

Investigation of the influence of molecular structure at interfaces in polymer
photovoltaic devices

By

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Preface

The following dissertation relates a story about the design, fabrication and operation of polymer-based photovoltaic devices. Recently, the development of clean, renewable energy technologies has become very popular as the environmental effects of continued fossil fuel consumption are becoming socially recognized. The following research focuses upon a niche technology which currently serves only as a laboratory curiosity. Although they have the potential to fulfill the need for inexpensive, renewable energy production, polymer based solar cells are not yet understood well enough to practically implement. The physics which govern the operation and degradation of these devices have yet to be holistically described and the design parameters of their constituent materials are not always clearly linked to device performance. Moreover, the length and time scales over which the important processes occur in these devices are very short (nanometers and femto to nanoseconds). However, the devices are easily made via solution based film casting routes and the chemical structure of the device films is broadly tuneable. The research interest in these devices is thus motivated by the ease of entry into this field and the diversity of investigation specialties whose unique perspective may contribute to its advancement. As such, the achievement of useful device performance will only be realized as the result of highly collaborative research and the combination of efforts from chemists, physicists and other engineering scientists.

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List of Abbreviations

BHJ – Bulk heterojunction

FF – Fill factor

HOMO – Highest occupied molecular orbital energy level

ITO – Indium-tin oxide

J_{sc} – Short circuit current density

LUMO – Lowest unoccupied molecular orbital energy level

OCSC – Off center spincoating

OPV – Organic photovoltaic

P3HT – Poly(3-hexylthiophene)

PCBM – Phenyl C61 butyric acid methyl ester

PCE – power conversion efficiency

PEI – Poly(ethylenimine)

PPE – Poly(phenylene ethynylene)

PSC – polymer solar cell

PSS – Poly(sodium 4-styrenesulfonate)

PTFE – Poly(tetrafluoroethylene)

TCB – 1,3,5-trichlorobenzene

V_{oc} – Open circuit voltage

π - π – Refers to interaction between the pi-bonds which make up the conjugation of a molecule

λ – Refers to photon wavelength

$h\nu$ – Refers to photon energy

Abstract:

Organic photovoltaic devices embody the promise of inexpensive renewable energy. However, before these devices can become commercially successful a stronger understanding of the relationships between material structure, properties and device performance must be built. Interfaces within polymer photovoltaic devices are sites of processes critical to effective device function and are thus the focal point for ongoing research. We systematically investigated the effect of placing molecular spacers at the donor-acceptor interface. As we increased the thickness of the spacer layer we observed suppressed charge transfer, reduced dark current and reduced polaron binding which contributed to a decrease in current density and an increase in open circuit voltage. This result guides the design of materials which seek to mitigate the interfacial distance dependent trade-offs between charge transfer and recombination in order to improve device performance. We also investigated the influence of the molecular structure of the electrode-active layer interface. We found that insulating interfacial layers ensure diode rectification by breaking percolative-active material contact between non-selective electrodes. We also found that strong active layer-electrode interaction leads to charge blocking phase separation in the devices which deleteriously effects performance. This unwanted phase separation can be avoided by inserting a non-interacting interlayer. We also observed that acid- or base-like moieties can be used to modify the work function of ITO in order to achieve good electrical contact with the active layers of a device. These results provide molecular design guidelines for the fabrication of materials for the electrode interface of high performance devices. Besides the interface issues, the low charge carrier mobility of conjugated polymers (CPs) intrinsically limits the thickness, absorption, and performance of photovoltaic devices. We made aligned poly(3-hexylthiophene) films with an epitaxially directing additive and an off-center spincoating technique in order to take advantage of their anisotropic charge carrier mobility. These aligned films are applied in novel in-plane devices where the charge transport direction is abutted with the polymer alignment, providing large enhancements in the open circuit voltage. These results motivate the continued pursuit of CP alignment in devices in order to correlate molecular orientation with device performance.