Molecular Electronics: Ensembles & Dynamics

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July 25, 2009

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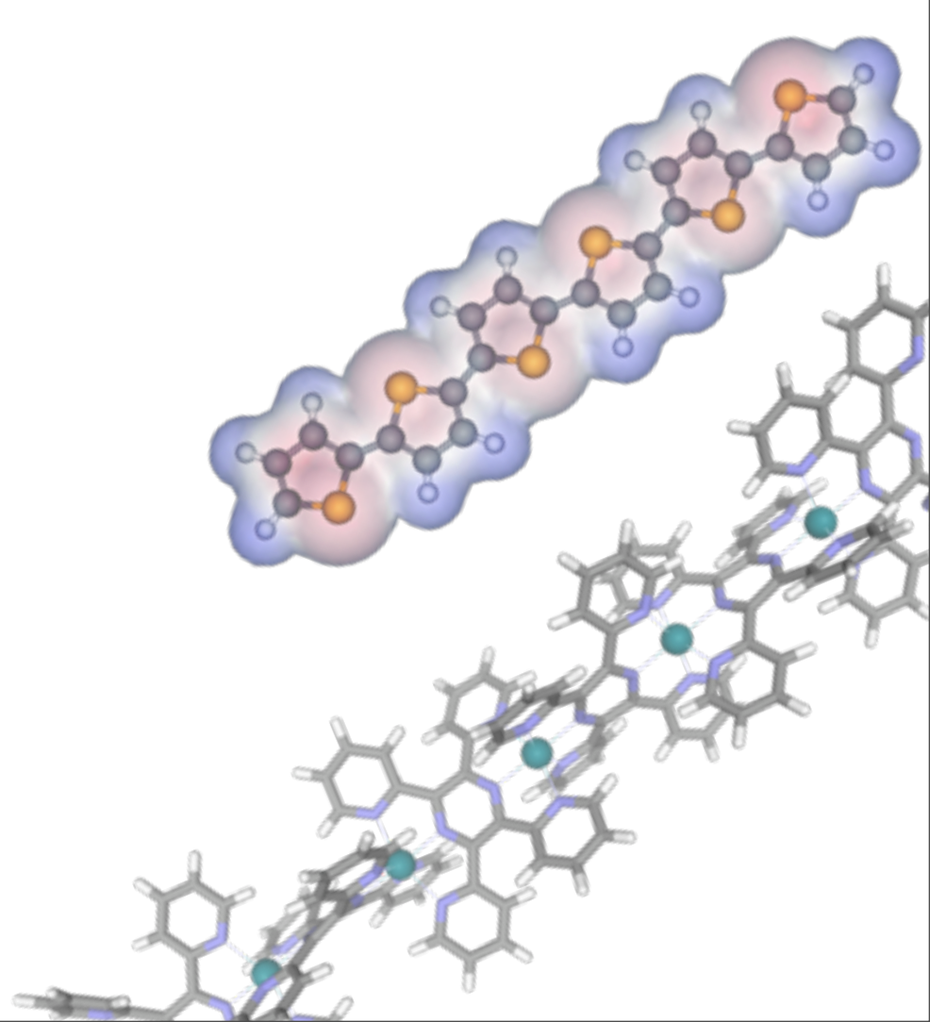
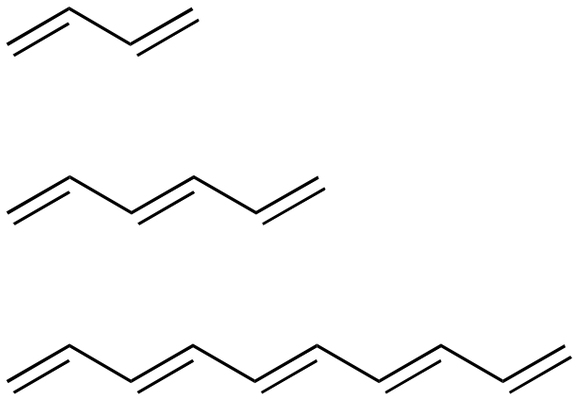
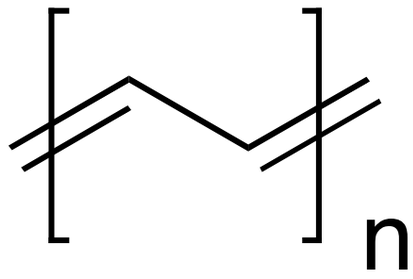
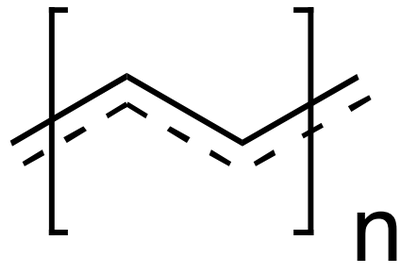


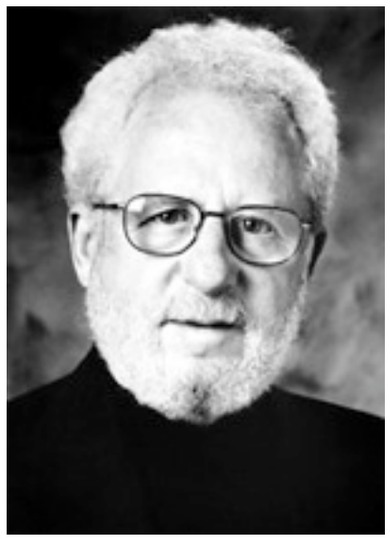
Particle in a Conjugated Box

How do electronic properties scale with box length?





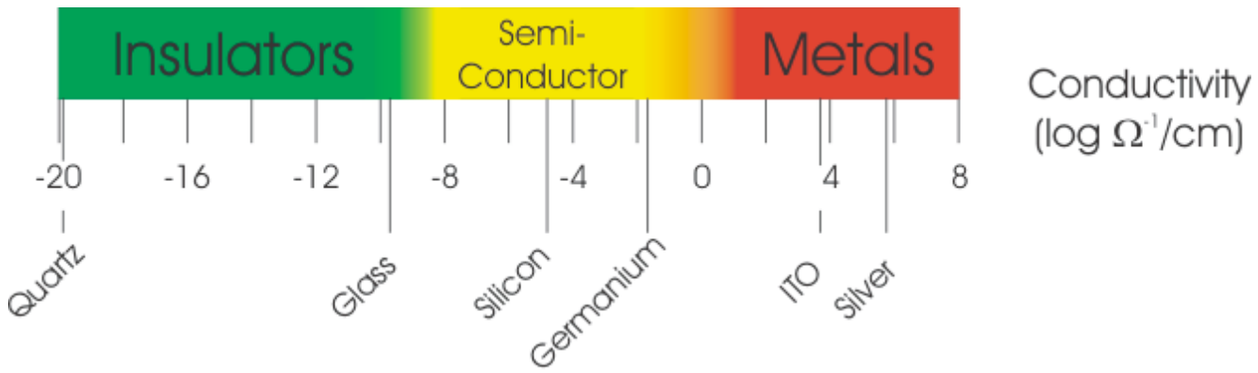




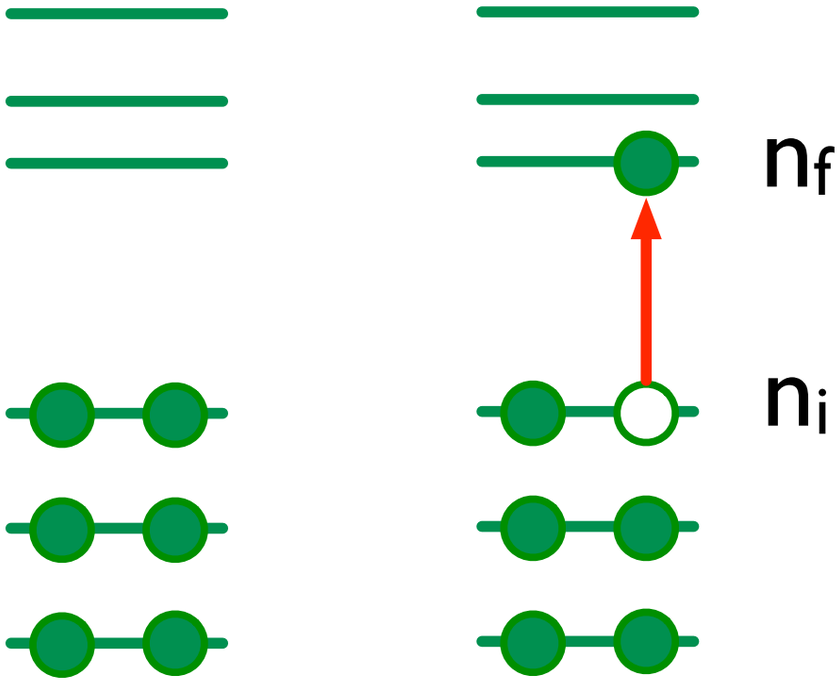
Heeger MacDiarmid Shirakawa

Nobel Prize, 2000

"For the discovery and development of conducting polymers"



Optical Excitations and Free-Electron Model

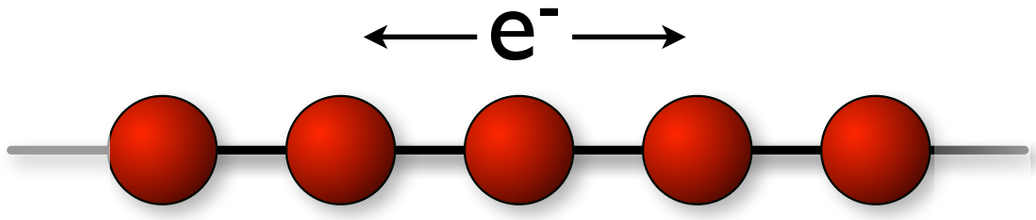


$$E = \frac{h^2 n^2}{8ma^2}$$

$$\Delta E = ?$$

Particle-In-A-Box for Conjugated Systems

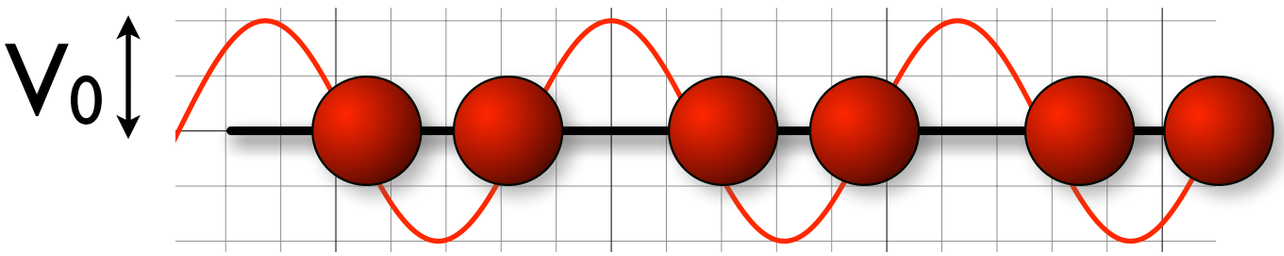
Conjugated systems are frequently treated like "particle in a box"



$$\Delta E = \frac{h^2(2N+1)}{8mL^2}$$

but $\Delta E \rightarrow 0$ as $L \rightarrow \infty$

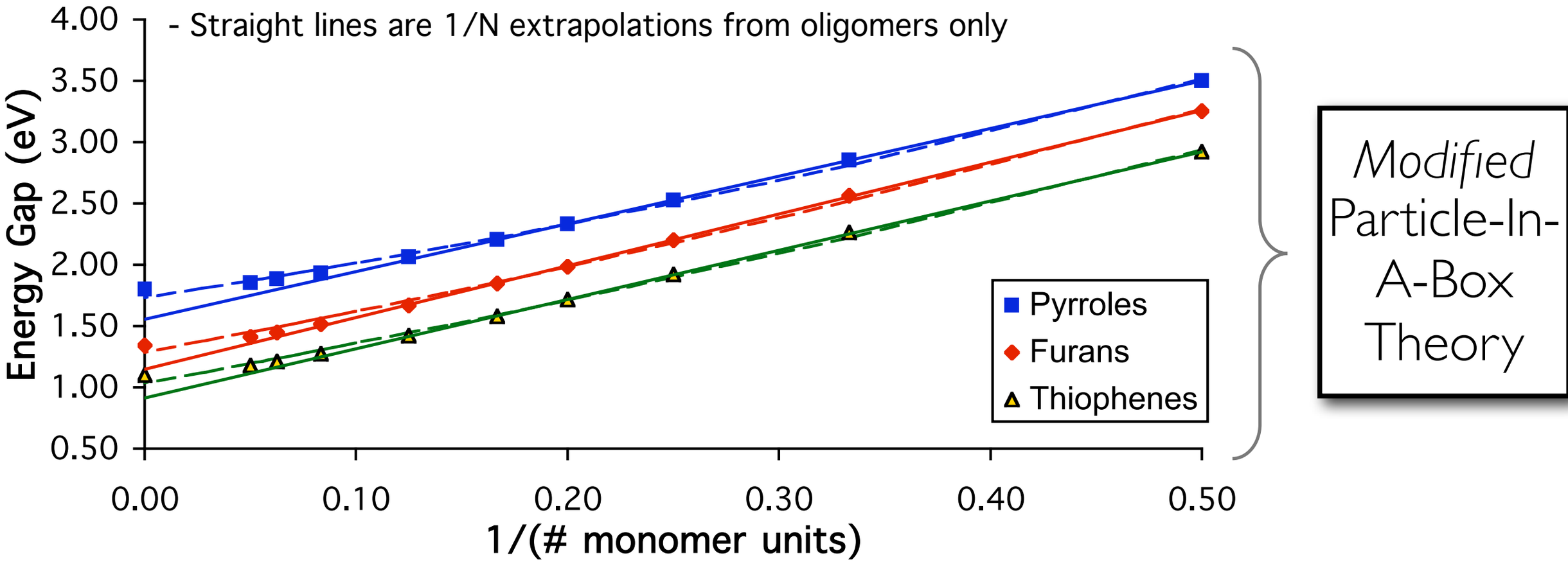
In reality, Peierls distortion implies a nonzero potential energy (e.g. sine wave): dimerization & finite band gap V_0



$$\Delta E = \frac{h^2(2N+1)}{8mL^2} + V_0(1-\frac{1}{N})$$

Since N and L both increase with # of units
$\Delta E \propto N/L^2 \propto 1/(\#\text{ of units})$

How Does Optical Band Gap Scale with Oligomer Length?



Full idealized polymer calculations show deviations from 1/N starting at ~10-20 monomer units

Hutchison, et. al. *Phys. Rev. B* **2003** *68* no.035204.

Improving Bulk Conductivity?

$$\sigma = ne\mu$$

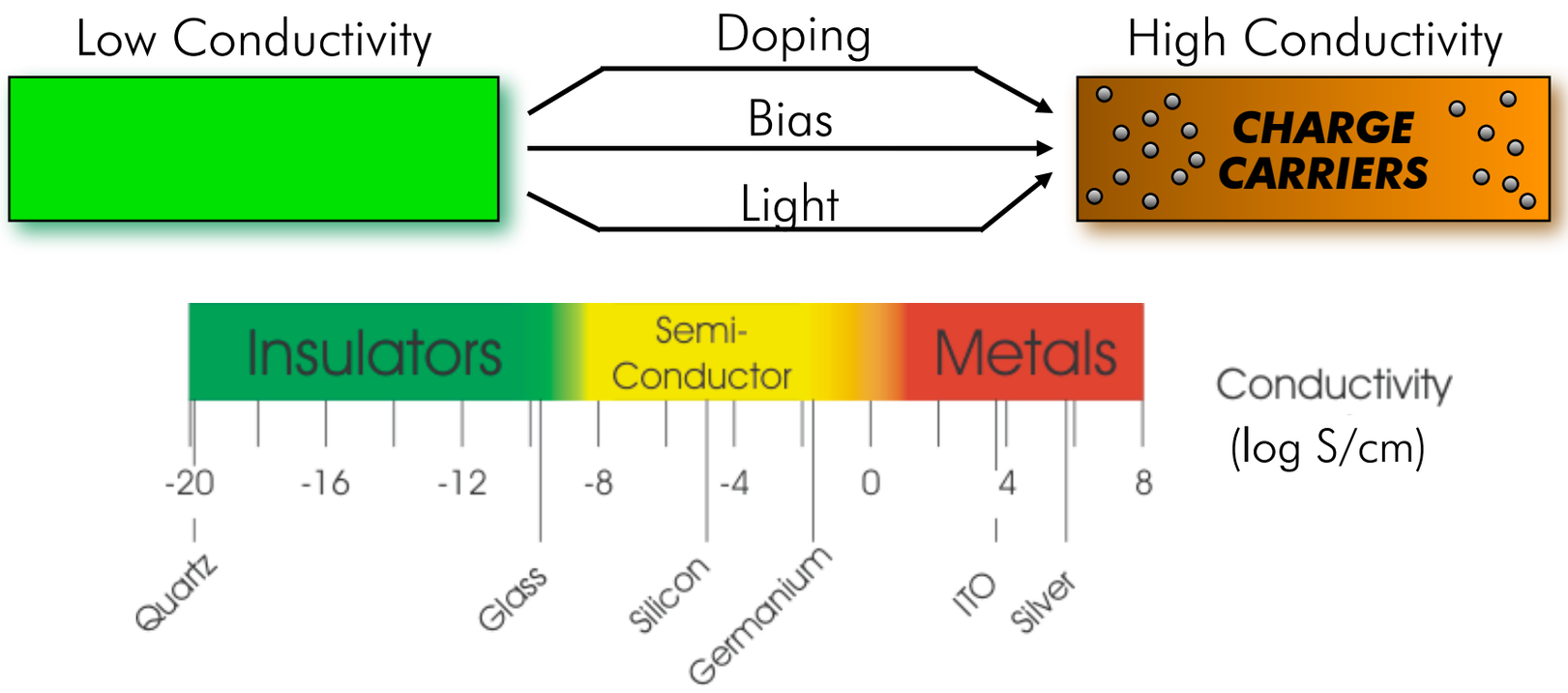
- **n** concentration of carriers
- **e** charge per carrier
- **μ** mobility of carriers

- There's a limit to improvement in n
- Carrier charge e is fixed!
- Must improve mobility

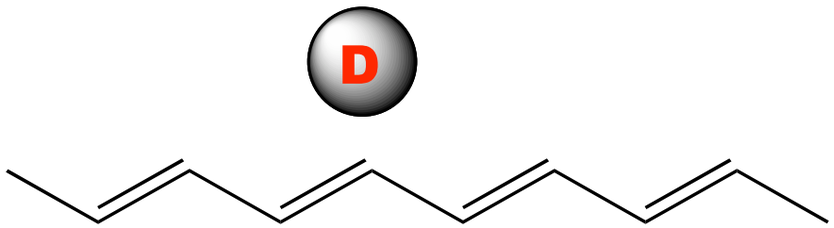
Organic Conductors and Semiconductors

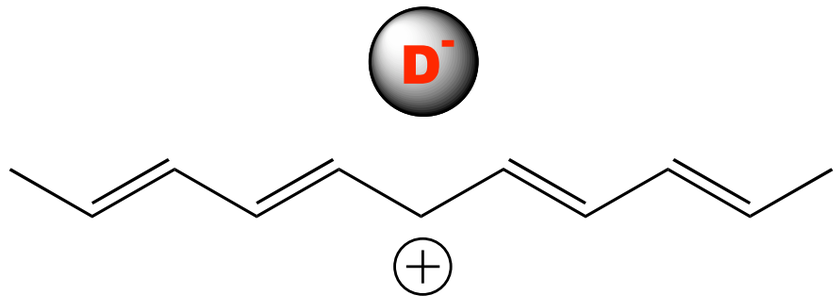
Conjugated organic materials can be converted from insulators/semiconductors

- *Doping (conductive polymers e.g., doped polyacetylene)*
- *Bias (electrical switching for field-effect transistors)*
- *Light (photoconductivity/photovoltaics)*



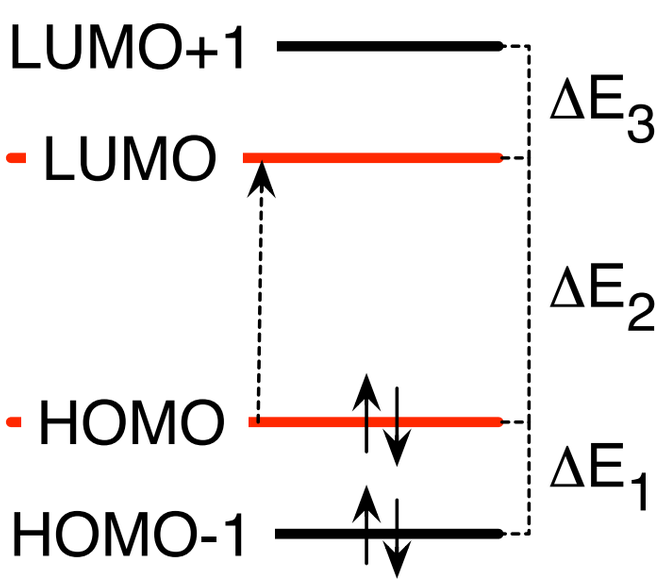
Band Theory and Doping: Midgap States and Carriers



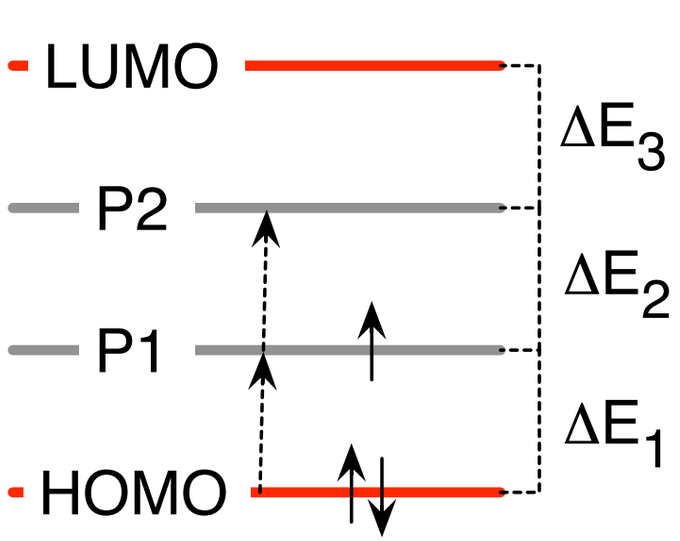


Energy

Neutral

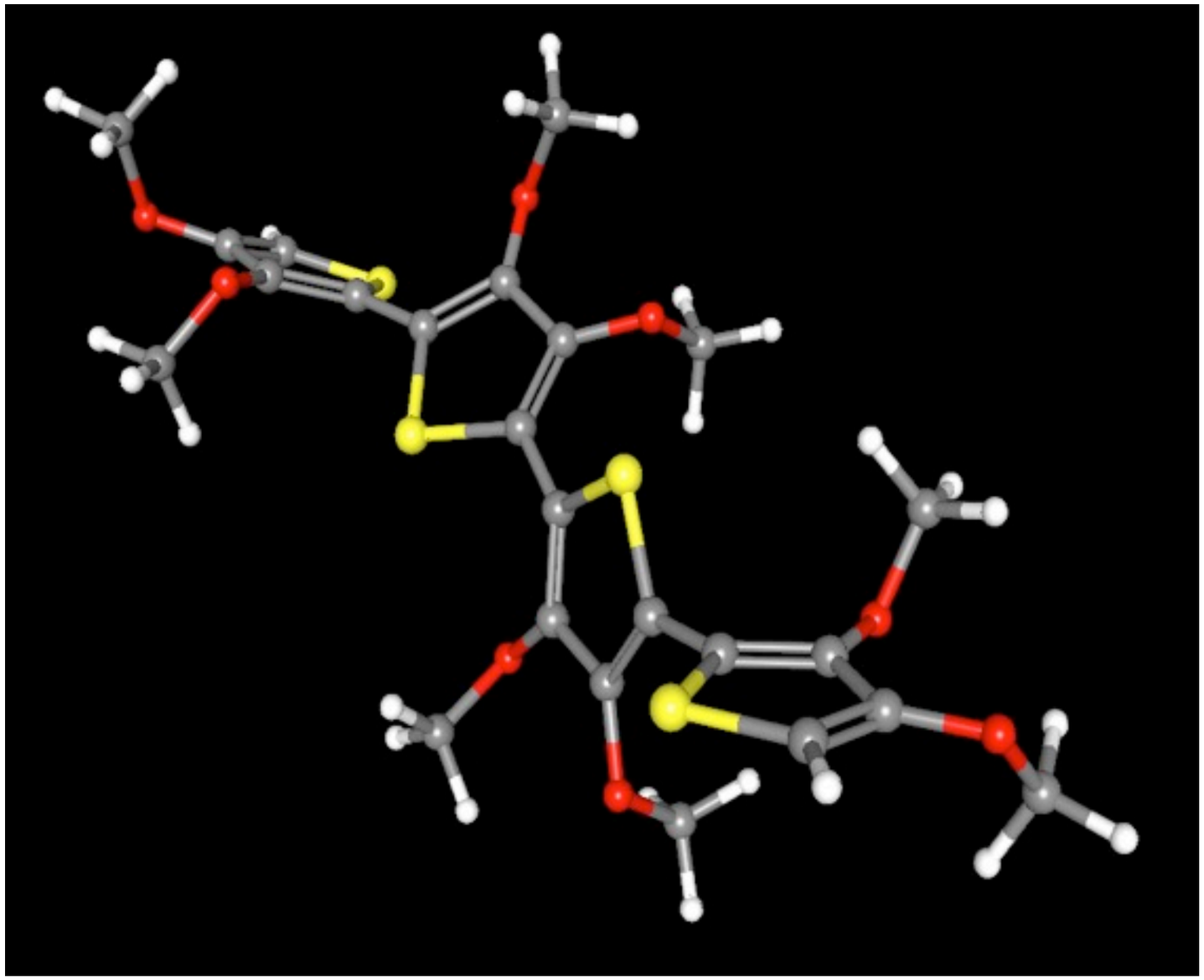


(+) Polaron

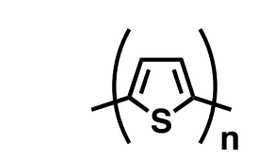


But... are the Chains Completely Planar?

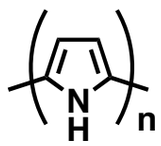
No!



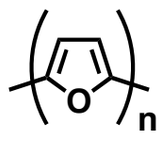
Predicting First Excited States
Survey Set: 60 Oligoheterocycles



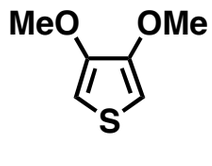
1-6 (n=1-6)



7-11 (n=1-3, 5, 7)



12-15 (n=1-4)



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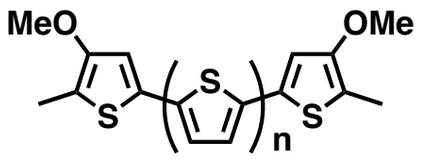
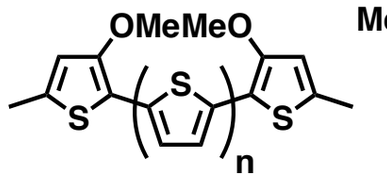
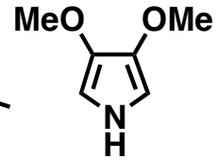


17-19 (n=0-2)



20-23 (n=0-3)



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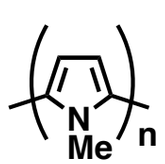
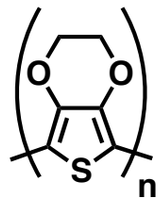
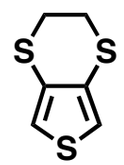


25-30 (n=2-6,8)



31-33 (1-3)



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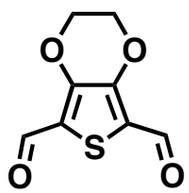
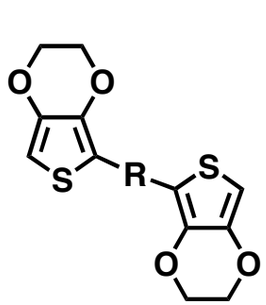
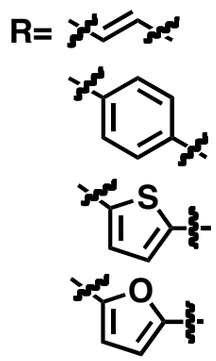


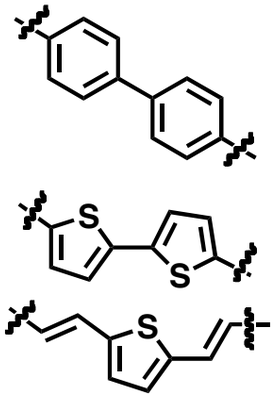
35

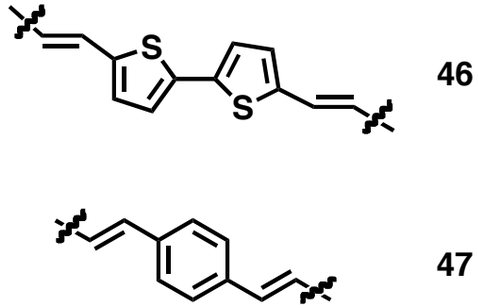
36-38 (n=2-4)

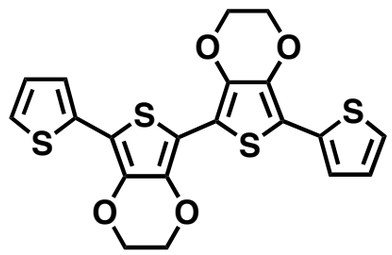


39-47









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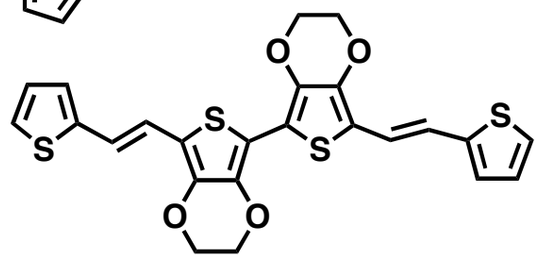

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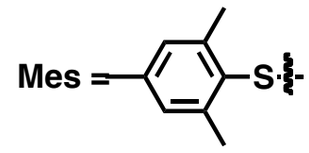
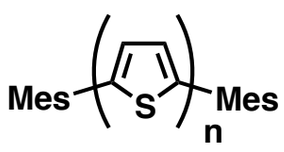
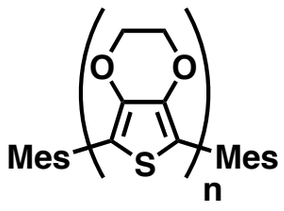
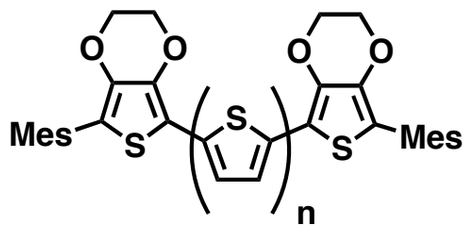




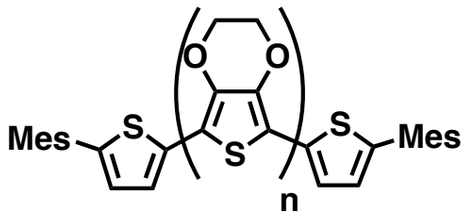
50-53 (n=1-4)



54-56 (n=1-3)



57-58 (n=1,2)

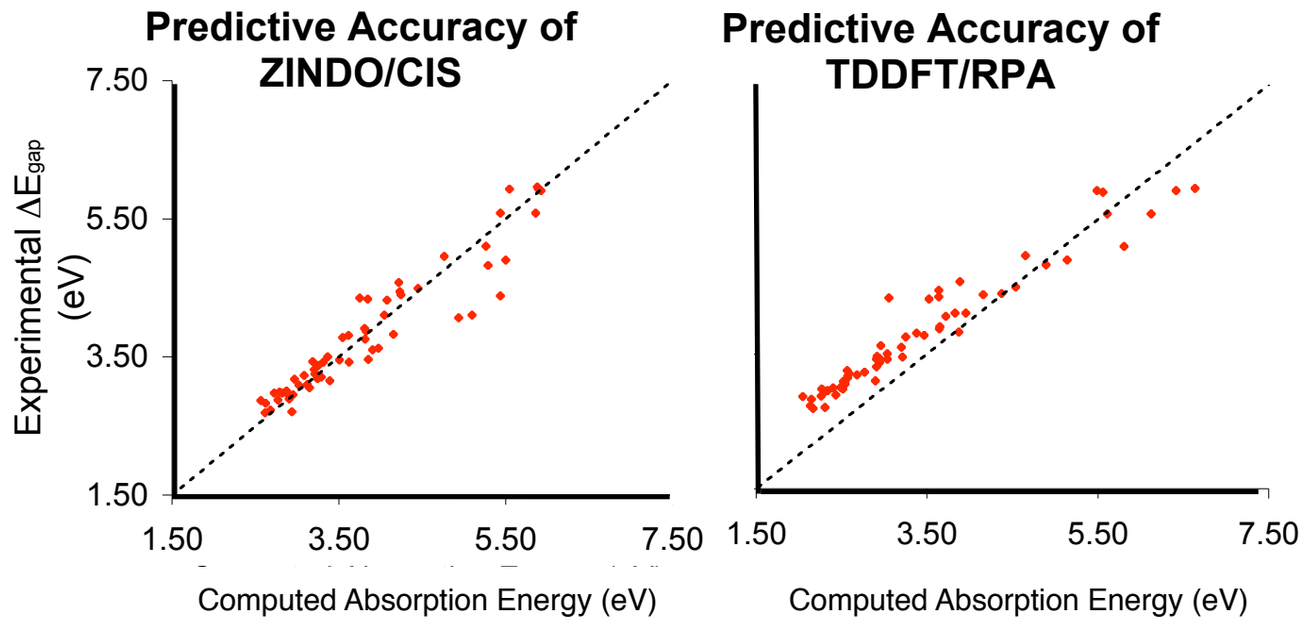


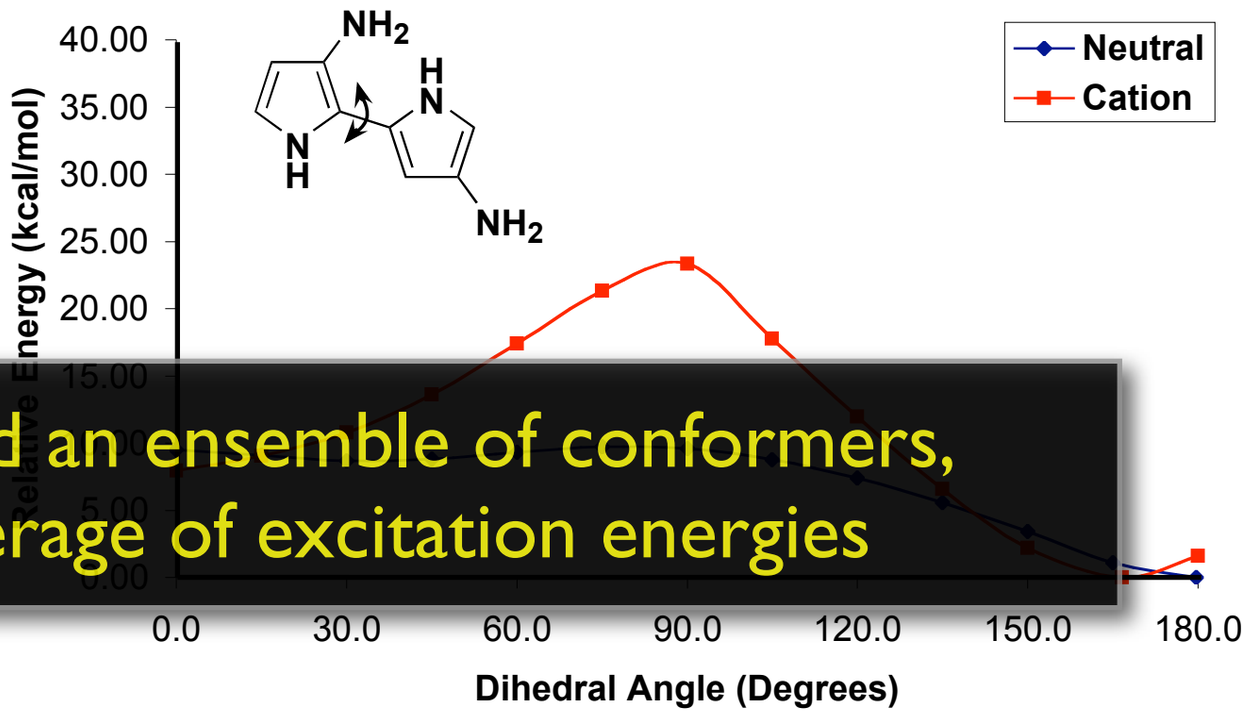
59-60 (n=1,2)

Predicting Optical Excitations for Neutral Oligomers

Set of 60 neutral oligomers shows high accuracy for several theoretical methods relative to experimental ΔE_{gap}

- TDDFT most accurate, consistent method
- Systematic skews (i.e., slope ~0.8) from torsional motion in solution

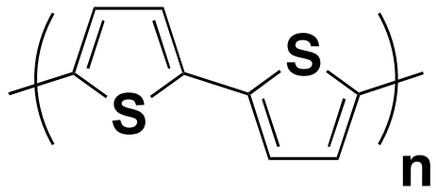




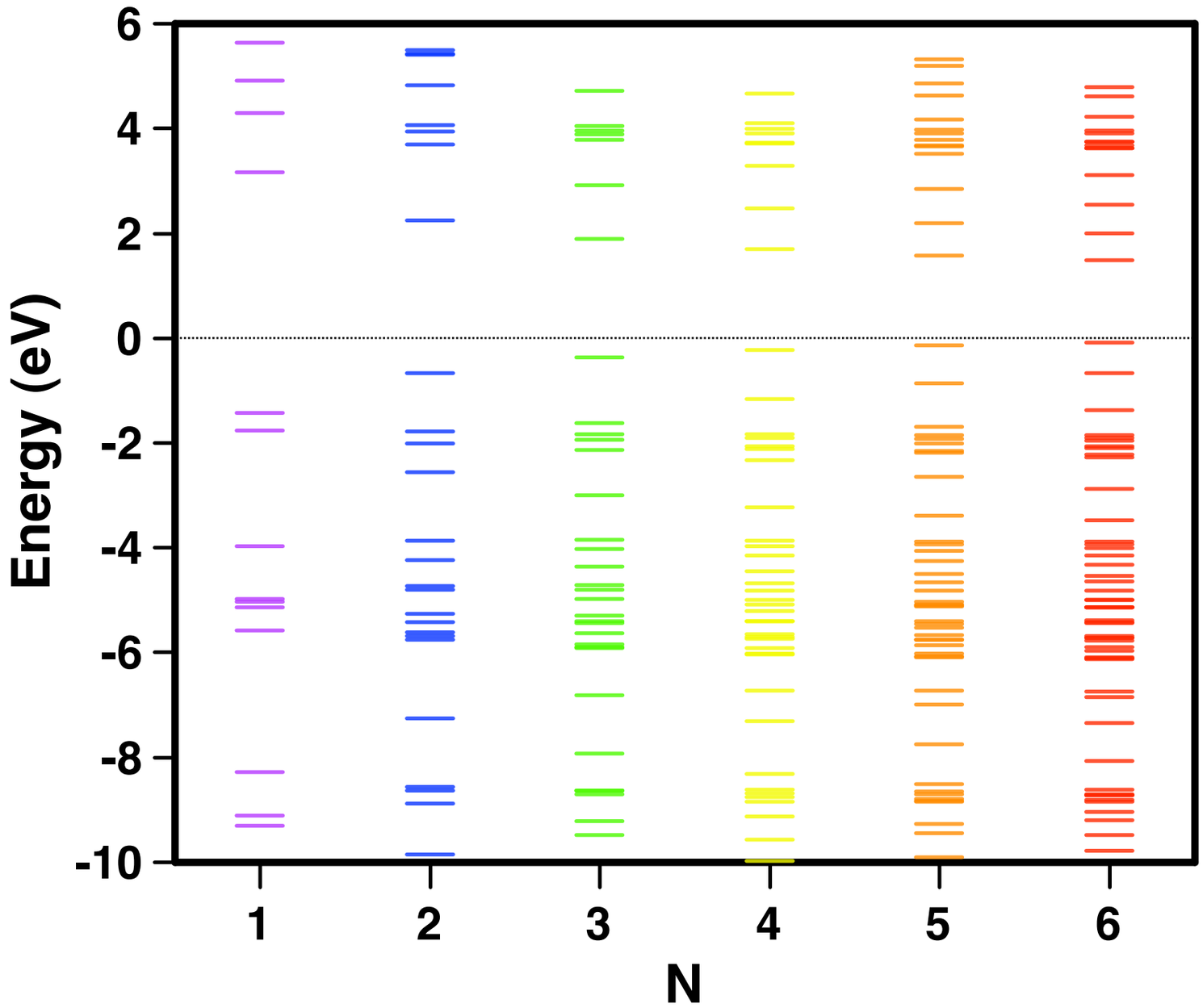
To do it right, we need an ensemble of conformers, take a weighted average of excitation energies

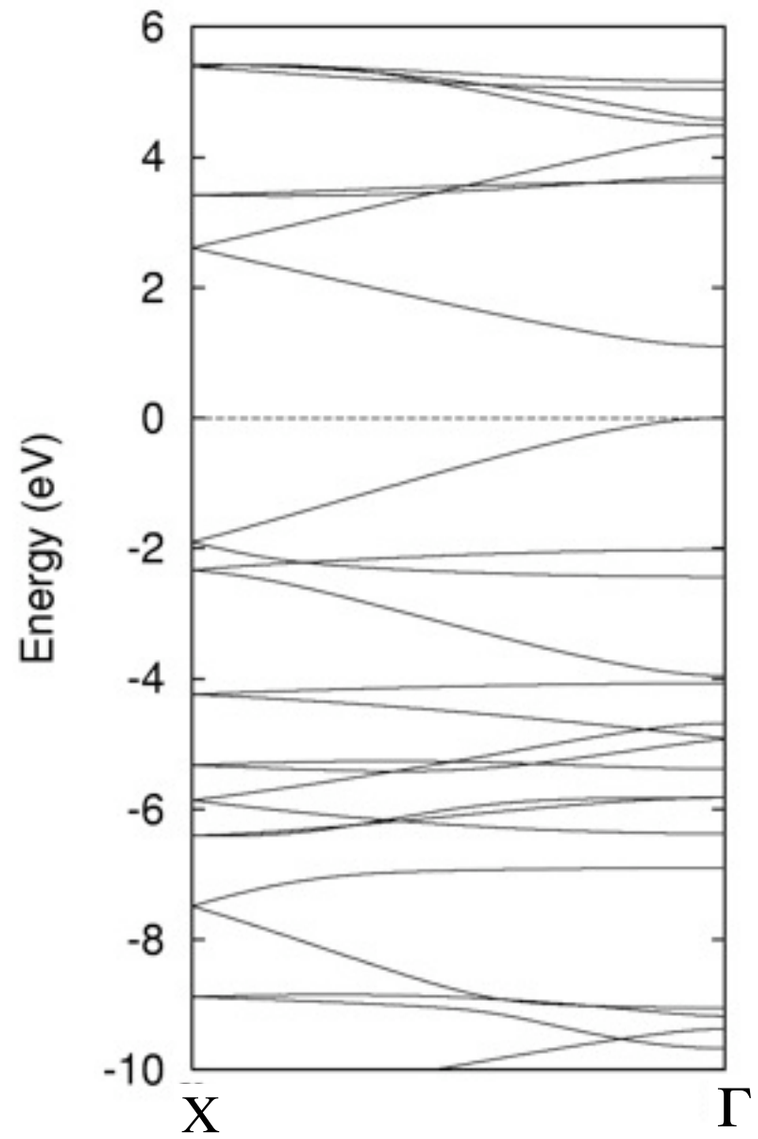
Hutchison, et. al. *J. Phys. Chem. A* **2002** *106* p.10596.

Evolution of Band Structure



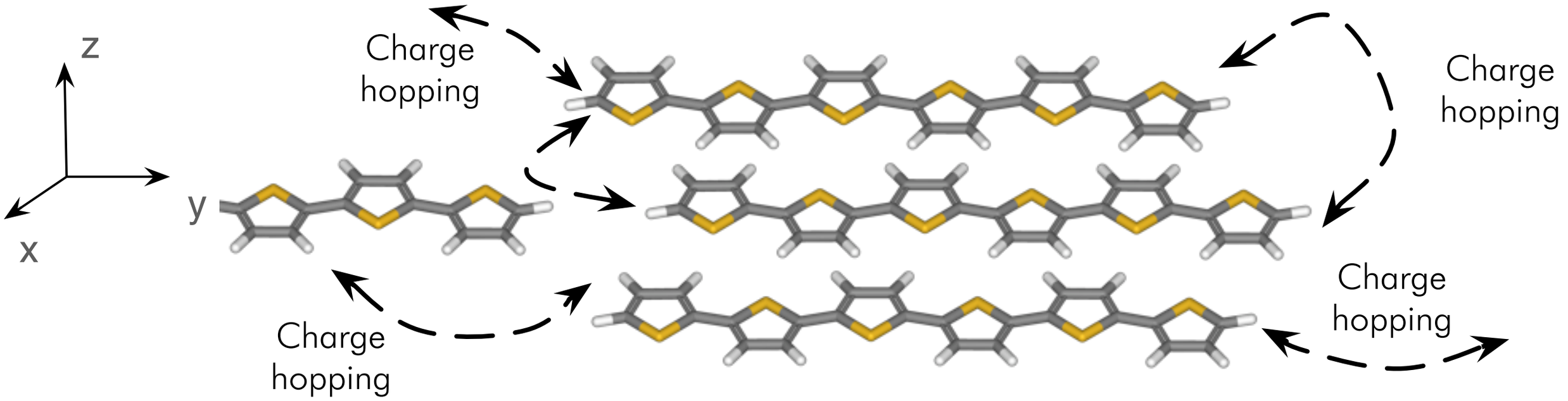
Effective mass: ~0.15m_e





Hutchison, et. al. *Phys. Rev. B* **2003** *68* no.035204.

Conduction is a 3D Process



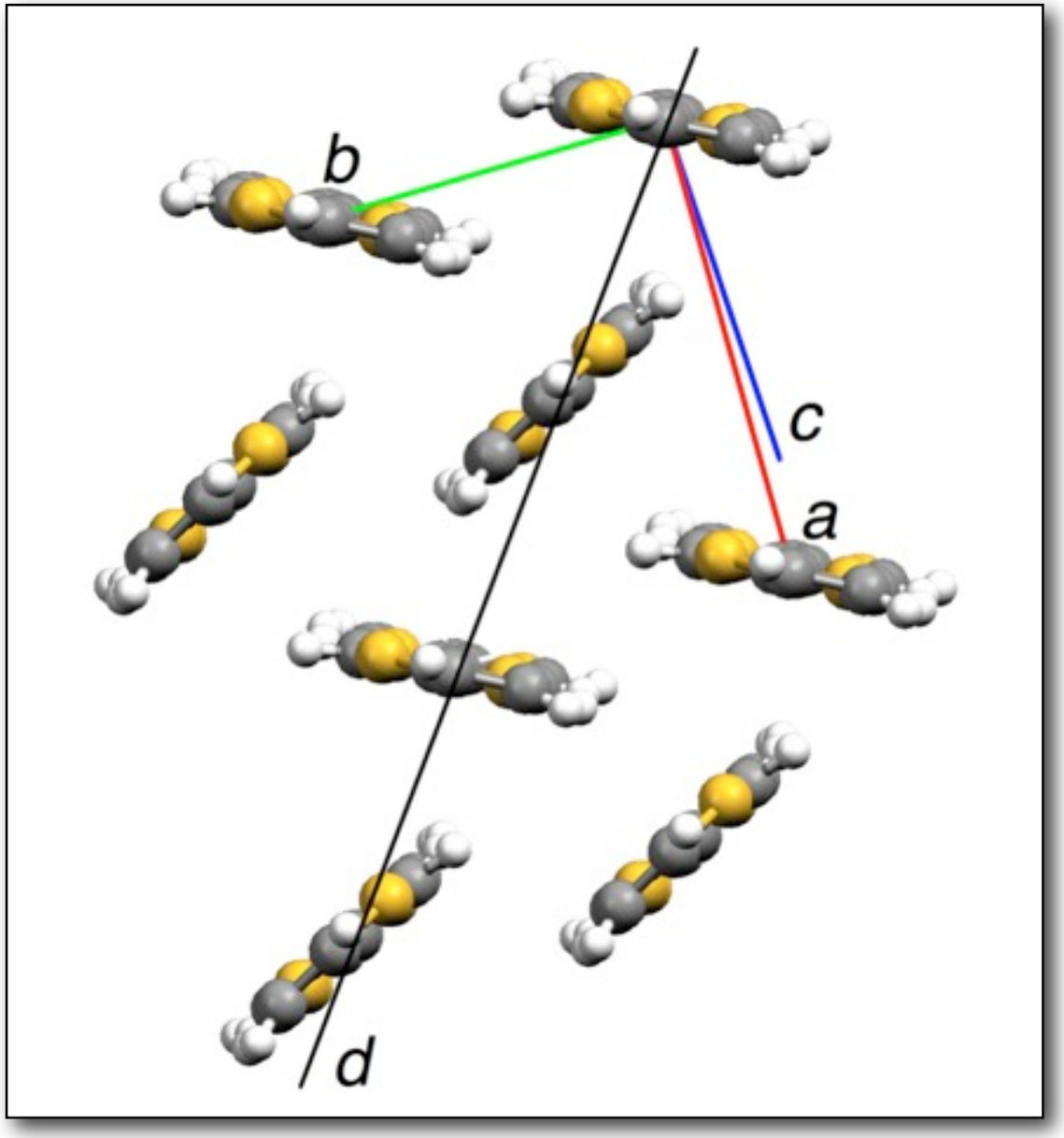
Conjugated materials are intrinsically disordered

- Band structures useful for optical properties
- Transport certainly ***not*** band-type (e.g., hopping)

Multiple factors important

- Intrachain transport (torsional disorder, chain defects)
- Interchain transport (π-stacking, intermolecular interactions)

Back to the Crystal Structure

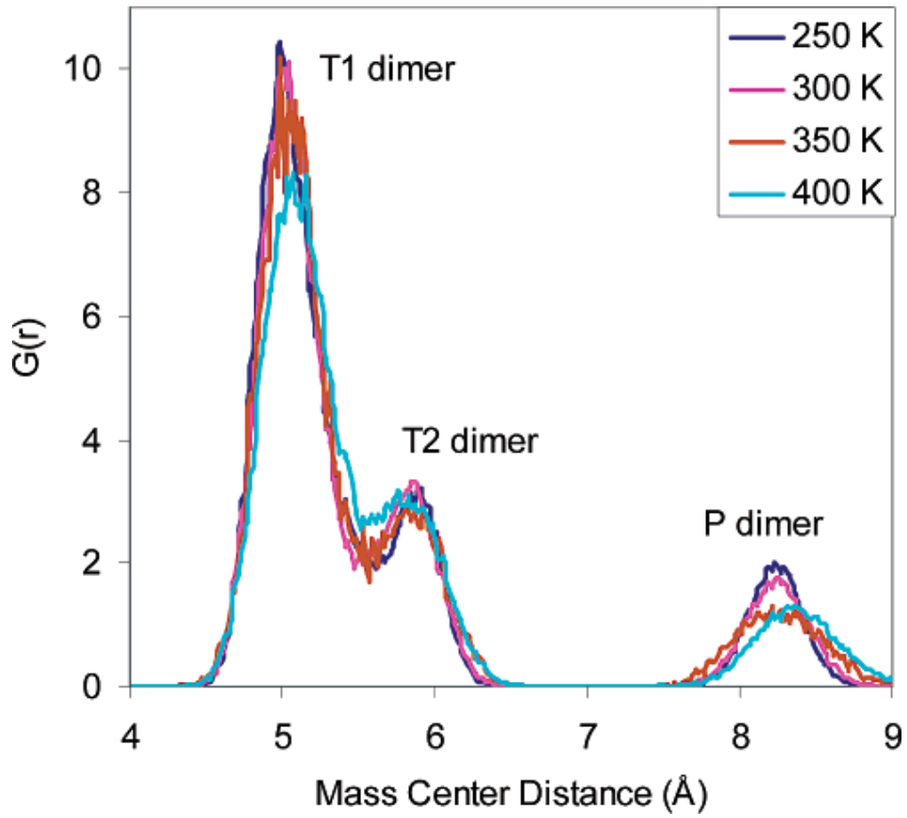


Temperature Variation

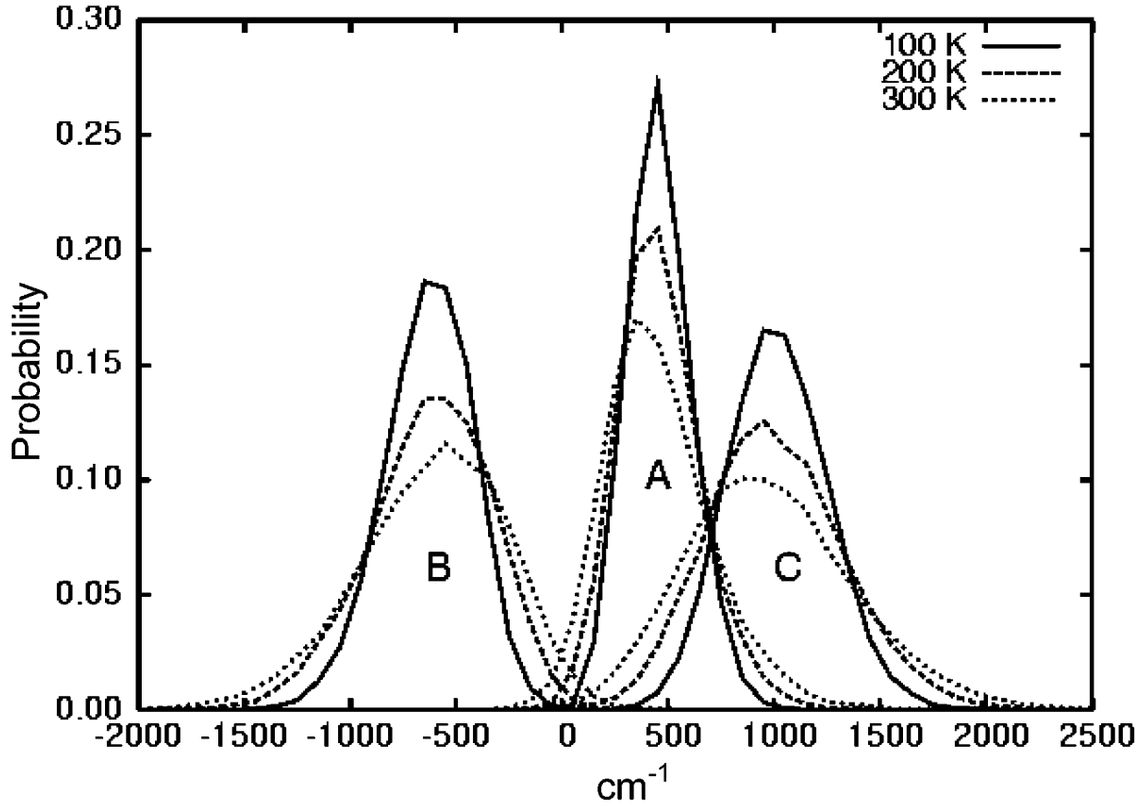
$$k = \left(\frac{\pi}{\lambda k_b T}\right)^{\frac{1}{2}} \frac{H_{ab}^2}{\hbar} e^{-\lambda/4k_b T}$$

Using the Einstein relation:

$$\mu = \frac{e}{k_b T} D = \frac{eL^2 k_{ct}}{k_b T}$$



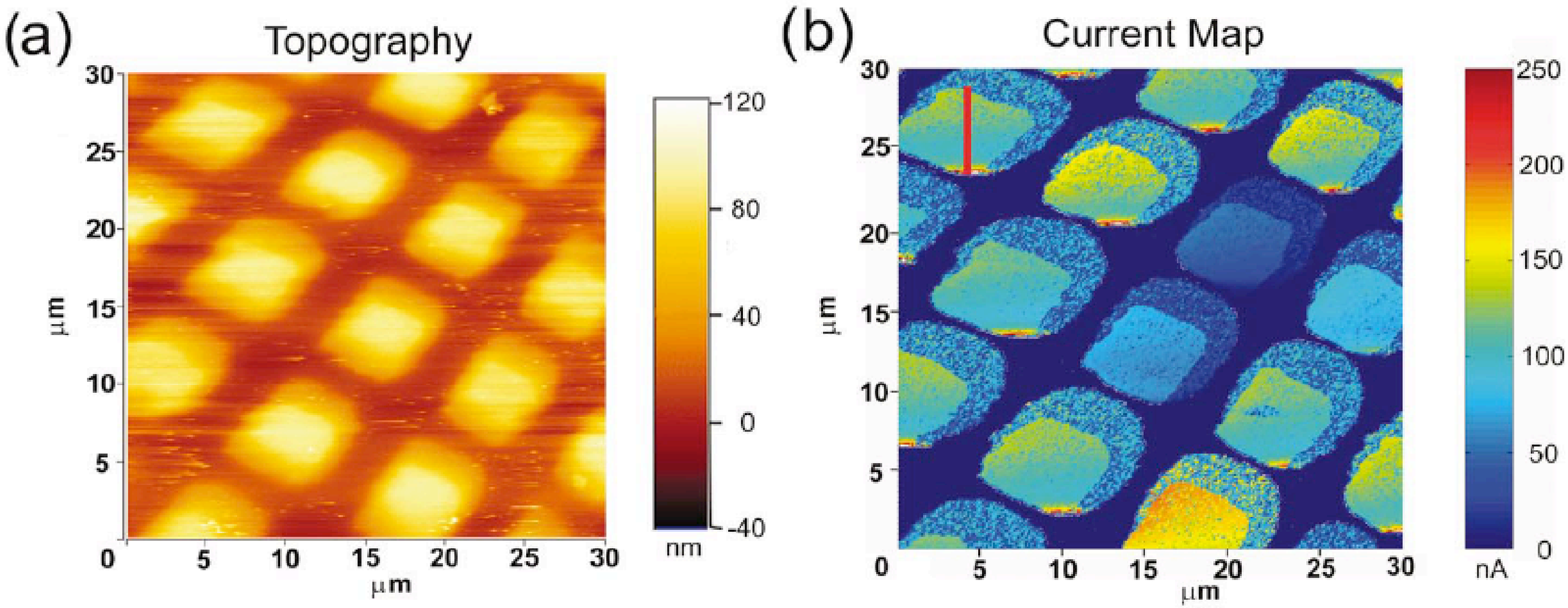
J. Phys. Chem. B **2004,** *108,* 8614



J. Phys. Chem. A **2006,** *110,* 4065

Spatial Variation of Charge in Organic Conductive Devices

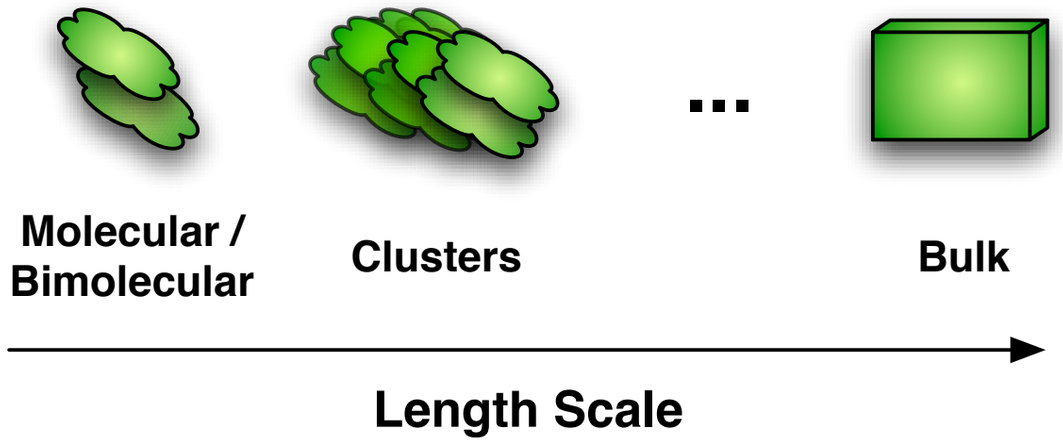
"Spatially-resolved electroluminescence of operating organic light-emitting diodes using conductive atomic force microscopy"



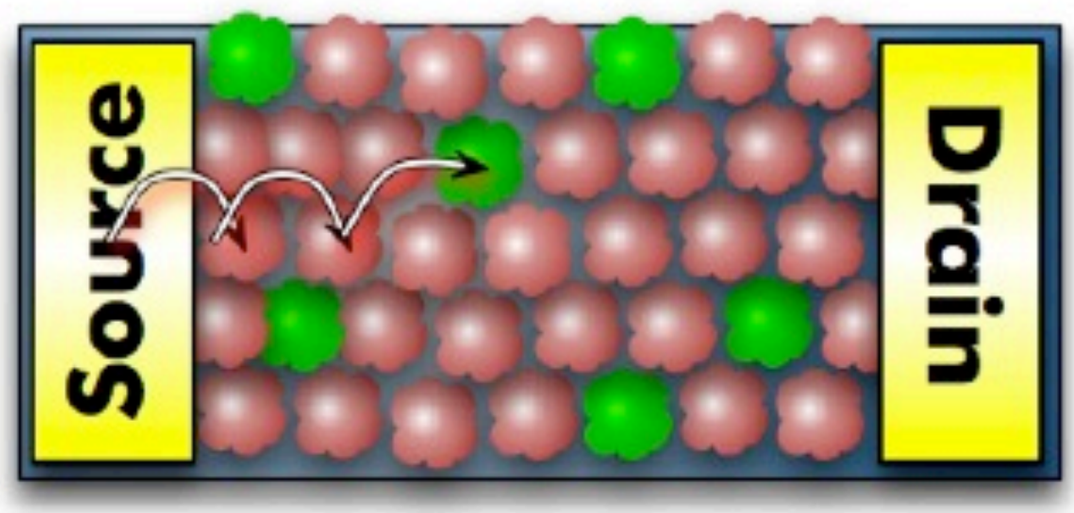
M. Hersam, T.J. Marks, et. al. *Appl. Phys. Lett.* **2004** 85*(2)* 344-346.

What About Defects?

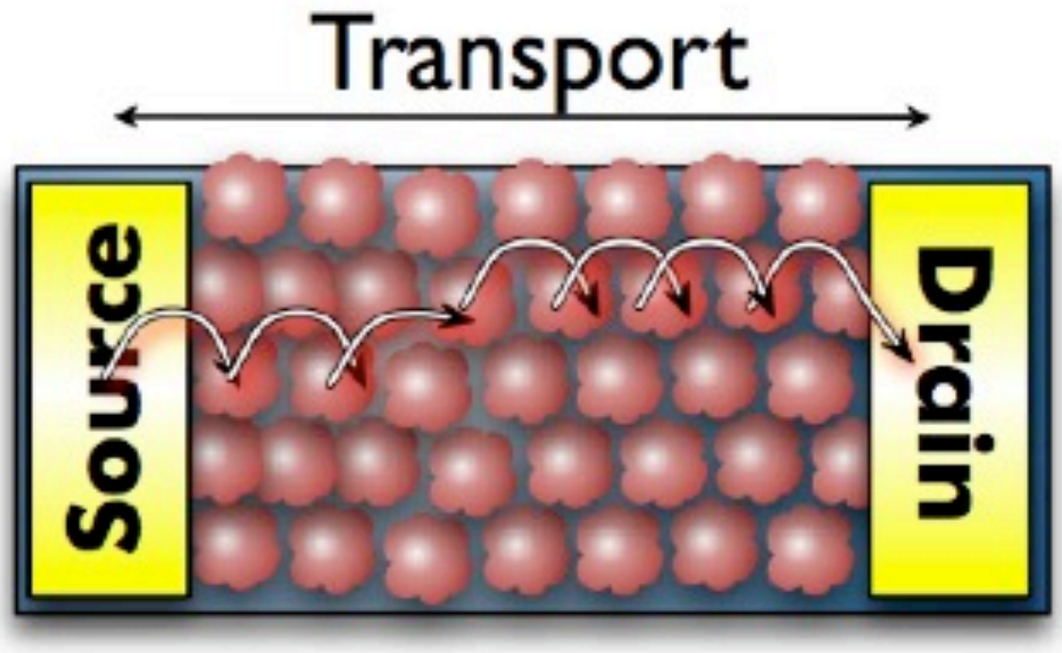
- Defects clearly influential in experiments
- Intermediate length scale is important!



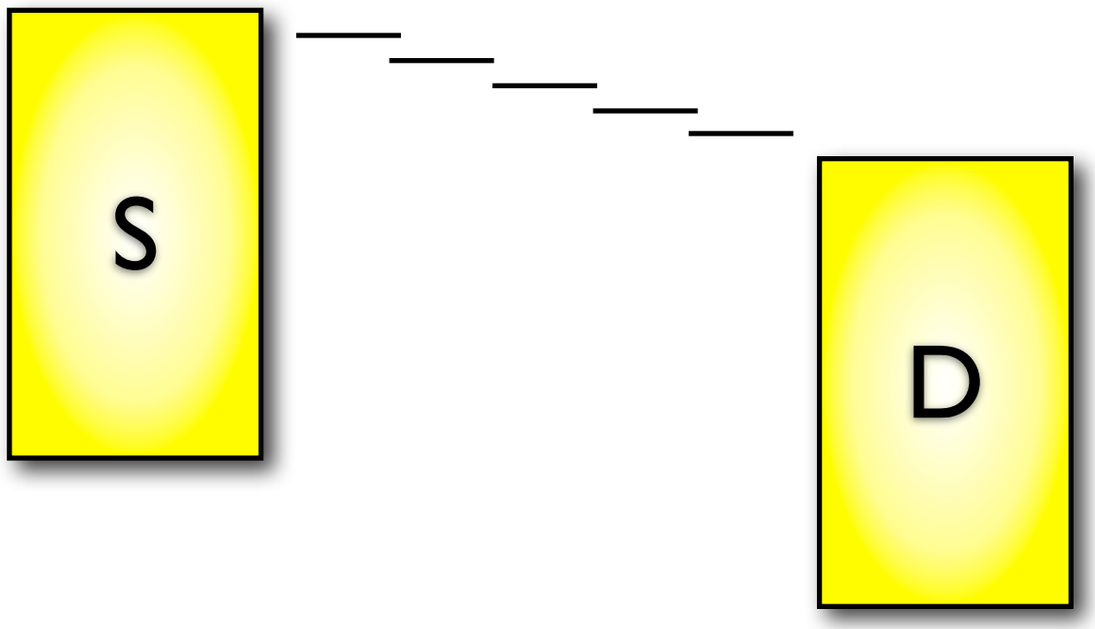
- So... let's do Monte Carlo dynamics for charge transport trajectories
- Get all parameters from electronic structure



Our Model:

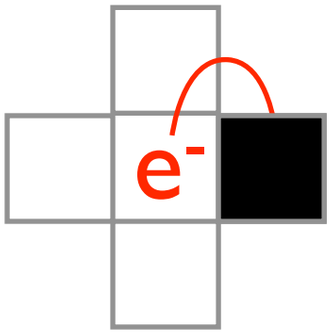


Energy Landscape

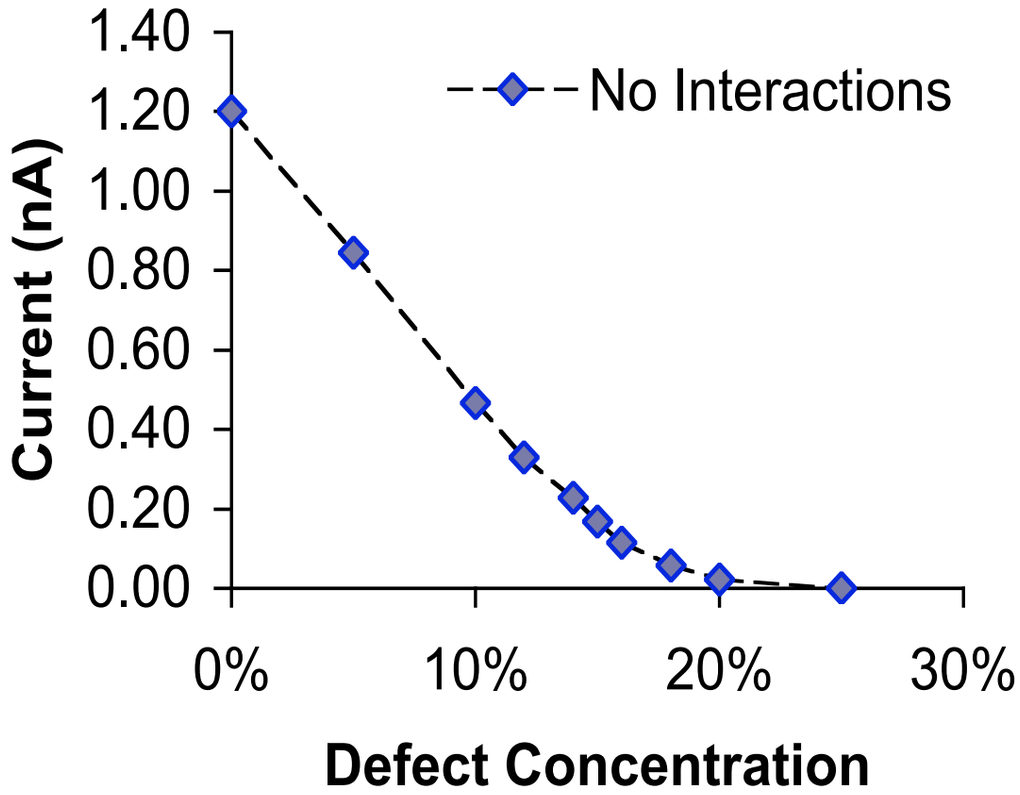


Trajectories are very linear:
Straight from source to drain

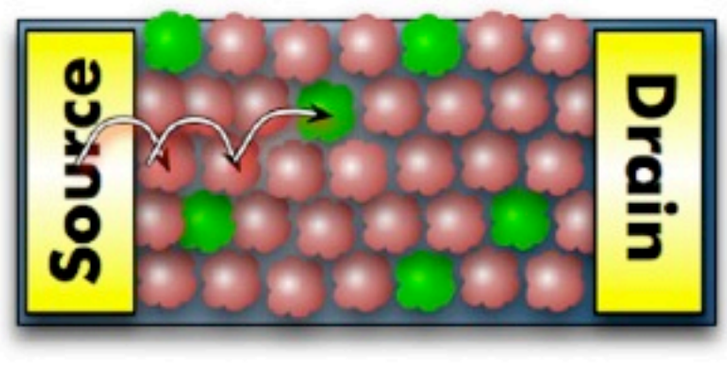
Percolation Theory of Defects

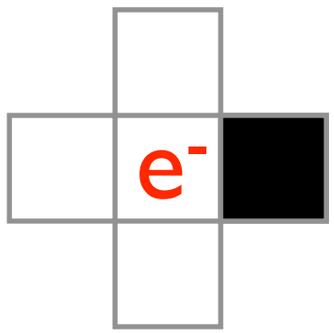


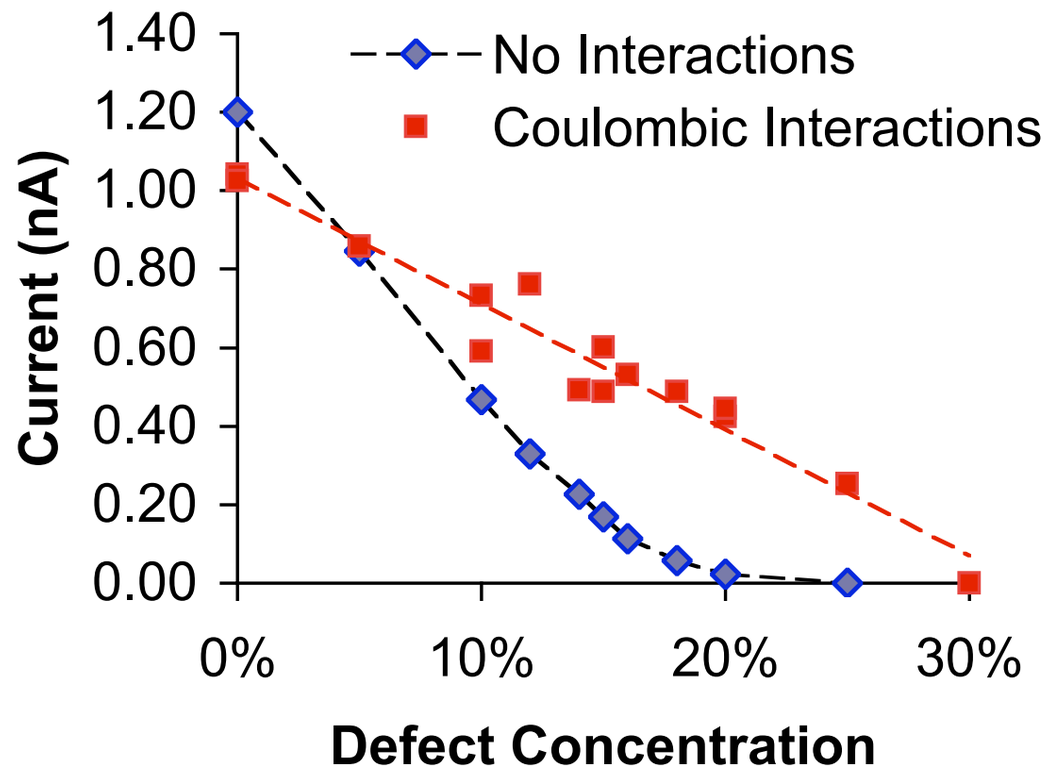
- As defects appear, conduction paths "turn off"
- With no interactions, "phase change" occurs quickly



Coulomb Interactions







- Electron repulsion coats the edges of the film: surface traps
- As defects appear, *some* e^- get trapped
- BUT... other electrons will force onto open pathways

Summary

- Electronic structure determines many properties in organic electronic materials
- BUT... dynamics are important, and treatment of ensembles is critical
- Ideal situation is to combine multiple areas of theory