

## Organic Electronics and Photovoltaics

### Objective

Organic electronics and photovoltaic technology are reaching critical mass with the establishment of a U.S. consortium and the recent introduction of new products into the marketplace. Manufacturing of products based on organic semiconductors, however, continues to be hindered by poor reproducibility and process-dependent properties. We develop an integrated suite of measurement methods to tie the electrical and photovoltaic performance of organic semiconductor devices to the materials structure of the layers produced by the manufacturing processes. By providing the measurement link for the structure-processing-performance paradigm, our methods will rationally accelerate product development, enable standard measurements and increase manufacturing output through science-based process design and process control approaches.



Merck Chemicals

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Corning

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National Renewable  
Energy Laboratory

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Luna Innovations

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Plextronics

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Polyera

### Impact and Customers

Organic electronic devices have applications in displays, photovoltaics, sensors, logic, lighting and radio-frequency identification tags. Their market is predicted to be more than \$44 billion globally by 2018 (Transparency Market Research, April 2012).

Our measurements have provided structural insight to help guide materials development at Merck Chemicals, Corning, and other manufacturers.

NIST is an organizer of the yearly International Summit on Organic Photovoltaic Stability hosted in 2011 on the National Renewable Energy Laboratory (NREL) campus. NREL is also a scientific collaborator.

We have engaged the Flextech Alliance by organizing a special session at its annual meeting and hosting a Flextech workshop for measurements and standards.

Collaborators include Luna Innovations, Plextronics and Polyera. A solar company embedded one of its employees at NIST in Gaithersburg for a Cooperative Research and Development Agreement collaboration.

### Approach

Developing commercial products based on organic electronics requires materials that deliver predictable and reproducible performance. One advantage of these materials is their compatibility with versatile solution processing methods. However, this advantage can lead to unpredictable performance and poor reproducibility because the critical microstructure of the material forms dynamically as the solution dries during manufacturing. Many process parameters influence the drying process and the microstructure formation is often hard to control.

To address these challenges, we develop quantitative methods to correlate chemical structure and process control variables to performance via microstructure measurements. A combination of spectroscopic tools (infrared, visible and X-ray), diffraction and scanning probe microscopy provides sufficiently detailed characterization to isolate the contributions of individual structure and processing variables. This integrated measurement platform provides a rational basis for informing process design, and it will further accelerate materials development by separating the molecular basis for electric performance from the process-induced variability. *In situ* variations on fast and low-cost versions of these techniques will provide a robust platform for science-based process control.

## Accomplishments

Conjugated, fused ring polymers with alkyl side chains constitute a general class of organic semiconductors, offering some of the best thin film charge mobilities to date. Determining how the packing structure of these polymers impacts their charge mobility can be challenging. In early work, we focused on the characterization of a class of polymer semiconductors (pBTTTs) with extremely high crystallinity. The high charge mobility in these materials was thought to originate in facile two-dimensional transport both along the polymer chain and between chains via  $\pi$ - $\pi$  stacking.

More recent work has caused us to revise this perspective. In collaboration with Imperial College London, we have discovered that several materials can exhibit excellent charge mobility even while having predominantly face-on orientation or lacking long range order entirely, both of which should dramatically limit charge transport via  $\pi$ - $\pi$  stacking. Other work with highly aligned polymer films has shown that transport occurs predominantly along the polymer backbone, with charge transport via  $\pi$ - $\pi$  stacking being poor. Together

these results offer a new picture of charge transport in these polymers: it is predominantly one-dimensional along the polymer backbone, with occasional hopping via  $\pi$ - $\pi$  stacking sufficient to move between chains. The structural figure of merit is therefore not the long range order, but the local molecular order (e.g., local ring co-planarity). An important implication of this is that new materials can simultaneously have high ductility and high charge mobility, a great combination for new flexible electronics products.

We have also investigated the role of order in organic photovoltaic devices. In collaboration with the University of Chicago, we measured the structure of a bulk heterojunction solar cell with an active layer of the polymer PTB7 blended with the fullerene PC71BM. This blend is produced by Solarm Energy, Inc. and features power conversion efficiency greater than 7%. By reconciling order information from scattering with orientation information from spectroscopy, we determined that the polymer was only  $\approx 20\%$  ordered. The importance of order in organic solar cells is still hotly debated, but

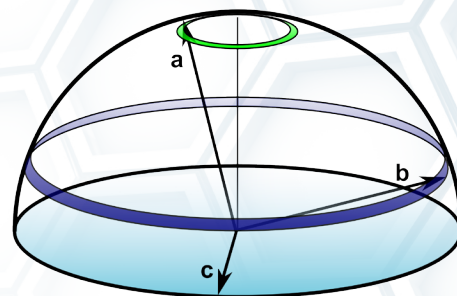


Figure 2: Solid angle considerations can create the illusion of orientation in grazing incidence diffraction of an isotropic material.

our work shows conclusively that high order is not a prerequisite for high efficiency.

We provided a critical review and guide to measurements for the nanoscale structure of organic photovoltaic devices in an invited article in the journal Energy and Environmental Science. We discussed organic bulk heterojunction structural measurements of contemporary interest and importance including vertical stratification, molecular orientation and order, and nanoscale morphology. Specific recommendations were made regarding the technical implementation of some popular techniques, with an eye toward the elimination of artifacts, ambiguous data and misinterpretation.

Moving forward, we are adapting our methods to measure aspects of structure *in situ* during manufacturing. Our early work has focused on fast spectroscopic and frequency-based electrical techniques, but we will soon add fast X-ray scattering. These techniques will be implemented on a slot-die coater for roll-to-roll manufacturing, and our work will be focused toward informing process design choices and providing robust, science-based process control.

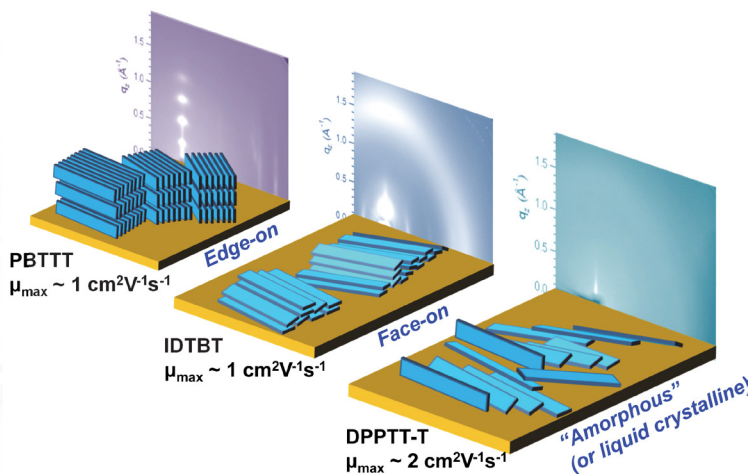


Figure 1: X-ray diffraction patterns show that some materials with high charge mobility, such as DPPTT-T, have very little long-range order.

## Learn More

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## Publications

DM DeLongchamp, RJ Kline and A Herzing, Nanoscale structure measurements for polymer-fullerene photovoltaics, *Energy & Environmental Science*, **5**, (3), 5980-5993 (2012).

MR Hammond, RJ Kline, AA Herzing, LJ Richter, DS Germack, HW Ro, CL Soles, DA Fischer, T Xu, LP Yu, MF Toney and DM DeLongchamp, Molecular Order in High-Efficiency Polymer/Fullerene Bulk Heterojunction Solar Cells, *ACS Nano*, **5**, (10), 8248-8257 (2011).

XR Zhang, LJ Richter, DM DeLongchamp, RJ Kline, MR Hammond, I McCulloch, M Heeney, RS Ashraf, JN Smith, TD Anthopoulos, B Schroeder, YH Geerts, DA Fischer and MF Toney, Molecular Packing of High-Mobility Diketo Pyrrolo-Pyrrole Polymer Semiconductors with Branched Alkyl Side Chains, *Journal of the American Chemical Society*, **133**, (38), 15073-15084 (2011).

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