## Nanoscale Morphological Characterization of Bulk-heterojunction Organic Photovoltaics via Energy-filtered Transmission Electron Microscopy

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A commonly employed design for producing high-efficiency photovoltaic cells using organic semiconductors is the bulk-heterojunction (BHJ) architecture. Typically, this consists of an interpenetrating, three-dimensional (3-D) network of donor and acceptor materials [1] produced via spin- or blade-coating from a co-solution of the two precursors. A number of morphological features are expected to produce a high-performance device, including a degree of phase separation that is on the order of the mean-free-path for excitonic recombination (typically, 10 nm – 20 nm) and a network configuration which allows for an uninterrupted vertical pathway to facilitate charge transport to the relevant electrode [2]. These and other features are strongly influenced by the processing parameters used in fabrication such as the film drying rate after deposition, the extent of polymer crystallization, and any subsequent thermal or chemical treatments. In order to more fully understand the complex interplay between fabrication conditions, morphology, and device performance, robust characterization techniques are required that, ideally, can reveal the 3-D distribution of the two phases within the film at nanometer length scales.

In this talk, the use of energy-filtered transmission electron microscopy (EF-TEM) for morphological characterization of several BHJ systems will be detailed. EF-TEM is an analytical technique where real-space images are formed using electrons which have lost a specific amount of energy. In the case of BHJ films, a difference in the electron density between the constituent phases produces spectral shifts in the plasmon-loss region of the energy loss spectrum. This provides an avenue to generate contrast between the donor and acceptor materials and to spatially map their extent. In cases where bright-field imaging produces insufficient contrast between the two materials, as is often the case in BHJ devices, this approach is especially powerful. In addition, compositional differences between the two phases can be quantitatively assessed by imaging with those electrons which have lost a characteristic amount of energy due to inner-shell ionization of atoms within the material [4,5]. Finally, the EF-TEM signals just described are largely incoherent and obey the projection requirement for electron tomography [6]; thus enabling three dimensional characterization of these complex, nanoscale architectures [3].

## References

- [1] G. Yu *et al.*, "Polymer photovoltaic cells: enhanced efficiencies via a network of internal donoracceptor heterojunctions," *Science*, vol. 270, pp. 1789-1791, no. 5243, Dec. 1995.
- [2] C. Brabec et al., Organic Photovoltaics: Concepts and Realization. Berlin: Springer, 2003.
- [3] A. A. Herzing *et al.*, "3D nanoscale characterization of thin-film organic photovoltaic device structures via spectroscopic contrast in the TEM," *J. Phys. Chem. C*, vol. 114, no. 41, pp. 17501-17508, 2010.
- [4] D. R. Kozub *et al.*, "Polymer crystallization of partially miscible polythiophene/fullerene mixtures controls morphology," *Macromolecules*, vol. 44, no. 14, pp. 5722-5726, 2011.
- [5] A. A. Herzing *et al.*, "Visualization of phase evolution in model organic photovoltaic structures via energy-filtered transmission electron microscopy," *ACS Nano*, to be published.
- [6] M. Weyland and P. A. Midgley, "Extending energy-filtered transmission electron microscopy (EFTEM) into three dimensions using electron tomography," *Microsc. Microanal.*, vol. 9, no. 6, pp. 542-555, 2003.