Detailed analysis of ultrathin fluorescent red dye interlayer for organic photovoltaic cells*

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The influence of an ultrathin 4-(dicyanomethylene)-2-t-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyran (DCJTB) fluorescent dye layer at donor/acceptor heterojunction on the performance of small-molecule organic photovoltaic (OPV) cell is studied. The structure of OPV cell is of indium-tin oxide (ITO)/copper phthalocyanine (CuPc)/DCJTB/fullerene (C_{60})/bathophenanthroline (Bphen)/Ag. The results show that open circuit voltage (V_{OC}) increases to 0.57 V as the film thickness of DCJTB layer increases from 0.2 to 2.0 nm. By using an equivalent circuit model, the enhancement of V_{OC} is found to be attributed to the reduced reverse saturation current density (J_S) which is due to the lower highest occupied molecular orbital (HOMO) level in DCJTB than that in CuPc. Also, the short circuit current density (J_{SC}) is affected when the DCJTB layer becomes thicker, resulting from the high series resistance $R_S A$ due to the low charge carrier mobility of fluorescent red dye.

Keywords: organic photovoltaic (OPV) cells, DCJTB, interlayer thickness, ultrathin red dye
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1. Introduction

Organic photovoltaic (OPV) cell as one of the promising green energy systems possesses many advantages, such as low cost, light weight and mechanical flexibility, which make this new field attract more and more attention.[1−4] In the past few years, lots of new concepts and approaches like tandem structure, buffer layer or doping proper materials into donor or acceptor have been introduced, and the performances of the OPV devices have been greatly improved.[5−8] To date, the highest power conversion efficiency of 7 % for polymer: fullerene bulky heterojunction cell has been achieved.[9]

Optimizing the donor/acceptor energy levels by doping appropriate materials is considered as a simple and effective method of improving device performance. For a small-molecular OPV cell fabricated by thermal vacuum deposition, it has been reported that by introducing 5, 6, 11, 12-tetraphenylnaphthacene (rubrene) as a dopant, the power conversion efficiency increased to 4.72 %.[8] It was attributed to the high V_{OC} resulting from a low highest occupied molecular orbital (HOMO) level in rubrene. In addition, the complementary absorption of rubrene broadens the absorption spectrum in a range of 500–550 nm. Also, an ultrathin layer can be used to substitute doping in order to make the fabrication process more controllable and precise, which has been widely used in organic light-emitting devices (OLEDs).[10] A very thin layer also acts as dopant to improve the device performance. OPV cell with an ultrathin layer of metal phthalocyanine inserted between pentacene and fullerene (C_{60}) to form multicharge separation (MCS) interfaces was developed by Kinoshita *et al.*[11] Compared with the performance of the device with single charge separation interface, the performance of this kind of device has been significantly improved. The interface of exciton dissociation has a great influence on the OPV cell.

Fluorescent red dye DCJTB is used as a conventional red dopant in OLEDs, and it has a low HOMO level with a complementary light absorption for CuPc and C_{60}. But there is a little of work on DCJTB dye and its application in OPV cell. Therefore, herein we investigate DCJTB as an ultrathin interlayer in OPV

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cell systematically. The variations of photovoltaic performance with the interface between CuPc, C_{60} and DCJTB are analysed. The current density–voltage (J–V) characteristics, separation interface morphologies and absorption spectra of OPV cell are also compared and discussed.

2. Experiment

The configurations of OPV cell are of indium-tin oxide (ITO)/CuPc (20 nm)/DCJTB (x nm)/C_{60} (40 nm)/Bphen (2.5 nm)/Ag (100 nm), x = 0, 0.2, 0.5, 1.0 and 2.0. Bathophenanthroline (Bphen) was used as a buffer layer.[12] The devices were fabricated onto the ITO coated glass substrates by an OLED-V organic multifunctional vacuum deposition equipment with commercially available materials, i.e., CuPc (sublimed before use, Aldrich), C_{60} (99.9 %, Aldrich), Bphen (99 %, Fluka) and DCJTB (99 %, Aldrich). The molecular structures of major materials are shown in Fig. 1. ITO coated glass substrates with a sheet resistance of 10 Ω/□ were cleaned consecutively in ultrasonic baths containing detergent, acetone, ethanol, deionized water for 10 min each, and finally dried by high purity nitrogen blow. The substrates were treated by O_2 plasma for 5 min prior to the deposition of organic layers. And organic layers were deposited onto the ITO substrates successively at a pressure of 3×10^{-4} Pa with a deposition rate of 1–2 Å/s (1 Å = 0.1 nm). Then Ag top electrode was deposited through a mask with 3 mm×4 mm at a pressure of 3×10^{-3} Pa with a deposition rate of ∼10 Å/s. The deposition rate and the film thickness were *in situ* monitored using a quartz crystal oscillator mounted on the substrate holder.

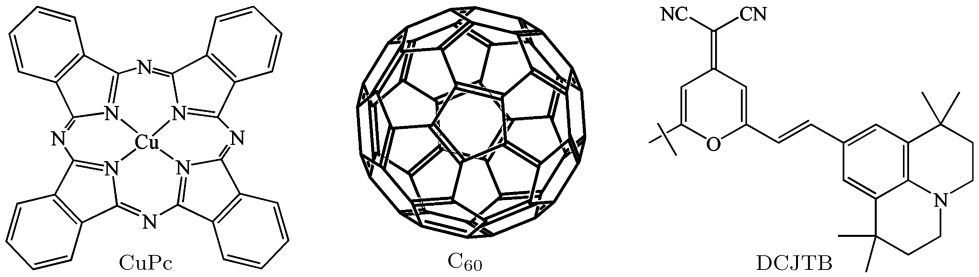


Fig. 1. Molecular structures of CuPc, C_{60} and DCJTB in this study.

The current density–voltage (J–V) curves in dark and under illumination were measured with a Keithley 4200 programmable voltage–current source. A xenon lamp (CHF-XM35) with an illumination power of 100 mW/cm^2 was used as a solar simulator. The absorption spectra were measured with a SHIMATZU UV1700 system. All the measurements were performed in air at room temperature.

3. Results and discussion

Figure 2 shows the J–V characteristics of ITO/CuPc (20 nm)/DCJTB (x nm)/C_{60}(40 nm)/Bphen (2.5 nm)/Ag devices under illumination. The thickness of DCJTB layer in the OPV cell was varied from 0 to 2 nm. The device with 2 nm DCJTB layer shows an open circuit voltage (V_{OC}) of 0.57 V, short circuit current density (J_{SC}) of 3.2 mA/cm^2, and fill factor (FF) of 0.29. The power conversion efficiency (η_p) of OPV cell can be described as

$$\eta_p = \frac{P_{max}}{P_{in}} = \frac{V_{OC}\cdot J_{SC}\cdot FF}{P_{in}}, \qquad (1)$$

where P_{in} is the incident optical power density. From Eq. (1), the calculated power conversion efficiency (η_p) is equal to 0.53 %. It is obvious that V_{OC} is enhanced after an ultrathin DCJTB layer has been inserted between CuPc and C_{60}. The enhancement of V_{OC} in the device with a 2 nm DCJTB layer can be ascribed to the change of charge separation interface from CuPc/C_{60} to DCJTB/C_{60} and to CuPc/C_{60} and the decrease of reverse saturation current J_S due to the lower HOMO level of DCJTB than CuPc (as shown in Fig. 3). In contrast, J_{SC} and FF do not increase correspondingly. Particularly, there is an anomalous S-shape J–V curve of the devices with 0.5 and 1 nm DCJTB layers. As discussed by Kumar *et al.*,[13] in-

terface properties have been speculated to be responsible for such a kind of curve feature and the barriers created by interfacial dipoles, defects, and traps can prevent charge carrier from being extracted.[13]

Based on the theory for p–n junction solar cell, the J–V characteristic can be expressed as

$$J = \frac{R_{\rm P}}{R_{\rm S}+R_{\rm P}}\left\{J_{\rm S}\left[\exp\left(\frac{V-J\cdot R_{\rm S}A}{nk_{\rm B}T/q}\right)-1\right]+\frac{V}{R_{\rm P}A}\right\}-J_{\rm ph}(V), \quad (2)$$

where A is the active area of solar cell, $k_{\rm B}$ and T are Boltzmann constant and Kelvin temperature, respectively, n is ideality factor, q is electronic charge, $J_{\rm S}$ and $J_{\rm ph}$ are reverse saturation current density and photocurrent, respectively. The main parameters extracted from the fitting results of the J–V characteristics of OPV cells are summarized in Table 1. It can be seen that as the thickness of DCJTB layer increases, the $J_{\rm S}$ significantly decreases. This is due to the lower HOMO level of DCJTB than that of CuPc, and it eventually leads to an improvement on $V_{\rm OC}$. In particular, when a 2 nm thick DCJTB layer was inserted between CuPc and C_{60}, the open circuit voltage was increased from 0.40 to 0.57 V.

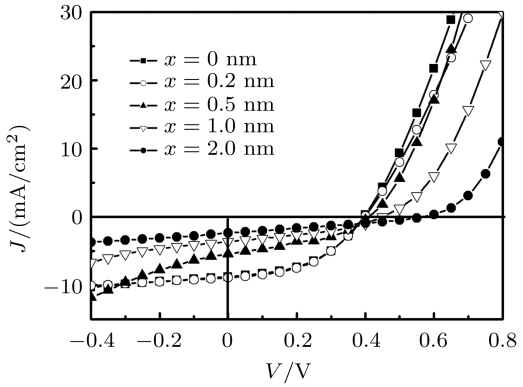


Fig. 2. Current density–voltage (J–V) characteristics of ITO/CuPc (20 nm)/DCJTB (x nm)/C_{60} (40 nm)/Bphen (2.5 nm)/Ag devices under illumination with an intensity of 100 mW/cm^2.

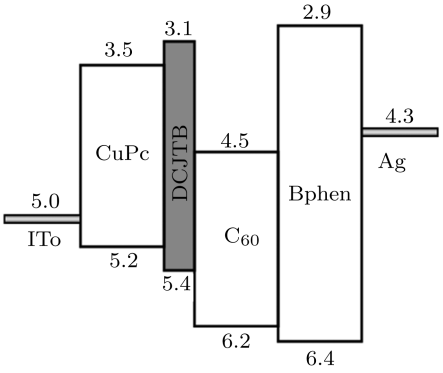


Fig. 3. Energy level diagram of OPV cell.

Table 1. Performances of cells with different thicknesses of DCJTB layer. The value is the median of four individual samples for each configuration.

thickness of DCJTB layer/nm	$V_{\rm OC}$/V	$J_{\rm SC}/(\mathrm{mA/cm^2})$	FF	$\eta_{\rm p}/(\%)$	$R_{\rm S}\mathrm{A}/(\Omega\cdot\mathrm{cm^2})$	$J_{\rm S}/(\mu\mathrm{A/cm^2})$
0	0.40	8.78	0.47	1.62	4.09	1.22×10^{2}
0.2	0.40	7.44	0.46	1.37	4.47	1.42×10^{1}
0.5	0.41	5.44	0.40	0.90	4.33	1.66×10^{-2}
1.0	0.45	3.66	0.38	0.63	5.12	6.71×10^{-3}
2.0	0.57	3.20	0.29	0.53	10.46	1.66×10^{-4}

Also, $J_{\rm S}$ can be described as,[14]

$$J_{\rm S} = J_{\rm SO}\exp\left(\frac{-E_{\rm g}}{2nk_{\rm B}T}\right), \quad (3)$$

where, $E_{\rm g}$ is the energy difference between the highest occupied molecular orbital (HOMO) of donor material (D) and the lowest unoccupied molecular orbital (LUMO) of the acceptor material (A), which equals $E_{\rm g} = \mathrm{HOMO_D} - \mathrm{LUMO_A}$, and $J_{\rm SO}$ is a temperature independent prefactor.

The relationship between dark current and $V_{\rm OC}$ in Eq. (4) can be inferred by setting $J = 0$ from Eq. (2) to be

$$V_{\rm OC} = \frac{nk_{\rm B}T}{q}\ln\left[\frac{J_{\rm ph}(V_{\rm OC})}{J_{\rm S}}+1-\frac{V_{\rm OC}}{R_{\rm P}AJ_{\rm S}}\right]. \quad (4)$$

Assuming infinite shunt resistance and zero series resistance, the open circuit voltage is described as

$$V_{\rm OC} = \frac{nk_{\rm B}T}{q}\ln\left[\frac{J_{\rm ph}(V_{\rm OC})}{J_{\rm S}}+1\right] \approx \frac{nk_{\rm B}T}{q}\ln\left[\frac{J_{\rm ph}(V_{\rm OC})}{J_{\rm S}}\right]. \quad (5)$$

From Eq. (5) it follows that when $J_{\rm ph}/J_{\rm S} >> 1$, $V_{\rm OC}$ is proportional to $\ln(J_{\rm ph}/J_{\rm S})$, suggesting that a low $J_{\rm S}$ can result in an increase in $V_{\rm OC}$. From Eq. (3), it can be seen that $J_{\rm S} \propto E_{\rm g}^{-1}$. Therefore, increasing $E_{\rm g}$ by choosing a donor material with lower HOMO level such as DCJTB, can reduce the reverse saturation current $J_{\rm S}$, and finally improve $V_{\rm OC}$. This is consistent with the report in which $V_{\rm OC}$ was predominately determined by the energy difference between the highest occupied molecular orbital (HOMO) of donor material (D) and the lowest unoccupied molecular orbital (LUMO) of acceptor material (A).[15] The energy level diagram of OPV cell is depicted in Fig. 3. When an ultrathin DCJTB layer is inserted, a higher $E_{\rm g}$ formed between DCJTB and C_{60} can result in a reduction of $J_{\rm S}$ and finally increase $V_{\rm OC}$.

On the other hand, the drop of $J_{\rm SC}$ with the increase of DCJTB film thickness can be attributed to the high series resistance $R_{\rm S}A$ due to a low charge carrier mobility of DCJTB layer. Series resistance includes the bulk resistances of organic materials and electrodes and the contact resistance between organic layer and electrodes.[16] In our experiment, the bulk resistance of organic materials would be the key parameter for the decrease in $J_{\rm SC}$. The reason is that the electrodes and the interface between electrode and organic layer are always identical in material, which leads to an unchanged bulk resistance of electrodes and the contact resistance. The increment of DCJTB thickness leads to high series resistance $R_{\rm S}A$ originating from the increased bulk resistance of organic layer. Also, charge carrier mobility in dye material is on the order of 10^{-5}–10^{-7} $\rm cm^2 \cdot V^{-1} \cdot s^{-1}$, which is lower than those in CuPc and C_{60}. Hole mobility in CuPc is on the order of 10^{-4} $\rm cm^2 \cdot V^{-1} \cdot s^{-1}$, and the electron mobility in C_{60} is on the order of 10^{-2} $\rm cm^2 \cdot V^{-1} \cdot s^{-1}$.[17] As a result, the conductivity of organic layer reduces after an interlayer of DCJTB has been inserted between CuPc and C_{60}. In addition, previous studies have demonstrated that the increase of series resistance leads to the reduction of fill factor.[18] As shown in Table 1, it can be seen that the fill factor was reduced with the thickness of DCJTB layer increasing, which is due to the $R_{\rm S}A$ increasing from 4.09 to 10.46 $\Omega \cdot \rm cm^2$.

To get more insight into the relationship between the performance of the OPV cell and the thickness of the thin fluorescent dye layer, a schematic diagram of the interfaces between CuPc, C_{60} and DCJTB is shown in Fig. 4. In the case of device with no DCJTB layer, the exciton dissociation only occurs at the CuPc/C_{60} interface. Subsequently, free electrons and holes transport from C_{60} and CuPc towards two electrodes, thereby producing the photocurrent. In Fig. 4(b), when an ultrathin DCJTB layer was inserted, the multicharge separation (MCS) interfaces were formed.[11] As $V_{\rm OC}$ is determined by $\rm HOMO_D$-$\rm LUMO_A$ and the HOMO of DCJTB is lower than that of CuPc, the device with the interface formed by DCJTB and C_{60} obtains a higher $V_{\rm OC}$ than that of standard structure. However, when transporting to the corresponding electrodes, electrons and holes may meet each other and be recombined in DCJTB layer due to the low carrier mobility of DCJTB. When a thicker DCJTB film is inserted between CuPc and C_{60}, the possibility of recombination between electrons and holes is increased. As a result, this causes the reduction of $J_{\rm SC}$. Therefore, in order to improve the performance of organic solar cell with MCS interfaces, novel materials with low HOMO and high carrier mobility such as ZnPc and SubPc should be introduced as an interlayer to yield a balance between $V_{\rm OC}$ and $J_{\rm SC}$.

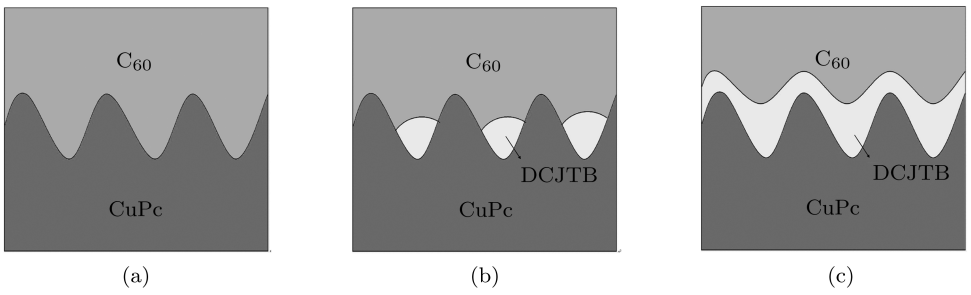


Fig. 4. Schematic diagram showing the variations of exciton separation interface between CuPc, C_{60} and DCJTB with the thickness of DCJTB layer.

The absorption spectra of devices with different thicknesses of DCJTB layer are shown in Fig. 5.

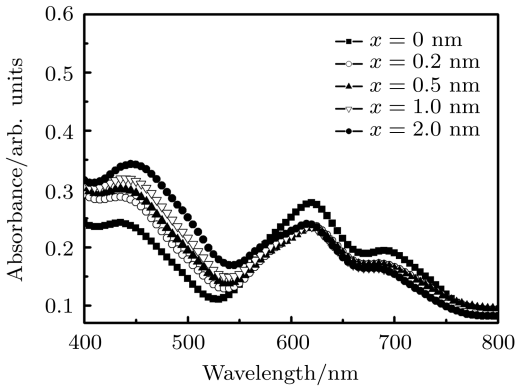


Fig. 5. Absorption spectra of CuPc/DCJTB/C_{60} devices.

DCJTB has two absorption peaks at 359 and 538 nm broadening the absorption spectra, while CuPc and C_{60} do not absorb any light. It is obvious that the absorption in a range from 400 to 500 nm is enhanced with the increase of DCJTB thickness. This suggests that a DCJTB interlayer improves the light absorption efficiency, which was reported to be the main reason for the improvement of OPV cells.[8] Compared with the absorption spectra of ITO/CuPc (20 nm)/DCJTB (x nm)/C_{60} (40 nm)/Bphen (2.5 nm)/Ag, with a very thin DCJTB layer inserted, the absorption spectra have the peaks shifting from 620 to 450 nm. Also, the light absorption distribution in the device can be changed by inserting different thicknesses of the DCJTB layer. However, the short circuit current density (J_{SC}) is not correspondingly improved due to the low charge carrier mobility of DCJTB.

4. Conclusions

Small-molecular organic photovoltaic cell has been realized by inserting an ultrathin DCJTB interlayer between CuPc and C_{60} in. By increasing the thickness of DCJTB layer, a large V_{OC} of 0.57 V has been obtained. This can be attributed to the change of exciton dissociation interface and the reduced reverse saturation current density (J_S) due to the high HOMO level of DCJTB. In addition, the absorption spectra show that by inserting an ultrathin layer of DCJTB between CuPc and C_{60}, the total visible light absorption of cell is enhanced. However, the low charge carrier mobility of fluorescent red dye material, which increases the recombination in DCJTB layer between electron and hole, leads to a high series resistance of R_SA. When a thicker DCJTB layer is used, J_{SC} decreases. Therefore, balancing the contradictory between V_{OC} and J_{SC} is essential to improve the device performance in organic solar cell with MCS interfaces. The results show that by selecting appropriate fluorescent red dyes with low HOMO and high carrier mobility, it will be beneficial to further optimize the OPV cell with broader spectral absorption and higher device performance.

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