

Fourier-Transform Photocurrent Spectroscopy for a fast and highly sensitive spectral characterization of organic and hybrid solar cells

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## Title

Fourier-transform photocurrent spectroscopy for a fast and highly sensitive spectral characterization of organic and hybrid solar cells

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## **Abstract**

Two modes of Fourier-Transform Photocurrent Spectroscopy (FTPS) are presented for a fast and sensitive determination of photocurrent spectra of organic and dye-sensitized solar cells. Furthermore, FTPS allows to spectrally resolve sub-bandgap absorption phenomena in P3HT, in organic P3HT:PCBM bulk heterojunctions and in hybrid P3HT/TiO<sub>2</sub> solar cells. The sub-bandgap absorption in the P3HT:PCBM blend is dominated by a band due to the formation of a ground-state charge-transfer complex between the polymer and PCBM. In P3HT/TiO<sub>2</sub> junctions such a charge-transfer complex band is not observed. Long-lived light induced sub-bandgap states appear in pure P3HT and in P3HT/TiO<sub>2</sub> junctions after irradiation with  $E > 1.9$  eV.

## **Keywords**

Organic solar cells ; Dye sensitized solar cells ; FTPS ; optical spectroscopy

## 1. Introduction

New types of solar cells such as organic bulk heterojunction (BHJ) solar cells and dye sensitized solar cells (DSSC) are based on three dimensional, nanoscale interpenetrating networks of different electron and hole transporting materials. At the large internal interface, excitons created upon illumination are split, resulting in separated electrons and holes, which are transported in different materials. Power conversion efficiencies up to 5 % were reported for fully organic BHJ devices using a blend of the conjugated polymer poly(3-hexylthiophene) (P3HT) and the fullerene derivative [6-6]-phenyl C61 butyric acid methyl ester (PCBM) [1]. DSSCs consisting of a nanoporous TiO<sub>2</sub> network, a dye and an electrolyte nowadays reach power conversion efficiencies over 10 % [2]. The use of conjugated polymers in DSSCs as a replacement for the liquid electrolyte as the hole transporting material can avoid encapsulation and stability problems. Because of the conjugated polymer's ability to absorb light, it is also possible to omit the dye [3]. On the other hand, the replacement of the morphologically instable organic fullerene network [4-5] in organic BHJ devices by a metal oxide network could improve the stability of the morphology of such devices. In this way both the organic and dye sensitised solar cell evolve to hybrid organic/inorganic solar cells.

An important step in the further development of these types of solar cells is the need for a better insight in the electronic structure and density of trapped states of the used materials, and their influence on the device performance. States in the bandgap will have a strong influence on transport, recombination and

trapping properties of the used materials. Fourier-Transform Photocurrent Spectroscopy already has proven to be a valuable measurement technique to study sub-bandgap features in amorphous silicon [6] and polymer/fullerene [7] photovoltaic devices. FTPS uses the output light beam of a Fourier-Transform Infrared (FTIR) spectrometer to illuminate the photovoltaic device under test [6]. The spectral dependence of the incident light is measured with a calibrated photodetector and converted to light irradiation power. In this way, a photocurrent spectrum in A/W can be obtained.

The output light beam of an FTIR spectrometer is an intensity-modulated light beam. In this work, two modes of the FTIR spectrometer are used: The Continuous Scan mode (CS-FTPS) and the Amplitude Modulated step scan mode (AM-FTPS). In the CS-FTPS mode, the incident light is modulated with a different frequency  $f$ , depending on its wavenumber  $\sigma$ :

$$f = 2\sigma v \quad (1)$$

Hereby is  $v$  the mirror velocity of the FTIRs moving mirror [8]. In the AM-FTPS mode the output beam is modulated with a fixed chopping frequency for every wavenumber. In this mode, spectral information is extracted by measuring the photocurrent signal for different mirror retardations [8].

In this work, absolute photocurrent spectra of an organic P3HT:PCBM solar cell and a DSSC are obtained by the FTPS method. The extremely high sensitivity of this method will be demonstrated by the detection of sub-bandgap features in P3HT, PCBM, P3HT:PCBM and the hybrid P3HT/TiO<sub>2</sub> device.

## 2. Experimental Details

### 2.1 Solar cells

Organic devices with an active layer of P3HT, PCBM and the P3HT:PCBM 1:1 blend were constructed using a standard procedure in N<sub>2</sub> atmosphere. A 40 nm thick poly(3,4-ethylenedioxythiophene-polystyrenesulfonate (PEDOT-PSS, Bayer) layer was spincoated from an aqueous solution onto indium tin oxide (ITO, 100 nm) coated glass. These substrates were dried for 20 min on a hotplate at 120 °C. Subsequently the active layers of the pure and blended materials were spincoated from a chlorobenzene solution (2 wt %) on top of the PEDOT-PSS layer. Finally, the Al top electrode of 80 nm was evaporated on top of the active layer.

Hybrid, P3HT/TiO<sub>2</sub> devices were prepared in the following way: an aqueous citratoperoxo-Ti(IV)-gel precursor was spincoated onto SnO<sub>2</sub>:F coated borosilicate glass (Solaronix). After a heat treatment of 1 hour at 650 °C a 60 nm, thin dense layer of TiO<sub>2</sub> was formed [9]. On top, a Solaronix nanoxide T paste was tape casted and was given a heat treatment of 450 °C for 30 min in air. This resulted in the formation of a nanoporous TiO<sub>2</sub> layer with a thickness of 4 μm. Afterwards, a P3HT layer was spincoated on top from a 2 wt% chlorobenzene solution. After spin coating, the sample was annealed for 10 minutes at 110°C on a hotplate. As top electrode, a 40 nm thick layer of gold was evaporated.

Both the P3HT:PCBM and P3HT/TiO<sub>2</sub> devices have an active area of 0.25 cm<sup>2</sup>

A larger area DSSC (area = 70 cm<sup>2</sup>) has been purchased from Solaronix.

## 2.2 Measurement setup

The organic and hybrid photovoltaic devices were mounted in a N<sub>2</sub> filled measurement chamber. For the FTPS measurements, the modulated illumination beam of a Thermo Electron Nicolet 8700 FTIR with an external detector option was used. For the CS mode, the produced photocurrent upon illumination was amplified by a Stanford Research Systems (SRS) low noise current preamplifier (SR). When using the AM mode, an optical chopper and a SRS SR830 lock-in amplifier were used to modulate and to measure the photocurrent. For both modes the amplified photocurrent was fed back to the FTIR. The resolution of the FTIR spectrometer was set to 32 cm<sup>-1</sup>. For the absolute photocurrent measurements, the light was filtered with an IR blocking filter with a cut-on at 1.5 eV. As reference, a calibrated silicon photodetector was used.

For the sub-bandgap absorption measurements a long wave pass filter with a cut-off frequency of 2 eV was used. The reference detector was the internal DTGS detector of the used spectrometer. Spectra were set to absolute absorption scale (cm<sup>-1</sup>) by matching the high energy region with data obtained from transmission and reflection measurements. In this approach the measured absorption coefficient is the actual  $\alpha(E)$  scaled with the quantum efficiency for free carrier generation, as the photocurrent in organic devices is proportional to  $\alpha(E)\eta(E)$ , in which  $\eta$  can also be spectrally dependent [10].

### **3. Results and discussion**

#### **3.1. Absolute photocurrent spectra**

##### **a. Organic bulk heterojunction solar cells**

A high measurement speed, while maintaining a high resolution, makes CS-FTPS very interesting for a fast and accurate measurement of absolute photocurrent spectra. In Fig. 1, the photocurrent spectrum of the P3HT:PCBM device measured by FTPS is shown and is compared to the one measured with the classical technique using monochromatic light. The advantage of FTPS is that a high resolution (0.004 eV) spectrum between 800 and 400 nm is obtained in a few seconds. For the shorter wavelengths, the FTPS spectrum becomes noisier. This is due to the fast decreasing light intensity of the FTIRs light source in this spectral area.

The inset of Fig. 1 shows the modulation frequency response of the organic photovoltaic device. It was deduced by an algorithm using formula (1) and the data obtained for different mirror velocities. When a mirror velocity of  $0.1581 \text{ cm.s}^{-1}$  is used, the modulation frequencies are between 4 kHz and 8 kHz. From the inset it is clear that for this mirror velocity, the frequency response is still in its quasi DC mode. When using this mirror velocity, the modulation frequency response will not influence the measurement.



## **b. Dye Sensitized Solar Cells**

The use of CS-FTPS causes problems for the measurement of DSSCs containing an electrolyte. These device usually have a cut-off frequency well below 1 kHz. The photocurrent for light modulation frequencies above 1 kHz is very low and the spectrum will undergo mayor deformations. For this kind of long response time solar cells, the use of the AM-FTPS mode at low chopping frequencies is more appropriate. In Fig. 2 the photocurrent of the DSSC obtained from Solaronix is shown for different modulation frequencies and compared with the photocurrent spectrum obtained by the monochromatic technique at a chopping frequency of 8 Hz. For this DSSC a bandgap of 1.7 eV with an Urbach slope of 52 meV can be deduced. The inset of the figure shows the photocurrent at 1.85 eV versus the modulation frequency. It is clear that the photocurrent signal decreases fast for an increasing chopping frequency, even for low frequencies.

## **3.2. Sub-bandgap absorption**

### **a. Organic Bulk Heterojunction solar cells**

Due to the extremely high sensitivity of FTPS, it is possible to measure light absorption in the low absorbing region between 1 eV and 1.9 eV, corresponding to the bandgap of the photovoltaic devices. Fig. 3 shows the measured absorption spectra on a logarithmic scale of the pure P3HT and PCBM, and the P3HT:PCBM blended devices. In the high energy part of the measurement, a bandgap of 1.9 eV for P3HT and 1.7 eV for PCBM could be deduced. Below

this bandgap the absorption decreases exponentially. an Urbach slope of 33 meV and 29 meV could be deduced for respectively P3HT and PCBM.

An interesting effect is observed when examining the FTPS spectrum of the P3HT:PCBM composite. In comparison with the pure spectra, the composite one shows a new absorption band, which can be fitted by a Gaussian centred at 1.9 eV and having a width of 0.4 eV. This extra absorption band has also been previously detected for the MDMO-PPV:PCBM blend [11] and for blends of PCBM with polyfluorenes [12], and has been assigned to the formation of a charge transfer complex (CTC) between the conjugated polymer and PCBM. The presence of this CTC is determined by the ionization potential of the used conjugated polymer. It is argued that it has a role in charge transfer, transport and recombination processes in these types of solar cells [12]. CS-FTPS is a suited technique to rapidly and accurately detect the presence of this CTC, directly on the solar cell device and to perform further investigation to reveal the exact influence of this extra state.

#### **b. Illumination induced long lived states in P3HT and P3HT/TiO<sub>2</sub> blends**

Fig. 4 a) and b) show the respective spectra of a pure P3HT and a hybrid P3HT/TiO<sub>2</sub> device, both before and after an illumination of 30 min with a tungsten-halogen lamp with an intensity of approximately 1 sun. For both, a low energy absorption band due to the illumination is appearing. This sub-bandgap absorption band does only appear if the illumination contains energies above 1.9 eV. When the samples are kept in the dark for 2 days, the sub-bandgap

absorption decreases and disappears again. An annealing treatment at 100 °C for 5 minutes also eliminates the illumination-induced absorption. A similar effect of increasing sub-bandgap absorption upon above bandgap illumination was detected in the absorption spectrum of TiO<sub>2</sub>, measured with PDS [13].

This light induced sub-bandgap absorption is caused by the presence of trapped charge carriers, created upon illumination. In the studied devices most of the photocurrent originates from excitons split at the P3HT/Al or P3HT/TiO<sub>2</sub> interface. The sub-bandgap photocurrent measured by FTPS after illumination is therefore attributed to carriers trapped at the interfaces. This large amount of trapped carriers will influence the interface properties such as semiconductor band bending and charge carrier generation. In reference [14] it is argued that these trapped charges have a large influence on the open circuit voltage ( $V_{oc}$ ) and that the build up of charge at the P3HT/TiO<sub>2</sub> interface may cause the observed decrease in  $V_{oc}$  during illumination.

The broad sub-bandgap absorption band created upon illumination of P3HT/TiO<sub>2</sub> devices has different characteristics than the CTC band, as observed in P3HT:PCBM blends. While illumination has no measurable influence on the sub-bandgap absorption in blends of P3HT with PCBM, it has a large influence on the sub-bandgap absorption in pure P3HT and P3HT/TiO<sub>2</sub> devices.

#### 4. Conclusion

In conclusion, it is shown that FTPS is a favourable technique for a fast and accurate measurement of absolute photocurrent spectra of organic bulk heterojunction and dye sensitised solar cells. The fast, continuous scan mode, produces light modulation frequencies directly proportional to the wavenumber or energy of the light source. These frequencies are practically above 1 kHz. For fast responding organic bulk heterojunction solar cells, this mode produces a photocurrent spectrum in a matter of seconds and no corrections due to the frequency response are needed. For the measurement of long response time dye sensitised solar cells, the step scan mode is used. This mode allows lowering the modulation frequency and to measure the photocurrent spectrum for a certain, fixed frequency.

Because of the high sensitive nature of the FTPS technique, not only classical photocurrent spectra can be measured, but also photocurrent generated by sub-bandgap optical transitions can be detected. The detected low energy bands in pure P3HT and in P3HT/TiO<sub>2</sub> junctions appear after irradiation with  $E > 1.9$  eV. This absorption may be explained by the presence of light induced, trapped charge carriers. For the P3HT:PCBM blend, the sub-bandgap absorption is dominated by a band due to the formation of a ground-state charge-transfer complex between the polymer and PCBM, and no light induced features could be detected.

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Fig. 1. The photocurrent spectrum of a P3HT:PCBM bulk heterojunction solar cell measured by the monochromatic technique and by CS-FTPS. The inset shows the modulation frequency dependence of the device.

Fig. 2. The photocurrent spectrum of a dye-sensitized solar cell measured by the monochromatic technique and by AM-FTPS for different frequencies. The inset shows the signal at 1.85 eV versus chopping frequency.

Fig. 3. Absorption coefficient below the bandgap of P3HT, PCBM and P3HT:PCBM as measured by FTPS.

Fig. 4. The absorption coefficient below the bandgap of a freshly prepared and illuminated a) P3HT and b) P3HT/TiO<sub>2</sub> device.

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Fig. 1

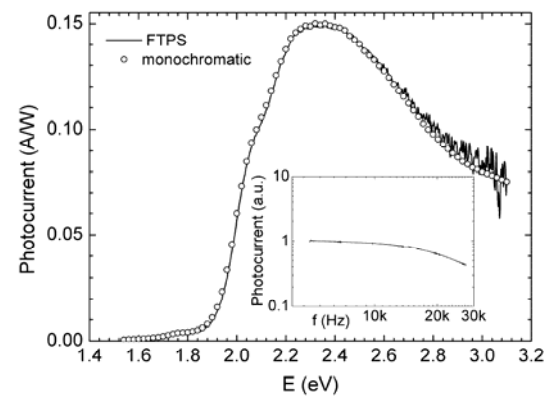


Fig. 2

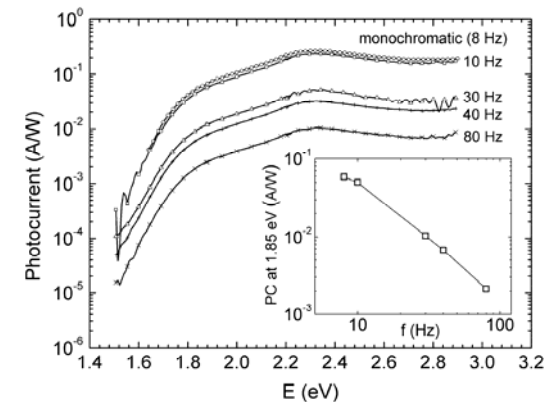




Fig. 3

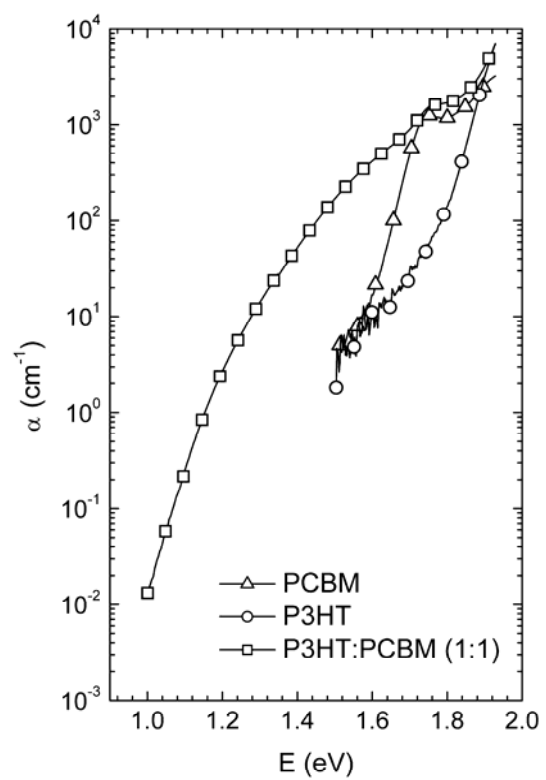


Fig. 4

