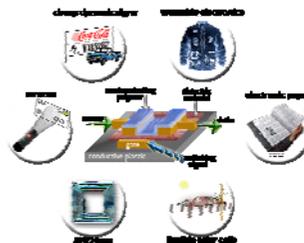




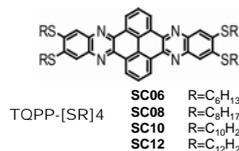
Structural Investigation of Pyrene Discotics for Organic Field Effect Transistors

Motivation

- Organic field effect transistors (OFETs) can be used in the backplane electronics for many applications such as displays, photovoltaics, and radio-frequency identification tags
- Measuring organic semiconductor microstructure and establishing how it can relate to carrier mobility continues to challenge the development of new materials for organic electronics
- Establishing these relationships is a necessary step toward asserting control over thin film crystallization processes to realize greater carrier mobility and more facile processing
- Advancing OFET technology requires understanding of structure-performance relationship, yet current measurement tools used for traditional semiconductors cannot always be directly transferred



Objective

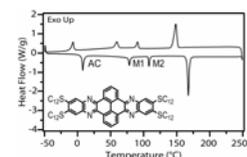


Semiconducting 6,7,15,16-tetrakis(dodecylthio)quinoxalino[2',3':9,10]-phenanthro[4,5-*abc*]phenazine (TQPP-[SR]4) is a promising solution-processable OFET active layer. We characterize the thin film microstructure using a combination of polarized photon absorption spectroscopies (X-ray, vis, and IR), X-ray diffraction, and scanning probe techniques. The combined techniques reveal molecular orientation and order. This strategy enables the nearly complete determination of thin-film molecular packing style for this complex molecule.

Experimental Approach

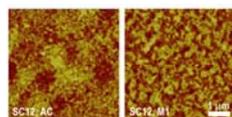
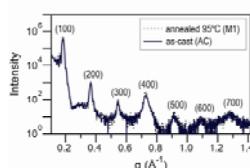
Let's start with SC12

Thin films of TQPP-SC12 spun on OTS-modified Si substrates were first prepared according to the AC, M1 and M2 mesophase regions determined by DSC



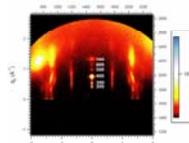
Specular XRD measures long-range positional order along the thin film normal (out-of-plane).

- Minimal effect of thermal processing
- M2 similar to M1
- d-spacing of 34.2 Å
- XRD indicates lamellar structure with reproducible out-of-plane spacing



Surface morphology (AFM) differs with temperature.

- Lateral crystal size increases
- Terrace formation (height ~3.4 nm)



Grazing incidence XRD (GIXRD) measures out-of-plane (q_z) & in-plane order (q_x).

- Complements specular XRD
- SC12 shows in-plane order

Comparing the molecular dimensions of the conjugated core and the side chains with the d-spacing, parts of the molecule must be tilted in order to fit into this lattice.

How can the molecular orientations be determined?

Complement XRD by using polarized photon spectroscopies!

Near-Edge X-ray Absorption Fine Structure (NEXAFS) Spectroscopy

Features

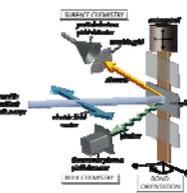
- Synchrotron soft X-ray source
- High sensitivity to π -bonding
- Directly measures molecular orientation
- Depth sensitive
- Collects chemistry & orientation info simultaneously

Quantitation

- Signal is dot product of transition dipole and E-field
- Figure of merit, dichroic ratio (R)

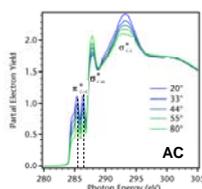
$$R = \frac{I(90^\circ) - I(0^\circ)}{I(90^\circ) + I(0^\circ)}$$

- Conjugated plane oriented normal to surface (R=-1) and if parallel (R=0.7)



In NEXAFS, tunable soft X-rays are absorbed to excite core 1s electrons to unfilled σ^* or π^* molecular orbitals.

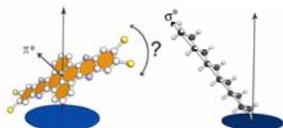
- Consistent with XRD, minimal thermal effect, R ~ -0.38 for AC and M1
- R of OTS/SC12 interface same as top surface (via PDMS film delamination)
- Based on the comprehensive crystallinity (XRD), assume



$$R = \frac{I(90^\circ) - I(0^\circ)}{I(90^\circ) + I(0^\circ)} = \frac{P(1 - 3 \cos^2 \theta >)}{2(1 - \cos^2 \theta + P(\cos^2 \theta > -))}$$

Conjugated plane tilt $48^\circ \pm 1$
Side chain tilt 45°

angles are off surface normal



Variable Angle Spectroscopic Ellipsometry

Features

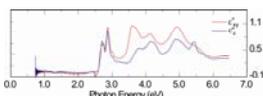
- Film thickness measurement
- Absorption spectrum
- Film anisotropy - transition dipole orientation

Quantitation

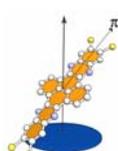
- Multiple angles+multiple samples (thin/thick oxide) provide dielectric function directly, $\epsilon = \epsilon' + i\epsilon''$
- ϵ'' is the first single $\pi-\pi^*$ transition and in-plane (xy) and out-of-plane elements (z) can be separated
- $\epsilon''_z / \epsilon''_{xy}$ sensitive to long axis tilt
- Figure of merit (azimuthally isotropic sample)

$$\frac{\epsilon''_z}{\epsilon''_{xy}} = 2 \frac{\cos^2 \theta}{\sin^2 \theta}$$

In SE, transition dipole moment for $\pi-\pi^*$ transition is along main-chain axis.



- Conjugated plane is not symmetric (long and short axis of core)
- $\epsilon''_z / \epsilon''_{xy} = 0.7$ to 1.0 at 2.7 eV, indicating tilt out-of-plane



Core long axis is tilted ($57^\circ \pm 2$)

Polarized IR Absorption (FTIR)

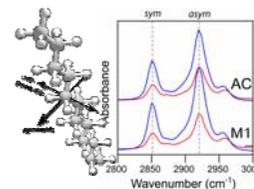
Features

- Highlights individual functional groups
- Vibrational frequencies characteristic of conformation (CH stretches)
- conjugation length (C=C stretches)
- Film anisotropy - transition dipole orientation

Quantitation

- Brewster angle transmission spectra recorded for s- and p-polarization
- Figure of merit, absorbance ratio (A_p/A_s)

Alkyl side chains resonances (2800-2930 cm⁻¹)

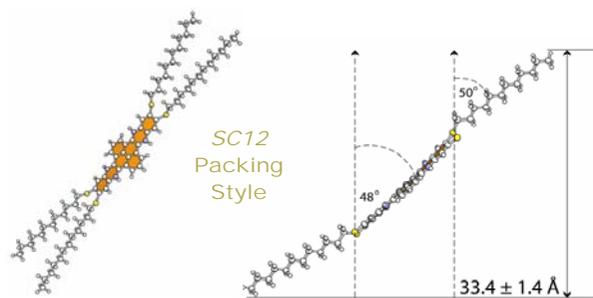


- Asym-CH₂ stretch centered at 2919 cm⁻¹
- Side chains highly ordered since all trans (2918 cm⁻¹) vs liquid (2928 cm⁻¹)
- From orthogonal axes, possible to calculate the chain and core π -directors

Core short axis $90^\circ \pm 3$
Core long axis $54^\circ \pm 3$ (agrees with SE)
Side chain $50^\circ \pm 3$ (agrees with NEXAFS)

1. Leah A. Lucas, Ghassan E. Jabbour
2. Dean M. DeLongchamp, Lee J. Richter, R. Joseph Kline, Dan A. Fischer, Michael J. Fasolka, Eric K. Lin
3. Brigette Wex, Bilal Kaafarani

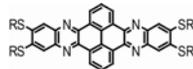
TQPP-SC12 Summary



- If assume a narrow, monomodal orientation distribution can obtain tilts from spectroscopies
- Lamellar spacing determined from spectroscopy in agreement with d-spacing from XRD
- Possible rotation of short axis in above/below lamellae
- Difficult to determine the exact in-plane geometry
 - Short axis is in-plane so probably not herring-boned
 - In-plane slip possible
 - Could explain different in-plane spacings (GIXRD)
- Good agreement of molecular orientation although independent determination by various spectroscopies

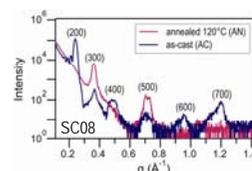
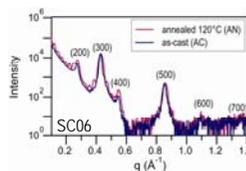
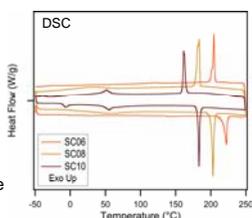
TQPP-[SR]4 Synthetic Series

What is the effect of side chain length on the microstructure?



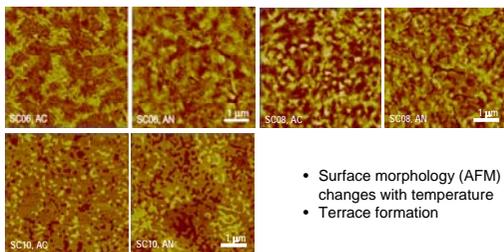
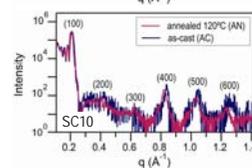
SC06 R=C₆H₁₃
 SC08 R=C₈H₁₇
 SC10 R=C₁₀H₂₁

Like SC12, SC10 shows multiple mesophase transition, however, SC06 and SC08 do not

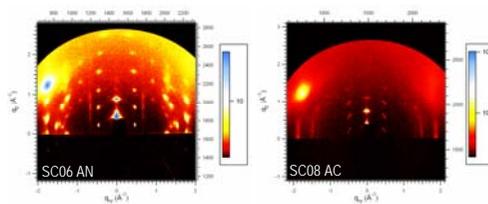


Specular XRD

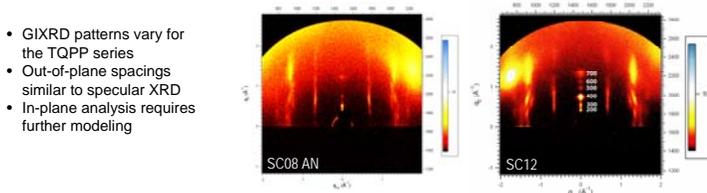
- As with SC12, no thermal effect for SC06 and SC10, but thermal effect present in SC08
- SC06, d = 45 Å
- SC08, d = 53.2 Å
- SC10, d = 30.7 Å



- Surface morphology (AFM) changes with temperature
- Terrace formation



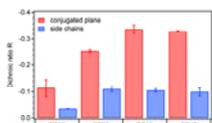
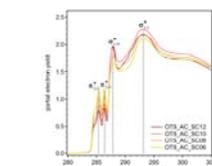
Interesting thermal effect present in SC08 – in-plane crystal shape is changing – becomes more like SC12



- GIXRD patterns vary for the TQPP series
- Out-of-plane spacings similar to specular XRD
- In-plane analysis requires further modeling

NEXAFS

- Chemistry trend is generally correct – decrease in π^{*} content as side chains increase in length
- SC10 and SC12 are most highly orientationally ordered and SC06 is least ordered
- All derivatives exhibit similar orientation to AN except SC08 which improves in order with anneal



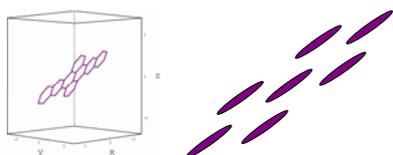
SC06 Packing Style

From the various spectroscopies (angles off surface normal),

- Conjugated plane tilt 51°±1 (NEXAFS)
- Side chain tilt 45°±1 (NEXAFS) & 53°±3 (FTIR)
- Core short axis tilt 44°±3 (FTIR)
- Core long axis tilt 73°±3 (SE) & 70°±2 (FTIR)

Using various molecular orientations,

- Calculated single molecule spacing is 15.1 Å ± 1.6
- XRD spacing spans 3 molecules



TQPP Series Summary

- If assume a narrow, monomodal orientation distribution can obtain tilts from spectroscopies
- Molecular orientations obtained through polarized photon spectroscopies can be used to complement diffraction results
- NEXAFS result that SC10 and SC12 are most highly orientationally ordered and SC06 is least ordered trends with p-type OFET behavior
- Decreasing sidechain lengths cause cores increase “face-on” tendency of TQPP core
- Initial results indicate that decreasing sidechain lengths increases “face-on” tendency of TQPP core yet decreases core-core registry

	μ (cm ² /Vs)	V _{th} (V)
SC6	no observable OFET behavior	
SC8	1.7E10 ⁻⁴	-43.9
SC10	3.8E10 ⁻⁵	-50.7
SC12	1.1E10 ⁻³	-43.7

TQPP Future Work

- To complete series, perform spectroscopic analysis on SC08 and SC10
- XRD simulations required to fully model in-plane order and symmetry
- Acknowledgements: L.A.L. would like to thank the Bell Labs Graduate Research Fellowship Program