



Sustainable Energy Authority of Ireland

National Energy Research,
Development & Demonstration
Funding Programme

FINAL REPORT TEMPLATE

SECTION 1: PROJECT DETAILS – FOR PUBLICATION

Project Title	Optical Antennas and the Purcell effect: Towards efficient solar concentration
Lead Grantee (Organisation)	Dublin City University
Lead Grantee (Name)	Daragh Byrne
Final Report Prepared By	Daragh Byrne
Report Submission Date	

	Name	Organisation
Project Partner(s)	N/A	
Collaborators	N/A	

Project Summary (max 500 words)

This project sought to develop novel technology based on luminescent solar concentrators to improve the efficiency of photovoltaic cells operating in low light conditions. A range of approaches were investigated to improve LSC device performance, including plasmonic based enhancement, carbon quantum dots, novel fluorophores and biodegradable based LSC waveguides. A range of plasmonic based devices were modelled, fabricated and tested. Whilst individually these devices shown significant enhancements in the optical output of the individual fluorophores near of within the optical antenna, the enhancement observed by the ensemble device was limited by a number of factors. The critical issues arose from the ohmic losses from the antennas and limits in the doping concentration achievable within the optical cavity. The fluorescence arising from carbon quantum dots was investigated where it was found that much of reported scientific literature was in accurate in ascribing the source of observed emissions to the carbon dots. Based on the study of the chemistry of carbon dots, a range of novel molecular fluorophores were developed. These fluorophores were derived from modification of citrazinic acid a key component in the fluorescence observed from carbon dots. Two particular derivatives showed promise for further development, having a high quantum efficiency approaching unity. To address the issues surround product end of life arising from the use of petrol chemical based plastics, more environmentally benign

biopolymer waveguides were investigated in conjunction with both conventional molecular fluorophores and the fluorophores developed in this project.

Keywords (min 3 and max 10)

Luminescence solar concentration, Carbon Quantum dots, photovoltaics, fluorescence

NB – Both Section 1 and Section 2 of this Final Report will be made publicly available in a Final Technical Report uploaded online to the National Energy Research Database.

In the following Section, please provide a clear overview of your project, including details of the key findings, outcomes and recommendations. The section headings below are provided as a guide, please update or add to these as best suits your project.

By submitting this project report to SEAI, you confirm you are happy for Section 1 and Section 2 of this report to be made publicly available. If you wish to request edits to this section in advance of publication, please contact SEAI at EnergyResearch@seai.ie.

SECTION 2: FINAL TECHNICAL REPORT – FOR PUBLICATION

(max 10 pages)

2.1 Executive Summary

The concept of luminescent solar concentration has been explored for several decades as means for boosting photovoltaic cell performance in low light conditions. In its simplest form, luminescence solar concentrators (LSCs) consist of a glass or polymer sheet which has been doped with a luminescent moiety such as organic dye, fluorescent ions, phosphor or quantum dots. Light entering the sheet is absorbed by the luminophore and reemitted at a longer wavelength, closer to the maximum absorption of a photovoltaic cell. Current LSC designs have a number of draw backs which limit their efficiency. This project examined a range of approaches to enhance the efficiency and improve the LSC design and improve the device performance and environmental profile. Optical antennas, while enhancing the performance of individual fluorophores, had minimal impact on the overall device performance. The carbon quantum dots regularly reported to yield broad spectral emissions are in general contaminated by small quantities of high quantum yield fluorophores. In this project methods to directly synthesis these fluorophores directly have yielded a range of novel fluorophores. To minimise the impacts of end-of-life pollution, a broad range of biopolymer-based waveguides have been tested, the most promising of which is cellulose acetate.

2.2 Introduction to Project

This project aims to improve the sustainability and reduce the environmental impact of urban areas by exploring new approaches to solar energy harvesting. Solar cells need bright light in order to operate efficiently. In built up areas such as cities, the shadows cast by buildings reduce the ambient light levels, limiting the range of locations where solar panels can be installed. Greater urbanisation and increased building heights, limit the ability to increase solar capacity and to reduce a buildings carbon footprint. However, if diffuse or low intensity light can be concentrated onto smaller solar cells, the increase in performance will enable a much wider range of urban surfaces to be exploited for energy

harvesting. Current fluorescence-based methods to concentrate light are hampered by relatively low levels of efficiency, limiting their potential usefulness and widespread applicability. In contrast, nanoscale metal structures such as optical antennae can efficiently capture solar energy and transmit energy with greater control over direction. These attributes make them an attractive alternative to current solar concentration technologies. By focusing on the fundamental physics, antennae design, material properties and optical configurations, this project aims to explore the potential of large area optical antenna arrays to function as highly efficient solar concentrators.

2.3 Project Objectives

The principal aim of this project was to develop methods to collect low intensity light and concentrate it for enhanced photovoltaic applications using luminescent solar concentrators. A range of strategies were employed, including plasmonic based optical antennas, carbon quantum dot-based fluorescence, other novel fluorophores and biopolymer-based waveguides.

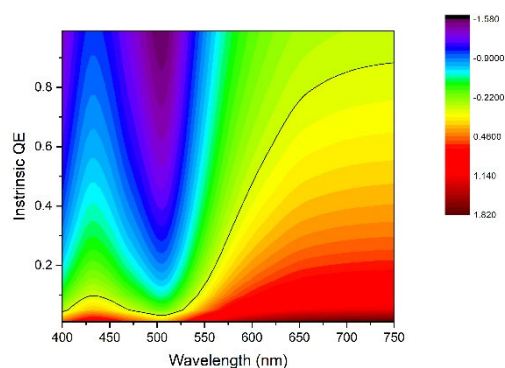
2.4 Summary of Key Findings/Outcomes

Plasmonics

Initial work on this project examined plasmonic nanostructures and their incorporation into LSC devices. This work consisted of two strands, finite element modelling of optical antennas to calculate the field enhancements and Purcell enhancements and secondly device fabrication and testing.

The finite element modelling performed looked at both silver and gold based isolated antenna in both the free space and encapsulated states

using a single particle size and incidence angle. These models have been used to produce full spatial and spectral maps of both electric field distribution within an antenna and Purcell enhancements for all quantum efficiency fluorophores (i.e. QE = 0 to 1, an example of which is shown in figure 1.) The impact of encapsulation on the plasmonic structures was investigated using a nominal polymer material with purely real refractive index of 1.4,



is the threshold point between enhancement and quenching

equivalent to a PMMA type matrix. Later this modelling was expanded to look at the influence of excitation angle and the impact of neighbouring antennas. The emission directionality of individual fluorophores was explored as a function of the fluorophore dipole moment, in tandem with experimental approaches. Interparticle scattering appears to play a significant role in the experimental measurements. However, such effects are difficult to model as they require large domain sizes beyond the computing processor power available.

Fabrication and characterisation of optical antenna arrays

Fabrication and testing of optical antenna arrays focused on conventional fluorophores across a range of quantum efficiencies, using silver nanoparticles in conjunction with gold films. Net enhancements were obtained for most configurations tested. As explored by the FEM modelling significant enhancements were only achieved using the lowest quantum efficiency fluorophores which emit at longer wavelengths of the spectrum ($\lambda > 500$ nm). While enhancements have been achieved, the general light output is still relatively low. Two factors limited the net output. First, the ability to achieve sufficient fluorophore density within the active region of the optical antenna and second the dipole orientation of the fluorophore. In the encapsulated state, it was found that the enhanced optical cross-section of the optical antenna in conjunction with the significant ohmic losses of the nanoparticle lead to significant reabsorption losses. One approach to limit these losses would be to optically isolate the antenna array from the waveguide, however practical approaches to achieve this were not investigated as restrictions arising from covid forced a change in project direction.

In addition to free space antenna arrays, a wide variety of encapsulated devices were tested, yielding mixed results. Both enhancements in emission and quenching were observed. The finite element modelling suggested that the impact of encapsulant refractive index would have less impact on the fluorescence than observed. Whilst unconfirmed, the variations observed may arise from factors such as nanoscale delamination of the optical antennas, chemical quenching of the fluorophores from the curing polymers, or increased scattering/reduced collection efficiency at the detector waveguide interface.

Carbon Dots and fluorophores

Carbon quantum dots (C-dots) are widely hailed as a revolutionary optical material with tuneable properties such as absorption and emission wavelengths. C-Dots are small fragments of graphene with dimensions in the order of a couple of nano-meters. These particles are found to readily form via the thermal decomposition of a wide range of organic materials. One of the most widely used synthetic routes to C-Dot formation is via the hydrothermal and solvothermal decomposition of a citric acid / urea mixture. It has been reported in the scientific literature that by varying parameters such as the reagent concentrations, temperature and choice of solvent it is possible to tune the emission characteristics of the C-Dots across the full visible spectrum. Furthermore, it has been reported that the C-Dots formed by this method are bio-compatible, stable and have fluorescence quantum yield between 0.05 and 0.4. These characteristics make them ideal for a diverse range of applications. However, because of the stochastic nature of the decomposition process, one of the principal challenges in producing high quality C-Dots is purification. In addition to these processing challenges, much debate still surrounded the origins of the observed optical properties. In order to optimise their optical properties for solar concentration applications, an essential component of the research focused on studying the origins of the fluorescent emissions.

Green and Blue emitters

Initially, significant progress was made in replicating the synthetic procedures described in the literature to produce a range of C-Dot solutions with emission wavelength ranging from 430 nm to 630 nm. Focus then turned to methods to purify the C-dots so as to enhance their quantum yield, by removing broadly absorbing carbonaceous impurities. A range of approaches were examined such as centrifugation, dialysis, precipitation and phase transfer. As successive purification methods were examined it became increasingly apparent that increases in the C-Dot quantum yield for blue and green emissive species correlated with the removal of the carbon dots themselves. Concurrently, a range of publications revealed that within this spectral range, molecular fluorophore produced as a by-product of the hydrothermal decomposition were largely responsible for the observed blue and green emissions. These reports identified citrazinic acid, citrazinic acid clusters and a citrazinic acid derivative (4-hydroxy-1H-pyrrolo[3,4-c]pyridine-1,3,6(2H,5H)-trione or HPPT) as being the primary origins of the short wavelength fluorescence. These results largely agreed with data obtained in this project. Photobleaching studies were undertaken so as to further understand the nature of the relationship between C-Dots and the molecular fluorophores, revealing that under some

conditions the molecular fluorophores were free in solution and consequently unprotected from oxidative attack whilst under different processing conditions the C-Dots preserved UV-deactivation. However, this performance enhancement came at a cost, specifically, reduced quantum yields. Furthermore, it was unclear whether the presence of C-Dots was acting as an internal filter, reducing the generation of oxidative free radicals or if the molecular fluorophores were incorporated within the C-Dot structure and physically protected from damage. In either case, in a solid matrix such as a solar concentrator, the rate of oxidative damage would be attenuated anyway, so as to render the issue less critical.

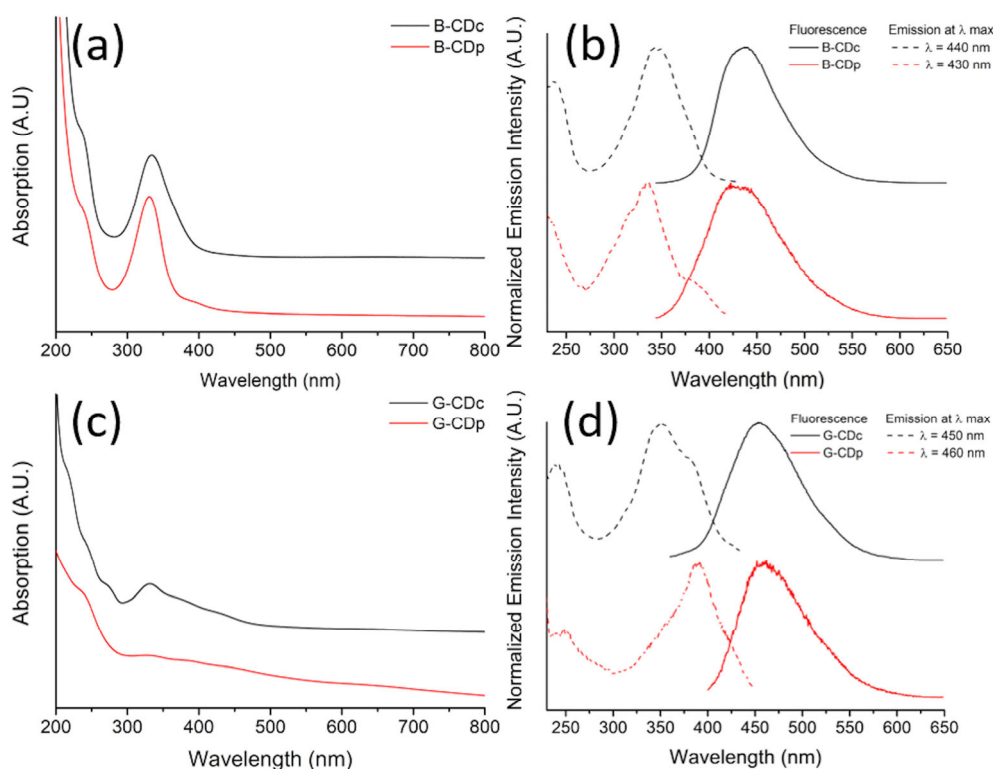


Figure 2: (a) Absorption spectra of (black line) Blue-CD crude (red line) B-CD purified (b) Fluorescence spectra of (solid black line) Blue-CD crude (solid red line) B-CD purified. Excitation spectra at $\lambda =$ fluorescence max of (black dashed line) Blue – CD crude (red dashed line) B-CD purified (c) Absorption spectra of (black line) Green-CD crude (red line) Green-CD purified (b) Fluorescence spectra of (solid black line) Green – CD crude (solid red line) G-CD purified. Excitation spectra at $\lambda =$ fluorescence max of (black dashed line) Green – CD crude (red dashed line) G-CD purified.

A detailed study of the optical properties of both molecules (an extract of which is shown in figure 2), revealed that both had a high quantum yield and relatively high stokes shift making them excellent candidates for a multi-layered solar concentrator device. In particular, the HPPT molecular had a quantum yield close to unity (and beyond the range of accuracy achievable with the available equipment). Both molecules possessed a large stokes shift of circa 80 nm, which would reduce the reabsorption losses in a solar concentrator.

Orange and Red emitters

As with the blue and green emitters, much uncertainty surrounded the origins of the observed orange and red fluorescence derived from dimethylformamide (DMF) processed citric acid carbon quantum dots. Two opposing views were expressed in the literature. First, the DMF promoted carbonation leading to larger carbon dots. The increased graphene domain size leads to increased thermalisation of the excited state electrons shifting the observed emission to longer wavelengths. Alternatively it was proposed that the DMF increase nitrogen incorporation into the graphene molecule thereby modifying the band structure leading to a lower energy bandgap and longer emission. In both instances, it has been proposed that edge states on the graphene moiety lead to non-radiative recombination. Passivation of the molecule with NaOH or other cationic species decreases the non-radiative recombination rate, thus increasing the quantum

yield. Typically the quantum yield reported for these materials were circa 10%. Given the relatively low quantum yield and reported spectral position, it was believed that these carbon dots would make ideal emitters for plasmonic amplification as highlighted by the earlier finite element modelling. However, as with the blue and green emitters it was first essential to optimise and purify the C-Dots before use.

During the early stage of purification, it was observed that filtering the crude reaction solutions lead to a high degree of adhesion between the fluorescent moiety and the filter paper. This property was subsequently confirmed using paper chromatography and exploited as a means to purify the carbon dots. Using preparative chromatography, with microcrystalline cellulose as a stationary phase all other impurities present could be successfully removed in a single stage operation. Under the correct conditions, the fluorescent material could be preserved on the cellulose, dried and packaged for later recovery on demand. Furthermore, the high degree of purification, increased the quantum yield of the material to close to 40% matching the highest reported yields for this material. Examples of the materials properties and usage are shown in figure 4.

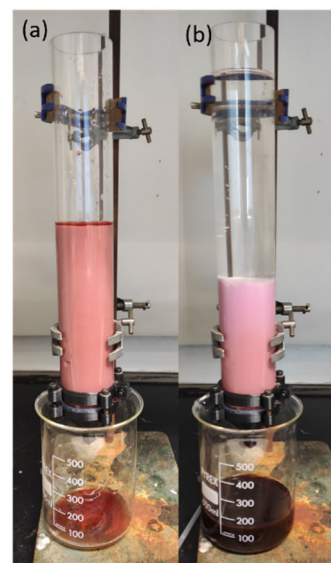


Figure 3: C-Dot purification process (a) crude suspension (b) crude suspension 50% purified.

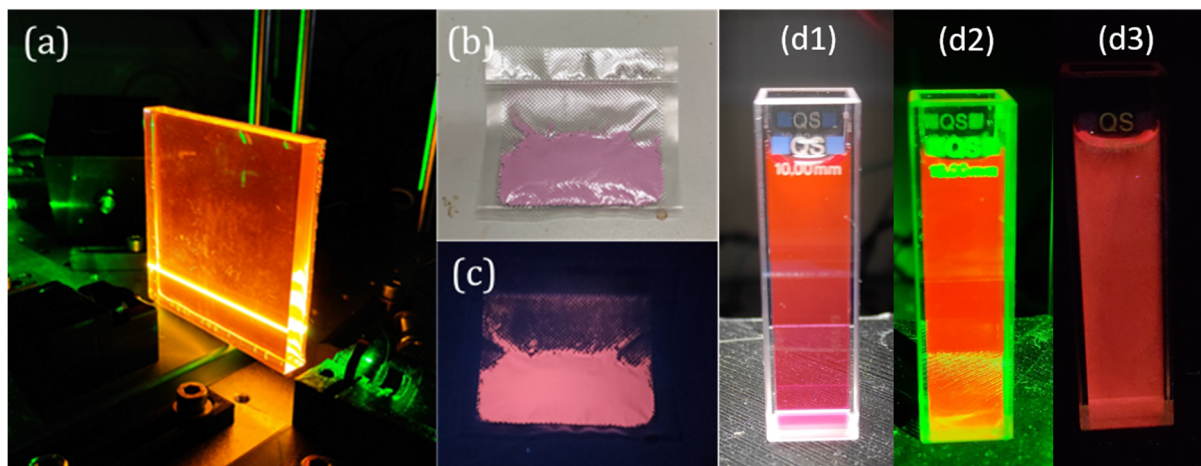


Figure 4: (a) Epoxy slab doped with “C-Dots” and illuminated with a green 530 nm laser. Dried composite material under (b) room light (c) UV illumination. Reconstituted solutions (sodium salt) under (d1) white light (d2) green 530 nm illumination (d3) UV 360nm illumination.

Despite the apparent success of this purification process, sever difficulties were encountered in characterising the C-Dots. They simply could not be detected by any means at our disposal. As with the blue and green emitters one again it became apparent that the presence of carbon quantum dots was unrelated to the observed fluorescence and damaging to the net quantum yield of the material generated.

By carefully examining the reaction conditions it was found that derivatives of citrazinic acid were once again responsible for the mis-identification of C-Dot fluorescence. Furthermore, a method of synthesising the fluorophore direct was established by directly substituting the citrazinic acid ring via a Leuckart reaction on the ketone functional group at moderate temperatures as compared to the C-Dot synthesis. Purification via column chromatography revealed a related range of fluorophores consisting of the free acid of an amine substituted citrazinic acid, the ammonium salt of this acid and a doubly substituted derivative, each with unique optical properties, previously ascribed to C-Dots in the literature. Of these, the free acid derivative yielded the greatest quantum yield, again approaching unit. However, unlike other citrazinic acid derivates, the stoke shift was exceptionally small (2 nm), leading to a large concentration dependent fluorescence signal variation. It appears that the apparent need to pacify the C-Dot edge states was in fact the precipitation of the sodium (or other cation) salt onto the C-Dot solution or as nanocrystals of dye. Whilst precipitating the free acid dye shifts the emission to longer wavelengths apparently increasing the stokes shift, it does so at the expense of the quantum yield, reducing it to the higher end of what has been reported for “carbon quantum dots”. The net conclusion for each of the spectral regions examined was the carbon dots play little to no role in the emissions observed, and in each case the fluorophore responsible can be synthesised and purified directly to yield a material with a high quantum

efficiency. However, from an applications standpoint the high quantum efficiencies achieved and, in some instances, large Stokes shift make this family of fluorophores an intriguing prospect for solar concentrator applications.

Biopolymer waveguides

As a general rule, well-constructed solar cells have a design lifespan of 20 to 30 years. In contrast, fluorophores can readily undergo chemical reactions which deactivate them reducing their life span significantly. Even when fully embedded within a polymer matrix, significant loss in activity can occur within a matter of days to weeks, depending on the chemical robustness of the



Figure 5: Sample sheet of a transparent biopolymer composite sitting over SEAI logo

molecule. Consequently, the useable lifespan of a luminescent solar concentrator is only a fraction of the PV cell used to harness their power. To address this mis-match, a range of biodegradable and environmentally friendly composite biopolymer waveguide material were tested in conjunction with the fluorophores discussed earlier. Whilst no one biopolymer was found satisfactory for all fluorophores, cellulose and its derivatives were most promising. The table below summarises the general findings from the range of polymers examined.

Material	Method	Results summary
Cellulose	Dissolution and regeneration of doctor bladed films	Difficult and time consuming to prepare with freeze thaw cycle. Works well with citrazinic acid derivatives (orange and red). Moderate haze. Insoluble in water. Can be coated with cellulose acetate or casein to yield high gloss finish with lower haze.
Methyl cellulose	Hot solution casting from DMSO	Forms good films with low absorption. Good for conventional fluorophores. Moderate results with citrazinic acid derivatives (red & orange). Soluble in water.
Sodium carboxy methyl cellulose	Freeze thaw casting from water	High degree of transparency but very high degree of optical haze. Insoluble in water if prepared correctly but swells badly.
Cellulose acetate	Hot solution casting from DMSO	Forms good films with low absorption. Good for conventional fluorophores. Moderate results with citrazinic acid derivatives (red & orange) Insoluble in water.

Cellulose triacetate	Hot solution casting from DMSO	Forms good films. However too much internal absorption in the blue spectral region. Insoluble in water
Casein	Water casting	Post casting can be doped well with citrazinic acid derivates (blue and green). Plastiser required or it becomes excessively brittle. Can be rendered water insoluble with formaldehyde at same time as dye doping. Yellowes with age.
Sodium Caseinate	Water casting	Post casting can be doped well with citrazinic acid derivates (blue and green). Plastiser required or it becomes excessively brittle. Can be rendered water insoluble with formaldehyde at same time as dye doping. Easier to prepare than casein.
Polylactic acid	Casting from Acetone	Very difficult to prepare good quality films. More suited to extrusion processes.

Development of this system progressed rapidly and a number of very promising results have been obtained. A composite biopolymer with low haze / high clarity and good optical properties has been developed by combining cellulose films with a thin coating of either casein or cellulose acetate. Cellulose acetate and methyl cellulose formed the best quality films, and in conjunction with Rhodamine B, the highest optical output. However, further optimisation of the film forming processes are required.

Innovations

- *Innovation 1: Finite element modelling of the complete parameter space for nano patch optical antennas*

The complete parameter space for nano-patch antennas based on gold films – silver particles was mapped using finite element modelling. Both the localised field enhancement effects and Purcell enhancement effects were calculated for a range of optical configurations and for the entire visible spectrum

- *Innovation 2: Novel fluorophore development*

A broad range of novel fluorophores were developed based on modified citrazinic acid. Two of these fluorophores had a quantum efficiency approaching unity. In addition, one of the fluorophores developed had an exceptionally large stoke shift making it ideal for solar concentration applications. The second high quantum yield

fluorophore, had a tuneable emission and absorption spectral profile based on the degree of protonation.

- *Innovation 3: The origins of carbon quantum dots' fluorescence discovered*

Carbon quantum dots have been widely hailed as an emerging technological tool for fluorescence-based applications. Careful study of these structures has shown that much of their properties arise from poorly soluble cationic dyes produced as a by-product in the carbonisation of the precursor materials.

- *Innovation 4: Biodegradable waveguide development*

One drawback of conventional luminescent solar concentrators is the difficulties of end-of-life recycling of the petrochemical based polymers. An extensive range of biopolymers was tested for their suitability as a replaceable element in thin film luminescent solar concentrators, thus limiting the impact of end-of-life treatment.

2.5 Project Impact

Meeting Ireland's future energy demands in a sustainable and environmentally responsible manner will demand a diverse mix of renewable energy sources. Solar energy will undoubtedly play key contribution in diversifying Ireland's energy supplies away from fossil fuels. Factors which improve the efficiency of PV cells and enable a greater diversity in the physical location where solar energy can be harvested will facilitate Ireland transition toward a low carbon society. This project sought to develop novel technology which contribute towards reducing Ireland carbon emissions, by increasing the efficiency of PV systems where only low intensity light is available. This project has developed a range of high quantum efficiency fluorophores in conjunction with biopolymer waveguides which could potentially be used to enhance the efficiency of PV systems, thereby increasing the range of locations surfaces and places where solar energy can be effectively used.

2.6 Recommendations

The role of biodegradable solar concentrators and its potential to reduce the impact of conventional luminescent solar concentrators has not been studied to any large extent. While this project briefly examined a range of potential polymers, more detailed studies by groups with suitable polymer processing equipment and expertise may yield more significant impact. In contrast, whilst plasmonic structures have the ability to amplify the emissions from fluorophores across a broad range of the optical spectrum when taken as part of a fully

concentrator device, their contributions are less significant. When balanced with the increased complexity material usage and difficulties surrounding end of life product treatment, the modest gains are unsatisfactory. Consequently, beyond some speciality applications I do not believe that plasmonics will offer significant advantages over conventional solar concentrators.