Small is Different:
Introduction and Examples in Nanoscale Materials Science

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Outline

- Introduction to Nanoscience
  - "There is plenty of room at the bottom"
  - "Small is different"
- Examples from Nanoscience Research
  - Materials assembly by DNA templates
  - Capacitive properties of nanoscale metal clusters
  - Oriented semiconducting polymer nanostructures
- Oak Ridge National Laboratory
- Summary

Introduction to Nanoscience

- Nanoscience is an emerging area of science that concerns itself with the study of materials and systems having very small size.
  - The prefix “nano” is derived from the Greek for “dwarf”. In the SI system, it refers to 10^{-9}.
  - Nanoscience definitions:
    - The study of materials, systems, and devices of size range of the order 1nm to 100nm.
    - The ability to observe, measure, predict, and construct on the nanometer scale and exploit the novel properties found at that scale.

- It is interdisciplinary science incorporating chemistry, biology, and physics.
  - Example: Hybrid organic and inorganic materials.

"There's Plenty of Room at the Bottom":
An Invitation to Enter a New Field of Physics

- Classic talk given by Richard Feynman, December 29, 1959.
  - http://www.zyvex.com/nanotech/feynman.html
  - "Why cannot we write the entire 24 volumes of the Encyclopedia Britannica on the head of a pin?"
  - "I want to build a billion tiny factories, models of each other, which are manufacturing simultaneously."
- See "Feynman Prize" Winners: http://www.foresight.org/FI/2003Feynman.html.

“Small is different”

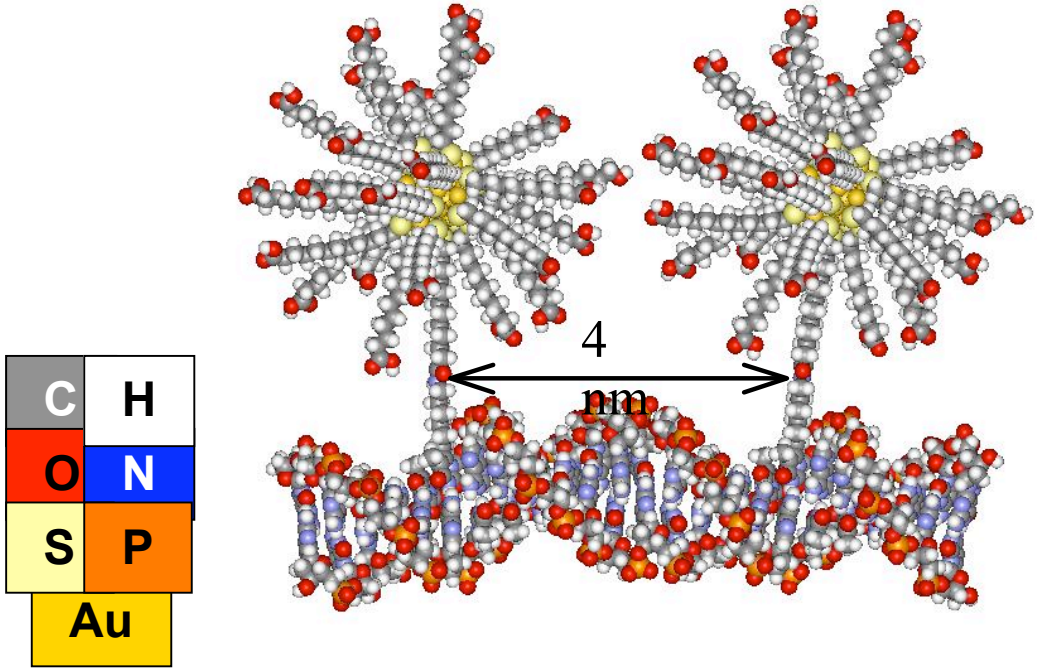
Within the nanoscale, the size scaling of well-known phenomena in bulky materials is no longer valid.

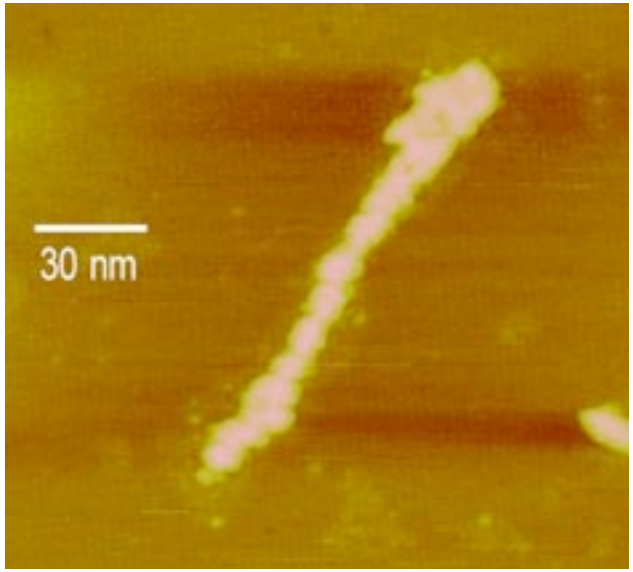
- Materials synthesis and assembly “from the bottom up”.
  - Self assembly
- Size-dependent phenomena
  - Capacitive charging
    - Coulomb blockade of current
  - Quantum size effect
    - Size-dependent control of electronic structure
- Access to quantum phenomena not observed in larger structures.
  - The “realm of the dwarfs” leads to the “Quantum World”.
- C***omplexities such as these promise materials and systems that may exhibit classes of behavior fundamentally different from those of both molecular and micro-scale structures.***
- National Nanotechnology Initiative: www.nano.gov

Example #1: Materials Synthesis via DNA Templates

DNA and Gold Nanoparticle complexes

$Au_{38}(S(CH_2)_{11}COOH)_{24}$





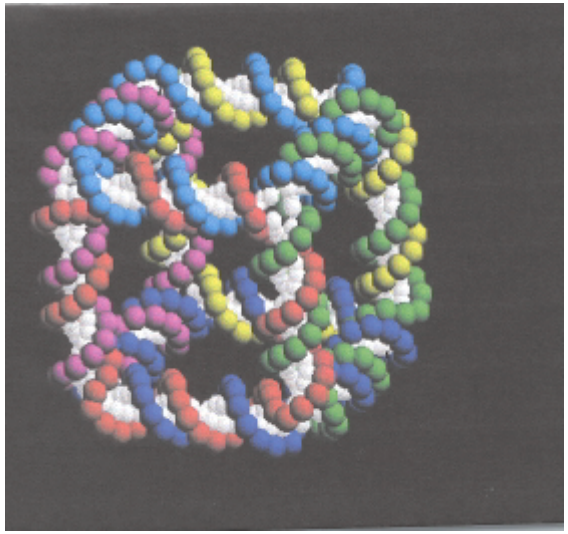
- Construction of Linear Arrays of nanoscale metal clusters via DNA templates.

"Covalent Attachment of Gold Nanoparticles to DNA Templates"

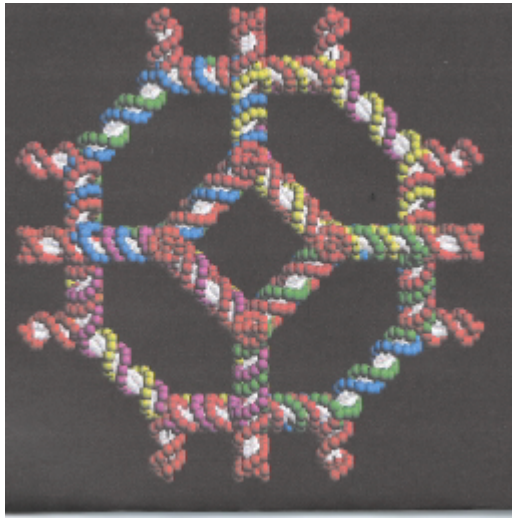
Stevenson, Muralidharan, Maya, Wells, Barhen, and Thundat, *J. Nanosci. Nanotech*. **2** (2002)

Seeman's DNA Constructs

- **DNA CUBE**



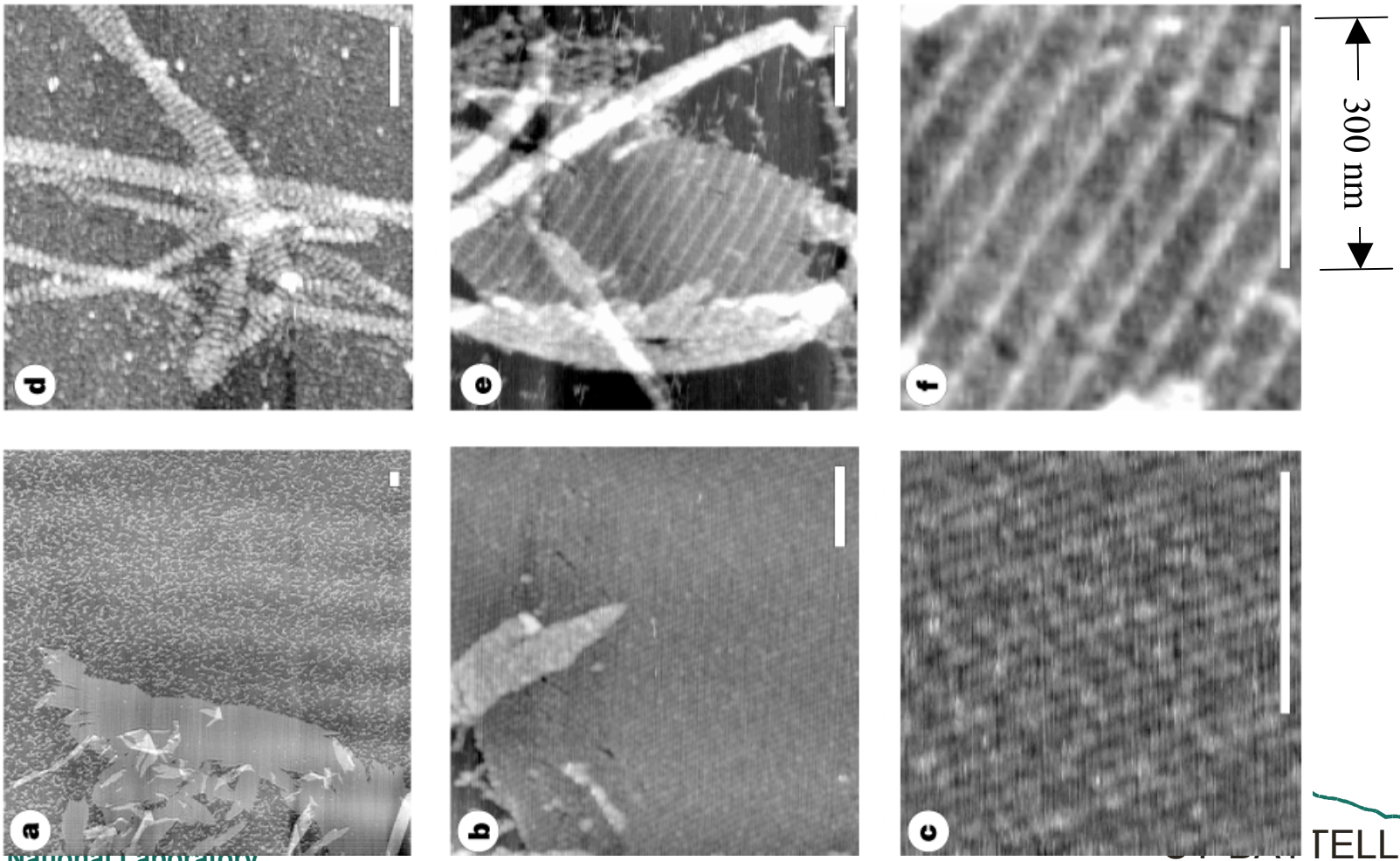
- **DNA TRUNCATED OCTAHEDRON**



http://seemanlab4.chem.nyu.edu/homepage.html

2D Lattices from DNA Cross-linked Structures

- **Seeman and coworkers have produced DNA in regular 2D geometries**
  - **N.C. Seeman, *J. Vac. Sci. Technol A* 12, 1895 (1993);**
  - **E. Winfree, *et al., Nature* 394, 539 (1998).**



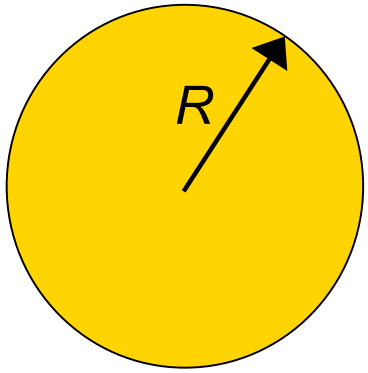
Example #2: Capacitive nature of nanoscale metal clusters

- **Isolated conducting sphere**

$$C \equiv \frac{\Delta Q}{\Delta V} = \frac{Q}{Q/4\pi\varepsilon_0 R} = 4\pi\varepsilon_0 R$$

- **(Coulomb) Energy to charge sphere with single electron**

$$\Delta E = \frac{e^2}{2C}$$



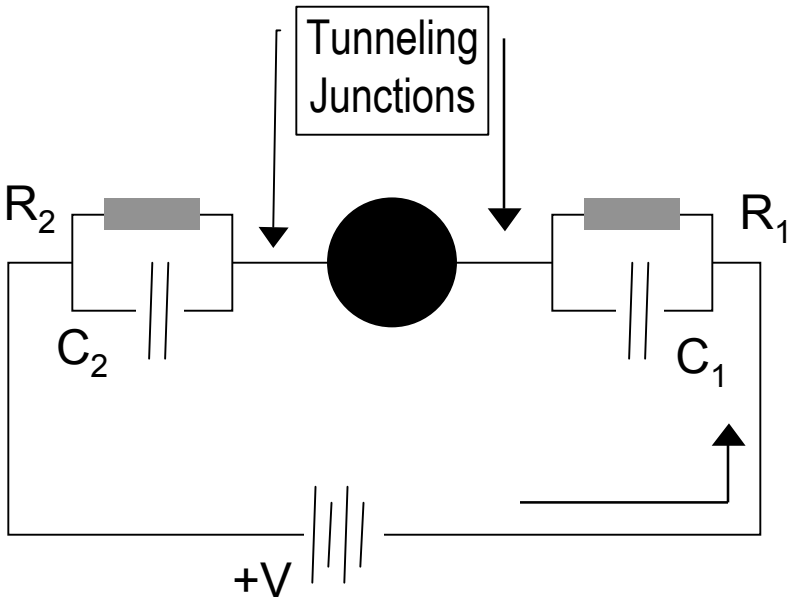
- **Find energy to add single electron to ideal conducting sphere with R=5 nm:**

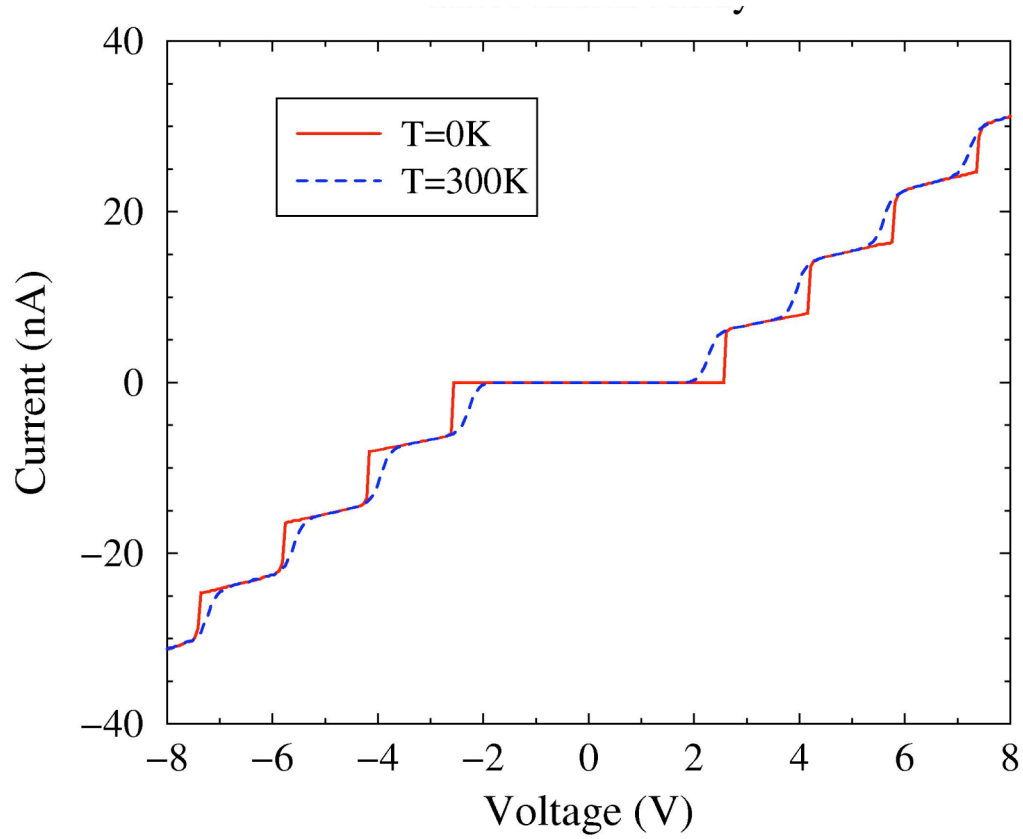
$$\Delta E = \frac{e^{2=}}{2C} = \frac{e^2}{8\pi\varepsilon_0 R}$$

$$\Delta E = \left(\frac{\left(1.6\times10^{-19}\,C\right)^2}{8\pi\left(8.85\times10^{-12}\,\frac{C^2}{N\cdot m^2}\right)\left(5\times10^{-9}\,m\right)} \right) = 2.3\times10^{-20}\,J$$

$$= 0.14\,eV$$

“Single-electron” Devices and “Coulomb Blockade”





Basic Assumptions

- Electron tunneling on and off con
  - $R_T >> h/e2 \approx 25.8\ k\Omega$.
- Overcome thermal fluctuations,
  - $EC = e^2/C >> k_B T \approx 0.026$ eV.
- Tunneling rates from Fermi’s Golden Rule

References:

Likharev and coworkers (1991)

UT-BATTELLE

Energy levels of electrons in the metal cluster

- According to quantum mechanics, electrons have extra energy from being localized in the cluster, i.e., a "box".
- Energy to add an electron is a difference in chemical potential, e.g., of the neutral cluster and its anion.
- Capacitance concept can be extended to atomic-sized structures.
  - $C=C(N_{electrons})$
- Capacitive properties may be measured or computed from Quantum Mechanics.

$$\boxed{\varepsilon_{Box} = \frac{\pi^2\hbar^2}{2mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)}$$

$$e\Delta V = \Delta\mu = \mu(N+1) - \mu(N),$$

$$\mu(N) \equiv E(N) - E(N-1)$$

$$C(N) \equiv \Delta Q / \Delta V(N)$$

$$\Delta E(N) = \frac{e^2}{C(N)}$$

$$= E(N+1) - 2E(N) + E(N-1)$$

$$= I(N) - A(N) = 2\chi(N)$$

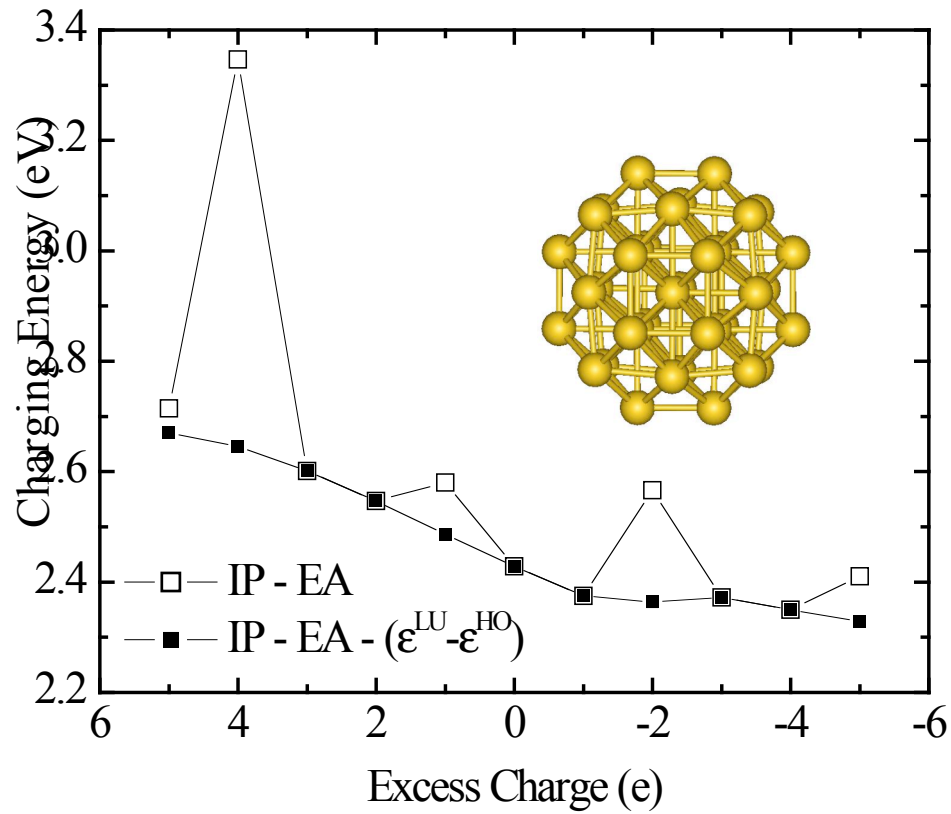
χ: "Absolute hardness" of electron transfer

Charging Characteristics of Au_{38} from Density Functional Theory

- Using a result from DFT, the difference in IP and EA may be written the sum of a term depending of the size of the charge density and the HOMO-LUMO gap.

$$\Delta E(N) = I(N) - A(N)$$
$$= B_0(R) - \Delta\varepsilon_{HOMO-LUMO}$$

- Predictions from numerical calculations:
  - Truncated octahedron.
  - Charge –2 is the lowest energy configuration.
  - Capacitance is constant over several charge states.
  - Electronic shell closings result in particularly configurations → large charging energies.



Apra, Krstic, Wells, et al., *Comp. Mat. Sci.* (2003)

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).

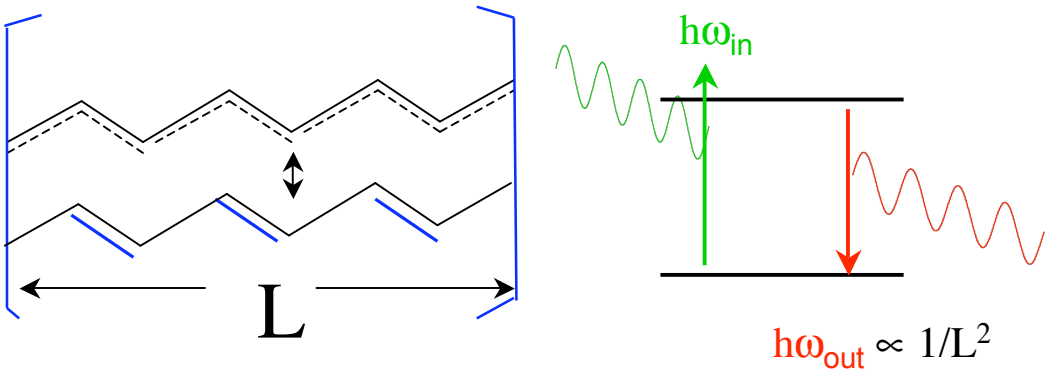
Applications:

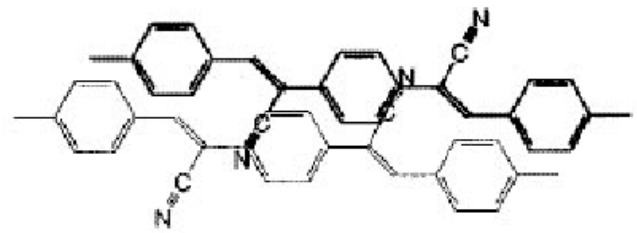
- Electronic paper, luminescent clothing, display technologies, etc.!

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

What are the issues in nanoscale applications??

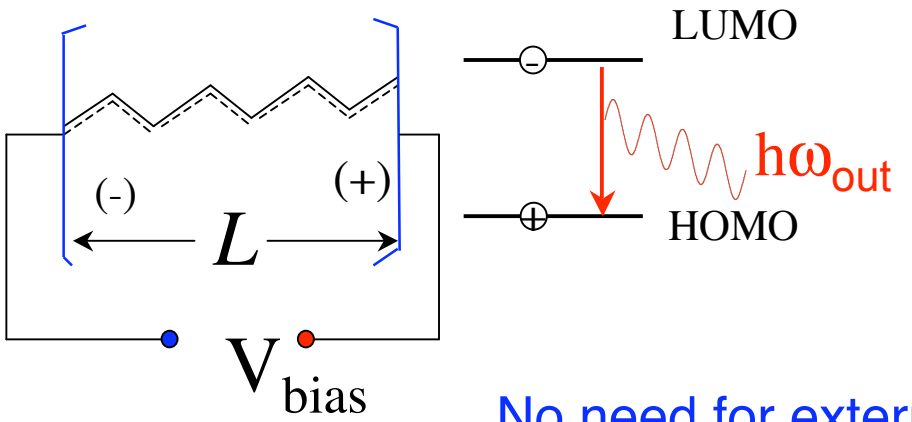
Semiconducting Polymers ??





- 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

Electroluminescence



No need for external light pump.

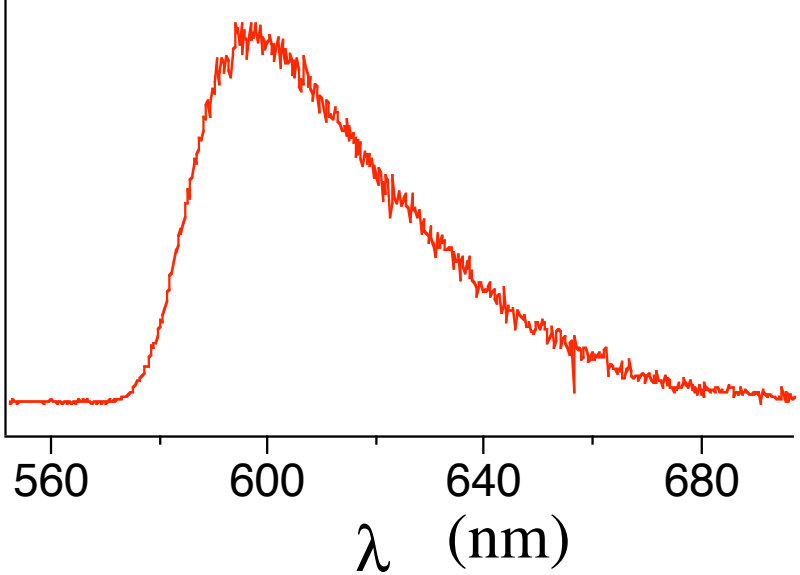
Semiconducting Polymers:
Photo-physical Limitations in thin-film formats

The bad news:

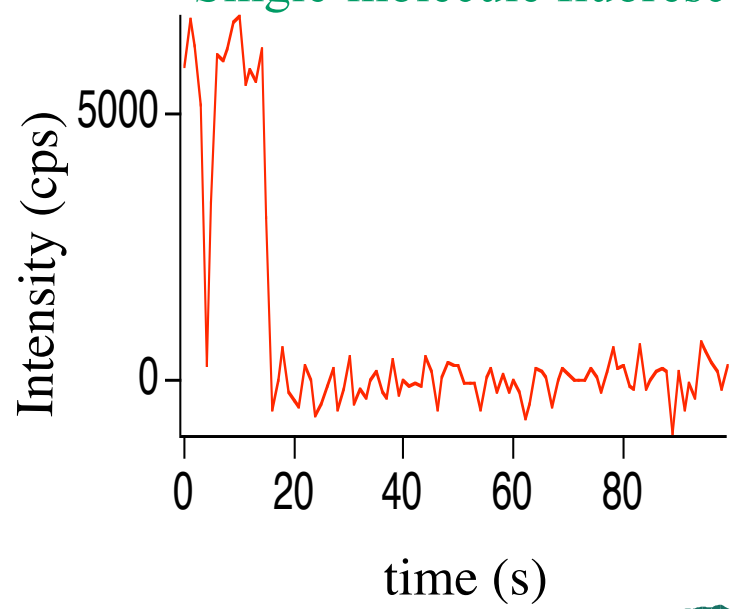
- Random, disordered chain structure for thin films;
- Broad emission spectrum, poor photo-stability and charge-transport properties

→ nanoscale photonics applications are "short-circuited"!

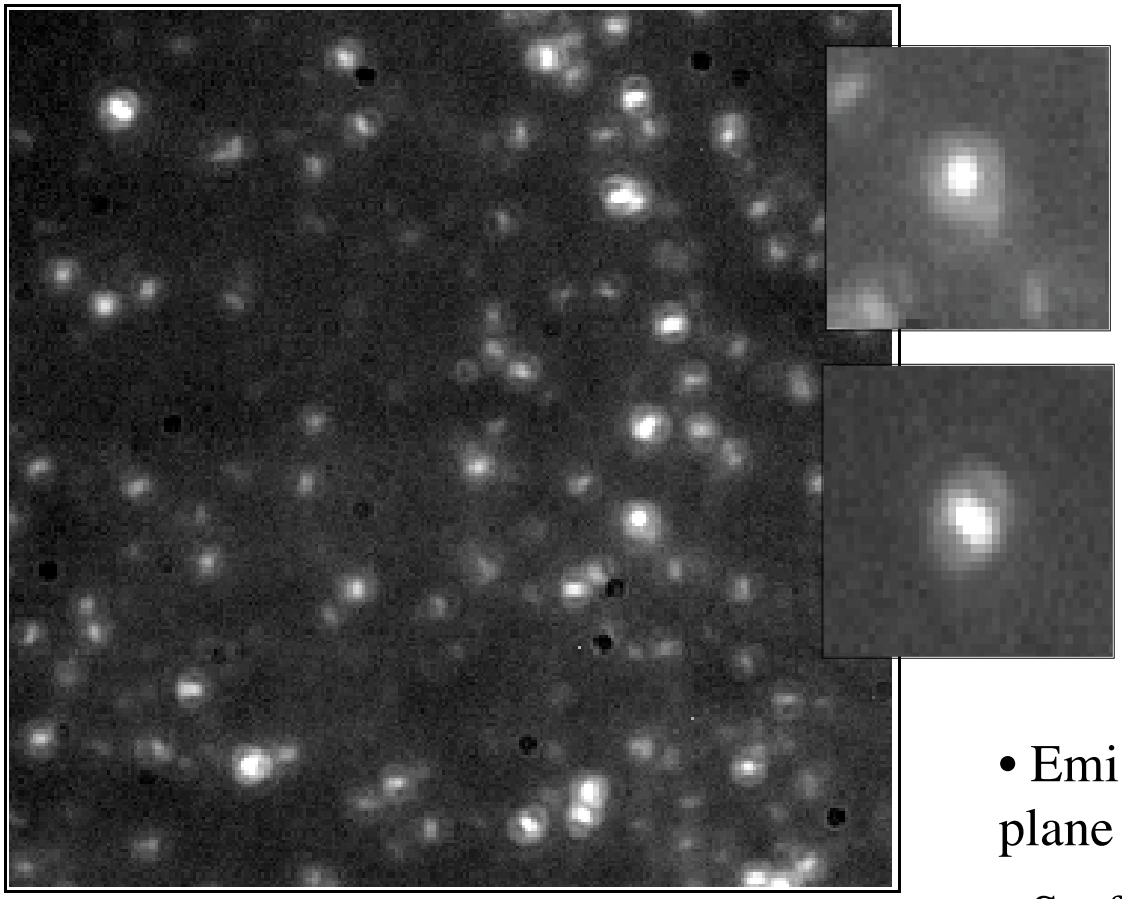
Broad ensemble emission spectrum



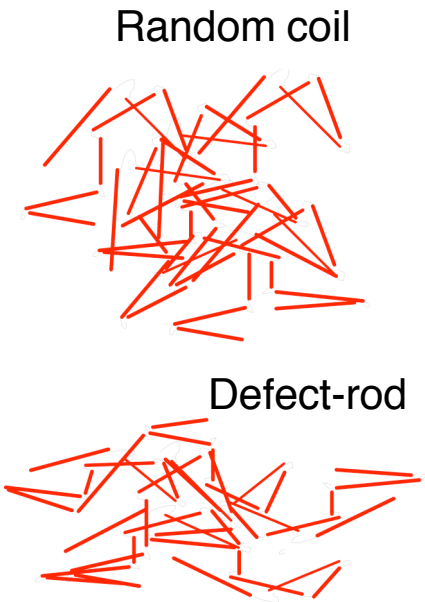
Single-molecule fluorescence



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



Fluorescence of single MEH-PPV molecules under 400x magnification



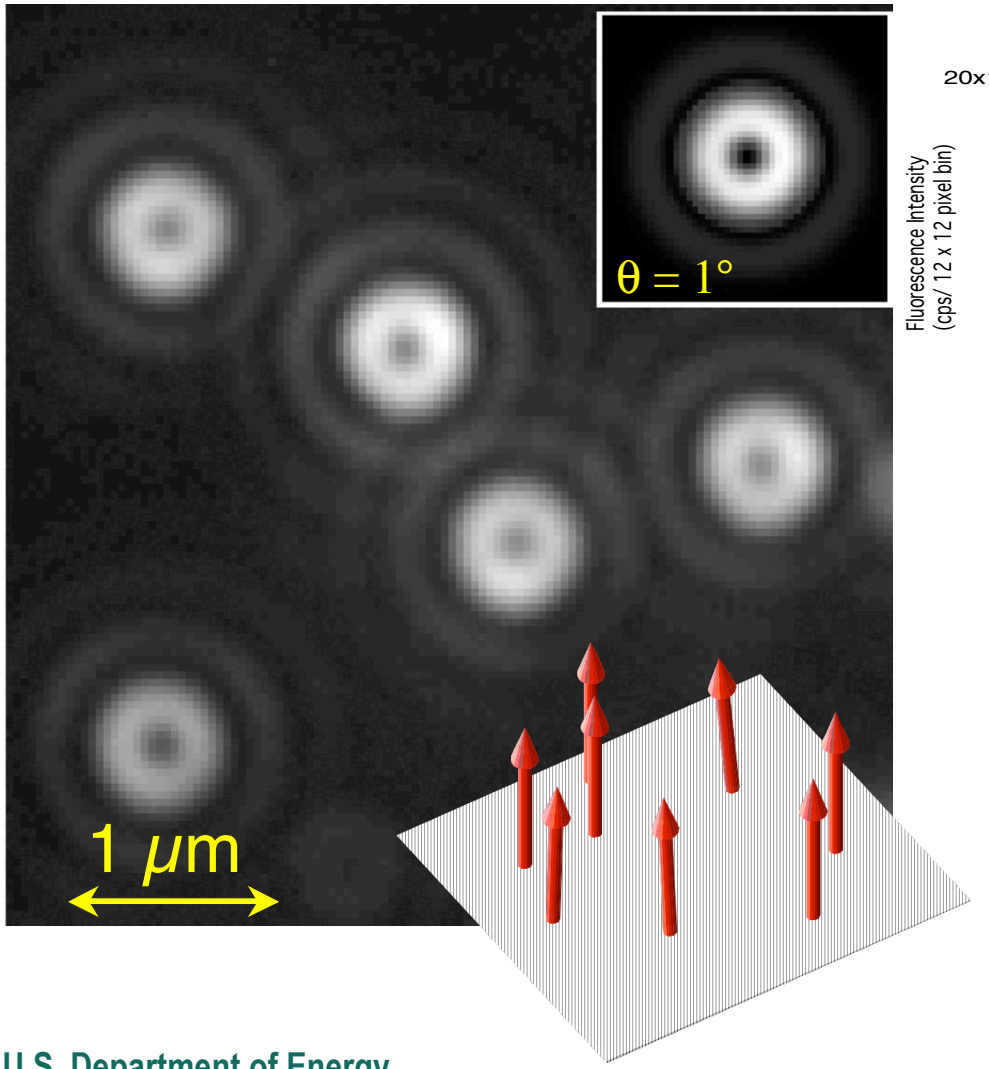
- Emission dipoles oriented in the plane of the substrate.
- Surface interaction/charge states
- Oxidation events

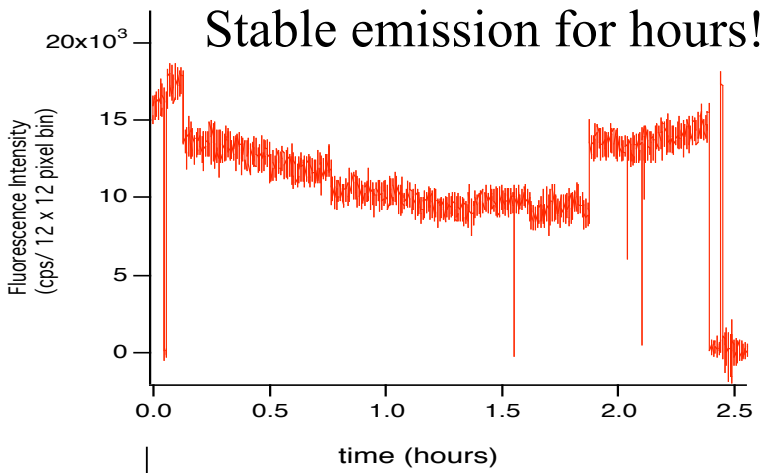
Example #3: Oriented nanostructures from single-molecules of conjugated polymers

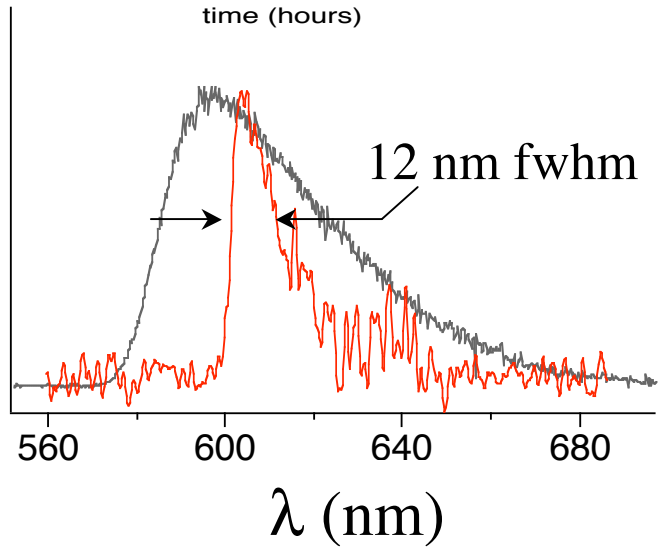
P. Kumar, *et al.*, JPCB **107**, 6252 (2003)

- 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 oriented polymer nanoparticles (cyano-substituted PPV)







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

Generating an Electromagnetic Wave

- Maxwell's Equations predict the generation and free propagation of EM radiation.

<u>Physics</u>, Halliday, Resnick, and Krane 5th Ed., Section 38-4

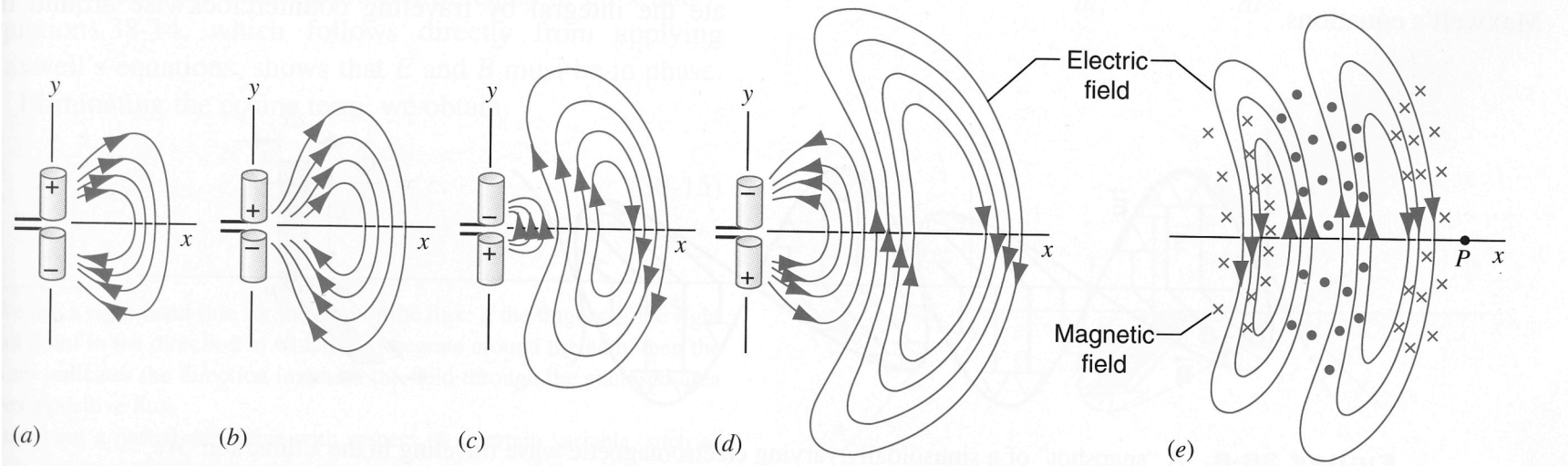


FIGURE 38-6. Successive stages in the emission of an electromagnetic wave from a dipole antenna. In (*a*)–(*d*), only the electric field patterns are shown. In (*e*), the magnetic field is shown as perpendicular to the plane of the page.

Radiation emission from oscillating dipole

- Far-field
  - Propagation to large distance: Radiated energy
  - Transverse field only
  - Distance dependence: 1/r
  - Angular dependence: *sinθ*
- Near field
  - Instantaneous dipole field
  - Distance dependence: $1/r^3$
  - Additional longitudinal component.
- Induction field (Intermediate)
  - Distance dependence: $1/r^2$

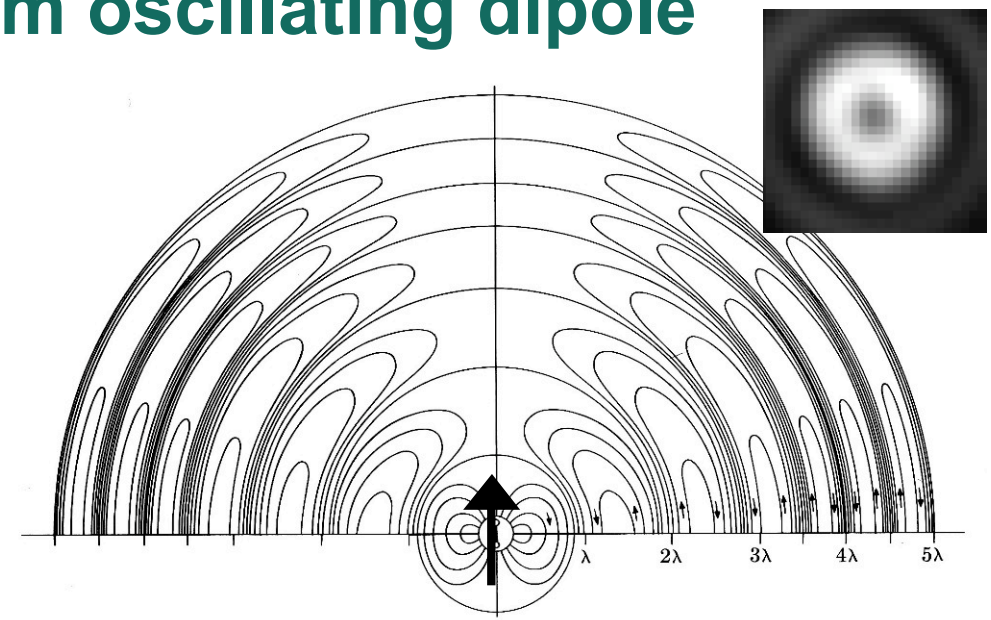


Figure 20–3 Electric field lines produced by an oscillating electric dipole.

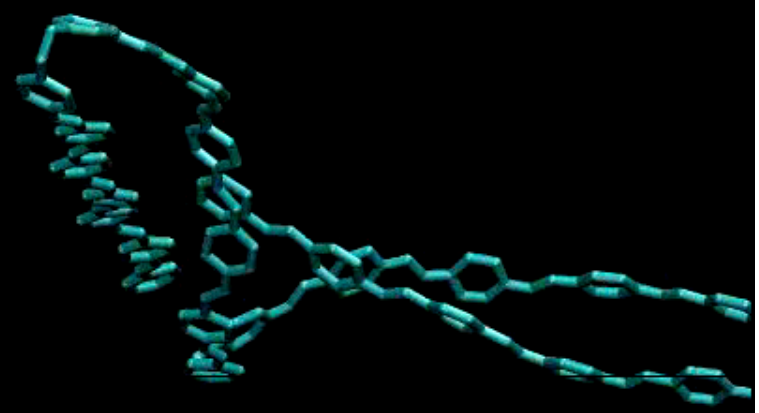
$$\vec{p}(t') = p\vec{k}e^{-i(\omega t-\kappa r)}, \kappa = \omega/c$$

$$E_\vartheta = \frac{p\kappa^3}{4\pi\varepsilon_0}\sin\vartheta\left[-\frac{1}{\kappa r} - i\frac{1}{(\kappa r)^2} + \frac{1}{(\kappa r)^3}\right]e^{-i(\omega t-\kappa r)}$$

$$E_r = \frac{p\kappa^3}{2\pi\varepsilon_0}\cos\vartheta\left[\qquad -i\frac{1}{(\kappa r)^2} + \frac{1}{(\kappa r)^3}\right]e^{-i(\omega t-\kappa r)}$$

Foundations of Electromagnetic Theory, 3rd Ed., Reitz, Milford, and Christy, Ch. 20

Molecular Dynamics Simulation of Polymer:
Initial Stages of Folding

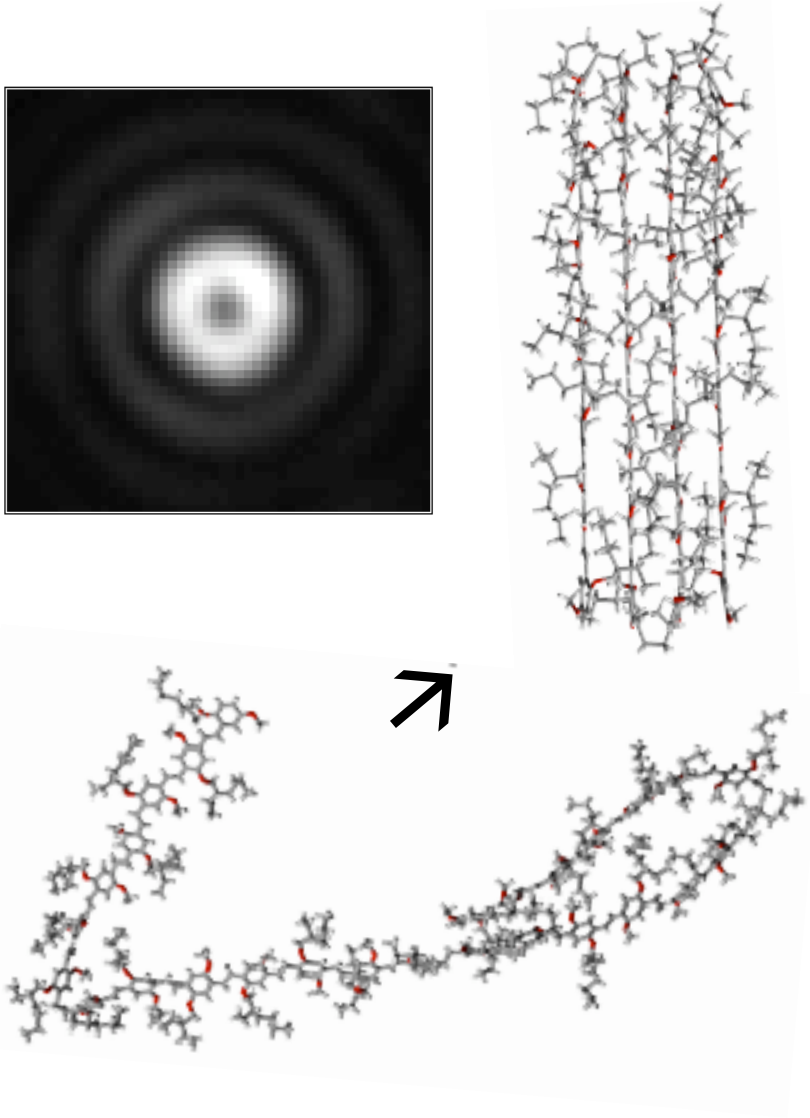


Connection between orientation and particle structure?

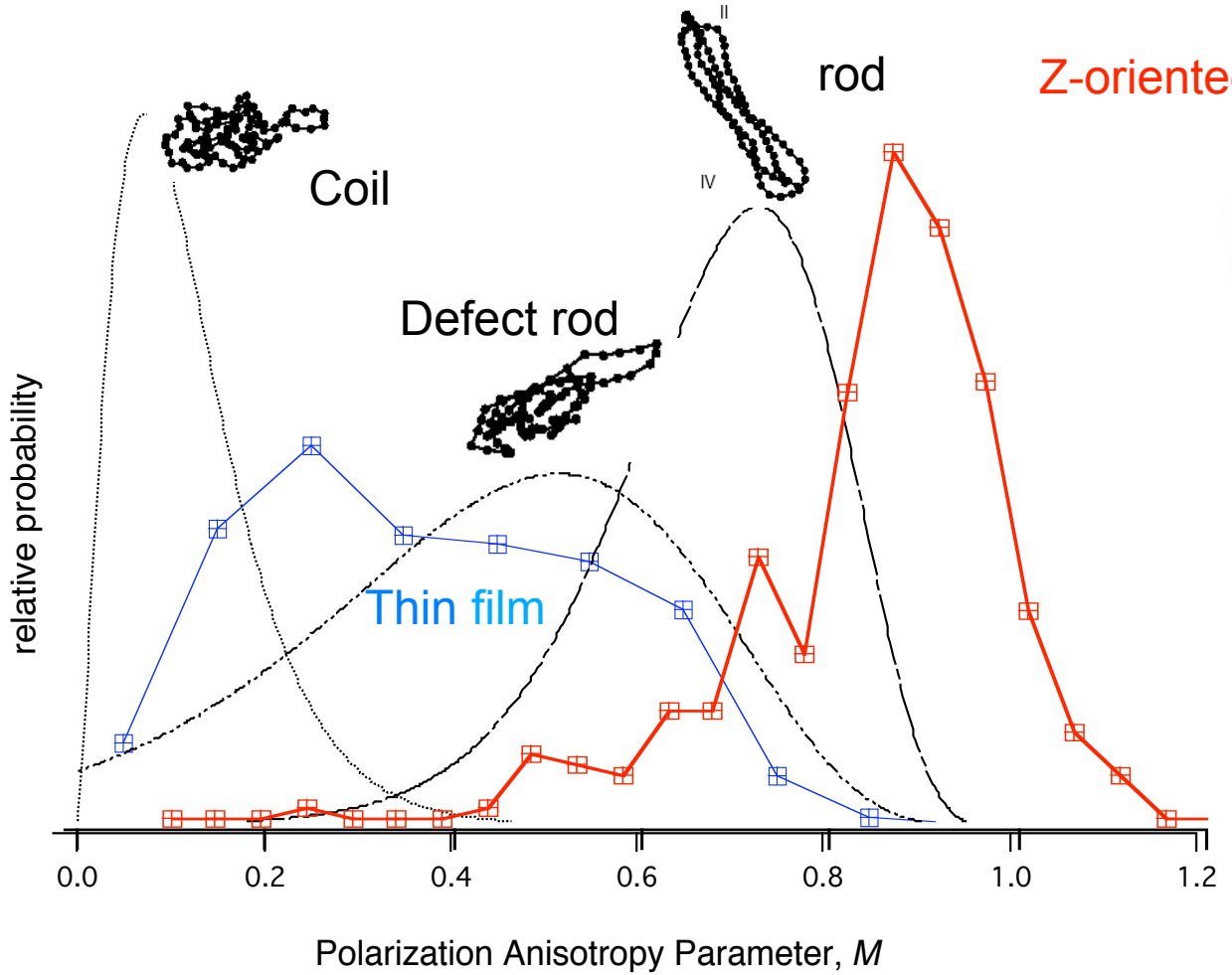
MM simulations of polymer folding & collapse

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

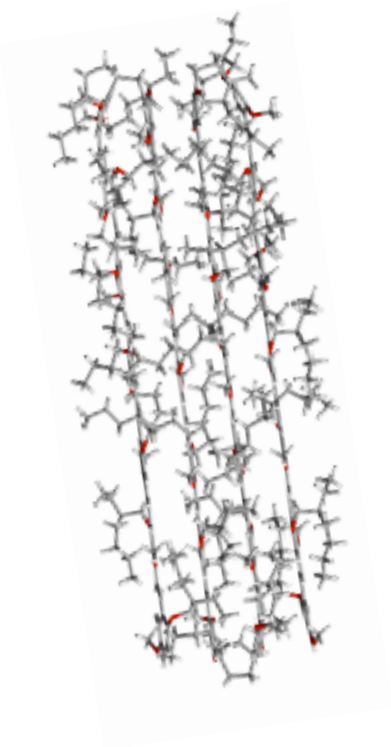
- **3D confinement in droplet**
  - **High-pressure environment from surface tension**



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

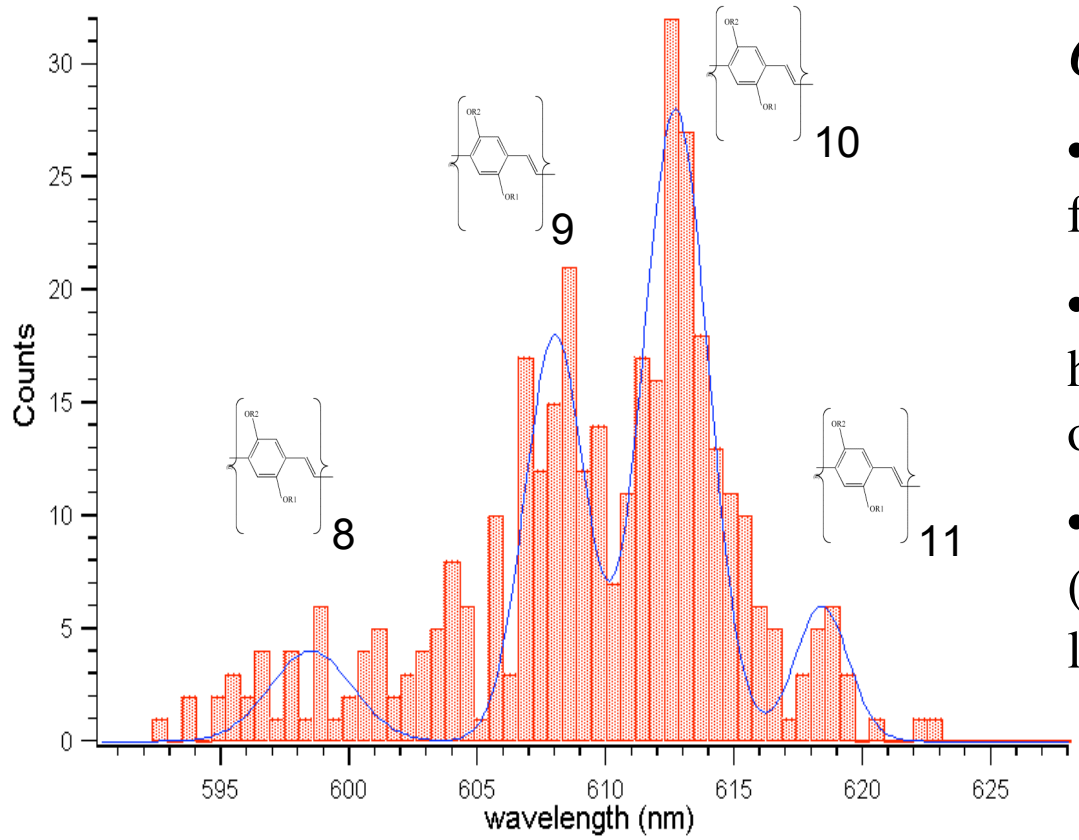


Z-oriented nanoparticles:



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

Discrete center frequency distribution



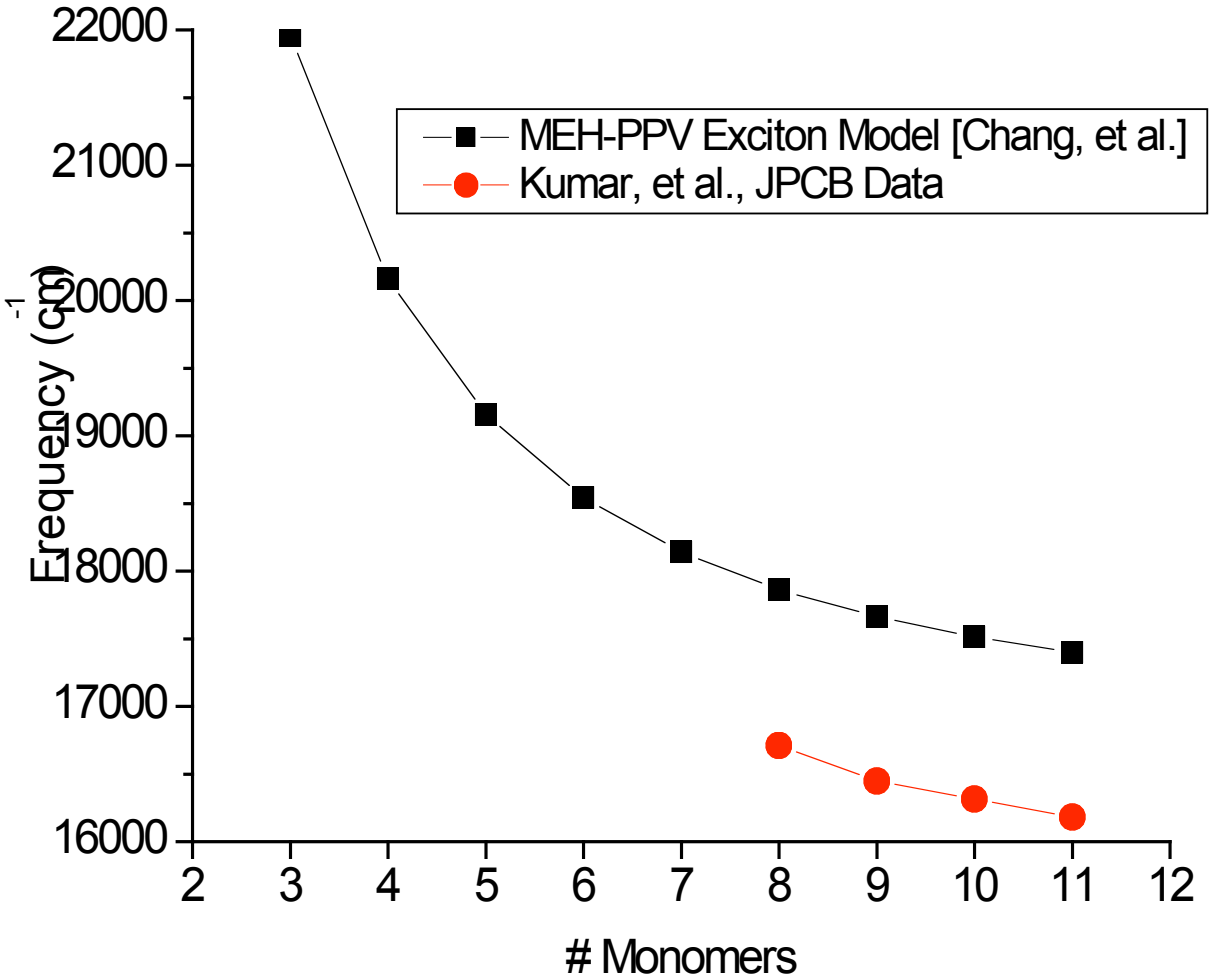
Observations:

- 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)

Observed center frequencies vs. exciton model



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

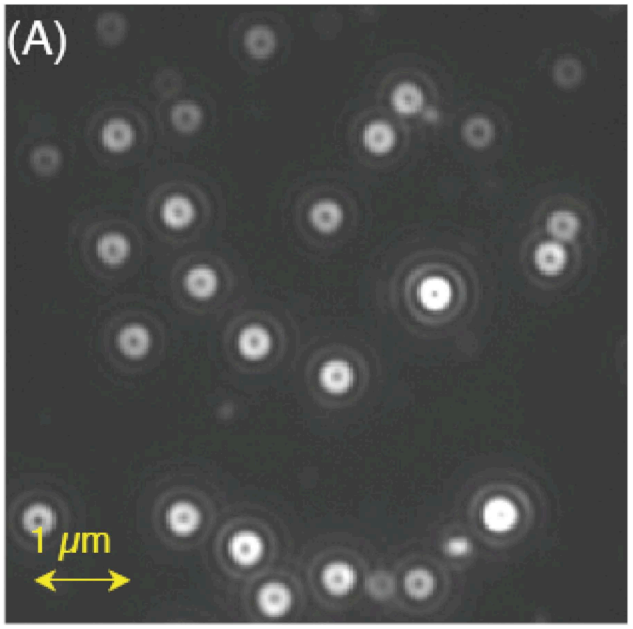
$$E_j = E_0 + 2\beta \cos\left(\frac{j\pi}{N+1}\right)$$

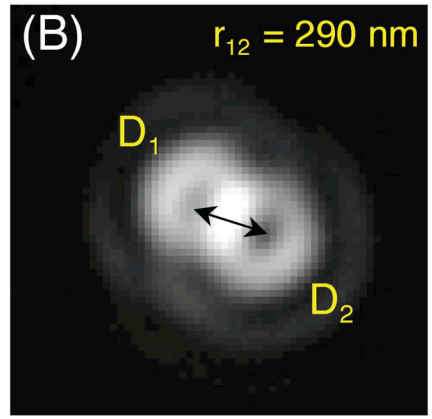
$$\beta = -8{,}800\, cm^{-1} = -1.1\, eV$$

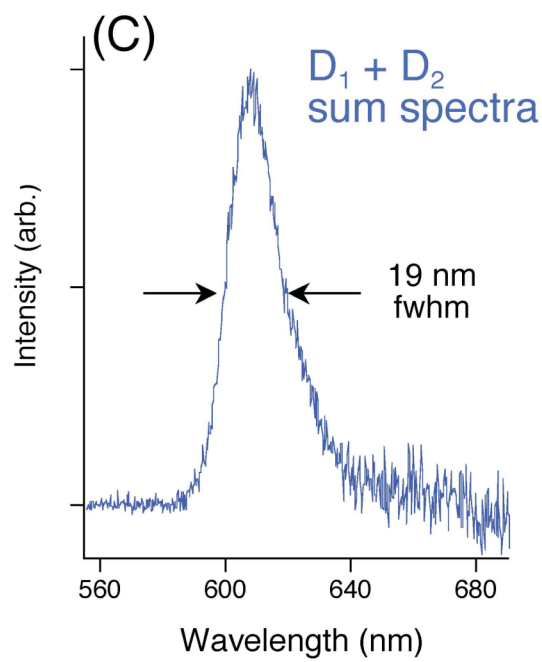
$$E_0 = 34{,}000\, cm^{-1} = 4.3\, eV$$

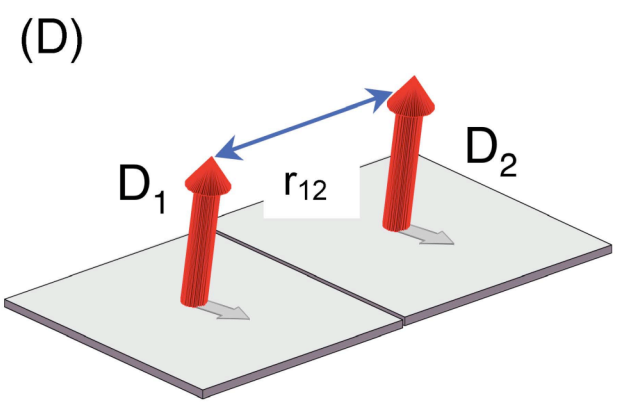
Exciton Model:
R. Chang, *et al.*, *Chem Phys. Lett.* **317**, 142 (2000).
J. Yu, *et al., Syn. Met.* **66**, 143 (1994).

Nanoscale Antennae: Are the dipoles coupled?









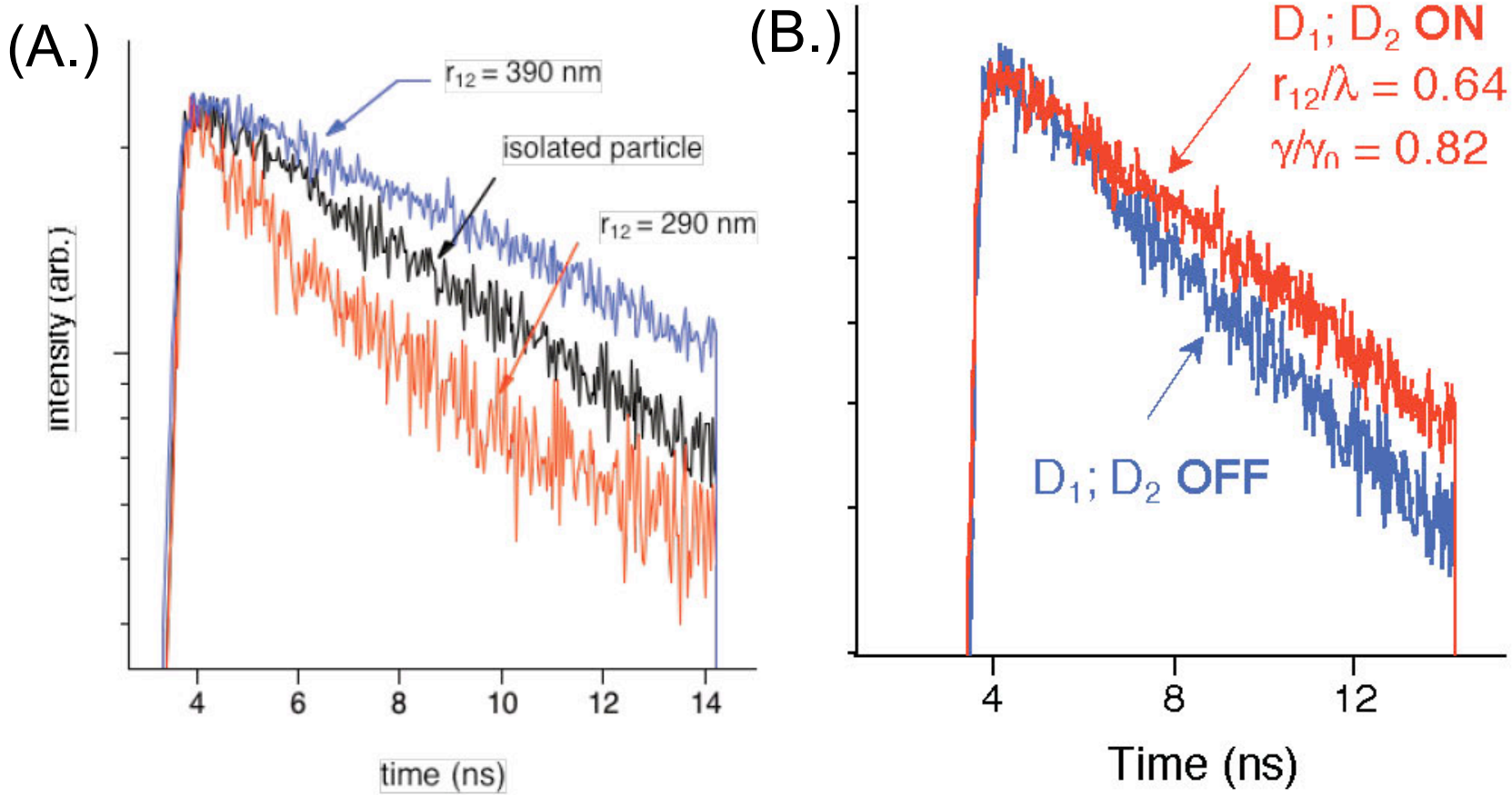
A. Wide-field view of oriented PPV nanostructures.

B. Close up of particle "dimer" with 290 nm spacing

C. Summed emission spectrum for the dimer (D_1+D_2).

D. Dipole D_1 is the "probe" particle in the presence of the second dipole D_2

Fluorescence decay



A. Fluorescence decay functions compared with a typical isolated particle transient (γ_0=0.11 nsec^{-1}).

B. D_1 fluorescence decay function in presence of D_2, and after photo-bleaching of D_2.

Radiation emission from oscillating dipole

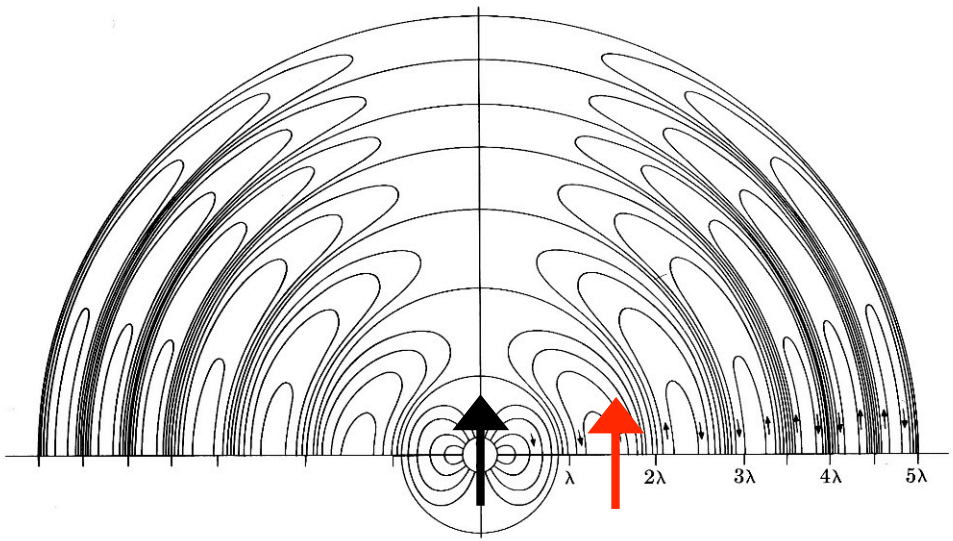
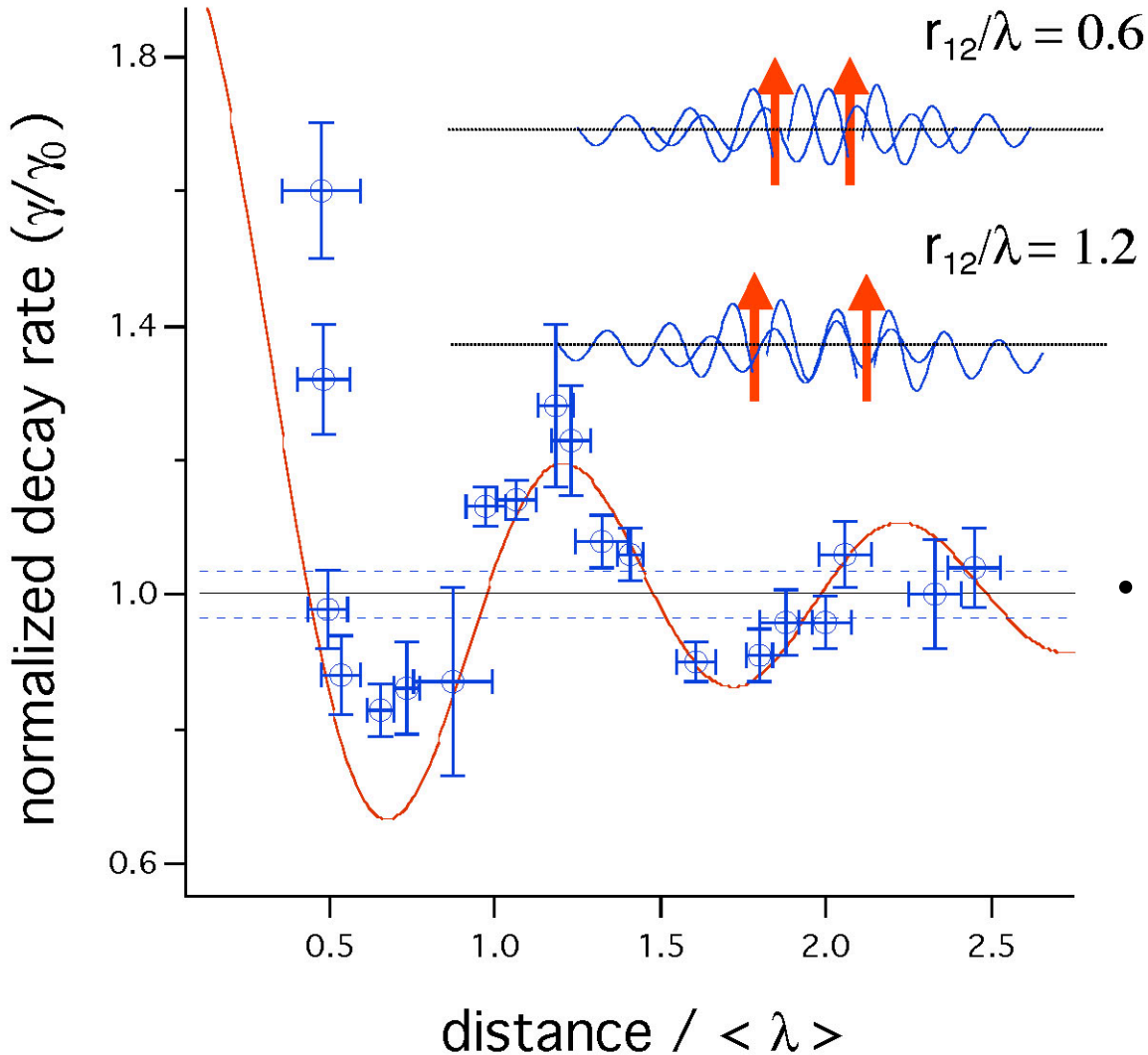


Figure 20–3 Electric field lines produced by an oscillating electric dipole.

$$\frac{\gamma}{\gamma_0} = 1 + \frac{3}{2}\left\{\frac{\sin\alpha}{\alpha} - \frac{\cos\alpha}{\alpha^2} + \frac{\sin\alpha}{\alpha^3}\right\}; \alpha \equiv 2\pi\frac{r_{12}}{\lambda}$$

Barnes, Krstic, Kumar, Mehta, and Wells, *Phys. Rev. Lett.* Submitted (2004)

Far-field fluorescence decay rate modulation

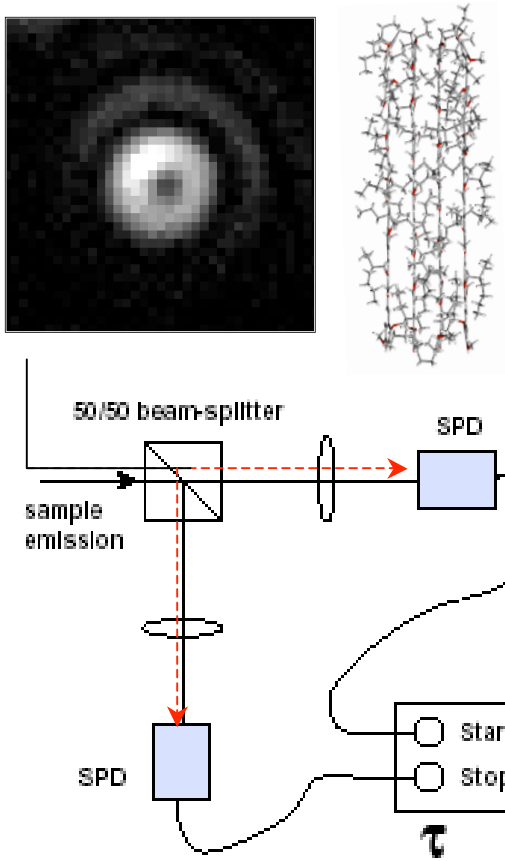


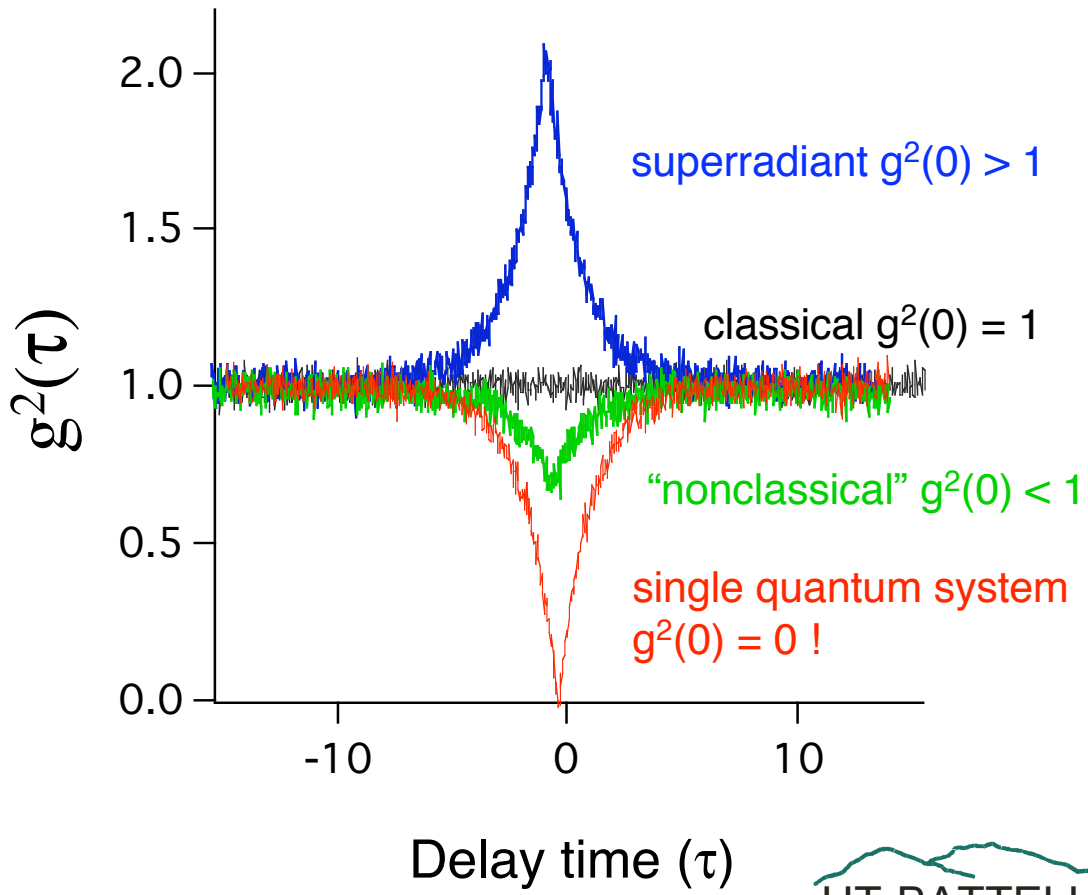
- For two coupled oscillators, the external driving force has an oscillatory dependence on the distance between the dipoles.

Photon statistics from single polymer nanostructures:

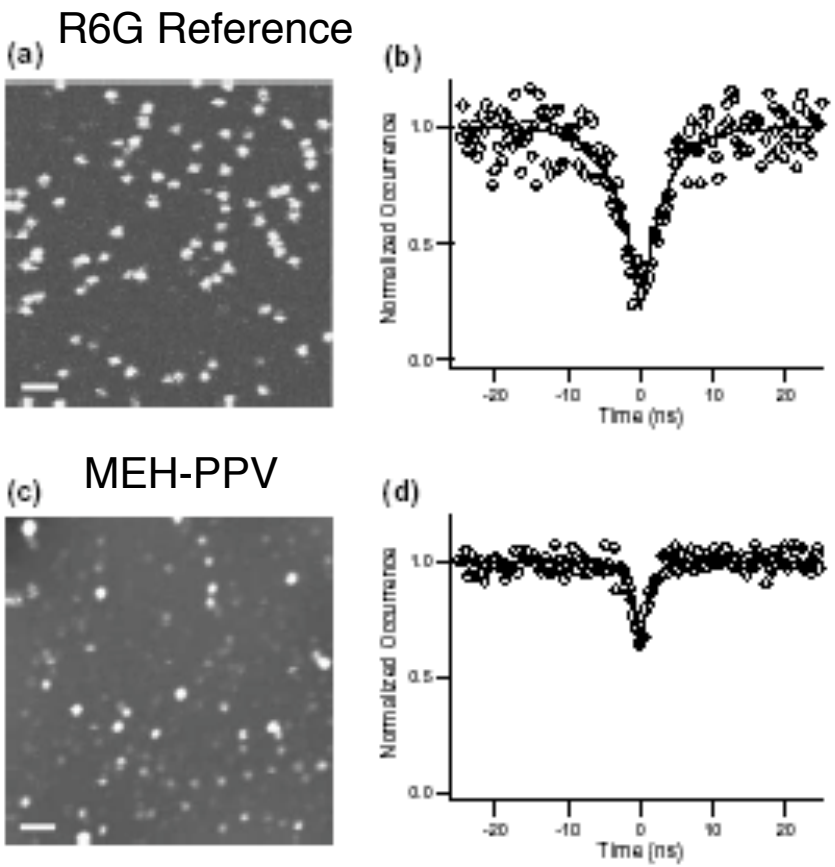
Single or multiple emissive sites ?

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





Photon correlation statistics from single polymer molecules in thin-films

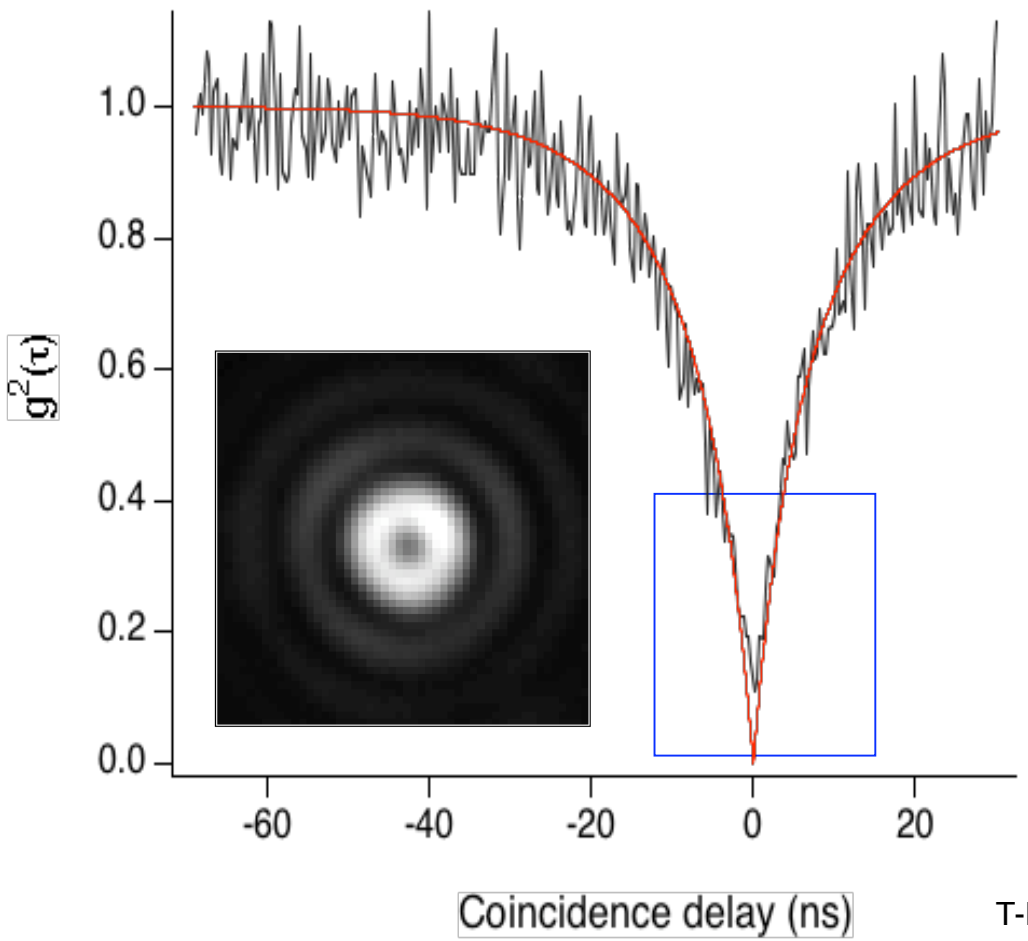


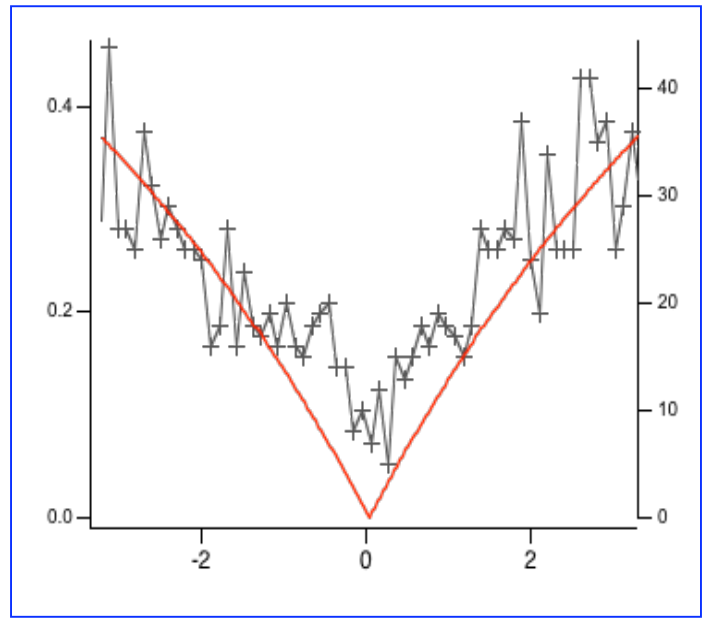
- Summed contribution from over ≈ 1000 molecules
- Relatively poor contrast (≈ 35%)
  - suggests $\langle N \rangle \approx 3$
- *Short-lifetimes*?
  - averaging over configurations?

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

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



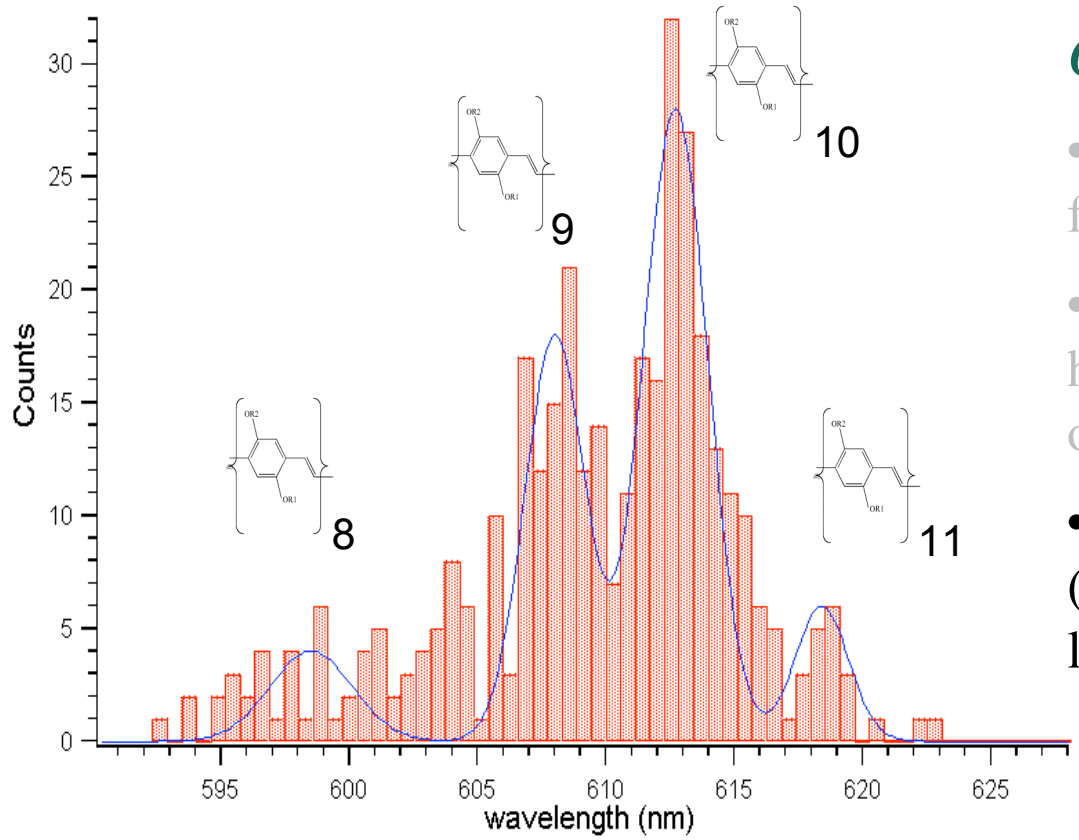


$g^2(0) = 0.08 \pm 0.02$

•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.*

Discrete center frequency distribution



Observations:

•Frequency is fixed, (but different for each particle).

•Frequency correlated not with rod height but with conjugated oligomer length.

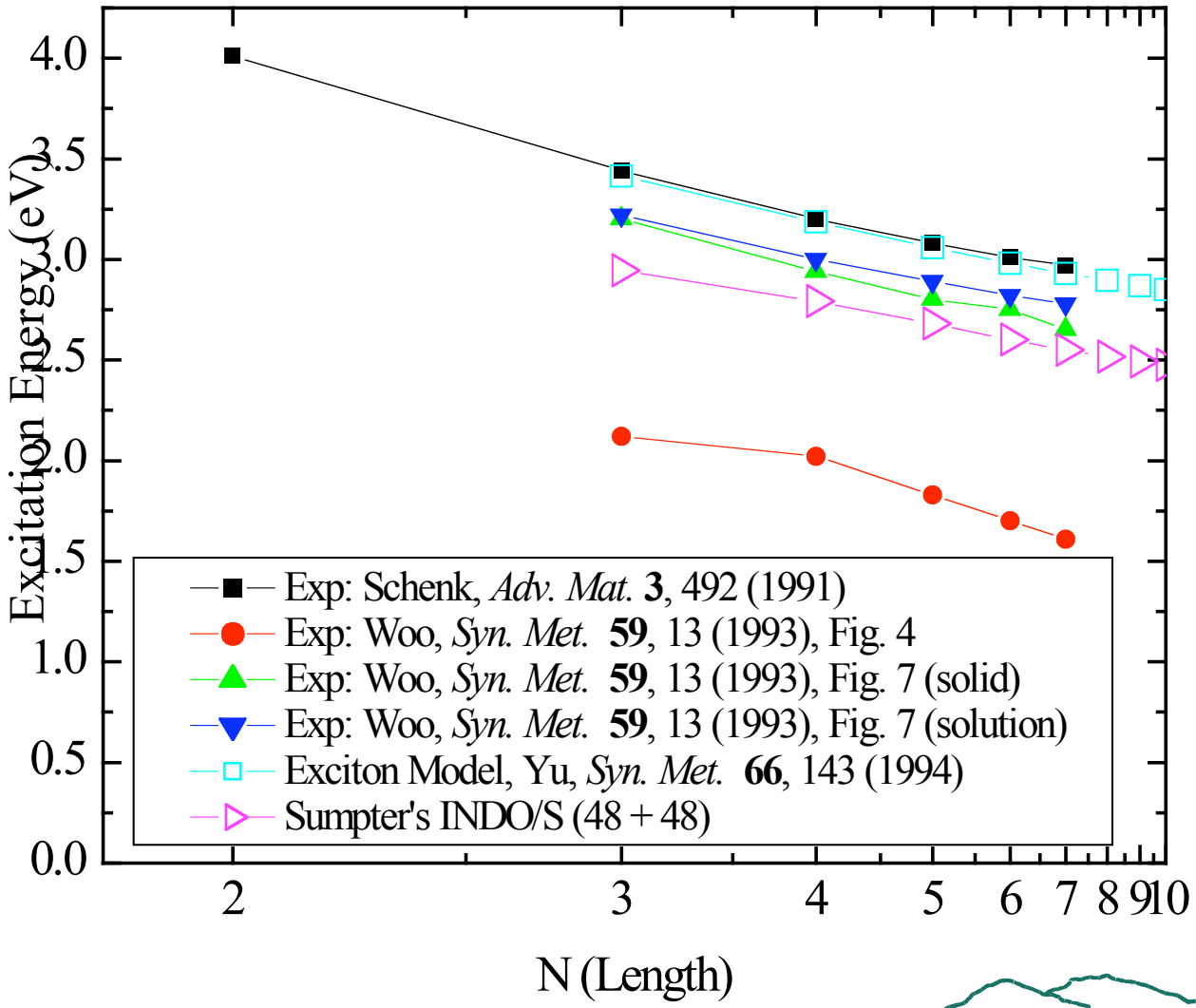
• Absolute frequencies red shifted (Possibly due to local LUMO lowering due to structural order).

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

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

Individual PV Oligimers: Lowest Singlet Excitation

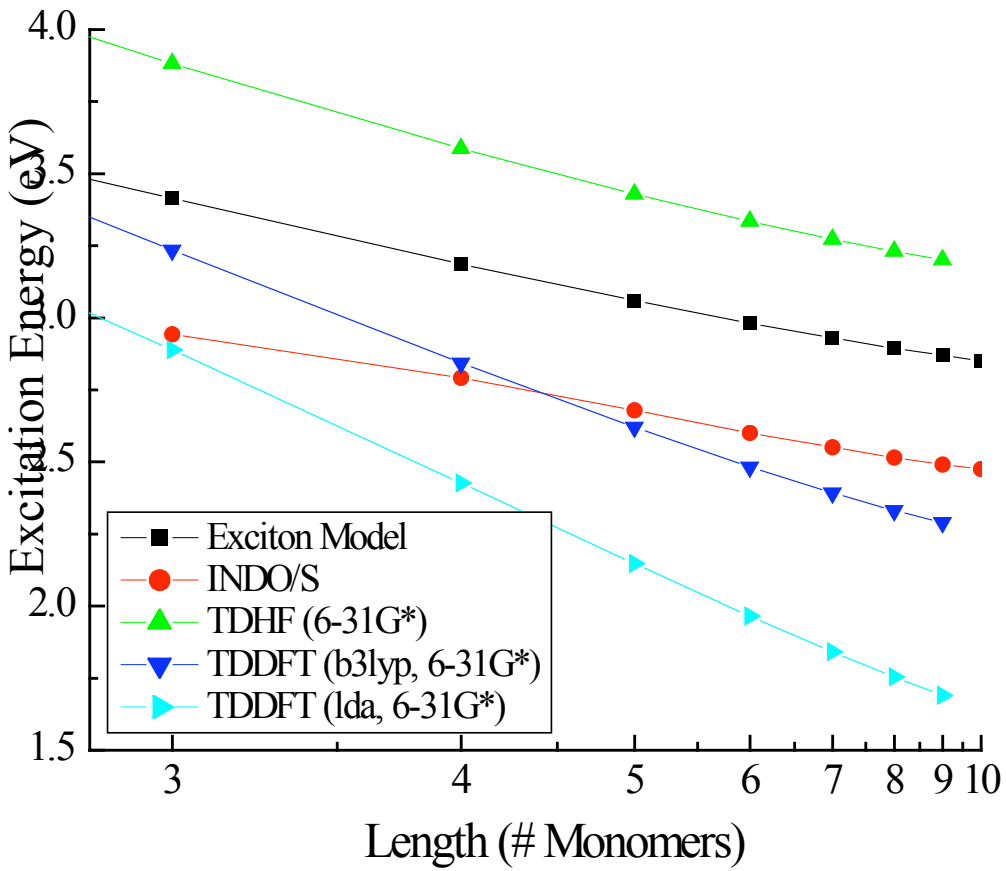
Compare experiment with model and semi-empirical predictions



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 π -conjugated systems**

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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