

# Recombination losses in organic solar cells

Study of recombination losses in organic solar cells by light intensity-dependent measurements

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Rekombinationsförluster i organiska solceller  
Undersökning av rekombinationsförluster i organiska solceller genom  
ljusintensitets mätningar

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## Abstract

Easy manufacturing, light weight and inexpensive materials are the key qualities of organic solar cells that makes them a highly researched area. To make organic solar cells adequate for the market, the efficiency of power conversion has to increase further, and the lifetime of organic solar cells has to improve. Avoiding recombination losses is a piece in the puzzle that can make organic solar cells more efficient. Organic solar cells with two different hole transport layers were therefore examined by I-V measurements. It was found that the organic solar cell with MoO<sub>3</sub> as the HTL possesses a higher current density in both the reverse region and forward region. The higher current density in both regions points towards a less successful blocking of electrons travelling to the anode (reverse region) and a better ability to transport holes from the active layer to the anode. Insight to different state of recombination was also found from the slope values in the  $V_{oc}$  and  $J_{sc}$  as a function of light intensity plots. It was concluded that both solar cells experience a dominant monomolecular recombination under short circuit condition and evolved into bimolecular recombination under open circuit condition. However, the cell with CuSCN showed a more dominant bimolecular recombination, which was shown from a slope closer to one unity  $\frac{kT}{q}$  in the  $V_{oc}$  as a function of light intensity plot.

## Sammanfattning

Organiska solceller används framförallt på grund av deras lätta vikt, billiga material och lätttilverkning. För att organiska solceller ska få en utvidgad kundkrets behöver deras effektivitet (PCE) och livslängd öka. Genom att minska rekombinationsförluster är det möjligt att uppnås. Två olika håltransportlager kommer därför att undersökas i detta arbetet. Insikt till olika rekombinationsstadier av elektron-hål par hittades från lutningarna av  $V_{oc}$  och  $J_{sc}$  som funktion av ljusintensitet. Det visade sig att båda solcellernas elektron-hål par rekombinationer var dominerande av monomolekylära rekombinationer under kortslutnings förhållanden och rekombinationsdominansen utvecklades till bimolekyläriska rekombinationer under öppen krets förhållanden. Dock, solcellen med CuSCN visade på ett mer dominant tillstånd av bimolekylära rekombinationer under öppen krets förhållanden, vilket visades av en lutning närmare en enhet  $\frac{kT}{q}$  i plotten  $V_{oc}$  som funktion at ljusintensitet.

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# 1 Introduction

Renewable energy resources are important to slow the global warming, stop pollution in water and air, and to create a sustainable future. Fossil fuels are still heavily used as a non-renewable energy resource in many countries, but will ultimately deplete in the future. It is therefore important to improve current techniques for harvesting energy from renewable energy resources. In specific, to make solar cells adequate for current global energy needs, their efficiency must be increased.

Solar cells uses the photovoltaic effect to convert light from the sun into electric current. There are different types of solar cells, one of those are organic solar cells. They are used due to their inexpensive materials, easy manufacturing and light weight.

Every layer of a solar cell is complex and requires substantial research and understanding in order to maximize the efficiency of solar cells. A solar cell that is subjected to light can only successfully convert a limited amount of the photons to free charge carriers (electrons and holes), this is due to losses. The photon-to-free charge carriers conversion process is a complex process and there are different types of losses. Recombination losses is one of those losses that will be studied throughout the work. By using different materials as hole transport layers and comparing the I-V characteristics of the solar cells under different illumination intensities, it is possible to gain insight about the origin of recombination losses.

The report will first give some theoretical background on organic solar cells, in order to prepare the reader for the results. Thereafter the experimental set-up will be discussed, which will describe how the light intensity measurements are done. The third section is going to be graphical analysis, which will be followed by discussion, and conclusions will be drawn in the last chapter.

## 2 Theory

### 2.1 Organic solar cells

Single-junction organic solar cells will be the focus in this report, they usually consist of five different layers, see Figure 1.

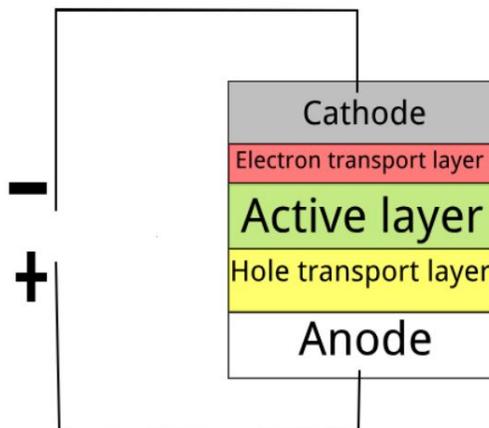


Figure 1: The general appearance of a single-junction organic solar cell

The photon-to-free charge carriers process can be affected by many aspects. The general purpose for each layer in an organic solar cell will therefore be discussed briefly here.

#### 2.1.1 Active layer (Donor and Acceptor)

The active layer consists of a blend between two materials, one donor and one acceptor. Different electron affinities in the acceptor and donor are required to separate the excitons into electrons and holes. The acceptor material needs a high electron affinity, since the electrons must be accepted by the acceptor material. Morphology of the active layer is another aspect that must be considered when constructing the optimal organic solar cell. The change in photocurrent can be correlated to the morphology [1] of the active layer. The morphology of the active layer can be altered using different solvents and additives to achieve the best results.

### 2.1.2 Electrodes (Anode and Cathode)

A solar cell also requires two electrodes (one anode and one cathode), in order to conduct electricity. These two electrodes are the outer layer of a solar cell, which collect the respective free charge carriers.

There are two types of configurations, the conventional (direct) or the inverted configuration, see Figure 2.

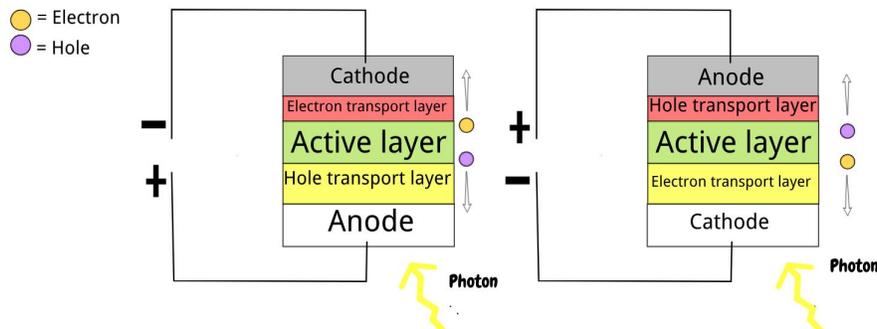


Figure 2: Conventional and indirect configuration, respectively.

The difference between the two comes down to the reversion of the electrodes. In the direct configuration the electrons will be collected at the cathode (top layer), while the holes are collected at the anode (bottom layer). For the inverted configuration the anode will instead be the top layer and the cathode the bottom layer, which means the free charges are transferred in the opposite directions, contrary to the conventional configuration.

The inverted configuration comes with both its benefits and downsides. One big advantage is the increased lifetime of the inverted configuration, but they can struggle to keep up with the efficiency [2]. It should also be kept in mind that the energy levels should be suitable and the transmittance rate should be high for the electrode facing the sun.

### 2.1.3 hole/electron transport layer

Energy levels between the cathode, active layer and anode should match and layers called hole/electron transport layers (HTLs/EELs) can be used for this purpose. These two layers are placed in between the active layer and the electrodes see Figure (7). The goal of the transport layers is to make the transition of the free charge carriers from the active layer to the electrodes easier. Transport layers are therefore often chosen due to their

energy levels and their ability to reduce recombination losses. It should be remarked that these layers can cause resistance, they can hinder electrons and hole and thus form space charge regions.

## 2.2 How organic semiconductors conduct electricity.

Organic and inorganic semiconductors transport electrons and holes differently and also have various properties. Conjugated organic molecules are used in organic solar cells to absorb light and to conduct electricity. For instance, the two materials used in the active layer for the experimental analysis (Section 3) are both conjugated organic molecules, see Figure 3.

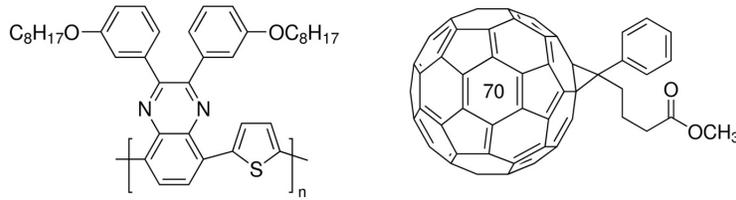


Figure 3: a) TQ1 donor polymer with n repetitive units b) PC<sub>70</sub>BM acceptor material, single organic molecule.

TQ1 used as the donor material, is a conjugated organic polymer, while the acceptor material, PC<sub>70</sub>BM is a conjugated molecule. Conjugated organic systems have both  $\sigma$  and  $\pi$  bonds for the electrons, but  $\pi$ -electrons are more mobile with respect to the  $\sigma$ -electrons and can move in the conjugated chains, due to their mutual overlap of  $\pi$ -orbitals[3]. The  $\pi$ -electrons are the electrons that makes it possible for the active layer in organic semiconductors to conduct electricity.

It should also be remarked that even though the delocalized electrons makes it possible for organic conjugated molecules to conduct electricity, there are other material properties with respect to inorganic material for example Si, that lack behind. One of those material properties is the dielectric constant. The dielectric constant for organic materials are generally much lower, this results in the stronger bonded excitons created when a solar cells is subjected to light[4]. Organic solar cells therefore require higher energy to overcome the Coulomb interaction of the excitons.

## 2.3 Equivalent circuit diagram

The electric behaviour of a solar cell can be understood with an equivalent circuit diagram. The characteristics of the equivalent circuit diagram must therefore represent the electrical behaviour of a solar cell identical see Figure 4.

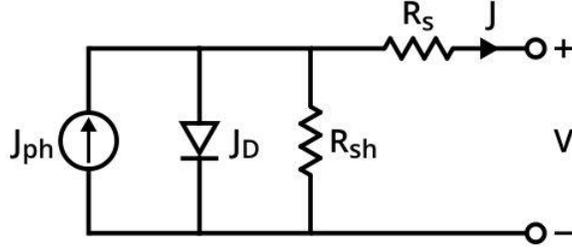


Figure 4: Equivalent circuit diagram for single-junction organic solar cell.

An ideal solar cell can be modelled using the Shockley diode equation[5]

$$J(V) = J_{ph} - J_D = J_{ph} - J_0 \left[ \exp\left(\frac{eV}{K_B T}\right) - 1 \right]. \quad (2.1)$$

Here  $J_{ph}$  represents the photogenerated current density,  $J_D$  the dark current,  $J_0$  the saturated current,  $V$  the voltage and  $T$  is the temperature. The notations  $e$  and  $K_B$  are both two constants, namely elementary charge and Boltzmann constant, respectively. This equation is eligible here since a solar cell works in the same way as a diode. It should be clarified that this equation is only valid under the assumptions that  $R_s \rightarrow 0$ ,  $R_{sh} \rightarrow \infty$  and the ideality factor  $n = 1$ . Since solar cells always have some sort of imperfection, Equation (2.1) must be modified to account for these losses. Introducing

$$J(V) = J_{ph} - J_0 \left[ \exp\left(\frac{e(V + JR_s)}{nK_B T}\right) - 1 \right] - \frac{V + JR_s}{R_{sh}}, \quad (2.2)$$

where the losses in a solar cell have been accounted for. Notations used in Equation (2.1) and what they represent is still the same, but  $n$ ,  $R_s$  and  $R_{sh}$  have been introduced.  $n$  is the ideality factor,  $R_s$  the series resistance and  $R_{sh}$  the shunt resistance. It should also be remarked when  $R_s \rightarrow 0$ ,  $R_{sh} \rightarrow \infty$  and the ideality factor  $n = 1$  that Equation (2.2) goes to Equation (2.1). The series resistance of an organic solar cell depends on the interfaces between the layers.[6]. Shunt resistance is on the other hand due to impurities in the materials. The two resistances can furthermore be related by

$$J_{sc} = J_{ph} - \frac{J_{sc} R_s}{R_{sh}}. \quad (2.3)$$

Here  $J_{sc}$  is the short circuit current density, which means  $V = 0$  when  $J = J_{sc}$ .

## 2.4 How to analyse solar cell performance

Power conversion efficiency is often a unit used to evaluate solar cells. Efficiency for solar cells can be expressed as[7]:

$$\eta = \frac{P_{max}}{E_{tot}A} 100. \quad (2.4)$$

Here  $P_{max}$  represents the measured peak power of the cell,  $E_{tot}$  the total incident irradiance and  $A$  the area of the solar cell. Although this general formula is applicable to every solar cell, standardised measurements must be applied to give comparable results.

A standardised spectrum used is the 100 ( $\frac{mW}{cm^2}$ ), AM 1.5 global spectrum (AM:Air mass)[8], while maintaining the temperature of the solar cell at 25 degrees Celsius. It is hard to achieve a close spectral match between a solar simulator and the AM 1.5 spectrum. Solar simulators are required to have a spectral mismatch  $<1.25\%$  from AM 1.5 spectrum to receive the top rating in that category[8].

(Eq 2.1) can also written as:

$$\eta = \frac{J_{sc}V_{oc}FF}{P_{in}} 100 \quad (2.5)$$

Where  $J_{sc}$  represents the short circuit current,  $V_{oc}$  the open circuit voltage,  $FF$  the fill factor and  $P_{in}$  the input power from the light. The reason why this notation was adopted for efficiency instead of (Eq 2.1) is to make the interpretations later on more straightforward.

The three parameters  $J_{sc}$ ,  $V_{oc}$  and  $FF$  used in Equation (2.5) can be extracted by performing I-V measurements of a solar cell and can be visualised graphically see Figure 5.

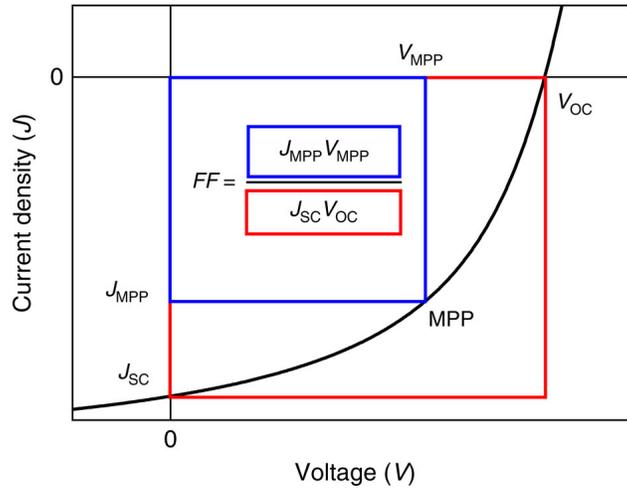


Figure 5: General curve from a I-V measurements, that shows the how the fill factor can be calculated, alongside how to interpret the parameters used in the experiment in a graphical fashion.

In this graph, short circuit current density  $J_{sc}$  is shown instead of  $I_{sc}$ , often used to neglect the area dependence. Another thing to remark in this graph is the property *MPP*, which represents the maximum power point, previously expressed as  $P_{max}$ . The fill factor ( $FF$ ), can be expressed as the ratio between the two areas see Figure 5. The  $V_{oc}$  is the maximum voltage for a solar cell, this is also the point when the current becomes zero. The last parameter that will be discussed is the  $J_{sc}$ , which represents the maximum current density and is also the point where the voltage is zero.

In conjunction with previous statement (Equation 2.5), it is apparent that for an ideal solar cell the  $FF$  would be equal to 1, which is only possible if the maximum power point for the voltage and current is equal to the open circuit voltage and the short circuit current density, respectively. The fill factor can also be seen as the squareness of the curve, which can be useful for later interpretations.

## 2.5 Recombination losses.

when the photoactive layer of an organic solar cell is subjected to light, electrons in the donor material are excited. When an electron is excited from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), a hole will be left behind and hence create an exciton (electron-hole pair), held together by Coulomb forces. In order to not waste the energy of the photon, the exciton must be separated into free charge carriers which are then collected at their respective electrodes. The separation of an exciton to free charge carriers can be seen as a three stage process see Figure 6.

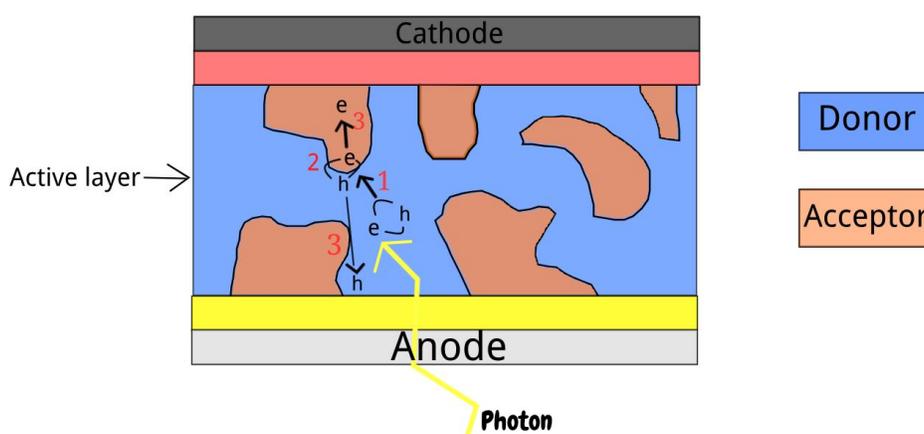


Figure 6: Three step process for exciton to separate into free charge carriers

The first step is diffusion of the exciton in the donor material. It can either diffuse to the interface of the donor/acceptor or, in the unwanted case decay to the ground state, yielding luminescence. If the exciton diffuses to the interface between the donor and acceptor, then dissociation can take place and form a geminate pair[9]. A geminate pair is the state when the electron has been transferred to the acceptor, while the hole is still in the donor, although they are still held together by Coulomb forces. In the two stages mentioned above, mono-molecular recombination can occur by trap-assisted recombination, such as imperfections or space charge regions.

In the final step of the exciton separation process, the driving force pulling  $e$  and  $h$  apart overcome the Coulomb forces and thus form free charge carriers. Even though the electron and hole are free charges, recombination losses can still occur. The electron moving in the acceptor can meet an oppositely charged carrier (originally from a different source) and recombine with it, this is called bimolecular recombination. If the electron is able to move in the acceptor material without coming across a hole and recombine, then

the electron can travel to the cathode, while the hole travel to the anode. The free charge carriers will then be transferred to an external circuit, where the power can be harvested.

### 3 Experimental details

#### 3.1 Materials and sample preparation

The two different solar cells used in this work were fabricated in Karlstad university, except the bottom layer (ITO/glass), which was purchased from luminescence technology corp (Lumtech) with a thickness  $\sim 150$  nm, see Figure 7.

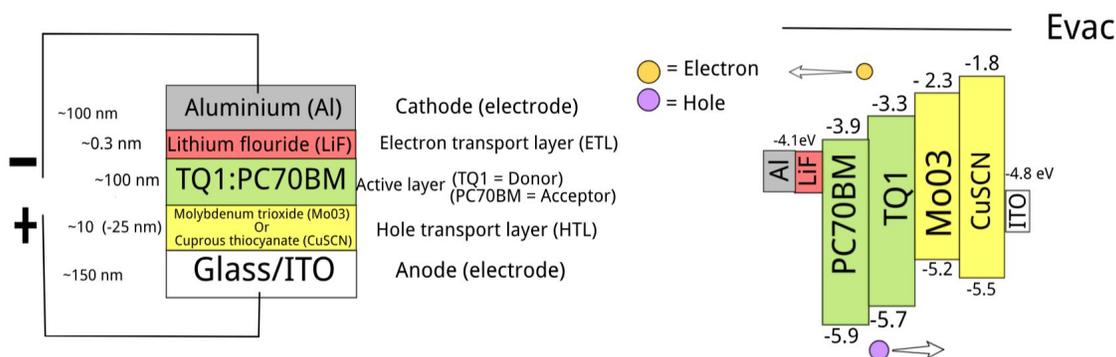


Figure 7: a) The general appearance of an organic solar cell, with two different hole transport materials. b) Energy diagram, showing the LUMO and HOMO for respective layer

Two different hole transport layers (HTLs) were used to perform the experiments, CuSCN (cuprous thiocyanate) and MoO<sub>3</sub> (molybdenum trioxide). CuSCN and MoO<sub>3</sub> materials were purchased from Sigma-Aldrich. The method used for depositing the two different HTLs onto the ITO/glass was different. First, glass/ITO substrate is cleaned with Isopropanol for 60 minutes in ultrasonic bath. The cleaned glass/ITO substrates were then treated in a UV ozone for 15 minutes prior to the coating of the HTMs. The glass/ITO substrates were treated to ensure that the HTLs reacted with the glass/ITO. The CuSCN HTL, which is solution processed from ammonia (NH<sub>3</sub>), was then dropped onto the ITO/glass and spin coated to obtain a thickness  $\sim 25$  nm.

When MoO<sub>3</sub> instead was to be used as the HTL, then the cleaned glass/ITO substrate was directly moved to a vacuum chamber in a N<sub>2</sub> environment. The MoO<sub>3</sub> HTL was then evaporated onto the surface of the ITO/glass layer with a thickness  $\sim 10$  nm.

The active layer for both material was made by mixing TQ1:PC70BM, 1:3 w/w in orthodichlorobenzene (ODCB) solvent with 1-chloronaphthalene additive inside a glove box. The blend was then allowed to stir at 80 °C overnight prior to spin-coated on the surface of the respective HTL. The blend was then moved to a glove box ( $N_2$  atmosphere,  $O_2$  level and  $H_2O$  vapour level < 1 ppm), where it was deposited onto the surface of the HTLs and then spin coated, to obtain a thickness roughly around 100 nm.

The last two layers, Lithium fluoride(LiF) and Aluminium (Al) electrode, were sequentially evaporated onto the active layer in a vacuum chamber at base pressure of  $10^{-6}$ . Evaporation continued for both materials until it reached a thickness of  $\sim 0.3$  nm and  $\sim 100$  nm for LiF and Al electrode, respectively.

Both samples were then stored in the glovebox under aluminium cover to prevent degradation until measurements took place.

### 3.2 Measurements

The solar cells were mounted one at a time, by using a measurement board with 6 pins (4 pins for top electrode and 2 for bottom electrode) see Figure 8.

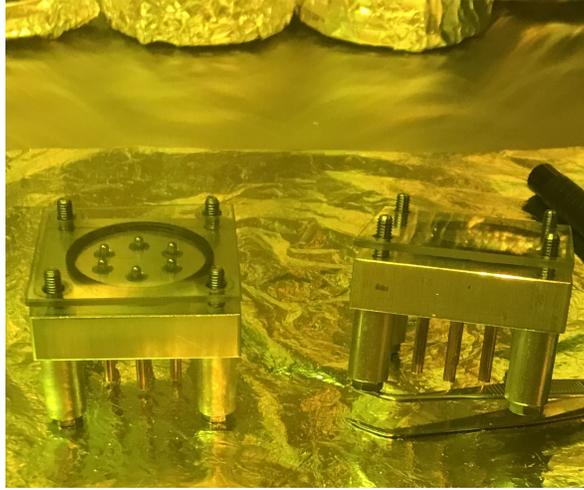


Figure 8: Two measurement boards.

The solar cells were then sealed by placing a rubber ring around the solar cells and a transparent glass layer was screwed on top of it, this was to ensure the solar cells were kept under inert  $N_2$  atmosphere and did not degrade by reacting with the oxygen. The devices were then connected one at a time by the pins to a Keithley2600 source meter,

one cable to the top electrode and one to the bottom electrode. Once the device is connected with the source meter, I-V measurement is then carried out first in dark and then light. The measurement is done one cell at a time, by moving the cables connected to the top electrode, pin to pin until all four cells were done.

After the device has been hooked up, settings had to be tuned for the measurements. Keithley2600 controller was used on the computer to adjust the settings for the measurements. The following settings were used: min. voltage = 1.5 V, max. voltage = -0.5 V, with a step voltage of -0.05 V and the active area was adjusted to 0.04 cm<sup>2</sup> to match the area of the solar cell. I-V measurements were then carried out, one cell at a time, by moving the cable connected to the top electrode, pin to pin until all four cells were done.

For light measurements, the devices were then placed under an Oriel sol 2A solar simulator, which produce 1 sun illumination. The same procedure is then repeated with different intensities. The measurements were done for each hole transport layer, with a total of 4 cells per sample.

The intensities were adjusted by using a set of neutral density filters. Neutral density filters have the ability to block a certain amount of the light, which reduces the intensity. The transmittance rate can be calculated by [10]

$$OD = \log_{10}\left(\frac{I_0}{I_T}\right), \quad (3.1)$$

where OD stands for optical density.  $I_0$  and  $I_T$  represent the intensity of the incident light (from original source) and the intensity of transmitted light (intensity after  $I_0$  passed through the filter), respectively. The transmittance rate can then be derived by raising both sides to the power of 10 and introducing

$$T = \left(\frac{I_T}{I_0}\right). \quad (3.2)$$

Here  $T$  represents the percent transmission, hence  $T$  can be expressed as

$$T = 10^{-OD}. \quad (3.3)$$

The transmittance rate can then be calculated for respective optical density filter. The optical density filters and OD values were supplied by Edmund Industrial Optics, see Table 1.

Optical density filter values	Light intensity ( $\frac{mW}{cm^2}$ )
0.15	71
0.30	50
0.40	41
0.60	25
0.90	13

Table 1: Calculated values for light intensity using Equation 3.3

The experimental I-V data were then exported to an excel file where the average values were taken for each parameter per sample. The I-V curve is then plotted for each light intensity. All other photovoltaic parameters are also extracted and plotted as a function of light intensity, see Section 4.

## 4 Results/Discussion

Figure 9 shows the dark current under different voltages. The region  $-0.5V \rightarrow 0V$  represents the reverse bias. In this region the current density for CuSCN is lower, compared to MoO<sub>3</sub>.

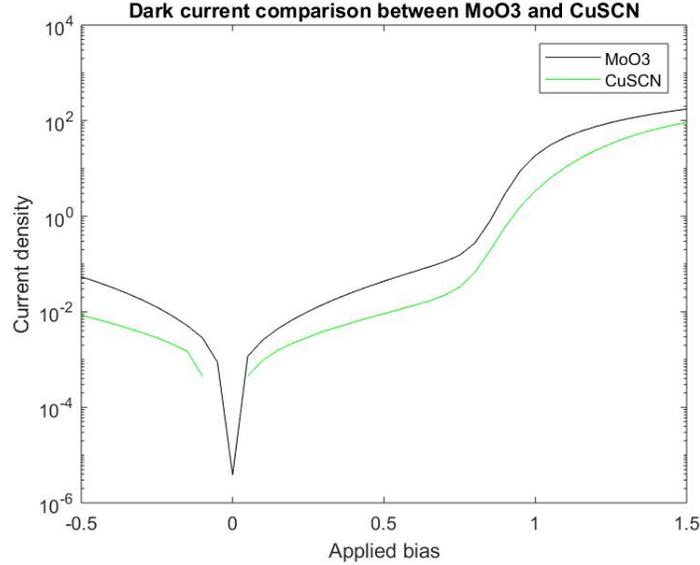


Figure 9: Dark current comparison by using two different hole transport layers

MoO<sub>3</sub> as the HTL retained the higher current density in the reverse region due to the less successful blocking of the electrons traveling to the anode (reverse direction). Failure in blocking electrons comes from the energy levels of the hole transport layer which is -2.3 eV and -5.2 eV for the LUMO and HOMO, respectively[11].

However, the lower current density is a more favourable shape for the curve, since the current density in the reverse bias region represents leakage current[12]. Leakage current can be seen as a unwanted current injected by the electrodes before the voltage turn on. The region to the right of the reverse bias represents the operating regime, which ranges from  $0 \rightarrow V_{oc}$ .

Figure 9 shows that the solar cell with MoO<sub>3</sub> also possesses a higher current density in the operating regime in conjunction with the higher current density in the reverse region. The higher current density in the operating regime signals that the solar cell with MoO<sub>3</sub>/(anode) accomplishes a better ability to transport holes. On the other hand, the

current density in this region will reduce the photocurrent, since it flows in the opposite direction to the photocurrent.

The higher current density in the operating regime is a factor that influence the fill factor and short circuit current density in a negative perspective and ultimately reduces the fill factor and short circuit current density[11]. The lower current density for the solar cell with the CuSCN HTL can be a consequence of worse transport of charges.

Diode parameters have also been extracted from the dark curve,see Table 2.

HTL	$n$	$R_s$ ( $\Omega cm^2$ )	$R_{sh}$ ( $\Omega cm^2$ )	$J_0(mA/cm^2)$
<i>CuSCN</i>	2.2	3.5	165 000	$8.5 \cdot 10^{-8}$
<i>MoO<sub>3</sub></i>	1.8	2.4	48 664	$2.7 \cdot 10^{-8}$

Table 2: Extracted diode parameters from the dark curve.

There are many ways to extract these parameters and there are more accurate ways to extract them than will be presented here, although those methods exceed the scope of this report. The series resistance, saturated current density and ideality factor for both solar cells were extracted using

$$J = J_0 \left[ \exp\left(\frac{e(V - JR_s)}{nK_B T}\right) - 1 \right]. \quad (4.1)$$

Here  $J$ ,  $J_0$  and  $V$  represents the current density, saturated current density and voltage, respectively.  $e$  is the elementary charge,  $K_B$  Boltzmann constant and  $T$  is the temperature in Kelvin.  $R_s$  is the series resistance and  $n$  the ideality factor.  $n$  shows how solar cells follows an ideal diode and it is apparent from Table 3 that the cell with CuSCN has a  $n$  value closer to one. Interpretation of  $n$  values will be discussed later in conjunction with different recombination states. The shunt resistance  $R_{sh}$  for the two solar cells were extracted using

$$\left. \left( \frac{dJ}{dV} \right) \right|_{V \rightarrow 0} = \frac{1}{R_{sh}}, \quad (4.2)$$

which gives a good approximation of the  $R_{sh}$  values.

All the I-V curves for the different light intensities are presented in Figure 10. Light intensity measurements are varied from 1 sun, which reflects  $\frac{100mW}{cm^2}$ . It is apparent from Figure 10 that the cell with MoO<sub>3</sub> has given a higher short circuit current density ( $J_{sc}$ ) than the cell with CuSCN. It should also be remarked that the current starts to increase at a lower voltage for the solar cell with MoO<sub>3</sub> and has higher slope at the open circuit voltage with respect to the solar cell with CuSCN. The rate of decrease in the short circuit current density ( $J_{sc}$ ) measured with different light intensities is similar, except a larger  $J_{sc}$  at 1 sun and 0.71 sun for MoO<sub>3</sub>.

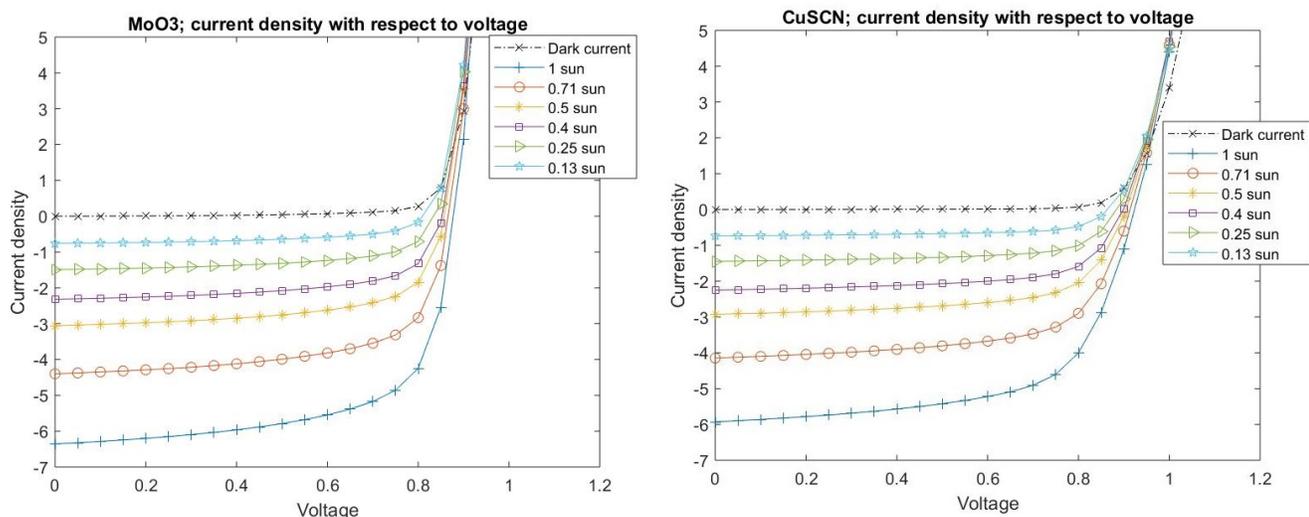


Figure 10: current density plotted against voltage in the dark (black) and under white illumination with different intensities. with different neutral density filters.

HTL	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	$FF$ (%)	$PCE$ (%)
<i>CuSCN</i>	0.93	5.93	63.2	3.47
<i>MoO<sub>3</sub></i>	0.88	6.36	65.2	3.66

Table 3: Extracted values from I-V measurements under 1 sun illumination.

Table 3 shows the extracted solar cell parameters under 1 sun illumination. These values were obtained by using previous presented methods for extraction, see section 2.4. The higher  $J_{sc}$  at 1 sun and the higher slope at open circuit voltage for the solar cell with MoO<sub>3</sub> are in agreement with the higher fill factor at 1 sun, which can be calculated using the equation in Figure (5). For an ideal solar cell  $R_s \rightarrow 0$  while  $R_{sh} \rightarrow \infty$ , which is in agreement with the higher FF for the cell with MoO<sub>3</sub> compared to the cell with CuSCN

at 1 sun.

Further investigation of the two hole transport layer is done by plotting  $V_{oc}$ ,  $FF$ ,  $J_{sc}$  and  $PCE$  versus the light intensity. Figure 11 a) shows the  $V_{oc}$  versus the natural logarithmic of light intensity.

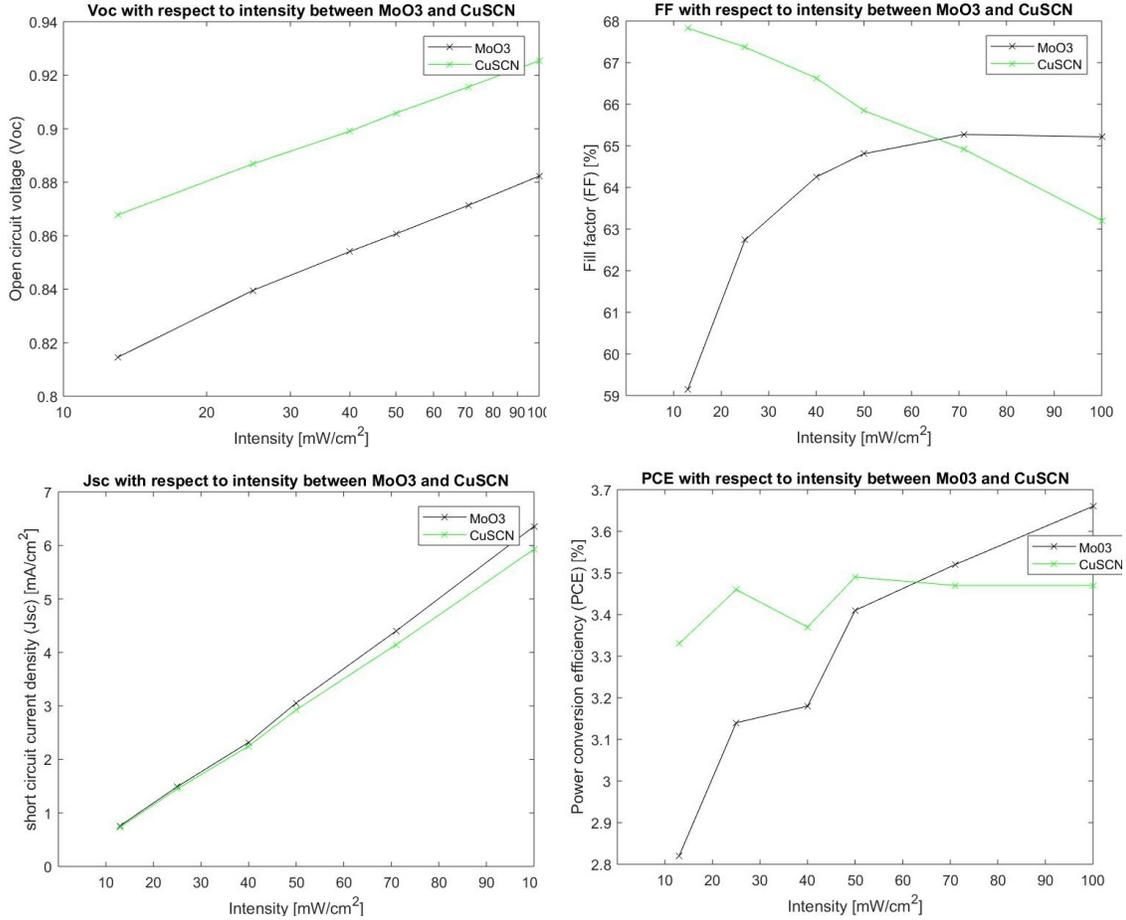


Figure 11: solar cell parameters a) Open circuit voltage b) fill factor c) short circuit current density and d) power conversion efficiency, plotted as a function of light intensity for both HTLs.

It is apparent that the solar cell with the CuSCN as the hole transport layer exhibits higher  $V_{oc}$  at every intensity. A linear increase of  $V_{oc}$  with logarithmic intensity was found. The cell with MoO<sub>3</sub> shows a small deviation from a linear dependence at lower intensities. On the other hand, the maximum  $V_{oc}$  at 1 sun is governed by the band gap of

the donor and acceptor, in other words the LUMO of the donor material and the HOMO of the acceptor material [11].

$$V_{oc} = \frac{E_{gap}}{e} - \frac{kT}{q} \ln \left( \frac{(1 - P_D) \delta N_c^2}{P_D G} \right). \quad (4.3)$$

Here  $E_{gap}$  represents the energy of the band gap (energy between LUMO of donor and HOMO of acceptor).  $T$  is the temperature and  $k$ ,  $q$  and  $\delta$  are three constants: Boltzmann constant, elementary charge and Langevin recombination constant, respectively.  $P_D$  is the probability of dissociation for electron-hole pair, while  $N_c$  is the effective density of states and  $G$  the generation rate of bound electron-hole pairs.

The expected value of  $V_{oc}$  is governed by the band gap as mentioned earlier, although an exchange in hole transport material can alter the  $V_{oc}$ . A mismatch in HOMO levels can create injection barriers at the electrodes, since carriers will get accumulated at the electrodes and change the electric field in the organic solar cell[13]. The lower voltage for the cell with MoO<sub>3</sub> in Figure 11 a) can therefore be linked to the disjointed HOMO of TQ1 and MoO<sub>3</sub> compared to TQ1 and CuSCN, since an induced hole injection barrier(HIB) is generated at the anode.

Figure 11 b) displays the  $FF$  vs intensity and it is apparent that the cell with CuSCN has a  $FF$  that decreases with increasing light intensity, contrary to the cell with MoO<sub>3</sub>, which presents an increase in  $FF$  with increasing light intensity. It has been reported in the past that a decreasing fill factor have two origins: series resistance and bimolecular recombination[12].

An estimated value can be obtained for the series resistance from Figure 6 b) in conjunction with Equation (4.1), to deduce which of the two HTLs experience the higher series resistance. It is therefore obvious the solar cell with CuSCN experience a higher series resistance, which is in agreement with the decreasing  $FF$  with increasing light intensity. The bimolecular recombination is another parameter that can affect the decrease in  $FF$  with increasing light intensity, but the different states of recombination will be discussed at length later on.

$J_{sc}$  as a function of light intensity is plotted in Figure 11 c). Both curves are fairly linear and are almost identical at low intensities. As the light intensity increase, the  $J_{sc}$  values for respective sample starts to deviate from each other. However the deviation between the two samples is very small and the  $J_{sc}$  values almost coincide at 1 sun. The linear curves are to be expected, since one absorbed photon generates one exciton.

The dependence of  $V_{oc}$ ,  $FF$  and  $J_{sc}$  on light intensity are shown simultaneously using the PCE see Figure 11 d). The increase in PCE with increasing light intensity for the solar cell with MoO<sub>3</sub> can be correlated to the increasing FF and the small increase in the

current density. The appearance of the solar cell with CuSCN on the other hand shows small oscillations, but ultimately, the deviations under different light intensities are negligible. This behaviour can be directly correlated to the  $FF$  and  $J_{sc}$  curves.

further investigation of open circuit voltage versus intensity can be done by using

$$V_{oc} \propto n \frac{kT}{q} \ln(I) \quad (4.4)$$

Notations used in Equation (4.4) are the same as in Equation (4.3), while the new notations  $n$  and  $I$  stands for the ideality factor and light intensity, respectively. This formula is applicable when studying the open circuit voltage, since most of all excitons will recombine in the blend under open circuit voltage conditions.

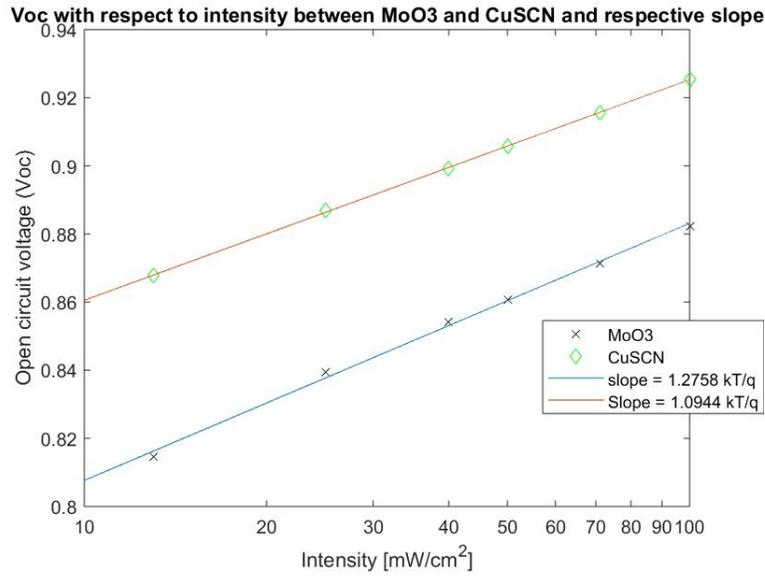


Figure 12: open circuit voltage plotted as a function of light intensity and line regression fitting for both HTLs, in order to find recombination states under open circuit conditions.

Figure 12 shows the same values as in Figure 11 a) but with a linear regression fitting, which is used to extract  $n$  from Equation (4.4). The  $n$  values can be used to decide which of the two recombinations is dominant, monomolecular or bimolecular recombination. A value of  $n$  close to unity indicates a dominant bimolecular recombination, while a higher  $n$  indicates monomolecular recombination [11]. From the linear fitted curve, the  $n$  value for the cell with MoO<sub>3</sub> is  $n = 1.2758$  and  $n = 1.0944$  for the cell with CuSCN. The two different values of  $n$  for the solar cells with MoO<sub>3</sub> and CuSCN points towards a higher

presence of bimolecular recombination in the cell with CuSCN. This conclusion is also in agreement that the fill factor is decreasing with increasing light intensity for the solar cell with CuSCN see Figure 11 b).

It is also possible to gain further insight of different state of recombination by using the power law dependence of the short-circuit current density

$$J_{sc} \propto I^\alpha. \quad (4.5)$$

The power law proportionality can be taken as indicative that an  $\alpha$  close to unity points to a weak bimolecular recombination. Both curves exhibit a similar trend and show small deviations from an  $\alpha$  equal unity see Figure 13. It has previously been argued that a deviation from  $\alpha$  equals unity points towards: Formation of space charge regions, variety in mobility between electron and holes and also bimolecular recombination [14].

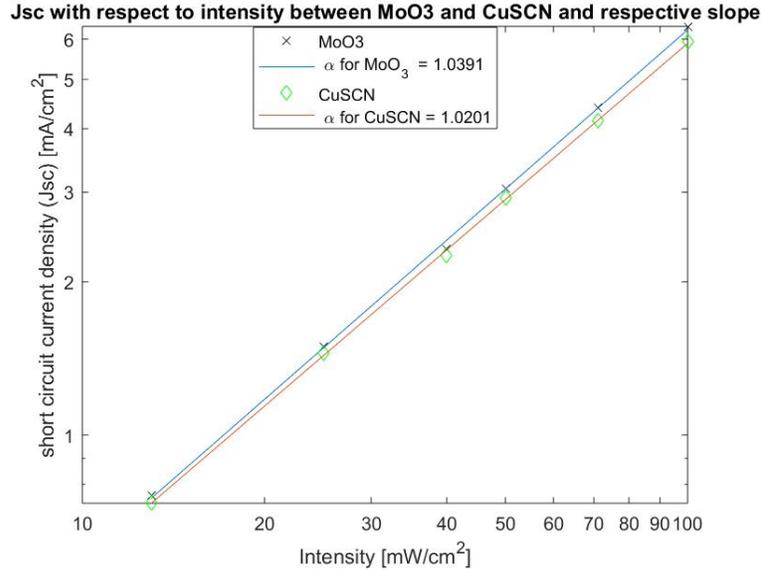


Figure 13: Power law dependence  $J_{sc} \propto I^\alpha$  and line regression fitting for both HTLs, in order to find recombination states under short circuit conditions.

It is therefore highly likely that both HTLs experience a weak bimolecular recombination under short circuit current density conditions. It can therefore be concluded that a monomolecular recombination is dominant under short circuit conditions for both solar cells with different HTLs. However under open circuit conditions as previously discussed, bimolecular recombination is dominant for both solar cells, slightly more dominant for the solar cell with CuSCN compared to the solar cell with MoO<sub>3</sub>. This is compatible with

previous findings that monomolecular recombination evolve into bimolecular recombination when passing the MPP [14], see Figure 5.

## 5 Conclusion

In this study, I-V measurements were performed to give insight to different states of recombination. It was found that the organic solar cell with MoO<sub>3</sub> as the HTL possesses a higher current density in both the reverse region and forward region. The higher current density in both regions points towards a less successful blocking of electrons travelling to the anode (reverse region) and a better ability to transport holes from the active layer to the anode. Knowledge of different recombination mechanism was found when  $V_{oc}$  was plotted as a function of the natural logarithmic of light intensity. Both solar cells experienced bimolecular recombination under open circuit conditions. However, the solar cell with the CuSCN HTL had a slope value closer to one unity  $\frac{kT}{q}$ , which indicated a more dominated bimolecular recombination.  $J_{sc}$  as a function of light intensity was also plotted and showed an  $\alpha$  close to unity for both solar cells. This points towards a monomolecular recombination. Both solar cells therefore experienced a monomolecular recombination under short circuit conditions, which evolved into bimolecular recombination when it passed the *MPP*.

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## Appendix

### Dark current plot example.

```
clear all [v1,T1,vT1] = xlsread('Samp2_MoO3_voltage_current.xlsx') ;
t1=v1(:,1); % X-axis, voltage, 1 means the first column that have numbers in
it. y1=abs(v1(:,6)); % Dark current, column 6

[v2,T2,vT2] = xlsread('Samp8_CuSCN_voltage_current.xlsx') ; %Import
t2=v2(:,1); % X-axis, voltage, 1 means the first column that have numbers in
it. y2=abs(v2(:,6)); % Dark current, column 6

figure

semilogy(t1,y1,'k-',t2,y2,'g-')
legend('MoO3','CuSCN')

xlim([-0.5 1.5]);

xlabel('Applied bias');
ylabel('Current density');
title('Dark current comparison between MoO3 and CuSCN')
```

### current density with respect to voltage plot example.

```
[v,T,vT] = xlsread('MoO3_voltage_current.xlsx') ; t=v(:,1); % X-axis,
voltage, 1 means the first column that have numbers in it.

y1=v(:,6); % Dark current, column 6
y2=v(:,12); % 1 Sun
y3=v(:,18); % 0.71 sun
y4=v(:,24); % 0.50 Sun
y5=v(:,30); % 0.40 sun
y6=v(:,36); % 0.25 sun
y7=v(:,42); % 0.13 sun

plot(t,y1,'k-.x',t,y2,'-+',t,y3,'-o',t,y4,'-*',t,y5,'-s',t,y6,'->',t,y7,'-p')
legend('Dark current','1 sun','0.71 sun','0.5 sun','0.4 sun','0.25 sun','0.13
sun')
xlabel('Voltage');
ylabel('Current density');
yticks(-7:1:5);
xlim([0 1.2]);
ylim([-7 5]);
title('MoO3; current density with respect to voltage')
```

### Voc with respect to light intensity plot using polynomial fit.

```
clear all
%Minstakvadratanpassning med polynom av grad 1
[v1,T1,vT1] =
xlsread('Samp2_Voc_Jsc_FF_PCE_reg.xlsx'); %import
t1=(v1(:,1))*100; % X-axis, log values of the intensity
y1=v1(:,2); % Y-axis, Voc values from second coloumn p1 =
polyfit(log(t1),y1,1); %Polyfit med polynom av grad ett.
x=10:0.01:100; % X values for least square method
y3=p1(1).*log(x)+p1(2); % equation for least square method

[v2,T2,vT2] =
xlsread('Samp8_Voc_Jsc_FF_PCE_reg.xlsx'); %Import
t2=(v2(:,1))*100; % X-axis, log values of the intensity y2 =
v2(:,2); % Y-axis, Voc values from second coloumn p2 =
polyfit(log(t2),y2,1); %Polyfit med polynom av grad ett.
x=10:0.01:100; % X values for least square method
y4 =p2(1).*log(x)+p2(2); % equation for least square method

figure
semilogx(t1,y1,'k x',t2,y2,'g d',x,y3,x,y4); %plot logarithmic x-axis
xlim([10 100]); %Limit of the x axis
set(gca, 'XTick', 10:10:100); %How many values on axis axis

%plot(t1,y1,'k-x',t2,y2,'g-x')
slope1 = (p1(1).*1.602*10^-19)/((273.15+25)*1.381*10^-23)
slope2 = (p2(1).*1.602*10^-19)/((273.15+25)*1.381*10^-23)
xlabel('Intensity [mw/cm^2]');
ylabel('Open circuit voltage (Voc)');
s1 = num2str(slope1)
s2 = num2str(slope2)
legend('MoO3','CuSCN',['slope = ' s1 ' kT/q'],['Slope = ' s2 ' kT/q'])
title('Voc with respect to intensity between MoO3 and CuSCN and respective slope')
```

### Jsc with respect to light intensity plot using power law.

```
clear all
%Minstakvadratanpassning med Jsc=I^(alpha)
[v1] = xlsread('Samp2_Voc_Jsc_FF_PCE_reg.xlsx'); %import
t1=((v1(:,1))*100) % X-axis, log values of the intensity
y1=v1(:,4) % Y-axis, Jsc values from fourth coloumn (mA)
%We then solve the system by taking ln on both side resulting
in %Jsc = a*I^b, log on both sides gives log(Jsc)=log(a)+b*log(I)
%Ax=b => x=A\b
A1=log10(t1) %log10 on the x axis
B=log10(y1) %log10 on the y axis
i=1
for i = 1:length(A1)
    A(i,1)=(1);
    A(i,2)=(A1(i));
    i=i+1;
end x=A\B
a1 = x(1) % log(a)
b1 = x(2) %slope
```

```

a=10.^(a1)
h=@(t)(a.*t.^(b1));
t=13:1:100;
z=h(t);
%
[v2] = xlsread('Samp8_Voc_Jsc_FF_PCE_reg.xlsx') ;
t2=((v2(:,1))*100)
y2=v2(:,4)
A2=log10(t2) %log10 on the x axis
B2=log10(y2) %log10 on the y axis
i=1
for i = 1:length(A2)
    A3(i,1)=(1);
    A3(i,2)=(A2(i));
    i=i+1;
end
x2=A3\B2
a2 = x2(1) % log(a2)
b2 = x2(2) %slope
a3=10.^(a2)
h=@(t)(a3.*t.^(b2));
t=13:1:100;
z2=h(t);
figure s1 =
num2str(b1) s2
= num2str(b2)
loglog(t1,y1,'k x',t,z,t2,y2,'g d',t,z2);
set(gca, 'XTick', 0:10:100); %How many values on axis axis
set(gca, 'YTick', 0:1:10); %How many values on axis axis
xlabel('Intensity [mW/cm^2]');
ylabel('short circuit current density (Jsc) [mA/cm^2]');
legend('MoO3', [' \alpha for MoO_{3} = ' s1], 'CuSCN', [' \alpha for CuSCN = '
s2]); title('Jsc with respect to intensity between MoO3 and CuSCN and respective
slope')

```

### Extraction of diode parameters.

```
%CuSCN values
Jcuscn = [0.189206967 0.5932605 1.567883917 3.3895575 6.327640833 10.64673583
          16.52516167 24.01187 33.02614167 43.36011667 54.78553333 67.01779167
          79.59951667
          91.07906667]; Vcuscn = [0.85 0.9 0.95 1 1.05 1.1 1.15 1.2 1.25 1.3
          1.35 1.4 1.45 1.5];
fun = @(c,Jcuscn) Jcuscn*c(1)+ 0.02585*c(2)*log(1+Jcuscn/c(3));
c0 = [1, 1^-5, 0.001];
c = lsqcurvefit(fun,c0,Jcuscn,Vcuscn)
Rs =
c(1)*1000 n=
c(2) j0 =
c(3)
%MoO3 values
Jmo03 = [0.087519125 0.111304763 0.153017706 0.273144381 0.788003625 2.94387625
          8.84430375 18.66948813 31.05695625 44.96064375 59.8176 75.336225 91.3553
          107.7357313 124.3928 141.2399625 158.0993438 174.5704313];
```

```
Vmo03 = [0.65 0.7 0.75 0.8 0.85 0.9 0.95 1 1.05 1.1 1.15 1.2 1.25
          1.3 1.35 1.4 1.45 1.5];
fun2 = @(m,Jmo03) Jmo03*m(1)+ 0.02585*m(2)*log(1+Jmo03/m(3));
m0 = [1, 1^-5, 0.001];
m = lsqcurvefit(fun2,m0,Jmo03,Vmo03)
Rs2 =
m(1)*1000 n2=
m(2) j02 =
m(3)
Cu = ['CuSCN values: Rs = ',num2str(Rs), ' n = ',
      num2str(n), ' j0 = ', num2str(j0)];
disp(Cu)
Mo = ['MoO3 values: Rs = ',num2str(Rs2), ' n = ',
      num2str(n2), ' j0 = ', num2str(j02)];
disp(Mo)
```