



The  
University  
Of  
Sheffield.



# E-Futures

**Mini-project report**

**Organic Photovoltaics**

**Rob Raine – [dtp11rdr@sheffield.ac.uk](mailto:dtp11rdr@sheffield.ac.uk)**

**10/2/2012**



The  
University  
Of  
Sheffield.



## ASSIGNMENT COVER SHEET 2010/2011

A completed copy of this sheet **MUST** be attached to coursework contributing towards theme 2 assessment.

<b>Name :</b>	Rob Raine
<b>Degree Course:</b>	<b>E-Futures DTC</b>
<b>Supervisor:</b>	<b>Prof. David Lidzey</b>
<b>Signature:</b>	R D Raine

I declare that this work is my own and that I have made appropriate reference to any sources used. I am aware of the handbook section on 'Plagiarism' and declare that this work is consistent with those guidelines.

## Mini-Project Mark Sheet

**Student:**

**Grade:** fail/satisfactory/good/very-good/excellent

**Supervisor:**

**Feedback:**

	Excellent	Good	Average	Poor	Very Poor	Not Done	Not applicable
Introduction to the problem / subject							
Statement of aims							
Experimental description							
Presentation of results / findings							
Quality and depth of discussion / interpretation							
Relevance of conclusions							
Quality of English							
Use of reference material							
Evidence of external reading							
Quality of presentation							
Use of figures							

**Comments:**

# Organic Photovoltaics

Robert Raine, dtp11rdr@shef.ac.uk

Energy Futures Mini-Project

December 2011-February 2012

Supervised by Prof. David Lidzey,

Department of Physics,

University of Sheffield.



E-Futures



## Abstract

The main aim of this project was to familiarise myself with techniques for creating organic, polymer-based photovoltaic test devices and to find their efficiency. A further aim was to vary aspects of our method to achieve better results for the specific sample of polymer material we were given. In our experiments, we produced devices that were up to 5.6% efficient at converting sunlight energy to electrical energy.

**Introduction** Conventionally, solar power is generated in devices containing semiconductor crystals. The energy gap between electrons held fixed in the crystal structure and those that are free to move allows energy to be captured when electrons move between these states. There are now efforts to use similar energy gaps in polymer molecules to capture solar energy.

In these new polymer solar cells, unlike what is generally seen in semiconductor examples, after excitation by light the negatively charged electron and the positively charged vacant location (the 'hole') often remain in a bound state called an 'exciton'. This exciton state has greater energy than the ground state and separation of the charges in this state is the basis of electricity production. The energy is lost if the opposite charges in the exciton recombine and emit a photon of light; this outcome is of no use for generating electricity.

Electron acceptor and electron donor molecules are chosen so that when an exciton diffuses to an interface of the materials, electrons are transferred and the exciton is permanently separated. One material in the device is chosen to have a high electron affinity in order to help charge separation, usually a fullerene; the other material is usually a polymer with good light absorbing properties as it is easy for charges to move along the

long polymer chains. At the interface of these materials, excitons are separated and the component charges move through the separate phases to the electrodes where they are extracted from the device and result in an electric current in the external circuit. A good summary of the technology is found in (Frechet et al)<sup>1</sup>

In this study the electron donor is a polymer called PCDTBT\* and the electron acceptor is a fullerene called PC<sub>70</sub>BM<sup>†</sup>. The molecular structures appear in Figures 1 and 2.

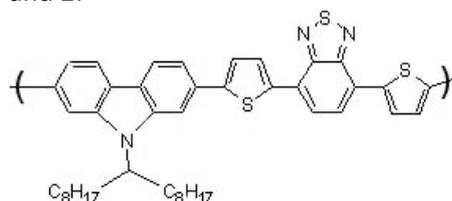


Figure 1 Chemical structure of PCDTBT monomer, Ossila.com<sup>2</sup>

The polymer sample we were given came directly from the polymerisation process and is called 'crude', it contains a large range of polymer lengths. Usually this mixture is washed in various solvents and these each pick up a range of polymer lengths. For example, washing with dichlorobenzene dissolves longer polymers than washing with chlorobenzene solvent<sup>1</sup>.

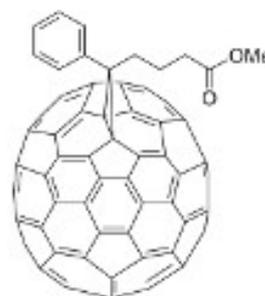


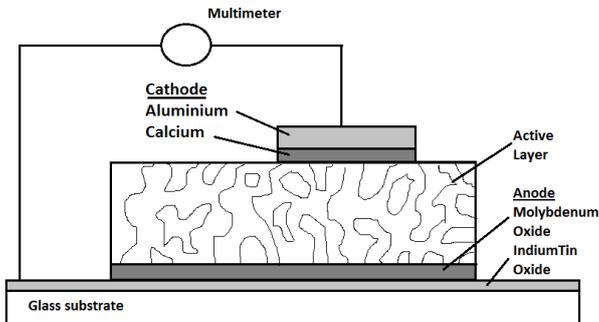
Figure 2 Chemical structure of PC(70)BM, Ossila.com<sup>3</sup>

\* PCDTBT is poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)]

<sup>†</sup> PCBM is [6,6]-phenyl-C71-butyric acid methyl ester

## Method

The photovoltaic test devices consist of a series of layers that are added during fabrication. The substrate is a glass slide which has partial covering with transparent semiconductor indium tin oxide (ITO). This covering allows electrical connection from the pixels in the middle of the device, where the separated charges are generated, to the edges of the device where the electrodes are attached. The layered structure is shown in Figure 3.



**Figure 3** Structure of the bulk heterojunction cell, light enters into the active layer after traversing the glass substrate and ITO.

For deposition of the active layer on the device, the polymer donor is dissolved in solvent and mixed well with the PCBM acceptor; a hotplate and magnetic stir-bar were used to aid this process. In our polymer sample there is a wide range of polymer lengths and the longer chains are less soluble. The solution is put through a filter before use in order to remove undissolved particulates that would affect the microstructure of the device active layer.

The active layer is deposited by a process called 'spin coating'. In this process, the active solution is dropped onto a spinning glass substrate and the rotation causes the droplet to spread out into a thin layer. The spin speed can be varied and this alters the layer thickness.

The other layers in the devices are made from metal or metal oxides. These coatings are added by heating the material and causing it to evaporate inside a vacuum chamber and allowing the vapour to settle onto the device surface.

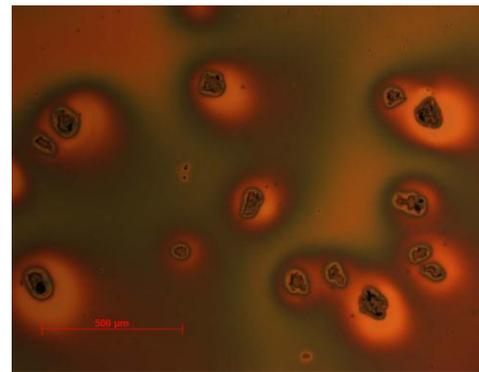
The layers are susceptible to degradation in air and in the presence of moisture and so the devices are fabricated in a dry nitrogen atmosphere inside a glovebox and sealed using a glass cover slip secured with epoxy resin before it leaves the glovebox.

Metal electrodes are added so that the devices can be connected to a circuit board for electrical testing. A

solar simulator lamp is used to provide a known intensity of light and the electrical power output then tells us how efficient the photovoltaic device is. A multimeter measures the current derived at different levels of bias voltage across the device. The voltage varies from -1 to +1 and the point where  $V=0$  is known as the 'short circuit' point and the point where the curve passes  $I=0$  is known as the 'open circuit' point. The values of current voltage respectively at these points, highlighted as  $J_{sc}$  and  $V_{oc}$  in Figure 5, in combination with the curve shape between these points are what determine the efficiency.

## Results

We found that using a  $5\mu\text{m}$  filter was much more effective than  $0.45\mu\text{m}$  in terms of practicality and also seemed to lead to better results. We blocked many filters during processing and this was the main processing difficulty. The sub-millimetre scale particles causing blockage were clearly visible under the microscope in Figure 4. Moving from the smaller to the larger filter alleviated much of the blockage problem.



**Figure 4** Optical micrograph of polymer aggregate particles in the blend solution just before filtering, large particles that block the filters are clearly visible.

From previous research we took a blend ratio for the polymer compared to the PCBM as 1:4. However, towards the end of our project, with help from the microscope, we realised that a significant fraction of the polymer was not dissolving so we needed to reduce the amount of PCBM being used, to compensate for this, and produce a correctly weighted mixture.

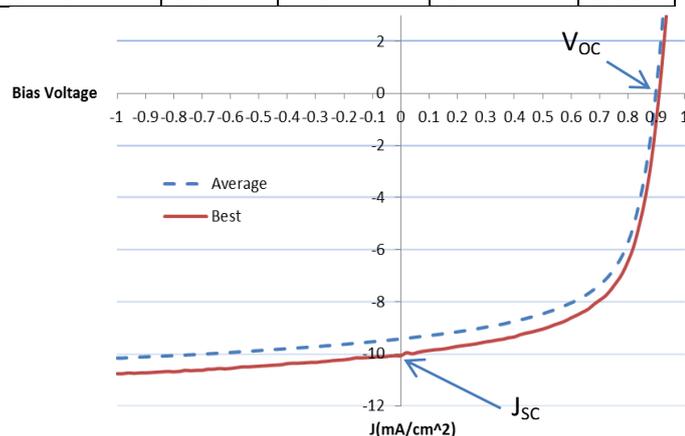
We found that a blend ratio of between 1:2 and 1:3 worked much better in this instance and resulted in devices of efficiency up to 5.6% compared to around 2% in earlier attempts.

Our optimum efficiency pixel was on a device with a blend ratio of 2:1 PCBM to PCDTBT. We made four devices with this blend, spun cast to a thickness of

70nm. The average characteristics over the devices and their 24 working pixels are shown in the table, along with the best pixel's characteristics. The J-V curve for our best pixel is shown in Figure 5.

**Table 1** Showing for a 2:1 blend the average voltage-current characteristics over 24 working pixels on four devices, as well as for the most efficient single pixel.

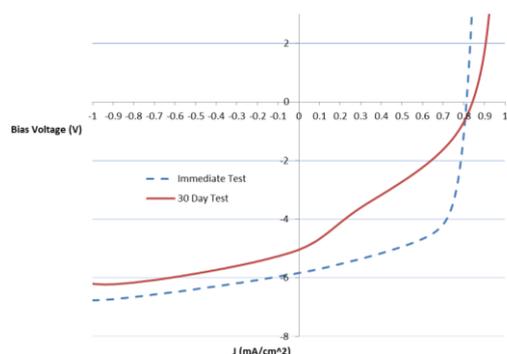
Sample	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	Fill Factor (%)	PCE (%)
Average Pixel	0.90	-9.43	61.0	5.16
Best Pixel	0.91	-10.1	61.2	5.60



**Figure 5** J-V curve for 2:1 blend devices showing the best performing pixel and the average performance.

With a 3:1 blend we showed that there was a local maximum in efficiency for thicknesses of active layer around 70nm.

We looked too at degradation of the devices, finding that when we stored the devices in a dark environment for 30 days the efficiency of the devices fell to around half its initial value; see Figure 6.



**Figure 6** Degradation of device performance after a 30-day period.

**Discussion** It appears that the use of PCDTBT with a 5 $\mu$ m filter produced good devices. High  $V_{oc}$  values and fill factors made for devices that rivalled the best made in the department so far. This result is promising as there are likely improvements to be found

by altering the blend ratio slightly as well as trying different temperatures in the solution preparation stages.

Apparent improvements with using a larger filter pore size suggest that more of the polymer is passing through as PCBM is generally in solution in particles of size much less than 1 $\mu$ m, whereas the longer chains in the crude sample may be on this scale. (Jamieson et al. refer to monomer lengthscale<sup>4</sup>).

Degradation of our devices was significant but reflects that the epoxy resin encapsulation is only meant to keep the devices from deteriorating before testing, which follows quickly after fabrication. Larger devices would last better as oxygen and moisture, which cause damage, enter from the edges of the device layers.

**Conclusions** The fact that the crude polymer sample performed well points to reduced processing need and therefore cost. This is potentially very good news for OPV technology but there is still the problem of a lot of the polymer being lost in filters. Ossila, a spin out company based in Sheffield, are working with the suppliers of the polymer to make the polymer easier to use and filter as a follow-up step to our work. Further work can be carried out to see if variations in processes, such as higher temperatures for dissolving the polymer, are beneficial. X-ray scattering investigations may be useful to better understand the differences at a molecular scale, such as those conducted on similar polymers by (Beiley et al.)<sup>5</sup>

**Acknowledgements** Many thanks to David Lidzey, Darren Watters, James Kingsley and Ed Bovill for their guidance. Thanks to Ossila for providing materials for making our devices. Thanks too to Alex Barrows for cooperating on making devices.

*I am grateful to the EPSRC for providing funding for my studentship as part of the Energy Futures Doctoral Training Centre at the University of Sheffield.*

<sup>1</sup> *Polymer-Fullerene Composite Solar Cells*, B.C. Thompson and J.M.J Frechet.

<sup>2</sup> Figure from Ossila data sheet at [ossila.com/oled\\_opv\\_ofet\\_catalogue3/M131-PCDTBT.php](http://ossila.com/oled_opv_ofet_catalogue3/M131-PCDTBT.php)

<sup>3</sup> Figure from Ossila data sheet at [ossila.com/oled\\_opv\\_ofet\\_catalogue3/M113-C70\\_PCBM.php](http://ossila.com/oled_opv_ofet_catalogue3/M113-C70_PCBM.php)

<sup>4</sup> *Fullerene crystallisation as a key driver of charge separation in polymer/fullerene bulk heterojunction solar cells*, Jamieson et al., Chem. Sci., 2012, 3, 485

<sup>5</sup> *Morphology-Dependent Trap Formation in High Performance Polymer Bulk Heterojunction Solar Cells*, Beiley et al. - Adv. Energy Mater. 2011, 1, 954–962