

# Towards Increasing the Photon Harvesting in Bulk Heterojunction Polymer Solar Cells

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## Abstract

Organic solar cells based on interpenetrating networks of conjugated polymer donors and fullerene-based acceptors with AM 1.5 efficiencies up to 3 % were presented recently. For further improvement of the efficiency, the absorption of the solar light should be increased. This can be done by matching the active layer absorption better to the terrestrial solar emission spectrum and by increasing the absorption coefficient.

In this contribution we present a combined spectroscopic and device study of novel materials that extend the absorption to the red. The systems studied are, among others, low bandgap polymers as electron donors or dye sensitized fullerene compounds.

The photophysical properties are investigated by excited state spectroscopy and the materials are discussed with regard to their suitability for efficient photoinduced charge generation.

The photovoltaic activity is demonstrated by photocurrent action spectra as well as by AM 1.5 efficiencies of prototype devices made using these novel materials.

Keywords: organic solar cells, photoinduced charge transfer, photon harvesting, sensitization, fullerene, phthalocyanine

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## 1. Introduction

Conjugated polymer based photovoltaic devices have gained great interest within the scientific community during the last years [1-3].

Photoinduced charge transfer from excited polymeric donors to  $C_{60}$  fullerene like acceptors [4] has been established as an efficient way of charge creation. This process is known to happen quantitatively in a time regime of approx. 50 fs in excess of fullerene [5]. The recombination is hindered and happens in the  $\mu$ s regime [6]; therefore the charges live long enough to be collected at the electrodes.

The bulk heterojunction concept [1], i.e. the intimate mixing of donor and acceptor, enlarges the interface between the two phases. This ensures charge creation by absorbed photons throughout the volume of the bulk.

Optimization and consequent engineering of cells with poly-[2-methoxyl, 5-(3',7' -dimethyloctyloxy)] para phenylene-vinylene (MDMO-PPV) as donor and [6,6]-phenyl  $C_{61}$  butyric acid methyl ester (PCBM) as acceptor resulted in AM 1.5 efficiencies of to 3 % [7,8]. Several parameters are known to influence the cell function and have to be optimized to reach higher efficiencies.

a) Energy levels of the active materials [9] and

b) the choice of contacts [8] influence the open circuit voltage  $V_{oc}$  and the fill factor FF.

c) In addition, the processing conditions influence the blend nano- morphology [7] and film quality and thereby the efficiency.

However, the main limiting factor of polymer solar cells today is the low amount of absorbed photons [10]. The main reasons are the thin active layer and the mismatch of the absorption spectrum to the terrestrial sun spectrum. MDMO-PPV has its absorption maximum around 500 nm, whereas the maximal solar photon flux is in the range between 600 and 800 nm (see figure 1). Film thickness of the blend cannot be increased further due to low mobility of the charges. To overcome this problem the strategy is to use photoactive materials with a low bandgap.

In this contribution we present new conjugated polymer as well as fullerene materials absorbing light more in the spectral range for photovoltaics.

For the polymers, we present the new conjugated polymer poly [*N*-dodecyl-2,5-bis(2-thienyl)pyrrole-2,1,3-benzothiadiazole] (PTPTB) with an absorption onset at 750 nm; this corresponds to a bandgap of 1.6 eV. The material shows, in blends with PCBM, photoinduced charge transfer and photovoltaic device efficiencies of 1 % under AM 1.5 simulated illumination when incorporated in bulk heterojunction solar cells.

For the fullerene, we present a dyad molecule zinc-tri-tert.-butyl-phthalocyanine fulleropyrrolidine (Pc- $C_{60}$ ) consisting of a fulleropyrrolidine  $C_{60}$ -P covalently linked with a zinc-phthalocyanine (ZnTBPC). Since fullerenes absorb in the UV, and therefore hardly contribute to the solar photocurrent, absorbing fullerene materials would be very welcome for polymer bulk heterojunction solar cells. Experimental proof for charge creation upon photoexcitation is presented by photoinduced absorption measurements. Photovoltaic devices using this novel dyad molecule are presented.

## 2. Experimental

The syntheses of PTPTB [11, 12] and Pc-C60 [13] have been described previously. The molecular structure of the compounds is presented in figure 2 together with MDMO-PPV and PCBM.

Absorption of thin films is measured on a HP 8453. Photoinduced absorption PIA, a pump-probe technique, is measure on a homemade setup at 100 K. Excitation is performed with mechanically chopped laser light from an  $Ar^+$  laser with 40 mW. The transmission changes of a tungsten lamp beam are measured phase sensitively with a lock-in amplifier, after passing a monochromator. As detectors, a Si -InGaAsSb sandwich photodiode is used.

The geometric structure of the photovoltaic devices is shown in figure 2. On precleaned ITO glass, a layer of ~ 150 nm of pEDOT:PSS, Baytron P, is spincoated as hole transport layer from an aqueous dispersion. The photoactive layers are spin cast from chlorobenzene or toluene. As top electrode, 6 Å of LiF and subsequently 60 nm of Al is evaporated in a vacuum better than  $10^{-5}$  mbar. Device testing is done in an argon glovebox. Current vs. voltage curves are measured with a Keithley 2400 source meter in the dark and under illumination of a Steuernagel solar simulator with  $800 \text{ W m}^{-2}$  to simulate the AM 1.5 solar spectrum. Incident photon to collected electrons IPCE, (i.e. the external quantum efficiency), is measured with a lock-in amplifier after illumination with monochromatic light from a tungsten lamp.

### 3. Results and Discussion

#### 3.1 Low Bandgap polymer PTPTB

The absorption spectrum of a thin film of PTPTB is presented in figure 3. The absorption maximum is shifted by more than 100 nm as compared to for example MDMO-PPV. The optical bandgap is determined with 1.6 eV and corresponds with electrochemically-determined gap of 1.7 eV.

Dhanabalan et al. could show photoinduced electron transfer from excited PTPTB to PCBM acceptor [12] by PIA measurements. The performance of devices of PTPTB/PCBM 1/3 blend is presented in figure 4. The photovoltaic efficiency, as product of  $V_{oc}$ ,  $I_{sc}$ , FF and divided by the light intensity, is around 1%. It is mainly limited by the low FF. Possible origins are a high series resistance or a low shunt resistance. Since series resistance can be excluded as limiting factor from the high injection current in forward direction, small shunts due to the bad film forming properties of the blend are likely to cause the limitation of the FF. The  $V_{oc}$  is reduced by less the 100 mV, as compared to MDMO-PPV, although the bandgap has been reduced by more the 600 meV. The onset for the electrochemical doping for both materials is in the same region (+ 0.53 V vs. NHE for PTPTB, +0.5 V vs. NHE for MDMO-PPV), therefore the effective distance between the donor HOMO and the acceptor LUMO is similar in both cases. The IPCE spectrum, figure 5, closely follows the absorption and demonstrated the contribution of PTPTB to the photocurrent.

#### 3.2 Fulleropyrrolidine- Phthalocyanine dyad photophysics

The absorption spectrum of the Pc-C<sub>60</sub> dyad is presented in figure 3. The absorption spectrum is in first approximation the sum of that of the single reference component's absorption.

PIA spectra of the single components Zn-TBPc and C<sub>60</sub>-P as well as of the covalently linked dyad Pc-C<sub>60</sub> is presented in figure 6. The spectrum of the dyad shows distinct features compared to the parent molecules.

Zn-TBPc shows a negative band around 750 nm, which we assign to the ground-state bleaching of the Q-band, and a broad absorption around 1300 nm, we assign it to a triplet-triplet absorption.

The C<sub>60</sub>-P is excited in the UV, since the visible absorption is too weak. The PIA spectrum shows an intense peak at 690 nm, which is known as the triplet transition in fullerene [14, 15].

In the Pc-C<sub>60</sub> film, both triplet transitions are quenched. The PIA spectrum shows the negative band at 750 nm, a narrow absorption peak at 1100 and a broad absorption increasing in the near infrared. The negative band we assign to the ground-state bleaching of the Zn-TBPc unit, the band at 1100 nm is characteristic for the fullerene anion. The broad absorption in the far red is probably due to the positive charge located on the phthalocyanine-unit. The luminescence of the Zn-TBPc is significantly reduced in the Pc-C<sub>60</sub> molecule.

From these results we conclude that a photoinduced electron transfer occurs from the phthalocyanine unit to the fullerene.

#### 3.3 Fulleropyrrolidine-Phthalocyanine photovoltaic devices

Figure 7 shows the I-V curve of a Pc-C<sub>60</sub> photovoltaic device in the configuration showed in figure 2. The devices show a rectification of ~ 10 at +/- 2V and a clear photoeffect under AM 1.5 illumination. A low shunt resistivity due to bad film morphology obtained by spin cast films probably causes the low FF of 0.23. Figure 8 shows the IPCE spectrum in comparison with the optical absorption. Quantum efficiency up to 1 % at the peak maximum is observed. The IPCE spectrum matches the absorption spectrum well, showing symbatic behaviour. Both, the phthalocyanine and the fullerene contribute to the photocurrent. Studies with additional donor and acceptor molecules/polymers for increased photon harvesting and improved charge transport are under way.

#### **4. Conclusion**

Photon harvesting by shifting the optical absorption spectrum to the red is a viable way to increase the efficiency of polymer based solar cells. PTPTB shows photoinduced charge transfer to PCBM. Devices from the blends of the two materials show AM 1.5 efficiencies up to 1 %. The onset of the photocurrent is at the absorption onset at 750 nm.

In the fulleropyrrolidine-phthalocyanine dyad, photoinduced charge transfer from the ZnTBPC unit onto the C<sub>60</sub>-P takes place. Devices with this molecule show a photovoltaic effect with a short circuit current of 0.2 mA cm<sup>-2</sup> under illumination of 800 W m<sup>-2</sup>. Light with the energy of the Q band absorption of phthalocyanine is harvested for the photocurrent by the dyad molecule, proving the concept of spectral shift for photon harvesting. Optimization of these systems is necessary for utilizing the full potential of this approach

#### **Acknowledgments**

The authors thank David Muehlbacher and Harald Hoppe for their support in the experimental work. Further we thank Helmut Neugebauer and Dieter Meissner for helpful discussions.

This work has been performed within the Christian Doppler Society's dedicated laboratory on Plastic Solar Cells funded by the Austrian Ministry of Economic Affairs, Quantum Solar Energy Linz Ges. m. b. H. and the European commission, within the framework of Human Potential- Research Training Network, contract No HPRN-CT-2000-00127. Further, the financial support by the Land Oberösterreich (ETP) and the Magistrat Linz. Financial support by E.E.T (EETK97115) and by the Council for Chemical Sciences of the Netherlands Organization for Scientific Research (CW-NWO) and the Eindhoven University of Technology in the PIONIER program (98400) is acknowledged.

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## Figure Caption

**Figure 1:** AM 1.5 solar spectrum (full line) and integrated photon flux (circles) in comparison with the absorption of an MDMO-PPV/PCBM 1/4 (dotted line) blend as used in photovoltaic cells.

**Figure 2:** Chemical structure of PTPTB poly [*N*-dodecyl-2,5-bis(2'-thienyl)pyrrole-2,1,3-benzothiadiazole] , MDMO-PPV (poly-[2-methoxyl, 5-(3',7' – dimethyloctyloxy)] para phenylene-vinylene), PCBM ([6,6]-phenyl C<sub>61</sub> butyric acid methyl ester), Pc-C<sub>60</sub> (zinc-tri-tert. -butyl phthalocyanine fulleropyrrolidine) and the device structure of the thin film solar cells.

**Figure 3:** absorption spectrum of PTPTB (open triangles) and Pc-C<sub>60</sub> (open squares) thin film, both spin cast from toluene.

**Figure 4:** device characteristics of a PTPTB/PCBM 1/3 solar cell: I-V curve in the dark (dots) and under AM 1.5 illumination (full line); active layer is spin cast from toluene.

**Figure 5:** device characteristic of a PTPTB/PCBM device: IPCE spectrum compared to the amount of absorbed photons of the active film.

**Figure 6:** Photoinduced absorption spectra at 100 K of thin films of fullerene (dotted line), excited at 352 nm, Zn-phthalocyanine (full line) excited at 685 nm and Pc-C<sub>60</sub> dyad (open circles), excited at 685 nm.

**Figure 7:** device characteristics of a Pc-C<sub>60</sub> device: I-V curve in the dark (dots) and under AM1.5 illumination (full line), active layer is spin cast from toluene.

**Figure 8:** IPCE (full line) in comparison with the optical absorption (dotted line) of a Pc- C<sub>60</sub> device in sandwich geometry between ITO-PEDOT and LiF-Al contact.

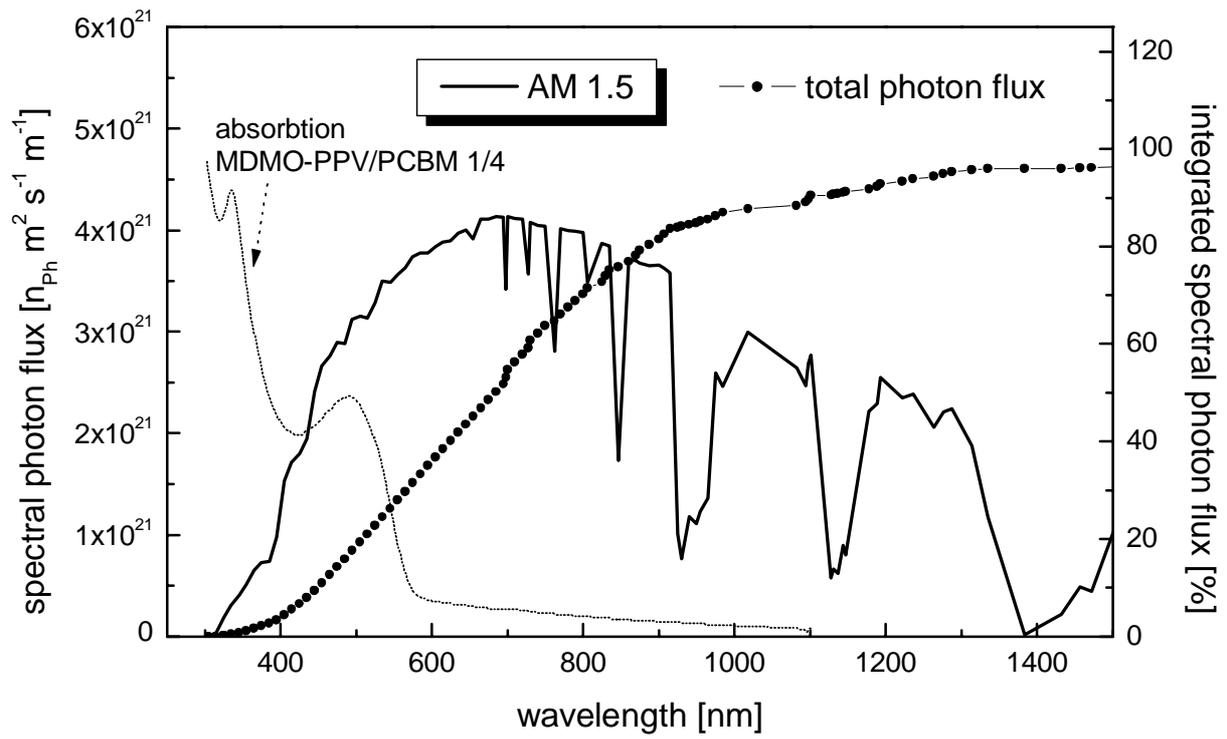


Figure 1: Christoph Winder et.al.



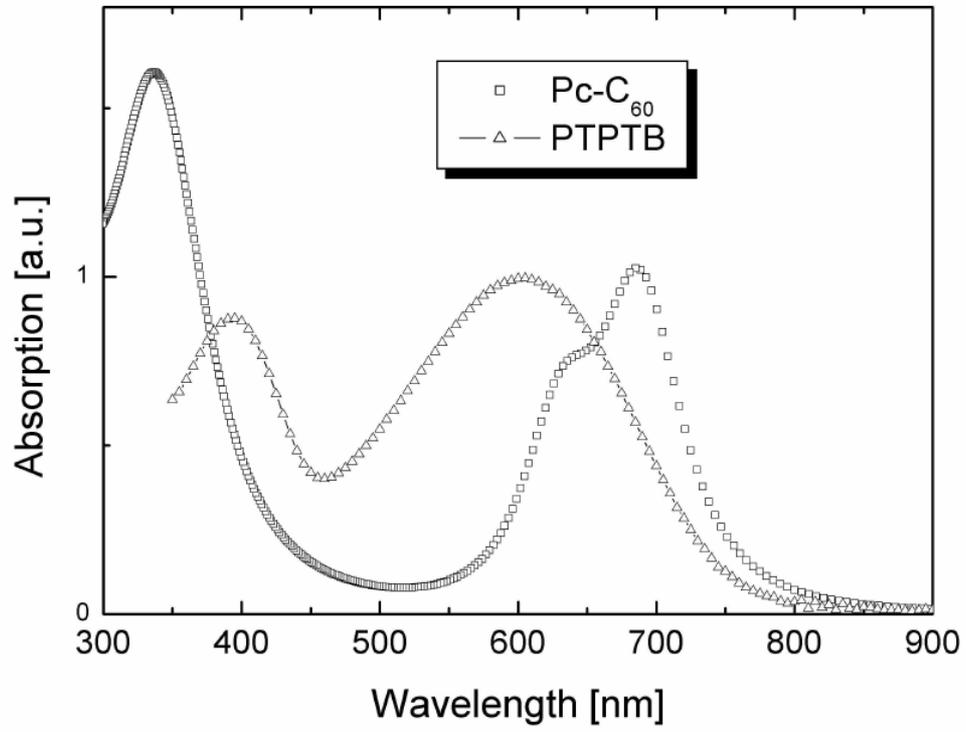


Figure 3: Christoph Winder et.al.

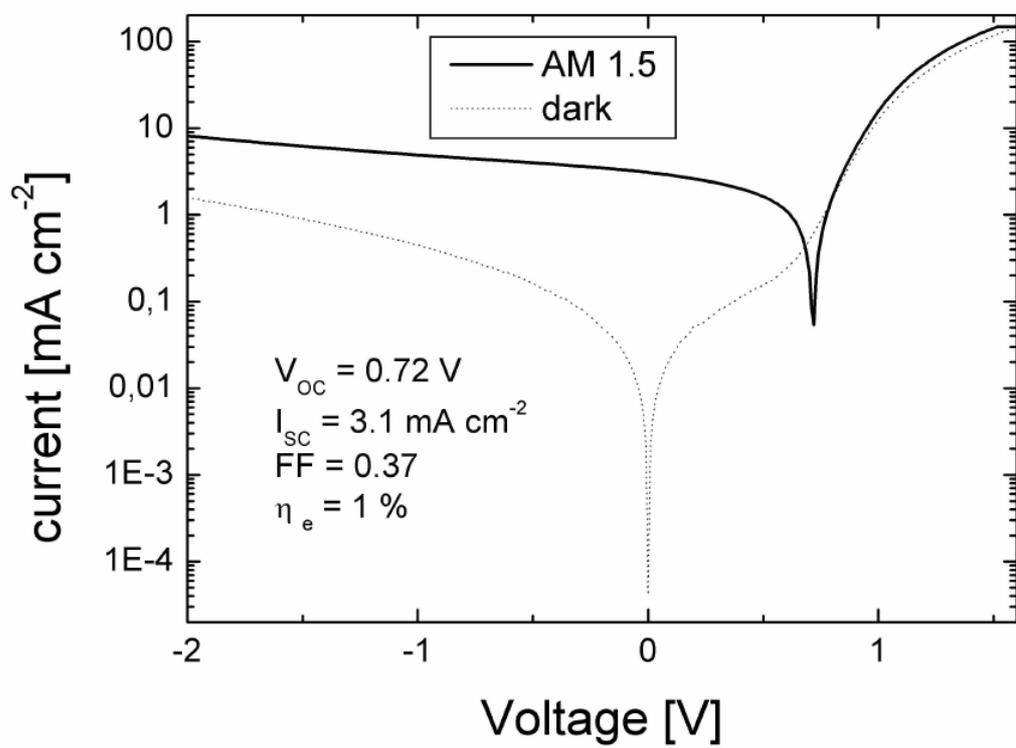


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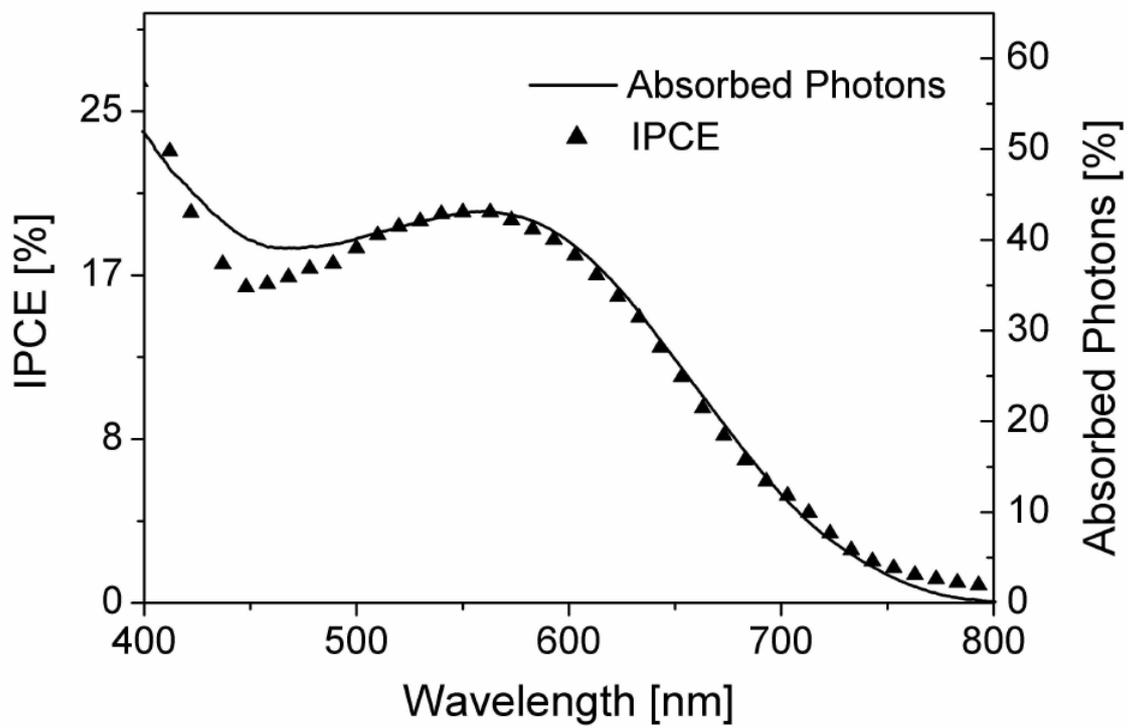


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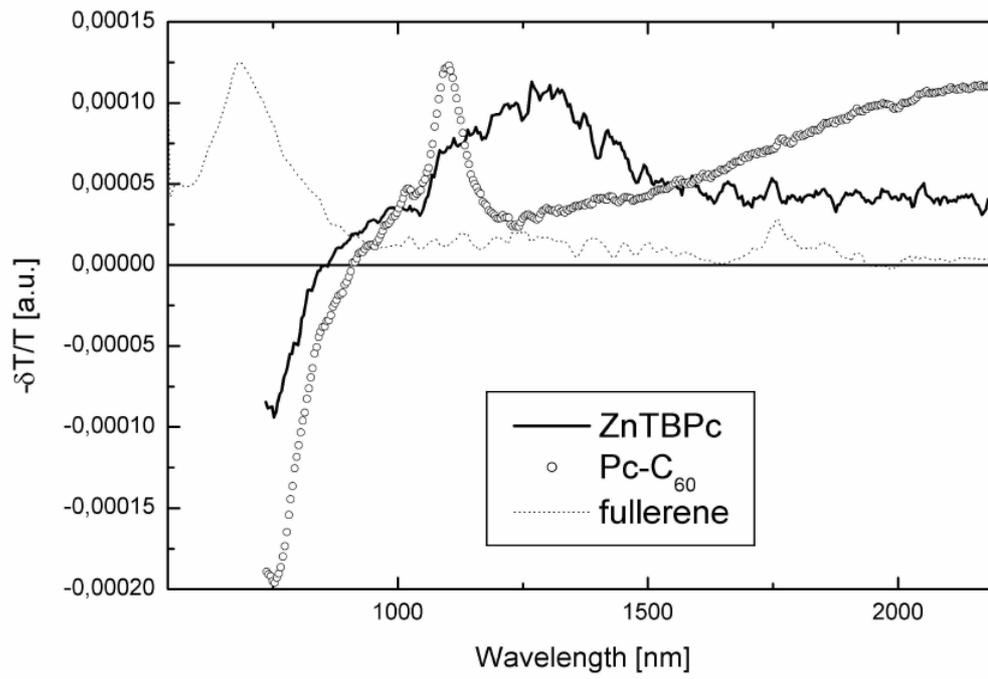


Figure 6: Christoph Winder et.al.

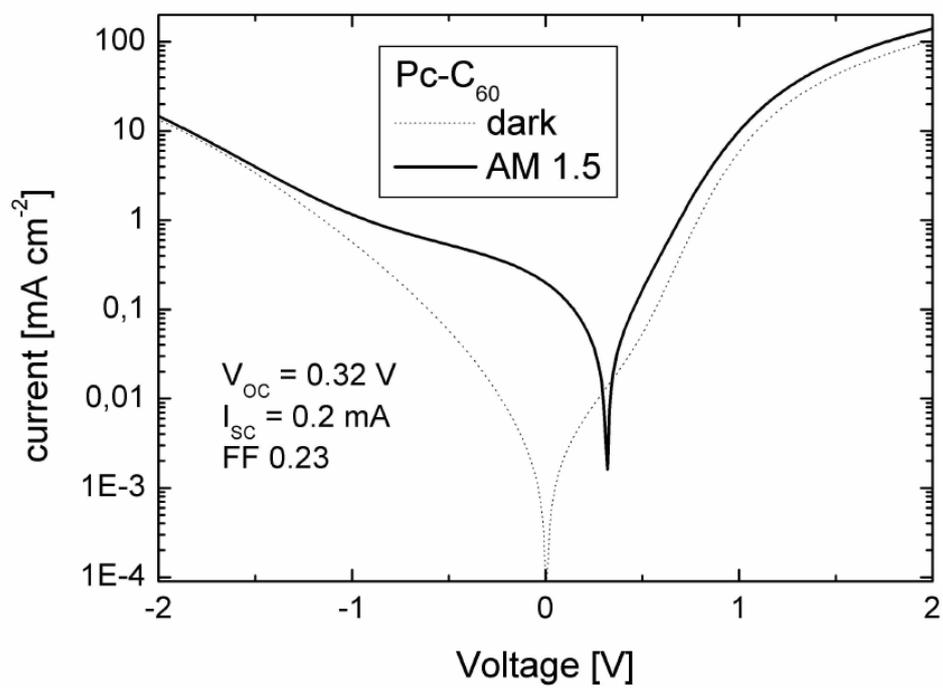


Figure 7: Christoph Winder et.al.

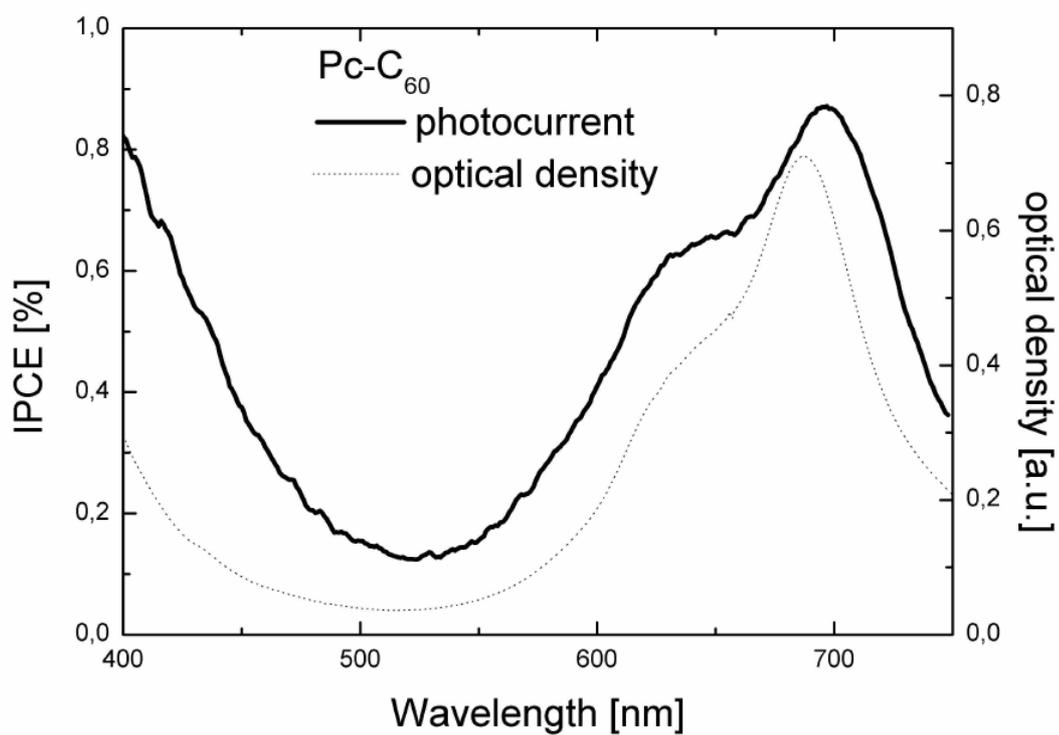


Figure 8: Christoph Winder et.al.