AIP Applied Physics Letters

Cascade-energy-level alignment based organic photovoltaic cells by utilizing copper phthalocyanine as bipolar carrier transporting layer

Guang Zhang, Wenlian Li, Bei Chu, Lili Chen, Fei Yan et al.

Citation: Appl. Phys. Lett. **94**, 143302 (2009); doi: 10.1063/1.3114379

View online: http://dx.doi.org/10.1063/1.3114379

View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v94/i14

Published by the American Institute of Physics.

APPLIED PHYSICS LETTERS **94**, 143302 (2009)

Cascade-energy-level alignment based organic photovoltaic cells by utilizing copper phthalocyanine as bipolar carrier transporting layer

Guang Zhang,[1] Wenlian Li,[1,a)] Bei Chu,[1,a)] Lili Chen,[1] Fei Yan,[1] Jianzhuo Zhu,[1]
Yiren Chen,[1,2] and C. S. Lee[2]
[1]*Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, People's Republic of China*
[2]*Department of Physics and Materials Science and Center of Super-Diamond and Advanced Films (COSDAF), City University of Hong Kong, Hong Kong SAR, China*

(Received 19 September 2008; accepted 15 March 2009; published online 6 April 2009)

We demonstrate a cascade-energy-level alignment based organic photovoltaic cell by using stacking three materials with appropriate energy levels. A cell with a structure of ITO/4,4′,4″-tris[*N*,(3-methylphenyl)-*N*-phenylamino]-triphenylamine (*m*-MTDATA)/copper phthalocyanine (CuPc)/fullerene (C_{60})/4,4′-*N*,*N*′-dicarubreneazolebiphenyl (BCP)/LiF/Al was shown to have a power efficiency enhancement in more than 30% over that of a standard reference cell (ITO/CuPc/C_{60}/BCP/LiF/Al), which has only one exciton-dissociation interface. The efficiency improvement was mainly ascribed to the ingenious cascade-energy-level alignment and the application of the bipolar carrier transporting property. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3114379]

The investigations on the organic solar cells have been considerably developed due to their promising cost effectiveness and environmental benignity compared with traditional solar cells.[1–7] Power conversion efficiency (PCE) of organic photovoltaic (OPV) cell has steadily increased by the introduction of various device concepts, such as the donor/acceptor (D/A) heterojunction (HJ), exciton blocking layer,[1] blended and tandem structures,[6] as well highly doped crystalline materials,[4,5] and so on. Performances of earlier bilayer HJ-OPV cells are often limited by the short exciton diffusion length (L_D) ($L_D \leq 100$ Å) in comparison with the optical absorption length (L_A) of ~1000 Å.[8] To extract a maximum photocurrent, an optimum balance between sufficient L_A and larger L_D must be achieved simultaneously.[7] The tandem structure-based PV cell may also partly solve the problem, but such a configuration contains two or more subcells that act as the individual PV unit so that its current was limited by the smaller one.[6,9,10]

In this letter we introduce a PV cell structure based on *cascade-energy-level alignment* (CELA) in three photoactive organic layers of 4,4′,4″-tris[*N*, (3-methylphenyl)-*N*-phenylamino]-triphenylamine (*m*-MTDATA), copper phthalocyanine (CuPc), and C_{60}. In the *m*-MTDATA/CuPc/C_{60} cell, *m*-MTDATA and C_{60} are used, respectively, as the donor and the acceptor. Due to its medium energy levels and bipolar characteristics, CuPc behaves as an acceptor and a donor, respectively, at its interfaces with *m*-MTDATA and C_{60}. In comparison with a standard CuPc/C_{60} bilayer cell, an efficiency enhancement of over 30% was achieved in the three layer CELA device.

Schematic energy level diagrams of the bilayer reference cell and the three-layer CELA cell are shown in Fig. 1. All devices were fabricated on precleaned indium-tin-oxide (ITO) glass with a sheet resistance of 25 Ω/sq. The substrates were UV ozone treated immediately before device fabrication. Organic layers were then deposited at a rate of 2 Å/s by vacuum evaporation at a pressure of about 10^{-7} Torr. Evaporating rates for LiF and Al were controlled to be 0.5 and 10 Å/s, respectively. All organic materials were purified by sublimating for two times before used. Absorption spectra of organic films deposited on quartz substrates were measured with a Shimadzu UV-3101PC spectrophotometer. The

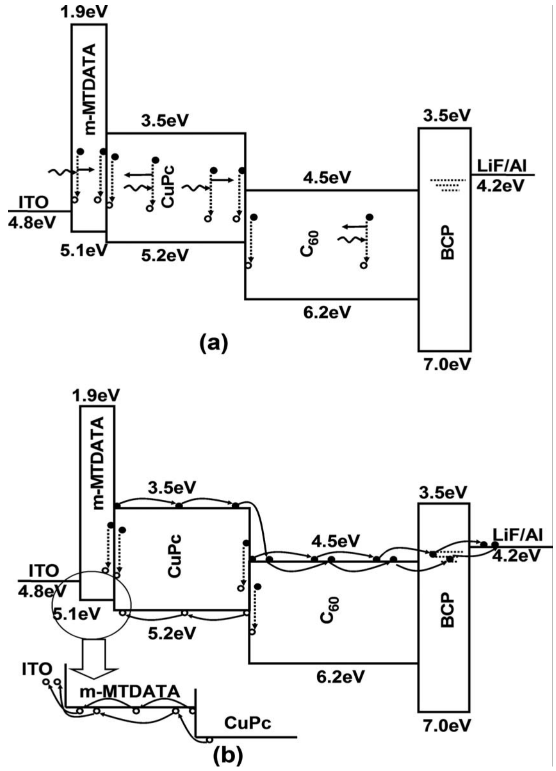

FIG. 1. The schematic energy level diagrams of the bilayer reference cell and the three-layer CELA cell. (a) Photoabsorption as well the generation and diffusion of excitons. (b) The separation hole and electron, i.e., exciton dissociation, and carrier transport toward the respective charge collection electrodes.

[a)] Authors to whom correspondence should be addressed. Electronic addresses: wllioel@yahoo.com.cn and beichubox@hotmail.com.

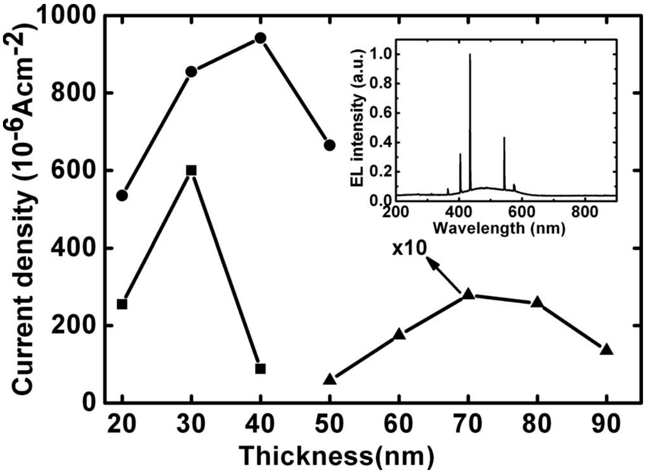

FIG. 2. The dependence of J_{sc} on the thickness of CuPc layer in three PV diodes. D-a was illuminated by a 365 nm UV lamp of 1.5 mW/cm^2 (filled triangle); D-b (filled block) and D-c (filled circle) were under an illumination of a fluorescent lamp with an illumination power of 20 mW/cm^2 and its emissive spectrum is shown at the insert.

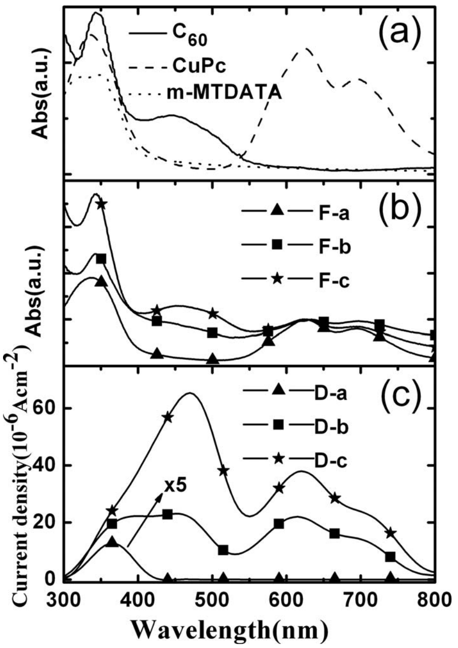

FIG. 3. (a) Absorption spectra of the three neat films of *m*-MTDATA, CuPc, and C$_{60}$. (b) Absorption spectra of the three complex films: *m*-MTDATA (30 nm)/CuPc (70 nm) film (F-a), CuPc(30 nm)/C$_{60}$(50 nm) /BCP (15 nm) film (F-b), and of *m*-MTDATA (10 nm)/CuPc(40 nm)/C$_{60}$(50 nm)/BCP (15 nm) film (F-c). (c) The corresponding photocurrent response curves of device -a, -b, and -c.

photocurrent spectral responses were determined with a Hitachi F-4500 fluorescence spectrophotometer. Energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the organic materials were cited from literatures.[2,11]

Figure 2 shows the dependence of short circuit current density J_{sc} on the thickness of CuPc layer in three PV diodes, D-a, D-b (control), and D-c CELA diodes, with their optimum architectures of ITO/*m*-MTDATA (30 nm)/CuPc (60 nm)/LiF (1 nm)/Al, ITO/CuPc(30 nm)/C$_{60}$(50 nm)/BCP (15 nm)/LiF (1 nm)/Al, and ITO/*m*-MTDATA (10 nm)/CuPc(40 nm)/C$_{60}$(50 nm)/BCP (15 nm)/LiF (1 nm)/Al. The maximum PCE obtained by optimizing the CuPc thickness as well the open circuit voltage, V_{OC}, J_{sc}, and fill factor (FF) of each PV cells are shown in Table I. We observe that the PCE of the CELA diode structure increases by about 33% compared with the control diode with a single active interface. It should be pointed out that the illumination intensity of the fluorescent lamp in our laboratory is far lower than that of 1 sun AM1.5 illumination (100 mW/cm^2). Besides, the emission spectra of the lamp is low in the red and the near infrared regions (see inset of Fig. 2) compared with the solar spectrum.

Figure 3(a) shows the absorption spectra of the neat films of *m*-MTDATA, CuPc, and C$_{60}$. Figure 3(c) shows the photocurrent spectral responses of the three devices and Fig. 3(b) shows the absorption spectra of the corresponding multilayer films on quartz substrates. As shown in Fig. 3, we can see that the absorption of F-c is an overlap of F-a and F-b, while the spectral response of D-c is greatly enhanced compared with that of D-b diode in a wide wavelength region. This result may be attributed to the photocurrent contribution from the formed active interface of *m*-MTDATA/CuPc. It is well known that photogenerated exciton can be dissociated into free electron polaron in the acceptor molecule and free hole polaron in the donor molecule[7] as the D and A have lower ionization potential (IP) and high electron affinity, respectively. If both the LUMO and the HOMO energy levels of the donor material locate at an appropriate higher position than those of the acceptor material, the excitons diffused to the interface can easily be dissociated into free carriers.[7] In the present CELA device, both the LUMO and the HOMO levels of the three active materials are in the order of *m*-MTDATA < CuPc < C60. Hence, there will be two D/A interfaces connected in series. In addition to the medium energy levels of CuPc, the high carrier mobilities for both electron (9.04×10^{-4} cm^2/V s) (Ref. 12) and hole (7×10^{-4} cm^2/V s) (Ref. 13) also enable its dual roles. It is expected that excitons generated in the CuPc layer can diffuse toward both of the interfaces (*m*-MTDATA/CuPc and CuPc/C60) and lead to a more effi-

TABLE I. The optimum performances based on the maximum PCE of different PV cells fabricated by using our experiment conditions.

PV cell	The cell structure	V_{OC} (V)	J_{sc} (μA/cm^2)	FF	PCE (%)
D-a	*m*-MTDATA (30 nm)/CuPc (70 nm)[a]	1.050	54.6	0.30	1.03
D-b	CuPc(30 nm)/C$_{60}$(50 nm)/BCP(15 nm)[b]	0.464	581	0.40	0.54
D-c	*m*-MTDATA(10 nm)/CuPc(40 nm)/C$_{60}$(50 nm)/BCP(15 nm)[b]	0.439	942	0.35	0.72
D-d	TPD(5 nm)/*m*-MTDATA(5 nm)/CuPc(40 nm)/C$_{60}$(50 nm)/BCP(15 nm)[b]	0.440	723	0.37	0.59

[a] Reference 11.

[b] Under an illumination intensity of 20 mW/cm^2.

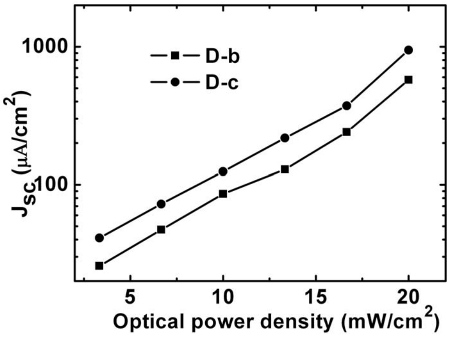

FIG. 4. The relation of I_{SC} as a function of the incident optical power density of the fluorescent lamp with an illumination power of 20 mW/cm^2 for D-b and D-c, respectively.

cient exciton dissociation. This is in agreement with the observed increases in I_{SC} and photocurrent spectral response.

It can be seen from Figs. 3(a) and 3(c) that the absorption of C_{60} offers more contribution to photocurrent response than the CuPc layer. It is because the holes resulted from CuPc/C60 interface would partly recombine with the electrons that come from *m*-MTDATA/CuPc interface and this can lead to exciton formation or probable relaxation and energy loss in the CuPc layer. This would thus decrease the photocurrent response in the CuPc layer. As a result, the photocurrent response is larger at around 400–500 nm (the absorption of C_{60}) than at around 550–700 nm (the absorption of CuPc).

Figure 4 plots the J_{sc} of D-b and D-c as a function of the illumination intensity. Both devices show clear nonlinear increase in J_{sc} as the illumination intensity increases. We speculate that the illumination intensity with low level would lead to the lower V_{OC} compared with normal value (~0.45 V). As a result, it could not efficiently dissociate photogenerated exciton.

To clarify the photocurrent contribution of the *m*-MTDATA/CuPc interface, we fabricated another PV diode (D-d) in which the 5 nm *m*-MTDATA layer adjacent to ITO was replaced by another diamine derivative, *N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)-(1,1′-biphenyl)-4,4′-diamine (TPD) which has a lower IP (5.4 eV).[14] As a result, the PV diode only delivers an I_{SC} of 683 μA/cm^2, which is lower than that of the *m*-MTDATA based (942 μA/cm^2) diode (see Table I). We suppose that this is due to the unmatched energy level alignment between the TPD and the *m*-MTDATA layers, which lead to an inefficient transport of holes. However, the PCE of this diode is almost the same with that of the control diode, indicating that modification function of TPD in the ITO surface may also offer a smaller contribution to the improvement of I_{SC}. In short, the performance improvement in the *m*-MTDATA/CuPc/C60 device is benefited by the formation of two active exciton dissociation interfaces, where CuPc layer simultaneity plays the roles of donor and acceptor.

Based on the above results, the detailed PV process in the CELA structure is interpreted as follows. Upon illumination, the *m*-MTDATA layer absorbs photons in the UV region, while the visible photons penetrate through the *m*-MTDATA layer and then can be successively absorbed by the CuPc and the C_{60} layers. These lead to the formation of localized Frenkel or charge-transfer excitons [see Fig. 1(a)]. Then, the excitons were dissociated into holes and electrons by the built-in electric field in the two HJ-interfaces [see Fig. 1(b)] due to the appropriate energy level difference of the three materials. At the *m*-MTDATA/CuPc interface, holes were transported via the *m*-MTDATA HOMO level and were collected by ITO anode, while the electrons were transported via the LUMO levels of CuPc and C_{60}, and the defect state of the BCP layer[7] and eventually to the cathode. At the CuPc/C60 interface, electrons were transported through the C_{60} LUMO level and the defect state of BCP, and then they were eventually collected by cathode, while holes were transported from CuPc and *m*-MTDATA HOMO levels and then eventually to anode [see Fig. 1(b)]. So, the V_{OC} of D-c is determined by the difference between the HOMO of *m*-MTDATA and the LUMO of CuPc, which is the reason that the V_{OC} of D-c slightly is lower than that of D-b (see Table I).

In summary, we demonstrate an efficient CELA organic PV cell structure by using CuPc as a bipolar carrier transporting layer. Due to the presence of two exciton-dissociation interfaces in the cell, higher PCE was achieved. The improvement in the PV performances is mainly attributed to the contribution of the exciton-dissociation interfaces. It is expected that if some more appropriate materials that excelled *m*-MTDATA and CuPc would be found, much higher efficient PV cell could be harvested in terms of the above argument.

This work was supported by the National Natural Science Foundation of China under Grant No. 60877027 and Knowledge Innovation Project of Chinese Academy of Sciences under Contract No. KJCX2-YW-M11.

[1] C. W. Tang, Appl. Phys. Lett. **48**, 183 (1986).
[2] P. Peumans and S. R. Forrest, Appl. Phys. Lett. **79**, 126 (2001).
[3] P. Peumans, S. Uchida, and S. R. Forrest, Nature (London) **425**, 158 (2003).
[4] M. Y. Chan, S. L. Lai, M. K. Fung, C. S. Lee, and S. T. Lee, Appl. Phys. Lett. **90**, 023504 (2007).
[5] J. H. Schon, Ch. Kloc, E. Bucher, and B. Batlogg, Nature (London) **403**, 408 (2000).
[6] G. Dennler, H.-J. Prall, R. Koeppe, M. Egginger, R. Autengruber, and N. S. Sariciftci, Appl. Phys. Lett. **89**, 073502 (2006).
[7] P. Peumans, A. Yakimov, and S. R. Forrest, J. Appl. Phys. **93**, 3693 (2003).
[8] J. Xue, S. Uchida, B. P. Rand, and S. R. Forrest, Appl. Phys. Lett. **85**, 5757 (2004).
[9] A. Yakimov and S. R. Forrest, Appl. Phys. Lett. **80**, 1667 (2002).
[10] A. Colsmann, J. Junge, C. Kayser, and U. Lemmer, Appl. Phys. Lett. **89**, 203506 (2006).
[11] L. L. Chen, W. L. Li, H. Z. Wei, B. Chu, and B. Li, Sol. Energy Mater. Sol. Cells **90**, 1788 (2006).
[12] L. S. Hung and M. G. Mason, Appl. Phys. Lett. **78**, 3732 (2001).
[13] B. P. Rand, J. Xue, F. Yang, and S. R. Forrest, Appl. Phys. Lett. **87**, 233508 (2005).
[14] C. Gielbeler, H. Antoniadis, D. D. C. Bradley, and Y. Shirota, J. Appl. Phys. **85**, 608 (1999).