Photo-induced phenomena in Organic Field-Effect Phototransistors based on Conjugated Polymer/Fullerene Blends and Organic Dielectric

N. Marjanović [a], Th. B. Singh [a,*], G. Dennler [a], S. Günes [a], R. Koeppe [a], H. Neugebauer [a], N. S. Sariciftci [a], S. Bauer [b]

[a] Linz Institute for Organic Solar Cells (LIOS), Physical Chemistry, Johannes Kepler University Linz, Altenbergerstrasse 69, Linz, A-4040, Austria

[b] Soft Matter Physics, Johannes Kepler University Linz, Altenbergerstrasse 69, Linz, A-4040, Austria

Abstract

Photo-induced phenomena were investigated in photoresposive organic field-effect transistors (photOFETs) based on conjugated polymer/fullerene solid-state mixtures as active semiconductor layer and divinyltetramethyldisiloxane-bis(benzocyclobutene) (BCB) as gate dielectrics. The devices were characterized both in under dark showing n-type transistor behaviour with linear and saturated mobility of 1.7 x 10^{-3} cm^2/Vs and 2.7 x 10^{-2} cm^2/Vs respectively, and under white light illumination condition, where large shifts in the threshold voltage in the transfer characteristics were obtained. A typical phototransistor behaviour in a wide range of illumination intensities are observed in these devices.

[*] Corresponding author. Tel: + 43 732 2468 1767; Fax: + 43 732 2468 8770.
E-mail address: birendra.singh@jku.at

Organic Optoelectronics and Photonics II, edited by Paul L. Heremans, Michele Muccini, Eric A. Meulenkamp, Proc. of SPIE Vol. 6192, 61921D, (2006) · 0277-786X/06/$15 · doi: 10.1117/12.663042

1. Introduction

Photo-induced effect in organic field effect transisors (photOFETs) are interesting since they are the basis for light sensitive transistors. PhotOFETs can be used *e.g.* for light induced switches, light triggered amplification, detection circuits and, in photOFET arrays, for highly sensitive image sensors. The realisation of photoactive organic field-effect transistors has been demonstrated using various organic and polymeric semiconductors. Responsivity as high as 0.5 to 1 A/W has been achieved using pristine poly (3-octylthiophene) [1], polyfluorene [2], bifunctional spiro compounds [3] and polyphenyleneethynylene derivative [4]. Among the various concepts for achieving a highly efficient photoinduced charge generation, one of the well-known routes is "the bulk heterojunction concept", [5(a)] which uses acceptor materials with high electron affinity (such as C_{60} or soluble derivatives of C_{60}) mixed with conjugated polymers as electron donors [5(b)-5(c)]. The behaviour of OFETs based on conjugated polymer/fullerene blends as active layers in FET configuration has been reported [6(a),6(b),7]. However, photOFET based on conjugated polymer/fullerene blends, have not been reported.

In this paper, we report on photOFETs based on conjugated polymer/fullerene blends as the photoactive semiconductor layer and divinyltetramethyldisiloxane-bis(benzocyclobutene) (BCB) as a highly transparent polymeric gate dielectric. When characterised in dark, these devices exhibit n-channel OFET with linear and saturated mobility of 1.7×10^{-3} cm^2/Vs and 2.7×10^{-2} cm^2/Vs respectively. Under various illumination intensities of white light, transistor characteristics shows a large shift in threshold voltage, a typical behaviour of phototransistors.

2. Experimental

A scheme of the device structure is presented in Fig. 1 together with the chemical structure of the materials used. PhotOFETs were fabricated on cleaned and patterned indium tin oxide (ITO) glass substrates. BCB precursor solution (used as received from Dow

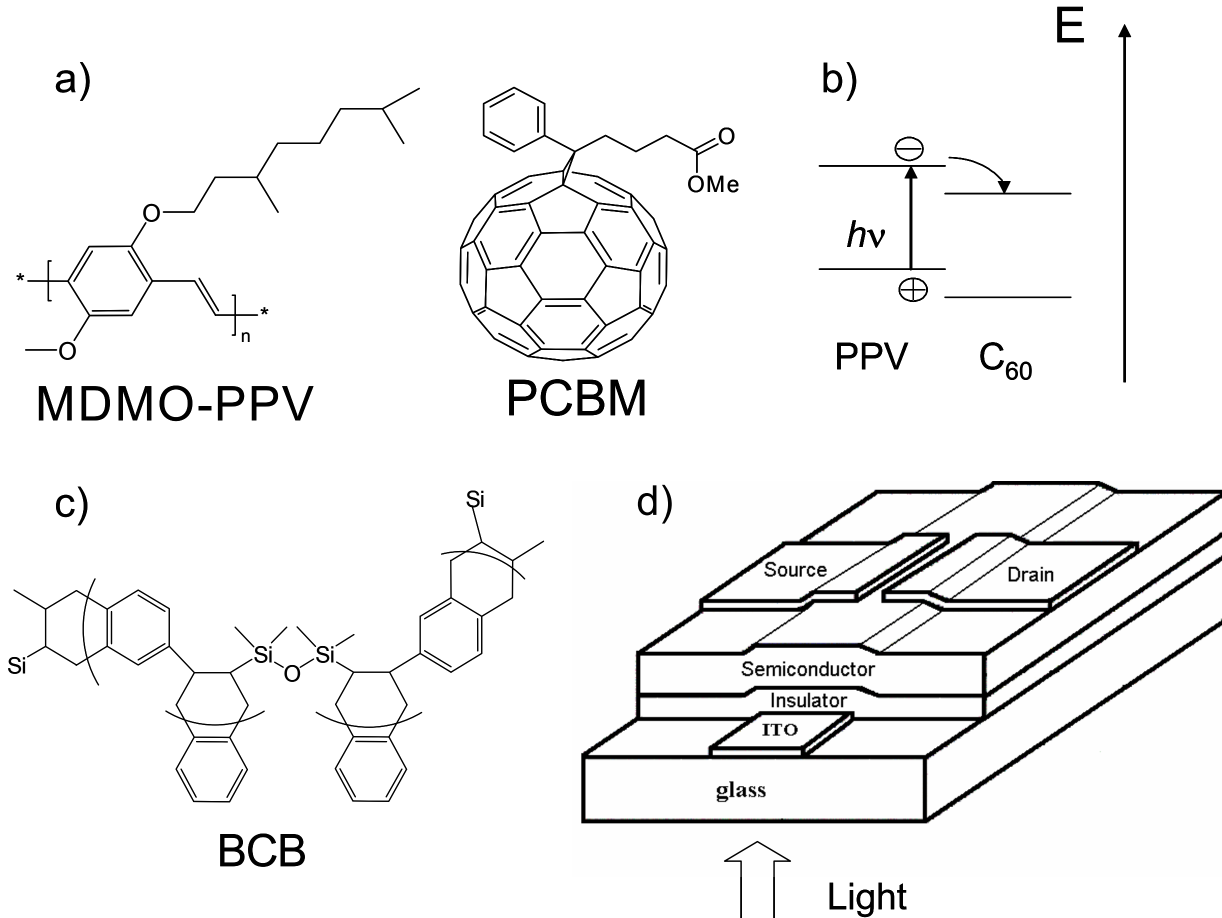

Fig. 1: (a) Molecular structure of MDMO-PPV and PCBM; (b) scheme of the photoinduced charge transfer between the PPV donor and the C_{60} acceptor; (c) molecular structure of BCB; (d) photOFET device structure.

Chemicals) was spin coated at 1500 rpm resulting in a 2-µm thick film. The cross linking to BCB was done as described previously [7]. BCB forms an inert dielectric layer with excellent mechanical

properties and chemical stability, however with a rather low dielectric constant ε_{BCB}= 2.6 (C_{BCB} = 1.2 nF/cm^2). As photoactive material, a blend of MDMO-PPV (poly[2-methoxy-5-(3,7-dimethyloctyloxy)]-1,4-phenylenevinylene) and (PCBM) methanofullerene [6,6]-phenyl C_{61}-butyric acid methyl ester (1 : 4 wt. ratio) was spin coated at 1500 rpm from 0.5% wt. chlorobenzene solution, yielding films with a thickness of 170 nm, inside a glove box under argon atmosphere. The surface morphology and the thickness of the dielectric and the blend film were determined with a Digital Instrument 3100 atomic force microscope (AFM) and a Dektak surface profilometer. As top source and drain contacts, LiF/Al (0.6/60 nm) was evaporated under vacuum (5 x 10^{-6} mbar) through a shadow mask. The channel length, *L,* of all devices was 35 µm and the channel width, *W,* was 2 mm. All electrical characterisations were carried out under inert argon environment inside a glove box system or under vacuum. For the steady state current-voltage measurements, Keithley 2400 and Keithley 236 instruments were used. For the characterisation of the devices under illumination, a solar simulator (K.H. Steuernagel Lichttechnik GmbH) with intensities varying from 0.1 to 100 mW/cm^2 by using neutral density filters was used. The devices were illuminated through the ITO glass and the transparent dielectric layer as shown in Fig. 1(c).

3. Results and discussion

Output characteristics of a photOFET based on MDMO-PPV: PCBM (1:4) blends fabricated on top of a BCB gate-insulator with LiF/Al top source-drain contacts in dark are shown in Figure 2(a). Electron accumulation mode is achieved with a positively biased gate voltage, V_{gs}, demonstrating n-type transistor behaviour, similar to the behaviour reported in pristine PCBM based devices [8]. It is assumed that LiF/Al forms ohmic contacts with the blend layer, especially with respect to charge injection and collection from the fullerene phase [9(a),9(b)]. Electron enhanced mode under AM1.5 (100 mW/cm^2) illumination is achieved by biasing the devices with positive

gate-source voltages, V_{gs} (Fig. 2(b)). The light response of the device is clearly observed by comparing the values of the drain-source current in dark (Fig. 2(a)) and under illumination (Fig.

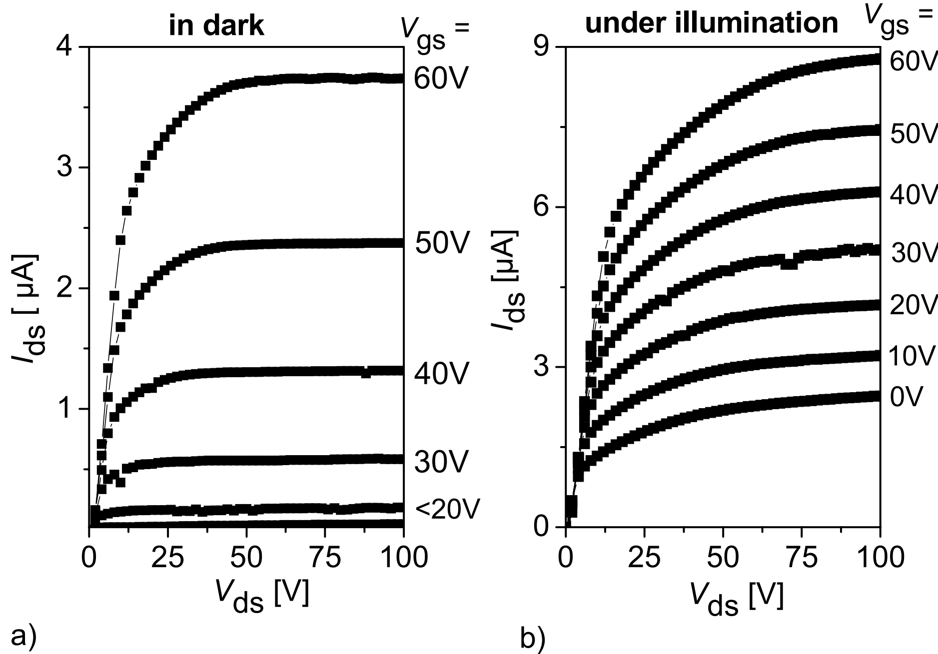

Fig. 2: Output characteristics of the MDMO-PPV: PCBM (1:4) based photOFET fabricated on top of a BCB gate insulator with LiF/Al as top source and drain electrodes (a) in dark and (b) under AM1.5 (100 mW/cm^2)

2(b)). Figure 2(b) shows photOFET output characteristics under illumination due to the photo-induced charges. The photOFETs transfer characteristics in dark is shown in Figure 3 for linear V_{ds} of 2 V and saturated V_{ds} of 20 V which indicate a threshold voltage, V_{th} of ~ 3 V. From these curves, linear and saturated field-effect mobility, μ of 1.7 x 10^{-3} cm^2/Vs and 2.7 x 10^{-2} cm^2/Vs respectively was calculated from the standard transistor equations [10]. In pristine PCBM based OFETs, electron mobility as high as 0.2 cm^2/Vs has been observed [8], at least one order of magnitude higher than in

the present blend devices. We presume that, in the blend, polymer chains significantly disturb the inter-molecular hopping transport in the fullerenes.

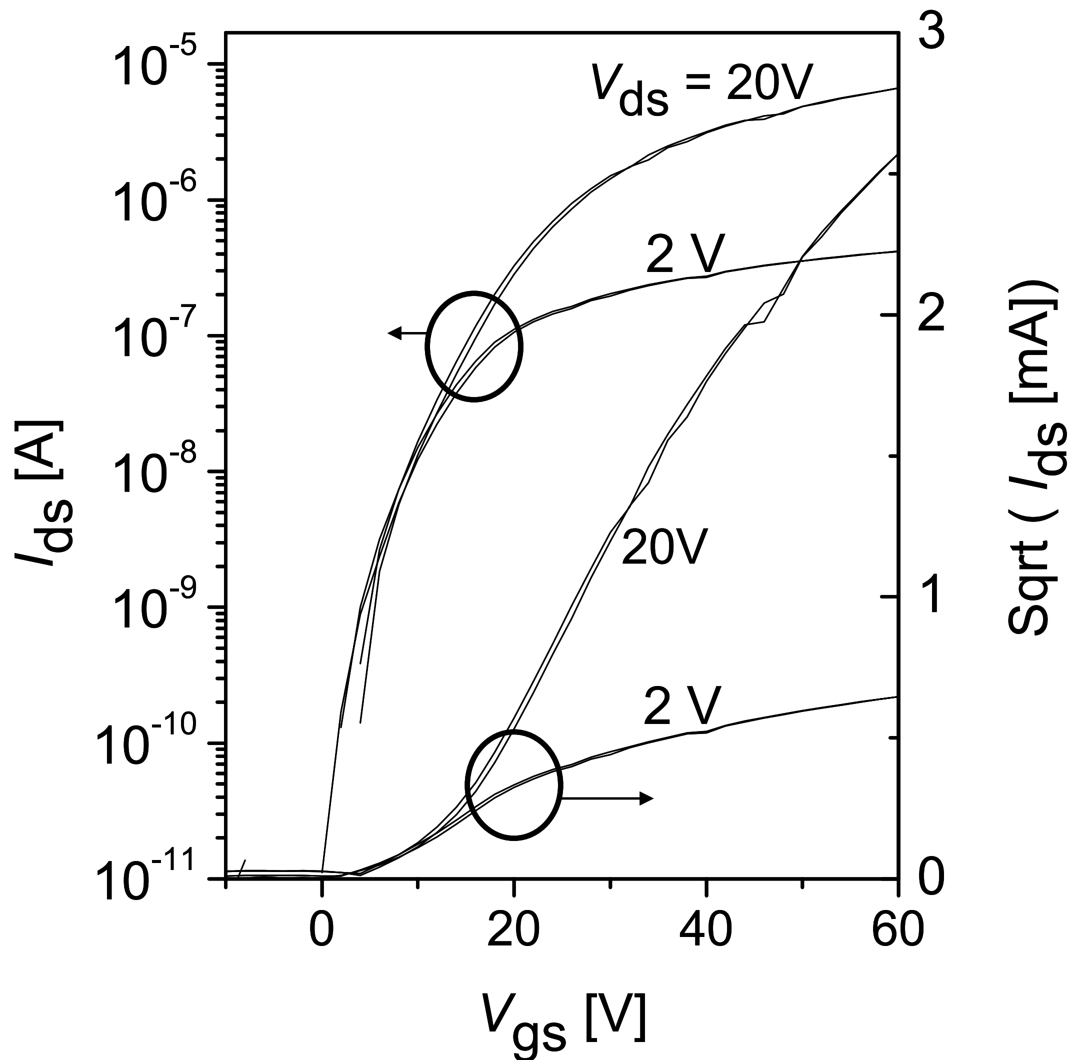

Fig. 3: (b) Transfer characteristics of the device in dark for linear V_{ds} of 2 V and saturated V_{ds} of 20 V. left scale: I_{ds} vs. V_{gs} and right scale: $\sqrt{I_{ds}}$ vs. V_{gs}. A linear mobility of ..and saturated mobility .. is extracted from these curves.

The transfer characteristics with applied large V_{ds} of 80 V in dark and under illumination with white light (AM1.5) and under different illumination intensities (from 0.1 – 100 mW/cm^2) are shown in

Fig 4. The drain-source current of the device is increased as a function of illumination intensity, especially in the depletion regime. In the accumulation regime, the increase of the drain-source current is less pronounced. The reason for shift of V_{th} upon for large applied lateral voltage, V_{ds} in dark condition is not known. A large shift of V_{th} from 15 V to -25 V upon given illumination conditions was clearly observed. We presume the shift of V_{th} originating from an additional photovoltage developed upon illumination in the photOFETs.

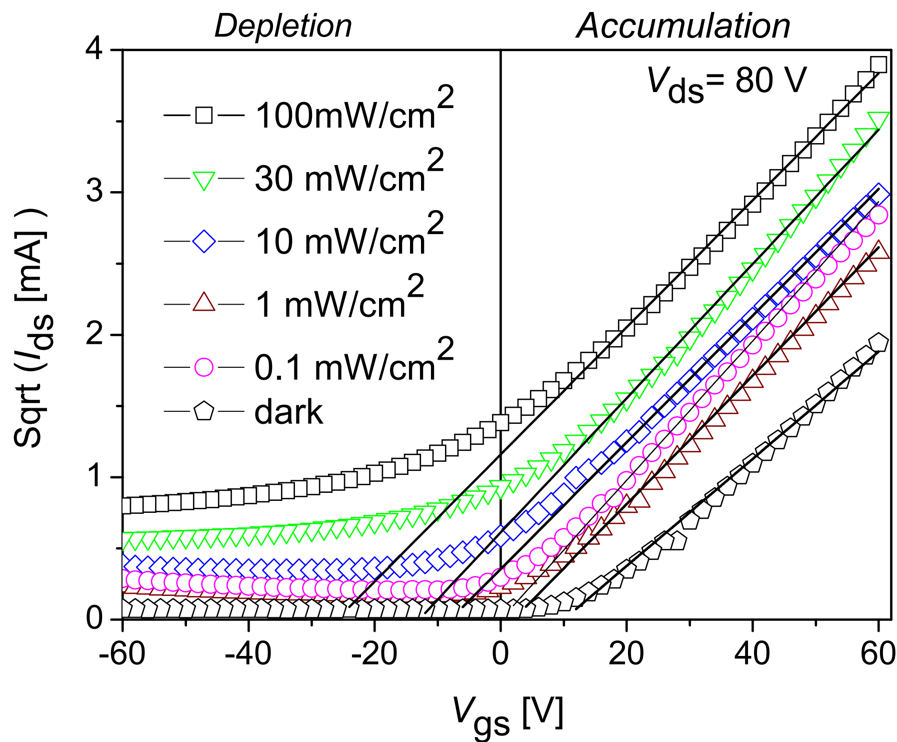

Fig. 4. $\sqrt{I_{ds}}$ vs. V_{gs} at V_{ds} = 80V, for the device from Fig. 2 clearly showing the threshold voltage shift caused by photo-induced effects in dark and under different illumination intensity.

Upon illumination two different effects *i.e. photoconductivity* and the *photovoltaic effect* are assumed to be taking place depending on the applied V_{gs} regime. When the transistor is in the *accumulation-mode*, the photocurrent is given by Equation (1) [11]:

$$I_{ph,pv} = G_M \Delta V_{th} = \frac{AkT}{q} \ln\left(1 + \frac{\eta q \lambda P_{opt}}{I_{pd} hc}\right) \qquad (1)$$

where η is the quantum efficiency (i.e. the number of charge carriers generated per incident photon), q is the elementary charge, P_{opt} the incident optical power, I_{pd} the dark current for electrons, hc/λ the photon energy, G_M the transconductance, ΔV_{th} is the threshold voltage shift, and A is a fit parameter. The photovoltaic effect together with the shift of the threshold voltage is caused by the large number of trapped charge carriers under the source contact [11].

When the transistor is in the *depletion-mode*, the photocurrent is dominated by photoconductivity as described by Equation (2) [10]:

$$I_{ph,pc} = \left(q \mu n E\right) W d = B P_{opt} \qquad (2),$$

where μ is the charge carrier mobility, n is the carrier density, E the electrical field in the channel, W the gate width, and d the thickness of the active layer. $I_{ph,pc}$ is therefore directly proportional to P_{opt} with a proportionality factor B.

The argument of development of photovoltaic action in our photOFET is further confirmed from the measurement of photocurrent as a function light intensity at different bias condition as shown in Fig. 5. The photocurrent tend to saturate as a function of light intensity in the case of *accumulation* voltage (V_{gs} = 60 V). A linear dependence of the photocurrent as a function of intensity for applied *depletion* voltage (V_{gs}= 0,-60 V) is observed with a large photocurrent gain which is a typical characteristics of a phototransistor.

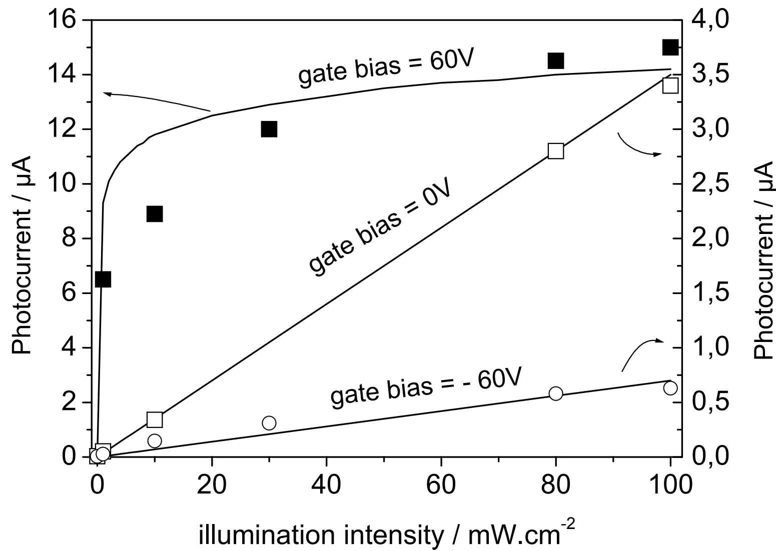

Fig. 5. Photocurrent as a function of the illumination intensity in the *accumulation-mode* (V_{gs} = 60 V, filled square symbols), under *depletion-mode* (V_{gs} = 0 V, open square symbols) and in (V_{gs} = -60 V, open circle symbols). Solid lines are the fits based on Eqs. (1) and (2)

4. Summary

In summary, we demonstrate photoresponsive OFETs (photOFET) based on MDMO-PPV: PCBM (1:4) blends with transparent insulating BCB layers as gate-dielectric. The devices show n-type transistor characteristics with LiF/Al as top source and drain electrodes. PhotOFETs show phototransistor behaviour in a wide range of illumination intensities.

ACKNOWLEDGMENTS

We acknowledge Reinhard Schröwdiauer of Soft Matter Physics, JKU Linz and Gilles Horowitz of ITODYS, CNRS-UMR 7086, University Denis-Diderot, Paris for stimulating discussion. We also acknowledge financial support from Austrian Science Foundation, FWF project No. P16891-N08 and N00103000.

References:

[1] K. S. Narayan and N. Kumar, Appl. Phys. Lett. 79 (2001) 1891.

[2] M. C. Hamilton, S. Martin, and J. Kanicki, IEEE Trans. Electron Devices 51 (2004) 877.

[3] T. P. I. Saragi, R. Pudzich, T. Fuhrmann, and J. Salbeck, Appl. Phys. Lett. 84 (2004) 2334.

[4] Y. Xu, P. R. Berger, J. N. Wilson, and U. H. F. Bunz, Appl. Phys. Lett. 85 (2004) 4219.

[5] (a) Semiconducting polymers, edited by G. Hadziioannou and P. F. van Hutten (Wiley-VCH, Weinheim, 2000); (b) N. S. Sariciftci, L. Smilowitz, A. J. Heeger, and F. Wudl, Science 258 (1992) 1474; (c) C. H. Lee, G. Yu, D. Moses, K. Pakbaz, C. Zhang, N. S. Sariciftci, A. J. Heeger, and F. Wudl, Phys. Rev. B 48 (1993) 15425.

[6] (a) E. J. Meier, D. M. de Leeuw, S. Setayesh, E. van Veenendaal, B. -H. Huisman, P. W. M. Blom, J. C. Hummelen, U. Scherf, and T. M. Klapwijk, Nature Mater. 2 (2003) 678;
(b) W. Geens, T. Martens, J. Poortmans, T. Aernouts, J. Manca, L. Lutsen, P. Heremans, S. Borghs, R. Mertens, and D. Vanderzande, Thin Solid Films 451-452 (2004) 498.

[7] Th. B. Singh, S. Günes, N. Marjanović, N. S. Sariciftci, and R. Menon, J. Appl. Phys. 97 (2005) 114508.

[8] Th. B. Singh, N. Marjanović, P. Stadler, M. Auinger, G. J. Matt, S. Günes, N. S. Sariciftci, R. Schwödiauer, and S. Bauer, J. Appl. Phys. 97 (2005) 083714.

[9] (a) V. D. Mihailetchi, J. K. J. van Duren, P. W. M. Blom, J. C. Hummelen, R. A. J. Janssen, J. M. Kroon, M. T. Rispens, W. J. H. Verhees, and M. M. Wienk, Adv. Func. Mater. 13 (2003) 43;
(b) G. J. Matt, N. S. Sariciftci and T. Fromherz, Appl. Phys. Lett. 84 1570 (2004); C. J. Brabec, A. Cravino, D. Meissner, N. S. Sariciftci, T. Fromherz, M. T. Rispens, L. Sanchez, and J. C. Hummelen, Adv. Funct. Mater. 11 (2001) 374.

[10] S. M. Sze, Physics of Semiconductor Devices, Wiley, New York, 1981.

[11] H-S. Kang, C.S. Choi, W.-Y. Choi, D.-H. Kim, and K.-W. Seo, Appl. Phys. Lett. 84 (2004) 3780.