

DOCTORAL THESIS

Transport, material characterization, and device applications of photovoltaic polymers used in bulk heterojunction solar cells

Lee, Ka Hin

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**Transport, Material Characterization, and Device Applications of
Photovoltaic Polymers Used in Bulk Heterojunction Solar Cells**

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A thesis submitted in partial fulfillment of the requirements
for the degree of
Doctor of Philosophy

Principal Supervisor: Prof. SO Shu Kong

Hong Kong Baptist University

November 2014

Declaration

I hereby declare that this thesis represents my own work which has been done after registration for the degree of PhD at Hong Kong Baptist University, and has not been previously included in a thesis or dissertation submitted to this or any other institution for a degree, diploma or other qualifications.

Signature: _____

Date: November 2014

Abstract

This thesis presents the transport, material characterization, and device applications of photovoltaic polymers used in bulk heterojunction solar cells. These three areas were found to be well correlated. Materials properties affect charge transport behaviors. Charge transport behaviors affect organic photovoltaic (OPV) cell performances. Two typical PV polymers were selected for investigation. They were poly(3-hexylthiophene) (P3HT) and poly[N-9''-heptadecanyl-2,7- carbazole-alt-5,5-(4',7'-di-2- thienyl-2',1',3'- benzothiadiazole)] (PCDTBT).

Different charge transport measurement techniques were employed to study how charge carriers move in OPV materials including space-charge-limited current (SCLC) measurement, dark-injection space-charge-limited current (DI-SCLC) measurement, and admittance spectroscopy (AS). For hole transport measurement on P3HT, electron leakages were found in a presumed hole-only device structure resulting in ill-defined DI-SCLC and AS signals. After inserting a thin electron blocking and trapping (EBT) layer between the active layer and the Au cathode, the electron leakages can be significantly suppressed leading to well-defined transport measurement signals. Applying the EBT layer to the polymer:fullerene bulk heterojunction (BHJ) blends, the transport properties can also be studied.

Charge transport measurements were carried out at different temperatures for Gaussian Disorder Model (GDM) analysis to extract energetic disorders σ and high-temperature limit mobilities μ_{∞} . For P3HT BHJ films, σ were found to be

much smaller than PCDTBT BHJ films. Within the same polymer system, similar σ were extracted. σ can be correlated to the device parameters such as open-circuit voltage V_{OC} and fill factor FF . Large σ was found to limit both V_{OC} and FF .

With the experience of transport measurement for PV materials gained, we focused on a common problem of batch-to-batch variations in device performance. Five batches of amorphous polymers PCDTBT were purchased from two vendors. From gel permeation chromatography, bimodal distributions of molecular weight were observed in all five batches of PCDTBT with different fraction of small molecular weight component. The corresponding charge carrier mobilities and device performances drop significantly with the small molecular weight component. From GDM, all five batches of polymers have similar σ . However, μ_{∞} for each batch of PCDTBT appear to have significant differences. The differences originate from the variation of charge carrier hopping distances caused by different amounts of the small molecular weight component of PCDTBT.

At last, ZnO prepared by low temperature annealing sol gel method was used as functional layers for OPV cells and charge transport measurements. Structural, elemental, energetic, optical, and electrical characterizations were performed to examine the ZnO. The results suggested that the ZnO should be suitable for organic device applications. The applications of the ZnO on inverted OPV cells and charge transport measurements were demonstrated.

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