Systematic Investigation of Morphology of Polymer:Bis-Fullerene Blends for Bulk Heterojunction Organic Photovoltaics

Joseph Smalley
Engineering Science, The Pennsylvania State University (graduated),
Electrical and Computer Engineering, University of California, San Diego

NNIN iREU Site: Interuniversity Microelectronics Center (imec), Leuven, Belgium
NNIN iREU Principal Investigator: Dr. Barry Rand, Polymer and Molecular Electronics, imec
NNIN iREU Mentor: Eszter Voroshazi, Polymer and Molecular Electronics, imec, Katholieke Universiteit, Leuven, Belgium
Contact: jsmalley@ucsd.edu barry.rand@imec.be, eszter.voroshaz@imec.be

Abstract:

Active layer morphology plays an essential role in determining the performance of polymer:fullerene bulk heterojunction (BHJ) organic photovoltaic (OPV) cells. Upon processing with several amorphous polymers, a promising new bis-fullerene—bis-oquino dimethane C_{60} (bis-oQDMC$_{60}$)—was recently found to exhibit undesired formation of holes at the surface with diameter on the order of 10's of nanometers at a density of approximately 25 μm^{-2} (~ 0.1-1.0% of film surface area). This poor film formation significantly hinders device performance. We prepared and characterized BHJ thin films to systematically study the processing conditions under which these holes arise. Spin-coated blends of poly(3-hexylthiophene) (P3HT):bis-oQDMC$_{60}$ and P3HT:bis-phenyl-C_{61}-butyric acid methyl ester (PCBM) were investigated by comparison to the well-known P3HT:PCBM system. The blends were characterized by atomic force microscopy (AFM), ultraviolet-visible (UV-Vis) spectrophotometry, and contact angle measurements. Throughout the annealing temperature range of 27°C-130°C, we found P3HT:bis-oQDMC$_{60}$ (1:4 ratio) always exhibited hole formation. Furthermore, at room temperature, films of P3HT:bis-PCBM (1:4) also exhibited holes, indicating hole formation may be a general property of bis-fullerene derivatives at high loadings within polymer films. Measurement of the absorption spectra and contact angle of our samples revealed the likelihood that the nanoholes form a porous network in the bulk.

Introduction:

Because they can be fabricated inexpensively, OPV cells need have neither the efficiency nor lifetime of inorganic solar cells. To date, researchers have reported a record power conversion efficiency of 8.3% [1], and outdoor operating lifetimes of more than one year [2], with hopes of reaching an efficiency of over 10%. One route by which efficiency can be improved is through the use of novel acceptor materials that enable a high open circuit voltage, V_{oc}. Whether this increased V_{oc} can be realized without a related reduction in short circuit current density, J_{sc}, is an essential question for determining the utility of these new materials.

With a higher V_{oc} than the reference P3HT:PCBM, and a comparable J_{sc}, the P3HT:bis-oQDMC$_{60}$ (1:1) blend demonstrates that bis-oQDMC$_{60}$ is a promising acceptor [3]. In contrast, Figure 1 shows the performance of an OPV cell made of poly(2-methoxy-5-(3',7'-dimethyl-octyloxy))-p-phenylene vinylene (MDMO-PPV):bis-oQDMC$_{60}$(1:3). In this unfortunate case, we see that V_{oc} is improved at the expense of a much lower J_{sc}. AFM scans revealed that the unannealed blend of MDMO-PPV:bis-oQDMC$_{60}$ exhibited nanoholes whose properties are explained in the abstract. Whether the loading factor or annealing conditions

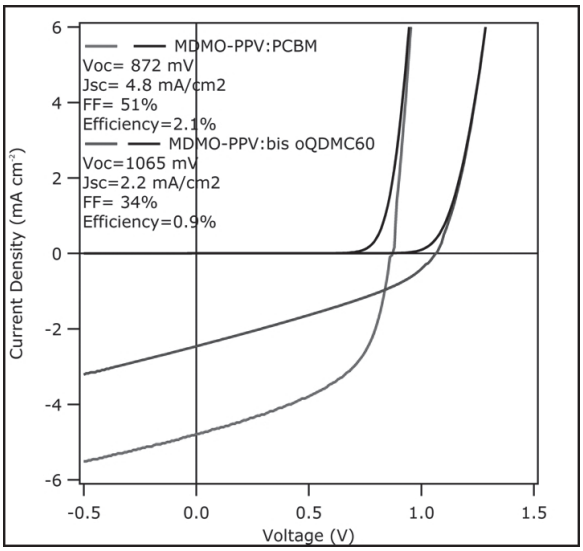

Figure 1: Current density vs. voltage characteristics of MDMO-PPV:PCBM and MDMO-PPV:bis-oQDMC$_{60}$, measured under AM1.5G simulated solar illumination.

were responsible for formation of theses holes, and hence the reduced current density, was an open question, as was the extent of the holes in the bulk.

Methods:

Blends of P3HT:bis-oQDMC$_{60}$ and P3HT:bis-PCBM were investigated by comparison to the well-known P3HT:PCBM system. Substrates consisted of glass coated with indium tin oxide (ITO) that were cleaned with sequential ultrasonic baths in soapy water, deionized water, acetone, and isopropyl alcohol, followed by an ultraviolet radiation cleaning. Afterwards, a 25 nm thick poly(3,3-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) film was spin-coated and the samples were annealed in nitrogen for 10 min at 130°C. Solutions of P3HT and bis-oQDMC$_{60}$, each dissolved in odichlorobenzene, were prepared and then combined in respective ratios. These blends were deposited by spin-coating on the PEDOT:PSS layer and followed by an optional 10 min annealing in nitrogen at 130°C, or a variable temperature.

The blends were characterized by AFM, UV-Vis spectrophotometry, thickness, and contact angle measurements.

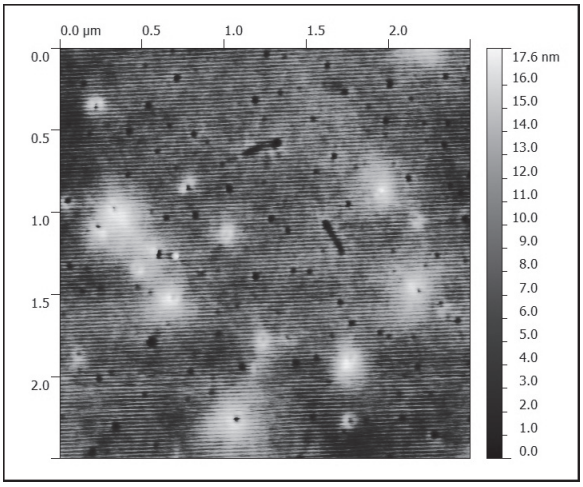

Figure 2: AFM scan of unannealed P3HT:bis-oQDMC$_{60}$ (1:4).

Results and Discussion:

Throughout the annealing temperature range of 27°C-130°C, we found P3HT:bis-oQDMC$_{60}$ (1:4) to always exhibit hole formation. Figure 2 shows the surface of an unannealed sample of P3HT:bis-oQDMC$_{60}$ (1:4). At room temperature, films of P3HT:bis-PCBM (1:4) also exhibited holes, indicating hole formation may be a general property of bis-fullerene derivatives at high loadings within polymer films.

Absorption measurements suggested that the holes affect absorption in the bulk of the film. As seen in Figure 3a, higher loading ratios of P3HT:PCBM had higher attenuation coefficients, resulting from the fact that absorption of PCBM was strongest between 300 and 400 nm. For P3HT:bis-oQDMC$_{60}$, a similar trend was expected, because bis-oQDMC$_{60}$ also absorbs more strongly at lower wavelengths. However, the opposite trend was exhibited; viz, higher loading ratios have lower attenuation coefficients. We attributed this unexpected trend to the presence of a porous network of nanoholes at the 1:4 and 1:3 ratios, which was supported by contact angle measurements.

The contact angles of water on the active layer of the 1:4 and 1:3 ratios of P3HT:bis-oQDMC$_{60}$ were measured to be much lower than any of the other samples. During measurement, we observed that the water dissolved the PEDOT:PSS layer underneath the active layer upon which water was dropped. The dissolved PEDOT:PSS then effectively washed away the active layer, causing the measurement to record values similar to water in contact with the glass substrate. Based on this observation and our absorption measurements, we concluded that the holes do indeed form a porous network throughout the bulk, allowing water to pass through and limiting the absorption considerably.

Conclusion:

We have prepared and characterized samples of P3HT:bis-oQDMC$_{60}$ and compared them to P3HT:PCBM and P3HT:bis-PCBM. Our results indicate that hole formation may be a general occurrence for bis-fullerenes blended with polymers. Additionally, we have strong evidence from UV-Vis and contact angle measurements suggesting that the nanoholes form a porous network. These results are valuable for continued study of polymer:bis-fullerene adducts, and ultimately for high-performance OPV.

Acknowledgments:

Foremost, I thank my mentor, Eszter Voroshazi, for her guidance throughout all of this work. I also thank Dr. Barry Rand, for overseeing the progress of this research. Finally, I thank the National Nanotechnology Infrastructure Network International Research Experience for Undergraduates (NNIN iREU) Program and the National Science Foundation for financial support.

References:

[1] M.A. Green et al. Progress in Photovoltaics: Research and Applications, 19, 562-572 (2011).

[2] J. Hauch et al., Solar Energy Materials and Solar Cells, 92, 7, 727-731 (2008).

[3] E. Voroshazi et al. J. of Materials Chemistry, submitted May 2011.

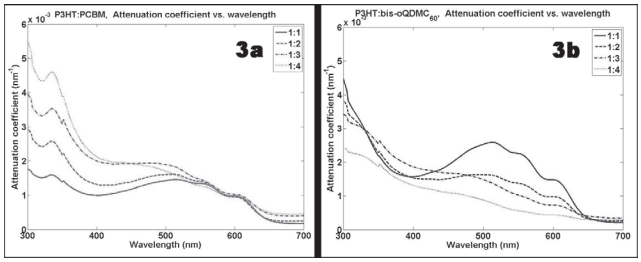

Figure 3: Absorption of P3HT:fullerene for various ratios: (a) P3HT:PCBM, (b) P3HT:bis-oQDMC$_{60}$.