Temperature Effect on the Performance of H_2Pc/C_{60} Photovoltaic Device

Dr. Hemant Kumar
Government Degree College, Kasganj, UP, India.
drhemantgdc@gmail.com

We present the investigations carried out on the effect of temperature on the performance of hydrogen phthalocyanine (H_2Pc)/fullerene (C_{60}) bilayer organic photovoltaic (OPV) devices. Prior to these investigations the thicknesses of the active layers were optimised to get the best performance. The optimised device had an efficiency of ~0.5% at 307 ^oK. The investigations on the best device showed that temperature has significant effect on the photovoltaic performance. Short circuit current density (J_{sc}) and fill factor (*FF*) decrease while open circuit voltage (V_{oc}) increases with reduction in temperature. In overall the efficiency first increases and then decreases with reduction in temperature. The reduction in J_{sc} and *FF* is because of the temperature dependent electronic properties of the organic materials. We have developed a model which shows that the built in voltage (V_{bi}) of the devices increases with reduction in temperature. The increment in V_{oc} with reduction in temperature has been attributed to the increment in V_{bi}.

1. INTRODUCTION

In the last two decades a new branch of photovoltaic research, known as organic photovoltaic has evolved. Researchers and technologist have found a new playground in the face of organic photovoltaic devices (also know as solar cells). Organic solar cells (OSCs), which are now considered to be an alternative to conventional inorganic solar cells, have lots of potential advantages, such as light weight, flexibility, and fabrication of large area devices at very low cost. These technological potentials are now driving the attention of researchers towards further improvement in the performance of these cells. There are various parameters, which can be played with to improve the performance, for example the performance of OSCs can be improved by introduction of new materials, proper donor-acceptor combinations and by different treatments to the materials and devices. Power conversion efficiency (η) of ~ 6.5% has been achieved in tandem OSCs based on a polymer: fullerene bulk heterojunctions [1]. Stability and reliability are the major concerns for these devices therefore intense research is also being done to understand the stability and reliability issues. Because of continuous efforts and hard work of the researchers, several thousand hours outdoor life time of OSCs has been achieved [2-4]. The efficiency of a solar cell is related to the V_{oc}, J_{sc} and *FF* as

$$\eta = \frac{J_{sc} V_{oc} FF}{P_{in}} \tag{1}$$

Received: 15.11.16, Accepted: 02.12.16

where P_{in} is the incident optical power.

For reliability of these devices in different environmental conditions is becomes very important to investigate the effect of various physical parameters e.g. temperature, electric field, magnetic field, cosmic rays, humidity etc. on their performance. In this paper we investigate the effect of temperature on the performance of small molecular OSCs based on hydrogen phthalocyanine (H_2Pc) and fullerene (C_{60}) which are respectively the important donor and acceptor material. First of all the thicknesses of active layers were optimized to get the best efficiency with this system. The best performance was obtained for indium tin oxide (ITO)/H_2Pc (23 nm)/C_{60} (40 nm)/bathophenanthroline (BPhen) (8 nm)/Al (150 nm) device which exhibited an efficiency of ~ 0.53 % with V_{oc} = 0.43 V and J_{sc} = 2.3 mA/cm^2 at room temperature. Temperature variation has been found to have a remarkable effect on the performance.

2. EXPERIMENTAL PROCEDURE

The devices were prepared on the pre-patterned and pre-cleaned ITO substrates in ITO/H_2Pc/C_{60}/BPhen/Al configuration, where ITO, H_2Pc, C_{60}, BPhen and Al are respectively the transparent anode, donor, acceptor, exciton blocking and cathode materials.

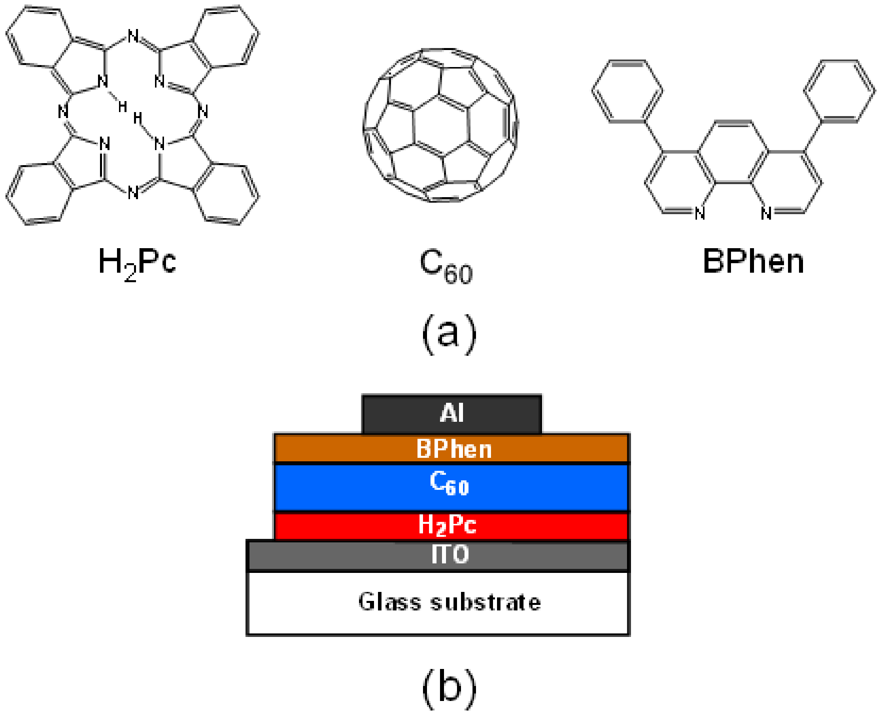

Fig. 1(a): Molecular structures of the materials used; **1(b):** Schematic structural diagram of the H_2Pc/C_{60} solar cell.

Figure 1 shows the molecular structures of the materials and schematic structure of the device. Application of exciton blocking layer reduces the exciton quenching at cathode and improves the cell performance [5]. Prior to any deposition the ITO substrates were exposed to air plasma for 5 min and then transferred to a vacuum chamber, where thin film depositions were carried out via thermal evaporation of the materials at the base pressure ~ 5×10^{-6} Torr. All the materials were purchased from Sigma-Aldrich USA and were used as such. To eliminate the performance variance due to fabrication conditions the devices were fabricated in a controlled way under the identical conditions. For low temperature measurements the device was transferred to a laboratory made low temperature measurement assembly, where the *J-V* characteristics were carried out in dark and under halogen lamp illumination with irradiance of 80 mW/cm^2. A Keithley 2400 Source-Measure unit, interfaced with the computer, was used to measure the *J-V* characteristics. The UV-visible absorption spectroscopic studies of the materials have been carried out in thin films on fused silica substrates, using SHIMADZU 2401-PC spectrophotometer at the room temperature.

3. RESULTS AND DISCUSSION

The power conversion efficiency of an OSC depends upon the absorption efficiency, exciton dissociation efficiency, transport of charge carriers and charge collection efficiency. Absorption of incident photons and exciton dissociation are decided by the thickness of the photoactive layers. The best performance can only be achieved by the optimisation of various parameters. For the same objective we varied the thicknesses of H_2Pc and C_{60} in the configuration ITO/H_2Pc (x nm)/C_{60} (y nm)/BPhen (8 nm)/Al (150 nm), where x and y have been varied. The optimum thickness of H_2Pc and C_{60} were found to be 23 and 40 nm respectively and the cell exhibited V_{oc} = 0.43 V, FF = 40 % J_{sc} = 2.3 mA/cm^2 and an efficiency of 0.53%. We found an interesting result that with the variation of active layer thickness V_{oc} was observed to vary (results not shown). It is interesting because in the literature V_{oc} has been correlated with the difference (I_g) between the lowest unoccupied molecular orbital (LUMO) of acceptor and highest occupied molecular orbital (HOMO) of the donor material at the heterojunction interface [6,7], and with the difference of work functions of the electrodes used [8]. In the present studies neither the materials nor the electrodes have been changed still a change in V_{oc} has been observed just because of thickness variation. The change in V_{oc} on the variation of active layer thickness has also been observed in boron subphthalocyanine chloride (Sub-Pc)/C_{60} OPV devices by other authors as well [9] but the reason is not well understood. So these types of observations open the new doors for noble research in the area of OSCs.

Once the device was optimized, we studied the effect of temperature on its performance. Figure 2 shows the dark *J-V* characteristics of the optimized device on semi-log scale, measured at different temperatures in the range 307-252 ^{0}K. The dark current is determined by the charge carriers injected through the electrodes and is observed to decrease with reduction in temperature. At low temperatures the reduction in reverse bias current is relatively low compared to that in the forward bias (+ve voltage to ITO) current.

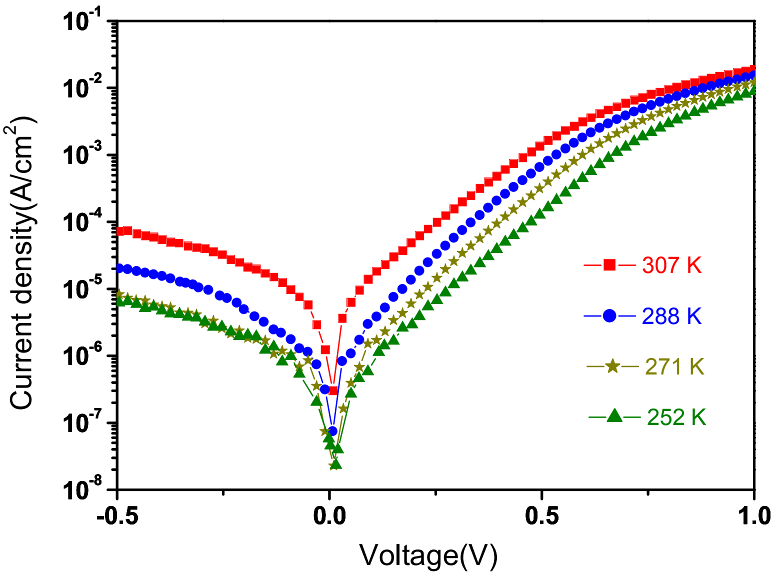

Fig. 2: *J-V* characteristics of ITO/H_2Pc(23 nm)/C_{60}(40 nm)/Bphen(8 nm)/Al OSCs device measured in dark at different temperatures in the range 307-252 ^{0}K.

The reduction in dark current with reduction of temperature can be explained by the temperature dependent charge transport properties of the active organic layers. In the reverse bias (+ve voltage to Al) below 271 ^{0}K the current became almost temperature independent. Temperature independency of the current below 271 ^{0}K in the reverse bias suggests that the current might be controlled be the tunnelling of the charge carriers through large injection barriers [10]. The current shows ohmic behaviour at 307 ^{0}K in the reverse bias. This ohmic behaviour in the reverse bias can probably be attributed to the high charge injection barriers in the reverse bias [11]. At low temperatures charges do not have sufficient energy to overcome the injection barriers and therefore are injected into the semiconductor via tunnelling through the barriers.

It is thus established that the reverse bias current in the present OPV device is governed by tunnelling mechanism at low temperatures. Figure 3 shows the illuminated *J-V* characteristics of the same device at different temperatures on a semi-log scale. The temperature exhibited significant effect on the current under illumination as well. The current is observed to decrease with reduction in temperature.

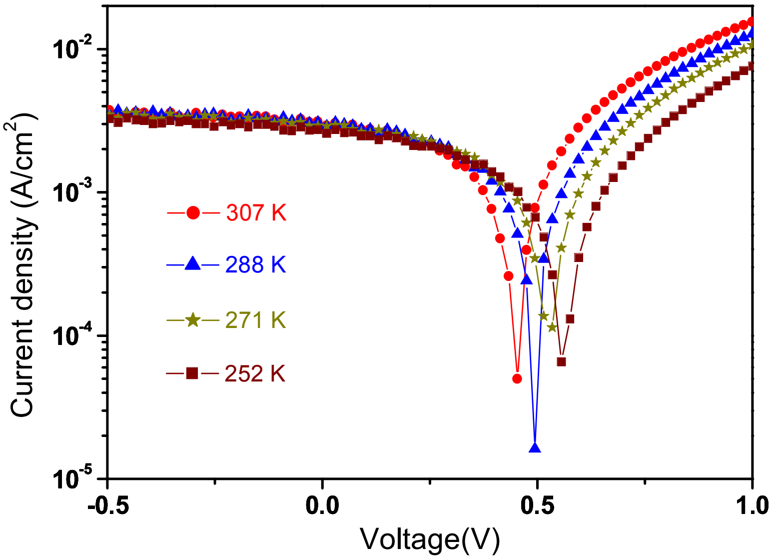

Fig. 3: *J-V* characteristics of ITO/H_2Pc(23 nm)/C_{60}(40 nm)/Bphen(8 nm)/Al solar cell under 80 mW/cm^2 irradiance of halogen lamp at different temperatures.

Figure 4 shows the effect of temperature on J_{sc} and V_{oc}. It is observed that the J_{sc} decreases while V_{oc} increases with reduction in temperature. Organic semiconductors are generally amorphous in nature and contain traps.

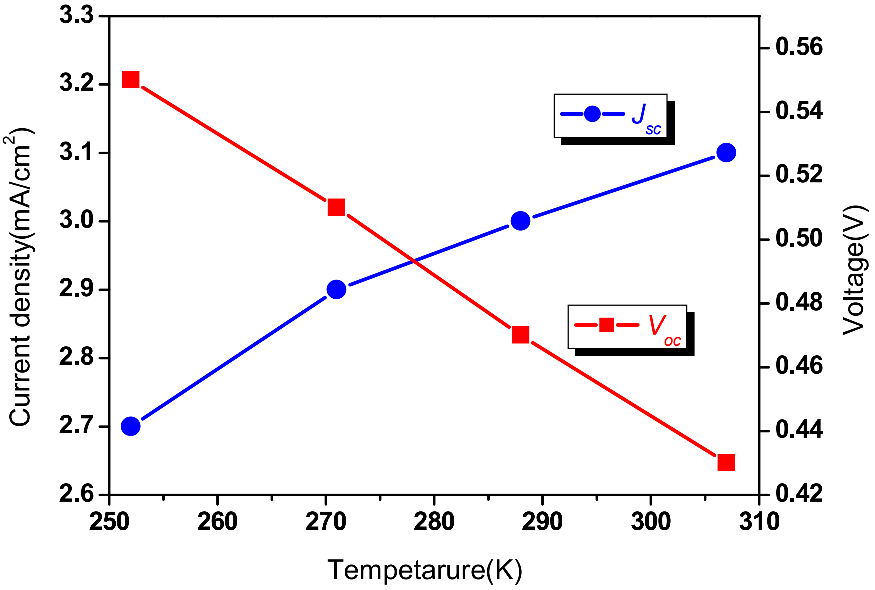

Fig. 4: Variation of V_{oc} and J_{sc} as a function of temperature.

The temperature dependence of J_{sc} can be attributed to the electronic transport properties of the active organic materials. Their charge carrier mobilities are very low and depend on the temperature. Furthermore it is negatively influenced by the capture of charge carriers by traps. One would expect that the lowering of temperature will reduce the current [12]. Therefore reduction in J_{sc} can be interpreted in terms of trapping effect and the reduction of charge carrier mobility with temperature.

Regarding the variation of V_{oc} with temperature, the origin of V_{oc} itself is not well understood. Different models have been presented to explain the experimental observations [7,13]. However the temperature variation of V_{oc} could not directly be explained by these models. The temperature dependence of V_{oc} in the present case makes it further difficult to explain the explicitly origin of V_{oc}. In conventional Si solar cells the temperature dependence of V_{oc} is given by

$$V_{oc} = \frac{nkT}{q} \ln\left(\frac{J_{sc}}{J_0} + 1 \right) \tag{2}$$

where J_0 is the reverse saturation current in the device and n is the diode ideality factor. Here both the J_{sc} and J_0 also depend on temperature and increase with increase in temperature [14,15]. Though increase in J_{sc} would slightly increase V_{oc} but due to large increase in J_0 (J_0 is proportional to n_i^2, where n_i is intrinsic charge carrier density) would rapidly decrease V_{oc} with increment in temperature [14]. Katz *et al.* investigated the effect of temperature on J_{sc}, V_{oc}, FF and η in a poly(2-methoxy, 5-(3,7 dimethyl-octyloxy))-*p*-phenylene-vinylene (MDMO-PPV): [6,6] phenyl C_{61}-butyric methyl-ester (PCBM) based bulk-heterojunction OPV device in the temperature range 25-60 ^{o}C [14]. V_{oc} was observed to increase linearly with temperature and Eq. (2) was used to explain the temperature dependence of V_{oc}. The temperature dependence of V_{oc} has directly been correlated to the temperature dependence of quasi-Fermi levels of the polymer and the PCBM under illumination. Alternatively the temperature dependence of the V_{oc} in the present case has been attributed to the temperature dependence of built-in voltage (V_{bi}) [16]. The structure of an OPV device contains a thin active organic layer sandwiched between two metal electrodes. For the devices containing electrodes with different work-functions, in thermal equilibrium the Fermi level alignment takes place and an electric field is developed which is known as built-in electric field. The corresponding voltage between the two electrodes is known as the built-in voltage (V_{bi}). The built-in electric field for electrons is directed from anode to cathode. Generally V_{bi} is given by the difference of the work-function of the two electrodes (ΔW). But if electrodes make ohmic contact with the organic materials, an accumulation of charge carriers takes place in the vicinity of the electrodes and band bending takes place. Because of this band bending V_{bi} now becomes less than the ΔW. As the temperature reduces V_{bi} increases and because of increment in V_{bi}, V_{oc} increases. The results of Eq. (2) are good enough for inorganic solar cells but their applicability to OPV devices is an open question, though they have been used to interpret V_{oc} in OPV devices [14]. Figure 5 shows the variation of FF and the η with temperature. The observed temperature dependence of FF is almost similar to that of J_{sc}. This behaviour can qualitatively be understood in terms of temperature dependent series resistance of the OPV devices.

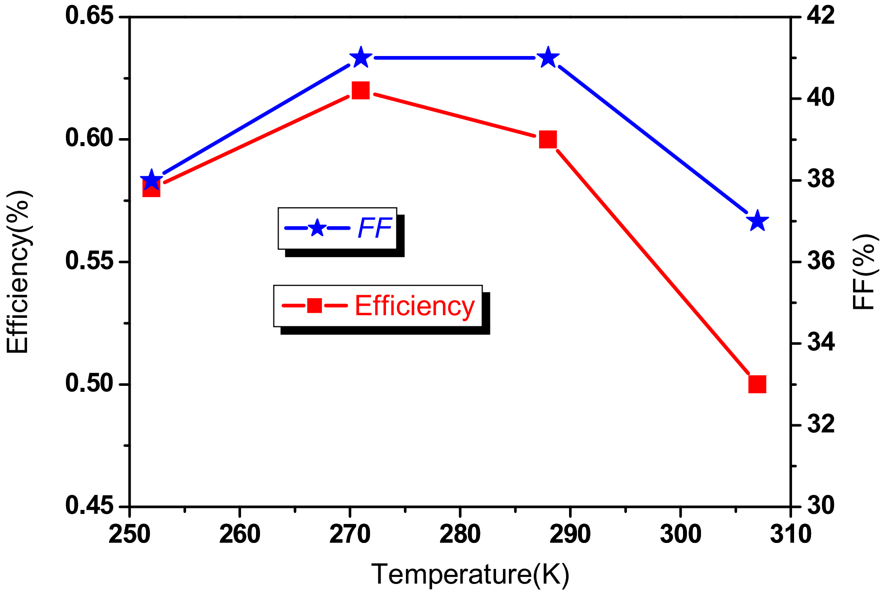

Fig. 5: Variation of *FF* and *η* as a function temperature.

In case of inorganic semiconductors the resistivity of the active semiconductor material is very low and the series resistance is solely determined by the metal-semiconductor interface and is independent of the temperature. On the other hand OPV devices have relatively high resistivity of the organic active layers (bulk resistivity) that increases with decreasing temperature. The increase in resistivity with decrease in temperature can be attributed to the trapping effect and lowering of the charge carrier mobility. It is this increase in resistivity, which reduces *FF* with lowering of the temperature. As regards the efficiency, it increases first and then decreases with the decrease in temperature.

4. ACKNOWLEDGMENT

This work done at the time of Ph.D., I would like to pay my heartfelt gratitude to my supervisor Dr. S. Chand for their kind help and support. I heartily thank him for providing me the facilities and a healthy working environment at NPL.

REFERENCES

[1] J. Y. Kim, K. Lee, N. E. Coates, D. Moses, T. Q. Nguyen, M .Dante and A. J. Heeger; “Efficient tandem polymer solar cells fabricated by all-solution processing”, Science, Vol. 317, pp. 222-225, 2007.

[2] J. A. Hauch, P. Schilinsky, S. A. Choulis, R. Childers, M. Biele and C. J. Brabec; “Flexible organic P3HT:PCBM bulk-heterojunction modules with more than 1 year outdoor lifetime”, Sol. Energy Mater. Sol. Cells, Vol. 92(7), pp. 727-731, 2008.

[3] F. C. Krebs and H. Spanggaard; "Significant improvement of polymer solar cell stability", Chem. Mater., Vol. 17(21), pp. 5235-5237, 2005.

[4] C. Lungenschmied, G. Dennler, H. Neugebauer, S. N. Sariciftci, M. Glatthaar, T. Meyer and A. Meyer; "Flexible, long-lived, large-area, organic solar cells", Sol. Energy Mater. Sol. Cells, Vol. 91(5), pp. 379-384, 2007

[5] T. Noda, H. Ogawa and Y. Shirota; "A blue-emitting organic electroluminescent device using a novel emitting amorphous molecular material, 5,5'-Bis(dimesitylboryl)-2,2'-bithiophene", Adv. Mater., Vol. 11(4), pp. 283-285, 1999.

[6] H. Kumar, P. Kumar, R. Bhardwaj, G. D. Sharma, S. Chand, S. C. Jain and V. Kumar; "Broad spectral sensitivity and improved efficiency in CuPc/Sub-Pc organic photovoltaic devices", J. Phys. D: Appl. Phys., Vol. 42(1), pp. 15103-15108, 2009.

[7] C. J .Brabec, A. Cravino, D. Meissner, N. S. Sariciftci, T. Fromhertz, M.T.Rispens, L. Sanchez and J. C. Hummelen; "Origin of the open circuit voltage of plastic solar cells", Adv. Funct. Mater., Vol. 11(5), pp. 374-380, 2001

[8] V. D. Mihailetchi, P. W. M. Blom, J. C. Hummelen and M. T. Rispens; "Cathode dependence of the open-circuit voltage of polymer:fullerene bulk heterojunction solar cells", J. Appl. Phys., Vol. 94(10), pp. 6849-6855, 2003.

[9] K. L. Mutolo, E. I .Mayo, B. P. Rand, S. R. Forrest and M. E. Thompson; "Enhanced Open-Circuit Voltage in subphthalocyanine/C_{60} organic photovoltaic Cells", J. Am. Chem. Soc., Vol. 128(25), pp. 8108-8109, 2006.

[10] M. A. Lampert and P. Mark, "Current Injection in Solids", Academic Press, New York, 1970.

[11] (a) P. Kumar, S. C. Jain, V. Kumar, A. Misra, S. Chand and M. N. Kamalasanan; "Current–voltage characteristics of an organic diode: Revisited", Synth. Met., Vol. 157(22-23), pp. 905-909, 2007. (b) P. Kumar, A. Misra, M. N. Kamalasanan, S. C. Jain and V. Kumar; "Charge transport through conducting organic poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene)", J. Phys. D:Appl. Phys., Vol. 40(2), pp. 561-, 2007. (c) P. Kumar, S. Chand, S. Dwivedi and M. N. Kamalasanan; "Effect of interface layer, curing temperature, and polarization on the hole transport in poly(3-hexylthiophene) thin films", Appl. Phys. Lett., Vol. 90(2), pp. 23501, 2007.

[12] S. C. Jain, M. Willander and V. Kumar; "Conducting Organic Materials and Devices", Academic Press, San Diego, 2007.

[13] P. Schilinsky, C. Waldauf, J. Hauch and C. J. Brabec; "Simulation of light intensity dependent current characteristics of polymer solar cells", J. Appl. Phys., Vol. 95(5), pp. 2816, 2004.

[14] E. A. Katz, D. Faiman, S. M. Tuladhar, J. M. Kroon, M. M. Wienk, T. Fromherz, F.

Padinger, C. J. Brabec and N. S. Sariciftci; “Temperature dependence for the photovoltaic device parameters of polymer-fullerene solar cells under operating conditions”, J. Appl. Phys., Vol. 90(10), pp. 5343-5350, 2001.

[15] Peumans and S. R. Forrest; “Very-high-efficiency double-heterostructure copper phthalocyanine/C_{60} photovoltaic cells” Appl. Phys. Lett., Vol. 79(1), pp. 126-128, 2001.

[16] P. Kumar, S. C. Jain, H. Kumar, S. Chand and V. Kumar; “Effect of illumination intensity and temperature on open circuit voltage in organic solar cells”, Appl. Phys. Lett., Vol. 94(18), pp. 183505-183505.3, 2009.