

Examining Spectral Converters for Emerging Photovoltaic Technologies

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Declaration

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Barry McKenna M.Sc.

Acknowledgements

This part is far more nerve wracking than I expected but I'll start first and foremost with the most important, my supervisor Dr Rachel Evans. Rachels dedication to getting the best out of her students and (oft tested) patience are the only reason I have gotten this far. Her guidance with work has allowed me to mature professionally, and her commitment to fostering a friendly atmosphere within the group has meant I am not only leaving with experience but with friends for life. I can't imagine many other supervisors who would join their new student in a stirring rendition of a Seal song (Kiss From A Rose) on their first group night out, it made me feel right at home. I would like to thank Rachel for allowing me to be part of her group, the last four (and a bit) years have been an amazing experience that without you would not have been possible.

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Abstract

Spectral converters are photoluminescent layers which can selectively absorb solar photons of wavelengths which are not efficiently converted to electricity by a photovoltaic (PV) cell, and re-emit these photons at wavelengths more suitable for use. These materials are attractive for complementary application with PV devices due to the versatility afforded to them by the choice of luminophore which can be tuned to the PV cell in question. The ability of these materials to harvest ultraviolet (UV) radiation and emit it at longer, less harmful wavelengths means they can potentially improve the photostability of emerging PV technologies, in particular, perovskite solar cells (PSCs). PSCs are limited currently by their instability to moisture, which when present in conjunction with light and heat can cause irreversible degradation.

In order to address the current limitations of PSCs, the first part of this work will investigate a two-fold approach of both polymer encapsulation to improve the resistance of the device to moisture-induced degradation (**Chapter 3**) and the addition of luminescent down-shifting (LDS) layers to act as UV-filters (**Chapter 4**). To investigate the requirements of an encapsulant for PSCs, bare perovskite layers were thermally degraded with and without polymer encapsulation. This degradation was monitored by X-ray diffraction, UV/Vis absorption spectroscopy and epifluorescence microscopy. It was found that the water vapour transport rate within the polymer had the greatest impact on its ability to act as an encapsulant for PSCs. Poly(methyl methacrylate) (PMMA) performed the best, with stabilities of over 400 h achieved for elevated temperatures (60 °C) and thus, was used as the host material for the LDS layers coated on the PSCs in **Chapter 4**. LDS coatings applied to $\text{CH}_3\text{NH}_3\text{PbI}_3$ PSCs using the luminophores Lumogen F Violet 570, polyfluorene and 2-(2-hydroxyphenyl)quinazolin-4(3H)-one exhibited enhanced power conversion efficiencies (PCE) and external quantum efficiencies (EQE). The device photostability, however, was not measurably enhanced upon coating due to device degradation caused by alternative degradation pathways (thermal, moisture) occurring on a faster timescale.

The use of nanocrystals for spectral converters was then investigated. The tunable emission properties of $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{I}_x$ mixed-halide perovskite nanocrystals (PNCs) upon dilution was examined in **Chapter 5**. It was determined by photoluminescence spectroscopy and transmission electron microscopy that a red-shift in PNC emission occurred due to aggregation and uncontrolled growth of the PNCs caused by decreasing capping ligand concentration in solution. This growth led to particles with dimensions *ca.* 1 μm and the uptake of the excess iodide bound within the capping ligands. This red-shift occurs independently of the makeup of the precursor solution and is directly related to the iodide content and anti-solvent utilised.

Finally, due to the issues with the solution phase instability of PNCs, in **Chapter 6** CdSe@ZnS/ZnS QDs were investigated as luminophores for large-area luminescent solar concentrators (LSCs). Due to the inhomogeneity of the edge emission observed for these LSCs, a detailed study into the optical characterisation protocols for large planar LSCs was undertaken. It was found that determining the mean edge emission from multiple overlapping intervals is the most accurate characterisation method. The LSCs were coupled with a thin strip DSSC and a photocurrent was obtained.

These examples illustrate the versatility of spectral converters and highlight the range of applications they can be used for with emerging PV technologies. The stability and efficiency of PV cells can be improved, the materials required can be minimised and the optical properties of our conversion techniques can be carefully tuned for the application and device architecture required.

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Abbreviations

AFM	– Atomic force microscopy
AIE	– Aggregation induced emission
AIEgen	– Aggregation induced emitting molecule
AM	– Air-mass
BCP	– Bathocuproine
BIPV	– Building integrated photovoltaic
C153	– Coumarin 153
CCD	– Charge coupled device
CIGS	– Copper indium gallium selenide
c-Si	– Crystalline silicon
CZTS	– Copper zinc tin sulfide
DLS	– Dynamic light scattering
DMF	– Dimethylformamide
DMSO	– Dimethyl sulfoxide
DS	– Down-shifting
DSC	– Differential scanning calorimetry
DSSC	– Dye-sensitised solar cell
EC	– Ethyl cellulose
EDGM	– Ethylene glycol dimethacrylate
EDX	– Energy dispersive X-ray spectroscopy
EQE	– External quantum efficiency
ETL	– Electron transport layer
EVA	– Ethylene vinyl acetate
FA	– Formamidineum
FDSC	– Fibre dye-sensitised solar cell
FK209	–tris(2-(1 <i>H</i> -pyrazol-1-yl)-4- <i>tert</i> -butylpyridine)cobalt(III) tri [bis(trifluoromethane) sulfonimide]
FM	– Epi-fluorescence microscopy
FRET	– Förster resonance energy transfer
FTIR	– Fourier transform infrared spectroscopy
FTO	– Fluorene doped tin oxide
FWHM	– Full-width half-maximum
HAADF	– High angle annular dark field
HTL	– Hole transport layer
IC	– Internal conversion
IPCE	– Incident photon to current efficiency
IQE	– Internal quantum efficiency

IR – Infrared
 IS – Integrating sphere
 ISC – Inter-system crossing
 LARP – Ligand assisted re-precipitation
 LDS – Luminescence down-shifting
 LED – Light emitting diode
 LMA – Lauryl methacrylate
 LR305 – Lumogen F Red 305
 LSC – Luminescent solar concentrator
 LV570 – Lumogen F Violet 570
 MA – Methyl ammonium
 N719 - Di-tetrabutylammonium cis-bis(isothiocyanato) bis(2,2'-bipyridyl-4,4'dicarboxylato) ruthenium(II)
 NC – Nanocrystal
 ND – Neutral density
 NIR – Near-infrared
 OA – Oleic acid
 ODE – Octadecene
 OPV – Organic Photovoltaic
 OY – Oleylamine
 P3HT – Poly(3-hexylthiophene-2,5-diyl)
 PC – Polycarbonate
 PCBM – Phenyl-C61-butyric acid methyl ester
 PCE – Power conversion efficiency
 PDI – Perylenediimide
 PDI-sil – *N,N*-bis(3-triethoxysilylpropyl)-1,6,7,12-tetra-*tert*-butylphenoxyperylene-3,4:9,10-tetra-carboxdiimide
 PDMS – Polydimethylsiloxane
 PFO – Poly (9,9-di-*n*-octylfluorenyl-2,7-diyl)
 PHPS – Perhydropolysilazane
 PL – Photoluminescence
 PLMA – Poly(lauryl methacrylate)
 PMMA – Poly(methyl methacrylate)
 PMP – Poly(4-methyl-1-pentene)
 PNC – Perovskite nanocrystal
 PSC – Perovskite solar cell
 PTFE – Polytetrafluoroethylene
 PV – Photovoltaic

PVC – Poly(vinylchloride)
PXRD – Powder X-ray diffraction
QC – Quantum cutting
QD – Quantum dot
RH – Relative humidity
RT – Room temperature
SEM – Scanning electron microscopy
spiro-OMeTAD – 2,2',7,7'-tetrakis[*N,N*-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene
STEM – Scanning transmission electron microscopy
tBP – 4-tert-butylpyridine
TCO – Transparent conducting oxide
TCSPC – Time-correlated single photon counting
TEM – Transmission electron microscopy
TFSI – Bis(trifluoromethane)sulfonimide
TGA – Thermogravimetric analysis
TIR – Total internal reflection
TOP - trioctylphosphine
TPE – Tetraphenylethene
TTA – 2-thionyltrifluoroacetone
UC - Upconversion
UV – Ultra-violet
WVTR – Water vapour transport rate
XPS – X-ray photoelectron spectroscopy
XRD – X-ray diffraction

Symbols

A	– Area
AM	– Air mass coefficient
C	– Luminophore doping concentration
d	– Distance
d_h	– Hydrodynamic diameter
E_g	– Bandgap energy
F	– Concentration factor
FF	– Fill-factor
G	– Geometric gain factor
I	– Intensity
i	– Intrinsic
I_d	– Diode current
I_p	– Current produced by the photoelectric effect
I_{SC}	– Short-circuit current
$I-V$	– Current voltage
J	– Current density
J_{SC}	– Short-circuit current density
k	– Extinction coefficient
k_B	– Boltzmann constant
k_{nr}	– Non-radiative decay rate
k_r	– Radiative decay rate
K_{sp}	– Solubility parameter
M_w	– Molecular weight
n	– Refractive index
n	– Negative
OP_{in}	– Optical power input
OP_{out}	– Optical power output
p	– Positive
P_{in}	– Power input
P_{max}	– Max power point
P_{out}	– Power output
q	– Electron charge
R	– Fresnel reflection coefficient
R_s	– Series resistance
R_{sh}	– Shunt resistance
S	– Total spin angular momentum
s_i	– Spin angular momentum

S_n – n^{th} singlet excited state
 t – Time
 $\%T$ – Percentage transmittance
 T_g – Glass transition temperature
 T_n – n^{th} triplet excited state
 V_{OC} – Open circuit voltage
 η_{opt} – Optical efficiency
 η_{trap} – Trapping Efficiency
 θ – Solar zenith angle
 θ_c – Critical angle
 λ - Wavelength
 λ_{abs} – Absorption wavelength
 λ_{em} – Emission wavelength
 λ_{ex} – Excitation wavelength
 $\langle \tau \rangle$ – Average fluorescence lifetime
 τ_i – Characteristic lifetime for the i^{th} component of a fluorophore
 Φ_{PL} – Photoluminescence quantum yield
 χ^2 – Chi squared statistic

Chapter One

Introduction

Portions of this Chapter have been published in:

B. McKenna and R. C. Evans, Towards Efficient Spectral Converters through Materials Design for Luminescent Solar Devices, *Adv. Mater.*, 2017, **29**, 1606491.

1.1 Introduction

World energy consumption has increased by over ten-fold since the early 20th century, with fossil fuels providing approximately three quarters of the total 558 EJ (5.58×10^{18} J) consumed in 2016.^{1,2} Considering the world population is approximately 7.6 billion, the average annual energy consumption per person is about 73 GJ (7.3×10^9 J) per year, equivalent to nearly 6 litres of oil per day for every person.² This is an oversimplified reality, however, with the average consumption of people in the developing world only using approximately one fifth of that used by people in the developed world. As more countries become industrialised, energy consumption will greatly increase. It has been predicted by Jones *et al.* that, due to this increase in industrialisation, in order to meet the goal of preventing a 2 °C global temperature increase put forward in the 2015 United Nations Climate Change Conference, up to 50% of our global energy consumption must be from renewable sources by 2028.³ This increased energy consumption and the increasing scarcity of fossil fuels, combined with the threat of climate change, is driving research into alternate forms of energy generation. One of the most promising natural sources to meet our energy requirements is solar power, which is the most abundant source of energy available to us. The incident sunlight upon the earth in one year is 1.5×10^{18} kWh of energy; in comparison, the sum of the known reserves of coal, gas and oil comes to just 8.65×10^{15} kWh.⁴

The focus of this thesis is the application of complementary spectral converters with third generation photovoltaic (PV) devices, particularly perovskite solar cells (PSCs) with the aim overcoming the current limitations of these emerging renewable energy technologies. The first part of the thesis will investigate the inherent stability issues with perovskite solar cells, and will explore resolving this limitation through both polymer encapsulation and the addition of luminescent down-shifting layers. In the second half of the thesis, perovskite-based nanocrystal luminophores will be investigated to improve their solution phase stability during processing and a detailed study on the characterisation of large area luminescent solar concentrators with quantum dot luminophores will be presented. This chapter will provide background on the spectral converters investigated, contemporary and emerging PV technologies.

1.2 Solar Energy

Solar energy is the most abundant natural source of energy available to us and it is also perhaps the most versatile. Almost all energy comes from the sun either directly through radiation or indirectly.^{2,5} Direct solar radiation can be used for applications such as solar water heating, reflected concentrated solar light for energy generation and direct conversion to electricity through PV cells. Solar radiation can be used indirectly as energy through the usage of hydroelectric power, wind power and bioenergy. The solar energy incident on the earth is typically represented by the air mass coefficient (AM), which represents the spectral power distribution of the incident solar radiation at different optical path lengths through the Earth's atmosphere. AM is calculated by:^{6,7}

$$AM = \frac{1}{\cos \theta} \quad (1.1)$$

where θ is the angle of the sun from its zenith position. An AM value of 0 or 1 thus represents radiation from the sun outside the Earth's atmosphere and when the sun is at its zenith position (directly overhead $\theta = 0^\circ$), respectively. Typically, when considering the characterisation of PV cells AM 1.5 is used as standard, and represents a thickness of 1.5 atmospheres and a solar zenith angle of 48.2° .⁸ AM 1.5 is used due to many of the major population centres being located at temperate latitudes; this is further specified by AM 1.5G where G represents an averaged value of global data, giving an irradiance of 1000 W m^{-2} . The AM 0 and AM 1.5G spectra are shown in **Fig. 1.1**.⁸

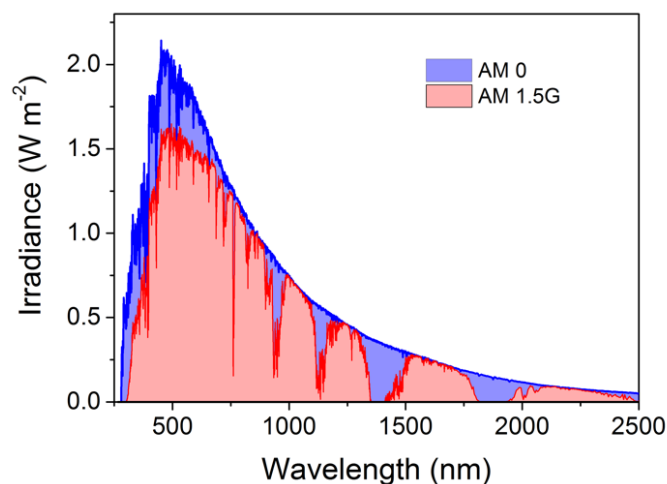


Figure 1.1. Solar irradiance spectrum (ASTM G173-03) above the atmosphere (AM 0) and at a zenith angle of 48.2° (AM 1.5G).⁸

1.3 Spectral Converters

While solar energy can be used to heat water, which can be used to power an engine and thus generate electricity, photovoltaic devices offer a more direct and better controlled method to generate electricity from solar energy. However, intrinsic spectral losses due to non-absorption and thermalisation of photons represent a major efficiency shortfall for all PV cells. The photogeneration of charge carriers can only occur upon absorption of solar photons with energies corresponding to that of the bandgap energy (E_g) or greater. All photons of wavelengths longer than those analogous to E_g which fall on the PV cell will be transmitted through the device and lost. However, the absorption of photons greater than E_g is also inefficient, with the excess energy gained being lost as heat through non-radiative recombination of the photoexcited charge carriers. Spectral converters exhibit great potential for integration with solar cells to overcome fundamental non-absorption and thermalisation losses.⁹ In their simplest form they can be applied to an existing solar cell in the form of an active photoluminescent layer. This photoluminescent layer can selectively absorb solar photons of wavelengths which are not efficiently converted to electricity by the PV cell, and re-emit them at wavelengths more suitable for use. These spectral converters can be used with standard solar cell architectures without any alteration of the intrinsic device materials, and are thus easily integrated with established manufacturing processes. Judicious selection of the luminophore used allows for facile optimization towards a specific PV cell type. Moreover, the space requirements of traditional PV cells, coupled with their reduced performance in diffuse sunlight conditions,^{10,11} mean that arrays of conventional solar panels may not be the most cost-effective nor practical solution in built-up areas. Spectral converters may help overcome some of these limitations, through the application of colourful photoluminescent films to any available surface (*e.g.*, façades, roofs, windows, walls etc.) coupled to highly efficient, smaller PV cells enabling the transformation of everyday buildings into solar harvesting machines.

1.3.1 Theory of Operation

1.3.1.1 Photoluminescence

In order for a spectral converter to function it has to undergo photoluminescence (PL), whereby light is emitted from a substance in an electronically excited-state.¹² Excitation of the molecule occurs when an energy source (in this case a photon) promotes an electron from the electronic ground-state to an excited state. These transitions occur very quickly (10^{-15} s) and as such there is no time for significant displacement of the nuclei (*Franck-Condon principle*). For organic luminophores the nomenclature used to describe these electronic states is derived by the equation for *spin multiplicity* $2S+1$, where S is the total spin angular momentum ($S = \sum s_i$ where $s_i = \pm\frac{1}{2}$) (s_i represents the spin angular momentum of a single electron).¹³ Individual spins are either up ($s = +\frac{1}{2}$) or spin down ($s = -\frac{1}{2}$). When the luminophore is in a ground or excited singlet state (S_n) the spin multiplicity is 1 as $S = 0$. In contrast, if the spin multiplicity for the excited state is 3 (electron spin in the ground and excited state are parallel), $S = 1$, which results in a triplet excited state (T_n). The difference between the spins of ground singlet, excited singlet and excited triplet state is shown in **Fig. 1.2**.

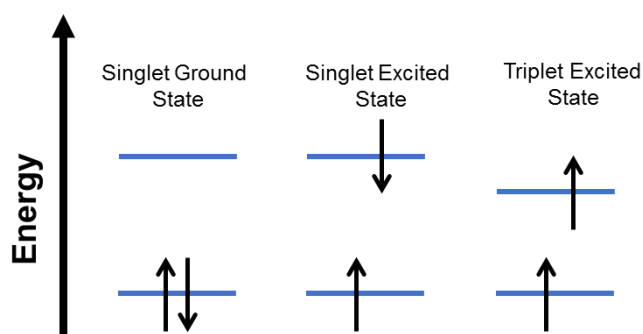


Figure 1.2. Schematic representation of the energy levels and electron spins of singlet and triplet excited states.

Upon formation of the excited state there are a number of transitions which can occur before deactivation of the excited state, both radiative and non-radiative. These processes are typically represented by a Jablonski diagram (**Fig. 1.3**). The radiative processes are depicted as straight lines and non-radiative as curved lines. The processes by which these excited states can deactivate, depicted in the Jablonski diagram are: internal conversion (IC); intersystem crossing (ISC); fluorescence and phosphorescence. Internal conversion and intersystem crossing involve the non-

radiative transition between excited states with the same and different multiplicities respectively.¹⁴ Intersystem crossing is a formally forbidden transition, although it can occur if there is significant spin-orbit coupling, a phenomenon typically observed for heavy atoms.¹⁵ These non-radiative processes occur quickly for electronic levels with similar energies (S_n to S_1) due to better overlap of the vibrational wavefunctions of the electronic states. As the energy gap between the states increases the rate of non-radiative processes decreases rapidly as described by the ‘*energy gap law*’.¹⁴ These processes are usually followed by rapid vibrational relaxation to the lowest vibrational level of the new electronic state (10^{-12} s). This relaxation is the basis for *Kasha’s rule*, which states that emission occurs from the lowest excited state for a given multiplicity of a molecule, thus, the emission observed through these radiative processes is typically independent of the excitation wavelength.¹⁶

Fluorescence describes radiative transitions between electronic states of the same multiplicity (*e.g.* S_1 to S_0) and phosphorescence between states of different multiplicity (*e.g.* T_1 to S_0).¹² Fluorescence typically occurs at longer wavelengths than the absorbed light due to Kasha’s rule. The difference between the absolute maximum of the first absorption band and the maximum of the fluorescence emission band is known as the *Stokes’ shift*.¹⁵ Fluorescence processes typically occur on timescales of 10^{-7} to 10^{-10} s.¹⁷ Deactivation occurs to higher vibrational levels which then reach equilibrium, thus, vibrational structure is observed in emission spectra. Due to the forbidden nature of the transitions, phosphorescence occurs at a much slower rate than fluorescence, as such non-radiative decay processes typically occur preferably.¹⁸ The Jablonski diagram depicted in **Fig. 1.3** is simplified and does not consider quenching, energy transfer and solvent interactions as they have limited impact on the systems investigated in this thesis.

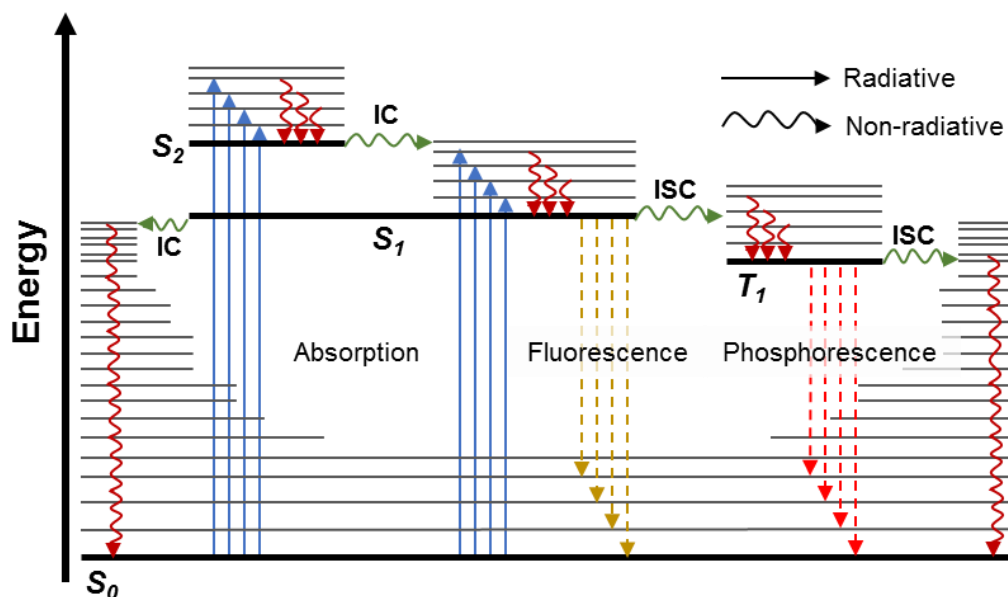


Figure 1.3. Jablonski diagram showing the processes of absorption, fluorescence, phosphorescence, internal conversion and intersystem crossing. The radiative processes are represented by straight lines and the non-radiative processes by curved arrows.

1.3.1.2 Spectral Conversion Mechanisms

While all spectral converters exploit photoluminescence to tune the spectrum of the light incident on the surface of a PV cell, the mechanisms by which they achieve this are quite varied. The most common methods of spectral conversion are: luminescence down-shifting (LDS); quantum cutting (QC); upconversion (UC); and luminescent solar concentrators (LSCs).¹⁹ **Fig. 1.4** presents a schematic illustration of the three photoluminescence processes currently exploited for the improvement of PV efficiency, down-shifting (DS), UC and QC and demonstrates the architectures they are applied to integrate with single junction PV cells.

Down-shifting involves the absorption of a high energy photon and the emission of a lower energy photon which can be more effectively harnessed by the PV cell. Down-shifting is typically used in two distinct architectures, i) as a planar design, where the down-shifting layer is applied to the top surface of a solar cell (usually referred to as an LDS layer),²⁰ and ii) an LSC structure in which the luminophore down-shifter is coated on, or doped within, a transparent waveguide slab that has PV cell(s) coupled to one or more of the edges.²¹

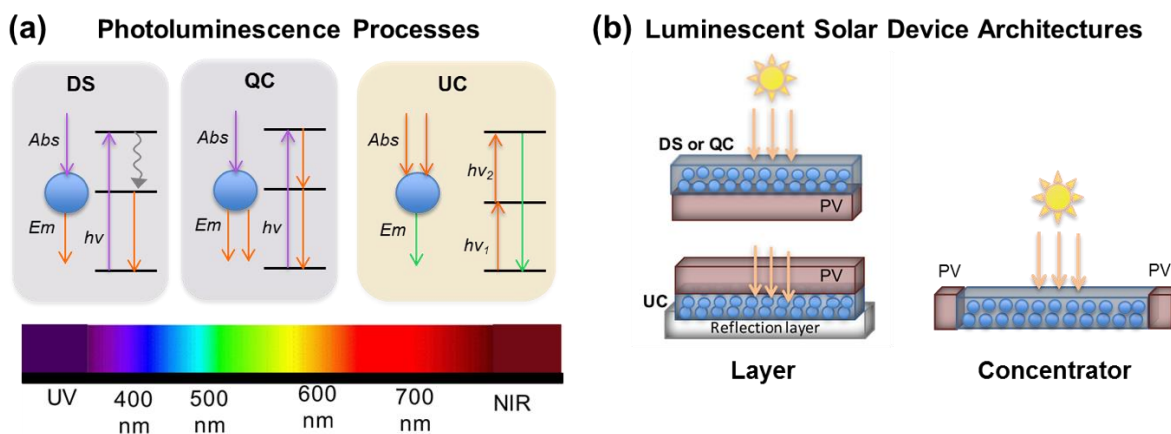


Figure 1.4. Photoluminescence processes used in spectral converters and their integration architectures with PV cells to form photoluminescent solar devices. (a) Simplified energy level diagrams for DC, QC and UC. DS converts a single high energy photon and emits it as a single lower energy photon that is closer to the band gap energy of the PV cell. In QC a single high energy photon is down-converted into two (or more) lower energy photons. UC is a nonlinear process in which two (or more) low energy photons are absorbed by a luminophore and converted to one emitted high energy photon. (b) LDS and QC architectures typically involve a coated layer on top of the surface of the PV cell, while UC typically involves a layer coated on the back surface of the device to absorb the transmitted photons, with a reflector layer to ensure the upconverted photons are directed back to the cell. LSCs typically consist of a DS luminophore doped or coated onto a transparent waveguiding plate, with PV cells coupled to one or more plate edges.¹⁹

Upconversion aims to utilise the photons lost due to non-absorption in the low energy region of the spectrum. The upconverting molecule absorbs two or more low energy ($<E_g$) photons and converts them into one higher energy photon which can be effectively exploited by the PV cell.²² These UC layers are typically applied under the active PV layer so that they can effectively exploit the photons transmitted through the cells, a reflective layer is placed below the UC layer to ensure the emitted photons are directed back into the PV cell. QC is a process in which the thermalisation losses are reduced by taking high energy photons ($>2E_g$) and “cutting” into two or more photons ($>E_g$) which can be utilised effectively by the cell.²³

The effectiveness of these spectral conversion techniques varies with the architecture and PV cell used. DS in both LDS and LSC architectures can reduce energy losses due to surface, Auger or Shockley-Read-Hall recombination of the electron hole pairs.¹⁹ The efficiency of DS is capped by the photoluminescence quantum yield (Φ_{PL}) which cannot exceed 100%, as such DS devices cannot break the Shockley-Queisser limit.²⁴ UC and QC can overcome the Shockley-Queisser limit as both mechanisms generate more than one photon for each photon absorbed, thus more electron hole pairs

are generated in the cell and the short-circuit current (I_{sc}) increases. The theoretical efficiency limit for UC²⁵ and QC²⁶ materials applied to crystalline silicon (c-Si) cells are 47.6% and 39.63% respectively.

1.3.2 Tuning Spectral Converters to Photovoltaic Devices

Which of the above spectral conversion methods is used is typically dictated by the type of PV cell, the architecture of the cell and the external quantum efficiency (EQE) of the device. The EQE is defined as the ratio of electron hole pairs generated to the number of photons hitting the front surface of the device, as a function of wavelength.²⁰ The regions of the AM 1.5G spectrum which can be effectively used by DS and UC for a PSC ($E_g = 1.55$ eV) are highlighted in **Fig. 1.5**. The blue region illustrates where DS can minimise the thermalisation losses and the red region where UC is required to enable absorption of photons of energy $< E_g$.

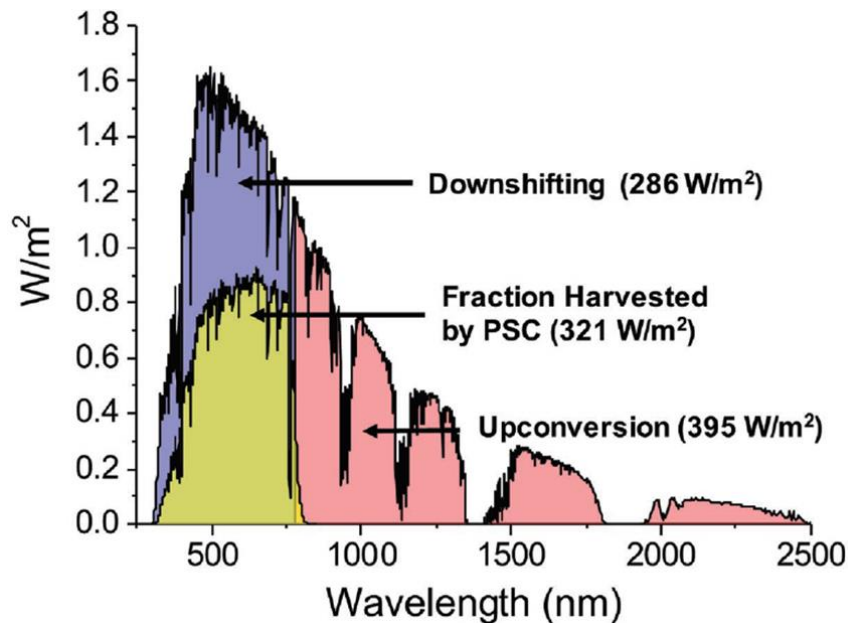


Figure 1.5. The AM 1.5G solar spectrum (solid black line), the fraction of incident radiation effectively harvested by a reference perovskite solar cell (yellow), and the spectral regions in which downshifting (blue) and upconversion (red) spectral converters can be exploited to improve the cell efficiency. The maximum fraction of the solar spectrum efficiently harvested by the PSC was determined from the product of the maximum fraction of incident photons which can be harvested by the cell ($E_g = 1.55$ eV) and the corresponding EQE spectrum.¹⁹

As can be seen from **Fig. 1.5**, at wavelengths higher and lower than the EQE spectrum there is a rapid drop off in the fraction of the solar spectrum which can be harvested. The specific EQE

spectrum varies from cell to cell with silicon, both crystalline and amorphous ($E_g \approx 1.1$ eV), showing high EQEs in the visible to near infra-red (NIR) region ($\approx 450 - 1000$ nm).²⁷ Thin film chalcogenide cells such as copper indium gallium selenide (CIGS) and copper zinc tin sulfide (CZTS) typically show much narrower window of performance ($\approx 500 - 800$ nm).²⁷ Third generation PV such as organic photovoltaic cells (OPV), dye-sensitised solar cells (DSSC) and PSCs can show tunable spectral windows by varying the absorbing molecules for each architecture. The devices typically display maximum EQE in the ranges of $\approx 400 - 700$ nm for PSCs ($E_g \approx 1.6$ eV),²⁷ $\approx 350 - 750$ nm for OPV ($E_g \approx 1.6$ eV)²⁸ and $\approx 450 - 800$ nm for DSSCs ($E_g \approx 1.55$ eV)²⁹ While the tunability of these third generation PV technologies is a distinct advantage when applying them in conjunction with spectral converters, they are still affected by reduced efficiencies in the blue/ultraviolet (UV) region of the solar spectrum. At these wavelengths parasitic absorption from the glass encapsulants and increased reflectance can limit the absorption of the cell, while, particularly for third generation PV, the light in this region can be harmful to the absorber materials used causing degradation.

In this thesis, luminescence downshifting will be the only mechanism of spectral conversion presented, in both its LDS and LSC forms. These spectral converters will be utilised to both improve the light response of the PV cells and prevent light induced degradation.

1.4. Luminescence Down-Shifting

1.4.1 Working Principle and Figures of Merit

Fig. 1.4 depicts an LDS device in its most simple and common configuration, a luminescent layer coated on the surface of a PV device. Since LDS layers neither concentrate the incident light nor produce more photons than are incident, they can only improve the power conversion efficiency (PCE) of the PV cell by tuning the window of spectral absorption, particularly in the blue/UV region.³⁰ After absorption of this high energy radiation (where the cells have low EQE), the photons are re-emitted by the luminophores at a lower energy and collected by the PV cell, thus, generating more electron hole pairs and increasing the cell I_{SC} .²⁰ An increased I_{SC} should lead to an improvement in the EQE response of the devices at these shorter wavelengths (when characterised with the LDS layer applied) although there are examples where this is not always the case.³¹ The open circuit

voltage (V_{OC}) and the fill factor (FF) of the PV devices should not change upon application of an LDS layer as these values are related to the intrinsic materials in the PV cell. Theoretical calculations to determine the maximum efficiency gains from applying LDS layers to Si PV cells predict an increase of 0.6–1%.³²

Unlike other types of spectral conversion, the LDS efficiency is typically quantified by characterising the coated cell identically before and after coating and comparing the observed changes in the EQE and the I - V curves.^{31,33,34} The reliance on the actual cell performance allows a degree of consistency between characterisation of the bare and coated device, particularly in comparison with other spectral conversion architectures such as LSCs, which often rely only on characterisation of the spectral converter itself.^{19,21} The EQE, in particular, enables the direct characterisation of the LDS layer as it measures both the wavelength (λ)-dependent response of the PV cell and the I_{SC} of the device.

1.4.2 LDS Components and Requirements

LDS layers typically consist of a luminophore doped into a host matrix which can be easily coated onto the cell surface and retain its luminescent properties. The requirements of an effective LDS luminophore are: i) strong absorbance in the region of interest for the PV cell used; ii) a high Φ_{PL} ; iii) a large Stokes' shift to minimise reabsorption losses which may occur; iv) high photostability; and v) high optical transmittance in the host material.^{9,20} The most commonly used luminophore materials for LDS are organic dyes,^{33,35,36} quantum dots (QD)^{37–40} and lanthanide metal ions/complexes.^{41–44} There are few requirements for LDS host materials, including high transparency in the UV/visible region and a suitable refractive index ($n = 1.4 - 2.4$) to minimise both surface reflection and escape cone losses.⁴⁵ Polymers,^{46–49} silica hybrids^{50–52} and glasses^{41,42,53} are typically used as host materials, however, there are examples of luminophores coated directly onto the PV cell surface.^{34,54} The host material thickness has to be minimised to limit the amount of edge emission which occurs.^{16,55} Most of the recent research on LDS has aimed at optimising the host-luminophore combinations to both minimise losses and improve the stability and efficiency of the PV cells.

1.4.2.1 LDS Luminophores

As described above the luminophores used for LDS typically fall into three categories: lanthanide metal ions/complexes; organic dyes and QDs. Much of the earliest LDS research was performed using lanthanide-based phosphors. Eu^{2+} and Eu^{3+} ions were doped into polymer hosts and coated onto Si cells.^{56,57} These materials, however, suffered from limited efficiencies due to the low absorption coefficients of free lanthanide ions. The most commonly used family of luminophores for LDS are organic dyes, due to their relative cheapness, high Φ_{PL} values and ease of processing.¹⁹ LumogenTM dyes are the most common as they are compatible with most polymer host materials and their properties are well known.^{20,21,35,49,58–60} This has led to the use of this family luminophores as benchmarks for theoretical modelling aimed at predicting LDS efficiencies. Richards *et al.*, for example, compared experimental results of six Lumogen organic dyes, alone and in mixtures (photoluminescence quantum yield (Φ_{PL}) > 87%), in two polymer hosts, with three different cell types (c-Si, CdTe and CIGS), with a theoretical model based analytical description of the LDS layer (created by comparing figures of merit) and ray-tracing simulations (**Fig. 1.6**).³⁶ Organic luminophores are primarily used in conjunction with thin film solar cells due to their narrower EQE ranges. For example, Solodovnyk *et al.* have recently achieved a 2.93% enhancement of the PCE of a CIGS cell by applying a thick LDS layer of poly (vinyl butyral) doped with a mixture of Lumogen Yellow 083 and Violet 570 (LV570).³³

A variation on the standard organic dye molecules which has received some recent attention for LDS applications is aggregation-induced emitter (AIE) luminophores. These materials overcome the concentration dependant limitations of conventional organic dyes, in which aggregation typically leads to emission quenching due to preferential relaxation *via* non-radiative channels.^{61,62} AIE active molecules (AIEgens) typically contain twisted molecular cores which hampers π - π stacking interactions.^{63–65} Upon aggregation steric effects limit the intramolecular rotations/vibrations thus switching on luminescence. Dong *et al.* have recently investigated tetraphenylethene (TPE) based AIEgens in a poly(methyl methacrylate) (PMMA) host material as LDS layers.^{37,60} A family of TPE derivative luminophores were synthesised which exhibited Stokes' shifts of over 100 nm and Φ_{PL}

values of up to 99%. When applied to CdTe cells, an increase in device I_{SC} of 5–10% was obtained compared to a 3–4% for Lumogen Yellow 083.

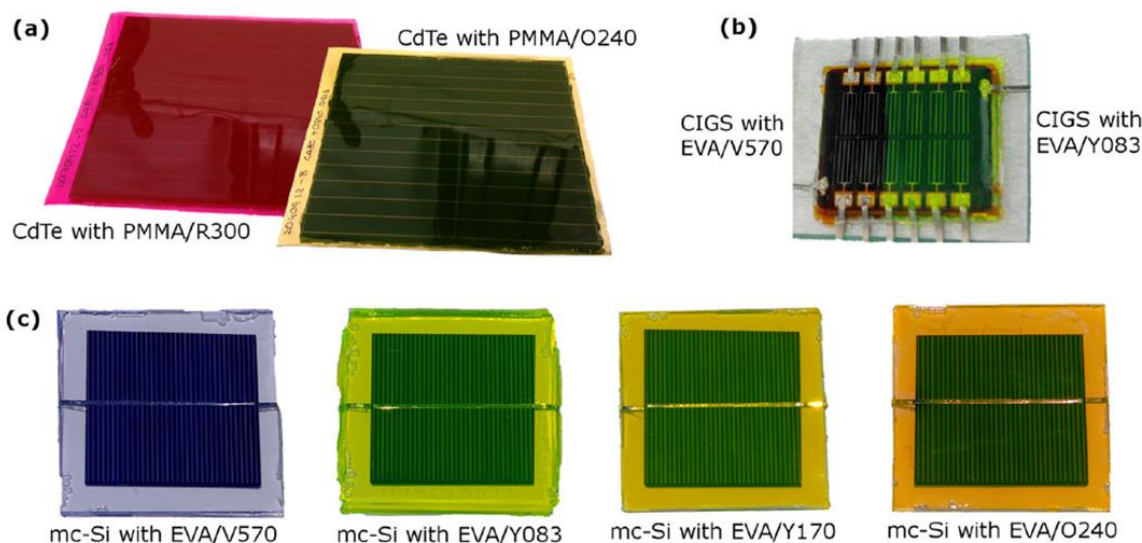


Figure 1.6. Examples of PV cells coated with different LDS layers. (a) CdTe, (b) CIGS and (c) c-Si. Hosts: poly (methyl methacrylate) (PMMA), ethylene vinyl acetate (EVA). Luminophores: Lumogen Red 300, Orange 240, LV570, Yellow 083, Yellow 170. Adapted with permission from ref.³⁶ Copyright AIP publishing 2018.

While Eu-ion doped glasses showed relatively low efficiencies when applied as LDS layers, the use of Eu^{2+} and Eu^{3+} complexes and phosphors have achieved better results. Chen *et al.* applied a $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$ LDS layer to the surface of a Si PV cell, which upon doping with Ag nanoparticles and an SiO_2 spacer, showed an increase in PCE from 17.1 to 17.7%.⁶⁶ An LDS layer composed of $\text{Gd}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ doped in poly(vinylpyrrolidone) has also been demonstrated, in which the $\text{Gd}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ spherical particles improved the anti-reflection properties of the material. This, coupled with the increase in the I_{SC} increase led to an improvement in the PCE from 10.44 to 12.97%.⁴⁴ While Eu is predominantly used for lanthanide-based LDS, there are examples of Tb luminophores operating comparably. Fix *et al.* demonstrated that $[\text{LnL}_3]-(\text{Et}_3\text{NH})_3$, ($\text{Ln} = \text{Eu(III)}, \text{Tb(III)}$) ($\text{L} = \text{triazole-pyridine-bis-tetrazolate antenna}$) doped EVA films performed comparably for the Eu^{3+} and Tb^{3+} analogues.⁴³

Recently attention has shifted towards the use of QDs as luminophores for LDS applications, with studies of CdTe and CdSe/CdS QDs doped in PMMA or EVA for both Si and thin film (CdTe/CdS) solar cells performed.⁶⁷ Li *et al.* have recently addressed the need for inert atmospheric

conditions when synthesising certain QDs by performing microwave synthesis.^{38,50} CdSe/CdS/ZnS and CuInS₂/ZnS QDs have been synthesised by this method and when doped in a host matrix (SiO₂ and PMMA respectively) gave a PCE increase of 15.34 to 16.14% and 15.6 to 16.21% respectively, for Si cells. A PCE increase of 14.48 to 18.05% was achieved for green-emitting CdSe/ZnS QDs when applied directly without a host matrix to the surface of GaAs cells.⁵⁴

1.4.2.2. LDS Hosts

LDS host materials have few requirements compared to luminophores and this is reflected in the research - there are very few variations between polymer hosts, silicates and glasses used in LDS layers, with PMMA and EVA appearing most commonly. Much of the research on the host materials for LDS has been focussed on adding multi-functionality to the layer, for example, anti-reflectivity,^{40,68} hydrophobicity⁶⁹ and other barrier properties. Xu *et al.* used nanosphere lithography to pattern their Si substrate to lower surface reflectance and then applied a Si-QD/SiO₂ composite LDS layer to achieve a PCE increase from 3.1 to 3.8%.⁶⁸ This demonstrates the advantages of using LDS with other light management techniques.

Ghyman *et al.* used a combination of a QD-LDS layer with a ‘moth-eyed’ antireflective coating.⁴⁰ Polydimethylsiloxane (PDMS) films were doped with CdZnS/ZnS core-shell quantum dots and nanopatterned using a Si mould to imprint the ‘moth eyed’ pattern on the PDMS. This moth-eyed pattern decreased surface reflection leading to a PCE increase from 27.8 to 28.7% for these dual functional films. The deposition of a semiconductor passivation layer onto an InGaP PV cell with an LDS layer of commercial Trilite 585 and Trilite 665 QDs allowed Förster resonance energy transfer (FRET) to occur between the passivation layer and the QDs.⁷⁰ This design enabled a two mechanism LDS process, from both direct illumination and FRET, which increased the absolute PCE by 2%.

Nam *et al.* demonstrated nanopatterned LDS layers for OPV by the direct nanoimprinting of spin-coated Ln (Eu³⁺ and Tb³⁺) doped perhydropolysilazane (PHPS) polymer ceramics to give red and green emission, respectively (**Fig. 1.7**).⁶⁹ Soft-imprint lithography was used to form both ‘nanocone’ and ‘nanocylinder’ patterns regularly on the film surface. These nanopatterns acted as

scattering centres to increase the photoluminescence intensity compared with the non-patterned films. A degree of tunability was also observed with a red-shift observed upon increasing the cone diameter. These nanopatterned films displayed hydrophobicity and high transparency and upon characterisation with the OPV cells a maximum PCE increase from 4.1 to 4.6% was observed.

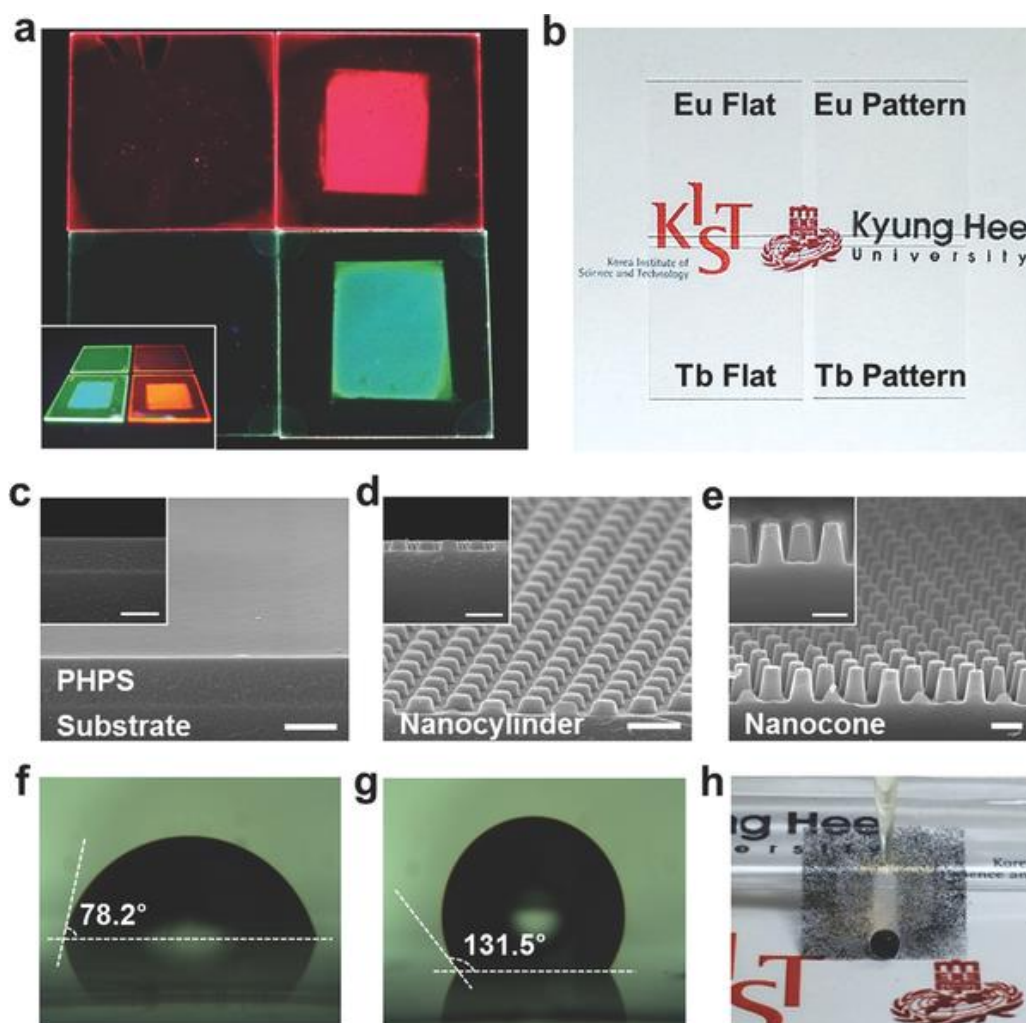


Figure 1.7. Surface structure and hydrophobicity of nanopatterned LDS layers. (a) Tb³⁺ (green) and Eu³⁺ (red) doped PHPS films prepared with or without imprinted nanopatterns on a quartz substrate, under 254 nm illumination. The inset shows the same samples under AM 1.5G illumination through a UV short pass filter (cut-off 400 nm). (b) Photograph of the samples showing high transparency under natural light. (c - e) Tilted and cross-sectional SEM images of the flat, nanocylinder (diameter = 200 nm, pitch = 400 nm, height = 180 nm) and truncated nanocone (diameter = lower 390 nm/upper 220 nm, pitch = 500 nm, height = 550 nm) samples, respectively. The scale bars indicate 500 nm. Optical microscopy images of water droplets on the surfaces of the nanocylinder patterns (f) prior to and (g) after hydrophobic treatment. (h) A water droplet effectively removed dust particles on the hydrophobic nanopatterns indicating the self-cleaning nature of the surface. Adapted with permission from ref.⁶⁹ Copyright Wiley 2018.

1.4.3 LDS for Emerging PV Technologies

Most of the above examples have involved LDS layers for commercially available Si and thin film PV cells, however, there has been a considerable amount of research on using this spectral conversion technology for emerging third generation PV devices. LDS layers applied to third generation PV cells such as OPV, DSSCs and PSCs offer not only efficiency enhancement but also can improve the photostability of the devices by filtering much of the high energy blue/UV radiation and re-emitting it at more favourable wavelengths. One of the earliest applications of LDS to a 3rd generation PV device was the application of a $\text{LaVO}_4\text{:Dy}^{3+}$ film to a DSSC to act as both an LDS layer and a UV-filter.⁷¹ Recently, Griffini *et al.* have demonstrated LDS layers tailored for DSSC applications based on both Eu^{3+} complexes⁷² or LV570⁷³ doped fluoropolymer host materials. These coating caused a 1.82% and 1.31% increase in the PCE, respectively. Long term outdoor stability testing (>2000 h) of the LDS coated DSSCs resulted in a 2–7% decrease in PCE with time, compared to *ca.* 30% for the uncoated devices. Hosseini *et al.* applied an LDS/reflective layer to the bottom of a DSSC in a similar architecture to that typically used for UC.⁷⁴ The combination of LDS from the $\text{CaAlSiN}_3\text{:Eu}^{2+}$ luminophore and back reflection led to an increase in PCE from 3.3 to 4.8%.

OPVs, similarly to DSSCs, have had limited commercialisation due to the UV instability of the organic materials used in both the photoactive and charge extraction layers.⁷⁵ Lanthanide based luminophores are commonly used with OPV, as with the example highlighted in **Fig. 1.7**. The first example of LDS with OPV used a $\text{YVO}_4\text{:Eu}^{3+}/\text{Bi}^{3+}$ luminophore and after coating the device stability increased to three times compared to the uncoated cells.⁷⁶ Krebs *et al.* used luminophores based on commercial tris(hexafluoroacetylacetonate) mono(1,10-phenanthroline) europium and PMMA inks as LDS layers.⁷⁷ These layers were applied to OPV cells by both doctor-blading and screen-printing, thus allowing for high throughput application of the layers. These layers both improved device half-life by 850% for indoor light stability testing and improved the PCE by $\sim 0.25\%$. Recently, the Zhang group synthesised fluorescent carbon dots from L-ascorbic acid, in conjunction with a host agent based on (N-(2-aminoethyl)-3-aminopropyl)tris-(2-ethoxy)silane to stabilise and passivate the carbon dots.⁷⁸ Hydrolytic condensation of the silica network gave a solid LDS film when applied to

the OPV cell through spin coating. Application of the LDS layer gave an increase in the PCE from 2.85 to 3.18% and passivation of the carbon dots increased their Φ_{PL} from 3.6 to 8.6%.

Among the third generation PV technologies, PSCs offer both the highest potential for commercialisation and the greatest stability issues, with long term stability hindered by susceptibility to moisture-, thermal- and UV-degradation.⁷⁹ LDS is an attractive method to minimise the UV-degradation which occurs in PSCs. The first example of LDS with PSCs was by Chander *et al.* who used spray deposition to apply a YVO_4/Eu^{3+} nanophosphor to the top surface of a PSC.⁸⁰ The coated PSC showed higher efficiencies after continuous light soaking, with a PCE increase from 7.42 to 7.93% and displayed increased device stability compared to uncoated devices. A novel method to apply an LDS layer was demonstrated by Hou *et al.* who incorporated the $ZnGa_2O_4:Eu^{3+}$ LDS layer into the mesoporous TiO_2 , resulting in a PCE increase of over 3%.⁸¹ Recently, a PSC coated with an LV570 and fluoropolymer layer on the top of the PV cell, and an undoped polymer encapsulation coating on the back side (encapsulating the active layer) was demonstrated by Bella *et al.*⁸² The dual coated PSCs showed improved stability compared to both the bare devices and those only coated with the LDS layer over six months continuous UV-illumination. The single layer LDS coated cells outperformed the bare cells with PCE enhancements from 17.31 to 18.67% observed and only showed notable efficiency losses after 75 days continuous illumination in an inert atmosphere. This highlights the potential of LDS layers to improve device stability. Due to the relative youth of PSCs as a technology, there is still a huge potential for research to improve both efficiencies and stabilities through LDS.

1.5 Luminescent Solar Concentrators

1.5.1 Working Principle and Figures of Merit

In its most prevalent architecture an LSC consists of a transparent waveguiding plate either doped or coated with a down-shifting luminophore (**Fig. 1.8**). As with the LDS layers described above, high energy photons absorbed by the luminophores are subsequently re-emitted at longer wavelengths. However, unlike LDS layers, a portion of the re-emitted light is guided by TIR to the edges of the waveguide plate where coupled PV cells can effectively harvest the concentrated

emission. LSCs concentrate light by absorbing the light incident on the large area top surface of the plate and emitting at the smaller area edges (geometric concentration). The influence of these dimensions is represented by G , the geometric gain factor, which is given for planar LSCs by:^{83,84}

$$G = \frac{A_{\text{surface}}}{A_{\text{edge}}} \quad (1.2)$$

where A_{surface} and A_{edge} are the area of the top surface and the total summed area of the four edges, respectively. This concentration effect both reduces the area and number of PV cells required and makes the use of high efficiency PV more cost effective, and while the LSC efficiency is lower than an equivalent area of PV cell, their flexibility in design and low cost make them an attractive prospect for building integrated photovoltaics (BIPV).²¹

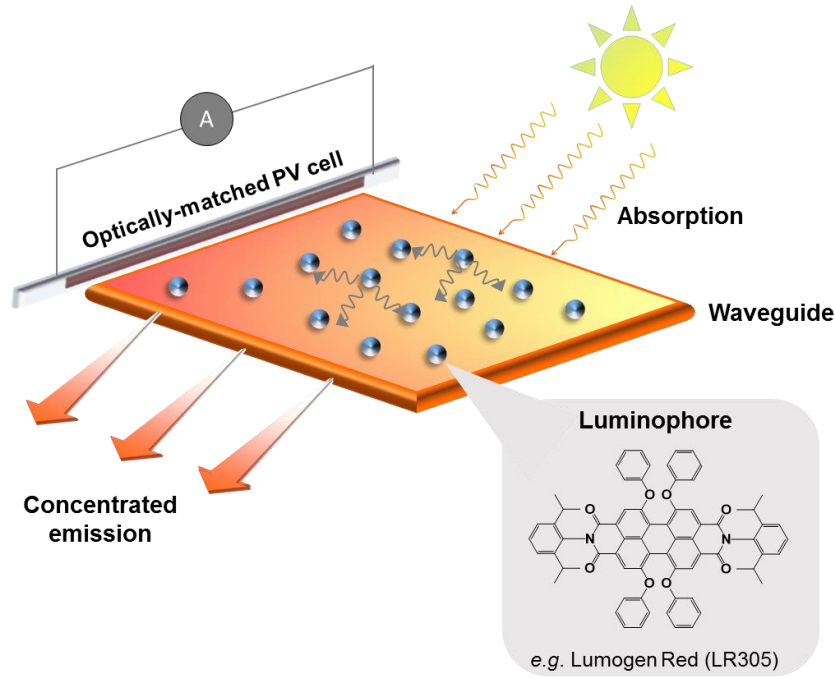


Figure 1.8. Operating principle of a luminescent solar concentrator. Light incident on the LSC top surface is absorbed by the luminophores and re-emitted at longer wavelengths. The emitted photons are propagated through the waveguide by TIR, resulting in concentration of the emission at the slab edges. The concentrated emission can be used to sensitise an optically matched PV cell, placed at one or more the edges.¹⁹

The most important figure of merit when characterising the performance of an LSC is the optical conversion efficiency (η_{opt}) which measures the efficiency of the LSC in terms of the total power of light emitted compared to the total power of light incident. It is given by:^{83,84}

$$\eta_{\text{opt}} = \frac{OP_{\text{out}}}{OP_{\text{in}}} \quad (1.3)$$

where OP_{out} is the total optical power output obtained over the sum of the four LSC edges and OP_{in} is the total optical power incident on the top surface of the waveguide plate. The combination of η_{opt} with the geometric gain factor, give the quantifiable expression for the overall efficiency of an LSC, the concentration factor F :^{83,84}

$$F = \eta_{\text{opt}} G \quad (1.4)$$

These three figures of merit are widely used to evaluate the performance of LSCs. However, there is much debate in the literature on the experimental methods of determining η_{opt} , which can lead to difficulties comparing results between research groups. This lack of a standard testing protocol will be expanded on in **Chapter 6**.

1.5.2 LSC Components and Requirements

While most LSCs consist only of two components, similar to LDS layers, they are more complicated systems due to the longer propagation distances of the light compared to LDS. There are several intrinsic loss mechanisms, which are directly related to both the luminophore and the waveguide used (**Fig. 1.9**). Luminophore-associated losses include: incomplete harvesting of the incident solar spectrum, low Φ_{PL} , low absorption efficiency, photodegradation of the luminophore and reabsorption losses by neighbouring luminophores. An ideal luminophore should have a large Stokes' shift, possess a near-unity Φ_{PL} , have broad absorption in the visible region of the spectrum with a high absorption coefficient and high photostability.^{19,21} The emission wavelength of the luminophore should also be as close the E_g or the maximum point on the EQE spectrum as possible to minimise losses within the PV cell. Waveguide losses typically include: losses through the escape cone of the waveguide, reflection from the waveguide surface, parasitic absorption by the waveguide itself and scattering cause by defects in the waveguide. The ideal waveguide typically has a refractive index between 1.5 and 2.5 to both ensure a significant portion of the incident light undergoes total internal reflection (TIR) and to minimise the losses through reflection. It should also be free of defects and show a high transmittance in the visible spectrum. These requirements mean the combinations of luminophore and waveguide have to be carefully tailored to ensure a synergistically optimised LSC is obtained.

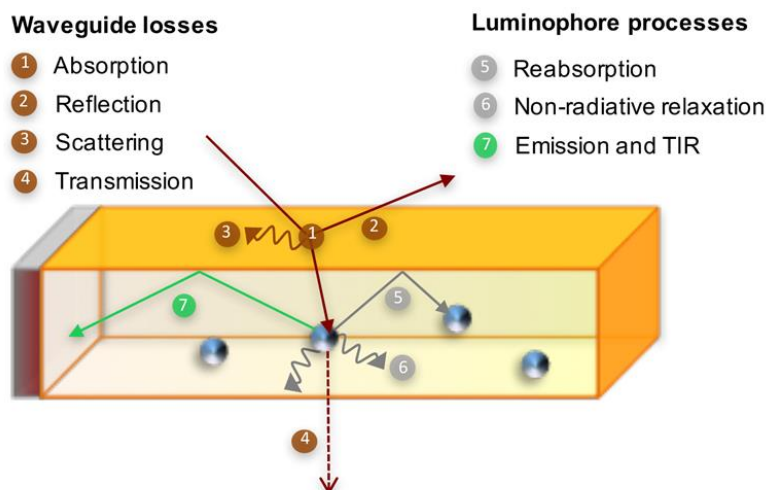


Figure 1.9. Schematic illustration of common loss mechanisms in planar LSCs. Straight arrows indicate radiative processes, curved arrows represent non-radiative processes. Waveguide losses include absorption, reflection and scattering of incident light at defects in the plate, or transmission. Luminophore losses include non-absorption, non-radiative relaxation, reabsorption by neighbouring luminophores and emission within the escape cone of the waveguide.¹⁹

1.5.2.1 LSC Luminophores

The most common luminophores used in LSCs have historically been organic dyes such as perylenes, naphthalimides, coumarins and rhodamines.²¹ These materials have attracted the most attention due to their high Φ_{PL} , ease of processability, high absorption coefficients and reasonable photostability. Lumogen Red 305 (LR305) is a perylene bisimide dye (perylen-1,7,8,12-tetraphenoxy-3,4,9,10 tetracarboxylic acid-*bis* (2'-6' diisopropylanilide)) which is widely used as a performance benchmark for LSCs due to its Φ_{PL} of 97% in PMMA and its bright red emission which favours applications with Si PV cells.^{58,85–90} Some of the issues with this material, however, include a small Stokes' shift which gives rise to reabsorption losses and aggregation which occurs at high concentrations.⁹¹ These issues both can result in non-radiative decay of the absorbed light leading to efficiency losses within the device.

Strategic design of new luminophores has allowed LSCs to progress beyond the traditional organic dyes, with new luminophores being synthesised specifically for application in LSCs showing engineered Stokes' shifts and high Φ_{PL} values. While lanthanide ions show large Stokes' shifts and high photostability they commonly display low absorption coefficients and low Φ_{PL} values.^{56,92} These limitations can be overcome by Ln^{3+} complexes utilising the antenna effect where coordinated

ligands absorb light and transfer energy to an Ln^{3+} centre from which emission occurs.⁹² Moudam *et al.* demonstrated a highly red-emissive Eu^{3+} complex, $\text{Eu}(\text{hexafluoroacetylacetonate})_3(\text{bis}(2\text{-disphenylphosphino})\text{phenyl})\text{ether oxide}$, which exhibited a $\Phi_{\text{PL}} = 80\%$ when immobilised in a PMMA film, upon ligand excitation.⁹³ Similarly Correia *et al.* obtained a $\Phi_{\text{PL}} = 85\%$ for $\text{Eu}(\text{tta})_3 \cdot 2\text{H}_2\text{O}$ (tta = 2-theonyltrifluoroacetone) embedded in an organic-inorganic hybrid matrix.⁸³

AIEgens have also been investigated as luminophores for LSC devices. Wong, Ghiggino *et al.* prepared an LSC from TPE cast in a PMMA matrix onto a glass film.⁹⁴ While this device showed effective concentration of light, the emission range of TPE ($\lambda_{\text{em}} \approx 450 \text{ nm}$) is not well matched for the Si or GaAs cells it was tested with. The use of other TPE derived AIEgens was investigated to shift the emission towards the red-region of the spectrum. It was observed that by increasing the number of polyaromatic rings from 2 to 4, a red-shift occurred; however, it was accompanied by a decrease in Φ_{PL} from 49.5 to 31.2%. The same group reported using an AIEgen, 2-(4-(diphenylamino)phenyl)-3,3-diphenylacrylonitrile, as an energy transfer donor for an emissive acceptor dye, 4-(dicyano-methylene)-2-tert-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyran. By optimising the relative concentrations in the blend, a max Φ_{PL} of 92% was achieved.⁹⁵

QDs show huge potential as luminophores for LSCs, due to the possibility of engineering their photophysical properties through judicious choice of their size and the architecture employed (*e.g.* core-shell,⁹⁶ alloyed⁹⁷ or doped⁹⁸ QD structures). The structural versatility allows for a tunable band gap energy and thus it is possible to synthesise QDs which both absorb and emit across the entire spectral region. Theoretical models using Monte-Carlo simulations have predicted that η_{opt} values of up to *ca.* 24% can be achieved for CdSe/CdTe core-shell QDs with a Φ_{PL} of 95%.⁹⁹ “Giant” core-shell QDs have been presented as a method of incorporation in which a large shell of a wide bandgap semiconductor is grown on narrower bandgap semiconductor to minimise reabsorption losses.^{100–103} This method was first demonstrated by Krumer *et al.* who compared the self-absorption behaviour of CdSe and CdTe/CdSe QDs with common organic dyes including LR305. They demonstrated negligible self-absorption losses for the CdTe/CdSe QDs compared to the other luminophores and showed an emission close to that of the Si bandgap ($\lambda_{\text{em}} \approx 900 \text{ nm}$)

1.5.2.2 LSC Waveguides

The performance of an LSC waveguide is primarily determined by its refractive index. The light trapping efficiency (η_{trap}) is given by:

$$\eta_{\text{trap}} = \left(1 - \frac{1}{n_{\lambda}^2}\right)^{1/2} \quad (1.5)$$

where 1 represents the refractive index of air, and n_{λ} is the refractive index of the waveguide at wavelength λ . This value is a measure of the fraction of emitted photons in the waveguide which will undergo TIR. The proportion of light reflected by the surface of the LSC is given by the Fresnel reflection coefficient R :

$$R = \left|\frac{1-n_i}{1+n_i}\right|^2 \quad (1.6)$$

where n_i is the refractive index of the waveguide at the incident wavelength. Escape-cone losses occur for light rays which impact the surface of the waveguide plate at an angle $< \theta_c$. θ_c is the critical angle given by:

$$\theta_c = \sin^{-1}(1/n_{\lambda}) \quad (1.7)$$

The most common waveguide materials used are polymers, in particular, PMMA and polycarbonate (PC). These materials show favourable refractive indices (1.49 and 1.59 respectively), are cheap, easily processable, and suitable hosts for most luminescent species.²¹ While these materials are still widely used, there have been advances in the polymers used for LSCs with Griffini *et al.* utilising cross-linked fluoropolymers as host materials for thin film LSCs.⁵⁹ The LSCs fabricated using these fluoropolymers displayed efficiencies comparable to PMMA based reference devices, however they exhibited long term stability (>500 h) compared to PMMA, which can undergo photo-oxidation after prolonged exposure.¹⁰⁴ Other work on polymer waveguides has been aimed at making biodegradable host materials using L-poly(lactic acid) or silk fibroin, which showed n values of 1.45 and 1.54 respectively for eco-friendly LSCs.^{105–107}

Organic-inorganic hybrid materials have recently received considerable attention for applications as LSC host materials due to their combination of functionality and processability of the organic moiety with the stability and transparency of the inorganic.¹⁰⁸ Silsesquioxane-based materials have been examined as hosts for Eu^{3+} and Tb^{3+} ions as thin film LSC materials by Carlos *et al.*^{109–111} More recently, however, there has been a drive towards using ureasil-based materials as waveguides for LSCs with both organic dye based luminophores⁹¹ and Eu^{3+} β -diketonate complexes.^{112,113} For example, a planar flexible LSC based on a di-ureasil host (d-U(600)) and using an LR305 luminophore exhibited an η_{opt} of 14.5% and a PCE of 0.54% with a c-Si cell coupled (Fig. 1.10).⁹¹

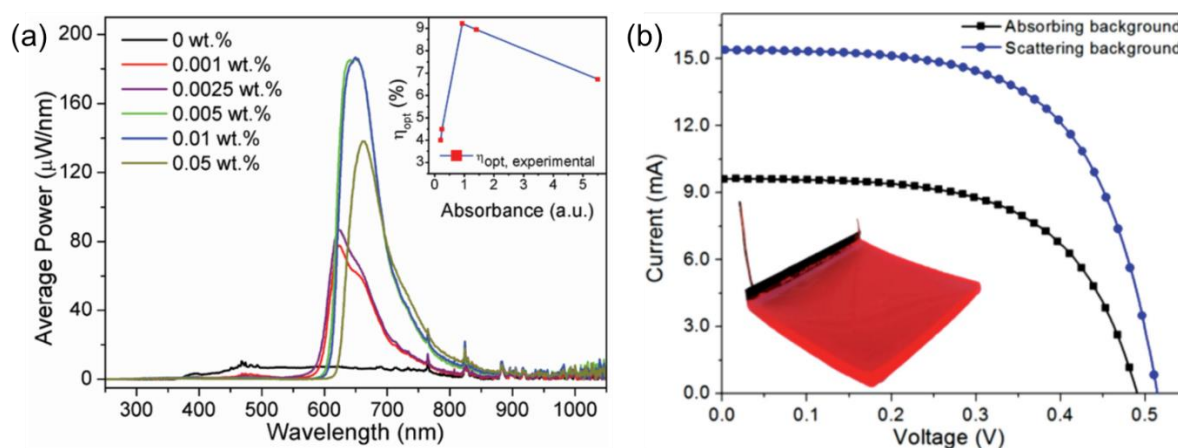


Figure 1.10. Optical and PV characterisation of LR305 di-ureasil planar LSC. (a) Optical power spectra of doped LR305-d-U(600) LSCs with a dark absorbing background, averaged over all four edges. (Inset) Variation of the experimental optical (red squares) efficiencies of the LSCs with a dark background, determined over the 300–800 nm spectral range, with respect to the LSC absorbance. (b) Current–voltage characteristics of c-Si solar cell coupled to 0.005 wt% LR305-d-U(600) LSC under absorbing and scattering background conditions. A photograph of this sample is shown in the inset. Adapted with permission from ref.⁹¹ Copyright Wiley 2018.

Interestingly, these materials have been demonstrated to allow controlled alignment of luminophores within the waveguide material to both inhibit or enhance FRET and self-absorption as required. A perylene carboxydiimide-bridged triethoxysilane (PDI-Sil) luminophore synthesised to replicate LR305 was covalently grafted within the siliceous domain of the ureasil backbone. Through tuning the branching and the molecular weight of the organic backbone, the energy transfer between the ureasil host and the PDI-Sil could be tuned to give emission colours from pink to orange.¹¹⁴ Further exploration of this immobilisation produced LSCs fabricated utilising a poly(fluorene-alt-

phenylene) (PFP) copolymer containing on-chain perylenediimide (PDI) chromophore units as the luminophore (PBS-PFP-PDI) immobilised within a ureasil waveguide.¹¹⁵ These devices achieved an η_{opt} of 5.6% using a scattering background, which was boosted to 13.1% by increasing the percentage of PDI units per PBS-PFP chains through doping with LR305.

1.5.3 LSCs for Emerging Photovoltaic Devices

Due to the requirement of thin strips of high efficiency PV cells, planar LSCs have for the most part been limited to applications with Si cells. To facilitate integration with third generation PV cells alternative architectures have to be investigated. One potential architecture which can overcome the need for thin strip PV cells are cylindrical LSCs, which show higher concentration factors than conventional LSCs and would allow end-on mounting of solar cells.¹¹² Correia *et al.* reported the fabrication of large area LSCs (up to 2.5 m length) in which bulk and hollow core LSCs were coated or filled with luminophores of rhodamine 6G or Eu(tta)₂·2H₂O doped into a ureasil matrix.⁸³ These LSCs gave an η_{opt} of 0.6% and an F of 6.5 for the bulk coated and an η_{opt} of 72.4% for optimised hollow core devices ($F = 12.3$). LSCs have been integrated with DSSCs through the usage of optical fibres, with Peng *et al.* demonstrating the effective combination of a fibre architecture DSSC with commercial LSCs using a connective envelope made of aluminium foil.¹¹⁶ A maximum PCE of 0.1% was observed for a red LSC coupled with four fibre DSSCs. Chen *et al.* recently took advantage of surface plasmon resonance to manage the emission behaviour of an LSC fabricated from nanofibers of poly[2,7-(9,9-dihexylfluorene)-alt-4,7-(2,1,3-benzothiadiazole)] and Ag nanoparticles.¹¹⁷ The nanofibers were integrated into OPV cells as an aligned network in check patterns, this led to an increase in PCE of 18% compared to the reference device; the total PCE obtained was 7.12%.

1.6 Silicon Photovoltaic Cells

To understand the limitations and potential of third generation PV, contemporary and historical devices have to be studied. PV cells are in their simplest form a doped semiconductor p - n junction and the most ubiquitous semiconductor material used in PV cells is crystalline silicon. A p - n junction consists of positive (p -) and negative (n -) doped semiconductors which act as hole and

electron transporters respectively, c-Si solar cells consist of a top layer of n -doped Si and a lower layer of p -doped Si. They operate via the *photovoltaic effect*, which describes how, as photogeneration of charge carriers in the n -type material occurs, there is also an increase in the number of holes in the p -type material. This charge separation creates an electric field which is in opposition to the intrinsic electric field of the p - n junction. This acts as a barrier to diffusion of charge carriers across the depletion region of the p - n junction, which in turn creates a voltage across the device (**Fig. 1.11**). Thus, as the n -type semiconductor absorbs light creating an electron-hole pair, the electron flows through the external circuit performing work as the hole diffuses through the p - n junction to the p -type side where it can recombine with the electron.

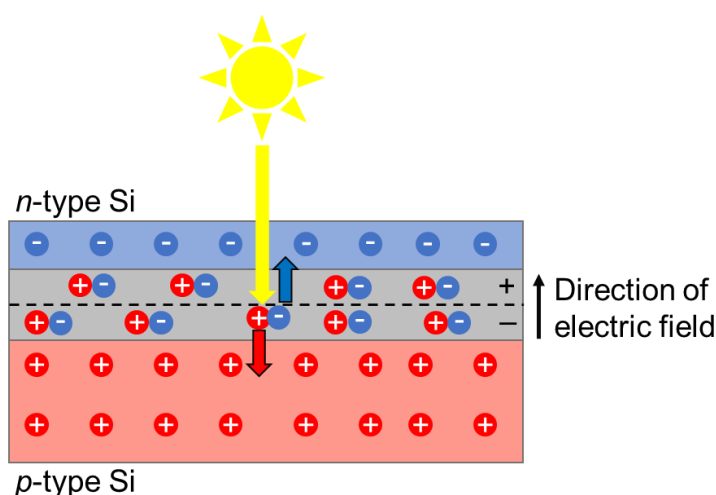


Figure 1.11. Schematic of the photovoltaic effect for a Si p - n junction. Grey area represents the depletion region formed due to diffusion of charge between the p -type and n -type Si.

The first c-Si solar cell was reported in 1941 and had an efficiency of $<1\%$.¹¹⁸ Cell efficiencies increased when diffusion fabricated junctions became possible with increases in cell efficiency from 4.5% to $>10\%$ reported between 1953 and 1955.^{118–120} By 1961 terrestrial efficiencies of 14.5% were achieved,¹²¹ however much of the research was focussed on space applications of the technology.¹²² It was not until the mid-1970s that Si-PV technology was considered for terrestrial applications and at this stage the cost was prohibitively high (*ca.* $\$70\text{ W}^{-1}$).¹²³ The price has massively decreased since then as innovations in device processing and further uptake in PV technology have led to “economy of scale” price reductions. This price drop has been described as Swanson’s Law, whereby, the price of PV modules decreases by approximately 20% for every doubling of cumulative

production, with current prices at $<\$0.40 \text{ W}^{-1}$.¹²³ Currently c-Si cells have a record cell efficiency of 26.7% and a record module efficiency of 24.4%, under standard testing conditions.¹²⁴

Si PV has many advantages, including: low cost;¹²³ high market share;^{125,126} a broad absorption window;¹²⁴ high stability;^{127,128} high efficiency.^{124,129} Although it is currently the technology of choice for most commercial PV applications, there are still some limitations. Crystalline Si for use in PV is currently manufactured by the Czochralski process, a high temperature process (1350 °C) which involves the slow growth of a single large Si crystal with defects $<10^{-10}\%$.¹³⁰ This crystal is then cut to wafers with material losses of up to 50%. While there have been innovations in the fabrication of mono and polycrystalline Si cells to minimise material losses, these methods are not yet industrially feasible.¹³¹ Despite silicon's broad absorption range into the infra-red (IR) region (bandgap *ca.* 1200 nm), it suffers from a lower absorption coefficient in the visible range than other technologies such as thin film chalcogenide and perovskite cells.¹³² This low absorption coefficient means in order to efficiently harvest high-energy short-wavelength light, the Si layers have to be thicker, which contributes to device weight and limits applications. The inability to effectively harvest all wavelengths of solar light is in itself a limitation, with the maximum efficiency achievable for Si, as described by the Shockley-Queisser limit, of 29.6%.^{24,30} Other issues with Si devices include low-flexibility¹³³ and poor performance in diffuse light conditions.^{10,11} These limitations offer an opportunity for both Si complementary technologies and emerging third generation PV technologies to capitalise on.

1.7. Perovskite Solar Cells

Since 1991, when Grätzel and O'Regan first developed DSSCs, there has been a drive to develop low-cost, high stability, high efficiency third generation photovoltaics.¹³⁴ The initial DSSC showed a PCE of *ca.* 7% and was highly attractive due to the low cost of the materials, and facile processing. However, currently the record certified efficiency of DSSCs is 11.9%, which is still considerably lower than silicon PV.¹²⁴ From DSSC architectures, PSCs have emerged as a separate family of next generation cells, which have shown ease of processability and efficiencies comparable to c-Si PV on a lab scale. In 2009 Miyasaka *et al.* used $\text{CH}_3\text{NH}_3\text{PbBr}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_3$ as absorber materials in DSSC architectures.¹³⁵ These cells showed a PCE of 3.13 and 3.81% respectively;

however, they quickly degraded due to reaction of the halides in the perovskites with the halides in the liquid electrolyte. This efficiency was greatly increased in 2012 when $\text{CH}_3\text{NH}_3\text{PbI}_3$ was coupled to a 2,2',7,7'-tetrakis[*N,N*-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (spiro-OMeTAD) solid-state hole transporting layer (HTL) to give cell efficiencies of 9.7%.¹³⁶ Later that year, Lee *et al.* coupled a mixed halide perovskite $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ to a mesoporous Al_2O_3 scaffold layer giving a cell efficiency of 10.9%.¹³⁷ The use of solid state HTL led to an explosion of research in the field of PSCs to improve both the efficiency and the stability of these devices in the past five years. At the time of writing, state of the art perovskite-based solar cells have certified efficiencies of 22.1%.¹²⁴

1.7.1 Working Principle of PSCs

Perovskites are materials which possess the chemical formula the ABX_3 , where A and B are typically two cations of very different sizes and X is an anion that binds to both (**Fig. 1.12a**).¹³⁸ The perovskites used as absorber materials in PSCs are typically organic-inorganic hybrids, the most common being methylammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$), which since its first use in 2009 has become the archetypal absorber for incorporation in PSCs.¹³⁹ **Fig. 1.12b** shows the general configuration of a PSC, which typically consists of a transparent conducting oxide (TCO) coated glass substrate, usually fluorine-doped tin oxide (FTO), the photoactive perovskite layer and the charge transport layers consisting of an electron transport layer (ETL) and a HTL.¹⁴⁰

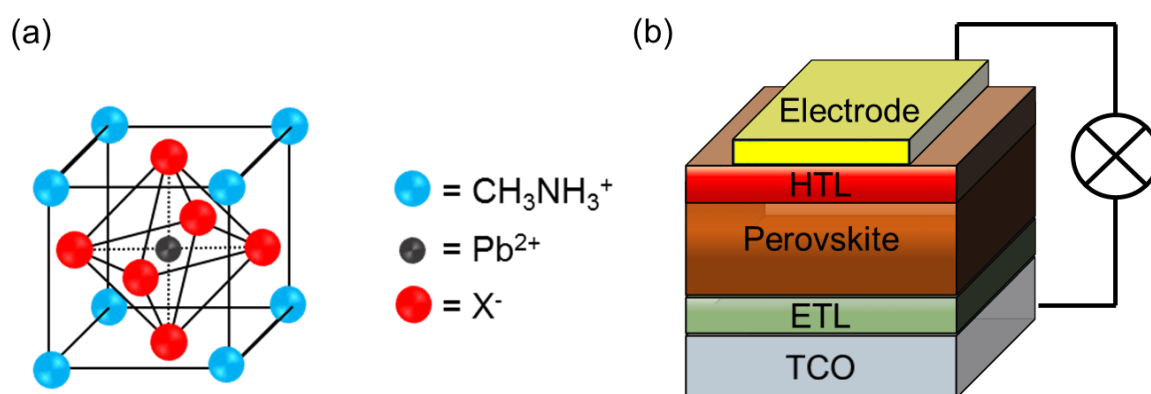


Figure 1.12. (a) Crystal structure of a $\text{CH}_3\text{NH}_3\text{PbX}_3$ organo-lead halide perovskite. (b) Schematic of the general constituents of a PSC.

In PSCs, like in any photovoltaic device, the conversion begins with light-induced charge generation. $\text{CH}_3\text{NH}_3\text{PbI}_3$ has a direct bandgap of *ca.* 1.55 eV, which corresponds approximately to a

wavelength of 800 nm. This, coupled with a high absorption coefficient in the visible range, means that thin $\text{CH}_3\text{NH}_3\text{PbI}_3$ films can be used to lower transport losses.^{141–143} The valence and conduction band consist only of Pb and I orbitals, with the methylammonium cation only contributing to the formation of the 3D perovskite crystal and thus only impacts the optical properties.¹⁴⁴ Upon charge generation, charge separation typically occurs when either the electron or hole comes into contact with the ETL or HTL respectively, so the efficiency of charge generation is dictated by the dimensions of the device and the charge carrier diffusion length. It was observed by Snaith *et al.* and Grätzel *et al.* that upon excitation of these materials, the charge carrier diffusion lengths for $\text{CH}_3\text{NH}_3\text{PbI}_3$ are up to 100 nm, with Snaith *et al.* further demonstrating charge carrier diffusion lengths of 1 μm for $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskites.^{145,146} These long carrier diffusion lengths contribute to the high efficiencies observed for PSCs as it means that there is limited recombination within the dimensions of the device. Interestingly, the same group then discovered that in the perovskites the exciton binding energy was so low that upon photoabsorption there is spontaneous generation of free electrons and holes, which enables the impressive performance of these materials in PV cells through ambipolar charge transport.¹⁴⁷ This charge separation and ambipolarity means that perovskites can effectively separate charge even in the absence of an ETL or HTL.^{148–150} Upon reaching the ETL the electron generated then diffuses to the cathode, where it performs work in the external circuit and recombines with the generated holes at the anode.

1.7.2 Architectures and Components of PSCs

While PSCs were originally developed from DSSCs, the device architectures have diverged considerably. The most common device architecture mimics a solid-state DSSC and consists of FTO glass coated with a compact TiO_2 layer, upon which a mesoporous TiO_2 layer followed by a $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer is deposited. Spiro-OMeTAD is then typically applied as the HTL, followed by a gold electrode to give an *n-i-p* junction. This is the architecture which was used by Grätzel *et al.* when efficiencies of *ca.* 10% were first achieved.¹³⁶ Through improvement of processing techniques, cells with this architecture have achieved efficiencies of over 17%.¹⁵¹ While this architecture is still commonly used to benchmark cells, there have been significant variations to achieve higher efficiencies and stabilities, the most common device architectures are highlighted in **Fig. 1.13**.

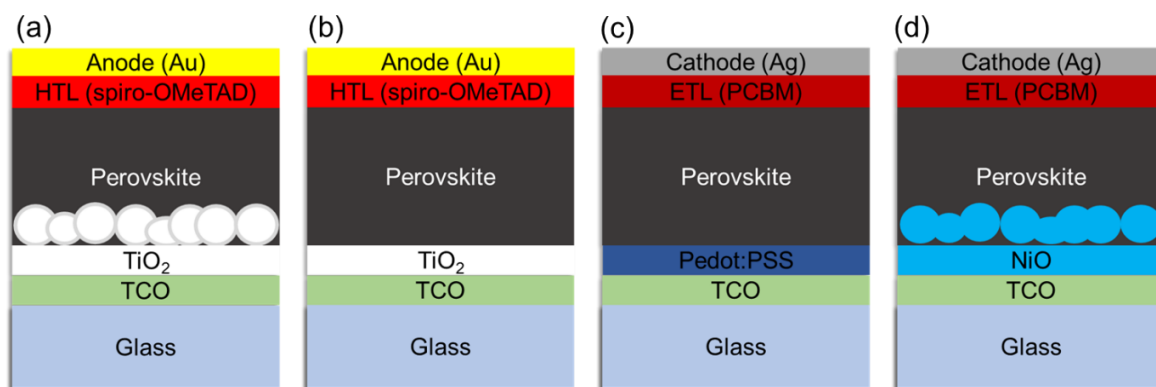


Figure 1.13. Common PSC device architectures. (a) Mesoscopic TiO_2 ($n-i-p$). (b) Planar ($n-i-p$). (c) Planar ($p-i-n$). (d) Mesoscopic NiO ($p-i-n$).

An important alteration of the mesoscopic TiO_2 architecture initially used was by Lee *et al.*, who replaced the TiO_2 with insulating Al_2O_3 to give cell efficiencies of *ca.* 11%. This indicated electron transport could occur in the perovskite material without an ETL. By removing the mesostructured host material, the planar device architecture was developed, with early examples showing efficiencies of >15%.¹⁵² The observation that these materials could both act as electron ‘donor’ (similar to those in OPV) and that an infiltrated HTL was not required for the PSCs to function, led to the development of what is commonly referred to now as the ‘*inverted*’ architecture. Chen and co-workers prepared planar inverted $p-i-n$ type perovskite solar cells based on the common planar-heterojunction type OPV as depicted in **Fig. 1.13c**.¹⁵³ These first cells used poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) and fullerene derivatives as HTL and ETL, respectively, and only achieved cell efficiencies of *ca.* 3%. However, later that year Malikiewicz *et al.* demonstrated inverted type PSCs with 12% efficiencies.¹⁵⁴ **Fig. 1.13d** shows the inverted mesoscopic cell architecture, which was first demonstrated by Wang *et al.*, with the intention of combining the benefits of both architectures by using mesoporous NiO as the HTL.¹⁵⁵

The four architectures described above are the most commonly encountered, but the constituents of these devices, in particular the perovskite absorber used, are varied considerably to achieve high efficiencies. One of the first methods used was to replace the methyl ammonium (MA) cation with formamidinium (FA), to achieve a narrower bandgap¹⁵⁶ or caesium to achieve a wider bandgap.¹⁵⁷ FA-based PSCs achieved a 20.1% efficiency through intramolecular exchange between dimethyl sulfoxide (DMSO) intercalated in the PbI_2 layers with FA to produce FAPbI_3 films with

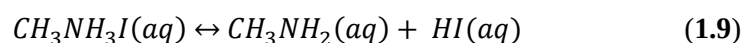
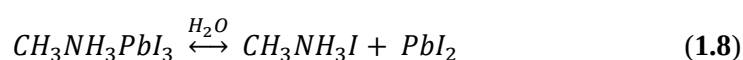
(111)-preferred crystallographic orientation, large-grained dense microstructures, and flat surfaces.¹⁵⁸ Saliba *et al.* demonstrated “triple-cation” type perovskites with a general formula $\text{Cs}_x(\text{MA}_{0.17}\text{FA}_{0.83})_{(100-x)}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$, which showed a high PCE (21.1%), high stabilities and less impurities.¹⁵⁹ One of the most attractive methods to increase efficiency is using graded band-gap PSCs, in which compositions of the perovskite materials, both the organic molecules methyl and ammonia, the metals tin and iodine, and the halides are combined using a single atom thick hexagonal boron-nitride separation layer to ensure no ion diffusion occurs.¹⁶⁰ These cells can then effectively harvest the entire solar spectrum and function as *pseudo*-tandem cells.

1.7.3 Device Instability

Despite the meteoric rise of PSCs in terms of efficiency over the last five years, there are still significant questions regarding their suitability for scalable applications due to poor device stability. The organolead halide perovskites used in these solar cells undergo rapid degradation upon exposure to moisture, high temperatures and UV-illumination. This degradation is typically accompanied by a colour change from dark brown/black to bright yellow representing the conversion of $\text{CH}_3\text{NH}_3\text{PbI}_3$ to PbI_2 .

1.7.3.1 Moisture Degradation

Niu *et al.* suggested the following series of reactions occur to cause the degradation of the perovskite layer:¹⁶¹



In these reactions it is suggested water acts as the catalyst for the degradation by forming hydrogen bonds with the methylammonium cations which, in turn, causes bond dissociation in the perovskite crystal.¹⁶² Frost *et al.* suggested an alternative degradation pathway in which an acid-base

reaction occurs between water and the perovskite, bringing about the initial decomposition of the perovskite layer.¹⁶³ The production of volatile CH_3NH_2 and the decomposition of HI which follows the above dissociation causes the irreversible degradation of the perovskite. The reduced PCE is not the only issue with device degradation: the decomposition product of PbI_2 raises environmental concerns due to its toxicity and water solubility. The role of moisture as the initiator for the degradation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskites was investigated using *in situ* techniques by Yang *et al.*¹⁶⁴ By constructing an environmental chamber which flowed gas of controlled humidity over the perovskite, in conjunction with UV/Vis absorption and X-ray diffraction (XRD) techniques, the decay of perovskite features was monitored. They observed no decay occurring when N_2 or low humidity air were used as carrier gases. The authors suggested the formation of a hydrated intermediate $(\text{CH}_3\text{NH}_3)_4 \text{PbI}_6 \cdot 2\text{H}_2\text{O}$ occurred prior to degradation, contrasting the one step degradation mechanism of $\text{CH}_3\text{NH}_3\text{PbI}_3$ suggested by Niu *et al.*¹⁶¹ This intermediate was also observed by Christians *et al.* through XRD studies of $\text{CH}_3\text{NH}_3\text{PbI}_3$ after exposure to moisture.¹⁶⁵ They further confirmed the formation of this intermediate by synthesising it and comparing the XRD pattern of the intermediate with the pattern of $\text{CH}_3\text{NH}_3\text{PbI}_3$ exposed to 90% relative humidity (RH). They suggest that the formation of the hydrated intermediate is dependent on the relative strength of the hydrogen bonding between either the cation MA or H_2O with PbI_6 . Thus, inherently strengthening the bond between the cation and metal halide may improve the resistance of the perovskite to moisture.

1.7.3.2 Thermal Degradation

Thermal degradation is a significant concern for perovskite materials due to the thermal annealing step that is typically required to form the perovskite upon deposition.¹⁶⁶ Phillippe *et al.* performed a detailed study on the impact of temperature on both $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskites.¹⁶⁷ They exposed the perovskite films to different environmental conditions and characterised the changes using X-ray photoelectron spectroscopy (XPS). The main result of the different exposures was that the perovskite is decomposed into PbI_2 , but this degradation occurs at temperatures as low as 100 °C and is not only related to humidity. Even in an inert atmosphere such as argon, slow degradation to PbI_2 was observed. The authors suggested a reaction similar to that

shown in (Eqn. 1.9) occurs and that the high temperature exacerbates the removal of the volatile CH_3NH_2 . Conings *et al.* performed studies on ‘half-finished’ perovskite cells, consisting of an TCO substrate coated with TiO_2 and a $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer, in different environmental conditions to monitor the degradation of the perovskite layer.¹⁶⁸ Topographical scanning electron microscopy (SEM) images showed structural changes occurred even at temperatures as low as 85 °C. Using conductive atomic force microscopy (AFM) in conjunction with XRD, the areas of topological changes were confirmed to be PbI_2 . Delamination was also observed to occur for the films heated in ambient conditions.

Divitini *et al.* performed a detailed study on the effect of temperature on the degradation of PSCs by fabricating cells by four different methods; three of them involved a two-step synthesis of the perovskite layer in either vacuum, glove box and ambient conditions, and one by a single-step in glove box conditions.¹⁶⁹ The devices were heated and analysed by transmission electron microscopy *in situ*, allowing the deformation of the perovskite layers to be observed as it occurred. **Fig. 1.14** shows an example of a high angle annular dark-field (HAADF) scanning transmission electron micrograph (STEM), with energy dispersive X-ray spectroscopy (EDX) elemental maps. They observed that the signal decay in the samples fabricated in air was slower than in the sample fabricated in the glove box. They suggest this is due to the incorporation of low concentrations of oxygen and water in the perovskite film which induces pinning sites and prevents the diffusion PbI_2 .

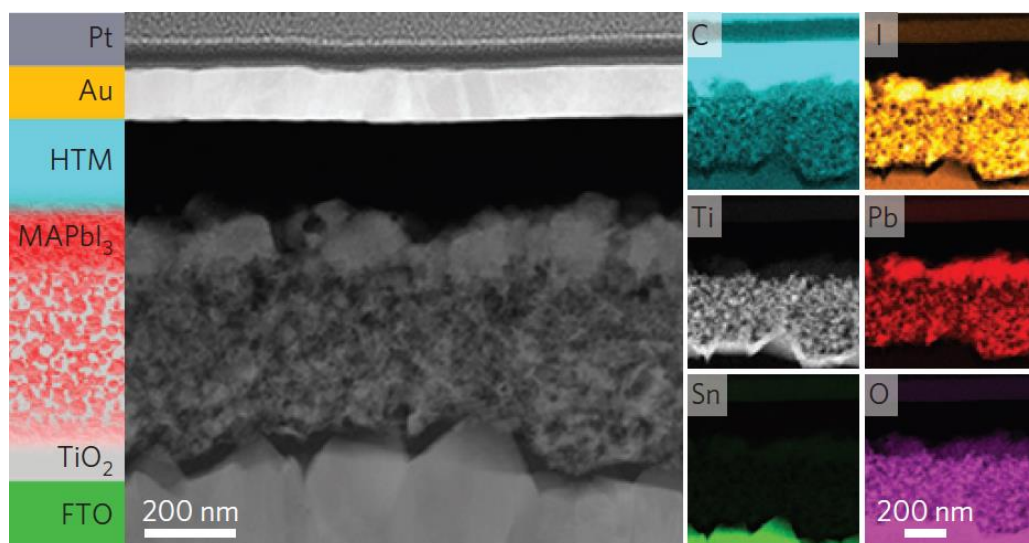


Figure 1.14. Cross-sectional image of a $\text{CH}_3\text{NH}_3\text{PbI}_3$ PSC taken by HAADF STEM. PSC layers are labelled in the schematic representation on the left. The EDX elemental maps are on the right showing well defined layers. Adapted with permission from ref.¹⁶⁹ Copyright Nature 2018.

1.7.3.3 UV Degradation

As with other third generation PV such as DSSCs and OPVs, PSCs are susceptible to UV degradation. If we look at (Eqn. 1.11), it can be seen that UV radiation can help to bring about the irreversible degradation of HI to H₂ and I₂. Leijtens *et al.* noted that for PSCs under UV-illumination, the TiO₂ mesoporous layer is vulnerable to degradation, which can in turn bring about degradation of the perovskite layer.¹⁷⁰ This was studied by measuring the device efficiency under 5 h continuous UV-illumination for encapsulated and non-encapsulated devices, with and without a UV filter. It was observed that the encapsulated devices degraded quicker than the non-encapsulated, due to the trapping of electrons injected into the TiO₂ in unoccupied sites, with the trapped electrons then recombining with the holes of the HTL. The density of these trap states was related to the rate of oxygen desorption, hence encapsulated cells showed lower efficiencies. It was also demonstrated by Konrad *et al.* that the compact TiO₂ layer, which has been seen as essential in all *n-i-p* type PSCs, can cause a decrease in the PCE.¹⁷¹ They overcame this by using a phenyl-C₆₁-butyric acid methyl ester (PCBM)-based compact layer. While mixed halide PSCs, such as the triple cation have achieved high efficiencies, they come with their own intrinsic instabilities.¹⁷² These mixed halide systems can undergo halide segregation upon illumination. This nanoscale segregation causes multiple perovskite compositions to occur throughout the thin film.¹⁷² This segregation of halides takes place *via* halide defects in the perovskite layer and can significantly limit any efforts to tune the bandgap of mixed halide layers.¹⁷³

1.7.4 Improving Device Stability

1.7.4.1 Tuning the Perovskite Layer

In order to improve the stability of PSCs there has been significant research has already been undertaken to improve the intrinsic stability of the active perovskite layer. One of the most effective methods to improve both the moisture and thermal stability is to use mixed halide perovskites. Seok *et al.* synthesised mixed bromide-iodide PSCs of varying ratios to see the effect that the bromide content has on the stability.¹⁷⁴ PSCs with even a small ratio of Br to I (1:4) showed improved stabilities and efficiencies. This stability increase is due to a move from a tetragonal CH₃NH₃PbI₃

structure to a more compact cubic $\text{CH}_3\text{NH}_3\text{PbBr}_3$ structure, which limits the ease of intercalation by moisture. The use of formamidinium in place of methylammonium as the organic counterion has been demonstrated to both improve the efficiency and thermal stability of PSCs, with cells showing stability at 150 °C.¹⁷⁵ However, it has also been demonstrated that formamidinium-based perovskites are highly sensitive to humidity. Wozny *et al.* showed that upon raising RH to 30–40% there was an observed decay in morphology, carrier lifetime, optical property and crystallinity.¹⁷⁶

Karunadasa *et al.* also varied the cation used in the PSC to improve the stability using $(\text{PEA})_2(\text{MA})[\text{Pb}_3\text{I}_{10}]$ absorbers ($\text{PEA} = \text{C}_6\text{H}_5(\text{CH}_2)_2\text{NH}_3^+$).¹⁷⁷ These materials formed 2D layered structures in which the outer organic groups can act to repel moisture. After 46 days the crystal structure of these materials was retained while the structure of the $(\text{MA})[\text{PbI}_3]$ had decayed. Li *et al.* pioneered the use of cross-linking agents by including an additive, butylphosphonic acid 4-ammoniumchloride, into a one-step spin-coating method to modify the $\text{CH}_3\text{NH}_3\text{PbI}_3$ surface.¹⁷⁸ This cross-linking prevented the interaction of moisture with the perovskite layers and improved stability.

1.7.4.2 Encapsulation

While altering the perovskite layer is an attractive option to improve the stability, much of the research has been to improve the stability of the most common PSC architecture (based on $\text{CH}_3\text{NH}_3\text{PbI}_3$) by encapsulation. Encapsulation seems an obvious solution for the stability issues faced by PSCs, however, most of the encapsulation performed at the laboratory scale involves manual coverage of the device with a glass cover slip and sealing using an epoxy resin.^{179–181} While this method has proven to be effective in small devices it is not practical for mass production. Roll-to-roll fabrication will require encapsulation of the devices using polymer layers similar to what has already been demonstrated with OPV cells.¹⁸²

A variety of materials have been investigated as device encapsulants, to act as a barrier layer to prevent moisture-initiated degradation. Hwang *et al.* coated PSCs with Teflon by simply spin-coating the hydrophobic polymer on the completed devices.¹⁸³ It was observed that upon encapsulation the stability of the PSCs increased significantly, with no observable UV/vis absorption degradation over 30 days storage in air and after 900 s immersion in water. The uncoated cells saw

a drop in PCE from *ca.* 11 to 6% after 30 days, whereas the encapsulated devices only decreased from 11.8 to 11.1% over the same timescale. Al_2O_3 , which itself has been demonstrated to be an effective mesoporous host material for PSCs has been used as an encapsulant for PSCs.^{161,184} This was first demonstrated by Niu *et al.* who used dip-coating into triethylaluminium to deposit an Al_2O_3 layer¹⁶¹ and later Kim *et al.* used water-free atomic layer deposition to grow films of Al_2O_3 on perovskite.¹⁸⁴ These methods both resulted in improved thermal and moisture stability of the perovskite films. PMMA and polycarbonate PC films have been demonstrated to similarly act as effective barrier layers.^{162,185} Habisreutinger *et al.* compared perovskite layers encapsulated by PMMA and PC at 80 °C for 96 h with bare perovskite.¹⁶² The encapsulated layers showed no degradation of note in the timescales investigated when monitored by UV/Vis absorption spectroscopy and no degradation was observed when the films were placed under water flow. Krebs *et al.* used polyethyleneterephthalate as a substrate and to encapsulate the first roll-to-roll fabricated PSC, which showed a PCE of 4.9%.¹⁸⁶

1.8 Perovskite Nanocrystals

The uptake of perovskite-based semiconductors as absorber materials in solar cells has drawn attention to their unique physical properties, such as large charge carrier diffusion lengths,¹⁸⁷ high absorption coefficients,¹⁸⁸ ambipolarity,¹⁸⁹ and tunable bandgaps.¹⁹⁰ These properties have led perovskites to be investigated for use in other devices, in particular, light-emitting diodes (LEDs). Perovskite LEDs have been explored since the 1990's, however they were limited by poorly understood photophysical properties.^{191,192} Recent attempts at making thin film perovskite devices have been more successful. Tan *et al.* fabricated infrared-, red- and green-emitting perovskite LEDs by varying the ratio of bromide to iodide in $\text{CH}_3\text{NH}_3\text{PbX}_3$.¹⁹³ They demonstrated high EQE and internal quantum efficiency (IQE) of 0.76 and 3.4% for their infrared LEDs, however the visible green-emitting devices only achieved an EQE and IQE of 0.1 and 0.4%, respectively. These low values are due to the low Φ_{PL} value of 7% for the green-emitting perovskites.

Recent work for optical sensing and LED applications has focussed on perovskite nanocrystals (PNC) due to their high Φ_{PL} values and tunable optical properties.^{194,195} Interestingly much of the PNCs presented in initial research showed negligible quantum confinement, due to an

average particle size greater than the Bohr radius.¹⁹⁵ Schmidt *et al.* presented the first example of PNCs in 2014, which were $\text{CH}_3\text{NH}_3\text{PbBr}_3$ based.¹⁹⁶ Despite not exhibiting quantum confinement effects these particles showed Φ_{PL} values of 20%. Since then, Φ_{PL} values near unity have been obtained for these materials. Song *et al.* fabricated CsPbX_3 which displayed Φ_{PL} values between 60–90% and achieved values of $\Phi_{\text{PL}} > 85\%$ for all inorganic perovskite CsPbBr_3 PNC thin films.¹⁹⁷ These films were used to fabricate LEDs which showed EQEs up to 0.12% with little optimisation. Similar results were achieved for $\text{CH}_3\text{NH}_3\text{PbBr}_3$ PNCs soon after, with up to 85% Φ_{PL} achieved by Ling *et al.*¹⁹⁸ These $\text{CH}_3\text{NH}_3\text{PbBr}_3$ PNCs when incorporated into LEDs gave EQE values up to 0.48%. By using the *quasi*-spherical shaped 2-adamantylammonium bromide as a capping ligand, a Φ_{PL} of *ca.* 100% was achieved for $\text{CH}_3\text{NH}_3\text{PbBr}_3$ PNCs in N_2 and air by Gonzalez-Carrero *et al.*¹⁹⁹ Recently, Xing *et al.* synthesised mixed halide PNCs to tune the emission colour, but utilised amorphous $\text{CH}_3\text{NH}_3\text{PbBr}_3$ PNCs to make a record high efficiency PNC LED with an EQE of 3.8% and a maximum luminance efficiency of 11.49 cd/A.²⁰⁰

1.8.1 Quantum Confinement in Nanocrystals

Quantum dots and nanocrystals (NC) have been described above as effective luminophores for spectral converters due to their tunable emission properties, which are often size dependent. The size dependence of the photophysical properties of QDs and other nanoparticles is a result of quantum confinement.²⁰¹ Quantum-confined nanoparticles were first observed in CuCl crystals grown on silicate glass in 1981.²⁰² These materials began to be known as artificial atoms because their behaviour was between that of atoms and semiconductors.^{203,204} The observation with these artificial atoms was that as the size of the particles was decreased the bandgap increased and the energy bands began to appear quantised. Due to their small size, the electrons in quantum dots are confined in a small space. As the size decreases (geometric constraint) the electron wave functions are confined to the physical dimensions of the particles and when the radius of the semiconductor nanocrystal is smaller than the exciton Bohr radius (the average distance between the electron in the conduction band and the hole it leaves behind in the valence band), quantisation of the energy levels occurs (**Fig. 1.15**).²⁰¹ Thus, by adjusting the size of these materials, the bandgap and emission wavelengths can be varied.

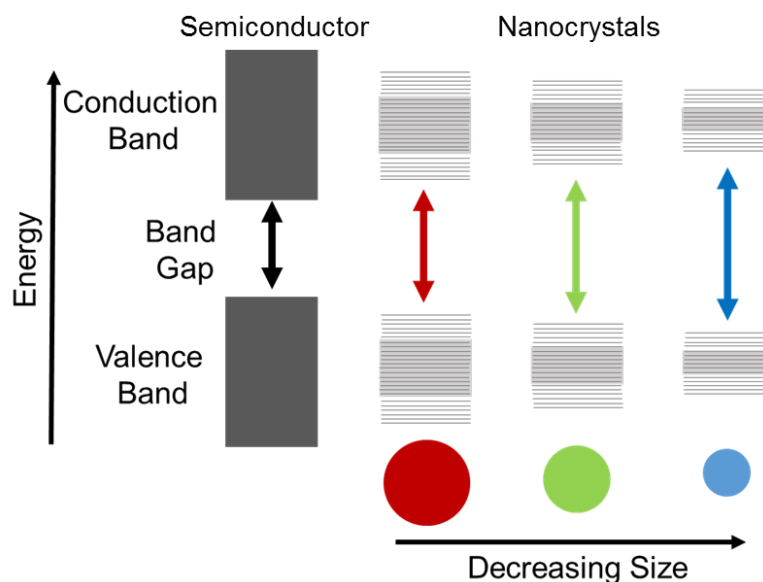


Figure 1.15: Schematic representation of the energy levels in a bulk semiconductor and quantum-confined nanoparticles as a function of particle size. In quantum confined particles the energy levels split and the semiconductor bandgap increases with decreasing size.

1.8.2 Perovskite Nanocrystal Synthesis and Emission Properties

The first examples of the synthesis of PNCs relied on using a mixture of long and short chain alkylammonium cations in ligand-assisted reprecipitation reactions (LARP).¹⁹⁶ The long chain cations cannot be incorporated into the perovskite structure and thus lead to self-termination of the PNC growth, and passivation of the new crystal facets.¹⁹⁵ Upon synthesis, $\text{CH}_3\text{NH}_3\text{PbBr}_3$ PNCs were initially obtained as large platelet like structures with thicknesses of *ca.* 20 nm and lateral dimensions of *ca.* 100 nm. By increasing the concentration of the long chain (octylammonium) capping ligand relative to the MA ligand, quantum confinement effects were first observed for PNCs by Urban *et al.*²⁰⁵ The thickness of the platelets was observed to decrease until it was near monolayer thickness and a blue-shift of the emission properties occurred. Levchuk *et al.* observed similar thickness tailoring of PNCs by varying the ratios of oleylamine (OY) and oleic acid (OA) capping ligands.²⁰⁶ This LARP technique was first utilised to fabricate mixed halide PNCs by Zhang *et al.*, who demonstrated that by simply varying the ratios of the PbX_2 and MAX precursors emission colour tunability could be achieved through the whole visible range (**Fig. 1.16**).²⁰⁷

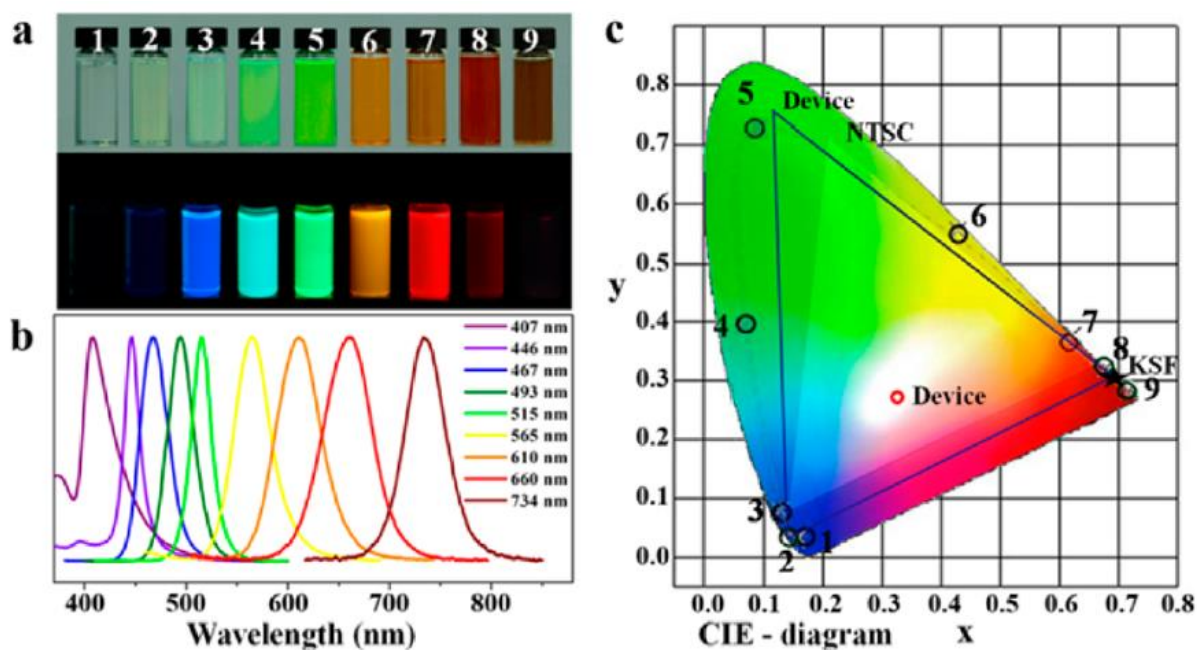


Figure 1.16. Emission properties of mixed halide $\text{CH}_3\text{NH}_3\text{PbX}_3$ PNCs. (a) Photographs of $\text{CH}_3\text{NH}_3\text{PbX}_3$ QDs under ambient light and a 365 nm UV irradiation (Cl – Br – I left to right). (b) Steady-state PL spectra of $\text{CH}_3\text{NH}_3\text{PbX}_3$ QDs. (c) CIE colour coordinates corresponding to the $\text{CH}_3\text{NH}_3\text{PbX}_3$ QDs. Adapted with permission from ref.²⁰⁷ Copyright 2018 American Chemical Society.

While the emission properties are significantly affected by the anion used, the cation can also affect the properties, in particular if the MA cation is replaced with caesium.²⁰⁸ All inorganic CsPbBr_3 PNCs are synthesised by a hot injection method, which typically means these PNCs require high temperatures (*ca.* 300 °C), however they typically show improved stability and Φ_{PL} values to the mixed organic-inorganic perovskites. Despite the advances in the development of the thickness and halide dependant optical properties of these PNCs, there is a lack of understanding on what the synthesis and storage conditions have on these properties, with different groups reporting different morphologies for similar fabrication conditions.

1.9 Aims

This thesis aims to investigate the use of spectral converters, such as luminescence down-shifting layers and luminescent solar concentrators, to improve the efficiency and stability of third generation PV cells, particularly perovskite solar cells, which currently limits the uptake of these technologies on a large scale.

The first part of this thesis will investigate a two-fold approach of both polymer encapsulation to improve the resistance of the device to moisture-induced degradation and the addition of luminescent down-shifting (LDS) layers to act as UV-filters. **Chapter 3** will focus on the relationship between the physical properties of polymer encapsulation layers and their effectiveness as encapsulants for PSCs through a time dependant stability study. The effect of the encapsulation by polymer layers (PMMA, PC, ethyl cellulose (EC) and poly(4-methyl-1-pentene) (PMP) applied directly to the $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite layer will be investigated through thermally induced degradation and characterisation at timed intervals. The mechanism of this degradation will then be further elucidated using fluorescence microscopy. PMMA will be demonstrated as the most effective encapsulant due to its low water vapour transport rate. Following from this result PMMA will be presented as the most suitable host material for LDS coatings for PSCs.

In **Chapter 4** minimising the light induced degradation of PSCs will be investigated through LDS coatings. A variety of luminophores doped into a PMMA host material and coated onto PSCs will be subjected to stability testing under simulated solar illumination for extended periods of time. This chapter will aim to demonstrate the relationship between luminophore optical absorption and emission properties, doping concentrations and layer thickness on the effectiveness of the LDS layer to both improve device PCE and to minimise light induced cell degradation. The luminophores coated consisted of organic dyes, conjugated polymers and AIEgens, however, as discussed above, quantum confined nanocrystals show attractive properties for use in spectral converters. The second part of the thesis will investigate the potential of nanocrystals as luminophores for spectral conversion.

Chapter 5 will investigate the effect of dilution on $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{I}_x$ PNC solutions to give insight into the solution phase behaviour of the materials. We will present observations that the emission and absorption properties can be tuned by dilution with the anti-solvent used in the fabrication process due to a combination of both ion exchange and particle growth. We will thus aim to understand the dilution effect on the PNCs to reliably minimise any unwanted side reactions which cause significant alteration of the morphology, optical properties and stability of the PNCs.

Chapter 6 will detail the use CdSe@ZnS/ZnS QDs with a composition gradient shell in a polymer matrix for fabrication of large-area QD-LSCs. A detailed study into the characterisation of large-area LSCs will be presented and three proposed methodologies will be compared as well as the sources of error which can arise when investigating large-area LSCs. The effect of the luminophore concentration on the optical efficiency of the QD-LSCs will be presented, together with the relative contributions of reabsorption and scattering processes along the length of the device. These LSCs will be integrated with a planar, thin strip DSSC. **Chapter 7** summarises the conclusions and future research directions arising from this work.

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Chapter Two

Experimental

2.1 Materials

2.1.1 Perovskite Encapsulation

Methylamine solution (33 wt% in absolute ethanol), hydroiodic acid (57 wt% in H₂O), lead chloride (99.999%), ethanol (99%), poly(methyl methacrylate) (PMMA) (molecular weight (M_w) (av.) 120,000 g mol⁻¹), ethyl cellulose (EC) (48% ethoxyl) and poly(4-methyl-1-pentene) (PMP) were all obtained from Sigma Aldrich. Polycarbonate (PC) (M_w (av.) 45,000 g mol⁻¹) was obtained from Acros Organics. Dimethyl formamide (DMF) (99.8%), toluene (99.8%), chloroform (99.8%), cyclohexane (99.8%), dimethyl sulfoxide (DMSO) (99.8%) and dichloromethane (DCM) (99.8%) were obtained from Fisher. Encapsulation epoxy was purchased from Ossila. All reagents were used as received.

2.1.2 Perovskite Cell Fabrication

Lead iodide (99%), titanium diisopropoxide bis(acetylacetonate) (75% in isopropanol), chlorobenzene (99.8%), bis(trifluoromethane)sulfonimide lithium salt (Li-TFSI) (anhydrous 99.8%), 4-tert-butylpyridine (tBP) (96%), tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)cobalt(III) tri[bis(trifluoromethane)sulfonimide] (FK209) (98%), nickel (II) acetate tetrahydrate (98%), 2-methoxyethanol (anhydrous 99.8%), ethanolamine (98%), DMF (anhydrous 99.8%), DMSO (anhydrous 99.8%), and bathocuproine (BCP) (99.99%) were purchased from Sigma Aldrich. Spiro-OMeTAD (99%) and phenyl-C61-butyric acid methyl ester (PCBM) (99%) were purchased from Ossila. FTO glass substrates (TEC 7) were purchased from NSG Pilkington. TiO₂ paste (30NR-D) and methylammonium iodide were purchased from Dyesol. Silver pellets and gold wire (1 mm diameter) were purchased from Kurt J. Lesker. All materials were used as received.

2.1.3 Perovskite Nanocrystal Synthesis

Lead (II) iodide (PbI₂, 99.999% trace metal basis), oleylamine (tech. 70%), hydroiodic acid (57 wt% in H₂O), methylamine solution (33 wt% in ethanol), chloroform (98%) and *N,N*-dimethyl formamide (99.8% anhydrous) were purchased from Sigma-Aldrich. Toluene (anhydrous, 99.8%) and oleic acid (90%) were purchased from Alfa Aesar. Lead (II) bromide (PbBr₂, 98%) was

purchased from Acros Organics. Hydrobromic acid (47%) was purchased from VWR. All chemicals were used as received.

2.1.4 Luminophores

Lumogen F Red 305 and Lumogen F Violet 570 were supplied by BASF. Poly(9,9-di-*n*-octylfluorenyl-2,7-diyl) ($M_w > 20000$) (PFO) was purchased from Sigma Aldrich. Coumarin 153 (C153) was purchased from Tokyo Chemical Industry. 2-(2-hydroxyphenyl)quinazolin-4(3H)-one (HPQ) was a kind gift from Professor Ben Zhong Tang at Hong Kong University of Science and Technology. All luminophores were used as received.

2.1.5 Large Area Quantum Dot LSC Synthesis

Cadmium acetate (anhydrous), zinc oxide, sulfur, selenium (99.99%), oleylamine (97%), 1-octadecene, trioctylphosphine (97%), zinc acetate dihydrate, lauryl methacrylate (LMA), 2,2-dimethoxy-1,2-diphenylethan-1-one, 1-butyl-3-methyl imidazolium iodide (0.6 M) iodine (0.03 M), guanidium thiocyanate (0.10 M) and 4-*tert*-butylpyridine were purchased from Sigma Aldrich. Ethylene glycol dimethacrylate (EDGM) was purchased from Santa Cruz Biotechnology. TiO₂ paste, Pt paste (platisol), N719 sensitising dye (*cis*-di(thiocyanato)-*N*-*N'*-bis(2,2'-bipyridyl-4-carboxylic acid-4'-tetrabutylammonium carboxylate) ruthenium (II)) were purchased from Dyesol Ltd. All chemicals were used as received.

2.2 Instrumentation

2.2.1 UV/Vis Absorption Spectroscopy

UV/Vis absorption spectroscopy was performed on either a Lambda 35 UV/Vis spectrometer or a Lambda 1050 UV/Vis-NIR spectrometer using slit widths of 2 nm. Solution phase measurements were performed using matched quartz cuvettes (path length = 10 mm) at room temperature, with HPLC or higher-grade solvents. Solid-state UV/Vis absorption spectroscopy was performed on thin film samples by attaching the films to the sample holders in normal operation mode.

2.2.2 Steady-State Photoluminescence Spectroscopy

Solution phase steady-state PL spectroscopy measurements were performed at room temperature on either a FluoroMax-4 or a Fluorolog-3 (Horiba Jobin Yohn) spectrophotometer using a 10 mm path length quartz cell. Solid-state PL spectroscopy was performed using the Fluorolog-3 spectrophotometer in the front-face configuration. PL spectra were corrected for the wavelength response of the system and the lamp profile using correction factors supplied by the manufacturer. The slit widths for excitation and emission spectroscopy, and integration time, were varied according to the sample emission intensity for the PL measurements.

2.2.3 Photoluminescence Quantum Yield Measurement

Photoluminescence quantum yield measurements were performed using an F-3018 integrating sphere (IS) accessory mounted on a Fluorolog FL 3-22 (Horiba). The reported values are the mean of three repeat measurements. This method is accurate to within 10%. Corrections to the Φ_{PL} obtained to account for self-absorption were performed as described in **Section 2.3.1**.

2.2.4 Photoluminescence Lifetime Measurement

Fluorescence lifetime measurements were performed with a Horiba Fluorolog FL 3-22 equipped with a FluoroHub v2.0 single photon controller using the time-correlated single photon counting method (TCSPC), run in reverse mode. Samples were excited at 458 nm with a pulsed nanosecond light-emitting diode (NanoLED®). The time distribution of the lamp pulse (1.3 ns), also called the instrument response function, was recorded prior to lifetime measurements in a separate experiment using a scattering solution (30 wt% SiO₂ Ludox, Aldrich). All the measurements were performed at room temperature (RT).

2.2.5 Dynamic Light Scattering

Dynamic light scattering (DLS) measurements were carried out on a Malvern Instruments Zetasizer Nano-ZS. The apparatus is equipped with a He-Ne laser (4.0 mW) emitting at 633 nm. The instrument uses a backscattering configuration, with detection at a scattering angle of 175°.

2.2.6 Thermogravimetric Analysis

Thermogravimetric Analysis (TGA) was performed using a Perkin Elmer Pyris 1 TGA thermogravimetric analyser in the range 30-900 °C in an N₂ atmosphere using *ca.* 2-5 mg sample, at a heating rate of 10 °C/min in a ceramic crucible. The instrument was calibrated with In and Ni standards in an air atmosphere.

2.2.7 Fluorescence Microscopy

Fluorescence microscopy images were obtained using a Nikon Labophot epi-fluorescence microscope fitted with a B2-A filter cube (excitation 450-490 nm, dichroic mirror with a 500 nm cut-on (longpass), and 515 nm cut-on emission filter (longpass)) and a QImaging QIClick camera. Image integration time was varied depending on the brightness of the sample to ensure image quality was maintained. For stability measurements, the integration time was kept constant across the measurement series.

Fig. 2.1 shows the components of a fluorescence microscope. Fluorescence microscopy utilises the luminescence of the sample as an imaging method, which can provide insight into the localisation of defects or luminophores themselves in the sample, which may not otherwise be observable through conventional optical or electron microscopy. As depicted in **Fig. 2.1** the fluorescence microscope functions using a filter cube which typically contains an excitation filter, a dichroic mirror and an emission filter. The role of these components is to let the excitation source irradiate the sample with a specific band of wavelengths and selectively collect the lower intensity emitted light. Light from the mercury arc lamp source is passed through the excitation filter removing all but the selected excitation wavelengths. These wavelengths are then reflected by the dichroic mirror at an angle of 45° from the mirror, where it illuminates and excites the sample. The dichroic

mirror is an interference filter that reflects short wavelength light and allows longer wavelengths to pass through. Therefore, when the sample fluoresces, only the light emitted from the sample at longer wavelengths can pass through the dichroic mirror. The emitted light then passes through the emission filter, cutting off unwanted excitation wavelengths of light. As a result only the light emitted from the luminescent sample reaches the eyepiece or charge-coupled device (CCD) camera.

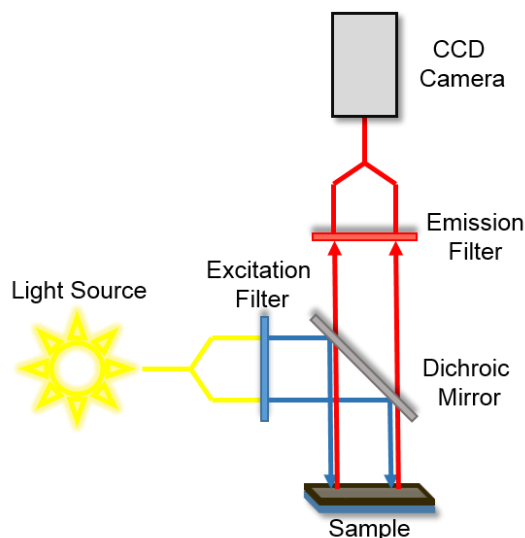


Figure 2.1 Operating scheme of an epi-fluorescence microscope.

2.2.8 Transmission Electron Microscopy

Transmission electron microscopy (TEM) and STEM were performed on a FEI Titan operating at 300 kV. Samples were prepared by dropping two aliquots (15 μ L) onto a carbon type B on 200 mesh Cu grid. Imaging was performed in TEM and STEM modes using the HAADF detector. All EDX analysis was performed in STEM mode.

2.2.9 Scanning Electron Microscopy

SEM were recorded on a Zeiss-Ultra Scanning Electron Microscope at an accelerating voltage of 2-5 kV. Images were collected using an In-lens (Carl Zeiss) detector. Thin film samples were prepared for SEM by attaching the coated glass substrates to stubs using conductive copper tape to minimise charging on the substrate.

2.2.10 Atomic Force Microscopy

AFM measurements were performed using an Asylum Research MFP-3D™ Atomic Force Microscope mounted on an anti-vibration plinth, in the tapping mode at room temperature under ambient conditions. The silicon cantilevers used were 125 µm in length and had a resonance frequency of approximately 150 kHz. All raw AFM images were visualised and analysed using the Gwyddion 2.44 software.

2.2.11 Thin Film Reflectance

Thin film reflectance measurements used to determine film thickness and refractive index were performed using a Filmetrics F20 thin film analyser in contact mode. This technique works by measuring the intensity of light that is reflected upon illumination normal to the film surface over a number of wavelengths. This reflected light is then fitted to a calculated reflectance spectrum to determine the optical constants. For light incident normal to the surface of a film, the reflectivity can be determined by the Fresnel equation for refraction:¹

$$R = \left| \frac{n_1 - n_2}{n_1 + n_2} \right|^2 \quad (2.1)$$

where n_1 and n_2 represent the refractive indices of the film material and the medium the light is travelling through, respectively. When considering multiple interfaces, such as a thin film on top of a substrate, the total amount of light reflected is the sum of the individual reflections at the interfaces. The reflected light will undergo either constructive or destructive interference depending on the phase of the light, which is in turn dependant on the thickness of the film, the wavelength of light and the optical constants of the film. These dependencies mean it is not possible to solve for the reflectance in a closed form, or to solve for n and extinction coefficient (k) for each wavelength. Consequently, the film properties are determined by using models to fit the observed spectra by constraining values of n , k and film thicknesses to within known values or reasonable ranges and judging the quality of the fit. All thicknesses measured had a goodness of fit values >0.99.

2.2.12 Current-Voltage Measurement

Current-Voltage (I - V) measurements were performed using a Keithley 2401 source meter and either an AAA-rated solar simulator (Oriel Sol3A) calibrated against a KG5-filtered reference diode (Oriel 91150-KG5) or an ABB-rated solar simulator (Abet Technologies 10500) calibrated against a quartz-filtered reference diode (RR 230 O). Solar cells were masked to 0.1 cm^2 and scanned both in both forward and reverse between 1.1 V and -0.1 V at 100 mV/s to observe any hysteresis effects.

2.2.13 Quantum Efficiency Measurement

External quantum efficiency measurements were performed using a PV Measurements Inc. QE X10 spectral response measurement system with a 300-1100 nm wavelength range. The measurements were performed in direct current mode under no bias light illumination. The setup was calibrated with a Si reference photodiode before each measurement.

2.2.14 AM 1.5G Light Soaking

Stability testing of PSCs was performed using a Solaronix Solixion A-20 solar simulator (Class ABB) coupled to a Keithley 2401 source meter while under continuous illumination. Solar cell pixel active areas were masked to 0.1 cm^2 and scanned automatically both from forward to reverse bias and *vice versa* between 1.1 V and -0.1 V at 100 mV/s at timed intervals to characterise degradation. The solar simulator intensity was either 0.8 or 1 sun illumination.

2.2.15 X-ray Diffraction

Powder x-ray diffraction (PXRD) measurements were performed on a Bruker D2 Phaser Powder diffractometer. Samples were exposed to Cu $K\alpha$ radiation ($\lambda = 1.54\text{ \AA}$) at RT in the range $5\text{--}55^\circ 2\theta$. PXRD measurements were performed on perovskite thin films by placing the films into an acrylic plastic holder at a height which allowed them to be scanned as normal powder samples. Grazing-incidence XRD analyses of the crystalline properties of perovskite films were carried out using a Bruker D8 Discover instrument with a Cu $K\alpha$ beam at 40 kV and 40 mA, scan parameters of 0.1 s/step at $0.01 2\theta$ step size.

2.2.16 LSC Optical Efficiency Measurements

Optical efficiency measurements were performed by illumination of the LSCs at room temperature using either a Class ABB solar simulator (Abet Technologies, Model 10500) calibrated to 1 sun using a ReRa Technologies reference silicon cell, with an irradiation area of 9.6 cm^2 , or an AAA-rated solar simulator (Oriel Sol3A) calibrated against a KG5-filtered reference diode (Oriel 91150-KG5), with an irradiation area of 103.2 cm^2 . Measurements were performed on black absorbing backgrounds, with and without masking of the LSC area. Further information can be found in **Chapter 6**. The emission from each of the four edges of the LSC was measured using an INS 125 integrating sphere coupled with a spectroradiometer (International Light Technologies ILT950) with a Sony silicon CCD detector over the range 250-1050 nm (**Fig. 2.2**). The analysis of the data was performed with SpectrILight III software, using the manufacturer provided calibration file for the optical power (ILT1007131U1NS125).

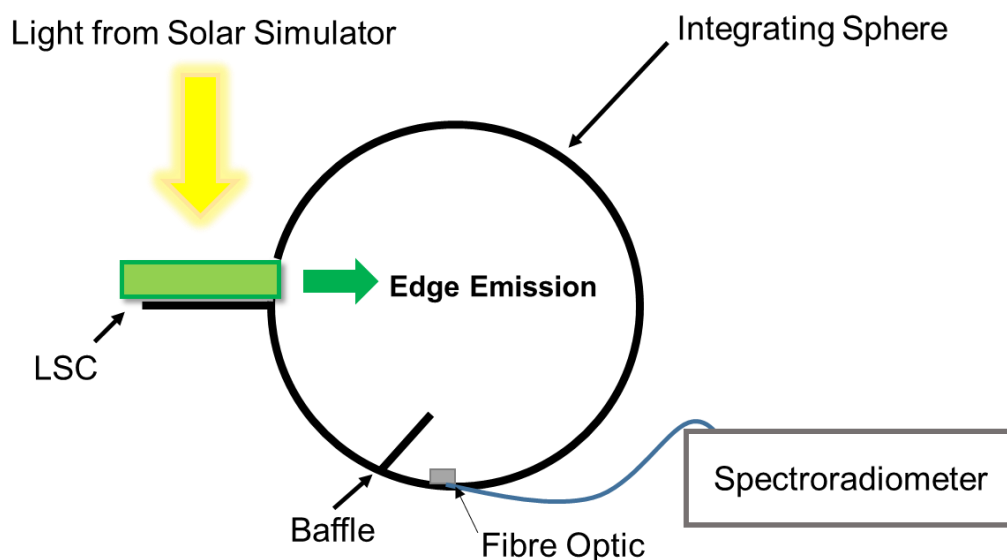


Figure 2.2 Schematic diagram of the characterisation procedure for an LSC. Sources of error stem from misalignment of the solar simulator light source and discrepancies in the positioning of the LSC in relation to the integrating sphere. The LSC has to be positioned to ensure it is correctly in contact with the port on the integrating sphere to ensure no edge emitted light is lost.

2.3 Data Analysis

2.3.1 Determination of Photoluminescence Quantum Yield of PNC solutions

Due to the sensitivity of PNC solutions to the external environment, in particular concentration (**Chapter 5**), special care was taken when characterising the emission properties of these materials. To determine Φ_{PL} , the high concentration of the PNC solution has to be accounted for, as low transmission of light and a large amount of reabsorption occurs. Typically, there are two methods for determining the Φ_{PL} . The comparative method involves using known luminescence standards as references and comparing the measured spectrum of the sample with that of a reference standard obtained under the same experimental conditions to obtain the Φ_{PL} . However, the sensitivity of the PNC solutions to dilution and capping ligand concentrations prevented the comparative method of determining Φ_{PL} to be used here.^{2,3} Instead, to account for the high optical density, the inability to dilute the samples without causing a change in the emission properties, and the small sample volumes available, an integrating sphere was utilised to measure the absolute Φ_{PL} . Φ_{PL} is defined by the relationship:

$$\Phi_{\text{PL}} = \frac{\text{number of photons emitted}}{\text{number of photons absorbed}} \quad (2.2)$$

The method used to determine Φ_{PL} using the F-3018 integrating sphere was first reported by de Mello *et al.*⁴ and later refined for solution phase work by Porrès *et al.*⁵ In the method outlined by de Mello *et al.*, there are three configurations of the experimental apparatus (**Fig. 2.3**): (a) no sample is placed in the sphere and the excitation light alone is recorded by the detector; (b) the sample is placed in the sphere but out of the direct path of the excitation port; (c) the sample is placed in the sphere in the path of the monochromatic light.

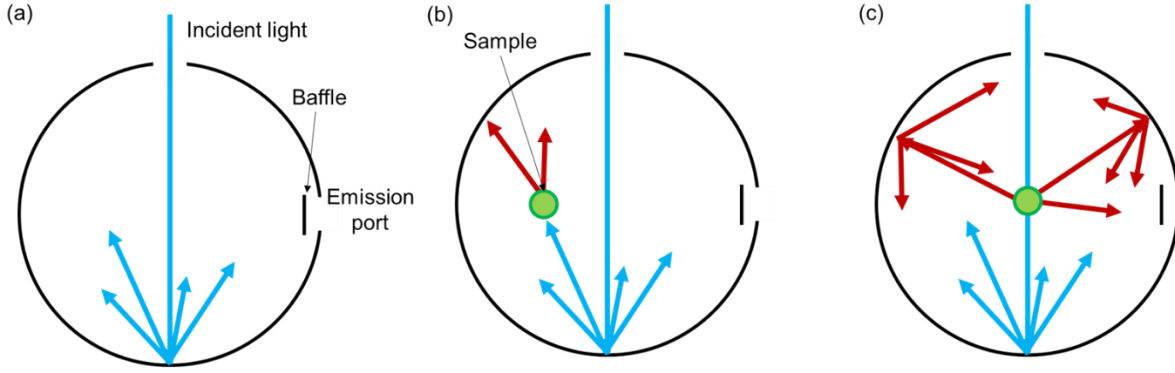


Figure 2.3 Schematic representation of three integrating sphere configurations for determination of Φ_{PL} : (a) sphere is empty; (b) sample is in the sphere but not directly illuminated and (c) sample is in the sphere and directly illuminated by the incident monochromatic light. Blue and red arrows represent incident and emitted/reflected light, respectively.

By comparing the integrated area under the curves resulting from both emitted and scattered light for the emission spectra of each of these three experiments, Φ_{PL} can be expressed by the equation:

$$\Phi_{PL} = \frac{P_c + (1 - A)P_b}{L_a A} \quad (2.3)$$

where P_x and L_x represent the area under the emission peak and under the scattering peak, respectively, and x denotes the experimental configuration (a, b or c). A represents the fraction of incident light absorbed by the sample in configuration (c). $(1-A)$ represents the fraction of light either transmitted or reflected from the sample in configuration (c). According to de Mello *et al.* A can be represented as:⁴

$$A = 1 - \frac{L_c}{L_b} \quad (2.4)$$

We can approximate the fraction of the beam in configuration (b) which will scatter off the sphere and be absorbed by the sample to be 0. Thus $L_b = L_a$ and by extension $P_b = 0$, which, when these new values are substituted into 2.4 and 2.5, leads to a new expression for Φ_{PL} :

$$\Phi_{PL} = \frac{P_c}{L_a - L_c} \quad (2.5)$$

This simplified expression removes the need to perform experiments in configuration (b). However, it is not practical when the contribution of the scattered excitation light is several orders of magnitude higher than the emitted light. To attenuate the light intensity at the excitation wavelength, λ_{ex} , a neutral density (ND) filter has to be used. The ND filter was placed between the emission port of the integrating sphere and the detector and its contribution can be expressed as:⁵

$$\Phi_{PL} = \frac{P_c}{(L_a - L_c)ND\%} \quad (2.6)$$

where $ND\%$ represents the percentage of light that the ND filter allows to pass through. These values can be calculated using the integrating sphere where, P_c is the integrated area under the emission peak of the luminophore solution under investigation, L_a is the integrated area under the Rayleigh peak of the blank sample and L_c is the integrated area under the Rayleigh peak in the emission spectra of the solution under investigation.⁶ These measurements must be taken in identical conditions. Re-absorption is a considerable issue when determining Φ_{PL} using an integrating sphere for samples with a low Stokes' shift, as a percentage of the emitted light will in turn be reabsorbed due to overlap between the absorption and emission bands.⁴ This re-absorption can lead to errors in the calculated Φ_{PL} . One of the methods to overcome this limitation is to correct the measured spectra by matching the red edge of the emission spectra to that of a sample whose spectrum is not distorted.^{4,7} However, due to the extremely high optical density of our stock PNC solutions across the visible range, and the inability to dilute them, there were no low concentration samples to correct to.⁸ Thus, in order to minimise the contribution of re-absorption events, the Φ_{PL} was determined using a low sample volume (50 μL).

2.3.2 Emission Decay Measurements

The lifetime of the excited state is a fundamental characteristic of a luminophore. It can be described for a typical singlet emitter by considering a sample excited by an infinitely sharp pulse of light.⁹ This results in an excitation of an excited singlet state. Vibronic relaxation occurs as dictated by Kasha's rule until we have an initial concentration, c_0 , of fluorophores in the lowest vibronic state of the first excited singlet state S_1 . Emission occurs spontaneously and randomly, thus, the

concentration of fluorophores in this excited state can be expressed as an exponential function where after time, t , is c_t given by:¹⁰

$$c_t = c_0 e^{-t/\tau_0} \quad (2.7)$$

where τ_0 is the excited state lifetime defined as the reciprocal sum of all the decay processes available for the excited state:

$$\tau_0 = \frac{1}{k_R + k_{NR}} \quad (2.8)$$

where k_R is the radiative decay rate constant and k_{NR} is the non-radiative decay rate constant ($k_{NR} = k_{IC} + k_{ISC}$, where k_{IC} and k_{ISC} are the rate constants for internal conversion and intersystem crossing, respectively). As the intensity of a luminescent species, I_t , is proportional to c_t , its lifetime can be expressed as a function of the luminescence intensity:¹¹

$$I_t = I_0 e^{-t/\tau_0} \quad (2.9)$$

where I_0 is the intensity of luminescence at $t = 0$. This expression can be utilised to calculate the lifetime of an emissive species by plotting $\log I_t$ versus t and calculating the slope or, more commonly, fitting the data to assumed decay models.⁹ However, it is necessary to note that this expression is not accurate for multi-component systems. In the case of multi-component decays, the total intensity observed is assumed to be the sum of the multiple single exponential decays, given by the following expression:

$$I_t = \sum_i a_i e^{-t/\tau_i} \quad (2.10)$$

a_i is the pre-exponential factor and τ_i is the characteristic lifetime for the i^{th} component. The pre-exponential factor represents the fractional amount of molecules which make up each decay component at $t = 0$. The average lifetime for multicomponent systems is the emission decay curve fitted to a multiple exponential decay and given by:¹²

$$\langle \tau \rangle = \frac{\sum a_i \tau_i^2}{\sum a_i \tau_i} = \sum f_i \tau_i \quad (2.11)$$

where f_i is the fractional contribution of the lifetime of the i^{th} species to the steady-state intensity, given by:

$$f_i = \frac{a_i \tau_i}{\sum a_j \tau_j} \quad (2.12)$$

In the case of the measurements presented in this work the emission decay curves were analysed using IBH DAS6 software. Data were fitted as a sum of exponentials as described in equation 2.11. The errors in these fittings are accounted for by considering non-linear least squares analysis for error minimisation. The quality of the fitted data was assessed quantitatively by determining the χ^2 values given by:¹³

$$\chi^2 = \sum_{i=1}^n \frac{(N(t_i) - N_c(t_i))^2}{\sigma_i^2} \quad (2.13)$$

where $N(t_i)$ and $N_c(t_i)$ represent the measured and calculated data, respectively, and σ_i is the standard deviation of each datapoint. The data quality was also assessed qualitatively by examining the distribution of the weighted residuals which represent the difference between the fitted and observed points. Any non-random behaviour in a plot of the weighted residuals with respect to time suggests an error with the fit.

2.3.3 Photovoltaic Device Characterisation

Photovoltaic cells can be modelled on a diode with a parallel current source: when there is no light incident on the device to produce current, the cell behaves as a diode, when light is incident on the cell, the total current is the current produced by the photoelectric effect (I_p) minus the diode current (I_D):¹⁴

$$I = I_p - I_D = I_p - I_0 \left(e^{\frac{qV}{nk_B T}} - 1 \right) \quad (2.14)$$

where I_0 is the saturation current of the diode, q is the charge of an electron, V is the measured cell voltage, k_B is the Boltzmann constant, n is the diode ideality factor and T is the temperature in Kelvin. While this expression provides a decent approximation for the generation of current in a PV cell, it

is an idealised version. If we account for the parasitic resistances within the PV cell, the expression becomes:

$$I = I_P - I_0 \left(e^{\frac{q(V+I.R_S)}{nkT}} - 1 \right) - \frac{V + I.R_S}{R_{SH}} \quad (2.15)$$

where R_S and R_{SH} are the series and shunt resistances, respectively.

By sweeping the voltage across the illuminated cell, an I - V plot is obtained. In the I - V plot of a solar cell there are several parameters which are used to characterise a solar cell performance, including the I_{SC} , V_{OC} and FF , highlighted in the representative I - V curve in **Fig. 2.4**.¹⁵ The short-circuit current is the current produced by the solar cell when the voltage is zero. I_{SC} is related to cell area and the light intensity. To remove the dependence of cell area, the current density (J_{SC}) in mA/cm² is often used instead. The open circuit voltage is the maximum voltage achievable for the solar cell and it occurs when the current is zero. It is related to the amount of electron-hole recombination taking place in the device. The fill factor of a cell relates V_{OC} and I_{SC} to the maximum power (P_{max}) of the PV device. It can be described as the “squareness” of the I - V curve and is the ratio of the maximum power of the cell to the max theoretical power determined by the product of I_{SC} and V_{OC} .¹⁵ It can also be determined by the ratio of the area of the square (FF) to the total area under the curve. The overall power conversion efficiency (PCE) of the cell is given by:¹⁵

$$PCE = \frac{P_{max}}{P_{in}} = \frac{V_{OC} \cdot I_{SC} \cdot FF}{P_{in}} \quad (2.16)$$

where P_{in} is the incident power. P_{in} can be given in terms of absolute power input or in terms of irradiance if J_{SC} is plotted.

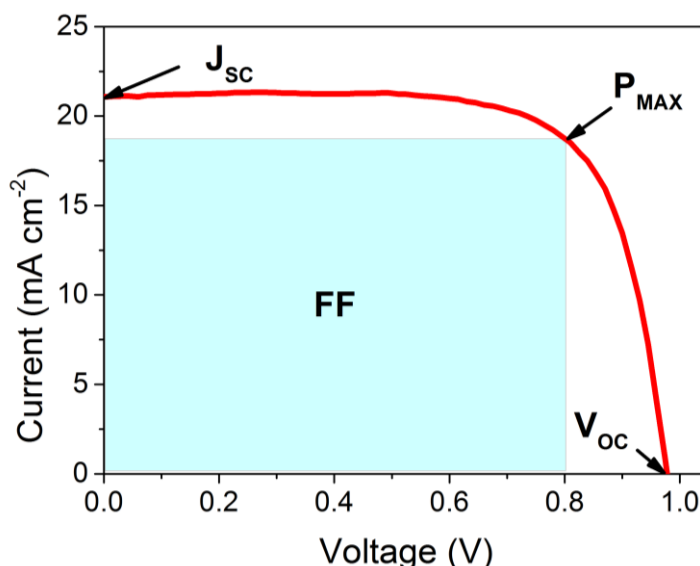


Figure 2.4 Example of a current-voltage curve for a photovoltaic cell showing the short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), maximum device power (P_{max}) and fill factor (FF).

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Chapter Three

Enhancing the Stability of Organolead Halide Perovskite Films through Polymer Encapsulation

The work in this Chapter has been published in:

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3.1 Introduction

While perovskite-based solar cells have achieved both high efficiencies ($>20\%$)¹ and show remarkable ease of processability, the technology has not yet become commercially viable. The inherent instability of PSCs continues to be a limiting factor in the growth of the technology towards large scale applications.² The bi-product of this degradation process as outlined in **Chapter 1**, PbI_2 , is water soluble ($K_{\text{sp}} = 9.8 \times 10^{-9}$ at $25\text{ }^\circ\text{C}$) and toxic, leading to environmental concerns about the technology.^{3,4} Encapsulation represents an attractive and facile method to improve device stability; however, the encapsulation materials used to protect finished cells must be rigorously tested to ensure that the accidental discharge of lead compounds from both working and legacy devices into the environment is prevented. As described in **Chapter 1**, the categories of materials used for encapsulation are broad, and include Teflon,⁵ Al_2O_3 ,^{3,6} PMMA and PC.^{7,8} The most common and promising method for device encapsulation is through coating the device with a polymer film. This methodology can be implemented through roll-to-roll fabrication, similar to that currently under investigation for OPV.⁹

However, while encapsulation presents an attractive option to increase the stability of PSCs, there has been little work to investigate what properties control the efficiency of a polymer encapsulant as a barrier layer. The issue with the existing studies in which a PSC is encapsulated is they often only use one polymer and offer little insight into why it was selected. Elevated temperatures ($20\text{--}90\text{ }^\circ\text{C}$) are commonly used to accelerate the decomposition of the perovskite material allowing for a greater control over the degradation rate and characterisation.^{7,10,11} One of the few studies where direct comparison of the polymer encapsulants was performed was by Habisreutinger *et al.* who used PMMA and PC, poly(3-hexylthiophene-2,5-diyl) (P3HT) and a carbon nanotube composite as a dual barrier-hole transport layer, with the resultant devices displaying improved stability for up to 96 h upon heating at $80\text{ }^\circ\text{C}$ in air.⁷ This was achieved by doping a hole conducting P3HT-nanotube composite within the hydrophobic PMMA and PC stock solutions and depositing this mixture onto the bare perovskite layer. This work directly correlated the effectiveness of the polymers as encapsulation barriers with their glass transition temperature (T_g) and thus showed slightly improved stability when using PC ($T_g = 154\text{ }^\circ\text{C}$)¹² rather than PMMA

($T_g = 105\text{ }^{\circ}\text{C}$).¹² However, the specific role of temperature and the other material properties of the encapsulation layer were not investigated in detail.

The most common characterisation methods typically used to monitor the degradation of perovskite films are XRD and UV/Vis absorption spectroscopy. $\text{CH}_3\text{NH}_3\text{PbI}_3$, for example, shows diffraction peaks at 14° and 28° and 43° 2θ , corresponding to the (110), (220) and (330) planes of the tetragonal perovskite lattice, respectively. However, upon degradation, these peaks are replaced by a single peak at 12.8° 2θ , corresponding to PbI_2 .^{13,14} XRD has been utilised to observe the effects of different conditions/treatments, including substrates and Cl^- doping concentrations¹⁵ the effect of different atmospheres,^{10,16} effect of temperature,^{10,11} humidity,¹⁷ and moisture⁷, by comparing the relative intensities of $\text{CH}_3\text{NH}_3\text{PbX}_3$ to PbX_2 diffraction peaks throughout the degradation process. UV/Vis absorption spectroscopy can be used to monitor the characteristic colour change from dark brown/grey to bright yellow, which occurs upon degradation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ or $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ into PbI_2 . By monitoring the decay of characteristic perovskite features in the absorption spectrum, the rate of degradation can be quantitatively determined.¹⁷ There are issues, however, which occur for perovskite thin films upon measuring the UV/Vis absorption spectrum. High optical density and high scattering due to the crystallite size can result in a spectrum which is largely featureless across the visible range, thus due care has to be taken when using this method as the spectrum observed may not represent the “true” spectrum of the perovskite material.¹⁸ Interestingly, Watson *et al.* have developed a novel approach to characterise the degradation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin films using the colour change observed upon degradation using RGB (red, green, blue) colour analysis to track the degradation of the perovskite layer to PbI_2 through time-lapse photography.⁸ The same group demonstrated spectrothermal evaluation of the thermal annealing step of perovskite formation through a combination of TGA, differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR) and showed that degradation of a $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ thin film did not occur for temperatures less than $150\text{ }^{\circ}\text{C}$ over the timescale investigated (80 min).¹⁹ This work highlighted the need for a combination of techniques to accurately characterise the formation/degradation of the perovskite layer.

Other techniques which have been used to monitor perovskite degradation include XPS, which has been used to investigate the stability of perovskites to moisture, inert atmospheres, thermal and X-ray beam damage,²⁰ and photoluminescence characterisation, which has been exploited to monitor the layer uniformity of PSCs under operating conditions.^{21,22} However, such methods are generally not suitable for rapid, real-time analysis and early indication of device degradation on the production line. Sheng *et al.* have utilised the intrinsic photoluminescence of the perovskite layers through confocal fluorescence microscopy to observe grain growth in $\text{CH}_3\text{NH}_3\text{PbBr}_3$ films in the presence of moisture and oxygen, and showed that larger crystals have a higher number of defects, despite no obvious change in the XRD pattern of the films.²³ This increase in defect concentration results in a shorter charge-carrier lifetime, which negatively impacts the efficiency of the perovskite as a light-absorber.

3.1.1 Aims

The aims of this chapter are to combine both a study into the favourable properties of a polymer encapsulant and to develop a robust characterisation procedure to monitor the stability of perovskite layers in a rapid and non-invasive manner. Time-dependent stability studies of both encapsulated and non-encapsulated $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films with characterisation at timed intervals will be presented. These studies allow direct comparison of the effectiveness of the polymer encapsulants, which can in turn be related to the physical properties of the polymers to determine the most relevant to their performance as a barrier. The physical properties which will be investigated for comparison include the T_g , water vapour transport rate (WVTR), O_2 permeability and hydrophobicity. Time-dependent stability studies will be performed by coating $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films with polymer layers of known thickness before accelerated thermal degradation at a series of temperatures to enable the stability of both the active perovskite layer and the polymer barrier to be probed. Visual inspection, UV/Vis absorption spectroscopy, PXRD, SEM, AFM and epi-fluorescence microscopy (FM) will be examined as potential techniques investigated to characterise the extent of degradation of the perovskite film.

3.2 Experimental

3.2.1 Perovskite Layer Deposition

$\text{CH}_3\text{NH}_3\text{I}$ was initially synthesised through the gradual addition of HI (57 wt% in H_2O) to methylamine (33 wt% in ethanol) in a 2:1 molar ratio in ethanol (50 mL), with stirring in an ice bath under nitrogen flow. After stirring for 2 h the product was isolated by rotary evaporation and vacuum filtration before it was washed with diethyl ether several times to remove unreacted precursor and left to dry in an oven at 60 °C. The $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ stock solution was prepared by dissolving $\text{CH}_3\text{NH}_3\text{I}$ (1.19 g, 10.6 mmol) and PbCl_2 (978 mg, 3.52 mmol) in DMF (4 mL). This solution was stirred vigorously at RT to ensure complete dissolution of the perovskite precursors before filtration through a 200 nm polytetrafluoroethylene (PTFE) syringe filter. $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films were then deposited on microscope glass slides by spin coating a fixed volume (400 μL) of the stock solution at 2000 rpm for 45 s, followed by annealing at 100 °C for 60 min.

3.2.2 Polymer Layer Deposition

Post annealing, the perovskite films were allowed to cool to RT before coating with the different polymer layers. The polymer layers were applied directly to the bare $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite films by spin-coating. To ensure an accurate comparison between the polymer encapsulants, the layer thicknesses were kept uniform (~800 nm measured using Filmetrics F-20 in contact mode). Due to the varying viscosities of the polymer stock solutions, the spin rates and conditions were carefully controlled to achieve a standard and uniform thickness for all barrier layers. PMMA (560 mg in 4 mL toluene (16.1 wt%)) and PMP (100 mg in 4 mL cyclohexane (3.2 wt%)) films were deposited by spin-coating at 8000 rpm for 60 s, PC (200 mg in 4 mL dichloromethane (3.8 wt%)) and EC (200 mg in 4 mL 80:20 toluene:ethanol (5.9 wt%)) were spun at 2000 and 1000 rpm for 60 s respectively. After spinning, the polymer-coated perovskite layers were placed on a hot plate at 80 °C for 5 min to ensure complete evaporation of the solvent.

3.2.3 PSC Device Fabrication

Etched FTO glass substrates were cleaned sequentially in detergent, deionised water, acetone and ethanol before undergoing 10 min of O₂ plasma treatment. A compact TiO₂ layer was deposited on the glass substrates through spray pyrolysis of a 0.2 M solution of titanium diisopropoxide *bis*(acetylacetonate) in isopropanol at 450 °C. Upon cooling, a mesoporous layer of TiO₂ nanoparticles was spin-coated from a 2:7 (w/w) suspension of Dyesol 30NR-D paste in ethanol (4,500 rpm for 30 s), followed by sintering at 550 °C for 30 min.

A CH₃NH₃PbI₃ perovskite precursor solution was prepared by dissolving PbI₂ (576 mg, 1.25 mmol), and CH₃NH₃I (199 mg, 1.78 mmol) in 1 mL 4:1 (v/v) solution of DMF:DMSO. A volume (100 µL) of the perovskite precursor solution was deposited onto the TiO₂ film and spin-coated at 4,000 rpm for 30 s, with a small volume (200 µL) of ethyl acetate dropped onto the spinning substrate 10 s prior to the end of the spin-coating process to act as an anti-solvent and instigate crystallisation of the perovskite layer. The perovskite films were annealed at 100 °C for 10 min.

Spiro-OMeTAD (80 mg, 0.065 mmol) was dissolved in chlorobenzene (1 mL) and doped with tBP (30 µL), Li-TFSI (20 µL, 1.81 M in acetonitrile) and FK209 TFSI solution (20 µL, 0.2 M in acetonitrile) before being spin-coated onto the perovskite layer at 4000 rpm for 30 s. Finally, gold electrodes were evaporated at 10⁻⁴ Torr using an Edwards 306 thermal evaporator. All perovskite and HTL deposition was performed in under N₂ in glove box conditions.

3.3 Results and Discussion

3.3.1 Selection of Polymers

In order to effectively screen the physical properties that allow for effective encapsulation of a perovskite film, four different polymers were selected to be coated. These polymers showed varied values for oxygen permeability, WVTR, water absorption and glass transition temperature, thus allowing for effective screening of these properties to determine the most relevant when considering an encapsulant (**Table 3.1**). Oxygen permeability and WVTR measure the rate at which gas molecules pass through polymer films, in this case oxygen and water vapour. Permeability is

determined by measuring the amount of the gas which passes through a film of the polymer at uniform thickness (typically 1 mm) in a constant pressure environment in a *time lag* experiment.²⁴ Water absorption measures the percentage weight gain of a polymer after immersion for 24 h at 23 °C.²⁵ The polymers selected were PMMA, PC, EC and PMP; their chemical structures are shown in **Fig. 3.1**. PMMA and PC were selected as encapsulants based on work previously performed, where they were demonstrated as effective hole transport layers when doped with P3HT and single-walled carbon nanotubes.⁷ These HTMs increased the thermal stability of the perovskite layers for over 96 hours upon heating at 80 °C and even after it was placed under a flowing tap. EC is commonly used as a thin film coating material and it possesses the highest WVTR of the polymers investigated here, along with a relatively high T_g of 129 °C.^{24–26} PMP has a very low T_g of only 29 °C, and so some structural distortions may be expected to occur as the layer is heated and cooled. However it also has an extremely low water absorption percentage, which should improve its ability to act as a barrier for moisture.^{12,27}

Table 3.1. Physical properties of polymer encapsulants.

Polymer	Glass Transition Temperature, T_g (°C)	O ₂ Permeability (cc.mm/m ² /24 h/ bar)	Water Vapour Transmission Rate (g.mm/ m ² /24 h/bar)	Water Absorption (%)	Reference
PMMA	105	4.8	55.2	0.35	12
PC	154	116.57	115	0.35	12
EC	155	952	594,000	2	24–26
PMP	29	12,434	775	0.01	12,27

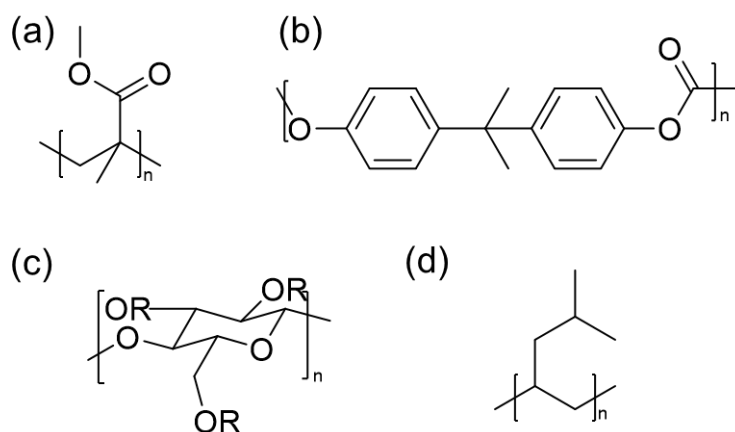


Figure 3.1. Chemical structures of the polymer encapsulants investigated: (a) PMMA, (b) PC, (c) EC and (d) PMP.

3.3.2 Thermal Degradation of Pristine and Polymer-Coated $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ Films

To characterise the degradation of the encapsulated perovskite layers over reasonable timescales accelerated conditions were required. Perovskites undergo rapid degradation at increased temperatures, and thus the perovskite films were subjected to temperatures of 60, 80 and 100 °C to both accelerate degradation and give us insight into the stability of perovskites in the range of possible operating temperatures for solar cells in different climates.²⁸ Interestingly, the TGA thermogram of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite powder performed in an inert N_2 atmosphere (**Fig. 3.2**) showed that thermal degradation takes place in three steps, with onset temperatures at ~200, 300 and 450 °C. These steps correspond to the loss of HI, CH_3NH_2 and PbCl_2 and occur beyond the range of our temperature increases.²⁹ Thus, the heating process instigated in the present acts to accelerate the moisture-induced degradation described in **Chapter 1**, rather than induce thermal dissociation of the perovskite lattice. This TGA was performed in an inert atmosphere in order to characterise the thermal degradation of the perovskite lattice without any contribution from moisture, however, measurement of the thermogram in air would provide a more accurate representation of the actual degradation processes which occur in the film under ambient conditions. Thermal degradation of bare and polymer-encapsulated $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ thin films was then performed under identical ambient conditions (relative humidity 50-70%, indoor lighting) by placing the perovskite films face

up onto a hotplate at 60, 80 or 100 °C. The films were only removed briefly at intervals of 24 h for characterisation by the methods outlined below.

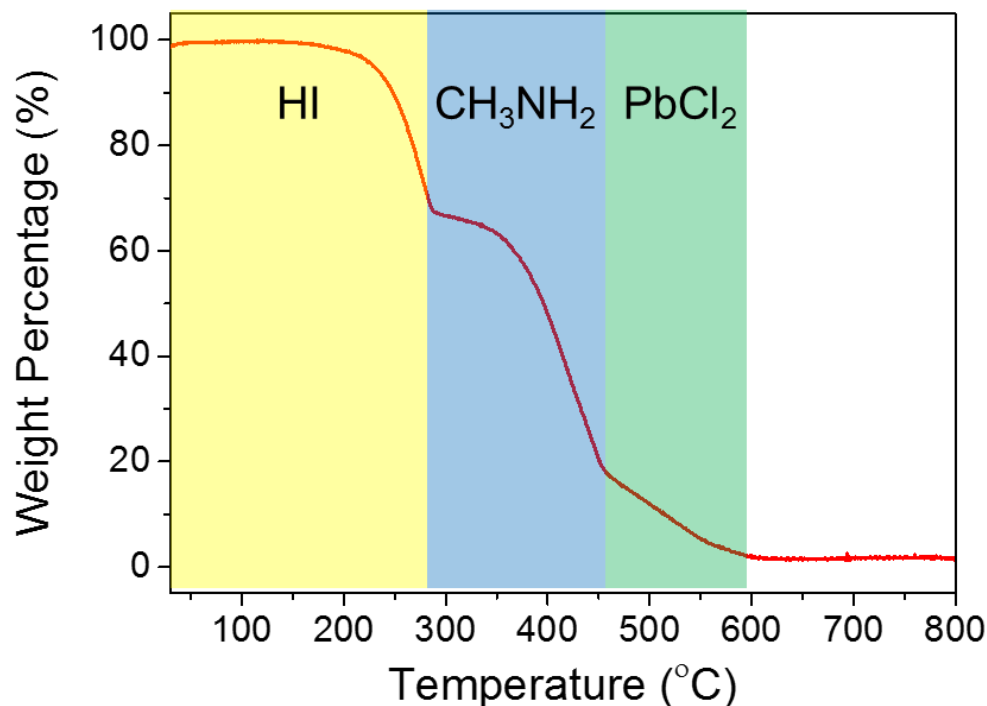


Figure 3.2. TGA thermogram of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite powder performed in an inert N_2 atmosphere. Heat rate = $10\text{ }^\circ\text{C min}^{-1}$.

3.3.2.1 UV/Vis Absorption and Photoluminescence Spectroscopy

In order to compare the effects of polymer encapsulation, the physical changes associated with degradation of uncoated perovskite films ($\sim 500\text{ nm}$ thickness) need to be shown. While pristine $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films are grey-brown in colour, following heating at $60\text{ }^\circ\text{C}$ (a typical operating temperature for a solar panel) in air for 72 h they turn yellow (**Fig. 3.3a**). This colour change has previously been assigned to complete degradation of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ and formation of PbI_2 .¹⁹ This colour change can be monitored quantitatively using UV/Vis absorption spectroscopy (**Fig. 3.3b**). Pristine $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films exhibit a characteristic step-like feature with an onset at $\sim 750\text{ nm}$, corresponding to a bandgap energy of approximately 1.56 eV and typically absorb strongly across the UV/Vis region with increasing absorbance as you move towards shorter wavelengths. Upon thermal degradation, the step-like feature disappears. Pristine $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films are also

photoluminescent, exhibiting an emission maximum at approximately 770 nm upon excitation at 500 nm.

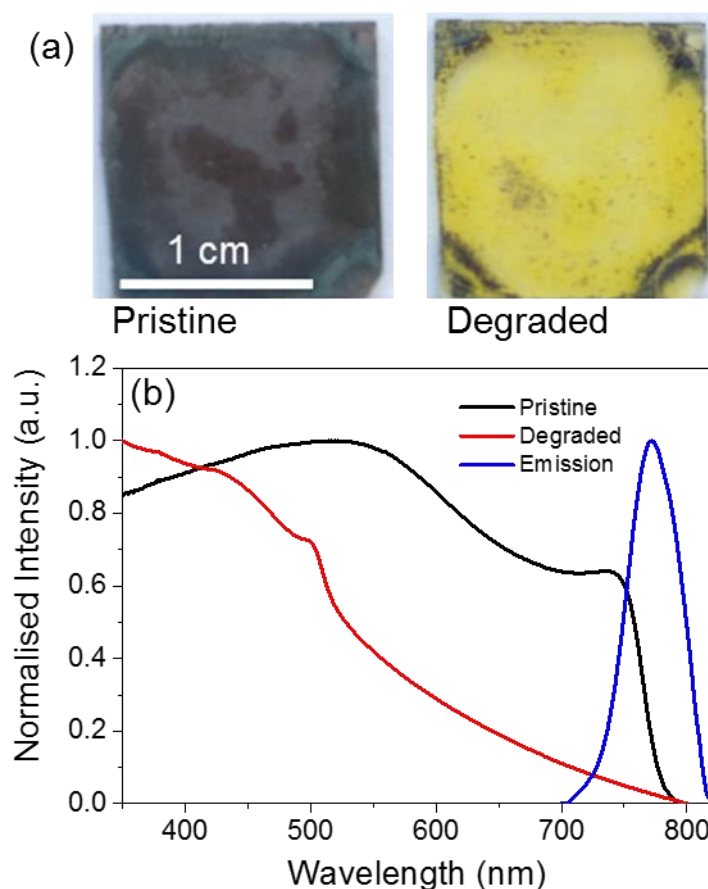


Figure 3.3. Comparison of the optical properties of a pristine and thermally degraded (60 °C for 72 h in air) $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ film (~500 nm thick). (a) Photograph illustrating the colour change that occurs upon degradation. (b) Normalised UV/Vis absorption spectrum of an uncoated $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ film before (black line) and after (red line) thermal degradation. The photoluminescence spectrum (blue line) of the pristine film of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ ($\lambda_{\text{ex}} = 500$ nm) is also shown.

The polymer encapsulants described above were spin-coated as uniform films (~800 nm thick) onto pristine $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ to investigate their potential to act as a barrier to the ambient environment and decrease the rate of thermal degradation. Upon addition of the polymer coating, changes in the shape and intensity of the UV/Vis absorption spectrum were observed for the $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films (**Fig. 3.4**). This behaviour can be attributed a combination of partial re-dissolution of the perovskite layer and rapid-crystallization due to the solvents used to dissolve the polymer encapsulants during the spin coating process.

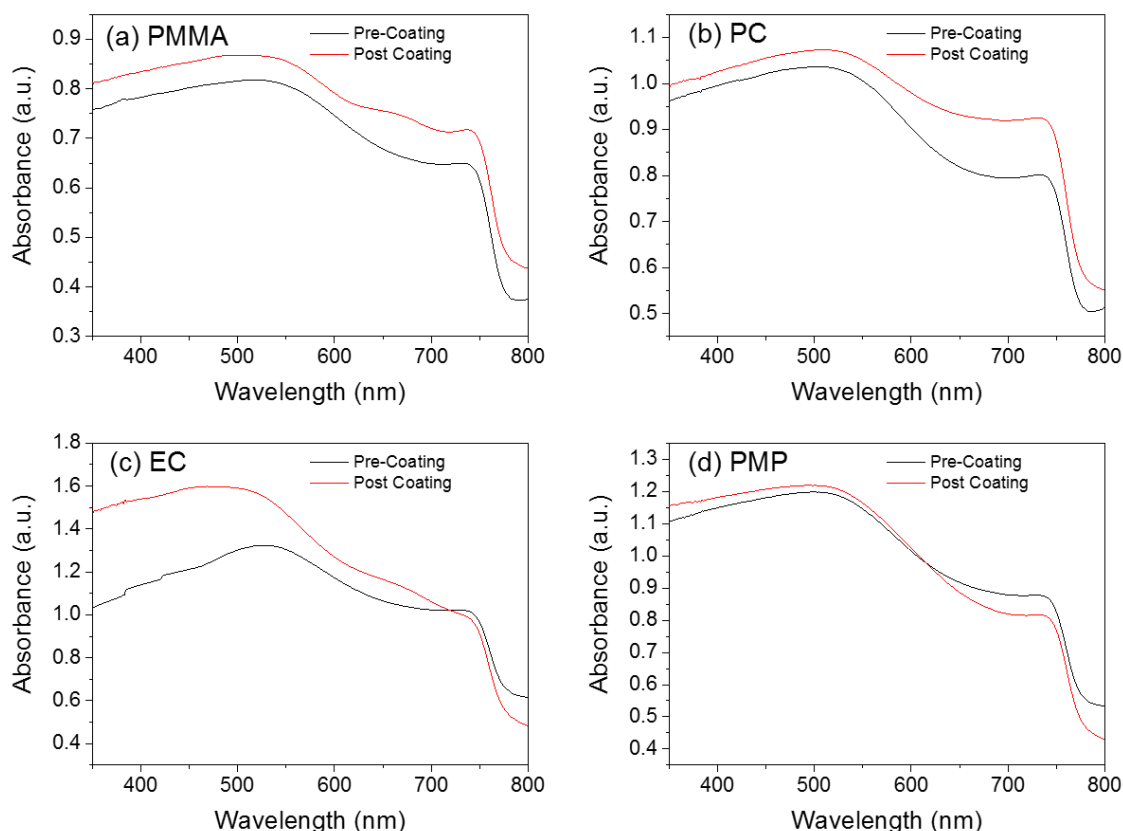


Figure 3.4. UV/Vis absorption spectra of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ layers before and after coating with (a) PMMA, (b) PC, (c) EC and (d) PMP thin films.

The partial dissolution and self-healing of the $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ can bring about increased coverage of the substrate leading to increased optical density across the perovskite absorption spectrum. Similar rapid-crystallization due to poor solvents has been well described in the literature as a means to improve the perovskite film uniformity and crystallinity for device fabrication.^{30,31} EC- and PMP-coated samples display an increase in absorbance towards the higher energy spectral region giving spectra which better represent the “true” absorption spectrum of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite films.¹⁸ PMMA- and PC-coated $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films show an increase in optical density at all wavelengths. With polymer stock solutions made up in different solvents the extent of any effects is varied and determined by the solubility of the perovskite in that solvent. The transmittance spectra of the 800 nm polymer coatings on glass show that negligible absorbance occurs across the visible spectrum, and thus, the increase is not related to the polymer layer (**Fig. 3.5**). All four polymers showed high transmittance (>80%) in the visible region and, as such, do not contribute to the observed changes.

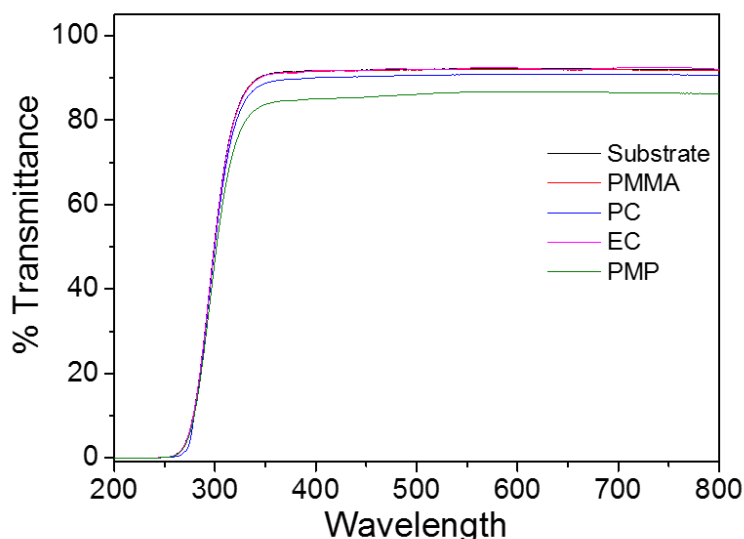


Figure 3.5. Light transmittance of polymer thin films (~800 nm) coated on glass substrates

3.3.2.2 X-Ray Diffraction

PXRD was utilized to characterise the polymer-encapsulated films both before and after prolonged degradation at elevated temperatures. $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films show characteristic reflections at 14° and 28° and a less intense peak at 43° , which correspond to the (110), (220) and (330) planes of the tetragonal perovskite lattice, respectively.¹⁴ It was observed that upon coating the perovskite films with the encapsulating polymers there was no change in the PXRD patterns, which indicates that no changes occurred in the $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ crystal lattice during the spin-coating procedure (**Fig. 3.6a**). The encapsulated films were then subjected to an elevated temperature of 60°C for 432 h, following which they were re-characterised. The levels of degradation were found to vary depending on the polymer coating applied. The degradation of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ can be monitored both by the disappearance of the characteristic peaks outlined above and the appearance of a peak at 12.8° , characteristic of PbI_2 .¹⁷ After this extended degradation period only the PMMA-coated film showed no evidence of degradation, retaining its characteristic peaks at 14° and 28° and showing no discernible PbI_2 peak. PC-, EC-, and PMP-encapsulated films still exhibited some of the characteristic reflections of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ but these were of low intensity, with the highest intensity peak in each case being that of PbI_2 . Despite the decay of each of the polymer-encapsulated films (with the exception of PMMA), they retain some characteristic perovskite reflections in their

PXD patterns. In contrast, the uncoated film was degraded to an extent that the PXD pattern corresponds more to that of the amorphous glass substrate than $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$, with only a low intensity residual PbI_2 peak observable. This is due to material loss from the substrate with degradation and repeated characterisation.

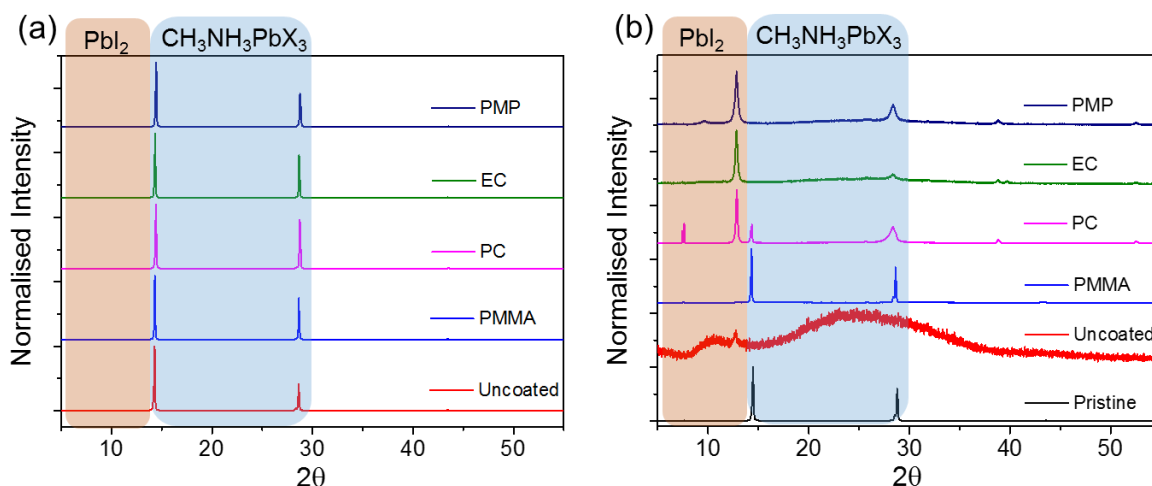


Figure 3.6. PXRD patterns of (a) pristine (uncoated) and polymer-encapsulated $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films before thermal degradation, (b) uncoated and polymer-encapsulated $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films following thermal degradation in 60 °C in air for 432 h. The PXRD pattern of the pristine uncoated $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ film prior to thermal degradation is also shown for comparison (black line). The pattern corresponding to the degraded uncoated sample appears amorphous due to loss of material as the degradation progressed.

3.3.2.3 Scanning Electron and Atomic Force Microscopy

Microscopy is an effective tool to monitor the morphological changes which accompany the degradation of the perovskite material.^{16,17} **Fig. 3.7** shows the SEM and AFM images of pristine and degraded perovskite samples. Both techniques revealed that a clear structural change occurs, from relatively featureless “islands” of coverage for the pristine samples, to the formation of flake-like and amorphous layers after degradation, corresponding to the growth of PbI_2 dendrites from the $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ film. While the microscopy techniques outlined above are a convenient method to image the degradation of the unencapsulated perovskite layers, they proved difficult to image the degradation process for the polymer-encapsulated films. SEM was ineffective due to the large amount of charging which occurred due to the polymer encapsulants. This made it impossible to

image the samples as the charge built up in the polymer layer affected both the contrast and shift of the images.

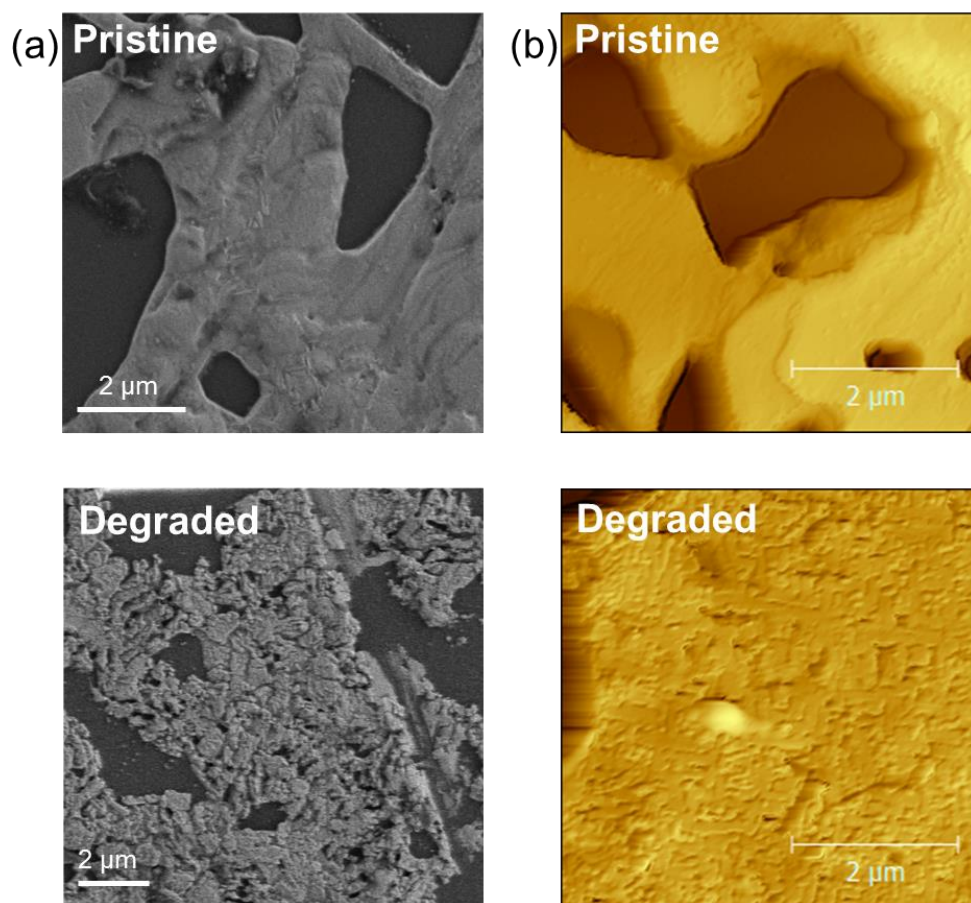


Figure 3.7. Morphological changes induced in an uncoated $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ film after heating in air. (a) SEM images of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films before and after degradation at 120 °C for 4 h. (b) AFM images of pristine $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films and after degradation at 60 °C for 72 h.

AFM allowed the imaging of the surface morphologies of the encapsulated perovskite films both before and after degradation. The transition from planar perovskite structures to the more dendritic PbI_2 was postulated to result in deformation of the encapsulating polymer layers, resulting in an increased surface roughness. **Fig. 3.8** shows the AFM images of encapsulated perovskite films before and after degradation for 168 h at 80 °C. Upon degradation an increase in both the surface roughness values for the EC- and PMP-coated samples from 0.26 to 0.73 nm and from 0.28 to 0.66 nm, respectively, is observed, thus indicating that the degradation process deforms the polymer films in some way. This deformation is likely to be due to a combination of PbI_2 growth and heat-induced stresses on the polymer films themselves. As the films were removed and replaced on the hotplate

to be characterised it is possible that the expansion and contraction associated with the heating process will affect the film's stability. This effect can be further exacerbated in the case of polymers with low glass transition temperatures such as PMP. A decrease in the surface roughness is observed post degradation of the PMMA- and PC-coated samples. This corresponds to a loss of the pinhole-like features observed in the AFM samples pre-heating. In both samples these pinhole like features show depths of > 15 nm (**Fig. 3.8e,f**) and are a result of rapid solvent evaporation during the spin-coating process.³² These features disappear after heating the perovskite film, with only shallow craters left after 168 h. While the deformation of the polymer films leading to changes to both roughness and the visible features can be observed by AFM, the technique does not allow the isolation of whether the observed changes in the film morphology are in fact due to the growth of PbI_2 or simply due to repeated heating and cooling cycles of the polymer films.

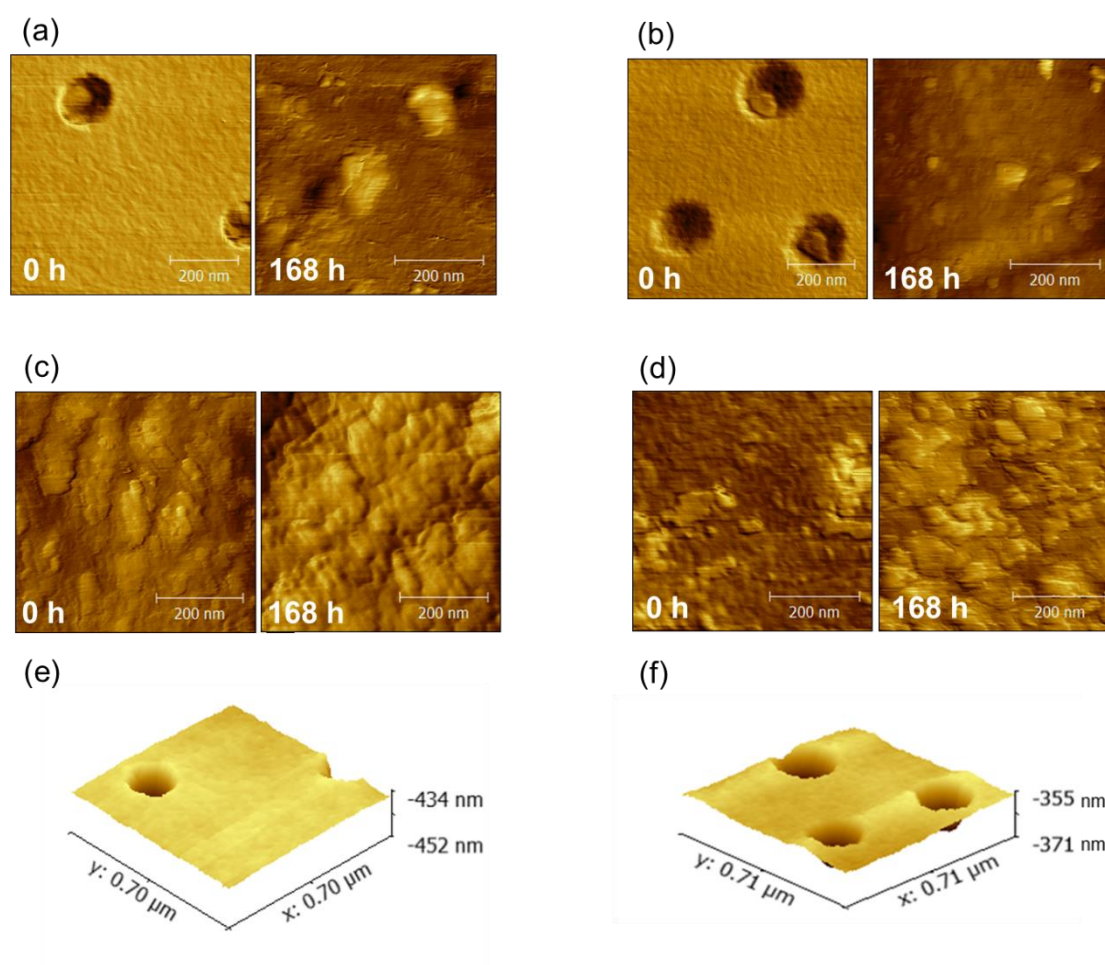


Figure 3.8. AFM images of polymer-encapsulated perovskites before and after 168 h degradation at 80 °C: (a) PMMA, (b) PC, (c) EC and (d) PMP. Depth profiles of pinhole like features observed for (e) PMMA- and (f) PC-coated perovskite films.

3.3.3 Time-dependent Thermal Degradation Monitored by *ex-situ* UV/Vis Absorption Spectroscopy and Visual Characterisation.

To quantitatively determine the efficacy of the polymers as encapsulation layers a time dependent stability study was performed on the coated $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films. The perovskite films were heated to 60, 80 or 100 °C on a hot plate in ambient conditions before removal at 24 h intervals for characterisation. Visual inspection (of photographs) allows rapid qualitative characterisation of perovskite film condition, with any discolouration or yellowing of the films representing the onset of conversion to PbI_2 . As described above, Watson *et al.* demonstrated the potential of visual characterisation through simple red, green, blue colour analysis to provide quantitative data on the extent of degradation in the perovskite layer.⁸ In this study, UV/Vis absorption spectroscopy was also utilised to quantify the degradation in the encapsulated and bare $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films. As shown in **Fig. 3.3b**, upon degradation the step-like absorption feature at 750 nm is lost. By measuring the decrease in the band edge at 750 nm relative to the absorbance at 800 nm the extent of the perovskite film degradation can thus be quantified.

3.3.3.1 Photographs of Degradation

As described above, visual characterisation can be used to rapidly determine whether or not a perovskite layer has been degraded. Images of the polymer-encapsulated perovskite films were meticulously taken throughout the time-dependent stability study to allow us to quickly monitor which of the encapsulants were performing the best. **Fig. 3.9** shows photographs of the encapsulated and bare perovskite films after they were subjected to 100 °C and how their degradation can be monitored visually with time as a representative example. The examples for temperatures at 60 °C and 80 °C are found in the appendix (**Fig. A3.1–A3.2**).

As expected, visual characterisation showed that the degradation of the uncoated film occurred rapidly, with the sample appearing completely yellow within 24 h. PMMA performs the best out of all the encapsulation layers at all degradation temperatures, with no observable discolouration occurring over the timescales investigated. This supports the results observed using PXRD. PC performed the second best, with slight yellow discolouration observable after 120, 96

and 48 h for temperatures of 60, 80 and 100 °C, respectively. EC and PMP showed similar trends in their stability with near complete degradation observable after 24 h at temperatures of 80 and 100 °C and PMP performing better at 60 °C.

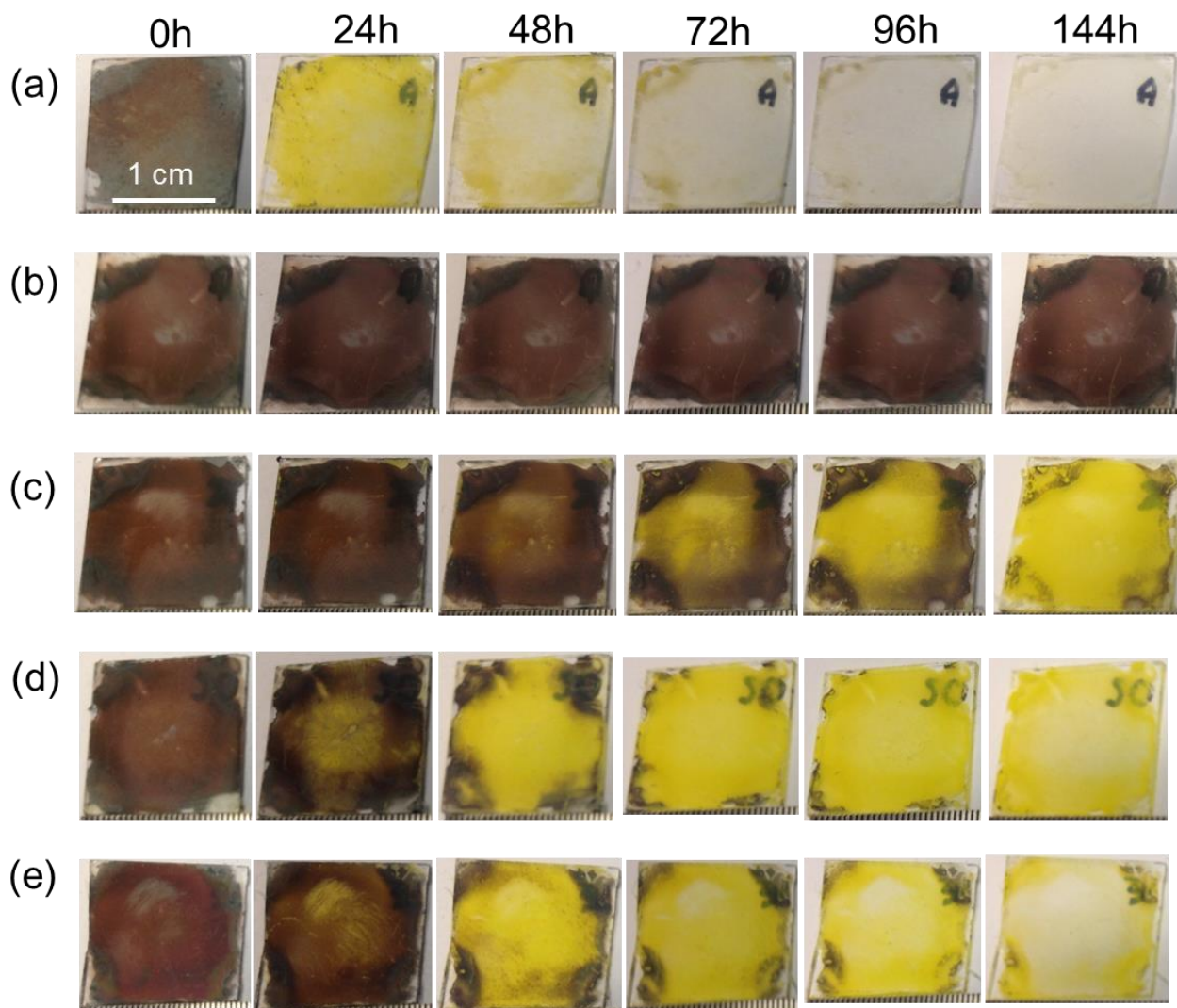


Figure 3.9. Photographs of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite films upon degradation at 100 °C in ambient conditions as a function of time. The films are coated with (a) uncoated, (b) PMMA, (c) PC, (d) EC and (e) PMP.

3.3.3.2 UV/Vis Absorption Spectroscopy

While visual characterisation was useful to observe when degradation is complete, UV/Vis absorption spectroscopy allowed the effectiveness of the polymer encapsulants to be quantitatively compared. Concurrently with the visual characterisation, UV/Vis absorption spectroscopy was performed on the bare and encapsulated $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films. The UV/Vis absorption spectra for polymer-encapsulated perovskite films at 80 °C is shown in **Fig. 3.10** as a representative sample.

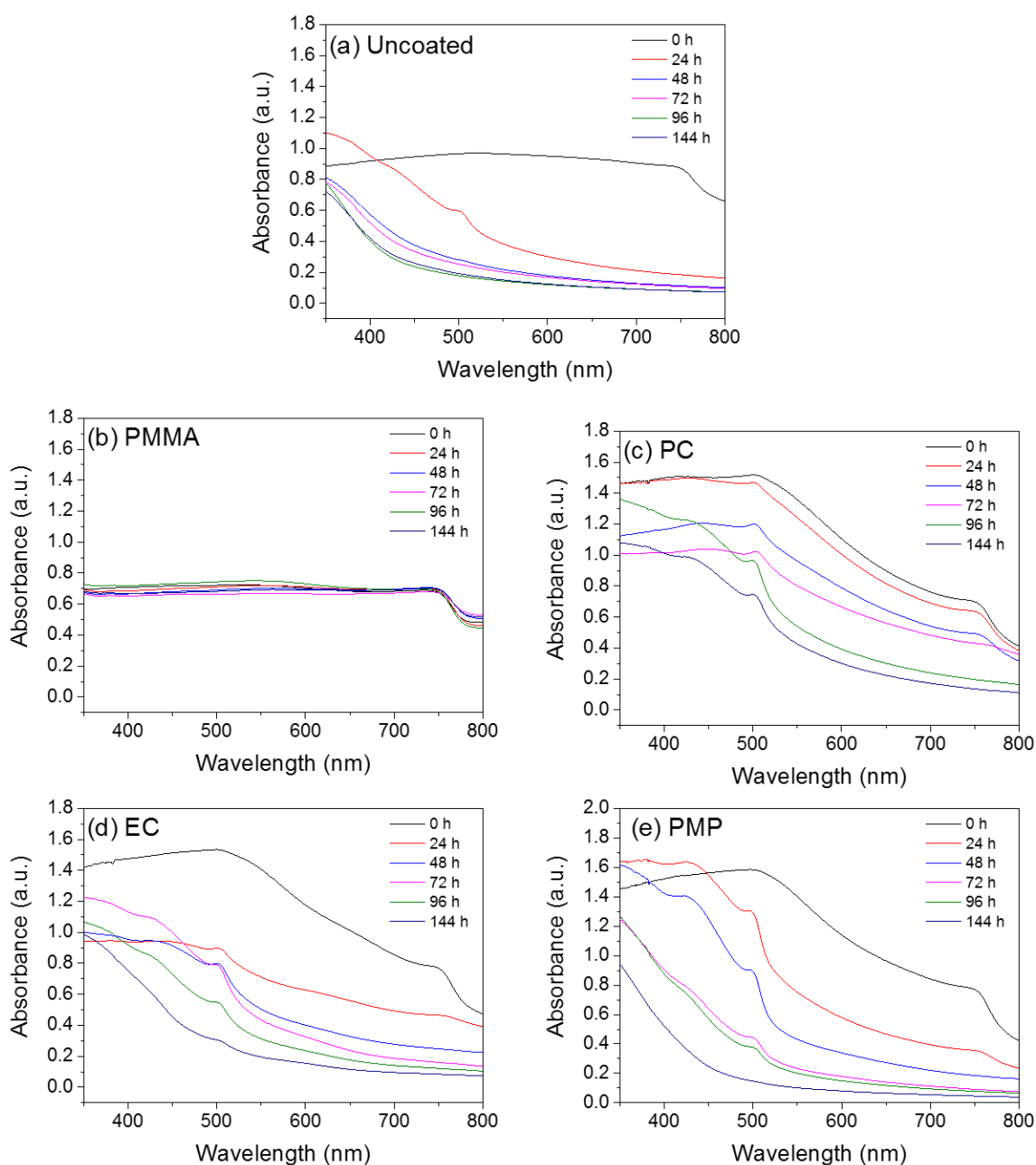


Figure 3.10. *Ex-situ* UV/Vis absorption spectroscopy of perovskite films degraded at 80 °C as a function of time, t coated with (a) uncoated, (b) PMMA, (c) PC, (d) EC and (e) PMP.

With the exception of the PMMA-coated film, the step-like feature at 750 nm disappears for all polymer encapsulants with increasing degradation time. The time taken to reach total degradation was the only differentiator between the coatings. A similar trend was observed for the samples degraded at 60 and 100 °C (**Appendix Fig. A3.3–A3.4**). **Fig. 3.10** also highlights the variation in the appearance of the perovskite films prior to degradation, particularly in **Fig. 3.10b** where the PMMA-coated sample appears to be almost completely flat across the visible range. This is indicative of poor microscale film coverage and also implies that limited dissolution/recrystallization effects are occurring for the toluene dissolved PMMA samples, which is to be expected considering toluene is a very poor solvent for perovskites.^{18,33}

To quantify the rate of degradation of the $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ polymer-encapsulated films at different temperatures, the absorbance at 750 nm relative to the absorbance at 800 nm was normalised and plotted varying with time, $t = 0$, to monitor the decay of the band edge (**Fig. 3.11**). Interestingly, several of the samples showed increased absorbance between 0 and 24 h heating before the expected band edge decay was observed. This increase is typically associated with additional annealing of the film and the removal of any unevaporated solvent during the first 24 h, which results in rearrangement of crystallites and improved surface coverage of the film due to moisture present in the solvents.^{19,30}

The trends in the band edge decay observed using UV/Vis absorption spectroscopy match those seen through visual characterisation, with PMMA-encapsulated layers showing no significant degradation at any temperature including 384 h at 60 °C, which shows good agreement with the PXRD data. Uncoated $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films exhibit significant loss in absorbance corresponding to near complete degradation after 24 h. Notably, despite the complete disappearance of the band edge after 24 hours, the normalised absorbance continues to decrease. This can be observed as loss of material from the substrate with time (**Fig. 3.9a**). The fluctuations visible for the PMMA coated sample in **Fig. 3.11b** were due to variations in film position between measurements, however, no band edge decay was observed in the investigated timescales (**Fig. 3.10b**). The rate of band edge decay was retarded through the application of each of the polymer layers, however, the extent of their impact on the rate of decay varied considerably. As with the visual characterisation a clear trend

emerged in the efficacy of the polymer layer as encapsulants. At all temperatures, it became apparent that WVTR of the polymer (**Table 3.1**) showed the greatest impact on the stability of the polymer coated perovskite films. PMMA, with the lowest WVTR, vastly outperforms the other polymers, confirming, as expected, that water vapour plays a key role in the thermal degradation mechanism. Habisreutinger *et al.* showed similar results for their carbon nanotube-doped polymer hole transport layers using PMMA and PC when placed under running water.⁷ While PMMA-coated films showed no noteworthy degradation on the timescales measured, all the other polymers eventually showed complete degradation and an increased rate of band edge decay with increasing temperature. PC performed better than EC and PMP with total degradation observed at ~380 h, 340 h and 190 h at 60 °C, 80 °C and 100 °C, respectively. However, as encapsulants, EC and PMP exhibited a similar performance, with degradation occurring after ~50 h at all temperatures despite EC's significantly higher WVTR.

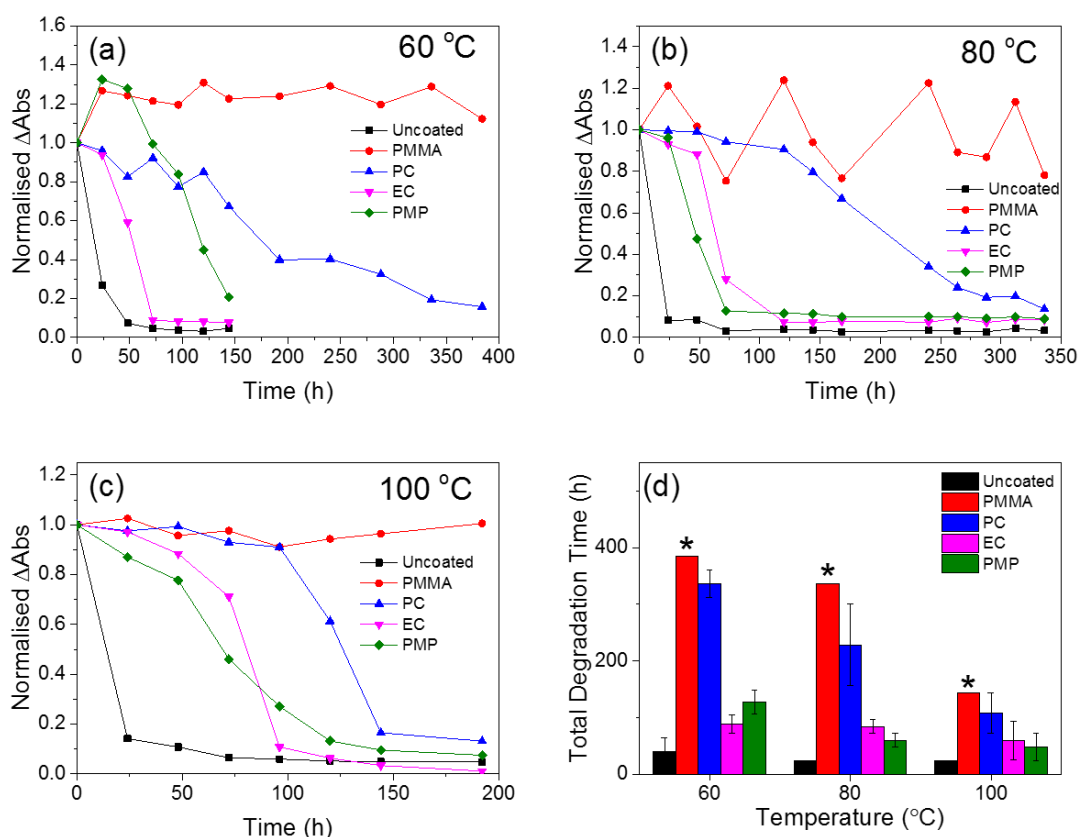


Figure 3.11. Results of time-dependent $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ stability studies monitored by UV/Vis absorption. (a) Difference in absorbance between 750 nm and 800 nm (ΔAbs) as a function of time, normalised to $t = 0$ h for films degraded at 60 °C in air, (b) 80 °C in air and (c) at 100 °C in air. The solid lines serve only to guide the eye. (d) The mean times required for complete degradation of the UV/Vis absorption band edge (750 nm) for pristine and polymer-encapsulated $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films as a function of degradation temperature. The error bars represent the standard deviation of three measurements. * indicates that at that time no indication of degradation was observed.

A plot of the average times for complete band-edge decay for the four encapsulants is shown in **Fig. 3.11d**. It can be observed that the rate of degradation of the encapsulated $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films increases as the temperature is increased. Interestingly, contact angle measurements on polymer films demonstrated that while WVTR has a significant impact on the ability of a polymer to act as an encapsulant, the hydrophobicity of the film shows a negligible contribution. **Fig. 3.12** shows the contact angle measurements for films of each polymer-coated on a glass substrate. These measurements revealed that while PMP exhibits the lowest wettability ($\theta_c = 105.9^\circ$) and the EC surface is highly hydrophilic ($\theta_c = 18.5^\circ$), both polymers exhibit similar trends in the thermal degradation rates at all temperatures investigated. The poor performance of PMP, despite its lower WVTR than EC, can be attributed to its low glass transition temperature ($T_g = 29^\circ\text{C}$ for amorphous PMP, however this can decrease with crystallinity), which upon heating can result in the formation of defects in the film, which allow moisture to permeate through facilitating degradation.²⁷

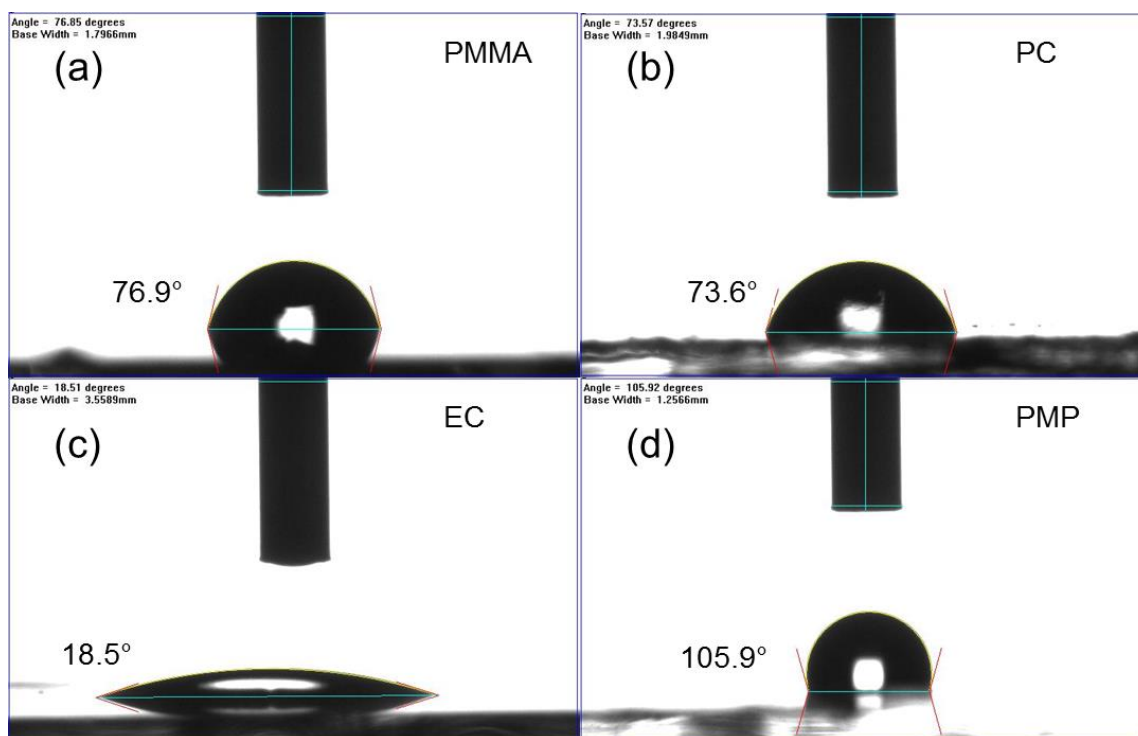


Figure 3.12. Determination of the surface hydrophobicity of polymer films coated on glass slides using contact angle measurements: (a) PMMA, (b) PC, (c) EC and (d) PMP.

3.3.4 Real-Time Evaluation of Thermal Degradation using Fluorescence Microscopy

The use of well-established techniques such as X-ray diffraction and UV/Vis absorption spectroscopy to characterise the degradation has been demonstrated above. However, these methods are quite invasive and can be time consuming, limiting their applications in a large-scale fabrication process. Similarly, while visual inspection is useful to determine if degradation has occurred, by the time the yellow colour is obvious to the naked eye degradation has already progressed significantly. Furthermore, techniques such as AFM and SEM, while effective for imaging uncoated perovskite films, do not allow imaging of the degradation of the encapsulated perovskite film. Thus, in order to determine the quality of the $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite films in a rapid and non-invasive way, epifluorescence microscopy was utilised. FM takes advantage of the characteristic red emission of the $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite which is subsequently lost as PbI_2 is formed upon degradation. **Fig. 3.13** shows a non-encapsulated film of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ before and after degradation at 60 °C for 48 h. A darkening of the film was observed upon thermal degradation, thus allowing a qualitative determination of the extent of degradation by comparison between the pristine and degraded samples.

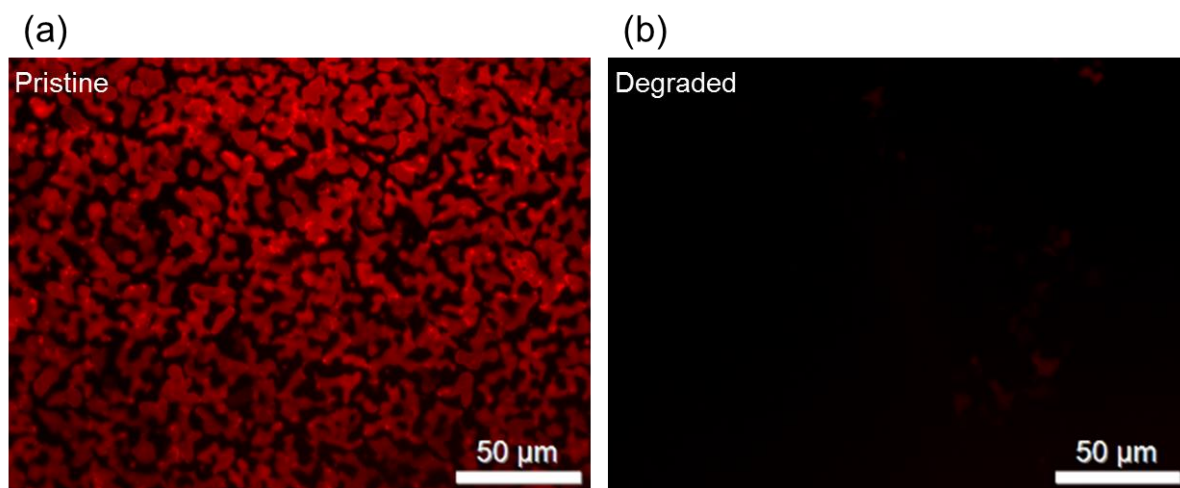


Figure 3.13. Fluorescence microscopy images of uncoated $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite (a) before and (b) after thermal degradation at 60 °C for 48 h.

3.3.4.1 Time-Dependent Thermal Degradation Monitored by FM

It has been shown above that FM can be utilised to characterise the degradation of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films. However, to investigate if it is a useful technique for comparing the ability of the polymers to act as encapsulants for perovskite layers, the polymer-encapsulated films were imaged as they underwent thermal degradation at 24 h intervals at temperatures of 60, 80 and 100 °C. **Fig. 3.14** shows the FM images of polymer-encapsulated $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films as a function of degradation time at 60 °C.

Prior to heating, the encapsulated films exhibit a homogeneous red emission that is characteristic of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$, and matches that observed for the non-encapsulated samples (**Fig. 3.13**) with no evidence of darkening or loss of photoluminescence observed upon application of the polymer encapsulants. As with the previous studies using UV/Vis absorption spectroscopy and XRD, the rate of degradation varied significantly depending on the polymer encapsulant used. Fluorescence imaging revealed the same trends in the efficacy of the polymer encapsulants at inhibiting thermal degradation at all temperatures. PMMA-encapsulated films showed only a slight drop in the emission intensity after 384 h degradation at 60 °C, thus further supporting its claim as the champion barrier layer. Interestingly, this darkening in **Fig. 3.14a** is observable before any signs of degradation had appeared visibly or through UV/Vis absorption spectroscopy. For example, when PC-coated films were characterised by UV/Vis absorption spectroscopy, they showed no significant band edge decay until 144 h, whereas there is an almost complete loss of fluorescence after 96 h degradation in the FM image (**Fig. 3.14b**). Similarly, the films encapsulated by EC and PMP showed darkening 24 h before any significant decay was observed in the UV/Vis absorption spectra with nearly complete loss of fluorescence after 24 h and 72 h, respectively. When examining the more stable encapsulated samples a brightening effect was often observed between $t = 0$ h and $t = 24$ h. This brightening can be attributed to additional thermal annealing of the perovskite films within the timescales investigated due to no changes made in the microscope settings between measurements.

Similar trends were observed in the efficacy of the polymer encapsulants at 80 °C, however the rate of film darkening is onset earlier for PMMA with evidence of significant degradation appearing after only 120 h, well before any degradation was observed through other experimental

techniques (**Fig. 3.15a**). PC shows complete loss of fluorescence after 120 h and darkening after 48 h, whereas EC and PMP show significant darkening after 24 h.

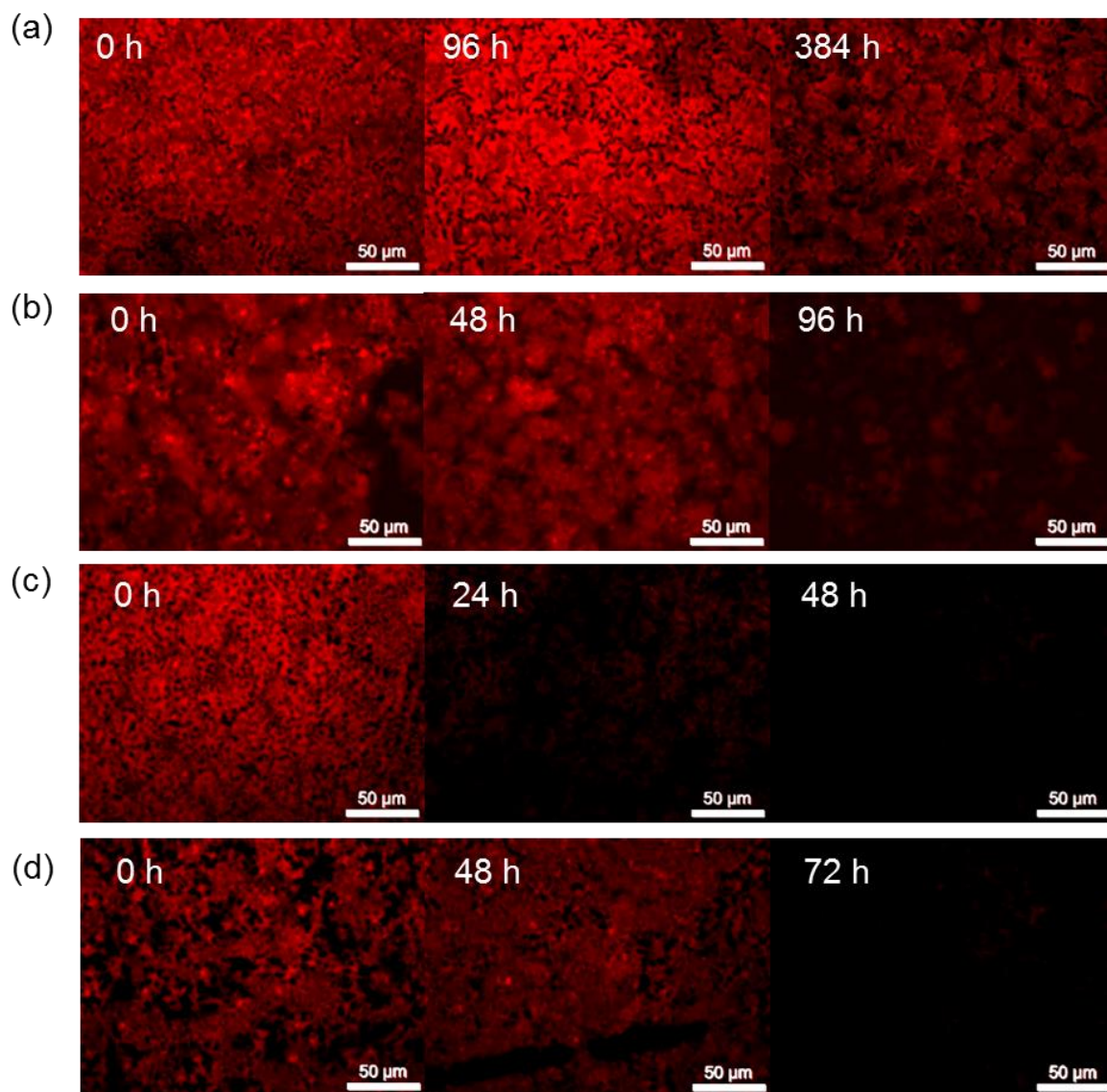


Figure 3.14. Thermal degradation of polymer-encapsulated $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films at 60 °C as a function of time monitored by fluorescence microscopy. $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ degradation is accompanied by a decrease in emission intensity and hence darkening of the image. (a) PMMA shows negligible degradation after 384 h, (b) PC degrades completely after 96 h, (c) EC shows an onset of degradation after 24 h and (d) PMP shows complete degradation after 72 h.

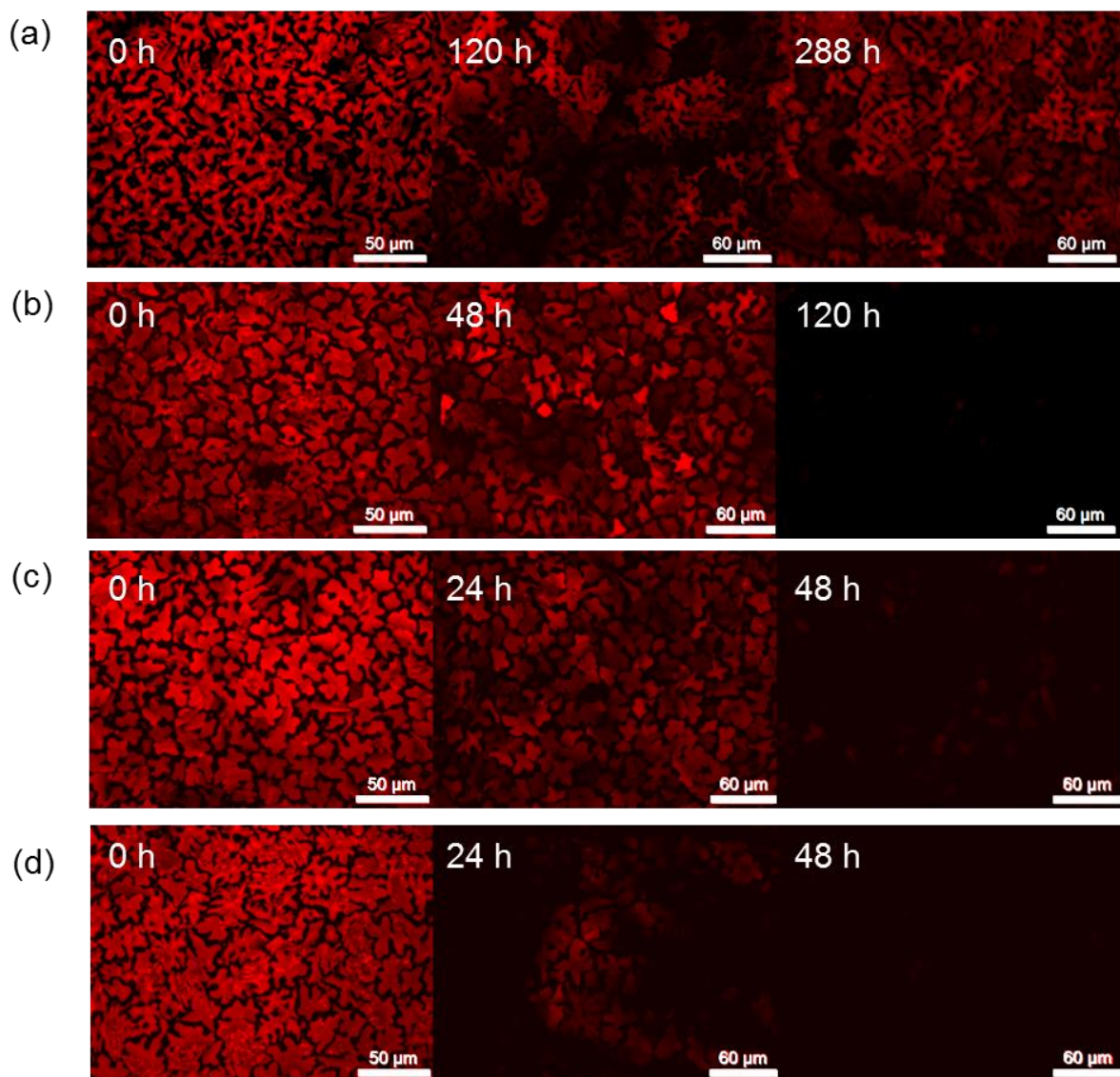


Figure 3.15. Time-dependent fluorescence microscopy images of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films undergoing degradation at 80 °C encapsulated by (a) PMMA (b) PC (c) EC and (d) PMP.

As the degradation temperature was further elevated to 100 °C, this decrease in the fluorescence intensity is observed for all samples, including those encapsulated in PMMA, after only 48 h, thus indicating that even with an effective barrier layer to the local environment a significant decrease in the fluorescence intensity is observed (**Fig. 3.16**). This phenomenon is observed well before the other characterisation techniques begin to show evidence of degradation and, thus, cannot be described by the conversion of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ to PbI_2 alone. This film darkening can be attributed to a combination of effects, including the inherent degradation of the $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ to PbI_2 and to the agglomeration of crystal grains under ambient conditions to form larger aggregates.²³ It has been documented that under storage in ambient conditions for 2 weeks spontaneous grain

growth occurs for $\text{CH}_3\text{NH}_3\text{PbBr}_3$.²³ In this work, after two weeks Sheng *et al.* demonstrated a change in grain sizes from relatively homogeneous $<1\ \mu\text{m}$ grains to variable grains sizes $>2\ \mu\text{m}$, with the larger grains showing less intense emission. Spatially-resolved confocal fluorescence-lifetime imaging experiments on pure $\text{CH}_3\text{NH}_3\text{PbBr}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_3$ films have also shown that an increase in grain size leads to a decrease in the PL intensity.^{23,34} The observed grain growth can be attributed to the aggregation of smaller grains, resulting in the formation of localised defect sites which enhance the rate of non-radiative recombination.^{23,34}

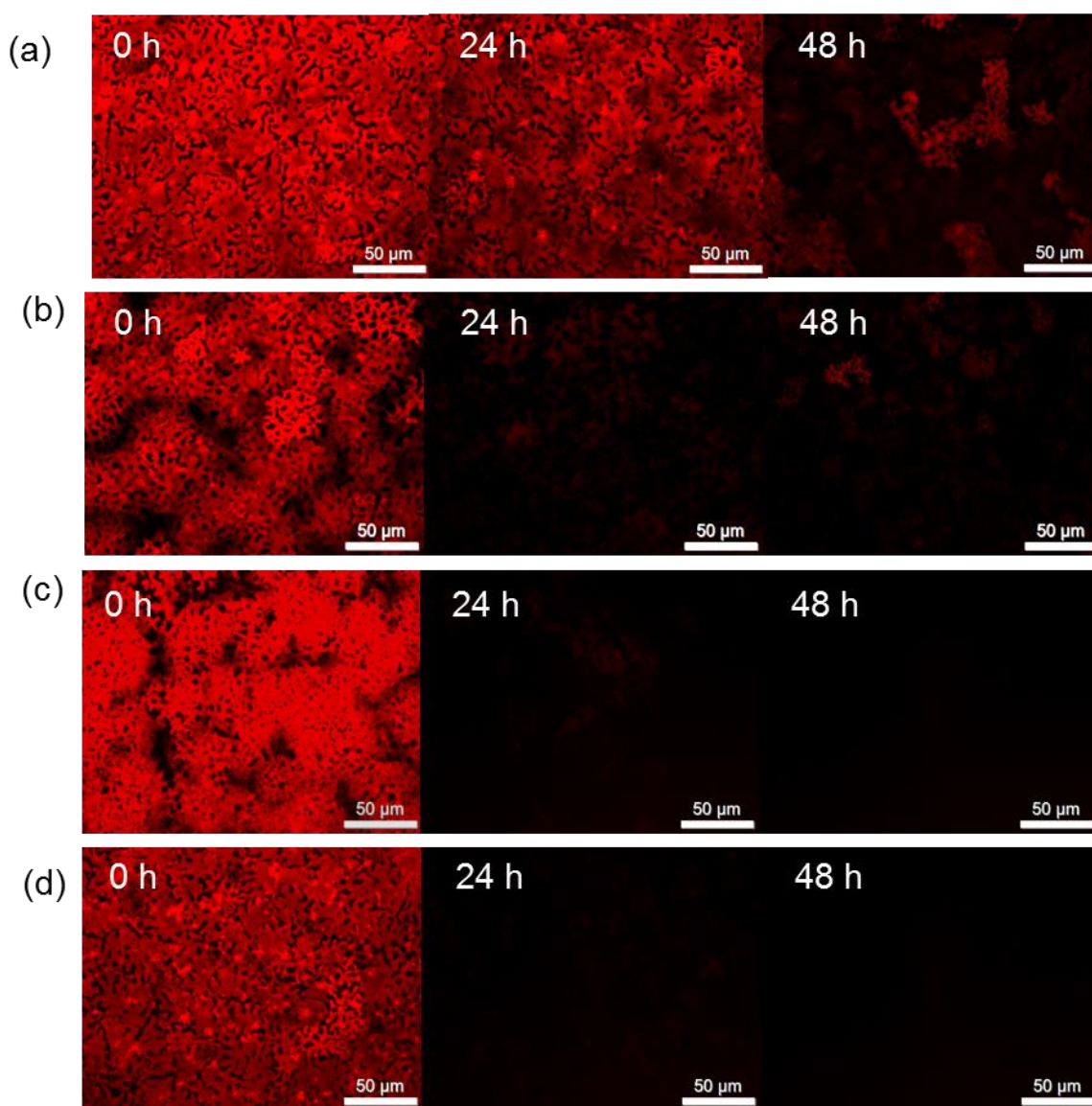


Figure 3.16. Time-dependent fluorescence microscopy images of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films undergoing degradation at $100\ ^\circ\text{C}$ encapsulated by (a) PMMA (b) PC (c) EC and (d) PMP.

The spatial resolution of epifluorescence imaging coupled with the subsequent darkening of the films renders this technique inappropriate to image the grain growth. However, utilising the results from the complementary techniques (UV/Vis absorption spectroscopy, XRD and visual characterisation) for timescales where no degradation was observed, (PMMA-coated sample following thermal degradation at 100 °C) (**Fig. 3.11c**) and where FM revealed a similar pattern of film darkening to that observed for the other polymer encapsulants (**Fig. 3.16a**), it can be concluded that the observed darkening of the $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ layer is due to spontaneous grain growth (and associated formation of non-radiative trap sites) and that this growth is temperature dependent. The existence of these trap states can act as recombination centres which limit the efficiency of charge transport in PSCs, thus is a mechanism for cell degradation which occurs in parallel with the chemical degradation to PbI_2 .

While it has been shown that FM can be utilised to observe rapid degradation of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films through grain growth in a non-invasive way, before it is observable by UV/Vis absorption spectroscopy or PXRD, the limitations of the technique need to be established. Thus, pristine and EC-coated $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films were degraded at 60 °C and images were recorded at shorter time intervals of 1 h in order to observe the lowest time detection limit for the onset of degradation by FM. **Fig. 3.17** shows the images of the samples pre-degradation and when the first instance of film darkening is observed. An increase in fluorescence intensity was observed in the first 2 hours of the stability test, which can be attributed to a combination of additional thermal annealing causing increased crystallinity of the films, as was observed by UV/Vis absorption, and potentially a photobrightening effect caused by halide exchange upon illumination by the FM light source.^{30,35} Film darkening is observed for the uncoated $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ sample after only 8 h, which is reasonable given that both UV/Vis absorption and PXRD measurements show complete degradation of the film to PbI_2 within 24 h. For the analogous EC-coated films, significant film darkening was observed by FM after 29 h. In contrast, UV/Vis absorption studies only revealed the onset of thermal degradation after 50 h of heating (**Fig. 3.11c**). These results demonstrate that FM imaging can be used as a rapid, non-invasive approach to screen the quality of perovskite films and to identify the onset of film degradation before other commonly used techniques.

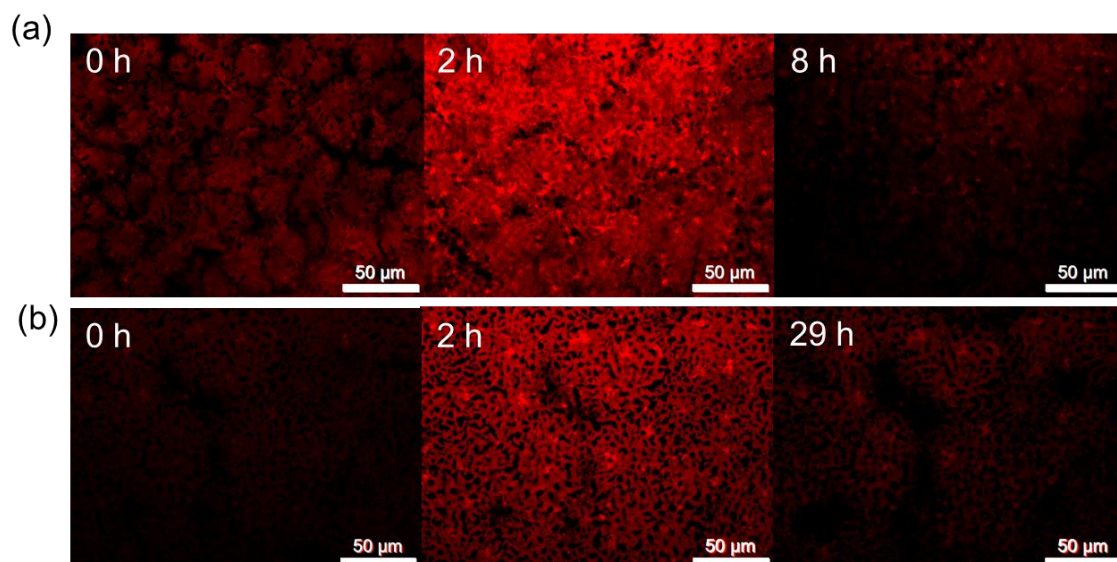


Figure 3.17. Thermal degradation of pristine and EC-encapsulated $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films at 60 °C as a function of time, as monitored by fluorescence microscopy. (a) The uncoated $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ film exhibits significant darkening after 8 h. (b) The EC-encapsulated film exhibits significant darkening after 29 h. After 2 h at 60 °C, the fluorescence of both films is more intense due to additional annealing and a contribution of photobrightening effects.

3.3.4.2 Degradation of Finished PSC Device

In order to confirm that this technique is applicable to finished PSC devices, and not simply the perovskite layer itself, a non-encapsulated $\text{CH}_3\text{NH}_3\text{PbI}_3$ cell was thermally degraded at 100 °C for 14 h to observe if the early onset degradation through crystal growth could (i) be observed by FM and (ii) negatively impacts on the current-voltage (I - V) performance of the cell. The cell fabrication method used a standard TiO_2 , $\text{CH}_3\text{NH}_3\text{PbI}_3$, and spiro-OMeTAD architecture. $\text{CH}_3\text{NH}_3\text{PbI}_3$ was utilised due to large hysteresis observed for cells fabricated using $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$. Interestingly, upon thermal degradation of the PSC, despite a significant loss of cell PCE from 8% to 1%, there was no obvious discolouration of the perovskite that made up the cell active layer. **Fig. 3.18** shows a comparison of the J - V curves measured both before and after thermal degradation and the corresponding FM images of the device. The lack of a film darkening is likely due to the anti-solvent treatment of the perovskite film. By depositing the anti-solvent as the perovskite is spin-coated the film rapidly crystallises to form uniform large grains and not the flake-like structures which was previously observed for the investigated $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films. Upon heating, however, the degradation of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ films can be observed by an increase in the number of pinhole

type defects in the film (**Fig. 3.18b**). This formation of pinholes has previously been shown to be a result of degradation of uniform perovskite films by Soufiani *et al.*²¹ They reported an increase in the number and size of pinhole defects for a $\text{CH}_3\text{NH}_3\text{PbI}_3$ PSC aged in an inert atmosphere for 2 months.²¹ The noteworthy decay of the PCE upon degradation is likely not to be due entirely to degradation of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ to PbI_2 , but can also be explained by evaporation of the 4-tert-butylpyridine dopant ($T > 85\text{ }^\circ\text{C}$)^{36,37} in the spiro-OMeTAD hole transport layer. However, the possibility of using FM to rapidly assess the film quality in a non-invasive manner at any stage of the device fabrication process still presents an attractive option.

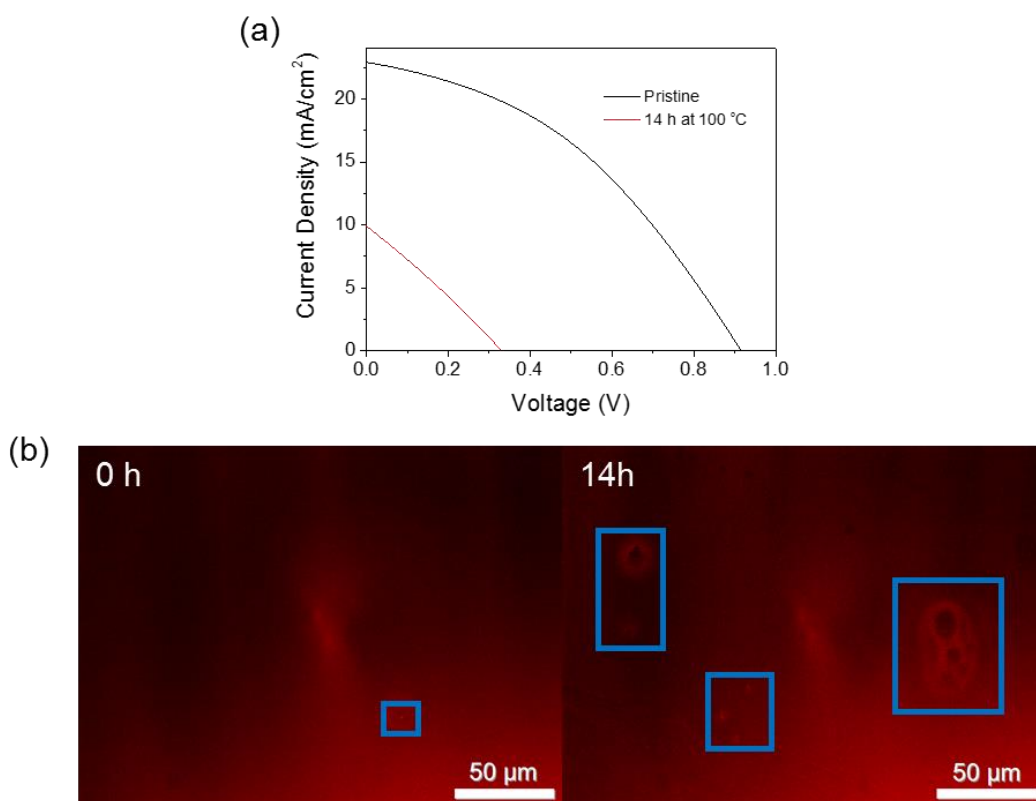


Figure 3.18. (a) *I*-*V* curves of a $\text{CH}_3\text{NH}_3\text{PbI}_3$ PSC before (black) and after (red) heating at $100\text{ }^\circ\text{C}$ for 14 h. (b) Fluorescence microscopy images of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ PSC before and after heating at $100\text{ }^\circ\text{C}$ for 14 h. The blue boxes highlight the visible pinhole defects.

3.4 Conclusions

To determine the physical properties of polymers which have the most impact on their ability to act as barriers to moisture when coating perovskite solar cells, controlled degradation experiments

have been performed on $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite thin films uncoated and coated with four common polymer encapsulants (PMMA, PC, EC and PMP). These encapsulants act as a physical barrier to prevent moisture induced degradation, which currently limits the commercial application of PSC technology. Time-dependent thermal degradation of pristine and polymer-encapsulated $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films at 60 °C, 80 °C and 100 °C was utilised as the basis for the comparative study. The degradation was monitored by a combination of PXRD, UV/Vis absorption spectroscopy, visual characterisation and epifluorescence microscopy. PMMA performed the best of the four polymers studied as encapsulants at all temperatures investigated, extending the lifetime of the $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ film from 24 h to >400 h upon continuous heating at 60 °C. PC was the next best performing encapsulant, with total degradation observed at ~380 h at 60 °C. In contrast, EC and PMP only moderately enhanced the thermal stability compared to the uncoated $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ film, with the onset of degradation occurring rapidly after 50 h at all temperatures. WVTR was determined to be the most important physical property when selecting a polymer encapsulant; however, a T_g well above the typical device operating temperatures and/or the ambient conditions is also advisable. It was observed that while PXRD and UV/Vis absorption provide quantitative analysis of the degradation of the $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ film to PbI_2 , epifluorescence microscopy provides an indication of the early onset deterioration of the film quality due to grain growth and associated defect formation. This suggests that FM may be an attractive technique for rapid and non-invasive screening of device quality in real-time during the fabrication process. Through the judicious study of these polymers a robust methodology for both polymer film deposition and perovskite characterisation has been achieved. PMMA is the best performing encapsulant which presents an attractive option for both device encapsulation and LDS coatings for PSCs to improve their photostability.

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Chapter Four

Luminescence Down-Shifting for Perovskite Solar Cells: A Study of Film Thickness and Luminophore Concentration.

4.1 Introduction

Chapter 3 has demonstrated that encapsulation can be used to effectively enhance the stability of PSCs by acting as a barrier to moisture intercalation. The effectiveness of the PMMA encapsulating layer in particular, and its facile application to perovskite layers makes it an attractive host material for LDS layers. As outlined in **Chapter 1**, LDS is a highly attractive method to improve the UV-stability of third generation PV devices. LDS as a technique has not been widely investigated for use with PSCs because moisture and thermally induced degradation are viewed as more critical.¹ However, as we move towards long term applications and potential commercialisation of PSCs, the issues regarding UV-degradation must be addressed.²

Chander *et al.* in their first example of LDS for PSCs, used a $\text{YVO}_4/\text{Eu}^{3+}$ LDS layer to achieve both a PCE increase from 7.42 to 7.93 % and increased device stability compared to uncoated devices, which has proven the effectiveness of this technique.³ The recent paper by Griffini *et al.* utilising a fluoropolymer layer doped with LV570 as an LDS coating,⁴ demonstrated the viability of LDS for PSC applications. In this example, addition of the polymer coatings both as LDS layers on the front and as a hydrophobic barrier on the back of perovskite solar cells resulting in an increase in PCE to *ca.* 19%, along with greatly increased stability under illumination and high-humidity conditions. Since this paper, there have been several other examples of LDS specifically tailored for PSCs.⁴ Jiang *et al.* reported an LDS layer similar to that originally presented by Chander *et al.*³ in which an $\text{Eu(III)-4,7-diphenyl-1,10-phenanthroline}$ luminophore was applied in a polyvinylpyrrolidone host to the FTO of a PSC as an LDS layer.⁵ Three concentrations of the Eu(III) complex were investigated (0.5, 1.0 and 1.5 wt%) with the 1.5 wt% samples exhibiting a significant increase in the device PCE from 13.14 to 15.44 % and a stability increase after 10 h UV-illumination. However, in this work they do not characterise the devices before and after coating, but rather present examples made with and without the LDS layer. The authors acknowledge that some of the improved performance of the 1.5 wt% sample may be simply due to a better perovskite layer. However, the effect of the LDS coating can be seen in the EQE spectrum, where significantly enhanced EQE is observed in the region corresponding to luminophore emission.

Wang *et al.* provided a detailed study on the performance of CsPbCl₃:Mn NCs as LDS layers for PSCs and other PV cells.⁶ The blue-emitting perovskite CsPbCl₃ luminophore showed both low Φ_{PL} and a short Stokes' shift (<20 nm), but upon doping with Mn²⁺ energy transfer was observed to occur leading to yellow/orange emission and an increase in Φ_{PL} to 60%. Upon direct coating as LDS layers to PSCs, these doped PNCs increased the obtained PCE values, from 17.97 to 18.57%, with a general increase in J_{SC} obtained for the coated samples as seen in the EQE spectra. An increased stability was observed for the champion LDS-coated device, with a *ca.* 2% degradation observed after 100 h UV-illumination in an N₂ environment compared to a *ca.* 15% degradation for the uncoated cells. Anizelli *et al.* compared the effectiveness of an LDS layer comprised of the organic dye, Kremer fluorescent blue, doped into a PMMA host matrix, with a UV-filter to improve the stability of PSCs.⁷ The absorption spectrum of this dye significantly overlapped with the EQE spectrum of the CH₃NH₃PbI_{3-x}Cl_x perovskite cell, thus there was an average drop in the PCE from 9.1 to 7.9% for the LDS layer, compared to 7.6% for the UV-filter. The UV-filter and LDS layer performed similarly, with a *ca.* 40% decrease in the PCE observed under AM 1.5G illumination over 30 hours, whereas the uncoated cells showed complete degradation in the same timeframe.

An increase in device stability after 450 minutes of continuous UV-irradiation at 40 % RH was achieved for both bare perovskite layers and PSCs, upon coating with an LDS layer, by Tian *et al.*⁸ The LDS layers in question were fabricated by spin-coating a suspension of ZnSe QDs directly onto the top of a mesoporous TiO₂ CH₃NH₃PbI₃ PSC. The QDs showed bright blue photoluminescence, and for QD concentrations of 2 mg/mL and 5 mg/mL, an increase in the PCE was obtained. The bare perovskite layers showed near complete degradation in the absence of the LDS layer after 12 hours continuous illumination, whereas the LDS coated layers only began to show degradation onset yellowing after 18 hours. The PSCs performed similarly with a 50% drop in efficiency for the LDS devices after 450 minutes, compared to complete loss of efficiency for the uncoated cells. Very recently, Gheno *et al.* investigated a tetrazine-based downshifting layer to improve the stability of a CH₃NH₃PbI_{3-x}Cl_x PSC.⁹ The down-shifting layer consisted of a polystyrene host which was doped with *N*-(2-(6-chloros-tetrazin-3-yloxy)ethyl)-naphthalimide. The naphthalimide moiety causes similar absorption behaviour to LV570 which is also naphthalimide

based, the luminophore then exhibits *quasi*-complete Förster energy transfer to the tetrazine, giving a large Stokes' shift (*ca.* 230 nm). Despite the carefully tailored emission properties, the LDS layer was applied as a removable polystyrene film for the EQE measurements and this meant there were significant losses upon incorporation due to waveguiding by the LDS plate and the air gap between the PSC and the LDS layer.

4.1.1 Aims

As can be seen above there have been several recent examples of LDS layers applied to PSCs with the aim of improving the photostability and efficiency of the devices. These examples will typically vary the concentration of a luminophore and examine the effects on device efficiencies and stabilities, however there have been no studies which have examined the effect of film thickness on the cell efficiencies.

The aim of this Chapter is to provide a detailed study on the effect of LDS layer thickness and luminophore concentration on device efficiencies and stabilities. The fabrication and characterisation of two distinct PSC architectures (mesoporous TiO₂, and inverted) will be presented. LDS layers utilising several different organic luminophores will be deposited at different spin rates and concentrations to allow a detailed study of the effects of each coating to be obtained. The PSC-LDS devices will be characterised by EQE and *J-V* methods, with long term stability tests performed on both encapsulated and non-encapsulated devices under *AM* 1.5G conditions.

4.2 Experimental

4.2.1 Fabrication of Perovskite Solar Cells

4.2.1.1 Mesoporous TiO₂ Cell Fabrication

The fabrication of the mesoporous TiO₂-based perovskites cells followed the procedure previously reported by Troughton *et al.*¹⁰ FTO-coated glass (7 Ω/sq, Solaronix) substrates were sonicated in a solution of detergent, followed by deionised water, acetone and isopropanol before undergoing 10 min of oxygen-plasma etching. A 10% vol. solution of titanium diisopropoxide bis(acetylacetonate) in isopropanol (10 mL total) was repeatedly sprayed onto FTO glass substrates

at a temperature of 250 °C to deposit the compact TiO₂ layer. This layer was then sintered at 550 °C for 30 min. Upon cooling, a suspension of mesoporous TiO₂ nanoparticles (Dyesol 30NR-D : terpinol : isopropanol, 2:6:4.5 wt) was spin-coated onto substrates at 4500 rpm for 30 s before re-sintering at 550 °C for 30 min.

The CH₃NH₃PbI₃ perovskite precursor solution was prepared by dissolving PbI₂ (576 mg, 1.25 mmol) and methylammonium iodide (199 mg, 1.78 mmol) in 4:1 (v/v) DMF:DMSO (10 mL). To deposit the CH₃NH₃PbI₃ perovskite layer, 100 µL of the precursor solution was spin-coated onto FTO glass substrates at 4000 rpm for 30 s. During spin-coating, 100 µL of the ethylacetate anti-solvent was dropped onto the spinning substrate 20 s prior to the end of the spin cycle to rapidly crystallise the perovskite layer. The resultant films were then left to anneal at 100 °C for 1 h. Spiro-OMeTAD (80 mg, 0.065 mmol) was dissolved in chlorobenzene (1 mL) and doped with tBP (30 µL), Li-TFSI (20 µL, 1.81 M in acetonitrile) and FK209 TFSI solution (20 µL, 0.2 M in acetonitrile) before being spin-coated onto the perovskite layer at 4000 rpm for 30 s. Finally, gold electrodes were evaporated at 10⁻⁴ Torr using an Edwards 306 thermal evaporator. All perovskite and HTL deposition was performed under N₂ in glove box conditions.

4.2.1.2 NiO ‘Inverted’ Cell Fabrication

To fabricate inverted perovskite solar cells, the procedure previously described by Troughton *et al.* was used.¹⁰ FTO glass samples were cleaned as described in **Section 4.2.1.1** before being coated with a NiO hole transporting layer. This layer was spin-coated (4000 rpm, 30 s) from a 0.2 M solution of nickel acetate tetrahydrate (50 mg, 0.2 mmol) dissolved in 2-methoxyethanol (1 mL) and doped with ethanolamine (12 µL). After spin-coating, samples were annealed at 500 °C for 30 min before cooling to room temperature. The perovskite layers were prepared following the same procedure as described above in **Section 4.2.1.1**. PCBM ETL (20 mg, 0.02 mmol in chlorobenzene (1 mL)) was applied by spin-coating (2000 rpm for 30 s), then a buffer layer of bathocuproine (BCP, 0.5 mg, 0.001 mmol in anhydrous ethanol (1 mL)) was deposited by spin coating (6000 rpm for 10 s). 100 nm thick silver counter electrodes were evaporated at 10⁻⁴ Torr using an Edwards 306 thermal evaporator. All perovskite, ETL and buffer layer deposition was performed under N₂ in glove box conditions.

4.2.2 Device Encapsulation

Completed PSCs were encapsulated by evenly applying a photocurable encapsulation epoxy to the surface of a glass coverslip. This coverslip was then pressed into contact with the active surface of the PSC. The PSC was then placed under AM 1.5G illumination for *ca.* 5 minutes until the epoxy had hardened. Conductive silver paste was then applied to the contacts of the device. Cells were tested immediately before and after encapsulation to observe if the encapsulation process negatively affected the performance. All encapsulations were performed in ambient conditions.

4.2.3 LDS Layer Deposition

The LDS host stock solution was made by adding PMMA (1400 mg) to toluene (10 mL, 16.1 wt%) and alternating sonication and stirring until completely dissolved. To this stock solution, various concentrations of luminophore were added directly and sonicated until fully dissolved. The luminophores investigated were: LV570, LR305, Coumarin 153 (C153), polyfluorene (PFO) and 2-(2-hydroxyphenyl) quinazolin-4(3H)-one (HPQ) (**Fig. 4.2**).

Deposition of the LDS layer took part as a one-step spin-coating process. The luminophore-doped PMMA stock solutions were dropped onto the top face of the PSC and spread using the pipette tip before spin-coating. The thickness of the LDS layer was determined by the spin-rate, with film thicknesses corresponding to *ca.* 3.5, 1.7 and 0.8 μm achieved for spin rates of 500, 2000 and 8000 rpm respectively. Film thicknesses were determined using a Filmetrics F-20 thin film analyser in contact mode. The LDS layers were spin-coated for 60 s to achieve the desired thickness before, ramping to 10000 rpm for 5 s to remove any excess PMMA. A schematic of the cell architectures and LDS deposition is given in **Fig. 4.1**.

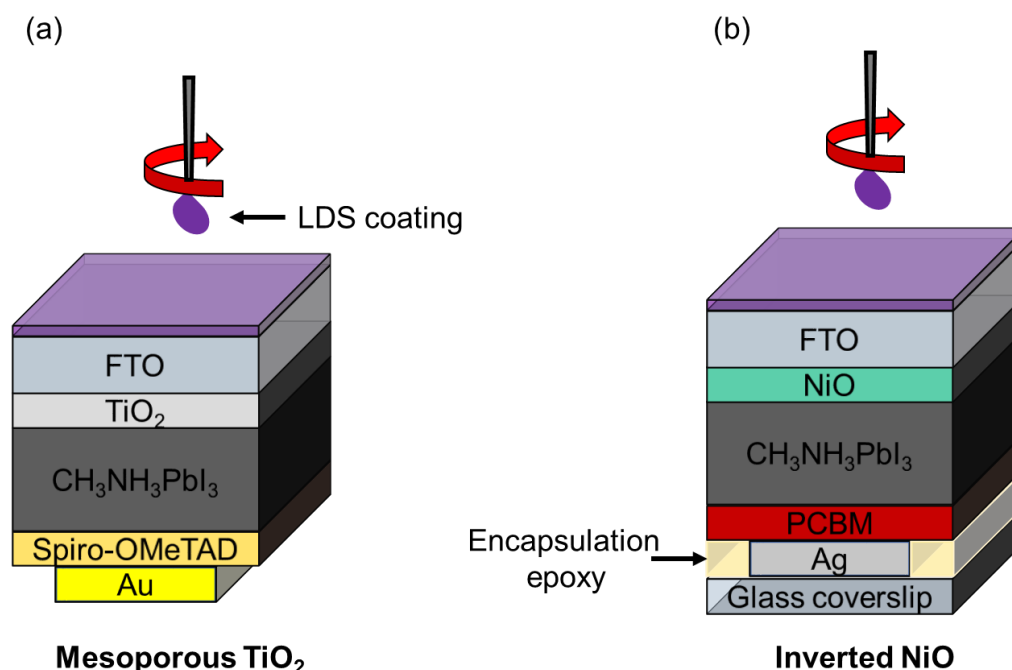


Figure 4.1. Schematic representation of the PV device architecture and LDS layer deposition for (a) unencapsulated mesoporous TiO_2 PSCs, and (b) encapsulated inverted NiO PSCs.

4.3 Results and Discussion

4.3.1 Selection of Luminophores

The luminophores investigated were selected to have a variety of emission wavelengths to allow the study of the effects that LDS layers emitting across the visible range have on the PSCs. **Fig. 4.2** shows the chemical structures of the luminophores used in this chapter. LV570 was the first luminophore selected as it has been frequently used to improve the PCE of PV cells as an LDS material.^{11–13} Its more recent application in LDS layers for both DSSCs¹⁴ and PSCs⁴ has demonstrated its effectiveness as a UV-filter, as well as an efficiency increasing layer for third generation PV. LV570 can thus act as a performance benchmark in this study, and by comparing different thicknesses with different concentrations we can potentially further optimise the performance of LDS layers based on LV570. PFO was selected due to its UV/blue absorption and emission and its high Φ_{PL} (>50%) upon incorporation into PMMA in low doping concentrations.¹⁵ Conjugated polymers such as PFO have been relatively under investigated for use in spectral converters, though some promising recent results suggest their unique behaviours in host materials

such as controllable phase separation and alignment in host matrices.^{16–18} HPQ is highly attractive as an LDS luminophore due to a combination of its aggregation-induced emission, and its favourable photophysical properties. HPQ shows absorption in the region of 250–350 nm; however, its Stokes' shift is approximately 250 nm which will both minimise reabsorption losses and allow direct absorption of high energy UV photons.¹⁹

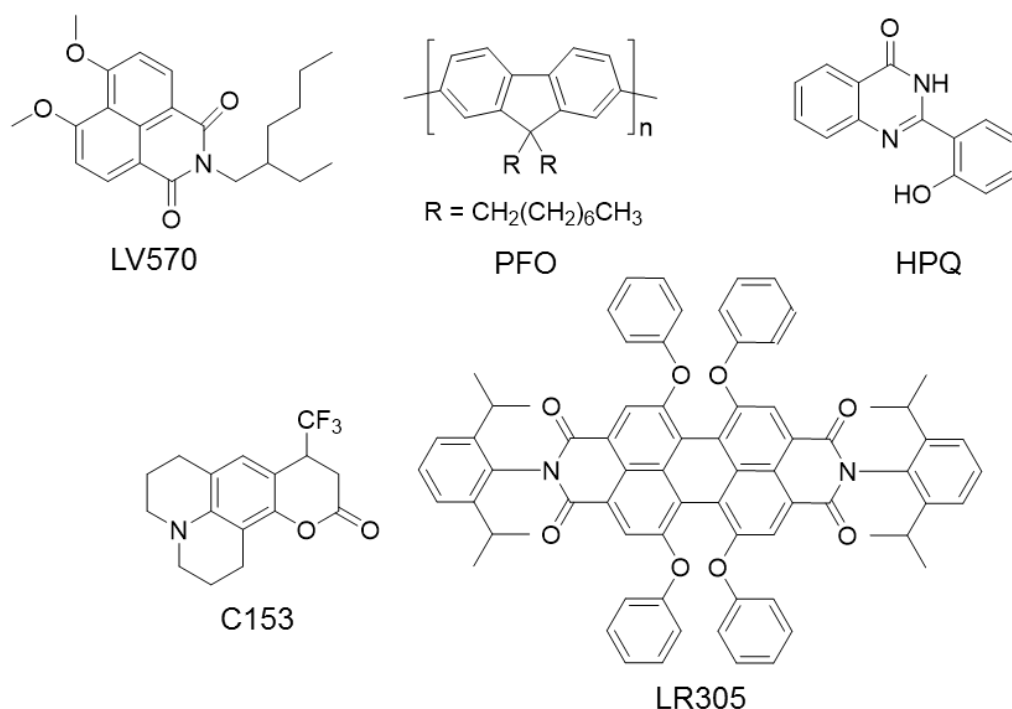


Figure 4.2. Chemical structures of the luminophores investigated in LDS layers for PSCs.

The above luminophores were selected due to their absorption properties which will act to enhance the UV-stability of PSCs without a significant impact on the EQE spectrum. However, in order to investigate whether luminophores which absorb in other ranges of the spectrum can improve the device stability, C153 and LR305 were also examined. Coumarin dyes have been used in spectral converters since the 1980s²⁰ and C153 was selected due to its absorption which is slightly red-shifted to the UV-absorbing luminophores described above, with an absorption maximum (λ_{abs}) at *ca.* 400 nm and an emission maximum (λ_{em}) at *ca.* 500 nm in the solid state.²¹ LR305, as detailed in **Chapter 1**, is one of the most common luminophores used in spectral converters, which shows red emission

and Φ_{PL} values of >90% in PMMA. As such it was used as an LDS layer in this study to see if red-emitting dyes can impact the stability/efficiency of PSCs.²²

The luminophores investigated generally showed good solubility in the PMMA matrix. HPQ required prolonged sonication (>6 h) at temperatures *ca.* 80 °C to be fully dissolved; however, since HPQ is an AIEgen the lower solubility is advantageous. In order to examine the effectiveness of the luminophores as LDS layers their photophysical properties, in particular, their absorption and emission behaviours must be understood. **Fig. 4.3** shows the UV/Vis absorption and PL spectra of the LDS luminophores in PMMA films (800 nm thick) at the standard doping concentrations used in this chapter. **Table 4.1** give the standard doping concentrations for the luminophores used in this chapter and the emission and absorption maxima.

Table 4.1. Steady-state photoluminescence and UV/Vis absorption maxima of the LDS luminophores applied to PSCs in PMMA host films (800 nm thickness) at their standard doping concentrations.

Luminophore	Concentration (wt%)	λ_{abs} (nm)	λ_{em} (nm)
LV570	0.25	376	432
PFO	0.1	389	435
HPQ	0.15	255	503
C153	1	416	504
LR305	0.25	574	603

The standard concentrations were selected for the Lumogen and coumarin dyes by varying the doping concentrations of the luminophore in 800 nm thick films, these films were then characterised by steady-state PL spectroscopy in identical conditions. The doping concentration which displayed the highest PL emission intensity was selected (**Appendix, Fig. A4.1**). The standard concentration for LR305 was initially 1 wt%, however due to high absorbance limiting the ability to characterise PSC performance upon coating, this was changed to 0.25 wt% and the tests were repeated. The Lumogen- and coumarin-based luminophores investigated show red-shifted absorption and emission maxima compared to the solution phase spectra, which can commonly occur

for organic dyes (**Appendix, Fig. A4.2**).²³ The PFO doped thin films, due to the high molecular weight of the luminophore ($M_w - > 20,000$) are highly optically concentrated in comparison, and as such the absorption peaks are slightly red-shifted (*ca.* 15 nm) compared to their solution phase counterparts.¹⁸ Notably, the emission profile of the PFO in PMMA is consistent with the formation of the β -phase. β -phase PFO corresponds to a planar conformation of the conjugated backbone, which is consistent with the planar separation which occurs between PFO doped into PMMA observed by Chappell *et al.*¹⁶ The λ_{em} of the HPQ-doped films matches the literature value of 500 nm for the concentration investigated,¹⁹ however some of the fine features of the absorption spectrum are lost for wavelengths < 300 nm due to the onset of absorption from the PMMA host and the glass substrate. (**Chapter 3, Section 3.3.2.1, Fig. 3.5**).

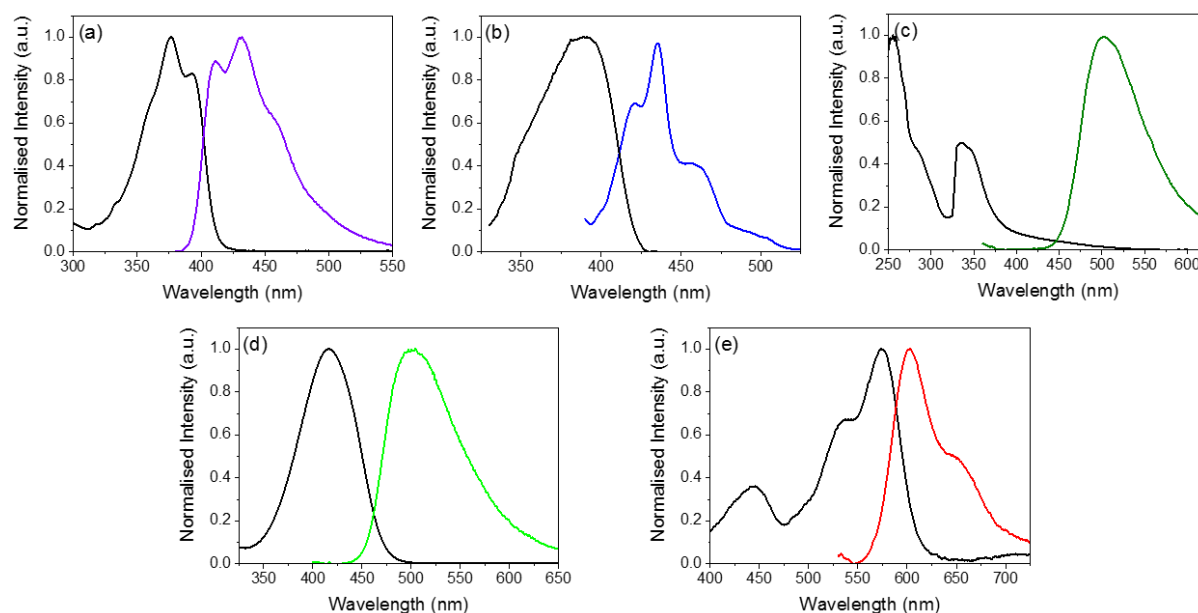


Figure 4.3. Optical properties of luminophores employed in LDS layers. UV/Vis absorption (black lines) and steady-state PL (coloured lines) spectra of PMMA films (800 nm) doped with the LDS luminophores on borosilicate glass slides. (a) LV570 0.25 wt% ($\lambda_{ex} = 360$ nm). (b) PFO 0.1 wt% ($\lambda_{ex} = 370$ nm). (c) HPQ 0.15 wt% ($\lambda_{ex} = 340$ nm). (d) C153 1 wt% ($\lambda_{ex} = 380$ nm). (e) LR305 0.25 wt% ($\lambda_{ex} = 515$ nm).

4.3.2 Characterisation of PSCs

In order to comprehensively characterise the effectiveness of the LDS layers on the performance of the PSCs, two of the most common architectures were investigated: mesoporous TiO_2 and inverted mesoporous NiO . The perovskite used in these devices was $\text{CH}_3\text{NH}_3\text{PbI}_3$. Many of the degradation processes which occur upon UV-illumination of PSCs are due to TiO_2 , both in the

device mesoporous layer and in the compact electrode-coating layer.^{24,25} This degradation needs to be addressed, as the use of TiO_2 in PSCs is ubiquitous in standard PSC architectures. The inverted NiO cell architecture has no TiO_2 and as such should be more resistant to UV-radiation. As the perovskite material itself is unstable under UV-illumination, the magnitude of the contribution of TiO_2 to degradation can thus be estimated.²⁶ While the absence of TiO_2 suggests inherent increased stability in inverted NiO cells, in **Chapter 3** pinholes were observed to form within the perovskite absorber film upon degradation. The detrimental effect of these pinholes is mitigated somewhat by the presence of the additional TiO_2 layer in conventional mesoporous device architectures, as the presence of this layer between charge-selective contacts can block recombination.¹⁰ However, with a purely planar device structure, a pinhole within the perovskite represents direct contact between electron and hole transport layers, leading to increased recombination.¹⁰ Here, both PSC architectures were fabricated in glovebox conditions using an ethyl acetate anti-solvent deposition to improve film quality.^{27,28} This anti-solvent treatment causes intermediate phase to form between the $\text{CH}_3\text{NH}_2\text{-PbI}_2$ perovskite precursors and the DMSO solvent. This intermediate slows the reaction between the MA and lead iodide, and leads to a high-quality perovskite film.²⁹

Fig. 4.4 shows a J - V curve and EQE spectrum for the champion devices of both cell types. The PCEs of the cells shown were 16.4% and 14.2% for the TiO_2 and NiO cells, respectively. Device efficiencies fluctuated between batches, although generally the mesoporous TiO_2 devices achieved higher efficiencies than the inverted NiO cells. This is likely to be due to a combination of pinhole caused recombination as outlined above and a non-optimised NiO layer thickness leading to transport losses in the HTL. Interestingly, the EQE spectrum of the TiO_2 based cells typically gave low EQE values across the visible range, not corresponding to the I_{SC} values actually observed by the cells during AM 1.5G testing. This can be seen in **Fig. 4.4b**, where the NiO cell with a lower efficiency shows a broader EQE response. Similar trends were observed for all TiO_2 cells with most of them showing a max EQE of approx. 70% in the blue-green region, followed by a sharp drop-off in the red region of the spectrum. Due to the absence of this loss in the NiO cells, it is likely to be due to the TiO_2 requiring a bias voltage to initiate the optimum cell operation.³⁰ While this could be applied by shining a light onto the PSCs while performing EQE measurements and using a chopper to isolate

the contribution of the monochromatic light source, the EQEs in this chapter will be used for characterisation before and after LDS application, as such the absolute values are not as important as the relative changes observed.

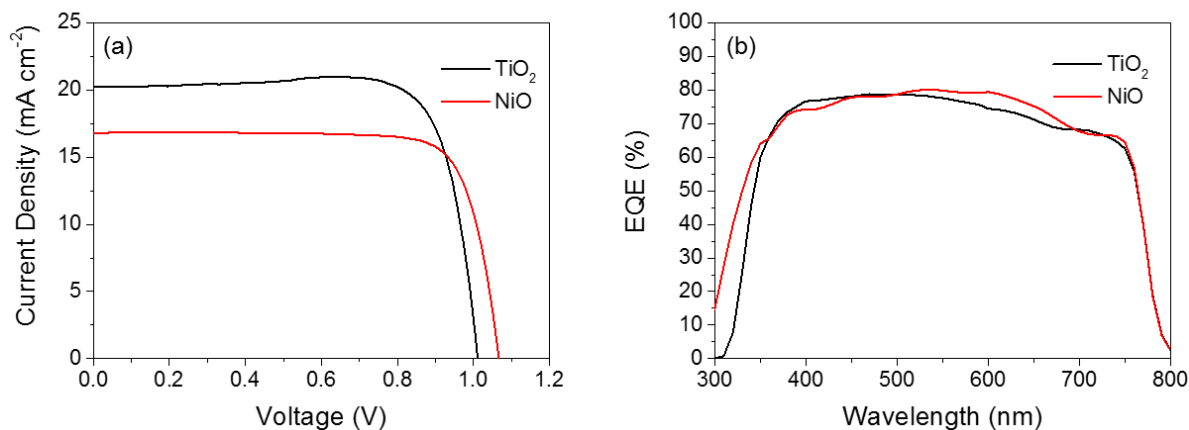


Figure 4.4. Photovoltaic characterisation of champion CH₃NH₃PbI₃ PSCs. (a) *J*-*V* curve of the champion mesoporous TiO₂ PSC (black line) and champion NiO PSC (red line). (b) EQE spectra of champion mesoporous TiO₂ PSC (black line) and NiO PSC (red line).

Fig. 4.5 shows the average performances of the cells for both architectures used for LDS studies before layer application or device encapsulation. This gives a representative of the performance of each of the architectures as a whole. As can be seen from **Fig. 4.5a**, the NiO cells typically achieved higher V_{OC} values than the mesoporous TiO₂ cells. The voltage in PSCs is influenced by a number of factors, however, typically both the surface coverage and thickness will impact the V_{OC} obtained.^{31,32} Since a higher J_{SC} is typically obtained for thicker perovskite films, it follows that better coverage (thus less defects) is the cause of the increased V_{OC} for the inverted cells.³³ The mesoporous TiO₂ cells performed better in all other categories, which indicates that for these inverted NiO devices a thicker perovskite layer may be beneficial. In general, PCE values of between 9 and 13% were achieved for the NiO devices and efficiencies between 11 and 16% were achieved for those made using mesoporous TiO₂ (**Fig. 4.5d**).

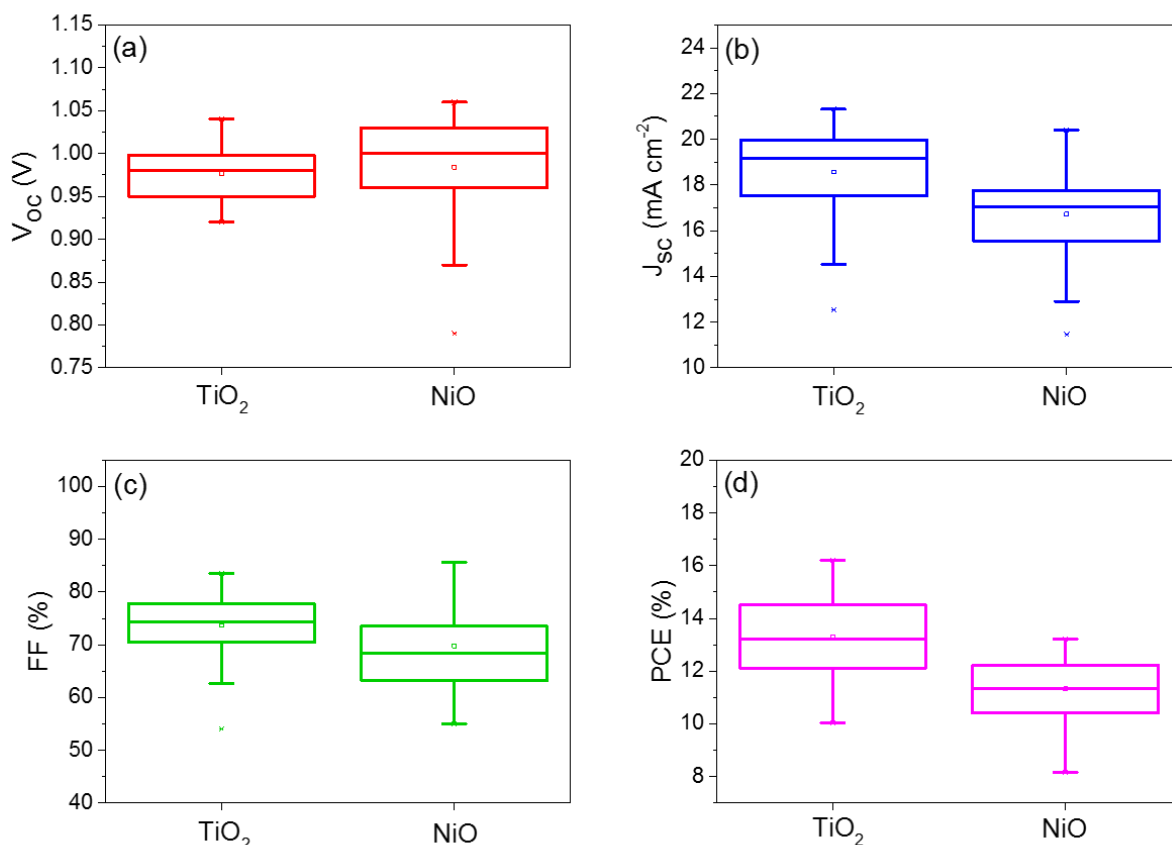


Figure 4.5. J - V characteristics of PSCs fabricated both using mesoporous TiO_2 and NiO prior to further treatment by LDS layer application or encapsulation. (a) V_{oc} , (b) J_{sc} , (c) FF and (d) PCE . Data calculated from 48 devices per architecture.

4.3.3 Deposition of LDS Layers

To demonstrate the effect of film thickness on the performance of LDS layers for PSCs, film depositions were performed at three spin rates (500, 2000 and 8000 rpm) with a fixed luminophore doping concentration (C). However, in order to screen the effect of layer thickness the concentration of luminophore in the LDS layers needs to be constant. This was achieved by both doping the 500 rpm layers ($3.5 \mu\text{m}$) with half the standard concentration and doping the 8000 rpm ($0.8 \mu\text{m}$) with twice the standard luminophore concentration. Thus, the amount of luminophore in the 500 rpm ($0.5 C$), 2000 rpm (C) and 8000 rpm ($2 C$) are comparable and the effect of layer thickness on the LDS performance can be determined. **Table 4.2** summarises the LDS coatings investigated for the TiO_2 and NiO PSC architectures, respectively.

Table 4.2. List of the compositions and thicknesses of luminophore-doped PMMA LDS layers applied to PSCs.

Architecture	Luminophore	Concentration (wt%)	Spin Rate (rpm)	Thickness ^a (μm)
TiO ₂	LV570	0.25 ^b	500	3.5
		0.25 ^b	2000	1.7
		0.25 ^b	8000	0.8
		0.125	500	3.5
		0.5	8000	0.8
	PFO	0.1 ^b	500	3.5
		0.1 ^b	2000	1.7
		0.1 ^b	8000	0.8
		0.05	500	3.5
		0.2	8000	0.8
	HPQ	0.15 ^b	500	3.5
		0.15 ^b	2000	1.7
		0.15 ^b	8000	0.8
		0.075	500	3.5
		0.3	8000	0.8
	C153	1.0 ^b	500	3.5
		1.0 ^b	2000	1.7
		1.0 ^b	8000	0.8
		0.5	500	3.5
		2	8000	0.8
	LR305	0.25 ^b	500	3.5
		0.25 ^b	2000	1.7
		0.25 ^b	8000	0.8
		0.125	500	3.5
		0.5	8000	0.8
NiO	LV570	0.25 ^b	500	3.5
		0.25 ^b	2000	1.7
		0.25 ^b	8000	0.8
		0.125	500	3.5
		0.5	8000	0.8
	PFO	0.1 ^b	500	3.5
		0.1 ^b	2000	1.7
		0.1 ^b	8000	0.8
		0.05	500	3.5
		0.2	8000	0.8
	HPQ	0.15 ^b	500	3.5
		0.15 ^b	2000	1.7
		0.15 ^b	8000	0.8
		0.075	500	3.5
		0.3	8000	0.8

^a Thickness values are approximations based on the average thickness obtained for undoped PMMA layers.^b Denotes the standard concentration for that luminophore.

4.3.4 Effect of LDS Layers on PSC Efficiencies

4.3.4.1 Mesoporous TiO_2 Devices

Mesoporous TiO_2 PSCs were selected as the primary architecture for this LDS study due to the higher PCE values obtained and the inherent instability issues due to the mesoporous layer. The PSCs were fabricated by the method outlined above and characterised by J - V and EQE measurements before and after application of the LDS coatings. Initially thick LDS films ($3.5\ \mu\text{m}$) of each luminophore, at their standard concentration, were applied to the PSCs. It was observed that upon spin-coating of the LDS layers onto the PSCs, with the exception of the PFO layer, the PCEs obtained indicated decreased performance upon application of the LDS layer. The PFO-coated cell exhibited a moderate increase in PCE from 15.5 to 15.7 % (**Appendix, Fig. A4.3**), but overall these thick LDS layers performed poorly compared to the uncoated samples.

Upon increasing the spin rate to 2000 rpm, corresponding to a film thickness of $1.7\ \mu\text{m}$, better results were obtained. Cells coated with LDS layers doped with LV570, PFO, HPQ and C153 displayed increased PCE, the J - V plots of which are shown in **Fig. 4.6**. No increase in device PCE was observed upon application of LR305-doped LDS layers. Upon closer investigation it is noteworthy that the increased PCE observed in these devices is primarily due to an increase in V_{OC} and not J_{SC} as would be expected for an LDS layer. This means that the observed increases are likely to be due to light-soaking effects from repeated characterisation.³⁴ Migration of ions and vacancies under photovoltage conditions results in localised charge redistribution manifested as positive charge accumulation at the TiO_2 , which affects the rate of charge recombination at the ETL, significantly increasing the observed V_{OC} .^{35,34} Upon increasing the spin-rate to 8000 rpm, the HPQ and LV570-doped LDS layers showed a champion PCE increase from 11.9 to 13.1 % and from 10.4 to 11.9%, respectively (**Fig. 4.6e, f**). This efficiency enhancement was due to an improved J_{SC} value, as well as an increased V_{OC} . The other luminophores showed no increased efficiency at these spin rates. While the overall performance of the LDS layers is quite low it is worth noting that the spin-coating of these layers onto the top of the glass, as shown in **Fig. 4.1a**, for finished perovskite cells means that the active layer itself is placed face down on the spin coater and thus, was prone to damage.

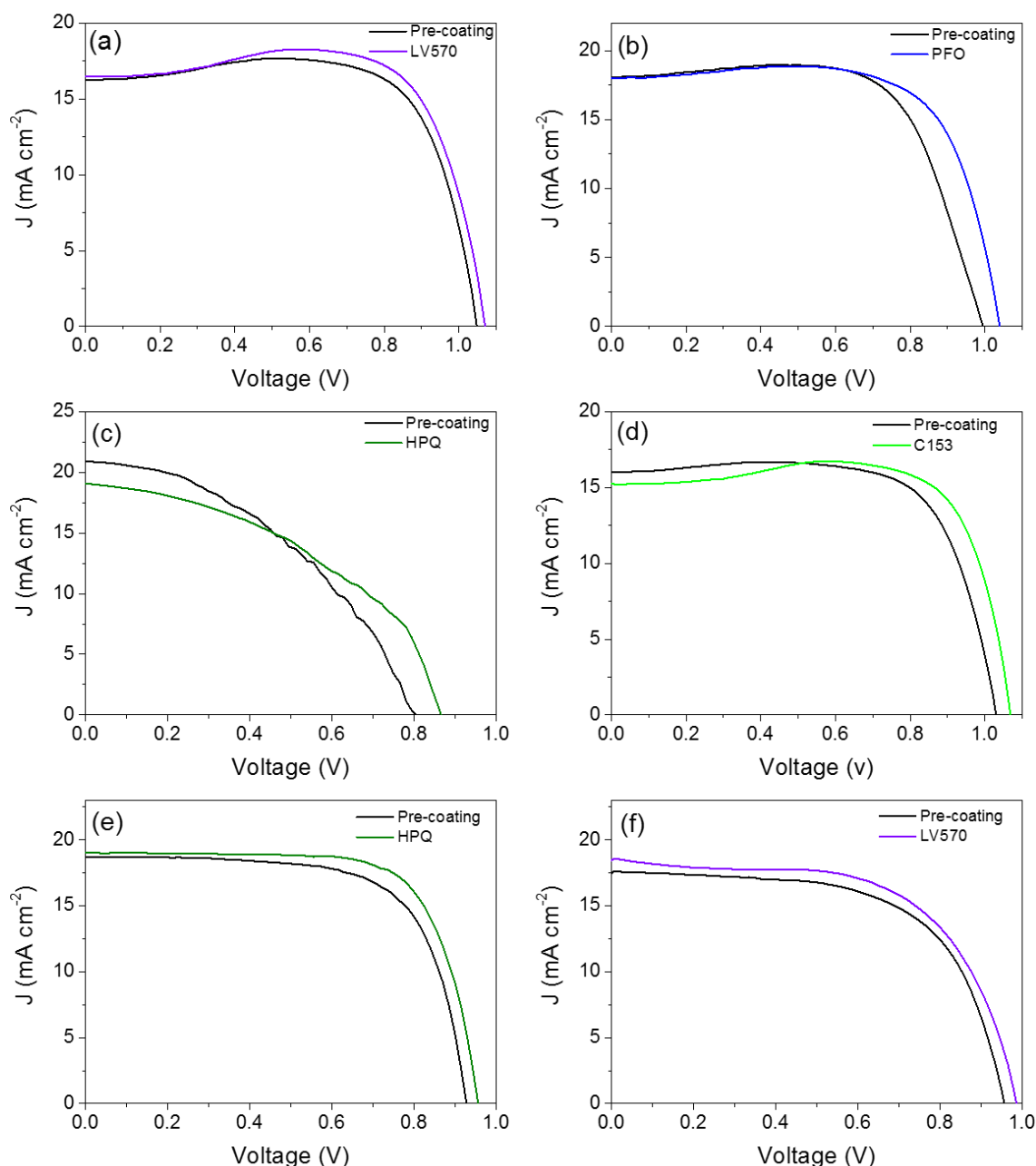


Figure 4.6. *J-V* sweeps of mesoporous TiO_2 $\text{CH}_3\text{NH}_3\text{PbI}_3$ PSCs before and after the application of LDS layers under AM 1.5G illumination: (a) LV570 (0.25 wt%, 2000 rpm); (b) PFO (0.1 wt%, 2000 rpm); (c) HPQ (0.15 wt%, 2000 rpm); (d) C153 (1.0 wt%, 2000 rpm); (e) HPQ (0.15 wt%, 8000 rpm); (f) LV570 (0.25 wt%, 8000 rpm). Three devices tested per coating, results present champion values.

Despite some minor increased efficiencies observed through the *J-V* sweeps, upon investigation of these films using EQE measurements, the spectra obtained showed a decrease across the visible range for all the samples and typically showed no increase in I_{SC} , despite the *J-V* curves indicating an increase. **Fig. 4.7** shows representative EQE spectra for the samples deposited at 2000 rpm. As can be seen in all the spectra presented, there is a steady drop in EQE observed across the

visible range. This drop is inconsistent with literature reports¹⁰ and the magnitude varies between PSCs. As mentioned above, this feature is only observed in the TiO_2 based cells. The decrease at longer wavelengths corresponds to the area of the spectrum where TiO_2 absorbs less,^{36–38} and is thus likely caused by a lack of the migration of ions and vacancies observed under light soaking conditions. In the regions of low TiO_2 absorption, there is less defect passivation and a lower EQE is observed. This could be mitigated by measuring the EQE spectrum under a bias voltage illumination however, that was not possible using the experimental setup used here. In general, however, the absorption of the luminophores overlaps considerably with the EQE spectrum of the PSCs. This is not ideal as it means a loss of efficiency in the regions where the luminophore absorbs, which is particularly evident for the high doping concentration of C153 (**Fig. 4.7d**). These effects can be mitigated by varying the perovskite composition to red-shift alter the onset of EQE spectrum. However, despite no enhancement of device performance these LDS layers may still improve device stability by acting as light filters.

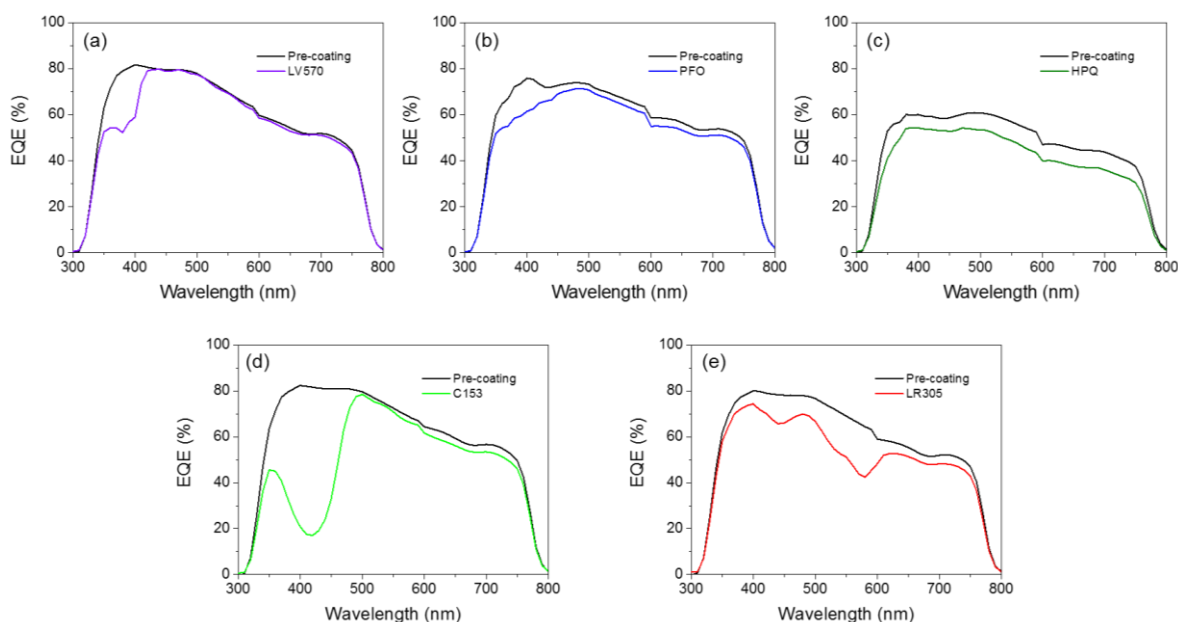


Figure 4.7. EQE spectra of mesoporous TiO_2 $\text{CH}_3\text{NH}_3\text{PbI}_3$ PSCs before and application of LDS layers by spin-coating at 2000 rpm: (a) LV570 (0.25 wt%); (b) PFO (0.1 wt%); (c) HPQ (0.15 wt%); (d) C153 (1.0 wt%) and (e) LR305 (0.25 wt%).

Upon investigation of different concentrations of luminophore in the LDS films, the results were similar to those observed above. Upon doubling the luminophore concentration and halving the thickness, only the PFO films showed any increased PCE, due to a slight increase in the measured

J_{SC} . Upon decreasing the dopant concentration in the thick films (3.5 μm), the PFO, LV570 and HPQ LDS layers all showed some PCE increase. However, the values fluctuated significantly between cells making any predictions on the effect of concentration and thickness on the LDS properties purely speculative. To solve these inconsistencies a move away from the mesoporous TiO_2 architecture was required.

4.3.4.2 Inverted NiO Devices

A number of issues affected the results obtained using the mesoporous TiO_2 architecture PSCs, including, not-representative EQE spectra, potential cell damage during spin-coating, damage to contacts through repeated characterisation. To minimise these sources of error, which can impact the characterisation of the LDS layers, a number of steps were taken including: use of TiO_2 free NiO inverted devices and the encapsulation of the devices prior to LDS layer application. By encapsulating the PSCs using a glass coverslip and a photocurable epoxy, the cells can be spin-coated without potential damage to the active surface. The ability to repeatedly spin-coat cells without damage allows for more consistency in characterising the LDS layers. When characterising the performance of an LDS layer on the encapsulated NiO PSCs, the same devices were used for each coating to ensure consistency. After characterisation the LDS layer was removed using a razor blade and the glass surface was carefully cleaned before the next coating was applied. Because of the overall poor performance of the LDS layers doped with LR305 and C153, these were not applied to the NiO PSCs to improve the efficiencies.

The encapsulated NiO-based devices showed more consistent LDS results than the mesoporous TiO_2 cells. Interestingly, the performance of the LDS layers displayed different trends in the PCE improvement, depending on the film thickness and the luminophore used. PFO showed the best performance of the three luminophores investigated, with increases in PCE and J_{SC} obtained for films spun at 2000 (1.7 μm) and 8000 rpm (0.8 μm). The 1.7 μm PFO doped films with 0.1 wt% luminophore performed the best, with an average PCE increase of 1.6 % upon application of the LDS layer. By comparing to the 0.8 μm thick film with a 0.2 wt% doping, which showed a PCE increase of 0.8%, we can see that a thicker film with a lower luminophore concentration performs better. The poor performance of both thick (3.5 μm) films doped with PFO, suggests that the high

luminophore concentration and thickness in these layers results in re-absorption losses. **Fig. 4.8** shows the J - V and EQE characterisation of the champion performing LDS layers for each luminophore.

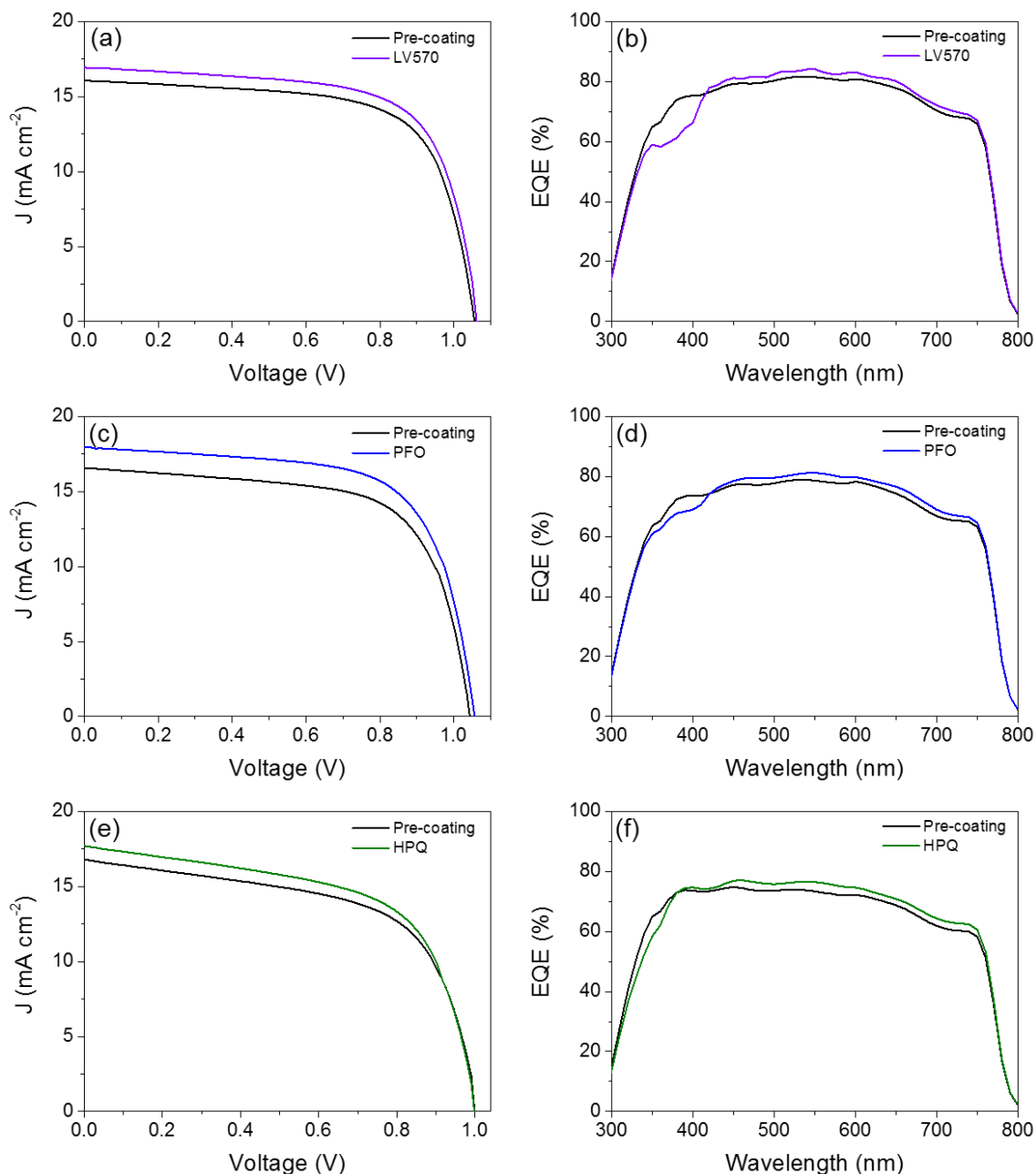


Figure 4.8. Photovoltaic characterisation of champion LDS coatings for NiO inverted $\text{CH}_3\text{NH}_3\text{PbI}_3$ PSCs. J - V curve under AM 1.5G illumination and EQE spectrum for (a, b) LV570-PMMA LDS layer (0.125 wt%, 500 rpm), (c, d) PFO-PMMA LDS layer (0.1 wt%, 8000 rpm) and (e, f) HPQ-PMMA LDS layer (0.3 wt%, 8000 rpm).

LV570 showed the opposite trend to the PFO-PMMA layers, with the best performance obtained for the films deposited at 500 rpm ($3.5 \mu\text{m}$). For a direct comparison, the films with standard

dopant concentration (0.25 wt%) deposited at 2000 rpm (1.7 μm) showed an average ΔJ_{SC} of -0.04 mA cm^{-2} , whereas the films with thickness 3.5 μm with a concentration of 0.125 wt% achieved a ΔJ_{SC} of 0.93 mA cm^{-2} . The 3.5 μm LDS layer with 0.25 wt% did not perform as well, indicating that in the case of LV570, as with PFO, a low dopant concentration in a thick film provides the best enhancement of the device photocurrent. HPQ-LDS layers did not exhibit the same trends as the aforementioned luminophores, with the high concentration thin film showing the only noteworthy average increase in J_{SC} of 0.82 mA cm^{-2} . This can be ascribed to the AIE properties of HPQ.¹⁹ It follows that a higher luminophore concentration in a thinner film would mean more aggregation of the luminophore molecules, thus enhancing the photoluminescence intensity.

The EQE spectra shown in **Fig. 4.8** do not exhibit the decrease across the visible range shown in the TiO_2 samples, instead, these samples are flat until *ca.* 650 nm where they start to decrease. For the samples investigated, the increased J_{SC} observed in the J - V curves appeared as a general increase in EQE across the visible range. The areas which showed decreased EQE correspond to the absorption wavelengths of the luminophores (**Fig. 4.3**). For the champion devices shown, the ΔJ_{SC} values obtained using the EQE were positive but showed a lower magnitude, for example the LV570 sample which showed a ΔJ_{SC} of 0.93 mA cm^{-2} from the J - V curve, had a ΔJ_{SC} of 0.24 mA cm^{-2} for the EQE. This is likely to be due to differences in the measurement techniques, which can occur from non-uniform illumination by the solar simulator etc. The ΔJ_{SC} values determined using the EQE are thus more accurate. The results of this study of LDS coatings on NiO cells are summarised in **Table 4.3**.

For all three investigated luminophores for NiO-PSCs, increased PCE and J_{SC} values were obtained and verified by EQE. These results have thus demonstrated that for non-AIEgen luminophores thicker LDS layers with lower concentration of luminophores perform better as LDS layers for PSCs. The minimisation of reabsorption losses by having the luminophores separated is the cause for this, as evidenced by the reverse effect observed for the AIE luminophore, in which a high concentration thin film provided the best results. As thickness is increased however edge emission becomes a more prominent loss mechanism. Hence, care has to be taken to ensure the

correct balance of luminophore concentration and film thickness to maximise LDS layer performance.

Table 4.3. Summary of photovoltaic characterisation LDS coated NiO CH₃NH₃PbI₃ PSCs. Δ PCE represents the average difference in PCE upon coating with the LDS layer. ΔJ_{SC} represents the average difference in J_{SC} upon coating with the LDS layer.

Luminophore	Concentration (wt%)	Thickness (μ m)	Δ PCE (%)	ΔJ_{SC} (mA cm ⁻²)
LV570	0.25	3.5	0.53 ± 0.06	0.40 ± 0.06
	0.25	1.7	0.04 ± 0.003	-0.05 ± 0.06
	0.25	0.8	0.07 ± 0.015	-0.04 ± 0.02
	0.125	3.5	$0.58^a \pm 0.12$	$0.93^b \pm 0.06$
	0.5	0.8	-0.10 ± 0.12	-0.43 ± 0.18
PFO	0.1	3.5	-1.29 ± 0.06	-1.79 ± 0.14
	0.1	1.7	$1.67^a \pm 0.02$	$1.76^b \pm 0.2$
	0.1	0.8	0.86 ± 0.36	0.93 ± 0.4
	0.05	3.5	-1.09 ± 0.007	-1.82 ± 0.11
	0.2	0.8	0.79 ± 0.12	0.80 ± 0.12
HPQ	0.15	3.5	-0.26 ± 0.17	-0.67 ± 0.09
	0.15	1.7	-0.06 ± 0.05	-0.40 ± 0.2
	0.15	0.8	0.10 ± 0.09	-0.01 ± 0.005
	0.075	3.5	0.24 ± 0.04	0.01 ± 0.08
	0.3	0.8	$0.61^a \pm 0.09$	$0.82^b \pm 0.08$

^{a, b} Denote the max PCE and J_{SC} increase for each luminophore, respectively.

4.3.5 Effect of LDS on PSC stability

To test the effectiveness of the LDS coatings to improve the photostability of PSCs, they need to be tested under operating conditions. Cells were subjected to extended periods of illumination in a large-area light soaker (class ABB solar simulator) to approximate outdoor illumination. After coating with the LDS layer, the PSCs were placed into the light-soaker which was programmed to test the cells automatically at 30-minute intervals. By monitoring the decrease in the PCE with time, the effectiveness of the LDS layer to improve photostability can be quantified.

The non-encapsulated TiO₂ devices were tested using all five luminophores with each of the film thicknesses and concentrations described in **Table 4.2**. These PSCs typically showed complete

loss of PCE in less than 12 hours illumination. This degradation however in several cases occurred in timescales of <1 h illumination, and as such there was little consistency between measurements. The addition of LDS layers had no obvious impact upon the rate of degradation as the uncoated reference samples similarly showed no consistent rate of degradation. **Fig. 4.9** shows the normalised PCE degradation curves of a LV570-PMMA LDS coated TiO_2 cells and uncoated TiO_2 cells. Similar decay rates were observed for all luminophores under the stability testing conditions investigated (**Appendix, Fig. A4.4**). The PCE decay was observed as a decrease in V_{OC} , J_{SC} and FF thus making it difficult to identify the direct cause of the degradation.

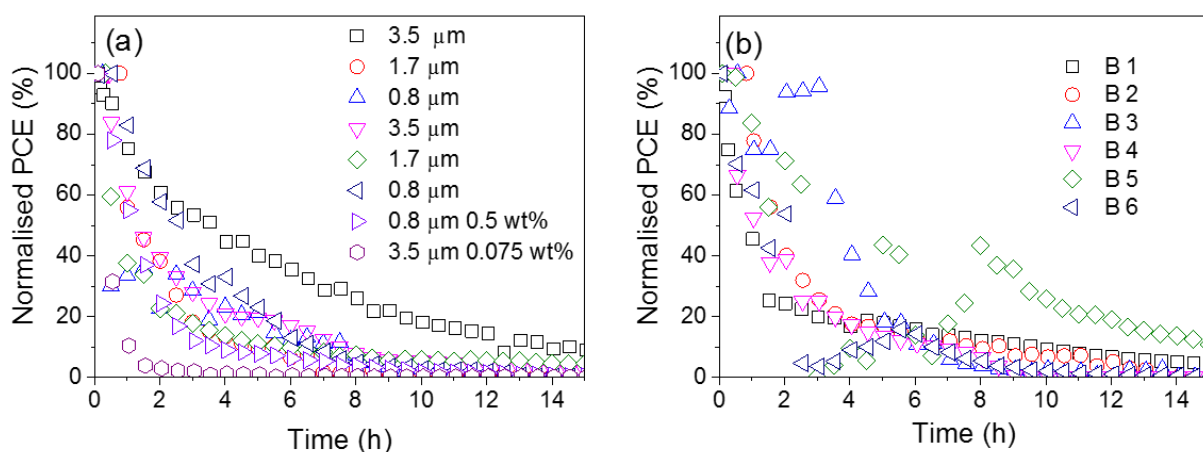


Figure 4.9. PCE degradation plots for mesoporous TiO_2 $\text{CH}_3\text{NH}_3\text{PbI}_3$ PSCs under illumination by simulated AM 1.5G light. (a) LV570-PMMA (0.25 wt% unless otherwise stated) LDS layers of varying thickness. (b) Uncoated blank cells (B1-B6).

To investigate if the rapid device degradation was due to decomposition of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ to PbI_2 and to attempt to characterise the performance of the LDS layers as photostability enhancers, bare $\text{CH}_3\text{NH}_3\text{PbI}_3$ films, deposited on FTO without charge transport layers, were coated with LDS layers of each luminophore and placed in the light-soaker. The time-dependent degradation of the perovskite films was characterised by grazing-incidence XRD (**Fig. 4.10**) and UV/Vis absorption spectroscopy (**Fig. 4.11**). **Fig. 4.10** shows the region of the XRD pattern where the characteristic PbI_2 (ca. 12.5°) and $\text{CH}_3\text{NH}_3\text{PbI}_3$ (110, ca. 14°) peaks appear. In the diffraction patterns shown, there is a decrease in the intensity of the (110) perovskite peak with time, however, PbI_2 peaks only appear after $t = > 6$ h illumination for all the samples (with the exception of the C153-PMMA LDS layer); thus, we can assume that there has been no significant $\text{CH}_3\text{NH}_3\text{PbI}_3$ degradation in this time period.

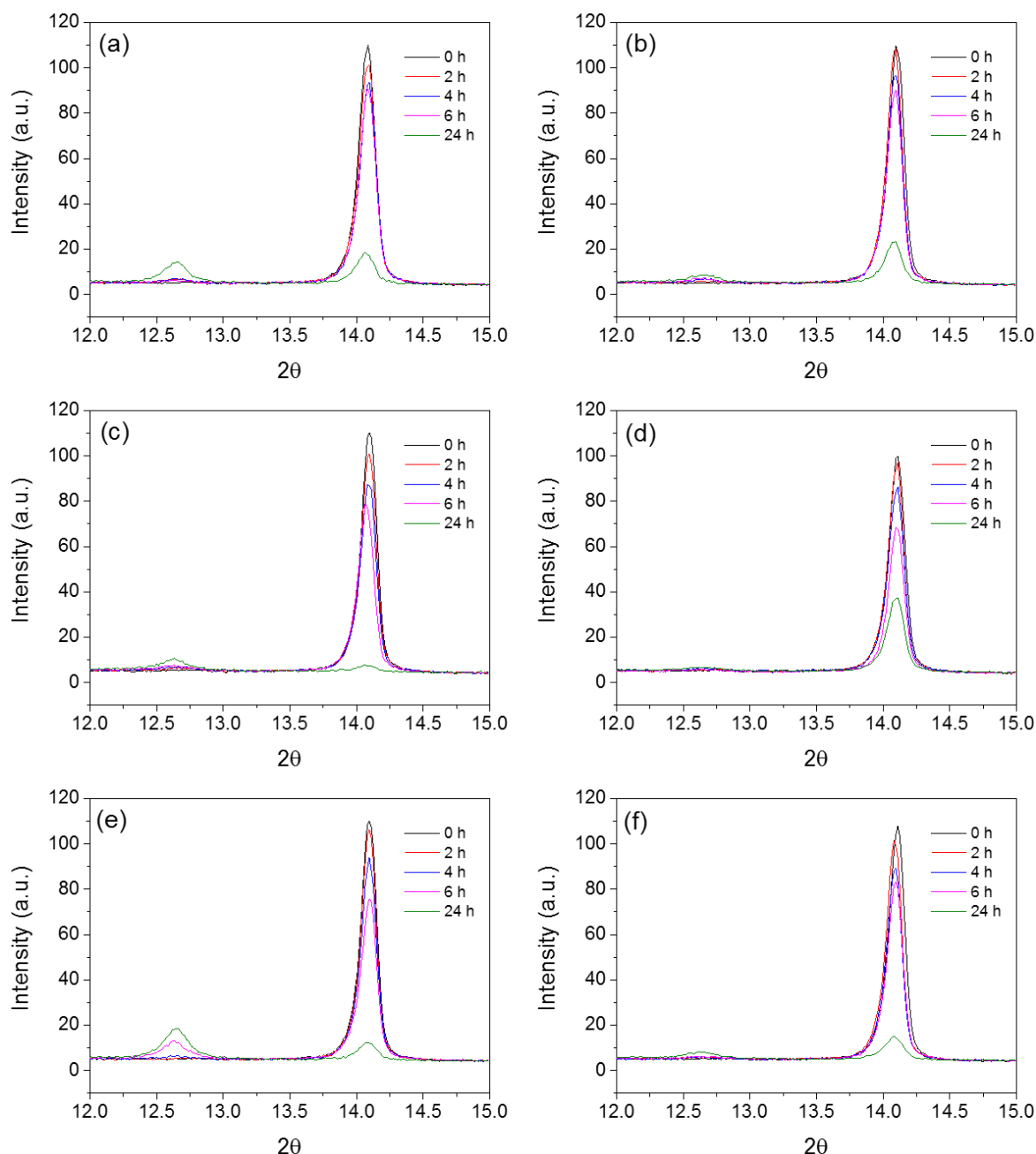


Figure 4.10. Grazing-incidence XRD patterns for blank and LDS coated $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin films exposed to simulated AM 1.5G radiation and removed for characterisation at timed intervals. (a) Blank $\text{CH}_3\text{NH}_3\text{PbI}_3$ film, (b) LV570 -PMMA film (3.5 μm , 0.25 wt%), (c) PFO-PMMA film (3.5 μm , 0.1 wt%), (d) HPQ-PMMA film (3.5 μm , 0.3 wt%), (e) C153-PMMA film (3.5 μm , 1.0 wt%) and LR305-PMMA film (1.7 μm , 0.25 wt%).

The UV/Vis absorption spectra in **Fig. 4.11** show there is no loss of the band edge feature for cells illuminated for 2–6 hours, but by 24 h the perovskite layers are completely degraded. However, **Fig. 4.9** shows near complete PCE loss in timescales less than 2 h for certain devices. By examining the XRD and UV/Vis absorption data, we can conclude that the experimental conditions under which the PSCs were characterised (AM 1.5G illumination) did not cause degradation of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer over the timescales at which loss of the PCE was observed. The absence of

significant degradation to PbI_2 implies that the deterioration in the device performance is due to degradation of the charge transport layers.

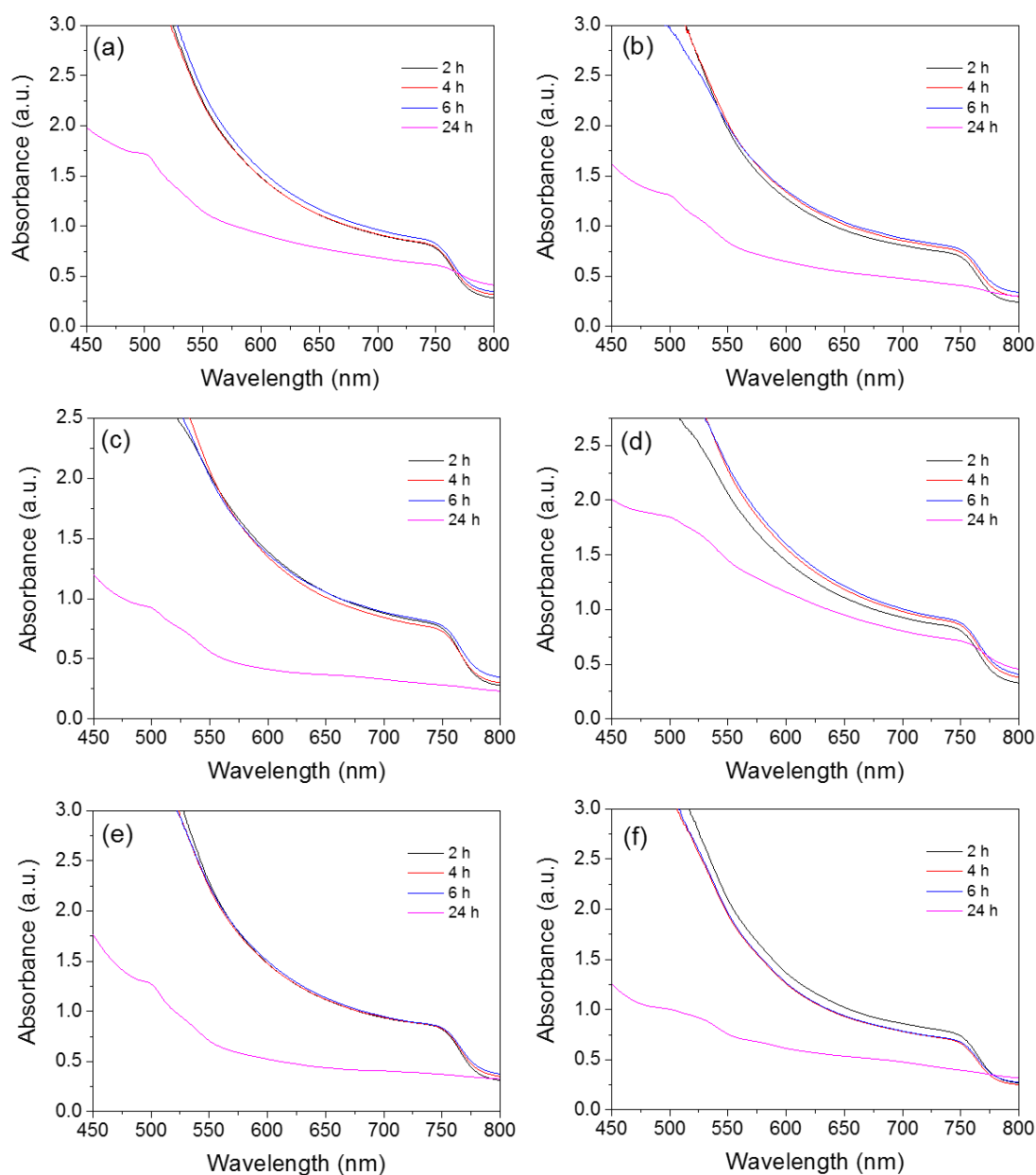


Figure 4.11. UV/Vis absorption spectra of blank and LDS-coated $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin films exposed to simulated AM 1.5G radiation and removed for characterisation at timed intervals. (a) Blank $\text{CH}_3\text{NH}_3\text{PbI}_3$ film, (b) LV570 PMMA layer (3.5 μm , 0.25 wt%), (c) PFO-PMMA layer (3.5 μm , 0.1 wt%), (d) HPQ-PMMA layer (3.5 μm , 0.3 wt%), (e) C153-PMMA layer (3.5 μm , 1.0 wt%) and LR305-PMMA layer (1.7 μm , 0.25 wt%).

Stability issues with spiro-OMeTAD as a HTL are well documented, with degradation of the HTM due to evaporation of the Li-TFSI and tBP dopants occurring at temperatures *ca.* 90 °C.³⁹ Very recently, however, Jena *et al.* examined the role of spiro-OMeTAD in the performance deterioration of PSCs at temperatures as low as 60 °C.⁴⁰ This work found that even at these lower

temperatures, where the perovskite layer itself was undegraded, deformation of the HTL occurred, which caused an increase in recombination losses due to poor active layer/HTL interface. The temperature of the stage in the Solaronix light soaker used for these stability tests has an in-built thermocouple which typically gave values *ca.* 25 °C. However, upon placing an independent thermometer on the stage during stability tests temperatures of *ca.* 55 °C were measured. If we couple this with the black tape used to mask the PSC active area it is likely the cells themselves were at higher temperatures during testing. Encapsulated NiO PSCs were thus used to test the LDS layers to remove the potential instability of the spiro-OMeTAD layer.

Encapsulated NiO PSCs performed better than their TiO₂ counterparts, however, they still exhibited poor stability and performances, which varied significantly between tests even for blank cells in identical testing conditions. These encapsulated cells typically exhibited <50 % of their original PCE within 20 hours testing. **Fig. 4.12** shows the PCE decay curves of the blank encapsulated NiO cells and coated with LDS layers doped with LV570, PFO and HPQ. These cells show no trends based on which LDS coating was applied and the stability seems to vary from cell to cell. That these encapsulated spiro-OMeTAD free cells exhibited poor stability upon repeated testing suggests that there may be inherent instabilities in the PSCs which occurs upon repeated testing in operating conditions. It was observed for some of the devices (**Fig. 4.12a, 4.12b**) that the PCE would immediately drop to zero before recovering in a later measurement. The devices were not moved or removed during the testing period so these drops in PCE have to be due to temporary loss of charge transport in the devices. Charge trapping under light illumination has been described recently for PCEs under operating conditions.^{41,42} Ahn *et al.* demonstrated for PSCs fabricated using TiO₂ or PCBM ETLs that under illumination, accumulation of charge occurs, and that these trapped charges contribute to the moisture-induced degradation of the PSCs.⁴² These trapped electrons have been stated as one of the primary causes for the hysteresis observed in PSCs,⁴³ which was observed to increase upon encapsulation of the NiO devices (**Appendix, Fig. A4.5**), thus, it is likely the encapsulation process impacts the performance of the PCBM ETL in these inverted architectures causing a trapped-charge induced degradation.

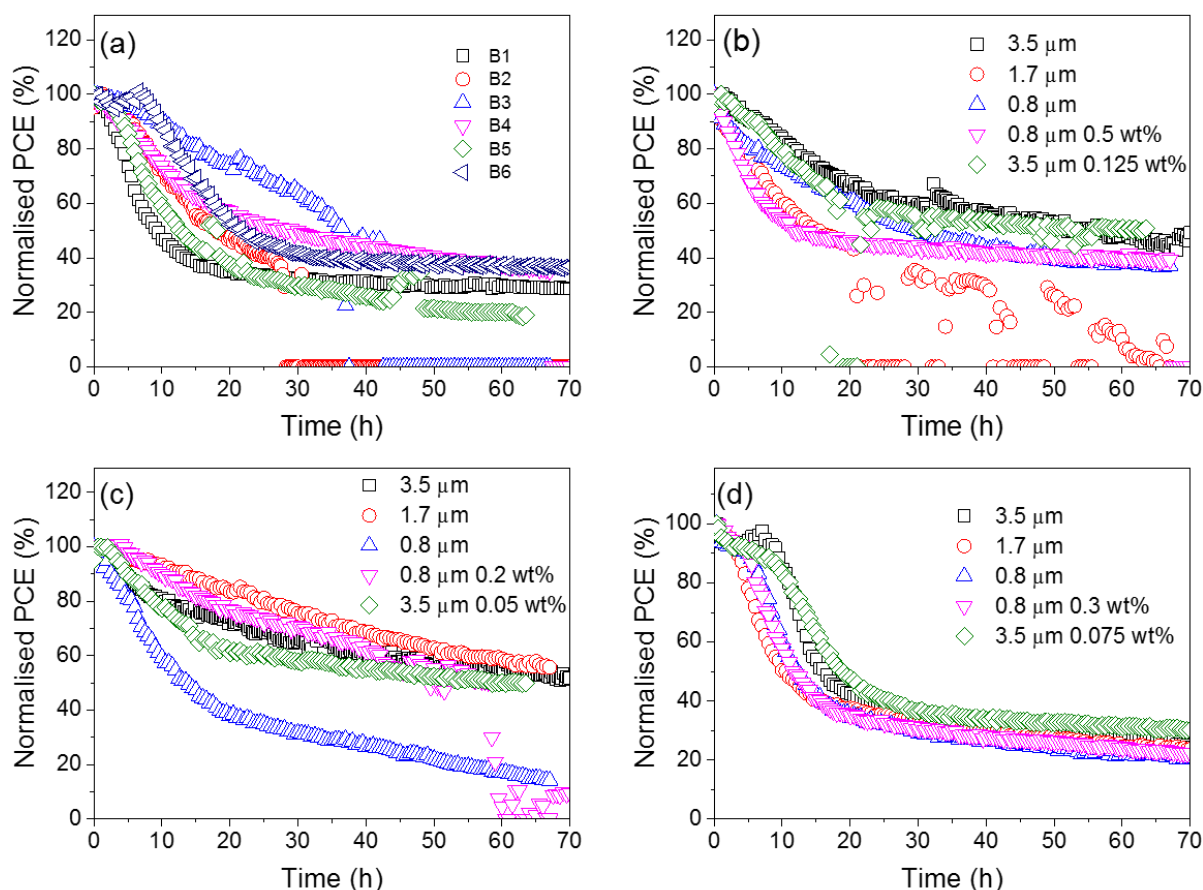


Figure 4.12. PCE degradation plots for both blank and LDS layers of varying thickness coated, encapsulated, NiO $\text{CH}_3\text{NH}_3\text{PbI}_3$ PSCs under illumination by simulated AM 1.5G light. (a) Uncoated blank cells (B1-B6). (b) LV570-PMMA layers (0.25 wt% unless otherwise stated) (b) PFO-PMMA layers (0.1 wt% unless otherwise stated). (c) HPQ-PMMA layers (0.15 wt% unless otherwise stated).

Nie *et al.* demonstrated that light-induced trap states can be prevented by alternating AM 1.5G exposure and dark storage.⁴¹ To attempt to gain some insight into the relative performance of the LDS layers as long term stabilisers for PSCs, a stability test was performed using non-encapsulated NiO cells using PFO-PMMA as the LDS layer and characterising the degradation of the cells by placing them in the light-soaker, but removing them to perform *J-V* sweeps (**Fig. 4.13**). These results showed again very little consistency in the performance of the LDS layers compared to the blank. This indicates that the loss of PCE for these cells is not due to photodegradation in the timescales investigated. The stability of these non-encapsulated devices can also be limited by degradation induced by reaction with the silver electrode.⁴⁴

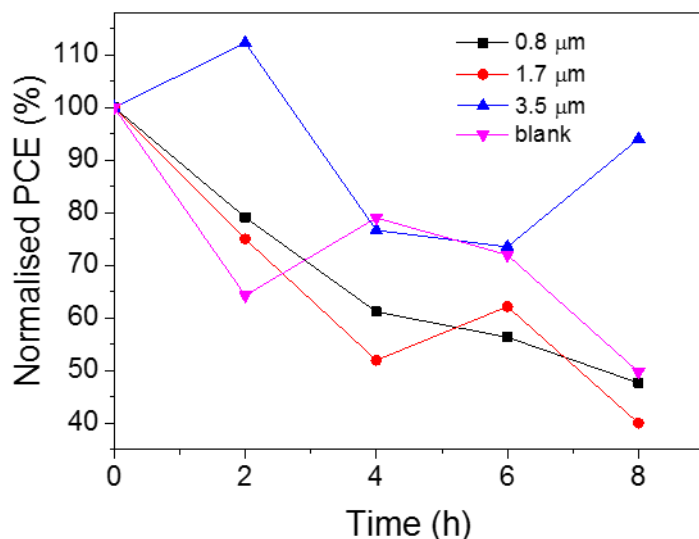


Figure 4.13. PCE degradation plots for non-encapsulated NiO PSCs, with and without LDS coating of PFO-PMMA. LDS layer thicknesses indicated on plot. The solid lines serve only to guide the eye.

The lack of discernible trends in degradation between the characterised devices, with and without LDS coatings, highlights that while stability is one of the continuing issues with PSCs, under AM 1.5G illumination at elevated temperatures, the photostability occurs on longer timescales than other degradation methods for $\text{CH}_3\text{NH}_3\text{PbI}_3$ PSCs. To minimise these degradation processes careful tuning of the perovskite material itself is necessary. It has been demonstrated that $\text{Cs}_{0.17}(\text{FA}_{0.83})\text{Pb}(\text{I}_{0.8}\text{Br}_{0.2})_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ are more resistant to the light-induced trap generation under AM 1.5G operating conditions due to the removal of the volatile MA cation and improved film morphology respectively.⁴⁵ While this work has not presented the effectiveness of the LDS coatings to enhance the long term operational stability of PSCs, it has highlighted that $\text{CH}_3\text{NH}_3\text{PbI}_3$ as an absorber layer is not suitable for long term AM 1.5G stability tests for LDS layers. In order to accurately compare these layers as stability enhancers, either a different perovskite material should be used or the testing conditions should be modified, for example by only using UV-light to induce photodegradation.

4.4 Conclusions

To examine the effect of concentration and LDS layer thickness on the efficiency and photostability of PSCs, two architectures of $\text{CH}_3\text{NH}_3\text{PbI}_3$ cells were fabricated based on mesoporous

TiO₂ and NiO, respectively. To these devices LDS layers of five different luminophores were applied with varying dopant concentrations and layer thicknesses to both examine the efficiency of different luminophores and to examine if any trends in behaviour could be elucidated. By characterising the perovskite cells before and after LDS layer application by both *J-V* sweeps and EQE measurements, the effect of the LDS layers on the device properties could be established. It was observed that for the mesoporous TiO₂ based cells the ETL itself can affect the characterisation of the PSCs through EQE measurements. By using NiO cells consistent improvements in both device PCE and *J*_{SC} were obtained for devices coated with LV570, PFO and HPQ doped films. Through varying the thicknesses and concentrations of these films it can be concluded that for conventional luminophores, lower doping concentrations and thicker films were advantageous to minimise reabsorption losses, whereas for AIEgens, high concentration thin films displayed better performance due to the increased interactions between the luminophores.

It was observed that upon testing of LDS layers as photostability enhancers under operating conditions, the device stability is rapidly compromised. This degradation can be attributed to charge trapping, which occurs for CH₃NH₃PbI₃ PSCs of both architectures. However, there are other contributions to the degradation rate which are unique to their respective architectures. In TiO₂-based cells, the instability of the spiro-OMeTAD HTL to high temperatures causes irreversible degradation,⁴⁰ while for NiO cells the degradation can be attributed to a combination of parasitic leeching of silver from the electrode,⁴⁴ and encapsulation interfering with the PCBM ETL. These stability tests have demonstrated the unsuitability of CH₃NH₃PbI₃ for long term applications in perovskite devices, and that irrespective of device architecture or encapsulation/LDS coating, the intrinsic degradation mechanisms are pervasive.

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Chapter Five

Exploring the Colour Tunability and Stability of Organolead Halide Perovskite Nanocrystals

5.1 Introduction

As it has been demonstrated in **Chapter 3** and **Chapter 4**, perovskite-based absorbers are becoming increasingly viable for device applications, particularly in the fields of photovoltaic and light-emitting devices due to their favourable optoelectronic properties. While many of the initial applications have focussed on thin film perovskites,^{1–3} recent developments of PNCs which show high Φ_{PL} ^{4–6} and tunable emission have led to a shift towards PNC-based devices,⁷ for example as LEDs^{8–13} and lasing materials.^{14–16} PNCs are typically either organic-inorganic hybrids of the formula $\text{CH}_3\text{NH}_3\text{PbX}_3$,¹³ or all-inorganic CsPbX_3 ,¹⁷ where X = halide. PNCs based on $\text{CH}_3\text{NH}_3\text{PbX}_3$ or CsPbX_3 show analogous behaviour with similar morphologies and emission properties, which are predominantly dependent on the nanocrystal size and the halide anion.^{18,19} There have been considerable efforts in the literature to explore different methods to control the emission properties of PNCs. When considering bulk perovskite-based materials perhaps the most common method to alter the emission properties is to vary the type and stoichiometric ratio of the halide anion during the synthetic process.²⁰ Several groups have demonstrated that this approach is also applicable to PNCs, with pure Cl^- , Br^- and I^- analogues showing blue, green and red emission, respectively.^{12,13,21} For example, Zhang *et al.* achieved an impressive tunable emission maximum (λ_{em}) across the entire visible spectrum (407–734 nm) and Φ_{PL} up to 70% by using mixed-halides of varying ratios.¹³ Similar effects have also been demonstrated for mixed-halide CsPbX_3 PNCs¹⁷ and formamidinium $(\text{CH}(\text{NH}_2)_2\text{PbX}_3)$ PNCs.²²

Although halide composition has the largest impact on the emission properties of PNCs, smaller particles show increased quantum confinement and thus, exhibit a blue-shift in emission maximum compared to a bulk perovskite.^{23,24} The first synthesis of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ PNCs by Schmidt *et al.* was achieved by adding long chain octylammonium bromide or octadecylammonium bromide to replace some of the surface, shorter-chain methylammonium bromide and thus prevent aggregation through steric repulsion.²⁵ These particles, however, showed no evidence of quantum confinement as no blue-shift of the emission spectrum from that of the bulk $\text{CH}_3\text{NH}_3\text{PbBr}_3$ was observed. Nonetheless, long-chain capping ligands have been used to control the size of PNCs fabricated through the LARP process^{26–28} and concentration effects have been demonstrated to be

important.²³ For example, Urban *et al.* demonstrated that quantum confinement effects were induced in $\text{CH}_3\text{NH}_3\text{PbBr}_3$ PNCs upon increasing the capping ligand concentration. This led to a significant shift in the λ_{em} of nearly 90 nm from the green emission of the bulk material to the blue spectral region upon formation of small PNCs.²³ Notably, the capping ligand concentration had a significant effect on the morphology of the nanomaterials obtained. For example, large platelet-like structures with dimensions >100 nm were observed for low concentrations, which were postulated to be exfoliated to form increasingly thin, almost 2D-like platelets as the concentration of capping ligand was increased. Ma *et al.* reported similar quantum confinement-like behaviour for PNCs of the general formula $(\text{RNH}_3)_2(\text{CH}_3\text{NH}_3)_{n-1}\text{Pb}_n\text{Br}_{3n+1}$, as a function of chain length of the alkyl ammonium (RNH_3). The long chain ammonium cations were added during the synthesis procedure along with the standard methylammonium cations.²⁹

While varying the halide content can provide a high degree of control over the emission colour, it has been shown that the excited state lifetime and Φ_{PL} are both highly dependent on the morphology of the PNC.³⁰ For example, it has previously been demonstrated that ligand-assisted exfoliation of layered all-iodide $\text{CH}_3\text{NH}_3\text{PbI}_3$ PNCs resulted in a decrease in the excited state lifetime from ~ 25 ns to 5 ns upon shearing of the nanocrystal morphology from 3D to 2D, which was attributed to a combination of increased exciton binding energy (due to reduced screening) and an increase in trap-assisted recombination (due to increased surface area).³¹ In another report, Levchuk *et al.* showed that Φ_{PL} of up to 90% could be obtained by varying the capping ligand concentration for $\text{CH}_3\text{NH}_3\text{PbBr}_3$ PNCs.³² Tunable thickness and thus emission properties have also been achieved by tip sonication during the synthesis for all inorganic PNCs (CsPbX_3) with varying halide composition.³³ It was observed for tip sonication that the PNC thickness depended on both the precursor ratios and the reaction time.

Other methods investigated to control the morphology and emission properties include varying temperature,^{18,34} substituting Sn^{2+} in place of Pb^{2+} ,¹⁹ varying the antisolvent,³⁵ controlling lateral PNC growth³⁶ and more recently, dilution.^{37,38} Interestingly, the dilution of PNC dispersions has a somewhat unpredictable effect on both the size and emission properties. For example, dilution of stock solutions of both $\text{CH}_3\text{NH}_3\text{PbBr}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_3$ PNCs with the antisolvent used in the

LARP reaction resulted in *fragmentation* and *exfoliation* of the nanocrystals to give 2D nanoplatelets stabilised by excess capping ligand, whose emission maximum was blue-shifted and exhibited a decrease in the Φ_{PL} .³⁷ A recent study has investigated the effect of dilution by a polar solvent on the nucleation and growth of CsPbX₃ PNCs.³⁸ In this case it was found that PNC formation proceeded through a seed-mediated nucleation step, where Pb⁰ nanoparticles acted as seeds and the polarity of the environment determined the shape and size of the resultant PNCs. However, upon controlled addition of a polar species, *self-assembly* and *growth* of the nanoparticles was observed, which was attributed to the destabilisation and removal of surface ligands, which caused a transformation from a 2D to a 3D structure.

5.1.1 Aims

The opposing behaviour upon dilution in the above examples presents a somewhat significant issue for the use of these materials in larger scale applications. While dilution is an attractive method to control the properties of PNCs due to its simplicity, the precise regulation of the solution phase emission properties of these materials is key to their scalability for use in devices, and thus, needs to be studied to ensure any negative alteration of the optical properties does not occur. Herein, the effect of dilution on mixed halide PNC solutions is examined to both understand and control the solution phase properties. Mixed halide PNCs have been presented as one of the most attractive methods to tune the emission properties for large scale applications, and as of yet there has been no investigation on the effect of dilution on these systems. In this chapter a mechanism for the particle growth and shift in the spectral properties observed for mixed halide systems is presented, through judicious study of the PNCs under varying synthetic and post synthetic conditions in the solution phase. The effect of varying these conditions will be probed through a combination of spectroscopic and structural techniques. This study thus allows a better oversight on the behaviour of these PNCs in solution and how to best control the emission properties for scalable applications.

5.2 Experimental

5.2.1 Synthesis of $\text{CH}_3\text{NH}_3\text{X}$ (X= Br, I)

Methylamine (24 mL, 33 wt % in ethanol) was vigorously stirred, diluted with ethanol (50 mL) and then placed under nitrogen flow in an ice bath. HBr (9 mL, 76 mmol) or HI (10 mL, 76 mmol) was then slowly added. The solution was then stirred for 2 h until a precipitate formed. The precipitate was isolated by vacuum filtration, washed three times with diethyl ether (approx. 100 mL) and allowed to dry in an oven at 60 °C.

5.2.2 Synthesis and Dilution of Colloidal $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{I}_x$ NCs

PNCs were synthesised using the LARP method. In a representative synthesis, PbBr_2 (73.4 mg, 0.20 mmol) and methylammonium iodide (MAI) (25.4 mg, 0.16 mmol) were dissolved in anhydrous DMF (5 mL). Oleylamine (OY, 50 μL , 0.15 mmol) and oleic acid (OA, 500 μL , 1.6 mmol) were added to the mixture under ultrasonic agitation to give the precursor solution. An aliquot (500 μL) of this precursor solution was quickly injected into anhydrous toluene (5 mL) at 40 °C under vigorous stirring. Immediately after mixing, the solution turned bright yellow/green. After stirring for 15 min, a cloudy orange precipitate formed. The suspension was centrifuged at 13,000 rpm for 6 min and the precipitate was discarded. The remaining yellow/green supernatant solution containing the PNCs was retained. Variations on this synthetic procedure, which included increasing the concentration of the capping ligand between 0.18–0.30 mmol and changing the ratio of bromide to iodide by replacing PbBr_2/MAI with PbI_2/MABr , are further detailed in **5.3 Results and Discussion**. **Table 5.1** gives the full synthetic composition of the $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{I}_x$ PNCs prepared in this chapter. The as-prepared PNC suspensions were diluted by addition of anhydrous toluene to give different dilution factors. Samples are denoted according to the dilution factor, for example sample **D₂₀** has a dilution factor of 20, *i.e.* 1 mL of the precursor solution was added to 19 mL of toluene. The synthesis of all-bromide PNCs was achieved using an identical method to that outlined above using PbBr_2 (73.4 mg, 0.20 mmol) and MABr (18 mg, 0.16 mmol). All-iodide PNCs were fabricated through a variation of this synthetic method, outlined by Zhang *et al.* in which acetonitrile was used as the solvent in place of DMF.³⁹ In this synthesis, PbI_2 (45.9 mg, 0.1 mmol), and $\text{CH}_3\text{NH}_3\text{I}$ (0.0127

g, 0.08 mmol), OA (200 μ L, 0.64 mmol) and n-octylamine (20 μ L, 0.12 mmol) were dissolved in acetonitrile (2 mL). An aliquot (1 mL) of this precursor solution was added dropwise to toluene (10 mL). The suspension was centrifuged at 13,000 rpm for 6 min and the precipitate was discarded. The remaining red supernatant solution containing the PNCs was retained. The steady-state PL and UV/Vis absorption spectra of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ and $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{I}_x$ PNC stocks are shown in **Appendix, Fig. A5.1**.

Table 5.1. Summary of the synthetic reagents used for the fabrication of mixed halide $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{I}_x$ PNC precursor solutions.

Sample	PbBr ₂ (mmol)	PbI ₂ (mmol)	MAI (mmol)	MABr (mmol)	OY (mmol)	OA (mmol)	Ratio (Br ⁻ :I ⁻)	Solvent
Std.	0.2		0.16		0.15	1.6	2:0.8	Toluene
OY ₆₀	0.2		0.16		0.18	1.6	2:0.8	Toluene
OY ₇₀	0.2		0.16		0.21	1.6	2:0.8	Toluene
OY ₈₀	0.2		0.16		0.24	1.6	2:0.8	Toluene
OY ₉₀	0.2		0.16		0.27	1.6	2:0.8	Toluene
OY ₁₀₀	0.2		0.16		0.30	1.6	2:0.8	Toluene
R ₁	0.13	0.7	0.056	0.104	0.15	1.6	2:1.1	Toluene
R ₂	0.13	0.7	0.07	0.13	0.15	1.6	2:1.1	Toluene
R ₃	0.1	0.1		0.16	0.15	1.6	2:1.1	Toluene
R ₄	0.1	0.1		0.2	0.15	1.6	2:1	Toluene
R ₅		0.2		0.16	0.15	1.6	0.8:2	Toluene
R ₆	0.1	0.1	0.08	0.08	0.15	1.6	1:1	Toluene
R ₇	0.2		0.08	0.08	0.15	1.6	5:1	Toluene
S ₁	0.2		0.16		0.15	1.6	2:0.8	CHCl ₃

5.3 Results and Discussion

5.3.1 Effect of Dilution on the Emission Properties of PNC dispersions

An attempt was made to prepare $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{I}_x$ mixed halide PNCs using a mixed precursor solution of $\text{CH}_3\text{NH}_3\text{I}$ and PbBr_2 . The LARP method was used by injecting a mix of PbBr_2

and MAI dissolved in a good solvent (DMF) into a poor solvent (toluene) to bring about supersaturation of the solution in the presence of long chain organic capping ligands (OY and OA), as illustrated in **Fig. 5.1a**. OY controls the kinetics of crystallisation by competing with CH_3NH_3^+ for surface sites in the crystal lattice.²⁹ This competition contributes to the size control of PNCs, while OA plays an important role in suppressing aggregation effects and contributes to colloidal stability.¹³ The precursor solution was made up of a non-stoichiometric mixture of MAI and PbBr_2 (0.8:1 molar ratio). The ratio of MAI to PbBr_2 can act as the limiting reagent for the size of the PNCs. In general, small nanoparticles can show non-stoichiometric behaviour due to anion or cation rich surfaces.²¹ Due to the small size, there is a higher concentration of surface atoms relative to the bulk. In the case of PNCs, the particles are made up of a $[\text{PbX}_6]^{4-}$ crystal lattice with the halide ions on the surface, thus, an excess of PbBr_2 means a higher surface area is required to incorporate the halide.²¹ The small size of the PNC particles dictates that the ratio of Pb^{2+} to X^- will not be 1:3, as would be observed in the stoichiometric bulk sample, due to the effect of the anion rich surface, which has previously been demonstrated for CdSe QDs⁴⁰ and PNCs.^{13,21} Thus, for PNCs prepared with excess PbBr_2 , the ratio of bromide to iodide anions will not be 2:1 as expected from the stoichiometry of the reaction mixture, but will show an increased effective contribution of bromide.

Upon injection of the precursor solution into toluene at 40 °C, an orange precipitate consisting of large $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{I}_x$ particles was formed and removed by centrifugation. The remaining supernatant was yellow/green coloured, and exhibited bright green photoluminescence under UV illumination (**Fig. 5.1b**). Since $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{I}_x$ perovskites with an approximate $\text{Br}^-:\text{I}^-$ ratio of 2:1 typically emit in the yellow-red spectral region,^{13,17,22,31,32} the green fluorescence observed in **Fig. 5.1b** supports the hypothesis that the stoichiometric ratio of halides incorporated into the PNC structure differs from the reaction medium. The emission wavelength of bulk PbBr_2 is 520 nm,²⁵ thus the observed green emission ($\lambda_{\text{em}} \sim 525$ nm, **Fig. 5.2**) while slightly red-shifted is indicative of negligible incorporation of the iodide in the PNCs. This can be explained by a combination of the role of PbBr_2 as the seed for PNC growth, meaning that Br^- is favourably incorporated into the PNC crystal structure, thus, the free I^- ions are likely to undergo hydrogen bonding with the excess OY capping ligand.^{13,21} STEM analysis of the samples indicated that platelet-like architectures with

dimensions of ~ 10 nm are formed, which is characteristic for quantum-confined PNCs (**Fig. 5.3a**). However, EDX analysis showed no iodide peaks, which typically can be observed at *ca.* 5 keV (**Fig. 5.5d**), indicating that despite the inclusion of MAI in the reaction mixture, the resultant PNCs were predominantly all-bromide in composition, or that the concentration of iodide present is difficult to observe within the spectrum obtained (**Fig. 5.3b,c**).

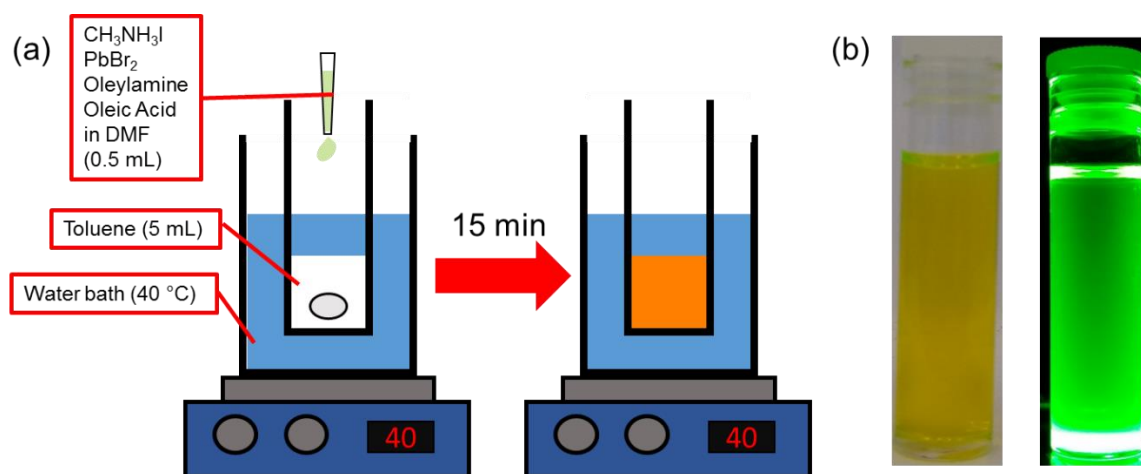


Figure 5.1. Fabrication and characterisation of mixed halide $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{I}_x$ PNC samples synthesised in toluene. (a) Scheme of the LARP synthesis protocol. (b) Photographs of a $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{I}_x$ PNC suspension obtained after centrifugation under white and UV (365 nm) light illumination.

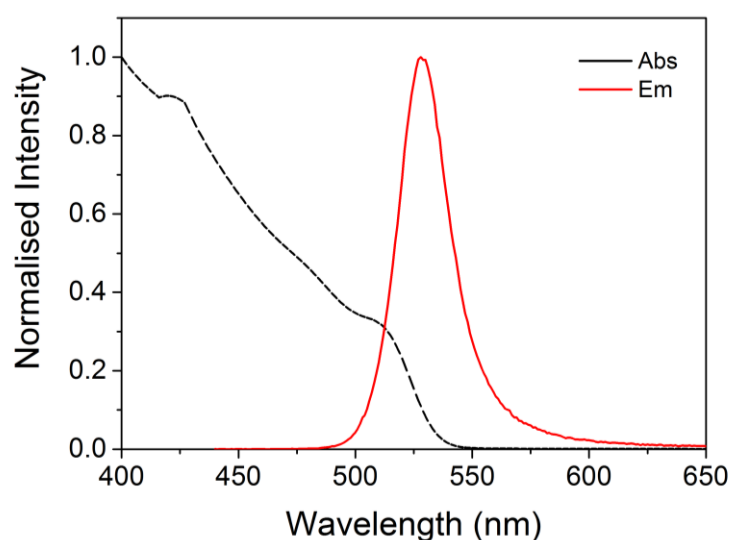


Figure 5.2. UV/Vis absorption and steady-state photoluminescence spectra of $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{I}_x$ PNCs ($\lambda_{\text{ex}} = 400$ nm).

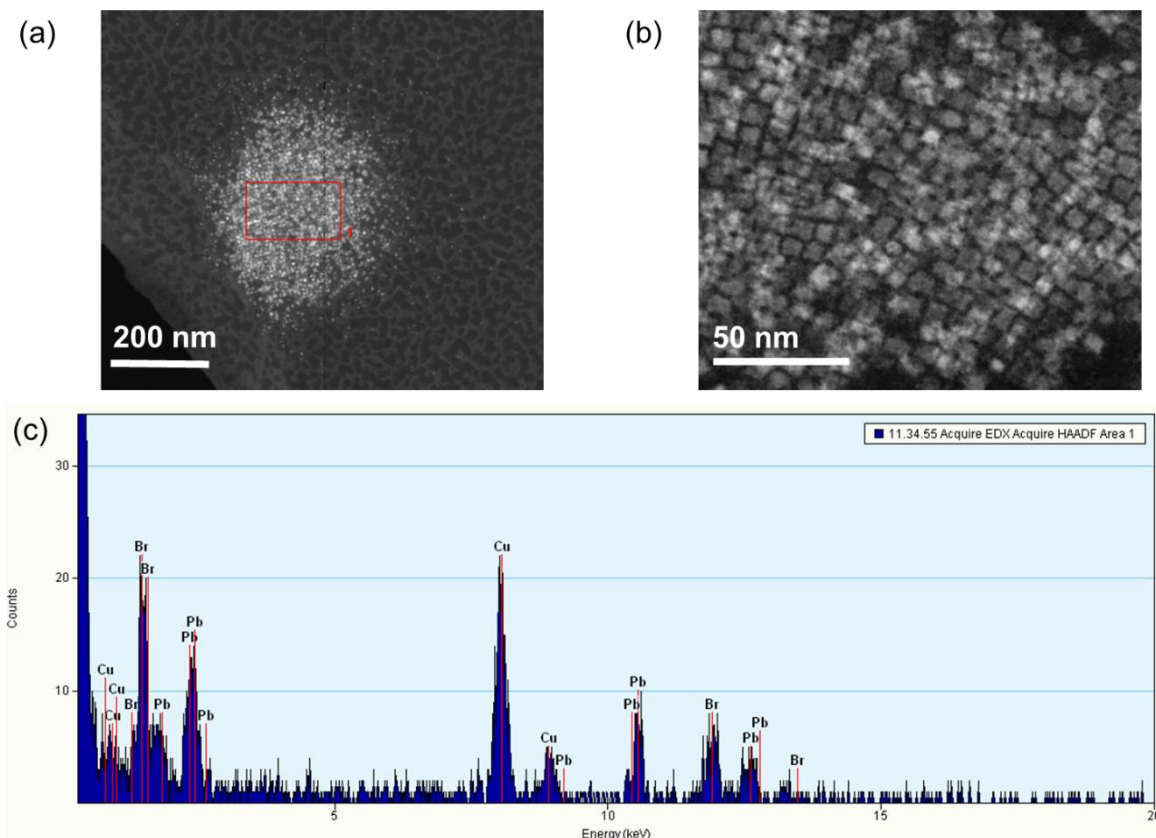


Figure 5.3. Compositional analysis of the parent solution of $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{I}_x$ PNCs by STEM. (a) STEM image of a large population the sample; the red box represents the area investigated by EDX image. (b) Magnified image highlighting the *ca.* 10 nm square platelet-like structures. (c) Corresponding EDX spectrum of the parent $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{I}_x$ PNC solution.

Significant changes in the photoluminescence properties of the $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{I}_x$ PNC suspension were observed upon dilution with toluene, the magnitude of which is dependent on the dilution factor (D_x). **Fig. 5.4a** presents the UV/Vis absorption and PL spectra as a function of dilution. While the absorption spectrum remained effectively unchanged, the emission maximum was red-shifted by ~ 20 nm for dilution between D_0 and D_{10} . Further dilution of the sample beyond D_{10} resulted in no further spectral change. As described above, using a similar LARP procedure Urban *et al.* synthesised $\text{CH}_3\text{NH}_3\text{PbBr}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_3$ PNCs with dimensions >100 nm, which fractured to give smaller ~ 10 nm PNCs upon dilution.³⁷ Interestingly, however, in this example, a blue-shift of the emission maximum was observed immediately upon dilution, attributed to solvent fragmentation and exfoliation of larger multilayer PNCs to yield thinner NCs, which were stabilised by excess capping ligand.

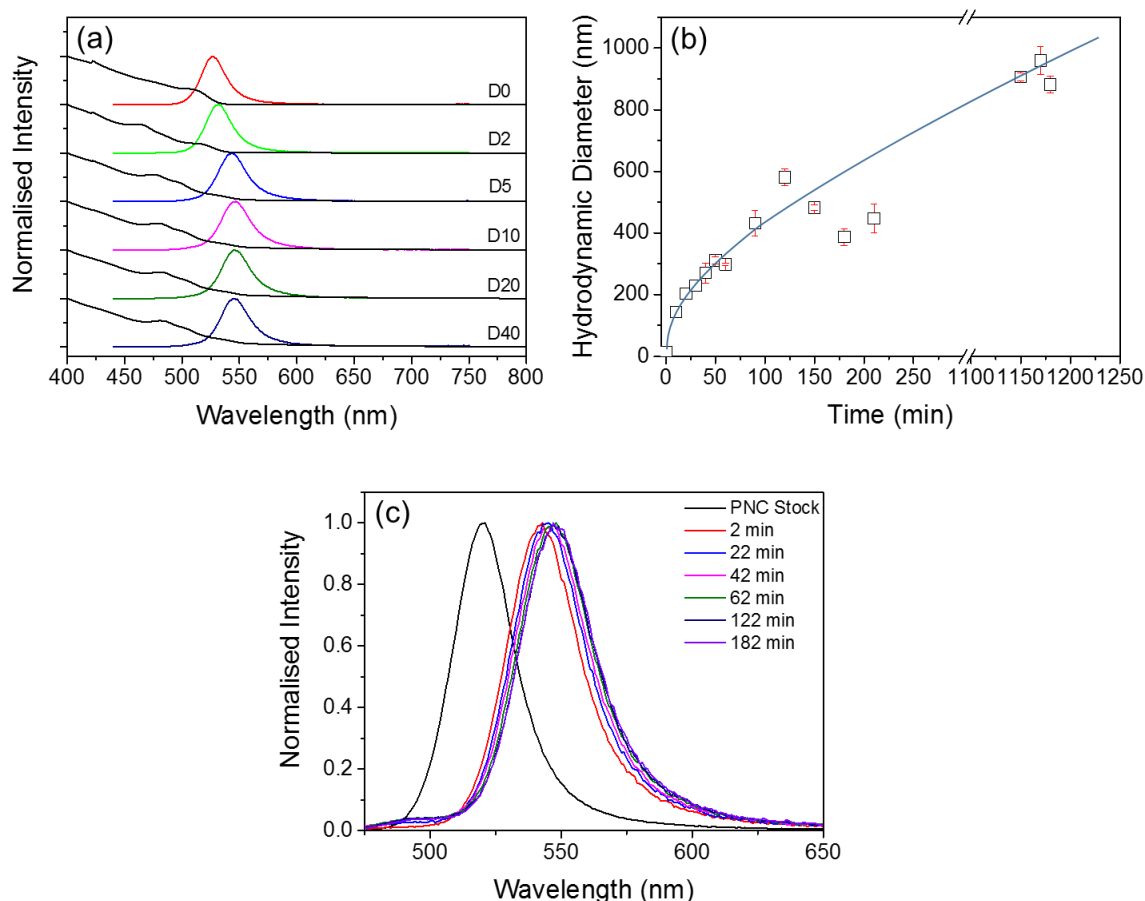


Figure 5.4. Variation of optical properties and size of CH₃NH₃PbBr_{3-x}I_x PNCs upon dilution. (a) UV/Vis absorption and steady-state PL ($\lambda_{\text{ex}} = 400$ nm) spectra for CH₃NH₃PbBr_{3-x}I_x PNCs with dilution factors of D₀ to D₄₀. (b) Variation in the hydrodynamic diameter, d_h , upon dilution (D₂₀) with time. The blue line serves only to guide the eye. (c) Steady-state PL spectra of the CH₃NH₃PbBr_{3-x}I_x parent solution before dilution by a factor D₂₀ and at timed intervals after dilution ($\lambda_{\text{ex}} = 400$ nm).

PNCs, like other semiconductor nanoparticles, show size-dependent optical properties, with quantum confinement typically leading to a blue-shift in the emission spectrum, while particle growth leads to a red-shift back towards the PL spectrum more typical of the bulk material.²⁴ Due to their planar structure, PNCs will often only show quantum confinement as the thickness of the nanoplatelets approaches that of a monolayer.^{23,31,41} To explore the origin of the red-shift of the PL spectrum observed in the mixed halide system, DLS experiments were performed on PNC suspensions for both the parent and diluted samples as a function of time. The mean hydrodynamic diameter, d_h , of the PNCs in the parent suspension (D₀) was ~14 nm (**Appendix, Fig. A5.2**). Upon dilution, however, the observed d_h increased with time until values of ~1 μm were obtained (*e.g.* **Fig. 5.4b** for D₂₀). This trend indicates that dilution results in growth of the CH₃NH₃PbBr_{3-x}I_x PNCs,

rather than the fragmentation and exfoliation of layers as previously reported for single halide $\text{CH}_3\text{NH}_3\text{PbBr}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_3$ PNCs.³⁷ A similar trend of particle growth upon dilution has been observed for CsPbX_3 PNCs, where destabilisation of the capping ligands occurred upon dilution with a polar solvent.³⁸ Steady-state PL measurements were performed concurrently with the time-dependent DLS study (**Fig. 5.4c**). Interestingly, the predominant red-shift in the emission maximum occurred very quickly after dilution (2 min), with only subtle spectral changes observed at increasing times after dilution, suggesting a very rapid growth/aggregation rate.

Fig. 5.5 shows the STEM images of $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{I}_x$ PNCs before and after dilution by factor $\mathbf{D}_{20}$. Prior to dilution, square-shaped nanoplatelet structures were observed with dimensions ~ 10 nm (in good agreement with the observed $d_h \sim 14$ nm). Following dilution, the small nanoplatelet-like structures were observed to aggregate into larger cubic structures, reaching dimensions of >100 nm in size (**Fig. 5.5b**). EDX was used to determine the elemental composition of the diluted PNC samples. Upon dilution, only the extremely thick particles showed detectable iodide peaks (**Fig. 5.5c**), suggesting that while particle growth results in incorporation of iodide ions present in the reaction medium, it occurs only to a small extent. The large particle examined in **Fig. 5.5c** appears to be made up of several overlapping platelets thus the thickness of the layer is likely greater than the *ca.* 250 nm surface dimensions. The peak ratios in the EDX spectrum of the $\mathbf{D}_{20}$ sample indicate a bromide to iodide mass ratio of 4:1, this corresponds to a molar ratio of *ca.* 2.5:1, thus the diluted PNCs composition moves toward that of the precursor solution.

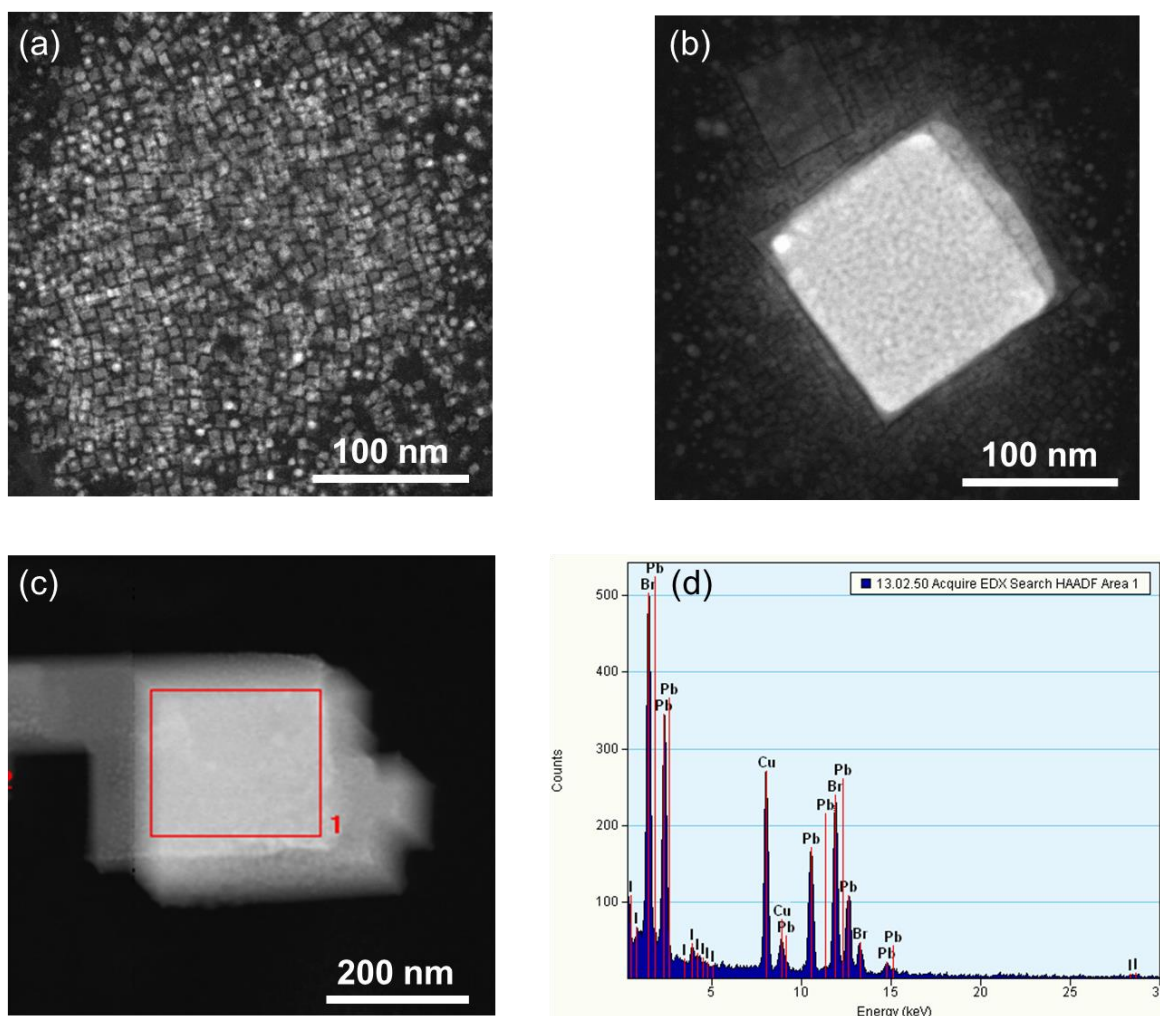


Figure 5.5. Growth of $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{I}_x$ PNCs upon dilution by a factor D_{20} . STEM images of $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{I}_x$ PNCs (a) before and (b) after dilution (D_{20}) in toluene. (c) STEM image of a large population the sample; the red box represents the area investigated by EDX. (d) Corresponding EDX spectrum of the dilute $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{I}_x$ PNC solution.

EDX analysis confirmed that the observed red-shift in the PL maximum is not due to significant halide exchange in the small PNCs, which would have suggested the formation of all-iodide $\text{CH}_3\text{NH}_3\text{PbI}_3$ PNCs. Instead, it is likely that the spectral shift is caused by a decrease in the effective capping ligand concentration in the diluted sample. **Fig. 5.6** presents a proposed hypothesis for the mechanism of particle growth observed upon dilution. Partial dissolution of the capping ligand on the surface of the nanocrystal due to this concentration decrease leads to uncontrolled aggregation of the PNCs. As this aggregation occurs some of the excess iodide, which underwent hydrogen bonding to the capping ligand, was incorporated through halide exchange. This was supported by both the observation that the red-shift in the PL maximum did not further shift after initial particle growth, and that this growth upon dilution (as imaged by STEM) was accompanied

by an increase in the iodide content in the crystal structure. Anion exchange reactions, which cause a red-shift of the emission properties are well documented for CsPbX_3 PNCs.^{42–45} However, it has not been reported to occur spontaneously upon dilution without addition of excess PbX_2 salts. It is worth noting that particle growth was not observed by Urban *et al.* who initially synthesised large (>100 nm) all-bromide or all-iodide PNCs.³⁷ From which, no red-shift of the emission properties will occur due to no incorporation of iodide, and due to the large initial thickness of the particles exfoliation by the excess solvent molecules occurs, leading to thinner particles and an increase in quantum confinement.

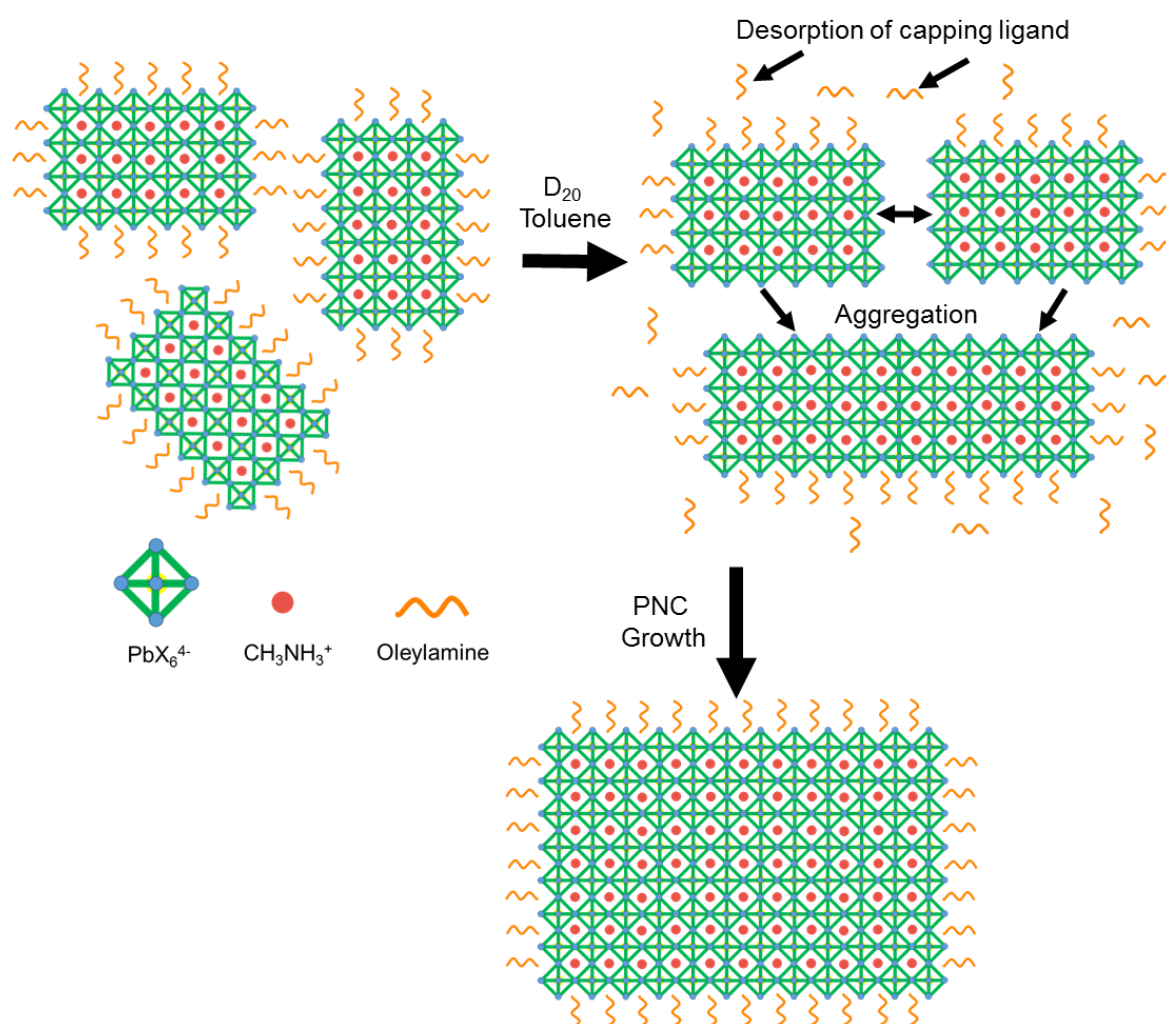


Figure 5.6. Schematic representation of the proposed mechanism of nanocrystal growth upon dilution.

5.3.2 Role of Capping Ligand Concentration

If the proposed mechanism is correct, and particle growth is directly related to a decrease in the effective concentration of the capping ligand upon dilution, similar behaviour should be observed for different capping ligand concentrations. There have been numerous examples of previous work whereby the thickness of PNCs has been tailored by varying the capping ligand content.^{31,32} Typically, increased capping ligand concentration results in thinner nanocrystals, with the excess capping ligand stabilising the increased surface area associated with smaller particles.³² To further explore the effect of the capping ligand on the optical properties of the resultant PNC suspensions, a series of analogous $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{I}_x$ PNC samples was prepared, in which the volume of the OY capping ligand added during the LARP process was varied. Samples are designated as **OY_n**, where $n = 50-100$ (μL) and **OY₅₀** corresponds to the standard fabrication procedure. Increases in the OY concentration (**OY₆₀** – **OY₉₀**) resulted in a slight blue-shift in the photoluminescence spectrum compared to the standard **OY₅₀** sample (**Fig. 5.7**), as expected for a higher capping ligand concentration.

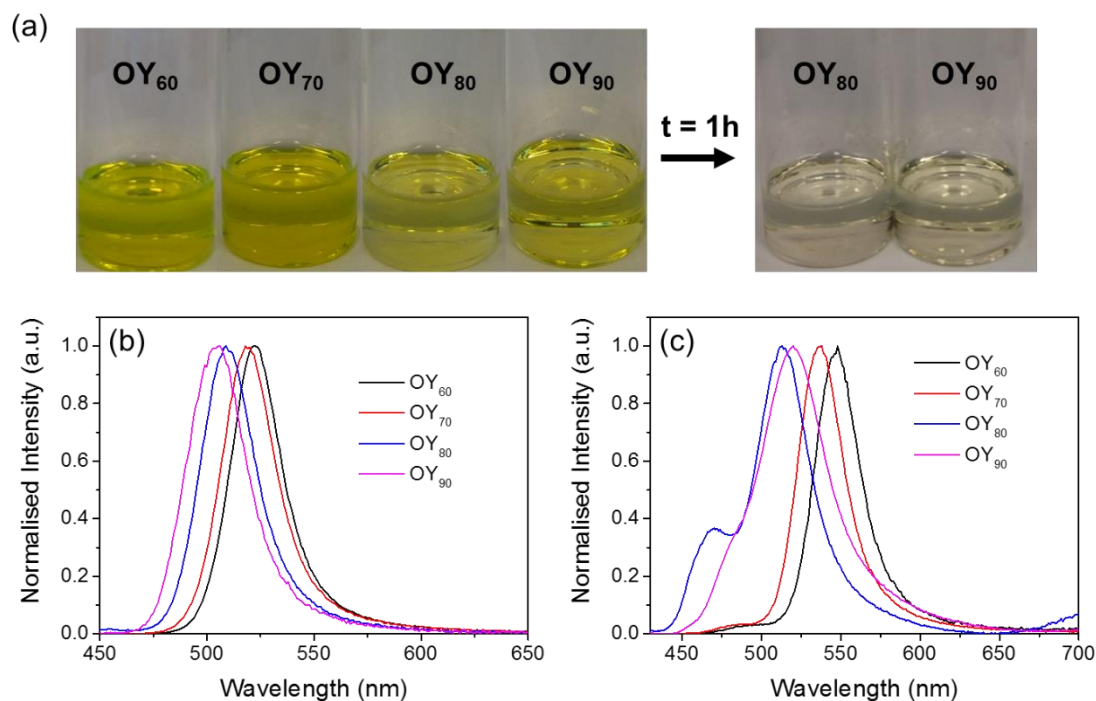


Figure 5.7. (a) Photographs of $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{I}_x$ PNC stock solutions synthesised with increased oleylamine capping ligand volumes. (b) Steady-state photoluminescence spectra of PNC stock solutions synthesised with OY₆₀ – OY₉₀ (right to left). (c) Steady-state photoluminescence spectra of the high oleylamine concentration stocks upon dilution by a factor D_{20} .

These samples, however, still displayed a characteristic red-shift of 20–30 nm upon dilution (**D**₂₀). Conversely, at concentrations **OY**₈₀ and **OY**₉₀ the samples were observed to turn from pale yellow to colourless with time (**Fig. 5.7a**). Moreover, while these samples initially showed an emission maximum at *ca.* 500 nm, an almost complete loss of visible photoluminescence was observed as the solution turned transparent.

Interestingly, for the samples synthesised with the highest capping ligand concentration (**OY**₁₀₀), the initial yellow solution was not observed, but rather a colourless transparent solution was obtained immediately after centrifugation (**Fig. 5.8a**). This solution showed a low intensity blue emission ($\lambda_{\text{em}} \sim 410$ nm) with several additional peaks, including peaks at *ca.* 500 nm indicating that a variety of particle sizes and compositions are present in the solution (**Fig. 5.8b**). The drop in PL intensity observed was likely due to be due to dissociation of the PNCs caused by the excess capping ligand altering the polarity of the stock solution. A similar occurrence has been previously documented by Nishikubo *et al.* who described the formation of 1D PbBr₂ nanoparticles upon solvation of the excess MA and Br⁻ by the capping ligands.³⁴ They reported blue emission from the 1D PbBr₂ nanoparticles, with a λ_{em} of 415 nm with minor peaks visible at *ca.* 500 and 550 nm.

The **OY**₁₀₀ sample similarly shows an immediate red-shift in the emission maximum from 410 nm to 480 nm upon dilution (**D**₂₀), with a blue-green emission observed (**Fig. 5.8a**). STEM images of the samples before and after dilution interestingly show no large growth in particle size immediately after dilution. **Fig. 5.8c** and **Fig. 5.8d** show spherical particles corresponding to dot-like structures with dimensions <10 nm. The blue emission of the PL spectrum similar to that observed by Nishikubo *et al.* suggests these particles in the non-dilute sample are PbBr₂. PbBr₂ 0D nanoparticles have been well documented as acting as seeds for the growth of PNCs.^{13,21,34} It follows that upon dilution, as described for the standard PNC samples (**Fig. 5.6**), the relative concentration of the capping ligand in the solution decreases, decreasing the solubility of the excess MA and Br⁻ allowing particle growth to occur. The increased intensity blue/green emission observed and the small size of the particles observed in **Fig. 5.8d** suggests the formation highly quantum confined CH₃NH₃PbBr_{3-x}I_x PNCs from the PbBr₂ seed particles is occurring.

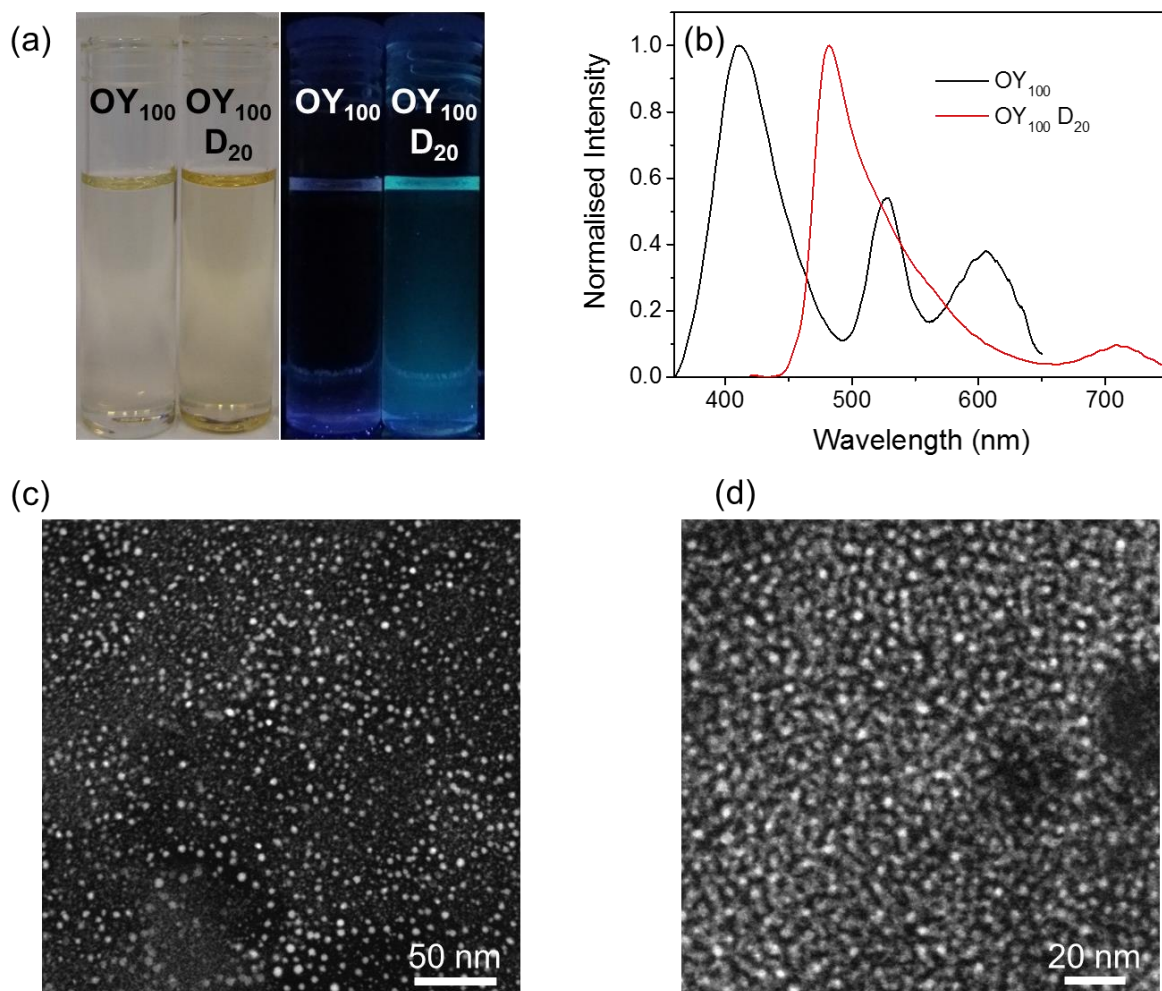


Figure 5.8. Characterisation of OY₁₀₀ CH₃NH₃PbBr_{3-x}I_x PNC solution before and after dilution (a) Photographs of stock and dilute (D₂₀) OY₁₀₀ under visible and 365 nm UV light. (b) Steady-state PL spectra of stock and dilute (D₂₀) OY₁₀₀ solution. STEM images of a drop-cast OY₁₀₀ solution with (c) before ($\lambda_{\text{ex}} = 360$ nm) and (d) after dilution by a factor D₂₀ ($\lambda_{\text{ex}} = 400$ nm).

After 24 h, the OY₁₀₀ sample with a high concentration of capping ligand showed bright red fluorescence (**Fig. 5.9a**). Upon investigation by steady-state PL spectroscopy there was a second emission peak at 580 nm with similar intensity to the peak at 490 nm (**Fig. 5.9b**); after 48 h this peak became the $\lambda_{\text{em (max)}}$ indicating that this solution was not stable. Upon centrifugation the red colour was lost and a non-photoluminescent solution was obtained, indicating large PNC particles were the cause of the red emission. It can be postulated that the red-emission of these particles indicates a high uptake of the iodide ions upon aggregation.

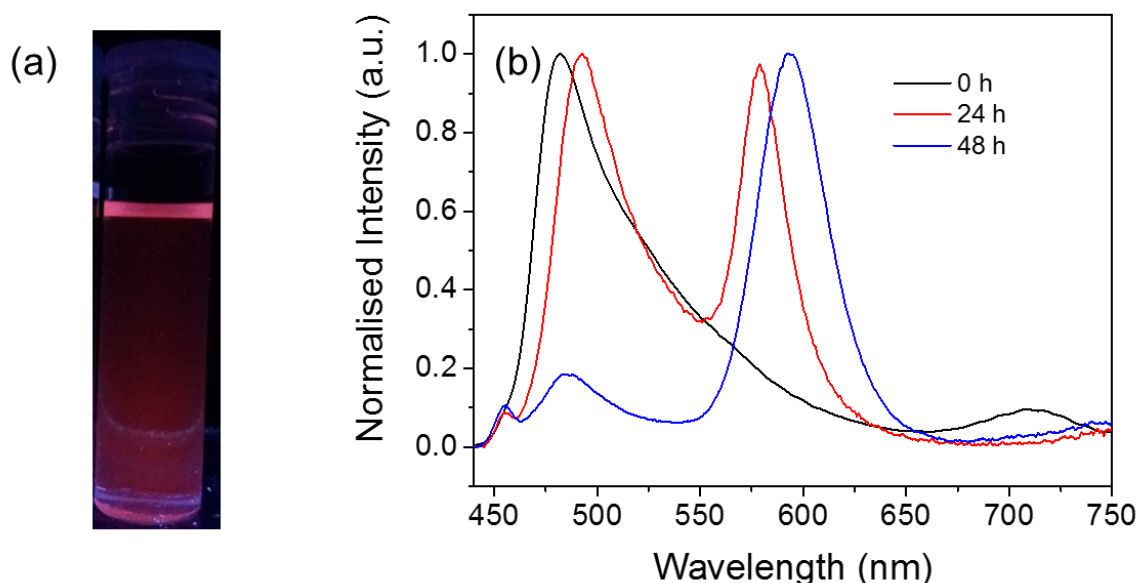


Figure 5.9. Time dependent characterisation of D₂₀ OY₁₀₀ CH₃NH₃PbBr_{3-x}I_x PNC solution. (a) Picture of OY₁₀₀ CH₃NH₃PbBr_{3-x}I_x PNC solution, 24 h after dilution by a factor D₂₀ under UV illumination at 365 nm. (b) Steady-state PL spectra of OY₁₀₀ CH₃NH₃PbBr_{3-x}I_x PNCs, upon dilution by a factor D₂₀ after 0, 24 and 48 h ($\lambda_{\text{ex}} = 400$ nm).

5.3.3 Effect of Halide Content

To confirm that the observed red-shift in the emission maximum upon dilution is due to a move towards the bulk emissive properties of CH₃NH₃PbBr_{3-x}I_x and uptake of iodide, the halide content in the precursor solutions was varied. Initially, the concentration of MAI was increased to give a stoichiometric mixture of MAI/PbBr₂ (1:1), with the synthetic procedure unchanged, giving an approximate ratio of Br⁻ to I⁻ of 2:1 in the precursor solution. Upon increasing the concentration of MAI, a slight red-shift in the emission maximum (~5 nm) was observed for the resultant parent PNC dispersion. Upon dilution (D₂₀), a more significant red-shift of *ca.* 30 nm was detected, compared to 25 nm for the standard 2:0.8 Br:I sample. This would support our hypothesis that a higher iodide content in the reaction medium thus leads to an increased red-shift in the emission for both the parent and dilute samples.

Interestingly, the magnitude of the red-shift observed can be tailored by varying which of reactants provides the halides. To demonstrate this, similar ratios of Br⁻ to I⁻ (*ca.* 2:1), PNC stock solutions were synthesised using varying amounts of PbX₂, (PbBr₂ + PbI₂ = total 0.2 mmol) and

MAX (MABr + MAI total 0.16 or 0.2 mmol). Samples of varied reagent ratios were designated **R**₁-**R**₄ with the exact compositions outlined in **Table 5.2**.

Table 5.2. Reagent compositions for CH₃NH₃PbBr_{3-x}I_x PNC precursor solutions with a Br⁻:I⁻ ratio of *ca.* 2:1, to investigate the consequence of varying the halide source on the optical properties.

Sample	PbBr ₂ (mmol)	PbI ₂ (mmol)	MABr (mmol)	MAI (mmol)	Ratio Br ⁻ :I ⁻
R ₁	0.13	0.07	0.104	0.056	2 : 1.08
R ₂	0.13	0.07	0.13	0.07	2 : 1.08
R ₃	0.1	0.1	0.16	0	2 : 1.1
R ₄	0.1	0.1	0.2	0	2 : 1

All four of the investigated PNC solutions with a *ca.* 2:1 Br⁻ to I⁻ ratio showed the characteristic green emission as expected, with λ_{em} varying between 530 nm and 538 nm prior to dilution (**Fig. 5.10a**). This obtained green emission again indicates that there is a non-stoichiometric incorporation of the iodide into the PNCs. However, considering these PNC samples exhibit variation of λ_{em} and that these values appear at wavelengths longer than the 525 nm observed for the standard samples, this indicates that there is some iodide present. When these samples were subsequently diluted, the effect on λ_{em} varied based on the combinations of reagents used in the synthetic procedure. The sample showing the largest emission red-shift (**R**₂) was prepared from a 1:1 ratio of PbX₂ and MAX and using a combination of all four reagents. This sample showed a red-shift of 28 nm compared with 12 nm for the equivalent sample which used a 2:1.6 ratio of PbX₂ to MAX (**Fig. 5.10c,d**). This demonstrates that even for identical ratios of bromide to iodide, the magnitude of the red-shift can vary significantly if a different halide source is used. If each PNC is considered as a [PbX₆]⁴⁻ crystal lattice, with MAX and excess halides bound to capping ligands on its surface, it follows that the higher the relative concentration of iodide anions bound in the capping ligand, which can undergo incorporation as the PNC grows, the greater the red-shift will be.²¹ The largest emission red-shifts occurred for samples with the highest concentration of MAI (**R**₂) (**Fig. 5.10d**), compared to the samples where the iodide came from PbI₂ (**R**₃,**R**₄), thus, supporting the

hypothesis that the iodide bound to the capping ligand on the surface is favourably incorporated upon dilution and subsequent growth.

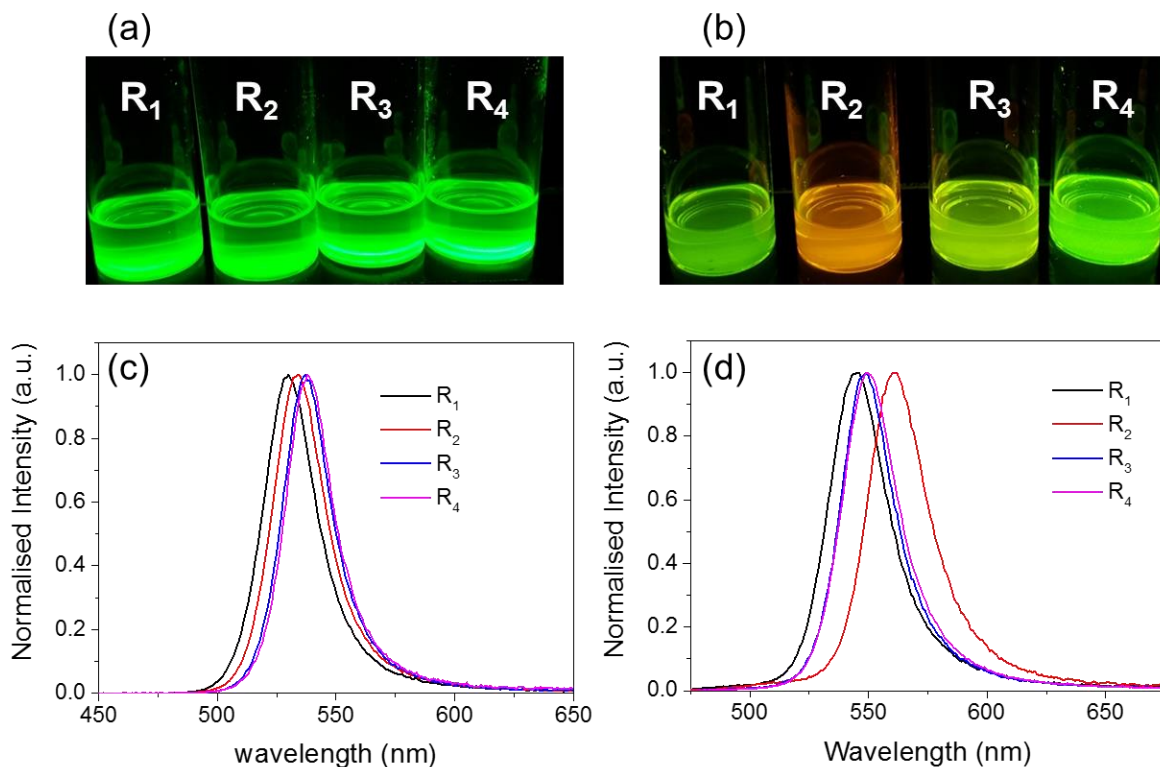


Figure 5.10. Visual and PL characterization of $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{I}_x$ PNC solutions to investigate the impact of the halide source on the emission properties. PNC synthesised using a precursor solution with $\text{Br}^-:\text{I}^-$ ratio of *ca.* 2:1 with different reagent combinations (R_1 - R_4). Photographs under 365 nm illumination (a) before and (b) after dilution (D_{20}). Steady-state photoluminescence spectra of the PNC samples (c) before and (d) after dilution D_{20} ($\lambda_{\text{ex}} = 400 \text{ nm}$).

After successfully demonstrating that a slight increase in the iodide content of the PNC solutions can result in an increase in the magnitude of the emission red-shift observed, PNC stocks with different bromide to iodide ratios were synthesised by varying the ratios of the precursors as shown in **Table 5.3**. The investigated $\text{Br}^-:\text{I}^-$ ratios were 0.8:2 (R_5), 1:1(R_6) and 6:1(R_7). These PNC solutions were synthesised identically to the standard and were diluted by factor D_{20} to observe if any red-shift occurred.

Table 5.3 Reagent compositions for $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{I}_x$ PNC precursor solutions with varying $\text{Br}^-:\text{I}^-$ to investigate the contribution of iodide content to the optical properties.

Sample	PbBr_2 (mmol)	PbI_2 (mmol)	MABr (mmol)	MAI (mmol)	Ratio $\text{Br}^-:\text{I}^-$
R₅	0	0.2	0.16	0	0.8 : 2
R₆	0.1	0.1	0.08	0.08	1 : 1
R₇	0.2	0	0.08	0.08	6 : 1

After centrifugation, **R₅** was a transparent solution and showed a weak blue emission. These emission properties appeared similar to those observed for the **OY₁₀₀** with a similar λ_{em} . This indicates that these solutions likely consist of PbBr_2 seed particles, as described above. This is not surprising if we consider the instability of iodide-based perovskites and the difficulty of fabricating stable all-iodide PNC solutions.³⁹ In many cases a more polar solvent such as chloroform is required to stabilise the suspension.³² Upon dilution, however, a change of the λ_{em} from *ca.* 420 to 530 nm was observed, showing a bright green emission characteristic of the standard undiluted $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{I}_x$ PNC samples using a *ca.* 2:1 $\text{Br}^-:\text{I}^-$ ratio precursor solution (**Fig. 5.11a**). This further supports the hypothesis that the low intensity blue emission seen for **R₅** and **OY₁₀₀** originates from PbBr_2 NCs which act as seeds for growth of the larger platelets. The green emission obtained for **R₅** and the green/blue emission for **OY₁₀₀** is likely to be related to a higher degree of quantum confinement in the high capping-ligand concentration sample. **R₆**, the PNC stock made with a 1:1 ratio of $\text{Br}^-:\text{I}^-$, behaved similarly to the standard samples, with an emission red-shift of approximately 25 nm observed upon dilution **D₂₀** (**Fig. 5.11b**). This shift however was observed to take place much more slowly than previously observed for the standard, with two peaks of equal intensity observed at 528 nm and 595 nm upon dilution. However, approximately 13 minutes post dilution, the relative intensity of the peak at 528 nm had decreased, while the peak at 595 nm blue-shifted back to 555 nm and became the most prominent emission peak. This behaviour can be explained by the ion exchange observed in the standard samples. We hypothesise that, upon dilution, two populations with different halide compositions are present and a gradual move towards a single mixed halide population occurs as the PNCs agglomerate and homogenise to form the micrometre size particles. **R₇**, prepared from

a 6:1 Br⁻:I⁻ ratio, gave a green emission with an emission maximum of 520 nm and upon dilution no shift was observed (**Fig. 5.11c**). This further indicates that the change in the spectral properties upon dilution is due to the presence of iodide in the PNC stock solution and that in a low iodide concentration sample, no red-shift is observed. The emission properties of this suspension look identical to that of bulk CH₃NH₃PbBr₃, both before and after dilution, thus implying that no change in the chemical makeup of the crystal lattice is observed.²⁵

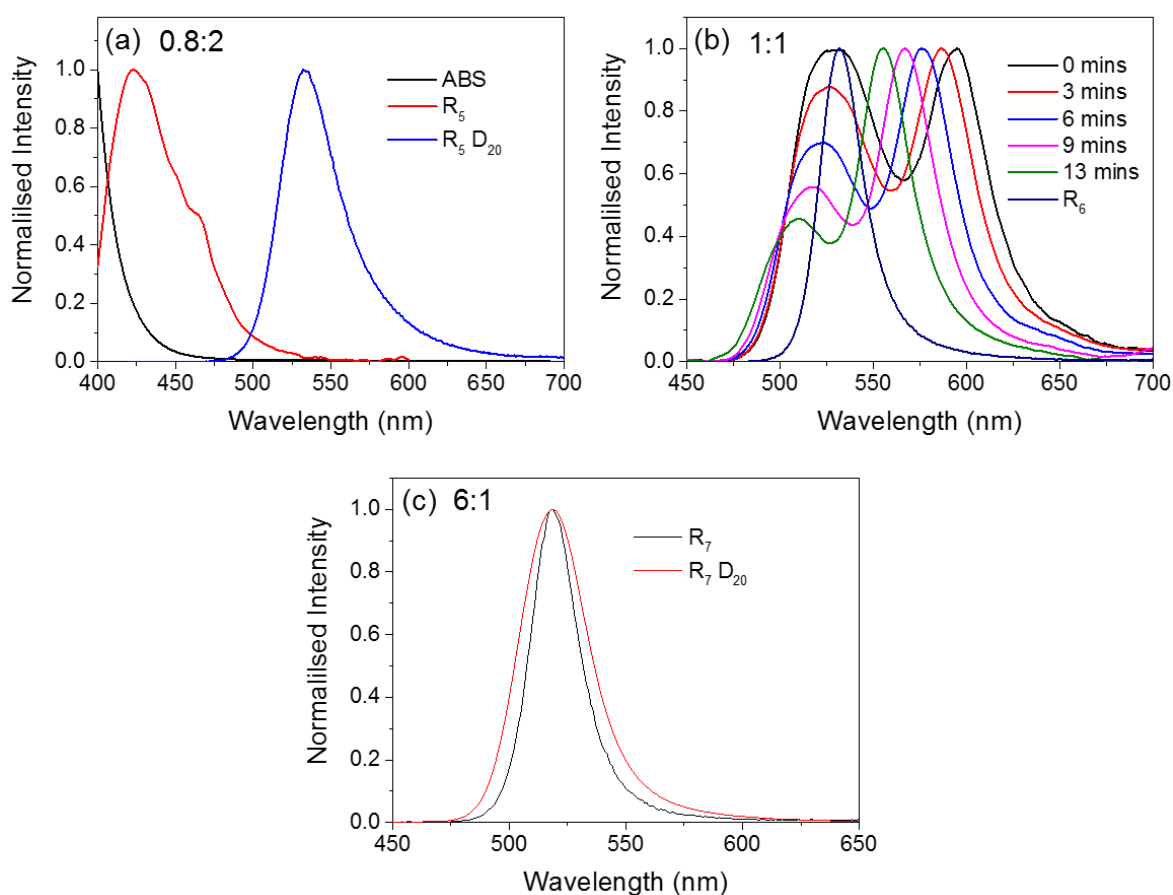


Figure 5.11. (a) Absorption and emission spectra of CH₃NH₃PbBr_{3-x}I_x PNC stock prepared with a 1:2 Br⁻:I⁻ ratio and emission spectra after a dilution by a factor of 20 (D₂₀). (b) Time dependent emission spectra of CH₃NH₃PbBr_{3-x}I_x PNC stock prepared with a 1:1 Br⁻:I⁻ ratio upon dilution (D₂₀). (c) Emission spectra of CH₃NH₃PbBr_{3-x}I_x PNC stock prepared with a 5:1 Br⁻:I⁻ ratio before and after dilution (D₂₀). For all λ_{ex} = 400 nm.

5.3.4 Role of Solvent

In order to confirm that the dilution-induced changes in the optical properties can be explained by the partial desorption of the capping ligands causing both growth and anion exchange, a standard $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{I}_x$ PNC sample was prepared using chloroform as the antisolvent in place of toluene (**S**₁). The increased polarity of chloroform (dielectric constant, $\epsilon = 4.81$, vs. $\epsilon = 2.38$ for toluene) is advantageous as it facilitates improved ionic dissociation, and thus acts to prevent excessive agglomeration of particles on mixing with DMF ($\epsilon = 37.8$).³² From the Hansen solubility parameters, it can also be observed that the capping ligands (oleic acid, $\delta_t = 16.81 \text{ MPa}^{1/2}$) are less soluble in chloroform ($\delta_t = 18.94 \text{ MPa}^{1/2}$) than in toluene ($\delta_t = 17.95 \text{ MPa}^{1/2}$);⁴⁶ thus less aggregation should be observed upon dilution if the proposed mechanism is valid (the solubility parameter for oleylamine is likely to be similar to that of oleic acid due to the structural similarities).⁴⁶ It should also be noted that Urban *et al.* observed a larger blue-shift in the emission maximum upon dilution with chloroform compared to toluene.³⁷ The chloroform antisolvent sample is shown in **Fig. 5.12a** before and after dilution (**D**₂₀). A bright green emission with a maximum at 545 nm was observed for the non-dilute sample, which is slightly red-shifted compared to the analogous toluene sample (**Fig. 5.12b**). Upon dilution, a bright blue emission is observed with a λ_{em} at 475 nm. The blue-shift in the emission maximum can be attributed to both solvent exfoliation of the PNC layers to increase quantum confinement effects, or anion doping of chloride from the chloroform solvent molecules to PNC which has been observed previously.³⁷ The observed emission behaviour confirms the effect the solvent can have on the dilution-induced behaviour of the PNCs. Toluene is able to better solvate the capping ligands, initiating solvent dissociation and particle growth, whereas, chloroform, which exhibits poor solvation of the capping ligand, exhibited blue-shifting of the emission maximum.

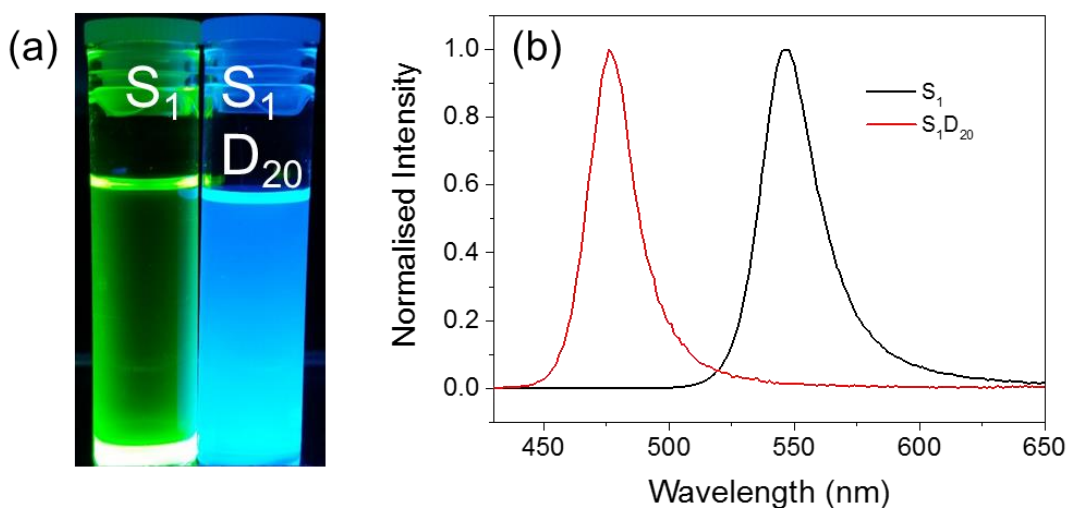


Figure 5.12. (a) Photographs of the stock solution before and after dilution by a factor D_{20} under illumination at 365 nm and (b) steady-state PL spectra of $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{I}_x$ PNC stock synthesised using chloroform as an antisolvent before and after dilution (D_{20}) ($\lambda_{\text{ex}} = 400$ nm).

5.3.5 Photoluminescence Properties of $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{I}_x$ PNCs

It has been demonstrated above that $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{I}_x$ PNCs can undergo rapid crystal growth upon dilution and that a change in the relative concentration of bromide/iodide ions occurs as the crystals grow. This tendency will have a significant effect on their eventual use in device fabrication through solution processing, as the optical performance may be unintentionally modified. In particular, PNCs have been shown to typically display a higher Φ_{PL} than their bulk counterparts.^{21,22} The measured Φ_{PL} for the standard mixed halide $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{I}_x$ PNC dispersion was $54 \pm 4\%$, whereas upon dilution (D_{20}) the Φ_{PL} decreased dramatically to $10 \pm 0.5\%$. The Φ_{PL} value of the stock is in good agreement with that previously reported ($\Phi_{\text{PL}} = 60.1\%$) for non-dilute $\text{CH}_3\text{NH}_3\text{PbBr}_3$ PNC systems.³⁷ Previous reports indicated that as PNCs become thinner, a drop in the Φ_{PL} is observed due to enhanced non-radiative decay pathways due to an increase in lattice strain upon thinning.^{32,47} The mechanism for the observed loss of Φ_{PL} for the standard samples upon dilution can be explained by the observed particle growth resulting in bulk-like optical properties. This significant loss in the Φ_{PL} upon dilution indicates that while tunable emission is achievable for these systems, it comes at the cost of efficient emission. Nevertheless, it demonstrates that careful control of the solution phase storage of PNC dispersions and their deposition methods are required in order to prevent discrepancies during the device fabrication process.

Time-correlated single photon counting (TCSPC) experiments were performed to determine the fluorescence lifetimes of the standard samples. Similar to the Φ_{PL} measurements, significant differences were observed between the lifetimes of the parent and diluted (**D₂₀**) PNC samples, although they both exhibited biexponential decay curves (**Fig. 5.13**). Upon dilution the lifetimes of the samples were observed to increase with both the exponential components of the decay increasing from 10.7 ns to 12.4 ns and from 24.2 ns to 28.8 ns for τ_1 and τ_2 , respectively. The biexponential nature of this decay represents localised (τ_2) and delocalised (τ_1) exciton recombination.^{47,48} The amplitude of the slower localised decay rate can thus provide an estimate for the quantity of defects in the perovskite lattice. Interestingly, as the samples were diluted, a decrease in the amplitude of the localised recombination was observed, thus, as the PNCs aggregate, a loss of defect sites occurs. This is to be expected as a loss of surface area as the particles aggregate would mean a significant decrease in the concentration of surface trap sites. The photoluminescence properties of the standard $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{I}_x$ PNC solutions before and after dilution by a factor **D₂₀** are summarised in **Table 5.4**.

Table 5.4. Photoluminescence properties of standard $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{I}_x$ PNC solutions. Lifetimes (τ), pre-exponential coefficients (α), and chi squared (χ^2) values obtained from fitting of the emission decays ($\lambda_{\text{ex}} = 400$ nm) of both stock ($\lambda_{\text{em}} = 525$ nm) and dilute **D₂₀** ($\lambda_{\text{em}} = 560$ nm) $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{I}_x$ PNC solutions, respectively. Radiative (k_{R}) and non-radiative (k_{NR}) decay rate constants and photoluminescence quantum yields (Φ_{PL}) obtained before and after dilution **D₂₀** are also shown.

$\lambda_{\text{ex}} =$ 400 nm	τ_1 (ns)	τ_2 (ns)	α_1	α_2	χ^2	k_{R} (ns ⁻¹)	k_{NR} (ns ⁻¹)	Φ_{PL} (%)
PNC Stock	10.7 ± 0.1	24.2 ± 0.2	0.66 ± 0.02	0.34 ± 0.01	1.14	0.031	0.024	54 ± 4
PNC D₂₀	12.4 ± 0.2	28.8 ± 0.2	0.72 ± 0.01	0.28 ± 0.01	1.2	0.005	0.044	10 ± 0.5

The average lifetimes, $\langle \tau \rangle$, of the parent and dilute (**D₂₀**) samples were 18 ns and 20.5 ns, respectively. Given that bulk $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{I}_x$ films have shown lifetimes greater than 100 ns,⁴⁹ the increase in the lifetime upon dilution supports the hypothesis of nanocrystal growth.³² The Φ_{PL} and the average excited-state lifetime are related by the following equations:

$$\langle \tau \rangle = 1 / (k_R + k_{NR}) \quad (5.1)$$

where k_R and k_{NR} are the radiative and non-radiative decay rate constants, respectively, and

$$\Phi_{PL} = k_R / (k_R + k_{NR}) \quad (5.2)$$

Using these equations, k_R and k_{NR} were determined to be 0.031 ns^{-1} and 0.024 ns^{-1} , respectively, for the parent PNC sample. Upon dilution, a significant drop in k_R to 0.005 ns^{-1} was observed, along with the expected increase in k_{NR} to 0.044 ns^{-1} . This decrease in k_R is typically assigned to a decreased exciton binding energy, with thinner PNC layers showing much higher binding energies compared to thick bulk-like structures, due to both the transition from 3D to 2D structures and the decreased Coulombic screening between the electrons and holes as the layers become thinner.^{31,37,50}

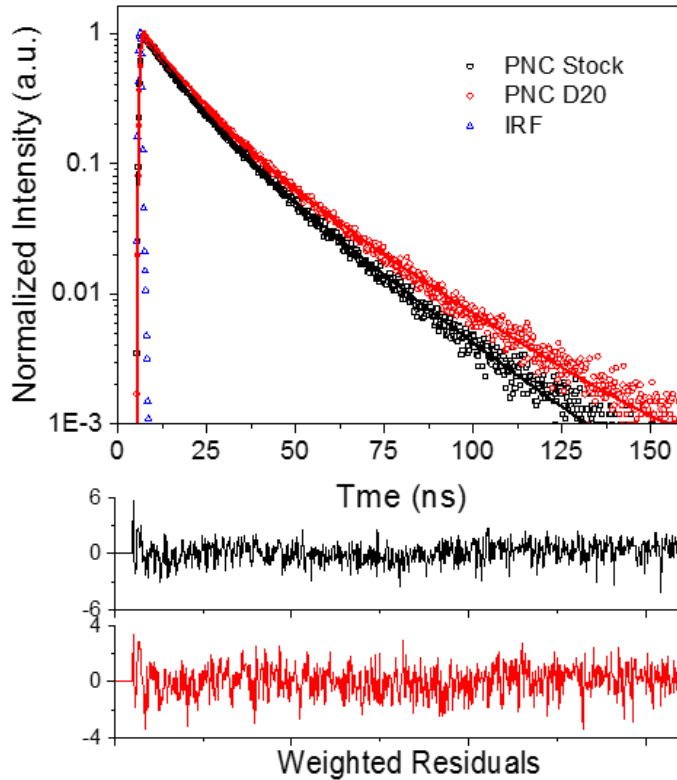


Figure 5.13. Emission decay curves (red circles and black squares), fits (solid lines) and instrument response function (IRF, blue triangles) for a standard $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{I}_x$ PNC solution in toluene upon excitation at 458 nm both before (black line, detection $\lambda_{\text{em}} = 525 \text{ nm}$) and after dilution by a factor D_{20} (red line, detection $\lambda_{\text{em}} = 560 \text{ nm}$). For each fit the residuals are also shown.

5.4 Conclusions

The spectral shifts and associated particle growth observed for $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{I}_x$ PNCs highlights one of the most pressing issues with the development of PNCs as a technology; the difficulty of morphological control. In this chapter attempts were made to fabricate mixed halide PNCs with a 2:1 $\text{Br}^-:\text{I}^-$ ratio using a LARP method. However, upon fabrication these PNCs were bright green emissive which indicated a negligible iodide content. It was demonstrated that dilution of as-prepared mixed halide $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{I}_x$ PNC solutions using a toluene antisolvent results in a red-shift in the emission maximum. Using a combination of STEM, EDX and DLS it can be concluded that this red-shift is due to uncontrolled growth of the PNCs to crystals with dimensions >100 nm almost instantaneously, over 24 h these particles grow to dimensions *ca.* 1 μm . The resultant crystals thus display PL properties of the bulk $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{I}_x$ perovskite and not those originally obtained (and desired) for quantum-confined nanocrystals.

To attempt to control the observed particle growth, high capping ligand concentrations were investigated. It was found that a slight blue-shift of the emission properties would occur for higher capping ligand concentrations up to a point at which, due to increased solubility of the CH_3NH_3 and Br^- in the antisolvent, the PNCs themselves would decompose. The weakly fluorescent particles remaining were identified as PbBr_2 NCs by PL spectroscopy and STEM. Upon dilution of these particles an increase in the emission intensity and a red-shift in the emission maximum were observed, indicating the same mechanism of growth occurs independently of capping ligand concentration.

Through variation of the reagents used in the precursor solution for a fixed halide ratio of *ca.* 2:1 $\text{Br}^-:\text{I}^-$, it was determined that a higher content of iodide on the surface through increased MAI concentration contributed to a greater change in the spectral properties. The excess iodide hydrogen bonded to the capping ligand was favourably incorporated upon particle growth. Alteration of the $\text{Br}^-:\text{I}^-$ ratio further elucidated the causes for the particle growth, with a 1:1 ratio precursor solution, indicating the formation of two populations upon dilution which, over time homogenise to one. A high bromide ratio (6:1) exhibited no red-shift in the emission maximum upon dilution, demonstrating the role of iodide in the observed emission behaviour. Similarly, by replacing the

toluene with chloroform, particle growth is arrested and a blue-shift of the emission maximum was obtained.

The significant drop in the Φ_{PL} and k_{R} upon dilution indicates that this method of tuning the emission is not attractive for device applications and raises an issue with the use of solution processed mixed-halide PNCs in these devices. This work has demonstrated that careful control over the antisolvent used is required to minimise any unwanted side reactions causing significant alteration of the morphology, optical properties and stability of the PNCs. For example, by focussing on solvents which will not dissolve the capping ligand, and in the synthetic procedure by either using all bromide/iodide PNCs or minimising the excess unwanted halides bonded to the capping ligands.

5.5 References

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Chapter Six

Establishing an Optical Characterisation Protocol for Large Area Luminescent Solar Concentrators

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6.1 Introduction

Chapter 1 highlighted the demand for technologies which can effectively harvest solar energy, in particular, the potential application of spectral conversion systems such as LDS (**Chapter 4**) and LSCs with emerging PV technologies has driven a renaissance in the field. LSCs, specifically, fulfil a distinct role due to their tunable transparency and colour which allow them to be used as solar harvesting windows or as other architectural features for BIPV technologies in an urban environment.¹⁻⁸ As has been highlighted in **Chapter 5** quantum-confined nanocrystals are highly attractive emitters for a variety of applications due to the possibility of tuning their photophysical properties through the careful variation of the materials and architectures employed. While PNCs are an attractive future prospect for use in spectral conversion technologies, they are still somewhat limited by their instability to different solvent environments. All-inorganic QDs have, however, shown great promise as LSC luminophores due to their stability and structural versatility, which enables judicious control of the band-gap,⁹ Φ_{PL} ¹⁰ and the Stokes' shift.¹¹ This tunability allows for spectral converters which can be tailored to the wavelengths of highest quantum efficiency for different solar cell architectures and also allows for tunable device colours for application in architectural features.

Recent research involving the use of QDs and nanocrystals as luminophores has been aimed at minimising optical losses in the LSC due to reabsorption by neighbouring fluorophores by tuning the Stokes' shift and bandgap. Erickson *et al.* recently demonstrated “zero-reabsorption” LSCs by utilising Mn²⁺-doped ZnSe/ZnS core-shell quantum dots as the luminophore.¹² Devices of 25 mm × 75 mm × 0.42 mm dimensions showed no luminescence reabsorption and optical quantum efficiencies of 37%. Transparent LSCs have been demonstrated using hexanuclear metal halide nanoclusters of the form M₆(II)X₁₂ (M = Mo, W, X = Cl, Br, I) encapsulated in poly(butyl methacrylate-co-methacrylate/poly(ethylmethacrylate) composites.¹³ These LSCs exhibit a Stokes' shift of 400 nm and effectively sensitise Si photovoltaics.

While these NC LSCs can show negligible reabsorption through Stokes' shift engineering, in larger area LSCs, with sizes representative of those needed for application in the built environment, the increased distance for the photons to travel means that other parasitic losses can

cause dramatic drops in concentration efficiencies.¹⁴ Despite these optical losses occurring commonly in LSCs, there have been few studies on how best to fabricate and characterise three-dimensional (3D) large-area QD-LSCs which more effectively represent practical-scale devices. Stokes' shift engineered core-shell CdSe/CdS nanocrystals were used by Meinardi *et al.* as luminophores for large-area (10 cm × 1.5 cm × 0.2 cm) QD-LSCs, which under A.M 1.5G illumination (100 mW cm⁻²) and, coupled with white diffusing reflectors along the long faces of the LSC, exhibited an optical concentration efficiency of ~10.2 %.⁴ The same group subsequently developed colourless LSCs (12 cm × 12 cm × 0.3 cm) employing heavy-metal free CuInSe_xS_{2-x} QDs embedded in a poly(laurylmethacrylate) and ethylene glycol dimethacrylate co-polymer (PLMA-co-EGDM) waveguide, which achieved an optical concentration efficiency of 3.2 % in the absence of light diffusers or reflectors.⁵ More recently, a similar PLMA-co-EGDM host was utilised by Rosei *et al.* to fabricate rectangular near-infrared LSCs (5 cm × 1.5 cm × 0.3 cm) utilising PbS/CdS core/shell QDs, with a reported optical efficiency of 6.1%.¹⁵

Though there have been recent examples of large-area Stokes' shift engineered QD-LSCs which have enabled reabsorption losses to be overcome to some extent, the lack of standardised characterisation methods to ensure reproducible reporting of the optical efficiency has become a limitation for these larger devices. The development of synthetic methodologies to enable the incorporation of high QD dopant concentrations and the design of 3D large-area prototypes of sufficient optical quality remain significant challenges for the realisation of larger QD-LSC devices. Moreover, as highlighted in **Chapter 1** and **Chapter 4**, LSCs and other spectral conversion approaches in general have been relatively overlooked for implementation with third generation photovoltaic devices. In particular there has been very few applications of LSCs with DSSCs.¹⁶⁻¹⁸

6.1.1 Aims

In this chapter a study into the optical characterisation of large-area green-emitting CdSe@ZnS/ZnS QD-LSCs with a composition gradient shell in a PLMA-co-EGDM matrix will be reported.¹⁹ CdSe@ZnS/ZnS QDs were selected as the luminophore due to both a high photoluminescence quantum yield (Φ_{PL} = 79-83 % in chloroform) and bright green fluorescence, which coincides with the maximum in the IPCE (incident-photon-to-current-efficiency) spectrum of

an N719 sensitised DSSC. The large area of these LSC devices ($10\text{ cm} \times 9\text{ cm} \times 0.3\text{ cm}$) means inhomogeneity in the optical power output along the edge of the LSC occurs. In this chapter several different methods for determining the optical output power of these LSCs will be presented for both full area and masked illumination and it will be demonstrated that extrapolation of the edge emission can lead to erroneous values of the optical efficiency for large-area devices, indicating the need for caution in these measurements and that masked illumination cannot reliably be used to characterise large area LSCs. The effect of the luminophore concentration on the optical efficiency of the QD-LSCs will be presented. The champion LSC will be incorporated with a thin strip DSSC and characterised.

6.2 Experimental

6.2.1 Synthesis and Purification of CdSe@ZnS/ZnS Quantum Dots

The synthesis and purification of the CdSe@ZnS/ZnS QDs was performed by Dr Finn-Purcell Milton, based on the procedure previously outlined by Lee *et al.*¹⁹ In a single step 0.42 mmol Cd(CH₃CO₂)₂ (0.1119 g) and 10.23 mmol ZnO (0.834g) were mixed with OY (21 mL) in a 200 mL three-neck round-bottom flask. The mixture was degassed at 150 °C for 30 min before it was placed under an argon atmosphere. Following this, 45 mL degassed 1-octadecene (ODE) was injected, and the solution was heated to 310 °C. Upon reaching at 310 °C, the (Se/S)-trioctylphosphine (TOP) solution (6 mL) was swiftly injected and 10 min was allowed to elapse to initiate the growth of CdSe@ZnS QDs. The (Se/S)-TOP stock solution was prepared by dissolving Se (15 mmol, 1.185 g) and S (15 mmol, 0.4809 g) in TOP (15 mL).

The ZnS shell was grown by injecting 0.1539 g of S (4.8 mmol) dissolved in ODE (7.2 mL) into the solution of CdSe@ZnS QDs at 310 °C, followed by a growth time of 12 min. Next, Zn acetate dihydrate (8.58 mmol, 1.575 g) was dissolved in a mixture of OY (3 mL) and ODE (12 mL) and injected into the reaction mixture at 310 °C, after which the temperature of reaction was lowered to 270 °C. Finally, 0.9483 g S (28.95 mmol) dissolved in TOP (15 mL) was added drop-wise at a rate of $\sim 0.5\text{ mL min}^{-1}$ and the growth of the additional ZnS shell continued at 270 °C for a further 20 min.

The CdSe@ZnS/ZnS QDs were precipitated by the addition of 1:5 MeOH:EtOH (100 mL) and separated through centrifugation (10 min, 4,000 rpm). The precipitate was then dissolved in a minimum volume of hexane, and re-precipitated using a 10:1 EtOH:MeOH mixture. This step was repeated twice. Following this, the precipitated QDs were then re-dispersed in a minimum volume of hexane, after which acetone was added to the sample giving a 1:1 ratio of acetone to hexane. The QDs were then separated from the solution using high-speed centrifugation (15,000 rpm) for 10 min. This step was repeated twice more. The QDs were dispersed in hexane (30 mL) and separated from solution *via* centrifugation at 15,000 rpm for 30 min. Finally, the QDs were then dissolved in hexane ready for use.

6.2.2 Fabrication of Large Area QD-LSCs

Fabrication of large area QD-LSCs was performed by Dr Lorcan. J. Brennan. The LMA-*co*-EGDM *co*-polymer host material was prepared by adding lauryl methacrylate (80 wt%) and ethylene glycol dimethacrylate (20 wt%) to a three-neck round-bottom flask under continuous stirring at room temperature. The photoinitiator, 2,2-dimethoxy-1,2-diphenylethan-1-one (IGACURE 651), was added to this solution at 1 wt%. This host solution was ultrasonicated for *ca.* 30 min to ensure adequate dispersion of the components throughout the mixture. The solution was then degassed under vacuum-assisted ultrasonication for 1 h to ensure removal of residual oxygen from the mixture.

A custom built mould was utilised to enable the fabrication of the large area (90 cm²) QD-LSCs reproducibly (**Fig. 6.1**). The mould consisted of a cavity created between two optically transparent glass plates. This cavity was sealed using a strip of poly(vinylchloride) (PVC) wire (*ca.* 4 mm thick), which acted as an impenetrable gasket. The spring-loaded clamps were used to hold the glass moulding plates in place. The pre-polymerised solution was injected into the cavity between the glass plates. Following injection, excess PVC gasket was used to seal the cavity; which ensured that the external atmosphere did not enter the cavity and quench the photopolymerisation reaction. Photopolymerisation was initiated by illuminating the top surface of the custom mould with UV radiation (366 nm) for up to 90 min with frequent inversion of the polymerisation chamber to ensure uniform illumination of the host polymerisation matrix through both faces. Upon completion of the reaction, the clamps were carefully removed from the glass plates, the PVC gasket was slowly

opened and the top glass plate removed from the moulding chamber. This allowed the freestanding LMA-co-EGDM slab to be removed, which was subsequently cured with UV radiation (366 nm) for an additional 30 min.

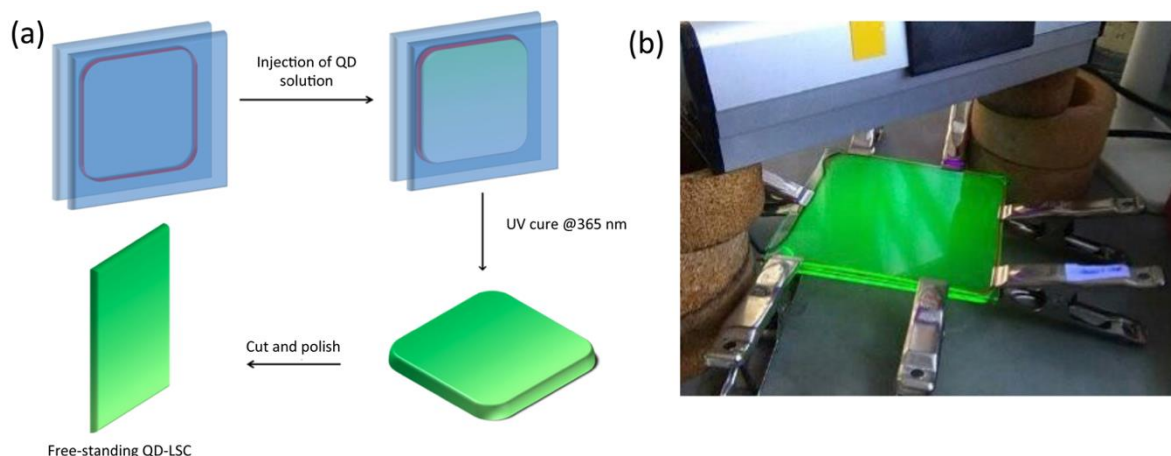


Figure 6.1. (a) Schematic representation of the fabrication procedure for a large-area QD-doped LSC. (b) Photographic image of the pre-polymerised solution encapsulated within the mould. (Figure prepared by Dr L. J. Brennan).²⁰

To fabricate the LMA-co-EGDM QD-LSCs the same curing procedure was employed. The QD hexane solutions were added to a vessel and the solvent was subsequently removed under vacuum. Pre-polymerised QD-LSC solutions were then prepared adding a volume of LMA (typically 40-50 mL) to the dry QDs to re-disperse them, with sonication to aid dissolution. To this mixture, EGDM and IGACURE-651 were added to make a 50 mL solution, which was then degassed with vacuum-assisted ultrasonication, and backfilled with argon before curing as described above.

6.2.3 Characterisation of QD-LSCs and QD-LSC-DSSCs

The optical power output (OP_{out}) of the LSCs was calculated as outlined in **Chapter 2**. A variety of irradiation and collection geometries were evaluated in order to effectively characterise these large area LSCs. The characterisation of the LSCs was performed under full AM 1.5G illumination by AAA-rated solar simulator with an irradiation area of 103.2 cm². Three geometries of the LSC and integrating sphere were investigated as described in **Section 6.3.2, Fig. 6.5**. Characterisation was then performed on the LSCs under masked illumination, with a black mask of aperture diameter 4 cm placed both in the centre of the LSC plate (3 cm distance from edge) and at

the LSC edge (2 mm distance from edge) and characterisation performed using the optimised configuration from **Section 6.3.2**.

Reabsorption losses were evaluated using a Class ABB solar simulator (Abet Technologies) equipped with an AM 1.5G filter and suitable for small area illumination in conjunction with the integrating sphere and spectroradiometer set-up described in **Chapter 2, Section 2.2.16**. A reference Si solar cell (ReRa Technologies) was used to calibrate the distance between the top face of the LSC and the illumination source until an illumination of 1 sun ($990 \pm 30 \text{ W m}^{-2}$) was obtained. A black mask was used to confine irradiation of the top surface to a single circular spot (diameter = 4 cm) which was systematically moved from the centre to the LSC to the edge to vary the optical path length. Relative reabsorption losses were determined from the integrated OP_{out} spectrum measured at the centre of a single edge using the 4 cm port on the IS. The optical scattering properties of the PLMA-co-EGDM slab were analysed using a collimated beam (diameter = 4 cm) of light centred at 750 nm, which was generated by attaching a 750 nm band pass filter (THOR Labs) to the output terminal of the same solar simulator. The optical path length was varied as described for the reabsorption loss measurements.

6.3 Results and Discussion

6.3.1 Characterisation of CdSe@ZnS/ZnS Polymer Composites

A modified hot-injection method was utilised to synthesise the CdSe@ZnS/ZnS QDs with a composition gradient shell. TEM measurements, performed by Dr F. Purcell Milton, revealed a monodisperse distribution of spherical nanoparticles. These QDs exhibit distinct lattice fringes, thus indicating a high degree of crystallinity (**Fig. 6.2a**). The mean particle diameter achieved was $12.9 \text{ nm} \pm 1.7 \text{ nm}$ ($n = 400$) (**Fig. 6.2b**), which is in good agreement with the literature.¹⁹

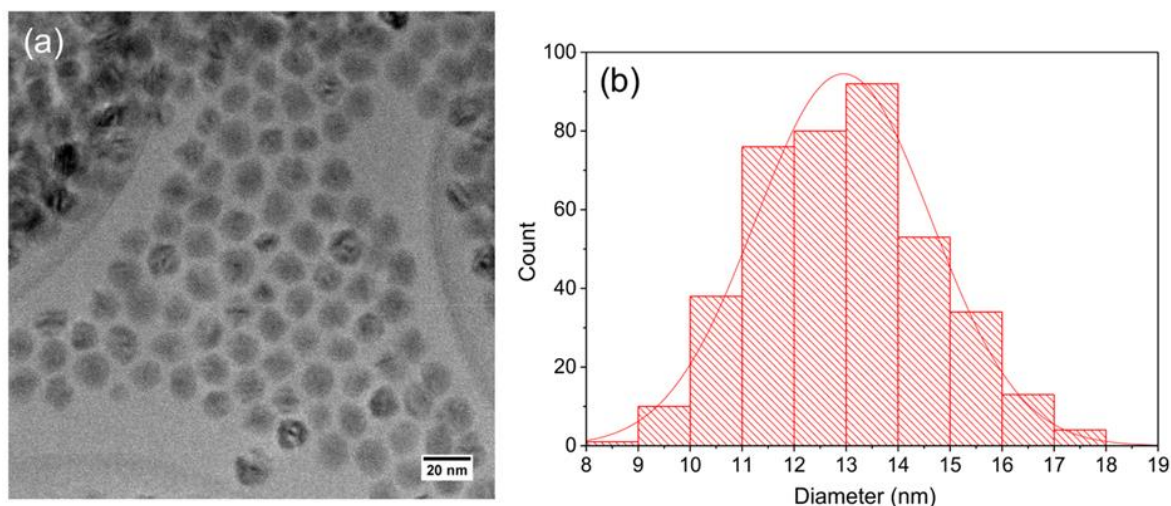


Figure 6.2. Size-characterisation of CdSe@ZnS/ZnS nanoparticles (a) Representative HRTEM image of CdSe@ZnS/ZnS nanoparticles and (b) histogram of the corresponding diameter of the nanoparticles as analysed by TEM using the ImageJ programme showing an average particle size of $12.9 \text{ nm} \pm 1.7 \text{ nm}$ ($n = 400$). The solid line represents a Schulz distribution fit to the data. (Figure prepared by Dr F. Purcell-Milton).²⁰

Fig. 6.3a shows the UV/Vis absorption and PL spectra of the CdSe@ZnS/ZnS QDs in hexane and embedded in the PLMA-co-EGDM host matrix ($\sim 2.5 \text{ mm}$ thick). The UV/Vis absorption spectrum exhibits two distinct features: firstly, a small excitonic band centred at 506 nm , assigned to absorption of the CdSe core, and second, a significantly more intense broad shoulder below 400 nm which can be attributed to the onset of absorption for the ZnS shell. The ZnS shell shows the broad absorption window of these QDs, the shoulder of which extends through the UVA to the UVB region to $\sim 300 \text{ nm}$ (**Fig. 6.3a**, inset). The position of the CdSe first excitonic band is slightly red-shifted (507 nm) upon incorporation of the QDs within the PLMA-co-EGDM host matrix. This shift is commonly observed when studying the optical absorption properties of nanostructured objects in the solid-state and is most commonly associated with optical scattering of the incident light.²¹ The moderate overlap between the absorption of the first excitonic band (CdSe) and the emission spectrum suggests that reabsorption processes may be expected in the resultant LSC devices.

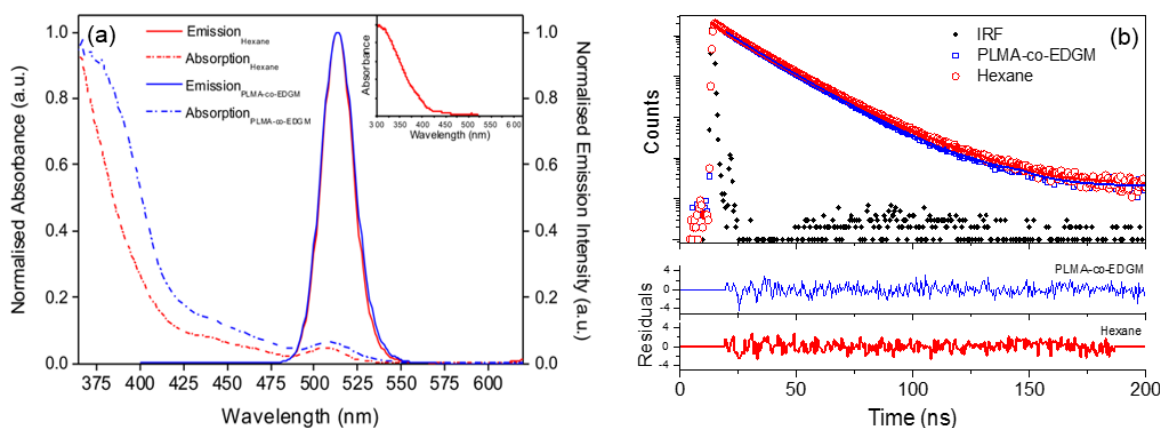


Figure 6.3. Optical characterisation of CdSe@ZnS/ZnS QDs. (a) UV/Vis absorption and steady-state PL spectra ($\lambda_{\text{ex}} = 350$ nm) of CdSe@ZnS/ZnS QDs dissolved in hexane (red dashed/solid line) and embedded in a PLMA-co-EGDM film (blue dashed/solid line). The inset highlights the broad absorption profile of the QDs with the observation window extended to 300 nm. (c) PL decay curves of CdSe@ZnS/ZnS QDs in hexane (open red circles), the PLMA-co-EGDM matrix (open blue squares) and the instrument response function (IRF, black diamonds). Emission and excitation wavelengths were $\lambda_{\text{em}} = 510$ nm and $\lambda_{\text{ex}} = 458$ nm, respectively. Solid lines show the corresponding fits and residuals to a biexponential decay functions. (Data measured by Dr F. Purcell-Milton)

As can be seen from **Fig. 6.3a**, the PL spectra for CdSe@ZnS/ZnS QDs appear identical in solution and the PLMA-co-EGDM matrix, exhibiting a narrow emission band centred at 513 nm and a full-width-half-maximum (FWHM) of 21.35 nm and 22.55 nm, respectively. The radical polymerisation process used to form the PLMA-co-EGDM matrix thus, does not significantly affect the optical characteristics of the QDs. The photoluminescence quantum yield was determined to be 65 ± 3.4 % for CdSe@ZnS/ZnS QDs dispersed in hexane (**Appendix, Table A6.1**). The excited-state decay kinetics of the CdSe@ZnS/ZnS QDs were further investigated by examining the PL lifetime dynamics. Almost identical emission decay curves were obtained for CdSe@ZnS/ZnS QDs in hexane and the PLMA-co-EGDM matrix (**Fig. 6.3b**). As for the PL spectra, the decay curves appeared almost identical for the CdSe@ZnS/ZnS QDs in solution and the PLMA-co-EGDM matrix. Both decays were fitted with a biexponential function, yielding observed lifetimes of $\tau_1 = 9.8 (\pm 0.2)$ ns and $\tau_2 = 14.9 (\pm 0.1)$ ns in the polymer composite, and $\tau_1 = 10.6 (\pm 0.2)$ ns and $\tau_2 = 16.2 (\pm 0.1)$ ns in solution. The deposition of CdSe@ZnS/ZnS QDs as a 40 nm-thick film has previously been shown to result in a significant reduction in the observed lifetime (27.2 ns and 9.2 ns in solution and the film respectively), which was attributed to the introduction of additional non-radiative processes such as energy transfer and/or the exposure to an inhomogeneous environment.¹⁹ The observed

comparable decay dynamics between the CdSe@ZnS/ZnS QDs in solution and in the solid PLMA-co-EGDM matrix confirm the absence of additional non-radiative decay channels, indicating that the excitonic emission is neither affected by the dispersion of the CdSe@ZnS/ZnS QDs within the polymer composite nor by the action of the radical initiator used to form it. The PL decay curve for QDs in the PLMA-co-EGDM matrix was recorded for a sample that was stored in a pre-polymerised solution mixture for six weeks prior to polymerisation and characterisation, highlighting that the QDs are stable in the presence of the copolymer and the initiator for extended time periods.

6.3.2 Characterisation of Large Area QD-LSCs Under Full Illumination

To evaluate the potential of CdSe@ZnS/ZnS core-shell QDs as luminophores for LSCs, seven large area devices (10 cm × 9 cm × 0.3 cm) were fabricated, in which the QD loading was varied between 0-0.9 wt%. PLMA-co-EGDM (80:20 wt%) was chosen as the polymer waveguide as it both minimises QD aggregation in the matrix, a problem often observed with hosts such as PMMA and allows for facile design of QD-loaded polymer slabs, which retain high optical quality. **Fig. 6.4** shows the high optical transparency of the CdSe@ZnS/ZnS LSCs under standard indoor illumination conditions (**Fig. 6.4a**) and across the visible spectrum (88% transmittance (%*T*) at 550 nm, **Fig. 6.4b**). This property is crucial for the application of such devices in BIPV and for the development of smart solar windows, which allow transmitted light to be used for indoor lighting or secondary solar harvesting applications. **Fig. 6.4c** shows the green concentrated emission from the CdSe@ZnS/ZnS QD-LSCs which can clearly be observed from the slab edges upon illumination at 365 nm. The intensity of the QD emission increases with the concentration of QDs incorporated within the LSCs (0.15 - 0.90 wt%).

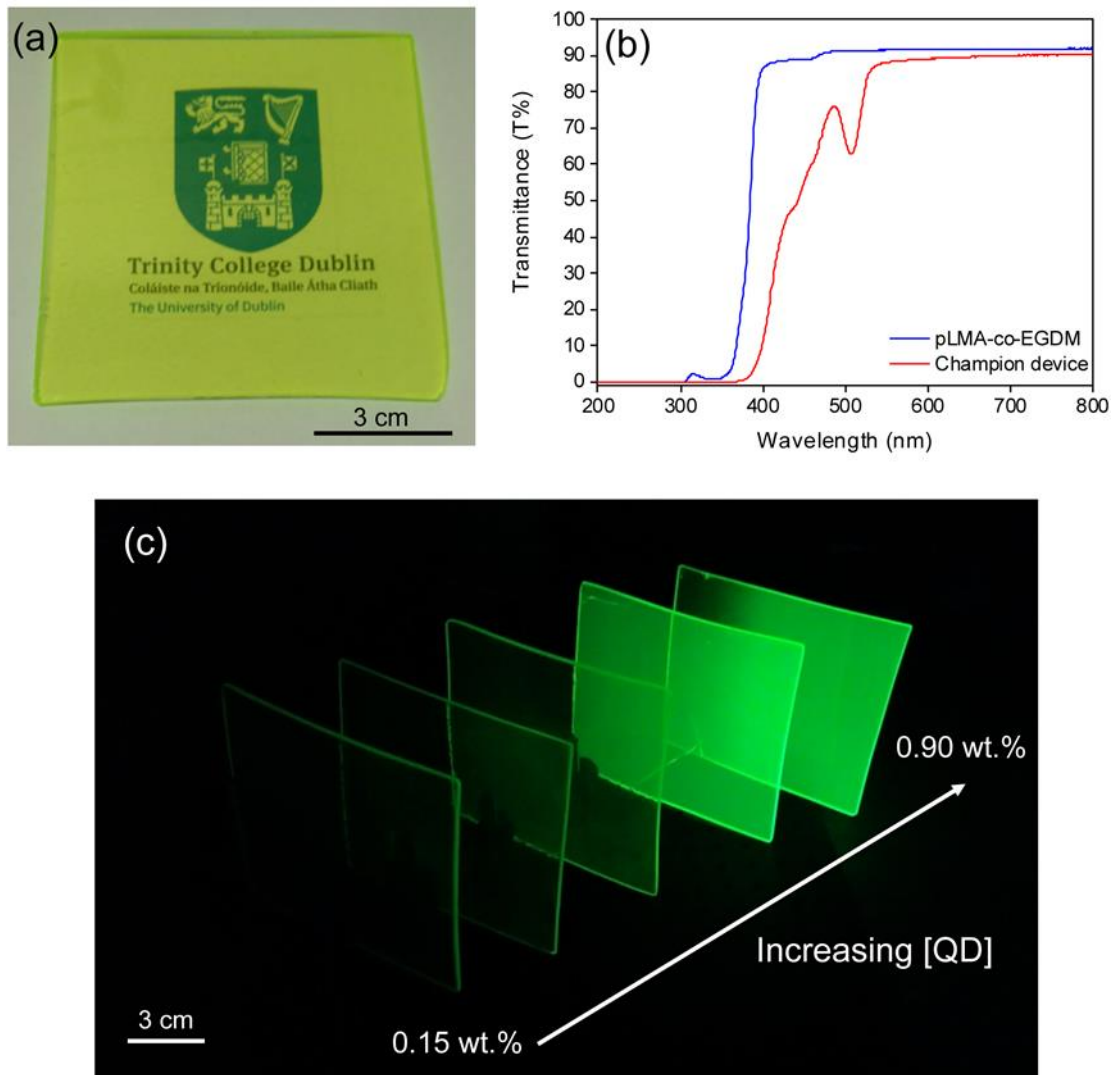


Figure 6.4. Optical properties of CdSe@ZnS/ZnS-LSCs. (a) Optical image of a QD-loaded LSC under standard indoor lighting conditions. (b) Optical transmission of an undoped PLMA-co-EGDM slab (ca. 3 mm thick) and CdSe@ZnS/ZnS-LSC (0.9 wt%, ca. 2.5 mm thick). (c) Optical concentration of emitted light by freestanding large area (10 cm × 9 cm × 0.3 cm) CdSe@ZnS/ZnS-LSCs as a function of luminophore dopant concentration (0.15 – 0.90 wt%) under illumination at 365 nm. (Figure prepared by Dr L. J. Brennan).²⁰

As highlighted in **Chapter 1**, the performance of LSCs is typically quantified on the basis of the optical conversion efficiency (η_{opt}), which can be determined experimentally by measuring the OP_{out} and dividing by the total power input (OP_{in}):

$$\eta_{\text{opt}} = \frac{OP_{\text{out}}}{OP_{\text{in}}} \quad (1.3)$$

OP_{out} is obtained by summing the total power output of the four edges of the LSC and OP_{in} is the incident irradiance in W m^{-2} by the illuminated top area of the LSC. While η_{opt} is currently used to characterise LSCs throughout the literature, there is no standardised protocol for experimentally-

determining it, which can make it challenging to benchmark the performance of devices between research groups.²¹ Similarly, experimental approaches which work well for small scale prototypes may not be directly applicable to larger devices. **Fig. 6.5** shows a schematic representation of the three experimental configurations used to characterise these LSCs. All measurements were performed using a dark background, without the use of reflective foil or scattering background to reflect photons emitted outside of the escape cone back into the waveguide for recycling.

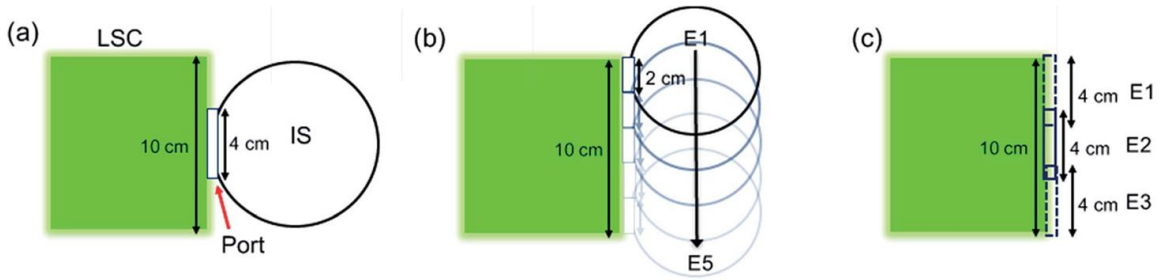


Figure 6.5. Top view of the different experimental geometries used to collect edge emission from QD-LSCs. The entire top surface of the LSC is irradiated with AM 1.5G solar simulated light. In (a) the edge emission is collected at the centre of the LSC using a 4 cm port to the IS. The integrated OP_{out} (250-1050 nm) value is extrapolated to estimate a value for the full edge length (9 or 10 cm). (b) OP_{out} spectra are collected using a 2 cm port, across the full edge length by moving the IS at 2 cm intervals. The integrated OP_{out} (250-1050 nm) at each interval is summed to give the total edge OP_{out} . (c) OP_{out} spectra are collected across the full edge length using three overlapping intervals (4 cm). The mean integrated OP_{out} (250-1050 nm) is determined and extrapolated to estimate a value for the full edge length (9 or 10 cm).²⁰

As depicted in **Fig. 6.5**, an integrating sphere coupled to a spectroradiometer was used to measure the optical power output at each edge of the LSC, an approach which is used by a number of research groups.^{21–23} A limitation of this method is that the collection area is restricted by the size of the entry port to the IS, thus, larger LSCs would require a prohibitively large IS. In this section, the variety of collection geometries given in **Fig. 6.5** have been evaluated for large area LSCs under full area AM 1.5G illumination, in order to explore both the inhomogeneity of the concentrated emission across the edge length and the consequences of this on the subsequently calculated η_{opt} value.

6.3.2.1 Single Measurement Extrapolation

In the first configuration, the entire top surface of the LSC was irradiated with calibrated solar simulated light ($OP_{in} = 9000$ mW over the 90 cm^2 top surface) and the emission was collected from the centre of the edge using a 4 cm entry port on the IS (**Fig. 6.5a**). The obtained spectra shown in **Fig. 6.6** were integrated between 250-1050 nm to give the power output measured from the centre 4 cm of the LSC edge. This obtained value was then extrapolated for the entire edge length of each of the four sides of the LSC (38 cm) to give the total OP_{out} . This can be expressed by:

$$OP_{out} = (OP_{measured}/4) \times 38 \quad (6.1)$$

The edge outputs shown gave values of η_{opt} which showed very little difference for concentrations from 0 to 0.55 wt% with values only ranging from 0.46–0.67%. The peak corresponding to the CdSe@ZnS/ZnS QDs exhibited low intensity for these samples, thus, the emission behaviour of these samples is similar to the blank. This means slight differences in thickness or roughness of the edge can alter the total output significantly. These variations in the edge are compounded by the fact the extrapolations were only based on one area of the four LSC edges. This method resulted in an efficiency η_{opt} of 1.2% for the 0.7 wt% sample and 1.3% for the 0.9 wt% samples, which due to the high intensity QD emission were more reliable than the low concentration samples. This characterisation method however, can be considered an overestimation, as LSCs have been demonstrated to emit non-uniformly across the slab edge, with output varying between the centre and edges by up to 20%.^{7,24,25} Greater luminophore doping led to incomplete polymerisation of the PLMA-co-EDGM host matrix, thus 0.9 wt% was the highest concentration attempted.

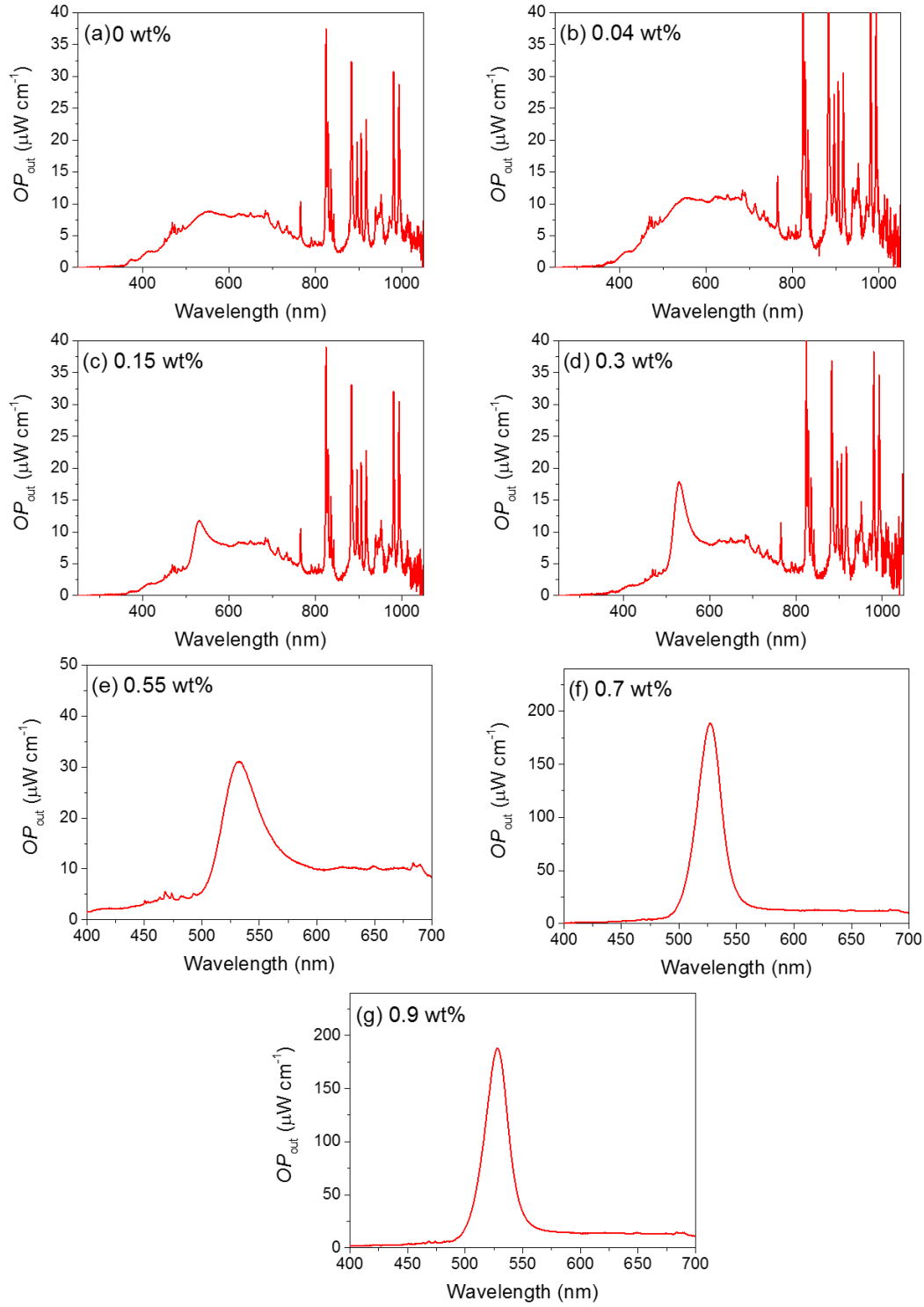


Figure 6.6. Edge emission spectra obtained for the QD-LSC samples obtained using configuration 1, whereby, one 4 cm port measurement was taken in the centre of the LSC edge. These spectra were then integrated between 250 and 1050 nm and extrapolated to estimate a value for the full edge length (38 cm). (a) 0 wt% sample, ($OP_{out} = 41.2$ mW). (b) 0.04 wt% sample, ($OP_{out} = 53.4$ mW). (c) 0.15 wt% sample, ($OP_{out} = 41.3$ mW). (d) 0.3 wt% sample, ($OP_{out} = 46.4$ mW). (e) 0.55 wt% sample, ($OP_{out} = 59.9$ mW). (f) 0.7 wt% sample, ($OP_{out} = 108.6$ mW). (g) 0.9 wt% sample, ($OP_{out} = 117.0$ mW)

6.3.2.2 Full Edge Measurement

To prevent the overestimation and errors outlined above a second geometry was investigated, in which, the emission was collected across the entire edge length through successive measurements, at consecutive increments, using the 2 cm entry port on the IS (**Fig. 6.7**); OP_{out} for a single edge was obtained from the sum of the integrated optical power obtained at each interval, the total OP_{out} was obtained by summing the values of the individual sides of the LSC.

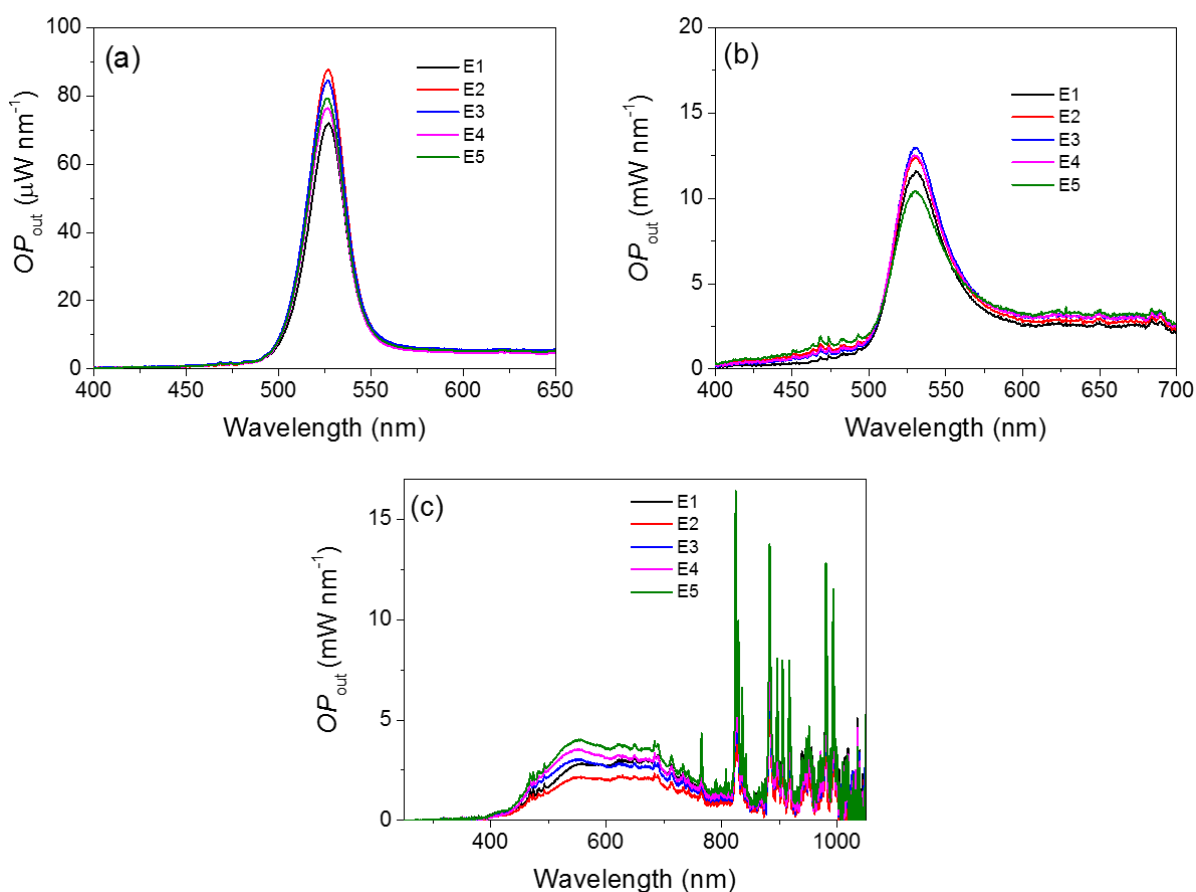


Figure 6.7. Representative OP_{out} spectra obtained for a single edge of the CdSe@ZnS/ZnS LSCs using configuration 2. The entire top surface of the LSC is irradiated with AM 1.5G solar simulated light. OP_{out} spectra are collected across the full edge length by moving the IS at 2 cm intervals for (a) 0.7 wt%, (b) 0.55 wt% and (c) 0 wt%. The integrated OP_{out} (250-1050 nm) at each interval is summed to give the total edge OP_{out} .

When using this configuration, it became apparent that the emission is inhomogeneous across the edge length as predicted, with the maximum intensity typically occurring at the centre of the LSC edge, which drops off as the entry port is moved towards the edge extremity. This geometry gave an OP_{out} value 83% of that determined through the first configuration for the 0.7 wt% sample,

thus resulting in an efficiency η_{opt} of 1%. To confirm this discrepancy between the measured and extrapolated value the same method was investigated for the 0.55 wt% sample and the 0 wt% sample (**Fig. 6.7c,d**). In the 0.55 wt% sample the variation between the extrapolated and measured value was more pronounced than the 0.7 wt% sample, giving η_{opt} values of 0.67% and 0.35% respectively. The 0 wt% sample showed similar differences in the measured OP_{out} with the measured full edge sum only totalling 26.3 mW, 63% that of the extrapolated value. While the measurement geometry used in **Fig. 6.7** is undoubtedly more accurate than the extrapolation method used in **Fig. 6.6**, fluctuations in the measured power output were also observed using this configuration. Notably, for the same edge region, the sum of the emission measured consecutively using the 2 cm port twice led to a significantly lower output compared to a single measurement performed using the 4 cm port at the same edge location. This is understandable, since accurate alignment of the port to perform sequential measurements proved difficult. This factor, coupled with increased number of measurements required when using the smaller port, inherently leads to a greater systematic error in the data obtained using this approach.

6.3.2.3 Average Edge Emission Measurement

To address the shortcomings of the first two measurement configurations, a third method was investigated. In this final arrangement, the edge output was collected across the entire length, with 3 overlapping intervals using the 4 cm entry port (**Fig. 6.5c**). These measurements were used to determine the mean integrated optical power for a 4 cm slice of the edge and this was extrapolated to obtain OP_{out} for the full edge length (9 or 10 cm). The geometry illustrated in **Fig. 6.5c** overcomes the limitations of the previous configurations by taking into account the non-homogeneity of the emission across the edge, while eliminating the systematic errors introduced by using the smaller port. The graphs obtained from using this configuration for all four sides of the 0.7 wt% sample are presented in **Fig. 6.8**, giving a total OP_{out} of 106.25 mW and thus an η_{opt} of 1.18%. The calculated η_{opt} values obtained for all CdSe@ZnS/ZnS LSCs as a function of luminophore concentration using this approach are presented in **Table 6.1** (see **Appendix, Fig. A6.1–A6.6** and **Table A6.2** for edge-emission spectra for remaining LSC samples and calculations, respectively). At low QD concentrations (<0.55 wt%), η_{opt} is comparable within experimental error. However, as the QD

loading is increased further, η_{opt} also increases reaching a maximum value of 1.22% for a loading of 0.9 wt%. The increase in η_{opt} with QD concentration suggests that the threshold for η_{opt} is not yet achieved at the dopant concentrations studied and that any decrease in the optical efficiency due to reabsorption is determined primarily by the intrinsic spectral overlap integral of the luminophore rather than the nearest neighbour distance. It must be noted, however, that higher dopant concentrations lead to incomplete polymerisation of the PLMA-co-EGDM matrix, even with extended curing time.

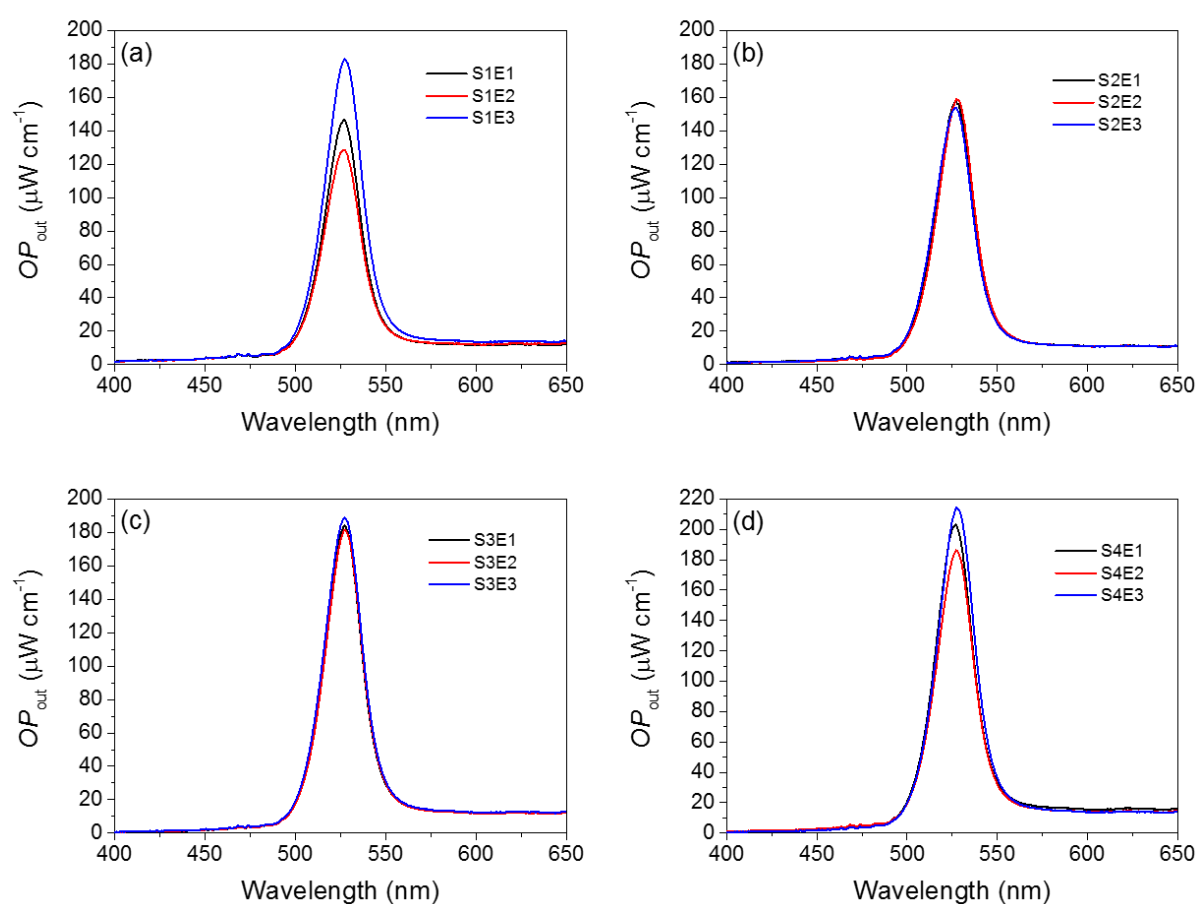


Figure 6.8. Edge emission obtained for the 0.7 wt% QD-LSC sample obtained using configuration 3, whereby, three overlapping 4 cm port measurements were taken across the edge of the LSC (E1/E2 = corner, E3 = centre). The mean integrated OP_{out} (250-1050 nm) is determined and extrapolated to estimate a value for the full edge length (9 or 10 cm). (a) Side 1 $OP_{\text{out}} = 27.6$ mW, (b) Side 2 $OP_{\text{out}} = 22.3$ mW, (c) Side 3 $OP_{\text{out}} = 27.8$ mW and (d) Side 4 $OP_{\text{out}} = 28.6$ m.

Table 6.1. Optical efficiencies (η_{opt}) obtained for CdSe@ZnS/ZnS LSCs under 1 sun illumination. OP_{out} is the sum of the optical power measured for each edge as described in the text.

QD concentration (wt%)	OP_{out} (mW) ^a	η_{opt} (%) ^b
0	46.0	0.51
0.04	47.9	0.53
0.15	48.4	0.54
0.30	50.8	0.56
0.55	56.9	0.63
0.70	106.3	1.18
0.90	109.8	1.22

^a Sum of OP_{out} measured for each edge using the arrangement shown in Figure 6c. ^b Determined from Eqn. 1 using $OP_{\text{in}} = 9000 \text{ mW}$ ($90 \text{ cm}^2 \times 100 \text{ mW/cm}^2$).

As described in **Chapter 1** LSCs can be typically characterised by several figures of merit including G , the geometric gain factor (**Eqn. (1.2)**)^{6,26} and F , the concentration factor (**Eqn. (1.4)**).²⁶ A value of $G = 7.9$ is obtained for the CdSe@ZnS/ZnS LSCs fabricated in this work, with a max. $\eta_{\text{opt}} = 1.22\%$. This corresponds to a concentration factor of $F = 0.10$. For comparison, the recent work by Zhou *et al.* reported an η_{opt} of 6.1% for a PbS/CdS-doped QD-LSC, where $G = 2.14$ if the contribution from all 4 edges of the slab is considered, and $F = 0.15$.¹⁵ Similarly, using the same approach for the CdSe/CdS LSC reported by Meinardi *et al.*, a G value of 1.22 is obtained and $\eta_{\text{opt}} = 10.2 \%$, with $F = 0.12$.⁴ Large area, planar LSCs have also been fabricated by Meinardi *et al.* utilising $\text{CuInSe}_x\text{S}_{2-x}$ QDs, with a reported efficiency of $\eta_{\text{opt}} = 3.2\%$ when $G = 10$, leading to $F = 0.32$.⁵

6.3.3 Characterisation of Large Area QD-LSCs Under Masked Illumination

While characterisation of LSCs under full illumination is undoubtedly the most accurate method of characterisation, it may not be possible as research moves towards large area LSCs. In this section the CdSe@ZnS/ZnS QD LSCs were masked and characterised, to observe if through masking any comparable results to full illumination can be obtained. The LSCs were masked using a circular aperture (diameter 4 cm), both in the centre of the LSC (3 cm from the edge) and at the edge of the LSC (*ca.* 2 mm from LSC edge). The masked samples were then characterised using configuration 3 outlined above. The masked samples tested were 0 wt%, 0.55 wt% and 0.7 wt%. **Fig.**

6.9 shows representative single-edge emission for the LSCs masked at 3 cm from the edge using configuration 3.

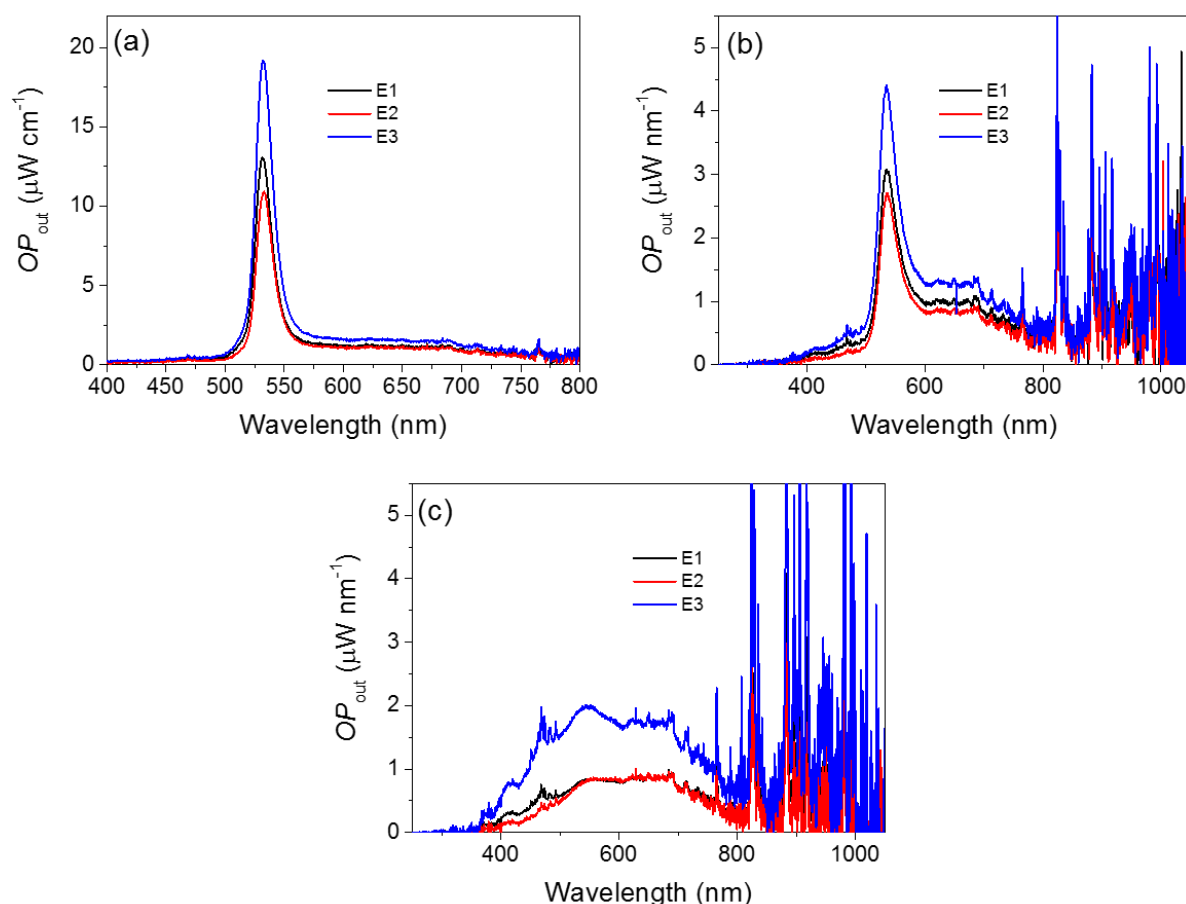


Figure 6.9. Representative OP_{out} spectra obtained for a single edge of the CdSe@ZnS/ZnS LSCs using configuration 2. The top surface of the LSC was masked with an aperture 4 cm diameter in the centre, 3 cm from the edge and irradiated with AM 1.5G solar simulated light. OP_{out} spectra are collected across the full edge length sample using configuration 3, whereby, three overlapping 4 cm port measurements were taken across the edge of the LSC (E1/E2 = corner, E3 = centre). (a) 0.7 wt%, (b) 0.55 wt% and (c) 0 wt%.

The OP_{out} calculated for the single edge shown in **Fig. 6.9a** representing the 0.7 wt% sample was *ca.* 2.2 mW, over ten times less than the average edge output under full illumination (26.6 mW). If we extrapolate this value across all four edges of the device and divide by $OP_{in} = 1257 \text{ mW}$ ($\pi r^2 \times 100 \text{ mW/cm}^2$) an η_{opt} of 0.65% is obtained. This value is only 55% of the η_{opt} achieved with full illumination, indicating that the transport losses due to self-absorption by the luminophores and waveguide losses are limiting the effectiveness of the LSC. If we compare the efficiencies obtained for the 0.55 wt% and 0 wt% samples contribution of the CdSe@ZnS/ZnS QDs to these optical losses can be approximated, for example, in the 0 wt% sample any transport losses are due to the

waveguide. The 0 wt% and 0.55 wt% samples showed efficiencies of 0.43% and 0.47%, respectively, which corresponds to 84% and 74% of the values obtained under full illumination. It can thus be demonstrated that the transport losses related to luminophore reabsorption increase with concentration, and that for the 3 cm propagation distance only a *ca.* 16% loss in η_{opt} is due to the waveguide material itself.

Fig. 6.10 shows the obtained edge output spectra for the CdSe@ZnS/ZnS QD LSCs masked with a 4 cm diameter aperture, 2 mm from the waveguide edge. The OP_{out} of these spectra at Edge 3 (waveguide centre) are considerably higher than when masked at 3 cm from the edge. It was observed that the emission spectra measured for the 0.7 wt% (shown in **Fig. 6.10a**) exhibited a higher intensity output for the two measurements taken at the corners of the slab than the centre measurement in **Fig. 6.9a**. Considering losses in η_{opt} are directly related to the propagation distance of the light through the LSC (3 cm for centre illumination vs <3cm for E1, E2 at 2mm illumination) this is as expected. By applying the same approximations to calculate the efficiency as performed on the sample masked at 3 cm from the slab edge, we obtain η_{opt} values of 0.92, 1.02 and 1.84% for the 0, 0.55 and 0.7 wt% samples respectively. These are impossibly high as they assume homogeneous emission across all 4 edges despite the illumination only occurring near one side, with no loss mechanisms through transport across the slab considered. Without further consideration of the transport losses which occur in the LSC plates masked illumination cannot approximate the emission of the plate under full illumination.

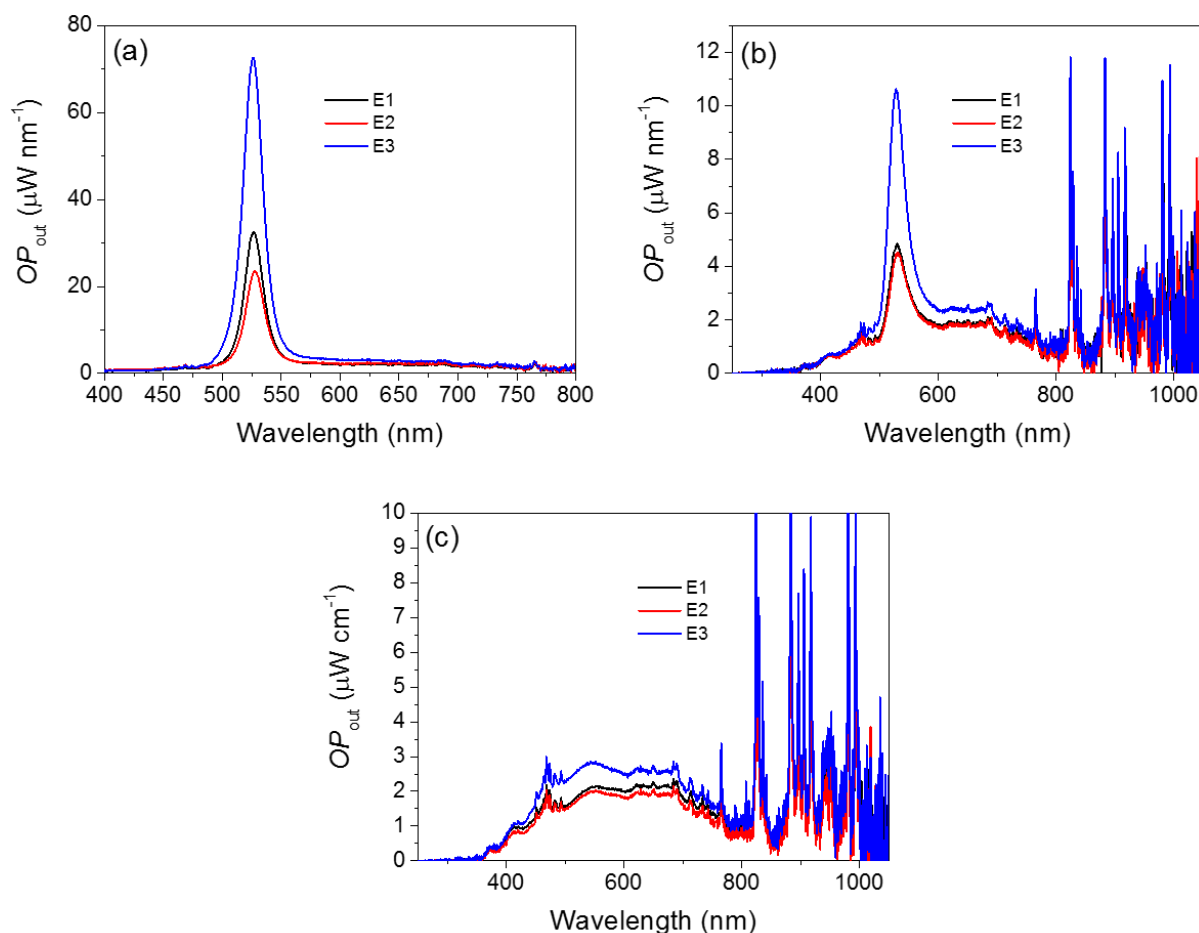


Figure 6.10. Representative OP_{out} spectra obtained for a single edge of the CdSe@ZnS/ZnS LSCs using configuration 2. The top surface of the LSC was masked with an aperture 4 cm diameter, *ca.* 2 mm from the edge and irradiated with AM 1.5G solar simulated light. OP_{out} spectra are collected across the full edge length sample using configuration 3, whereby, three overlapping 4 cm port measurements were taken across the edge of the LSC (E1/E2 = corner, E3 = centre). (a) 0.7 wt%, (b) 0.55 wt% and (c) 0 wt%.

6.3.4 QD-LSC Optical Loss Mechanisms

The observed overlap between the absorption and emission spectra of the CdSe@ZnS/ZnS QDs (**Fig. 6.3a**) means that there will be reabsorption losses occurring in the QD-LSC devices which will limit the optical efficiency achievable. However, it is likely that other intrinsic loss mechanisms will similarly limit the efficiency achieved, particularly light scattering by the embedded QDs and imperfections present in the host matrix will also affect the device performance. The large distances for photons to travel in the QD-LSCs fabricated means that these scattering losses are more likely to occur than in smaller LSCs. By determining the magnitude of the transport losses for masked illumination at increasing distances the efficiencies under full illumination can potentially be

approximated. **Fig. 6.11** shows the influence of reabsorption and scattering losses to the champion CdSe@ZnS/ZnS-LSC output.

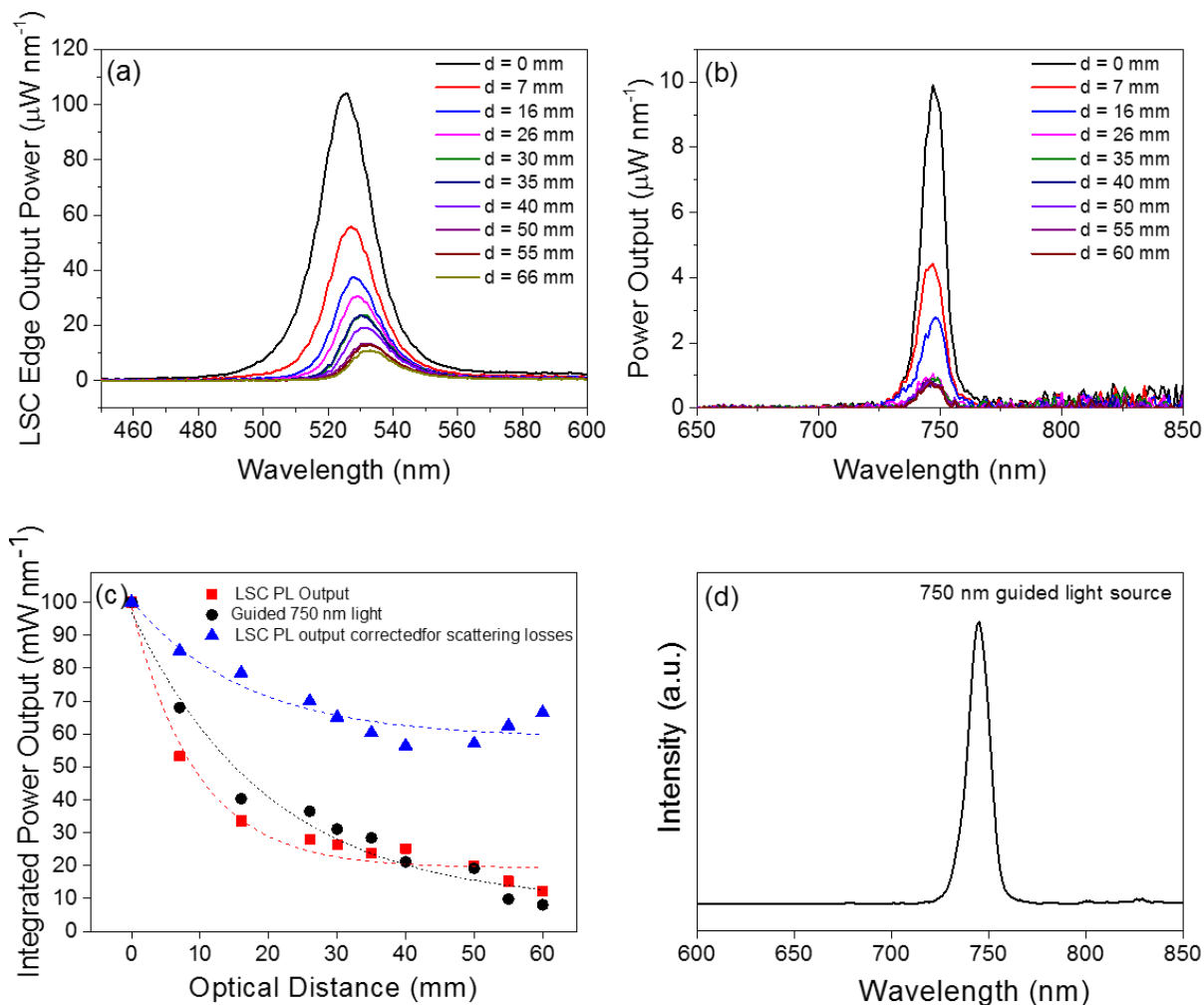


Figure 6.11. Determination of reabsorption and scattering losses in the champion CdSe@ZnS/ZnS-LSC (0.9 wt%). (a) Optical power output (OP_{out}) at the centre of a single edge ($4.0 \text{ cm} \times 0.3 \text{ cm}$) as a function of distance, d , from the illumination site under irradiation with solar simulated light (1 sun). A red shift (525 – 530 nm) and decrease in optical power was observed with increasing d due to the reabsorption of emitted photons. (b) Optical power output under the same measurement conditions using guided 750 nm light. A decrease in optical power was observed but no red-shift with increasing d using this irradiation source. (c) Intensity normalised decay of the integrated optical power output as a function of d under 1 sun illumination (red squares) and using 750 nm guided light (black circles). The calculated integrated optical power output corrected for scattering losses (blue triangles) is also shown. The dashed lines represent an exponential fit to the data. (d) Spectral profile of the 750 nm source used for the guided light experiments. (Data measured by Dr L. J. Brennan).

Reabsorption losses were determined by illuminating a spot of diameter 4 cm on the LSC surface and measuring the OP_{out} at the centre of a single edge for the LSC as a function of the optical path length from the irradiation spot, d , under 1 sun illumination. As d increases, the PL output gradually decreases and a slight red-shift in the emission maximum (from 525 nm to 530 nm) is

observed up to $d = 30$ mm (**Fig. 6.11a**). At distances greater than 30 mm the position of the emission maximum is unchanged suggesting that losses due to reabsorption become saturated at this point. Any subsequent losses in the OP_{out} observed are thus related to scattering and other optical losses.

If the LSCs are illuminated with monochromatic light at wavelengths longer than the absorption wavelengths of the CdSe@ZnS/ZnS QDs scattering losses can be isolated from those due to reabsorption. In these measurements the optical edge output of the LSCs was also monitored as a function of distance, using monochromatic light centred at 750 nm. Since CdSe@ZnS/ZnS QDs do not absorb at this wavelength (**Fig. 6.3a**), any losses in the optical output can be attributed to scattering from either polymer matrix defects and/or the QDs. As with the previous optical loss measurements a decrease in the OP_{out} was detected with increasing optical path length (**Fig. 6.11b**). However, the red-shift in the emission maximum was no longer observed, confirming that reabsorption effects are negligible in this wavelength region.

Under both illumination conditions (1 sun or 750 nm), the optical power decays exponentially with increasing distance from the illumination point, decreasing to ~10-15 % of the initial power output for $d > 50$ mm. The contribution of reabsorption to the optical efficiency can therefore be isolated by subtracting for scattering losses at a given d , as shown in **Fig. 6.11c**. Using this approach reabsorption losses are estimated to be ~40% at optical distances up to 65 mm from the irradiation centre. By multiplying the normalised transport losses as a function of distance by the OP_{out} values determined by masked illumination in the LSC centre in **Fig. 6.9a**, we can approximate the efficiency of the 0.7 wt% device under full illumination conditions. At distances of 3 cm and 4 cm (approximately the distance from the illumination spot to the centre of E1 and E2) the OP_{out} is *ca.* 30% of the initial value. If the OP_{out} measured for the centre edge of **Fig. 6.9a** (OP_{out} E3 = 1.01 mW) is divided by 30% the value obtained is 3.36 mW which is almost identical to the measured value at 2 mm distance for **Fig. 6.10a** (OP_{out} E3 = 3.35 mW). By multiplying the values for the E1 and E2 measurements an η_{opt} of *ca.* 2% resulted, this is an overestimation, thus, further indicating it is non-trivial to determine the η_{opt} of an LSC using masked illumination and to accurately calculate the efficiencies the geometry of the measurement position in relation to the illumination spot has to be considered.

6.3.5 Integration with Third Generation Photovoltaic Technologies

For an LSC to operate effectively as an energy-harvesting device, the LSC needs to be coupled with an appropriate solar cell. Ideally, the solar cell attached will exhibit a high quantum efficiency in the wavelength range of the emission from the LSC luminophore and thus, the light edge emitted from the LSC edges will be more effectively utilised than a similar irradiance of white light, producing a maximum possible photocurrent. Predominately the literature is focussed on examples of LSCs coupled to Si based PV cells due to the ubiquitous use of that technology presently.^{2,27,28} This reliance on Si, however, has meant that few attempts have been made at coupling LSCs to other classes of PV cells. This is most likely due to the limited exploration of LSCs containing luminophores whose emission properties are compatible with the spectral response of third generation PV technologies such as DSSCs and PSCs and also the challenge of fabricating prototypes of such devices in architectures compatible with LSCs. For example, Peng *et al.* have reported on the integration of fibre DSSCs (FDSC) with commercially-available LSCs, demonstrating an increase in efficiency for the FDSCs coupled to both red- and green-emitting LSCs.^{17,18} Further attempts have been made at increasing the short-circuit current density of DSSCs with the use of LDS.^{29–32} As highlighted in **Chapter 4** LDS layers have been successfully integrated in perovskite solar cells, whereby unabsorbed UV light is down-shifted to optical frequencies that can be harnessed by the absorber to improve both the stability and the efficiency.^{33,34} There are as of yet no examples of LSCs coupled to perovskite cells.

In an effort to address this gap, a CdSe@ZnS/ZnS LSC has been integrated with a thin-strip DSSC to demonstrate proof-of-concept viability of this approach. The champion LSC (0.9 wt%, $\eta_{\text{opt}} = 1.22\%$) exhibits an emission maximum centred at 520 nm in the single edge optical power output spectrum (**Fig. 6.12a**). This λ_{em} is almost perfectly matched with the IPCE maximum recorded for an N719-sensitised DSSC (1 cm $\times$ 1 cm), where N179 is the commonly used sensitizer dye di-tetrabutylammonium cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4' dicarboxylato)ruthenium(II).^{35,36} The optical power obtained from an undoped LSC (*i.e.* a blank PLMA-co-EGDM slab of the same dimensions) is also shown for comparison and confirms that the waveguide host makes zero contribution to the optical output of the slab in the visible region.

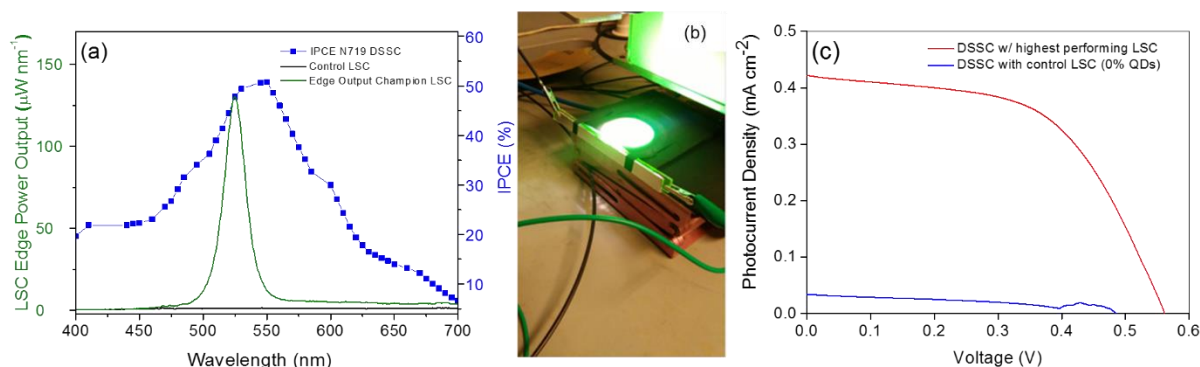


Figure 6.12. Characterisation of an integrated CdSe@ZnS/ZnS-LSC-DSSC device. (a) Edge emission for the champion LSC device (green) and an undoped PLMA-co-EGDM slab (black) and the IPCE spectrum of an N719 DSSC. All measurements performed under 1 sun illumination with an edge area of $0.4 \times 0.3 \text{ cm}^2$ for the LSCs. (b) Photograph of the integrated CdSe@ZnS/ZnS-LSC-DSSC device. (c) Current-voltage characteristics of the DSSC obtained following illumination of either the champion LSC (red) or a control device (undoped PLMA-co-EGDM slab, blue). (Data measured by Dr L. J. Brennan).²⁰

To quantify the ability of the CdSe@ZnS/ZnS LSCs to effectively sensitise an N719-DSSC, a thin strip DSSC (active area = $9 \text{ cm} \times 0.2 \text{ cm}$) was fabricated by Dr L. J. Brennan (fabrication procedure, **Appendix, Section A6.1**) and adhered to one edge of the champion LSC using an optical grade sealant (**Fig. 6.12b**). The LSC was illuminated by a calibrated solar simulator (AM 1.5G) and the current-voltage (J - V) performance of the attached DSSC was measured. Notably, the short-circuit current density obtained for the CdSe@ZnS/ZnS LSC-DSSC device, $J_{\text{SC}} = 0.42 \text{ mA cm}^{-2}$, was greater than the corresponding photocurrent recorded for the undoped PLMA-co-EGDM slab ($J_{\text{SC}} = 0.032 \text{ mA cm}^{-2}$) (**Fig. 6.12c**). Given the large dimensions of the thin-strip DSSC, it was difficult to obtain an accurate value for the overall efficiency of the bare device, since only masked (4 cm diameter) illumination of the front face of the DSSC was possible with the experimental configuration utilised. However, the PCE of the DSSC upon sensitisation by the edge emission of the coupled LSC can be estimated as described in **Chapter 2** by:

$$PCE = \frac{I_{\text{SC}} V_{\text{OC}} FF}{OP_{\text{in}}} \quad (2.16)$$

where I_{SC} is (0.76 mA), V_{OC} is (0.56 V) and FF is (0.55). Here, OP_{in} is taken to be the optical power of the corresponding LSC edge emission (8.64 mW), which gives a PCE of 2.71% for the DSSC. If

the actual light incident on the top surface of the CdSe@ZnS/ZnS LSC 1257 mW (12.57 cm^2 at 100 mW cm^{-2}) is considered as OP_{in} , a PCE of 0.02% is obtained for the entire LSC/DSSC system.

6.4 Conclusions

The fabrication of large-area LSCs utilising green-emitting CdSe@ZnS/ZnS QDs with a composition gradient shell as the luminophore was achieved. The judicious selection of the PLMA-co-EGDM as host matrix facilitated the incorporation of the CdSe@ZnS/ZnS QDs to high dopant concentrations (up to 0.9 wt%), without affecting the intrinsic photophysical properties of QD luminophores. These semi-transparent CdSe@ZnS/ZnS-LSCs displayed both high optical quality and demonstrated a maximum operating efficiency of 1.22 % for a G of = 7.9 under AM 1.5G illumination with no additional light scattering or reflective layers employed. A detailed study into the characterisation techniques for large planar LSCs was then undertaken, where, through comparative measurements using three different LSC/IS configurations a method was obtained to both minimises systematic errors, whilst accounting for the inhomogeneity in the edge emission. It was observed that due to the inhomogeneity of the emission across the edge length, extrapolation of the OP_{out} measured at the LSC centre will lead to an overestimation. Similarly, measurements utilising a small port and the entire LSC edge result in larger systematic errors due to repeated measurements. Thus, a suitable approach for large area devices is to determine the mean edge emission from multiple overlapping intervals over the entire edge length.

By investigating masked illumination as a characterisation method for LSCs it was determined that due to transport losses and non-uniform emission across the edge, these characterisation techniques are not accurate for large are LSCs, however masked illumination can be used to measure the transport losses which occur in LSCs. Investigation of these loss contributions in the large area QD-LSCs revealed that reabsorption saturate at distances $>30 \text{ mm}$ and that any further losses in efficiency are due to scattering. Thus, reabsorption losses are estimated to be $\sim 40\%$ at optical distances up to 65 mm. The champion LSC was integrated with a DSSC and was shown to boost the short-circuit photocurrent, when compared to an undoped polymer slab. This work highlights the challenges and possibilities for combining spectral converters with emerging PV technologies such as DSSCs, organic and perovskite solar cells. These technologies have been

heralded as low-cost, lightweight alternatives to established inorganic semiconductor PV cells for the urban environment which presents a significant opportunity for the rational design of hybrid LSC/PV systems where third generation solar cells are a viable prospect.

6.5 References

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Chapter Seven

Conclusions

This thesis has investigated the use of spectral converters, such as luminescence down-shifting layers and luminescent solar concentrators, to improve the efficiency and stability of third generation PV cells, particularly perovskite solar cells, which currently limits the uptake of these technologies on a large scale.

The first part of this thesis investigated the inherent stability issues with perovskite solar cells, with the aim of resolving this limitation through a two-fold approach of polymer encapsulation to improve the resistance to moisture-induced degradation¹ and the addition of luminescence down-shifting layers to act as UV-filters.² Both perovskite thin films and complete PSCs of different architectures were subjected to rigorous testing to mimic operating conditions and to identify the properties which make materials effective as both encapsulants and luminophores for down-shifting layers.

Chapter 3 examined the relationship between the physical properties of polymer encapsulation layers and their ability to act as encapsulants for PSCs through controlled degradation experiments on uncoated $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite thin films and films coated with four common polymer encapsulants (PMMA, PC, EC and PMP). The effect of the encapsulation by the polymers applied directly to the $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite was examined comparatively through thermal degradation at 60 °C, 80 °C and 100 °C. A combination of PXRD, UV/Vis absorption spectroscopy, visual characterisation and epi-fluorescence microscopy was used to monitor the degradation. The water vapour transmission rate was determined to be the most important physical property when selecting a polymer encapsulant; however, the polymers which exhibited T_g near the degradation temperatures exhibited accelerated degradation, thus, a $T_g >$ operating temperatures is essential to effective encapsulation. Of the four polymers studied as encapsulants, PMMA performed the best at all temperatures investigated due to its low WVTR. It demonstrated increased stability of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films from *ca.* 24 h to >400 h upon continuous heating at 60 °C. EC and PMP exhibited rapid degradation at all investigated temperatures with very slight improvements in stability over the bare film and PC performed well with stability of over 300 h at $T = 60$ °C. The onset of the degradation of the perovskite layers was observable through epi-fluorescence microscopy, seen as deterioration of the film quality due to grain growth and associated defect

formation, while PXRD and UV/Vis absorption provided quantitative analysis of the degradation of the $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ film to PbI_2 . It was notable that epi-fluorescence microscopy provided a qualitative method of characterisation for the perovskite layers before any other techniques could detect degradation, thus, it has potential use in a scaled fabrication procedure. PMMA presents an attractive option for both device encapsulation and LDS coatings for PSCs to improve their photostability

Chapter 4 investigated using PMMA as a host matrix for LDS layers to improve the UV-stability of PSCs. A variety of luminophores based on organic dyes, conjugated polymers and AIEgens, were doped into a PMMA host material, and coated onto two $\text{CH}_3\text{NH}_3\text{PbI}_3$ cell architectures based on mesoporous TiO_2 and NiO. The PSCs were characterised before and after LDS layer application, by a combination of *J-V* sweeps and EQE measurements, to establish the effect the LDS layers had on device performance. LDS layers of different thicknesses and with varying luminophore concentrations were produced to determine any trends between these parameters and the performance of the LSC layer. The architecture of the devices themselves had a significant impact on the effect the LDS layers had on device efficiency. Poor performances were obtained for mesoporous TiO_2 devices compared to the NiO-based devices, which showed consistent improvements in both device PCE and J_{SC} when coated with LV570, PFO and HPQ doped films. It was observed that for conventional luminophores, lower doping concentrations and thicker films were advantageous to minimise reabsorption losses, whereas for AIEgens, highly concentrated thin films displayed better performances due to the increased interactions between the luminophores. Extended stability tests of the devices under operating conditions resulted in rapid degradation of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ PSCs, which was attributed to a combination of architecture specific degradation mechanisms, such as degradation of the spiro-OMeTAD HTL in the TiO_2 ,³ Ag electrode-induced degradation in the NiO devices⁴ and inherent $\text{CH}_3\text{NH}_3\text{PbI}_3$ degradation caused by trap formation.⁵ Therefore, the outcome from this stability study was that $\text{CH}_3\text{NH}_3\text{PbI}_3$ is an unsuitable candidate for comparative studies performed under operating conditions, as intrinsic degradation is too rapid to allow for an adequate comparison between the performance of different LDS layers.

The chapters above highlight the limitations of these PSC devices, notably that moisture-induced degradation occurs on such a rapid scale that other degradation methods are only secondary concerns. The first part of this thesis has demonstrated a facile method of encapsulation to increase device stability. PMMA was found to be particularly versatile as both a device encapsulation layer and LDS host, achieving improved stability and an increase in device PCE. Therefore, this material is attractive for scaled application with PSC devices. However, this work has also highlighted that the stability of $\text{CH}_3\text{NH}_3\text{PbI}_3$ based perovskites is inherently limited under operating conditions. Future work in this area will focus on testing dual functional encapsulation/LDS layers to improve the stability of different perovskite materials such as “triple-cation” $(\text{Cs}_x(\text{MA}_{0.17}\text{FA}_{0.83})_{(100-x)}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3)$ type materials which display enhanced stability compared to $\text{CH}_3\text{NH}_3\text{PbI}_3$.

While the above work has demonstrated there is still a place for organic luminophores in spectral converters, they are currently limited by concentration induced loss mechanisms, poor Stokes' shifts and low UV-stability. The second part of this thesis aims to address these limitations by investigating nanocrystal-based luminophores were investigated with the aim of application in spectral converters for third generation PV devices.

Chapter 5 examined how the photophysical properties of $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{I}_x$ PNCs can be tuned by dilution with the anti-solvent used during fabrication following the LARP procedure. It was demonstrated that upon fabrication there was negligible incorporation of iodide in the PNCs despite a ratio of *ca.* 2:1 Br⁻ to I⁻ in the precursor solution, and that upon dilution a red-shift of the emission properties occurred. Using a combination of STEM, EDX and DLS it was determined that this red-shift is due to aggregation and uncontrolled growth of the PNCs caused by decreasing capping ligand concentration in solution. This growth led to particles with dimensions *ca.* 1 μm and the uptake of the excess iodide bound within the capping ligands. Consequently, the resultant crystals displayed PL properties representative of the bulk $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{I}_x$ perovskite. By increasing the capping ligand concentration, it was observed that the changes in the emission properties occurred regardless of the initial concentration, with the amount of capping ligand only dictating the extent of the emission shift observed. It was demonstrated by varying the precursors used to provide the halides

(in a constant ratio of *ca.* 2:1 Br⁻ to I⁻), that a higher content of iodide provided by an increased MAI concentration contributed to a greater change in the spectral properties, thus, excess surface iodide bound to the capping ligands was favourably incorporated upon particle growth. Changing this ratio and increasing the concentration of the bromide relative to the iodide resulted in a loss of the red-shift, thus, demonstrating the role of iodide uptake in the observed emission behaviour. This chapter demonstrated that careful control over the anti-solvent used is required to minimise any unwanted side reactions causing significant alteration of the morphology, optical properties and stability of the PNCs. These unwanted solution phase side reactions can limit the applicability of PNC based materials for use in devices and highlights a limitation of mixed halide perovskites, which has not been addressed thus far.

The solution phase instability of the optical properties of mixed halide PNCs has meant that they are not yet ready for use as spectral converters. **Chapter 6** presents the fabrication and characterisation of large-area LSCs utilising green-emitting CdSe@ZnS/ZnS QDs with a composition gradient shell as the luminophore and PLMA-co-EGDM as host matrix. Upon fabrication of the CdSe@ZnS/ZnS QD LSCs, with high dopant concentrations (up to 0.9 wt%), issues with the characterisation procedures for large area LSCs became apparent. Thus, a detailed study into the characterisation protocols used for large planar LSCs was undertaken, where, through comparative measurements using three different LSC/IS configurations under full illumination by simulated AM 1.5G light, a robust characterisation method was obtained to both minimise systematic errors, whilst accounting for the inhomogeneity in the edge emission. It was demonstrated that the most suitable method to characterise large area devices is to determine the mean edge emission from multiple overlapping intervals. This method takes into account both the inhomogeneity of the emission across the edge length, which, extrapolation of the OP_{out} measured at the LSC centre will underestimate, and minimises systematic error associated with multiple measurements utilising a small port. By masking the LSCs and characterising the decrease in OP_{out} , the transport losses which occur in LSCs could be measured. It was observed that reabsorption losses saturate at distances of >30 mm and that further losses are due to scattering. A boost in PCE was obtained when the champion LSC was coupled to a DSSC, compared to the undoped waveguide plate.

This thesis highlights the potential for spectral converters to be combined with 3rd generation PV, as well as the limitations which are inherent. The ability to vary the luminophore, waveguide and architecture lends a versatility to spectral converters which allows their application to be tailored for any PV cell. In addition, this thesis has demonstrated that through careful consideration of the materials used, spectral converters can fulfil a variety of roles for emerging PV devices, including efficiency enhancing layers, encapsulation materials and concentrators to minimise cell area. However, despite the potential of these materials they are unable to address all of the current limitations of PSCs. Degradation pathways such as trap driven decay will limit the efficiency of these devices. For spectral converters to be successful with third generation PV on an industrial scale a synergistic approach needs to be adopted. Innovation needs to continue to develop new luminophores, such as PNCs and AIEgens, new host materials, such as organic-inorganic hybrids, new perovskite absorber materials, such as $\text{Cs}_x(\text{MA}_{0.17}\text{FA}_{0.83})_{(100-x)}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$, and new spectral conversion architectures to couple with PV devices.

Future work will focus on the use of PNC-based luminophores in spectral converters. While there have been examples of PNCs applied to LDS layers⁶ and LSCs⁷, this work has thus far shown limited use of the unique tunability and emissivity of these materials. Integration of LSCs with perovskite solar cells is an attractive method to minimise both the UV-degradation of the perovskite layer and the potentially harmful lead content. Recent examples of printed PSCs means device fabrication in the dimensions required should be facile.⁸ In this work PFO has been demonstrated as an effective luminophore for PSC LDS coatings, and as an effective luminophore for LSCs upon incorporation into organic-inorganic ureasil hybrid materials.^{9,10} Such conjugated polymer-based hybrid spectral converters will be investigated for applications with PSCs and other PV devices.

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Appendix

1.1 Chapter 3

Figure A3.1 Photographs of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite films upon degradation at 60 °C.

Figure A3.2 Photographs of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite films upon degradation at 80 °C.

Figure A3.3 UV/Vis absorption spectroscopy of perovskite films degraded at 60 °C.

Figure A3.4 UV/Vis absorption spectroscopy of perovskite films degraded at 100 °C.

1.2 Chapter 4

Figure A4.1 PL spectra of 0.8 μm thick PMMA films doped with LV570, C153 and LR305 at varying concentrations.

Figure A4.2 UV/Vis absorption and PL spectra of LV570, C153 and LR305 in dilute solutions.

Figure A4.3 *J-V* sweep of TiO_2 $\text{CH}_3\text{NH}_3\text{PbI}_3$ PSC before and after application of a PFO LDS layer.

Figure A4.4 PCE degradation plots for mesoporous TiO_2 $\text{CH}_3\text{NH}_3\text{PbI}_3$ PSCs, coated with luminophore doped PMMA.

Figure A4.5 *J-V* curves of a NiO inverted $\text{CH}_3\text{NH}_3\text{PbI}_3$ PSC before and after encapsulation.

1.3 Chapter 5

Figure A5.1 UV/Vis absorption and PL spectra of $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($\text{X}_3 = \text{Br}_3, \text{I}_3$) PNC solutions in toluene.

Figure A5.2 Dynamic light scattering intensity distribution plot for $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{I}_x$ PNCs.

1.4 Chapter 6

Table A6.1 Photoluminescence quantum yields measured for CdSe@ZnS/ZnS quantum dots

Figure A6.1 Edge emission obtained for the 0 wt% QD-LSC obtained using configuration 3.

Figure A6.2 Edge emission obtained for the 0.04 wt% QD-LSC obtained using configuration 3.

Figure A6.3 Edge emission obtained for the 0.15 wt% QD-LSC obtained using configuration 3.

Figure A6.4 Edge emission obtained for the 0.3 wt% QD-LSC obtained using configuration 3.

Figure A6.5 Edge emission obtained for the 0.55 wt% QD-LSC obtained using configuration 3.

Figure A6.6 Edge emission obtained for the 0.9 wt% QD-LSC obtained using configuration 3.

Table A6.2 Summary of total optical power output and optical efficiencies of QD-LSCs. Determined by configuration 3.

Section A6.1 Fabrication of thin strip DSSCs.

1.1 Chapter 3

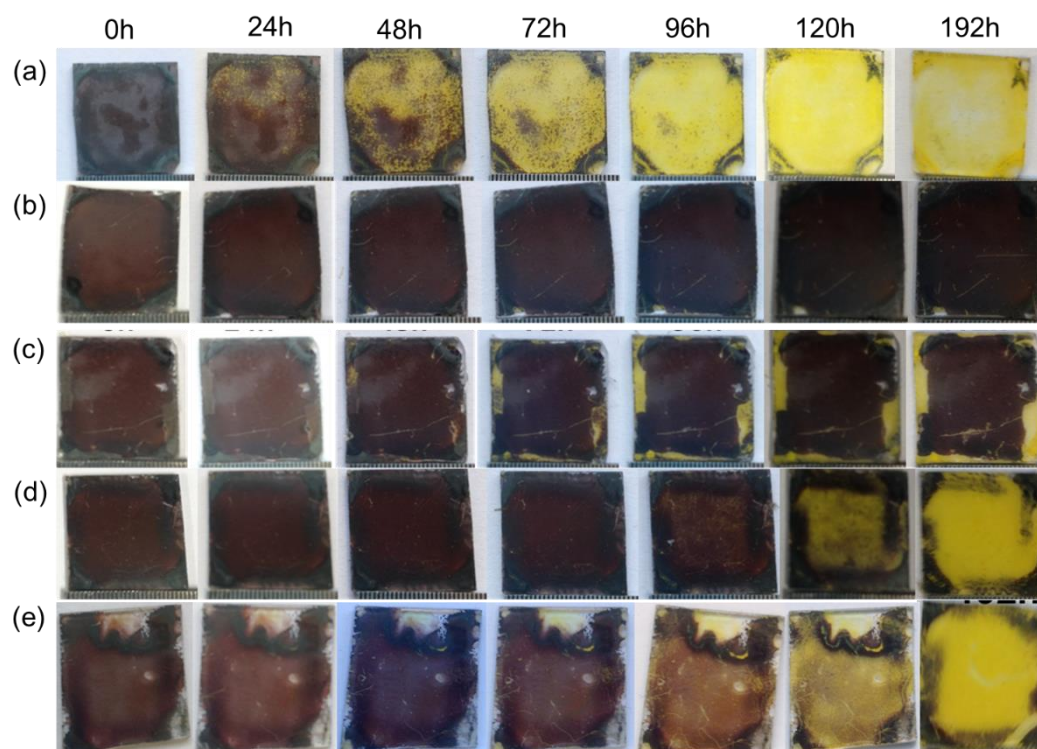


Figure A3.1. Photographs of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite films upon degradation at 60 °C in ambient conditions as a function of time. The films are coated with (a) uncoated, (b) PMMA, (c) PC, (d) EC and (e) PMP.

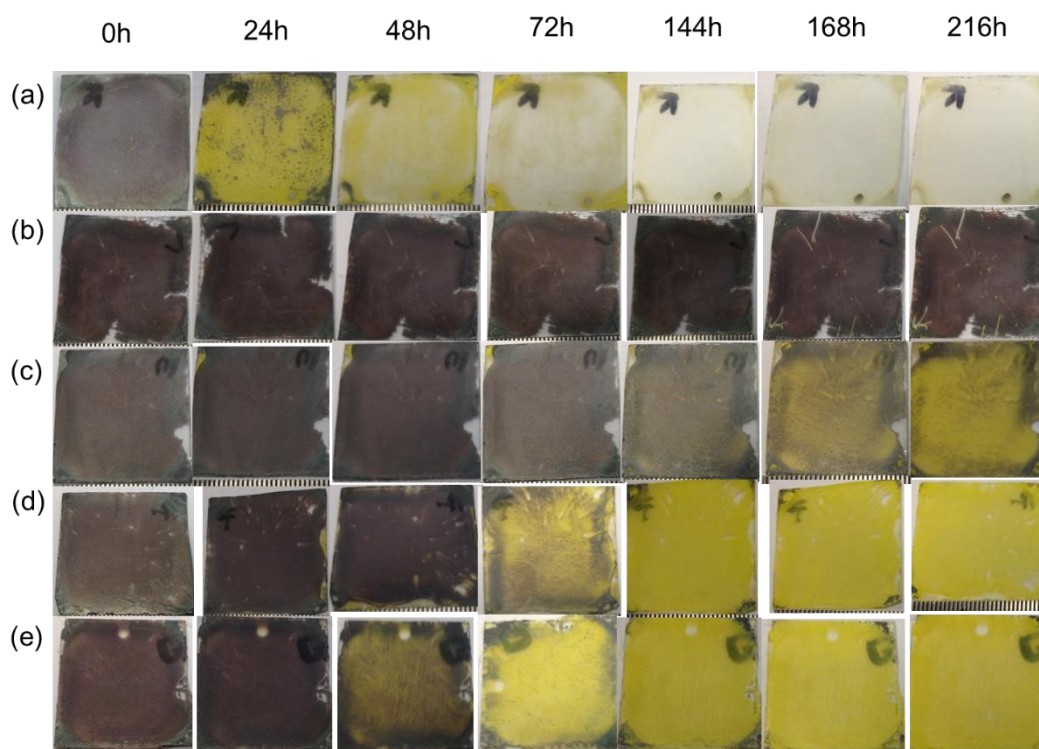


Figure A3.2. Photographs of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite films upon degradation at 80 °C in ambient conditions as a function of time. The films are coated with (a) uncoated, (b) PMMA, (c) PC, (d) EC and (e) PMP.

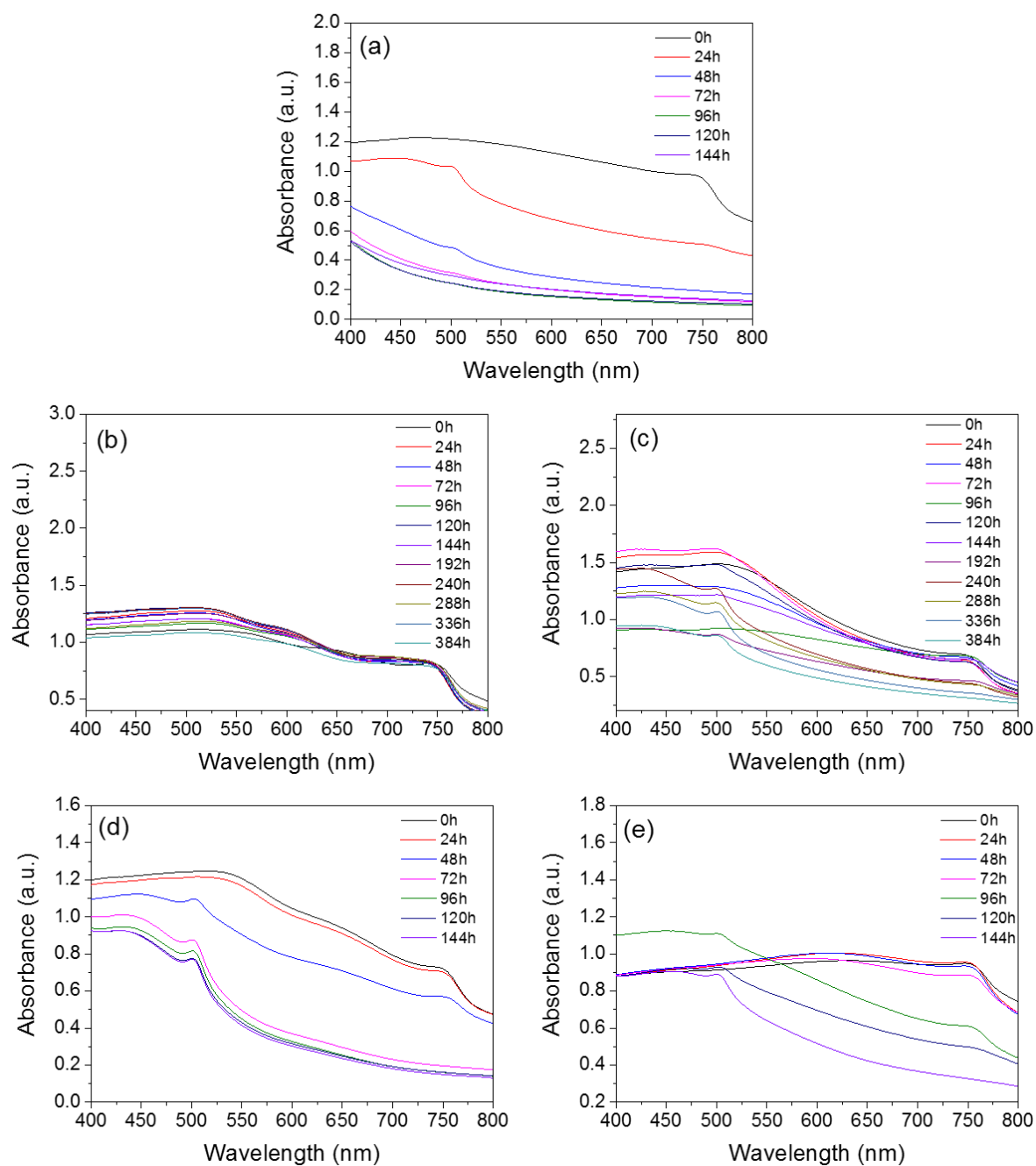


Figure A3.3. *Ex-situ* UV/Vis absorption spectroscopy of perovskite films degraded at 60 °C as a function of time, t coated with (a) uncoated, (b) PMMA, (c) PC, (d) EC and (e) PMP.

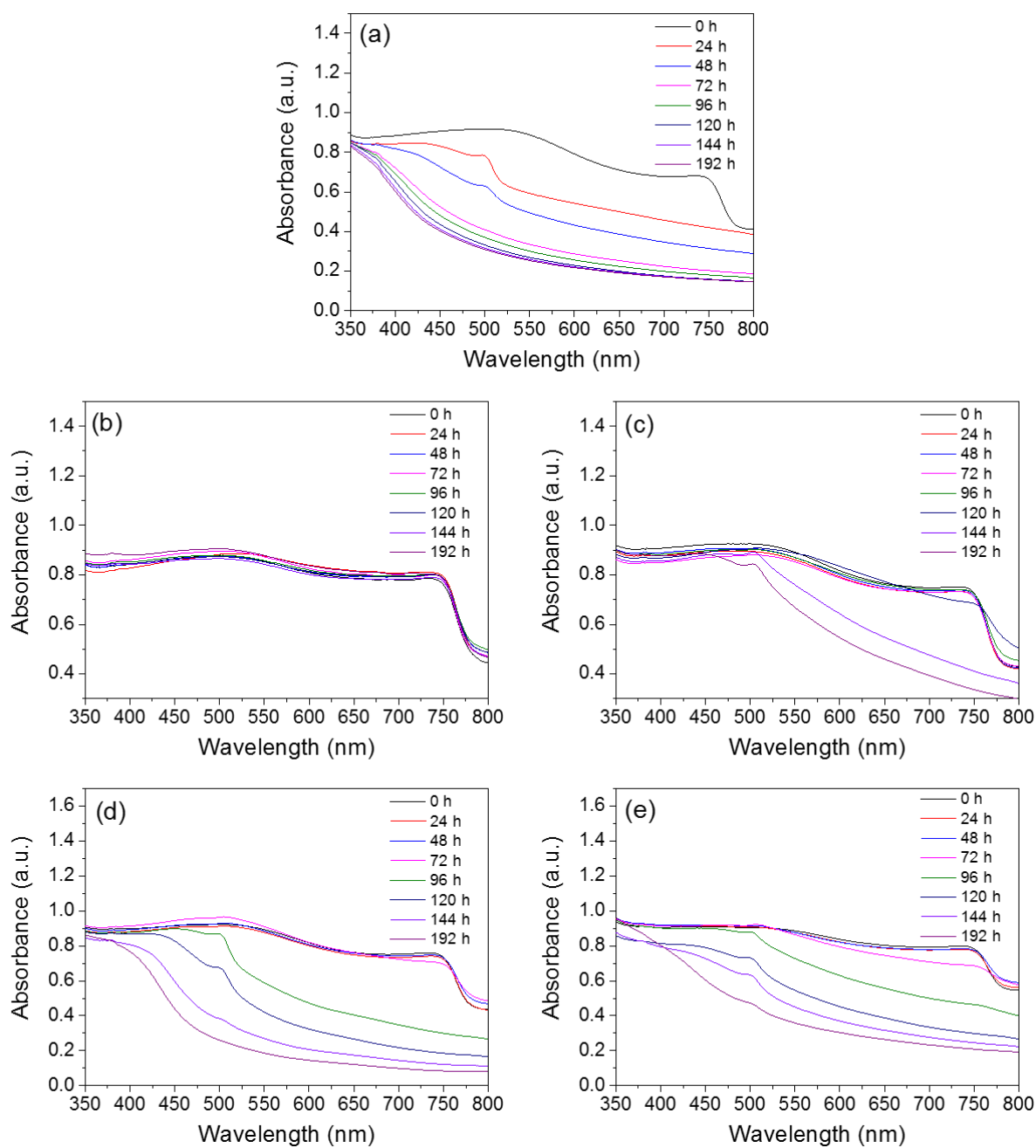


Figure A3.4. *Ex-situ* UV/Vis absorption spectroscopy of perovskite films degraded at 100 °C as a function of time, t coated with (a) uncoated, (b) PMMA, (c) PC, (d) EC and (e) PMP.

1.2 Chapter 4

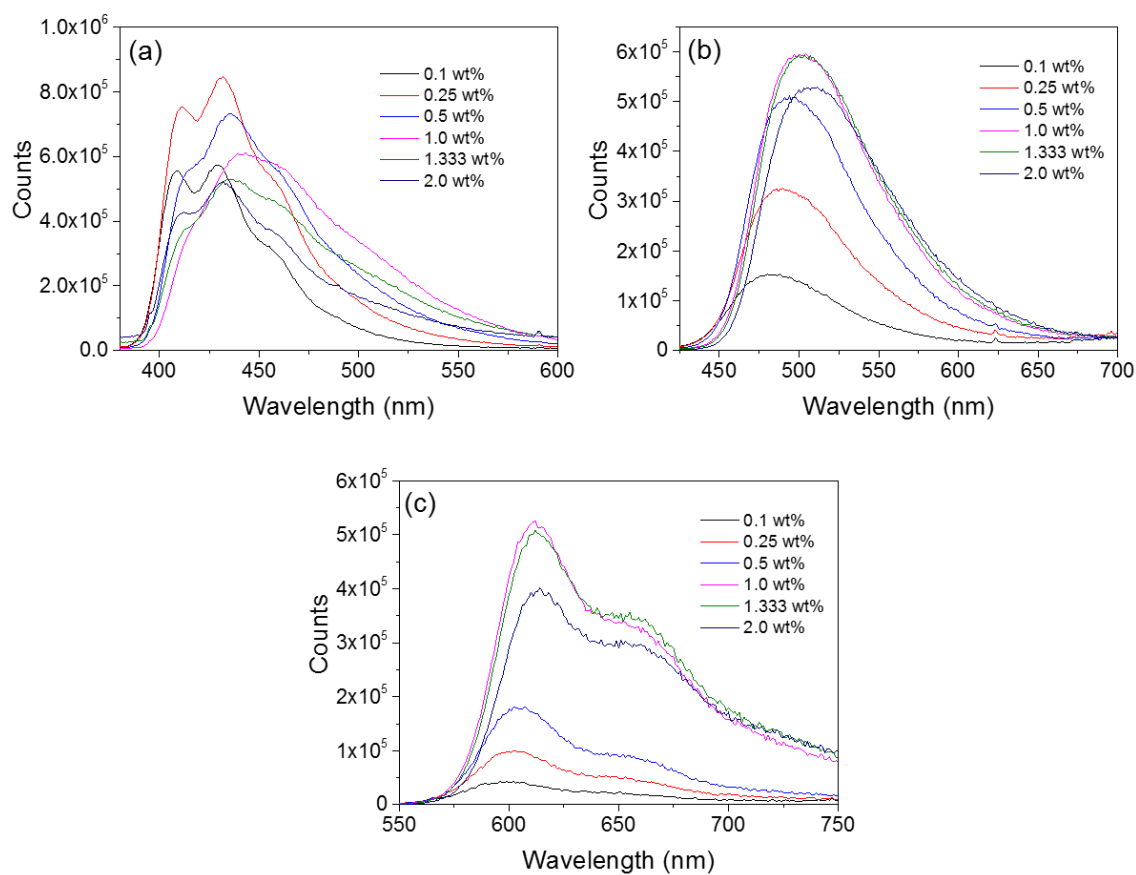


Figure A.4.1. Steady-state PL spectra of 0.8 μm thick PMMA films with luminophore doping of various concentrations. (a) LV570, (b) C153 and (c) LR305.

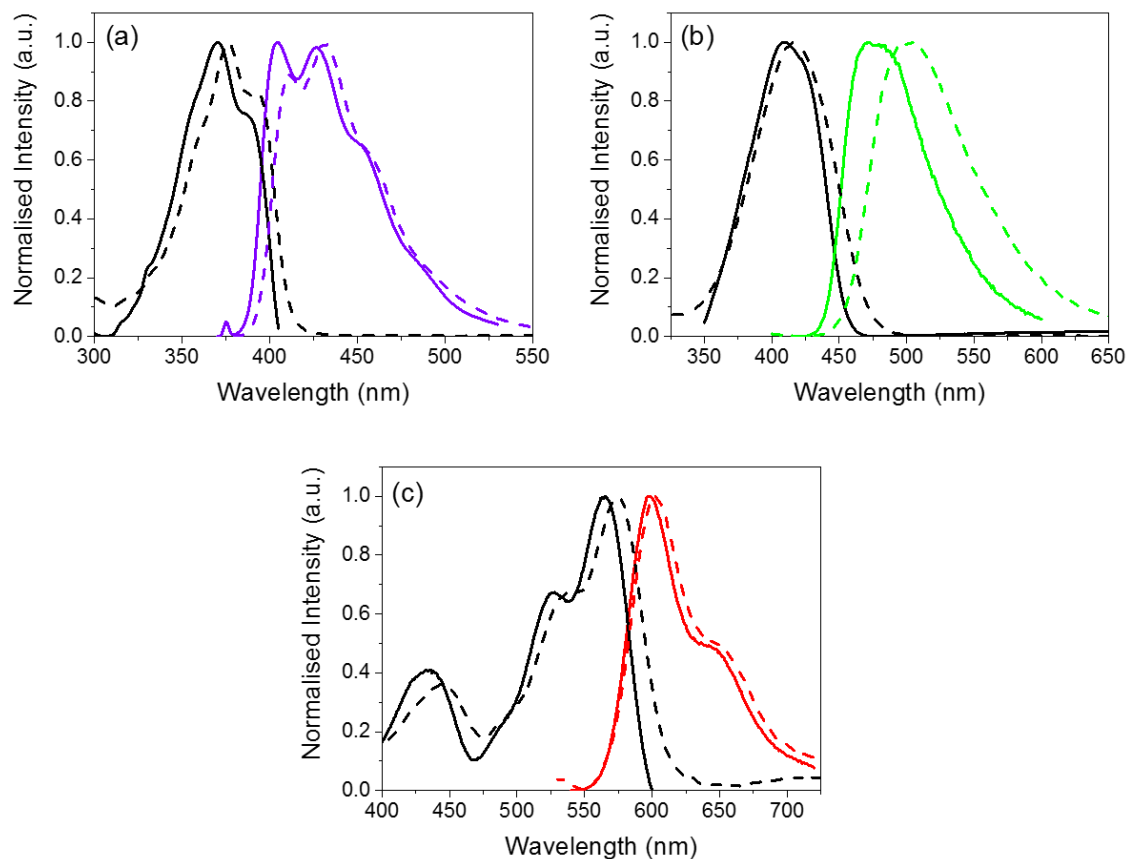


Figure A.4.2. Normalised UV/Vis absorption and steady state PL spectra of luminophores in dilute solutions (absorption at $\lambda_{\text{abs}} = \text{ca. } 0.1$) (solid lines) and in 0.8 μm thick PMMA films at standard concentration (dashed lines). (a) LV570 (film = 0.25 wt%), (b) C153 (film = 1.0 wt%) and (c) LR305 (film = 0.25 wt%).

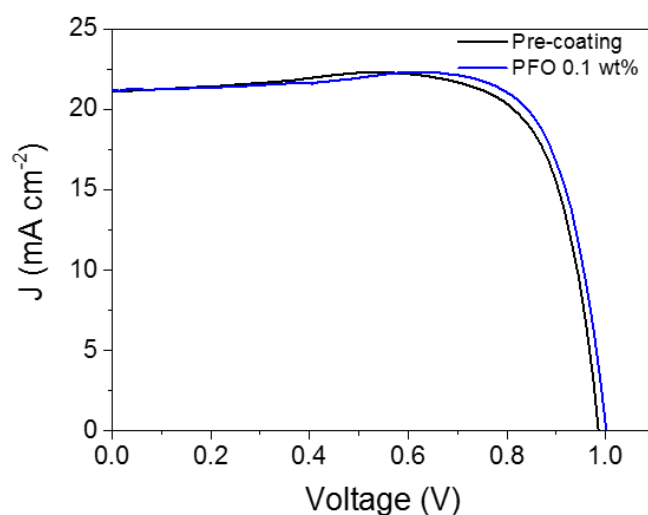


Figure A.4.3. J-V sweep of mesoporous TiO_2 $\text{CH}_3\text{NH}_3\text{PbI}_3$ PSC before and after the application of a PFO LDS layer (3.5 μm , 0.1 wt%) under AM 1.5G illumination.

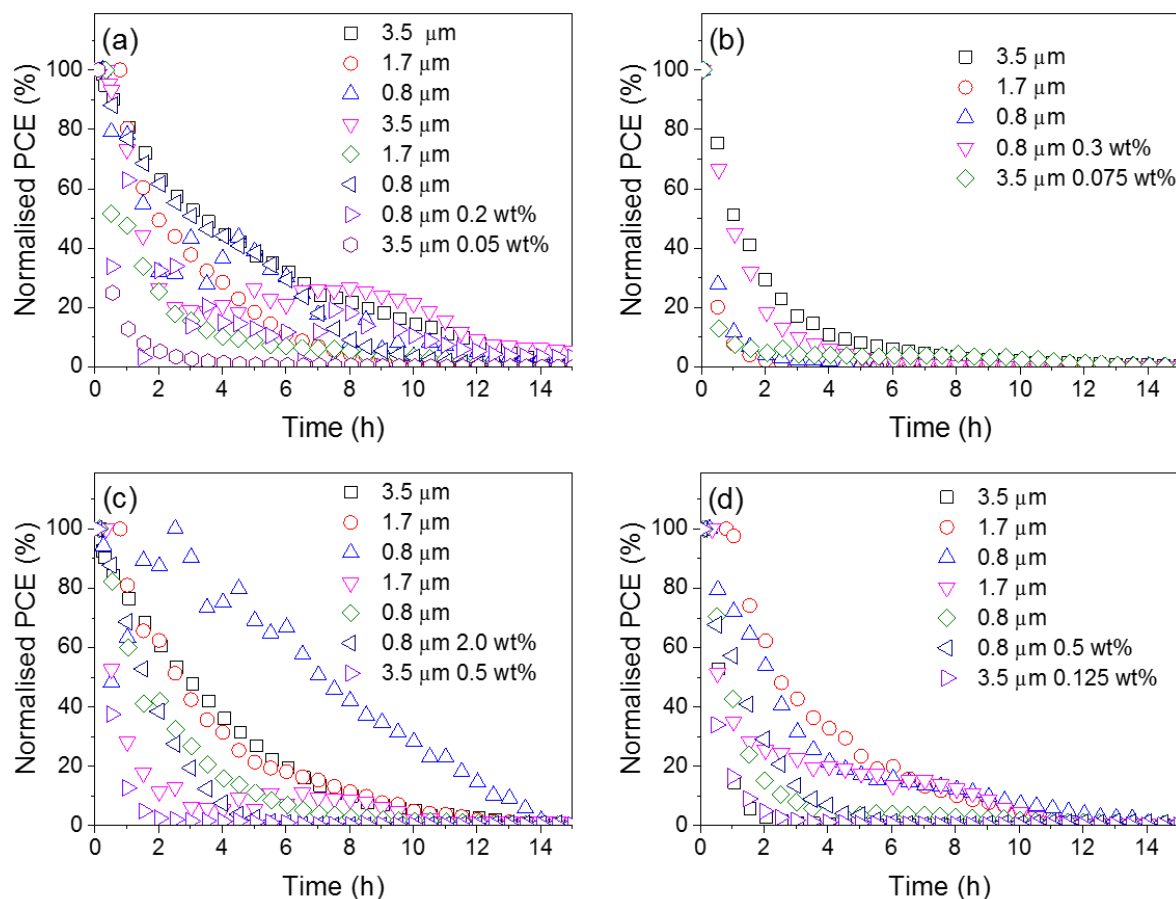


Figure A.4.4. PCE degradation plots for mesoporous TiO_2 $\text{CH}_3\text{NH}_3\text{PbI}_3$ PSCs, coated with luminophore doped PMMA, under illumination by simulated AM 1.5G light. (a) PFO (0.1 wt% unless otherwise stated) LDS layers of varying thickness. (b) HPQ (0.15 wt% unless otherwise stated). (c) C153 (1.0 wt% unless otherwise stated). (d) LR305 (0.25 wt% unless otherwise stated).

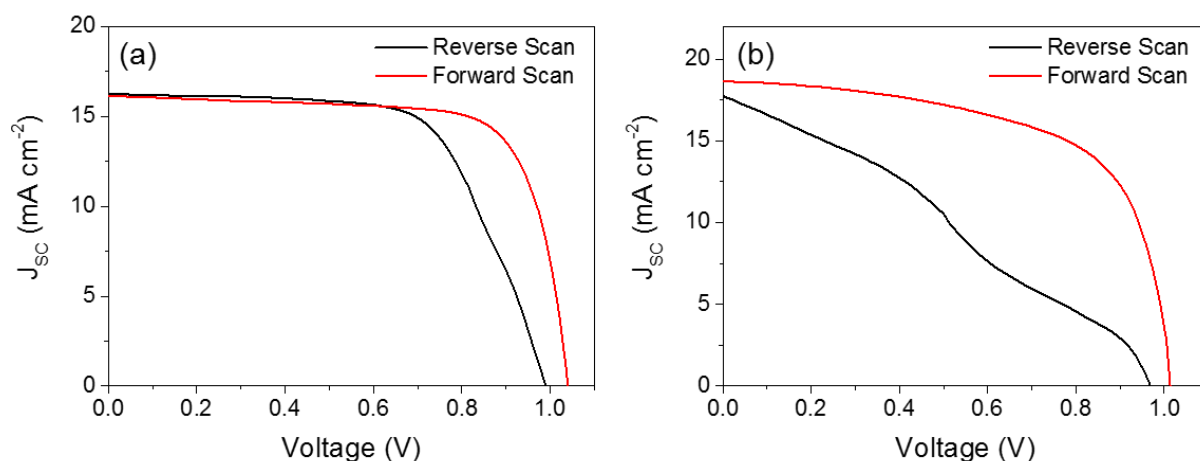


Figure A.4.5. J - V curves of a NiO inverted $\text{CH}_3\text{NH}_3\text{PbI}_3$ PSC (a) before and (b) after encapsulation using a photocurable epoxy and glass coverslip.

1.3 Chapter 5

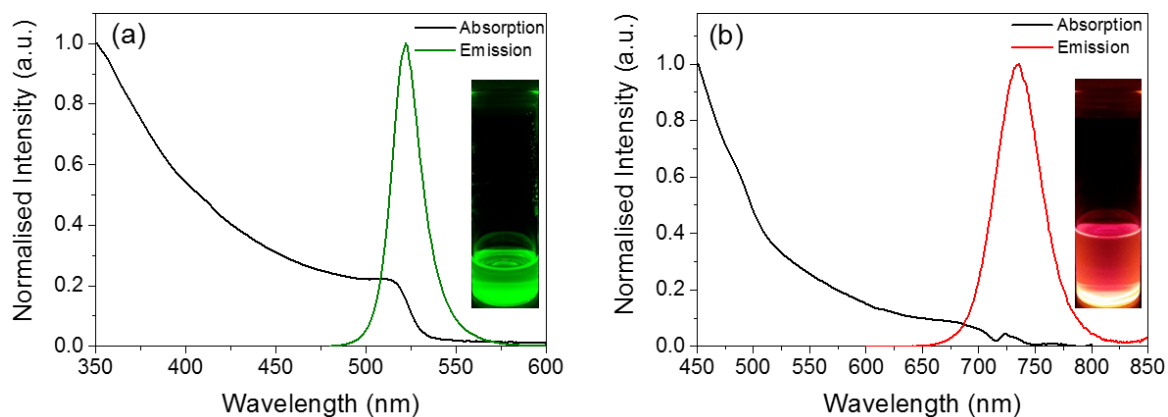


Figure A5.1. UV/Vis absorption and steady state PL spectra of $\text{CH}_3\text{NH}_3\text{PbX}_3$ PNC solutions in toluene. (a) $\text{CH}_3\text{NH}_3\text{PbBr}_3$, (b) $\text{CH}_3\text{NH}_3\text{PbI}_3$. Inset shows PNC stocks under 365 nm UV-illumination.

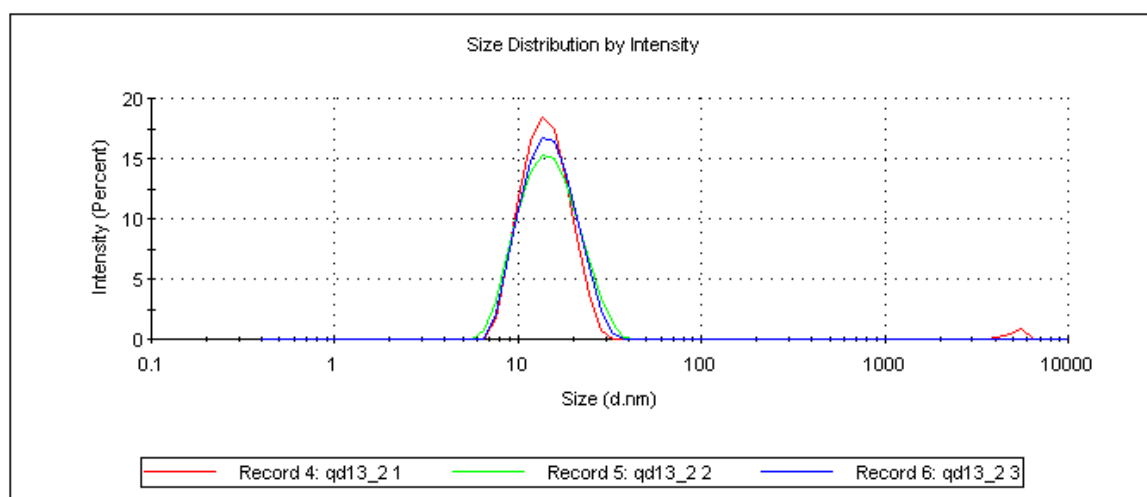


Figure A5.2. Dynamic light scattering intensity distribution plot for $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{I}_x$ PNCs in toluene. The mean hydrodynamic diameter is *ca.* 14 nm.

1.4 Chapter 6

Table A6.1. Absolute photoluminescence quantum yields (Φ_{PL}) measured for CdSe@ZnS/ZnS quantum dots in hexane. Measurements were performed using an F-3018 integrating sphere 194 mounted into a FluoroMax-4 spectrophotometer (Horiba Jobin-Yvon). Samples were excited at 460 nm with a band pass of 1.1 nm. (Data Measured by Dr L. J. Brennan).

Trial no.	Φ_{PL} (%)
1	63.1
2	62.3
3	68.4
Mean	65 $\pm$ 3

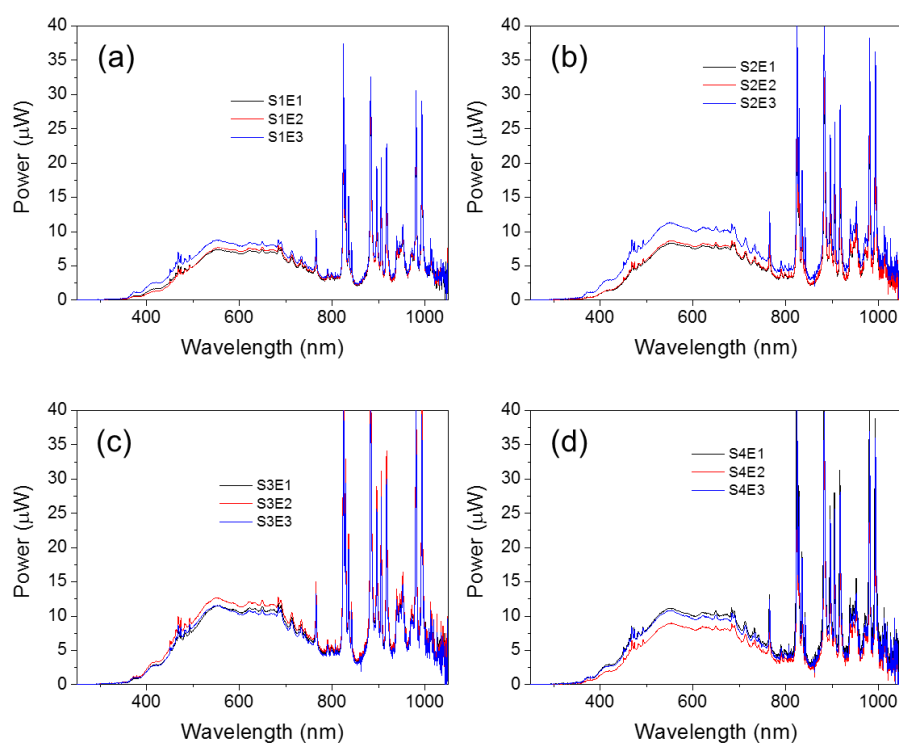


Figure A6.1. Edge emission obtained for the 0 wt% QD-LSC sample obtained using configuration 3, whereby, three overlapping 4 cm port measurements were taken across the edge of the LSC (E1/E2 = corner, E3 = centre). The mean integrated OP_{out} (250-1050 nm) is determined and extrapolated to estimate a value for the full edge length (9 or 10 cm). (a) Side 1 OP_{out} = 9.82 mW, (b) Side 2 OP_{out} = 10.2 mW, (c) Side 3 OP_{out} = 14.8 mW and (d) Side 4 OP_{out} = 11.3 mW

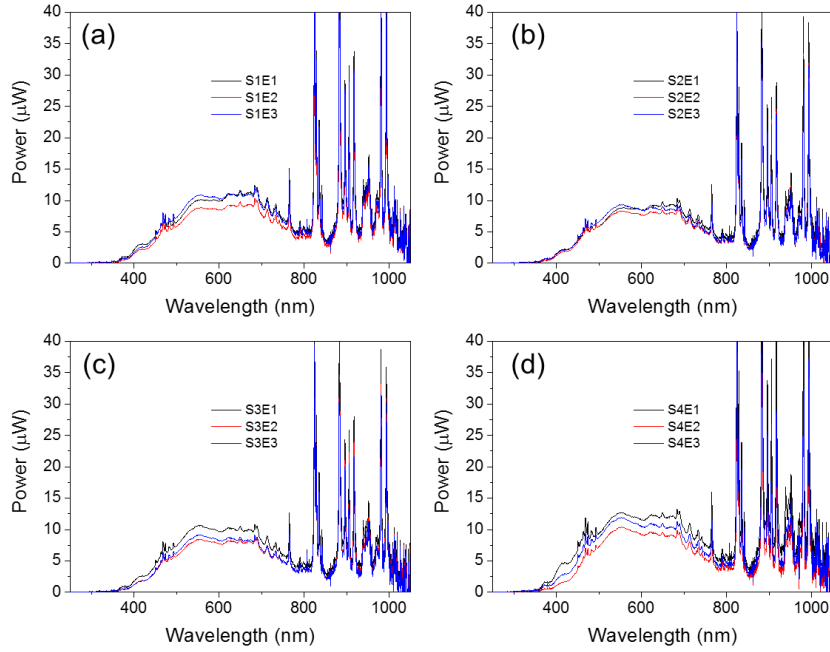


Figure A6.2. Edge emission obtained for the 0.04 wt% QD-LSC sample obtained using configuration 3, whereby, three overlapping 4 cm port measurements were taken across the edge of the LSC (E1/E2 = corner, E3 = centre). The mean integrated OP_{out} (250-1050 nm) is determined and extrapolated to estimate a value for the full edge length (9 or 10 cm). (a) Side 1 OP_{out} = 13.6 mW, (b) Side 2 OP_{out} = 10.2 mW, (c) Side 3 OP_{out} = 11.3 mW and (d) Side 4 OP_{out} = 12.7 mW

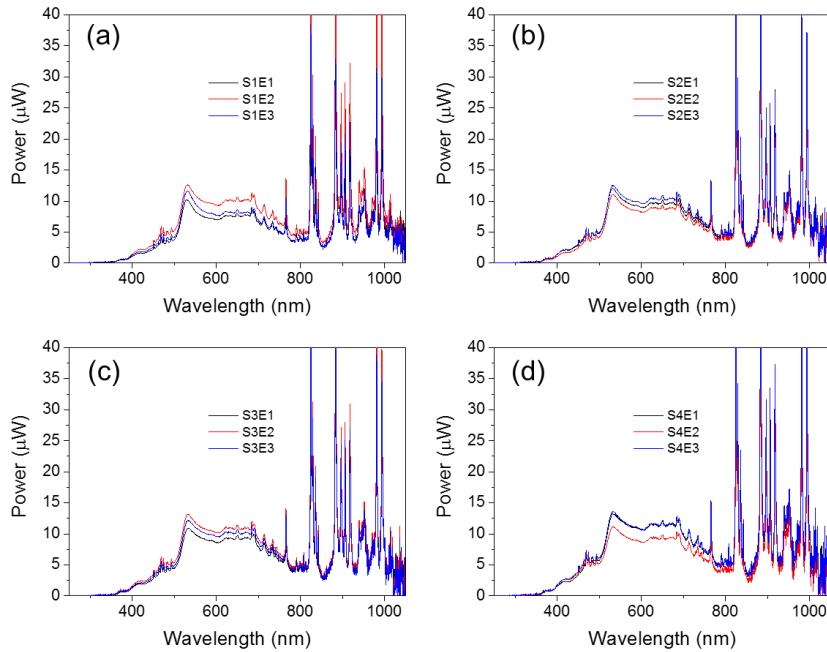


Figure A6.3. Edge emission obtained for the 0.15 wt% QD-LSC sample obtained using configuration 3, whereby, three overlapping 4 cm port measurements were taken across the edge of the LSC (E1/E2 = corner, E3 = centre). The mean integrated OP_{out} (250-1050 nm) is determined and extrapolated to estimate a value for the full edge length (9 or 10 cm). (a) Side 1 OP_{out} = 11.6 mW, (b) Side 2 OP_{out} = 11.1 mW, (c) Side 3 OP_{out} = 12.8 mW and (d) Side 4 OP_{out} = 12.7 mW

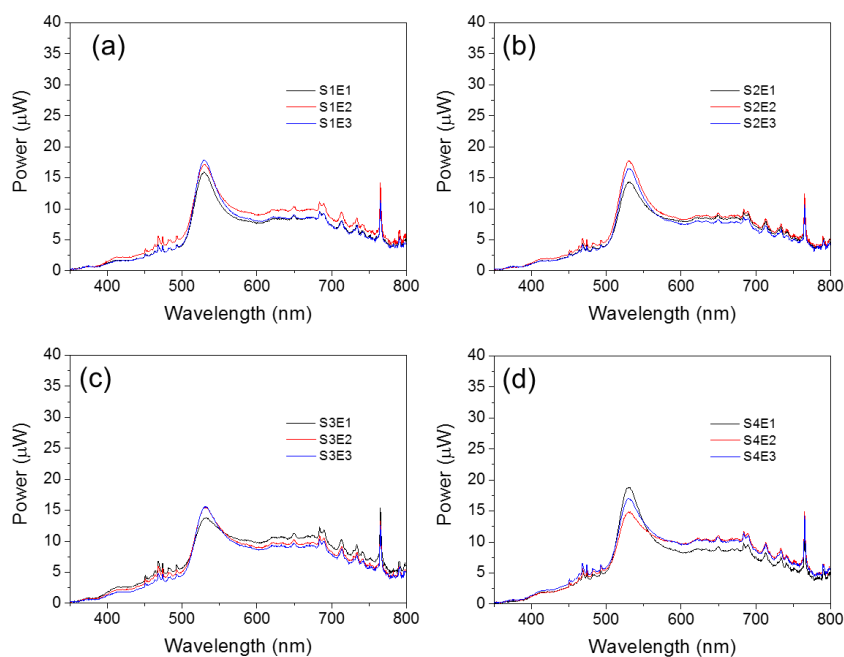


Figure A6.4. Edge emission obtained for the 0.3 wt% QD-LSC sample obtained using configuration 3, whereby, three overlapping 4 cm port measurements were taken across the edge of the LSC (E1/E2 = corner, E3 = centre). The mean integrated OP_{out} (250-1050 nm) is determined and extrapolated to estimate a value for the full edge length (9 or 10 cm). (a) Side 1 OP_{out} = 11.6 mW, (b) Side 2 OP_{out} = 11.1 mW, (c) Side 3 OP_{out} = 12.8 mW and (d) Side 4 OP_{out} = 12.7 mW

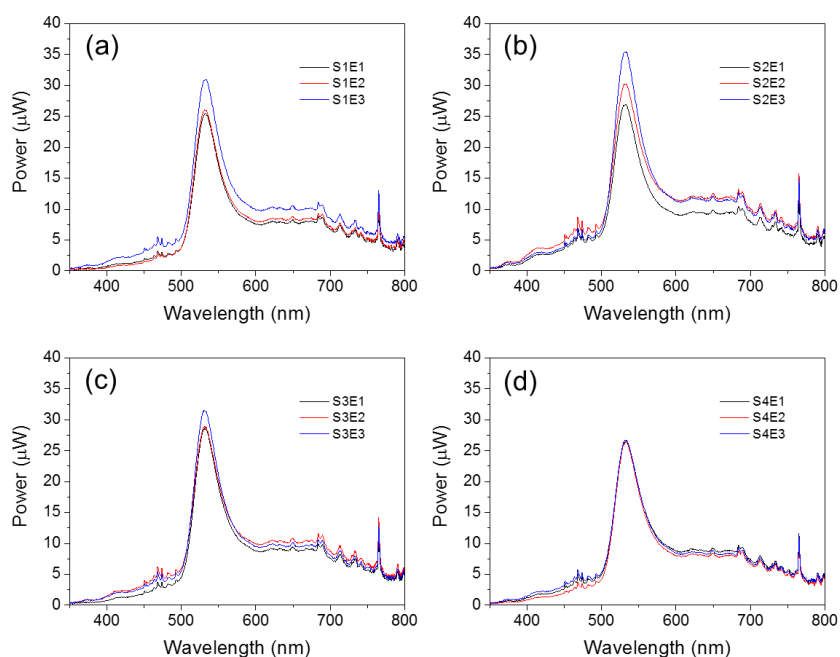


Figure A6.5. Edge emission obtained for the 0.55 wt% QD-LSC sample obtained using configuration 3, whereby, three overlapping 4 cm port measurements were taken across the edge of the LSC (E1/E2 = corner, E3 = centre). The mean integrated OP_{out} (250-1050 nm) is determined and extrapolated to estimate a value for the full edge length (9 or 10 cm). (a) Side 1 OP_{out} = 13.5 mW, (b) Side 2 OP_{out} = 15.7 mW, (c) Side 3 OP_{out} = 15.5 mW and (d) Side 4 OP_{out} = 12.2 mW

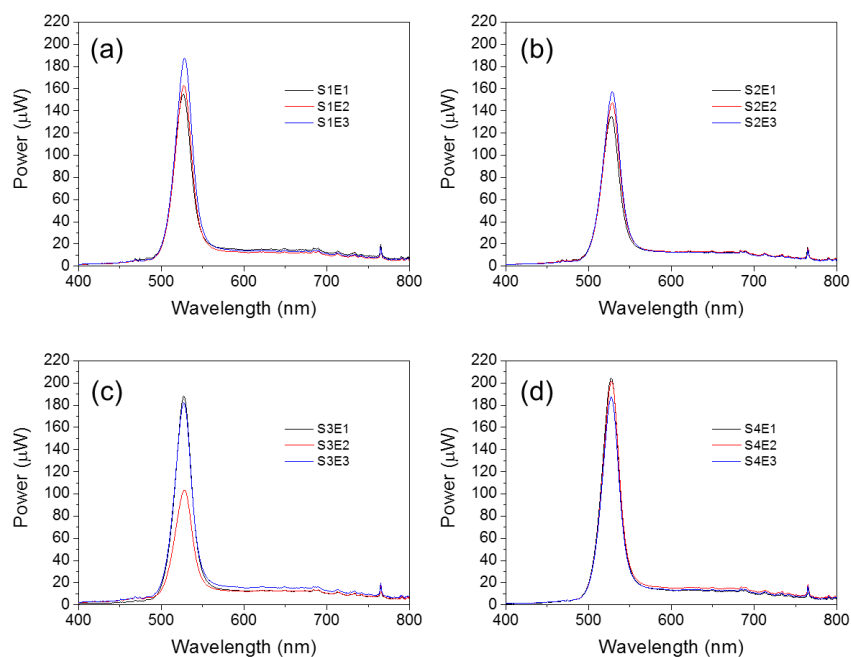


Figure A6.6. Edge emission obtained for the 0.9 wt% QD-LSC sample obtained using configuration 3, whereby, three overlapping 4 cm port measurements were taken across the edge of the LSC (E1/E2 = corner, E3 = centre). The mean integrated OP_{out} (250-1050 nm) is determined and extrapolated to estimate a value for the full edge length (9 or 10 cm). (a) Side 1 OP_{out} = 29.6 mW, (b) Side 2 OP_{out} = 24.1 mW, (c) Side 3 OP_{out} = 28.5 mW and (d) Side 4 OP_{out} = 27.6 mW

Table A6.2. Measured edge emission, total optical power output (OP_{out}) and optical efficiencies (η_{opt}) of QD-LSCs. Determined by configuration 3, whereby, three overlapping 4 cm port measurements were taken across the edge of the LSC (E1/E2 = corner, E3 = centre).

QD Conc. (wt%)	Side 1 (μW) ^a			Side 2 (μW) ^b			Side 3 (μW) ^a			Side 4 (μW) ^b	
	E1	E2	E3	E1	E2	E3	E1	E2	E3	E1	E2
0.0	3706	3778	4298	3996	4130	5475	5841	6284	5575	5545	4321
Mean			3927.333			4533.667			5900		
Full Edge			9818.333			10200.75			14750		
0.04	5835	4864	5641	4864	4235	4452	5185	4187	4232	6796	4630
Mean			5446.667			4517			4534.667		
Full Edge			13616.67			10163.25			11336.67		
0.15	4197	5466	4344	5030	4547	5251	4787	5546	5049	5924	4930
Mean			4669			4942.667			5127.333		
Full Edge			11672.5			11121			12818.33		
0.3	4970	5791	4353	4795	5225	4636	6411	5532	5192	5222	6030
Mean			5038			4885.333			5711.667		
Full Edge			12595			10992			14279.17		
0.55	4749	5150	6308	6229	7438	7240	5646	6649	6260	5535	5070
Mean			5402.333			6969			6185		
Full Edge			13505.83			15680.25			15462.5		
0.7	10279	10516	12303	9955	9538	10219	11095	10858	11433	13554	11920
Mean			11032.67			9904			11128.67		
Full Edge			27581.67			22284			27821.67		
0.9	12210	10941	12325	10583	10932	10560	11744	9617	12844	11899	13030
Mean			11825.33			10691.67			11401.67		
Full Edge			29563.33			24056.25			28504.17		

^a Edge Length = 10 cm, ^b edge length = 9 cm. Full edge power = (mean/4 $\times$ edge length), η_{opt} = total OP_{out} /
 OP_{in} . OP_{in} = 9000 mW

A6.1 Fabrication of Thin Strip DSSCs

A6.1.1 Electrode Fabrication

The DSSC TiO_2 electrodes were prepared on FTO-coated glass substrates. Glass substrates were cleaned in a Hellmanex detergent solution with ultra-sonication for 15 min followed by sonication in ethanol (10 min) and acetone (10 min). A compact TiO_2 layer was applied by submerging the FTO-glass substrates in a hydrolysed TiCl_4 solution (40 mM) at 70 °C for 30 min. The substrates were removed and washed with water and ethanol. In order to form the mesoporous electrode, TiO_2 paste was applied to FTO-coated substrates using the doctor blade method. In short, a mask was fabricated using commercially available scotch tape. The mask was placed on top of the FTO-coated glass substrate and allowed to adhere to the surface. TiO_2 paste was placed at the mask edge and carefully coated along the mask by moving a glass rod at a steady pace across the substrate. This procedure allowed the TiO_2 paste to fill the void created by the mask. Electrodes were produced with two coatings of light-absorbing TiO_2 paste (20 nm) (GCell 180B). Following this, one layer of light-scattering TiO_2 (150–200 nm particle size) (Dyesol WERO-2) was deposited. The deposited electrodes were air dried for approximately 30 min to allow for excess solvent evaporation. The TiO_2 working electrodes were finally treated to a sintering profile which consisted of a drying period at 125 °C for 6 min, ramping to 350 °C and holding for 15 min, ramping to 450 °C and holding for 15 min and finally sintering at 500 °C for 15 min. Once cooled, the electrodes were re-immersed in an aqueous TiCl_4 solution (40 mM) and heated to 70 °C for 30 min. Upon removal from the bath, electrodes were cleaned with water and ethanol and treated to a second sintering step at 500 °C for 30 min.

A6.1.2 Dye Adsorption

TiO_2 electrodes were soaked in a solution of di-tetrabutylammonium *cis*-Bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II) (N719) dye in a *t*-butanol/acetonitrile mixture (1:1 (v/v)) for 16 h. This process enables adsorption of a monolayer of the light-harvesting dye onto the mesoporous TiO_2 electrode. Upon removal from the dye solution, the

electrodes were washed with ethanol to remove unadsorbed dye molecules from the surface and dried under nitrogen flow.

A6.1.3 Cell Construction

A surlyn sealant (25 μm) was placed around the active area of the dye-sensitised electrode and the counter electrode (CE) was placed on top. The CE was fabricated by depositing plastisol adhesive paste (Dyesol) onto cleaned FTO-coated glass and thermally treating at 400 °C for 15 min. The device was sealed by clamping both electrodes together and heating to 130 °C. At this temperature the surlyn seal melts and once cooled acts as a sealant between both electrodes. The organic electrolyte was prepared from the following formulation: 1-butyl-3-methyl imidazolium iodide (0.6 M) iodine (0.03 M), guanidium thiocyanate (0.10 M) and 4-tert-butylpyridine (0.5 M) were dissolved in a solvent mixture of acetonitrile and valeronitrile (85:15 vol. ratio) as described by Ito *et al.*¹ The electrolyte (25 μL) was dropped over a 1 mm² hole drilled into the back of the counter electrode and when placed under vacuum the electrolyte was driven into the chamber between the electrodes in the cell. The hole in the CE was then sealed using a small portion of surlyn and a piece of glass.

A.6.1.4 References

- 1 S. Ito, T. N. Murakami, P. Comte, P. Liska, C. Grätzel, M. K. Nazeeruddin and M. Grätzel, *Thin Solid Films*, 2008, **516**, 4613–4619.