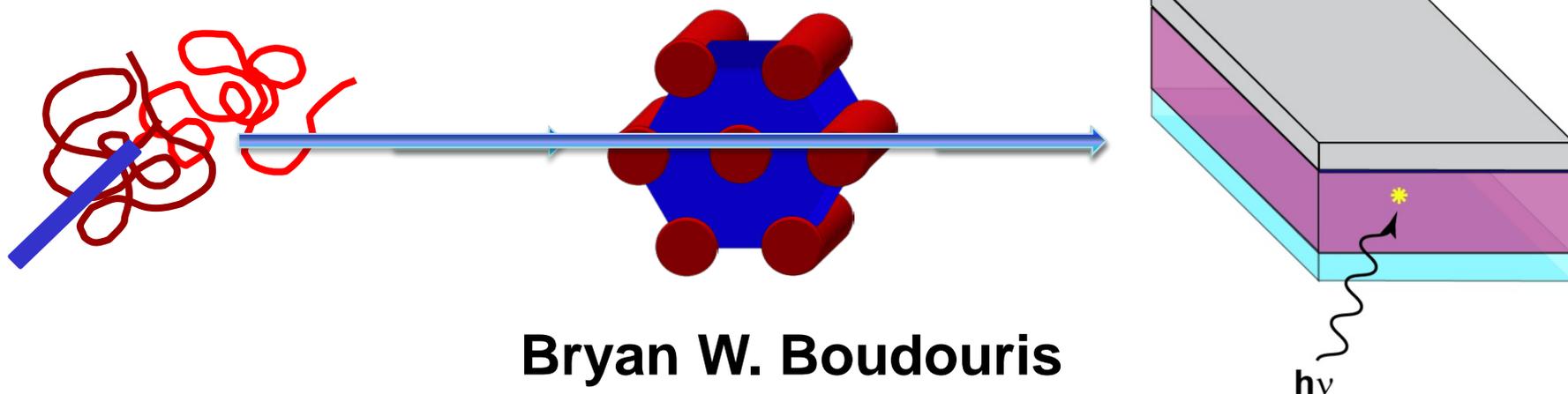


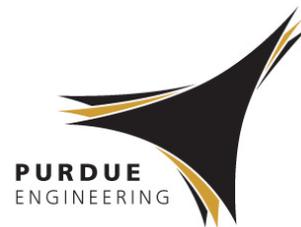
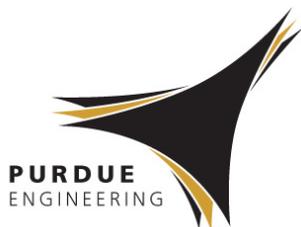
Design of Optoelectronically-active Polymers for Organic Photovoltaic Applications



Bryan W. Boudouris

*School of Chemical Engineering
Purdue University*

Spring 2013 Solar Research Series
Purdue University Energy Center, Discovery Park, and
Birck Nanotechnology Center

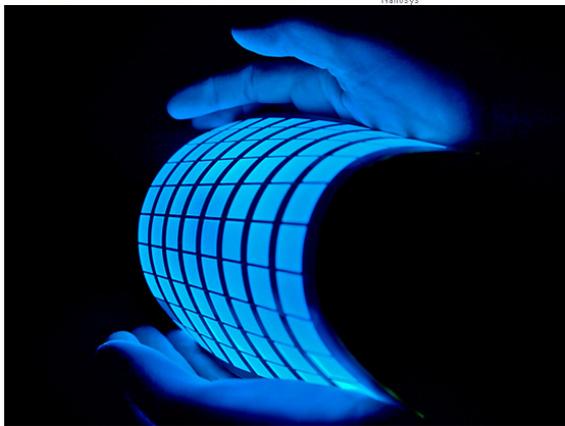
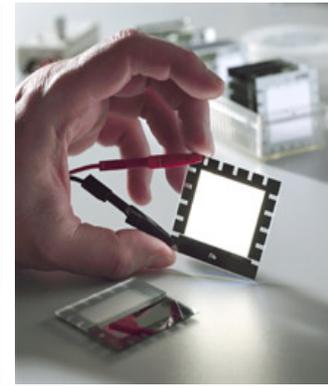


Thursday, January 24, 2013

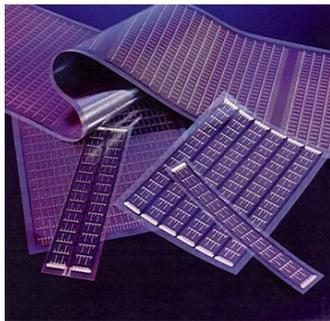
Novel Materials Caused Plastic Electronics to Emerge



GE Research, 2004
16 x 6" x 6" OLED panels
1600 lumens – 15 lm/W



Konarka, 2004



Konarka, 2004

Konarka, 2010



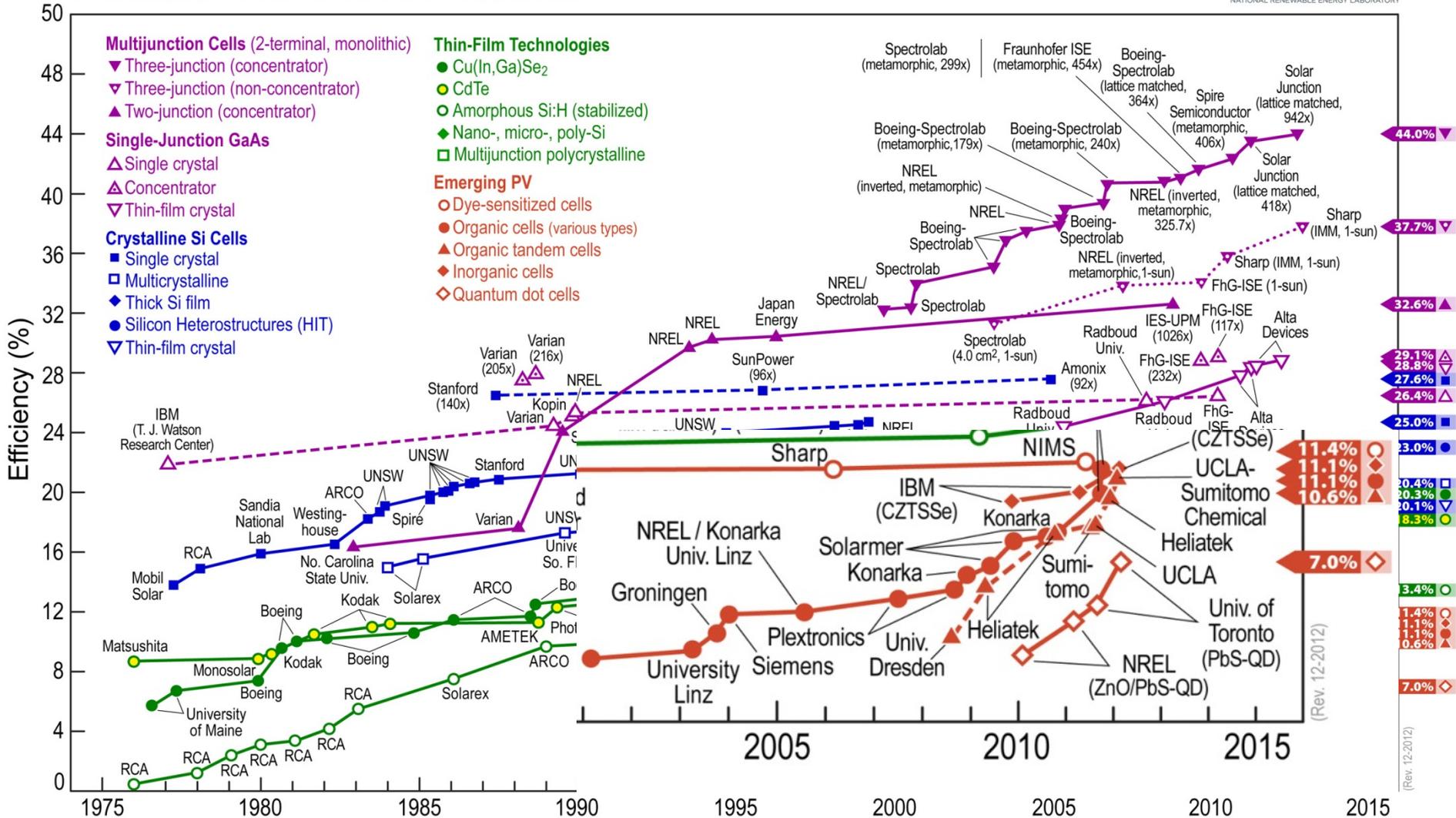
Konarka, 2010



Rapid Efficiency Increases in Laboratory-scale OPV Devices

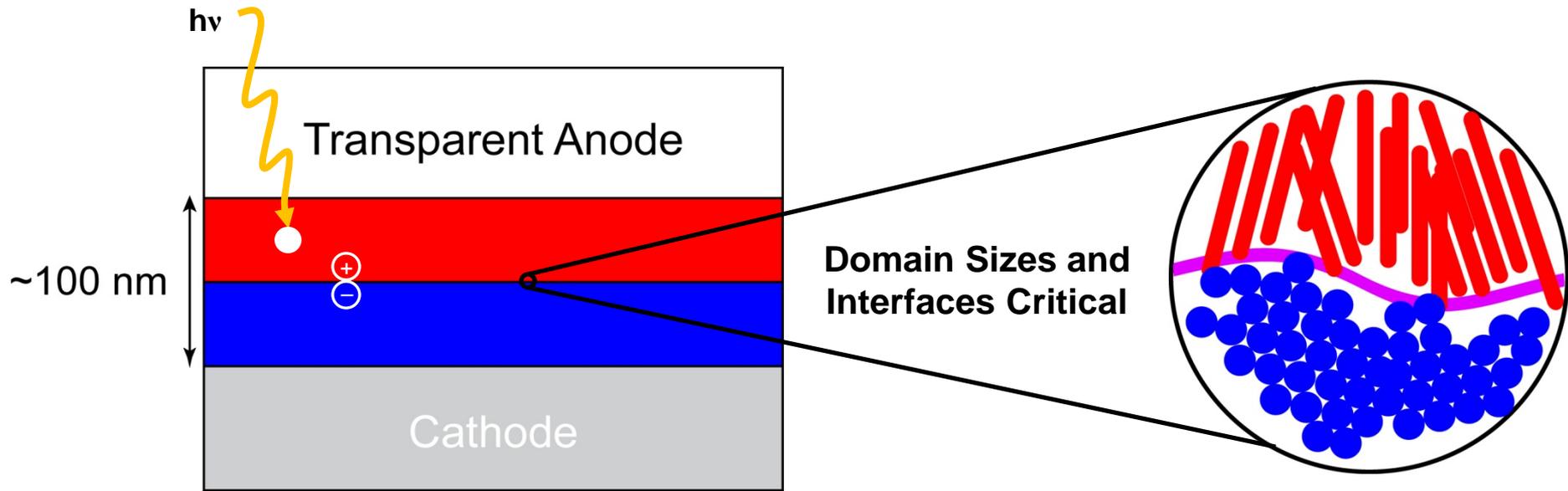


Best Research-Cell Efficiencies



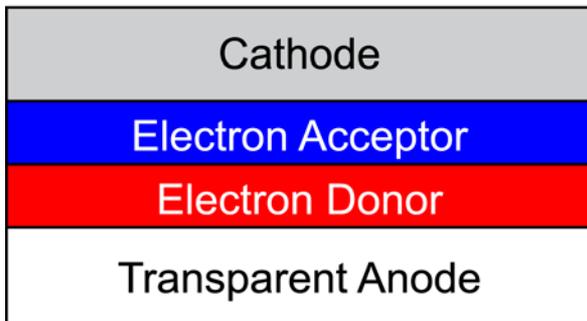
As compiled by the National Renewable Energy Laboratory (NREL)

Nanoscale Morphology and Interfaces Are Crucial in OPVs

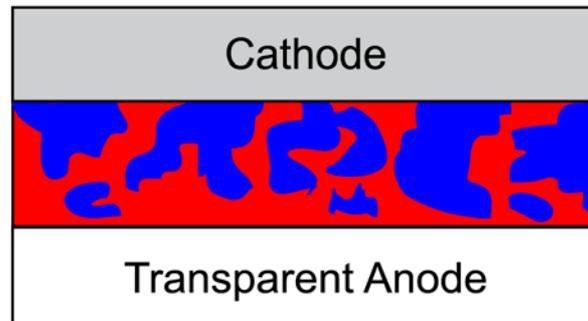


Three Common Polymeric Photovoltaic Device Geometries

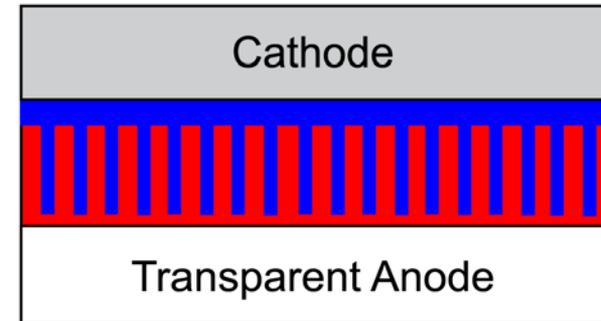
Bilayer Cell



Bulk Heterojunction



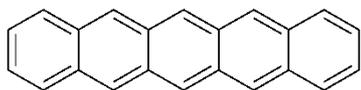
Ordered Bulk Heterojunction



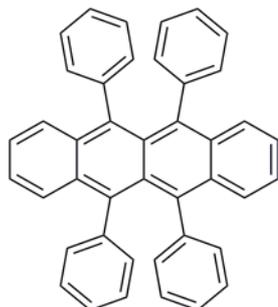
Organic Semiconductors Generally Are Highly Conjugated

Small Molecule Semiconductors

p-type Materials



Pentacene

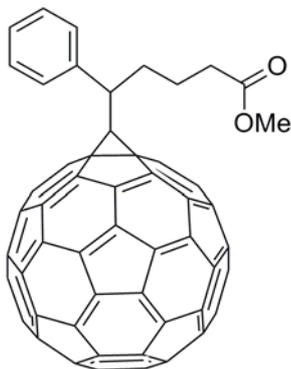


Rubrene

n-type Materials



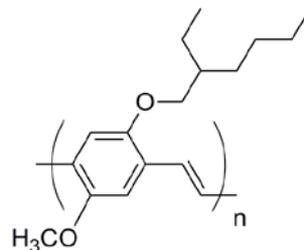
Buckminsterfullerene



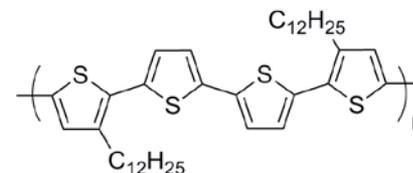
PCBM

Polymeric Semiconductors

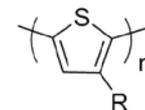
p-type Materials



MEH-PPV

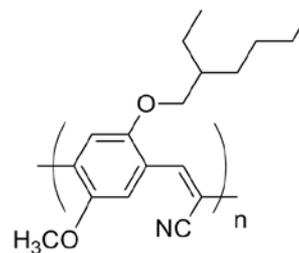


PQT-12

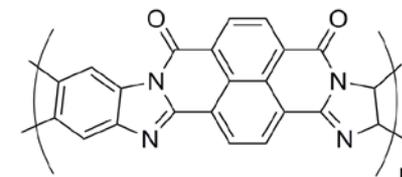


P3AT

n-type Materials

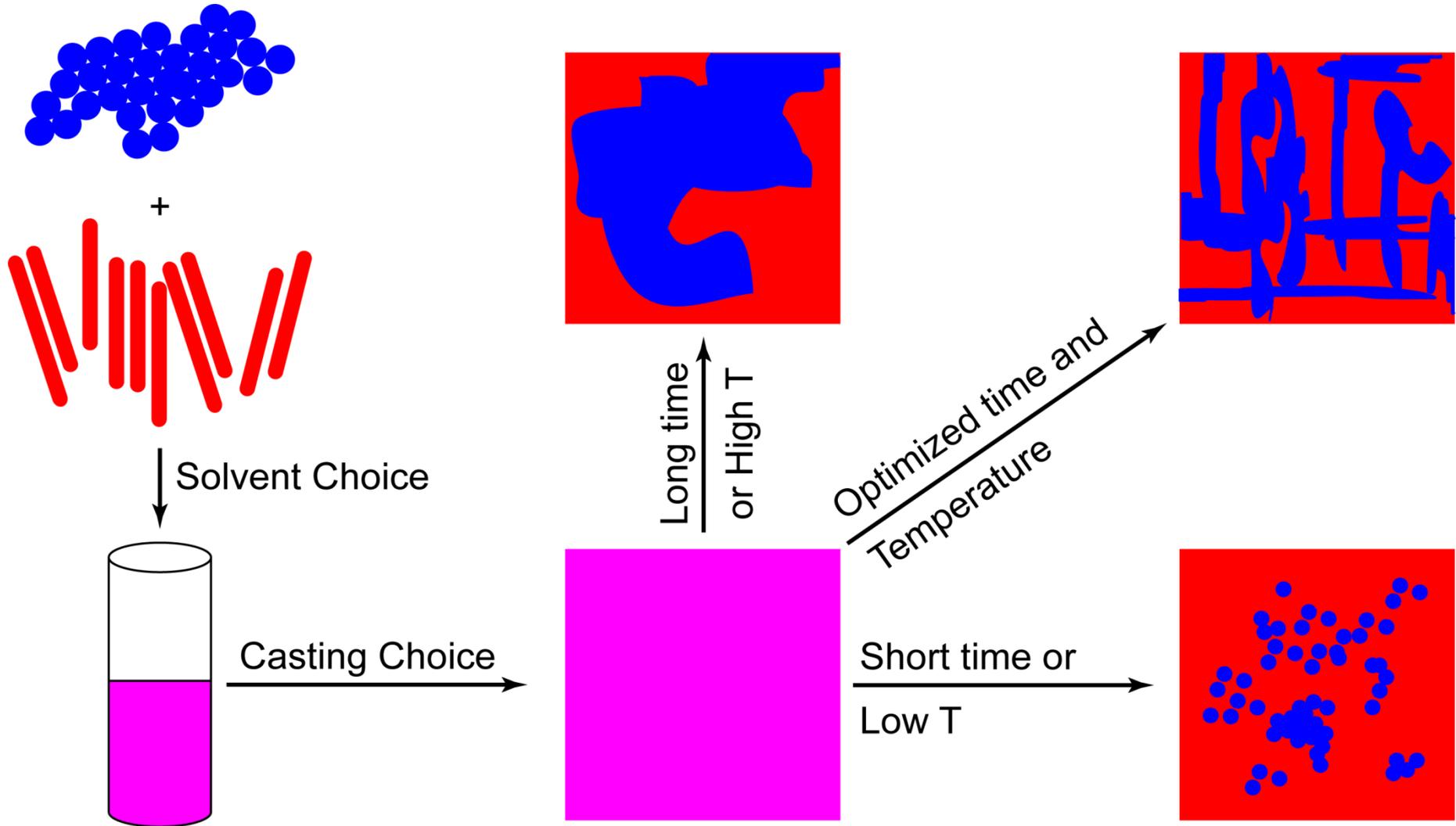


CN-MEH-PPV



BBL

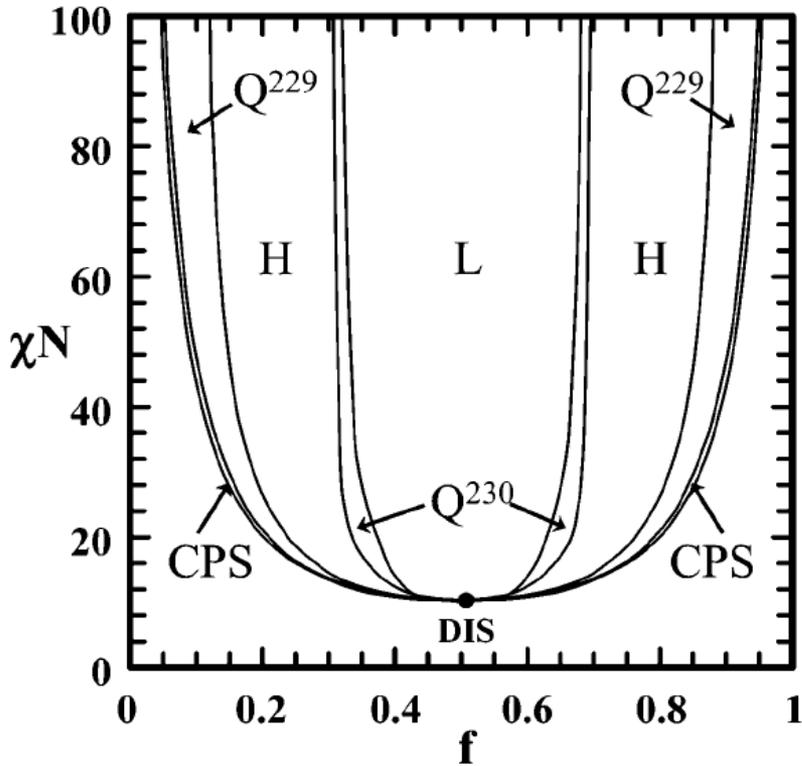
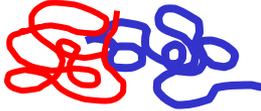
Current Active Layer Microstructures are History Dependent



Is there an alternate route that is thermodynamically stable?

Block Copolymers Self-assemble on a Useful Scale

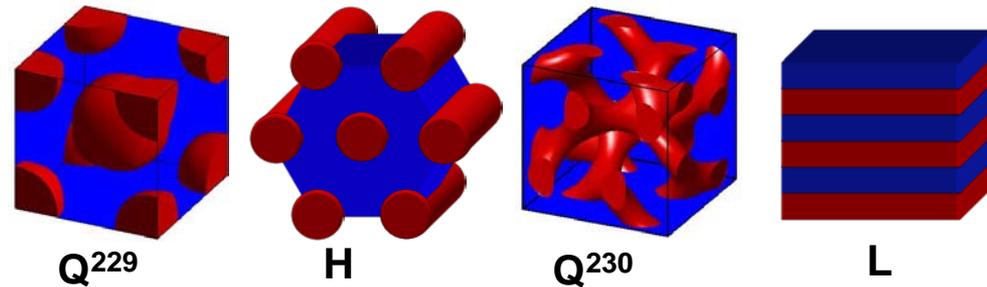
Theoretical Coil-Coil Diblock Copolymer Phase Diagram



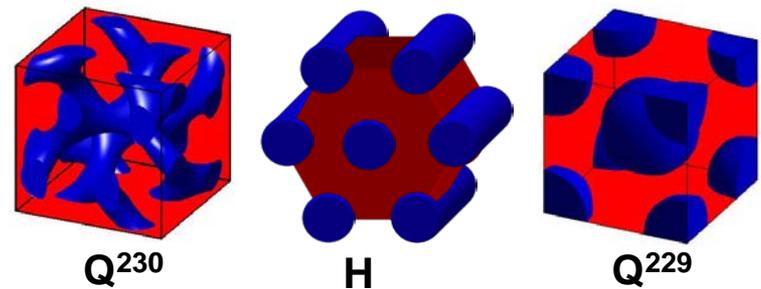
N = number of segments
 χ = interaction parameter
 f = polymer volume fraction

Unit Cell Schematics

Red Polymer *MINORITY PHASE*



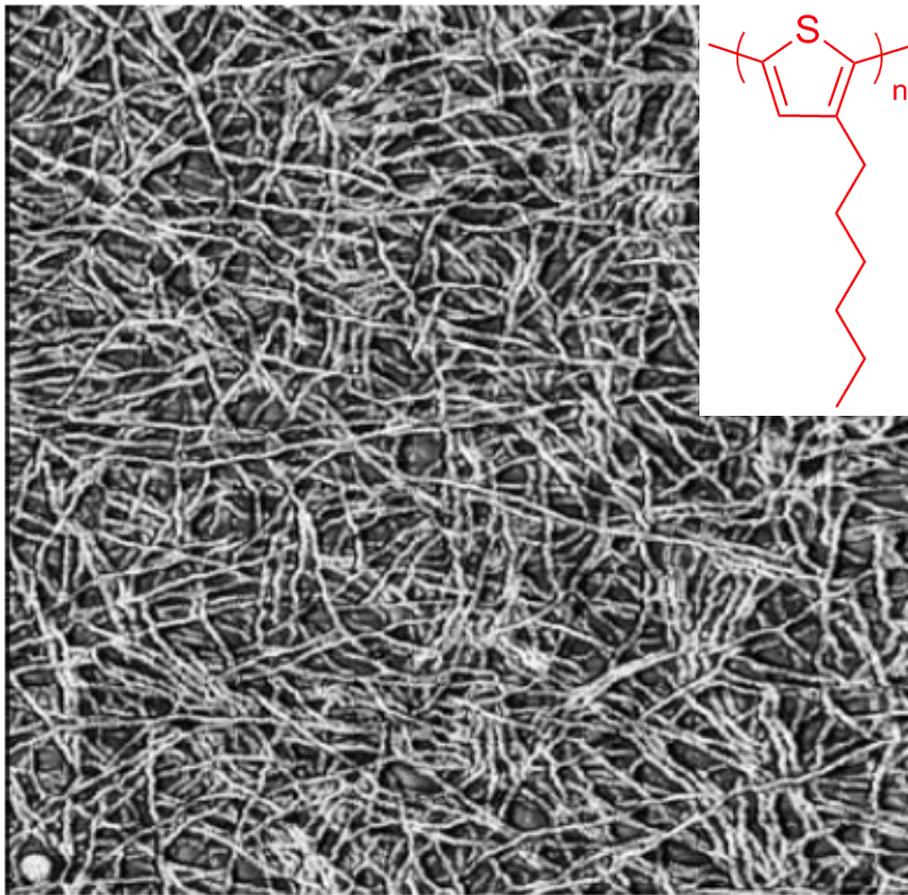
f_{Red} →



f_{Red} →

Poly(3-hexylthiophene) (P3HT) Self-Assembly is Complex

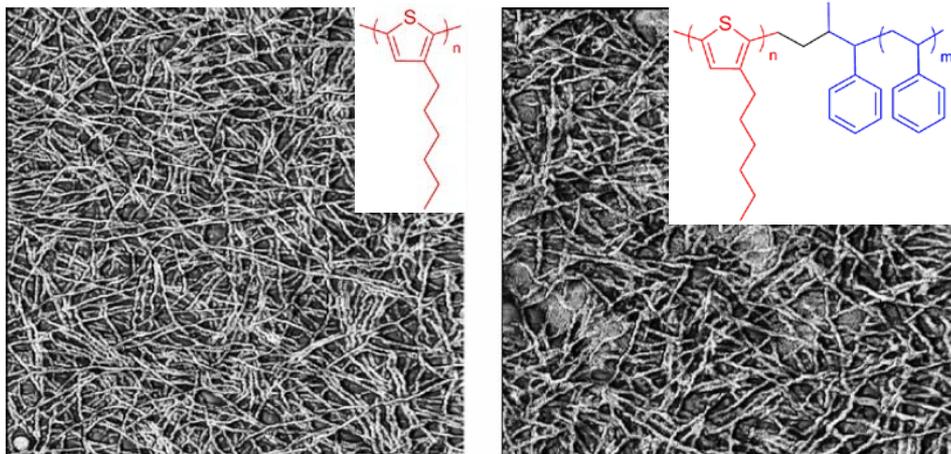
P3HT Homopolymer



2 x 2 μm AFM Tapping Mode Phase Images

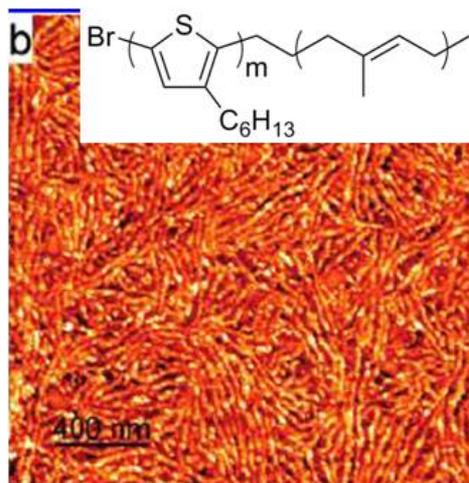
lovu, M. C. et al. *J. Macro. Sci. Part A* **2006**, 43, 1991.

P3HT Block Copolymers Lack Long Range Order

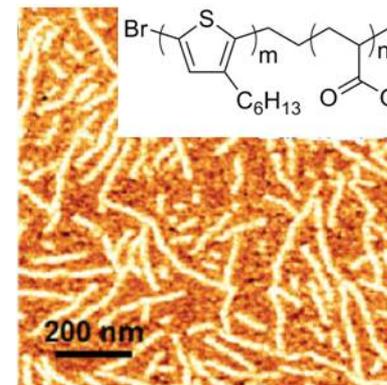


2 x 2 μm AFM Tapping Mode Phase Images

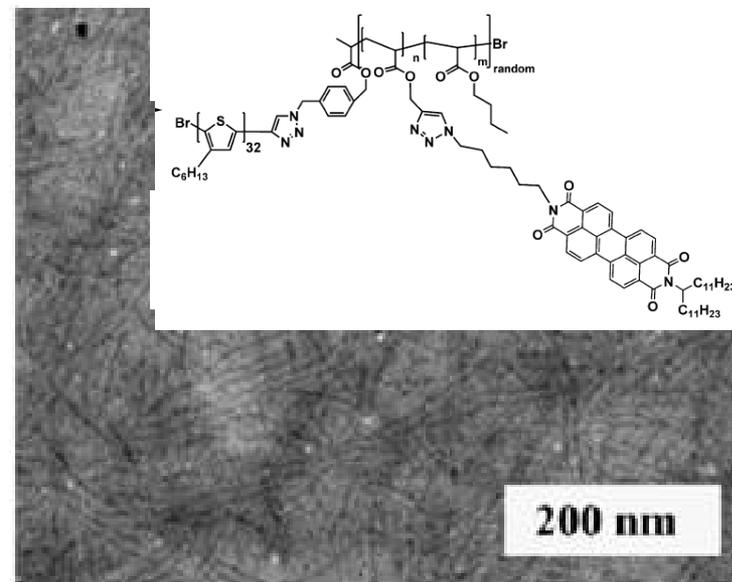
Iovu, M. C. *et al. J. Macro. Sci. Part A* **2006**, 43, 1991.



Iovu, M. C. *et al. Macromolecules* **2007**, 40, 4733.

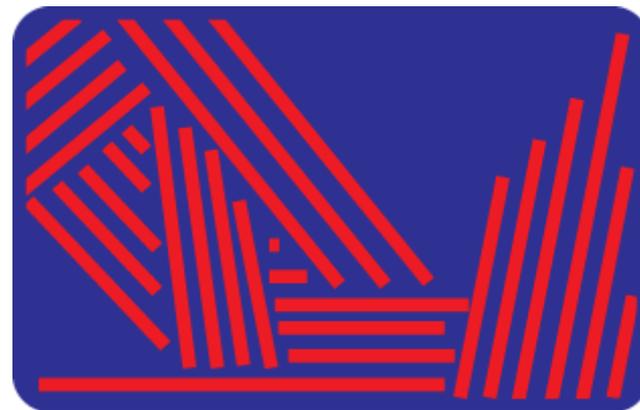
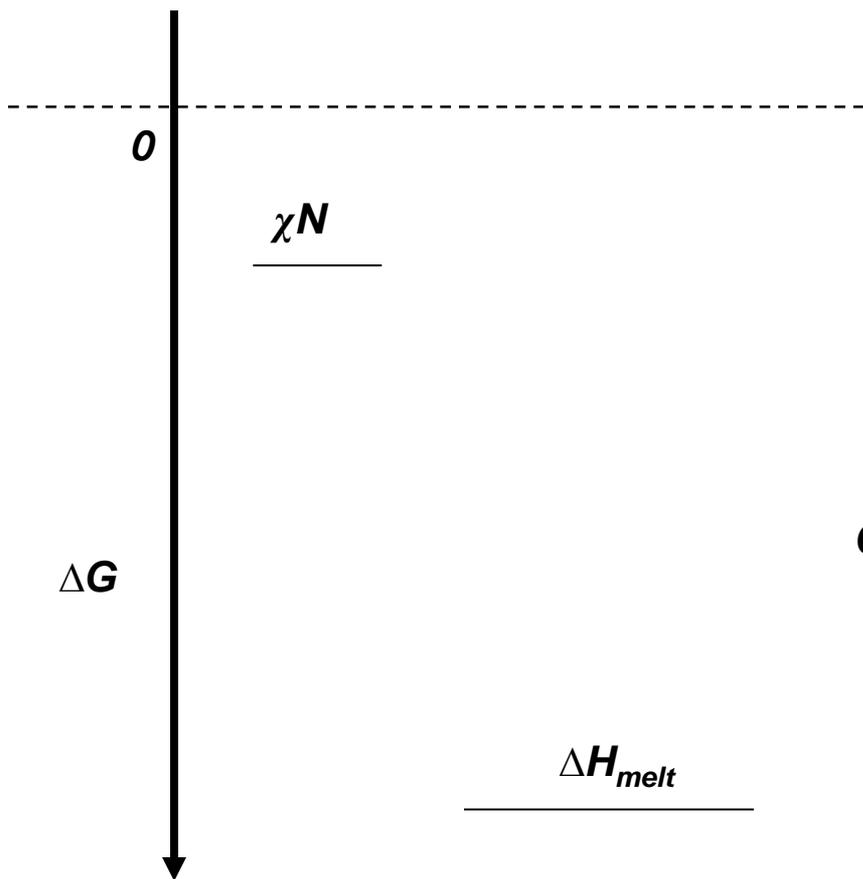


Iovu, M. C. *et al. Macromol. Rapid Commun.* **2007**, 28, 1816–1824.

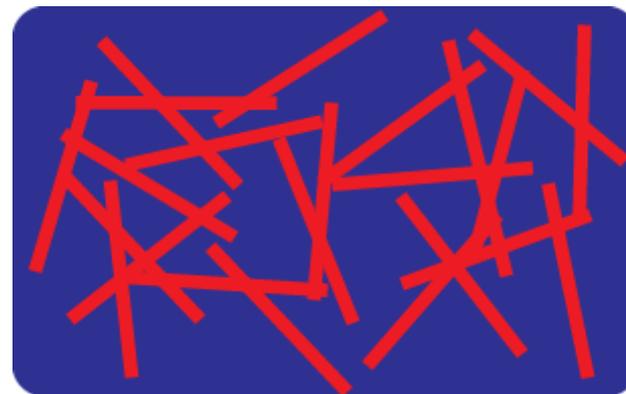


Tao, Y. *et al. Soft Matter* **2009**, 5, 4219.

Strong Crystallization Forces can Override Self-Assembly



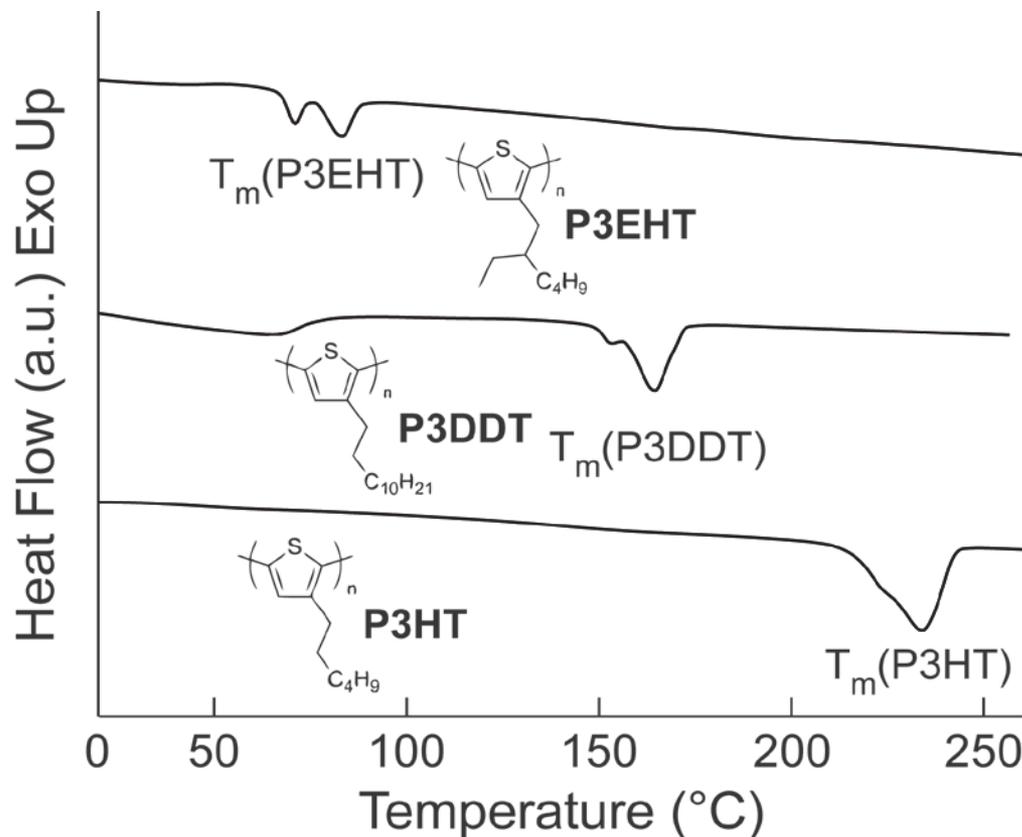
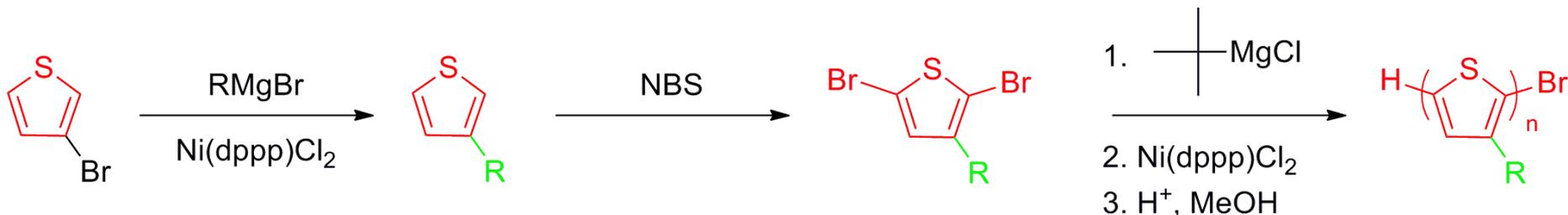
*Self-Assembly dominates crystallization.
Crystallization occurs "after" phase separation.*



*Crystallization has large driving force.
Occurs "faster" and kinetically traps structure.*

**Can our P3AT design cause
SELF-ASSEMBLY TO
OCCUR PRIOR TO
CRYSTALLIZATION?**

Poly(3-alkylthiophenes) are Readily Synthesized e^- Donors

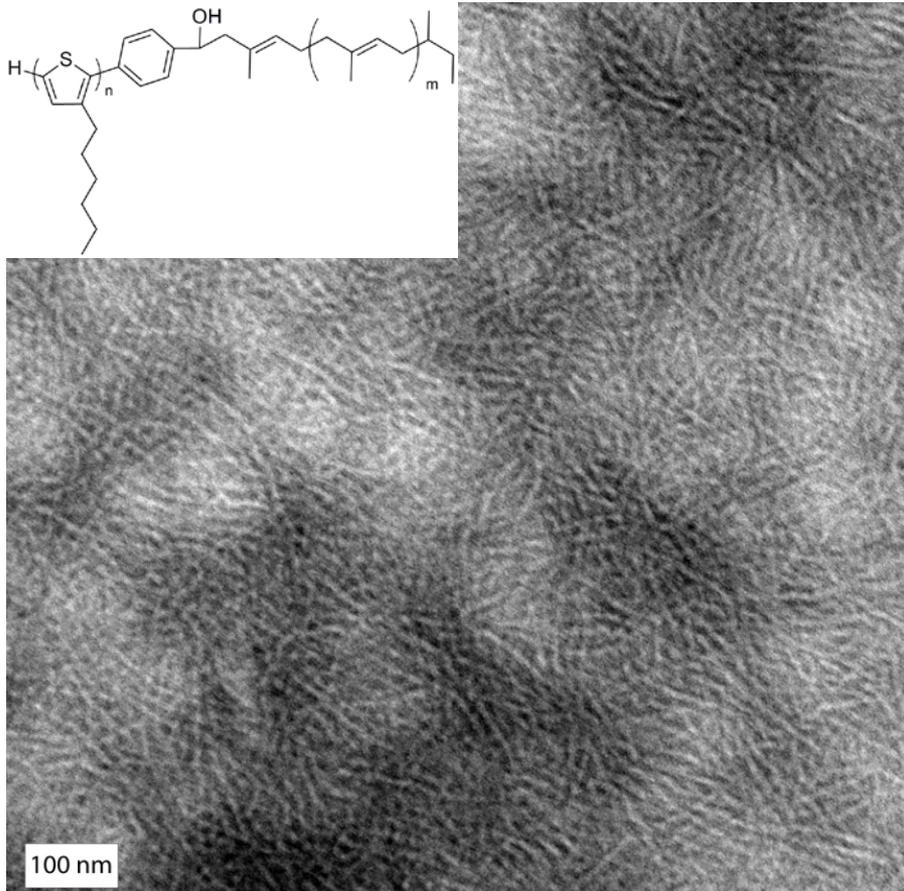


Macromolecules **2010**, *43*, 7895-7899.

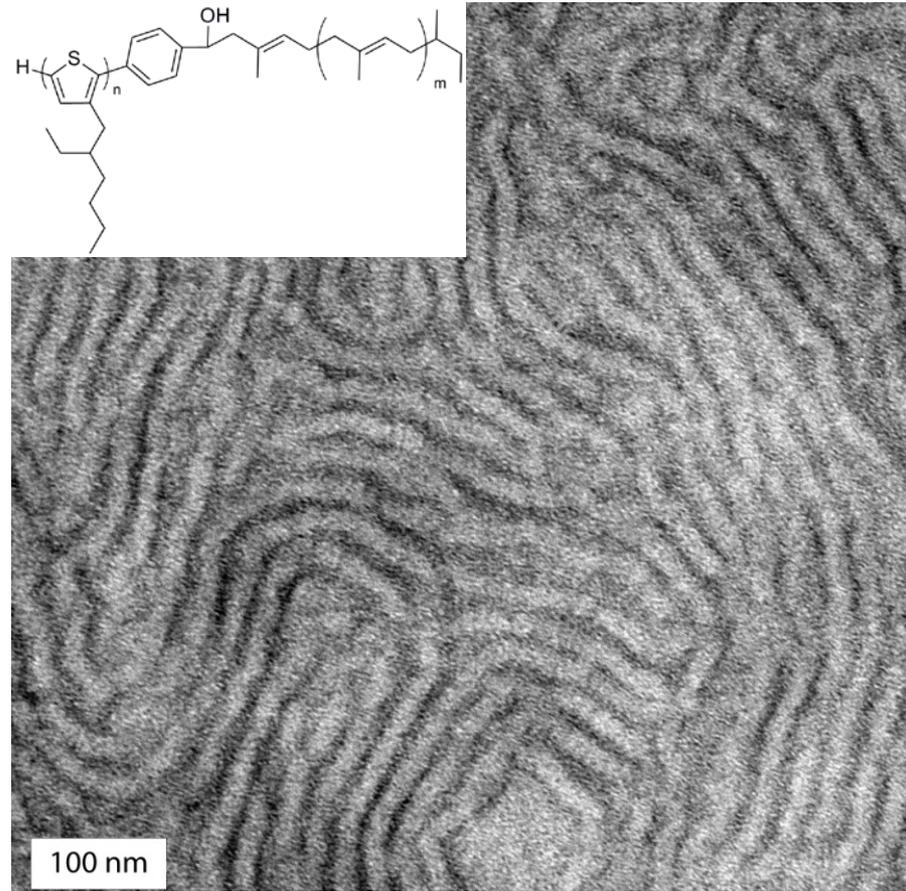
Macromolecules **2011**, *44*, 6653-6658.

P3EHT BCPs Can Be Used to Generate Nanostructured OPVs

P3HT-PI TEM Image

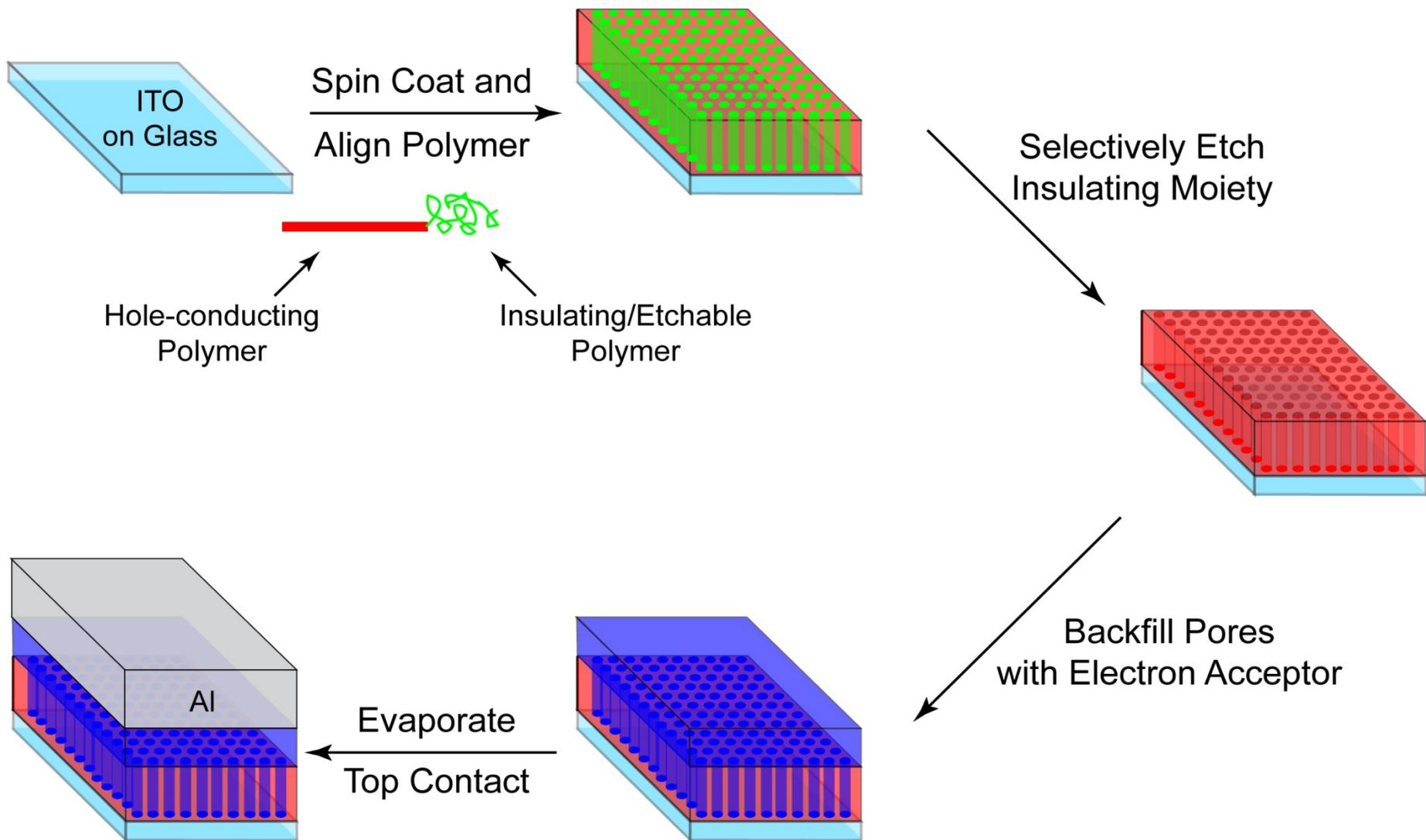


P3EHT-PI TEM Image

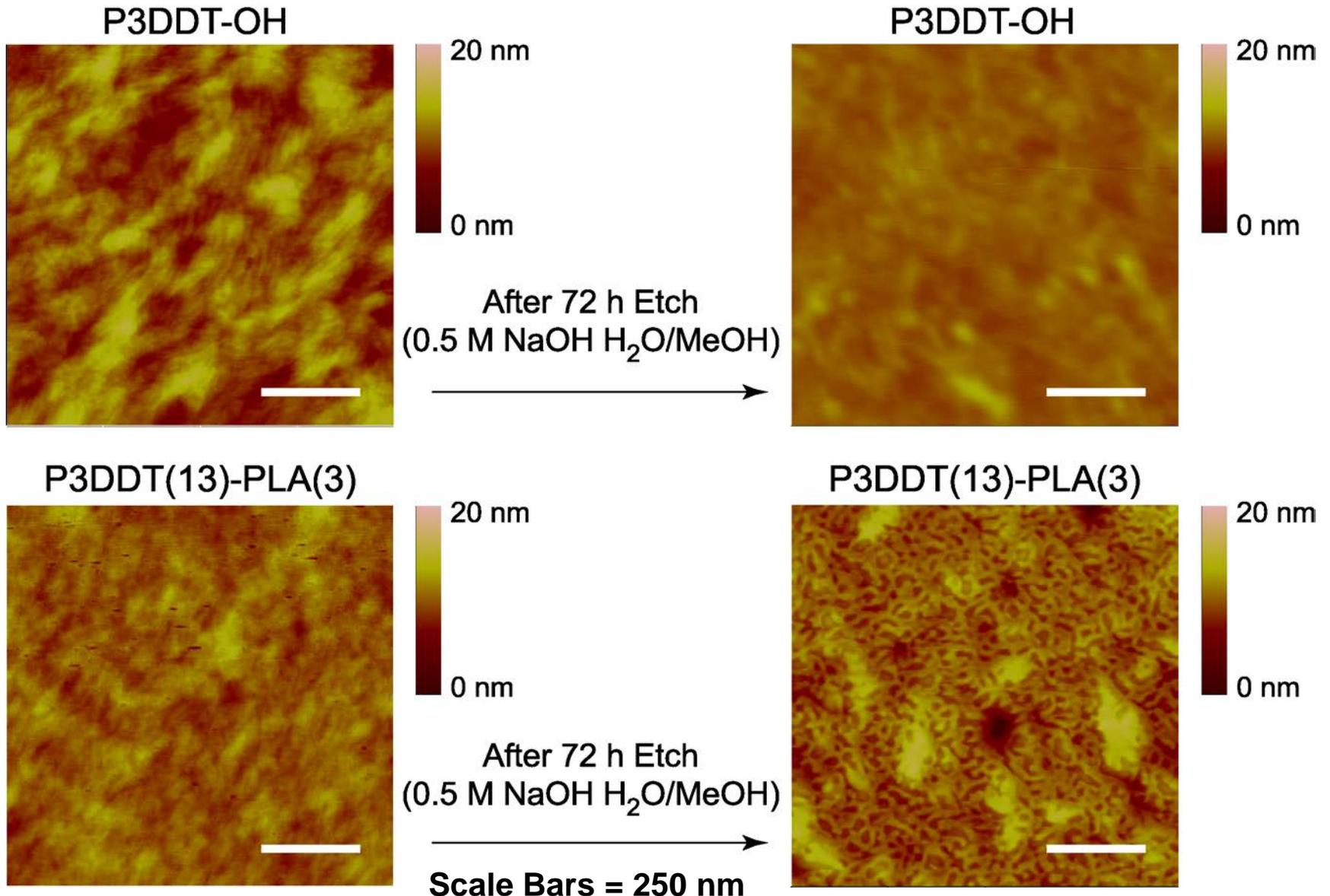


Polyisoprene selectively stained dark with OsO_4 .

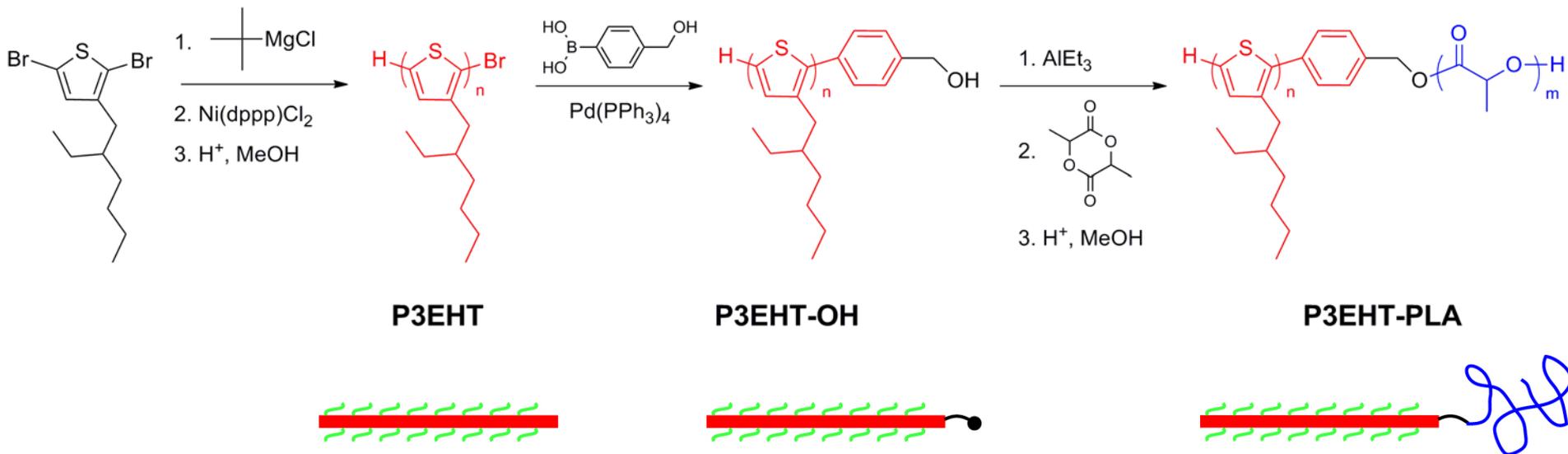
P3EHT Block Copolymers for Ordered BHJ Photovoltaics



Poly lactide (PLA) Selectively Etched from a Polythiophene Matrix



Two Controlled Polymerizations for P3EHT-PLA Synthesis



The Grignard Metathesis (GRIM) and Ring-Opening Polymerization (ROP)
Combination Leads to Rod-Coil Block Copolymers with:

Easily-Controlled Molecular Weights and Tunable Compositions

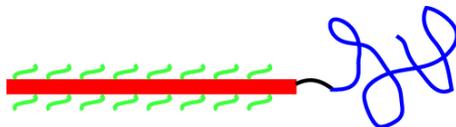
Parent P3EHT Block



$M_n(\text{P3EHT}) \sim 7 \text{ kg/mol}$

$M_w/M_n = \text{PDI} = 1.06$

P3EHT-PLA BCPs



10 BCPs Studied

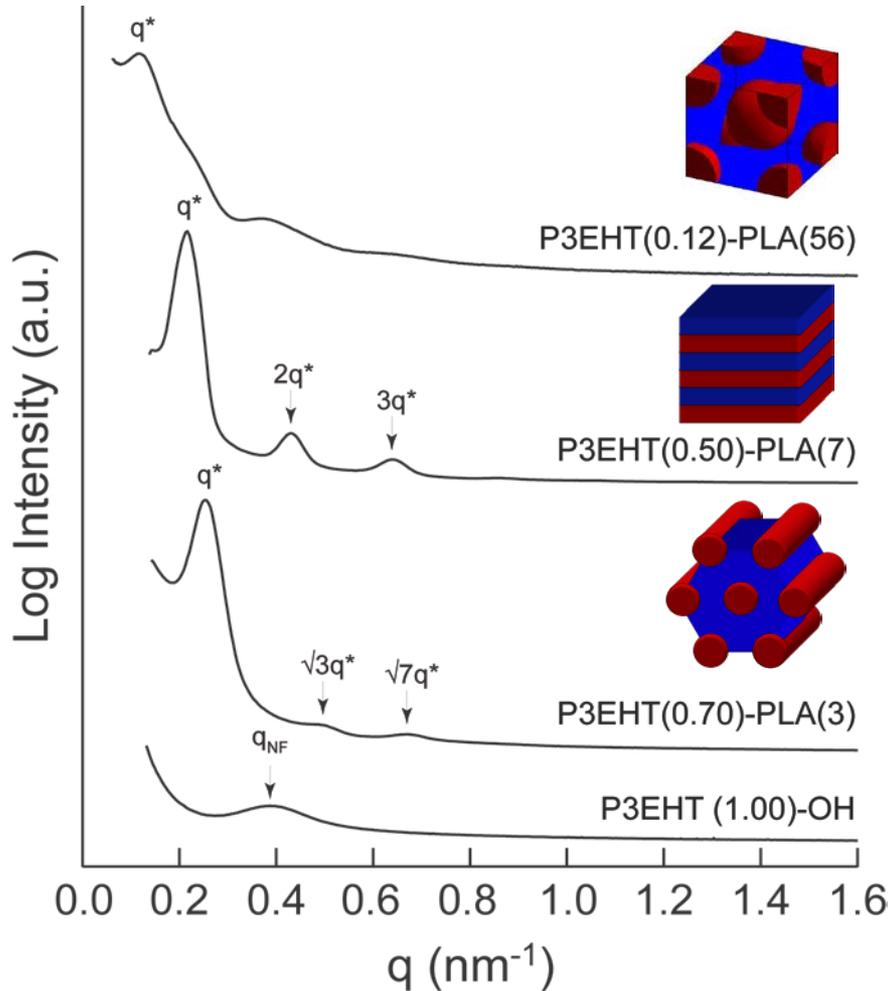
$3 \text{ kg/mol} < M_n(\text{PLA}) < 56 \text{ kg/mol}$

$M_w/M_n = \text{PDI} < 1.21$

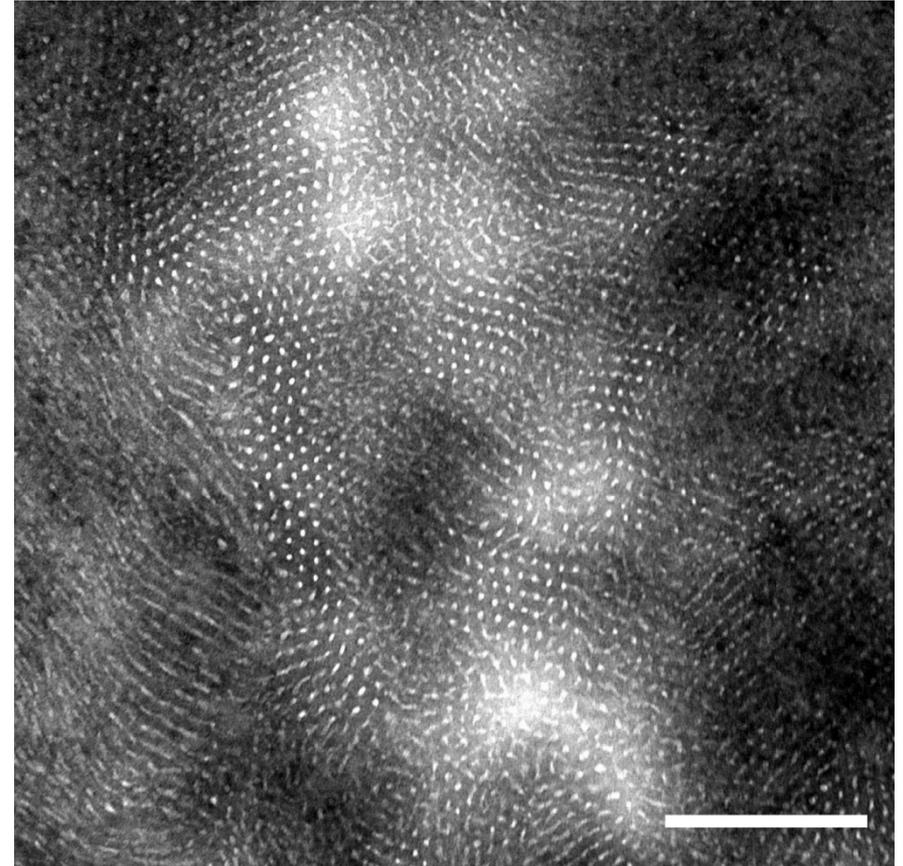
$0.12 < w_{\text{P3EHT}} < 0.70$

Examples of P3EHT Block Copolymer Microphase Separation

Powder SAXS Spectra



Electron Micrographs

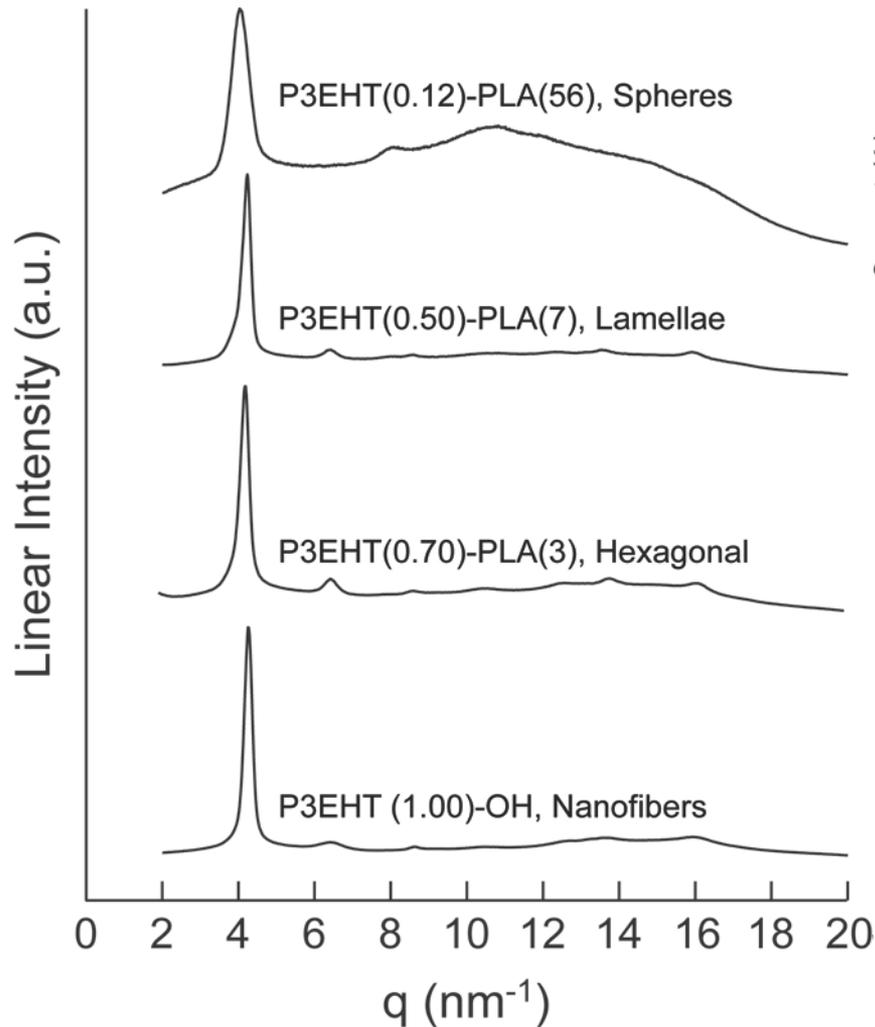


Red domains of the Block Copolymers are stained dark with RuO_4 , selectively.

All scale bars represent 200 nm

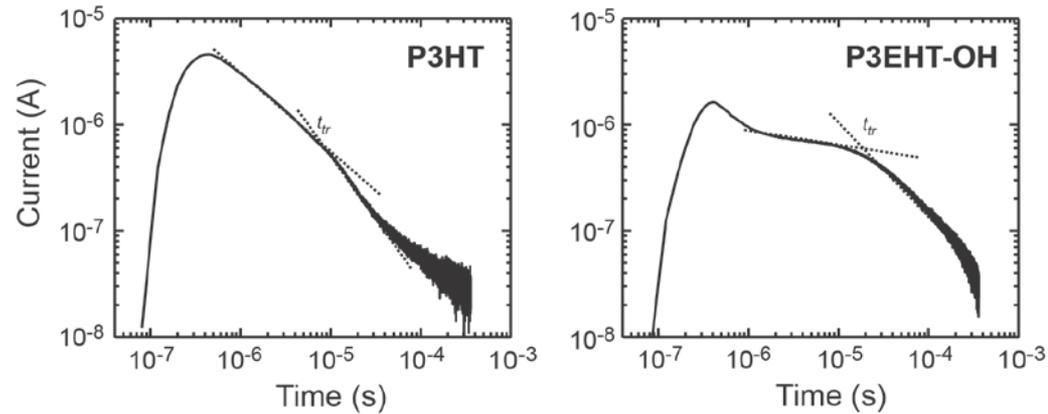
P3EHT-PLA Block Copolymers Retain Crystallinity

Powder WAXS Spectra



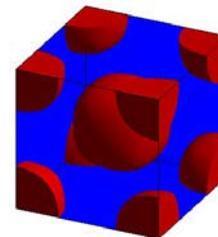
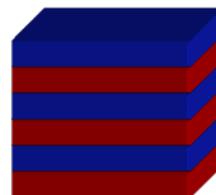
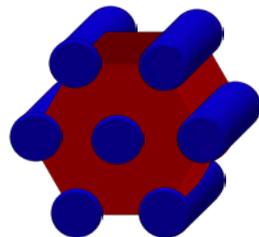
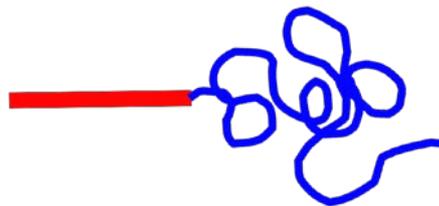
Data acquired at 50 °C

TOF Mobility Measurements



All Bulk Mobility Values $\sim 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$

Many Ordered Microstructures Observed in P3EHT-PLA

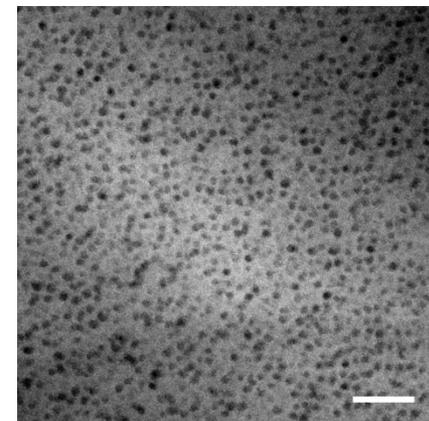
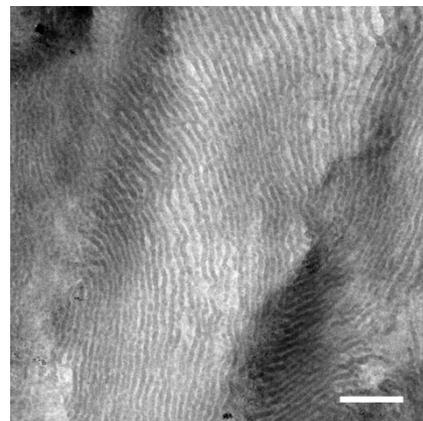
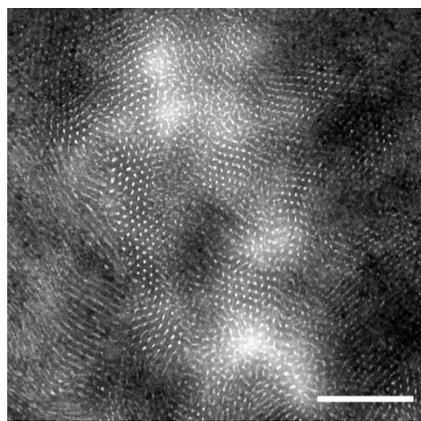
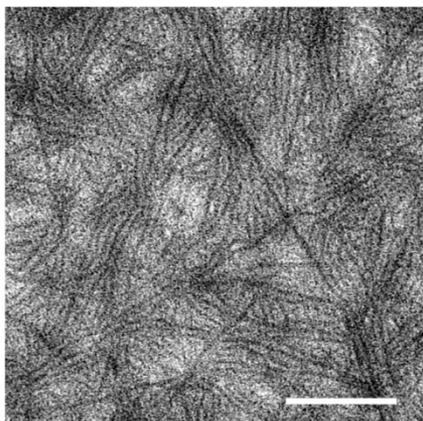


Nanofibers

HEX

LAM

Micelle



$$w_{P3EHT} = 1.00$$

$$0.63 < w_{P3EHT} < 0.70$$

$$0.25 < w_{P3EHT} < 0.50$$

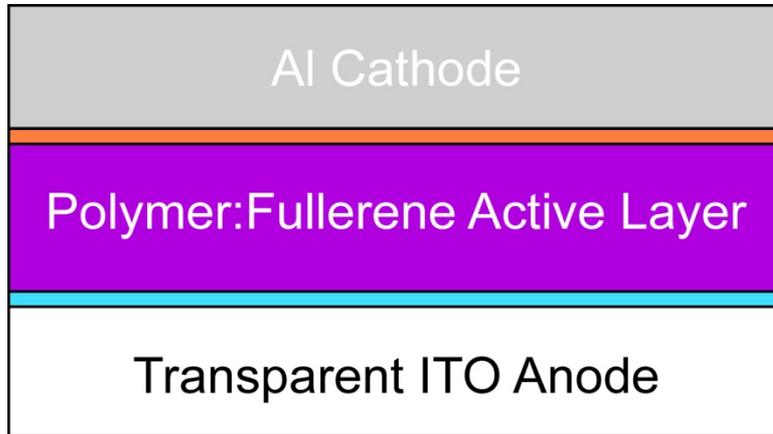
$$w_{P3EHT} = 0.12$$

All scale bars represent 200 nm

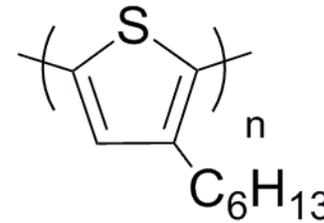
J. Am. Chem. Soc. **2011**, *133*, 9270.

Organic-Metal Interface Critical in Free Charge Collection

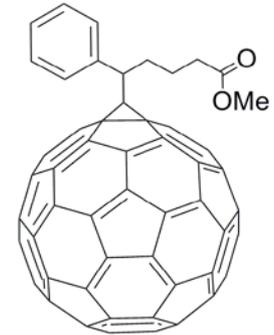
OPV Schematic



P3HT



PCBM

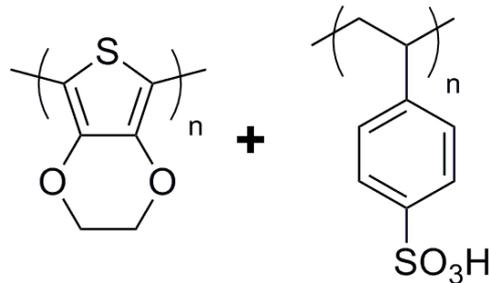


Blocking Layer

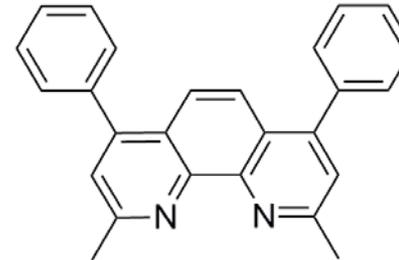
PEDOT:PSS

Blocking Layers

PEDOT:PSS



BCP



LiF

TiO_x

- Makes near ohmic contact with P3HT HOMO
- Smoothens ITO surface
- Improves wetting of organic active layer ink
- Protects active layer from metal damage
- Changes wave optics inside thin film device
- Improves electronic alignment
- Fills dipole traps at active layer interface

Radical Polymers for Organic Electronic Devices: A Radical Departure from Conjugated Polymers?

By *Kenichi Oyaizu* and *Hiroyuki Nishide**



Aliphatic Polymer Backbone

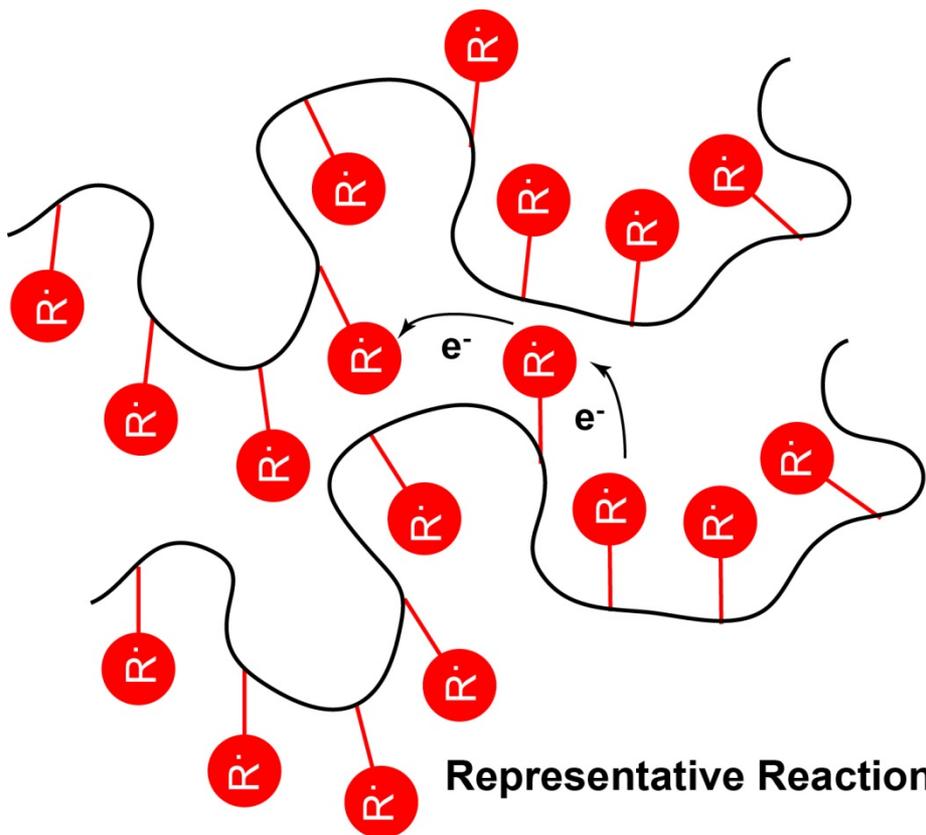


- Charge hopping transport mechanism
- SOMO Levels define electronic levels
- Currently used in flexible electronics

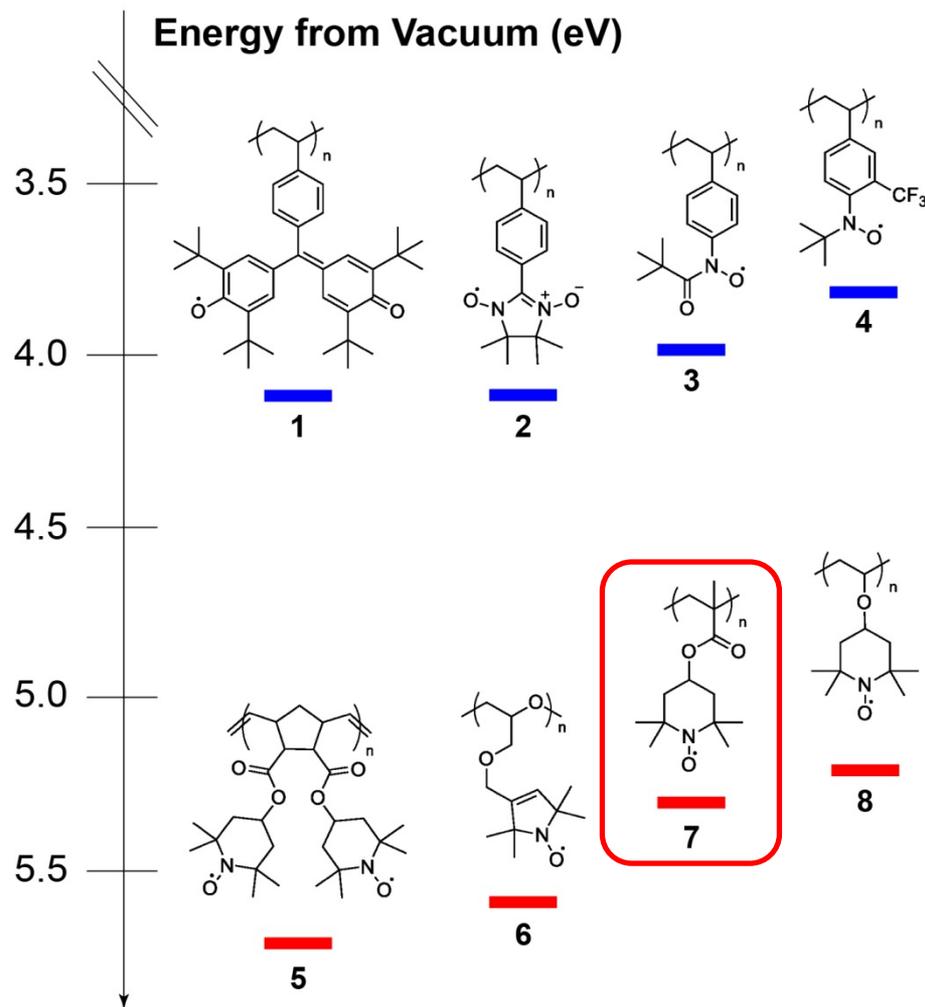
**Can we design a SOLUTION
PROCESSIBLE molecule that
has
ELECTRONIC properties that
avoids the synthetic and
microstructural challenges of
conjugated polymers?**

Pendant Group of Radical Polymers Dictate Transport Levels

Transport Occurs Through Charge Hopping



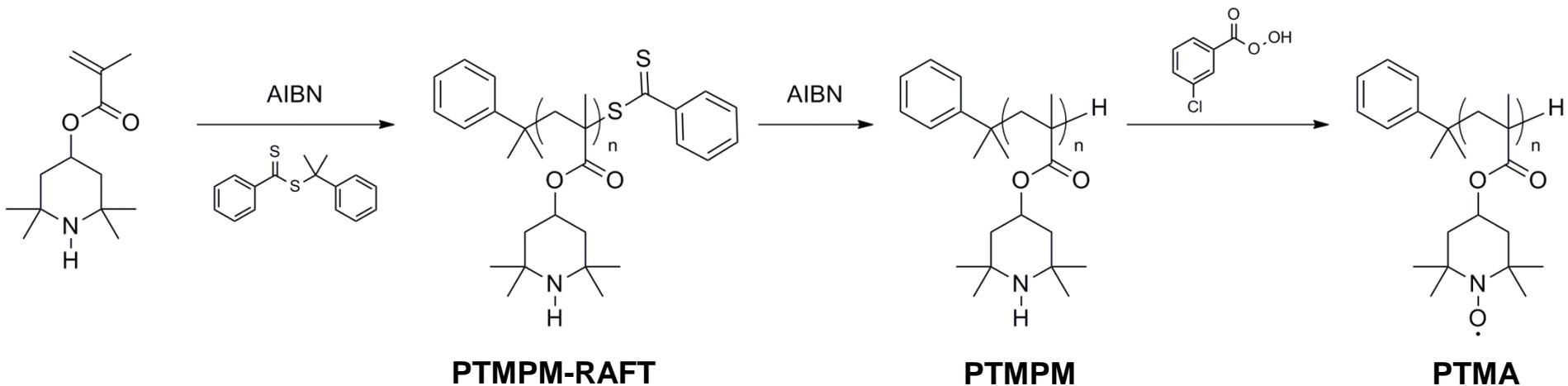
Representative Radical Polymer SOMO Energy Levels



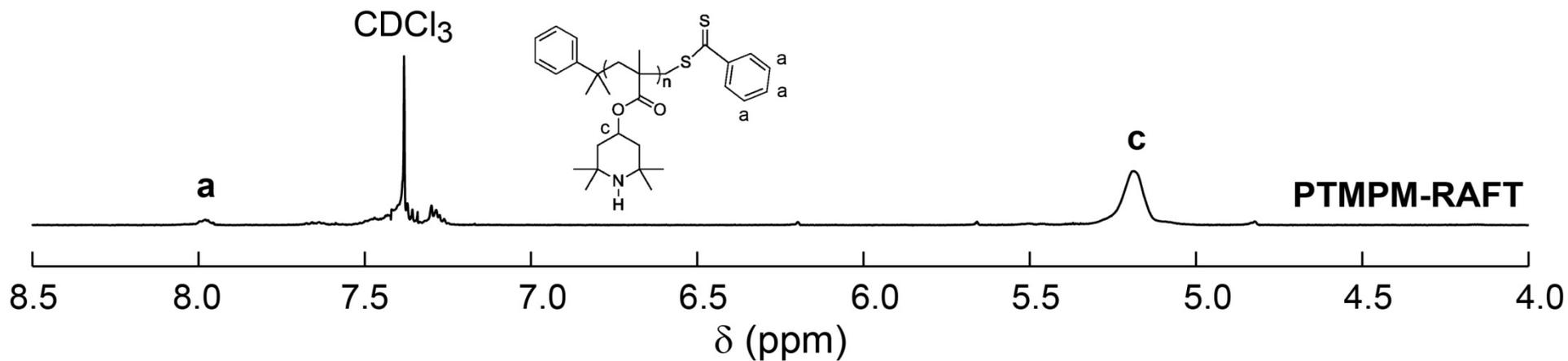
Oyaizu, K.; Nishide, H. *Adv. Mater.* **2009**, *21*, 2339.

Janoschka, T.; Hager, M. D.; Schubert, U. S. *Adv. Mater.* **2012**, *24*, 6397.

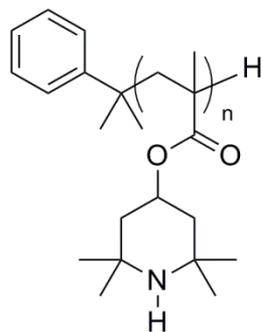
Facile Synthesis of PTMA via RAFT-Mediated Polymerization



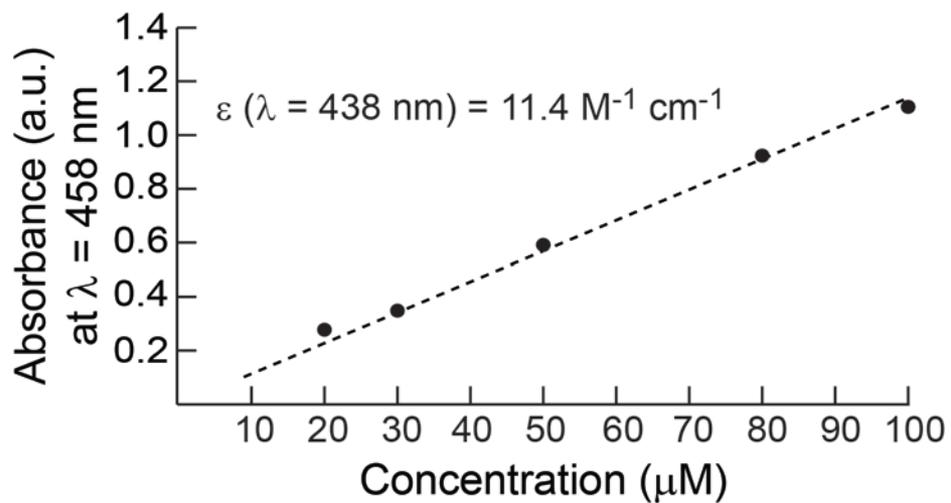
Removal of RAFT end group CRITICAL to Solution-Coating Methodology



Spectroscopy Shows Radical Conversion at ~80-90%



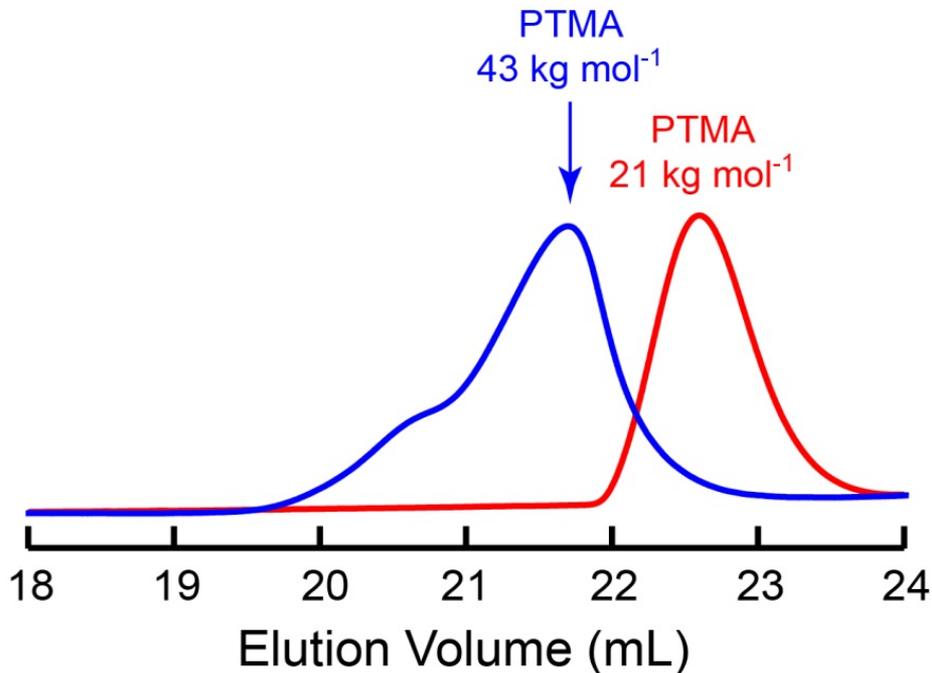
Utilizer the Beer-Lambert Law to Calculate Conversion of Radicals $A = \epsilon b C$



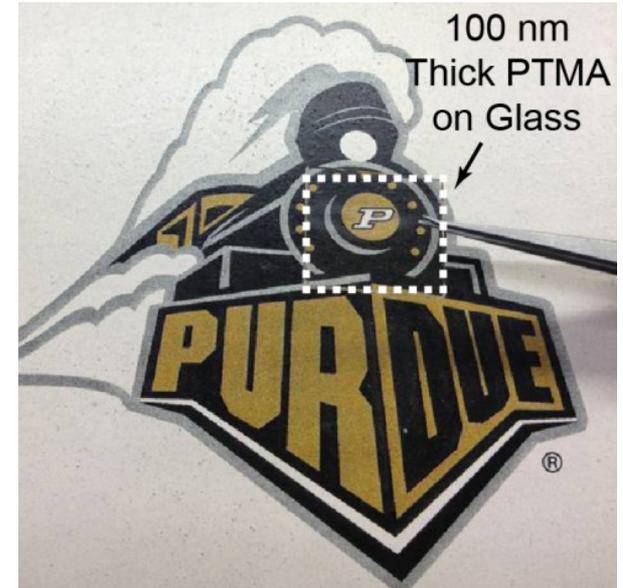
PTMA Has Many Unique Properties Relative to Conjugated Polymers

PTMA Synthesis is Much More Flexible Than for Conjugated Polymers

- Molecular Weights Ranging from:
5 kg mol⁻¹ to 120 kg mol⁻¹
Readily Made Using This Technique
- All PDI Values are PDI < 1.15 as measured against polystyrene (PS) standards
- Total Synthetic Scheme is Relatively High Throughput and Requires Only 4 days to Go From Monomer to Radical Polymer and Large (> 5 g) Batches Can Be Made

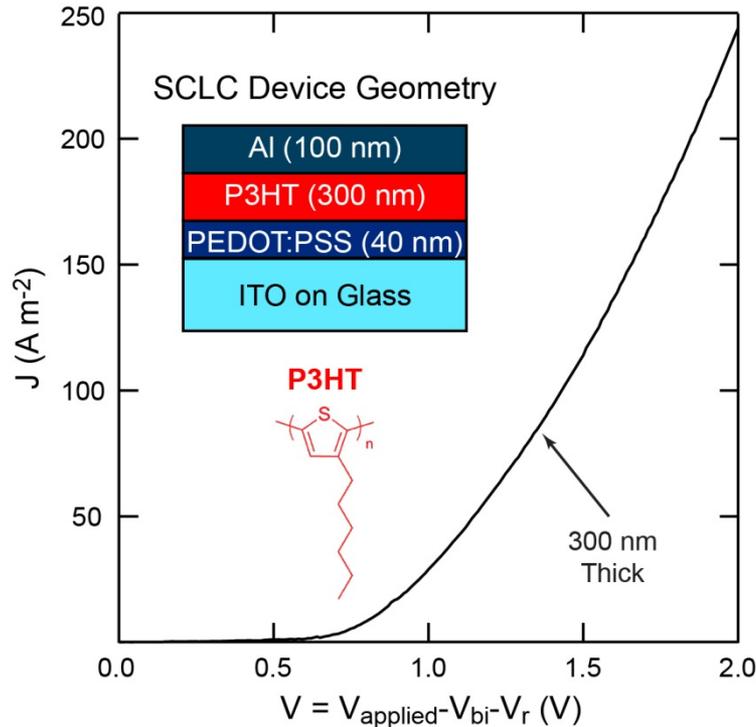


PTMA Thin Films are Transparent



PTMA Capable of Transporting Holes in Diode Structure

SCLC Sandwich Structure for P3HT

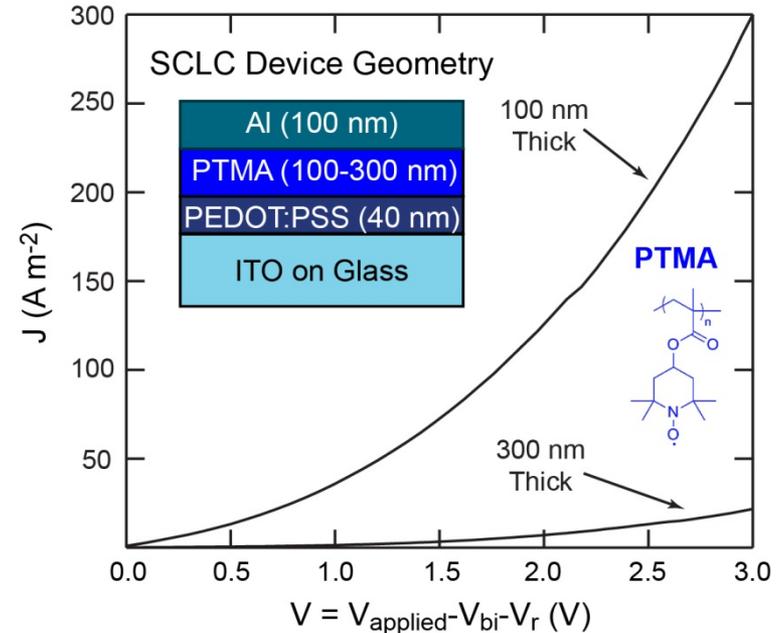


SCLC Mobility Calculation

$$V = V_{\text{applied}} - V_{\text{bi}} - V_r \quad ; \quad J = \frac{9}{8} \epsilon_0 \epsilon \mu \frac{L^3}{V^2}$$

$$\therefore \mu_{\text{P3HT}} \sim 8 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$$

SCLC Sandwich Structure for PTMA



SCLC Mobility Notes

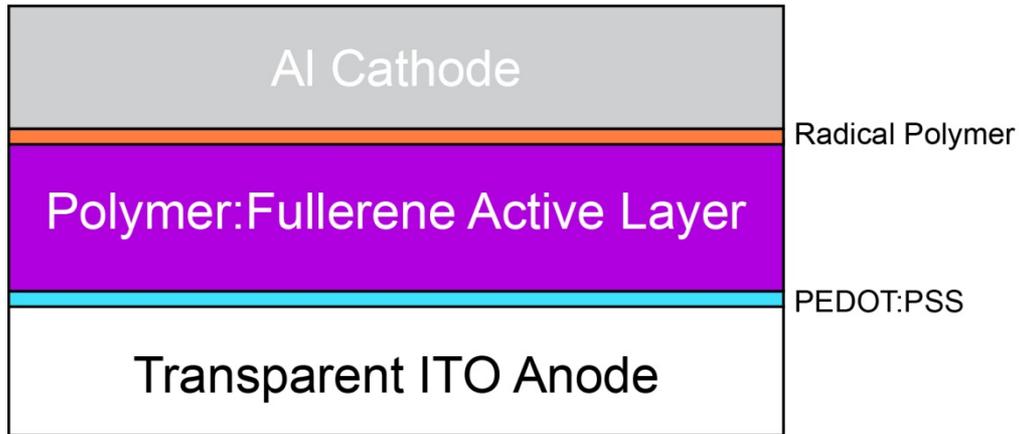
Mobility is Thickness Independent
(as expected for SCLC) and is:

$$\mu_{\text{PTMA}} \sim 6 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$$

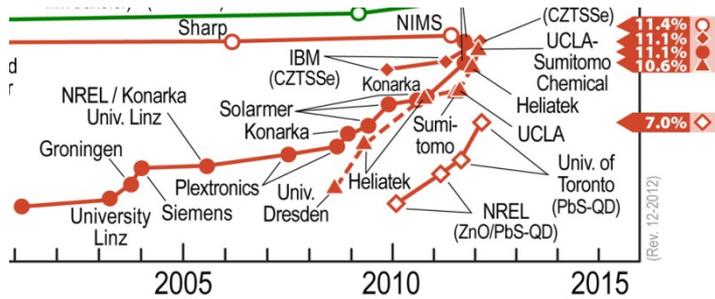
Recent Doping Studies Show High Promise for PTMA as a Transparent Conductor

Altering Molecular Architecture Changes SOMO Levels

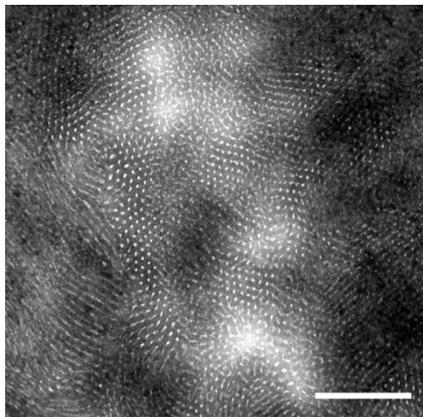
OPV Schematic



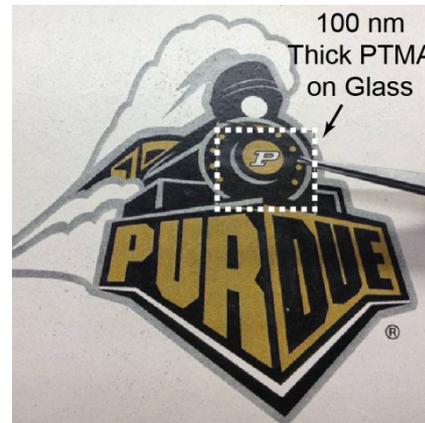
Summary and Future Outlook



The future of polymer solar cells is bright, and the design of new materials will continue to be a key role, with processing refinement and novel devices, in achieving higher device performance efficiencies.

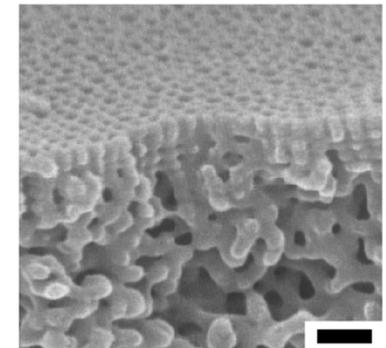
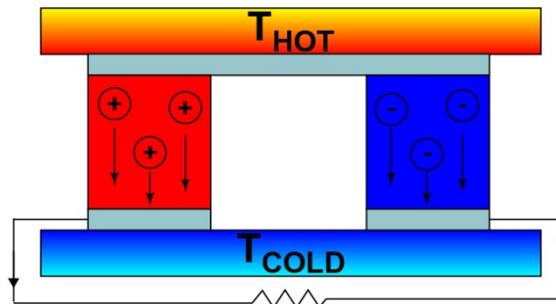
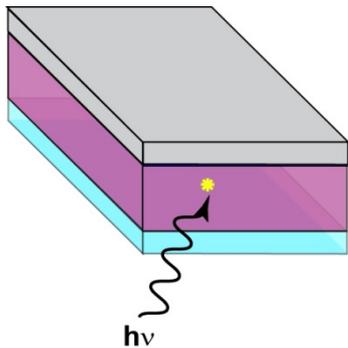


Diblock copolymers containing a semiconducting block can self-assemble into very useful structures for polymer solar cell active layers



Radical polymers have been synthesized and initial transport measurements are very promising for use as electrode modifiers in polymer solar cells

Creating New Materials Opens Many Applications Not Envisioned Originally



Acknowledgements

Boudouris Laboratory Research Team

Segalman Research Team

University of California, Berkeley
Lawrence Berkeley National Lab
Department of Energy

Collaborators

- **Ashraf Alam (Purdue)**
 - Biswajit Ray
- **Rakesh Agrawal (Purdue)**
 - Bryce Walker
 - Nathaniel Carter
 - Charles Hages
 - Erik Sheets
- **William Phillip (Notre Dame)**
 - Jacob Weidman

Lizbeth Rostro and Aditya Baradwaj

We Gratefully Thank the Agencies Funding The Radical Polymer Work

