

Ultra-sensitive determination of the optical absorptance of donor/acceptor blends for organic photovoltaics with Fourier-transform photocurrent spectroscopy

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ABSTRACT - A new spectroscopic approach to investigate the optical absorption of organic semiconductors is introduced. This research is focussed on polymer-fullerene blends in photoactive thin films for bulk heterojunction solar cells, which have gained an established place in the wide range of organic solar cell concepts. This is due to the promising efficiencies reported up till now and their vast increase at short timescale¹. Moreover, the prospect to produce them on large scale, at low cost and on flexible support are supplemental assets of this class of photovoltaics. Solar cells with a photoactive layer of MDMO-PPV:PCBM and with regioregular P3HT:PCBM have been investigated with the brand new technique of FTPS.

FOURIER-TRANSFORM PHOTOCURRENT SPECTROSCOPY (FTPS) - In FTPS, the photocurrent spectrum of the sample (solar cell) is recorded by replacing the conventional detector of the spectrometer (KBr, DTGS) by the photoconductive sample. To accomplish this the light source is directed out of the spectrometer and the photocurrent signal coming from the sample is, after A/D conversion, Fourier analysed. The FTIR signal from the sample is normalized to the FTIR signal coming from a spectrally independent deuterated triglycine sulphate (DTGS) detector. In this way the absorption spectrum can be obtained at very short timescales and with very high sensitivity, revealing sub-bandgap absorption phenomena not to be uncovered with conventional spectroscopic methods. An extensive description of the FTPS principles can be found in ref. 2. The FTPS signal for each sample has been checked for its dependence on the light intensity, employing neutral density filters. All samples showed a linear dependence, a prerequisite for the correct interpretation of the measured spectra. All FTPS spectra cover absorption data ranging from the IR into the visual spectral region, leaving out a small part around the frequency of the HeNe laser of the Michelson spectrometer. This drawback of the FTPS technique was circumvented by applying the Constant photocurrent method (CPM) on the films in order to fill in the missing part.

EXPERIMENTAL RESULTS - Solar cells were constructed conform the standard procedure described in literature³, with this difference that an interfacial layer of LiF between the active layer and the Al electrode was omitted in the architecture. To exclude any influence on the absorption spectrum due atmospheric O₂ and H₂O, all cells were sealed with a thin glass cover.

In fig. 1, the FTPS spectrum of a solar cell with an active layer of MDMO-PPV:PCBM (1:4) is displayed. The spectra show the absorptance of the layers (absorptance $A=1-T-R$, where T is transmittance and R reflectance) over a dynamical range covering nine orders of magnitude. They are matched together at the saturation region around 2.5 eV. The band-to-band transitions of the constituting compounds are clearly observed. The absorption peak at 2.30 eV can be assigned to the $\pi \rightarrow \pi^*$ transition in MDMO-PPV. The distinct peak at 1.77 eV is due to the orbitally forbidden HOMO-LUMO transition ($h_u \rightarrow t_{1u}$) in PCBM, analogous to the forbidden transition in C₆₀ at approximately the same energy. The symmetry breaking originates from a Herzberg-Teller distortion, characteristic for C₆₀ and methanofullerenes. The broad absorption band between 1.77 eV and 2.30 eV is due to the transition from HOMO and HOMO-1 to higher excited states⁴. A remarkably broad fall-off in the optical absorption below 1.77 eV is present in all spectra, and ends in an exponential, Urbach like decay below 1.40 eV and extends to 1.2 eV. Below this energy supplemental sub-bandgap absorption features could be observed.

INTERPRETATION -To account for the observed Urbach like tail, two possible explanations are proposed :

- 1) The absorption spectrum of conjugated polymers, including MDMO-PPV exhibit a Gaussian absorption profile, tailing off in an exponential decay at lower energies^{5,6}. The origin of the Urbach tail in organic semiconductors has been considered in literature and is explained in terms of absorption due to self-trapped excitons, a consequence of the strong exciton-phonon coupling present in these materials^{7,8}. Adding PCBM to the polymer matrix, which acts as a charge transfer centre, would enhance the chance of exciton dissociation significantly, prevent self-trapping and elevate the photocurrent production at the sub-band gap level. This mechanism could account for the broadening of the absorption spectrum below 1.77 eV and the shift of the exponential decay to start at 1.40 eV.
- 2) The creation of a charge transfer complex (CTC) should be considered. Wang et. al. proved that complexation between fullerenes and *N*-polyvinylcarbazol (PVK) is the crucial step in the creation of

free charge carriers in their blends⁹. The interaction between MDMO-PPV and the fullerene derivative, as studied in the present paper, could result in the analogous CTC, which absorbs in the spectral region below 1.77 eV.

EFFECT OF UV-IRRADIATION - To investigate the origin of the absorption features below 1.2 eV, the solar cell was subjected to UV irradiation in a first series of 3 steps of 5 minutes each, followed by a more profound degradation regime of 3 steps of 1 hour each. The spectra suggest the absorptance increases with each step, as depicted in the inset of fig. 1, to eventually saturate at long degradation time, suggesting the creation of optically active defects created upon UV irradiation. This effect has been observed for the first time in dangling bond formation upon degradation of a-Si:H and seems to play an important role in organic solar cells all the same¹⁰.

EFFECT OF POST-ANNEALING - To conclude, the FT-PS spectrum of a P3HT:PCBM 1:2 (by weight) was compared before and after annealing at 80°C for 5 min (fig 2). In general, the same features can be observed as in the MDMO-PPV:PCBM 1:4 (by weight) solar cells, except for the initial presence of defect related absorption processes below the exponential decay. Remarkable however is the pronounced change in spectral shape before and after annealing. A profound red-shift of the exponential tail is observed, an effect of which no satisfying explanation has been found to this time. On the other hand, a strong increase absorption is measured at 1.9 eV, coinciding with the bandgap of regioregular P3HT. It is known that, introducing PCBM in a matrix of regioregular P3HT does interfere with the structural order present in a pure film of P3HT, resulting in a considerable increase of the bandgap. The annealing procedure can re-establish this order, an effect which has been studied by optical absorption spectroscopy in ref. 11. This is confirmed by the pronounced presence of the P3HT absorption at 1.9 eV in the FT-PS spectrum of the annealed film.

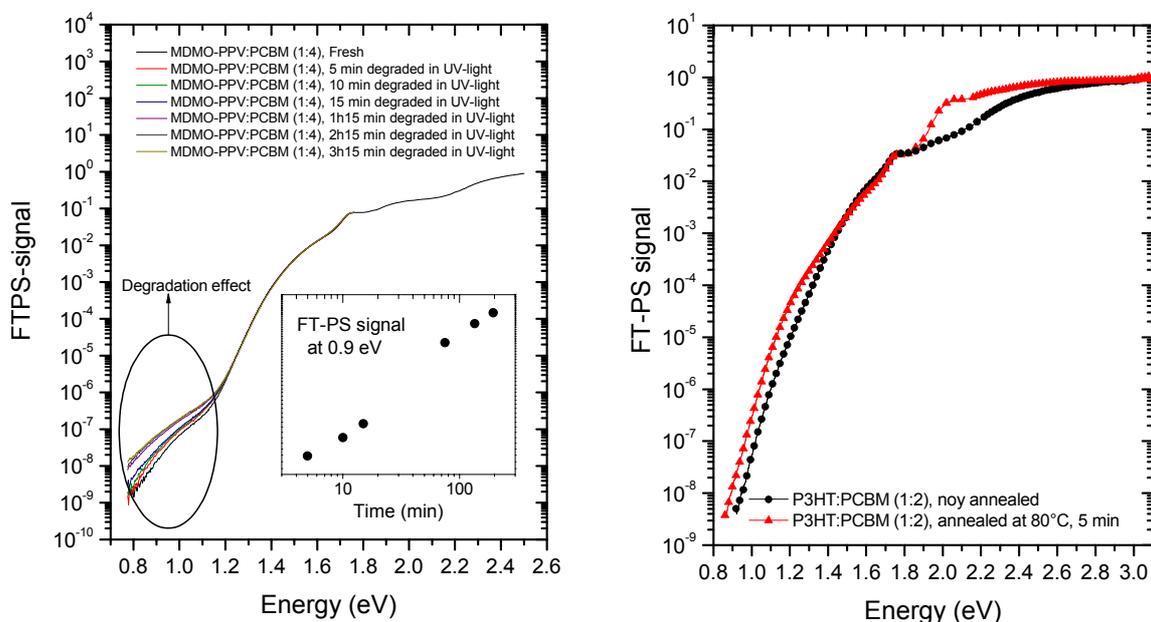


Fig. 1: FT-PS spectrum of solar cell with active layer layer of MDMO-PPV:PCBM (1:4), fresh and under after subsequent degradation steps Fig. 2: FT-PS spectrum of solar cell with active layer layer of P3HT:PCBM (1:2), not annealed and annealed, 80°C for 5 min

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1. C. J. Brabec, *Solar Energy Materials and Solar Cells* **83**, 273 (2004)
2. M. Vaneček, A. Poruba, *Applied Physics Letters* **80** (5), 719 (2002)
3. C. J. Brabec, N. S. Sariciftci, J. C. Hummelen, *Advanced Functional Materials* **11** (1), 15 (2001)
4. R. V. Bensasson, E. Bienvénute, C. Fabre, J. J. Janot, E. J. Land, S. Leach, V. Leboulaire, A. Rassat, S. Roux, P. Seta, *Chemistry-A European Journal* **4** (2), 270 (1998)
5. B. Jarzabek, E. Schab-Balcerzak, T. Chamenko, D. Sek, J. Cisowski, A. Volozhin, *Journal of Non-Crystalline Solids* **299-302**, 1057 (2002)
6. L. Goris, K. Haenen, M. Nesládek, P. Wagner, D. Vanderzande, L. De Schepper, J. D'Haen, L. Lutsen, J.V. Manca, presented at the International Conference on the Physics, Chemistry and Engineering of Solar Cells (SCCELL), Badajoz, Spain, 2004 (accepted for publication in *Journal of Materials Science: Materials in Electronics*)
7. K. Mizuno, A. Matsui, G. J. Sloan, *Journal of the Physical Society of Japan*, **53** (8), 2799 (1984)
8. A. Aziz, K. L. Narasimhan, *Synthetic Metals* **131**, 71 (2002)
9. Y. Wang, A. Suna, *Journal of Physical Chemistry B* **101**, 5627 (1997)
10. M. Stutzmann, W. Jackson, C. C. Tsaj, *Physical Review B*, **32**, 23 (1985)
11. D. Chirvase, J. Parisi, J. C. Hummelen, V. Dyakonov, *Nanotechnology*, **15**, 1317 (2004)