

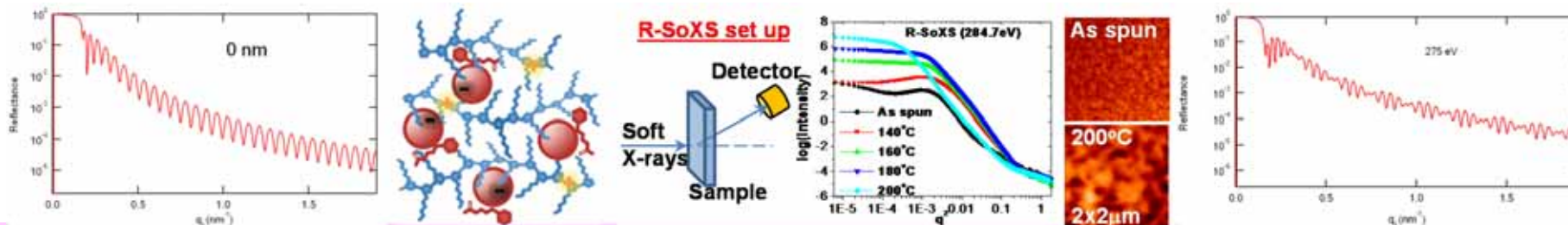
Critical Needs in Characterizing Organic Devices

In reply to Sol: What I would really like to do!
 Janos' demand: We need to solve problems!

XDL workshop,
 Cornell, June 7, 2011

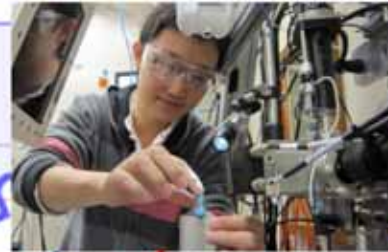
Harald Ade
 Department of Physics
 North Carolina State University
<http://www.physics.ncsu.edu/stxm/>

Thanks to organizers for inviting me
 Research supported by: DOE Office of Science, Basic Energy Science, Division of Materials Science and
 Engineering, National Science Foundation



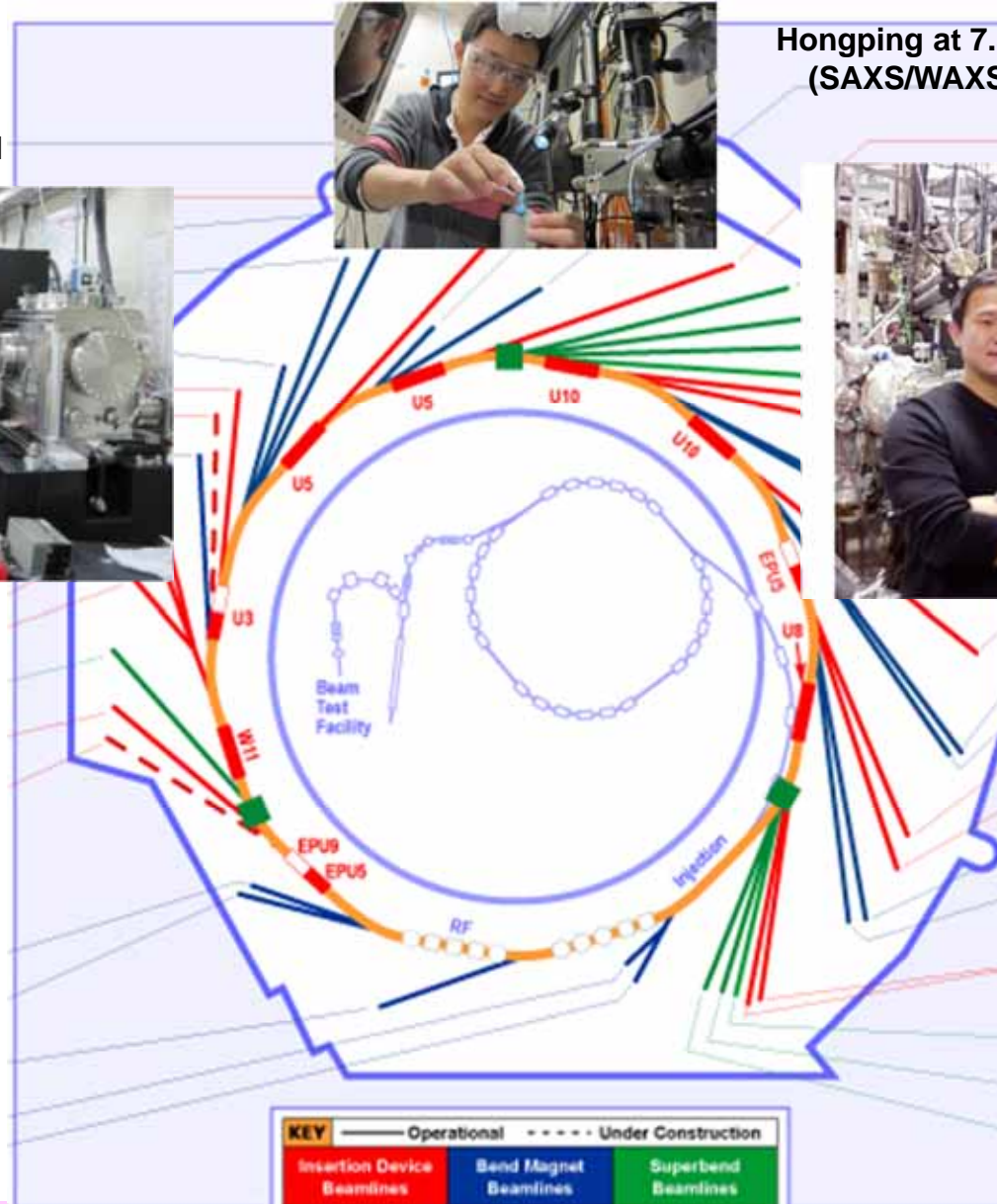
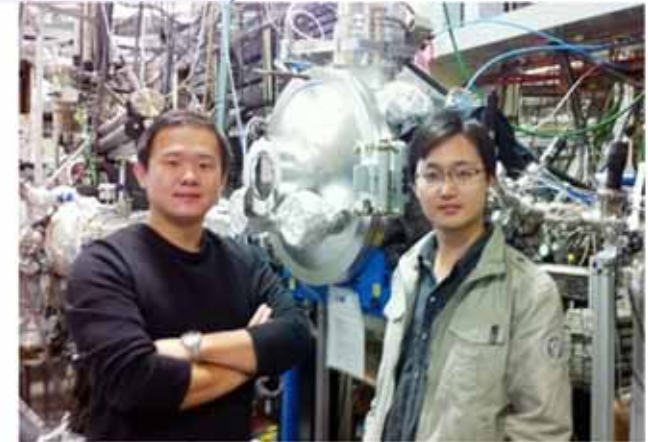
Beamlines we use are: 5.3.2.2 (STXM), 6,3.2 (SoXR), 7.3.3. (WAXS), 11.0.1.2 (SoXS), 11.0.2.1 (STXM)

Brian at 5.3.2.2 STXM



Hongping at 7.3.3.
(SAXS/WAXS)

Cheng and Hongping
at 11.0.1.2. (R-SoXS)



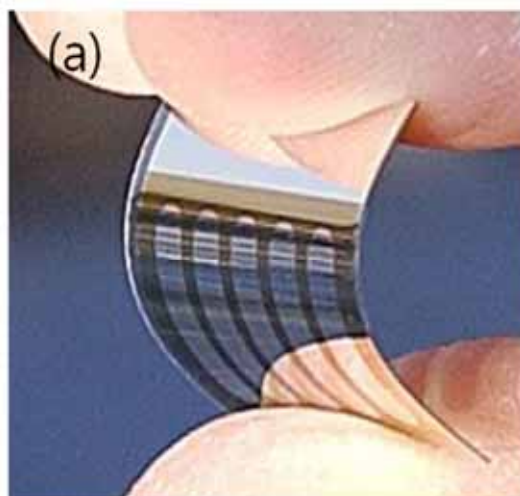
11.0.2.1 STXM



My energy range might
be below the Cornell
ERL target range

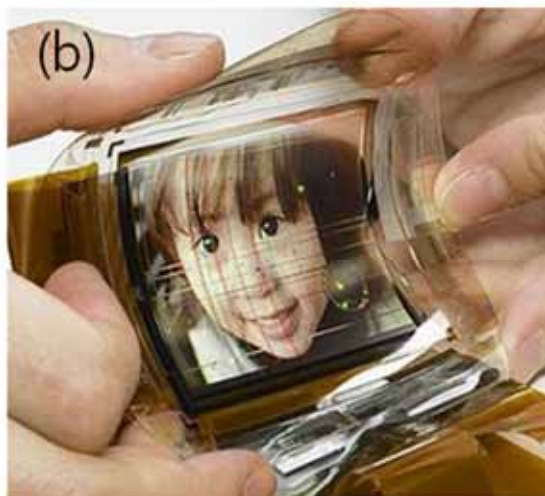
Organic Electronics: An interesting area of applications and characterization needs

Context: Energy Security/Independence, Global Warming



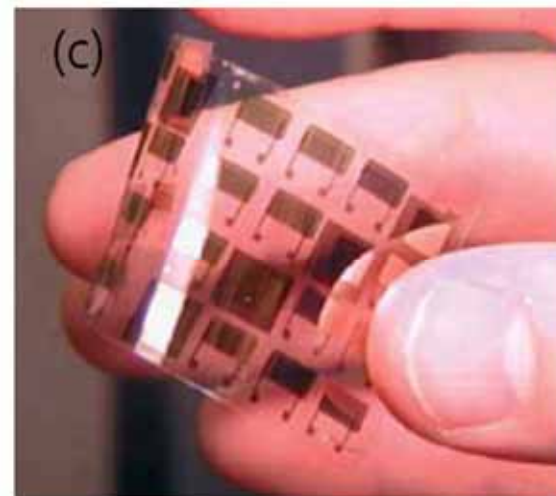
organic photovoltaics
(OPV)

(from Nicole Cappello,
Gatech)



Flexible organic
light emitting
diodes (OLED)

(from Sony)



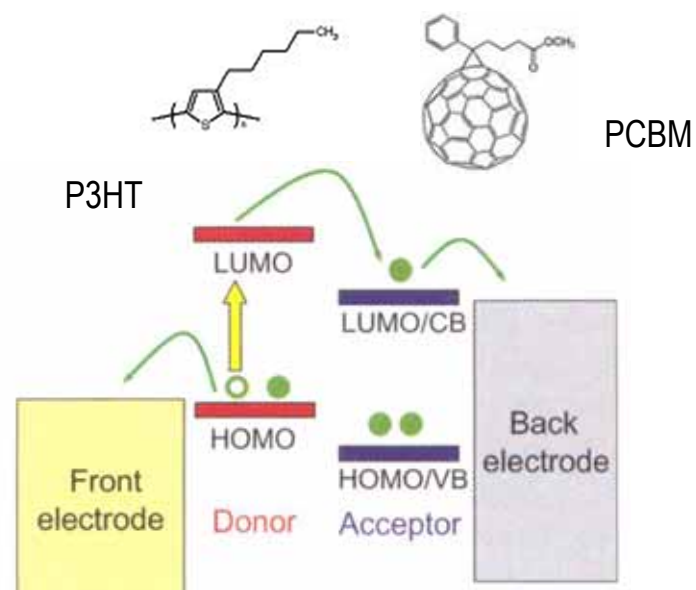
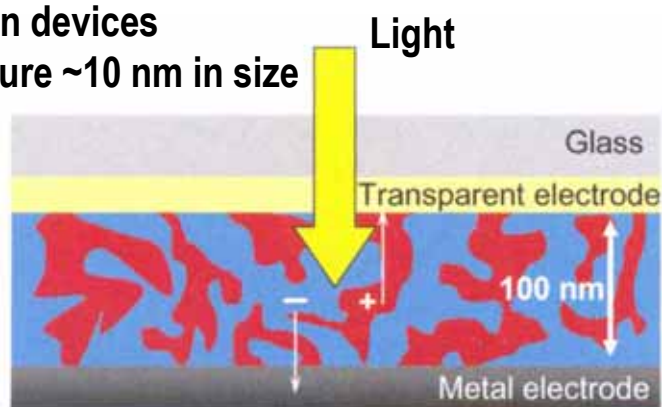
organic thin film transistors,

(from www.livescience.com.)

Critical Factors in Organic Photovoltaic Devices: Morphology, interfaces, domain purity, and energy levels

Bulk heterojunction devices

Need lateral structure ~10 nm in size



“Organic Photovoltaics: Materials, Device Physics, and Manufacturing Technologies”, Wiley-VCH (August 25, 2008)

What makes fullerene-based devices to successful?

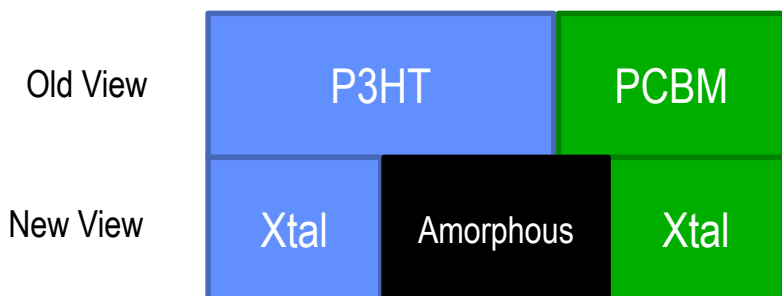
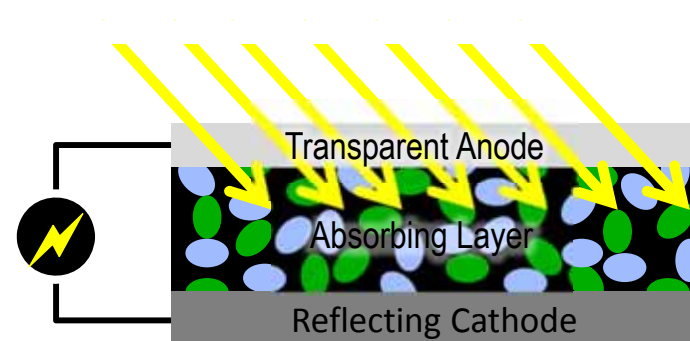
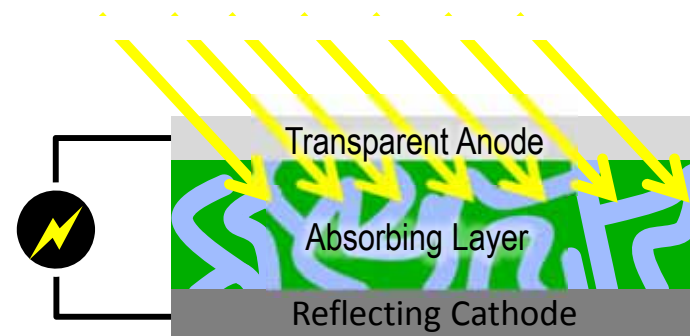
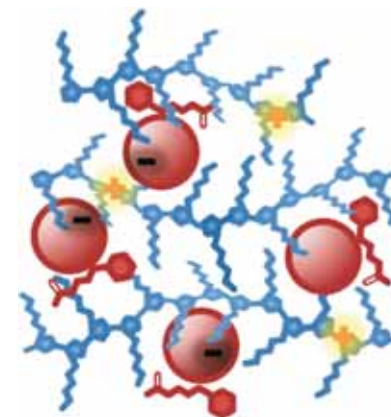
What are the primary shortcomings of polymer-polymer devices and can they be overcome?

What role can soft x-ray characterization methods play?

- **Morphology (including crystallinity):** scattering and microscopy
- **Interfaces:** scattering and reflectivity
- **Purity:** quantitative compositional microscopy and scattering

Actual Device Morphology: Not two but at least three phases!

- Three phases inferred in P3HT:PCBM
 - ◆ Pure P3HT crystals
 - ◆ “Pure” PCBM agglomerates
 - ◆ Amorphous phase w/ 15-20 wt.% PCBM
- No Pure amorphous phases exist in devices
 - ◆ Two-phase model based on pure components incorrect
- Volume breakdown of the phases: ~1/3 is mixed amorphous phase



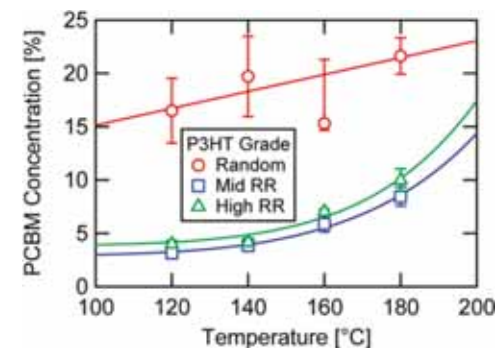
There is a lack of excellent tools to characterize OPV device morphology

- **Need quantitative mapping**
 - **Better than analytical TEM**
- **~10 nm spatial resolution**
- **3D**

Even present tools are very powerful

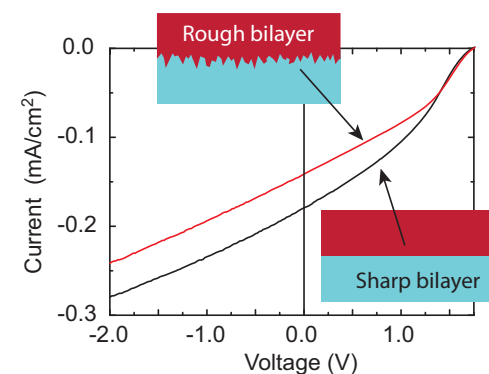
B. Collins et al. J. Phys Chem Lett 1, 3160 (2010)

- ◆ X-ray microscopy shows PCBM is partially miscible with P3HT (~15% PCBM in amorphous portion of P3HT)
- Three, not two domains in BHJ devices of this important system



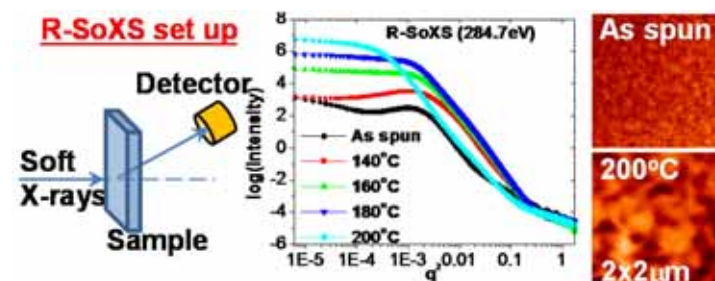
H. Yang, et al. Adv Funct Mater. 20, 4209 (2010)

- ◆ X-ray reflectivity coupled to device data and MC simulations shows that interface structure in PFB/F8BT bilayers contributes 50% to the poor performance.
- Non-equilibrium, sharp interfaces are best



S. Swaraj et al., Nano Letters 10, 6863 (2010)

- ◆ Scattering and microscopy shows that domains in all-polymer blends are too large or too impure
- Need better control. Use of BCP?



Characterization power based on Soft X-rays' unique interaction with organic materials

Scattering factors and optical constants of C,N, and O

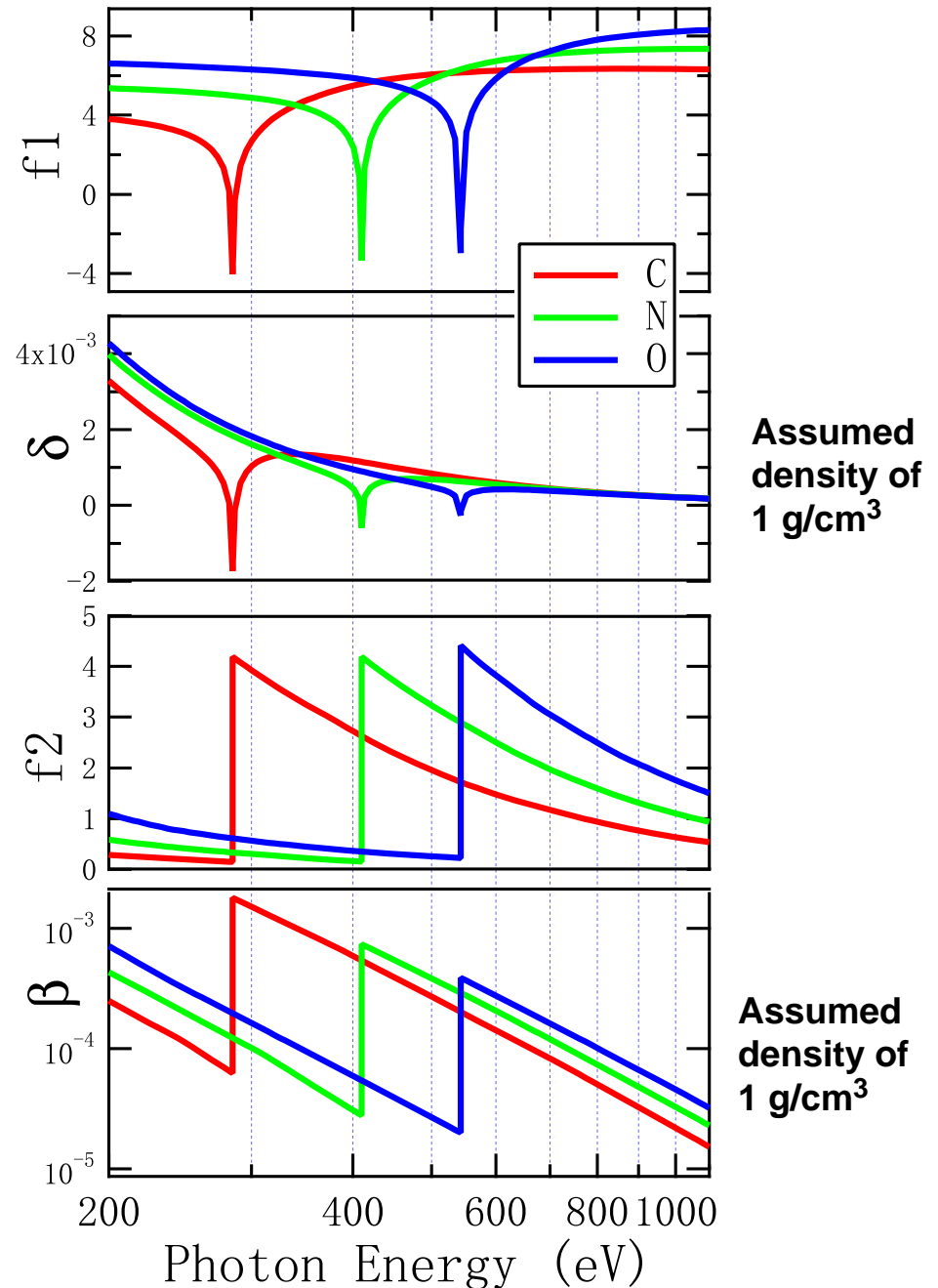
Complex index of refraction:
 $n = 1 - \delta + i\beta$

“Natural” scattering contrast:

$$I(E) \propto F^2(E) \propto E^4 |\delta(E) + i\beta(E)|^2$$

Quantitative absorption microscopy:

- Beer's Law: $I = I_0 e^{-\mu \rho t}$
 → 20-200 nm thick samples



Resonant Scattering/Reflectivity R-SoXS/R-SoXR

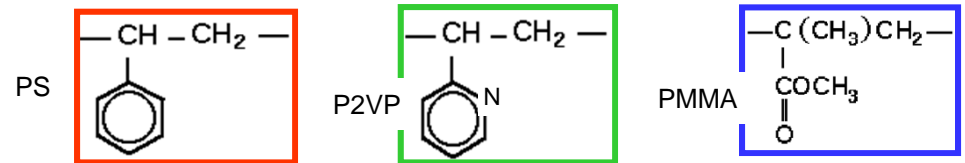
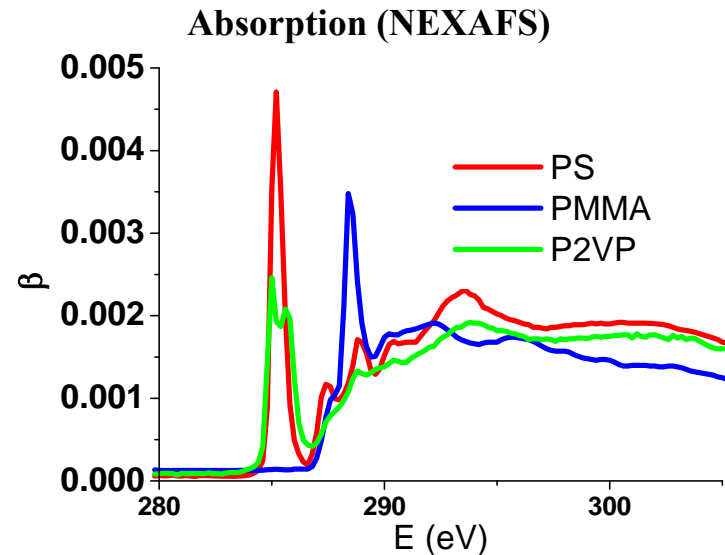
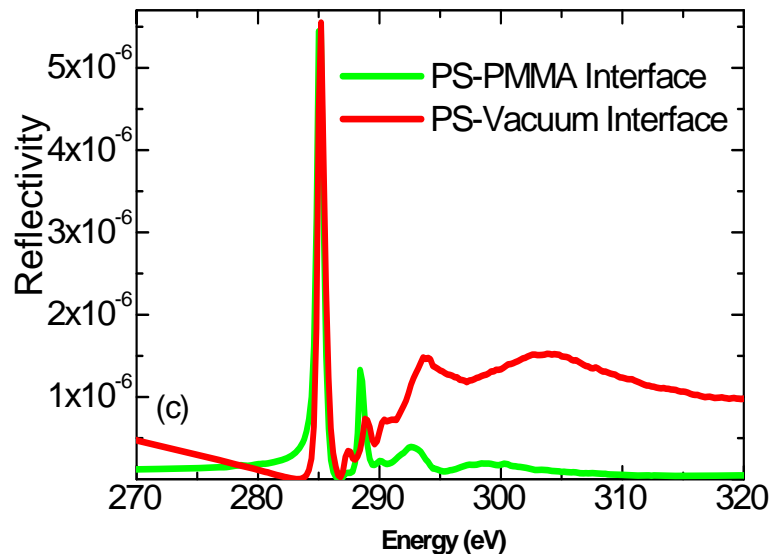
(contrast is almost as good as selective deuteration)

Scattering factors f' and f'' (optical const. δ and β , respectively) show strong energy dependence

$$n = 1 - \delta + i\beta$$

Neutron community use different terminology: complex scattering length density

$$R_{12} = |r_{12}|^2 = \left| \frac{n_1 \sin \theta_1 - n_2 \sin \theta_2}{n_1 \sin \theta_1 + n_2 \sin \theta_2} \right|^2 \propto \Delta\delta^2 + \Delta\beta^2$$

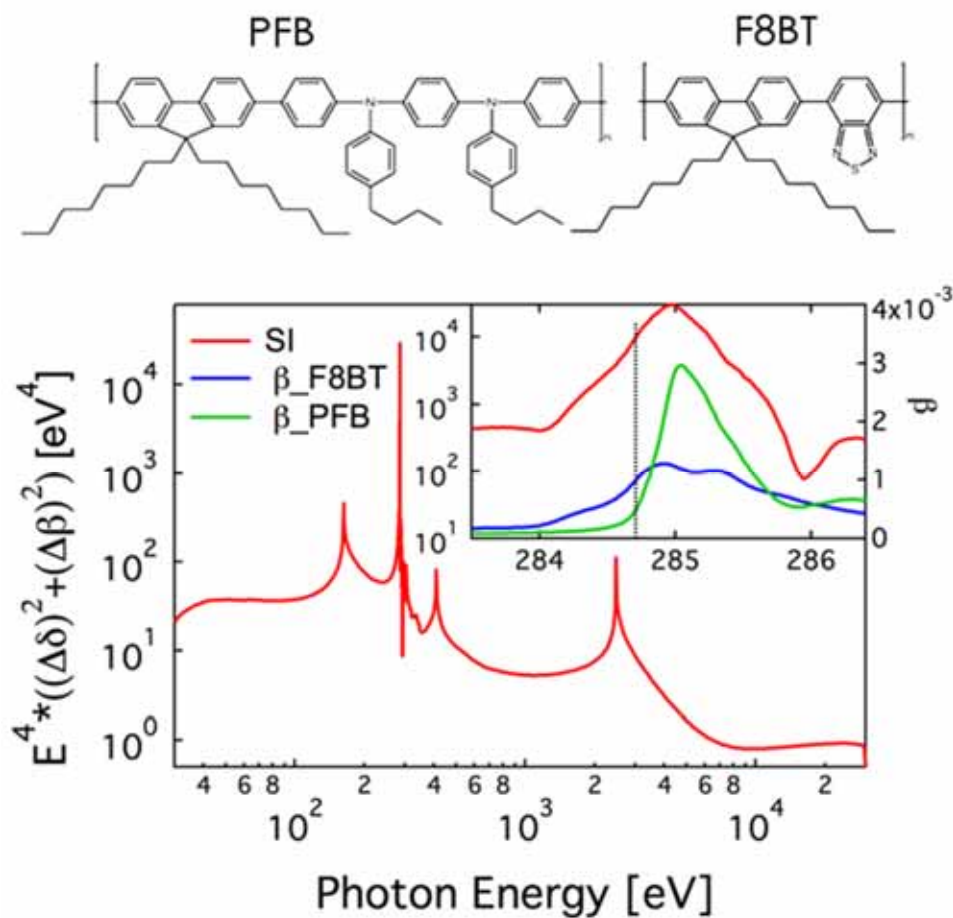
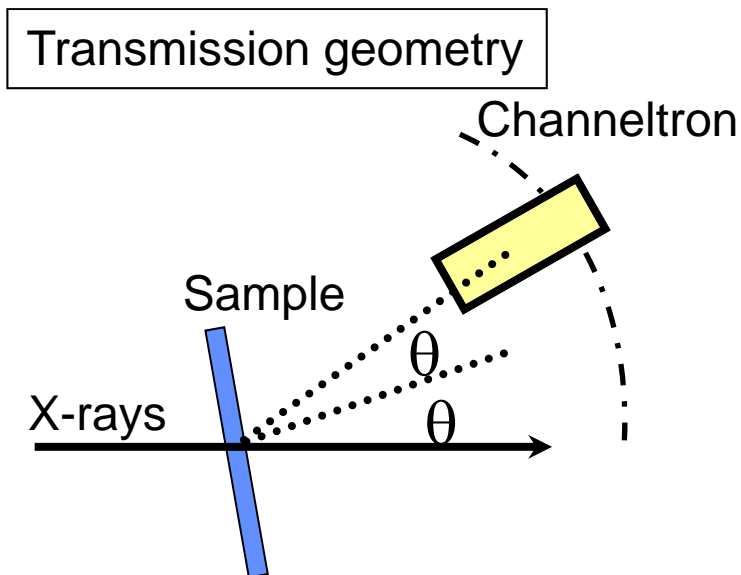


$$R \text{ or } I \propto (\Delta\delta^2 + \Delta\beta^2)$$

- “Bond specific” scattering!
- Substantial potential as complementary tool!

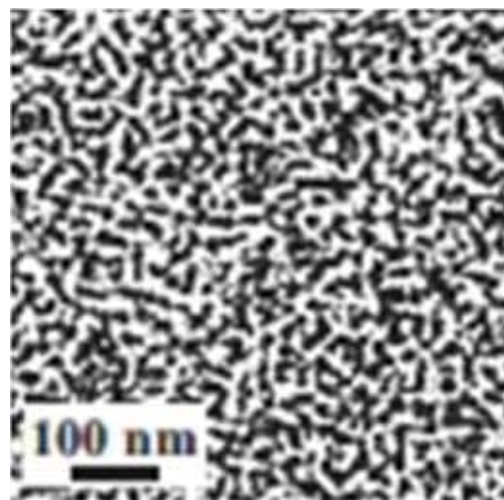
Resonant Soft X-ray Scattering (R-SoXS) of PFB:F8BT blend

High enough scattering contrast for transmission experiment



Are donor and/or acceptor domains pure in OPV devices?

Binarized phase contrast TEM of P3HT:PCBM BHJ

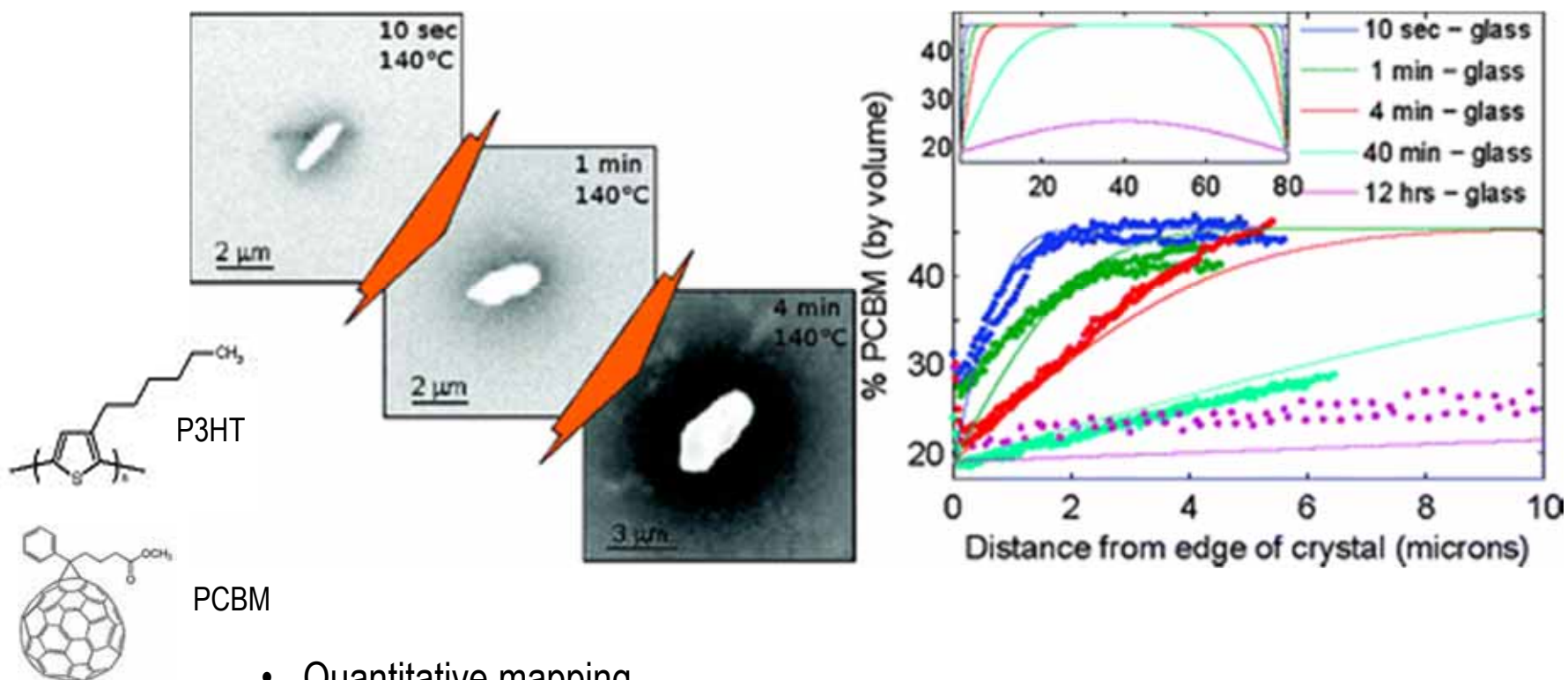


Are there just two phases?

Ma W., Gopinathan A., & Heeger A.,
Adv. Mater. **19**, 3556 (2007).

Thermodynamics of blends used in organic solar cells

P3HT:PCBM 1:1 w/w

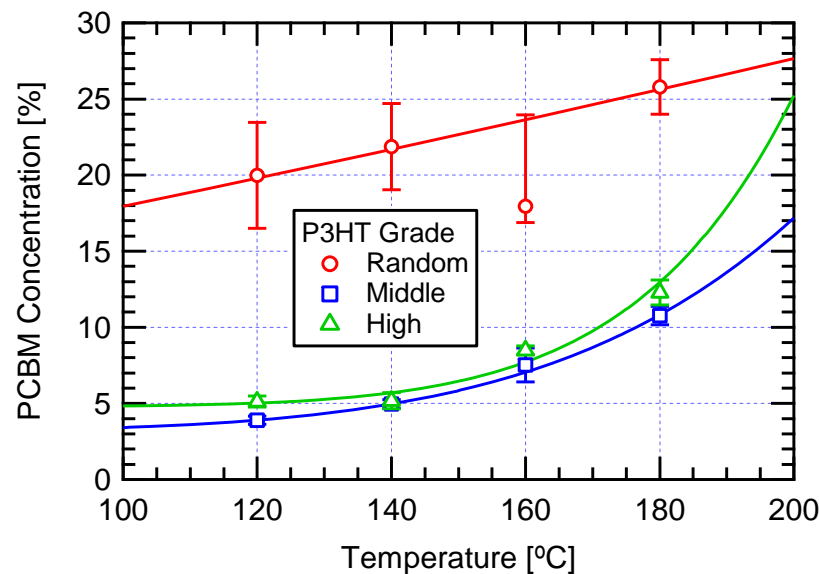
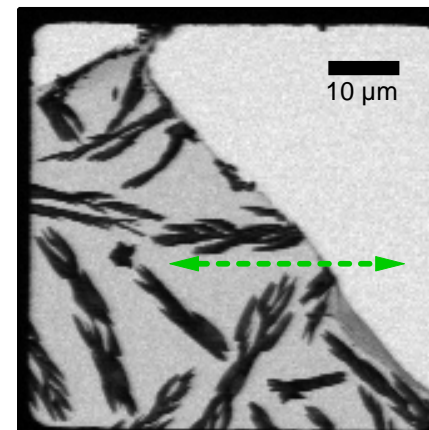
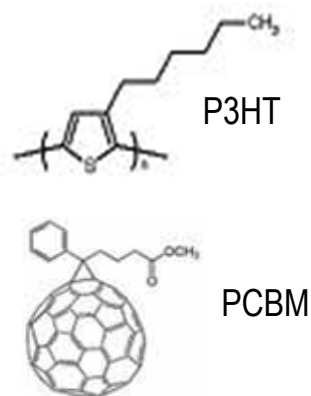
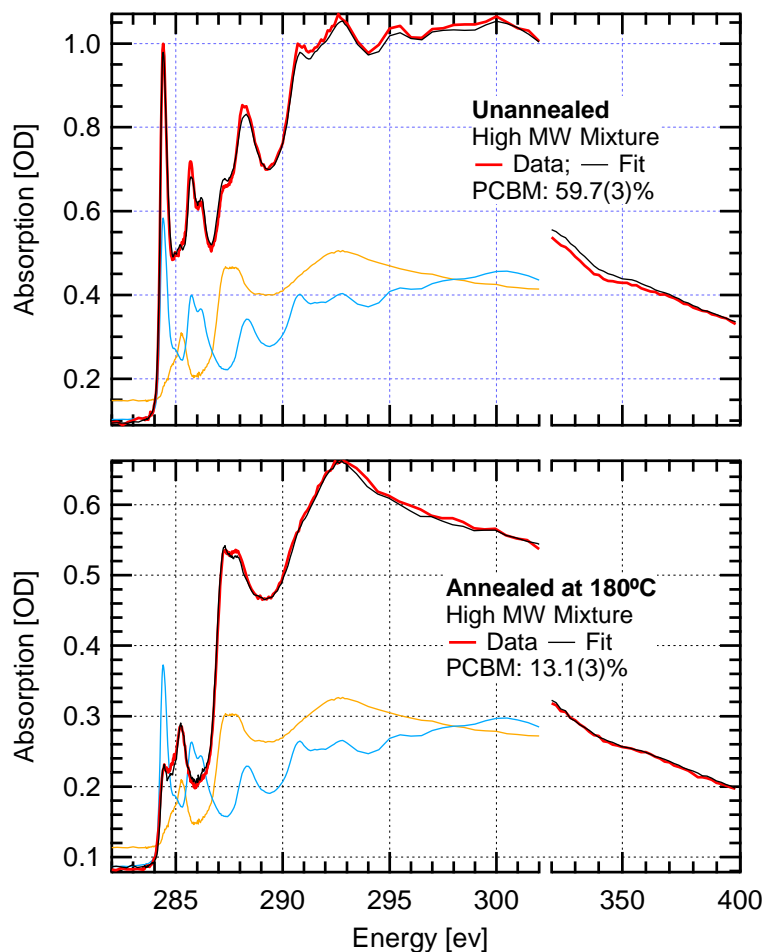


- Quantitative mapping
- Diffusion constant $\sim 2.5 \times 10^{-14} \text{ m}^2/\text{s}$.
- **The PCBM concentration at the crystal boundary was found to be $\sim 19\%$ (v/v)**

Watts, B., Belcher, W. J., Thomsen, L. et al., *Macromol.* **42**,. 8392 (2009)

Miscibility in P3HT:PCBM from NEXAFS microscopy

1:1 blends annealed 48 hrs, large PCBM crystals next to “equilibrium” matrix

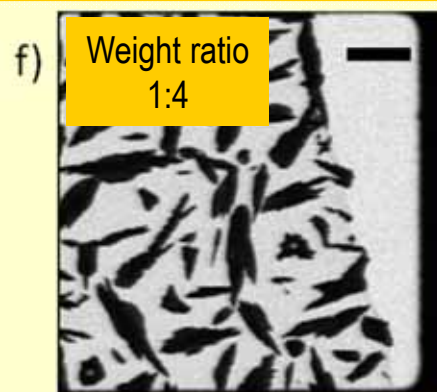
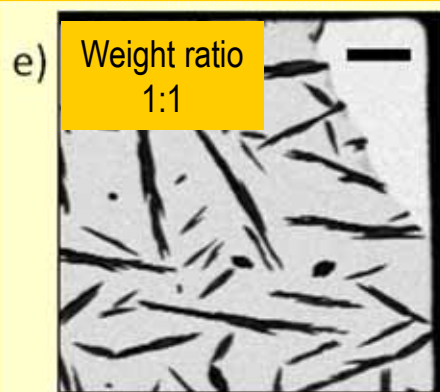
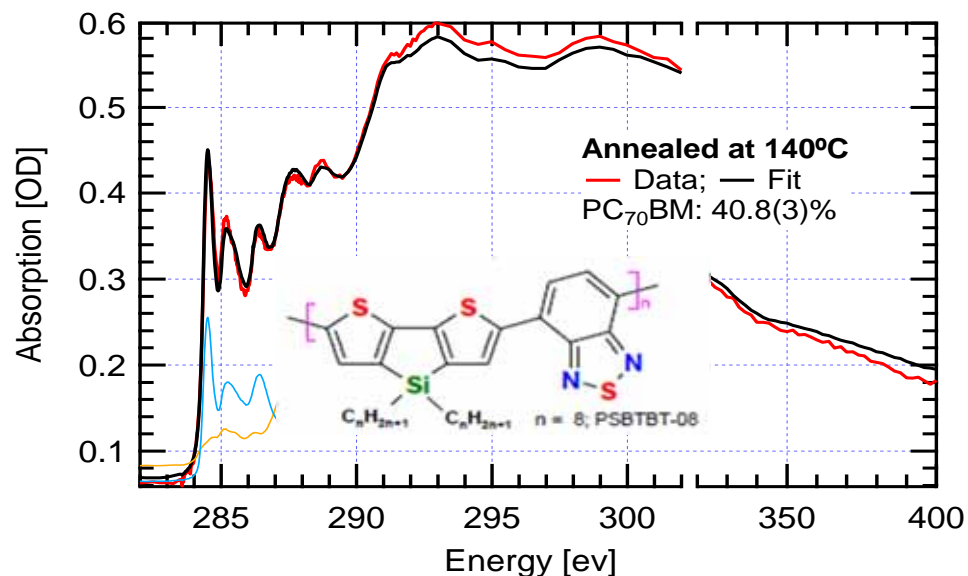


Absolute accuracy <1%

All grades of P3HT are partially miscible

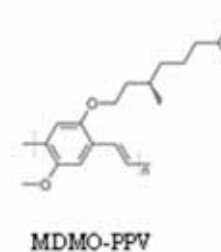
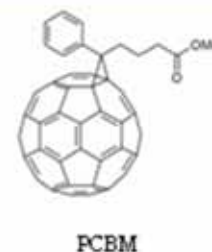
Miscibility seems to be a general phenomena

This has not been contemplated until recently



MDMO-PPV:PCBM blends

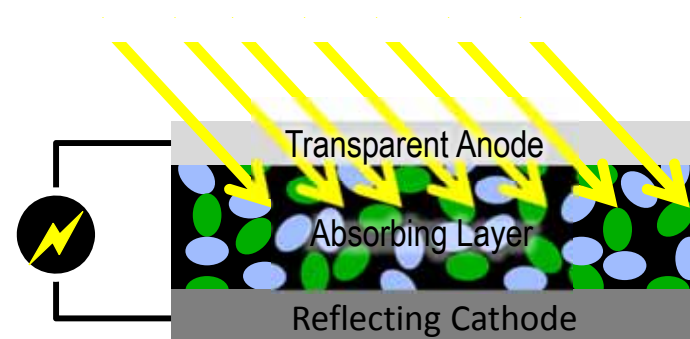
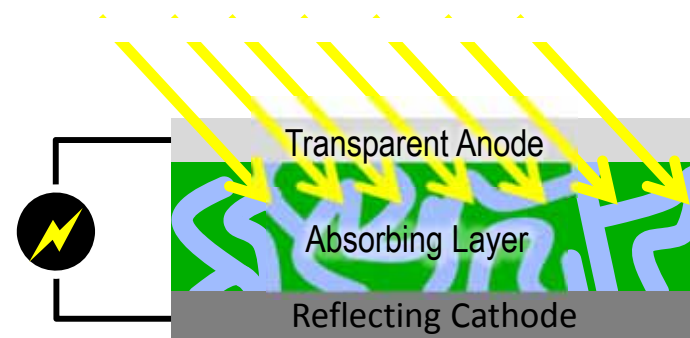
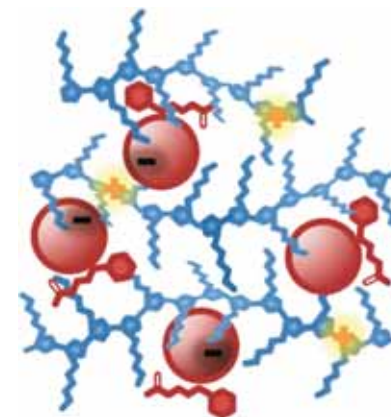
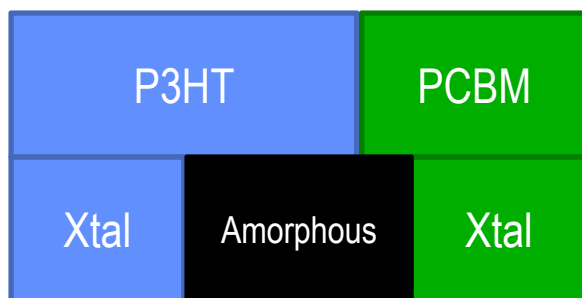
→ 9% miscibility



→ Domains seem to be always impure → implications for device physics?

Actual Device Morphology: Not two but at least three phases!

- Three phases inferred in P3HT:PCBM
 - ◆ Pure P3HT crystals
 - ◆ “Pure” PCBM agglomerates
 - ◆ Amorphous phase w/ 15-20 wt.% PCBM
- No Pure amorphous phases exist in devices
 - ◆ Two-phase model base on pure components incorrect
- Volume breakdown of the phases: ~1/3 is mixed amorphous phase

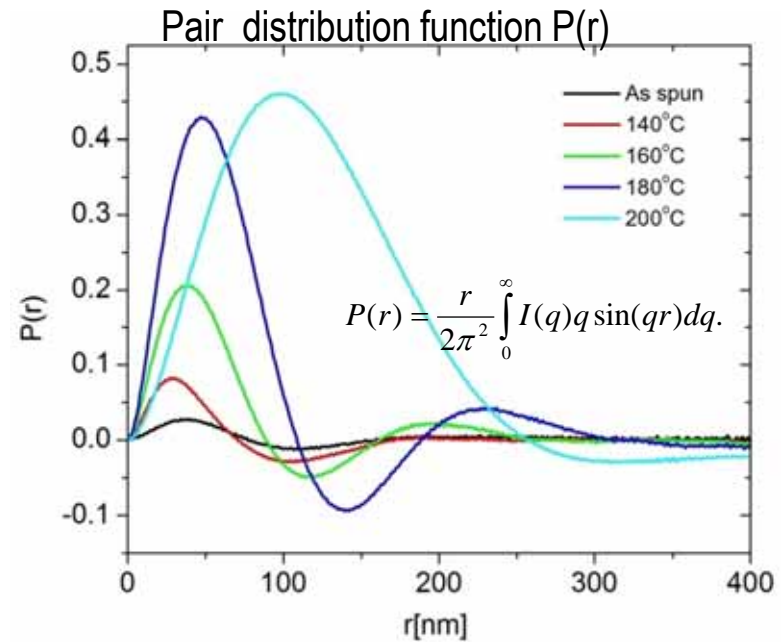
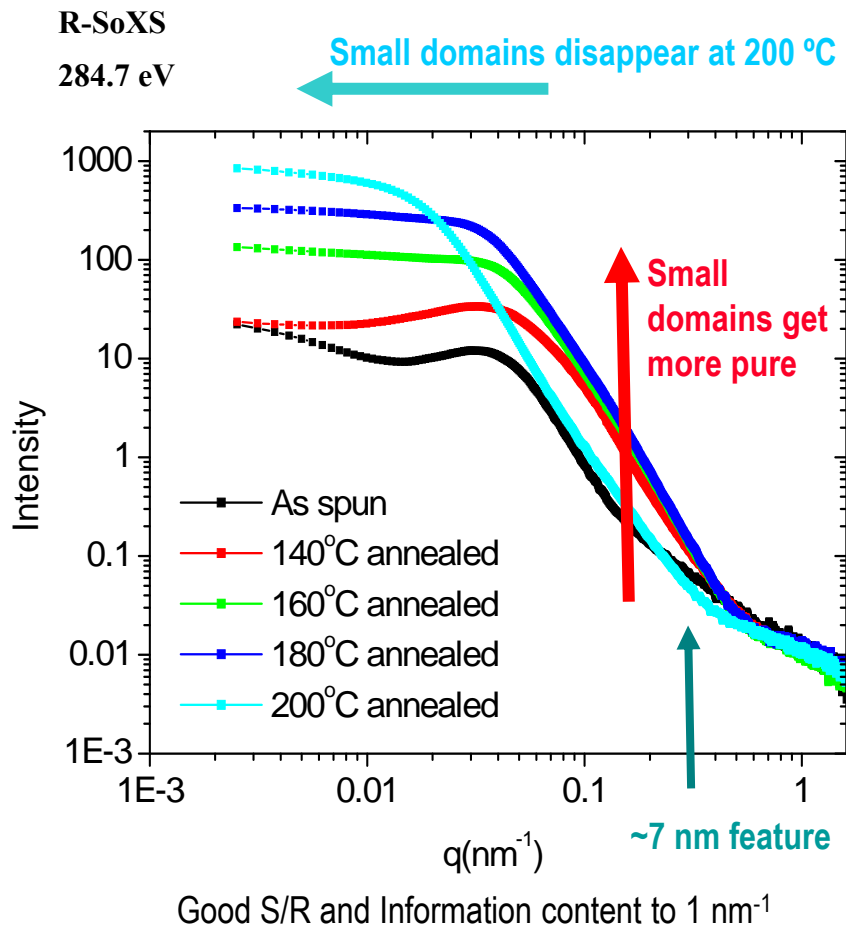


Morphology

Polymer:Polymer blend devices

Domain size analysis with R-SoXS

1:1 PFB:F8BT blends cast from chloroform

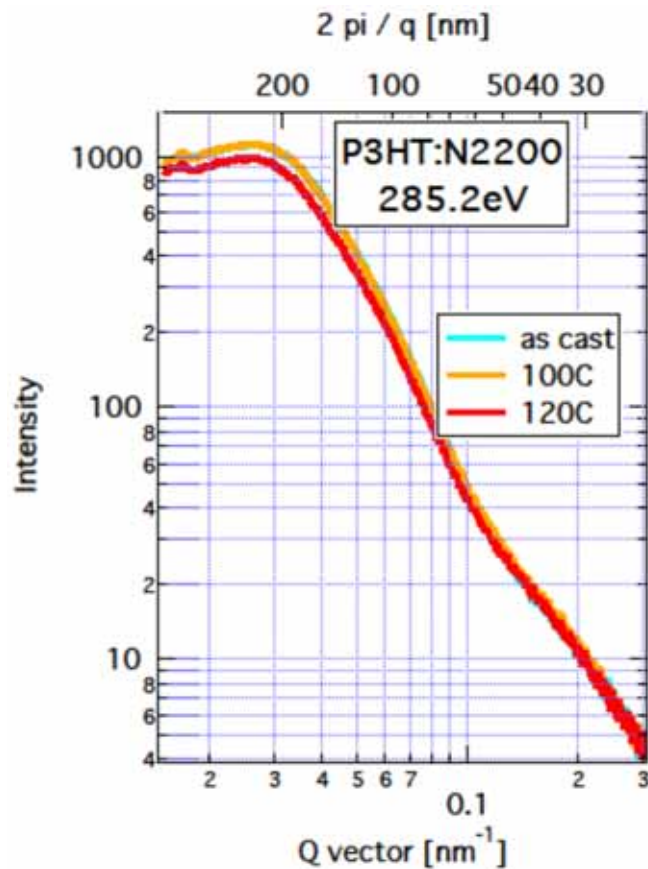
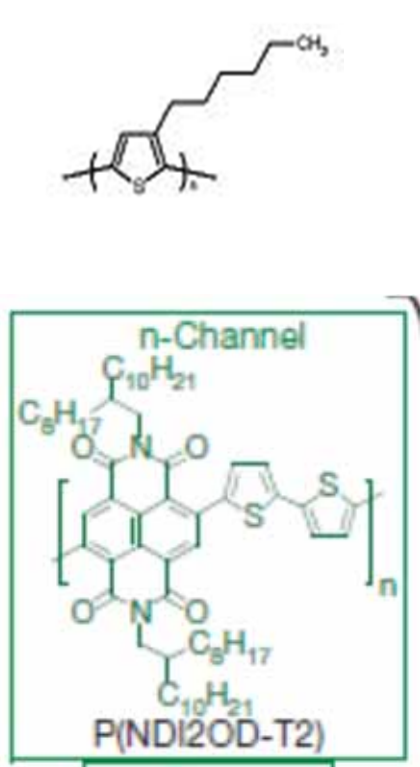


Sample		As spun	140 °C	160 °C	180 °C	200 °C
Domain size /nm	RSOXS	~77	~71	~89	~110	~260
	STXM	~80	~80	~85	~100	~250

Average domain much larger than exciton diffusion length and/or too impure
 → poor efficiency (partially) explained

Another all-polymer blend: P3HT:N2200

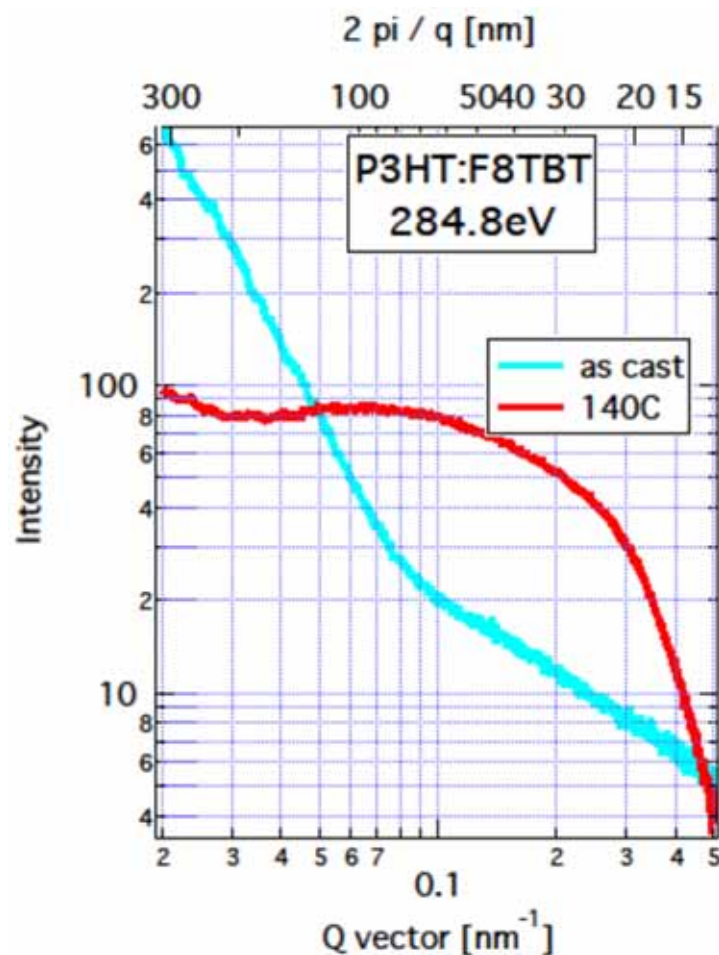
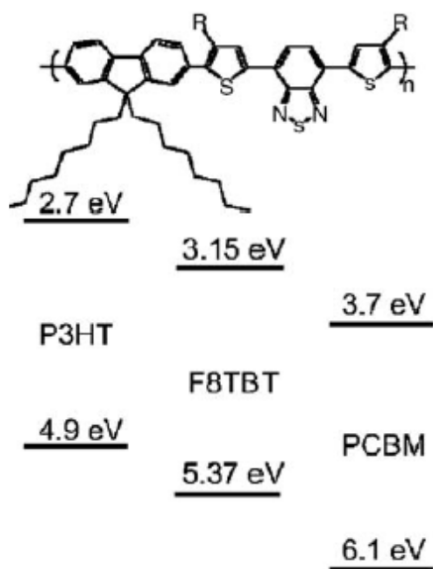
Initial data/analysis



→ Domains way too large from the beginning

Third all-polymer blend: P3HT:F8TBT Initial data/analysis

PCE=1.8% at 140 °C
McNeill APL **90**, 193506 (2007)

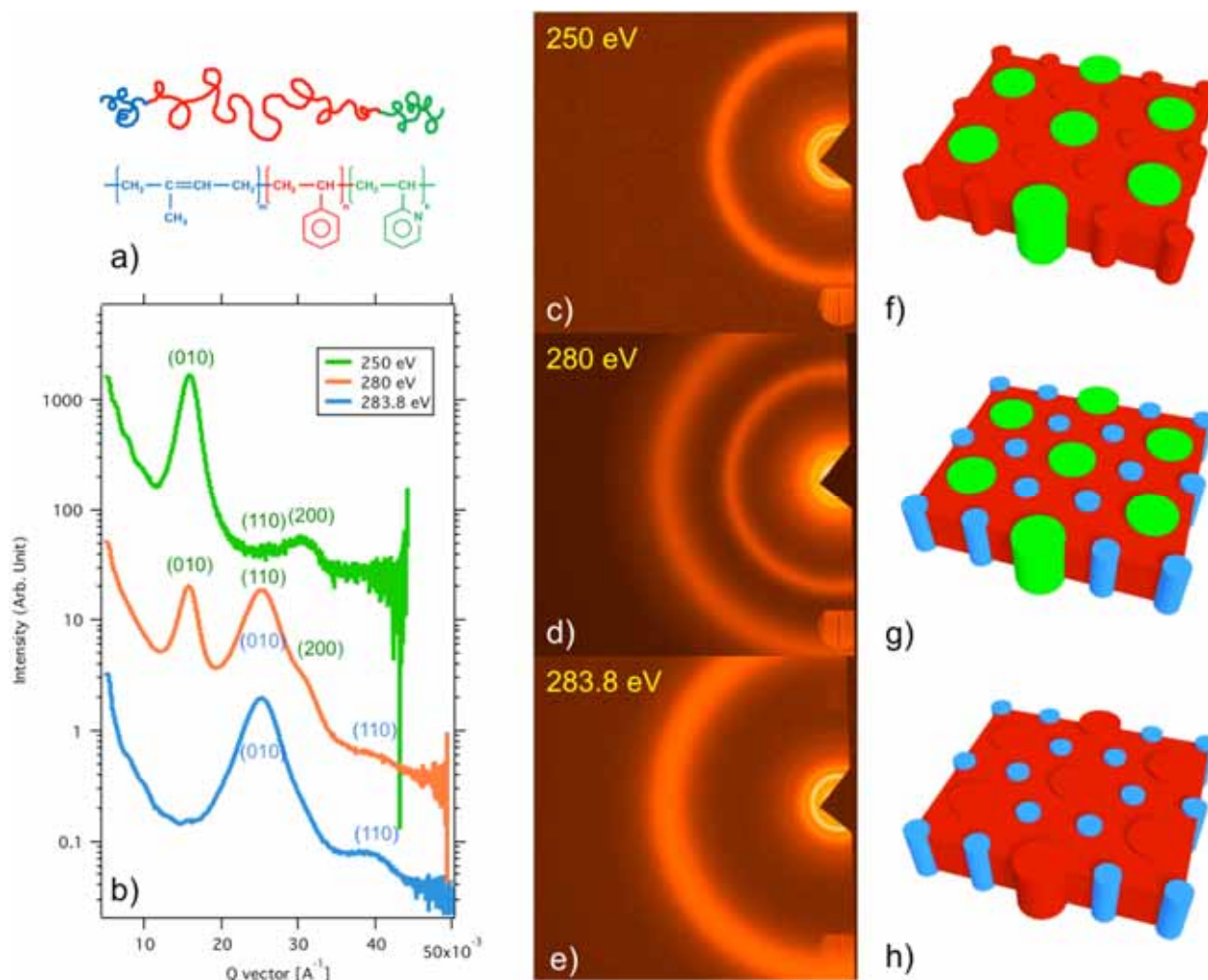


→ Unfavorable large range of domain size once annealed

Characterization needs

- 10 nm 3D spatial resolution
- Quantitative compositional analysis that exceeds analytical TEM capabilities
- Artifact free
- Engineering applications
 - ◆ Rapid analysis
 - ◆ Many samples with different processing conditions
 - ◆ Preliminary analysis online
- Avoid radiation damage for high resolution data
 - phase contrast
- ptychography
- Just below the carbon absorption edge

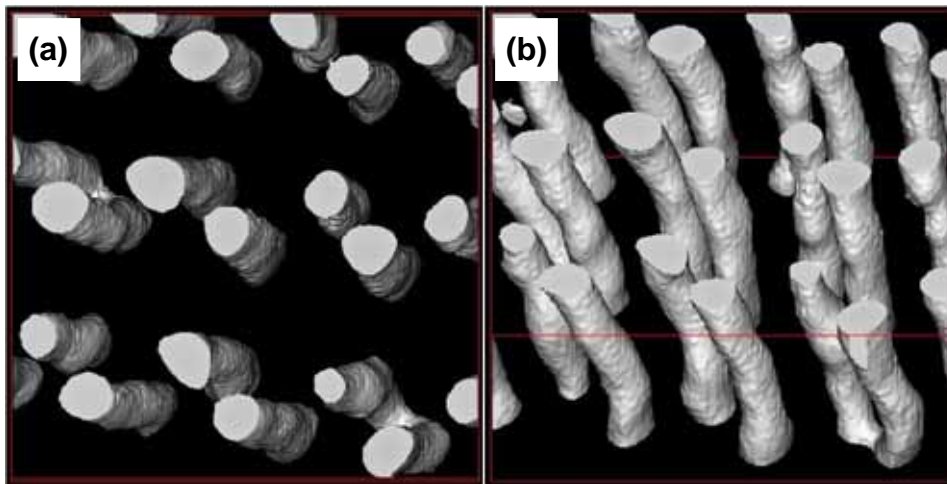
How about we test ptychography at C-edge with a good test samples?



Cheng Wang^{1,†,*}, Dong Hyun Lee^{2,†}, Alexander Hexemer¹, Myung Im Kim³, Wei Zhao⁴, Hirokazu Hasegawa⁵, Ting Xu³, Harald Ade⁶, Thomas P. Russell^{4,*} (in preparation)

How about we test ptychography at C-edge with triblock copolymer test samples?

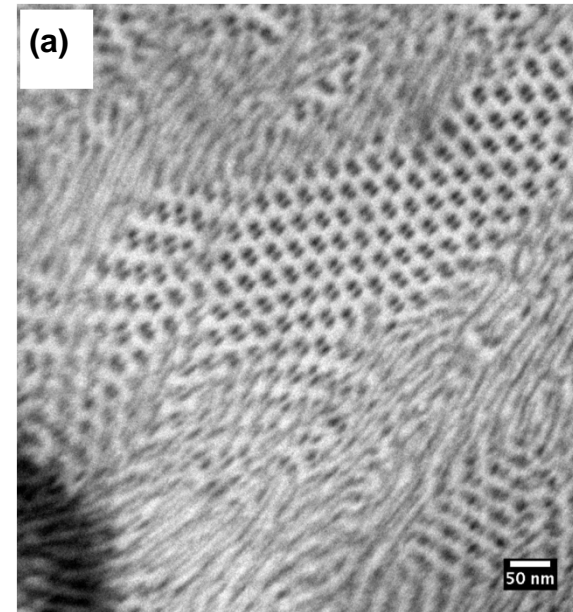
Good mix of complexity and sample knowledge



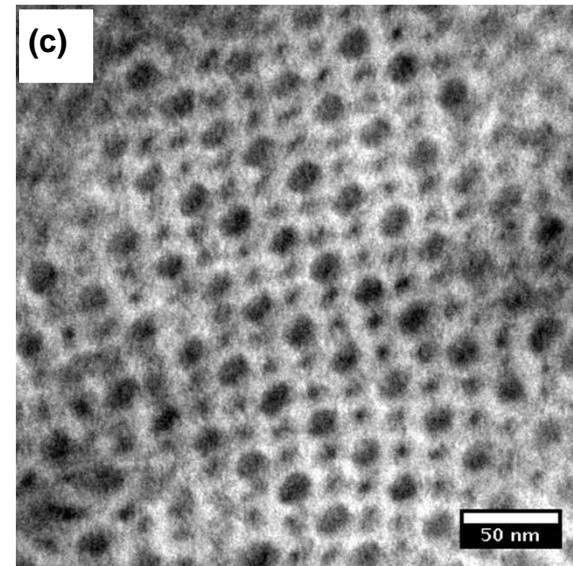
osmium tetroxide → PI domains

Cheng Wang^{1,†,*}, Dong Hyun Lee^{2,†}, Alexander Hexemer¹, Myung Im Kim³, Wei Zhao⁴, Hirokazu Hasegawa⁵, Ting Xu³, Harald Ade⁶, Thomas P. Russell^{4,*} (in preparation)

osmium tetroxide



di-iodobutane and osmium tetroxide



50 nm

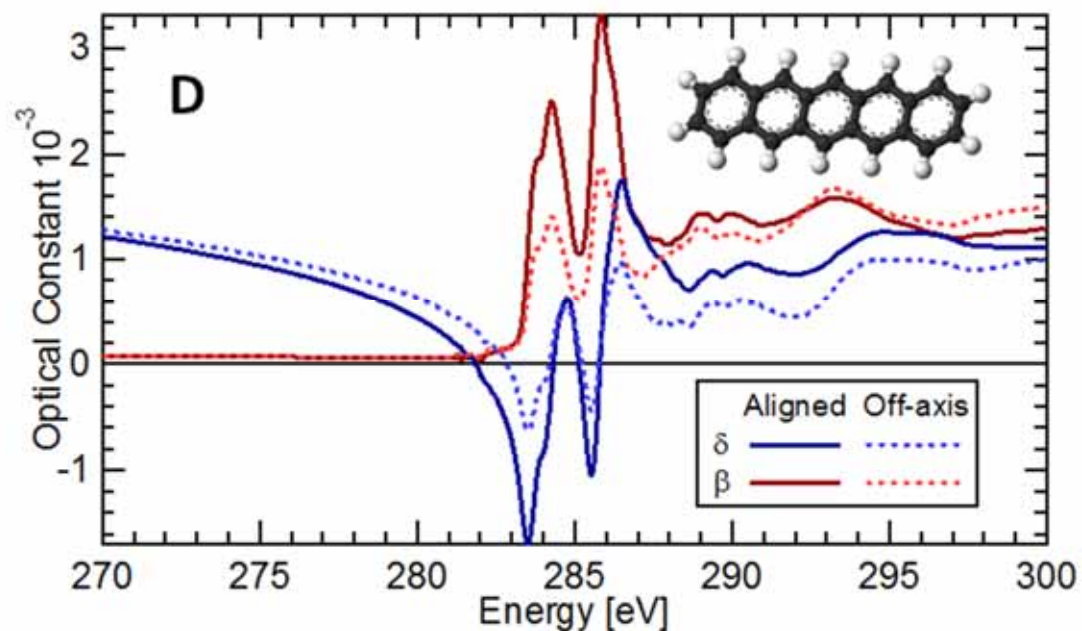
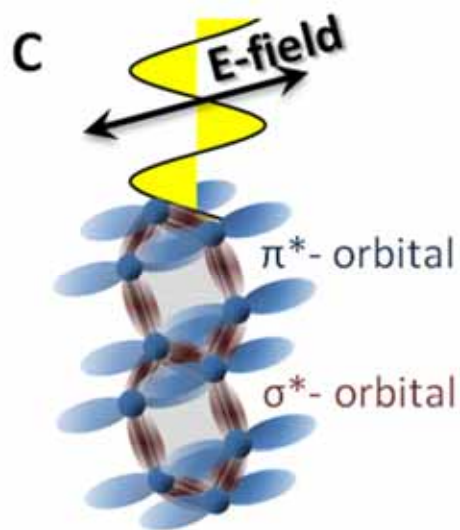
Polarization in STXM and Scattering

Another interesting and unique contrast mechanism

→ probing domain size and domain correlation in TFT applications

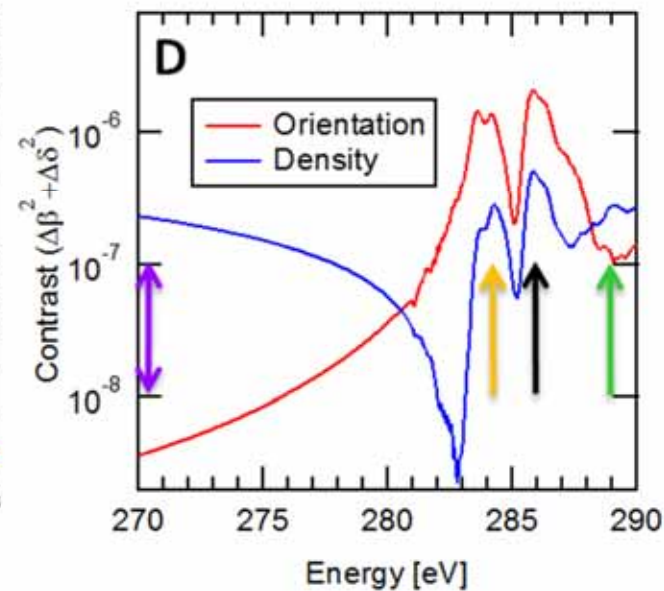
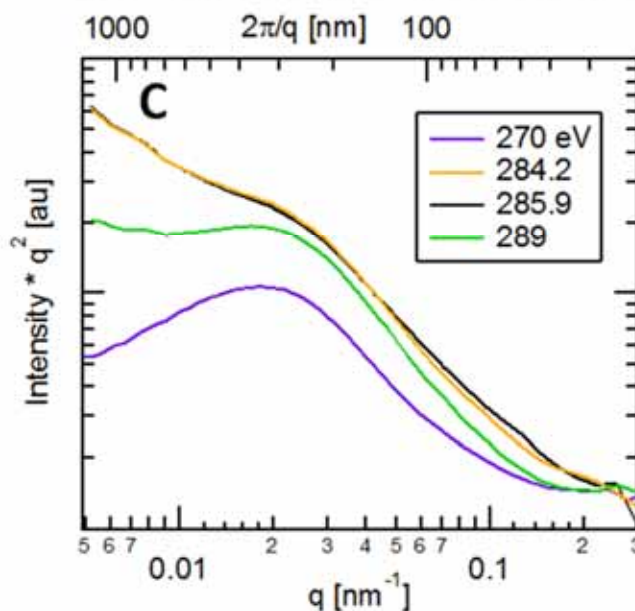
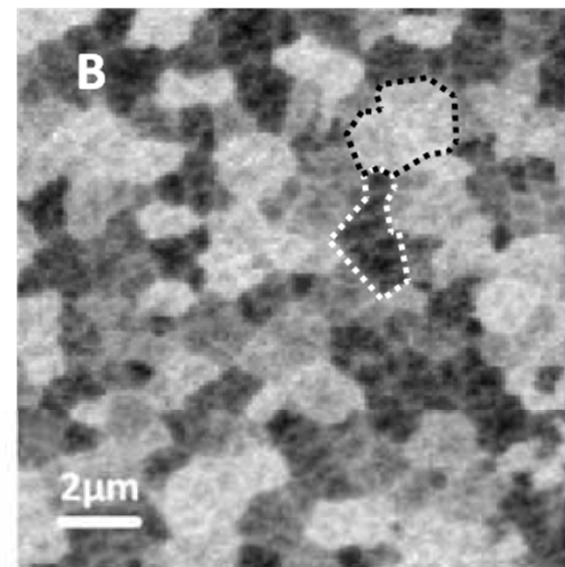
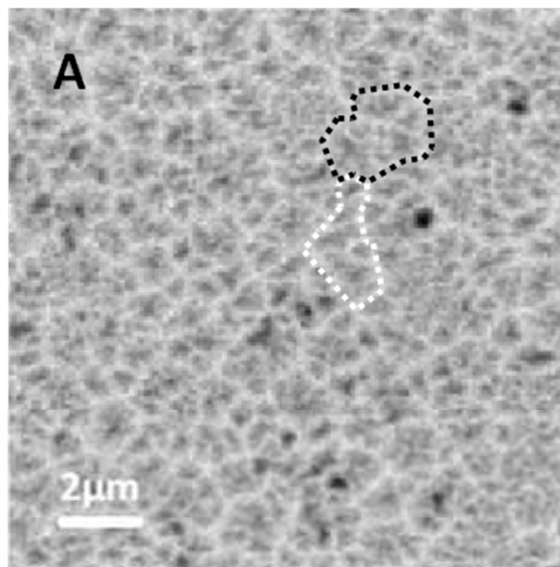
Polarization contrast in STXM and Scattering

- Specific molecular orbitals are probed via x-ray photons at resonant energies
- Absorption/Scattering enhanced if photon polarization is *parallel* to orbital dipole moment



Collins et al. (2011).

Scattering can assess average domain size
 First results from polarization scattering of pentacene

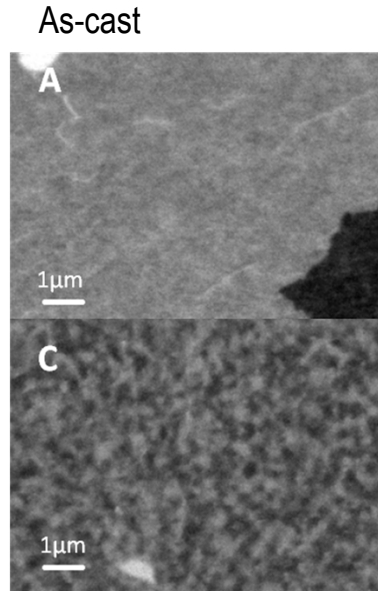


→ Use scattering when domains are too small for STXM

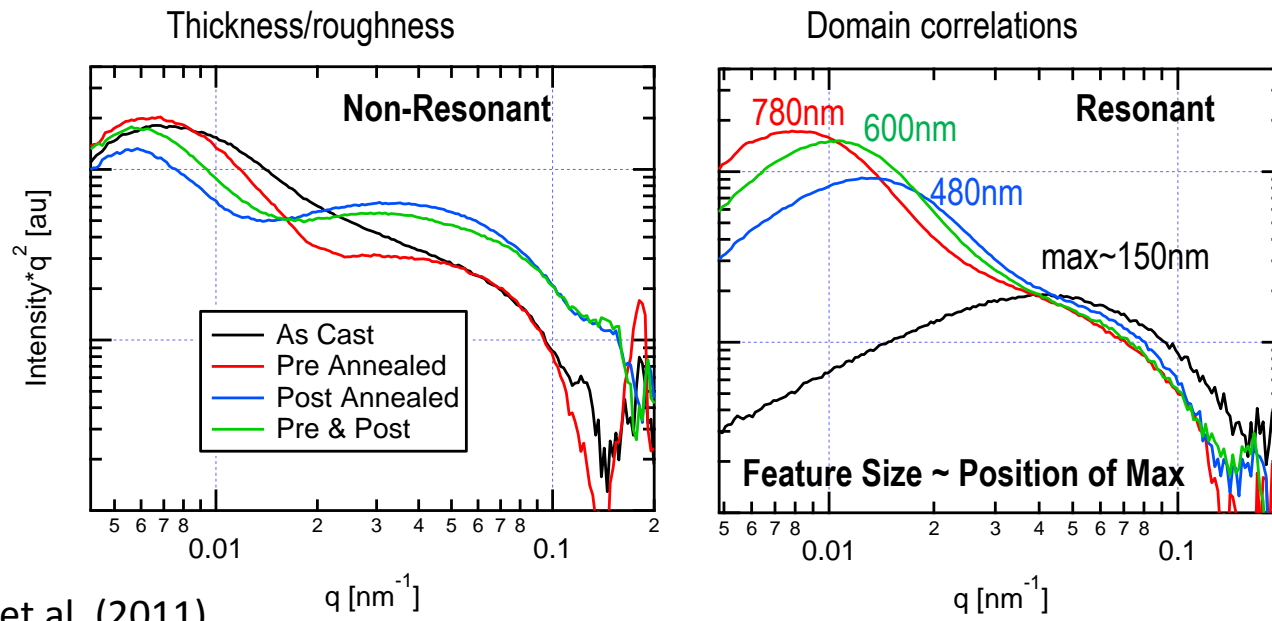
Scattering Results from PBTTT/PMMA TFTs:

$$I(q) \cdot q^2$$

- Non-Resonant scattering sensitive to mass-thickness
 - ◆ Similar to scattering using hard x-rays
- Resonant scattering profiles completely different, showing definite trend
 - ◆ Clear trend of both feature size and feature contrast



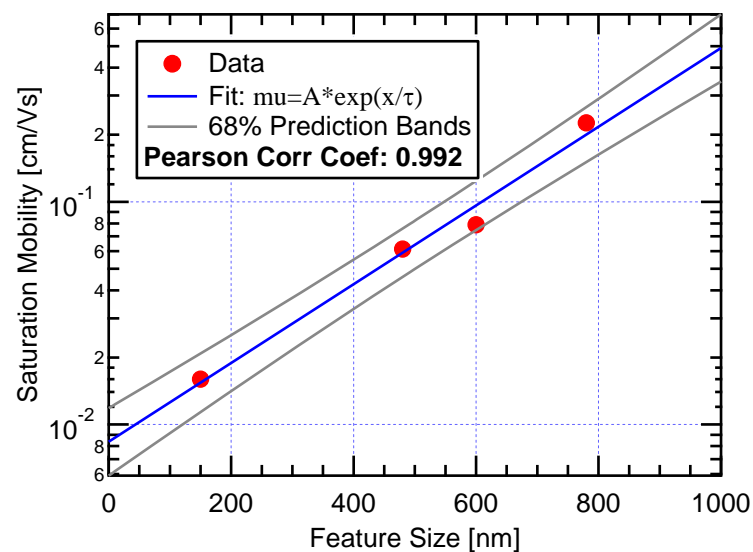
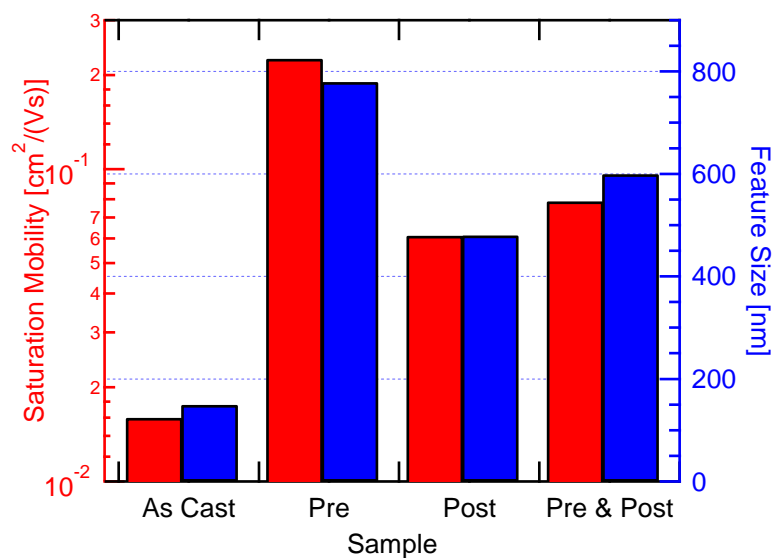
Annealed



Collins et al. (2011).

Device mobility related to domain size

- correlation of feature size with device saturation mobilities
- **Corr. Coef = 0.992**

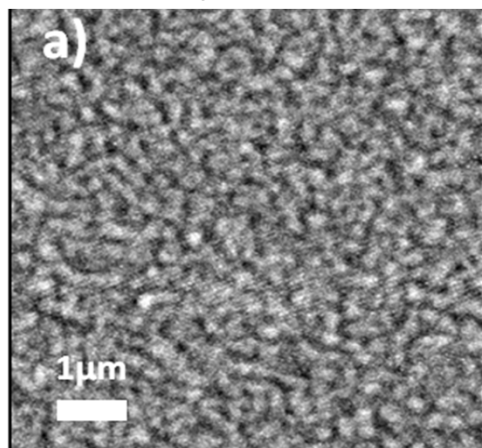


Collins et al. (2011).

P-SoXS signal from P3HT:F8TBT blends

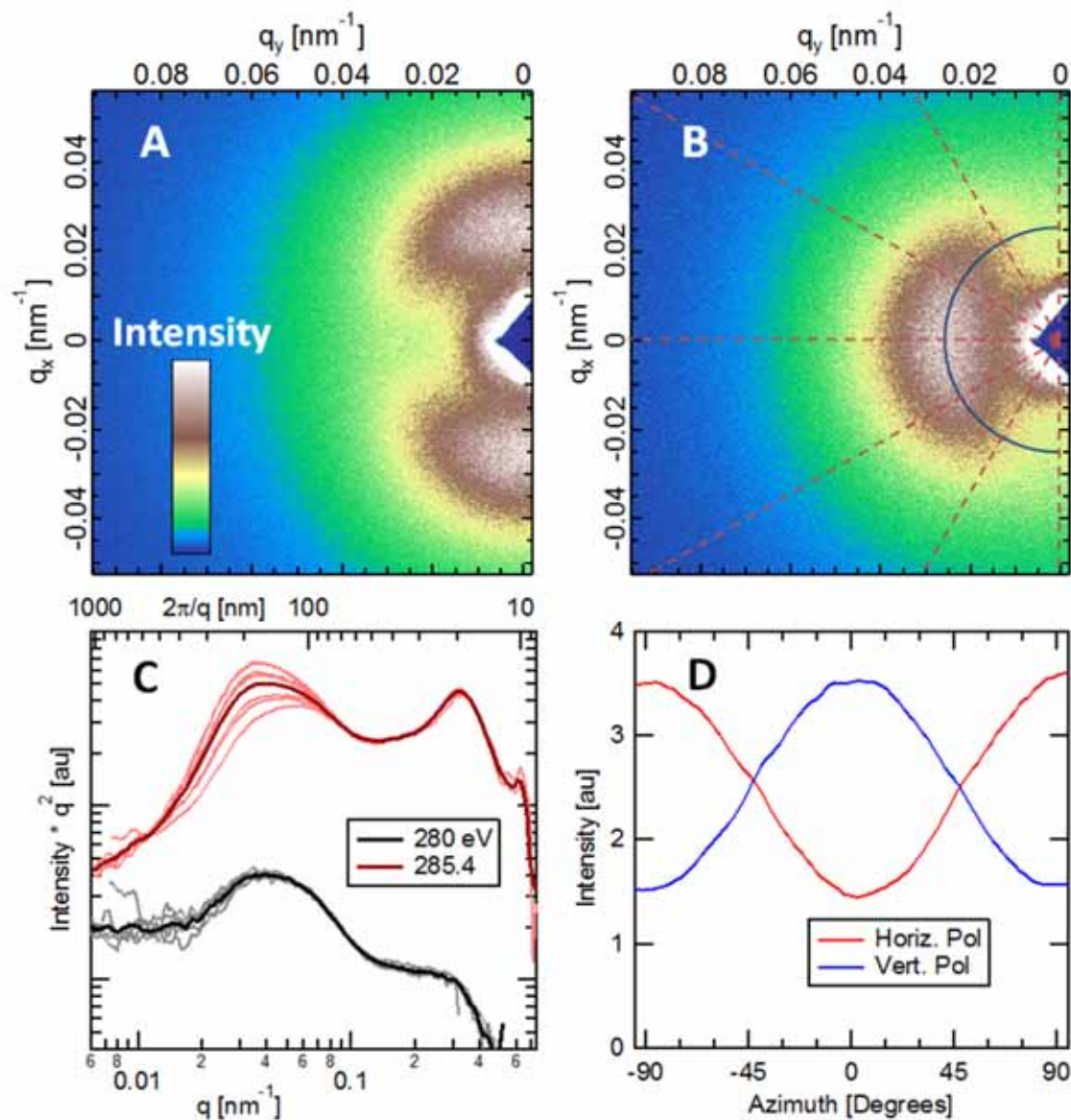
~150 nm thick, annealed at 180C

STXM image at 285.4 eV



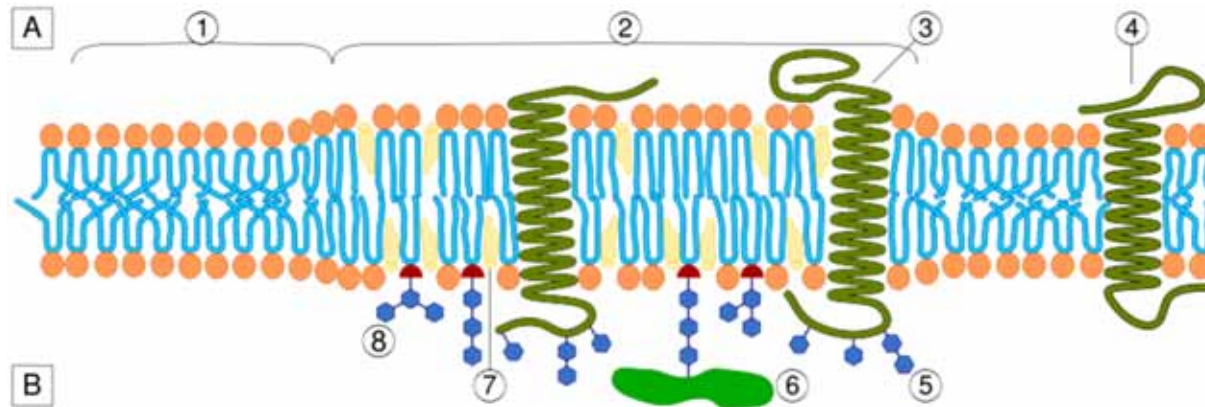
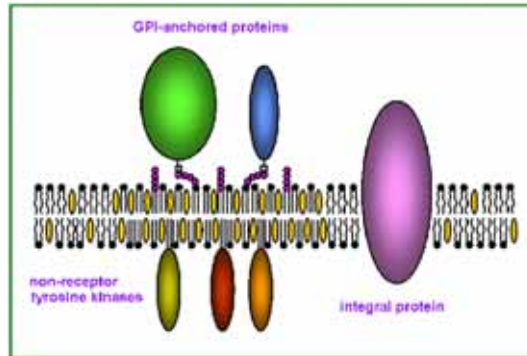
Not sure yet what this all means,

→ Better real space method would be really helpful



Lipid Rafts

ISI search: 6370 hits



1. Non-raft membrane
2. Lipid raft
3. Lipid raft associated transmembrane protein
4. Non-raft membrane protein
5. Glycosylation modifications (on glycoproteins and glycolipids)
6. GPI-anchored protein
7. Cholesterol
8. Glycolipid

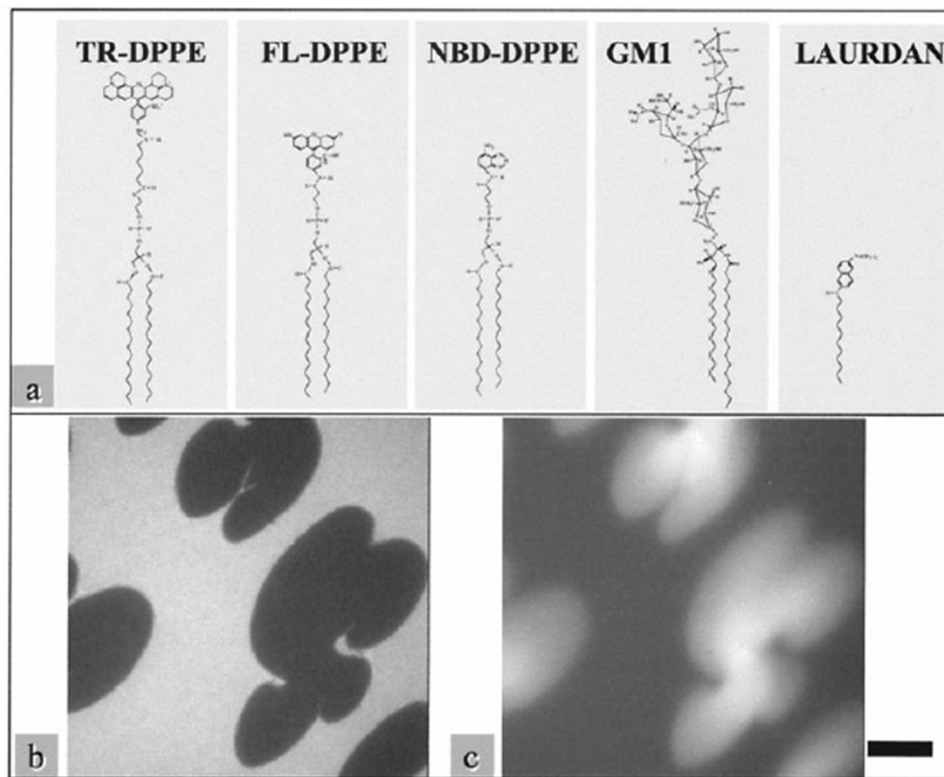
- Cell plasma membrane patchy and locally differentiated into domains
- some domains seem to arise through the confinement of diffusible membrane proteins
- other domains may arise through lipid-lipid interactions
- Domains are transient on a biological timescale
- both could create local conditions that enhance molecular interactions (e.g. receptor-mediated signaling)

Lipid Rafts

Biophysical Journal Volume 80 March 2001 1417-1428

Lipid Rafts Reconstituted in Model Membranes

C. Dietrich,^{*} L. A. Bagatolli,[†] Z. N. Volovyk,[‡] N. L. Thompson,[‡] M. Levi,[§] K. Jacobson,^{*,¶} and E. Gratton[†]



RAFTS are a 4+ “Dimensional” problem

- **2 if not 3 space dimensions**
- **Fluctuations over a large time range**
 - ◆ **FLASH diffraction imaging would require statistical analysis of many images and interpretation using models. Might not be able to capture fluctuations dynamics.**
- **Need to isolate specific chemical components**

XPCS of lipid rafts

- ERL with high rep rate offers opportunity to investigate rafts with high time resolution

Needs:

- Adjustability near carbon K-edge
- Resolving power of ~2000
- Coherent, high intensity beam
 - ◆ Rafts are weak scatters
- Unknown time scale of fluctuations requires large t-domain
- Unsure about need for polarization
- Sample geometry and preparation needs to be sorted out

Utility of Soft X-rays

- Lots of great science possible (It's also fun!)
- How low in energy will the Cornell ERL go?
 - ◆ Reaching Oxygen would be useful
 - ◆ Carbon would be clearly best

Thank you for your attention

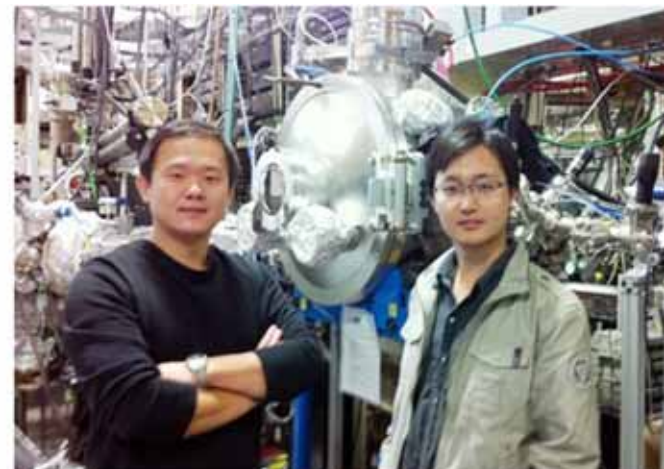
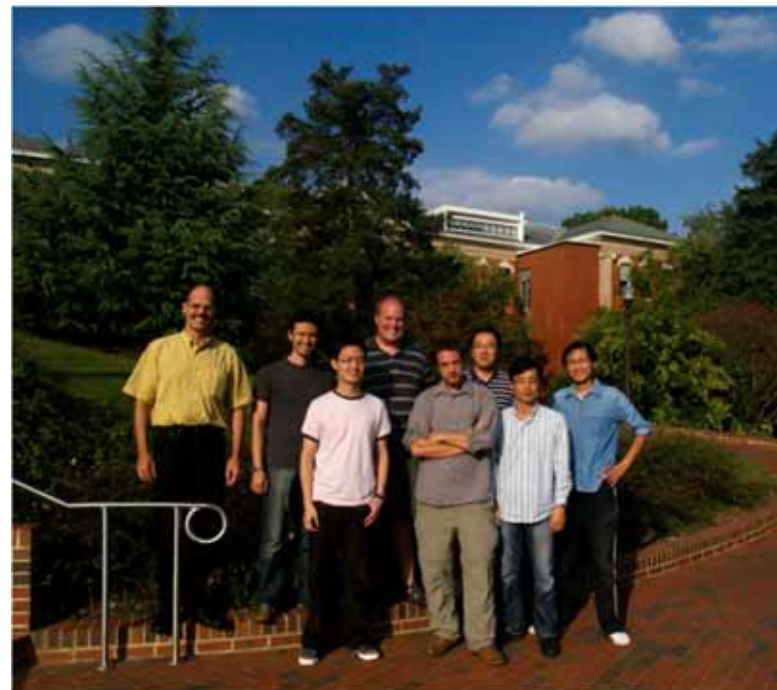
Thanks to members of my group:
B. Collins, S. Swaraj (now Soleil),
H. Yan, E. Gann, Z. Gu, J. Seok

and

C. McNeill, N. Greenham, I. Hwang
(Cambridge), C. Wang (ALS), M. Chabynec, and
J. Cochran (UCSB)



Financial support:
DOE Office of Science, Basic Energy Science,
Division of Materials Science and Engineering
Contract: DE-FG02-98ER45737



Cheng and Hongping at the ALS