Tuning the Energy Level Offset between Donor and Acceptor with Ferroelectric Dipole Layers for Increased Efficiency in Bilayer Organic Photovoltaic Cells

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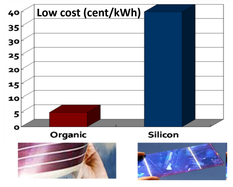
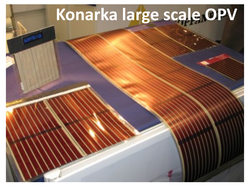
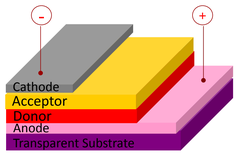
Research motivation

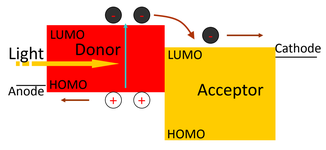




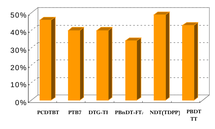
➢ Organic photovoltaic (OPV) technology is one of the most attractive candidates for solving future energy shortage problem due to its advantage of light weight, flexibility, low cost and large scale production.



Typical device structure



Device working principle

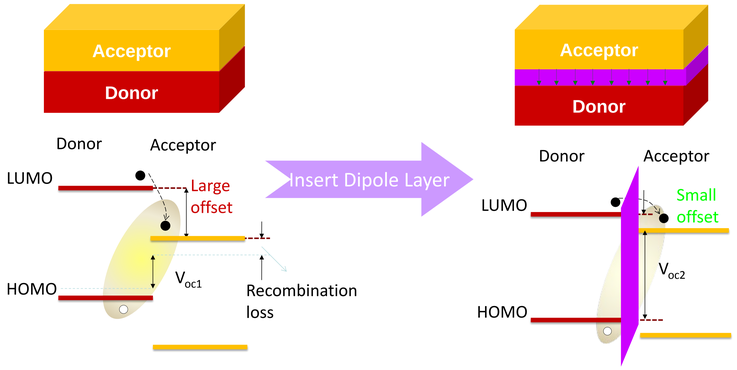


V_{oc} / Bandgap of polymer

➢ Power conversion efficiency (PCE) of OPV devices already exceeds 10%, further increasing the PCE to over 15% is needed for OPV to compete with silicon solar cells and other thin film photovoltaic technologies.

➢ In polymer solar cells with PCE over 6%, none of them has open circuit voltage (V_{oc}) reaching half of the optical bandgap of the semiconducting polymers, caused by the too large lowest unoccupied molecular orbital (LUMO) offsets between the donors and the acceptors.

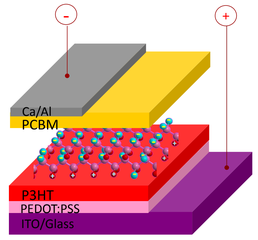
Proposed mechanism

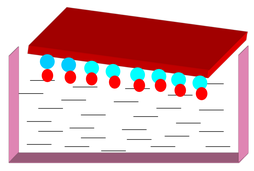


➢ The V_{oc} of OPV devices is determined by the difference of LUMO (or conduction band) of the acceptor material and HOMO (or valence band) of the donor material. A small LUMO offset between the donor and the acceptor is preferred for a high V_{oc}.

➢ A tunable dipole layer, consisting of an ultrathin ferroelectric polymer film, was inserted between the donor and the acceptor semiconductor layers, which shifts the relative energy levels of the donor and the acceptor. Therefore, the V_{oc} could be increased by tuning the LUMO offset between the donor and the acceptor without changing their chemical structures. It is thus a general method to increase the efficiency of OPV devices consisting of any active materials.

Device fabrication and maximum attainable V_{oc}





Langmuir-Blodgett deposition

Real device

➢ In this work, a polyvinylidene fluoride (70%)-trifluoroethylene (30%) copolymer, P(VDF-TrFE), was used as the tunable dipole layer, which was coated by Langmuir-Blodgett (LB) deposition technique.

➢ The P(VDF-TrFE) layer was sandwiched between P3HT and PCBM bilayers which can precisely grow the ferroelectric layer thickness by monolayer (ML) and generates P(VDF-TrFE) with excellent crystallinity.

$$d = \frac{\varepsilon_0 \varepsilon_{FE} E}{\sigma_P q}$$

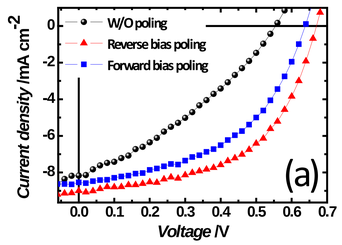
➢ According to above equation, a thickness as thin as 0.6 nm P(VDF-TrFE), about one monomolecular layer, is needed to induce an energy level shift of 0.8 eV.

➢ The P3HT/PCBM system, however, has a V_{oc} output of only about 0.6 V, which is significantly lower than the optical bandgap (~2.0 eV) of P3HT. This discrepancy is caused by a very large LUMO offset close to 1.0 eV.

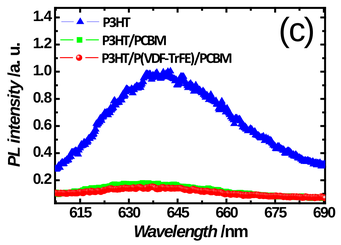
➢ The maximum attainable V_{oc} of 1.5 V which assumes LUMO offset 0.2 V loss for the efficient charge transfer and a V_{oc} loss of 0.3 V due to the non-ideal diode in P3HT/PCBM OPV devices.

Experimental results and discussion

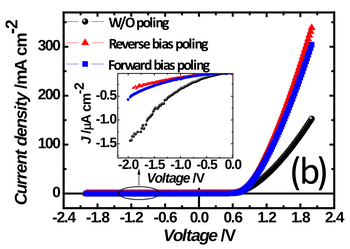
J-V curve measurement



Under light 100 mW cm^{-2}



PL change after insertion P(VDF-TrFE) between P3HT and PCBM layers



Under dark

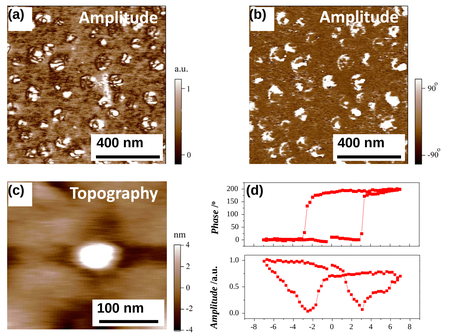
➢ After insertion 1 ML P(VDF-TrFE) LB film between the P3HT and PCBM layers, the photoluminescence (PL) intensity only showed little change, which demonstrated that the 1 ML P(VDF-TrFE) LB film does not hinder photoinduced charge transfer from the donor to the acceptor.

➢ The V_{oc} was increased from 0.55 V to 0.67 V after poling the P(VDF-TrFE) layer by applying a reverse bias on the device, and was poled back with an opposite bias on the device.

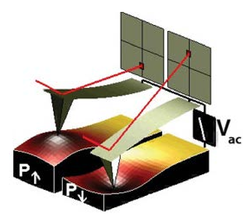
➢ The dark current density was also reduced due to the decreased charge transfer exciton recombination after poling the P(VDF-TrFE) layer by applying a reverse bias on the device.

➢ Thus, the PCE was more than doubled from 1.5% to 3.3%.

Piezoelectric force microscopy measurement



Local piezoelectric response of the P(VDF-TrFE) grains imbedded under thin PCBM layer (20 nm)

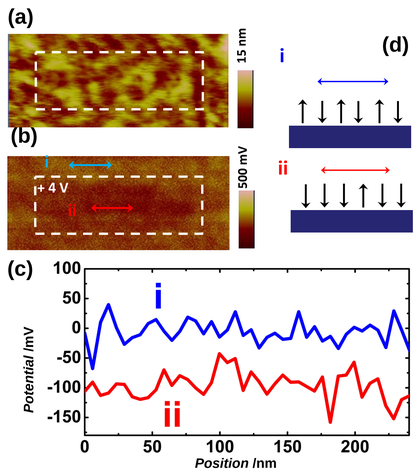


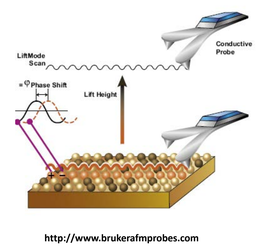
http:// www.asylumresearch.com

➢ As shown in Figure a-b, only approximately 20% of the P3HT surface was covered by the ferroelectric P(VDF-TrFE) nanoislands. It could explain why the obtained V_{oc} is far less than the maximum attainable V_{oc} of 1.5 V since most of the P3HT polymers directly contact with PCBM molecules.

➢ Figure c-f showed that the inserted P(VDF-TrFE) layer was in the ferroelectric state which could be switched between two states by applying opposite bias.

Electrostatic force microscopy measurement





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➢ As shown in the figure a-d, the average surface potential difference is 0.1 V, which is consistent with tuned V_{oc}.

➢ The fluctuation of surface potential is consistent with the nonuniform distribution of the ferroelectric P(VDF-TrFE) nanoislands on P3HT layer.

➢ This result indicates a large potential to further increase the energy tuning capability by the ferroelectric dipoles with increased coverage of the dipole layer.

Conclusions

➢ We demonstrated a method to increase the V_{oc} of bilayer OPV devices by tuning the energy level offset of the donor and the acceptor with tunable ferroelectric P(VDF-TrFE) dipole layers.

➢ Both J_{sc} and FF also increased due to the reduced recombination loss of charge transfer excitons. Thus, a double efficiency was achieved for P3HT and PCBM based bilayer OPV devices.

➢ We expect that a further increase of V_{oc} can be achieved by improving the coverage of the P(VDF-TrFE) dipole layer on P3HT.

➢ The V_{oc} can be potentially improved to above 1.0 V without compromising other photovoltaic parameters such as J_{sc} and FF.

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