

ORGANIC SINGLE CRYSTAL FOR SOLAR CELL APPLICATIONS

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ABSTRACT

Organic Single Crystals of two materials have been grown in this research. P-type Rubrene, 5,6,11,12-tetraphenylnaphthacene, single crystals were *cm*-sized. N-type PDI-FCN₂, fluoroalkylated dicyanoperylene-3,4:9,10-bis(dicarboximides), single crystals were *mm*-sized. Photodiode devices have been fabricated using Rubrene as single layer device with asymmetric work-function electrodes. A bilayer structure with Rubrene and PDI-FCN₂ with asymmetric work-function electrodes has been fabricated to obtain solar cell behavior. The bottom electrodes were modified with a thin organic layer, which can reduce the electrode work-function. For all device configurations, photoactive behavior has been observed. A bottom electrode of silver modified with PEI has got the best photodiode characteristics. For the bilayer structure a small short-circuit current and open-circuit voltage has been observed. Nevertheless, the shifts were too small to call it solar cell behavior.

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1. INTRODUCTION

1.1 SOLAR ENERGY

The search for alternative energy source began, since people became more aware for the exhaustion of fossil fuels in the near-future. Solar, wind and nuclear energy are among the most promising energy sources to be utilized, besides the new unconventional usage of fossil fuels, like oil-sands, shale gas and coals. In the last decade, the use of solar energy as energy supply start to increase drastically.

Besides the problem with the exhaustion of the fossil fuels, the environmental effects of the fuel usage also became an important concern. The emission of carbon dioxide (CO_2) from burning the fossil fuel gives dramatical effect on the earth's atmosphere, which became the main cause for the global warming. CO_2 forms a thick blanket around the Earth's surface. When sunlight reaches the Earth's surface, it cannot escape on its way back. Therefore, a so-called 'Greenhouse'-effect occurs.

The utilization of solar energy provide a huge spectrum of advantages. Besides that solar energy is a 'green' energy (with 'zero' CO_2 -emission), the way to use it is also nice. People do not need to be connected to the central grid of a city or area. They are totally independent in producing their energy supply. Moreover, electricity also can be possible in inhospitable places in the world (figure 1). Therefore, solar cell research has gained a lot of interest in the last years. Scientists want to produce low-costs solar cells with high efficiency and lifetime.

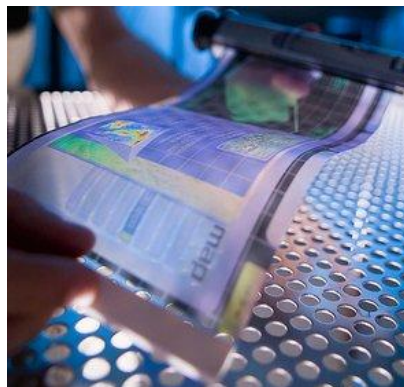


Figure 1. The independency of solar cells is a great advantage for energy generation in more places.[†]

[†] http://www.copper.org/publications/newsletters/innovations/2007/05/solar_energy.html (June, 2012)

1.2 ORGANIC ELECTRONICS

In the last decade, the research on organic electronics has start to flourish significantly, because of their prospects to provide huge advantages compared with the traditional inorganic electronics. Organic electronic devices can be made flexible and light-weight. Figure 2 shows an organic flexible display, which can be used in future for wearable molecular computers.



*Figure 2. Flexible organic displays are already fabricated**

So far, most focus on organic materials are on the applications for Organic Field-Effect Transistor (OFET) and Organic Light-Emitting Diode (OLED). OFET of Rubrene single crystal has shown carrier mobility of $20\text{-}40\text{ cm}^2/\text{Vs}$, comparable to the value of amorphous silicon transistor. On the other hand, OLED, a device that can emit light due to an electric current (electroluminescence), is of great interest, since their potential for low cost displays and lightings in the future. Recently, it has been reported that OLED can have 100% quantum efficiency. Therefore, OLED televisions have better performance than plasma or LCD-televitions. In 2008 Sony released the World's first commercial available OLED television. Meanwhile, some companies such as Philips start to release OLED lightings to the market.

Because organic materials can have very high absorption coefficients, the production of thin optoelectronic devices is possible. This requires much less material and can lead to cheaper devices. Moreover, organic solar cells can be made flexible and light-weight. The large-scale production of organic solar cells can be also more easily than for the traditional silicon-based cells, which also leads to cheaper products [12]. The biggest challenge for organic solar cells is the relative low efficiency, because carrier mobility is relatively low and charge carriers are difficult to dissociate. Organic materials have relative high band gap, which is an important property for the device performance. Impurities should be as low as possible in organic materials, because this also can lead to efficiency limitations. Despite, the promising status of organic photovoltaics in the future, research on stability of devices due to reduction and oxidation of the organic materials is still lacking.

Nevertheless, the record efficiency for OSC claimed to be 10,7% by Heliateg[‡], based on a so-called tandem solar cell. This is a solar cell based on two separate active organic layers, connected in series with each other. OSC's did not reach yet power conversion efficiencies of 15-20% for

[‡] <http://www.gizmag.com/heliateg-organic-solar-cell-efficiency-record/22358/>

inorganic solar cells, but researchers think that OSC's can reach 15% in the near-future. The problem with the values of carrier mobility is still the most important issue to be addressed, since most of the organic solar cell only rely on organic thin film. By far, organic single crystals are still not well explored for this purpose, despite their high carrier mobility.

1.3 OUTLINE

In this research we are going to fabricate photovoltaic devices based on organic single crystals. Rubrene and PDI-FCN₂ are the materials we use to grow organic single crystal using Physical Vapor Transport (PVT). We try to make different device configuration like single layer devices and bilayer devices to obtain photovoltaic processes which can lead to solar cell applications.

2. THEORETICAL BACKGROUND

2.1 SEMICONDUCTOR THEORY

Solar cells are based on a piece of semiconductor material, which makes photo voltage and photocurrent generation possible. Therefore, the understanding of semiconductor physics is necessary to establish an underlying principle to fabricate solar cells. A semiconductor can behave like insulator or conductor in different situations. The highest energy band in which an electron is bound is called the valence band. The lowest energy band towards which an electron can be excited is called the conduction band. There are no allowed energy levels inside the material's band gap, therefore the band gap is often called the forbidden energy gap. Silicon is the most common semiconductor because it is one of the most common materials in nature[§]. When a bound electron is excited by a photon with energy higher than the material's band gap ($E_{\text{photon}} \geq E_g$), electron is excited to the conduction band and hole is formed. The formed electron and hole can move through the solid and contribute to the conductivity of the material (figure 3).

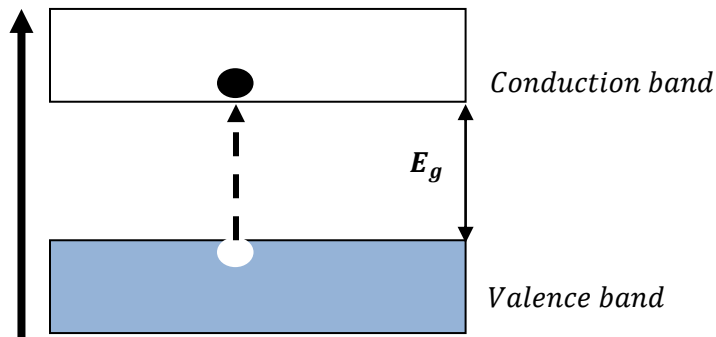


Figure 3. Schematic of semiconductor principle. Electrons can overcome the forbidden energy gap (band gap) due to photon or phonon absorption. The conductivity can be controlled by these processes.

[§] Wikipedia, 'Silicon' (July 2012)

2.1.1 ORGANIC SEMICONDUCTOR

The main differences in organic semiconductor compared to inorganic, is the formation of a strong exciton (bound excitation) in organic semiconductors, rather than a free electron/hole pair in inorganic semiconductors [15]. The first developments in using organic materials for semiconductor applications started with melanin [20]. Later, it was also possible to synthesize semiconductor polymers. The semiconductor properties of organic materials relies on the hybridization of the atomic orbital's [1]. The electronic configuration of carbon, which is the main backbone-atom of an organic molecule, is $[2s^2 2p^2]$. In this configuration only 2 valence electrons could make chemical bonds. Orbital hybridization means that the last four orbital's of carbon are mixed up and make four different orbital's: sp^3 -, sp^2 - or sp^1 -hybridization. The sp^2 hybridization allows one double bond per carbon atom. This is the overlap of 2 p-orbital's across a single σ -bond. When we have a polymer with alternating single and double bonds (figure 4), the π -electrons are no longer restricted to a single atom but rather to a group of atoms. Materials based on this sp^2 hybridization are called conjugated polymers. In organic semiconductor, the semiconducting properties originate from a conjugated system in an organic material, because the double ' π '-bonds (1,5-3,0 eV) are significantly weaker than the single ' σ '-bonds ($>6,0$ eV) in sp^1 -hybridization [2].

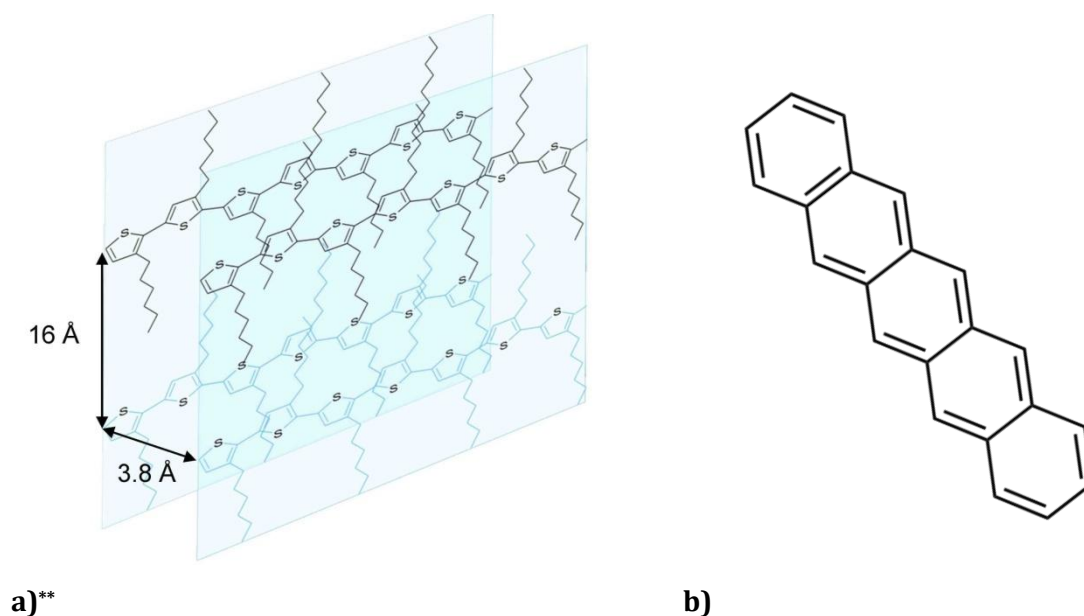


Figure 4. a) Examples of semiconductor a) polymers and b) small molecules (pentacene). Clearly it can be seen that most molecule have in common a conjugated system [2].

** <http://www.phys.umontreal.ca/~silva/pmwiki/uploads/Main/lamella.jpg>

In the ground state at $T=0\text{ K}$, the electrons in a small molecule or polymer fill the orbital's only until the Highest Occupied Molecular Orbital (HOMO). There can be two electrons with opposite spin (Pauli Exclusion Principle) for each orbital. The HOMO and the Lowest Unoccupied Molecular Orbital (LUMO) are very important concept for the semiconducting properties of the organic material, since they act in similar manner as valence and conduction bands in inorganic material.

When light is absorbed, electron can excite from the HOMO to the LUMO of the material, to form an exciton. The light absorption, exciton creation and several possible exciton decay processes are illustrated in figure 5. When an absorbed photon energy is higher than the material's band gap, the excited electron undergo non-radiative decay giving up energy to the surroundings. When the exciton reaches S_1 or T_1 , it can decay radiative (fluorescence or phosphorescence). However, if we can dissociate this exciton before it decays, a photovoltaic and photocurrent can be generated.

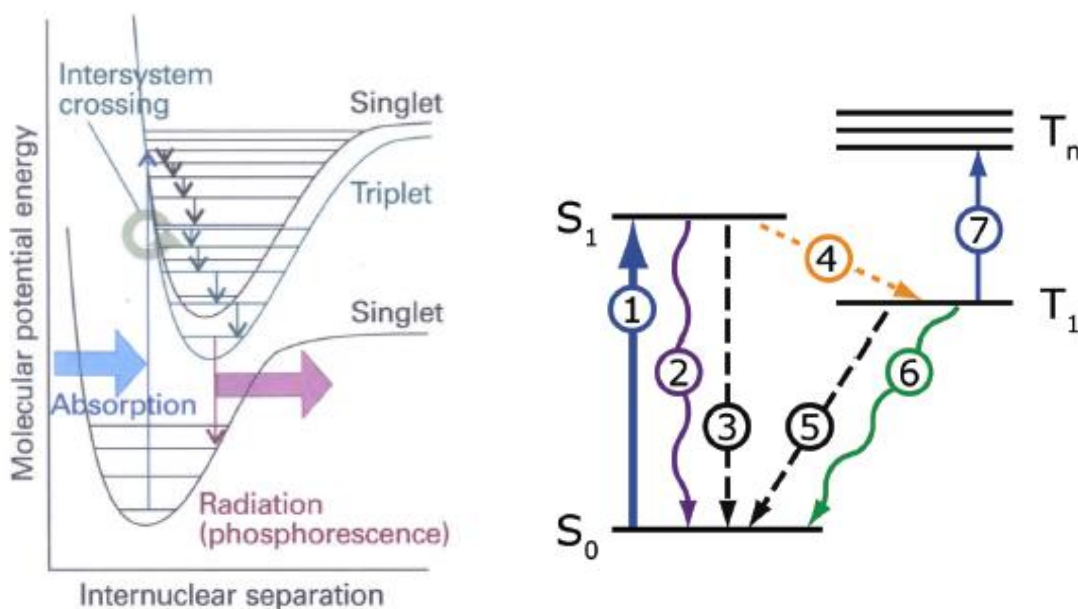


Figure 5. 1) Absorption of photon leading to $S_0 \rightarrow S_1$ transition; 2) and 3) Radiative (fluorescence) and non-radiative decay from $S_1 \rightarrow S_0$; 4) Intersystem crossing $S_1 \rightarrow T_1$; 5) and 6) Radiative (phosphorescence) and non-radiative decay from $T_1 \rightarrow S_0$;

2.2 ORGANIC PHOTOACTIVE DEVICES

The basic principle of photoactive devices like Solar Cells and Photodiodes Diodes, are based on the absorption of photons leading to excited electrons. There are four main steps in converting the photon's energy to electrical energy in the form of photocurrent and/or photo voltage.

2.2.1 WORKING PRINCIPLE

i) Absorption

The first requirement for a good operating photoactive device is a high absorption of photons. The main advantage of the organic materials is the high absorption coefficient ($\sim 10^5/cm$) in the visible part of the solar spectrum, which is sufficient for the fabrication of very thin devices ($\sim 0,1-1\mu m$) [4]. To obtain the same absorbance, a silicon solar cell should be two orders of magnitude thicker. That is the reason why the single crystalline silicon solar cell always looks bulky. This absorption property can reduce the costs of the device because less material is necessary. The band gap for well investigated organic semiconductors materials for OLEDs and OFETs are typically $>2,0eV$. For solar cell applications this is not ideal, because the optimal band gap for efficient absorption of the solar spectrum, lies at $1,1eV$ [3]. Nevertheless, organic materials are synthesizable and constant improvements of semiconducting material design can be achieved.

ii) Exciton diffusion

When an electron is excited to the Lowest Unoccupied Molecular Orbital (LUMO), it leaves a vacant position, called an hole, in the Highest Occupied Molecular Orbital (HOMO). In particular for organic materials, the formed electron-hole pair is electrostatically bound (exciton). This exciton can be seen as an uncharged semi-particle. An exciton can dissociate or decay. Dissociation takes place as the exciton is able to reach a region where there is an electric field to break it up to become charges. Exciton decay takes place as the exciton cannot reach the dissociation site and the electron goes back to the ground state by releasing the energy radiative or non-radiative. Due to defects, impurities or traps in the bulk material, excitons can decay non radiative at energy levels within the band gap. If we assume that there are no such traps in the material, electrons can fall back to the HOMO band-to-band with the emission of a photon. The decay of singlet excitons and triplet excitons leads to fluorescence and phosphorescence, respectively, which have been described before. For Solar Cell triplet excitons are preferred because phosphorescence is a relative long process compared to fluorescence. Now the exciton has longer time to dissociate before it recombines.

The length an exciton can travel before it decays, is called the exciton diffusion length, and is typically 10-100nm for polymers and dyes thin film. This short exciton diffusion length can limit dramatically the thickness of the photoactive device, which results in lower absorption [5].

iii) Exciton dissociation

The exciton have to be separated in free electron and holes, to produce photocurrent and-voltage. In single layer devices, called often Metal-Semiconductor (MS) devices, this typically occurs at the metal-semiconductor (MS) interface. In bilayer devices, this happens at a donor/acceptor interface. There is high local electric field at such interfaces which can break up the Coulombian bound excitons.

iv) Charge collection

When the exciton dissociates, the free electron and hole have to be collected at the electrodes to produce photocurrent. It is important to choose organic materials with good charge carrier transport properties and metal electrodes with well-matched work functions in respect to the semiconductor HOMO or LUMO level. The charge transport is dominated by the charge carrier mobility μ . This is the ability of an electron/hole to move through a certain electric field.

2.2.2 SOLAR CELL DEVICE ARCHITECTURES

In general, it can be said that a solar cell absorbs incident photons, create voltage and generate current. This can be realized when a p-n junction of semiconductors is formed. A solar cell does not need an external power supply. The generated photocurrent passes through an external load to generate power [2]. In this part, the principles of two different possible devices will be explained: the Schottky diode and the Bilayer Heterojunction.

When a semiconductor is sandwiched in between two metal electrodes of different work function (energy needed to remove an electron from a metal atom), as so-called Schottky Barrier is formed at the interface of at least one of the MS-junction. The difference between the lower-work function electrode and the LUMO of the organic material determines the barrier height for the electron. For holes this works the other way around: the difference between the higher-work function and the HOMO of the organic materials determines the barrier height. A Schottky diode obtains its rectifying behavior due to the formed Schottky barrier at this interface. If we look at the band scheme from one side of a single layer device (figure 6), we can see that band bending occurs

at the MS-interface which results in the formation of the Schottky barrier. The energy bands can bend when two materials of different work-function come in contact. At the interface between these materials charge carriers can exchange from one side to the other, changing their energy. This results in local band bending near the junction or interface.

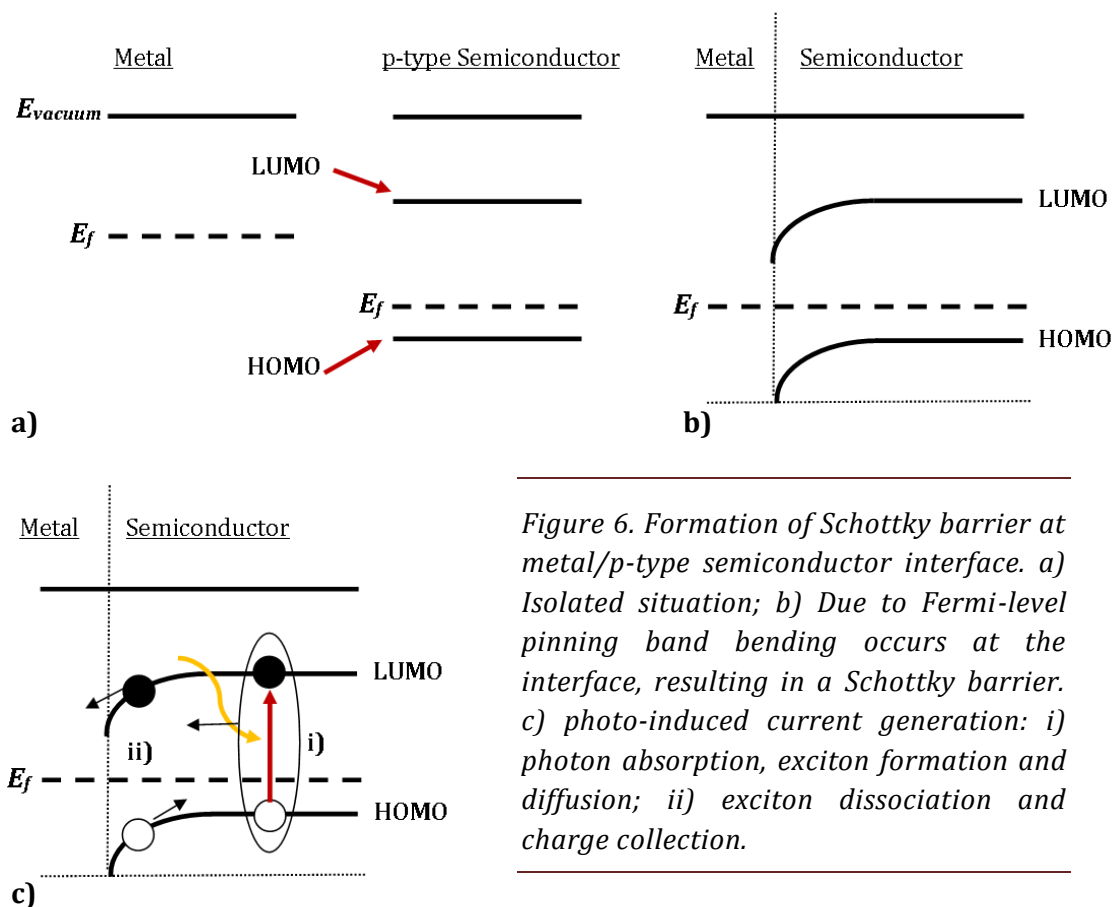


Figure 6. Formation of Schottky barrier at metal/p-type semiconductor interface. a) Isolated situation; b) Due to Fermi-level pinning band bending occurs at the interface, resulting in a Schottky barrier. c) photo-induced current generation: i) photon absorption, exciton formation and diffusion; ii) exciton dissociation and charge collection.

When excitons are generated in the semiconductor, some of them diffuse to the depletion zone at the MS-interface. Electrons can be collected at the metal on the left, holes can travel to the other electrode, which is normally assumed to be Ohmic. Such devices are normally not suitable for solar cells, because often the barrier is too small to break up the excitons. Moreover, both types of charge carriers travel through the same material, which results in high self-recombination rates [5]. Nevertheless, it is possible to get some photovoltaic response but the power conversion efficiencies are low [6]. Schottky diodes are useful in many sensors, like the usage as detector or mixer in RF (Radio Frequency)-applications, because of their high switching speeds^{††}.

More efficient solar cells can be realized using a donor/acceptor heterojunction. The principle of this configuration is more less the same as the well-known p-n junctions used in most

^{††} Wikipedia, 'Schottky diode' and 'Schottky barrier' (July 2012)

inorganic solar cells. In p-n junctions, photon absorption leads directly to free electron and hole formation in the same material around the space charge layer. They can move in a built-in electric field (due to n-type and p-type materials). In organic heterojunction solar cells, photon absorption leads to the formation of an exciton. The charge dissociation takes place at the donor/acceptor interface (figure 7). The electron and hole are formed (after dissociation) in different materials (donor and acceptor) (figure 8). The former is a good hole conductor and the latter a good electron conductor. The built-in electric field at the charge dissociation site is generally stronger than the Schottky barrier in the metal/semiconductor device. Therefore, more exciton dissociation and charge collection at the electrode can occur. The work function should match the HOMO and the LUMO of the donor and acceptor material. Since most common metals like aluminum and silver have a pristine work function $>4.0\text{eV}$, modification of these electrodes can be useful to lower this work function if the acceptor has a low LUMO like rubrene, which is 3.1eV . Pristine low-work function metals like calcium and magnesium are also possible, but very unstable and difficult to work with.##

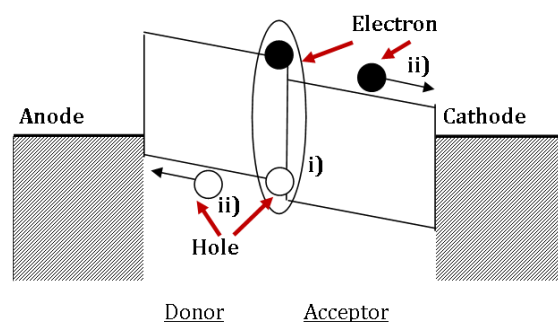


Figure 7. Band scheme of heterojunction. i) Excitons are formed in the bulk material and diffuse to the donor/acceptor interface; ii) At the D/A-interface the excitons are dissociated and the free electron and hole are collected at the cathode (electrons) and anode (holes).

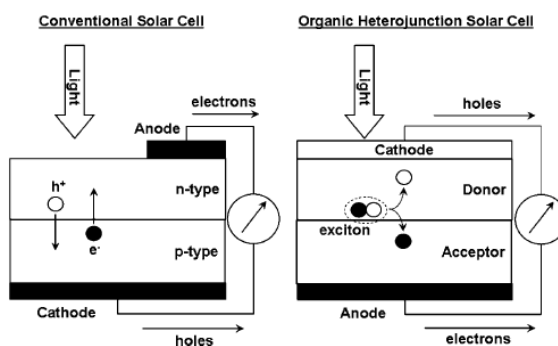


Figure 8. Conventional (inorganic) p-n junction solar cell (left) compared to an Organic bilayer solar cell (right).

Wikipedia, 'Calcium' (August 2012)

2.3 MOLECULAR SINGLE CRYSTALS

Organic single crystals are organic solids with a periodic arrangement of the molecules or polymers. Because this highly ordered structure, single crystals have lower numbers of traps, defects or dislocations compared with amorphous or polycrystalline materials [7]. The major advantage of single crystals are the nice intrinsic properties for device performance.

2.3.1 RUBRENE

Rubrene is a strong red-emitting molecule which is a very promising aromatic polycyclic HC (figure 9) for organic electronic devices. Especially Organic Light Emitting Diode (OLED) and OFET applications based on Rubrene are widely used. Besides, Rubrene in single crystal form is the organic semiconductor with the highest reported hole mobility [8] for organic materials (20-40 cm^2/Vs). Moreover, high quantum efficiency can be achieved for Rubrene molecules [21]. Recently, Najafov *et al.* found that Rubrene single crystal have exciton diffusion length in micrometer scale [9], which attracts interest for the exploration of its usage in organic solar cells.

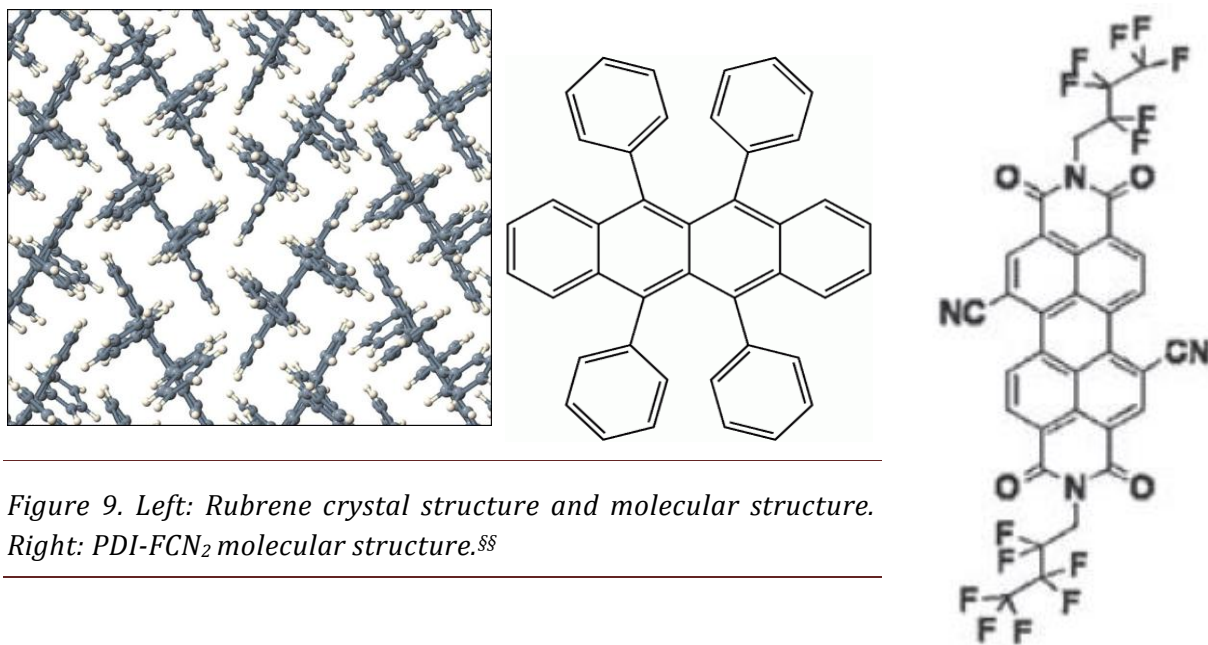


Figure 9. Left: Rubrene crystal structure and molecular structure. Right: PDI-FCN₂ molecular structure.^{§§}

2.3.2 PDI – FCN₂

High quality acceptor organic materials (n-type) are hard to obtain compared to donor (p-type) materials such as Rubrene [10]. N-type organic materials are weakly soluble in common organic solvents, which makes device fabrication, like transistors, difficult [17]. Moreover, stable n-type materials, which means consistent to air and water, are quite rare. Water and oxygen can accept

^{§§} <http://www.physics.ntua.gr/~tsetseris/orgel.html>

electrons from the semiconductor molecule due to matching the LUMO of the semiconductor. Therefore, n-type material with deeper LUMO level are necessary to avoid this effect. The best-known mobility for electron transport is achieved in an Organic Field-Effect Transistor (OFET) with PDI-FCN₂ (figure 9) single crystals [11], which is 2-5 cm²/Vs. Thin single crystals were grown by Physical Vapor Transport, which were stable in ambient operating conditions [11]. The high electron mobility and ease of producing PDI-FCN₂ single crystal, makes this material suitable for this research.

2.4 OVERVIEW OF THESIS

Organic single crystals are grown using the PVT-technique. Several device structures are fabricated and measured. Because of the high periodic arrangement of organic single crystal high exciton diffusion length and carrier mobility are expected leading to good device performance. Schottky devices using Rubrene (p-type) and heterojunction structure with PDI-FCN₂ (n-type) are made with several bottom electrode. I-V characteristics are measured, analyzed and explained.

3. METHODOLOGY AND EXPERIMENTAL

3.1 CRYSTAL GROWTH

In this study, the growing of the single crystals was done using Physical Vapor Transport (PVT)-method, which was introduced by R.A. Laudise *et al* [12]. The working principle of PVT is as follows: a powder is sublimating in the 'hot zone' of a glass tube. With the help of carrier gas (argon), the sublimed molecules are transported under a certain temperature-gradient to the 'cold zone' of the tube. The tube is heated by a metal heating filament coiled around the tube. The difference in coil density can tune the temperature gradient in the horizontal direction. The temperature is regulated by a thermal controller in combination with a single thermocouple at the hot zone of the tube. A sketch of the principle can be seen in the figure 10.

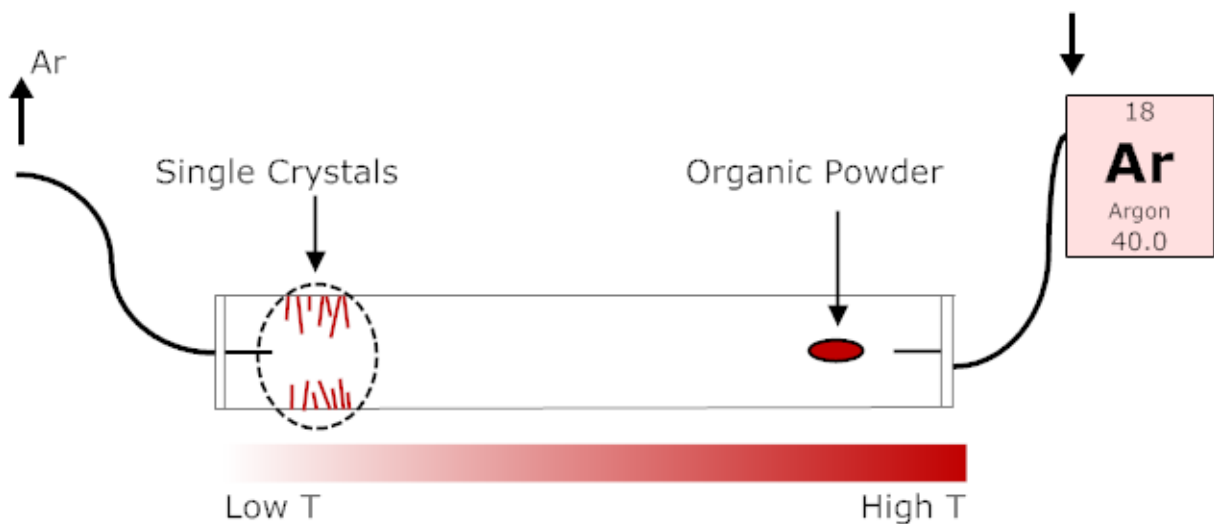


Figure 10. Physical Vapor Transport (PVT). A organic powder is sublimed under a certain temperature gradient. With the use of a carrier gas there occurs crystal growing at the cold-end of the tube.

The forced convection, due to the carrier gas, does not really transport the sublimed molecules itself. However, the buoyancy driven convection, which is the result of horizontal temperature gradient, dominates over the forced convection to transport the molecules. The approximate velocity of the carrier gas is much smaller than the natural convection. Nevertheless, the carrier gas is essential in PVT, because of the local low-pressure it creates at the powder surface, which leads to sublimation. Moreover, it can remove impurities and eventual-decomposed molecules of the source, before they can affect the single crystals quality [12]. In this research a gas-

flow of 40-60 *ml/min* was used. There were no big differences in crystal quality and size with variable gas-flow.

Compared with alternative crystal growth methods, the merit of PVT is the free standing growth of crystals without any substrate. For example, solution-based crystal growth, crystals grow directly on substrates.

3.1.1 TEMPERATURE-REGIME

Like the flow of the carrier gas, the temperature at the crucible and the temperature gradient are of great importance. A well-matched subliming temperature has to be used, in order that the organic powder totally sublimed with minimum amount of decomposition [12]. The temperature gradient limits the diffusion through the tube and takes the impurities away from the growing-region, because of the lower/higher sublimation temperature of the impurities [13]. For Rubrene optimum growth-temperature was 310K and for PDI-FCN₂ 308K. This temperature is measured between the inner and outer tube, resulting in a slightly higher optimum value as in literature, because the organic powder itself is placed inside the inner tube and no temperature measurements have been done inside the inner tube. Lower or higher temperature led to decreased or no total crystal area at all. Single crystal at optimum growth temperature were big, thin platelets in *cm*-scale for Rubrene (figure 11) and small, thin foil-like crystal for the PDI-FCN₂.

3.1.2 CRYSTAL QUALITY

The main advantage of PVT is the relative high purity of the single crystal. This is demonstrated in several field-effect transistors (FET's) based on organic single crystal [16], since intrinsic charge transport can be realized. Impurities and imperfections in the organic powder can be physically removed from the powder as described before. This effect can be seen clearly in Rubrene single crystals, where large exciton diffusion lengths are measured [9]. With PVT, it is also possible to grow mm-sized (sometimes cm-sized) single crystals. The relative big size of the crystals is a main advantage in processing them in device fabrication. The ultra-flatness of the single crystal surface is a nice property for making nice metal/semiconductor or organic/organic interfaces.

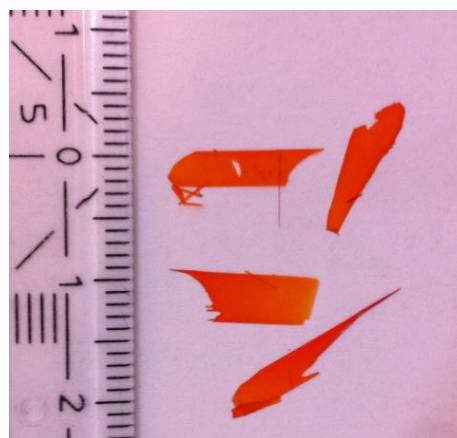


Figure 11. mm-sized Rubrene single crystals grown by Physical Vapour Transport.

3.2 DEVICE FABRICATION

The device build-up consist out of bottom substrate with electrode, single crystal(s) and top electrode. The electrodes are working as electron or hole collector. Especially the lamination of the single crystal has to been done carefully, because picking up and laminating the fragile crystal is very difficult. In each following section the fabrication, cleaning and processing of the different device parts is described.

3.2.1 SUBSTRATES PREPARATION AND ELECTRODES FABRICATION

The bottom electrodes are evaporated on top of glass substrates. These substrates are ultra-cleaned before lamination of the single crystals take place. Firstly, the substrates are immersed after each other in acetone and isopropanol. The immersed substrates stayed for 10 minutes in the ultrasonic cleaner. This machine consists out of a water container, to which ultrasonic waves are generated. The solvent can remove contaminants from the surface of the substrate.

After substrate washing with organic solvents, the remaining droplets of the chemical residues were removed with nitrogen stream. For 30 minutes the substrates were dried in an oven at 120°C. Finally, the substrates were treated in an UV-ozon-plasma cleaner for 10 minutes. In the plasma cleaner, the oxygen inside becomes ionized due high voltage at low-pressure (in the order of 1/1000 atmosphere). The VUV-light (vacuum ultra-violet light) breaks most of the covalent, organic bonds on the substrate surface. UV emission is emitted from the cleaner. The remaining organic molecules react with the formed oxygen species in the plasma, like O_3 , O_2^- , O_2^+ and free resulted electrons, to decompose and form the molecules H_2O and CO_2 . These molecules are evacuated during the cleaning process by continuous vacuuming.

Aluminum and Silver bottom electrodes are evaporated as thin layer ($\sim 100nm$) on top of the glass substrates. The evaporator works at very low-pressure ($P < 10^{-6} bar$). The evaporation rate was $1 \text{ \AA} \cdot s^{-1}$ and the substrate was rotated at 30 rpm to ensure the quality of the metal film. On the other hand, the ITO (Indium-Tin oxide) bottom electrode has been prefabricated, , so only cleaning was needed.

3.2.2 SURFACE MODIFICATION OF THE ELECTRODE

The ultra-clean bottom electrodes are modified with polyethylenimine (PEI) or polyethylenimine ethoxylated (PEIE) (figure 12). Recently, these thin polymer modification layers are known to reduce the electrode's work function [14]. The work function of a metal is the energy needed to remove an electron from a metallic atom ($W = E_{vac} - E_f$). For Schottky devices, as described in the introduction, the work function of one electrode determines the height of the Schottky barrier. For a bilayer device, the work function of both electrodes need to match the HOMO of the donor and the LUMO of the acceptor molecule as good as possible, leading to more efficient charge extraction, for case of photovoltaic operation, and injection, for the case of diode.

The PEIE was dissolved in water with a concentration of 35-40 wt%. This solution was further diluted with 2-methoxyethanol till a concentration of 0,4 wt%. On the other hand, PEI was dissolved also in methoxyethanol till a concentration of 0,4 wt%.

The modification layer is deposited using spin coating. The substrate is placed in a holder, and an excessive amount of solution is placed on top. Due to the high rotation velocity of the spin coater, the solution is spread out uniformly on the substrate because of the centrifugal force. The velocity and acceleration rate determine the layer thickness. For the PEI/PEIE layers the velocity was 5000 rpm and the acceleration rate 1000 rpm/s, leading to a target layer thickness of $\sim 10\text{nm}$ [14]. The main advantage of spin coating is the property that the deposited layer is uniform in thickness. For this research, this is a crucial factor since a good lamination of the single crystals on the electrode is required.

3.2.3 CRYSTAL LAMINATION

The grown organic crystals now can be laminated on the modified electrodes. Because of the small size ($10\text{-}50\text{nm}^2$) and thickness ($150\text{nm}\text{-}5\mu\text{m}$) of the crystals as well as the delicate nature of the crystal, it is important to be very careful during the storage, transport and lamination. The

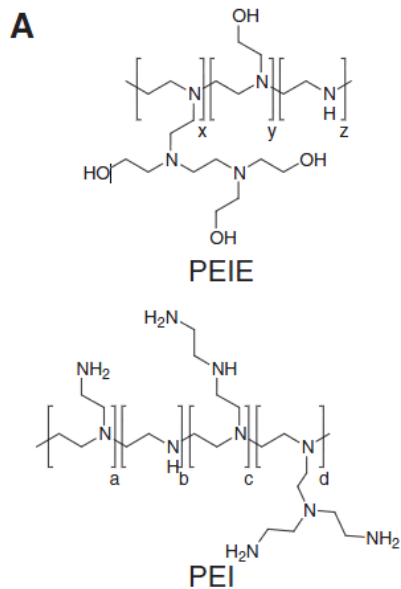


Figure 12. Molecule structure of PEI and PEIE [14].

evacuation and lamination of the crystals is performed using a thin horse-hair, since the crystals are electrostatically bound to this hair. With a certain 'flipping' technique, the crystals can be evacuated from the growing tube and laminated in the storage container of on the modified substrates (figure 13).

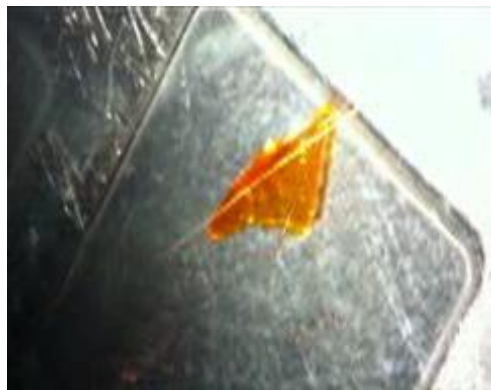


Figure 13. Picture of misprocess of crystal lamination on substrate. Note that the hair still attach to the crystal, which was use as manipulator to evacuate and laminate the crystal.

3.2.4 TOP ELECTRODE

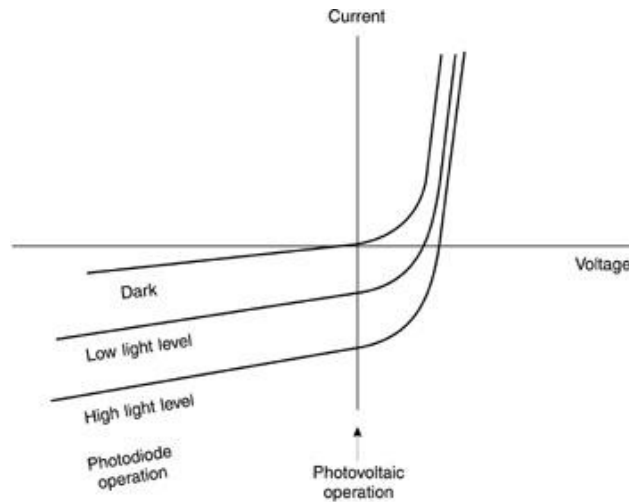
For the top electrode, we used silver paste. Silver paste is dispersed silver micro/submicroparticles in organic solvent, which is easy to handle for its application on organic single crystals. Silver paste was used, instead of evaporated thin metal layers, on top of the single crystal because of its simplicity. The first organic FET's based on single crystals also utilized silver paste electrodes [18, 19]. The work function of the silver paste is assumed to be the same as normal silver (4.7eV). The deposition of the silver paste on top of the crystal was done by utilizing small wooden stick, due to its capillary effect. The disadvantage of this silver pasting is the lack control of thickness, uniformity and size area of the top electrode.

3.3 OUTPUT CHARACTERISTICS MEASUREMENT OF THE PHOTOACTIVE DEVICE

Device measurements are performed in a nitrogen-filled glove box using a two-terminal probe station, connected to Agilent E5270B semiconductor parameter analyzer. With the two probes, a potential bias can be applied over the device and the flowing current can be measured. During the measurements the source was connected to the ground, while the drain is biased.

What can one expect with photodiode characteristics? When a positive bias is obtained (forward), the Schottky barrier in the single-layer device is lowered, resulting in a larger net current flow from the semiconductor to the metal. When a reverse bias is obtained, only a small amount of current flow occurs from the metal to the semiconductor, because the potential barrier becomes higher (figure 14).

*Figure 14. Typical output characteristics for a photodiode. At increasing illumination the current conduction become higher. The dark curve illustrate the normal diode characteristics without illumination.****



The ideal diode behaviour showed in figure 8 is described by the ideal Schottky equation:

$$I = I_s(e^{V_D/(nV_T)} - 1)$$

Where I is the current through the diode, I_s the saturation current, V_D is the voltage across the diode, n the ideality factor and V_T the thermal voltage.

There are two important parameters in the photocurrent generated in the solar cell. The voltage across the cell when it is connected to an open circuit (no current), is called the open circuit voltage, V_{oc} . When the output is short circuited (no voltage), we call the current the short circuit current I_{sc} . For the conversion efficiency of the cell:

*** http://agamemnon.cord.org/cm/leot/course04_mod08/8_fig3.jpg

$$= \frac{I_{generated} \times V_{generated}}{P_{in}}$$

$$P_{in} = G_{in} \times A$$

With P_{in} the power of the incoming radiation, G_{in} the density of the illuminated power and A the surface of the cell. The Fill Factor FF is also an important parameter for solar cells, it determines the 'squareness' of the power output quadrant (figure 15). High FF leads so low series and high shunt resistance, resulting in low internal energy losses:

$$FF = \frac{(I \times V)}{(I_{sc} \times V_{oc})}$$

Where $(I \times V)$ is the maximum power point on the curve.

Ideal light and dark I-V characteristics of a solar cell are shown in figure 15. The processes and its limitations which take place in creating photocurrent, are briefly discussed in this chapter.

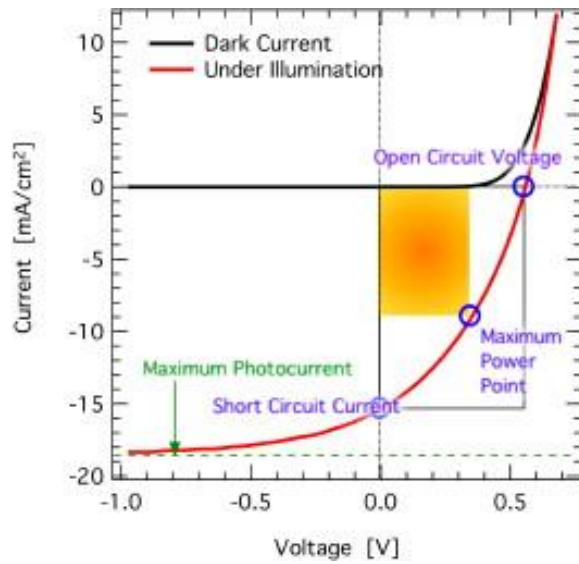


Figure 15. Typical output characteristics for a solar cell device. Power output can be obtained when the device operates in the fourth quadrant.^{†††}

^{†††} <http://deibel.files.wordpress.com/2008/03/osc-i-v-lin-sketch-english.jpg?w=270&h=254>

4. RESULTS & DISCUSSION

In the experiment, different photoactive devices are fabricated using organic single crystal of Rubrene and/or PDI-FCN₂. Bottom electrodes are custom modified with thin organic, buffer layer which lowers the electrode work-function. The analysis of data has been performed looking at the device performance for photodiode or solar cell application. Measurements under illuminated conditions have been done using a Leica KL 1500 LCD light source.

4.1 SCHOTTKY DEVICES

The first photosensitive device configuration is the single layer, or Schottky device. These devices were fabricated as the following configurations: a Rubrene single crystal is sandwiched in between two electrodes of different work functions. For all devices, The top electrode was Ag, deposited from silver paste. The bottom electrode were varied: Ag/PEI, Ag/PEIE, Al/PEIE, and ITO/PEIE. The selection of these electrodes determines the performance of the photosensitive device (figure 16). Electrons, for example, can be injected from the modified electrode to the Rubrene. For the Ag/PEI, Ag/PEIE, ITO/PEIE an energy barrier of 0,4-0,5eV needs to be overcome since the work function is higher than the LUMO of Rubrene. Electron injection from Al/PEIE to Rubrene can occur without a barrier since the work function of the Al/PEIE is lower than the LUMO of the Rubrene.

In general, Schottky devices have poor solar cell characteristics. Nevertheless, we try this configuration to see if there is any photo response and diode behavior for the crystal in combination with the modified electrode.

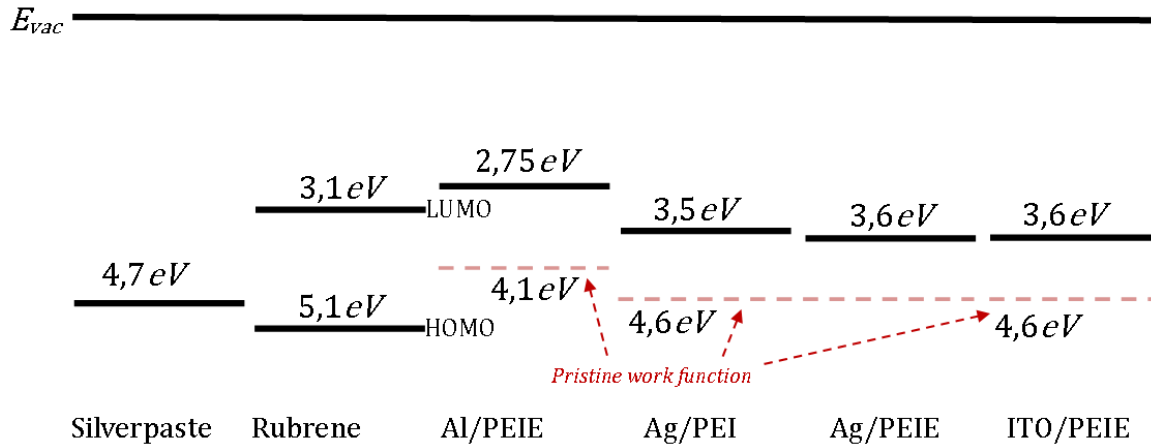


Figure 16. Schematic of work function of the modified electrode and HOMO/LUMO position of the Rubrene. The work function is defined as the difference between the vacuum energy level and the Fermi level of the metal.

The final outlook of this single layer devices are illustrated in figure 11. For the voltage-current characteristics it is important to know the size of the silver paste electrode for correcting the output current to current density. Optical pictures were taken for all of the working devices and the area of the electrodes were estimated using a method shown in figure 17.

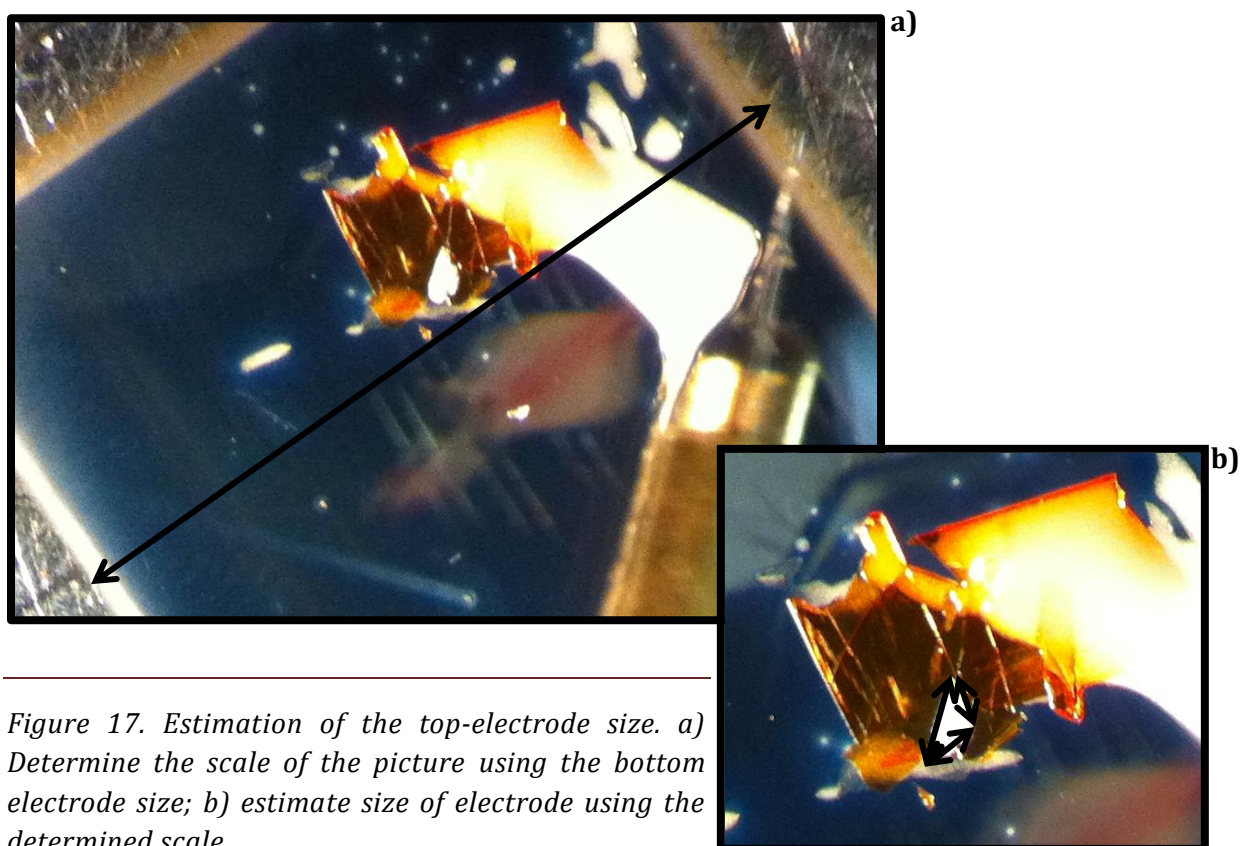


Figure 17. Estimation of the top-electrode size. a) Determine the scale of the picture using the bottom electrode size; b) estimate size of electrode using the determined scale.

Device	Configuration	Area (cm ²)	+/-
B	Ag/PEIE	0,00342	0,0005
D	Ag/PEI	0,00119	0,0002
F	Ag/PEIE	0,000360	0,00005
G	Ag/PEI	0,000825	0,00015
I	Al/PEI	0,000562	0,00008
J	Al/PEIE	0,000427	0,00005
K	ITO/PEIE	0,00463	0,0006

I-V measurements have been done in nitrogen surroundings and under dark and illuminated conditions. Because we fabricated two devices for both Ag/PEIE and Ag/PEI, the results from those measurements were averaged. There are no Al/PEI and ITO/PEI devices because of limited supply of high quality Rubrene single crystals.

4.1.1 DARK CHARACTERISTICS

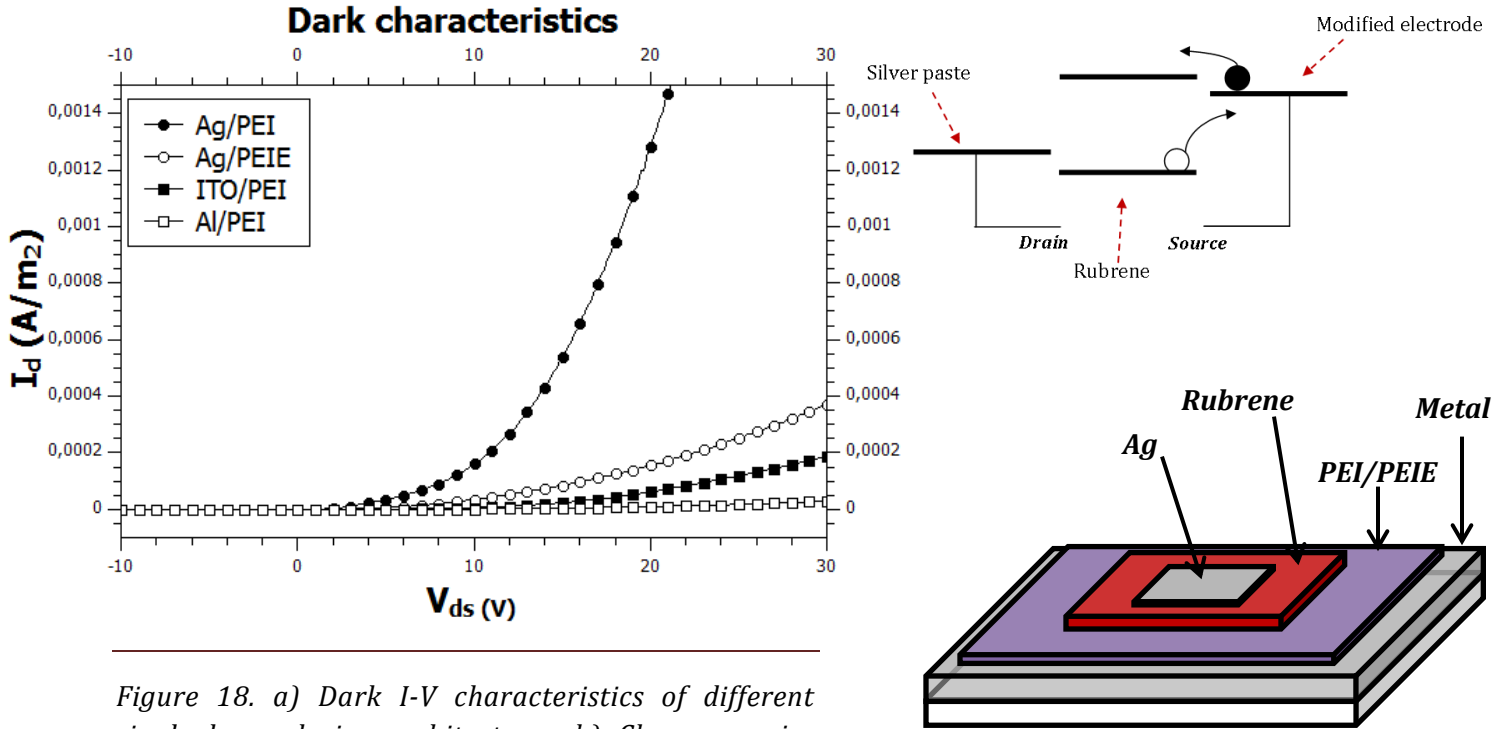


Figure 18. a) Dark I-V characteristics of different single layer device architectures b) Charge carrier transport in this c) configuration (single layer device).

If one sees the I-V characteristics in figure 18, typical diode behavior can be observed. It is obvious that the Ag/PEI device has got the highest current conduction. The red line, Ag/PEIE device, is a factor five time worse than the Ag/PEI device. If we recall the work function of the Ag/PEI and Ag/PEIE, this can be explained by the bigger charge injection barrier of the Ag/PEIE, which results in lower response. For the ITO/PEI device, the current conduction is relatively low, possible due to bad ITO/PEI-Rubrene single crystal interface. Unpolished ITO substrates have a relatively large surface roughness. The aluminum device has got the worst characteristics, probably due to a native oxidized surface of the aluminum, leading to an insulating barrier between the single crystal and the modified electrode, which makes charge injection difficult.

4.1.2 LIGHT CHARACTERISTICS

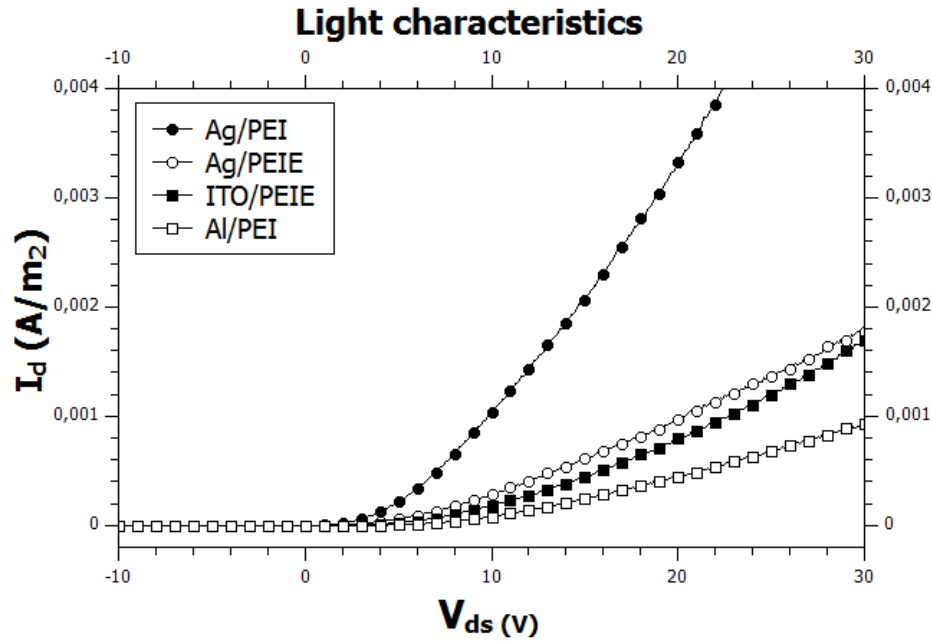


Figure 19. a) Illuminated I-V characteristics of different single layer device architectures

The I-V characteristics under illuminated conditions are shown in figure 19. For every device we observed an increment in current conduction, which is caused by the photo generated current. The dissociated charge carriers can be extracted by the silver paste (electrons) and the modified electrode (holes). Also under illumination the Ag/PEI device has got the best diode characteristics. Nevertheless, the other device structures have big improvements with respect to their dark characteristics. When every active layer (Rubrene) of every devices shave the same thickness, the generated photocurrent should be more less the same, since the electron collector electrode is the same for all devices, silver paste. The hole collector electrode, is not the same in work function. This means that the energy which is lost per collected hole is the greatest for the aluminum electrode, since the difference between the HOMO of the Rubrene (3,1eV) and the Al work function (2,75eV) is the greatest.

4.1.3 PHOTODIODE PERFORMANCE

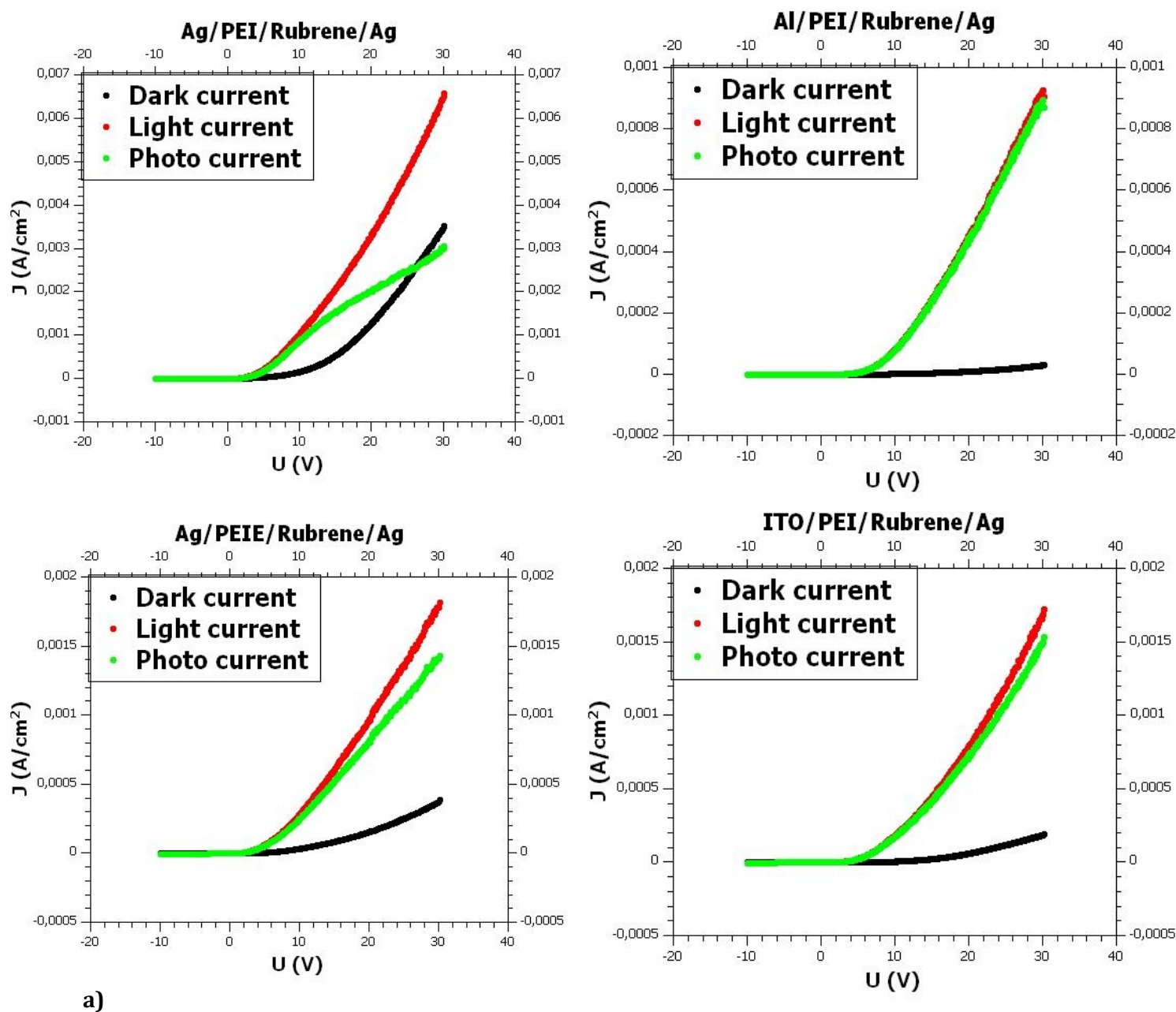


Figure 20. a) Photodiode characteristics for all different device configurations; b) Rectification ratio of the devices.

Device	Ag/PEI	Ag/PEIE	Al/PEI	ITO/PEI
R (10 V)	1470	70	100	160

b)

Photodiode characteristics are shown in figure 20. It can be seen that the Ag/PEI/Rubrene/Ag device has the highest rectification ratio compared to the other modified bottom electrodes. The maximum photocurrent generated at 30V is for the Ag/PEIE, Al/PEI and ITO/PEI devices more less the same ($0,0010\text{--}0,0015\text{ A/cm}^2$). For the Ag/PEI device the maximum photocurrent is a factor 2/3 higher. This possibly could be explained by the thicker single crystal used in the Ag/PEI device. On the other hand, thicker single crystal tends to more exciton decay (recombination) which counteracts more exciton dissociation. Although thickness measurements haven't been done, so we cannot be sure about that.

4.2 BILAYER SOLAR CELL

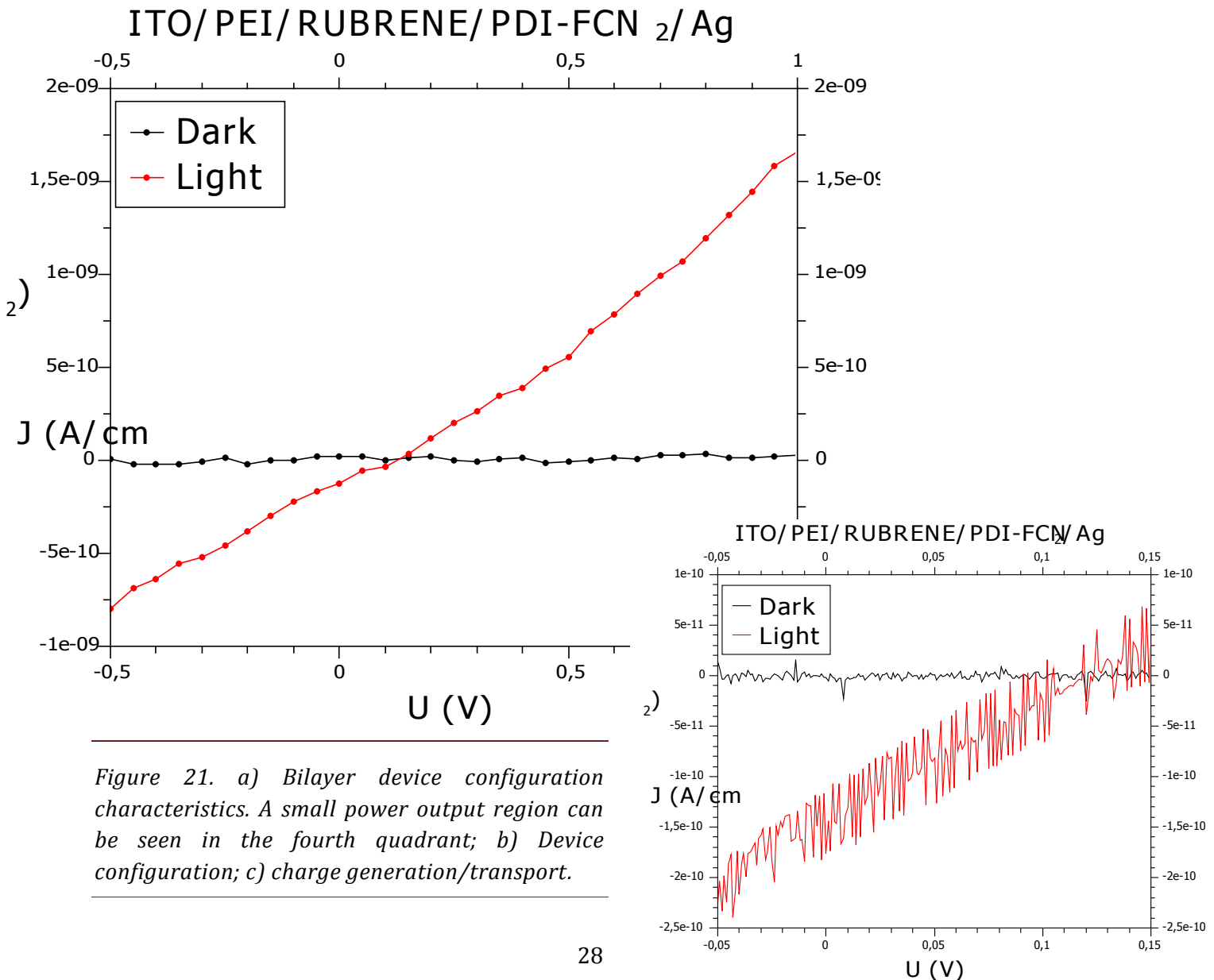


Figure 21. a) Bilayer device configuration characteristics. A small power output region can be seen in the fourth quadrant; b) Device configuration; c) charge generation/transport.

For the bilayer device, we used ITO/PEI as bottom contact because of the transparency of the ITO substrate. PDI-FCN₂ is used as n-type (electron carrying) and Rubrene as p-type (hole carrying). The HOMO and LUMO of PDI-FCN₂ are respectively 6,6eV and 4,5eV. Figure 22c) shows the energy scheme of this bilayer device in more detail.

Clearly some photoactive response can be seen in the form of small open circuit voltage and short circuit current, but it is too small to call is photovoltaic. It is possible that we created two Schottky diodes back-to-back connected. To be sure, single layer device with only PDI-FCN₂ needs to be fabricated and measured. Measurements of both Rubrene and PDI-FCN₂ Schottky devices should give more explanation if we do have a heterojunction solar cell in this bilayer configuration. Nevertheless, the characteristics (figure 21) are very poor for solar cell applications. Optimizing and future measurements are necessary to gain more information about the modified electrode/single crystal interface, the crystal quality and crystal thicknesses.

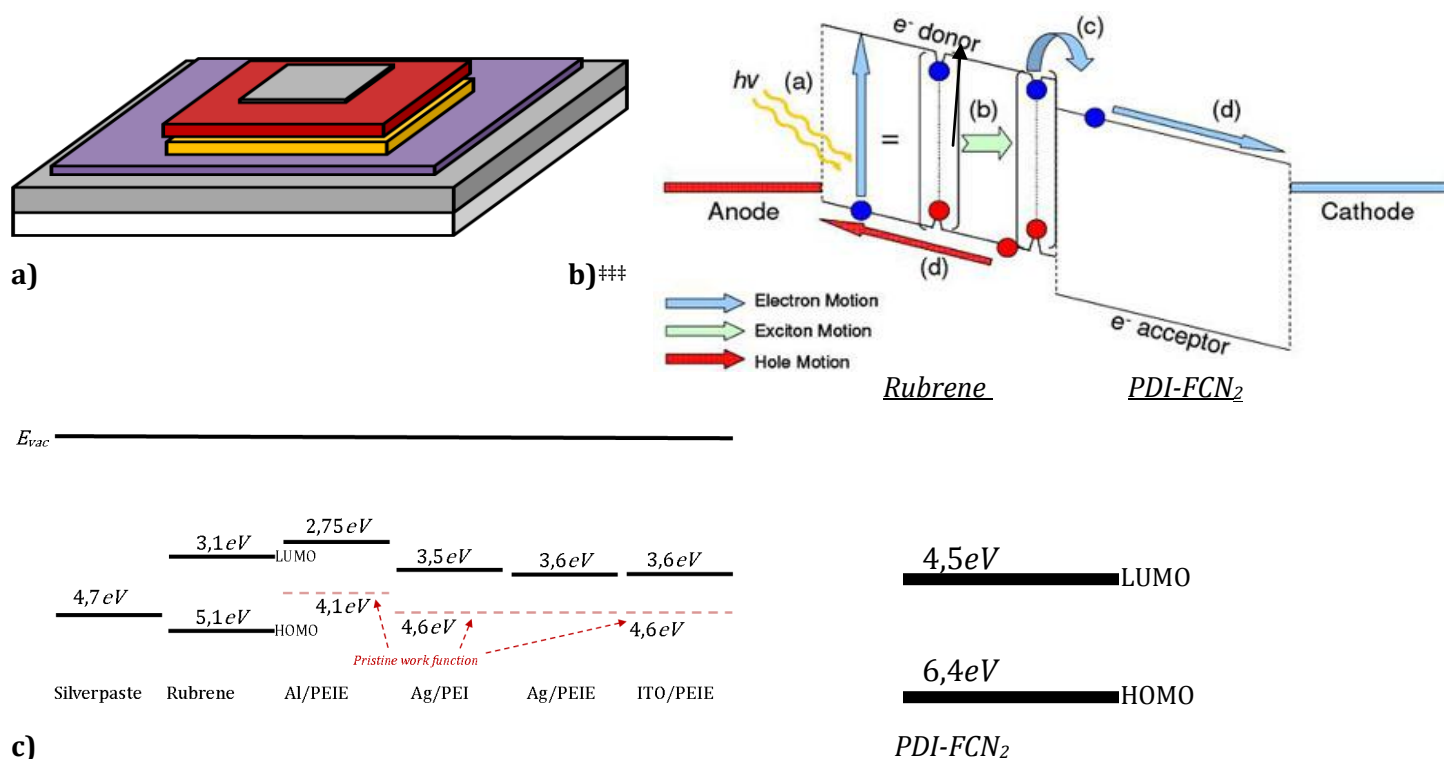


Figure 22. a) Bilayer device configuration (schematic); b) Energy band scheme of bilayer device if we imagine a vertical slice through figure 22a). Processes like photon absorption, exciton diffusion and dissociation and charge carrier collection are denoted; c) Band structure PDI-FCN₂.

###<http://www2.warwick.ac.uk/fac/sci/chemistry/research/jones/jonesgroup/research/organicelectronics/>

5. CONCLUSIONS

Single crystal have successively been grown of Rubrene and PDI-FCN₂. Photoactive device have been fabricated and measured, resulting in working photodiode device based on Rubrene single crystal, in combination with stable, low-work function bottom electrode. For the first time a double-layer photo-active device based on organic single crystal heterojunction has been successively been made. This bilayer device is made using Rubrene and PDI-FCN₂ sandwiched between asymmetric work-function electrodes. Photovoltaic response was not observed, but we did see photoactive response, which can be evidence for realizing solar cell based on organic single crystal in future studies. Optimizing parameters like organic crystal thickness, interface quality and crystal quality can lead to usable solar cells based on thin organic single crystal.

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