Semi-Transparent Organic Solar Cells for Agrivoltaic Application

A Thesis submitted to Indian Institute of Science Education and Research Pune in partial fulfilment of the requirements for the BS-MS Dual Degree Programme

by

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Certificate

This is to certify that this dissertation entitled Semi-Transparent Organic Solar Cells for Agrivoltaic Applications towards the partial fulfilment of the BS-MS dual degree programme at the Indian Institute of Science Education and Research, Pune represents study/work carried out by Your Name at Indian Institute of Science, Bengaluru under the supervision of Dr. Satish Patil, Professor, Solid State and Structural Chemistry Unit (SSCU) during the academic year 2024-2025.

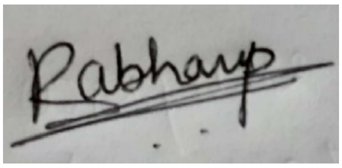
Satish patil

Prof. Satish Patil

This thesis is dedicated to my family from home and ROOM 249

Declaration

I hereby declare that the matter embodied in the report entitled “Semi-Transparent Organic Solar Cells for Agrivoltaic Applications” are the results of the work carried out by me at the Solid State and Structural Unit (SSCU), Indian Institute of Science (IISc), under the supervision of Prof. Satish Patil, and the same has not been submitted elsewhere for any other degree. Wherever others contribute, every effort is made to indicate this clearly, with due reference to the literature and acknowledgement of collaborative research and discussions.



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Abstract

Energy demands grow exponentially every year, and our reliance on conventional energy sources has significantly posed a threat to our existence. With carbon emissions increasing the global average temperatures and causing climate change, there is an urgent need to incorporate alternative energy sources into our daily lives that are environmentally friendly. This has made the solar energy research community extremely interested in finding ways to implement solar energy in areas that were previously deemed unsuitable for solar energy generation, as the traditional Silicon-wafer solar cells were opaque and often heavy due to the nature of encapsulation.

One such interesting area of research is Agrivoltaics using Semi-Transparent Organic Solar Cells (ST-OSCs) as a roofing material in greenhouses that can allow wavelengths of light essential for plant growth to pass through, and the rest to be absorbed for solar energy harvesting.

In this study, I mimicked the environment inside of a greenhouse with an ST-OSC absorber material PM6:Y6 filter over a petri plate and studied its effects on a model plant, *Arabidopsis thaliana.* In order to conduct my study, I had to scale up and optimise an ST-OSC fabrication technique and use it for the plant-based study. This study paves the way for future agrivoltaic research and its scale-up processes.

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Acknowledgements

I would like to firstly thank Prof. Satish Patil for giving me an opportunity to explore this side of his academic research and my lab mates for their support during the entirety of this project. I would also like to thank my plant bio collaborator, Prof. Naresh Loudya, who has been a crucial player in enabling me to work on this interdisciplinary project. Lastly, I would like to thank my family for being supportive and taking care of me throughout this MS Thesis period. I envision this technology to be commercialised soon to democratise solar power in areas that require reliable, clean energy the most, and I hope through this project, I have developed the skills that would serve as the foundation stone of my upcoming startup, “UrjAgri”.

Chapter 1: Introduction

1.1 : Agriculture and the need for green practices

It is expected that by the year 2060, there will be more than 10 billion humans on the planet[1], which is considered the theoretical limit for the human population to exist sustainably on the planet [2]. With this ever-growing population, the world needs to adopt productive and environmentally friendly agricultural methods to be able to sustainably feed the population.

Figure 1: Describes the state of food production by 2050[28]

Agriculture is one of the major consumers of energy and a significant contributor to greenhouse gas emissions[3]. Traditional farming relies heavily on fossil fuels for irrigation[4], mechanization, and synthetic fertilizers[5], leading to high carbon footprints estimating to about 20 gigatons of CO_2 every year, which accounts for nearly 35% of all global greenhouse gas (GHG) emissions[6]. It is estimated that the total agricultural land will increase from 165 million to 600 million hectares by the year 2050, further aggravating the issue of rising GHG emissions[7]. Hence, it is imperative to find sustainable ways to seamlessly integrate environmentally friendly energy generation facilities on the agricultural fields.

1.2 : Potential Green Energy Solutions

Innovations in the last few decades have shown great improvement in developing many green energy solutions to the current energy crisis[26]. It is estimated by the year 2050, we could mitigate 36.9 Gt of CO_2 emissions by utilising a combination of green energy technologies as shown below.

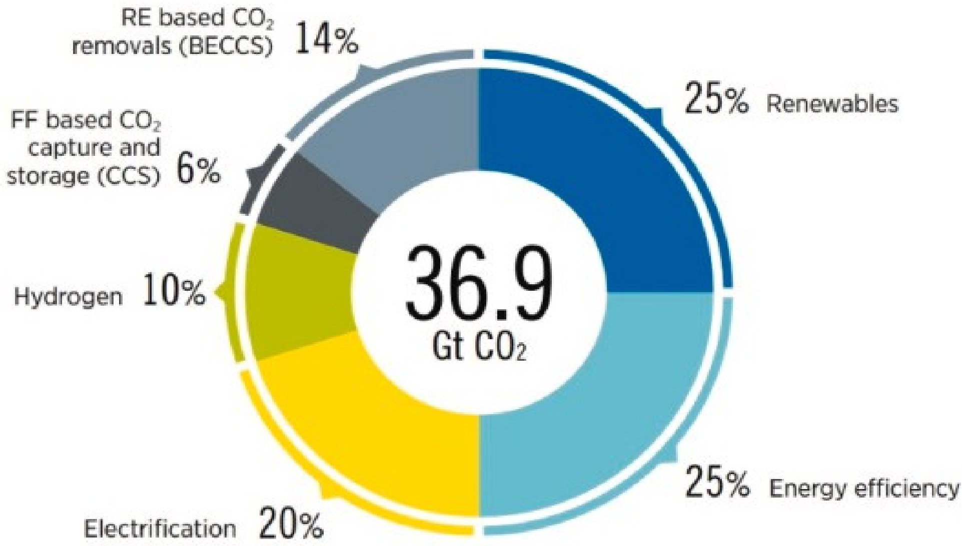


Figure 2: Decreasing emissions by 2050 using six technical pathways [27]

The renewable energy sources widely used today are hydro power, wind power, geothermal power, nuclear power, solar power, etc. However, excluding solar energy, a lot of power is lost during conversion into electricity as most of these methods implement the use of mechanical converters that transform energy into usable form, which is prone to mechanical inefficiencies. Therefore, harnessing solar energy is considered the most efficient way of obtaining energy since solar energy is abundant and readily available.

1.3 : Solar radiation

The sun emits radiation that spans from ultraviolet to infrared in the electromagnetic spectrum. Only a part of this solar energy reaches the earth's surface as they are reflected, scattered, and absorbed by gas molecules, dust particles and aerosol suspended in the atmosphere, leaving only a small section of the total solar radiation spectrum that is available to us for solar energy conversion.

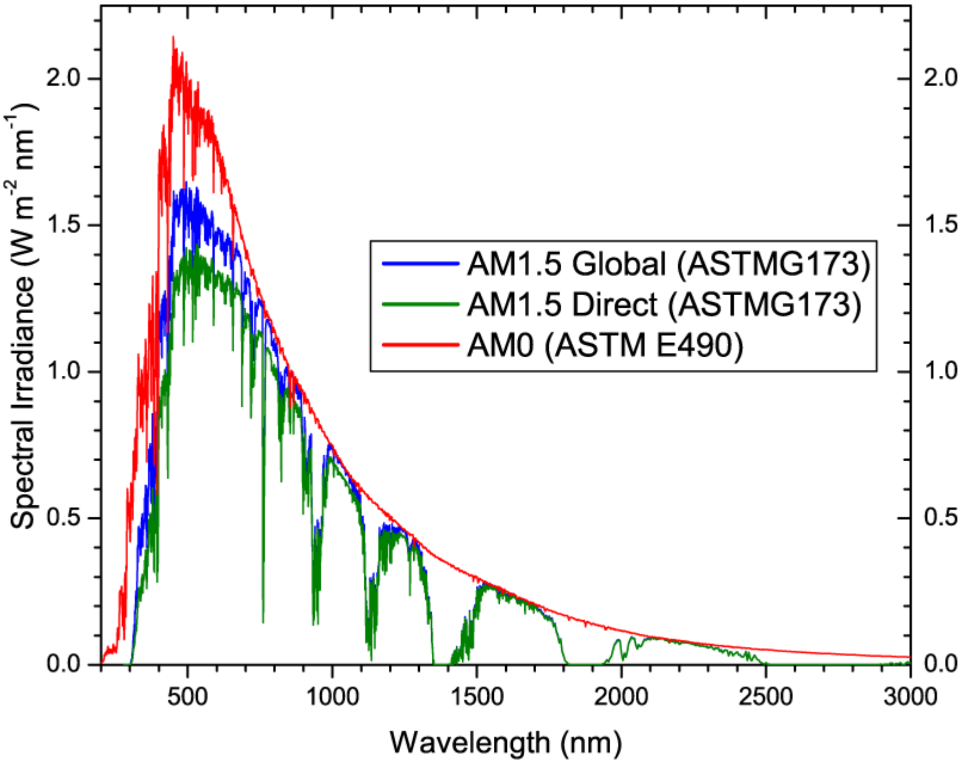


Figure 3: A schematic that shows the amount of solar radiation that reaches the earth's surface.[21]

This reduction in solar energy depends on the path it covers in the atmosphere, which is quantified using an index known as Air Mass. Mainly, 3 air mass indices are defined as AM_0, AM_1, and $AM_{1.5}$.

$$AM = \frac{L}{L_0}$$

where L represents the actual length of the sunlight through the atmosphere, and L_0 is the normal distance covered by the sunlight with the sun at the zenith position. AM_0 refers to the light path outside the earth's atmosphere, AM_1 represents sunlight that reaches the earth's surface at normal incidence and $AM_{1.5}$ which refers to the light path that is 1.5 times of the normal incidence path, that is observed when the angle that the sunlight makes at the ground becomes 48.2 as shown in the diagram below.

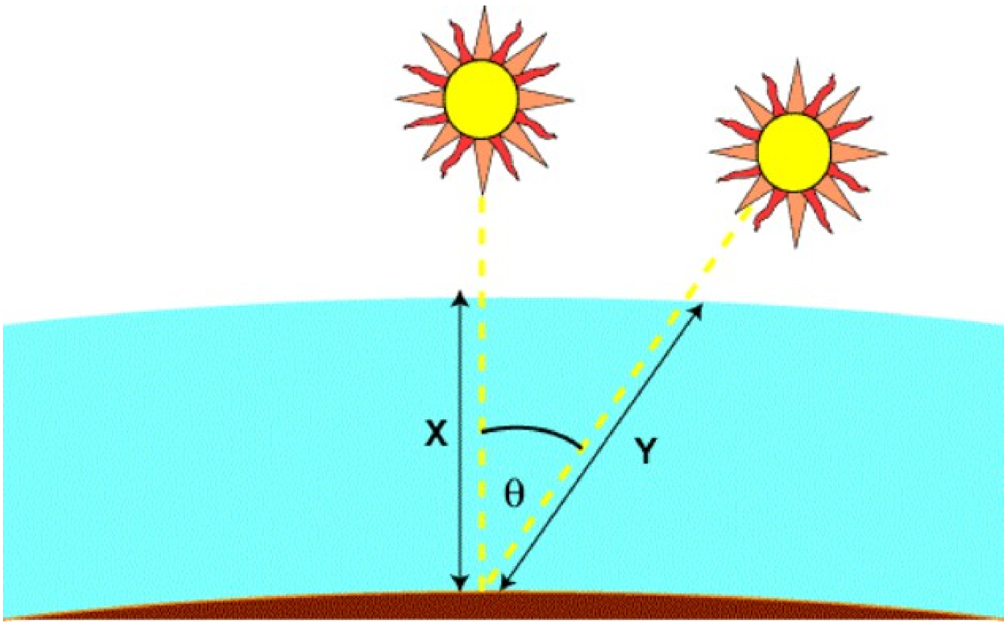


Figure 4: The picture depicts how the sunlight travels an extra distance upon reaching a different position in the sky[22].

Even though this radiation is significantly reduced upon entering the atmosphere, it is seen to have a harsh impact on the plants. Therefore, many modern-day farmers use greenhouses with specialised films that diffuse the light for growing plants.[23]

1.4 : Relevance of Diffused Light in Agriculture

It has been well-studied that exposure to bright light could reduce photosynthetic activity[18] as increased light intensity leads to photosynthetic saturation[19], which is tied to a decrease in the Light utilisation efficiency (LUE)[20], which often occurs under direct light condition. Therefore, direct light usually wastes photons by concentrating the light resource to only a fraction of all leaves, leading to a less efficient photosynthetic use of light by plants. Hence, having a material that can be used to diffuse light over a greenhouse that can also filter out certain wavelengths of sunlight can be very beneficial to the growth of plants.

1.5 : Greenhouses and current energy needs

Most modern-day plant-growing institutions involve the usage of a glass structure called a greenhouse, which modifies and manages environmental factors that allow plants to be grown in suitable climates that may not be well suited for their growth and development[12]. These structures are often equipped with various electronic devices such as soil sensors, humidifiers, drip irrigation sets and IoT-based monitoring systems, which require a significant amount of electricity[13] that is meted out through local electrical grid connections or through diesel generators in remote areas which adds to the existing problem of GHG emissions[14].

1.6 : Agrivoltaics

Popularly known as Agrivoltaics, it is the method of growing plants under solar cells. Traditionally, monocrystalline silicon wafer photovoltaic technology (Si-PV) being the commercial choice for solar installations, is currently used to cover agricultural areas, but due to their brittle nature, Si-PV has to be encapsulated in heavy materials and is often opaque. Hence, they are placed spaced apart to optimise maximum land use productivity[8]. This causes a lot of space to be unused and makes it difficult to ensure that every plant gets an adequate amount of sunlight without sun tracking and constantly moving the panels throughout the day.

1.7 : Semi-transparent Organic Solar Cells (ST-OSCs)

In the last couple of years, some new types of solar cells were developed that could be made semi-transparent and have a wavelength selective absorption curve. Therefore, it can be used like a filter and absorb certain wavelengths of light for solar energy generation that would otherwise not be used by the plant. These solar cells were lightweight and could be made flexible, making them ideal for Agrivoltaic applications[9]. One of the front runners in this field is Organic Solar Cells which is relatively cheaper and has less environmental health concerns than its counterparts but has lesser power conversion efficiency (PCE) and degrades under sunlight. However, with the advent of non-fullerene acceptors being used in OSCs, researchers have been able to achieve a record efficiency of 19.7% in lab conditions [10], and studies are underway to make OSCs more reliable and photostable under extended periods of exposure to light [11].

Combining the benefits of using Semi-Transparent Organic Solar Cells (ST-OSCs) and the practices of using greenhouses, we can maximise the land use productivity that is currently under agriculture[15]. However, there have been only a handful of projects that are proposed to study the effect of Agrivoltaics on plant growth in India. Most of these projects are either simulations[16] or data that are based on data from farms that have implemented Si-PVs[25]. In my thesis project, I aim to conduct an experimental setup to study the effects of using an Organic Non-Fullerene Acceptor (NFA) PM6:Y6 as a light absorber fabricated into a wavelength selective filter when placed over a model plant *Arabidopsis thaliana*.

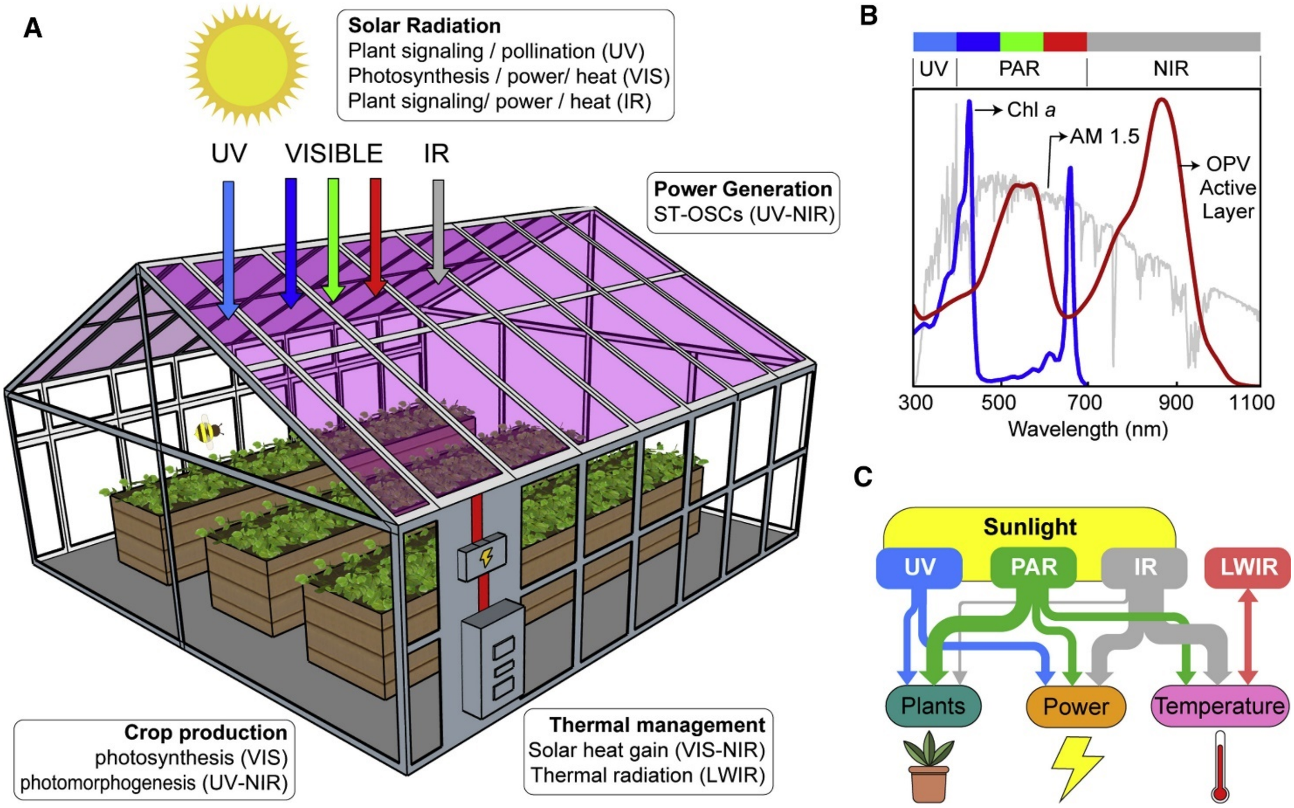


Figure 5: Schematic showing the benefits of using Agrivoltaic Greenhouses[17]

Chapter 2: Materials and Methods

This section shall be classified into two broad sections: Semi-transparent Filter Fabrication and the subsequent plant-based study.

2.1: **Semi-transparent Filter Fabrication**

The generally accepted method for scaling up fabrication of OSCs in the Organic Solar Cell Research community is as follows:

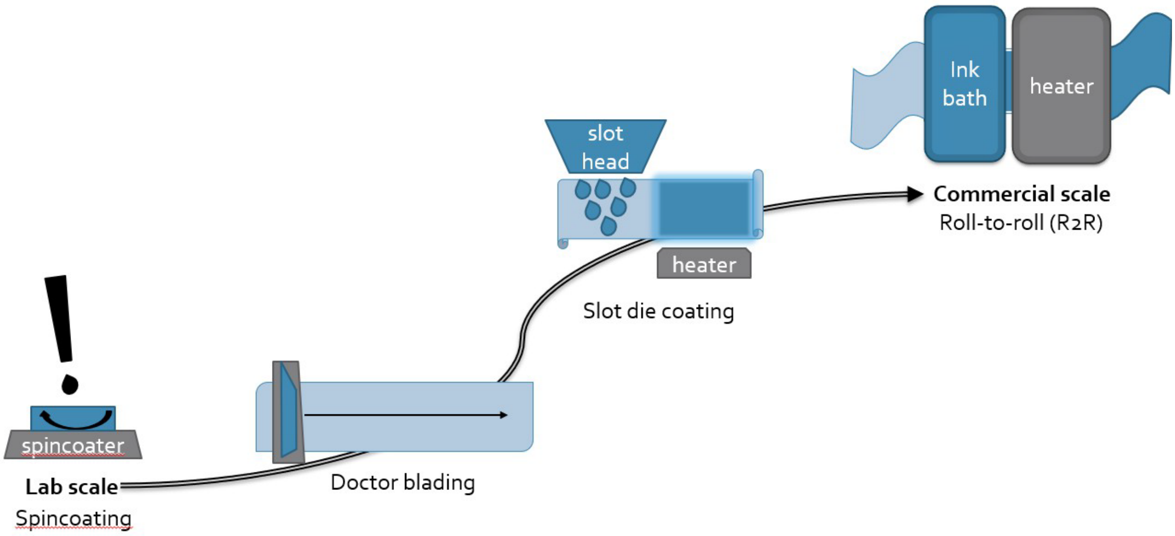
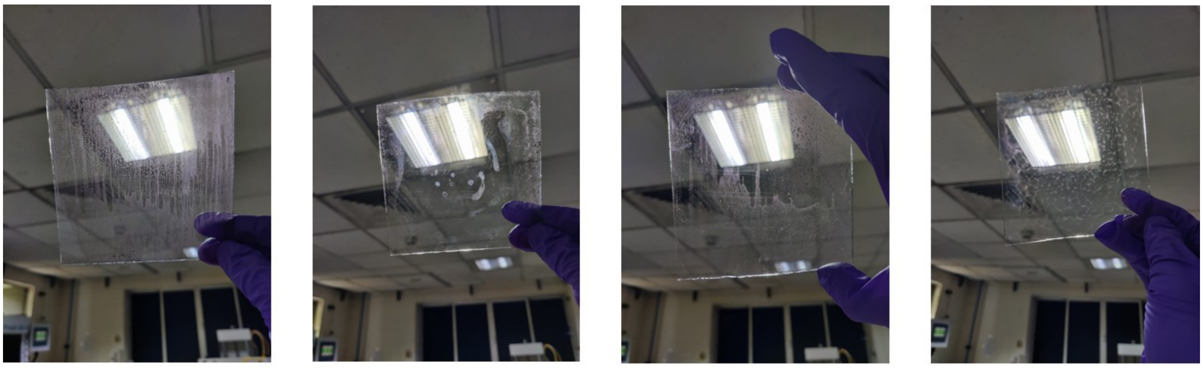


Figure 6: Schematic representation of scale-up fabrication processes for Organic Solar cells (OSCs).

2.1.1: Doctor Blading

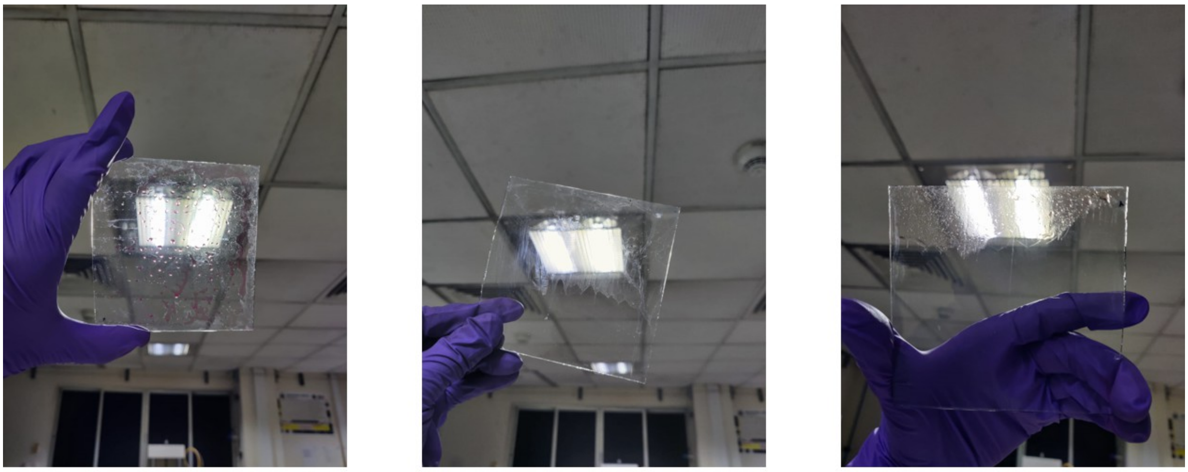
The fabrication method of doctor blading was first tested using DPP-OD-OD (a Diketopyrrolopyrrole-based polymer) that has a similar molecular weight to PM6:Y6 in order to learn and optimise the technique. The images of the first few attempts are shown below.



Chloroform ($CHCl_3$) | Dimethylformaldehyde (DMF) | Dichlorobenzene (DCB) | Dioxane

Figure 7: Showcases the film quality from different solvents while using the doctor blading technique.

As the film was not uniform, an experiment was devised with increasing amounts of Poly(methyl methacrylate) (PMMA) polymer added to the solution and the following films were obtained.



0% PMMA | 10mg/ml PMMA in $CHCl_3$ | 100mg/ml PMMA in $CHCl_3$

Figure 8: Depicts the thin film quality seen with increasing PMMA concentration in the coating polymer solution.

2.1.2 : Spray coating

Since. getting a desired uniform film was difficult using the doctor blading technique. Spray coating was employed, and the following thin films were obtained.

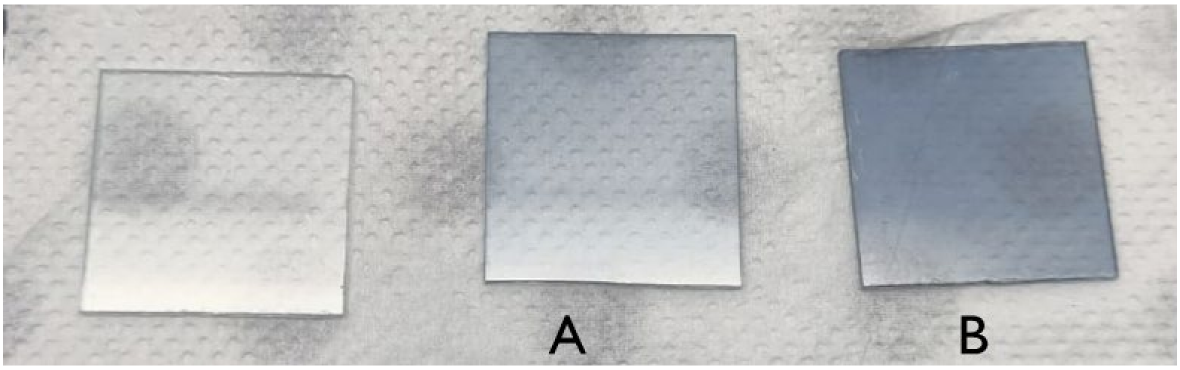


Figure 9: Depicts the quality of thin films produced through spray coating next to a cleaned 4x4cm^2 soda lime glass (control). a) spray-coated with PM6:Y6 at 4mg/ml in Chloroform ($ChCl_3$) (b) PM6:Y6 solution in Chloroform ($ChCl_3$) and Tetrachloroethane (TCE) at a 1:1 ratio.

Upon achieving a decently uniform film thickness using the spray coating method. The remaining PM6:Y6 solution (~20ml) was used to coat on a cleaned 10x10 cm2 soda lime glass substrate to obtain the large area filter, as shown below.

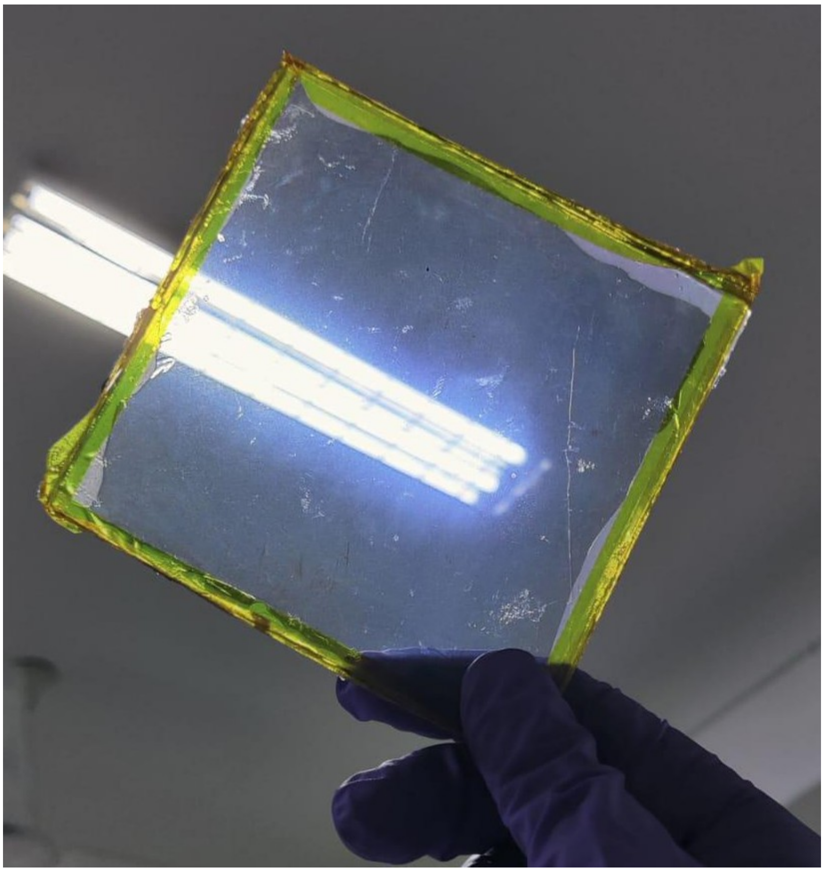


Figure 10: Showcases the encapsulated wavelength selective filter made using PM:Y6 for the plant-based studies.

The coated surface was encapsulated using another soda lime glass substrate and sealed with an Araldite epoxy. This fabricated setup was then placed on top of the plant-growing petri plate to study the effects of the wavelength selective filter on the growth of plants.

2.2: **Plant-based study**

In order to study the effects of the absorber filter fabricated, a plant-based model system, *Arabidopsis thaliana,* was grown, as shown below.

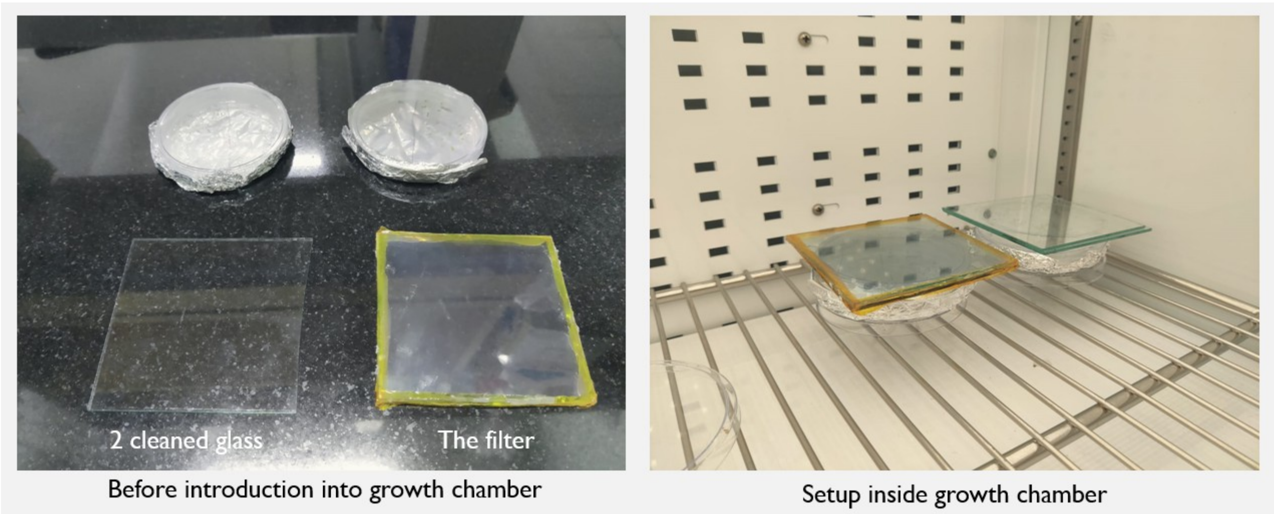


Figure 11: Images of the experimental setup used for the plant-based studies.

The seeds were first washed in 70% ethanol first, followed by 100% ethanol and vortexed for 10 mins each. Then, in a laminar flow hood, the washed seeds were carefully placed onto a clean petri plate containing Murashige and Skoog (MS) media one by one using an autoclaved toothpick.

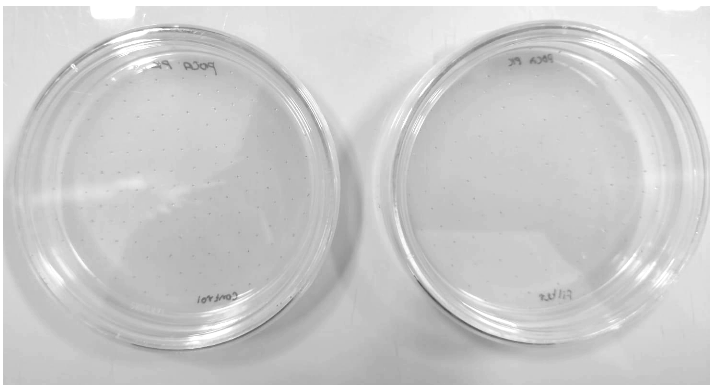


Figure 12: Freshly prepared petri plates with MS media

Two such petri plates were prepared and sealed with a lid using a Parafilm tape. The Petri plates were covered in Aluminium foil and kept under 4ºC for 3 days for a process called stratification to make the seeds resilient by mimicking the winter season. Then it was transferred to a Percival Growth chamber with the top side of the Petri plate exposed to the 450.8mW/cm2 white LED illuminated environment Growth Chamber from Percival for 5 days while the bottom side of the Petri Plates were still covered using an Aluminium foil to restrict any other source of light entering the petri plate.

2.2.1 : Chlorophyll estimation

Upon completion of the 5 days, the petri plates were opened inside the laminar flow hood again, and healthy-looking seedlings were transferred into each of the 3 eppendorf tubes containing 500µl Dimethylformamide (DMF). The Eppendorfs were then wrapped in Aluminium Foil and kept under 4ºC for 2 days. Later, the chlorophyll content in the seedlings was estimated using the absorbance values of the solution obtained from an IMPLEN NanoPhotometer P300 UV-Vis Spectrophotometer.

IMPLEN NanoPhotometer P300

Figure 13: Image of the UV-Vis spectroscope used for chlorophyll estimation.

2.2.2 : Chloroplast visualisation

To study if there is any difference in the plant's chlorophyll production ability, we conducted a study looking into chloroplast compartments using a Differential interference contrast (DIC) Microscope the same day the seedlings were removed for chlorophyll estimation. Some healthy looking seedlings were selected and immersed in an Eppendorf of 500µl fixing solution (Glyceraldehyde (3.5% w/v)) and kept in a dark environment for 1 hour, followed by 15mins in a low-pressure environment using a pump and a desiccator. The Glyceraldehyde (3.5% w/v) was then removed, and 500µl of EDTA was introduced into the Eppendorf tubes to break the cell walls and to enable the samples' boundary to be clearly visualised. The samples were then cooked at 65℃ using a heat block and were mounted onto the microscope slides using glycerol and a cover slip.

DIC Microscope

Figure 14: Image of the Differential interference contrast (DIC) Microscope used for chloroplast visualisation.

The chloroplasts were visualised, and their areas were measured using the NIS Elements Imaging Software the cell index was then calculated using the formula given below:

Cell index = (Average chloroplast area x Number of chloroplasts) / Total cell area

Chapter 3: Results and Discussion

We first analysed the unique absorbance curve that our wavelength selective filter had in comparison to the plants' absorbance and plotted using origin graphing software.

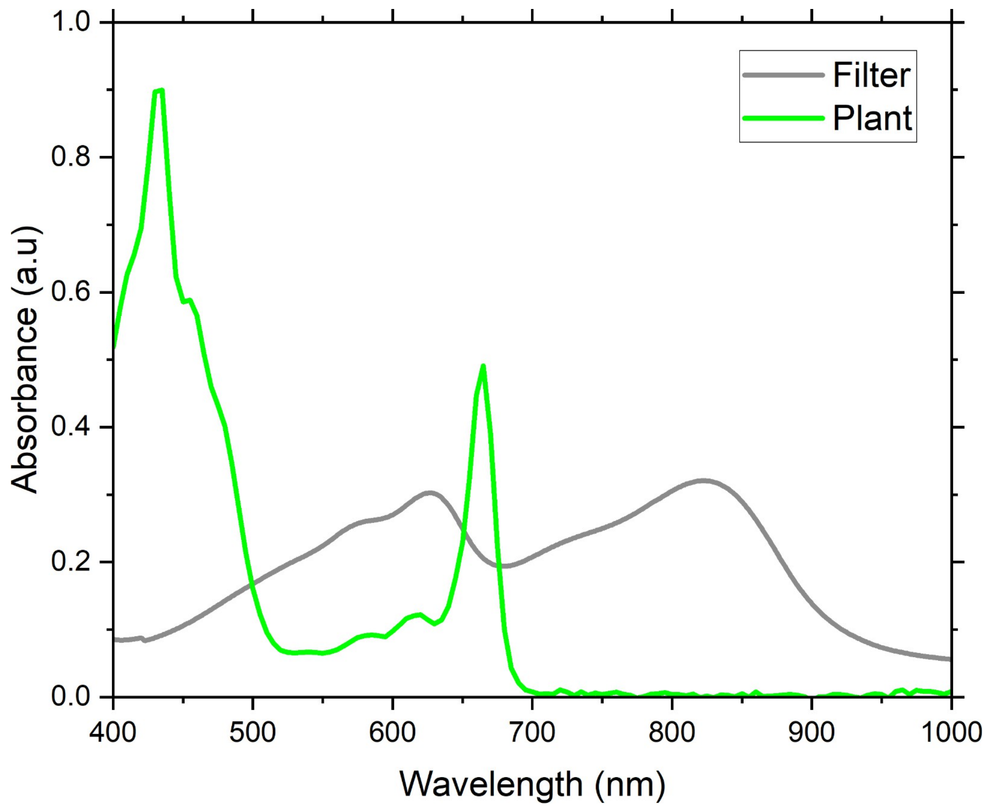


Figure 15: Depicts the complimentary absorbance curves of the filter material (PM6:Y6) and the plant.

This wavelength selective filter was placed above the growing plants to study whether the filter would have an effect on plant chlorophyll production. The following graphs depict the chlorophyll content that was present in the plants, and a student t-test was run to verify their statistical significance using the GraphPad Prism.

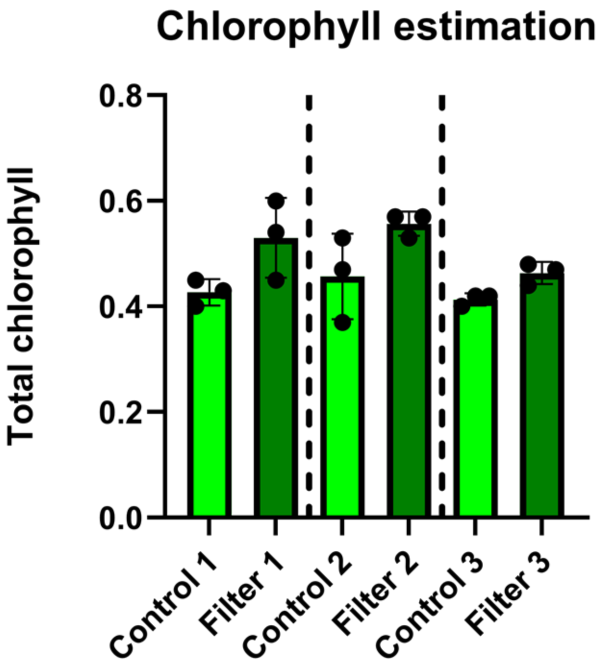


Figure 16: Showcases the amount of chlorophyll content in the plants grown in control and under the filter.

UV-visible spectrophotometer results indicate the absorbance and the amount of chlorophyll present in both systems.

Following this, DIC Microscopy images were taken to observe any changes in the chloroplast compartments in both systems, as shown.

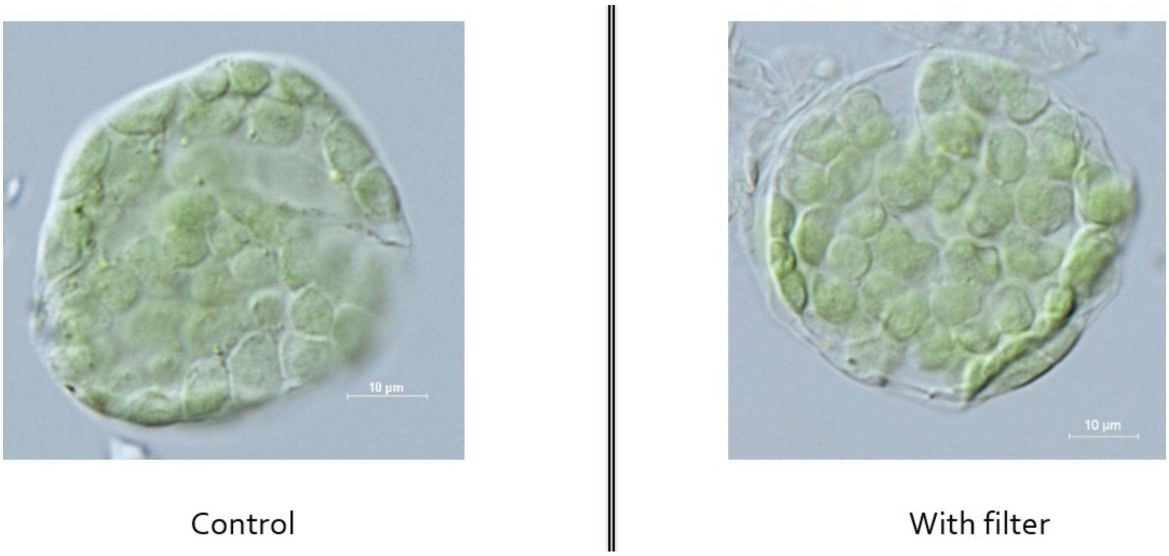


Figure 17: DIC Microscopy images depicting the plant cells from control and grown under the filter.

The Cell indexes were calculated and they are depicted as follows:

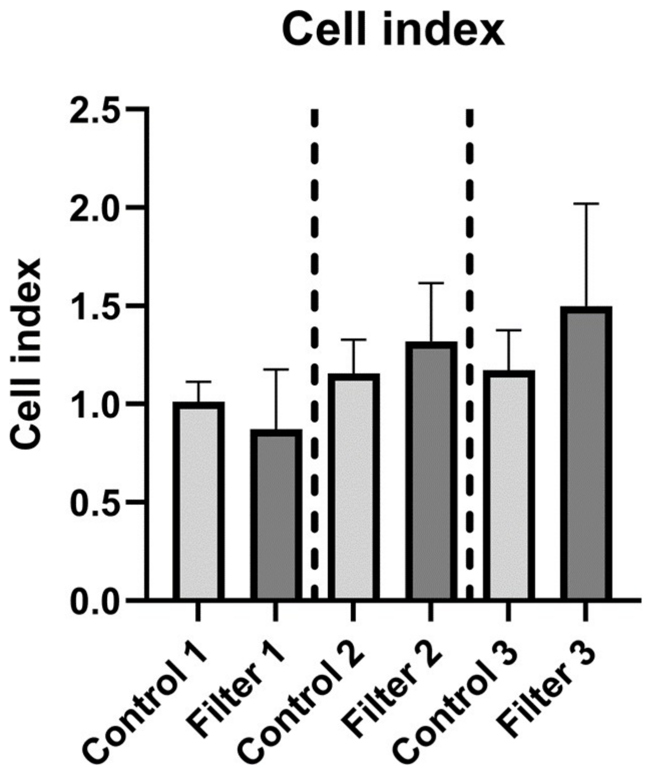


Figure 18: Depicts the variation in cell indexes obtained in the plant cells grown under the control and filter setting.

The results from the UV-visible spectrophotometer show there is no significant difference in absorbance values, which corresponds to the amount of chlorophyll available in the plants. Suggesting that the filter did not harm the plants' growth and that it was comparable to the plants grown in control. The images from the DIC microscope can further help us validate the above claims.

However, it is noticed in every batch of the plants grown that the control petri plates had developed a layer of condensed water vapour on the lid but almost negligibly on the petri plate with the filter. This could be associated with the IR range absorption of the filter that could reduce the internal temperature of the petri in turn reducing the evaporation rate of the material inside the plate. Further studies are necessary to prove this hypothesis.

Future research is necessary to materialise this concept of ST-OSCs for agrivoltaics before it becomes ergonomically feasible, along with studies involving larger installations to study its effects in the later stages of the plant's growth.

Chapter 4: Appendix: Organic Solar Cell Fabrication and Characterisation

Organic solar cells using PM6:Y6 as their absorber layer were fabricated on a 1.5cmx1.5cm indium tin oxide (ITO) coated glass substrate (sheet resistance ~15Ω) with an inverted device architecture of ITO/ZnO/PM6:Y6/MoO_3/Ag. Fabricated in a PIN arrangement it has a bulk heterojunction layer of organic absorber material sandwiched between ETL and HTL made of metal oxides. The figure below showcases the PIN solar cell architecture of the fabricated Organic Solar Cells (OSCs).

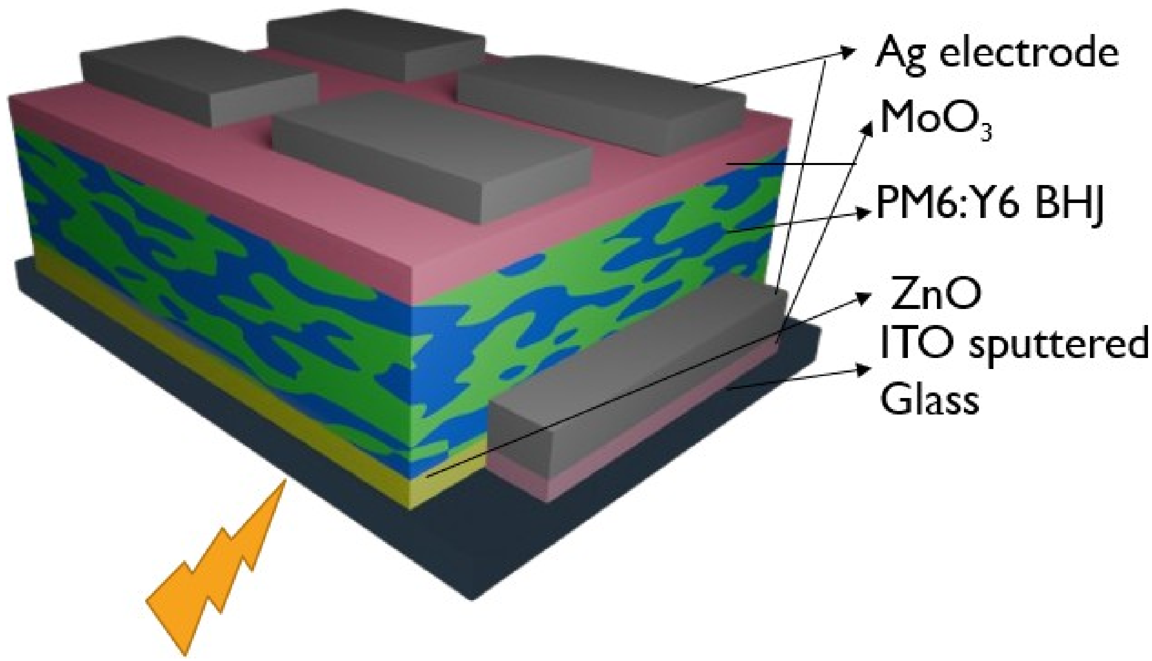


Figure 19: 3D schematic of an inverted architecture Organic Solar Cell.

The pre-patterned ITO sputtered glasses were first thoroughly cleaned with 10% soap solution, De-ionised (DI) Water, acetone and Isopropyl alcohol (IPA) for 20 mins in an ultrasound sonicator each, followed by N_2 blow drying prior to oxygen plasma treatment to ensure that the substrate was free from any debris and improved surface energy to allow easy wetting of the succeeding solutions onto the substrate. A ZnO nanoparticle solution was made using the sol-gel method in which 100mg of Zinc Acetate dehydrate was dissolved in 1ml of 2-methoxy ethanol followed by 27.7μl of ethanol amine and stirred for 3hrs at 45°C before spincoating it onto the cleaned ITO sputtered glass substrate at 5000 rpm for 60s and annealed at 110°C for 15mins. These substrates were then transferred in the argon filled glove box. The absorber layer PM6:Y6 solution was made using a mixed solvent of chloroform/1-chloronepthalene (100:0.5v/v) that had a total blend concentration of 14mg/mL. This solution was stirred for 6hrs before spin coating onto the substrate at 2500 rpm for 30s and annealed at 80ºC for 10 mins. The substrates were scratched using a clean blade to expose the ITO layer at the ends to create space for the back contacts and then transferred to a thermal evaporator to deposit 9 nm of MoO_3 and a 100 nm Ag layer under a vacuum of 2×10^{-6} Pa.

The Organic Solar Cells were then tested for their Power Conversion Efficiency (PCE) using a Newport solar simulator using AM 1.5G spectra (100mW/cm^2), Semi-Transparency using a Perkin Elmer Lambda 35 UV-visible spectrometer and the following J-V curves were obtained under AM1.5.

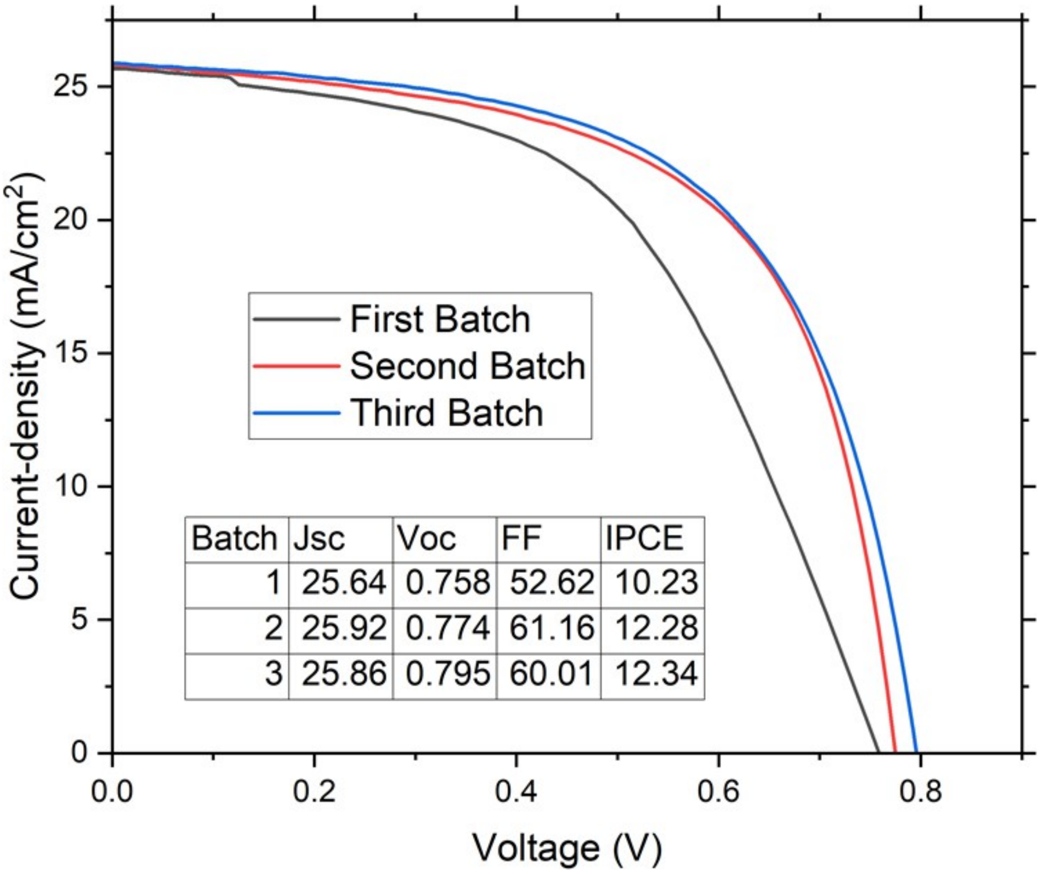


Figure 20: Current density vs voltage for the Organic Solar cells across different batches.

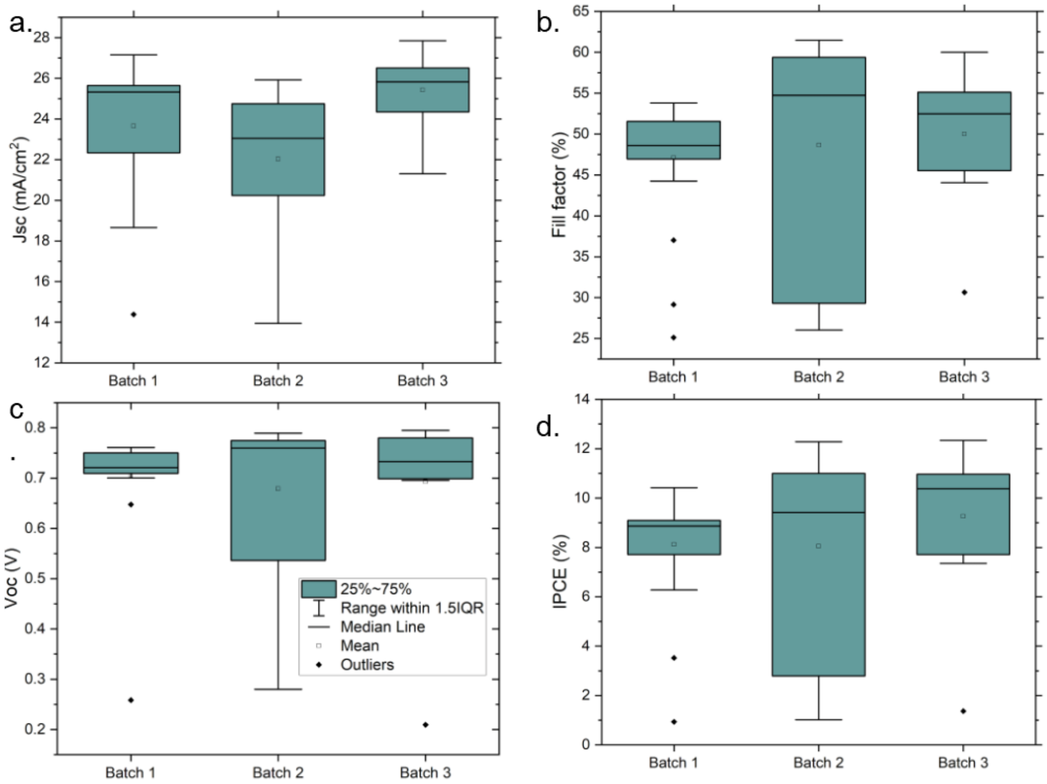
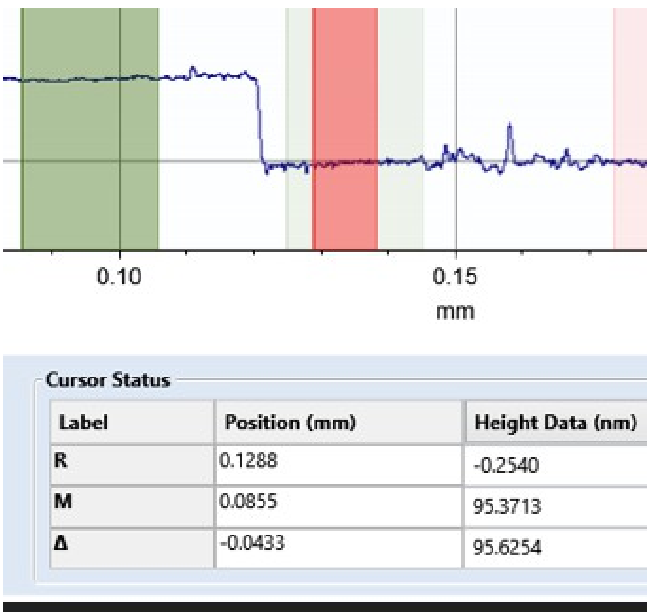


Fig: The data from the J-V cure were then interpreted in a box plot as shown above

Its thickness was measured using a Bruker Dektak XT profilometer to reveal the thickness to be about 100nm as per literature[24] .



Label	Position (mm)	Height Data (nm)
R	0.1288	-0.2540
M	0.0855	95.3713
Δ	-0.0433	95.6254

Figure 21: Thickness measurement of the fabricated Organic Solar cell

Semi-transparent thin films containing only PM6 and Y6 were used to study the selective wavelength absorbance nature of the thin films fabricated and how it influences the BHJs absorbance curve, as shown below.

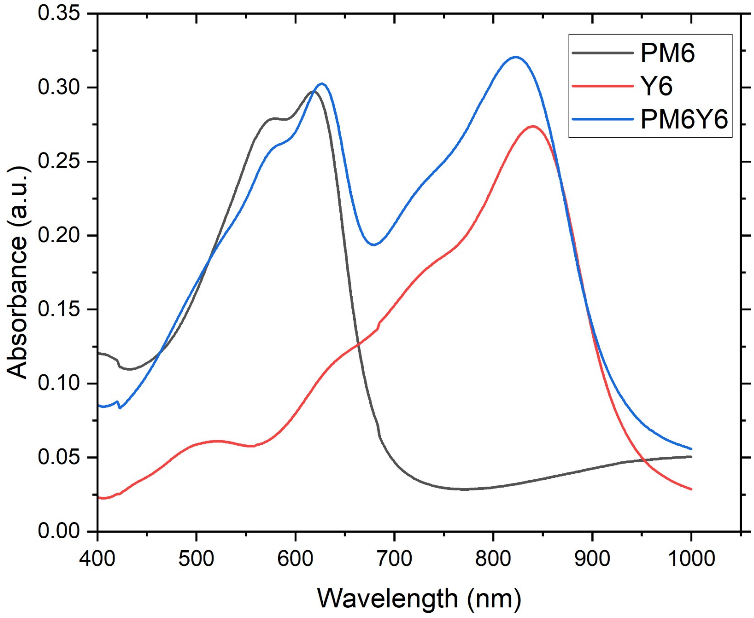


Figure 22: UV-Vis spectroscopy of the thin films containing PM6, Y6 and their mixture at a 1:1.2 ratio.

Chapter 5: Appendix: TMM Simulations

In order to find the optimal thickness of the absorber layer, a calculation using the Transfer Matrix Method (TMM) was carried out. The light management in a solar cell can be analysed by considering multiple cross-sections of the different layers. The set of electromagnetic eigenmodes that exist in each layer of the solar cell was then numerically calculated to obtain eigenvalues. These eigenvalues describe how light propagates in the longitudinal direction through the solar cell and depict the propagation constants of the eigenmodes. They can then be used to calculate light's propagation through each layer as the light's longitudinal path is assumed to be analytical. This calculation also assumes that the layer is uniform and the light's path is not affected throughout the length of the individual layers. Hence, these layers can be of any size, and the eigenvalues can be calculated with no additional computational burden. At the interfaces, the boundary conditions between the layers are enforced such that the tangential field components are equated on either sides. In this manner, propagation through the entire device is modelled rigorously.

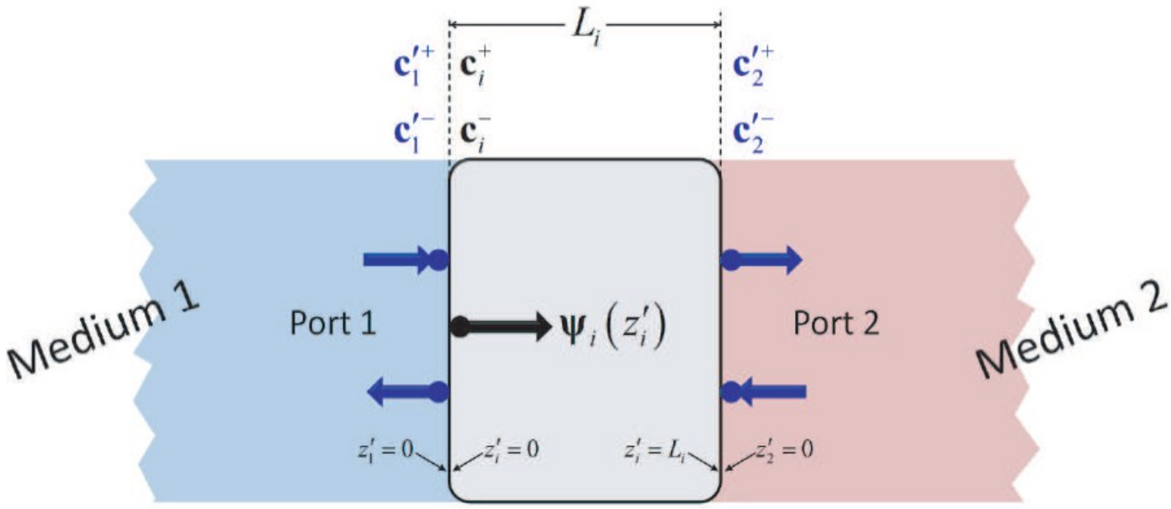


Figure 23: Illustration depicting the boundary conditions as light enters a medium[29].

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