

The photodegradation of polymers and small molecular materials applied in organic optoelectronic devices

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Abstract

This contribution is focused on study of photo-degradation of a several photoconductive organic materials such as polymeric (high T_g -PPV – block copolymer of derivates of poly(p-phenylene-vinylene) and P3HT – poly(3-hexylthiophene-2,5-diyl) as small molecular weight material a derivate of diphenyl-diketopyrrolo-pyrrole – DPP 36 was used. These materials are used for construction of optoelectronic devices like organic solar cells, transistors, optical sensors and others. Photo-degradation processes were studied by optical characterization (UV-VIS spectroscopy,) and by analysis of photographs obtained by means of optical microscope.

Keywords: UV-VIS spectroscopy, polymers, photodegradation

Introduction

Opto-electrical devices use absorption of light for generation of charge carries. The photogeneration process competes with several photophysical processes as fluorescence, phosphorescence, thermal relaxation and others, which don't have destructive effect on material, and with chemical reactions initialized by light, which lead to decomposition of the organic functional materials. Rate of photo-degradation depends on many factors, but mainly on light intensity and oxygen concentration, sample thickness, multilayer construction, used solvent, etc. (Jorgensen et al. 2008).

In this work, rate of photo-degradation was studied, which is very important parameter for future application and lifetime assessment of organic materials in optoelectronics.

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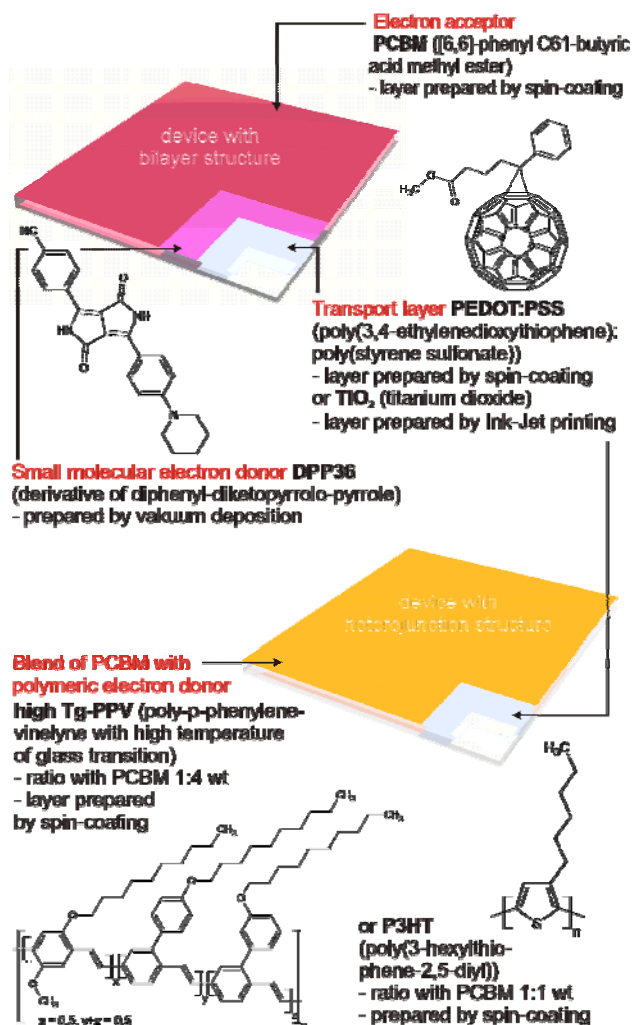


Figure 1: The scheme of the studied prepared samples and structures of used materials

Materials and Methods

Two polymers and one small molecular material were studied. For the experiment a π -conjugated block copolymer of derivatives of poly-*p*-phenylene-vinylene with high glass transition temperature (Tg-PPV) and P3HT (poly(3-hexylthiophene-2,5-diyl)) which were blended with PCBM ([6,6]-phenyl C61-butyrac acid methyl ester) were chosen. Tg-PPV was mixed with PCBM in the ratio 1:4 w/w and P3HT in ratio 1:1 w/w. Solutions were prepared in chlorobenzene. Polymer layers were created employing spin-coating.

As a small molecular weight material the derivative of diphenyl-diketopyrrolo-pyrrole (here abbreviated as DPP 36, see Fig 1) was used. The layer was created by vacuum evaporation. Layer of PCBM was prepared by spin-coating onto the DPP36. In all cases these active materials were deposited on charge transporting layer of PEDOT:PSS (poly(3,4-ethylenedioxy-thiophene):poly(4-styren sulfonate)) or TiO₂ (titanium dioxide). As a substrate quartz glass was used. Assessed samples were prepared without encapsulation and at ambient air atmosphere.

Samples were irradiated in Qsun Xe test chamber; model Xe-1-B with outdoor filter. Temperature in test chamber was 45 °C. Degree of degradation of materials was studied by measuring of UV-VIS absorption spectra on Varian Cary 50 Spectrophotometer. Simultaneously appearance of surface of samples was studied by the optical microscope NIKON Eclipse E200 and documented by photographs.

Table 1: The resulting rate constants of the studied samples, where n is the order of reaction

Active layer	n	Rate constants (10 ⁻² mol ⁿ h ⁻¹)	
		/PEDOT	/TiO ₂
Tg-PPV:PCBM (1:4)	1	15,7 ± 0,6	13,7 ± 0,6
P3HT:PCBM (1:1)	0	2,85 ± 0,09	2,066 ± 0,003
DPP36/PCBM	0	0,231 ± 0,011	1,16 ± 0,02

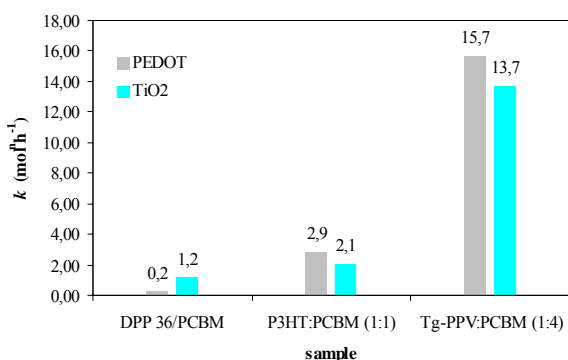


Figure 2: The diagram of the resulting rates constants of the studied samples.

Results and Discussion

These photo-degradation tests took 55 hours each. Kinetics of photo-degradation was obtained from the decay of characteristic absorbance maxima of UV-VIS spectra of researched electron donor materials. P3HT and DPP 36 presented zero order kinetic reaction while Tg-PPV showed more complex degradation kinetics, however for a first approach; it was possible to simplify it to the first order reaction.

Significant difference has been found between use of TiO₂ and PEDOT transport layers for DPP 36, when kinetic decay constant for PCBM/DPP 36/TiO₂ was found 5 times bigger as for PCBM/DPP 36/PEDOT. Type of transport layer does not play such an important role in photo-degradation processes of used polymers. The rate of photo-degradation of the low molecular DPP 36 was slower than in the polymers, while PCBM/DPP36 presented 4 times lower average rate constant when compared to P3HT:PCBM and 24 times lower if compared to Tg-PPV:PCBM respectively. Decomposition kinetics of Tg-PPV:PCBM was almost 6 times faster as P3HT:PCBM. The results are showed in diagram on Fig 2 and in Table 1.

Simultaneously, appearance of samples' surfaces was analyzed by means of the optical microscopy and documented. Expected color changes were observed during the whole experiment while the TiO₂ layer cracking was presented for the first four hours of the experiment. This cracking contributed to mechanical disintegration of DPP 36 layer. This fact naturally influenced trend of absorbance decay (disintegration of layer caused faster decay of absorbance with time of light irradiation of samples).

Conclusions

These photo-degradation assessments presented the enhanced stability of the studied DPP 36 dye with PCBM layer over the polymer blends Tg-PPV:PCBM (1:4) and P3HT:PCBM (1:1). Moreover, significant difference in stability between blends of P3HT and Tg-PPV was found.

The importance of charge transport layer selection was observed mainly for DPP 36 while in case of polymers the influence was negligible. Although the DPP 36 as a low molecular photoconductive material was found more photo stable against the the polymer materials, it showed lower mechanical endurance, because the TiO₂ cracking contributed to the disintegration of the DPP 36 layer, but not of the polymer layers. DPP 36 layer on PEDOT remained compact during the entire photo-degradation test.

Acknowledgement

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References

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