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Origin of the open-circuit voltage in multilayer heterojunction organic solar cells

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From temperature dependent studies of pentacene/ C_{60} solar cells in the dark, the reverse saturation current is found to be thermally activated with a barrier height that corresponds to the difference in energy between the highest occupied molecular orbital of the donor and the lowest unoccupied molecular orbital of the acceptor corrected for vacuum level misalignments and the presence of charge-transfer states. From the reverse saturation current in the dark and the short-circuit current under illumination, the open-circuit voltage can be predicted. Examination of several donor materials supports the relationship between reverse saturation current, this barrier height, and open-circuit voltage. © 2008 American Institute of Physics. [DOI: 10.1063/1.3027061]

Organic photovoltaic devices have been the subject of intense research in recent years due to their potential to lead to a new generation of low-cost portable power sources with highly flexible form factors. Despite significant advances, the power conversion efficiency of organic solar cells remains rather small with maximum values in the range of 5%–6%. In order to compete with other thin-film technologies, it is critical that progress is made toward increasing the performance of organic photovoltaic cells. A critical factor, which remains the subject of active research, is the understanding of the physical processes that determine the open-circuit voltage in organic solar cells. Recent studies in small molecule multilayer heterojunction devices^{1,2} and in polymeric bulk heterojunctions^{3–8} have confirmed that the magnitude of the open-circuit voltage correlates with the energy difference between the highest occupied molecular orbital (HOMO) level (also approximated to the ionization potential) of the donor and the lowest unoccupied molecular orbital (LUMO) level (also approximated to the electron affinity) of the acceptor molecules that form the multilayer or bulk heterojunction, provided that good electrical contacts are formed between the electrodes and the organic layers.^{9,10}

Here, we report on temperature dependent studies of the reverse saturation current in multilayer organic solar cells based on the well-known pentacene/ C_{60} heterojunction.^{11–13} We find that its magnitude is thermally activated with an activation energy ϕ_B , which is related to the energy difference ΔE_{HL} between the HOMO of the donor and the LUMO of the acceptor before heterojunction formation. By combining this result with the expression of the open-circuit voltage derived from the Shockley equivalent circuit of solar cells, an analytical expression of the open-circuit voltage is proposed. To test the predictive capabilities of the proposed model, values of ϕ_B and open-circuit voltage are calculated for different multilayer heterojunction devices, in which the energy difference ΔE_{HL} is varied by using donor molecules with different HOMO energies [pentacene, copper phthalocyanine (CuPc), and titanyl phthalocyanine (TiOPc)] combined with the acceptor molecule C_{60} . Good agreement is found between the measured and calculated values of the open-circuit voltage and reverse saturation current densities.

All of the devices were fabricated by vacuum thermal evaporation onto cleaned indium tin oxide (ITO) substrates. The layer thicknesses of the three solar cells studied here along with the HOMO levels of the donors are as follows: ITO/pentacene (45 nm, 5.0 eV)/ C_{60} (50 nm)/BCP (8 nm)/Al, ITO/CuPc (15 nm, 5.3 eV)/ C_{60} (50 nm)/BCP (8 nm)/Al, and ITO/TiOPc (20 nm, 5.4 eV)/ C_{60} (40 nm)/BCP (10 nm)/Al.^{14–16} Details of the fabrication and testing of the TiOPc and pentacene devices can be found in Refs. 2 and 11, respectively. The CuPc devices were produced and tested with the same procedures as the pentacene devices. The chemical structures and basic device geometry are shown in Fig. 1. Temperature dependent measurements were made by placing the pentacene device in a copper holder in contact with a thermoelectric cooler/heater used to control the temperature.

As with conventional p - n solar cells, an organic photovoltaic device can be described by a Shockley equivalent circuit, and the current-voltage characteristic can be approximated by

$$J = \frac{1}{1 + R_S/R_P} \left[J_0 \left\{ \exp\left(\frac{V - J R_S A}{nkT/e}\right) - 1 \right\} - \left(J_{ph} - \frac{V}{R_{PA}} \right) \right], \quad (1)$$

where e denotes the elementary charge, kT the thermal en-

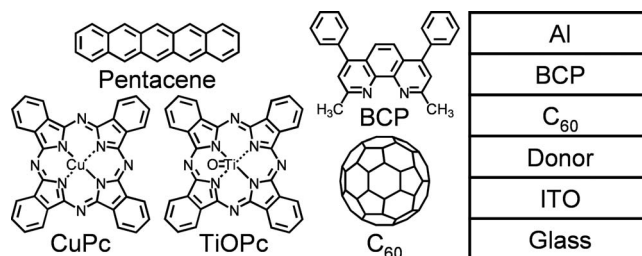


FIG. 1. Chemical structures of the materials used in the devices with a basic schematic of the device geometry.

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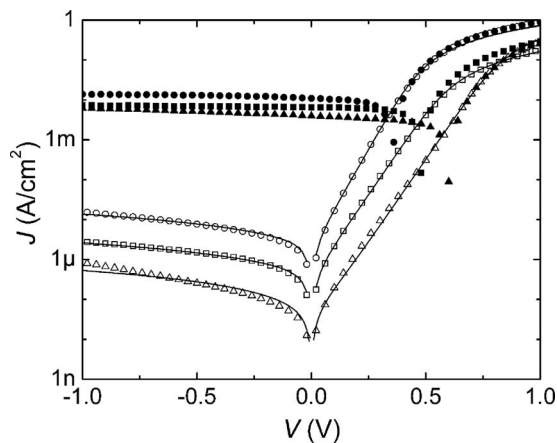


FIG. 2. Experimental J - V characteristics of solar cells with an acceptor layer of C_{60} and a donor layer of either pentacene (circles), CuPc (squares), or TiOPc (triangles) both in the dark (empty shapes) and under illumination (filled shapes). Solid lines are fits to the experimental data in the dark using the equivalent circuit model and the parameters in Table I.

ergy, A the area of the cell, n the ideality factor of the diode, J_0 the reverse saturation current density, J_{ph} the photocurrent, and R_S and R_P the series and shunt resistance, respectively.^{17,18} From Eq. (1), the following simplified expressions can be derived for the open-circuit voltage V_{OC} :

$$\begin{aligned} V_{OC} &= n \frac{kT}{e} \ln \left\{ 1 + \frac{J_{ph}}{J_0} \left(1 - \frac{V_{OC}}{J_{ph} R_P A} \right) \right\} \\ &\approx n \frac{kT}{e} \ln \left\{ 1 + \frac{J_{SC}}{J_0} \right\} \\ &\approx n \frac{kT}{e} \ln \left\{ \frac{J_{SC}}{J_0} \right\}. \end{aligned} \quad (2)$$

Figure 2 shows the measured current-voltage characteristics of three different devices based on pentacene/ C_{60} , CuPc/ C_{60} , and TiOPc/ C_{60} heterojunctions and fits in the dark using the equivalent circuit model. The fitting parameters are summarized in Table I. It is apparent from the curves shown in Fig. 2 that the open circuit is improved as the HOMO of the donor molecule is increased as predicted from previous studies on a large class of donor materials.^{1,4,6} Also evident from Fig. 2 is that the reverse saturation current is reduced as the HOMO energy of the donor molecule is increased. Turning back to Eq. (2), the open-circuit voltage can be computed with the knowledge of the ideality factor n , the short-circuit current density J_{SC} , and the reverse saturation current density J_0 . This observation motivated us to study in greater detail the origin of the reverse saturation current in a device with selected materials.

TABLE I. Open-circuit voltage (V_{OC}), short-circuit current density (J_{SC}), fill factor (FF), and power conversion efficiency under broadband illumination (η) of solar cells with the geometry ITO/donor/ C_{60} /BCP/Al, in which the donor material was varied. Shockley parameters derived from fitting the electrical characteristics in the dark with the equivalent circuit model: diode ideality factor (n), reverse saturation current density (J_0), series resistance ($R_S A$), and shunt resistance ($R_P A$).

Donor	V_{OC} (V)	J_{SC} (mA/cm ²)	FF	η (%)	n	J_0 (μ A/cm ²)	$R_S A$ (Ω cm ²)	$R_P A$ (k Ω cm ²)
Pentacene	0.35	11.0	0.53	2.1	1.68	1.37	0.480	110
CuPc	0.47	6.45	0.62	1.9	2.00	0.33	1.98	43.9
TiOPc	0.60	3.99	0.51	1.2	2.02	0.023	0.413	1970

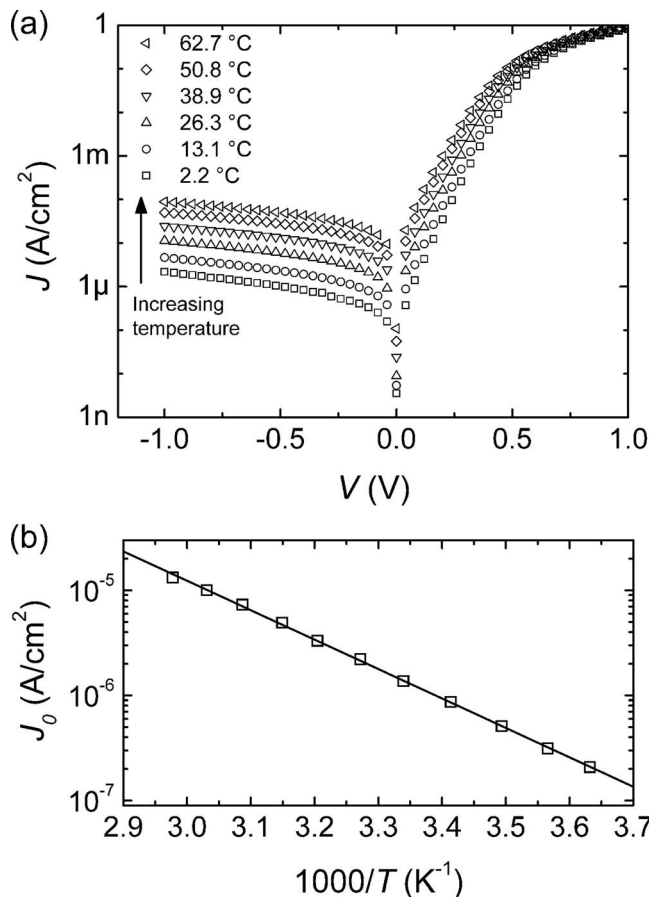


FIG. 3. (a) Experimental J - V characteristics of pentacene/ C_{60} devices in the dark at various temperatures between 2.2 °C and 62.7 °C. Current density can be seen to increase with temperature. (b) J_0 calculated at different temperatures by fitting the equivalent circuit model to the experimental data plotted as a function of $1000/T$ (symbols) and fit to the data according to Eq. (3) with $J_{00}=3090$ A/cm² and $\phi_B=0.55$ eV (solid line).

Figure 3(a) shows the temperature dependence of the electrical characteristic of a pentacene/ C_{60} device in the dark. Analysis of the data showed that it could be best fitted with a thermally activated injection expression of the form

$$J_0 = J_{00} \exp\left(\frac{-\phi_B}{kT}\right) = J_{00} \exp\left(\frac{-\Delta E_{HL}}{n'kT}\right), \quad (3)$$

where ϕ_B is the activation energy and J_{00} is a prefactor. The effective barrier ϕ_B can also be written as ΔE_{HL} adjusted by an ideality factor n' , the reasons for which are described later. As shown by the solid lines in Fig. 3(b), the reverse saturation current density of the dark characteristics can be well fitted within the temperature range studied (275–336 K)

TABLE II. For each donor/C₆₀ combination, effective barrier height (ϕ_B), calculated reverse saturation current density (J_{0th}), and calculated open-circuit voltage (V_{OCth}). Experimental J_0 and V_{OC} can be found in Table I. The value of the prefactor J_{00} was 3090 A/cm² and the temperatures for the calculations of J_{0th} in the dark and of V_{OCth} under illumination were set to 300 and 323 K, respectively.

Donor	ϕ_B (eV)	J_{0th} ($\mu A/cm^2$)	V_{OCth} (V)
Pentacene	0.55	1.55	0.34
CuPc	0.60	0.26	0.47
TiOPc	0.67	0.02	0.59

with this model using $J_{00}=3090$ A/cm² and with $\phi_B=0.55$ eV. Combining now the simplest expression of V_{OC} given by Eq. (2) with the expression of the reverse saturation current density given by Eq. (3), the following equation can be derived:

$$eV_{OC} = n\phi_B - nkT \ln \left\{ \frac{J_{00}}{J_{SC}} \right\} \\ = \frac{n}{n'} \Delta E_{HL} - nkT \ln \left\{ \frac{J_{00}}{J_{SC}} \right\}. \quad (4)$$

Table II shows calculated values of open-circuit voltages and reverse saturation current densities using Eq. (4) obtained in devices with heterojunctions of pentacene/C₆₀, CuPc/C₆₀, and TiOPc/C₆₀, which can be compared with the experimental values in Table I. Good agreement between experiment and calculation is found between the reverse saturation current density and V_{OC} for devices with different effective barrier heights ϕ_B . Note that the second term in the right hand side of Eq. (4), based on the values of the reverse saturation current densities measured in the devices used for this study, is in the range of 0.4–0.7 eV and can partially explain the empirical expression of V_{OC} derived by Scharber *et al.*⁶ The effective barrier height ϕ_B is related to ΔE_{HL} but renormalized by the ideality factor n' to include effects such as vacuum level misalignments at the heterojunction caused by energy level bending and interface dipoles and the formation of charge-transfer states.¹⁹ These changes at heterojunction interfaces have been discussed for CuPc/C₆₀ with measured values of ~0.7 eV in line with the $\phi_B=0.6$ eV used in our calculations.^{2,20,21} Since comparison of the calculated ϕ_B with measured ΔE_{HL} suggests that n' is in the range of 1.5–2, the n/n' term in Eq. (4) will be close to one, reinforcing the importance of ΔE_{HL} for open-circuit voltage. The exact nature of n' will be the subject of future studies.

To relate the values of the prefactor J_{00} to corresponding physical processes, we now turn back to Eq. (3) and discuss the possible origin of the thermal activation of the reverse saturation current density with an effective barrier height ϕ_B . By analogy with the origin of current in a conventional inorganic *p-n* diode that is assigned to the thermal generation of minority carriers on either side of the junction within a minority carrier diffusion length, we tentatively assign the origin of reverse saturation current in organic heterojunctions

to the thermal generation of carriers through the cross reaction $A+D \rightarrow A^-+D^+$, in which an electron is excited from the HOMO level of neutral donor molecules to the lowest energy charge-transfer state formed with the acceptor molecules at the heterojunction over the effective barrier ϕ_B .

In conclusion, a parametrized analytical expression of the open-circuit voltage in organic solar cells is proposed. Its derivation was enabled by the observation that the reverse saturation current can be modeled by a thermally activated injection with an effective barrier height ϕ_B , related to the difference in energy between the HOMO level of the donor and the LUMO level of the acceptor molecules that form the heterojunction, but corrected for vacuum level misalignments and for the formation of charge-transfer states. Thermal excitation of charge carriers is tentatively assigned to thermally activated electron transfer reactions between the donor and the acceptor molecules at the heterojunction.

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