Innovative Nanomaterial Approaches For Solar Energy Applications

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Innovative Nanomaterial Approaches
For Solar Energy Applications

By
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A thesis submitted to the Technological University for Dublin,
For the degree of Doctor of Philosophy (PhD)

Supervisors:
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Assoc. Prof. Sarah McCormack
Dr. Hind Ahmed

School of Physics & Clinical & Optometric Sciences,
College of Sciences and Health
Technological University for Dublin
June 2020
Abstract

The fundamental limitation of the conversion efficiency achievable with solar energy solutions (which includes photovoltaic and photothermal technology), requires the adaptation and integration of a series of innovative material strategies to continue the process of sustainably decarbonizing the global economy. Through the passive integration of additional nanoscale features which exploit and modify the solar spectrum through its interactions with luminescent molecules, metal nanoparticles, and/or thin-film optical coatings – the solar spectrum can be modulated and accordingly the collection efficiency of each respective technology enhanced. However, irrespective of the type of spectral conversion integrated into the technology (luminescent down-shifting, nanofluids, plasmonic luminescent down-shifting, or spectral beam splitting), a series of additional loss mechanisms are introduced as a result of the architectural modifications. Through a proposed series of innovative & iterative advancements in each one of these material strategies, the objective of alleviating the additional loss mechanisms through a suitable combination of the individual approaches could potentially be realised.

In this investigation, a novel series of 27 imidazole[4,5-f][1,10]phenanthroline derivatives were characterised and evaluated for their role in solar energy conversion applications. From this library of fluorescent materials, a selected few of the highest performing candidates were integrated into luminescent down-shifting photovoltaic devices, and spectral beam splitting photovoltaic-thermal collection systems. The presence of these molecular species in either type of collection device resulted in significant enhancements in the standalone collection efficiency, the optical collection efficiency, the thermal performance, the economic value of the energy captured, as well as the capability to modulate the thermal and electrical outputs of a combined heat and power system. The thermal performance of these phenanthroline derivatives in static stagnation tests also revealed their cross-application potential for photothermal collection
applications. In this same static scenario, the implementation of a silver based nanofluid containing a diverse set of individual particle morphologies and particle size-distributions was shown to enhance the photothermal collection efficiency of a standardized thermal collection device. Finally, a hypothetical architecture which builds upon the luminescent down-shifting (LDS) and plasmonic luminescent down-shifting (PLDS) approaches to light management in photovoltaic devices was designed and analysed using a transfer matrix model. The results of the simulations have shown how the collection efficiency of a traditional LDS and PLDS device is predicted to be enhanced by the incorporation of spectrally selective thin-film optical coatings. Overall, the results have shown the potential of a series of alternative material strategies to increase the conversion efficiency of a range of standalone solar energy solutions including photovoltaic, photothermal, and combined photovoltaic-thermal collection devices.
Declaration

I certify that this thesis which I now submit for examination for the award of PhD, is entirely my own work and has not been taken from the work of others, save and to the extent that such work has been cited and acknowledged within the text of my work. This thesis was prepared according to the regulations for graduate study by research of the Technological University for Dublin and has not been submitted in whole or in part for another award in any other third level institution. The work reported on in this thesis conforms to the principles and requirements of the TUD’s guidelines for ethics in research. TUD has permission to keep, lend or copy this thesis in whole or in part, on condition that any such use of the material of the thesis be duly acknowledged.

Signature ___________________________ Date ____________

James Walsh
Acknowledgements

If you are reading this document, then I guess I made it out of alive after all! Throughout all the trials and tribulations along the journey into intellectual self-mastery, one confronts a litany of challenges at both the professional and personal level. Having survived relatively unscathed the series of challenges prompted throughout my PhD, I would like to take the time to express my appreciation for those who helped me achieve my full potential along the arduous journey. First and foremost are my supervisors; Prof. John Doran, Dr. George Amarandei, Assoc. Prof. Sarah Mc Cormack, and Dr. Hind Ahmed who never ceased in offering their endless support and expert advice. I am sure throughout the numerous group meetings, impromptu coffee mornings and amazing conferences I had the pleasure of attending, I no doubt tested your patience at least more than once. You all helped create a friendly and familiar environment, which made the last four years working both as an independent researcher as well as being involved in the collaborative effort ongoing in the SEAG group a real pleasure.

Jake Green once provocatively stated that “you only get better by playing a better opponent” and while the attribution of the term ‘opponent’ remains questionable, the motto has consistently reverberated throughout my short time here at the FOCAS institute. Special thanks to Dr. George Amarandei and Dr. Pauraic Mc Carron for their collaborative involvement throughout different stages of the project, you both helped to continuously push my knowledge basis into areas outside of my original projects scope. The project would not have been possible if not for the availability of the research facilities and technical advice offered within the FOCAS Institute. I would like to extend my gratitude to all the staff members within the research institute as well as the Dublin Energy Lab, Solar Energy Applications Group, and the School of Physics at the Technological University for Dublin for your advice, support, and cooperation.
The day to day operations which became mundane at the best of times were illuminated by the array of characters I had the fortune of encountering during my time at the FOCAS research centre. I would love to include everyone here, but I must keep within the word count limit, so I will keep it short and snappy. Thanks to Martin Quirke, Modan Wu, and Andrew Reynolds for brightening up the office environment, as without fail they managed to dredge up everyday something for me to take my intellectual frustrations out on, even if they were albeit misdirected, misinformed, or for purely comical reasons which I cannot go into detail. Given all the negativity (self-directed and otherwise) you will inevitably encounter during your time as a postgraduate, you better make sure you have one or two positive people within your circle, after all the universe favours balance and neutrality, right! The soon to be Dr. Eline Manaloto fulfilled these job requirements and then some, even at times unbeknownst to her.

Last, but by no means not least I would like to thank my loving parents for their unconditional support, love, and encouragement during the countless debacles, crazy periods and unadulterated scientific debauchery they had the pleasure and/or misfortune of experiencing.
### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Acceptor</td>
</tr>
<tr>
<td>Ag</td>
<td>Silver</td>
</tr>
<tr>
<td>AgNO₃</td>
<td>Silver nitrate</td>
</tr>
<tr>
<td>Al-BSF</td>
<td>Aluminium back surface field</td>
</tr>
<tr>
<td>Al-ZnO</td>
<td>Aluminium zinc-oxide</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>Aluminium oxide</td>
</tr>
<tr>
<td>a-Si</td>
<td>Amorphous silicon</td>
</tr>
<tr>
<td>Au</td>
<td>Gold</td>
</tr>
<tr>
<td>A.U.</td>
<td>Arbitrary units</td>
</tr>
<tr>
<td>CdTe</td>
<td>Cadmium telluride</td>
</tr>
<tr>
<td>CIGS</td>
<td>Copper Gallium Indium Selenide</td>
</tr>
<tr>
<td>C-PVT</td>
<td>Concentrated photovoltaic-thermal</td>
</tr>
<tr>
<td>C-SBS-PVT</td>
<td>Concentrated spectral beam-splitting photovoltaic-thermal</td>
</tr>
<tr>
<td>Cu</td>
<td>Copper</td>
</tr>
<tr>
<td>CuO</td>
<td>Copper oxide</td>
</tr>
<tr>
<td>D</td>
<td>Donor</td>
</tr>
<tr>
<td>DC</td>
<td>Down conversion</td>
</tr>
<tr>
<td>DCM</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>DLS</td>
<td>Dynamic light scattering</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl sulfoxide</td>
</tr>
<tr>
<td>DSSC</td>
<td>Dye synthesized solar cell</td>
</tr>
<tr>
<td>EQE</td>
<td>External Quantum efficiency</td>
</tr>
<tr>
<td>Eu</td>
<td>European union</td>
</tr>
<tr>
<td>Eu³⁺</td>
<td>Europium</td>
</tr>
<tr>
<td>EVA</td>
<td>Ethylene-vinyl acetate</td>
</tr>
<tr>
<td>FF</td>
<td>Fill factor</td>
</tr>
<tr>
<td>FPSTC</td>
<td>Flat plate solar thermal collector</td>
</tr>
<tr>
<td>FRET</td>
<td>Förster resonance energy transfer</td>
</tr>
<tr>
<td>FSEM</td>
<td>Field emission scanning electron microscope</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full-width at half maximum</td>
</tr>
<tr>
<td>GaInP/GaAs/GaInAs/GaInAs</td>
<td>Four junction solar cell: gallium indium phosphate / gallium arsenide / gallium indium arsenide / gallium indium arsenide</td>
</tr>
<tr>
<td>GW</td>
<td>Gigawatts</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>ICT</td>
<td>Intramolecular charge transfer</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium tin oxide</td>
</tr>
<tr>
<td>LDS</td>
<td>Luminescent down-shifting</td>
</tr>
<tr>
<td>LQY</td>
<td>Luminescent quantum yield</td>
</tr>
<tr>
<td>LSPR</td>
<td>Localised surface plasmon resonance</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>mc-Si</td>
<td>Monocrystalline silicon</td>
</tr>
<tr>
<td>MEF</td>
<td>Metal enhanced fluorescence</td>
</tr>
<tr>
<td>MF</td>
<td>Merit function</td>
</tr>
<tr>
<td>MgF₂</td>
<td>Magnesium fluoride</td>
</tr>
<tr>
<td>MNP’s</td>
<td>Metal nanoparticles</td>
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</table>
MPP  Maximum power point
MTPP  Maximum theoretical power point
NaBH₄  Sodium borohydride
ncSi  Nanocrystalline silicon
NIR  Near infrared
NP  Nanoparticle
N₂H₄  Hydrazine
pc-Si  Polycrystalline silicon
PDI  Polydispersity index
PEP  Plasmon enhanced photoluminescence
Phen  1,10-phenanthroline
PLA  Polylactic acid
PLDS  Plasmon enhanced luminescent down-shifting
PLQY  Luminescent quantum yield (solid samples)
PMMA  Poly(methyl methacrylate)
PT  Photothermal
PTE  Photothermal conversion efficiency
PV  Photovoltaic
PVA  Poly-vinyl alcohol
PVT  Photovoltaic-thermal
QY  Quantum yield
SBS  Spectral beam splitting
SE-LDS  Structure enhanced luminescent down-shifting
SEM  Scanning electron microscope
SE-PLDS  Structure enhanced plasmonic luminescent down-shifting
SiC  Silicon carbide
Si₃N₄  Silicon nitride
SiO  Silicon oxide
SiO₂  Silicon dioxide
SQ  Shockley-Queisser
STC  Solar thermal collector
S₀  Ground singlet state
S₁  First excited singlet state
TE  Transverse electronic
Ta₂O₅  Tantalum pentoxide
TiC  Titanium carbide
TiO₂  Titanium dioxide
TM  Transverse magnetic
TMM  Transfer matrix model/method
TSC  Tri-sodium citrate
TTA  Thenoyltrifluoroacetone
T₁  First excited triplet state
UC  Up-conversion
UV  Ultraviolet
VIS  Visible
V/V%  Volume percent
WLI  White light interferometer
<table>
<thead>
<tr>
<th>Wt%</th>
<th>Weight percent</th>
</tr>
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<tbody>
<tr>
<td>ZnS</td>
<td>Zinc sulphide</td>
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## Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>S.I. units</th>
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<tbody>
<tr>
<td>A</td>
<td>Absorbance</td>
<td>A.U.</td>
</tr>
<tr>
<td>A</td>
<td>Area</td>
<td>m²</td>
</tr>
<tr>
<td>α</td>
<td>Absorption coefficient</td>
<td>m⁻²</td>
</tr>
<tr>
<td>α</td>
<td>Temperature coefficient of resistance</td>
<td>°C⁻¹</td>
</tr>
<tr>
<td>c</td>
<td>Concentration</td>
<td>Mole m⁻³</td>
</tr>
<tr>
<td>C_w</td>
<td>Specific heat capacity of water</td>
<td>J kg⁻¹ k⁻¹</td>
</tr>
<tr>
<td>C_np</td>
<td>Specific heat capacity of nanoparticle</td>
<td>J kg⁻¹ k⁻¹</td>
</tr>
<tr>
<td>d</td>
<td>Diameter</td>
<td>m</td>
</tr>
<tr>
<td>d</td>
<td>Distance</td>
<td>m</td>
</tr>
<tr>
<td>D</td>
<td>Translational diffusion coefficient</td>
<td>m² s⁻¹</td>
</tr>
<tr>
<td>e</td>
<td>Fundamental unit of charge</td>
<td>Coulomb</td>
</tr>
<tr>
<td>E</td>
<td>Enhancement in the conversion performance due to a specific structural alteration in the PV devices architecture</td>
<td></td>
</tr>
<tr>
<td>E_g</td>
<td>Energy bandgap</td>
<td>eV</td>
</tr>
<tr>
<td>f</td>
<td>Concentration factor for C-PVT systems</td>
<td></td>
</tr>
<tr>
<td>F_ABS</td>
<td>Absorbed photon flux</td>
<td>No. of photons</td>
</tr>
<tr>
<td>F_b</td>
<td>Photon flux with a ‘blank’ sample</td>
<td>No. of photons</td>
</tr>
<tr>
<td>F_EMI</td>
<td>Emission photon flux</td>
<td>No. of photons</td>
</tr>
<tr>
<td>F_s</td>
<td>Photons flux with a ‘doped’ sample</td>
<td>No. of photons</td>
</tr>
<tr>
<td>FF</td>
<td>Fill factor</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>Irradiance</td>
<td>W m⁻²</td>
</tr>
<tr>
<td>I_max</td>
<td>Current delivered at maximum power</td>
<td>Amps</td>
</tr>
<tr>
<td>I_R</td>
<td>Current running through the platinum wire</td>
<td>Amps</td>
</tr>
<tr>
<td>I_sc</td>
<td>Short circuit current</td>
<td>Amps</td>
</tr>
<tr>
<td>J_sc</td>
<td>Short circuit current density</td>
<td>A m⁻²</td>
</tr>
<tr>
<td>j_00</td>
<td>Reverse saturation current</td>
<td>Amps</td>
</tr>
<tr>
<td>K_b</td>
<td>Boltzmann constant</td>
<td>m² kg s⁻²</td>
</tr>
<tr>
<td>L</td>
<td>Length</td>
<td>m</td>
</tr>
<tr>
<td>LQY</td>
<td>Luminescent quantum yield</td>
<td></td>
</tr>
<tr>
<td>LQY*</td>
<td>Luminescent quantum yield modified in the presence of another species i.e. nanoparticles</td>
<td></td>
</tr>
<tr>
<td>MF</td>
<td>Merit function</td>
<td></td>
</tr>
<tr>
<td>MPP</td>
<td>Maximum power point</td>
<td>Watts</td>
</tr>
<tr>
<td>MTPP</td>
<td>Maximum theoretical power point</td>
<td>Watts</td>
</tr>
<tr>
<td>n</td>
<td>Refractive index</td>
<td></td>
</tr>
<tr>
<td>PLQY</td>
<td>Luminescent quantum yield (solid samples)</td>
<td></td>
</tr>
<tr>
<td>P_max</td>
<td>Maximum power</td>
<td>Watts</td>
</tr>
<tr>
<td>P_PV</td>
<td>Power output of PV device</td>
<td>Watts</td>
</tr>
<tr>
<td>PTE</td>
<td>Photothermal conversion efficiency</td>
<td></td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
<td>Unit</td>
</tr>
<tr>
<td>--------</td>
<td>------------------------------------------------</td>
<td>---------------</td>
</tr>
<tr>
<td>$P_{th}$</td>
<td>Thermal power output</td>
<td>Watts</td>
</tr>
<tr>
<td>$R$</td>
<td>Reflectance</td>
<td></td>
</tr>
<tr>
<td>$R$</td>
<td>Resistance</td>
<td>$\Omega$</td>
</tr>
<tr>
<td>$R_e$</td>
<td>Effective weighted average reflectance</td>
<td></td>
</tr>
<tr>
<td>$R_w$</td>
<td>Weighted average reflectance</td>
<td></td>
</tr>
<tr>
<td>$U$</td>
<td>Hydrodynamic radius</td>
<td>nm</td>
</tr>
<tr>
<td>$S$</td>
<td>Resistance</td>
<td>$\Omega$</td>
</tr>
<tr>
<td>$SR$</td>
<td>Spectral response</td>
<td>$A\ W^{-1}$</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
<td>Kelvin</td>
</tr>
<tr>
<td>$T$</td>
<td>Transmittance</td>
<td></td>
</tr>
<tr>
<td>$T_C$</td>
<td>Solar cell temperature</td>
<td>Kelvin</td>
</tr>
<tr>
<td>$T_{LIQUID}$</td>
<td>Optical transmittance of liquid</td>
<td></td>
</tr>
<tr>
<td>$V_{mp}$</td>
<td>Voltage derived at maximum power production</td>
<td>Volts</td>
</tr>
<tr>
<td>$V_{OC}$</td>
<td>Open circuit voltage</td>
<td>Volts</td>
</tr>
<tr>
<td>$w$</td>
<td>Worth factor (ratio of price of electricity to thermal energy)</td>
<td></td>
</tr>
<tr>
<td>$X$</td>
<td>Optical path length</td>
<td>Metres</td>
</tr>
<tr>
<td>$Z$</td>
<td>Zeta potential</td>
<td>Volts</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>Thermal conductivity</td>
<td>$W\ m^{-1}\ k^{-1}$</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Viscosity</td>
<td>$m^2\ s^{-1}$</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Conversion efficiency</td>
<td>$%$</td>
</tr>
<tr>
<td>$\varphi$</td>
<td>Solar irradiance</td>
<td></td>
</tr>
</tbody>
</table>
Table of Figures

Figure 1.1: (a) The cumulative installed PV capacity and its regional breakdown from 2010 – 2017. (b) The percentage (%) of total power production (MWp) derived from photovoltaics 1997 – 2017 and its regional breakdown. (c) solar PV module price (€/kWp) as a function of the cumulative installed photovoltaic capacity (GWp) 1980 – 2018. (d) Average price (€ / kWp) for commercial PV rooftop systems in a European Union context, 2006 – 2018, and the distinction between the system costs (monitoring electronics, inverters, installation, etc. – shown in navy) and the modules cost (shown in orange). (e) Advancements in the conversion efficiency of PV cells based on various technologies and different materials from 1975 to 2019. ................................................................. 7

Figure 1.2: Inter-comparison between the conversion efficiency η (%) and projected costing (US $ m-2) for 1st generation (I), 2nd generation (II) and 3rd generation (III) photovoltaic technologies including the highest reported conversion efficiency in 2018 as well as the fundamental thermodynamic limit of the conversion process. .................... 10

Figure 1.3: The typical I-V curve (black) and power sweep (red) of a PV cell under illumination of a AM1.5G spectra. The key electrical characteristics i.e. the short circuit current (Isc), the open circuit voltage (Voc), the current (Imp) and voltage (Vmp) values which yield the maximum power point (MPP), as well as the theoretical maximum power point (MTPP) are presented. The fill factor (FF) is the ratio of the device’s performance (area under the I-V response curve) as a ratio of the same device’s theatrical performance (area under the green curve). ........................................................................................................ 11

Figure 1.4: (a) The disparity between the Shockley-Queisser limit of theoretically attainable efficiency (ηSQ – orange), and the highest efficiency achieved with modules (ηModule - blue) and cells (ηLab - green) based upon different major PV technologies including; mc-Si, pc-Si, CdTe, GaAs, Organic, CIGS, Perskovite, aSi-ncSi, mc-Si (x80) and InGaP/GaAs/InGaAs. Where mc-Si(x80) and aSi-ncSi stand for monocrystalline silicon under an illumination of 80 suns, and amorphous/nanocrystalline silicon respectively. (b) The fraction (%) of sunlight (AM 1.5G standard spectrum) lost to different intrinsic loss mechanisms within an ideal PV device, as a function of the fundamental absorption band of the active material, under the scenario envisioned by Shockley & Queisser: (1) light may not absorbed due to the finite energy bandgap (yellow), (2) The excess energy of an absorbed photon is turned into heat (orange), (3) The emittance of energy, in response to the recombination of pairs of holes and electrons (green), and (4) the flow of charges throughout the electrodes generates entropy (blue) ........................................................................................................ 13

Figure 1.5: The energy distribution within the solar spectrum (AM1.5G – solid line) and the accompanying spectral responsivity of a monocrystalline silicon cell (highlighted in grey): signifying the large amount of irradiance left uncaptured even by the most highly commercialised form of PV technology available. Approaches towards spectral conversion can be separated into two distinctive spectral regions (1) those in which the molecules activity is confined towards λ < 400 nm – which includes down-conversion (DC) and down-shifting (DS) strategies and (2) those whereby the molecules activity is within the infrared region (λ > 1100nm) – up-conversion strategies. The energy available for potential harvesting within each target spectral window is 149 w m-2 (LDS and DC) and 164 w m-2 (UC) respectively: with these values dependent upon the type of PV technology which the device is built upon. The conversion mechanism underpinning each
strategy is also provided in the form of a simplified Jablonski diagram, where the excitation (red arrow) event promotes the photoluminescent species into an excited state before returning to the ground state via one or more radiative emission events; down conversion (green arrow), luminescent down-shifting (violet arrow), and up-conversion (blue arrow).

**Figure 1.6:** (a) Schematic of an LDS-fitted PV device showing the various pathways an incident photon (blue arrows) can take within the optical system (red arrows), and (b) the corresponding aggregate spectral properties stemming from the series of interactions for an LDS fitted mc-Si device: whose external quantum efficiency (EQE) in response to the solar irradiance (AM1.5G – grey) is highlighted with a dashed line. An incident photon [1] can pass straight through the LDS layer without interacting with the photoluminescent material [5]. Alternatively, a photon can be reflected from the front surface of the LDS layer [2] or interact with the luminescent species [3] prior to undergoing reflection and exiting the side of the layer [8]: such losses are collectively bundled as the escape cone losses. Finally, the photons which interact with the encapsulated photoluminescent material [3] can undergo reflection [6] or undergo a successive series of photoluminescent events [7] before finally reaching the underlying cell.

**Figure 1.7:** (a) Geometry, (b) quadrupole moment and (c) electrostatic surface potential (where red is positive and blue is negative) of typical π-π interactions (stacked, T-shape, and parallel displaced) found in aromatic based systems.

**Figure 1.8:** Schematic overview of a metal coordination complexes key components (1) a series of aromatic ligand derivatives which act as “antennae” shuttling the energy they absorb directly into the (2) metal ion (Eu coordination centre – shown in red) and (3) the accompanying sensitizing co-ligand (in this instance 1,10-philanthroline) which acts to enhance the structures stability whilst also ensuring the distinctive transitions within the metal, which perturbate their signature emission spectrum (shown in red within the accompanying spectrum) are encouraged. An example of the absorption (red/green) and emission (red) spectra one of the most widely studied coordination complexes – Eu(TTA)3Phen, where TTA is 2-Thenoyltrifluoroacetone, is provided to showcase the dramatic stokes shift achievable with similar structures.

**Figure 1.9:** (a) Schematic structure of 1,10-philanthroline (I) with related ring numbering and the bidentate ligands corresponding normalised (b) absorption – (black), emission – (red) and phosphorescence – (blue) spectra in CH2Cl2. (c, e, f) Substituted phenanthroline architectures, where R denotes the specific moiety introduced and the corresponding absorption (d) and emission spectra (g) of the compounds for which (II) R = H (absorption spectrum shown in d – black) or R = OCH3 (absorption profile shown in d – blue), and (IV) R is alternated between H, CH3, OCH3 and N(CH3)2 [110]. The luminescent quantum yield (LQY) of the each phenanthroline derivative is also provided as a mean of comparison, with the LQY of the compounds abbreviated in (f & g) varying from 0.41 (R = H), 1 (R = CH3), 0.64 (OCH3) to ~ 0 (N(CH3)2) .

**Figure 1.10:** Energy levels (\(\pi_1\), \(\pi_2\) and \(\sigma_N\)) existing in pristine phenanthroline and their corresponding molecular origin within the aromatic ring (highlighted in black).

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(iii) Dispersal of 1ml of the fluorophore doped PMMA resin, directly onto a thoroughly cleaned glass substrate

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**Figure 6.1:** (a) Schematic of a structure-enhanced photovoltaic device, highlighting the individual design components; a semi-transparent host matrix encapsulating a photoluminescent material in isolation or in combination with a metal nanostructure, the underlying photovoltaic technology as well as a ‘spectrally selective’ structure element. (b i & ii) Initial architectures for a structure-enhanced plasmonic luminescent down-shifting (SE-PLDS) device and (b iii) the operating principle upon which the device is based. (b iii) The structural elements reflection profile (b iii – green) is tailored to yield a maximum reflectance within the absorption window of the fluorescent material utilised (b iii – blue) while minimising the reflectivity across the emission range (b iii – red) and high responsivity window (b iii – grey) of the underlying photovoltaic technology upon which the device is built. (c) The complex 3-dimensional structure of a SE-PLDS device, consisting of a cascading series of layers of differing refractive index (n₁, n₂ …) can be represented as a one-dimensional periodic structure within the confines of a transfer matrix method: assuming the refractive index within each individual layer is homogenous. The transfer matrix method models the optical behaviour of a plane wave composed of two mutually orthogonal linearly polarised components (Transverse electronic – TE and transverse magnetic - TM modes) as they propagate through the structure along the direction of propagation (r).

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Chapter 1  
Solar Energy Technologies

1.1 Introduction  
This chapter will serve as an introduction through the overarching application of solar energy and its many technical and economic challenges, as well as the material strategies aimed at circumventing these limitations. Delving into the fundamental constraints imposed on photovoltaic and photothermal conversion technology through the selection of the raw materials employed in the construction of solar collection systems demonstrates the need for identifying alternative hybrid materials which possess enhanced optical and thermal characteristics. Through highlighting the primary material strategies which have been appointed to assist in enhancing the energetic and economic merit of solar collection devices, the inherent physical limitations of the approaches become even more evident. Building upon these concepts the possibility of leveraging a completely organic/organometallic synthetic strategy - from which an expansive series of unique molecular frameworks can be derived, for enhancing the conversion processes within photovoltaic and photothermal collectors is presented. The fundamental molecular building block behind this strategic approach 1,10-phenanthroline, is additionally discussed in terms of its electronic band structure and what functionalisation strategies have previously been exploited to augment and heighten its luminescence. The expensive series of topics covered in this chapter will ultimately serve to contextualise the significance and overall merit of the results presented in later chapters.

1.2 The Renewable Revolution  
As the global economy continues to grow in terms of its technological prowess and economic development, the increase in the energy consumption requirements must be accommodated by an ever-evolving electrical grid [1-5]. For example, in 2017 the cumulative worldwide energy consumption reached nearly 600 terawatts, and it is
expected that it will increase substantially (23% - 64%) by 2040 under the different environmental and climate scenarios envisioned [1]. In its current fragile, aging and outdated configuration, the electrical grid is becoming radically overhauled in an attempt to transition away from its heavy reliance on fossil fuels to meet the increased demand for ‘clean’ electricity [1, 6-9]. Once passive, the role played by the electrical grid as a singular isolated network of power distribution is being steadily redesigned to handle the implementation of more variable forms of energy production, specifically renewable sources [1, 6-9]. Renewable energy sources provide a ‘cleaner’ alternative to conventional fossil fuel-based approaches, through deriving energy from naturally occurring resources (solar, wind, wave and geothermal) that are continuously regenerated over short timescales. Transitioning to a grid where renewable energy is used to meet a larger percentage of the global energy demand would increase our chances of a more environmentally sustainable and energy-secure global economy in the future [1, 3, 5, 8, 9].

This inexorable need to alter and diversify the world’s current grid configuration is one of the greatest challenges facing the global economy in the coming years [5]. The ramifications of anthropogenic climate change on global economic development and globalisation are increasingly being recognised at a governmental, commercial, and industrial level [3, 5, 9, 10]. For example, large scale economies such as Germany (40%), the United Kingdom (33%), and Spain (40%) are already starting to become increasingly powered by renewable energy in 2018 [10]. In the same year more than 130 leading corporations including Google, Microsoft, Ikea, General Motors, and J.P Morgan had joined the renewable energy 100 (RE100) initiative, promising to commit to being 100% powered by renewable energy [11, 12]. Even at a corporate level, more and more companies are looking to disengage from fossil fuel backed financial assets and investments, with ENGIE (a French utility company) selling off fossil fuel based assets
worth $15 billion during the 2016 to 2017 period [12]. The same company was promoting the research and development of renewable energy technologies through reinvesting a further €22 billion by the end of 2018 [12]. When combined with the fact that renewable technologies had accounted for ~70% of the net-additions to the global power generation capacity in 2018, it is clear that the transition towards a more sustainable means of energy generation and overall energy efficiency is well underway [7, 9, 10, 12].

However, for a complete “green” transition to be fully realised, some of the underlying limitations inherent in these renewable technologies must be addressed before they can truly become cost competitive sources of energy production. This delay of technological advancement in the development of highly energy-efficient renewable based technologies has resulted in a drawback of the capital investments allocated towards low-carbon alternatives such as solar energy (photovoltaic, photothermal) technologies in 2018 [3]. Crucially, the additional capital investments, required to rearrange the energy sector in-line with the legislative changes adopted to make renewable energy an international priority (Paris agreement, Kyoto protocol, etc.), are 40% lower than the projections under the different scenarios envisioned [3, 10]. This is despite the falling costs associated with the manufacture of these technologies [3, 7, 9, 10, 12]. It is clear that, in order to sustain the continued growth, development, and market penetration of renewable energy sources, their capability to capture and convert energy must be increased substantially if they are to become the prevailing energy solution [3, 7, 9, 10, 12].

1.3 Photovoltaics

Photovoltaics (PV’s) is the renewable sector which has received the greatest interest, investment and uptake throughout the last two decades [3, 6, 7, 9, 10]. This is due to the significant reduction in the costs associated with manufacturing technology, its modularity and adaptability for integration into sustainable architectures, as well as its
energy harvesting potential [3, 10, 13, 14]. The year 2018 was the 8th consecutive year in a row for which photovoltaics captured the largest share of the capital flow allocated towards low-carbon technologies, securing ~60% of all funding initiatives issued [15]. Within the same year, the newly installed photovoltaic capacity had increased almost 32% (figure 1.1 a), with the annual growth reported compounding on the fact that between 2008 and 2015 the average price of a photovoltaic module had deceased by more than 80% (figure 1.1 c) [3, 10, 15]. This substantial reduction in cost has been primarily driven by major advancements in materials research and by the progress made in developing the streamlining manufacturing technology [8, 9, 16]. The latter can be exemplified by the well documented correlation between the cumulative installed photovoltaic capacity and the reduction exhibited in the price of an individual PV module (figure 1.1c). As the fabrication process becomes further refined, the costs associated with manufacturing the technology is reduced with the average module price falling by 20% for every doubling of the production volume [15-18]. Even in the commercial sector, where PV efficiencies can be moderately lower than those reported within a research environment, the contribution of the module cost towards the overall PV system price (monitoring electronics, inverter, etc.) had been decreased from 71% to 45% of the total cost from 2006 to 2018 (figure 1.1 d) [15, 16]. Nevertheless, despite the technology’s rapid deployment and the reduction in manufacturing costs, the gradual increases in the conversion efficiencies achieved remains a fundamental limitation of the PV technology [19-22]. This can be observed in the plateauing of the PV modular pricing since as early as 2014 (see figure 1.1 d) [16]. The ramifications of this limitation have heavily influenced the rates of market penetration for the technology (figure 1.1 b), especially within the European region where the rate of PV implementation peaked as early as 2008 (figure 1.1 b). In order to better understand the core of the problem, the following sections
of this chapter delve into the operation of photovoltaic devices, the different types of architecture available, and the inherent limitations underpinning them.

1.3.1 Photovoltaic Architectures & Their Economics

All photovoltaic (PV) devices are based upon the physical phenomenon in which electromagnetic radiation is directly converted into usable electricity via the photoelectric effect [23]. The material properties of the semiconducting material (such as its crystal structure, the presence of lattice defects, and/or the level of impurities introduced) heavily influence the devices capability to capture and convert a specific spectral range from within the solar spectrum [22, 24, 25]. The current PV market consists of a diverse range of different technologies, each of which is built upon a particular material, whose architecture continues to undergo modifications as the understanding of the internal loss mechanisms associated with each material intensifies [26]. Depending upon the material utilized and its level of commercial maturity, the different classes of PV technology are grouped into three distinct generations (1\textsuperscript{st} – silicon based, 2\textsuperscript{nd} – thin film technologies, and 3\textsuperscript{rd} – emerging technologies) as shown in figure 1.1 e [24-26].

1.3.1.1 1\textsuperscript{st} Generation Technology

The 1\textsuperscript{st} generation technology is the oldest and most commercially developed form of PV technology available today, with these types of devices still accounting for 95\% of all of the PV panels produced in 2018 [16]. Their structure and the resulting loss mechanisms have been thoroughly explored and addressed through improvements made in the device configuration at the manufacturing stage [23, 24, 26]. Their architecture consists of a single-junction built upon different allotropes of silicon, including monocrystalline (mc-Si) and polycrystalline (pc-Si) forms [26]. The conversion efficiency achieved with commercial modules, based upon the mc-Si and pc-Si cells, stands at \( \sim \) 16 $\%$ – 24 $\%$ and \( \sim \) 12 $\%$ – 20 $\%$, respectively [27-29]. In the laboratory testing environment, efficiencies as high as 27$\%$ for mc-Si and 23$\%$ for pc-Si cells have been
realized – see figure 1.1 e [27, 29, 30]. Although this generation of materials has endured a long period of technological success, the need to increase the efficiencies achievable and further enhance the market competitiveness of photovoltaics has forced the industry to consider alternative material solutions [3, 16, 24].

1.3.1.2 2nd Generation Technology

The driving force behind the development of the 2nd generation (thin-film) PV technologies was the integral need to drive down the fabrication costs involved in the production of high quality, low defect materials, imposed by 1st generation designs [24, 26]. Interleaving alternating layers of semiconducting material such as cadmium telluride (CdTe), copper gallium indium selenide (CIGS) or amorphous silicon (a-Si) onto relatively inexpensive substrates (glass, metal or polymer-based) has delivered single-junction devices whose designs are economically viable [15, 16, 26]. Efficiencies achieved with the technology range from 5% - 10% (a-Si) [32], 16% - 22% (CdTe) [27], and 18% - 23% (CIGS) [27, 33] in commercially available large-scale modules, with higher efficiencies reported with smaller scale lab modules (see figure 1.1 e – green). The impact of these devices in the market has been small; just 5% of global PV power production being derived from 2nd generation thin-film technologies in 2017 [16]. The lack of market penetration is due to the fact that for new and emerging technologies to enter the market the prices must be comparable to the existing market prices that have been established by the longstanding silicon-based technologies [15, 16]. Ample opportunity remains to promote the continued reduction in the materials consumed and the associated costs experienced throughout the manufacture of photovoltaics. This could be obtained, for example, through further refinements in thin-film solar cell architecture (figure 1.2).
Figure 1.1: (a) The cumulative installed PV capacity and its regional breakdown from 2010 – 2017 [16].
(b) The percentage (%) of total power production (MW\textsubscript{p}) derived from photovoltaics 1997 – 2017 and its regional breakdown [16]. (c) Solar PV module price (€/kW\textsubscript{p}) as a function of the cumulative installed photovoltaic capacity (GW\textsubscript{p}) 1980 – 2018 [16]. (d) Average price (€/kW\textsubscript{p}) for commercial PV rooftop systems in a European Union context, 2006 – 2018, and the distinction between the system costs (monitoring electronics, inverters, installation, etc. – shown in navy) and the modules cost (shown in orange) [16]. (e) Advancements in the conversion efficiency of PV cells based on various technologies and different materials from 1975 to 2019 [31].
1.3.1.3 3rd Generation Technology

As thin-film technologies continue to drive down the cost of the active material within PV devices, they will ultimately encounter a physical limit, whereby the amount of semiconducting material cannot be reduced any further within the confines of a single-junction design [22, 23, 34]. 3rd generation technologies were designed on the premise of capitalising on the merits of each prior iteration of the technology. Using a diverse combination of highly efficient materials in conjunction with low-cost substrates, energy intensive techniques are developed to deliver conversion efficiencies beyond even the theoretical limit of single-junction systems performance [23-25]. Thus, advanced energy and time intensive strategies such as the creation of multiple junctions [24, 25, 35], hot-carrier extraction [36, 37], intermediate bandgap formation [24, 25, 38], as well as modulation of the incoming solar spectrum [24, 39, 40] have been developed and deployed to help promote the energy harvesting potential of photovoltaic technology [21, 22].

The most eloquent of which seems to be the inclusion of different semiconducting materials, each possessing its own distinct bandgap energy and, thereby, allowing the cascading series of single junctions (sub-cells) to capture and convert energy across a much larger bandwidth of frequencies [41, 42]. For example, the typical spectral response ranges of 1st and 2nd generation technologies extend anywhere from 200 nm – 1200 nm [43, 44], while 3rd generation technologies expand this collection and conversion range to 200 nm – 2500 nm or larger [41, 42]. Utilizing a multijunction architecture consisting of GaInP/GaAs/GaInAs/GaInAs sub-cells, conversion efficiencies of 46% have been realised under a heavily concentrated irradiance of ~600 suns [27]. However, under the normal irradiance conditions (1000 Wm\(^{-2}\) or 1 suns-equivalent) outlined in the ASTM-G173-03 standard [45, 46] this efficiency diminishes to 33% [27]. Still, the non-modular nature of the technology, and its typical requirement of a concentrated solar flux in
combination with high precision manufacturing techniques has resulted in a lack of commercial application to date [24-26, 36]. The underlying strategy here is to drastically drive down the energy production costs, often expressed in terms of $/watt, through significantly increasing the devices conversion efficiency. Figure 1.2 demonstrates the projected cost savings attainable with each generation of PV technology as a function of their existing and theoretically attainable conversion efficiencies [24].

Another promising avenue of exploration is represented by synthetic polymer-based solar cells. In these cells the internal electronic transport processes integral to PV devices are replicated using specifically designed molecular species, which drive the semiconducting push-pull dynamics within an organic or organometallic framework [24, 47, 48]. They represent some of the most promising forms of PV technology due to the flexibility of their design and their capability to be integrated into modern, aesthetic and sustainable architectural features [49]. These characteristics coupled with their functionality under extremely low intensity lighting conditions, like those encountered in indoor environments or the diffuse lighting situations frequently experienced throughout the temperate climate zones, makes them highly versatile [23, 24, 26]. In addition, there are low-cost, facile, and chemically flexible synthesis routes from which the structures derive, making them the potential pinnacle of PV development [23, 24, 26]. This category of devices includes dye synthesized solar cells (DSSC’s) [50], purely organic based solar cells [47], as well as the renowned perovskite solar cells [48]. The maximum efficiency achievable with each so far has been 12 % [51], 12 % [52] and 23 % [53], respectively (see figure 1.1 e). Unfortunately, in their current form, they suffer from instabilities (photodegradation of active molecules, ion migration in the bulk material, and the vulnerability of the material(s) to heat and moisture) arising in their electrical performance over their relatively short (<500 hours) operational lifetime [24, 26].
Figure 1.2: Inter-comparison between the conversion efficiency \( \eta \) (%) and projected costing (US $ m^{-2}) for 1st generation (I), 2nd generation (II) and 3rd generation (III) photovoltaic technologies including the highest reported conversion efficiency in 2018 as well as the fundamental thermodynamic limit of the conversion process. [25]

1.4 Conversion Efficiency, Loss mechanisms and its fundamental limit

The conversion efficiency \( \eta \) represents the most realistic indicator used throughout the evaluation and differentiation of PV performance. This can be defined as the ratio of electrical-output to energy-input for a given device [24]. The term \( \eta \) embodies many constituting parameters of the system, such as its open circuit voltage \( (V_{\text{OC}}) \), short-circuit current \( (I_{\text{SC}}) \) (sometimes short-circuit current density \( (J_{\text{SC}}) \) is used), and fill factor \( \text{(FF)} \). These parameters are dependent upon the fundamental properties of the material [23, 24] which include the band-gap energy of the substance as well the mobility of charge carriers (electrons and holes) within it, both of which are heavily influenced by the lattice structure and the defect density [23, 24]. Through modelling the behaviour of charge carriers permeating throughout an ideal solar cell of infinite mobility, unity luminescent efficiency, zero contact resistance, and zero junction loss, the balance between photogeneration (figure 1.4 b - cyan) and radiative recombination processes (figure 1.4 b
– violet & dark yellow) can be studied as they will be important in limiting the efficiency of the conversion process [21, 22, 24, 25]. This approach (i.e. to understand the fundamental energy harvesting potential of PVs and its subsequent limitations) was first developed and applied by Shockley and Queisser (SQ) and it is still the prominent method used to evaluate the theoretical performance of PV devices [21, 22, 24, 25]. The method yields a signature, predicted I-V response curve, like that shown in figure 1.3, from which all the performance metrics previously stated (I_{sc}, V_{oc}, and FF) are derived.

**Figure 1.3:** The typical I-V curve (black) and power sweep (red) of a PV cell under illumination of a AM1.5G spectra. The key electrical characteristics i.e. the short circuit current (I_{sc}), the open circuit voltage (V_{oc}), the current (I_{mp}) and voltage (V_{mp}) values which yield the maximum power point (MPP), as well as the theoretical maximum power point (MTPP) are presented. The fill factor (FF) is the ratio of the device’s performance (area under the I-V response curve) as a ratio of the same device’s theatrical performance (area under the green curve)

Any optical, electrical, or conversion losses introduced through the non-ideality of the material properties would result in efficiencies lower than that predicted under the SQ scenario. This comes in addition to the losses introduced through the difficult integration of individual cells, typically 156 mm x 156 mm in size into larger-scale modules (~1.6 m x 1 m) [24, 54]. The divergence between η achieved with small form factor cells (η_{Lab} – figure 1.4 a – green), full scale modules (η_{Module} – figure 1.4a – blue) and the maximum efficiency conceivable (η_{SQ} – figure 1.4 a – orange) across a host of
different PV technologies is provided in figure 1.4 a. The disparity between the highest efficiencies realised thus far ($\eta_{\text{Lab}}$) and those ideally attainable ($\eta_{\text{SQ}}$) highlights the room for improvement on a fundamental architectural level [24, 26, 35]. The divergence observed in scaling up the technology from a small form factor ($\eta_{\text{Lab}}$) to a larger more commercialised application ($\eta_{\text{Module}}$) pinpoints the improvements that have to be attained to develop the transfer and adaptation of laboratory prototypes into integrated systems [24]. The most mature technologies (figure 1.4 a - mc-Si, GaAs, and pc-Si) display very little integration losses, while for new and emerging types of technology (figure 1.4 a - perskovite and organic based cells) the losses can reach 50% [24]. As mature technologies approach the SQ limit (~33% for a single junction), their evolution has begun to show little change (figure 1.1 e), showing the need for rethinking the approach towards curtailing the primary loss mechanism, i.e. the nonideality of the fundamental semiconducting materials.

The fundamental loss mechanisms, stemming from the non-ideal reality of the materials available, are summarised in figure 1.4 b. Taking mc-Si as an example, whose bandgap energy ($E_G$) is ~1.12 eV, the maximum energy convertible into usable electrical power is 29%, while at the forefront of solar cell development $\eta \sim 27\%$ have been realised with the material [22, 24, 25]. The remaining energy is lost due to a combination of: (1) a large portion of the solar spectrum possessing energies well below the spectral region that can be converted by the cell (this energy is not absorbed (figure 1.4 b - yellow)); (2) another equally large percentage of the solar irradiance is constituted of high energy photons, producing carriers which, upon relaxation within the lattice, generate heat (figure 1.4 b – orange); and (3) some of the energy absorbed is lost internally due to the radiative (figure 1.4 b – light yellow) or non-radiative (figure 1.4 b – purple) recombination processes -[20, 24, 26, 35]. The first two mechanisms alone amount to ~19 % and ~30 %, respectively, decrease in the theoretical solar cell efficiency, even before
the considerations of adapting the technology towards larger scale applications. This spectral mismatch between the optoelectronic properties of the active material and the incoming solar flux constitutes, depending upon the material, 50% - 80% (figure 1.4 b) of the losses incurred throughout the conversion process [24].

An important question presents itself: is there another way through which some of these spectral losses could be alleviated post-manufacture? Borrowing concepts implemented in the design of organic based PVs (highly absorbing molecular species), the energy intensive strategies devised for 3rd generation PV technology (modulation of
the incoming solar spectrum), as well as those encountered throughout the development of dye synthesized cells (prolonging the operational lifespan through molecular modifications) a method, now generically known as spectral conversion, can be proposed to overcome some of these losses.

1.5 Spectral Converters

Conventional solar cell structures are fine-tuned towards the efficient capture and conversion of light across the visible region (400 nm – 800 nm), where a considerable fraction of the solar energy is distributed – see figure 1.5. The premise of spectral converters lies in the utilisation of adaptive material strategies, to modulate the incident solar spectrum to better suit the photoactive material responsivity to better utilise the spectrum, rather than altering the architecture as in the case of 3rd generation PV technologies [20, 26, 55-57]. Their structure offers the flexibility to be integrated directly onto a finished PV device, in the form of a semi-transparent photoluminescent layer, whose role is to absorb photons which are ineffectively utilised and convert them to wavelengths more suitable for the photoactive PV material [20, 56, 57]. More electron-hole pairs per incident photon are produced thus increasing the overall device external quantum efficiency (EQE) and short circuit current density ($J_{sc}$)[20, 56, 57].

The modulation of the incident spectrum is achieved through a plethora of different molecular species, each of which can be categorized into two distinct types of converter based upon the spectral window of activity. The structures tailored towards the capture and conversion of highly energetic photons from deep within the ultraviolet region ($\lambda < 400$ nm) to more moderate energies are referred to as downconverters and include both down-conversion (DC – figure 1.5, green arrow in Jablonski diagram) and luminescent down-shifting (LDS - figure 1.5, purple arrow in Jablonski diagram) approaches [26, 55-57]. The divergence between these two analogous approaches lies in
the internal conversion mechanism which facilitates the energy exchange process [26, 55-57].

**Figure 1.5:** The energy distribution within the solar spectrum (AM1.5G – solid line) and the accompanying spectral responsivity of a monocrystalline silicon cell (highlighted in grey): signifying the large amount of irradiance left uncaptured even by the most highly commercialised form of PV technology available.

Approaches towards spectral conversion can be separated into two distinctive spectral regions (1) those in which the molecules activity is confined towards λ < 400 nm – which includes down-conversion (DC) and down-shifting (DS) strategies and (2) those whereby the molecules activity is within the infrared region (λ > 1100 nm) – up-conversion strategies. The energy available for potential harvesting within each target spectral window is 149 W m$^{-2}$ (LDS and DC) and 164 W m$^{-2}$ (UC) respectively: with these values dependent upon the type of PV technology which the device is built upon [55]. The conversion mechanism underpinning each strategy is also provided in the form of a simplified Jablonski diagram, where the excitation (red arrow) event promotes the photoluminescent species into an excited state before returning to the ground state via one or more radiative emission events; down conversion (green arrow), luminescent down-shifting (violet arrow), and up-conversion (blue arrow).

The LDS approach relies on conventional photoluminescence, whereby, at best, a single photon is emitted for every absorption event (figure 1.5). This restricts the definition to molecular species whose luminescent quantum yield (LQY) is ≤ 1 [20, 26, 55-57]. As such, this strategy is focused on alleviating the energy losses arising from Auger, Shockley-Read-Hall and surface recombination of charge carriers, which confines devices (integrated spectral converter– PV cell systems) solely based on LDS to remain
bound by the Shockley-Quiesser barrier [56, 57]. The DC approach, on the other hand, utilises the quantum-cutting to transfer energy from one radiative centre to another in order to generate multiple low-energy photons from a single high-energy absorption event and, hence, by definition, it encompasses structures which can possess quantum yield’s (QY’s) ≥ 1 [26, 55-57]. In contrast to the LDS approach, devices incorporating DC materials have the capability to circumvent the Shockley-Quiesser barrier as they can generate a higher number of photons and, consequentially, electron-hole pairs than their single-emission LDS counterparts [56].

Alternatively, structures with the potential to combine two or more low-energy photons from within the infrared part of the spectrum (λ > 1100 nm) to produce one higher energy electron-hole pair are known as up-converters (UC) [26, 56, 57]. The UC layers are usually positioned beneath the PV cell to aid in the capture and transformation of any sub-bandgap photons and a reflective layer ensures the up-converted photons are redirected back towards the PV cell for conversion [26, 56, 57]. Comprehensive theoretical studies have shown that idealised DC and UC materials have the capacity to boost the conversion performance within a single-junction mc-Si solar cell from 29% to 36.75% [58] and 47.6% [59], respectively. However, both avenues remain limited in their experimental application by the shear lack of availability of material candidates possessing suitable optical properties in conjunction with low-cost scalable fabrication routes [26, 55-57].

LDS, conversely, offers considerable scope for the addition of multifunctionality into the application of PV devices through the capability of the retrofitted layer to act as an external protective, hydrophobic and antireflective coating [60-64]. This, in combination with the extensive library of material candidates already catalogued, the well exhibited and understood loss-mechanisms at play and the highly developed readily deployable fabrication pathways, have made LDS an alluring application [20, 56, 57].
1.5.1 Luminescent Down-Shifting (LDS)

In its simplest architecture, LDS embodies a planar photoluminescent layer coated on the top surface of a PV device (figure 1.6 a). As a result of the photoluminescent process, a fraction of the incident UV spectral irradiance, where most PV cells exhibit low EQE’s, is absorbed before being re-radiated at longer wavelengths, where the photoconductive material responds better [20, 56, 57]. A simple example of how the LDS process modulates parts of the spectrum toward a spectral region of higher EQE is provided in figure 1.6 b. The mc-Si cell exhibits a decrease in EQE for $\lambda < 400$ nm (figure 1.6 b – dashed line). A photoluminescent organic dye derivative that absorbs within this spectral region (figure 1.6 b – cyan) and emits at $\lambda > 500$ nm (figure 1.6 b – red) transforms parts of the incident radiation where the cells performance is “poor” (EQE $< 0.6$) to more energy efficient conversion windows where the EQE $\geq 0.8$. The energy distribution available within the standardised air mass 1.5 global (AM1.5G) spectrum is also provided in figure 1.6 b (grey), in order to consider the process in terms of the photons available for ‘down-shifting’. The lower energy photons emitted by the luminescent species are subsequently absorbed by the Si cell, producing more electron-hole pairs and thus an increased $J_{sc}$ [65-70]. An increase in $J_{sc}$ is typically, but not always, correlated with an accompanying improvement in the devices EQE within the absorption window of the LDS layer [56, 71]. Consequently, the LDS efficiency is quantified by a combination of the relative changes in the EQE and IV curves measured before and after the LDS coating is applied [56, 65-71].

The introduction of an LDS layer into the PV system creates a cascade of additional interactions with the incoming radiation, resulting in the emergence of extra loss mechanisms – the majority of which are highlighted in figure 1.6 a. Therefore, any potential enhancement offered by modulating the spectrum must compensate for these losses before offering an overall improvement [56, 65-71]. These additional losses stem
Figure 1.6: (a) Schematic of an LDS-fitted PV device showing the various pathways an incident photon (blue arrows) can take within the optical system (red arrows), and (b) the corresponding aggregate spectral properties stemming from the series of interactions for an LDS fitted mc-Si device: whose external quantum efficiency (EQE) in response to the solar irradiance (AM1.5G – grey) is highlighted with a dashed line. An incident photon [1] can pass straight through the LDS layer without interacting with the photoluminescent material [5]. Alternatively, a photon can be reflected from the front surface of the LDS layer [2] or interact with the luminescent species [3] prior to undergoing reflection and exiting the side of the layer [8]: such losses are collectively bundled as the escape cone losses. Finally, the photons which interact with the encapsulated photoluminescent material [3] can undergo reflection [6] or undergo a successive series of photoluminescent events [7] before finally reaching the underlying cell.

As a direct consequence, most of the research effort since the early 1970’s [72] has been funneled into the development, characterisation and enhancement of the array from the host material; (ii) the non-ideal optical characteristics of the luminophore, particularly its luminescent quantum yield (LQY), where LQY is defined as the ratio between the number of photons emitted and the number of photons absorbed by the molecular structure; (iii) re-absorption from the luminophore due to partial overlapping of its absorption and emission bands (figure 1.6 b – cross section between the two spectra); (iv) the isotropic nature of the emission process, resulting in optical losses through the top and side planes of the layer (figure 1.6 a – [2] and [8]); and (v) increased reflection from the front surface due to the introduction of an additional interface [20, 55, 56, 65, 66, 68-70].

As a direct consequence, most of the research effort since the early 1970’s [72] has been funneled into the development, characterisation and enhancement of the array
of material combinations suitable for exploitation within LDS devices [20, 56, 57]. An ideal ‘down-shifting’ material should exhibit: (1) an LQY close to unity, (2) an absorption band confined within the spectral region where the EQE of the cell is low, (3) a high absorption coefficient, (4) a good degree of separation between the absorption and emission bands, in order to minimise reabsorption losses, (5) a highly cost-effective yet scalable synthesis route, and (6) a prolonged photostability under harsh environmental conditions [20, 39, 56, 57].

1.5.1.1 Photoluminescent materials
1.5.1.1.1 Organics Dyes

The class of LDS materials spawned the inception of spectral conversion applications in the mid 1970’s due the phenomenal optical properties they exhibit [73-79]. They possess a close to unity LQY, relatively high absorption coefficients and are easily processed into a wide array of different host media [73-79]. When combined with the abundance of different robust low-cost synthesis routes from which they can be obtained, it is easy to see why the organic dyes remain one of the most widely utilised materials in the design of spectral conversion devices [20, 56, 73-79]. However, their molecular structure tends to favour a large degree of overlap between the absorption and emission bands, leading to the onset of significant re-absorption losses [5, 20, 70, 80]. The same structural features are responsible for the pronounced susceptibility of these molecules to UV radiation, particularly over prolonged periods, where their photostability remains questionable [20, 56, 78]. This is particularly evident when comparing the stability of an organic dye, synthesised using different fabrication techniques, to various climate and/or environmental scenarios [20, 56, 78]. The renowned Lumogen F range developed by BASF, which includes the Violet 570, Red 300 and Yellow 083 perylene and naphtylamide based derivatives, is typically quoted as having an operation lifespan matching that of the PV modules they are designed to improve [81-83]. However, there
are numerous instances where the photostability of the same structures is reported as being less than 100 days, even under very moderate temperate climate conditions [83, 84].

**Figure 1.7:** (a) Geometry, (b) quadrupole moment and (c) electrostatic surface potential (where red is positive and blue is negative) of typical \( \pi-\pi \) interactions (stacked, T-shape, and parallel displaced) found in aromatic based systems. *source [93]

Besides these drawbacks organic based dyes frequently suffer from fluorescent self-quenching when encapsulated within solid state frameworks, particularly of the polymeric variety [20, 56, 66, 85-87]. The planar nature of the coumarin, phenyl, naphthylamide and perylene derivatives, which form the molecular scaffolding of most organic photoluminescent dyes, energetically favours \( \pi-\pi \) stacking (figure 1.7) [88-92]. This electrostatic interaction between neighbouring planar moieties serves to increase the energy lost through non-radiative pathways within the LDS structure and it is typically responsible for the divergence between the solid (referred to as PLQY) and liquid phase
LQY [56, 87, 88, 91]. Depending upon the physiochemical properties of the surrounding host media and the control exercised over the encapsulation environment, this reduction can be quite dramatic, with some luminophores LQY decreasing by as much as 20% once embedded within a matrix material [85-87].

To avoid these problems and improve their application in LDS, research and development of molecular systems, whose carefully constructed network of donor (D) and acceptor (A) moieties provide the desired intramolecular charge transfer (ICT) characteristics, specific to an individualised application, is well underway [87, 94-97]. Studies have shown how the careful manipulation of the donor and/or acceptor charge densities can fine-tune the absorption and emission characteristics of such a fluorophore and help combat the self-absorption losses stemming from the classically small Stokes shift [86, 87, 98-100].

A similar approach is explored in relation to the material candidate studied throughout this thesis [1,10] Phenanthroline in chapter 4. Further refinements in the structures rigidity minimise or prevent the propensity of the system to favour π-π interactions once embedded within the chosen host material [87, 94, 95, 97, 101]. This concept has even been adapted, through aggregation-induced-emission, to ensure that certain forms of molecular rotation are restricted, lessening the energy lost through these non-radiative pathways and further reducing the divergence between the systems solid and liquid state QY’s [87, 94, 95, 97, 101].

1.5.1.1.2 Metal coordination complexes

Metal coordination frameworks or coordination complexes that incorporate lanthanide (III) ions such as europium (Eu$^{3+}$) represent a promising alternative to the other luminescent materials due to their extremely narrow emission bands, very large Stokes shifts and highly luminescent nature [56, 102]. Their unique electronic configuration, which consists of partially filled d- and f- subshells, elicits a distinctive
emission spectrum at wavelengths close to 615 nm, directly within the optimum conversion window for most PV based technologies - particularly mc-Si [102, 103]. Although the photoluminescence exhibited by the lanthanide ions is an extremely efficient process, their relatively weak absorptivity (for example the molar absorptivity of most lanthanide ions is less than 100 mol⁻¹ cm⁻¹ [103]) results in only a small amount of radiation being absorbed by direct excitation of their 4f energy levels. However, this problem of weak absorption can be overcome through harnessing the so-called ‘antenna effect’ (intersystem crossing - figure 1.9) of intramolecular charge transfer (ICT), once a free lanthanide ion has been coordinated with suitable organic ligands or fluorescent dyes [103-107]. The intense absorption band(s) of the organic chromophores act as ‘antennae’, which in turn transfer their excitation energy to the rare-earth ion before emission [103-107]. Within a complex, this transfer of energy is highly dependent on the alignment between the excited states available within the lanthanide and those accessible in the triplet state of the polydentate ligand or fluorescent dye molecule [103-107]. The more energetically favourable this triplet to singlet transition becomes, through refinements in the synthetic chemistry protocol, the stronger the resulting complexes photoluminescent emission grows [5, 15, 103-105]. For illustration, switching the configuration of the bidentate ligand used to construct a series of tridentate ligands and their europium (III) complexes pushed the absolute quantum yield of the thin film LDS layers produced from 13% to 92% within a PMMA encapsulant [106].

The absolute LQY of a complex is an aggregate of the efficiency of the ICT processes and the intrinsic quantum yield of the ion located at the centre of the complex, the latter being lanthanide dependent and strongly influenced by the corresponding coordination geometry of the complex and its surrounding environment [108]. The capability to tune a metal coordination framework’s photophysical, mechanical and
chemical properties through the diligent selection of the proper ‘antenna’, potentially through utilising non-toxic precursors (unlike quantum dots), has made this type of material an area of increased interest in recent years [104, 106, 108, 109]. There is a particular interest in the photoluminescent enhancement of lanthanide ions with aromatic molecules as these structures (aromatics) are frequently used as structural and functionalised probes in biological systems. In addition, they are playing integral roles across an assortment of optoelectronic applications [104]. For organic functionalised compounds to be practically incorporated into an application, it is important that their solubility in organic solvents such as those typically encountered throughout the processing of polymeric materials and/or PV modules (toluene, acetone, ethanol or chloroform) is readily achievable [107]. However, many functionalised compounds do not dissolve sufficiently in these media due to their largely π-conjugated systems, which induce strong π-π interactions among neighbouring molecules [107]. Hence, there is an incessant need to identify organic

**Figure 1.8:** Schematic overview of a metal coordination complexes key components (1) a series of aromatic ligand derivatives which act as “antennae” shuttling the energy they absorb directly into the (2) metal ion (Eu coordination centre – shown in red) and (3) the accompanying sensitizing co-ligand (in this instance 1,10-philathroline) which acts to enhance the structures stability whilst also ensuring the distinctive transitions within the metal, which perturbate their signature emission spectrum (shown in red within the accompanying spectrum) are encouraged. An example of the absorption (red/green) and emission (red) spectra one of the most widely studied coordination complexes – Eu(TTA)_3Phen, where TTA is 2-Thenoyltrifluoroacetone, is provided to showcase the dramatic stokes shift achievable with similar structures.
derivatives which not only possess favourable optoelectronic properties when paired with an ionic centre but retain their desirable functionality for adoption in practical applications. Nevertheless, these strongly absorbing polydentate ligands (a ligand which can provide more than one bonding site for a metal atom or ion located at the centre of a coordination complex) on their own, although shuttling more energy through the complex, do not produce sufficient excitation of the lanthanide ion due to the forbidden nature of such intra-configurational transitions [102, 104, 107, 109].

To further enhance the effectiveness of the lanthanide excitation process, a photosensitising co-ligand is typically additionally incorporated into the coordination sphere of the metal [102, 104, 107, 109] – see figure 1.8. The co-ligand serves not only to augment the electronic environment around a metal ion, but also acts as a building-block upon which different chemical moieties can be attached to further expand the variety of coordination geometries that are possible [110, 111] – figure 1.8. The rich coordination chemistry achievable with 1,10-phenanthroline, a neutral bidentate ligand, represents one of the most widely exploited sensitising-agents encountered throughout all of coordination chemistry [110, 111]. Its inclusion in a coordination framework (figure 1.8) has not only been shown to enhance the overall structural, thermal and optical behaviour of the complex, but its presence is also well correlated with a reduction in the availability of non-radiative decay modes, further enhancing the fluorescent intensity of the emission process [102, 104, 109]. For instance, increasing the molar ratio \(x\) of phenanthroline (Phen) within an Eu(DBM)\(_3\)Phen\(_x\) complex has been shown to enhance the fluorescent intensity of the characteristic Eu emission by a factor of \(~10\), with the enhancement retained even after subsequent embedding within a polymeric network [104].

The inclusion of coordination complexes within polymeric networks, such as those used for the encapsulation of the photoluminescent material within LDS
applications or the active structures encountered in organic PV devices, has produced composite materials with excellent thermal properties [102, 104, 108, 109, 112, 113]. Recent studies [102, 104, 108, 109, 112, 113] have reported and revealed the prolonged photo- and thermo- stability of luminescent down-shifting layers composed of Eu(III) complexes, and have alluded towards operational lifetimes exceeding 10 years [114]. The enormous interest in these composite materials stems from their advantageous luminescent characteristics, excellent mechanical properties and their lightweight and low temperature processability [104, 108, 112-114]. The well documented long-term susceptibility of certain solar module constituents, particularly the encapsulation utilised to provide protection to the module from moisture and impact, to photodegradation under the continuous UV-irradiation makes this radiation undesirable [56, 106, 109]. Classically this is combated, directly, through the inclusion of UV absorbers within the poly-methyl methacrylate (PMMA) or ethylene-vinyl acetate (EVA) encapsulating materials, consequentially decreasing the potential solar cell efficiency [109]. Considering the excellent dispersion behaviour of many derivatives of metal coordination complexes within polymeric matrixes, particularly of the same variety as those used for the encapsulation of solar modules, their adoption into alternate cost-effective spectral conversion structures remains warranted [20, 56]. Coinciding with a reduction in the photodegradation experienced by the encapsulating material, improvement in the short wavelength responsivity of the photoconductive material is an enhanced capability of such an organic-lanthanide down-shifting structure to more rapidly conduct heat away from the cell during its operation, which is favourable if the systems energy harvesting potential is to be maximised.

1.5.2 Phenanthroline

Over the last few decades 1,10-Phenanthroline (figure 1.9 a) has been extensively studied for its application as a chemically versatile, fundamental building-block of an
extensive ensemble of luminescent molecules, materials and metal complexes [110, 111]. Its exhibition of a fortuitous combination of chemical (aromaticity, basicity, inertness and its chelating capability) and structural properties (planarity and rigidity) has enabled the development of sophisticated synthetic strategies that have produced such diverse alluring molecular architectures as mono- and poly-nuclear complexes [110, 111]. Compared to its analogues, the 1,10-phenanthroline’s (Phens) substantially more rigid aromatic framework is reflected in the structure of the spectral features resolved within its absorption (figure 1.9 b – black) and emission spectra (figure 1.9 b – red). The confinement of the pristine molecule’s absorption band to the ultraviolet spectral region (200 nm - 320 nm), its short emission wavelength ($\lambda_{\text{emission}} = 360$ nm) and its extremely low LQY (< 0.01) are a direct consequence of its electronic band structure [110, 111]. Phens exhibition of $\pi - \pi^*$ (strongly emissive, radiative decay pathway) and $n - \pi^*$ (poorly emissive, non-radiative decay pathway) singlet excited states of a similar energy stems from the two very close-lying molecular orbitals of the structures [110, 111]. Hence, an effective strategy to augment the photophysical properties of pristine Phen is to increase the energy separation between these two alternate energy levels ($\pi - \pi^*$, $n - \pi^*$) through introducing suitable substituents onto the Phen ring (figure 1.10).

The synthetic strategies adopted have primarily focused on the substitution of various functional groups at the 2,9- and 4,7- positions (figure 1.9 a), whereas the 3,8- and 5,6- sites on the aromatic system have been less common [110, 111]. The attached functional groups served to either (1) extend the $\pi$-conjugation of the system or (2) inject/withdraw electron density from the aromatic ring [110, 111]. Symmetric substitution of Phen with aromatic residues at the 2,9- positions (figure 1.9 c and e) has proved to be a very effective method of enhancing the bidentate ligands photoluminescent performance (see figure 1.9 d). For instance, as the substituted aromatic (R) is switched from phenyl (figure 1.9 d – blue) to anisyl (figure 1.9 d – red), there is an inherent
bathochromic shift in the absorption spectrum indicating a progressive lowering of the $\pi - \pi^*$ level, which, in turn, diverges from the $n - \pi^*$ level and promotes the growth of radiative transitions [110, 111]. This is apparent in the almost doubling experienced in

![Figure 1.9](image_url)

**Figure 1.9:** (a) Schematic structure of 1,10-phenanthroline (I) with related ring numbering and the bidentate ligands corresponding normalised (b) absorption – (black), emission – (red) and phosphorescence – (blue) spectra in CH$_2$Cl$_2$ [110]. (c, e, f) Substituted phenanthroline architectures, where R denotes the specific moiety introduced and the corresponding absorption (d) and emission spectra (g) of the compounds for which (II) R = H (absorption spectrum shown in d – black) or R = OCH$_3$ (absorption profile shown in d – blue), and (IV) R is alternated between H, CH$_3$, OCH$_3$ and N(CH$_3$)$_2$ [110]. The luminescent quantum yield (LQY) of the each phenanthroline derivative is also provided as a mean of comparison, with the LQY of the compounds abbreviated in (f & g) varying from 0.41 (R = H), 1 (R = CH$_3$), 0.64 (OCH$_3$) to ~ 0 (N(CH$_3$)$_2$) [110]
the compounds LQY (16 % to 32 %) as this alternation occurs with an even more impressive 89 % LQY achieved when the two aromatic moieties (anisyl and phenyl) are interlinked (figure 1.9 e) forging further conjugation [110, 111].

An alternative set of strategies [115] targets the electronic delocalization along the 3,8- positions of the aromatic scaffolding to further fine-tune the photophysical properties of Phen in order to achieve an intense emission in the visible region (figure 1.9 g). This modulation of the delocalised electrons in their excited state results in these compounds (figure 1.9 f, where R is alternated through; H, CH₃, OCH₃ and N(CH₃)₂) displaying a gradual red-shift in their emission spectra (figure 1.9 g), directly in line with the electron donating abilities of the substituent [115]. For example, in the prevalence of radiative transitions, an unsubstituted phenylacetylene derivative (figure 1.9 e, R = H) elicits a relatively high photoluminescent quantum yield (LQY = 0.41), while methyl substituted derivatives (figure 1.9 e, R = CH₃) produce a unity luminescent quantum yield (LQY = 1) [115]. Alternate electron-donating fragments, such as methoxy (figure 1.9 e, R = OCH₃) and N,N-dimethyl derivatives (figure 1.9 e, R = N(CH₃)₂), produce a more polarised excited state, which may be responsible for their suppression of radiative transitions and their correspondingly low LQYs of 0.64 and ~0, respectively [110, 115].

Even though the behaviour of 1,10-Phenanthroline towards chemical and structural alterations within its scaffolding remains well-explored [110, 111], the need to continue to discover and diversify the synthetic strategies available for augmenting its photophysical characteristics remains amplified [110, 111]. This takes place especially in the pursuit of highly luminescent energy-harvesting materials, where ample room for expansion remains in the utilisation of Phen as both a basis and a standalone material candidate for expanding and enhancing the functionality of photovoltaic and photothermal applications.
1.6 Photoluminescence

Deconvolution of the molecular transitions afforded by a chromophore is classically represented in a Jablonski diagram (figure 1.11), in which the internal energy configuration of a photoluminescent molecule is visually represented [117]. As radiation strikes a chromophore, electrons within the molecule can become promoted into an excited state either through electronic ($\lambda = 200$ nm to $800$ nm) or vibrational ($\lambda = 3$ $\mu$m – $100$ $\mu$m) transitions [117]. Immediately after this excitation ($\sim 10^{-15}$ s), any excess vibrational energy from an absorption event becomes dissipated through thermal relaxation ($\sim 10^{-12}$ s), allowing the excited electron to minimise its vibrational energy within a given excited electronic state before any further transitions occur [117]. From this excited state ($S_1$, $S_2$…), the electron can subsequently undergo a series of different decay pathways on return to its original ground state ($S_0$) through a combination of non-radiative and radiative processes. Radiative processes (luminescence and phosphorescence) are typically favoured from a structural standpoint due to their widespread applicability across a host of different applications including the construction of energy adaptive architectures, environmental monitoring, molecular diagnostics and
many more [117]. Their non-radiative counterparts (intersystem crossing, thermal relaxation, collisional quenching, etc.), on the other hand, result in the exogenous production of thermal and electronic interactions with the surrounding solvent and are favourable in applications where the generation of localised heat fluctuations is warranted i.e. solar-thermal energy systems. These two defining characteristics (radiative and non-radiative processes) of a chromophore are embodied in the luminescent quantum yield (LQY). The LQY, representing the efficiency of the radiative processes in relation to their non-radiative counterparts, is highly dependent upon the decay rate of the individual processes responsible for returning to the ground state (S0) [117];

\[ LQY = \frac{\Gamma}{\Gamma + k_{nr}} \]  

(1.1)

where \( \Gamma \) is the emissive (photoluminescent) rate constant and \( k_{nr} \) is the collective rate constant for all non-radiative decay processes, individual to the chromophore. Consequently, the LQY of a luminophore can be modified through careful control of either one of the rate constants (\( \Gamma \) or \( k_{nr} \)) [117]. A promising synergistic alternative not only offers to enhance the functionality of the luminescent materials, in terms of their natural LQY’s, but also has the capability to further expand the architectures imagined for optoelectronic devices is plasmon-enhanced photoluminescence.

### 1.7 Plasmon-enhanced photoluminescence

It is well known that when a luminescent species comes into close proximity to a metal nanoparticle’s (MNP’s) surface, its luminescent properties can become altered [118, 119], sometimes significantly. The LQY, the emission intensity, and the directionality of the emission process of diverse luminophores (quantum dots, luminescent dyes, metal coordination complexes) are susceptible to these interactions and have been widely studied [120-124]. The cooperative interaction between the two species (luminophore and MNP), is broadly termed metal-enhanced fluorescence (MEF) or...
plasmon-enhanced photoluminescence (PEP), as the interaction is manifested through an aggregate of many different energy-transfer mechanisms [125].

![Figure 1.11: Jablonski diagram showing the electronic and vibrational energy levels of a photoluminescent molecule such as an organic dye, quantum dot or heteroaromatic fluorescent ligand. Electronic excitation of a delocalized electron within the molecule promotes the electron to an excited singlet state (S₁, S₂ …) whereby there are a number of radiative (fluorescence – red arrows, phosphorescence – blue arrow) as well as non-radiative (intersystem crossing – dark orange arrows, thermal relaxation & internal conversion -gold arrows) transitions available allowing the molecule to return to its ground state (S₀). The electrons orientation in both singlet (paired electrons) and triplet (unpaired electrons) states is also provided](image)

The collective oscillation of electrons across a metal’s surface (figure 1.12 a) in response to electromagnetic irradiation provides the capability of these nanostructures to manipulate light and light-matter interactions in an extremely controlled fashion – a phenomenon referred to as localised surface plasmon resonance (LSPR) [125]. This intense concentration of light around a nanostructure gives rise to highly locally intensified-electromagnetic fields (the near-field), whose distribution is dependent upon the modulation of the interaction [126]. The exact nature of the modulation is highly dependent upon the composition of the metal [127], the size and the shape of the NP’s [128, 129], the intersection of the luminophores absorption and emission bands with the
LSPR band produced by the NP’s [130-132], the fluorophores intrinsic LQY [133] and by the physical separation between the particles of the luminescent and NP species [128, 134]. Noble metals such as silver (Ag) or gold (Au) are the most widely explored as their electron-rich surfaces facilitate the formation of plasmonic properties within the ultraviolet/visible spectral region, where most of the extensive range of luminophores are active [118, 120, 125, 126].

Figure 1.12: (a) Schematic of localised surface plasmon resonance (LSPR) phenomena arising through the interaction of conduction band electrons within a spherical metal nanoparticle, with an external electromagnetic field. (b) Classical Jablonski diagram for the free-space (no metal present) condition and the modified form in the presence of metallic nanoparticles, islands or colloids [126]. The coinciding of the metals LSPR absorption within the absorption (c) and emission (d) bands of a luminophore, resulting in the excitation enhancement of the luminophore through near-field Förster resonance energy transfer (FRET) or scattering, or the emission enhancement of the luminophore through FRET respectively [135].

When a MNP is introduced, the simple free-space Jablonski diagram envisioned for conventional photoluminescence (figure 1.11 & re-represented for convenience in figure 1.12 b) becomes modified to account for the additional excitation and radiative decay modes facilitated by the MNP (figure 1.12 b). The corresponding amplified \( LQY^* \) is given by [118];

\[
LQY^* = \frac{\Gamma + \Gamma_M}{\Gamma + \Gamma_M + k_{nr}}
\] (1.2)
where $\Gamma_M$ corresponds to the decay rate from the MNP’s and $k_{nr}^*$ represents the collection of non-radiative modes available in the coupled system i.e. those in the luminescent species as well as those in the MNP. These photophysical properties of a luminescent species are typically augmented through the careful consideration of the correspondence between the optical properties of the luminophore and the LSPR frequency of the metal - figure 1.12 d and e [125, 136]. The changes induced through the presence of a MNP are being strongly mediated through careful control of the distance between the two species [125, 126]. As an excited luminophore is brought closer to a MNP, the oscillating near-field of the decaying molecule excites surface plasmons (waves of coherently oscillating delocalised electrons on the metal surface) provide the frequency of the transitions match [137, 138]. In such cases the energy from the donor (the luminophore) is transferred into the metal, via a process called Förster resonance energy transfer (FRET), before being re-radiated and, thereby, increasing the radiative decay rate ($\Gamma_M$) [125, 139, 140]. Hence, a luminescent species located within this near-field interaction distance (20 nm – 50 nm from the MNP’s surface) experiences an increase in excitation intensity ($E_M$ in figure 1.12 b) followed by an enhancement in the emission rate [118]. As an excited luminophore is continuously brought closer in proximity to the metals surface, the energy from the excited states of the molecule begin to energetically favour quantum tunnelling into the MNP and becomes lost through dissipative and ohmic heating process inherently favoured by the metals band structure [125, 141-143].

As such, the enhancement in LQY involves the competition between radiative and non-radiative modes, both of which increase as the luminophore approaches the surface of the MNP [136]. In the case of highly efficient luminophores, the increased rate of enhanced radiative emission becomes marginalised and the interaction can become dominated by the enhancement of non-radiative modes, even though the overall
fluorescent intensity increases [136]. Conversely, the interaction favours molecular structures whose intrinsic LQY is low, as under these circumstances the enhancement initiated in the non-radiative modes effectively lags the enhancement initiated in the radiative decay rate [136]. Leveraging the collective dipole-dipole interactions activated within MNP networks offers an alternative route to further enhance and fine-tune the photoluminescent emission intensity exhibited by a luminophore [125, 144-148]. Each metal nanostructure within the network (which can be a cluster, pattern, or even a collection of aggregates) can receive energy from all the neighbouring components and couple this energy into the induced electromagnetic fields [125, 144-148]. The strength of the fields established within this collective network are of a much greater magnitude than those generated in isolated non-interacting MNP’s systems [125, 144-148]. For example, the fluorescent intensity of polystyrene beads has been shown to be enhanced by more than 270 % of its original value when placed within the localised “hot-spot” established through the interactions of two neighbouring Au NP’s [144], while the enhancement was only 150 % of the original value, when the luminescent beads were located near a single Au NP [144].

1.8 Photothermal

Despite the amplified uptake in the number of renewable pathways, from which we continue to derive an ever-increasing portion of our electrical demands, ‘heating and cooling’ remains the largest single sector of the European energy system that awaits decarbonisation [149, 150]. This sector alone accounted for 50% of total energy consumption in 2015 with 84% of this demand being generated from fossil fuels while only 16% stemmed from renewable sources such as biomass, geothermal and photothermal (solar thermal) technologies [151]. In the same year, across EU households, the heating and hot water demand singlehandedly accounted for 79% of the residential energy consumption [149, 151]. In an Irish context, 90% of the heating (spatial and hot
water production) demands are met through fossil fuel resources, while a further 8% is created using electricity from the electrical grid [150]. To promote decarbonisation within the heating and cooling sector, the EU plans to have up to 50% (~200 GW\textsubscript{thermal}) of its low to medium temperature water (utilised throughout the residential, building and industrial sectors) delivered by photothermal energy systems by 2050 [150]. Currently, photothermal technologies only deliver ~ 0.5% of this estimated spatial and water heating demand within the European region [149, 150].

Solar thermal collectors (STC’s) work as heat exchangers in which the incoming solar energy is selectively absorbed and transformed into heat before being transferred to a working fluid which carries the energy, either to directly produce electricity or alternatively store it for periods of high demand [152-154]. Flat plate solar thermal collectors (FPSTC’s), like that shown in figure 1.13.a, represent the most widely produced collection device operating within the low temperature regimes (25 \(^\circ\)C - 80 \(^\circ\)C above ambient) typically encountered in the production of hot water [155-157]. Although their cost-effective production and installation has made them an essential component in residential applications of solar-thermal systems, they remain limited by the low thermal efficiencies achievable [155-157]. The principal strategies to improve the thermal performance of the collection system are: (1) modify the geometry of the collector design; (2) develop innovative working fluids; or (3) integrate different collection systems into a single hybrid design [154]. Improving the thermal characteristics of the working fluid has proved to be the most fruitful avenue due to the dominant role played by the fluid in establishing the performance and transfer dynamics within a STC system [153, 156, 158, 159]. The hybridisation of solar thermal systems with other alternative renewable sources
offers the potential to capitalise on the synergistic interactions between the two or more cooperative co-dependent systems [160-163].

Figure 1.13: (a) Examples of the different types of flat plate solar thermal collection (FPSTC) systems commercially available, as well as their key design features. (b) The limiting factor effecting the thermal efficiency achievable with solar thermal collector’s lies is the ‘poor’ thermal properties possessed by conventional single-phase heat transfer fluids, particularly their extremely low thermal conductivity, some of which are highlighted for comparison. (c) schematic of the operating principle underpinning spectral beam splitting (SBS) technology, in which the working fluid (nanofluid, composite fluid or a hybrid fluid) acts to selectively absorb the spectral regions ineffectively utilised by the cell, shown in (d – spectral windows highlighted as ‘thermal’), whilst remaining highly transmissive in the ideal operating window

1.8.1 Heat Transfer Fluids

Conventional single-phase heat transfer fluids (water, ethylene glycol or glycerol) were originally utilised because of their natural abundance, chemical inertness and relative ease of handling [164]. However, their relatively short-lived commercial success
is now being overthrown in the search for highly efficient heat transfer fluids whose chemical, physical and thermal properties can be controlled on the molecular level [164-169]. The remarkably high thermal conductivity (figure 1.13 b) and heat transfer coefficient produced by nanoscale structures (spheres, cubes, prisms, triangles, fibres, etc.) when dispersed throughout a suitable base fluid (water, ethylene glycol, etc.) has made the so-called ‘nanofluids’ a serious contender for improving the thermal performance of STC’s [164-169]. Through careful control of the nanoparticle’s composition, size, shape, size-distribution and concentration within a fluid, thermal collection efficiencies of up to 93 % can be realised [164-169]. However, the high surface area to volume ratio of the nanostructures, coupled with the high surface energy, leads to an unstable fluid whose thermal characteristics vary with temperature and time [156, 170-173]. The plethora of robust synthesis routes allow us to control the nanoparticles photophysical characteristics and to fine-tune them for a given application. Usually, these routes also employ particularly expensive raw materials and very often they involve environmentally unfriendly precursors [174-178]. Consequently, there is a need to develop a highly stabilised nanofluid which offers a superior solar-energy absorption property and derives from an environmentally friendly synthesis route[153, 173-178].

In efforts to promote and control the thermophysical properties of different base fluids, many material avenues have been explored including metals (Ag, Au, Cu), oxides (TiO₂, CuO, Al₂O₃), carbides (TiC, SiC), and various allotropes of carbon (Carbon nanotubes, graphite, carbon black). However, given the innumerable synthetic protocols available and the continual development of ever more intricate particle geometries there remains ample room for expansion of the final fluid’s configuration.

1.8.2 Hybridisation

Solar thermal power is an ideal technology to hybridise with other existing forms of energy technology for power generation as heat is a typical by-product of the inefficient
conversion processes already ongoing within the standalone technology [155, 179, 180]. It can be readily united with other types of energy (coal, natural gas, biofuels, etc.) into a synergistic hybrid system which has many benefits including improved efficiency, increased dispatchability, reduced capital costs through equipment sharing, and the opportunity for flexible operating conditions through alternating between the different energy sources. Thus, hybridisation can lead to an overall enhanced net-efficiency through synergy between the distinct energy sources [155, 179, 180]. As photovoltaic and photothermal technologies share the same energy source (the sun), the combination of the two presents some strong synergies. PV technologies classically exhibit a decline in their performance under elevated temperature [155, 179, 180]. Because of this, the PV cells are largely designed to be cooled, either actively or passively, to keep them functioning at peak operating conditions [180-184]. Instead of simply cooling them, and wasting potentially harvestable thermal energy, hybrid photovoltaic-thermal (PVT) systems use this thermal energy to increase the overall efficiency of the system [155, 179, 180].

The heat transfer fluid is either in direct contact with the surface of the PV or kept separated depending upon the specifics of the application [155, 179, 180]. Thus there is a delicate balance between the recoverable waste-heat and the electricity generated by the complementary PV component [155, 179, 180]. But what if there was a way to preserve the enhanced thermal properties offered by two-phase heat transfer fluids, while allowing for a reduction in the electrical energy scarified through the inclusion of the thermal component?

Spectral beam splitting (SBS – shown in figure 1.13 c) offers the potential to include all three of these design aspects in a single hybrid system. In a spectral beam splitter a liquid optical filter serves as both a heat transfer fluid and a spectrally selective absorber, heavily absorbing the wavelengths ineffectively captured by a PV cell (‘thermal’ regions outlined in figure 1.13 d), and highly transmissive within the spectral
region where the PV cell elicits peak performance (‘electricity’ region outlined in figure 1.13 d)[180, 185-190]. Separating the liquid filter from the PV component in SBS PVT systems has several advantages as the absorptive liquid is usually inexpensive and it can serve multiple purposes simultaneously: (1) it absorbs the solar irradiance that is inefficiently utilised by PV; (2) the thermal energy generated can be stored and transported by the fluid; and (3) the filter characteristics can be easily modified by altering the liquid’s optoelectronic and thermophysical properties [180, 185-190]. In order to achieve the high operating temperatures (150 °C - 700 °C) required to facilitate the penetration of SBS-PVT systems into a greater number of industrial and energy production applications, concentration optics must be also employed [155, 180]. Concentrated PVT (C-PVT) systems with spectral beam splitting technology could offer significantly higher heat transfer fluid temperatures and markedly broaden the spectrum of integration options for C-SBS-PVT systems as the technology continues to develop [155, 180]. However, for these systems to be realised a long-term thermally stable liquid, which is also environmentally friendly, with suitable absorption spectra remains to be identified [155, 180].

1.9 Project Outlook
1.9.1 Photovoltaic

In this work a systematic approach towards addressing the extent of the losses introduced through the inclusion of an LDS layer within a PV system is developed and demonstrated in conjunction with novel luminophores. A set of 27 heteroaromatic chelating ligands, built upon a phenanthroline scaffolding, were evaluated and explored in terms of their photoluminescent properties and suitability for LDS and PLDS applications. The leading candidates were embedded within a relatively thin (~10 µm) poly-methyl-methacrylate (PMMA) layer and their fluorescent properties (absorption, emission intensity, and LQY) explored and optimised for the fabrication of thin-film LDS
devices constructed upon mc-Si technology. The subsequent impact of each molecule on the energy harvesting capabilities of the resulting LDS devices was thoroughly explored through electrical characterisation using I-V and EQE measurements. A complementary series of photostability trials were also carried out to further refine the viable lifetimes of these candidates under different climate conditions.

To counteract the combination of reflection losses (introduced through the creation of an additional optical interface within an LDS-PV system) and the losses stemming from the non-ideal nature of most photoluminescent materials, a set of supplementary optical structures was devised. The structures, comprised of single-layer and double-layer antireflection coatings, were designed to generate maximum reflection suppression within the typical absorption window of commonly used fluorophores. The impact of this additional optical structure’s composition, thickness, and complexity on the electrical performance of an underlying mc-Si architecture was evaluated and explored using the transfer matrix method. The premise of the structure, within these augmented solar cell designs, lies in the possibility of offering a cost-effective alternative to the already complex series of frames, sealants, protective glass casings and polymeric encapsulants currently embodied within the design of a typical PV full scale module. Through a combination of theoretical and experimental approaches, the initial design considerations behind these structural-enhanced LDS (SE-LDS) or PLDS (SE-PLDS) devices was established.

1.9.2 Photothermal

In the pursuit of highly efficient heat transfer fluids for STC’s, a hybrid nanofluid conformation was considered and investigated. The hybrid fluid, comprised of a diverse set of distinct particle morphologies (spheres, prisms, hexagons, and other non-spherical geometries), was obtained through a two-step wet chemical synthesis route which utilised readily available reagents. The photophysical properties of the nanostructures, controlled
through subtle refinements in the concentration of the aqueous solutions, were optimised before their redispersion in a suitable base fluid (water in this particular case). The possible interaction(s) between different types of particle morphology and complexity of their size-distribution were considered for their role in enhancing the heat transfer dynamics of the resulting working fluids. To further validate the thermophysical characterisation of the nanofluids developed, their thermal conductivity was measured using a transient hot-wire technique. The photothermal conversion efficiency of the working fluids was evaluated within a stationary STC system, under a standardised AM1.5G weighted spectrum to access the fluid’s suitability for solar thermal applications.

1.9.3 Photovoltaic-thermal

From the series of organic and organometallic ligands catalogued in 1.8.1., several ligands were selected to be explored for their role in liquid spectral beam splitting agents in a combined heat and power hybrid-system. The structure’s molecular scaffolding offers an abundance of desirable physical features for further developing the SBS-PVT applications including: (1) thermal stability up to ~200 °C; (2) readily modified photophysical properties through simple substitution(s) with alternate functional moieties; (3) controllable photoluminescence; (4) non-corrosivity; and (5) ability to be derived from a cost-effective, scalable one-pot synthesis method that offers a substantially lower environmental impact than what is typically encountered throughout the fabrication of conventional nanofluids. The range of working fluid candidates employed represented structures which favoured radiative decay pathways as well as non-radiative transitions. The basis of this strategy lies in trying to identify whether radiative transitions could be leveraged to minimise the electrical power sacrificed through the inclusion of the thermal element or whether their non-radiative counterparts should be further exploited to substantially enhance the thermal energy captured within a hybrid design. The interplay between the absorption and emission band of each chelating ligands, optical
transmittance, and contribution towards enhancing the heat transfer dynamics of an ethylene glycol-based working fluid, on maximising the collective (thermal and electrical) power efficiency of a hybrid SBS-PVT system was evaluated. However, not only is the net conversion efficiency of a hybrid device design important, but also the economic viability of the configuration, and this is considered throughout the evaluation of the SBS-PVT configuration proposed herein through the adoption of a merit function.

1.10 References


[157] M.J. Muhammad, I.A. Muhammad, N.A. Che Sidik, M.N.A.W. Muhammad Yazid, Thermal Performance Enhancement Of Flat-Plate and Evacuated Tube Solar Collectors


Chapter 2
Experimental Techniques and Instrumentation

2.1 Introduction
The focus of this chapter will be a discussion of the experimental and analytical methods & techniques implemented throughout this research. A series of spectroscopic techniques were employed to assess the impact of the substituent moiety, introduced into a phenanthroline based conjugated system, on the photoluminescent properties of the resulting structures. The identified optimal conjugated structures were subsequently loaded into a highly versatile polymer host material, and the resulting film’s optical, topological and photostability further explored for their role in spectral conversion applications. The optimised structures were subsequently deployed on a commercial silicon based photovoltaic technology, and the electrical performance of the down-shifting devices evaluated under standard testing conditions. The impact of additional design considerations, including the exploitation of the enhanced near-field characteristics generated close to a metallic nanostructure as well as added thin-film components to minimise the reflections losses within the system were also investigated.

The instruments used, their features, and any consideration or revision to outstanding methodologies adopted throughout the study are discussed below. In later chapters, the role of the methods and techniques outlined herein will be further expanded upon, in terms of the materials utilised and system parameters employed.

2.2 Spectroscopic Characterisation
2.2.1 Electronic Spectroscopy
2.2.1.1 Absorption Spectroscopy
Absorption represents one of the most fundamental forms of light-matter interaction and stands as the basis of absorption spectroscopy, which remains one of the most advantageous and well explored material characterisation techniques available [1, 2]. Underpinning the quantitative aspect of absorption spectroscopy is the application of
the well-known Beer-Lambert law, which relates the transmittance (T) through a given material of known concentration (c) and thickness (L), to the optical properties of the absorbing material:

\[ T = \frac{I}{I_o} = 10^{-\alpha L} = 10^{-(\epsilon_M c) L} \]  

(2.1)

where transmittance is defined as the ratio of the transmitted light intensity (I) to the intensity of the incident light (I<sub>o</sub>), and the properties of the absorbing material are conveyed through its wavelength specific absorption coefficient (\(\alpha\)), which can alternatively be expressed in terms of molar absorptivity (\(\epsilon_M\)) depending upon the nature of the analysis being carried out. The measured transmittance, in turn gives the corresponding absorbance (A) according to:

\[ A = -\log_{10} \left( \frac{I}{I_o} \right) \]  

(2.2)

This implies that the absorbance becomes linear in response to the concentration of the absorbing species present, provided there are no chemical or physical alterations within the medium \([1, 2]\). However, this linear relationship only holds true for absorbance values less than two, as under these conditions \(~100\%\) of the light is being absorbed within the sample.

The absorption spectra of the materials characterised throughout this study were recorded using a Perkin Elmer Lambda 900 UV/VIS/NIR spectrometer, shown in figure 2.1. The Lambda 900 is a double beam spectrometer, allowing the absorbance (A) to be measured at a specific wavelength, for both the reference and sample material simultaneously. The reference material should be identical to the sample in every aspect, except for the absence of the absorbing species being considered. The device uses a combination of a tungsten-halogen and deuterium lamps to provide illumination over the 170 nm - 3300 nm wavelength range (figure 2.1 d). The Lambda 900 allows the conventional sample compartment shown in figure 2.1 b to be replaced by an alternative
integrating sphere compartment (figure 2.1 c), which aids in the analysis of samples which are prone to producing a large degree of scattering, e.g. colloidal dispersions, nanofluids, fine particulate suspensions or thin films polymer samples such as those encountered in spectral conversion applications. The integrating sphere capturing light, previously lost through the excessive scattering encountered in these types of samples, through the highly reflective coating on the inside surface of the sphere (figure 2.1 e).

**Figure 2.1:** (a) Perkin Elmer Lambda 900 UV/VIS/NIR spectrometer with (b) standard sample compartment and (c) integrating sphere compartment and the accompanying schematics of each compartment type (d – standard sample compartment & e – integrating sphere compartment): the optical components within each highlighted
2.2.1.2 Derivative spectroscopy

UV-VIS absorption spectra typically consist of broad absorption bands, with the particular wavelength region at which they occur providing information about the presence of certain chromophores such as organic dyes, quantum dots, or coordination complexes. However, given the subtle variability in a chromophore’s absorption characteristics when exposed to fluctuations within its molecular environment (pH, temperature, as well as the physical properties of the solvent), the broad absorption bands registered through conventional UV-VIS spectroscopy often provide very little qualitative information about these types of interactions. Consequently, the narrow absorption bands, often introduced into a conjugated system through chemical and physical alterations made to the molecule’s structure can go unresolved. Alongside the dramatic improvements in the resolution and precision of modern instrumentation, the simultaneous development of analytical techniques has synergistically enhanced the resolution of these systems through a purely mathematical approach [2-6].

![Figure 2.2](image)

**Figure 2.2:** (a) Unprocessed broadband absorption spectra of a silver colloidal solution (b) baseline identification (i.e. noise floor) and its subsequent subtraction (c) and the corresponding 2nd order \( \frac{d^2 A}{d\lambda^2} \) derivative spectra of the baseline corrected absorption spectrum showing in (c) indicating the presence of three distinctive components at ~345nm, ~410nm and ~545nm
The premise of this technique lies in the effective differentiation of the raw unprocessed spectral information captured with the derivative simply taken as the rate of change in the absorbance ($\delta A$) with respect the accompanying change in wavelength ($\delta \lambda$). The order of the derivative taken (1$^{\text{st}}$ order, 2$^{\text{nd}}$ order, 3$^{\text{rd}}$ order….) is flexible within the technique, with higher orders typically avoided due to the complexity of the resulting spectrum as well as the inherent loss of information introduced through over-processing the raw data [1, 4, 6]. The application of this technique is illustrated in figure 2.2, which shows a broad band before, and after a 2$^{\text{nd}}$ order derivative has been implemented, with the peaks resolved in the derivative spectra corresponding to the presence of multiple different species. Throughout this study, a 2$^{\text{nd}}$ order derivative was adopted when analysing and fitting raw unprocessed spectral data generated by both the Perkin Elmer Lambda 900 UV/VIS/NIR spectrometer and a Malvern Nano series ZS Zetasizer.

2.2.1.3 Deconvolution

Further expanding upon the enhanced capability to distinguish between overlapping spectral features and the improvement in quantitative analysis offered by derivative spectroscopy is the computer-aided ‘deconvolution’ procedure. This powerful technique, allows for not only the key spectral contributions to be resolved, but also their corresponding spectral area to be estimated, and utilised to monitor the growth or decay of specific spectral contributions in response to environmental constraints including UV-irradiation, temperature, and pH, as well as the effects of the solvent on the analyte molecule’s molecular structure [4, 7-10]. This overarching analytical framework consists of several stages, with a general overview of the approach shown in figure 2.3, highlighting the individual stages involved and the order in which they are applied.

Typically, the technique involves an initial smoothing and/or filtering of the unprocessed spectrum, to reduce the levels of noise present. This in conjunction with the application of a baseline correction (figure 2.2 b) removes any inherent background noise
Figure 2.3: Schematic overview of the spectral ‘deconvolution’ technique as it is applied to UV-VIS spectra: highlighting the individual stages as well as some of the controlled variables associated within each stage. The entire process entails (1) smoothing of the unprocessed spectral information via a Fourier transform or polynomial based smoothing protocol followed by the application of a (2) baseline correction – further removing any noise inherent in the signal. (3) Performing a 2nd order derivative of the ‘smoothed’ spectrum to identify the number of individual spectral contributions and their corresponding wavelengths. (4) Constructing a simulated spectrum using a Gaussian function to represent each spectral component, adjusting their individual parameters (λ, band width as well as the integrated area) until the simulated spectrum matches the original ‘smoothed’ spectrum within the tolerance criteria established.

in the signal, which could otherwise lead to the introduction of artefacts during the spectral-fitting stage, later in the protocol. The subsequent stage involves an estimation of the number of overlapping bands present within the spectrum, and this is facilitated by performing the 2nd derivative of the spectrum (figure 2.3). The original spectrum is then recreated using approximation functions (Gaussian, Lorentzian or a mixture of the two) which attempt to recreate the spectral shape attributed to the electronic band structure registered through a substance’s absorption spectrum [1, 4, 6]. Given the implicit random
distribution of vibrational energy levels in an absorption band, the Gaussian function is most widely attributed to the accurate fitting of UV-VIS absorption spectra [4]. The contribution of the individual bands (wavelength, intensity, bandwidth, and the corresponding integrated area) constructing a ‘simulated’ spectrum is then continuously adjusted until the difference between this ‘simulated’ spectrum and the measured spectrum, exceeds the curve fitting criterion required. The bands within such a system must conform to a few basic requirements, in order to ensure the information extracted is indeed valid and they are as follows:

- The number of overlapping bands used must be determined via one of the following methods; derivative spectroscopy [2, 4, 6], spectral stripping [11, 12] or spectral deconvolution [13, 14].
- The minimal number of component bands must be used reach the confidence interval required.
- Contributions of negative amplitude are not considered, as they are not physically viable solutions.
- Adoption of a strict confidence interval (> 95%) when optimising the least-squares procedure, which is used to re-evaluate the simulated spectrum ‘quality of fit’ [4, 6].

2.2.2 **Fluorescent emission spectroscopy**

How a molecule dissipates absorbed energy via radiative processes such as photoluminescence reveals structural information about its internal molecular structure as well as its vibrational energy conformation. The highly sensitive nature of the emission process means that it can be used to probe the impact of specific structural alterations on the internal energy dynamics of a luminescent species (fluorescent ligand, quantum dot, or a coordination complex). Coupled with the susceptibility of the conversion mechanisms available (internal systems crossing, internal conversion, fluorescence and
phosphorescence) toward the physical and chemical properties of the surrounding medium, makes emission spectroscopy a powerful tool for sensing subtle deviations in the environment surrounding a molecular species.

2.2.2.1 Liquid samples

The luminescent spectra for all of the liquid-based samples studied, including the organic and the organometallic fluorescent candidates were recorded using a Perkin Elmer LS 55 luminescent spectrometer (shown in figure 2.4 a). A pulsed xenon discharge lamp acts as the excitation source to provide constant illumination over the 200 nm – 800 nm range. Two Monk-Gillieson-type monochromators provide the wavelength selectivity, which enables the excitation and emission spectra from a sample to be scanned over the 200 nm – 800 nm and 200 nm – 900 nm ranges, respectively (figure 2.4 c). The excitation and emission collection ports are located at 90° with respect to each other, to avoid potential light contamination occurring from stray light generated within the system. The excitation (d_{ex}) and emission (d_{em}) slit widths are controllable, offering a spectral resolution range of 2.5 nm – 15 nm depending upon the measurement requirements and/or the sample configuration. The variations within the spectral irradiance produced by the Xenon discharge lamp (figure 2.4 d) are automatically corrected. The instrument facilitates two types of measurement; (1) keeping the excitation wavelength constant while monitoring the emission spectrum – the classical emission spectrum or alternatively (2) keeping the emission wavelength constant while altering the excitation wavelength through a series of different values (an excitation spectrum).

2.2.2.2 Solid samples

The AvaSpec-2048 fibre optic based set-up sown in figure 2.5 was used to measure the emission spectrum of the diverse range of solid sample types encountered
throughout this study. This included the organic and organometallic based luminescent
down-shifting layers. Light from a GRIVEN 1200 MSR metal-halide discharge lamp

![Figure 2.4](image)

**Figure 2.4:** (a) Perkin Elmer LS55 luminescent spectrometer and conventional sample holder compartment (b). (c) The accompanying schematic highlighting the operating principle of the spectrometer, showing the selection of a narrowband of light, used to excite a liquid sample, and the subsequent screening of the emission spectrum prior to the application of a correction for the lamps varying spectral irradiance (d).

provided the high intensity excitation power required to excite and produce an appreciable signal within the spectrometer. A band-pass filter was used to produce light in wavelength region (380 nm ± 10 nm), within the absorption band of the fluorescent species categorized herein, with the light transmitted through the filter coupled into a fibre optic cable using a collimating lens as shown in figure 2.5. The coupled light is subsequently guided into an integrating sphere in which the sample is mounted on a highly reflective surface in order to reflection minimise losses within the system.

The accumulated spectrum, containing elements of scattering, excitation, reflection, and emission was coupled via an additional optical fibre directly into the AvaSpec-2048 spectrometer. The capability to adjust the integration time from one millisecond to ten seconds allowed for the detection of very low intensity signals, like
those typically encountered in thin or ultrathin fluorescent polymer-composite systems. A spectral correction, to transform the emission spectra captured into natural units of spectral irradiance, was applied through the implementation of a Bentham CL6 halogen standard. This translated spectral information was later used to optimise the loading concentration of the optimal photoluminescent candidates identified (organic and organometallic based) within the polymer matrix of choice – PMMA. This set-up was also used in the determination of the photoluminescent quantum yield (PLQY*) of the fluorescent candidates, once embedded within their respective host media. The measurement specific parameters involved for each type of measurement will be further expanded upon in the later sections of this chapter.

Figure 2.5: Schematic of the experimental set-up used to measure the emission spectrum of all solid sample types prepared: highlighting each of the individual components as well as the physical principle of operation occurring within the integrating sphere

2.2.3 Luminescent quantum yield

Determination of the fluorescent quantum yield of a fluorophore offers one of the only methods capable of directly measuring the structures capability to convert the
absorbed light into emitted light. The highly sensitive nature of the decay processes, facilitated through a fluorophores physiochemical structure, to the prevailing conditions within their surrounding environment becomes further manifest through this quantitative measurement. Thereby allowing the impact of subtle refinements in the host material, or the interaction between two different species (fluorophore and nanoparticle), on the energy transfer dynamics of the fluorophore to be more resolutely provided. The resulting information helping to refine an LDS or PLDS devices design from early on during the design process, minimising potential losses arising from a mismatch in material selection.

The fluorescent quantum yield of transparent samples such as solutions containing molecular fluorophores, or the semi-transparent host materials encountered throughout LDS and other assorted spectral conversion applications can be determined via two alternative approaches: (1) a relative method and (2) an absolute method. The main difference between these two approaches lies in the requirement for a fluorescent standard of known quantum yield, which also possesses stable optical properties in the solvent/matrix of choice for the relative type measurement. Another divergence between both approaches is their capability to handle different sample types. For example, samples producing significant scattering, some of which may be lost within the conventional spectrometers used in the relative method, require a more practical absolute methodology. The absolute methodologies centre around performing a series of photonic measurements within a calibrated integrating sphere set-up, like that shown in figure 2.5.

2.2.3.1 Relative method

For a typical relative measurement, the comparative method [15-18] was implemented using a combination of three independent fluorescent standards: harmane (figure 2.6 – a & b – purple, dissolved in toluene), harmine (figure 2.6 – a & b – green – dissolved in toluene) and quinine sulphate (figure 2.6 – a & b – orange – dissolved in 0.1 M H$_2$SO$_4$). Three independent standards were used in order to ensure the viability and
validity of the method when applied across the wide range of fluorescent candidates explored throughout this study [18-20]. The choice of the standard materials employed was based upon the guidelines and suggested standards outlined in the different reviews conducted by the International Union of Pure and Applied Chemistry (IUPAC) [19, 21]. Through the careful selection of the excitation wavelength, the influence of the excitation source (inner-filter effects) on the emission spectra resolved and hence resulting LQY determined were minimised [18]. The excitation wavelength ($\lambda_E$) of 380 nm provided the optimal spectral region, across both the standard(s) utilised as well as the catalogue of materials under investigation, in terms of its occurrence in a relatively flat region of the absorption band [18]. A typical measurement for an unknown material was conducted through the successive steps outlined below:

1. A small amount of the material under consideration (~50 mg) was dissolved in 2 ml of a suitable solvent, forming a stock solution of known molarity (~ 1.25 x10$^{-4}$ M). DMSO was used as solvent. The solution was shaken vigorously using a Vortex mixer before being transferred into an oven set to a temperature of 100$^\circ$C to enhance any partial solubility that may have arisen. The solution was removed after 15 minutes and allowed to reach room temperature before spectroscopic measurements were carried out.

2. One millilitre of the stock solution was transferred into a 10 mm path-length quartz cuvette and the absorption and corresponding emission spectra recorded using the Perkin Elmer Lambda 900 UV/VIS/NIR spectrometer and Perkin Elmer LS-55 spectrophotometer, respectively. The measurement parameters (excitation and emission slit widths, PMT accelerating voltage etc.) were kept constant.

3. The original solution was then serially diluted, adopting a dilution factor of 2, until the absorption at the excitation wavelength selected (380 nm) had reached
-0.1 A.U., taking care to ensure the material’s response followed the well-known Beer-Lambert relationship (figure 2.6 c – inset). Any deviation from this response was indicative of chemical (dissociation) or physical (aggregation) changes ongoing within the solution. The same process was repeated for each of the fluorescent standards employed - for example the absorption and emission response of Quinine sulphate is presented in figure 2.6 c and figure 2.6 d, respectively.

4. Finally, the emission spectra registered at each concentration were integrated and the corresponding rate of total emission intensity variation with peak absorbance, at the excitation wavelength (380 nm), determined (figure 2.6 e). The difference between the rate of change of the integrated emission intensity vs. absorption between the material under consideration and the fluorescent standard(s) utilised (figure 2.6 e) is used to determine the LQY [18, 20, 22, 23] according to:

\[
LQY_x = LQY_{ST} \left( \frac{S_x}{S_{ST}} \right) \left( \frac{n_x}{n_{ST}} \right)^2
\]

where LQY represents the fluorescent quantum yield, \(n\) is the refractive index of the solvent utilised, and \(S\) is the gradient of the integrated emission response curve (determined as a function of peak absorbance at the excitation wavelength (figure 2.6 e)). The subscripts \(x\) and \(ST\) denote the material under evaluation and the fluorescent standard, respectively. The abbreviation LQY will subsequently be adopted when specifically referring to a material’s fluorescent quantum yield in liquid form, this being to avoid confusion when discussing the results of the alternative absolute method. All measurements were repeated independently in triplicate with the following strict confidence criteria established throughout the measurement [18, 20, 22, 23]:

- Absorption at the excitation wavelength \(\leq 0.1\) A.U. using 10 mm path-length cuvettes.
- A 95% or greater confidence interval on all fit criteria.
- A maximum allowable tolerance level of ~10% on the standard deviation across the trio of measurements.
- The most up to date value of the standard materials LQY used.

2.2.3.2 Absolute method

Measurement of the absolute fluorescent quantum yield across the different types of solids samples encountered throughout this research was performed using the calibrated set-up outlined in section 2.2.2.2. Samples were typically prepared through the careful removal of a section of the layer (0.025 m x 0.01 m), from the substrate using a scalpel, in order to minimise any influence that may arise due to multiple reflections from the front surface of the substrate. A comparable excitation wavelength of 380 ± 10 nm was adopted throughout the study, as it was similar to the excitation wavelength during the use of the relative method and corresponded to a spectral region of low absorbance. Thereby the inner filter effects typically encountered in integrating spheres were minimised [18]. A typical measurement for an unknown material was carried out using the following steps:

1. An initial adjustment of the measurement parameters available was initiated until the excitation peak registered was maximised within the linear range of the detector. This was completed using a sample fabricated under the same conditions as those used to deposit the layers containing the fluorophore (under evaluation) and was of the same thickness and material properties. This sample is often referred to as the ‘blank’.

2. A series of spectra spanning the 200 nm – 1100 nm range were recorded for both the ‘blank’ and the sample, ensuring that an adequate number of scans (~10) was made across each sample’s surface in order to account for local deviations within the layers optical properties and corresponding thickness.
Figure 2.6: Normalised absorption (a) and emission (b) spectra of the fluorescent standards utilised throughout the study: Harmane (purple), Harmine (green) and Quinine Sulphate (orange). The absorption and emission spectra of one of the material candidates – P282 (cyan) is also shown for comparison. The variation in the absorption (c) and emission (d) intensity of Quinine Sulphate in 0.1M H$_2$SO$_4$ as the concentration is varied from 1.25x10$^{-4}$ M to 1.55x10$^{-6}$ M: the insets in each highlighting the adherence to the Beer Lambert law (c) as well as the linear dependence of the integrated emission spectra within a specific concentration range (d). (e) The rate of change in the integrated fluorescent intensity of each of the fluorescent standards as a function of the absorbance at the excitation wavelength (380 ± 2.5 nm): the fit criterion for each material also displayed.
3. The measured spectra were converted to their respective photon flux \( (F) \) equivalents, through the application of the calibration derived from the Bentham CL 6 – see figure 2.7 for an example of the spectra acquired.

Figure 2.7: Example of the signals of an absolute quantum yield measurement for the sample (LDS – solid black line) and the blank (Blank polymer – dotted black line). The example shows the position of the separation between the excitation and emission, the latter whose spectral profile is enlarged within the inset for further comparison.

4. The photon flux absorbed by the embedded fluorophore \( (F_{abs}) \) was determined according to:

\[
F_{abs} = \int_{\lambda_{ex}} F_b(\lambda_{ex}) - F_x(\lambda_{ex}) \, d\lambda_{ex} \tag{2.4}
\]

where \( F_b \) and \( F_x \) represent the photon flux of the ‘blank’ and sample under consideration, respectively, and the limits of the integration are determined by the excitation bandwidth of light \( (\lambda_{ex}) \) used to excite the sample. For example, in figure 2.7 this integration was performed over the 375 nm – 385 nm wavelength range.
5. The photon flux emitted from the sample ($F_{emi}$) was determined according to:

$$F_{emi} = \int_{\lambda_{emi}} F_{x}(\lambda_{emi}) - F_{b}(\lambda_{emi}) d\lambda_{emi}$$  \hspace{1cm} (2.5)

where $F_{b}$ and $F_{x}$ are as in 4 above and with the integration now performed over the emission range of the sample ($\lambda_{emi}$). For example, with reference to the inset in figure 2.7 the limits of the integration in this example were 400 nm and 600 nm.

6. Finally, the resulting fluorescent quantum yield of the material (*PLQY) was subsequently calculated using the values obtained through expressions 2.4 and 2.5:

$$PLQY = \frac{F_{emi}}{F_{abs}}$$  \hspace{1cm} (2.6)

Depending upon the properties of the material, the PLQY can become highly susceptible to concentration dependent effects such as self-absorption or fluorescent quenching [18, 22]. Given the overlap that typically exists for most classical luminescent materials between the absorption and emission bands, there is a high probability that the photons emitted can become re-absorbed within the sample and accompanied by an apparent reduction in the measured PLQY. This is routinely identified through the onset of deviations within the material’s unique emission spectrum as the loading concentration is increased, specifically the occurrence of a distinguished red-shift [24]. It is possible to account for these effects through the determination of the self-absorption coefficient for each individual concentration employed [24]. Such approaches were not employed throughout this study.

*The PLQY acronym is chosen to avoid confusion when comparing the results discovered through the application of the alternative relative method discussed previously.*
2.3 Reflection spectroscopy

Reflection measurements were carried out using the simple reflection spectroscopy set-up outlined in figure 2.8. The reflectance spectra measured served as a comparative, to ensure the accuracy and reliability of the spectra derived through the transfer matrix models predictive capabilities. Light generated by an Ocean Optics deuterium-hydrogen (DH-2000-BAL) lamp, coupled via a high sensitivity 600 μm thick reflectance probe, provided the illumination for the sample. The sample was housed within the Ocean Optics RPH-1 reflectance holder, with all of the measurements carried out under normal incidence conditions. The light reflected from the sample was coupled into a sensitive Ocean Optics Flame UV/VIS/NIR miniature spectrometer, via an accompanying connection provided by the reflectance probe. The system was calibrated using an Ocean Optics WS-1 diffuse reflectance standard, with a series of independent measurements (~10 - 15) performed across each sample surface to ensure any variability in the samples thickness and/or the uniformity of the fluorophore dispersed throughout was accurately reflected in the spectra acquired.

2.4 Dynamic Light Scattering & Zeta Potential

2.4.1 Dynamic Light Scattering

Dynamic light scattering (DLS), also referred to as photon-correlation spectroscopy, is a highly versatile technique which offers the capability to study the in-situ size, size-distribution, molecular weight, and in some cases the range of particle morphologies present within a solution. The technique relies upon the characteristic behaviour exhibited by sub-micrometre sized particles suspended within a fluid of known viscosity and temperature as the particles continuously undergo Brownian motion. This, in conjunction with the characteristic interference pattern produced when monochromatic light interacts with the particle, creates a cascade of scattering events, whose contributions
Figure 2.8: Schematic of the reflection spectroscopy set-up used throughout the optical characterisation of solid samples, as well assisting in the evaluation and revision of the mathematical model developed: with all the individual components highlighted directly derive from the distinct location and size of the particles within the solution at any given instant: an example of such a pattern is showcased in figure 2.9 a. This signature speckle interference pattern fluctuates as the particles traverse throughout the liquid undergoing a continuous bombardment from the solvent molecules present. The modulations within the signal, monitored on a pixel-by-pixel basis within the detector, exhibit a characteristic rate of decline in intensity, with the rate of decline signifying the particle size [25-28]. This aspect of the signal is expressed through the time-based correlation function, which is rapidly calculated in real time through the computer-controlled element called a correlator, see figure 2.9 a. Monitoring the subtle changes ongoing within the interference pattern registered by the detector, over an extended period allows the particle size-distribution to be derived through the application of the well-known Stokes-Einstein relation:

\[ D = \frac{k_B T}{6\pi\eta R} \]  

(2.7)
Where \( k_b \) is the Boltzmann constant, \( T \) is the absolute temperature of the fluid, \( \eta \) is the viscosity of the medium (typically taken to be the solvent used), \( R \) is the hydrodynamic radius of the particle and \( D \) is the translational diffusion coefficient, which was derived through the analysis of the variability in the interference pattern produced [25-28]. Hence, for a broad distribution of particles sizes, a range of diffusion coefficient values is determined and revealed. The information captured, is classically represented within a size-distribution plot weighted in terms of the intensity contribution derived across each size grouping; an example of such a distribution is presented in figure 2.9 a (size-distribution -black line).

However, this information can be transformed to accommodate other type of weighting distributions, including according to the ‘number of particles’ and ‘particle volume’. An example of the transformation of the information contained within an intensity-weighted plot (figure 2.9 a – black line) to one weighted in terms of the ‘number of particles’ is provided in figure 2.9 a (red line) for comparison. As no single method can produce a fully reliable and valid set of information concerning the photophysical properties of a sample, the DLS technique is typically utilised in conjunction with other techniques, including scanning electron microscopy or tunnelling electron microscopy. The particle size-distribution and polydispersity index (PDI) and the colloidal dispersions encountered were measured using a Malvern Nano series ZS Zetasizer (Malvern Instruments Ltd, Malvern, United Kingdom). The PDI is a measure of how narrow or broad the overall size-distribution is. A PDI above 0.7 is considered inadequate for DLS analysis [27]. Hydrodynamic size measurements were performed in poly-methylmethacrylate cuvettes at a temperature of 25 °C using a He-Ne Laser (\( \lambda = 633 \) nm) with a detector angle of 173°.
2.4.2 Zeta Potential

Alongside the recent advancements within synthetic chemistry has come the ability to tune the optoelectronic properties of materials on the nanoscale, via a plethora of readily available synthesis routes. The unique optical and electrical properties exhibited by these nanomaterials is a direct by-product of their size and shape, with these properties refined through exercising extreme control of the synthesis parameters available. At the small size-regime encountered throughout the preparation of
nanoparticles or similar sized particle-dispersions (nanometre-sized particles dispersed throughout a fluid), the large surface area of the particles begins to dominate the interactions between the nanoparticles and any additional chemical species present. Each particle experiences a torrent of attractive and repulsive forces as it traverses throughout the fluid by way of Brownian motion. The delicate balancing act ongoing within a dispersion between these long-range attractive forces (typically, London - van der Waals) and repulsive forces (e.g. steric interactions) determines the tendency of the nanoparticles to clump together via a process called agglomeration or the capability of the fluid to remain relatively stable [29, 30].

Typically, the attractive molecular forces are more energetically favourable and hence, over time, the particles within a two-phase fluid coalesce, forming larger and larger aggregates, and destabilising the dispersion as the process continues. The susceptibility of particle-dispersions to tend towards favouring particle-agglomeration as a means of reducing their surface energy can be controlled through modifications in the nanoparticle’s surface chemistry [29, 30]. The addition of surfactants or stabilising agents during the preparation of the nanoparticles offers one of the most simple and cost-effective routes for preparing stable particle-dispersions [29, 30]. A stabilising agent, consisting of a polymeric hydrocarbon containing hydrophobic and hydrophilic elements at opposite ends of the molecule, selectively binds to the surface of the nanoparticles altering the repulsive forces existing between neighbouring particles within the dispersion. The stability of a dispersion, in response to changes within its surrounding environment or chemical revisions adopted at the synthesis stage, was ascertained through monitoring the characteristic absorption spectra derived within a conventional UV-VIS-NIR spectrometer over prolonged periods of time [29, 30]. Subtle deviations within the absorption spectra give indications of the struggle ongoing between the competing forces. Developed as a rapid and efficient alternative, the zeta potential measurement provides a
single snapshot from which a dispersion’s stability can be determined without the need for repeating measurements over prolonged periods [29, 30].

The measurement principle revolves around the application of a fixed potential across the solution (shown in figure 2.9 b) with the externally applied potential driving a rearrangement of the charge distribution within the solution. Eventually, to neutralize the surface charges accumulated across the nanoparticle surface, counter-ions, freely available within the medium, begin to form an immovable layer around each nanoparticle called the Stern layer – see figure 2.9 c. Although there exists a strong coupling between the counter ions and their surface charge equivalents, now accommodated within the Stern layer, a weak electrostatic force is still felt by neighbouring ions and counter-ions alike, both of which are freely available within the dispersion. As more ions begin to attach to the nanoparticles, in an attempt to counteract the remaining surface charges, a secondary more diffuse layer is created around the Stern layer, whereby ions and counter-ions from within the bulk fluid can continuously migrate into and out of this diffusion region (slipping plane) as shown in figure 2.9 c. The potential that exists along this slipping plane boundary is called the zeta potential (Z), and its magnitude i.e. the cumulative charge built up in the response to the externally applied potential, provides the qualitative information regarding the particle’s stability [30].

Given the non-monomodal nature of most fabricated dispersions, there exists a distribution of zeta potentials whose peak magnitude and corresponding distribution reveal the cumulative effect of the electrostatic interactions unfolding within the particle ensemble. The larger the magnitude of the Zeta potential, the more particles within the solution are undergoing electrostatic repulsion amongst themselves, prolonging the occurrence of the aggregation process. Peak values of approximately $\pm \geq 30$ mV are considered highly stable [30].
2.5 Scanning Electron Microscopy

Focusing a beam of high energy electrons towards a sample surface and analysing the characteristics of the secondary electrons, backscattered electrons, and distinct x-rays subsequently produced through the electron-sample interactions, forms the basis of scanning electron microscopy (SEM). Electrons generated within the tip of the electron gun – shown in figure 2.10 a, are rapidly accelerated towards a sample, due to the potential bias established between the sample and the electron source, with the magnitude of the applied potential controlling the penetration depth within the sample. Electromagnetic optical components like those shown in figure 2.10 a (condenser lens, objective aperture as well as the objective lens) are used to help collimate and adjust the spot size of the electron beam, to provide the desired degree of spatial resolution.

Figure 2.10: (a) Schematic of a generic scanning electron microscope (SEM) including all the key components, and the accompanying combination of SEM devices (b - Hitachi SU 6600 field emission scanning electron microscope (FESEM) and c - Hitachi SU 70 Analytical FESEM) used throughout this research.
SEM was primarily used in this work to probe the impact of key synthesis parameters, such as the concentration of the reagents utilised throughout the synthesis of Ag Nanoparticles (see chapter 3), on the resulting structure’s optical and morphological properties. The technique was also deployed, in conjunction with DLS (section 2.4) to develop an accurate representation of the nanoparticle population complexity (particle size, size-distribution, and the existence of different anisotropic particle morphologies) in response to the synthesis configuration and surrounding environment conditions, e.g. re-suspension or polymer encapsulation.

2.6 White light interferometry

White light interferometry (WLI) is a well-developed and extremely powerful measurement tool, frequently utilised to rapidly analyse the surface topography of an object over a large area or alternatively perform a high-resolution thickness measurement [34, 35]. The interferometer’s design (shown in figure 2.11) is basically that of a Michelson Interferometer. Light, from a broadband light source is split along two different optical paths within the system – see figure 2.11 a; one of the paths contains a reference mirror (shown in red) and the other incident upon the surface of the sample. The additional phase accumulated through the beam’s interaction (figure 2.11 b) with the sample is effectively coupled into the light returning to the CCD detector yielding a characteristic interference pattern. The result is a measurement area (82 µm x 62 µm - 264 µm x 200 µm), that can be accurately mapped in detail to deliver topographical information about the surface features existing on a test sample. For performing a high-resolution thickness measurement, the sample, if bound to a substrate (which is common throughout the fabrication of polymers), is carefully perforated at different locations along its surface. The corresponding divergence between the interference pattern registered along the substrate and at the different locations scattered across the layer
provide an accurate estimation of the layer’s thickness as well as its overall surface roughness. WLI measurements were carried out using a MicroXAM white light interferometer and were used in this study to determine the thickness of the various structures deposited (LDS, as well as the ARC’s studied), while also aiding in the corroboration of the thickness profiles used to validate the TMM model, as outlined in chapter 6.

Figure 2.11: (a) Optical schematic of a white light interferometer, used to analyse the fine structure of a test samples surface: highlighting each of the primary components within the devices design. (b) the interaction scheme of light within the bottom part of the interferometer, Whereby the additional phase component introduced into the beam, through the interaction of light with the samples surface (represented in red arrows) is coupled back through the beam splitter and combined with the reference beam (represented in black arrows) before being subjected back into the remainder of the system.
2.7 Stylus Profilometry

An alternative contact-based approach to analysing the surface properties of a material is the classical stylus based profilometer shown in figure 2.12. The stylus profilometer works through bringing an extremely sharp tip (“stylus”), frequently composed of diamond, ruby or sapphire, directly into contact with the sample surface. Manoeuvring the stylus across the surface of the sample, whilst monitoring the deviations in its position by the surface topography, enables a two-dimensional image of the surface to be reconstructed [34, 35]. The resolution of the images obtained are limited by the physical dimensions of the stylus itself, which provides a filtered representation of the surface rather than a true profile. The resolution provided is also a function of the type of stylus implemented (composition and geometry) as well as the magnitude of the force applied to drive the tip into direct contact with the surface [34, 35]. For “soft” samples such as polymers the forces utilised can prove too great and they inevitably introduce a degree of degradation into the sample during the analysis.

![Figure 2.12: (a) Veeco Dektak 6M stylus profilometer and (b) accompanying schematic of a stylus based profilometer and the measurement principle involved](image)
In order to ensure the additional optical structures devised in chapter 6 were accurately replicated in a modelling environment, simple AR coated structures were used to verify the models’ output(s), with the samples physically characterised using a host of different characterisation techniques. A Veeco Dektak 6M (shown in figure 2.12 a) was utilised to provide a cross calibration of the thickness values provided by the WLI technique outlined in section 2.7 specifically in the pursuit of accurate thickness values for the structures utilised in the experimental validation of the model.

2.8 Q-SUN XE-3 xenon lamp chamber

In order to investigate whether the material solutions proposed, could withstand the typically harsh environmental conditions encountered throughout the various solar applications applicable to the technology (building integrated photovoltaics, combined PVT systems or spectral beam splitting applications), their durability under similar conditions were assessed. Accelerated ageing, carried out under a high intensity spectral lamp, designed to replicate the spectral irradiance conditions found under a cloudless sky in a mild summer climate, paves the way for rapidly assessing a photoactive material’s longevity in a highly reproducible manner [36-38]. The Q-SUN XE-3 chamber, shown in figure 2.13 a, is one such irradiator capable of subjecting the materials enclosed within its test area (highlighted in figure 2.13 a) to spectral irradiation similar to that found within warm & humid tropical climates south of the equator - see figure 3.13 c for examples highlighted in red. The test chamber also facilitates the capability to simulate realistic weather conditions including relative humidity, temperature, and moisture content. Ideally, the three separate lamps adopted within the Q-SUNs design would allow for an accurate replication of the entire solar spectrum; however, the materials utilised always limit this from becoming a reality. Instead, most sources are calibrated at a single wavelength (340 nm for the Q-SUN XE-3) and the rest of the lamp’s spectrum scaled accordingly. The XE-3 model comes equipped with a series of built in filters, with the
“daylight Q-filter” providing the best spectral match to that of a noon summer sun, see figure 2.13 b for a comparison.

Figure 2.13: (a) Schematic of the Q-LABS Q-SUN XE-3 xenon test chamber highlighting the fundamental internal components. (b) Comparison between the spectral irradiances achievable with the Q-SUN, when adopting some of the different optical filters (‘daylight’ or ‘UVA’) available, as well as its correlation with the natural irradiance conditions. (c) Global breakdown of the different climate regions (tropical – red, subtropical – yellow, temperate– green, and polar & subpolar – cyan), which facilitated in the design of the photo-stability trials conducted.

To pinpoint the locations and climates most feasible for integrating the LDS/PLDS proposed devices, the photo-stability trails conducted were divided up into two categories. (1) Those simulating a moderate European temperate climate – see the
countries highlighted in green in figure 2.13 c, and (2) those simulating harsher more tropical climate conditions – see the countries highlighted in red in figure 2.13 c. In the temperate climate zones (Ireland, England, Germany and other European countries) an irradiance of 0.30 - 0.35 W m$^{-2}$ nm$^{-1}$ at 340 nm is considered adequate [36]. Whereas in the extreme tropical climates of, e.g., Florida, sub-Saharan Africa or northern Australia an irradiance above 0.45 W m$^{-2}$ nm$^{-1}$ at 340 nm is commonplace for most of the year, and throughout the entire duration of the daily light cycle [36].

To expand upon the divergence between the two simulated climate conditions the irradiance values lying within the range identified to correspond to each specific climate classification were taken to be the extreme case. This corresponded to an irradiance of 0.30 W m$^{-2}$ nm$^{-1}$ for temperate climates and an irradiance of 0.50 W m$^{-2}$ nm$^{-1}$ for tropical climates at 340 nm, respectively. LDS layers used in this study were fabricated under the conditions outlined in chapter 4 and embodied a wide range of loading concentrations (0.007825 wt-% - 3 wt-%) to see if the degradative effects were indeed concentration independent. The layers were subjected to the irradiance conditions outlined in conjunction with an allowable temperature range: 15 °C – 25 °C for temperate climates and 25 °C – 40 °C for the tropical climates. Regular spectroscopic evaluation of the absorption spectra of the layers was carried out, until the resulting absorption spectra had diminished, or the test had reached a specific period of exposure (~100 hrs). Given the likely variation in the intensity producible across the XE-3 sample tray [39, 40], the sample’s position on the tray was continuously rotated, upon the removal of the layers for spectroscopic evaluation.
2.9 Electrical characterisation
2.9.1 External Quantum Efficiency

One of the primary techniques used to determine the conversion efficiency of a solar cell is the external quantum efficiency (EQE) measurement. The EQE, characteristically defined as:

$$EQE(\lambda) = \frac{\text{number of charge carriers collected}(\lambda)}{\text{number of incident photons}(\lambda)}$$  \hspace{1cm} (2.8)

and offers insights into the conversion processes and losses occurring within specific wavelength ranges [41-45]. Contrasted with the traditional current-voltage (I-V) relationship, from which the maximum power achievable is derived, and which can only provide information regarding the collective behaviour of the cell across its complete spectral response range [41, 42, 45]. Given the rich information retrieved from a sample using the EQE measurement, commercial companies have begun offering stand-alone single units capable of handling a diverse range of cell architectures including silicon derivatives, cadmium telluride, perovskite, as well as other organic based technologies [42, 45-47]. The instrument used in this work is a Rerea Solutions Ltd spec-quest solar cell EQE measurement unit shown in figure 2.14 a. The unit combines all the required components (calibrated illumination source, monochromator and lock-in amplifier) under one external shell. A calibrated quartz-halogen lamp provides illumination over the 250 nm – 2500 nm range, with the lamps output stabilised via a dedicated current limited power supply – see figure 2.14 b.

For a typical EQE measurement, the system was started and allowed 30 minutes to reach a stable operating temperature before commencing any measurements. The system was successively calibrated over the 250 nm – 1100 nm range using a calibrated silicon photodiode (10 mm x 10 mm, NIST traceable) by determining its spectral response as a function of wavelength, with an incident beam area of 2 mm$^2$ narrowly focused on the centre of the reference diode. The current collection device was AC coupled to
discriminate the photocurrent generated within the photodetector from that produced within the cell when under DC loading conditions, which occur throughout the measurement process [45]. The reference diode was replaced with the sample, and the process repeated using an average of five independent scans, taken from across its surface, in order to account for any variations in performance stemming from the physical properties of the fitted structures (LDS, PLDS, anti-reflective coatings, etc.).

![Figure 2.1](image)

**Figure 2.14:** (a) The Spec-Quest External Quantum Efficiency (EQE) solar measurement instrument from Rera Solutions, with all of the key components highlighted. (b) Accompanying schematic outlining the interplay between the components throughout the measurement.

### 2.9.2 Current-voltage (I-V) characterisation

The most fundamental solar cell characterisation technique is the measurement of the cell’s efficiency under the standardised ASTM E1021-15 test conditions [48]. Considering the strenuous control required by a system in order to achieve and maintain these operating conditions, most measurements are carried out under custom-made test rigs that only roughly approximate these standardised conditions [45, 46, 49]. The efficiencies reported utilising such a set-up serve to form an inter-comparison between
the cells characterised under the exact same conditions (irradiance, intensity, temperature and beam size). In this manner, the conversion efficiency of alternative cell designs including LDS fitted devices are compared to the “bare” cell’s performance [46, 49-52]. The “bare” cell is an uncoated solar cell accompanied by a host layer (non-doped) of the same thickness as that utilised within the spectral conversion device [46, 49-52]. This is an adequate assertion, considering that PMMA and other semi-transparent polymers are frequently used throughout the solar industry to form protective cover sheets for the photovoltaic panels [53, 54]. The technique involves evaluating the junction’s performance and quality under artificial loading conditions through alteration of the potential applied across the cell. Monitoring the resulting photocurrent generated within the cell, through the implementation of a suitable source meter such as that shown in figure 2.15, enables the cells distinctive I-V response curve to be measured. The performance metrics commonly used to convey the quality of a cell including maximum power, fill factor and overall efficiency are derived from this curve [55].

For a typical measurement, spectral conversion devices (LDS) consisting of 2 cm x 2 cm monocrystalline silicon solar cells (Solar Capture Technologies Ltd, England) were fitted to glass substrates in order to ensure they remained completely flat throughout the measurement. The substrates were then carefully placed within a makeshift sample holder (shown in figure 2.15), which further secured the devices throughout the measurement, whilst also ensuring that the diameter of the incident beam was maintained at 10 mm. A Keithley 2400 source meter was used to perform the measurements, with the resulting I-V curve generated through a LabVIEW interface. A series of three independent measurements were performed across the entirety of each device in order to ensure the accuracy and validity of the measurement.
2.10 Transient Hot Wire Technique

To determine the thermal conductivity of the nanofluids and of the base fluid (water in this case), the transient hot-wire technique was used as it is a rapid, cost-effective, and widely accepted method applicable across a diverse range of fluids [56-61]. In this method a platinum wire is immersed in the sample fluid and it is used as both heat source and temperature probe as the controlled transfer of heat through the wire is initiated. As the temperature of the wire increases under ohmic heating, the heat transfer mechanisms within the fluid begin to curtail the temperature instabilities arising within the liquid. The rate of heating within the fluid can be directly related back to its fundamental thermal properties [56-61]. Restricting the analysis to very short timeframes limits the capability of natural convection to occur. The temperature variations consequently arise solely from the conductive heat transfer within the fluid and allow for the determination of the thermal conductivity of the liquid [56-61].

Figure 2.15: Schematic of the set-up used to perform the characteristic current-voltage (I-V) measurement, with all of the key components highlighted.
In this experiment a platinum wire (diameter $d = 10 \, \mu m$ and length $L = 4 \, \text{cm}$) was secured into a plastic cell where the liquid is placed. The wire is connected to one arm of a Wheatstone bridge circuit, as shown in Figure 2.16. This facilitates the arrangement of a highly temperature-sensitive circuit whose potential imbalance ($V_{out}$) is correlated with the dynamic heat conduction conditions within the surrounding liquid [56-61]. Monitoring the temperature- and time-response of the wire, when subjected to an abrupt electrical pulse, allows for the thermal conductivity ($\kappa$) and thermal diffusivity (D) of the fluid to be determined [56-61].

![Figure 2.16: Schematic representation of the transient hot-wire experimental set-up used to explore the thermal conductivity of the nanofluids developed.](image)

The mathematical model used to characterize the situation within a hot-wire cell (as the one shown in Figure 2.16) considers an infinitely long and thin uniform heat source (the wire) embedded in an infinite homogeneous medium, i.e. the sample fluid [56, 57].
An infinitesimal line source, such as that described by the model, is realised by using an ultrathin wire of relatively long length \(d \ll L\) effectively simulating a line segment of length \(L\) from an infinite wire [56, 57]. Here, the wire has diameter \(d = 10 \mu m\) and its length \(L\) is 4 cm. Consequently, the model conditions are fulfilled. The model uses the assumption that as result of the conductive heat transfer from the wire into the fluid, the temperature, and hence the resistance of the wire (test cell), varies with time. The equation governing this physical process is derived from the application of the transient heat diffusion Fourier equation in the presence of adequate boundary conditions [56-61]. The solution to this problem is well known [56, 57] and, when applied to a circuit resembling that outlined in Figure 2.16, yields the following expression [2]:

\[
\kappa = \frac{(IR)^3 \alpha S R^2}{4\pi L(R+S)A'}
\]  

(2.9)

where \(I_R\) is the current flowing through the wire, \(\alpha\) is the temperature coefficient of resistance for the conducting wire (for platinum this is taken to be \(3.85 \times 10^{-3} \degree C^{-1}\)), \(L\) is the length of the wire, \(S\) and \(R\) are the resistances of the potentiometer and the wire, respectively, while \(\kappa\) is the thermal conductivity of the fluid. The quantity \(A'\) is the slope of the following linear relationship [57]:

\[
V_{out} = A' \ln(t) + B
\]  

(2.10)

where \(V_{out}\) represents the potential imbalance registered across the Wheatstone bridge circuit after the switch shown in figure 2.16 has been open for a time period \((t)\). Hence, monitoring the voltage drop across the bridge as a function of time and ensuring the measurements are acquired over very short time-scales allows for the thermal conductivity of a liquid to be obtained using the equations 2.9 and 2.10.

In this study, a hot-wire cell (5 cm x 4 cm x 4cm), as depicted in Figure 2.16, was designed to be used with a reduced sample volume (~30 ml), the cell being manufactured using a 3D printer utilising polylactic acid (PLA). The cell was designed to be flexible in
terms of its capability of replacing the sample or to be completely disassembled to clean the parts involved. Platinum wire was used due to its relatively high thermal conductivity and well characterised resistance variation across a wide temperature range [56, 57]. The resistance of the two resistors in the bridge was selected to maximise the sensitivity of the set-up [56, 57].

The potentiometer S allows the elimination of any potential imbalance within the bridge before an abrupt electrical pulse is sent through the circuit. The voltage readings across the bridge were acquired using a Keithley 2110 multimeter configured to record the data every 25 milliseconds. For a typical measurement the electrical pulse was delivered for a period of approximately 15 seconds and, typically, 5 minutes was allowed between successive measurements. This allows the proper cooling of the system and the removal of any residual thermal energy from the system. The data gathered was subsequently processed using equations 2.9 and 2.10 to obtain the thermal conductivity of the fluid investigated.

To ensure that the direct exposure of the wire to the various types of working fluid will have a minimum impact on the sensitivity of the uncoated platinum wire, the thermal conductivity of ultrapure water (\( \rho = 18.2 \text{ M\Omega cm}^{-1} \)) was measured before and after each nanofluid was investigated. The thermal conductivity of the water (\( \kappa_W \)) prior each nanofluid test was then used to calculate the ratio (\( \kappa_{NF} / \kappa_W \)) for the subsequent nanofluid concentration considered.

2.11 References


Chapter 3

Development of Poly-Vinyl Alcohol Stabilized Silver Nanofluids for Solar Thermal Applications


3.1 Introduction

At present, there are two main types of solar energy systems: those reliant on the direct conversion of the incident solar irradiance into usable electricity (solar-photovoltaic) and those based on harnessing the solar irradiance to use it as an alternative source of thermal energy (solar-thermal) to meet a proportion of a buildings cooling and heating demands [1-5]. Typically, in solar thermal plants or in a conventional flat plate solar thermal collection (FPSTC) system, the solar radiation captured by a heat sink is in turn transferred to a working fluid (e.g. water, ethylene glycol etc.) which passes through the enclosed system under flow conditions specific to the application [6-10]. Therefore, the working fluid plays a dominant role in enhancing the efficiency of the energy transfer, which, in turn, is dependent upon the composition, arrangement, stability and photothermal properties of the fluid. To enhance the physical properties of a working fluid nanometer sized particles can be suspended into a base fluid [11-16]. The presence of such particles, commonly composed of highly conductive materials, dominate the thermal and physical properties of the resulting fluid [12,15,17,58-59]. The resulting fluid suspensions, generically called nanofluids or nanosuspensions, have become a leading candidate for the cost reduction of the solar-thermal energy [11,13-14,18,20,28-29,45-48].

Typically, the nanoparticles utilized in nanofluid studies embodied a single mode narrow-distribution of the particle size [23-26,35-36]. However, using a poly-disperse particle size-distribution can influence the interaction between the collective ensembles of particles and promote the thermal properties of the base fluid. Within such a wide-
ranging particle size-distribution, the larger sized particles form an antenna effectively coupling the higher order LSPR modes available on these nanostructures to the nearly smaller size particles. These smaller size particles can in turn act as resonators, creating localized ‘hot-spot’ regions [32,39,50-53]. The enhanced electric field established through such an interconnected particle network is greater in magnitude than that created through isolated narrow particle size-distributions [50-53]. Typically, the commercially purchased nanoparticles employed in the design and characterization of nanofluids are lacking in the variety of particle morphologies, shapes and sizes [21,23,34,54-55]. This can be mainly due to the product control existing within a commercial environment, which requires narrow particle size-distributions and similar morphologies for the nanoparticles as a commercial product. Consequentially, in the research pursuit of efficient and stable nanofluids, the possibility of particle-particle interactions between different anisotropic shape and sizes has been, typically, overlooked. However, such interactions can have the potential of enhancing the absorption and/or thermal capabilities of the nanofluids [56-60].

The present experimental study focuses on the influence of the nanoparticle population complexity on the thermal properties of the nanofluid through developing and characterizing nanofluids containing nanoparticles of different particle size-distribution, configurations, and shapes. Water based silver-nanofluids (developed via a two-step method in which the nanoparticles were formed through a wet-chemical synthesis route using widely available reagents) are explored as potential candidates for working fluids within a direct absorption solar-thermal collection system. The synthesis route allows for the stabilization of the nanofluids through the employment of the surfactant poly-vinyl alcohol (PVA) to aid and control the nanoparticle growth. The main advantage of this approach is represented by the fact that the nanofluids manufacturing procedure is simple, relatively low-cost and it can be easily scaled up to be used in real-world solar thermal
applications. The optical properties of the colloidal dispersions fabricated were tuned throughout the synthesis stage to deliver a dynamic absorption profile over the 300 nm – 800 nm spectral window. The impact of the particle size-distribution, particle morphology, particle concentration and dispersion stability on the photo-thermal conversion efficiency and thermal conductivity of the nanofluids is discussed.

3.2 Materials and Methods

3.2.1 Ag nanoparticle Synthesis

3.2.1.1 Reagents

Silver nitrate (AgNO₃, 99.99%), sodium borohydride (NaBH₄, 99%), poly-vinyl alcohol (PVA, 87% - 89% hydrolyzed, typical M_W 13 000 – 23 000 g/mol), tri-sodium citrate (TSC, 99.5%) and hydrazine (N₂H₄, hydrate, reagent grade, 50% - 60%) were all purchased from Sigma Aldrich Co (St. Louis, Missouri, United States) and used without further purification. Ultrapure water (ρ = 18.2 MΩ cm⁻¹) was used throughout the experiment to form the numerous aqueous solutions required for the nanoparticle synthesis route employed.

3.2.1.2 Particle Nucleation and the formation of Ag Seeds

In this study, silver nanoparticles were synthesized using a two-stage seed mediated process (Figure 3.1) consisting of (I) particle nucleation and (II) particle growth [61-63]. In the first stage silver seeds, prepared by the chemical reduction of silver nitrate (AgNO₃) with sodium borohydride (NaBH₄) in the presence of a stabilizing and capping agent poly-vinyl alcohol (PVA), constitutes a ‘reference frame’ upon which nanoparticles of various sizes and shapes can be formed (Figure 3.1, (i) – (iii)). In a typical synthesis process 2 ml of chilled (T < 4 °C) NaBH₄ (0.001 M) were added dropwise to 2 ml of AgNO₃ (0.001 M) and 2 ml of PVA (1% w/v in g/ml) while the solution underwent constant agitation via magnetic stirring.
Figure 3.1: Schematic representation of the seed-mediated method (i – v) used to synthesize and control the size of silver (Ag) nanoparticles. Subsequently, the nanoparticles were dispersed in a base fluid to form silver nanofluids (vi). The individual stages of heterogeneous particle growth that is taking place during each stage of the synthesis procedure are also presented.

### 3.2.1.3 Controlled Ag Particle Growth

In the second stage, various volumes of AgNO$_3$ were added to a ‘growth solution’ leading to the formation of colloidal dispersions with various colours tuned through the crystals growth (Figure 3.1 (iv) - (v)). In a typical synthesis process, 1 ml of seed solution prepared in stage I was added to 1 ml PVA (1 % w/v), under magnetic stirring. Then, to this resulting dispersion, 3 ml TSC (0.1 M) and 5 ml N$_2$H$_4$ (0.1 M) were added sequentially forming the ‘growth solution’. The nanoparticle dispersions of various colours were produced by adding, under constant agitation, various volumes (0.4 ml – 20 ml) of AgNO$_3$ (0.001 M) to the ‘growth solution’ in a slow and controlled manner (~ 0.03 – 0.06 ml/s).
3.2.2 Nanoparticle Characterization

The formation of Ag nanoparticles was monitored by UV-VIS spectroscopy. The absorbance spectra of a colloidal sample were recorded over the 200 nm – 800 nm spectral range using a Perkin Elmer Lambda 900 spectrometer (Perkin Elmer Inc., Massachusetts, USA) and having ultrapure water as a reference. An integrating sphere configuration was adopted to minimize the scattering losses occurring due to the presence of Ag nanoparticles within the colloidal dispersions. The dispersions formed were diluted with ultrapure water in a ratio of 1:5 and the measurements were carried out using 10 mm path length quartz cuvettes. The underlying spectral components, corresponding to the different particle size-distributions present, were determined using spectral deconvolution, Gaussian peaks being considered for curve-fitting in each case. The evolution of the individual spectral components allowed monitoring the growth and the decay of nanoparticles size distributions within the dispersions. The spectral deconvolution consisted of three steps: (1) baseline subtraction, (2) identifying the possible number of peaks by performing the second derivative and (3) curve-fitting of the overall spectrum using Gaussian peaks [64-66]. The fitting criteria adopted in each case were in correspondence with the guidelines available in the references [64-66].

The particle size-distribution, polydispersity index (PDI) and zeta potential of the colloidal dispersions fabricated were measured using a Malvern Nano series ZS Zetasizer (Malvern Instruments Ltd, Malvern, United Kingdom). Hydrodynamic diameter measurements were performed in poly-methyl-methacrylate cuvettes at a temperature of 25 °C using a He-Ne Laser (λ = 633 nm) with a detector angle of 173°. The refractive index and the viscosity values used were that of pure water. Hydrodynamic size and zeta potential are reported as the mean of the three repeated measurements. The error bar values represent the standard deviation of these measurements.
The surface morphology and shape of the Ag nanoparticles were examined using a Hitachi SU-6600 Field Emission Scanning Electron Microscope (FESEM) and/or a Hitachi SU-70 FESEM (Hitachi Ltd, Tokyo, Japan). A typical sample preparation for SEM investigations involved placing a drop of the diluted Ag nanoparticle solution on a copper grid and allowing 12 hours (hrs) to dry at room temperature before imaging. The images were analysed using ImageJ software, employing an automatic threshold routine. The algorithm used to determine the threshold for each case was selected from the methodologies available in Image J. The mean (Sauter) diameter was subsequently calculated using at least 250 particles per sample.

3.2.3 Preparation and characterization of silver nanofluids

Silver nanofluids were prepared by the method schematically summarized in Figure 3.1 (i) – (vi). In this method, colloidal silver dispersions containing particles of different sizes and shapes were first prepared using the aforementioned synthesis route (Figure 1 i – v). In each case, a certain volume (0.05 µl – 2.50 ml) of the dispersion was re-dispersed into a base fluid – ultrapure water in this work – as presented in Figure 3.1 vi. After the addition of the nanoparticles, the resulting nanofluid solution was transferred to an ultrasonication bath for 30 minutes to reduce possible particle agglomeration, which could have occurred during the transfer of the particles into the base fluid [13-14,27]. Characterization at each stage of the nanofluids preparation was carried out to ensure adequate stability of the nanofluids and their photo-thermal property measurements.

UV-VIS spectrophotometry was used to investigate the stability of the nanoparticles within different types of nanofluid, i.e. those containing different particle size-distributions and/or a variety of particle shapes. As the plasmon absorption band of a nanoparticle is highly influenced by its size, shape and surrounding environment, the Perkin Elmer Lambda 900 spectrophotometer was used to aid in the identification of possible aggregation, upon transferring the particles from the colloidal dispersion into the
base fluid [13,22,27,42,44]. This test was carried out in conjunction with dynamic light scattering and Zeta-potential analysis, post particle re-dispersion in the base fluid, to identify subtle changes in the particle size and surface charge distribution. The measurements were performed using a Malvern Nano Series ZS Zetasizer (Malvern Instruments Ltd, Malvern, United Kingdom).

### 3.2.4 Photo-thermal Conversion Efficiency

The capability of the nanofluids to capture and convert light across a broad spectral range into usable thermal energy was studied and evaluated using the set-up shown in Figure 3.2 (a). A halogen lamp (Griven© 1200 MSR), working as a solar simulator, was used to reproduce the natural solar irradiance. This solution was chosen to alleviate the uncertainties which can arise due to the instabilities experienced in the natural lighting conditions. The Griven lamp provided a spectral irradiance closely matching that of the standard AM1.5G reference spectra (Figure 3.2 c), commonly used within controlled testing environments to replicate the sun's spectral distribution under certain idealized conditions [67]. The Griven lamp delivered a consistent spectral irradiance to within a 4% - 9% tolerance range over the entire spectral range of the lamp (Figure 3.2 c) with fluctuations in the overall irradiance approaching 4% over the course of an individual nanofluid characterization cycle (Figure 3.2 d). The light produced by the lamp was sent to the bottom of a borosilicate glass cell (length × diameter = 7 cm × 2.3 cm and a wall thickness of 0.3 cm) using a plane mirror oriented at 45° (Figure 3.2 a). The borosilicate glass has a high transparency (~95%) over the broadband range of frequencies present within the incident spectrum. The glass cell was placed within a polyester insulating foam (used to provide an insulating environment for the cell) with only the bottom surface area of the cell directly exposed to the centre of the beam produced by the solar simulator. The possibility of thermal and radiative losses to the
surrounding environment were minimized through encasing the entire set-up in an external wooden wall.

For a typical nanofluid characterization measurement, the power of the halogen lamp was adjusted, the irradiance arriving at the nanofluids location being \(1220 \pm 50 \text{ Wm}^{-2}\). This value was measured at the sample location using a pyranometer (Delta-T BF-3 sunshine sensor) that has a measurement uncertainty of \(\pm 5 \text{ Wm}^{-2}\). A period of 30 minutes was allocated for the lamp to reach stable operating conditions. After this, the glass collector containing the nanofluid under consideration was placed under the illumination of the solar simulator for 90 minutes. Typically, 25 ml of working fluid was employed
within the direct solar absorption collection system, with the 0.05% - 10% v/v nanofluid loadings prepared by collecting a quantity from the stock nanoparticle solution (step V in Figure 3.1) and re-dispersing them into ultrapure water for each type of nanofluid considered.

Four K-type thermocouples (with an uncertainty of ± 0.5 °C) were positioned at the top and at bottom of the glass collector (as depicted in Figure 3.2 b) to monitor the temperature changes within the nanofluid (using the temperature differences between the two thermocouples within the fluid) and with its surrounding environment (using the temperature differences between the thermocouples within and outside the cell) in real time. The temperature probe closest to the inlet was used to resolve changes within the photo-thermal efficiency of the working fluid as a result of the alterations made to the nanoparticles size, shape, and concentration within it. The divergence between the two temperature readings, within the fluid, reveals information on the homogeneity of the heat transfer within the volume of fluid. As the temperature of the working fluid increased during constant irradiation, losses to the surrounding environment became more prevalent. Placing two thermocouples outside the working fluid allowed for these losses to be resolved and quantified. The temperature variations were monitored and recorded every second using a data acquisition system composed of a data logger (Pico TC-08 data logger) interfaced to a computer.

The photo-thermal conversion efficiency (PTE) is commonly defined as the ratio between the energy stored within the nanofluid and the total incident solar irradiation [19,26,45,49]:

\[
PTE = \frac{(c_w m_w \Delta T_w + c_{np} m_{np} \Delta T_{np})}{I A \Delta t} \approx \frac{c_w m_w}{I A} \left( \frac{\Delta T_{nf}}{\Delta t} \right)
\]  

(3.1)

where \(c_w\) and \(c_{np}\) are the specific heat, \(m_w\) and \(m_{np}\) are the mass, \(\Delta T_w\) and \(\Delta T_{np}\) are the rise of the temperatures over the measurement period \(\Delta t\) of the water (w) and the nanoparticles.
(np), respectively; \( I \) is the irradiation flux and \( A \) is the illumination area of the nanofluid. Under low intensity conditions, the temperature difference between the particles and the base fluid is negligible [19,26,68]. The low concentrations of particles employed allows the nanoparticles mass contribution to be assumed negligible [26,69-70]. This allows for a general accepted simplification of general equation 3.1, PTE being now directly proportional to the temperature gradient at a point within the bulk nanofluid \( \Delta T_{nf} \), measured by the thermocouples. The contributions to the PTE arising from latent heat (i.e. due to evaporation) are not considered in the outlined definition of PTE [26,69-70]. The relatively low temperatures (< 50 °C) involved in this study allow the assumption that these contributions are negligible. The expression employed does not have to consider the losses to the surrounding environment through both radiative and convection processes, as the system was placed in an insulator environment. The enhancement (equation 3.2) in the PTE of the nanofluid, as compared to the base fluid, offers a clearer metric of the overall impact of design parameters on the performance of the nanofluid.

\[
\text{Enhancement} = \left( \frac{PTE_{nf} - PTE_w}{PTE_w} \right) \times 100
\]  

The thermal conductivity of the water (\( \kappa_W \)), the base fluid in this study, and the thermal conductivity of each nanofluid (\( \kappa_{NF} \)) for various concentrations were measured using the hot-wire method as described in detail in section 2.10. The values obtained for the thermal conductivities were used to calculate the ratio (\( \kappa_{NF} / \kappa_W \)). These results were then compared with the PTE behavior for the various nanofluids.

### 3.3 Results and Discussion

#### 3.3.1 Seed Formation

Seed solutions containing a narrow distribution of particle sizes are essential to the development of controlled nanoparticle growth during the second stage of the synthesis. Deviations within their optical properties can be used as indicatives of the
control exerted over the growth kinetics during heterogeneous particle growth [61,63,71-72]. Seed solutions exhibiting a rich golden yellow colour (like that presented in Figure 3.3 a, inset) represent the ideal case, reflecting the best control granted over the particle formation [61-63]. Darker colours are indicative of increased scattering due to the presence of larger particles [38,61,63,66,88]. This implies that during the initial stages of particle growth, a larger variation in the size of the ‘seed’ particles was formed. The origin of this variation is owing to either subtle differences within the growth kinetics of the reaction [38] or, alternatively, to the formation of a larger number of ‘seed’ particles during nucleation [73]. The larger number of seeds particles formed can allow for a higher predisposition of the seed solutions towards agglomeration and, hence, at a later stage, for a larger variation in the nanoparticle size in the resulting nanofluid.

Typically, a colloidal dispersion containing seed particles 2 nm – 15 nm in diameter (Figure 3.3 a - inset) has a LSPR absorption band extending from 300 nm to 700 nm (Figure 3.3 a), with a maximum peak situated at ~ 450 ± 5 nm and a small ‘shoulder’ peak occurring at ~ 350 ± 5 nm. These peaks are characteristic for the formation of spherical Ag nanoparticles [37]. These seeds will be used to tune the growth of the nanoparticles and their optical properties (Figure 3.3 b - d). The approximately spherical shape of the seeds is confirmed through SEM (Figure 3.3 e - f), where the presence of small particles (~ 10 nm – 20 nm) with approximately spherical shape can be observed. The SEM images (Figure 3.3 f) also reveal the presence of clusters of seed particles (~ 50 nm – 200 nm).

The presence of clusters could suggest that possible aggregation might have occurred in the seed solution prior to particle growth. However, in this figure, the cluster formation might also be the result of the deposition technique used for SEM sample preparation. These facts reinforce the need of using the seed solutions immediately after
Figure 3.3: (a) UV-VIS absorption spectrum of a typical stable colloidal solution containing the Ag-Seeds. The particle size-distribution and a photograph of the solution are shown as an inset. The rich golden yellow colour can be seen. (b) Different colloidal solutions produced when the volume of AgNO$_3$ (0.001 M) is varied during the growth stage of the nanoparticle synthesis and (c) their respective plasmonic absorption bands. As the volume of AgNO$_3$ is varied the formation of two peaks within the LSPR absorption band of the colloidal dispersions becomes discernible. (d) The wavelength ($\lambda_{\text{max}}$) of the peak absorption as a function of the volume of AgNO$_3$ leads to two components (1) static – in red and (2) dynamic – black. (e - f) SEM images showing the variation in the size and in the morphology of the particles present within the seed colloidal dispersion prior to the growth stage.
preparation to avoid possible aggregation prior to particle growth.

3.3.2 Fine-Tuning of Colloidal Dispersions Optical Properties

Colloidal dispersions of different colours (Figure 3.3 b) were produced by altering the volume of AgNO₃ (0.001 M) added to the growth solution during the heterogeneous particle nucleation process. The colour of the dispersions shifts from yellow to red and from red to green as the volume of silver nitrate was varied from 0.4 ml – 20 ml (Figure 3.3 b). Variations within the colour of the colloidal dispersions were registered through the modifications in the LSPR absorption band (Figure 3 c). These deviations are directly related to the changes in the particle size-distribution [41,61,63]. Consequently, it is expected that the shift in peak absorption wavelength (λ_max) of the dispersions to larger wavelengths (Figure 3.3 c) reflects the changes in the particle size-distributions.

As the volume of AgNO₃ is increased, the formation of two peaks in the absorption spectra of the dispersions becomes prominent (Figure 3.3 c), indicating the presence of more than one species of nanoparticles. The absorption spectra contain two spectral components (1) a ‘static’ component that retains absorption characteristics similar to the seeds used to grow the nanoparticles (Figure 3.3 d - red circles), and (2) a ‘dynamic’ component which shifts from 450 nm to 650 nm as the amount of added AgNO₃ varies from 0.4 ml to 20 ml (Figure 3.3 d –black squares). Thereby, the particles absorption band can be tuned to cover the entire 350 nm – 800 nm spectral window (Figure 3.3 c). This wide absorption will be very beneficial to the solar applications as the amount of energy collected from the sun will be increased. The deconvolution of the spectra (Figure 3.4 a – f) revealed the presence of more spectral bands contributing to the overall spectrum, with some of the spectra containing as many as five individual contributions (Figure 3.4 e). These higher order modes are corresponding to larger particles present within the colloidal dispersions and/or to the existence of anisotropic morphologies [40,74]. The individual spectral contributions arising from higher
frequency modes within the colloidal dispersion need to be used to monitor these changes in particle size-distributions and morphologies.

Figure 3.4: Spectroscopic analysis of colloidal dispersions containing Ag nanoparticles produced by increasing the volume of AgNO$_3$ (0.001 M) in the growth stage of a two-step mediated synthesis methodology. Growth solution consisted of 1ml PVA (1% w/v), 1ml seed, 3ml TSC (0.1 M), 5ml Hydrazine (0.1 M) and X ml AgNO$_3$ (0.001 M) added in that particular order, with X being: (a) 0.5 ml, (b) 1 ml, (c) 1.5 ml, (d) 2.5 ml, (e) 8 ml and (f) 20 ml. The deconvoluted spectral components presented indicate the presence of one or more size-distributions of nanoparticles within a dispersion.

The changes seen in Figure 3.4 lead to the conclusion that the nanoparticles present in the dispersions have various size distributions and/or a variety of particle morphologies. The competition between these species within a dispersion can also lead to the observed variation in colour (Figure 3.3 b). The wide range of particle morphologies is also revealed by the SEM images (Figure 3.5 a – b and Figure 3.6), where the presence of cubes, prisms, spheres and other hexagonal and/or non-spherical geometries can be seen.
The origin of the individual absorption properties of each colloidal dispersion lies in the particle-size distribution and morphologies existing within it [75-76]. The scattering and the absorption of the light, as well as the characteristics of the locally enhanced electric field (EF) established through LSPR, are controlled by the shape and the size of the nanostructures [74-76]. By controlling the volume of silver nitrate employed during crystal growth, the size of the particle distribution can be tailored from 10 nm – 50 nm at low volumes (0.2 ml to 0.6 ml) to 5 nm – 110 nm at larger volumes (20 ml and above). The particle sizes reported (Figure 5 d) have been resolved through SEM size analysis carried out on different ‘coloured’ colloidal dispersions produced using the aforementioned synthesis route. This is correlated with the relationship between the volume of AgNO$_3$ and the PDI (Figure 3.5 c) of the colloidal dispersions formed. PDI, a measure of particle distribution broadness, increases rapidly within the 0.4 ml to 2.5 ml added range before tapering-off gradually towards 10 ml. At this critical point (2.5 ml), as the particle size-distribution undergoes a transition from an almost purely monomodal to bimodal distribution (Figure 3.4), the increasing population of larger particles begins to dominate the scattering characteristics of the signal registered in the photodetector of the DLS device. The formation of the secondary size distribution at this point can be attributed to a gradual decrease in the stability of the dispersion, as the interplay of the competing processes of agglomeration, coalescence and colloid stabilization start to become important.

Within a particle dispersion, the delicate balance between the long-range attractive (typically, London - van der Waals) forces, which act as the driving force behind the aggregation process, and the repulsive (e.g. steric) interactions will determine the long-term stability of a solution [31]. The aggregation tendency can be retarded by the inclusion of a surfactant or stabilizing agent. The surfactant, in this case PVA, forms
a protective layer around the particles allowing for the (steric) stabilization of the dispersions.

**Figure 3.5:** (a) Overall low-magnification (b) and zoomed SEM images of the Ag nanoparticles in the dispersions. The inset in (a) shows higher magnification of the various clusters in the nanofluid solutions. The scale bar in the inset is 200 nm. The wide range of particle morphologies and sizes present within the polydisperse colloidal dispersions formed can be observed. The presence of multiple different size distributions within a given sample can explain the changes in the spectral observations. (c) The deviations in the zeta potential (black squares) and PDI (red circles) of the colloidal dispersions produced as the volume of AgNO$_3$ (0.001 M) is changed in the growth process, and the (d) corresponding change in the particle size throughout this range: as determined through SEM.

The Zeta potential (Figure 3.5 c) represents a rapid and efficient method to determine and predict the stability of a particle dispersion [77]. The solutions formed in this study displayed a rapid increase in the stability, with the average zeta potential increasing from -22 mV (0.4 ml AgNO$_3$) to -50 mV (2.5 ml AgNO$_3$). The uncertainty on
the Zeta potential is indicative of the variation of particle stability within the collective particle ensemble. As particles can coalesce to form larger structures, their charge distribution will also be altered, affecting the electrostatic interactions within the particle dispersion. This will lead to a distribution of Zeta potential values whose extent will depend upon the internal structure of the fluid.

Figure 3.6: High resolution SEM images showing different nanoparticle morphologies present within the fabricated colloidal dispersions (a) spherical and non-spherical geometries (b) triangles (c) vertically stacked disks and (d) nano-aggregates containing the various morphologies presented.

Therefore, developing an understanding of the degree of control, granted through the many synthesis routes available, over the optical and morphological properties of the nanostructures employed in the development of nanofluids seems to be crucial. Gaining an insight into the impact of specific properties of the structures and their correlation with variations in the photo-thermal performance will allow revisions for design at the
synthesis stage. However, such studies are beyond the purpose of the present paper, but we note that these insights should be considered in future studies to maximize the cooperation between the base fluid and nanostructures to enhance the performances and the efficiencies of the photo-thermal energy systems.

3.3.3 Nanofluids and Their Optical Properties

Three different types of nanofluid (Table 3.1) were designed based on the variation in particle size and morphology of the dispersions previously mentioned. Each type has a distinctive absorption bandwidth and a characteristic particle size distribution, allowing for the effect of each of these parameters on the photo-thermal performance of the fluid to be evaluated. The prepared nanofluids are shown in Figure 3.7 a–c with most of the working fluids appearing transparent, but this effect changes at the higher concentrations (2% - 10% v/v) where the scattering due to the presence of nanoparticles start to become appreciable. The optical properties of the nanofluids were explored by UV-VIS spectroscopy (Figure 3.7 (i) – (iii)). The absorption within the 350 nm – 800 nm spectral window increased with increasing the particle concentration. In accordance with the Beer-Lambert law, the relationship between the absorbance and concentration of nanoparticle was found to be linear (see the insets in Figure 3.7 (i) – (iii):). An exception from this linear dependence can be noted at very low concentration (less than 1% v/v).

Table 3.1: The different types of nanofluid designed through varying the volume of silver nitrate (0.001 M) added during the growth stage of the synthesis employed, and their respective typical particle sizes, absorption range & particle distribution type

<table>
<thead>
<tr>
<th>Volume of AgNO₃ (0.001 M) required for particle growth (ml)</th>
<th>Particle Diameter (nm)</th>
<th>Particle distribution Type</th>
<th>Absorption Range (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type A 0.4</td>
<td>10 – 50</td>
<td>Single mode</td>
<td>300 - 500</td>
</tr>
<tr>
<td>Type B 4</td>
<td>10 – 85</td>
<td>Bi-modal</td>
<td>300 - 700</td>
</tr>
<tr>
<td>Type C 20</td>
<td>5 – 120</td>
<td>Bi-modal</td>
<td>300 - 750</td>
</tr>
</tbody>
</table>

Type A nanofluids (Figure 3.7 (i)) presented a more confined absorption window that is localized within the 350 nm – 450 nm region, while Type B (Figure 3.7 (ii)) and
Type C (Figure 3.7 (iii)) nanofluids absorb the light over a much larger (350 nm – 800 nm) spectral range. Nevertheless, differences in the absorption profiles of these two types of nanofluid can be observed. Type B nanofluids present a peak absorption at 550 nm owing to the presence of larger particles ~ 30 nm – 80 nm in diameter. Type C nanofluids have a similar level of absorbance at this wavelength but this type of nanofluid also has an LSPR mode occurring at 420 nm. This mode LSPR seems to correspond to the abundance of particles with sizes (as noticed through SEM and DLS) that are closely matching the size of the seed particles (2 nm – 20 nm) used in the nanofluids production. The absorption profile is produced due to the interaction of electromagnetic radiation with the silver nanostructures suspended within water. Therefore, the Ag nanoparticles can provide a more efficient method of capturing and converting the energy within the UV/VIS range i.e. in the region where water is a poor absorber.

3.3.4 Photo-thermal Performance

The photo-thermal performance of the nanofluids (Types A - C) were evaluated under the continuous irradiation provided by the solar simulator (Figure 3.2). As the working fluid is exposed to the constant irradiation, the temperature of the fluid increases (Figure 3.8 a, d and g). Even though water is transparent, most of the near-infrared radiation available is absorbed by the water molecules before being converted into thermal energy [87]. This enables the water to undergo a temperature variation of 12 °C over 90 minutes of exposure time. The silver nanofluids capability to capture and convert visible and ultraviolet light into thermal energy resulted in a much larger temperature variation within the initial few minutes of exposure as compared to pure water (Figure 3.8 a, d, and g). Thus, during this period the radiation that is transmitted through the glass collector is absorbed and scattered by the nanoparticles. The presence of nanoparticles decreases the optical path within the working fluid leading to the partial transmission of spectral radiation within the working volume [31-32,78]. The particles are forming a
collecting’ area within which the interactions between the chemical species present lead to a rapid transfer of heat to the residual working volume. The temperature of the working fluid reaches the value of 42 °C. Further increases in temperature start to become less pronounced, as reflected by the PTE values at the later stages of the experiment (Figure 3.8 b, c and h). This is owing to the gradual increase in the temperature difference between the working fluid and the surrounding environment, as the working fluid is under the constant electromagnetic flux.

Enhancement gained through the inclusion of PVA stabilized silver nanoparticles within the base fluid did not follow the typical relationships commonly reported in metal-based nanofluids [12-14,27]. Thus, typically, the presence of smaller particle size and an increasing particle concentration are reported to lead to significant enhancements in the photo-thermal performance of the working fluid [16]. Nonetheless, in the system studied, these trends were not observed. Moreover, for some of the nanofluids in this study, a rather non-linear variation of the PTE enhancement with exposure time was observed (Figure 3.8 c, f and i), with the rate of increase or decrease in photo-thermal performance varying from sample to sample. However, this might be explained by the fact that there is a capability of the particle size to overwrite the particle-concentration effect [12].

The type A fluids displayed the lowest increase in the PTE enhancement value among the three nanofluids, but, even in these conditions, it still exhibited a PTE larger by 10% - 19% than the PTE of the base fluid (Figure 3.8 c). The presence of a narrow absorption bandwidth of the particles (Figure 3.7 i) that captures less solar irradiance can explain their performance when compared with the other two types. The smaller size particles present within the fluid (~ 10 nm – 50 nm) should have led to better heat transfer kinetics for this type of nanofluid [16,79]. However, the low (~ 20 mV) zeta potential of
Figure 3.7: Photographs of different types of Ag based nanofluids (a – c) and their corresponding absorption spectra (i – iii). The peak intensity of each working fluid as a function of concentration is presented in the inset. Each inset including a linear fit, emphasizing the Beer-Lambert relationship between absorbance and concentration for each nanofluid considered.
colloidal dispersions produced using such small volumes of AgNO₃ (Figure 3.5 c) could lead to the onset of thermally aided aggregation during the exposure and this aggregation can hamper the thermal properties. The substantial increase in the fluid temperature, especially for certain concentrations (0.2%, 0.4% and 1% v/v), within the first 1000 s of exposure can suggest that these nanofluids could be tailored towards applications where their short-time enhanced performances (i.e. when exposed to such short bursts of high intensity spectral irradiance) are more suitable. In some instances, e.g. for certain nanoparticle concentrations, the photo-thermal performance of the base fluid was unfavourably affected by the inclusion of the nanoparticles (Figure 3.8 c – 0.5% v/v and 0.8% v/v) as this inclusion lead to a decrease of the fluids performance by as much as 10%.

Similar effects have been reported, typically, when employing surfactants or stabilizing agents. These molecules can effectively reduce the extensive hydrogen-bonding network found in water [37], this network being considered responsible for water increasing thermal conductivity with temperature [37]. Therefore, nanofluids containing a much larger concentration of type A particles (~10% v/v) represent a better candidate for solar thermal applications, which typically require lengthy exposure times and fluid lifetime cycles [10,80-81].

The type B nanofluids exhibited, depending upon the particle concentration, PTE values with 11% – 26% larger than the PTE of the base fluid as reflected by the PTE enhancement (Figure 3.8 f). However, the rate of variation in the PTE with exposure time differ across the nanoparticle concentration range investigated. Thus, some nanofluids are displaying a more steeply decline in their photo-thermal performance than others. A similar behavior as for type A nanofluids was observed, with some of the nanofluids (0.4% and 0.8%) initially performing well within the first 2000 s of exposure. During the later stages of the exposure time, and as the temperature of the fluid increases (Figure 3.8
e), their photo-thermal performance was overcome by nanofluids containing much smaller concentrations of particles (0.05% v/v).

The difference between the two types of fluid can be lying in the prevalence of the high concentrations of type A nanoparticles in providing the largest enhancement reported, while the lowest concentration of Type B nanoparticles investigated provided the best compromise between thermal performance and photo-stability. Another noticeable difference between the two types of nanofluid is the emergence of an enhancement in the photo-thermal efficiency of type B fluids when compared with type A. This is valid irrespective of the concentration of particles present, exception being the 0.1% v/v (Figure 3.8 e) sample. The improvement in performance is likely to be due to the interaction of the type B nanoparticles with a much larger band of frequencies. This is due to the presence of a bi-modal size-distribution (Figure 3.4) as well as to the different particle morphologies present within each size distribution (Figure 3.5 a and b and figure 3.6).

The best performances were obtained with the type C nanofluids, that showed an increase in PTE of up to 32% when compared with the base fluid (see PTE enhancement in Figure 3.8 i). All the nanofluids within this category exhibited an enhancement in the performance when compared with the base fluid irrespective of the concentration of particles present. The large ensemble of particle sizes present within these fluids (Figure 3.4, 3.10 and 3.11), enables a much stronger coupling between the electric fields within the incident irradiance and the oscillating waves of electrons established on the dispersed structures surface (Figure 3.7 (iii)). Similarly, with the type B nanofluids the dominance of low concentration (0.05% v/v) working fluids in providing the best enhancement in the photo-thermal performance was once again observed.
Figure 3.8: Temperature variation (instantaneous – initial temperature) within the working fluid for three types of silver nanofluid: (a) Type A (d) Type B & (g) Type C. The photo-thermal conversion efficiency (PTE) as a function of the working fluid temperature (b, c, h) and the corresponding enhancement in the PTE at various time during the 90-minute exposure period (c, f, i).
The different modes of particle sizes present within the collective network of particles, are possibly responsible for the dominating characteristics displayed by type C nanofluids [82]. The larger particles in the collective ensemble allow the higher order LSPR modes to be involved in the particle-particle interactions within the nanofluid [31,50]. Thus, these can generate local enhancements in electromagnetic fields to values that are many orders of magnitude above those achievable through monomodal particle size-distributions [50-52]. The capability of different particle morphologies to facilitate in the formation of a more tightly or loosely packed particle network chain, during the particle agglomeration process, must be also considered. As more particles, which can be effectively packed within the extended particle networks, are formed the higher the thermal conductivity a nanofluid can exhibit [56-57,60,82]. In fact, the thermal conductivity measurements performed for these nanofluids show that the thermal conductivity ratio ($\kappa_{NF}/\kappa_{W}$) has a similar non-linear behaviour as the PTE as the concentration increases - see Figure 3.9.

The results in Figure 3.9 highlight a strong correlation between the behaviour of the photo-thermal conversion efficiency (PTE) and the ratio of the thermal conductivity ($\kappa_{NF}/\kappa_{W}$) as the concentration of the nanoparticles is increased. However, the dependencies on the concentration exhibited by both parameters is non-linear. These dependencies are expected to be related with the ability of the nanofluids (and of the nanostructure within) to promote or suppress heat transfer. As the concentration of nanoparticles increases, the subtle differences in their molecular structure are becoming more concentration dependent. This can make some of the possible interaction pathways more or less energetically favourable, depending upon the molecular re-arrangement within the fluid. The changes in the structural conformation of the nanofluid investigated, in response to changes within its local environment (such as particle concentration), require further investigations. These investigations should be performed from both experimental
Figure 3.9: The photo-thermal conversion efficiency (PTE) after 1000 seconds (as presented in Figure 3.8) and the thermal conductivity ratio ($\kappa_{\text{NF}} / \kappa_{\text{W}}$) as influenced by the nanoparticle concentration present in the various working nanofluid.

and theoretical perspective in order to reveal the mechanism underpinning the non-linear concentration dependence of the particles photo-thermal properties. Additionally, the interactions between neighbouring particles can destabilize the nanofluid via aggregation as the attractive forces between nanoparticles lead to the formation of clusters, islands and even fractal networks in an attempt to minimize the free energy within the nanofluid [83-84]. However, while establishing the role of these interactions and explaining the molecular mechanism behind these effects should be investigated, such investigations are beyond the purpose of the present study.

The heat transfer mechanics of a nanofluid can be affected by a number of interactions possible within it: (1) the Brownian motion of particles within the liquid,
resulting in the formation of a ‘convection like’ effect. In this case the particles can collide during their random path within the fluid influencing the thermal properties; (2) the interaction of particles with molecules of the base fluid; (3) layering of the liquid at the liquid/nanoparticle interface altering the thermal boundary resistance between the particles and the base fluid; (4) the highly localized near field radiation created through the LSPR phenomena and (5) the formation of loose particle chains or particle networks within the fluid as aggregation begins to occur [15-16,43]. Theoretical studies aimed at removing the veil on the impact of nanoparticle properties (composition, shape and size), interaction pathways and environmental factors (temperature and pH) on the heat transfer mechanisms within nanofluids suggest that the presence of aggregates can be primarily responsible for some of the high thermal conductivities of nanofluids [30-31,48,73,78,85,89].

The more particles are present the more by-products of the aggregation process are observed within the nanofluids. This is indicated by the emergence of more modes (blue star in Figure 3.10) as well as a larger range of particle sizes post exposure to the solar simulator (Figure 3.11). This confirms that the individual spectral contributions resolved within the colloids plasmon absorption band (Figure 3.4) are corresponding to the presence of multiple particle size distributions within it. The best performing nanofluids, i.e. type C nanofluids, display an array of size-distributions, whose peak size lies in close proximity to each other (Figure 3.10 e). The other two types of nanofluid, A and B, contain mostly non-overlapping size distributions (see the presence of the error bars overlap in Figure 3.10). This can limit the interactions between similar sized particles within the numerous distributions present within nanofluids and, consequently, their photo-thermal properties. The origin of the effectiveness of the heat transfer process, across all three nanofluids, seems to lie in the upper limit imposed on the maximum size of the particles, which are able to produce the best enhancement in the photo-thermal
Figure 3.10: The post-exposure particle size-distributions (black squares, red triangles, green circles and blue stars) present within the three different types of silver nanofluid (a) type A (c) type B and (e) type C as a function of the particle concentration within the fluid. The error bars represent the full width half maximum of each individual size distribution within the collective particle ensemble. The error bars are also an indication of the presence of overlapping between the various particle size-distributions. The percentage (%) contribution from each individual component to the overall size-distribution for each type of fluid (b) type A (d) type B and (f) type C is also presented.
performance of the base fluid [86]. The best performing concentrations (5% v/v type A, 0.05% v/v type B and 0.05% v/v type C) contained particles no more than 150 nm in diameter (Figure 3.10 and 3.11). Once particles, whose size exceeds this threshold, become involved in the heat transfer process their physical properties appear to dominate the thermo-physical characteristics of the nanofluid, resulting in a decrease in the nanofluids photothermal performance.

Examples of the individual particle size distributions present in solutions whose concentrations resulted in ‘poor’ and ‘good’ photo-thermal performance is provided in Figure 3.11. This confirms that the presence of particles with sizes no greater than 150 nm in the best performing nanofluids. The highest performance from the nanofluids is obtained when a degree of overlap exists between the particle size-distributions (Figure 3.10 red triangles/green circles). The variation in the particle size-distribution seen in the best performing nanofluids can allow for a better packing order of the nanoparticles, which, along with the particle size, has a significant influence on the enhancement of the thermal conductivity [78]. The deterioration in the performance of the remaining fluids is likely to be the result of the emergence of additional modes (Figure 3.10 - shown in blue stars and in Figure 3.11) corresponding to particle sizes above 150 nm in diameter. Thus, the delicate balance of the competitive processes between the multiple modes already present within the nanofluid, is deteriorated as the aggregation process accelerates. However, further studies should be performed in order to understand the underlying molecular mechanism that stands behind the changes in the photo-thermal properties of these nanofluids. Such studies should involve both experimental and theoretical investigations and should contain a well-defined mixture ratio of nanoparticle with various sizes, morphology and concentration.
Figure 3.11: Typical individual particle size-distributions present within nanofluids classified as ‘good’ and ‘bad’ performers in terms of their photo-thermal conversion efficiency: (a) 5 % type A (b) 0.8 % type A (c) 0.05 % type B (d) 2 % type B (e) 0.05 % type C (f) 2 % type C.
3.4 Conclusion

Nanofluids can become a suitable and low-cost alternative to improve the efficiencies of the heat transfer fluid employed within solar-thermal and photovoltaic-thermal collection systems. Here, nanofluids containing multimodal silver nanostructures of a rich morphology were synthesized and their thermo-optical properties were studied. The synthesis method presented allows the bandwidth of energy captured by the structures to be tuned, through controlling the concentration of silver nitrite used during the heterogeneous growth of the nanoparticles. This synthesis procedure is simple, relatively low-cost and it can be easily scaled up to be used in real-world solar thermal applications. Different variations of silver nanofluids have been designed. Thus, different types of particle size-distribution have been incorporated in the base fluid and their impact on the thermo-optical properties of the resulting nanofluid was explored. Low concentrations (0.05% - 0.1% v/v) provided the best improvement in the photo-thermal conversion efficiency, with 5% - 32% enhancements in the PTE being achieved. The variations emerging in the photo-thermal conversion efficiency, can be correlated to changes in the individual populations of the numerous size-distributions contained within the internal structure of the nanofluid. The existence of an upper threshold in the particle size was observed to limit the enhancement in thermal properties, a strong degree of correlation between the individual size-distributions and increased performance being noted. The different particle size modes present show that using one (and/or narrow) particle size-distribution does not represent the best choice in controlling and optimizing the heat transfer properties of a nanofluid. Therefore, more work is required to understand the process through which a wide distribution of particle sizes enhances the thermal properties, as this could allow a faster implementation of the nanofluids into more solar applications in the future.
3.5 References


Suspensions in Unsteady Thermal Convection. Sci Rep 6, 39446. https://doi.org/10.1038/srep39446


Chapter 4

LDS: A Bottom Up Approach Toward the Development of Highly Luminescent Organic Alternatives

4.1 Introduction

In the pursuit of highly efficient ‘emitters’, various material structures have been explored in efforts to identify the fundamental molecular building block(s) which will facilitate the expansion of PV’s energy harvesting potential. Organic dyes [1-7], quantum dots [2, 5, 6, 8-10], metal coordination complexes [5, 6, 11-15] and rare-earth ion doped phosphors [5, 6, 11-15] encapsulated within a diverse set of polymeric, ceramic and composite host materials have shown great promise in their capability to deliver enhanced spectral responsivities, when paired with commercial and non-commercial PV technologies [5, 6]. These structures exhibit some of the idealised physical and optical characteristics required for spectral conversion applications, which include: (1) a high absorption coefficient, (2) a relatively large absorption bandwidth, (3) an emission spectrum closely matching the peak responsivity of the PV material, (4) a high luminescent quantum yield (LQY), (5) prolonged photostability, (6) a cost effective synthesis route, and (7) ease of handling and processing for scalability [5, 6]. Even with this ever-expansive catalogue of material candidates, the merits identified throughout the literature are often overshadowed by an inherent lack of addressing the limitations or weaknesses of each candidate [5, 6]. This is accompanied by an additional lack of diversity in the commercially available luminescent materials, which further restricts the analysis and discussion to only a handful of key molecules. Hence there is an ever present need to revisit the fundamental material aspects and continue in the pursuit of developing and refining the material selection criterion for spectral conversion applications [5, 6]. As the number of synthetic strategies continues to grow, offering ever more intricate,
adaptable and scalable molecular frameworks, the promise afforded by these alternative structures warrants exploration.

One such alluring alternative is phenanthroline based luminophore’s whose molecular structure affords an abundance of desirable chemical and physical attributes for spectral conversion applications [16, 17]. The considerable photostability exhibited by 1,10-phenanthroline even prior to functionalisation [11, 12, 14, 15, 18] could help address the longstanding limitation of spectral conversion devices, namely, the short operational lifetime of the luminophore under the continuous exposure to irradiation. Combining this with phenanthroline’s flexibility to be integrated with a host of already well-developed and renowned emissive structures including quantum dots and transition metal elements (Ag, Au, Eu) makes such a synthetic strategy much more attractive. Furthermore, discovering newly conceived structural conformations of phenanthroline and exploiting their capability to tune the chemical structure’s photophysical and thermophysical properties towards a specific energy harvesting application remains paramount [16, 17]. Although most of the literature has focused on supporting the inclusion of numerous phenanthroline derivatives into ever more complex and intricate metal coordination complexes, the need to further develop the library of polydentate ligands used to synthetically adapt the complexes overall chemical and physical behaviour remains ever present [16, 17]. In this premise, the precedent is to identify suitable molecular structures which can act both as a polydentate ligand used to sensitise a metal centre during the formation of a metal complex and simultaneously exhibit significant standalone luminescence. The iterative refining of the organic structure of phenanthroline using an efficient synthetic strategy in terms of yield, functional group variability, time and cost in order to produce highly luminescent, photostable and commercially viable standalone luminophore(s), holds significant potential. Such an approach has not been fully explored to date and could potentially offer new organic
phenanthroline based luminophores and highly efficient coordination complexes for LDS applications.

Herein, we report the use of a novel synthetic strategy used to systematically substitute the core structure of 1,10-phenanthroline with various amine, phenyl and other heteroaromatic moieties to form a series of known and novel imidazo[4,5-f][1,10]phenanthroline fluorescent ligands. The role played by the substituted moiety in enhancing or curtailing the photophysical properties of the newly established set of fluorophores which all contain the core 1,10-phenthroline structure fused to an imidazole ring (27 in total) was explored thorough a comprehensive evaluation of the structural-activity relationship, exhibited by the molecular structures. Each iteration of the molecule was evaluated for its optical properties in conjunction with its suitability for photovoltaic (LDS) and photothermal (STC’s, PVT and SBS) applications. The set of fluorophores, whose material properties corresponded to the criterion for LDS, were selected for additional complementary optical characterisation, including the determination of their LQY. The leading candidates identified were subsequently embedded within one of the most widely recognized host materials, poly-methyl-methacrylate (PMMA), and their optical behaviour within the relatively thin (10 µm) encapsulating framework was considered and optimised. The optimal loading concentration was identified for each material, and this optimal loading was deployed within LDS-devices, which were based upon the most commercially mature mc-Si technology. The impact of the fluorescent material’s optical properties on the conversion performance of the underlying Si architecture was established through determination of the devices I-V response curves. Finally, the photostability of the principle structures was examined by subjecting them to accelerated artificial exposure conditions and monitoring their deterioration spectroscopically. This study serves as a foundation, upon which further refinements and
modifications can yield even more efficient structures and conceivably more pronounced enhancements in PV efficiency.

4.2 Methods and Materials
4.2.1 Materials

To modulate the relationship between radiative and non-radiative transitions, a series of distinct chemical moieties were substituted onto the phenanthroline ring shown in figure 4.1, with each substitution’s role in enhancing or curtailing the radiative emission process considered. The molecular architectures explored, as well as their respective formula, nomenclature, molecular weight and the abbreviation used to identify it, are presented in table 4.1.

![Molecular Structure](image)

**Figure 4.1:** The molecular structure underpinning the range of unique luminophores explored, where each iteration had a distinct chemical substitution at R.

4.2.2 Solubility

The active role played by the solvent cage surrounding a fluorescent molecule, in facilitating a variety of different quenching mechanisms is well known [19]. Hence, to enhance the accuracy and reliability of the measurements performed throughout the study, it was essential that the solvent variability across the large range of potential fluorescent candidates be reduced as much as possible in order to avoid solvatochromic effects for the various different structures tested. This makes the key insights gained into the role played by the molecules chemical and physical structure in aiding and enhancing the
Table 4.1: Structural iterations of the [1,10]phenanthroline molecular scaffold and their corresponding abbreviation, chemical formula, chemical name and molecular weight. Noted exclusions from this table are the P122, P135, P136 and P138 structures, whose initial spectroscopic details are presented but their structural features require further exploration before the full results can be presented.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Chemical formula</th>
<th>Name</th>
<th>Molecular weight (g mol⁻¹)</th>
</tr>
</thead>
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<tr>
<td>Phen</td>
<td>C₁₂H₁₈N₂</td>
<td>[1,10]phenanthroline</td>
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<tr>
<td>Phenend</td>
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<td>[1,10]phenanthroline-5,6-dione</td>
<td>210.19</td>
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<td>P7</td>
<td>C₂₂H₂₄N₂O₂</td>
<td>6-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)-2H-chromen-2-one</td>
<td>364.35</td>
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<tr>
<td>P121</td>
<td>C₂₅H₂₂N₂O₆</td>
<td>(2S,3R,4R,5S,6R)-2-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)phenoxo)-6-(hydroxyethyl)tetrahydrafuran-2H-pyran-3,4,5-triol</td>
<td>474.47</td>
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<td>P125</td>
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<tr>
<td>P126</td>
<td>C₁₀H₁₂N₄</td>
<td>2-phenyl-1H-imidazo[4,5-f][1,10]phenanthroline</td>
<td>296.33</td>
</tr>
<tr>
<td>P133</td>
<td>C₂₀H₂₀N₂O</td>
<td>2-(4-methoxyphenyl)-1H-imidazo[4,5-f][1,10]phenanthroline</td>
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</tr>
<tr>
<td>P166</td>
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<td>C₁₀H₈N₂O</td>
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<td>C₂₃H₁₈FeN₄</td>
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<td>C₂₅H₁₆N₄</td>
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<td>P183</td>
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<td>1,4-bis(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)benzene</td>
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<td>C₁₀H₁₂N₂O₂</td>
<td>4-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)benzene-1,2-diol</td>
<td>328.31</td>
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<td>P245</td>
<td>C₂₀H₁₂N₂O₂</td>
<td>4-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)benzoic acid</td>
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<td>341.31</td>
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<td>P273</td>
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<td>4-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)aniline</td>
<td>311.35</td>
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<td>P282</td>
<td>C₂₀H₁₀N₄</td>
<td>2-(pyren-1-yl)-1H-imidazo[4,5-f][1,10]phenanthroline</td>
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<td>P284</td>
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<td>C₁₀H₁₁FN₄</td>
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<td>2-(3,5-bis(trifluoromethyl)phenyl)-1H-imidazo[4,5-f][1,10]phenanthroline</td>
<td>432.33</td>
</tr>
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</table>
chemical and physical structure in aiding and enhancing the radiative emission process more consistent when limited to a small range of solvents.

The solubility of each ligand was determined in a series of solvents typically utilised in the preparation and fabrication of luminescent down-shifting (LDS) and plasmon-enhanced luminescent down-shifting devices (PLDS). These included Ethanol, Methanol, Dimethylformamide (DMF), Dichloromethane (DCM), Dimethyl sulfoxide (DMSO), Acetonitrile, Toluene, Chloroform, Acetone as well as ultrapure water ($\rho = 18.2 \text{ M}\Omega \text{ cm}^{-1}$). For a typical trial, 1 mg of the solid was placed in 2 ml of the solvent under consideration and the solution shaken vigorously with a Vortex mixer under standard temperature and pressure conditions. The resulting solution was visually examined and classified under one of the following categories; solution, suspension or non-soluble. Partial solubility or fine suspensions were also considered as they offered the possibility of enhancing the solubility of the compound under elevated temperatures [20], which are frequently encountered the polymer processing or high efficiency heat-transfer applications.

4.2.3 Spectroscopic characterisation

Throughout the study, a bottom-up approach was adopted, starting from a wide basis of material candidates and reducing the scope of the investigation to only the highest quality materials identified at each stage of the study. Evaluating each compound under the same concentration and measurement parameters (slit width, optical path length, PMT acceleration voltage etc.) enabled an inter-comparison to be performed, between the absorption and emission capabilities of each compound. Each material was evaluated under the following criteria;

- Absorption bandwidth
- Absorption efficiency
- Emission bandwidth
- Emission efficiency
- Degree of spectral overlap between absorption and emission bands
- Further functionalization possibilities
- Novelty

The absorption and emission efficiency were quantified through integrated spectroscopy [21, 22]. From these 27 different ligands the top 10 candidates were further investigated in terms of their luminescent quantum yield (LQY) in solution.

4.2.3.1 Absorption and fluorescence inter-comparison

Solutions containing each compound at a concentration of $1.25 \times 10^{-4}$ M - $1.25 \times 10^{-6}$ M were prepared in DMSO, and their absorption spectra determined using a Perkin Elmer Lambda 900 UV/VIS/NIR spectrometer using 10 mm path-length quartz cuvettes. DMSO was selected as the solvent based on its excellent solvent properties ascertained across the entire library of ligands catalogued. The subtle differences in the absorption spectrum of a ligand were monitored as the concentration of the ligand was varied, to identify any occurrences of aggregation (a common feature among heteroaromatic molecules [23-29]). Subsequently the fluorescence spectra of each compound were resolved using a Perkin Elmer LS-55 spectrophotometer to capture the light emitted at a $90^\circ$ orientation to the excitation beam path, thus mitigating the impact of the excitation source on the spectra recorded. Given the conjugated nature of the structures within the library of materials evaluated, their emission spectra were studied under different excitation wavelengths (285 nm – 425 nm); namely those corresponding to the $\lambda$ maximum absorption peaks for the numerous chromophores evident within each molecule’s absorption spectra.
4.2.3.2 Quantum yield measurement

The luminescent quantum yield (LQY) of each translucent liquid sample (ligand immersed in DMSO) was determined using the relative method (full protocol outlined in section 2.2.3.1). A combination of independent fluorescent standards including quinine sulphate, harmane and harmine were employed to ensure the methods viability and validity across the series of ligands investigated. The series of standards were selected due to their well-established absorption range and photostability in their respective solvents; 0.1 M H₂SO₄ (quinine sulphate) and toluene (harmane and hamine) [30-32]. This option was selected to minimise the uncertainties that can arise, when relying solely on the optical properties of one fluorescent standard to compute the LQY of an unknown material [30-33]. The absorption and corresponding fluorescent spectra of the leading 10 candidates identified from the initial library of ligands were recorded using the combination of a Perkin Elmer Lambda 900 UV/VIS/NIR spectrometer and a Perkin Elmer LS-55 luminescent spectrometer. Using 10 mm path-length quartz cuvettes, a stock solution of known molarity (~1x10⁻⁴ M) was serially diluted until the absorption at the excitation wavelength selected (380 nm) was ~ 0.1 A.U. Once this limit had been achieved the sample was immediately transferred into the LS-55 luminescent spectrometer and its fluorescence spectra recorded at the known concentration. The sample was consecutively further diluted, and its absorption and emission spectra recorded after each dilution under the same measurement parameters and experimental conditions (temperature and relative humidity). This process was repeated until multiple distinct absorption & emission spectra had been attained, allowing the fluorophore’s characteristic correlation between its (1) absorbance at the excitation wavelength and (2) accompanying integrated emission intensity, has been obtained. All measurements were repeated independently in triplicate [30-32].
4.2.4 Fabrication of LDS layers and devices

LDS layers were prepared on glass substrates of size 25 x 25 x 0.01 mm (L x W x H) through the multi-stage protocol developed and outlined in figure 4.2. For a typical preparation procedure, a 50 wt% Plexit 55 Röhm (Carl Roth Ltd) solution was prepared with DMSO. DMSO was ideal, due to its complementary compatibility across the wide range of fluorophore candidates adopted and studied within the PMMA matrix. The resulting polymer solution was vigorously agitated (figure 4.2 i) via magnetic stirring at 500 RPM – 800 RPM for 60 minutes, to ensure the solvent was homogeneously dispersed throughout the resin and that no trapped air remained prior to the addition of the fluorophore. From a stock solution of known molarity (the fluorophore under evaluation dissolved in pure high grade DMSO), the volume necessary to attain the required loading concentration was added to 1 ml of the polymer solution in a separate PTFE beaker (figure 4.2 ii). A loading concentration range of ~0.008 wt% - 3 wt% (a wt% to molarity conversion for each material is included in the appendix) was employed for each one of the highest performing candidates identified in the inter-comparative study (section 4.2.2.1). The concentration of the stock solution was adapted to ensure that the volume utilised was less than 80 μL, minimising any potential impact on the resulting layers viscosity and corresponding thickness.

The fluorophore doped polymer solution was subsequently agitated via magnetic stirring at 400 RPM for five minutes (figure 4.2 ii) in order to ensure a uniform distribution of the fluorescent material throughout. Consecutively, using a pipette (or in some cases a syringe), 1 ml of the solution was transferred onto a thoroughly cleaned glass substrate (figure 4.2 iii). The substrate was housed within a G3-P8 Spin Coater
(Speciality Coating Systems) and spun at 4000 RPM for 180 s, allowing 10 s for the spin-up and spin-down processes.

**Figure 4.2:** The protocol developed for the production of good quality, highly fluorescent LDS layers for solar applications, including all the individual stages involved: (i) PMMA polymer preparation using the solvent of choice – DMSO (ii) Dispersal of the specific amount of the fluorophore stock solution (fluorophore in DMSO), required to yield the wt-% loading, desired within the PMMA resin (iii) Dispersal of 1 ml of the fluorophore doped PMMA resin, directly onto a thoroughly cleaned glass substrate (iv) Spin coating applied using the optimal spin coating parameters identified during trials (4000 RPM for 180 s with a 10 s dwell time either side of the primary stage) (v) the resulting LDS layers (2.5 cm x 2.5cm x 10 μm), which require extensive annealing (vi) and further drying (vii) to remove any localised stress introduced through the evaporation of the solvent during the spin process

Once completed, the substrate was carefully removed from the spin coater and placed directly onto a preheated hot plate at temperature 50 °C to begin the annealing process. This stage proved crucial as the low volatility of the DMSO ensured that even after spinning at such high spin-speeds, a large amount of residual solvent remained. Consequently, a marked reduction in the optical clarity of the films directly after spinning had occurred. This initial annealing stage helped to remove the inherent stresses built-up
in the layer throughout the spinning process [34-36] and improve its optical clarity. The accelerated drying and annealing capabilities offered within a low-pressure environment [34-36] were employed throughout the final stage of the preparation (figure 4.2 vii) whereby the layer was placed within a vacuum oven set to a pressure of 100 mbar at 25 °C for a total of 24 hours. Thereby, ensuring that any remaining internal stress or residual solvent was minimalised if not totally removed.

4.2.5 LDS characterisation

To investigate dispersion of the fluorophore throughout the PMMA matrix a Perkin Elmer Lambda 900 UV/VIS/NIR spectrometer was used adopting an undoped ‘blank’ replica layer as the reference. This allowed for any subtle deviations, owing to the onset of aggregation or other chemical changes induced through the high spin speeds and subsequent heat treatments to be monitored. Additionally, any divergence between the solid structure’s spectra, and their corresponding molecular spectral counterparts could be observed. The emission spectra of the solid layers were measured using an integrating sphere in conjunction with a solar simulator (see section 2.2.2.2 for full description) to deliver a simulated irradiance through a narrow band-pass filter (380 ± 10 nm) and excite the samples within their optimal absorption window. The accumulated spectrum, containing elements of scattering, excitation, reflection and emission was coupled into an AvaSpec-2048 spectrometer. A spectral correction was applied to transform the emission spectra into natural units of spectral irradiance, from which the sample’s absolute quantum yield (PLQY) could be determined. As the loading concentration for each molecule was increased, the emission spectra and the respective PLQY gives insight into the development and progression of fluorescent quenching. The corrected emission spectra also facilitated the identification of the optimal loading concentration, which was deemed to be the concentration that maximised the number of emitted photons.
4.2.6 LDS device performance

Small form factor (2.5 cm x 2.5 cm) aluminium back surface field (AL-BSF) monocrystalline silicon solar cells (Big Sun Community Solar, Texas, USA) were used, to examine the influence of each LDS iteration on the electrical conversion performance of the PV cell. The devices were fabricated using an identical protocol to that outlined in section 4.2.3, with an additional set of thicker (thickness ~ 300 μm) layers cast using the same optimal loading concentrations identified during the optical characterisation stage. The thicker layers, cast by the simple drop-casting technique, offered an insight into the impact of the optical-thickness of the retrofitted structures on the dynamics of the conversion process. The electrical performance of the modified devices was determined through their current-voltage (I-V, see section 2.9.2 for full description of methodology) response curve. The enhancement, offered by the optical and physical properties of the distinct molecular structures, was determined by comparing the performance of the down-shifting devices with the performance of a non-doped replica. This allowed for any variation in the device’s electrical performance, to be directly correlated with structural alterations made to the phenanthroline ring.

4.2.7 LDS Photodegradation Study

To pinpoint the location and climate most feasible for integrating the proposed LDS devices, the photo-stability trials were divided up into two categories: (1) simulating a moderate European temperate climate – see the countries highlighted in green in figure 2.14 c; and (2) those simulating harsher more tropical climate conditions – see the countries highlighted in red in figure 2.14 c. In the temperate climate zones (Ireland, England, Germany and other European countries) an irradiance of 0.30 - 0.35 W m$^{-2}$ nm$^{-1}$ at 340 nm is considered representative [37], whereas in the extreme tropical climates of Florida, sub-Saharan Africa or northern Australia an irradiance above 0.45 W m$^{-2}$ nm$^{-1}$ at 340 nm is common for most of the year and throughout the entire duration of the daily
light cycle [37]. The irradiance values lying within the identified range corresponding to each specific climate classification were taken to be the extreme case. This corresponded to an irradiance of 0.30 W m\(^{-2}\) nm\(^{-1}\) for temperate climates and an irradiance of 0.50 W m\(^{-2}\) nm\(^{-1}\) for tropical climates at 340 nm, respectively.

LDS layers utilised throughout the study were fabricated under the protocol outlined in section 4.2.3 and embodied a wide range of loading concentrations (~0.008 wt% - 3 wt% - see the appendix for loading concentrations in their respective molarities) to see if the degradation effects were indeed concentration independent. The layers were subjected to the irradiance conditions outlined in conjunction with temperature range: 15 °C – 25 °C for temperate climates and 25 °C – 40 °C for the tropical climates. Regular spectroscopic evaluation of the layer’s absorption spectra was carried out using the Perkin Elmer Lambda 900, until the resulting absorption spectra had diminished completely, or the test had reached a considerable period of exposure (~100 hrs). Given that the intensity across the XE-3 sample tray might vary [38, 39], the samples position on the tray was continuously rotated.

4.3 Results and Discussions
4.3.1 Ligand Inter-Evaluation: Selecting The Highest Performing Candidates

The push-pull dynamics of the transfer of charge within Phen was carefully controlled through modifications in its molecular architecture at the 5,6- position (figure 1.8 a) which drove a divergence between the aromatic scaffolding’s characteristic closely overlapped molecular orbitals. These changes in the electronic configuration were initiated using the electron-rich five-membered heteroaromatic imidazole, whose nitrogen atoms provided the protonation point for the substitution reactions, and thereby allowed the various functional moieties to be included along the conjugation pathway. The chromophoric nature of each iteration of the ligand, i.e. the energy separation between the highest occupied molecular orbital (HOMO) and the lowest unoccupied
molecular orbital (LUMO) originated through the incorporation of heterocycles which were excessive (‘donors’) or deficient (‘acceptors’) in electron density. Within such a system the electron excessive/deficient heterocycles behaved as secondary donors/acceptors, complimenting or diminishing the electronic characteristics of the pristine framework, once they had been interconnected alongside the electron deficient Phen heterocycle. The impact of each substituent (see table 4.1) on the electronic absorption and the corresponding fluorescent emission spectrum, of the series of newly developed π-conjugated heteroaromatic Phen derivates are provided in figures 4.3 (a – l), 4.4 (a – l) and 4.5 (a – e).

The absorption band across all the ligands explored exhibited a confinement to the ultraviolet spectral region (250 nm – 400 nm), which is not only the targeted spectral window for LDS applications but remains the minimal requirement for highly efficient approaches towards effective ‘down-shifting’ [5, 6]. Although the position of the absorption band remained strongly influenced by the overall structure of the substituted heterocycle, a signature absorption contribution corresponding to the imidazo[4,5-f][1,10]phenanthroline core remained strikingly evident across the family of ligands, especially within the 250 nm – 300 nm window where Phen (figure 4.3 a) is classically active [16, 17]. The higher wavelength (300 nm – 400 nm) components evident in the absorption spectra originated from the individual contributions arising from the substituent chromophore (anthracene, coumarins, phenyls, and/or other benzene derivatives), incorporated onto the Phen ring. In addition, further augmentation of the molecule’s planarity and conjugation pathway through the substituted heterocyclic moiety aided in the extension of the absorption tail into the visible region; specifically P166 (figure 4.3 l), P183 (figure 4.4 d), P185 (figure 4.4 e), P205 (figure 4.4 i), P254 (figure 4.4 l) and P282 (figure 4.5 b). Although the structure of P122 (figure 4.3 e), P135 (figure 4.3 i), P136 (figure 4.3 j) and P138 (figure 4.3 k) have been excluded from figure
4.3, they can for deliberation be considered alkylated versions of P205, P282 and P183. The addition of an alkyl substituent serves to further stabilise the phenanthroline ring, through electron donating inductive effects [16, 17, 40, 41]. This translated either into an immense enhancement in the strength of the absorption contribution arising from the core of the ligand (figure 4.3 i, j, k) or an even greater extension of the absorption tail into the visible region (figure 4.3 e). However, although these alkylated derivatives are presented here for spectroscopic comparison, they will remain the subject of a 2nd phase trial in the future, which will build upon the structures, insights and performances gathered from this initial phase of the study. A complementary overview of the absorption contribution across the family of ligands, partitioned into distinct spectral windows including UV-A (315 nm – 400 nm), UV-B (280 nm – 315 nm), UV-C (200 nm - 280 nm) and the visible region (400 nm and above) is presented in figure 4.5 f for convenient comparison.

An ideal fluorophore for LDS applications must not only capture the energy from within the target spectral window where the energy is inefficiently harvested by the PV technology, but re-radiate the energy across a wavelength range where the PV material exhibits a much greater spectral response. This wavelength range is highly dependent upon the material characteristics of the technology. Thus, developing technologies such as dye synthesized solar cells exhibit peak responsivities ~600 nm [42], while older more developed technologies such as Si based architectures have peak conversion performances close to 1000 nm [43-45]. Across the library of candidates catalogued (figure 4.3 a – l, figure 4.4 a - l, figure 4.5 a - e) the spectral position of the emission band as well as the intensity of the emission were influenced by the overarching structures planarity, rigidity, conjugation and the presence or absence of certain known fluorescent quenchers. Although most of the structural iterations emitted close to the 450 nm – 500 nm range, the intensity of the emission was heavily modified through the inclusion of well-known fluorescent quenchers including aniline (P273, figure 4.5 a), (P254, figure 4.4 l),
Figure 4.3: (a - l) Absorption (cyan) and emission (wine) spectra of the fluorescent candidates (phen – P166) at a fixed concentration of $1.25 \times 10^{-6}$ M in pristine DMSO. The spectra were acquired using the same measurement parameters (slit width, optical path length, PMT amplification, integration time etc.) and are corrected for the spectral response of the detector. The candidates’ molecular structure as well as its assigned abbreviation is also provided in the inset. The structure of P122, P135, P136 and P138 have been excluded as they can for deliberation be considered alkylated versions of P282, P205 and P183.
Figure 4.4: (a - l) Absorption (cyan) and emission (wine) spectra of the fluorescent candidates (P172 - P254) at a fixed concentration of 1.25x10^{-6} M in pristine DMSO. The spectra were acquired using the same measurement parameters (slit width, optical path length, PMT amplification, integration time etc.) and are corrected for the spectral response of the detector. The candidates’ molecular structure as well as its assigned abbreviation is also provided in the inset.
Figure 4.5: (a - e) Absorption (cyan) and emission (wine) spectra of the fluorescent candidates (P273 - P287) at a fixed concentration of $1.25 \times 10^{-6}$ M in pristine DMSO. The spectra were acquired using the same measurement parameters (slit width, optical path length, PMT amplification, integration time etc.) and are corrected for the spectral response of the detector. With each candidates’ molecular structure as well as its assigned code is also provided in the inset. (f) spectral breakdown (%) in the absorption bandwidth of each fluorophore into the following spectral regions UV-A (315 nm – 400 nm, wine), UV-B (280 nm – 315 nm, cyan), UV-C (200 nm - 280 nm, green), and Visible (> 400 nm, yellow). (g) Integrated absorption ($Q_A$ - green) and emission ($Q_E$ - orange) spectra for each candidate at a concentration of $1.25 \times 10^{-6}$ M in pristine DMSO, with the top performers indicated via red asterix
fluorophenyl (P286, figure 4.5 d), bromophenyl (P284, figure 4.5 c) and coumarin (P7, figure 4.3 c). Structures whose molecular scaffolding contained pyrene (P282, figure 4.5 b) or assorted benzene derivatives (P183 – figure 4.4 d, P205 – figure 4.4 i and P166 – figure 4.3 l) offered the best balance in terms of their absorption bandwidth and the intensity of the emission they provided. Another key consideration, when designing a photoluminescent material is the Stokes-shift that the structures exhibit, which is typically defined in terms of the difference between the luminophores peak absorption and emission wavelengths [46].

The emission spectra of most of the ligands studied, shown in figures 4.3 (a - l), 4.4 (a - l) and 4.5 (a - e), indicates that there is very little spectral overlap between the absorption and emission bands. This represents another advantageous aspect of the molecular design as, typically, ligands suffer some major drawbacks in terms of their small Stokes shift, which, in turn, can lead to fluorescent quenching, increasing the energetic favourability of non-radiative decay modes in the process [5, 47-51]. The energy transfer mechanisms available within the internal structure of a specific candidate are reflected through modifications in the photophysical behaviour of the material, within the confines of the inter-comparison performed. Hence, the structures which were identified as absorbing heavily over the targeted spectral region (250 nm – 450 nm) do not directly correspond to the structures which can effectively convert this energy into a more energetically favourable spectral window. This is evident across the series of ligands classified when comparing the intensity of the absorption (QA - figure 4.5 g, green) and the emission (QE – figure 4.5 g, orange) they provide at a fixed concentration of 1.25 x 10^{-6} M. Adopting this approach allowed only the best candidates to be selected for the subsequent parts of this trial, screening out the molecular alterations that delivered a ‘poor’ optical performance for the intended application. Based on the spectroscopic performances highlighted in figures 4.5 f & g, the top ten candidates selected for inclusion
in the next stage of the tests were, in no particular order, P204, P282, P187, P205, P183, P166, P121, P182, P245 and P197 (highlighted in figure 4.5 g with red asterixis). Given the active role of ligands in sensitizing metal coordination centres during the formation of coordination complexes, these same candidates represent favourable consideration as polydentate ligands used to fine-tune the optoelectronic properties of the rare earth-based coordination complexes.

4.3.2 Luminescent Quantum Yield (LQY) of the most promising candidates

Determination of the LQY remains the pre-eminent method used to assess the potential of a fluorescent material and judge its suitability for spectral conversion applications such as LDS, PLDS or SBS [7, 30-33]. Given the qualitatively high performance exhibited by the promising materials in the spectroscopic inter-comparison, a more quantitative definition of their spectrofluorometric capability remained warranted. The LQY of the top-performing candidates originally drafted is presented in figure 4.6, with the values presented calculated through the implementation of two standalone fluorescent standards - harmine and quinine sulphate. Harmine, although formerly proposed as an additional fluorescent standard was excluded from the study, due to its lack of ability to accurately predict the known LQY of the other two materials during the standardised calibration of the fluorescent standards.

Three of the organic ligands (P205, P282 and P205) previously recognized as the most versatile molecular frameworks during the initial spectroscopic evaluation exhibited close to unity quantum yields (figure 4.6), making them ideal candidates for LDS and SBS applications. The presence of the highly electronegative substituents benzonitrile (P205), benzene (P183) and pyrene (P282) contributed to the extremely luminescent nature of these species, whose LQY’s were determined as 0.98 ± 0.05, 0.84 ± 0.04 and 0.85 ± 0.04, respectively. The molecular backbone of the remaining ligands incorporated less electronegative substituents, and, in turn, they exhibited a large degree of non-
radiative energy transfer as elucidated through the moderately low LQY’s (< 0.6) they promoted (figure 4.6). The increased non-radiative decay modes evident in these ‘poorly’ emitting fluorophores (figure 4.6) makes their potential role more appealing and rewarding in solar thermal applications where localised heat generation and transfer is a favourable consideration.

Figure 4.6: Luminescent quantum yield (LQY) of the top 10 performing fluorophores identified during the spectroscopic inter-comparison, with the values shown representing the resultant average of the LQY ascertained through the implementation of two-standards, quinine sulphate and harmane. The candidates are divided into two main applications, those which favour radiative transitions (LDS candidates, green) and those which favour localised heat generation through non-radiative modes (heat transfer fluid candidates, black).

To gain a deeper understanding of the factors responsible for the LQY modulation, density functional theory (DFT) and time-dependent density functional theory (TDDFT) would need to be performed using the empirical spectroscopic data acquired for this family of ligands [52, 53]. The combination of these computational approaches would not only allow a detailed depiction of each ligand’s electronic band structure and for the corresponding transition states to be fully resolved, but they will further permit the rationalization of the factors effecting the radiative and non-radiative
pathways through additional functionalisation attempts [52, 53]. However, such calculations are beyond the scope of the present work.

4.3.3 Photophysical characterisation and optimisation of the LDS layers

The optical spectral features of the P282, P205 and P183 fluorophores encapsulated in moderately thin (10 µm) PMMA films are reported in figure 4.7. The three fluorophores in PMMA displayed absorption features (figure 4.7; P282 – a, P205 - d, P183 - g) in accordance with their molecular counterparts (figure 4.5 b – P282, figure 4.4; P205 - i, P183 – d) and showed very little signs of aggregation over the 0.0078 wt% - 3.0 wt% concentration range explored (figure 4.7, P282 – a, P205 – d, P183 -g). It is noted that the absorbance of the films was dramatically increased by increasing the concentration of the P282 (figure 4.7 a) and P205 (figure 4.7 d) ligands. This increase could be potentially accompanied by an expansive vibrational profile as the molecular transitions acutely resolved in the molecular spectra became less discernible [54]. However, this assertion would need to be clarified by an independent infrared spectroscopic examination of the photo-selective polymers behaviour, under differential loading concentrations. When combined with the amorphous nature of the polymer, the distribution of the fluorophore throughout and the surface roughness (~0.5 µm) of the films provided via the deposition method, the source of this spectral broadening becomes convoluted. Conversely P183, owing to its modest solubility in the phase transfer solvent (i.e. DMSO), proved difficult to disperse homogeneously throughout the PMMA network (figure 4.7 g). Slight deviations from the Beer-Lambert law (insets of figure 4.7 a, d, g) were reported at moderate (< 0.1 wt%) to extremely high (> 2 wt%) loading concentrations. Their origin is likely stemming from the formation of dimers and other higher-order aggregates whose formation is expected in molecular systems containing aromatic derivatives, especially at the loading percentages employed [4-6, 23-29]. This suggests suitable favourability of the P282 and P205 fluorescent ligands towards
interaction with the PMMA host-matrix, which could assist in the promotion of the molecule’s stability within the polymeric network [54].

Figure 4.7: (a, d, g) Absorption spectra of the PMMA based LDS layers, encapsulating the top three performing candidates (P282, P205 and P183) over the 0.00078125 wt% - 3.00 wt% concentration range: with the absorption as a function of concentration provided in each inset. (b, e, h) Emission spectra of the LDS layers as a function of loading concentration, with the integrated emission intensity vs concentration displayed in each inset: whereby the optimal loading for each material is highlighted with a blue circle. (c, f, i) Absolute photoluminescent quantum yield (PLQY) of the LDS layers as a function of loading concentration, with the optimal loading identified for each candidate specified with a blue square – whereby each inset provides the corresponding variation in the peak emission wavelength (λe)
In contrast the fluorescent spectra of the photo-selective PMMA films (figure 4.7; P282 – b, P205 - e, P183 – h) showed a remarkable dependence on the concentration of the ligand and allowed significant insights into the aromatic systems physical behaviour within the polymeric framework to be inferred. Consider the emission spectrum of P282 shown in figure 4.7 b, upon transfer from the highly polar phase-transfer solvent DMSO (\(\varepsilon \sim 47\)) into the moderately non-polar PMMA (\(\varepsilon \sim 3\)) the full width at half maximum (FWHM) of the emission profile becomes narrower, reducing from 81 nm (figure 4.5 b) in the solvent to 53 nm in the solid film (figure 4.7 b), while the peak emission wavelength (\(\lambda_e\)) remained close to 460 nm. Given the rigidity of PMMA, the narrowing of the emission profile likely originated in the restriction of specific vibrational and rotational transitions, once the ligand had become fully immersed in the polymeric lattice [54]. However, this aspect of the molecules’ physical behaviour within the layer would need to be investigated in the future.

As the concentration of the ligand within the layer was gradually increased, further significant changes in the overall spectral profile become observable (figure 4.5 b). Most noticeable is the distinctive shift in \(\lambda_e\) often accompanied and characterised by the formation of dimers and other higher molecular-weight aggregates - whose contribution(s) negatively influence the emissive capabilities of the molecule [23-29, 55, 56]. This simplified analogy of the molecular behaviour does not even begin to consider the negative impact of self-absorption and/or the possibility of the formation of other more intricate molecular arrangements within the host material [23-29, 55, 56]. Two fundamental types of molecular aggregates (J-type, H-type) are typically created when aromatic and/or planar molecules are infused throughout a polymeric material, namely side-by-side (or J-type) or face-to-face (or H type) aggregates. The distinction between the two is arising from subtle differences in the molecular arrangement instigated between neighbouring species [29, 54]. Ligand molecules distributed across a single plane within
the overarching PMMA film can form side-by-side molecular arrangements called J-aggregates. Alternatively, the ligands can organise into face-to-face molecular arrangements with adjacent molecules residing above or below the plane called H-aggregates [29, 54]. The behaviour of J-aggregates of similarly structured fluorophores is well explored and their continued formation is correlated with a distinguished red-shift in the emission spectra [29, 54]. The formation of H-aggregates is linked with an opposing blue-shift in the emission wavelength [29, 54]. Furthermore, excimers also known as ‘excited state dimers’ can also be formed through the association of excited and unexcited molecules, which additionally encourages non-radiative relaxation pathways within the hybrid material. The aggregates formed often prove not only to be weakly emissive and quenching the fluorescent intensity, but their presence also prompts a reduction in the overall LQY of the encapsulated material [23-27, 29, 51, 54, 55]. Given the finite dimensionality of the photo-selective PMMA films deposited, a dynamic combination of the competing H-aggregate, J-aggregate and excimer formation processes is anticipated.

The formation of each type of aggregate within the P282 system was tracked spectroscopically through the subtle modifications registered in the emission intensity (figure 4.5 b - inset) in association with the spectral-shift induced in the emission peak (figure 4.5 c – inset). The behaviour of the P282 molecular framework in PMMA exhibit a tendency to energetically favour side-by-side molecular arrangements, evidenced through the characteristic red-shift revealed in $\lambda_e$ (figure 4.5 c - inset). In addition, a small contribution deriving from the formation of H-aggregates was also noted at moderate loading concentrations – the blue shift seen in the inset of figure 4.5 c.

The influence of concentration on the LQY of P282 (PLQY in figure 4.7 c) provides even more insight into the dispersion and aggregation state of the molecule(s) dispersed throughout the matrix. An initial 20 % reduction in the LQY (figure 4.6) was observed upon the successful transfer of the molecule to within the PMMA network.
Although PMMA was chosen because of its excellent optical transparency, film-forming properties, and ease of solution processability, the polarity of the phase transfer solvent used can have a strong influence over the luminophores LQY [51, 57]. Hence, the extremely high LQY values resolved through the comparative method (figure 4.6) may have been influenced by the choice of solvent – DMSO [51, 57]. The continuous decline experienced in the LQY under increased loading concentrations (figure 4.7) resonates with the formation of aggregates. Their modestly emissive nature contributes to an apparent broadening of the quantum yield at certain loading percentages, indicated through the deviation in the LQY value reported (error bars in figure 4.7 c for example). The LQY of the remaining candidates (figure 4.7; P205 – f, P183 – i) suffered an even greater deterioration in their photoluminescent efficiency, once constrained within the polymer. Both P205 and P183 experienced an almost 50 % reduction in their LQY (figure 4.8), and while these LQY’s may seem sufficient, it must be remembered that any non-unity quantum yield will increase the losses from re-absorption which occur in an LDS device. The possible reactivity of the fluorophores towards chemical additives present in the Plexit 55 resin (PMMA) may be additionally intertwined with the reduction in performance, as a commercial PMMA based resin is frequently known to be stabilised through the inclusion of several additives [58]. Although the exact chemical structure of these additives was not explored (their list also being protected by the manufacturers), stabilising agents are typically known to embody a reducing character and be selectively destabilising towards certain fluorescent compounds [58]. This divergence between the behaviour of the P183, P205 and P282 molecular systems when embodied within the PMMA lattice (and their preference to form discrete molecular arrangements) within it is likely to be influenced by the chemical and physical properties generated by the substituent moiety present [54, 59]. A direct comparison between the optical properties
of each of the materials in their respective solid (PMMA) and liquid (DMSO) phases is provided in figure 4.8.

![Spectroscopic summary](image)

**Figure 4.8:** Spectroscopic summary of the top three performing organic materials (P282, P205 and P183) at their respective optimal loading concentrations (P282 - 0.0625 wt%, P205 - 0.015625 wt%, P183 - 0.0078125 wt%) in liquid and solid states. Each materials LQY is also highlighted, with LQY* referring to the PLQY of the solid fluorescent polymer layers.

4.3.4 **Electrical characteristics of the optimised LDS devices**

The optimal loading concentration for each ligand was identified through the loading percentage that yielded the maximum fluorescent intensity (blue square in the inset of figure 4.7; P282 - b, P205 - e, P183 - h) and it was found to be 0.063 wt%, 0.016 wt% and 0.0078 wt% for P282, P205 and P183, respectively (see the appendix section for the concentration in terms of molarity). The equivalent concentration of each distinct molecular scaffold was subsequently incorporated in LDS devices built upon a mc-Si architecture, thereby, ensuring that the most intense luminescence from each molecule was imparted upon the conversion dynamics of the cell. Before any correlation between the optical properties of the LDS layer and the electrical performance exhibited through
retrofitting of the cell can be concluded, it is important to first understand the influence of the pristine polymer on the overall properties of the device [5, 18].

Including an additional semi-transparent layer into a PV collection system is well known to further promote the reflection losses arising from the front surface [5, 6]. This was confirmed through the amendments registered in the reflection spectra of the blank device(s) in figure 4.9 a. The extremely low reflectance of the pristine device (figure 4.9 a – black line) reveals just how effective the industrial standard of anti-reflective structures are at addressing the front surface reflections, and why the majority of the loss mechanisms inherent in this commercially mature technology have been largely addressed at manufacturing stage. Regardless of the thickness of the polymer deposited, either in the form of relatively thin (10 µm – figure 4.9 a, red line) or moderately thick (300 µm – figure 4.9 a- blue line) films, the result was a 4 % - 5 % and 5 % - 6 % increase in the reflectance across the entire 200 nm – 1000 nm window. This indicates that even without the presence of an absorbing species (luminophore), the encapsulating layers introduce additional losses into the system which must be compensated by the fluorescence provided by the P282, P205 and P183 ligands. The two alternative thickness profiles were chosen as they allowed the interplay between the casting method and the molecular structure of the ligand on the resulting distribution of each luminophore to be examined once the luminescent species had been added into the device. The subsequent impact of each PMMA film on the current-voltage (I-V) characteristics of the cell (figure 4.9 b) confirms a decrease in efficiency (1 % - 2 %) accompanies the heightened surface reflectivity. SEM analysis of the pristine cells front surface (figure 4.9 c) reveals the source of this behaviour, displaying a surface textured with a multitude of randomly distributed three dimensional pyramids – synonymous with a surface textured antireflection coating [60, 61]. The textured elements with feature sizes on the order of several micrometres (figure 4.9 c) provide: (1) a reduction in the surface reflectivity, (2)
an increase in the amount of internal reflection – which in turn prevents more light from escaping the cell and (3) an increased optical path length inside the architecture which leads to an enhanced optical absorption [60, 61]. Hence, through the consecutive deposition of LDS layers it is highly likely that one or more of these mechanisms will be undermined. Ideally, an LDS system should not only outperform the retrofitted blank devices performance, but it should improve upon the efficiency of the pristine device. However, this expected idealised scenario is non-practical as upon interweaving the individual mc-Si solar cells into industrial scale modules - a complementary encapsulation layer (individual layers of glass and a polymer) is always added to help protect the panels from moisture and impact [62, 63]. Therefore, it was more appropriate to compare the performance between the undoped (blank) and doped (LDS) devices – when analysing the influence of each molecule on the conversion efficiency.

Alternatively, the LDS layers could be inserted at the manufacturing stage i.e. prior to the addition of the encapsulating layer. Moreover, the LDS layer could play its role as well as it has the required mechanical and physical properties reducing, consequently, the cost and improving the cell efficiency.

The influence of each molecular structure on the conversion performance of the mc-Si when retrofitted with relatively thin spin-coated (a, c, e) and moderately thick drop casted (b, d, f) LDS layers is highlighted in figure 4.10. The increase in the photo-current generated through the inclusion of the P282 (figure 4.10 – a), P205 (figure 4.10 – c), and P183 (figure 4.10 – e) molecules when encapsulated in relatively thin spin-coated LDS can be observed. Surprisingly, the highest improvements in efficiency were obtained using the two molecular structures (P205, P183) which displayed significantly lower LQY’s once they were immersed in the polymer (figure 4.8). Considering the moderate solubility of the two materials in the phase transfer solvent DMSO – showcased in the insets of figure 4.10 b and figure 4.10 e, the possible influence of the formation of larger
clusters and/or differences in crystallisation behaviour within the polymeric matrix cannot be ruled out. Furthermore, the scattering contributions stemming from these divergences in physical characteristics could have further altered the interaction of light with the textured surface lying underneath the protective photo-selective polymer coating. Consequently, these contributions could promote the enhanced collection of light registered in the I-V response curves of the two devices (P205 – figure 4.10 c and P183 – figure 4.10 e). Despite these differences all three molecules still gave an absolute enhancement in the conversion efficiency ranging from 0.4 ± 0.05 % (P282 – figure 4.10 a) to 0.93 ± 0.05 % (P183 – figure 4.10 e) – further highlighting the potential of the

Figure 4.9: Reflectance spectra of the pristine mc-Si cell (black) and the accompanying increased reflectance introduced through the incorporation of a drop cast (blue) and spin coated (red) ‘blank’ PMMA coating. (b) The I-V response curve of the pristine (black) device in addition to the drop cast (blue) and spin coated blank’ devices, and their corresponding conversion efficiency (η). (c) The textured antireflective coating etched into the Si cells surface, as revealed through SEM analysis.
molecular arrangements for LDS applications. Although this enhanced effect may seem inconsequential in magnitude, one should consider the advancements in conversion efficiency achieved through modifying the fundamental architecture of the same technology over the last decade – ~2% (highlighted in figure 1.1 e)

Increasing the optical-path length within the down-shifting layer while keeping the concentration of the fluorophore fixed resulted in a significant impairment in the underlying devices capacity to effectively convert light into usable electrical power (figure 4.10 – d, f). Conversely, the P282 molecule still retained its promise as an effective emitter (figure 4.10 - b) despite the larger polymeric manifold – leading to a 1.2 ± 0.1% enhancement in the conversion efficiency. This effect is seen despite the lack of compensation required through the concentration of the ligand to account for the additional increase in optical thickness, indicating that an even greater enhancement may be available through further refinements in the concentration of this ligand. One possible explanation for this divergence between the behaviour of the spin-coated and drop-casted P282-LDS devices is the additional temperature the thicker layers were subjected to in order to ensure they were fully cured and annealed prior to testing.

This additional 2 – 4 hrs in the low-pressure drying environment (figure 4.2) could have supported additional thermal diffusion and molecular rearrangement of the dispersed fluorophore within the matrix and, thereby, altered the spectrofluorimetric properties of the photo-selective layer [29,51]. Therefore, through limiting the thickness of the LDS layer the quantity of materials consumed and the corresponding cost of the retrofitted structure can be decreased, with very little if any noticeable decline in the enhancement offered through the molecular strategy adopted. In addition, the P282 ligand warrants further exploration in thicker and more heavily absorbing films as the possibility of even greater enhancements in performance seems reasonable.
Figure 4.10: I-V response curve and conversion efficiency of LDS fitted mc-Si devices fabricated using spin coating (a – P282, c – P205, e – P183) and drop casting (b – P282 at 0.0078125 wt%, d – P205 at, f – P183 at) fabrication pathways, with the accompanying structure of each molecular framework provided for convenient comparison.

4.3.5 Photostability

The evolution of the UV-VIS absorption spectra of thinly coated LDS layers containing the P282 (a & b), P205 (b & c) and P183 (d & e) ligands at their optimal
loading concentrations - under the exposure of a continuous irradiance is depicted in figure 4.11. In order to highlight any differences in the rate of photodegradation experienced by the two prominent peaks characteristic of the two absorbing groups present within the phen based chromophores, their relative intensities were monitored throughout the entire exposure cycle (presented as insets in figure 4.11). The shorter wavelength absorption peak situated at 280 nm – 285 nm (black squares) is associated with the absorption of the phenanthroline core of the heteroaromatic molecule, while the longer-wavelength absorption peak (340 nm – 375 nm, green triangle) is considered the substituent moiety on the aromatic phen ring. Under the moderate exposure conditions representative of a European climate the substituent molecule (282 – pyrene, 205 – benzonitrile, 183 - benzene) shows considerable degradation after less than 10 hrs exposure , whereby a 33 % (P282 - figure 4.11 a), 37 % (P205 - figure 4.11 c) and 25 % (P183 - figure 4.11 e) relative decrease in absorption intensity was observed.

Over the remaining 90 hrs of exposure a further 25 % (P282), 20 % (P205) and 40 % (P183) decline in the intensity of this spectral component was witnessed, while the short-wavelength absorption contribution revealed an insignificant variation. This may suggest that the degradation mechanism for the heteroaromatic molecule initiates with the disruption of the substituent attached to the phen core, the latter appearing to be much more resilient to photo-degradation as showcased in figures 4.11 a, c and e – green triangle. The disruption is most probably facilitated through the rupture of the imidazole aromatic which effectively binds the substituent moiety onto the phenanthroline ring. As a result of the combined action of the irradiation and oxygen rich atmospheric conditions, the radical species formed as a consequence of the photoreduction of the imidazole structure can subsequently undergo a series of oxidation or crosslinking interactions with other neighbouring reactive species [64]. Eventually even the polymer matrix itself
Figure 4.11: Structural integrity of the top three performers (P282, P205, P183) encapsulated within a 10 µm thick PMMA network under the continuous bombardment of photoirradiation simulating two alternate climate scenarios, temperate (a, c, e) and tropical (b, d, f). With the peak absorption at two different spectral windows (285 nm, black squares) and (350 nm – 375 nm, green triangles) as function of exposure time highlighted in each inset. The decoupling of the two absorption peaks, allowing any changes in the phenanthroline ring or the substituted moiety to be monitored continuously.
experiences photoinduced degradation effects, which in turn can further contribute to the destabilisation of the heteroaromatic molecules [64]. In order to support the proposed degradation mechanism a complementary in-depth structural analysis of the LDS films would need to be carried out at various exposure intervals in order to conclusively register the acute chemical changes induced in the photo-selective PMMA films [64]. In a more extreme tropical climate condition, the same scenario enfolded, but at a substantially faster pace (figure 4.11 – b, d, f). Even at these elevated irradiance conditions the absorption component correlated with the core of each ligand remained structurally intact, with the intensity of the signal in some instances even increasing over the exposure cycle (P183 - figure 4.11 f). Structurally this can be attempted to be explained by carefully examining the structure of P183 in figure 4.4 d, whose distinctive structure symmetrically includes two phenanthroline moieties. Under the continuous bombardment of irradiation, the benzene moiety becomes liberated from the ligand through photoinduced dissociation, leaving the two phenanthroline cores directly exposed to the incoming solar flux. Given the intense absorption contribution arising from even minute amounts of pristine phenanthroline in figure 4.3 a, the twofold increase in its presence directly in line with the deterioration of the imidazole linking-molecule, when exposed to such an extreme irradiance, could help to explain the structures behaviour within the photo-selective PMMA film. Again, this would need to be confirmed through a complete structural study of the film’s chemical and physical structure when subjected to these environmental conditions.

4.4 Conclusion

The influence of a series of monosubstituted heteroaromatic moieties over the photophysical properties of an imidazole[4,5-f][1,10]phenanthroline ligand was investigated for their potential role in solar energy conversion applications. Through the changes initiated in the aromatic molecules structure the absorption profile was fine-tuned
to heavily absorb over the 300 nm – 500 nm region, where most commercial and non-commercial PV technologies suffer from low conversion efficiencies. Three of the structural iterations seem to adequately surpass the optical requirements imposed on LDS material candidates as they exhibit an extremely high LQY (0.8 – 0.95). The physical behaviour of the three candidates when immersed in relatively thin (10 µm) PMMA films was thoroughly explored and the optimal concentration determined. The absolute quantum yield of the photo-selective PMMA films revealed aggregation processes which resulted in a deterioration in the LQY by 20 ± 5 % - 50 ± 8 % depending upon the fundamental properties of the substituent moiety. Fitting of the optimised LDS layers onto a series of mc-Si cells promoted an 0.40 ± 0.05 % - 0.93± 0.05 % absolute enhancement in the conversion efficiency of the tested technology. In addition, the photo-degradation of the films was studied to access the long-term susceptibility of the layers towards the in-situ environmental conditions typically encountered across solar applications. Although the layers exhibited degenerative effects under the artificial climate conditions instigated, the molecular strategies developed show great premise for further expanding the library of fluorescent candidates suitable for LDS, PLDS and SBS applications. Alternatively, through modification of the substituent moiety the fluorescent processes deemed favourable for spectral conversion applications can be diminished to yield moderately to lowly fluorescent candidates whose quantum yield ranges from 0.2 – 0.6; making them ideal candidates for solar thermal applications whereby non-radiative energy transfer is a favourable consideration.

4.5 References


Chapter 5
Splitting The Solar Spectrum Using Organic Luminescent Down-Shifting Optical Filters For Hybrid PVT Collector Applications

5.1 Outline

In efforts to bridge the gap between the maximum conversion efficiencies achievable and those currently attained with standalone photovoltaic (PV) and photothermal (PT) technology, merging the two approaches into a single hybridized photovoltaic-thermal (PVT) collector represents one of the most promising avenues. When combined with the capability of spectral beam splitting (SBS), provided either through highly tuned optical cavities or specifically designed liquid filters, to modulate the thermal and electrical output of the combined heat and power unit - the potential application of the device’s become endless. In order to effectively control the spectral characteristics of the partitioning of the solar spectrum into its distinctive ‘thermal’ and ‘electrical’ components, liquid optical filters represent a more readily adaptable, scalable and cost-effective approach. Traditionally, the liquid optical filter has been comprised of nanoscale structures suspended in a suitable base fluid in order to capitalise on the enhanced heat transfer capabilities afforded through the highly attuned surface morphology of the nanostructures. However, for this type of working fluid to offer a tangible alternative to some of the more commercially mature (single-phase) heat transfer fluids currently employed in PVT collection systems, allot of underlying issues (instabilities, costly fabrication, environmentally hazardous) must be addressed.

In this study an alternative strategy in which a set of newly developed organic and organometallic derivatives of [1,10]phenanthroline were employed as hybridised heat transfer fluids within an SBS-PVT system. This type of working fluid was designed to mimic the behaviour of luminescent down-shifting structures in a liquid, whilst also affording enhanced thermophysical characteristics over the corresponding base fluid. This complementary optical and thermophysical behaviour contributed to an intensified
rate of heating within the working fluid’s, while their fluorescent capability makes them exceedingly suitable for addressing some of the shortcomings identified in alternative working fluid strategies. Integration of the hybridised working fluid’s (as liquid optical filters) within a conventional SBS-PVT system enabled optical efficiencies as high as 63% to be realized, a marked improvement over the 18% to 20% captured with standalone PV technology. These additional modifications in the spectroscopic properties of the fluid resulted in a subsequent 2% to 61% increase in the economic value of the energy captured, when compared with the PVT system employing the pristine base fluid. Overall, the results of the present work provide a novel organic basis for effectively designing high performance spectrally selective heat transfer fluids for SBS-PVT applications.

5.2 Introduction
As the need for affordable, scalable and dispatchable alternative energy solutions remains ever present [1-5] coupling photovoltaic (PV) and photothermal (PT) technologies together can offer a more effective way to minimise energy loss as it exploits the potential synergy between the two or more conversion processes [6]. Thermal energy remains an unwanted remnant of most conversion processes and its abundance is also correlated with a decrease in the ability of some conversion technologies, including PV, to perform at their peak conversion efficiencies [7-9]. One attractive hybridisation option seems to be coupling of PV and PT systems into a combined photovoltaic-thermal (PVT) unit capable of maximising the cooperative interactions between the two conversion technologies [6, 10-12]. In a classical hybridisation, the two similar elements, the electrical component (PV) and the thermal component (PT), are encased in a standardised PVT collector in which both remain in physical contact [5, 6]. These standardised collector designs are restrictive in terms of their fixed spectral characteristics and their inability to enable high operating temperatures within the thermal component [5, 6, 13, 14]. The heat leakage emanating from the physical proximity of the two competing
technologies, additionally served to increase the operating temperatures in which the PV component was subjected to. These factors are forcing the system to operate under submaximal conditions [5, 6, 13, 14]. Within a standard PVT collector design, this ‘wasted’ heat resulted in the PV module operating at electrical efficiencies ~22 % below their peak performance criterion [15]. Thereby, this is forcing an even greater compensatory heat generating capacity to be imposed upon the heat transfer fluids evaluated within such systems.

An alternative to this classic approach is the partitioning of the two energy sources through volumetric spectral beam splitting (SBS), in which a liquid optical filter serves as both a spectral modulator and a heat transfer fluid. Such an approach has the ability to enable substantially higher fluid temperatures to be realised [13, 14, 16-22]. The decoupling of the thermal component allows for the optical and thermal properties of the working fluid to be readily modified to meet the various demands imposed by an application. This can be achieved through dynamic control of the light-matter interactions within the fluids internal structure [13, 14, 16-22]. Classical single-phase heat transfer fluids such as water, glycols, mineral oils and liquid salts proved the initial viability of splitting the solar spectrum conversion into its thermal and electrical applications by their characteristic infrared absorption spectra [11, 12, 23, 24]. However, the rigidity in the classical working fluid’s spectral properties do not sufficiently match the spectral responsivity of the PV cell used throughout the hybrid applications. This led to lower collective conversion efficiencies [11, 12, 23, 24]. Single-phase fluids absorption capabilities across the ultraviolet-visible spectral window (290 nm – 600 nm), where the intense solar flux is distributed, are small. This, together with inefficiencies in infrared absorption, suggests, a further need for spectral tuning of the working fluids optical properties [11, 12, 23, 24]. This could be achieved by controlling the molecular dynamics of a 2nd phase additive suspended within the fluid. Consequently, the fluids capability to
modulate the output of heat and electricity can be further attuned for these applications [11, 14, 16, 18-20]. Traditionally this has been achieved through the dispersion of a wide range of nanomaterials within a suitable base fluid, where the unique optoelectronic properties elicited by the nanoscale features augmented the heat transfer dynamics of the aptly named ‘nanofluids’ [11, 14, 16, 18-20]. However, the improvements in efficiency granted through the inclusion of these materials is often overshadowed by their costly synthesis [25-27], the requirement of toxic precursors [28], their inability of offering the required solar energy conversion over a broad spectral range and the lack of control over the instabilities which arise as aggregative processes proceed [29-34].

Here, an alternative set of organic/organometallic hybrid heat transfer fluids was explored through modifications in a cost-effective, scalable, high-yield one pot synthetic strategy. Each molecular architecture of these fluids was built upon a [1,10]Phenanthroline scaffolding which afforded an abundance of desirable physical features for further developing the SBS-PVT application. These features included (1) thermal stability up to ~250 °C, (2) readily modified photophysical properties through simple substitution(s) with alternate functional moieties, (3) controllable photoluminescence, (4) non-corrosivity and (5) capability of being derived from a synthesis method which offers a substantially lower environmental impact that anything encountered throughout the fabrication of conventional nanofluids. The molecules selected for the initial study were chosen based on the physical and spectroscopic characterisation presented in chapter 4. These results also reflected the molecular structures for which the radiative and non-radiative transitions were dominant. The aim was to identify whether through the careful control of the optical filters’ fluorescence, the electrical energy sacrificed through the inclusion of the thermal component could be minimised, or alternatively whether non-radiative transitions should be further exploited to substantially enhance the thermal energy captured within a hybrid design. The interplay
between each chelating ligand’s absorption and emission bands, optical transmittance and contribution towards enhancing the heat transfer dynamics of an ethylene glycol based working fluid, on maximising the collective (thermal and electrical) power efficiency of a hybrid SBS-PVT system was evaluated. In addition, the economic viability of each structural iteration throughout the European region during the evaluation of the SBS-PVT configuration proposed was considered using a merit function which incorporated the most up to date financial information.

5.3 Materials and methods

5.3.1 Materials

Since crystalline silicon based solar cells remain the most widely used PV devices in low to medium concentrated-PVT (C-PVT) systems. Therefore, an aluminium back surface field (Al-BSF) monocrystalline silicon (mc-Si) cell designed and fabricated by BigSun Community Solar (Big Sun Community Solar, San Antonio, TX, USA) was selected for this study. The spectral responsivity of the PV material, shown in figure 5.1 a, reaches peak conversion efficiency when the incoming energy closely matches that of the PV materials band gap (ideal PV window highlighted in figure 5.1 a), while the remaining wavelengths within the solar spectrum contribute to an unwanted production of heat. To capitalise on the ‘waste’ heat, generated through the spectral mismatch between the incident solar irradiance and the conversion dynamics of the PV material and also to enhance the combined conversion efficiency of C-PVT systems, spectrally selective optical filters were designed to target these ‘thermal regions’ shown in figure 5.1 a. In other words, the optical filters developed facilitate the splitting of the incident spectrum into its corresponding PV and thermal components as shown in figure 5.1 a. Unlike conventional heat transfer fluids, which exhibit heightened heat transfer capabilities, the fluids developed and characterised herein exhibit complementary strongly emissive fluorescent properties. This allows for a potential reduction in the
electrical energy sacrificed through the inclusion of the thermal component within C-PVT systems.

![Image](108x312 to 542x722)

**Figure 5.1:** (a) Separating or ‘splitting’ of the solar spectrum into its respective idealised photothermal (thermal) and photovoltaic (electricity) conversion windows. (b) The interaction pathways available within a luminescent down-shifting (LDS) material which includes absorptive (3, 7), emissive (4, 6, 7), reflective (2, 8) and non-interaction (5) processes. (c) Zoomed in spectral response window (250 nm – 1100 nm) for silicon PV, highlighting the capability of luminescent materials (organic dye, quantum dot or fluorescent ligand) to capture (LDS candidate’s absorption – cyan) and convert (LDS candidate’s emission - wine) part of the incoming solar irradiance into more easily harvestable electrical energy: potentially reducing the electrical energy sacrificed through the thermal components inclusion within a PVT or CPVT system. (d) the molecular scaffolding underpinning the range of hybridised

Traditionally luminescent down-shifting (LDS) materials have been employed as solid, semi-transparent, retrofitted layers used to enhance the short-wavelength (300 nm – 500 nm) conversion performance across a host of different PV technologies [35, 36].
As light interacts with the LDS material it can undergo a series of different radiative and non-radiative pathways before reaching the underlying PV material, as outlined in figure 5.1 b. An incident photon (1) can pass straight through the LDS material without interacting with the photoluminescent species present (5) or alternatively be reflected from the front surface of the LDS structure (2). Otherwise the photon can interact with the luminescent species (3) prior to undergoing reflection and exiting out the side of the structure (8) - with such losses collectively bundled as ‘escape cone’ losses. Finally, the photons which do interact with the suspended luminophore (3) can undergo reflection (6) or a successive series of photoluminescent events (7) before finally reaching the underlying PV cell. These light-matter interactions within the LDS material (figure 5.1 b) are controlled through careful consideration of the luminophore's molecular structure (figure 5.1 d), the dynamics between competing radiative and non-radiative processes, and the concentration and thickness of the LDS material [35-38]. In this study, the same photoluminescent mechanism is exploited to absorb irradiance (figure 5.1 c - cyan) from within the targeted wavelength range (300 nm – 400 nm) where almost all PV cells exhibit poor conversion capabilities (figure 5.1 c) and convert this energy into more readily convertible wavelengths (figure 5.1 c - wine) within a C-PVT system. The liquid LDS layer is acting as both a spectrally selective filter, complementing the absorption profile of conventional heat transfer fluids such as ethylene glycol, whilst also affording an enhanced transmission intensity within the ideal PV window (figure 5.1 c) on account of the materials luminescence. To modulate the interplay between the two competing processes (radiative and non-radiative transitions) a series of distinct chemical moieties were substituted onto the phenanthroline ring at R in figure 5.1 d, and their role in enhancing or curtailing the thermophysical properties of the corresponding hybridised heat transfer fluid examined. The molecular architectures explored as well as their
respective formula, nomenclature, molecular weight and their abbreviation (which will be adopted throughout the discussions) are presented in table 5.1.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Chemical formula</th>
<th>Name</th>
<th>Molecular weight (g mol⁻¹)</th>
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<tr>
<td>P166</td>
<td>C₂₇H₁₆N₄</td>
<td>2-(anthracen-4-yl)-1H-imidazo[4,5-f][1,10]phenanthroline</td>
<td>396.45</td>
</tr>
<tr>
<td>P181</td>
<td>C₂₃H₁₆FeN₄</td>
<td>2-ferroceny-1H-imidazo[4,5-f][1,10]phenanthroline</td>
<td>404.25</td>
</tr>
<tr>
<td>P183</td>
<td>C₃₂H₁₈N₈</td>
<td>1,4-bis(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)benzene</td>
<td>514.55</td>
</tr>
<tr>
<td>P187</td>
<td>C₂₆H₁₈N₄</td>
<td>2-(9H-fluoren-3-yl)-1H-imidazo[4,5-f][1,10]phenanthroline</td>
<td>384.44</td>
</tr>
<tr>
<td>P205</td>
<td>C₂₀H₁₁N₅</td>
<td>4-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)benzonitrile</td>
<td>321.44</td>
</tr>
<tr>
<td>P282</td>
<td>C₂₉H₁₈N₄</td>
<td>2-(pyren-1-yl)-1H-imidazo[4,5-f][1,10]phenanthroline</td>
<td>420.42</td>
</tr>
</tbody>
</table>

5.3.2 LDS fluid preparation

Stock solutions of a known molarity (~0.025 M) were prepared using pristine ethylene glycol. Each stock solution was subsequently subjected to an initial temperature of 100 °C for 30 minutes to 1 hr to ensure that any partial solubility which arose was addressed. Once cooled to room temperature the solutions were placed in an ultrasonication bath for 1 hr to ensure that any remaining inhomogeneities were removed, before the working fluids were prepared. After each stage, the absorption and the emission spectra were measured to ensure that no degradation in the molecule’s optical characteristics had been initiated as a result of the processing. A series of working fluids (0.005 wt% - 0.5 wt%) for each material candidate were prepared through the removal of aliquots (5 μL - 700 μL) from each stock solution, with the remainder of the working volume coming from pristine ethylene glycol.
5.3.3 Optical transmittance of liquid LDS filters

Optical transmittance measurements were performed using a Perkin Elmer Lambda 900 UV-VIS-NIR spectrometer (Perkin Elmer Inc., Massachusetts, USA) employing highly transparent quartz cuvettes. For each liquid considered, a combination of 5 mm and 10 mm optical path-lengths was used with all measurements being performed twice before using the average value in all subsequent calculations. Transmittance spectra were acquired over the 250 nm to 2000 nm range under ambient conditions, using 1 nm wavelength intervals, as this corresponded to 97% of the solar irradiance reaching Earth’s surface. The utilisation of multiple path-lengths is essential to measure the value of the fluids transmittance at a particular wavelength, as the measurements performed using only a single path-length contain unaccounted absorptive (within the cuvette) and reflective (at each optical interface) interactions [39-42]. Based on the Beer-Lambert law, the optical transmittance of a liquid \( \tau(\lambda) \) at a wavelength \( \lambda \) is directly related to its absorption coefficient \( \alpha(\lambda) \) and to its optical path length \( x \) as follows [39-42];

\[
\tau(\lambda) = e^{(-\alpha(\lambda) \cdot x)} \quad (5.1)
\]

However, the measured transmittance \( T \) using the spectrometer at an individual path-length is an accumulation of the interactions between the liquid layer and two cuvette walls, immersed in air [39, 40]. At each interface (air-cuvette, cuvette-liquid), absorption within the walls of the cuvette and Fresnel losses owning to the differences in refractive index, contribute to a diminished intensity, particularly in the ultraviolet region (300 nm – 400 nm) [39, 40]. With the assumption of no scattering, negligible coherent effects [43] and a single reflection emanating from each interface, the cumulative transmittance \( T(\lambda) \) can be written as [39, 40];

\[
T(\lambda) = \tau(\lambda)(1 - R_1)^2(1 - R_2)^2 e^{(-\alpha_g \cdot d)} \quad (5.2)
\]
where $R_1$ and $R_2$ are the reflection at the air-cuvette and cuvette-liquid interface respectively, $\alpha_q$ is the absorption coefficient of the cuvette wall (in this case quartz) and $d$ is the thickness of the cuvette wall. Consequently, with air as a reference, measuring the transmittance of a liquid at two different optical path lengths $X_1$ and $X_2$, facilitates the determination of the liquid’s true absorption coefficient $\alpha_L$ via [39, 40];

$$\alpha_L(\lambda) = \left[-\frac{1}{X_2 - X_1}\right] \ln \left[\frac{X_2(\lambda)}{X_1(\lambda)}\right]$$

where $X_2$ and $X_1$ correspond to the individual path lengths. Finally, according to the absorption coefficient of the liquid $\alpha_L(\lambda)$ obtained through equation 5.3, the optical transmittance of the liquid $\tau(\lambda)$ at any optical path length $X$ can be readily determined through equation 5.1.

### 5.3.4 LDS fluid characterisation

#### 5.3.4.1 Performance evaluation of LDS liquid filters

The purpose of this study was to examine the impact of each type of liquid filter on the electrical characteristics of the C-PV silicon cell and further probe the filtering performance of the down-shifting hybrid heat transfer fluids developed. Figure 5.2 presents the experimental set-up used throughout the study, which includes; (1) solar simulator – a combination of a Griven 1200 MSR and an accompanying ultraviolet lamp, (2) current-voltage (I-V) curve generator (Keysight B2901A source-meter), (3) data collector (Pico TC-08), (4) K-type thermocouples, (5) quartz glass cuvette with a 120 mm x 2 mm x 75 mm L x W x H, (6) computer to collect and record the data and (7) mc-Si C-PV cell (25 mm x 25 mm).

Under the 1000 W m$^{-2}$ irradiance provided by the combination of the two complementary lamps, the I-V curve of the mc-Si C-PV cell without any liquid filter (the ‘unfiltered’ case) was first measured. The temperature of the solar cell ($T_{\text{cell}}$) was monitored throughout the illumination cycle (33 minutes) using a K-type thermocouple.
Figure 5.2: Schematic of the experimental set-up used to evaluate the performance of a concentrator PV cell (C-PV) incorporating various liquid LDS filters designed for C-PVT systems in order to ensure that the electrical performance of the cell could be adequately compared across the range of liquid filters investigated. Preventing the cell from being actively cooled throughout an exposure cycle also enabled the partial shading capabilities provided by the various liquid filters to be expanded upon and investigated. Subsequently the quartz glass cuvette (2 mm optical path-length) was filled with 1 ml of a hybrid heat transfer fluid and then placed between the PV cell and the solar lamp as shown in figure 5.2. An additional K-type thermocouple was inserted into the quartz glass cuvette to monitor the working fluid’s temperature (T_{FLUID}) at 1s intervals throughout the exposure cycle. After each exposure cycle had been completed a cool down window of 20 to 30 minutes was allocated in order to ensure the initial cell and fluid temperatures remained as replicable as possible within the confines of the experimental design. The principal electrical characteristics of the solar cell including short circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and conversion efficiency (\eta) were derived from the I-V curves generated at 30 s intervals throughout the exposure cycle. Throughout the study an optical path-length of 2 mm was adopted, as it enabled a larger range of concentrations to be explored for the material candidates considered.
5.3.4.2 Merit function of PVT system with LDS liquid optical filter

Although the test outlined above adequately allows for the impact of a specific liquid filter on the conversion performance metrics of the C-PV cell to be evaluated under differential temperature loads it cannot distinguish the dynamics of the thermal and electrical collector performances. Therefore, a theoretical approach was additionally employed to reveal the combined power output \( P_{\text{th}} \) - thermal and \( P_{\text{pv}} \) - electrical delivered by each liquid LDS filter when it is utilised in a C-PVT system. The electrical properties of the cell in response to the incoming filtered irradiance spectra were modelled using the electrical model established by [44, 45]. Firstly, the reverse saturation current density \( J_{00} \) of the solar cell can be calculated by the following correlation [41, 44];

\[
J_{00} = K' T^3/n e^{\frac{-E_g}{m k_B T_c}}
\]  

where \( K' \), \( n \) and \( m \) are empirical constants, \( E_g \) is the bandgap energy of the PV material, \( k_B \) is the Boltzmann constant, \( T \) is the ambient temperature, and \( T_c \) is the cell temperature. Based on the optical transmittance measured for each liquid filter \( T_{\text{LIQUID}}(\lambda) \), the measured spectral response of the solar cell \( (\text{SR}(\lambda)) \), in unification with a direct normal incident irradiance AM1.5D spectrum \( \phi_{\text{AM1.5D}}(\lambda) \) the short circuit current density generated within the solar cell with each liquid filter \( J_{\text{sc}}(\text{filtered}) \) can be written as follows [41, 45];

\[
J_{\text{sc}}(\text{filtered}) = \int_{250 \text{ nm}}^{2000 \text{ nm}} \phi_{\text{AM1.5D}}(\lambda) \cdot \text{SR}(\lambda) \cdot T_{\text{LIQUID}}(\lambda) \cdot d\lambda
\]  

where the limits of the integration represent 97% of the solar energy reaching the Earth’s surface. The open-circuit voltage \( V_{\text{oc}} \) can be calculated as follows [41, 44, 45];

\[
V_{\text{oc}} = \frac{A' k_B T_c}{e} \ln \left( \frac{f J_{\text{sc}}}{J_{00}} + 1 \right)
\]  

where \( e \) is the fundamental unit of charge, \( f \) is the concentration factor (in this case 1) and \( A' \) is the ideality factor. In addition, the fill factor \( FF \) is given by [41, 44, 45]
\[ FF = \frac{V_{mp}}{V_{OC}} \left[ 1 - e^{\frac{eV_{mp}}{kBT_C} - 1} \right] \]  

(5.7)

where \( V_{mp} \) is the maximum voltage derived at the maximum power point of the cells I-V response curve, which can be approximated by the following relationship [41, 44, 45]:

\[ V_{mp} = k \ast V_{OC} \]  

(5.8)

where \( k \) is typically between 0.7 – 0.8 [41, 46]. For convenience all the constants utilised throughout equations 5.4 – 5.8 are presented in table 5.2. Furthermore, the electrical power output \( P_{pv} \) derived by the silicon C-PV cell with an accompanying hybrid liquid filter can be determined by multiplying the corresponding \( V_{OC} \) and \( FF \) for the \( J_{sc} \) (filtered), as given by [41, 44, 46];

\[ P_{PV} = J_{sc} V_{OC} FF \]  

(5.9)

The thermal power output for the hybrid filters \( P_{th} \) is attained according to the absorption properties exhibited by the spectrally selective filters as follows [41, 44, 46];

\[ P_{th} = \eta_{collector} \int_{2000 \text{ nm}}^{250 \text{ nm}} \varphi_{AM1.5D}(\lambda) \cdot [1 - T_{LIQUID}(\lambda)] \cdot d\lambda \]  

(5.10)

where the absorption of the liquid filters is \( I - T_{LIQUID}(\lambda) \) and we assume the collector efficiency \( \eta_{collector} \) of the thermal component within the C-PVT system is 67%, which is based on the literature value [41, 42, 47, 48].

The dynamic competition between the percentage of the solar irradiance partitioned into usable thermal and electrical energy for each hybrid fluid was revealed through the following expression [41, 42, 47, 48];

\[ \eta_* = \frac{P_{*}}{\int_{250 \text{ nm}}^{2000 \text{ nm}} \varphi_{AM1.5D}(\lambda) d\lambda} \]  

(5.11)

where \( P_{*} \) embodies the thermal (\( P_{th} \)) or electrical (\( P_{PV} \)) power output of the system and \( \eta_* \) represents the energy conversion percentage for this type of energy. It is not enough for
Table 5.2: Values of empirical and constant parameters utilised throughout this work [44,45]. The values represent empirical data derived from longstanding measurements of the performance of a mc-Si cell, under laboratory testing conditions [44, 45].

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Parameter</th>
<th>Value used</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K'$</td>
<td>Empirical parameter in equation (3)</td>
<td>0.01</td>
</tr>
<tr>
<td>$n$</td>
<td>Empirical parameter in equation (3)</td>
<td>0.96</td>
</tr>
<tr>
<td>$m$</td>
<td>Empirical parameter in equation (3)</td>
<td>1.15</td>
</tr>
<tr>
<td>$E_g$</td>
<td>Bandgap energy of silicon C-PV cell</td>
<td>1.12 ev</td>
</tr>
<tr>
<td>$A'$</td>
<td>Ideality factor of silicon cell</td>
<td>0.79</td>
</tr>
<tr>
<td>$k$</td>
<td>Empirical parameter in equation (7)</td>
<td>0.7</td>
</tr>
</tbody>
</table>

A newly designed heat transfer fluid to simply increase the total energy converted within a C-PVT or PVT system, but rather the additional thermal energy captured through the fluids inclusion must compensate for the electrical energy sacrificed through the thermal components integration within the hybrid system [10, 16, 18, 41, 42]. In addition, the modification in the fluids thermophysical or optoelectronic properties must contribute an additional enhancement over the performance dynamics offered by the base fluid in which these additives are suspended [10, 16, 18, 41, 42]. To evaluate whether a hybrid working fluid converted solar energy into thermal and electrical energy more effectively within C-PVT and PVT systems, a merit function was implemented [16, 18, 41, 42].

$$MF = \frac{w \cdot P_{PV} + P_{th}}{w \cdot P_{PV\ (unfiltered)}}$$ (5.12)

where $P_{PV\ (unfiltered)}$ is the electrical power output of the silicon C-PV cell without any liquid filter, and $w$ is the worth factor of electricity to thermal energy. Classically, heat transfer fluids for such applications are evaluated using a 3:1 worth factor of electricity to thermal energy, based on the literature values [41, 42, 48]. However, the magnitude of the worth factor remains highly susceptible to geographical and temporal fluctuations in the price of gas and electricity, which stem from regional differences in political, geological and socioeconomic policy [48]. For example, within the confines of the global...
the worth factor can vary anywhere from 0.79 (mainland China, [49]) to 31.3 (Canada, [49]). Even within Europe, the divergence between the localised gas pricing and affordable electricity push the worth factor from 1.98 in the Netherlands [50] to 4.93 in Germany [50]. Hence the performance and selection of a hybrid heat transfer fluid for PVT application remains inextricably linked to the local dynamics of an economy [48]. The category of fluids proposed in this study were evaluated using an average value of the worth factor derived across the entire European region using economic data from 2018 [50, 51], which corresponded to a worth factor of 3.09 ± 0.89. This can allow for the individual molecular structures characterised to be uniquely tailored towards deployment in specific geographical locations, in order to maximise their combinatory conversion efficiency when deployed within a PVT system.

5.4 Results and Discussions
5.4.1 Optical transmittance and fluorescence of liquid LDS filters

The optical transmittance of the fluid remains the main material attribute through which the electrical and thermal performance of each liquid filter is evaluated. The optical transmittance of all six fluids listed in table 5.1 are presented in figure 5.3 (P166 – a, P282 – d, P183 – g) and figure 5.4 (P187 – a, P181 – d, P205 – g) with the accompanying spectral properties of the base fluid and ideal conversion window of the underlying PV cell provided for comparison. The figures illustrate how the base fluid, i.e. ethylene glycol, demonstrated a substantial 95% - 98% transmittance over the 250 nm – 1000 nm range while also absorbing a considerable fraction of the longer wavelength irradiation (1000 nm – 2000 nm). These same optoelectronic features highlight why ethylene glycol has become one of the most prominent heat transfer fluids for moderate temperature solar thermal applications and, correspondingly, why it was selected as the basis of the proposed candidate fluids. Moreover, the absorption selectivity offered through its characteristic structure directly aligns with the idealised partitioning of the solar spectrum.
into its respective electrical and thermal components identified in figure 5.1 a. As the entire assortment of organic structures outlined in table 5.1 are known to heavily absorb within the 250 nm to 500 nm range (see chapter 4), then their addition into the base fluid should further complement the spectral matching between the two collection elements (thermal and electrical) as is reflected in figures 5.3 (a, d, g) and 5.4 (a, d, g).

Taking into consideration the shape of the ideal PV window for mc-Si highlighted in figures 5.3 and 5.4 (grey shaded region), any subtle deviations introduced into the optical properties of the fluid through a lack of molecule’s suitability in ethylene glycol could negatively influence the overall merit of the fluid’s configuration. The onset and later development of this behaviour can be clearly seen when examining the variation in optical transmittance experienced by each type of fluid with the continuous increase of the loading concentration of each molecule. At low loading concentrations (5 x 10^{-3} wt%) the molecular structure of P205 (figure 5.4 g), P187 (figure 5.4 a) and P181 (figure 5.4 d) displayed remarkable solubility in ethylene glycol as demonstrated by the minor loss in transparency (< 5 %) within the optimal PV window, sustained through each molecules inclusion. Other structures (P282, P183, and P166) suffered a more pronounced deterioration within the noteworthy spectral region ranging from 12% (P183 – figure 5.3 g) to 20% (P166 – figure 5.3 a), owing to their partial solubilities within the solvent. As the concentration of each distinct molecule was gradually increased the divergence between the spectral properties of each hybridised working fluid became further evident. Under moderate loading conditions significant changes in the absorption band of each luminescent down-shifting fluid was registered, with the emergence of partial solubilities contributing to a 10% (P205 – figure 5.4 g) to 40% (P166 – figure 5.3 a) decrease in transmittance over the 375 nm – 1025 nm region. Finally, at the highest loading concentration of 0.5 wt% all the structural iterations of the phenanthroline molecule excluding P181 (figure 5.4 d) had exhibited substantial reductions (30% - 80%) in their overall transparency. However, considering that
solubility remains a function of temperature, any partial solubilities that arose may be 
accommodated under the considerably higher operating temperatures (100 °C – 250 °C) 
typically encountered throughout combined heat and power applications. Consequently, in 
order to effectively identify the optimal loading concentration of each heteroaromatic 
molecule, the electrical energy lost through the emergence of partial solubility (and any other 
accompanying scattering losses which may arise as a result) must be compensated for by the 
additional thermal energy captured by the hybridised material. Nevertheless, the intense 
absorption contributions generated with small amounts of each molecule even when 
encapsulated in considerably thinner filters (traditional filters are 10 mm – 20 mm thick while 
the configuration investigated was 2 mm) indicate that a more compact PVT design may be 
achieved with phenanthroline based hybridised heat transfer fluids.

Unlike conventional heat transfer fluids which solely offer enhanced thermophysical 
properties, the fluorescent nature of the fluids investigated here require an accurate depiction 
of their fluorescent characteristics. This ensures that the impact of each molecule’s 
fluorescent contribution towards the performance of the PV cell within the PVT system can 
be systematically examined over the concentration range explored. Fluorescent pigments are 
often added to commercial heat transfer fluids to assist in the identification of leaks in both 
PT and PVT systems. Thereby, the use of these materials ensures that any deterioration in the 
temperature of the working fluid(s) are readily recognisable. To the knowledge of the author 
this is the first-time when controlled fluorescence has been strategically deployed to 
counteract the electrical energy lost. This was achieved through modification of the heat 
transfer fluid in SBS applications.

The structure of the six organic and organometallic working fluids outlined in table 
5.1 can be further classified according to their luminescent intensity, which is provided in 
figures 5.3 (P166 – b, P282 – e, P183 -h) and 5.4 (P187 – b, P181 – e, P205 – h) – with the 
integrated emission intensity as a function of concentration provided in each inset. The internal
Figure 5.3: Optical transmittance of P166 (a), P282 (d) and P183 (g) loaded ethylene glycol based hybrid heat transfer fluids - with the optimal conversion bandwidth of the mc-Si cell highlighted in grey, and their corresponding fluorescent intensity as a function of the loading concentration highlighted in b, e, and h respectively. The integrated emission intensity ($I_{\text{integrated}}$) as a function of the concentration is provided in the insets. The impact of each liquid optical filter on the short circuit current density ($J_{sc}$, A cm$^{-2}$) of the ‘filtered’ cell in response to an increased loading of each organic fluorophore (c – P166, f – P282, i – P183) at a cell temperature of 35 ± 1°C: with the performances of the pristine base fluid (ethylene glycol – black dotted line) and unfiltered (no liquid filter – red dotted line) provided for comparison.
Figure 5.4: Optical transmittance of P187 (a), P181 (d) and P205 (g) loaded ethylene glycol based hybrid heat transfer fluids - with the optimal conversion bandwidth of the mc-Si cell highlighted in grey, and their corresponding fluorescent intensity as a function of the loading concentration highlighted in b, e, and h respectively. The integrated emission intensity (I_{\text{integrated}}) as a function of the concentration is provided in the insets. The impact of each liquid optical filter on the short circuit current density \(J_{\text{sc}}, \text{A cm}^{-2}\) of the ‘filtered’ cell in response to an increased loading of each organic fluorophore (c – P187, f – P181, i – P205) at a cell temperature of 35 ± 1 °C: with the performances of the pristine base fluid (ethylene glycol – black dotted line) and unfiltered (no liquid filter – red dotted line) provided for comparison.
structure of each fluid exhibited an emission band characteristic of the distinctive molecular framework(s) outlined in chapter 4, with every one of the working fluids except P181 (figure 5.4 e) exhibiting weak to strong fluorescence over the 400 nm – 550 nm range. The lack of fluorescent intensity was accredited with an intense manifestation of non-radiative relaxation pathways within some of the fluids considered. This was primarily driven by the molecular structure of each candidate - see chapter 4. The fluorescence intensity attributed to each distinct species allowed the fluids to be classified as either emitters (indicating a moderate degree of fluorescence) or absorbers (indicating a strong degree of non-radiative relaxation pathways). Under this scenario P282, P205, P183 and P166 were all considered emitters while P181 and P187 were considered absorbers. Although the purpose of this study was to examine the influence of the loading concentration over the corresponding fluids optical properties and additionally, to identify the optimal loading concentration of each molecular species, a more detailed study into the physical and thermophysical behaviour of these materials when subjected to extreme temperature and irradiance remains warranted. Such a study would not only allow the expected operational lifetime of each fluid to be determined, but also assist in pinpointing which environmental factors (temperature, pH, reactivity of encasing material) drive each molecular additives’ degradation over more moderate to long term timeframes. The insights gathered throughout the study would also serve to further refine the synthesis strategy, with additional functionalisation of the phenanthroline backbone through subsequent substitutions with potentially innumerable different moieties providing an ever-expansive catalogue of potentially enhanced hybridised fluids.

5.4.2 Performance of C-PV solar cell with liquid LDS filters

The short circuit current density (J_{sc}) of the mc-Si C-PV solar cell with and without the optical filters at a fixed temperature is provided in figures 5.3 (P166 – c, P282 – f, P183 – i) and 5.4 (P187 – c, P181 – f, P205 – i). It can be observed that, independently
of the internal structure of the fluid, a reduction in the short circuit current density of the cell transpires with the magnitude of this reduction in $J_{sc}$ varying for the different fluids employed. Even at the lowest concentration of $5 \times 10^{-3}$ wt% the inclusion of the molecular species contributed to a 12% (P282, P187), 15% (P205, P183) or 23% (P166, P181) decline in $J_{sc}$ as compared to that achieved with the base fluid. These differences in the rate of decline in $J_{sc}$ originate from the subtle alterations in optical transparency as well as from the emissive capability across the range of materials selected. As the concentration was increased the $J_{sc}$ of the cell was reduced further, with the absorption band of the higher concentration fluids directly affecting the silicon C-PV cells spectral response bandwidth. It is expected that the reduced transmittance of the hybrid fluids over the Si cells spectral response bandwidth could lead to a reduction in the overall conversion efficiency of the PVT system, when compared with base fluid. This is primarily due to the energetic and financial favourability of generating sustainable electricity over the substitute thermal energy, making the thermal performance requirement imposed on the fluids much more heightened.

To resolve whether the fluorescent contributions emanating from each candidate could indeed mitigate some of this sacrificial electricity, closely examine and compare the transmittance and $J_{sc}$ for the emitter - P282 and the absorber - P187 at the lowest concentration. P282 sustains a large deterioration in the signature 375 nm – 1005 nm spectral window (figure 5.3 d) whilst still maintaining a modest ~12% decrease in the $J_{sc}$ (figure 5.3 f). Conversely the absorption band of P187 remains constrained outside of this spectral window (figure 5.4 a). Its emission intensity is lower by a factor of 3 (figure 5.4 b), but the loss incurred in the $J_{sc}$ remains the same in magnitude i.e. ~12% (figure 5.4 c). This could indicate that some of the energy lost through the extension of the fluids’ absorption band directly into the spectral responsivity window of the C-PV cell is being redistributed back through luminescence into the PV cell for capture. At the same
concentration the combination of the intense emission delivered by P205 (figure 5.4 h) and its lack of absorption within the Si C-PV cells responsivity bandwidth (figure 5.4 g) should have resulted in an even greater re-distribution of this lost energy. Consequently, the enhancement originally identified as a result of the fluorescent properties of P282 may in fact be a combination of fluorescence and scattering contributions which arise as a result of the partial solubility of the P282 compound in ethylene glycol. Over the relatively short Stokes-shift (~150 nm) exhibited by each molecular structure the spectral responsivity of the C-PV cell increases dramatically from 0.008 A W\(^{-1}\) to 0.31 A W\(^{-1}\) (figure 5.1a). However, this modulation of the incoming solar spectrum may not be substantial enough to induce a clear enhancement in PV performance. Subsequent modification of the phenanthroline molecular scaffolding through the inclusion of metal ions such as EU(III) could push the spectral-shift in energy further into the 650 nm – 700 nm region - where the spectral responsivity of the mc-Si C-PV cell increase to 0.5 A W\(^{-1}\) - 0.6 A W\(^{-1}\) (figure 5.1a). This modification of the molecular species would permit a more detailed correlation between the down-shifting effect of the incident spectrum and its contribution towards the C-PV cells performance to be carried out.

The reduction in short circuit current density (\(J_{sc}\)) and open circuit voltage (\(V_{oc}\)) as a function of the mc-Si C-PV solar cells temperature is provided in figure 5.5. The figure clearly illustrates the C-PV cell’s filtered and unfiltered response to fluctuations in the cells’ temperature created as a result of the irradiance transmitted through each liquid filter. The behaviour of the C-PV cell under the different filtered scenarios outlined in figures 5.3 and 5.4 is further confirmed through the trends observed in both \(J_{sc}\) and \(V_{oc}\). This highlights how the unfiltered and filtered cell’s electrical performance followed a well-established relationship over the 25 °C to 38 °C operating conditions. The separation between the decrease in \(I_{sc}\) and \(V_{oc}\) sustained through the application of different liquid filters remains relatively unchanged over the temperature range explored. This behaviour
confirms that any enhancement reported through the subsequent modelling of the PVT system when fitted with the same liquid optical filters is representative of tangible improvements in the fluid’s physical and optical properties.

Figure 5.5: Variation in the short circuit current density \(J_{sc}, \text{A cm}^{-2}\) and open circuit voltage \(V_{OC}, \text{Volts}\) of the mc-Si cell in response to variations in cell temperature, with various 2 mm thick liquid optical filters (P282 – square, P205 – circle, P187 – triangle, P183 – inverted triangle, P181 – pentagon, P166 – diamond). The unfiltered cells performance as well as that achieved with the pristine base fluid (ethylene glycol) is provided for comparison.

5.4.3 Heating rate and stagnation temperature of hybrid fluids

Ideally, the enhanced filtering capabilities stemming from the inclusion of each molecule within the hybridised fluid will lead to an improvement in the rate of heating experienced by each working fluid, under the modulated solar spectrum. In this study,
although all the hybrid fluids yielded lower electrical outputs, their temperature response and the C-PV cells response when shielded by the different configurations of liquid filter revealed a compensatory thermal output of the system (figures 5.6 and 5.7). The temperature of the working fluids (figure 5.6; P166 - a, P282 - c, P183 – e & figure 5.7; P187 – a, P181 - c, P205 - e) remained in most cases moderately lower than that achieved with the pristine base fluid, with the noticeable exceptions of P205 (figure 5.7 e), P187 (figure 5.7 a), P183 (figure 5.6 e) and P181 (figure 5.7 c). Even when considering the shielding effect provided for the C-PV cell by the liquid optical filters, their addition into the system appeared to create additional unwanted thermal fluctuations (2 °C – 3 °C) in the C-PV cells operating temperature. However, considering the close physical proximity between the thermal and electrical collection elements of the PVT system, and the fact that the thermal collector remained uninsulated from the surrounding ambient conditions, thermal cross leakage between the elements could help explain the relationships reported in both the C-PV cells temperature and that of the working fluid.

In this manner the instantaneous change in the temperature of the system ($\Delta T_{\text{system}}$) is the by-product of the instantaneous fluid temperature ($\Delta T_{\text{fluid}}$) and filtered cell temperature ($\Delta T_{\text{cell}}$). Assuming negligible thermal transfer to the surrounding environment, the impact of the alterations in the constitution of each fluid can be correlated with their corresponding thermal performance. The enhancement in performance achieved through each compound is best evaluated at the lowest concentration, where the extent of intermolecular interactions and aggregative processes such as $\pi-\pi$ stacking becomes greatly diminished. Under this scenario the fluorescent compounds delivered a 15 % (P181), 14% (P187), 13% (P205), 12% (P183) and 4% (P282) enhancement in the stagnation temperature of the fluid, when compared with the base fluid. The presence of P166 contributed to a 2% decline in the thermal performance of the fluid, this effect being reversed by increasing the amount of the molecular species.
dispersed throughout the working fluid. The enhancements are striking when considering how more intricate, complex and expensive constituents such as silica-coated silver nanoplates or silver nanospheres have delivered 17% - 44% improvements in the temperature response of similar base fluids [41, 48]. Taking into consideration the organic and organometallic nature of the constituents studied, and their more environmentally friendly and scalable synthesis procedure - which can consistently deliver high yields, the premise of these phenanthroline derivatives for SBS-PVT applications looks promising.

The physical origin of the enhanced thermal capabilities presented by the hybrid fluids lies in the physical properties of the substituted functional moiety. P187, for example, contains fluorine, whose importance in charge transfer throughout many different mineral species is well documented [52] and could account for the enhanced thermophysical properties reported here. Similarly, P181 contains the moderately conductive element iron whose thermal conductivity (~ 94 W m⁻¹ k⁻¹) significantly exceeds that of the pristine base fluid whose thermal conductivity is 0.25 W m⁻¹ k⁻¹ [53]. While the thermal conductivity of iron is not as high as silver (thermal conductivity of 403 W m⁻¹ k⁻¹) the adaptability of the synthetic protocol enables the inclusion of metal and metallic elements through simple substitution reactions in the synthetic synthesis, and this will be the focus of a future study. Considering the enrichment in the thermophysical and optical properties of the working fluid accessible through the completely organic and organometallic additives outlined in table 5.1, their application in SBS-PVT systems at low concentrations appears exceedingly practical. When combined with the plethora of additional synthetic alterations of the phenanthroline scaffolding, forming ever more
Figure 5.6: Variation in the temperature response ($\Delta T$) of various liquid optical filters (a – P166, c – P282, e – P183) and the accompanying change in the operational temperature ($\Delta T$) of the mc-Si solar cell (b – P166, d – 282, f – P183) under 1000 W m$^{-2}$ solar simulator exposure. The performance of the unfiltered system as well as that achieved with the pristine base fluid (ethylene glycol) is provided for comparison.
Figure 5.7: Variation in the temperature response ($\Delta T$) of various liquid optical filters (a – P187, c – P181, e – P205) and the accompanying change in the operational temperature ($\Delta T$) of the mc-Si solar cell (b – P187, d – 181, f – P205) under 1000 W m$^{-2}$ solar simulator exposure. The performance of the unfiltered system as well as that achieved with the pristine base fluid (ethylene glycol) is provided for comparison.
intricate and diverse sets of suitable derivatives of the starting materials studied herein, may prove even more fruitful in the future. To further complement and enrich the insight into the relationship between each molecular constituent and its contribution towards the thermophysical properties of the resulting fluid requires a more detailed standalone physical characterisation of the hybrid fluids.

5.4.4 Impact of hybrid fluids on performance of PVT system

Although the detailed optical and physical characterisation of each fluid candidate revealed the promise of each molecule for PVT and SBS applications, understanding the actual influence of each working fluid and its expected behaviour within the system remained essential. The model outlined in section 5.2.4.2 in conjunction with the empirical optical data acquired was used to derive the electrical and thermal output efficiency and the corresponding merit function of each fluid, when operating within a fixed PVT architecture specified in the models’ formalism. The culmination of these metrics is often used to describe the beneficial aspects of modifying any one parameter of a candidate fluids properties, rather than alternatively trying to justify the possible combination of an overabundance of alternatives [14, 39, 41, 42, 48]. Figures 5.8 and 5.9 present the merit function (MF), thermal output efficiency (‘thermal energy’ in cyan) and electrical output efficiency (‘electricity’ in green) as calculated by the theoretical model provided in section 5.2.4.2.

The electrical output efficiency of the unfiltered C-PV cell (‘unfiltered electricity’ in yellow) is provided in the figures for comparison. It should be noted that the optical transmittance of the fluids shown in figures 5.3 and 5.4 were used to determine the MF for each fluid, and that the worth factor value adopted represented the average market value of electricity to thermal energy (derived through natural gas) across the entire European region in 2018 [50,51].
In terms of overall optical efficiency, figures 5.8 (P166 – b, P282 – d, P183 - f) and 5.9 (P187 – b, P181 - d, P205 – f) clearly demonstrate how using phenanthroline based ‘absorbers’ and ‘emitters’ as liquid SBS filters for Si based PVT collectors yields a considerably superior optical efficiency. The intense absorption contribution arising from the inclusion of the molecular species within the base fluid (figures 5.3 and 5.4) resulted in optical efficiencies ranging from 25.3 % (figure 5.9 f – P205 at 0.005 wt%) to 62.6 % (figure 5.8 b – P166 at 0.5 wt%). Furthermore, when compared with the standalone PV system the enhancements translate into an additional 8 % - 45 % increase in the economic value of the energy captured. The MF value of the PVT systems, independently of the selected filters, is larger than 1, as shown in figures 5.8 (P166 – a, P282 – c, P183 - e) and 5.9 (P187 – a, P181 - c, P205 – e), implying that the luminescent fluid-based SBS systems exhibit superior performance when directly compared to the classical PV systems.

In particular, the P166 filter produced the highest MF value at the most extreme loading concentration employed (0.5 wt%), yielding a 71% greater economic value in return, when compared with the standalone PV. The immense improvement in the performance of the combined heat and power system is due to the substantial increase in the performance of the thermal collector, as more and more of the distinctive molecule is dispersed throughout the working fluid. In the case of P166 the electrical and thermal output efficiencies at the lowest concentration were 12.4% and 22.4%, respectively (figure 5.8 a), with the threefold increase in concentration pushing the efficiencies of each element to 2.0 % and 60.7 %, respectively (figure 5.8 a). In addition, the presence of the organic and organometallic derivatives within the PVT system provided MF values exceeding that of the PVT system with the typical ethylene glycol filter. These additional modifications in the spectroscopic properties of the fluid resulted in a 1.7 % (P166 at 0.005 wt%) to 60.9 % (P205 at 0.5 wt%) increase in the economic value of the energy captured, when compared with the pristine base fluid. Evidently the series of organic and
Figure 5.8: Merit function of a C-PVT system incorporating mc-Si solar cells for each liquid optical filter (a – P166, c – P282, e - P183) according to the average worth factor derived across the European (EU – black circle) region, with the Irish (IRE – red triangles) economy added for comparison: where the path length of the filter was 2 mm the filled region (light blue) represents the performance of the base fluid under the same conditions. Variation in the percentage of thermal energy (photothermal - cyan) and electricity (photovoltaic -green) delivered by the combined heat and power system for each liquid filter configuration (b – P166, d – P282, f - P183), where the electricity delivered via an unfiltered system (unfiltered electricity – yellow) is provided for comparison.
Figure 5.9: Merit function of a C-PVT system incorporating mc-Si solar cells for each liquid optical filter (a – P187, c – P181, e – P205) according to the average worth factor derived across the European (EU – black circle) region, with the Irish (IRE – red triangles) economy added for comparison: where the path length of the filter was 2 mm and the filled region (light blue) represents the performance of the base fluid under the same conditions. Variation in the percentage of thermal energy (photothermal - cyan) and electricity (photovoltaic - green) delivered by the combined heat and power system for each liquid filter configuration (b – P187, d – P181, f – P205), where the electricity delivered via an unfiltered system (unfiltered electricity – yellow) is provided for comparison.
organometallic filters developed seems to present significant advantages over other alternative filters for PVT applications.

The susceptibility of the worth factor to geographical and economical fluctuations in the dynamic between the widespread availability of electrical and thermal energy allows a strategic selection of the locations where full-scale PVT systems can be established to further help, explore and refine the approach developed herein. As the value of the worth factor depreciates the economic merit of the additional energy captured through the adaptations in the fluids’ spectral properties becomes even more heightened [48]. Within the context of the initial European case study conducted, the countries identified as most favourable for full-scale testing are Spain (2.83), Portugal (2.92), Italy (2.27), Sweden (1.63), Netherlands (1.98), Greece (2.52) and Bulgaria (2.29). In the case of Ireland where the residential price of electricity and natural gas is 0.254 €(kWh)$^{-1}$ and 0.08 €(kWh)$^{-1}$ respectively [50, 51], the compensatory heat output offered by the fluid’s enhanced absorption capabilities is further constrained by having to compensate for the economic divide between the two (electrical and thermal) alternative energy sources. Hence, in the Irish economy a higher concentration of each material would be required in order to sustain a noticeable enhancement over the economic merit already achieved with the pristine base fluid, and this is indeed reflected in figures 5.8 and 5.9. Outside of the European (EU) region, international countries which offered cost-effective alternatives locations included mainland China (0.79) and New Zealand (2.71). Considering that an insufficient amount of previous work has attempted to address the massive divergence in the applicability of the fluid augmentations towards specific geographical locations [48]. The tangible capability of the additives developed, to surmount the economic factors imposed by this lack of awareness makes the identification of structures which offer a real economic value more convoluted. This reinforces the need to evaluate each candidate fluid under the socioeconomic conditions of where it is planned on being implemented,
in order to adequately ensure the full justification of the semi-empirical modelling results retrieved.

Although the semi-empirical model outlined in section 5.2.4.2 allowed for the merit of including each phenanthroline derivative in an SBS-PVT system to be revealed, the possible influence of aggregative or other intermolecular interactions pathways on the transmittance spectra registered is not considered. Considering that the influence of such interaction mechanisms on the resultant thermophysical properties of the working fluid remains unknown. Consequently, the lack of consideration of these unwanted molecular interaction mechanisms within the model necessitates the strict corroboration between the semi-empirical relationships resolved and those revealed through physical characterisation of the same working fluids. Evidently even at the lowest concentration, where very little evidence of the apparent unwanted interactions is manifested, the fluids developed exhibited a 2 % - 10 % increase in the economic value of the energy captured by the system, as compared with pristine ethylene glycol. When combined with the fact that at the same loading concentration the hybrid fluids exhibited a 4 % - 15 % increase in their stagnation temperature, the fluids improved thermal performance seems more realistic.

5.5 Conclusion

A series of luminescent phenanthroline based liquid filters was developed for spectrum beam splitting PVT applications with monocrystalline silicon cells. The series of molecular compounds were dispersed in ethylene glycol and their optical transmittance, fluorescence, and thermal response to the solar flux measured. The hybrid fluids exhibited a significantly higher absorption in the ultraviolet and visible wavelengths, as compared with the pristine base fluid. This complementary absorption contribution towards the composite fluids resultant spectroscopic properties attributed to a 4 % - 15 % increase in the stagnation temperature reached by the working fluid. In
addition, indoor static stagnation tests were conducted to investigate the effect of each hybridised fluid on the electrical performance of a mc-Si C-PV cell. Regardless of the filter’s internal structure a lower short circuit current, and, thus, lower electrical conversion efficiency was reported. To minimise the electrical energy loss through merging the thermal and electrical components, lower concentrations of each compound were more appropriate. This combined with the capability of the molecular structures to elicit not only an intensified rate of heating, but also complementary fluorescence, makes them exceedingly suitable for addressing some of the shortcomings identified in alternative working fluid strategies. The ability of the proposed fluids to more effectively convert solar irradiance into electricity and thermal energy within a PVT system was evaluated using a merit function. The intense absorption contribution, arising from the inclusion of the molecular species within ethylene glycol, resulted in optical efficiencies ranging from 25 % to 63 %. The additional modifications in the spectroscopic properties of the fluid yielded a subsequent 2% - 61 % increase in the economic value of the energy captured, when compared with pristine ethylene glycol. Overall the results of the present work provide a new organic basis for effectively designing high performance spectrally selective heat transfer fluids for SBS-PVT applications.

5.6 References


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Chapter 6
Designing and Optimising The Efficiency of Plasmonic Luminescent Down-Shifting Systems Using a Transfer Matrix Modelling Approach

6.1 Overview
In the pursuit of highly efficient solar collectors the fundamental interactions of light with the semiconducting material must be modulated, to increase the collection efficiencies achievable. Incorporating luminescent species within a semi-transparent framework which can be retrofitted onto small- or large-scale photovoltaic devices, offers a passive approach toward expanding the range of wavelengths over which the conversion process can effectively occur. This passive strategy is called luminescent down-shifting (LDS) and it has undergone many iterations since its inception in the early 1970’s. The most recent of which has been the inclusion of metal nanoparticles (plasmonic luminescent down-shifting – PLDS), which have assisted in promoting the photoluminescent and physical characteristics of the semi-transparent frameworks, in which they are embedded. However, with each additional component comes a cascade of additional loss pathways which must be addressed, if the PLDS application is to offer a tangible alternative to some of the more invasive fundamental strategies being pursued.

In this study through a set of simple modifications in the design of an LDS/PLDS device, some of these additional loss pathways have been addressed. Two initially proposed device designs were considered, with the deviations between the optical response of each iteration helping to establish a set of design considerations for this type of architecture. The optical behaviour of the device’s was modelled utilising a transfer matrix approach, whose outputs were validated and correlated with the behaviour and performance of physical devices, characterised under real world experimental conditions. The newly aptly proposed structure-enhanced LDS (SE-LDS) and structure enhanced PLDS (SE-PLDS) designs generated a predicted 7% to 20% enhancement in the collection
efficiency, as inferred through the short-circuit current. Through downsizing the thickness of the LDS/PLDS layer an additional 0.4 % to 3% increase in the enhancement was obtained. The structures proposed also offer an advantageous flexibility to incorporate innumerable additional optical structures to help further enhance and promote the potential synergetic interactions between the individual design components.

6.2 Introduction

In conventional efforts to modularize photovoltaic (PV) cells into large-scale industrial panels, a series of polymeric and glass layers are integrated into the panel architecture to provide a protective shield from the harsh environmental conditions (temperature, humidity etc.) [1]. The encapsulating materials, typically a combination of poly-methyl-methacrylate (PMMA) and tempered glass derivatives, impinge upon the conversion dynamics of the underlying PV technology [2-4]. Consequently, the addition of the encapsulants heavily-influences the spectral response [2-4] and short-circuit current density [2-4] generated within a PV device, particularly within the ultraviolet region (300 nm – 400 nm) where PMMA exhibits a sharp spectral cut-off [2-4]. To counteract these additional modular losses, the fundamental architecture of the active material is drastically altered through surface passivation [1, 4-6], surface texturing [1, 4-6], or through tailoring the materials band-gap dynamics through selectively doping the crystal lattice [1, 4-6]. However, for each additional processing stage implemented into the devices design, the fabrication costs grow [7-9]. To continue the reductions experienced in PV pricing [7-10], alongside the continuously improving conversion efficiencies [7-10], various alternative intricate architectures has been suggested, developed, manufactured and characterized [2-6]. As the complexity in PV architecture is growing, optical modelling starts to become the preferred tool to resolve and decouple the complex physical phenomena. Often, the optical modelling is used for the stratified structures, to maximize their energy harvesting potential [2, 3, 11].
As previously mentioned in this thesis, the plasmon enhanced luminescent down-shifting (PLDS) is a strategy focused on alleviating the narrow responsivity of PV technologies through the incorporation of energy adaptive materials that can offer an alternative approach in which no alteration of the active material is required [3, 4, 6]. Replacing the inactive encapsulating material with a semi-transparent framework, doped with selectively absorbing species which modulate the solar spectrum, alleviates the losses stemming from the parasitic absorption exhibited by PMMA or other encapsulating materials [2-6, 11, 12]. Through the inclusion of metal nanoparticles (MNP’s) within the encapsulating layer, a higher degree of control and promotion of the photoluminescent behaviour of the embedded luminescent material is achieved. The intense highly localised electromagnetic fields created on the surface of the MNP’s are altering not only the photoluminescent properties of the luminescent polymer, but also advantageously attune the physical properties of the nanocomposite encapsulant [13-17]. However, the non-ideal optical properties exhibited by most encapsulating materials (n ~ 1.4 -1.6) in combination with the myriad of additional loss mechanisms introduced through the presence of the luminescent material and MNP’s, requires further improvement from the classical PLDS approach.

Typically, the influence of each PLDS iteration on the conversion dynamics of a PV device has been ascertained through experimental trial and error [3, 11]. This implies fitting each combination of encapsulant, luminescent material and MNP directly onto a PV structure and recording the difference in performance acquired [3, 11]. In efforts to further understand the impact of the optical properties of a PLDS layer on the electrical characteristics of a pristine solar cell architecture, several complementary modelling approaches have been developed [18-22]. This schema consists of either utilising wave based optical relationships or more probabilistic photon-based approaches to derive information about the fundamental properties and performance of the simulated optical
These PLDS strategies, in conjunction with the capability of thin-film structures to suppress the reflection losses arising from the front surface of a device, offer further means of alleviating the additional losses introduced through the PLDS layer [23-25]. Through further refinements in the spectrally selective properties produced by the thin film, a set of additional synergies between the luminophore and the anti-reflective coating (ARC) could potentially be established [23-25]. Consequently, in order to understand the behaviour of this complex design a combination of theoretical and experimental approaches is required.

In this study a generalized transfer matrix model was modified to examine the impact of simple single- and double-layer thin-films, on the optical and electrical behaviour of a pristine monocrystalline silicon cell. Each type of structure was represented using optical materials frequently encountered in the deposition of highly transparent thin-film coatings. The cost-effective feasibility of each materials integration into the solar cell manufacturing process was also considered in their selection. Through the successive experimental fabrication and optical characterization of different encapsulating, substrate, and thin-film structures, the outputs generated by the model were correlated to performances achieved under laboratory conditions. This enabled any divergences between the expected behaviour (modelled) and the actual behaviour (measured) of the device to be quantified, resolved and utilised to re-calibrate the performance metrics employed in the modelling environment. The design considerations encountered with each type of thin-film structure, and their capability to modulate the optical interactions of light within it, was explored and optimised before their subsequent inclusion in the proposed structure enhanced luminescent down-shifting (SE-LDS) devices. Two initial designs of the SE-LDS device were developed and characterised theoretically, with the impact of each individual optical component (LDS layer, thin-film element) on the collective performance of the device, investigated. The impact of the
film’s composition, structure, and optical thickness on the underlying architectures conversion efficiency was further expanded upon to ensure that the device’s energy-harvesting potential was maximized. Finally, the study outlines the initial design requirements for passive SE-PLDS devices, which can offer an elegant alternative design whose efficiency is enhanced beyond that achieved with conventional PLDS approaches.

6.2.1 Structure Enhanced Plasmonic Luminescent Down-Shifting Devices

The number of potential loss mechanisms available within a photovoltaic device increases through the direct addition of a luminescent down-shifting layer [11]. The non-ideal optical properties of the photoluminescent materials available, coupled with the additional losses arising as a result of the parasitic absorption and poor photo-stability of the encapsulating materials employed [3, 11], allow for further design revisions. This is further compounded by increased reflection losses which arise at the front surface, as a direct result of the typically low refractive index \( n = 1.2 – 1.6 \) of the encapsulating materials employed in the fabrication of LDS devices to date [3, 11]. This series of different loss mechanisms does not even begin to consider the lack of control granted over the optical properties of the nanomaterials, utilized in plasmonic luminescent down-shifting (PLDS) devices to augment the optical characteristics of the photoluminescent material present [2, 13, 26-30]. Additionally, the inclusion of nanomaterials within a polymeric network, also supports their tendency to aggregate upon exposure to fluctuations in the surrounding environmental conditions (thermal, electrical etc.) [2, 13, 26-30].

Incorporating additional optical structures into the PLDS architecture (figure 6.1.a), whose design is based upon simple thin-film antireflection coatings, could help address and mitigate some of these additional loss mechanisms [23-25]. This aptly defined SE-PLDS device offers the potential to reduce the reflection losses arising from the divergence between the refractive index of commonly utilised encapsulating materials.
and the underlying substrate material. Through the careful control and consideration of the structure’s optical properties, the reflection suppression capabilities of the additional structure can be tailored to offer maximum reflectivity close to the peak absorption of the photoluminescent species (figure 6.1.b.iii – green). Thereby, allowing for the potential recycling of those photons which did not previously undergo photoluminescence (figure 6.1.b.iii). Curtailing the structure’s reflectivity across the remaining high responsivity window of the underlying solar cell (figure 6.1.b.iii – grey), ensures that the majority of the photons impinging the device within this spectral range can generate charge carriers within the semiconducting material. These structures in combination with silver nanoparticles embedded within the encapsulating material, offer a multi-teared targeted design approach capable of alleviating the primary loss mechanisms instigated via the addition of the PLDS/LDS layer. Moreover, they offer the possibility of increasing the longevity of such retrofitted devices [13, 29].

6.3 Experimental and Modelling Approaches
6.3.1 Modelling the SE-PLDS Devices
6.3.1.1 The Transfer Matrix Method

The proposed solar cell architecture is assumed to consist of two distinct layers (figure 6.1.b); an optically thick down-shifting layer whose thickness is on the order of 10 μm – 100 μm and a thin-film constituent whose thickness ranges from 20 nm – 200 nm depending on the spectral responsivity of the underlying photovoltaic material upon which the device is constructed. The thin-film structural component is sandwiched between the substrate (figure 6.1.b.ii) and the down-shifting layer or, in an alternative design, directly on-top of the down-shifting device (figure 6.1.b.i). Within the multi-layered structure, each material of different thickness (d), refractive index (n) and extinction coefficient (k) is assumed to have uniform optical properties along the x- and y-axis, with the individual interfaces stratified along the z direction. Throughout the design process, a broad range of commonly utilised material candidates within the device.
**Figure 6.1:** (a) Schematic of a structure-enhanced photovoltaic device, highlighting the individual design components; a semi-transparent host matrix encapsulating a photoluminescent material in isolation or in combination with a metal nanostructure, the underlying photovoltaic technology as well as a ‘spectrally selective’ structure element. (b i & ii) Initial architectures for a structure-enhanced plasmonic luminescent down-shifting (SE-PLDS) device and (b iii) the operating principle upon which the device is based. (b iii) The structural elements reflection profile (b iii – green) is tailored to yield a maximum reflectance within the absorption window of the fluorescent material utilised (b iii – blue) while minimising the reflectivity across the emission range (b iii – red) and high responsivity window (b iii – grey) of the underlying photovoltaic technology upon which the device is built. (c) The complex 3-dimensional structure of a SE-PLDS device, consisting of a cascading series of layers of differing refractive index \((n_1, n_2, \ldots)\) can be represented as a one-dimensional periodic structure within the confines of a transfer matrix method: assuming the refractive index within each individual layer is homogenous. The transfer matrix method models the optical behaviour of a plane wave composed of two mutually orthogonal linearly polarised components (Transverse electronic – TE and transverse magnetic-TM modes) as they propagate through the structure along the direction of propagation (r).
Throughout the design process, a broad range of commonly utilised material candidates were incorporated into both single- and double-layered thin-film structural components within the device. This included magnesium fluoride (MgF\(_2\)), silicon oxides (monoxide – SiO and dioxide -SiO\(_2\)), silicon nitride (Si\(_3\)N\(_4\)), zinc derivatives (sulphide – ZnS, oxide – ZnO and aluminium zinc oxide –Al-ZnO), tantalum pentoxide (Ta\(_2\)O\(_5\)), titanium dioxide (TiO\(_2\)), indium tin oxide (ITO), as well as hypothetical ideal materials.

To examine the impact each design consideration had on the overall SE-PLDS device, a transfer matrix model was adopted to model the reflectance and transmittance behaviour of the system under each individual design revision. The merit of the transfer matrix models approach is its simple, yet computationally effective determination of the optical interference matrix for a particular multilayer structure [31-37]. Considering a system of N layers prepared on a substrate as shown in figure 6.2, with each layer (i) within the system specified via its complex refractive index (\(n_i = n + jk\)) and thickness (\(d_i\)). Under normal incidence conditions (\(\theta_i = 0^\circ\)) and in an external surrounding medium of refractive index (\(n_0 – \text{air}\)) a characteristic interference matrix for each layer (\(M_i\)) in the system can be determined as follows [38]:

\[
M_i = \begin{bmatrix}
\cos \varphi_i & j \frac{\sin \varphi_i}{n_i} \\
j n_i \sin \varphi_i & \cos \varphi_i
\end{bmatrix} = \begin{bmatrix}
M_{11} & M_{12} \\
M_{21} & M_{22}
\end{bmatrix}
\]

(6.1)

where \(j^2 = -1\), \(n_i\) is the refractive index of the \(i^{th}\) layer and \(\varphi_i\) is the effective optical thickness of the layer at a given wavelength (\(\lambda\)) i.e. the phase difference accumulated between the reflected waves occurring from layers \(i\) and \(i+1\) [38]:

\[
\varphi_i = \left(\frac{2\pi}{\lambda}\right) n_i d_i \cos \varnothing
\]

(6.2)

where \(\varnothing\) is the angle of wave propagation within the \(i^{th}\) layer. The equivalent characteristic matrix for the multi-layered structure (\(M_T\)) is simply the mathematical product of the individual single layer matrices which comprise the overall device [38]:

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\[ M_T = \prod_{i=1}^{N} \begin{bmatrix} \cos \varphi_i & j \sin \varphi_i / n_i \\ j n_i \sin \varphi_i & \cos \varphi_i \end{bmatrix} \] (6.3)

The resulting reflection \( (r) \) and transmittance \( (t) \) coefficients for one of the key modes of electromagnetic wave propagation (transverse electric – TE or transverse magnetic – TM, figure 6.1c) is obtained by incorporating the individual equivalent matrix components \( (M_{11}, M_{12}, M_{21} \text{ and } M_{22}) \) into the well-known Fresnel equations [33, 38-47]:

\[ r = \frac{n_o M_{11} + n_o n_s M_{12} + M_{21} - n_s M_{22}}{n_o M_{11} + n_o n_s M_{12} + M_{21} + n_s M_{22}} \] (6.4)

\[ t = \frac{2 n_o}{n_o M_{11} + n_o n_s M_{12} + M_{21} + n_s M_{22}} \] (6.5)

where \( n_s \) is the refractive index of the substrate. The reflectance \( (R) \) and transmittance \( (T) \) power of the overall multi-layered structure is now determined by [38]:

\[ R = |r|^2 \] (6.6)

\[ T = \left( \frac{n_s}{n_o} \right)^2 \frac{\cos \varphi}{\cos \varphi_i} |t|^2 \] (6.7)

**Figure 6.2:** The optical representation of a multilayer structure similar to that found in SE-PLDS devices, within the transfer matrix model. Indicating the orientation of the electric \( (\vec{E}) \) and magnetic \( (\vec{H}) \) field components after the incident electromagnetic waves (green arrow) series of interactions (reflection – red arrow and transmission – blue arrow) with the first media \( (n_1) \) of thickness \( d_1 \) within the structure. With similar behaviour occurring at every interface where the wave is propagating from a medium of lower refractive index to a medium with a higher refractive index.
where $\theta_i$ and $\theta_E$ are the angles of incidence and angles of light exiting the multi-layered structure respectively. Given the probability that natural light consists of an equal mixture of TE and TM modes, the resulting reflectance will have equal contributions arising from the Fresnel coefficients corresponding to each individual mode [46]. Thus, the effective reflectance ($R_{\text{effect}}$) and transmittance ($T_{\text{effect}}$) of each design configuration was taken as the average of the TE ($R_{\text{TE}}$, $T_{\text{TE}}$) and TM modes ($R_{\text{TM}}$, $T_{\text{TM}}$) [38]:

$$R_{\text{effect}} = \frac{R_{\text{TE}} + R_{\text{TM}}}{2} \quad (6.8)$$

$$T_{\text{effect}} = \frac{T_{\text{TE}} + T_{\text{TM}}}{2} \quad (6.9)$$

### 6.3.1.2 Optimisation of the Structural Component

Typically, in the pursuit of effective antireflective coatings (ARC’s) the design process and subsequent optimisation is heavily orientated towards the minimization of the structures overall reflectance within the visible region i.e. in the region where solar cells are typically most proficient at energy harvesting [33, 39, 40, 42-45, 47]. Considering the broad range of wavelengths contained within the solar spectrum it is necessary to incorporate the Sun’s spectral characteristics into the design of antireflective coatings [33, 39, 40, 42-45, 47]. Moreover, depending on the type of technology upon which the device is envisioned, the electrical contributions derived from the conversion of light into electrical energy can become increasingly wavelength dependent. Consequently, it is important to consider the internal quantum efficiency (IQE) of the photovoltaic technology underpinning the device during the design process [40, 41]. The most commonly used metric to evaluate and revise an ARC’s capability to maximise the transmission of light directly onto an underlying solar cell is the weighted average reflectivity ($R_w$) [39, 43]:

$$R_w = \frac{\int_{\lambda_1}^{\lambda_2} I(\lambda) \cdot R(\lambda) \cdot IQE(\lambda) \cdot d\lambda}{\int_{\lambda_1}^{\lambda_2} I(\lambda) \cdot IQE(\lambda) \cdot d\lambda} \quad (6.10)$$
where I(\(\lambda\)) is the spectral irradiance from the global standardised air mass 1.5 spectrum (AM1.5G) [48], IQE(\(\lambda\)) is the internal quantum efficiency of the photovoltaic technology under consideration, and R(\(\lambda\)) is the reflectivity of the structure at the given wavelength [39]. Here, \(\lambda_2\) and \(\lambda_1\) represent the upper and lower limits of the photovoltaic technologies spectral response [39]. However, because of the very subtle difference existing in the IQE’s across light in most practical applications [39, 42, 43], the more convenient and readily computable effective weighted average reflectance (Re) metric was adopted throughout this study [39, 42, 43]:

\[
R_e = \frac{\int_{\lambda_1}^{\lambda_2} I(\lambda) \cdot R(\lambda) \cdot d\lambda}{\int_{\lambda_1}^{\lambda_2} I(\lambda) \cdot d\lambda}
\] (6.11)

with an emphasis placed on structural solutions whose peak reflectivity was confined to the 300 nm – 500 nm absorption window, where most of the typically utilised photoluminescent materials are heavily active.

6.3.1.3 Potential Efficiency Enhancement

In order to assess the impact of each individual design consideration on the conversion efficiency of the underlying photovoltaic material it is not sufficient to rely solely upon the variation in the transmittance produced as a direct result of the specific structural configuration [33, 40, 41, 44-47, 49]. The capability of commercial and non-commercial photovoltaic technologies to produce an electrical output is highly dependent upon the material characteristics of the absorbing material as well as the wavelength at which the conversion occurs [2, 3, 11]. Consequently, the spectral irradiance characteristics widely adopted in the evaluation of solar cell performance should also be considered during the optimisation process [34, 36, 40, 41, 45-47, 49]. Essentially the criterion for optimising the antireflective elements design was to maximise the photo-generated current produced by the cell under the standardised AM1.5G weighted solar spectrum [49-51]. Assuming that other electrical parameters of the solar
cell which can influence the cells efficiency (open circuit voltage, serial resistance etc.), remain unchanged throughout the addition and revision of the ARC’s structure, the photogenerated current becomes equivalent to the short circuit current density ($J_{sc}$). The experimental evidence accumulated across numerous ARC’s studied on both encapsulated (additional air/glass interface) and non-encapsulated mono-crystalline silicon (mc-Si) solar cells, substantiates these assumptions made about the cell’s electrical properties [49, 50, 52]. Increases in $J_{sc}$ of up to 25% have been reported while at the same time the open circuit voltage remained relatively unchanged, increasing by a mere 2% [49, 50, 52]. Consequently, the gain in the open circuit voltage will be neglected in the analysis and discussion, which will focus instead on the variation within $J_{sc}$ given by [49, 50, 52]:

$$J_{sc} = \frac{\lambda_2 - \lambda_1}{\int \Phi(\lambda) \cdot SR(\lambda) \cdot d\lambda}$$

where $\Phi(\lambda)$ is the photon flux under the AM1.5G spectrum, $SR(\lambda)$ is the spectral response of the photovoltaic material i.e. the photo-current produced as a direct result of the conversion process, which is influenced by the prevalent loss mechanisms inherent within the architecture, and $\lambda_2$ and $\lambda_1$ represent the upper and lower limits of the spectral response of the material respectively. The expression 6.12 allows an effective coupling between the reflectivity $R(\lambda)$ and absorption $A(\lambda)$ characteristics of the additional antireflective element and the overall device’s electrical performance [33, 44, 49, 51]. Hence, the enhancement ($E$) in $J_{sc}$ due to the addition of the antireflective structure was treated as:

$$E(\%) = \frac{J_{sc} (\text{with ARC}) - J_{sc} (\text{without ARC})}{J_{sc} (\text{without ARC})}$$

6.3.1.4 Model Validation

The output generated from the transfer model can be classified to operate via two distinct predictive pathways (1) the determination of the structure’s reflection suppression
capability and (2) the enhancement in the short-circuit current achieved through the subsequent fitting of the structure onto a PV substrate. Each mechanism was independently investigated through the deposition, and subsequent optical and electrical characterisation of single-layer ARC’s (comprised of ZnO, AZO, ITO, and TiO$_2$) deposited across a host of different substrate materials (commercial Si cell, untreated pure Si). The resulting structures reflection spectra was characterised using the methodology outlined in section 2.3 in order to ensure that the reflection properties of the material library considered were accurately represented within the modelling environment. This validation ensured that any insights into the correlation between the reflection suppressive behaviour of the structural element (incorporated into the SE-PLDS device designs) and the improvements reported reflected a true enhancement in device performance.

The conversion performance aspect of the validation process was facilitated through the adoption of relatively inexpensive substrates for the layer deposition, namely a silicon wafer (‘witness’). The ‘witness’ sample was subjected to the specific deposition parameters utilised to coat the commercial grade Si cells (Solar Capture Technologies Ltd, England) employed in the comparison of the model’s efficiency enhancement metric. The reflection spectra generated using the model, were based upon the thickness values derived from measurements made using ellipsometry (Horiba Jobin Yvon Universal ellipsometer with accompany Delta Psi software suite) and stylus profilometry (section 2.8). The spectral features, observed in the reflectance spectra registered were compared with those produced by the model, until both spectra (the measured spectra and the simulated spectra) were in agreement within the confines of statistical significance. The operational ARC-fitted Si devices were characterised experimentally using the set-up and protocol outlined in section 2.10.2, with the order of merit dictated by the simulated evaluation of the structure’s performance, and its performance under experimental conditions compared.
6.4 Results and Discussions
6.4.1 Modulating The Reflection Suppression Capabilities Of Simple Antireflection Elements

Before the optical and electrical behaviour of the conceived SE-LDS and SE-PLDS devices could be accurately modelled, it was first necessary to demonstrate the behaviour of each individual design component (PV cell, polymeric encapsulant layer, and the antireflective structure) within the overarching composite device. The evaluation process was broken down into three distinctive aspects (1) the assessment of the optical tunability afforded through single- and double-layer antireflection coatings (ARC’s) and their subsequent impact on the electrical performance of the PV cell, (2) the verification of the model’s predictive capabilities when describing the optical and electrical behaviour of the various materials encountered throughout this study, and (3) the determination of the possible enhancement in the conversion efficiency, achievable with the initial SE-LDS and SE-PLDS device designs considered and developed herein. The first component of this evaluation process is discussed in the following sections.

6.4.1.1 Single-layer Structures

Silicon (Si) in its pristine and untreated form endures a substantial 35% - 40% loss in light-collection efficiency (figure 6.3.a, broken black line) over the spectral region where the semiconducting material exhibits peak conversion efficiencies, i.e. the 450 nm – 1100 nm spectral bandwidth. An intensified reflection loss of 55% - 60% (figure 6.3.a, broken black line) arises over the ultraviolet spectral region (300 nm – 400 nm) and stems from silicon’s considerably high extinction coefficient within the narrowband of frequencies [53], and, thus, it dominates the total losses of the untreated PV device. Figure 6.3.a also highlights the ability of simplified single-layer ARC’s composed of common optical materials to suppress the reflection losses arising from the front surface of the PV device. It is evident from figure 6.3.a that selecting even a single-layer AR coating to include in the SE-LDS and SE-PLDS designs facilitates the suppression of reflections
over a relatively large (250 nm – 300 nm) spectral bandwidth. Furthermore, through the subtle modification of the thin-films optical thickness this spectral bandwidth can be controlled. The optical thickness of an ARC is typically expressed as the wavelength (λ₀) at which the film(s) are designed to act as a quarter-wavelength thick optical medium [32, 38], and it is calculated using the optical materials refractive index (n) at the given wavelength [32, 38].

Additionally, figure 6.3.a highlights that irrespective of the ARC’s optical properties, the reflectance of the PV device becomes dramatically diminished, especially within the 450 nm to 1100 nm spectral window. Furthermore, through monitoring of the variation in the reflectance at a fixed wavelength of 600 nm as a function of the refractive index of the material (figure 6.3.b), used to construct the AR coating, the enhancement and subsequent optimisation of the coating through the careful selection of the optical material becomes clear. For single-layer AR coatings this translates to an ideal refractive index of ~1.97 (figure 6.3.b), which is closely matched by silicon oxide (SiO) and silicon nitride (Si₃N₄). Thus, through the selection of a material whose refractive index closely aligns with the optimal 1.8 - 2.2 range identified in figure 6.3.b, the reflection losses can be largely supressed. However, the optical materials utilised in an ARC must not only possess a suitable refractive index and be highly transmissive across a broad range of wavelengths. They must also accommodate a favourable combination of chemical, physical and mechanical attributes [54]. This includes; chemical, optical and mechanical stability under the intense solar spectrum for prolonged periods of time, readily achievable adhesion to the Si substrate, little or no reactivity with other thin-film materials, and the absence of a tendency to crack under mechanical stress [54]. Deposition of the AR material(s) should also be completely compatible with the state-of-the-art solar cell manufacturing and processing techniques. Indeed some, if not all, of these design requirements are fulfilled by the materials selected and investigated in this study.
Figure 6.3: (a) Reflection spectra of single-layer antireflection coatings (ARCs) designed to act as a quarter-wavelength film at a wavelength ($\lambda_0$) of 600 nm and (b) the corresponding variation in the reflectance at this wavelength as a function of the materials refractive index ($n$) – with the ideal ARC material properties highlighted. (c) The deviation in the effective-weighted average reflectance ($R_e$) as a function of each antireflection coatings optical thickness, as specified by its quarter-wavelength thickness ($\lambda_0$). (d) The enhancement in the short-circuit current density (Jsc) achieved through incorporating each antireflective structure onto an untreated pristine mc-Si cell, with the error bars representing the divergence in the enhancement achieved through different optical thickness of each material.

Furthermore, the magnitude of the reflection losses originating from the front surface of the PV device can be further alleviated through complementing the choice of design material(s) with the appropriate optical thickness ($\lambda_0$). This is acutely demonstrated
in figure 6.3.c where the behaviour of the effective-weighted average reflectance ($R_e$) of the fitted PV device in response to an amending optical thickness of the single-layer ARC is provided. Figure 6.3.c confirms the notion that selecting the right material for the AR component can result in a substantial decrease in the spectral losses of the PV device, losses that are stemming from the reflection interactions with the incident solar flux. Consequently, this can lead to a 26% to 44% enhancement in the light directly transmitted into the photoconductive material (figure 6.3.c). Through the optimisation of the film’s thickness to act as a quarter-wavelength thick optical medium at 600 nm – 650 nm, this enhancement was pushed as high as 71% (Si$_3$N$_4$, figure 6.3.c). The controlled modification of the PV device’s optical properties resulted in a 25% (MgF$_2$) to 48% (SiO) increase in the short-circuit current density generated within the photoconductive material, when compared to the untreated pristine PV architecture (figure 6.3.d). The only limitation affecting single-layer ARC designs is their limited ability to offer reflection suppression over a single relatively narrow band of frequencies. In order to effectively target a much wider range of frequencies within the solar spectrum and leverage the power of multiple different types of AR material, the architecture of this simplistic design must be adapted to include more than one AR layer.

### 6.4.1.2 Double-layer Structures

Enhancing the complexity of the AR coating design through the addition of a similar supplementary thin-film (also designed to act as a quarter-wavelength thick optical medium at the same wavelength) provides ample opportunity to further refine the reflection profile of the PV device [32, 38]. A schematic of a typical double-layer AR coating is provided in the inset of figure 6.4.a. Such coating is comprised of a relatively low refractive index material ($n_1$ - MgF$_2$, SiO$_2$, ZnO) followed by a higher index material ($n_2$) directly on-top of the Si substrate. Depending upon the refractive index of the individual stratified components ($n_1$, $n_2$) within the composite coating, the reflection
losses can now be repressed at two distinct wavelength bands within the solar spectrum, with a moderate localised central maximum originating between the two reflectance minima (figure 6.4.a). Additionally, the spectral position(s) of these reflectance minima could be shifted accordingly to accommodate very specific spectral bandwidths (e.g. like the absorption and emission band of a luminophore) by independently varying the thickness of each film. This optical behaviour is expected from double-layer thin films and stems from the two independent criteria required for zero-reflectance to be achieved [32, 38]. Since the working principle of AR coatings is based upon the destructive inference of light reflected from the interface between the two AR materials, the interaction is conditionally dependent upon the thickness of each material as well as its respective refractive index. As such, the optical thickness is determinant for the occurrence of destructive interference while the index criteria control the extent of the phenomena i.e. zero-reflectance requires both conditions to be mutually satisfied [32, 38]. This divergence within the optical response of the ARC architecture is reflected in figure 6.4.a, whereby the isolated reflectance minima (~ 5%) centred at 450 nm and 1050 nm diminish in intensity and begin to coalesce into a single v-shaped broadband minimum localised around 600 nm. This change in the optical behaviour occurred as the refractive index of the higher index layer \( (n_2) \) was alternated from \( \sim 1.8 \) (ITO – figure 6.4.a) to 2.6 (TiO\(_2\) – figure 6.4.a). Consequently, through the incorporation of the right materials the characteristic W-shaped reflectance band synonymous with double-layer ARC’s can be transformed into a V-shape profile, allowing for an almost complete absence of reflection \( (R \leq 0.005, \text{figure 6.4 b) over a specific band of frequencies. Alongside the expansion of the full width at half maximum (FWHM) of the individual reflectance contributions (\( \Delta \lambda = 100 \text{ nm} – 300 \text{ nm} \)) comes a broadening in the range of wavelengths over which the reflection losses are curtailed.
Figure 6.4: (a) Reflection spectra of double-layer antireflection coatings designed to act as quarter-quarter wavelength films at a wavelength ($\lambda_0$) of 600 nm and (b) the corresponding variation in the reflectance at this wavelength as a function of the materials refractive index ($n$) – with the ideal ARC material for each layer ($n_1$ – filled shapes, $n_2$ – partially filled shapes) highlighted. (c) The deviation in the effective-weighted average reflectance ($R_e$) as a function of each antireflection coatings optical thickness, as specified by its quarter-wavelength thickness ($\lambda_0$). (d) The enhancement in the short-circuit current density ($J_{sc}$) achieved through incorporating each antireflective structure onto an untreated pristine mc-Si cell, with the error bars representing the divergence in the enhancement achieved through different optical thickness of each material.

Considering that the most expansive FWHM achieved with single-layer designs was ~300 nm (figure 6.3.a) the additional AR layer assisted in promoting this enhanced
suppression well beyond a 450 nm targeted spectral window, once the two interference criteria had been established. For this type of coating the criteria was a combination of a low-index (ideal $n_1$ material – figure 6.4.b) and high-index (ideal $n_2$ material – figure 6.4.b) material having a refractive index of ~1.57 and ~2.47, respectively, in correspondence with a quarter-quarter wavelength optical thickness. This optical behaviour is confirmed through modulations in the $R_e$ of the PV device shown in figure 6.4.c, as the optical thickness of each film was shifted from the infrared region towards the ultraviolet-visible. Under this scenario the $R_e$ was effectively reduced from 0.2 (Zno-Al-ZnO – figure 6.4.c) to 0.01 (MgF$_2$-TiO$_2$ – figure 6.4.c) representing a marked 80% improvement upon that attained with the single-layer coating.

Figure 6.4.d shows the impact of each double-layer AR coating on the short-circuit density generated within the Si cell and reveals a considerable 12% - 56% enhancement in the overall light collection efficiency, when compared with the untreated architecture. By comparison, this is an 18% improvement over the current density achieved with an optimised single-layer ARC. The minimal improvement in the performance with a more complicated AR design may be not worth the added device complexity, the additional cost, or the extra processing time that would be required. This is, indeed, reflected in the state-of-the-art architecture of silicon solar cells, whereby double-layer coatings are almost completely absent [55]. Nevertheless, it was essential to investigate their optical behaviour for the inclusion and exploitation in the proposed SE-LDS and SE-PLDS designs as they offer additional flexibility through accommodating a larger ability to tune the optical behaviour of the front surface of the PV device. Thus, this is making them a potential alternative for assisting the coordination of the spectral properties of the additional thin-film element with the spectroscopic characteristics of the luminescent species embedded within the polymeric component of the structure enhanced (SE-LDS, SE-PLDS) devices.
6.4.1.3 Multilayer Structures

To reduce the reflection losses even further, the application of a multilayer system consisting of a cascading series of distinct ARC’s was explored. In this case the multilayer structure was exploited to establish a graded-index profile in which the refractive index of each successive quarter-wavelength layer was gradually increased, i.e. air < 1st layer < 2nd layer ... < nth layer < silicon. Each layer within the composite structure(s) was assumed to be of ideal refractive index \( n_{\text{ideal}} = (n_{\text{top}}n_{\text{bottom}})^{-1/2} \), where \( n_{\text{top}} \) and \( n_{\text{bottom}} \) are the refractive indexes of the layers adjacent to the layer in question, and have an accompanying optical thickness of 600 nm. This ensured that only the highest performance(s) from each thin-film were imparted upon the light collection efficiency of the underlying solar cell. Additionally, this simultaneously allowed for the enhancement provided by the more complex AR designs to be effectively determined without the additional need to independently refine the optical thickness of each film within the overarching design. Although the materials utilised embodied idealised optical properties, their characteristic optical behaviour can be recreated through the application equivalent layers. Whereby, the refractive index that is unavailable or unpractical is simply replaced by a symmetrical combination of “equivalent layers” - made up of higher and lower index materials [56]. In this manner the “equivalent layers” are essentially the same optical thickness and refractive index as the single-layered coating they are emulating [56].

Figure 6.5.a shows the dependence of the pristine Si device’s reflectance spectrum, when fitted with an ideal multi-layered ARC incorporating an increasing number of additional layers. As the number of layers within the ARC design was gradually increased significant changes in the reflectance spectrum were registered. The single relatively broad reflectance minima achieved with a single-layer coating becomes drastically extended (figure 6.5.a) as two or more layers are integrated into the composite structure. Including three or more layers contributed towards an almost complete nullification of the reflectance
Figure 6.5: (a) Reflectance spectra of ideal multi-layered antireflection coatings (ARCs) consisting of 1 to 6 individual layers, each with its own distinct material properties. (b) The corresponding effective-weighted average reflectance (Re, black triangles) and short-circuit current density (Jsc, blue circles) derived from an untreated pristine mc-Si cell when fitted with the stratified structures.

losses (< 5%) which extend well beyond the entire spectral response range (400 nm – 1100 nm) of the photoconductive PV material, with the noticeable exception of the ultraviolet spectral region (300 nm – 400 nm). These residual reflectance contributions stem from the large divergence in Si’s refractive index coupled with the materials amplified absorption coefficient within this wavelength range (300 nm – 400 nm). However, considering that the spectral responsivity of Si remains limited to 0.1 A W⁻¹ - 0.2 A W⁻¹ within this narrow spectral band, this optical limitation can be largely overlooked in the pursuit of highly efficient ARC’s.

The enhanced curtailment of the reflection losses allowed for an even greater proportion of the incoming solar flux to be captured and converted into usable electricity. This is reflected in the changes registered in the Jsc generated within the PV cell, as shown in figure 6.5.b. Initially, through adding an additional optical layer into the ARC the Re and Jsc of the cell experience a marked 56% and 5% improvement, respectively, as
compared to their single-layer counterpart. As the AR structure begins to exceed a double-layer design, the enhancement afforded through fitting each additional successive film becomes less and less pronounced. This is exemplified in figure 6.5.b whereupon transitioning from a double- to six-layer coating offered a 62% and 2% increase in the $R_e$ and $J_{sc}$ of the device, respectively. Thus, through enhancing the complexity of the AR coating an additional degree of control over the capability to modify the reflectance profile at the front end of the PV device is enabled. However, the corresponding improvement in the amount of additional solar energy captured remained negligible when considering the enhancements and advantages offered by alternative strategies such as structured or textured AR coatings and/or surfaces [1].

6.4.2 Model Validation
6.4.2.1 Reflection Spectral component

Within the modelling environment the accurate representation of the device’s architecture is dependent upon the strict definition of the material’s optical properties and its corresponding optical thickness [38]. The accurate description of the refractive index of each one of the optical materials utilised to model and predict the enhancement offered through the series of proposed SE-LDS and SE-PLDS designs remained essential. Considering the interaction between the incident solar irradiance and the structure considered is predominantly controlled by the numerical value of the refractive index, any perturbations within its description could potentially influence the insights, associations and results discovered when predicting the optical behaviour of the corresponding PV device’s. This aspect is further compounded by the susceptibility of a material’s refractive index to its porosity [57], deposition method [58], deposition temperature [59], oxidation conditions [60], etc. [61]. Even under the same deposition conditions (temperature, atmosphere, deposition rate etc.) deviations in the refractive index (and the thickness) of a material are still present [62]. Ideally, the optical properties
of the materials would be the prerequisite condition for independently ensuring the accuracy of the optical constants utilised to simulate the library of materials employed throughout this body of work. Unfortunately, this criterion remains impractical as in most cases, even with highly specialised equipment required for the deposition and characterisation method’s, deviations are still present. Consequently, most of the theoretical studies which have explored the behaviour of ARC fitted solar devices relied on sourcing this optical data from external material databases such as SOPRA [63], FilmMetrics [64], Refractiveindex [65], and many more.

Therefore, the optical data utilised throughout this study was gathered from a number of different material databases, with the accumulation of these optical properties presented in figure 6.6. Some of the materials including Si₃N₄, SiO₂, PMMA, ZnO and MgF₂ display very little variation in their refractive index over the spectral response range of Si (300 nm – 1100 nm) due to their internal crystal structure [66], while other materials such as Al-ZnO, ITO, SiO and pristine Si demonstrate a large degree of variance in their respective refractive index, especially over the 300 nm – 400 nm range (figure 6.6). These spectral features are also accompanied by an absorptive contribution which is elucidated through the magnitude of the extinction coefficient \( k \) provided in figure 6.6.c and in figure 6.6.d. Additionally, this spectral range (300 nm – 400 nm) proves challenging to the accurate determination of the transparent material’s optical behaviour [67]. This is evident in figure 6.6 by the lack of availability of refractive index and extinction coefficient values for some of the materials studied.

Another essential design consideration which had be evaluated, before any comparison between the theoretical and experimental reflectance spectrum of a given device could be effectively conducted, was the optical thickness of each device component (substrate, thin-film and polymeric encapsulant). This aspect was carried out through the deposition of different single-layer ARC’s on a pristine Si substrate and
Figure 6.6: Refractive index (n) and extinction coefficient (k) of the materials used to represent the (a,b) different antireflection coating designs and (c,d) the substrate materials upon which they were modelled [63-65].

subsequently comparing their optical thickness using a combination of interferometry, profilometry and optical modelling (transfer matrix) techniques. In this manner the thickness values derived through both profilometry and interferometry measurements were utilised to obtain a reflectance spectrum for each structure, with the modelling parameters carefully adjusted until a statistically significant fit between the two spectra (measured and modelled) had been obtained. The optical thickness determined by each
technique for the series of different materials (ITO, TiO$_2$, Al-ZnO, ZnO) is presented in figure 6.7 and shows a close agreement between the different independent methods.

The large discrepancy between the thickness value derived with ellipsometry and the alternative techniques for ZnO in figure 6.7 likely stems from the large uncertainty in the fit criteria of the model, used to simulate the materials behaviour in conjunction with the ellipsometric data. The statistical significance of the fit criteria required for chi-squared ($\chi^2$) when fitting ellipsometric data is restricted to an upper-limit of ~10 [68, 69]. Considering the $\chi^2$ of the fit for ZnO was ~16, this could have influenced the thickness value determined for this material, when using this approach. However, the accuracy and applicability of ellipsometry to precisely define the optical thickness of a thin-film coating when deposited on a high-index substrate, such as Si, is depicted in figure 6.7, provided that the standards imposed on the fit-criterion are met.

**Figure 6.7:** Inter-comparison between the thickness values derived for a series of single-layer antireflection coatings by three independent characterisation methods: (1) ellipsometry (black squares) using a series of distinct analytical models to predict the materials optical behaviour and corresponding optical properties, (2) profilometry (green triangles) using a Veeco Dektak 6M (full method outlined in section 2.7), and (3) the transfer matrix model, iterating the layers thickness until a statistically significant correlation had been achieved between the ‘measured’ and ‘modelled’ optical properties of each structure.
Based on the optical thickness values presented in figure 6.7 the reflectance spectrum of each corresponding structure was modelled utilising the optical data highlighted in figure 6.6. Additionally, the reflectance spectrum of pristine PMMA and pristine Si was also considered, as they represented essential building-blocks of SE-LDS and SE-PLDS devices. Figure 6.8 shows the consistency between the spectral features present in the experimental (solid black line) reflectance spectra and those of the accompanying modelled architectures (solid red line), when considering a Si substrate fitted with the various single-layer polymeric or AR coatings. Some small discrepancies between the ‘measured’ and ‘modelled’ spectra are visible in figure 6.7, some of the spectral features being less or more intense in magnitude over a specific range of wavelengths. These deviations are a direct consequence of the uncertainties which arise throughout the deposition process (irrespective of the methodology employed), and their presence contributes to the resulting film exhibiting inhomogeneous optical properties throughout – see the associated uncertainty on the film thickness in figure 6.7 for example.

In comparison, the structures representation within the modelling environment assumed complete uniformity of the optical properties (refractive index, optical thickness) and as a result, the modelled spectra lack some of the spectral information which originates from this divergence in the optical characteristics. Additionally, the presence of high frequency contributions in the reflectance spectra of the 10 μm thick PMMA layer (figure 6.8.b) are are a testament to the limited capability of the transfer matrix model (TMM) in its generalised form, to effectively handle relatively thick optical layers [32, 38]. Nonetheless, the close agreement between the modelled and measured reflectance spectra shown in figure 6.8 ensured the suitability of the TMM to effectively handle the more complex SE-LDS and SE-PLDS optical designs.
Figure 6.8: Comparison between the reflectance spectra derived using the transfer matrix model (broken red line) and the reflectance spectra determined experimentally (black solid line) for a number of different types of material: (a) pristine untreated silicon, (b) pristine 10 µm thick poly-methyl methacrylate also known as PMMA, (c) zinc Oxide (ZnO), (d) indium tin oxide (ITO), (e) titanium dioxide (TiO2), and (f) aluminium zinc oxide (Al-ZnO)
6.4.2.2 Short-Circuit Current Density component

Considering the TMM in its generalised formalism cannot accurately describe the optical behaviour of a structured/textured PV architecture [31, 38], it was essential to find a suitable ARC structure which could effectively imitate the spectral and electrical characteristics of this type of architecture. The ultra-low reflectance (< 2%) achieved with the most commercially mature textured/structured Si architecture is demonstrated in figure 6.9.a (mc-Si PV Cell) and shows almost complete suppression of the reflection losses over the 300 nm – 1100 nm range. Recreating this optical behaviour in its entirety using completely planar optical interfaces of differing refractive index is challenging but not impractical. Through utilising a multi-layered ARC design like that depicted in figure 6.5.a, a reflectance spectrum approximately matching that of the commercial grade mc-Si cell was obtained (figure 6.9, imitated PV cell – red triangles). However, a reflectance loss of 5% - 25% remained over the 300 nm – 450 nm range for the imitated architecture. Coincidentally, the spectral response of Si over this narrow band of frequencies is relatively low (0.1 A W⁻¹– 0.2 A W⁻¹). Consequently, the discrepancy between the ‘imitated’ and ‘real’ PV devices reflectance spectra is expected to have very little influence over the performance metrics (Rₑ, Jₑ), utilised to evaluate and optimise the collection efficiency of the newly proposed solar cell designs. This aspect is highlighted by the close agreement between the Rₑ of the two devices (simulated - imitated PV cell, measured – mc-Si PV cell), as shown in the inset of figure 6.9.a. Through the subsequent fitting of single-layer transparent thin-films and polymeric encapsulants onto the imitated PV cell, the predicted electrical behaviour of these modelled devices was effectively compared to their real-world experimental counterparts.

The comparison between the electrical performances exhibited by the ‘imitated’ modelled devices and those fabricated and characterised experimentally is presented in figure 6.9.b. A divergence between the expected (modelled) and real-world (experimental)
Figure 6.9: (a) Divergence in the reflectance spectrum exhibited by untreated pristine silicon (pristine Si, broken black line), a commercial high-grade monocrystalline silicon photovoltaic cell (mc-Si PV cell, black squares) and a similar antireflective fitted mc-Si device designed to mimic the optical and electrical behaviour of the commercial PV cell (imitated PV cell, red triangles). A direct comparison between the effective-weighted average reflectance ($R_e$) of the commercial PV cell and the imitated PV device is additionally provided in the inset. (b) The short-circuit current density ($J_{sc}$) of the physical devices fabricated and measured experimentally (black squares) and the corresponding behaviour of the imitated device (red triangles) when fitted with the same series of antireflection coatings (ARCs). A magnified image of the PV cells front surface revealed through scanning electron microscopy is additionally provided in the inset. (c) External quantum efficiency (EQE) of the PV cell when equipped with the different ARC’s or polymer coatings and (d) their corresponding reflection spectra. Performances of each iteration of the PV device is evident in figure 6.9.b, with the discrepancy in the $J_{sc}$ ranging from -5.1 mA cm$^{-2}$ (figure 6.9.b - TiO$_2$) to +3.5 mA cm$^{-2}$ (figure 6.9.b - mc-Si PV Cell) for the modelled devices. Differences between the
behaviour of the modelled and actual PV devices are expected as the fundamental nature of the interactions of light with the highly ordered textured surface (shown in the inset of figure 6.9.b) are unaccounted for in the modelling environment. Additionally, solar simulators with a “class A” match to the AM1.5G spectrum (utilised to simulate the natural climate conditions in the modelling environment) are allowed tolerances of ±25% under the standardised testing guidelines [11]. Consequently, the spectral mismatch between the spectral irradiance provided to the modelled and experimental devices could have influenced the resulting current densities generated within them.

Furthermore, in the simplification of the calculations involved in modelling the PV devices a number of additional loss pathways (including back surface reflection losses, band offsets, changes in the sheet- and serial-resistance, thermalisation losses, and the possibility of ‘poor’ electrical contact as a result of preparing the cells for indoor characterisation) were excluded from the analysis. Meanwhile, the origin of the deviations in the actual PV devices electrical and optical properties, upon the addition of each extra optical structure, is presented in figure 6.9.c and figure 6.9.d, respectively. The changes in the external quantum efficiency (EQE) of the device’s over the 350 nm – 500 nm region with the addition of the supplementary ARC’s was negligible, while the addition of the relatively thick PMMA layer resulted in a significant deterioration in the EQE across the entire 300 nm – 1100 nm range. This behaviour is expected to stem from the disruption of the antireflection properties exhibited by the textured surface of the Si. Indeed, this is reflected in the abrupt change in the reflectance spectrum upon the addition of the polymeric layer (figure 6.9.e). Nevertheless, the data generated throughout this comparison was used to recalibrate the short-circuit current density generated in the subsequently modelled SE-LDS and SE-PLDS device architectures. In order to ensure that the performance of the modelled SE-LDS and SE-PLDS devices was in-line with a tangible improvement over their conventional LDS and PLDS counterparts, a cautionary
adjustment of -5.1 mA cm\(^{-2}\) (the most severe divergence reported in figure 6.9.b) was henceforth implemented in all of the calculations involved.

### 6.4.3 Structure Enhanced Luminescent Down-Shifting (SE-LDS) Devices

In the pursuit of highly efficient LDS devices many different configurations of optical thickness have been employed, ranging from 5 µm to 5 mm [2, 3, 11]. However, in order to maximise the potential of the structure enhanced designs proposed in this study, the restrictions imposed on the embedded luminophore through this important design consideration must be carefully considered. Integrating a relatively thick LDS layer would allow for significantly more interactions between the embedded luminescent material and the incident solar irradiance, while leaving the embedded luminophore(s) susceptible to the unwanted aggregation processes which can negatively influence the layer’s photoluminescent properties [70, 71]. Conversely, selecting a thinner LDS layer not only allows for the quantity of luminescent material utilised to be reduced but, additionally, it offers more control over the intramolecular interactions between the embedded luminescent molecules [70, 71]. Thus, adopting a thinner LDS layer could potentially offer more advantageous design considerations, in terms of assisting in the mitigation of some of the unfavourable considerations encountered in optically thick LDS devices.

For this model, the LDS layer which is homogeneously doped with a luminescent material similar to that developed and characterised in chapter 4 was effectively modelled as a pristine PMMA film containing no impurities. Although the refractive index of the LDS layers in chapter 4 was never measured in response to the loading concentration of the luminescent material(s) employed, the presence of analogous molecular structures within PMMA networks has shown to have an inconsiderable impact on the refractive index of the corresponding fluorescent polymer [72]. The variation in the optical \(R_e\) and electrical \(J_{sc}\) response of a conventional LDS device to an increase in the optical
thickness (1 nm – 100 μm) of the encapsulating layer is presented in figure 6.10. As the LDS layer is extended from 1 nm to 150 nm the polymeric layer acts like an ARC, reducing the $R_e$ (figure 6.10 – black squares) and enhancing the photocurrent $J_{sc}$ (figure 6.10 – blue circles) generated by the LDS device. This is expected as the addition of a supplementary thin-film layer of relatively low refractive index ($n_{pmma} \sim 1.5$) further extends the device’s graded-index profile, leading to less light being lost at each optical interface. At intermediate thicknesses of 150 nm – 500 nm the variation in performance becomes more chaotic (figure 6.10).

![Figure 6.10: Variation in the effective-weighted average reflectance ($R_e$, black squares) and short-circuit current density ($J_{sc}$, blue circles) of a polymer encapsulated mc-Si PV device, as a function of the thickness of the pristine polymethacrylate (PMMA) layer. The broken lines ($R_e$ – black, $J_{sc}$ - blue) correspond to the pristine PV devices electrical performance.](image)

This change in the optical behaviour of the LDS layer originates in the transition from conditions favourable to coherent light propagation (often synonymous with thin-film interference), to conditions which promote narrowband oscillations in the calculated reflectance and transmittance spectra [32, 38]. These oscillations occur when the layer
becomes sufficiently ‘thick’ compared with the wavelength of the incident irradiance [32, 38]. Considering how these oscillations are rarely observed in practical measurements, either due to a phase incoherency within the optically thick layer or because of the limited resolution of the measurement – they are often referred to as ‘incoherent interference interactions’ [32, 38]. Beyond a film thickness of 500 nm these fluctuations in the properties of the LDS device become less striking, as the thickness is continuously increased (figure 6.10). Consequently, through adopting a 1 μm – 100 μm thick LDS layer a 35% and 20% improvement in the device’s $R_e$ and $J_{sc}$ was achieved, respectively. Therefore, in order to maximise the cooperation between the different optical elements within the SE-LDS devices proposed, two alternative configurations of the LDS layer were incorporated into the SE-LDS designs. Those integrating a relatively thick 90 μm LDS layer (figure 6.11 - red triangles) and an alternative option which incorporated a much thinner 9 μm LDS layer (figure 6.11 – green circles).

Single-layer and double-layer ARC’s, constructed using the library of materials previously employed, were incorporated into two different configurations of the SE-LDS device. A design in which the ARC was located directly below the LDS layer (design option #1 – figure 6.11 inset) and an alternative design where the ARC was directly situated above the LDS layer (design option #2 – figure 6.11 inset). Integrating the ARC below the LDS layer ensured that the graded step-down refractive index profile of the device ($n_{PMMA} < n_{ARC} < n_{Si}$) was maintained, with the noticeable exception of MgF$_2$ (figure 6.11.a). Once this condition has been broken (as in the case of the MgF$_2$), the fixed-phase relationship between the multiple reflections originating from each optical interface within the stratified architecture, no longer accumulate in the sole production of destructive interference [32, 38]. Instead, a combination of constructive interference and destructive interference occurs with the constructive component contributing to an
increase reflection loss at the front side of the device (figure 6.11.a). Otherwise, the presence of a single-layered ARC contributed to an 8% (figure 6.11.a, SiO) - 16% (figure 6.11, ZnS) improvement in the photocurrent generated within the hybrid devices. Accordingly, through the careful consideration of the AR structure’s composition and optical thickness, the cooperative interactions between the individual optical components (LDS layer, Si substrate, ARC) was maximised. For the same single-layer SE-LDS devices shown in figure 6.11.a, the thickness of the integrated LDS layer had very little impact (0.1% - 0.4%) on the subsequent enhancement provided through the inclusion of the thin-film component.

Through alternatively adopting a double-layer ARC into the design as depicted in the inset of figure 6.11.b, the optical coupling initiated between the different retrofitted elements within the SE-LDS design was further supported. Switching from the simple single-layer designs to a double-layer thin-film alternative contributed to a 7% (figure 6.11.b, MgF2-SiO) to 20% (figure 6.11.b, Ideal material) enhancement in the performance of the hybrid devices, when compared to the classical LDS device. However, the improvement in the collection efficiency of the device (4% over a single-layer design) must be weighed against the increase in the structural complexity and the additional costs occurred, when transitioning from a single-layer to a double-layer coating. This evaluation of each modification to the retrofitted SE-LDS structure is necessary to ensure that its impact on the conversion performance of the underlying PV device, offers a tangible cost-effective alternative to effectively restructuring the fundamental photoconductive architecture. Additionally, any divergences in the performance of the double-layer SE-LDS devices were further intensified by an adjustment in the thickness of the LDS layer (figure 6.11.b). Considering the importance of the narrowband contributions in the reflectance spectrum of a conventional LDS device (figure 6.8.b), the possibility of competing behaviour between the coherent and incoherent optical domains
within the stratified SE-LDS structures is considered. Hence, through consolidating these two optical domains into a single architecture, the susceptibility of the retrofitted SE-LDS structure towards subtle optical deviations introduced through the AR component becomes intensified. Consequently, adopting a much thinner LDS layer moderated the extent of the ‘incoherent’ interactions within the LDS layer, as demonstrated by the ~3% increase in the enhancement attained when downsizing the LDS layer from 90 µm to 9 µm (figure 6.11.b).

In the alternative SE-LDS design (illustrated in the inset of figure 6.11.c) the inherent lack of suitably transparent materials, which possess a refractive index lower than 1.5 [65, 73, 74] disrupted the interaction of light with the cascading series of distinct optical layers within the SE-LDS structure. Thus, incorporating single-layer ARC’s into this type of configuration contributed to a 5% (Figure 6.11.c, SiO) to 20% (figure 6.11.c, ZnS) decline in the energy harvesting potential, when compared to a conventional LDS device. A similar effect occurred within the double-layer designs portrayed in the inset of figure 6.11.d, but the extent of the increased reflection losses introduced through the additional optical element was less extreme. This deviation in the optical behaviour of single- and double-layer ARC’s when embedded within the SE-LDS is expected to arise as a result of the effective refractive index of the double-layer films closely matching that of the LDS layer ($n_{PMMA} \sim 1.5$) [38, 75, 76]. In the context of thin films, the effective refractive index is derived from the observation that a multi-layered film (composed of a mixture of different materials) often behaves as a single homogeneous film exhibiting an effective refractive index that does not equal the refractive index of any of its individual constituents [32, 38].
Figure 6.11: The enhanced short-circuit current density (Jsc) achieved with two different types of structure enhanced luminescent down-shifting (SE-LDS) layer design (1) structures incorporating a (a) single or (b) double layer antireflection element below the LDS layer as highlighted in the device schematics provided in the insets or alternatively (2) structures incorporating the (c) single or (d) double layer antireflection element above the LDS layer as shown in the device schematics provided in the insets. Two different thickness profiles of the LDS layer were evaluated within the initial designs considered – 90 µm (red triangles) and 9 µm (green circles), as well as host of different abundantly available materials frequently utilised in the fabrication of ARC’s. The error bars represent the variability of the enhancement offered through different optical thickness.

Through the careful modification of each individual layer’s optical thickness the effective refractive index of the SE-LDS structure could have been tailored towards emulating a classical quarter-quarter wavelength coating [38, 75, 76], but this option was not considered in this study. Consequently, this type of SE-LDS design (inset of figures 6.11 c & d) was not considered when
exploring the expected optical behaviour of the device, upon the homogeneous dispersal of nanoparticles throughout the polymeric network.

6.4.4 Structure Enhanced Plasmon Luminescent Down-Shifting (SE-PLDS) Devices

Exploiting the localized surface plasmon resonance (LSPR) exhibited by metal nanoparticles (MNP’s) when embedded in a composite material produces an interesting series of non-linear effects in the optical response of the nanocomposite by modulating its effective refractive index [15-17]. Controlling the size, shape and dispersion state of the MNPs within the nanocomposite material (e.g. a polymer nanocomposite) determines the spectral bandwidth over which the non-linear effects are initiated, as well as their extent [15-17]. However, in order to achieve a significant modulation in the real part of the refractive index \( n(\lambda) \), a substantially high number of MNP’s per unit volume is required [15-17]. For example, for silver-based polymer nanocomposite materials a filling factor on the order of 2.5% is required for modulations in the refractive index to become discernible [78]. If the number of MNP’s is insufficient, the optical properties of the nanocomposite material become dominated by the contributions from scattering interactions [78]. However, the inclusion of MNP’s within a polymeric network (such as an PLDS layer) can still readily impact the imaginary part of the refractive index \( k(\lambda) \) which is indicative of the state and extent of attenuation within the material [78].

In PMMA-based nanocomposite systems containing spherical silver NP’s (10 nm – 50 nm in diameter) the modulations in the real part of the refractive index were less than ~0.1, when utilizing NP concentrations of 1 wt% - 6 wt% in conjunction with a relatively thick film thickness of 20 µm to 30 µm [14-17]. Even in ultrathin (20 nm – 40 nm) films of PMMA, adopting a suitably low concentration of silver (Ag) NP’s (0.15 wt%) introduces a very small (~0.1) alteration in the real part of the refractive index, with this modification solely extended to the frequencies within the MNP’s LSPR band.
However, the accompanying modification in the magnitude of $k(\lambda)$ over the same spectral bandwidth is not so insignificant and it can achieve extinction coefficient values as high as 3 over this relatively narrow spectral window [13, 29]. Consequently, considering that the LSPR band of MNPs is tuned to occupy a spectral region (300 nm – 450 nm) that is inefficiently utilised by PV technology in order to maximise the positive interactions between the MNP’s and a luminescent material, these severe divergences in the $k(\lambda)$ of a PLDS layer can be neglected in the model. For PLDS applications, in which the objective is to utilize the MNPs to further promote the photoluminescent characteristics of a luminophore, the optimal loading concentration for a variety of different silver nanostructures has been identified to correspond to 0.013 wt% - 0.1 wt%, and is dependent upon the optical thickness of the layer [14-17]. wt% - 0.1 wt%, and is dependent upon the optical thickness of the layer [14-17]. Considering the structural merit of including thinner LDS layers in the SE-LDS designs (and the tangible possibility of the MNP interactions becoming optimised at concentrations well below the limit of the effective refractive index changes), the PLDS layer can subsequently (as a first order approximation) be represented as a pristine LDS layer with a modified $k(\lambda)$ to account for the scattering contributions which arise as a result of the presence of the Ag NP’s.

The enhancement in the $J_{sc}$ of a mc-Si cell when equipped with a SE-PLDS structure (illustrated in the inset of figure 6.12.a) in response to the simulated scattering contributions from the Ag NP’s is provided in figure 6.12.a. The figure reveals that even subtle deviations in the extinction coefficient of the PLDS layer drastically impacts the capability of the SE-PLDS devices to outperform the highly modified bare Si architecture. Through further optimizing the optical properties (refractive index, optical thickness) of the single-layer ARC, the attenuation can be compensated to a certain degree. Consequently, adopting a material of higher refractive index like SiO (figure 6.12.a – red
circle) or ZnS (figure 6.12.a – blue off-centre triangle) allows for more Ag NP’s \((k(\lambda) \propto \text{No of MNP’s})\) to be included within the PLDS layer, without sacrificing the enhanced collection efficiency. Integrating a more complex AR structure into the SE-PLDS design (as depicted in the inset of figure 6.12.b) has little influence on the performance of the hybrid device. This is demonstrated by the 5% increase in the performances attained, when switching from the highest performing single-layer design (figure 6.12.a, ZnS) to an optimised double-layer design (figure 6.12.b, Ideal-Ideal). The optical behaviour of the SE-PLDS devices summarized in figure 6.12.a and figure 6.12.b restricts the extinction coefficient to values below \(1.5 \times 10^{-4}\), if the primary objective of the adaptations in the PLDS design is to outperform the pristine uncoated PV device.

However, this description does not reflect most LDS or PLDS devices as the underlying photoconductive architecture of high-performance commercial PV cells has undergone a complex reconfiguration to attain their near maximum conversion efficiencies [1, 77]. Consequently, the addition of an encapsulating material such as PMMA, disrupts many of the advantageous structural adaptations made to the fundamental architecture of the semiconducting materials, resulting in a decrease in their performance [3, 11]. Furthermore, in the modularization of PV technology from small scale laboratory test cells like the ones utilised in chapter 5, to fully operational PV modules, a polymeric encapsulant is required for protection and stability of the framework [1]. However, in the development of new and emerging technologies (such as SE-LDS or SE-PLDS devices) an alternative approach which involves a revision in the state-of-the-art solar cell manufacturing process would be introduced to ensure maximum positive impact of the structures proposed. Under this scenario the textured surface frequently encountered in mature grade Si technology would be replaced with an optimised SE-LDS/SE-PLDS structure, and the disruptions typically introduced into the device collection efficiency circumvented. Under this scenario, irrespective of the magnitude of
the scattering losses introduced through the inclusion of the Ag NP’s, the fitting of the additional optical structure still offered a substantial 10% (figure 6.12.c, SiO) to 20% (figure 6.12.c, ZnS) enhancement in the collection efficiency of the cell, as compared to the conventional PLDS device.

**Figure 6.12:** Enhancement in the short-circuit current density (J_{sc}) of a structure enhanced plasmonic luminescent down-shifting (SE-PLDS) device, incorporating (a) single layer and (b) double layer antireflection coatings of different compositions, as a function of the encapsulating layers (polymethylmethacrylate – PMMA) extinction coefficient (k): with a schematic of each device design included in the insets. (c) The average enhancement in the J_{sc} of a monocrystalline silicon photovoltaic cell when fitted with a number of different single- and double-layer antireflection coatings. The error bars represent the variation in the device’s performance exhibited by adopting different optical thicknesses of each individual coating.
6.5 Conclusion

A series of highly transparent thin-film optical coatings were designed to exploit the optical properties of conventional LDS and PLDS devices which were built upon a monocrystalline-silicon photovoltaic cell. The capability to tune the optical properties of the standalone thin-film coatings (single-layer and double-layer designs) was theoretically explored in response to changes in the effective refractive index and the optical thickness of the coating. The associated influence of each iteration of the supplementary optical structures on the conversion efficiency of the PV cell was also explored, and the optimal design criteria for each type of structure (single-layer, double-layer) was identified. Through a combination of experimental and theoretical approaches, the reflectance spectra of the individual components of the SE-LDS device (the LDS layer, the Si substrate, and the thin-film component) were accurately predicted within the modelling environment. Comparing the corresponding short-circuit current density generated within these modeled and experimental devices, enabled the performance output of the model to be directly correlated with the performances achieved under real world laboratory conditions. As a result, the modelled integration of a single- or double-layer coating into the SE-LDS device, predicts a 7.5 % - 20% enhancement in the collection efficiency, as inferred through the $J_{sc}$. Downsizing the LDS layer from a thickness of 90 µm to 9 µm also assisted in promoting an additional 0.4% – 3% increase in the enhancement. The divergence in the optical response of the two initially proposed SE-LDS designs facilitated the development and refinement of an initial set of design considerations for this type of architecture. The more complex SE-PLDS device designs were examined using a 1st order approximation of the modulation in their effective refractive index upon the inclusion of silver nanoparticles, and the subsequent optical and electrical behaviour of the hybrid devices was investigated. The simulations indicate that irrespective of the magnitude of the modulation in the extinction coefficient of the PLDS
layer (owing to the presence of metal nanoparticles), the additional thin-film coatings can still offer substantial benefits to counteracting and curtailing the optical losses within the SE-PLDS structure. Through correspondingly fine-tuning the structural element in the SE-PLDS devices, a 7% - 20% increase in the energy harvesting potential of a conventional PLDS device was predicted. Considering that the enhancement stemmed purely from optical matching of the construction materials, the possible occurrence of spectral modulations in the incoming solar flux (initiated through photoluminescence), and its subsequent interactions with the embedded silver nanoparticles, could offer further synergistic interactions between the individual design elements.

6.6 References


Chapter 7
Conclusions and Future Work

7.1 Introduction

In recent years the need to address the limitations inherent in solar technology (photovoltaic - PV, photothermal - PT) has become of paramount importance, as the decarbonisation of the global economy continues. Many different iterations of the luminescent down-shifting structure have been explored in attempts to push the efficiencies achievable with PV applications beyond that which is attained with conventional PV architectures. These retrofitted device add-ons have been studied and developed utilising different combinations of luminescent materials and metal/metallic nanoparticles. Additionally, these very same molecular strategies to a lesser extent have also been deployed in PT applications, in the promise of promoting the heat transfer capabilities of a diverse range of classical heat transfer fluids.

The first part of this work has involved the fabrication, characterisation, and utilisation of silver nanoparticles to enhance the collection efficiency of a standardised flat plate solar thermal collection system. This is one of the first instances in which experimentally the interactions between neighbouring nanoparticles of different sizes and morphologies have been exploited to further promote the thermophysical behaviour of a working fluid.

The second part of this work has involved the characterisation of a series of novel organic and organometallic luminescent species exclusively developed for LDS applications, which were built upon a highly adaptable imidazole[4,5-f][1,10]phenanthroline scaffolding. Some of these luminescent materials are completely new from a structural standpoint, while for others this is the first time the phenanthroline derivatives have been extensively studied and exploited for solar applications.
The third part of this work investigated the novel application of some of these same luminescent down-shifting phenanthroline derivatives as a hybridised heat transfer fluid within a combined spectral beam splitting photovoltaic-thermal (SBS-PVT) system. This is the first time this type of molecular structure has ever been employed in a combined heat and power system. Additionally, the synthetic strategy applied also represents the first instance of trying to utilise luminescent down-shifting in a liquid optical filter, to modulate the thermal and electrical outputs more efficiently within a PVT system.

In the fourth and final part of this work a newly proposed solar cell architecture which builds iteratively upon the plasmonic luminescent down-shifting (PLDS) strategy was theoretically explored for PV applications using a transfer matrix model. The hypothetical structure’s devised represent the first instance of integrating a spectrally selective antireflection coating whose optical properties have been tailored towards maximising the efficiency enhancement afforded through down-shifting approaches to light-management in PV applications. A summary of these works is concluded in the following sections.

7.2 Nanomaterials: Synthesis, Characterisation and Performance in Solar Thermal Applications

A simple and relatively cost-effective nano-synthesis protocol was adapted to investigate the optical and thermophysical behaviour of different types of nanoparticle size-distributions, when employed as silver-based nanofluids within a solar-thermal collection system. The adapted synthesis method allowed for the bandwidth of energy captured by the nanofluids to be readily tuned through straightforward modifications in the concentration of the precursor chemicals used during the heterogeneous growth of the nanoparticles. Thereby, the optical and morphological characteristics of the individual size-distributions contained within the nanofluids particle ensemble were attuned for studying the impact of interparticle interactions on the thermal behaviour of the working
Employing low concentrations (0.05% - 0.1% v/v) of nanoparticle ensembles containing a diverse set of individual particle morphologies and particle size-distributions, was demonstrated to provide a 10% - 15% improvement in the thermal collection efficiency of the working fluid, when compared with their monomodal counterparts. The emergence of this diverging behaviour in the thermal collection efficiency, was correlated to changes in the individual populations of the numerous size-distributions contained within the internal structure of the nanofluid. Hence, through the incorporation of different particle size modes, it was effectively demonstrated how using one (and/or narrow) particle size-distribution to control and optimize the heat transfer properties of a nanofluid does not represent the best approach. Furthermore, within the multimodal size-distributions contained within the nanofluids internal structure, an upper threshold in the particle size was (with a strong degree of correlation) associated with restrictions in the enhancement of the fluid’s thermal properties. Consequently, the principle of exploiting a wide distribution of particle sizes to enhance the collection efficiency in solar thermal applications was experimentally established.

7.2.1 Contribution to Knowledge

➢ One of the first experimental instances of demonstrating the enhanced photothermal collection efficiency of a metal based nanofluid containing a multitude of different particle shapes and individual particle size-distributions

➢ One of the first experimental examples to corroborate the modification of the thermophysical behaviour of a multimodal silver-based nanofluid (stagnation temperature, PTE, and thermal conductivity) with deviations in the individual populations of the numerous particle size-distributions contained within the nanofluid

➢ The interparticle interactions which promoted the enhanced thermophysical performance of the multimodal nanofluid were controlled (to a strong degree), by
the maximum size of the particles contained within the collective particle ensemble

➢ The existence of an upper threshold (diameter ~ 150 nm) in the nanoparticle size was discovered, above which an increasing particle size was strongly linked to a decrease in the enhancement afforded through the multimodal approach

7.2.2 Suggestion for Future Work

Although the presence of numerous individual particle size-distributions was correlated with an enhanced photothermal conversion efficiency in the nanofluid, the molecular mechanisms by which the heat transfer processes were intensified remains to be investigated and identified. Through a combination of experimental and theoretical approaches the impact of each one of the nanofluids internal attributes (composition, particle size-distribution, particle morphology, presence or absence of stabilising agents etc.) should be evaluated and utilised to further probe the thermophysical behaviour of the multimodal working fluids. Under this scenario, the fundamental mechanisms could be resolved and be potentially further exploited to promote the thermal properties of the silver based nanofluids. Additionally, although the nanostructures explored exhibited a relatively broad LSPR absorption band extending from 250 nm to 800 nm, the broadband nature of the solar spectrum leaves ample opportunity for incorporating additional molecular species into the nanofluid. Under this schema, the additional molecular species (carbon-based nanomaterials, fluorescent ligands, or upconverting nanocrystals) would be utilised to enable the hybridised working fluid to interact with the totality of the solar spectrum. Thereby, allowing for potentially even greater enhancements in the photothermal conversion efficiency to be realised in solar thermal applications.

7.3 LDS Materials: Characterisation, Evaluation and Device Fabrication

A new basis for organic LDS materials was investigated through the structural activity relationship established between the functionalization of a imidazole[4, 5-
f][1,10]phenanthroline core and the resulting photoluminescent properties exhibited by the series of adapted frameworks. The optical properties and structural merits of 27 individual phenanthroline derivatives was evaluated to assess their suitability for integration in LDS applications. From this library of starting materials, a total of 10 candidates were selected for further optical characterisation including measuring their LQY in solution. The P282, P205 and P183 adaptations of the phenanthroline scaffolding exhibited a promising combination of properties for inclusion in LDS applications, namely their near unity (80% to 100%) LQY in solution. The optical behaviour of P282, P205 and P183 when independently embedded within a 10 µm thick PMMA film was studied under an expansive range of concentrations, ranging from 0.0078 wt% to 3 wt%. The dispersion state of the luminophore’s throughout each polymeric matrix was assessed by the deviations introduced into the absorption spectrum, the emission spectrum, and the LQY of the LDS films under the increased loading concentrations employed. From these divergences in the optical behaviour, the optimal concentration of the P282, P205 and P183 molecules within each LDS layer was identified as 0.063 wt%, 0.016 wt% and 0.0078 wt%, respectively. The capability of each molecular structure to effectively down-shift and modulate the solar spectrum when incorporated in the optimised 10 µm thick LDS layers was assessed using state-of-the-art commercial grade mc-Si cells (2 cm x 2 cm). The conversion performance of the mc-Si cells with and without the optically active component of the LDS layer’s (i.e. the photoluminescent species), was characterised using a simulated solar spectrum under artificial climate conditions. The presence of all three molecules promoted an absolute enhancement in the conversion efficiency of the mc-Si cells ranging from 0.4 ± 0.05 % to 0.93 ± 0.05 %, due to the photoluminescent nature of each molecule. Additionally, the stability of each photo-selective LDS layer was investigated under accelerated artificial aging conditions, with the P282 structure exhibiting the most promising photostability of the three LDS candidates.
7.3.1 Contribution to Knowledge

➢ Established a well-developed structural activity relationship between the specific chemical moiety substituted onto a imidazole[4, 5-f][1,10]phenanthroline scaffolding and the subsequent photoluminescent properties of a series of novel organic/organometallic fluorescent materials

➢ Several promising new materials were identified for inclusion in solar energy applications including LDS, SBS and PT technologies, namely: P282, P205, P187, P183, P181 and P166

➢ This is the first instance of the optical behaviour of P282, P205 and P183 being characterised in PMMA films for LDS-PV applications

➢ An improved conversion efficiency was achieved in state-of-the-art commercial grade mc-Si solar cells using novel standalone phenanthroline based LDS layers for the first time

➢ Preliminary trials were performed to assess the photostability of a series of highly fluorescent phenanthroline based ligands designed for LDS-PV applications for the first time

➢ The highly luminescent materials catalogued represent innovative alternatives for modifying the photophysical behaviour of metal coordination complexes as polydentate ligands – leading to potential advancements in down-shifting strategies for PV applications

7.3.2 Suggestion for Future Work

Considering the incredible capability of nanoparticles to modulate the photoluminescent and physical properties of an LDS device, the nanosynthesis protocol adopted in chapter 3 could serve to further extend the enhancement offered through the phenanthroline based approach to LDS. Incorporating such a diverse set of nanoparticle shapes and sizes could possibly promote an enhanced light coupling effect far exceeding
that achieved with conventional narrow particle size-distribution approaches to plasmonic luminescent down-shifting. Consequently, the decreases in the LQY incurred for the P282, P205 and P183 molecules when embedded within the PMMA network could potentially not only be compensated for by the interactions with the nanoparticles, but their fluorescent intensity could become enhanced well beyond their performance reported in the liquid state. In addition, the integration of nanoparticles within the LDS layers would also promote an enhanced degree of photostability, making progressive improvements over the moderate stability reported for the standalone phenanthroline based fluorophores.

Finally, the series of highly fluorescent ligands catalogued could be incorporated into metal coordination complexes as polydentate ligands and serve as a 2nd generation of the phenanthroline based approach to LDS. Thus, their inclusion in a coordination complex could promote a spectral shift of the light captured by these light sensitive chromophores further into the red end of the visible spectrum (600 nm – 650 nm), where solar cells are more efficient.

7.4 LDS Optical Filters for SBS-PVT Applications

From the series of luminescent species catalogued for solid-state LDS applications, a selected group of the novel luminophores were integrated as liquid LDS optical filters within an SBS-PVT system. The capability of the molecular compounds to modulate the spectral characteristics of the transmitted solar flux, and to modify the thermophysical behaviour of an ethylene glycol based working fluid was established. The complimentary ultraviolet and visible wavelength absorption contributions provided by the inclusion of the molecular species resulted in a 4% to 15% increase in the stagnation temperature reached by the composite working fluids, when compared with the pristine base fluid. In addition, the impact of each liquid optical filter on the electrical performance of a mc-Si PV cell demonstrated the decrease in the electrical conversion
efficiency as more of the solar spectrum was converted into thermal energy within the working fluid. Furthermore, the ability of the LDS fluid’s to more effectively convert solar irradiance into useable electricity and thermal energy within a standardized PVT system was demonstrated using a semi-empirical merit function. The results showed how incorporating the phenanthroline based compounds within a PVT system contributed to an optical collection efficiency of 25% to 63%, a marked improvement over the 20% conversion efficiency attainable with the standalone PV. The additional modifications in the spectroscopic properties of the composite fluid also yielded a subsequent 2% to 61% increase in the economic value of the energy captured, when compared with the pristine base fluid. Consequently, the combined capability of the molecular structures to elicit not only an intensified rate of heating, but also complementary fluorescence, makes them exceedingly suitable for addressing some of the shortcomings identified in alternative working fluid strategies. Overall the results provide a new organic basis for effectively designing high performance spectrally selective heat transfer fluids for SBS-PVT applications.

7.4.1 Contribution to Knowledge

➢ This is the first instance of the optical and thermal behaviour of the P282, P205, P187, P183, P181 and P166 phenanthroline derivatives being investigated for PVT applications

➢ First reported instance of exploiting LDS in a PVT system to mitigate the electrical energy sacrificed through merging the thermal and electrical components

➢ A series of promising new materials were identified for inclusion in combined heat and power applications
The organic/organometallic phenanthroline derivatives studied showcase a favourable combination of thermophysical, optical and fluorescent characteristics when employed as hybrid heat transfer fluids within an SBS-PVT system.

The inclusion of the catalogued series of phenanthroline derivatives within ethylene glycol increased the optical efficiency of the PVT collection system as well as the economic value of the energy captured.

The economic merit of modifying the spectral characteristics of the phenanthroline based working fluids was assessed in relation to fluctuations in the geographical and socio-economical energy-landscape for the first time.

### 7.4.2 Suggestion for Future Work

Although the capability of the materials to modify the stagnation temperature and rate of heating within ethylene glycol was physically demonstrated, a more thorough characterisation of the composite fluids thermophysical properties remains warranted. Particularly, the thermal conductivity of the working fluids under increased loading concentrations and increased fluid temperatures should be determined. This would enable and develop a deeper understanding of the chemical parameters which dominate the enhancement or curtailment of the thermophysical properties of this type of working fluid. Additionally, more of the library of materials catalogued in chapter 4 should be evaluated for their application in PVT systems – especially the 2nd generation of materials which exhibited an intensified absorption band when compared with the 1st generation of luminophores. Studying the behaviour of these alternative phenanthroline derivatives would allow for refinements to be made in the molecular design process, and thereby maximise the performance of the materials.

In order to further intensify the unique luminescent characteristics of this type of working fluid two different aspects of their design should be considered (1) integrating the individual phenanthroline ligands into a metal coordination complex for enhanced...
down-shifting of the solar spectrum, (2) including metal nanoparticles such as those characterised in chapter 3 to assist in promoting the fluorescent intensity and the thermal properties of the hybrid working fluid. These two alternative approaches would not only allow for the photoluminescence to be fine-tuned to a region of higher PV spectral responsivity, enhance the intensity of the emission process, but would also complementarily modify the thermal properties of the working fluid.

7.5 Structure Enhanced-LDS and PLDS devices: A Theoretical Study

A newly proposed hypothetical architecture which builds upon the LDS and PLDS approaches to light management within PV applications was theoretically investigated using a transfer matrix model. The new type of architecture consisted of a series of highly transparent thin-film optical coatings (single-layer and double-layer designs) designed to exploit the optical properties of conventional LDS and PLDS devices, which were built upon a monocrystalline-silicon photovoltaic cell. The capability to attune the optical properties of the standalone thin-film coatings was theoretically explored, and the optimal criteria for maximising the collection efficiency of the PV cell with each type of structure (single-layer, double-layer) was identified. Through a combination of experimental and theoretical approaches, the outputs of the model were accurately correlated with the behaviour of physical devices under real world laboratory conditions, to within experimental uncertainty. The modelled integration of the single- or double-layer coatings into the newly created SE-LDS device, predicted a 7.5 % to 20% enhancement in the collection efficiency, as inferred through the $J_{sc}$. Downsizing the LDS layer from a thickness of 90 µm to 9 µm also assisted in promoting an additional 0.4% – 3% increase in the device performance. In Addition, the divergences in the optical response of two initially proposed SE-LDS designs assisted in the development and refinement of an initial set of design considerations for this type of architecture. The simulations also indicated that irrespective of the magnitude of the modulation in the
optical properties of a PLDS layer (owing to the presence of metal nanoparticles) the additional thin-film coatings still offer substantial benefits to counteracting and curtailing the optical losses within the SE-PLDS structure. Consequently, through correspondingly fine-tuning the structural element in the SE-PLDS devices, a 7% to 20% increase in the energy harvesting potential of a conventional PLDS device was predicted. Therefore, through the concept of effectively optically matching the construction materials of LDS-PV and PLDS-PV devices, a more energy efficient conversion process can be realised.

7.5.1 Contribution to Knowledge
➢ The promise of incorporating additional thin-film optical components into LDS and PLDS light management strategies in PV applications theoretically demonstrated using a transfer matrix model
➢ Simple ARC’s were exploited for enhancing the optical matching of the construction materials utilised in LDS/PLDS devices for the first time
➢ The simulated optical and electrical behaviour of the newly proposed SE-LDS/SE-PLDS device architecture was systematically verified through experimental comparison between the behaviour exhibited by each one of the individual ‘modelled’ device components
➢ A set of initial design considerations were established for the SE-LDS and SE-PLDS structures when integrated into mc-Si PV technology

7.5.2 Suggestion for Future Work
Considering the predicted enhanced conversion efficiencies stemmed purely from a more effective optical matching of the construction materials, the additional interactions of the solar flux with the luminescent species and MNP’s present within the LDS/PLDS layer should be considered. This would allow for the modulations in the solar flux by the down-conversion process, and the augmentation of the luminescent material’s optical
properties (through its interactions with the MNP’s present) to be included in the calculations considered throughout the evaluation process.

Through a few straightforward assumptions about the LDS layer the absorption spectra, the emission spectra, and the LQY of the LDS layer’s fabricated and characterised in chapter 4 should be used to model the behaviour of the interactions of the luminescent species with the AM1.5G solar spectrum. The additional interaction of the MNP’s within the polymer layer, both on its effective refractive index and its refinement of the modified AM1.5G spectrum, should be incorporated through experimentally casting PLDS layers which contain the NP’s synthesised using the protocol outlined in chapter 3. Through the subsequent characterisation of the PLDS layers produced, the influence of the concentration of the MNP’s on the PLDS layers optical representation within the modelling environment would be more accurately realised. Consequently, any predictions made using the theoretical model established would be made more realistic.

7.6 Publications

**Journal Publication**


**Conference Publications**


- James Walshe, Pauraic Mc Carron, Hind Ahmed, Sarah McCormack, John Doran, Metal Coordination Complexes: A Bottom-Up Approach Tailored Towards Solar
8.0 Concentration Conversions

*Table 8.1:* The concentration of P282 employed (wt%) in the casting of the 10 μm thick solid LDS layers discussed in chapter 4, with the conversion between wt% and molarity (mM) displayed for convenience

<table>
<thead>
<tr>
<th>Loading concentration of material in Plexit 55 Röhm (wt%)</th>
<th>Molarity of the luminophore/resin mixture pre-casting (x10^{-3} M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0078</td>
<td>0.161</td>
</tr>
<tr>
<td>0.0157</td>
<td>0.322</td>
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<tr>
<td>0.0313</td>
<td>0.643</td>
</tr>
<tr>
<td>0.0625</td>
<td>1.287</td>
</tr>
<tr>
<td>0.125</td>
<td>2.302</td>
</tr>
<tr>
<td>0.250</td>
<td>4.603</td>
</tr>
<tr>
<td>0.500</td>
<td>9.206</td>
</tr>
<tr>
<td>0.750</td>
<td>13.810</td>
</tr>
<tr>
<td>1.000</td>
<td>18.413</td>
</tr>
<tr>
<td>2.000</td>
<td>36.826</td>
</tr>
<tr>
<td>3.000</td>
<td>55.238</td>
</tr>
</tbody>
</table>

*Table 8.2:* The concentration of P205 employed in the casting of the 10 μm thick solid LDS layers discussed in chapter 4, with the conversion between wt% and molarity (mM) displayed for convenience

<table>
<thead>
<tr>
<th>Loading concentration of material in Plexit 55 Röhm (wt%)</th>
<th>Molarity of the luminophore/resin mixture pre-casting (x10^{-3} M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0078</td>
<td>0.206</td>
</tr>
<tr>
<td>0.0157</td>
<td>0.412</td>
</tr>
<tr>
<td>0.0313</td>
<td>0.824</td>
</tr>
<tr>
<td>0.0625</td>
<td>1.648</td>
</tr>
<tr>
<td>0.125</td>
<td>2.947</td>
</tr>
<tr>
<td>0.250</td>
<td>5.894</td>
</tr>
<tr>
<td>0.500</td>
<td>11.787</td>
</tr>
<tr>
<td>0.750</td>
<td>17.681</td>
</tr>
<tr>
<td>1.000</td>
<td>23.574</td>
</tr>
<tr>
<td>2.000</td>
<td>47.149</td>
</tr>
<tr>
<td>3.000</td>
<td>70.723</td>
</tr>
</tbody>
</table>
Table 8.2: The concentration of P183 employed in the casting of the 10 μm thick solid LDS layers discussed in chapter 4, with the conversion between wt% and molarity (mM) displayed for convenience

<table>
<thead>
<tr>
<th>Loading concentration of material in Plexit 55 Röhm (wt%)</th>
<th>Molarity of the luminophore/resin mixture pre-casting (x10³ M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0078</td>
<td>0.127</td>
</tr>
<tr>
<td>0.0157</td>
<td>0.254</td>
</tr>
<tr>
<td>0.0313</td>
<td>0.508</td>
</tr>
<tr>
<td>0.0625</td>
<td>1.016</td>
</tr>
<tr>
<td>0.125</td>
<td>1.816</td>
</tr>
<tr>
<td>0.250</td>
<td>3.633</td>
</tr>
<tr>
<td>0.500</td>
<td>7.265</td>
</tr>
<tr>
<td>0.750</td>
<td>10.898</td>
</tr>
<tr>
<td>1.000</td>
<td>14.530</td>
</tr>
<tr>
<td>2.000</td>
<td>29.061</td>
</tr>
<tr>
<td>3.000</td>
<td>43.591</td>
</tr>
</tbody>
</table>