Combinatorial thermal platform for study of polythiophene thin film structure and OFETs

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MERCK

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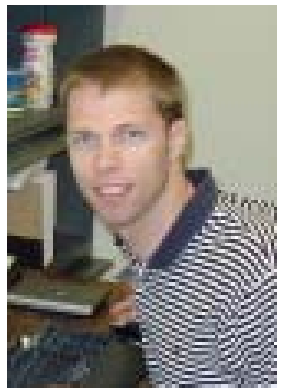

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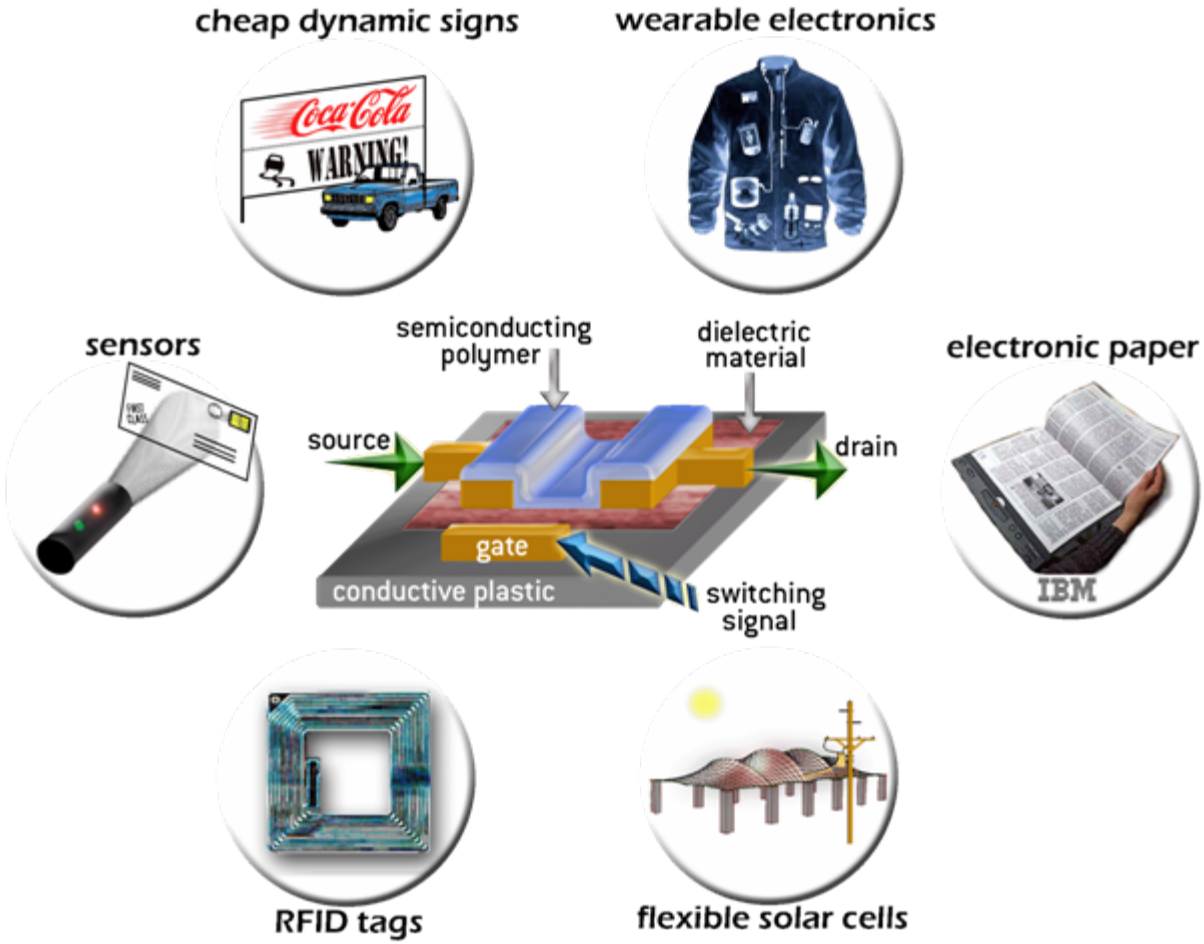
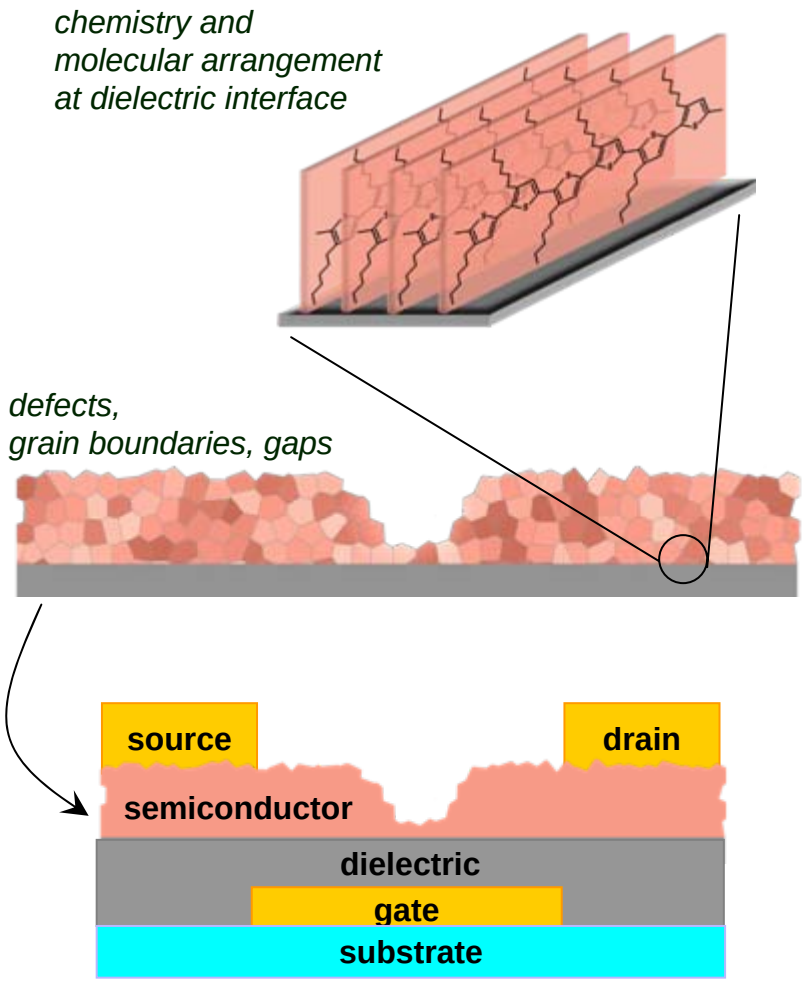


Alternative technology to Si-based

- Lower performance, disposable applications
- Potential advantage → cheaper processing costs
- Solution, large area & R2R processing (flexible substrates)
- New form functionality → conformable, rollable, lightweight

The dominant role of structure



device structure

… and on to circuits

- Structural knowledge required to understand & control electronic properties
- Data needed over multiple length scales

(Å to nm)	Molecular orientation
(Å to nm)	Interfacial width
(nm to μm)	Crystal / amorphous domain morphology
(μm)	Macroscopic defects
(μm to mm)	Device architecture

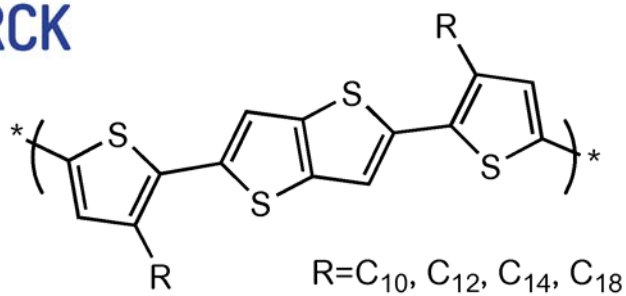
Compromise carrier mobility, device performance, and reliability.

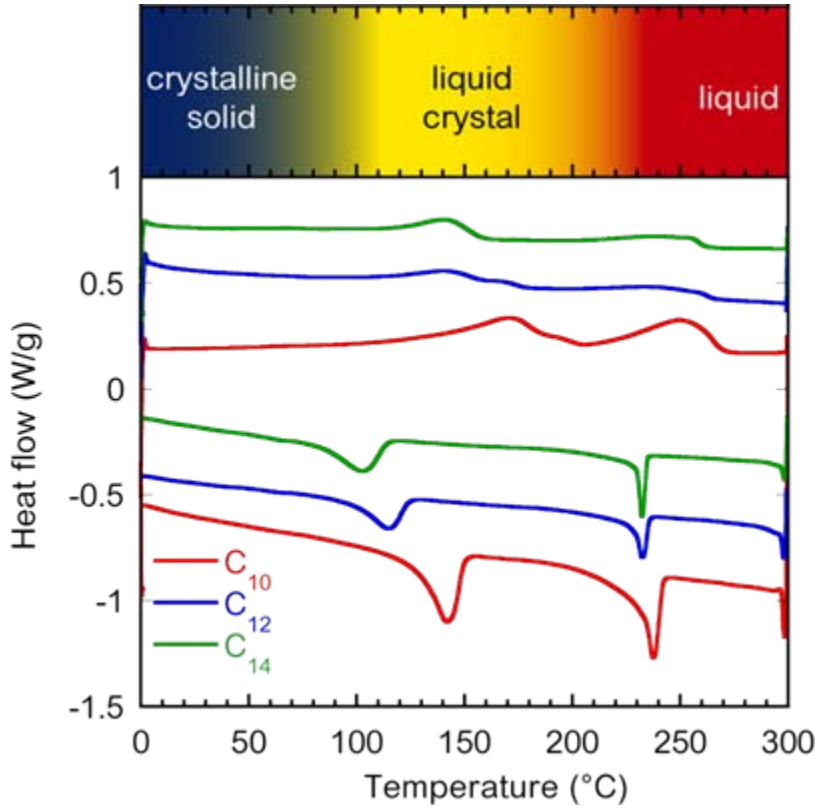
- Our goal: correlate processing to structure to performance, with quantifiable structural measurements.

How can we assess structure of organic semiconductors ***especially at the buried interface****?*

Truly high performance polymer semiconductors

*poly(2,5-bis(3-alkylthiophen-2-yl) thieno[3,2-b]thiophenes) (**pBTTT**)*



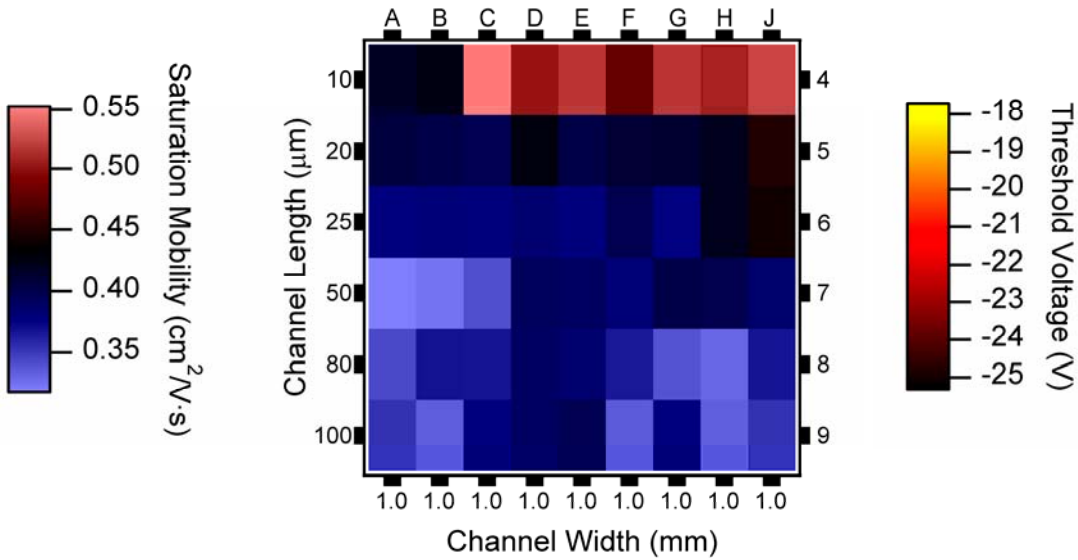


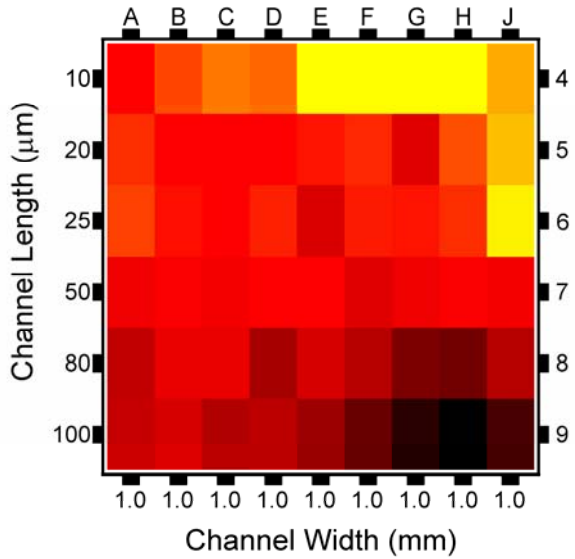
- **Solution processible**
- Saturation hole mobility **0.2 to 0.6 cm²/V·s** (comparable to *a*-Si)
- Improved mobility after annealing to liquid crystal

	M_N/M_W (Da)
pBTTT-C_{10}	27,400 / 62,700
pBTTT-C_{12}	29,600 / 54,000
pBTTT-C_{14}	28,000 / 61,000
pBTTT-C_{18}	26,100 / 41,800
DP ≈ 40 - 43	

McCulloch et. al. *Nature Materials* 2006, **5**, 243

Typical Saturation Mobility & Vt



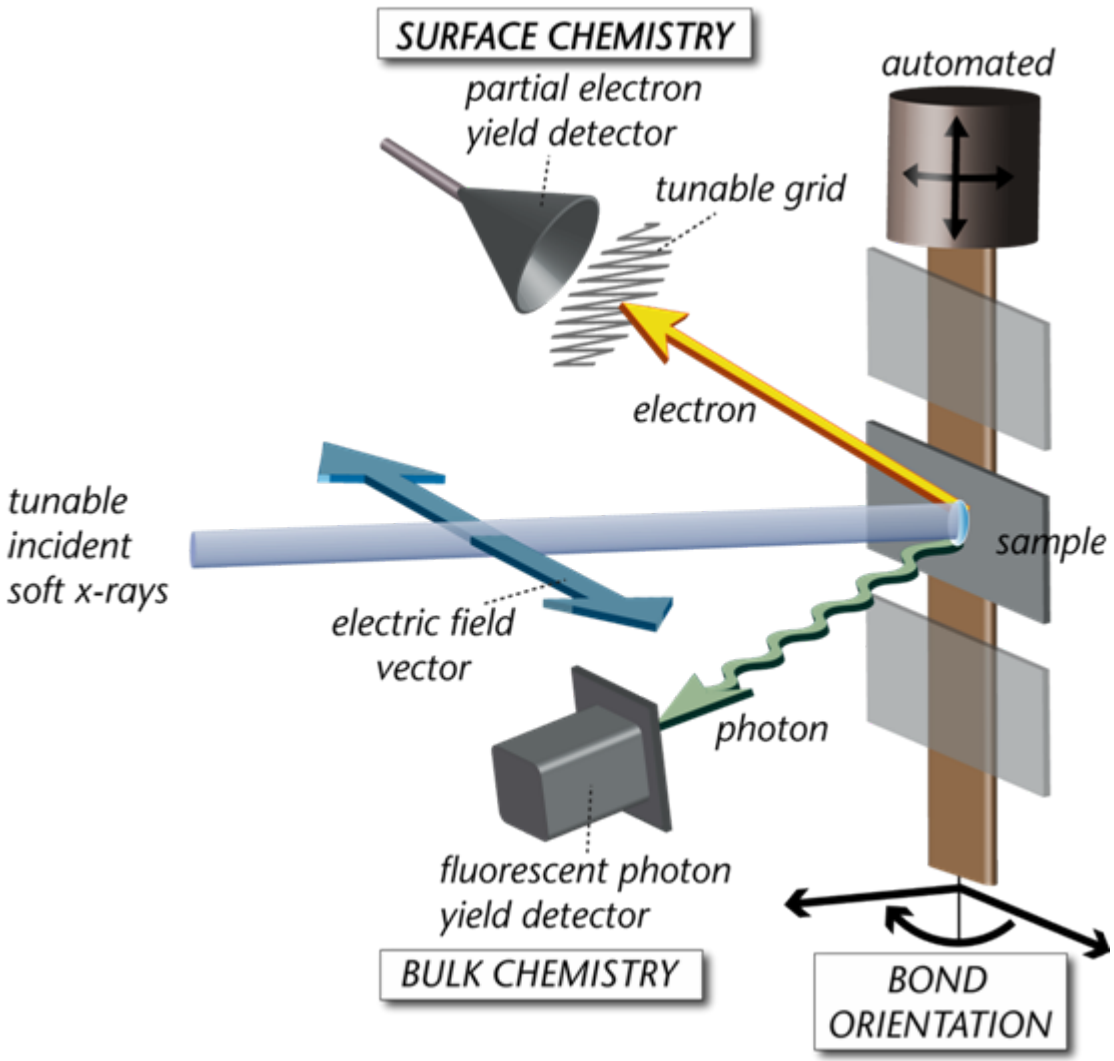


- No exotic dielectric (octyltrichlorosilane on oxide)
- No exotic post-spinning treatments (other than annealing)
- **Simple processing** - Just spin and anneal
- In agreement with Merck measurements

What is behind the high performance of the pBTTT? How can we quantitatively assess its structure?

	μ_{AVG} ($cm^2/V \cdot s$)
pBTTT-C_{10}	~0.2
pBTTT-C_{12}	~0.3
pBTTT-C_{14}	~0.4
pBTTT-C_{18}	~0.2

NEXAFS for structure and chemistry



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

Strengths for Organic Electronics:

- Detects C, N, O, & F bonds. High sensitivity to π bonding.
- Directly measures molecular orientation.
- Depth sensitive.
- Collects chemistry and orientation information simultaneously.
- Detects defects.

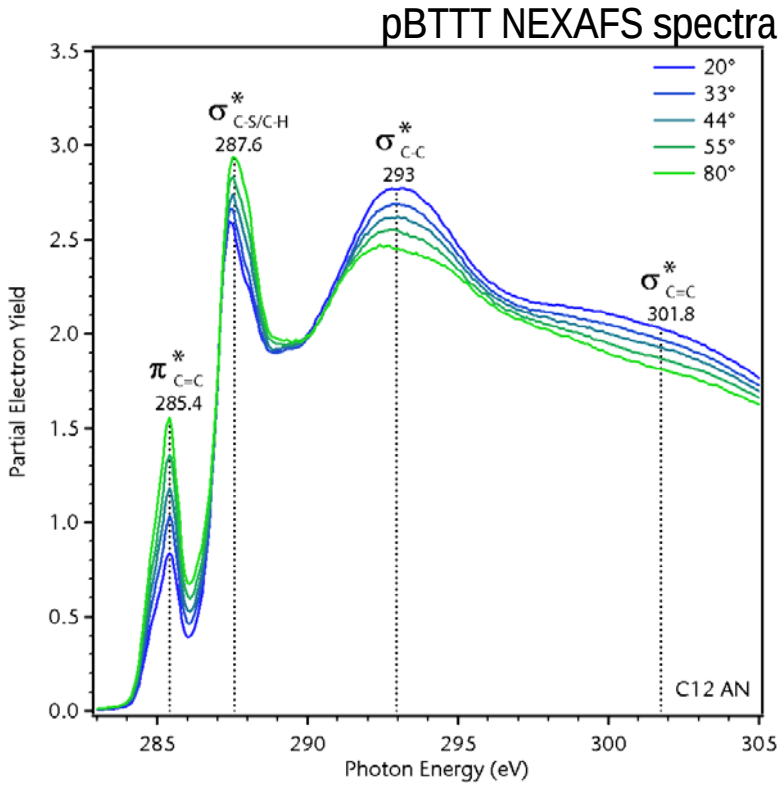
Does NOT measure :

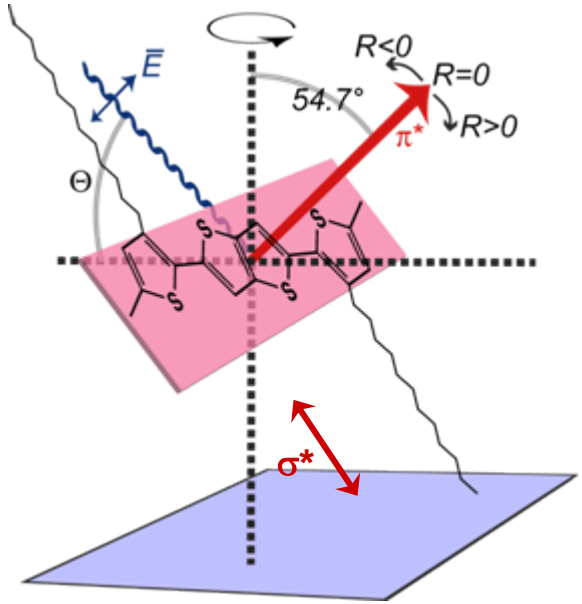
- Crystal packing style, prevalence, size, shape.
- HOMO, bandgaps.
- Secondary chemical interactions (e.g. vib / rot structure).

A powerful technique complementary to AFM, GIXD, and *XPS*.

Often sufficient for solo investigations.

NEXAFS - Conjugated plane tilt

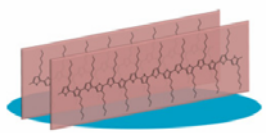




Resonance Intensity:

$$I(\Theta) = \int_{peak} PEY(\Theta)$$

Edge-On

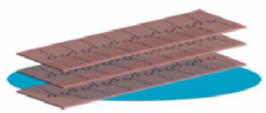


R = 0.70

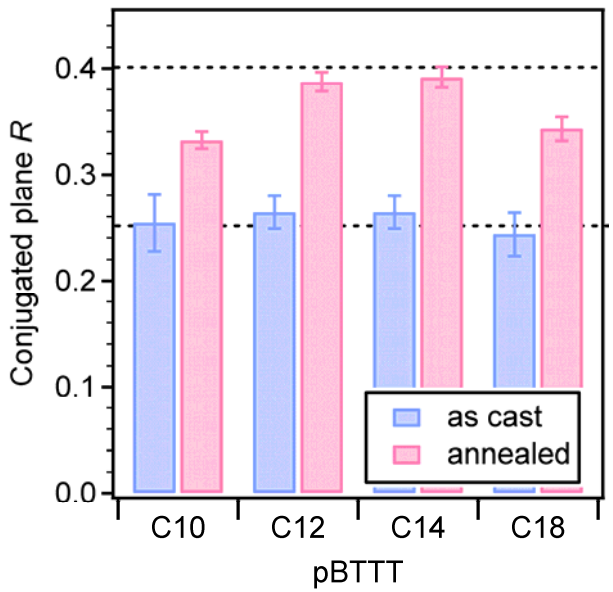
Dichroic Ratio:

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

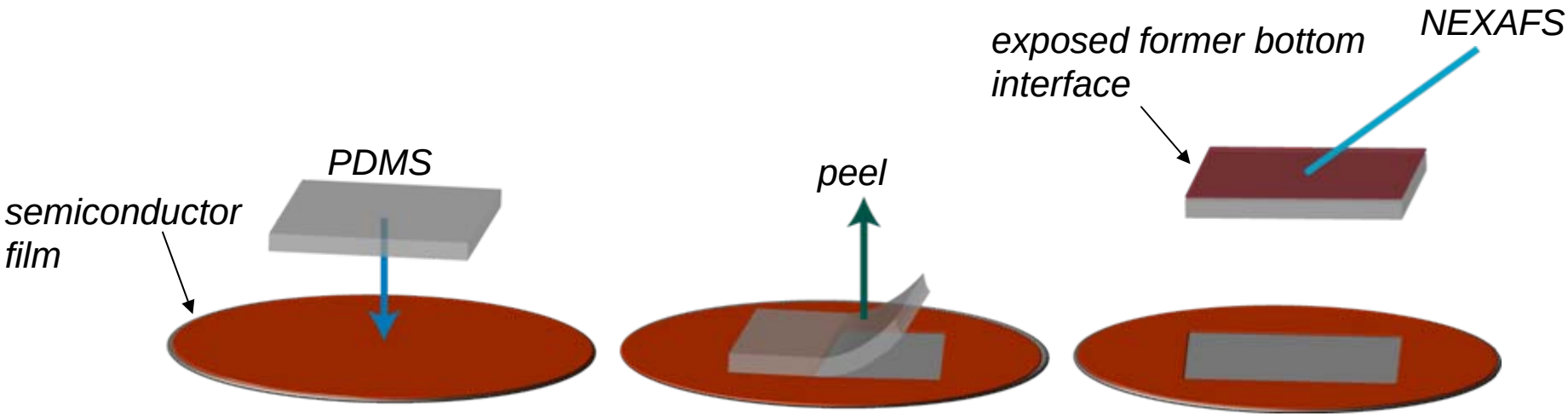
Plane-On



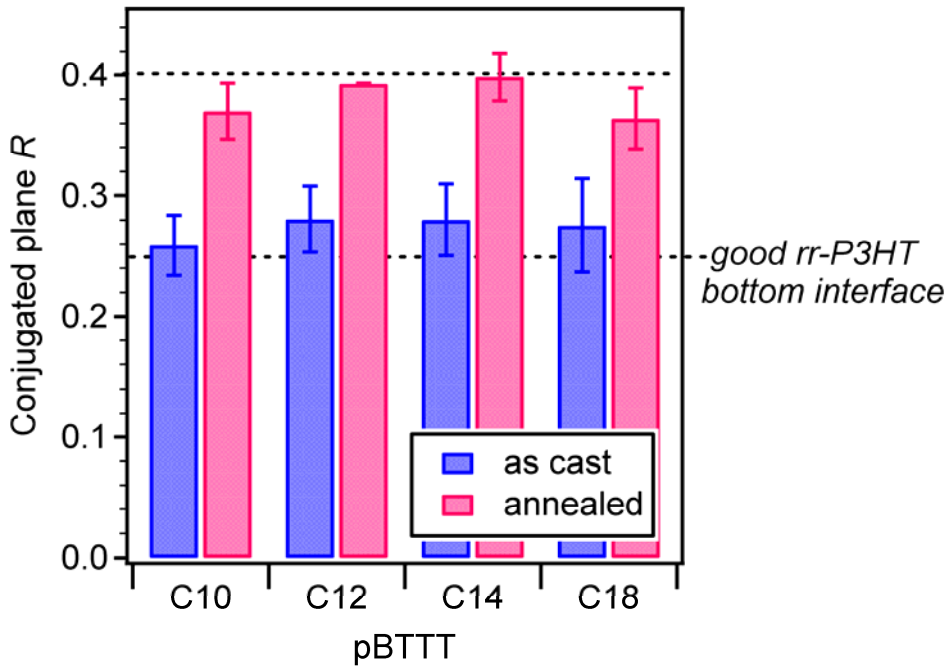
R = -1.00



Ex-situ bottom interface orientation measurement w/ NEXAFS



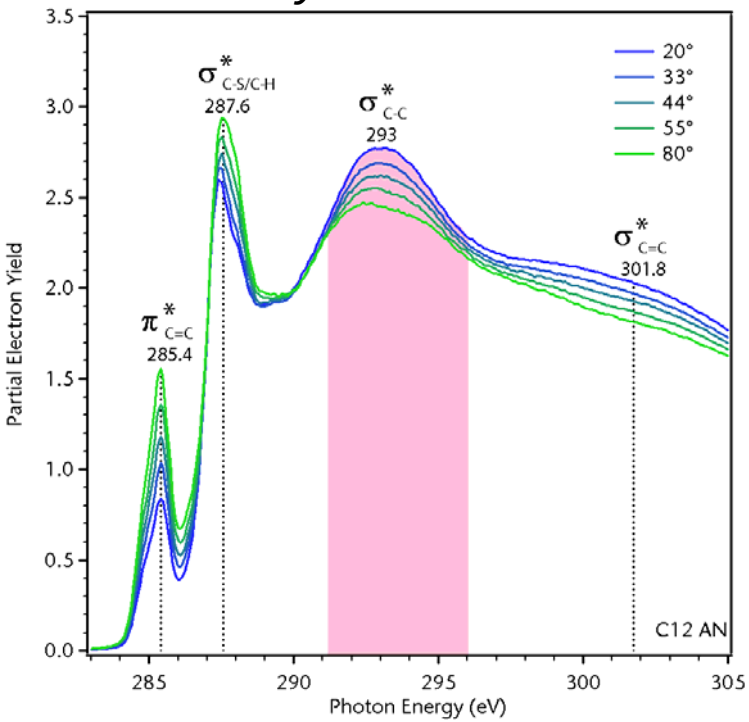
*Chabinyc et al. JACS, 2004, **126** ,13928*

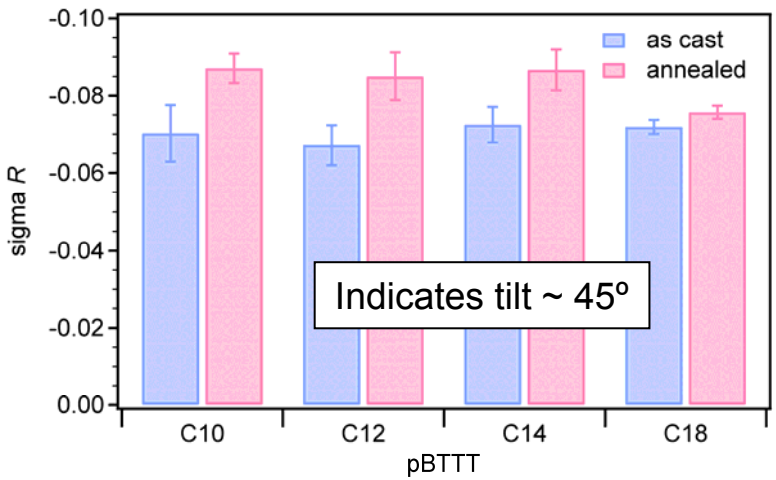


- **Bottom interface orientation is very similar to top interface orientation.** (Remember films are ~20 nm thick)
- pBTTTs have more vertical conjugated plane than P3HT
- But, the conjugated plane orientation is *not* as vertical as for pentacene / oligothiophenes (*R*=0.5-0.6)

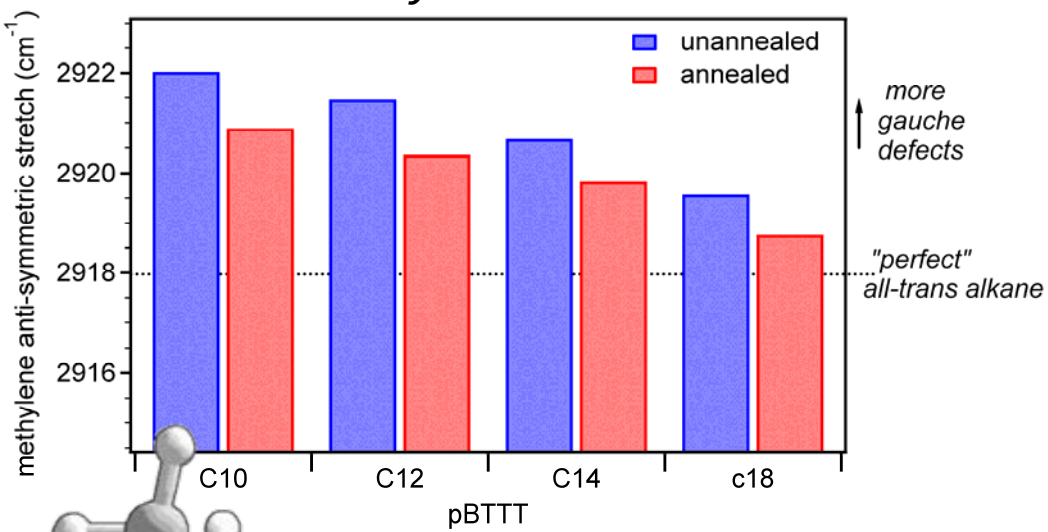
Consistent side chain orientation from two spectroscopies

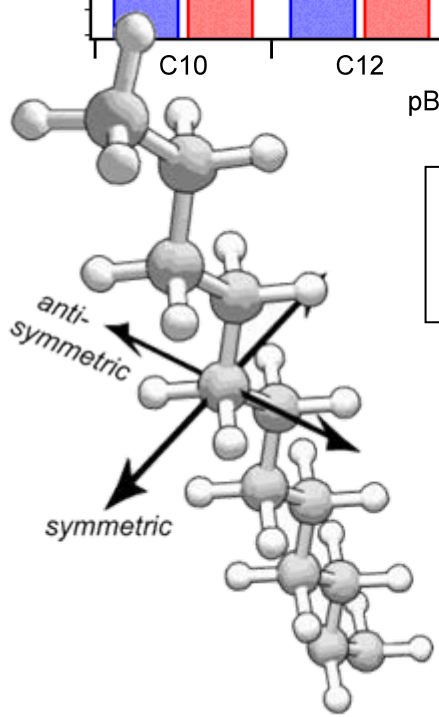
by NEXAFS





by FTIR

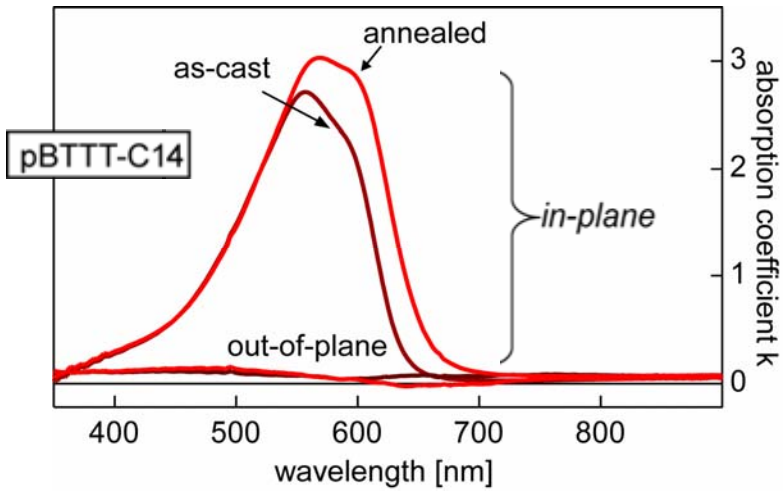


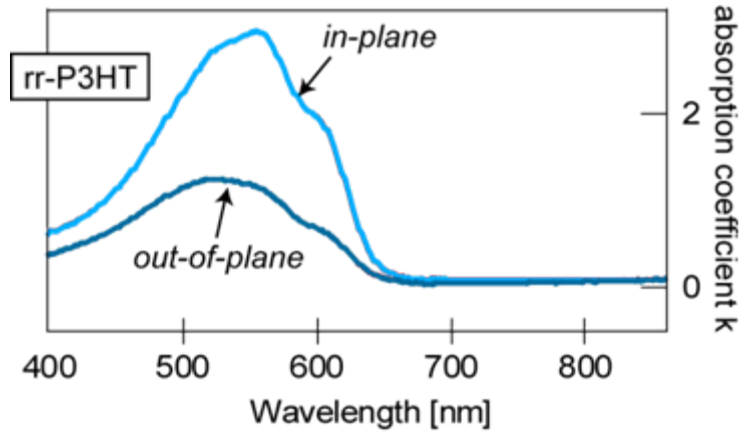


Ap/As = 0.3-0.4 indicates sidechain tilt ~45º

What about the conjugated plane long axis?

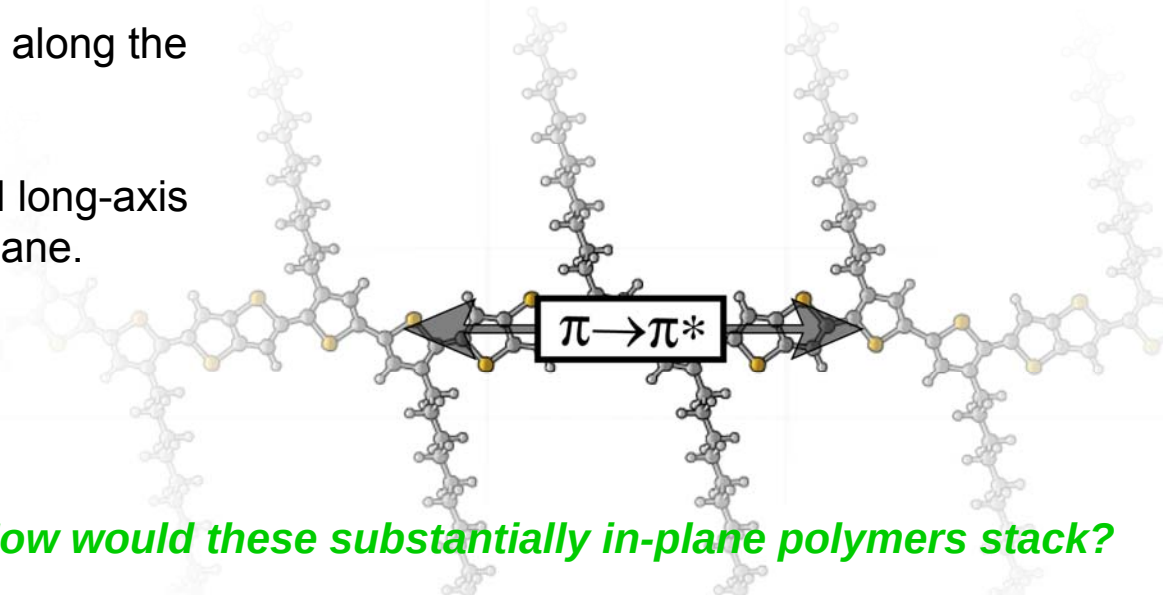
Polymer long axis orientation by Spectral Ellipsometry





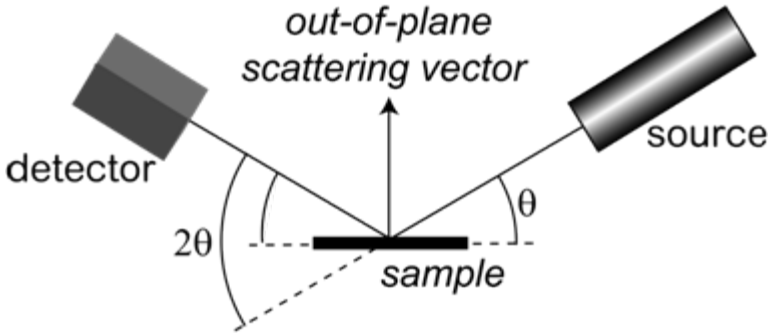
- The $\pi \rightarrow \pi^*$ excitation is oriented along the conjugated long axis.

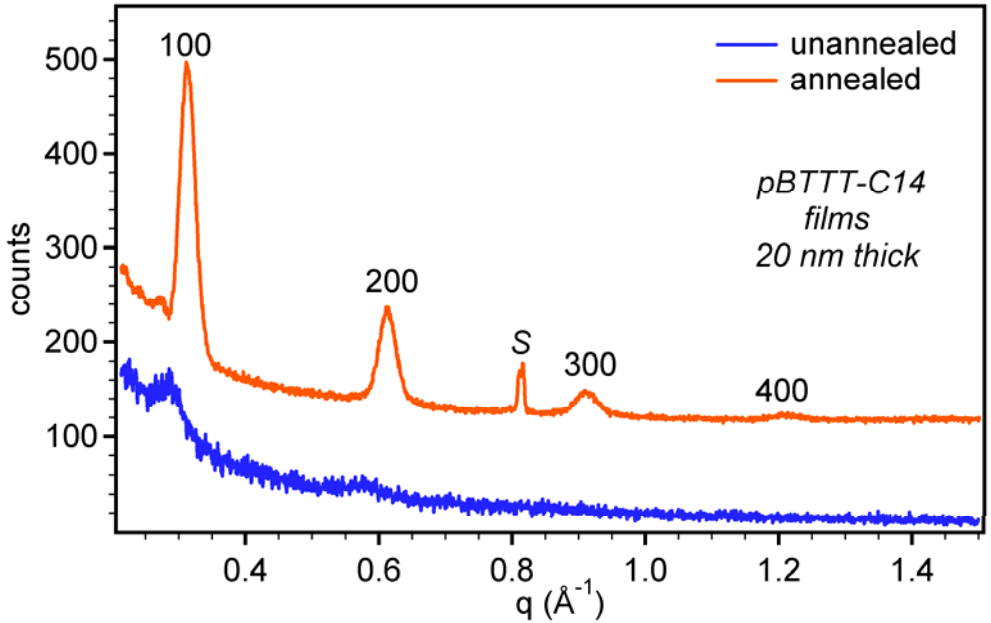
- pBTTT films exhibit **substantial** long-axis orientation within the substrate plane.



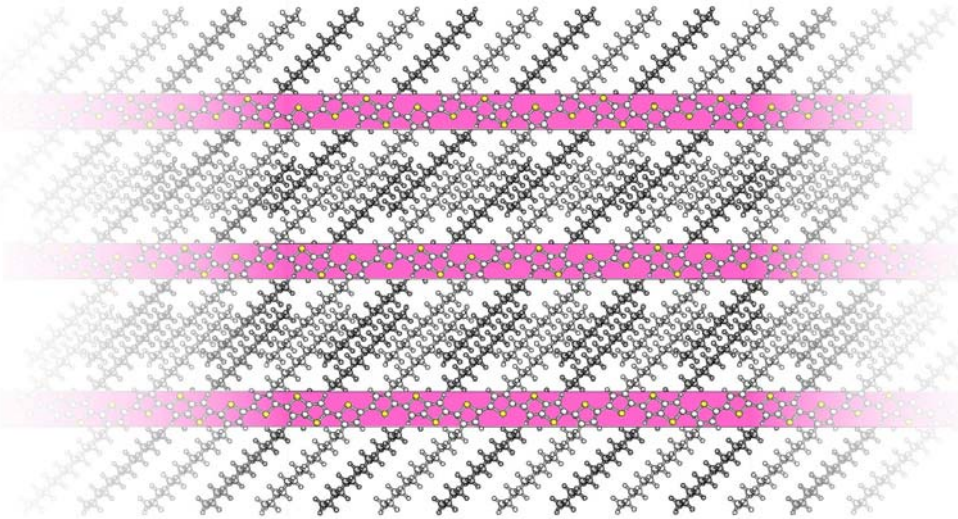
How would these substantially in-plane polymers stack?

Specular X-ray diffraction reveals molecular layers



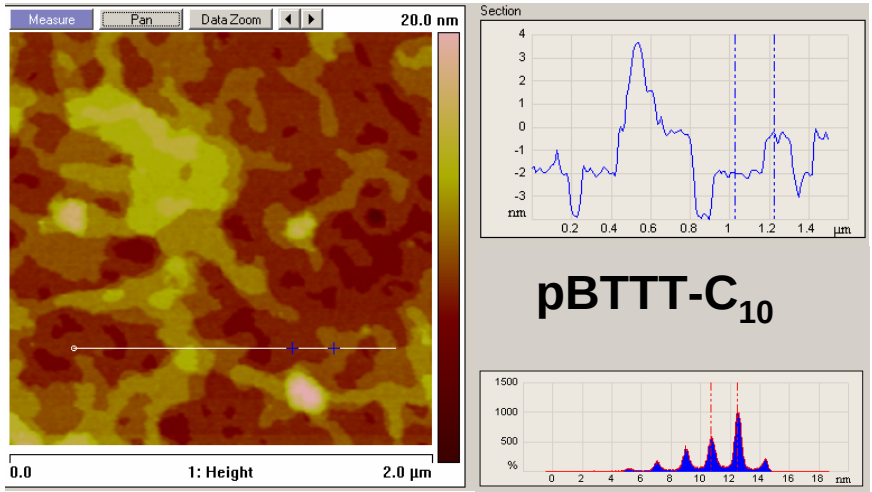


- Clear indication of regularly spaced layers with different electron density.
- Lamellae of packed cores separated from lamellae of packed side chains. Also consistent w/ long axis orientation.
- d-spacing ~2.1 nm
- **4 orders of diffraction from 20 nm thick films - indicates highly ordered and oriented structure!**

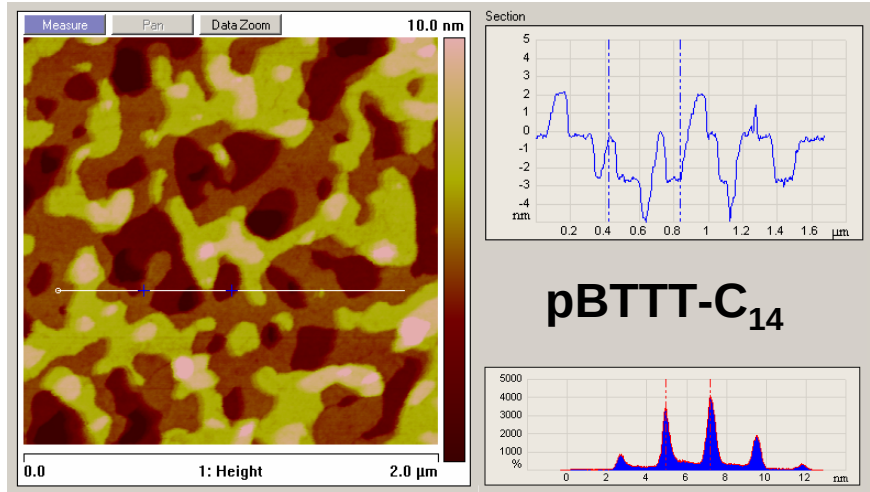


How would these lamellae be distributed laterally?

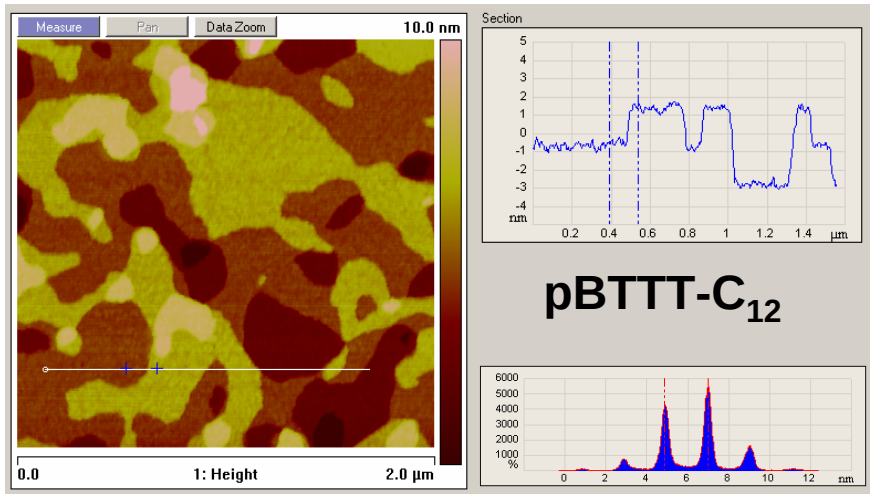
Atomic force micrographs of annealed films reveal wide terraces of molecular height



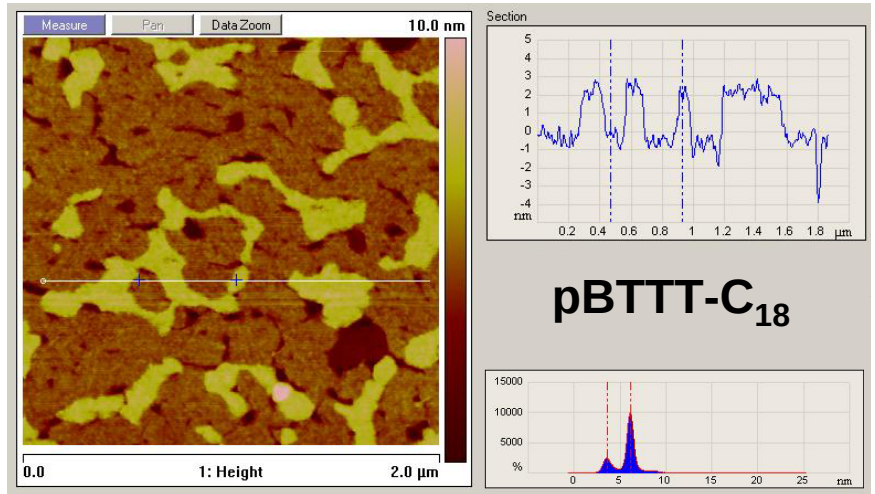
pBTTT-C_{10}



pBTTT-C_{14}



pBTTT-C_{12}

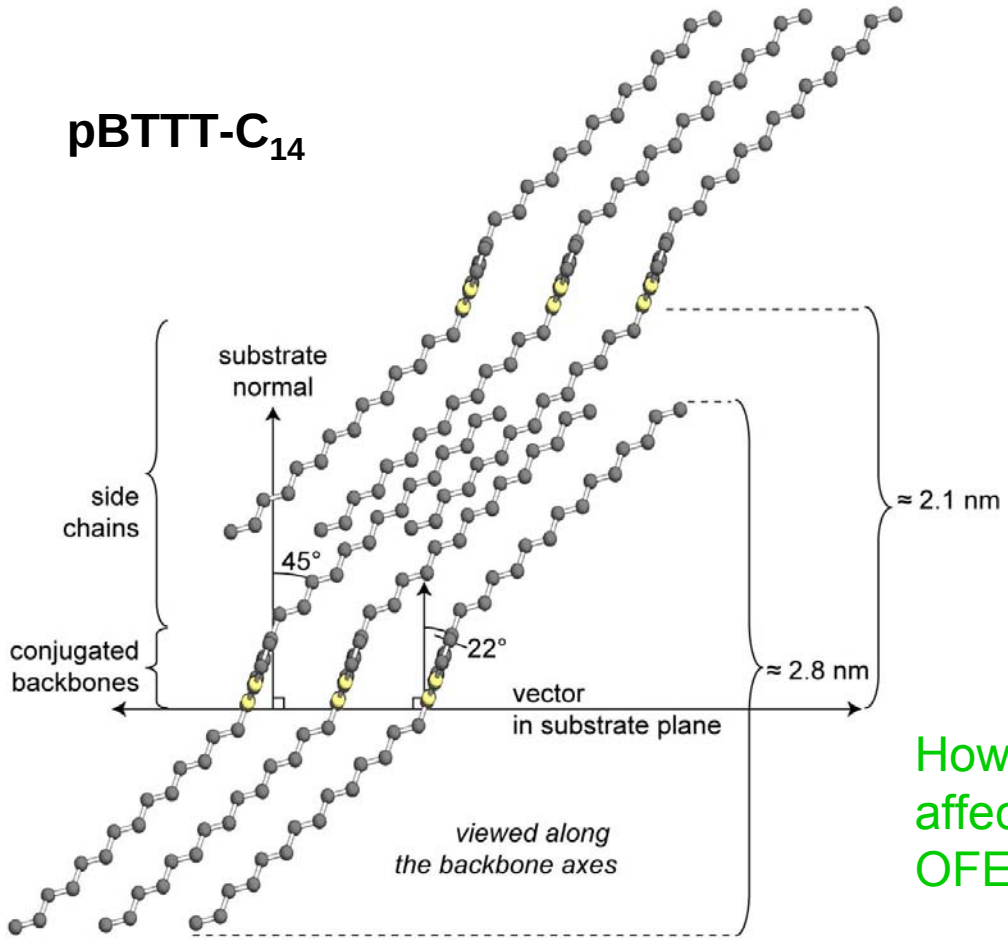


pBTTT-C_{18}

We now know the plane tilt, side chain orientation, the long axis tilt, lamellar packing w/ spacing, and lateral distribution of terraced domains.

Bringing it together: detailed microstructure of pBTTT-C14

- AFM and X-ray diffraction indicate comprehensive crystallinity of a single type.
- We can assume a narrow, monomodal orientation distribution and extract tilts from spectroscopies
- Further details: DeLongchamp, D. M. et al., Advanced Materials, in press, 2007



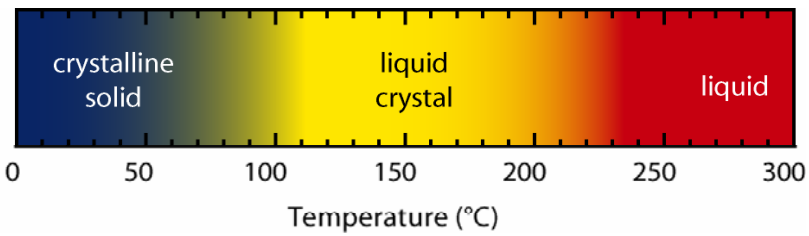
How does temperature affect the structure and OFET properties?

Combinatorial approach:

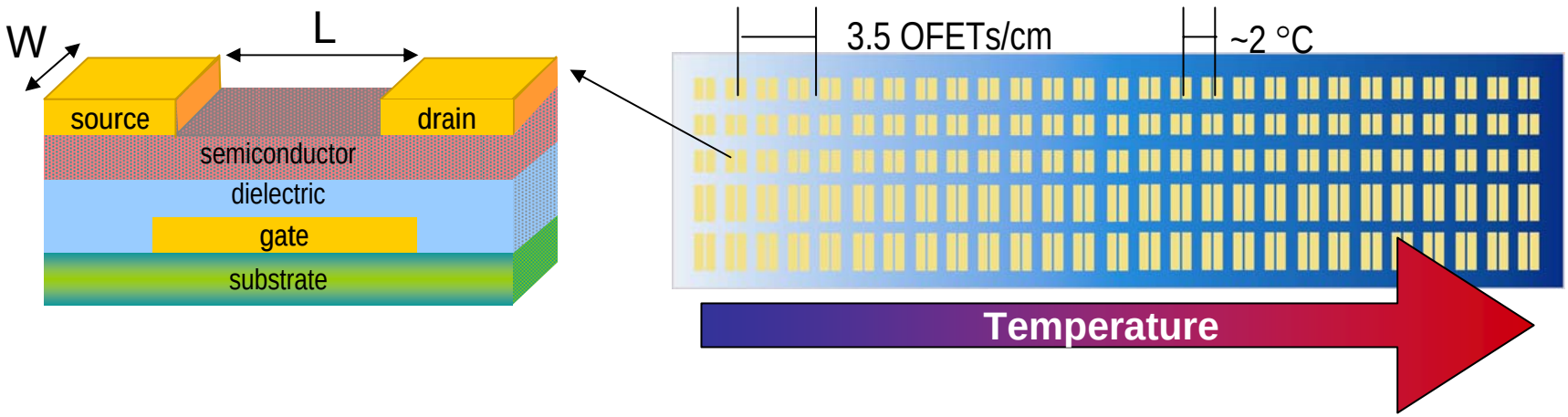
How does temperature affect the structure and OFET properties?

- Distinct structure/morphology difference in as-cast vs. annealed pBTTT films
- Previous structure study used ***arbitrary*** annealing temperature
- Combinatorial methods provide means to access this wide parameter space

Apply a temperature gradient to systematically evaluate the influence of thermal history on pBTTT-C12 OFETs



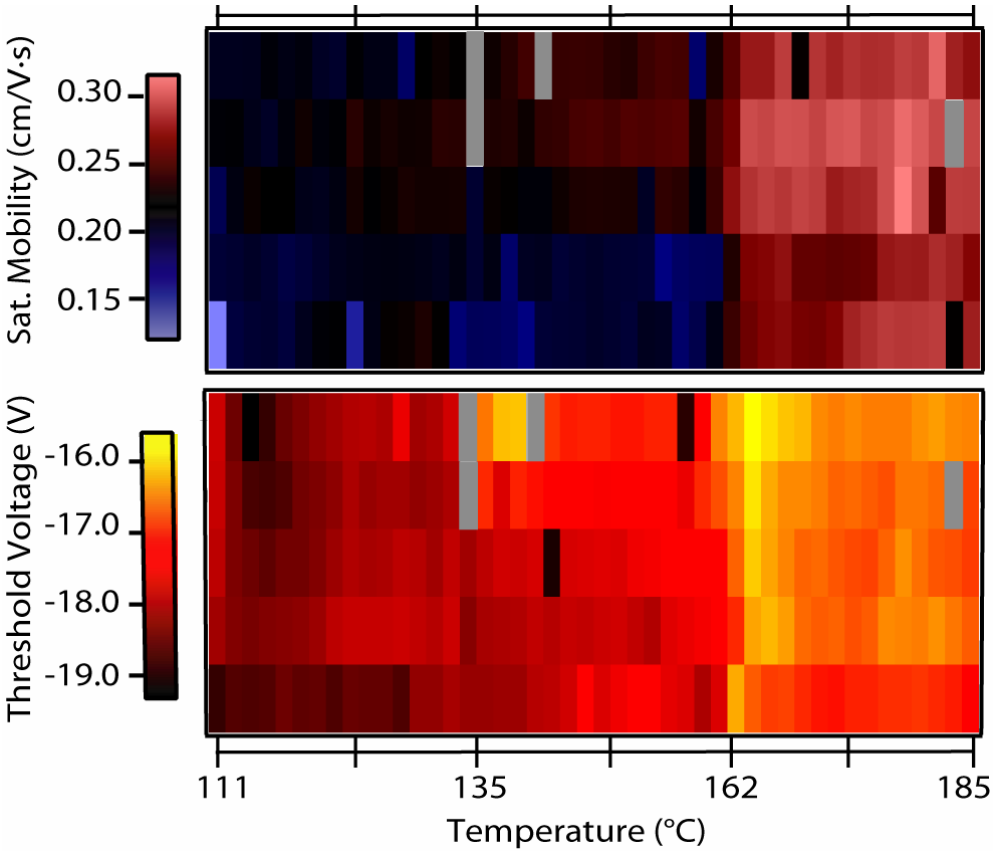
pBTTT-C12 OFET fabrication & thermal gradient



- pBTTT-C_{12} spin coated from warm dichlorobenzene onto OTS-SiO_2
- Top contact gold S/D electrodes
  - Channel width (W) = 1 or 2 mm
  - Channel length (L) = 80 to 220 μm
- Thermal gradient anneal in nitrogen
  - $\Delta T \sim 75°C$
  - Heated for 5 min, cooled to 80 °C (15 min)
- OFET characterization in N_2 purge

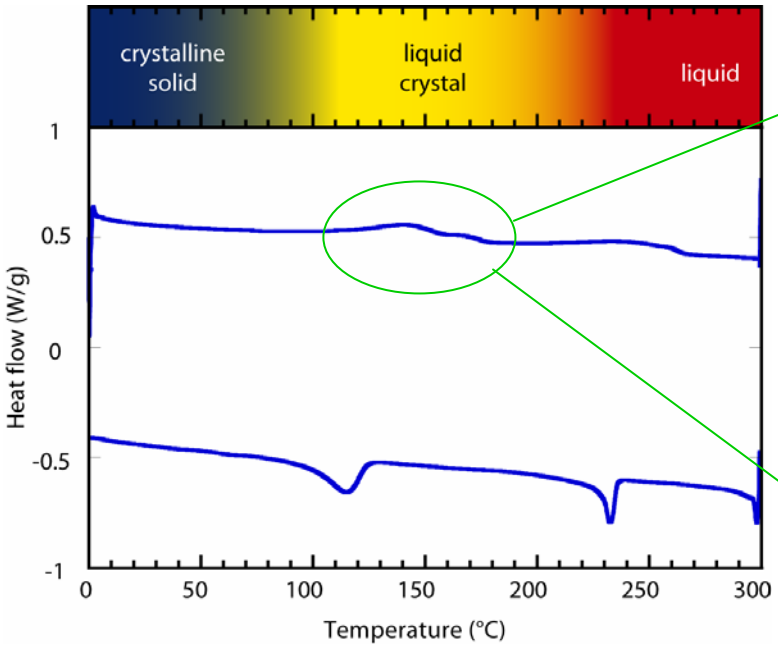
$$I_D = \frac{WC_i}{2L}\mu(V_G - V_T)^2$$

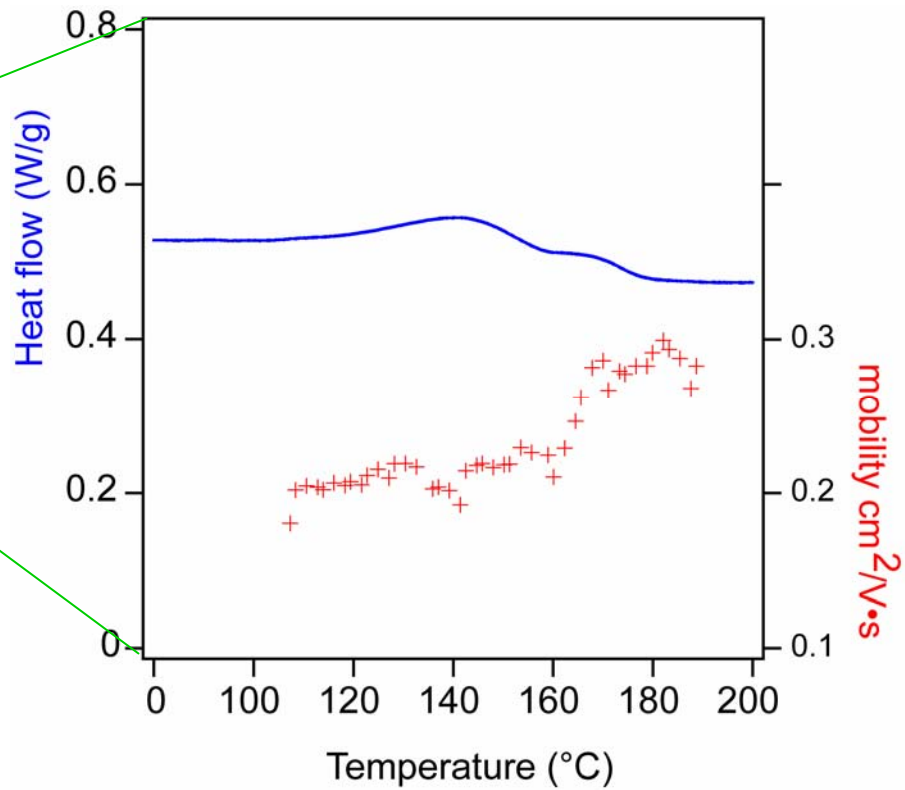
OFET characterization of pBTTT-C12



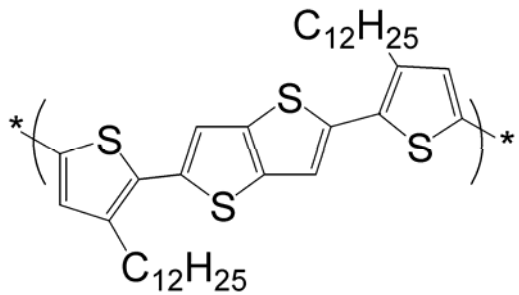
- Each pixel represents individual OFET (230 OFETs processed simultaneously)
- Gray pixels represent OFET with excessive gate leakage
- Mobility increases with temperature with transition region (160 to 165)ºC
- Highest mobility ~ 0.3 $cm^2V^{-1}s^{-1}$

Differential Scanning Calorimetry of pBTTT-C12

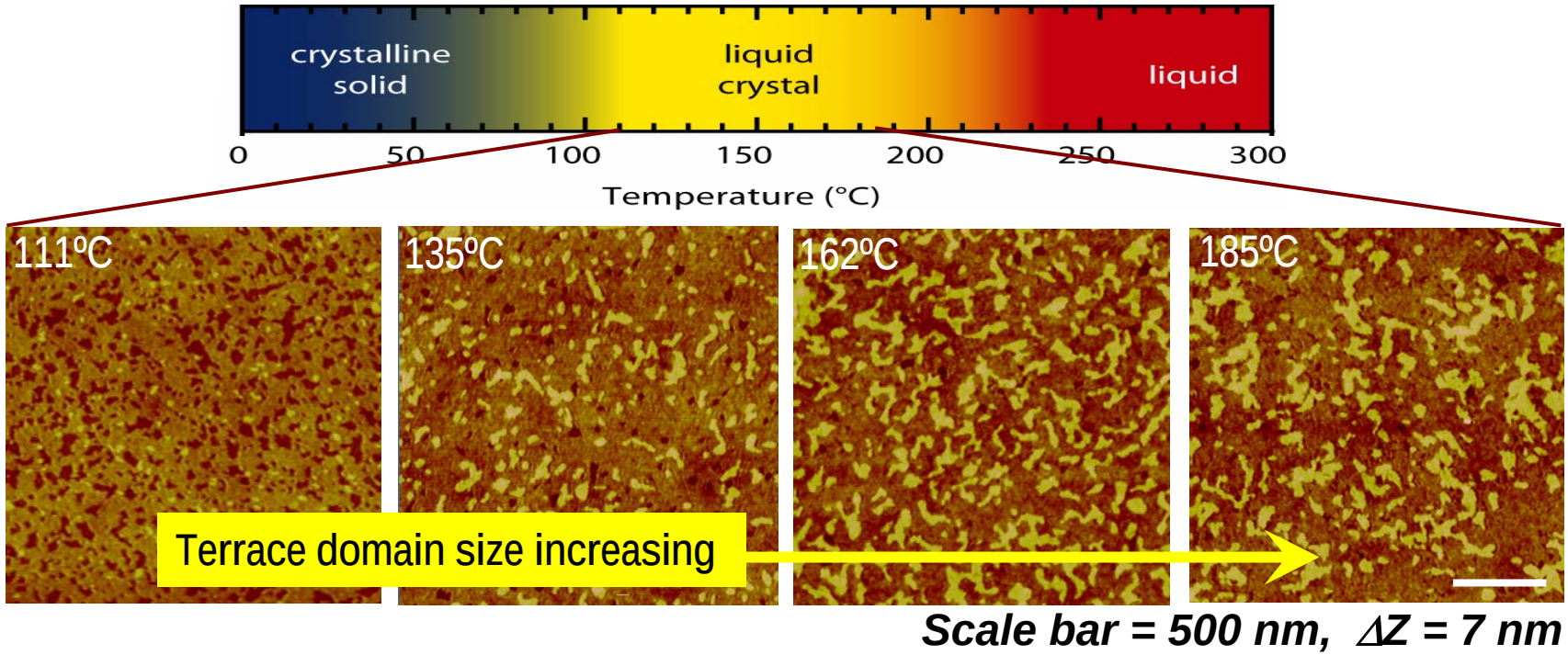




- Increased μ coincides with heating into LC phase (DSC)
- Powder DSC reveals melting transition from crystalline solid to liquid crystal occurs at 150-160°C

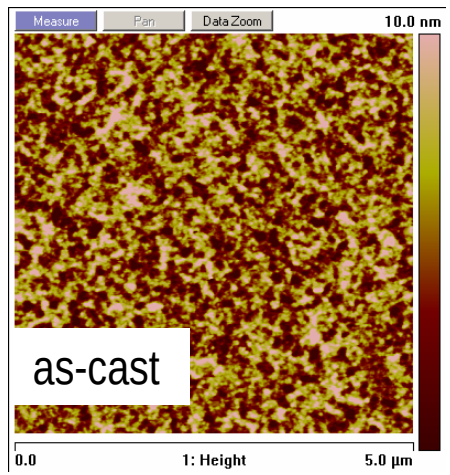


Atomic Force Microscopy of pBTTT-C12



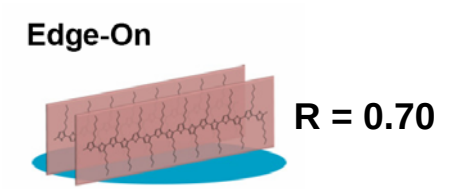
Scale bar = 500 nm, ΔZ = 7 nm

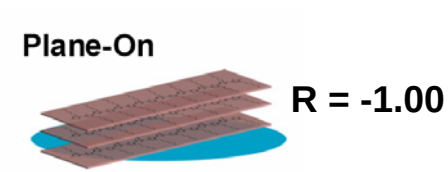
- As cast-films are featureless
- Lamellar terraces(~2 nm height) form during annealing
- Step height corresponds to lamellar spacing

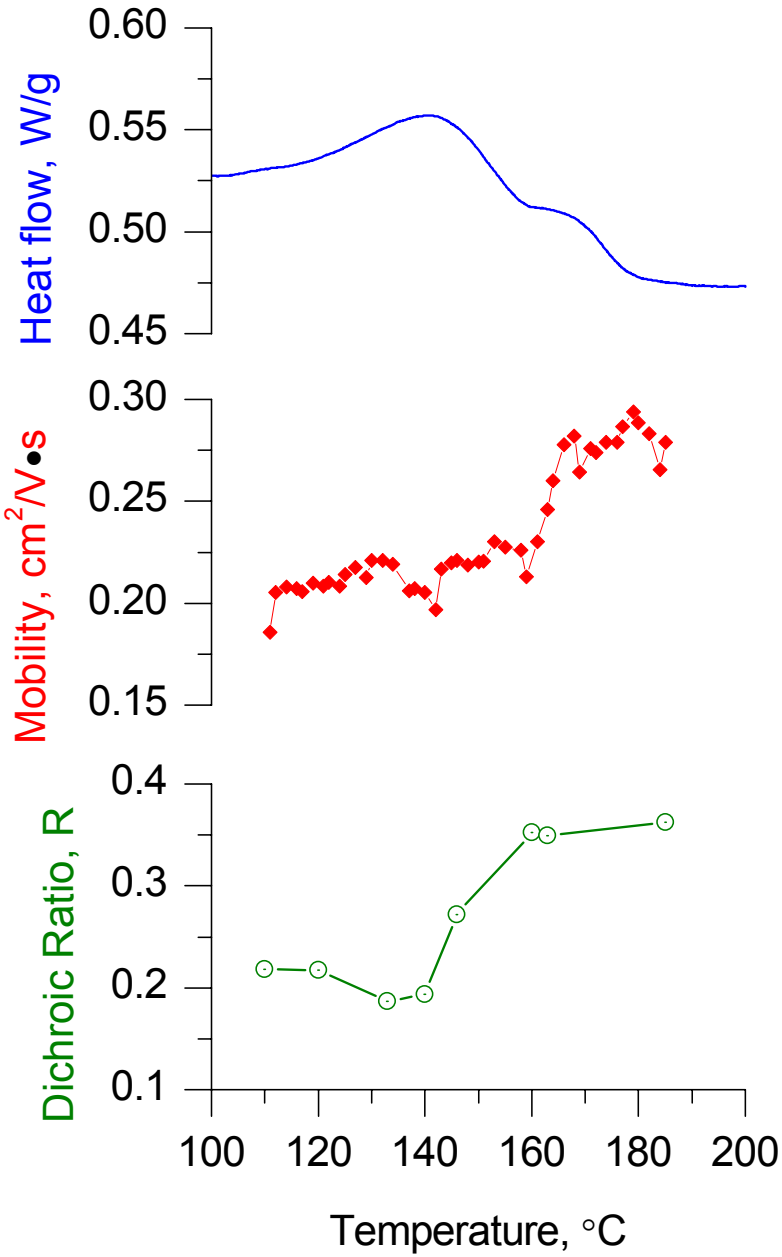


NEXAFS of pBTTT-C12

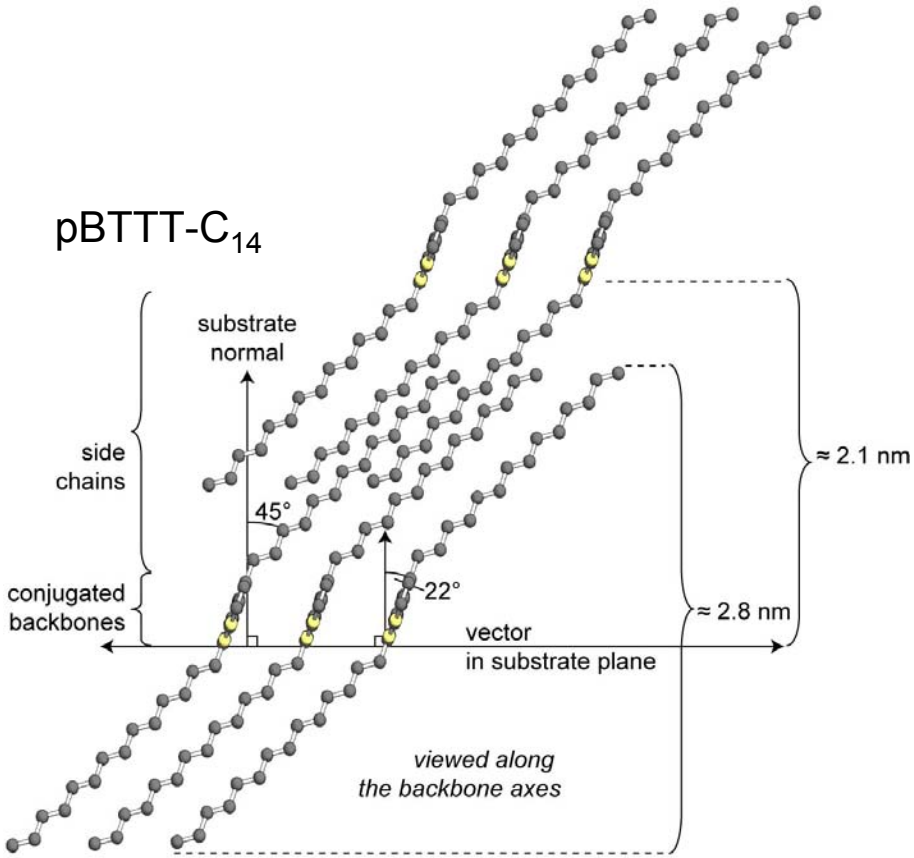
Edge-on orientation of conjugated plane increases with temperature due to decrease in disorder of the film







Conclusions



- Improved OFET characteristics result from increased crystalline domain size and molecular ordering when pBTTT-C12 heated into LC state
- Smooth correlation (temperature, structure) made possible by use of combinatorial temperature gradient
- Robust and practical method in new materials development
  - lowest thermal budget necessary
  - screening materials with multiple thermal transitions
  - optimize OFET performance
- Lucas, L. A. *et al*, Appl. Phys. Lett. **90**, 012112, 2007

Acknowledgements

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