BROADBAND SPECTRAL STUDY OF THE IMPACT OF THE PHOTO-OXIDATION ON ABSORPTION STRENGTH OF P3HT:PCBM

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1. Introduction

Poly(3-hexylthiophene-2,5-diyl) (P3HT)is one of the most suitable and extensively studied donor polymeroften blended with methanofullerene (PCBM) as acceptor inbulk heterojunction organic solar cells (OSC). P3HT:PCBM benefits from low-cost production and absorption spectrum well compatible with the solar irradiance spectrum (Fig.1) [1,2]. However degradation upon UV Vis radiation is reported to be one of the main agents to affect the OSC stability and lifetime and degrade its electrical parameters and efficiency [3-5].Incident photons usually provide sufficient energy to oxygen to react chemically with organic semiconductors. This process is referred to asthe photo-oxidation leading to structural and/or chemical changes dependent on the radiation intensity and wavelength [6,7].

In this paper broadband UV-Vis-IR optical spectroscopy of photo-oxidized P3HT:PCBM blends is reported.UV-Vis and IR absorbance spectra of P3HT:PCBM blends have been monitored over tens of minutes/hours of the photo-oxidation and the changes have been considered in light of absorption degradation. The observed absorption quenching indicates the destruction of ordering.

2. Experimental

The non-encapsulated 120±10 nm layer was spin-coated (27 rps for 50 seconds)on indium thin oxide (ITO)-coated glass substrate from 2 wt% P3HT:PCBM (1.5:1) in 1,2-dichlorobenzene and processed by solvent and thermal annealing in glove box to prevent oxygen to penetrate.

The photo-oxidation was carried out under AM 1.5G solar irradiation of the intensity of 1000 W/m^2 with Sun 2000 Solar Simulator (Abet Technologies)in the ambient air. Photo-oxidation exposure times of the P3HT:PCBM layer for UV-Vis absorbance measurements were set to 5, 10, 20, 30, 40, 50, and 60 minutes. Optical absorbance of samples was measured using Shimadzu UV-Vis-NIR spectrophotometer in the double beam operation with ITO-glass substrate as a reference sample. UV-Vis difference absorption spectrophotometry was used as a sensitive and high-resolution approach allowing deeper insight in absorbance changes upon prolonged solar illumination. Difference absorbance spectra are depicted in Fig. 2 together with the absorbance spectrum of the reference fresh non-degraded P3HT:PCBM sample (divided by 100). Fourier Transform Infrared (FTIR) DIGILAB FTS 3000MX Excalibur spectrophotometer equipped with anHATR accessory with a diamond crystal was used to collect FTIR absorbance spectra of P3HT:PCBM. Due to much lower sensitivity of FTIR measurements in comparison with UV-Vis the exposure times were set as

1, 2, 3 and 6 hours (Fig.3). For lower exposure times no systematic changes in FTIR absorbance were found.

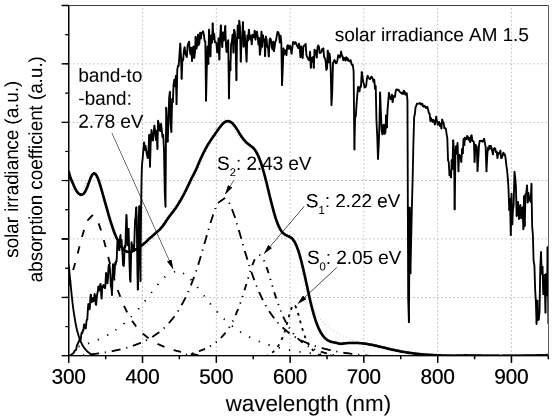

Fig.1:*Comparison of the standard AM1.5 terrestrial solar irradiance and illustrative absorption spectrum of P3HT:PCBM(dotted line) decomposed into individual excitations (for the assignments see the text below, the cumulative fit peak drawn with thick full line).*

3. Results and discussion

The wavelength dependent P3HT:PCBMabsorbance (Fig. 1) shows broad asymmetric peaks as often reported. In Fig. 1 the absorbance spectrum decomposed into individual excitations can be seen compared with the solar irradiance spectrum. The peak at photon energy ~2.78 eV corresponds to the band-to-band transition. P3HT excitonic features are positioned at photon energies of ~ 2.43 eV (~510 nm, S_2), ~ 2.22 eV (~560 nm, S_1) and ~ 2.05eV (~ 610 nm, S_0). S_0 indicates a single exciton generation, S_1an exciton + one phonon, S_2 an exciton + two phonons generation. The exciton generation via absorption is a key process in organic solar cells. Clearly pronounced excitonic peaks demonstrate a certain degree of P3HT chain ordering. In [8] we have shown significant effects of the photo-oxidation on UV-Vis absorbance. In Fig. 2 we see that sunlight exposure influences individual absorbance features in a various way.

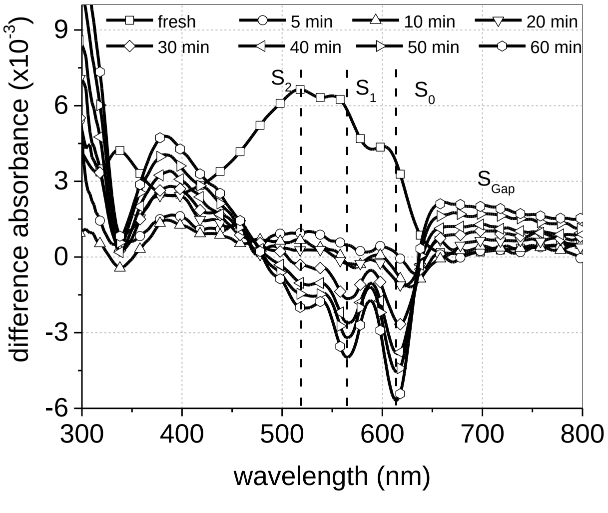

Fig.2:*Difference absorbance spectra. The line with squares represents the absorbance spectrum of the fresh non-degraded sample divided by 100. Dashed straight lines indicate S_0, S_1, S_2 positions. S_{Gap} corresponds to gap defect states.*

The minima in Fig.2 corresponding to S_0, S_1, S_2 almost coincide with the maxima of the fresh non-degraded sample although are slightly shifted due to the changes in ordering. Peaks in difference absorbance spectra related to S_0, S_1, S_2 steadily decrease with increasing the exposure as a result of π-bonds breaking leading to the decrease of the exciton generation rate. The absorbance loss is accelerated after 20 min of the photo-oxidation. This observation often referred to as the photobleaching is caused by the loss of π-conjugation by chemical changes under the photo-oxidation and hence the reduction of light absorbance.

π-bonds breaking may also be accompanied by the formation of defect states acting as charge traps.In near IR spectral region (at wavelengths > 640 nm) the absorption enhancement can be noticed with increasing the exposure time (Fig.2). On the contrary to the photobleaching, enhanced absorbance can be referred to as the photoinduced absorption, where new states located in the bandgap (labelled as S_{Gap}) are generated to absorb light undesirably and contribute significantly to the OSC degradation.

FTIR spectra in Fig.3 indicate mainly C-H vibrations in P3HT chains and C-C, C=C vibrations in the P3HT ring. The assignments of vibrational modes is as follows: CH_2 and CH_3aliphatic stretch in P3HT alkyl side chains at ~2900 cm^{-1}, C=O ester stretch at ~1740 cm^{-1}, noticeable P3HT ring-related peaks in the vicinity of ~ 1500 cm^{-1}(C=C symmetric stretch at ~1460 cm^{-1}, weak C=C antisymmetric stretch at ~1515 cm^{-1} and 1560 cm^{-1}), C-C skeletal stretch at ~1380 cm^{-1} and weak C-H thiophene ring out-of-plane bend at ~820 cm^{-1}.

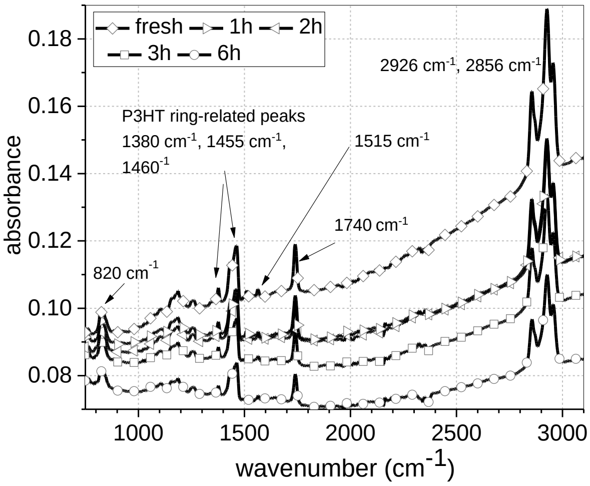

Fig.3:*FTIR spectra of P3HT:PCBM upon a prolonged photo-oxidation.*

Background subtracted spectra offer a detailed insight into the C-H stretching modes in the vicinity of ~2900 cm^{-1}(Fig.4). The decrease of C-H vibrational absorbance after the exposure to sunlight is caused by P3HT side chain degradation via breaking the molecular backbone resulting in a loss of conjugation. The integrated area of C-H band absorbance was found to be an exponentially decreasing function of the exposure time. After normalizing the spectra in Fig.4 no changes in peak shapes, positions and ratios between related peaks were observed indicating no special modifications of alkyl side chain lengths.

In Fig.5 background subtracted FTIR spectra corresponding to C-C and C=C skelet on ring vibrations are depicted. The peak at ~1460 cm^{-1} is obviously asymmetric. Its decomposition into two peaks at ~ 1455 and 1465 cm^{-1}indicates the presence of both, aromatic and quinoid forms of polymer rings as observed also in Raman spectra [9]. The similar exponential decrease of ring-related vibrational integrated absorbance with the exposure time was detected as in case of backbone C-H bonds. After normalizing the spectra to the 1460 cm^{-1} peak height no specific changes in peak shapes and ratios were noticed announcing that carbon bonds breaking occurred after reactions with oxygen. The only exception is aweak unsystematic change of the peak at 1455 cm^{-1} belonging to the quinoid form of the P3HT chain.

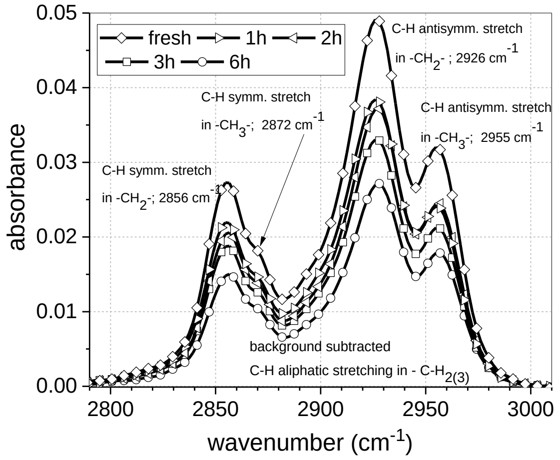

Fig.4:*Background subtracted FTIR spectra corresponding to C-H stretching obviously decreasing upon the photo-oxidation.*

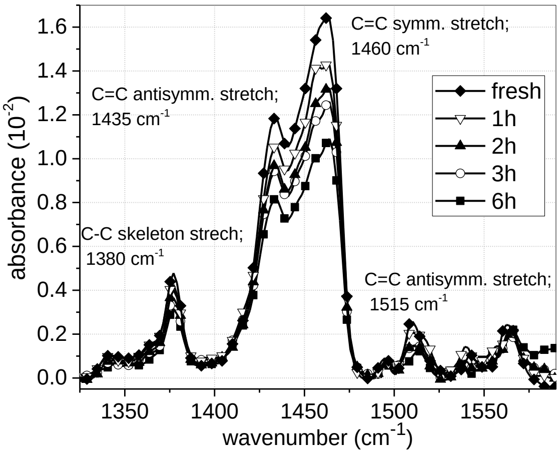

Fig.5:*Background subtracted FTIR spectra ofP3HT ring-related C-C and C=C stretching. The strongest feature corresponds to symmetric C=C stretching.*

4. Conclusions

In this paper broadband UV-Vis-IR absorption spectra are used to consider the photo-oxidative stability of P3HT:PCBM blend for solar cells. From UV-Vis studies we conclude that under prolonged solar irradiation the photobleaching in excitonic absorption and defect states creation in the bandgap occur which can have negative impact on the solar cell performance. FTIR studies imply that the prolonged photo-oxidation causes C-H and ring-related vibrational integrated absorbance decrease.

Acknowledgement

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