Correlating Composition, Morphology and Performance Metrologies Performed on Organic Photovoltaics: A Combinatorial Challenge

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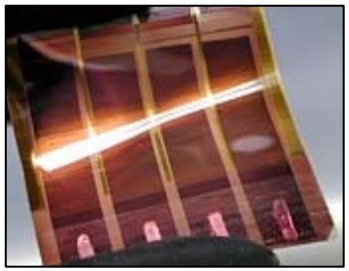
National Institute of Standards and Technology
Technology Administration
U.S. Department of Commerce

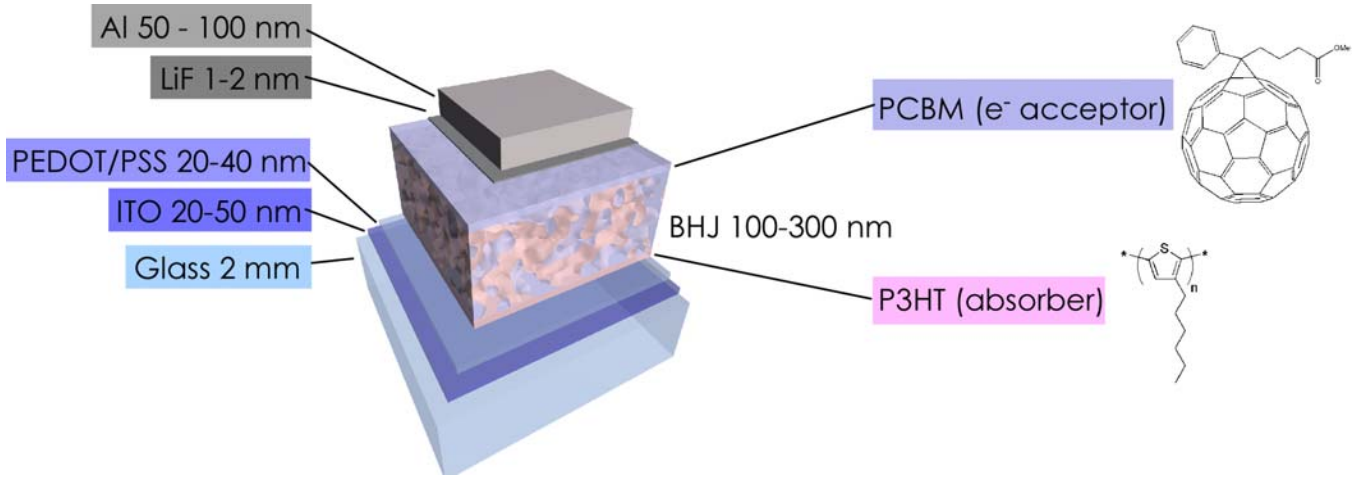
NIST Combinatorial Methods Center
Meeting No. 14: A DOE-EERE/ NIST Joint Workshop on Combinatorial Materials Science for Applications in Energy

Next-Generation Photovoltaics: The Big Deal About a Small Thing

Next-gen photovoltaics: *printable & flexible thin-film, organic, and hybrid solar cells, which rely on complex nanostructured morphologies of multiple components.*



The Promise: low-cost, large-area fabrication (printing, doctor-blading, painting), light weight, flexible/ foldable/ rollable substrates.

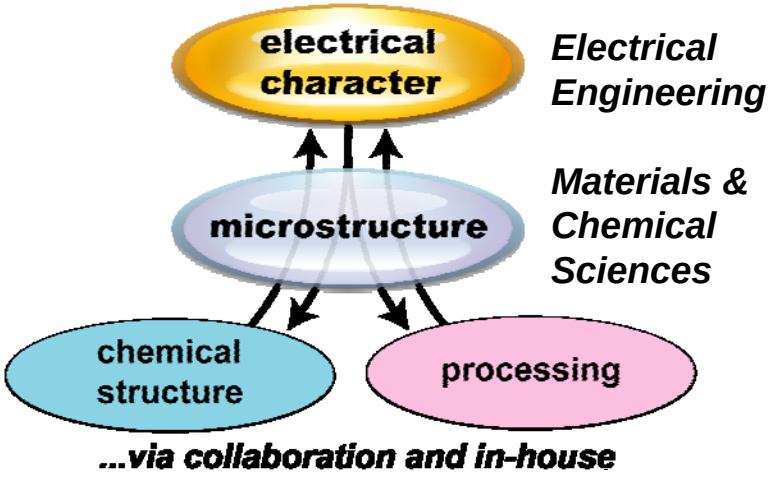


The Reality: low efficiencies related to uncontrolled and poorly understood interface composition and active layer morphology, poor solar spectrum overlap, band-gap mismatches and short useful device lifetimes.

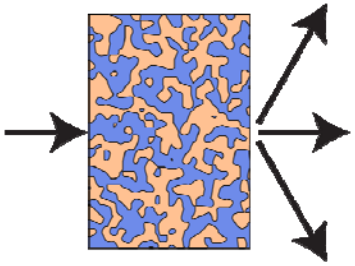
NIST Organic Photovoltaics Program

Metrology to Enable the Realization of Organic Electronics (Started in '05)

- to "*provide the integrated measurement and standards tools needed to accelerate progress in organic electronics*"
- Satisfies a ubiquitous need expressed by organic electronics technology developers.

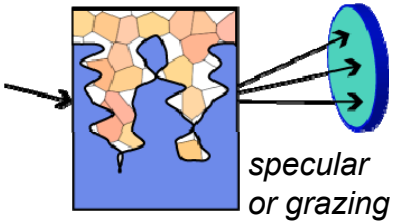


Scattering

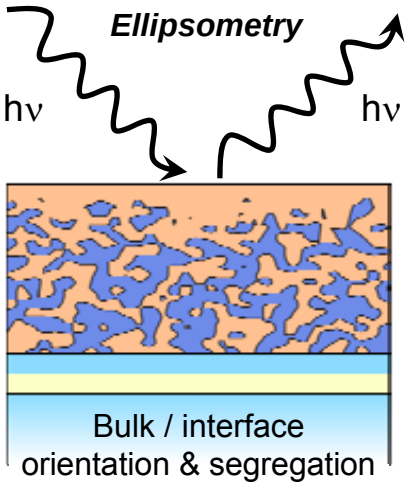


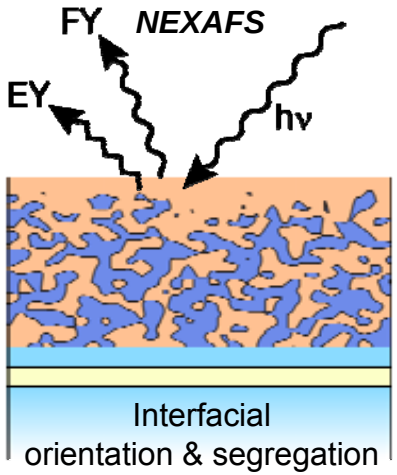
domain size, shape, distribution

Diffraction/ Reflectivity



Crystal size, orientation, & interface segregation





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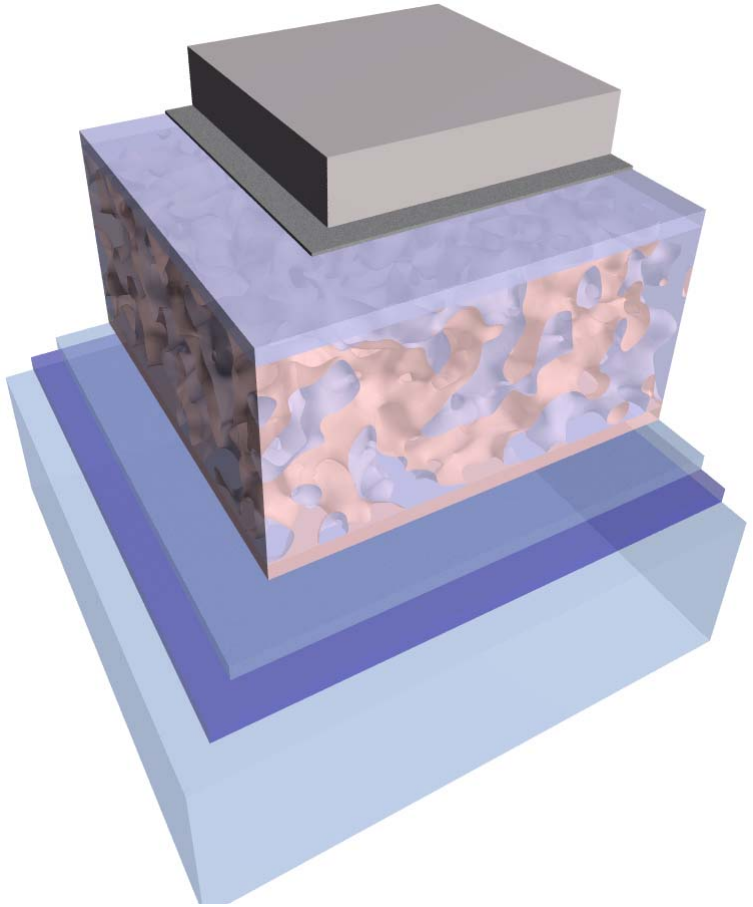
Developing bulk heterojunction structural model



Molecular orientation

- Light absorbance (by P3HT)
- Transport anisotropy
- Interpretation of model-dependent methods

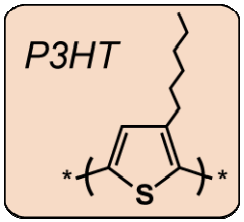
Vertical composition gradient

- Relates to series resistance, could affect device characteristics.
- Necessary to know this to interpret measurements of domain size and shape.

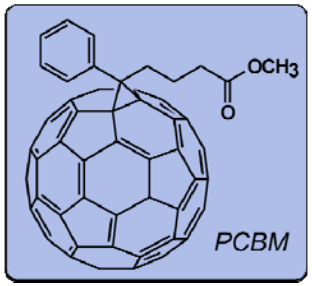
Surface segregation control by SAMs

Substrates of different surface energy

- Vertical composition profile is likely to be influenced by substrate chemistry
- Solution-deposited SAMs provide model substrates
- In "real" OPV devices, the surface energy of the HIL influences the composition profile

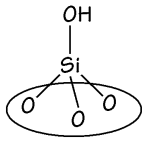


γ =27 mN/m^2



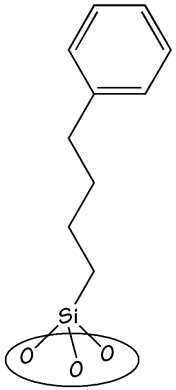
γ =38 mN/m^2

Model surface for PEDOT:PSS



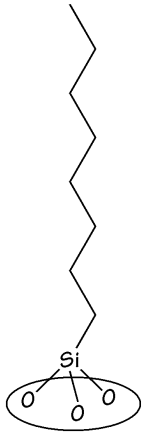
silicon oxide

γ =77 mN/m^2



PBTS

γ =26 mN/m^2

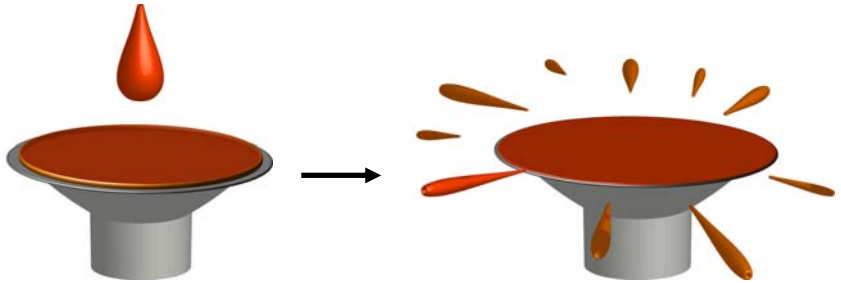


OTS

γ =20 mN/m^2

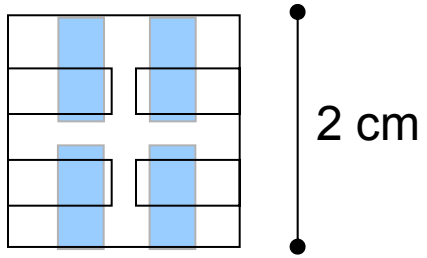
Device Fabrication

Bulk heterojunction (BHJ) Recipe:
- 30 mg/mL (total solids) in *o*-dichlorobenzene, 60 °C
- 1:1 weight ratio of P3HT:PCBM
- 500 rpm, 60 seconds, A = 001
- "As Cast" = solvent annealed†
- "Annealed" = 140 °C, 40 min



Substrate Preparation:
- Sonication 10 min in Acetone and IPA
- UV Ozone for 10 minutes
- Water rinse and N_2 Dry

SAMs
- 2 mM OTS in Hexadecane overnight
- Sonication in $CHCl_3$, IPA, and H_2O followed by 10 min at 150 °C
- 10 mM PBTS in toluene overnight ‡
- Sonication in toluene, acetone, and IPA followed by 10 min at 150 °C

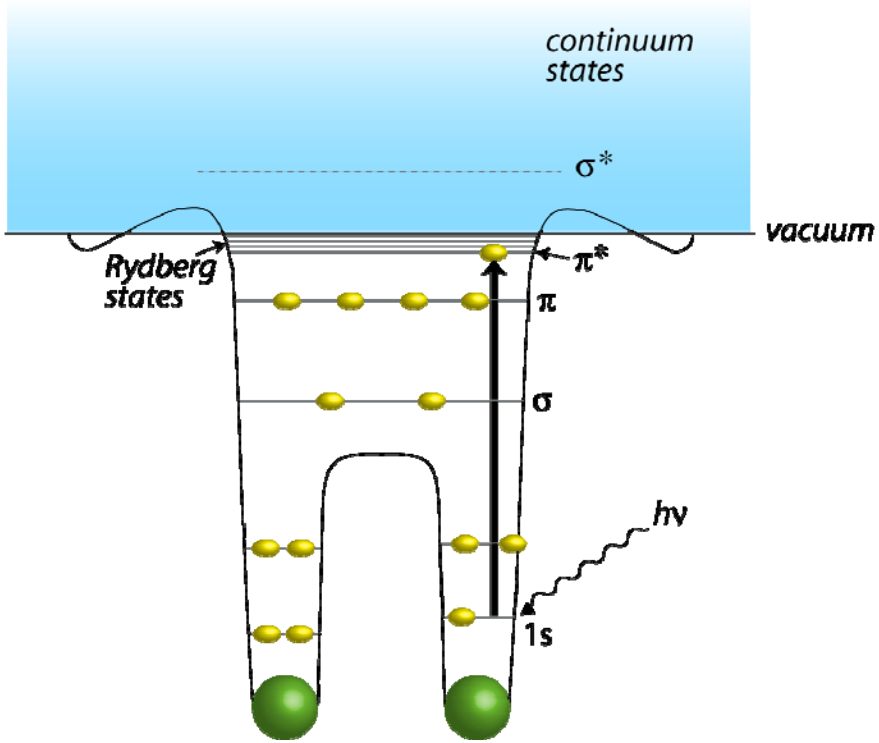


† Li, G. *et al. Adv. Funct. Mater.* **2007,** *17 (10),* 1636-1644
‡ Kumaki, D. *et. Al. Appl. Phys. Lett.* **2007**, *90*, 133511

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

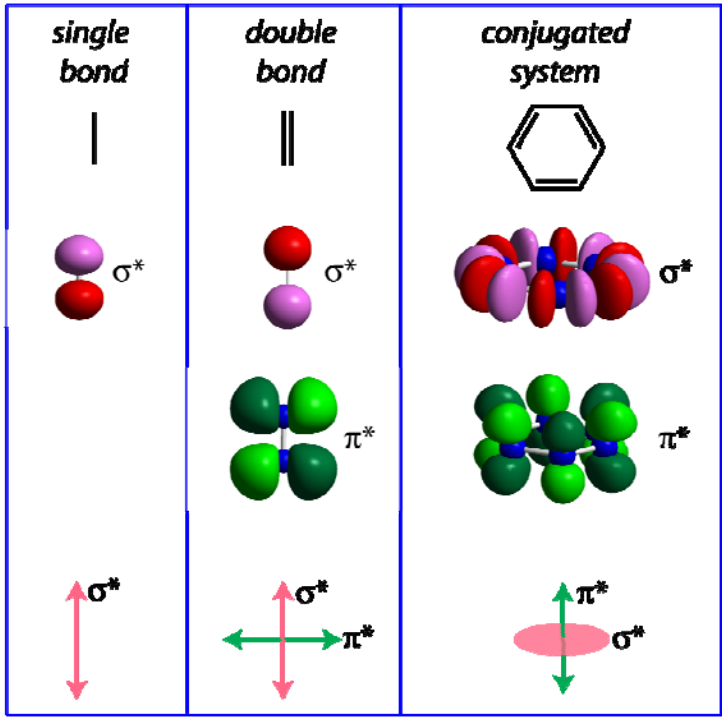
Resonant bound-state excitations

- Atomic electrons excited to unfilled molecular orbitals
- Element specific, and bond-sensitive
- Absorbance measured by Auger or fluorescence.



Resonance orientations

- Defined by end state orbital
- Can be decomposed into vector and plane representations
- The π* resonance of organic semiconductors is especially useful because it is a single vector for any conjugated plane.



The Nuts and Bolts of NEXAFS Measurements: NIST/Dow Beamline U7A at the NSLS

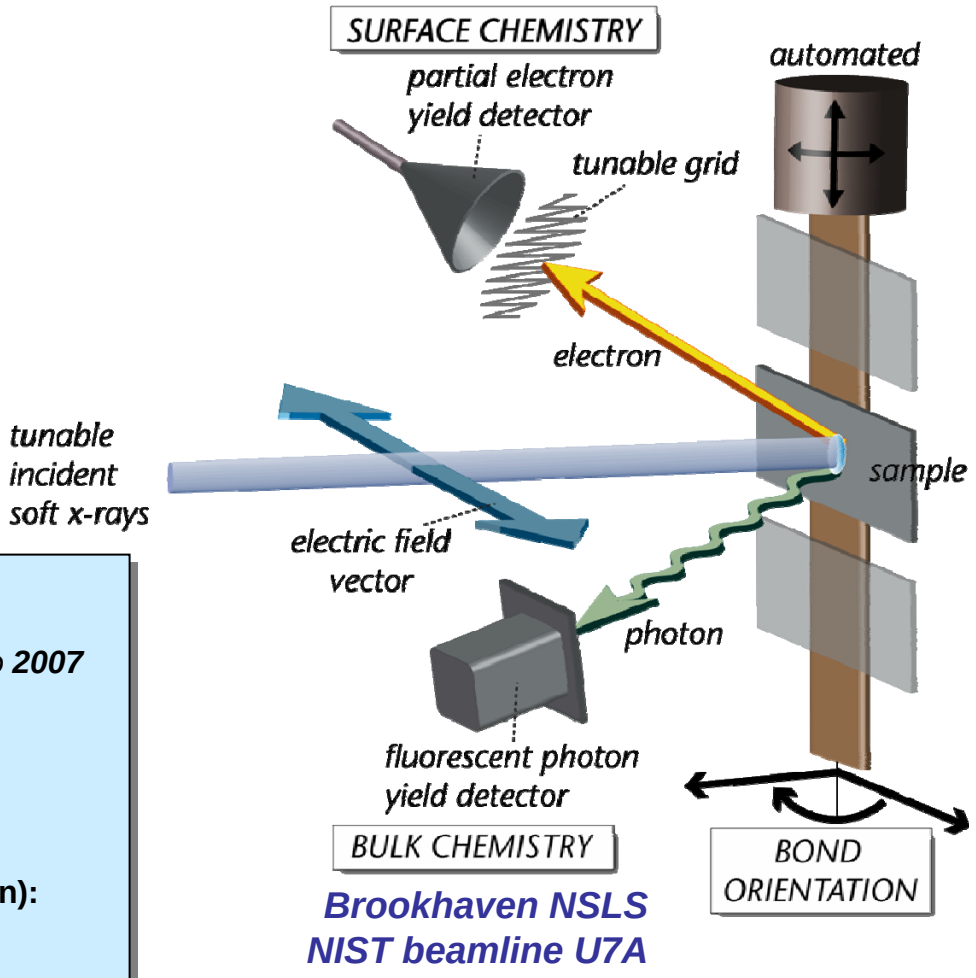
Polymers Division

Strengths for Organic Electronics:

- Detects C, N, O, & F bonds.
- High sensitivity to π bonding.
- Directly measures orientation.
- Depth sensitive.

Does NOT measure :

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



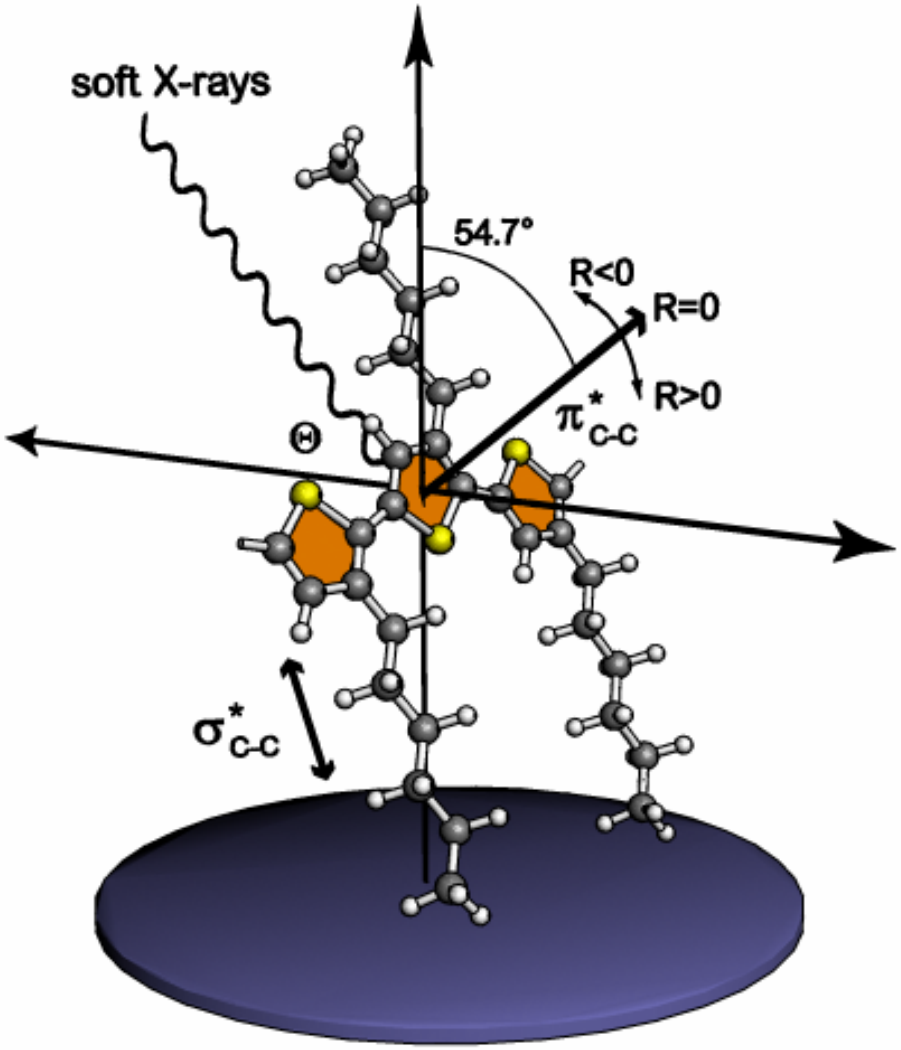
Brookhaven NSLS NIST beamline U7A

How to apply NEXAFS to P3HT & pentacene:
- *Proc. SPIE OFET IV* ***2005*** *p54*
- *In "Organic Field Effect Transistors" eds. Locklin & Bao* ***2007***

P3HT:
- *Chem. Mater.* ***2005*** *p5610 (spin speed)*
- *Langmuir* ***2007*** *p834 (liquid side chains)*

Oligothiophenes (w/ J.M.J. Frechet & V. Subramanian):
- *Adv. Mater.* ***2005*** *p2340*
- *Chem. Mater.* ***2006*** *p6033*
- *J. Phys. Chem. B.* **2006** *p10654*

NEXAFS Example: P3HT



Resonance Intensity:

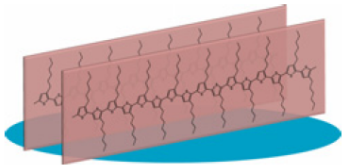
$$I(\Theta) = \int_{peak} PEY(\Theta)$$

Dichroic Ratio:

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

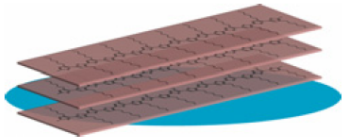
for conjugated plane

Edge-On



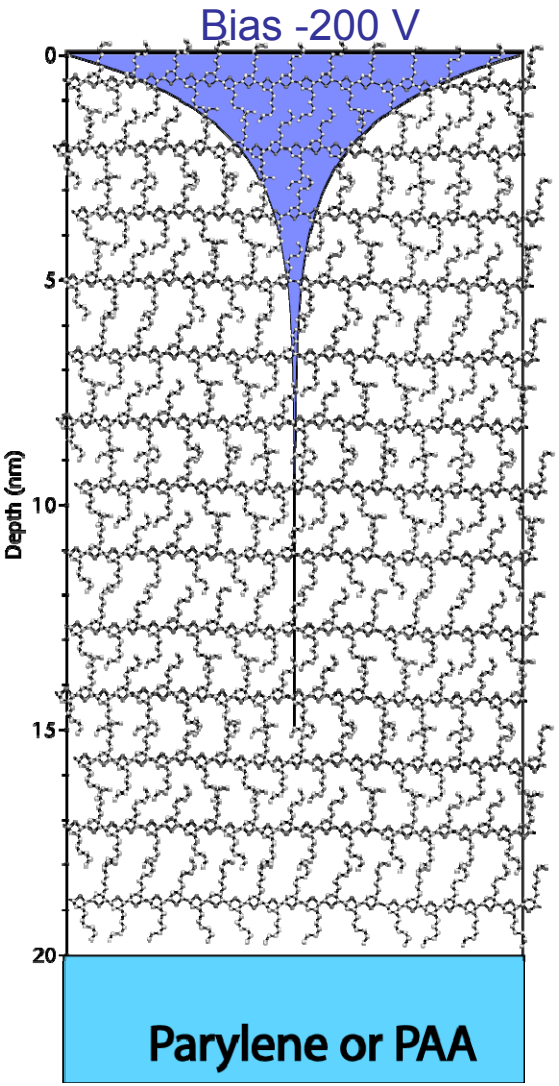
R = 0.70

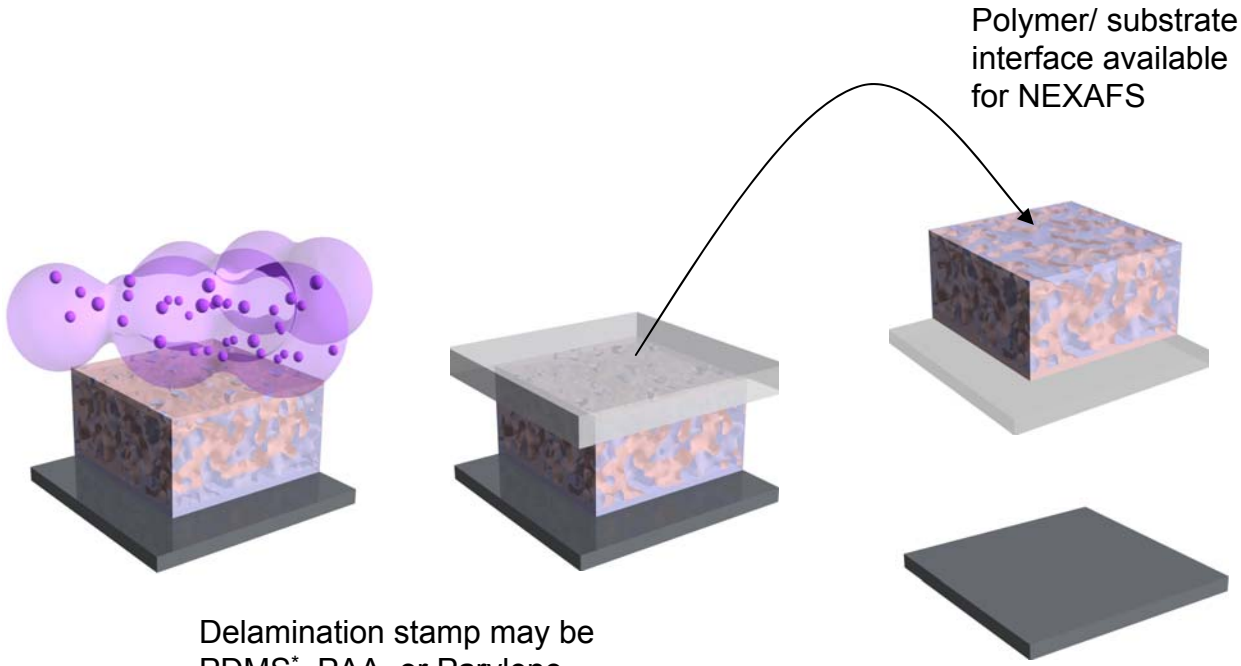
Plane-On



R = -1.00

NEXAFS Probes Surfaces: Delamination Exposes the Polymer/ Substrate Interface

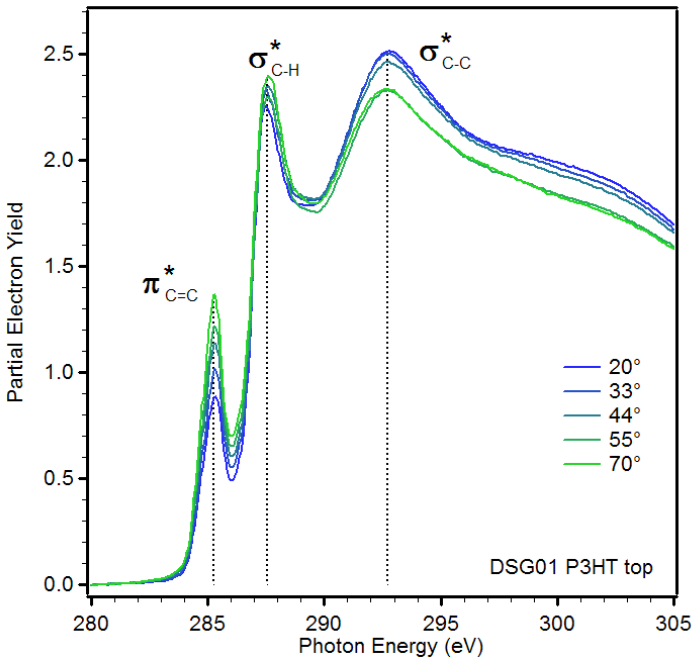


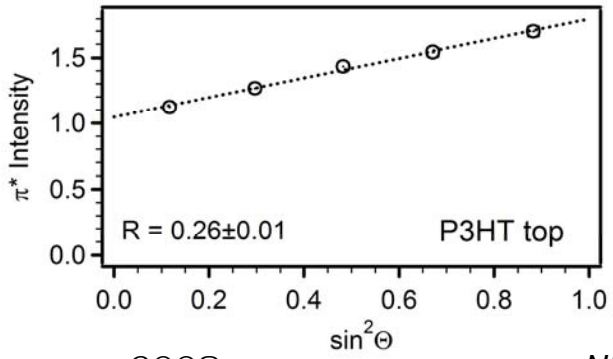


* Chabinyc *et al. JACS* **2004,** *126 (43),* 13928-13929

P3HT and PCBM Polymer/Air Interface Spectra

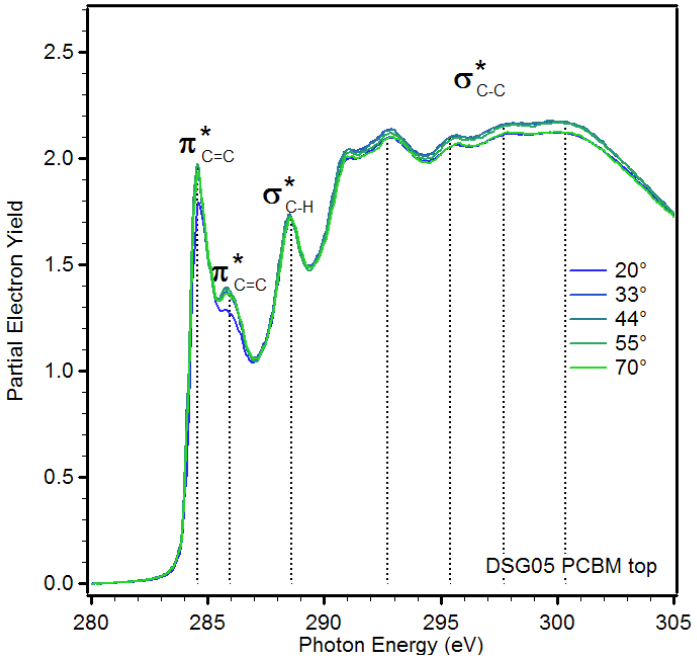
P3HT

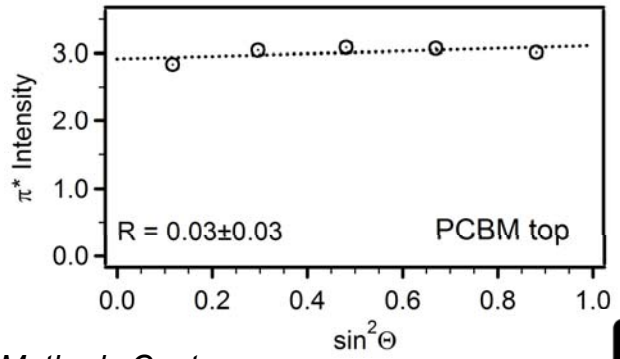




edge-on

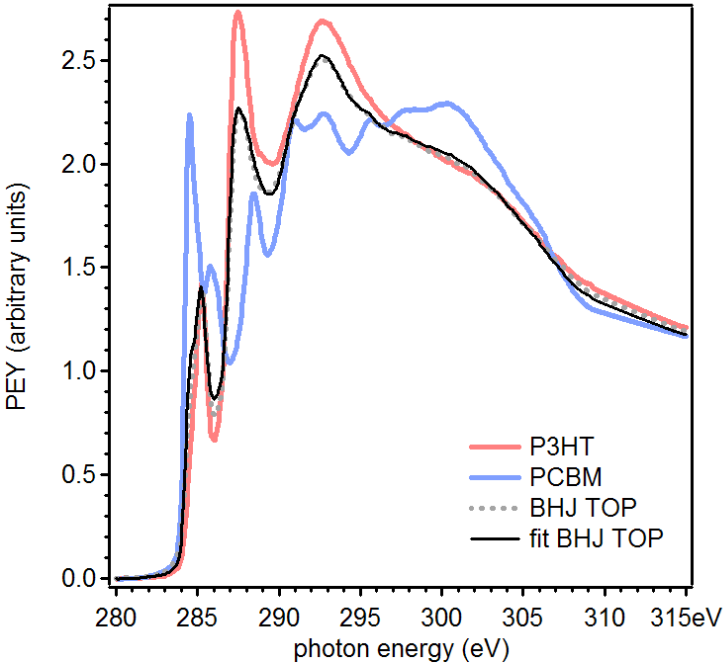
PCBM

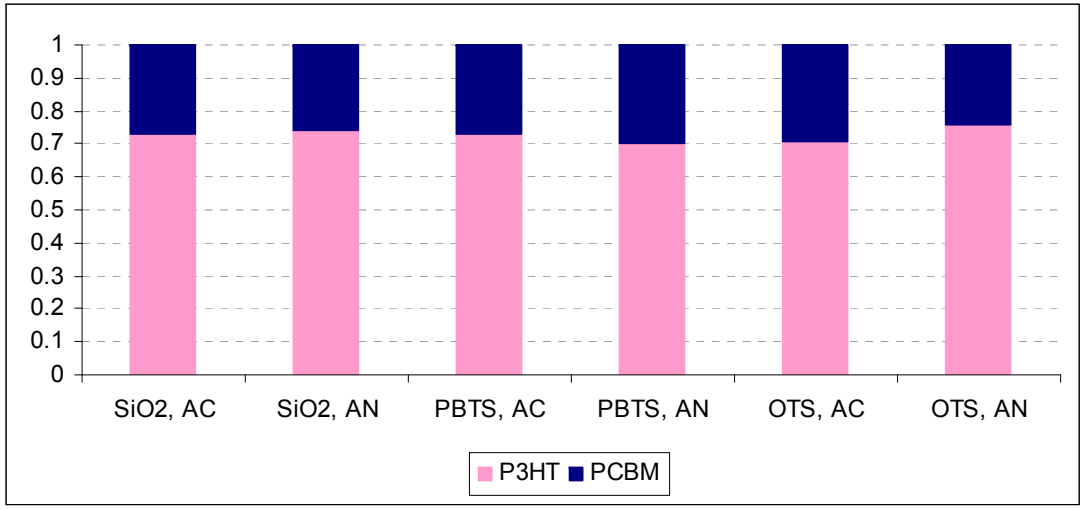




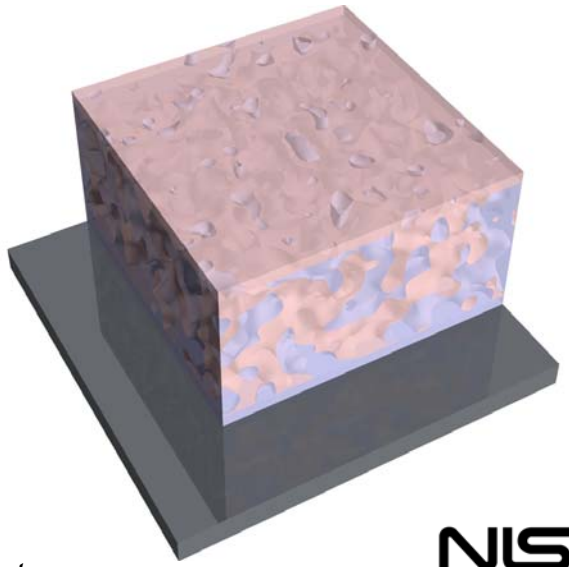
unoriented

BHJ Polymer/ Air Surface Spectra: P3HT Enrichment Under All Circumstances

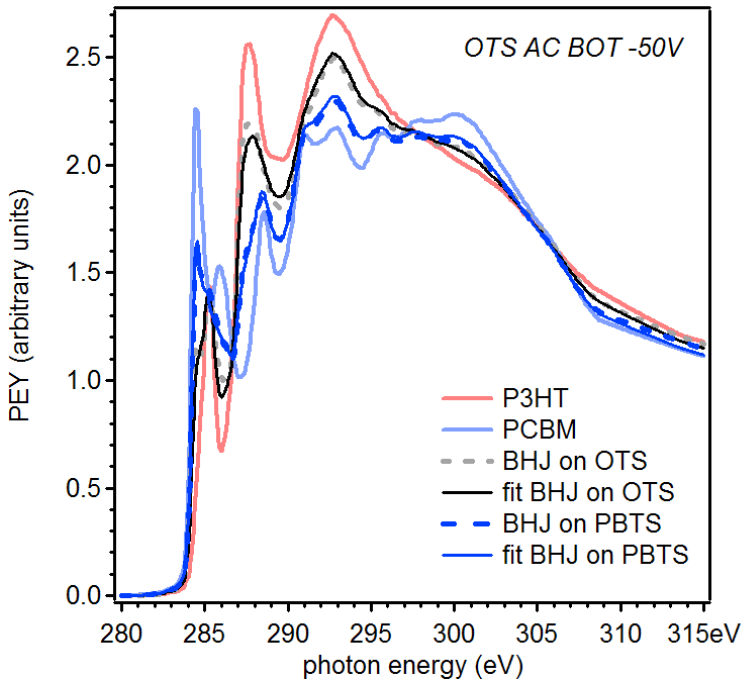


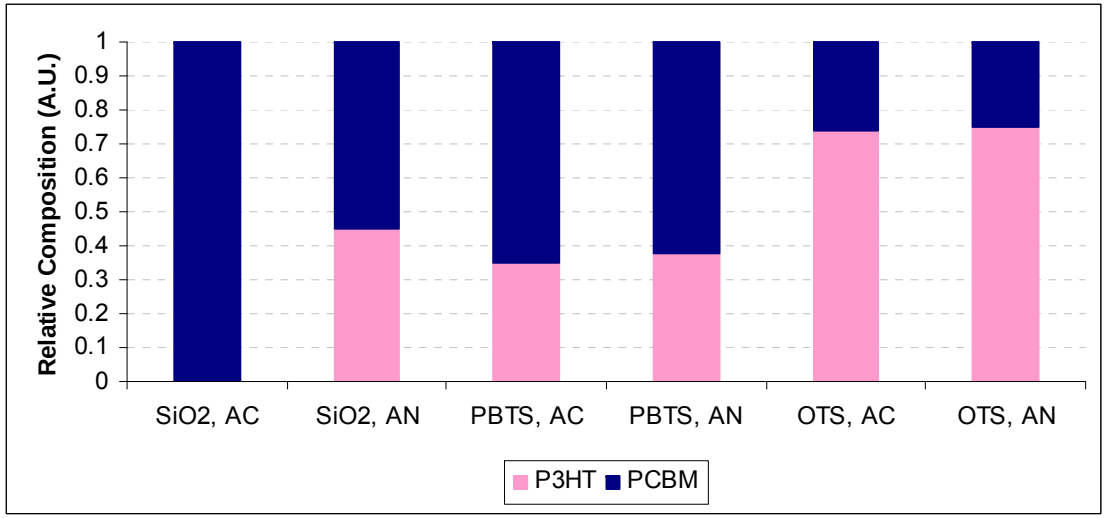


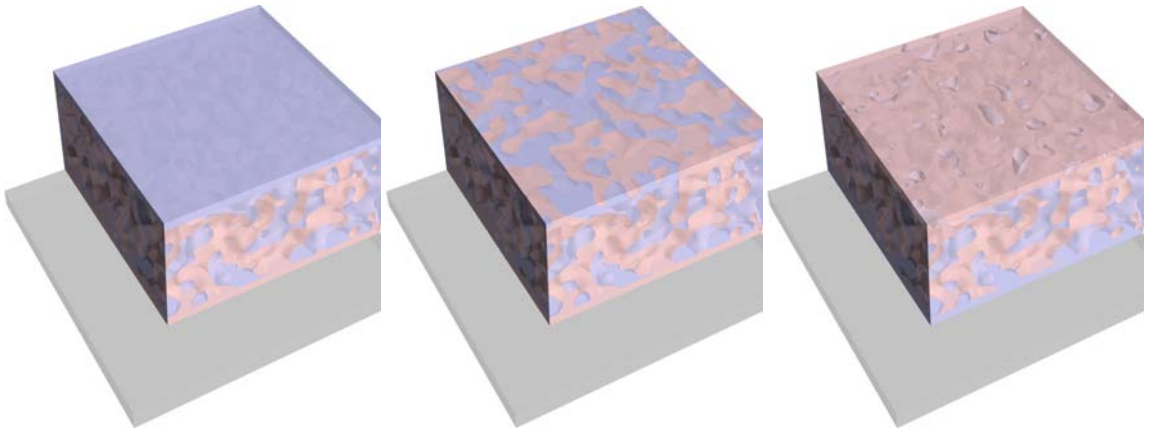
Subs.	Sample	P3HT	PCBM	R
SiO_2	BHJ AC	0.73	0.27	0.12 ± 0.03
SiO_2	BHJ AN	0.74	0.26	0.09 ± 0.01
PBTS	BHJ AC	0.73	0.27	0.26 ± 0.01
PBTS	BHJ AN	0.70	0.30	0.09 ± 0.02
OTS	BHJ AC	0.71	0.29	0.16 ± 0.02
OTS	BHJ AN	0.76	0.24	0.13 ± 0.05



BHJ Polymer/ Substrate Interface Spectra: Composition Changes with Surface Energy (γ)



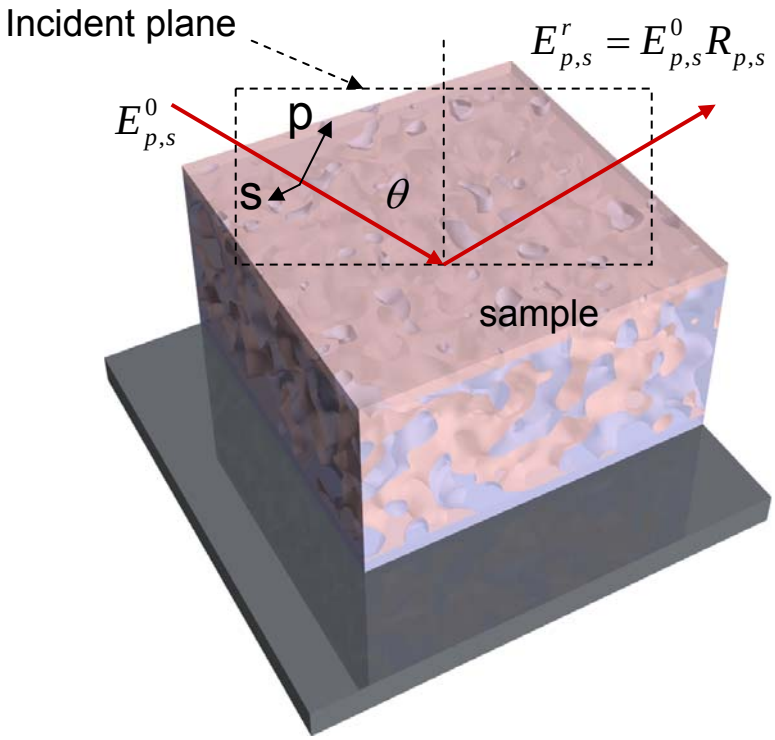




Subs.	Sample	P3HT	PCBM	R
SiO_2	BHJ AC	0.00	1.00	0.02 0.01
SiO_2	BHJ AN	0.45	0.55	0.05 0.01
PBTS	BHJ AC	0.35	0.65	0.10 ± 0.03
PBTS	BHJ AN	0.38	0.62	0.01 ± 0.00
OTS	BHJ AC	0.74	0.26	0.25 ± 0.03
OTS	BHJ AN	0.75	0.25	0.24 ± 0.00

Variable Angle Spectroscopic Ellipsometry

In a VASE experiment a UV-Vis (or IR) spectrum and an ellipsometric measurement are simultaneously collected allowing for the analysis of samples with complex or unknown dielectric constants to be analyzed.



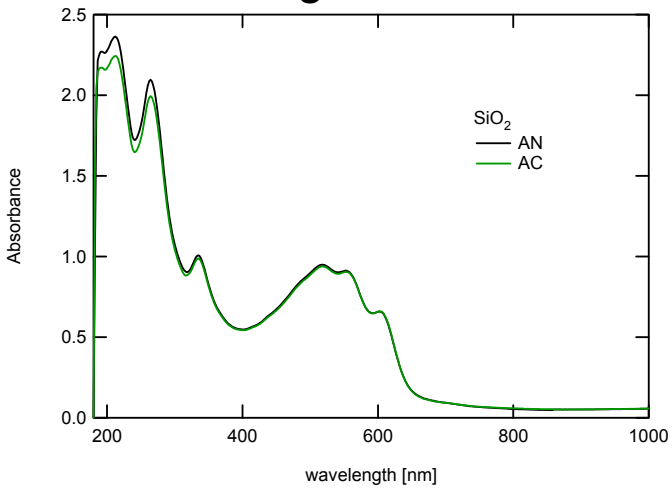
$$\rho \equiv \frac{R_p}{R_s} \equiv \tan\Psi e^{i\Delta}$$

- VASE is model dependent
- complimentary optical techniques inform the model and provide checks on the "physicality" of the model
- models can include materials properties like optical anisotropy and conductivity

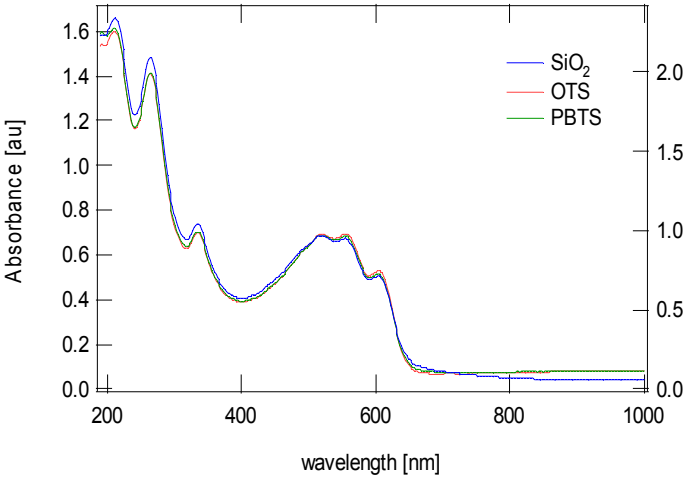
Example of VASE applied to BHJs:
Campo-Quiles, M. *et al. Nature Materials* **2008,** *7,* 158-164

Before Constructing a VASE Model it Helps to Know Some Things

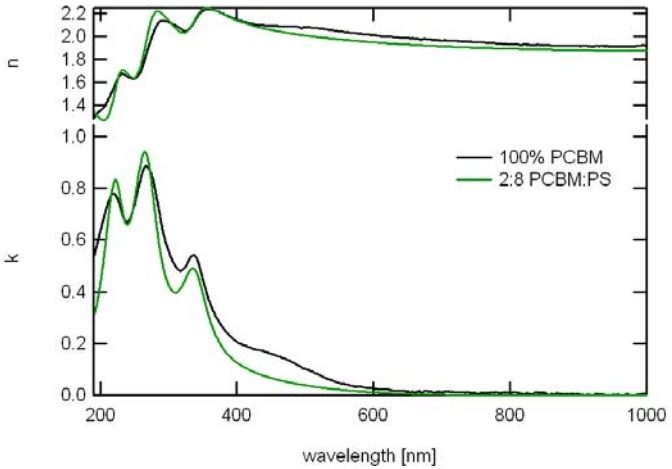
Thermal Budget: BHJ



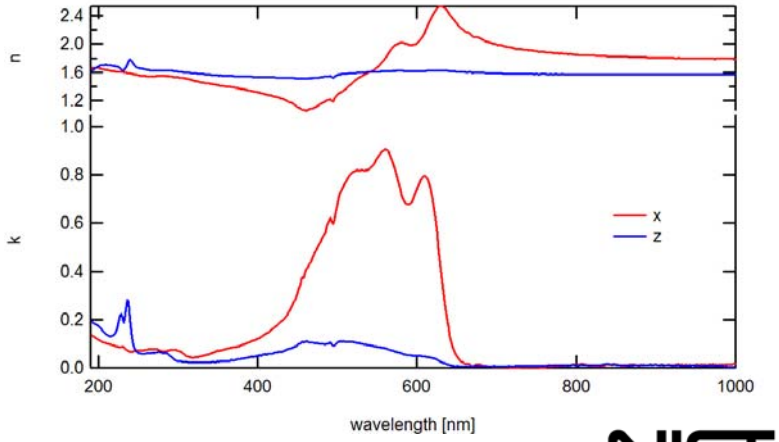
Surface Energy: BHJ



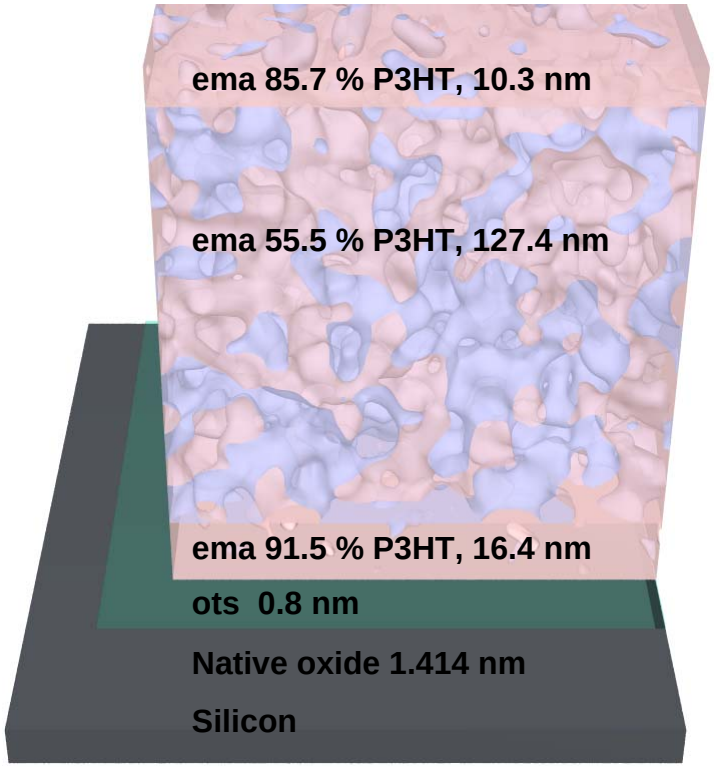
Aggregation: PCBM



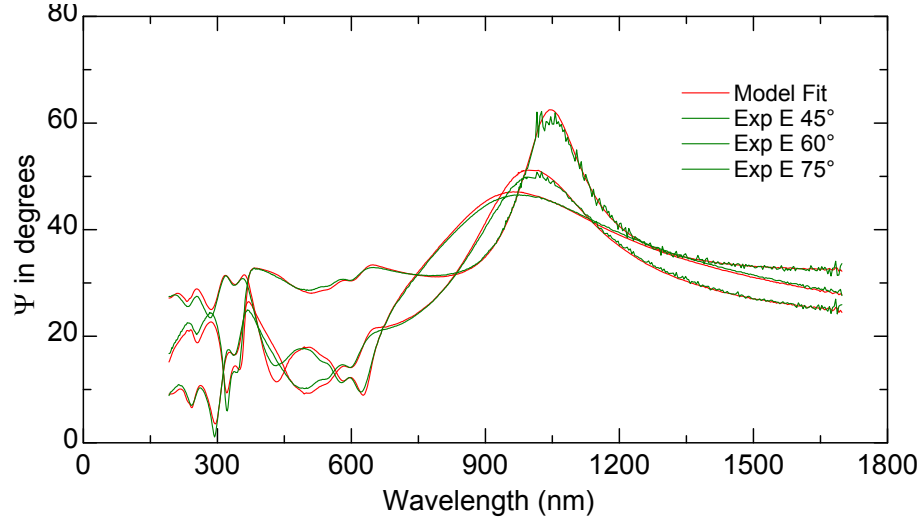
Orientation: P3HT

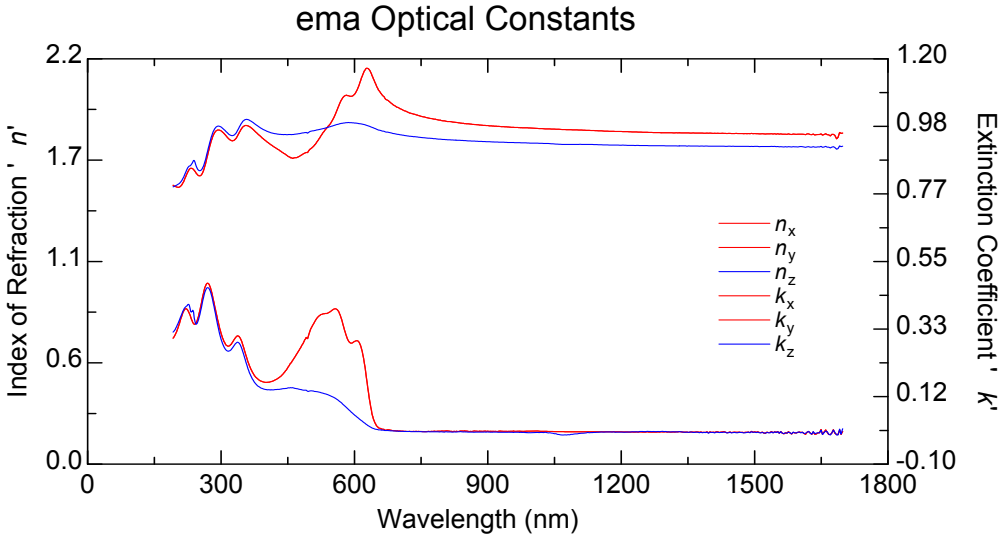


Raw VASE Data, Fitted Curves and Model



ema = effective medium approximation
describes bulk properties based upon the "mixing" of its constituents, in this case PCBM and P3HT



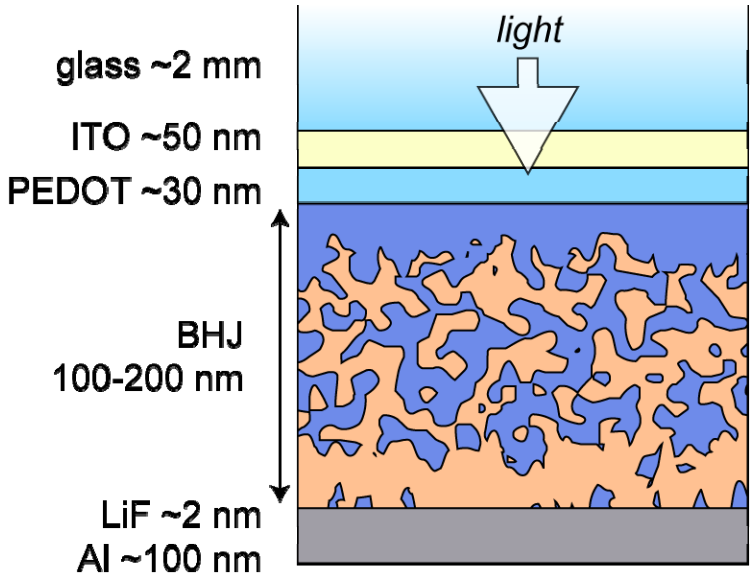


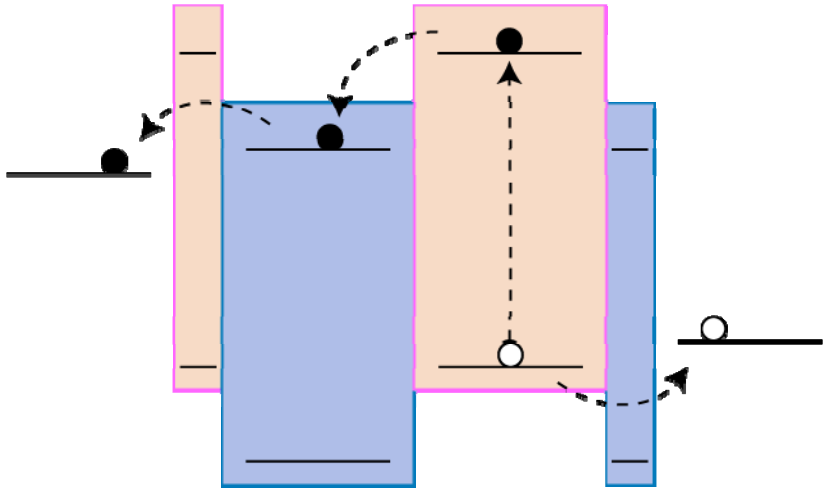
Optimized VASE Model: Good Agreement with NEXAFS

		Top			Middle			Bottom		
	γ (mN/m^2)	% P3HT$_N$	% P3HT$_{SE}$	t_{SE} (nm)	% P3HT$_{SE}$	$\varepsilon_x : \varepsilon_z$	t_{SE} (nm)	% P3HT$_N$	% P3HT$_{SE}$	t_{SE} (nm)
SiO_2	77.36*	74	100	10	59	4:1	68	0	28	8
PBTS	26.23*	74	83	13	56	3:1	132	35	100	7
OTS	20.03*	75	86	10	56	4:1	127	74	92	16
P3HT	26.9†	-	-	-	-	-		-	-	-
PCBM	37.8‡	-	-	-	-	-		-	-	-

* Janssen, D. *et. al. Thin Solid Films* **2006**, *515*, 1433-1438
† Wang, X.; Ederth, T.,; Inganäs, O., *Langmuir* **2006**, *22*, 9287-9294
‡ Nilsson, S.; Bernasik, A.; Budkowski, A.; Moons, E., *Macromolecules* **2007**, *40* 8291-8301

Vertical Phase Distribution Atop PEDOT:PSS

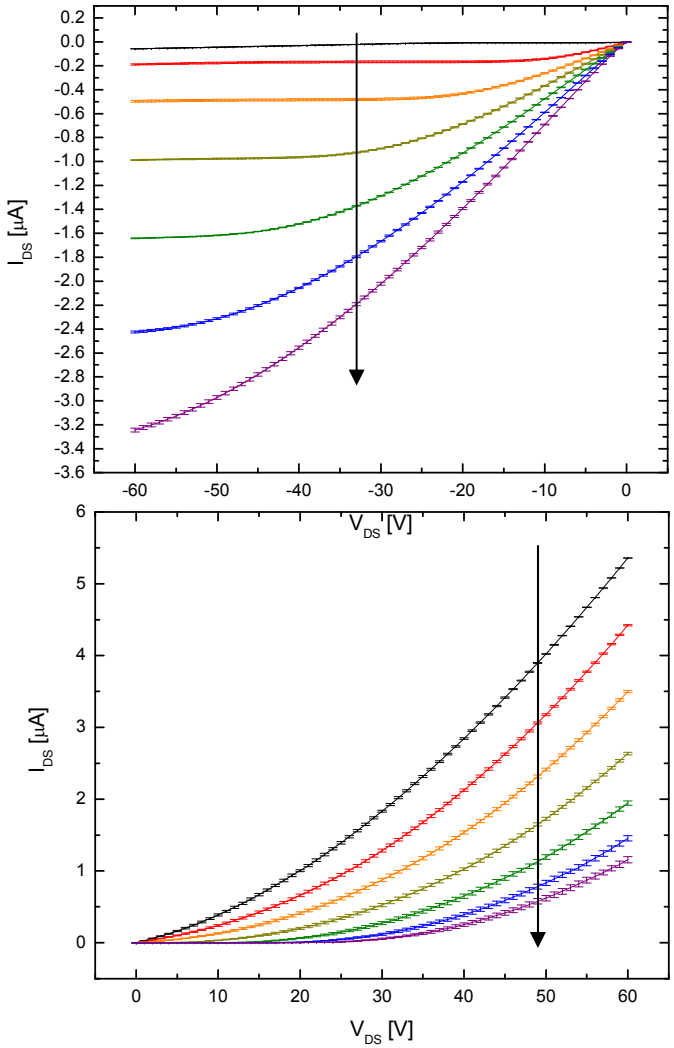


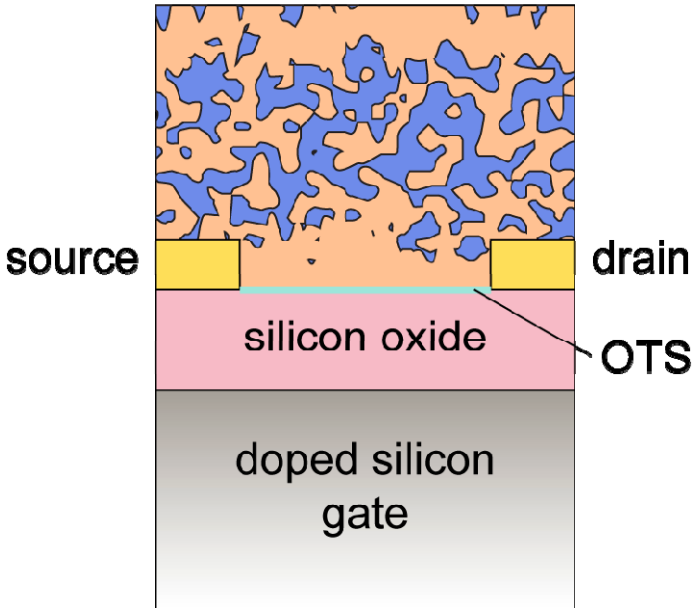


Potential cause of poor ff?

- But, blocking layers are very thin relative to BHJ (each is 5-10% BHJ thickness)
- P3HT layer might be removed or changed by metal evaporation
- Blocking layers are not "perfect," so lateral percolation might allow carriers to go around them (at the cost of some additional series resistance).
- Suggests that surface energy of HIL might be an important optimization variable for more reasons than simple solvent wetting.

OTFTs of Bulk Heterojunctions: Dependence on Dielectric Surface Energy

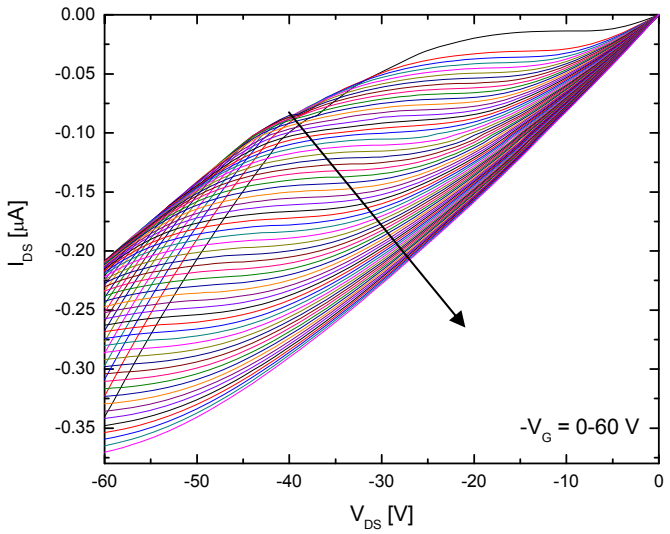


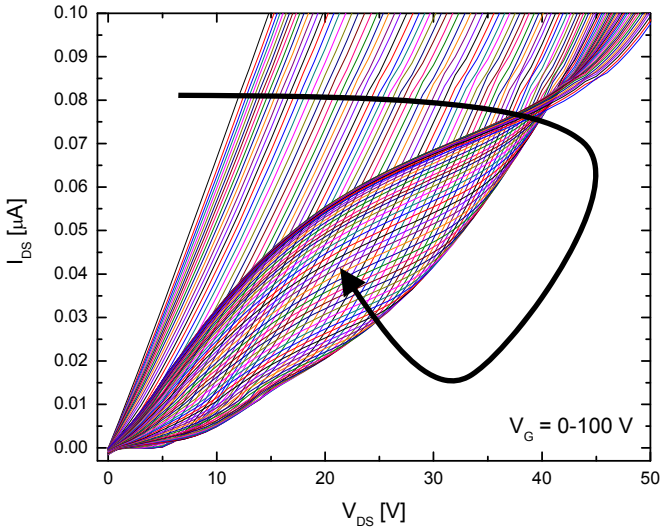


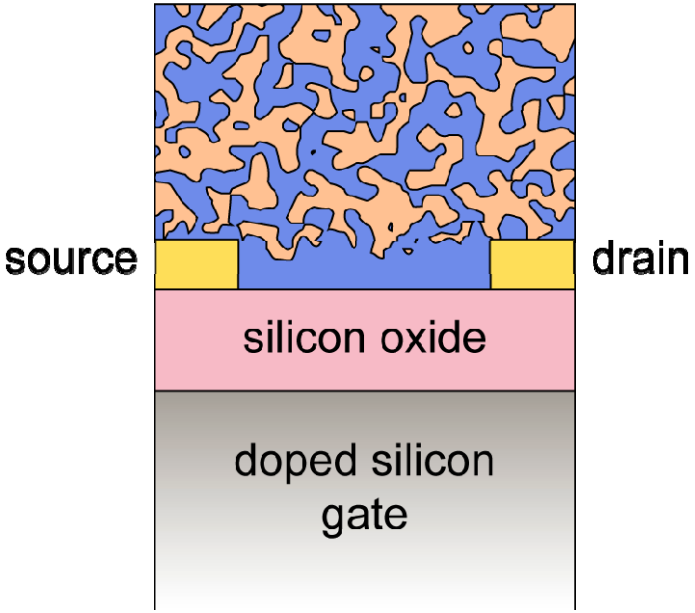
On OTS

- P3HT-rich bottom layer
- Only observe hole transport
- μ_h = 1.75 x 10^{-3} $cm^2V^{-1}s^{-1}$

OTFTs of Bulk Heterojunctions: Dependence on Dielectric Surface Energy





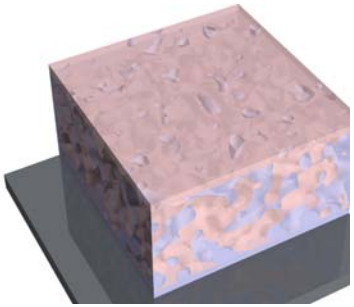


On bare oxide

- PCBM-rich bottom layer
- Observe ambipolar transport
- Difficult to extract hole and electron mobilities independently.

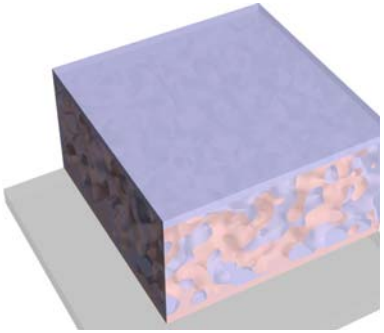
Summary

Polymer/ Air Interface:
aka Cathode

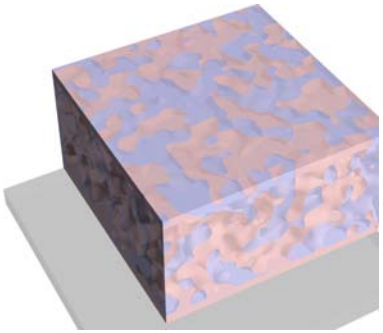


All Cases

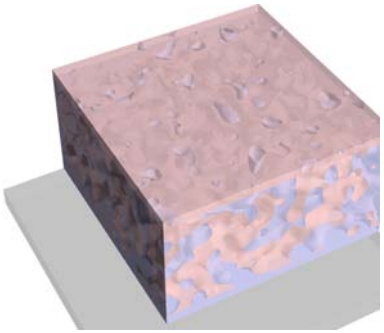
Polymer/ Substrate Interface:
aka Anode



As Cast Oxide



Annealed Oxide/ PBTS



OTS

TFT – like orientation of P3HT chains throughout the BHJ is non-ideal for vertical transport of holes

Future Work

- Interrogate BHJ layers on HTL *via* VASE
- Apply knowledge gained here to OPV devices by assembling SAMs on HTL surfaces
- Explore relationship of Anode/BHJ and Cathode/BHJ interfaces and device aging
- Correlate VASE model to reflectivity/ diffraction/ scattering results

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