

Organic semiconductor structure and chemistry from Near-edge X-ray absorption fine structure (NEXAFS) spectroscopy.

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ABSTRACT

The ability to measure the structural development of organic semiconductor films and correlate it to the electrical characteristics of organic devices such as thin film transistors (OTFTs) is needed to facilitate the commercialization of this technology. Synchrotron-based Near-Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy is a powerful tool that meets this need because it can non-destructively reveal both the structure and chemistry of thin organic films. The density of bonds involving carbon, nitrogen, oxygen, and fluorine can be quantified, a depth profile can be developed, and bond orientation can be determined. Here, we outline the principles of NEXAFS experimentation and data analysis with an emphasis on their application to organic semiconductor thin films. NEXAFS spectra of model organic semiconductors such as pentacene and poly(3-hexylthiophene) (P3HT) are used to demonstrate how NEXAFS can enhance understanding of the complex processing–structure relationships of semiconductor film formation and identify processing methods that may optimize device performance.

Keywords: NEXAFS, X-ray absorption spectroscopy, organic semiconductors, pentacene, poly(3-hexylthiophene), P3HT, organic thin film transistor, flexible electronics

1. INTRODUCTION

Organic semiconductors may soon enable the low-cost, high-volume manufacture of electronic circuitry to support emerging applications such as flexible displays, radio frequency identification (RFID) tags, and plastic photovoltaics. A key advantage of organic semiconductors is their ability to be solution processed, which allows the use of bottom-up device fabrication as an alternative to conventional photolithography. The direct patterning of organic semiconductors with inkjet, gravure, or web printing onto a continuous roll could allow device production at the speed and volume of printing presses.

Additive fabrication brings with it significant characterization challenges. Most organic semiconductor fabrication methods begin with a solution or vapor containing the semiconductor. Upon application to a substrate, a solid semiconductor layer is formed in a dynamic assembly process at the substrate interface that may include the nucleation, growth, and orientation of crystalline material. Chemistry, chemical interactions, or heat processes may be employed to optimize these processes. The resultant film is typically (10 to 100) nm thick and often exhibits a rough surface texture. The field effect mobility, trap depth and distribution, and injection properties of the semiconductor layer strongly depend on the film microstructure, morphology, and interfacial details.

Characterizing these aspects of structure is necessary to establish relationships between processing and performance. Techniques such as atomic force microscopy (AFM) and grazing-incidence X-ray diffraction (GIXD) are often used to obtain structural information that is then correlated to electronic performance. However, these techniques characterize different aspects of structure. AFM is a local probe of nanometer-scale heterogeneity, and GIXD is a non-local measurement of unit cell dimensions and preferential orientation for crystalline regions. A single measurement that

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unambiguously quantifies chemical composition, orientation, and defects for broad classes of organic semiconductor films (amorphous or crystalline) would enhance the rational development of new materials and processes. Here, we demonstrate how Near-Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy may meet this need.

1.1. NEXAFS Background

NEXAFS was developed in the 1980s with a focus on the structure and chemistry of molecules physisorbed or chemisorbed at interfaces. Synchrotron-based NEXAFS measures the absorption of linearly polarized soft X-rays within 30 eV of the K-shell threshold into resonant electron excitations. This X-ray absorption results in the “fine structure,” a collection of absorption peaks observed near the ionization edge. The technique is element sensitive by energetic selection of the K-shell that is accessed. Typically, NEXAFS is performed on the K-edges of low-Z elements with binding energies less than 1 keV such as carbon (285 eV), nitrogen (400 eV), oxygen (535 eV), and fluorine (685 eV).¹

The excitation of K-shell (1s) electrons by soft X-rays can result in either a bound state or a continuum state. Bound state excitations occur as either Rydberg transitions or excitations of 1s electrons to unfilled (typically antibonding) molecular orbitals, which may have either π or σ symmetry. A potential energy diagram is shown in Figure 1a to illustrate these transitions. A $1s \rightarrow \pi^*$ transition typically occurs at energies less than the vacuum level, and a $1s \rightarrow \sigma^*$ transition typically occurs at energies greater than the vacuum level. Among $1s \rightarrow \sigma^*$ transitions, the resonance position varies systematically with σ bond length; lower-energy resonance positions are expected for longer σ bonds. The energy separation between transitions creates the fine structure of X-ray absorbance, and allows one to determine intramolecular bonding.

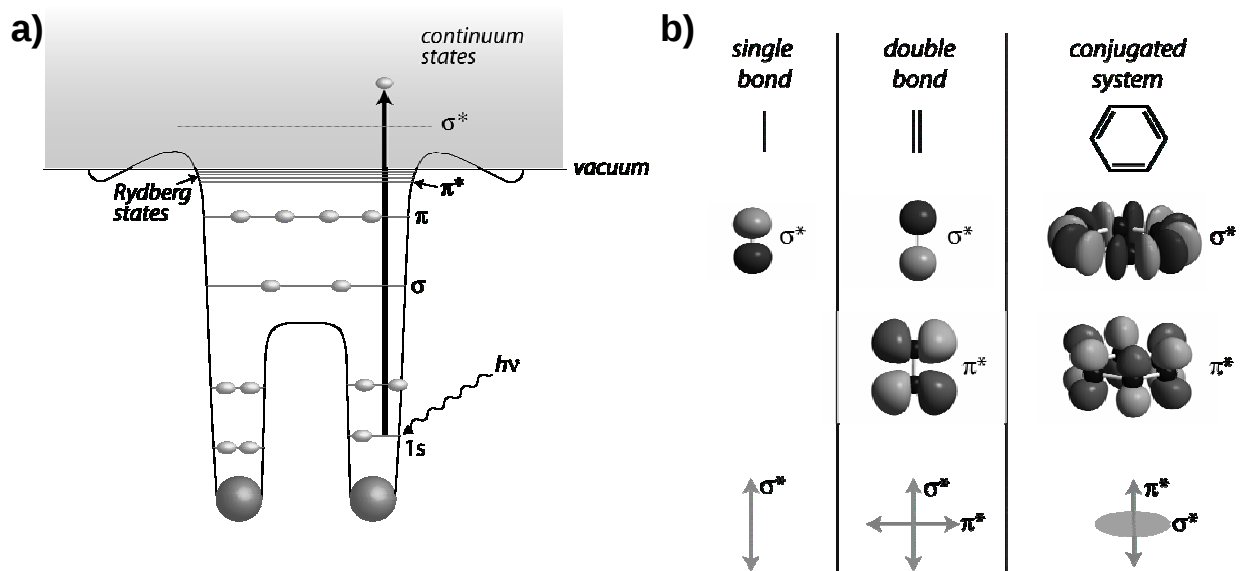


Figure 1: a) Band energy diagram depicting NEXAFS resonant excitations. Incident soft X-ray photons excite 1s electrons to unfilled molecular orbitals such as the π^* or σ^* . Excitation to the continuum, as shown here, can occur at energies above the absorption edge. b) Directional resonances are dependent on the spatial location of the final state orbital, and can be expressed as vectors or planes. These figures adapted from reference 1.

Spectrum interpretation is best illustrated with an example. In Figure 2, the carbon K-edge NEXAFS spectrum for poly(3-hexylthiophene) (P3HT) is shown. There are four distinct peaks. The lowest energy peak, near 286 eV, is the $1s \rightarrow \pi^*$ peak associated with the carbon-carbon double bonds of thiophene² (for P3HT, they are delocalized over the backbone). The second resonance at 288 eV is a combination of carbon-hydrogen, carbon-sulfur, and Rydberg excitations. The edge jump, where continuum states are accessed, appears at ≈ 289 eV. This edge jump causes a step

change in the absorbance, so that all energies above the edge jump exhibit a constant absorbance that has been normalized to 1 in Figure 2. The peak near 293 eV is associated with the $1s \rightarrow \sigma^*$ of carbon-carbon single bonds, and the peak near 303 eV is associated with the $1s \rightarrow \sigma^*$ of carbon-carbon double bonds. This peak hierarchy follows Figure 1a. The intensities of these peak shapes are equivalent to the stoichiometric bond densities within the sampled volume. Because peaks in NEXAFS are typically well-separated as in Figure 2, quantitative chemical analyses can be performed by fitting a sum of peak shapes to the spectrum, then integrating for the resonance intensity.

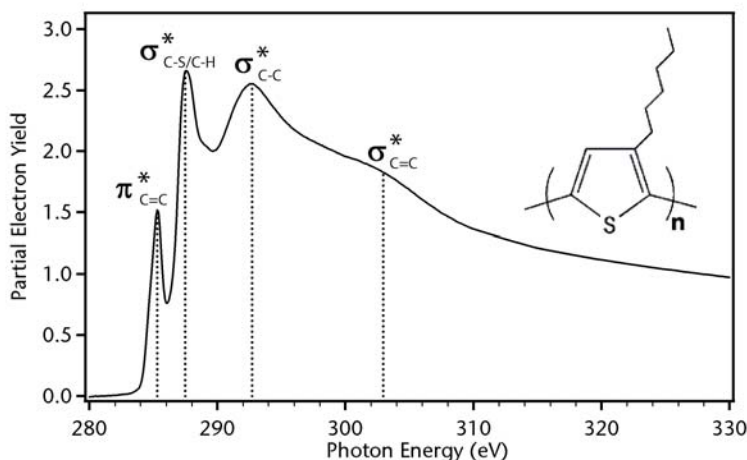


Figure 2: NEXAFS spectrum of poly(3-hexylthiophene) (P3HT). Resonances are labeled. PEY standard experimental uncertainty is $< 2\%$.

One of the advantages of NEXAFS as a surface spectroscopy is that it can determine bond orientation. The initial state of K-edge excitations is always $1s$, which is spherically symmetric. However, the final state is typically an antibonding orbital closely correlated to a bond and highly directional. The transition dipole matrix element will therefore be dominated by this directional final state orbital. The maximum final-state orbital amplitude relative to the atomic center of excitation will determine the directionality of the resonance, as shown in Figure 1b. The spatial orientation of a σ^* orbital is along a bond. The spatial orientation of a π^* orbital is orthogonal to a bond. When more than one resonance exists, these vectors add to form planes, such as the $1s \rightarrow \sigma^*$ resonances in benzene.

For simple molecules, the σ^* and π^* orbital directions can always be decomposed into a series of vectors and planes. The resonance intensity for a vector final state will be proportional to $\cos^2\delta$, where δ is the angle between the electric field vector of polarized incident soft X-rays and the vector of the resonance orbital. From this simple relationship, a surface-relative bond orientation can be determined. Often one or two bond orientations are sufficient to uniquely specify a molecular orientation.

1.2. NEXAFS for organic electronics

NEXAFS spectroscopy has several key advantages for investigating organic semiconductor thin films. Most importantly, it is highly sensitive to π bonds, which are detected in spectra as $1s \rightarrow \pi^*$ resonances. Carbon K-edge $1s \rightarrow \pi^*$ resonances typically appear at incident energies between (284 and 287) eV, as in Figure 2. This excitation appears at energies less than the absorption edge, and is more easily deconvoluted than most peaks in a typical NEXAFS spectrum. Because of this sensitivity, NEXAFS is particularly well suited to characterizing the extended π -conjugated networks of organic semiconductors.

In addition to their π networks, semiconducting organics also require a high level of surface-relative orientation to support the efficient delocalization and transport of mobile carriers in the form of holes or electrons. The preferred molecular orientation of an organic semiconductor in a thin film transistor (OTFT) is an edge-on orientation where the

conjugated plane is normal to the substrate and π overlap is facilitated in the source-drain plane. This π overlap can be partial or full, and various crystalline architectures such as herringbone or π -stacked motifs have been described.

Because of the strong link between molecular orientation and carrier mobility in organic semiconductors, the ability of NEXAFS to determine bond orientation is particularly attractive in the context of organic electronics. Most organic semiconductors feature a single conjugated plane. The directionality of the $1s \rightarrow \pi^*$ transition can typically be expressed as a *single* vector normal to any conjugated plane, as shown in Figure 1b for benzene. From a single set of NEXAFS spectra taken at different incident angles, it is straightforward to establish whether conjugated molecules within the sampled volume are oriented preferentially edge-on or preferentially plane-on. The extent of orientation can also be extracted, within limits that will be discussed later.

The controlled NEXAFS sampling volume is also attractive for organic electronics measurements. NEXAFS spectra taken in partial electron yield (PEY) mode are measured by counting Auger electrons ejected from the film. The depth within the film from which sensed electrons originate can be controlled by adjusting a bias on a grid covering the detector entrance. A low grid bias (e.g., -50 V for the carbon edge) will admit most electrons, even those inelastically scattered after originating from deep within the film. A high grid bias (e.g., -250 V) will reject most electrons except for those originating near the free surface. Bias adjustment in PEY mode allows the sampled depth to be controlled from $\approx(2 \text{ to } 10) \text{ nm}$.^{3,4} This depth range compares favorably to $\approx(5 \text{ to } 6) \text{ nm}$ dimensions of the mobile carrier region near the dielectric in organic TFTs. If the bottom interface of the semiconductor can be exposed, NEXAFS will provide a measurement of molecular orientation that is localized to the mobile carrier region.

The capabilities listed above can be combined to use NEXAFS spectroscopy as a tool to follow the simultaneous chemical conversion, molecular ordering, and defect formation of complex organic semiconductor systems such as convertible precursors. These materials can be cast from solution and then thermally converted to an insoluble active semiconductor layer. The sensitivity of NEXAFS to π bonds and other resonances can be used to follow conversion; spectra can be fit to a combination of peaks for stoichiometric quantification. The development of orientation can be tracked by varying the incident angle of polarized soft X-rays. Finally, defects such as dewetting can be detected and quantified by evaluating the exposure of the underlying substrate within the controlled sampling volume. With these capabilities, NEXAFS spectroscopy can often succeed as a solo technique for structure/function investigations of organic electronics materials systems.

Although NEXAFS has great potential as a solo technique, there is important structural information that NEXAFS does not provide. NEXAFS cannot measure the extent of crystallinity, the mode of crystal packing, or the crystal orientation in thin films. The molecular orientation provided by NEXAFS is the azimuthally averaged mean of the individual orientations of all the molecules within the sampled volume. Often, a high level of crystallinity can be deduced when this mean exhibits a high degree of surface-relative orientation. However, in cases where less order is observed it is impossible to know whether the film contains unoriented crystals or is simply amorphous. In these cases, complementary techniques such as GIXD should be employed. This information could then be compared with NEXAFS orientation information to determine whether the amorphous regions of the film also exhibit preferential orientation. Another aspect of organic film structure that NEXAFS does not directly measure is the nanometer-scale surface heterogeneity. This information, which sometimes includes crystal size and connectivity, can be determined using techniques such as AFM. NEXAFS, GIXD, and AFM are complementary in many cases, and could be combined to develop a comprehensive and self-consistent understanding of the semiconductor film formation process.

2. EXPERIMENTAL CONSIDERATIONS

Most photon absorption spectroscopies use transmission geometry in which a beam is measured before and after passing through a sample. NEXAFS spectra of solids are rarely collected in transmission because the sample would have to be a freestanding film less than 100 nm thick, which is difficult to fabricate and maintain. The beam would need to be extremely intense to penetrate the film, and degradation of the material would be a likely result. An exception to this generalization is NEXAFS microscopy, which normally uses a tightly focused beam in transmission.

Most NEXAFS beamlines measure soft X-ray absorbance by monitoring the decay of bound-state excited electrons, which occurs nonradiatively as Auger electron emission, and radiatively as photon fluorescence. Auger electron emission provides the most common quantification of soft X-ray absorption into bound states. Auger emission occurs when an electron decays into the core hole formed by soft X-ray excitation. The decay energy is transferred to a second electron, which is ejected from the molecule. This nonradiative decay is preferred over radiative decay by over two orders of magnitude. The kinetic energy of Auger electrons will remain constant over a NEXAFS K-edge, and spectra are collected in Auger electron yield (AEY) mode by selecting a detector energy window to reject lower energy electrons. Inelastic collisions will cause many Auger electrons to lose energy before leaving the film. This circumstance gives rise to partial electron yield (PEY) collection mode, where the detector energy window is broadened to include electrons with lower kinetic energy. By controlling the PEY electron rejection bias on a tunable grid (see Figure 3), depth selectivity can be achieved.⁵ Higher biases admit only electrons emitted near the free surface, whereas lower biases admit additional electrons emitted deep within the film and inelastically scattered.⁵ Finally, the total electron emission of a sample can be measured from the current flowing into the grounded sample. This mode, called total electron yield (TEY),^{6,7} has a small signal-to-noise ratio because of a large background from photoelectron emission.

Fluorescent photon counting is an alternative to electron yield.⁸ The strongest advantage of fluorescence yield (FY) is that the mean free path of photons through solids is longer than that of electrons. Therefore, FY mode reveals X-ray absorption from deeper into the film bulk (≈ 100 nm) than EY modes can measure (≈ 10 nm). A comparison of EY and FY NEXAFS spectra can reveal surface segregation and heterostructure formation.⁹⁻¹¹ This comparison might be used in evaluating organic semiconductor films to determine whether interface and bulk molecular orientations are different.

Orbital orientation can be determined experimentally by varying the tilt of the sample, as shown in Figure 3. The sample may be tilted from 20° to 90° with respect to the incident beam (by extension, with respect to the electric field vector). An orientation tendency is sometimes reported by comparing spectra taken at these two extremes. Robust discrimination between different orientations, however, is only possible if more angles are used. We find that the standard deviation of fits based on the data analysis outlined in Section 3 is minimized by including spectra taken at five to seven different angles, spaced between 20° and 90° . In most cases, using fewer than five angles adds uncertainty, and using more than seven angles does not reduce uncertainty. The standard deviation of a two angle fit is infinitely large. These five to seven scans may be collected at different points on the sample surface to avoid sample degradation and to confirm that orientation is constant across the surface. Using many angles also ensures that no experimental artifacts influence the orientation conclusions.

Sample charging is important to consider in NEXAFS measurements because it can introduce experimental artifacts.¹² Electron emission is a necessary product of soft X-ray excitation, but it does cause the sample to become positively charged. Electron emission is then reduced because of increased electrostatic binding, attenuating EY signals. The extent of charge buildup depends on the beam intensity and energy, the spot size, the exposure duration, and the quality of sample grounding. The spectral signature of charging is an artificially low post-edge intensity, which causes normalization errors.

A NEXAFS spectrum is typically normalized to account for changing spot size by dividing it by the intensity in the post-edge beyond bound-state resonances (≈ 330 eV for carbon).¹³ If the post-edge is artificially depressed due to charging, then the rest of the spectrum will be artificially increased after normalization. This increase can cause misinterpretation of orientation because charging varies with incident angle. Charging is typically strongest at 20° , where the spot is largest, and it decreases as the angle comes closer to 90° , where the spot is smallest. The normalized peak intensities may appear to vary in a systematic manner with angle, leading to a false assessment of their orientations.

Sample charging usually causes *all* of the bound state intensities to appear most intense at 20° and least intense at 90° , a situation that rarely occurs in properly measured and normalized spectra. Most angular collections of NEXAFS spectra exhibit isosbestic points where the intensity variation with angle “crosses over,” or multiple regions of common intensity. If sample charging is suspected, a different grounding scheme using an all-metal substrate and thin organic semiconductor film can be employed to check. Avoiding charging with substrates common to organic electronics can be difficult, because they are typically gate oxides or other insulators intended for low current leakage.

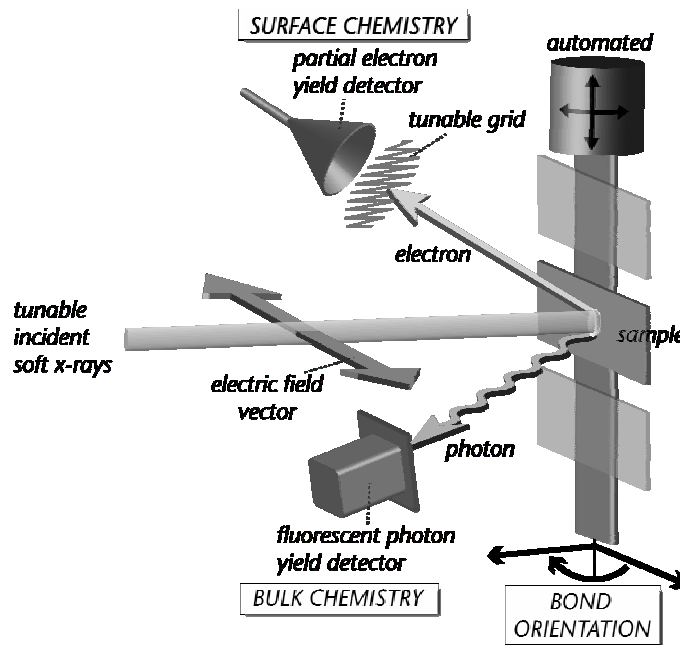


Figure 3: NEXAFS experimental setup at the NIST/Dow soft x-ray materials characterization facility, beamline U7A at Brookhaven National Laboratory.

3. DATA ANALYSIS FOR ORIENTATION

NEXAFS data analysis to extract orbital orientation follows simple equations that are trigonometric expansions of the $\cos^2\delta$ relationship described in Section 1.2. The typical orientation of interest for organic semiconductors is a surface-relative orientation uniformly distributed about the surface normal. In this case, the azimuthally averaged tilt of the orbital can be determined. For a vector orbital, the intensity in this case can be expressed as¹

$$I = A \cdot \left\{ \frac{P}{3} \left[1 + \frac{1}{2} (3 \cos^2 \Theta - 1) (3 \cos^2 \alpha - 1) \right] + \frac{(1-P)}{2} \sin^2 \alpha \right\} \quad \text{Equation 1}$$

I is the bound state resonance intensity, the integrated area of a normalized and deconvoluted peak;

A is a constant, roughly analogous to the extinction coefficient of conventional optical spectroscopy;

P is the polarization factor of the beamline;

Θ is the angle of the beam relative to the substrate plane;

α is the angle of the vector orbital relative to substrate normal.

The polarization factor, P , is usually known. The intensity, I , is measured as a function of Θ for many angles. Equation 1 can therefore be reduced to a linear fit of I vs $\cos^2 \Theta$, where the slope and intercept can be transformed into the two remaining unknowns A and α .

A linear fit of I vs $\cos^2 \Theta$ or I vs $\sin^2 \Theta$ will reveal whether orientation is consistent for the collected spectra. If no systematic deviation from linearity is observed, there are probably no gross experimental artifacts. The sample charging artifact described in Section 2, however, can sometimes result in a linear fit. The standard deviations of the fit parameters provide the statistical uncertainty of the orientation measurement. With sufficient points, a confidence

interval can be determined. Small differences in orientation can then be judged on a statistical confidence basis. The parameters A and α can also be fit directly using nonlinear least-squares methods.

The angle α describes the orientation of a vector orbital, but it is important to understand the meaning of this orientation. It is the *azimuthal mean* orientation of an ensemble of orbitals within the sampled volume. The underlying distribution of orientations within the ensemble usually cannot be determined. This consideration is important when analyzing organic semiconductors, because some of their crystallization motifs have a bimodal surface-relative orientation (e.g. some herringbone structures). It is tempting to assign α to every molecule, but this is only appropriate when reasonable, such as for a filled self-assembled monolayer (SAM) surface.

The azimuthal mean gives rise to an ambiguous quantity - the “magic angle” of 54.7°. If the vector orbital is tilted at 54.7°, there will be no variation in I with Θ . Conversely, if there is no variation in I with Θ , Equation 1 will reveal that $\alpha = 54.7^\circ$. An infinite number of orientation distributions can result in an azimuthal mean orientation of 54.7°, but the most important of these is complete disorder. If there is no variation in I with Θ , one may speculate but not prove that a sample is disordered.

Because of these considerations, it is impossible to separate the orientation itself from the “extent of orientation.” This information is hidden in the orientation distribution. The exception to this generalization occurs when the orbital is strongly oriented far from the magic angle. If the orbital exhibits a strong horizontal or vertical tendency, fewer orientation distributions will fit. For the extremes of perfect horizontal or vertical orientation, unique distributions of comprehensive, single-angle orbital orientation at $\alpha = 0^\circ$ or $\alpha = 90^\circ$ could be rigorously proven. In general, the farther α is away from 54.7°, the greater the allowable confidence that the orientation distribution is tight.

The magic angle ambiguity disappears if molecular orbitals are highly oriented in the substrate plane.^{6,14,10,11} The tilt angle still represents a mean, but the magic angle is now 45°, and only occurs if the in-plane projection of the electric field vector is aligned with that of the orbital. The three dimensional orbital orientation is determined by both tilting and turning the sample in the beam. Equation 1 is no longer valid, but a slightly more complex form can be employed. This measurement is potentially useful for organic semiconductor characterization because in-plane orientation between an OTFT source and drain is desirable, and is often created by mechanical alignment or casting upon oriented substrates.

To avoid confusion, it is often desirable to use a quantity other than α to express the orientation tendency of a distribution. One possibility is the orientational order parameter S ,^{15,16} which traditionally describes the mean orientation of liquid crystals. Assuming a surface-normal director,

$$S = \frac{1}{2}(3\cos^2\alpha - 1)$$

The parameter S will vary from +1 for a vertical orbital, to 0 for magic angle orientation, to -0.5 for a horizontal orbital. S is not symmetric about the disorder condition, and it is useful for expressing “how good” the ordering is in a purposefully aligned material (e.g. how closely orientation follows the director). For general comparisons of orientation tendency, we prefer a dichroic ratio defined as

$$R = \frac{I(90^\circ) - I(0^\circ)}{I(90^\circ) + I(0^\circ)}$$

Intensities at 0° and 90° are extrapolated from Equation 1, fitted to spectra from at least five angles. The parameter R varies from +0.7 for a horizontal orbital (not 1 because $P \approx 0.85$), to 0 for magic angle orientation, to -1 for a vertical orbital. R is roughly symmetric about the disorder condition and it is useful for general comparisons. We emphasize that α , S , and R all express the same orientation information. One parameter does not reveal more than the others.

4. SOME EXAMPLES

4.1. Pentacene

NEXAFS orientation analysis can be applied to any organic semiconductor film. In this example, a pentacene film was thermally evaporated to 50 nm thick on the native oxide of a silicon wafer. NEXAFS spectroscopy was performed on this film at the NIST/Dow soft x-ray materials characterization facility at the National Synchrotron Light Source (NSLS) of Brookhaven National Laboratory. The carbon K-edge was collected at several incident angles, shown in Figure 4. Collection bias was -50 V, so the sampled volume penetrates ≈ 10 nm into the top surface.

The most prominent absorbance is the carbon-carbon $1s \rightarrow \pi^*$ transition, which is split here into two peaks at 284.2 eV and 285.8 eV. The resonances at 294.8 eV and 301.0 eV are carbon-carbon $1s \rightarrow \sigma^*$ transitions. All transitions exhibit angular variation, and there is a clear isosbestic point. The π^* orbital intensity is greatest near normal incidence, and the σ^* orbital intensity is greatest near glancing incidence.

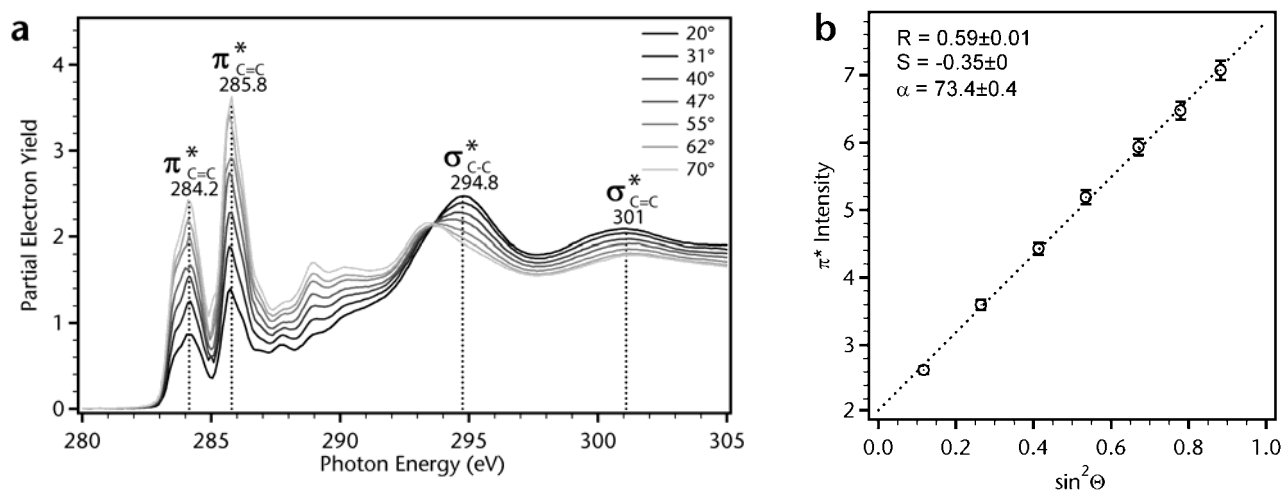


Figure 4: a) NEXAFS spectra of a 50 nm thick evaporated pentacene film. These spectra are post-edge normalized to the intensity at 330 eV to account for changing spot size. b) The intensity of the π^* resonances calculated by integrating the spectra from 282 eV to 286.5 eV, displayed vs. the squared sine of incident angle. The standard experimental uncertainty of PEY and its integrated intensity is < 2 %.

The orientation of pentacene can be extracted from Figure 4a by considering the pentacene carbon-carbon molecular orbital orientations. A rough sketch of these is shown in Figure 5. The π^* direction is represented as a single vector normal to the molecule, as for benzene in Figure 1b. The σ^* direction of pentacene is more complex. It is a plane, but there are more σ^* bonds along the long axis of the molecule than there are along the short axis. An elliptical plane is therefore the best representation of the σ^* direction.

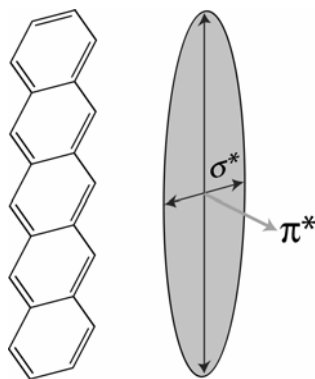


Figure 5: Antibonding orbital directions of pentacene.

We determine the molecular orientation of pentacene by comparing the angular variation of peaks in Figure 4a with the respective orbital orientations in Figure 5. The π^* orbital resonance is most intense near normal incidence, where the electric field vector is in the substrate plane. Thus, the π^* orbital is preferentially oriented in the substrate plane, and pentacene is oriented edge-on in the thin film. The π^* variation indicates only the conjugated plane tilt; we cannot determine the long axis tilt from this resonance.

The long axis tilt can be determined from the σ^* intensity variation. The σ^* intensity is most intense near glancing incidence, where the electric field vector is normal to the substrate plane. Thus, the long axis of the σ^* ellipse is preferentially normal to the substrate, and the long axes of pentacene are normal to the substrate. The edge-on orientation from the π^* is self-consistent with the standing up orientation from the σ^* .

The orientation of pentacene can be quantified using the analysis outlined in Section 3. The π^* intensity from Figure 4a is integrated from 283 eV to 286.5 eV. The intensity I varies with Θ according to Equation 1, as shown in Figure 4b. From Equation 1, R , S , and α can be determined, which quantify the extent of edge-on ordering in pentacene molecules. With $R = 0.59 \pm 0.01^*$, pentacene exhibits a high degree of edge-on character, and its orientation distribution is narrow. We assume that edge-on character is correlated to enhanced π interactions in the source-drain plane, consistent with pentacene's high hole mobility in OTFT architectures. Differences in pentacene orientation with film thickness, substrate chemistry, and substrate temperature can be quantified and compared by this technique.

4.2. Poly(3-hexyl thiophene)

NEXAFS orientation analysis can also be applied to polymer semiconductors. Films of regioregular and regiorandom poly(3-hexylthiophene) (P3HT) were spin-coated from chloroform to approximately 20 nm atop the native oxide of silicon, then melted at 250 °C and slowly cooled under vacuum. NEXAFS carbon K-edge spectra were collected at the same conditions as for pentacene. The resultant spectra are shown in Figure 6a-b below.

The regiorandom P3HT spectra exhibit no angular variation, and we may assume that the film is completely disordered. The regioregular P3HT spectra exhibit the same direction of π^* variation as pentacene, indicating that the conjugated plane is edge-on. We quantify the π^* orientation using the fits in Figure 6c-d. The regioregular P3HT exhibits $R = 0.26 \pm 0.01$ for the conjugated plane. This dichroic ratio is far less than that of pentacene, and the distribution of tilts cannot be known. These samples are not likely represented by a single, uniform orientation; R reflects an average of the edge-on, plane on, and amorphous orientations present.

* Uncertainty is the standard deviation of R from a direct nonlinear fit.

We could quantify the σ^* orientation, but in this case it is difficult to define the orbital directions relative to the molecule. The σ^* peaks appear to have a vertical orientation, which is consistent with the expectation that these peaks arise from hexyl sidechains, which should be vertical if the backbone is edge-on.

We find that P3HT ordering is well-described by comparing R for π^* . Here, the diagnostic is simply tested by comparing regioregular and regiorandom P3HT. More positive R values for the regioregular P3HT indicate a greater prevalence of edge-on orientation, which is presumably correlated to better π stacking in the source-drain plane. In more extensive studies of regioregular P3HT, we find that R varies with the solvent employed in spin-processing, the molecular weight of the P3HT, and thermal history. Correlation of R to field effect mobility has been possible in a number of these studies.

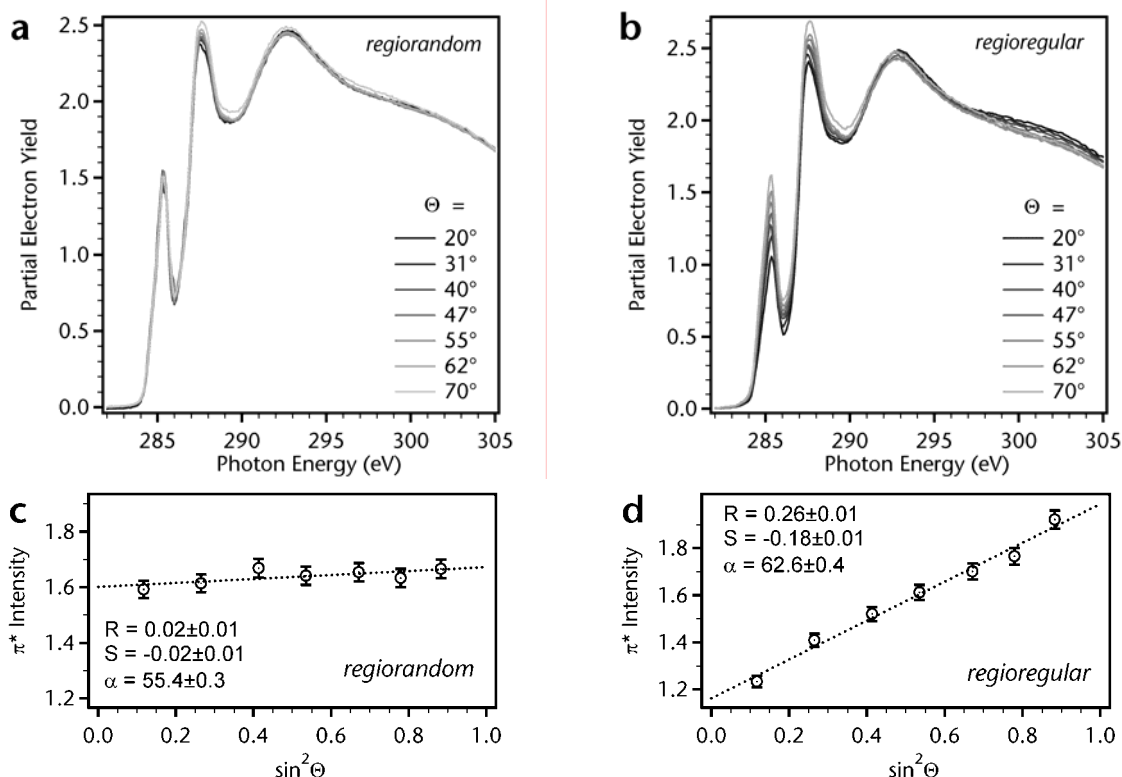


Figure 6: a) NEXAFS spectra of a spin-cast regiorandom P3HT film. b) NEXAFS spectra of a spin-cast regioregular P3HT film. These spectra are post-edge normalized to the intensity at 330 eV to account for changing spot size. c), d) The intensity of π^* resonances calculated by integrating the spectra from 282 eV to 286 eV, displayed vs. the squared sine of incident angle. The standard experimental uncertainty of PEY and its integrated intensity is $< 2\%$. The uncertainties of order parameters are standard deviations from direct fits of the parameters to intensity trends.

5. SUMMARY

NEXAFS spectroscopy is a valuable tool for investigating the structure and chemistry of organic semiconductors. The advantages of NEXAFS are its chemical sensitivity, its identification of bond orientation, and its tunable sampling volume. Orientation determination is straightforward, with simple dipole moments and simple math. NEXAFS can be applied to organic semiconductors on native substrates such as oxides or even device test beds. Flexible plastic substrates are equally suitable, so NEXAFS will remain useful for analyzing high-throughput fabrication. With these capabilities, NEXAFS can help establish the complex processing–structure relationships of semiconductor film formation. NEXAFS and complementary techniques will uncover the chemical motifs and processing methods that result in favorable structure and, ultimately, enhanced performance.

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