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Material Characterization of Luminescent Down-Shifting Layers for Solar Cells Application

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Abstract

High energy photons in the UV region are not efficiently used in solar cells and limit the overall efficiency of the cell. Luminescent Down-Shifting (LDS) layers can be used to convert the high energy photons to a lower energy before it reaches the cell, which is more efficiently absorbed. In this study, an investigation of the optics of polymer thin-films LDS layer when comprising of mixed organic dyes, against single dye thin-films was investigated. The effect of creating a layer comprising of an equal ratio of BASF Lumogen Yellow 083, Lumogen Orange 240, and Lumogen Violet 570 in a polymethyl methacrylate (PMMA) polymer was investigated and compared to the experimental results from each single dye. This aided in determining whether using multiple organic dyes in a single film was beneficial for use as an LDS material. The concentration of each individual dye was then optimised with the EQE determined and then tested outdoors over three months. There was a large degradation of the thin films in the short range of time, so due to the limitations of Lumogen dyes, focus moved to quantum dots (QDs). The absorption, emission, and quantum yield of a range of QDs was determined for introduction into the Lumogen layers.

Declaration

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Abbreviation

A.U.	Arbitrary unit
a-Si	Amorphous silicon
CdSe	Cadmium-Selenide
CdTe	Cadmium-Telluride
CIGS	Copper-Indium-Gallium-Selenide
c-Si	Crystalline silicon
CSQD	Core-shell quantum dot
DSSC	Dye sensitized solar cells
EQE	External quantum efficiency
EVA	Ethylene vinyl acetate
GaAs	Gallium arsenide
LDS	Luminescent down-shifting
LQY	Luminescent quantum yield
LSC	Luminescent solar concentrator
mc-Si	Multicrystalline silicon
PLMA	Poly(lauryl methacrylate)
PMMA	Poly(methyl methacrylate)
PV	Photovoltaic
PVB	Polyvinyl butyral
QD	Quantum dot
Si	Silicon
SPR	Surface plasmon resonance
TIR	Total internal reflection
UV	Ultraviolet
VIS	Visible spectra
ZnS	Zinc sulphide

Chapter 1 - Statement of Motivation

1.1. Motivation and Aims

A strain is being caused on traditional fuel sources such as coal, natural gas, and oil. These fuel sources are creating pollution which is placing the world's ecosystem in danger and to the point of extinction. It is vital that an energy source that is sustainable and renewable is developed. Solar cells are photovoltaic (PV) devices which harness solar energy and convert it to electrical energy using the photovoltaic effect. This technology has grown rapidly since the 1950s due to the strain created from an ever-growing population. PV cells which unfortunately suffer large energy losses due to numerous factors. Many of these losses can be attributed to spectral losses in the conversion process. This is where the high energy photons are not efficiently absorbed by the solar cell. Therefore, the maximum efficiency is not being reached. Luminescent Down-Shifting (LDS) is a process which converts high energy photons to a lower energy. This can be achieved using a planar sheet on top of the existing solar cell. It is an inexpensive process as the planar sheets can be fitted to existing solar cells with ease. The photons which have been shifted are absorbed in the photoconductive layer. This creates more electron-hole pairs and increases the external quantum efficiency. The main overall objective of this study was to increase the efficiency of a silicon (Si) solar cell. This study aims to do this by investigating a range of materials for inclusion in a thin-film which will act as a luminescent down-shifting layer. With the introduction of this thin-film onto a solar cell, the efficiency of a solar cell should be improved.

The first aim was to determine an appropriate host material and successfully optimise the spin-coating method to form a thin-film. The objectives in this aim included identifying a suitable polymer and then refining the spin-coating method until it repeatably forms a uniform thin-film, which can be easily removed from a glass substrate to allow for characterisation tests. With this first aim completed, the attention turns to introducing Lumogen dyes (BASF) into the thin-film. Three dyes were looked at and directly introduced into the host material. The concentrations of

the three dyes were varied until an optimum concentration could be determined for each. This was determined from examining the integrated absorption and emission curves at each concentration tested. Additionally, a layer was produced which contained an equal ratio of the three dyes, referred to as the 'mixed' layer. The absorbance and emission of this 'mixed' layer was then compared to layers which contained each dye individually. The combinatory effect on the absorption and emission of the 'mixed' layer was investigated and explained.

The next aim was to test the stability of the optimised concentrations, as organic dyes have been found to suffer from poor photostability. Lumogen dyes are a commercially available dye so a higher photostability would be anticipated. The layers were placed outdoors and exposed to sunny, snowy, and various other weather conditions for three months. This is the longest outdoor photostability test the Lumogen dyes have been exposed to in this research. The change in the absorption and emission of the layers must be regularly measured and integrated to determine the reduction in the absorbance and emission ranges. The optimised layers were also placed on Si cells and their EQE determined. With the results of this, the cells were also compared to the EQE of other cells which may be more suitable.

From the results gathered for the Lumogen dyes, the next aim was to look at quantum dots as a method to improve the performance of the dyes. A range of eight quantum dots were sourced, half being Hydrophobic CdSe/ZnS Quantum Dots kit and the other half being hydrophobic Zn-Cu-In-S/ZnS Quantum Dots Kit. These QDs had their absorbance and emission determined to compare to the Lumogen dyes to see which QD was best suited for which dye. To narrow in on an optimum QD, the quantum yield in solution of each QD was determined.

1.2. Organisation of the Thesis

This report consists of five chapters. Chapter 2 contains the literature review which covers Ireland's energy sector and how it has changed in recent years which is followed by the theory relevant to the project. The theory covers the progression of photovoltaic technology and the losses present in different cells that lead to the development of LDS layers. The process of luminescent down-shifting is described with the losses and recent developments discussed.

Chapter 3 outlines the various experimental techniques used in this study. A spin-coater, which is used to form the thin-films for this study, is discussed in full detail. For characterisation, the spectroscopic characterisation is described for two different luminescent materials which were tested. For further testing of these luminescent materials, the techniques used for photostability tests, the external quantum yield and the quantum yield were also discussed.

Chapter 4 describes the results obtained from the experimental techniques used. A detailed description of the optimisation process for the host material and thin-films is included. The various characterisations of the organic dyes, which include the absorption and emission ranges of the optimised thin-films, their outdoor performance over a range of three months, as well as the external quantum efficiency of these layers on a Si cell. As well as this, a comparison of single dye layers to a layer containing multiple dyes and how this effects the absorbance and emission range is described. The absorbance and emission of a range of quantum dots, as well as their quantum yield in solution is also provided.

Finally, chapter 5 contains the discussions and conclusions which were obtained from this study in relation to the aims initially described in section 1.1.

Chapter 2 - Introduction and Background

2.1. Introduction

In recent history, the world's population has seen rapid growth, reaching over 7 billion people in 2011 [1,2]. This is an increase of over 5 billion people in just 100 years. The UN Medium Fertility Variant predicts the World population to reach 11.2 billion by the year 2100. This population increase has been a large driving force of global change particularly in fuel consumption. Fossil fuels have a large part to play in human history, which include coal, oil and natural gas and have taken millions of years to form. During the industrial revolution, fossil fuels became a great source of power as they were cheap and efficient. Large scale industrial activity using fossil fuels soon became the norm and has largely been that way for nearly two centuries [3].

The use of fossil fuels is now known for the release of carbon dioxide (CO_2) into the atmosphere. CO_2 has caused an overall increase to the average temperature of the Earth's surface. According to NASA/GISS the average temperature has increased by 1 °C since 1940 as shown in figure 2.1 [4]. This increase in temperature appears small but has a significant effect on weather patterns, agriculture, water supplies, sea levels, animals. This will only worsen as the temperature rises.

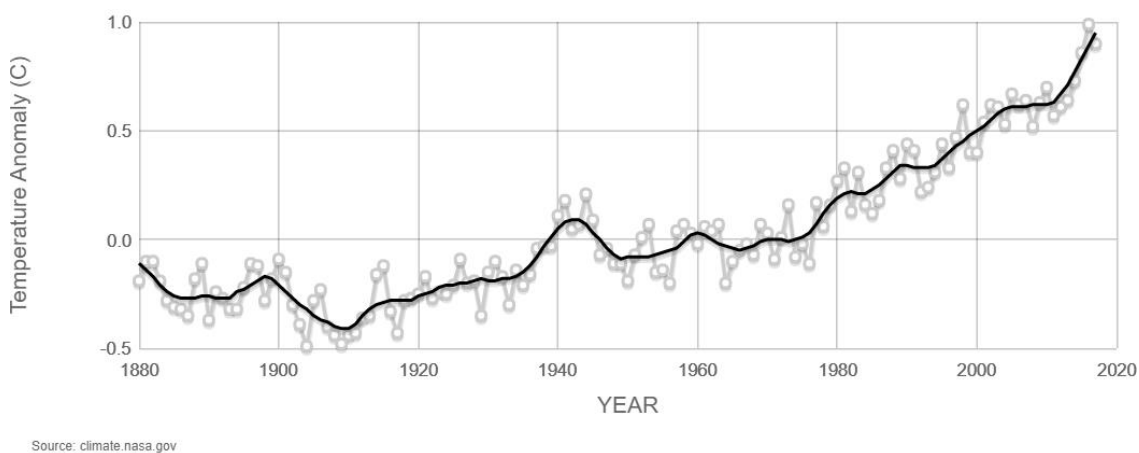


Figure 2.1: Global annual mean temperature increase in Celsius from 1880 to 2018 [4]

The threat of these effects has led to the Paris Agreement which was agreed in December 2015. The Paris Agreement has a long-term goal to limit the earth surface temperature rise to 1.5 °C as the consequences of 1°C can already be seen from rising sea levels and diminishing Arctic sea

ice [5]. Ireland has joined the Agreement under the EU acting as Member State and has committed to reducing EU-wide emissions by 40% of the 1990 levels by the year 2030.

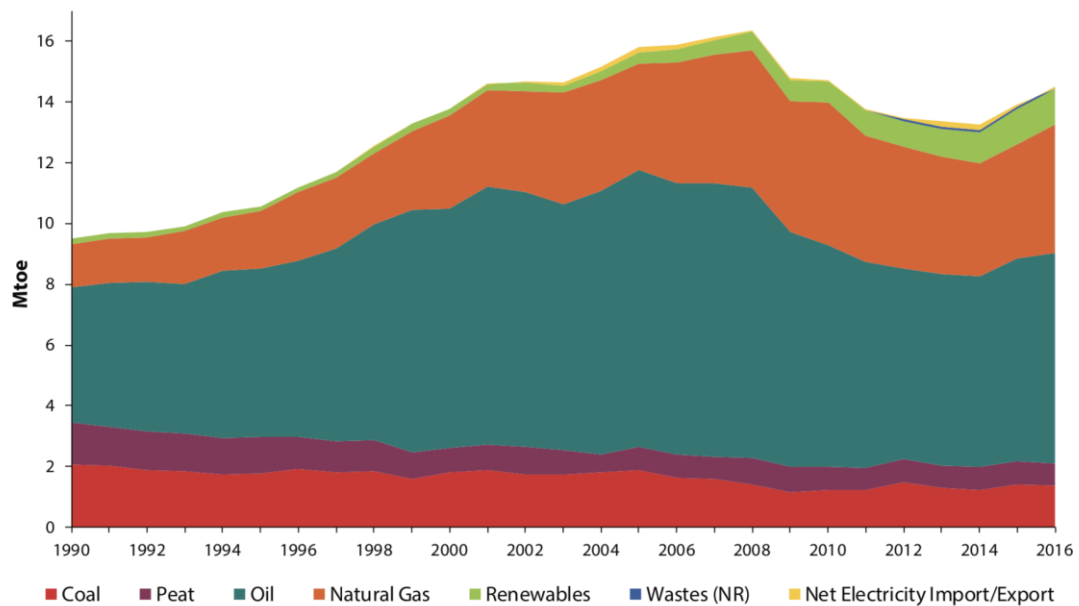


Figure 2.2: Total energy requirement in Ireland from 1990 to 2016 [6]

Ireland's population has increased by nearly 2 million in the past 60 years and the average sea level around Ireland has increased by over 3 cm per decade since 1993. Ireland's greenhouse gas emissions peaked in 2001. In 2014, it was 18% lower than the peak value, but still remains higher than the 1990 level target that have been set out. In 2005 in Ireland, fossil fuels still account for 96.5% of the total energy used. 2.4% was the gross amount of energy used was renewable, which increased to 8.0% in 2016, as shown in figure 2.2 and table 1. Ireland has been given the mandatory target of having 16% of the gross energy used be renewable by 2020. This goal breaks down further into specific targets for electricity, heat/cooling, and transportation [7].

Table 1: Growth of Irish energy sectors from 1990 to 2015 [6]

	Overall Growth %		Average annual growth %			Quantity (ktoe)		Shares %	
	1990 – 2016	2005 – 2016	'05 – '16	'10 – '16	2016	2005	2016	2005	2016
Fossil Fuels (Total)	42.0	-13.1	-1.3	-0.9	5.0	15,254	13,250	96.5	91.9
Coal	-34.1	-27.0	-2.8	1.8	-3.7	1,882	1,373	11.9	9.5
Peat	-46.7	-4.0	-0.4	-0.5	-4.3	765	734	4.8	5.1
Oil	56.3	-24.3	-2.5	-0.9	3.8	9,130	6,911	57.8	48.0
Natural Gas	192.6	21.7	1.8	-1.7	12.4	3,477	4,231	22.0	29.4
Renewables (Total)	590.5	210.2	10.8	9.1	0.3	373	1,158	2.4	8.0
Hydro	-2.3	7.9	0.7	2.2	-15.6	54	59	0.3	0.4
Wind	-	453.0	16.8	13.9	-6.5	96	529	0.6	3.7
Biomass	217.6	85.7	5.8	8.0	17.6	180	335	1.1	2.3
Other Renewables	9883.6	448.3	16.7	4.2	0.3	43	236	0.3	1.6
Wastes (Non-Renewable)	-	-	-	40.6	-3.8	-	66	-	0.5
Electricity Imports (net)	-	-	-	-	-	176	-61	1.1	-0.4
Total	51.8	-8.8	-0.8	-0.4	3.7	15,803	14,413		

Renewable energy includes solar energy, hydro, wind and biomass. The form of renewable energy which this study is concerned about is solar energy which harnesses the light and heat from the sun. This can be harnessed by solar thermal collectors for solar heating to provide hot water for homes or using photovoltaics to generate electricity when exposed to light.

2.2. Photovoltaic Technology

There have been numerous developments in photovoltaic (PV) technology throughout history. The general principle of a PV cell utilises the photovoltaic effect, which produces an electrical current when sunlight strikes a particular semiconductor material such as silicon (Si) or gallium arsenide (GaAs). In each generation there is a slow rise of increasing efficiency from year to year. The chart displaying the best efficiencies attained between 1957 and 2018 for the three generations of cells are shown in figure 2.3.

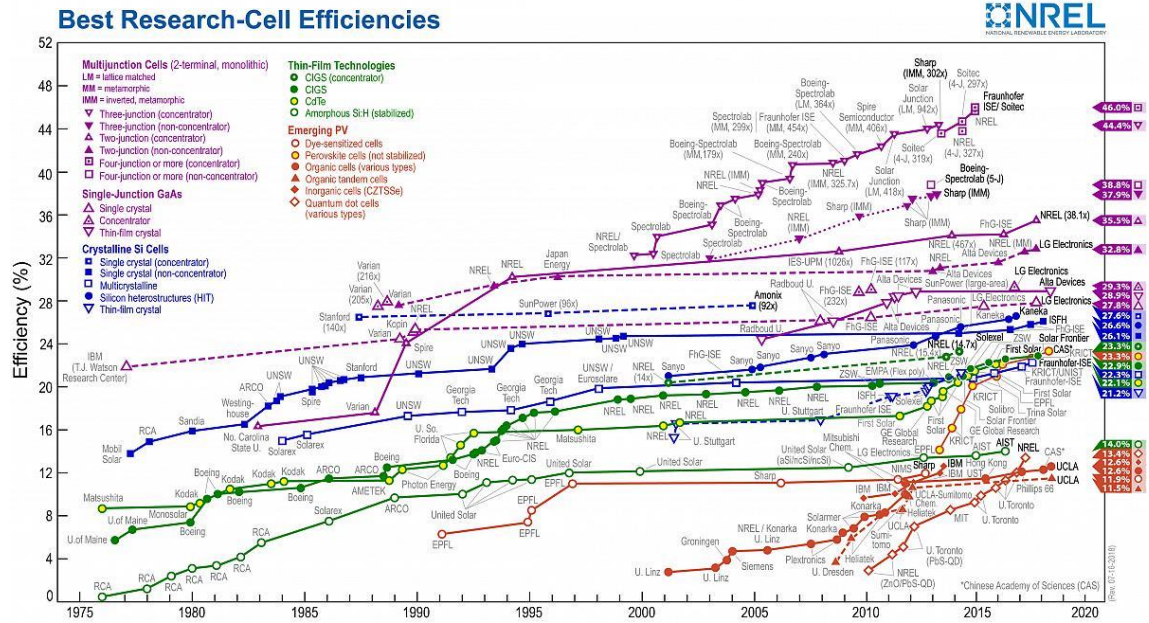


Figure 2.3: Best cell efficiencies from 1957 to 2018 [8]

The first generation of PV cells utilise Si wafers or crystalline Si for single crystalline (c-Si) and multi-crystalline Si (mc-Si), represented by blue in figure 2.3. This represents ~90% of the global market [9]. The highest efficiency reached for a single crystal crystalline Si cell was 27.6 % by Amonix [10].

Second generation PV reduces material costs by developing thin-film PV while still maintaining the efficiencies achieved by first generation PV. This is represented by the green data in figure 2.3. This consists of amorphous Si (a-Si), Cadmium-Telluride (CdTe) and Copper-Indium-Gallium-Selenide (CIGS). The highest efficiency reached for this generation is 23.3% at 14.7 sun concentration for a CIGS concentrator solar cell. Coming at a close second for this generation, in 2017 an efficiency of 22.9% was achieved for a CIS cell [11]. For CdTe solar cells an efficiency of 22.1% was attained by First Solar in 2016 [12].

Third generation PV is for multijunction cells and single junction GaAs cells, shown as purple on figure 2.3. This is the category with the highest efficiency reached, which was by a four-junction cells at 46% in 2014 which was measured at a concentration of 508 suns [13]. There is also emerging PV technologies which ranges from dye-sensitized solar cells (DSSC), perovskite cells, quantum dot (QD) cells, organic cells, inorganic cells, and organic tandem cells denoted by

red on figure 2.3 The fastest improvement in efficiency is by the perovskite cells in this generation. The efficiency has reached a record 27.3% from Oxford PV in June 2018 [14]. QD cells reached an efficiency of 13.4% due to the use of a new type of QD known as caesium lead triiodide (CsPbI_3) and an improvement in understanding the connectivity between QDs [15].

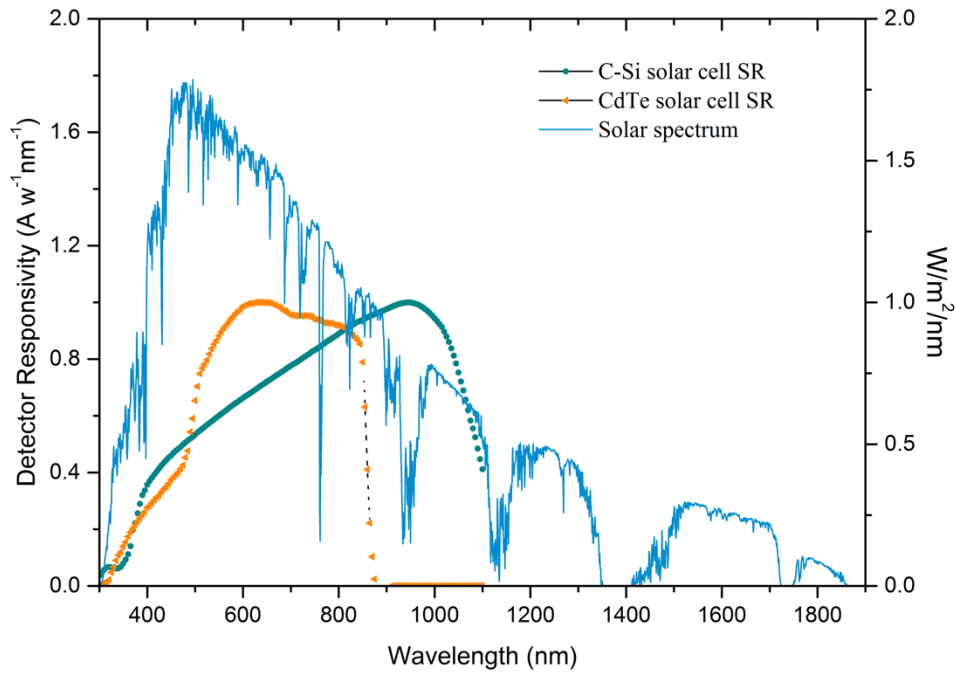


Figure 2.4: Response of C-Si and CdTe solar cells compared to the solar spectrum

With the development in PV technologies, energy losses are the biggest challenge for PV technology. For various types of technologies, the major loss mechanisms are due to the short wavelength photons not being absorbed by the solar cell [16]. Figure 2.4 shows the optical response of the silicon and cadmium telluride (CdTe) solar cells at 300 to 1900 nm. The region in which the solar spectrum is at a maximum, the response from the two cells is significantly lower. Commonly in all PV technologies, the optical response of the solar cell is extremely poor and/or sharply reduced at shorter wavelengths. These loss mechanisms are described [16] for some solar cells as follows in table 2;

Table 2: Solar cells and their loss mechanisms

<u>Solar Cell</u>	<u>Loss Mechanisms</u>
Monocrystalline Silicon (c-Si)	• Emitter recombination. • Increased reflectance. • Absorption from anti-reflective coating.
Multicrystalline Silicon (mc-Si)	• Recombination at the “dead” front surface layer due to heavily doped emitter. • Increased reflectance. • Absorption from anti-reflective coating.
Amorphous Silicon (a-Si)	• Absorption in transparent conducting oxide layer. • Recombination due to heavily doped semiconducting layers.
Cadmium Telluride (CdTe)	• Absorption in buffer (typically cadmium sulphide (CdS) and transparent conducting oxide layers).

With so many losses at short wavelengths, the maximum efficiency is limited. This study focuses on the process of luminescent down-shifting which can create a potential for improving the efficiency by shifting the short wavelength photons to a region which is more suitable for the cell. This shift in wavelength occurs before the photon reaches the cell. This is described further in the following section.

2.3. Luminescent Down-Shifting

Luminescent down-shifting (LDS) is an optical method used to increase the response of a solar cell at short wavelengths by shifting the incident rays with higher energy, to longer wavelengths with lower energy. The latter can easily be absorbed by the solar cell and can contribute to the

overall cell efficiency [16,17]. The luminescent down-shifting process is achieved by placing a sheet of fluorescent material doped polymer on top of the solar cell as presented in figure 2.5.

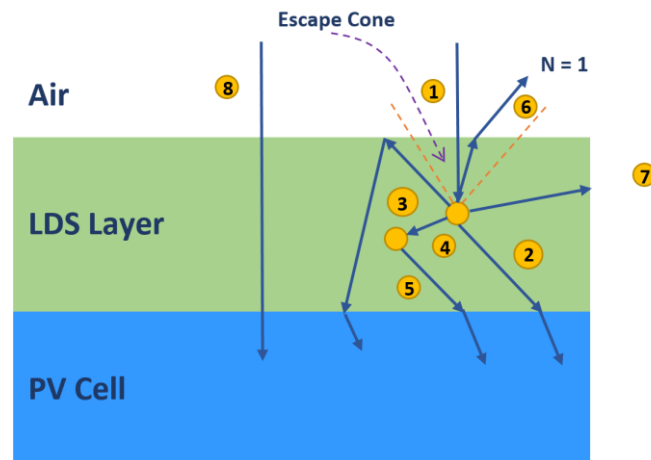


Figure 2.5: Schematic diagram of PV cell with LDS layer on top [16]

Incident light, shown as ray 1, will be absorbed and re-emitted at a longer wavelength. The majority of light is directly emitted to the cell (ray 2) or also via total internal reflection at the boundary between air and the LDS layer (ray 3). Light can also reach the cell via reabsorption (ray 4) and re-emission by another luminescent specific (ray 5). A portion of light will be lost from the cell through the top of the LDS layer due to the escape cone (ray 6) or side (ray 7). Light may also be transmitted directly to the cell if not absorbed by the luminescent species (ray 8).

This method was first described by Hovel et al in 1979 [18]. The LDS layer absorbs in the region of 300 to 560 nm and emits in a region with a longer wavelength which varies dependent upon on the material used. The photons which are shifted to a longer wavelength before reaching the photoconductive layer responds better to the shifted spectrum than the original spectrum. This creates more electron-hole pairs, and increases the external quantum efficiency (EQE) [16]. It is necessary that the gain obtained by LDS photoconversion is greater than the losses from shifting the solar spectrum [19]. Such losses include for example reabsorption, emission at less than unity photo-luminescent quantum yield, reflection, these are explained further in the proceeding section.

2.3.1. Losses in LDS

The presence of an LDS layer on the PV cell will increase the number of interactions with the photons, creating more loss mechanisms. The losses were summarised by [16] and are described below;

- Parasitic absorption: A loss mechanism from the host materials used in the LDS layer.
- Emission from the luminescent species at less than unity photo-luminescent quantum yield (PLQY).
- Losses through the top and side planes of the layer because luminescent light is not emitted towards the underlying solar cell only.
- Reabsorption from the luminescent species due to partial overlapping of the absorption and emission bands, where that is the case, which will increase the losses from the top and side planes of the LDS layer.
- Higher reflection losses due to the introduction of an additional interface between the LDS layer and the PV device.

2.3.2. Development of LDS

Initial work on LDS layers was performed by Hovel et al [18], as mentioned previously. The concept was then utilised in a different device used for optical concentration known as a luminescent solar concentrator by Weber and Lambe which is explained further in the following section. However, for LDS there has been a lot of work in recent decades to improve performance. In 2005, Van Sark et al [20] designed a LDS layer incorporating CdSe QDs in a transparent host material deposited on top of a mc-Si solar cell. After testing it in different light conditions, an increase in power was experienced in every condition. McIntosh et al. [21] then did some work on introducing Lumogen dyes (BASF) 570, 083, 240, and 300 into PMMA. Under an illumination of AM 1.5G there was an increase in performance of 0.37 mA/cm². Ahmed et al. [22] fabricated a LDS layer which combined the materials used in the two previous papers; a plasmonic LDS (pLDS) which comprises of silver nanoparticles and Lumogen 083 which is a yellow organic dye. The pLDS layer was placed on top of CdTe cells and significant improvements to the EQE in the

region below 500 nm were found to reach 25 – 40%. Ross et al. [23] combined Lumogen yellow and violet onto a CdTe cell and showed a 9 % increase in the short circuit current. Parel et al [24] combined LDS and LSC (Luminescent Solar Concentrator) to create a concentrated-LDS (C-LDS). Different mixtures of yellow, orange and violet were fabricated and tested. It showed that yellow and orange dyes are more suited to light concentration most likely due to a larger number of excitation photons present at the absorbing wavelengths of these dyes. Violet is more useful for enhancing the wavelength shifting as the EQE is poor at the absorbing wavelengths for violet. A 20% increase in the current output was found for a yellow-orange mixture on the C-LDS which shows potential for this setup.

The luminescent material and polymer allow for a variation of colours, shape, and size. This allows for customizability and more choice. The transparency of the polymer allows the LSC to be introduced as a light control measure or a window with the PV cells on the edges out of view for the building user.

2.4. Host Material for LDS

For LDS there is a range of requirements for the polymer; it must be transparent to visible light with no parasitic absorption in UV, the luminescent material chosen must remain stable in the polymer, and high photostability is ideal, but UV-stabilizing agents can be added [25]. Ethylene vinyl acetate (EVA) is a polymer which is in flake form and typically dissolves in toluene with stirring for 24 hours. The quantum yield (QY) of Lumogen dyes was determined in EVA with the dyes retaining a high QY. Yellow was the only dye not at 100% QY, obtaining a QY of 88%. If multiple dyes were combined, the lowest QY was violet-yellow at 89%. The IV measurements for these dyes only produced an overall improvement for the violet dye, a 1.19% improvement relative to the cell [26].

Polymethyl methacrylate, otherwise known as PMMA, is a suitable and well-established host material to be used with luminescent materials that is low in cost. It is a highly transparent

polymer which has proven to have long term stability when it was tested to be stable for over 17 years in desert sunlight after a 1975 test by Rainhart et al. Long-term stability is important for long lasting applications in the real world as devices are expected to have a lifetime of at least 10 years. The QY of PMMA was found to be very high at nearly 100% [27]. PMMA is also commonly used in spin-coating to form uniform thicknesses which makes it ideal for creating LDS thin-films via spin-coating [28]. As PMMA is a highly viscous material, toluene was added to make it more workable for spin-coating. [28].

Polyvinyl butyral (PVB) is also in flake form, which is dissolved in benzyl alcohol in 12 hours [25]. The stability of PVB is higher than EVA [16] and is soluble in simple alcohols. It is also used for encapsulation of PV modules. The QY of Lumogen dyes in PVB is lower than the QY obtained for PMMA, only reaching a high of 91% for yellow and 85% for violet [29].

2.5. Luminescent Materials

There is a large range of materials available for use within LDS which ideally have the following properties: A near unity luminescent quantum yield (LQY), a wide absorption band where the external quantum efficiency (EQE) of the cell being used is low, a large Stokes shift to reduce reabsorption losses, high absorption coefficient, a narrow emission region occurring where the EQE of the cell is highest, low cost [16], and a high photostability. The different materials which have been investigated in this study are discussed below and include organic dyes and quantum dots (QDs).

2.5.1. Organic Dyes

Organic dyes are a type of luminescent material with many qualities that can be utilised in LDS layers such as: high absorption coefficients, a luminescent quantum efficiency (LQE) close to unity, easily dissolve in polymers [16], and are low in cost. However, organic dyes also have a low Stokes shift with a narrow band of absorption which limit the utilisation of the solar spectrum and therefore the overall efficiency of the system [30]. An example of this can be seen in figure

2.6 for Lumogen orange. Dyes can be easily combined in solution to create layers with a larger absorption band. However, by creating a larger absorption band, the overlap of the absorption and emission curves could increase. This overlap increases the potential of reabsorption of emitted photons, which will decrease the efficiency. Organic dyes also have had their photostability increased in recent years with commercially available photostable dyes which can remain stable over many years of exposure to UV [31] which has renewed the interest in organic dyes [30].

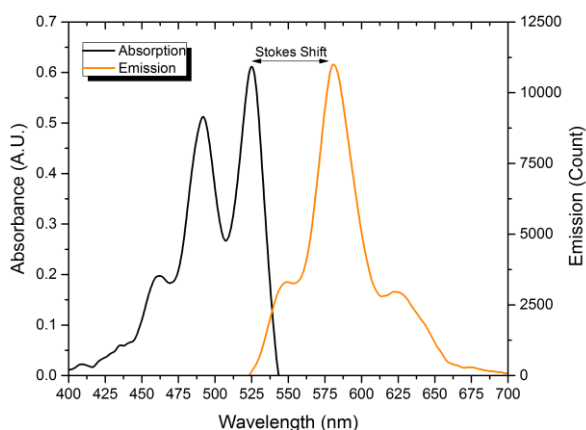


Figure 2.6: Stokes Shift of Orange Lumogen between absorption and emission spectra

2.5.2. Quantum Dots

Quantum dots are another material for LDS which have been characterized in this study. QDs were first discovered in the early 1980s by Alexei Ekimov [32]. As they are composed of crystalline semiconductor materials, QDs do not degrade as easily in UV light and therefore have a good photostability. QDs typically consist of materials such as Cadmium Selenide (CdSe) or Zinc Sulphide (ZnS). The advantage of QDs is that they can be spectrally tuned by varying their size and composition to absorb and emit at specific wavelengths, which is portrayed in figure 2.7 below. Smaller dots are closer to the blue end of the spectrum while larger QDs will emit closer to the red area of the spectrum. This tuning can occur due to their small size on the scale of nanometres, ranging from 2 to 10 nm in diameter. At this size, the quantum confinement effect controls the emission wavelength. Unfortunately, QDs also cost a lot more than dyes and can have surface defects that can act as traps and increase the recombination of electrons and holes, but this can be reduced with the QD core being encapsulated in a material of a higher band gap.

The quantum yield, which is the ratio of the number of photons emitted to the number of photons absorbed by a material, of QDs is lower than that of organic dyes but is compensated by the larger absorption region.

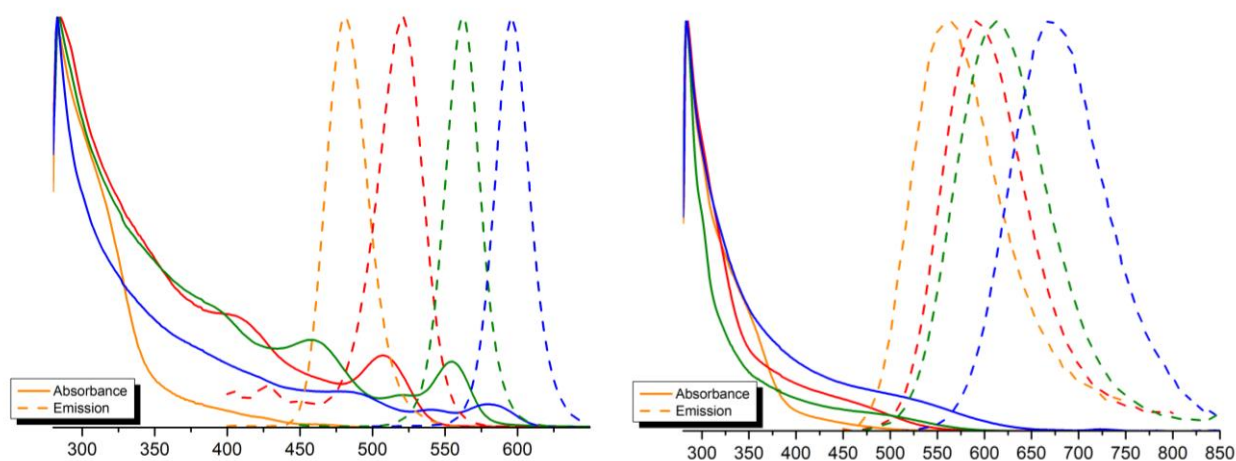


Figure 2.7: Redshift in emission peak of quantum dots from this study.
 Left: Hydrophobic CdSe/ZnS Quantum Dots kit Right: Hydrophobic Zn-Cu-In-S/ZnS Quantum Dots Kit

QDs consist of two main types; Core QDs and Core-shell QDs. Core QDs only consist of one semiconductor material. Core-shell QDs (CSQD), shown in figure 2.8, consist further of different types; type I which have a core with a larger band gap than the shell, inverse type I which has a shell with a larger band gap than the core, and type II which consists of the conduction or valence band of the core being located within the bandgap of the shell. QDs which are encapsulated with a shell consisting of a larger band gap can create an improvement in the quantum yield of photoluminescence due to surface recombination. QDs are also capped with a coating to enhance their stability in air.

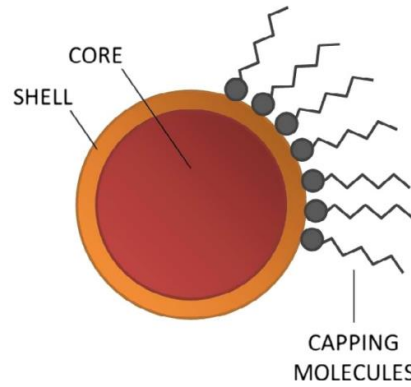


Figure 2.8: Structure of a core-shell quantum dot [32]

2.5.2.1. Development of Quantum Dots

In 2014, Han et al tested a range of QDs on GaAs solar cells in a hybrid design. After optimising the concentration of QDs, the power conversion efficiency was increased by 25 % compared to the cells without a layer of QDs. Additionally, the EQE had a 1.3-fold enhancement. The enhancement was mainly attributed to the photon downshift and antireflection [33]. Kalytchuk et al presented a simple model to analyse the wavelength-dependent efficiency of solar cells with a planer LDS layer on CdTe/CdS and c-Si cells. A short circuit increase of 16% for CdTe/CdS and 50% for c-Si cells was demonstrated [34].

2.6. Conclusion

With the World temperature increasing, mainly, due to CO₂ levels there is a desire for renewable energy sources. This study focuses on PV technology wherein an electrical current is produced when sunlight strikes a semiconductor material such as silicon (Si) or gallium arsenide (GaAs). Over the past 40 years, there have been multiple generations of PV cells, increasing in efficiency from year to year. First generation PV cells utilised Si wafers and reached 27.6 % efficiency. Second generation cells reduced in cost and used materials like a-Si and CdTe, reaching 23.3% for a CIGS concentrator solar cell. Third generation PV has achieved the highest efficiency of 46% by a four-junction cell at a concentration of 508 suns.

Energy losses are the biggest challenge for PV technology. For various types of technologies, the major loss mechanisms are due to the short wavelength photons not being absorbed by the solar

cell. Luminescent down-shifting creates a potential to improve the efficiency by shifting the photons to a region which is more suitable for the cell. For LDS development, Parel et al showed that a mixture of yellow and orange Lumogen dye on a concentrated LDS had a 20% increase in current output.

PMMA was chosen as the host material for the LDS layers as it is a suitable and well-established host material to be used with luminescent materials. The luminescent materials examined in this study were organic dyes and QDs. Organic dyes have high absorption coefficients, easily dissolve in polymer and are low cost. However, the Stokes shift is low which limits the utilisation. Dyes can be easily combined to create layers with a larger absorption band, but the overlap between absorption and emission could consequentially increase. QDs are composed of crystalline semiconductor materials and have a good photostability. QDs can be spectrally tuned by varying the size and composition, this varies the wavelengths at which it absorbs and emits. This is beneficial as the QD can be varied to suit a specific required wavelength. Unfortunately, the cost is higher than organic dyes. When Han et al tested a range of QDs on GaAs solar cells, a 25 % increase in power conversion efficiency was achieved.

Chapter 3 - Experimental Techniques

3.1. Introduction

This chapter describes the experimental techniques and characterisation methods used in this study. The experimental techniques include:

- Spin Coating technique: The process for depositing thin-films consisting of the host material and luminescent material on glass substrate is described.
- Photostability: The stability of the LDS layers exposed in outdoor conditions is described.
- Spectroscopic techniques: The spectrometers used to measure the absorbance and emission of LDS materials in solution and thin-film form.
- Quantum Yield measurement processes tested.
- External Quantum Efficiency of the LDS layers on Si cells.

3.2. Spin Coating

The spin coating technique was developed to create thin-films of 50 μm thickness, containing the host material, on glass substrates of 2.6 x 2.6 cm. The Spincoat G3P-12 from Specialty Coating Systems shown in figure 3.1 was used for the deposition process. The rotational speed can be programmed between 0 to 9,999 RPM, an acceleration/deceleration time of 0.1 to 25.5 seconds, and a dwell time of 0 to 999 seconds. The thickness of the resulting substrate varies depending on the viscosity of the solution used, the spin RPM, the dwell time and the rate of evaporation. These variables were changed until a maximum thickness for the host material could be attained. A glass substrate was placed on the chuck, the solution was manually deposited via a pipette into the centre of the substrate, the chuck then begins rotating and accelerating the rotational speed causing the solution to spin off the substrate to the outer containing bowl. The substrate is kept at a constant RPM, the solution is allowed to evaporate, and a thin-film remains on the substrate which can be easily removed.

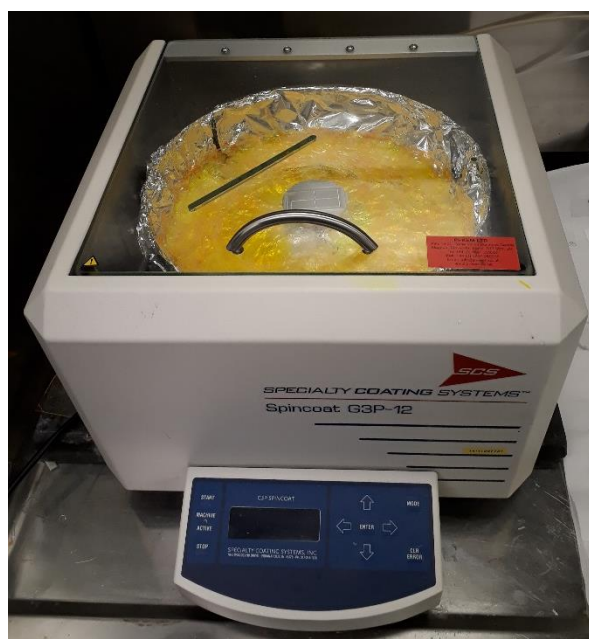


Figure 3.1: Spincoat G3P-12 spin coater

3.3. Spectroscopic Characterisation Techniques

3.3.1. Absorbance Measurements – StellarNet Inc

Absorbance measurements were performed in a StellarNet setup containing the SL5-DH UV-VIS Light source connected to a 1.3 cm width enclosed cuvette holder via optic fibre, which is then connected to the BLACK-Comet-SR Super Range Concave Grating Spectrometer which measures from 220 to 1100 nm. The light source has dual lamps of deuterium and tungsten halogen which can be individually turned on or off. It provides a range of 190 to 2500 nm. The schematic for this setup is shown in figure 3.2.

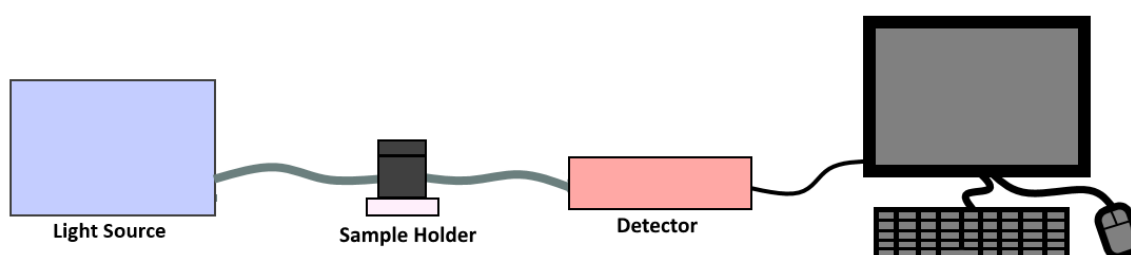


Figure 3.2: Schematic setup of cuvette holder absorbance measurements

This setup was used in the optimisation and photostability tests conducted for the thin-film LDS layers. The thin-films were cut to the correct width for testing in the cuvette holder and placed perpendicular to the incoming and outgoing light, as shown in figure 3.3. The setup is controlled by the software SpectraWiz wherein the integration time and number of averages can be set for sample readings. The resulting files are converted in an excel parser for analysis.

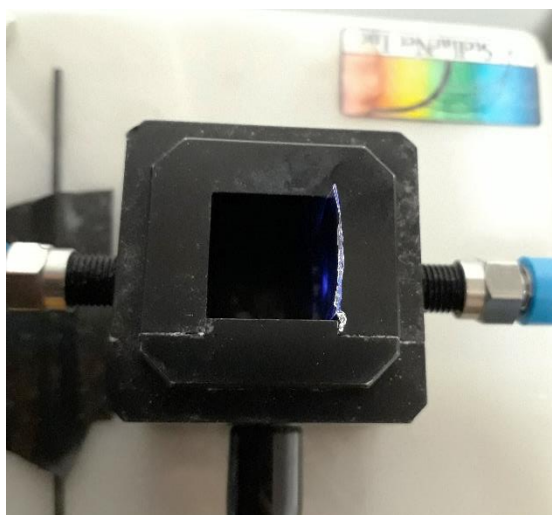


Figure 3.3: StellarNet Inc cuvette holder containing thin-film sample perpendicular to incoming and outgoing light

3.3.2. Emission Measurements – LabSphere Integrated Sphere

Emission measurements for the Lumogen dye optimisation and photostability tests were conducted using a solar light source focused at a wavelength filter, collimated to a LabSphere integrated sphere. This is connected to a BLACK-Comet-SR Super Range Concave Grating Spectrometer as used in the StellarNet Inc absorbance setup, which measures from 220 to 1100 nm. The band-pass filter used for a sample depends on the excitation wavelength needed; for instance, a 380 nm filter was used for Lumogen violet samples. This setup uses the SpectraWiz software, as used in section 3.3.1, so the integration time and averages are set by the user. The excitation light is collimated at a size of 5 to 11 mm depending on the fibre optic used. The schematic can be found in figure 3.4 below.

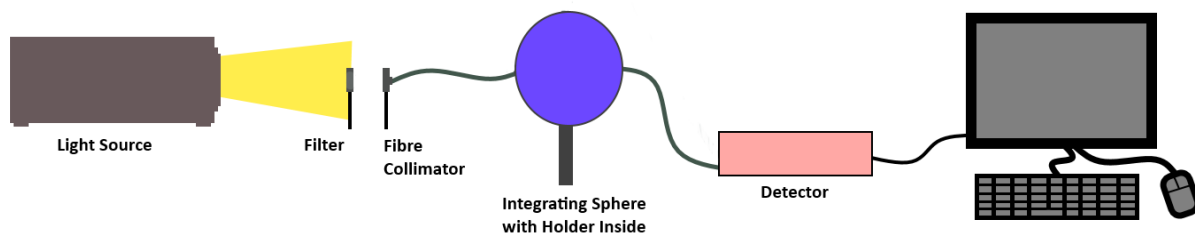


Figure 3.4: Schematic setup for emission measurements with integrating sphere

The Lumogen samples used in this setup were thin-films which were held suspended in the integrating sphere. As shown in figure 3.5, the input port and output port are at right angles, with the collimated beam striking the surface of the thin-film. The filter used for a Violet Lumogen thin-film was the 380 nm, whereas for the Yellow and Orange Lumogen, a 405 nm filter was used. Before a reading was taken, it was important to wait a minute or two for the spectra to stabilise.

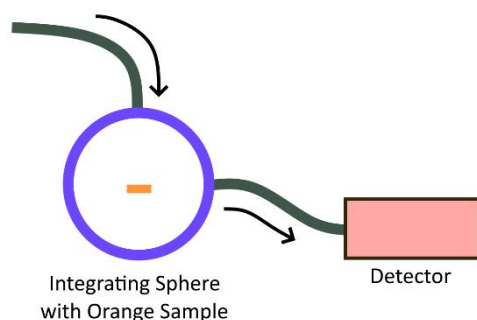


Figure 3.5: Top-down view of integrating sphere with orange sample inside

3.3.3. Absorbance – Perkin Elmer Lambda 35

The Perkin Elmer Lambda 35 is a double beam UV/Vis spectrometer shown in figure 3.6. It contains deuterium and halogen lamps prealigned with a wavelength detection range of 190 to 1100 nm. The slit width has four options of 0.5 nm, 1 nm, 2 nm, and 4 nm. The software automatically switches the lamps at 326 nm. The absorbance wavelength accuracy is ± 0.1 nm [35]. This machine was used to measure the absorbance characteristics of the QDs investigated in this study. The measurements were conducted with two quartz cuvettes. When taking measurements, a baseline was obtained first. This entailed both cuvettes being placed in the compartment (a) as illustrated in figure 3.6 where (b) contained the blank solvent, which was

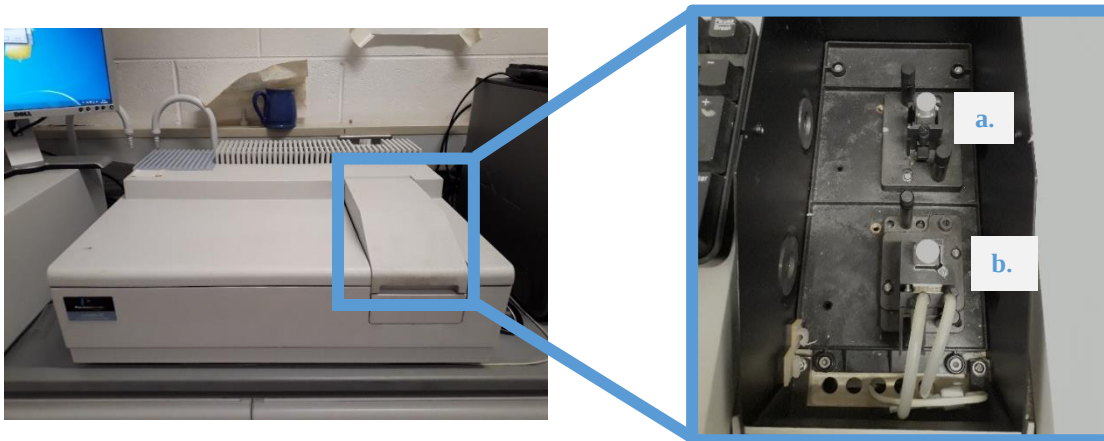


Figure 3.6: Perkin Elmer Lambda 35 Spectrometer with (a) reference sample and (b) tested sample

toluene for the QDs. Then the cuvette in holder (b) was removed and replaced with the QD sample dispersed in toluene. For consistency in measurements, the cuvettes were orientated in the same direction for every measurement and the fill level was the same for each measurement. A schematic diagram for this spectrometer is shown in figure 3.7. The visible range from the halogen lamp is reflected off the first mirror (M1) while then M1 is raised to allow the UV range from the deuterium lamp to pass. Both the UV and visible light will strike M2 and be reflected through an optical filter on the filter wheel. This spectra will then pass through slit 1 of the monochromator. The spectra is then dispersed, and the monochromator reflects a particular segment of the spectrum, which exits through slit 2 to M3. M3 then reflects the spectra to a beam splitter, which allows 50% of the spectra to pass to M4, and the other 50% to pass to M5. The beam from M4 passes to the sample cell (holder (b) in figure 3.7), while the beam from M5 passes to the reference cell (holder (a) in figure 3.7). Both beams are then passed through a lens to the photodiode detector.

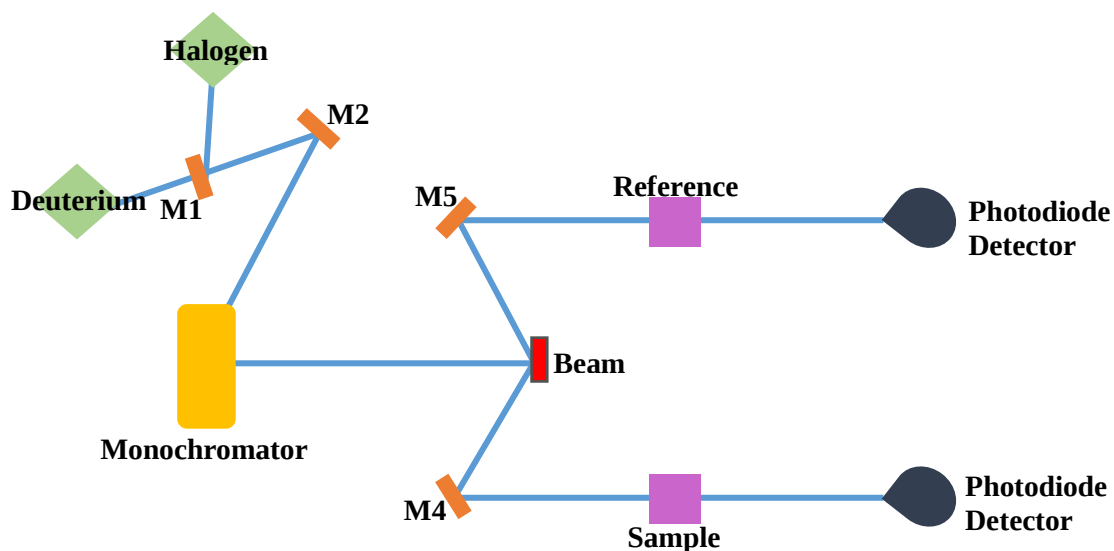


Figure 3.7: Schematic of Perkin Elmer Lambda 35

3.3.4. Emission – FluroMax-4

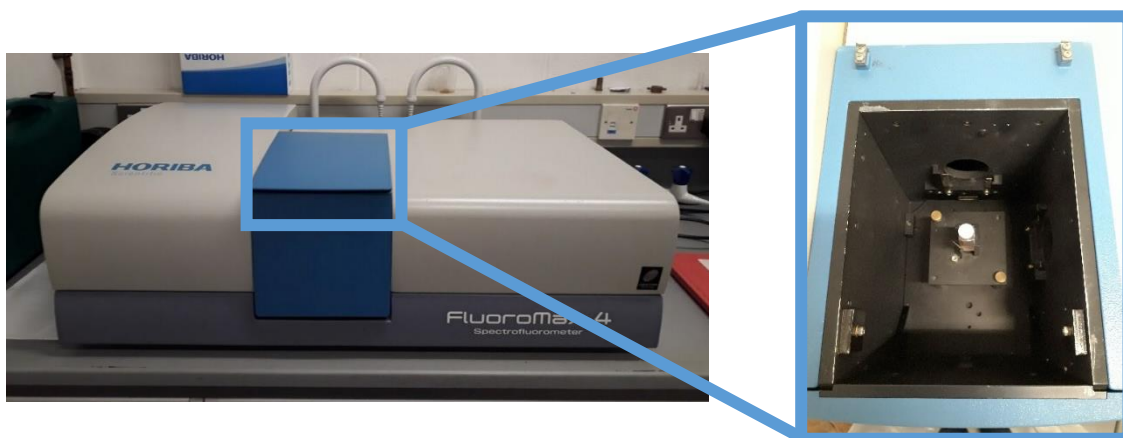


Figure 3.8: Horiba FluoroMax-4 Spectrofluorometer with sample holder highlighted

The Horiba FluoroMax-4 is a spectrofluorometer used to measure the emission wavelengths of the QDs in this study as shown in figure 3.8. It contains a xenon arc lamp, which passes through a monochromator. The monochromator selects a specific wavelength band as set by the user for

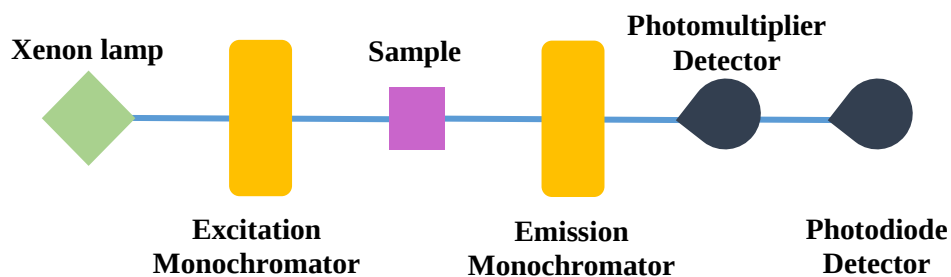


Figure 3.9: Schematic diagram of the Horiba FluoroMax-4 Spectrofluorometer

the sample as the excitation wavelength. This spectrum is directed onto the sample, of which the luminescence from the sample is then directed to a second monochromator for emission which selects a band of wavelengths and shines this onto the detector for the user to view the data. A schematic can be seen in figure 3.9. The excitation range for the first monochromator is 240 to 600 nm, and the emission detection range is 290 to 850 nm [36].

3.4. Photostability Tests

Photostability tests were conducted for thin-films LDS layers. The samples were placed outdoors on the 6th of December 2017, in a holder shown in figure 3.10 below, and experienced a wide range of conditions including sunny to snow to cloudy. To determine the effect the outdoor conditions were having on the samples, absorbance and emission measurements were taken under the same conditions for each measurement. After the measurement is taken, the samples were returned outdoors to the same location. The equipment used for these measurements are described in section 3.3.1 and 3.3.2.



Figure 3.10: Lumogen thin-films. L to R: PMMA, yellow, orange, and violet

3.5. External Quantum Efficiency



Figure 3.11: ReRa Solutions SpeQuest Quantum Efficiency setup

The external quantum efficiency (EQE) of a photovoltaic device is the ratio of the number of charge carriers, collected by the solar cell, compared to the number of photons of a given wavelength, which enter the solar cell. This is an indication of how well the solar cell can convert incident photons into electricity. To test the optimised concentrations of the Lumogen layers, the ReRa Solutions SpeQuest Quantum Efficiency is used, as shown in figure 3.11. The setup is a combination of a xenon light source with a range of 300 to 1100 nm, an IV converter, a bias light driver, a monochromator, and a chopper. The diameter of the light spot is between 2 mm up to 4 mm directed at the centre of the cell. The system measures the photocurrent generated by the cell at 10 nm steps in wavelength. The system is initially calibrated with a silicon reference cell between 300 to 1100 nm. If a wavelength up to 1800 nm is necessary, a germanium reference cell is also calibrated between 1050 and 1800 nm. As the machine is fully automated, the test sample needs to be mounted under the beam of light and the measurement begins using the Photor software.

3.6. Quantum Yield

The quantum yield (QY) of a material is defined as the ratio of the number of photons emitted to the number of photons absorbed by a material. The material this relates to for this study is the quantum dots (QD) obtained from PlasmaChem. These QDs are from two different kits, which are: Hydrophobic CdSe/ZnS Quantum Dots kit and the hydrophobic Zn-Cu-In-S/ZnS Quantum Dots Kit. Three different methods were tested until consistent results were obtained.

The first setup tested involved the comparative method with the use of the StellarNet Setup and LabSphere integrating sphere. The method involved comparing a standard dye of known QY to the QDs. The standard dye is required to have equivalent absorbance ranges and the same particular excitation wavelength so a comparison can be made. Samples are reduced to a starting point in which the excitation used has an absorbance value of 0.1 A.U. and the concentration lowered as low as possible with absorbance and emission measurements taken at each concentration. The integrated absorbance and integrated emission values are compared with the resulting slope to be used in equation 1. In this equation, 'x' represents the unknown QD and 'st' represents the standard dye used. Furthermore, 'A' denotes absorbance, 'E' denotes emission, 'I' is intensity, and 'n' is the refractive index of the solvents used. All absorbance and emission measurements were conducted using the equipment described in 3.3.3 and 3.3.4.

$$LQY_x = LQY_{st} \frac{A_{st}}{A_x} \frac{E_x}{E_{st}} \frac{I_{st}}{I_x} \frac{n_x^2}{n_{st}^2} \quad \text{Equation 1}$$

However, the resulting emission measurements did not give clear spectra and required a photomultiplier tube to enhance the emission intensity. The tests were then conducted in the Fluoromax-4 and the Perkin Elmer Lambda 35 and would be performed with the same method. This method was unable to give consistent and repeatable results, so a different method was used.

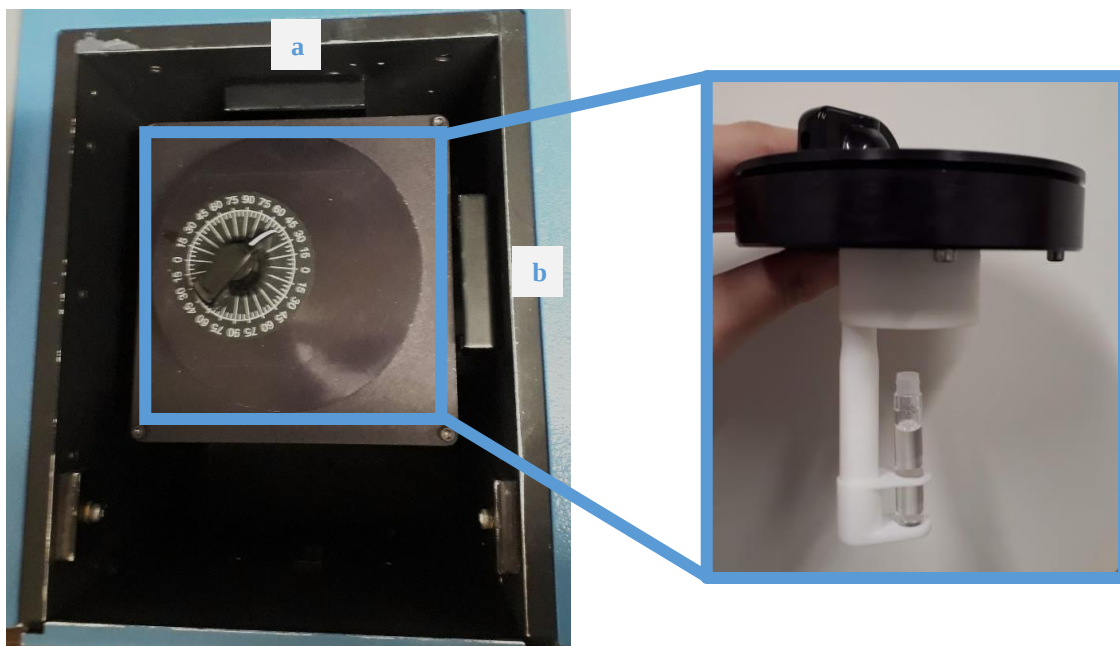


Figure 3.12: Fluoromax-4 with Integrating Sphere accessory containing vial holder. Filter locations denoted by 'a' and 'b'

The final method used an integrating sphere accessory which was placed in the Fluoromax-4 as shown in figure 3.12 above. The quantum yield is determined from the difference in the peak intensity between the measurement of the sample and of a blank, which contains the solvent used in the sample. The scatter, using the appropriate filter, and the fluorescence of the blank and sample are also measured. 'L_A' is the scatter of the blank, 'L_C' is the scatter of the sample, 'E_A' is the fluorescence of the blank, and 'E_C' is the fluorescence of the sample. The quantum yield (ϕ_f) is then calculated as shown in equation 2 below.

$$\phi_f = \frac{E_C - E_A}{L_A - L_C} \quad \text{Equation 2.}$$

Chapter 4 - Materials Characterisation

4.1. Introduction

This chapter describes the characterisation of different luminescent materials which will be incorporated into luminescent down-shifting (LDS) layers. A range of luminescent organic dyes and quantum dots were studied, and their suitability determined.

The first characteristic is the range in which the luminescent material absorbs and emits and whether that the luminescent material is suitable for LDS development.

Secondly, the photostability of the luminescent materials is tested outdoors over a range of three months.

Thirdly, the external quantum efficiency of the layers was determined. Finally, LQY for each quantum dot must be determined. LQY was determined with the material in solution form. The results are described in the following sections.

4.2. Host Material Optimisation

The first step in this study was to create a thin-film via spin coating that was uniform in thickness, easily removed from the substrate, and flexible. PMMA was chosen as the host material, specifically Plexit 55 acryl-resin. Toluene and PMMA were combined by magnetic stirring and deposited onto the centre of a 2.6 x 2.6 cm glass slide. Both the ratio of toluene to PMMA, the volume dispensed, and the controls on the spin coater were varied throughout the optimisation. Initially it was determined that a ratio of 1:1 was not viscous enough to create thick layers. The thickest layer achieved was only 20 μm with a volume of 500 μl at 1000 RPM and 180 s. These layers were too thin to remove from the glass substrate and had a textured surface, as shown in figure 4.1.

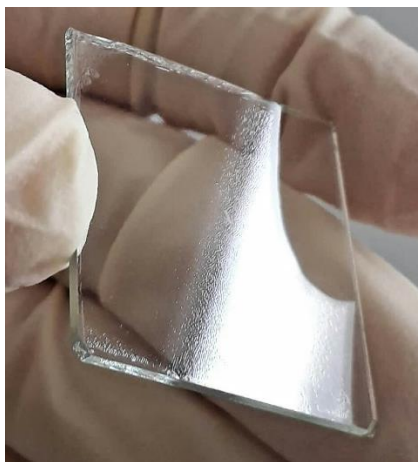


Figure 4.1: Initial host material thin-films - too thin and textured surface

The ratio was increased to 1:3 toluene to PMMA with 23 μm being the thickest layer created. At 1:4 ratio, 40 μm layers were formed, however there were defects in the layers. As shown in figure 4.2, the thickness of the host material caused pulling at the orders at the excess solution is spun off while the layer is forming. This creates a thinner layer in the centre and wrinkles forming at the sides.

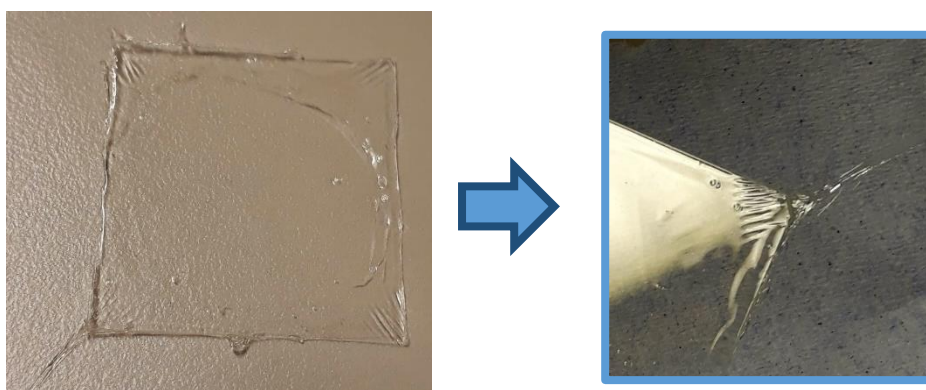


Figure 4.2: Wrinkling in corners of host material thin-films

The ratio was then reduced to 1:2.7 and the highest thickness was found to be 49 μm with 375 μl of host material spun at 1000 RMP for 240 s dwell time. This was determined to be the optimum concentration as it was easily removed from the glass substrate, no wrinkling occurred, the thin-films were flexible, and the thickness was uniform, as shown in figure 4.3. This was then used

for all further tests requiring host material. The layers only required 1 hour in an oven at 40°C or 16 hours in a fume cupboard to be easily removed from the substrate.



Figure 4.3: Optimised ratio of toluene to PMMA for host material displaying flexible properties

4.3. Organic Dye Characterisation

Three organic dyes from the Lumogen F range from BASF were characterised. This includes Yellow 083 and Orange 240 which are perylene based dyes, and violet 570 which is a naphthalimide based dye.

4.3.1. Absorbance and Emission Measurements

The different Lumogen dyes being used were dissolved into the host material being used which contains a 1:2.7 ratio of toluene to PMMA as determined in section 4.2. At this ratio, the dye is easily mixed in 45 minutes on a magnetic stirrer. The concentration was varied for each dye, and thin-films were formed using the spin coater described in section 3.2 and the method described in 4.2. The absorbance and emission measurements of the samples Yellow, Orange, and Violet at optimised concentrations are shown in figures 4.5, 4.7, and 4.9 respectively. The absorbance measurements were carried out using the StellarNet Inc setup while the emission measurements were performed using the LabSphere Integrated Sphere as described in sections 3.3.1 and 3.3.2. The method used to determine the optimised concentration was determined by comparing the integrated absorbance and emission curves at various concentrations. The concentration at which the absorbance and emission is at the highest and before reabsorbance occurs.

As shown in figure 4.4, the integrated emission of yellow begins to decrease from 0.25 wt% onwards, with the integrated absorbance still increasing until 0.5 wt%. It was determined to use 0.44 wt% as the optimum concentration.

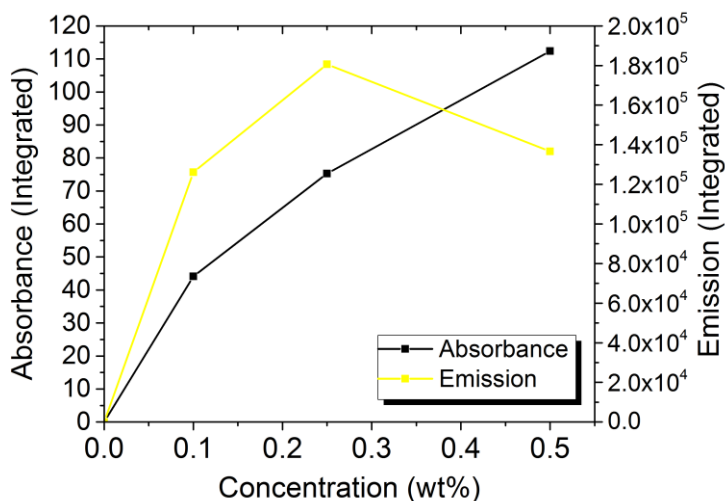


Figure 4.4: Integrated Absorbance and Integrated Emission at various concentrations for Lumogen yellow thin-film

The absorbance and emission of Yellow show a peak absorbance of 476 nm to a peak emission of 567 nm. This is a downshifting of 91 nm. This is a low Stokes shift and as a result there is an overlap between 480 and 530 nm, which causes reabsorbance of emitted photons and reduces the efficiency.

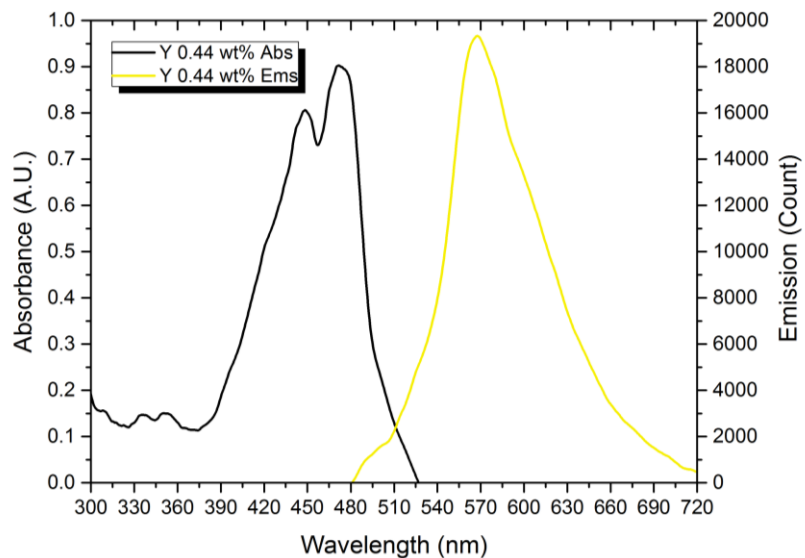


Figure 4.5: Absorbance and emission of Lumogen Yellow at 0.44 wt%

As shown in figure 4.6, the optimum concentration of orange was found to be 0.08 wt% as the integrated emission sharply decreases at all higher concentrations.

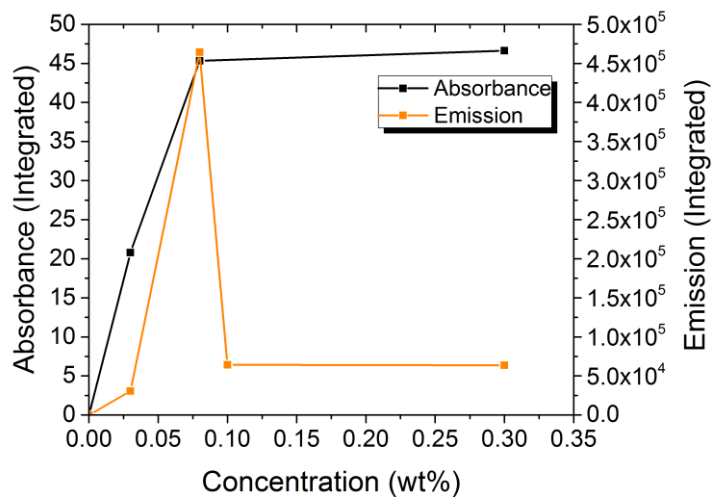


Figure 4.6: Integrated Absorbance and Integrated Emission at various concentrations for Lumogen orange thin-film

The absorbance and emission of Orange shows a peak absorbance of 525 nm downshifted to an emission peak of 581 nm, a difference of 56 nm. Once again, an overlap between the wavelengths of 523 and 543 nm which can reduced the efficiency due to reabsorbance.

Figure 4.4 displays how 0.08 wt% was determined as optimum for Lumogen orange.

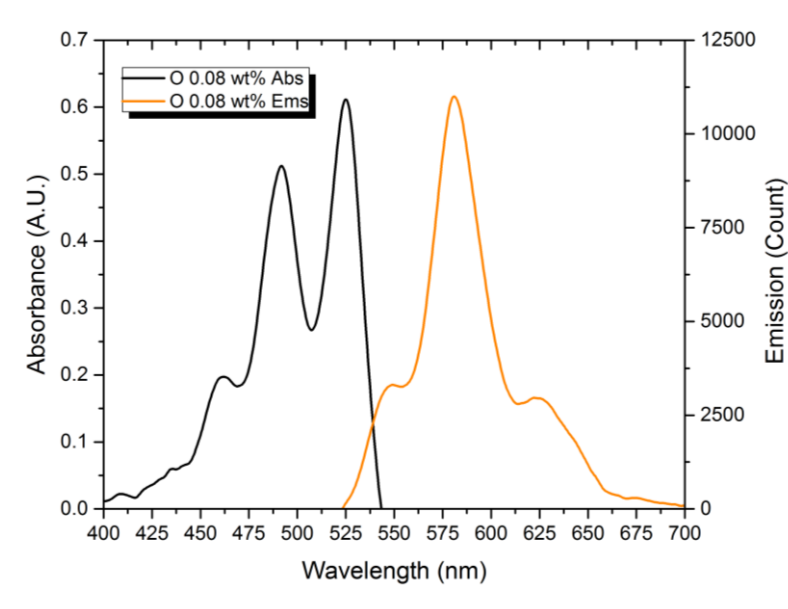


Figure 4.7: Absorbance and emission of Lumogen Orange at 0.08 wt%

As shown in figure 4.8 below, the optimum concentration of violet was found to be 0.18 wt% as the integrated emission sharply decreases at higher concentrations.

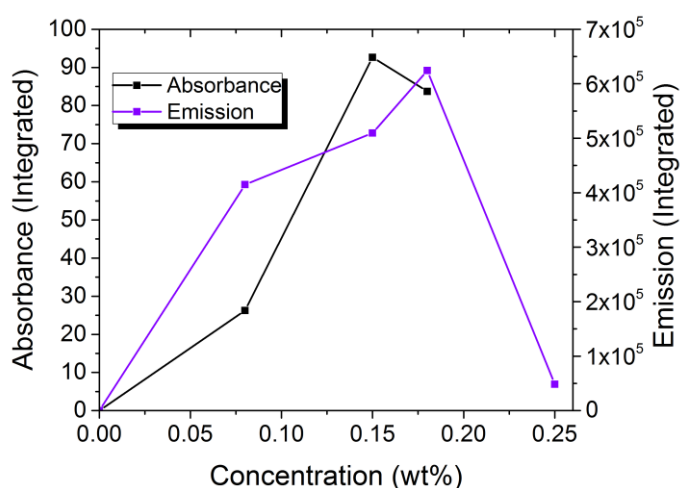


Figure 4.8: Integrated Absorbance and Integrated Emission at various concentrations for Lumogen violet thin-film

The absorbance peak of Violet shifts from a peak at 377 nm to an emission peak of 439 nm, a downshifting of 62 nm. An overlap is present between 402 and 412 nm which will cause reabsorbance.

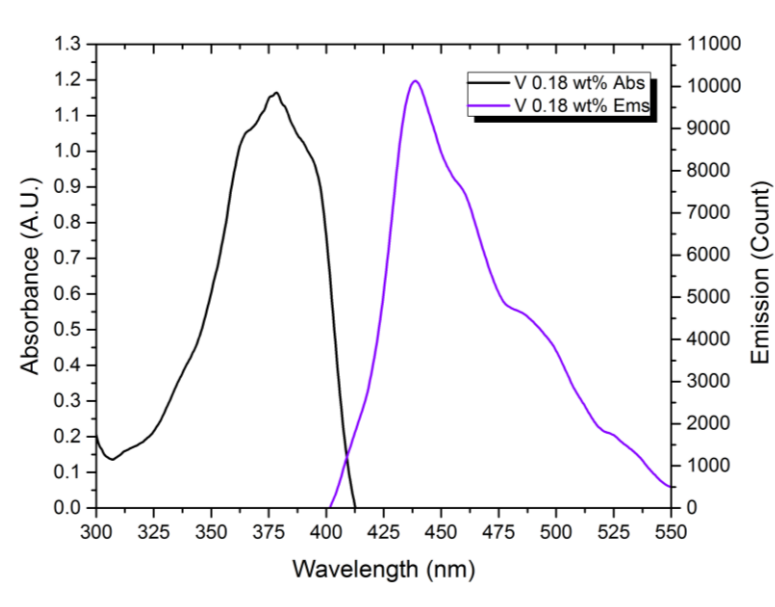


Figure 4.9: Absorbance and emission of Lumogen Violet at 0.18 wt%

Therefore, the optimum concentration for Yellow was determined to be 0.44 wt%, for Orange it was 0.08 wt% and for Violet it was 0.18 wt %.

4.3.2. Multi-Dye Layers

The effect of combining multiple Lumogen dyes in solution into a thin-film was also investigated. Initially, a solution of a third each of Lumogen yellow, orange, and violet at a concentration equal to 0.1 wt% overall was used. The results for this were compared to individual layers of yellow, orange and violet at 0.1 wt% concentration. The layers can be seen below in table 3.

Table 3: Images of Yellow, Orange, Violet and the Mixed layer at 0.1 wt%

Yellow 0.1 wt%	Orange 0.1 wt%	Violet 0.1 wt%	Mixed 0.1 wt%
			

The absorbance and emission of each layer were found using the setup described in sections 3.3.1 and 3.3.2. The absorbance and emission of the mixed layer can be seen in figure 4.10. The mixed layer has a peak at 480 nm with a large range from 300 to 550 nm with an emission peak at 581 nm with a range of 468 to 700 nm. This creates a large overlap between 468 and 550 nm. The absorbance begins where the violet absorbance also begins.

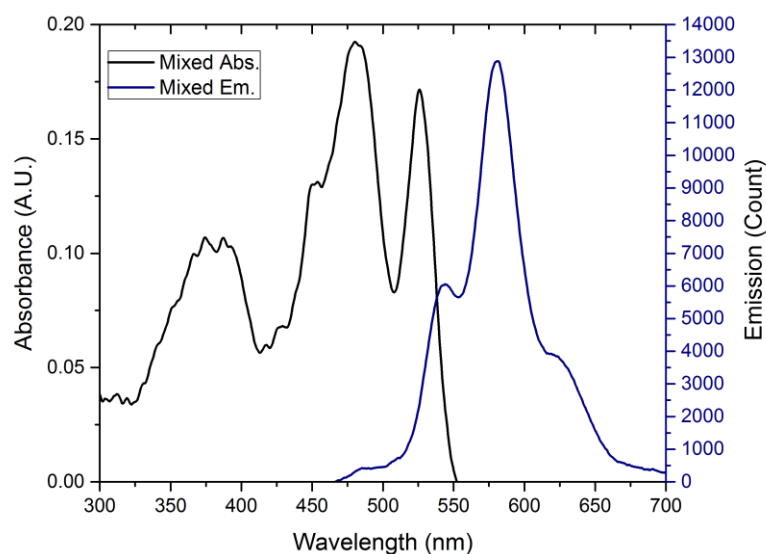


Figure 4.10: Absorbance and emission of mixed layer containing Lumogen yellow, orange, and violet at 0.1 wt% concentration

The absorbance of the mixed layer, with overall concentration 0.1 wt%, when compared to each individual component, shown below in figure 4.11, is at a much larger range. Each individual component is also at 0.1 wt%. Consequently, the height of the absorbance peaks is not as large as the organic dyes when not combined with each other. This is due to the reabsorbance present due to low Stokes shift, which created a large overlap of the absorbance and emission.

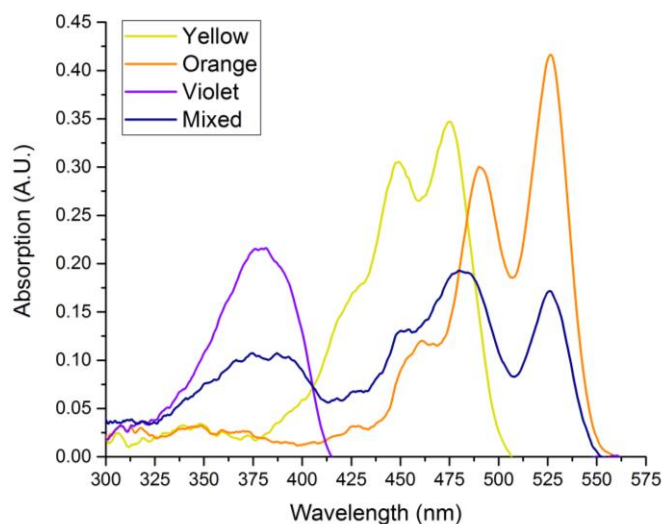


Figure 4.11: Absorbance of Lumogen yellow, orange, violet and mixed layer containing all three

To determine if the absorbance curve attained for the mixed layer, with three dye components adding up to 0.1 wt%, is as anticipated, a curve was calculated, shown in figure 4.12. The absorbance results from each layer, with concentration 0.1 wt%, were added together and divided by three, as they were combined in equal quantities. This curve when plotted against the experimental results are very similar.

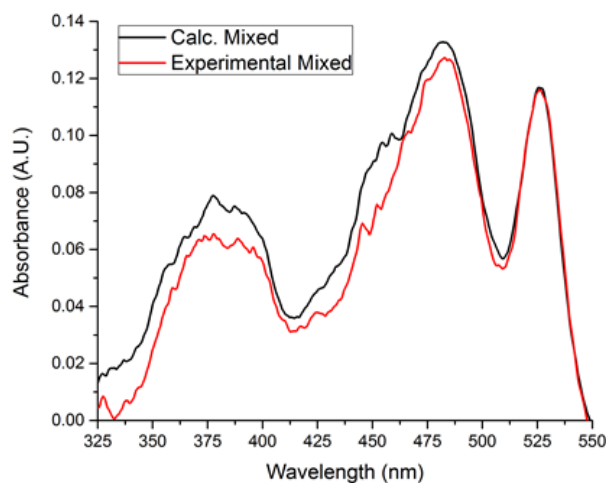


Figure 4.12: Mixed sample experimental results compared against calculated

The emission peak of the Mixed layer is blue shifted 1 nm off the emission peak of Lumogen orange. From the emission results, it can be seen that when a sample consists of materials which have various emission peaks, the resultant emission curve will take on the properties of the

samples at longer wavelengths without the same magnitude. As shown in figure 4.13, the mixed sample has properties from the peak in the yellow sample and the peaks present in the orange sample. Further tests were performed consisting of only two dyes – a thin-film containing violet and orange and a thin film of violet and yellow. When the characteristics were measured, they too had emission peaks matching the dye with the longest wavelength.

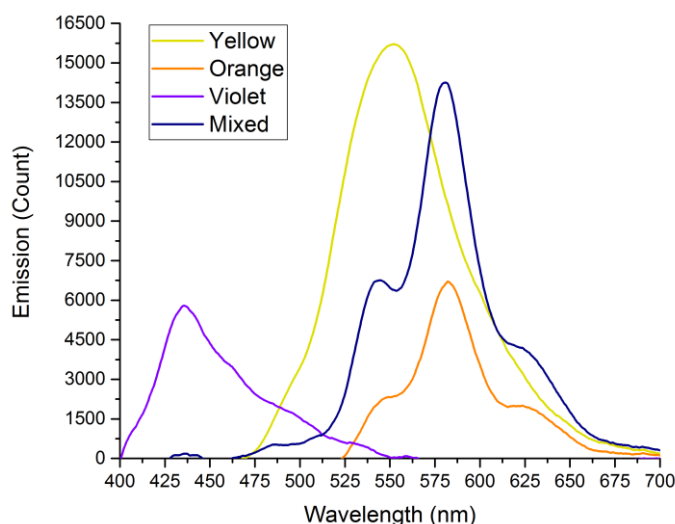


Figure 4.13: Emission of Lumogen yellow, orange, violet and mixed layer containing all three

4.3.3. Outdoor Exposure

The layers which had their concentrations optimised were placed outdoors between the period of the 6th of December to the 12th of March 2018 in a setup shown in figure 4.14. The optimised concentrations were 0.44 wt% for yellow, 0.08 wt% for orange and 0.18 wt% for violet. The average irradiance in this time was 164 W/m² but reached maxima of 846 W/m². Weather conditions during these tests varied from clear days to snow.

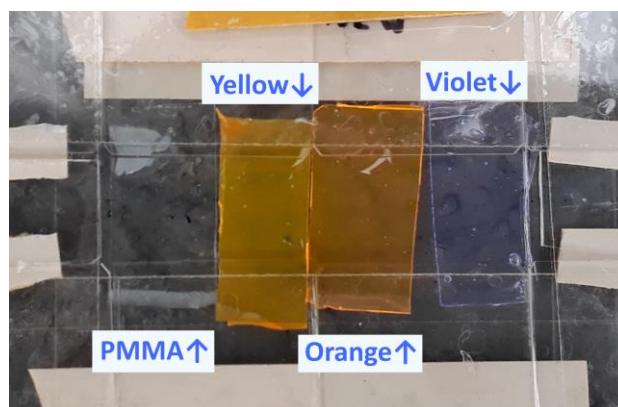


Figure 4.14: Samples placed outdoors in holder with window on top. L-R: PMMA, yellow, orange, and violet

The absorbance and emission were taken for each sample after outdoor exposure. The change in the absorbance and emission curves were observed with each measurement and the degradation determined comparing with the integral of the curve with no exposure.

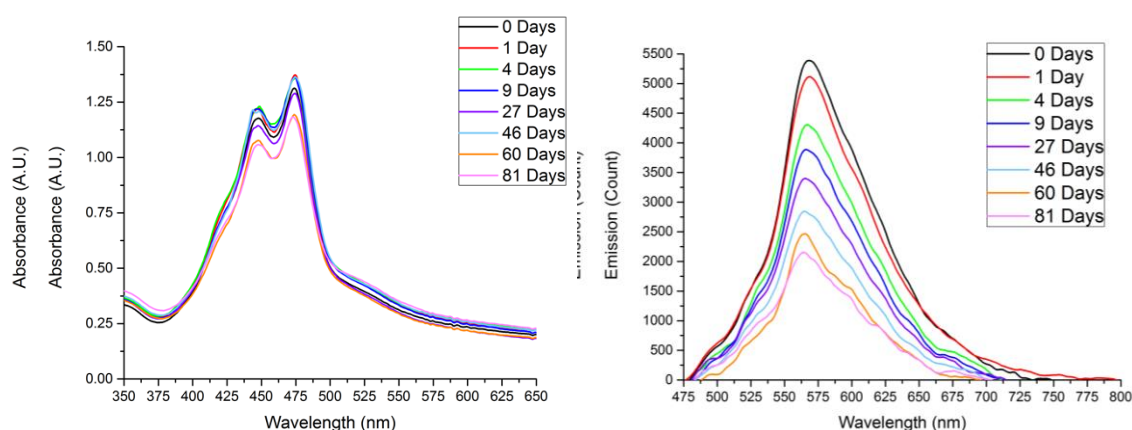


Figure 4.15: Left: Absorbance and Right: Emission of Lumogen Yellow after exposure from 0 to 81 days

It was found in figure 4.15 that the absorbance spectra of yellow reduced by 75% and the emission reduced by 64%. The reduction is clearer for the emission despite being a smaller value.

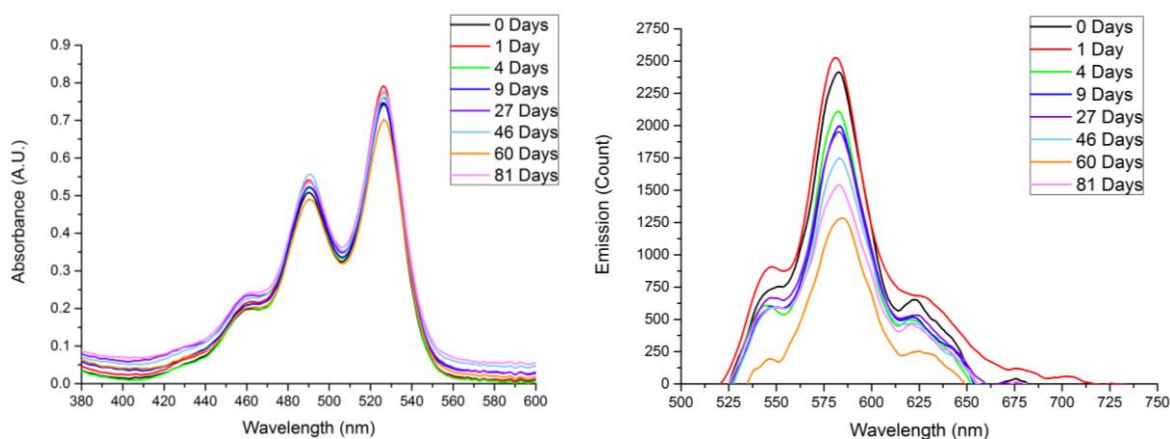


Figure 4.16: Left: Absorbance and Right: Emission of Lumogen Orange after exposure from 0 to 81 days

Shown above in figure 4.16, for Lumogen orange the absorbance reduced by only 0.22 % while the emission reduced by 31%.

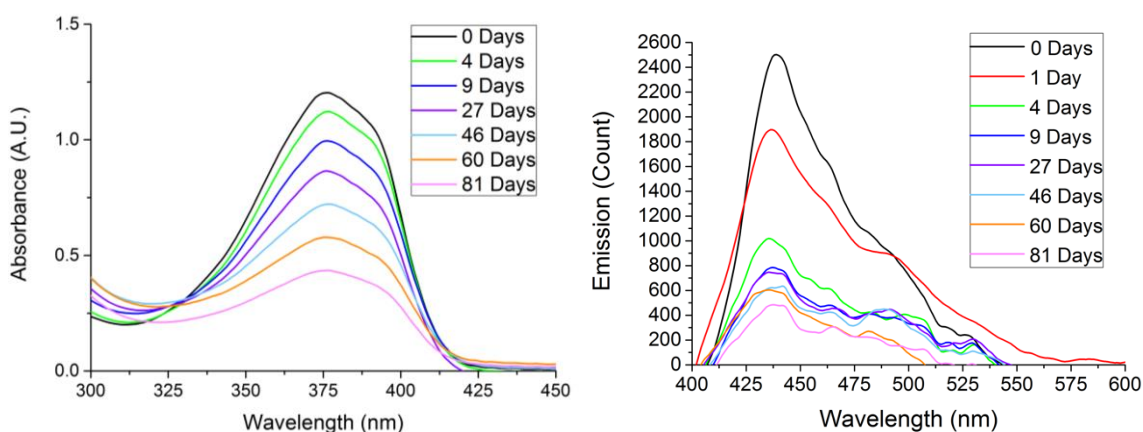


Figure 4.16: Left: Absorbance and Right: Emission of Lumogen Violet after exposure from 0 to 81 days

Finally, in figure 4.17, Lumogen violet had a 58% reduction in absorbance and an 82% reduction in emission over the period shown.

4.3.4. External Quantum Efficiency Measurements

EQE measurements were performed on the optimised concentration determined as described in section 3.5. Yellow with a concentration of 0.44 wt%, orange with a concentration of 0.08 wt%, and violet with a concentration of 0.18 wt%. The readings were taken of the bare Si cell, then the cell with a PMMA layer adhered on top, and then with each different optimised dye adhered on Si cells. A thin layer of PMMA was used as adhesive between the cell and the different layers,

for which the transmission is shown in figure 4.18 below. Figure 4.19 shows the full range of recordings from 300 to 1100 nm.

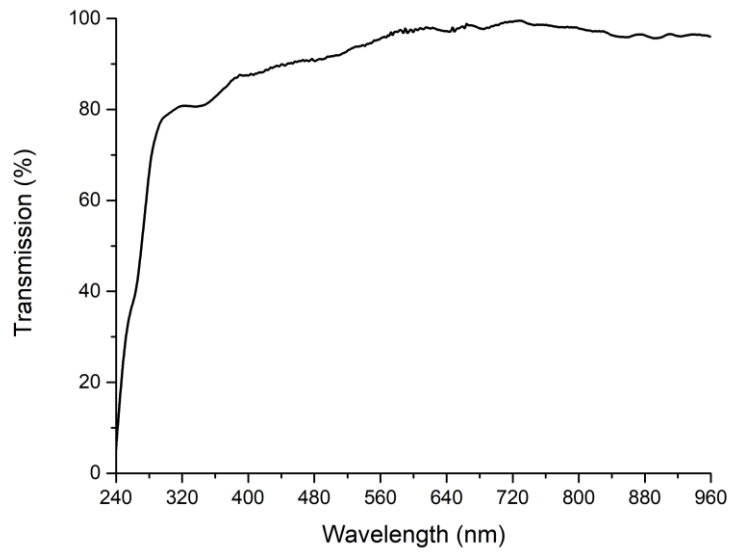


Figure 4.18: Transmission of PMMA used as host material and adhesive between Si cell and LDS layer

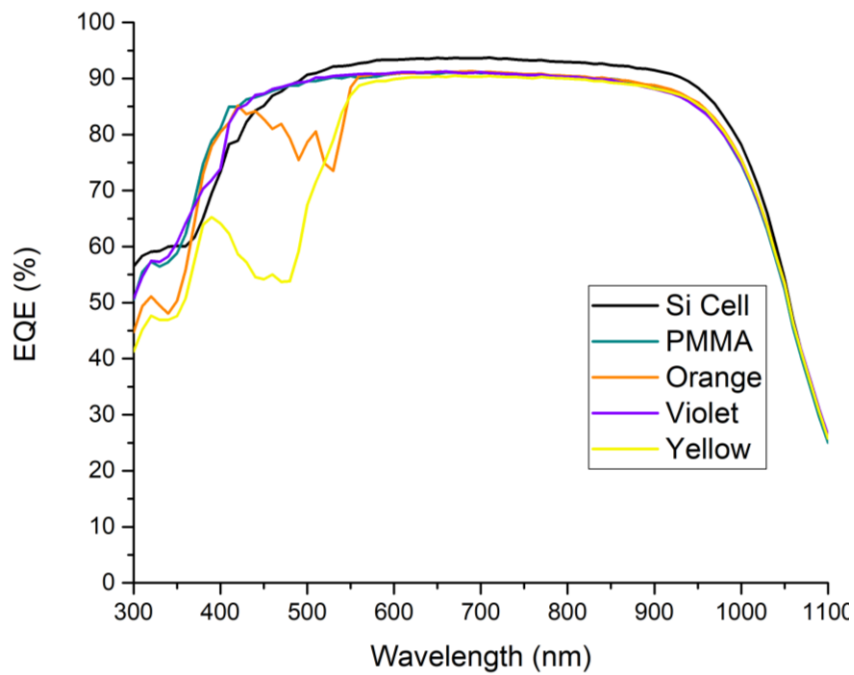


Figure 4.19: EQE curves of Si cell compared with various Lumogen dyes at their optimised concentration, as well as a blank PMMA layer, on Si cells.

The region in which the down-shifting process is occurring is between 300 to 600 nm, which is focused on in figure 4.20. It is very clear from the orange and yellow samples that there is a self-

absorption effect and escape cone losses between 380 to 600 nm which caused a significant decrease in the EQE compared to the bare Si cell. The largest decrease for orange was 18.6 % at 530 nm and for yellow was 34.0 % at 470 nm. This reabsorption is also present for the violet sample in the region of 380 to 410 nm but was only 7.3 %. The Si cell already had a very large EQE in the UV region with a range of 56.5% to 73.3% which unfortunately led to a decrease in EQE for every sample below 350 nm in the comparison.

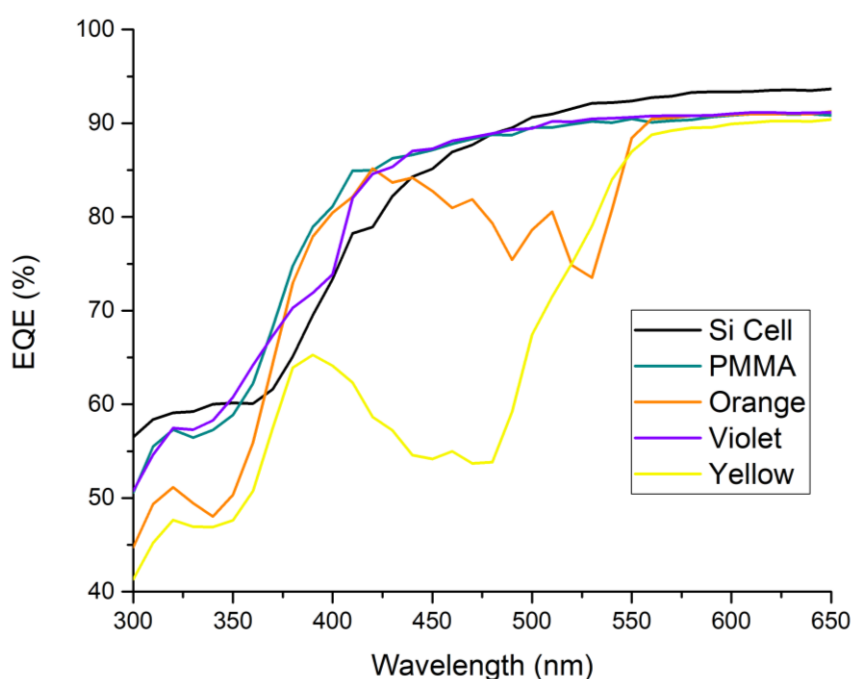


Figure 4.170: EQE curves of Si cell compared with various Lumogen dyes at their optimised concentration, as well as a blank PMMA layer, on Si cells focused on range where LDS absorbs

The EQE was integrated between the range of 300 nm to 650 nm and compared in figure 4.21. No enhancement of the EQE was found for the orange and yellow layers placed on the Si cell, the reduction being particularly significant for yellow. Violet provided a very slight enhancement as it has a greater EQE between 348 to 475 nm. Unfortunately, this gain is nearly entirely offset by the reduction in EQE between 300 to 348 nm and 475 nm onwards. The PMMA layer by itself provided the greatest, albeit slight, enhancement out of all the samples due to the EQE being greater than the Si cell between 355 to 475 nm. Over the range, PMMA consistently had an EQE higher than all the samples tested.

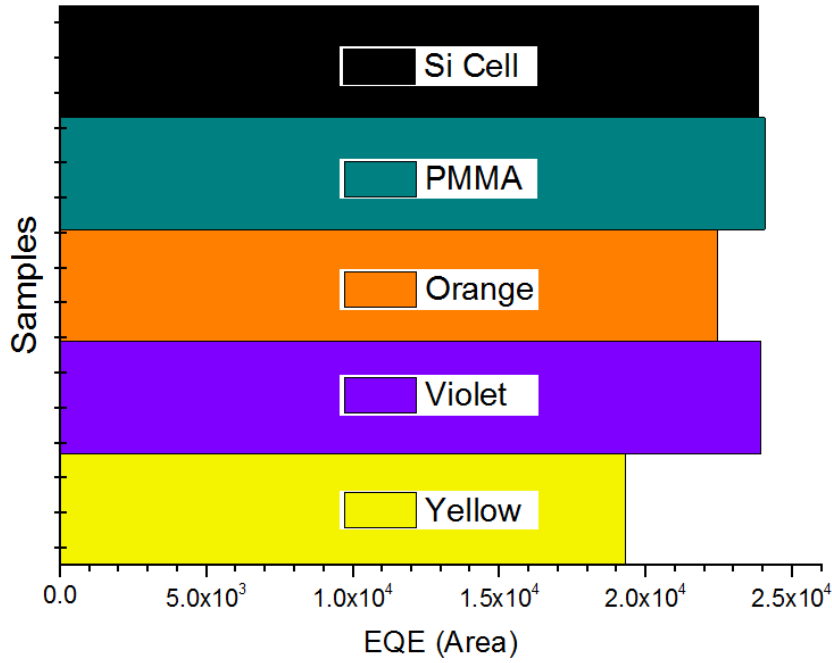


Figure 4.21: Integrated EQE spectra of Si cell with layers of PMMA and Lumogen Dyes placed on top as LDS layer

While the optimised samples were shown not to be suitable for a Si cell with an already high EQE, if the samples were placed on other cells such as DSSC or CdTe, or a Si cell with a lower response in the UV region, the samples may be more suitable and provide an overall enhancement. First, the EQE obtained for violet on the original Si cell is compared to the EQE of the Si cell used in H. Ahmed's thesis, along with their CdTe and DSSC EQE data [31]. This is shown in figure 4.22. In terms of Si cell, the cell labelled 'Si Hind' has a much lower EQE response in the UV region, which would be beneficial for the violet layer and cause a greater increase. For the DSSC and the CdTe cell, other dyes would be more suitable as the range in which violet emits is not where the EQE is highest for these cells.

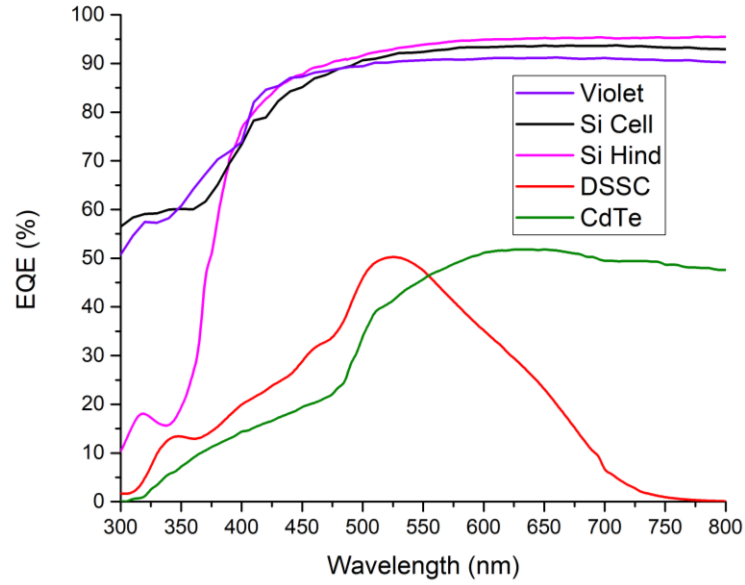


Figure 4.22: Violet and Si cell data compared to Si cell, DSSC and CdTe cell from H. Ahmed's previous work

The orange layer sample is compared to the same data in figure 4.23. It is shown that orange would be more suited to a CdTe or DSSC. CdTe overall has a lower EQE than Si, so the introduction of a layer could be more beneficial. The emission of orange is from 525 to 700 nm, which matches the region of DSSC which has a low EQE. However, the reabsorption which occurs in orange matches the wavelength at which the EQE of DSSC is maximum. Therefore, orange is well suited to a DSSC cell if this enhancement is greater than the reabsorption present.

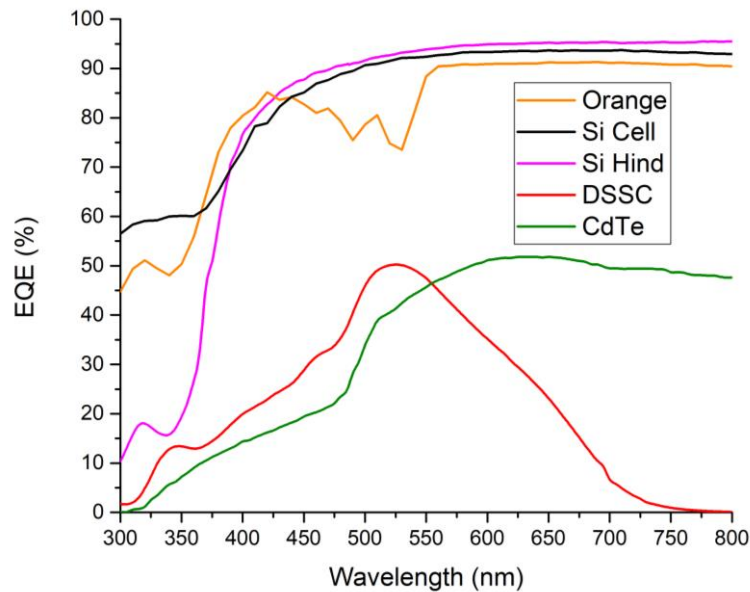


Figure 4.23: Orange and Si cell data compared to Si cell, DSSC and CdTe cell from H. Ahmed's previous work

When yellow Lumogen is compared to the same samples, as in figure 4.24, it is also a suitable sample for DSSC cells as it absorbs and emits in the regions in which the EQE is lowest for DSSC. Also, the CdTe cell's EQE is lowest from 300 to 480 nm, which covers the region in which yellow Lumogen absorbs and could allow some enhancement to be produced. This sample still would not suit 'Si Hind' as the reabsorption region is unsuitable for the cell.

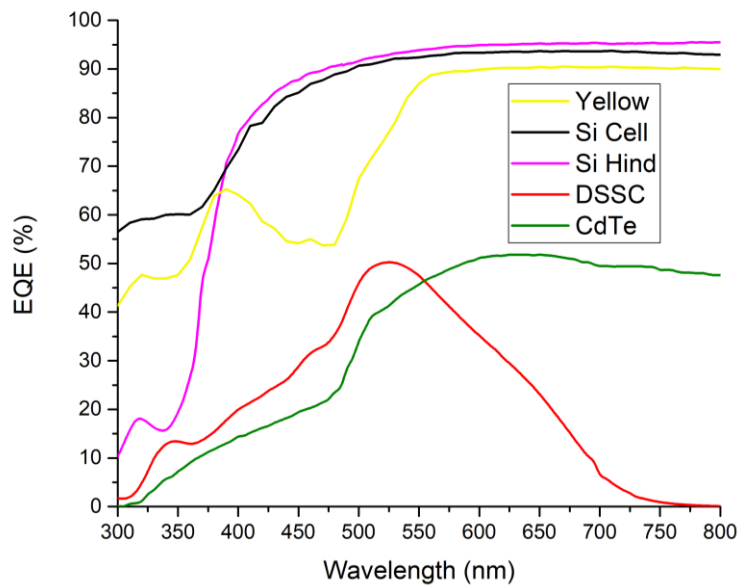


Figure 4.24: Yellow and Si cell data compared to Si cell, DSSC and CdTe cell from H. Ahmed's previous work

Many sources of error were identified while taking the EQE measurements. Errors can arise from the presence of bubbles in the adhesive layer of PMMA between the layer and the cell, and most noticeably from the placement of the sample in the EQE setup. As shown in figure 4.25, a PMMA sample was placed as flat as possible in the first reading, but in the second reading it was slightly angled and caused a significant reduction in the EQE for the sample. It is vital to ensure the layer is placed as flat as possible in the EQE setup. Overall, the change in angle caused a 5% overall reduction in the EQE over the entire spectra, and a difference of 12% at a single wavelength.

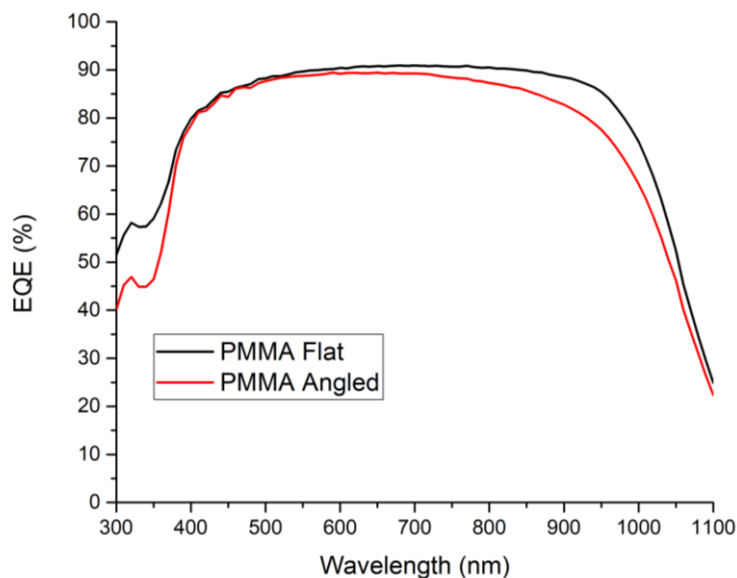


Figure 4.25: EQE of a PMMA sample placed flat and then placed at an angle

4.4. Quantum Dot Characterisation

Due to the limitations presented by the Lumogen dyes, focus moved to quantum dots (QDs). Two kits of QDs were purchased from PlasmaChem; Hydrophobic CdSe/ZnS Quantum Dots kit, to be referred to as Kit 1, and the hydrophobic Zn-Cu-In-S/ZnS Quantum Dots Kit, to be referred to as Kit 2. As no absorbance, emission, or QY data was provided from the manufactures, this information needed to be determined before introduction into a thin-film. After the quantum yield of each QD was determined, which QD should be introduced into the thin-films can be chosen.

4.4.1. Absorbance and Emission Measurements

Kit 1 contains 5 mg of QDs which emit at 480, 520, 560, 600, and 650 nm. The QDs are mixed in 5 ml of toluene. The absorbance and emission measurements were performed using the method described in sections 3.3.3 and 3.3.4. Unfortunately, QD650 did not successfully dissolve in toluene so no measurements could be taken. The absorbance and emission for kit 1 is shown below in figure 4.26 to 4.29.

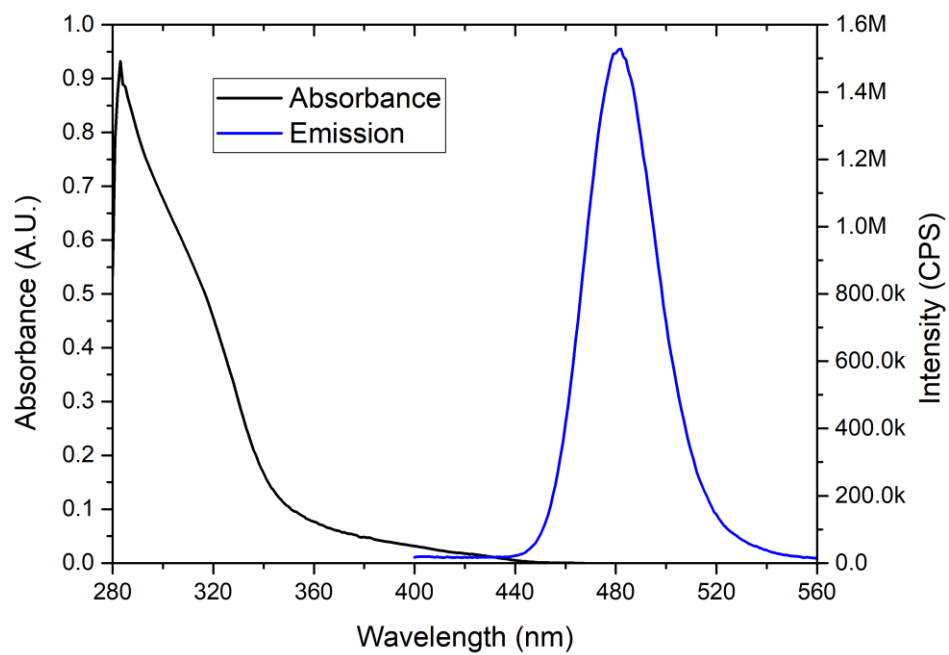


Figure 4.26: Absorbance and emission of QD480

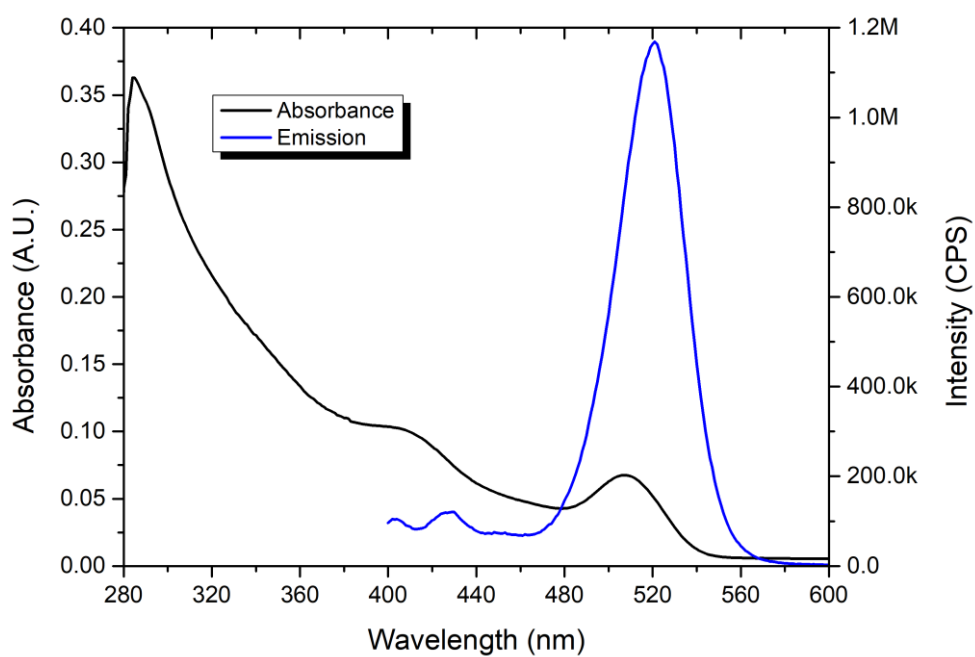


Figure 4.187: Absorbance and emission of QD520

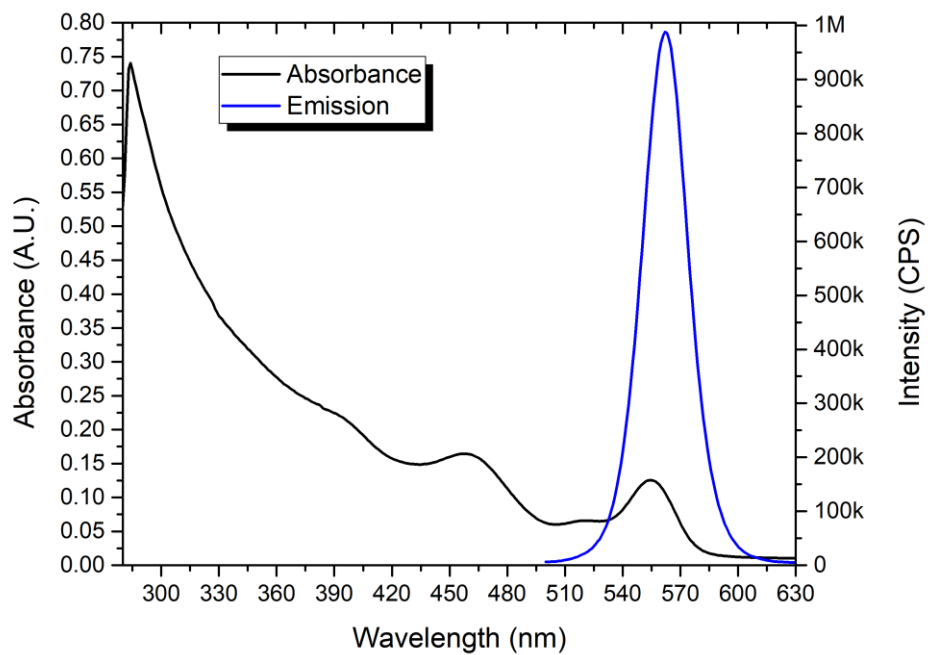


Figure 4.198: Absorbance and emission of QD560

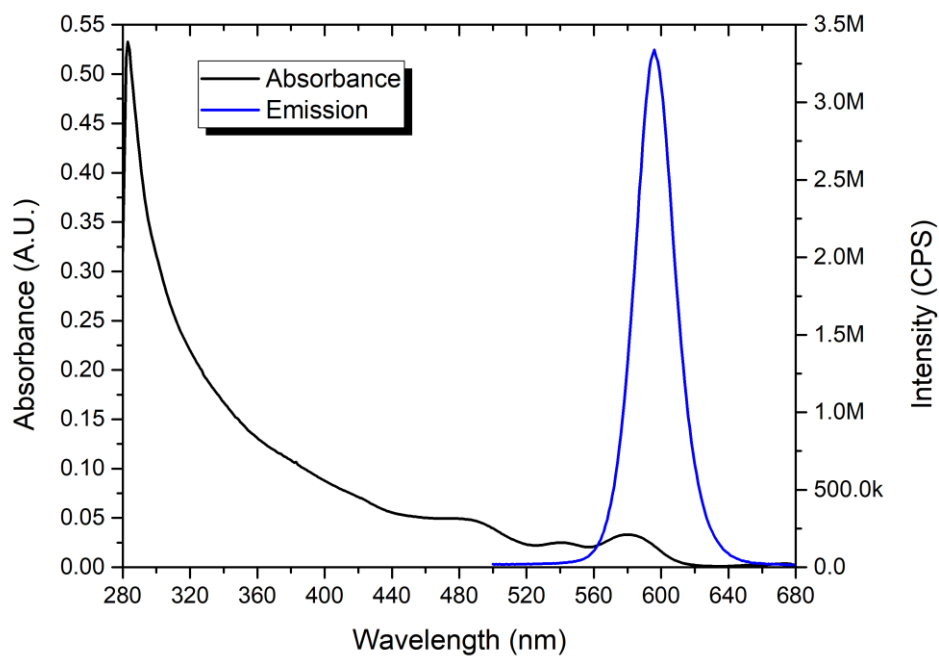


Figure 4.29: Absorbance and emission of QD600

The measurements were also taken for kit 2 which emit at 550, 590, 610, and 670 nm using the same method used for the previous QD kit described in sections 3.3.3 and 3.3.4. The results are shown in figures 4.30 to 4.33.

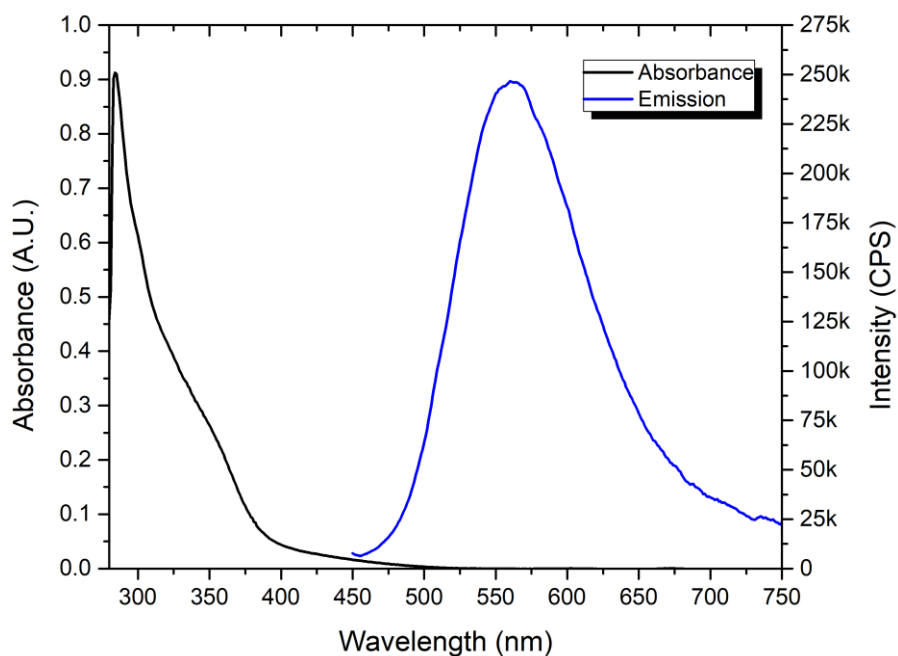


Figure 4.200: Absorbance and emission of QD550

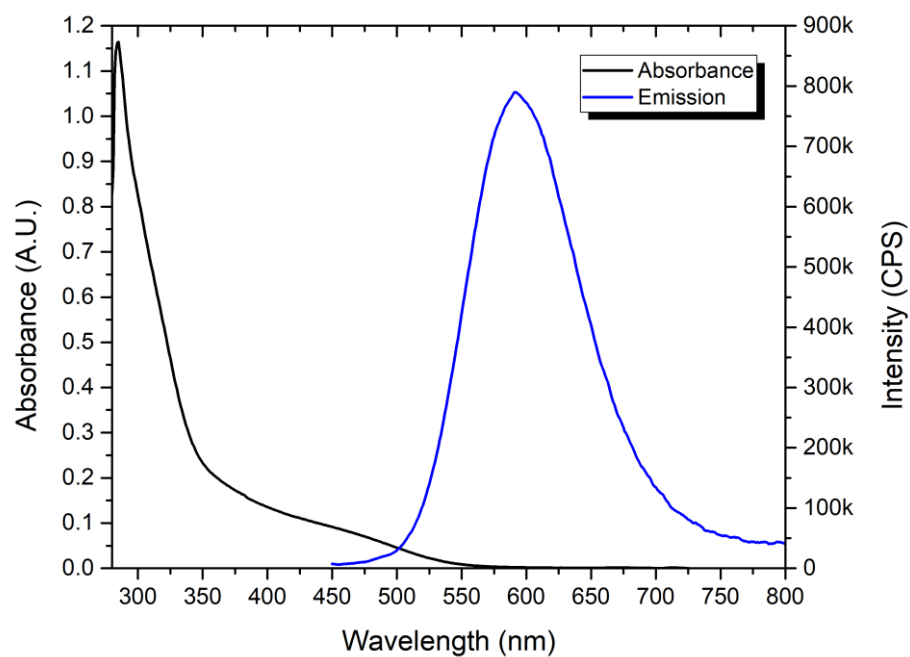


Figure 4.31: Absorbance and emission of QD590

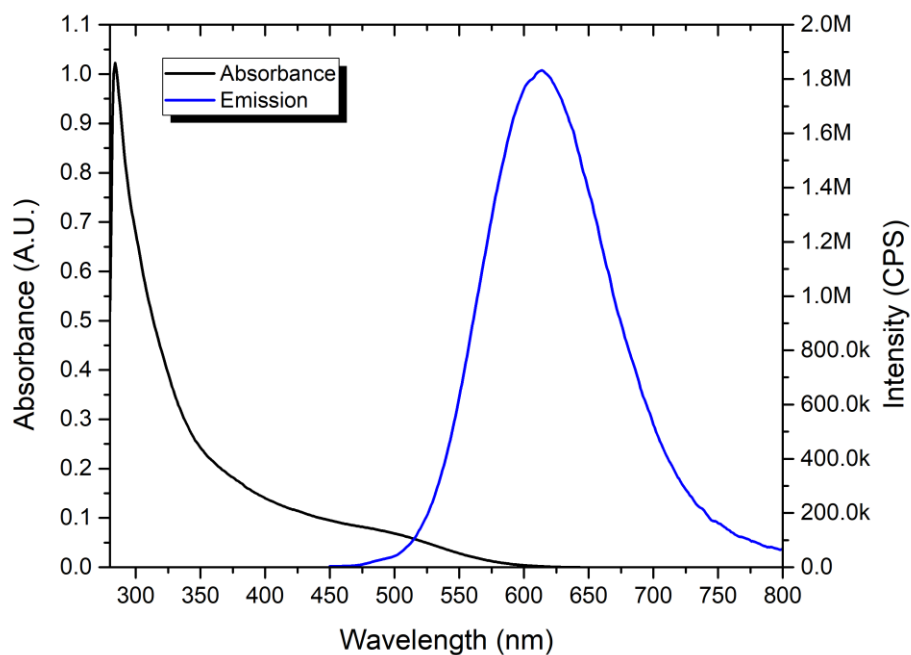


Figure 4.212: Absorbance and emission of QD610

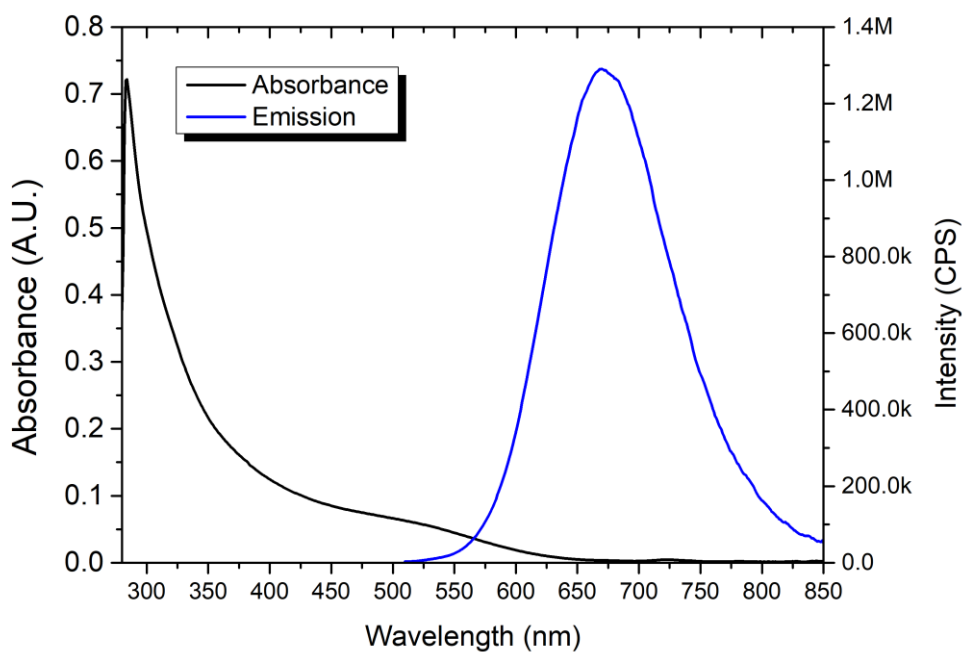


Figure 4.223: Absorbance and emission of QD670

4.4.2. Quantum Yield

The quantum yield (QY) of the QDs in solution took multiple attempts to get consistent and reliable results. Each method and setup used will be described and the results described.

4.4.2.1. Quantum Yield with StellarNet Inc and LabSphere Integrating Sphere Setup

The first tests conducted used a StellarNet Inc setup to measure absorbance, which worked perfectly, and a LabSphere Integrated Sphere for emission measurements. The method used for this measurement is described in 3.3.1 and 3.3.2. However, as this setup does not include a photomultiplier, the emission peak obtained was unreliable and contained a lot of noise as there were not enough photons present. The two standards; harmane and harmine, were tested.

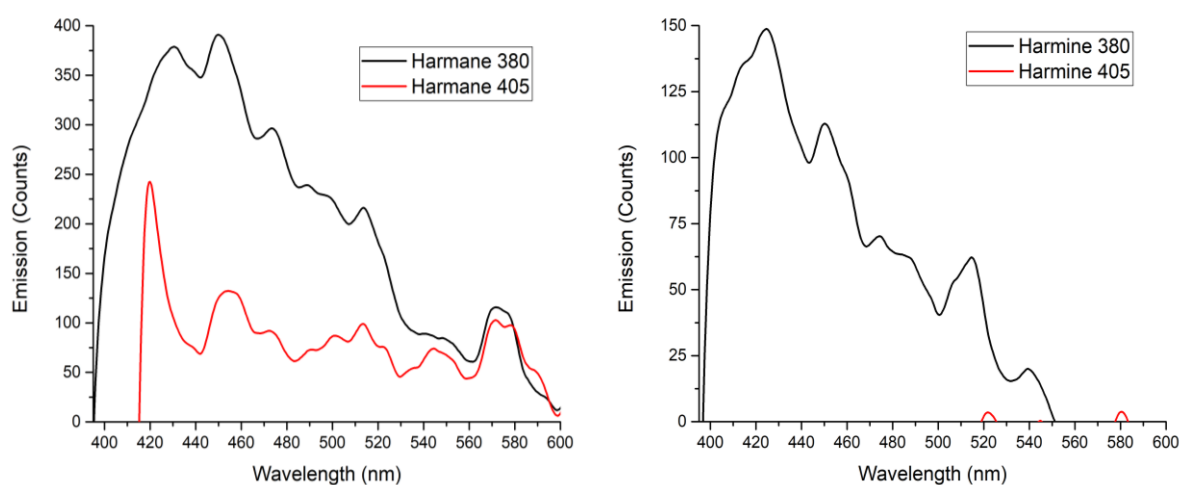


Figure 4.34: Emission of harmane (left) and harmine (right) excited at 380 and 405 nm

From the two graphs shown in figure 4.34 above, the emission counts of both samples were very low. Harmane reached a maximum of 400 counts while harmine only reached a maximum of 150 counts. Both samples were excited at 380 and 405 nm to ensure the excitation wavelength was not the cause of the low response. The spectra produced are also noisy with multiple peaks being produced. From this, it was determined to move to a setup which included a photomultiplier tube.

4.4.2.2. Quantum Yield with Lambda-35 and Fluoramax-4

The second setup uses the Lambda-35 for absorbance measurements and the Fluoramax-4 was used for emission measurements as it contains a photomultiplier tube. The method for taking measurements on this equipment is described in 3.3.3 and 3.3.4. Using the first method described in section 3.6, with the varying concentration shown in figure 4.35 below, was not providing repeatable results for determining the QY. When harmane was used as the standard, the QY obtained ranged from 1.7% and 9.9% while for rhodamine the QY ranged from 2.6% to

49.8%. Due to difficulty sourcing additional cuvettes to use in this test to increase the reliability of results, a new method was found.

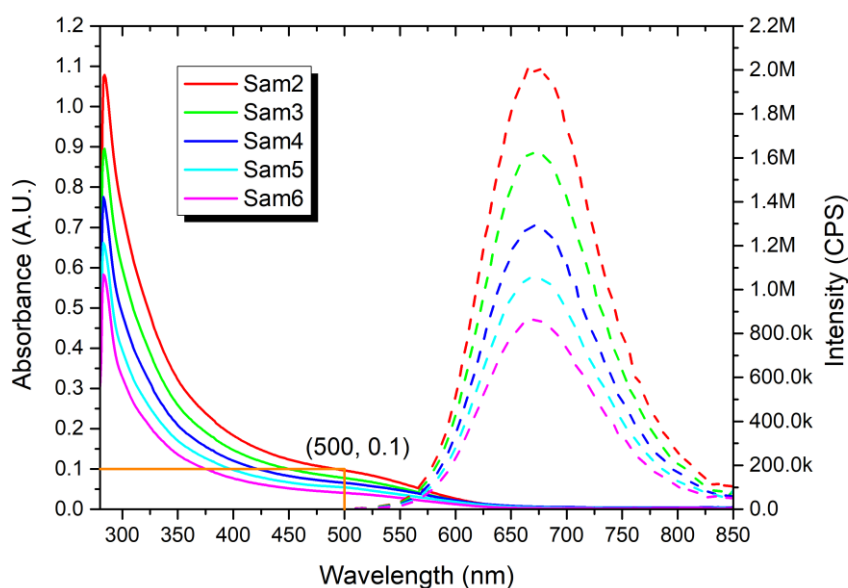


Figure 4.235: Absorbance and emission of QD670 over various concentrations to determine QY

4.4.2.3. Quantum Yield with Fluoramax-4 containing Integrating Sphere Accessory

The final setup to determine the QY used the Fluoramax-4 from the previous section with an Integrating Sphere accessory. When taking measurements, it is important to obtain three consistent readings for a sample. Readings were considered consistent if within 10% of each other. Initially, harmine was tested to ensure the setup was working correctly.

Table 4: Quantum yield values obtained for harmine in Fluoramax-4 with Integrating Sphere

Test no.	Quantum Yield (%)
1.	38.2
2.	36.8
3.	34.7
4.	37.8

The results shown in table 4 above gave an average QY of 36.9% which is within 10% of the expected value of 45% [37]. This allowed tests on the remaining eight samples from kit 1 and kit

2 to be conducted, as shown in table 5. Unfortunately, the highest obtained QY was only 33.8% which was for QD670. The best QDs from the two kits were and QD600 from kit 1 and QD610 and QD670 from kit 2 as they had the highest QYs.

Table 5: Quantum yield values obtained for kit 1 and 2

<u>Kit 1 – CdSe/ZnS QDs</u>		<u>Kit 2 – Zn-Cu-In-S QDs</u>	
Quantum Dot	Quantum Yield (%)	Quantum Dot	Quantum Yield (%)
<i>QD480</i>	6.7	<i>QD550</i>	10.0
<i>QD520</i>	3.1	<i>QD590</i>	10.4
<i>QD560</i>	0.1	<i>QD610</i>	27.5
<i>QD600</i>	25.1	<i>QD670</i>	33.8

4.5. Conclusion

The optimum ratio of PMMA to toluene was found to be 1:2.7 to create a thin-film with a thickness of 49 μm . 375 μl of the host material was spun at 1000 RPM for 240 s dwell time and after 16 hours in a fume cupboard, the thin-film was easily removed from the substrate for characterisation measurements.

When Lumogen dyes were introduced, the optimum concentrations were found. Yellow was optimised at 0.44 wt%, orange at 0.08 wt% and violet and 0.18 wt%. When these dyes are combined at an equal ratio with total concentration 0.1 wt%, the mixed layer absorbance is comprised equally of each dye, whereas the emission curve will take on the properties of the samples at longer wavelengths without the same magnitude.

After the optimised concentrations were determined for yellow, orange, and violet, the samples underwent an outdoor exposure test for 81 days. The absorbance of yellow reduced by 75% and the emission reduced by 64%. However, orange only reduced 0.22% in absorbance, but 31% for emission. Finally, violet absorbance reduced 58% and the emission had the largest reduction at 82%.

The optimised samples were then also glued to a Si cell using a thin layer of PMMA and their EQE was determined. The bare Si cell had a large EQE in the UV region, which led to a decrease in EQE for each sample below 350 nm. There was also a decrease in EQE in particular regions due to self-absorption and escape cone losses, for example orange decreased 18.6 % at 530 nm, and yellow decreased 34.0 % at 470 nm. Overall, violet provided a very slight enhancement, which is nearly offset by the reduction in EQE. PMMA had the largest enhancement due to the EQE being larger than the Si cell between 355 to 475 nm. When the samples were compared to other cells, it was determined that violet suits a Si cell with a lower EQE response in the UV regions. Orange is more suited to a DSSC cell due to the region in which the losses are located; the enhancement may be greater than the reabsorption present in this cell. Finally, yellow is more suited to a CdTe cell as the EQE of a CdTe cell is lowest from 300 to 480 nm, which is where yellow absorbs. This could allow some enhancement to be produced.

Finally, the absorbance and emission were determined for a range of quantum dots; one kit of Hydrophobic CdSe/ZnS QDs (which emit at 480, 520, 600, and 650 nm) and the other is hydrophobic Zn-Cu-In-S/ZnS QDs (which emit at 550, 590, 610, and 670 nm). The quantum yield was then determined for each. From kit 1, QD480 had a QY of 6.7 %, QD520 was 3.1 %, QD560 was the lowest at 0.1%, and the highest for kit 1 was QD600 at 25.1 %. For kit 2, QD550 had a QY of 10.0 %, QD590 was 10.4 %, QD610 was 27.5%, and the highest QY overall was from QD670 at 33.8%.

Chapter 5 - Discussion and Conclusions

5.1.1. Discussion Host Material Optimisation

PMMA was chosen as the polymer to be used for the thin-films. As the PMMA used is very viscous, toluene needed to be added to make it easier to work with. After varying the concentration of PMMA and toluene, the method used for the spin-coater was also varied. Current findings show that a ratio of 1:2.7 of toluene to PMMA forms a thin-film of 50 μm thickness. This is formed with a method of 1000 RPM for 240 s and only 375 μl of host material on the substrate. If there is less toluene in the host material, the layer formed on the substrate is thin in the centre and wrinkles form at the sides due to stretching during the spin.

5.1.2. Organic Dye Characterisation

Lumogen dyes were then successfully introduced to the thin-film. The concentration of multiple dyes was optimised. Lumogen Yellow was optimised at a concentration of 0.44 wt%, orange was optimised at a concentration of 0.08 wt% and violet at 0.18 wt%. This was determined by varying the concentrations and integrating the absorbance and emission. The concentration at which the absorbance and emission is at the highest and before reabsorbance occurs was determined to be the optimum concentration. Layers containing multiple dyes were also formed. It was shown that the absorbance range encompasses all dyes equal to the ratio used. It was also shown that the emission spectra takes the form of the dye with the longest wavelength emission. This is in agreement with the findings from Davos et al [38] in which the absorbance and emission of a layer which containing violet and yellow dye was determined. Davos determined that the emission occurs predominately from yellow which indicated an efficient excitation energy transfer from violet to yellow. Mixing dyes can also be very beneficial depending on the cell being used, the absorbance and emission spectra can be changed by combining the dyes to make it a more suitable material for the cell. This was also shown, as mentioned earlier, by Parel et al [24] when it was shown that a yellow-orange mixture increases current output by 20%.

The optimised single-dye thin-films were placed outdoors for three months, the longest real-world test of Lumogen dyes. Immediately, their low photostability was prominent. Organic dyes have

low photostability, but despite improvements in recent years the dyes suffer from UV exposure. These tests were performed in a wide range of conditions with the maxima irradiance reaching 846 W/m^2 . The optimised Yellow thin-film saw reductions of 75% and 64% for the absorbance and emission respectively. Orange only saw a reduction of 0.22% and 31% for absorbance and emission relatively. Finally, Violet had the largest reduction with 58% for absorbance and 82% for emission. These reductions are in agreement with the results obtained by Ahmed et al [31] in which a violet/PMMA LDS layer was placed in a sun chamber for 72 hours. The peak absorption reduced by 80% in the first 24 hours. The EQE was determined for the optimised single dye layers on Si cells. As the UV region of the bare Si cell already had a high EQE, only PMMA and violet showed a slight enhancement. The enhancement of the PMMA layer was due to the EQE being greater than the Si cell between 355 and 475 nm. For violet, the EQE only increased between 348 and 475 nm. However, there is a large reduction present for the remaining spectrum, which caused the EQE enhancement to be so low. Yellow and orange experienced large decreases in the EQE due to reabsorption. The largest decrease was for orange at 18.6% at 530 nm, and for yellow it was 34 % at 470 nm. As this was a Si cell with an already high EQE, the results obtained were compared to DSSC, CdTe cells, and a Si cell with a lower EQE. It was shown that yellow would be more suitable for CdTe or DSSC cells as the region in which the reabsorption occurs is not where the EQE is maximum. This finding is in agreement with the findings from the Ahmed et al [22] paper discussed previously in this thesis. Ahmed found improvements when a pLDS layer of silver nanoparticles and Lumogen yellow was placed on a CdTe cell. For orange, the reabsorption occurs at the maximum EQE for the DSSC cell, so it is vital that the enhancement can cancel out the reabsorption effects present as increasing the efficiency is the main objective. This led on to work with QDs.

5.1.3. Quantum Dot Characterisation

The absorbance and emission measurements were taken for the two kits of quantum dots. It was shown that for most samples in the hydrophobic Zn-Cu-In-S/ZnS kit there was a large overlap present between the absorbance and emission, which will cause some reabsorbance. For kit 2,

which comprised of CdSe/ZnS, there was less overlap present between the absorbance and emission.

After difficulty in characterising the QY of the QDs, it was shown that the QD610 and QD670, which contain Zn-Cu-In-S, have a QY of 27.5% and 33.8% respectively, and that QD600 was the highest for CdSe/ZnS QDs at 25.1%. Unfortunately, a majority of samples had QYs ranging from 10.4% to as low as 0.1%. When examining the absorbance and emission of the samples with high QY, none of the QDs spectra match well with the Lumogen dyes, so combining the two is not recommended. Other QDs would need to be sourced with a higher QY at a lower emission peak.

5.2. Conclusion

Luminescent down-shifting layers consisting of PMMA and a range of organic dyes were successfully spin-coated. Tests were conducted combining each dye in an equal amount in one layer, then examining the absorbance and emission. It was shown that the absorbance range encompasses all dyes equal to the ratio used. It was also shown that the emission spectra take form of the dye with the longest wavelength emission. The dyes were then optimised separately, Lumogen Yellow optimised at a concentration of 0.44 wt%, Lumogen Orange at 0.08 wt% and Lumogen Violet at 0.18 wt%. Additionally, these optimised samples were placed outdoors for a period of 81 days and their absorbance and emission measured over the period. It was found that due to the low stability of organic dyes, their absorbance and emission decreased. Yellow thin-film saw reductions of 75% and 64% for the absorbance and emission respectively, Orange only saw a reduction of 0.22% for absorbance and 31% for emission, and finally, Violet had the largest reduction with 58% for absorbance and 82% for emission.

After examining the photostability, the EQE was determined of the optimised sample glued to a Si cell using the same PMMA from earlier. As the UV region of the bare Si cell already had a high EQE, only PMMA and violet showed a slight enhancement. Due to reabsorbance and escape cone losses, there were large reductions in the dye samples at particular wavelengths; such as

orange decreasing 18.6% at 530 nm and yellow decreasing 34 % at 470 nm. Unfortunately, due to a large EQE in the Si cell below 350 nm, there was a decrease in the EQE for every sample below 350 nm. It was shown that if the samples were placed on a Si cell with a lower EQE, a DSSC cell, or a CdTe cell, the orange and yellow samples could be better suited to a DSSC cell if the enhancement is greater than the reabsorbance present. Additionally, the yellow sample is more suited to the CdTe cell than the Si cell.

Due to the low stability in organic dyes, attention turned to QDs for use in future work. The QDs examined were sourced from two kits of QDs; Hydrophobic CdSe/ZnS QDs denoted as kit 1, and hydrophobic Zn-Cu-In-S/ZnS QDs denoted as kit 2. Kit 1 emits at 480, 520, 560, 600, 650 nm, and kit 2 at 550, 590, 610, 670 nm. As the absorbance and emission was not supplied, it was determined. Furthermore, the QY was determined. The highest QY for kit 1 was found to be 25.1 % for QD600, and for kit 2 it was 33.8 % for QD 670. However, this is too low for inclusion with the organic dyes so other QDs should be sourced with a higher QY and a lower emission peak more suited for the organic dyes used.

5.3. Future Work

For future work it should include:

- Development of plasmonic QD LDS layers. For this, sourcing QDs with a higher QY for integration into an LDS layer with the Lumogen dyes is vital. As shown, the QDs sourced for this project had a very low QY. Therefore, obtaining a range of QDs with a higher QY in the appropriate region to create a plasmonic enhancement for each dye should increase the EQE of a cell.
- Further research should be done on using the other polymers mentioned in the background information for the host material, such as EVA or PVB. When concluding this study, the source of PMMA used is no longer easily found as production has ceased. PMMA powder is another option which could be investigated further to determine if there is a benefit to PMMA powder vs the PMMA epoxy resin used in this study.

- It was also shown that it is vital for an appropriate cell to be sourced. Namely a CdTe or DSSC cell for yellow or orange, or a Si cell with a low EQE in the UV region for violet would see the most benefit from a luminescent down-shifting layer with the Lumogen used in this project.
- Investigate the effect of PMMA to cause an improvement in EQE measurements compared to a bare Si cell.
- Finally, upscaling the dimensions of the LDS layer into a design which can be integrated into the façade of a building should be investigated further. This study only used thin-films with dimensions of 2.5 x 2.5 cm². Increasing the size will come with a whole other range of issues, such as maintaining a constant thickness throughout the layer and easy removal from a substrate. It is vital that large-scale samples are developed so that the true potential of LDS layers can be shown.

Appendix 1

Publications

Conference Proceedings

1. S. Gilligan, H. Ahmed, S. Chandra, and S. J. McCormack, Effects of multiple organic dyes for luminescent down-shifting layers application, EU Photovoltaic Solar Energy Conference and Exhibition (PVSEC), 25-29 Sep 2017, Amsterdam, The Netherlands.
2. Sethi, A., S. Chandra, H. Ahmed, Gilligan, S. and S. J. McCormack, 2017. Phase transfer and polymer compatibility of gold and gold core silver shell nanorods for luminescent solar devices, EU Photovoltaic Solar Energy Conference and Exhibition (PVSEC), 25-29 Sep 2017, Amsterdam, The Netherlands.
3. S. Gilligan, H. Ahmed, S. Chandra, S. J. McCormack, Optimization and Photostability Studies of Luminescent Organic Dyes for Solar Devices, 14th Photovoltaic Science, Applications and Technology Conference C99 (PVSAT-14), 18-19 April 2018, London, UK

Appendix 2

ECTS completed:

Creative Thinking and Innovation (10 ECTS)

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