# ON PRISTINE AND BLEND OPTICAL ABSORPTION IN NEW-GENERATION LOW BAND-GAP ORGANIC SEMICONDUCTORS FOR HETEROJUNCTION SOLAR CELLS

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## 1. Introduction

Newly synthesized organic semiconductors of low band-gaps have been appeared recently for applications in organic electronics and photovoltaics such as polymer solar cells with enhanced absorption in visible range, open-circuit voltage and efficiency [1-6]. Most of them are derivatives of poly(phenylene vinylene)s and polythiophenes such as PBDTTT or PTB. In promising applications in bulk heterojunction solar cells or tandem cells, PBDTTT and PTB as donors are binary blended with derivatives of methanofullerene (PCBM) as acceptors. A great effort is made for their characterization. Thermal annealing is reported to improve morphology or polymers by stacking in coplanar conjugated segments. Optical properties of pristine as well as blended polymers are of particular interest because the absorption spectrum can be modified, e.g. by synthesis, deposition or post-deposition treatment or the ratio of PCBM. Here we present a study of optical absorption in wide range from UV to near IR to inspect thin films of non-annealed and solvent and thermally annealed PBDTTT and its blends with $PC_{71}BM$. The Tauc's and Cody's optical band gap values of thin films were calculated from the absorption coefficient spectra and were found to be around 1.6 eV providing excellent absorption in the spectral region at about 700 nm.

## 2. Experimental

The pristine PBDTTT-CF derivative of the synonym poly[1-(6-{4,8-bis[(2-ethylhexyl)oxy]-6-methylbenzo[1,2-b:4,5-b0]dithiophen-2-yl}-3-fluoro-4-methylthieno[3,4-b]thiophen-2-yl)-1-octanone] (Sigma–Aldrich, $M$ = 53000–83000) was dissolved in dichlorobenzene (DCB, Sigma–Aldrich, 0.001% $H_2O$) and spin-coated at 16 rps on cleaned (ultrasonically in acetone and isopropanol and UV irradiated) commercial ITO substrate. Thermal annealing (referred to as TA) at 110 $^{o}$C for 5 min in argon atmosphere was used for the comparison with non-annealing effect. The PBDTTT-CF was blended with $PC_{71}BM$ (Sigma–Aldrich, HPLC grade ≥ 99.5%) in 1:1.5 wt.% ratio and dissolved in DCB and 1,8-diiodooctane (DIO) (Sigma–Aldrich, 98%) as additive solvent [6]. Then the investigated blends were spin-coated at 16 rps on cleaned (the same procedure as above) ITO substrates. During the solvent annealing (SA) several samples were covered by a Petri dish with 9 cm in diameter. Thermal annealing at 110 $^{o}$C for 5 min in argon atmosphere was used, too. The samples that were not post-deposition treated are referred to as NTA and NSA.

The thickness of the samples was measured by Dektak profilometer (Tab. 1). Optical absorbance of non-annealed and annealed samples was measured using Shimadzu UV-Vis-NIR spectrophotometer in the double beam operation with ITO substrate as a reference sample in one light path. To avoid the thickness dependence of absorbance, absorption coefficients were calculated and then the spectra were background subtracted. Absorption coefficients were found to be relatively high (~ $10^4$ – $10^5$ $cm^{-1}$) which is promising for maximizing the light absorption.

## 3. Results and discussion

The wavelength dependent absorption coefficients of pristine PBDTTT (Fig.1) are dominated by broad asymmetric absorption peak at ~ 500 – 700 nm. The peak is composed of two vibronic features at ~1.8 eV and 2 eV. These features can be attributed to strong intermolecular interactions [1]. At smaller wavelengths, an absorption feature at ~2.8 eV can be seen. Absorption coefficient spectra of PBDTTT:$PC_{71}BM$ blends presented in Fig.2 manifest broad and extensive absorption through wide UV and visible region at the values of not below ~ $10^4$ $cm^{-1}$. The region below ~ 350 nm corresponds to PCBM interactions whilst the peak at higher wavelengths with maximum at ~700 nm belongs to the PBDTTT absorption. This wide maximum is not as pronounced as in case of pristine PBDTTT and the two vibronic features are slightly blue-shifted (~ 2 eV and 2.2 eV). The influence of post-deposition treatment in the position of the absorption edge at the wavelengths > ~700 nm can be observed. The falling edge of the peak at ~ 700 nm (photon energy ~1.77 eV) corresponds to the band-to-band transition and is positioned at lower photon energies than in so-far most popular organic donors as P3HT (~2.6 eV). This shift could be beneficially applied in tandem solar cells based on organic semiconductors.

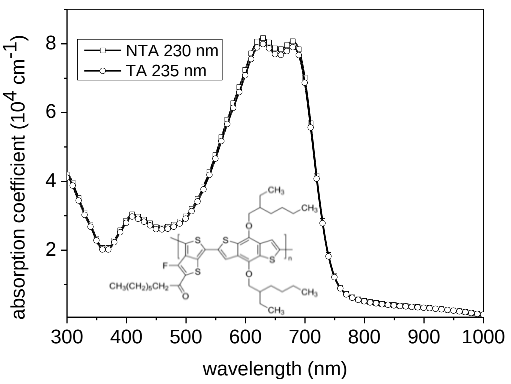

Fig.1: *Absorption coefficients of non-thermally annealed (NTA) and thermally annealed (TA) thin films of pristine PBDTTT.*

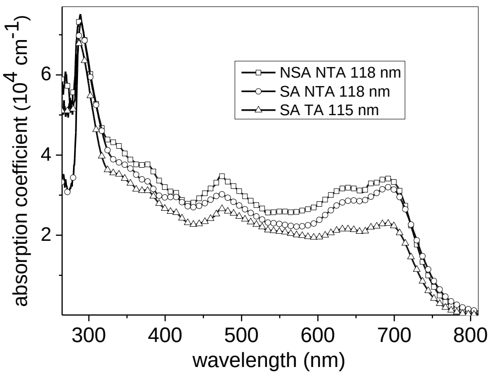

Fig.2: *Absorption coefficients of non-annealed (NTA) and annealed (solvent SA and thermally TA) thin films of PBDTTT:$PC_{71}BM$ blends.*

The optical energy gap is one of the important optical transition parameters of organic/inorganic semiconductors. It is often deduced from reflectance/transmittance/absorbance spectra. Considering the optical energy gap, the effect of solvent and thermal annealing can be identified. Absorption broadening in conjugated polymers arises from the coupling between conjugated segments and from the characteristic distribution of conjugation lengths. The onset of the absorption corresponds to the $\pi$–$\pi^*$ transitions between the allowed highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Due to the partial disorder in studied polymers the HOMO and LUMO edges are extended. The tail states play important role in optical and electronic properties of amorphous organic semiconductors but it is quite puzzling to determine the optical band gap from optical measurements only without some ambiguity. Differently defined optical gaps compared in this paper are Tauc's and Cody's gaps [7, 8]. Both approaches variously express the density of states distribution in the extended states near HOMO and LUMO edges and the transition matrix element, especially the relation of the momentum and energy of the excited charge carriers. The Tauc's model has served for years as an empirical procedure to determine the optical gap of amorphous semiconductors. The Tauc's approximation [7] is expressed as $(\alpha\hbar\omega)^{1/2} \propto (\hbar\omega - E_g^{Tauc})$ where $\alpha$ is the absorption coefficient, $\hbar\omega$ is the photon energy and $E_g^{Tauc}$ is Tauc's gap. Tauc's model originates from the assumption of constant matrix element squared. Cody [7] showed that assuming the photon-energy dependent transition matrix element the plot $(\alpha/\hbar\omega)^{1/2} \propto (\hbar\omega - E_g^{Cody})$ versus $\hbar\omega$ usually offers better linearity than Tauc's plot $(\alpha\hbar\omega)^{1/2}$. The related optical gaps are determined from extrapolation of the linear parts of Cody's and Tauc's plots to the photon energy axis.

Fig.3 and Fig.4 illustrate the determination of the optical gaps directly from the absorbance spectra extrapolating the linear part of absorbance to the photon energy axis. The results are in Tab.1. Tauc's and Cody's plots for PBDTTT:PC$_{71}$BM blends are in Fig.5 and Fig.6. All results are summarized in Tab.1. Noticeable differences in absorptive properties of pristine PBDTTT non-thermally and thermally annealed samples were not observed. However we observed stronger effect of post-deposition treatment (especially SA) in case of samples of smaller thickness. The iso-absorption gap $E_{04}$ (Tab.1) is also often used to characterize optical absorption in semiconductors. However owing to rather complicated absorbance features of organic materials this parameter might be confusing.

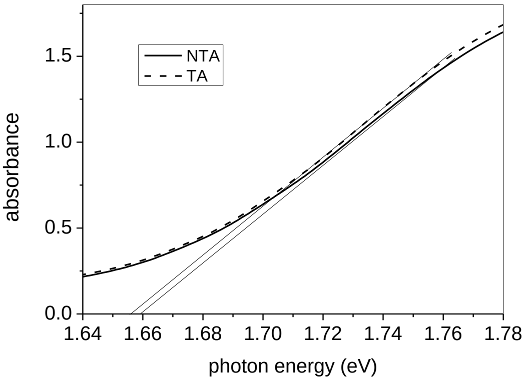

Fig.3: *Absorbance of non-thermally annealed (NTA) and thermally annealed (TA) pristine PBDTTT.*

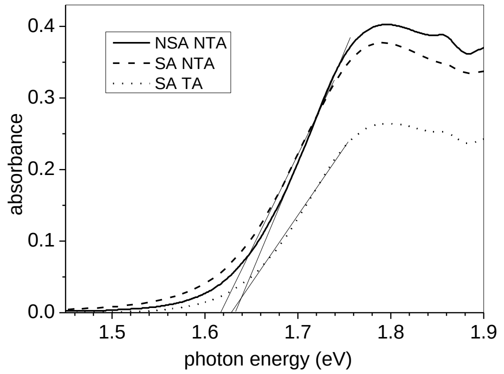

Fig.4: *Absorbance of non-annealed and annealed (solvent SA and thermally TA) PBDTTT:PC$_{71}$BM blends.*

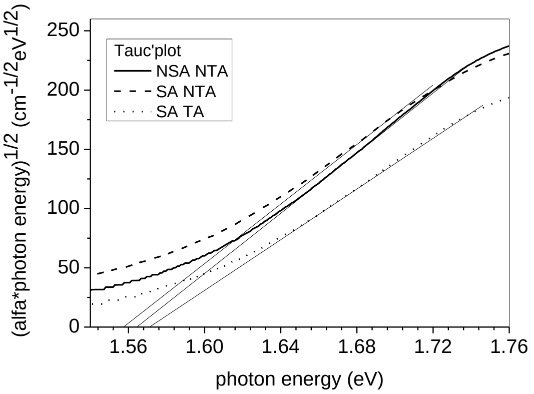

Fig.5: *Tauc's plots of non-annealed and annealed (solvent SA and thermally TA) PBDTTT:PC$_{71}$BM blends.*

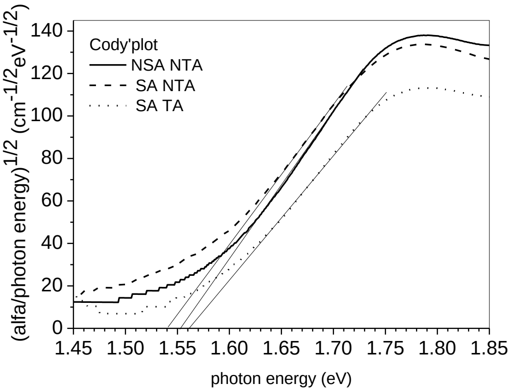

Fig.6: *Cody's plots of non-annealed and annealed (solvent SA and thermally TA) PBDTTT:PC$_{71}$BM blends.*

Tab.1. *Optical gaps of pristine PBDTTT and PBDTTT:PC$_{71}$BM blends.*

| Sample | Sample | Thickness (nm) | Absorbance edge (eV) | Tauc's gap (eV) | Cody's gap (eV) | $E_{04}$ (eV) |
|---|---|---|---|---|---|---|
| pristine | SA NTA | 230 | 1.66 | 1.59 | 1.58 | 1.64 |
| | SA TA | 235 | 1.66 | 1.59 | 1.58 | 1.64 |
| blend | NSA NTA | 118 | 1.63 | 1.57 | 1.55 | 1.67 |
| | SA NTA | 118 | 1.62 | 1.56 | 1.54 | 1.65 |
| | SA TA | 115 | 1.63 | 1.58 | 1.56 | 1.69 |

Similar values within experimental errors may be observed arising from the optical gaps determined by Tauc's and Cody's model. Therefore we can conclude that both models can be used for calculating optical gaps of organic semiconductors.

## 4. Conclusions

In this paper band-to-band absorption of spin-coated pristine PBDTTT and PBDTTT:PC$_{71}$BM blends with and without post-deposition treatment (solvent and thermal annealing) was investigated. Remarkable changes in absorption spectrum were detected after blending PBDTTT with PCBM. No special improvement was observed in case of pristine PBDTTT which might be caused by greater thickness of the films when compared with PBDTTT blends. The beneficial effect of solvent annealing was detected in PBDTTT:PC$_{71}$BM bringing slight but apparent red-shift of the optical gap that can be caused by more effective conjugation. To our knowledge solvent annealing supports at least the same improvements as known for thermal annealing. Applying both solvent and thermal post-deposition treatment upon one sample brought no special improvements.

## Acknowledgement

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## References:

[1] J. P. Kollender, J. Gosiorowski, N.S. Saricifti, A.I. Mardare, A.W. Hassel: *Sci. Technol. Adv. Mater.*, **15**, 054201 (2014).

[2] H.-Y. Chen, J. Hou, S. Zhang, Y. Liang, G. Yang, Y. Yang, L. Yu, Y. Wu, G. Li: *Nature Photonics*, **3**, 649 (2009).

[3] S. Zhang, L. Ye, W. Zhao, D. Liu, H. Yao, J. Hou: *Macromolecules*, **47**, 4653 (2014).

[4] J. You, L. Dou, Z. Hong, G. Li, Y.Yang: *Progress in Polymer Sci.*, **38**, 1909 (2013).

[5] Y. Liang, Z. Xu, J. Xia, S. – T. Tsai, Y. Wu, G. Li, C. Ray, L. Yu: *Adv. Mat.*,**22**, E135 (2010).

[6] A. Vojtko, M. Jergel, V. Nádaždy, P. Šiffalovič, M. Kaiser, Y. Halahovets, M. Benkovičová, J. Ivančo, E. Majková, M.O.A. Erola, S. Suvanto, T.T. Pakkanen: *Phys. Status Solidi A*, **212**, 867 (2015).

[7] J. Singh, K. Shimakawa, G. Kotliar, Y. Tokura: *Advances in Condensed Matter Science,* Taylor&Francis, London and New York, (2003).

[8] M.E. Sánchez-Vergarra, J.C. Alonso-Huitron, A. Rodrigez-Gómez, J.N. Reider-Burstin: *Molecules*, **12**, 10000 (2012).