Polymer-based structures for meso- and nano-scale photonics

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Overview

- Questions and research issues in meso- and nanoscale photonics
  - what are the scientific and technological payoffs?!

- *Polymer-based meso and nanostructures for photonics*
  - Photonic “molecules” and “polymers”
  - Polymer quantum rods

- What does the future hold ….

The future of photonics….

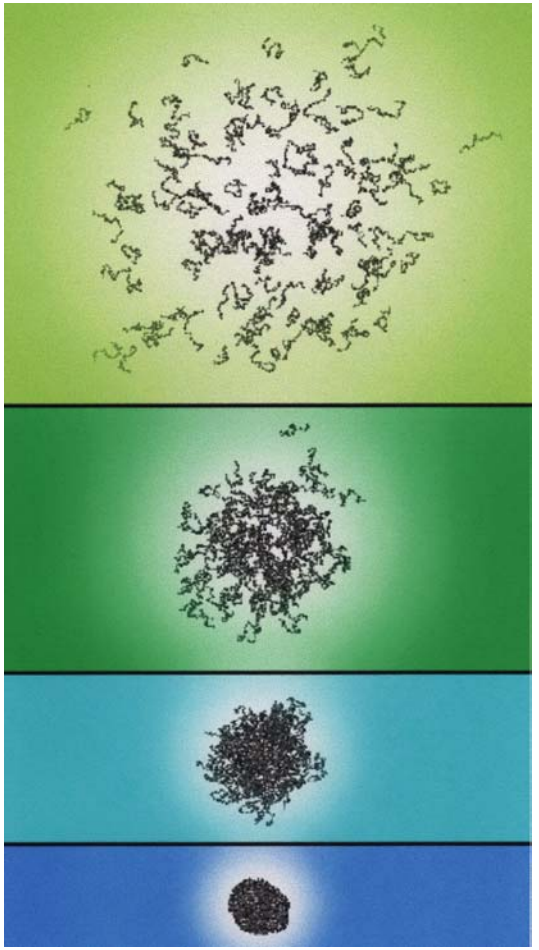
- ***Optical computing and information processing*** -
  - Spatial photon manipulation capability
    - (high density requirements imply subdiffraction-limit length scales)
  - Frequency selection/manipulation capability
    - (wavelength division multiplexing, add-drop filters, etc.)
  - Nonlinear / active "devices"
    - (transistors, gates, etc.)
  - "Circuit" integration

- ***Molecular scale optoelectronics*** -
  - optical (*wireless*) interface to molecular scale electronic circuits
  - tailored/multiplexed electro-optic response to a far-field optical input
  - electronic coupling??
    - *MATERIALS* ….

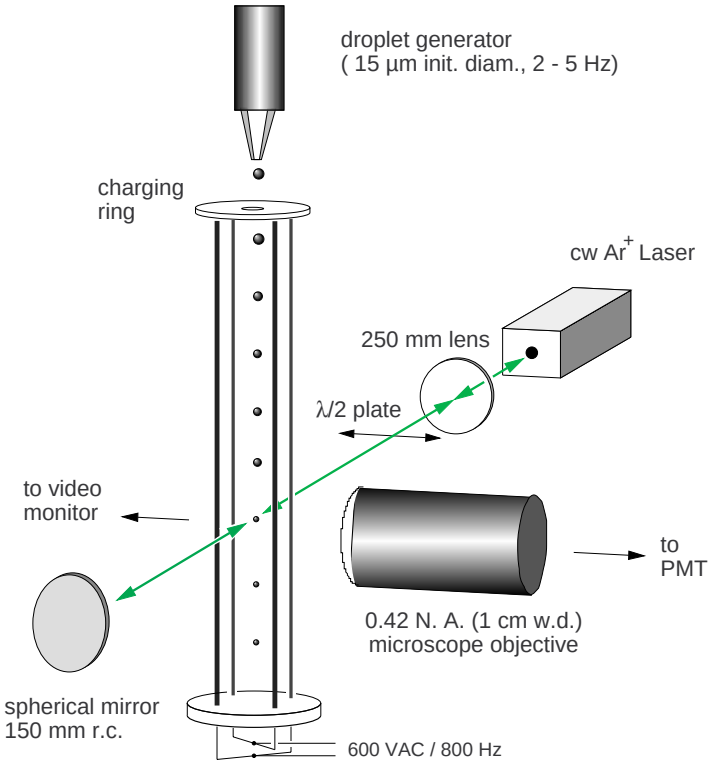
Polymer-composite micro and nanoparticles from solution - A new approach to nanoscale composites with tunable properties

- ***Nearly arbitrary size and composition***
  - Defined by droplet size and polymer concentration
- ***Tunable properties***
  - Suppression of phase-separation for small droplets
- ***Ultra-trace dopant capability***
  - Single-molecules, rare-earth ions, etc.

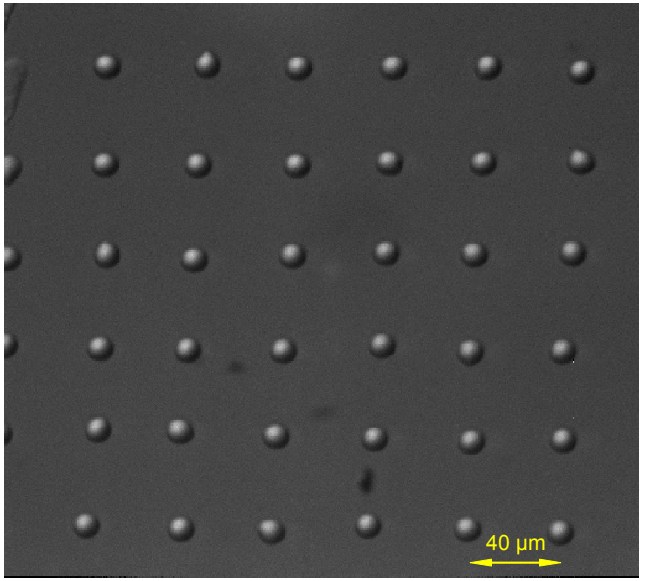
M. D. Barnes, et al. *Materials Today*, **2** (3), 25-28 (1999)



Electrodynamic particle focusing and manipulation



9.5 µm PEG (10 k MW) particles on silanated glass slides. Center-to-center spacing is 40 µm/ 40x phase-contrast objective with Nomarski DIC optics.



M. D. Barnes, et al. *Rev. Sci. Instrum* **71**, 2497 (2000)

Molecular Opto-electronics:

Marriage of photons and nanoscale electronics

Challenges :

- Materials? Design issues are daunting - need well-defined color (transition energies), position, orientation, as well as photon-modulated charge-transport properties
- Coupling with other nanoelectronic elements?
- Sub-diffraction limit spatial addressibility?

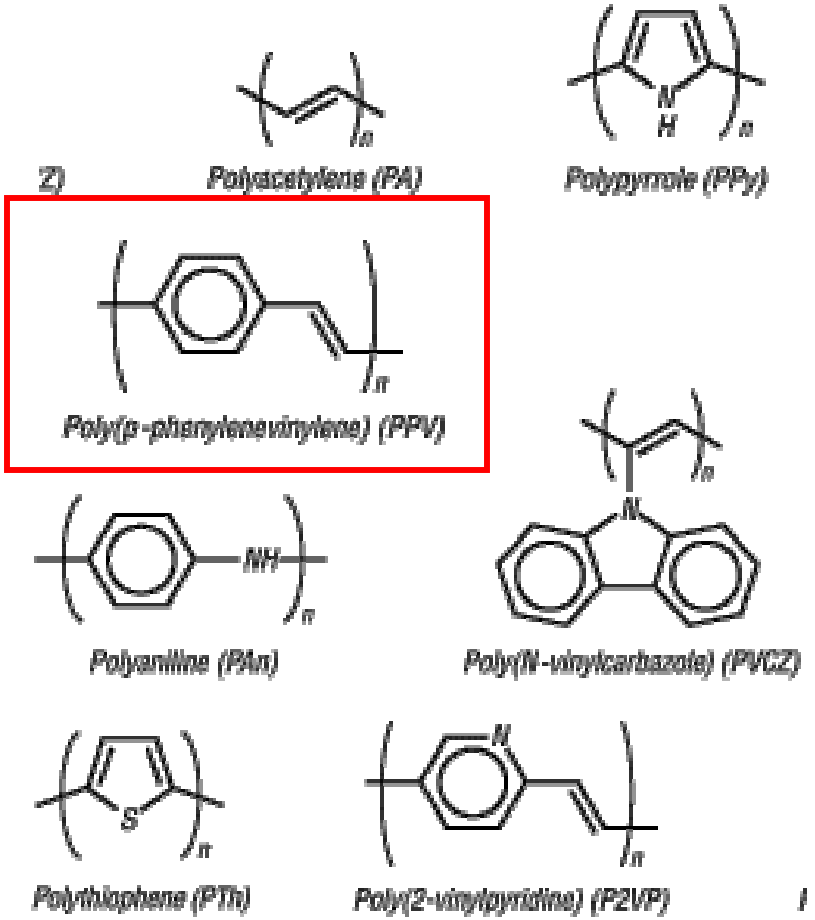
Benefits :

- Wireless interface strategy, large “optical toolbox”, multiplexing, etc.

Semiconducting Polymers: The ideal material for nanoscale optoelectronics?

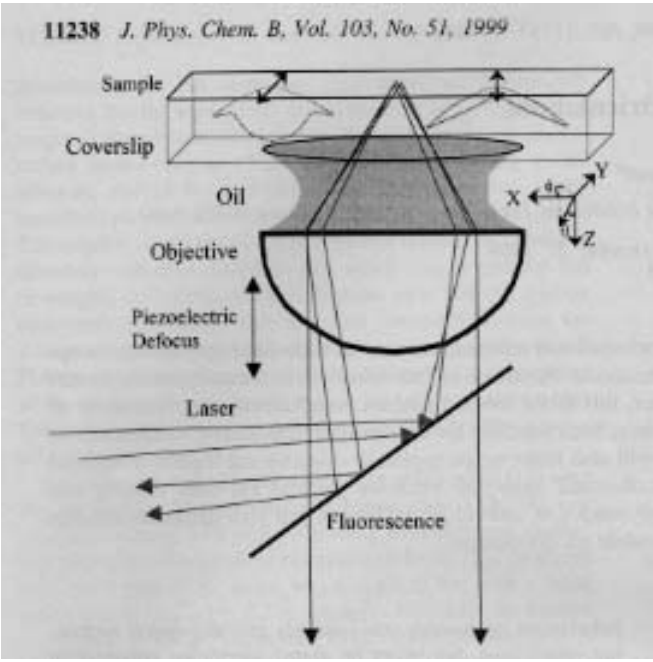
The good news:

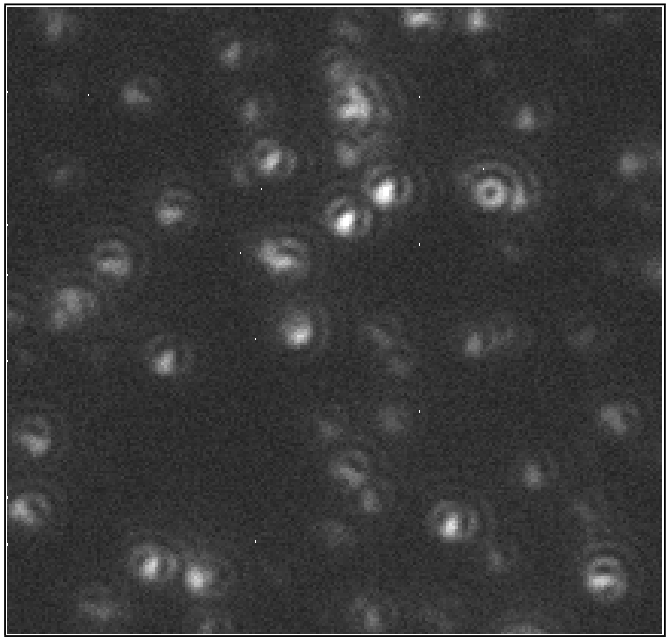
- enormous structural/electonic parameter space
- facile electron transport properties
- responsive to optical excitation
- size-scalabilty down to 10's of Å!



Emission Pattern Imaging: Probing Orientation and Chain-Organization of Semiconducting Polymer Nanoparticles

A. Bartko and R. M. Dickson J. Phys. Chem. B **103**, 11238 (1999)



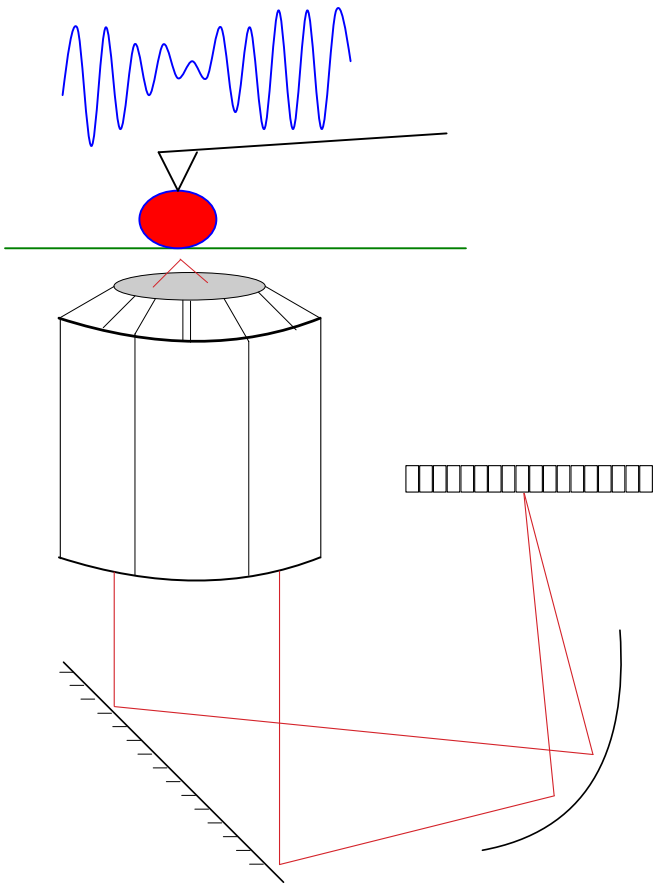


• Schematic of dipole emission pattern imaging apparatus: Laser light is brought in off-axis to produce TIR at sample plane. PZ-controlled objective produces emission patterns containing 3D orientation information

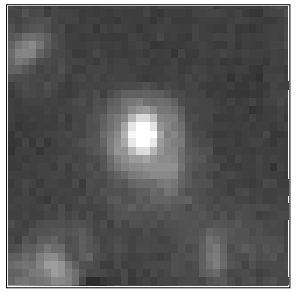
• Reference patterns from single DiI molecules in a polymer thin-film. Single dipoles oriented in the XY plane produce a characteristic “batwing” pattern, while much rarer Z-oriented molecules produce “donut” shaped pattern

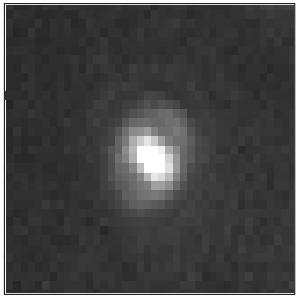
Combining Atomic Force Microscopy and Fluorescence Microscopy/Spectroscopy of Single Ions/Nanoparticles

- AFM surface imaging of particles above cover-slip
- High-NA optical imaging and spectroscopy using inverted geometry
- Register relative position of cantilever and laser spot with 2-µm pinhole or fluorescent nanoparticles



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





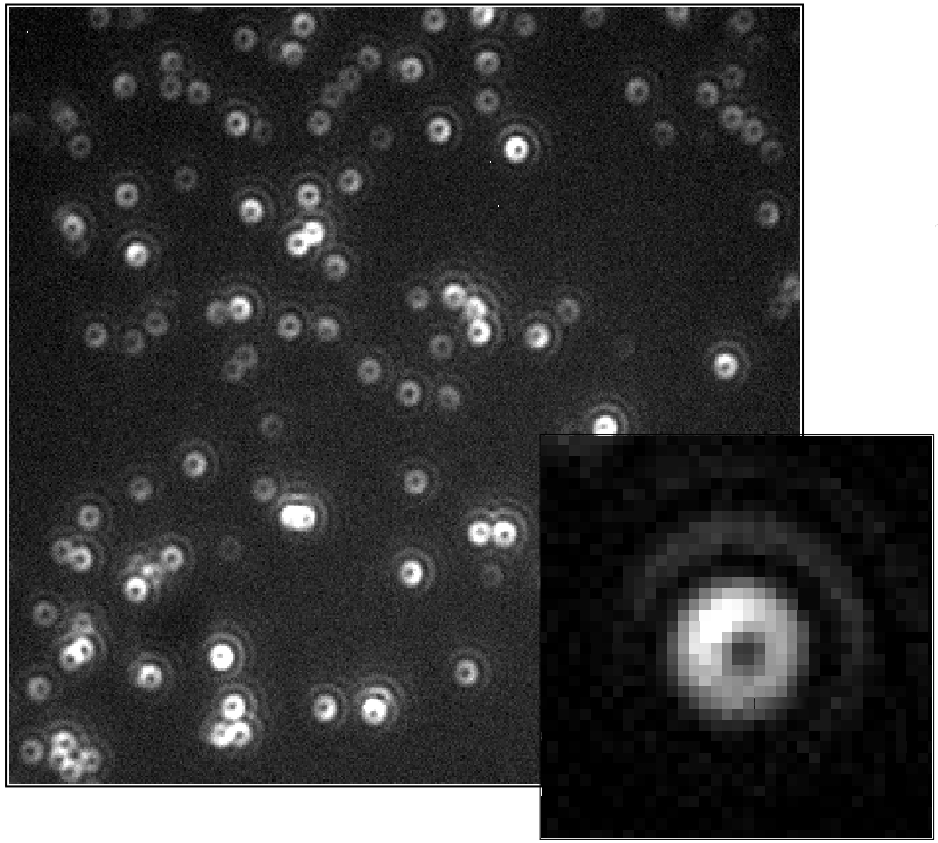
Random coil

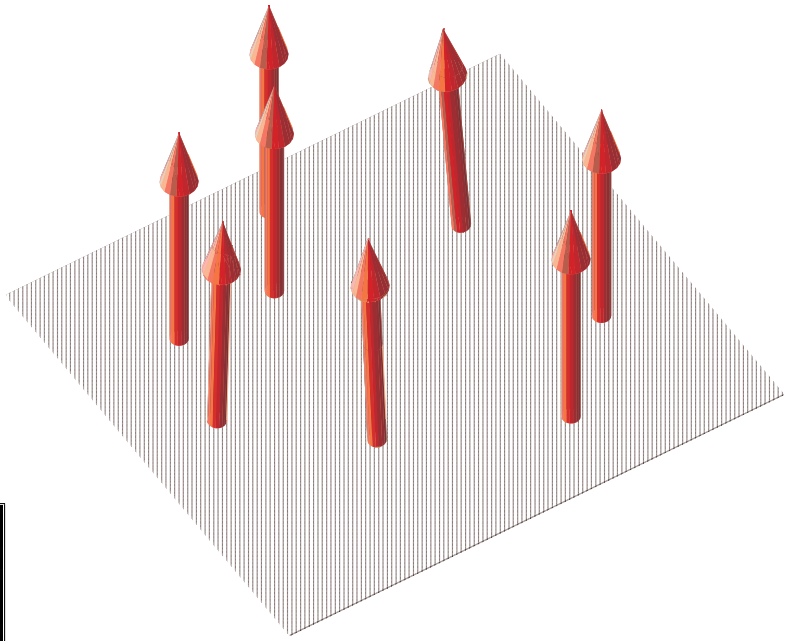
Defect-rod

Fluorescence of single MEH-PPV molecules under 400x magnification

The bad news: random, disordered chain structure; poor photostabilty and charge-transport properties, in-plane orientation in thin-films are "short-circuited" for photonics applications!

Polymer-based nanostructures for nanophotonics: Z-oriented nanoparticles of a semiconducting polymer via ink-jet printing





- Uniformly (to within < 10%) **Z**-oriented nanoparticles
- Particle structure? - single dipole pattern suggests high-degree of internal order

P. Kumar, A. Mehta, et al. "Oriented Semiconductor Polymer Nanorods" submitted to Science (pending Editorial decision)

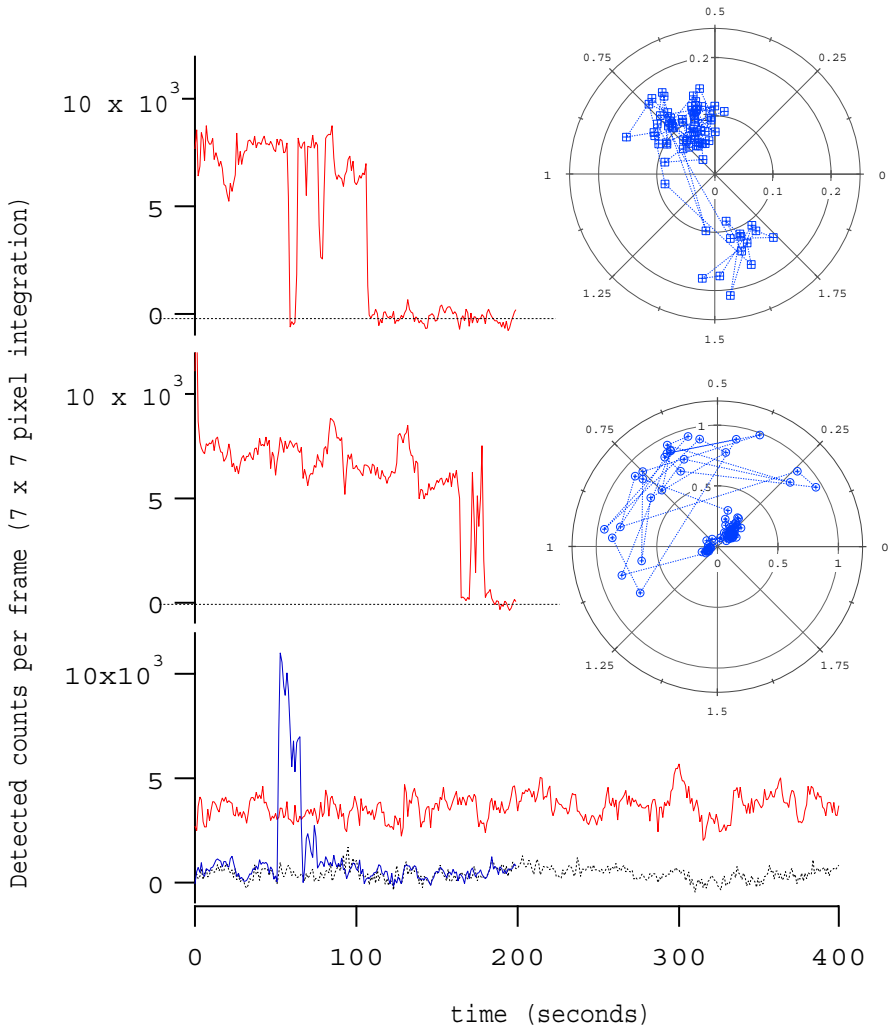
Luminescence dynamics of oriented MEH-PPV particles

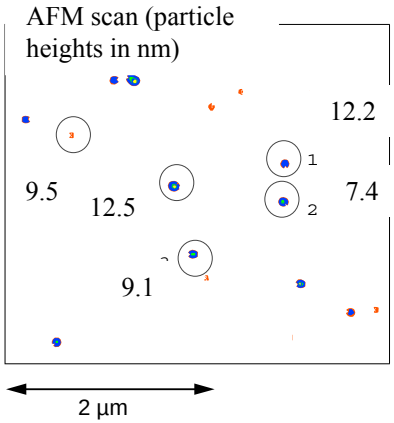
QuickTime™ and a
Animation decompressor
are needed to see this picture.

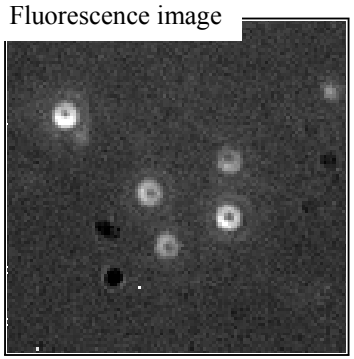
- Multiple intensity levels, on-off blinking
  - similar to observations with single (inorganic) q-dots/single molecules

- Note orientational instabilities (relative to lower pump power)!

Orientational and luminescence dynamics of MEH-PPV nanoparticles



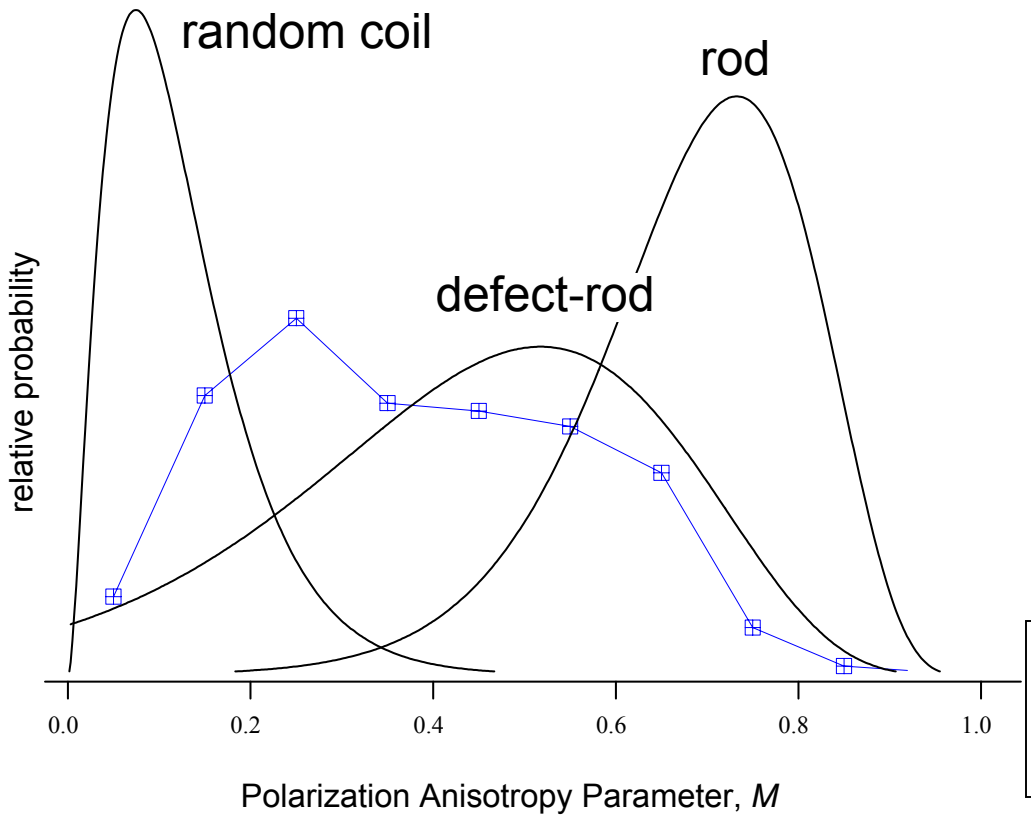


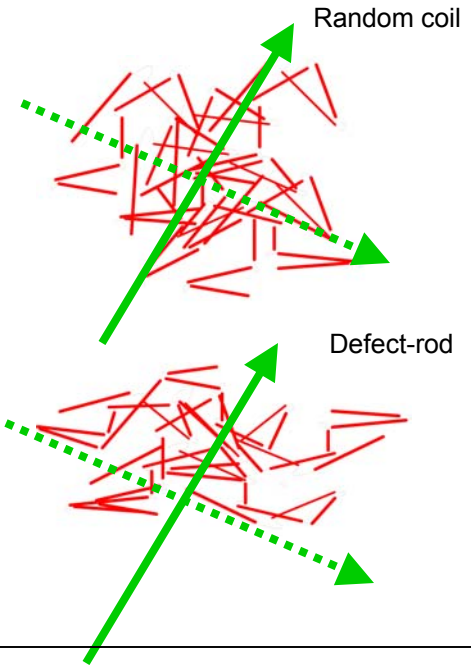


- Particle heights from AFM in good agreement with MEH-PPV persistence length (≈ 10 monomer units)

- Orientational instability related to pump intensity - oxidation of vinylene linkages cause a “wobbling” of the nanorod

Single-molecule polarization anisotropy measurements as a structural probe in thin-film geometries



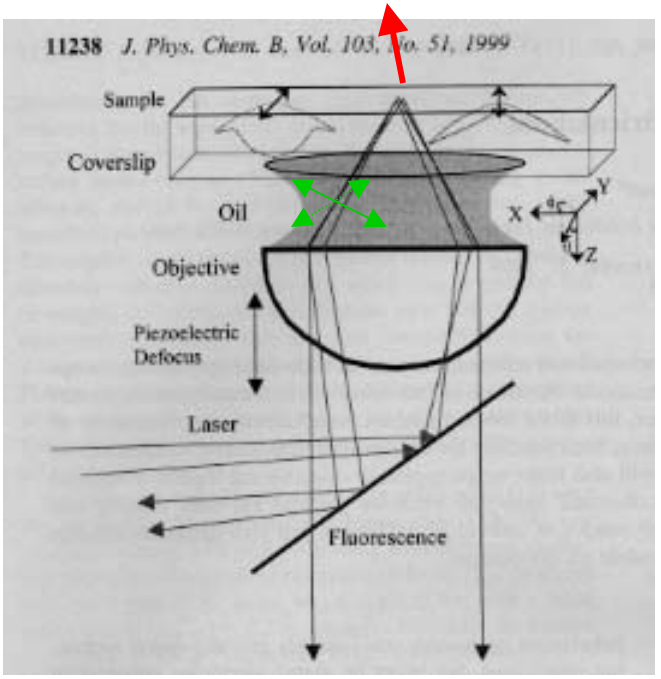


$$M = \frac{I_{parallel} - I_{perpendicular}}{I_{parallel} + I_{perpendicular}}$$

P. F. Barbara, et al. "Collapse of stiff conjugated polymers with chemical defects into ordered cylindrical conformations," *Nature* **405** 1030 (2000)

Thin film preparations result in broad Distribution of relatively poorly ordered chain structures !

Probing polarization anisotropy in z-oriented nanoparticles

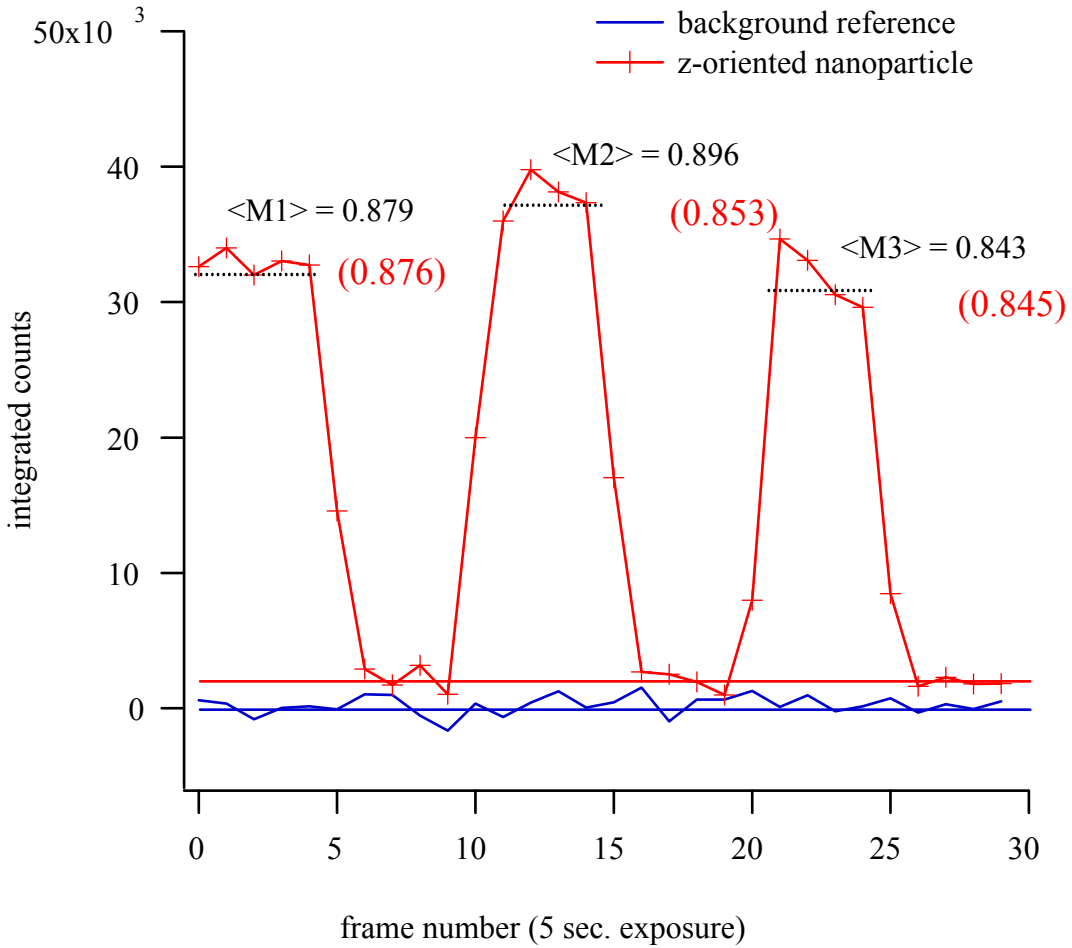


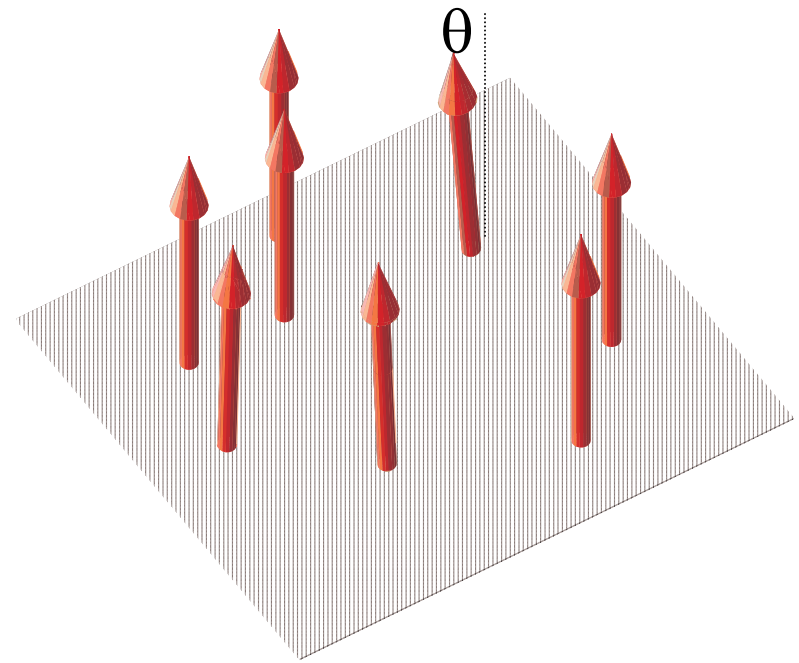
QuickTime™ and a
Animation decompressor
are needed to see this picture.

$$M = \frac{I_P - I_S}{I_P + I_S}$$

Modulate z-component in excitation field by rotating input polarization between *P* and *S*

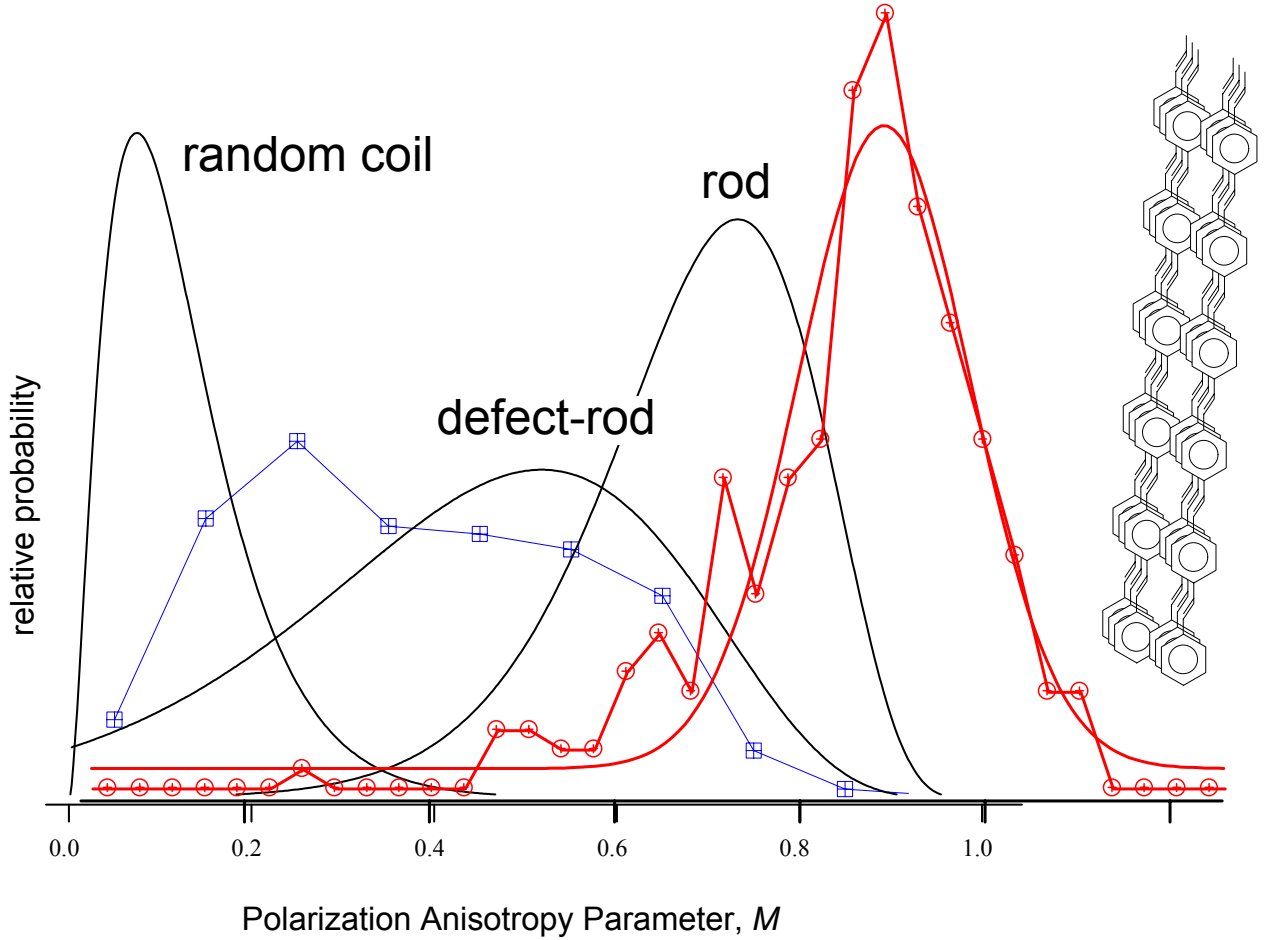
Probing structural order in z-oriented nanoparticles

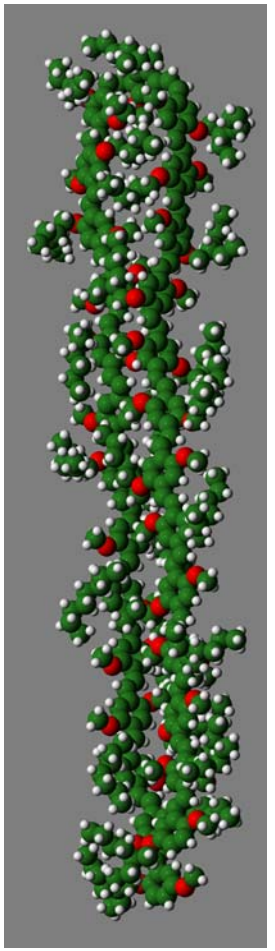




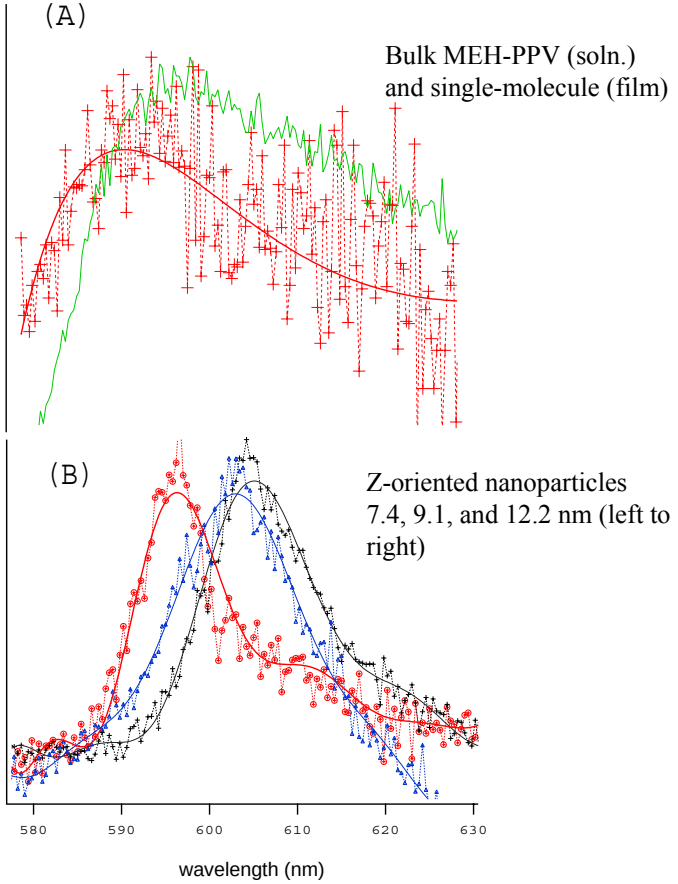
$$M_{\text{tilt}} = \frac{\cos\theta - \sin\theta}{\cos\theta + \sin\theta}$$

Polarization anisotropy evidence for a nanocrystalline phase of a semiconducting polymer





Observation of quantum-dot like spectroscopic properties of Z-oriented MEH-PPVnanoparticles



• Observation of quantum-dot like spectral signatures in z-oriented polymer nanoparticles

• Observe narrow (10-15 nm fwhm) emission spectra from individual nanoparticles

•Center frequency is stable (no spectral diffusion) for a given particle

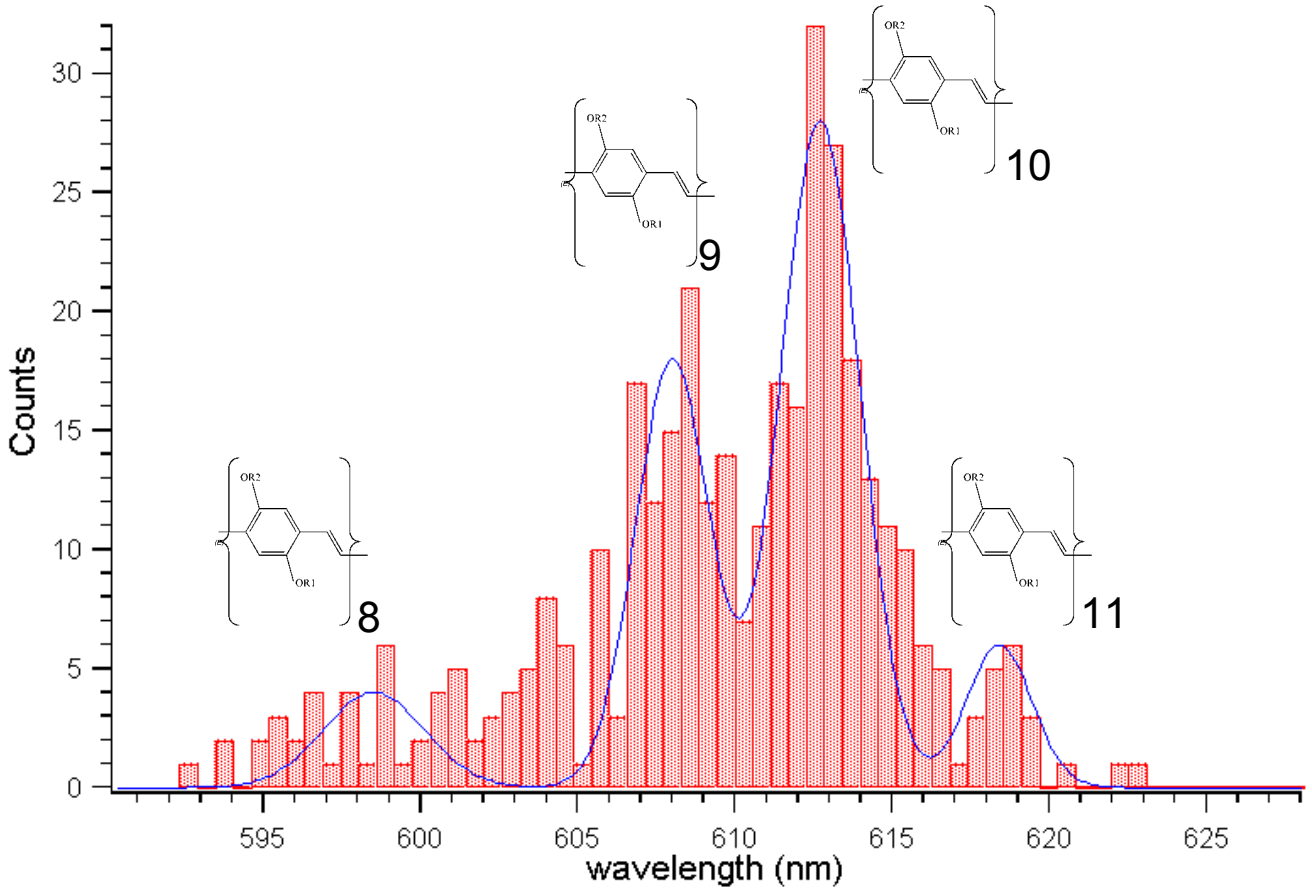
•Observe many different "colors" that are only weakly correlated with particle size

What's going on?

•Exciton delocalization - subvolume or whole particle?

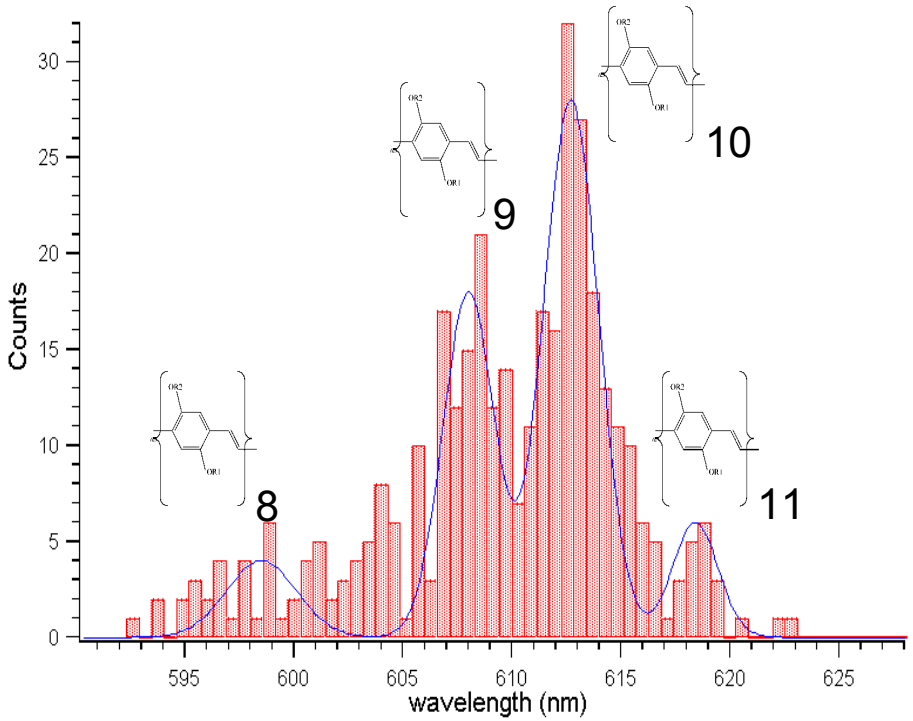
•LUMO structure - related to "crystallinity"

Distribution of PLE center frequencies - *correlation with integer conjugation lengths*



• Emission frequencies correlated with discrete confinement (box) lengths (R. Chang, et al. Chem. Phys. Lett **317**, 142 (2000)

Mechanism behind discrete center frequency probability distribution ? Emissive state is NOT necessarily lowest energy!



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

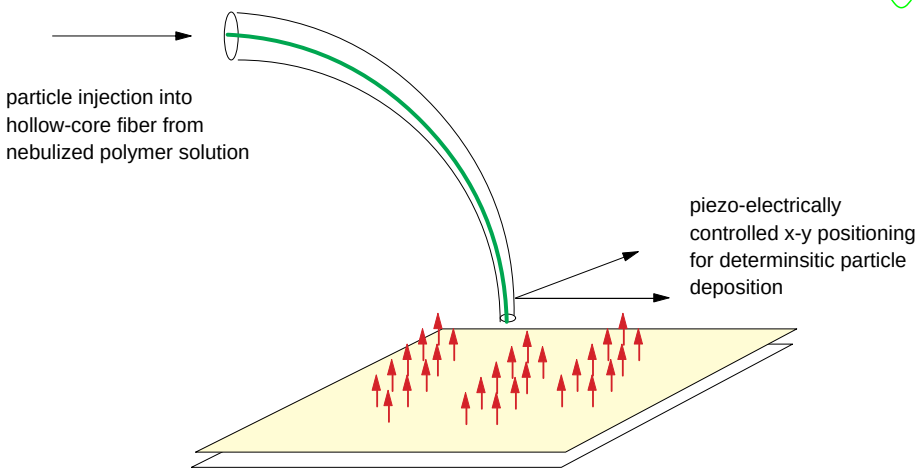
Observations:

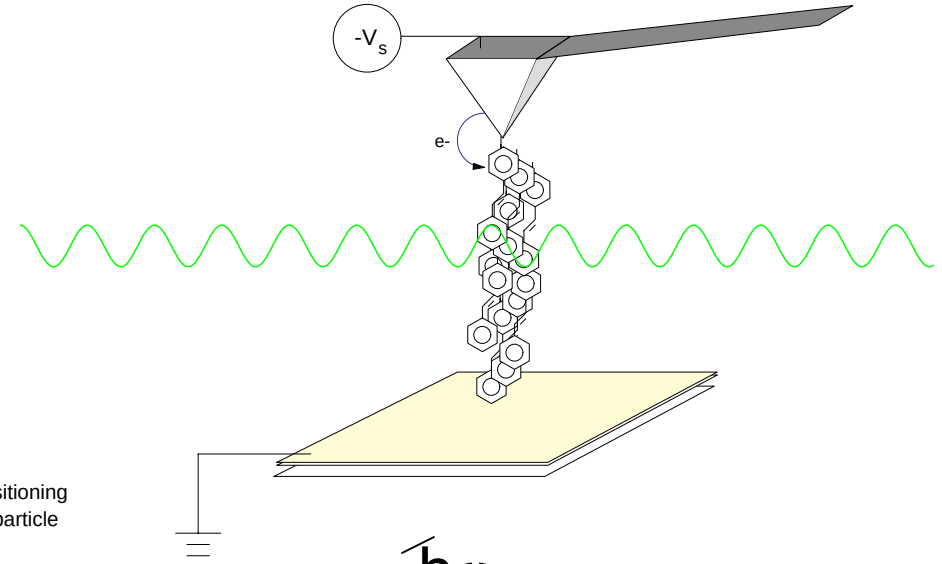
- Emission frequency is fixed, but different for each particle
- Emission frequency correlated not with 'box' size but with oligomer length
- Possibly due to local LUMO lowering due to structural order

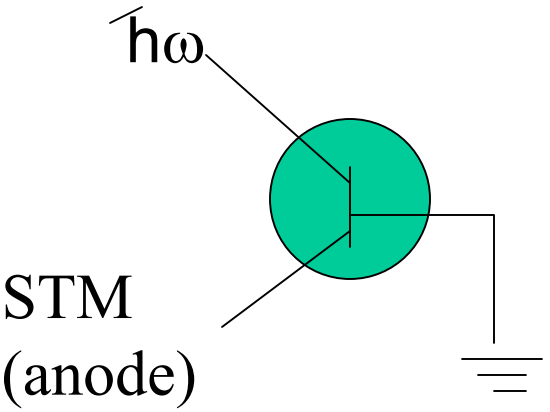
What's next?

- Controlled deposition of oriented polymer nanorods on conducting surfaces, microcavities

- Single-photon source?







- Probe optically modulated conductivity of z-oriented nanoparticles using STM (or modified AFM) probe

Electronic structure and quantum transport in polymers

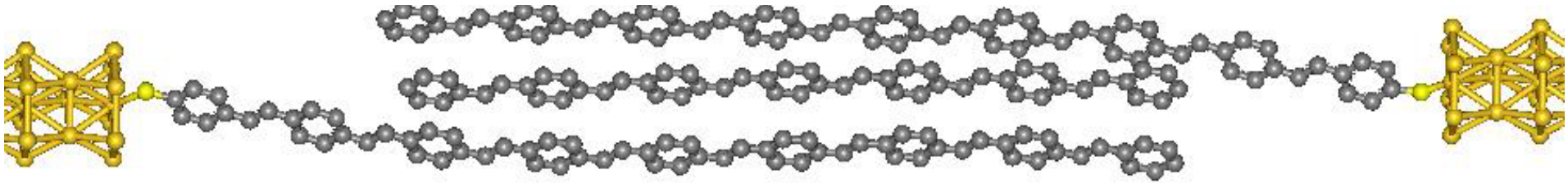
Molecular Structure

- Structure of the polymer nanorod?
  - Electric coupling between conjugated segments?
  - Solvation of chromophors?
- Role of electron correlation in photo emission?
- Effect of DC and AC fields on structure?
- Charge delocalization in polymer crystal?
- Methods:
  - DFT, Quantum Chemistry
  - Refine exchange-correlation functional via comparison with experiment.

Quantum Transport

Conductance for charge transport through polymer (w/ realistic leads).

- Field modulated electron transport
  - Static fields
  - AC fields, Photon-assisted transport.
- Mobility of charge carriers between conjugated segments?
- Methods:
  - Nonlinear transport theory.
  - Time-dependent transport in DC+AC fields.
  - Role of leads and contacts (structure, contact geometry).



Summary and Conclusions:

- Photonic polymers
  - Observed coupled resonances in fluorescence - characteristic mode splitting of a nearly degenerate system
  - Identified 3d classical trajectories corresponding to coupled resonances

- New technique for nanoscale processing of semiconducting polymers with a number of remarkable properties:
  - Photostability
  - Polarization
  - Structural
  - Spectroscopic

- *... and we've just scratched the surface!*

PEOPLE:

- Adosh Mehta (SPM and optical spectroscopy)
- Pradeep Kumar (Nanoparticle *Maestro*)
- Shannon Mahurin (3-d photonic structures)
- Bobby Sumpter/Don Noid (structural simulation)
- Brian Hathorn (3D ray optics)

- Keith Runge (Univ. of Florida, Dept. of Physics - 3D SOS)

- Rob Dickson (Ga. Tech, Dept. of Chemistry)
    - Andy Bartko, Jie Zheng, and Lynn Peyser

$$$ Office of Science and ORNL LDRD