Impact of dye interlayer on the performance of organic photovoltaic devices

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The influences of buffer interlayer at the donor/acceptor interface on the open circuit voltage (V_{OC}) of typical copper phthalocyanine (CuPc)/C_{60} organic photovoltaic devices are studied. Six fluorescent dyes with progressively increasing ionization potentials (I_P) were used to investigate the factors influencing the V_{OC}. The short-circuit current and fill factor of CuPc/C_{60} device incorporating dye interlayer are lower than those of standard bilayer device. On the other hand, the V_{OC} increases linearly with the I_P of dye material and falls off when the I_P is equal to or greater than 5.6 eV, in which the energy offset between the highest occupied molecular orbitals at the interlayer/C_{60} heterojunction is smaller than the C_{60} exciton binding energy. The findings underscore the importance of energy offsets in photovoltaic responses. © 2009 American Institute of Physics. [doi:10.1063/1.3243991]

It is well known that the short-circuit current density (J_{SC}) strongly depends on the absorption efficiency and the exciton diffusion length in the photoactive materials, while the open-circuit voltage (V_{OC}) is predominately determined by the energy difference between the highest occupied molecular orbital (HOMO) of the donor (D) and the lowest unoccupied molecular orbital (LUMO) of the acceptor (A), i.e., $HOMO_D - LUMO_A$.[1–6]

Currently, most organic photovoltaic (OPV) devices employ two photoactive materials to form the donor-acceptor junction where photogenerated exciton dissociation and charge transfer take place. To further improve the photovoltaic responses, the use of more complicated device structures with multiple photoactive layers is one feasible approach. Sista et al.[7] recently reported three-component OPV devices with a cascade-type energy level structure, in which a thin interfacial layer, copper phthalocyanine (CuPc), was inserted between the donor/acceptor interface. The requirements for such a cascade-type energy band structure is that the ionization potential (I_P) of the interlayer should be larger than that of p-type material (donor) while its electron affinity (E_A) should be smaller than that of n-type material (acceptor). This approach can effectively engineer the V_{OC} of OPV devices via choosing interlayers with appropriate energy levels. Kinoshita et al.[8] have also demonstrated the use of a thin zinc phthalocyanine interfacial layer (~ 2 nm) between pentacene and C_{60} to improve both J_{SC} and V_{OC}. On the other hand, Rand et al.[9] reported that the use of an interfacial layer would negatively affect the J_{SC} if the interfacial layer thickness exceeds 5 nm. While the cascade-type energy band structure provides a viable means to improve the photovoltaic response, there is little information on how the device performance is related to the constituent materials. In order to optimize the performance of such three-component OPV devices, systematic studies on the influence of the interlayer would obviously be desirable. In this work, we report the use

of six representative fluorescent dyes as interfacial layers to form the cascade-type energy band structure, from which we determine the ideal material parameters for the three-component OPV devices. In addition, the relation between the V_{OC} and the offset energies at the donor-acceptor interface is discussed.

Six representative fluorescent dyes, namely 4-(dicyanomethylene)-2-tert-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyran (DCJTB), 4-(dicyanomethylene)-2-tert-butyl-(1,3,3,7,7,-penta-methyljulolidyl-9-enyl)-4H-pyran (DCJPB), tetra(t-butyl)rubrene (TBRB), rubrene (RB), 10-(2-benzothiazolyl)-1,1,7,7-tetramethyl-,3,6,7-tetrahydro-1H,5H,11H-benzo[l]pyrano[6 7 8-ij]quinolizin-11-one (C545T), and 4,4'-bis(2,2'-diphenyl vinyl)-1,1'-biphenyl (DPVBi), were inserted as an interlayer between CuPc (donor) and C_{60} (acceptor). These six materials were selected because of their progressively increasing ionization potentials (I_P) that allow us to study the dependence of V_{OC} on the offset energies at the organic heterojunctions.[10–15] For comparison, a standard bilayer device with the structure of ITO/CuPc/C_{60}/bathocuproine (BCP)/Al was also fabricated. Current-voltage characteristics of OPV devices were measured with a programmable Keithley model 237 power source. The photocurrent was measured in the dark and under illumination with an intensity of 100 mW/cm^2 from an Oriel 150 W solar simulator equipped with AM1.5G (AM: air mass, G: global) filters, and the light intensity was measured with a calibrated silicon detector with a KG-5 color filter.[16] Absorption spectra of organic films on quartz substrates were measured with a Perkin Elmer Lambda 2S UV/VIS spectrometer.

Table I summarizes the key cell parameters for devices with the structure of ITO/CuPc (34 nm)/dye (5 nm)/C_{60} (40 nm)/BCP (5 nm)/Al (80 nm), in which DCJTB, DCJPB, TBRB, RB, C545T, and DPVBi were used as dye interlayer, respectively, together with the standard device. Under illumination, the standard device exhibits a J_{SC} of 6.40 mA/cm^2, a V_{OC} of 0.46 V, a fill factor (FF) of 0.52, and a power conversion efficiency (η_P) of 1.54%. However, the J_{SC} drops sharply when a thin dye interlayer is inserted between CuPc

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TABLE I. Key photovoltaic responses for devices without and with different dye interlayers.

Dye	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	η_P (%)
Standard	6.40	0.46	0.52	1.54
DCJTB	2.48	0.51	0.42	0.53
DCJPB	3.41	0.53	0.43	0.76
TBRB	2.90	0.60	0.39	0.67
RB	3.47	0.62	0.39	0.83
C5454T	3.98	0.48	0.45	0.86
DPVBi	0.67	0.54	0.44	0.16

FIG. 2. (Color online) V_{OC} of devices with different dye interlayers as a function of I_P of dye materials.

and C_{60}. The poor J_{SC} may be attributed to the absence of C_{60} exciton dissociation (see discussion below) and the relatively low absorption coefficients of dye materials. In particular, the absorption coefficients of all dye materials are on the order of 10^4 cm^{-1}, which are one order of magnitude lower than those of CuPc and C_{60}.[17] The low absorption would inevitably lead to a smaller number of photogenerated excitons, and thus a lower photocurrent. The low photocurrent may also be attributed to the relatively low carrier mobility in dye materials. Particularly, carrier mobilities in dye materials (on the order of $10^{-5}-10^{-7}$ cm^2 V^{-1} s^{-1}) are comparatively smaller than those in CuPc and C_{60}, provided that the hole mobility in CuPc is on the order of 10^{-4} cm^2 V^{-1} s^{-1} and the electron mobility in C_{60} is on the order of 10^{-2} cm^2 V^{-1} s^{-1}. The low carrier mobility would impede the charge carrier transport to the respective electrodes. It should be mentioned that the J_{SC} for the DPVBi-based device is exceptionally low (0.67 mA/cm^2), about one-fourth that of the devices with other dyes. One reason for the low J_{SC} is the extremely low absorption of DPVBi in the visible spectrum. Figure 1 depicts the normalized absorption spectra of the thin films of the dye materials on quartz substrates. Clearly, DPVBi absorbs light in the UV region that coincides with the absorption cutoff of the ITO coated glass substrate, i.e., wavelength $\lambda \leq 360$ nm. This definitely limits photon harvest in the DPVBi layer.

On the other hand, the V_{OC} increases from 0.46 to 0.62 V and then falls off to 0.48 V when a C545T interlayer is used. To investigate the controlling factors of V_{OC} in the three-

component OPV devices, the V_{OC} of devices are plotted as a function of I_P of the dyes in Fig. 2. The V_{OC} of a device with an interlayer of smaller I_P (i.e., $I_P \leq 5.5$ eV) is generally larger than that of a device with an interlayer having I_P equal or larger than 5.6 eV. In addition, by subtracting the V_{OC} of the former devices by 0.145 V, a linear fit to the data with a slope of 0.24 and a correlation coefficient (R^2) of 0.96 can be drawn. In particular, the line represents a linear relation between the V_{OC} and the I_P of dye materials. It is interesting to note that the linear fit intercepts the x-axis at 3.6 eV, which corresponds to the LUMO level of C_{60} measured by inverse photoelectron spectroscopy.[18] This is in good agreement with an increase in V_{OC} with increasing the energy difference, that is, HOMO (dye)–LUMO (C_{60}) as derived.

The voltage difference of 0.145 V may be attributed to the V_{OC} contribution from the presence of C_{60} exciton dissociation. Table II lists the energy levels of organic materials. All energy levels of organic materials are taken from the literature,[10–15,18] in which the LUMO levels of CuPc and C_{60} were measured by inverse photoelectron spectroscopy, so called "true LUMO", and those of dye materials were estimated from the optical absorption spectra, referred as "optical LUMO", in which the exciton binding energies (E_B) of the dye materials have not been considered. E_B is the minimum energy needed to overcome the Coulomb electric force to separate the exciton into free electron and hole, and is given by the energy difference between the true LUMO and the optical LUMO, i.e., $E_B = E_{\text{true LUMO}} - E_{\text{optical LUMO}}$. Djurovich *et al.*[18] recently reported that E_B in most molecular organic semiconductors linearly increases with increasing energy gap (either transport gap, E_T, i.e., $E_T = E_{\text{HOMO}}$
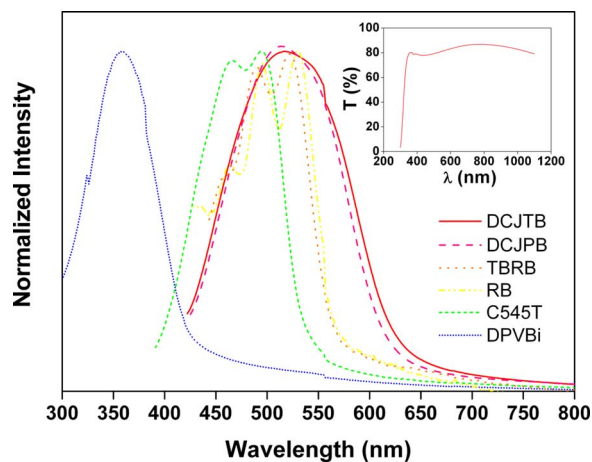

FIG. 1. (Color online) Normalized absorption spectra of thin films of dye materials on quartz substrates. Inset: Transmission of ITO coated glass substrate with reference to air.
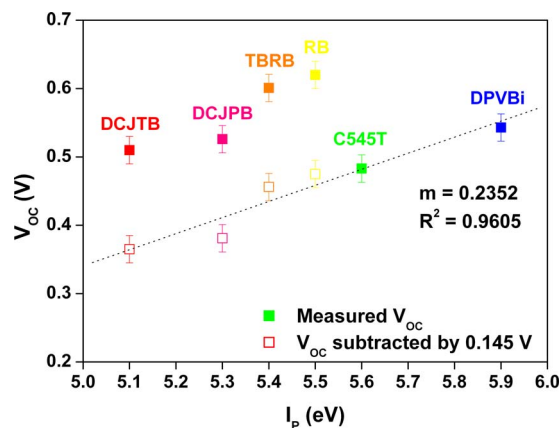
TABLE II. Energy levels of dye materials used. E_{opt}, E_T, and E_B are the optical bandgap, the transport gap, and the exciton binding energy in the organic materials, respectively. The electron affinities of CuPc and C_{60} were measured by the inverse photoelectron spectroscopy, in which $E_{\text{true LUMO}}$ levels were directly determined.

Material	CuPc	DCJTB	DCJPB	TBRB	RB	C545T	DPVBi	C_{60}
E_A (eV)	3.2	3.1	3.2	3.2	3.3	2.8	2.8	3.5
I_P (eV)	5.2	5.1	5.3	5.4	5.5	5.6	5.9	6.2
E_{opt} (eV)	$\cdots$	2.0	2.1	2.2	2.2	2.8	3.1	$\cdots$
E_T (eV)	2.0	2.3	2.4	2.6	2.6	3.4	3.9	2.7
E_B (eV)	0.3	0.3	0.3	0.4	0.4	0.6	0.8	0.7

TABLE III. Conditions for exciton dissociation at the organic/organic interfaces, given that E_B of CuPc and C_{60} are 0.3 and 0.7 eV, respectively. ΔE_{LUMO} is calculated from the difference between the $E_{true\ LUMO}$ (CuPc or C_{60}) and $E_{true\ LUMO}$ (dye), in which $E_{true\ LUMO}$ (dye) is estimated according to the equation $E_B = E_{true\ LUMO} - E_{optical\ LUMO}$. ✓ and ✗ show whether excitons can or cannot be dissociated in the particular layers at various interfaces.

Interface	ΔE_{LUMO}	ΔE_{HOMO}	CuPc	Dye	C_{60}
CuPc/C_{60}	0.3	1.0	✓	⋯	✓
CuPc/DCJTB	0.4	0.1	✓	✗	⋯
CuPc/DCJPB	0.3	0.1	✓	✗	⋯
CuPc/TBRB	0.4	0.2	✓	✗	⋯
CuPc/RB	0.3	0.3	✓	✗	⋯
CuPc/C545T	1.0	0.4	✓	✗	⋯
CuPc/DPVBi	1.2	0.7	✓	✗	⋯
DCJTB/C_{60}	0.7	1.1	⋯	✓	✓
DCJPB/C_{60}	0.6	0.9	⋯	✓	✓
TBRB/C_{60}	0.7	0.8	⋯	✓	✓
RB/C_{60}	0.6	0.7	⋯	✓	✓
C545T/C_{60}	1.3	0.6	⋯	✓	✗
DPVBi/C_{60}	1.5	0.3	⋯	✓	✗

$-E_{true\ LUMO}$, or optical bandgap, E_{opt}, i.e., $E_{opt} = E_{HOMO} - E_{optical\ LUMO}$), with a minimum of 0.25 eV for $E_T = 2$ eV to 1.5 eV for $E_T = 6$ eV.

For efficient exciton dissociation into free charge carriers at the donor/acceptor interface, the energy level offset for the HOMO or LUMO (ΔE_{HOMO} or ΔE_{LUMO}, respectively) should be larger than E_B.[19,20] In particular, ΔE_{HOMO} (ΔE_{LUMO}) should be larger than the acceptor (donor) exciton binding energy for efficient exciton dissociation in the acceptor (donor).[20] In other words, excitons in C_{60} would be dissociated if the ΔE_{HOMO} at the interlayer/C_{60} interface is larger than the E_B in C_{60} (0.7 eV); while excitons in CuPc only dissociate if the ΔE_{LUMO} at the CuPc/interlayer interface is larger than 0.3 eV.[18] At the same time, excitons in dye material would be dissociated if the ΔE_{HOMO} at the CuPc/interlayer and ΔE_{LUMO} at the interlayer/C_{60} interface, respectively, are larger than the E_B in dye material. Table III summarizes the conditions for exciton dissociation at different organic/organic interfaces, in which the ΔE_{LUMO} is calculated from the difference between the $E_{true\ LUMO}$ (CuPc or C_{60}) and $E_{true\ LUMO}$ (dye), as shown in Table II. At the interlayer/C_{60} interfaces, efficient C_{60} exciton dissociation takes place at the interfaces between the dye materials and C_{60}. Except at the C545T/C_{60} and DPVBi/C_{60} contacts, the close proximity of the HOMO levels of C_{60} and dye materials prohibits C_{60} exciton dissociation; particularly the ΔE_{HOMO} is much smaller than the exciton binding energy in C_{60} ($E_B = 0.7$ eV). On the other hand, all excitons in the interlayer are expected to dissociate at the interlayer/C_{60} interfaces [i.e., $\Delta E_{LUMO} \geq E_B$ (dye)], especially when the E_B in dye material has been counted. However, it is not the case at the CuPc/interlayer interfaces, in which only CuPc excitons can be efficiently dissociated. The close proximity of the HOMO levels of CuPc and dye materials prohibits the dye exciton dissociation; particularly the ΔE_{HOMO} is much smaller than the exciton binding energy in dye materials.

As C_{60} exciton dissociation only takes place under certain conditions, this may account for the origin of the voltage difference between devices with interlayer having smaller I_P

(i.e., $I_P \leq 5.5$ eV) and those having I_P equal or greater than 5.6 eV. This may also explain the loss of photocurrent when a 5 nm thick tin(II) phthalocyanine (SnPc) is inserted between the CuPc and C_{60} layers, as here the energy level offset is not sufficiently large for efficient CuPc exciton dissociation and thus results in the lower photocurrent, as reported by Rand *et al.*[9] It is worth noting that the present results suggest that V_{OC} is related to exciton dissociation in both the donor and the acceptor. The absence of either donor or acceptor exciton dissociation would result in a lower V_{OC}. The exact mechanism or physical basis for this is still unclear, and more investigation is definitely needed.

In summary, we have used fluorescent dyes as interfacial layers between CuPc and C_{60} to form the cascade-type energy level structure. With the insertion of the dye interlayer, photovoltaic responses such as J_{SC} and FF are reduced compared to those of the standard device. The decreased photocurrent may be attributed to the absence of C_{60} exciton dissociation, given that the absorption coefficients in CuPc and C_{60} are an order of magnitude higher than those in dye materials, as well as the relatively low carrier mobility in dye materials. On the other hand, the V_{OC} linearly increases with the I_P of the dye interlayer, provided that the energy offset of HOMO levels at the interlayer/C_{60} interfaces is larger than the C_{60} exciton binding energy. In particular, the V_{OC} falls off when the I_P of dye materials is equal to or greater than 5.6 eV, which may be attributed to the absence of C_{60} exciton dissociation. Our findings provide guideline in material and device design with respect to improving the photovoltaic responses of trilayer OPV devices.

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