



# **Picosecond Time-Resolved Studies of Exciton Transport in Conjugated Polymer Nanoparticles**

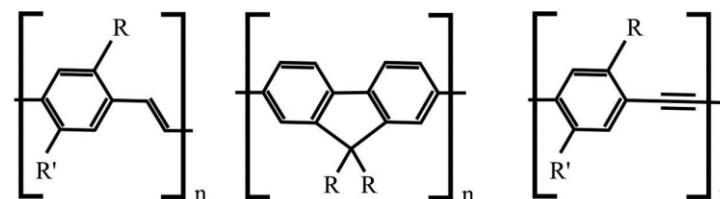
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# Outline

- Background
  - Conjugated Polymers & Nanoparticles
  - Why Study CPNs?
  - Excited States in CPs and CPNs
- Dye-Doped PFBT CPNs
  - Red-shifted Emission
  - Complex Fluorescence Lifetime Kinetics
  - Modeling to Determine Intrinsic  $L_D$
- Solvent-Induced Swelling of CPNs
  - Fluorescence Quantum Yield/Spectral Shifting
  - Picosecond Decay Kinetics
  - Fluorescence Anisotropy Decay
  - Lattice Model
  - Quantum Yield/Mobility Tradeoff
- Summary
- Acknowledgements

# Conjugated Polymers – Basic Photophysics

- Plastic, amorphous organic semiconductors
  - Useful for low cost, flexible photovoltaics, LEDs and solar cells
- Repurposing CPs to make nanoparticles
  - Have many useful optical properties



*Flexible Amorphous OLED Screen Prototype*

Dennler, G., Sariciftci, N.S., *Proc. IEEE* **2005**, 93 (8), 1429.

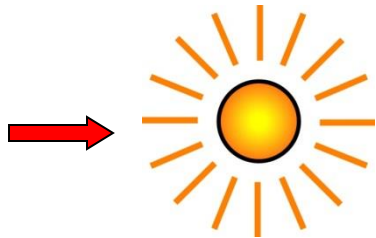
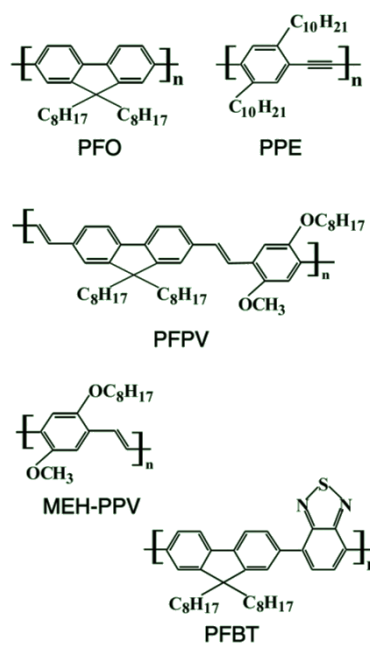
Yim, K., Kim, J. S. et al., *Adv. Func. Mater.* **2008**, 18, 1012.

Scholes, G., Rumbles, G., *Nature Mater.* **2006**, 5, 683.

[http://s1.ibtimes.com/sites/www.ibtimes.com/files/styles/v2\\_article\\_large/public/2014/01/15/samsungflexibleamoledphone.jpg](http://s1.ibtimes.com/sites/www.ibtimes.com/files/styles/v2_article_large/public/2014/01/15/samsungflexibleamoledphone.jpg)

# Conjugated Polymer Nanoparticles (CPNs)

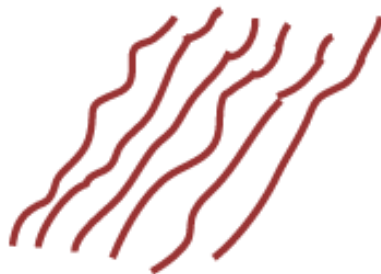
- Optical Properties
  - Extended  $\pi$ -conjugated chains
    - Structure, Heteroatoms: HOMO/LUMO gap in UV/Vis
    - Wide range of colors
  - High chromophore number density
    - Increased by nanoparticle formation
  - Highly fluorescent
  - Efficient Förster energy transfer hosts/dopants
    - Red-shifting, sensors
    - Wavelength tunability



## CP Properties and Structure



**conjugated  
polymer in  
solution**



**conjugated  
polymer film**

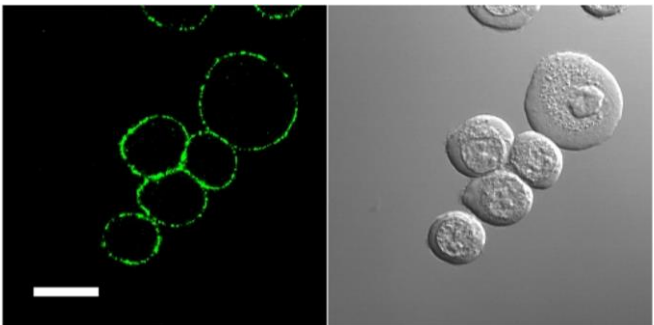


**conjugated  
polymer  
nanoparticle**

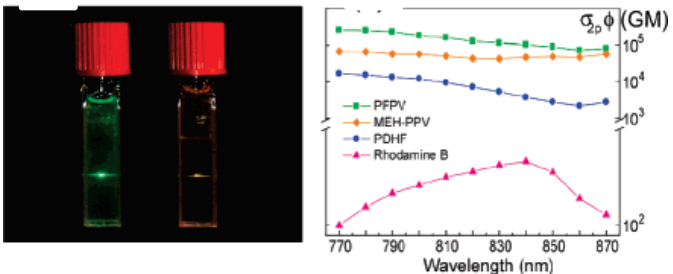
- Properties of conjugated polymers depend critically on nanoscale structure, heterogeneity, inter/intrachain interactions and other nm scale processes
  - Energy transfer and charge transfer
- CPNs comprised of one or more collapsed chains
  - Nanoscale, disordered, multichromophoric system
  - Studies of single CPNs provide unique perspective on nanoscale phenomena

# Milestones in CPN Research

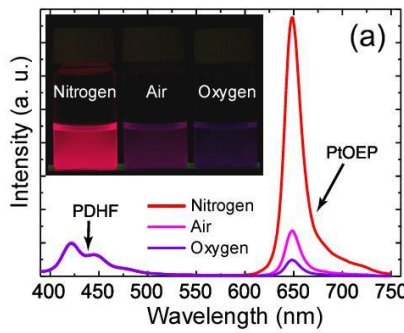
- Brightest (5-20 nm) nanoparticle probes reported to date
- 1000x brighter two-photon fluorescence compared to conventional dyes
- Effective fluorescent probes for imaging of cancer cells
- Novel oxygen sensing NPs



Confocal Imaging of Human Breast Cancer Cells



Two-Photon Brightness Comparisons



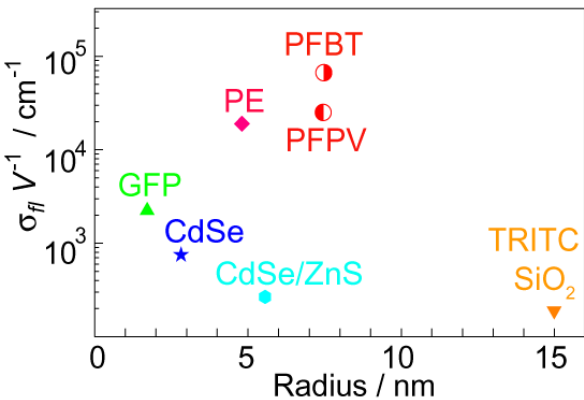
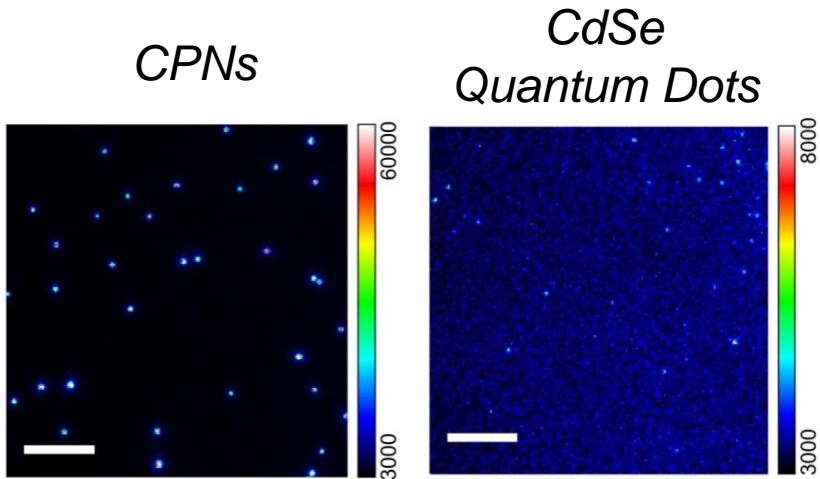
Oxygen Sensing CPNs

Wu, C. F., Szymanski, C., Cain, Z., and McNeill, J. D. *J. Am. Chem. Soc.* **2007**, 129, 12904-12905.  
Wu, C. F., Bull, B., Christensen, K., and McNeill, J. D. *Angew. Chem. Int. Ed.* **2009**, 48, 2741-2745.  
Wu, C. F., McNeill, J. D., Chiu, D. T., et. al. *J. Am. Chem. Soc.* **2010**, 132, 15410-15417.



# Why Study CPNs? – Imaging

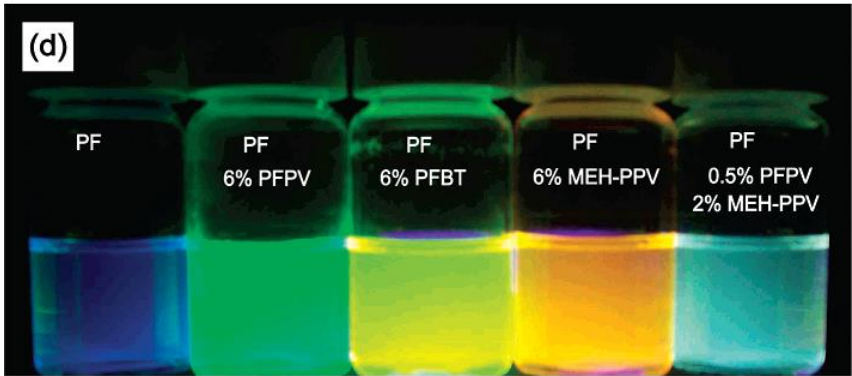
- Brighter fluorescent probes still needed for imaging applications
  - CPNs are the brightest small fluorescent probes reported to date
    - 30x higher emission intensity compared to Quantum Dots
    - High quantum yield, fluorescence cross sections
  - Improvements in quantum yield and photostability are still needed



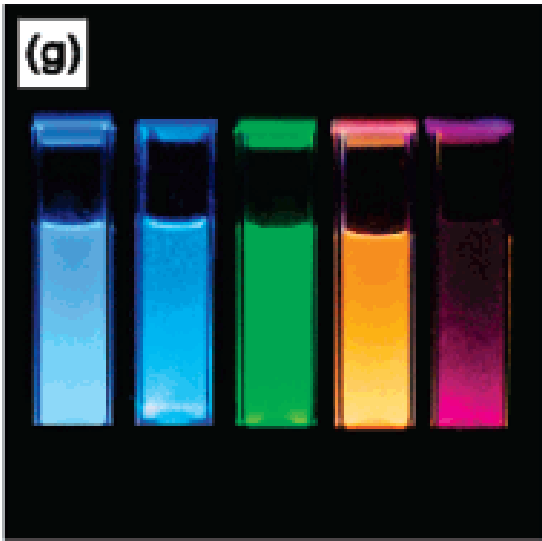
Brightness/Volume Ratios of Various Probes

# Why Study CPNs? – Imaging

- Red-shifting needed for imaging applications
  - overcome background cell autofluorescence
  - Improve brightness, photostability
  - Have previously accomplished this via doping CPNs with other CPs or dyes



*Red-shifting of fluorescence via polymer blending*



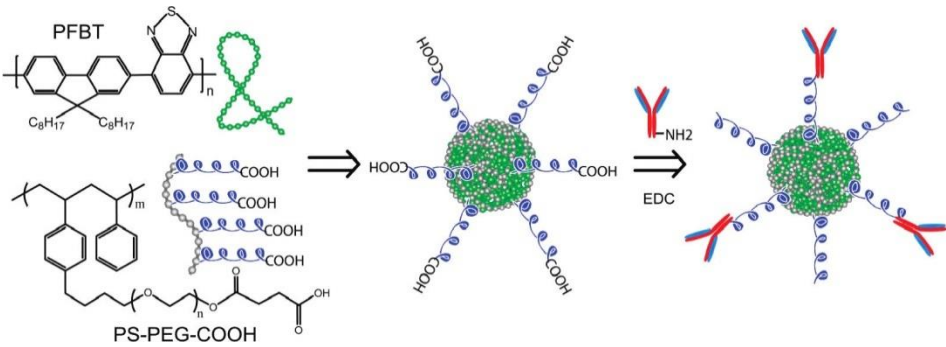
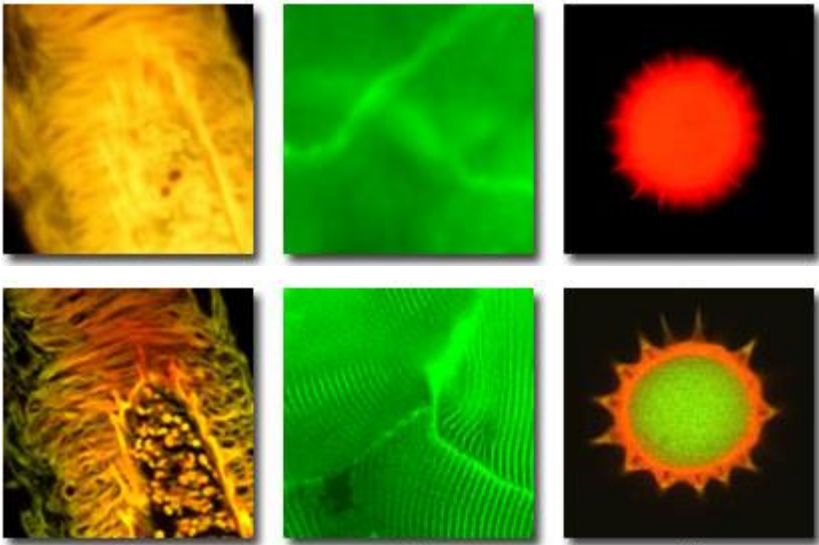
*Red-shifting of fluorescence via dye doping*

*Brighter, more photostable particles via doping*

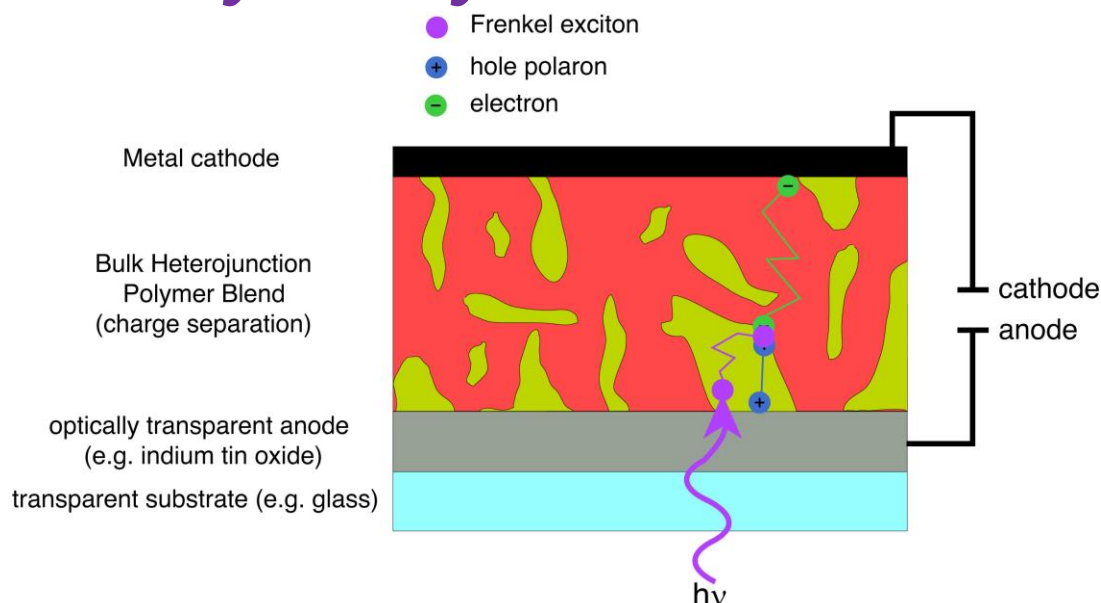


# Why Study CPNs? – Imaging

- CPNs are non-toxic to cells
  - No heavy metals
  - Allows for imaging in live cells
- Easily functionalized
  - Can functionalize or bioconjugate CPNs for use in cellular media
- Challenges:
  - Cell media are complex
    - Background autofluorescence
    - Requires bright, red-shifted particles



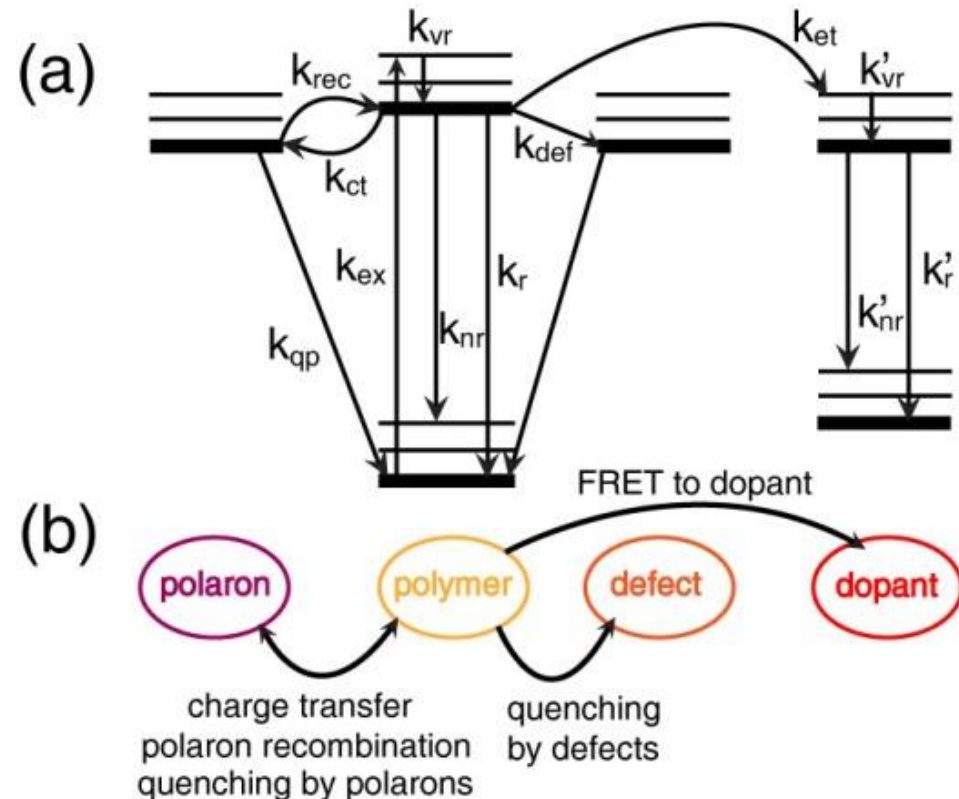
## Why Study CPNs? - Devices



- Optimize organic semiconductor devices such as LEDs, solar cells
- Conjugated polymer devices made by thin film casting
  - Bulk heterojunction film sandwiched between cathode/anode materials
  - Photoexcitation of film generates Frenkel excitons
  - Exciton transport to nano- microscale polymer interfaces
  - Charge transfer to generate electron and hole pair
  - Charges travel to cathode/anode materials

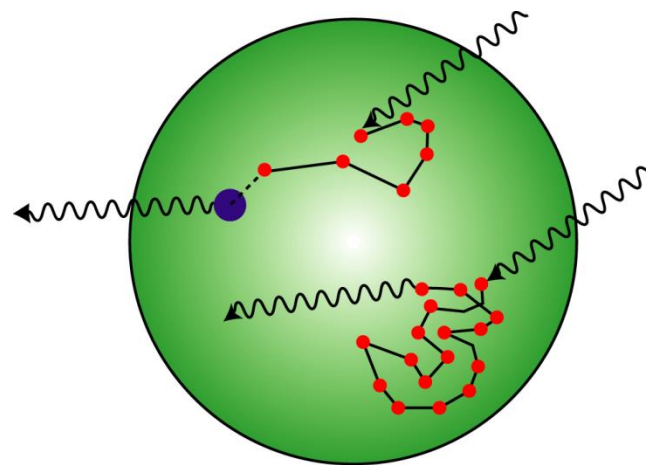
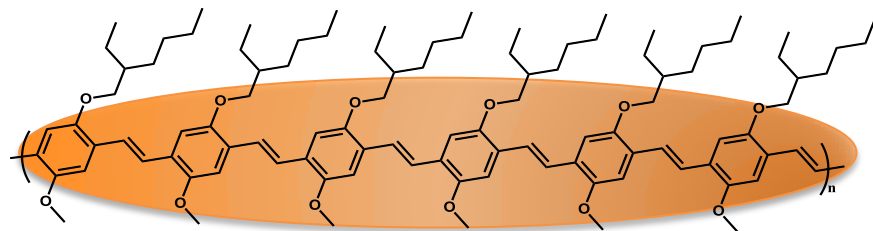
## Why Study CPNs? – Photophysics

- Many radiative and non-radiative processes occur in CPNs
  - Conventional radiative/non-radiative decay
  - Polaron generation/quenching by polarons
  - Quenching by defects
  - Energy transfer to dopants
- Interested in determining the rates of energy transfer in CPNs



# Excited States in Conjugated Polymers & CPNs: Frenkel Excitons

- Chromophore
  - Result of delocalized  $p_z$  orbitals
  - Individual chromophores are ~2-8 monomer units in length
- Molecular/Frenkel Exciton
  - Delocalized Excitation
  - Interacting transition dipoles between adjacent chromophores (perturbation theory)



# Excited States in Conjugated Polymers & CPNs: Exciton Dimer Model

- Simplest Case: Dimer
  - Zero-order: two isolated chromophores
  - Energies correspond to excitation at respective sites
  - Introduce perturbation  $\hat{V}$ 
    - Linear Combinations of Zero-Order States
    - Perturbed/Mixed states and energy  $\propto V_{dd}$  and  $\Delta E^{(0)}$
  - Different States/energy for non-degenerate and degenerate cases

$$\hat{H} = \hat{H}^{(0)} + \hat{V}$$

*Hamiltonian*

$$H^{(0)}|a\rangle = E_a^{(0)}|a\rangle$$

$$H^{(0)}|b\rangle = E_b^{(0)}|b\rangle$$

*Zero-order states/energy*

$$\hat{V} = V_{dd}\{|a\rangle\langle b| + |b\rangle\langle a|\}$$

*Perturbation*

$$|\pm\rangle = c_a|a\rangle \pm c_b|b\rangle$$

*Perturbed/Mixed States*

# Excited States in Conjugated Polymers & CPNs: Exciton Dimer Model

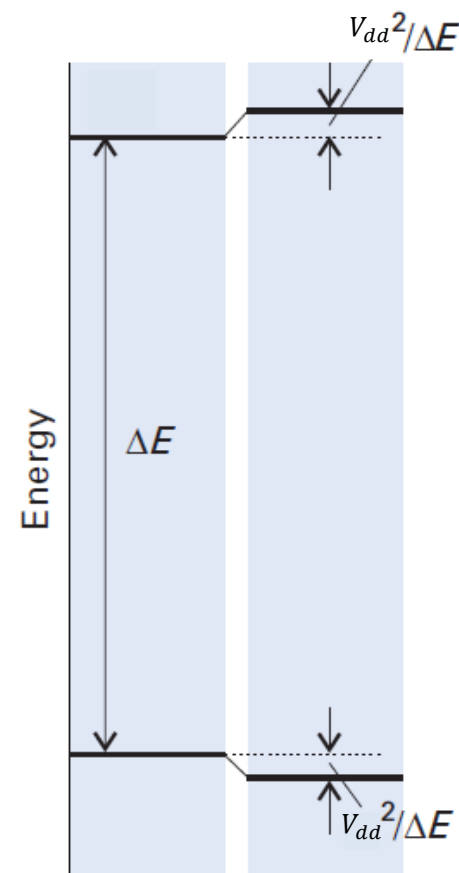
- Non-degenerate chromophores
  - Weakly mixed states
  - Small energy shift
  - Incoherent energy transport (FRET)
- Degenerate Chromophores
  - Evenly mixed states
  - Large energy shift
  - Coherent energy transport

$$|+\rangle = |a\rangle + \frac{|V_{dd}|}{\Delta E^{(0)}} |b\rangle$$

$$|-\rangle = |b\rangle - \frac{|V_{dd}|}{\Delta E^{(0)}} |a\rangle$$

$$E_+ = E_a^{(0)} + \frac{V_{dd}^2}{\Delta E^{(0)}}$$

$$E_- = E_b^{(0)} - \frac{V_{dd}^2}{\Delta E^{(0)}}$$





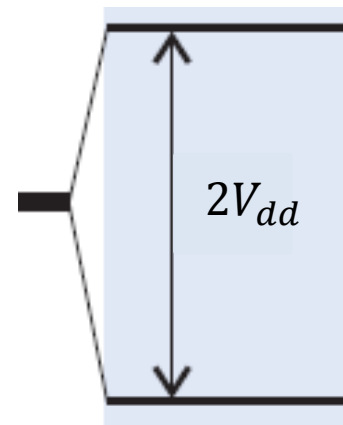
## *Excited States in Conjugated Polymers & CPNs: Exciton Dimer Model*

- Non-degenerate chromophores
  - Weakly mixed states
  - Small energy shift
  - Describes incoherent energy transport (FRET)
- Degenerate Chromophores
  - Evenly mixed states
  - Large energy shift
  - Describes coherent energy transport

$$\begin{aligned}|+\rangle &= \frac{1}{\sqrt{2}} [|a\rangle + |b\rangle] \\ |-\rangle &= \frac{1}{\sqrt{2}} [|a\rangle - |b\rangle]\end{aligned}$$

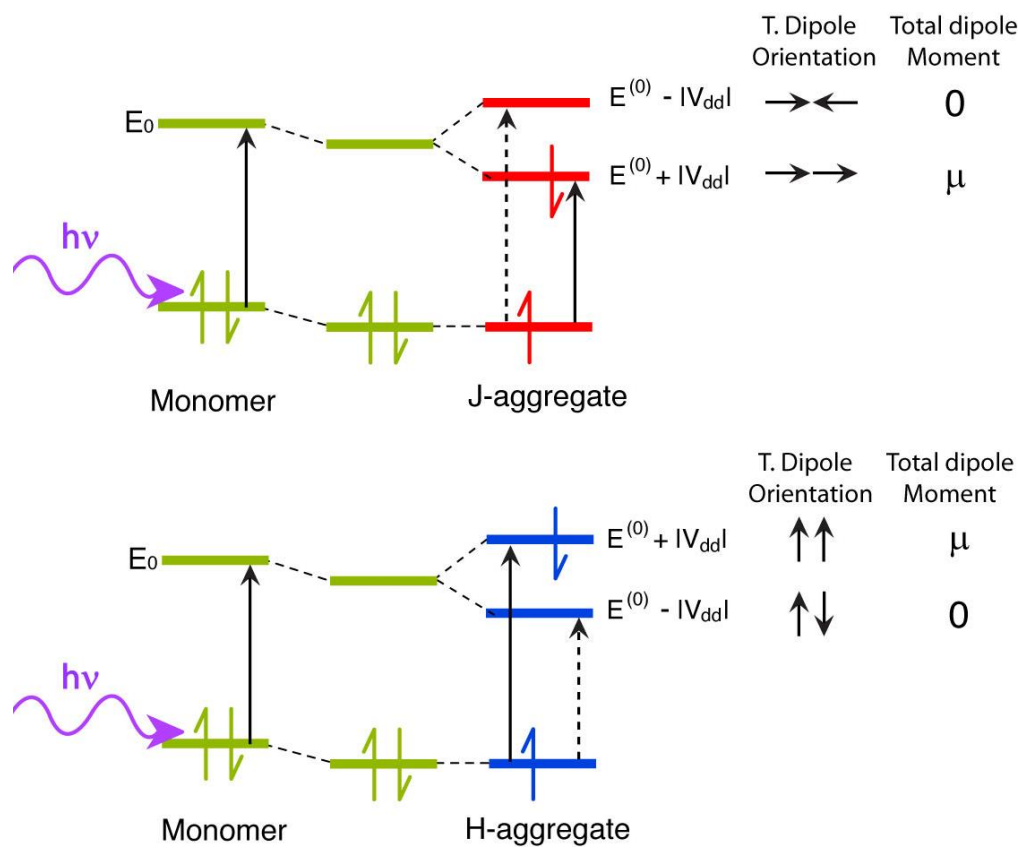
$$E_+ = E^{(0)} + |V_{dd}|$$

$$E_- = E^{(0)} - |V_{dd}|$$

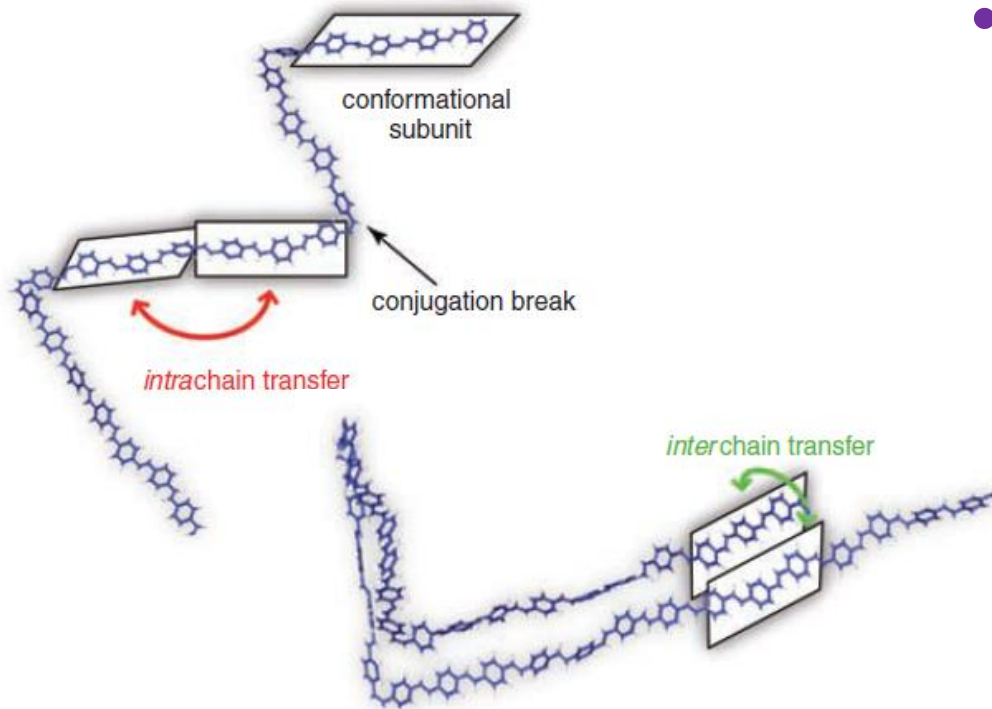


# Excited States in Conjugated Polymers & CPNs: Light and Dark Exciton States

- Transition dipole coupling splits energy levels of chromophores
  - T. dipole orientation dictates which state contributes to emission signal
  - Related to molecular orientation
  - Nonzero transition dipole vector sum → emissive state
- Basis of H- and J-aggregate spectral characteristics



# Excited States in Conjugated Polymers & CPNs: Exciton Transport

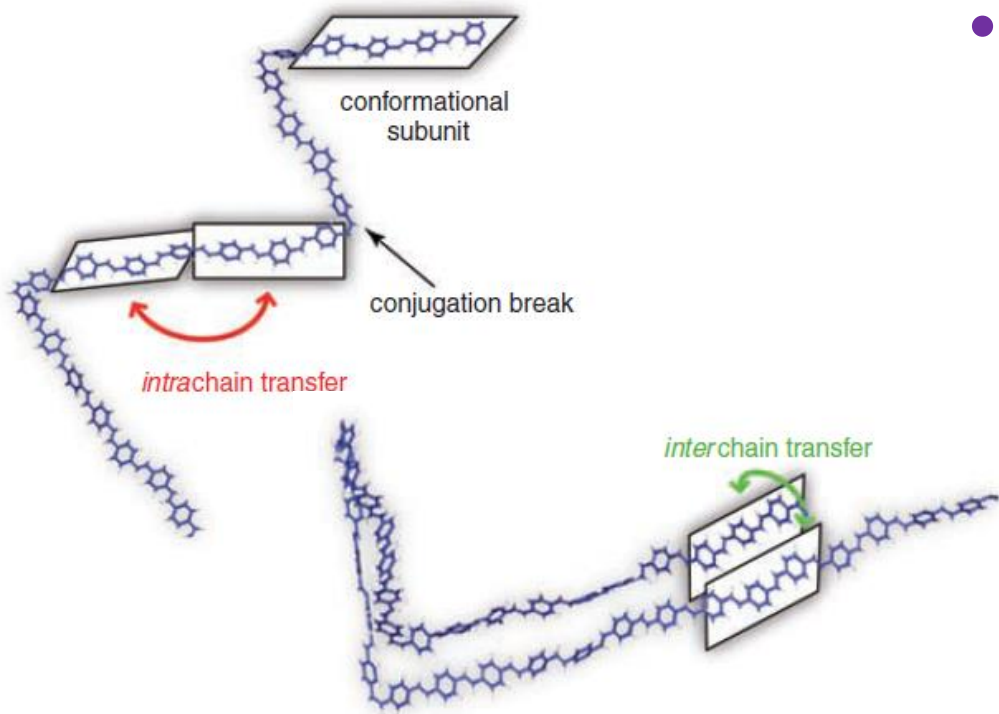


$$|A(t)|^2 = \sin^2 \left( \frac{V_{dd}}{\hbar} t \right)$$

*Coherent Energy Transfer Probability*

- Two types of energy transport
  - Coherent transport
    - Degenerate Chromophores
    - No/low disorder
    - Strong coupling
    - Low T
  - Oscillating excitation across chromophores (fs time scale)

# Excited States in Conjugated Polymers & CPNs: Exciton Transport

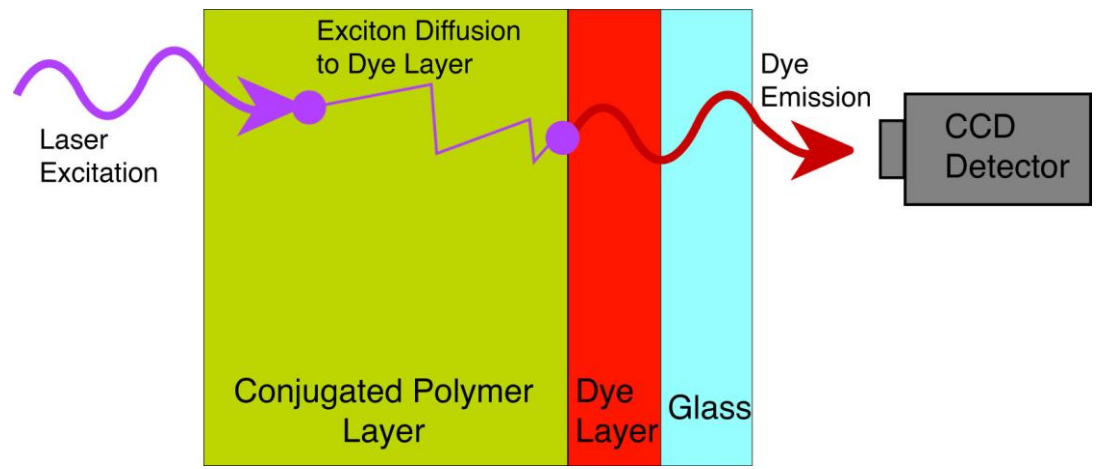


$$|A(t)|^2 = 2\pi\hbar|V_{dd}|^2\rho(E_{res})t$$

*Incoherent Energy Transfer Probability*

- Two types of energy transport
  - Incoherent transport
    - Non-degenerate chromophores
    - Significant disorder
    - Weak coupling
    - High (e.g. room) T
  - Energy transfer along or between chains, or to dopants (ps time scale)

# Conventional Exciton Diffusion Length Measurement



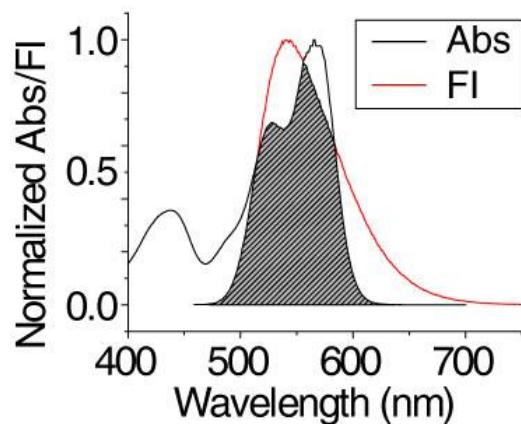
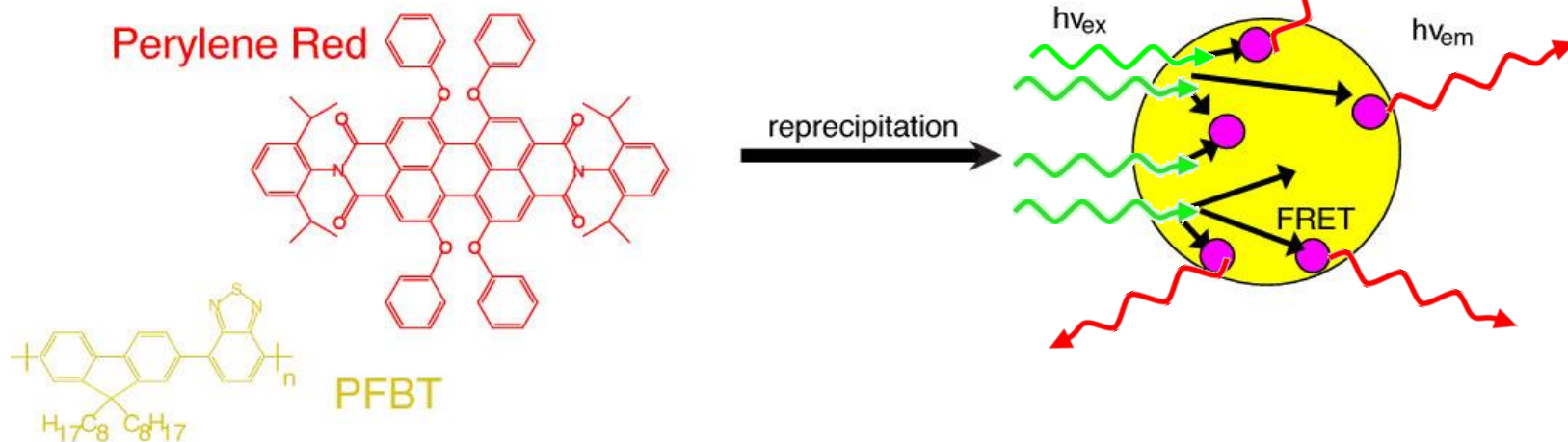
- Exciton Diffusion Length
  - Length exciton is transported during exciton lifetime
  - Measured using doped or layered film samples, or direct imaging methods (e.g. NSOM)
- CPNs exhibit similar photophysics to thin films
- Fewer challenges/pitfalls compared to films
  - Pinholes in film (direct acceptor excitation)
  - Optical penetration depths > length scales of energy transport
  - Layer segregation issues
  - Quenching by surface plasmons of metal anode/cathode (in electroluminescent samples)

## *CPN Photophysics*

- Want a model that can explain the complex photophysics of CPNs
  - Exciton Diffusion Energy Transfer Model
- Want to understand the underlying rate processes in CPNs as well as the length and time scales of nanoscale events in CPNs
  - Aid in optimizing CPNs for imaging applications and photovoltaic/OLED applications
  - Utilize a variety of time-resolved techniques to address these issues from multiple angles



# Red-shifted CPNs via Förster Resonance Energy Transfer



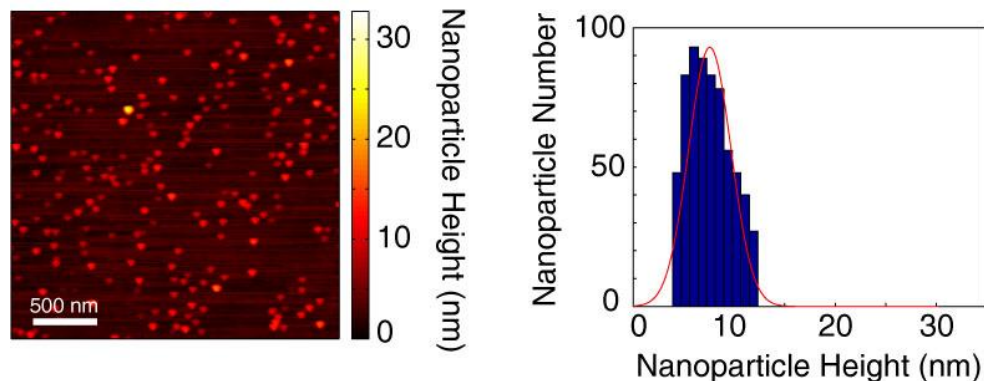
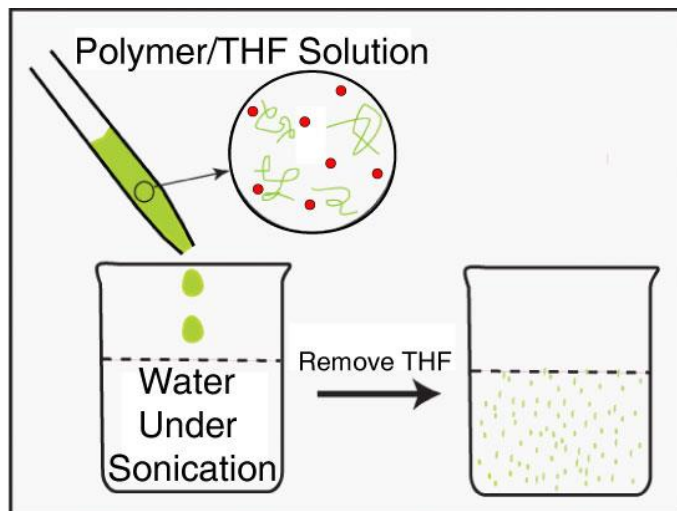
## PFBT – Host Polymer

- Very photostable ( $\sim 10^9$  photons/CPN emitted before photobleaching)
- High quantum yield (0.66 in THF)
- Broad emission spectrum

## Perylene Red – Nonpolar dye dopant

- High quantum yield (0.98 in DCM)
- Laser dye – highly photostable
- Excellent spectral overlap with PFBT
- Red-shifted emission spectrum

## Preparing Dye-doped CPNs



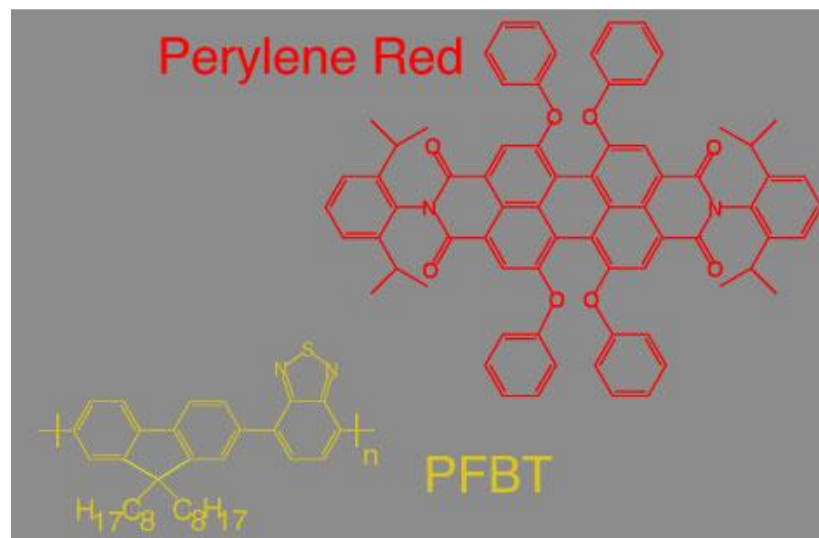
- **Reprecipitation method**
  - Polymer/dye dissolved in THF
  - Dilute solution
  - Rapidly mix with water under sonication (30 s)
  - Remove THF and filter to remove large aggregates
  - Mean particle size ~10 nm

# Förster Resonance Energy Transfer

- Interacting chromophore transition dipoles
  - Related to dimer model
  - $V_{dd} \propto R^{-3}$
  - $|A(t)|^2 = 2\pi\hbar|V_{dd}|^2\rho(E_{res})t$
  - Yields  $R^{-6}$  dependence
- Non-radiative energy transfer from donor to acceptor
- Donor/acceptor can be identical or different
  - Identical: Homotransfer
    - Degenerate chromophores
    - Thermal disorder causes incoherent transfer
  - Different: Heterotransfer
    - Transfer to dopants or defects

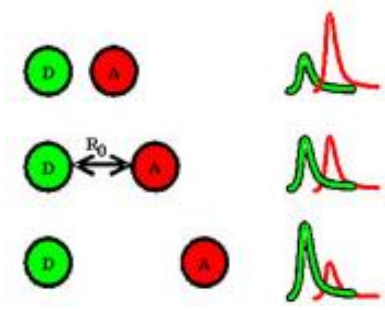
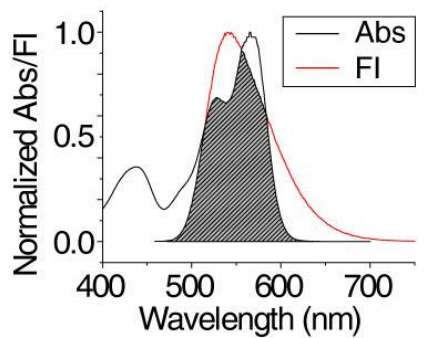
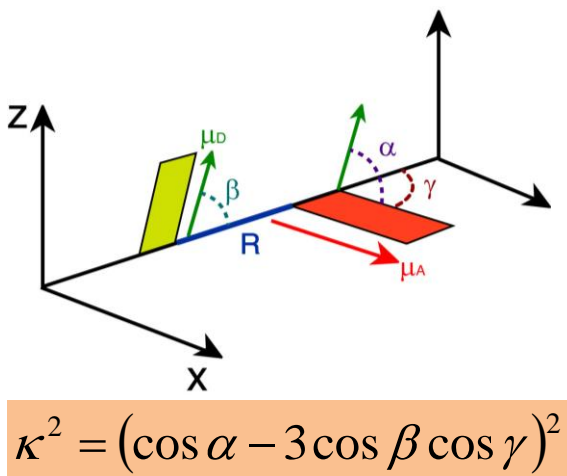
$$k_{et} = \frac{1}{\tau} \left( \frac{R_0}{R} \right)^6$$

Energy Transfer Rate Constant



# Förster Resonance Energy Transfer

- Energy transfer efficiency depends on spectral overlap, distance between donor/acceptor and orientation  $\kappa^2$ 
  - Scales as  $R^{-6}$
  - Useful as “molecular ruler”
- Förster Radius ( $R_0$ )
  - Distance at which energy transfer efficiency = 50%
  - Typically < 10 nm

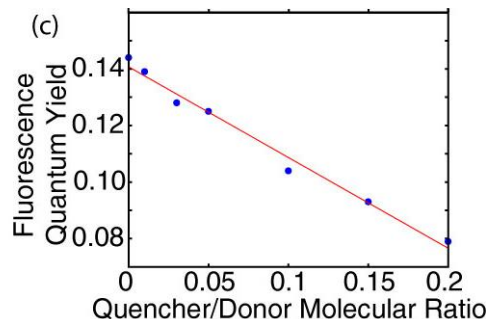
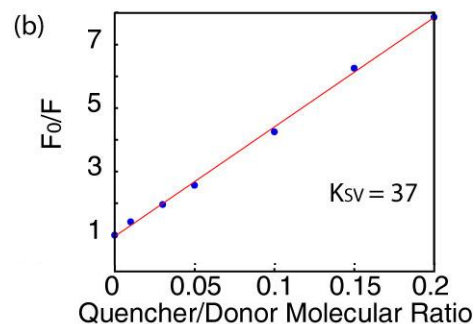
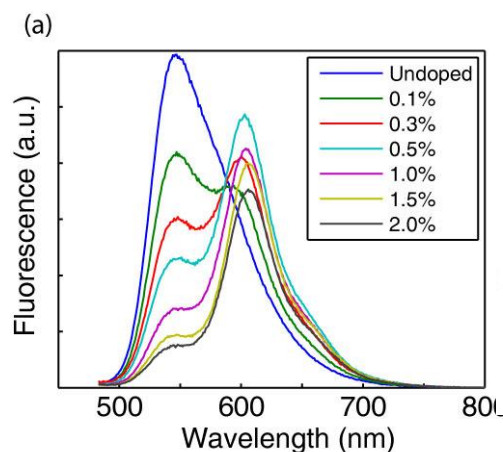


$$R_0^6 = \frac{9000 Q_D (\ln 10) \kappa^2}{128 \pi^5 n^4 N_A} \int f_D(\lambda) \epsilon_A(\lambda) \lambda^4 d\lambda$$

# Red-shifted, High Quantum Yield Dye-doped CPNs

$$\frac{F_0}{F} = 1 + K_{SV}[f]$$

*Stern-Volmer Equation*

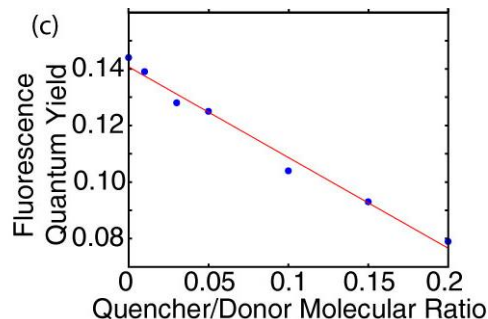
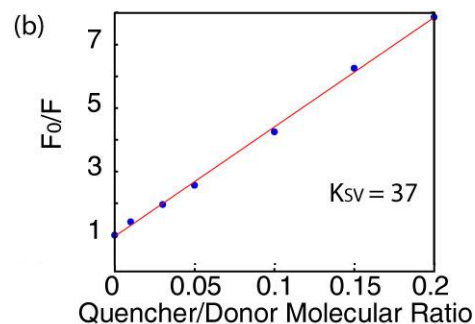
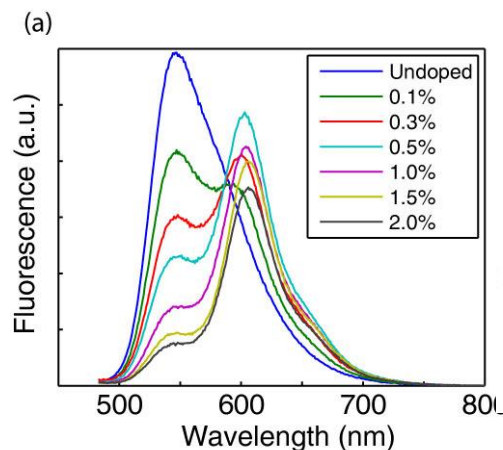


- Efficient quenching of PFBT emission by perylene red
  - 86% quenching at 2% perylene red
- Quenching obeys Stern-Volmer equation
- Perylene red emission red-shifts with increasing doping
- Aggregation quenching of acceptor at higher concentrations
  - Dynamic Quenching
  - Likely due to dye dimers in CPNs (J-aggregates)

# Red-shifted, High Quantum Yield Dye-doped CPNs

$$\frac{F_0}{F} = 1 + K_{SV}[f]$$

*Stern-Volmer Equation*



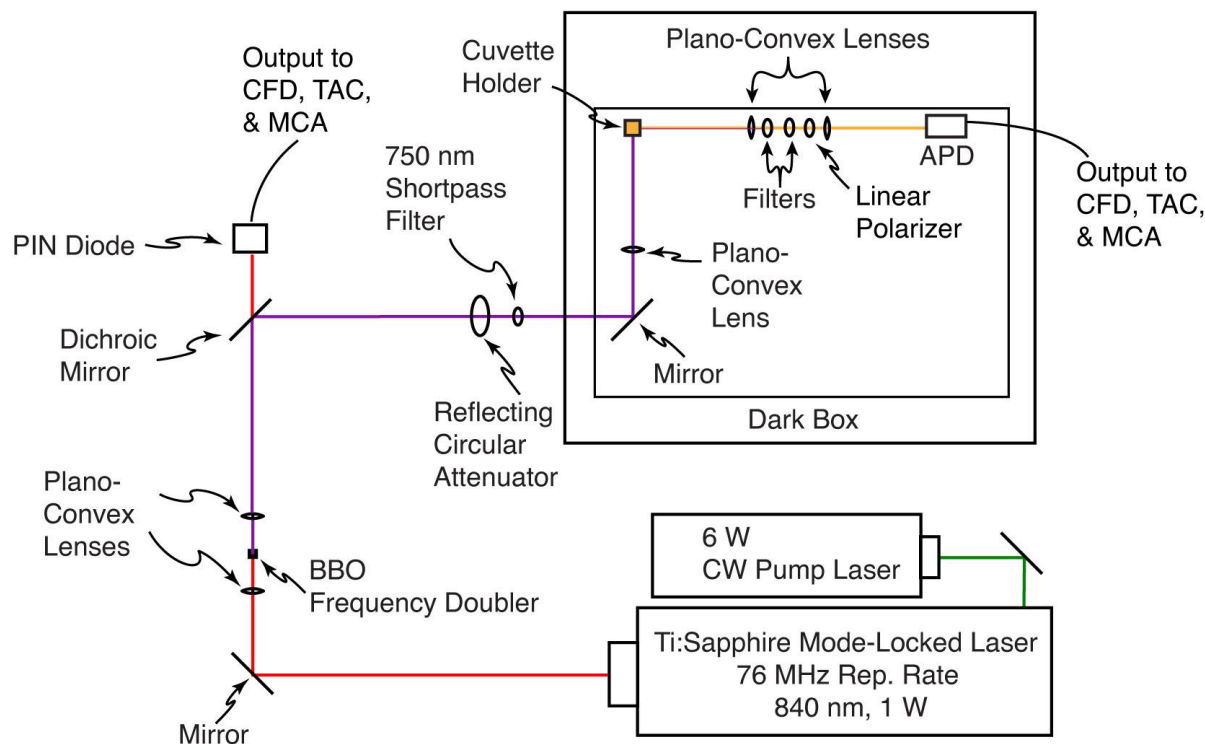
- Successfully red-shifted particle emission
- CPN quantum yield not substantially reduced from 0.1% to 1% doping while ET is high
  - Photostability may be improved by doping
  - Saturated emission rate may also be improved by doping



## *Fluorescence Quenching and Lifetimes*

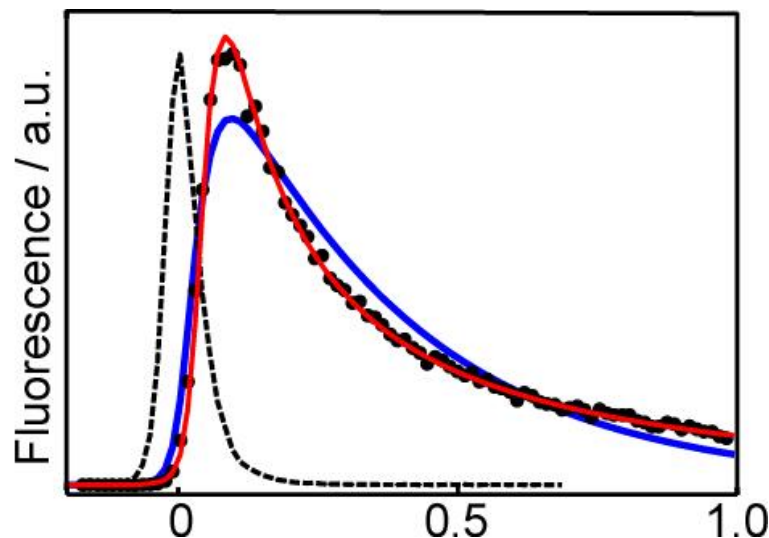
- It is evidenced by fluorescence spectra that perylene red efficiently quenches emission
  - Is this quenching static or dynamic?
- What are the fluorescence lifetimes of the doped samples?
  - Previous work indicates PFBT CPN lifetimes on the picosecond time scale
  - Do these samples exhibit complex decay kinetics?
- What is the correct physical picture in terms of rate processes?

# Picosecond Time-Correlated Single-Photon Counting (TCSPC) Spectroscopy



- Ultrafast, mode-locked, pulsed Ti:Sapphire laser source
- ~70 ps time resolution
- Frequency doubled for excitation
- Single-photon avalanche diode detector
- Fast electronics: arrival time measurements
- Histogram of detected photons

# Picosecond Fluorescence Lifetimes of Dye-doped CPNs



**Exponential**

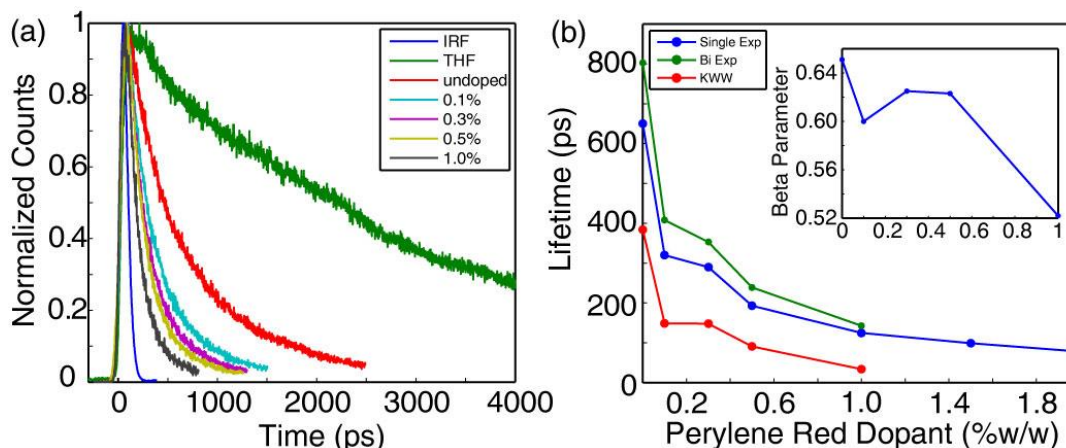
$$F(t) = F_0 e^{-t/\tau}$$

**Stretched Exponential**

$$F(t) = F_0 e^{-(t/\tau)^\beta}$$

- Previous experiments indicate CPNs exhibit complex decay kinetics
  - Stretched exponential lifetime decay
- $\beta$  is an indication of heterogeneity in exciton lifetimes
  - Number varying between  $\sim 0.2$  and  $1$
  - As  $\beta$  decreases, indicates a broadening distribution of exciton lifetimes
  - At  $\beta = 1$ , single exponential is recovered

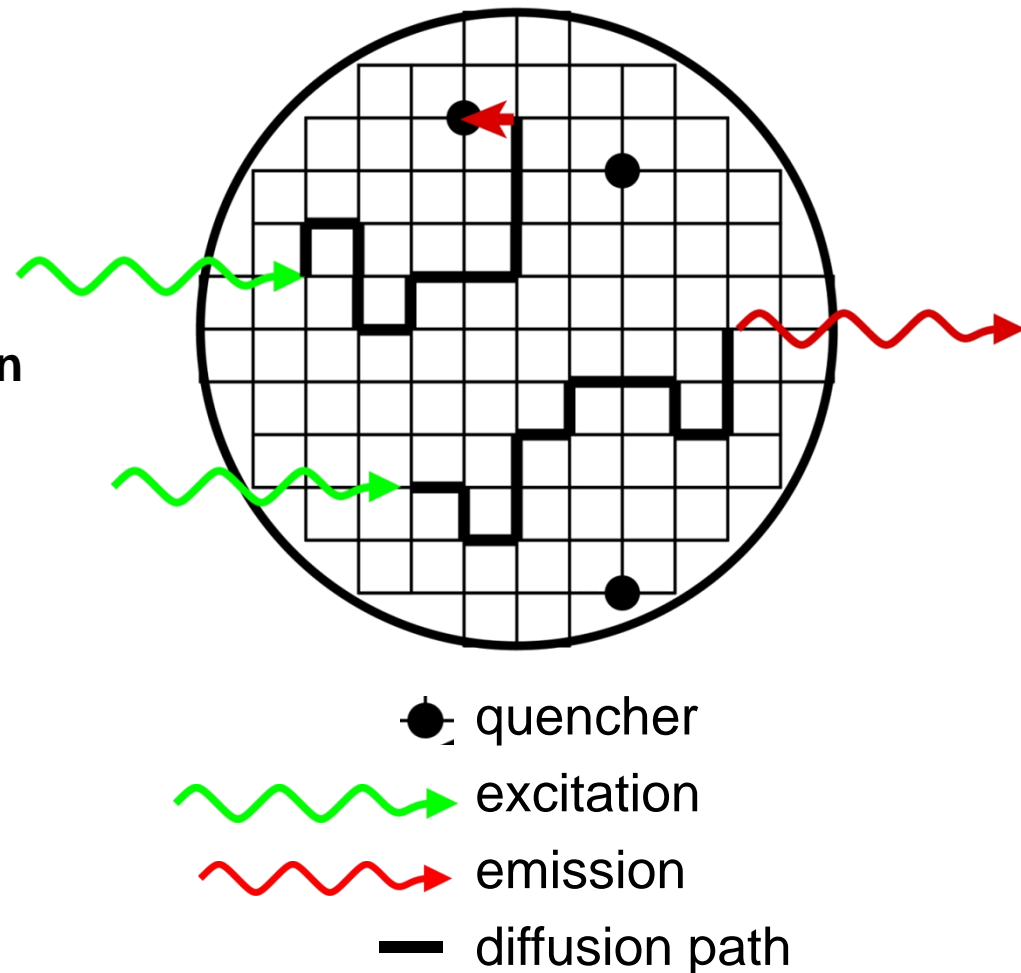
# Picosecond Fluorescence Lifetimes of Dye-doped CPNs



- Mean exciton lifetimes reduced by doping (dynamic quenching)
  - PFBT in THF fits well to single exponential (3 ns lifetime)
  - CPNs fit best to bi-exponential and stretched exponential decays
  - Decreasing trend in  $\beta$  as doping increases
  - Dynamic self-quenching of perylene red emission at high doping ratios
- Decreasing trend in  $\beta$  indicates a broadening distribution of exciton lifetimes as doping increases
  - Agrees qualitatively with physical picture of exciton multiple energy transfer
  - Range of exciton transfer distances broadens lifetime distribution

## Exciton Diffusion and FRET Random Walk Model

- Multichromophoric system--**Frenkel Exciton**
- Excitons hop from site to site: hopping between polymer chains and segments, exciton transfers to dyes, quenchers or defects--**Exciton diffusion**
- Hole polaron generation
- emission/decay
- Exciton transport modeled as a 3D random walk confined to a sphere
- **Results: excited state dynamics, quenching efficiency, blinking, twinkling**



# Exciton Diffusion Energy Transfer Model for Dye-doped NPs

- FRET rate

$$k_Q = \frac{1}{\tau_F} \sum_{\text{quenchers}} \left( \frac{R_0}{R} \right)^6$$

- Radiative emission rate  $k_F = \frac{1}{\tau_F}$

- Exciton diffusion
  - Gaussian RNG

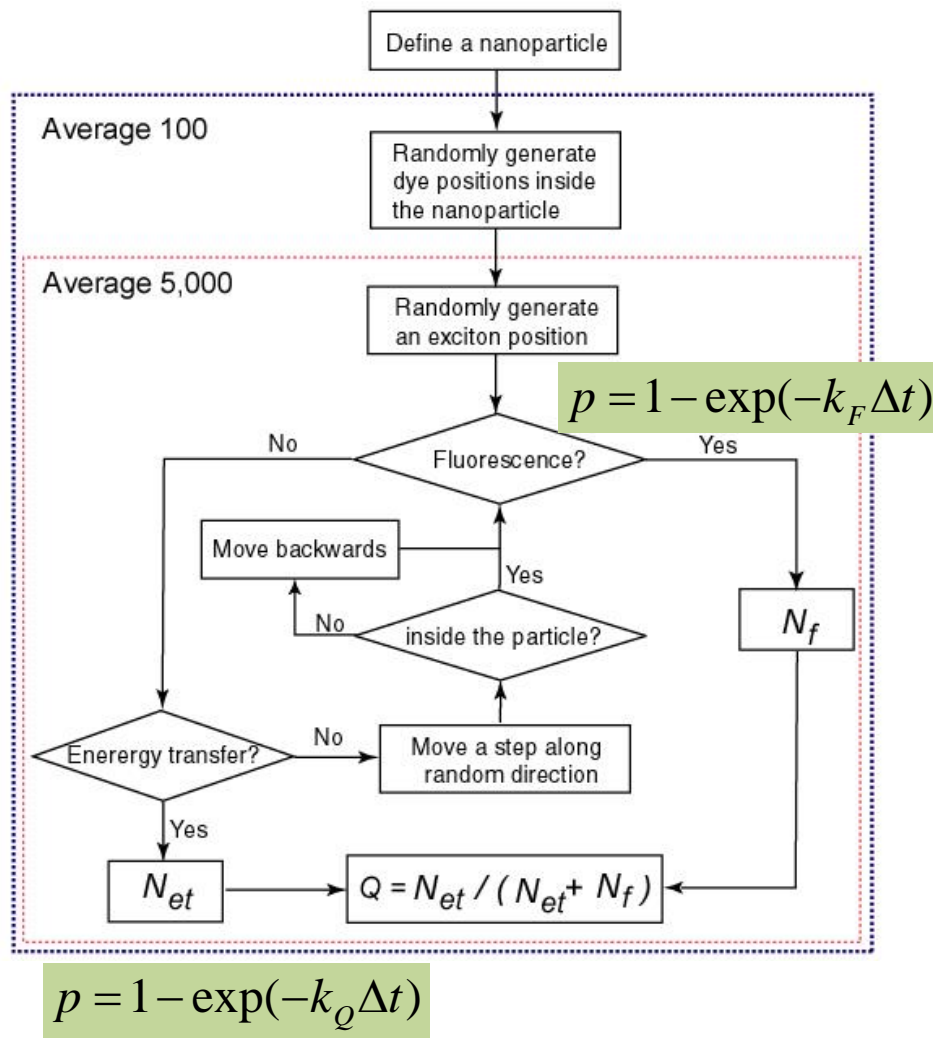
$$\sigma^2 = 2nD\Delta t$$

Displacement per  $\Delta t$

$$L_D = \sqrt{2nD\tau}$$

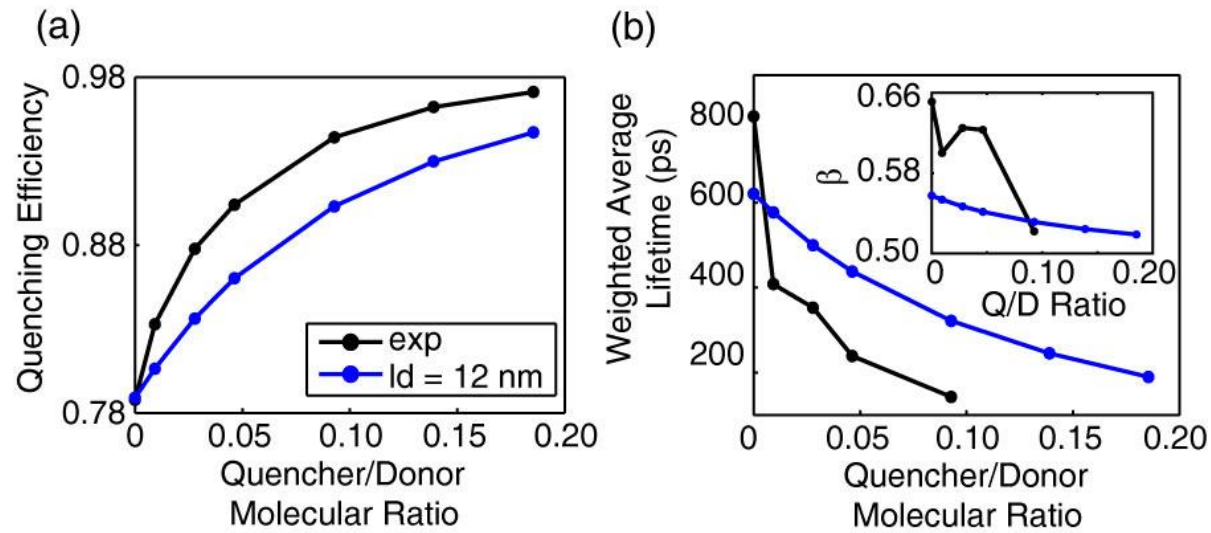
- Average over many exciton trajectories and quencher positions

- Results: Quenching efficiencies, Fluorescence decay kinetics





# Modeling of Dye-Doped PFBT Fluorescence

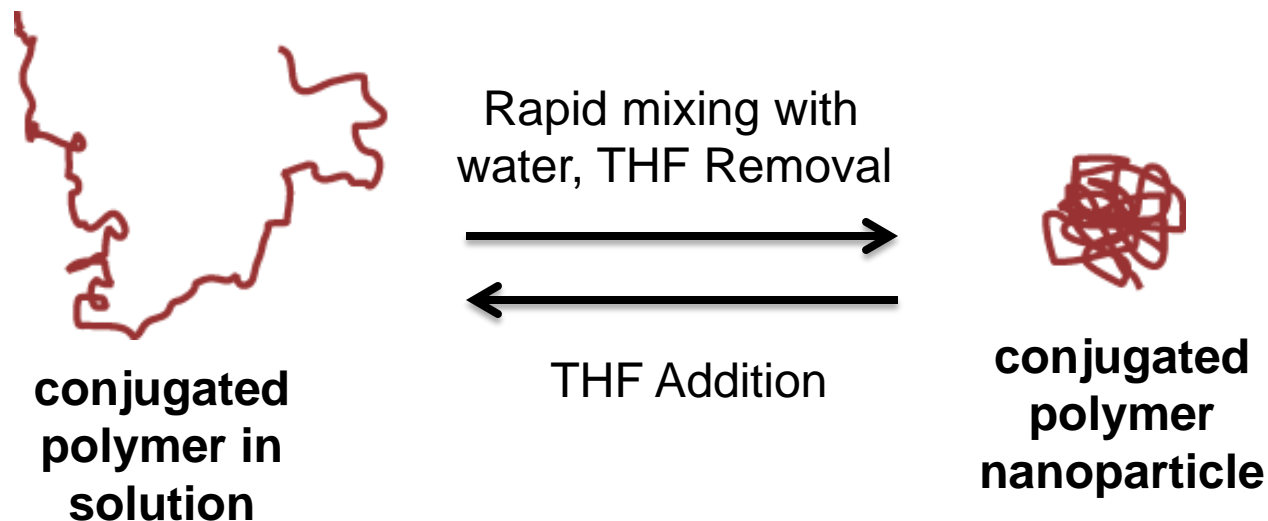


- Average over many excitons, particles, quencher positions
  - 3000 excitons per particle, 50 particles per data point
  - Poisson distribution of defects and quenchers
  - Exciton diffusion length  $L_D = 12$  nm, Förster radius  $R_0 = 4$  nm
- Approximate match to experimental TCSPC fitting results
  - At 0% dopant, 2.3 defect quenchers (dye equivalents) present
  - $\beta$  reduced by implementing Poisson statistics
  - Ignoring quenching by defects results in  $L_D$  2x lower, lower quality of agreement

## *Dye-Doped PFBT CPNs: Summary*

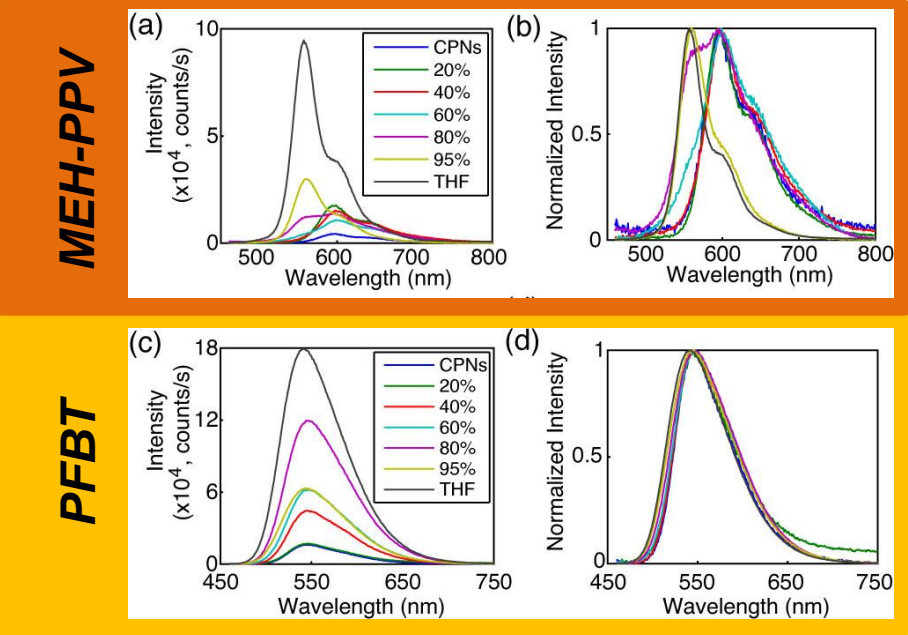
- Successfully red-shifted emission via dye-doping
  - High energy transfer efficiency and  $\Phi$  at moderate doping
- Nanoparticle samples exhibit complex decay kinetics
  - Described best by bi-exponential or KWW dynamics
  - Decreased lifetimes in doped samples (dynamic quenching)
  - Acceptor is dynamically quenched at high doping ratios
- Exciton diffusion, Energy Transfer Model matches experimental dynamics well
  - Poisson distribution of defects and quenchers
  - $\sim 2$  defects/CPN
  - Length scale of exciton transport  $\sim 12$  nm for PFBT  
( $D = 8 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ )

## Solvent-Induced Swelling of CPNs

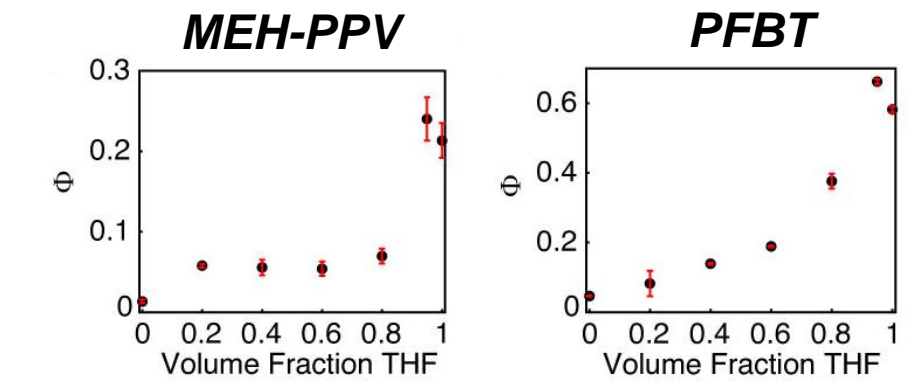


- Use solvent-induced swelling methods to probe the changes in nanoparticle photophysics
  - Probe rates of multiple energy transfer
  - Determine nature of quenching defects (aggregates vs. oxidative)
- Rate of exciton motion hypothesized to be amplified for CPNs
  - Densely packed chromophores
  - Access to more nearest neighbor chromophores in CPNs vs. polymer in solution
  - Probe via fluorescence anisotropy decay (FAD) and modeling

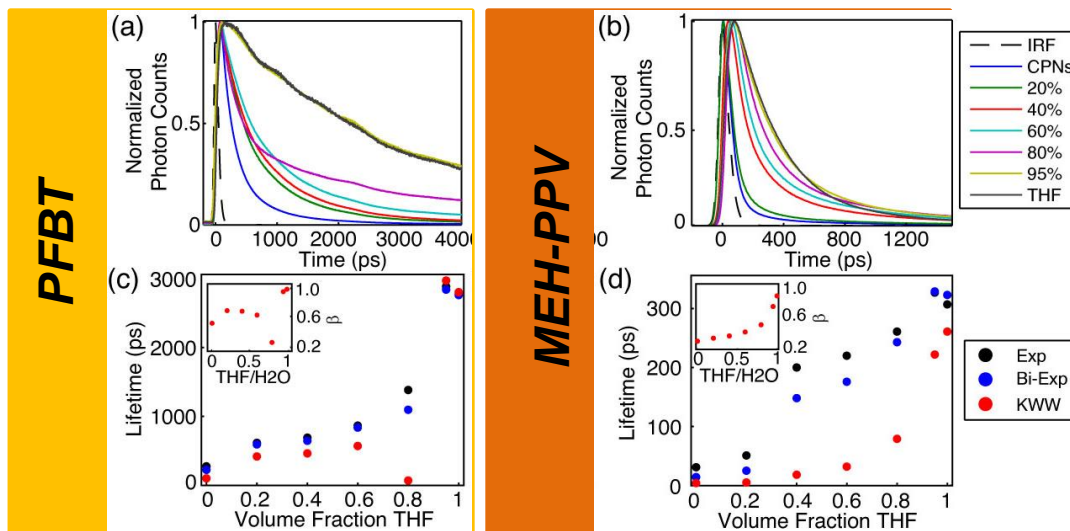
# Fluorescence Quantum Yield and Spectral Shifting



- Increase in  $\Phi$  as %THF increases
  - ~92% quenching at 0% THF
  - $\Phi_{\text{THF}}$  is recovered at high THF concentrations
- Normalized spectra show progressive blue shifting of emission peak
  - ~5 nm for PFBT
  - ~40 nm for MEH-PPV
  - Stronger dipole coupling in MEH-PPV

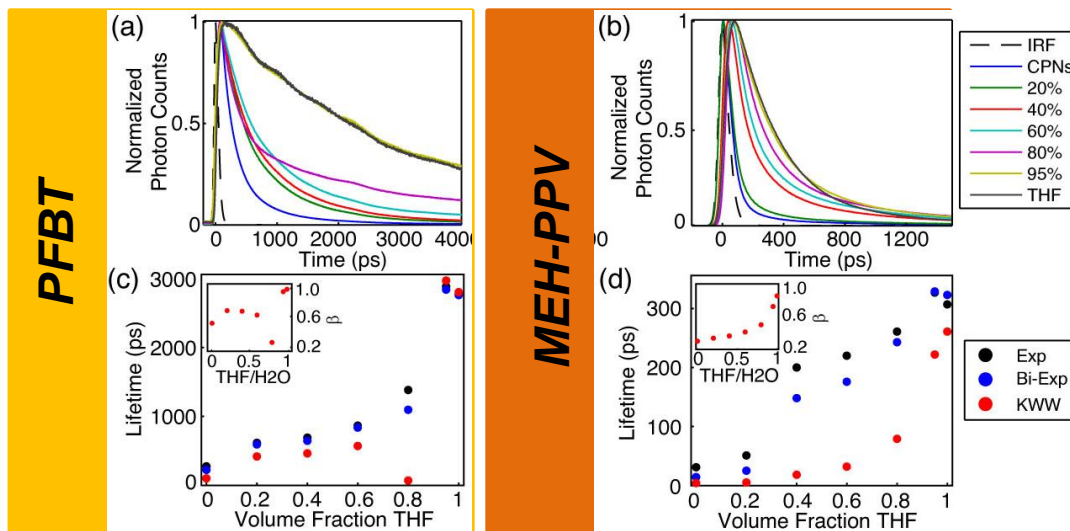


# Fluorescence Decay Kinetics of Swelled CPNs



- Exciton lifetimes increase with increasing THF volume fraction
  - PFBT in THF fits well to single exponential (3 ns lifetime)
  - All others fit best to bi-exponential and stretched exponential decays
  - $\beta$  increases with increasing THF, except PFBT in 80% THF
- Increasing trend in  $\beta$  indicates a narrowing distribution of exciton lifetimes as THF fraction increases
  - Multiple energy transfer is FRET mediated ( $R^{-6}$  dependence)
  - As CPN structure swells, neighboring chromophores become less accessible, reducing exciton mobility.

# Fluorescence Decay Kinetics of Swelled CPNs



- Evidence for possible dynamic equilibrium between CPNs and unassociated polymer
  - Drastic decrease in  $\beta$  to  $\sim 0.2$  at 80% THF for PFBT suggests sudden increase in lifetime distribution
  - Bi-exponential fitting results
    - PFBT Short time constant  $\sim$  CPN lifetime ( $\sim 275$  ps)
    - PFBT Long time constant  $\sim$  polymer lifetime ( $\sim 3$  ns)
    - Weighted amplitudes shift for higher THF concentrations
    - Similar lifetime behavior for MEH-PPV between 40-60% THF.



# Probing Energy Transport via Fluorescence Anisotropy Decay

- Challenge: Indistinguishable chromophores
  - Energetically degenerate, or near-degenerate
  - TCSPC can measure kinetics
  - Need method of measuring rate of energy transfer
- Time-resolved fluorescence anisotropy decay
  - Emission polarization is altered: rotational dynamics or energy transfer
  - Typical uses: rotational diffusion of macromolecules, small molecules
- Polarization changes due to energy homotransfer events
  - $\tau_r \propto 1/D_r$  (ns- $\mu$ s), depending on particle size
  - $\tau_r \gg \tau_{CPN}$  for 10 nm particle
  - Rotational motion is negligible for CPNs

$$D_r = \frac{k_b T}{8\pi\eta r^3}$$

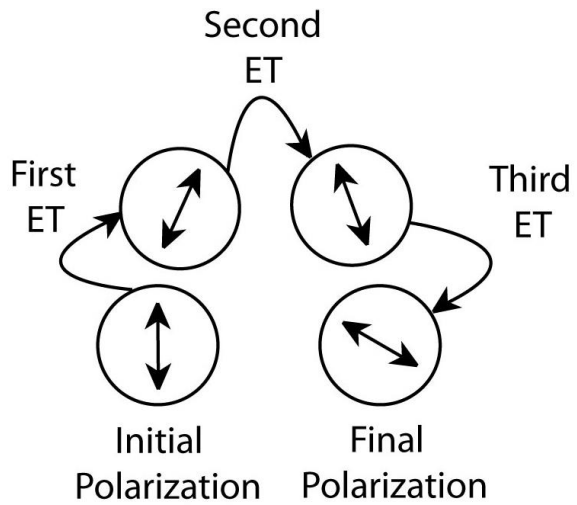
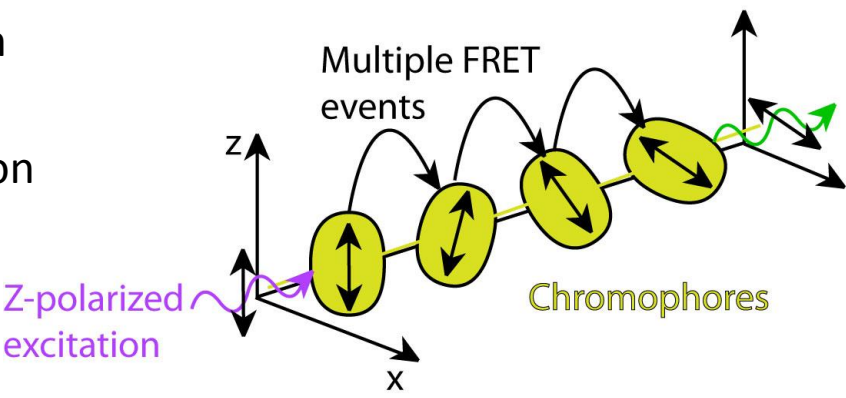
*Stokes-Einstein Equation*

$$r(t) = \frac{I_0(t) + I_{90}(t)}{I_0(t) - 2I_{90}(t)}$$

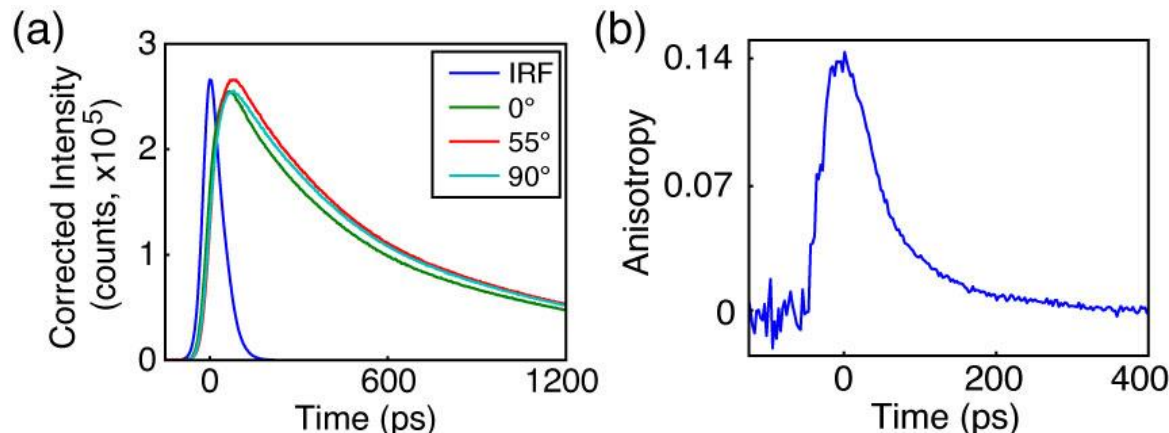
*Fluorescence Anisotropy Decay Equation*

# Polarization Loss via Exciton Diffusion

- Polarized excitation source
  - CPNs possess randomly oriented transition dipoles
  - Preferentially excite chromophore transition dipoles aligned relative to excitation
- FRET to neighboring chromophore with imperfectly aligned transition dipole
  - Each ET event alters polarization
  - Emission polarization depends on T. dipole alignment prior to decay
  - Measure intensity decays at 0°, 90°, 55° polarizations to construct anisotropy decay
- Fundamental Questions
  - How many transfer events occur within the exciton lifetime?
  - What is the length scale of these transfers?

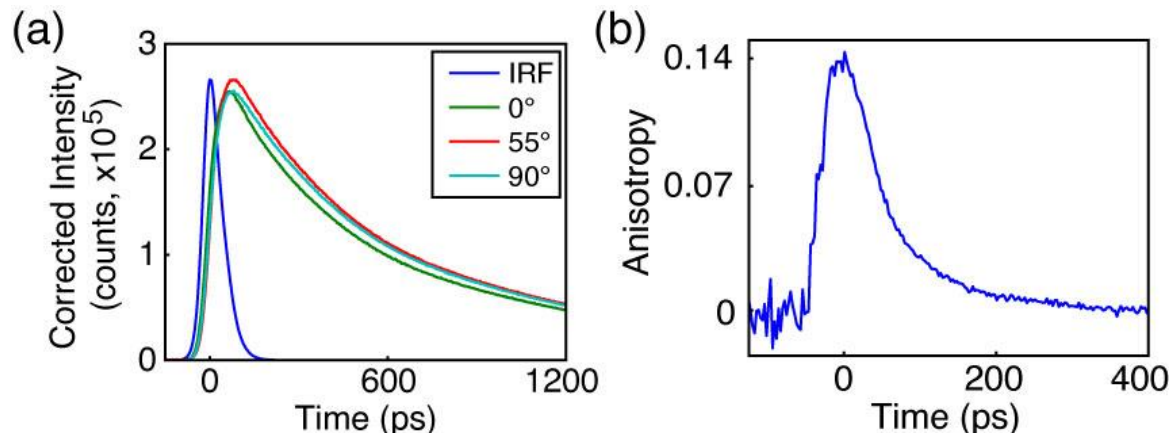


# Picosecond Fluorescence Anisotropy Decay



- Measure fluorescence polarization loss as a function of time
  - Collect intensity decays at 0°, 90°, 55° polarizations relative to excitation source
  - Rotational diffusion does not affect polarization loss
  - Polarization loss due to multiple energy transfer of excitons
- Intricate fitting analysis to extract anisotropy parameters
  - Convolution fitting of polarized intensity decays
  - Determine limiting anisotropy  $r_0$  and correlation time  $\tau_c$  from fit results
  - $r_0$  gives information about transition dipole alignment at  $t_0$
  - Able to measure rate constant  $k_{et}$  from correlation time,  $\tau_c$

# Picosecond Fluorescence Anisotropy Decay



- Multiple energy transfer rate constant amplified in CPNs
  - For moderately swelled PFBT CPNs (above)  $k_{et} \sim 3 \times 10^{10} \text{ s}^{-1}$
  - For PFBT in THF,  $k_{et} \sim 1 \times 10^9 \text{ s}^{-1}$
- Hypothesized to be due to quantity of nearest neighbor chromophores to move between
  - 6 neighbors in CPNs, allow for motion along or between chains
  - 2 neighbors in linear polymer, motion is restricted along chain

# Discrete Lattice Modeling of Nanoparticle Swelling

- Model Details
  - Cubic lattice
  - Energy transfer probability  $\propto$  chromophore densities
  - Initial lattice spacing determined from chromophore densities at  $\sim 1$  nm
- Defects/quenchers added to unswelled lattice until  $\Phi_{CPN}$ ,  $\tau_{CPN}$  reproduced
  - $R_q = 4$  nm
  - $\sim 10$  defects per CPN for both polymers
  - Oxidized defects assumed (defects present regardless of chromophore density)
- Quenching efficiency  $\eta$  defined via fluorescence quantum yield

$$p_{et} = 2D\Delta t / \Delta x_{np}^2$$

*Multiple energy transfer probability  
Defined from Random Walk*

$$f^{4/3} = (\Delta x_{np} / \Delta x_s)^4$$

*As lattice spacing increases,  
 $p_{et}$  reduced by  $f^{4/3}$*

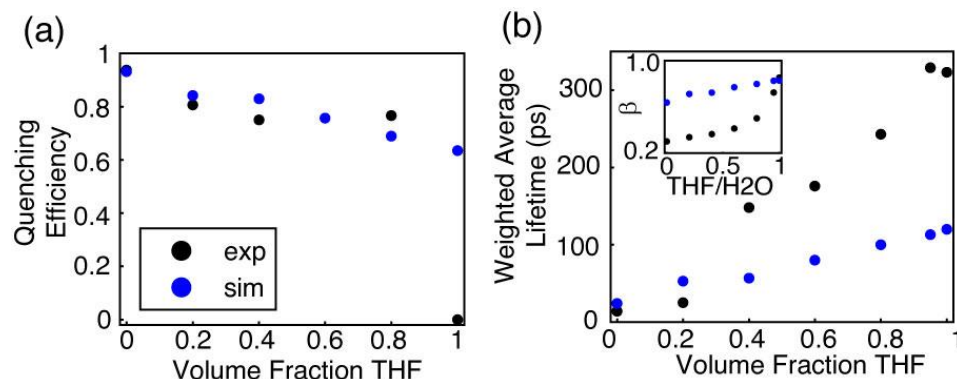
$$\eta_{exp} = 1 - (\Phi_s / \Phi_{poly})$$

*Experimental quenching efficiency*

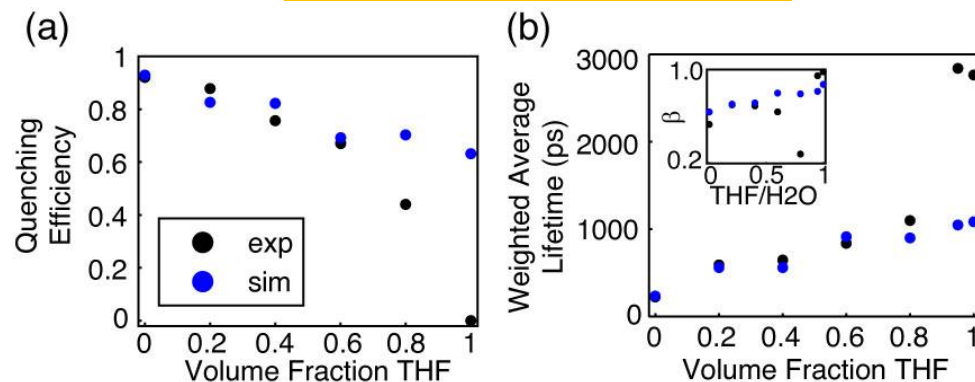
# Lattice Modeling Results

- Model reproduces experimental  $\eta$ ,  $\tau$  well
  - For low to moderate %THF
  - $\beta$  reproduced well for PFBT
- Model/experiment divergence at mid/high THF concentrations
  - ascribed to dynamic equilibrium
  - absence of nanoparticle dissociation in model
- Energy transfer rate constants extracted from  $p_{et}$ 
  - CPN ET rate constants 10-60x higher than polymer ET rate constants
  - Agrees with experimental anisotropy fit results
  - Agrees qualitatively with Förster exciton diffusion theory
    - Reduced chromophore number density reduces ET rate

## MEH-PPV Model Results



## PFBT Model Results



## *Fluorescence Quantum Yield/Exciton Mobility Tradeoff*

- $k_{\text{et}}$  is  $\sim 2\times$  higher for MEH-PPV CPNs compared to PFBT CPNs
  - Due to stronger transition dipole coupling in MEH-PPV
- $\Phi$  is  $\sim 4\times$  higher for PFBT CPNs compared to MEH-PPV CPNs
  - Weaker coupling/more isolated chromophores
- Increased exciton motion efficiently funnels excitons to defect quenchers
  - Reduction in lifetime
  - Reduction in  $\Phi$



## Summary

- Successfully prepared redshifted PFBT CPNs with high  $\Phi$
- Determined  $L_D \sim 12$  nm for PFBT
- Successfully used solvent-induced swelling to probe rates of exciton mobility using FAD
- Multiple energy transfer amplified 10x-60x in CPNs versus polymer in solution
- Lattice model results match well assuming oxidized defect quenchers
- Tradeoff between mobility and  $\Phi$  can be exploited for improvement of organic semiconductor devices

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- Dr. Jason McNeill
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  - Yifei Jiang
- NSF, NIH
- Clemson University Department of Chemistry
- You for your time and patience!



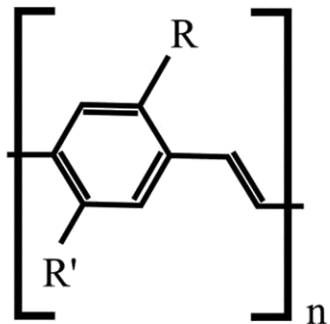
National Science Foundation  
WHERE DISCOVERIES BEGIN



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*Turning Discovery Into Health*

# ***Backup slides***

# Why are the particles nearly spherical?



- Pi-conjugated backbone is rigid
- Should yield oblong particles / rods

**However...**

- Very hydrophobic: high polymer-water interface tension
- Small particle size (High surface/volume ratio)
- Favors nearly spherical shape

***Confirmed by AFM, TEM, Preliminary Neutron Scattering***

# Stern-Volmer Derivations

## Static

$$K_{SV} = \frac{[F - Q]}{[F][Q]}$$

$$[F]_0 = [F] + [F - Q]$$


$$K_{SV} = \frac{[F]_0}{[F][Q]} - \frac{1}{[Q]}$$

## Dynamic

$$\frac{d[F]^*}{dt} = k_{abs} - (k_f + k_q[Q])[F]^* = 0$$

$$\frac{d[F]^*}{dt} = k_{abs} - k_f[F]^*_0 = 0$$

$$\frac{F_0}{F} = \frac{k_f + k_q[Q]}{k_f} = 1 + k_q\tau_0[Q]$$


$$F_0/F = 1 + K_{SV}[Q]$$

# Useful Equations

- Quantum Yield Calc

$$\phi_{F(x)} = \left(\frac{A_s}{A_x}\right) \left(\frac{F_x}{F_s}\right) \left(\frac{n_x}{n_s}\right)^2 \phi_{F(s)}$$

- Quantum Yield (Rates)

$$\phi_F = \frac{k_R}{k_R + k_{NR}}$$

- Absorption Cross-section

$$\sigma = \frac{2.303\varepsilon}{N_A}$$

## Hole Polarons: Photogeneration and Luminescence Quenching

- Quasiparticle, radical cation and local polarization field
- caused by reversible photoejection of  $e^-$
- Hole polaron can diffuse between chromophores or recombine with electron
- Extremely efficient fluorescence quenchers
  - One polaron quenches  $\sim 90\%$  of fluorescence from a polymer chain of  $>100$  chromophores
  - Significant quenching at  $5 \times 10^{17}$  holes per  $\text{cm}^3$  of polymer (exceeded in devices)

