Spray-Coating Deposition Techniques for Polymeric Semiconductor Bulk Hetero-Junctions

Aberystwyth University
Thesis submitted for the degree of M. Phil.

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20th of December 2016
Abstract

Organic Solar cells offer a promising route towards low-cost renewable energy production; however large-area production techniques and material deposition methods still represent a significant scientific and engineering challenge (1).

The characteristics and functionality of polymeric semiconductor photovoltaic heterojunctions where examined. Based on blends of polyfluorenes (F8TBT), polythiophenes (P3HT) and fullerenes (PCBM), using spray-coating deposition techniques suitable for large areas (2) (3). This can be achieved using blends of o-dichlorobenzene and Chlorobenzene as the solvent medium. Thermal / solvent – vapour post annealing of films were also studied.

Using a multi-faceted characterisation approach, studying photoluminescence quenching, optical microscopy, the morphological properties of these blend films are studied in detail by AFM methods, showing favourable results, in terms of layer thickness and uniformity, and micron-scale properties of these blends morphology. An optimal concentration for spray coating polymers was found to be 5mg ml$^{-1}$ of compound to solvent; with the compound being a 1:1 ratio of donor and acceptor polymers and the solvent being a 5:1 ratio of dichlorobenzene to chlorobenzene. This produced consistent thin films on the substrate for all combinations of polymers tested.

Thermal and solvent annealing was found to increase the photoluminescence quenching efficiency of the blends by 10% on average, aside from the F8TBT-PCBM blend, which did not seem to be affected by the either annealing process. Thermal and solvent annealing was also found to affect the morphology of the samples the roughness of the samples. Thermal annealing was found to decrease the roughness of the samples the most, with on average a decrease of 31.12%. Solvent annealing was found to decrease the roughness of the sample very little on average 6.23%, and in the case of F8TBT-PCBM, actually increased the roughness of the sample.
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Introduction

This work investigates and tests a method for spray coating blends of Polyfluorenes (F8TBT), Polyythiophenes (P3HT) and Fullerenes (PCBM), with in an in depth analysis investigating the optical and morphological properties of each blends.

Each of the blends will be deposited on to a substrate using an air brush set at the same pressure and distance away, the solvent / polymer mixture and concentration deposited shall also be kept the same. An in depth analysis of each blend studying their optical properties, their micro scale structures and their nano-scale structures shall then be conducted.

Then a method of either solvent vapour annealing (SVA) or thermal melt annealing (TMA) will be done and then once again an in depth analysis of each blend studying their optical properties, their micro scale structures and their nano-scale structures.

Reason of Interest

The need for electricity is increasing throughout the world; the electricity produced worldwide in 1973 was 6,131 tera-Watt hours this figure nearly quadrupled by 2013 to 23,322 tera-Watt hours. (4) Over 15,000 tera-Watt hours of which were generated by methods that causes harmful emissions of such as carbon dioxide into the atmosphere. This is responsible for over a third of the harmful emissions that contribute to global warming. (5)

Alternative sources of electricity generation have been sought after, such those which use wind, wave and solar energy. Solar energy was found to be the energy source that has the greatest future potential out of all of the renewable energy resources, with some models projecting it to becoming the one of the major sources of electricity generation by 2050. However this entire model has the cavitate that the cost of solar cell production greatly reduces in the next five years. (6)

The use of organics to produce solar cells is very important to future solar power generation as the current ways in which solar cells are manufactured using silicon chips are very expensive when compared to the costs of manufacturing organic solar cells. (7) However the current way of making organic solar cells requires the use of expensive equipment, which in-efficiently uses the expensive
chemicals needed, the up-scaling of the current process is almost impossible as it uses the method of spin coating that only allows one cell to be made at time meaning that it has a limited area and a large fraction of the material is wasted.

Spray coating is a promising new method for making organic solar cells, as it requires cheaper equipment to manufacture and uses resources more efficiently than the current spin coating methods and is much easier to upscale. However a universal method has yet to be found and is currently being tested. A universal method means a method which uses the same solvents and concentration of polymers to solvent for each blend used. It allows for the method of deposition to be the same as well. This universal method has yet to be tested with the three different polymers this project will be focusing on. This would be useful from a manufacturing standpoint as a similar set up could be used for each of the different polymers used for organic solar cell construction.

The ways in which this method will be evaluated will be how uniform the surface of the sample is and how photoluminescence quenching efficient the sample is. The uniformity of the sample is important as the current manufacturing techniques of organic solar cells are 250nm thick, with 100 nm reserved for the active layer of the polymer blends. This means that the thickness of the deposited layer needs to be within 100nm, a very rough surface would cause short circuiting of the cell, or not allow it to function. (8) (9)

In bulk heterojunction polymer solar cells the phase separation of the donor and acceptor polymers is important to the efficiencies of the cell. To reduce losses by recombination of excitons and increase device efficiency the domain sizes of slightly larger than the exciton diffusion length have been found to be beneficial, meaning sizes of ≈10nm. (10)

![Figure 1](image)

*Figure 1 this diagram shows the difference between a rough sample with poor phase separation (left) and a smooth sample with good phase separation (right) (11).*

The methods of annealing will also hopefully increase the phase separation of the polymers used and decrease the roughness further than the initial as made samples. The photoluminescence quenching efficiency of the sample is another way of analysing the phase separation of the sample and indicates the two polymers are working together to absorb light and generating electricity, which is what is wanted for solar cells.

This is analysed by finding the ratio of light absorbed by the sample to the light emitted by the sample .This gives a number between 1 and 0, 1 would be a sample that absorbs all of the light and emits none and 0 would be a sample that possibly absorbs light but then immediately emits all of it.
The light absorbed but not emitted is considered to be disassociated electron and electron holes carrying an electrical charge generating electricity, so the closer this ratio is to 1 indicates good electricity generation. The methods of annealing will hopefully also increase the ration towards 1 indicating good electricity generation and greater phase separation.

Applications of this research are to create a process that would make electricity generation through solar power much cheaper to produce, making it a more viable energy source than it currently is. If the up scaling of this method is found to be simple large scale sprayed solar cells could be produced and used for sides of sky scrapers or for car roofs, these are known as BIPV (Building Integrated Photovoltaics) (12).

Other application of this research could lead to effectively spray on solar panels which would have applications in the developing world, creating sources of electricity in areas that are hard to reach by conventional methods of electricity supply.

**Overview of Organic Solar Cells**

The most basic solar cells were single junction silicon cells, meaning that it used the Highest Occupied Molecular Orbit (HOMO) and Lowest Unoccupied Molecular Orbit (LUMO) of the silicon, organic solar cells that shall be discussed in this paper will be the far more efficient heterojunction organic solar cell. In a heterojunction organic solar cell uses a two polymer system, each with different HOMO and LUMO energies.

In these interactions it is helpful to use the term “exciton” an exciton is a bound state of an electron and an electron hole, attracted to each other by the electrostatic coulomb force.

![Figure 2 A diagram demonstrating exciton diffusion in organic semiconductors (Left (13))](image)

The way in which energy is generated in an organic solar cell is first that an exciton is generated by an incident photon of the correct wavelength becoming absorbed by the donor phase, creating the exciton, the exciton then diffuses to the donor / acceptor interface.

The exciton is disassociated by the energy step between the HOMO and LUMO energy levels, the free charge carries are transported to the electrons, supported by the attraction due to the different work function. In the diagram above it shows a basic view as to how an organic solar cell functions, however in reality the above diagram would look more like:
The manufacturing process of organic solar cells will now be discussed, starting with the most commonly used method spin coating. Spin coating is a method of creating films within the range of 100 – 10 nm, the method of which consists of, an excessive amount of the solution is applied to the substrate; the substrate is then spun up to several thousands of revolutions per minute, due to centrifugal force the solution is spread out evenly over the substrate. The surplus solution is spun off of the substrate leaving behind a thin film; the remaining solvent evaporates, leaving behind the less volatile polymer components on the substrate.

This method is a reliable method for creating thin films; it is very easy to control the speed at which the substrate is spun at and at what speed. It is also easy to control the concentration of the solution deposited on to the substrate. However this method is very expensive, the cheapest spin coaters are around £2000 (15). This method also uses the expensive materials in the solution in-efficiently as most is lost in the process as it is spun off in the surplus. The main problem however with this method is that it is very difficult to scale up, as each substrate must be coated individually. (16)

Another more common method for production of organic solar cells is that of drop casting. Drop casting is a method in which the solution is deposited on to the substrate, which is raised to a temperature the more volatile solvent will evaporate off leaving behind a thin film. The thickness of the film can be controlled by modifying the solvent concentration.
This method is far easier to scale up than that of spin coating, and is very easily the cheapest method of deposition with very little of the solution going to waste. However this method is in-effective over large areas of coverage, the thickness of the film is hard to control and give poor uniformity of the film, unless the concentration is controlled carefully.

The final method that shall be discussed is the method of spray coating, which will be the method that the rest of this project will focus on. The spray coating method involves an artist’s air brush set up in such a way that is elevated above the substrate, the solution is put in to the ink well of the air brush. The temperature of the substrate is raised to a temperature at which the solvent will evaporet, the air brush is pressurised to a required pressure and then the solution is sprayed on to the substrate, which is then allowed to dry.

From this method there are two techniques that can be used, either a single pass technique, making the droplets of the air brush to become fully wet before drying or the multiple pass technique, in which the droplets dry independently. The single pass technique produces a much smoother films however this has issues with the substrates ability to become fully wet. The multiple pass technique, though it creates less smooth films it does create far more repeatable results.

This method is very easy to scale up, is cheaper than spin coating and uses materials more efficiently than spin coating. This method also does not depend on the surface of the substrate to be smooth for a smooth surface. The main drawback of this method is the roughness of the surface after coating, with annealing the surface can hopefully be made smoother. Another drawback of this process is that for each compound used within each blend the correct solvent must be found to give the best solution for spray coating. (14) The specific methodology used in this work will be more distinctly laid out in the Theory and Methodology section.
**Brief History of Solar Power**

Energy generation by solar power was first discovered in 1839 by Edmond Becquerel, this was observed when Becquerel was experimenting with an electrolyte cell, made up of two metal electrodes placed in an electricity-conducting solution. He found that electricity was generated when it was exposed to light; Becquerel named this effect the Photovoltaic effect.

![Figure 7 Members of Bell Laboratory observing a solar cell](image)

Though this effect was observed in 1839 it was not until 1954 that Photovoltaic cells were invented in America by Daryl Chaplin, Callum Fuller and Gerald Pearson of Bell Laboratories, these primitive cells had a laboratory efficiency of 4%, later improved to 11%. The first use of Heterojunction Organic Solar cells was 1986 in a paper published by Tang, the polymers used were Copper PC and a Perylene derivative with an efficiency of 1%.

Bulk heterojunction organic solar cells were introduced by blending two polymers having donor and acceptor properties in a solution spin cast into a thin film resulting in a solid state mixtures of both polymers. A further approach was the lamination of both polymer layers leading to a diffusive interface of donor and acceptor giving a power conversion efficiency approaching 2%. In recent years organic solar cells have reached 1.5-4% power conversion efficiency for bulk heterojunction polymer-fullerene devices.

![Figure 8 The chemical structures of the first organic solar cells, phthalocyanine on the left and perylene on the right](image)
Materials used in organic solar cells were materials found to readily absorb sunlight and then create photo-generated charge carriers, then allows for transportation of these charge carriers. Both of these properties are commonly found for materials that an extended delocalised π – electron systems. Examples of such materials include phthalocyanine, is representative of the p-type hole conducting materials that work as an electron donor. Perylene and its derivatives show an n-type electron conducting behaviour, they serve as electron acceptor material. (16)

Figure 9A graph showing the different efficiencies of different types of solar cells (20)
The main competitor to organic solar cells continues to be in-organic solar cells which currently have a laboratory based efficiency of between 38.9 - 43.4% for a concentrated photovoltaic, which uses mirrors and lenses to focus the suns energy, using a GaInP/GaAs/GaInAsP/GaInAs cell architecture. This cell architecture is achieved by wafer bonding lattice matched grown on Gallium Arsenide and Lanthanide Phosphate substrates. (21)

Whilst this efficiency is impressive this has the drawback of expensive and complex cell construction and only has this efficiency because the focusing of the suns energy into one location, which itself must be maintained to keep the focal point of the energy on the cell itself. The current highest efficiency of organic solar cells is currently 11.5%. (20) Whilst this is lower than the current highest achieved inorganically the production of these organic solar cells is significantly less than its inorganic competitor meaning it can be more easily mass produced and used (22).

Bibliography


Literature Review

Spray coated thin film bulk-heterojunction photovoltaics are organic semiconductors comprised of two materials, often polymers, one of which will have high electron affinity the other with low electron affinity. These chemicals are dissolved in a more volatile solvent and sprayed on to a substrate leaving behind a thin film of the less volatile chemicals. This process produces substrates with high photoluminescence quenching efficiency which can be used in bulk-heterojunction photovoltaics.

In this work the main focus will be on testing a method of spray coating blends comprising of three different families of organic semiconductors, polyflurenes (F8TBT), poly thiophenes (P3HT) and fullerenes (PCBM), and closely examining the optical properties and the morphology of the samples then attempt to improve those properties through both solvent and thermal annealing processes.

Industrial Coating Techniques

Before establishing the scientific validity and methodology of the work, the industrial applications and future of the work must first be established. One of the seminal texts regarding industrial coating techniques is “Liquid Film Coating” by S. F. Kistler and Peter M. Schweizer (1).

This text goes into great detail regarding liquid film coating, an industrial technique for producing films typically in between 1-100 microns thick. This technique in one form or another accounts for most, if not all coating processes produced industrially and is worth in excess of $20,000,000 million per annum producing things from newspapers to blu-ray disks. The text details across several sections the different factors when it comes to industrial coating, including the fluid dynamics, the surface tension and viscosity of the liquid being coated itself and the problems with wetting and dewetting of the substrate being deposited on.

There are several methods of liquid film coating described in the work, detailing how the technique itself works and the drawbacks of the technique. These techniques are divided into two different overall methods, pre-metered coating processes and self metered coating processes.

An example of pre-metered coating processes is that of Curtain Coating, the section of which within the text is written by Kimiaki Miyamoto and Yoshinobu Katagiri (2). This is a process in which an uninterrupted curtain of liquid falls onto the substrate that is transported on a conveyor belt kept at a regular speed. The thickness of the coating is dictated primarily by the speed of the conveyor and the speed of the liquid leaving the tank. The flow of the liquid must remain un-interrupted to do this there is an edging along both sides of the slit that the curtain of liquid flows through is used; this is done to prohibit the surface tension from causing the coating to taper in. The flow rate of the liquid is also critical for accurate deposition of coatings, meaning that the viscosity and minimum flow rate is carefully controlled to produce the flow rate needed. This technique can produce coatings within ±0.5% of the target thickness.

The benefits of curtain coating and most pre-metered coating processes are that they are quicker processes that can be set to produce thinner coats than other methods; however they are dependant of the flow rate of the liquid itself and can generally only be done on flat substrates.

An example of self metered coating processes is that of Knife and Roll coating processes, the section of which within the text is written by Dennis J. Coyle (3). Knife coating is a process by which an excess of a liquid intended to be coated is loaded on to a substrate, the substrate then passes under a rigid knife that meters the thickness of the coating produced. The overall geometry of the coat can be determined by the distance between the substrate and the knife and the angle of the knife itself.
Knife coaters are simple low cost coaters that are typically used to apply thick coatings of high viscosity liquids creating films between 50-2500μm thick. The disadvantages for this method are that it often produces streaks in the coating as the process is very sensitive to thickness variations in the pre-metered liquid coat.

Roll coating processes are similar but different, once again a substrate is loaded up with an excess of liquid intended to be coated and then is passed through two or more rotating rolls causing the liquid to flow into the small gap between. The thickness of this coating method depends primarily on the gap between the two rolls and the speed at which the substrate is rolled through. This process is subdivided in to two categories forward rolling and reverse rolling, forward rolling goes in the same direction as the conveyer belt feeding the substrate in to the rollers and reverse rolling goes in the opposite direction.

Forward rolling is used to apply thin optical-quality coatings of low viscosity liquids, typically producing films between 25-60μm thick, this processes main disadvantages are that of low speed of the processes and the viscosities needed, and the thickness itself is sensitive to the speed, viscosity as well as the gap in the rollers. Reverse rolling is a much more versatile method being able to produce thicknesses between 10-1000μm in thickness, the main draw backs of this method are the complexity of the set up and the overall cost of the machinery itself. This problem with dependence on the viscosity, the gap through which the thickness of the coat is determined and the speed at which the process occurs all impact self-metered coating processes.

The simplest and most cost efficient methods of coating appear to be the pre-metered coating processes. These have the benefit that they also shown to produce thinner films of coating which is needed for the thinner films intended to be produced. Spray coating is the process that this work will be focusing on heavily, so the current state of industrialised spray coating needs to be taken into consideration.

The specifics of industrial spraying are discussed in “Industrial Sprays and Atomization: Design Analysis and Applications” by G. G. Nasr, A. J. Yule and L. Bendig (4). This text goes into detail behind each of the different industrial spray coating processes. The text details how spray coating technologies are used in food processing, pharmaceutical manufacturing, pulp manufacturing and paper manufacturing. However the area of interest is that of polymer spray coating as that begins to encompass to spray coating that needs to be conducted for spray coating the photosensitive organic material used in bulk heterojunction photovoltaics. There are many types of polymers which have applications when they are in a form of powder; the most common example is that of paint additives and coatings.

In spite of the huge potential market to production of polymer powders by spraying a molten polymer and allowing solidification in a chamber remains essentially a research area. Two fluid atomizers have been used experimentally to various levels of success for an industrial spray coating processes for polymers. The problems that arise when spray coating polymers are due to the high levels of viscosity in molten polymers, making it very difficult to control the atomization of the spray as such that it is completed before solidification occurs. The current challenge in industrial spray coating is to develop atomization processes that have clear cost advantages over the current conventional polymer coating techniques.

The text then goes on to state future developments in industrial spray coating, the spray coating of exotic carbon, such as Buckey Balls and nano-tubes has yet to be industrialised. Currently the experimental coating processes use a fine spray of liquid metal-organic compounds where clusters of metallic atoms act as seeds for crystallization growth. This also relevant to the work as the proposed materials for the spray coating process uses elements of exotic carbon, namely PCBM has a Buckey Ball structure.
Mechanisms behind Spray Deposition

For a more in-depth look in the mechanisms behind the actual spray coating process “Atomization” by John J Dunkley (5) shall be looked at. The overall characteristics of a spray are determined by the spray pattern and by the droplet sizes, spray patterns shall be discussed first.

Spray patterns are broadly divided into two different patterns, axis-symmetric and flat (or fan) patterns. These patterns are defined by the distribution of droplet mass within the spray itself; axis-symmetric patterns project the droplet mass over a wide circular area, either in a cone formation or in a broad hollow circular pattern, flat or fan patterns concentrate the droplet mass into a distinct flat line of spray.

The nozzle geometries effect how the spray coats the target substrate, the angle of the resulting spray is broadly defined into three categories; narrow sprays, where the angle is less than 30°, medium sprays, were the angle produced is between 30° and 70° and wide sprays are ones were the angle produced is greater than 70°. The type of geometry used is dependent on what is required of the spray itself, finer sprays are produced by narrower sprays, wider sprays are often used as they cover a larger area. There are two basic designs for nozzle designs, pressure jets and two fluid atomizers. Pressure jets are the most simple atomizer, these are the simplest atomizer they force the liquid through a small orifice (<0.3mm) at high pressure (>100mPa) and produces a very fine spray (average droplet diameter of 20μm). Two fluid atomizers fall into two different categories either internal mixing or external mixing. Internal mixing is used to mix a pressurised liquid and gas making for a very fine droplet size as the liquid and gases are mixed at high velocity and density. External mixing produces a relatively chaotic breakup and the droplet size distributions produced are generally wider.

The droplets shall now be discussed; the way in which droplets are created is through a process called atomization, which broadly fall into two categories, primary atomization and secondary atomization. Primary atomization is occurs nearest the nozzle caused by the pressure difference between the ambient air and the pressurised air liquid mixture present in the nozzle. Secondary atomization occurs further downstream of the nozzle, there are various parameter that can cause this secondary atomization, such as the relative speed between the gas and the droplet reaching a critical point, however the secondary atomization always leads to smaller droplets produced. As a general rule as the velocity of the spray increases the atomization increases and droplet size decreases. Droplets may have a wide range of shapes, particularly near the nozzle though are generally considered to be spherical. The likely deviation from spherical droplets increases with droplet size, for example droplets > 1mm are unlikely to be spherical.

Now the characteristics of the spray have been described, the deposition of the spray is now considered. The parameters that determine the behaviour of a drop when it hits the surface is the Weber number, a dimensionless number that dictates the relative importance of the fluid’s inertia compared to its surface tension. The impact behaviour is also dependent upon the surfaces characteristics, which are divided into three categories, Cold and dry surfaces, wetted surfaces and hot surfaces. On cold surfaces there is a border between a droplet “sticking” and “splashing”, “splashing” produces a range of droplet diameters ranging from 2% and 25% of the impacting diameter. In the final case of the droplet impacting on a hot surface is more complex as liquid film can only exist on the substrate below the Leidenfrost temperature. Heat transfer to the impacting droplets can be related empirically to their maximum spread on impact and their residences times.
Now the background in industrial coating techniques and general spray coating theory has been established and the gaps found in the literature point to very little data with regard to spray coating organic solar cell materials at an industrial level. The spray coating of polymers and exotic carbon compounds are still in the experimental phase. This leads on to establishing the scientific validity and methodology of the work.

**Establishing Experimental methodology**

Before establishing the methodology the usefulness of the materials being used needs to be established, this can be established by the paper “Polymers show versatility in organic solar cells” by Chris McNeil (6). In this paper the three materials, F8TBT, P3HT and PCBM are discussed as they pertain to organic solar cells. The external quantum efficiency of spin coated F8TBT–P3HT and spin coated F8TBT-PCBM are shown and the paper mentions that as an ambi-polar molecule the F8TBT can be used in both a donor and acceptor role. The paper also states that these particular chemicals may hold the key to reliable efficient plastic electricity.

Now that the materials have been established as useful for organic solar cells the method for spray coating organic electronics must be established before focusing in on what optical properties and morphology is to be expected for samples of each of the blends. The best methodology was found in the paper “Characterization of spray-coating methods for conjugated polymer blend thin films” by Mathias Noebels, et al (29). In this paper a series of tests were performed to find the optimal set up for an air brush to deposit the optimal thin film of PFB-F8BT two materials that commonly used in photovoltaics.

Though the chemicals used are different to the chemicals that are planned to be spray coated they are similar to the chemicals being used. Namely the polyfluorenes F8TBT and the F8BT used in the literature are very chemically similar, so the methodology used in the paper is worth testing against other organic semiconducting materials. The study found that the optimum solvent for spray coating using an air brush was a solvent mixture of Di-Chlorobenzene and Chlorobenzene, the optimum distance was found to be 17cm, the optimum substrate temperature was found to be 80°C and the optimum pressure was found to be 1.2 bars. This methodology gave results of high photoluminescence quenching (≈0.8) and with relatively low average roughness (≈15nm) for the blend used, leading to samples that could be manufactured into proto-typical solar cells that gave similar power output as that of a similar spin coated solar cell.

The future work that could be conducted following this paper would to be using more recent materials found in the field of bulk heterojunction semiconductors to produce the thin films with such as those discussed in” Active Layer Materials for Organic Solar Cells” by Jianhui Hou and Xia Guo (8) which include the materials discussed for this work. Another aspect that this paper did not consider was any post annealing processes as that too could increase the photoluminescence quenching and morphology of the samples produced. Now a methodology has been established a post annealing process should also be established. Upon reading the literature two different but similar processes emerged, that of thermal annealing and solvent annealing. The methodology of thermal annealing shall be established first.

To find a thermal annealing process that could be the same for each blend several factors had to be taken into consideration, for example what was the optimum time and temperature for each of the three blends and was there a common middle ground that allowed all of the blends to be processed similarly. The thermal annealing shall be addressed first; using both papers on the thermal annealing of PCBM-P3HT and the thermal annealing of P3HT-F8TBT the thermal annealing temperature and length of time annealed shall be established.
The annealing of the PCBM-F8TBT blend would also be discussed here, the common ground of which would then be taken into consideration when determining the annealing process. However there appears to be very little study done on the annealing of this blend and therefore it cannot be considered when determining the thermal annealing process. It must be stated this is a gap in the literature and therefore indicates an area of potential future work that could be addressed within this work.

“Efficient Polythiophene/Polyfluorene Copolymer Bulk Heterojunction Photovoltaic Devices: Device Physics and Annealing Effects” By Christopher R. McNeill, et al (9) is a paper in which the blend of P3HT-F8TBT is spin coated on to substrates, some of which go on to be thermally annealed, all of which are then tested to determine their photoluminescence quenching and external quantum efficiency and fill factor. In this paper the thermally annealing processes that was used was 140°C for ten minutes this lead to an increase in all areas being tested, the paper also indicates that 150°C could be the limit of improvement of the blend.

The annealing of PCBM-P3HT shall now be discussed in the paper “Effect of thermal annealing on P3HT: PCBM bulk-heterojunction organic solar cells: A critical review” by Xiaohan Yang and Ashraf Uddin (10). In this paper the results of several studies of various temperatures and times to try and show the optimum one for PCBM-P3HT. In this paper a table of results from all of the gathered studies show that the solvent used in the manufacture of the film could affect the result of the thermal annealing process, as such two of the figures leap out, a film created using Chlorobenzene gave the best results when annealed for thirty minutes at 150°C and a film created using dichlorobenzene gave the best results when held at 150°C for ten minutes.

Given that 150°C appears to be a temperature at which all of the chemicals in the blends appear to be able to be raised this shall be the temperature at which the annealing shall occur. The annealing times of both ten minutes and thirty minutes have been suggested in both papers; therefore an annealing time of twenty minutes will be used as a middle ground between them. Now that a methodology for the thermal annealing process has been established the solvent annealing process now needs to be established.

Once again papers on the solvent annealing of both PCBM-P3HT and P3HT-F8TBT will be discussed and the best common parameters will be used. The solvent annealing parameters of PCBM-F8TBT would also be discussed but once again it appears there is a gap in the literature with regards to the solvent annealing of PCBM-F8TBT. For this three papers were taken into consideration, two papers where used to find the best solvent, and one paper was used to find the solvent annealing time.

The first of the two papers that were used to find the best solvent for the annealing process are both “Investigation of nanoscale morphological changes in organic photovoltaics during solvent vapour annealing” by Steve Miller, et al (11). In this paper spin coated samples of P3HT-PCBM where exposed to CHCl₃, also known as chloroform and the photoluminescence of the blend was monitored from 30 seconds of expose until three minutes of exposure to the chloroform vapour.

As this was measured in situ more to observe how quickly the blend swells with the solvent and how that affects the photoluminescence quench, rather than give exact times for a solvent annealing process, the solvent used is useful information however with a lack of a clear annealing time a time must be found first.

The second paper that shall be considered is “Structure formation in P3HT/F8TBT blends” by Alessandro Sepe, et al (12) in which spin coated samples of P3HT-F8TBT where exposed to both
thermal and solvent annealing processes and the changes in both optical and electronic properties where recorded. In this paper the solvent chosen for solvent annealing was Carbon Disulfide (CS$_2$) as it was the solvent that could completely dissolve the P3HT crystals and the time for solvent annealing was that of 30 minutes.

The problem with Carbon Disulfide is that it is extremely volatile and unstable molecule with several health risks associated with using it, the paper however did indicate that a possible solvent that could be used would be chloroform, whilst it would not fully dissolve the P3HT crystals it would give similar results. Whilst this paper used a different solvent than chloroform the time at which the annealing was conducted gives a good indication for times for annealing processes.

Other papers such as “Controlled solvent vapour annealing for polymer electronics” by Sven Hüttner (13). In this paper perylene bisimide acrylate is spin coated onto a substrate and then exposed to chloroform as a means of solvent annealing it, as an example of solvent annealing, and its potential benefits for polymer electronics. The samples are shown to change in thickness at the 200 second mark, which the paper states that this indicates the thin films have absorbed the solvent vapour from the air. The annealing process continues with fluorescence and absorption analysis of the sample in situ as the process completes which takes 90 minutes. The paper indicates that there is a cut off point at which the solvent annealing no longer improves the optical properties and this cut of point is shown to be 30 minutes.

Each of the papers have either used or suggested Chloroform (CHCl$_3$) as the solvent used for the annealing process, that solvent shall be used for the solvent annealing process. The time of annealing is less clear in the literature, annealing has shown to be useful past 3 minutes in at two of the papers, in both cases this could be the time needed for thin films to absorb the solvent vapour in the air. In two of the papers the full time of completely annealing samples appears to be 30 minutes. Whilst in both papers suggesting this it was either using a different solvent or a different organic polymer these studies are similar enough to the work that 30 minutes shall be used for the time of solvent annealing.

Now the methodology by which the films shall be first made and then processed by has been established the metrics for improvement need to be established. First the morphology of the samples needs to be taken into consideration because as stated in the book “Short-Channel Organic Thin-Film Transistors Fabrication, Characterization, Modelling and Circuit Demonstration” by T. Zaki (36) the organic solar cell only has 100nm of active layer to work with in the current device fabrication processes used, therefore an exceedingly rough surface would lead problems, as discussed in “Efficient planar heterojunction perovskite solar cells by vapour deposition” by Mingzhen Liu, Michael B. Johnston and Henry J. Snaith (15) in which they discuss how if the active layer of a solar cell is uneven it can lead to a shunting path reducing overall fill factor and open circuit voltage of a solar cell which ultimately leads to a loss in efficiency of the cell.

As such several papers were found to find spin coated RMS roughness for each of the three blends and were possible the roughness of annealed blends for a point of comparison later.

<table>
<thead>
<tr>
<th>Blend</th>
<th>As Made Samples</th>
<th>Thermally Annealed</th>
<th>Solvent Annealed</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCBM-P3HT</td>
<td>2.50nm (16)</td>
<td>28.50nm (16)</td>
<td>5.0nm (17)</td>
</tr>
<tr>
<td>F8TBT-PCBM</td>
<td>0.40nm (18)</td>
<td>10.03nm (19)</td>
<td>2.0nm (18)</td>
</tr>
<tr>
<td>P3HT-F8TBT</td>
<td>0.9nm (20)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Each of these figures are gathered from studies which make spin coated samples of the blend indicated, some of which then go onto then anneal said blend. Whilst pristine spray coated samples
are expected to be more rough than the spin coated samples, for example the Mathias Noebels paper showed that “as made” samples could be as RMS rough as 15nm, the general trend shown here is to be expected. With thermally annealed samples increasing drastically in roughness and solvent annealed samples also increasing in roughness.

However it is not only morphology that is important but also the cells efficiency in separating electron- hole charge carriers without recombination, therefore producing a charge. One of the ways this can be calculated is through finding the photoluminescence quenching efficiency, as is discussed in “Exploration of spray-coating for producing polymer bulk-heterojunction solar cells” by Mathias Noebels as this is an established way in which the efficiency of solar cells are evaluated several papers were found and the photoluminescence quenching of each of the blends

<table>
<thead>
<tr>
<th>Blend</th>
<th>Photoluminescence Quenching</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCBM-P3HT</td>
<td>0.80 (21)</td>
</tr>
<tr>
<td>P3HT-F8TBT</td>
<td>0.83(12)</td>
</tr>
<tr>
<td>F8TBT-PCBM</td>
<td>0.90 (22)</td>
</tr>
</tbody>
</table>

For each of these figures the blend indicated was spin coated on to a substrate and through recording of both the fluorescence spectroscopy and absorption of the blend the photoluminescence quenching was found. However the annealing processes also need points of comparison

<table>
<thead>
<tr>
<th>Blends</th>
<th>Annealing Process</th>
<th>PL Quenching</th>
<th>Percentage difference when compared to pristine</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCBM-P3HT</td>
<td>Thermal</td>
<td>0.81 (21)</td>
<td>+10%</td>
</tr>
<tr>
<td></td>
<td>Solvent</td>
<td>0.74 (11)</td>
<td>+20%</td>
</tr>
<tr>
<td>P3HT-F8TBT</td>
<td>Thermal</td>
<td>0.46 (22)</td>
<td>-40%</td>
</tr>
<tr>
<td></td>
<td>Solvent</td>
<td>0.63 (22)</td>
<td>-20%</td>
</tr>
<tr>
<td>F8TBT-PCBM</td>
<td>Thermal</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>Solvent</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Each of these figures represent the effects of similar, if not identical, annealing processes that shall be used in the work occurring to a spin coated sample of the blend indicated.

This indicates what is to be expected from the solvent annealing process, if not finding similar photoluminescence quenching a similar percentage difference should be observed.

Bibliography


Theory and Methodology

In this section the theory behind much of the project shall be discussed, such as which polymers shall be used and their function within an organic solar cell. The morphology of the blended sample in both the macro and micro scale shall be discussed and what features are expected and optimal for organic solar cells.

The theory behind absorbance and fluorometric spectroscopy and how that relates to the photoluminescence quenching efficiency of the blends shall also be discussed. As will the way in which photoluminescence quenching efficiency can be calculated in practical terms to give quantities results.

For each of these subjects the methodology of each experiment shall also be laid out, the preliminary results will be referenced when appropriate for discussing how the parameters of the experiment where come to.

Semiconducting Polymers

When broken down into basic terms polymers are repeating structural units, monomers, which consist of mainly carbon atoms. These carbon atoms are connected to one another by valence bonds of electrons.

![Figure 10 formation of Sp² or Sp³ orbital due to hybridisation of a carbon atom (1)]

The carbon atom has the ability to form four bonds with neighbouring atoms with either a tetrahedral geometry, caused by four sp³ orbitals or a trigonal planar geometry caused by three sp² orbitals and one p orbital.

In the trigonal planar geometry the sp² orbitals can form σ bonds that are highly localised and cannot contribute to any charge carrier process. The remaining p orbital can form π bonds with other neighbouring p orbitals. Although more diffuse than σ, the π bonds still have a small overlap between orbitals so electron mobility is still limited.

The formation of carbon chains with single and double bonds makes steps toward conductive polymers, the simplest example of which are benzene rings.
The orbital overlap each other forming an orbital structure where electrons are delocalised along the whole polymer chain, as soon as an electron is removed by oxidation doping the sample the remaining electrons can move within the polymer chain. The polymers used within the work shall now be discussed.

The first polymer to be discussed is Poly [(9,9-dioctylfluorene)-2,7-diyl-alt-(4,7-bis(3-hexylthien-5-yl)-2,1,3-benzothiadiazole)-2',2''-diyl]( F8TBT) which can occupy both a donor and acceptor role when used in a bulk heterojunction with P3HT and PCBM as it has a HOMO of 3.15eV and a LUMO of 5.37eV. This polymer is ambipolar and has low electron affinity thiophene structures and high electron affinity benzothiadiazole structures, so it can act as both acceptor and donor.

The second polymer to be discussed will be Poly-3-Hexylthiophene (P3HT), a Polythiophene, it is a classic electron donor it has a HOMO of 2.7eV and a LUMO of 4.9eV. In this polymer the thiophene unit has a low electron affinity, making it an effective electron donor.

The final chemical to be discussed is [6,6]-Phenyl-C₆₁-butyric acid methyl ester (PCBM), a fullerene and a classic electron acceptor, has a HOMO of 3.7eV and LUMO of 6.2eV. This chemical has a very high electron affinity in the C₆0 buckyball present in the structure making it a very effective electron acceptor.
Thermodynamics of Mixing

The mixing of two polymers can lead to two different systems, a single phase system meaning effective or complete intermixing of the two polymers, or a two phase system with partial or complete de-mixing of the two polymers. A stable system is found when the lowest Gibbs free energy is found. This is dictated by both the energy of the system and the entropy of the system. The system is also dependant on the temperature and relative composition of the polymers to one another.

![Figure 13 the demonstration of phase separation of PFB and F8BT, two phases on the left and single phase on the right](1)

The energies of the system are dictated by; how well both polymers mix, dependent on how similar the polymers are to one another, and also how the energies change with donor-acceptor compared to donor-donor and acceptor-acceptor. The entropy of the system is dependant of the disorder when the donor and acceptor mix, which either promotes or inhibits the blend mixing. The stable system of minimized Gibbs free energy is dictated by the equation:

\[ \Delta G = \Delta H - T\Delta S \]

Equation 1 Gibbs free energy equation Where \( G \) =Gibbs free energy, \( H \) =enthalpy, \( S \) = entropy

It is usually more energetically favourable for like polymer chains to be neighbours to one another rather than different polymer chains. This usually means that \( \Delta H > 0 \). We therefore expect this to suppress mixing, unless the donor and acceptor are very similar.

However with the permutations of possible microstates within the overall macro-scale means the mixing of donor and acceptor leads to a less ordered state with higher entropy which is consistent with the second law of thermodynamics. This means that \( \Delta S \geq 0 \) and therefore strongly favours mixing.
In order for two substances to form a solution the Gibbs free energy of mixing must be negative and at its lowest possible value. As can be seen at any composition less than $X_1$ or greater than $X_2$, a single phase has a lower free energy than a two phase system.

For compositions in-between the two phase system has lower free energy than a single phase system. The blend will consist of two separate phases of donor and acceptor. The system also depends on temperature, above the critical temperature ($T_c$) entropic effects dominate and only single phase of mixing is possible.

**Spray Coating**

Spray coating is a method of creating a thin film of a substance using the previously an air brush. Semiconducting polymers lend themselves to being spray coated as they can be easily dissolved in any number of solvents.

There are many commercially available kits, with considerable levels of control and variability, such as distance from the substrate, pressure of the air brush, and concentration of polymer to solvent, this works well for this process.
In this project the process for creating a thin film of the polymer compound was to first load the polymer solvent solution into the ink well of the air brush, the temperature of the substrate for coating with the thin film was thermally controlled.

The basic working principle of the airbrush works on the Bernoulli Principle, which states that an increase in the speed of a gas or fluid causes a decrease in pressure and the atomisation of liquids. The size of the droplets produced by the atomisation process is directly related to the ratio of the pressurised gas and the polymer liquid passing the mixing point. The higher the ratio of gas to polymer liquid the smaller the droplets produced will be.

Using the airbrush this ratio can be regulated using the trigger on the airbrush (10). The gas from the pressurised container through the valve (20), at (2) the gas passes through a bottle neck that lead to an increase in speed of the gas. The pulling of the trigger (10) also move a needle (18) backwards opening a small aperture (3) towards the well that holds the solvent mixture.

The low pressure cause by the passing gas sucks the solvent mixture out of the well and leads towards the mixing point, which is the tip of the needle. At this point the atomisation of the mixture takes place via collisions caused by turbulent flow; this causes the surface energy of the solvent mixture to increase producing smaller droplets. At the opening droplets with a bigger size divide...
further because of the pressure step between the inside of the airbrush and the ambient air pressure.

The airbrush itself has internal systems that make the internal mix for a high amount of fine atomised droplets. The distance between the nozzle of the airbrush and the substrate is dependant on the air pressure in the air brush. The closer to the substrate the less air pressure is needed to allow the atomisation of the polymer solution. Using a higher pressure also decreases the size of droplets, this also leads to a more regular film, however if the pressure is too high the droplets will be blown away once they hit the substrate, this leads to a splash pattern and a higher waste of materials.

The shorter the distance leads to a more wet irregular film, the longer the distance leads to a dry and dusty films as the droplets already have evaporated on the way to the solvent. A good middle ground must be used in order to get a smooth even film. With the air brush pressurised, the polymer solvent mixture was then sprayed on to the substrate, an evaporation period was then left to allow the solvent to evaporate off leaving behind the less volatile polymer compound, this was then repeated until the require thickness was reached.

For the experiment the air brush used was the Aztek A270 Airbrush, the air compressor used was the Stanley Air Compressor DN55/8/5 and a generic heating plate. Taking into account the factors in play in the atomisation of the polymers a recommended setup found in the literature was used, distance from the air brush to the sample was 17cm (17x10^{-2}m), the pressure of the air brush was set at 1.4 bars and the substrate temperature was set at 80°C.

The solution used for each spray coating was a concentration of 5mg polymer mixture per millilitre of solvent. Each polymer mixture was a 1:1 ratio of donor and acceptor polymers and each solvent was a 5:1 ratio of dichlorobenzene and chlorobenzene. For each of the polymer mixtures the substrate was sprayed with three intervals of 10 seconds of spray, followed by 30 seconds of drying time.

These parameters were found when preliminary studies of other solvents, namely toluene and chlorobenzene found that either the films made were inconsistent, or where too thin for any meaningful analysis of the optical or morphological properties of the samples. This closely matches up with similar findings found in the literature. (6)

Though the solvent that gave the best results was the dichlorobenzene, chlorobenzene mixture the samples made where still quite thin, so very little meaningful analysis could be conducted, to help remedy this the number of intervals of coating where increased to three coatings as opposed to the single coating conducted in the preliminary tests, this was to allow for the creation of films thick enough that meaningful analysis can be made.

The pressure of the airbrush and distance from hot plate used where optimum parameters that were found in the literature for polymers similar the polymers used. In the preliminary studies these parameters produced the most consistent films when tested against other setups.
The temperature of the hot plate was set at a temperature above the vaporisation point of the solvent mixture ($66\,^\circ\text{C}$), but below the boiling point of the solvent mixture ($131\,^\circ\text{C}$) to allow the solvent mixture to evaporate off rapidly but not to the point where the polymer blend would be deposited as a basically dust.

### Annealing Processes

Annealing with heat is a well known and established process in many different areas of science, however in the case of organic electronics thermal melt annealing is a special variant. The temperature of the substrate is raised causing the film to reach thermodynamic equilibrium. Once the film is at thermodynamic equilibrium the increased polymer chain mobility allows it time to modify its morphology, after it reaches the required morphology and phase separation the system is cooled down, fixing the film. The advantage of thermal melt annealing over other methods is that the temperature of a substrate is very easy to control, that and the cooling process of the substrate after the annealing is another controllable process.

The setup used, according to recommendations from the literature, with a hot plate set to $150\,^\circ\text{C}$ the samples were exposed to the heat for 20 minutes then allowed to cool for 40 minutes, cooling at a rate of $3.75\,^\circ\text{C}$ per minute.\(^{(7)}\)\(^{(8)}\)

Other thermal annealing processes where considered such as $80\,^\circ\text{C}$ for an hour and a half, however the process used has more literature supporting the higher temperature for a shorter period of time, as the prolonged exposition to high temperatures could potentially damage the polymers.

The second method to be discussed will be solvent vapour annealing. Solvent vapour annealing is a well established post annealing process used to alter or induce the desired phase separation in organic electronics. This process involves exposing the film of a polymer to a closely controlled solvent rich atmosphere; this causes the film to swell up from the intake of solvent causing an increase in polymer chain mobility, similar to that of thermal melt annealing. The solvent chosen for this process must be compatible with both compounds present in the film, often it will be the case that one of the compounds in the blends is more soluble than the other, however to get the best annealing this difference should be minimal.

*Figure 17 shows the set up of the solvent vapour annealing processes.*

Increasing the polymer chain mobility gives the system more time to modify its morphology towards thermodynamic equilibrium. After the required phase separation and morphology are met the system is effectively “frozen” in place by removing the substance from the solvent rich atmosphere. The advantages of solvent vapour annealing are that it can be done at room temperature thus reducing the risk of thermal damage. The disadvantages of this method is that the compatibility of
the solvent to both parts of the blend, if there is difference in compatibility it could cause one of the compounds to be more mobile than the other, making one compound reach the phase separation and morphology required and not the other. (9)

Set up used, according to recommendations from the literature with a reservoir was filled with chloroform that was gently heated to just above room temperature (≈30°C) to facilitate the evaporation of the chloroform. The samples were kept in the chloroform rich environment for 30 minutes. (10) (11) Other solvents where considered for the annealing process such as dichlorobenzene, however chloroform seemed to fit the polymers within the blends better.

**Absorption Spectroscopy**

Ultraviolet, Visible Near infrared (UV-Vis-NIR) Spectroscopy is useful for characterising the absorption / transmission and reflectivity for many different materials such as pigments, coatings, windows and filters. Often referred to as Spectrophotometry, this is an analytical technique based on the amount of light absorbed by a sample at a given wavelength. The wavelength is commonly in the region between 190 – 1000nm.

When a molecule or part of a molecule can be excited by light absorption, it is called a Chromophore. In the case of organic molecules chromophores always consist of multiple bonds such as carbon - carbon bonds, carbon – oxygen bonds or carbon – nitrogen bonds.

The energy that is absorbed is often dissipated kinetically through heat, or by light emission known as fluorescence. In both cases the intensity of the transmitted light by a collection of chromophores is less intense than the incident light. An excited molecule can posses any one set of quantum energy states, dictated by quantum mechanics, each of these states are called energy levels. In spectroscopy the major levels are determined primarily by the density of states of the electrons, these are called electron levels.

Absorption of a photon results in a change of the electron energy as well as a change in vibrational and rotational energies. In liquids and solids the rotational lines are broad and overlapping so rotational structure cannot be distinguished, and is therefore not relevant. If all transitions where between lowest vibrational ground state and the first excited state this would yield a discreet narrow peaks, however the transition from one electron level to the next can occur between many vibrational levels giving a broader peak.
The quantised internal energy can be described by this equation:

$$E_{\text{int}} = E_{\text{eel}} + E_{\text{vib}} + E_{\text{rot}}$$

Equation 2 where $E_{\text{int}}$ is internal energy, $E_{\text{eel}}$ is electronic energy, $E_{\text{vib}}$ vibrational energy and $E_{\text{rot}}$ is rotational energy.

The electronic energy refers to the whether the state is either in the ground state or the excited state. The vibrational energy refers to the energy of atoms in the molecule in periodic motion while the molecule as a whole has a different rotational and translational energy. The rotational energy refers to the electric dipole moment of the molecule caused by incident electromagnetic waves.

The Beer Lambert Law may be written for a single absorber either gaseous or solution:

$$A = -\log_{10} \left( \frac{I_t}{I_0} \right) = -d\alpha$$

Equation 3 where $I_0$ is the initial monochromatic radiant power, $I_t$ is the monochromatic radiant power transmitted by the absorbing medium ($I_t/I_0$) is the internal transmittance, $\alpha$ is the absorption coefficient and $d$ is the absorption path length.

Absorbance measurements allow the following determination of the concentrations of a substance kinetic assay of the certain chemical reactions, identification of materials, however the most
common use of absorbance measurements is to determine the concentration of the solute. (13) The equipment used for this experiment was the Ocean Optics USB-650 Red Tide spectrometer. The software used was SpectraSuite.

SpectraSuite is a data processing program that takes in the data from the USB spectrometer used, processes it and then out puts the data in to spreadsheets for further analysis. SpectraSuite automatically processed the data to get the most accurate results possible, whilst at the same time not compromising the resolution of the spectrometer used. For each sample the back ground light levels were taken then removed, then the broadband light source was activated and a blank substrate was inserted and a baseline of light absorption. Then the sample was inserted and a reading taken. Before each test the parameters for data processing were set in the software. As the process is not time dependant the processing of the data will be to reduce general noise present in the data.

The setting found to give optimal signal / dynamic range without saturation is an integration time of 17μsec, this is the length of time during which the sensing elements are collecting charge between data transport. A spectral averaging of 5 was used meaning 5 scans were taken and then averaged for each part of the spectrum this is often done to increase the signal to noise ratio when the signal is weak. A boxcar averaging of 5 was used meaning that taking the five points either side of that point and averaging them together as well, this is done when a spectrum is relatively flat and there is relatively little variation expected from point to point, this gives a smoother spectrum reducing overall noise within the spectral resolution of the instrument.

These parameters where found during the preliminary results to give the best results when compared to other setups used, giving meaningful data that can be analysed.

**Fluorescence Spectroscopy**

Fluorescence is a type of luminescence, which is an emission of light from a “cold source” meaning non-blackbody source, in fluorescence spectroscopy an external energy source is used to “photo-excite” the sample, often an infrared, visible or ultraviolet light source, causing light emission.

The light emission is caused by the “photo-excited” sample relaxing back down to a lower energy state; it does this by emitting a photon of light, the energy of which corresponds to the energy of the excited state.

This emission is called fluorescence, which can be broadly defined into two types, photoluminescence and phosphorescence. Both processes involve light emission from any form of matter after the absorption of photons, Photoluminescence is characterised as a fast process and Phosphorescence is characterised as a slow process, with the light emission lasting minutes or hours. In this work photoluminescence is being studied, this takes place in fluorometric analysis.
The absorption and emission of light is measured in quantised energy levels described by this equation:

\[ E = hf = \frac{hc}{\lambda} \]

Equation 4 where \( f \) is frequency, \( \lambda \) is related wavelength; \( h \) is Planck’s constant (6.624x10^{-27} \text{ergs/sec}), \( c \) is the speed of light (3x10^8 \text{metres/second}).

In the analysis of the emission spectrum the most interesting sections for the purposes of organic electronics is that of ultraviolet and visible light for emission that equate to transmission of outer electrons, and Infrared that equates to molecular vibrations. (14)

The equipment used was an Ocean Optics USB 2000+ Spectrometer, and two different lasers, the Shanghai Dream Lasers DPSS Laser 473nm with a power of approximately 1mW-3mW and the Shanghai Dream Lasers DPSS Lasers DPSS laser 532nm with a power of between 1mW-3mW. The
software used again was SpectraSuite with the same automatic data processing described previously. For each sample the background light level is taken then removed, one of the lasers are then activated and the readings are taken. This process was repeated for each of the different lasers. The data was processed SpectraSuite in the same way as described for absorption spectroscopy.

### Photoluminescence Quenching

The simple definition of Photoluminescence (PL) quenching efficiency is the ratio of disassociated excitons to the number of photons absorbed by the material:

\[
\text{Photoluminescence Quenching} = \frac{\text{Number of Disassociated Excitons}}{\text{Number of Photons Absorbed}}
\]

Equation 5

If it is assumed that:

\[
\text{Number of Photons Absorbed} - \text{Number of Photons Emitted} = \text{Number of Excitons}
\]

Equation 6

Therefore

\[
\text{Photoluminescence Quenching} = 1 - \frac{\text{Number of Photons Emitted}}{\text{Number of Photons Absorbed}}
\]

Equation 7

Experimentally this can be shown by the intensity of light emitted over a certain time frame giving an intensity of the sample, however the amount of photons absorbed cannot be directly shown, photons absorbed can be indirectly observed if we use a reference with no quenchers as per equation 6 this would equate the photons absorbed by it as there are no exciton disassociated by it.

Assuming the absorption of both the sample and reference device are the same we come to the equation:

\[
\text{Photoluminescence Quenching} = 1 - \frac{I}{I_0}
\]

Equation 8 where \( I \) is the sample intensity and \( I_0 \) is the reference intensity

However the sample and the reference will often not have the same absorption so another factor must be introduced for a more general expression:

\[
\text{Photoluminescence Quenching} = 1 - \frac{A_0}{A} \times \frac{I}{I_0}
\]

Equation 9 where \( A \) is the absorption of the sample and \( A_0 \) is the absorption of the reference material

Experimentally this is done by referencing the blended samples against the donor of the blended sample as that will not have the quenchers and therefore work as the reference sample.
\[ \text{Photoluminescence Quenching} = 1 - \frac{A_P}{A_B} \times \frac{I_B}{I_P} \]

Equation 10 where \( B \) is blended sample, \( P \) is pristine sample, \( I \) is intensity of emission, and \( A \) is the intensity of absorption.

These was achieved experimentally by keeping the distance between the sample and laser the same between each test, by keeping the sample held at the same angle between each test, and by keeping the angle of observation at 30°, this was done to allow for such quantitative results to be calculated. Keeping a consistent geometry of laser, sample and detector. (8) (1)

Whilst absorbance and emission is wavelength based the overall spectrum is being used for measurements. For absorbance the full spectrum is used as the integral of each of the sample and reference material must be taken into consideration. For emission the emission across the whole spectrum is inferred by exciting and measuring at two different wavelengths.

**Optical Microscopy**

Optical microscopy is useful for determining many features at the microscopic scale, such as the morphology and size of structures on sample, the transparency of the sample, the colour of the sample (reflected or transmitted), the refractive indices of the sample, dispersion or refractive indices and the crystal system.

The difference between the two setups (reflected or transmitted), is where the light source is situated. In the reflected setup the light source is set above the sample so the image recorded is the reflected light of the sample, in the transmission the light source is put bellow the sample so the image recorded is the light once it has gone through the sample.

An example of a compound microscope and microscope ray diagram is shown below:

![Microscope and Ray Diagram](image)

Figure 22 an image of the microscope used in the experiments, and a basic microscope ray diagram. (16)

This basic view does not take into account real world defects that occur in with real lenses, such as Spherical Aberration, when peripheral rays and axial rays have different focal points, which causes the image to appear blurred or slightly out of focus.
Another example of defects that occur is that of axial and lateral chromatic aberration. Axial chromatic aberration occurs because blue light is refracted to the greatest extent, followed by green and red light, a phenomenon called dispersion. Lateral chromatic aberration is the chromatic difference of magnification, the blue image of a detail was slightly larger than the green image or red image of white light, causing colour ringing of detail at the outer regions of the fields of view.

The resolution of the image is another concern of optical microscopy; the theoretical maximum resolution is defined by the equation:

$$ R = \frac{(0.61 \cdot \lambda)}{N \sin \alpha} $$

Equation 11 where 0.61 is a geometric term based on the average 20/20 eye, $\lambda$ is the wavelength of light illuminating the sample, $N$ is the refractive index of the material, $\alpha$ is the angle of focus subtended by the lens.

The magnification of the lens is also a concern of optical microscopy defined by the equation:

$$ M = \frac{D \cdot M_1 M_2}{250 \text{mm}} $$

Equation 12 where $D$ is the projection tube length (usually around 250mm), $M_1M_2$ is the magnification of the objective and the ocular pieces, and 250mm is the minimal distance of distinct vision eyes.

The final equation of relevance to optical microscopy is that of depth of focus:

$$ DOF \approx \frac{\lambda}{N \sin \alpha} $$

Equation 13 where $\lambda$ is the wavelength of the light illuminating the sample, $N$ is the refractive index of the lens, $\alpha$ is the angle subtended by the lens. (17)

Each of the samples was analysed using a Meji mx 9000 series microscope and Meji Techno [Japan] objectives of both 10x and 40x magnification. Photographs of 2592 x 1994 pixels were taken at each magnification both before and after the annealing process by a CCD digital camera, SMP, Visi cam 630-1032.A

As an example of what will be looked for in the microscopy tests here is an example of a spray coated PFB-F8BT from the literature:
As these are spray coated samples a coffee-stain like structure is expected, mostly circular in form with a flatter bottom and higher surrounding walls.

These images of the samples also show that the structures are building on top of one another meaning that the sample is not de-wetting when it is drying on the surface, this allows for several layers of spray coating to be built up.

The uniformity of the colour of the samples shall also be observed. The colour itself is a product of the light absorbed by the sample, however the camera itself automatically white balances, making the centres of the “coffee-stain” like structures to appear whiter and the edges of the structure to appear darker. The uniformity is important as if the sample is of a single colour rather than several this indicates that the sample was well mixed.

For example black specs on the sample images would indicate that an element of the spray coated polymer solvent solution was not optimal for the samples used. Whether that would be either the concentration of the solution or the parameters of the spray coating process.

Other elements of the image shall be discussed such as the range of the “coffee-stain” structures, as this is an indicator as to how fine and consistent the spray coating process was, for example the example has coffee-stain structures ranging between 50-10μm which indicates a very relatively consistent spray.

**Atomic Force Microscopy**

The general principles of Atomic Force Microscopy (AFM) are best described by explaining each part of the equipment.

![Diagram of an AFM](image)

Figure 24 a diagram of an AFM (18) The cantilever spring which deflects as the atomically sharp tip scans across the sample surface, a position sensitive photo-detector, measures the deflection of the cantilever, the output of which feeds through an error detector and into a piezoelectric scanner which controls the samples X,Y,Z position with Å accuracy.
A properly set up AFM with a sharp tip can scan the topography with extremely high magnification of up to 1,000,000X and also records the topography in three dimensions. The limiting factors of the resolution of the AFM are the structural properties of the atomic wave functions of the probe tip and sample. There are mechanisms which the interactions of the sample with the tip vary, with a very small tip repulsion is the mechanism that operates the cantilever, the sample to tip distances is very small, within a few Å.

This repulsion originates in the exchange interaction due to the overlap of the electronic orbital at atomic distances, when this repulsive force is predominant the tip and sample are considered to be in “contact”. Another mechanism in which can affect the cantilever is that of attraction (Van der Waals) a polarisation interaction between atoms, instantaneous polarisation of an atom induces a polarisation in nearby atoms therefore an interactive interaction, the tip and the sample are considered to be in “non-contact”

![Figure 25](image)

Contact mode is heavily influenced by frictional and adhesive forces and can damage samples and distort image data. Non-contact imaging generally provides low resolution and can also be hampered by contamination and by layer interference with oscillation. Non-contact imaging is the most suitable for polymers and soft matter as damaging the sample is a greater concern than the image resolution. (18)

The AFM used was the PSIA XE.100 Advanced Scanning Probe Microscope using NSG 10 probe tips. The software used was the XE Data acquisition Program and XEI Data imaging program for the 2D images. For the 3D images the software Gwyddion was used as it produced better 3D images than the XEI data imaging program.

The AFM was set to non-contact scans, each scan was 40-40μm with a lateral resolution of 15Å and a vertical resolution of 0.25Å , with a drive of 100kHz provided by a piezoelectric resonator, the Z gain piezoelectric was set at 10v to apply constant cantilever deflection. This produced images of 256 – 256 pixels, which combined with the Z data produced 3D images.
For each sample they were attached to a metal base plate and put inside the AFM sample holder, the scanning tip was lowered automatically by the software until it was in range to begin scanning, which was then started and each scan took approximately 40 minutes.

The parameters used where found in the preliminary results to give the best AFM images and data, other set ups of a smaller scan size, such as 10-10μm where tested, however at these ranges more noise seemed to be present and the structures being studied could be interpreted as random noise rather than evidence of phase separation or other sub-micron structures.

As an example as what shall be looked for in the AFM images the images taken in the preliminary results shall be shown:

Figure 26 an example of PCBM-F8TBT with the 2D image on the left (A) and the 3D image on the right (B), this sample has a root mean square roughness of 72.80nm

The samples both show the “coffee-stain” like structure expected in this process and the roughness of the sample is 72.80nm. The roughness of the sample is measured in Roughness Root Mean Squared (RMS); this is the averaged height profile deviations from the calculated mean line. The lower the RMS roughness the smoother the surface, for example polished metal has an RMS of 5nm.

The small lines present in this example show possible evidence of microstructures present. This potentially shows the blend has sub-micron phase separation.

Bibliography

Morphological Results

The morphology of thin film organic transistors and other optoelectronics, such as solar cells, is strongly dependent on various parameters such as individual solubility of each of the polymers in the solvent, the interaction with the substrate surface, the layer thickness, the drying processes and the deposition method.

The morphology of each the blends has been attempted to be modified by two different annealing processes, either by thermally annealing or by solvent vapour annealing. Thermal annealing effectively “melts” the polymers giving them more chain mobility, leading to greater phase separation, this process also causes a “melt flow” of the material evening out the peaks and valleys present on the film. Solvent annealing effectively increases the drying time, dissolving the polymers giving them more chain mobility, leading to greater phase separation (1). This phase separation happens at the sub-micron level, usually showing at the <10nm, however any evidence of phase separation at a macroscopic level shall be commented on. Phase separation is directly linked to photoluminescence quenching efficiency so this will become more obvious in the Optical Properties results and discussion.

In the Optical Microscope results images shall be shown and discussed. For each sample the overall uniformity of the samples will be discussed. As the samples are spray coated, not spun, the structure of the sample will be of similar sized “coffee stain” like structures, often between 50-10μm in length, caused when the spray coated solution dried (2). This “coffee stain” structure comprises of higher walls surrounding a thinner base layer. As the uniform morphology of the substrates is important for device integration, a process that decreases the height of the walls or increases the thin base area creating a more uniform surface is preferable. These coffee stain structures occur at the micron level and therefore the change in their structure has very little if any influence on the phase separation present in the sample as well.

Other elements that shall be commented on will be any evidence of the compounds of the blend not clearly integrated into the thin film itself more on top of the film. This will be evidence of potentially the compound not dissolving entirely into the solvent itself or becoming separated from the solvent in the spray coating process. (3)

In the Atomic Force Microscopy (AFM) results images will be presented in both the 2D and 3D. The roughness of samples before and after the annealing process shall also be discussed. Whilst there is potential for sample bias when analysing the samples under AFM, each of the sample sites chosen where ones that best demonstrated the overall morphology of the sample so as to give the most accurate roughness and AFM imaging possible. The roughness of the sample will be measured in Roughness Root Mean Squared (RMS); this is the averaged height profile deviations from the calculated mean line. Any signs of microstructure phase separation present in the sample shall be discussed.
Optical Microscope Results

The first set of samples to be looked at will be PCBM-P3HT.

Magnification x10

“As Made”

Thermal Annealed

Solvent Annealed

Magnification x40

“As Made”

Thermal Annealed

Solvent Annealed

Figure 27 as can be seen the thermally annealed sample has made the “coffee stains” less distinct than the “As made” samples indicating a greater planarity of the sample; however the solvent annealed samples show far more distinct “coffee stains”, showing a possible increase in roughness of the sample.

All the samples show no signs of macroscopic phase separation. Each of the crater shapes fall into two categories, either they are relatively large, ranging in size from 30-40μm, when compared to the other shapes and distended out of the “coffee stain” shape expected, or are of a similar smaller size ranging in size from 5-20μm and in the “coffee stain” shape.

The larger distended “coffee stains” indicate that whilst mostly uniform spray coating, there were the occasional slightly larger droplets that caused these larger structures. The reason for them being not of the expected “coffee stain” shape is possibly due to a slightly longer drying process allowing the droplet to relax from the crater shape before drying. The samples also show a layering effect from the spray coating process, with a number of “coffee stain” structures clearly on top of other coffee stain structures.

There appears to be little difference between the “as made” samples and the thermally annealed samples from these microscope images. However the solvent annealed samples appear to have reinforced the walls of the coffee-stain structures and also created a rainbow effect on the images, possibly due to thin film interference. This may infer a thickening of the base area of the “coffee stain” structures as the rainbow effect is strongest in areas surrounded by walls.
The next set of samples will be F8TBT-PCBM.

**Magnification x10**

![Image of magnification x10 samples](image)

“As Made”  
Thermal Annealed  
Solvent Annealed

**Magnification x40**

![Image of magnification x40 samples](image)

“As Made”  
Thermal Annealed  
Solvent Annealed

Figure 28 as can be seen with the thermally annealed sample shows that the structure of the “coffee stains” appears to have become less distinct than the “as made” samples, the solvent annealed samples seem to have reinforced the structures.

At greater magnification however there appears to be very little difference between the different annealing and “as made “samples. In the “as made” samples and thermally annealed samples there appear to be black dots present on an overall uniform substrate. Given that in the solvent annealed samples these black dots do not appear it would imply that these are small amounts of an undissolved polymer lying on the surface of the substrate that the solvent annealing process dissolves back into the uniform substrate.

The crater structures are much larger than in the previous sample (40-50μm), yet more circular; implying that though the droplets may have been bigger than the previous samples the drying time was similar across all the droplet sizes. Also it can be seen whilst the majority of the droplets appear to be relatively large there are still some smaller droplets still present, showing that the spray was mostly large droplets interspersed with smaller ones. The samples also show a layering effect from the spray coating process, with a number of “coffee stain” like structures clearly on top of other coffee stain structures.
The final set of samples that shall be discussed will be the P3HT-F8TBT.

**Magnification x10**

![Image](image1.jpg)

- “As Made”
- Thermal Annealed
- Solvent Annealed

**Magnification x40**

![Image](image2.jpg)

- “As Made”
- Thermal Annealed
- Solvent Annealed

Figure 29 as can be seen both the thermal and solvent annealed have far less distinct “coffee stain” structures than the “as made” samples. The solvent annealed samples seem to show some lines of structure at 40x magnification.

All of the samples show a mostly uniform structure with clear some kind of macroscopic phase separation indicated by the black spots on all of the samples. This could be evidence of P3HT crystals present on the substrate, or like in the previous example of F8TBT-PCBM, an amount of un-dissolved polymer on the substrate. This however is unlikely as the solvent annealed sample still has evidence of these black spots.

In both annealed samples there appear to be fewer black spots, implying that both annealing processes incorporated the separated compound back into the sample. In all of the samples at the higher magnification show several areas of a rainbow effect, possibly due to thin film interference. This may once again indicate thickening of the base of the “coffee stain” structure.

These samples show the smallest crater size observed (5-10μm) so far, even the larger craters are still much smaller than the previous two samples and much more uniformly circular. This implies a very fine spray with the occasional larger drop; these larger drops are what possibly cause the black spots to appear.

The solvent annealed sample is very interesting showing a breaking down of the crater structures and an almost lining up of the sample; this may be due to possible microstructure present causing the lining up of the samples.

The microscope images show that in general the “coffee stain” structures seem to be less defined in the thermally annealed samples, implying greater planarity. Whereas most solvent annealed samples show a more defined “coffee stain” structure, implying greater roughness. The size of the “coffee stain” structures range from 5-50μm. For further discussion of the morphology of the samples AFM of each of the sample shall now be discussed.
Atomic Force Microscopy Results

The first set of samples to be discussed will be PCBM-P3HT.

As Made

Roughness (Root Mean Squared): 92.10±2.00 nm

Thermally Annealed

Roughness (Root Mean Squared): 50.74±1.12 nm

Solvent Annealed

Roughness (Root Mean Squared): 84.87±1.88 nm

Figure 30: The thermally annealed samples show the greatest reduction in roughness. There appear to be lines of microstructures on the surface of both the “as made” and the solvent annealed samples. This may indicate greater phase separation at the sub-micron level.
The next set to be discussed will be the F8TBT – PCBM.

Table:

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Roughness (Root Mean Squared)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As Made</td>
<td>39.01 ± 0.86 nm</td>
</tr>
<tr>
<td>Thermally Annealed</td>
<td>34.00 ± 0.75 nm</td>
</tr>
<tr>
<td>Solvent Annealed</td>
<td>53.00 ± 1.17 nm</td>
</tr>
</tbody>
</table>

Figure 31 the thermally annealed samples show the greatest reduction in roughness. The solvent samples have a roughness greater than the “as made” samples; this added roughness is possibly due to the greater height of the walls in the solvent annealed sample.
The final set of data that shall be discussed will be the P3HT-F8TBT.

As Made

**Roughness (Root Mean Squared):** 43.20±0.95nm

Thermally Annealed

**Roughness (Root Mean Squared):** 28.10±0.62nm

Solvent Annealed

**Roughness (Root Mean Squared):** 41.00±0.91nm

Figure 32 once again this shows the thermal annealing gives the greatest reduction in roughness of the sample. Both the "as made" samples and solvent annealed samples show evidence of the structures lining up not present in the thermally annealed sample, this may indicate greater phase separation as the two blends may be the cause of the lining up.
Here are the table of results for the RMS roughness of each sample:

<table>
<thead>
<tr>
<th></th>
<th>As Made Samples</th>
<th>Thermally Annealed</th>
<th>Solvent Annealed</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCBM-P3HT</td>
<td>92.10±2.03nm</td>
<td>50.74±1.21nm</td>
<td>84.87±1.88nm</td>
</tr>
<tr>
<td>F8TBT-PCBM</td>
<td>39.01±0.86nm</td>
<td>34.00±0.75nm</td>
<td>53.00±1.17nm</td>
</tr>
<tr>
<td>P3HT-F8TBT</td>
<td>43.20±0.95nm</td>
<td>28.04±0.62nm</td>
<td>41.00±0.91nm</td>
</tr>
</tbody>
</table>

Table 1 this table shows the roughness of each of the samples and annealing processes.

The table shows that the PCBM-P3HT produced the roughest samples by far, nearly twice as rough as the other samples studied. It also shows that thermal annealing produced the greatest reduction in roughness when compared to the solvent annealing process with the greatest reduction from the PCBM-P3HT, reducing the roughness by almost half. The solvent annealing process in most samples did very little to reduce the roughness but in the case of F8TBT-PCBM it in fact increased the roughness of the sample by 14nm.

The phase separation that was expected to be seen by the AFM, must be taking place at a sub-micron level as there is little to no evidence of it at these scales. The phase separation may be implied by the photoluminescence quenching efficiency of the blends as these two elements are closely tied.

In Figure 26 there appears to be a lining up of the sample at a submicron level, this could be for any number of reason, such as polymer chains aligning themselves together, indications of the P3HT crystalline growth, however without a further magnification of these interest areas there is little that can be discussed with any certainty.

<table>
<thead>
<tr>
<th></th>
<th>As Made Samples</th>
<th>Thermally Annealed</th>
<th>Solvent Annealed</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCBM-P3HT</td>
<td>2.50nm (4)</td>
<td>28.50nm(4)</td>
<td>5.0nm (5)</td>
</tr>
<tr>
<td>F8TBT-PCBM</td>
<td>0.40nm (6)</td>
<td>10.03nm(7)</td>
<td>2.0nm(6)</td>
</tr>
<tr>
<td>P3HT-F8TBT</td>
<td>0.9nm (8)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 2 Showing the RMS roughness of spin coated samples from the literature

Obviously when comparing spin coated samples to spray coated samples the spin coated samples will be have a lower RMS Roughness as the spin coating process will not produce the “coffee-stain” structures discussed for spray coated samples.

However the thermally annealed literature samples do approach the same range as the spray coated samples, indicating that the spray coated samples still have potential in creating working photovoltaic devices. Whilst vastly different in scale the literature broadly demonstrates what has been observed in the spray coated samples, PCBM-P3HT are the roughest as made samples, with P3HT-F8TBT being the next roughest and the F8TBT-PCBM being the least roughest.

Interestingly the roughness of samples in the literature increases with either annealing process, most of the literature put this down to either P3HT crystalline formations, or to the increasing phase separation causes the increase in roughness. For P3HT-F8TBT there does not appear to be any established results for the roughness of thermally annealed or solvent annealed P3HT-F8TBT.

In the Spray coated samples it was shown that the roughness generally decreased with each of the annealing processes, this is because of the breaking down of the macro-scale “coffee-stain” like structures, the process causing this loss of roughness will be the material itself melting, levelling out the hills and valleys present in the thin film itself as opposed to the phase separation becoming less.
This is because the scales that are being worked on, if the sample is down to ≈1nm of RMS roughness any increased phase separation will drastically affecting the RMS roughness. As the spray coated samples have RMS roughness’s ≈40nm the increased phase separation will be felt less than the decrease in the larger macro-structures decreasing the roughness.

Bibliography
Optical Properties Results and Discussion

As Made Results

Absorption Spectroscopy

The first section of this shall be looking at the optical properties of each of the blended samples. Each of the graphs will show one of the blended samples with another of the pristine samples which is the donor of the blended sample as a point of reference.

Graph 3 shows F8TBT-PCBM compared to the pristine sample of F8TBT, giving an overall absorbance factor of 0.80±0.028.

Graph 2 shows the absorbance spectroscopy of PCBM-P3HT compared to that of P3HT, giving an absorbance factor of 0.28±0.013.

Graph 1 shows P3HT-F8TBT compared to the pristine sample of F8TBT, giving an overall absorbance factor of 0.72±0.023. These graphs are so similar because the P3HT has little effect on the overall absorption profile, only increasing the height of the second feature.
Fluorescence Spectroscopy

For each blend both the fluorescence of the 473nm (blue) and 532nm (green) laser shall be shown

Graph 4 shows PCBM-P3HT when excited with the blue laser giving an emission of 0.95±0.040

Graph 5 shows the fluorescence of the P3HT-PCBM compared to P3HT when excited by the green laser giving an emission of 0.69±0.021

Graph 6 shows the fluorescence of P3HT-F8TBT compared to F8TBT when excited by the blue laser showing an emission of 0.71±0.022%

Graph 7 shows the fluorescence of P3HT-F8TBT compared to F8TBT when excited by the green laser giving an emission of 0.70±0.022

Graph 8 shows the fluorescence of F8TBT-PCBM compared to F8TBT when excited by the blue laser showing an emission of 0.065±0.00019

Graph 9 shows the fluorescence of P3HT-F8TBT compared to F8TBT when excited by the green laser giving an emission of 0.036±0.0001

As can be seen on each of the graphs on the left give far noisier data when compared to the graphs on the right, this is due to a weaker response to the excitation of the blue laser when compared to the green laser however the integration time was kept the same to keep consistency of measurements.
Photoluminescence Quenching

Using the data collected from the absorbance spectroscopy and from the fluorescence spectroscopy, the photoluminescence (PL) quenching efficiency can be found using equation 10 from the Theory and Methodology section, shown below:

\[
\text{Photoluminescence Quenching} = 1 - \frac{A_P}{A_B} \times \frac{I_B}{I_P}
\]

Equation 140 were B is blended sample, P is pristine sample, I is intensity of emission, and A is the intensity of absorption.

For each blend, the PL quenching efficiency shall be found for both the green and blue lasers, PL quenching efficiency found for both, then averaged to give an overall PL quenching efficiency for each blend.

<table>
<thead>
<tr>
<th>Blend</th>
<th>Wavelength of Excitation</th>
<th>Photoluminescence Quenching</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCBPM-P3HT</td>
<td>473nm</td>
<td>0.73±0.053</td>
</tr>
<tr>
<td></td>
<td>532nm</td>
<td>0.81±0.034</td>
</tr>
<tr>
<td>P3HT-F8TBT</td>
<td>473nm</td>
<td>0.49±0.045</td>
</tr>
<tr>
<td></td>
<td>532nm</td>
<td>0.50±0.045</td>
</tr>
<tr>
<td>F8TBT-PCBM</td>
<td>473nm</td>
<td>0.95±0.028</td>
</tr>
<tr>
<td></td>
<td>532nm</td>
<td>0.97±0.028</td>
</tr>
</tbody>
</table>

Table 3 shows the photoluminescence quenching of all the blends at the different wavelengths of excitations. As the table shows, PCBPM-P3HT gives an overall average PL quenching efficiency of 0.77±0.087, P3HT-F8TBT gives an overall average PL quenching efficiency of 0.49±0.09 and finally F8TBT-PCBM gives an overall average PL quenching efficiency of 0.96±0.058 all these averages are the PL quenching efficiency the post production processes will be compared to.

Overall the efficiencies obtained using the blue laser excitation shows the blends performing 2.5% less quenching efficient when compared to the green laser excitation. This indicates that either there is a systematic error creating the difference or, whilst unlikely, the blue and green lasers excite different components of the blend causing the difference.

<table>
<thead>
<tr>
<th>Blend</th>
<th>Photoluminescence Quenching</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCBPM-P3HT</td>
<td>0.80(1)</td>
</tr>
<tr>
<td>P3HT-F8TBT</td>
<td>0.83 (2)</td>
</tr>
<tr>
<td>F8TBT-PCBM</td>
<td>0.90 (3)</td>
</tr>
</tbody>
</table>

Table 4 shows the photoluminescence of each of the spin coated blends found in the literature. When comparing the results found to the results found in the literature the PCBPM-P3HT and F8TBT-PCBM blends compare well with the established literature results being within 10% of the published figures.

The P3HT-F8TBT however is significantly less than the established figures, nearly 40% less than the established figures. This may be due to the figures found in the literature are found using finely tuned spin coating which seem to lead to higher Photoluminescence quenching efficiency.
Annealed Results and Discussion

In this section each of the method annealed samples shall be analysed and then the Photoluminescence (PL) quenching efficiency shall be compared against one another and the “As made” samples.

Absorption Spectroscopy

For this first section the absorption spectrum of each of the annealed samples will be studied, for each blend the thermal annealed samples shall be compared and contrasted against the solvent annealed samples.

The absorption of both thermal and solvent annealed PCBM-P3HT shall first be discussed:

Graph 10 is thermally annealed PCBM-P3HT which has an absorption factor of 0.48±0.011

Graph 11 is solvent annealed PCBM-P3HT which has an absorption factor of 0.20±0.004

The next set of graphs is both the thermal and solvent annealed P3HT-F8TBT:

Graph 12 is the thermally annealed P3HT-F8TBT giving an absorbance factor of 0.98±0.022

Graph 13 shows the solvent annealed P3HT-F8TBT giving an absorbance factor of 0.63±0.014.

The final set of absorption graphs are that of both thermally and solvent annealed F8TBT-PCBM:

Graph 14 shows the thermally annealed F8TBT-PCBM giving an absorption factor of 0.85±0.019

Graph 15 shows the solvent annealed F8TBT-PCBM giving an absorption factor of 0.76±0.017
Fluorescence Spectroscopy

For each blend both the fluorescence of the 473nm (blue) and 532nm (green) laser shall be shown, the first set of graphs of fluorescence is the thermally annealed PCBM-P3HT.

Graph 16 is the fluorescence after excitation of the blue laser giving an emission factor of $0.52 \pm 0.011$

Graph 17 shows the fluorescence of the green laser excitation giving an emission factor of $0.30 \pm 0.007$

The next sets of graphs show PCBM-P3HT after solvent annealing.

Graph 18 shows the fluorescence of the blue excitation, giving an emission factor of $0.80 \pm 0.018$

Graph 19 left shows the fluorescence of the green excitation, giving an emission factor of $0.40 \pm 0.009$

These graphs show that solvent annealing increases the emission factor of the blend.

The next sets of graphs relate to annealed P3HT-F8TBT starting with the thermally annealed samples.

Graph 20 shows the excitation after the blue laser, giving an emission factor of $0.35 \pm 0.008$

Graph 21 shows the excitation after the green laser giving an emission factor of $0.41 \pm 0.009$
Optical Properties Results and Discussion

The graphs below show solvent annealed P3HT-F8TBT:

Graph 22 shows the emission after the blue laser giving an emission factor of 0.55±0.012.
Graph 23 shows the emission after the green laser giving an emission factor of 0.51±0.011.
Once again the graphs show that solvent annealing increases the emission factor in both the blue and green lasers.

The final sets of graphs relate to annealed F8TBT-PCBM, starting with the thermal annealed samples:

Graph 24 shows emission of the blue laser giving an emission factor of 0.054±0.0011.
Graph 25 shows the emission of the green laser giving an emission factor of 0.050±0.0011.
The final set of graphs show the F8TBT-PCBM after the solvent annealing process:

Graph 26 shows emission of the blue laser giving an emission factor of 0.062±0.0014.
Graph 27 shows the emission of the green laser giving an emission factor of 0.048±0.0011.
These graphs also show that either of the annealing processes did very little difference compared to one another.
Photoluminescence Quenching

Using the data collected from the absorbance spectroscopy and from the fluorescence spectroscopy the photoluminescence (PL) quenching is found using equation 10. For each of the blends annealing processes the PL quenching efficiency shall be found for both the green and blue lasers, and then averaged to give an overall PL quenching efficiency for each method.

Then these efficiencies shall be compared to the “as made” PL quenching efficiencies to see what effect the different types of annealing had on each blend.

<table>
<thead>
<tr>
<th>Blend</th>
<th>Annealing Processes</th>
<th>Wavelength Excitation</th>
<th>Photoluminescence Quenching</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCBM-P3HT</td>
<td>Thermal</td>
<td>473nm</td>
<td>0.75±0.022</td>
</tr>
<tr>
<td></td>
<td></td>
<td>532nm</td>
<td>0.85±0.018</td>
</tr>
<tr>
<td></td>
<td>Solvent</td>
<td>473nm</td>
<td>0.84±0.022</td>
</tr>
<tr>
<td></td>
<td></td>
<td>532nm</td>
<td>0.92±0.013</td>
</tr>
<tr>
<td>P3HT-F8TBT</td>
<td>Thermal</td>
<td>473nm</td>
<td>0.66±0.030</td>
</tr>
<tr>
<td></td>
<td></td>
<td>532nm</td>
<td>0.60±0.031</td>
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<tr>
<td></td>
<td>Solvent</td>
<td>473nm</td>
<td>0.66±0.026</td>
</tr>
<tr>
<td></td>
<td></td>
<td>532nm</td>
<td>0.68±0.025</td>
</tr>
<tr>
<td>F8TBT-PCBM</td>
<td>Thermal</td>
<td>473nm</td>
<td>0.96±0.015</td>
</tr>
<tr>
<td></td>
<td></td>
<td>532nm</td>
<td>0.96±0.015</td>
</tr>
<tr>
<td></td>
<td>Solvent</td>
<td>473nm</td>
<td>0.95±0.018</td>
</tr>
<tr>
<td></td>
<td></td>
<td>532nm</td>
<td>0.96±0.018</td>
</tr>
</tbody>
</table>

Table 5 shows the photoluminescence quenching of all the blends and different annealing processes at the different wavelengths of excitations.

Next the average annealed PL quenching efficiencies will be compared to the “as made” average PL quenching efficiencies.

<table>
<thead>
<tr>
<th>Blend</th>
<th>Annealing Process</th>
<th>Photoluminescence Quench</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCBM-P3HT</td>
<td>As Made</td>
<td>0.77±0.087</td>
</tr>
<tr>
<td></td>
<td>Thermal</td>
<td>0.80±0.040</td>
</tr>
<tr>
<td></td>
<td>Solvent</td>
<td>0.88±0.035</td>
</tr>
<tr>
<td>P3HT-F8TBT</td>
<td>As Made</td>
<td>0.49±0.090</td>
</tr>
<tr>
<td></td>
<td>Thermal</td>
<td>0.63±0.061</td>
</tr>
<tr>
<td></td>
<td>Solvent</td>
<td>0.67±0.051</td>
</tr>
<tr>
<td>F8TBT-PCBM</td>
<td>As Made</td>
<td>0.96±0.058</td>
</tr>
<tr>
<td></td>
<td>Thermal</td>
<td>0.96±0.03</td>
</tr>
<tr>
<td></td>
<td>Solvent</td>
<td>0.96±0.04</td>
</tr>
</tbody>
</table>

Table 6 shows the average photoluminescence quenching of all the blends comparing the “as made” blends to the different annealing processes.

For PCBM-P3HT, both methods of annealing improved the PL quenching efficiency; however the solvent annealing substantially increased the PL quenching efficiency by 11.02% when compared to the thermal annealing that only increased the PL quenching efficiency by 3.26%.

It could be implied that while the solvent annealing process was selected correctly for improving phase separation, the thermal annealing process was not as optimal and perhaps could be modified future work. (4)

For P3HT-F8TBT, both methods of annealing improved the PL quenching efficiency quite substantially with an increase of more than 10% for both methods, however solvent annealing shows the better results with an increase of 17.47% compared to the increase of 13.47% of the thermal annealing. Both these blends the increased PL quenching efficiency this could indicate a
greater phase separation of the individual components of the blends at a sub-micron level, as phase separation and PL quenching efficiency are closely linked. (5)

For F8TBT-PCBM, both methods of annealing had little to no effect on the PL quenching efficiency of the F8TBT-PCBM either increasing or decreasing the quench by ≈0.3%. Basically meaning both methods left the PL quenching efficiency unchanged. However this blend produced the most efficient pristine PL quenching of the blends tested. This would imply that at a sub-micron level this blend must have already been phase separated, so much so that the annealing processes did very little to improve the PL quenching efficiency and therefore the phase separation. (6)

<table>
<thead>
<tr>
<th>Blends</th>
<th>Annealing Process</th>
<th>PL Quenching</th>
<th>Percentage difference when compared to pristine</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCBM-P3HT</td>
<td>Thermal</td>
<td>0.81(1)</td>
<td>+10%</td>
</tr>
<tr>
<td></td>
<td>Solvent</td>
<td>0.74 (7)</td>
<td>+20%</td>
</tr>
<tr>
<td>P3HT-F8TBT</td>
<td>Thermal</td>
<td>0.46 (2)</td>
<td>-40%</td>
</tr>
<tr>
<td></td>
<td>Solvent</td>
<td>0.63 (2)</td>
<td>-20%</td>
</tr>
<tr>
<td>F8TBT-PCBM</td>
<td>Thermal</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>Solvent</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 7 a table showing the established figures for solvent and thermal annealing the various blends

When compared to the established figures for solvent and thermal annealing PCBM-P3HT results match closely to the established figures, with both the PL Quenching and the increase compared to the pristine blend.

The PL Quenching for both thermal and solvent annealing are within 10% of established figures and the percentage increase are similar too. The thermal annealing increased the efficiency less than the solvent annealing and the percentage increased by both methods are similar to the increases found in the results. When compared to the established figures there is a different story for the P3HT-F8TBT, whilst the PL Quenching of the results quite closely match the figures found in the literature especially the solvent annealing than came within 4% of the literature numbers, the percentage differences are almost the exact opposite.

Whilst in the literature both forms of annealing decreased the Photoluminescence Quenching when compared to the pristine blend, in the results discussed both methods increased the photoluminescence quenching when compared to the pristine blend. This could be for a number of reasons, potentially both methods of annealing have an upper limit that it can improve the phase separation of the blend to and potentially spin coated samples have a higher phase separation at the outset and therefore the phase separation must decrease, whilst spray coated samples a have a lower phase separation and the annealing processes increase the phase separation to this limit.

And finally the F8TBT-PCBM has no established figures for effects of either solvent annealing or thermal annealing, as the results show this could because the photoluminescence quenching of the F8TBT-PCBM blend is unaffected by either method of annealing leading to the lack of figures present in the literature.

**Bibliography**
Conclusion and Future Work

In conclusion the results show that a method for uniformly spray coating each of the different families of organic semiconducting compounds has been found. The described spray coating technique described in the Theory and Methodology section found in the literature worked well for all types of polymers and semiconducting compounds tested.

The films themselves are continuous films of dried droplet structures, ranging in size between 5-50μm, the AFM shows that these structures are “coffee-stain” like with higher walls and flatter more uniform centres. There is no clear evidence of macro-scale phase separation, however the range in height from the walls to the centres appear to be slightly higher than 100nm which is problematic for the usual engineering tolerances of 100nm found in thin film organic transistors, organic solar cells are most relevant here due to their planar structure. (1)(2)

It has been shown that aside from the F8TBT-PCBM samples that both photoluminescence quenching and root mean squared roughness have been improved by both annealing processes. Photoluminescence quenching efficiency increased with both of the annealing processes, with increases of on average of 11.31% overall. However the greatest increase of photoluminescence quenching came from the solvent annealing process, giving an average increase of 14.25%, 3% greater than the overall average and 5.89% greater than the thermally annealed samples.

It has also been shown that the root means squared roughness of each of the samples were decreased by both of the annealing processes, with an average decrease in roughness of 15.24nm overall. The process that reduced the root means squared roughness most effectively is the thermally annealed samples, giving an average decrease of 28.26nm, 85% more reduction in roughness than the global average and significantly more than the reduction in roughness from the solvent annealing process, which on average reduced roughness by 2.2nm.

In both cases the general results have not been applicable to the F8TBT-PCBM; in the case of photoluminescence quenching may just be because the “as made” samples were more than 90% quenching before either annealing process, meaning that any improvements would be negligible.
compared to the “as made” samples. Similarly in the case of the root mean squared roughness it was the lowest roughness of the “as made” samples, so the annealing processes could only marginally improve the surface and in the case of solvent annealing it actually increased the roughness by 13.99nm. This implies either that the annealing processes used were not optimal for F8TBT-PCBM or that there is a limit on how much the annealing processes can improve an already photoluminescence quenching efficient and smooth surface.

However this also shows the one of the first attempts at either solvent annealing or thermally annealing F8TBT-PCBM, though neither used seemed to affect the Photoluminescence quenching of the blend the thermal annealing did reduce the roughness of the surface. This means that potentially the F8TBT-PCBM blend could be the primary blend for spray coating solar cells in the near future.

Future work would be using the results found by this project to build organic solar cells using the same construction methods used in this project. As the construction and annealing processes shown in this project show a high photoluminescence quenching efficiency and good planarity which show promise for organic solar cells.

Other future work that could be conducted would be to investigate the micro-scale structures potentially shown in the AFM results, one of the ways this could be done is through an AFM set up and configured with different parameters needed for sub micron work focused in on the areas of interest. This could also be conducted through a structural study by X-Ray scattering. (3)

Other methods of annealing would also have been tried, including varying the temperature and time of the thermal annealing, for example the literature indicates that 80°C for an hour and a half would also have worked well with the blends used (4). Using different solvents and times for solvent annealing would have been done; the literature suggested several solvents for example using Di-Chlorobenzene for half an hour also works for the blends used (5). This would work towards finding a more optimal annealing process for all semiconducting organic polymer families.

Similarly this project was working on glass substrates, further work would be exploring deposition on other substrates, such as diamond, ITO substrates commonly used in organic solar cells or oxides such as titanium oxide commonly used in inverted organic solar cell construction. This work would also have to explore whether the solvents used are affected by the substrate being used as the inherent wet-ability of the different substrates.

Further applications of this project include building-integrated photovoltaics; this is the process of replacing elements in buildings with photovoltaic materials, often windows or pieces of roofing. This is often achieved with thin film organic solar cells. (6) However this is currently achieved using the spin coating method, spray coating would be a much more efficient use of materials and be much easier to up-scale potentially.

There may be further challenges in up-scaling with the spray coating process, as current literature and this project only focuses on with making relatively small sized samples. The issues with distance and solvent compatibility have yet to be resolved.
Bibliography


Acknowledgements

The author would like to acknowledge Dr. Chris Finlayson for all his help and patience, Nathan Davies for his help with the AFM and the technicians of the Aberystwyth University Institute of Maths and Physics for their help constructing sample holders, David Lewis especially.

The author would also like to acknowledge Sigma Aldrich and the Melville Laboratory, Cambridge for the supply of materials used in this work, and Scanwel Ltd for technical support with AFM measurements. This work is supported by a *University Research Fund* (URF) award from Aberystwyth University.