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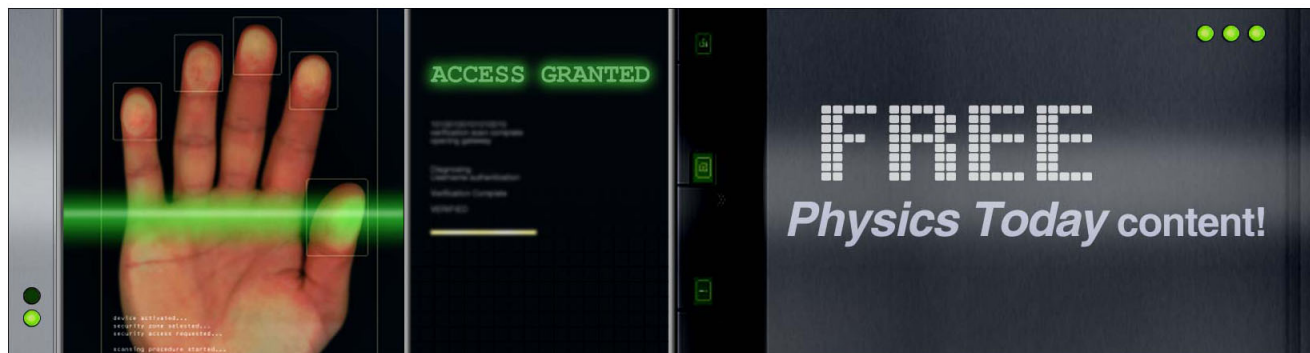
Influence of polymer ionization potential on the open-circuit voltage of hybrid polymer/TiO$_2$ solar cells

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We report studies of the dependence of the open-circuit voltage (V_{OC}) of polymer/titanium dioxide hybrid devices on the ionization potential of the polymer (I_P). Once corrected for differences in photocarrier generation by the polymers, the measured V_{OC} values vary linearly with the polymer I_P, with a slope of 0.8 ± 0.1. This behavior agrees with recent studies of polymer/fullerene photovoltaic devices and is consistent with the hypothesis that V_{OC} of an organic donor-acceptor solar cell is limited by the energy difference between the highest occupied molecular orbital of the donor (in this case, the polymer) and the lowest unoccupied electronic level of the acceptor (in this case, the conduction band edge of the TiO$_2$). © *2008 American Institute of Physics.*
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Hybrid conjugated polymer/metal oxide structures are of interest as alternatives to all organic donor-acceptor heterojunction structures as the active layer of low cost molecular solar cells.[1] Nanostructured and nanoparticulate metal oxides offer the potential advantages relative to organic acceptors of low cost, facile synthesis via wet chemical processing, control of heterojunction morphology, and the potential for higher physical and chemical stabilities. Devices with promising power conversion efficiencies of up to 1.5% have been reported,[2] and higher efficiencies are anticipated through improvement of the nanostructure morphology. The factors limiting short circuit current density, such as interface area,[3,4] intimacy of contact between the phases,[5,6] absorption of materials,[7] and transport properties[5,6,8] are reasonably well understood. Results from isolated studies show that the open-circuit voltage is influenced by the type of polymer,[7] the type of metal oxide,[2,9] and, in the case of TiO$_2$, by the degree of protonation[10] or the built-in dipole moment[11] of the metal oxide surface induced by any adsorbed species. However, the dependence of the open circuit voltage (V_{OC}) on the type of polymer used in these structures has not yet been studied in detail.

The origin of V_{OC} in organic donor-acceptor heterojunction devices has been the subject of much interest in recent years.[12–17] While arguments based on a traditional metal-insulator-metal picture indicate that V_{OC} should be limited by the difference in work functions between the two metal electrodes, experimental studies of polymer/fullerene devices showed a dependence of V_{OC} on the fullerene acceptor strength and negligible dependence on the cathode work function.[14] Experimental[12,17] and modeling[13,17] studies confirmed that in bilayer devices, V_{OC} can be controlled by the difference between the highest occupied molecular orbital (HOMO) of the donor and the lowest unoccupied molecular orbital (LUMO) of the acceptor, and is only partly dependent on the difference in work functions of the electrodes. In bulk heterojunctions, where both donor and acceptor phases contact both electrodes, the electrode work functions are also expected to influence V_{OC}. Nevertheless, the most detailed study of polymer/methanofullerene blend devices[15] found that V_{OC} varies linearly with the polymer oxidation potential, using a total of 26 different donor materials, thus confirming the linear dependence of V_{OC} on the energy difference between the LUMO of the acceptor and the HOMO level of the donor.[15] The result can be explained by arguing that, provided that the anode work function is high enough and the cathode work function low enough to form Ohmic contacts between anode and donor material and between cathode and acceptor material, the quasi-Fermi levels of the electrodes will be pinned to the active materials and variations in photovoltage therefore dominated by variations in the active materials. For non-Ohmic contacts, V_{OC} is expected to be determined by the work function difference of the electrodes.[16] (In the case of insufficiently selective electrode materials, where either donor or acceptor may exchange charges with both contacts, V_{OC} may be reduced by shunt pathways.[18]) On the basis of these studies, V_{OC} for polymer/metal oxide heterojunctions may be expected to vary linearly with the difference between conduction band edge position of the metal oxide and the HOMO of the polymer, provided that the contacts are Ohmic.

In this letter, we use polymers with different ionization potentials (I_P) as the donor in hybrid polymer/TiO$_2$ solar cell devices. We demonstrate that variations in polymer HOMO level influence device V_{OC} in a similar manner to the way they influence V_{OC} of the bulk heterojunction devices studied in Ref. 15. However, as with conventional solar cells, V_{OC} tends to increase logarithmically with light intensity in organic solar cells,[12] reflecting the influence of photogenerated carrier density on the quasi-Fermi level position. Hence, in order to obtain the correct relationship between V_{OC} and the ionization potential of the donor, variations in the photoge-

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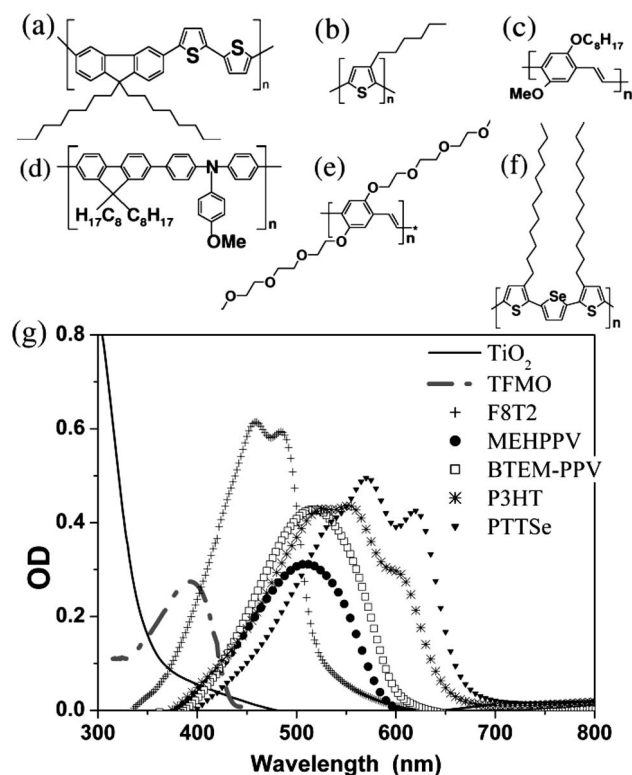a)Electronic mail: jenny.nelson@imperial.ac.uk.

FIG. 1. Chemical structures of the polymers used: (a) poly(9,9-dioctylfluorene-co-bithiophene)(F8T2), (b) poly(3-hexylthiophene)(P3HT) (c) poly[2-methoxy-5-(2′-ethylhexyloxy) paraphenylenevinylene] (MEH-PPV), (d) poly[9,9-dioctylfluorene-co-*N*-(4-methoxy-phenyl)diphenylamine](TFMO), (e) poly[2,5-bis(triethoxymethoxy)-1,4-phenylenevinylene](BTEM-PPV), (f) poly[2,5-bis(3-dodecylthiophen-2-yl)selenophene] (PTTSe), and (g) optical absorption spectra of 50 nm thick polymer films.

nerated carrier density between different polymer materials must also be taken into account.

A bilayer structure consisting of flat layers of dense TiO_2 and polymer was chosen for this study in order to simplify analysis and to avoid sample variation due to different degrees of polymer penetration into TiO_2 nanostructure pores. Dense TiO_2 electrodes of about 50 nm in thickness were deposited on indium tin oxide (ITO) coated glass substrates by the spray pyrolysis technique described in Ref. 3. A 50 nm polymer layer was then spin coated on the TiO_2 layer. The chemical names, structures, and optical absorption spectra of the polymers used are presented in Fig. 1. Optical absorption spectra of the spin coated polymers on spectrosil were taken using an UV-vis spectrometer (Jasco). Cyclic voltammetry measurements were carried out on polymer films, as described in Ref. 7, to determine I_P. A 50 nm layer of

TABLE I. Ionization potential of the studied polymers measured by the method in Ref. 7 except where indicated otherwise.

Polymer	I_p (± 0.05) (eV)
F8T2	5.5
MEH-PPV	5.30
PTTSe	5.20
TFMO	5.20[a]
P3HT	5.10
BTEM-PPV	4.97

[a]Reference 20.
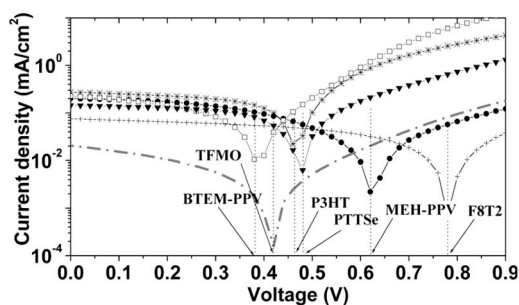

FIG. 2. (Color online) Current density–voltage (*J-V*) characteristics under simulated AM1.5 irradiation (50 mW/cm²) for bilayer ITO/TiO_2/polymer/PEDOT:PSS/Au devices with each of the six polymers.

poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) was deposited on the polymer before thermal evaporation of Au top contacts. Table I shows the I_P values of the polymers which were used in this study. Since the work function of PEDOT:PSS (5.2–5.3 eV) (Ref. 7) is similar to the I_P for each polymer, with a polymer/PEDOT:PSS energy step ≤ 0.3 eV, PEDOT:PSS is expected to provide a good Ohmic contact[19] in all cases.

Figure 2 shows the semilogarithmic *J-V* characteristics of the TiO_2/polymer bilayer devices under AM1.5 irradiance (50 mW/cm²). The short-circuit current density (J_{SC}) values of the devices vary by over one order of magnitude as a result of variations in the spectral range of the polymer as well as in its exciton and charge transport properties, while V_{OC} varies with the polymer I_P. Figure 3(a) shows that the measured V_{OC} values increase approximately linearly with I_P, although V_{OC} for the device made from the polymer with the weakest absorption in the visible region, poly[9,9-dioctylfluorence-co-*N*-(4-methoxy-phenyl) diphenylamine] (TFMO), appears to be anomalously low. The linear fit shows a slope of 0.7, indicating a weaker dependence of V_{OC} on I_P than expected from Ref. 15 for polymer/fullerene blend solar cells. However, in Fig. 3(a) and in previous studies,[12–17] the different photocurrent magnitudes generated by different organic materials was not considered. Variations in spectral sensitivity or charge generation efficiency result in different photocarrier densities under the same illumination spectrum. Since V_{OC} is determined by the separation between the quasi-Fermi levels of electrons and holes, and the position of the quasi-Fermi level relative to the relevant electronic energy level (HOMO for holes or LUMO for electrons) depends on the logarithm of the charge
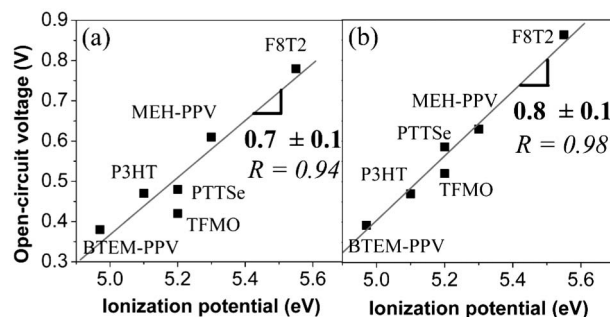

FIG. 3. Open-circuit voltage measured under simulated solar illumination (50 mW cm⁻²) of the TiO_2/polymer structures as *a* function of polymer ionisation potential (a) before and (b) after correction for variations in photocurrent density. The gradient and linear regression coefficient *R* of the best linear fit to the data is shown on each graph.
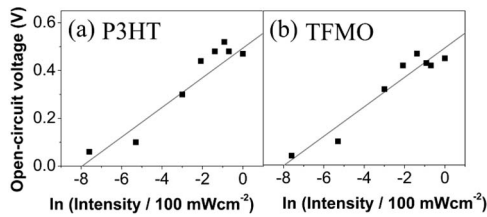
FIG. 4. (Color online) Open-circuit voltage as a function of the logarithm of light intensity for (a) the P3HT/TiO$_2$ device and (b) the TFMO/TiO$_2$ device. Straight lines represent the best fit to the data of the form $V_{oc} = kT/m \ln(\text{Intensity})$.

carrier density, these variations in charge carrier density result in variations in V_{OC}. Therefore, to make a valid comparison of V_{OC} between different material systems, the effect of different densities of photogenerated charge carriers should be accounted for.

To correct for differences in photocarrier densities generated by the different polymer materials, the short-circuit current densities generated by the devices were compared. For a solar cell that behaves as a nonideal diode, current density J is given approximately by $J = J_{SC} - J_0[\exp(eV/mkT) - 1]$, where J_0 is the dark saturation current density, m is the ideality factor, k is Boltzmann's constant, and T is the temperature. V_{OC} is then related to J_{SC} through

$$V_{OC} = \frac{mkT}{e} \ln\left(\frac{J_{SC}}{J_0}\right). \tag{1}$$

Since J_{SC} depends approximately linearly on light intensity, Eq. (1) implies a logarithmic dependence of V_{OC} on light intensity, and such behavior is indeed observed[12] except at the highest light intensities.

Figures 4(a) and 4(b) show the dependence of V_{OC} on light intensity for the polymer/TiO$_2$ devices with the strongest [poly(3-hexylthiophene) (P3HT)] and weakest (TFMO) visible light absorption. For the P3HT/TiO$_2$ and TFMO/TiO$_2$ devices, ideality factors of 2.58 and 2.38 were obtained, respectively. We take an ideality factor m_{ave} of 2.5 as representative of all the polymers in this study. To correct for differences in photogenerated carrier density, the V_{OC} for each device was corrected to the value that it would have if the short circuit current density was equal to that of the P3HT device, assuming that V_{OC} obeys Eq. (1) with an ideality factor of m_{ave}. The correction added to V_{OC} in each case is thus given by

$$\Delta V_{OC,X} = \frac{m_{ave}kT}{e} \ln\left(\frac{J_{SC,P3HT}}{J_{SC,X}}\right), \tag{2}$$

where $J_{SC,P3HT}$ denotes the measured J_{SC} of the P3HT/TiO$_2$ device at 50 mW cm^{-2} AM1.5 irradiation and the label X denotes one of the other polymer/TiO$_2$ devices.

The corrected V_{OC} values are plotted as a function of I_P in Fig. 3(b). The data show an improved linear fit with a gradient of 0.8 ± 0.1. This approaches the dependence (gradient of 1) expected when V_{OC} is controlled by the gap between the HOMO level of the donor and the TiO$_2$ conduction band edge. We note that, in this study, the contact between polymer and PEDOT:PSS anode is expected to be Ohmic in all cases, and should not affect V_{OC}. Taking the TiO$_2$ conduction band edge to lie at 4.2 eV below vacuum, we find

that the measured V_{OC} is less than the maximum V_{OC} determined by the difference between I_P and the TiO$_2$ conduction band edge, by a roughly constant amount of approximately 0.5 V. This is slightly larger than the voltage loss of approximately 0.3–0.4 V reported in Ref. 15 for polymer/([6,6]-phenyl-C$_{61}$-butyric acid methyl ester) (PCBM) cells, and would imply a lower limiting efficiency for polymer/TiO$_2$ than for polymer/PCBM devices. However, further studies on polymer/metal oxide bulk heterojunctions are necessary before the limiting efficiency for polymer/metal oxide devices can be determined.

In conclusion, we have found that the open circuit voltage of hybrid TiO$_2$/polymer devices is strongly dependent on the polymer ionization potential, supporting the view that V_{OC} is limited by the gap between acceptor conduction band edge and donor HOMO energy level. Thus the V_{OC} may be optimised through control of energy level alignment at the interface, either by choice of polymer of appropriate ionization potential, or by modifying the position of the conduction band edge through molecular modification or other surface treatments.

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