Available online at www.sciencedirect.com

ScienceDirect

Spectrochimica Acta Part A 70 (2008) 117–121

SPECTROCHIMICA ACTA PART A

www.elsevier.com/locate/saa

Photovoltaic response and values of state dipole moments in single-layered pyrazoloquinoline/polymer composites

E. Gondek[a], I.V. Kityk[c,*], A. Danel[b], J. Sanetra[a]

[a] Institute of Physics, Technical University of Cracow, Podchrazych 1, Krakow, Poland
[b] Department of Chemistry, Agricultural University of Krakow, Al. Mickiewicz 24/28, Krakow 30-059, Poland
[c] Institute of Physics, J. Dlugosz University Częstochowa, Al. Armii Krajowej 13/15, Częstochowa, Poland

Received 15 June 2007; received in revised form 9 July 2007; accepted 11 July 2007

Abstract

We report the photovoltaic response of composite films formed by polymer transport matrices poly(3-octylthiophene) (P3OT) and poly(3-decylthiophene) (PDT) with incorporated 1*H*-pyrazolo[3,4-*b*]quinoline (PAQ) chromophore (see the first figure). The photovoltage (PV) data were obtained for different substituted PAQ possessing different state dipole moments. The photovoltaic cells were formed between ITO and aluminum electrodes. We found that the PV signal of polymer/PAQ substantially depends on the state dipole moments of the pyrazoloquinoline chromophore. This fact indicates on a possibility of significant enhancement of PV efficiency by appropriate variations of the state dipole moments of chromophore. This results in photoinduced electron transfer from polymer serving as donors to PAQ being the electron acceptor. Despite an efficiency of the PV devices is below 1%, however, it may be substantially enhanced in future varying the chromophore state dipole moments appropriately.

Keywords: Photovoltaic response; Pyrazoloquinoline

1. Introduction

It is well known that PAQ chromophore demonstrate excellent optoelectronic and carrier transport properties [1], which allow using them as materials for creation of single-layer light emitting diodes. In the PAQ-based LEDs devices, the PVK or polysilane polymers were used as a conductive transport matrices [2].

Both of the matrices exhibit good transport properties required for efficient LED devices development, however they are not applicable yet for the photovoltaic. We decided to use the PDT and P3OT transport matrices with HOMO values of about −5.2 to 5.3 eV and LUMO levels of about −2.85 eV. The latter values correlate well with the energies of the LUMO in the PQ donors, providing an efficient charge transfer. The relatively large charge mobility in the PDT and P3OT polymer matrices allows expecting a high charge carrier separation. During exciton transport through the polymer chains, the main source of the exciton recombination of the transport kinetics will be dependent on the dipole–dipole interactions between the transport polymer chains and the PQ chromophore. This interaction seem to be crucial for polarons (electron vibration autolocalised states) forming effective trapping centers, that determine all the photo-kinetics processes.

In this article we have chosen the PQ chromophore molecules (see Fig. 1a) with different state dipole moments to study the PV parameters such as open circuit voltage (V_{OC}) and short current (I_{SC}) for different length polymer transport matrices—PDT and P3OT (Fig. 1b).

The overall efficiency η_{eff} of a solar cell can be calculated by the following formula:

$$\eta_{eff} = \frac{V_{OC} I_{SC}\,FF}{I_{light}}$$

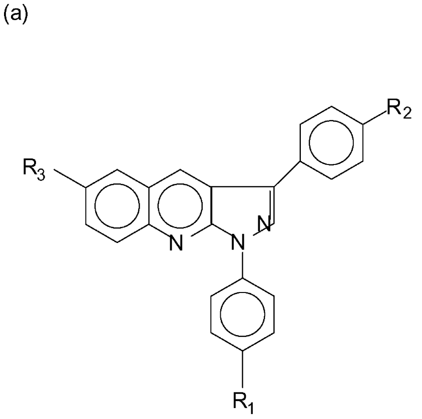
where V_{OC} is the open circuit voltage, I_{SC} the short circuit current, FF the fill factor, and I is the incident light solar radiation. All the parameters are indicated in Fig. 2. The fill factor of solar cells, which reflects their diode properties is determined by

$$FF = \frac{I_{mpp} V_{mpp}}{I_{SC} V_{OC}}$$

---

* Corresponding author.
E-mail address: i.kityk@ajd.czest.pl (I.V. Kityk).

1386-1425/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.saa.2007.07.014



Molecule	R1	R2	R3
DK11	H	OME	H
DK12	H	OME	OME
DK16	OME	OME	H
DK10	OME	H	H
DK7	OME	OME	OME
DK6	H	H	OME

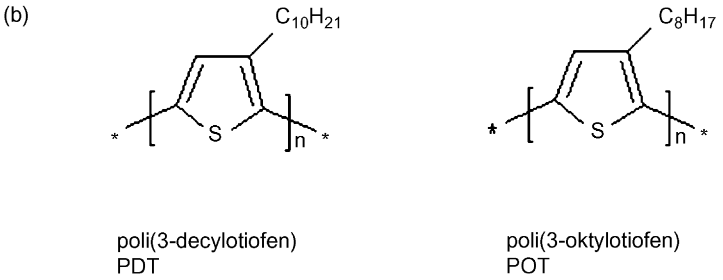


Fig. 1. (a) Investigated chromophore molecule of pyrazoloquinolines. (b) The principal molecular chemical formula for the transport polymers.

with I_{mpp} and V_{mpp} being the current and voltage at the maximum power point in the fourth quadrant of the I/V curve.

2. Experimental

2.1. Materials

Polythiophenes are among the most promising conducting polymers, as they combine chemical stability, good melt and solution process ability with the electronic and optical properties interesting for their various applications [3]. Semiconducting polymers can be used in combination with PAQ as electron acceptors to construct polymer photovoltaic cells. Poly(3-octylthiophene) P3OT and poly(3-decylthiophene) PDT with region regular structures were purchased from Aldrich.

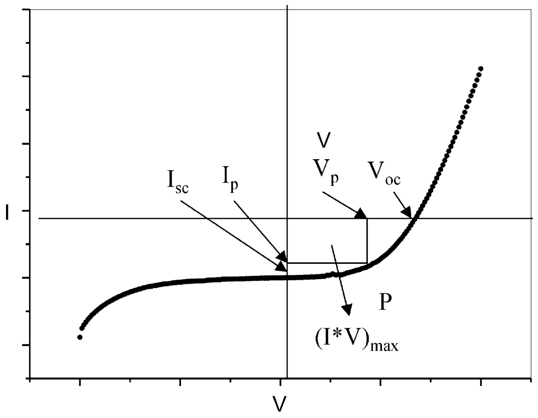
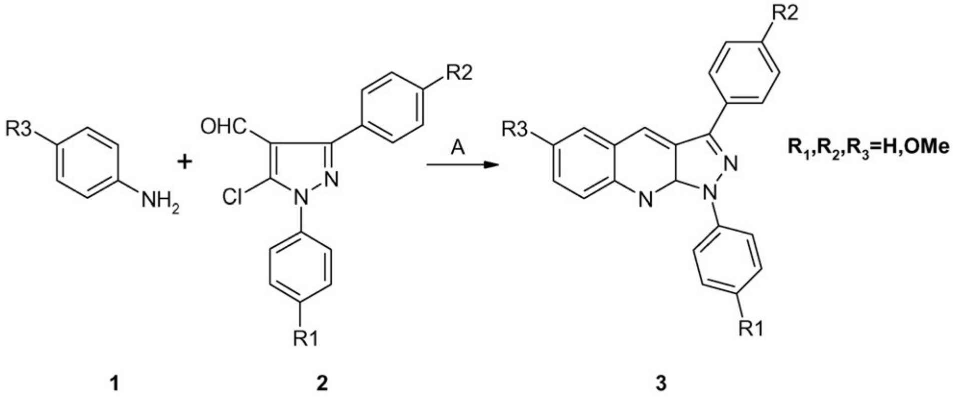


Fig. 2. The current vs. applied voltage of a solar cell. The extracted current is nagative. The fourth quadrant represents the voltage and current generated by the cell. An externally applied voltage is necessary to obtain date points in the first and third quadrants.

Pyrazolo[3,4-*b*]quinolines can be prepared by various method. The most important one is to include Fridländer condensation of *o*-aminobenzophenones, *o*-aminoacetophenones and *o*-aminobenzaldehydes with pyrazolones [4–6]. There may be some difficulties with the availability of ortho-amino carbonyl component (aldehyde or ketone) (see Scheme 1). The next one is the reaction of substituted anilines with 5-chloro-4-formyl-pyrazoles [7]. This method is very convenient and is characterized with short time of the reaction and relatively high yields. Formyl pyrazoles (**2**, Scheme 1) are prepared by DMF/$POCl_3$ formylation of pyrazolones. The third one is a three-component reaction of aldehyde (aromatic or aliphatic), substituted aniline and pyrazolone. In spite of low yield (30–33%) it is very versatile one-step procedure for pyrazolo[3,4-*b*]quinoline preparation substituted in pyridine ring (alkyl or aryl) [8]. This procedure avoids the synthesis of *o*-amino carbonyl component which is usually prepared in two to three stages.

For the synthesis of methoxy substituted pyrazolo[3,4-*b*]quinolines we have chosen the second procedure developed by Brack [7] (Scheme 1). Aniline **1** (R_3=H) or *p*-anisidine (R_3=OMe) reacts with aldehyde **2** at 140–190 °C for 20–40 min. After cooling the reaction mixture, it is dissolved in chloroform and filtered by short pad of alumina and finally subjected to column chromatography on silica gel (Merck 60, 70–230 mesh).



Scheme 1. 140–180 °C.

Thin polymer films were prepared on glass substrate covered partially with ITO. The films were obtained by spin coating from solutions of mixture of polymer and PAQ (polythiophene/PAQ = 1/1). The photovoltaic cell configuration was ITO/polymer + PAQ/Al. Aluminium electrode was evaporated on the surface of polymer under high vacuum conditions. The photocurrent as well as current–voltage (*IV*) characteristic were measured using the Kithley 2400 source meter (Fig. 3).

3. Results and discussion

Main factor responsible for quenching of the power conversion according to the current state-of-the-art for single-layer solar cells is relatively low energy conversion efficiency during the transformation process of an absorbed photon to an exciton (electron–hole coulomb pair) gathered at the electrodes. The absorption of light within the spectral range of 450–570 nm usually leads to an open circuit voltage of up to 760 mV, exhibiting approximately 80% energy losses. Contribution to the open circuit voltage of donor–acceptor heterojunction cell give both the photocurrent and the dark current. The LED efficiency influences different factors such as illumination intensity, organic heterojunction structure, electrode properties, and operating temperature. We also show that the common knowledge of using the “effective” gap of a donor–acceptor heterojunction used for determination for the maximum open circuit voltage needs to be carefully re-examined. Traditionally, dipole–dipole interactions between the chromophore and the transport polymer matrices are not considered in the sufficient way [9–15].

The proposed approach includes variation of position of the acceptor LUMO levels with respect to the donor HOMO ones. In general, enhancement of the efficiency may be achieved by formation of the many-layered structure with large number of the heterojunction to increase the charge separation, aggregation of the molecular complexes, incorporation of inorganic nanoparticles, etc. One of the restrained factors is relatively low mobility favoring a charge gathering near the electrodes and the thermo-destruction of the composites.

It is clear that the system, covered by donor-electron withdrawing side chains and acceptor-chromophore with electron donating side chains, enhances the process of carrier transporting. Consequently, the system has optimum performance of photoelectric conversion when the energy differences between the electrodes and the chromophore are small. However, processes of exciton transport are determined by dipole moments of the polymer chains and by the efficiency of the hole–electron interactions between the transporting materials and the chromophore. One can expect that for every type of donor polymers and of the acceptor chromophore it should be an optimal value of state dipole moments determining the optimal charge separation responsible for the open circuit voltage and the I_{sc} currents.

For the investigation in the present work we have chosen the PQ chromophore with relatively stable positions of the HOMO and LUMO levels, however due to the substitution of the backside groups there exists a possibility to operate by their state dipole moments. So there appears a rare possibility to operate by the dipole–dipole interactions without a necessity to change the positions of the HOMO and LUMO levels. Another factor was to investigate how to influence the space separation for the particular transport donor polymers that would influence on the principal parameters of the charge separation determining efficiency of the PV cells. For these reason two types of polymers

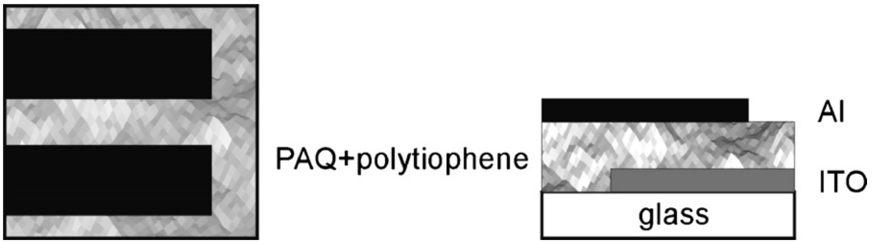


Fig. 3. Typical architecture of the photovoltaic devices.

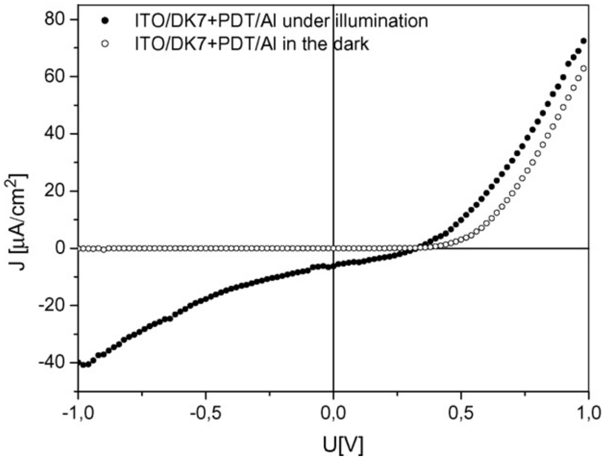


Fig. 4. Typical current–voltage features of the investigated PV devices without the photoexcitation (stars) and after the photoexcitations under the 1315 μW/cm² light.

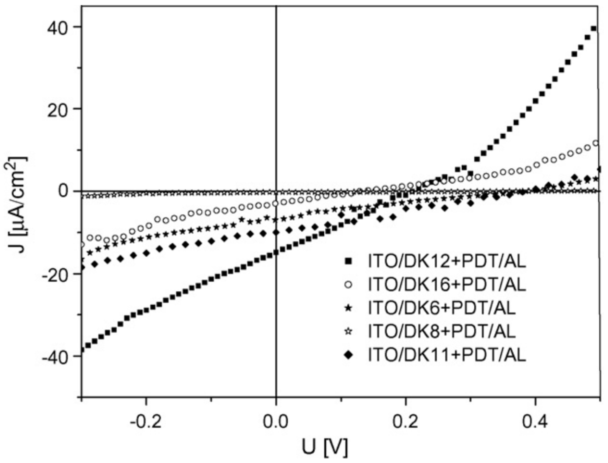


Fig. 5. *I–V* characteristics under illumination of ITO/active layer/Al devices ($P_{\mathrm{light}} = 1315$ μW/cm² light).

with different chain sizes—PDT and P3OT were chosen (see Fig. 1b).

Typical dependence for the PV current voltage features is given in Figs. 4–6. One can see that there exists photovoltaic response of 1315 μW/cm² light. From Table 1 one can see that the efficiency of the PV devices is below the threshold for organic materials, however one can see that the differences between the different chromophore are sufficiently large.

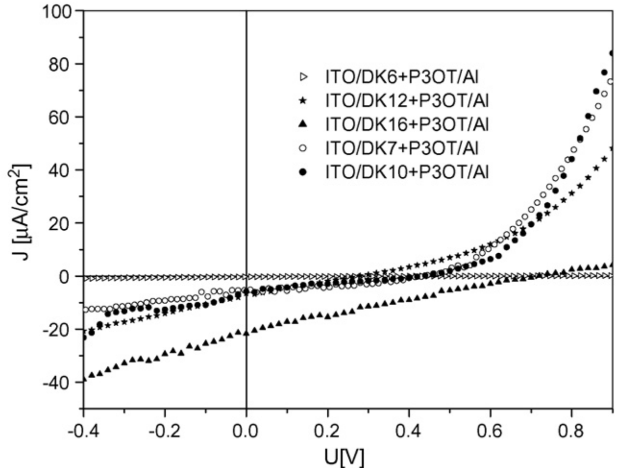


Fig. 6. *I–V* characteristics under illumination of ITO/active layer/Al devices ($P_{\mathrm{light}} = 1315$ μW/cm² light).

Energy conversion efficiencies of various organic solar cells including small molecular [16] as well as polymeric solar cells [17] are of the order of 1%. So, appropriately varying the state dipole moments one can achieve the desired effects in enhancement of the corresponding V_{OC}.

Following the fact that we deal with almost identical HOMO and LUMO parameters of the chromophores, one can understand that principal difference will be due to the polarizability of the chromophores and their interactions both with the same molecule within the aggregated molecular complexes as well as between the chromophore and the polymer chains.

For convenience of readers in Figs. 7 and 8 the dependences of the efficiency versus the dipole moments of the particular chromophore in different matrices are given.

From Figs. 7 and 8 one can see that for the both matrices with increase of the state dipole moments an enhancement of the V_{OC} is observed. Principal difference is that in the PDT matrix this dependence shows saturation whereas for the P3OT there is a drastic jump of V_{OC} for the molecule with larger dipole moments. The calculations of dipole moments were performed by B3LYP DFT method by taking into account of surrounding polymer matrix modifying the electronic states of the chro-

Table 1
Photovoltaic parameters for a sequenced of layers

Sequence of layers	V_{OC} (A)	I_{SC} (μA/cm²)	FF	R_{s} (Ω)	R_{sh} (Ω)	QE (%)
DK11 + PDT	0.382	9.84	0.25	1.0×10^5	3.69×10^5	7.15×10^{-2}
DK16 + PDT	0.131	2.95	0.25	7.6×10^4	2.93×10^5	7.35×10^{-3}
DK7 + PDT	0.337	5.83	0.32	5.5×10^4	2.96×10^5	4.78×10^{-2}
DK8 + PDT	0.39	9.85	0.249	1.1×10^6	2.87×10^6	7.27×10^{-2}
DK6 + PDT	0.388	6.69	0.209	2.5×10^4		4.12×10^{-2}
DK12 + PDT	0.207	15.00	0.255	4.5×10^4	1.10×10^5	6.02×10^{-2}
DK10 + P30T	0.407	5.51	0.271	1.8×10^4	3.67×10^5	4.62×10^{-2}
DK16 + P30T	0.713	22.00	0.236	2.94×10^5	4.29×10^5	0.28
DK7 + P30T	0.401	2.83	0.714	5.5×10^4	2.96×10^5	6.16×10^{-2}
DK6 + P3OT	0.63	0.32	0.19	2.50×10^4	1.35×10^5	2.91×10^{-3}
DK12 + P30T	0.279	6.70	0.254	4.55×10^4	1.10×10^5	3.61×10^{-2}

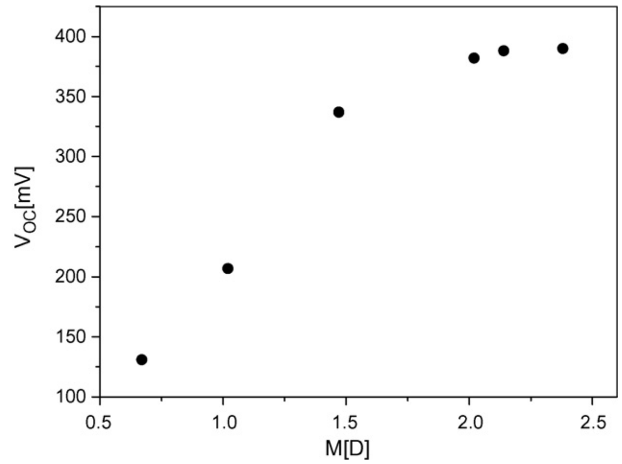


Fig. 7. Dependence of the V_{OC} vs. the state dipole moments in PDT matrix.

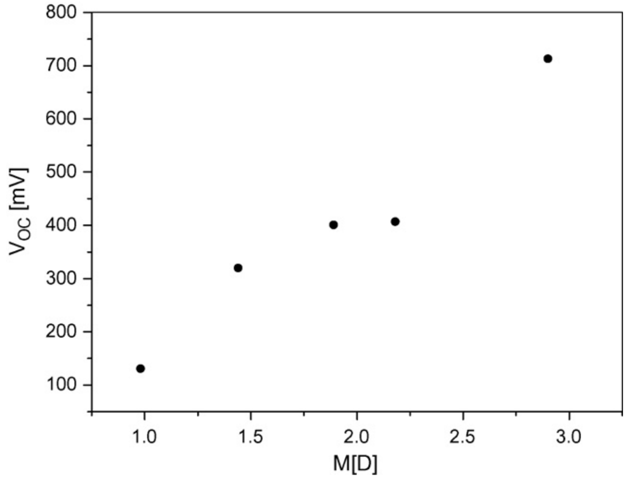


Fig. 8. Dependence of the V_{OC} vs. the state dipole moments in P3OT matrix.

mophore. So there is drastic enhancement of the V_{OC} or the molecule with the lowest sizes. POT may indicate that less separation of the thiophene rings may favor substantial enhancement of the charge transfer separation due to enhanced dipole moments. At the same time the excited dipole and transition dipole moments do not show any correlation with the observed PV efficiencies.

It is crucial that we did not find any significant correlation with the excited and transition dipole moments. This fact may reflect that the free carriers propagating in the polymer chains may be determined by the electrostatic dipole–dipole interactions.

Another crucial fact is a substantially lower I_{sc} for the P3OT matrices compared to the PDT ones. This fact may reflect shorter sides of the P3OT chains compared to the PDT. So the main potential for the use of the PQ molecule consists of an establishment of appropriate dipole–dipole interactions between the chromophore and the transport polymers. Variation of the HOMO and LUMO positions is not crucial for these kinds of devices, however it may become important during substantial substitution for the copolymer groups.

Following the obtained results one can expect that the appropriate operation by the values of the state dipole moments may open additional possibility to enhance the PV efficiency. From this point of view, promising materials may be considered as photopolymer matrices [18], allowing to enhance the efficient state dipole moments of the chromophore.

4. Conclusions

Photovoltaic effects in single-layer pyrazoloquinoline chromophore incorporated into thiophene-containing polymer matrices with different separation of the backbone molecule are reported. We have established principal role of the state dipole moments of the PQ dyes in the observed dependences of the open current voltage. Enhanced separation of the molecule leads to drastic enhancement of the open circuit voltage of up to two times achieving of about 750 mV. The performed quantum chemical calculations show a large potential of the investigated chromophore after appropriate modification of the backside group. The advantage for the use of the PQ molecule consists of an establishment of appropriate dipole–dipole interactions between the chromophore and the transport polymers.

References

[1] E. Gondek, I.V. Kityk, A. Danel, J. Phys. D: Appl. Phys. 40 (2007) 2747–2753.
[2] E. Gondek, I.V. Kityk, A. Danel, M. Pokladko, J. Sanetra, Mater. Lett. 61 (2006) 2018–2022.
[3] B. Kraabel, J.C. Hummelen, D. Vacar, D. Moses, N.S. Sariciftci, A.J. Heeger, J. Chem. Phys. 84 (1996) 4267.
[4] Z. Tomasik, Roczn. Chem. 8 (1928) 345.
[5] P. Tomasik, D. Tomasik, R.A. Abramovitch, J. Hetrocycl. Chem. 20 (1983) 1539.
[6] A. Danel, PhD Thesis, Cracow, 1996.
[7] A. Brack, Liebigs Ann. Chem. 681 (1965) 105.
[8] K. Chaczatrian, G. Chaczatrian, A. Danel, P. Tomasik, Pol. J. Chem. 77 (2003) 1141.
[9] C.J. Brabec, F. Padinger, N.C. Sacriciftci, J.C. Hummeln, J. Appl. Phys. 85 (1999) 6866.
[10] E. Bundgaard, F.C. Krebs, Solar Energy Mater. Solar Cells 91 (2007) 1019.
[11] S. Sahu, A.J. Pal, Mater. Sci. Eng. 27 (2007) 746.
[12] H. Imahori, Bull. Chem. Soc. Jpn. 80 (2007) 621.
[13] G.M. Philos, Trans. Roy. Soc. A: Math. Phys. Eng. Sci. 365 (2007) 993, 1853.
[14] S.S. Sun, Adv. Solar Energy 17 (2007) 74.
[15] P.L. Burhn, Chem. Rev. 107 (4) (2007) 1116.
[16] C.W. Tang, Appl. Phys. Lett. 48 (1986) 183.
[17] J.J.M. Halls, C.A. Walsh, N.C. Greenham, E.A. Marseglia, R.H. Friend, S.C. Moratti, A.B. Holmes, Nature (London) 376 (1995) 498.
[18] I.V. Kityk, M. Makowska-Janusik, E. Gondek, L. Krzeminska, A. Danel, K.J. Plucinski, S. Benet, B. Sahraoui, J. Phys. Condens. Matter 16 (2004) 231.