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Observation of the subgap optical absorption in polymer-fullerene blend solar cells

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This letter reports on highly sensitive optical absorption measurements on organic donor-acceptor solar cells, using Fourier-transform photocurrent spectroscopy (FTPS). The spectra cover an unprecedented dynamic range of eight to nine orders of magnitude making it possible to detect defect and disorder related sub-band gap transitions. Direct measurements on fully encapsulated solar cells with an active layer of poly[2-methoxy-5-(3',7'-dimethyl-octyloxy)]-p-phenylene-vinylene:(6,6)-phenyl-C61-butyric-acid (1:4 weight ratio) enabled a study of the intrinsic defect generation due to UV illumination. Solar cell temperature annealing effects in poly(3-hexylthiophene):PCBM (1:2 weight ratio) cells and the induced morphological changes are related to the changes in the absorption spectrum, as determined with FTPS. © 2006 American Institute of Physics. [DOI: 10.1063/1.2171492]

With the discovery of the ultrafast electron transfer between excited conjugated polymers and fullerenes, a promising destination was found for organic semiconductors, using them as low-cost, lightweight and easy-to-produce solar cells.¹ The combination of poly[2-methoxy-5-(3',7'-dimethyl-octyloxy)]-p-phenylene-vinylene (MDMO-PPV) and (6,6)-phenyl-C61-butyric-acid (PCBM) in a 1:4 weight ratio has long been the best performing system, attaining a 3% efficiency.² The continuous search for alternative materials realized an important breakthrough using regioregular poly(3-hexylthiophene) (P3HT) as a donor in conjunction with PCBM.³ Conversion efficiencies from 3.5% to 5% were reported,^{3,4} opening up commercial perspectives for organic solar cells, on condition that these efficiencies continue to improve substantially. Therefore, it is a great challenge to unveil the presence and nature of defects in the materials that limit the performance of these cells. To examine this and to meet the low absorption of light by defects, the extremely sensitive and fast technique of Fourier-transform photocurrent spectroscopy (FTPS) is used to measure the absorption spectrum of organic solar cells.

FTPS has been introduced to investigate the most dominant recombination center in $\mu\text{c-Si}$.⁵ In the current letter, solar cells of donor polymers MDMO-PPV and P3HT with PCBM as acceptor were prepared following the common procedure² and investigated by FTPS. The effect of compositional difference was evaluated by altering the PCBM content of an MDMO-PPV film around the standard proportion of 1:4 (80%) from 70%, 80% to 90% by weight. To decouple morphological effects from intrinsic defect generation a cell

of MDMO-PPV:PCBM (80 wt%) was subjected to a series of degradation tests using UV illumination (Xe lamp). To investigate the role of morphology, the FTPS absorbance of a P3HT:PCBM (66.66 wt%) cell was evaluated as a function of annealing temperature. It is known that these cells exhibit a huge increase in performance upon annealing at elevated temperatures, an effect correlated with the degree of P3HT packing.^{6,7}

Briefly, FTPS uses the photoconductive sample as an external detector of a Fourier-transform infrared spectrometer. The FTPS principles are well described in Ref. 5. Here, the white light source was used together with a CaF_2 or quartz beamsplitter, depending on the spectral range measured. All samples showed a linear dependence of the FTPS signal on the light intensity, a prerequisite for the correct quantitative interpretation of the spectra. All spectra have been measured at different mirror velocities and corrected for their frequency dependence, after which they are proportional to the absorbance A ($A=1-T-R$, T =transmittance, R =reflectance). The spectra cover absorbance data ranging from the near IR into the UV visible. A drawback of our FTPS apparatus is the inability to measure the spectrum below and above the HeNe laser frequency in one scan. When full scale spectra are displayed, the missing spectral part was measured by the constant photocurrent method. All measurements were performed on encapsulated cells, excluding any atmospheric influence.

The photothermal deflection spectra of MDMO-PPV, P3HT and PCBM and mixtures of MDMO-PPV with PCBM (80 wt%) and P3HT with PCBM (66.66 wt%) were measured and calibrated with absorption coefficient data calculated from independent transmittance and reflectance data obtained on dropcast and spin coated films [Figs. 1(a) and 1(b)]. The spectrum of the pure materials is characterized by

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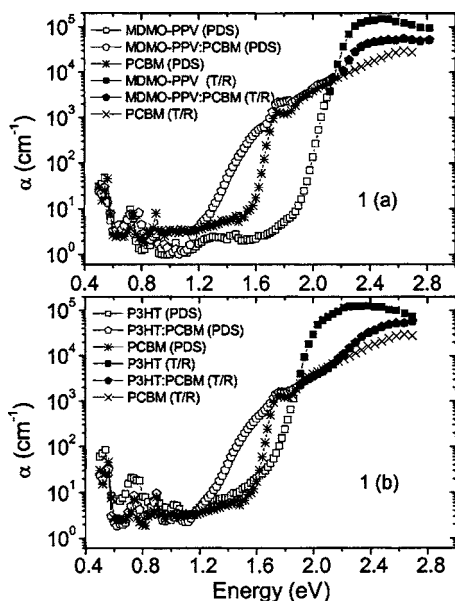


FIG. 1. (a): PDS-spectrum of dropcast layers of MDMO-PPV (square), PCBM (star) and MDMO-PPV:PCBM (80 wt%) (pentagon). (b): PDS spectra of dropcast layers of P3HT (square), PCBM (star) and P3HT:PCBM (66.66 wt%) (pentagon). The full symbols (PCBM=star) correspond to data obtained with transmittance and reflectance measurements.

a strong band gap absorption, which tails into the gap at low energies. The generated spectra are in accordance with the theoretically⁸ and experimentally⁹ established picture of the density of states (DOS) distribution in disordered organic semiconductors, describing the valence and conduction band as being Gaussian shaped and broadened to generate an exponential tail of states extending into the gap, in which charge carriers can be effectively trapped. Intermixing these compounds yields quite a different picture, with a more pronounced absorption tail. It is clear that mixing extends the exponential tail of valence and/or conduction band of one or both constituting semiconductors deeper into the gap, yielding a more complex DOS distribution. To get more precise data concerning this spectral region and to increase the experimental relevance for solar cell research, a series of FTPS measurements were performed directly on solar cells.

FTPS spectra of solar cells with an active layer of MDMO-PPV containing a PCBM percentage by weight ranging from 70, 80–90 wt% are displayed in Fig. 2(a). 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 forbidden highest occupied molecular orbital-lowest unoccupied molecular orbital transition in PCBM.¹⁰ As expected, the absorption peak at 1.77 eV is more pronounced with increasing PCBM content. A broad spectral response was measured below the band gap of both semiconductors, similar to the obtained PDS data. This spectral region is divided into two parts: (i) part E tentatively assigned to an exponential absorption tail (ii) part D tentatively assigned to the defect absorption. Varying the composition of the active layer induces a change in the exponential distribution of states, which could be related to the difference in disorder in the respective films. All the same, the defect absorption increases with the PCBM content. To investigate whether the absorption data in regions E and D reflect optical transitions due to structural defects, the cell was subjected to a sequence of “degradation” steps, involving a stepwise ex-

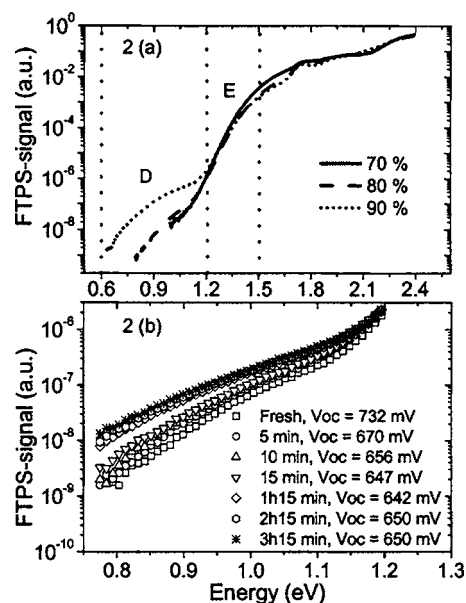


FIG. 2. (a): FTSP spectrum of solar cells with an active layer of MDMO-PPV:PCBM (70% by weight) (full line), MDMO-PPV:PCBM (80% by weight) (dashed line), MDMO-PPV:PCBM (90% by weight) (dotted line). Figure 2(b): evolution of the absorption in the D region of MDMO-PPV:PCBM (80% by weight) with increasing exposure to UV illumination, fresh (square), 5 min (circle), 10 min (up triangle), 15 min (down triangle), 1 h, 15 min (diamond), 2 h, 15 min (hexagon), 3 h, 15 min (star).

posure to UV light. After every step the FTSP spectrum was recorded and the open-circuit voltage (V_{oc}) measured under the low power illumination conditions of the spectrometer [Fig. 2(b)]. The absorption in region D is enhanced during the first series of steps (5 min). When subjecting the solar cell to longer exposure times (1 h), the absorption is strongly increased and has the tendency to saturate, while the E part stays unaltered. The V_{oc} decreased in every step and stabilized after 1 h, 15 min of degradation. This indicates the creation of (structural) defects, an intrinsic material property, rather than a difference in composition as erroneously could be concluded from Fig. 2(a).

More insight into the effect of film morphology on the spectral photocurrent response was provided by FTSP measurements on P3HT:PCBM (66%) solar cells. In Fig. 3(a), the spectrum of nonannealed and annealed cell (80 °C, 5 min) is displayed. Two major effects are observed: (i) an increase of spectral response by one order of magnitude around 2 eV and (ii) a spectral shift of the exponential tail of several tenths of meV to lower energy. The first effect is due to a reestablishment of the ordering in the P3HT chain, which was lost during spin coating of the polymer in a composite film with PCBM.⁶ This spectral shift is accompanied by a fourfold increase of the cell's short circuit current, measured under AM 1.5 illumination. The second effect can be explained in terms of an exponential tail of states extending deeper into the gap when the cell is exposed to an annealing procedure. This effect was investigated further, focusing on the spectral region in question, applying a stepwise annealing procedure (5 min) on a nonannealed cell [Fig. 3(b)]. A spectral shift towards lower energies is observed until a temperature of 150 °C is reached. This effect can be a result of the denser packing between the P3HT chains. Annealing the cell at 175 °C invokes an opposite shift, a possible consequence of the deterioration of the packing at higher temperatures. It

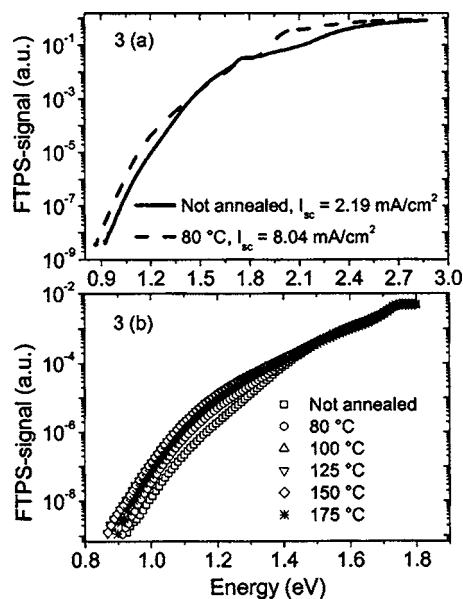


FIG. 3. (a): FTPS spectrum of a solar cell with an active layer of P3HT:PCBM (66% by weight): not annealed (full line), annealed (dashed line). Figure 3(b): evolution of FTPS spectrum applying a stepwise (5 min) annealing procedure: not annealed (square), 80 °C (circle), 100 °C (up triangle), 125 °C (down triangle), 150 °C (diamond), 175 °C (star).

is, however, important to mention that the formation of PCBM crystallites upon annealing, as observed in Ref. 6, can influence the spectral shift in its own way.

In conclusion, FTPS proved to be a very sensitive and fast method to record the absorption spectra of organic solar

cells. Typical spectra cover at least eight orders of magnitude, which enabled us for the first time to detect sub-band gap spectral features. These features were assigned to an exponential tail and defect related absorption processes. Degradation studies of encapsulated cells under UV illumination gave sound indication that structural defects are formed. The evaluation of the FTPS spectra during thermal annealing has shown that the exponential absorption tail is moving when the morphological (dis)order in the cell is changing.

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