608d Measuring Structure and Order Development in Organic Semiconductor Films with Soft X-Ray Spectroscopy

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Developing correlations between the structure of organic semiconductor films and their electrical performance will enhance the deterministic and rational design of new materials, composites, and processes to meet emerging industrial applications. We use Near-Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy as a powerful non-destructive method to evaluate the structure and chemistry of thin organic semiconductor films. Using NEXAFS, a depth profile of molecules containing C, N, O, and F bonds can be determined with nanometer resolution through the top (2 to 10) nm of the film. Average bond orientation relative to the substrate can be quantified, particularly the orientation of conjugated planes of organic semiconductors and conductors.

We present two examples of structural correlations for different types of organic semiconductors. First, we investigate how processing conditions such as solvent selection and drying rate can influence microstructure development in highly regioregular poly(3-hexylthiophene) (P3HT) films. The development of favorable morphology with enhanced π interactions in the film plane was quantified using NEXAFS and correlated to improved performance in a field effect transistor (FET) configuration. Even the best-performing P3HT films exhibit only a small preferred conjugated plane tilt away from isotropy or a balanced distribution. The small deviations in preferred ensemble tilt angle that we do observe are responsible for up to one order of magnitude variation in field effect mobility.

Second, we employ NEXAFS to examine the chemical conversion, order development, and defect formation of thermally convertible, soluble oligothiophenes. Microstructure development over a range of conversion temperatures was evaluated, and the FET mobility of these molecules was found to correlate strongly to structural development. We observe four distinct orientation regimes for these materials, two of which are highly ordered, and two of which are quite disordered. The orientations adopted within each regime change dramatically as the primary chemical structure of the core oligothiophene is extended from six to seven thiophene repeats. The best performance was realized at full conversion, where the oligothiophene long axes adopted a vertical orientation, enabling strong π interactions in the plane of hole transport.

The sensitivity of NEXAFS to π-bonds, its insensitivity to optical quality, and its ability to probe nanoscale films provide an ideal measurement platform for the systematic investigation of organic semiconductors and conductors. The correlations that result delineate clear routes to enhance operational field effect mobility in polymer and small molecule organic semiconductors.