizer material in combination with violanthrone-79 (V79) as the emitter species. Structures and spectra of the compounds are displayed in Figure 2. IR820 is a chlorinated heptamethine indocyanine dye possessing a singlet oxygen quantum yield of 7.7% in ethanol considered for photodynamic therapy,\(^{21,22}\) despite the low triplet quantum yield (~10\(^{-5}\)) reported for similar indocyanine dyes in oxygen-free solutions.\(^{23}\) The triplet yield was found to increase, however, in air-saturated solutions,\(^{23}\) an effect ascribed to the aforementioned interaction with paramagnetic ground-state oxygen. Indeed, IR820 was found to yield no transient absorption signal ascribable to the triplet state under deoxygenated conditions.\(^{23}\)

V79 is a chemically modified vat dye. Violanthrones like V79 are known to fluoresce when exposed to singlet oxygen, according to the SOSDF process.\(^{17}\) Differences in the polarity of these two compounds limited the choice of solvent for performing UC measurements. N,N-Dimethylformamide (DMF) was selected because both compounds displayed moderate to good solubility without significant shifting of their steady-state absorption and emission spectra. The overlap of the V79 fluorescence with the absorption band of IR820, however, leads to Förster-type resonance energy transfer (FRET) from V79 to IR820 that quenches a part of the V79 emission (vide infra).

Sensitizer/emitter mixtures were prepared under normal atmospheric conditions, and a weak delayed fluorescence signal from both V79 and IR820 was observed upon excitation with 830 nm laser light. However, after rigorous degassing of the sample by several freeze--pump--thaw cycles, no delayed fluorescence signal could be recorded. In contrast, after bubbling oxygen through the solution for several minutes, an increased delayed fluorescence signal was observed that was about a factor of 10 stronger than the untreated sample (Figure 3a). Because IR820 can generate singlet oxygen while V79 quenches the energy of (\(^{1}\Delta_g\))O\(_2\), the energy of the first excited triplet state
of IR820 is above the triplet state of V79. Despite this fact, the experimental results indicate that TET from IR820 to V79 is highly inefficient, presumably due to the low intersystem crossing (ISC) rate of IR820 as well as a small transmission coefficient for both compounds.

The increase of signal depending on the oxygen concentration was investigated in a series of measurements that recorded the delayed fluorescence every 2 s while the degassed sample was continuously bubbled through with a light stream of oxygen gas, as displayed in Figure 3b. After \(~\sim\) 150 s, the oxygen stream was slightly increased, resulting in a steeper increase of fluorescence signal. Both parts of the rise are single exponentials with respective rise times. Furthermore, the delayed fluorescence intensities from IR820 and V79 showed the same dependence on the oxygen concentration, indicating that the delayed IR820 fluorescence is indeed due to FRET from V79. Control experiments with pristine solutions of V79 in thoroughly oxygenated DMF showed no delayed fluorescence signal, excluding two-photon absorption induced by the employed laser pulses or direct excitation of oxygen as the origin of the delayed emission. Moreover, thoroughly oxygenated, pristine IR820 solutions were checked for emission at 634 and 703 nm, with the oxygen "dimol" bands resulting from pairs of singlet oxygen, which in principle could sensitize the observed fluorescence. However, Gorman et al. as well as Murphy et al. have shown that in their respective systems, sensitization from dimol oxygen is highly unlikely. Indeed, no dimol emission was found from the IR820 solutions, confirming that dimol sensitization is negligible in our system. However, the latter solutions of oxygenated IR820 showed weak delayed fluorescence with decay times on the order of 100 ns, which was not observed in degassed solutions; hence, it does not originate from residual natural fluorescence. We ascribe this to E-type delayed fluorescence, where the ISC processes are enhanced by the dissolved oxygen, despite its possible quenching of the triplet state.

We have measured the kinetics of the V79 delayed fluorescence signal, which are displayed in Figure 4 for three different mixtures of V79 and IR820 in oxygenated DMF. For all traces, a rise time of the signal is visible, verifying the sensitized nature of the emission. The decays are monoexponential, indicating that first-order processes are dominating. They match the respective decay kinetics of the delayed fluorescence of the IR820 band (gray symbols), further confirming FRET as an origin for this emission feature. However, the rise of the V79 fluorescence is not reproduced by the IR820 kinetics. A deconvolution reveals time constants for the initial decay on the order of 100 ns; thus, we ascribe this feature to the aforementioned E-type delayed fluorescence.

Despite being monoexponential, the tails of the kinetics are dependent on the respective concentrations, indicating that more than one UC mechanism is involved. A high concentration (\(\sim 10^{-3}\)) of emitter combined with a high concentration of IR820 yielded a decay constant of 0.9 µs (Figure 4a). While a decrease of the sensitizer concentration by a factor of 5 lead to similar kinetics, as shown in Figure 4b, the rise and decay times were prolonged when the V79 concentration was reduced to 1/5 (Figure 4c). Further reduction of the relative V79 concentration led to decay constants of up to \(~\sim\) 2.5 µs.

We can rationalize the differences in the kinetics by the relative contribution of the two UC processes depicted in Figure 1 to the overall delayed fluorescence signal. For high emitter concentrations, relative to the overall exciton population, singlet oxygen sensitized TTA (Figure 1a) is likely to dominate, whereas SOSDF (Figure 1b) is more likely at lower concentrations of the emitter species. In the former case, the observed decay time of the delayed fluorescence is mainly due to TTA, giving rise to a decay time of half of the \(T_1\) lifetime of the emitter. Indeed, experiments on pristine V79 in oxygenated DMF excited at 600 nm lead to a low delayed fluorescence signal due to (inefficient) ISC and subsequent TTA. Tail fits resulted in a decay constant of 0.9 µs, corresponding to a triplet lifetime of 1.8 µs. For lower relative V79 concentrations, the decay time should be governed by both the emitter \(T_1\) lifetime and the singlet oxygen lifetime, where the latter can vary between 7 and 25 µs, most probably dependent on the purity of the solvent.

As previously established, we obtained the efficiencies to generate singlet excited states in the emitter molecules, \(\Phi\), by comparison of the UC signal per input photon to that of the prompt fluorescence triggered by direct excitation of V79 with 630 nm light under otherwise identical experimental conditions. The delayed fluorescence signal per two input photons was the reference point for \(\Phi \sim 100\%\) because two low-energy photons can generate one upconverted photon at most. While the monoexponential decay behavior already intimates a low value for \(\Phi\), it was indeed found to be \(\Phi \leq 0.01\%\), which is ascribed to the low singlet oxygen yield of IR820 (<10%) as well as the relatively short lifetimes of triplet excited V79 and singlet oxygen (vide infra).

Indocyanine dyes are known to undergo photodegradation due to reaction with singlet oxygen. The photodegradation of the involved compounds was investigated by measurement of...
the absorbance of the compounds after irradiation with a xenon lamp emitting a white light beam. Three different samples were investigated, that is, solutions of the pristine compounds and a mixture containing the same concentrations as the pristine solutions. The samples were prepared under normal atmospheric conditions. The absorbance bands of the respective compounds were integrated and normalized, as displayed in Figure 5. After 50 min of irradiation time, the absorbance of the pristine V79 solution was reduced by less than 1%, indicating the high photostability of V79. In contrast, the absorbance of the IR820 solution decreased during the same irradiation time to ∼2.5% of the initial value. The initially green solution changed to a light gray, and a broad background was observed in the absorption spectrum, which is ascribed to the degradation products. However, in the mixture of V79 and IR820, the degradation of the latter was considerably reduced. The half-life of IR820 in the mixture with V79, considering a monoeponential behavior of the data of Figure 5, was increased by a factor of nearly 3. This is ascribed to the quenching of singlet oxygen by V79.

To further verify the observations that have been discussed so far, another set of experiments were performed using a palladium(II)-trisquinoxalinoporphyrin32 as the sensitizer and V79 as the emitter. The sensitizer has a T1 energy level at 830 nm, and its phosphorescence is efficiently quenched by oxygen. We monitored the delayed fluorescence of V79 upon selective excitation of the Soret band of the porphyrin at 480 nm for degassed and oxygenated DMF solutions of the two compounds. The delayed emission of the degassed samples is mostly dominated by the phosphorescence band of the porphyrin but exhibited a small amount of delayed V79 fluorescence that decays with the same kinetics as the phosphorless porphyrin. In contrast, for the oxygenated sample, the porphyrin phosphorescence vanished, and the V79 delayed fluorescence increased. It was found that the values of Φ of the samples were enhanced in the presence of oxygen by a factor of ∼5.

In conclusion, we have shown that the presence of molecular oxygen can be beneficial for photochemical UC if the sensitizer and emitter molecules are chosen in such a way that the energy of the ΔΣ=1Δt transition of dioxygen lies below the triplet—singlet gap of the sensitizer but above that of the emitter. The UC mechanism relies on singlet oxygen as a transmitter of the excitation energy from IR820 to V79. This leads to two different ways of combining two portions of energy, TTA in the emitter species and sequential energy transfer of singlet oxygen to one emitter molecule. Accordingly, the kinetics of the delayed fluorescence exhibits different behavior dependent on the relative emitter concentration. The mechanism utilizes the fast diffusion of oxygen in solution.33 Moreover, the dissolved ground-state oxygen adds allowed character to the spin-forbidden transitions of the involved molecules, thereby accelerating the IR820 ISC significantly and possibly inducing triplet energy transfer between IR820 and V79. The latter appears to be completely suppressed in degassed solutions.

Importantly, the employed IR820/V79 system facilitates the UC of NIR light (830 nm) into the visible region. As shown above, the emitter species V79 furthermore protects the singlet oxygen sensitizer from photodegradation, which is ascribed to the quenching of singlet oxygen. Despite the low generation efficiencies for emitter singlet excited states, Φ ≤ 0.01%, of the current dye system, several aspects can be significantly improved. The comparably low singlet oxygen yield of the sensitizer IR820 can be overcome by NIR-absorbing dyes such as metal bacteriochlorins,34 cadmium(II) benzotexaphyrin,35 and meso-β doubly fused diporphyrins,36 which are known to have high singlet oxygen quantum yields approaching unity. From the mechanisms for UC, the increase in singlet oxygen concentration is expected to affect Φ quadratically. Furthermore, these compounds are reported to have good solubility in nonpolar organic solvents such as chloroform, in which the lifetime of singlet oxygen is on the order of 250 μs,37 while the employed solvent DMF is known to quench singlet oxygen to a small amount by inherent impurities.38 Moreover, the triplet lifetime of the emitter species has an important influence on Φ.3 From a simple rate model, taking into account the mechanisms depicted in Figure 1 and estimates for the involved rate constants, we obtain an increase in Φ by more than a factor of 100 for a 10-fold increase in the singlet oxygen generation yield as well as the triplet lifetimes of oxygen and the emitter species. That is, optimizing these parameters will eventually lead to values of Φ and hence UC efficiencies in the several percent range for SOMUC.

**EXPERIMENTAL SECTION**

V79 and IR820 (80% dye content) were purchased from Sigma-Aldrich. V79 was found to be sufficiently pure for upconversion experiments, as assessed by thin-layer chromatography and 1H NMR spectroscopy. IR820 (∼1 g) was purified by Soxhlet extraction into dichloromethane to remove water-soluble impurities and then by silica gel chromatography eluting with methanol/chloroform (3:7, v/v). The major dark green fraction was collected, the solvents were removed, and the brown residue was recrystallized from methanol/diethyl ether to yield the purified dye as a light brown powder. Spectroscopic-grade DMF was used in the photophysical experiments and passed through a column of neutral alumina (Brockmann grade I) prior to use. Degasied samples were prepared through three freeze—pump—thaw cycles applying vacuum (10−3 mbar). Oxygen saturation was achieved by continuously bubbling a stream of oxygen gas through the solutions. The sample cuvettes were illuminated by the tunable output of a TOPAS OPA laser pumped by a Clark MXR CPA 2210 fs laser operating at 1 kHz. The ∼1 mm2 fluorescent spot on the front face of the
cuvette was entirely imaged with a spectrograph fitted with an iCCD detector (Acton/Princeton). The delayed fluorescence was recorded for 50 μs from 100 ns after the laser pulse, capturing the delayed signal, ignoring any prompt fluorescence.

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