Structural Order and Transport in Bulk Heterojunction Solar Cells

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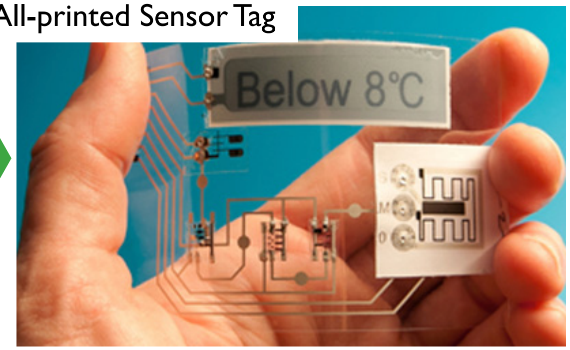
Organic Semiconductors

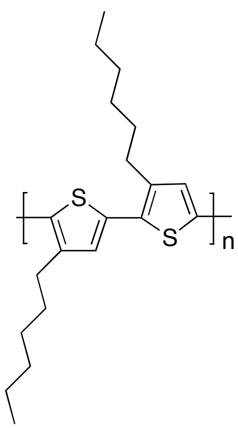
Organic semiconductors enable direct fabrication of electronics

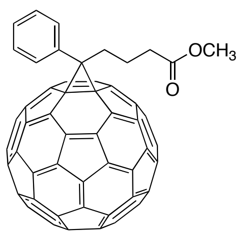
Fuji-Dimatix

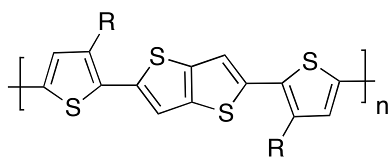
All-printed Sensor Tag

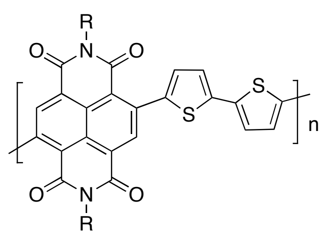


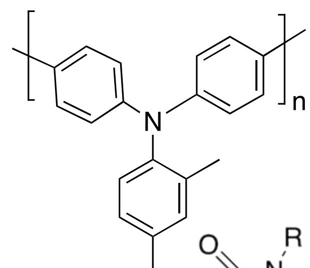
PARC/ThinFilm

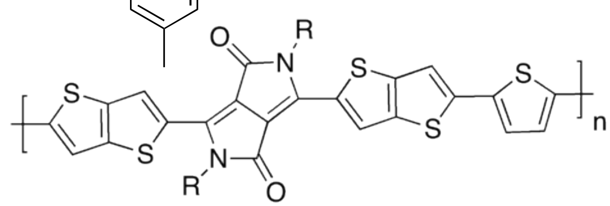




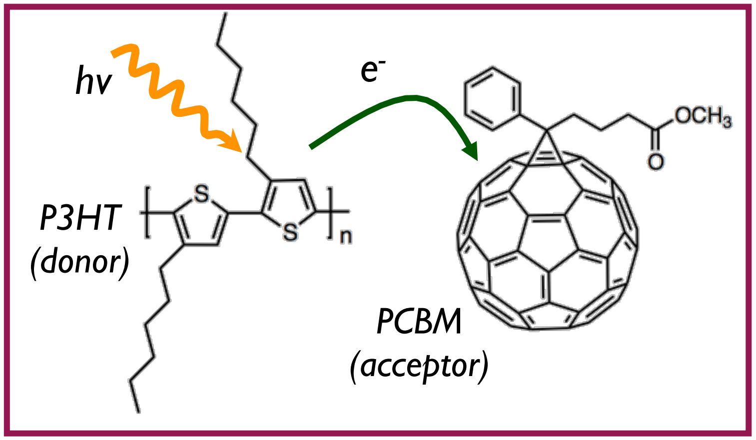


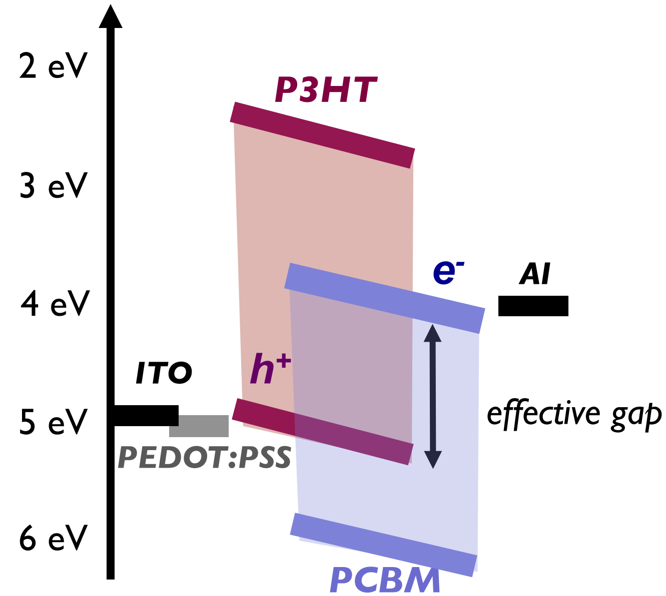


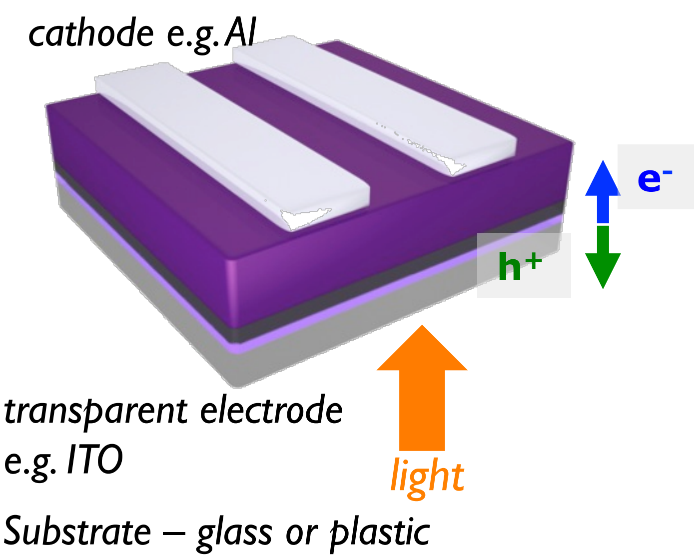


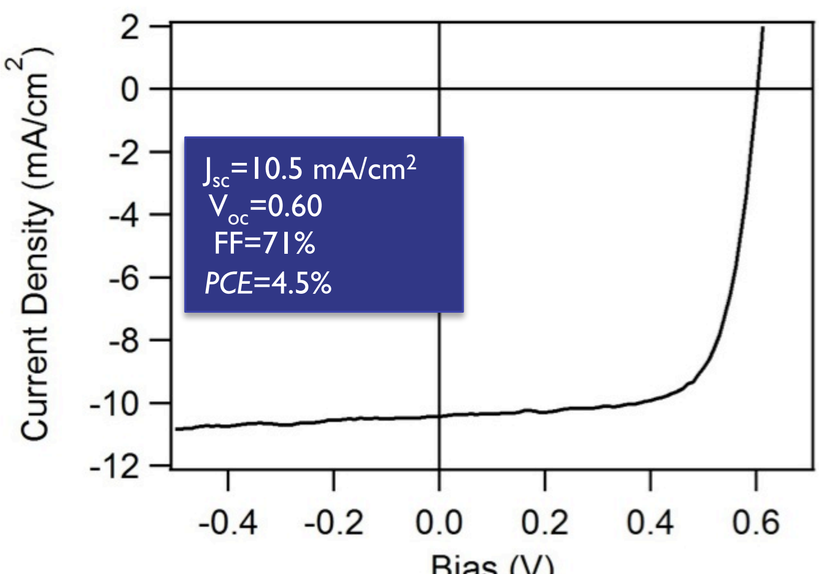


Bulk Heterojunction Organic Photovoltaics









ITO/PEDOT:PSS/P3HT:PCBM/Ca/Al

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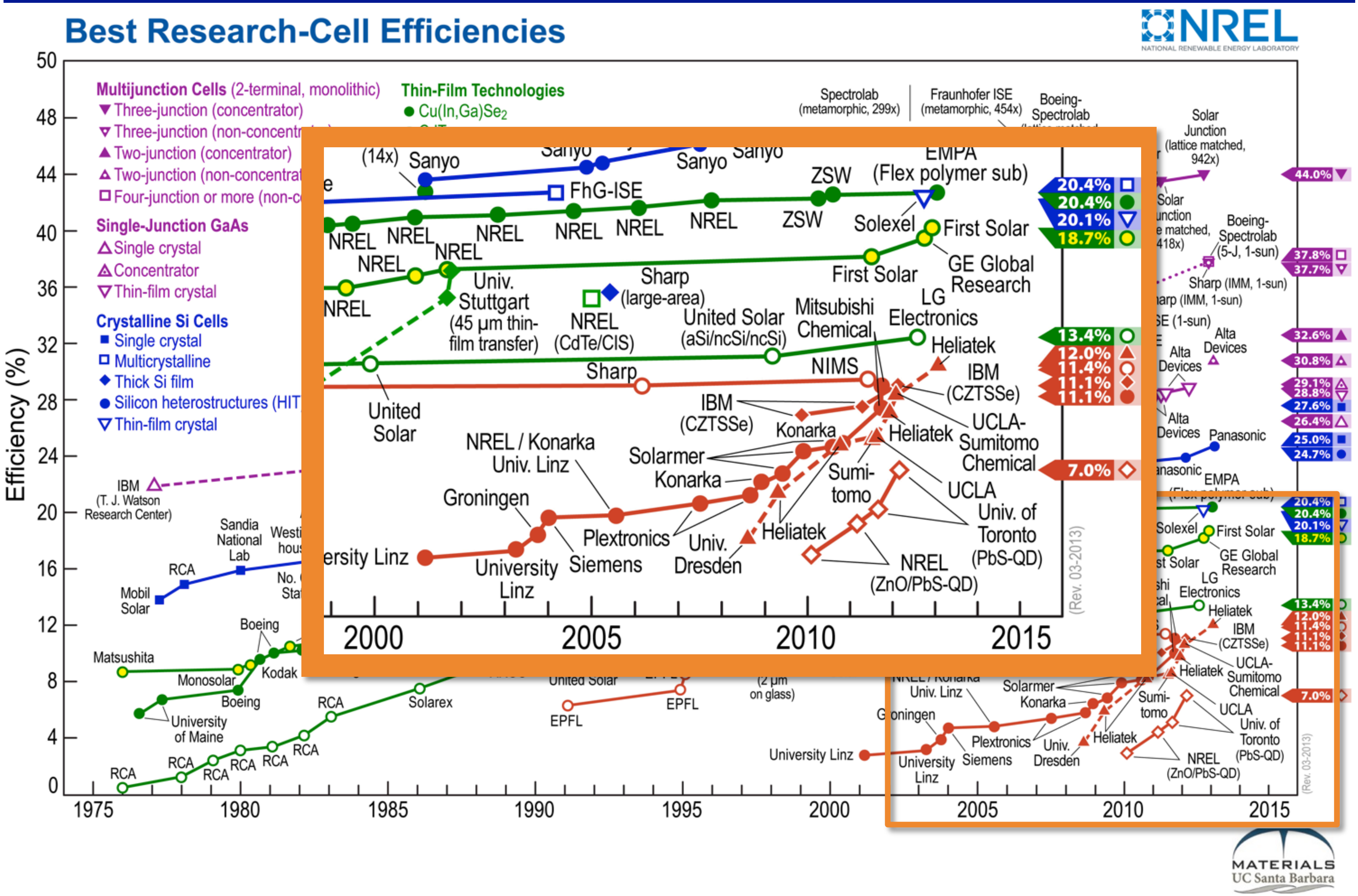
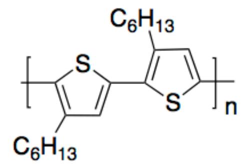
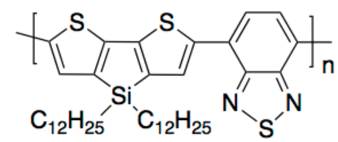
State of the Art Solar Cells



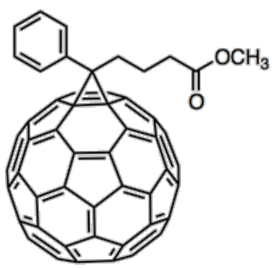
Structural Diversity in Efficient BHJs

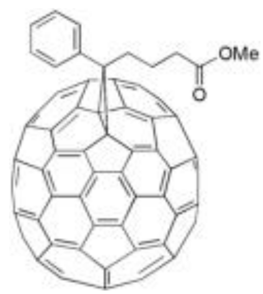
Donor: Many donor-acceptor co-polymers with PCE > ~5%

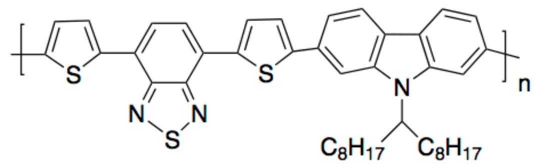


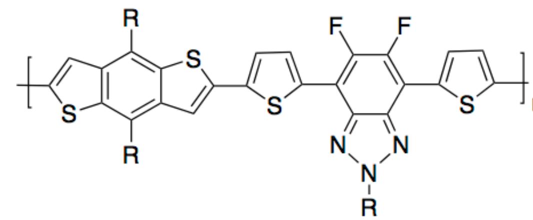


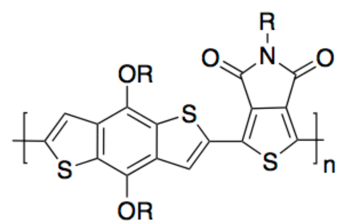
Acceptor:

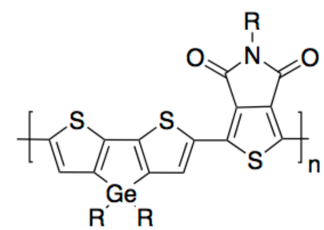




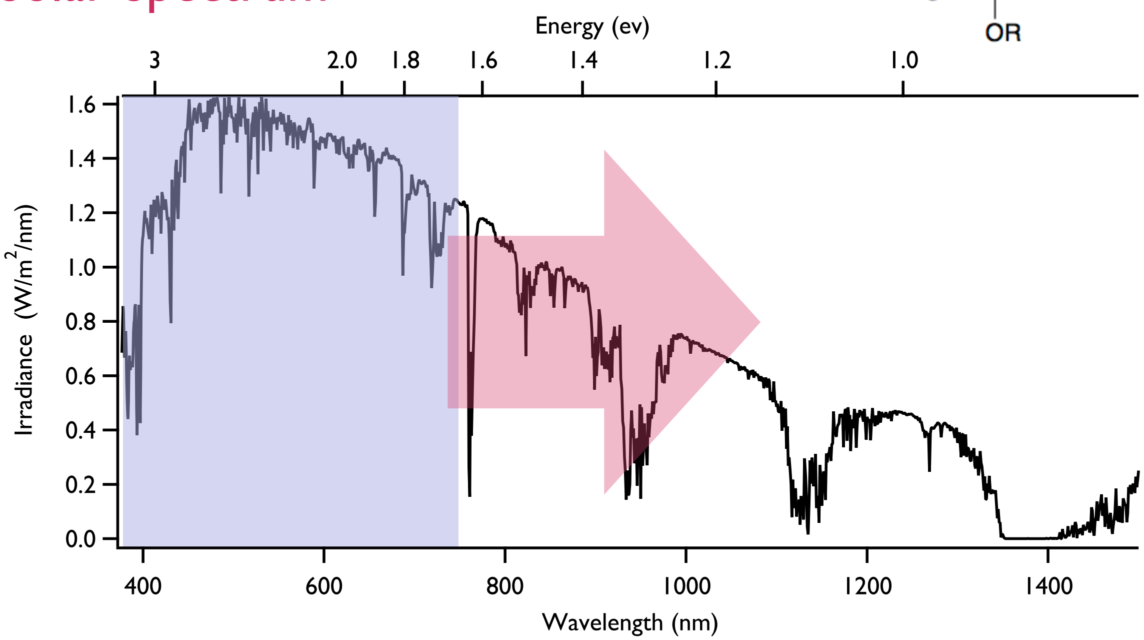








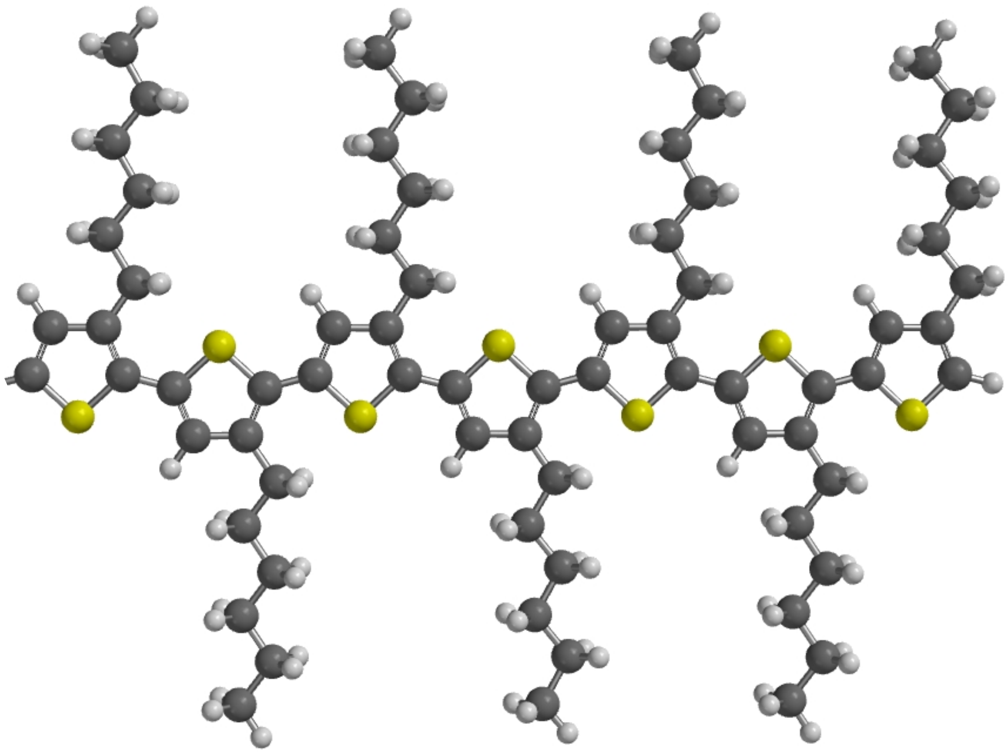
Solar Spectrum



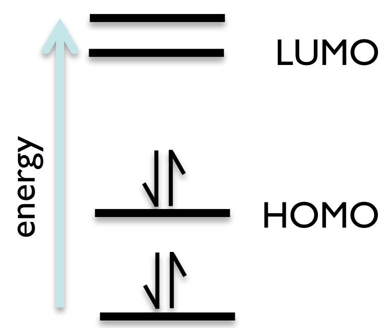
Few materials with absorption >800nm

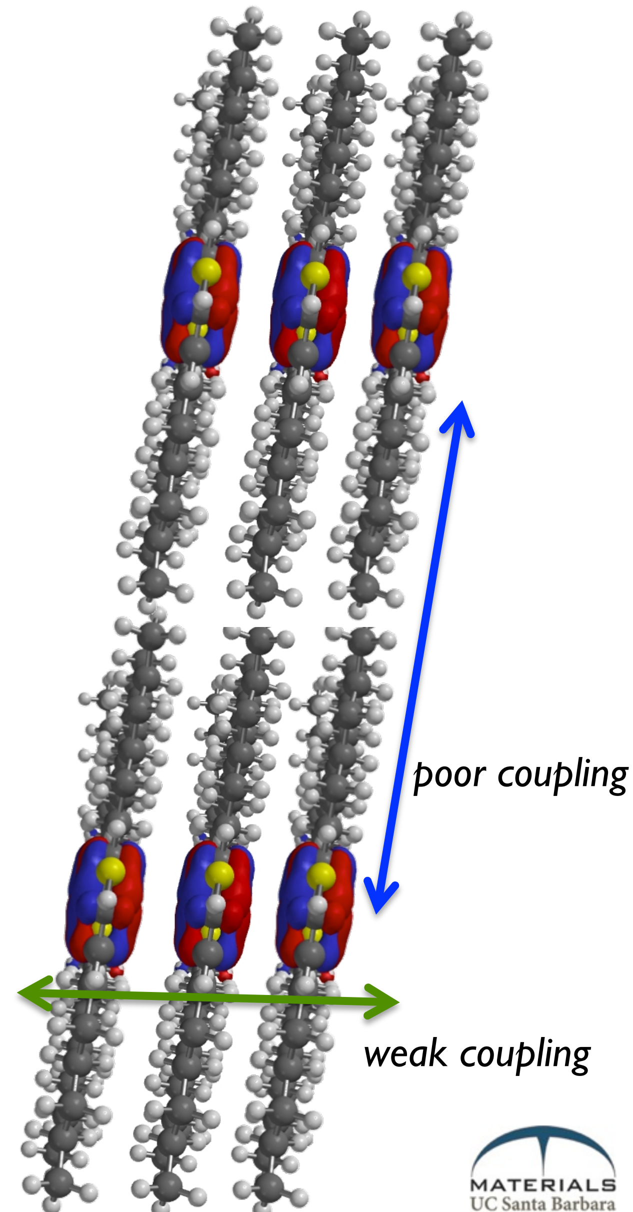
Electronic Structure of Semiconducting Polymers

poly(3-hexylthiophene)



Conjugated core controls electronic structure relevant for transport





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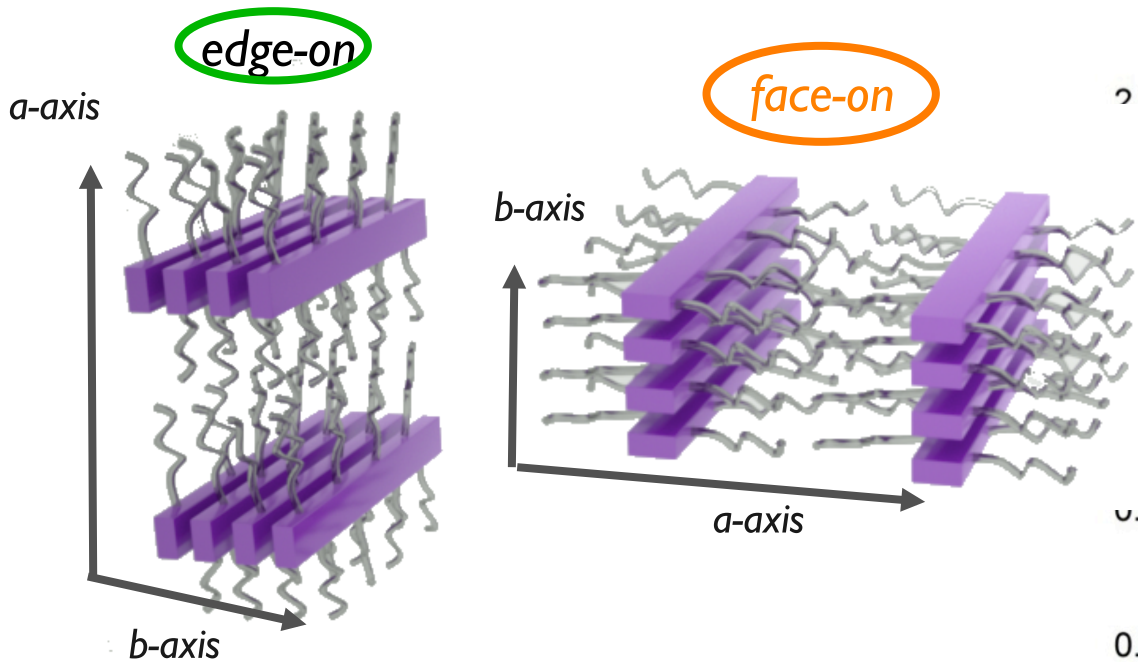
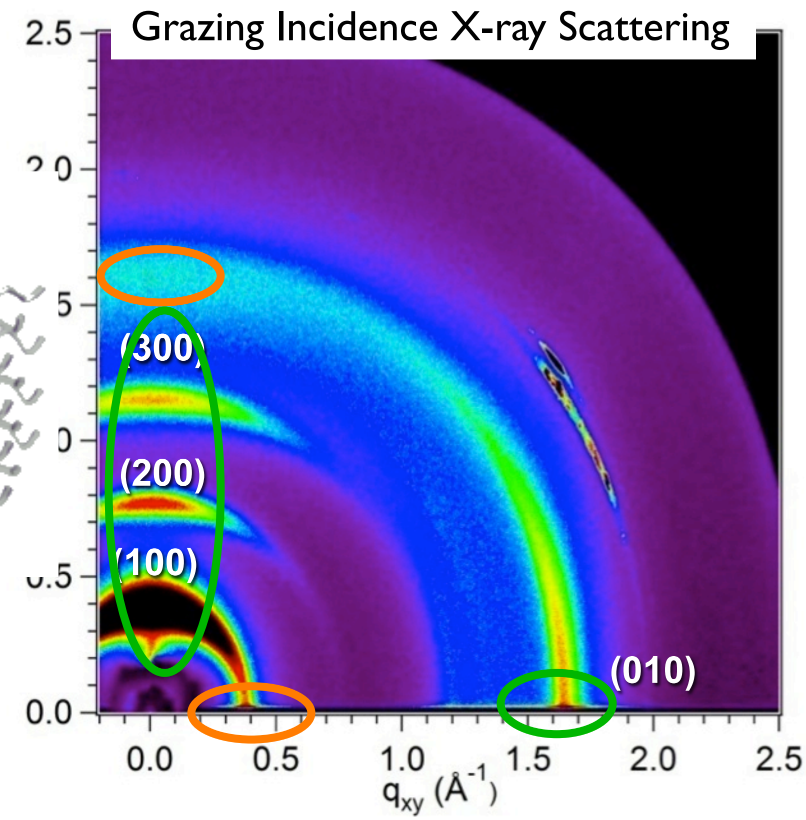
Crystallites in P3HT Have Two Main Orientations





P3HT thin films have dominant edge-on texture

out-of-plane – alkyl chains

in-plane – π -stacking

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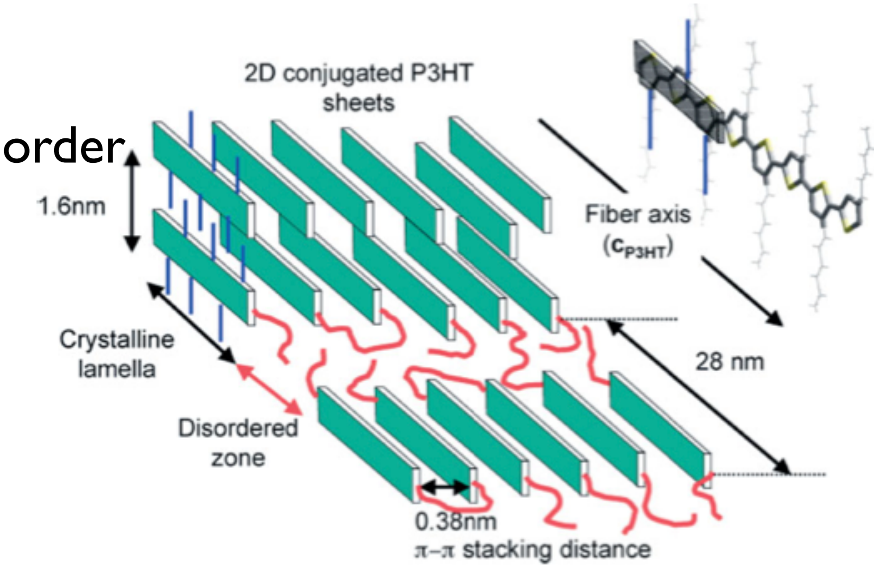
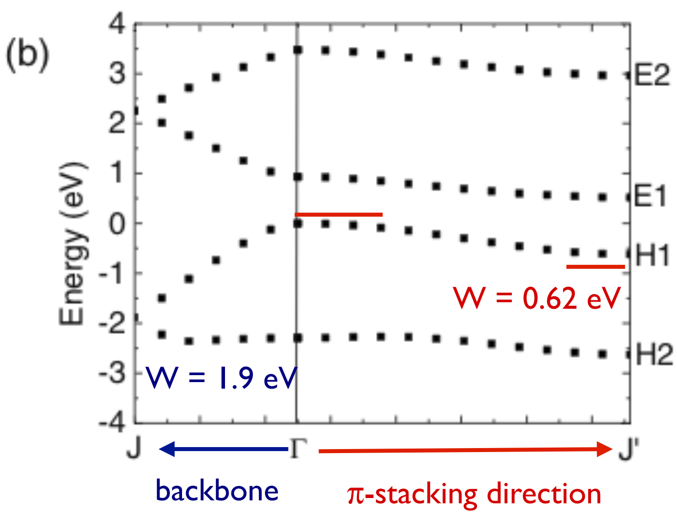
Disorder and Electronic Structure in Polymers

Polymer films have regions of order and disorder
- polydispersity
- packing defects
- domain boundaries



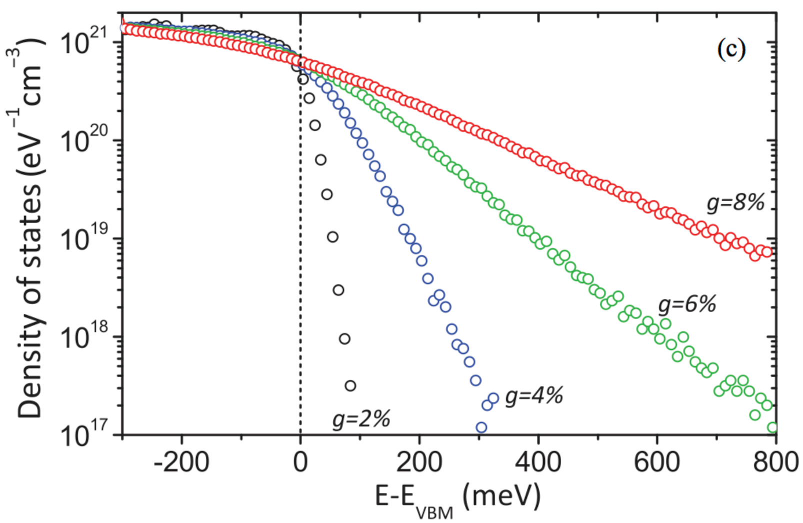
Brinkmann & Wittmann Adv. Mater. 18 860 (2006)

Band Structure of Perfect P3HT Crystal



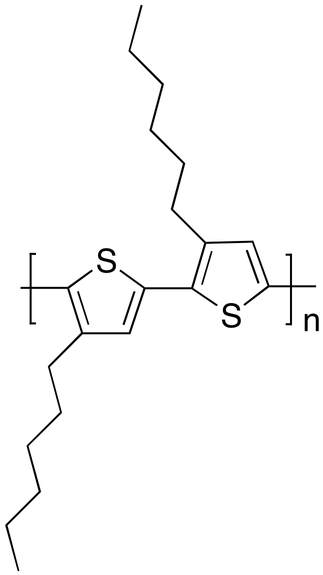
J. Northrup *Phys. Rev. B.* 76, 245202 (2008)

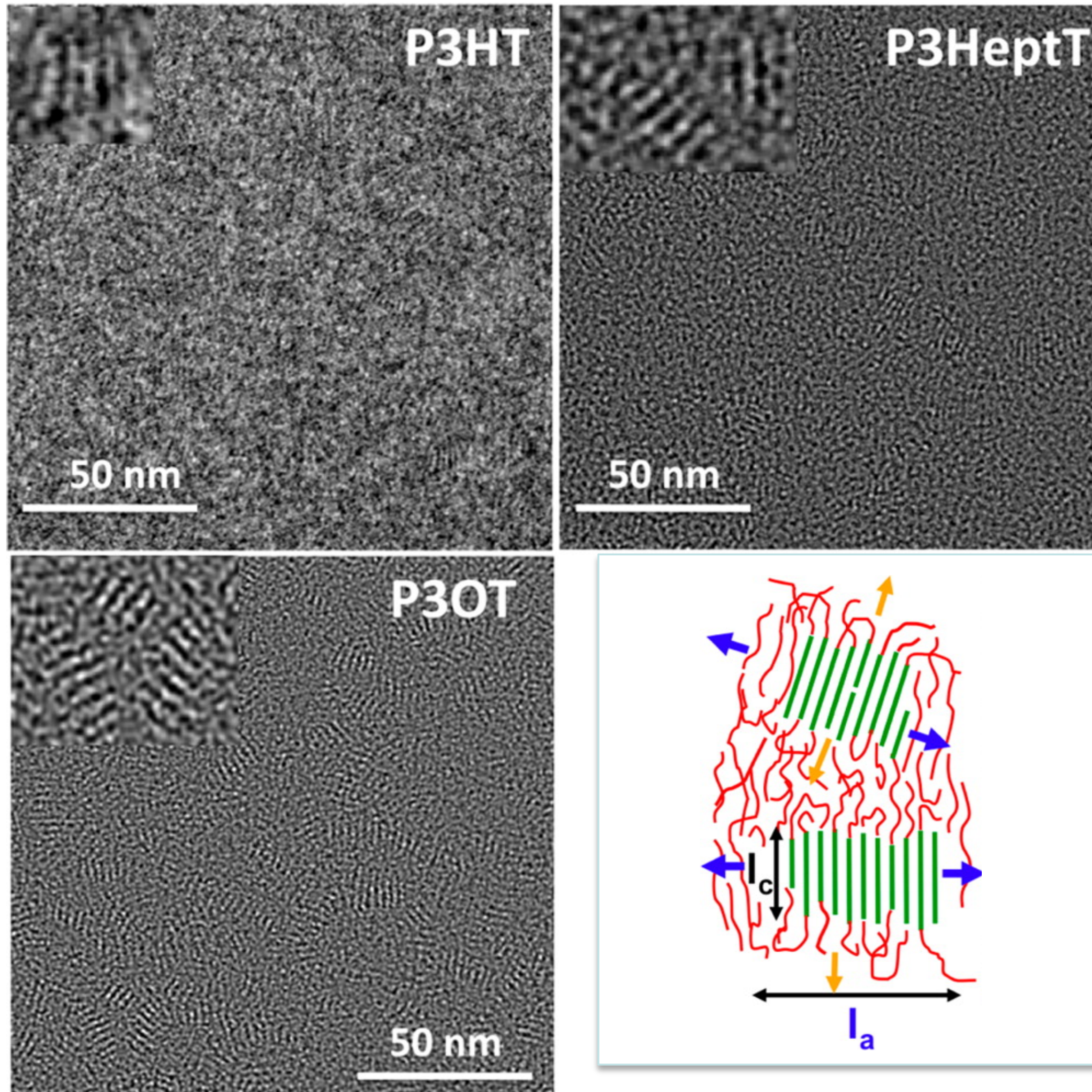
Disorder Broadens DOS



J. Rivnay, et. al. *Phys. Rev. B.* 83 121306(R) (2011)

Chain Ordering in Poly(alkylthiophenes)



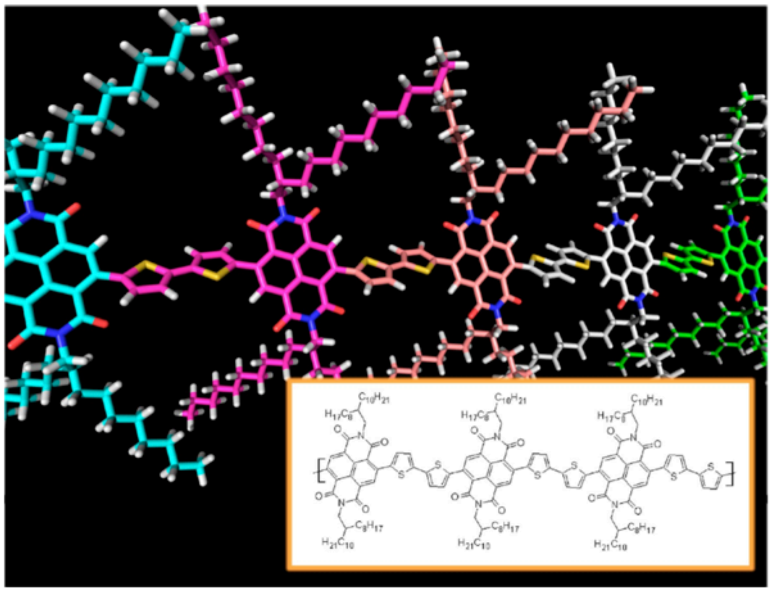


Small ~10 nm crystallites

No obvious long range order

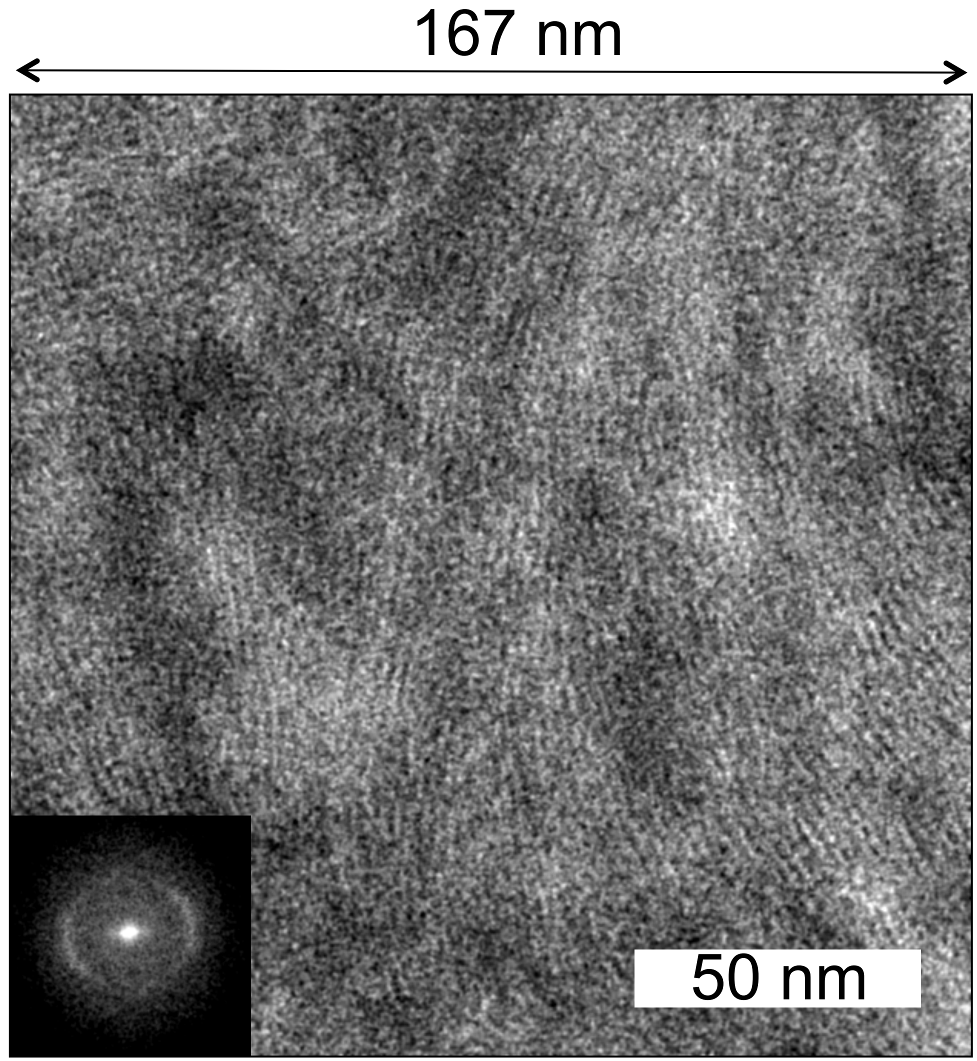
M. Brinkmann P. Rannou *Macromolecules* (2011)

Imaging Chains with Scanning Transmission Electron Microscopy



C. Takacs, et. al. *Nano Lett.* 2013

FT shows peaks at alkyl stacking spacing



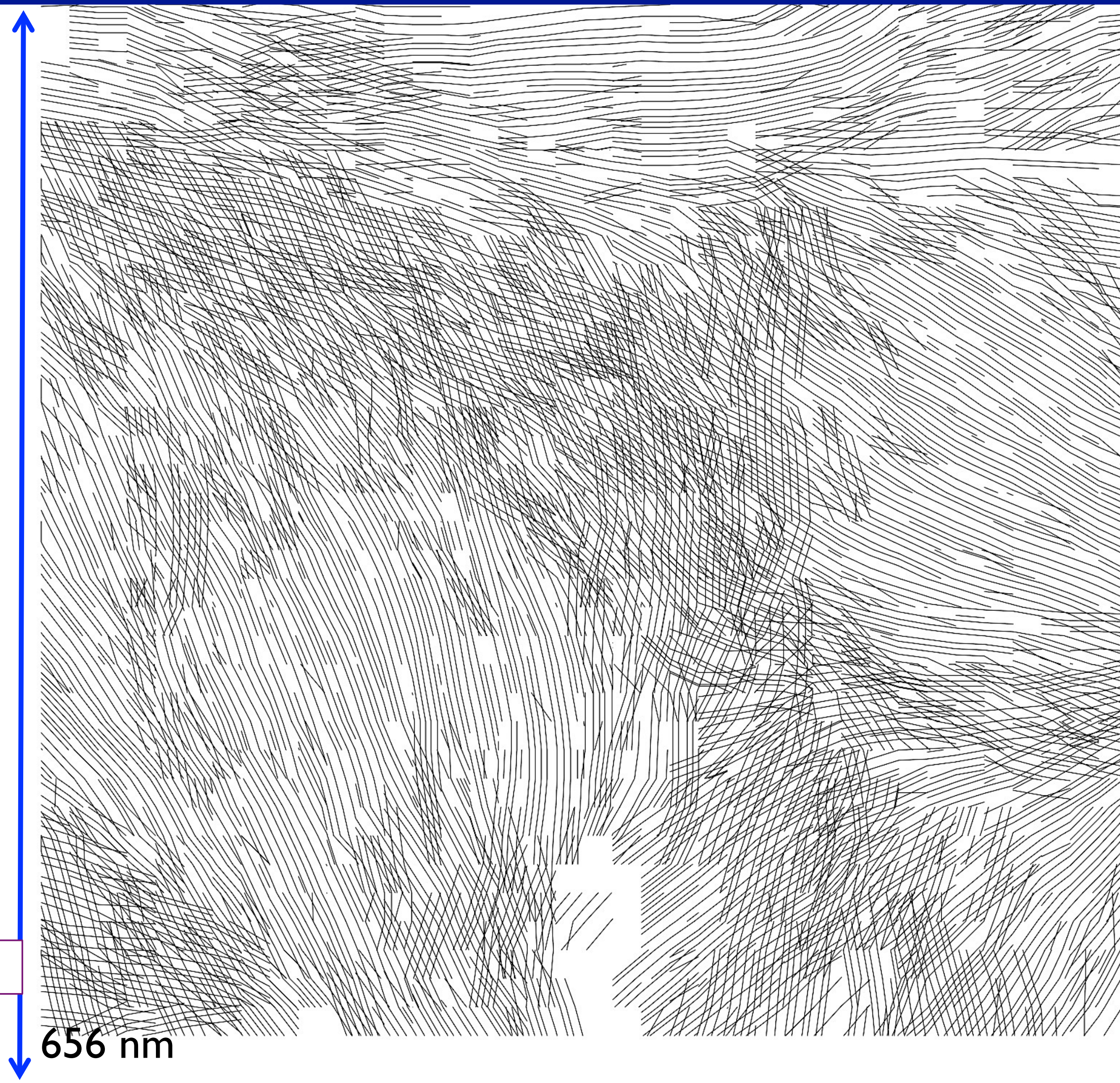
FEI Titan 300kV microscope

P(NDI2OD-T2) Chains in Have Long Range Correlation

Overlapping chains are resolved with long range alignment

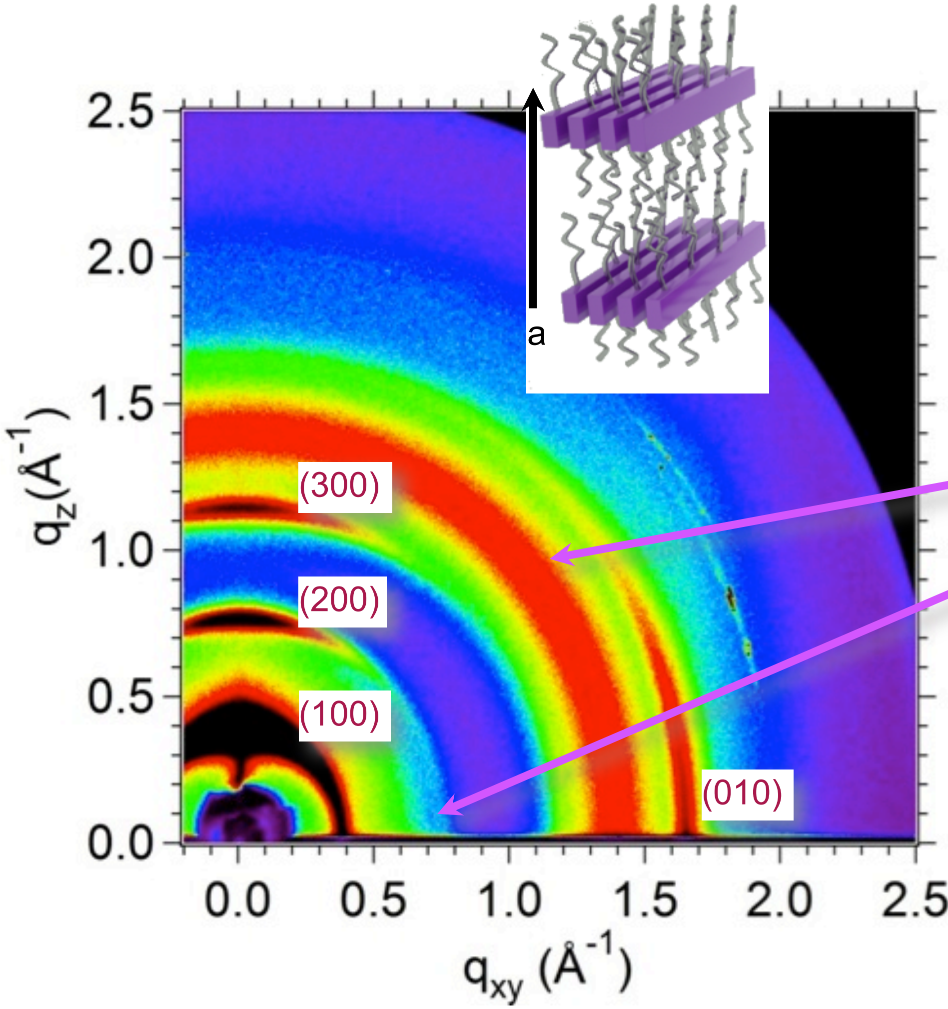
Chain correlation length should be considered for transport simulations

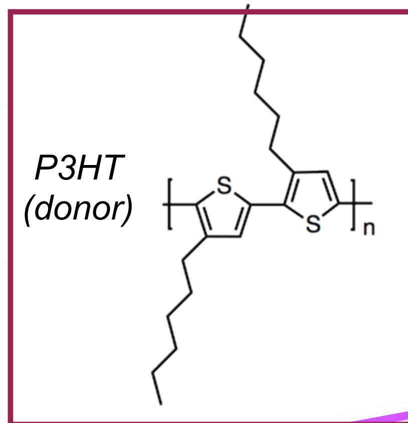
C. Takacs, et. al. *Nano Lett.* 2013

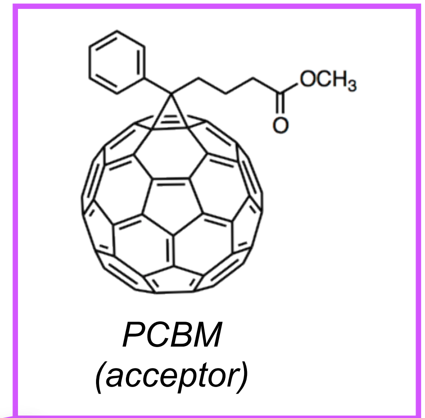


Molecular Order in Polymer:Fullerene BHJs

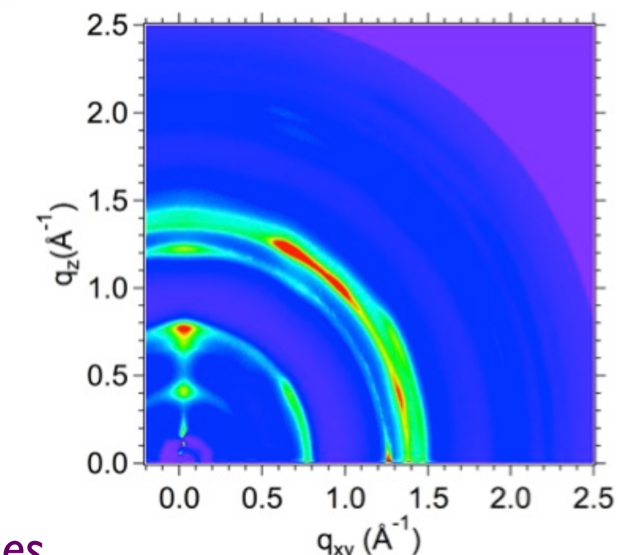
Grazing Incidence X-ray Scattering of BHJ







GIWAXS of crystalline PCBM



Domain sizes small and significant disorder in both phases

N. D. Treat et. al. *J. Mater. Chem.* **21** 15224 (2011)

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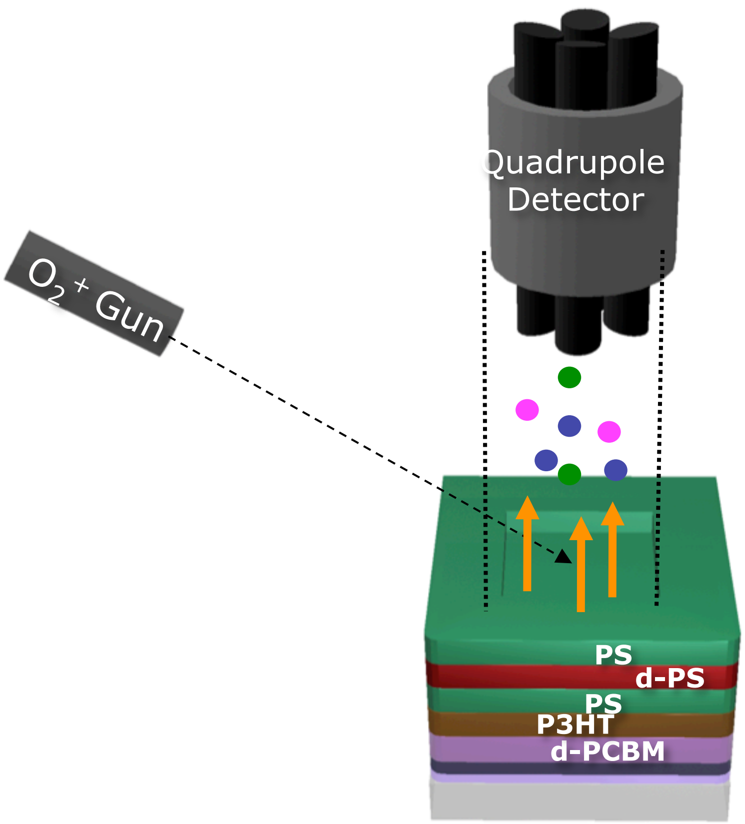
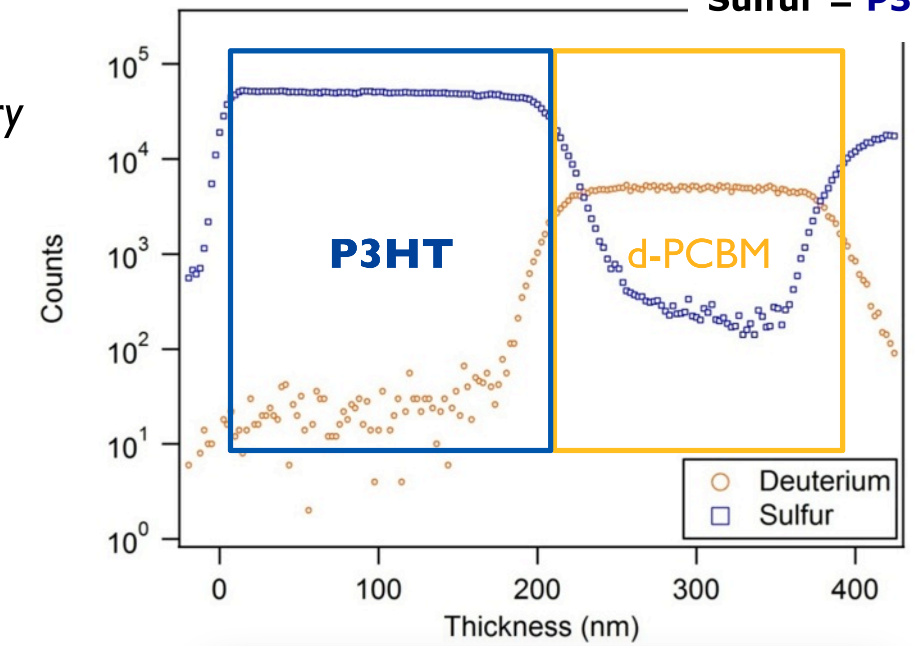
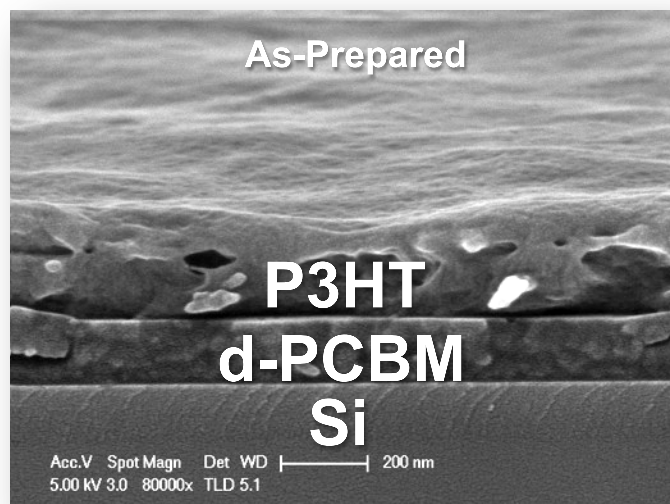
Depth Profile of a Bilayer Film

Dynamic Secondary Ion Mass Spectrometry



Deuterium = d-PCBM
Sulfur = P3HT





N. Treat, M. Brady, G. Smith, M. Toney, E. Kramer, C. Hawker, M. Chabinyc *Adv. Ener. Mater.* I (2011)

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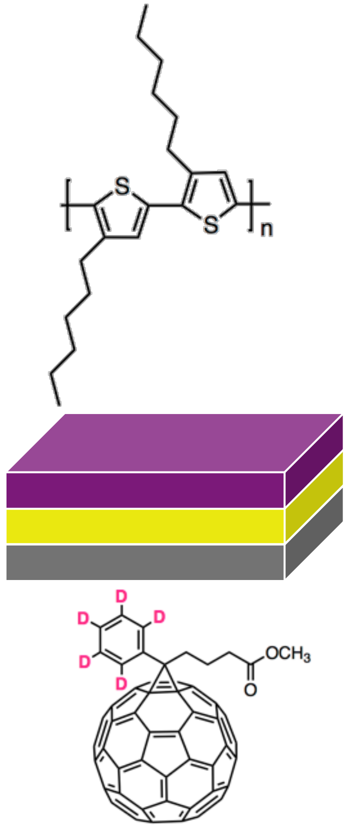
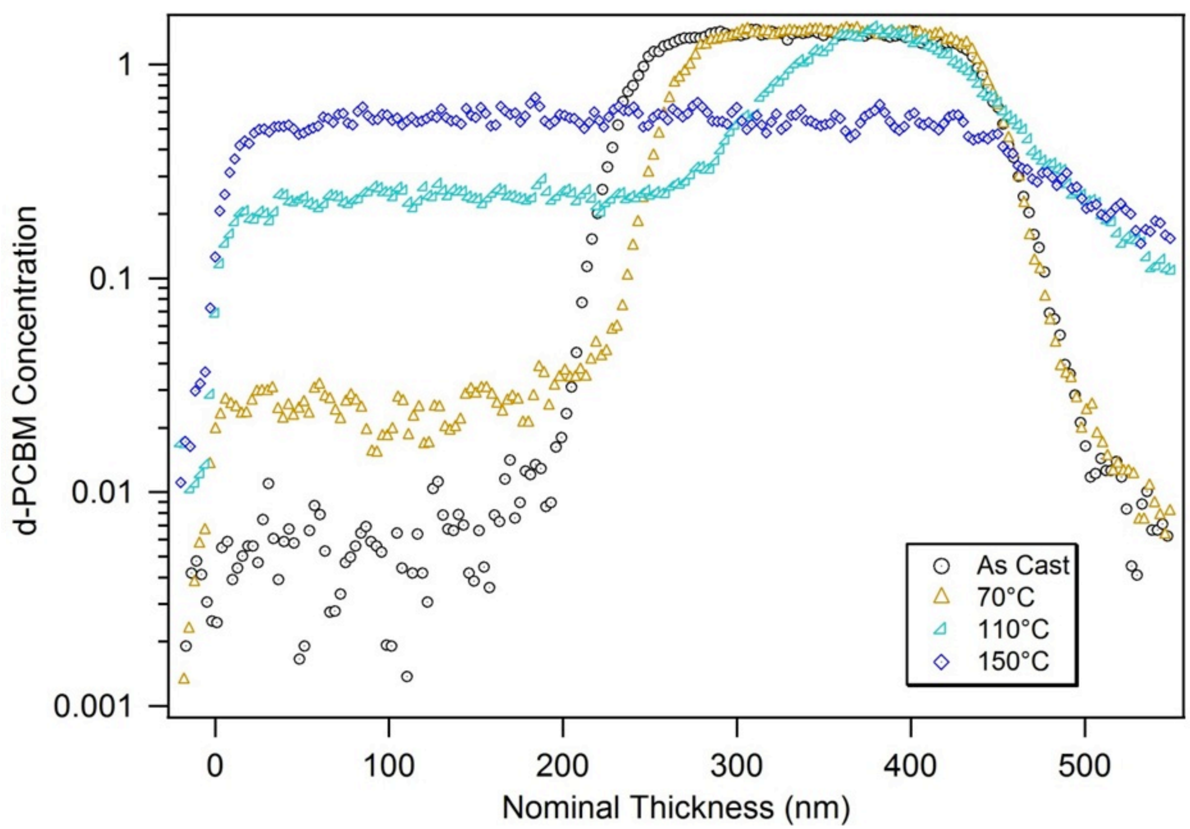
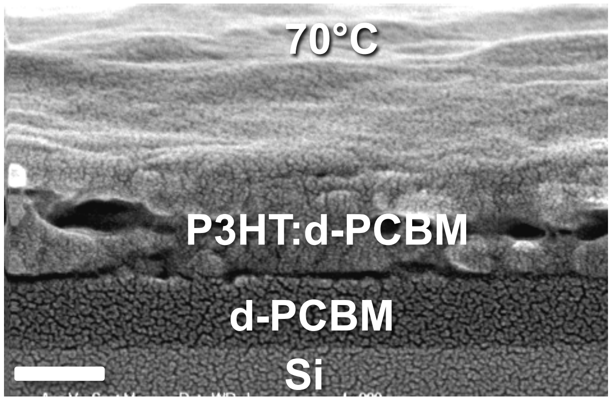
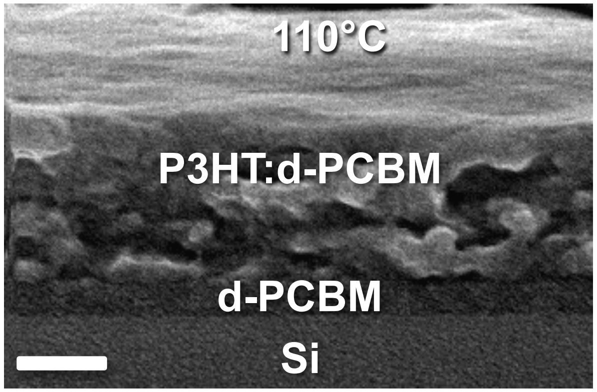
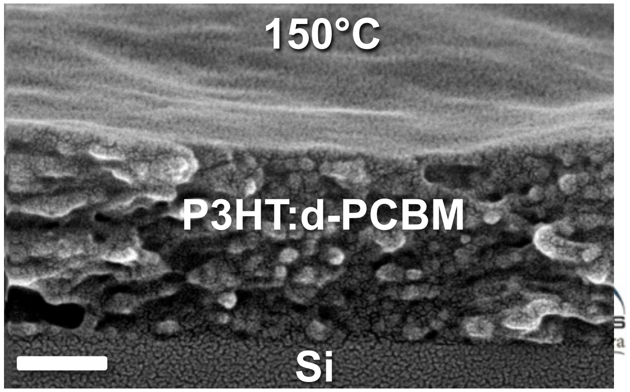
Layers Begin to Mix Upon Heating



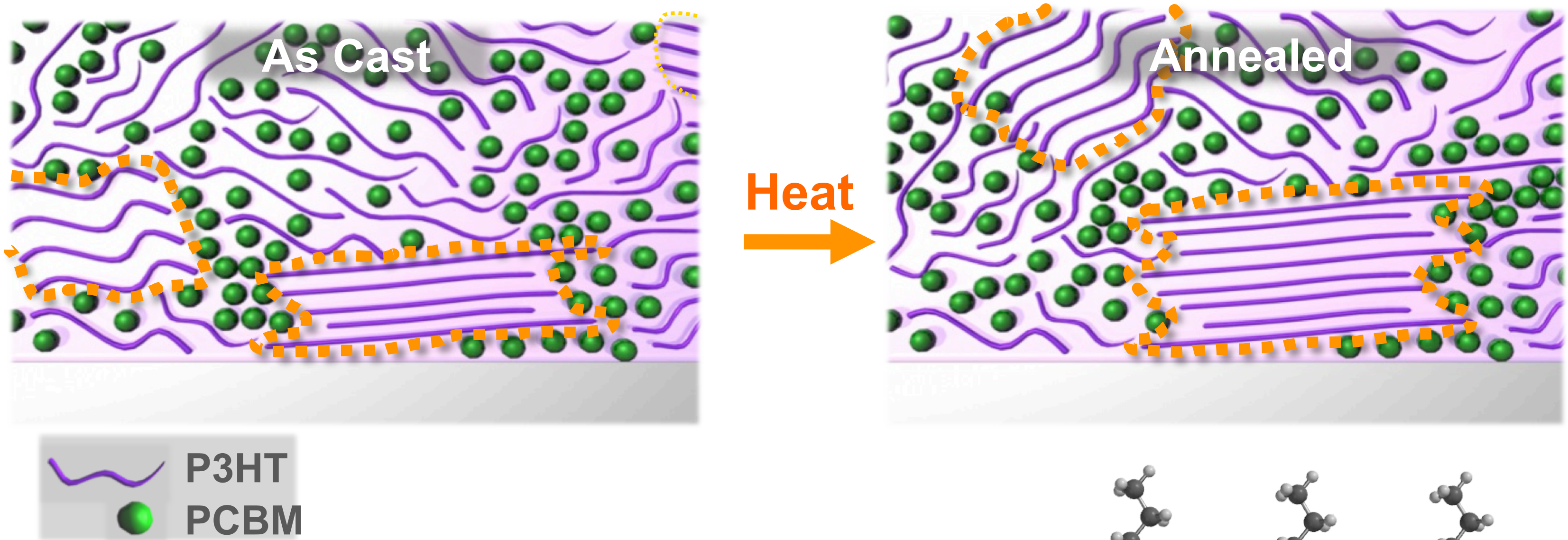


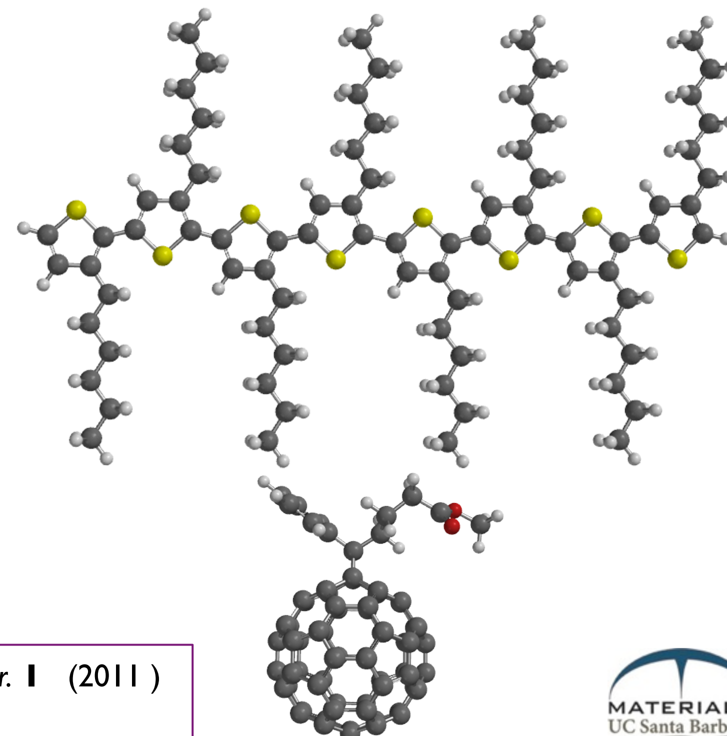






Thermal Annealing Process in P3HT:PCBM





- PCBM is highly mobile in P3HT
- At 1:1 ratio – PCBM has little effect on P3HT crystallinity

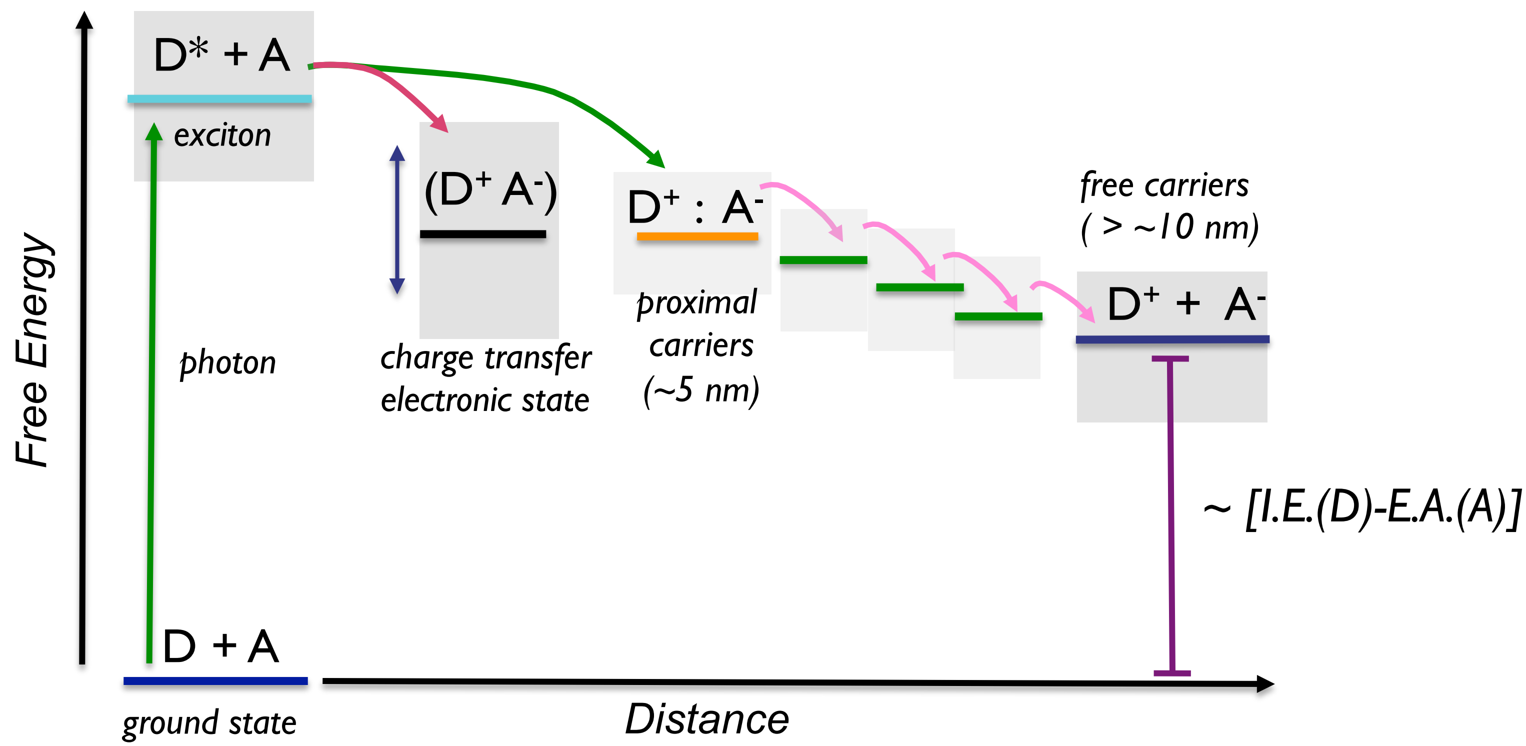
Efficient devices comprise a three phase blend

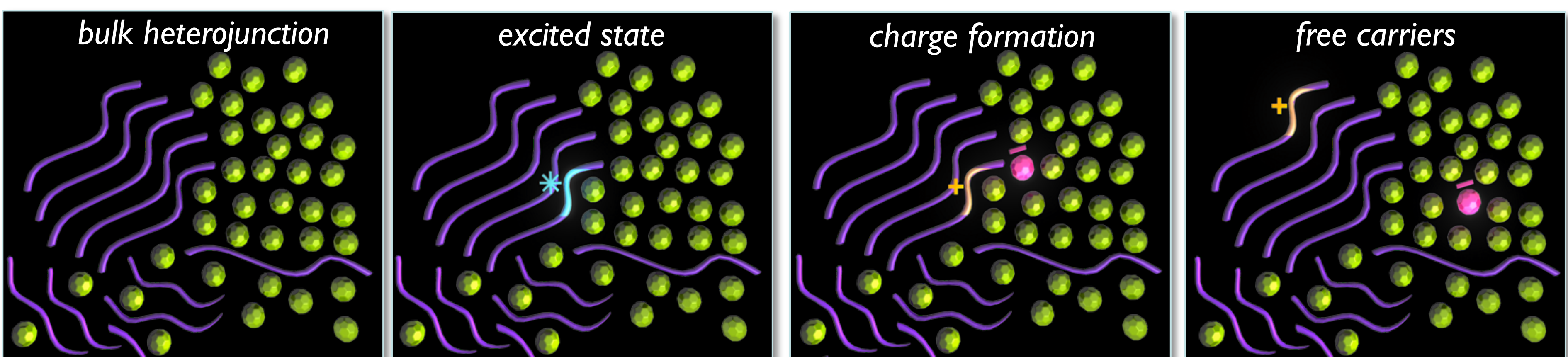
i) pure P3HT; ii) pure PCBM & iii) molecularly mixed P3HT:PCBM

N. Treat, M. Brady, G. Smith, M. Toney, E. Kramer, C. Hawker, M. Chabinyc *Adv. Ener. Mater.* **1** (2011)

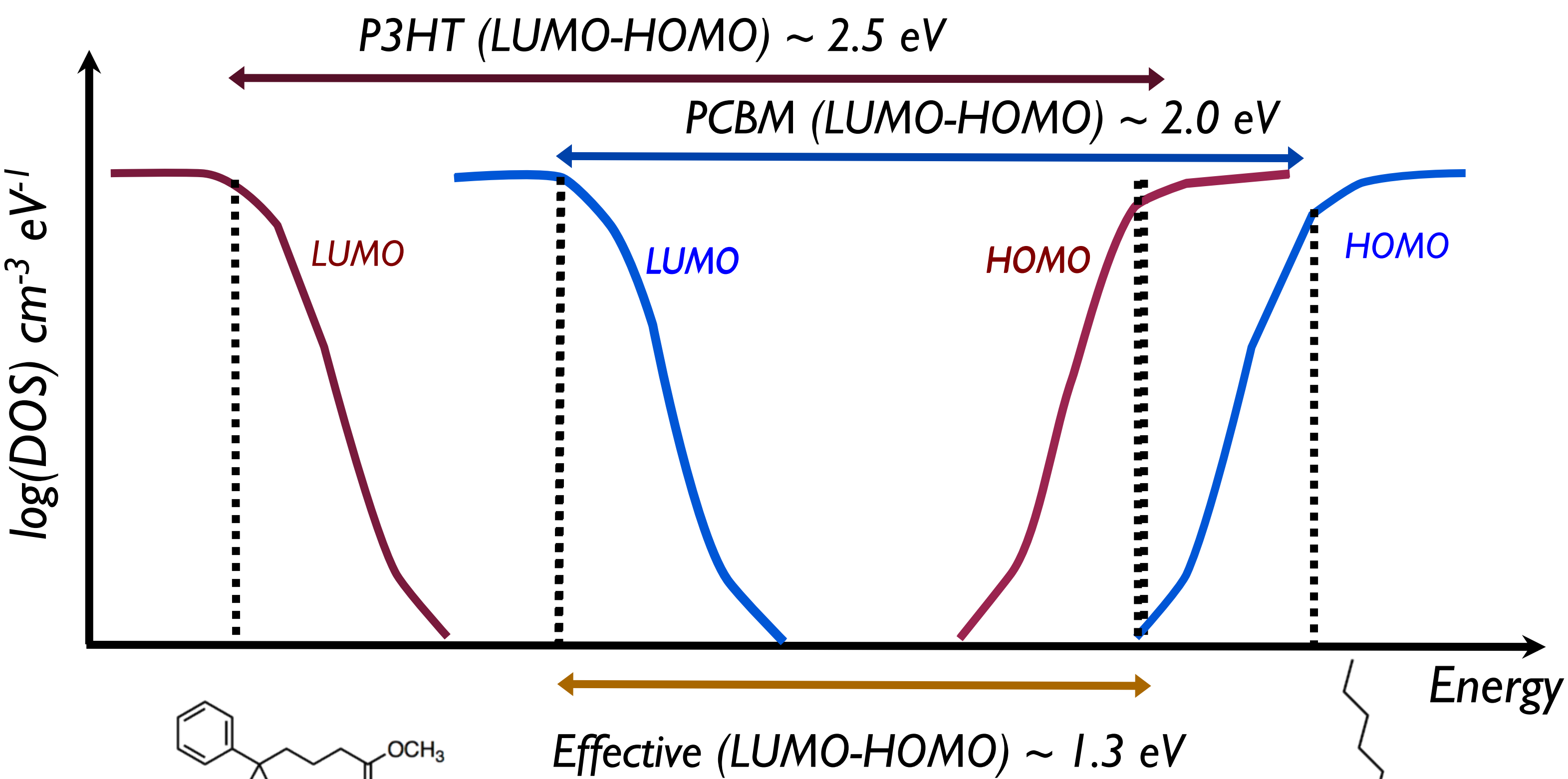
Similar observations by Ade, Russell, Dadmun, many others!

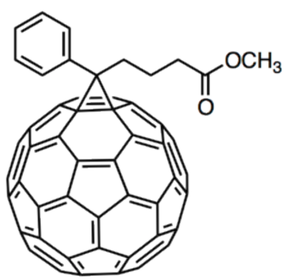
Charge Formation in Bulk Heterojunctions





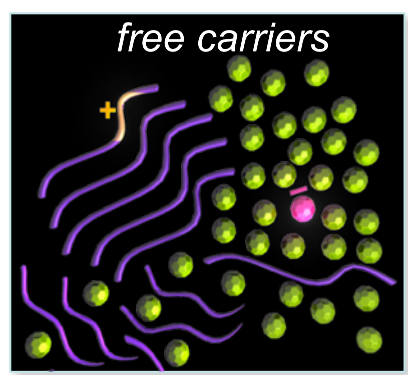
BHJ as an Effective Semiconductor

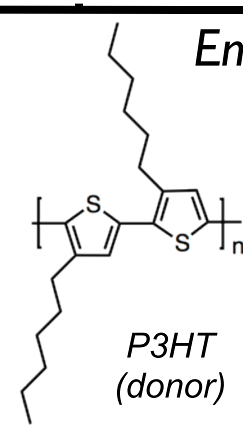




PCBM
(acceptor)

Z.L. Guan, et. al. *Org Elec.* 11 1779 (2010)

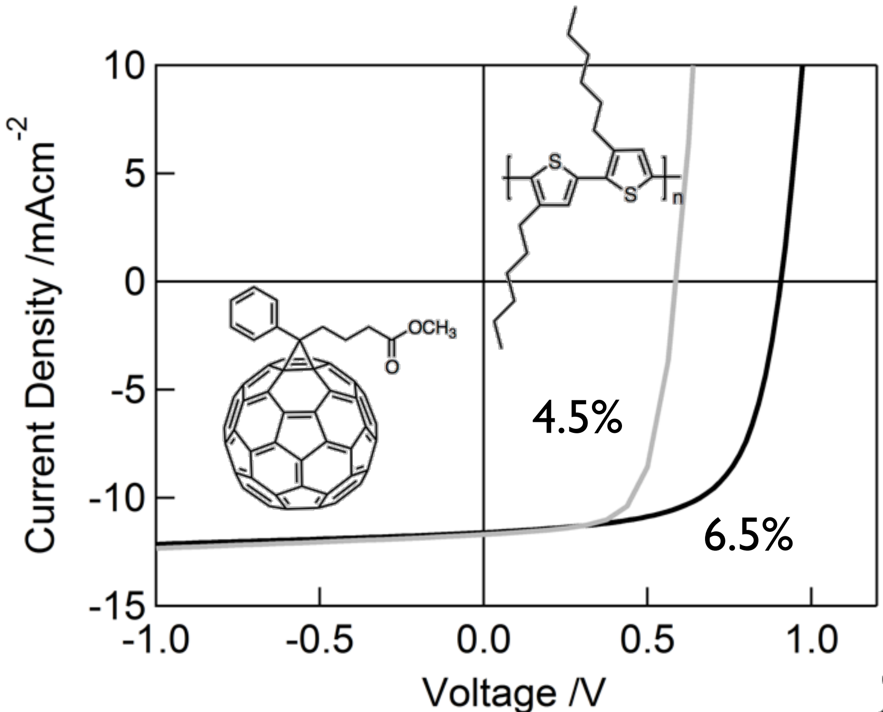


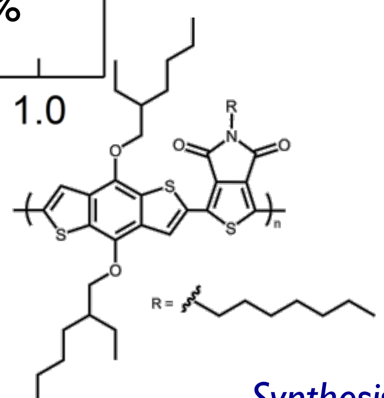


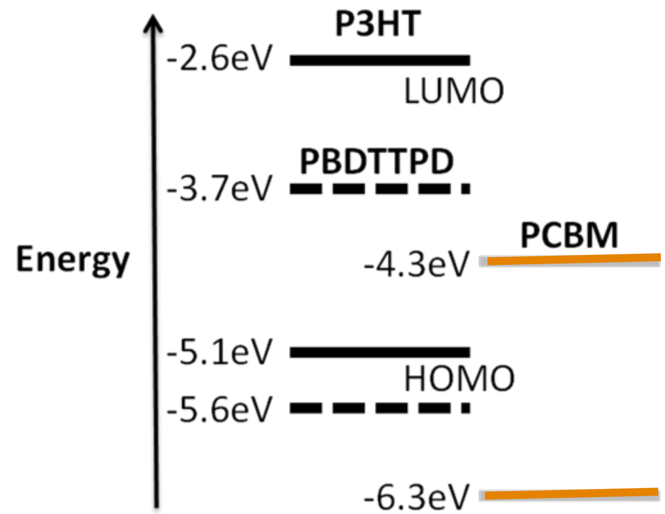
P3HT
(donor)

Transport in Efficient BHJs

Compare two polymers with nearly same optical gap





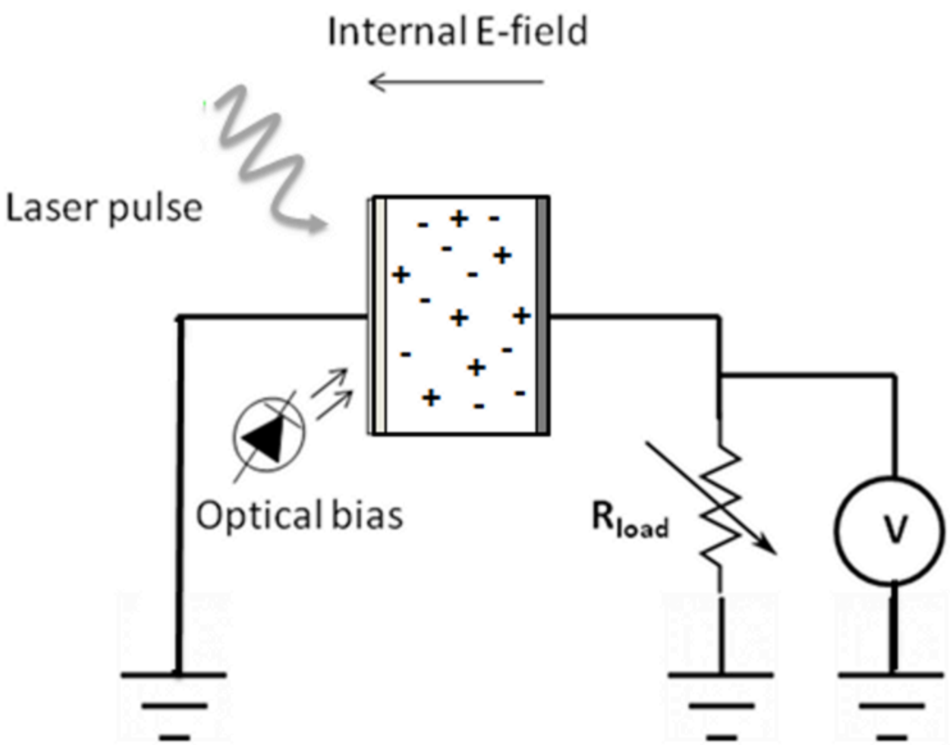


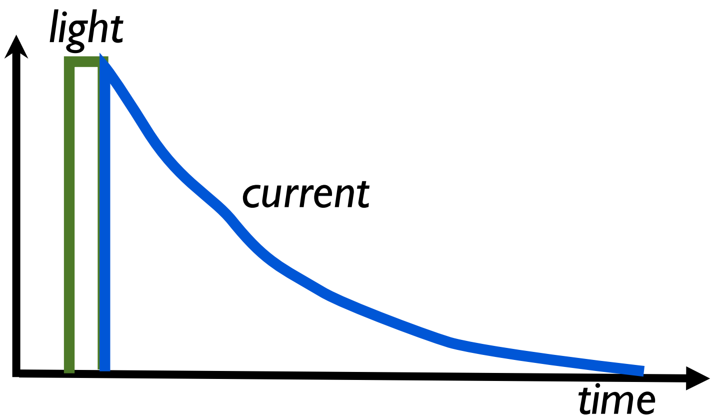
Both have FF ~ 65%;

Synthesis by J. Douglas & J. M. J. Fréchet

C. Shuttle, et. al *Adv. Ener Mater.* (2012)

Charge Extraction from BHJ Photovoltaics





Charges travel to the electrode in dark and have the chance to recombine

R. Street, et. al. *Phys. Rev. B.* 84 075208 (2011)
C. Shuttle, et. al *Adv. Ener. Mater.* **2** 111-119 (2012)

Transient photoconductivity provides timescale of transport and thereby energetics of electronic states

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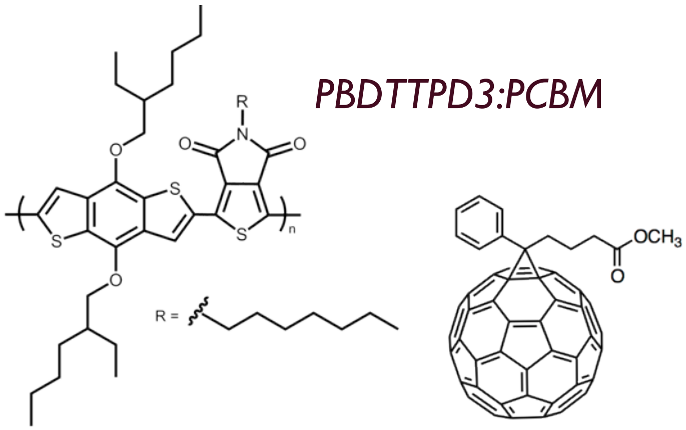
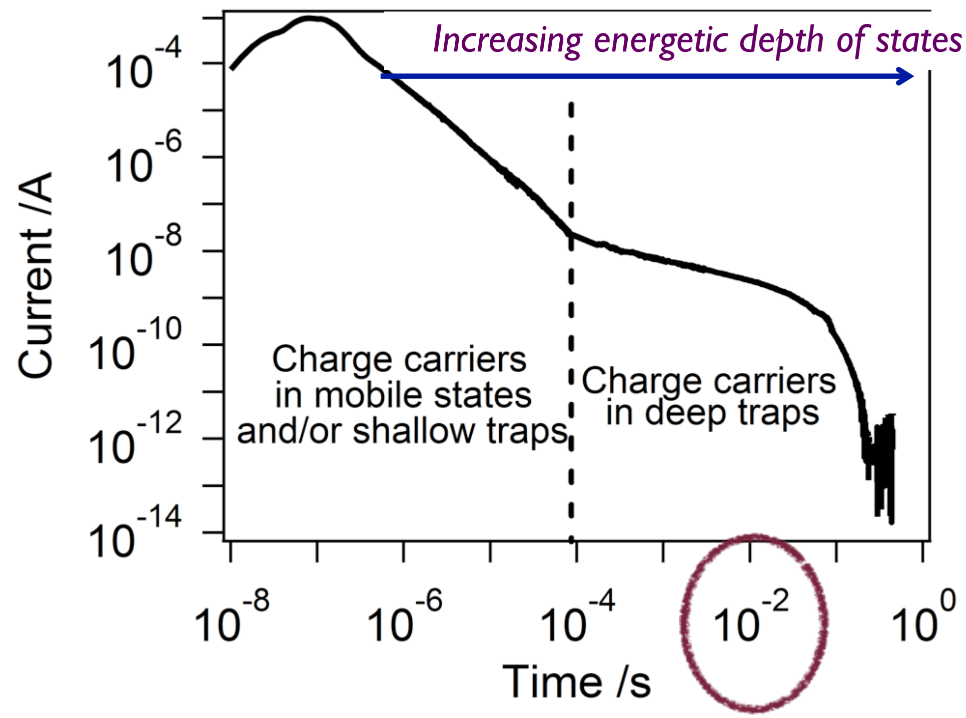
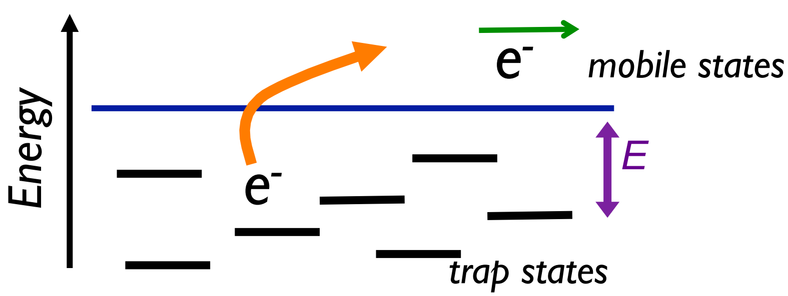
Charge Extraction Transient Shows Deep Lying States

PBDTTPD3:PCBM



C. Shuttle, et. al *Adv. Ener. Mater.*. **2** 111-119 (2012)





trap depth

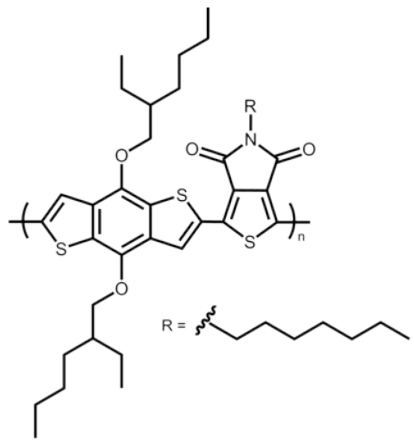
$$\nu e^{-E/k_bT}$$

attempt frequency

Charge extraction shows PBDTTPD3:PCBM has deep lying traps (~ > 0.45 eV away from transport level)

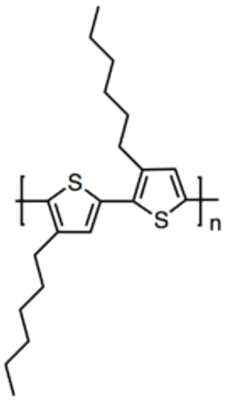
Charge Extraction from BHJ Photovoltaics

PBDTTPD3

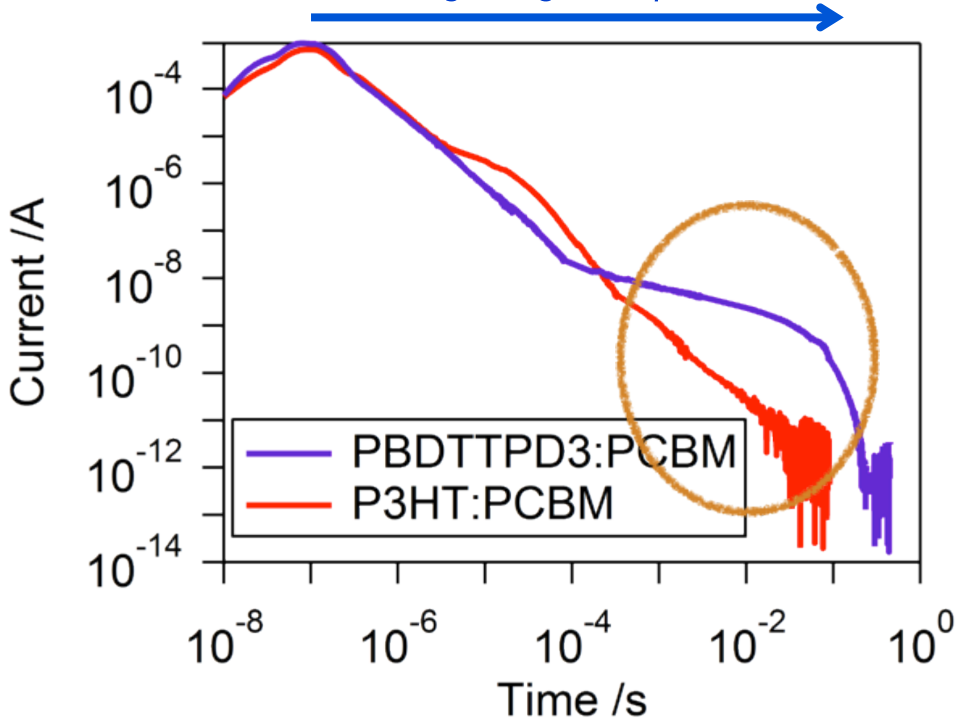


HOMO ~ 5.6 eV

P3HT



HOMO ~ 5.1 eV



C. Shuttle, et. al *Adv. Ener. Mater.*. **2** 111-119 (2012)

No deep states observed for P3HT!

- possible that there are no deep states (unlikely)

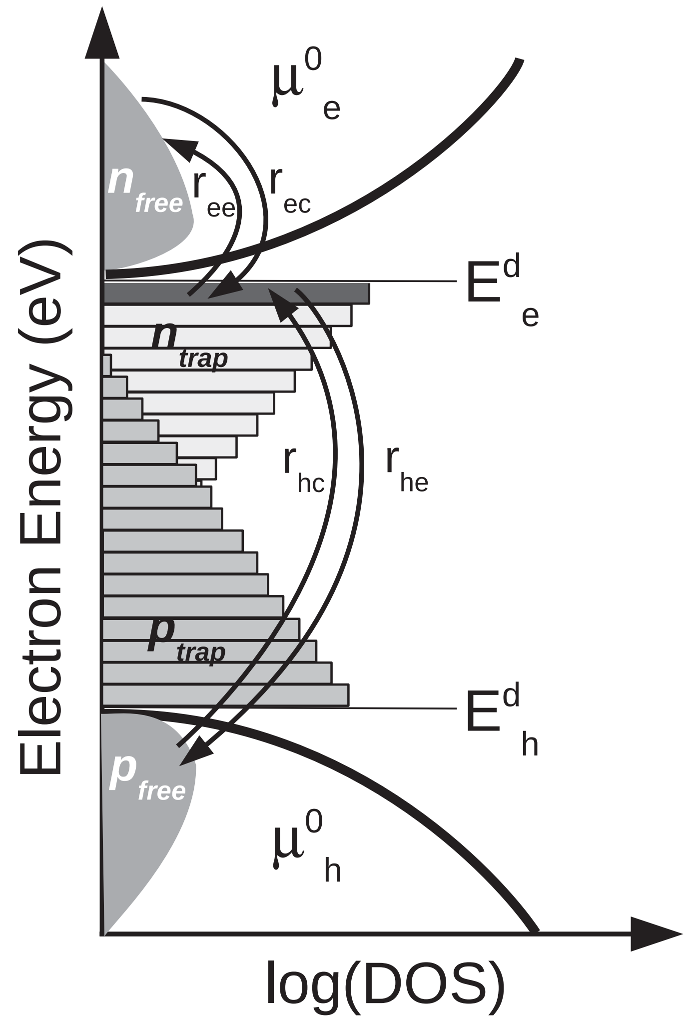
- most likely cause: doping of P3HT
  requires carrier concentration ~10^{15} cm^{-3} (confirmed by ESR)

Can We Learn More from Transients?

Use 1-D model to examine transport, i.e. reduce BHJ to an effective semiconductor

1) Solve Poisson Equation
2) Recombination by Shockley-Reed-Hall mechanism

Fit to combination of transient photocurrent measurements and steady state data



R. MacKenzie, et. al. *Adv. Ener. Mater.* (2012)

Downside: numerical simulation with many parameters

must be very careful to vary measurements and fit all data self-consistently

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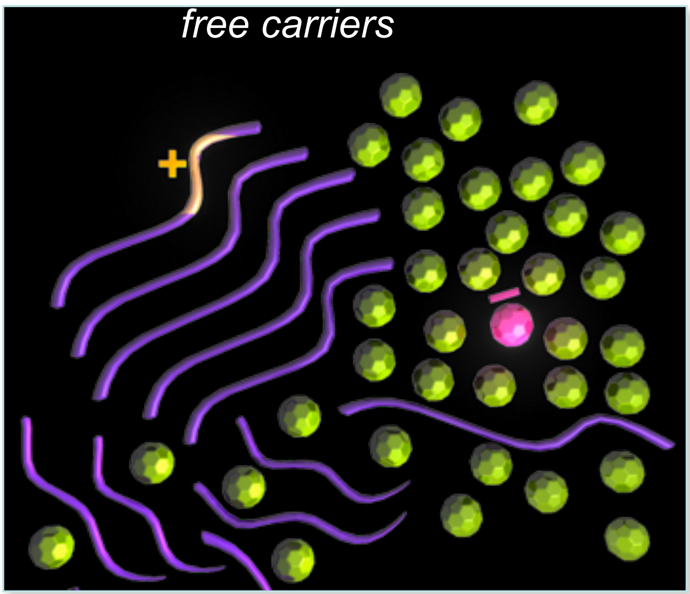
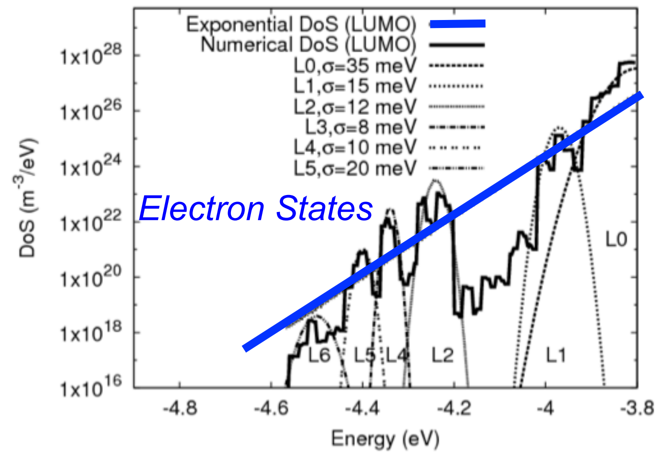
Simulation Reveals Complex Density of States

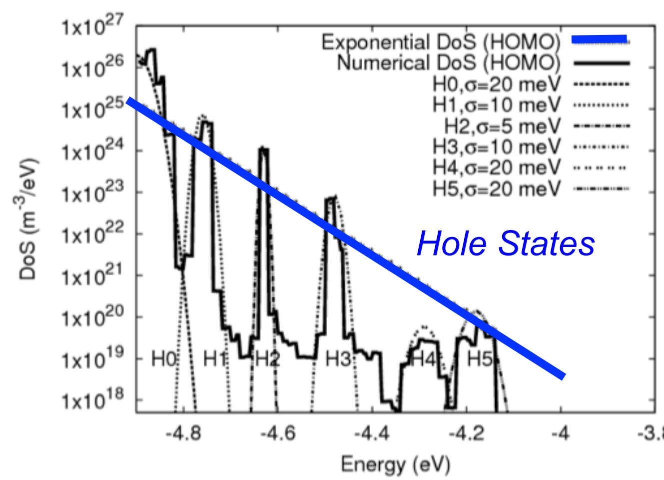
Disorder in BHJ blends leads to distribution of electronic states



P3HT:PCBM

Drift-Diffusion Model w/ SRH trapping

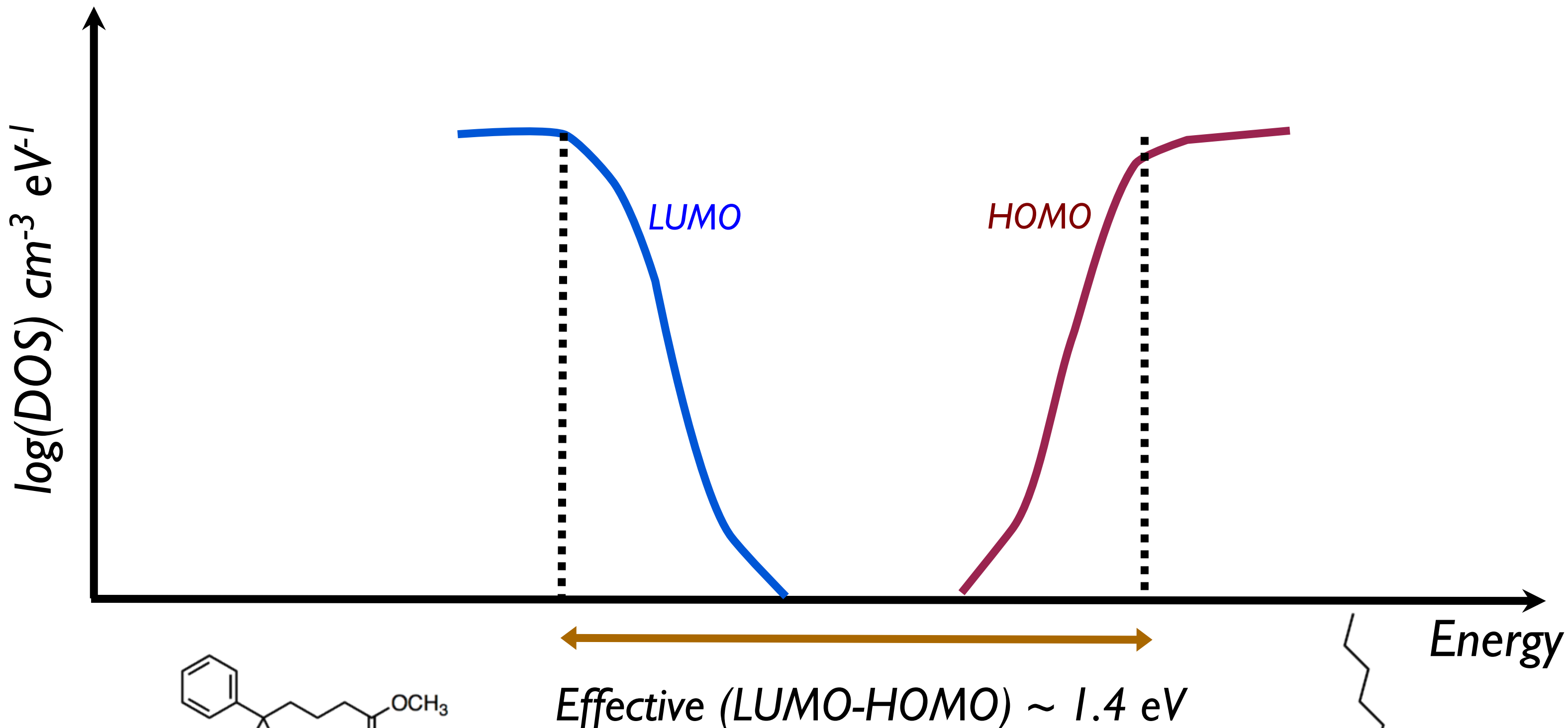


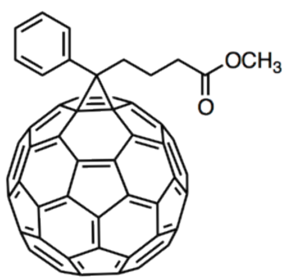


No reason to believe simple exponential or Gaussian is adequate to describe electronic landscape

R. MacKenzie, et. al *Adv. Ener. Mater. (2012)*

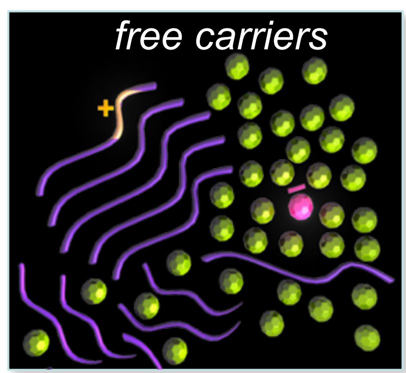
BHJ as an Effective Semiconductor

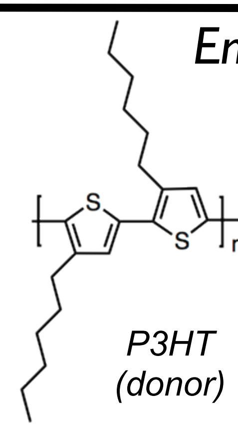




PCBM
(acceptor)

Z.L. Guan, et. al. *Org Elec.* 11 1779 (2010)





P3HT
(donor)

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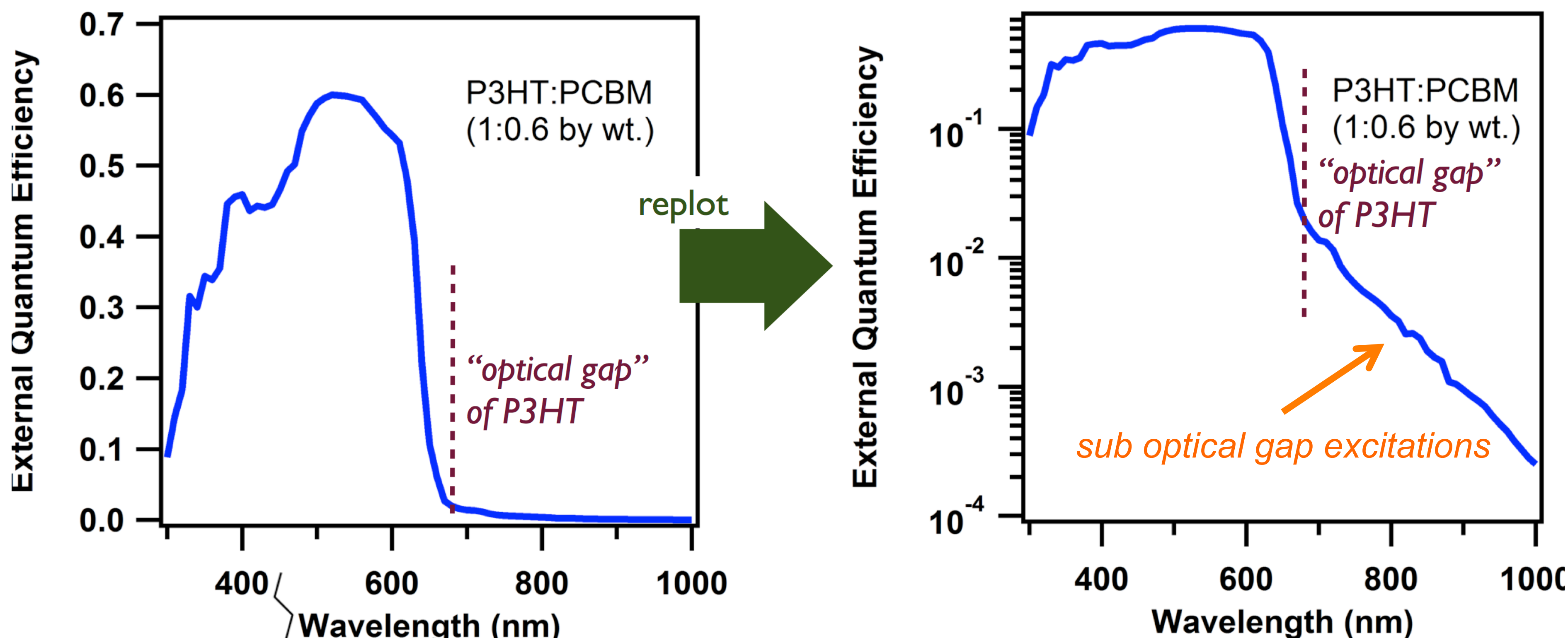
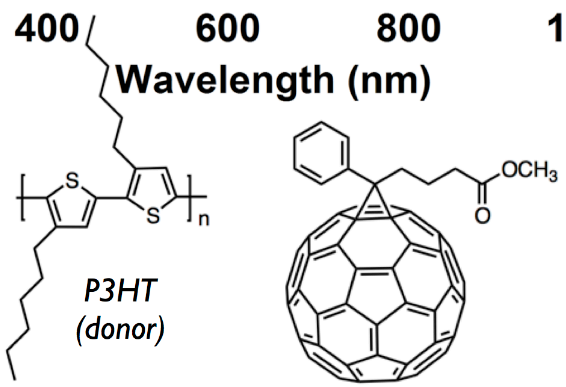
Interface or "Charge Transfer" States

$$EQE = \frac{\text{electrons collected}}{\text{photons incident}}$$





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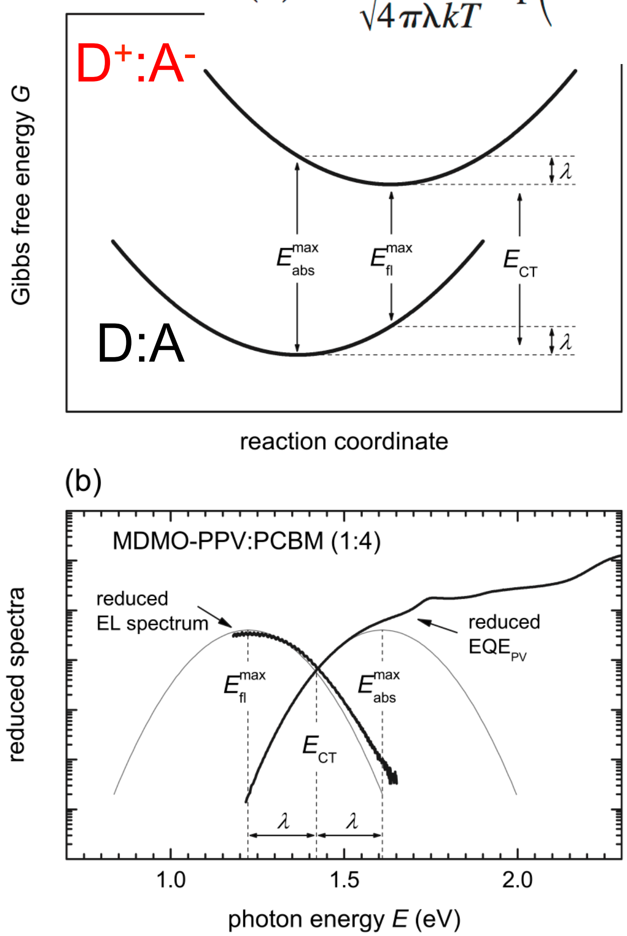
Models of Interface States

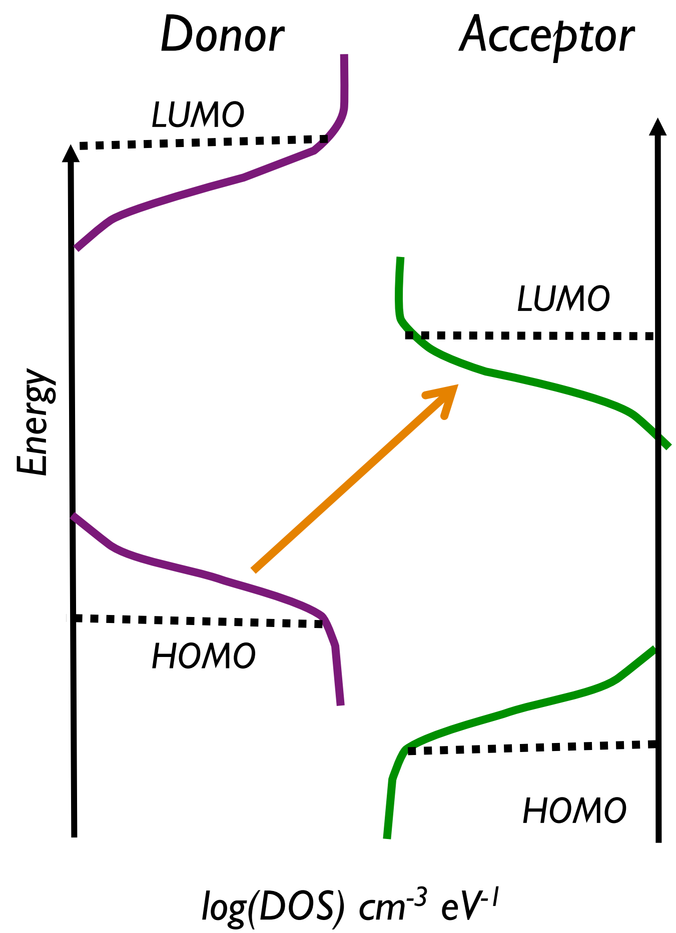
"Marcus" CT States of Donor:Acceptor

$$\sigma(E)E = \frac{f_\sigma}{\sqrt{4\pi\lambda kT}}\exp\left(\frac{-(E_{CT}+\lambda-E)^2}{4\lambda kT}\right)$$



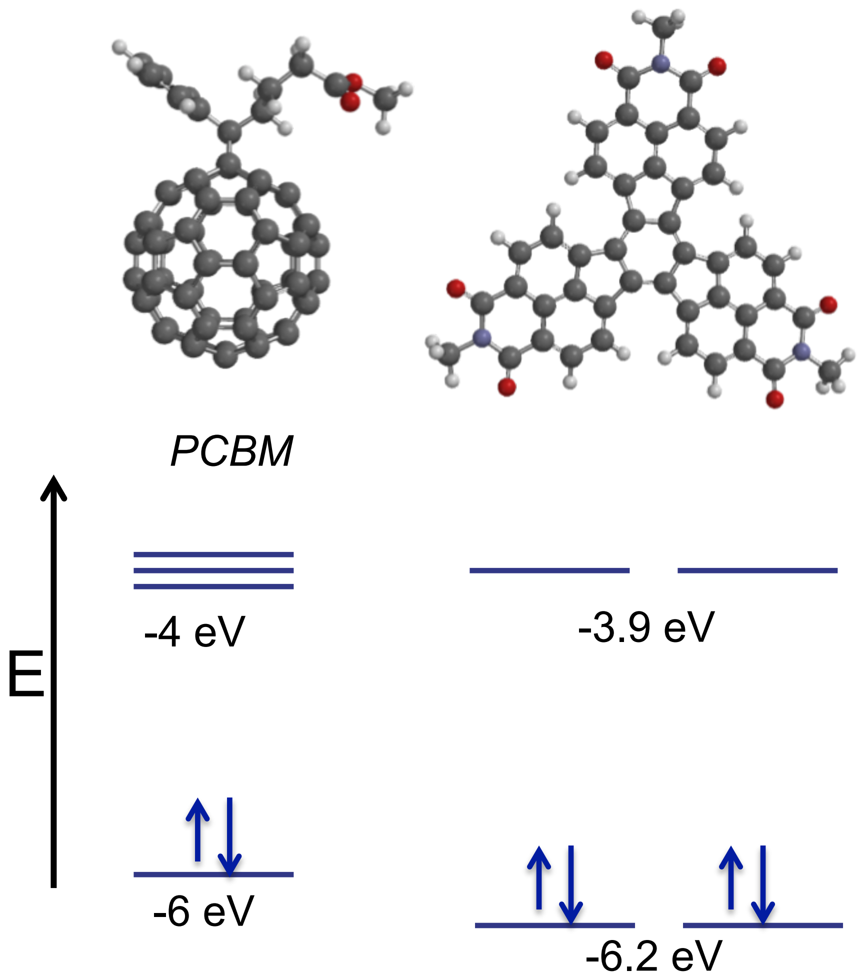
K. Vandewal, et. al. *Phys. Rev. B.* 81 125204 (2010)

Disorder – band tails



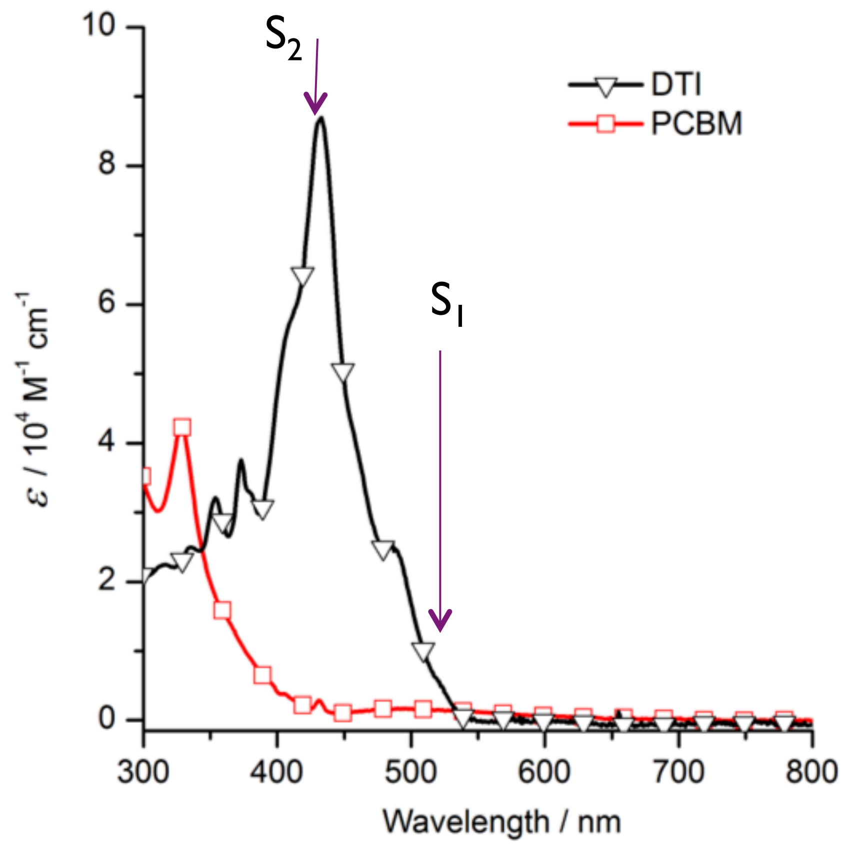
R. Street *Phys. Rev. B.* 83 165207 (2011)

Decacyclene-based Acceptors



Synthesis by T. Pho, F. Toma & F. Wudl

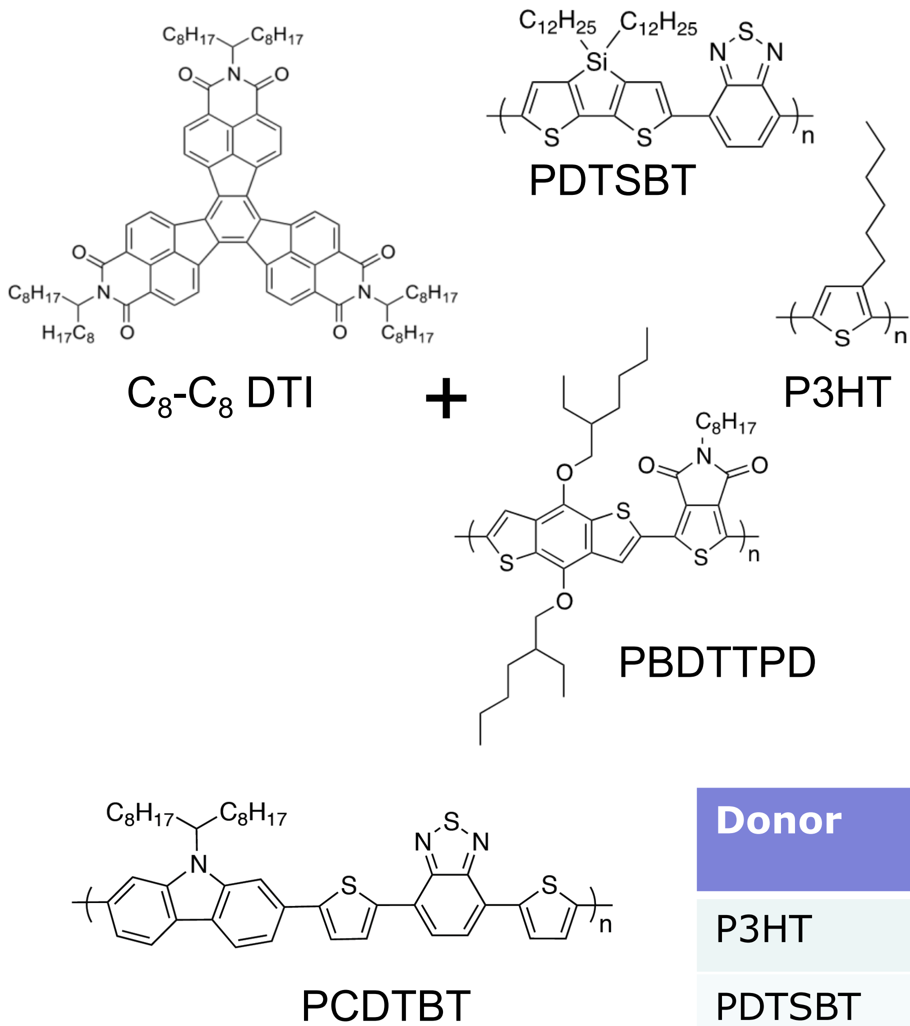
Optical absorption in chloroform

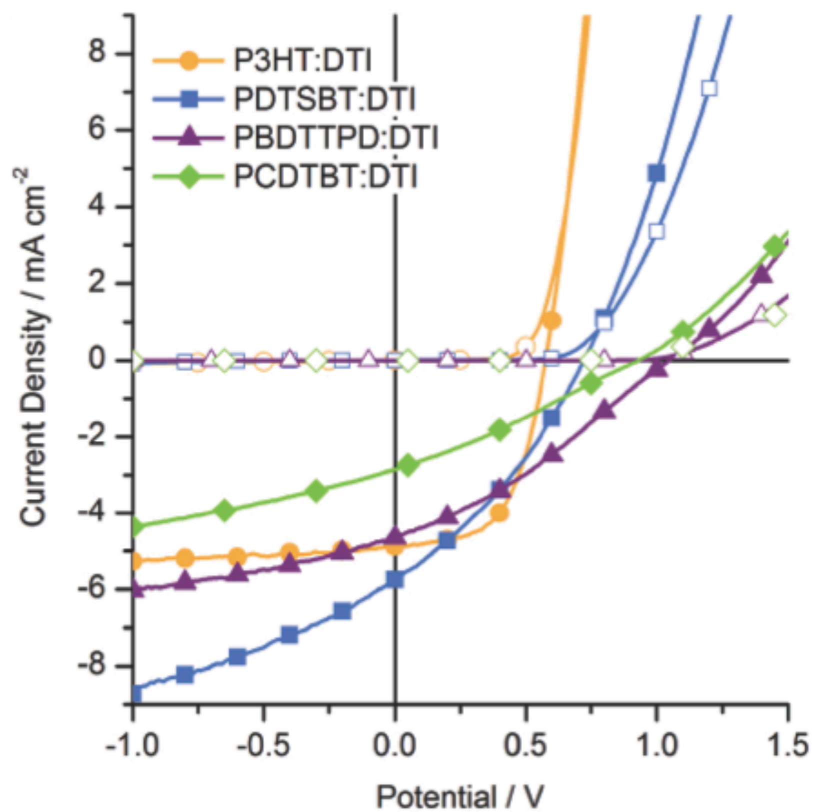


T. Pho, et. al *Angew. Chemie*
doi: 10.1002/anie.201207608 (2012)

- Similar electronic levels to PCBM; stronger optical absorption

DTI is a well-performing non-fullerene acceptor

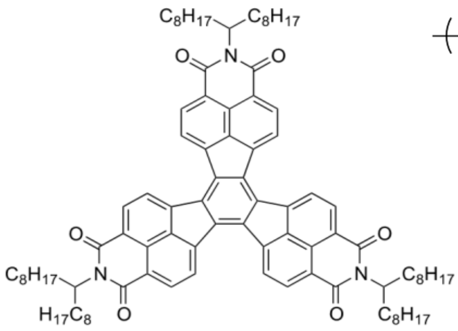




Donor	J_{SC} (mA/cm²)	V_{OC} (V)	FF	PCE (%)
P3HT	4.56	0.61	0.53	1.48
PDTSBT	5.75	0.72	0.33	1.36
PBDTTPD	4.65	1.05	0.31	1.5
PCDTBT	2.86	0.93	0.28	0.75

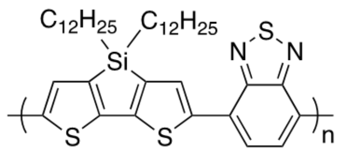
All devices as-cast

Excitation of DTI or Donor Leads to Charge Generation

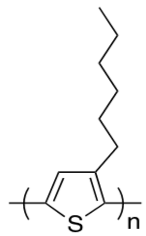


C_8-C_8 DTI

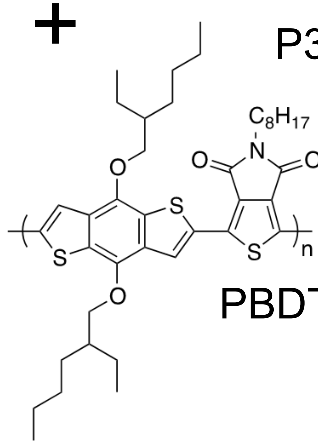
+



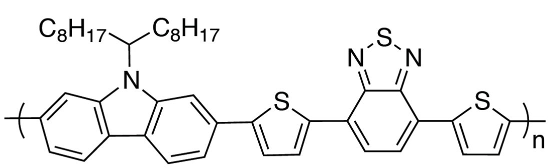
PDTSBT



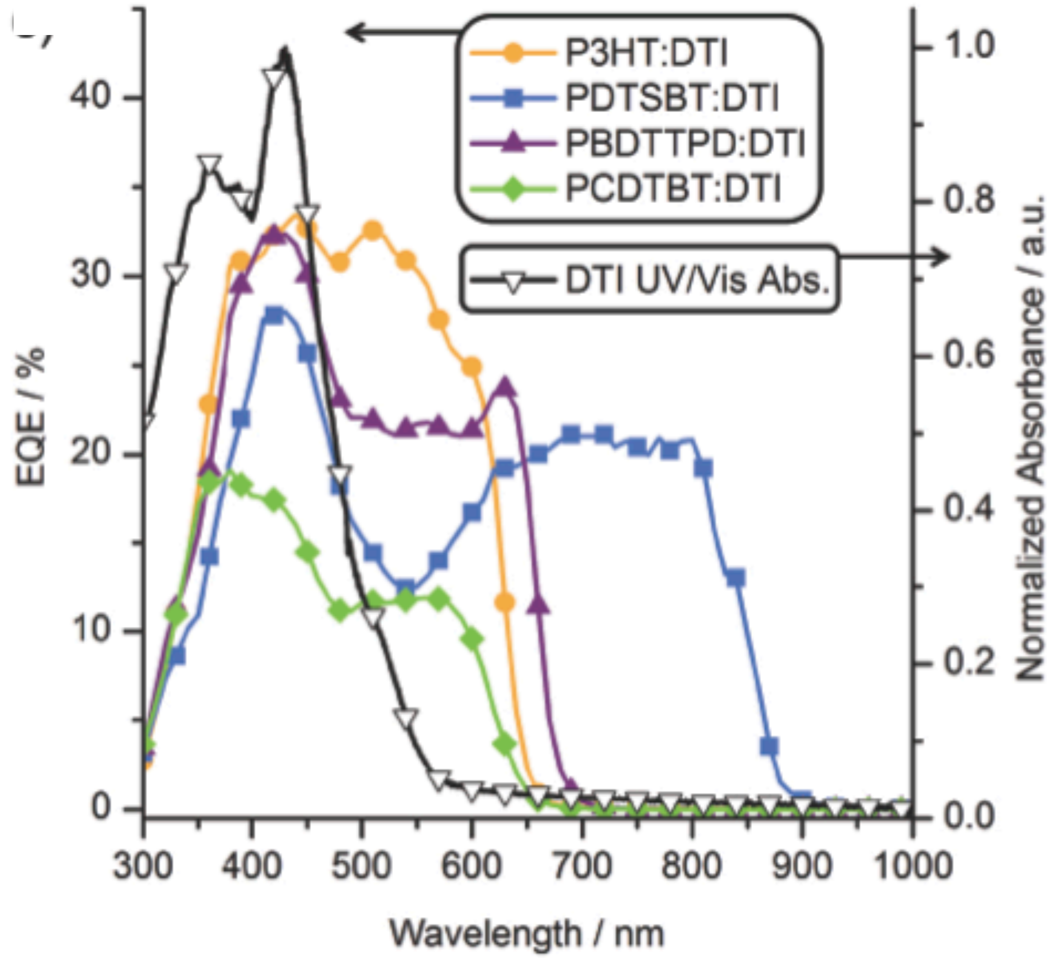
P3HT



PBDTTPD

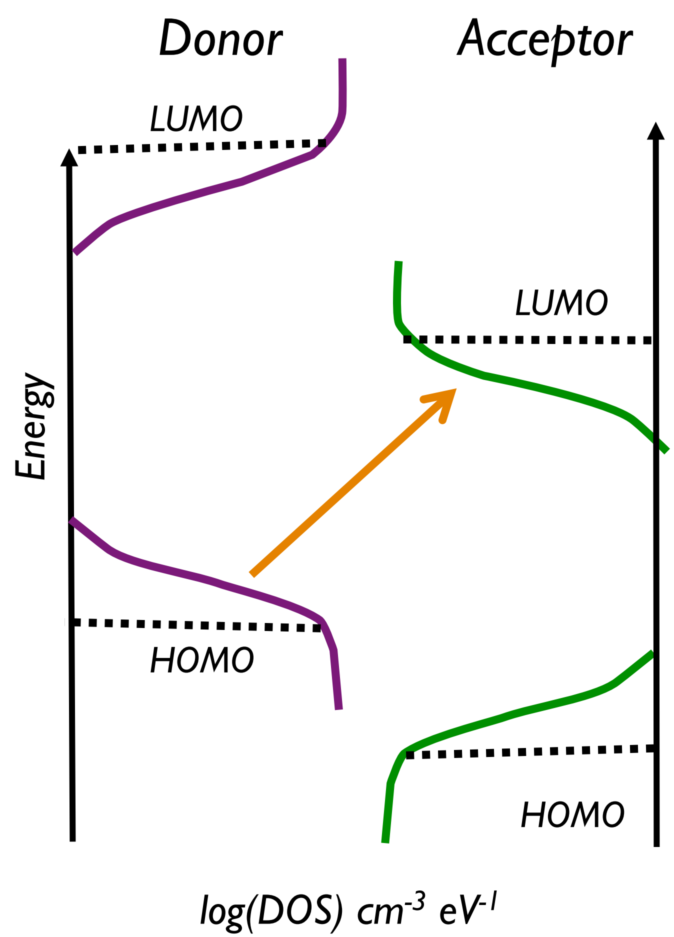


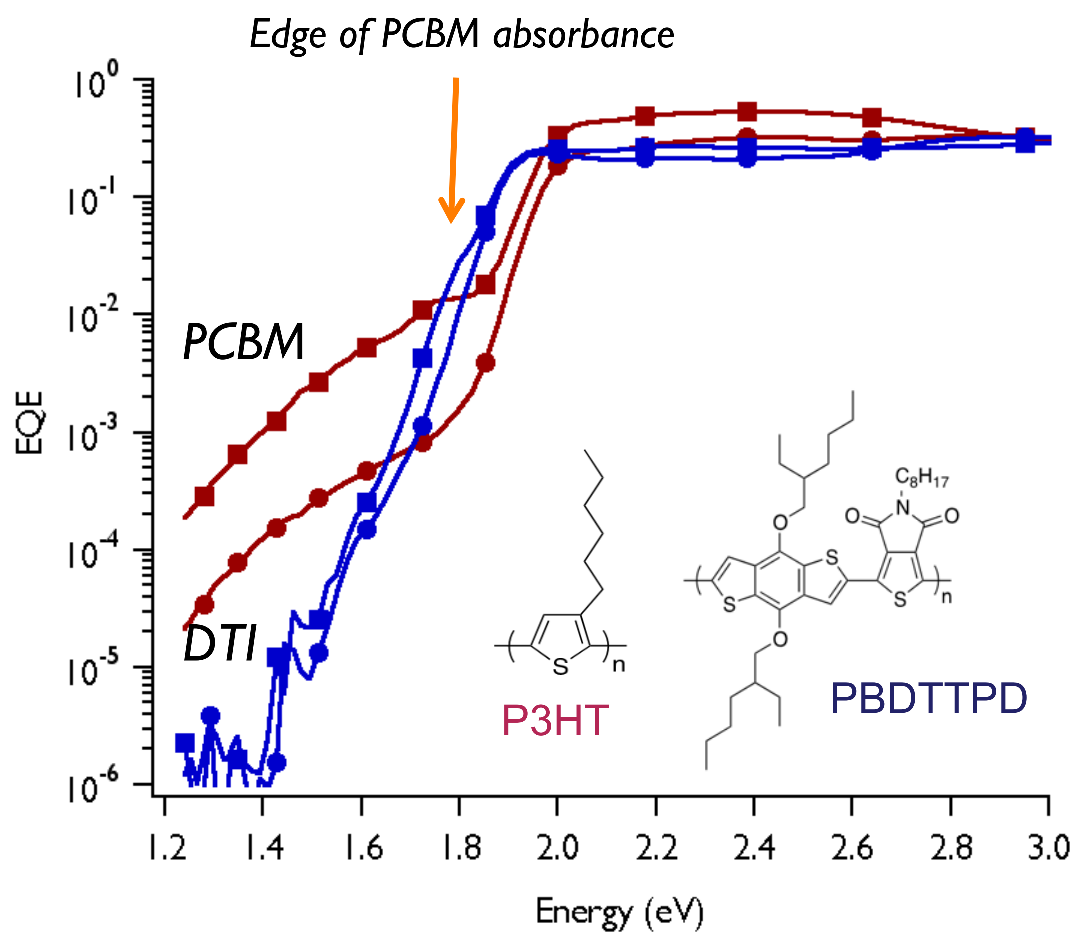
PCDTBT



All devices as-cast

Charge Transfer State Observed in Tail of EQE



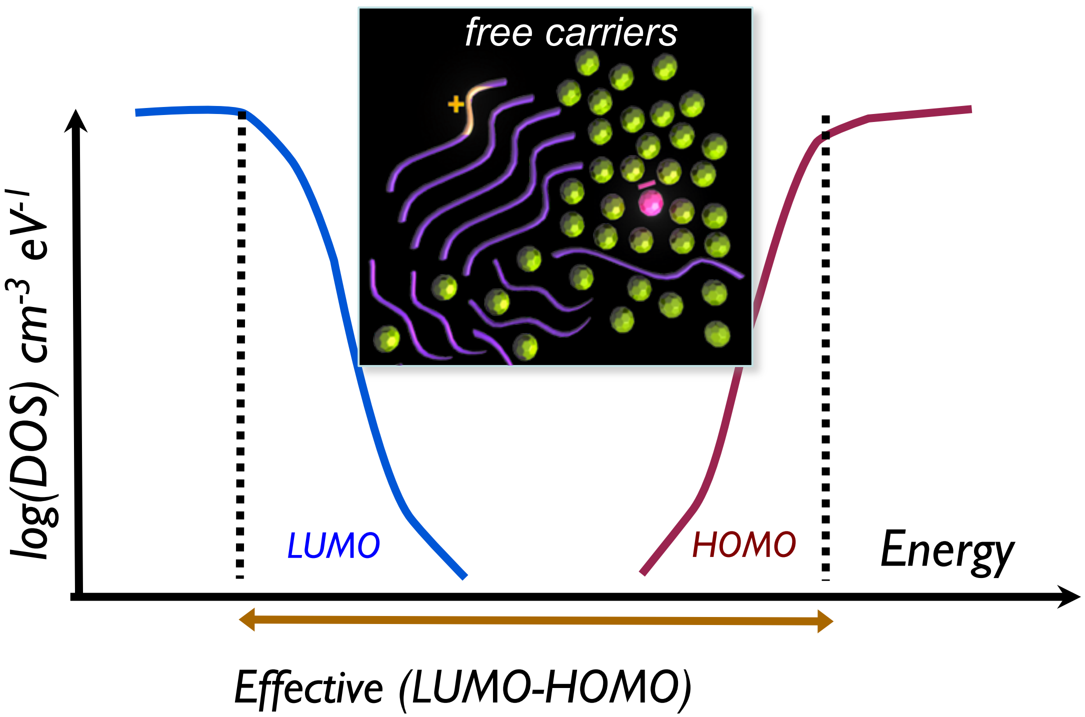


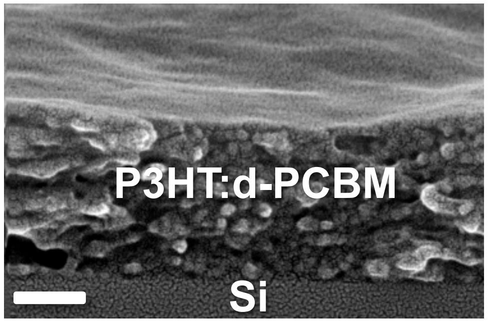
Reorganization energies unlikely the same

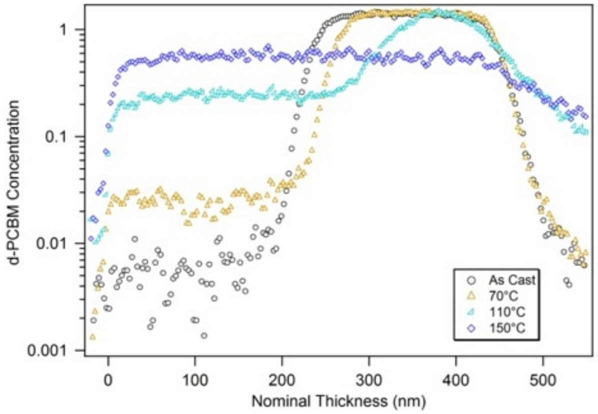
- suggests interfaces states due to disorder

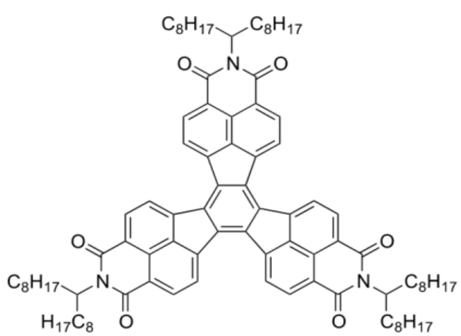
Summary

- Fullerenes have substantial molecular mobility in semiconducting polymers
- Mixing observed in BHJ occurs due to PCBM diffusion within amorphous P3HT
- Non-fullerene acceptors helpful to understand interfacial states









C_8-C_8 DTI

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- Dr. Betrand Tremolet de Villers
- Dr. Simon Bubel
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