Influence of the Work Function of Chemically Modified Indium–Tin–Oxide Electrodes on the Open-circuit Voltage of Heterojunction Photovoltaic Cells

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To understand the origin of the open-circuit voltage of heterojunction photovoltaic (HJ-PV) cells with small-molecular-weight organic thin films, HJ-PV cells with ITO/donor (20 nm)/fullerene (40 nm)/bathocuproine (10 nm)/Al were studied using three kinds of donors and four types ITOs with different work functions.

Since the first report of an organic photovoltaic (PV) cell with the donor (D)/acceptor (A) heterojunction (HJ) by Tang,[1] organic PV cells have attracted attention owing to their ease of fabrication, potential for low-cost productions, and compatibility with flexible substrates.[2] A fundamental understanding of the excitonic nature of organic materials is essential for device engineering.[2d] By the introduction of device concepts such as the mixed[3a] and blended[3b,3c] DA HJs, the exciton-blocking layer (EBL),[3d] and the tandem cell,[3e] the performance of small-molecular-weight[2b] and polymer[2c,2e] organic PV cells has been improved dramatically.

To achieve high power conversion efficiencies of such PV cells, the increase in the open-circuit voltage (V_{oc}) as well as the short-circuit current density (J_{sc}) and the filling factor (FF) is required. However, the origin of V_{oc} is not well understood.[2,4a] For metal/insulator/metal (MIM) type PV cells, the built-in potential (V_{bi}) results from the work function difference $\Delta\phi$ between the electron-collecting (EC) and hole-collecting (HC) electrodes. For so-called "bulk HJ" (Type I) PV cells, Al or Ag with low work functions (ϕ) (4.2 or 4.3 eV) in contact with an A molecule [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) blended with one of various conjugated D polymers is used as the EC electrode, while the polymer film of poly(3,4-ethylenedioxythiophene (PEDOT) doped with poly(styrenesulfonate) (PSS) acts as the HC electrode. ϕ of PEDOT:PSS (5.2–5.3 eV) is higher than that of indium–tin–oxide (ITO) (4.5–4.8 eV). Therefore, $\Delta\phi$ is kept almost constant to be $\approx$1.0 eV, since the Fermi level of the metal electrode is considered to be pinned to the lowest unoccupied molecular orbital (LUMO) level of PCBM (4.2–4.3 eV).[2c,4a] Under such high $\Delta\phi$ in Type I cells, V_{oc} has been found to change linearly with the highest occupied molecular orbital (HOMO) level or the oxidation potential (E_{ox}) of Ds.[2c,4b] In contrast, $\Delta\phi$ is 0.3–0.6 eV for HJ small-molecular-weight organic thin film PV (Type II) cells (i.e., ITO/D/A(C_{60})/bathocuproine(BCP)/Al(or Ag)),[2a] where the bare ITO electrode is mainly used as the HC electrode and the BCP layer functions as EBL and improves electron transport from the C_{60} film to the EC electrode.[3d,5] Recently, V_{oc} of Type II cells with a boron subphthalocyanine chloride (SubPc) D layer was found to be so low as 0.57–0.58 eV,[6] although HOMO of SubPc was estimated electrochemically to be 5.6 eV and thus V_{oc} was expected to be $>$1.0 V from the V_{oc} vs. HOMO level (or E_{ox}) relationship described above. It was also found that closer values (0.97–0.98 V) to the expected V_{oc} were measured only when the thickness of the D layer became very thin (13 nm).[6]

In the present work, we studied how the change in ϕ of chemically modified indium-tin-oxide[7] as the HC electrode affects observed V_{oc} of Type II cells (i.e. various ITO/D (20 nm)/C_{60} (40 nm)/BCP (10 nm)/Al (100 nm)) using three different Ds, i.e., zinc phthalocyanine (ZnPc), rubrene (Rub), and SubPc, and attempted to understand the origin of V_{oc} for the Type II cells.

As the HC electrode, three kinds of chemically modified indium-tin-oxide electrodes were prepared as previously as well as the as-cleaned (ac) ITO electrode.[7] Chemical structures of Ds, ITO modifiers, ϕ,[7] and abbreviations for the resulting ITOs are shown in Figure 1. The organic thin films and an Al top electrode on ITO substrates were deposited via high vacuum thermal evaporation at 7–9 $\times$ 10^{-4} Pa. The Al top electrode was evaporated through a shadow mask defining the device active area of 5 $\times$ 5 mm^2. Current–voltage characteristics were measured in the dark and under AM1.5G, 100 mW/cm^2 using a solar simulator (Yamashita Denso, YSS-50) in air.

Figure 2 shows schematic energy level diagrams for Type II PV cells with (a) Rub (solid line) or SubPc (dotted line) and (b) ZnPc as the D layer. HOMO energies are cited from UPS measurements, while LUMO energies are from the optical absorption edges. For the transport of free electrons, LUMO energies from IPES should be used.[6,8] For estimation of the driving force of the photovoltage generation (Δ_{ph}) from difference between the HOMO level of D and the LUMO level of C_{60},[4b,6] however, the LUMO energies shown in the diagrams are more appropriate, because the binding energy of the geminate e–h ($A^{\cdot -}$–$D^{\cdot +}$) pairs[2b,9] at the DA interface is approximately taken into account via the exciton binding energy.[2d]

Figure 3a shows the correlation between V_{oc} (as to J_{sc}, FF, and conversion efficiency[10]) and Δ_{ph} of three Ds for Type II PV cells with four kinds of ITOs having different ϕ. We expected

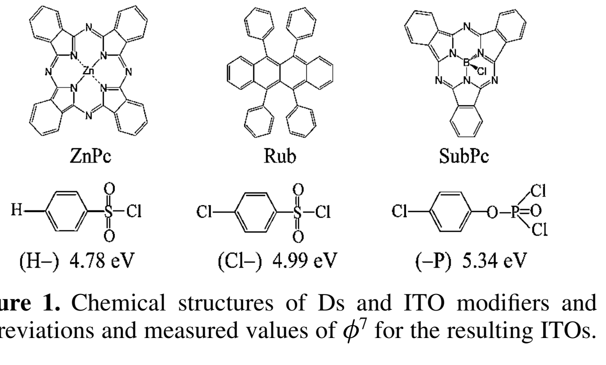

Figure 1. Chemical structures of Ds and ITO modifiers and abbreviations and measured values of ϕ[7] for the resulting ITOs.

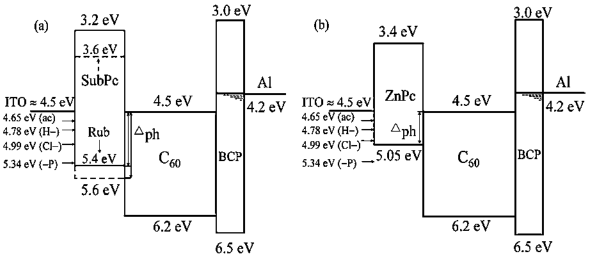

Figure 2. Schematic energy level diagrams for Type II PV cells with (a) Rub (solid line) or SubPc (dotted line) and (b) ZnPc as the D layer.

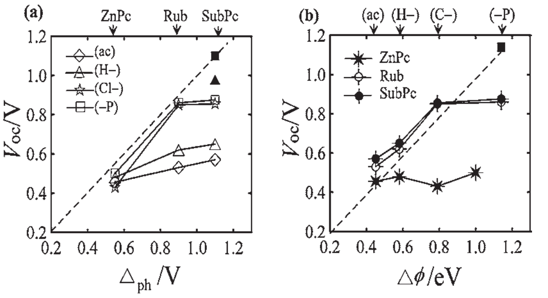

Figure 3. (a) Variation of V_{oc} with Δ_{ph} for three kinds of Ds on various ITOs with different ϕ and (b) a V_{oc} vs. $\Delta\phi$ plot from data in (a). The highest reported[6] and expected V_{oc} are also shown by closed triangle and square, respectively. See SI[10] for V_{oc} (ZnPc at $\Delta\phi = 1.0$ eV).

that V_{oc} would increase linearly with Δ_{ph} on chemically modified (–P) indium-tin-oxide with the highest ϕ (5.34 eV) in the same way as the V_{oc} vs. E_{ox} relationship for Type I,[2c] because $\Delta\phi$ (1.14 eV) is high enough to separate the charges for three Ds. It is likely that the low hole mobility and high reactivity with atmospheric H_2O[11] of SubPc is responsible for its deviated V_{oc}. The reason for this deviation is now under study. On the (ac) ITO ($\phi = 4.65$ eV)[7b] and (H–) ITO with low $\Delta\phi$ (0.45 and 0.58 eV, respectively), V_{oc} increased slightly with the increase in Δ_{ph}. These results suggest that i) high Δ_{ph} is necessary to form the e–h pairs with the high driving force but not sufficient to attain high V_{oc} and ii) high $\Delta\phi$ is needed additionally to separate the e–h pairs into the free charges and to transport them to the respective electrodes. For Rub with the high hole mobility, the expected V_{oc} from Δ_{ph} was observed on (Cl–) and (–P) ITO with high $\Delta\phi$ (0.79 and 1.14 eV, respectively), but much lower V_{oc} was observed on the two ITOs with low $\Delta\phi$. V_{oc} for ZnPc is limited by Δ_{ph} independently of ϕ of ITOs as described below.

In Figure 3b, all data except the highest reported V_{oc} for SubPc[6] in Figure 3a are replotted into a V_{oc} vs. $\Delta\phi$ relationship. As pointed out above, V_{oc} of SubPc on the (–P) ITO is deviated from the expected linear relationship. The expected maximum V_{oc} value from Δ_{ph} is also plotted as a closed square. If this point is included, it is clear that V_{oc} increases almost linearly with $\Delta\phi$ for Type II cells with SubPc (20 nm) on various ITOs. It is also clear from the plots for Rub and ZnPc that observed values of V_{oc} are limited by the expected maximum V_{oc} values from their Δ_{ph} values even if the ITOs with high $\Delta\phi$ are used. The $\Delta\phi$ dependence of V_{oc} observed here is similar to that observed on Type I PV cells with PEDOT HC electrodes having different ϕ adjusted electrochemically.[12]

In conclusion, we have studied the origin of V_{oc} for HJ PV cells (ITO/D/C_{60}/BCP/Al) using ZnPc, Rub, or SubPc as D with different HOMO levels and four types ITOs with different ϕ. The maximum V_{oc} values attainable by the present PV cells were always limited by Δ_{ph} between the HOMO level of D and the LUMO level of C_{60} estimated from the ionization potential and the optical absorption edge of C_{60}. Thus, Δ_{ph} corresponds approximately to the photoinduced energy to form the geminate e–h pairs at the DA interface. However, the selection of D giving high Δ_{ph} is a necessary but not a sufficient condition to obtain high V_{oc}. It was found that the simultaneous use of the chemically modified ITO or a polymer electrode such as PEDOT:PSS with high ϕ is necessary to create enough V_{bi} to separate the geminate e–h ($A^{\cdot -}$–$D^{\cdot +}$) pairs and transport the separated charges to the electrodes and thus to attain high V_{oc}.

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