Investigation of Temperature-Dependent Electrical Properties of Tc-CuPc:PCBM Bulk Heterojunction (BHJ) under Dark Conditions

Shahid M. Khan and Muhammad H. Sayyad

Abstract—An organic bulk heterojunction (BHJ) was fabricated using a blended film containing Copper (II) tetrakis(4-cumylphenoxy)phthalocyanine (Tc-CuPc) along with [6,6]-Phenyl C_{61} butyric acid methyl ester (PCBM). Weight ratio between Tc-CuPc and PCBM was 1:1. The electrical properties of Tc-CuPc:PCBM BHJ were examined. Rectifying nature of the BHJ was displayed by current-voltage (*I-V*) curves, recorded in dark and at various temperatures. At low voltages, conduction was ohmic succeeded by space-charge limiting current (SCLC) conduction at higher voltages in which exponential trap distribution was dominant. Series resistance, shunt resistance, ideality factor, effective barrier height and mobility at room temperature were found to be 526 Ω, 482 kΩ, 3.7, 0.17 eV and 2×10^{-7} $cm^2V^{-1}s^{-1}$ respectively. Temperature effect towards different BHJ parameters was observed under dark condition.

Keywords—bulk heterojunction, PCBM, phthalocyanine, spin coating.

I. INTRODUCTION

IN recent years, organic materials have become progressively important due to their diverse applications. Metallo-phthalocyanines (MPcs) have achieved substantial consideration because they have been incorporated with success in numerous application fields e.g. sensors [1], photovoltaic cells [2]-[4] and organic light-emitting diodes [5]. Thin films of Phthalocyanines are chemically and thermally durable and are prepared by vacuum thermal evaporation [4], [6], [7]. In contrast to relatively expensive technique i.e. vacuum evaporation, wet processing such as spin coating and drop casting have been established as low-cost, low-temperature and swift methods of obtaining organic thin films from solutions.

Low molecular weight semiconductors e.g metallo-phthalocyanines are unsuitable for wet processing because of their limited solubility in some well-known organic solvents. Therefore, their heterojunctions have generally been fabricated with layered [8] structures by vacuum evaporation.

A straightforward, and still an advantageous technique is the solution-processed bulk heterojunction (BHJ). In BHJ i.e. blended device, p and n-type organic semiconductors are co-dissolved in an organic solvent and spin-coated as a single organic blended film. This supports better charge transport. Hence, the main yield of the BHJ over the conventional (two layer) heterojunction is the tremendous increase of the interfacial area between p and n-type moieties throughout the bulk volume of the film. To examine the electrical and charge transport properties of metallo-phthalocyanines, their corresponding soluble derivatives can readily be incorporated in active layers of bulk heterojunctions. Thickness of film, quality of interface and temperature are some factors that influence the fundamental electrical traits of such semiconductors. Electrical behavior of organic semiconductor heterojunctions is greatly influenced by temperature [9]-[11]. Temperature-dependent parameters e.g ideality factor, *n*, leakage current, I_0, shunt resistance, R_{sh}, and series resistance, R_s, greatly influence heterojunction device performance, especially in photovoltaic devices that generally are installed in varying temperature ranges of 10-50°C. Study of electrical properties as function of temperature for these devices is vital to predict their performances at higher temperatures. For organic electronic devices, wide range temperature variation has been justified as an advantageous method for establishing deep concept of charge carrier transport.In this study, we examined the electrical properties of simple BHJ based on a blended film of a soluble phthalocyanine derivative Copper(II) tetrakis (4-cumylphenoxy) phthalocyanine (Tc-CuPc) with C_{60} derivative [6,6]-Phenyl C_{61} butyric acid methyl ester (PCBM) as a single organic active layer. Tc-CuPc is p-type semiconductor [3], and PCBM with high electron affinity was used as an n-type. Fig. 1 shows the molecular structure of both the semiconductors.
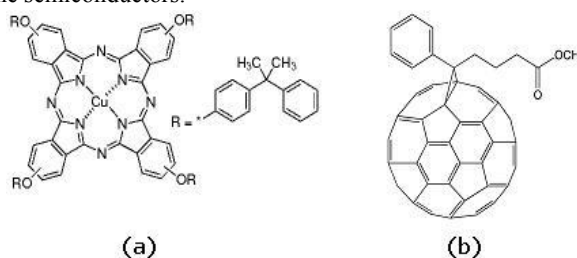

Fig. 1 Molecular structure of (a) Tc-CuPc and (b) PCBM

II. EXPERIMENTAL

The fabrication of BHJ was carried out in the following manner:

A hole extracting layer of Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)(PEDOT:PSS) complex was spin-casted over a pre-cleaned indium-tin-oxide (ITO) slide at 1400 rpm for 78 s and then allowed to dry at

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100 ºC for 10 minutes under ambient pressure. The blended solution was then prepared by dissolving 10 mg each of Tc-CuPc (Sigma Aldrich) and PCBM (Nano C) in 1 ml ortho-dichlorobenzene (o-DCB) solvent. The solution was kept stirring for 12 hours. The overall concentration of the solution was 2 % wt./vol. The Tc-CuPc:PCBM blend was spin-casted over the PEDOT:PSS film at 1200 rpm for 1 minute. The thickness of Tc-CuPC:PCBM layer was 70 nm. Finally, Al electrode of 70 nm thickness was evaporated over the Tc-CuPC:PCBM blended layer through shadow mask in vacuum better than 10^{-6} Torr by vacuum evaporator. The rate of Al deposition was maintained at 15-20 Å/s. The effective area of BHJ was 0.12 cm². Fig. 2. shows the schematic diagram of the fabricated Tc-CuPc:PCBM BHJ. Current-voltage (*I–V*) readings were acquired using Keithley 236 measurement system. Characterization of the fabricated Tc-CuPc:PCBM bulk heterojunction was done on basis of dark *I–V* curves recorded in temperature range of 296-363 K. Temperature gradient was maintained at 3-4 minutes/°C.
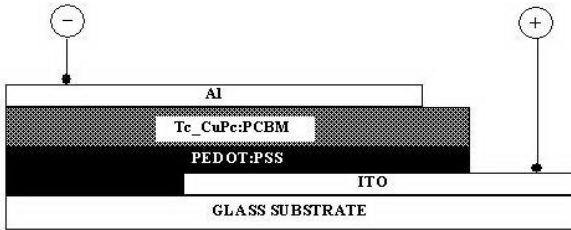

Fig. 2 Schematic diagram of fabricated Tc-CuPc:PCBM BHJ

III. RESULTS AND DISCUSSIONS

In forward and reverse bias, dark current-voltage-temperature (*I-V-T*) curves of the Tc-CuPc:PCBM bulk heterojunction are shown in Fig. 3. Apparently the *I-V* curves are asymmetrical, nonlinear and exhibiting rectifying behavior. At room temperature (23°C), rectification ratio (*RR*) i.e. ratio of current in forward bias to the current in reverse bias, at ±1 V was determined to be 14.7.
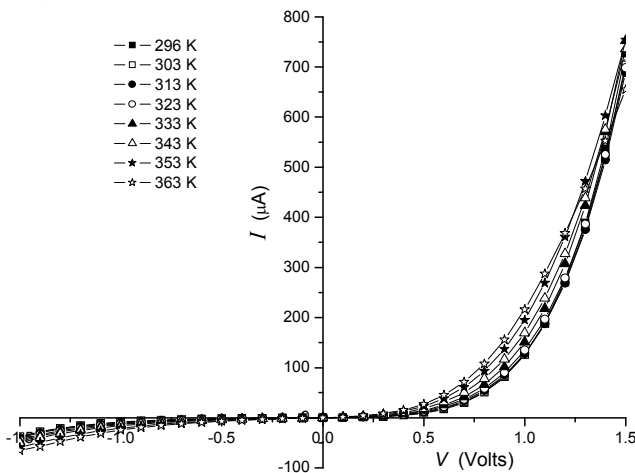

Fig. 3 Dark *I-V-T* curves of the ITO/PEDOT:PSS/Tc-CuPc:PCBM/Al BHJ

Apart from other parameters, shape of *I-V* curves of a heterojunction is also dependent on basic electrical parameters such as series resistance, R_s, and shunt resistance, R_{sh}. Fig. 4 shows differential resistance as a function of voltage at different temperatures in the range of 296-363 K. From room temperature curve of, series resistance (as minimum of curve) and shunt resistance (as maximum of curve) were determine as 526 Ω and 482 kΩ respectively.
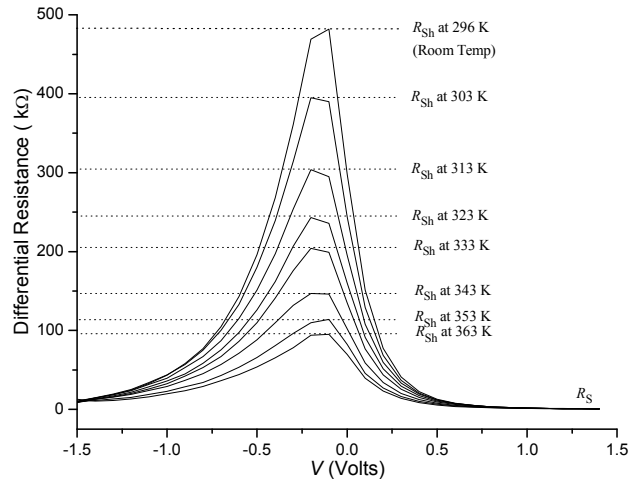

Fig.4 Dependence of differential resistance on voltage and temperature

Exponentially variation of current at small voltages e.g. $V \leq$ 0.1 Volts, is according to Shockley's relation [11], [12]:

$$I = I_0 \left[e^{\left(\frac{qV}{nkT}\right)} - 1 \right] \qquad (1)$$

The above equation leads to the following equation:

$$\ln I = \ln I_0 + \frac{qV}{nkT} \qquad (2)$$

where q is charge of electron, I_0 is reverse saturation current, , k is Boltzmann's constant, n is diode quality factor and T is absolute temperature.

Ideality factor and reverse saturation current found from y-intercept and slope of the room temperature semi-log *I-V* curve of Fig. 5, were 3.7 and 112 nA respectively.
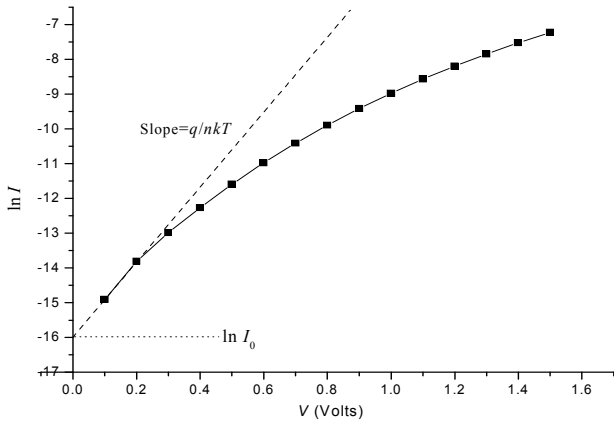
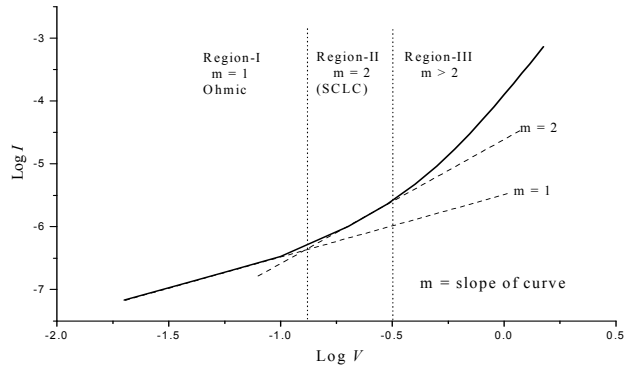Fig. 5 Semi-log of room temperature dark I-V curves.

Linear relation between current and voltage i.e Ohmic conduction attributed to carriers generated thermally, is observed at low voltages e.g. $V < 0.1$ Volts as shown in Fig. 6. Current density, J, for this region the is expressed as [6], [13]:

$$J_{ohmic} = \frac{\sigma V}{d} \qquad (3)$$

where V is the applied voltage, d is thickness of film and σ is the thermal conductivity.

Current dependence on higher voltages e.g. $V > 0.1$ Volts is of the $J \propto V^m$ form and m ≥ 2 (power law), indicating a space-charge limited current (SCLC) conduction. Hole injection by PEDOT:PSS into the highest occupied molecular orbit (HOMO) of Tc-CuPc besides electron injection by Al into the lowest unoccupied molecular orbit (LUMO) of PCBM represents forward bias.

Number of holes generated thermally at low voltages is small and the injected hole density is inadequate that the overall behavior emerges as ohmic. With the rise in voltage, density of injected holes rises, this dominates the blended layer's charge carrier transport capacity, and consequently a space of positive charge aggregates near the anode. Current is limited when applied electric field is dominated by the field due to space charge, this gives rise to space-charge limiting current (SCLC) conduction mechanism. Bulk relaxation time exceeding the transit time of any excess injected carrier gives rise to SCLC [14], in other words if the mobility of bulk layer is not high enough such that rate at which the extra injected are moved to the collecting electrode is not on a par with the rate at which they are being injected [6].

Fig. 6 Double-log of room temperature dark I-V curves.

Current generally varies with voltage according to the following relation:

$$I \propto V^m \qquad (4)$$

Taking log on both sides of (4) results in the following expression :

$$\log I \propto m \log V \qquad (5)$$

It is obvious from (5), that ohmic and SCLC regions can be differentiated on basis of the slope of the double log I-V curve shown in Fig. 6. In region-I, the slope of the curve is approximately unity, which reflects ohmic conduction as a result of charge carriers generated thermally whereas slope of 2 in region-II i.e. power law variation of current with voltage, reflects trap-free space-charge limited current (TFSCLC) conduction [6]. Remember absence of traps in the materials should not be necessarily inferred from a slope of 2. Due to the fact that in organic semiconductors charge carrier mobility is not high enough to sweep extra-injected charges to the receiving electrode at same instant at which they are being injected therefore trap-free space-charge limited current (TFSCLC) flows under such circumstances as given below [6], [14], [15]:

$$J_{TFSCLC} = \frac{9\varepsilon_S \mu V^2}{8d^3} \qquad (6)$$

where d is film thickness of blended layer i.e. 70 nm, μ is mobility and ε_S is the static relative dielectric constant of organic films i.e. the product of free space and average relative dielectric constants. Free space dielectric constant, ε_O, is 8.854×10^{-12} F·m⁻¹, whereas the average relative dielectric constant, ε_R, for Tc-CuPc ($\varepsilon_R \approx 3.6$) [16] and PCBM ($\varepsilon_R \approx 3.9$) [8] is 3.75. Slope above 2 in region-III, indicates traps dominant SCLC conduction mechanism. Organic spin-coated thin films have a common trait that structural and lattice defects along with different impurity centers introduced during film deposition gives rise to charge carrier traps. Child's law governs the variation of current density with square of voltage in this region, expressed as [4], [15], [17]:

$$J = \frac{9\varepsilon_S \theta \mu V^2}{8d^3} \qquad (7)$$

where N_T is trapped charge carrier density, N_0 is free charge carrier density and θ is the trap factor, given by the following expression:

$$\theta = \frac{N_0}{N_0 + N_T} \qquad (8)$$

Mobility, μ, of Tc-CuPc:PCBM blended layer was estimated from Fig. 6 by applying (6) in TFSCLC region. It was approximately 2.02×10^{-7} cm$^2\cdot$V$^{-1}\cdot$s^{-1}.

Plot of reverse saturation current density, J_0, at various temperatures in the range 296-363 K was used to extract barrier-height. The following relation expresses reverse saturation current density as a function of temperature [2], [11], [12]:

$$J_0 = A^* T^2 e^{\frac{-\Phi_B}{kT}} \qquad (9)$$

where Φ_B is the barrier height, A^* is the Richardson constant and prevailing meanings of other symbols

Equation (10) can easily be derived from (9):

$$\ln\left(\frac{J_0}{T^2}\right) = \ln A^* - \frac{\Phi_B}{kT} \qquad (10)$$

Fig. 8. shows effect of variation of temperature on reverse saturation current density. Since in applied voltage range of $V \leq 0.1$ Volts the predominant conduction is by thermionic emission, the behavior is linear indicated by an approximate straight line.
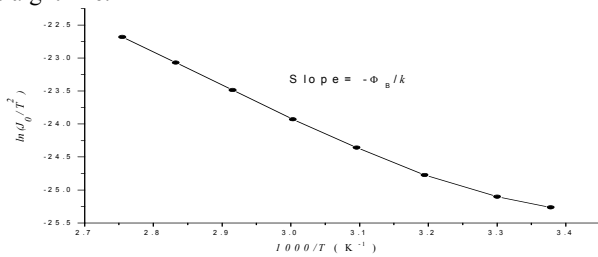

Fig. 8 Reverse saturation current density as a function of temperature

From Fig. 8, slope of the curve was used to determined effective barrier height , Φ_B, of the heterojunction as 0.17 eV at room temperature. With rising temperature, decrease in shunt resistance and increase in series resistances were observed. This change in both the resistances is not linear. With increase in temperature from 296 to 363 K, ideality factor, n, and rectification ratio, RR, show decreasing trends from 3.7 to 3.16 and 14.7 to 8.8 respectively. Decrease of ideality factor may be a result of the charge carrier recombination. However with increase in temperature, effective mobility, μ, and barrier height, Φ_B, exhibit increasing trend from 2.02×10^{-7} to 7.5×10^{-7} cm$^2\cdot$V$^{-1}\cdot$s^{-1} and 0.17 to 0.43 eV respectively. Variation of different heterojunction parameters with temperature is shown in Figs. 9-11.
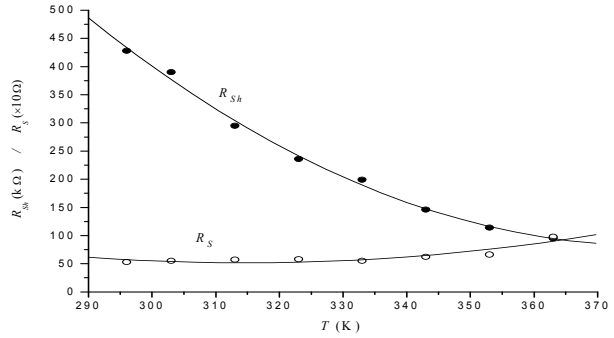

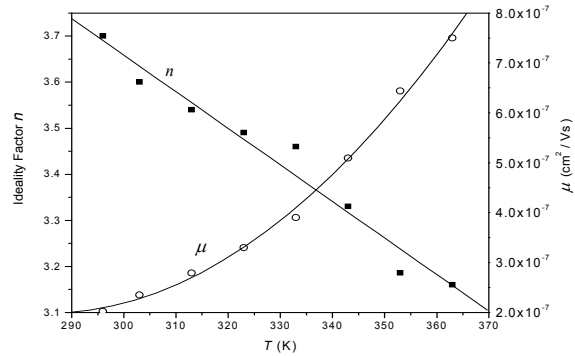Fig. 9 Temperature dependence of BHJ resistances

Fig. 10 Temperature dependence of ideality factor and mobility of BHJ
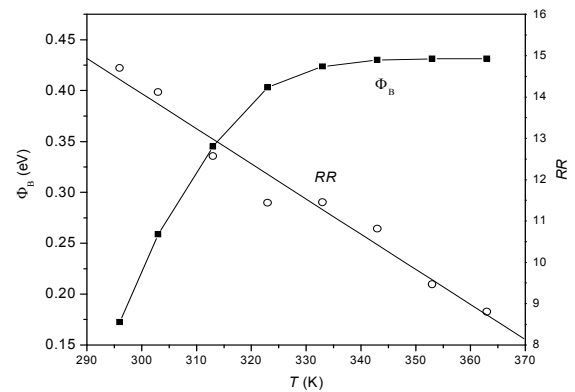

Fig. 11 Effective barrier height and rectification ratio variation with temperature

IV. CONCLUSION

Change in temperature resulted in variation of fundamental electrical properties of ITO/PEDOT:PSS/Tc-CuPc:PCBM /Al bulk heterojunction. Low resistivity of blended film was reflected by subtle series resistance. Existence of structural and lattice defects along with impurity centers were revealed by space-charge limiting current (SCLC) at higher voltages that might have been accommodated during spin coating of blended layer. Tc-CuPc:PCBM blended layer showed a mobility of 2.02×10^{-7} cm$^2\cdot$V$^{-1}\cdot$s^{-1}. The effective barrier height, Φ_B, of the BHJ was found to be 0.17 eV. Variation of different cell parameters with temperature was determined in temperatures range from 296 to 363 K.

REFERENCES

[1] K. S. Karimov, K. M. Akhmedov, A. A. Dzhuraev, M. N. Khan, S. M. Abrarov and M. I. Fiodorov, "Organic-on-inorganic Ag/n-GaAs/p-CuPc/Ag photoelectric sensor", Eurasian Chem. Technol. J. vol. 2, no. 3-4, pp. 251-256, 2000.

[2] A. Aruchamy, G. Aravamudan and G. V. S. Rao, "Semiconductor based photoelectrochemical cells for solar energy conversion—An overview ", Bull. Mater. Sci. vol. 4, no. 5, pp. 483-526, December 1982.

[3] R. Motoyoshi, A. Suzuki, K. Kikuchi and T. Oku, "Formation and characterization of copper tetrakis (4-cumylphenoxy) phthalocyanine:perylene solar cells", Synth. Met. vol. 159, no. 13, pp. 1345-1348, July 2009.

[4] M. M. El-Nahass, A. A. Atta, H. E. A. El-Sayed and E. F. M. El-Zaidia, "Electrical transport mechanisms and photovoltaic characterisation of MgPc/p-Silicon hybrid organic–inorganic solar cells", Curr. Org. Chem. vol. 14, no. 1, pp. 84-88, January 2010.

[5] P. C. Kao, S. Y. Chu, S. J. Liu, Z. X. You and C. A. Chuang, "Improved performance of organic light-emitting diodes using a metal-phthalocyanine hole-injection layer", J. Electrochem. Soc. vol. 153, no. 6, pp. H122-126, April 2006.

[6] M. S. Roy, P. Balraju, Y. S. Deol, R. K. Mishra, V. S. Choudhary and G. D. Sharma, "Charge transportation and photo generation process in polythiophene functionalized with tin (II) phthalocyanine (SnPc-PT) thin film", Sol. Energy Mater. Sol. Cells vol. 92, no. 11, pp. 1516-1525, November 2008.

[7] M. M. El-Nahass, K. F. Abd-El-Rahman and A. A. A. Darwish, "Fabrication and electrical characterization of p-NiPc/n-Si heterojunction", Microelectron. J. vol. 38, no. 1, pp. 91–95, January 2007.

[8] G. J. Matt, N. S. Sariciftci and T. Fromherz, "Anomalous charge transport behavior of fullerene based diodes", Appl. Phys. Lett. vol. 84, no. 9, pp. 1570-1572, March 2004.

[9] S. Darwish, A. S. Riad and H. S. Soliman, "Electrical conductivity and the effect of temperature on photoconduction of n-ZnSe/p-Si rectifying heterojunction cells", Semicond. Sci. Technol. vol. 11, no. 1, pp. 96-102, January 1996.

[10] A. Hussain, P. Akhter, A. S. Bhatti, A. A. Shah and S. Bilal, "Dominant conduction mechanism and the effects of device temperature on electrical characteristics of Al/ZnPc/n-Si structures", Vacuum vol. 84, no. 7, pp. 975-979, March 2010.

[11] A. A. M. Farag, E. A. A. El-Shazly, M. A. Rafea and A. Ibrahim, "Optical, electrical and photovoltaic characteristics of organic semiconductor based on oxazine/n-Si heterojunction", Sol. Energy Mater. Sol. Cells vol. 93, no. 10, pp. 1853-1859, October 2009.

[12] S. M. Sze, *Physics of semiconductor devices.* 2nd ed, New York: John Wiley and Sons, 1981, pp. 126,258-262.

[13] N. Amar, R. D. Gould and A. M. Saleh, "Structural and electrical properties of the α-form of metal-free phthalocyanine (α-H2Pc) thin films", Curr. Appl. Phys. vol. 2, no. 6, pp. 455-460, December 2002.

[14] M. Abkowitz, J. S. Facci and J. Rehm, "Direct evaluation of contact injection efficiency into small molecule based transport layers: Influence of extrinsic factors", J. Appl. Phys. vol. 83, no. 5, pp. 2670-2676, March 1998.

[15] K. C. Kao and W. Hwang, "Electrical transport in solids, with particular reference to organic semiconductors," in *International series in the science of the solid state*, 1st ed, vol. 14, Oxford: Pergamon Press, 1981, pp. 418-422.

[16] T. Basova, A. G. Gürek, V. Ahsen and A. K. Ray, "Electrical properties of dysprosium phthalocyanine films", Org. Electron. vol. 8, no. 6, pp. 784-790, December 2007.

[17] A. S. Riad, "Influence of dioxygen and annealing process on the transport properties of Nickel phthalocyanine Schottky-barrier devices", Physica B, vol. 270, no. 1-2, pp. 148-156, October 1999.