

Correlation between interface energetics and open circuit voltage in organic and hybrid photovoltaic cells

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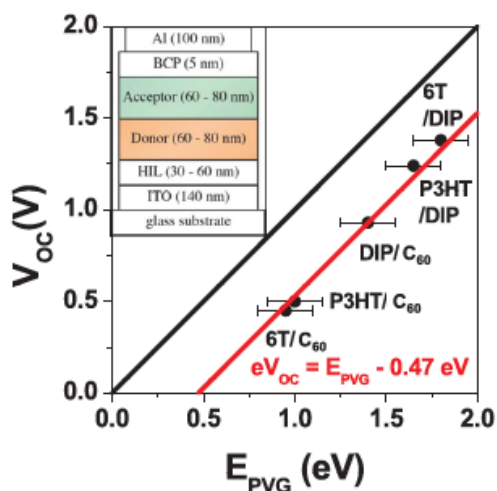
The full understanding of the relationship between solar cell open circuit voltage, V_{OC} , and the electronic structure of the cell, is a crucial step in the development of high performance devices. This is particularly true for excitonic solar cells based on organic small molecule or polymer donor-acceptor (D-A) heterojunctions, or for the new class of solar cells based on hybrid organic inorganic perovskites (HOIP) coupled with electron and hole extraction layers. Many factors ultimately limit the open circuit voltage of a cell, but the electronic structure of interfaces (heterojunctions, contacts) are often dominant.

In the former case, *i.e.*, the organic solar cell, the maximum open circuit voltage, $V_{OC(max)}$ has been loosely related to the energy gap, also called photovoltaic gap, E_{PVG} , between the free hole and free electron transport levels following exciton dissociation at the D-A interface, namely the highest occupied molecular orbital ($HOMO_D$) of the donor and the lowest unoccupied molecular orbital ($LUMO_A$) of the acceptor. Several investigations have shown a linear relationship between $V_{OC(max)}$ and E_{PVG} ,

$$eV_{OC(max)} = E_{PVG} - \delta,$$

although the interpretation of loss term δ between the two values varied significantly from one study to the next.¹⁻³ In order to understand the physical origin of δ , it is therefore necessary to obtain reliable values of E_{PVG} for comparison with the open circuit voltage. Yet, only few independently determined values of E_{PVG} are available for D-A pairs. As a consequence, E_{PVG} is generally assumed to be defined by vacuum level alignment between the two materials, or simply the difference between the ionization energy of the donor (IE_D) and the electron affinity of the acceptor (EA_A), whereas experimental determinations show that E_{PVG} is often increased with respect to this ideal value by the presence of an interface dipole between the two materials. The larger resulting gap implies a larger δ , which must be taken into consideration in the analysis of $V_{OC(max)}$. In the case of the HOIP solar cell, band offsets between the absorber and the hole and electron extraction layers are only beginning to be systematically determined to serve as a basis for the analysis of the device performance.

Therefore we emphasize in this talk the importance of direct determination of the electronic structure of all interfaces in organic and HOIP devices. We give examples of the experimental determination of the “real” E_{PVG} of some small molecule, single D-A heterojunctions, and of two widely used polymer bulk heterojunctions. All of which include a significant interface dipole. The energy level alignment of several HOIP-organic hole transport interlayers is also reviewed. We use ultra-violet, X-ray and inverse photoemission spectroscopies (UPS, XPS, IPES) to determine energy level alignment of *developing or buried interfaces*, which as nearly as possible represent the device interfaces.



The first set of interfaces corresponds to planar D/A heterojunctions formed via vacuum evaporation of small molecules, and for which the progressive formation of the interface can be followed systematically. Examples are C_{60} / diindenoperylene or sexithiophene/ C_{60} . These interfaces all exhibit an interface dipole of the order of 0.1-0.2 eV.⁴ The resulting correlation between $eV_{OC(max)}$ and E_{PVG} is shown in Figure 1, where δ has an average value of 0.47 eV.

The second set of systems are the solution processed D/A blend films, or bulk heterojunctions, such as poly(3-hexylthiophene) (P3HT) / [6,6]-phenyl-C61-butyric acid methyl

ester (PCBM)⁵ and P3HT / indene-C60 bisadduct (ICBA).⁶ We use a lift-off method to access the originally buried interface, which is rich in both P3HT and the acceptor, and thus representative of the bulk heterojunction. We show that the E_{PVG} in these blends are ~ 0.3 eV larger than the value anticipated based on simple vacuum level alignment, and put the loss in voltage at about 0.55-0.6 V for these blends.

Finally, we briefly review the electronic structure of selected interfaces between HOIPs such as MAPbI₃, MAPbBr₃ or CsPbBr₃, and show for some cases the impact of energy level alignment on the open circuit voltage of the cell.⁷

References

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