Mini-project report

Synthesis and Testing of a Solution Processable Transition Metal Charge Transport Dopant for Organic Solar Cells

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Abstract

Photovoltaic technology using organic polymeric semiconductors is one potential solution to the global energy crisis and offers a more cost-effect way of harnessing solar power than traditional Si-based panels. OPVs suffer with problems regarding stability, lifetime, and inadequate charge generation and extraction speeds. One line of research focuses on p-type dopants to increase conductivity but these must be solution-processable to fit in with the vision of low cost, large area fabrication methods. Some headway has been made into ascertaining the status of research into solution-processable p-type dopants and the project is at a stage that leaves scope for further assessment of two compounds that could be used as p-type dopants within an organic solar cell.

1. Introduction

Photovoltaic technology is one potential solution to the global energy crisis with solar power being an obvious alternative to fossil fuels. While traditional silicon-based solar panels are efficient, they are energy-intensive and costly to manufacture due to the sophisticated processing techniques required for inorganic semiconductor production.[1] It has been discovered that the inorganic components of photovoltaic cells may be replaced by semiconducting organic polymers, which are less expensive to synthesise. These polymeric materials also have the advantage of being solution processable [1-3] and, coupled with new manufacturing techniques, could revolutionise how solar energy is utilised. Dissolved organic semiconductors can be sprayed or printed onto lightweight, flexible substrates in a process very similar to newspaper printing, and this style of large-area, high throughput fabrication has the potential to make organic photovoltaics (OPVs) much more cost-effective than traditional solar panels.

There are problems with OPVs that are yet to be overcome, which include issues with the efficiency of charge extraction.[4] Research into the mechanisms at play in the active layer has gone some way to address the problems of charge transport, with the development of the bulk heterojunction. Early OPVs used a planar heterojunction (see Figure 1, below) to promote exciton separation but the efficiency of any junction is limited by the exciton diffusion length. The diffusion length describes the distance an electron-hole pair can travel before recombination occurs; this is usually in the order of 3-10 nm. If exciton formation should occur in a region of the polymer that is greater than 10 nm away from the electron acceptor, it is unlikely that the exciton would be harvested before recombination took place. The bulk heterojunction utilises an active composite that is a blend of the polymer and electron acceptor (commonly PCBM, see Appendix 6.1) and means that the electron acceptor is much more accessible when an exciton is formed in the donor. Another type of heterojunction currently under research is the ordered heterojunction, which uses an inorganic material instead of PCBM. Nanostructured oxide templates can be fabricated with pores that are the optimum length for exciton harvesting, although this research is at a very early stage and is not currently as efficient as the bulk heterojunction.[1]
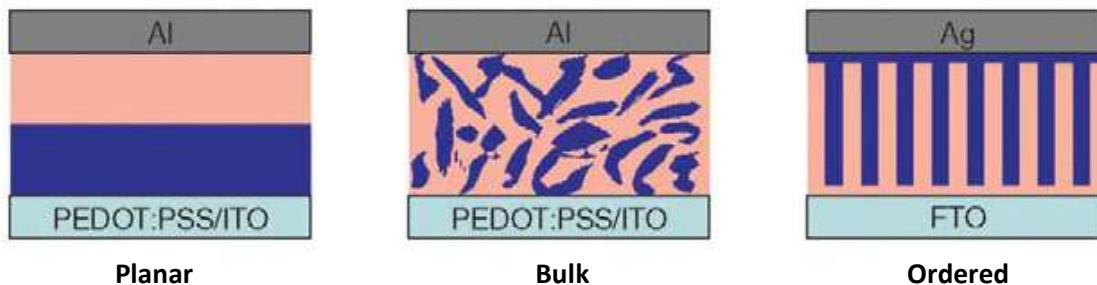

| Planar | Bulk | Ordered |

Figure 1. Schematic of heterojunctions found in OPVs.[1]

Although studies relating to the morphology of the active layer have contributed to increasing the efficiency of OPVs, this does not address the issue of energy gaps existing between the active materials. PCBM is considered to be an ideal electron acceptor,[2] having an energetically deep-lying LUMO at 4.2 eV. It is not beneficial for the donor LUMO energy to be greater than 3.9 eV, as energy is wasted and does not contribute to device performance. P3HT, a donor polymer commonly used in OPVs, has a LUMO energy of 3.2 eV and one way to address the issue of obtaining a better electronic equilibrium within the cell may be to use a p-type dopant. Dopants currently in use at the moment can be split into two obvious categories: organic and inorganic. The inorganic dopants include metal oxides [5-10] and complexes;[3-4, 11-12] the organic dopants taking a variety of forms [13-18] but F4-TCNQ and its derivatives [19-23] enjoying recent popularity. Although numerous dopants have been identified, there is much room for improvement with respect to compatibility with the roll-to-roll fabrication process. Inorganic dopants tend not to be fully soluble within the active layer and require evaporation onto the substrate, which does not fit with the printing process. Organic dopants, meanwhile, are soluble in the same solvents as the semiconductors but suffer with volatility and stability issues [19] that can translate to an uneven concentration within the active layer and, therefore, unpredictable conductivity effects.

The aim of this mini-project was to synthesise a novel p-type dopant and test its efficiency within an organic solar cell. As no such solution processable transition metal compound had been identified by the University, it was necessary to review the literature to ascertain the status of current research in this field. As I had no previous knowledge or experience of the physics of organic photovoltaic systems, the literature review was also useful in gaining an understanding of polymer-based solar cells, with particular emphasis on the effects of p-type dopants. In addition to the literature review, some laboratory skills were acquired via experimentation, such as: organic electronic cell assembly, clean room procedure, and cyclic voltammetry analysis. The project is now at a stage that leaves scope to synthesise p-type compounds and assess their properties and effectiveness as dopants within an organic solar cell.

2.   **Methods**

2.1   *Cyclic Voltammetry*

Cyclic voltammetry analysis was performed on BFE, PFB and TFB in order to determine their redox responses. A sample solution was prepared by adding just enough toluene to dissolve a few fragments of the polymer. The cyclic voltammeter was set up with three electrodes: a Pt disc working electrode, a Ag/AgCl reference electrode, and a Pt wire counter electrode. The instrument software was set up with the following parameters:

Parameter	Value
Start Potential	0 V
1st Vertex	2.0 V
2nd Vertex	-1.8 V
Step Potential	0.01007 V
Scan Rate	0.2 V/s

Table 1. Cyclic voltammetry parameters.

To prepare the cell, tetrabutylammonium hexafluorophosphate (TBAPF$_6$, 380-400 mg) was dissolved in acetonitrile (anhydrous, 5 mL) to produce a 0.2 M base electrolyte solution. The electrodes were positioned in the cell and the electrolyte solution sparged with N$_2$ for a short while to displace O$_2$. The background of the cell system was recorded prior to analysis of the polymer. The working electrode was removed from the cell and a drop of the sample solution placed on the Pt disc. The drop was carefully dried with a heat gun and the process repeated to build up three or four polymer layers. The working electrode was replaced and the measurement taken. The scan should be repeated until reproducible voltammograms are achieved. The data

was then transferred and plotted in Excel. (N.B. Care should be taken to fully remove the polymer film from the working electrode using toluene and acetone following analysis.)

2.2 Cell Assembly

In order to gain experience of inter-department cooperation, organic light emitting diodes were assembled using a dopant synthesised by Dr D Sykes from the Department of Chemistry, University of Sheffield. It was anticipated that the white light-emitting compound, DS057, would enhance the performance of OLEDs when doped into BFE and PFB at around the 1% level. When testing new materials or procedures, devices are made using glass substrates onto which an indium tin oxide (ITO) anode layer has already been deposited. As the construction procedure for OLED and OPV devices is similar, this task served to provide the clean-room experience required for the assembly of either type of cell.

The protective photoresist layer was removed from the substrates by sonicating in NaOH (aqueous, 5%) for 3 min and rinsing twice in water; this step was performed twice. After the final rinse, the substrates were dipped in propan-2-ol and blown dry in air. The substrates were transferred to a glove box and placed, ITO-side down, on a shadow mask for transfer into a vacuum chamber. The substrates then underwent a sputtering process with Mo in argon plasma, to form a MoO_3 hole-injection layer. Using pre-prepared polymer stock solutions (BFE and PFB, 15 mg/mL in toluene) and a solution of DS057 (1 mg/mL in toluene), the doped active layer was prepared as follows:

Final Dopant Concentration (mg/mL)	Dopant Solution Volume (µL)	Dopant Weight (mg)	Polymer Solution Volume (µL)	Polymer Weight (mg)	Ratio %
0.5	250	0.25	250	3.75	6.25
0.2	100	0.1	400	6.0	1.64
0.1	50	0.05	450	6.75	0.74
0.05	25	0.025	475	7.125	0.35
0.02	20	0.02	980	14.7	0.14

Table 2. Concentration of dopant vs. polymer. For calculations, see Appendix 6.2.

The substrates were initially coated with toluene to form a conditioning layer between the MoO_3 and the active

layer. Several drops of the doped polymer solution were placed on the surface of the substrate and the film cast at 2000 rpm for 45 s. Two devices for each dopant concentration were prepared. The cathode strip of the substrate was cleaned using toluene prior to thermal annealing in a glove box at 100 °C for 1 h. Upon cooling, the substrates were transferred to a shadow mask, and then to a vacuum chamber, where an aluminium cathode was evaporated over the doped active layer. The devices were encapsulated with glass cover slips using UV glue and dried in a UV light box for 40 min. Legs were attached to the devices for the activity to be measured, which was done at a later date by J Griffin, Department of Physics and Astronomy, University of Sheffield.
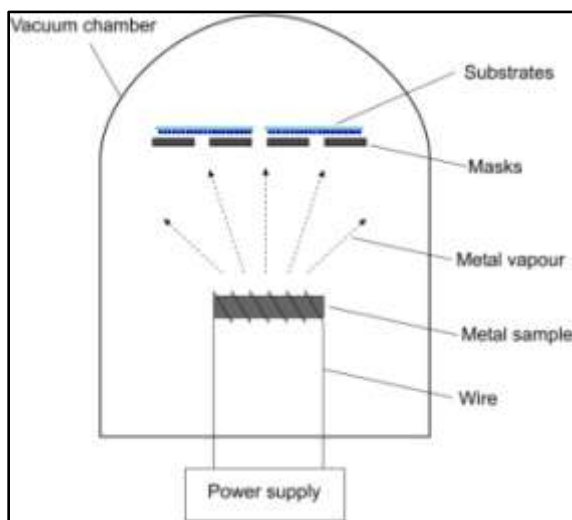
Figure 2. Schematic of vacuum evaporation chamber (courtesy of C J Hunter MSci, University of Sheffield).

3. Results and Discussion

3.1 Cyclic Voltammetry

As cyclic voltammetry is usually carried out in dichloromethane or acetonitrile, solubility of the polymers was tested in these solvents; all three polymers were insoluble in acetonitrile and sparingly soluble in dichloromethane. Initial experiments attempted to run the analysis from the polymer dissolved a dichloromethane base electrolyte solution. When a small aliquot of TFB was added to the system, no peaks were observed when the measurement was carried out. On closer inspection, it appeared that the polymer sample had not fully dissolved; the cell was removed, the solution sonicated and the analysis repeated. Again, no peaks were observed on the resultant voltammogram. The system was left to stand for several minutes while the literature [24-25] was consulted. As scans seen in the literature were run at 20 mV/s, it was decided that the scan rate should be reduced; peaks were visible at 20 mV/s and the measurement repeated at a scan rate of 200 mV/s, for which redox peaks were also visible. It was hypothesised that standing time was necessary to allow for coating of the working electrode. The experiments were continued with PFB – following recording of the background, a small aliquot was added to the dichloromethane base electrolyte solution and sonicated. The cell was replaced and left to stand with a N_2 sparge for approximately 25 min. An analysis was run at both 0.2 and 0.02 V/s but neither produced any results. Following further consultation of the literature,[24-25] it was decided that forming a polymer layer from toluene on the electrode, and using an acetonitrile base electrolyte solution, should be the next experiment (see method in section 2.1, above). This experiment yielded the results in the Table 3, below.

Compound	Scan Rate (V/s)	1st Oxidation (V)	2nd Oxidation (V)
BFE	0.2	1.1	1.6
PFB	0.2	0.7	1.0
TFB	0.05	1.0	n/a

Table 3. Oxidation results of analysis by cyclic voltammetry. For voltammograms, see Appendix 6.3.

When using films in cyclic voltammetry, an initial conditioning scan is required to achieve porosity within the polymer film, which then enables current to flow throughout the cell. Therefore, the second and subsequent scans only are used for analytical purposes. This is illustrated in Appendix 6.3, which shows both the conditioning and data-collection scans. TFB was the first polymer to be analysed, using an initial scan rate of 50 mV/s; Scan 3 shows a loop on the right-hand side of the voltammogram, which indicates that the scan rate was too slow. The scan rate was, therefore, increased to 200 mV/s for the analysis of BFE and PFB. Note that there is only one oxidation value for TFB as the compound contains only one triarylamine centre; BFE and PFB have two triarylamine centres and two corresponding oxidation values.

3.2 Cell Assembly

Current and photovoltage measurements were taken for all devices and the data plotted in Excel (see Appendix 6.4). For devices doped with a concentration of 0.5 and 0.2 mg/mL, the resultant data unusable due to short-circuiting. Reverse voltage current and little light emission was observed for the remaining devices with dopant concentrations of 0.1, 0.05 and 0.02 mg/mL. However, some of the PFB devices were marginally better than the BFE devices in showing slightly higher currents and some diode characteristics.

There are a number of possible explanations for the poor activity of the doped devices:
- Insufficient dopant concentration
- Dopant insolubility
- Behaviour of Eu within DS057
- Incompatible energy levels of dopant and polymer.

The devices were inspected under UV light and it appeared that any fluorescence came from the polymer itself and not from the dopant. This could indicate that the dopant was at too low a concentration to have any real effect on the diode characteristics of the device. However, as DS057 was only sparingly soluble in toluene (the preferred solvent for spin-coating BFE and PFB) it would not be possible to increase the concentration using this solvent. The preferred solvents for DS057 are methanol and acetonitrile, both of which are unsuitable for BFE and PFB; DS057 is also soluble in dichloromethane but the polymers only sparingly so. Light emission has been previously observed in devices using the same non-doped active polymers. During discussions with Dr Sykes, the idea was put forward that the lack of emission may be due to the europium centre of DS057 acting as a sink for electrons within the active layer. This idea is confirmed by the reduction of current with increasing dopant concentration, which implies that charge carriers are trapped and unable to make their way across the device. Also, should DS057 have energy levels that are incompatible with the polymers, no holes could be injected into the dopant compound; this would result in no emission occurring on the compound itself.

4. Conclusions and Future Work

The results obtained in the experimental work above are somewhat insignificant when considered in isolation but one would expect the results to be more relevant when used as part of a much larger research project. When considering a dopant for BFE, PFB or TFB, a compound with an oxidation value greater than those obtained for the polymers would be required in order for the polymer to be oxidised preferentially over the dopant molecule. With respect to the white light-emitting dopant for OLEDs, the next step of the experimental process may be to cast the polymer and dopant separately as a bilayer. It may be possible to use dichloromethane as the common solvent, although the solubility of the polymers should be taken into account when calculating dopant concentrations (the solubility of the polymers in dichloromethane was determined experimentally: BFE and PFB 8 mg/mL, TFB 4 mg/mL). The learning outcome of this mini-project has proved to be more literature-based than results-focused; this is due in part to the fact that the research is in its very early stages and also to my own inexperience in the field of OPVs.

There are numerous multifaceted requirements for a solution processable charge transport dopant to be successful, and it would be impossible to fulfil these requirements in the length of time allocated for a mini-project (2 or 4 months). However, two compounds have been identified as possible candidates for future research: a molybdenum dithiolene complex, $Mo(tfd)_3$, and a triarylamine compound, $C_{18}H_{12}Br_3N(SO_3)$, the structure of which was proposed by Professor Mike Ward (Department of Chemistry, University of Sheffield). $Mo(tfd)_3$ is currently being researched [11] as a p-dopant for hole transport materials at the Department of Electrical Engineering, Princeton University. The $Mo(tfd)_3$ complex is evaporated onto the substrate and solution processing has not yet formed part of their research. Investigation into the solubility of this compound may yield interesting results, or lead to the possibility of altering the structure in a way that affords solubility without negatively impacting upon the p-type activity of the complex. With respect to $C_{18}H_{12}Br_3N(SO_3)$, the triarylamine centre may already infer solubility as this moiety is commonly seen in existing polymeric semiconductors. The radical cation would act as an electron acceptor, while the sulphur trioxide group would balance the charges on the compound without the complication of a negative counter ion within the active layer.

OPVs have the potential to make a real contribution towards securing our future energy supplies and research is continuing into increasing the efficiency of this technology. Problems still exist with regard to lifetime, degradation and charge utilisation, and while reported conversion efficiencies still only reach the 5% mark [1] our understanding of the mechanisms involved with these processes is improving. OPV devices offer the potential for greater commercialisation of solar cells with new technologies offering the potential for large scale, low cost production. This, combined with research efforts into flexibility, transparency and colour for integration into building materials, means that OPVs may offer a greater accessibility to solar energy than experienced with traditional solar panels. Further knowledge to increase the stability and, therefore, match or

exceed the lifetimes enjoyed by Si-based photovoltaics would provide the general population with a cheap and effective way of harnessing the sun's energy; however, many hurdles are yet to be overcome before OPVs offer a real and tangible alternative to existing technologies.

5.   References

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6. **Appendices**

6.1 Abbreviations and non-IUPAC terms

PCBM – [6,6]-phenyl-C61-butyric acid methyl ester
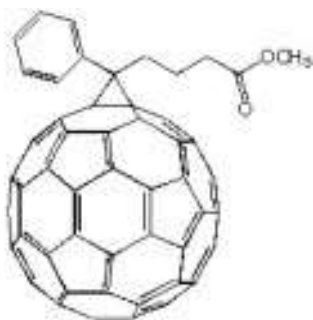
P3HT – Poly(3-hexylthiophene)
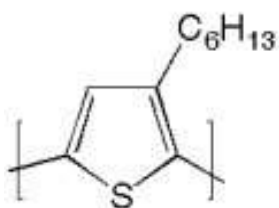
F4-TCNQ – 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane
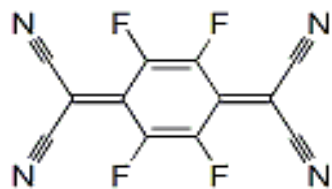
BFE – poly(9,9'-dioctylfluorene-*co*-bis-N,N'-(4-ethoxycarbonylphenyl)-bis-N,N'-phenylbenzidine)
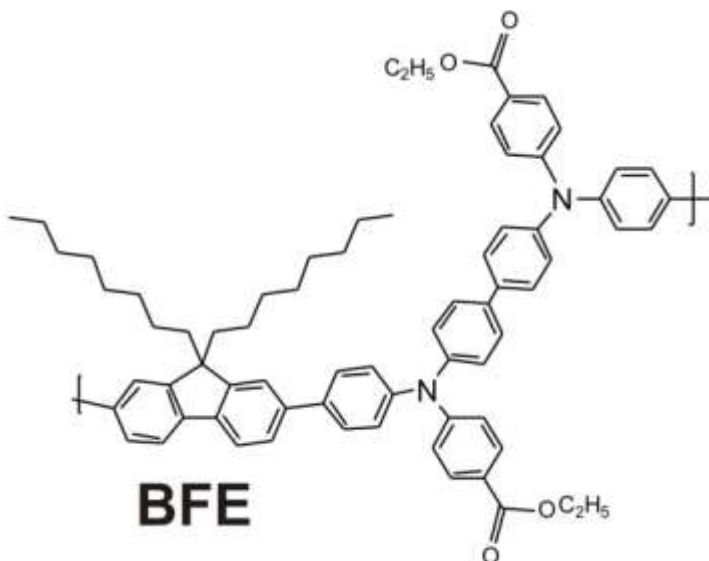
PFB – poly(9,9'-dioctylfluorene-*co*-bis-N,N'-(4-butylphenyl)-bis-N,N'-phenyl-1,4-phenylenediamine)
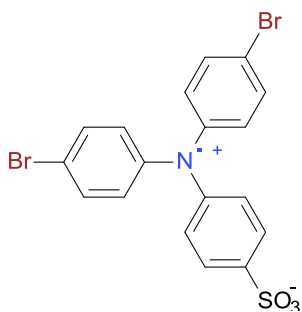
TFB – poly(9,9'-dioctylfluorene-*co*-bis-N,N'-(4-butylphenyl)-diphenylamine)
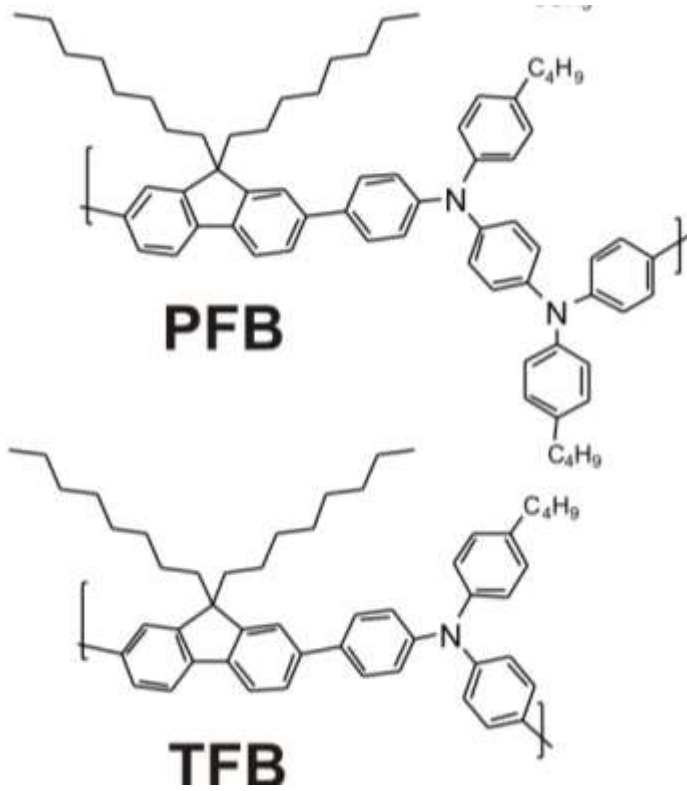
Mo(tfd)3 – Molybdenum tris-[1,2-bis-(trifluoromethyl)ethane-1,2-dithiolene]
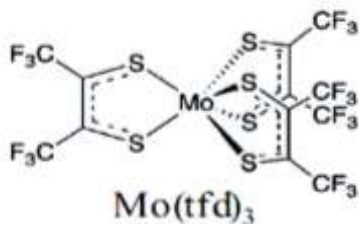
Triarylamine dopant (conceptual)

6.2 Calculations

To obtain a concentration of dopant in 0.5 mL of polymer solution:

$$Vol_{stock} \times Conc_{stock} = Vol_{dil} \times Conc_{dil}$$

For example:

$$Vol_{stock} \times 1\,mg/mL = 0.5\,mL \times 0.1\,mg/mL$$

$$Vol_{stock} = \frac{0.5 \times 0.1}{1} = 0.05\,mL = 50\,\mu L$$

of dopant solution, made up with 450 µL of polymer solution.

Weight of compound in a solution:

$$Weight\ of\ compound = Vol \times Conc$$

For example:

$$Weight\ of\ polymer = 0.45\,mL \times 15\,mg/mL = 6.75\,mg$$

Ratio of dopant in polymer solution:

$$\frac{Wt_D}{(Wt_D + Wt_P)} \times 100 = Ratio\ \%$$

For example:

$$\frac{0.05}{(0.05 + 6.75)} \times 100 = 0.735\%$$

BFE (four layers of film from Toluene) in MeCN with 0.2 M TBAPF6 vs. Ag/AgCl, 200 mV/s (two consecutive scans)
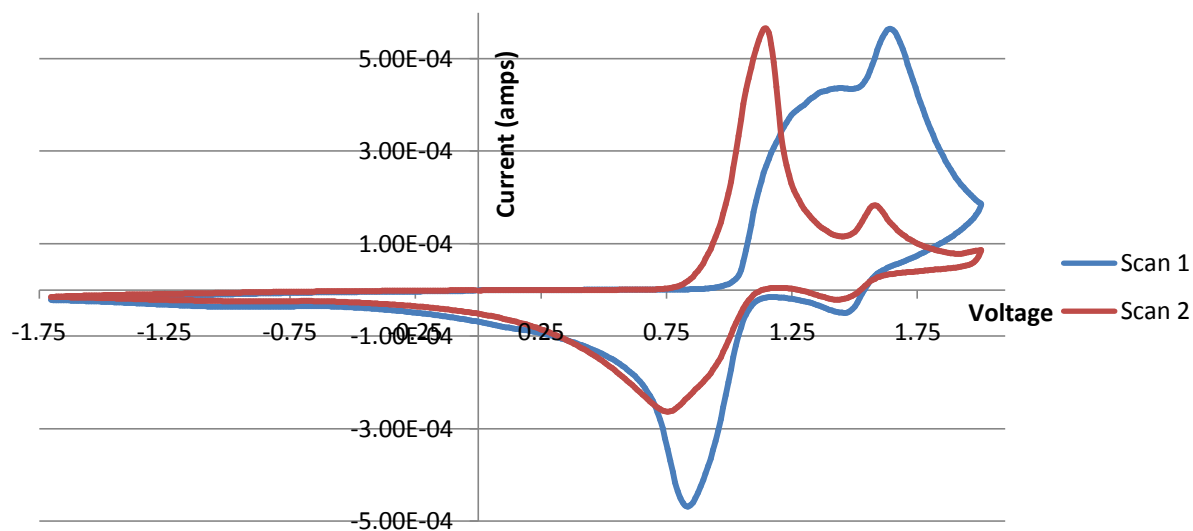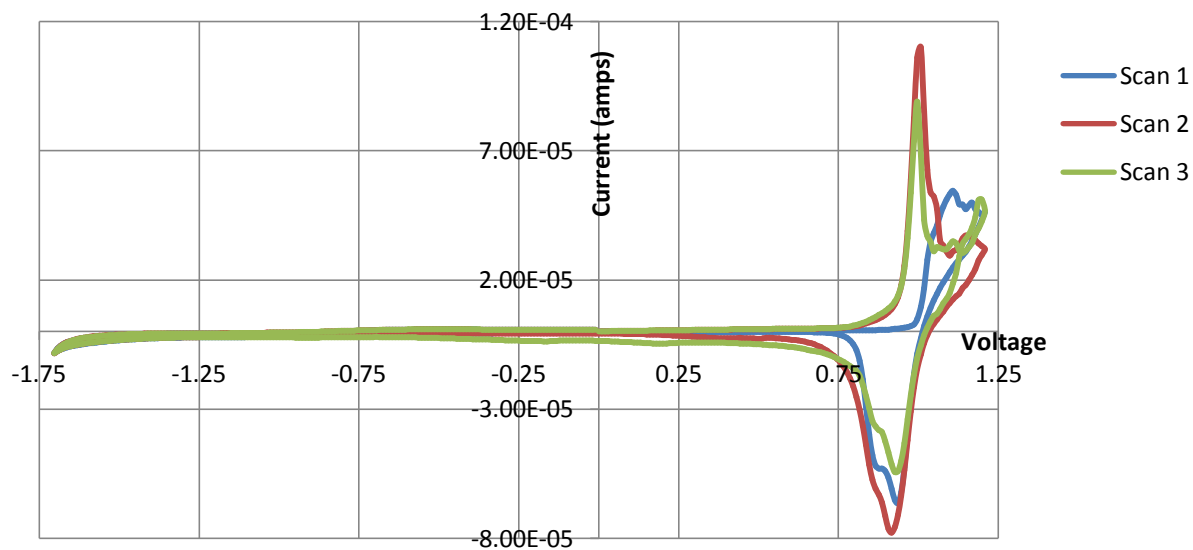

PFB (four layers of film from Toluene) in MeCN with 0.2 M TBAPF6 vs. Ag/AgCl, 200 mV/s (two consecutive scans)
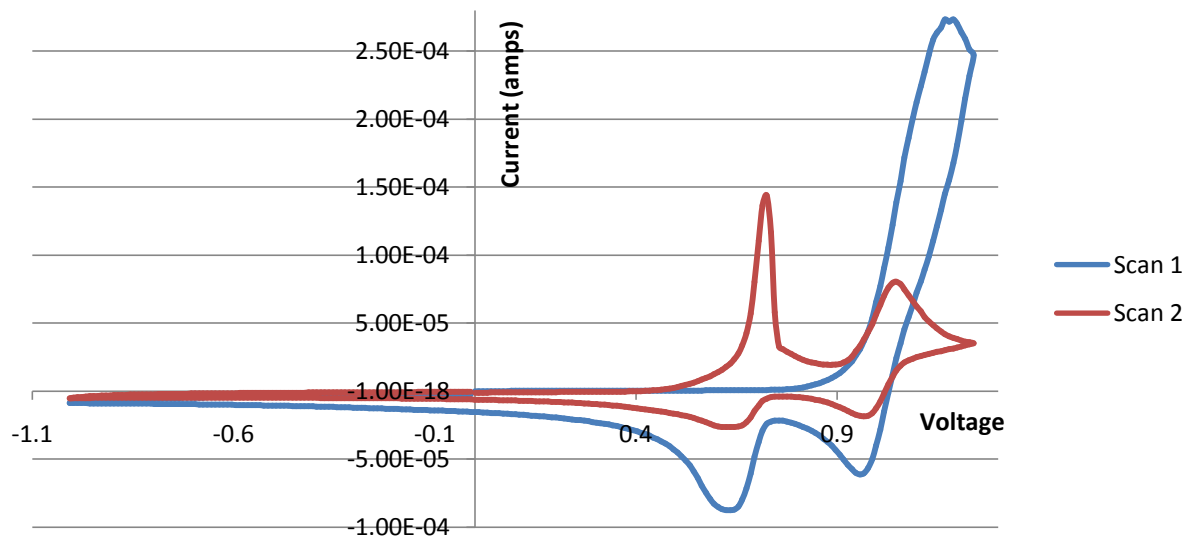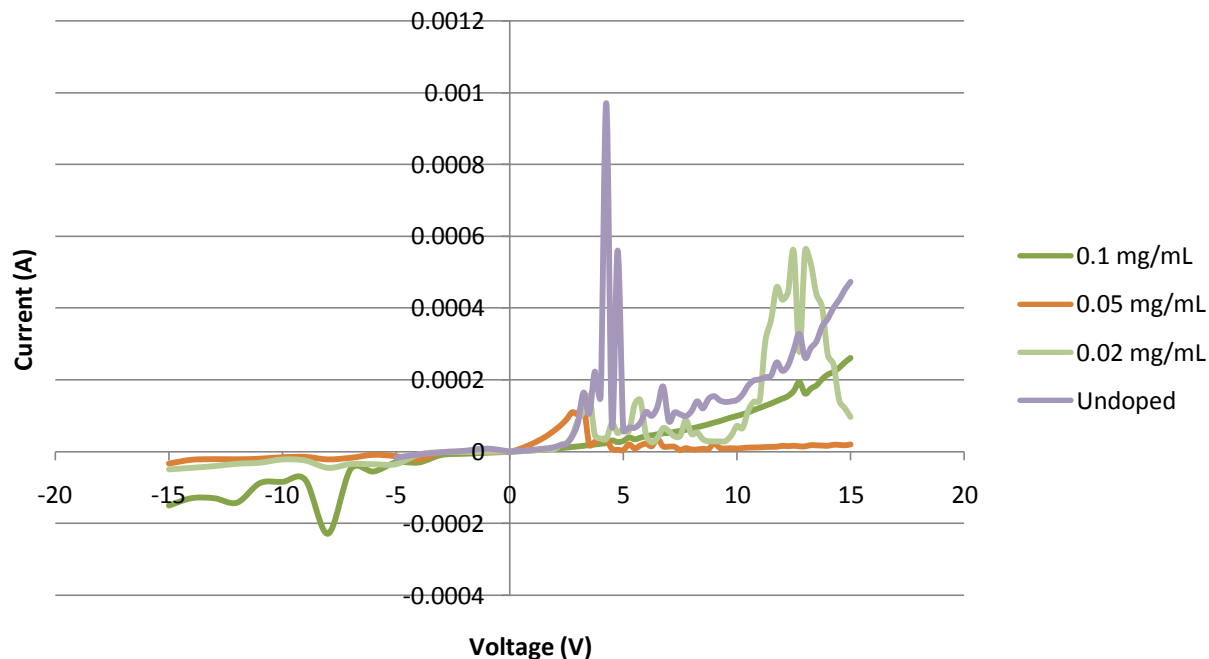
TFB (four layers of film from Toluene) in MeCN with 0.2 M TBAPF6 vs. Ag/AgCl, 50 mV/s (three consecutive scans)
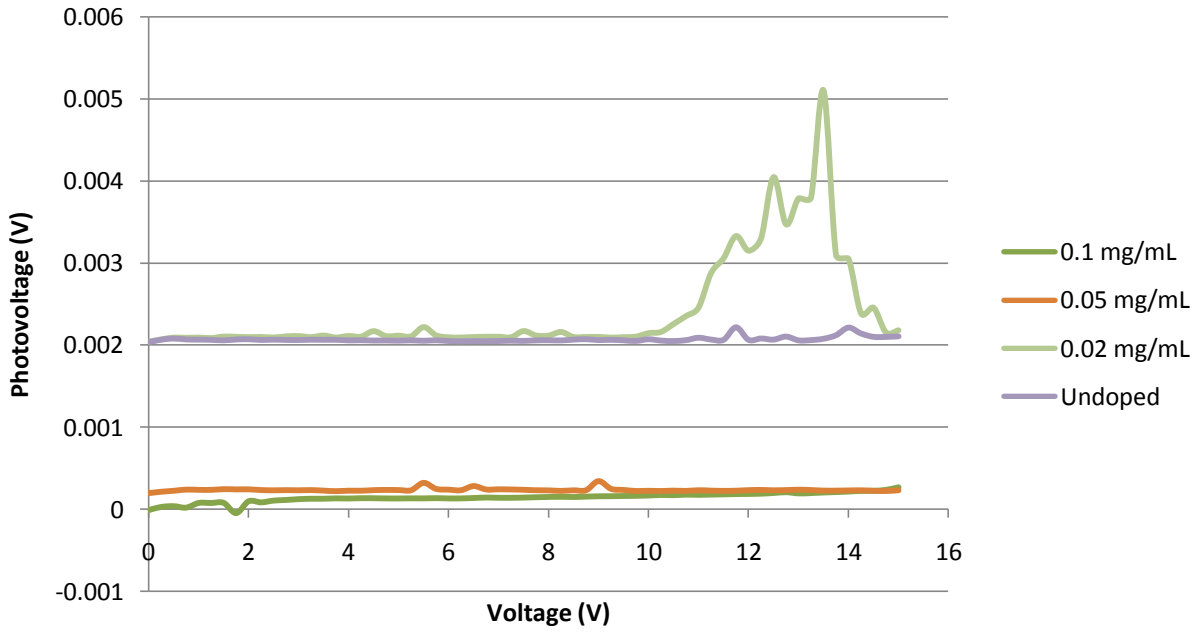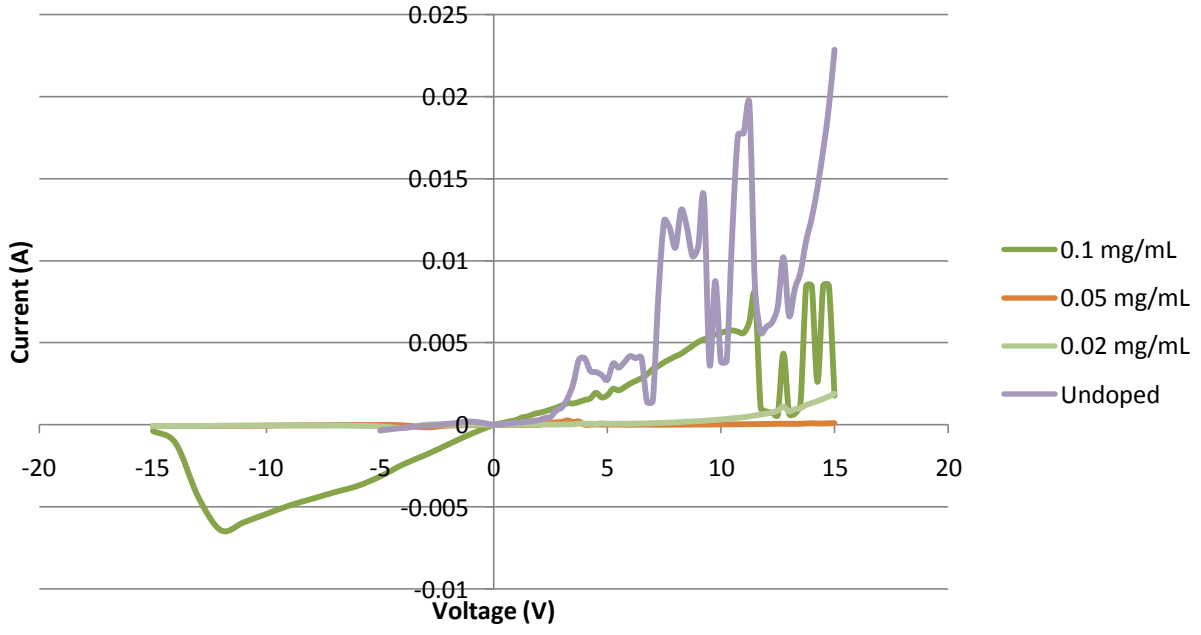
6.4   Current / Photovoltage Graphs

Devices with BFE active layer, doped with DS057 (2 device / 6 leg average)

Devices with BFE active layer, doped with DS057 (2 device / 6 leg average)

Devices with PFB active layer, doped with DS057 (2 device, 6 leg average)

Devices with PFB active layer, doped with DS057 (2 device, 6 leg average)