Stability of electron acceptor materials for organic solar cells

a work function study of C60/C70 derivatives and N2200

Stabilitet av elektron acceptor material för organiska solceller: en studie av utträdesarbetet i C60/C70 derivator samt N2200.

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**Abstract**

Thin films of the fullerenes PC$_{60}$BM and PC$_{70}$BM and the non-fullerene N2200, three popular electron acceptor materials in organic photovoltaics, have been studied, using both the Kelvin probe method as well as ultraviolet photoelectron spectroscopy. With these methods the work function was measured, as well as the highest occupied molecular orbital (HOMO) onset. Additionally band bending effects were studied by illuminating the samples while measuring the work function with the Kelvin probe so called surface photovoltage. Sample of each material was exposed to either air and simulated sunlight or N$_2$ and simulated sunlight, for different length of time, to observe how the materials work function evolves after exposure to the different conditions. It was observed that, as expected from previous studies, that PC$_{60}$BM was less photo-stable than PC$_{70}$BM. Additionally, the work function of PC$_{60}$BM changed significantly by storage in N$_2$. Each material after exposure for 24h to air and light, was annealed and measured with the Kelvin probe. A restoring effect was observed, for the non-fullerene material N2200. All three materials developed an increasing surface photovoltage, which suggest increased band bending, when exposed to air and light, indicating that due phot-oxidization, charges are redistributed at the surface of the film. The fullerenes showed a larger surface photovoltage effect than the non-fullerene materials. A difference between the work function values obtained from the Kelvin probe method and the ultraviolet photoelectron spectroscopy could be seen, however the exact reason for this couldn’t be isolated within this thesis, but was discussed.

**Sammanfattning**

Tunna filmer av fullerenerna PC$_{60}$BM och PC$_{70}$BM och den icke-Fullerene N2200, tre populära elektron acceptor material i organiska solceller, har studerats med både Kelvin probe metoden samt med ultraviolet photoelectron spectroscopy. Med dessa metoder mättes utträdesarbetet, samt början på "highest occupied molecular orbital" (HOMO) nivån. Dessutom studerades band böjnings effekter genom att belysa proverna samtidigt som utträdesarbetet mättes med Kelvin probe så kallad "surface photovoltage". Materialen hade före mätningen exponerats till både luft och simulerat solljus eller N$_2$ och simulerat solljus, under olika lång tid, för att bygga en förståelse för hur luft och ljust påverkas utträdesarbetet för varje material. Det konstaterades att, som väntat från tidigare studier, PC$_{60}$BM var mindre photo-stabil än PC$_{70}$BM. Dessutom ändrades utträdesarbetet för PC$_{60}$BM avsevärt utav förvaring i N$_2$. Varje material efter 24h luft och ljust exponering, glödgades och mättes med Kelvin probe. En återställande effekt observerades, för icke-fulleren materialet N2200. Alla tre materialen visade band böjnings effekter, men bara när de hade utsatts för luft och ljus som visar att på grund utav photo-oxidation så omfördelades laddningar på filmens yta. Fullerenerna visade en större surface photovolatage effekt än icke-fulleren materialet. En skillnad mellan Kelvin probe metoden och ultraviolet fotoelektronspektroskopi sågs, men den exakta orsaken till detta kunde inte isoleras i detta examensarbetet, men diskuterades.
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1. Introduction

A total of 195 countries has now signed the Paris Agreement COP21 [1]. Which means that a collaborative effort is made to reach a sustainable society. Emission can be regarded as one of the main areas where a lot of resources and knowledge has to be applied to achieve this goal [2]. The Swedish government responds to the Paris agreement by suggesting that a 50% emission reduction by the year 2030 reflects the EU’s responsibility and capability [3]. 2016 the global CO$_2$ emission from electricity and heat stood for a total of 13.41 GtCO$_2$, 42% of the global emission that year, which shows that there is much to gain in terms of emission reduction in said field [4]. To reach the proposed emission reduction, replacement of the existing fossil fuel power plants is of interest.

During the day the sun is consistently radiating energy, resulting in an average radiance of 1050W/m$^2$ on the surface of our earth. A great interest lies in converting this energy into electricity or heat without noise nor pollution, which has been on the mind of researchers and the general public for a long time. Applications such as the solar thermal collector are being used today to heat water. However, it’s more complicated to convert solar energy directly into electricity.

The photovoltaic effect was first discovered in 1839 by the french physicist Alexander-Edmond Becquerel, and in 1954 Daryl Chapin and Calvin Fuller at Bell Laboratories produced the first silicon solar cell, which uniquely at that time was able to produce enough electricity to run electrical devices[5]. To this day silicon solar cells is by far the most widely used cell on the market, however due to its theoretical limit, its problematic mechanical properties, as well as the complicated fabrication process, researchers are constantly looking for other materials and technologies to take its place [6].

In the year 2000 the Nobel prize in Chemistry was awarded jointly to Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa for the discovery of conductive polymers [7]. However, the work for which they received this prize was conducted in 1977 [8]. Previously, all polymers had been assumed to be insulators, but with this breakthrough came new research possibilities. The first donor/acceptor organic solar cell (OSC) was invented later in the year 1986, the materials used were copper phthalocyanine and a perylene tetracarboxylic derivative. However, the power conversion efficiency (PCE) was only measured to $\approx 1\%$ under AM2 illumination, where AM2 such as the standard AM1.5 are used to define the direct optical path through earth atmosphere. AM2 uses a zenith angle of 60° whereas AM1.5 uses a zenith angle of 48.2° [9]. In 1993 the fullerene material buckminsterfullerene C$_{60}$ was first used as the acceptor material in a rectifying heterojunction with the polymer donor material MEH-PPV yielding a PCE of only 0.04% [10]. The PCE of organic solar cells has been consistently increasing and in 2015 the PCE broke the 10% mark [11]. Even though this is still far below the PCE reached with crystalline solar cells, the advantages of possibly commercializing OSCs will bring great value. Some of the advantages of OSCs are low production costs, which comes from the ability to print the material, flexibility, color tunability and non-toxicity of the active material [12]-[14].

Up to present time the fullerene materials have been the most popular electron acceptor candidates and especially derivatives of C$_{60}$ and C$_{70}$, while for the electron donor the polymers PCDTBT, TQ1 and P3HT are usual electron donor materials. Challenges for the fullerene based OSC has been shown to be their strong tendencies to photo-oxidize. The degradation gives such a negative effect that after 10 minutes of exposure to ambient atmosphere conditions the power conversion efficiency (PCE) was reduced by 40% in a PCDTBT:PCBM (PC$_{60}$BM and PC$_{70}$BM) solar cell. After 1 hour exposure to ambient atmosphere the PCE decreased by 70% [16].
These problematic results regarding the fullerene based OSCs has initiated a movement to find more stable materials under ambient conditions. The focus has been concentrated on fullerene free electron acceptors, and one candidate that stands out has been the polymer Poly([N,N'-bis(2-octyldecyl)naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5'-(2,2'-bithiophene)) (N2200). N2200 has shown a high electron affinity, high electron mobility and also a light absorption ability at near-infrared wavelengths 700nm-1400nm [17]. The solar spectrum, showing the different intensities at different wavelengths is shown in figure 1 below.

Figure 1: Solar spectrum measured on Earth. The figure show the intensity of incident photons from the sun as a function of wavelength with the assumption AM1.5 [18].

In this thesis we aim at trying to understand how exposure to air and light affects the electron acceptor materials. Focus will be put on the work function as well as the HOMO (Highest occupied molecular orbital) band of the acceptor materials. The materials studied are two fullerenes PC\textsubscript{60}BM and PC\textsubscript{70}BM, and one non fullerene material, N2200. The methods used are Kelvin Probe to study both the work function but also the surface photovoltage effect of the materials. Ultraviolet photoelectron spectroscopy will be used to determine the work function (in UHV) and the HOMO band onset. The main goal will be to study specific trends for the different materials upon photo-degradation.
2. Theory

1. Conductive Polymers

Organic materials are materials that are mainly carbon based. Carbon has the electron configuration $1s^22s^22p^2$, which means that carbon has four valence electrons in the second shell. This configuration is the most energetically favorable one, however when participating in chemical bonds the electron orbitals become hybridized. Orbital hybridization is a central concept needed to understand the molecular geometry. Carbon can either be hybridized in a $sp^3$ hybridization or a $sp^2$ hybridization, where carbon participates in four single bonds or two single bonds and a double bond respectively. Hybridization of orbitals occur when the 2s orbital mixes the 2p orbitals due to electron cloud overlap. The $sp^3$ and $sp^2$ electron configuration can be seen in figure 3 and 4. Schematic figures of the different electron configurations are shown below,

When electrons from the s orbital and sp-hybridization orbital are shared to form a covalent bond it’s referred to as a $\sigma$ bond, when electrons from p orbitals are shared, it is known as $\pi$ bonds. The p orbitals can take the form of three different orientations, $p_x$, $p_y$ and $p_z$, where each of these orientations are orthogonal to each other in a Cartesian coordinate system.

![Figure 2: Atomic carbon.](image)

![Figure 3: $sp^2$ hybridization.](image)

![Figure 4: $sp^3$ hybridization.](image)

![Figure 5: Examples when $\sigma$ bonds are formed. Taken from [19].](image)
2. Theory

The orbitals shown in figure 5 and figure 6 shows the probability density of an electron $|\Psi(x, y, z)|^2$ where $\Psi(x, y, z)$ is the solutions to the Schrödinger equation for the system. $\pi$ bond orbitals are not rotation-symmetrical with respect to the bond axis which makes a structure consisting of $\pi$ bonds rigid.

In this thesis conjugated polymers will be treated. Conjugated polymers are polymers with alternating single and double bonds. What makes conjugated polymers special is that the $\pi$ bonds may be delocalized over the whole polymer. An illustration of a conjugated polymer chain is shown below in figure 7.

![Figure 7: The incomplete structure of Polyacetylene. Each carbon atom is also bound to an hydrogen atom.](image)

The alternating $\pi$ bonds are what allows charge transfer in the polymer chain as the electrons taking part in the $\pi$ bond are free to move as mentioned above. This phenomena is also known as a form of mesomerism which indicates that electrons within a specific bond can’t be localized in said bond at all times.

So far we have recognized that electrons in a conjugated polymer are mobile through the delocalized $\pi$ bonds, however this delocalization can also be extended over many molecules and this is why materials containing conjugated polymers may be produced with semiconducting properties.

Carbon bound to other materials can also be able to conduct electricity throughout the polymer. One example is polythiophene, which also contains sulfur atoms in the polymer backbone [7].
In the field of organic chemistry, it isn’t obvious what the electronic structure of conductive polymers looks like. In figure 8 the mesomeric structures of polythiophene are shown. These two structures are not energetically equal, and it’s the structure on top which is the more favorable one, where the delocalized π orbitals occupy the thiophene rings. This mainly shows that to study the exact electron configurations of conductive polymers isn’t obvious, and to determine the exact structure theoretical simulations have to be carried out [28].

2. Introduction to organic solar cells

From a theoretical point of view the solar cells I-V characteristics is given by the Shockley solar cell equation

$$I = I_{ph} - I_S \left( e^{\frac{qV}{k_B T}} - 1 \right)$$  \hspace{1cm} (1)

where $I_{ph}$ is the photo-generated current which is related to the photon incident flux, $I_S$ is commonly known as the diode saturation current where one can clearly see from eq (1), that a solar cell in the dark is simply a rectifying diode. T is the absolute temperature, $k_B$ is the Boltzmann constant, q is the electron charge and V is the voltage [29].
Figure 9 shows a general current-voltage curve characteristic for the solar cell. $V_{oc}$ is the open circuit voltage whilst $I_s$ is the short circuit current. Where $V_{oc}$ is defined by

$$V_{oc} = V_t \ln \left( 1 + \frac{I_{ph}}{I_s} \right)$$

and $I_s$ occurs when the resistance $R = 0$ so that $V=0$. However, when studying the I-V curve it’s just the blue area that gives the maximum power i.e. when $V = V_m$ and $I = I_m$. A common expression within the field of solar cells is the fill factor given by

$$FF = \frac{V_m I_m}{V_{oc} I_s} = \frac{P_{max}}{V_{oc} I_s}$$

Which is simply the blue area as a fraction of the total area in figure 9. The power conversion efficiency (PCE), previously mentioned is given by

$$PCE = \frac{P_{out}}{P_{in}}$$

where $P_{in}$ is the power of the incident light on a given area and $P_{out}$ is the power produced by the solar cell.

For inorganic solar cells, the silicon p-n junction is the most studied one. To understand organic solar cells one has to first take a look at the inorganic solar cells. The p-n junction solar cell consists of two regions of different doping (n-doped and p-doped), these sides when brought into contact form a depletion region at the interface. The depletion region indicated by its name depletes the region of mobile charge carries as a result of the potential difference of the two materials, which produces an electric field at the interface [29].
In figure 10 the photons are absorbed in the n or p region where excitons forms (bounded electron-hole pair). The electrons and holes pairs are split directly upon excitation, and after diffusing to the n-p interface the electrons and holes are sorted to the n side or p side respectively due to the electric field. The isolated electrons and holes will then be extracted by a front and back contact where they then becomes part of a circuit to produce electricity.

The operational principle of an organic solar cell is similar however the big difference is that the exciton is split at the heterojunction between the electron acceptor and the electron donor, this is because the excitons in organic materials are more strongly bound. The LUMO energy difference has to be larger than the Coulombic energy between the electron and hole. A schematic figure of the operation process in an OSC is shown below.
In figure 11 one can see the general operation principle of an organic solar cell. Radiation energy is absorbed by material 1, the electron donor, 1. An electron-hole pair (exciton) is formed due to the excitation of an electron from the HOMO level to the LUMO level in the material. The exciton diffuse to the donor/acceptor interface. The difference in LUMO energy has to be greater than the exciton binding energy, which in organic semiconductors is around 0.3-0.5 eV seen in step 2. The exciton diffusion length is between 5-20 nm, which means that step 4 (recombination) will be inevitable. In step 3 the electron and hole will be extracted by ohmic contacts by the cathode and anode respectively where they take part in the external circuit and produce energy. Materials used as the cathode need to have a low work function to be able to allow ohmic extraction, aluminum is commonly used as a cathode [28].

3. Degradation effects

In the OSC field a big obstacle in the development is the degradation of the active layer when exposed to different operating conditions. This section will be dedicated to present previous studies indicating degradation effects of the materials studied.

There’s been a lot of previous research indicating that the PCE of OSCs containing fullerenes or PCBM decreases when exposed to working conditions in air. A thorough study of this has been done by [15]. This has, as was mentioned in the introduction, halted the progress of these types of electron acceptors. Because of this, research groups all over the world has started to investigate the materials under different conditions, to get a clearer understanding what happens to the fullerenes when in contact with air.

In [22] it was shown that by simply exposing C\textsubscript{60} and PCBM films to the lamp light inside the preparation lab gave a change in the electronic structure of the materials. They also showed that by exposing the materials to air and light for a longer time destroyed the conjugated system of the fullerenes. This study was done using both UPS and NEXAFS, which gave results that both the filled and empty molecular orbitals had been significantly altered by exposure.
Further studies have been done with UV-Vis and FT-IR spectroscopy. By doing UV-Vis on photo-degraded PC₆₀BM and PC₇₀BM it was shown that both materials are getting bleached by exposure to light and air. However, PC₇₀BM was bleaching slower than PC₆₀BM. FT-IR measurements has shown that photo-oxidation occur faster for PC₆₀BM than for PC₇₀BM. The authors deduce that this is most probably because of the different shapes of both molecules [32]. There are many different ways oxygen could react with the fullerenes, and form bonds in different configuration on the cage. A thorough study of this can be found in [23].

As previously mentioned the fullerene cage was getting destroyed due to oxidization, which is detrimental for the conjugated electron system. In OSCs one can try to recover the loss in photo-current by annealing the devices[24]. One research group has shown that an OSC with an active layer of P3HT/PCBM,annealed at 140°C for different times, increased the efficiency of the solar cell. However, a maximum of efficiency was found after 30 min, while after 60 min of annealing the efficiency went back down. Thus shows that the annealing can also be devastating for device performance[26]. It has also been shown that annealing affects the molecular packing in such a way that it stabilize organic photovoltaic materials [27]. N2200 as the electron acceptor has also shown improvement in all polymer solar cell devices, where annealing seems to make the two polymers interact at the interface after annealing. This interaction made the device give a higher fill-factor [25].

4. Ultraviolet photoelectron spectroscopy (UPS)

By using photoelectron spectroscopy, information about the occupied electronic states in the material is obtained. The surface of the sample is exposed to monochromatic light which then allows the photoelectric effect to occur. By using incident light in the UV spectral range the method is called a Ultraviolet photoelectron spectroscopy or Ultraviolet photoemission spectroscopy (UPS). The photoelectric effect is regarded as a one-step process for which Albert Einstein earned the Nobel prize in physics 1921 [36]. However,a simplified but less accurate three-step model is usually used to explain the photoelectric effect:

a. Optical excitation from a lower to a higher electron state inside the crystal.

b. The electron propagates to the surface of the sample.

c. The same electron is then emitted from the surface into vacuum and its kinetic energy is measured by a detector (electron analyzer).

In the three-step model each step can be thought of as independent with its own contribution to the corresponding probabilities of the photo-emission of electrons [37]. The first step is given by the famous golden-rule transition probability which is given by

\[
W_{fi} = \frac{2\pi}{\hbar} \left| \left< f, \vec{k} \left| H \right| i, \vec{k} \right> \right|^2 \delta(E_f(\vec{k}) - E_i(\vec{k}) - \hbar\omega)
\]

\[
= \frac{2\pi}{\hbar} m_{fi} \delta(E_f - E_i - \hbar\omega)
\]

(5)

A UPS measurement is a surface sensitive measurement due to the propagation of the electron to the surface [37].The kinetic energy of the electron released is measured by an an electron-analyzer inside the analysis chamber. The signal is then given by an energy spectrum where the sharp peaks corresponds to the kinetic energy of the released electrons given by
\[ E_{\text{Kin}} = \hbar \omega - E_i - \phi. \] (6)

Where \( E_i \) is the energy of the initial state of the electron, \( \phi \) the work function of the material that the electron has to overcome to be released into the vacuum just outside the surface [37]. An illustrating figure of how a UPS spectra is produced is shown below.

![Schematic of UPS spectra](image)

Figure 12: A schematic figure of how an UPS spectra is produced. N(E) is the density of states, \( \Phi \) is the material work function and \( \hbar \omega \) is the incident photon energy. Inspired by [38].

In UPS a helium resonance lamp is connected with a high voltage DC discharge that goes along the capillary tube. The current is then used to allow the electrons in the helium gas to get excited. The transition back to its original state is responsible for the radiation. Commonly the He(\( \lambda_\alpha \)) spectral line is used which is the \( 1s^12p^1 \rightarrow 1s^2 \) transition giving an emission line of 21.218 eV (\( \lambda=58.4 \text{ nm} \)) [48].
In figure 13 above one can see the information generated from an ordinary UPS measurement. The x axis shows the binding energy however the electron analyzer measures the kinetic energy of the incident electron, the binding energy is then calculated from eq.(6). From the secondary electron cut-off (SECO) one can calculate the work function of the sample from the following equation

\[ \Phi = \hbar \omega - (\text{SECO} - E_F) \]  

The Fermi level is referred to the Fermi level of the system which is usually used as the reference given by \( E_F = 0 \). A negative bias is usually applied to the sample to separate the low energy cutoff from the spectrometer response [38].

5. **Kelvin Probe**

The Kelvin Probe is used to measure the contact potential difference (CPD) between a reference probe and the sample [41]. By bringing two materials with different work functions (WF) towards each other and regarding them as parallel plate capacitors, equal and opposite surface charges will form [42]. The voltage between these parallel plates is the contact potential difference eq.(8).
2. Theory

Figure 14: Two materials (metals) with different work function, not in contact.

The reference probe is usually made of gold and thus has a well known work function. The CPD is given by

\[ V_{CPD} = \frac{1}{e}(\Phi_2 - \Phi_1) \]  

where \( \Phi_1 \) and \( \Phi_2 \) are the work functions of the materials including adsorption layers on the surface [43].

Figure 15: Two materials brought close to contact such that equal and opposite surface charges form and how the CPD is measured. Inspired from [42]

The reference probe will then vibrate periodically, which induce an ac current in the circuit due to charging/discharging of the parallel plate capacitor.

\[ i(t) = V_{CPD} \Delta C \cos \omega t \]  

where \( \omega \) is the period and \( \Delta C \) is the change in capacitance. By applying a compensating dc-voltage such that the amplitude of eq.(9) goes to zero, one measures the \( V_{CPD} \) [43].

For the actual work function measurement, a calibration sample has to be used. It’s important that the work function of the calibration sample isn’t changing in the environmental condition it’s in. A common material that is used is gold (Au). However gold is used directly after the surface is cleaned, and is
When \( \Phi_{Ref} \) is known and both the \( V_{CPD}^{Ref} \) of the calibration sample and the \( V_{CPD}^{S} \) of the sample material are measured, the work function of the sample materials is found through

\[
\Phi^{S} = \Phi^{Ref} + (V_{CPD}^{Ref} - V_{CPD}^{S}).
\] (10)

### 5.1. Surface photovoltage

The surface photovoltage (SPV) is defined as the illumination-induced change in the surface potential. Commonly one assumes that no noticeable voltage drop occurs in the quasi-neutral bulk region even after illumination of the sample [47]. This means that the only effect occurring is on the sample surface. In the following piece the explanation will be of the more thoroughly studied semiconductor SPV effects. On the semiconductor surface electronic surface states appear which induce a perturbation to the local charge balance [37]. These surface charges can appear as either donor or acceptor type and depending on the position of the fermi level at the surfaces of the studied sample. This charge due to the surface state being occupied is screened by a mirror charge inside the sample. These surface charges are understood as a charge density per unit area. The screening charges inside the material are known as space charges \( Q_{sc} \) [37]. The overall neutrality requires that

\[
Q_{ss} + Q_{sc} = 0.
\] (11)

In figure 15 below a schematic figure how the screening of the charge of the surface states results in a band bending.
Band bending occurs in order to balance the charge and maintain charge neutrality, eq.(11). The band bending pushes away the conduction band electrons and leaves un-screened ionized bulk donors behind. The location of the Fermi level as well as the amount of band bending is decided by eq. (11).

Generally, when light is shone on the material both \( Q_{ss} \) and \( Q_{sc} \) may change drastically. The material absorbs the incident photons and which in turn produces either electron-hole pairs from a band to band transition of super-bandgap photons. These electron hole pairs are simply produced by an electron excited from the valence band to the conduction band. The other case is sub-bandgap excitations, this phenomena is produced by excitation or emitted from trap states inside the band gap. The recombination rate from and to these traps states are given by the Shockley Read Hall recombination rate given by

\[
R_n = R_p = \frac{C_n C_p N_t (np - n_i^2)}{C_n (n + n') + C_p (p + p')}.
\]

Where \( C_n \) and \( C_p \) are constants related to the capture of electron and holes, \( N_t \) trap density, \( n' \) and \( p' \) are constants related to to the trap energy [39]-[40]. In common for both situations are that charge carriers are getting redistributed throughout the semiconductor from the surface into bulk or vice versa. These charges following the Poission equation and the continuity equation changes both the electric potential and the charge distribution changes the surface potential.

To calculate the SPV value one simply subtracts the WF measured under illumination with the WF measured in the dark.

Figure 16: Schematic figure of how band bending occurs in an n doped semiconductor. It’s shown how the charge of the acceptor type surface states \( Q_{ss} \) are compensated by the charge of the ionized bulk donors \( Q_{sc} \). This results in a band bending of an energy difference equal to \( eV_s \). \( E_d \) is the energy of the bulk donors, \( E_F \) is the Fermi level and \( N_{ss} \) surface state density. \( E_c \) and \( E_v \) are the energy conduction band and valence band edge energies respectively. \( z \) is the distance normal to the surface.
3. **INSTRUMENTS AND MATERIALS.**

1. **Substrate Preparation**

   The substrates used were cleaned Si wafers, n-doped with orientation (100) and a resistivity of 0.001-0.003 \( \Omega \text{cm} \), cut down to about 1.5cm\(^2\). Si wafers were used due to the material's minimal surface roughness. The Si wafers had been stored in air for an unknown amount of time before use. So prior to using each 1.5cm\(^2\) tile of Si, they were cleaned using the RCA (Radio Corporation of America) method.

   The RCA method of cleaning was first invented by W. Kern and D. Puotinen in 1965 while working at RCA [21]. The RCA method consists of a total of six steps.

   a. Submerge the Si tiles into a solution consisting of 100ml of deionized H\(_2\)O, 20ml of hydrogen peroxide (H\(_2\)O\(_2\) (30\%)) and 20ml of ammonia solution (NH\(_4\)OH (25\%)).

   b. The solution is then put on a hot plate for 10-15 min at 70° to 80°.

   c. The tiles are then rinsed with deionized water.

   d. Then put in a solution consisting of 100ml deionized water, 20ml of H\(_2\)O\(_2\) and 20ml of hydrochloric acid (HCl (37\%)).

   e. Again put on a hot plate for 10-15 min at 70° to 80°.

   f. Finally the tiles are again rinsed with deionized water and dried by pressurized nitrogen gas.

   The first step is to remove any organic material that may reside on the surface of the Si tiles. This is done by the attack of the solvating action of the NH\(_4\)OH solution and the oxidizing effect of hydrogen peroxide. The ammonia hydroxide is also able to complex some group 1 and 2 metals [21].

   The fourth step is done to remove any heavy metals that contaminate the surface, and also to prevent displacements by forming soluble complexes with the exposed ions [21].

2. **PC\(_{60}\)BM and PC\(_{70}\)BM**

   [6,6]-phenyl C\(_{61}\)-butyric acid methyl ester (PC\(_{60}\)BM) and [6,6]-phenyl C\(_{71}\)-butyric acid methyl ester (PC\(_{70}\)BM) are one of the most used electron acceptor material in OSC. Both molecules as can be seen from figure 17 are C\(_{60}\) and C\(_{70}\) derivatives, respectively. The side chains seen in figure 17 are used to make the molecule more solvable [31].

(a) PC\textsubscript{60}BM

(b) PC\textsubscript{70}BM

Figure 17: The chemical structure of PC\textsubscript{60}BM (a) and PC\textsubscript{70}BM (b). Taken from [32].

3. N2200

Poly([N,N’-bis(2-octyldodecyl)naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5’-(2,2’-bithiophene)) (N2200) is a fullerene free electron acceptor.

Figure 18: The chemical structure of N2200. Taken from [33]

From figure 18 one can observe that the system does not consist of the same density of $\pi$-conjugate as the fullerenes however it still has high electron mobility, high electron affinity, and broad light absorption. However it’s absorbing light in the range of 300-840 nm where there are two distinct peaks at 380 nm from $\pi - \pi^*$ excitations and also a peak at 700 nm resulting from inter-molecular charge transfer band of the D/A co-polymer [35].

4. Glovebox

A glovebox is a sealed container, usually containing an inert gas. Here N\textsubscript{2} (can also be Ar). It is designed in such a way that it’s possible to perform tasks in absence of O\textsubscript{2} and water vapour. The glovebox has a see through side on which plastic gloves are mounted allowing the user to manipulate objects inside.
Figure 19: The image shows the two gloveboxes used. The yellow tinted light is used to avoid damaging UV and blue light that could photodegrade samples.

The glovebox used (MB200MOD, M. Braun Intergas-Systeme GmbH, Germany) (see fig.[5]) was kept at $O_2<0.1$ppm and $H_2O<0.1$ppm.

5. Sample preparation

$PC_{60}$BM (purity > 99.5%) and $PC_{70}$BM (purity >99.5%) had been purchased from Solenne B. V. (The Netherlands). The N2200 was also purchased from Solenne B. V.. Chloroform (purity 99%) was purchased from BDH Lab Supplies (UK). Both $PC_{60}$BM and $PC_{70}$BM were prepared under filtered (yellow) light in $N_2$ in the glovebox system. First, both materials were dissolved in Chloroform to a concentration of 15mg/ml. N2200 was also mixed with Chloroform at a concentration of 10mg/ml. These three solutions were left on a hot plate stirring at a temperature of 40°C for at least for 24h. The previously cleaned Si substrates (section 3.1) had been moved directly after cleaning into the glovebox. Thin films of the three solutions, $PC_{60}$BM, $PC_{70}$BM and N2200, were then spin coated on Si with the following spin-coating recipe:

a. 100rpm for 1 seconds with a 2 second ramp up.

b. 1500rpm for 80 seconds with a 3 second ramp up.

c. 2000rpm for 20 seconds with a 3 second ramp up.

The samples are then ready for measurements and were placed in Petri dishes inside the glovebox until they were used. ,

The photo-degradation was done with the solar-simulator (Sol2A, model 94022A, Oriel Instruments (USA)), a silicon photodiode reference cell was used to calibrate the intensity (model 91150V, Oriel Instruments).
6. Spin coating

To produce a thin film of a solution on top of a substrate a spin coater may be used. A substrate is placed on top of the spin coater and held in place through a vacuum suction. A small drop of the desired material in a solvent is then applied on top of the substrate, which is spun at a desired rate. The solution spreads evenly on the substrate. By changing either the concentration of solutions applied or the rotating speed, the thin film thickness is controlled.

![Figure 20: The working principle of a spin coater. Inspired from [34].](image)

7. Kelvin Probe setup

The Kelvin probe system (Besocke Delta Phi) consists of Kelvin Probe S / Kelvin probe S compact and the Kelvin control 07, which was used to do all measurements conducted by Kelvin Probe. The probe of the system is oscillating as result of a piezo electric drive. The system has a sensitivity of < 0.1 mV. The error of the system is unknown and the error it thus calculated by the largest deviation from the mean from three consecutive measurements. All CPD measurements were done with an applied bias of 2.390 V and HOPG as the calibration sample. Also the measurements were done in a humidity regulated room and measured every day a measurement were done in air with the instrument testo 605i-SmartProbes. The same system was moved into the glovebox system seen in figure 16 when measurements in N\textsubscript{2} were conducted.

8. Surface Photovoltage setup

The same Kelvin probe system was used for the surface photovoltage measurements. However to do the measurements a light source had to be mounted to the system. The light source used was a 230 V lamp with a luminous flux of 450 lm and a power of 6.5 W. This source was used to give an incident light beam consisting of a wide range of wavelengths. The light source was mounted ∼13.5 cm from the sample holder. All kelvin probe measurements were performed at room temperature.
9. UPS setup

The UPS measurements were conducted inside a UHV chamber using a UV-lamp and electron analyzer (Omicron Nanotechnology GmbH). The UPS system had been custom built to fit the UHV chamber. The pressure used during the measurements was $\sim 10^{-7}$ mbar. All measurements were also performed in room temperature. The UV-beam was produced by He(I$\alpha$) lamp with an energy of 21.218 eV. The Fermi level of the sample was also aligned to the Fermi level of the system. During measurements a bias of $-7$ V was applied.
4. Results

This section will be divided into three material sections i.e. PC$_{60}$BM, PC$_{70}$BM and N2200. In each of these sections we will present the result obtained by the two techniques i.e. Kelvin probe and UPS. Finally a figure is shown on how the materials work functions changed as a result of annealing. Three measurements were done of each time with the Kelvin probe. The error given in the tables is the largest deviation from the mean of the three measurements.

Regarding the Kelvin probe measurements. The work function of the probe was calculated when the Kelvin probe system was located in air and in N$_2$. The calculated values can be seen in the table below.

Table 1: Work function calculated for the gold probe in the Kelvin probe system in air and N$_2$. HOPG with a work function of 4.6 eV was used as reference.

<table>
<thead>
<tr>
<th>Location</th>
<th>Work function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>4.803 eV</td>
</tr>
<tr>
<td>N$_2$</td>
<td>4.698 eV</td>
</tr>
</tbody>
</table>

It can be seen in table 1 that the work function for the probe was 0.2 eV higher in air than in N$_2$.

1. PC$_{60}$BM

1.1. Kelvin Probe

Table 1 shows the results from Kelvin probe measurements where the PC$_{60}$BM film was kept in a Petri dish for a total of 48 hours. Measurements were taken during this time to see how only air exposure in the dark affects the work function. Humidity might have a great impact on Kelvin probe measurements, thus the humidity in the room during measurements in air was documented. During the measurements of the first 6 values the relative humidity in the room was 29.3% RH, during the 24h measurement 24.6% RH and during the 48h measurement 20.7% RH.

Table 2: Work function of PC$_{60}$BM kept in the dark in air, measured by Kelvin probe. The sample had been stored inside the glovebox system for 11 days prior to air exposure.

<table>
<thead>
<tr>
<th>Time (Hours)</th>
<th>Work function (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>4.615 ± 0.012</td>
</tr>
<tr>
<td>0.75</td>
<td>4.566 ± 0.008</td>
</tr>
<tr>
<td>1.25</td>
<td>4.561 ± 0.020</td>
</tr>
<tr>
<td>2.25</td>
<td>4.579 ± 0.015</td>
</tr>
<tr>
<td>3.25</td>
<td>4.629 ± 0.023</td>
</tr>
<tr>
<td>5</td>
<td>4.622 ± 0.005</td>
</tr>
<tr>
<td>24</td>
<td>4.619 ± 0.038</td>
</tr>
<tr>
<td>48</td>
<td>4.678 ± 0.007</td>
</tr>
</tbody>
</table>

As can be seen in table 2 the values seem relatively stable, with an initial decrease of 50 meV followed by a slight increase of 100 meV.

In table 3 one can see the measurements from when the Kelvin probe was inside the glovebox. This is because no exposure to air was allowed. The PC$_{60}$BM was spin coated and directly measured after
15 min, then measurements were taken until 24h. The measurement after 48h wasn’t done because the material was relatively stable inside the glovebox system.

Table 3: Work function of PC$_{60}$BM kept inside the glovebox and measured inside the glovebox. With measurements times after the spin coated material.

<table>
<thead>
<tr>
<th>Time (Hours)</th>
<th>Work function (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>4.560 ± 0.009</td>
</tr>
<tr>
<td>0.75</td>
<td>4.543 ± 0.032</td>
</tr>
<tr>
<td>1.25</td>
<td>4.507 ± 0.001</td>
</tr>
<tr>
<td>2.25</td>
<td>4.488 ± 0.001</td>
</tr>
<tr>
<td>3.25</td>
<td>4.538 ± 0.017</td>
</tr>
<tr>
<td>5</td>
<td>4.519 ± 0.014</td>
</tr>
<tr>
<td>24</td>
<td>4.479 ± 0.008</td>
</tr>
</tbody>
</table>

Table 3 shows that the PC$_{60}$BM work function seem stable during the first 24h inside a glovebox system. A total change in 80 meV was seen between the the first and the last measurement. The difference between the first measurement in table 2 and table 3 shows a magnitude of 70 meV. Important to consider is that the Kelvin probe or the calibration samples work function might change in the inert gas atmosphere.

In figure 22 one can see the SPV value measured done when the Kelvin probe was inside the glovebox. These measurements were taken simultaneously as the work function measurements of table 3.

Figure 22: SPV values of PC$_{60}$BM at different time intervals after the material had been spin coated. The measurements were done inside the glovebox. Light source used can be found in section 3.8.

As can be seen from figure 22 the work function changed less than 60 meV when light was striking the sample. This indicates that the material shows only weak SPV effect within these conditions.
Exposed to simulated sunlight.

Table 4 shows the measured work function of PC$_{60}$BM after exposure to air and sunlight for a total of 48 hours. During the first 6 measurements the humidity in the room was 16.6% RH, the measurement done at 24 hour of exposure had a room humidity of 21.3% RH and the measurement done at 48h of exposure had a room humidity of 26.0% RH.

Table 4: Work function of PC$_{60}$BM photo-degraded in air. Exposure was done to a simulated sun at the intensity of 0.93 suns. The sample was kept inside the glovebox for 19 days before exposure.

<table>
<thead>
<tr>
<th>Time (Hours)</th>
<th>Work function (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>4.754 ± 0.022</td>
</tr>
<tr>
<td>0.75</td>
<td>4.698 ± 0.044</td>
</tr>
<tr>
<td>1.25</td>
<td>4.842 ± 0.027</td>
</tr>
<tr>
<td>2.25</td>
<td>4.859 ± 0.009</td>
</tr>
<tr>
<td>3.25</td>
<td>4.892 ± 0.017</td>
</tr>
<tr>
<td>5</td>
<td>4.895 ± 0.022</td>
</tr>
<tr>
<td>24</td>
<td>4.819 ± 0.011</td>
</tr>
<tr>
<td>48</td>
<td>4.756 ± 0.017</td>
</tr>
</tbody>
</table>

The results of table 4 shows a clear change in work function, where a maximum change of 0.2 eV could be observed. Interestingly, after 48h the work function becomes again 4.75 eV as was seen after 15 min of exposure.

In figure 23 the SPV values taken after the work function measurements of table 4 can be seen.

Figure 23: SPV values measured of PC$_{60}$BM. Each measurement was done directly after the measurements done in table 3. Light source used can be found in section 3.8.
As is noted from the SPV result exposure of PC₆₀BM to air and simulated sunlight results in a clear SPV signal of >200 meV after 1.25 hours indicating that absorption of photons is happening close to the surface. The SPV signal increased fast to >180 meV after 15 min and increased until 1.25 hours after which the signal decreased. This indicates that two phenomena may be happening.

In table 5 the work functions of PC₆₀BM photo-degraded in nitrogen can be seen.

Table 5: Work function of PC₆₀BM photo-degraded in N₂. The sample was removed from the glovebox system inside a sealed container filled with N₂ with a quartz glass and placed under simulated sunlight. Light intensity was 1 sun. Prior to measurement the sample had been stored inside the glovebox for 4 days.

<table>
<thead>
<tr>
<th>Time (Hours)</th>
<th>Work function (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>4.371 ± 0.042</td>
</tr>
<tr>
<td>0.75</td>
<td>4.355 ± 0.010</td>
</tr>
<tr>
<td>1.25</td>
<td>4.312 ± 0.015</td>
</tr>
<tr>
<td>2.25</td>
<td>4.333 ± 0.021</td>
</tr>
<tr>
<td>3.25</td>
<td>4.402 ± 0.004</td>
</tr>
<tr>
<td>5</td>
<td>4.394 ± 0.019</td>
</tr>
<tr>
<td>24</td>
<td>4.457 ± 0.027</td>
</tr>
</tbody>
</table>

Table 5 shows that the PC₆₀BM work function was very stable upon exposure to 1 sun light intensity in N₂. One can see a clear difference between the work functions of table 3 when the system was exposed to air and the results of table 5. This will be discussed further in the discussion section.

Figure 24 shows the measured SPV values of the PC₆₀BM sample upon degradation in N₂ and air. These measurements were performed directly after each time stamp of table 5.

Figure 24: SPV values measured of PC₆₀BM photo-degraded in a N₂ atmosphere. Each measurement was done directly after the measurements done in table 5. Light source used can be found in section 3.8.
In the above figure when PC$_{60}$BM was exposed to simulated sunlight inside a N$_2$ filled container. No clear SPV effect (<20 meV) was observed in the beginning, the largest signal observed was 60 meV after 24h.

1.2. Ultraviolet photoelectron spectroscopy

Figure 25 shows how the HOMO band spectrum measured by UPS, with respect to the Fermi level of the system (0 eV) is behaving after exposure to different conditions. Storage in glovebox prior to exposure and measurement was; *Fresh*: 1 day, *48h air and light*: 6 days, *15 min air and light*: 11 days and *15 min N$_2$ and light*: 13 days.

![PC$_{60}$BM HOMO Leading Edge](image)

Figure 25: HOMO band spectra of PC$_{60}$BM UPS measurement focused on the HOMO leading edge. A comparison between different exposure conditions can be seen. **Leading edge values with respect to E$_F$**, *Fresh*: 1.8 eV, *15 min N2 and light*: 2.0 eV, *15 min air and light*: 2.4 eV, *48h air and light*: —. **Charging was observed for 15 min air and light**. (Information about the UPS can be seen in section 3.9.)

From figure 25 a clear indication that the HOMO level is moving away from the Fermi level, and that exposure to air gives a larger shift than exposure to N$_2$. After 48h of air and simulated light exposure the HOMO leading edge is completely destroyed.
2. PC$_{70}$BM

The results of this section will be divided in the same way as previous section.

2.1. Kelvin Probe

In table 6 the work function for PC$_{70}$BM is presented for films stored in air in the dark, as measured by Kelvin probe. The sample was stored for a total of 48 hours inside a Petri dish with aluminum foil protecting it from any external light in air. During the measurements of the first 6 values the relative humidity in the room was 29.3%RH, during the 24h measurement 24.6%RH and during the 48h measurement 20.7%RH.
Results

Table 6: Work function of PC\textsubscript{70}BM films kept in dark in air. The sample had been stored inside the glovebox system for 11 days prior to air exposure.

<table>
<thead>
<tr>
<th>Time (Hours)</th>
<th>Work function (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>4.555 ± 0.003</td>
</tr>
<tr>
<td>0.75</td>
<td>4.630 ± 0.021</td>
</tr>
<tr>
<td>1.25</td>
<td>4.637 ± 0.012</td>
</tr>
<tr>
<td>2.25</td>
<td>4.633 ± 0.014</td>
</tr>
<tr>
<td>3.25</td>
<td>4.641 ± 0.014</td>
</tr>
<tr>
<td>5</td>
<td>4.663 ± 0.014</td>
</tr>
<tr>
<td>24</td>
<td>4.632 ± 0.015</td>
</tr>
<tr>
<td>48</td>
<td>4.616 ± 0.053</td>
</tr>
</tbody>
</table>

In table 6 one can again see that after 45 minutes the work function became very stable at around ≈4.64 eV within the error.

In table 7 one can see how the work function of the PC\textsubscript{70}BM sample evolves when kept in the glovebox (N\textsubscript{2}) directly after spin coating inside the glovebox. For these measurements the Kelvin probe measurements were carried out inside the glovebox.

Table 7: PC\textsubscript{70}BM kept inside the glovebox and measured inside the glovebox. With measurements at times after the spin coated material.

<table>
<thead>
<tr>
<th>Time (Hours)</th>
<th>Work function (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>4.457 ± 0.037</td>
</tr>
<tr>
<td>0.75</td>
<td>4.507 ± 0.043</td>
</tr>
<tr>
<td>1.25</td>
<td>4.458 ± 0.033</td>
</tr>
<tr>
<td>2.25</td>
<td>4.514 ± 0.015</td>
</tr>
<tr>
<td>3.25</td>
<td>4.527 ± 0.064</td>
</tr>
<tr>
<td>5</td>
<td>4.529 ± 0.032</td>
</tr>
<tr>
<td>24</td>
<td>4.511 ± 0.055</td>
</tr>
</tbody>
</table>

As can be observed in table 7, the work function of PC\textsubscript{70}BM is relatively stable for 24 hours giving a work function of 4.5 eV within the error. Comparing these results with the work function of PC\textsubscript{70}BM in air (table 6) where the first measurement was done after 11 days exposed to the glovebox atmosphere, indicates that the work function of PC\textsubscript{70}BM is completely stable even after a long period inside N\textsubscript{2} atmosphere.

In figure 27 the SPV values are presented for PC\textsubscript{70}BM measured directly after the work function measurement presented in table 7.
4. Results

As for PC$_{60}$BM, PC$_{70}$BM doesn’t show any clear SPV effect after storage in N$_2$ where the signals shown in figure 27 could be majority noise.

Exposed to simulated sunlight.

In table 8 the work function value of a sample of PC$_{70}$BM are presented for a film that was exposed to simulated sunlight in air. During the 6 measurements the humidity in the room was 16.6% RH, while during the measurement done after 24 hour of exposure the room humidity was 21.3% RH and after 48h of exposure it was 26.0% RH.

Table 8: Work function of a PC$_{70}$BM film photo-degraded in air. Exposure was done to simulated sunlight at the intensity of 0.93 suns. The sample was kept inside the glovebox for 19 days before exposure.

<table>
<thead>
<tr>
<th>Time (Hours)</th>
<th>Work function (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>4.793 ± 0.020</td>
</tr>
<tr>
<td>0.75</td>
<td>4.815 ± 0.035</td>
</tr>
<tr>
<td>1.25</td>
<td>4.817 ± 0.014</td>
</tr>
<tr>
<td>2.25</td>
<td>4.843 ± 0.027</td>
</tr>
<tr>
<td>3.25</td>
<td>4.890 ± 0.009</td>
</tr>
<tr>
<td>5</td>
<td>4.885 ± 0.007</td>
</tr>
<tr>
<td>24</td>
<td>4.877 ± 0.009</td>
</tr>
<tr>
<td>48</td>
<td>4.760 ± 0.042</td>
</tr>
</tbody>
</table>

A difference in work function of 0.14 eV can be seen between the higher value after 3.25 hour exposure and 48 hour exposure, the difference between the 15 minutes and 48 hour measurements was only 0.033
eV indicating again that the system seems to be relatively stable.

Figure 28 shows the SPV values with respect to the work functions given in table 8.

![Figure 28: SPV values measured for PC$_{70}$BM films exposed to simulated sunlight with intensity of 0.93 suns in an air atmosphere. Each measurement was done directly after the (dark) work function measurements done in table 8. Light source used can be found in section 3.8.](image)

in figure 28 PC$_{70}$BM shows a clear SPV effect after the material was exposed to air. This follows the results for PC$_{60}$BM given in figure 23.

In table 9 below the results for PC$_{70}$BM work function exposed to simulated sunlight inside a sealed container with N$_2$ is shown.

Table 9: Work function of PC$_{70}$BM photo-degraded in N$_2$. The sample was removed from the glovebox system inside a sealed container filled with N$_2$ with a quartz glass and placed under simulated sunlight. Light intensity was 1 sun. Prior to measurement of the work function the sample had been stored inside the glovebox for a few days.

<table>
<thead>
<tr>
<th>Time (Hours)</th>
<th>Work function (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>4.405 ± 0.041</td>
</tr>
<tr>
<td>0.75</td>
<td>4.432 ± 0.020</td>
</tr>
<tr>
<td>1.25</td>
<td>4.431 ± 0.023</td>
</tr>
<tr>
<td>2.25</td>
<td>4.416 ± 0.021</td>
</tr>
<tr>
<td>3.25</td>
<td>4.476 ± 0.048</td>
</tr>
<tr>
<td>5</td>
<td>4.424 ± 0.045</td>
</tr>
<tr>
<td>24</td>
<td>4.400 ± 0.037</td>
</tr>
</tbody>
</table>

A work function change of 0.076 eV was seen. Again, this indicates that the materials work function is stable when it’s exposed to simulated sunlight in N$_2$. 
Figure 29: SPV values measured of PC$_{70}$BM photo-degraded in a N$_2$ atmosphere. Each measurement was done directly after the measurements done in table 9. Light source used can be found in section 3.8.

As for the SPV effect when PC$_{70}$BM was exposed to N$_2$, the maximum effect is only of a magnitude of \( \approx 60 \) meV, indicating that the materials absorption of photons doesn’t induce a shift of E$_F$.

2.2. Ultraviolet photoelectron spectroscopy

Figure 30 shows how the HOMO level as a reference to Fermi level of the system (0 eV) is behaving after exposure to different conditions.

Storage in glovebox prior to exposure and measurement was; Fresh: 21 days, 48h air and light: 6 days, 15 min air and light: 11 days and 15 min N$_2$ and light: 13 days.
Figure 30: HOMO band spectra of PC$_{70}$BM, UPS measurement focused on the HOMO leading edge. A comparison between different exposure conditions can be seen. **Leading edge values with respect to $E_F$:** Fresh: 1.6 eV, 15 min N$_2$ and light: 1.6 eV, 15 air and light: 1.8 eV, 48h air and light: —. (Information about the UPS can be seen in section 3.9.)

From figure 30 a clear indication that the HOMO level is moving away from the Fermi level, and exposure to air gives a larger shift than exposure to N$_2$. After 48h of air and simulated light exposure the HOMO leading edge has completely vanished.

In figure 31 below the work function using the UPS system can be seen.
A clear decrease of the work function can be observed in figure 31 when the film had been exposed to air. However, when exposed to 15 minutes of simulated sunlight in N₂, the work function shifts nothing in relation to the fresh sample. The work function was calculated from the SECO, Work Function: Fresh: 4.38 eV, 15 min N₂ and light: 4.38 eV, 15 min air and light: 4.12 eV, 48h air and light: 3.30 eV.

3. **N2200**

This section is divided in the same way as for the fullerenes.

3.1. **Kelvin Probe**

In table 10 the work function of N2200 is presented for films stored in air in the dark, as measured by the Kelvin probe. The sample was stored for a total of 48 hours inside a Petri dish with aluminum foil protecting it from any external light in air. During the measurements for the first 6 times the relative humidity in the room was 32.6% RH, during the 24h measurement 21.6% RH and during the 48h measurement 23.3% RH.
4. Results

Table 10: Work function of N2200 films kept in dark in air. The sample had been stored inside the glovebox system for 6 days prior to air exposure.

<table>
<thead>
<tr>
<th>Time (Hours)</th>
<th>Work function (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>4.448 ± 0.027</td>
</tr>
<tr>
<td>0.75</td>
<td>4.492 ± 0.016</td>
</tr>
<tr>
<td>1.25</td>
<td>4.495 ± 0.017</td>
</tr>
<tr>
<td>2.25</td>
<td>4.491 ± 0.009</td>
</tr>
<tr>
<td>3.25</td>
<td>4.507 ± 0.005</td>
</tr>
<tr>
<td>5</td>
<td>4.498 ± 0.015</td>
</tr>
<tr>
<td>24</td>
<td>4.460 ± 0.015</td>
</tr>
<tr>
<td>48</td>
<td>4.559 ± 0.015</td>
</tr>
</tbody>
</table>

A total difference in SPV of a magnitude of 0.11 eV was observed in table 10 between the values of 15 min and 48h.

In table 11 one can see how the work function of a N2200 sample evolves when kept in the glovebox (N$_2$) directly after spin coating inside the glovebox.

Table 11: Work function of N2200 films kept inside the glovebox and measured inside the glovebox. With measurements at times after the spin coated material.

<table>
<thead>
<tr>
<th>Time (Hours)</th>
<th>Work function (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>4.320 ± 0.017</td>
</tr>
<tr>
<td>0.75</td>
<td>4.267 ± 0.019</td>
</tr>
<tr>
<td>1.25</td>
<td>4.329 ± 0.043</td>
</tr>
<tr>
<td>2.25</td>
<td>4.353 ± 0.010</td>
</tr>
<tr>
<td>3.25</td>
<td>4.390 ± 0.074</td>
</tr>
<tr>
<td>5</td>
<td>4.302 ± 0.028</td>
</tr>
<tr>
<td>24</td>
<td>4.311 ± 0.025</td>
</tr>
</tbody>
</table>

Comparing table 10 and table 11 indicates that N2200 is very stable inside a glovebox system. Below in figure 32 the SPV was measured related to the work functions of table 11.
Figure 32: SPV values measured of N2200 films stored in the glovebox ($N_2$) after the material had been spin coated. The measurements were done inside the glovebox. Light source used can be found in section 3.8.

From figure 32 a clear indication, as for the fullerenes, no SPV effect is shown.

**Exposed to simulated sunlight**

In table 12 one can see how the materials work function behaves after exposure to air and simulated sunlight. During the first 6 measurements the humidity in the room was 20.7% RH, the measurement done at 24 hour of exposure had a room humidity of 30.6% RH and the measurement done at 48h of exposure had a room humidity of 29.1% RH.

Table 12: Work function of N2200 films, photo-degraded in air. Exposure was done to a simulated sunlight at the intensity of 0.93 suns.

<table>
<thead>
<tr>
<th>Time (Hours)</th>
<th>Work function (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>4.486 ± 0.013</td>
</tr>
<tr>
<td>0.75</td>
<td>4.597 ± 0.008</td>
</tr>
<tr>
<td>1.25</td>
<td>4.528 ± 0.019</td>
</tr>
<tr>
<td>2.25</td>
<td>4.571 ± 0.004</td>
</tr>
<tr>
<td>3.25</td>
<td>4.563 ± 0.019</td>
</tr>
<tr>
<td>5</td>
<td>4.594 ± 0.018</td>
</tr>
<tr>
<td>24</td>
<td>4.676 ± 0.005</td>
</tr>
<tr>
<td>48</td>
<td>4.630 ± 0.008</td>
</tr>
</tbody>
</table>

From table 12, one can deduce a clear increase in work function with increased exposure time.
As for the previous materials, N2200 shows some SPV effect when it has been exposed to light and air. However the effect is not as large as for the fullerenes, with a maximum amplitude of $\approx 117\text{meV}$ in relation to the $\approx 200\text{meV}$ that was measured by the fullerenes.

In table 13 the work function measurements of N2200 exposed to simulated sunlight inside an N$_2$ atmosphere can be seen.

Table 13: Work function measurements of N2200 photo-degraded in N$_2$. The sample was removed from the glovebox system inside a sealed container filled with N$_2$ with a quartz glass consisting placed under simulated sunlight. Light intensity was 1 sun. Prior to measurement the sample had been stored inside the glovebox for a few days.

<table>
<thead>
<tr>
<th>Time (Hours)</th>
<th>Work function (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>4.276 ± 0.053</td>
</tr>
<tr>
<td>0.75</td>
<td>4.248 ± 0.037</td>
</tr>
<tr>
<td>1.25</td>
<td>4.249 ± 0.055</td>
</tr>
<tr>
<td>2.25</td>
<td>4.258 ± 0.030</td>
</tr>
<tr>
<td>3.25</td>
<td>4.261 ± 0.037</td>
</tr>
<tr>
<td>5</td>
<td>4.225 ± 0.056</td>
</tr>
<tr>
<td>24</td>
<td>4.242 ± 0.024</td>
</tr>
</tbody>
</table>

From table 13 one can note that the work function doesn’t change much when exposed to simulated sunlight within N$_2$. Indicating that the work function is stable in this condition. The resulting SPV values measured in this condition can be seen in figure 34.
Figure 34: SPV values measured of N2200 photo-degraded in a N\textsubscript{2}. Each measurement was done directly after the (dark) work function measurements seen in table 13. (Light source used can be found in section 3.8.)

Figure 34 indicates that no significant SPV effect occur when the material had been exposed N\textsubscript{2} and simulated sunlight.

### 3.2. Ultraviolet photoelectron spectroscopy

Figure 35 the HOMO leading edge measured by the UPS with respect to the Fermi level of the system (0 eV) is shown for two different exposure conditions, fresh and 15 min in air and light. The reason why no more measurements were done on this material, was because the material didn’t behave well when measured with the UPS.

Storage in glovebox prior to exposure and measurement was; 
- **Fresh**: 1 day, 
- 48h air and light: 6 days, 
- 15 min air and light: 11 days, 
- 15 min air and light + 2h UV same sample as 15 min air and light.
Figure 35: HOMO band spectra of N2200. UPS measurement focused on the HOMO leading edge. A comparison between different exposure conditions can be seen. **Leading edge values:** Fresh: 1.2 eV, 15 min in air and light: —. (Information about the UPS can be seen in section 3.9)

Figure 35 shows a small bulge indicating density of states at 1.2 eV for the fresh sample. However, after just 15 min in air and light these density of states are completely gone.
Figure 36: Secondary cut-off spectrum of N2200, measured by UPS, after different exposure conditions. Information about the UPS can be seen in section 3.9. **Charging was observed for 48h air and light.**

In figure 36 above one can see that the work function decreases with increased exposure time. The work function is extracted from the SECO giving, **Work Function:** Fresh: 4.00 eV, 15 min air and light: 3.82 eV, 15 min air and light + 2h UV: 3.72 eV, 48h air and light: 2.69 eV.

### 4. Annealing

In figure 37 the work function after annealing for 10 minutes at 120°C can be seen. The humidity in the room for the fresh samples was 23.3% RH while for the measurements done 24 hours of exposure and after the annealing procedure the humidity was 22.1% RH.
4. Results

Fresh 24h light+air exposure After annealing

Work Function (eV)

Annealing Effects

PC$_{60}$BM, PC$_{70}$BM and N2200 measured with Kelvin probe. Fresh indicates that the samples were not exposed to sunlight but passed through air directly after they were spincoated in the glovebox and before measurement in air. After annealing indicates annealing the sample for 10 minutes at 120°C inside the glovebox. The samples were then extracted and exposed to roughly the same amount of air as the fresh measurements before measurement in air.

In figure 37 above one can see after 24h light+air exposure the work function has increased compared with those of the fresh samples for all three materials. The fresh work function correlate well with the previous measurements for all three materials if one relates this value to the values of table 3, table 5 and table 9 for PC$_{60}$BM, PC$_{70}$BM and N2200 respectively. This indicates a good reproducibility. The values for 24h light+ air exposure also corresponds well with the previous results for PC$_{60}$BM and PC$_{70}$BM in table 3 and 7, respectively. However, for N2200 the value for the work function after exposure in figure 37 compared to table 31 shows a difference of 0.174 eV.

After the annealing one can see that the work functions for the fullerenes didn’t change much indicating that there are no restoring effect for them during this annealing condition. N2200 however shows a clear decrease of its work function 0.0786 eV giving an indication that the change in work function is reversible.
5. Discussion

1. Kelvin probe in air or N$_2$.

It was shown in table 1 that the work function of the gold probe is changed by $\approx 0.1$ eV. The most probable reason for this change is that N$_2$ is an inert gas whereas air is not. The change seen in the work function of the probe (table 1) is correct if one assumes that the work function of HOPG isn’t changed and kept at a constant $\Phi = 4.6$ eV. This is however not necessarily true, as this is most probably due to a work function change for both the probe and the HOPG calibration sample. There is work done by Hansen W. and Hansen G. in [46], who showed that the actual work function of HOPG in air is $\Phi_{HOPG}^{air} = 4.475 \pm 0.005$ eV. This value was not used because the standard is to work with the value $\Phi_{HOPG}^{air} = 4.6$ eV. On top of that the work function of HOPG in N$_2$ seems to be still relatively unknown.

Because of this, it’s difficult to say anything concrete about the absolute work function of the materials with the Kelvin probe technique. However, the general trends observed are still true, and this is important for the understanding of work function behaviour during exposure to different environments.

2. Work function of PC$_{60}$BM seems unstable after exposure to yellow light in N$_2$.

First and foremost it’s interesting to see that when PC$_{60}$BM had been stored inside the glovebox for 4 days it gave a work function value after 15 min of degradation to simulated sunlight in N$_2$ of $\Phi = 4.371$ eV, which can be seen in table 5. However, in table 3 after 15 min exposure to N$_2$ in "dark" the work functions was measured to $\Phi = 4.560$ eV. A clear difference in WF can be seen of $\Delta \Phi = -0.189$ eV. If one does the same comparison for both PC$_{70}$BM and N2200 one gets $\Delta \Phi^{70} = -0.052$ eV and $\Delta \Phi^{N2200} = -0.044$ eV respectively, which is much lower, and near to the error of the measurements themselves. Important to keep in mind when doing this comparison is that the samples had been exposed 15 min to simulated sunlight in one case and not in the other. This means that the difference could be induced by effects due to the exposure of the simulated sunlight. The change in the work function for PC$_{70}$BM and N2200 during exposure to simulated sunlight in N$_2$ is $>0.1$ eV, for PC$_{60}$BM the maximum change was $\Delta \Phi_{60}^{max} = \Delta \Phi_{24h}^{60} - \Delta \Phi_{1.25h}^{60} = 0.145$ eV where it seems like the trend is that the work function decreases until 1.25h of exposure to simulated sunlight in N$_2$ (table 5) after which it starts to increase. A reason for the large work function decrease between the first measurements of table 3 and 5 could either be because of the simulated sunlight itself or if the work function had decreased significantly prior to the measurements of table 5.

To strengthen the hypothesis that the storage affects the sample can be seen by the reduction in the work function during the 24h of measurement of PC$_{60}$BM just from table 3 where an exact decrease of $\Phi_{24h}^{60} = \Phi_{15min}^{60} = -0.081$eV. For PC$_{70}$BM we see a change of $\Phi_{24h}^{70} = \Phi_{15min}^{70} = 0.054$eV from table 6 and for N2200 $\Phi_{24h}^{N2200} = \Phi_{15min}^{N2200} = -0.009$eV from table 30.

If the observations and assumptions are correct one would definitely have to be more careful when studying and manufacturing PC$_{60}$BM in similar conditions as have been used in this thesis. Optimally one would keep track on how long the material had been stored, and just compare samples with the same storage time.

3. Fullerenes has a clear increase in work function when exposed to light and air within 15 min.

If one compares the values of the work function for the materials after 15 min exposed to air and light (table 4, 8 and 12 for PC$_{60}$BM, PC$_{70}$BM and N2200 respectively) to the measurements done when the
material had just been exposed to air in dark for 15 min (table 2, 6, 10 for PC<sub>60</sub>BM, PC<sub>70</sub>BH and N2200 respectively) one finds:

\[
\Delta \Phi^{60} = \Phi_{a+l}^{60} - \Phi_{a}^{60} = 0.139eV
\]
\[
\Delta \Phi^{70} = \Phi_{a+l}^{70} - \Phi_{a}^{70} = 0.238eV
\]
\[
\Delta \Phi^{N2200} = \Phi_{a+l}^{N2200} - \Phi_{a}^{N2200} = 0.038eV.
\] (13)

In equation 13, a+l stands for air+light (table 4,8 and 12) where a is just air (table 2,6 and 10). From these values one can clearly see an increase in the work function after just 15 min exposure to light. This shows the importance of light for degradation in air, i.e. photooxidation has a much stronger effect on the work function than just oxidation, for PC<sub>60</sub>BH and even stronger for PC<sub>70</sub>BH. It also shows that for N2200, the mechanism of degradation is totally different, since photooxidation and oxidation does not have significantly different effect on the work function values. It’s important to remember that prior to exposure the samples had been stored inside the glovebox system for 11 days during the air+dark measurement and 19 days for the air+light measurement. From previous section one would assume that the work function decreases for PC<sub>60</sub>BH in a glovebox. This difference for PC<sub>60</sub>BH and PC<sub>70</sub>BH might be smaller than what is shown here.

It's clear that both fullerenes are very susceptible to photo-oxidation. Whereas for N2200 the degradation mechanism seems to be completely different.

4. Band bending effects seen with Kelvin probe.

If one combines all graphs regarding the SPV values for all three materials a clear relation can be seen. This is that for each material in air and light, the surface of films changes and an increasing band bending develops. This can be seen by the SPV experiment where light is used to flatten the bands, as a way to probe the band bending. Schematic clarification can be seen in the figure below where the maximum amount of band bending observed is depicted for all three materials.
5. Discussion

Figure 38: The figure depicts the band bending effect observed with the Kelvin probe for each material. Under the band diagram is the time stamp of each measurement that gave maximum band bending. The work functions can be found in table 4, 8, 12 for PC$_{60}$BM, PC$_{70}$BM and N2200 respectively. The band bending can be seen in figure 23, 28 and 33 respectively. Note also that the band gaps and band bending shown in the figure are not up to scale.

As can be observed from figure 38 is that the fullerenes has nearly double the band bending effect than N2200, this further strengthens the statement from the previous section that the degradation mechanism is different for N2200 than for the fullerenes. It’s very interesting to see this large difference with respect to what was seen for the materials in N$_2$ atmosphere.

5. Annealing results

The annealing results in figure 37 shows a clear indication that it’s only the non fullerene polymer that shows that annealing has any restoration effects of the work function. It has been shown that annealing of N2200 in all polymer OPV devices has improved efficiency [25]. A reason why one sees this effect is most probably due to the morphology of N2200 has been shown to change with annealing [50], whereas for the fullerenes the surface after 24 hours is already way too damaged to restore any of its previous features.

6. Charging effect in UPS

First of all it’s important to consider the fact that even though the sample had charging it was plotted and shown in the figures, this was indicated in the figure caption. Charging happens because photoelectrons are emitted from the surface, so the sample gets positively charged. If the sample can not dispose of these charges through the back contact that grounds the sample, the sample can build up a positive charge. Reasons for this could be a poor contact with the sample holder or that the film was to thick. When charging was observed only the first scan has been shown, this is because multiple scans on the sample just increases the charging effect. The general effect of charging and how it is observed is that
for consecutive scans the work function and the leading edge of the HOMO level is shifted more and more for each scan.

7. **UPS of N2200 was problematic**

As can be seen from the UPS measurements, N2200 wasn’t as thoroughly studied as the fullerenes. This can be seen in figure 35 where the fresh sample shows a small bulge indicating indicating HOMO density of states starting at 1.2 eV from the Fermi level. However, after just 15 min in air and light the leading edge of the HOMO couldn’t be observed, what is seen is instead a leading edge at around $\approx 3$ eV from Fermi, which is larger than the band gap (2.4 eV [49]) and indicating that it’s not N2200 that is observed here. However the work function was observable, and a decrease in work function could be seen with increased exposure time. It was also observed that the UV light is damaging the surface, after 2h UV exposure a decrease of 0.1eV was observed for the 15 min air and light sample.

8. **UPS results from the fullerenes.**

For both fullerenes one can clearly see that after 48h exposure to air and light, the density of states of the HOMO leading edge is completely gone or shifted outside the energy region which was measured. Also it is clear that PC$_{70}$BM seems to be more stable than PC$_{60}$BM i.e. a smaller shift in the work function was observed. In figure 25 the 15 min air and light suffered from charging so the shift that is seen could be a bit exaggerated. However a work function lower than the one after exposure to N$_2$ is expected as the UV light most probably flattens the bands for when the samples had been exposed to air prior to measurements.

Another feature that can be seen in figure 25 and 30 is that the valley behind the first HOMO peak is changing a clear indication that the surface is altered when exposed to different conditions. It’s interesting that this change is happening even for the case when both materials had been exposed to the inert gas.

In the work function figures 26 and 31 one can see that the change from fresh to 15 min N$_2$ and light is larger for PC$_{60}$BM than PC$_{70}$BM. It’s important to keep in mind that the samples for fresh and exposed had been stored for 1 day and 13 days respectively. While, for the PC70BM the samples had been stored for 21 days and 13 days respectively. If the discussion of section 5.2 is true this is a result one would most likely expect.

9. **Difference in KP and UPS work function measurements.**

The absolute values of the work function obtained with the Kelvin probe and with Ultraviolet photoelectron spectroscopy are systematically different, (see table below).
Table 14: Work function difference between UPS measurements and KP measurements. Samples that experienced charging has been marked by parentheses.

<table>
<thead>
<tr>
<th>Material and exposure condition</th>
<th>UPS work function (eV)</th>
<th>KP work function (eV)</th>
<th>Difference (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC$_{60}$BM:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15min air and light</td>
<td>(3.82)</td>
<td>4.75</td>
<td>-0.93</td>
</tr>
<tr>
<td>15min N$_2$ and light</td>
<td>4.12</td>
<td>4.37</td>
<td>-0.25</td>
</tr>
<tr>
<td>48h air and light</td>
<td>3.64</td>
<td>4.76</td>
<td>-1.12</td>
</tr>
<tr>
<td>PC$_{70}$BM:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15min air and light</td>
<td>4.12</td>
<td>4.79</td>
<td>-0.67</td>
</tr>
<tr>
<td>15min N$_2$ and light</td>
<td>4.38</td>
<td>4.40</td>
<td>-0.02</td>
</tr>
<tr>
<td>48h air and light</td>
<td>3.30</td>
<td>4.76</td>
<td>-1.46</td>
</tr>
<tr>
<td>N2200:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15min air and light</td>
<td>3.82</td>
<td>4.49</td>
<td>-0.67</td>
</tr>
<tr>
<td>15min N$_2$ and light</td>
<td>-</td>
<td>4.28</td>
<td>-</td>
</tr>
<tr>
<td>48h air and light</td>
<td>(2.69)</td>
<td>4.63</td>
<td>-1.94</td>
</tr>
</tbody>
</table>

From table 14 one can see that the difference in work function between the two methods is always smaller when the Kelvin probe was inside the glovebox. This indicates that the assumptions made when measuring with the Kelvin probe in air, are incorrect, as was discussed in section 5.1. Reasons for differences that can be observed between UPS and KP is further discussed in [51]. A comparison with the results in [51] and the results of table 14 shows a connection that the work function measured with UPS is consistently lower than the work function measured with KP. An important factor to keep in mind as well is the two completely different measuring environments. UPS spectra done in UHV and KP in air or N$_2$. The work function is also calculated differently for the two methods, work function with UPS is estimated but comparing the Fermi-edge and the SECO, whereas the work function with KP is an averaged value over the area of the gold probe.

Another interesting result is if one compares the results of 15 min air and light with 48h air and light measurements for all materials, one finds, that measured with the Kelvin probe the fullerenes work function doesn’t change much, however for N2200 one can see a clear increase. However, in the UPS the work function shows a clear decrease. It’s difficult to say why the difference is so severe, and especially why the trend is opposite for the two techniques. This difference is physically unreasonable and indicates that the measurements done on the samples exposed to air has gone wrong. An indication however is that the work function measurements done with the UPS could be the one reasonable for this large difference. The reason for this statement is because the work function in the Kelvin probe could be reproduced easily, however the work function measurement done with the UPS for 15 min air and light and 48h air and light were only done on one sample and a statement about the reproducibility of the UPS measurements couldn’t be stated. Therefore for future UPS and KP measurements it would be important to try to make a more thorough attempt at isolating the difference of the UPS and KP with more measurements with both methods on different samples from different batch with the same exposure times.
6. Conclusions
The surface electronic properties of three materials (PC$_{60}$BM, PC$_{70}$BM and N2200), commonly used as electron acceptor materials in organic solar cells, were studied in this thesis. A focus was made on the work function and how it evolves after different exposure conditions (air, N$_2$, air and light, and N$_2$ and light). It was shown that the PC$_{60}$BM was less stable to photo oxidation than its counterpart PC$_{70}$BM. Prior to the study an assumption was made that none of the materials work function would change considerably while stored in N$_2$. However, this was found to be not true for PC$_{60}$BM, whose work function changed significantly while exposed to yellow light inside the glovebox filled with a N$_2$ atmosphere. The exact mechanism for this observed work function change in PC$_{60}$BM films during storage in N$_2$ is not known, neither is the role of the yellow light. Band bending effects were observed for all materials but only after exposure to air and light. The fullerenes showed a larger band bending effect than the N2200. After annealing for 10 minutes and at 120°C, only N2200 showed a restoring effect.

A clear difference between the work functions extracted from KP and UPS measurements was seen, especially after exposure to air. Where the work function difference was so large that the results were physically unreasonable. Even the trend of the change in work function due to exposure was different for KP and UPS, the reasons for this couldn’t be isolated during this thesis.
7. Outlook

In general this project has gone very well, with only a few problems. Early in the project the gloveboxes were air contaminated, which delayed the experiments by approximately one and a half week. Contaminated samples were discarded.

A few open questions are left for future studies. First of all a thorough study of how N₂ storage affects organic materials especially PC₆₀BM would most probably clear up the question marks regarding the changes in work function of PC₆₀BM upon storage in N₂, seen within this thesis. The SPV effect could also be studied in more detail by using monochromated light instead of a white lamp. Due to time constraint the annealing effect couldn’t be further studied. If this was to be further studied, the annealing time and temperature would be changed to investigate the conditions for when the effect is reversible. With regards to doing Kelvin probe in air or N₂ a study would have to be done in order to determine which work function the calibration sample has in both atmospheres. To do this with a Kelvin probe one could use other materials as reference, where the work function is well known in both atmospheres to determine the exact work function of the HOPG. Assuming that the gold probes work function is known.

There is definitely information left to be extracted from the results within this thesis, which has not been done due to time constraint. Especially, one can see indications of multiple effects changing the work functions. It would probably be interesting to try and isolate these. Further some questions could probably be cleared up, by comparing the results with results from related studies.
8. Appendix

1. List of abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPV</td>
<td>Organic Photovoltaic</td>
</tr>
<tr>
<td>OSC</td>
<td>Organic solar cell</td>
</tr>
<tr>
<td>PCE</td>
<td>Power conversion efficiency</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>FF</td>
<td>Fill factor</td>
</tr>
<tr>
<td>UPS</td>
<td>Ultraviolet photoelectron spectroscopy</td>
</tr>
<tr>
<td>KP</td>
<td>Kelvin probe</td>
</tr>
<tr>
<td>WF</td>
<td>Work function</td>
</tr>
<tr>
<td>CPD</td>
<td>Contact potential difference</td>
</tr>
<tr>
<td>SPV</td>
<td>Surface photovoltage</td>
</tr>
<tr>
<td>HOPG</td>
<td>Highly oriented pyrolytic graphite</td>
</tr>
<tr>
<td>RH</td>
<td>Relative humidity</td>
</tr>
<tr>
<td>SECO</td>
<td>Secondary electron cut-off</td>
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</table>
References


