Organic photovoltaic cells with copper (II) tetra-methyl substituted phthalocyanine*

Xu Zong-Xiang(许宗祥)[a)†] and Roy V. A. L.[b)]

[a)] Department of Chemistry, South University of Science and Technology of China, Shenzhen 518055, China

[b)] Center of Super Diamond and Advanced Films (COSDAF), Department of Physics and Materials Science, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong SAR, China

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Efficient heterojunction organic photovoltaic (OPV) cells are fabricated based on copper tetra-methyl phthalocyanine (CuMePc) as donor and fullerene (C_{60}) as acceptor. The power conversion efficiency of CuMePc/C_{60} OPV cell (2.52%) is increased by 88% compared with that of the non-peripheral substituted copper phthalocyanine (CuPc)/C_{60} OPV cell (1.34%). The introduction of methyl substituent leads to stronger π–π interaction of CuMePc ($\sim$ 3.5 Å) than that of CuPc ($\sim$ 3.8 Å). The efficiency improvement is attributed to the enhanced carrier mobility of CuMePc thin film (1.1×10^{-3} cm^2/V·s) and better film morphology by introducing methyl groups into the periphery of CuPc molecule.

Keywords: organic photovoltaic cell, copper (II) tetra-methyl substituted phthalocyanine, π–π stacking, GIXRD

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1. Introduction

Heterojunction organic photovoltaic (OPV) cells are receiving a surge of interest in the context of developing low-cost, renewable energy sources.[1–5] There are four consecutive steps to accomplish the process of converting light into electric current in heterojunction OPV cells: (i) photon absorption leading to the generation of an exciton, (ii) diffusion of the exciton into a donor-acceptor (DA) interface, (iii) exciton dissociation by charge transfer at the DA interface, and (iv) collection of free charge carriers at the electrodes. In engineering science, many approaches have been discussed to improve these four steps, such as tandem[6] and doping technology,[7–9] and the power conversion efficiency (η_P) has been reported to reach as high as 9.2%.[10] However, in order to further enhance the η_P of heterojunction OPV cells, it is of paramount importance to develop robust organic semiconductors exhibiting broad solar spectral coverage in order to enhance the generation of excitons as well as better charge carrier transport properties.[2,4]

Metallophthalocyanines are robust materials that could be obtained in large quantity and high purity by evaporation. Metal free phthalocyanine (HPc) and copper phthalocyanine (CuPc) display remarkable semiconducting properties that have been used for photovoltaic cells and thin film transistors.[11–15] Reports on improving the semiconducting properties of metallophthalocyanines by varying the metal ion have been reported,[11,12,14] and efficient OPV cells based on chloroaluminum phthalocyanine with photon absorption extending up to near infrared region[14] and boron subphthalocyanine chloride cells possessing high open-circuit voltage (V_{OC}) have been demonstrated.[13,16] However the reported modifications on phthalocyanine ligands are mainly restricted to introducing carboxylic acid,[17] ester,[18] alkoxy,[19] or thioalkyl[20] groups into peripheral side chains, and these modifications are used to improve the performance of dye sensitized solar cells. Few studies on the enhanced performance of OPV cells by modification of

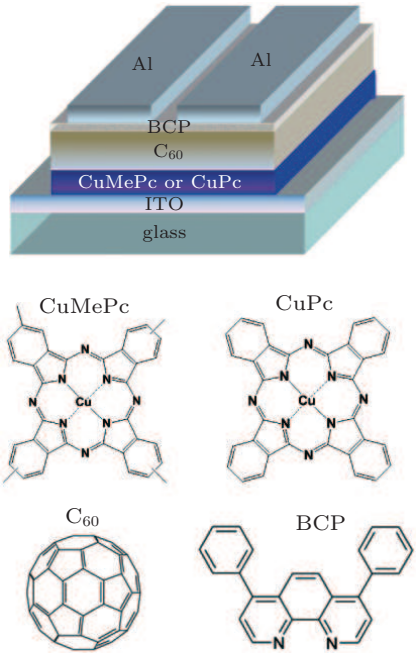


Fig. 1. (color online) Solar cell device configuration and chemical structures.

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†Corresponding author. E-mail: xu.zx@sustc.edu.cn

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phthalocyanine ligand have been reported.[21] Recently, we have incorporated copper tetra-methyl phthalocyanine (CuMePc) nanocrystals into P3HT/PCBM bulk heterojunction, and solar cells made from such ternary composites exhibited a power conversion efficiency up to 5.3%.[22]

In this work, copper tetra-methyl phthalocyanine (CuMePc) is prepared and used for bilayer OPV cells (Fig. 1). The η_P of CuMePc/fullerene (C_{60}) OPV cell (2.52%) is increased by 88% compared with that of standard CuPc/C_{60} OPV cell (1.34%). The enhancement in the efficiency is attributed to the high carrier mobility of CuMePc thin film.

2. Experimental details

CuPc was purchased from Aldrich. CuMePc was synthesized and characterized according to the reported procedure by using 4-methylphthalonitrile and copper (II) acetate. Both CuPc and CuMePc are dark blue solids and were purified by vacuum sublimation before use. The configuration of OPV cells was ITO/CuPc, or CuMePc (20 nm)/C_{60} (40 nm)/BCP (10 nm)/Al (100 nm) where indium-tin oxide (ITO) coated glass was the transparent anode and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) was the hole-blocking material (Fig. 1). All OPV cells were prepared on ITO coated glass.[23] The layer-by-layer thin film deposition was accomplished by thermal evaporation of the organic material under a vacuum of 4.0×10^{-4} Pa. Current density–voltage (J–V) characteristics of the fabricated OPV devices were measured in the dark as well as under AM 1.5 solar illumination at an intensity of 100 mW/cm^2.[22] Absorption spectra of CuPc and CuMePc thin films (50 nm) on ITO glass substrate were measured with a Perkin–Elmer Lambda 19 UV/VIS spectrophotometer. The carrier mobility values of the organic thin films, ITO/ CuPc (500 nm) or CuMePc (500 nm)/Al (100 nm), were measured by time-of-flight technique.[24,25] Incident photo-to-current collection efficiency (IPCE) was measured using a 250-W xenon lamp (Thermo Oriel Model 66901) with a monochromator (Corner Stone 74000) as a light source. The device was operated in the short-circuit mode. Keithley 2400 unit was used to catch the current characteristic. The power of the input monochromatic light was calibrated by NewPort Power Meter (Model 1930c). Ultraviolet photoemission spectroscopic (UPS) measurements of CuPc and CuMePc thin films deposited on p-type Si were performed using a VG ESCALAB 220i-XL UHV photoelectron spectroscopy system consisting of an analysis chamber interconnected to a preparation chamber.[26,27] The morphology of both of the CuPc and CuMePc layers (50 nm) deposited on ITO glass were inspected by an LEO1530 scanning electron microscopy (SEM) instrument. Grazing incidence X-ray diffraction (GIXRD) patterns of CuPc and CuMePc films (50 nm) formed on SiO_2/Si substrate were recorded using a Bruker D8 Advance (θ/θ) diffractometer with a Göbel mirror attachment.[23]

3. Results and discussion

Photovoltaic responses of CuPc-based and CuMePc-based OPV cells are depicted in Fig. 2. Under illumination, the standard CuPc-based OPV cell exhibits a short-circuit current density (J_{SC}) of 6.05 mA/cm^2, open circuit voltage (V_{OC}) of 0.47 V, fill factor (FF) of 0.47, and η_P of 1.34%. For CuMePc-based OPV cell, the J_{SC}, V_{OC}, FF, and η_P are found to be 11.4 mA/cm^2, 0.43 V, 0.52, and 2.52 %, respectively. The η_P of CuMePc-based OPV cell is increased by a factor of 88% compared with that of the standard CuPc-based OPV cell.

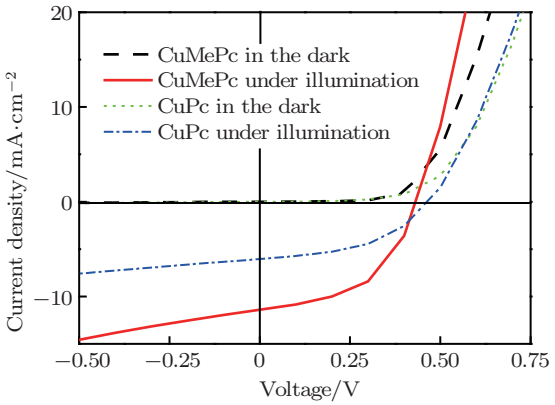


Fig. 2. (color online) Current density–voltage (J–V) characteristics of CuPc-based and CuMePc-based OPV cells.

From the device performance, it is understood that V_{OC} of CuMePc devices has not been improved in comparison with that of standard CuPc devices, because the V_{OC} of bulk heterojunction is strongly influenced by the energy level of the highest occupied molecular orbital (HOMO) of the donor.[13,14] It is expected that the HOMO values of CuPc would not be significantly affected by adding 4 methyl substituents to the phtahlocyanine core. This has been further confirmed by performing ultraviolet photoemission spectroscopy measurements. The HOMO level of CuPc is found to be reduced by a tenth of an electron volt (the HOMO level of CuPc and CuMePc are found to be 4.87 eV to 4.79 eV, respectively), which accords well with that of oligothiophene by modification.[28] For oligothiophenes, from 2TH (unmethylated dimer) to dimethyl (2TH44), the HOMO levels decrease from 7.95 eV to 7.60 eV. Clearly the effect of methylation is greater on such a small thiophene dimer than on the "giant" (CuPc). The slight change in HOMO level of CuPc tends to have a modest difference in absorbance compared with that of its alkylated counterpart. Compared with CuPc, the CuMePc exhibits a similar photon absorption ranging from 500 nm to 800 nm (Fig. 3), except for the second peak at 695 nm which

is found to be slightly prominent. In addition, we measure the IPCE spectra of solar cells fabricated from CuPc or CuMePc as donors. As exhibited in Fig. 3, each cell shows the spectral response that matches the absorption spectrum of the corresponding CuPc or CuMePc thin film.

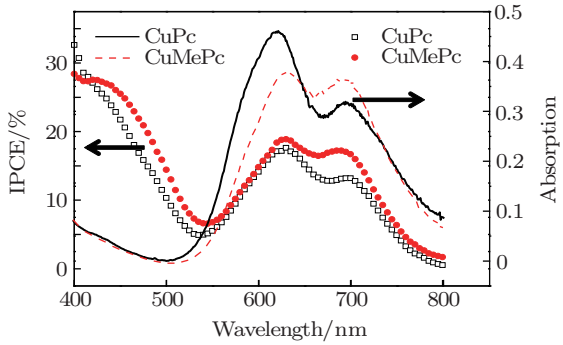


Fig. 3. (color online) Absorption spectra for the film samples of CuPc and CuMePc fabricated by vacuum deposition (film thickness = $\sim$ 50 nm) and IPCE spectra of solar cells fabricated with CuPc and CuMePc.

To investigate the enhancement in $\eta_{\rm P}$, the charge carrier mobility values of CuPc and CuMePc films ($\sim$ 500 nm) are measured by time-of-flight technique.[24,25] The hole carrier mobility of CuMePc layer (1.1×10^{-3} cm^2/V·s at 1.0×10^5 V/cm) is found to be much higher than that of CuPc layer (4.0×10^{-4} cm^2/V·s at 1.0×10^5 V/cm). The high charge carrier mobility of CuMePc is attributed to stronger intermolecular π–π stacking interactions, which are $\sim$ 3.5 Å and $\sim$ 3.8 Å for CuMePc and CuPc, respectively.[22] As expected, the high charge carrier mobility of the CuMePc device has higher $J_{\rm SC}$ than that of the standard CuPc device.[4]

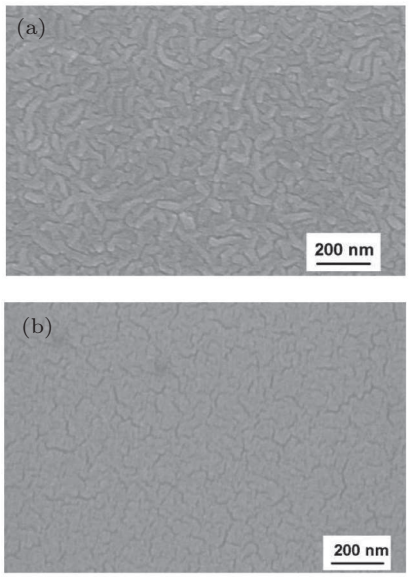


Fig. 4. SEM images of thin film samples made from (a) CuPc and (b) CuMePc.

Charge transports in metallophthalocyanines and other polycrystalline organic semiconductors have been proven to undergo a hopping mechanism at room temperature.[29] Hence, the morphology of film plays an important role in charge transport due to the grain boundary effect. Figures 4(a) and 4(b) show the SEM images of the vacuum deposited films of CuPc and CuMePc respectively. The thin film of CuPc contains big (about 100 nm long) crystal grains (see Fig. 4(a)). However, the thin film of CuMePc shows a continuous and smooth morphology with lesser grains than those in CuPc (see Fig. 4(b)). A smooth morphology is advantageous for thin film solar cells, for the increase of crystal size and surface roughness of thin film could induce pinholes or short circuit between cathode and anode contacts.[30]

The crystallinity of the film is examined by the grazing incidence X-ray diffraction (GIXRD). As shown in Fig. 5, CuPc film exhibits a sharp peak at $2\theta = 6.9°$, indicating that CuPc film is highly crystalline possessing a prominent molecular orientation with a d-spacing of 1.285 Å. CuMePc film exhibits an intensive peak ($2\theta = 6.3°$) indicating that CuMePc film possesses a similar crystallinity and molecules are oriented with d-spacing of 1.42 Å, which is consistent with its molecular length. The obtained interplanar distance matches well with the estimated length of the respective CuPc or CuMePc molecule, revealing that CuPc or CuMePc molecules are oriented to the direction nearly perpendicular to the SiO_2/Si substrate. Therefore, the stronger π–π stacking results in higher charge mobility and leads to better photovoltaic performance. Considering all this experimental evidence, it is found that the enhancement in the efficiency is attributed to the higher carrier mobility of CuMePc rather than the enhancement of photon absorption.

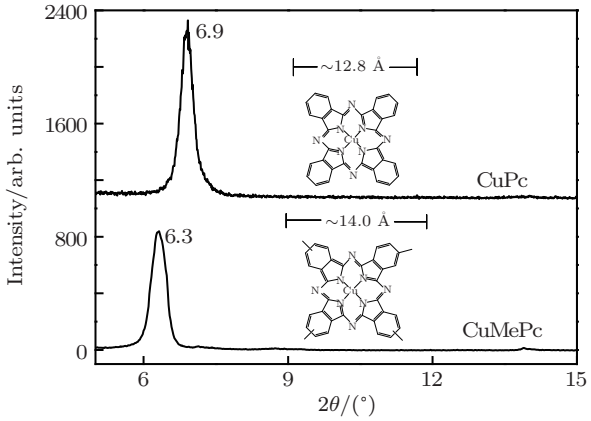


Fig. 5. GIXRD patterns of the thin film samples made from (a) CuPc and CuMePc.

4. Summary

An efficient OPV cell based on copper (II) tetra-methyl substituted phthalocyanine (CuMePc) is demonstrated. The peripheral methyl chains affect the intermolecular π–π interactions and lead to a higher charge carrier mobility. The power conversion efficiency of the CuMePc based OPV cell is found

to be 2.52%, an 88% increase in comparison with that of the standard CuPc based device (1.34%).

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