Harvesting the Light, The Photovoltaic Story

The influence of molecular orientation on organic bulk heterojunction solar cells

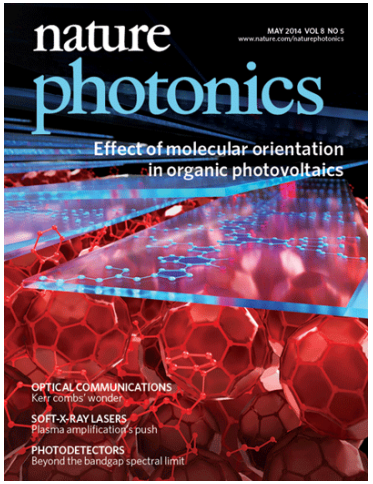
Ade Group

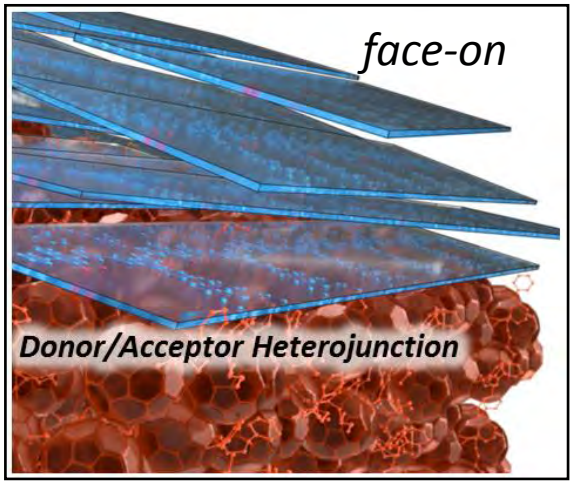
Prof. Wei You Group (Chemistry UNC)

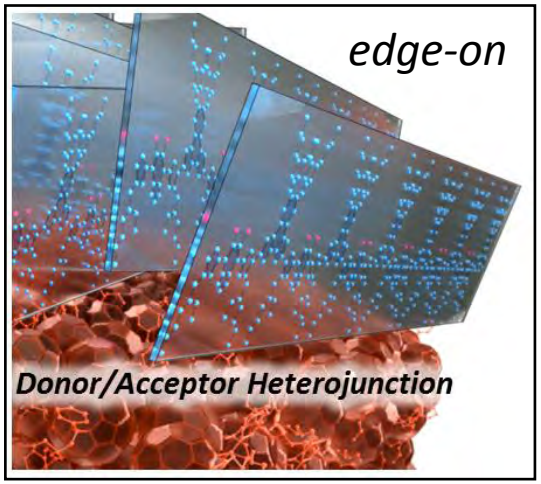
and other collaborators as indicated (by references)

NSLS-II User Meeting BNL

May 19, 2014







Some of our recent applications characterizing organic devices

J. Phys. Chem. C **117**, 26007–26012 (2013)
Energy Environ. Sci. **6**, 2756-2764 (2013)
Advanced Materials **25**, 3449–3455 (2013)
J. Mat. Chem. **C 1**, 33, 5023 (2013)
J. Am. Chem. Soc. **135**, 8464 (2013)
Phys. Rev. Lett. **110**, 177401 (2013)
Adv. Energy Mater. **3**, 7 (2013) - (Inside Cover)
Adv. Funct. Mater. **23**, 27 (2013)
Adv. Energy Mater. **3**, 364 (2013)
J. Am. Chem. Soc. **135**, 1806 (2013)
Energy Environ. Sci. **6**, 316 (2013)
J. Mater. Chem. C **1**, 187 (2013)
Adv. Energy Mater. **3**, 65 (2013) - (Front Cover)

Adv. Mater. **24**, 6335 (2012)
Appl. Phys. Lett. **101**, 093308 (2012)
ACS Nano **6**, 677 (2012)
Small **8**, 1920 (2012)
Rev. Sci. Instrum. **83**, 045110 (2012)
Nat. Mater. **11**, 536 (2012)
J. Phys. Chem. Lett. **2**, 3135 (2011)
Nano Letters **11**, 3906 (2011)
Adv, Funct. Mater. **20**, 4209 (2010)
Nano Letters **10**, 2863 (2010)
Applied Physics Letters **96**, 183305 (2010)
J. Phys. Chem. Lett. **1**, 3160 (2010)

+ 7 Advanced Materials, 1 JACS, 1 AFM and 1 Nat Photonics, + 4 more in 2014 so far

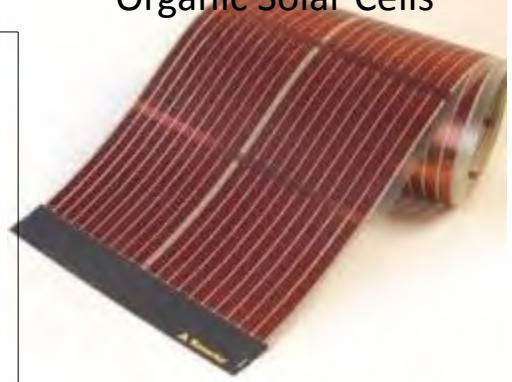
→ Found a lot of good nails! (???)
→ Our work changed the view/description how real bulk heterojunctions organic solar cells work

2

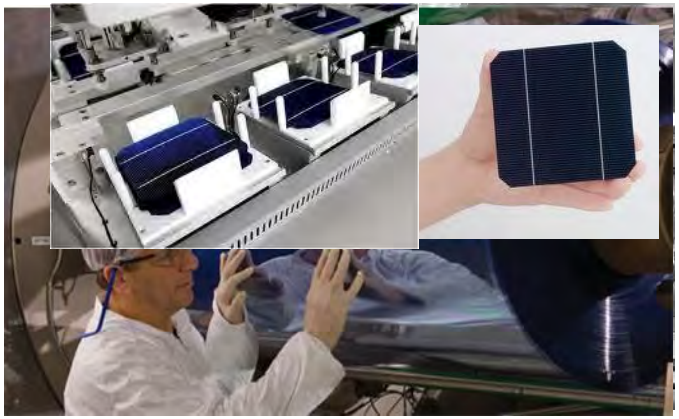
Context: ***Organic Electronics (and Photonics)***

Technologies for New Applications, Energy Security/Independence

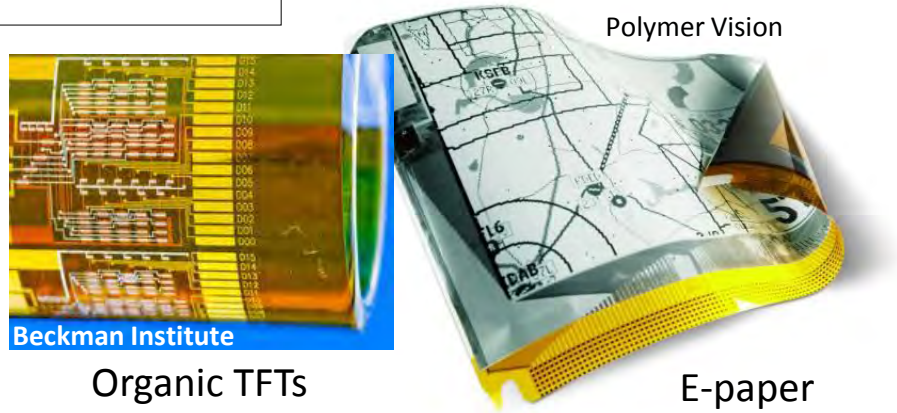
Organic Solar Cells



- Inexpensive materials
- Low thermal budgets
- Flexible applications
- Ease of scalability (R2R)



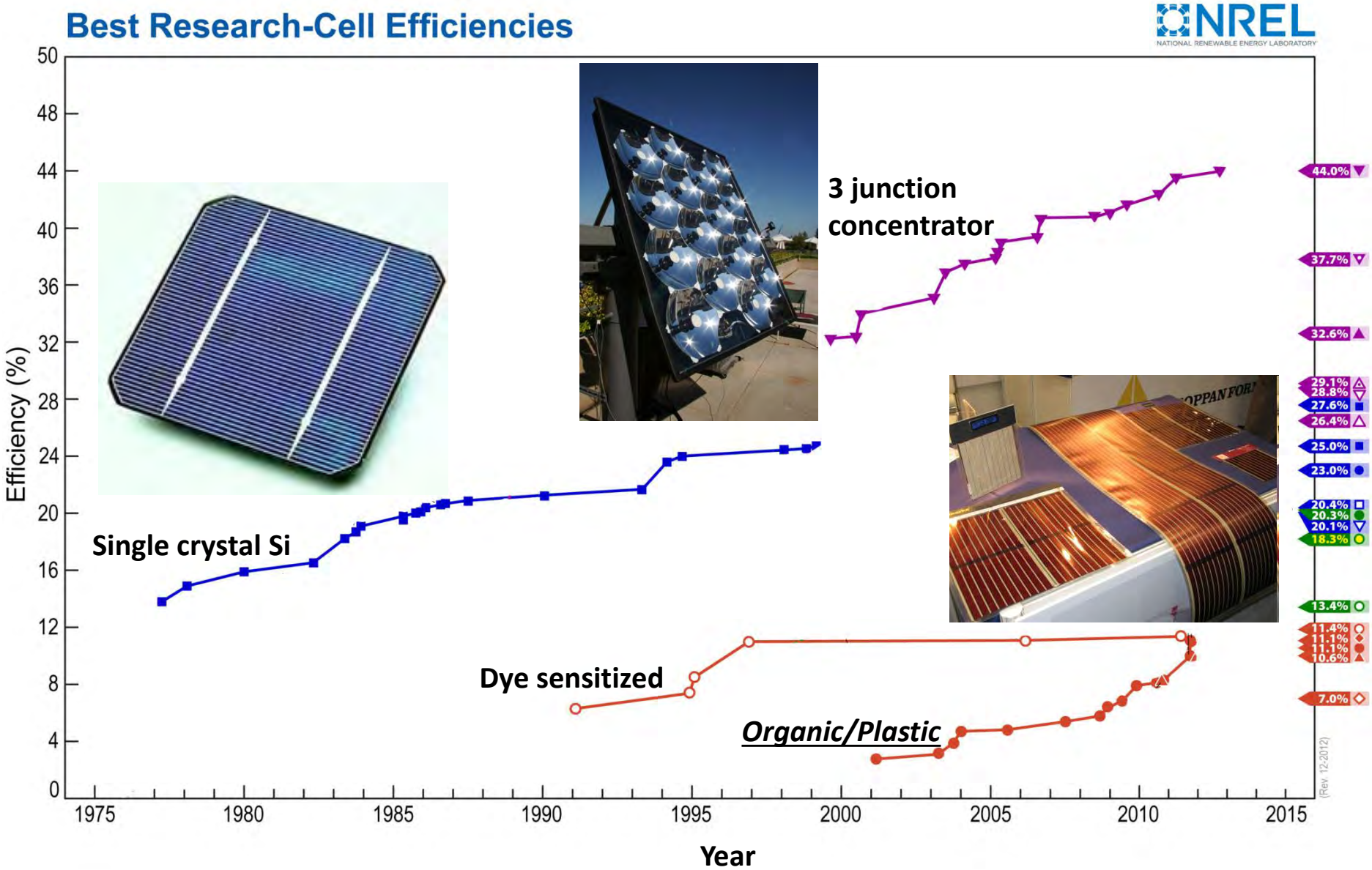
Polymer Vision



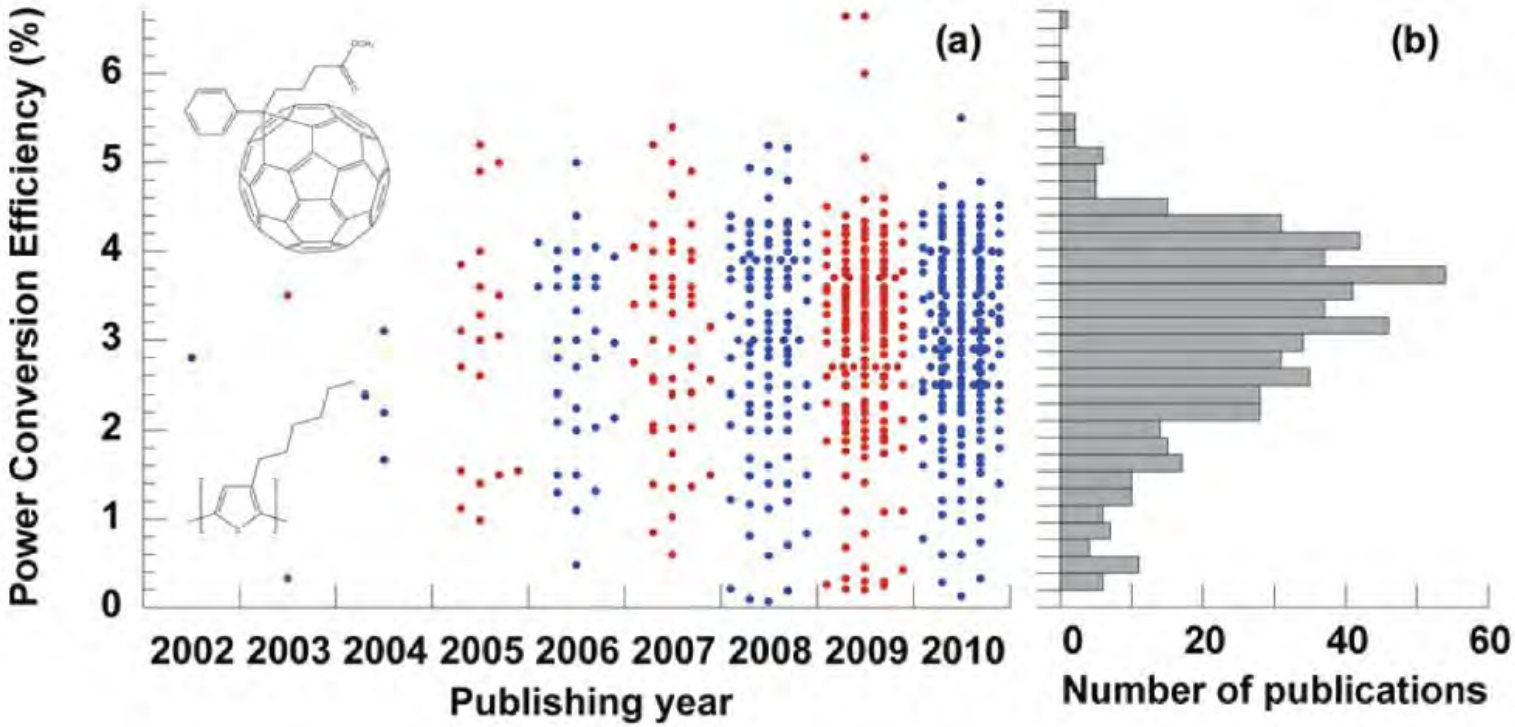
Organic TFTs

E-paper

Needs radically different materials, processing, and characterization!


Best Research-Cell Efficiencies
NREL
NATIONAL RENEWABLE ENERGY LABORATORY
Efficiency (%)
Year
3 junction concentrator
Single crystal Si
Dye sensitized
Organic/Plastic
44.0%
37.7%
32.6%
29.1%
28.8%
27.6%
26.4%
25.0%
23.0%
20.4%
20.3%
20.1%
18.3%
13.4%
11.4%
11.1%
11.1%
10.6%
7.0%
(Rev 12-2012)

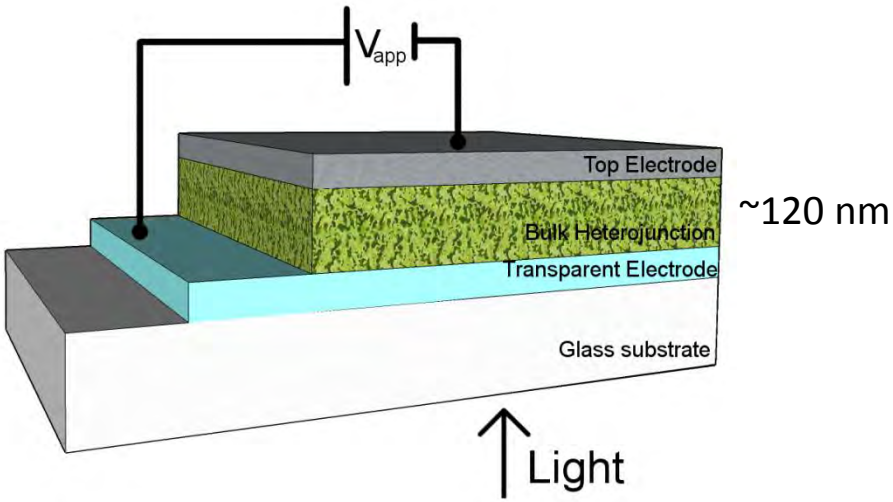
The “Fruit Fly”: P3HT:PCBM Device Efficiencies



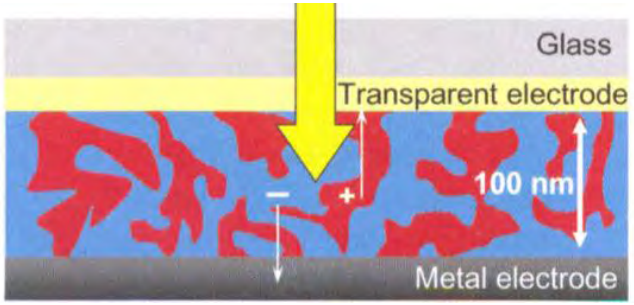
Dang M.T., Hirsch, L., Wantz, G.,
Adv. Mater. **2011,** *23*, 3597-3602.

- Hyperventilation!!!
- The limitations of “shake and bake”
- → golden opportunity

*Device Structure and **Basic(?)** Working Principles of Organic PVs*

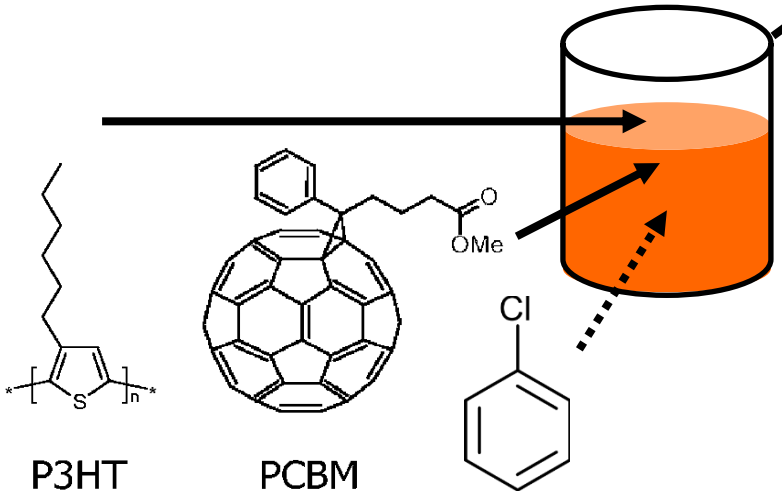


pure phases, bicontinuous (!?)



"Organic Photovoltaics: Materials, Device Physics, and Manufacturing Technologies", Wiley-VCH (2008) .

Cast a thin film



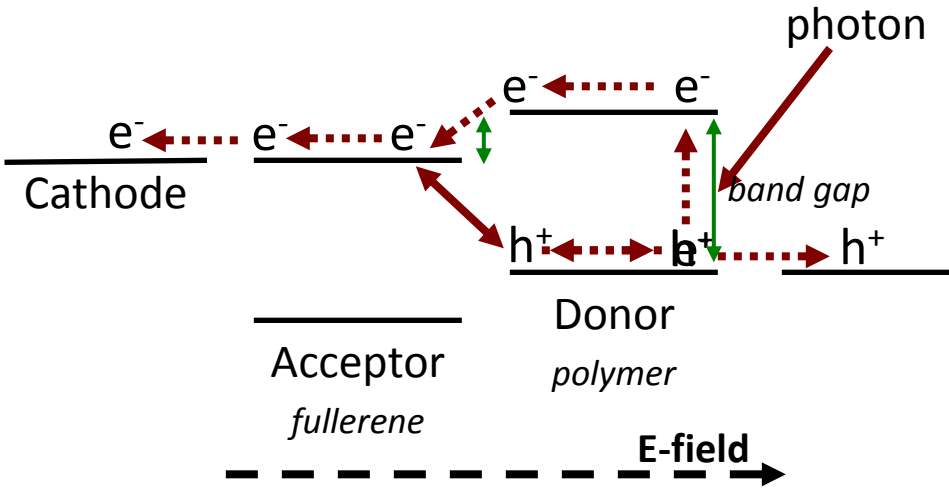
P3HT

conjugated polymer

PCBM

fullerene

Chlorobenzene (solvent)



Many Important Parameters: Impact of ordering/packing?

Materials Views
www.MaterialsViews.com

ADVANCED FUNCTIONAL MATERIALS
www.afm-journal.de

The Impact of Molecular Orientation on the Photovoltaic Properties of a Phthalocyanine/Fullerene Heterojunction

Barry P. Rand, David Cheyns, Karolien Vasseur, Noel C. Giebink, Sébastien Mothy, Yuanping Yi, Veaceslav Coropceanu, David Beljonne, Jérôme Cornil, Jean-Luc Brédas, and Jan Genoe*

Adv. Funct. Mater. **2012**, *22*, 2987–2995

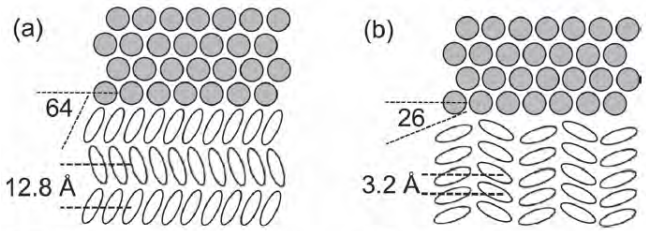
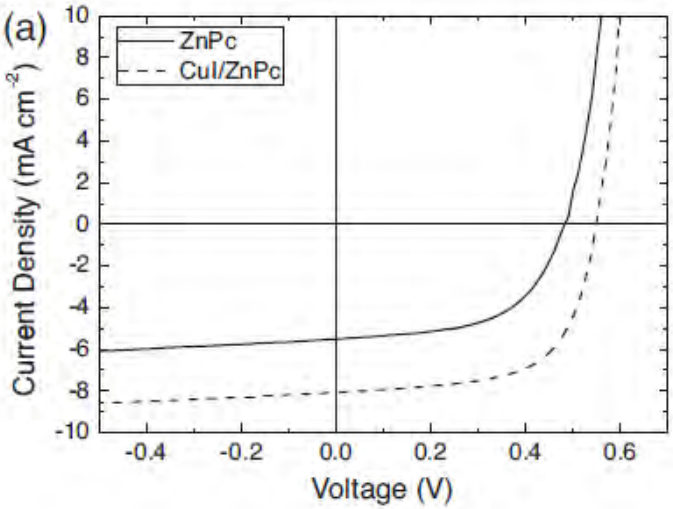


Figure 7. Schematics of the ZnPc/C_{60} heterojunctions for the cases of a) edge-on and b) face-on ZnPc orientations. ZnPc is represented by white ovals, whereas C_{60} is represented by grey circles. The expected angles between the ZnPc and C_{60} molecules are also given, as well as the lattice plane spacing in the stacking (growth) direction for the two orientations of ZnPc, as derived from the XRD results of Figure 1.



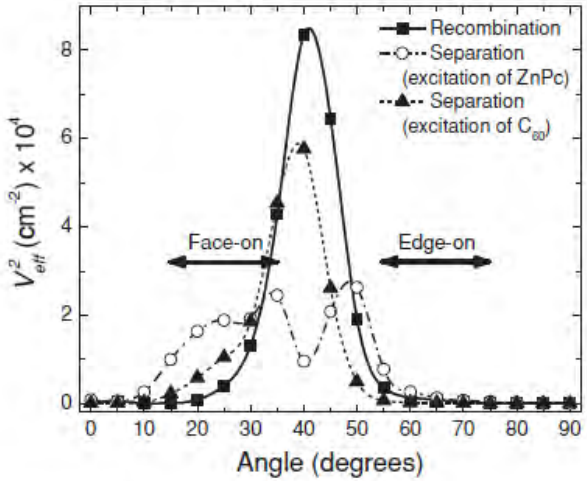
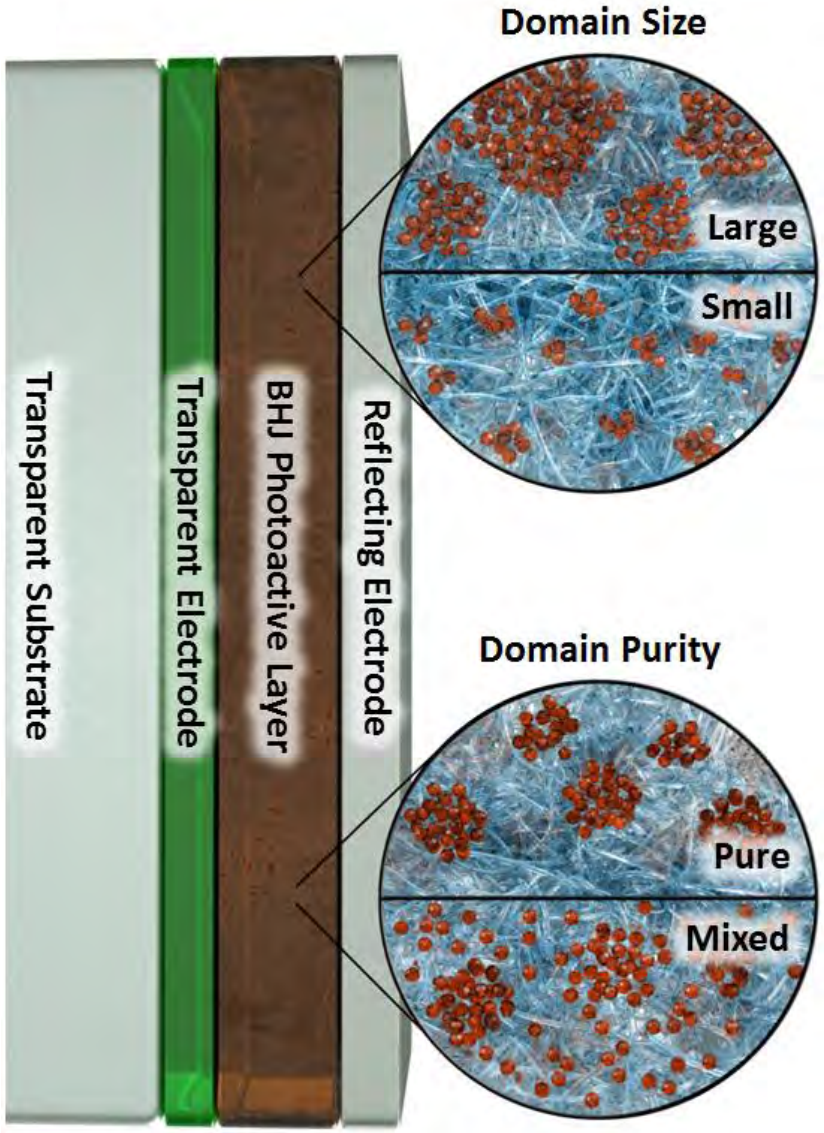
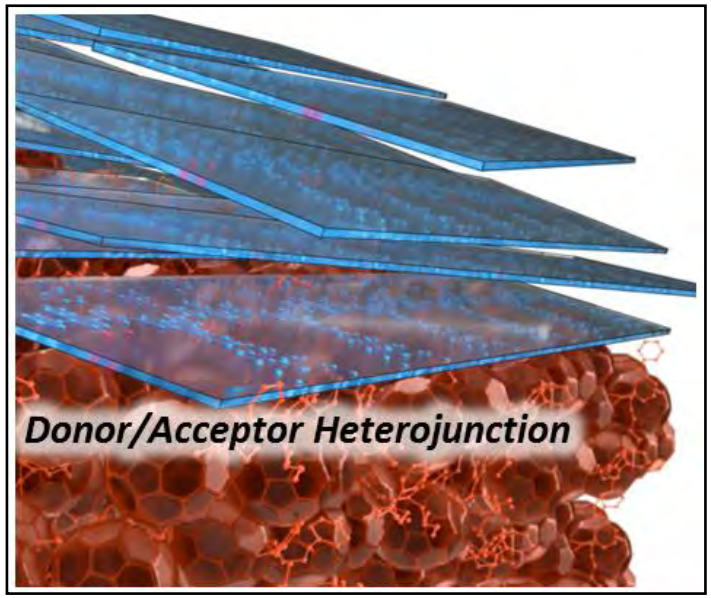


Figure 8. Calculated effective electronic coupling squared, V_{eff}^2, at the ZnPc/C_{60} heterojunction as a function of angle (cf. Figure 7) for the

Relevance and control in BHJ solar cells?

The "Mess" Makes High Demands on Characterization Methods



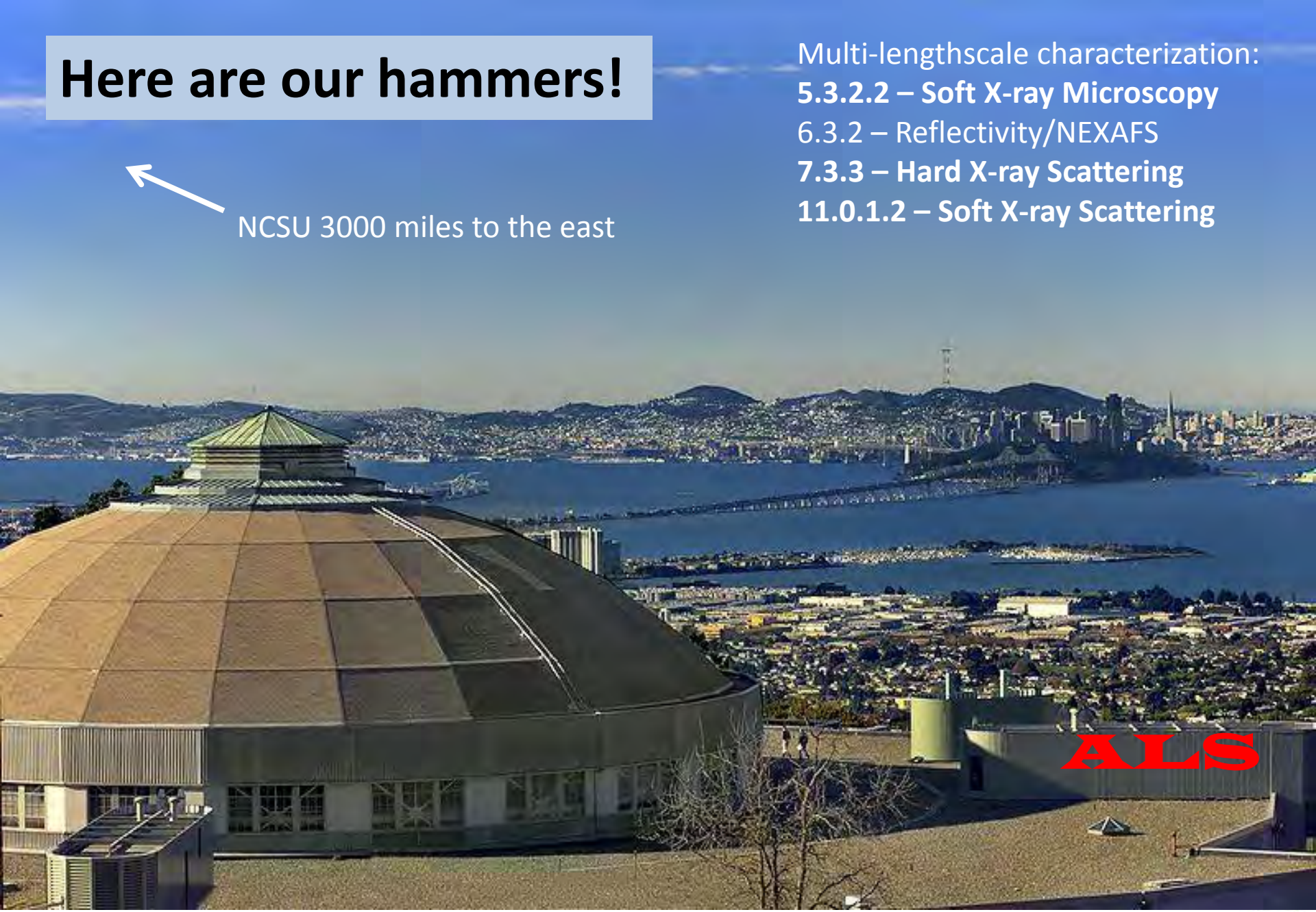


- **Important morphological parameters** –
  - Domain size, size distribution
  - Interface roughness/diffusivity
  - Electrode interface wetting layers
  - Domain purity, composition variations
  - Crystallization/aggregation
  - ***Molecular orientation "at" or relative to donor/acceptor interfaces***
  - *Connectivity*

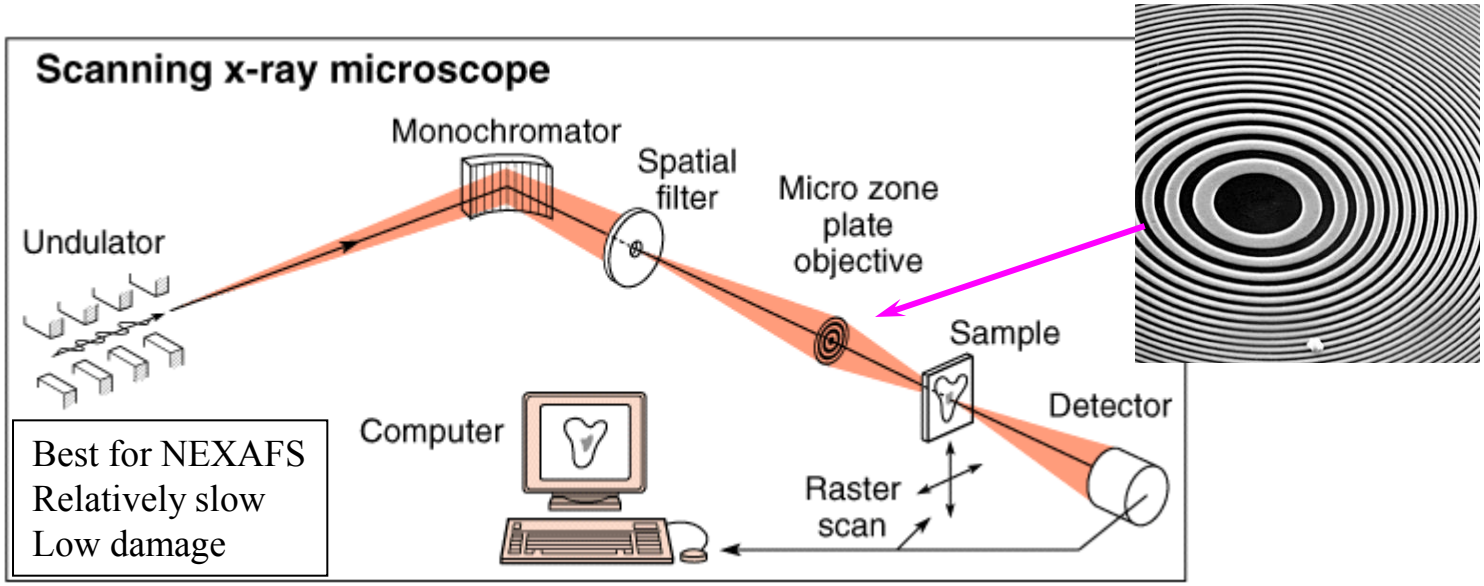
Here are our hammers!

NCSU 3000 miles to the east

Multi-lengthscale characterization:
5.3.2.2 – Soft X-ray Microscopy
6.3.2 – Reflectivity/NEXAFS
7.3.3 – Hard X-ray Scattering
11.0.1.2 – Soft X-ray Scattering



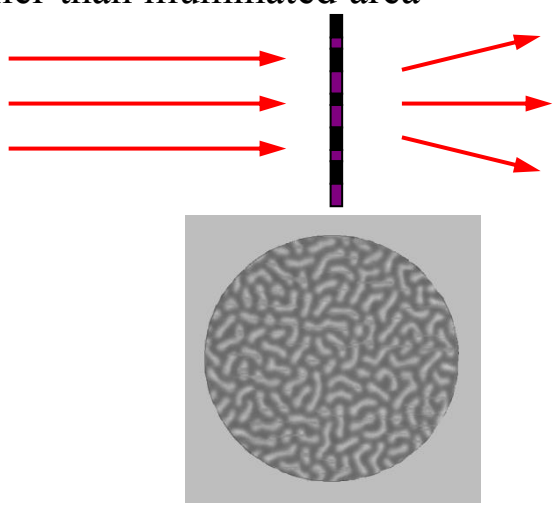
Structure/morphology Determination in Real Space: Absorption X-ray Microscopy

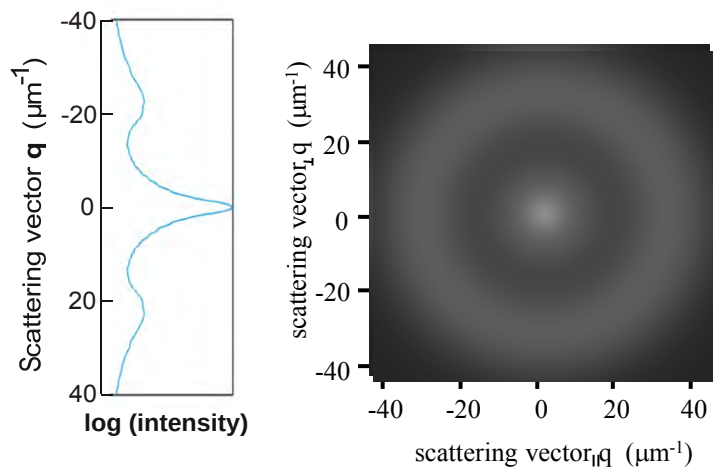


Small Angle Scattering/RSoXS

Coherence length larger than domains, but smaller than illuminated area

Structure/morphology Determination in Reciprocal Space: Resonant X-ray Scattering





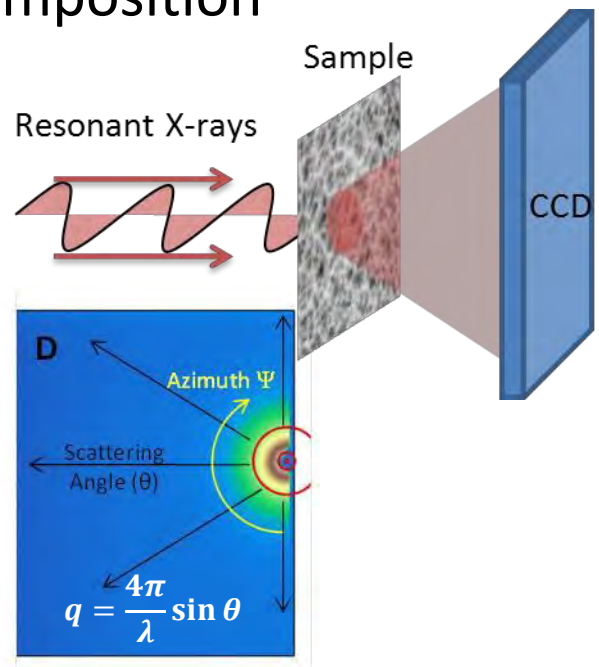
information about domain statistics

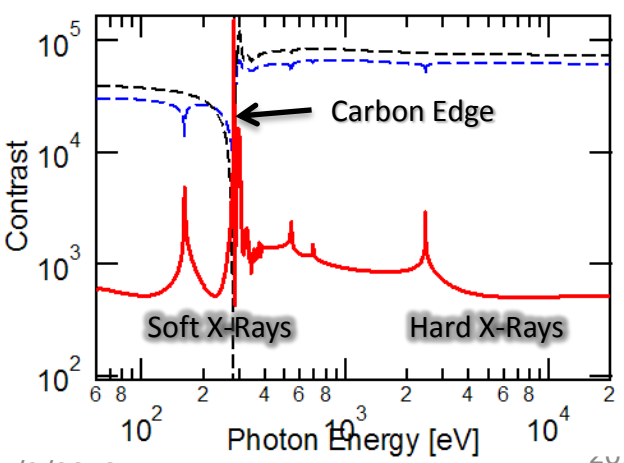
Figure courtesy of/after J. Stohr

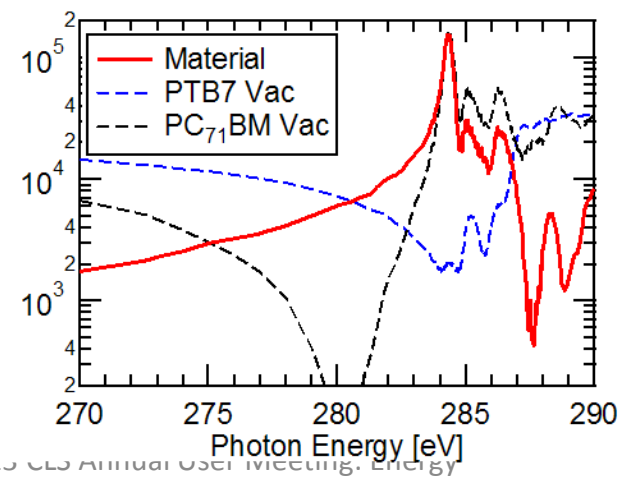
Resonant Soft X-Ray Scattering (RSoXS):

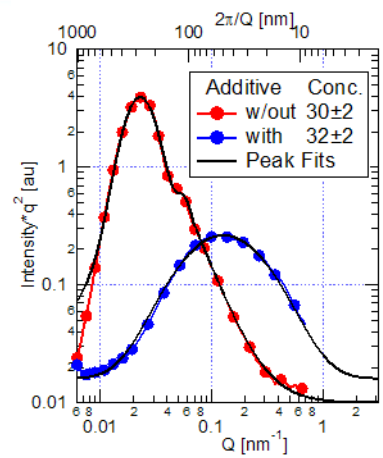
Domain size distribution and composition

- Molecular contrast rather than density contrast
  - $I(E) \propto E^4|\Delta\delta(E) + i\Delta\beta(E)|^2 = E^4|\Delta n(E)|^2$
  - Orders of magnitude more than hard x-rays
  - Like NEXAFS and STXM but also has *phase contrast*
- Tunable Contrast
  - At resonance: Material Domains
  - Non-resonant: surface roughness

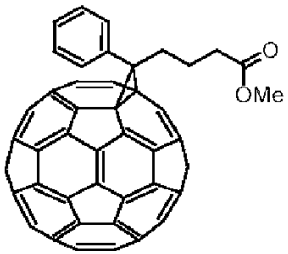




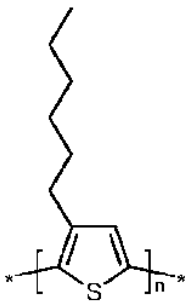




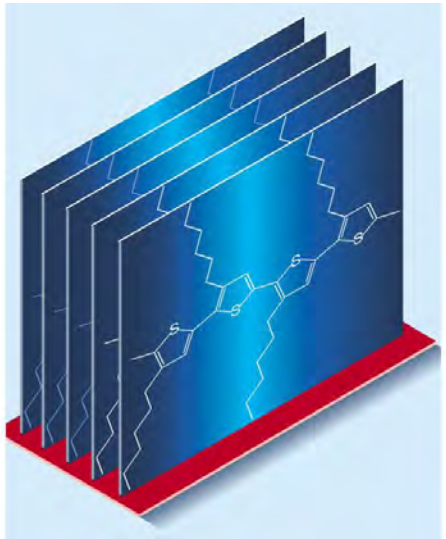
Gracing Incidence Wide Angel X-ray Scattering for Molecular Ordering



PCBM



P3HT



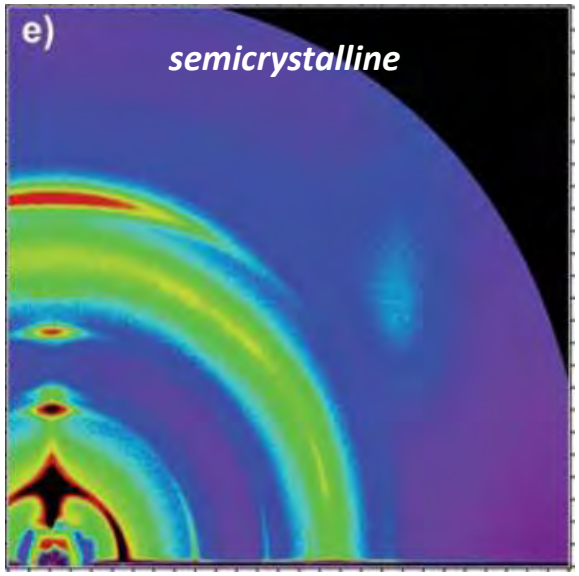
(010)

PCBM

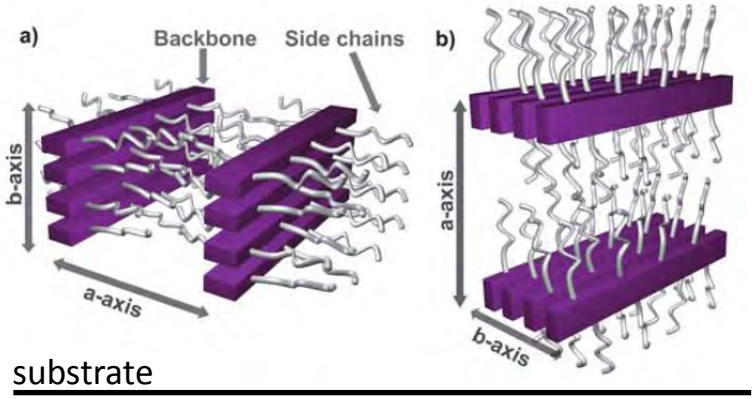
(300)

(200)

(100)

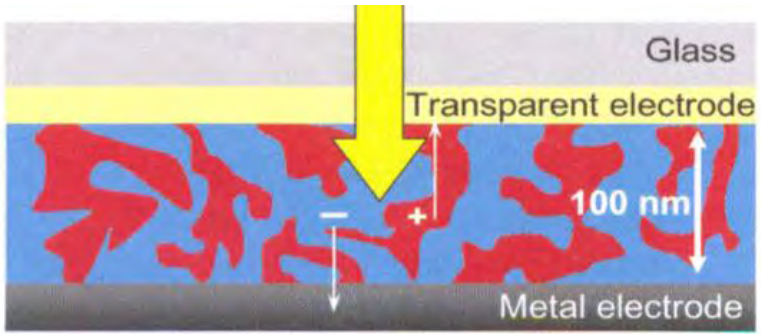


face-on ***edge-on***

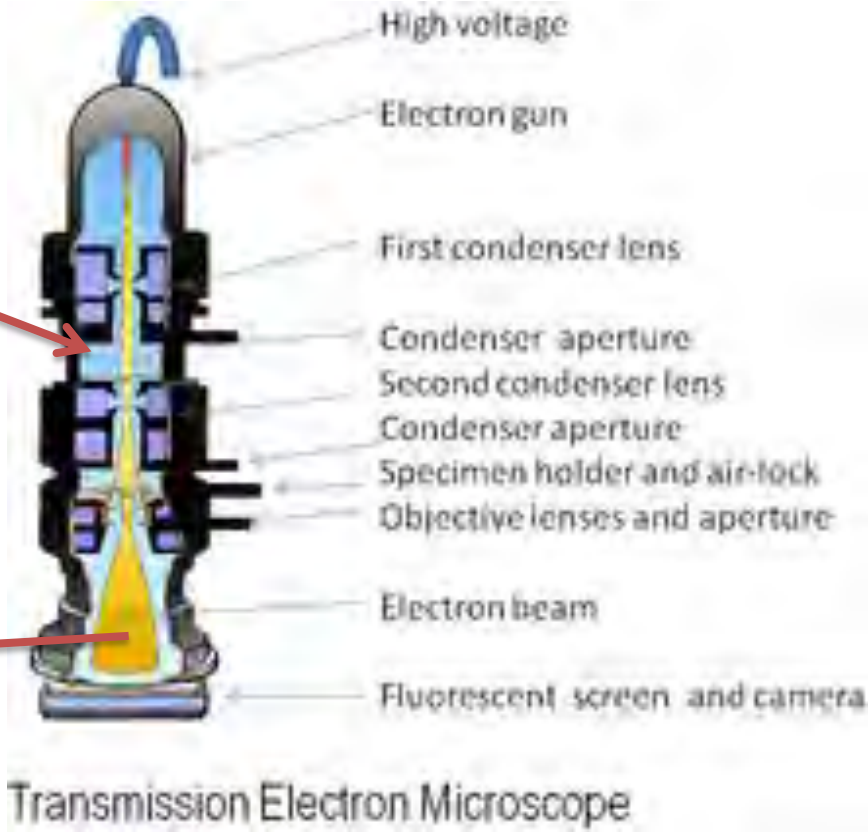


Simple Question: How pure are the phases?

Impure should lead to bad performance due to charge recombination



2D image



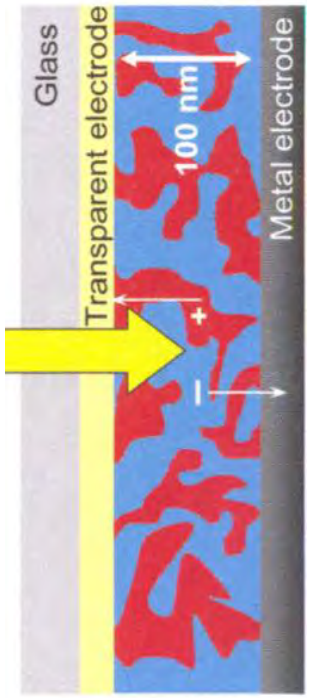
Purity hard to measure in projection in actual devices

→ Scattering will provide the solution

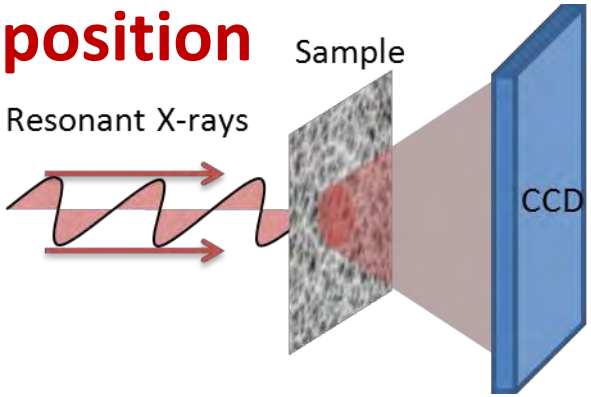
→ Or, we need quantitative tomography! Uh….. tough

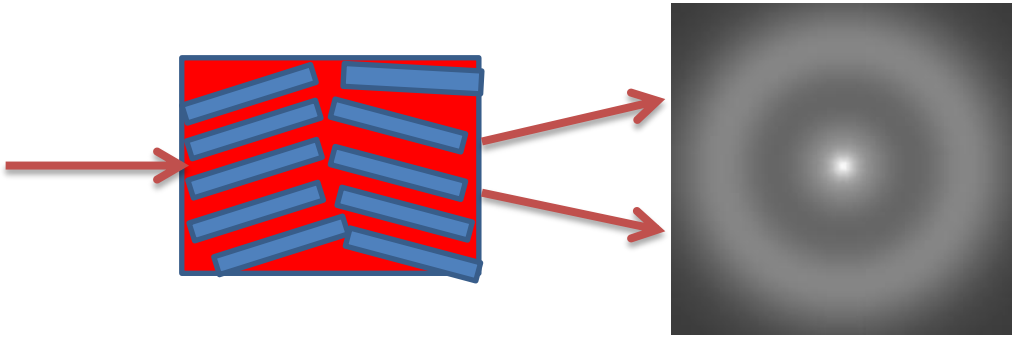
Scattering will help

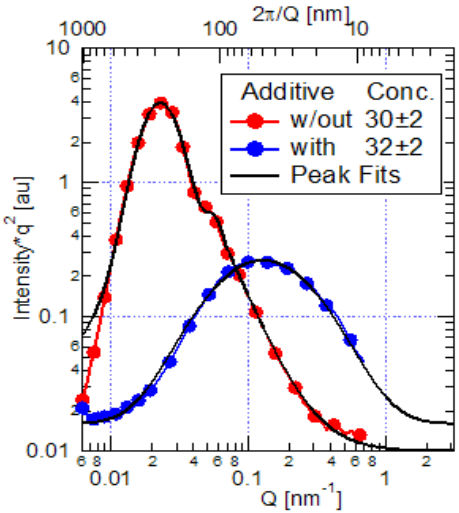
Domain size distribution and **relative composition**



"Wavefronts samples the size correlation in a given sample plane"





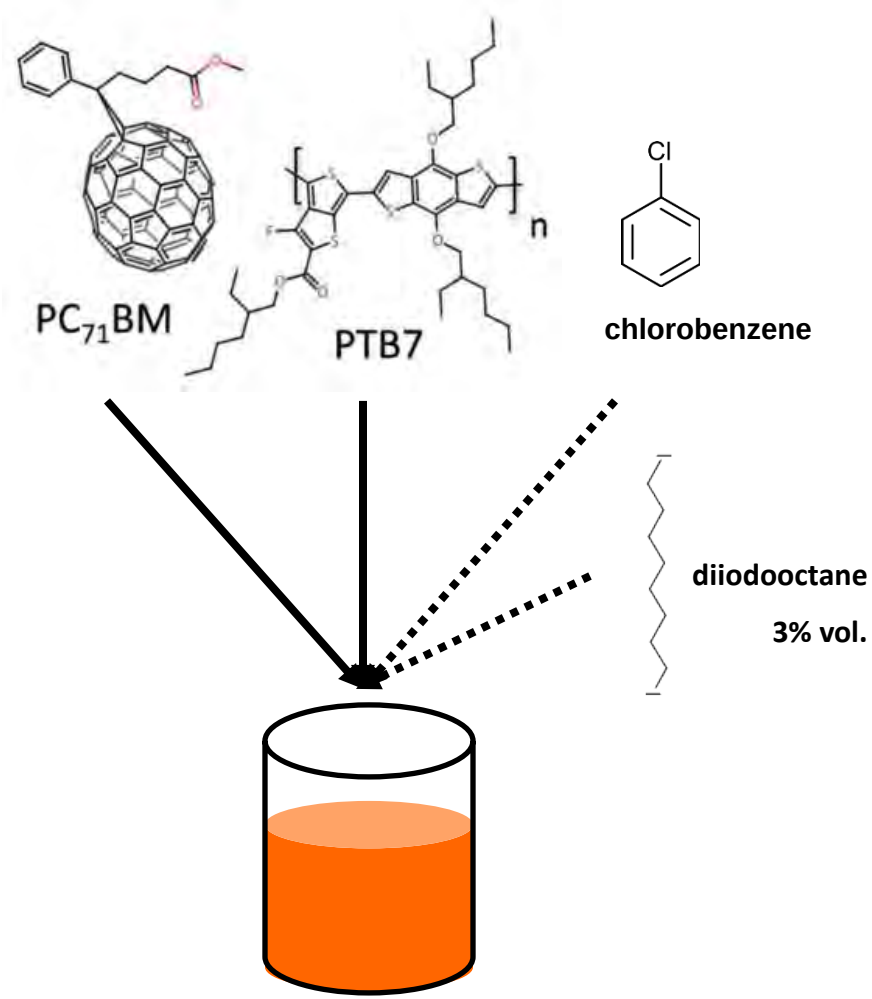


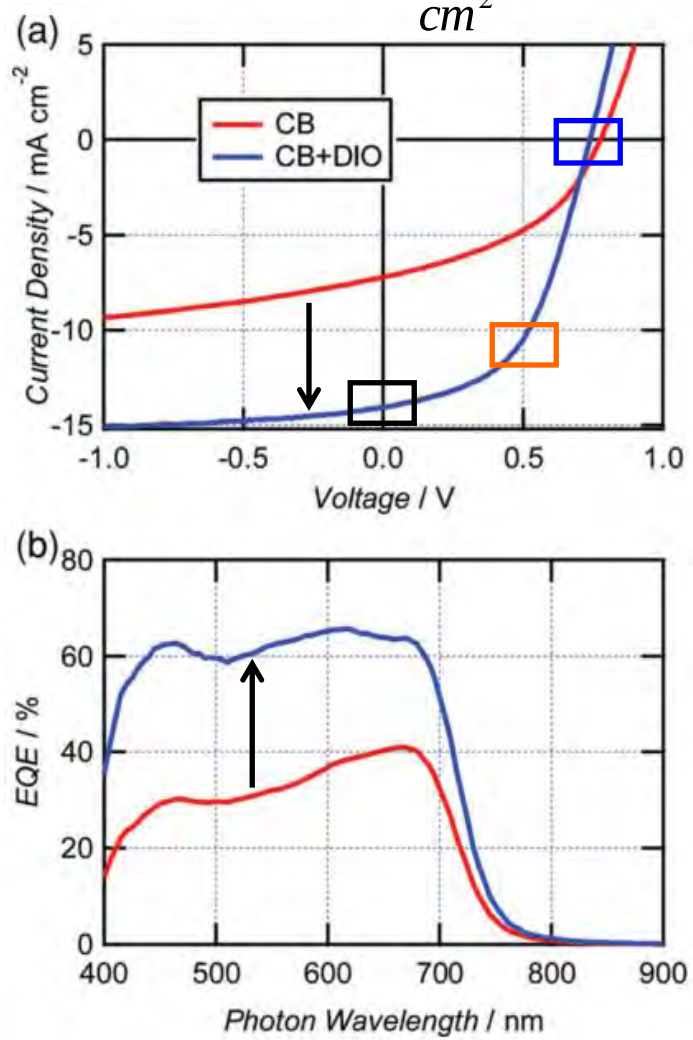
- **Relative domain compositions from Total scattering intensity (TSI, Porod Invariant)**

$$TSI = \int_0^\infty I(q)q^2 dq \propto \Delta Composition^2$$

Part 1. Introduction of Methods: PTB7:PCBM System as example

$$\mathrm{PCE} = \frac{J_{sc} \cdot V_{oc} \cdot FF}{100 \frac{mW}{cm^2}}$$



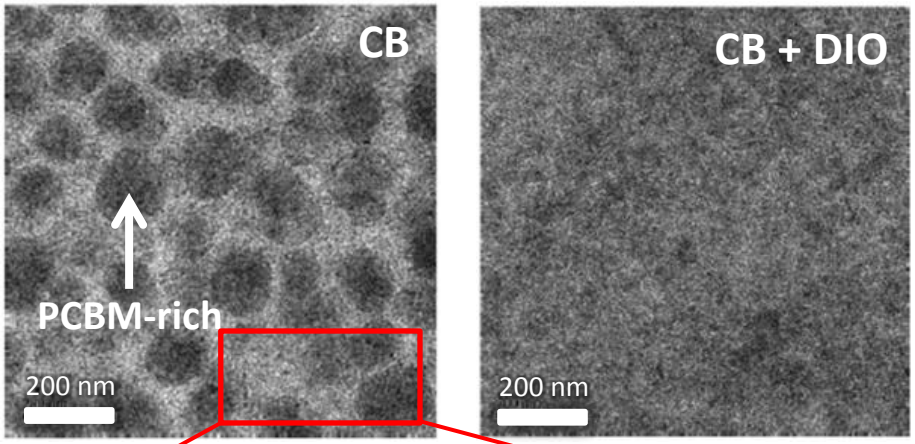


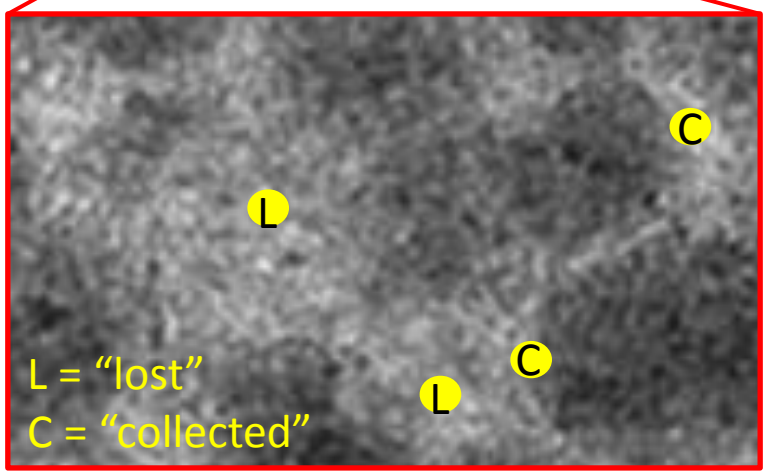
What happened to morphology?

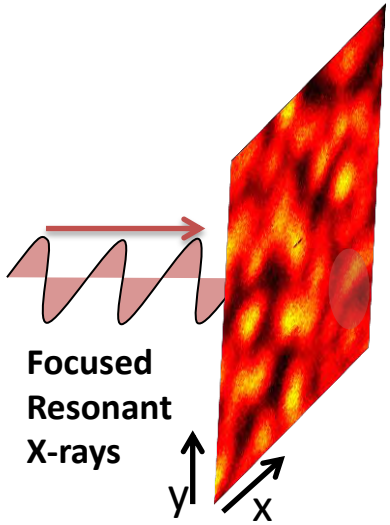
Collins et al., Adv. Energy Mater., 3, 65-74 (2013).

How Does Morphology Change with Processing for PTB7:$PC_{71}BM$?

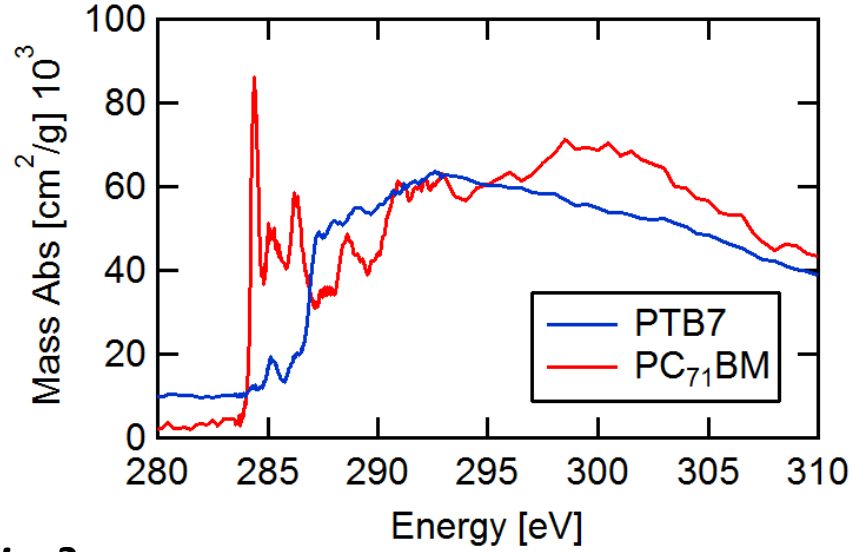
Bright field TEM: size gets smaller







Scanning Transmission X-ray Microscopy

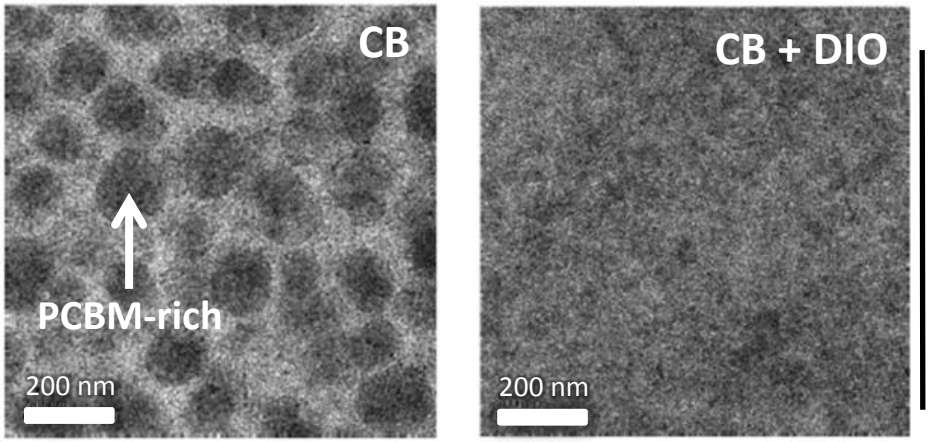


Question: What is the purity of the domains?

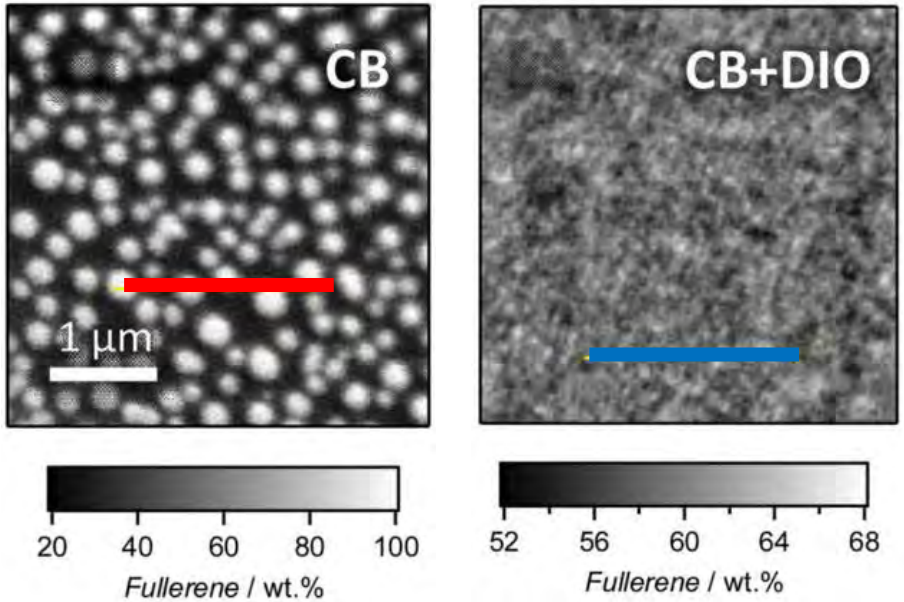
Liang et al., Adv. Mater., 22, E135 (2010).

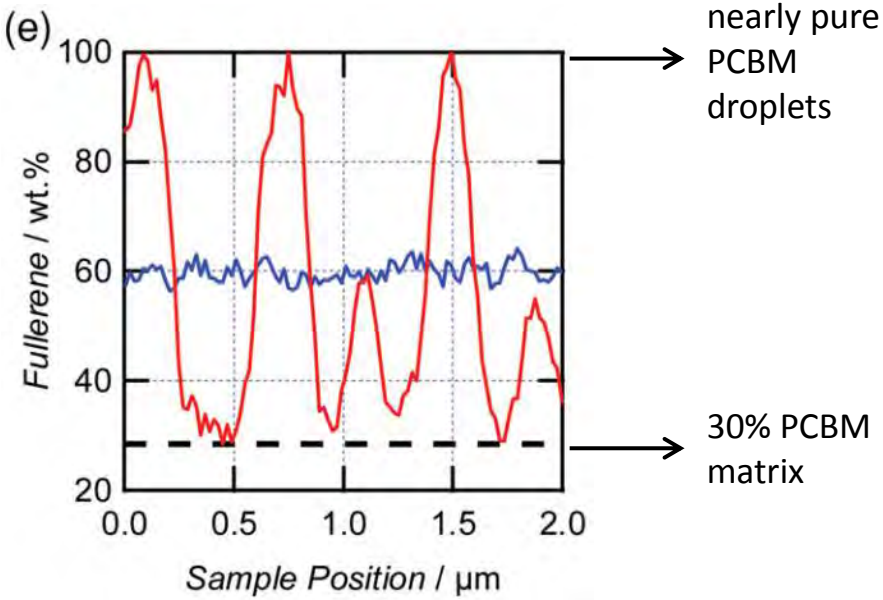
How Does Morphology Change with Processing for PTB7:$PC_{71}BM$?

Bright field TEM:



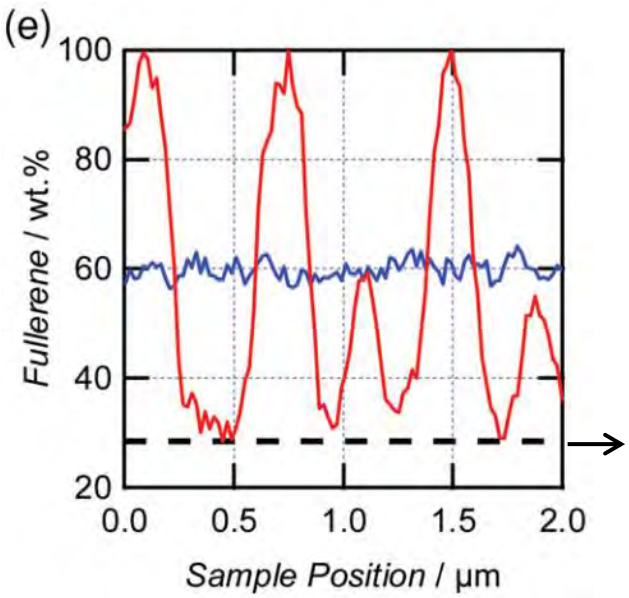
STXM:





*Collins et al., Adv. Energy Mater.**3**, 65 (2013)*

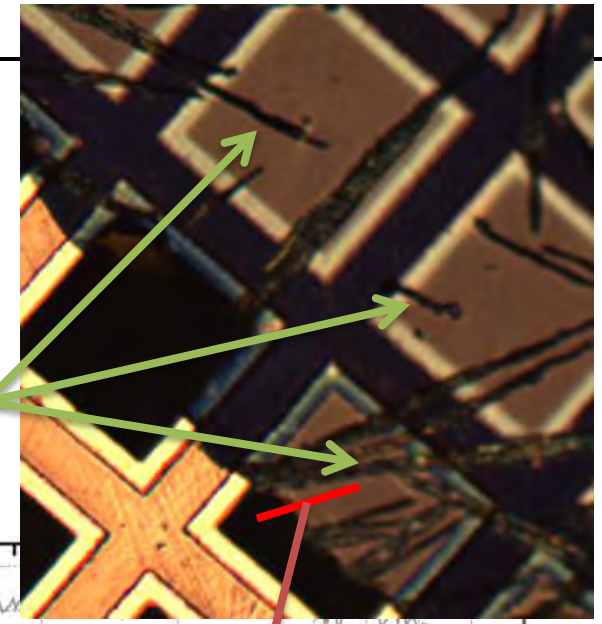
Connection to Fundamental Thermodynamics

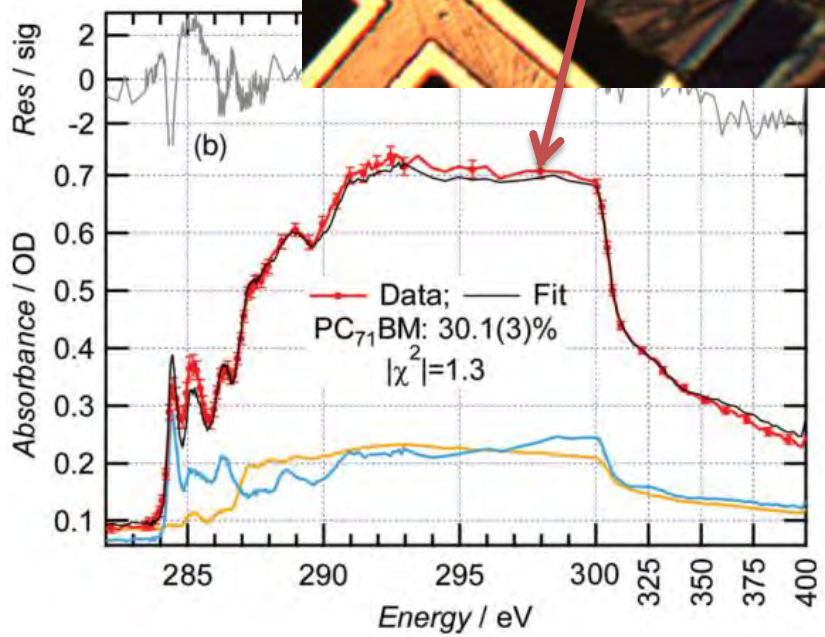


~30% PCBM matrix

thermally annealed for 5 days

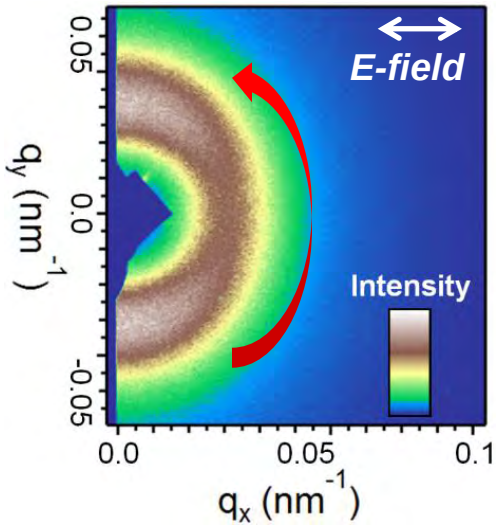
PCBM Xtals

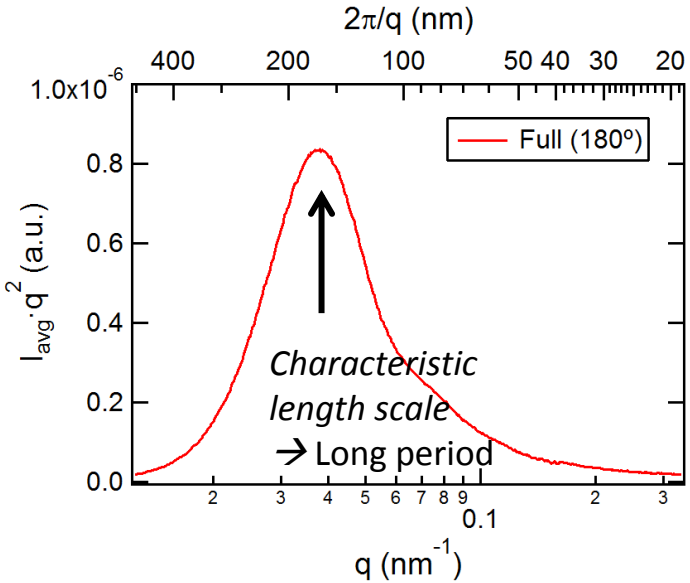




- Measured miscibility the same as composition in matrix: 30% PCBM
- Domain impurity does not kill devices. It actually might help in this case (see also *Bartelt, Adv. Energy Mater.* **3**, 364 (2013)).
- Ideal???? – Can study this now

Domain Distribution and Total Scattering

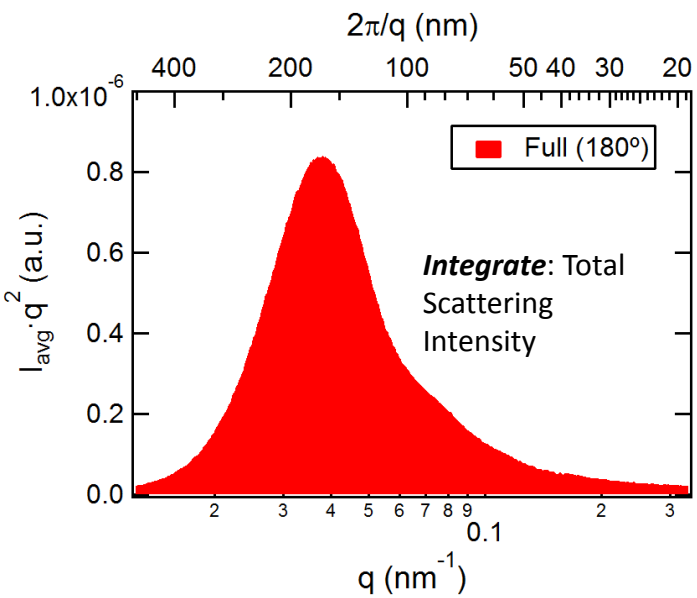


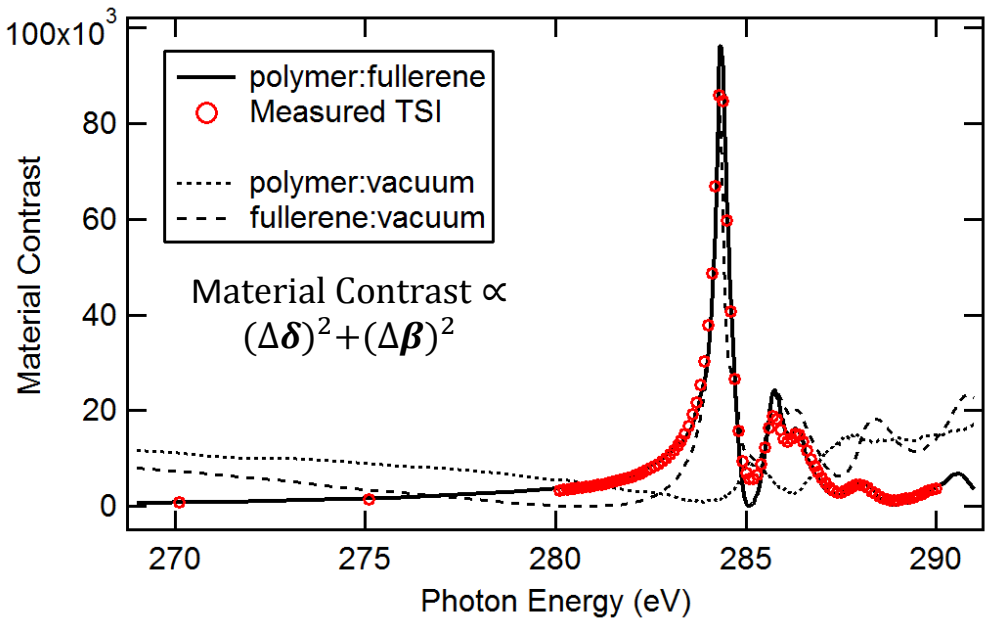


Total intensity at each q

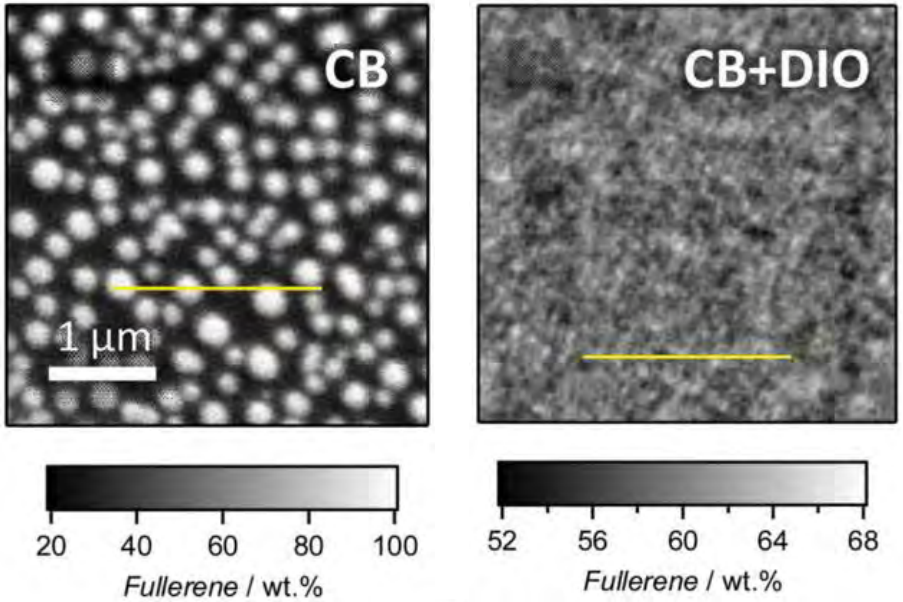
Peak represents mode in spatial frequencies

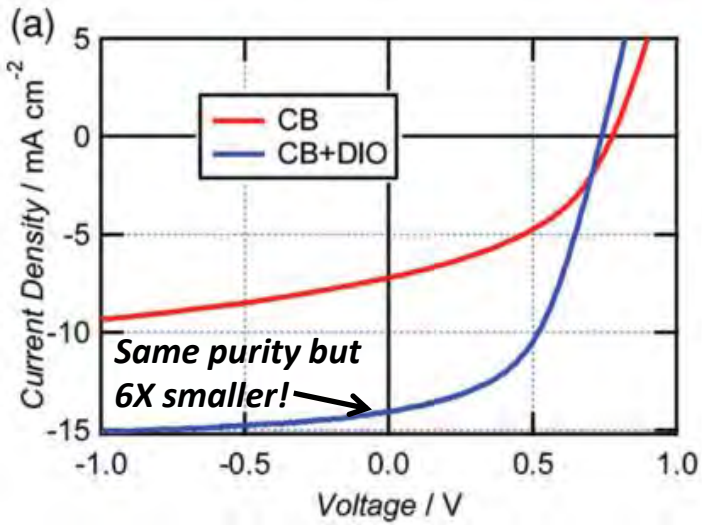
- Long period
- high polydispersity
- ~50/50 volume fraction

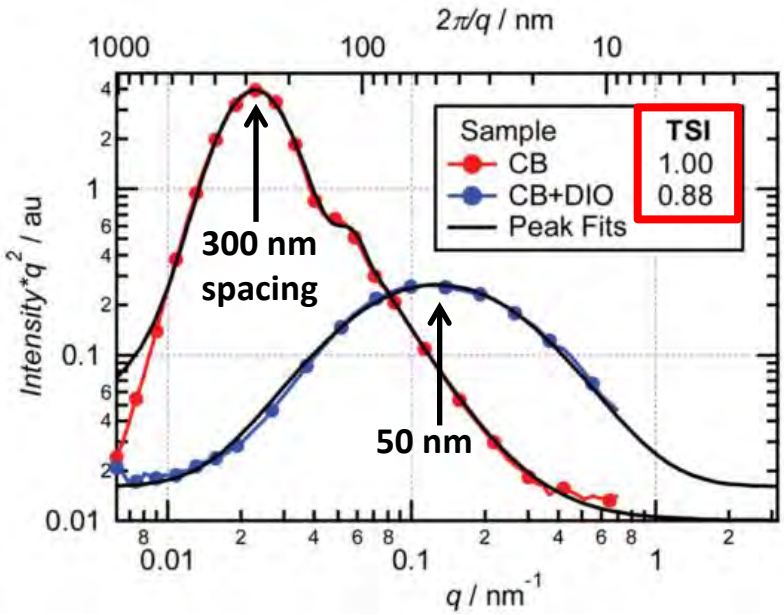


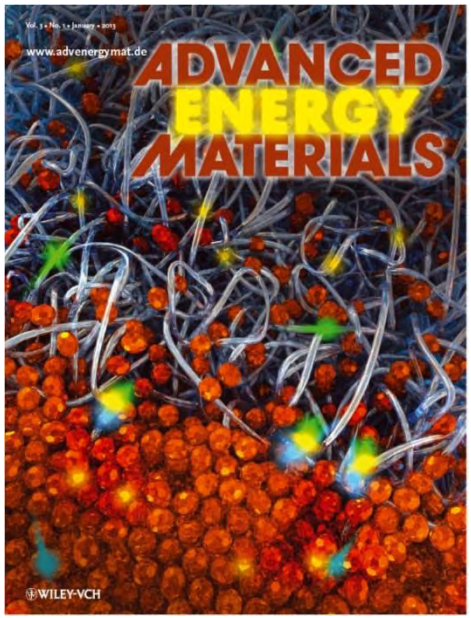


Relative Domain Purities Related to Total Scattering Intensity (TSI)







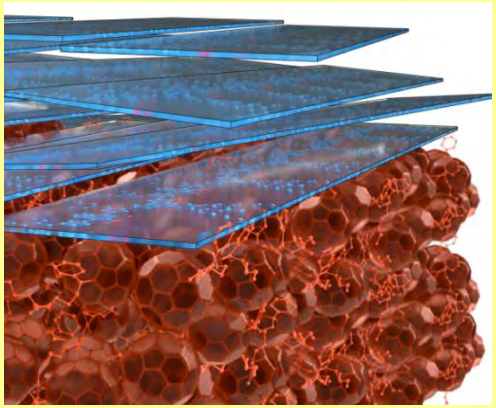


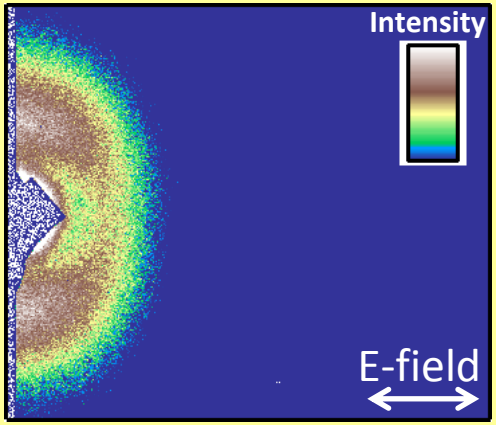
69 citations (CrossRef)

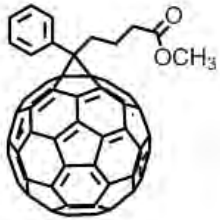
Collins et al., Adv. Energy Mater., 3, 65-74 (2013).

Part 2: Molecular Orientation with Respect to BHJ D/A "Interfaces"

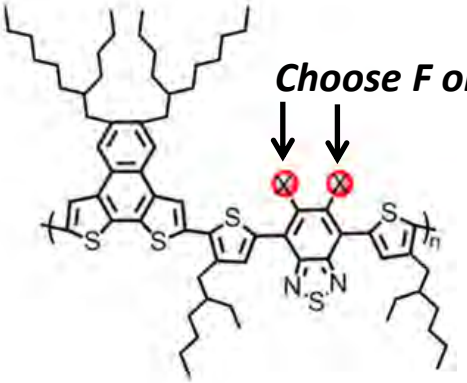
Fluorine: Face-on







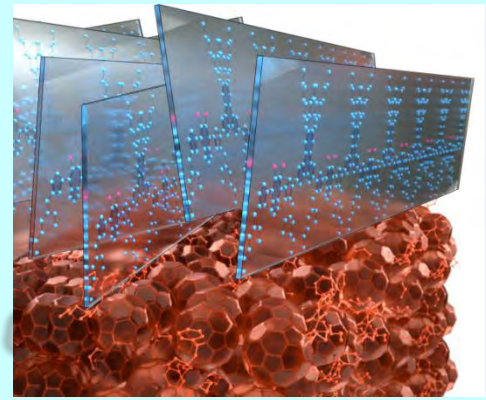
PCBM

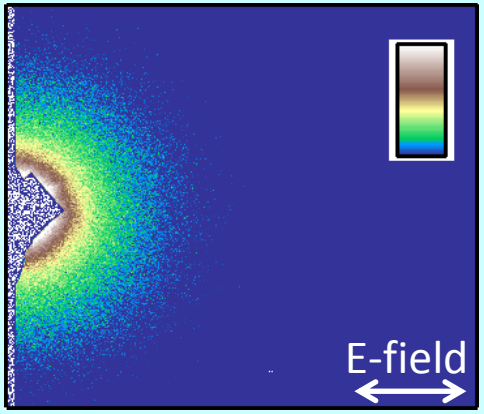


PNDT-DTBT

We can control and characterize this and it is critical to performance (in this system)

Hydrogen: Slightly edge-on



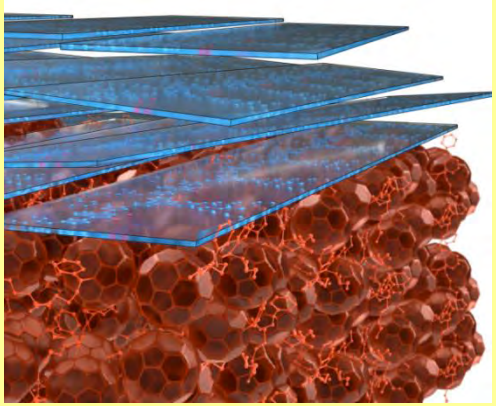


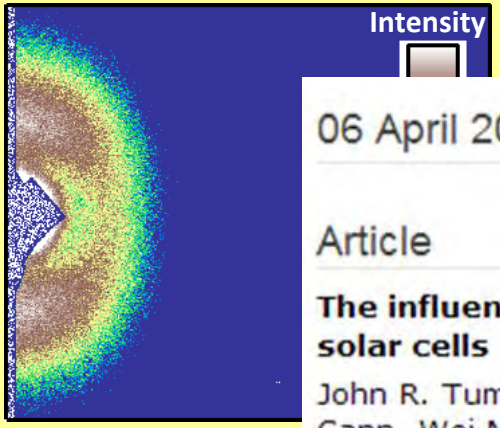
Collaboration with Wei You's group

Tumbleston et al. Nature Photonics (in press).

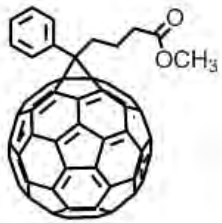
Part 2: Molecular Orientation with Respect to BHJ D/A "Interfaces"

Fluorine: Face-on

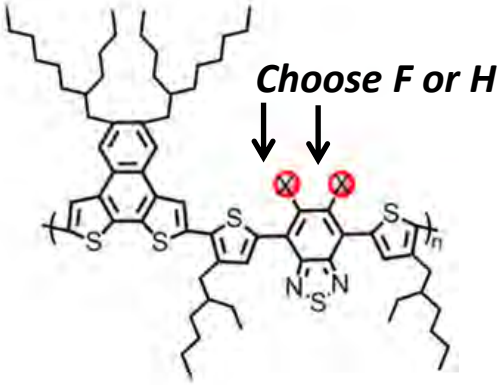




Collaboration with Wei You's group

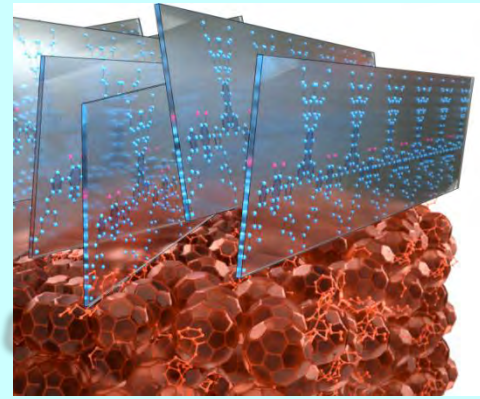


PCBM



PNDT-DTBT

Hydrogen: Slightly edge-on



06 April 2014 top

Article

The influence of molecular orientation on organic bulk heterojunction solar cells

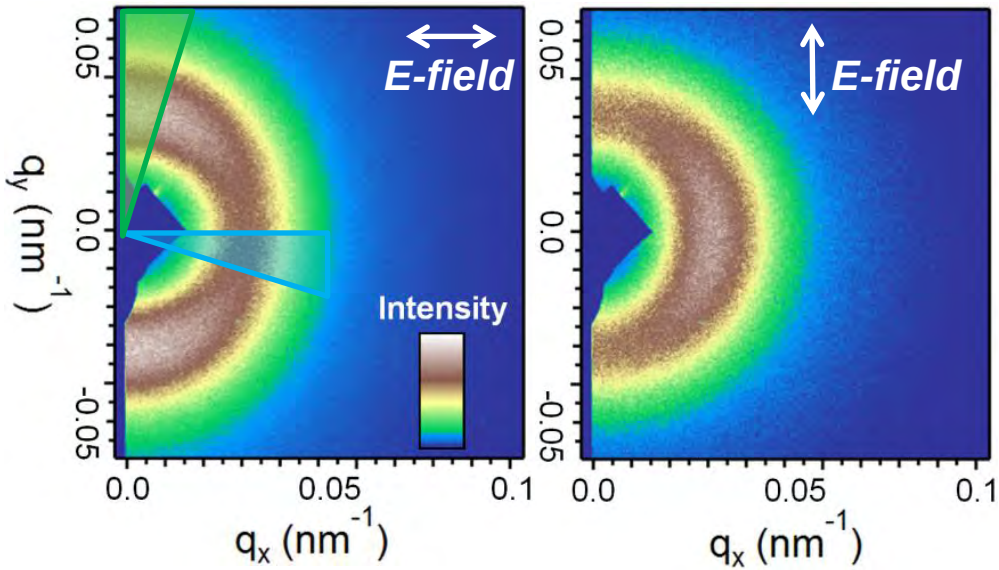
John R. Tumbleston, Brian A. Collins, Liqiang Yang, Andrew C. Stuart, Eliot Gann, Wei Ma, Wei You & Harald Ade

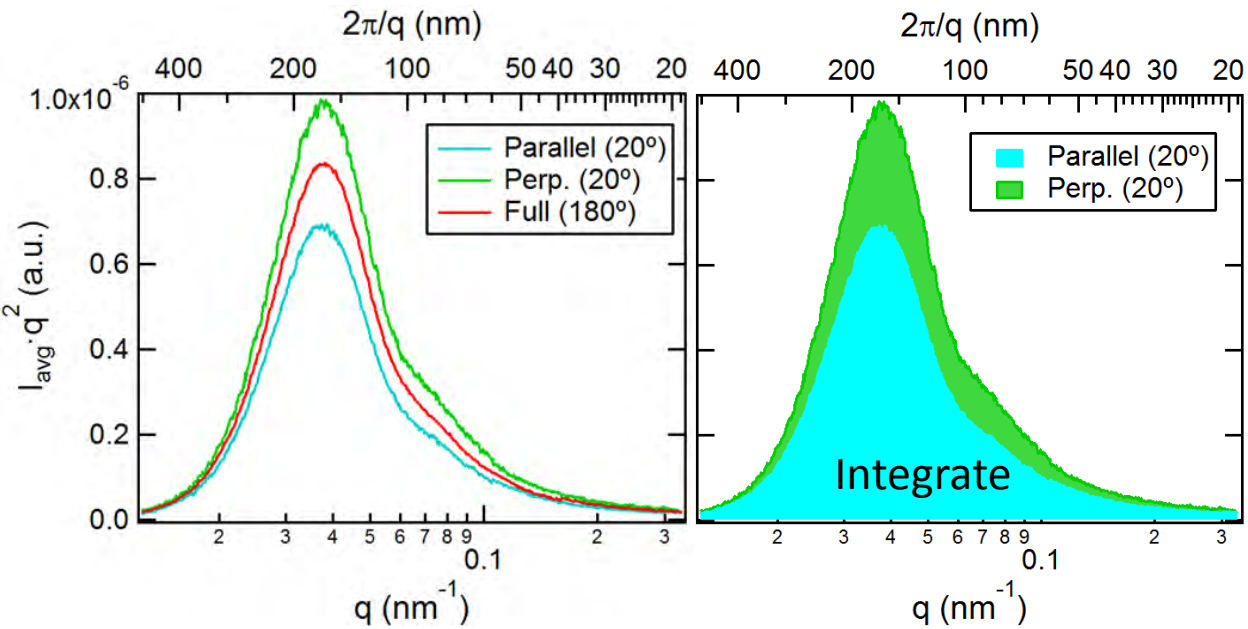
Published online: 06 April 2014 | doi:10.1038/nphoton.2014.55

X-ray scattering experiments indicate that the molecular orientation at the interfaces of bulk heterojunction organic solar cells influences the cells' fill factor and short-circuit current.

Abstract | **Full Text** | PDF (4,681 KB) | Supplementary information

Quantifying Scattering Anisotropy

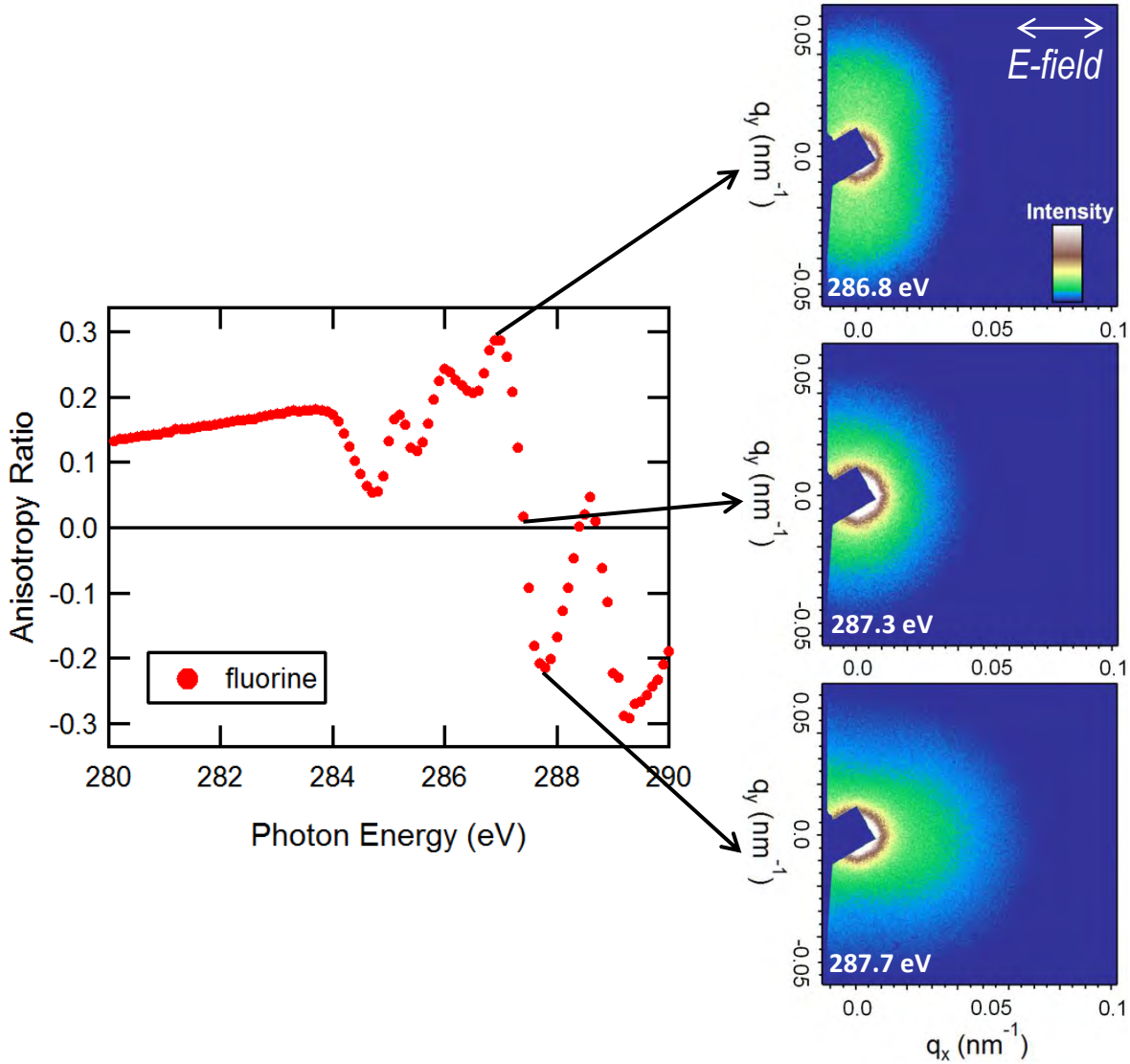




$$\textbf{Anisotropy Ratio} = \frac{\textbf{Perp.} - \textbf{Para.}}{\textbf{Perp.} + \textbf{Para.}}$$

$$\textbf{Anisotropy Ratio} = \frac{\textbf{Difference}}{\textbf{Sum}}$$

Observe Rich Energy Dependence

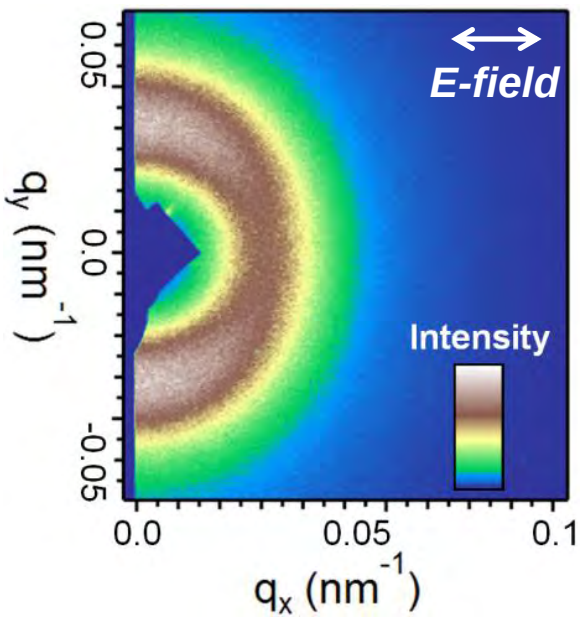


Optical properties depend on orientation (recall NEXAFS)

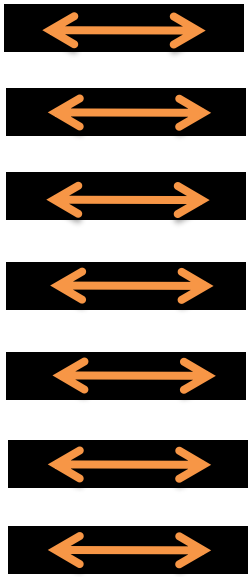
Tumbleston, submitted

Collins et al., Nature Materials, 11, (2012), 536-543

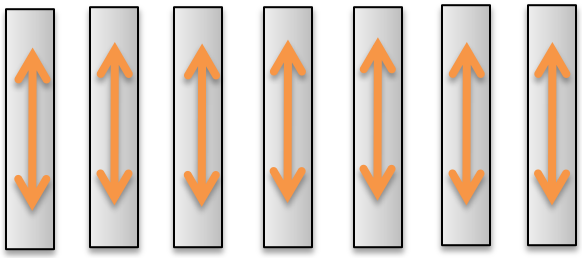
Simple Didactic Model: Gratings with oriented Transition Dipole Moment (TDM)



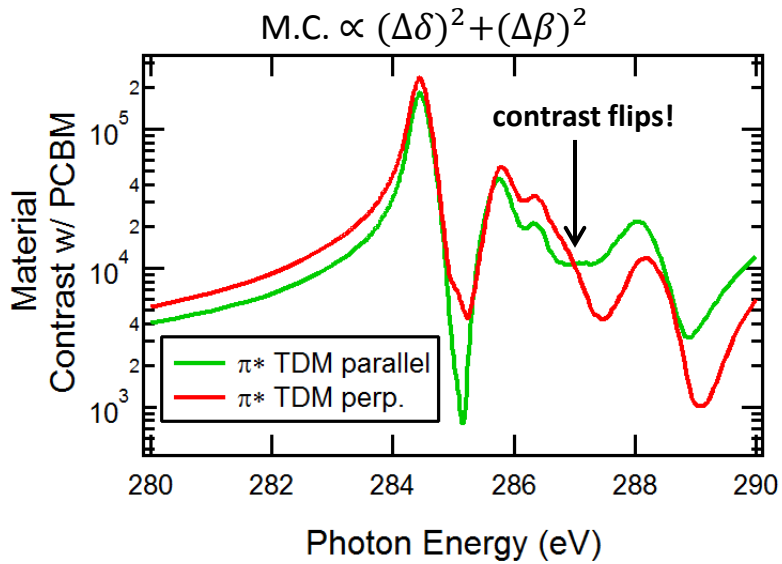
Parallel TDM:
more scattering
high contrast



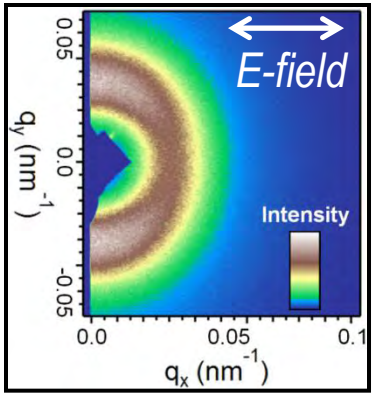
Perpendicular TDM:
less scattering
low contrast

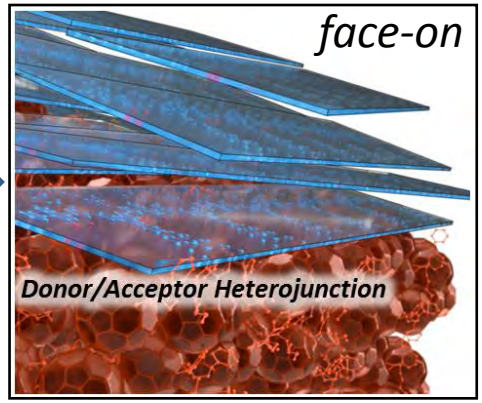


We Can Model the Energy Dependence (relatively well)



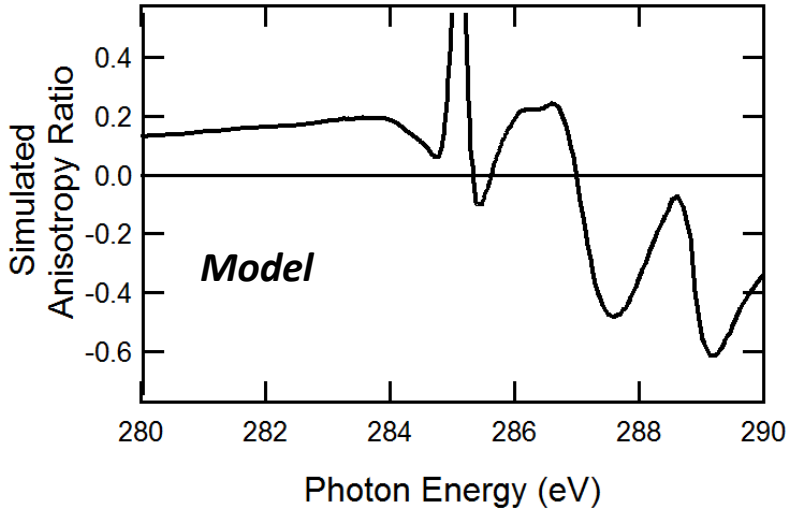
Greater optical contrast with PCBM when polymer π* is perpendicular to electric field (depending on energy)

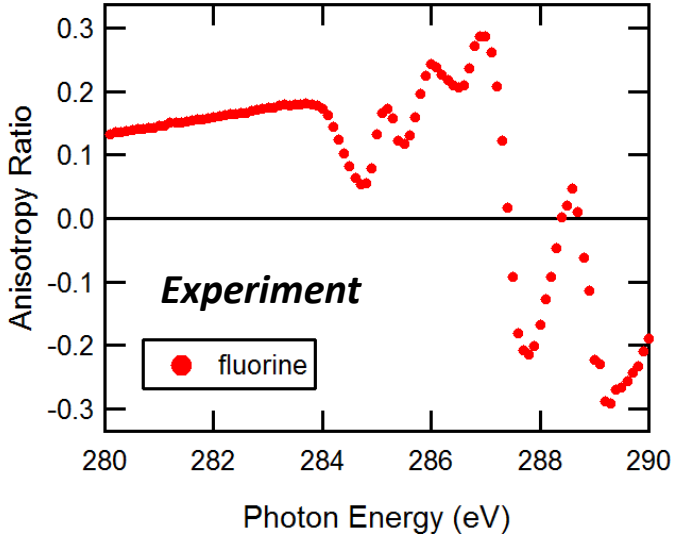




below ~287

$$\textit{Anisotropy Ratio} = \frac{\textit{Difference}}{\textit{Sum}}$$

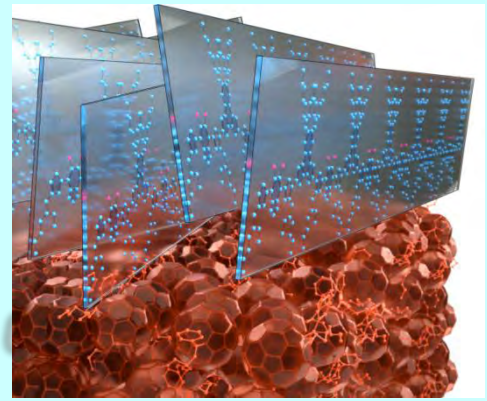


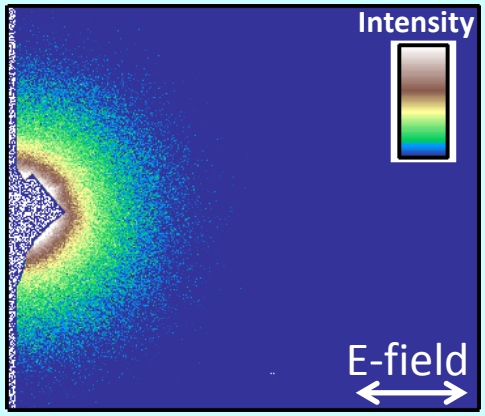


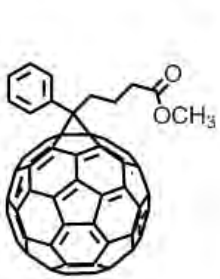
Tumbleston et al. Nature Photonics (in press).

What About Relation of Scattering Anisotropy to Device Performance?

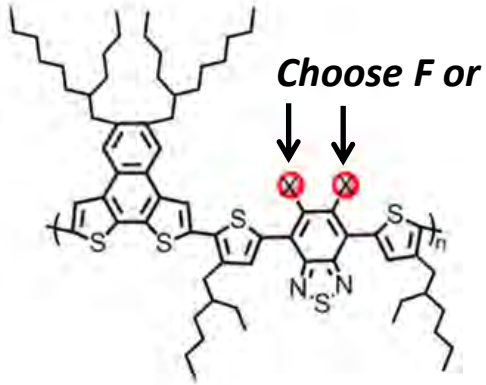
Hydrogen: Slightly edge-on
DCB



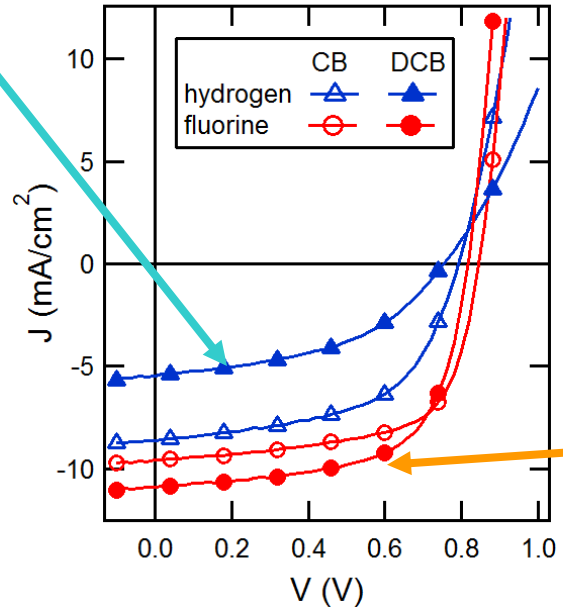




PCBM

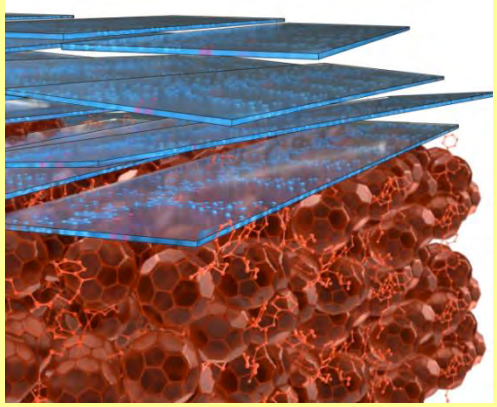


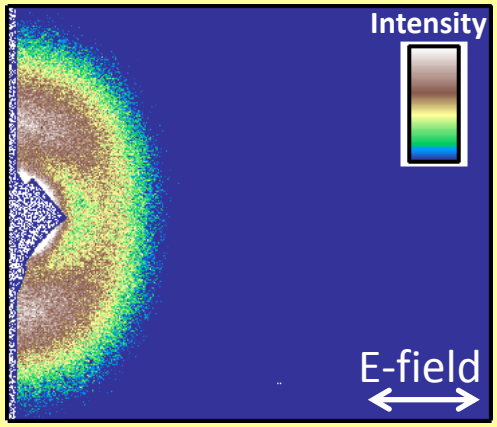
PNDT-DTBT



Choose solvent, too

Fluorine: Face-on
DCB



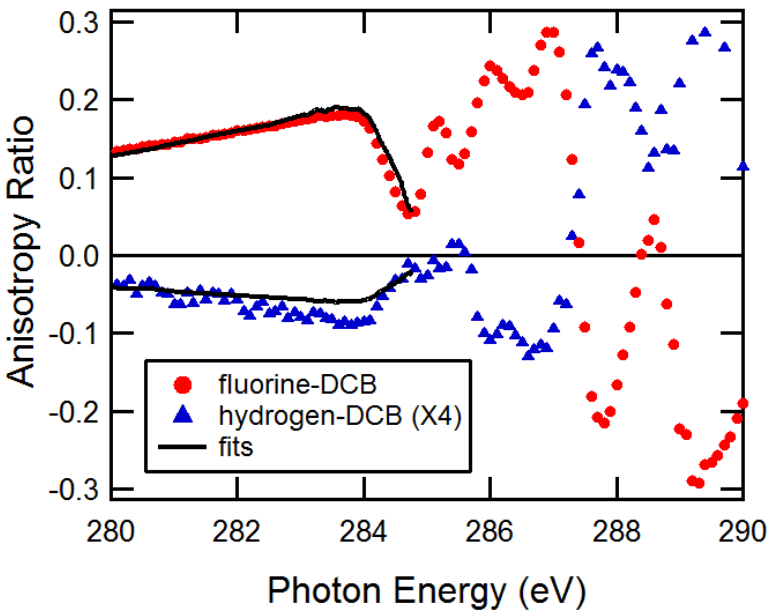


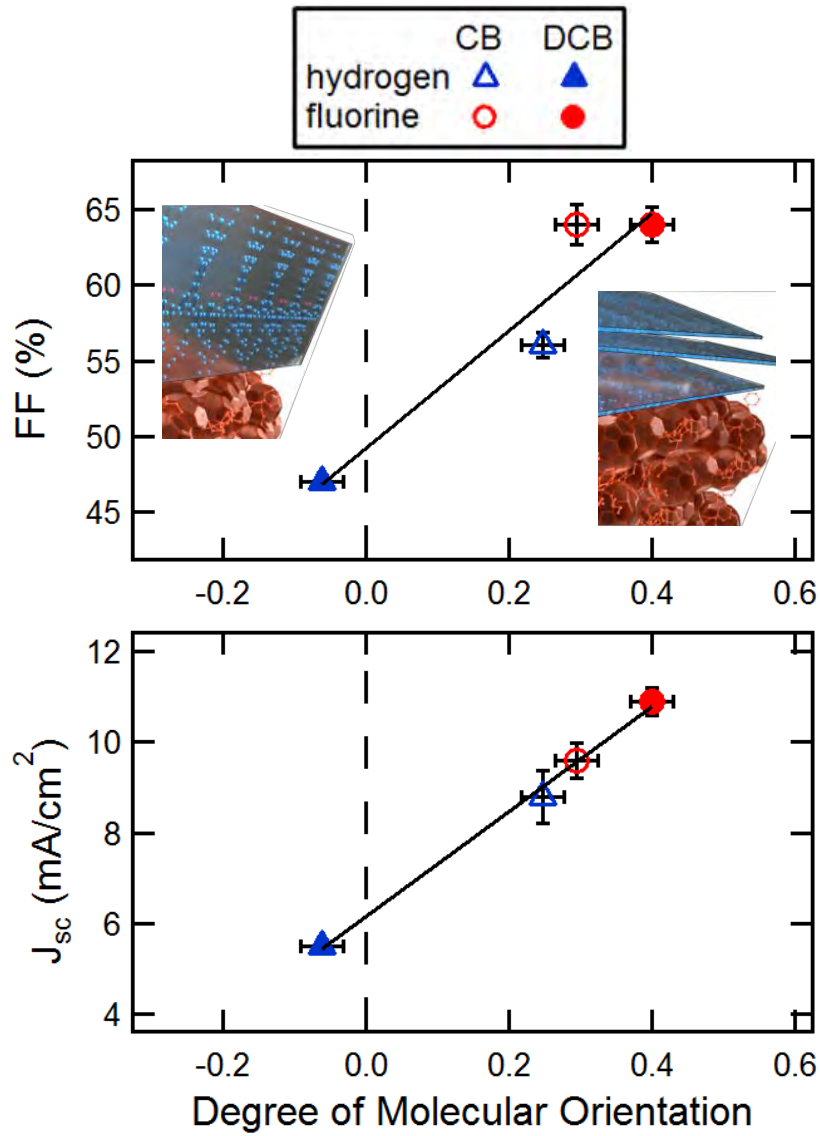
Other info:

- 1:1 wt. ratio with PCBM
- no thermal treatment

Tumbleston et al. Nature Photonics (in press).

Excellent Correlation with Performance



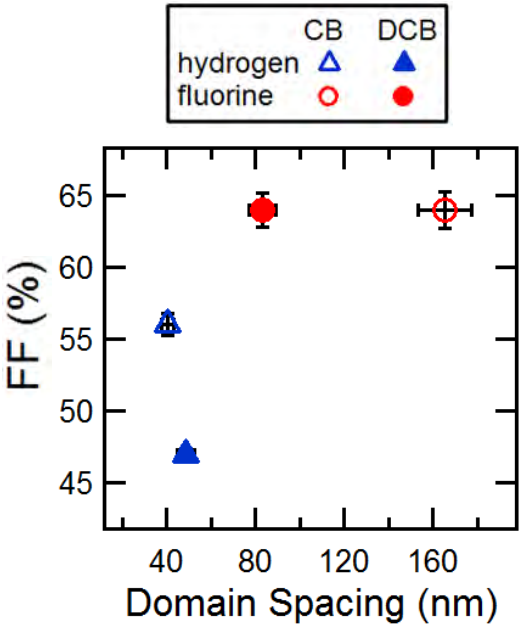


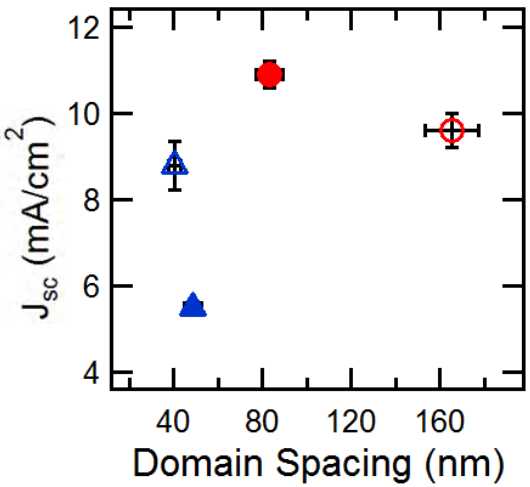
What about other aspects of the morphology?

- **Domain size**
- **Domain purity/composition variations**
- **Crystallinity**

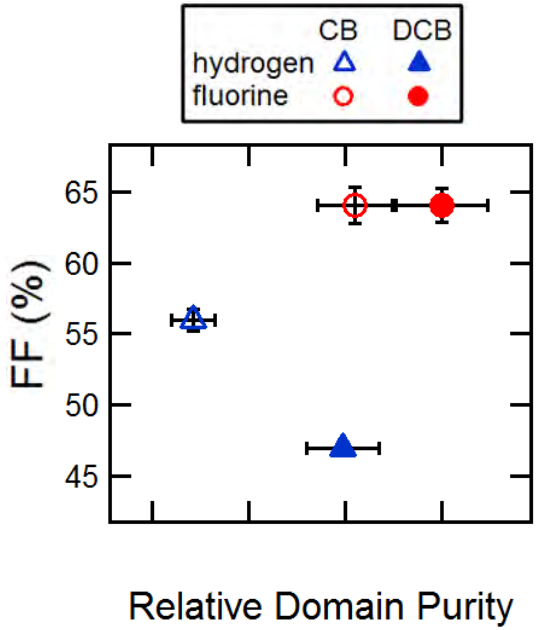
Tumbleston et al. Nature Photonics (in press).

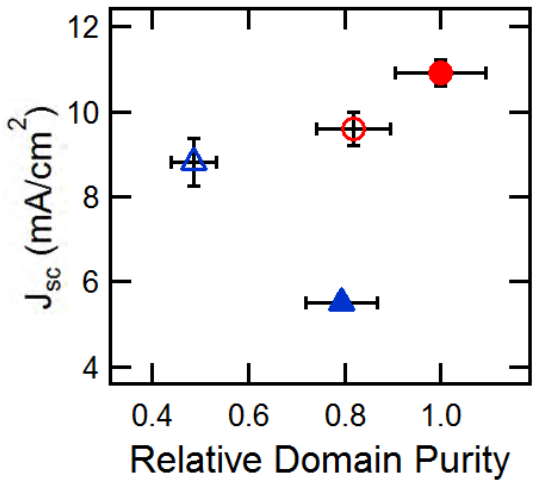
Preferential Orientation is Most Critical Parameter for this System



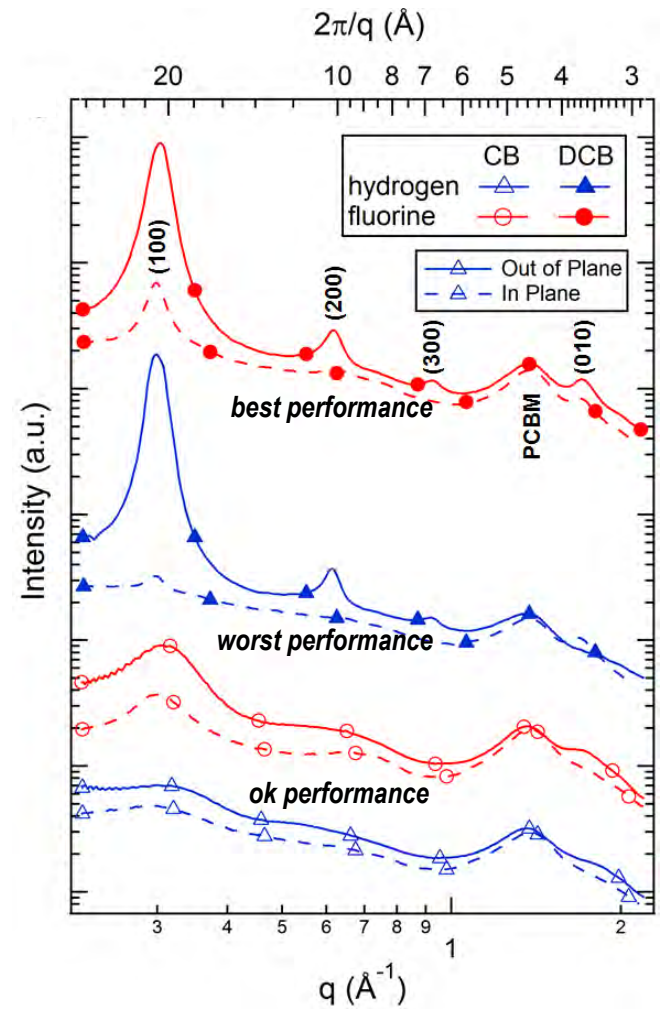


No Correlation!





No Correlation!



Crystallinity:
No Correlation!

Tumbleston et al. Nature Photonics (in press).

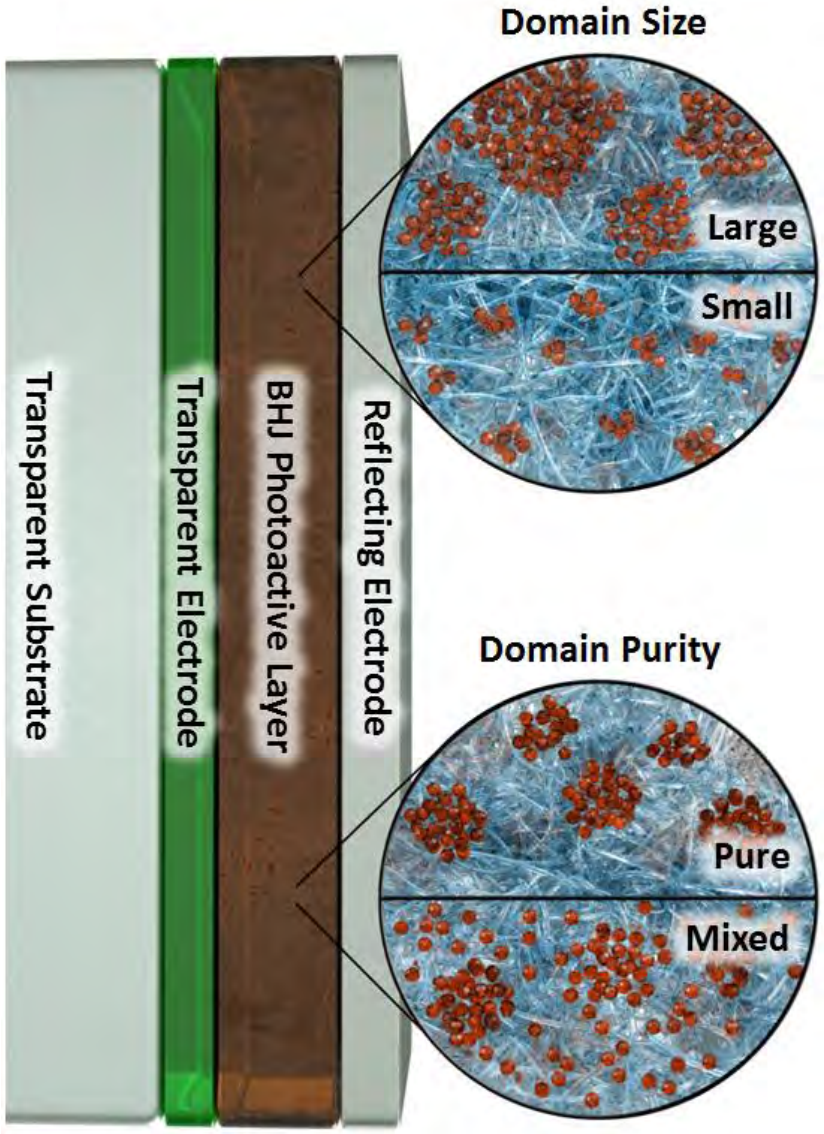
Big impact on charge dynamics

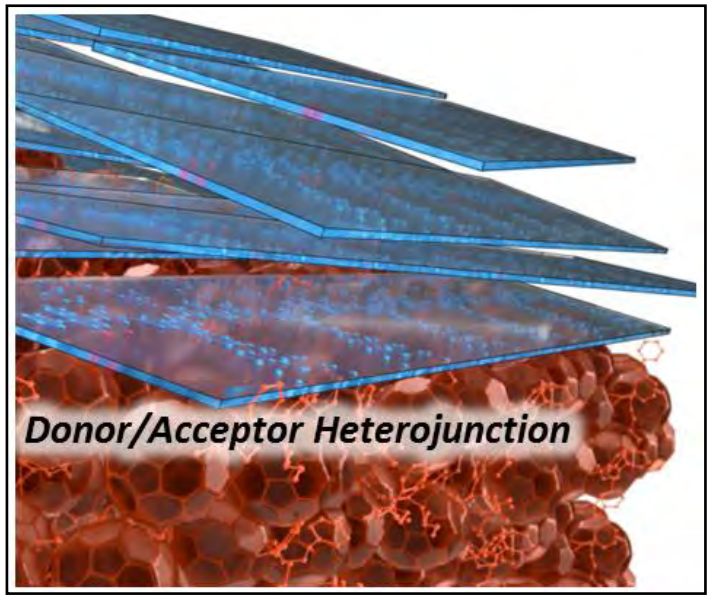
Transient absorption spectroscopy reveals polaron-pairs form faster in face-on **PNDT-DTBT:PCBM** samples

→ Different energies too

Unpublished data redacted

Summary on Methods (published results)





- Important morphological parameters –*can be measured with soft X-rays:*
  - Domain size and size distribution
  - Interface roughness/diffusivity
  - Electrode interface wetting layers
  - Domain purity/composition variations
  - Crystallization (with hard x-rays)
  - ***New: Molecular orientation "at"/relative to donor/acceptor interfaces***

What other important system characteristics did I not really characterize?

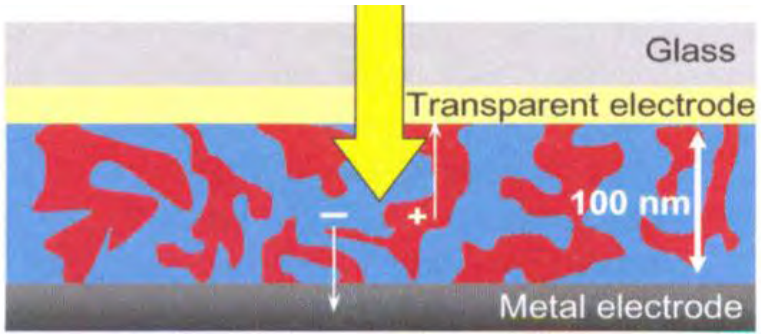
- Size, size distribution?
- Purity?
- Molecular orientation?

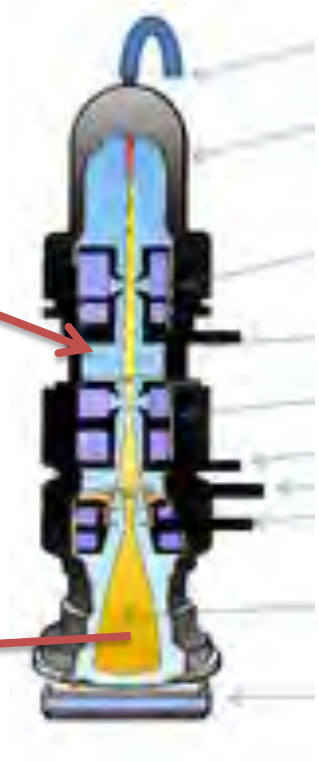
I only provided reciprocal space statistical description!

- Connectivity is not well described in this way

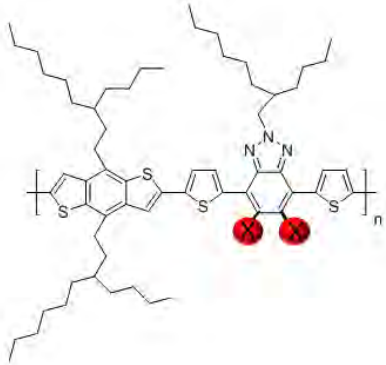
→ tomography by Prof. Spontak

Tilt series in Energy Filtered TEM

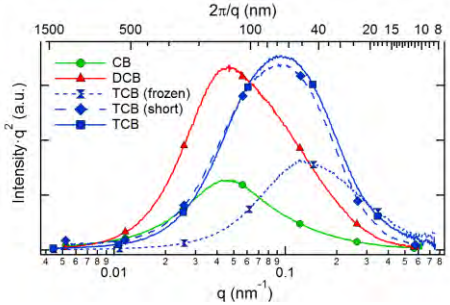




3D
reconstruction



Wei You's FTAZ in FTAZ:PCBM



Unpublished data redacted

Data courtesy of Prof. R. Spontak

Morphology? Ideal Morphology?

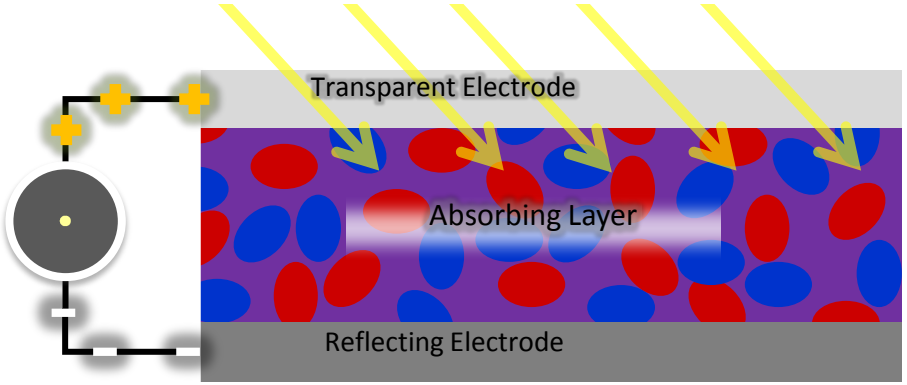
A lot has been learned, but a lot remains unknown: Mechanisms, control, relation to chemical structure?

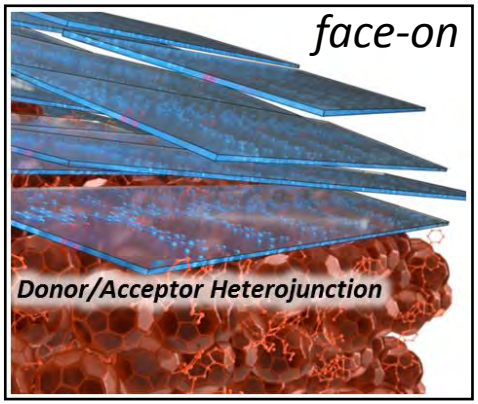
No predictive theory for operation or morphology

Limits of heuristic models and "shake and bake"

The field is still wide open

→ Still a good time to get involved!





Collins B.A., *ALS Science Highlights* (2011).

Challenges

Predictive theory for operation or morphology

How to we get from 10% to 25% (the theory limit)?

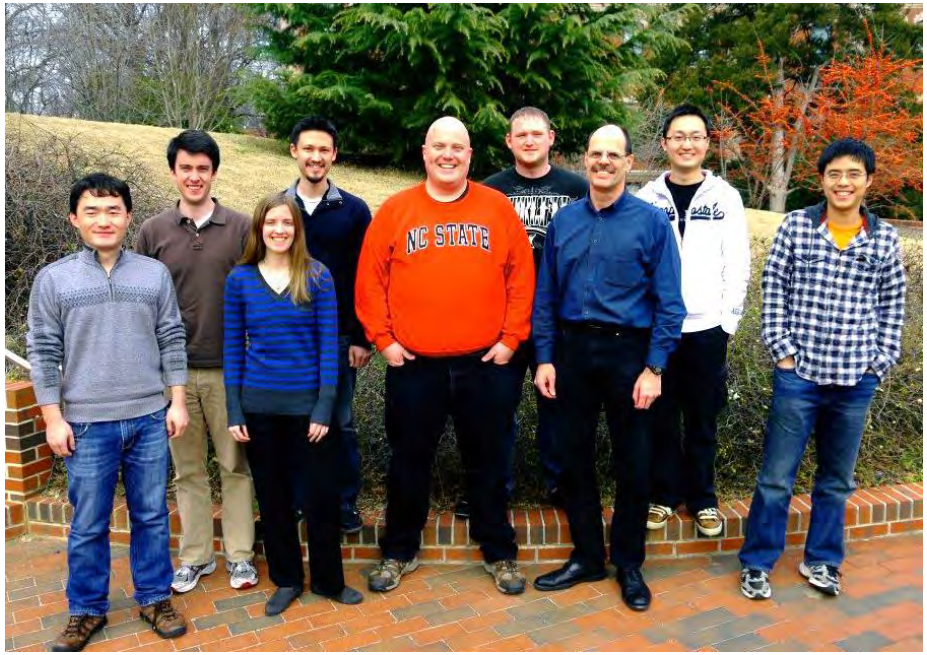
Can we make organics "hard", i.e more like classic seminconductors?

→ *high dielectric constant and low reorganization energies?*

→ ***Need 3D quantities compositional maps***

→ ***Need more advanced microscopy tools to complement the scattering***

Acknowledgements



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