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Heterocyclic Polymers Perspectives in Nanolayers of Donor Acceptor Heterojunction for Organic Photovoltaic Application

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In this work new polymers for organic photovoltaic that are stable to aggressive external environment influence are discussed. Heterocyclic "ladder" structure polymers poly(perylenebenzimidazole- with oxygen bridge between monomer units) (PPBI-O) and poly(naphthoylene benzimidazole – with oxygen bridge between monomer units) (PNBI-O) were studied as potential alternative to poly-3-methyl hexyl thiophene (P3HT) and fullerene {6, 6} -phenyl-C (61) butyric acid (PCBM). This subject is of current interest for goal of reducing cost and time for organic solar cells, where one of the main problems is still high cost of donor and acceptor synthesis. Solar cells based on new polymers were produced. Even after first device investigations it is detected that he electrical resistivity level and device efficiency is also comparable with the target analogue for comparison P3HT.

The possibility of molecular structural design provides a wide field for engineers to generate interest to heterocyclic structures based on die-perylene and naphthoyl, the possible combinations for the superposition of the absorption spectra. From this point of view, the creation of optically active polymers based on polybenzomidazofenantroline (PBF), 1, 4, 5, 8- naphthalene tetracarboxylic and 3, 4, 9, 10- perylenetetracarboxylic acids opens new opportunities in this important field of science and technology. The results are high absorption in visible spectrum and ability of morphology improvement. Advantages in the optical properties PPBI-O and PNBI-O above the target prototype P3HT, namely a peak absorption in the region of 555 nm to 700 nm red edge are detected.

Keywords: Organic solar cells, Polymers, Degradation, Scanning electron microscopy.

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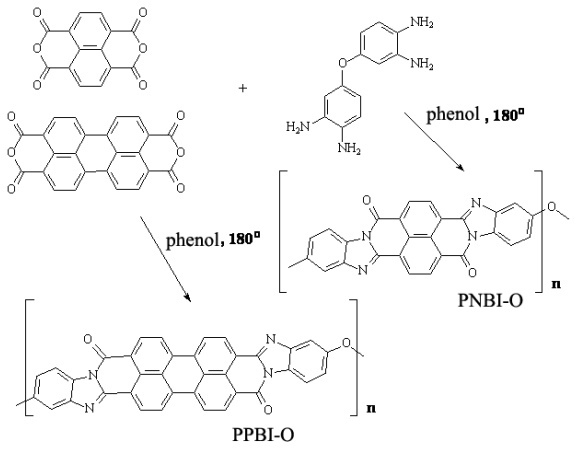
1. INTRODUCTION

Fullerene is rather expensive material, so the attention was paid to non-fullerene solar cells (SC) [1, 2]. The disadvantage of fullerene PCBM is a narrow absorption spectrum, which does not allow its expansion in contact with the photosensitive donor. Non-fullerene SC, which consist of a *p*-type semiconductor polymers and low molecule electron acceptors have certain advantages over the solar batteries based on fullerenes. Firstly, using non-fullerenes acceptors – it can be achieved broad and intense absorption through the structure of molecules. Secondly, their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels can be controlled to achieve a suitable driving force for charge separation. Thirdly, a SC non-fullerenes exhibits good long-term stability and a good stability under continuous bending.

To improve the stability of the materials, and achieving the desired energy conversion efficiency as photoactive materials the PPBI-O and PNBI-O "ladder" polymers were chosen and they are resistant to light, air and moisture, and also have extremely high heat resistance to organic Polymer to 400 °C. Their analogs show absorption in the range of 600-850 nm, the charge carrier mobility is about 0.1 $cm^2/V \cdot s$ [3], the efficiency is about 4 %. These polymers can be suggested as optimal and promising for research in terms of semiconductor properties and technological advantages. Their synthesis doesn't require expensive and low-temperature catalysts. The achievement of the targets is possible by using the optimal ratio of energy levels. The development of new approaches for a class of soluble, recycled polymers with photovoltaic properties, with improved efficiency of solar energy conversion and thermal stability, "ladder" polymers - polibenzimidazofenantrolinov based on 1, 4, 5, 8- naphthalene tetracarboxylic and 3, 4, 9, 10- perylenetetracarboxylic acids and studying results of their electrical, optical and photoelectric characteristics looks like rational choice, have the potential long-term and stable operation of photo devices with the ability to optimize SC.

2. EXPERIMENTAL PROCEDURES

Heterocyclic PNBI-O and PPBI-O polymers were synthesed by high temperature polycondensation of dianhydrides high-PNBI-O or PPBI-O acids with 3, 3, 4, 4-tetraaminodifenil ether (Fig. 1) in the phenol at 180 °C in a argon stream for 10 hours.



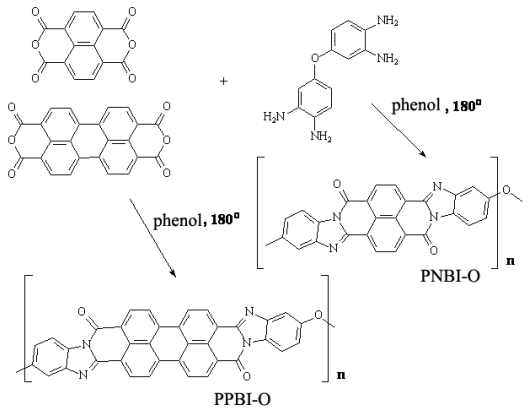


Fig. 1 – The synthesis scheme for PNBI-O and PPBI-O "ladder" polymers

As the catalysts a mixture of benzoic acid and benzimidazole was used. During polymers synthesis they were precipitated in the form of fine powders, which were filtered using a Shota filter and extracted by acetone from the solvent and catalyst residues in Soxhlet apparatus.

The polymers are soluble only in acidic solvents. For the preparation of solutions it was used the mixtures of volatile organic acids – 100 % formic acid and trifluoroacetic acid.

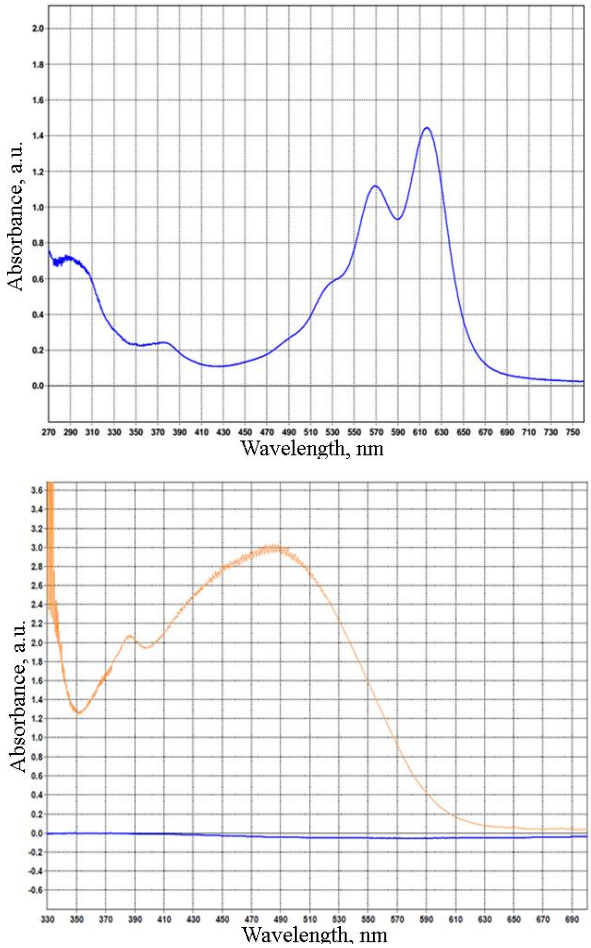


Fig. 2 – The absorption spectrum for PPBI-O and PNBI-O polymers

From 0.5 % solution it was obtained thin, deep burgundy colored coating (PNBI-O), and blue coating (PPBI-O).

Spectral characteristics were measured in the acid solution to determine the absorption peaks polymers by spectrometer Cintra 303 (Fig. 2).

3. RESULTS AND DISCUSSION

The optical band gap was determined by the "red edge" from the equation (1):

$$E_g = h\nu = h\frac{c}{\lambda} \qquad (1)$$

Consequently, E_g on the absorption edge of PPBI and PNBI solutions is about 1.8-1.9 eV.

This value is close enough to the desired analog giving solar cells efficiency about 5 % for the material P3HT and absorption peaks in the regions 480, 550 and 600 nm give reason to believe these materials are effective in terms of minority carriers generation to contribute to the photocurrent of the photovoltaic device. Moreover it looks quite promising to create a mixture of polymers provided for the absorption spectrum expansion. In comparison with the P3HT spectrum (Fig. 3) in three different solvents it was revealed the advantage in PPBI-O, with a peak of 550 nm – the maximum intensity of the solar spectrum, comparing with 470-510 nm for P3HT spectrum [4].

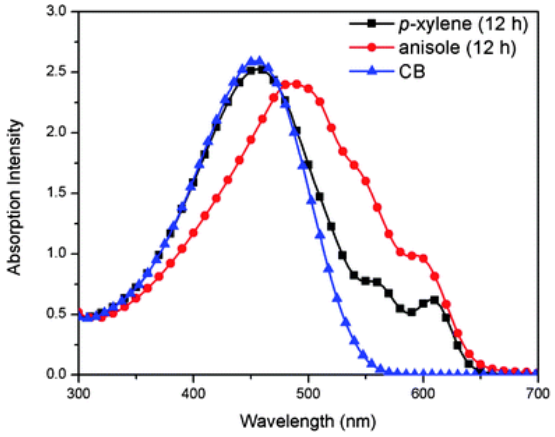


Fig. 3 – The absorption spectrum for P3HT polymer: black – xylene, red – anisole, blue – chlorobenzene

The morphology has been investigated by scanning probe microscopy for thin film nanolayers samples. For both investigated polymers the distribution was obtained (Fig. 4) with a peak in the region of 80-100 nm.

3D reconstructions of nanolayers films (Fig. 5) show the presence of roughness that indicates too fast exit of solvent vapor – volatile acids.

It is also could be seen the big structural formation (Fig. 6) in a polymer matrix, the structural units having dimensions orders 60-115 nm and 800 nm PNBI-O and PPBI-O, correspondently, which indicates the crystallization start.

It was also studied the absorption directly on thin films with thickness – 100 nm (Fig. 7).

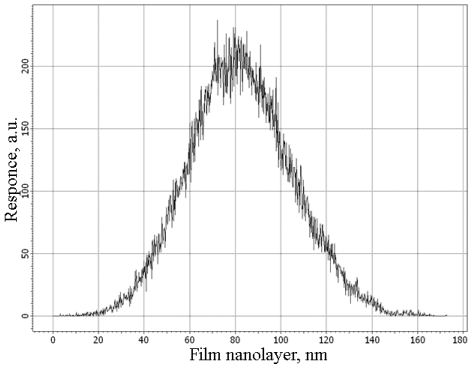


Fig. 4 – Typical thickness peaks distribution for samples PPBI-O

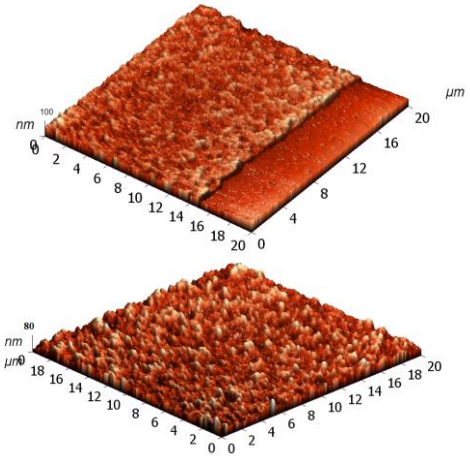


Fig. 5 – 3D reconstruction of a thin film – 20 × 20 mm PNBI-O (top) and PPBI-O (bottom)

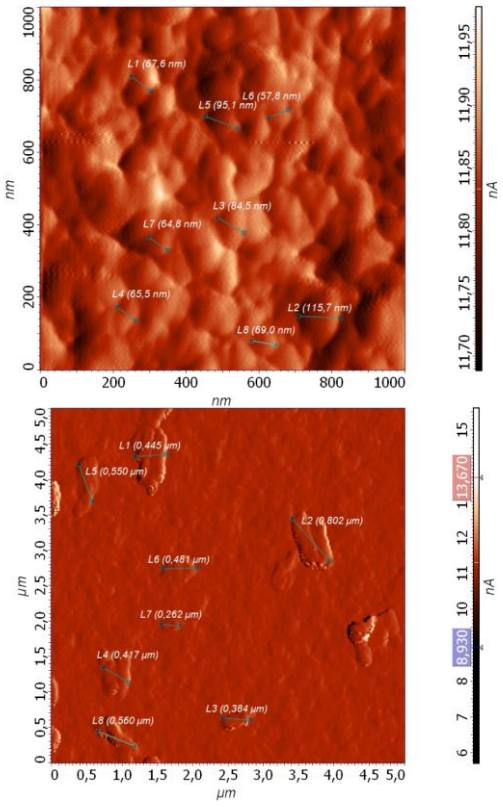


Fig. 6 – PNBI-O(top) and PPBI-O(bottom) polymer matrix view

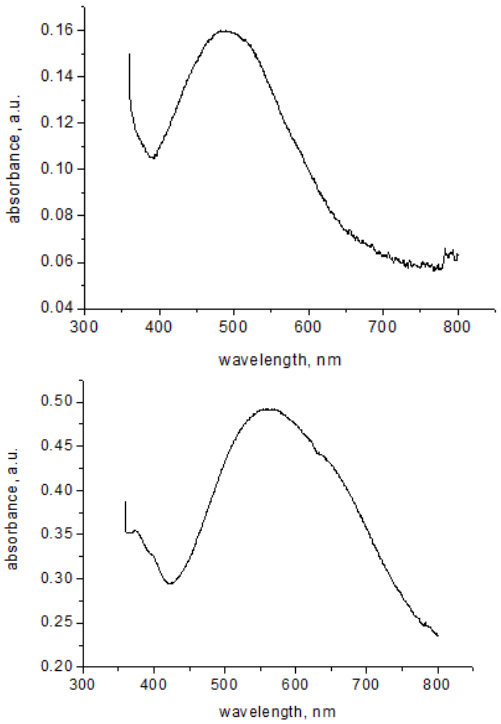


Fig. 7 – The absorption spectrum PNBI-O (top) and PPBI-O (bottom) 100 nm

The results show approximately similar picture on the absorption peaks for PNBI-O – 480 nm, and PPBI-O – 555 nm, it is seen the shift of about 20 nm to the infrared area on films PPBI-O with thickness – 100 nm.

In comparison with the P3HT spectrum (Fig. 8), the PNBI-O spectrum has almost the same borders in region about 650 nm, and the PPBI-O has more a wide range up to 700 nm [5].

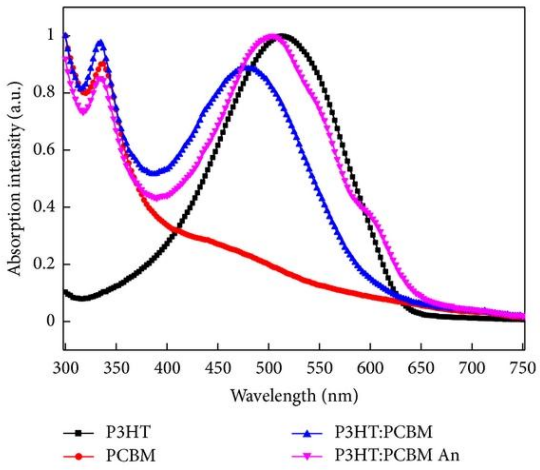


Fig. 8 – The absorption spectrum (P3HT 100 nm is indicated by a black line)

For the specific areas identification of new investigated materials application as a potential alternative to P3HT and PCBM, it is required further research in the measurement field of electrical conductivity and the HOMO and LUMO energy levels positions.

The energy levels position is determined by cyclic I-V using counter electrode – Pt, the electrode reference

– Ag/AgCl and ITO glass with PPBI-O or PNBI-O coated polymer as a working electrode. A supporting electrolyte was prepared based on acetonitrile (> 100 ppm H_2O) supplemented with 0.1 M tetrabutylammonium hexafluorophosphate. Results were adjusted for, based on the ferrocene scale 4.82 eV (equation 2):

$$E_{red/Ox} = -(\varphi_{red/Ox} + 4.82) \quad (2)$$

4. SUMMARY

It was identified certain advantages in the PPBI-O and PNBI-O optical properties above the target prototype P3HT. One of the advantages is absorption peak in the red edge region of 555 nm and 700 nm.

Even the first investigations of heterocyclic PNBI-O and PPBI-O polymers showed the comparable results by analogy with semiconductor properties, according to the application in organic solar cells. For example the HOMO and LUMO energy levels positions are in the optimum range – 3.4-3.6 eV and 5.3-5.6 eV, correspondently, which is typical for "ladder" polymers and donors. The electrical resistivity level is also comparable with the target analogue for comparison P3HT at 1 kOhm·cm. Results for solar cells current-voltage characteristics with two-layer structure showed rather good efficiency and average current I_{sc}.

The advantage of using "ladder" PPBI and PNBI heterocyclic donors is their immunity to oxygen influence during deposition that does not require additional conditions, such as inert atmosphere, heat resistance or sealed reactor which will lead to extended working device lifetime. Moreover, this polymers synthesis method does not require complicated chemical processes using low temperatures and catalysts, such as butyl lithium, all it makes the donors application very useful in organic photovoltaics and it will lead to the mainly increase of the device reliability, for reducing production price and time. Further work in this direction is necessary to continue system's optimization for the ability to use in polar solvent – chlorobenzene, chloroform and etc.

As a result, it will be possible to create the bulk heterojunction, achieve high-efficiency and stable solar cells, considering the PPBI-O and PNBI-O polymers oxidation resistance.

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