Optical Properties and Electronic Structure of Polymer Nanostructures

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Outline

- **Oriented semiconducting polymer nanostructures**
- **Attractive photo-physical properties**
  - Ensemble oriented dipole emission
  - Extreme polarization anisotropy
  - Narrow & stable photoemission
  - Single-photon source
- **Theory/Computational of structure and properties**
  - Molecular mechanics simulations of molecular configuration
  - Electronic structure
  - Linear response: Low-lying singlet exciton
- **Conclusions**

Polymer-based optoelectronics

Huge literature on macro/meso-scale polymer-based optoelectronic (LEDs, photo-voltaics, etc.) devices.

- R. H. Friend, et al. *Nature* **347**, 539 (1990).

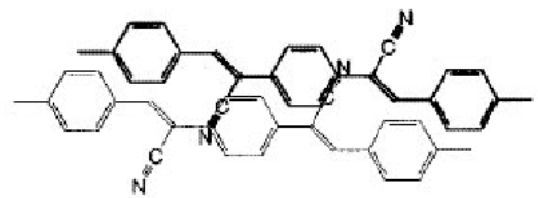
Applications:

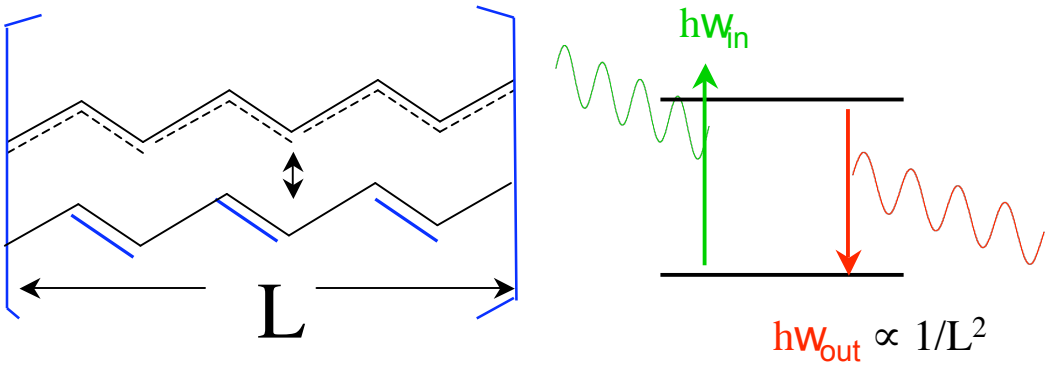
- Electronic paper, luminescent clothing, display technologies, etc.!

"*…brighter, thinner, lighter, faster*"

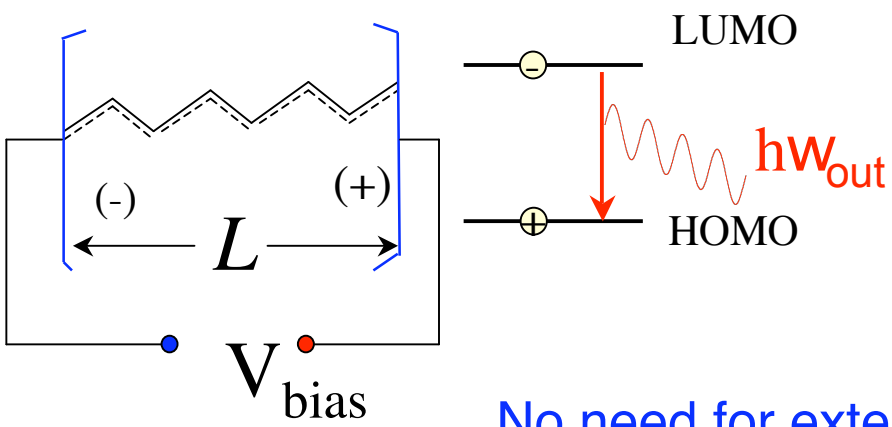
What are the issues in nanoscale applications??

Semiconducting Polymers ??





Electroluminescence



No need for external light pump.

- Many different 'flavors'
- Cheap to produce (many are commercially available)
- Convenient solution-phase processing
- Facile electron transport properties
- Responsive to optical excitation
- Size-scalability down to 1 nm

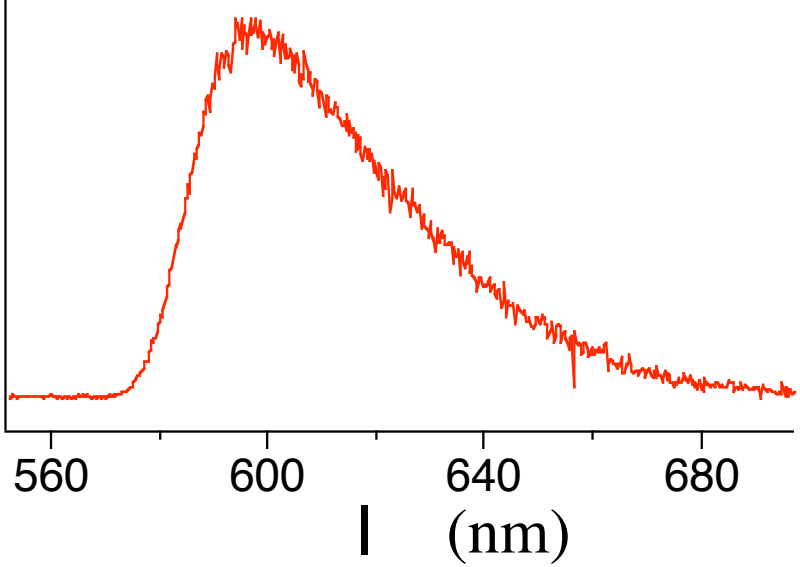
Semiconducting Polymers:
Photo-physical Limitations in thin-film formats

The bad news:

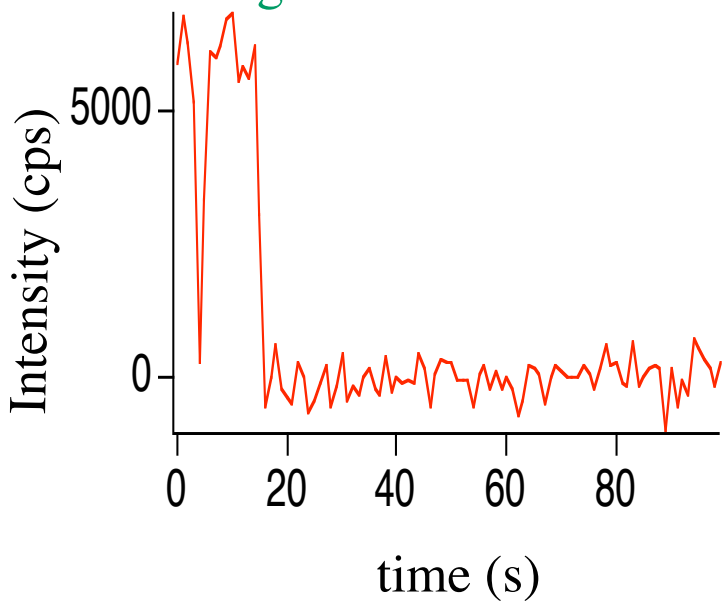
- Random, disordered chain structure for thin films;
- Broad emission spectrum, poor photo-stability and charge-transport properties

→ nanoscale photonics applications are "short-circuited"!

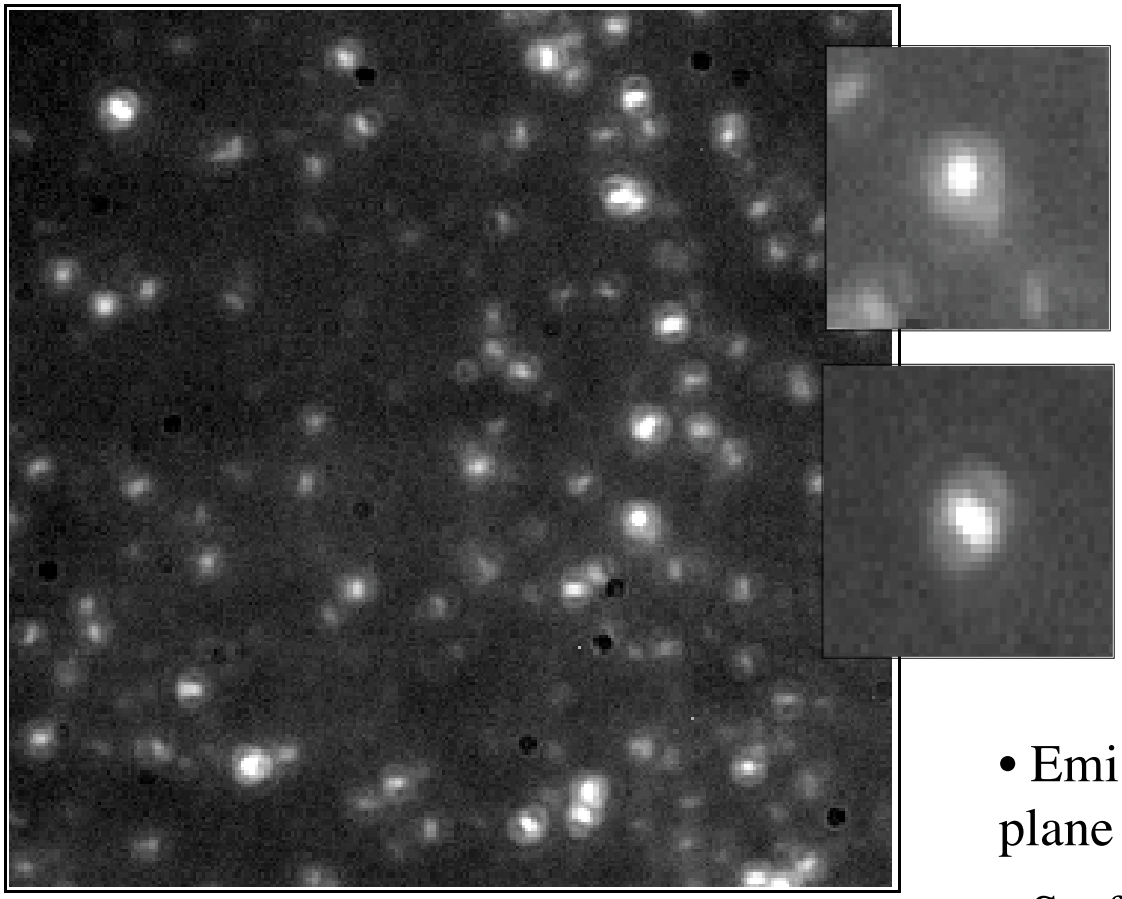
Broad ensemble emission spectrum



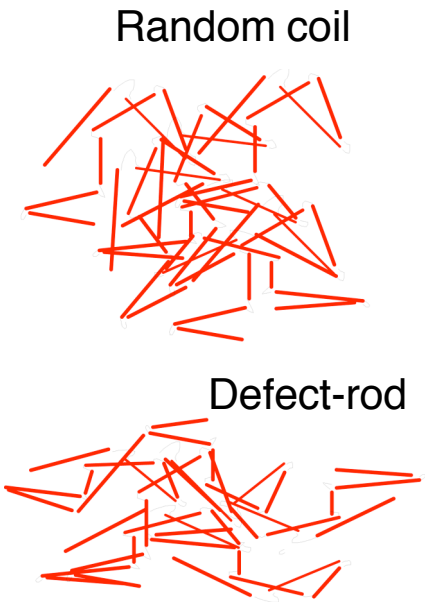
Single-molecule fluorescence



Semiconducting Polymers: Probing single-molecule chain organization and orientation in thin films



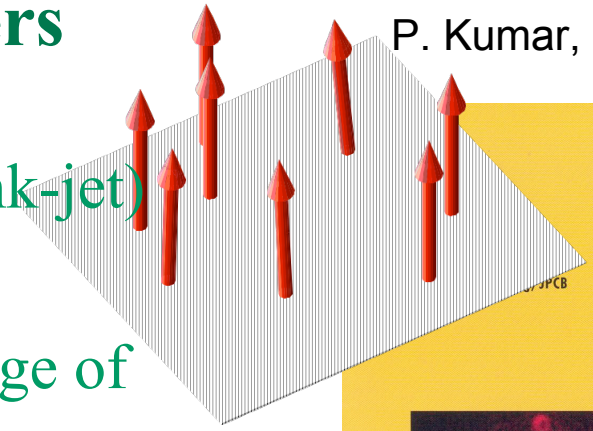
Fluorescence of single MEH-PPV molecules under 400x magnification



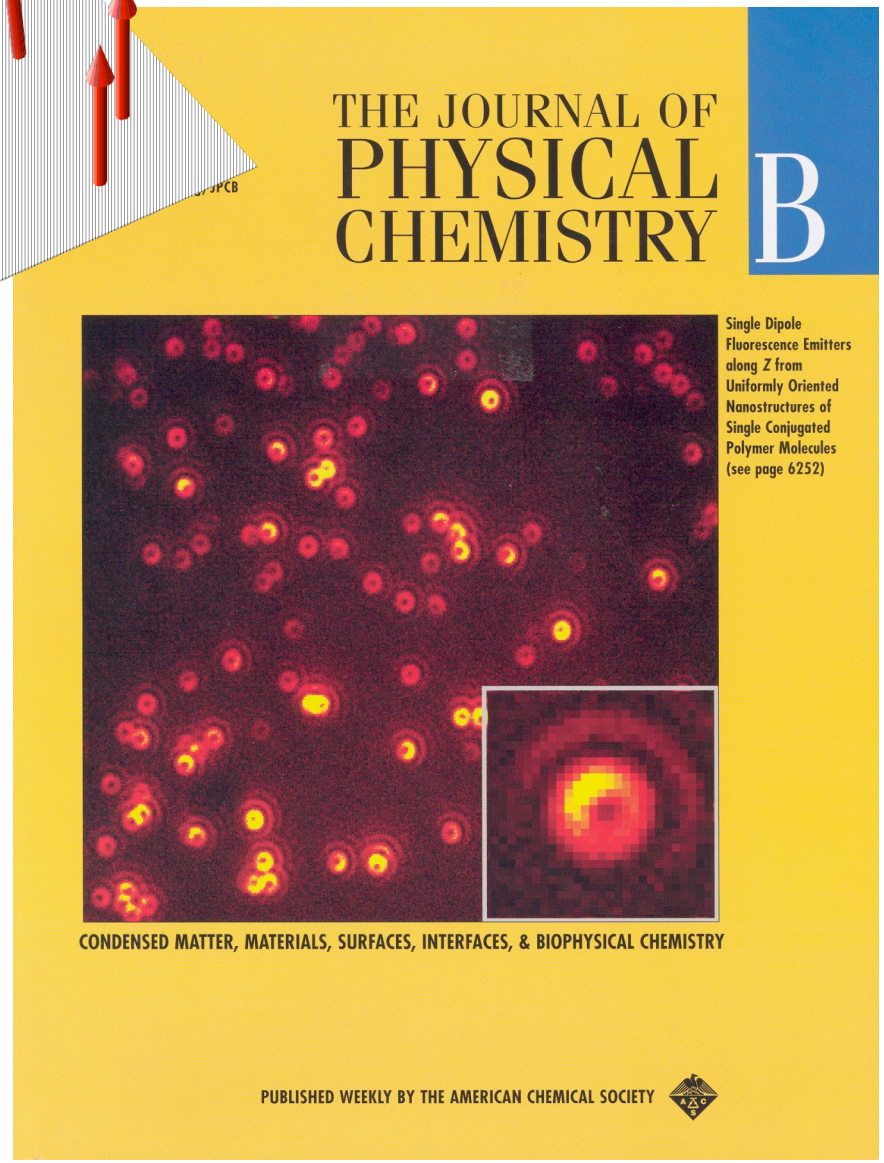
- Emission dipoles oriented in the plane of the substrate.
- Surface interaction/charge states
- Oxidation events

Oriented nanostructures from single-molecules of conjugated polymers

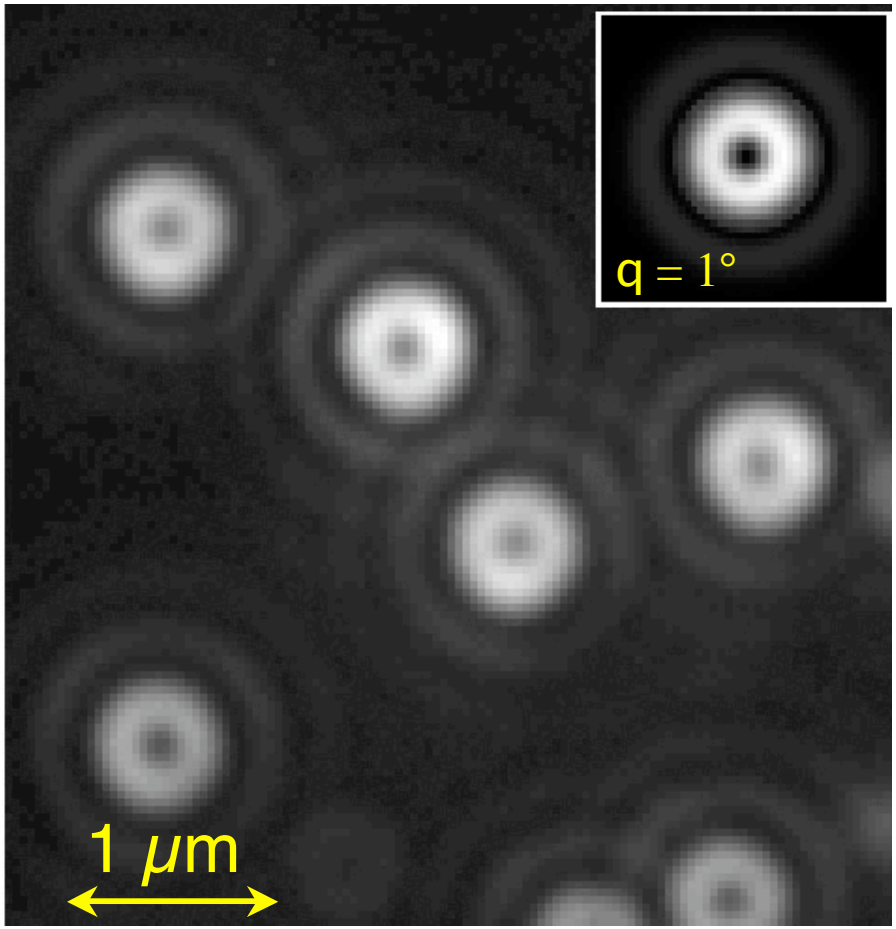
P. Kumar, *et al.*, JPCB **107**, 6252 (2003)

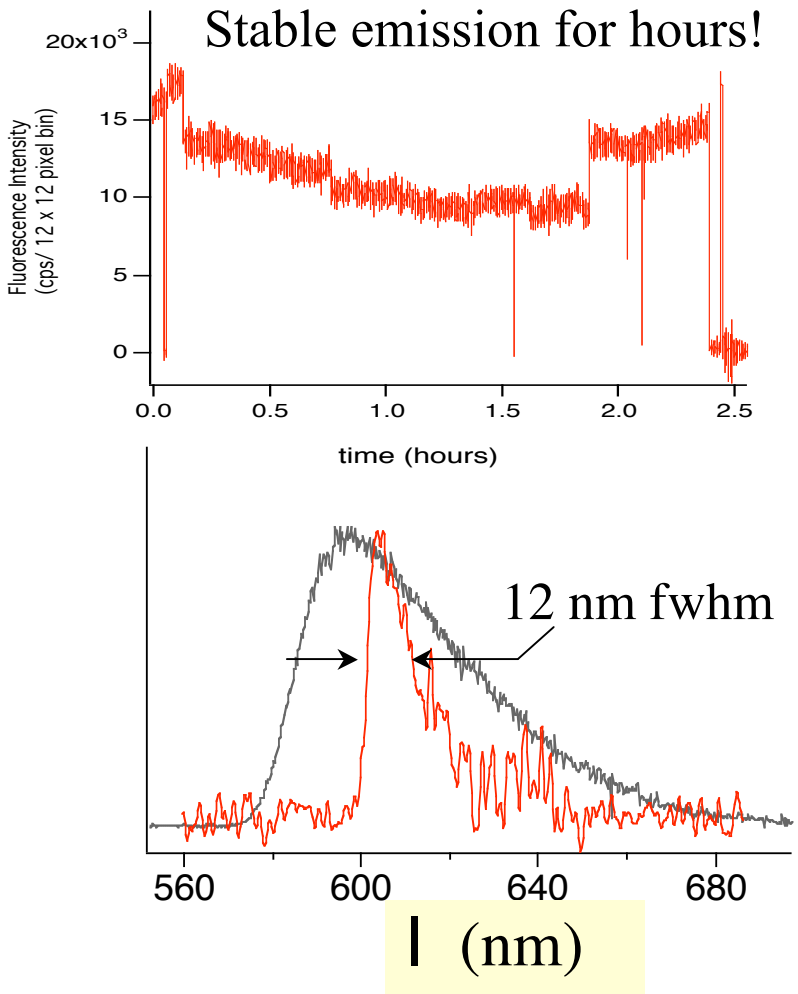


- Microdroplet-based (ink-jet) production
- Amenable to wide range of polymers
- Transition moments oriented perpendicular to substrate
- Single dipole pattern suggests high-degree of intra-molecular order
- *Profoundly* modified photo-physical properties



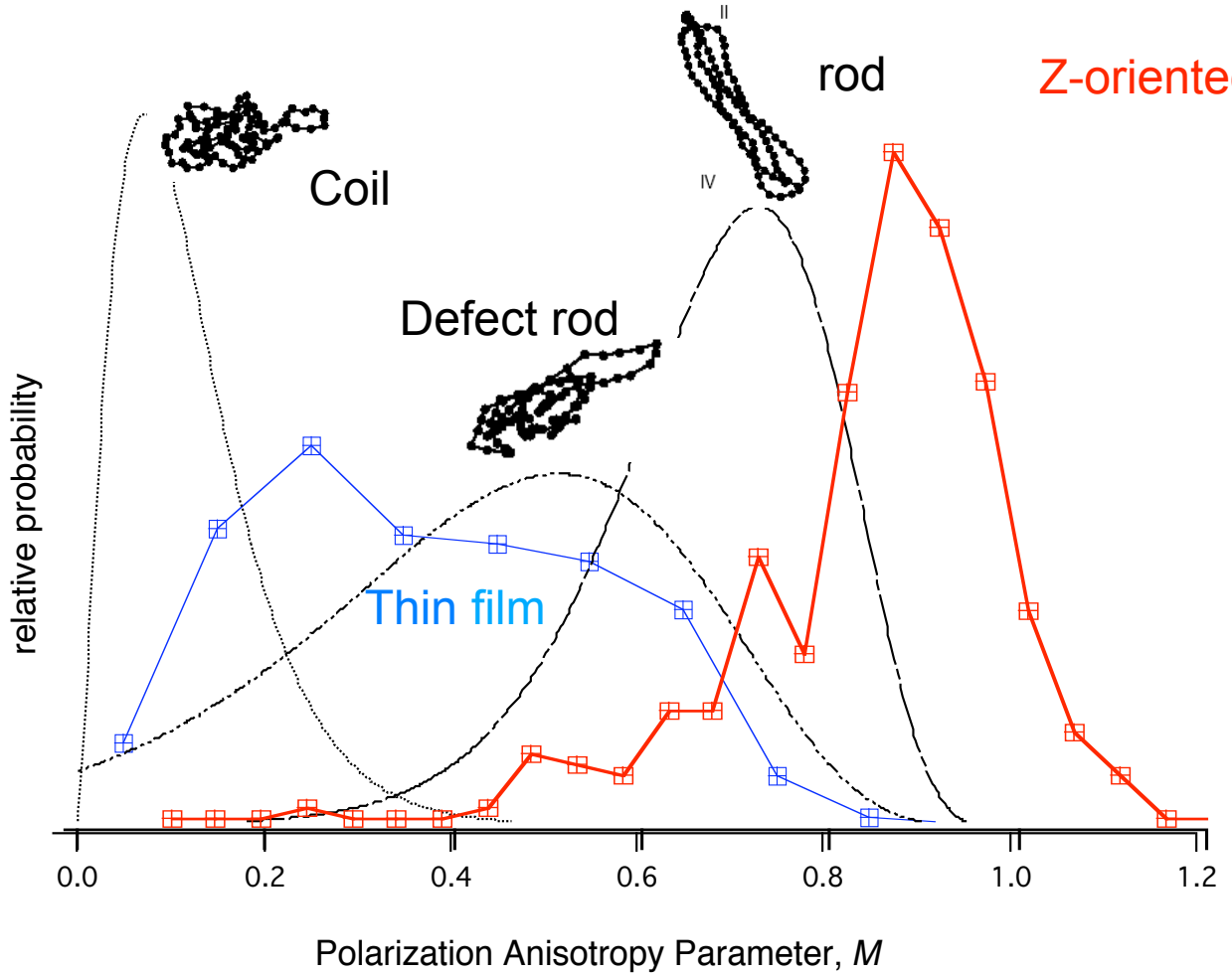
Enhanced photo-physical properties of z-oriented polymer nanoparticles (cyano-substituted PPV)



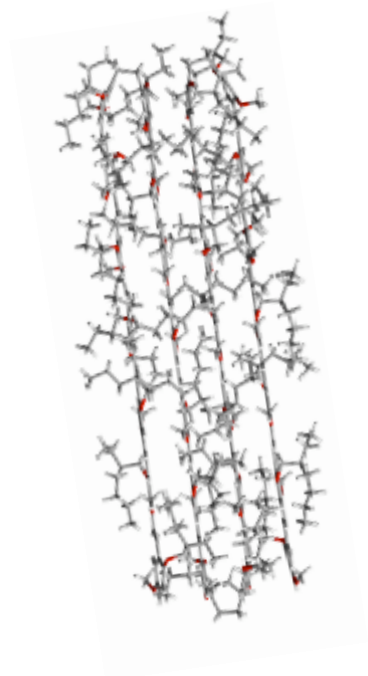


T-H. Lee, P. Kumar, A. Mehta, R. M. Dickson, and M. D. Barnes, *submitted to Phys. Rev. Lett.*

Distribution of Polarization Anisotropy Parameters:
Comparison with thin-film results

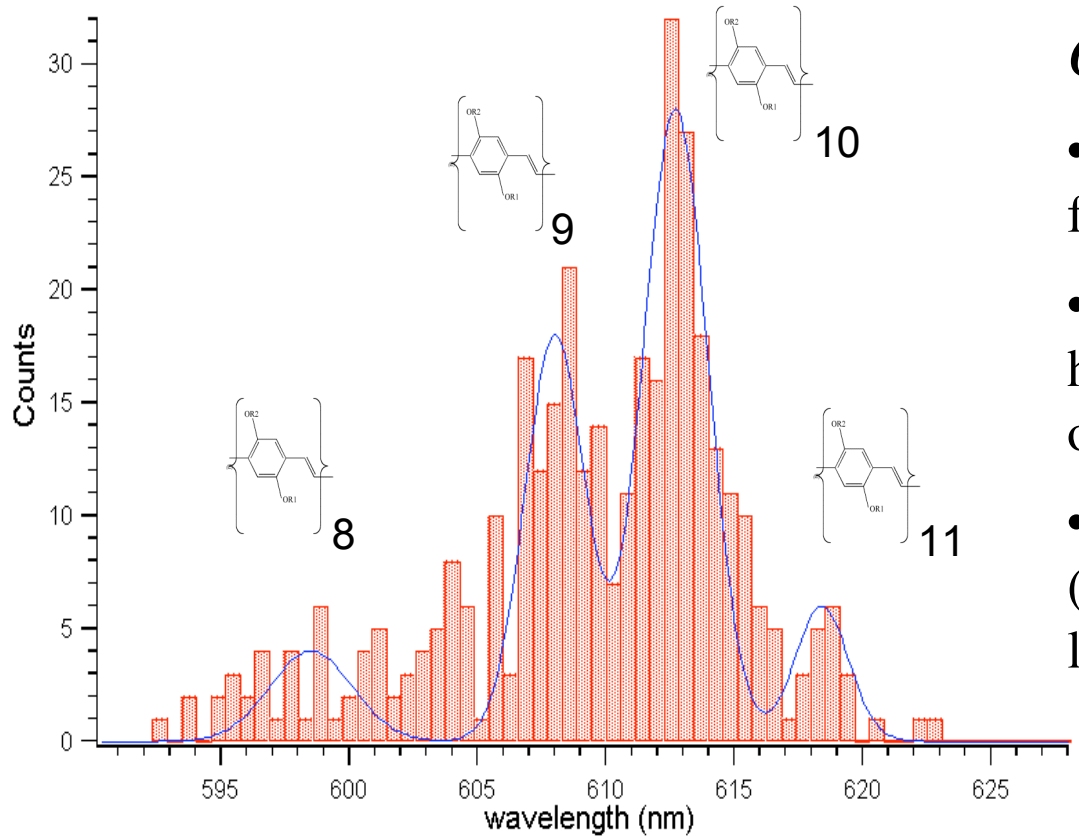


Z-oriented nanoparticles:



D. Hu, *et al.*, *Nature* **405**,1030 (2000).
A. Mehta, *et al. Nanoletters* **3** (5), 603-607 (2003).

Discrete center frequency distribution



Observations:

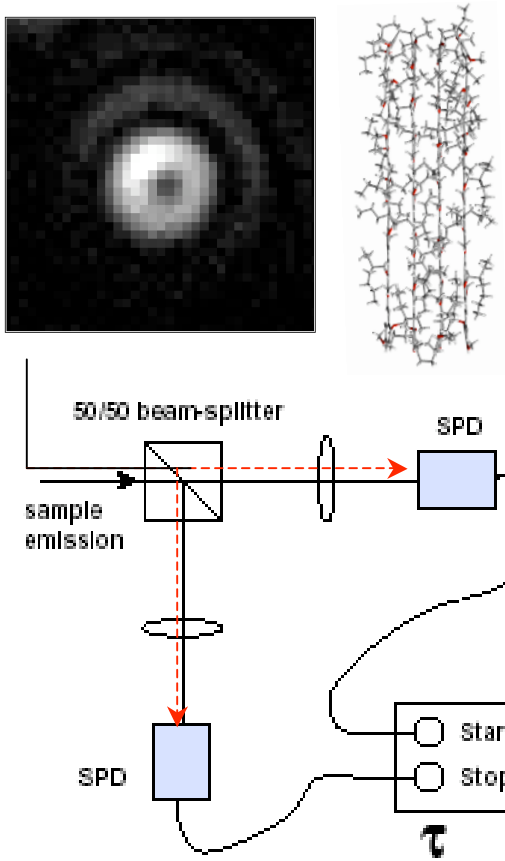
- Frequency is fixed, (but different for each particle).
- Frequency correlated not with rod height but with conjugated oligomer length.
- Absolute frequencies red shifted (Possibly due to local LUMO lowering due to structural order).

Emission frequencies correlated with discrete confinement (box) lengths - but not strongly correlated with molecular weight (size)!

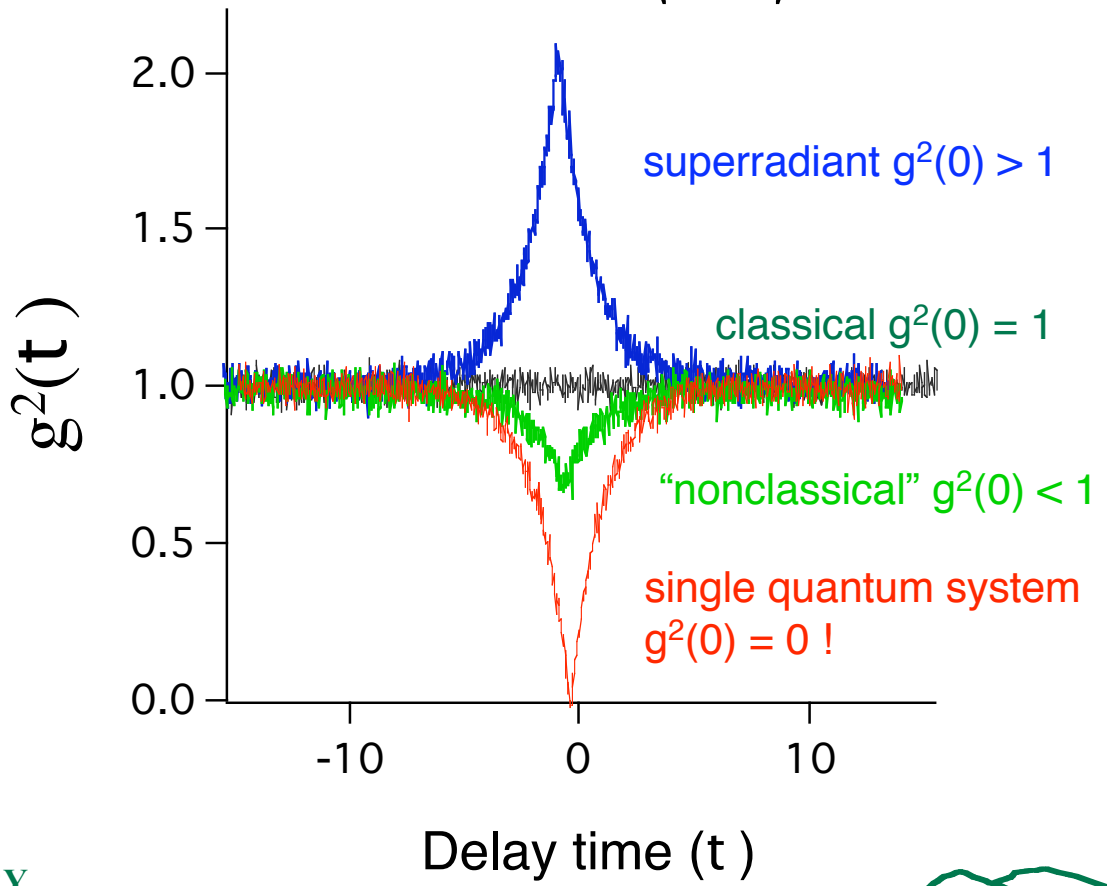
P. Kumar, *et al.*, JPCB **107**, 6252 (2003)

Photon statistics from single polymer nanostructures:

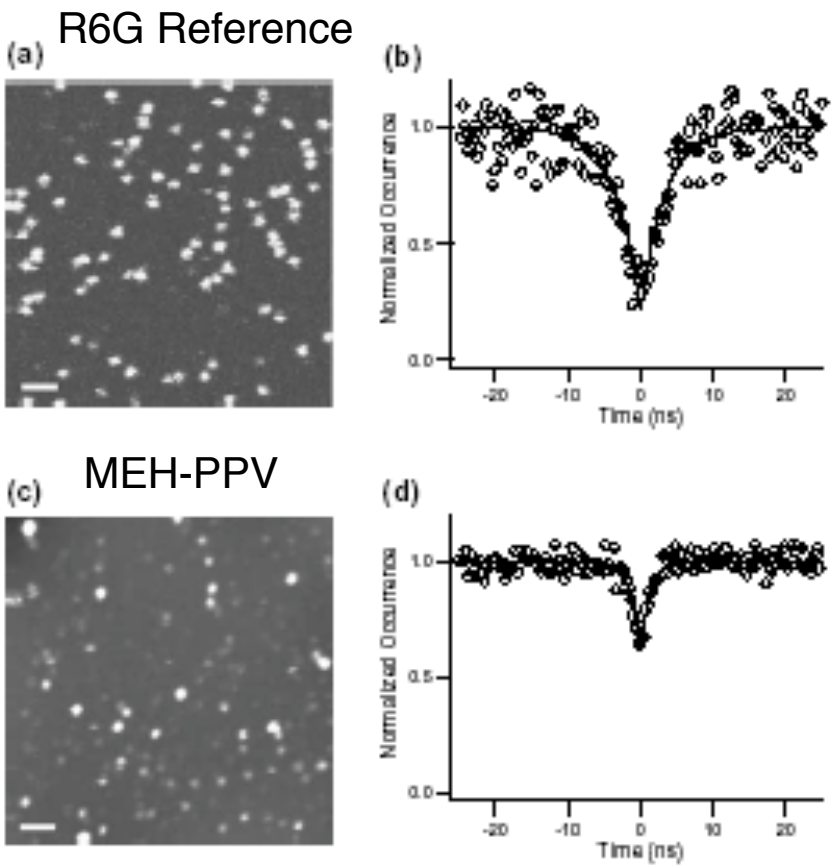
Single or multiple emissive sites ?



$$g_2(\tau) \equiv \frac{\langle I(t) I(t+\tau) \rangle}{\langle I(t) \rangle^2}$$



Photon correlation statistics from single polymer molecules in thin-films

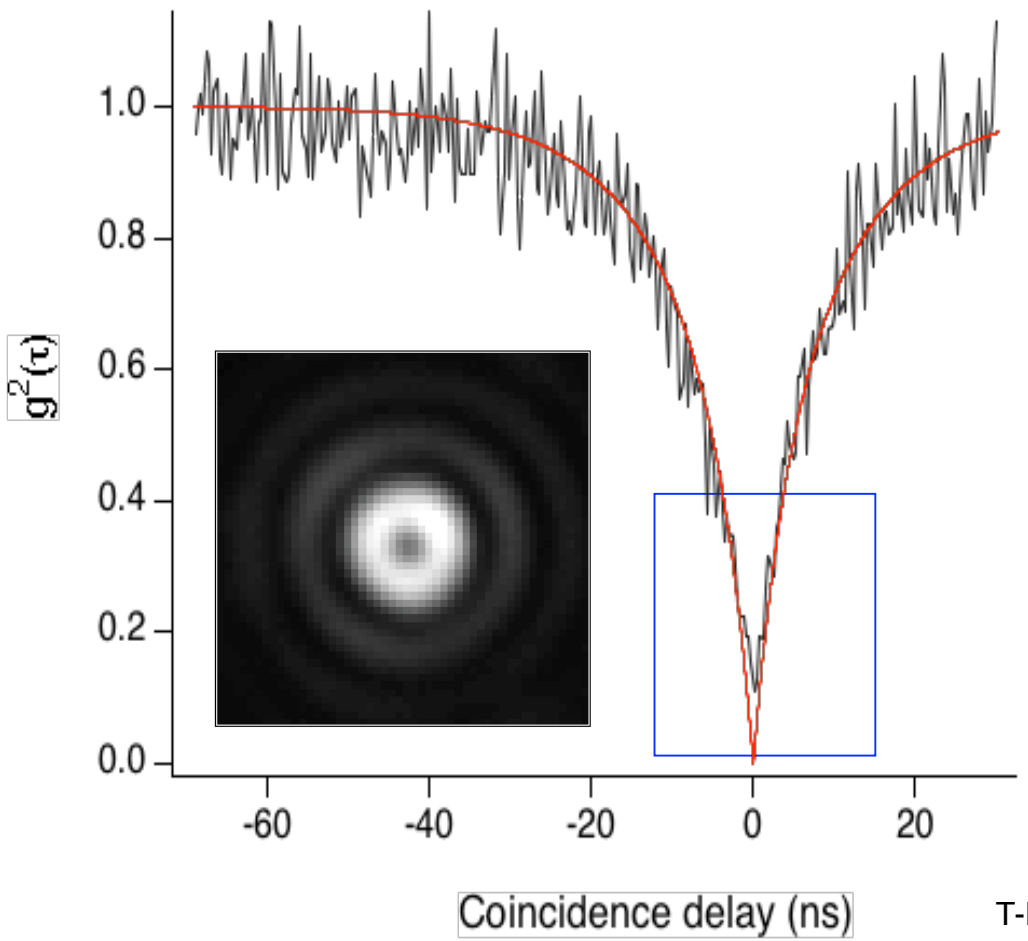


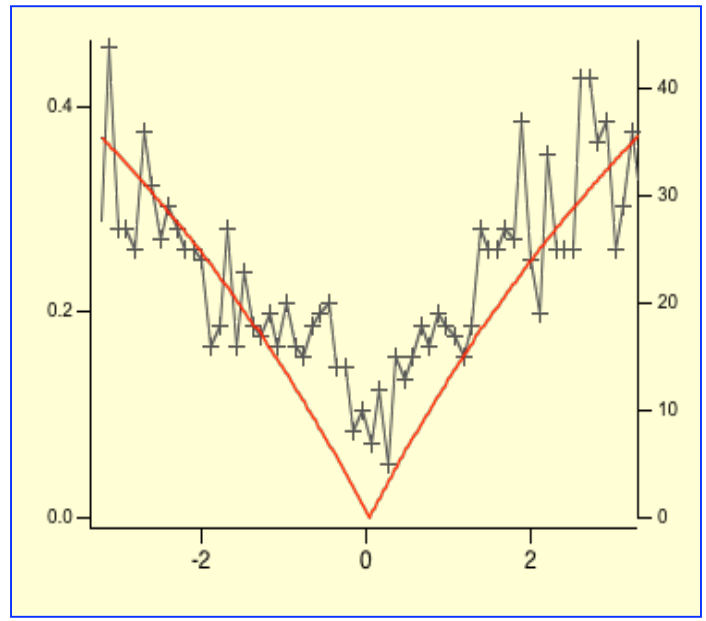
- Summed contribution from over ≈ <u>1000</u> molecules
- Relatively poor contrast (≈ 35%)
  - suggests $\langle N \rangle \approx 3$
- *Short-lifetimes*?
  - averaging over configurations?

C. W. Hollars, S. M. Lane, and T. Huser, *Chem. Phys. Lett.* **370**, 393 (2003).

Intensity correlation function from a *single* z-oriented CN-PPV nanostructure

$g^2(t) = 1 - (1/N)\exp[-| t *(W_p + G)|]$





$g^2(0) = 0.08 \pm 0.02$

- Definitive evidence of single-site emission!

T-H. Lee, P. Kumar, A. Mehta, R. M. Dickson, and M. D. Barnes, *submitted to Phys. Rev. Lett.*

Computational Methods

- Atomic-scale methods (MD & MM) provide information on the structure, dynamics, and thermodynamics of the system.
- *Ab Initio* (DFT-MD) methods used to compute electronic and molecular structure, interaction potentials, etc., as input into MD, kinetic MC, course grain approaches.
- Linear response methods (TDHF, TDDFT) for electronic spectra, excited-state configurations, etc.
- Correlated many-electron methods (MP2, CCSD)
- All codes are implemented in parallel and run on ORNL/CCS resources

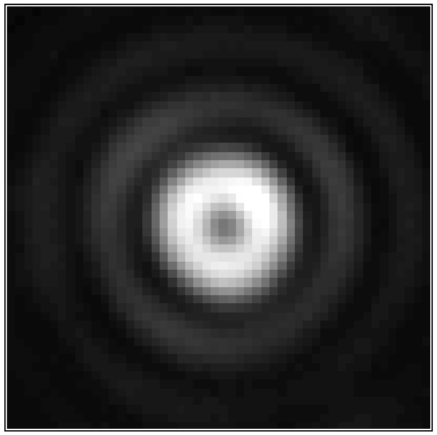
Use open source, community codes: NWChem, GAMESS

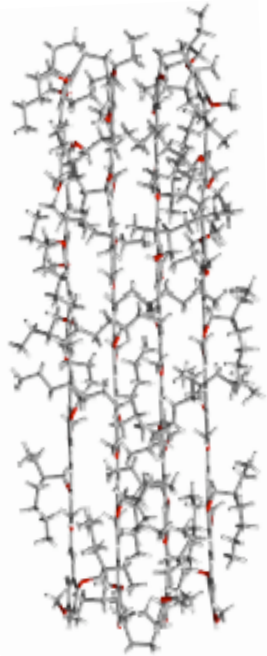
Connection between orientation and particle structure?

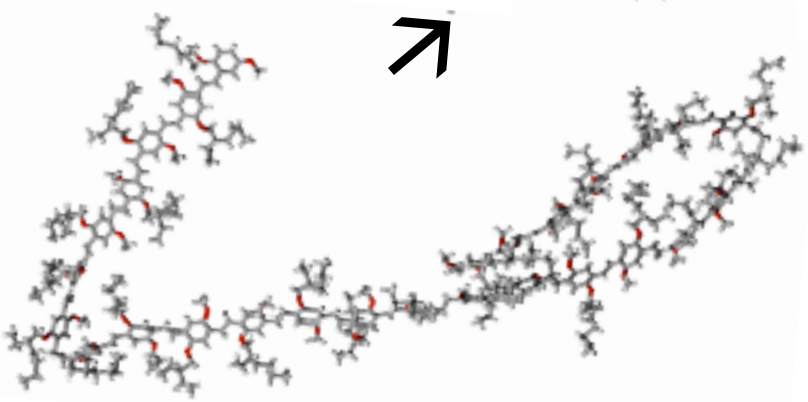
MM simulations of polymer folding & collapse

- Proceeds initially through solvent-solute interactions
  - "Good solvent" → No folding
  - "Bad solvent" → Rapid folding

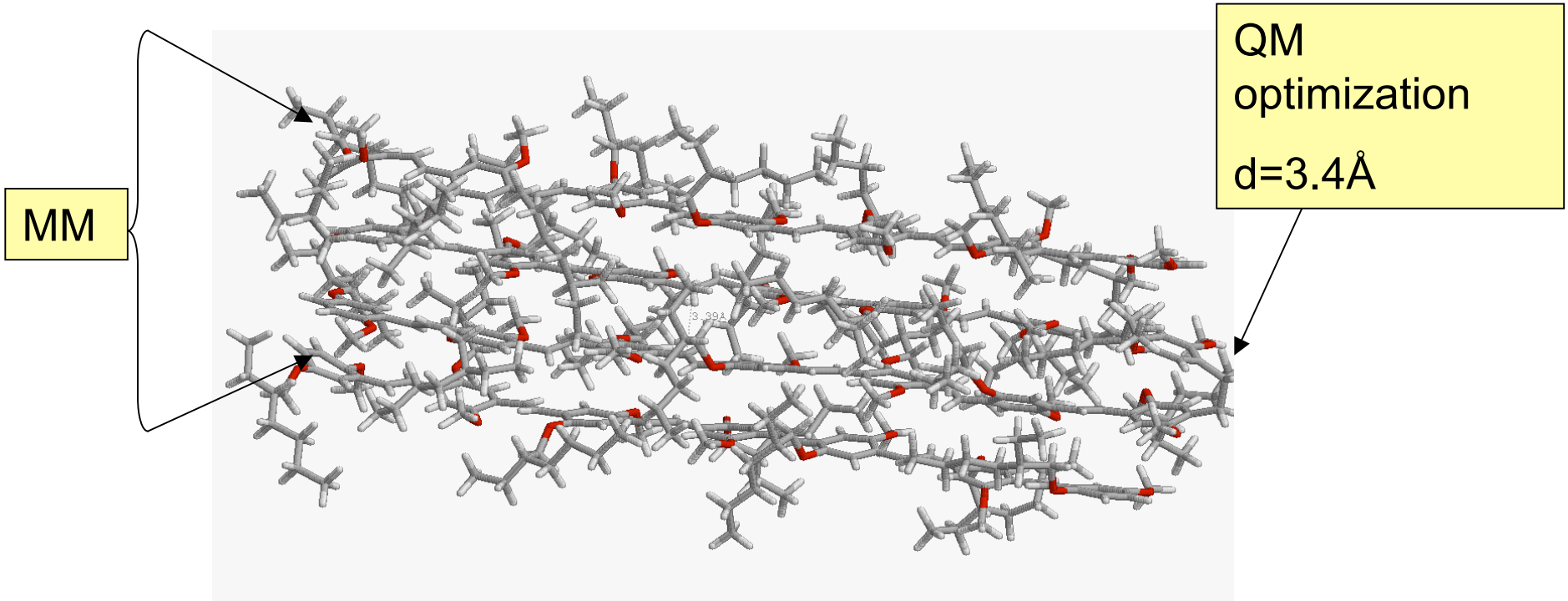
- 3D confinement in droplet
  - High-pressure environment from surface tension





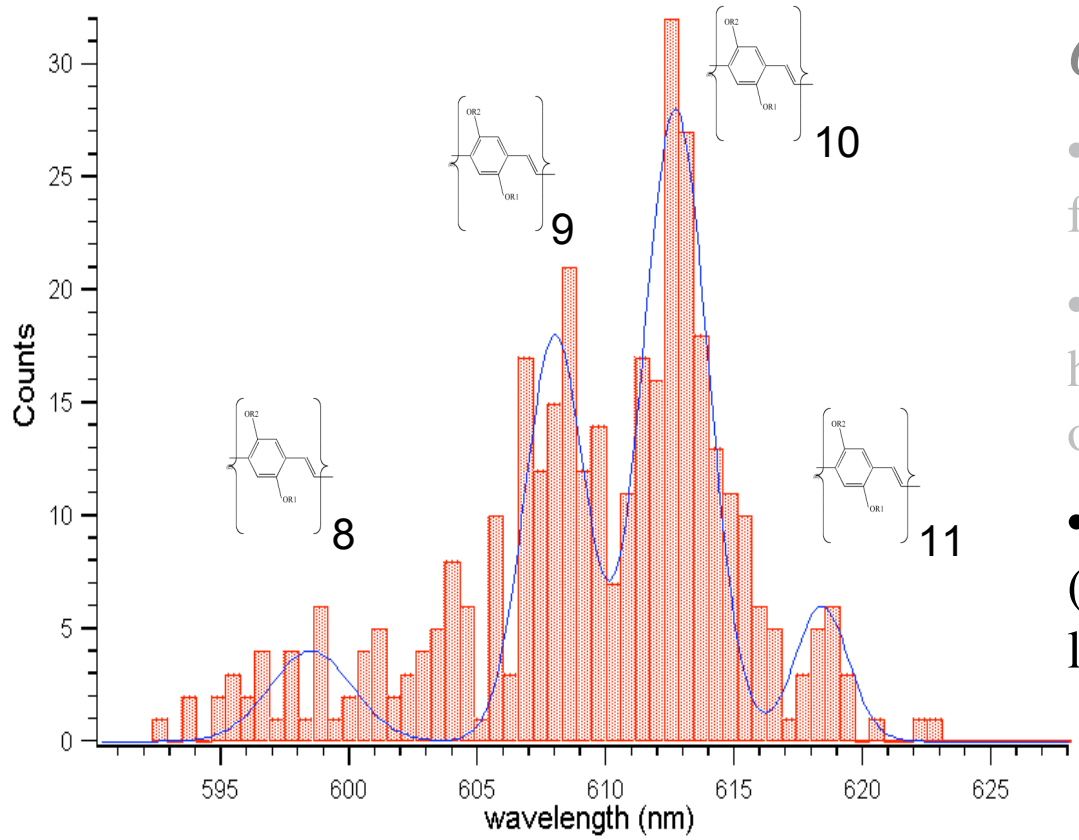


- Surface charge and inter-chain dispersive forces further compacts and orders the nanorod
  - Final 10% reduction in inter-chain distances



Hybrid QM/MM Multi-Scale Modeling

Discrete center frequency distribution



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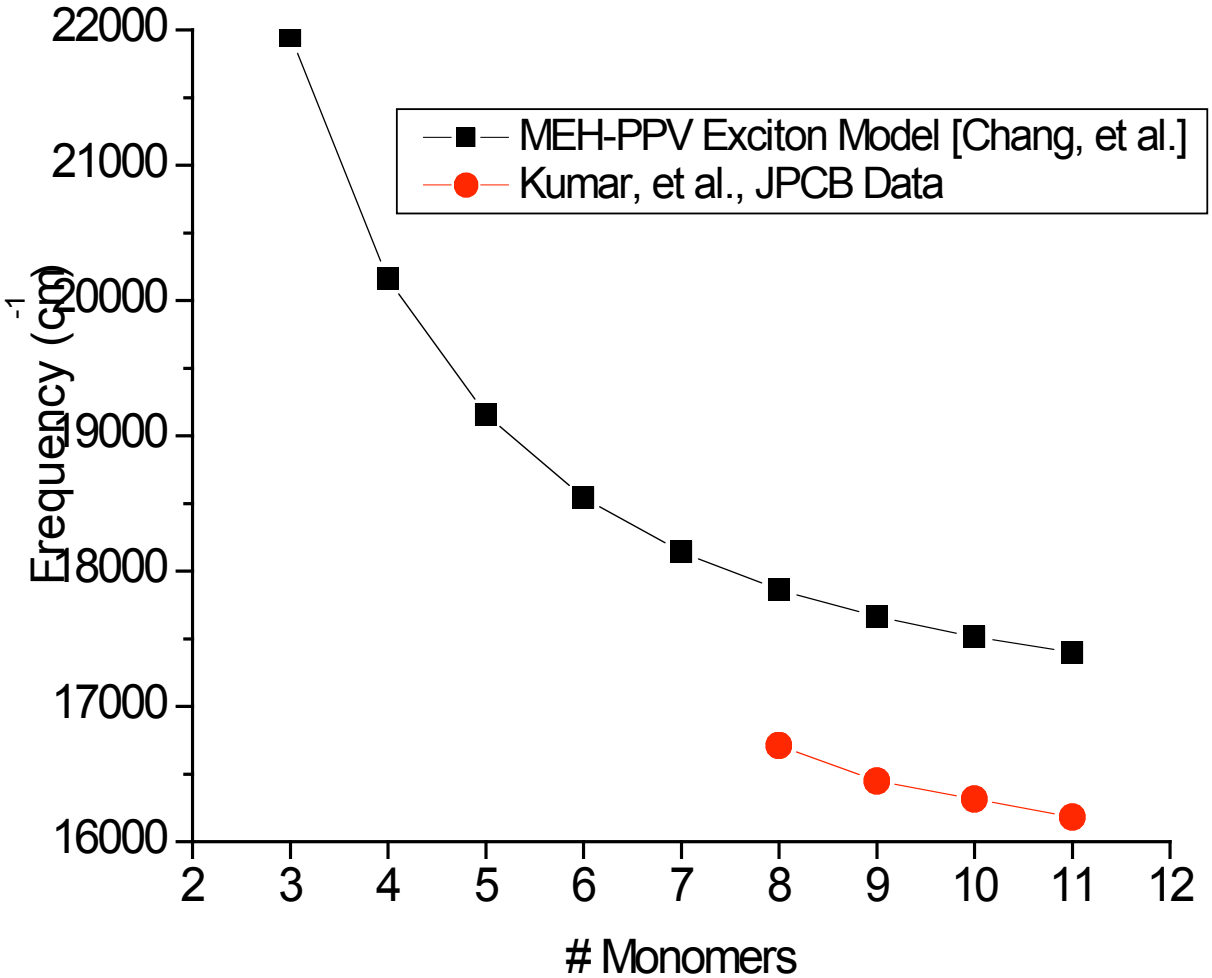
P. Kumar, *et al.*, JPCB **107**, 6252 (2003)

Observed center frequencies vs. exciton model



Exciton Model
Chang's to Yu et al.'s PPV Model fit of MEH-PPV

$$E_j = E_0 + 2\beta \cos\left(\frac{j\pi}{N+1}\right)$$

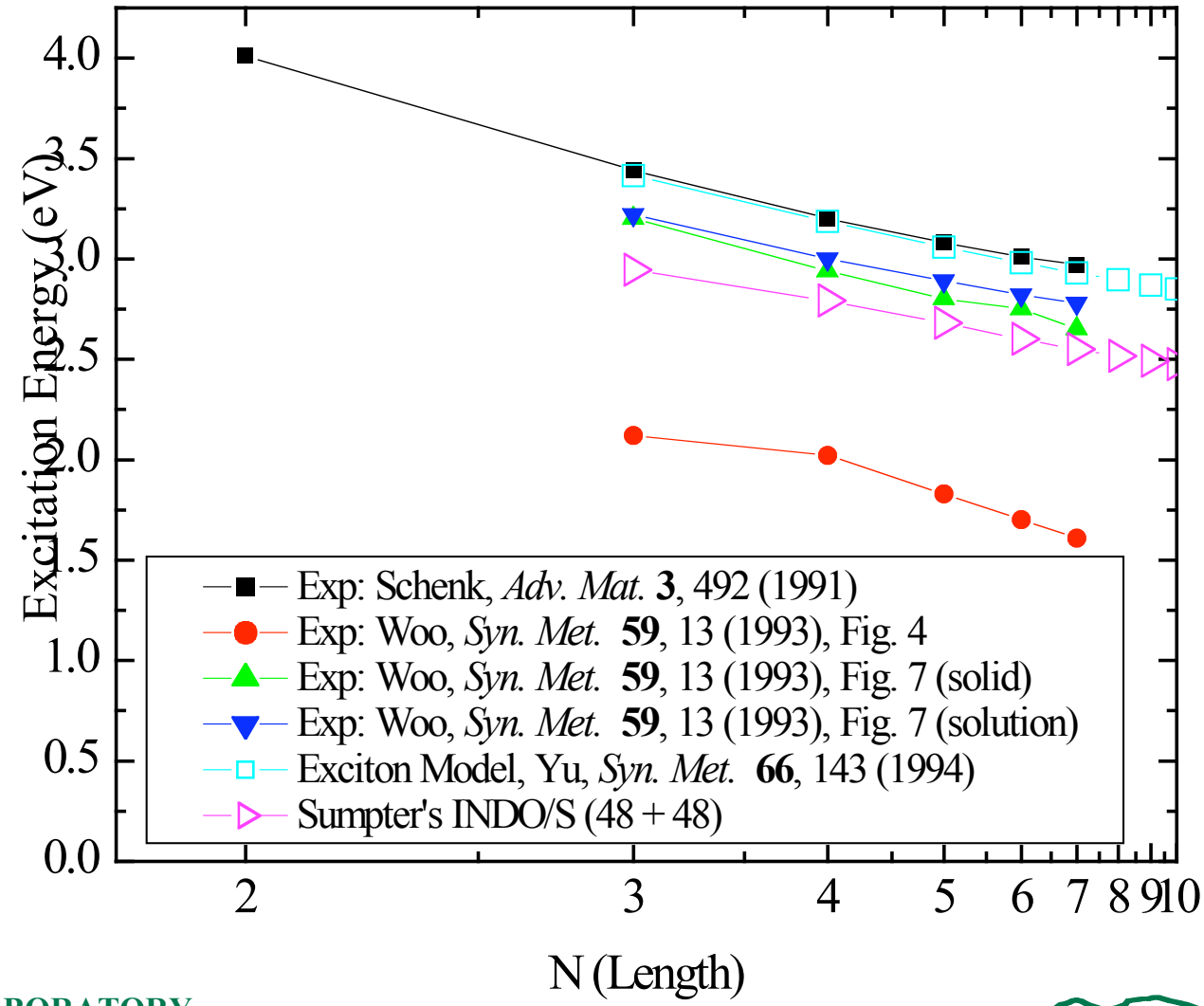
$$\beta = -8{,}800\, cm^{-1} = -1.1\, eV$$

$$E_0 = 34{,}000\, cm^{-1} = 4.3\, eV$$

Exciton Model:
R. Chang, *et al.*, *Chem Phys. Lett.* **317**, 142 (2000).
J. Yu, *et al., Syn. Met.* **66**, 143 (1994).

Individual PV Oligimers: Lowest Singlet Excitation

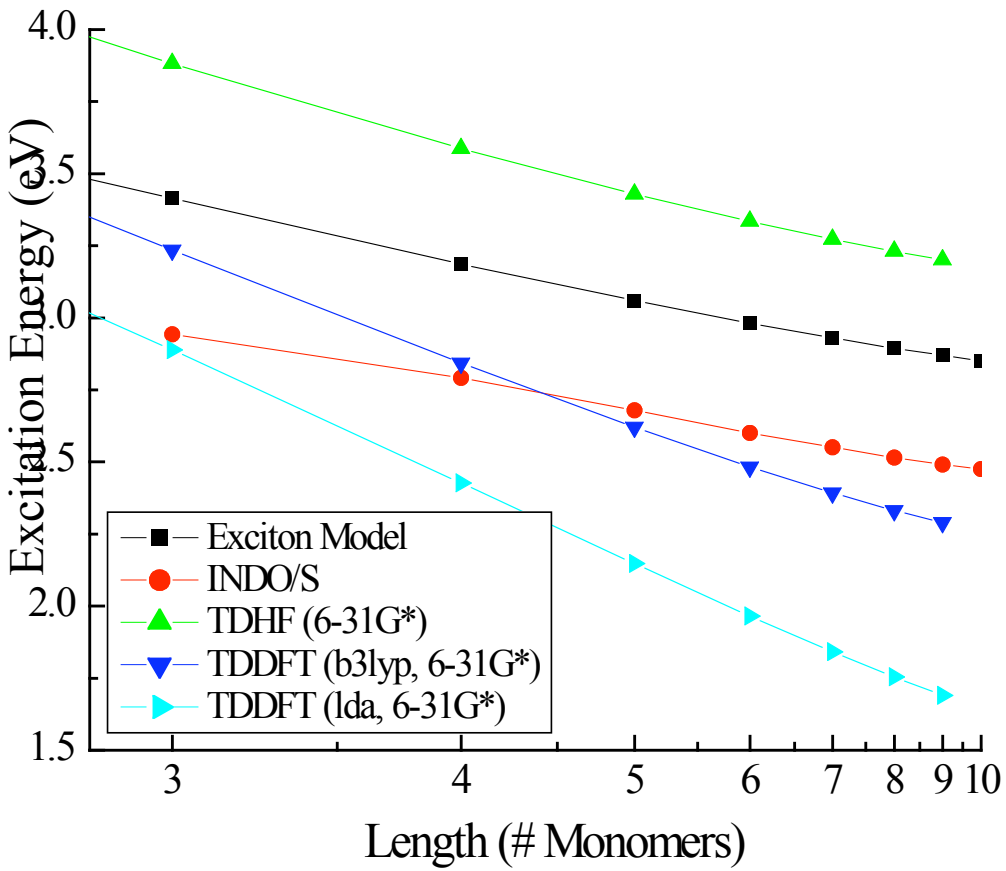
Compare experiment with model and semi-empirical predictions



Excitation of PV Oligimers:

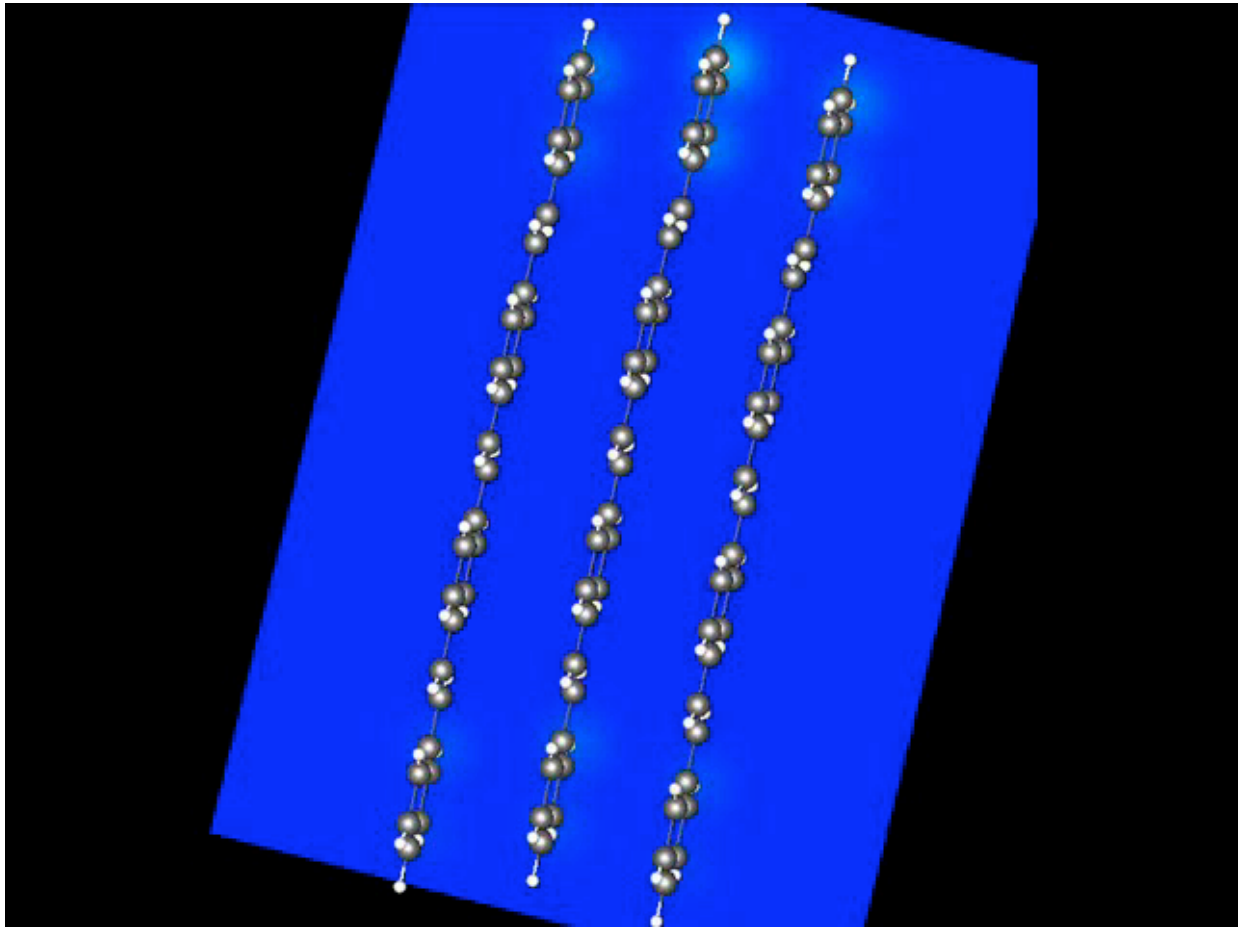
Comparison of Exciton Model, INDO/S, TDHF & TDDFT

First Singlet Excitation Length Dependence

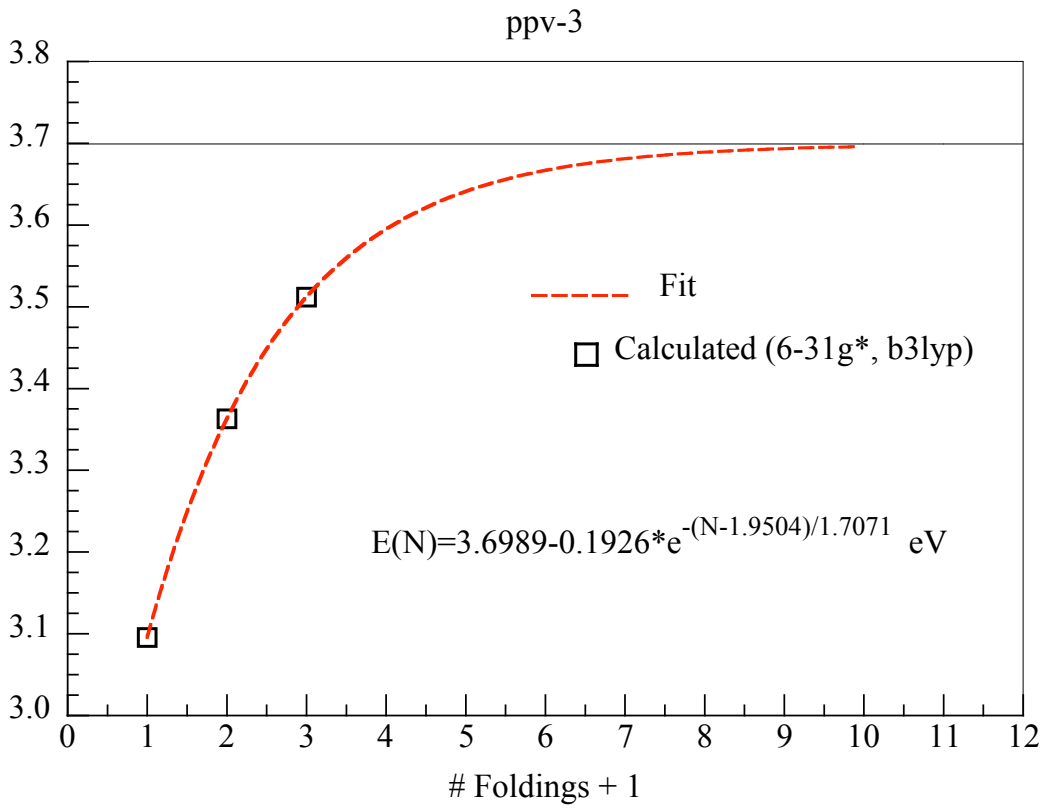


- TDHF:
  - Known to over predict excitations
- TDDFT (LDA):
  - "Method of choice" for large molecules.
  - OK for smallest oligimers
  - Errors grow with system size.
- Coupled-clusters linear response (EOM-CCSD) is too expensive.
- Exact exchange required for excitations in p -conjugated systems

Electron density distribution for a folded PPV



TDDFT:
Dominant vertical excitation vs. # of folding



- Collectively, spectrum red-shifts, consistent with larger box size.
- Transitions with dominate oscillator strength blue shift.
  - Persistent feature irrespectively of the oligomer length

?? Classical antenna in dielectric medium ??

- Classical antenna in dielectric experiences a red shift in frequency.
- Nanorods experience a large red shift from “self solvation”
- TDHF and TDDFT predicts a blue shift for dominate excitation.

Partial answers:

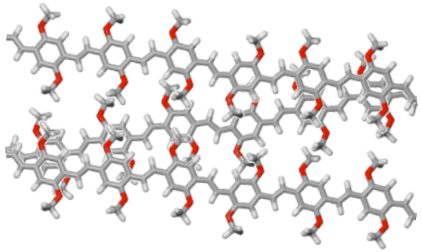
- Hybrid SE-QM/MM simulations of geometry relaxation (“self-solvation”) gives a red shift of ~23 nm. for vertical excitation.
- Excited state relaxation may contribute.
- Dielectric nanoparticle size << l .

Summary

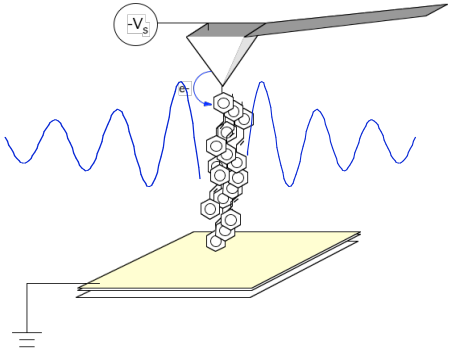
- Modified photo-physical properties of single polymer chains isolated by ink-jet printing!
- Photostability and spectral bandwidth superior to inorganic quantum dots under ambient conditions!
- First definitive evidence of single-site emission in conjugated polymer system
- Highly ordered nanorod structure confirmed by molecular modeling.
- Frontier, challenge system for theory and computation
  - Multiscale/multiphysics phenomena
  - Many electron methods with more accurate descriptions of exchange and correlation.
  - Time-dependent response of very large molecular systems.

New directions in macromolecular photo-physics and nanoscale optoelectronics

- ‘Designer’ oligomer and polymer synthesis?
  - *well-defined architecture*
  - *water-soluble variants*
  - *connection with electronic-structure theorists*
  - *designer light sources!*



- Single-nanoparticle electroluminescence?
  - *charge-transport properties*
  - *photovoltaic structures*



- Photonic quantum information processing?

People and Support

Experiment

- Mike Barnes (ORNL/Chemistry)
  - Pradeep Kumar (UT/Chemistry, Student)
  - Adosh Mehta (ORNL/LSD, Postdoc)
- Rob Dickson(GA Tech/Chemistry)
  - Tae-Hee Lee, Kewei Xu

Theory/Computation

- Predrag Krstić, (ORNL/Physics)
- Bobby Sumpter, Jack Wells (ORNL/CSMD)

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