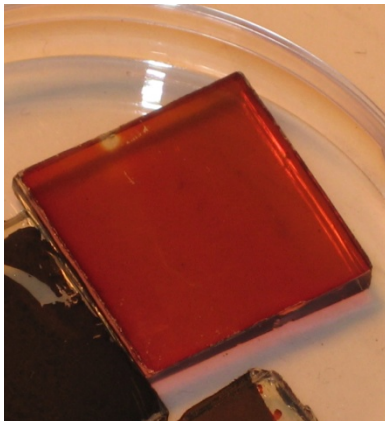
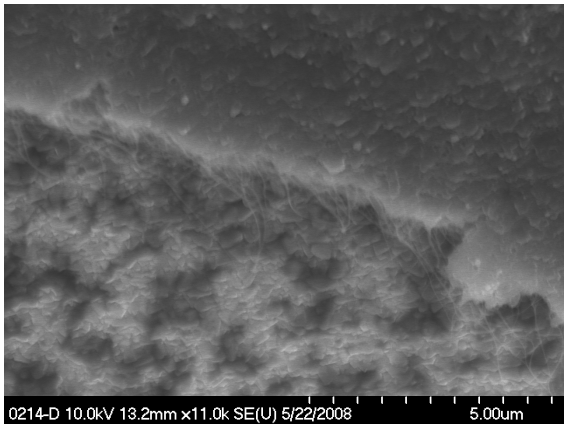
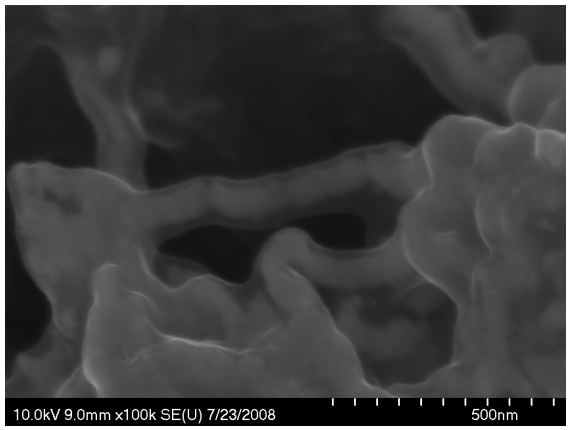
PENNSTATE

Poly(thiophene)/Carbon Nanotube Composites for Solar Cells







Romesh J. Patel,* Ilia N. Ivanov,+ Michael A. Hickner*

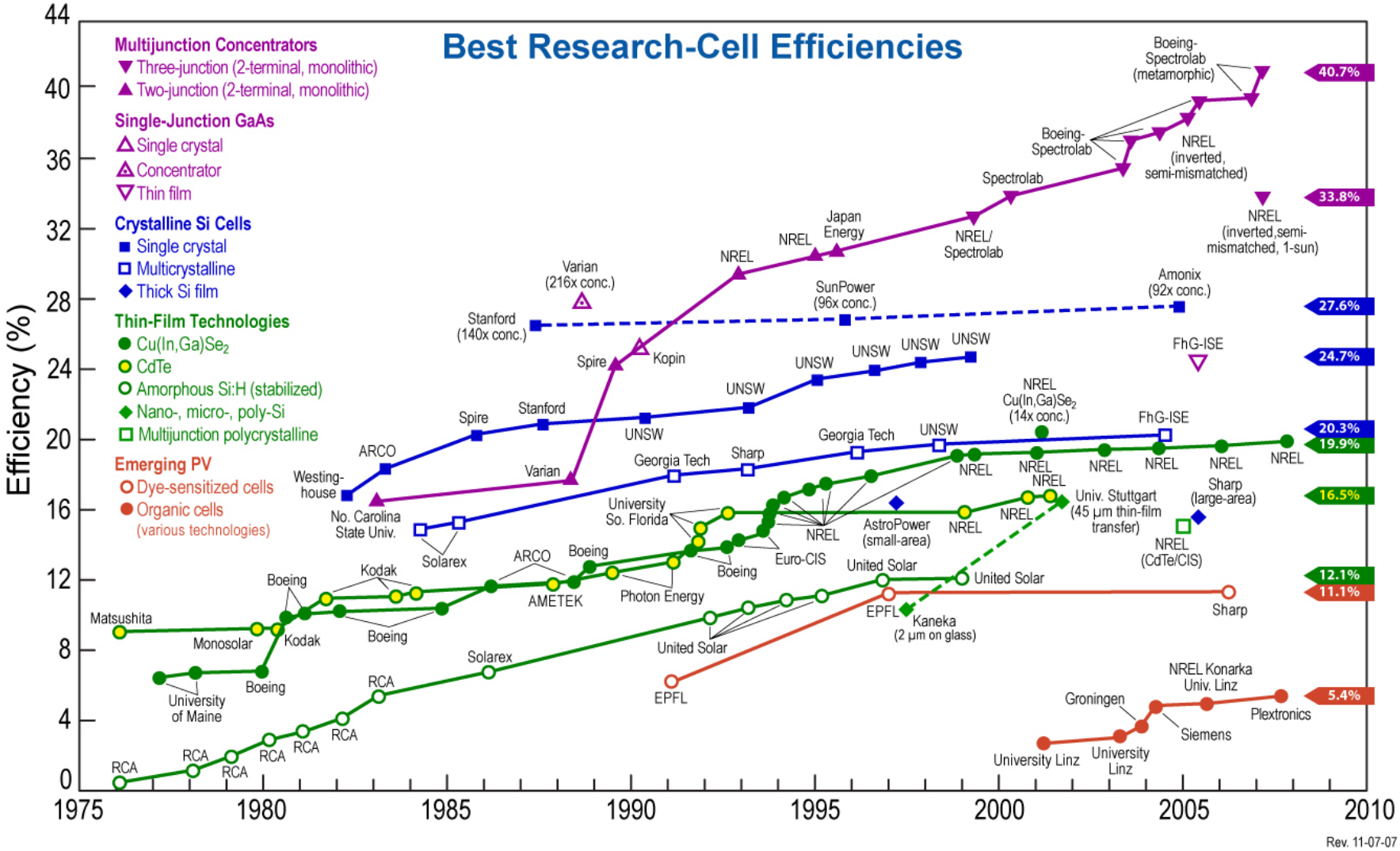
*Department of Materials Science and Engineering
The Pennsylvania State University

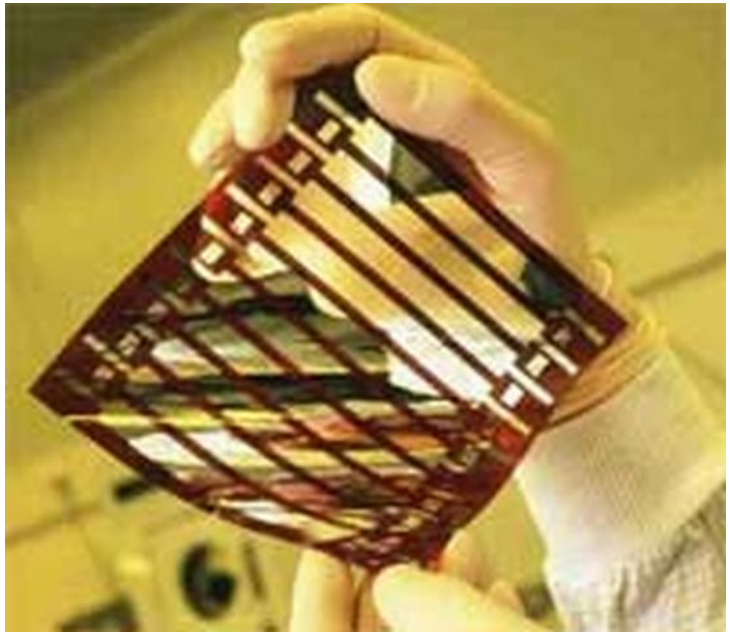
+Functional Hybrid Nanostructures Group
Center for Nanophase Materials Sciences, ORNL

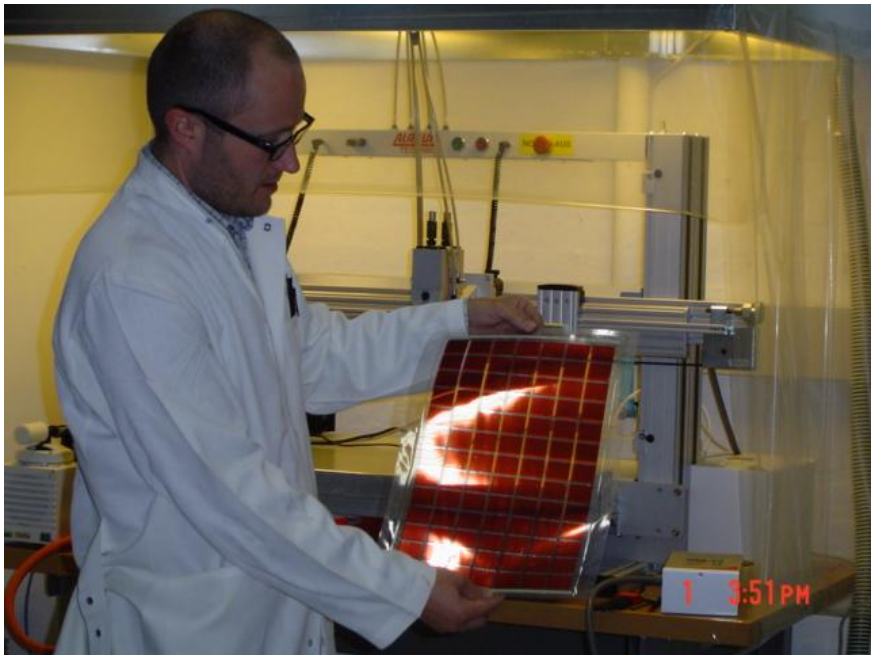
hickner@matse.psu.edu

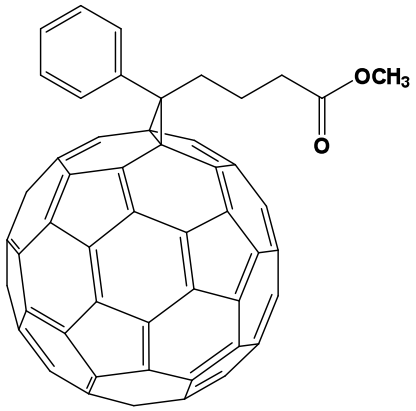
DEPARTMENT OF
MATERIALS SCIENCE AND ENGINEERING
COLLEGE OF EARTH AND MINERAL SCIENCES

CNMS User Meeting, Oak Ridge National Laboratory
September 14, 1020

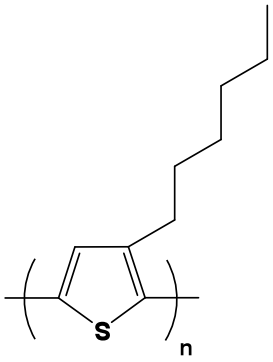

Best Research-Cell Efficiencies
Efficiency (%)
Multijunction Concentrators
Three-junction (2-terminal, monolithic)
Two-junction (2-terminal, monolithic)
Single-Junction GaAs
Single crystal
Concentrator
Thin film
Crystalline Si Cells
Single crystal
Multicrystalline
Thick Si film
Thin-Film Technologies
Cu(In,Ga)Se2
CdTe
Amorphous Si:H (stabilized)
Nano-, micro-, poly-Si
Multijunction polycrystalline
Emerging PV
Dye-sensitized cells
Organic cells
(various technologies)
40.7%
33.8%
27.6%
24.7%
20.3%
19.9%
16.5%
12.1%
11.1%
5.4%
Rev. 11-07-07



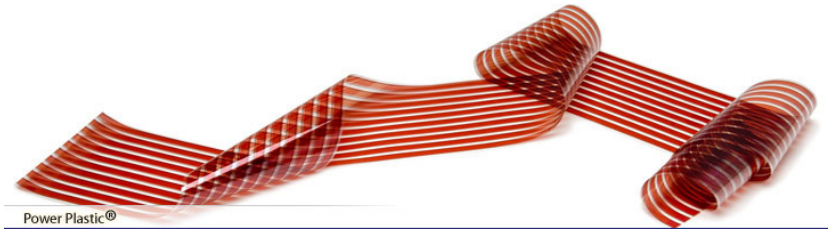




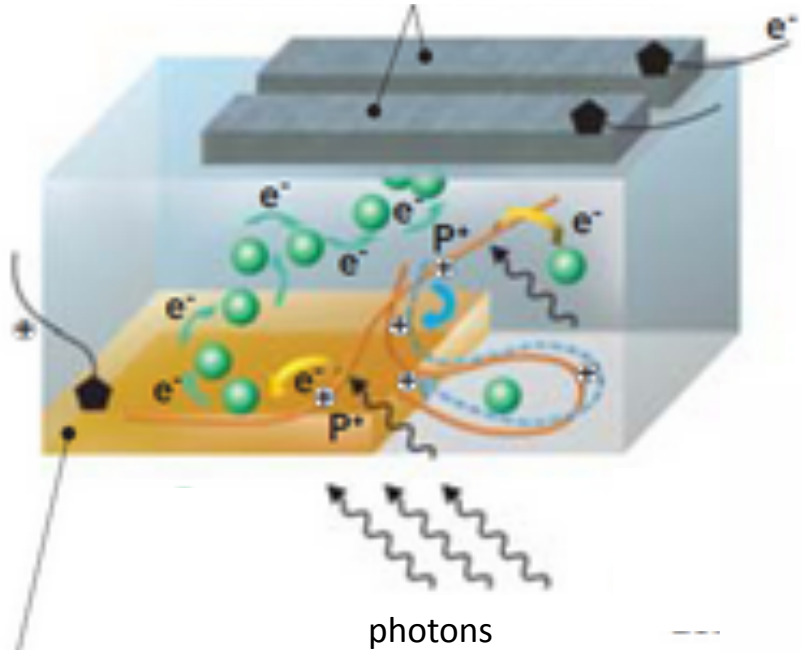
phenyl-C61-butyric acid methyl ester
PCMB

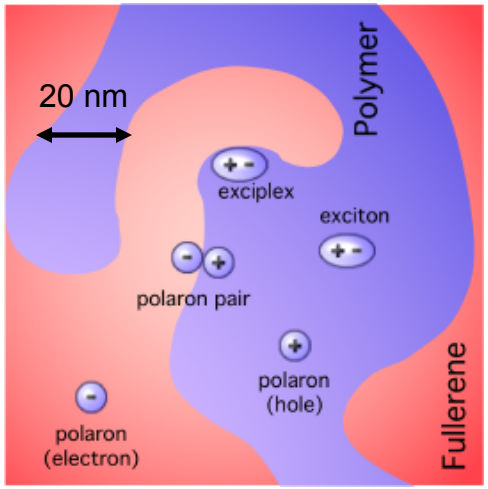


poly(3-n-hexylthiophene)
P3HT

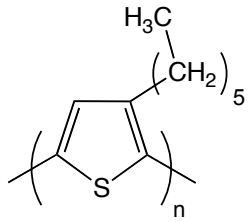


Photovoltaic structures and processes

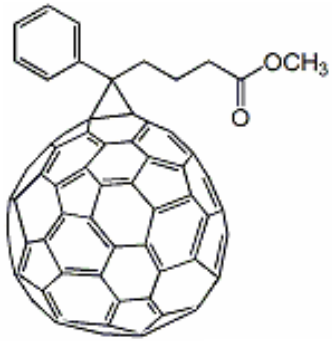


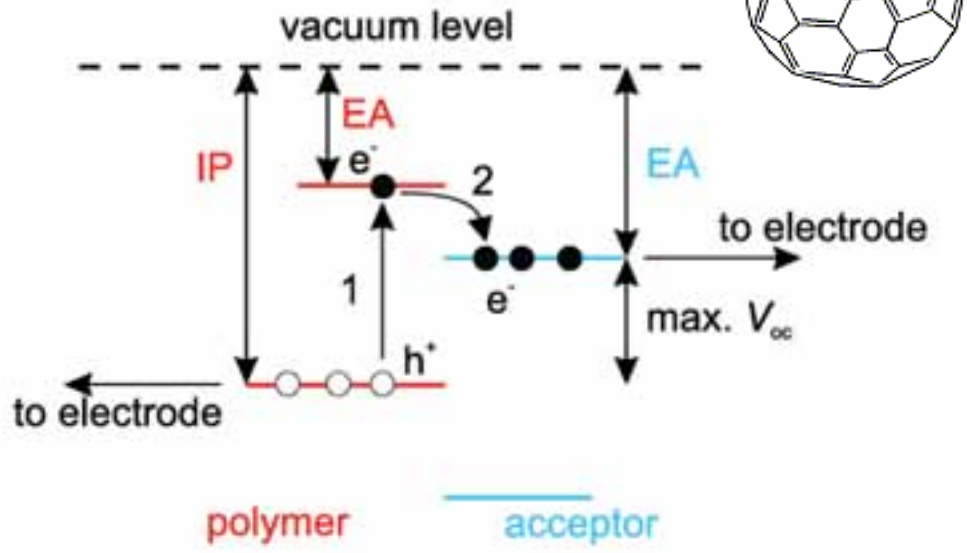


P3HT



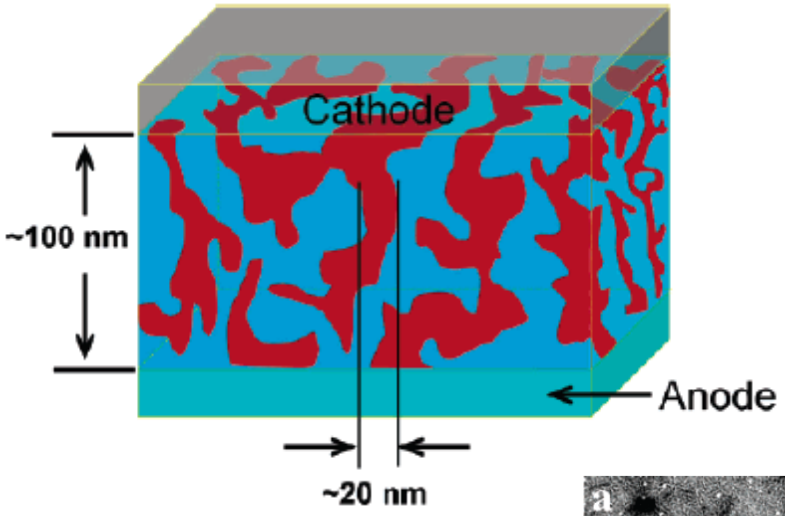
PCBM



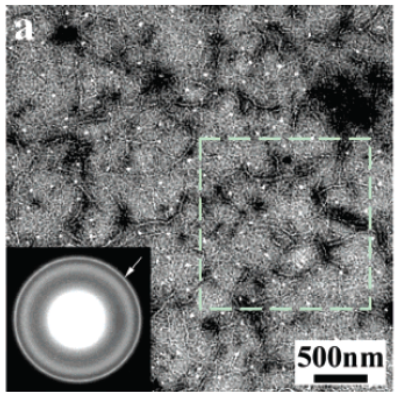


Bulk heterojunction concepts

Present



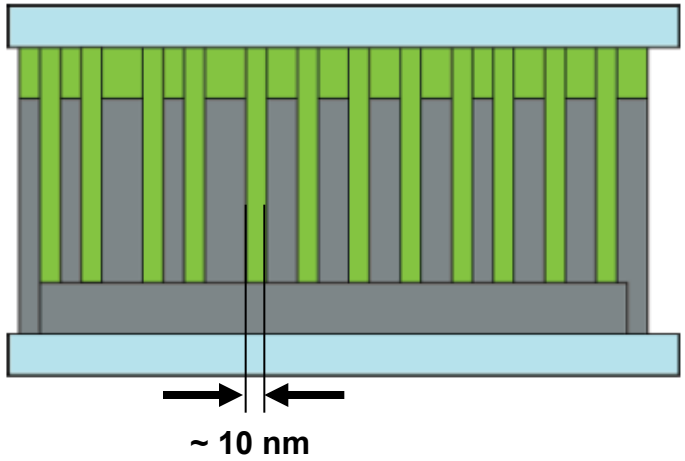
Acceptor **Donor**



Spinodal decomposition and annealing of donor acceptor blend as a primary approach.

X. Yang, J. Loos *Macromolecules* **2007.**
Loos, et al., *Nano Lett.* **2005**.

Ideal

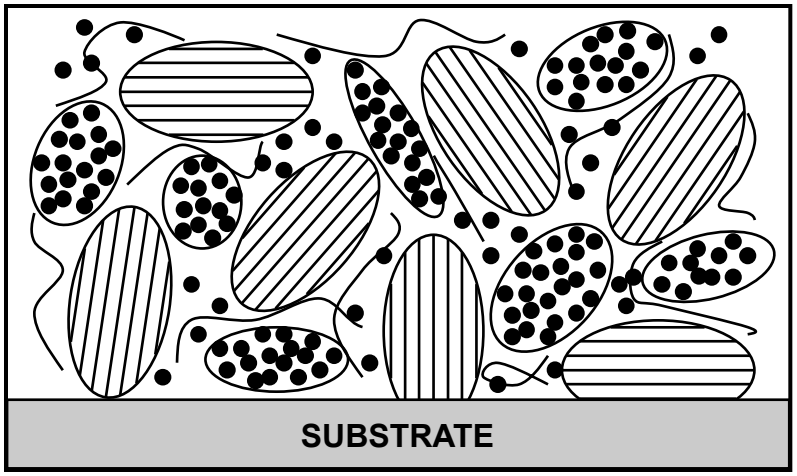


Acceptor **Donor**

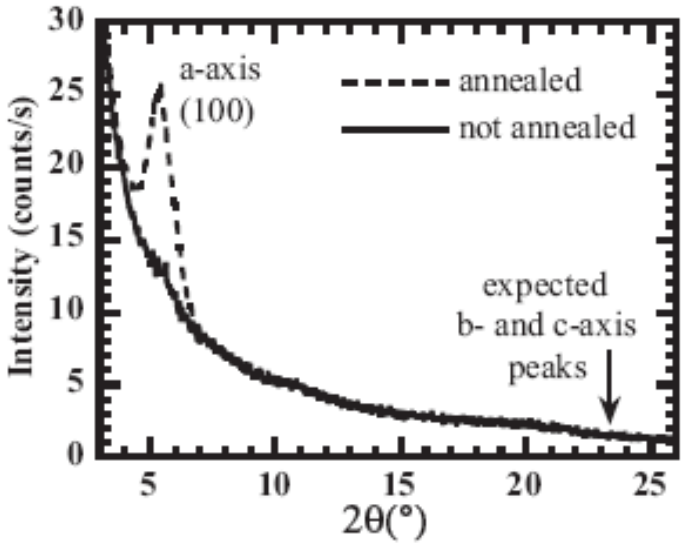
Structured interface with high interfacial area and direct paths for long-range transport.

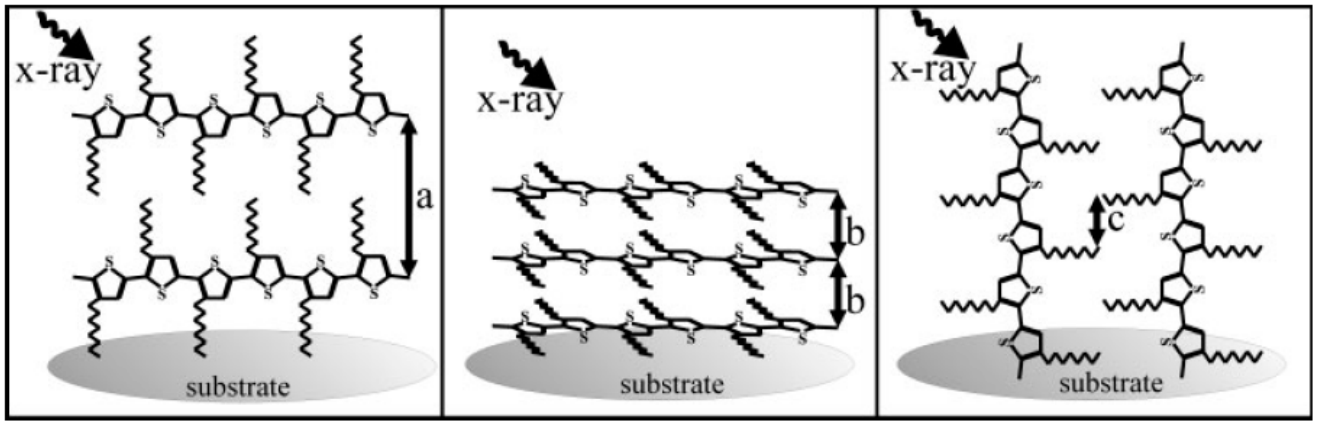
Sariciftci, et al. *Chem. Rev.* **2007.**

Polymer crystal alignment in PCBM/P3HT spun cast and annealed blends



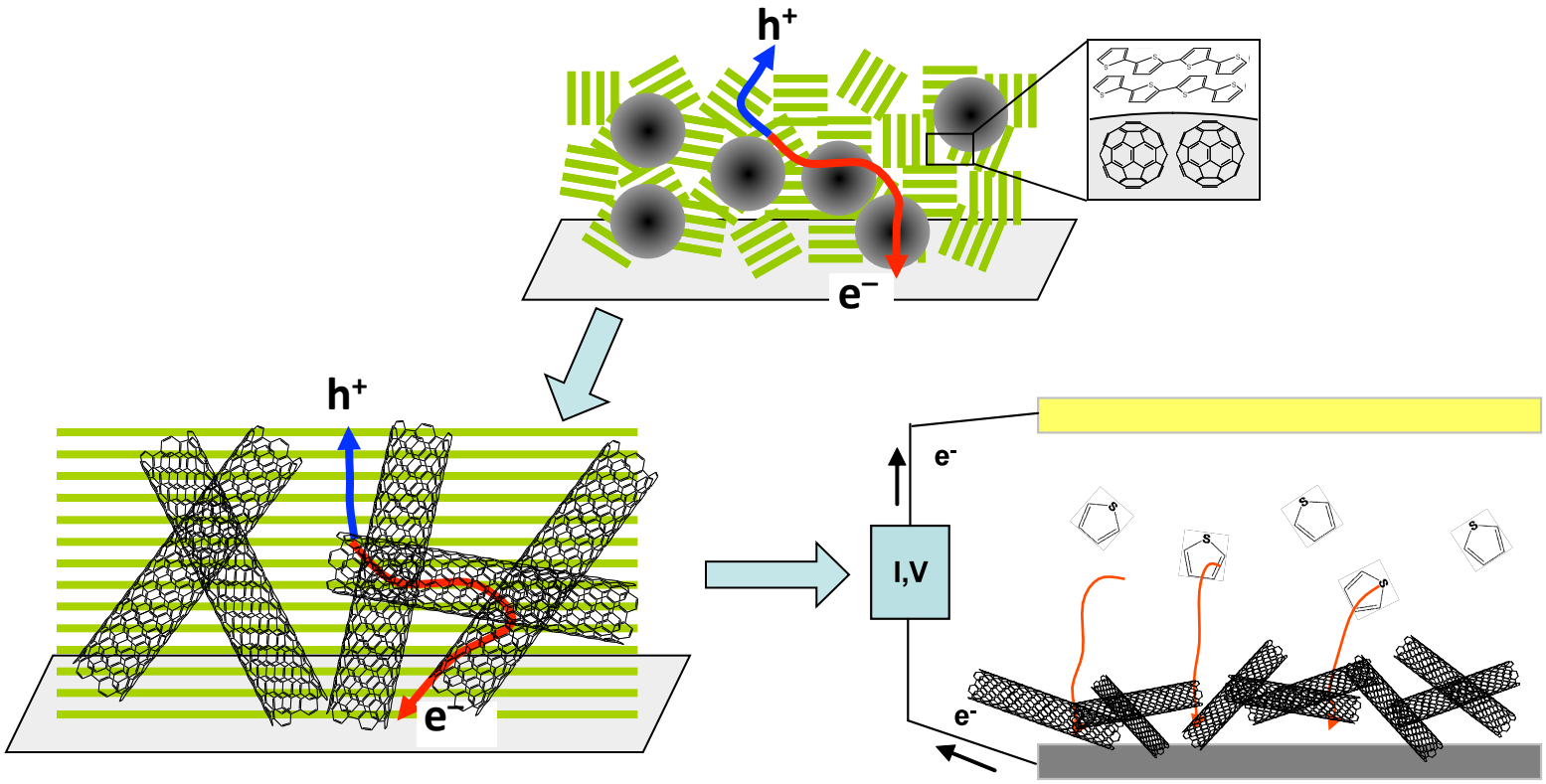
PCBM/P3HT blend





Gobsch., et al, *Adv. Funct. Mater.* **2005**, 15, 1193-1196.

Proposed layered polymers/CNT hierarchical morphologies



Requirements

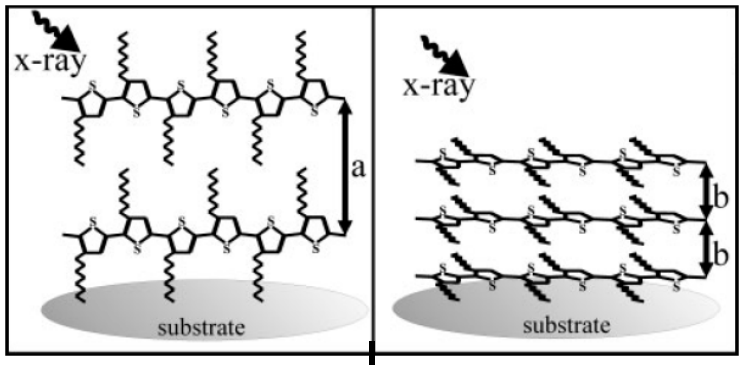
- light absorption
- charge transfer
- continuous pathways

Interesting possibilities

- π-π conjugated (stacked) polymer
- high aspect ratio electron acceptor

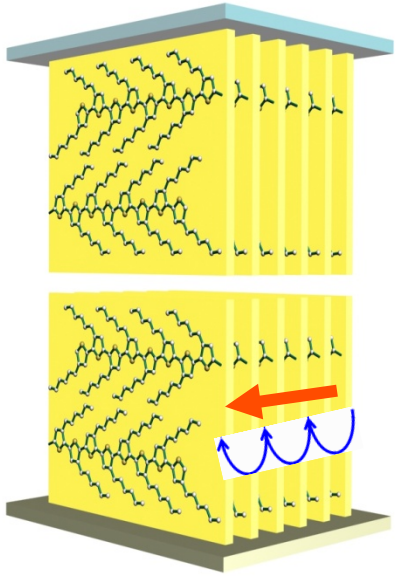
π-π stacking to facilitate interchain hopping

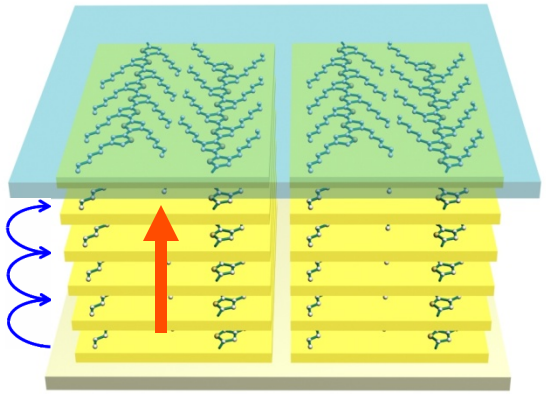
Spin-coating:
Perpendicular orientation



Electro-polymerization:

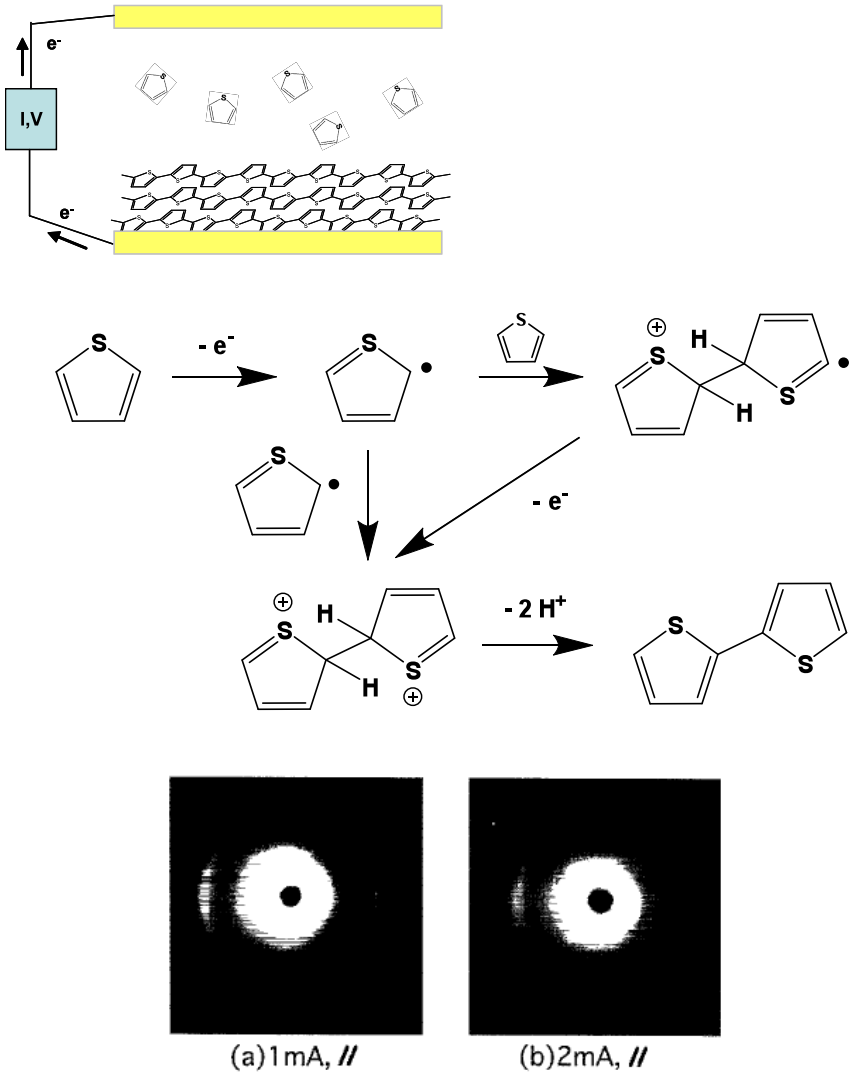
Parallel orientation



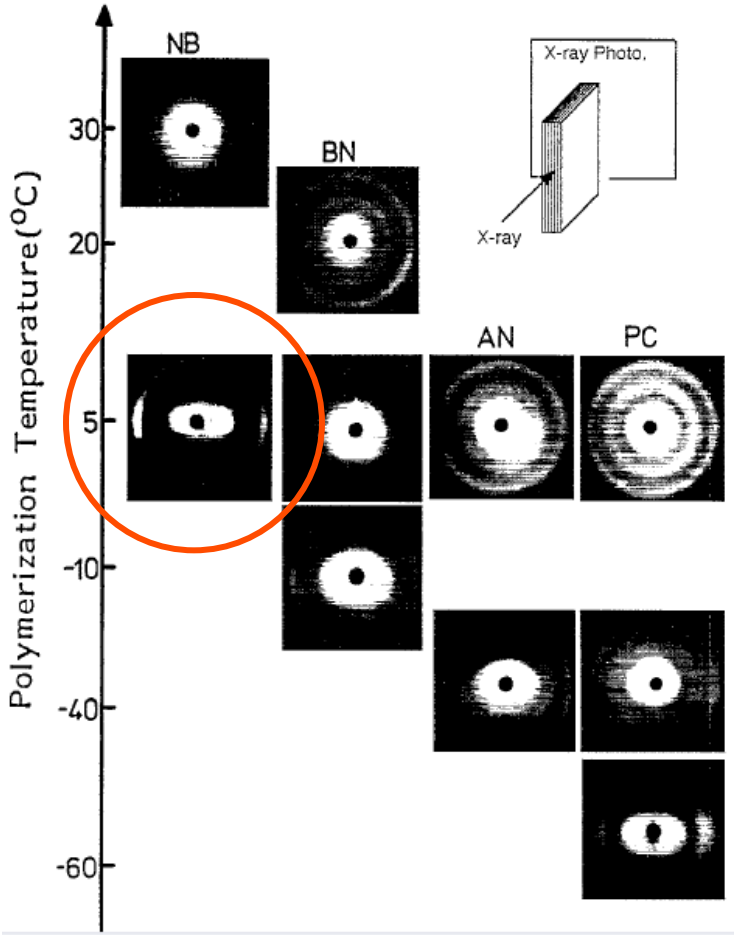


10 % efficiency possible by stacking
Blom, W. M.; et al *Phys. Rev. B*. 2005, 72, 085205.

Electro-polymerization and ordering of 3HT

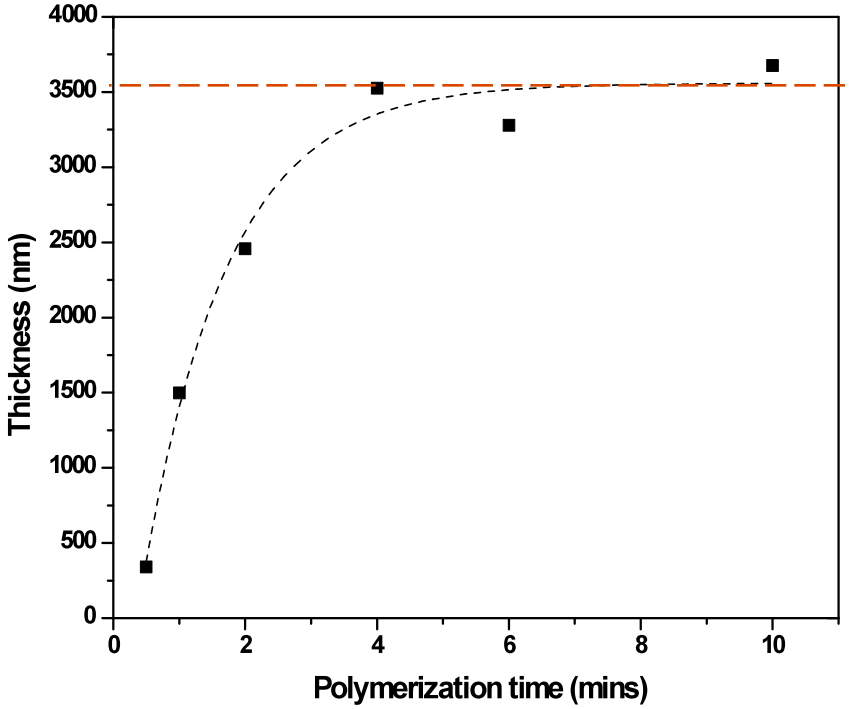


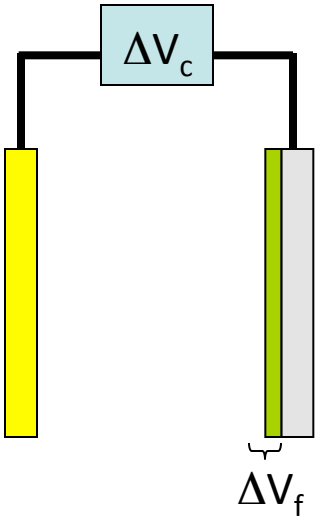
S. Osawa, T. Ogawa, M. Ito *Synthetic Metals* **1997.**



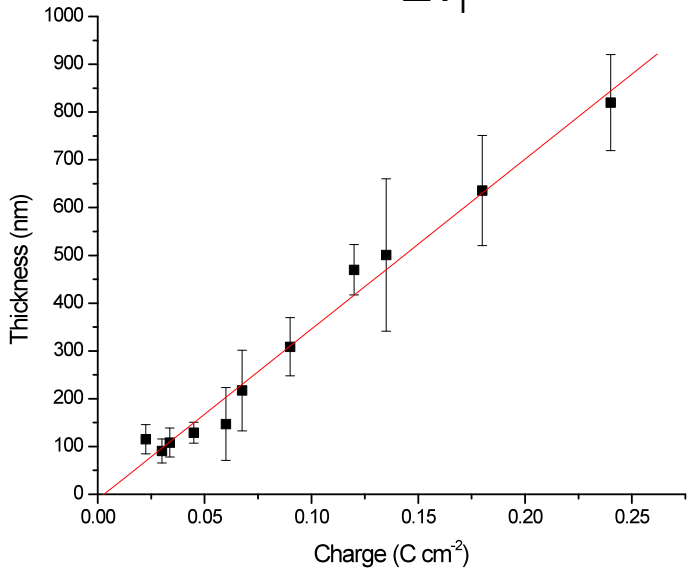
Slow down reaction kinetics to ensure parallel stacking by minimizing polymerization temperature and current.

Thickness control during electrochemical polymerization

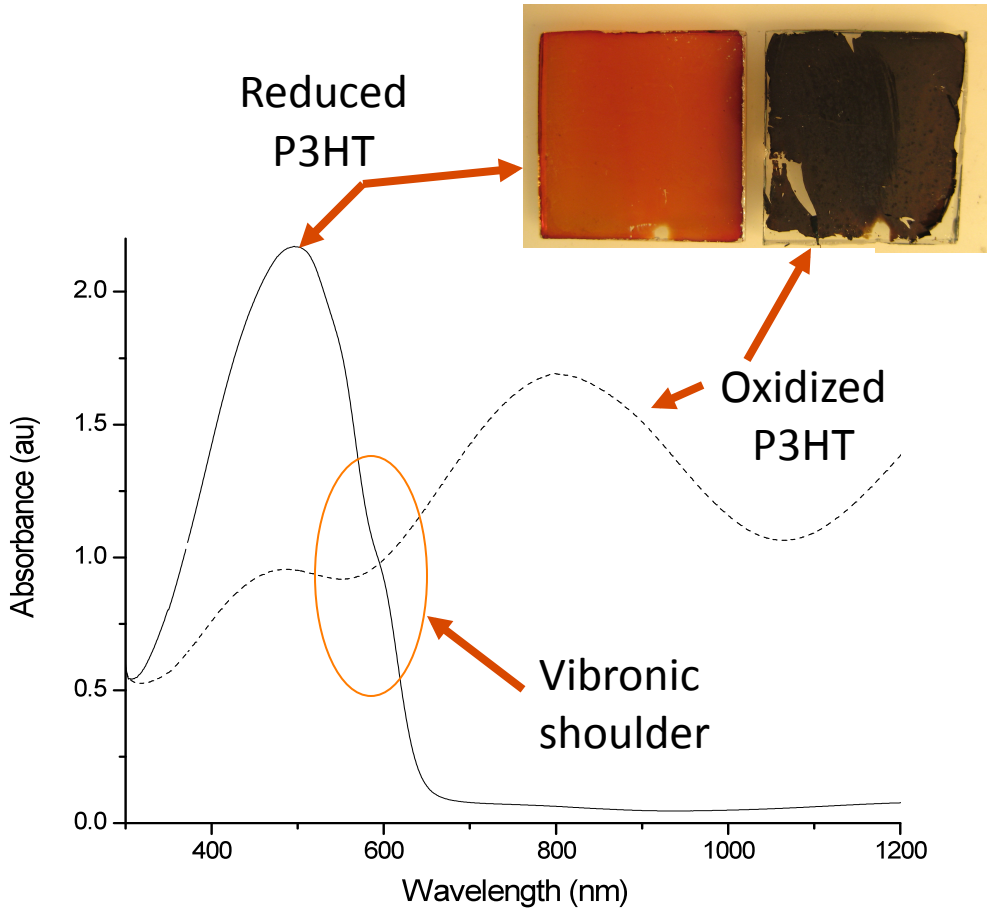




Film growth restricted by the oxidized film resistance

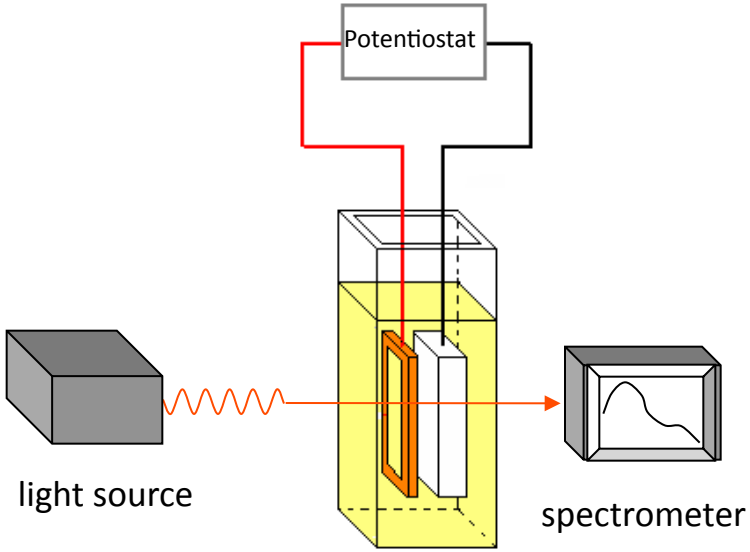


UV-vis of oxidized and reduced P3HT films

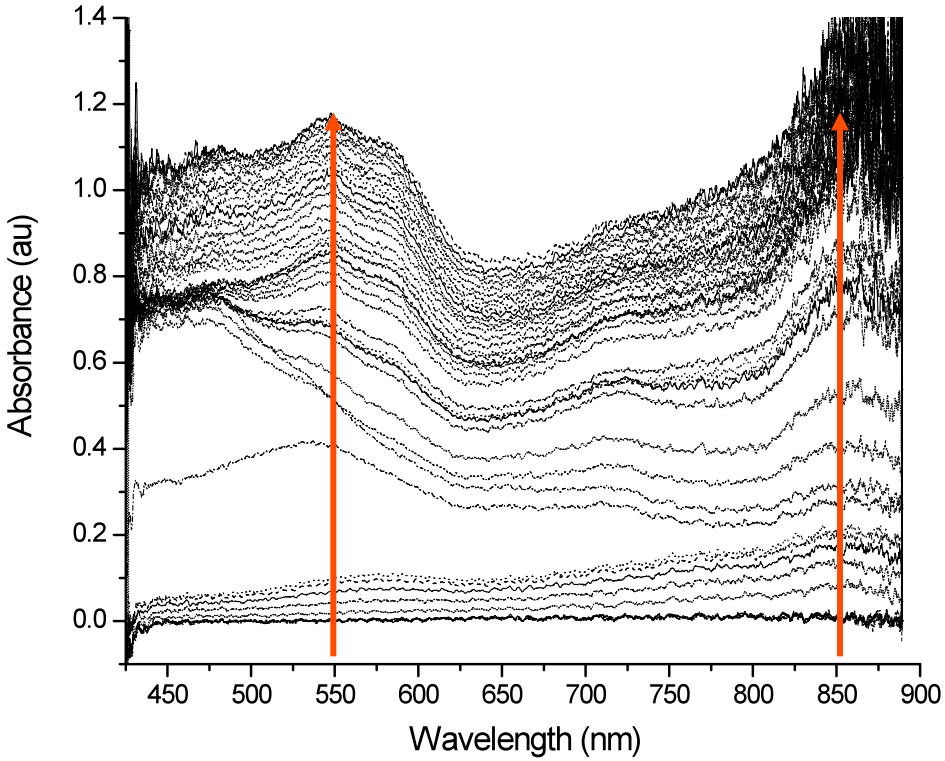


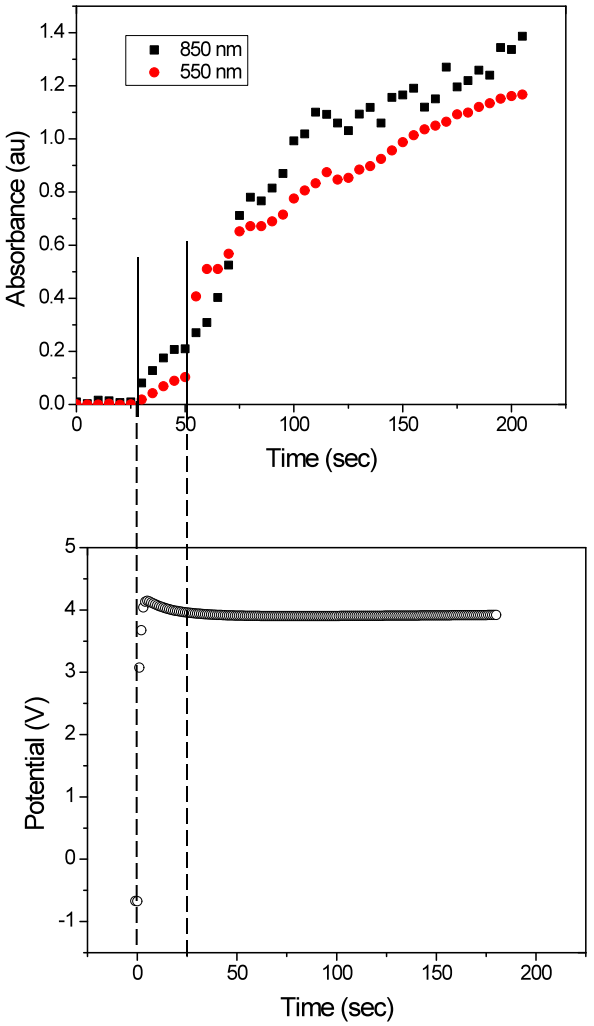
Peak at ~ 500 nm indicates reduced (conjugated) P3HT

Presence of vibronic shoulder indicates interchain order in P3HT



In-situ polymerization spectra

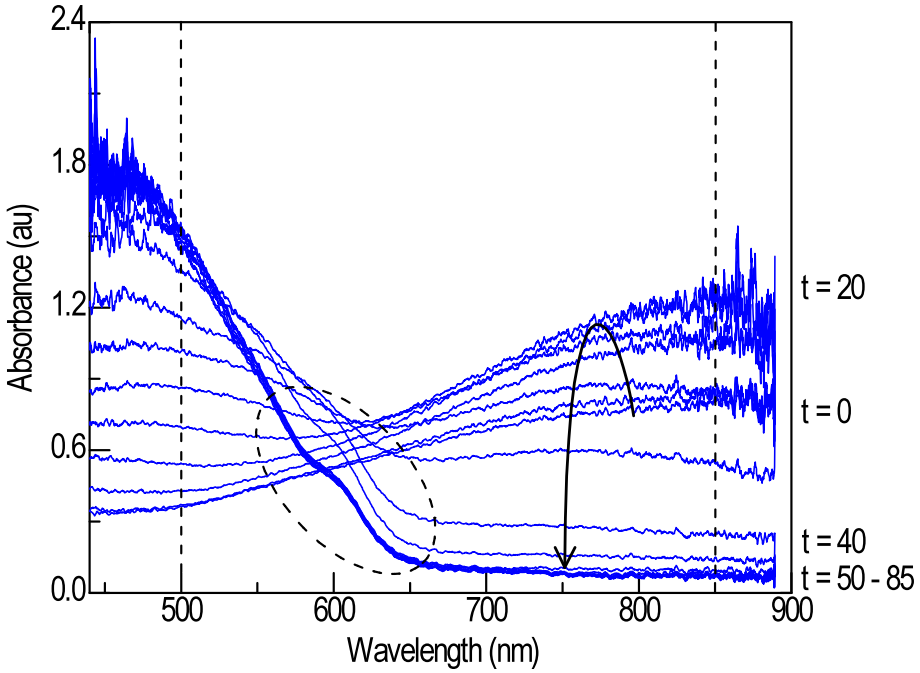


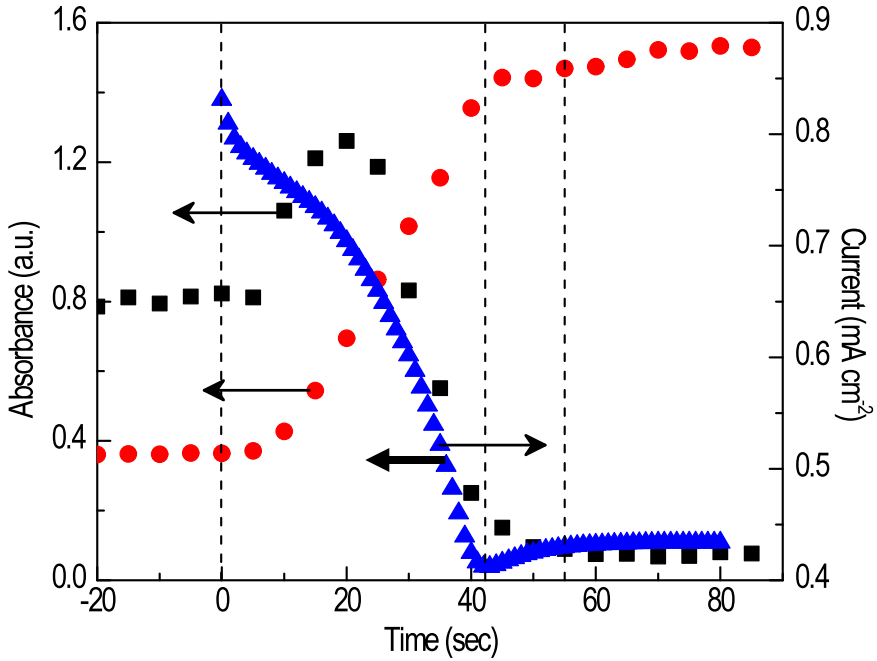


Spectra recorded every 5 sec.

550 nm → reduced P3HT in solution

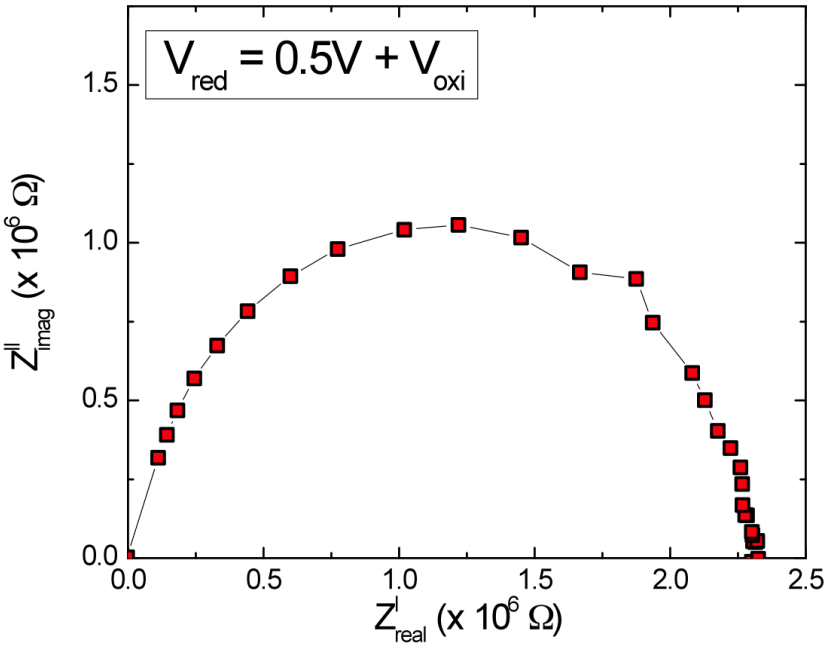
In-situ reduction spectra



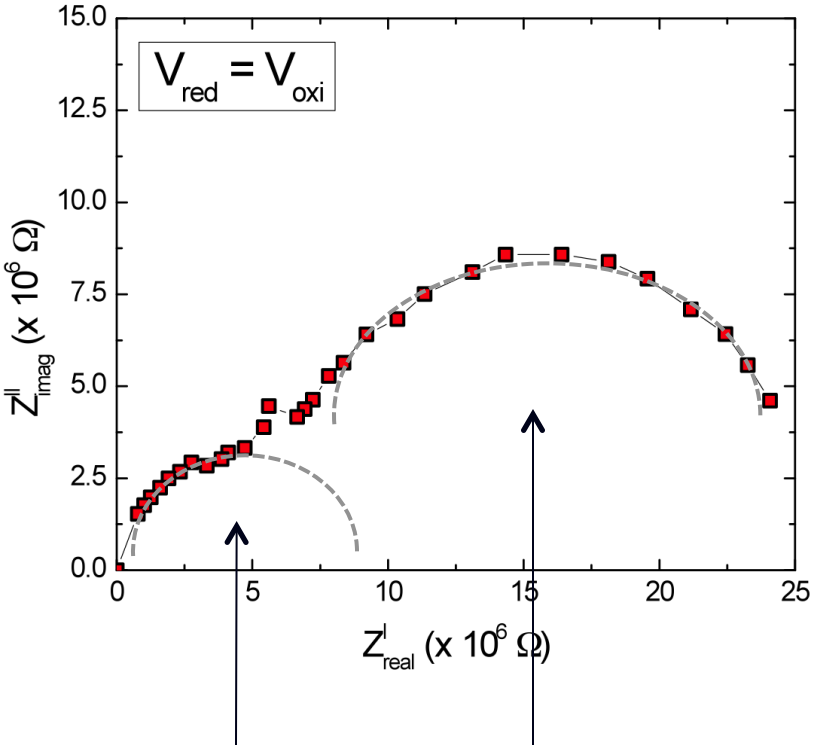


Vibronic shoulder develops ~ 10 sec after flattening of current-time curve

Reduction potential determines impedance response and charge defects of thin film

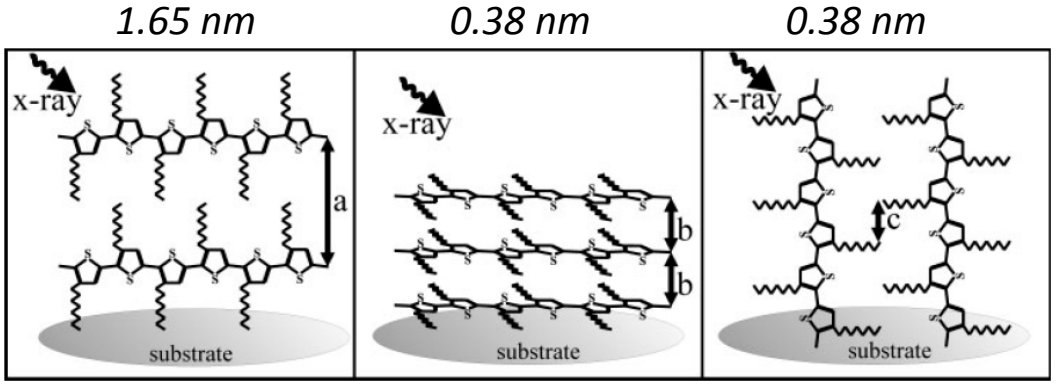


one capacitive process where all of the deep traps are filled



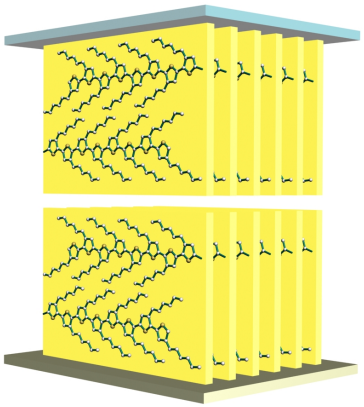
two capacitive processes
- may indicate presence of deep traps that are not completely filled during reduction of the film

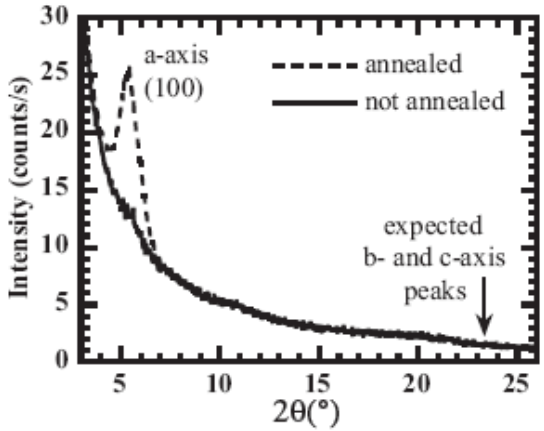
P3HT stacking at electrode surface



Spin-coating:

Perpendicular orientation



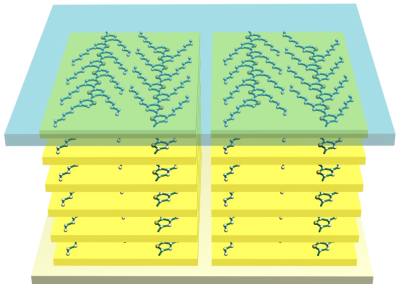


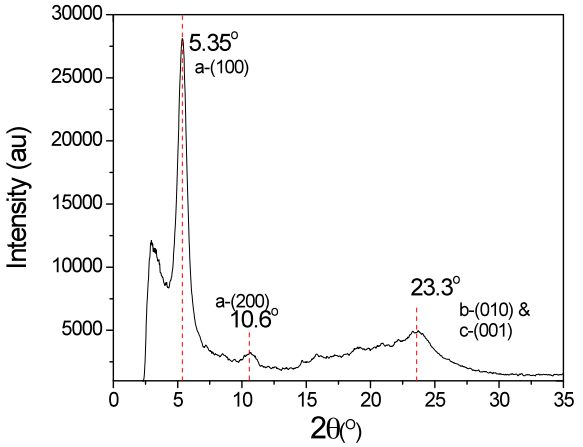
Need defects in perpendicular stacks for electrode injection.

Gobsch, Brabec, et al. *Adv. Func. Mater.* **2005.**

Electro-polymerization:

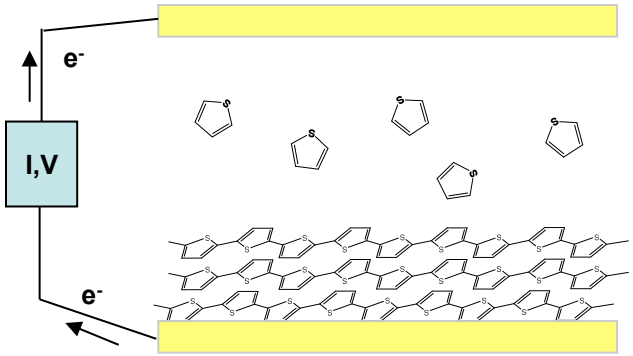
Parallel orientation

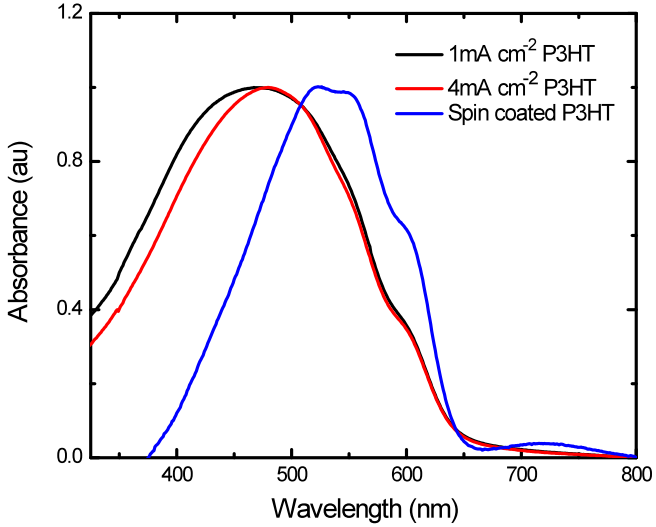


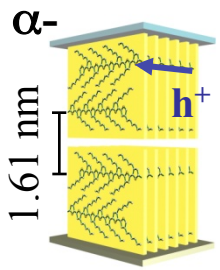


Parallel stacking offers a more direct path for hole transport

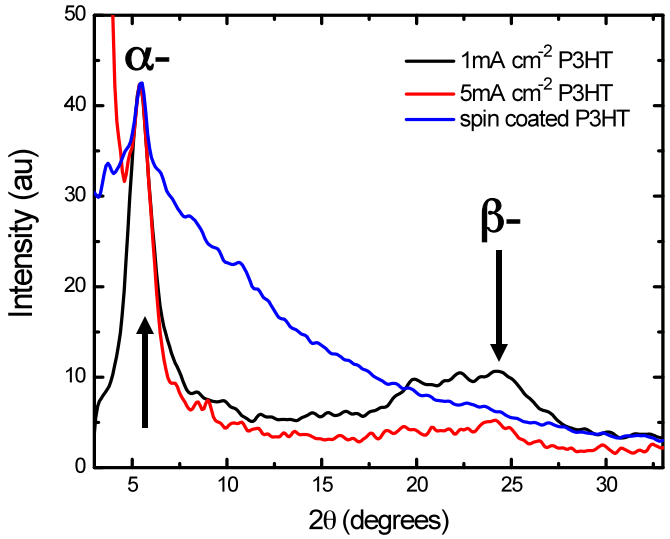
Preferential alignment: effect on absorbance

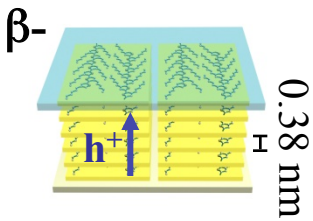






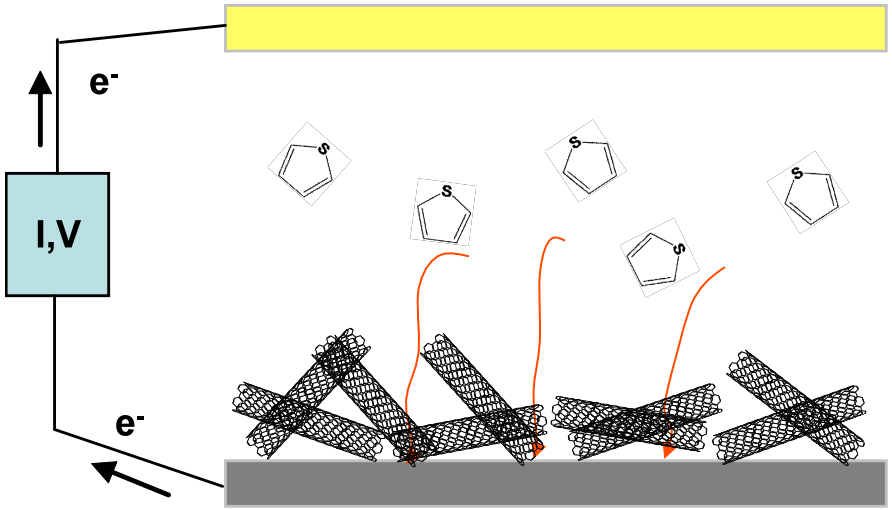
Undesired P3HT crystal orientation.

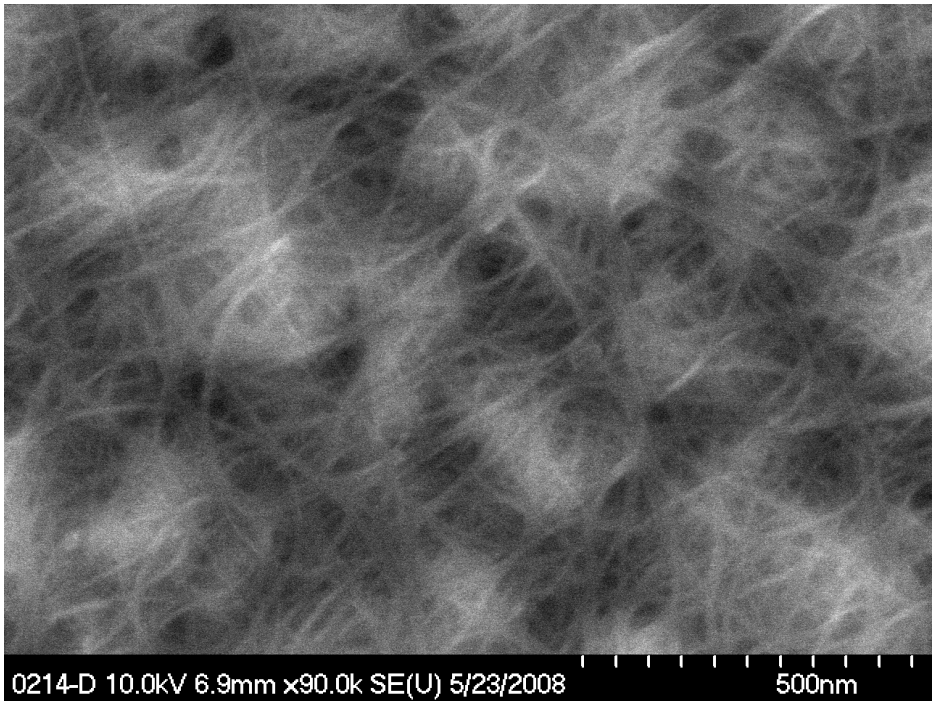




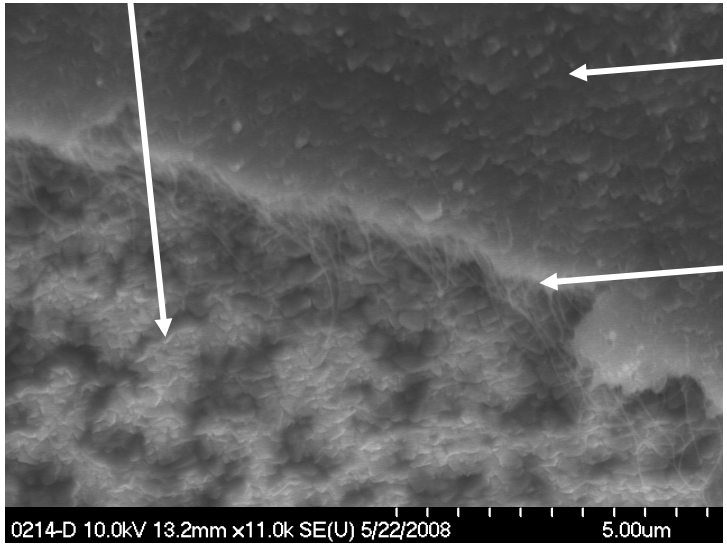
More direct path for charge transport.

Electro-polymerization in CNT mats



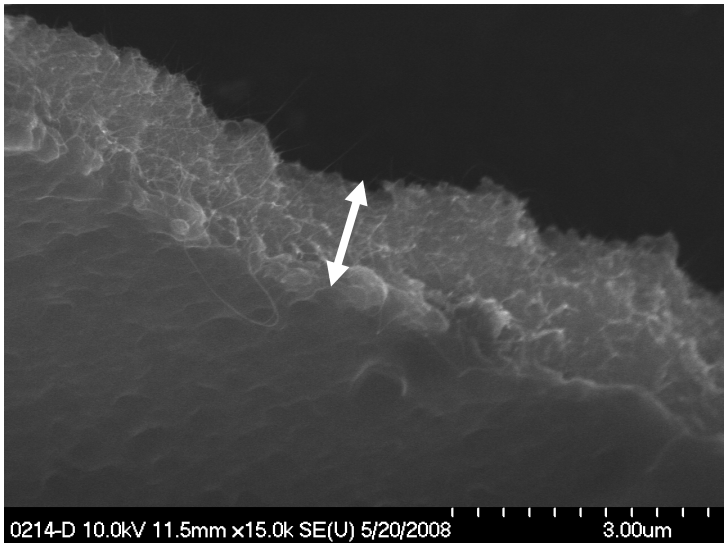


FTO substrate

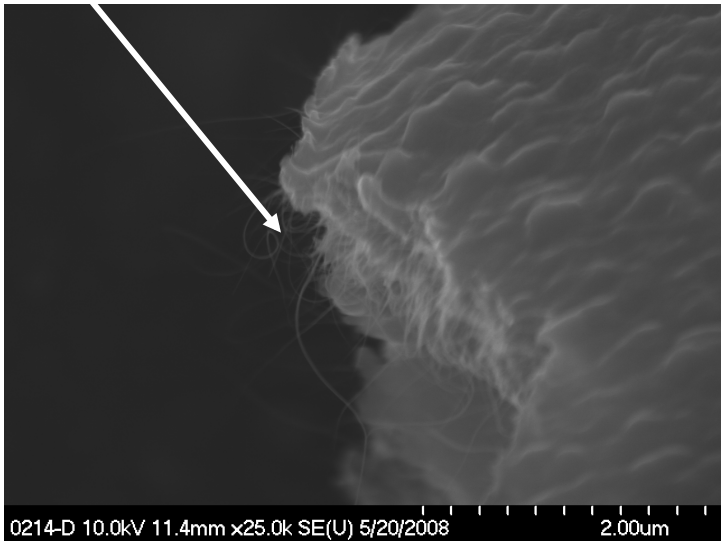


P3HT/SWNT composite film

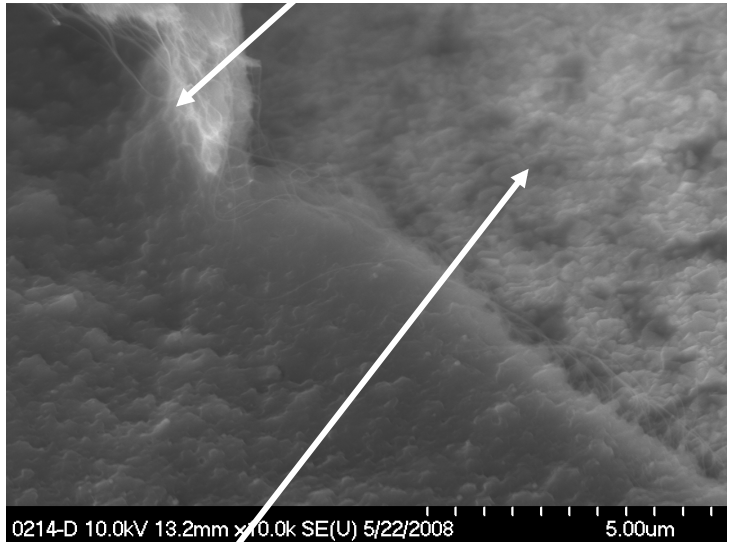
P3HT/SWNT edge



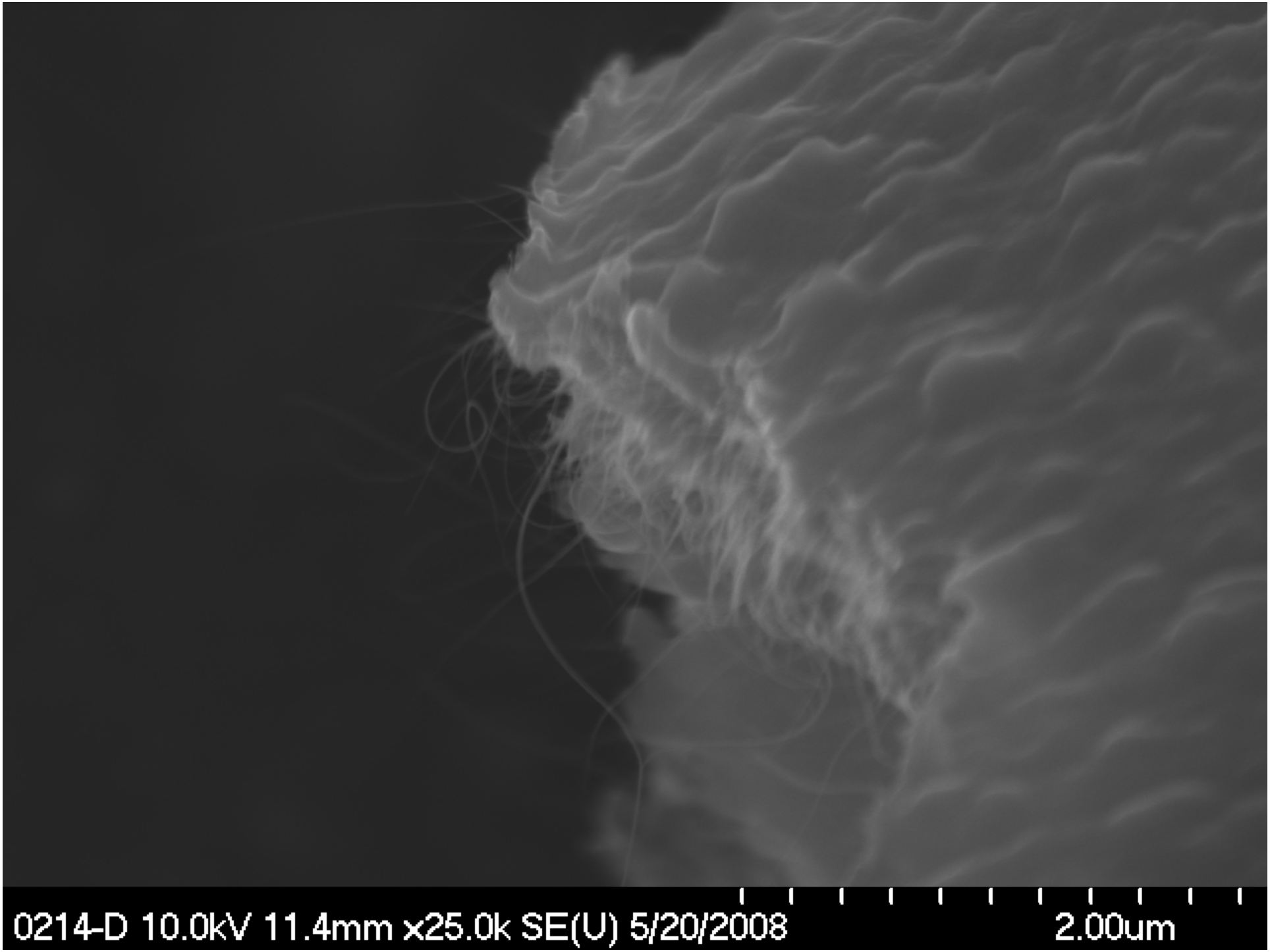
P3HT/SWNT edge



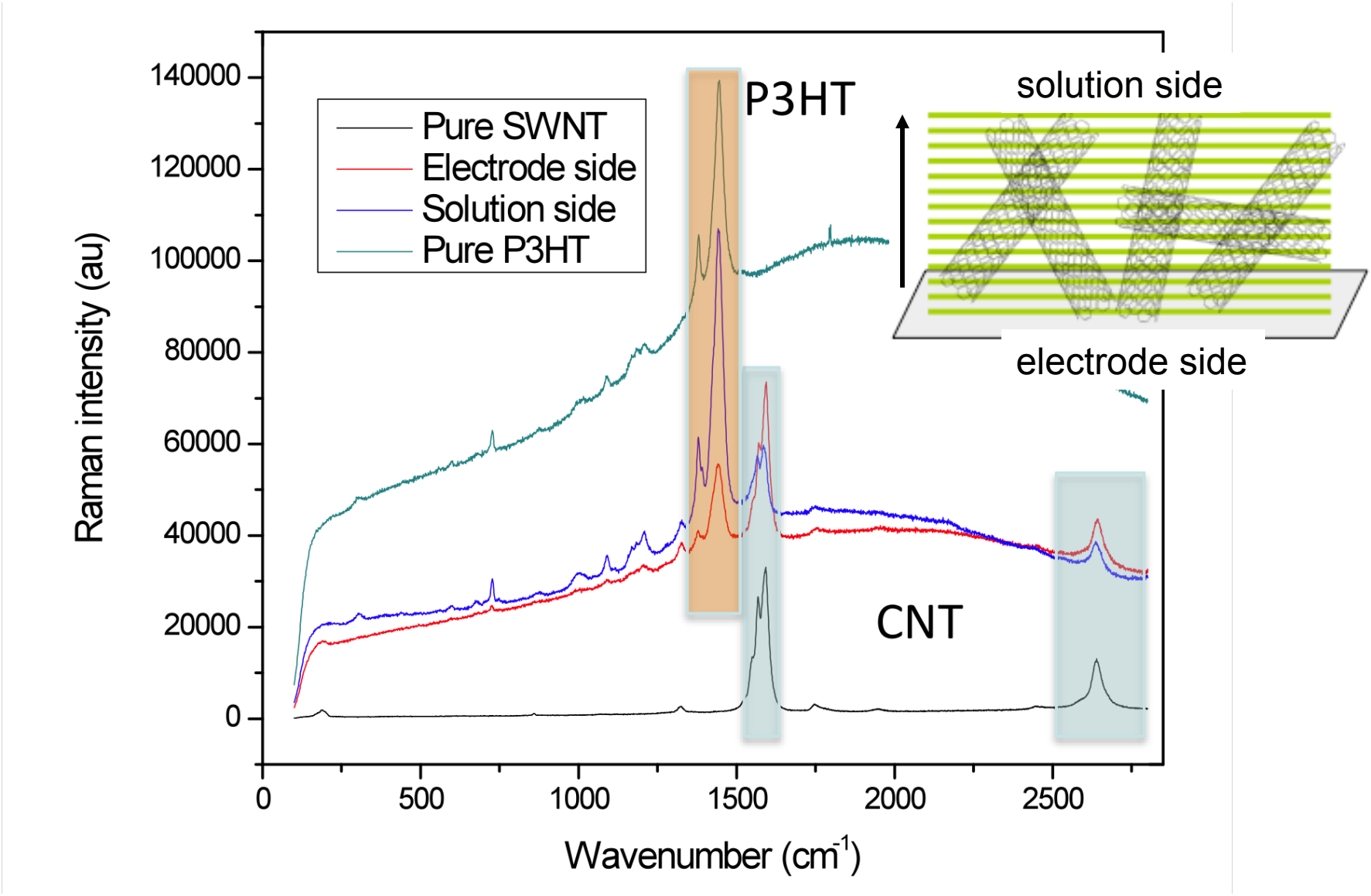
P3HT/SWNT edge



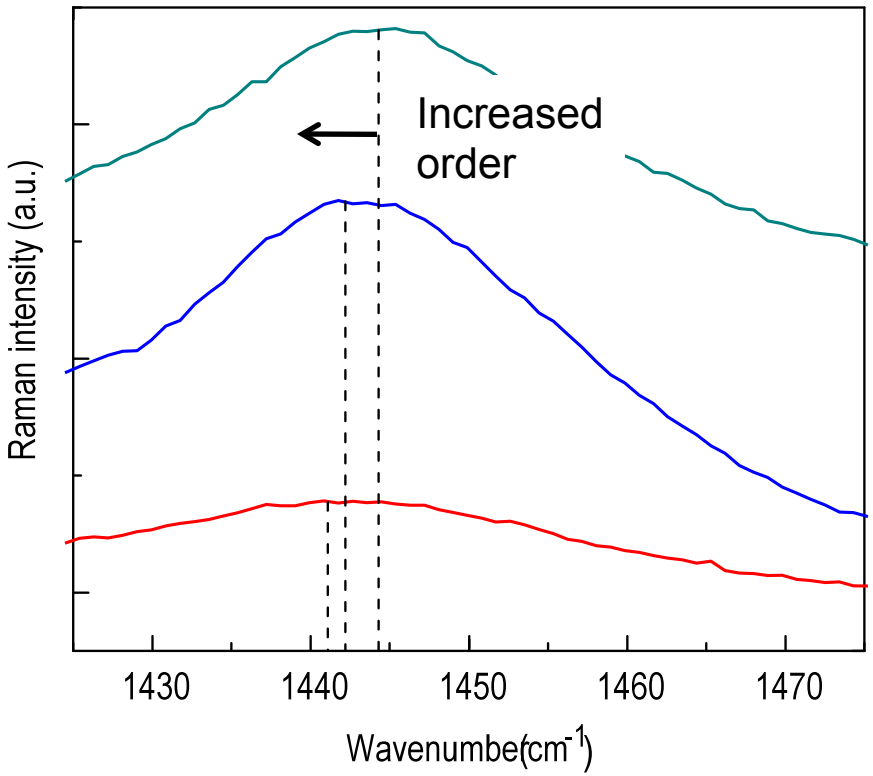
FTO substrate


0214-D 10.0kV 11.4mm x25.0k SE(U) 5/20/2008
2.00um

Raman spectroscopy of electropolymerized films



P3HT stacking at electrode surface



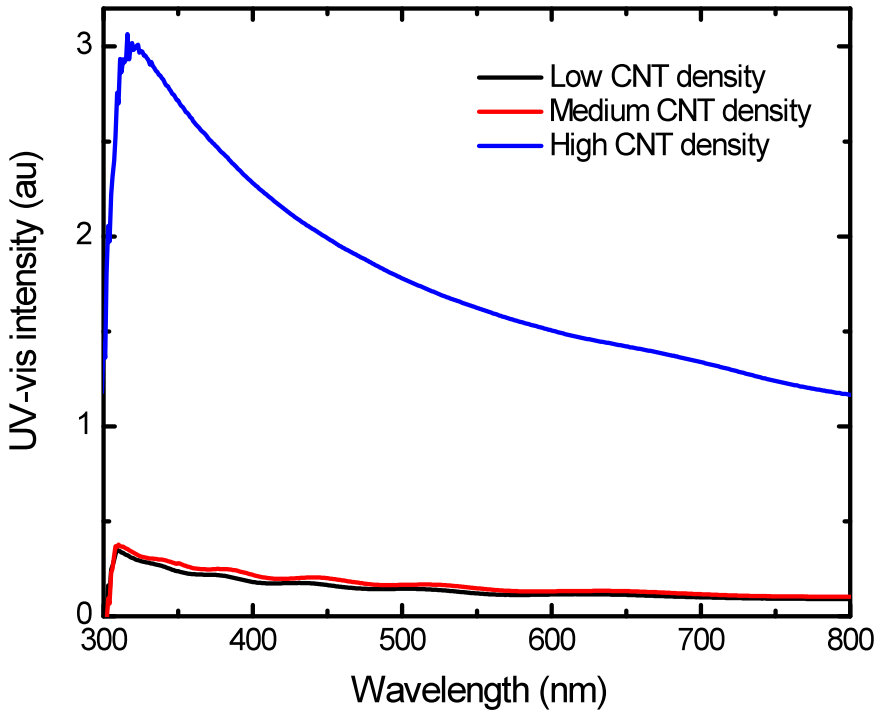
Surface	Peak position
Pure P3HT	1444.4 cm^{-1}
Solution side	1442.4 cm^{-1}
Electrode side	1441.5 cm^{-1}

Downward trend in wavenumber indicates an increase in P3HT stacking

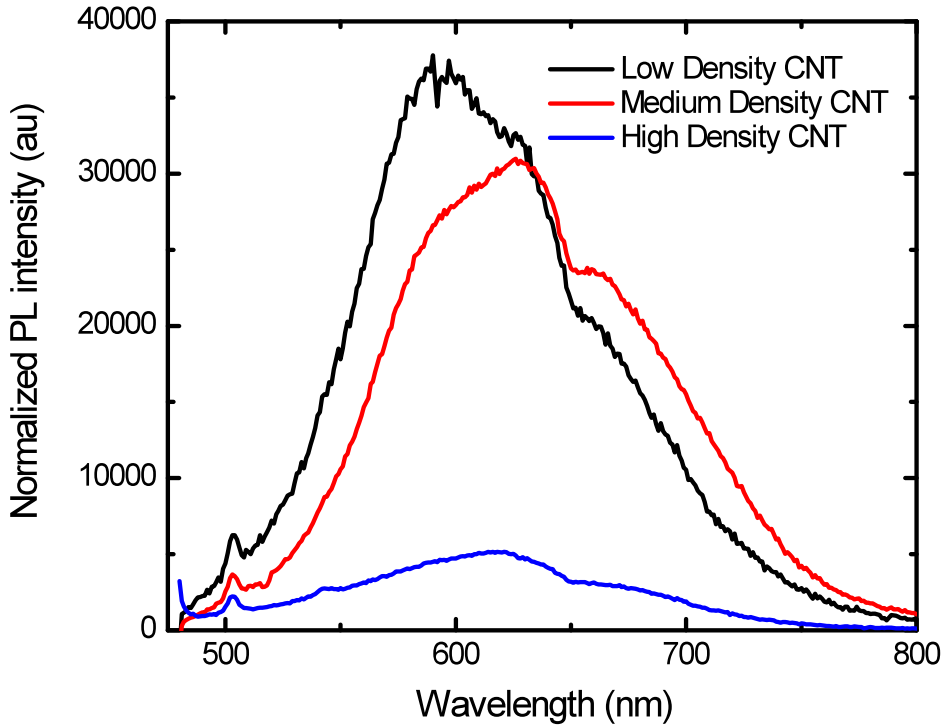
More stacking observed closest to the substrate

Guo, et al. *Thin Solid Films* **2008.**

Increasing CNT density decreases photoluminescence due to charge transfer

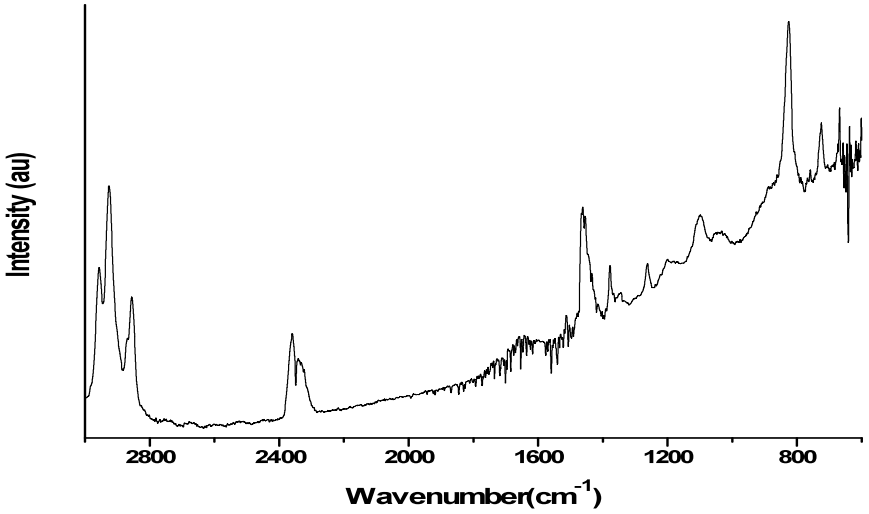


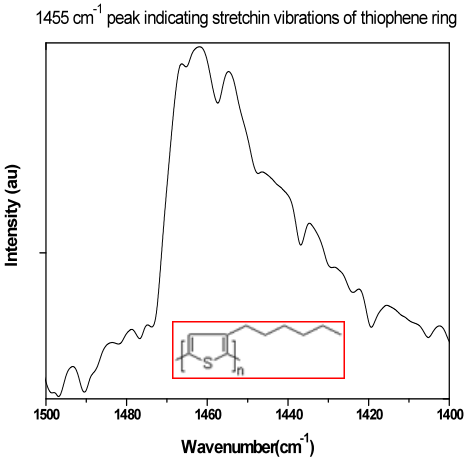
UV-vis spectra of CNT membranes, before polymerization

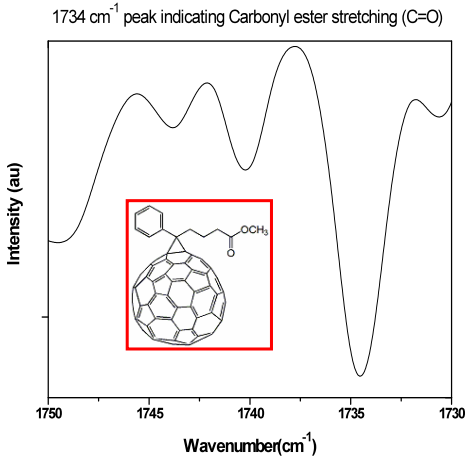


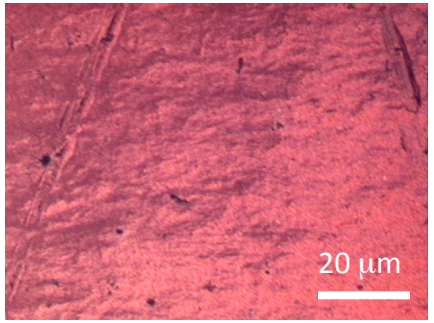
PL intensity quenched significantly with increasing CNT density

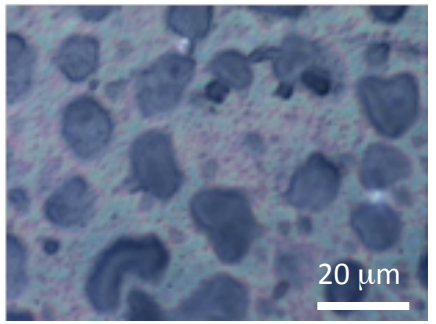
Electrochemical deposition of P3HT/fullerene blends

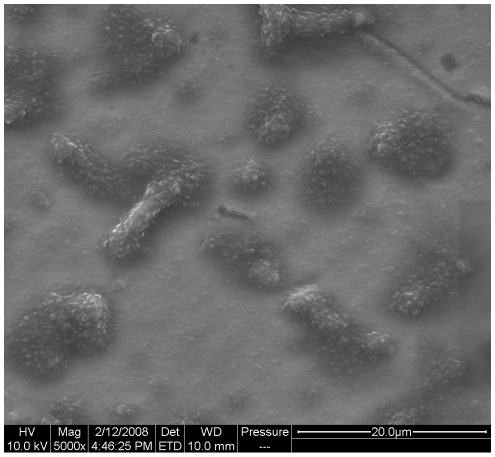




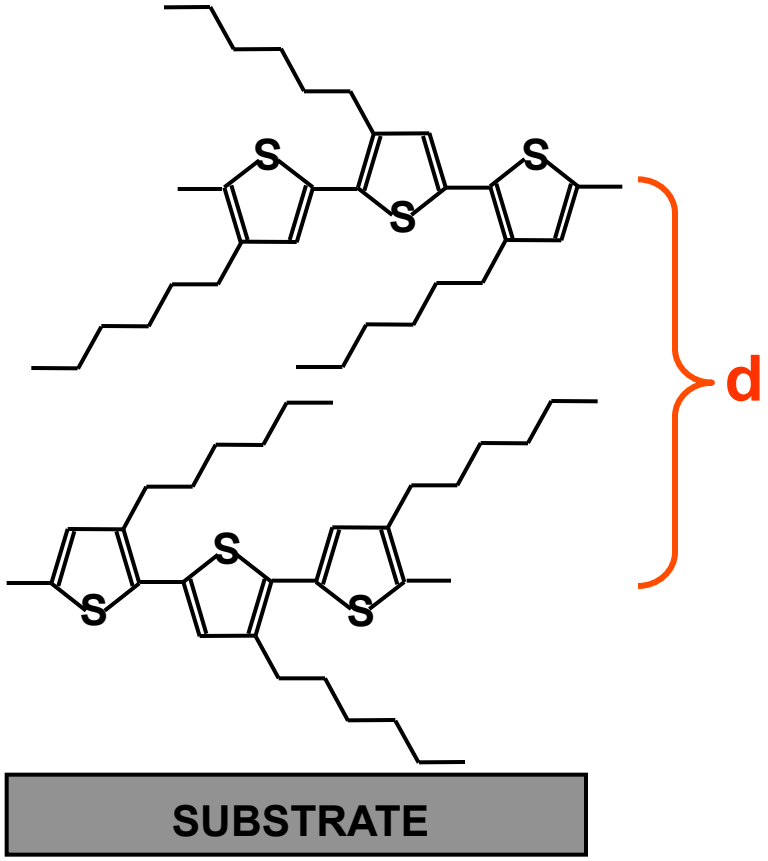


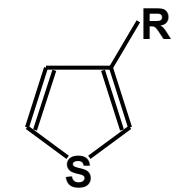




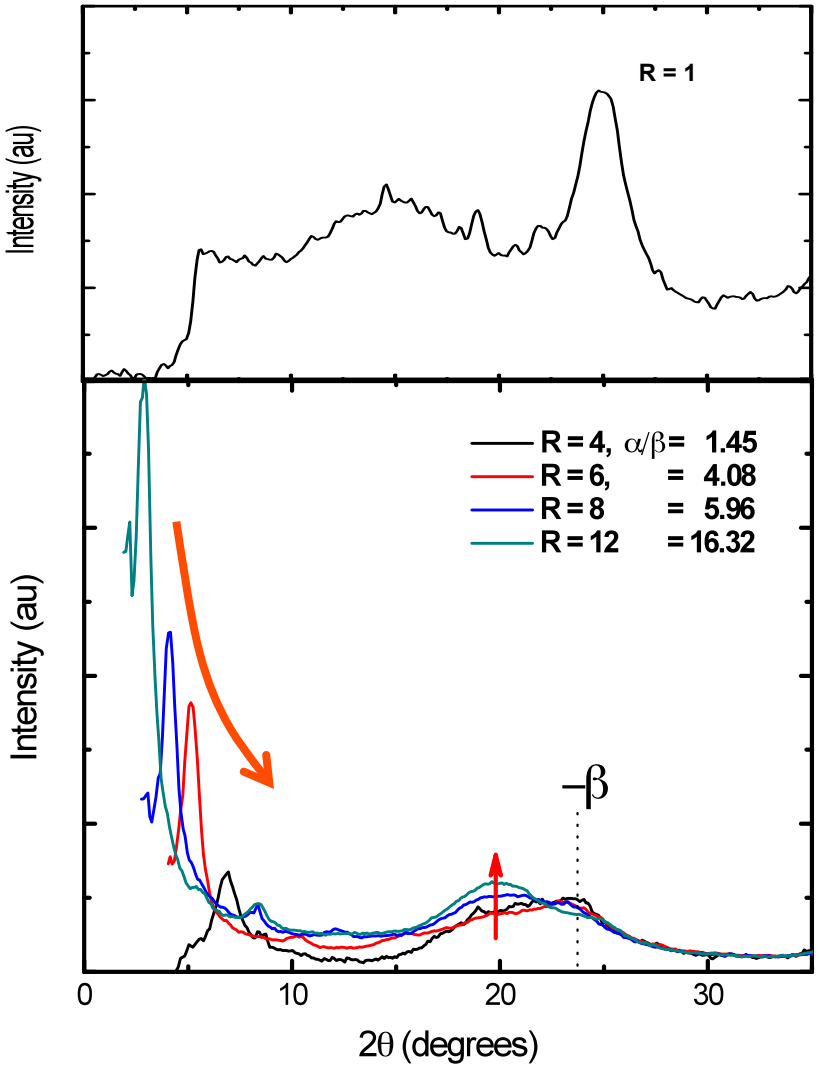


Thiophenes with variable side-chain lengths

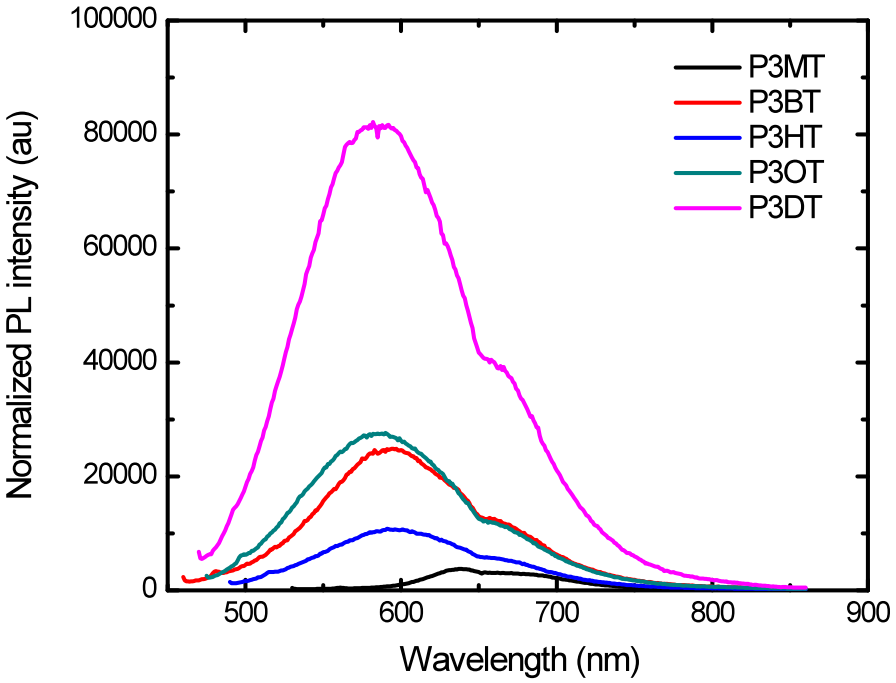




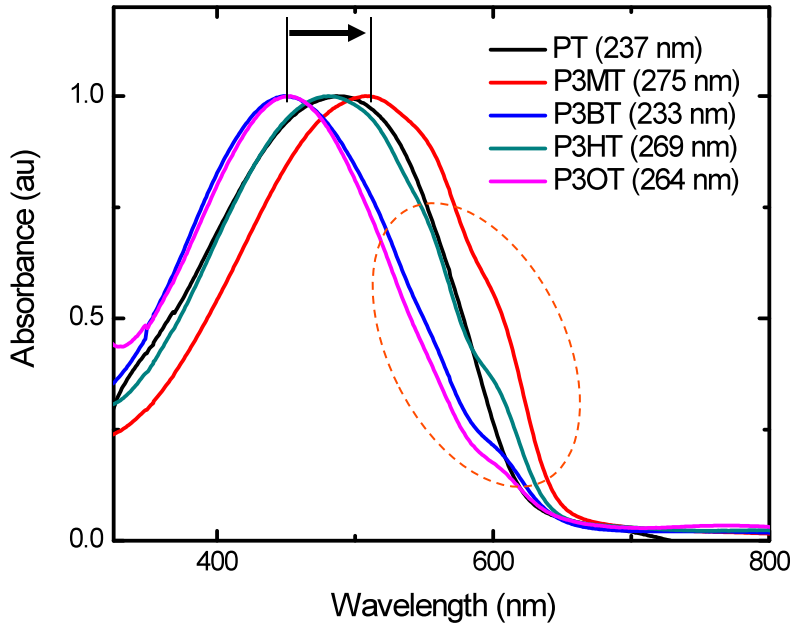
R_1 = -CH_3
R_4 = -$(CH_2)_3$-CH_3
R_6 = -$(CH_2)_5$-CH_3
R_8 = -$(CH_2)_7$-CH_3
R_{12} = -$(CH_2)_{11}$-CH_3



Influence of the side chain: photoluminescence and UV-vis spectroscopy



	Primary peak (nm)	FWHM (nm)
PT	487	210.1
P3MT	508	210.2
P3BT	448	193.6
P3HT	481	193.6
P3OT	453	186.5



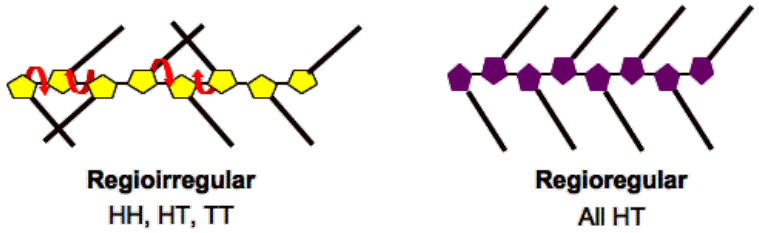
P3MT – red shift and broad absorption

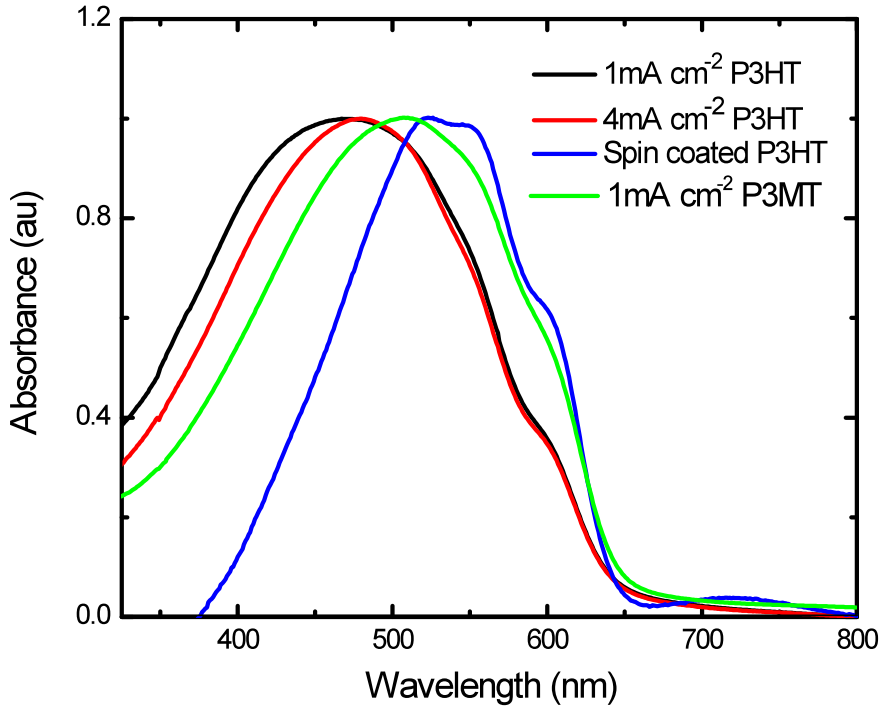
P3BT – larger than expected blue shift likely due to poor stacking

Trade-offs of electropolymerized thiophene

- Lack of regio-regularity

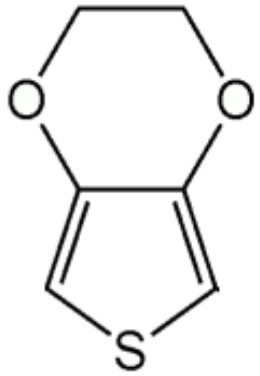
  Blue shift in UV-vis spectra





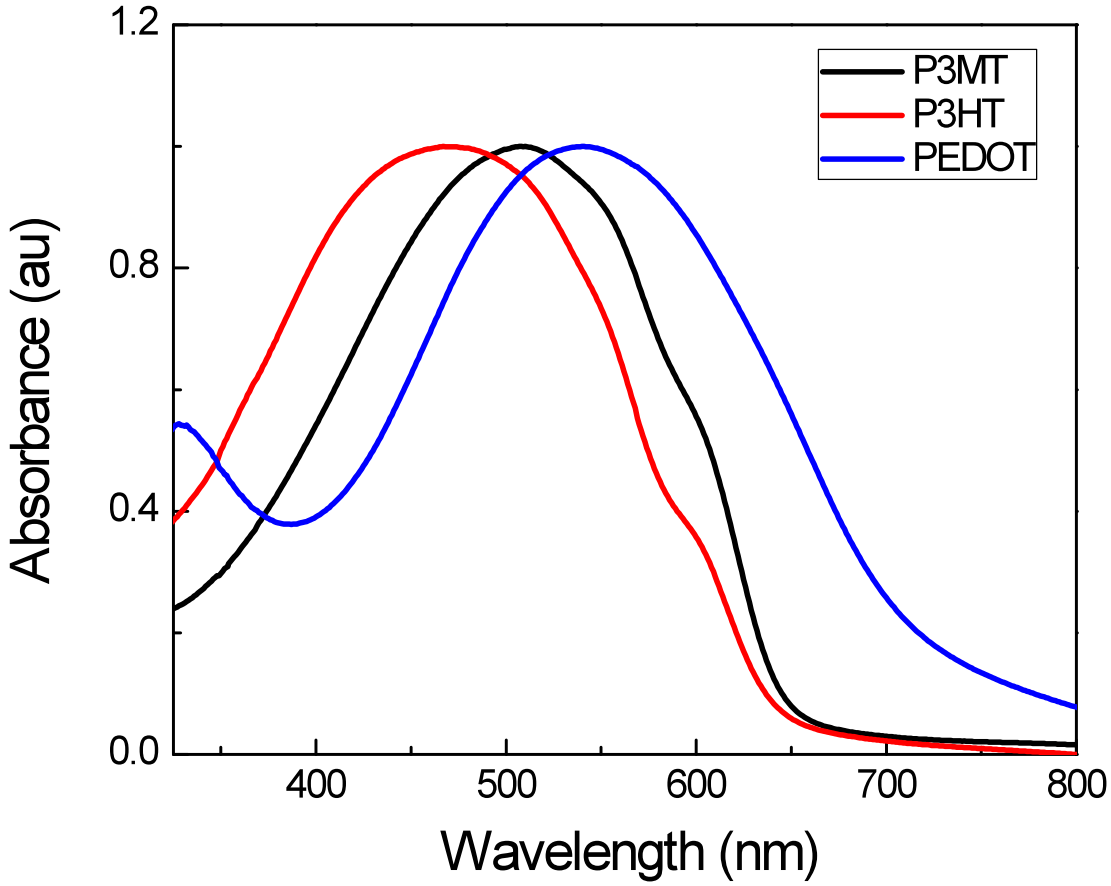
- Electrolyte and charge doping

Pursuing lower bandgaps for increased light adsorption



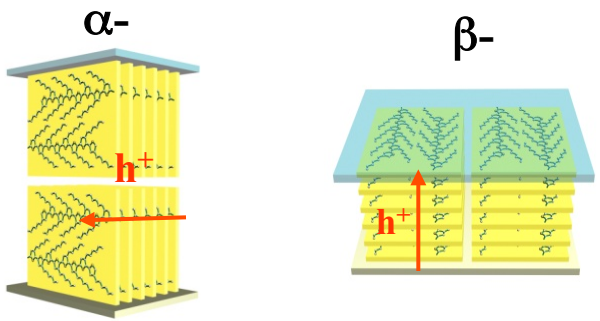
EDOT

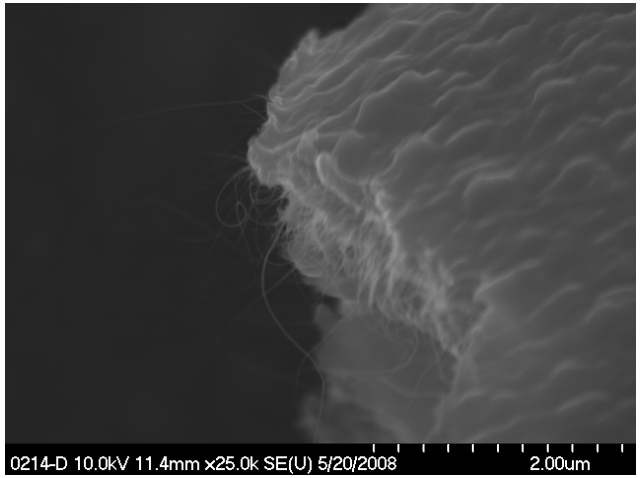
PEDOT
1.60 eV
*Low mobility



Concluding remarks

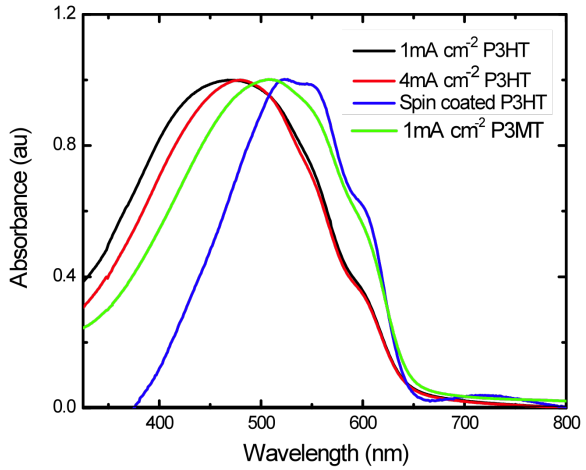
- Electrochemically synthesized P3HT→ better π–π stacking in the (010) plane
- Results in broader absorbance, especially at lower polymerization current





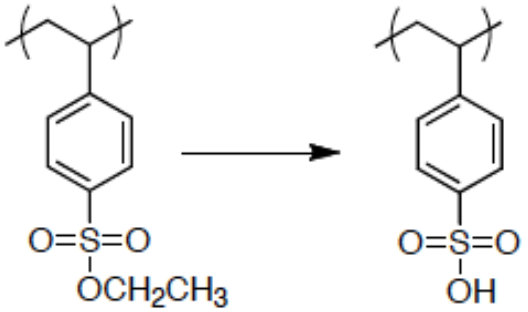
- Successful impregnation of CNT membranes with P3HT via electropolymerization
- Dense P3HT/CNT composite films had highly quenched photoluminescence indicating possible charge transfer to nanotubes

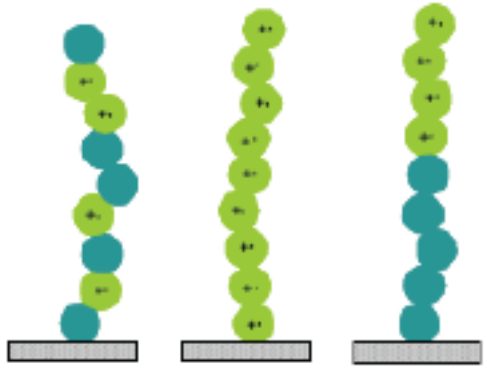
- Of all e-polymerized P3ATs, P3MT has the broadest absorbance and is most red-shifted.

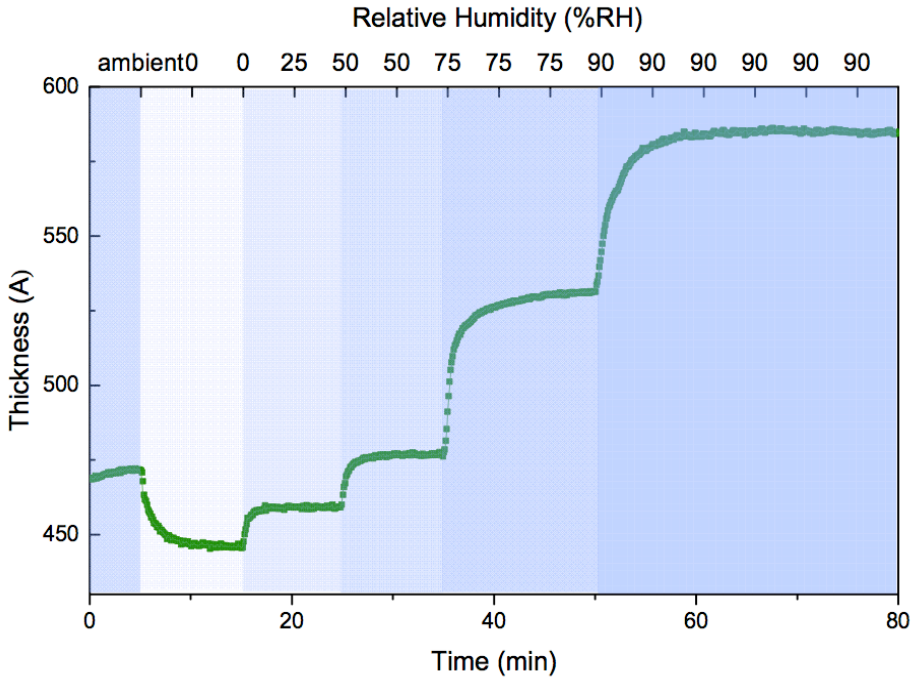


Swelling and relaxation dynamics of surface-tethered polymers

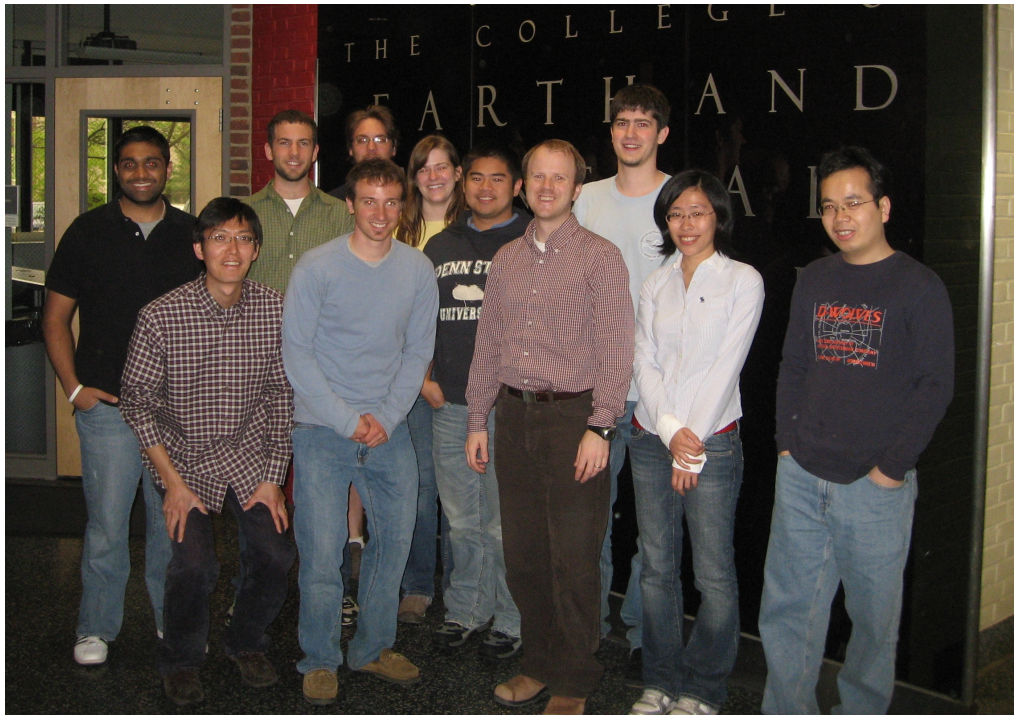
w/ Deanna Pickel and Brad Lokitz







Acknowledgements



Dr. Jingling Yan – Chinese Academy of Sciences, Changchun
Dr. Tomonori Saito – Virginia Tech
Dr. Tim Tighe – Penn State University
He Xie **Stephanie Petrina**
Romesh Patel **Alfonso Mendoza**
Hunter Moore **Brian Chaloux**
Matt Gross (MS) **Melanie Disabb**
Kevin Dicker (MATSE) **Chris Ewing (ChE)**
Kyle Bryson (MATSE Honors)

OAK RIDGE NATIONAL LABORATORY

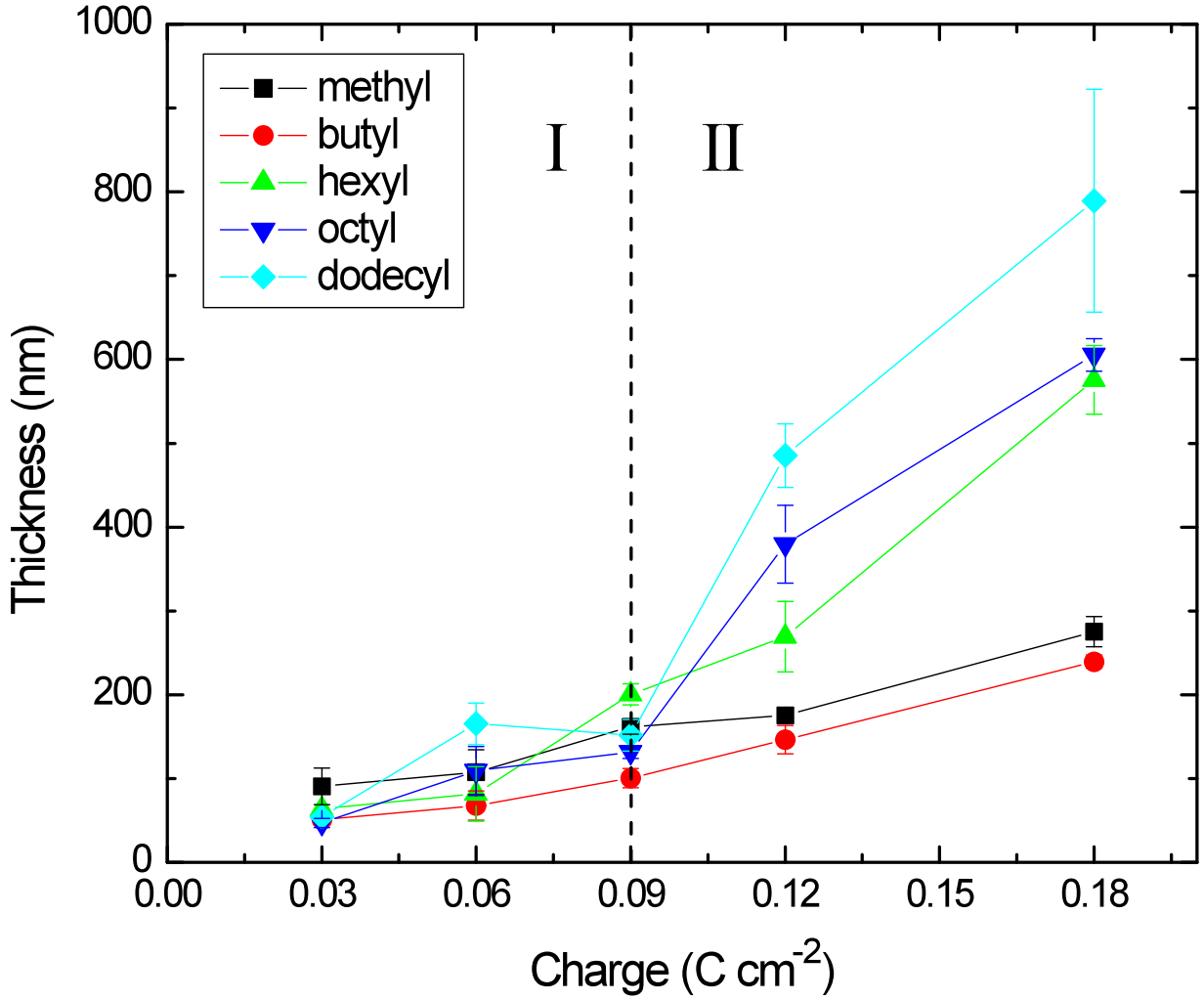
NSF # CMMI-1038007

CENTER FOR nanoscale science

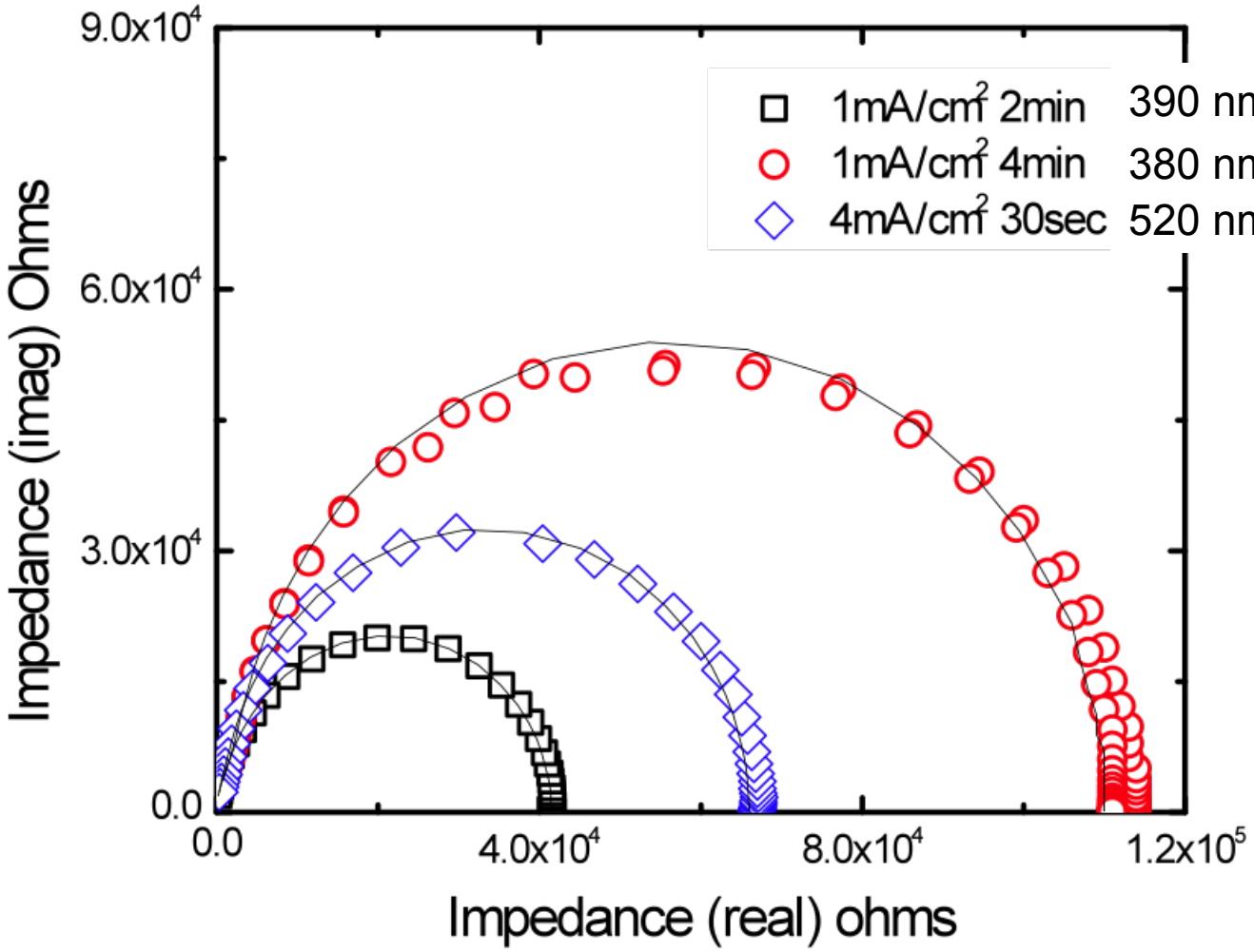
MRI MATERIALS RESEARCH INSTITUTE

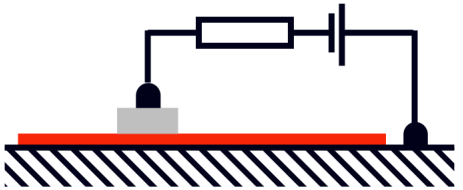
psiee

Electrodeposited film thickness with different P3AT monomers



Thin film impedance and stacking order

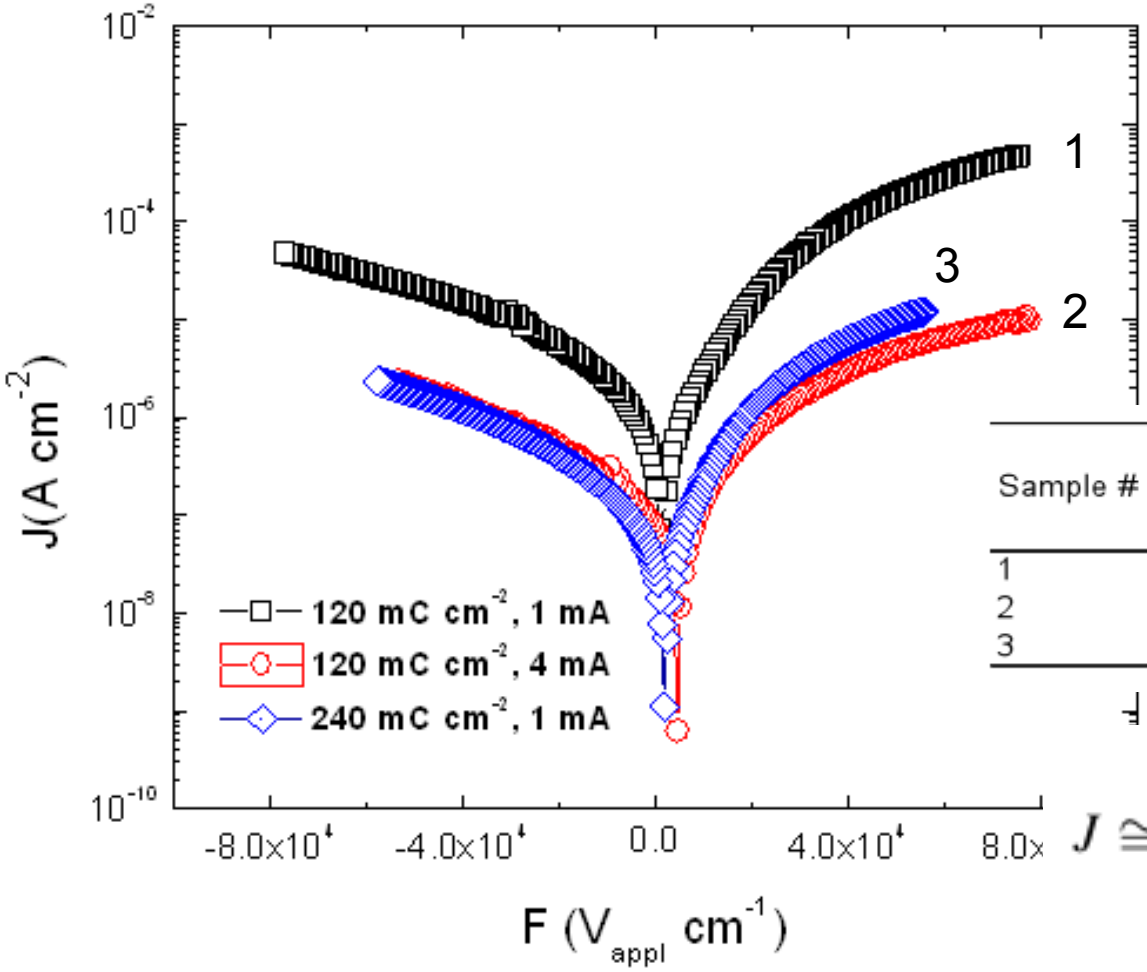


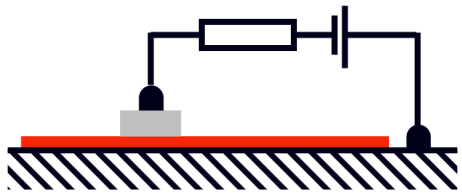


$$\rho = R\frac{A}{l}$$

■	1.21 MΩ - cm
▲	1.92 MΩ - cm
●	1.60 MΩ - cm

Charge mobility normal to the film plane





Sample #	Char. Field (V cm^{-1})	ZF mobility (μ_0) x 10^{-6} (cm^2 V^{-1} s^{-1})	Effective mobility (μ_{eff}) x 10^{-5} (cm^2 V^{-1} s^{-1})
1	9837	80.3	75.6
2	5358	3.2	7.0
3	5799	6.2	7.6

$$J \cong \frac{9}{8}\varepsilon\varepsilon_0\mu_0\frac{V^2}{L^3}\exp\left(0.89\sqrt{\frac{V}{F_0 L}}\right)$$

Roman and Inganas *Synthetic Metals* **2002**.