

Photovoltaic properties of bulk heterojunction devices based on CuI-PVA as electron donor and PCBM and modified PCBM as electron acceptor

G. D. SHARMA^{1,3*}, T. S. SHANAP², K.R. PATEL¹, M. K. EL-MANSY^{2†}

¹Molecular Electronic and Optoelectronic Device Laboratory
Physics Department, JNV University, Jodhpur (Raj.) 342005, India

²Department of Physics, Faculty of Science, Benha University, Benha, Egypt

³R & D Centre for Science and Technology JEC Group of Colleges, Kukas, Jaipur (Raj.), India

In this paper, we have investigated the bulk heterojunction organic solar cells based on CuI - polyvinyl alcohol (CuI-PVA) nanocomposite as electron donor and [6,6] - phenyl C₆₀ - butyric acid methyl ester (PCBM) or modified PCBM i.e. F as electron acceptor. The power conversion efficiencies (PCEs) of 0.46 % and 0.68 % were achieved for the photovoltaic devices based on as cast CuI-PVA:PCBM and CuI-PVA:F blend films, respectively. The higher PCEs of the organic solar cells based on F as electron acceptor resulted from the increase in both short circuit current (J_{sc}) and open circuit voltage (V_{oc}), due to the increased absorption of F in visible region and its higher LUMO level. After thermal annealing, the PCEs of the organic solar cells were further increased to 0.54 % and 0.80 % for CuI-PVA:PCBM and CuI-PVA:F blends, respectively. The increase in the PCEs was mainly due to the increase in J_{sc} , which has been attributed to the improvement in hole mobility and broadening of the absorption band in the longer wavelength region. The improved hole mobility resulted in more balanced charge transport in the devices based on the thermally annealed blends.

Keywords: *organic solar cells, bulk heterojunction, PCE*

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1. Introduction

Photovoltaic devices based on organic semiconductors are evolving into a promising cost effective alternative to the silicon based solar cells due to their low cost fabrication through solution processing, light weight, as well as excellent compatibility with flexible substrates [1–4]. According to theoretical models, the devices based on these materials are predicted to reach the power conversion efficiency (PCE) close to 10 % [5]. Up to now, the highest PCE of the bulk heterojunction (BHJ) polymer photovoltaic devices has been in the range of 6–8 % [6–10] for low band gap conjugated polymers as electron donors and fullerene derivatives as electron acceptors, and in

the range of 3–5 % for small molecules [11–17]. More recently, PCEs of 8.13 % and 8.3 % [18] for BHJ solar cells based on low band gap conjugated polymers as electron donors have been reported by Solarmer and Konarka, respectively.

Organic / inorganic nanocomposites are extremely promising for the applications in light emitting diodes, photodiodes and photovoltaic cells, smart microelectronics devices, and gas sensors [19, 20]. The properties of the nanocomposite films can be adjusted by varying their composition and size. Their fabrication shares the advantages of organic device technology, such as low cost production and the possibility of device fabrication on large areas and flexible substrates. Solar cells composed of hybrid conjugated polymers and semiconductor nanocrystals combine attractive characteristics of bulk inorganic materials with the solution

*E-mail: gdsharma273@gmail.com

†E-mail: mabrouk.almansy@fsc.bu.edu.eg

processability and low temperature chemical synthesis of polymers [21]. Furthermore, the polymers doped with inorganic nanoparticles, show novel and distinctive properties resulting from the unique combination of the inherent characteristics of polymers and the properties of nanoparticles [22–24]. In this regard, we have synthesized the nanocomposites of CuI embedded in the polyvinyl alcohol in order to employ them as electron donor component in organic bulk heterojunction solar cells.

The selection of PVA as the base material was caused by the possibility of good control of its conduction behavior by chemical doping and providing a good host matrix for the embedding of metal nanoparticles [25–30]. In this paper, an effort has been made to investigate the photovoltaic effect of BHJ organic solar cells using a CuI-PVA nanocomposite as electron donor and [6,6]–phenyl C₆₀–butyric acid methyl ester (PCBM) or modified PCBM i.e. F as electron acceptor. We achieved PCEs of 0.46 % and 0.68 % with the CuI-PVA:PCBM and CuI-PVA:F, respectively; this value has been improved up to 0.54 % and 0.80 %, when the thermally annealed blend was used as the photoactive layer.

2. Experimental Details

We have synthesized the CuI (7.5 % by wt)-PVA nanocomposite, as described in our earlier communication [31], that has an optical direct and indirect band gap about 1.7 eV and 1.45 eV, respectively and is used as an electron donor along with [6,6]–phenyl C₆₀–butyric acid methyl ester (PCBM) and modified PCBM i.e. F [32] as an electron acceptor for the BHJ active layer. The chemical structures of PCBM and F are shown in Fig. 1. In the modified PCBM i.e. F, the ester methyl group has been replaced by the large 4-nitro- α -cyanostilbene moiety. The chemical name of F is [6,6]–phenyl C₆₀–butyric acid 4-nitro- α -cyanostilbene. The ITO/PEDOT:PSS/CuI-PVA:PCBM or F/Al devices were fabricated on the pre-cleaned indium tin oxide (ITO) coated glass substrates. A layer of PEDOT:PSS (80 nm)

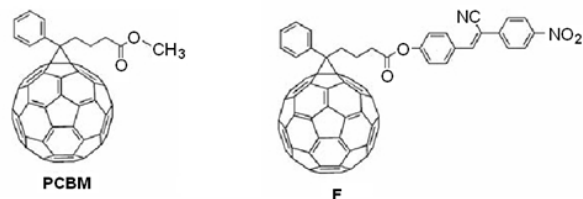


Fig. 1. Chemical structure of PCBM and modified PCBM i.e. F.

was deposited on the ITO coated glass substrate from poly (3,4-ethylenedioxythiophene): poly (styrenesulfonate) (PEDOT:PSS) aqueous solution at 2000 rpm. The layer was subsequently dried at 100 °C for 20 min in air. The CuI-PVA (2 mg/mL) and PCBM or F (2 mg/mL) were dissolved in DMF and THF solvent separately under constant stirring for 2 h and then mixed together. The thin film of the BHJ active layer was then spin cast (2000 rpm for 20 s) on the top of the PEDOT:PSS layer and then dried under ambient condition. The thickness of the active layer was about 90 nm. The device was completed after depositing a 100 nm thick layer of aluminum (Al) at a pressure below 1.33×10^{-3} Pa. The thermal annealing (140 °C for 30 s) of the BHJ active layer was performed placing it on a hot plate before the deposition of the final Al electrode. The current – voltage characteristics (J–V) of the devices were measured with a computer controlled Keithley electrometer in dark and under illumination of the intensity of 100 mW/cm², at room temperature. A xenon lamp coupled with an optical filter of AM1.5 was used as a light source to provide the stimulated irradiance of 100 mW/cm² at the surface of the device. To measure the hole and electron mobility, the devices with the structures ITO/PEDOT:PSS/CuI-PVA:PCBM or F/Au Al/CuI-PVA:PCBM or F/Al, respectively, were fabricated. The J–V characteristics of these devices were measured as described earlier, in dark.

3. Results and discussion

The optical spectra of CuI-PVA:PCBM and CuI-PVA:F thin films are shown in Fig. 2(a). It can be seen that the absorption spectra of the

blends are characteristic of the combination of individual components i.e. CuI-PVA and PCBM or F. The absorption band having a peak at 580 nm corresponds to the CuI-PVA and the peak in the shorter wavelength region corresponds to either PCBM or F. It can be seen from these spectra that the CuI-PVA:F blend shows a broad absorption band from 380 nm to 700 nm, which is closely matched with the solar spectrum. Therefore, we expect more photons to be absorbed by the CuI-PVA:F as compared to CuI-PVA:PCBM. The optical absorption spectra of thermally annealed CuI-PVA:PCBM and CuI-PVA:F films are also shown in Fig. 2(b). The thermally annealed blend shows not only a broader absorption band but also enhanced absorption intensity in the longer wavelength region. The broadening of the absorption band in the longer wavelength region indicates an increased intermolecular ordering and planarity in the CuI-PVA nanocomposite.

We have also estimated the energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the CuI-PVA composite from the cyclic voltammetry data. The energy levels of the CuI-PVA nanocomposite, PCBM and F are shown in Fig. 3. The difference between the LUMO energy level of the CuI-PVA composite and fullerene derivative (PCBM or F) is in the range of 0.5–0.6 eV, which is higher than the required energy difference of 0.3 eV to overcome the exciton binding energy of the material and ensure the electron transfer from the electron donor to electron acceptor used in the BHJ active layer [33–35]. Therefore, the CuI-PVA composites can be used as electron donors.

The LUMO level of CuI-PVA nanocomposite is higher than that of PCBM or F. Therefore, this composite can be used as an electron donor along with PCBM or F as an electron acceptor for the fabrication of BHJ photovoltaic devices. The current – voltage ($J-V$) characteristics of the devices based on the as cast blend, under illumination intensity of 100 mW/cm² are shown in Fig. 4(a). The photovoltaic parameters i.e. open circuit voltage (V_{oc}), short circuit current (J_{sc}),

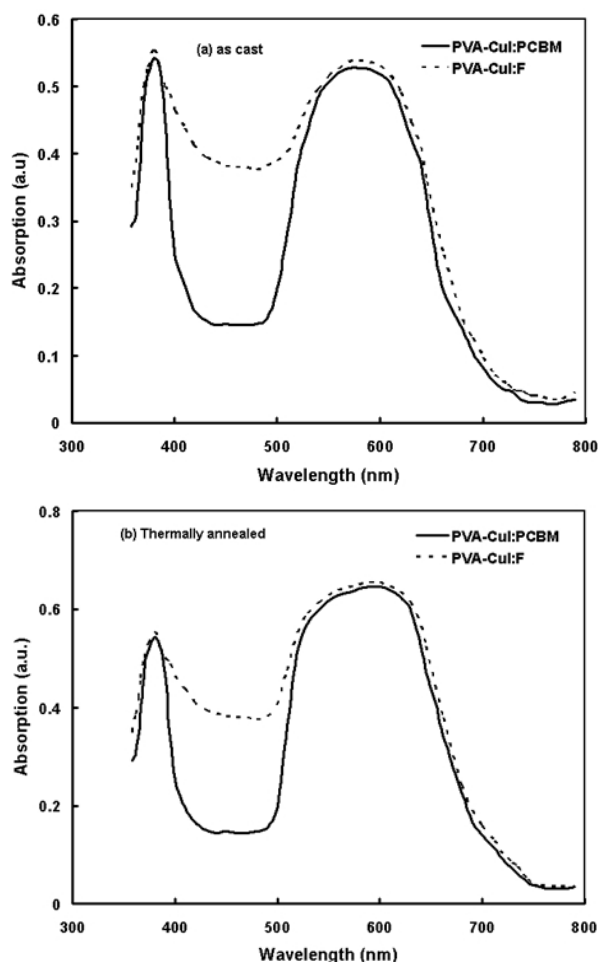


Fig. 2. Optical absorption spectra of PVA-CuI: PCBM or F thin films (a) as cast (b) thermally annealed.

fill factor (FF) and power conversion efficiency (PCE) are listed in Table 1. The V_{oc} of the device based on F as electron acceptor is higher than that of PCBM. Obviously, the V_{oc} increment in the organic solar cell benefits from the higher LUMO energy level of F (−3.75 eV) than that of PCBM (−3.95 eV), because it is well known that the V_{oc} of the BHJ organic solar cell is proportional to the difference between the HOMO of the donor and the LUMO of the acceptor [1]. The increase in J_{sc} in the photovoltaic device based on the blend containing F as electron acceptor, in comparison to PCBM as its counterpart, is attributed to the broader absorption band of the CuI-PVA:F blend, which results in the enhancement in the

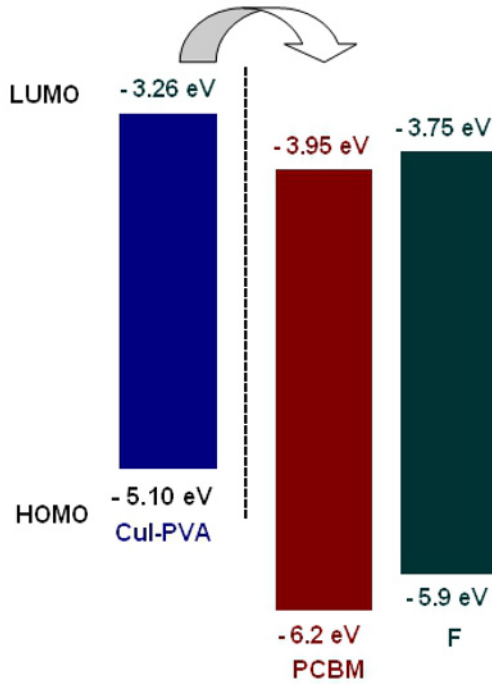


Fig. 3. Energy level diagram showing the LUMO and HOMO levels of CuI-PVA, PCBM and F.

photogenerated excitons in the blend, giving rise to higher photocurrent. The overall PCEs of the BHJ photovoltaic devices based on as cast CuI-PVA:PCBM and CuI-PVA:F blends are 0.46 % and 0.68 %, respectively.

The $J-V$ characteristics of the devices based on thermally annealed CuI-PVA:PCBM and CuI-PVA:F blends under illumination of 100 mW/cm^2 are shown in Fig. 4(b) and the photovoltaic parameters are summarized in Table 1. It can be seen from this table that the PCEs have increased (0.54 % and 0.80 % for the blends based on PCBM and F as electron acceptors, respectively). The improvement in the PCEs can be mainly attributed to the increase in J_{sc} and FF, while the V_{oc} has slightly decreased. The rise in the J_{sc} can be attributed to the increase in the light absorption capability of the BHJ active layer as it is evidenced from the absorption spectra of the BHJ active layers (Fig. 2(b)).

The J_{sc} of the BHJ photovoltaic device is the result of light absorption, exciton

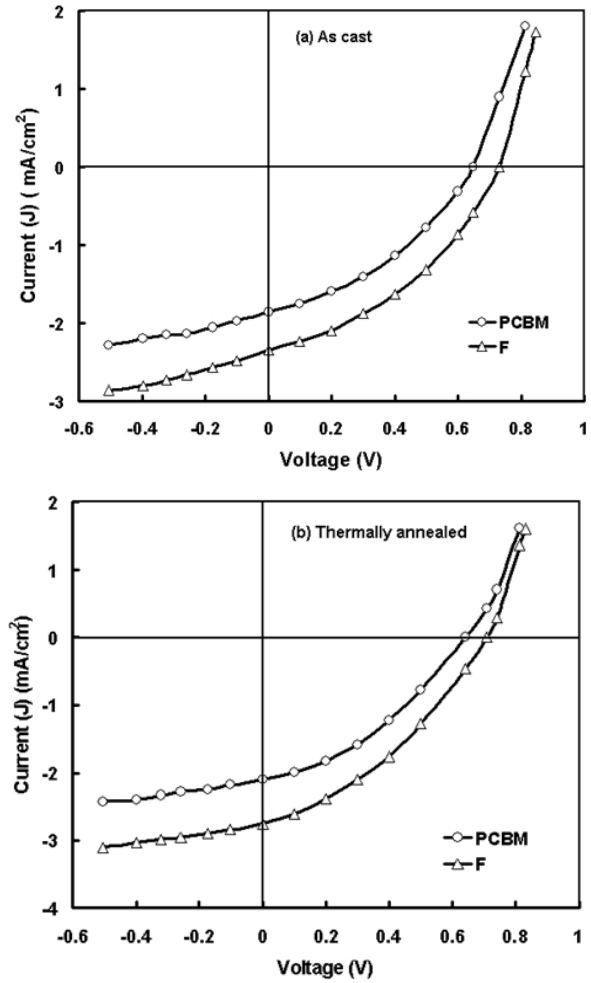


Fig. 4. Current – voltage characteristics of ITO/PEDOT:PSS/PVA-CuI:PCBM or F /Al devices based on (a) as cast and (b) thermally annealed films.

dissociation, charge transport and its collection by the electrodes. These three mechanisms are also crucial for the overall PCE of the BHJ photovoltaic device. To get information about the effect of thermal annealing on the charge transport and collection in the device, we have fabricated the hole-only devices i.e. ITO/PEDOT:PSS/CuI-PVA:PCBM or F/Au devices, and the electron-only devices i.e. Al/CuI-PVA:PCBM or F/Al, to estimate the hole and electron mobilities, respectively. When an appropriate voltage is applied to the device, the transport of holes or electrons in the hole-only

Table 1. Photovoltaic parameters of ITO/PEDOT: PSS/PVA-CuI: PCBM or F/ Al photovoltaic devices.

Blends	Short circuit current (mA/cm ²)	Open circuit voltage (V _{oc}) (V)	Fill factor (FF)	Power conversion efficiency (PCE) (%)
PVA-CuI:PCBM ^a	1.85	0.65	0.38	0.46
PVA-CuI:F ^a	2.34	0.73	0.40	0.68
PVA-CuI:PCBM ^b	2.12	0.64	0.40	0.54
PVA-CuI:F ^b	2.75	0.71	0.41	0.80

^a As cast

^b Thermally annealed at 140 °C for 30 s

or electron-only devices, through the blend layer is limited by the accumulated space charge. The space charge limited current density (J_{SCLC}) is described by the equation [36–38].

$$J_{SCLC} = (9/8) \epsilon_r \epsilon_0 \mu (V^2/d^3) \quad (1)$$

where ϵ_r is the dielectric constant of the blend, ϵ_0 is the permittivity of free space, μ is the charge carrier mobility, V is the effective voltage corrected with built-in potential and d is the thickness of the blend layer. Fig. 5(a) shows the experimental dark $J-V$ characteristics of the hole-only devices based on as cast and thermally annealed CuI-PVA: F blends. Similar results have been also observed for CuI-PVA:PCBM blends. The applied voltage was corrected with the built-in potential (V_{bi}), which is the difference between the electrodes used. We have also measured the dark current – voltage characteristics as a function of film thickness and found that the current in SCLC region follows the relationship $J_{SCLC} \propto d^3$. The hole mobility of the as cast CuI-PVA:F blend measured from Fig. 5(a) and by SCLC method was $2.3 \times 10^{-7} \text{ cm}^2/\text{Vs}$ and it increased up to $8.6 \times 10^{-7} \text{ cm}^2/\text{Vs}$ after thermal annealing. We assume that the increase in the hole mobility upon thermal annealing is due to the increase in the crystalline nature of the blend as reported for other polymer solar cells [39–42]. We also measured the electron mobility of the blends using the $J-V$ characteristics of the electron-only devices (as shown in Fig. 5b) and found that the electron mobilities are $5.8 \times 10^{-5} \text{ cm}^2/\text{Vs}$ and $6.5 \times 10^{-5} \text{ cm}^2/\text{Vs}$ for the as cast and thermally

annealed blends, respectively. For high efficiency organic solar cells, the balanced charge transport through the BHJ active layer is an essential prerequisite for increasing the J_{sc} and FF [43, 44]. The ratio between the electron mobility (μ_e) and hole mobility (μ_h) i.e. (μ_e/μ_h) is a very important factor for controlling the balanced charge transport in the BHJ organic solar cell. For efficient photovoltaic devices, this ratio should be very close to the unity. In our devices, these ratios are 252 and 76 for the device based on the as cast and thermally annealed blend, respectively. When the charge transport in the device is unbalanced (like in the as cast blend film), i.e. μ_h is much lower than μ_e , hole accumulation occurs in the device and the photocurrent is space charge limited [45]. A smaller value of μ_e/μ_h ratio for thermally annealed blend results in a more balanced charge transport in the device as compared to the device based on as cast blend, which contributes to the higher values of both J_{sc} and PCE.

4. Conclusions

We have fabricated organic bulk heterojunction solar cells with CuI-PVA: PCBM or modified PCBM i.e. F blends, (where CuI-PVA is used as an electron donor and PCBM or F is used as electron acceptor), sandwiched between ITO/PEDOT:PSS and Al electrodes. The PCE value of the devices based on as cast CuI-PVA:PCBM and CuI-PVA:F blends are about 0.46 % and 0.68 %, respectively. The increase in the PCE value for the device based on the blend using F as an electron acceptor

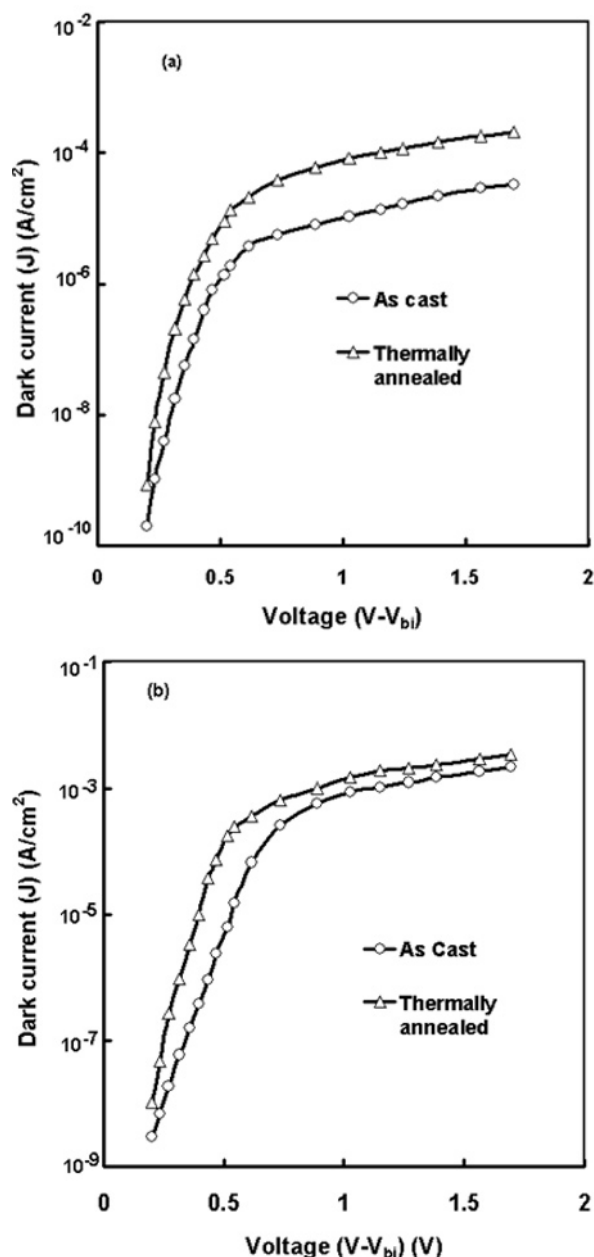


Fig. 5. Current – voltage characteristics of the (a) hole-only device and (b) electron-only devices based on as cast and thermally annealed CuI-PVA:F blends.

has been attributed to the stronger absorption of F in visible region in comparison to the devices based on PCBM. Furthermore, the higher value of V_{oc} has been ascribed to the higher value of LUMO level as compared to PCBM. The PCE

values of the devices were further improved up to 0.54 % and 0.80 %, for CuI-PVA:PCBM and CuI-PVA:F blends by their thermal annealing. The improvement in the PCE has been attributed to the increase in hole mobility of the thermally annealed films, which has led to more balanced charge transport.

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References

- [1] GUNES S., NEUGEBAUER H. AND SARICIFTCI N. S., *Chem. Rev.* 107 (2007), 1324
- [2] DELGADO J. L., BOUIT P. A., FILPPONE S., HERRANZA M. AND MARTYN N., *Chem. Commun.*, 46 (2010), 4853
- [3] BRABEC C.J. et al. *Adv. Mater.* doi: 10.1002/adma.200903697
- [4] LI C., LIU M., PSCHIRER N. G., BAUMGARTEN M. AND MULLEN K., *Chem. Rev.* 10.1021/cr100052z
- [5] SCHARBER M.C. et al., *Adv. Mater.* 18 (2006), 789
- [6] CHEN H. et al., *Nat. Photon.*, 3(2009), 649
- [7] PILIEGO C. et al., *J. Am. Chem. Soc.* 132, (2010), 7595
- [8] CHU T.Y. et al., *J. Am. Chem. Soc.*, 133 (2011), 4250
- [9] ZHOU H.X., YANG L.Q., STUART A.C., PRICE S.C., LIU S.B. AND YOU W., *Angew. Chem.Int. Ed.*, 50 (2011) 2995
- [10] LIANG Y.Y. AND YU L.P., *Acc. Chem. Res.* 43 (2010), 1227
- [11] MA C.Q. et al., *Angew. Chem. Int. Ed.*, 46 (2007), 1679
- [12] MA C.Q. et al., *Adv. Funct. Mater.* 18 (2008), 3323
- [13] MA W.W.H. et al., *Chem. Mater.* 22 (2010), 457
- [14] WALKER B., KIM C. AND NGYYEN T.Q., *Chem. Mater.* doi: 10.1021/cm102189g
- [15] WALKER B. et al., *Adv. Funct. Mater.*, 19(2009), 3063
- [16] LIU Y. et al., *Adv. Energy Mater.* doi: 10.1002/aenm.201100230
- [17] SHANG H., FAN H., LIU Y., HU W., LI Y. AND ZHAN X., *Adv. Mater.* doi: 10.1002/adma.201004445
- [18] www.solarmer.com (b) www.konarka.com
- [19] GODOVSKY D.Y., *Adv. Polym. Sci.*, 153(2000), 163
- [20] EL-SAYED M.A., *Acc. Chem. Res.* 34(2001), 257
- [21] COAKLEY K.M., LIU Y., GOH C. AND MCGEHEE M.D., *MRS Bull.* 30 (2005), 37
- [22] GAUTAM A. AND RAM S., *Mater. Chem. Phys.* 119,(2010), 266
- [23] BLOM P.W.M., SCHOO H.F.M. AND MATTERS M., *Appl. Phys. Lett.* 73(1998), 3914
- [24] RAY S., EASTEAL A.J., COONEY R.P. AND

- EDMONDS N.R., *Mater. Chem. Phys.* 113 (2009), 829
- [25] RAMYA C.S., SAVITHA T., SELVASEKARAPANDIAN S. AND G. HIRANKUMAR G., *Ionics*, 112, (2005), 436
- [26] BASAK D., KARAN S. AND MALIK B., *Solid State Commun.*, 141(2007), 483
- [27] RAM S., GAUTAM A., FECHT H.J., CAI J., BANSMANN H. AND BEHRM R.J., *Philos. Mag. Lett.*, 87(2007), 361
- [28] MALIK T.G.A., LATIF R.M.A., SAWABY A. AND AHMED S.M., *J. Appl. Sci. Res.*, 4, (2008), 331
- [29] ABDELAZIZ M. AND GHANNAM M. M., *Physica B* 405 (2010), 958
- [30] TRIPATHY S. K., *Nanoscale Res. Lett.* 3 (2008), 164
- [31] J EL-MANSY M.K., SHEHA E. M., PATEL K.R. AND SHARMA G D, Structural, Optical and electrical characterization of PVA /CuI polymer composites (Communicated)
- [32] MIKROYANNIDIS J. A., KABANAKIS A. N., SHARMA S. S. AND SHARMA G. D., *Adv. Funct. Mater.*, 21(2011), 7465
- [33] CHEN C., CHAN S., CHAO T., TING C. AND KO B., *J. Am. Chem. Soc.* 130 (2008), 12828
- [34] BRABEC C.J. et al., *Adv. Funct. Mater.* 12 (2002), 709
- [35] KRABEL B., MCBRANCH D., SARICIFTCI N.S., MOSES D. AND HEEGER A.J., *Phys. Rev. B: Condens. Matter.*, 50 (1994), 18543
- [36] REID O.G., MUNECHIKA K. AND GINGER D.S., *Nano Lett.*, 8 (2008), 1602
- [37] MEIZER C., KOOP E.J., MIHAILETCHI V.D. AND BLOM P.W.M., *Adv. Funct. Mater.* 14(2004), 865
- [38] MALLIARAS G.G., SALEM J.R., BROCK P.J. AND SCOTT C., *Phys. Rev. B*, 58(1998), R13411
- [39] CHEN H.Y. et al., *J. Phys. Chem. C*, 113(2009), 7946
- [40] LIU J.G. et al., *Org. Electron.*, 11(2010), 775
- [41] HWANG I.W. et al., *J. Appl. Phys.*, 104(2008), 33706
- [42] MIKROYANNIDIS J.A., TSAGKOURNOS D.V., SHARMA S. S. AND SHARMA G. D., *J. Phys. Chem. C*, 115 (2011), 7806
- [43] GUPTA D., MUKHOPADHAYA S. AND NARAYAN K.S., *Sol. Energy Mater. Sol. Cells*, 94 (2008) 1390
- [44] YUM M.H., KIM G.H., YANG C. AND KIM J.Y., *J. Mater. Chem.* doi. 10.1039/c0jm00790k
- [45] MOULE J. AND MEERHOLZ K., *Adv. Mater.*, 20 (2008), 240

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