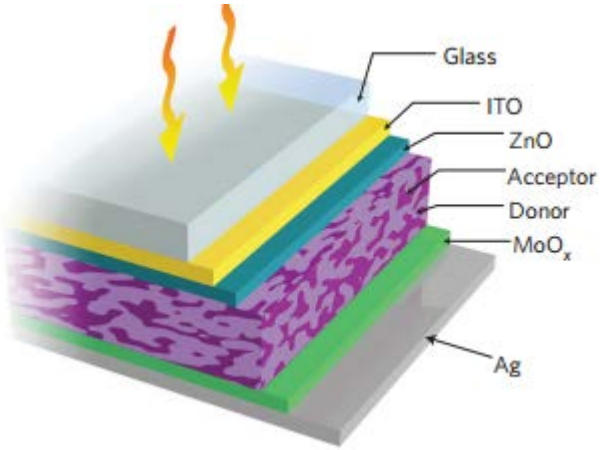
Beamline 8-ID-E: Enabling Grazing Incidence X-Ray Scattering for Organic Photovoltaics Research

Joseph Strzalka, 8-ID-E

Time-Resolved Research Group

X-Ray Science Division



Outline

- Introduction
  - Role of Organic PhotoVoltaics (OPVs) in Renewable Energy
- OPV Principles
  - Photovoltaic Effect
  - The Bulk Heterojunction (BHJ)
  - Organic Solar Cells
- Beamline 8-ID-E
- GIXS and OPV Morphology
  - Benchmark Material: P3HT
- Sample Environments: Influence of Processing on Performance
- Conclusions

Introduction:
Organic Photovoltaics (OPVs)

- Solar energy conversion from organic materials

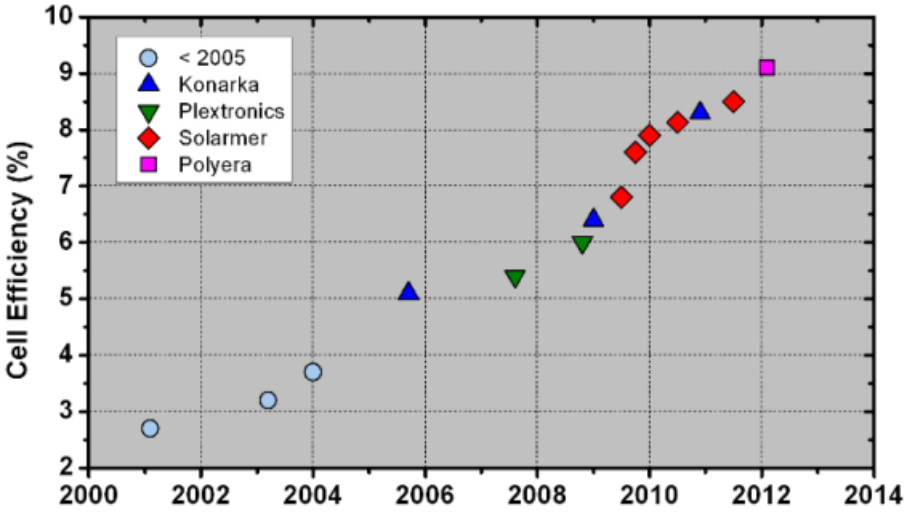
OPV Advantages

OPV Disadvantages

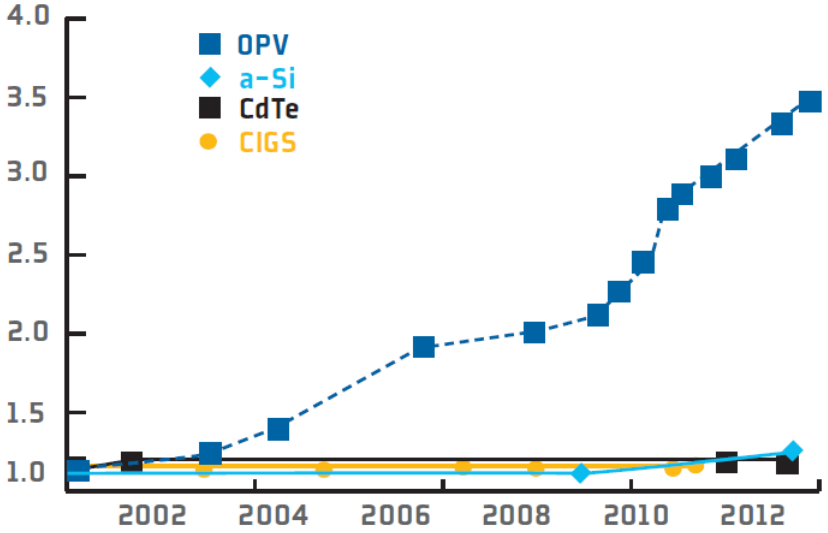
— **Lower efficiency**
— **Limited lifetime**

http://solarmer.com
F. C. Krebs et al, *Energy & Environmental Science*, 5, 5117-5132 (2012)

Introduction:
OPVs for a Renewable Energy Future



http://solarmer.com



Shrotriya, Industrial+Specialty Printing 4,22-25(2013)

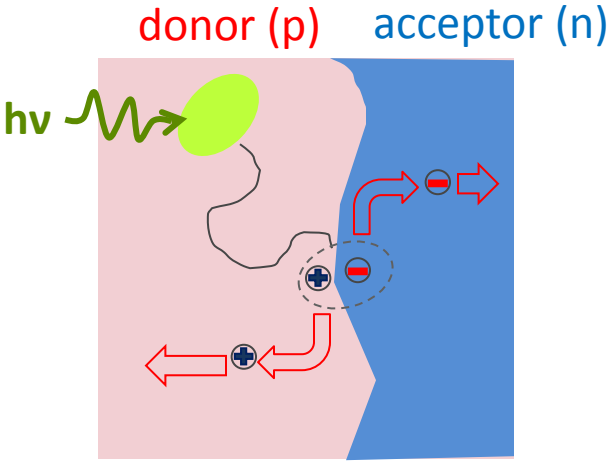
10% efficiency → widespread commercial application.

Energy payback time could be < 1 day!

F. C. Krebs et al, *Energy & Environmental Science*, 5, 5117-5132 (2012)

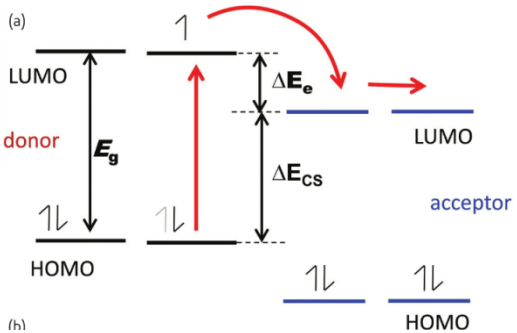
Darling & You, *RSC Advances*, 3, 17633-48 (2013)

OPV Principles:
Photovoltaic Effect for Organic Semiconductors



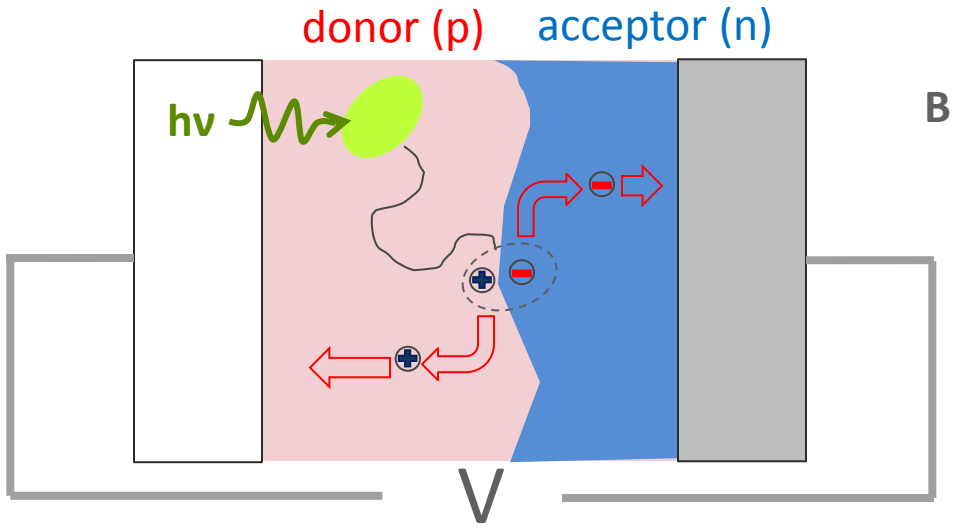
ε=3-4

E_g=1.5-2 eV



Nelson, *Materials Today* 14 462-470 (2011)

OPV Principles:
Photovoltaic Effect for Organic Semiconductors



Bilayer Organic Cell (1986)

ε=3-4

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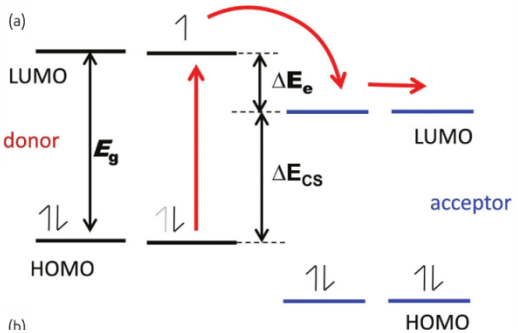
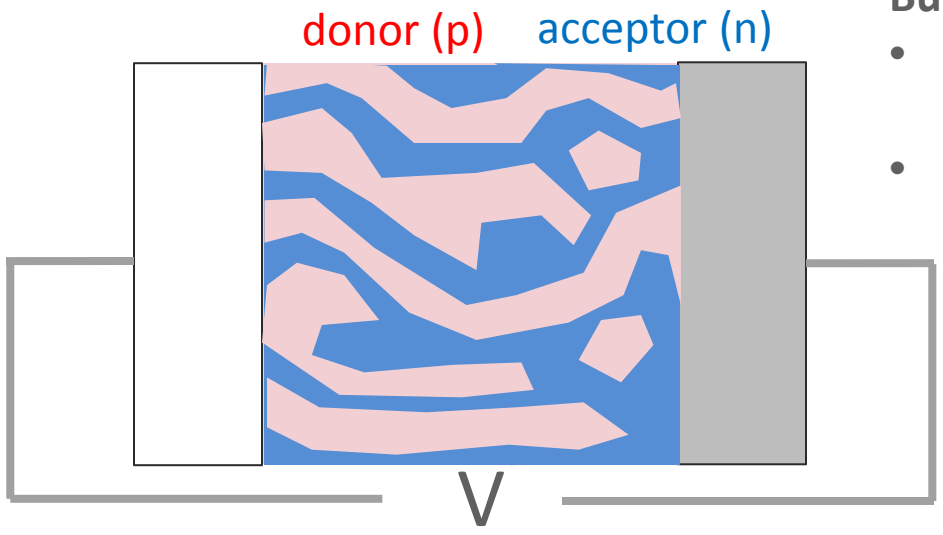


Tang, *Appl. Phy. Lett.* 48 183-185 (1986)

Nelson, *Materials Today* 14 462-470 (2011)

OPV Principles:
The Bulk Heterojunction (BHJ)

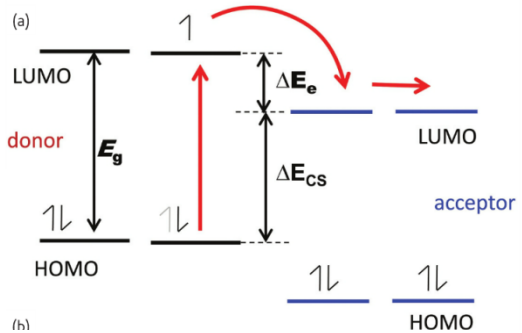


Bulk Heterojunction (1995)

- **Blending ~10 nm (exciton diffusion length)**
- **Bicontinuous phases for charge transport**

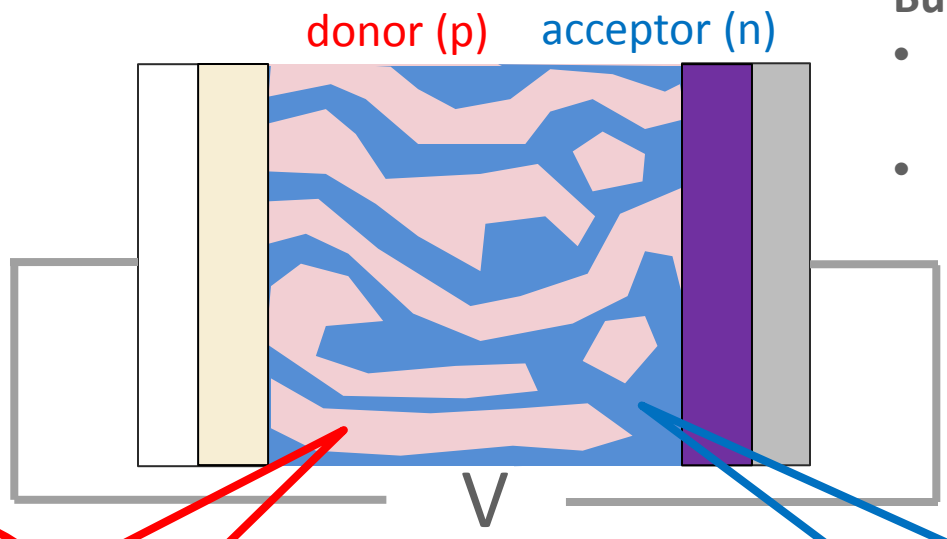
ε=3-4

E_g=1.5-2 eV



Nelson, *Materials Today* 14 462-470 (2011)

OPV Principles: Organic Solar Cells



Bulk Heterojunction (1995)

- **Blending ~10 nm (exciton diffusion length)**
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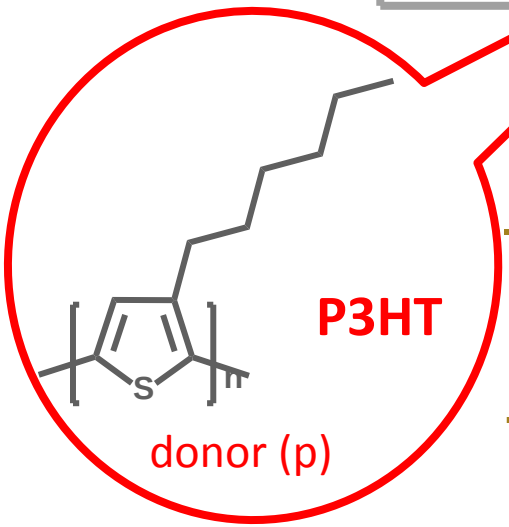

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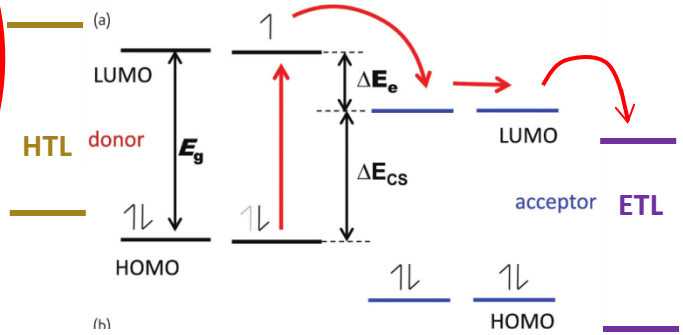
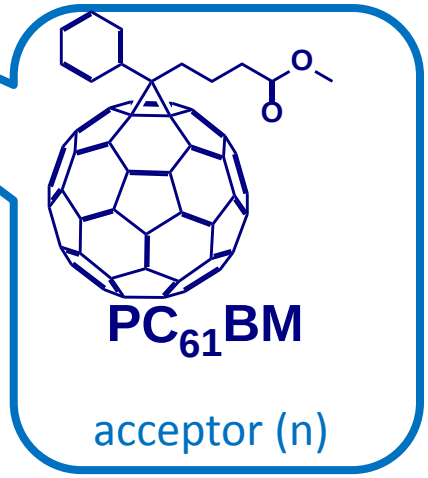




Heeger et al, *Science* 270 1789-1791 (1995)

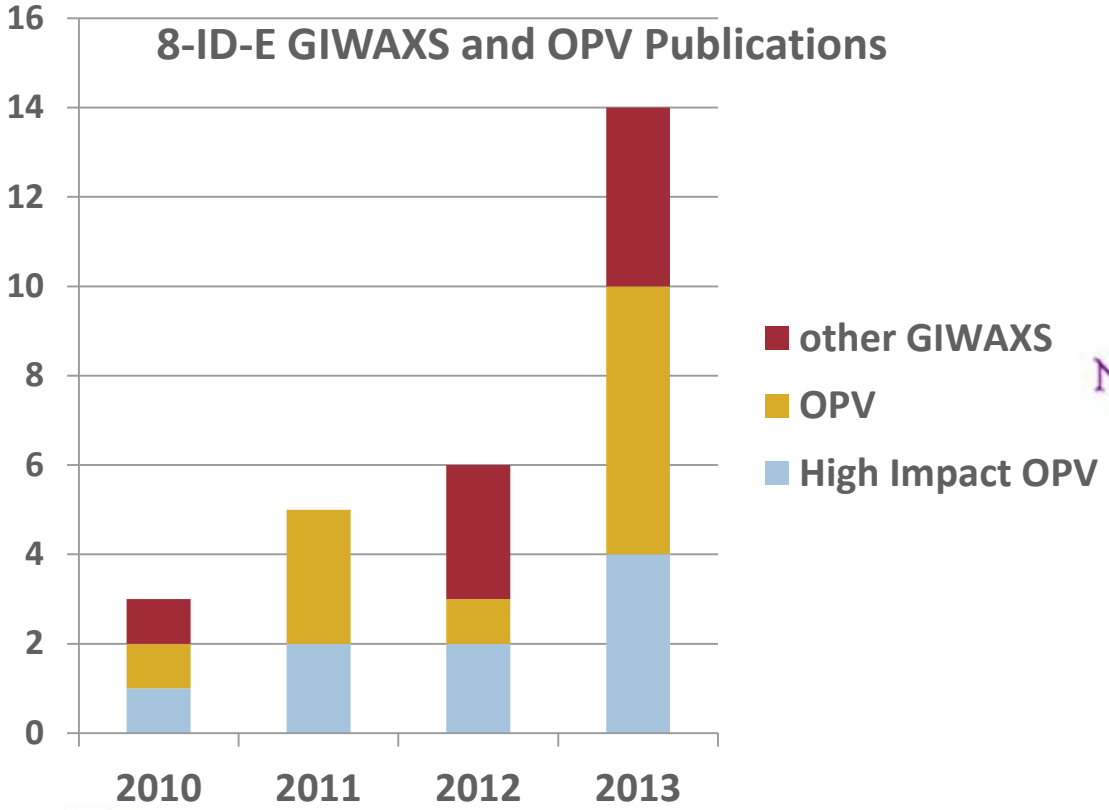
Halls et al, *Nature* 376 498-500 (1995)

Nelson, *Materials Today* 14 462-470 (2011)

OPV Principles: Summary

- Organics (ε ~ 3) require 2 materials, electron donor and acceptor, (p and n type) for photovoltaic function
- Since the introduction of the Bulk Heterojunction (BHJ) architecture, OPV materials have shown steady, ongoing performance gains
- Much effort in the synthetic direction, designing new materials
- We will see morphology over a hierarchy of lengthscales also plays a role
  - Microdomain structure – GISAXS
  - Molecular packing and orientation -- GIWAXS
- Beamline 8-ID-E has played a growing role over the last 5 years in OPV research

Beamline 8-ID-E: GIWAXS and OPV User Community



Argonne-Northwestern ANSER Solar Energy Research Center

NORTHWESTERN UNIVERSITY

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5 PIs

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- CSE, CNM, MSD

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Berkeley UNIVERSITY OF CALIFORNIA

서강대학교 SOGANG UNIVERSITY

WISCONSIN UNIVERSITY OF WISCONSIN-MADISON

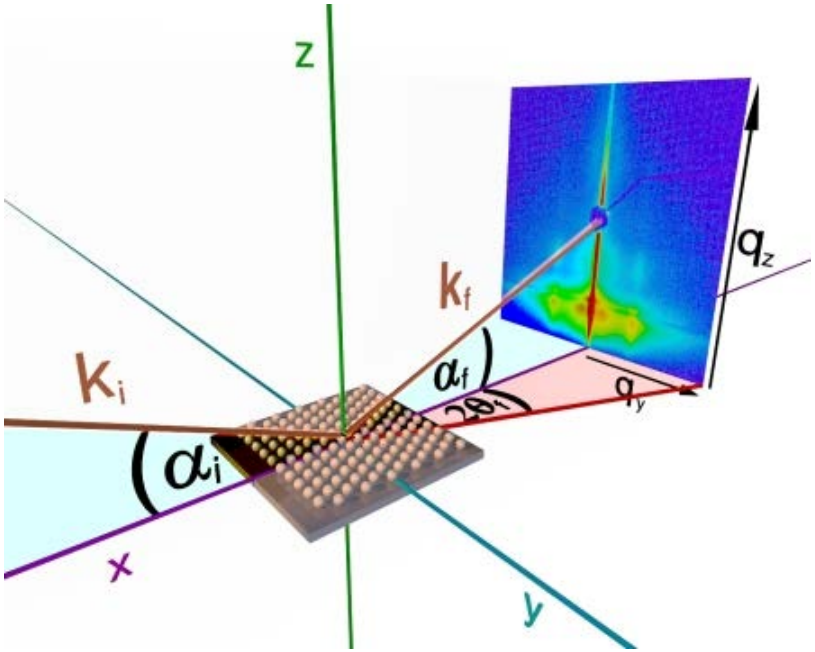
Georgia Institute of Technology

UCSB

Beamline 8-ID-E: Grazing Incidence X-ray Scattering (GIXS)

- Probe morphology at surfaces and interfaces
- Combine diffuse scattering & SAXS
- Access lengthscales:
  - 4 -220 nm (GISAXS)
  - 0.3 – 12 nm (GIWAXS)
- X-rays incident at grazing incidence

  $\alpha_{c,film} < \alpha_i < \alpha_{c,\ substrate}$
  - enhanced sensitivity to surface vs bulk
  - Probe entire depth of thin film
- Determine molecular packing, orientation, domain size, texture
- Area detector

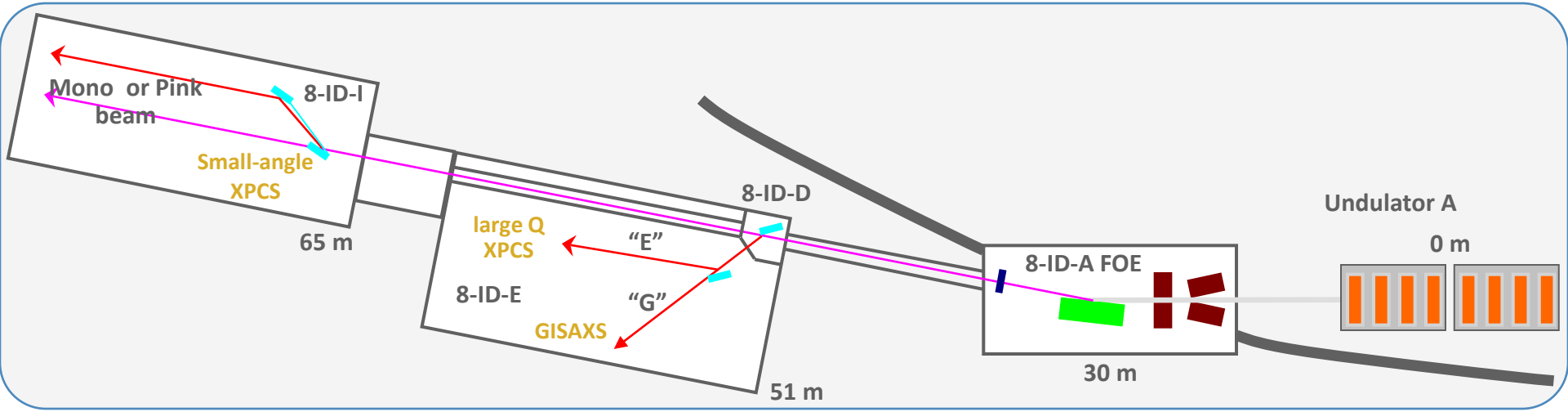


$$q_{x,y,z} = \frac{2\pi}{\lambda}\begin{bmatrix}\cos(\alpha_f)\cos(2\theta_f) - \cos(\alpha_i)\\ \cos(\alpha_f)\sin(2\theta_f)\\ \sin(\alpha_f) + \sin(\alpha_i)\end{bmatrix}$$

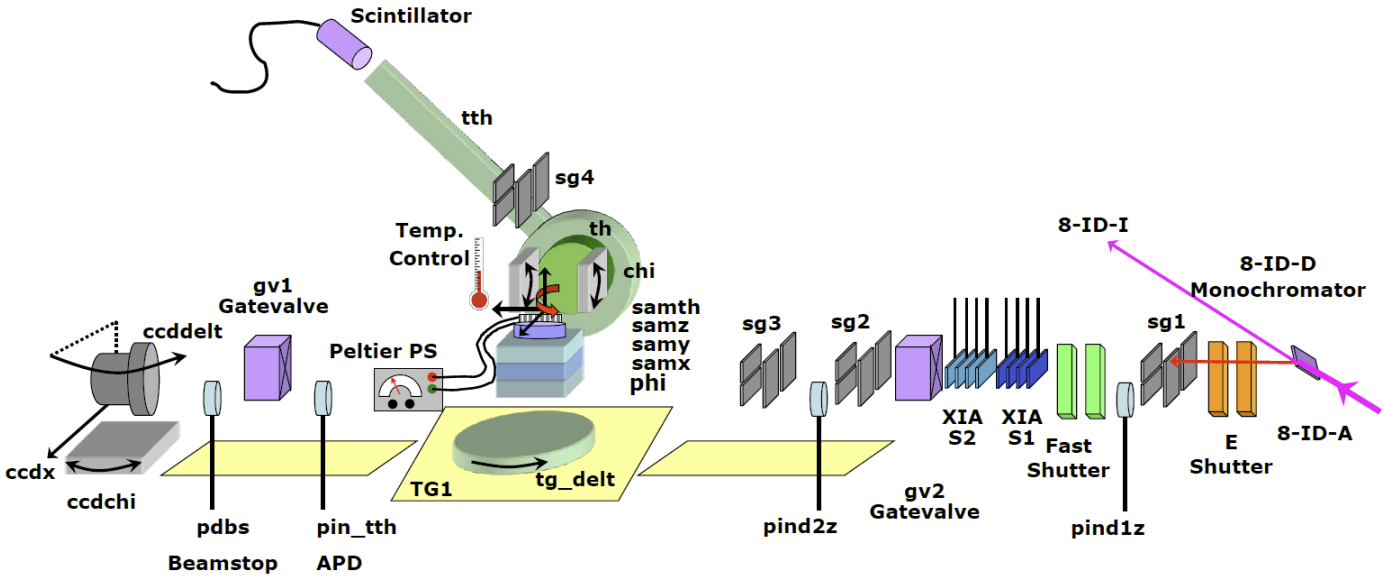
Images: Prof. Andreas Meyer, U. Hamburg, www.gisaxs.de

8-ID Introduction

- Undulator beamline supporting 2 scientific theme areas:
  - X-ray photon correlation spectroscopy (XPCS) in tunable end station
  - Grazing-incidence x-ray scattering (GIXS) on side station
  - Stations 8-ID-I and 8-ID-E operate independently/simultaneously at fixed energy 7.35 keV
- Coherence and stability essential for XPCS, determines optics
  - 300 micron diameter aperture
  - Mirror to reject higher energy components
  - Water-cooled mono
  - Transverse coherence lengths: ~200 microns vertical x 6 microns horizontal



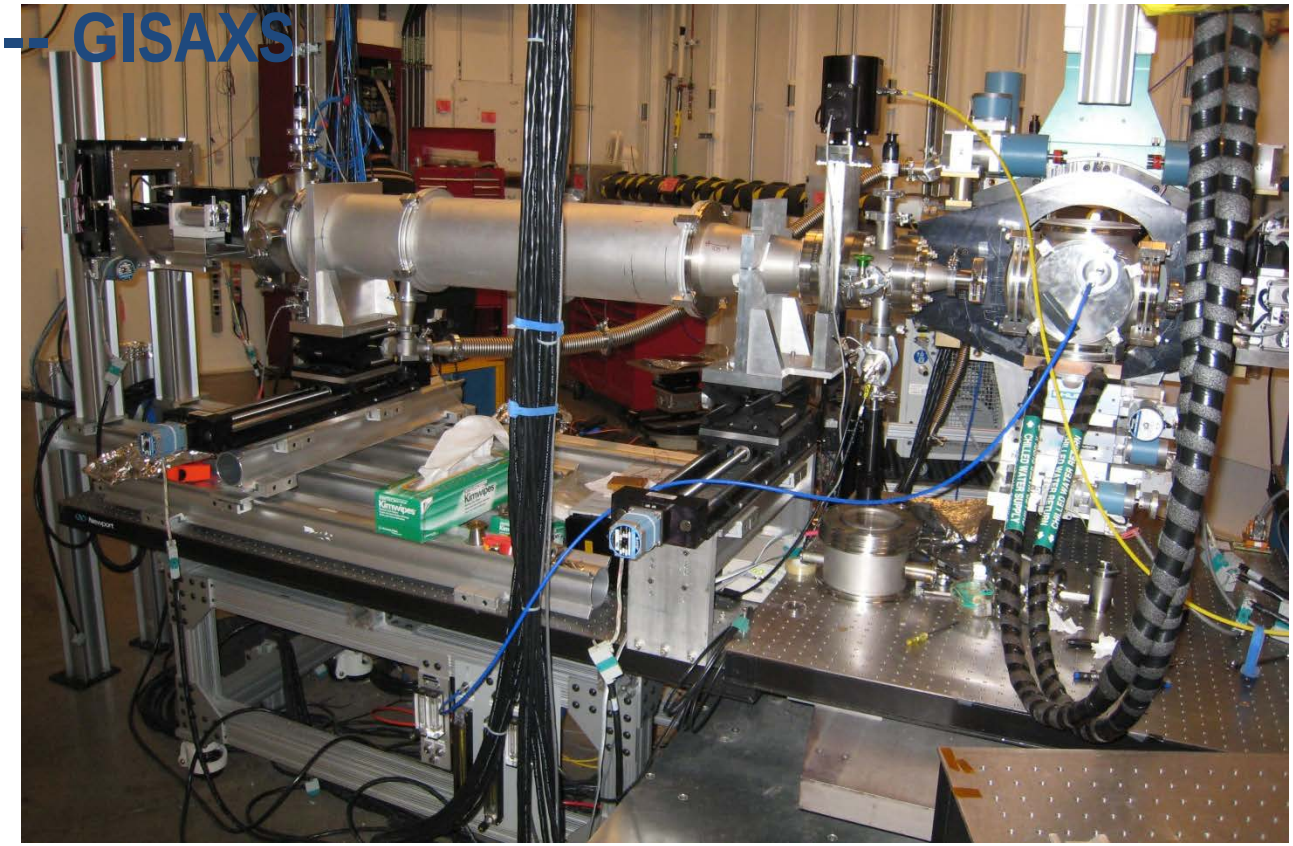
Beamline 8-ID-E: 2009 -- GISAXS



- Fixed energy side station: 7.35 keV
- Fixed sample-detector distance
  - Lengthscales > 10 nm
- Restricted sample access due to adjacent scientific program
- Slow, non-dedicated area detector

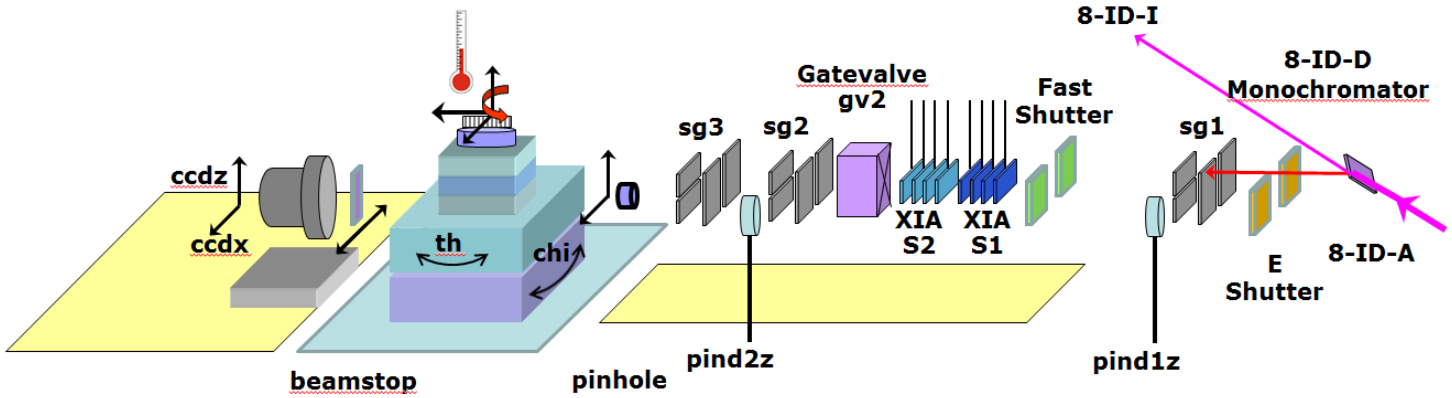
X. Li et al, *AIP Conf. Proceedings* **879** 1387-1390 (2007)

Beamline 8-ID-E: 2009 -- GISAXS



- Sample-detector distance ≥ 1.5 m
- Sample access restricted by diffractometer
- Mar165 from detector pool

Beamline 8-ID-E: 2010 -- GIXS

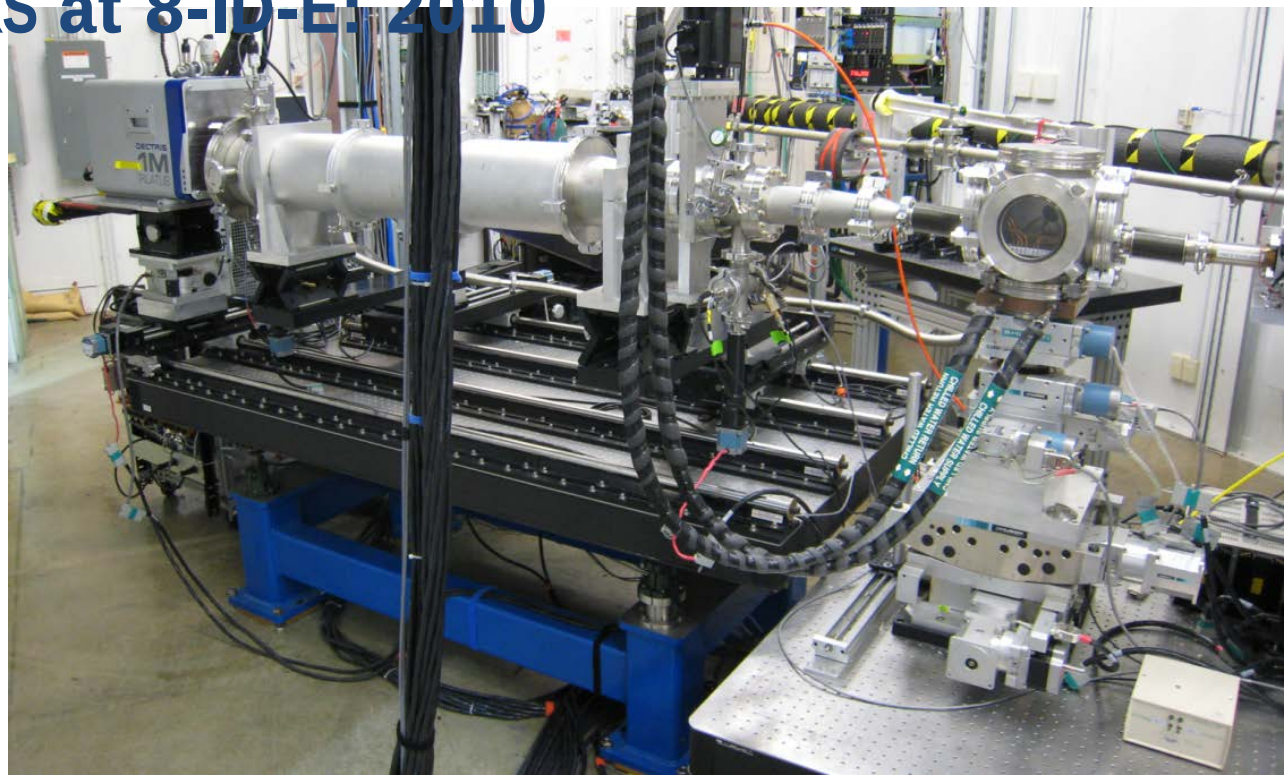


GIXS = GISAXS + GIWAXS

- Readily variable sample-detector distance
  - Lengthscales > 0.3 nm
- Accessible, flexible sample environment
- Fast, dedicated area detector with user-friendly data reduction/visualization

Z. Jiang, X. Li, J. Strzalka, M. Sprung, T. Sun, A. R. Sandy, S. Narayanan, D. R. Lee, J. Wang, *J. Synchr. Rad.* **19** 627 (2012)

Beamline 8-ID-E:
GISAXS at 8-ID-E: 2010



GISAXS

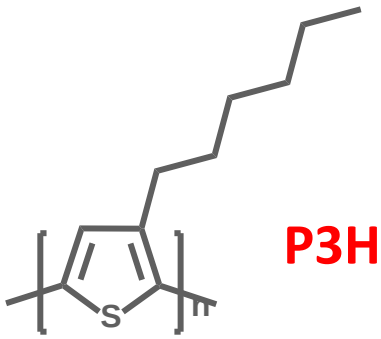
- Low-profile sample table
- Partial arc segment diffractometer
- Dedicated Pilatus 1MF (135 fps)
- Detector table with robust rails

Beamline 8-ID-E:
GISAXS at 8-ID-E: 2010

GIXS = GISAXS + GIWAXS

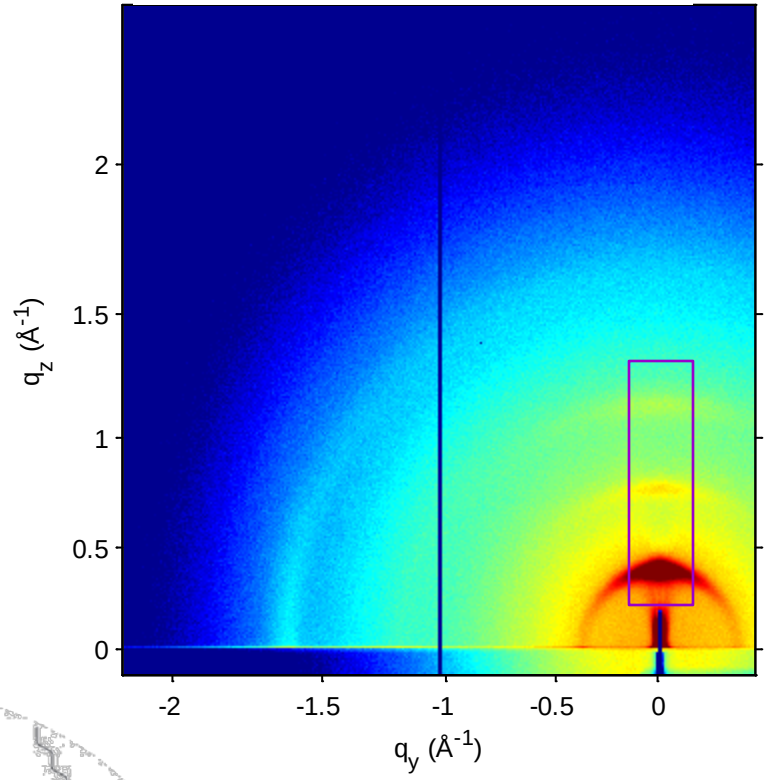
- Low-profile sample table
- Partial arc segment diffractometer
- Dedicated Pilatus 1MF (135 fps)
- Detector table with robust rails
- Sample-detector distance ≥ 0.2 m

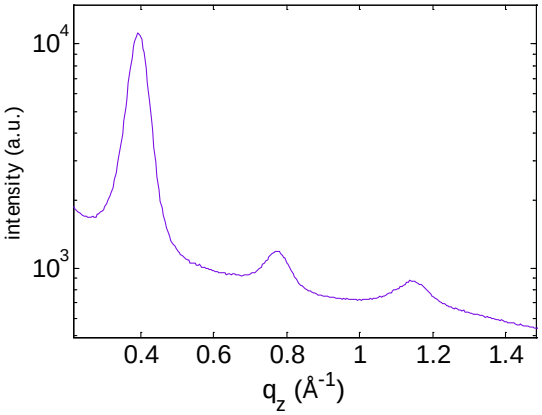
GIXS and Morphology - P3HT

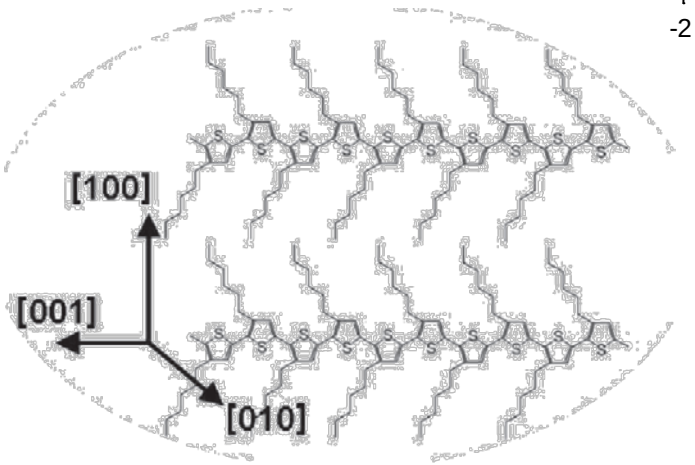


P3HT

donor (p)







P3HT forms lamellar structures:

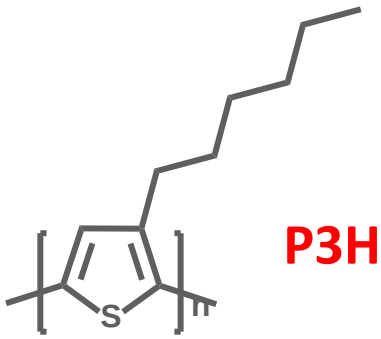
$q = n \times 2\pi/d_{lam}$

d_{lam} = 1.6 nm

width -> correlation length ~ nm

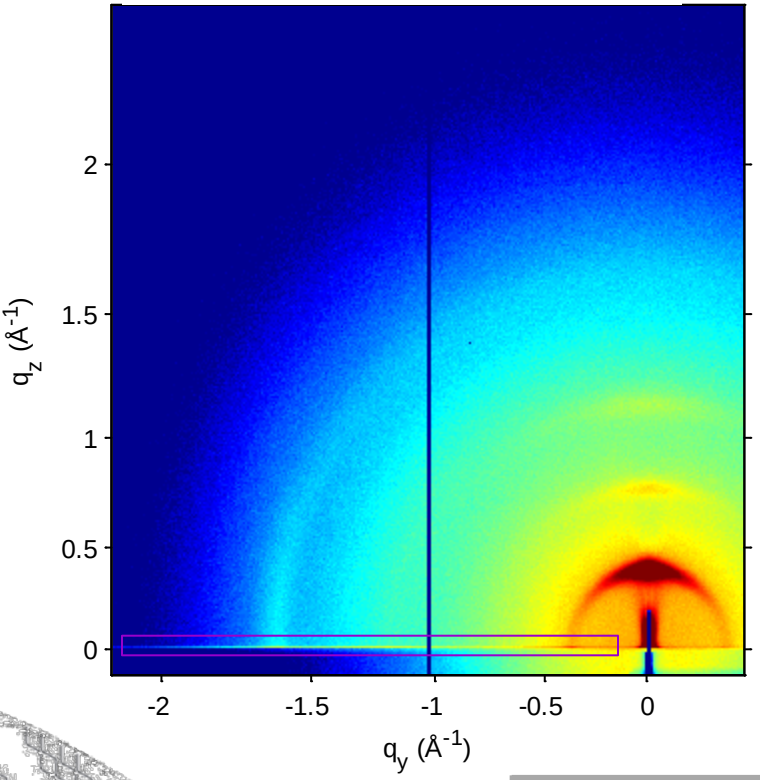
OPV Materials poorly ordered

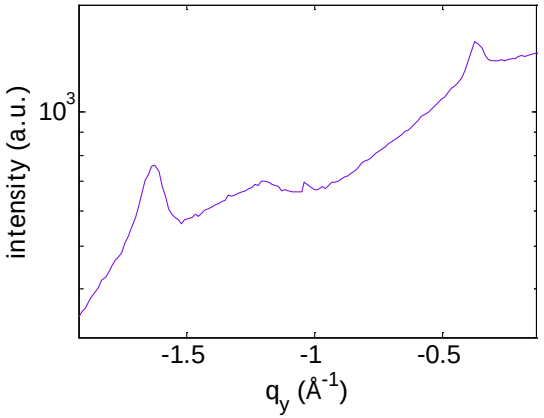
GIXS and Morphology - P3HT



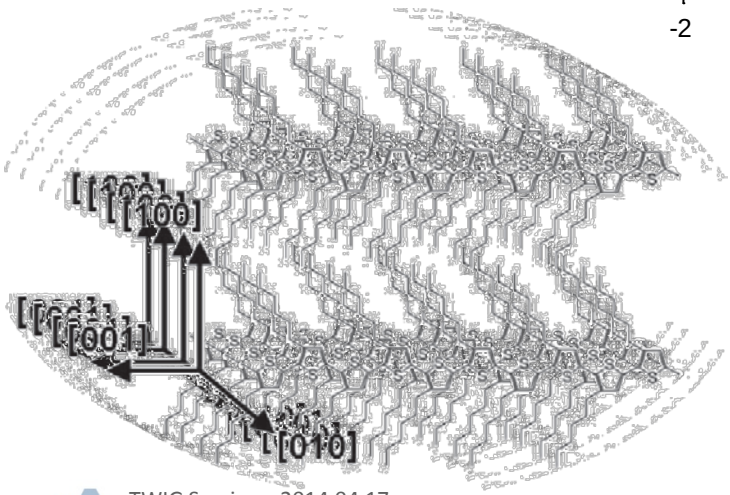
P3HT

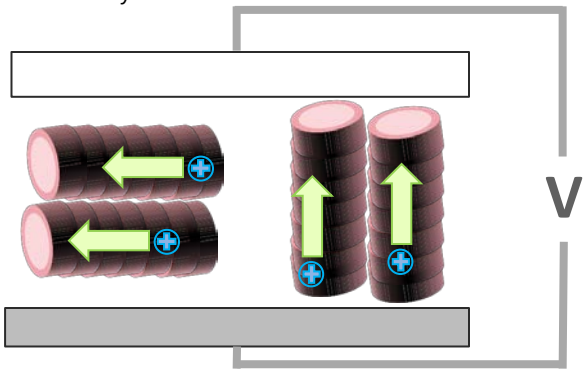
donor (p)





π-π stacking
q = 1.62 Å^{-1}
π-distance = 3.88 Å

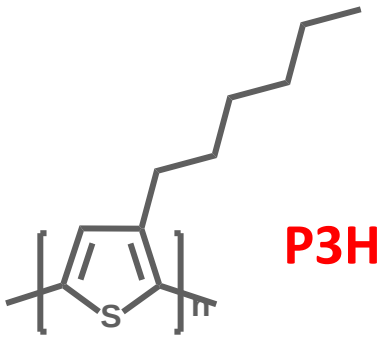




edge-on
unfavorable

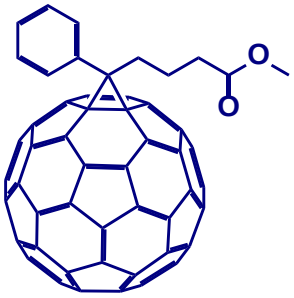
face-on
favorable!

GIXS and Morphology - P3HT:PCBM



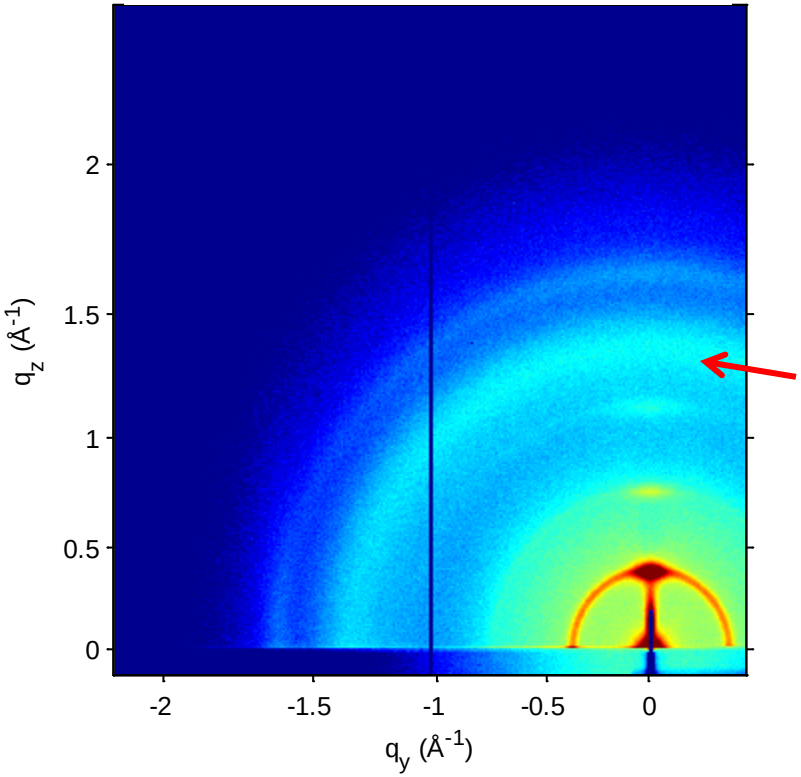
P3HT

donor (p)



$PC_{61}BM$

acceptor (n)

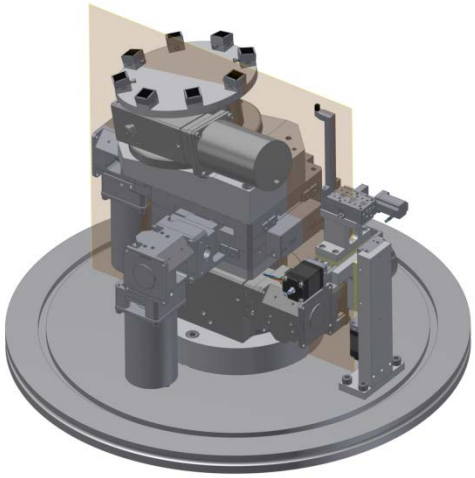


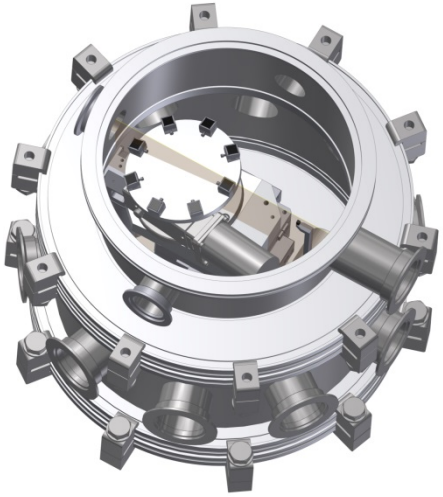
Adding fullerene adds isotropic ring

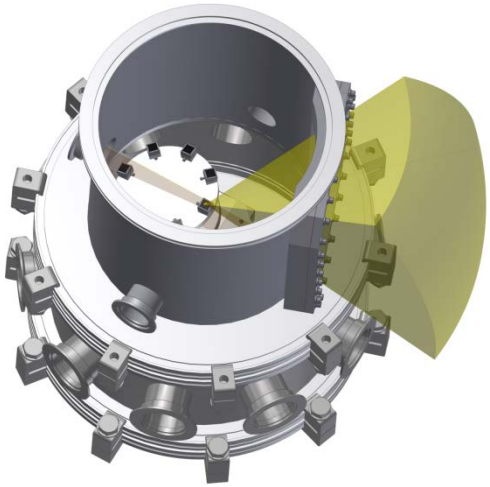
Blend results in superposition of features

Future Directions

Multiple sample changer vacuum environment for GISAXS/GIWAXS





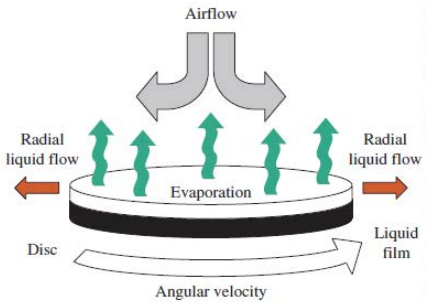


Design by Mike Fisher, Jusuf Haljiti

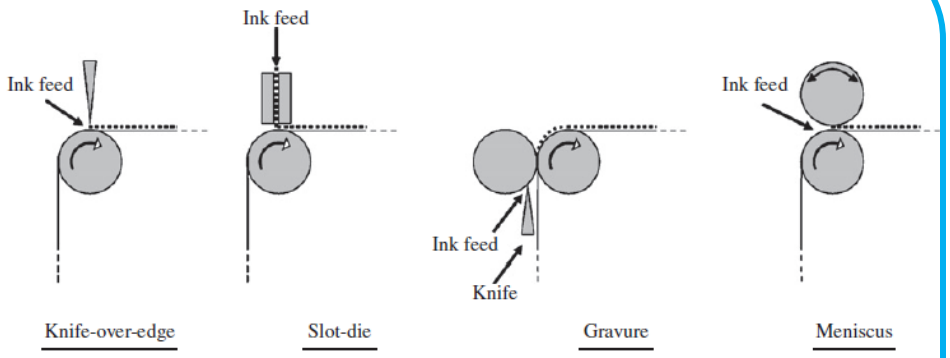
PUP with Paul Nealey (IME/U Chicago) and Wei Chen (MSD)

Future Directions

Time-resolved in situ studies to probe the Structure-Processing-Function Relationship



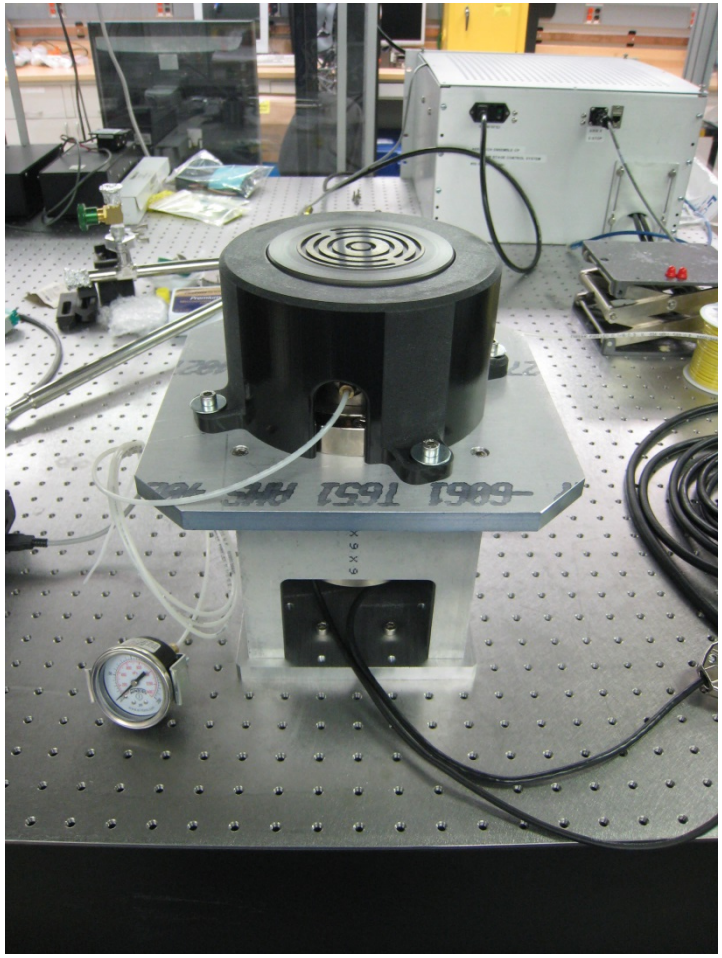
Spin coating: lab scale devices



scalable processing: manufacturing modules

F.C. Krebs / Solar Energy Materials & Solar Cells 93 (2009) 394–412

In Situ Spin Coater



New sample environment for spin coating:

Air bearing spindle motor and vacuum chuck by Aerotech

Specs:

- 500-4000 rpm
- stability < 1 millidegree
- acceleration: 2-3 sec to full speed

Commissioning in 2014-2

Be CRL for enhanced time resolution

With help from Oliver Schmidt, Ron Sluiter

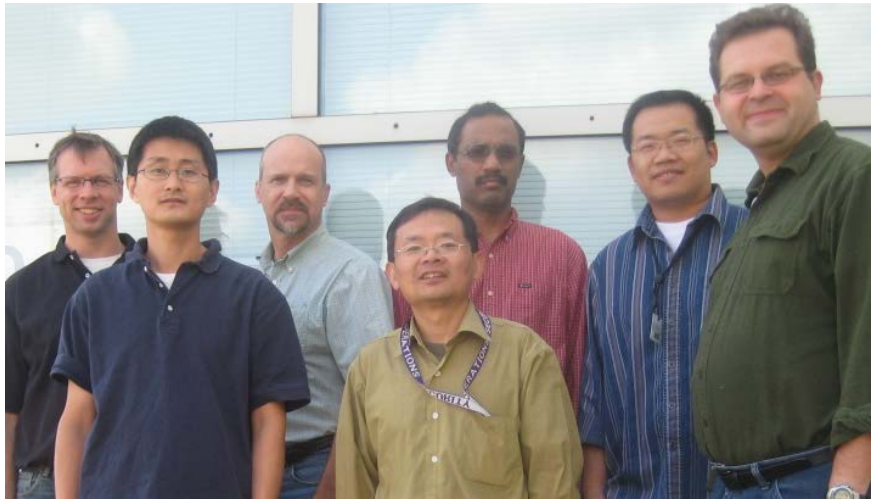
Conclusions

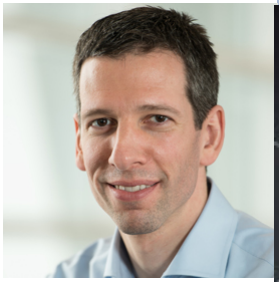
- Organic Photovoltaics poised to contribute to renewable energy future on terawatt scale
  - Further advances needed
- Grazing Incidence X-Ray Scattering is a key tool for probing OPV morphology and the interplay between materials, processing and performance
- 8-ID-E hosts a productive program in GIXS characterization of OPV materials
- Advances in materials design, informed by morphological studies, are steadily improving OPV performance
- Time-resolved studies of nanostructure kinetics are next frontier for understanding OPV processing

Thank you!

Acknowledgments



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Jodi Szarko
Mimi Lou
Brian Rolczynski
Tobin Marks

U. Chicago/ANSER Center
Yuping Lu

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Wei Chen

Argonne CNM
Seth Darling
Maxim Nikiforov

Rice University
Rafael Verduzco
Yen-Hao Lin
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