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## FOR MORE INFORMATION

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## Thickness Dependence of Microstructure in Semiconducting Films of an Oligofluorene Derivative

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*The measurement and optimization of microstructure development in organic semiconductor films is valuable because microstructure critically impacts performance. We use surface-sensitive near edge x-ray absorbance fine structure (NEXAFS) spectroscopy to study the thickness dependence of microstructure in thin films of an organic semiconductor. We find that the molecule exhibits two different microstructure phases: one with large terraces within which molecules exhibit a strongly vertical orientation, and one with much smaller domains within which molecules exhibit a mildly horizontal orientation. We create transistors from each phase and confirm that the vertical microstructure with optimal  $\pi$  orbital alignment delivers superior charge carrier mobility.*

Organic semiconductors will soon enable the low-cost fabrication of electronics on flexible substrates because they can be deposited directly from fluids. Unlike monolithic inorganic semiconductors such as silicon, organic semiconductors form a microstructure dynamically after deposition in a manner unique to each molecular structure. Measuring this microstructure is particularly challenging because the films are typically 20-50 nm thick, polycrystalline, and composed of complex molecules with chemically diverse subunits; x-ray diffraction alone is often not sufficient to solve the structure. The microstructure critically impacts performance because it determines the  $\pi$  orbital alignment in the film, and  $\pi$  orbital overlap enables charge carriers to move between molecules.

We used near edge x-ray absorbance fine structure (NEXAFS) spectroscopy to study the thickness dependence of microstructure in thin films of organic semiconductors. The application of surface spectroscopy to a well-ordered crystalline

film allows us to isolate the configurations of the diverse chemical moieties of the molecules forming the lattice. The surface sensitivity of NEXAFS allows us to follow the development of these configurations as a film grows. We apply this technique to an oligofluorene derivative DDFTTF, which consists of an aromatic fluorene – bithiophene – fluorene core that is end-substituted with aliphatic dodecyl groups, as shown in **Figure 1**.

The substrate-relative orientations of the aromatic core and aliphatic end chains of DDFTTF can be isolated by the Carbon K-edge

NEXAFS resonances illustrated in **Figure 1**. The  $1s \rightarrow \pi^*$  orientation is orthogonal to the aromatic conjugated plane, while the  $1s \rightarrow \sigma^*$  is dominated by the long axes of the aliphatic end chains. Incident angle-dependent NEXAFS spectra of thin DDFTTF films deposited on a heated substrate are shown in **Figure 2A**. The variation in the  $\pi^*$  resonance indicates that the conjugated plane is edge-on upon the substrate surface. This vertical microstructure is optimal for carrier mobility in transistors because the  $\pi$  orbitals are aligned in the plane of the film, which is the transport direction. The variation in the  $\sigma^*$  resonance indicates that the end chains are preferentially vertical but somewhat tilted. Comparing the allowed end chain tilt to the vertical lattice spacing proves that the end chains must be interdigitated or folded.

When DDFTTF is deposited on colder substrates, it exhibits a transition from this vertical microstructure to a more horizontal microstructure, which reverses the variations of the resonances, as shown in **Figure 2B**. By



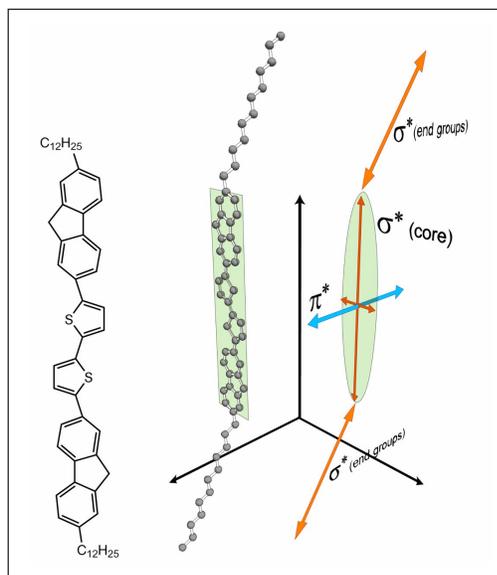
Authors Dan Fischer (left) and Dean DeLongchamp

varying thickness and temperature over a larger range, we find that the relative distribution of these two preferential microstructures depends on the distance of the domains from the substrate and the substrate temperature during deposition.

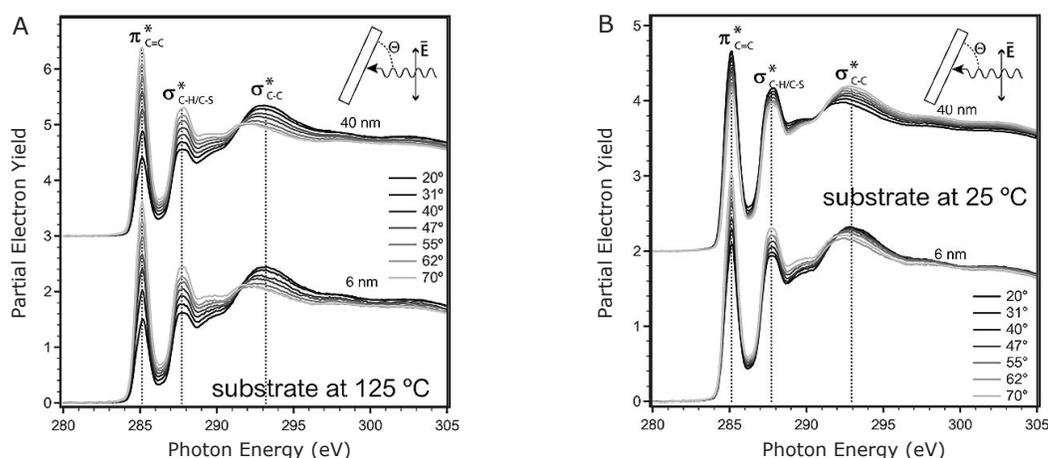
The value of this method is confirmed using a lamination tech-

nique to create field effect transistors that can be both bottom- and top-gated. A laminated elastomer is used as a dielectric on the top interfaces. From these transistors we measure the saturation hole mobility at the top and bottom interfaces of DDFTTF films. We find that local microstructures with greater  $\pi$  orbital alignment in the transistor source-drain plane, such as those

deposited in thin films at elevated substrate temperature, correlate directly to better local saturation hole mobilities. These correlations illustrate how fundamental microstructure studies can lead to practical guidelines for the knowledge-based process improvement and performance enhancement of organic electronics materials.



**Figure 1.** The DDFTTF molecule from three perspectives. From left to right: the DDFTTF primary chemical structure; an isometric view of DDFTTF as optimized by MOPAC (alone in vacuo); and a corresponding view of the directionality of DDFTTF carbon-carbon vector orbitals in the NEXAFS carbon K-edge. The conjugated plane is represented in green, the  $\sigma^*$  orbital vectors are in orange, and the  $\pi^*$  orbital vector is in blue.



**Figure 2 .** (A) NEXAFS PEY spectra variation with incident angle for films deposited on hot substrates to 6 nm and 40 nm. (B) NEXAFS PEY spectra variation with incident angle for films deposited on room temperature substrates to 6 nm and 40 nm.