

Understanding Thin Film Structure for the Rational Design of High-performance Organic Semiconductors for Plastic Electronics

Organic semiconductors are attracting considerable research interest due to their potential applications in low-cost electronics such as organic light emitting diode (OLED) displays, RF identification tags (RFID), smart cards and electronic paper. The development of π -conjugated materials, which are composed of alternating single and double chemical bonds, are the foundation of these applications. In the past decade research in this field has progressed to the extent that desirable charge transport in the organic semiconductor film in organic thin film transistors (OTFT) can be achieved through molecular design by selective placement of electron-rich, electron-withdrawing, and aromatic groups in different parts of the molecule. Although the electronic properties are easily tuned by molecular design, the molecular packing within the thin film and the film microstructure have a significant influence on the OTFT performance. Despite this importance, this interrelationship between molecular structure, thin film molecular packing and charge transport are only poorly understood.

Most previous structural characterization of organic semiconductors were performed on bulk crystals, and these bulk structures were correlated with thin film charge transport. However, thin film structures may be significantly different from bulk crystal structures. For example, in pentacene the thin film structure is known to be significantly different from its bulk structure. Hence to directly correlate molecular structure and packing with thin film charge transport, it is crucial to obtain the detailed structure of the organic semiconductor in thin film form.

A team of researchers from SSRL and Stanford University have developed a methodology to precisely determine the molecular alignment in organic thin films consisting of rigid molecules. The team used both grazing incidence X-ray diffraction (GIXD) and near edge X-ray absorption fine structure (NEXAFS) spectroscopy to elucidate the organic semiconductor film structure. The unit cell, crystallography symmetry and number of molecules in the unit cell were first identified from GIXD. The molecular orientations within the unit cell were then determined using crystallographic methods (assuming a rigid molecule). The molecular geometry was then checked using a semi-empirical computational method.

The methodology was applied to tetraceno[2,3-b]thiophene, a semiconductor material recently reported by the Bao research group at Stanford (see Figure 1 for chemical structure). For simplicity this is referred to as thiotetracene. This material has a high field-effect mobility of $0.45 \text{ cm}^2/\text{Vs}$. Its chemical structure closely resembles pentacene (i.e., the terminal benzene ring in pentacene is replaced by a thiophene ring), and it is of interest to compare its thin film structure with that of pentacene.

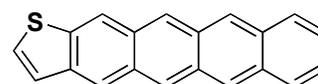


Figure 1: Chemical structure of tetraceno[2,3-b]thiophene (thiotetracene)

Figure 2(a) shows the GIXD pattern taken on SSRL beam line 11-3 for a 20nm thick thiotetracene film grown at 60°C on an OTS treated Si substrate. Using the diffraction intensities measured from this film, the molecular alignment in the unit cell was calculated by crystallographic refinement. The resulting empirically determined alignment of thiotetracene molecules in the unit cell has two molecules per unit cell with a herringbone motif: the molecular tilt angles are 3.7° and 10.5° and the herringbone angle (angle between the planes of the two molecules in the cell) is 59.5° (see Fig. 2(b)). The researcher

team verified this result using an energy minimization calculation. The theoretically predicted optimal arrangement also shows a herringbone-like alignment of the two molecules: the first molecule exhibits a tilt angle of 4.1° with respect to the surface normal, while the second molecule has a slightly larger tilt angle of 9.6° . The herringbone angle is 49° . The resultant structure is nearly identical to that obtained from crystallographic refinement.

Using NEXAFS spectroscopy, the researchers obtained an independent experimental verification of the tilt angle of the thiotetracene molecules. From the incidence angle dependence of the NEXAFS spectra, the projections of the molecular distribution function can be found. The NEXAFS spectra obtained on SSRL beam line 10-1 for a 2 nm thiotetracene film grown at 60°C on OTS treated silicon are shown in Figure 2 (c), exhibiting a clear incidence angle dependence. The resonances between 284 and 286 eV are related to excitation of carbon 1s electrons to the unoccupied π^* orbital of the sp^2 hybridized carbon atoms in the benzene and thiophene rings, which are oriented perpendicular to the ring plane. The higher intensity of the π^* resonances for normal incidence (90°) indicates that the molecules are approximately oriented along the surface normal. Quantitative analysis of the polarization dependence yields an

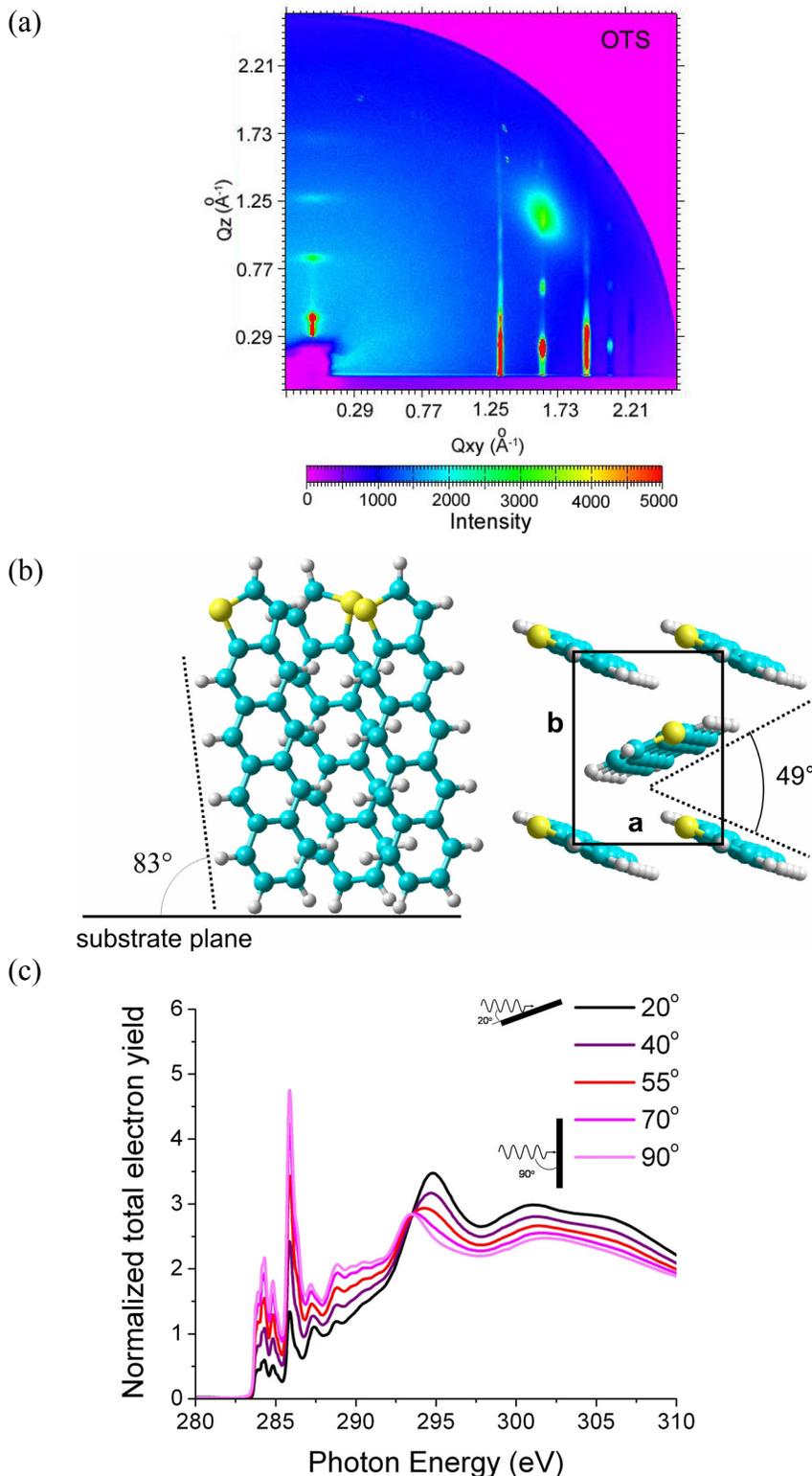


Figure 2: (a) 2D GIXD pattern of a 20 nm film of thiotetracene deposited at 60°C on an OTS treated Si substrate. The large green spot is due to diffuse scattering from the Si substrate. The diffuse vertical streaks are due to the thin film. (b) Thin film structure. (c) Normalized NEXAFS spectra for thiotetracene deposited at $T_D = 60^\circ\text{C}$ on an OTS treated Si surface with a nominal thickness of 2 nm.

average tilt angle of 10° to the surface normal consistent with both the GIXD structural model and the energy minimization calculation. The slightly larger tilt angle of the NEXAFS data could be indicative of the presence of non-crystalline regions within the film.

As a result of the application of a combination of theoretical and experimental techniques - GIXD and structure refinement of the diffraction data, energy minimization packing calculations and NEXAFS - detailed information was obtained on the molecular packing of the thiotetracene molecules in a thin film. The development of this methodology aids in understanding the influence of molecular structure on thin film microstructure and charge transport. Studies such as these will enable the development of predictive models of the dependence of transport on structure and will hence facilitate rational materials design.

Primary Citations:

Thin film structure of tetraceno[2,3-b]thiophene characterized by grazing incidence X-ray scattering and near-edge X-ray absorption fine structure analysis, Q. Yuan, S.C.B. Mannsfeld, M.L. Tang, M.F. Toney, J. Lüning, Z. Bao, J. Am. Chem. Soc. **130**, 3502 (2008)

High-performance organic semiconductors: Asymmetric linear acenes containing sulphur, M. L. Tang, T. Okamoto, Z. Bao, J. Am. Chem. Soc. **128**, 16002 (2006)

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