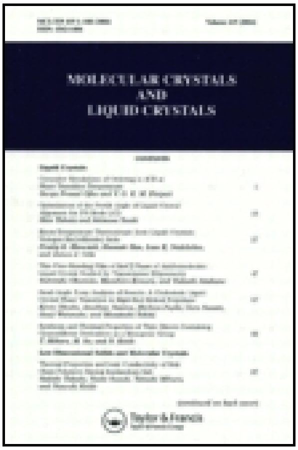

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Relationship Between Purity of CuPc and Properties of Organic Thin Photovoltaic Cells

Kohei Kato [a] & Tatsuo Mori [a]

[a] Department of Electrical Engineering and Computer Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Japan

To cite this article: Kohei Kato & Tatsuo Mori (2007): Relationship Between Purity of CuPc and Properties of Organic Thin Photovoltaic Cells, Molecular Crystals and Liquid Crystals, 471:1, 53-60

To link to this article: http://dx.doi.org/10.1080/15421400701545262

Mol. Cryst. Liq. Cryst., Vol. 471, pp. 53–60, 2007
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701545262

Taylor & Francis
Taylor & Francis Group

Relationship Between Purity of CuPc and Properties of Organic Thin Photovoltaic Cells

Kohei Kato
Tatsuo Mori
Department of Electrical Engineering and Computer Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Japan

Properties of organic thin photovoltaic cells using copper phthalocyanine (CuPc) with different purities are studied. When we change purity of CuPc, only open-circuit voltage (V_{OC}) increases as CuPc material purity increases while short-circuit current show a same value. Decrease in V_{OC} of cell using low-purity CuPc is maybe caused by impurities that are taken in CuPc layer. We show the model to explain this phenomenon and examine propriety of it.

Keywords: CuPc; organic photovoltaic cell; purity

1. INTRODUCTION

Although organic thin photovoltaic (PV) cells have been investigated for last three decades, the conversion efficiency had stayed in a low value for a long time [1]. But since Tang reported ca. 1% of conversion efficiency in single heterojunction cell that consist of donor-like and acceptor-like organic small molecules in 1986, organic PV cells have attracted attention [2]. The bulk heterojunction cell proposed by Hiramoto *et al.* improved the conversion efficiency rapidly [3]. Also in donor- acceptor heterojunction, the cell using the acceptor material C_{60} with long exciton diffusion length achieved high conversion efficienty of 3.6% [4]. In addition, very high efficiency of >5% is reported for tandem cell stacked two cells in series with Ag nanoclusters [5]. On the other hand, the high molecular PV cell has been paid attention due

---

The authors thank for a part of financial support of the Hibi Science Foundation.

Address correspondence to Tatsuo Mori, Department of Electrical Engineering and Computer Science, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan. E-mail: tmori@nuee.nagoya-u.ac.jp

to its advantage of no necessity of high vacuum for producing cell. Kim *et al*. reported conversion efficiency of ca. 5% by using conductive polymer P3HT and soluble fullerene derivative PCBM [6,7].

Purities of organic materials are important for achieving high efficiency in organic devices. But there are few reports about relationship between purity of source material and PV properties [8]. So we studied the purity dependence of PV properties. We paid attention to copper phthalocyanine (CuPc) that used widely in organic thin PV cells.

2. EXPERIMENTAL

We used CuPc as an electron donor and C_{60} as an electron acceptor and 3, 4, 9, 10-Perylenetetracarb$^-$ oxylicdianhydride (PTCDA) as an exciton-blocking layer. The cell structure is ITO/CuPc/C_{60}/PTCDA/metal cathode. We prepare purified and non-purified CuPc. Purified CuPc (purity $>$99.9%) is provided from Nippon Steel Chemical Co., Ltd. Non-purified CuPc (purity $>$90%) is purchased from Tokyo Chemical Industry Co., Ltd. We use a specific ITO substrate for organic light emitting diodes from Giomatic Co. as transparent anode. All organic layers are deposited by vacuum evaporation method at room temperature under ca. 3×10^{-4}Pa. Deposition rates are 0.15–0.20 nm/s. Metal cathodes are deposited at $3\text{–}6 \times 10^{-4}$ Pa. The area of sandwich cell is $2 \times 2\,\mathrm{mm}^2$. There is exposure of atmosphere between the organic layer deposition and the metal cathode deposition.

The PV properties are measured under AM1.5, $100\,\mathrm{mW/cm}^2$ using solar simulator (XIL-03E, SERIC) in vacuum after an exposure of atmosphere. We measure current–voltage characteristics using a source measurement unit (Keithley 2400; Keithley Instruments, Inc.). We measure absorption spectra using a spectrophotometer (U-3000; Hitachi Ltd.).

3. RESULTS AND DISCUSSION

Figure 1 shows the current density–voltage (J–V) characteristics of ITO/CuPc 10 nm/C_{60} 20 nm/PTCDA 20 nm/Al cells using purified or non-purified CuPc. Table 1 shows short-circuit current density (J_{SC}), open-circuit voltage (V_{OC}), fill factor (FF) and energy conversion efficiency (η) of both PV cells. B. P. Rand have already reported the effect of CuPc's purity on PV cell performance [8]. In this article, J_{SC}, V_{OC} and FF decreased with the decrease in purity of CuPc. But the authors could not observe the remarkable difference on CuPc's

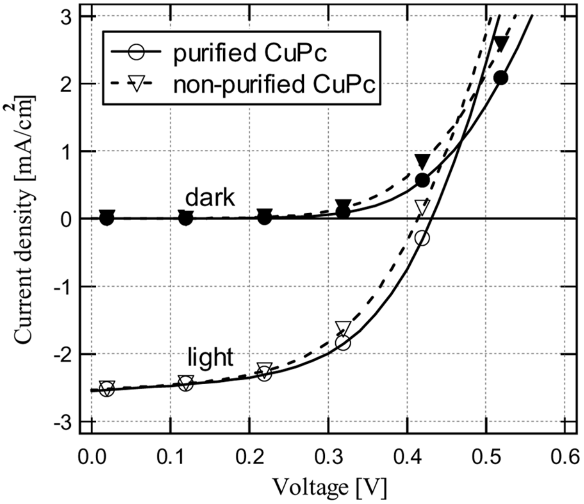

FIGURE 1 The J–V characteristics of ITO/CuPc (10 nm)/C_{60} (20 nm)/PTCDA (20 nm)/Al cells using purified or non-purified CuPc.

purity. The V_{OC} of 0.43 ± 0.002 V for the cell using purified CuPc is higher than that of 0.41 ± 0.002 V for the non-purified CuPc cell. Both J_{SC} show a same value of 2.4 0.1 mA/cm^2. It suggests that impurities including in our non-purified CuPc do not affect generation and diffusion processes of exciton exited in CuPc layer.

Figure 2 shows V_{OC}–workfunction of cathode metal characteristics. Figure 3 shows the energy diagram of organic layers with workfunction of four different cathode metals. V_{OC} decreases with decreasing workfunction of cathode metal. The origin of V_{OC} for organic thin PV cells may be due to difference of workfunctions between ITO and cathode metal. Although the authors will discuss the origin of V_{OC} using two-layer cell, this concept applied to two-layer cell can be also applied to three-layer cell. It is thought that the increase in difference of workfunctions cause the increase in built-in potential (V_{bi}) of cell. Figure 4(a) shows the energy diagram before ITO leads cathode metal. In short-circuit state of both electrodes (Fig. 4(b)), the internal electric

TABLE 1 Summary of PV Properties

CuPc	J_{SC}[mA/cm^2]	V_{OC}[V]	FF	η[%]
Pure	2.4	0.43	0.56	0.57
Non-pure	2.4	0.41	0.55	0.53

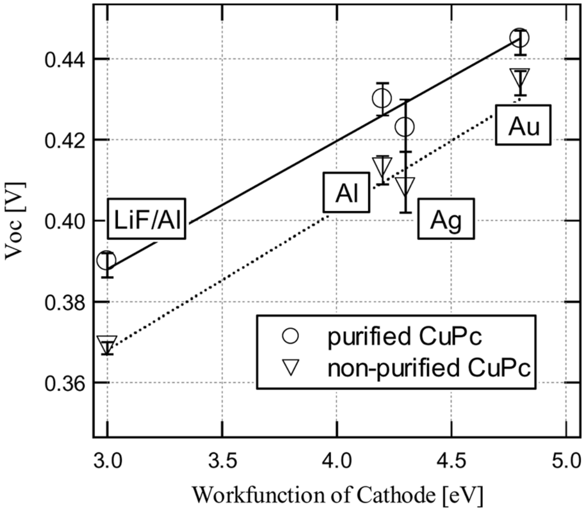

FIGURE 2 V_{OC} – workfunction of cathode metal plot in ITO/CuPc (10 nm)/C_{60} (20 nm)/PTCDA (20 nm)/cathode metal cells using purified or non-purified CuPc.

field, E_{int}, occurs in the cell on the based on V_{bi}. When positive voltage V_+ is applied to make ITO positive with respect to the cathode metal (Fig. 4(c)), the external electric field, E_{ext}, that is in the opposite direction to the E_{int} is applied to the cell. Then the electric field in the cell, that is the sum of E_{int} and E_{ext}, is diminished because E_{int} is cancelled by E_{ext}. When applied voltage reaches to V_{OC}, the photogenerated carriers cannot be collected to electrodes. If the cell has higher E_{int}, photogenerated carriers are thought to be collected to

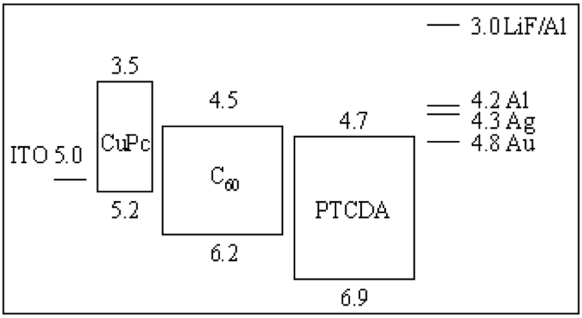

FIGURE 3 Energy diagram of devices with the workfunctions of cathode metals.

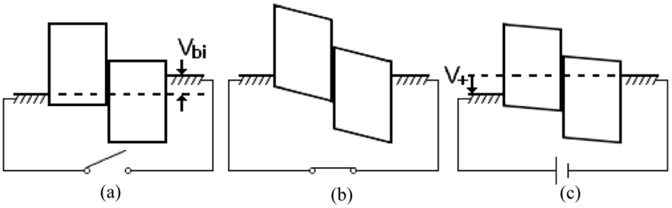

FIGURE 4 The energy diagram of two-layer cell for (a) open-circuit state (b) short-circuit state (c) positive external voltage is applied.

electrodes till higher external positive voltages. So higher V_{bi} is expected to increase V_{OC} due to its higher E_{int}. But the V_{OC} of our PV cells decreases with increasing the difference of workfunctions as shown in Figure 2. So the increase in V_{OC} cannot be explained by the increase in difference of workfunctions.

It is reported that the maximum V_{OC} of cell is determined by the difference between HOMO of the donor and LUMO of the acceptor [9,10]. According to these reports, if the voltage losses in carrier conduction process are minimized, the value of V_{OC} is reported to correspond to the difference between HOMO of donor and LUMO of acceptor. In the cell that the authors fabricated, the difference between HOMO of CuPc, 5.2eV, and LUMO of C_{60}, 4.5 eV, is 0.7 eV. But our V_{OC} are smaller than 0.7 V. Since the voltage losses of the cell using Au will be smaller than that of other cells using Ag, Al and LiF/Al, the largest V_{OC} is obtained when Au is used. However, it seems that the authors cannot explain about the origin of V_{OC} clearly.

Dark current of non-purified CuPc cell is higher than that of purified CuPc cell at a constant voltage. However, there is no difference between both single CuPc layers as shown in Figure 5. The increase in dark current of PV cell is not caused by CuPc layer. Generation of excitons due to light irradiation occurs in CuPc and C_{60} layer. The CuPc's excitons in CuPc are diffused toward CuPc/C_{60} interface. They are dissociated at the interface. This photo-generated current (I_{pg}) will be compensated by reverse dark current (I_d). The current flowing in external circuit (I) will be represented by $I = I_{pg}–I_d$. Figure 6 shows $I–I_d$ calculated from J–V characteristics of Figure 1. These two curves are almost same. The decrease in V_{OC} is suggested to be affected by the increase in J_d.

To investigate the CuPc/C_{60} interface, the 20 nm-thic CuPc layer divided in half (two 10 nm layers named ITO side and C_{60} side). The authors fablicate three cells, the first cell contain purified CuPc in both layers (pure/pure), the second cell contain non-purified CuPc

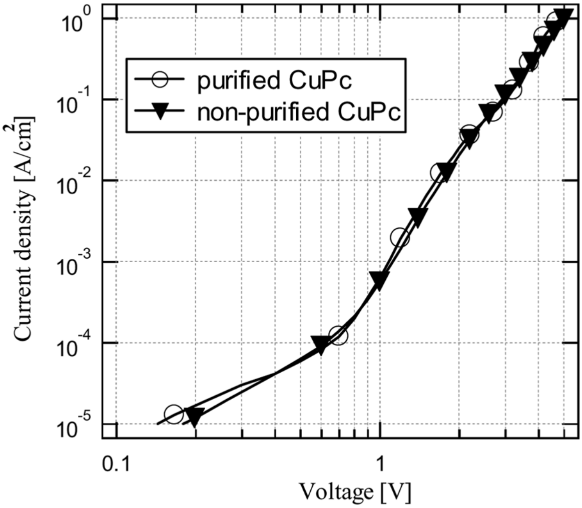

FIGURE 5 The J–V characteristics of ITO/CuPc (50 nm)/Au cells using purified or non-purified CuPc.

for ITO side and purified CuPc for C_{60} side (non/pure), and the third cell contain purified CuPc for ITO side and non-purified CuPc for C_{60} side (pure/non). Figure 7 shows J_d–V characteristics of cells with cell

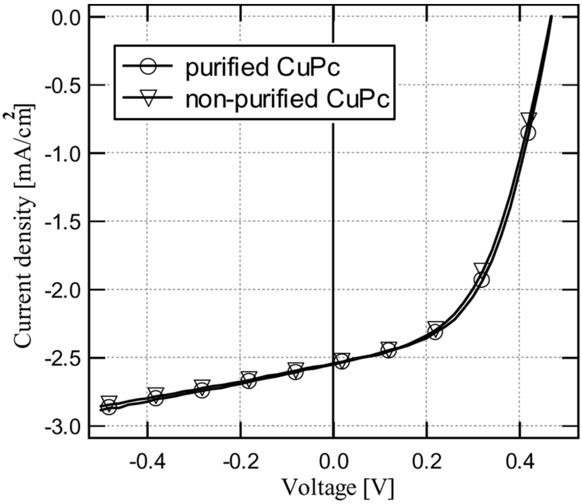

FIGURE 6 The J_{pg}–V characteristics of ITO/CuPc (10 nm)/C_{60} (20 nm)/ PTCDA (20 nm)/Al cells using purified or non-purified CuPc.

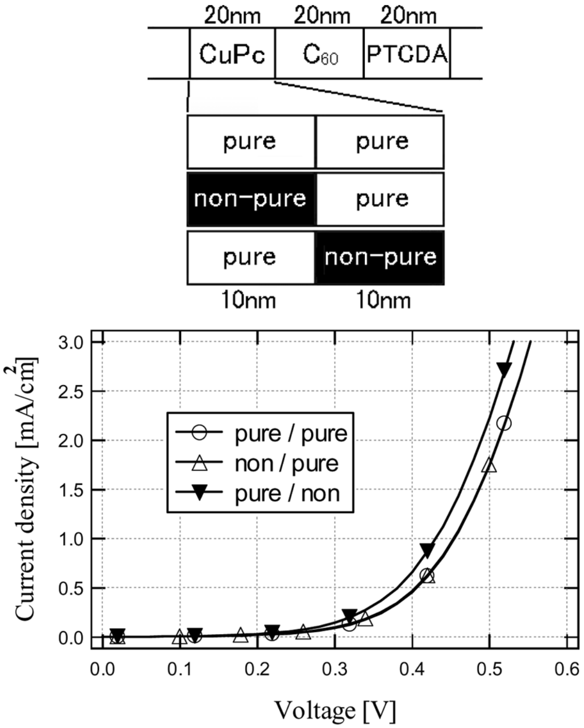

FIGURE 7 The J_d–V characteristics of ITO/CuPc (20 nm)/C_{60} (20 nm)/ PTCDA (20 nm)/Al cells using purified or non-purified CuPc. The cell structure is illustrated above.

structures. The non/pure cell shows similar characteristic to pure/ pure cell. But the dark current in the pure/non cell is higher than two other cells. The photocurrent shows same behavior. It is found that a dark current increases and Voc of photocurrent deceases when non-purified CuPc layer contacts on C_{60}. In the dark current flow of PV cell, holes and electrons are injected into organic layers from ITO and cathode metal, respectively. But the barrier height of electron injection from the LUMO of C_{60} to the LUMO of CuPc is estimated to be ca. 0.7 eV. In addition, the barrier heights of hole injection from the HOMO of CuPc to the HOMO of C_{60} and from the HOMO of C_{60} to the HOMO of PTCDA are estimated to be ca. 1eV and 0.7eV, respectively. Since the thermal energy around room temperature is regarded as 0.026 eV, these barrier heights are much higher than this thermal energy. Therefore, it is difficult to form the conduction pass of carriers in multilayer. However, the dark currents of PV cells are not small.

The conduction pass of dark current in multilayer is thought to be caused by the recombination with holes, injected from ITO to CuPc, and electrons, injected from cathode metal through the C_{60}/PTCDA interface, at the CuPc/C_{60} interface. And the impurities in non-purified CuPc are thought to enhance the recombination process. That is, they act as a recombination center. Unfortunately, the authors cannot have identified the impurities.

4. CONCLUSIONS

The authors studied the CuPc's purity dependence on the conduction property of organic PV cell. Although V_{OC} of non-purified CuPc cell is a little lower than that of purified CuPc cell, the J_{SC} of photocurrent little depended on CuPc's purity. It suggests that some impurities including in our non-purified CuPc do not affect generation and diffusion of exciton. The decrease in V_{OC} could be related to the increase in J_d at the non-purified CuPc cell. It could be caused by impurities at CuPc/C_{60} interface using partially deposition method. The authors suggested that the impurities at the CuPc/C_{60} interface enhance the carrier recombination of hole in CuPc and electron in C_{60}.

REFERENCES

[1] Ghosh, Amal K. & Feng, Tom. (1973). *J. Appl. Phys.*, *44*, 2781.
[2] Tang, C. W. (1986). *Appl. Phys. Lett.*, *48*, 183.
[3] Hiramoto, M., Fujiwara, H., & Yokoyama, M. (1986). *Appl. Phys. Lett.*, *58*, 1062.
[4] Peumans, P. & Forrest, S. R. (2001). *Appl. Phys. Lett.*, *79*, 126.
[5] Xue, J., Uchida, S., Rand, B. P., & Forrest, S. R. (2004). *Appl. Phys. Lett.*, *85*, 5757.
[6] Ma, W., Yang, C., Gong, X., Lee, K., & Heeger, A. J. (2005). *Adv. Funct. Mater.*, *15*, 1617.
[7] Kim, J. Y., Kim, S. H., Lee, H. H., Lee, K., Ma, W., Gong, X., & Heeger, A. J. (2006). *Adv. Mater.*, *18*, 572.
[8] Salzman, R. F., Xue, J., Rand, B. P., Alexander, A., Thompson, M. E., & Forrest, S. R. (2005). *Org. Elec.*, *6*, 242.
[9] Dyakonov, V. (2002). *Physica E*, *14*, 53.
[10] Taima, T., Sakai, J., Yamanari, T., & Saito, K. (2006). *Jpn. J. Appl. Phys.*, *45*, 995.