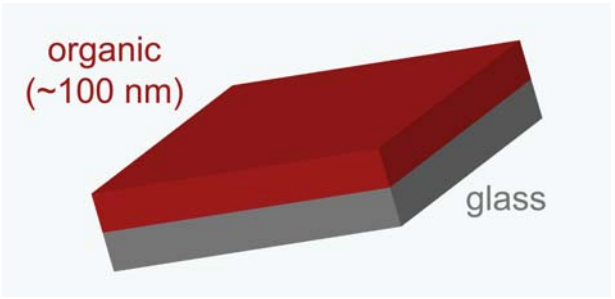
Organic LEDs – part 8

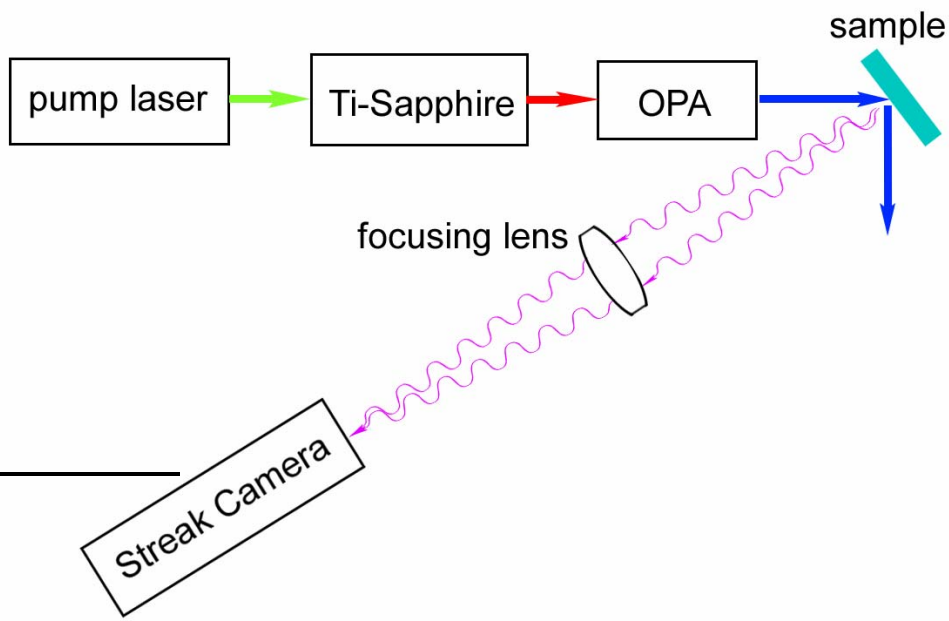
- Exciton Dynamics in Disordered Organic Thin Films
- Quantum Dot LEDs

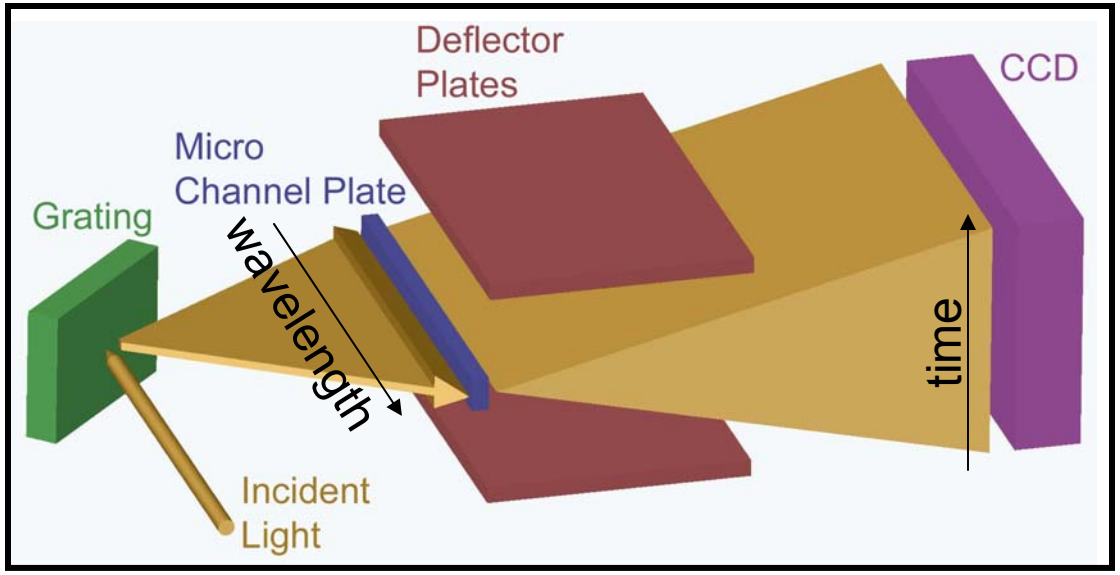
Handout on QD-LEDs: Coe et al., Nature 420, 800 (2002).

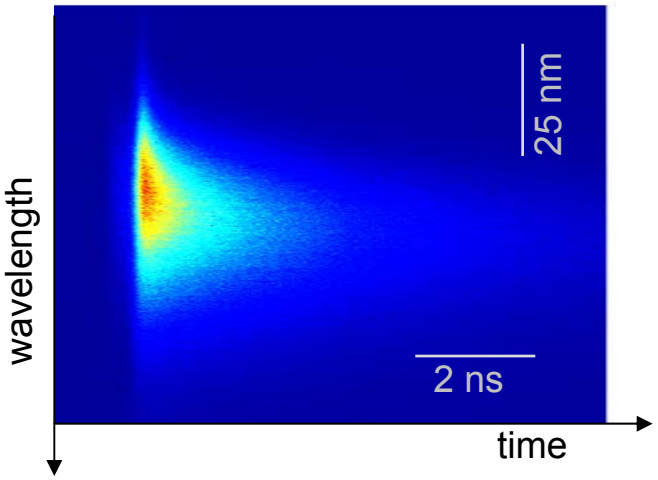
looe @ MIT

Exciton Dynamics in Time Dependant PL



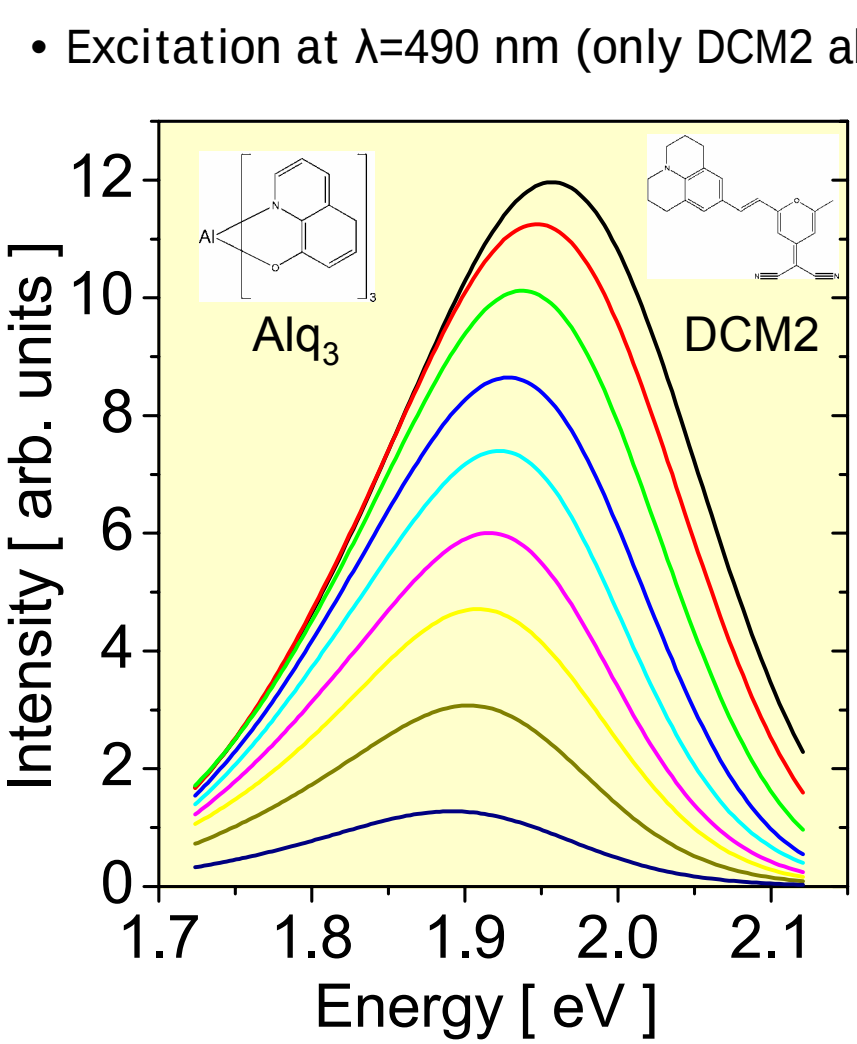


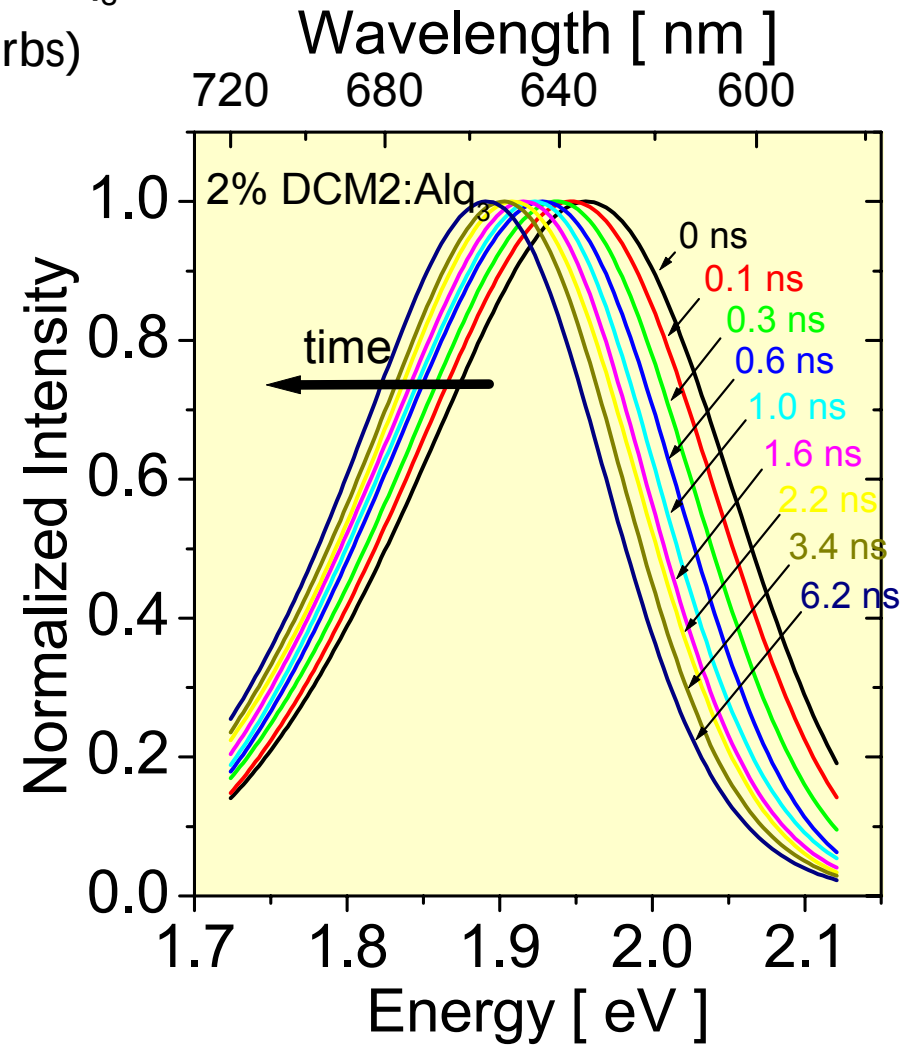




Dynamic Spectral Shifts of DCM2 in Alq_3

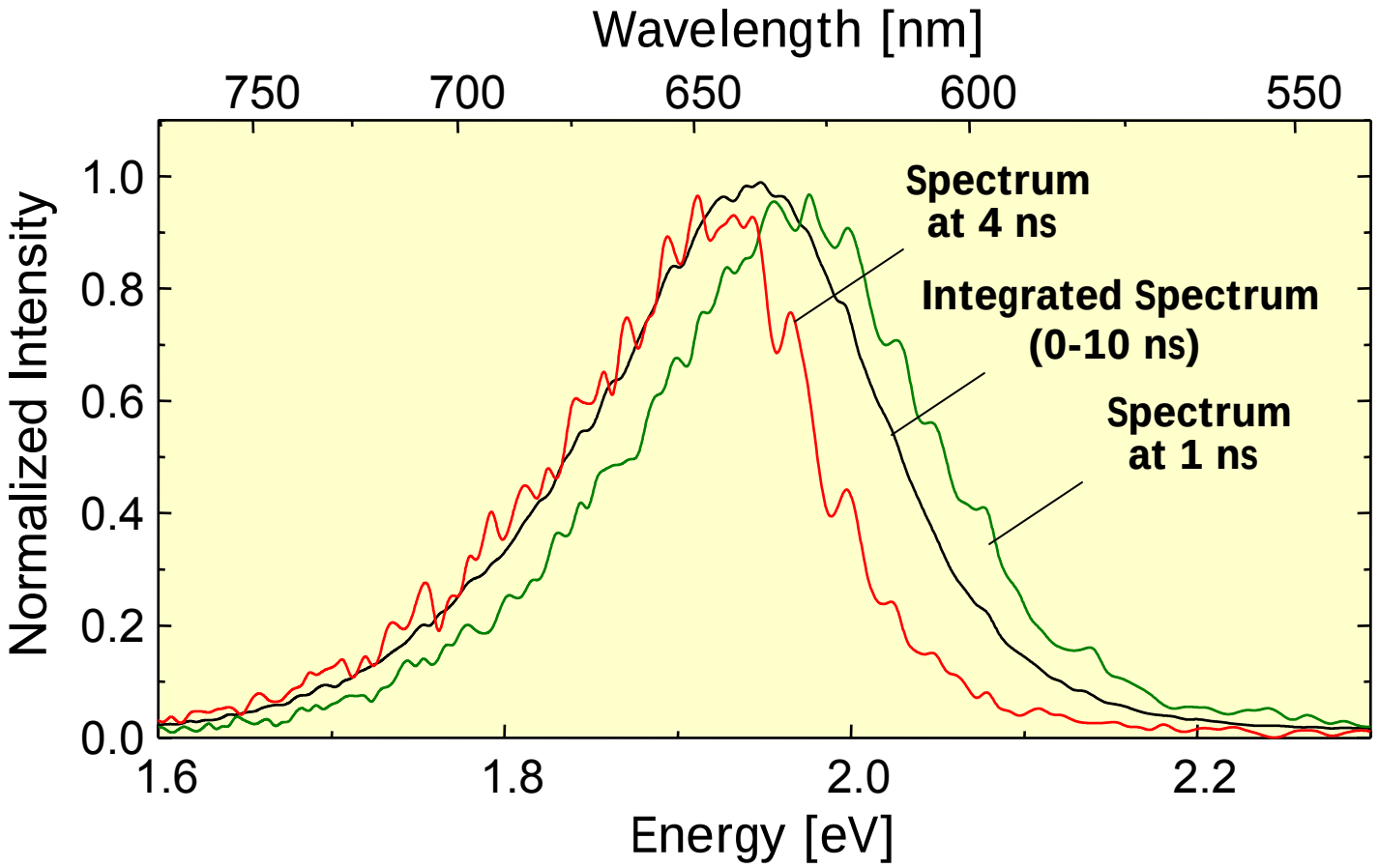
- Measurement performed on doped DCM2:Alq_3 films
- Excitation at λ=490 nm (only DCM2 absorbs)



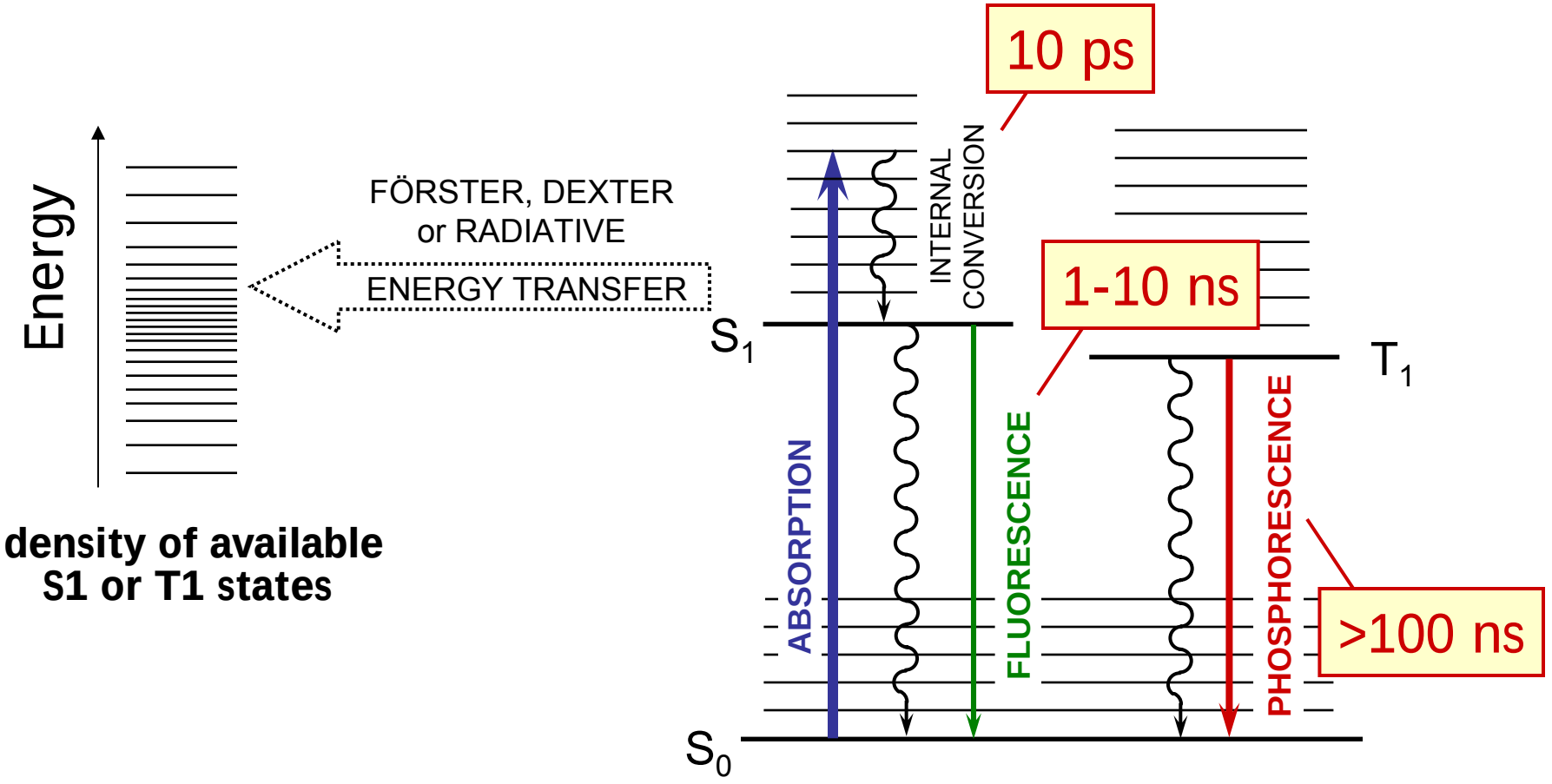


~ DCM2 PL red shifts > 20 nm over 6 ns ~

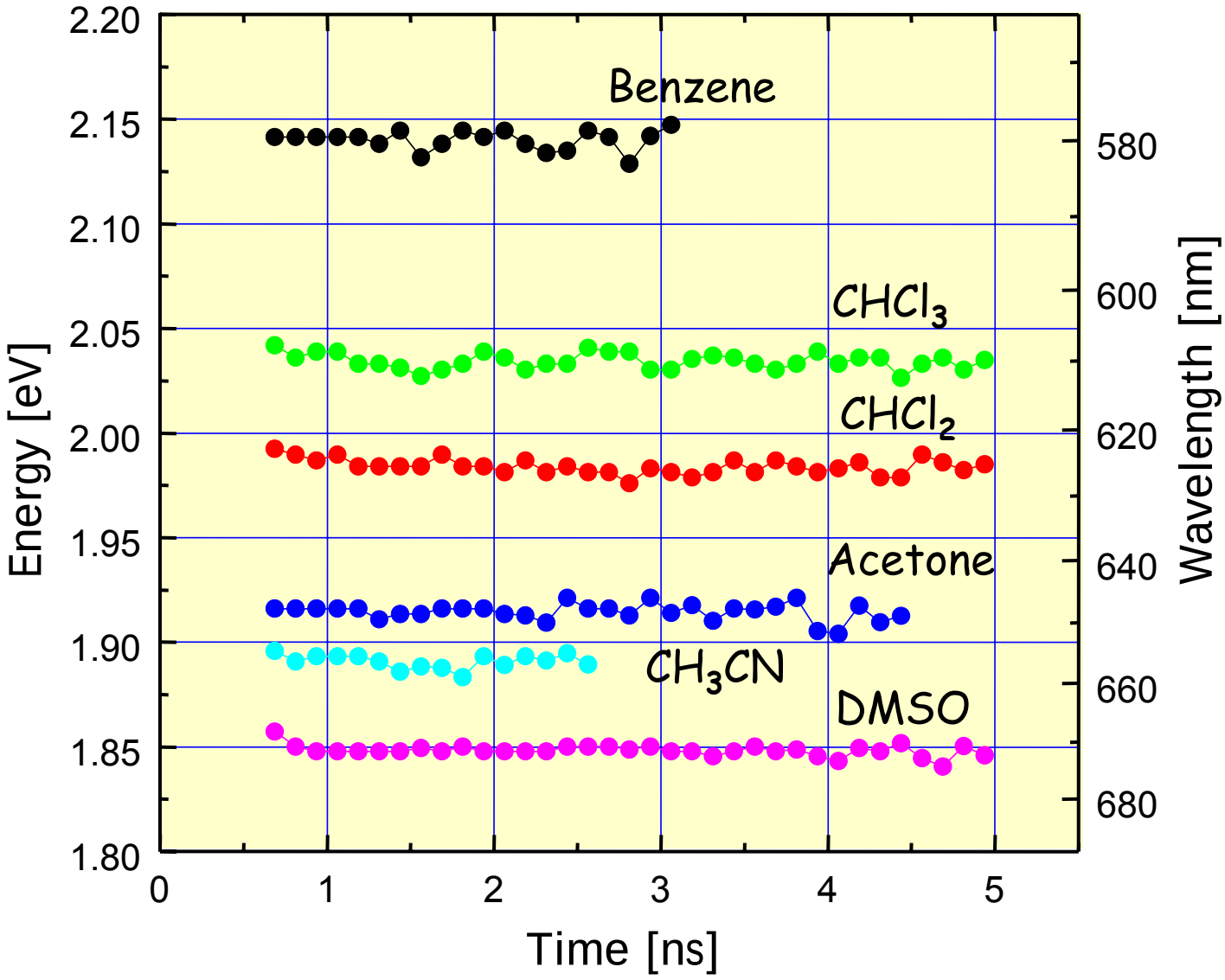
Time Evolution of 4% DCM2 in Alq_3 PL Spectrum



Electronic Processes in Molecules



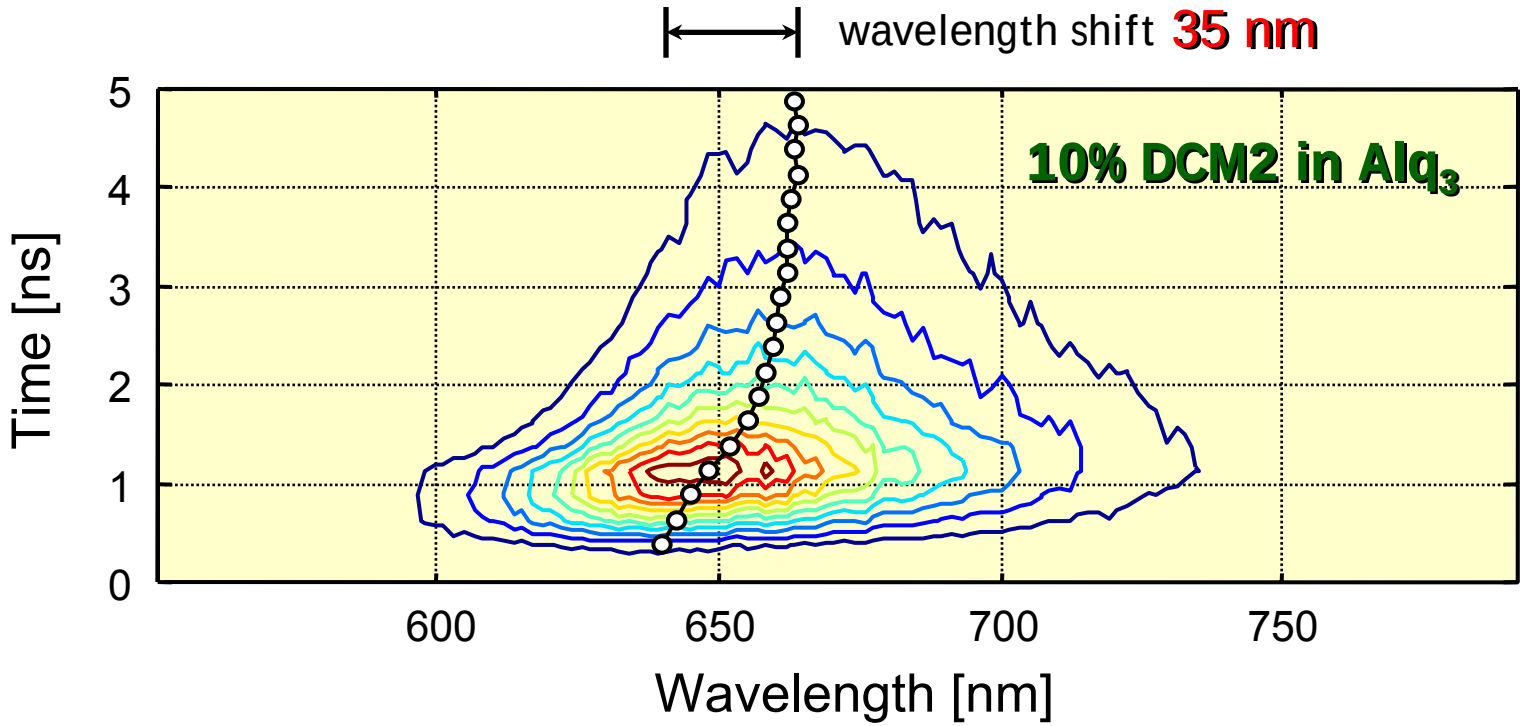
Time Evolution of DCM2 Solution PL Spectra



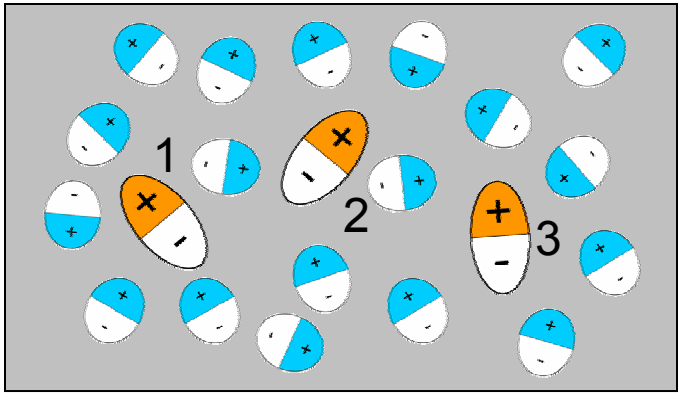
Spectral Shift due to

~ Exciton Diffusion ~

~ Intermolecular Solid State Interactions ~



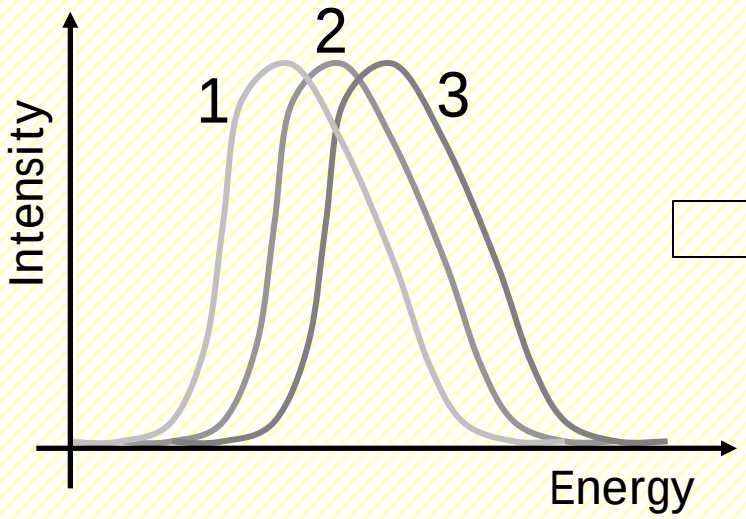
Excitonic Energy Variations



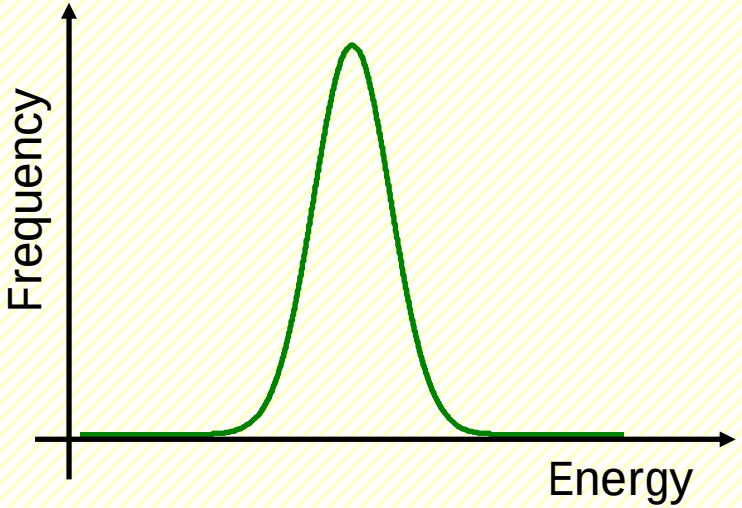
Each dye molecule experiences a different local medium
⇒ variations in excitonic energies

Non-zero width to excitonic density of states

Molecular PL Spectra

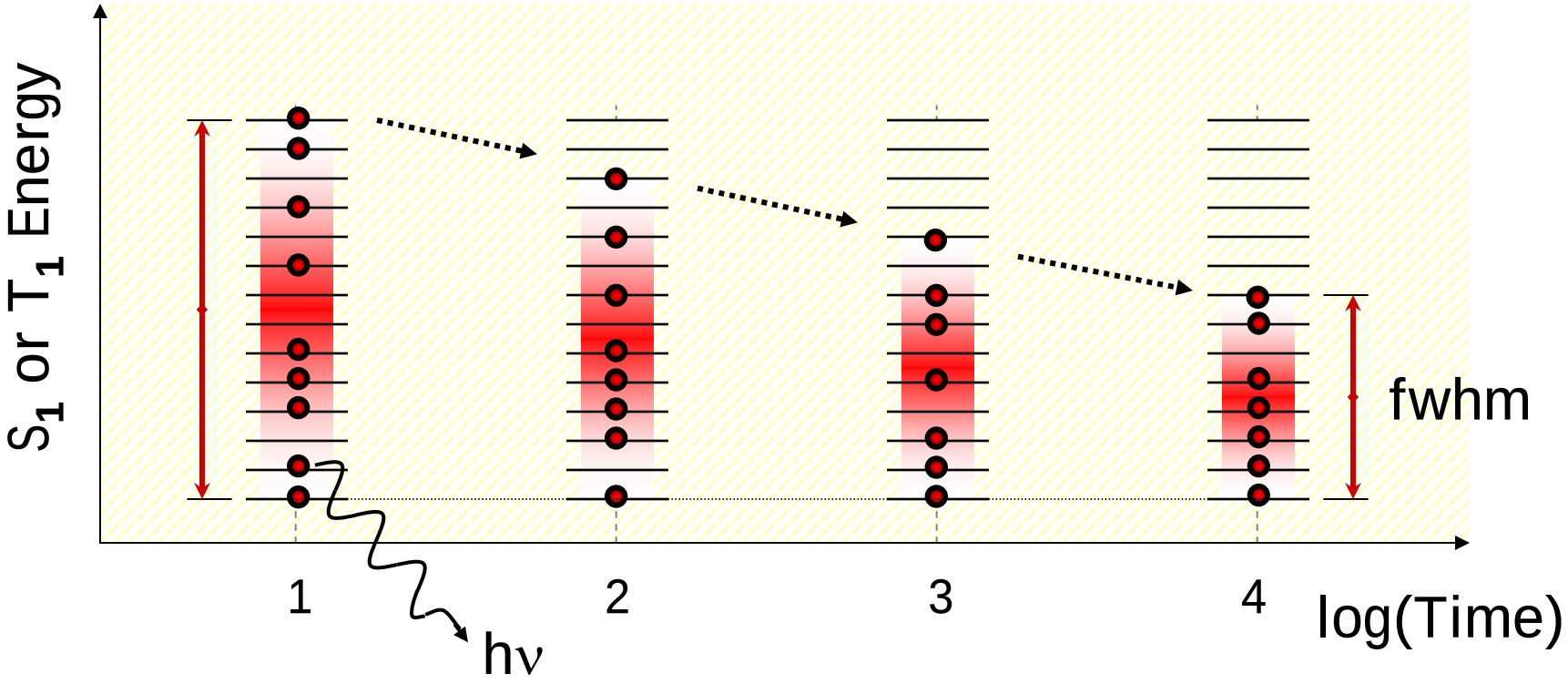


Excitonic Density of States

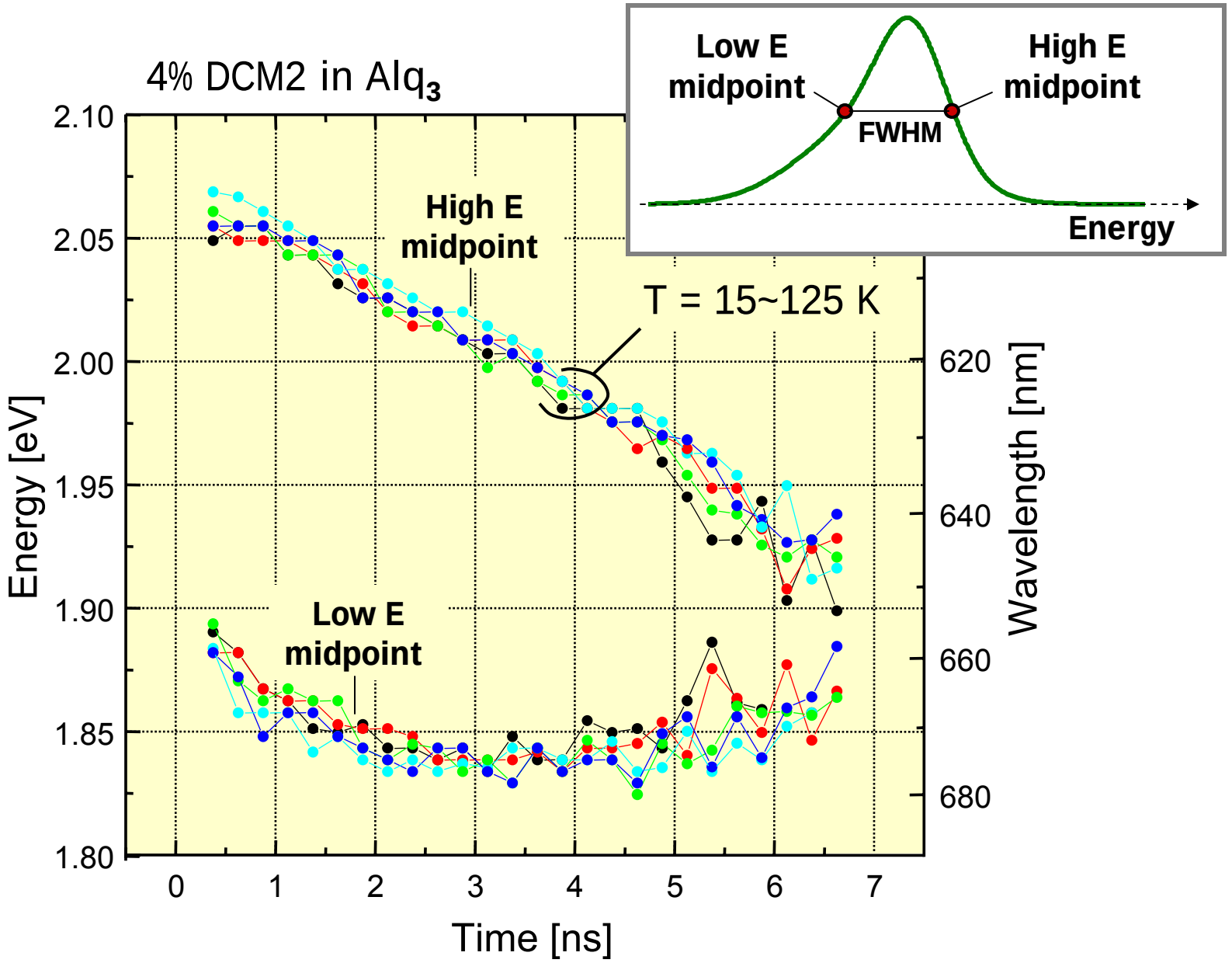


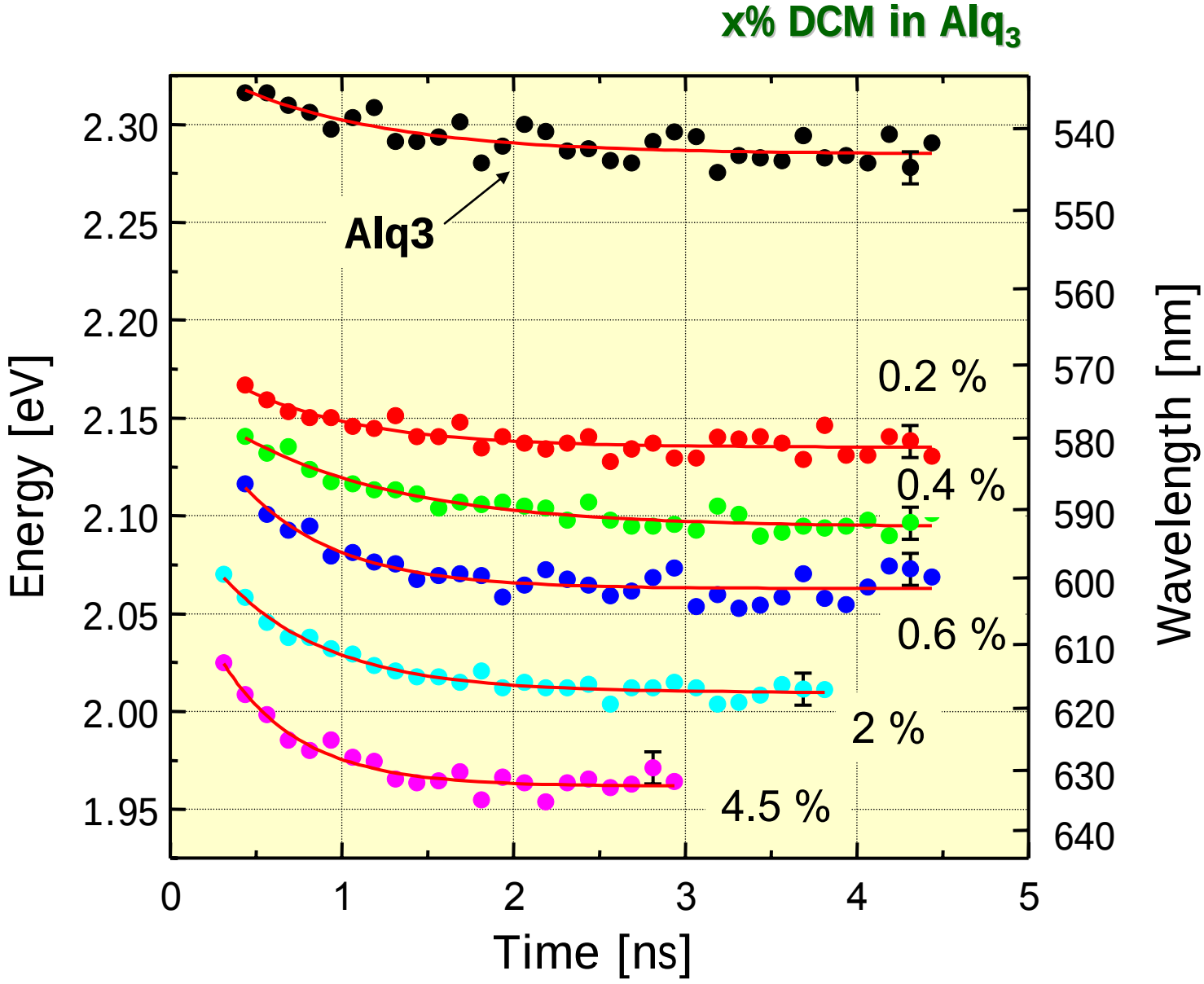
Exciton Distribution in the Excited State (S_1 or T_1)

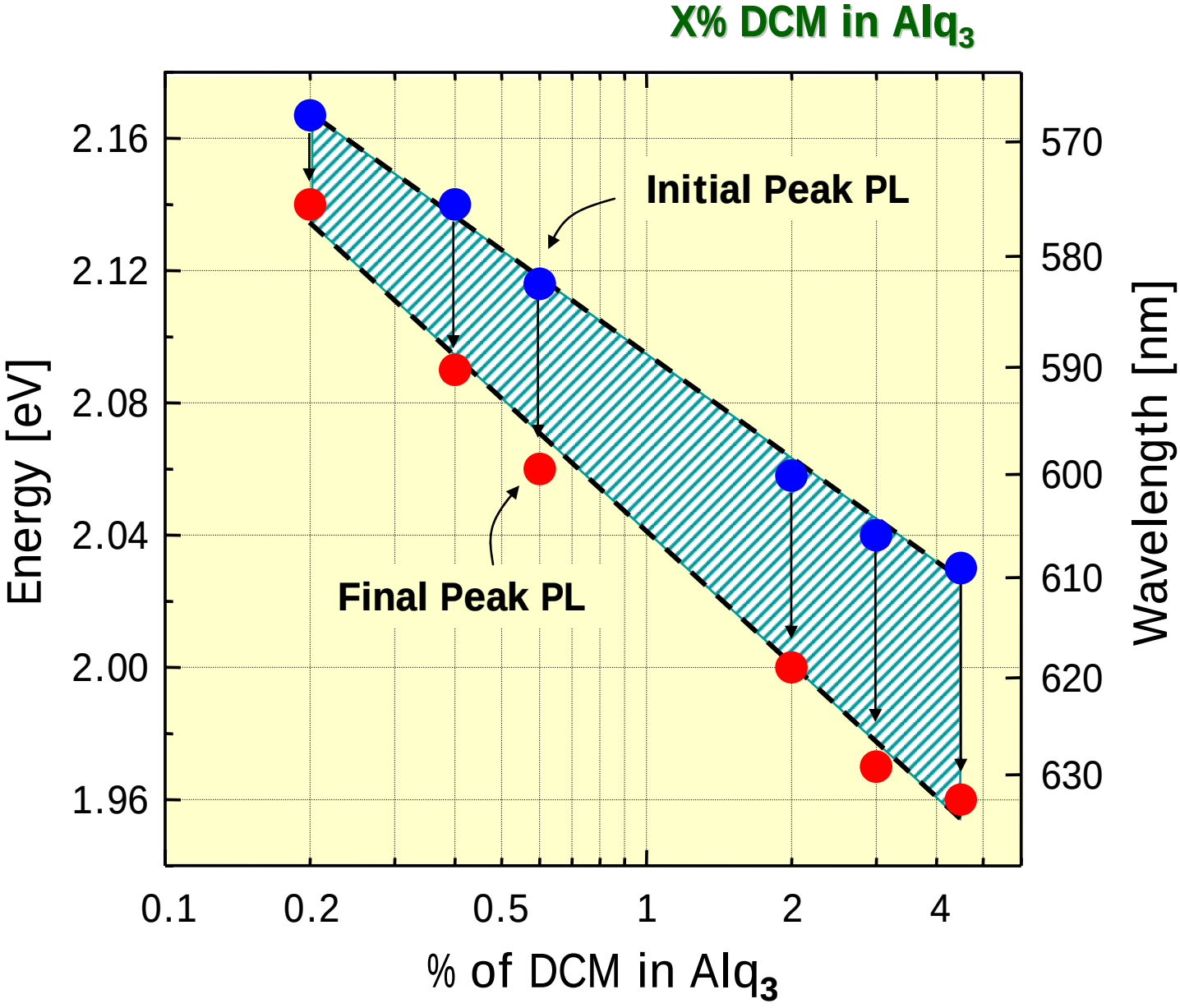
~ Time Evolved Exciton Thermalization ~



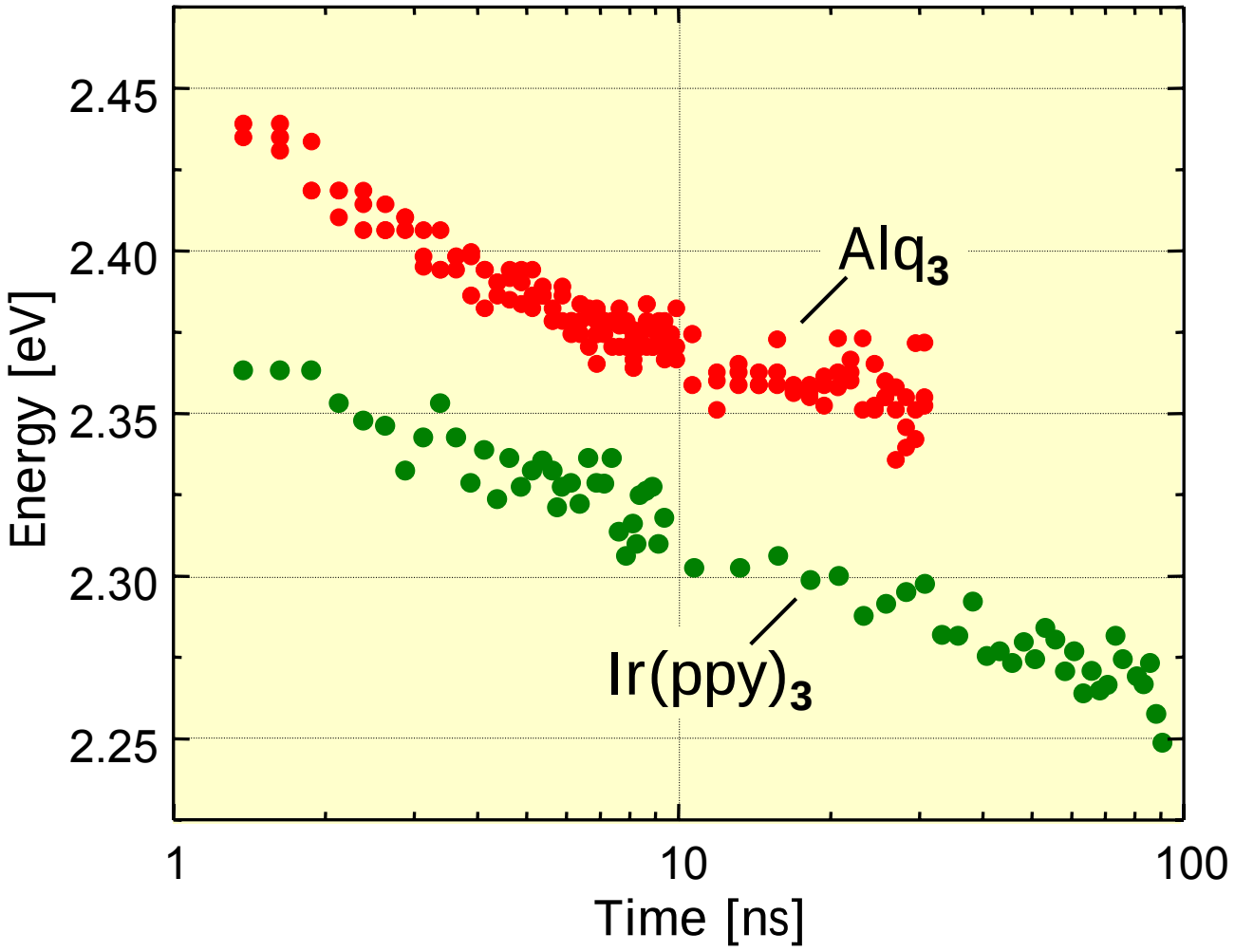
EXCITON DIFFUSION LEADS TO REDUCTION IN FWHM


4% DCM2 in Alq3
Low E midpoint
High E midpoint
FWHM
Energy
High E midpoint
T = 15~125 K
Low E midpoint
Energy [eV]
Wavelength [nm]
Time [ns]
2.10
2.05
2.00
1.95
1.90
1.85
1.80
620
640
660
680
0
1
2
3
4
5
6
7


x% DCM in Alq3
Alq3
0.2 %
0.4 %
0.6 %
2 %
4.5 %
Energy [eV]
Wavelength [nm]
Time [ns]
2.30
2.25
2.20
2.15
2.10
2.05
2.00
1.95
540
550
560
570
580
590
600
610
620
630
640
0
1
2
3
4
5

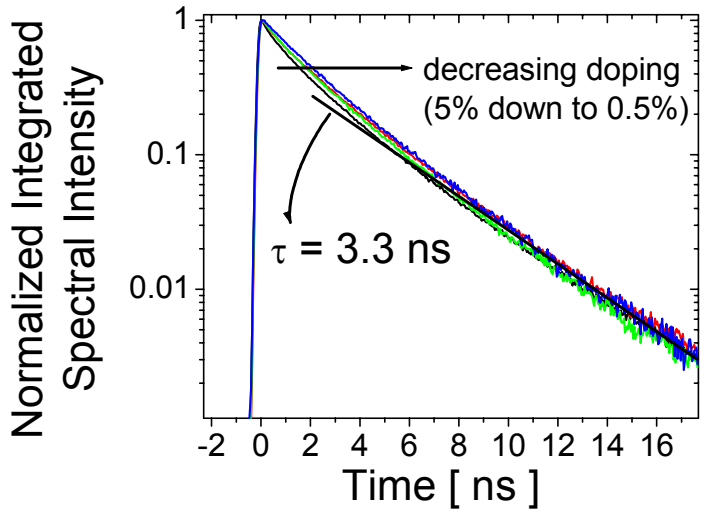

X% DCM in Alq3
Initial Peak PL
Final Peak PL
Energy [eV]
2.16
2.12
2.08
2.04
2.00
1.96
Wavelength [nm]
570
580
590
600
610
620
630
0.1
0.2
0.5
1
2
4
% of DCM in Alq3

Time Evolution of Peak PL in Neat Thin Films



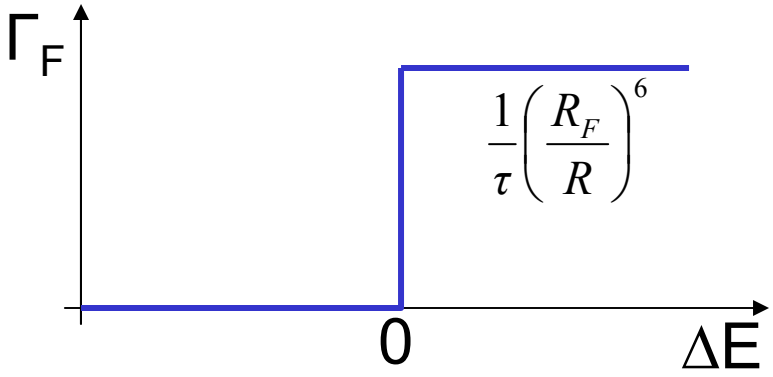
Parameters for Simulating Exciton Diffusion

observed radiative lifetime (τ)



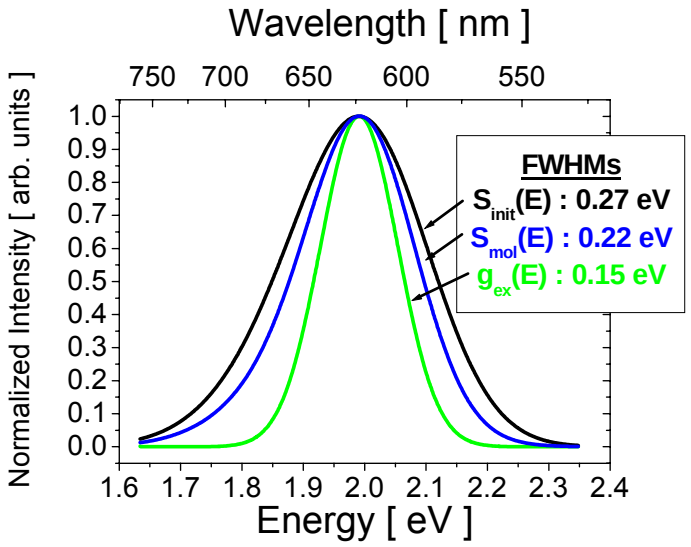
Förster radius (R_F)

- Assign value for *allowed* transfers:

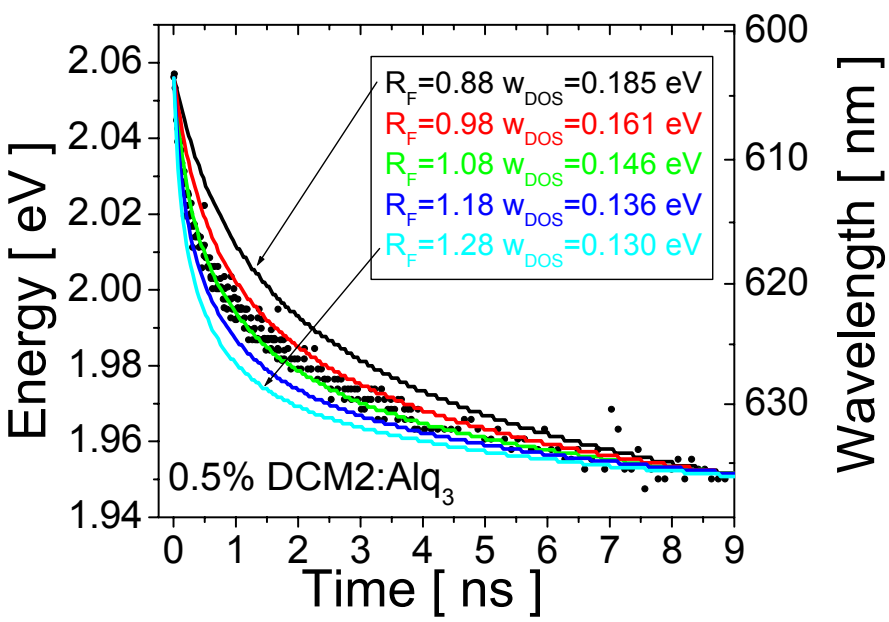


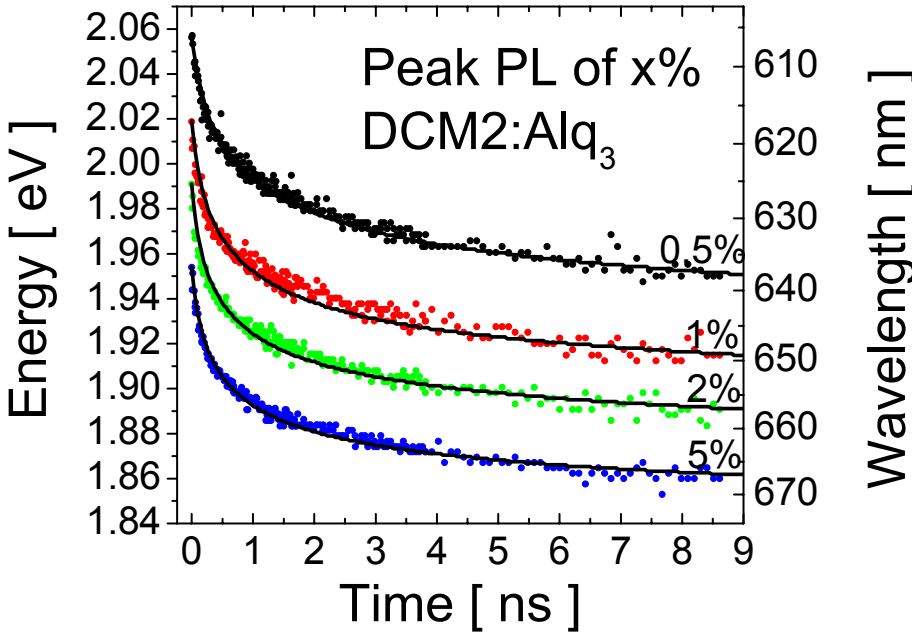
excitonic density of states ($g_{ex}(E)$)

- Assume Gaussian shape of width, w_{DOS}
- Center at peak of initial bulk PL spectrum
- Molecular PL spectrum implied…



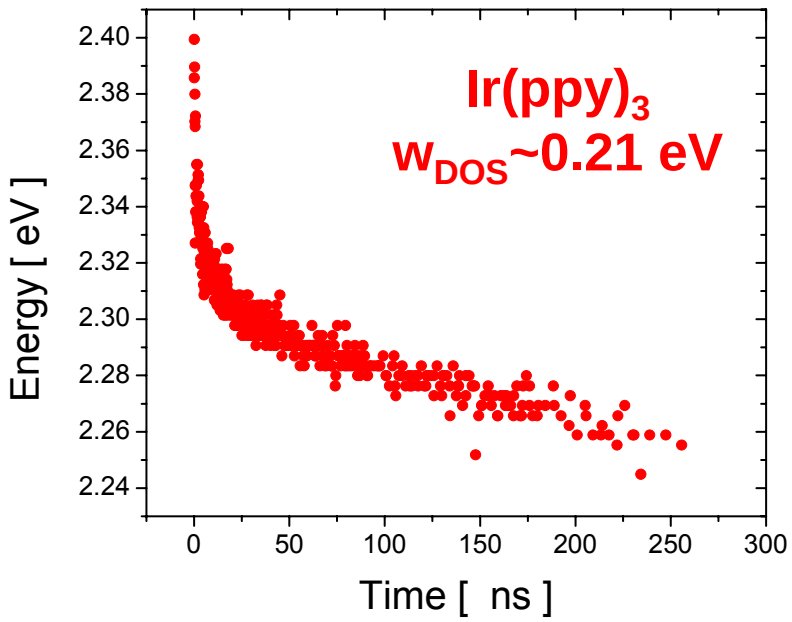
Fitting Simulation to Experiment – Doped Films



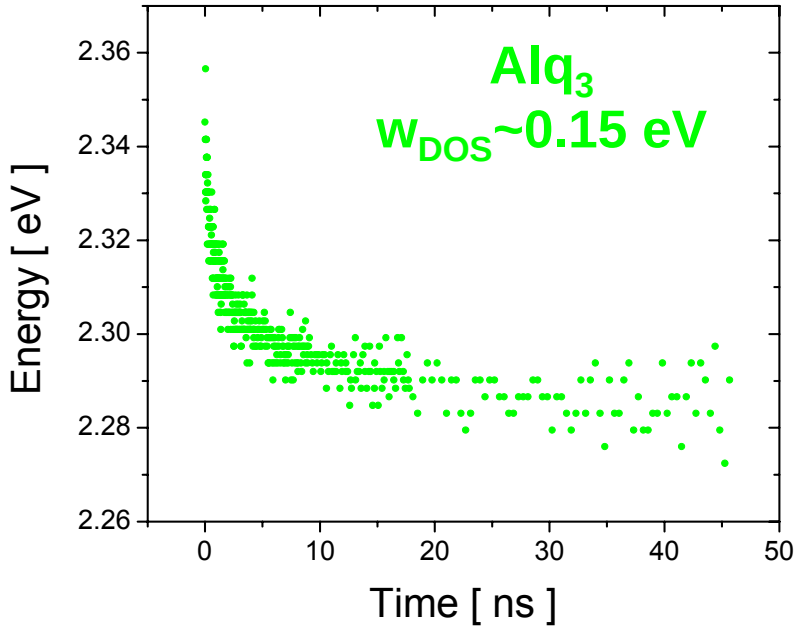


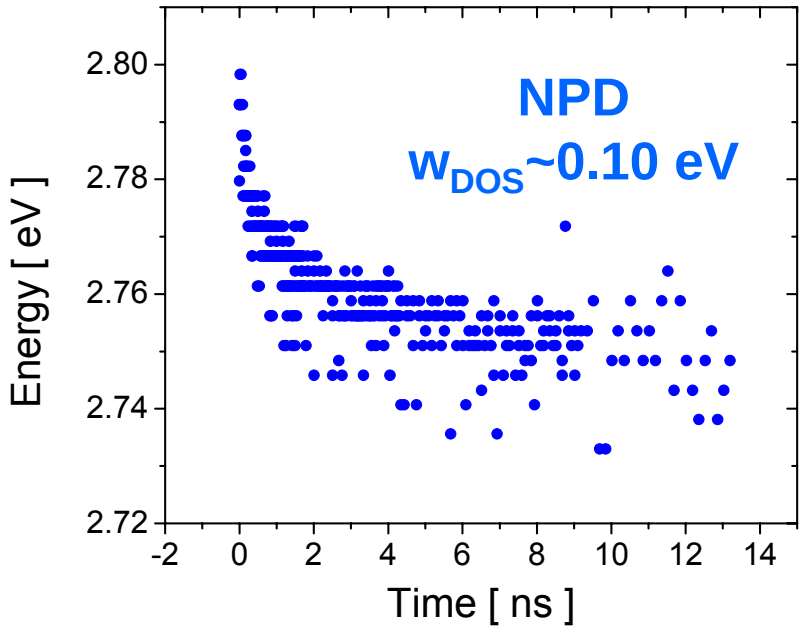
- Good fits possible for all data sets
- R_F decreases with increasing doping,
  falling from 52 Å to 22 Å
- w_{DOS} also decreases with increasing doping,
  ranging from 0.146 eV to 0.120 eV

Fitting Simulation – Neat Films



- Spectral shift observed in each material system
- Molecular dipole and w_{DOS} are correllated: **lower dipoles correspond to less dispersion**
- Even with no dipole, some dispersion exists
- Experimental technique **general**, and yields **first measurements** of **excitonic energy dispersion** in amorphous organic solids

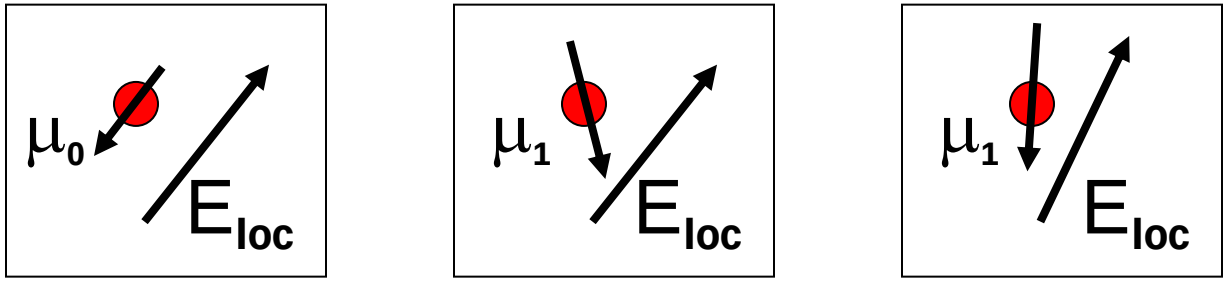




Temporal Solid State Solvation

upon excitation both magnitude and direction of lumophore dipole moment can change

FOR EXAMPLE for DCM: $\mu_1 - \mu_0 > 20$ Debye !
~ from 5.6 D to 26.3 D ~

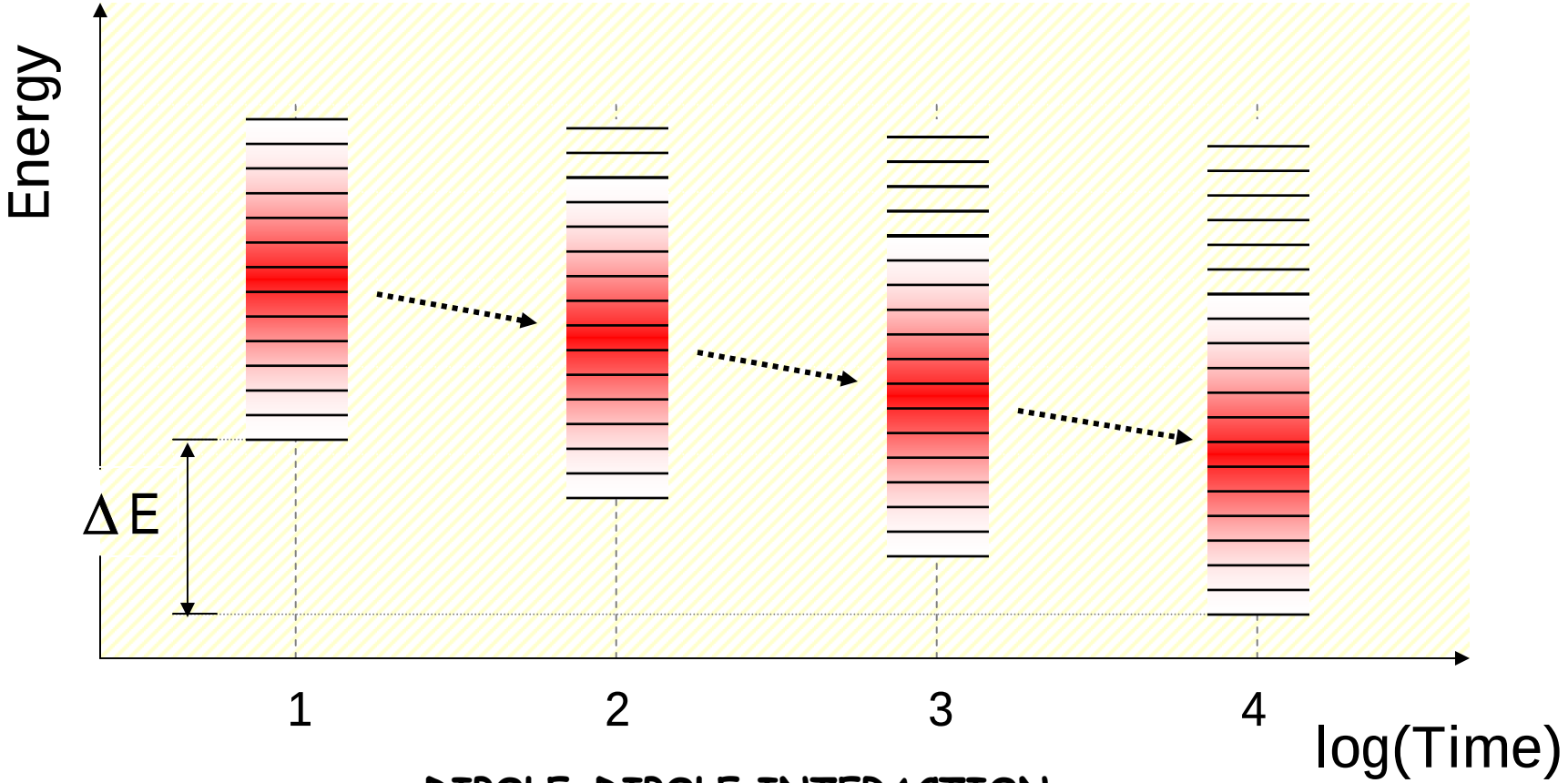


t < 0 t = 0 t ~ 1 ns

following the excitation the environment surrounding the excited molecule will reorganize to minimize the overall energy of the system (maximize $\mu \cdot E_{loc}$)

Exciton Distribution in the Excited State (S_1 or T_1)

~ Time Evolved Molecular Reconfiguration ~



DIPOLE-DIPOLE INTERACTION

LEADS TO ENERGY SHIFT IN DENSITY OF EXCITED STATES

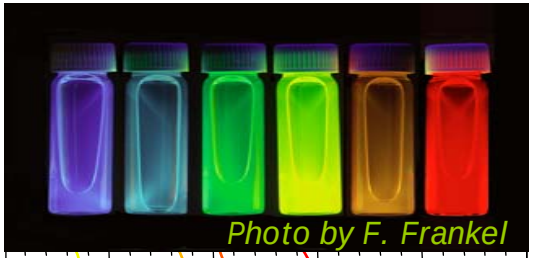
Fusion of Two Material Sets

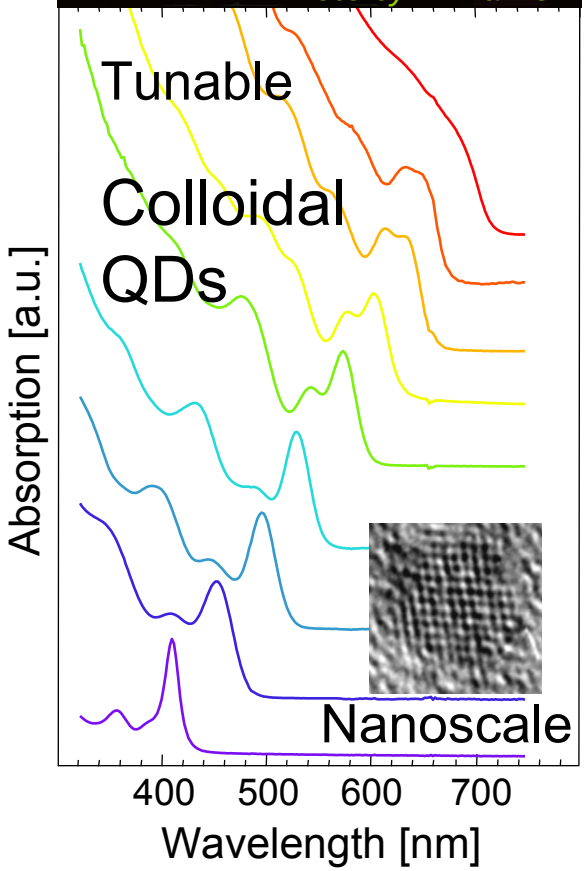
Efficient

Organic Semiconductors

Flexible

Emissive





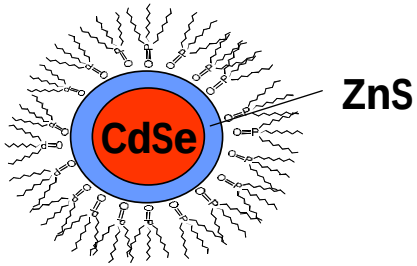
Hybrid devices could enable

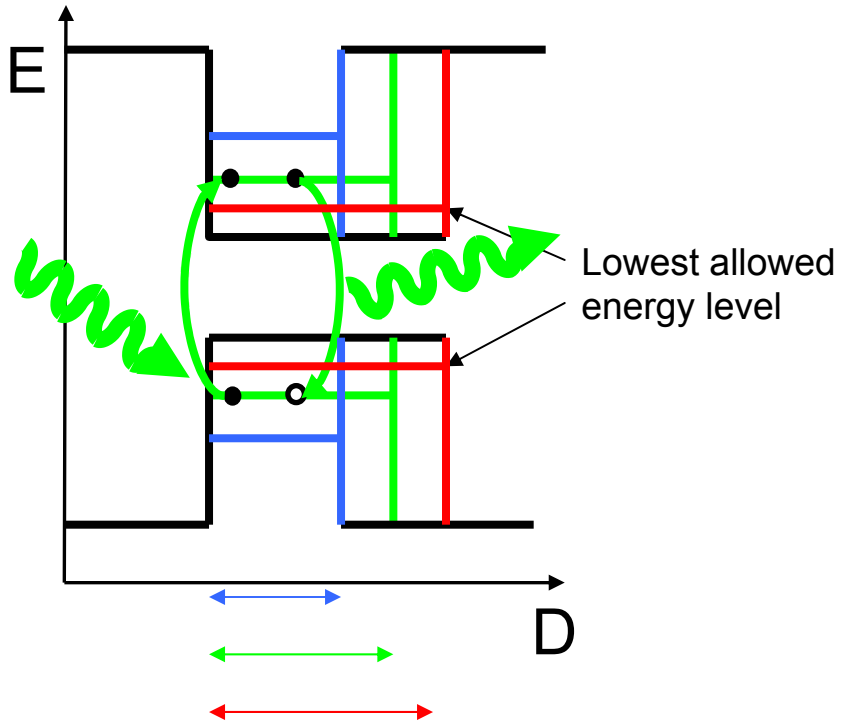
LEDs, Solar Cells, Photodetectors, Modulators, and Lasers

which utilize the best properties of each individual material.

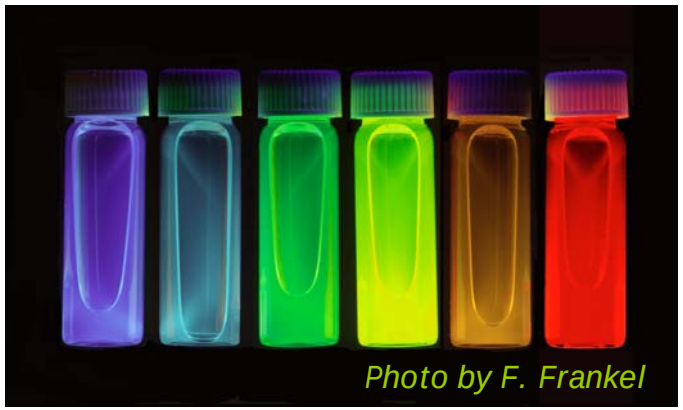
Fabrication of rational structures has been the main obstacle *to date*.

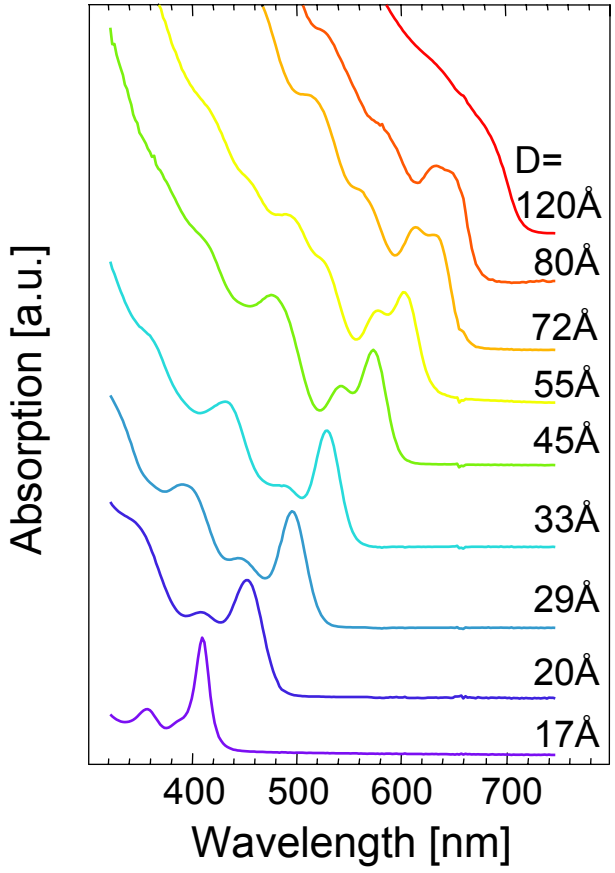
Inorganic Nanocrystals – Quantum Dots





Quantum Dot *SIZE*

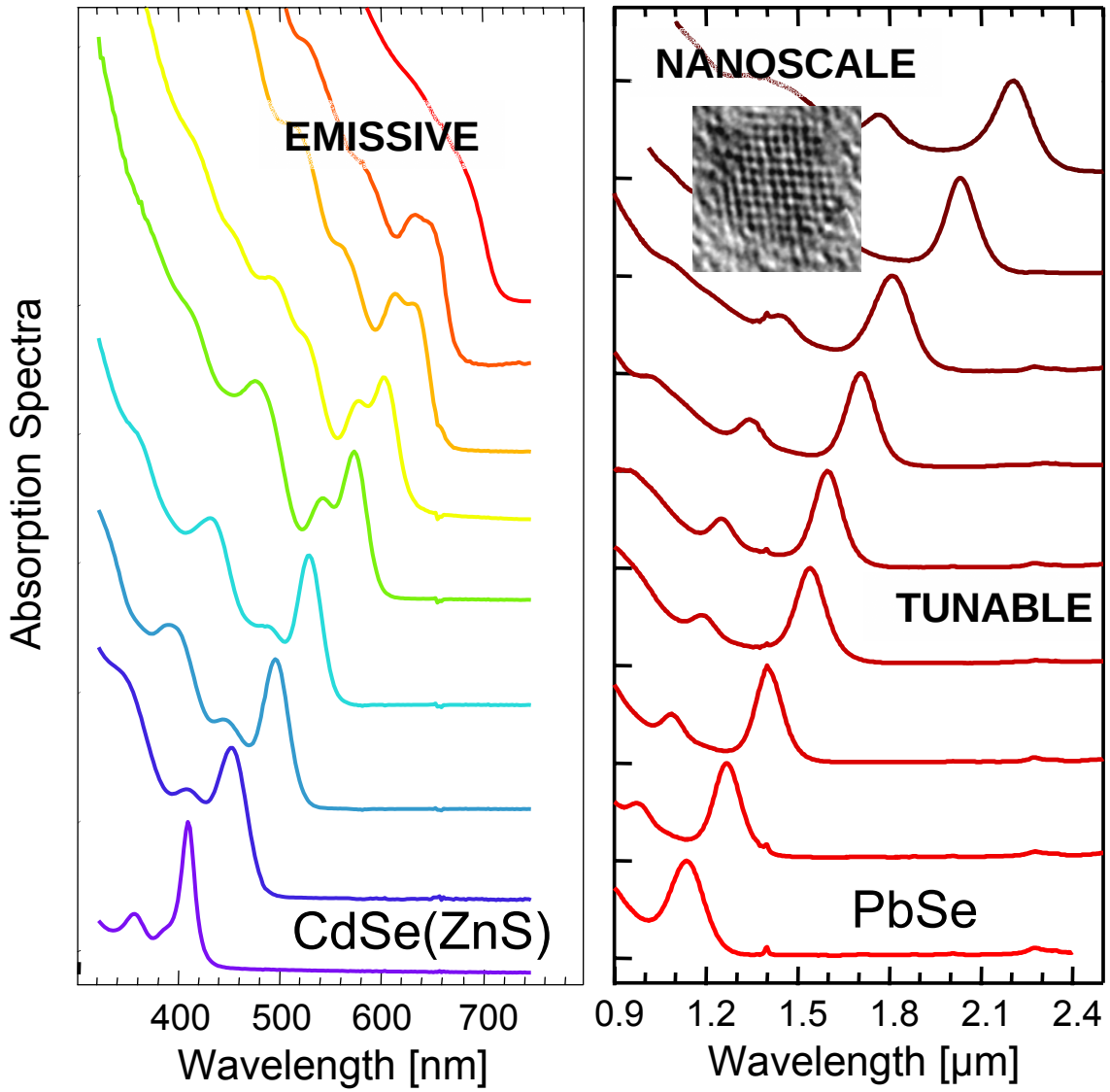




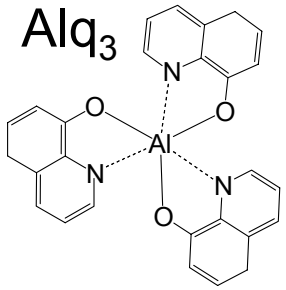
Synthetic route of Murray et al, J. Am. Chem. Soc. **115**, 8706 (1993).

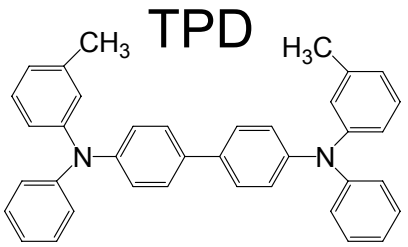
Fusion of Two Material Sets

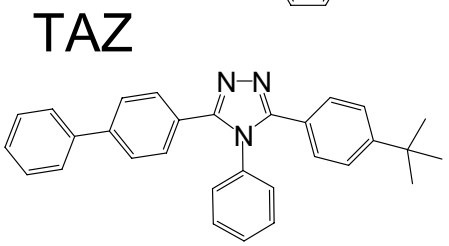
Quantum Dots

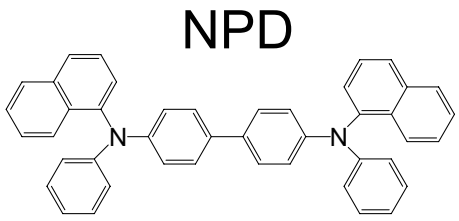


Organic Molecules









Integration of Nanoscale Materials

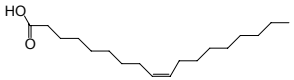
Quantum Dots and Organic Semiconductors

ZnS overcoating shell
(0 to 5 monolayers)

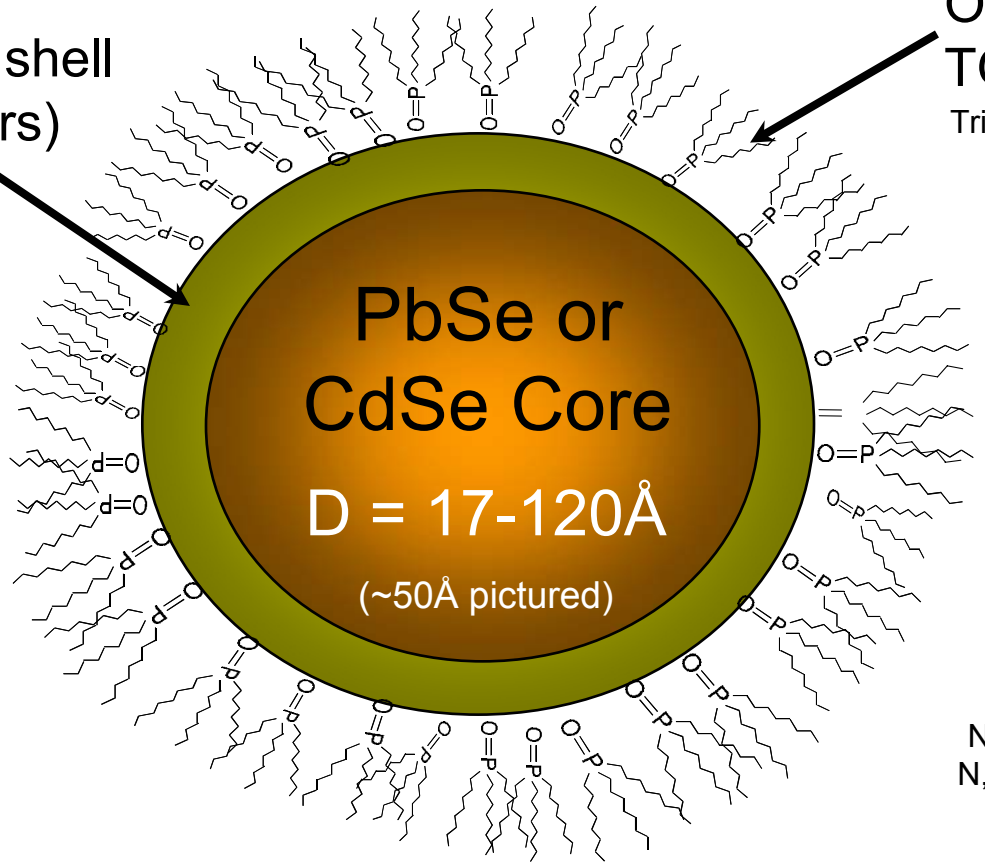
Synthetic routes of Murray et al, J. Am. Chem. Soc. **115**, 8706 (1993) and Chen, et al, *MRS Symp. Proc. 691,*G10.2.

Oleic Acid or
TOPO caps

Trioctylphosphine oxide

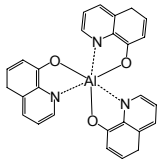


Oleic Acid



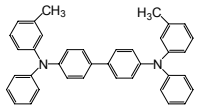
10Å

Alq_3



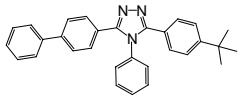
Tris(8-hydroxyquinoline)
Aluminum (III)

TPD



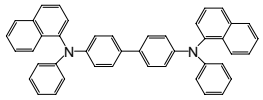
N,N'-Bis(3-methylphenyl)-
N,N'-bis-(phenyl)-benzidine

TAZ



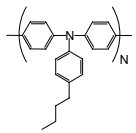
3-(4-Biphenylyl)-4-phenyl-5-
tert-butylphenyl-1,2,4-triazole

NPD



N,N'-Bis(naphthalen-1-yl)-
N,N'-bis(phenyl)benzidine

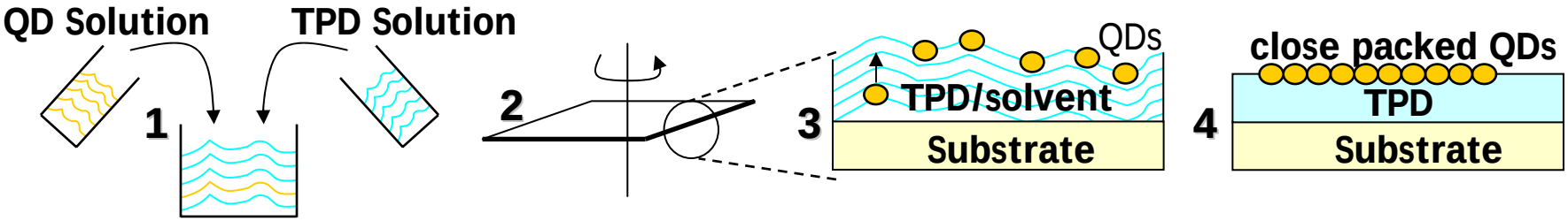
poly-TPD



Differences in:	Chemistry	Size
Molecular Organics	Aromatic	"Small"
Quantum Dots	Aliphatic Caps	"Big"

➔Phase Segregation

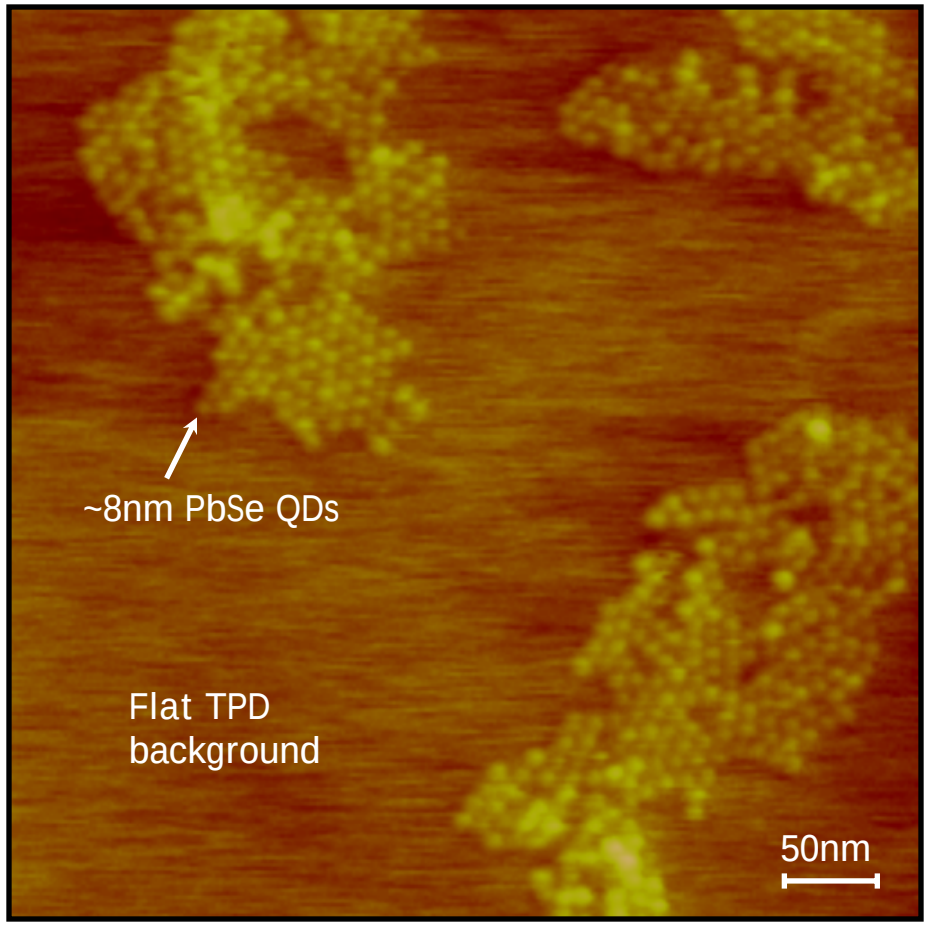
Phase Segregation and Self-Assembly



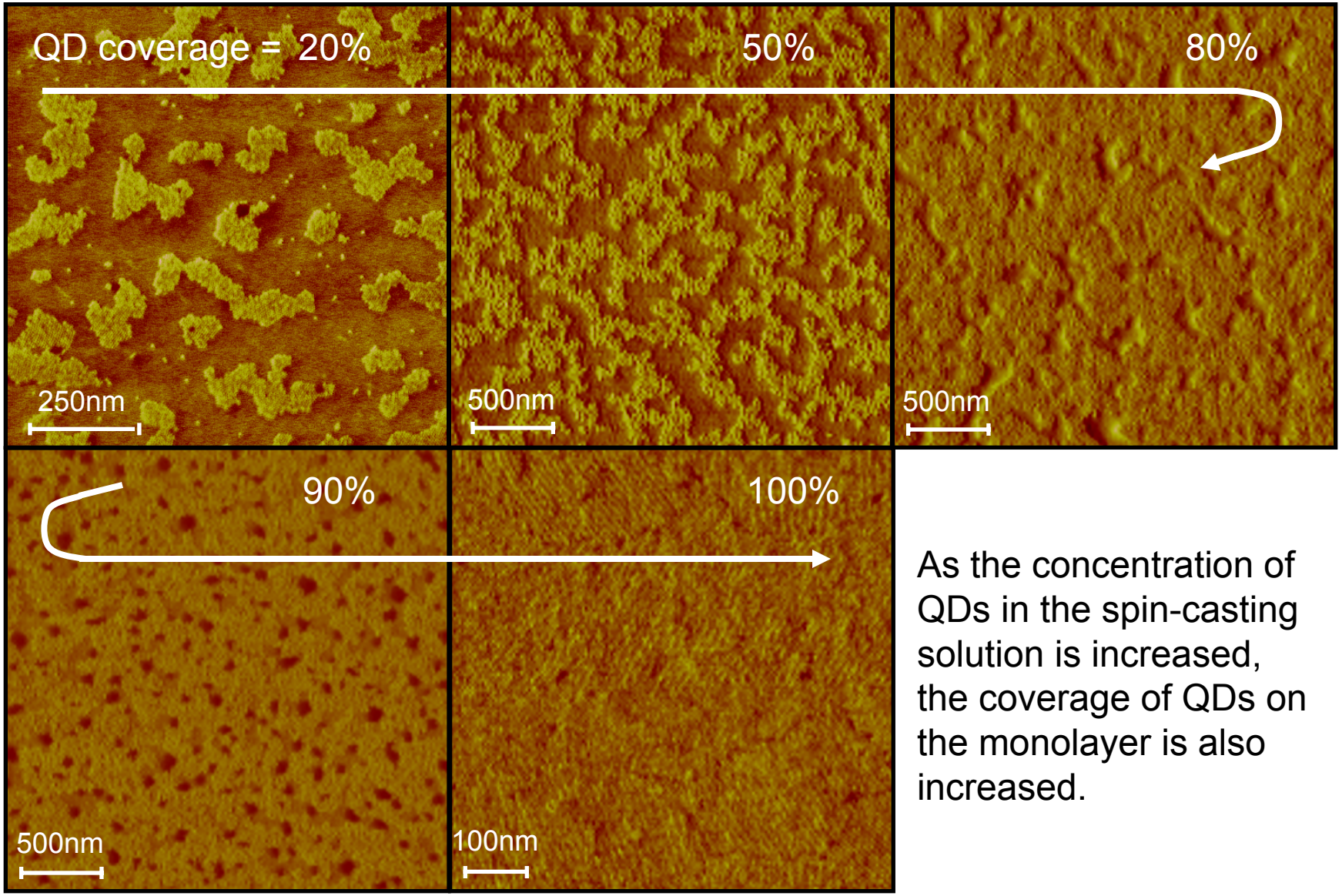
1. A solution of an organic material, QDs, and solvent…
2. is spin-coated onto a clean substrate.
3. During the solvent drying time, the QDs rise to the surface…
4. and self-assemble into grains of hexagonally close packed spheres.

Organic hosts that deposit as flat films allow for imaging via AFM, despite the AFM tip being as large as the QDs.

Phase segregation is driven by a combination of ***size and chemistry.***

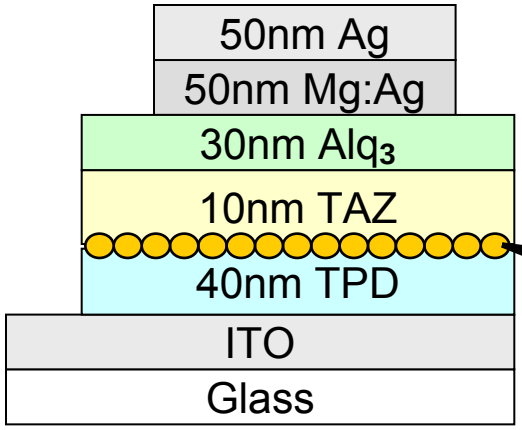


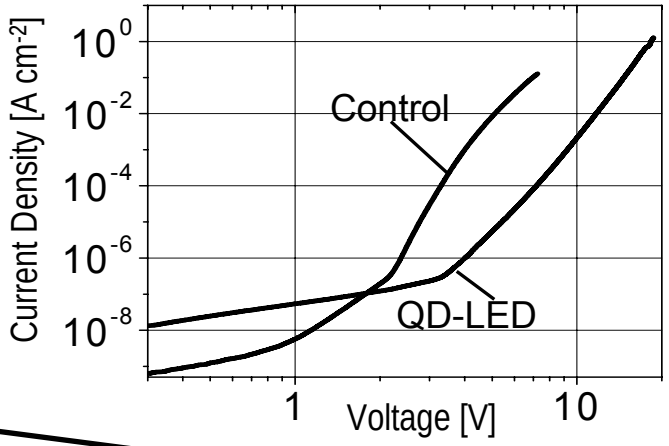
Monolayer Coverage – QD concentration

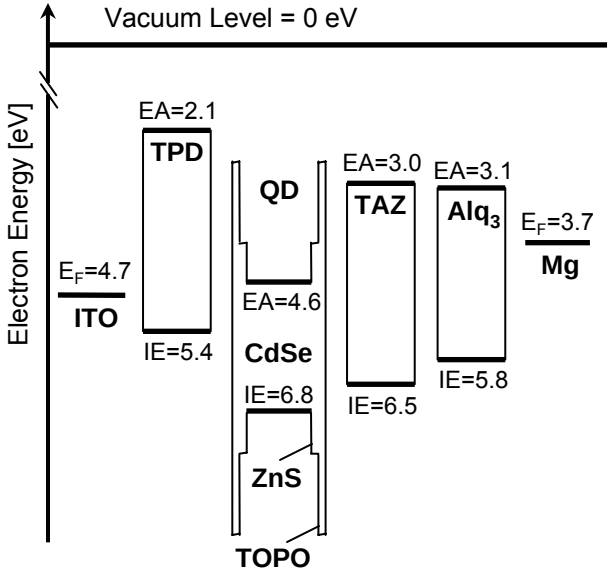


As the concentration of QDs in the spin-casting solution is increased, the coverage of QDs on the monolayer is also increased.

QD-LED Performance

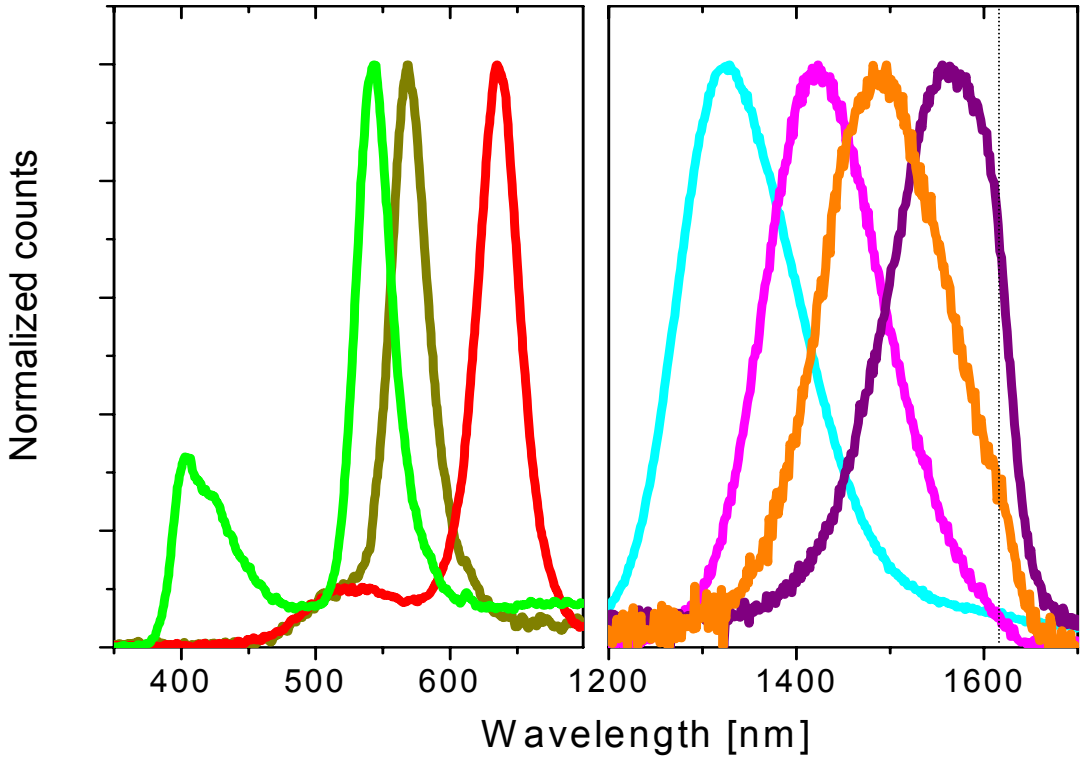


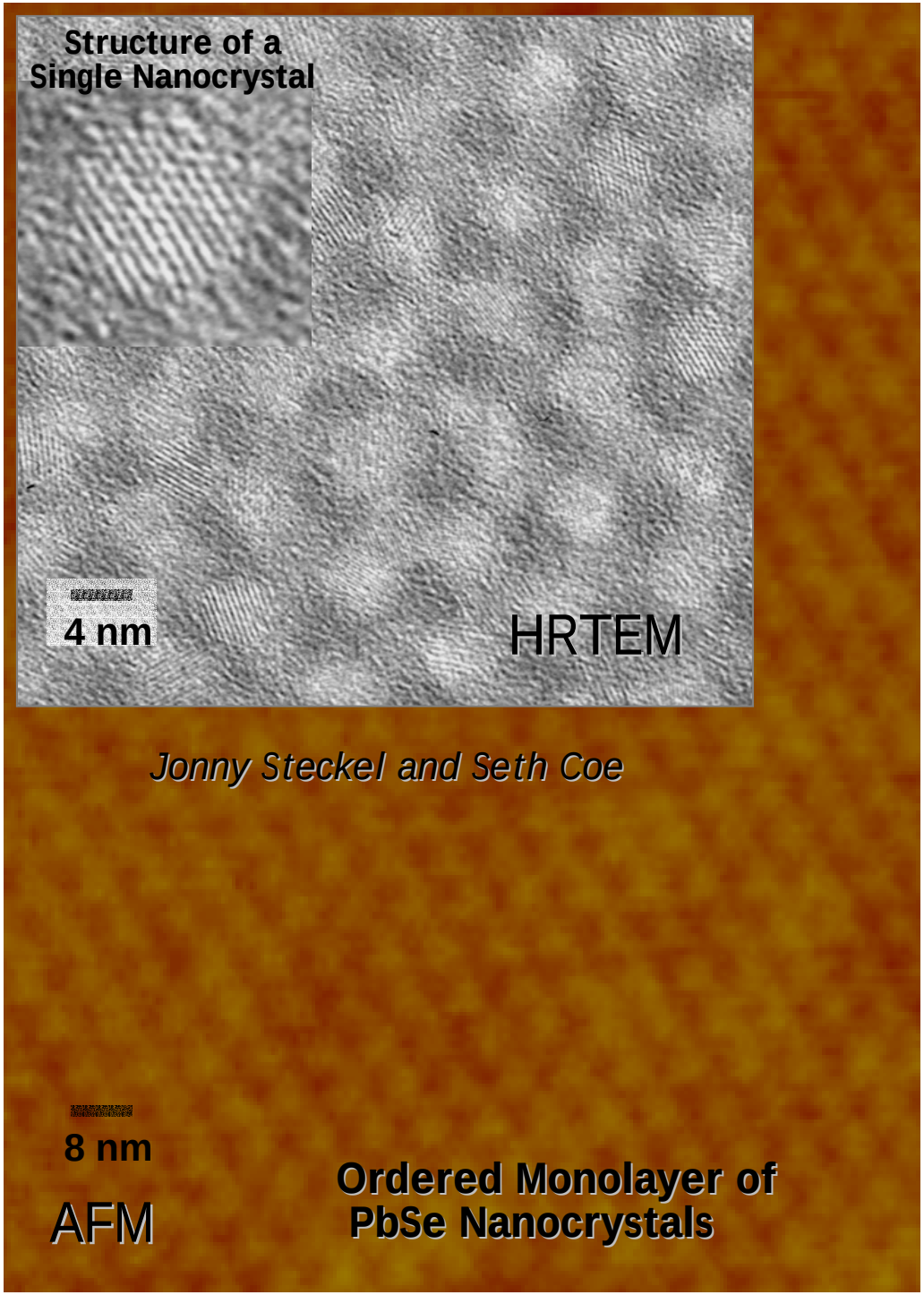


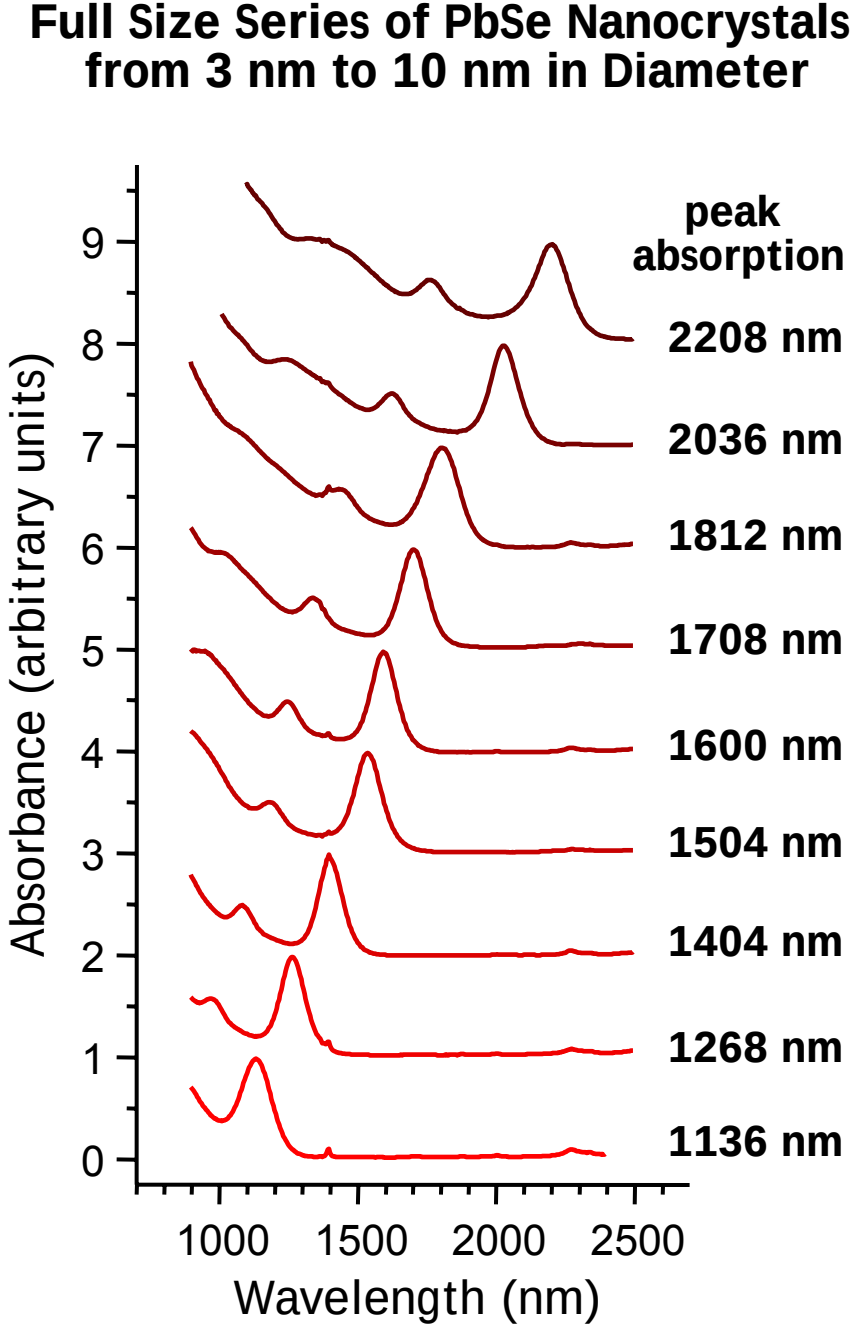


CdSe(ZnS)/TOPO

PbSe/oleic acid

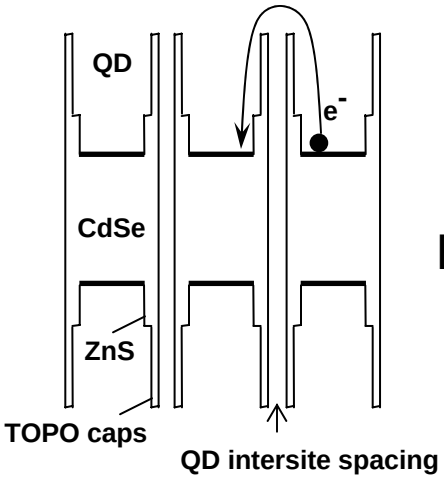



Structure of a
Single Nanocrystal
4 nm
HRTEM
Jonny Steckel and Seth Coe
8 nm
AFM
Ordered Monolayer of
PbSe Nanocrystals

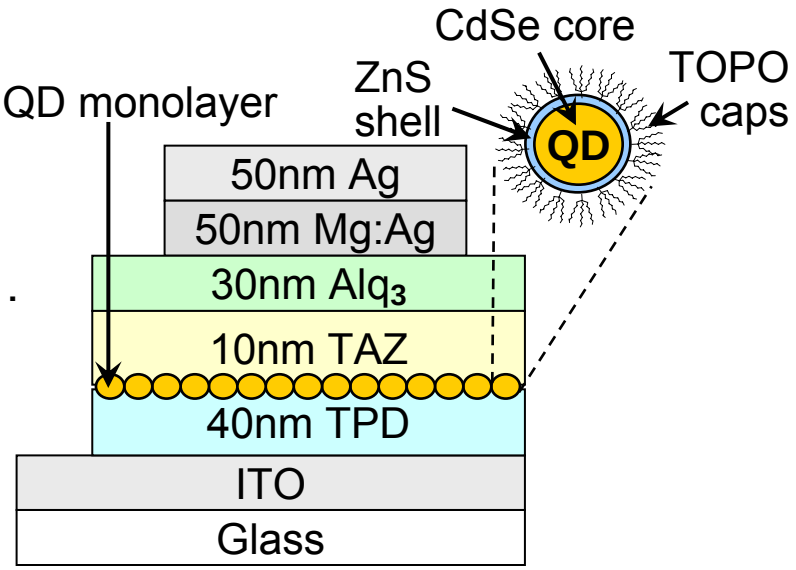

Full Size Series of PbSe Nanocrystals
from 3 nm to 10 nm in Diameter
peak
absorption
2208 nm
2036 nm
1812 nm
1708 nm
1600 nm
1504 nm
1404 nm
1268 nm
1136 nm
Absorbance (arbitrary units)
0
1
2
3
4
5
6
7
8
9
1000
1500
2000
2500
Wavelength (nm)

Design of Device Structures

QDs are poor charge transport materials...



But efficient emitters…



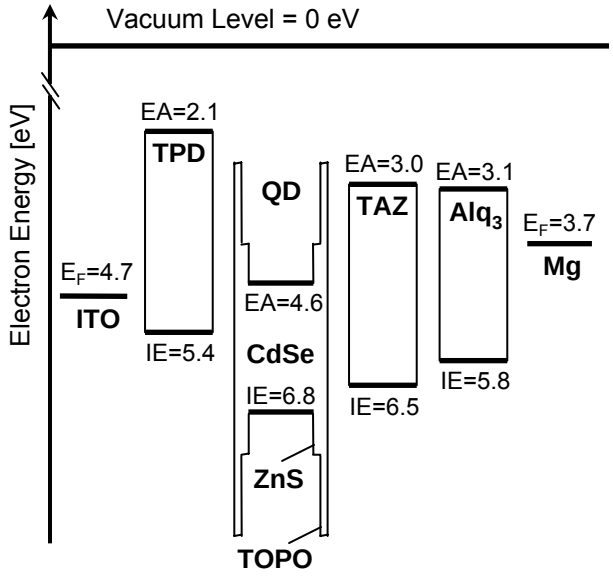
Isolate layer functions of maximize device performance.

1. Generate excitons on organic sites.
2. Transfer excitons to QDs via Förster or Dexter energy transfer.
3. QD electroluminescence.

Need a *new fabrication method* in order to be able to make such double heterostructures:

Phase Segregation.

Use organics for charge transport.



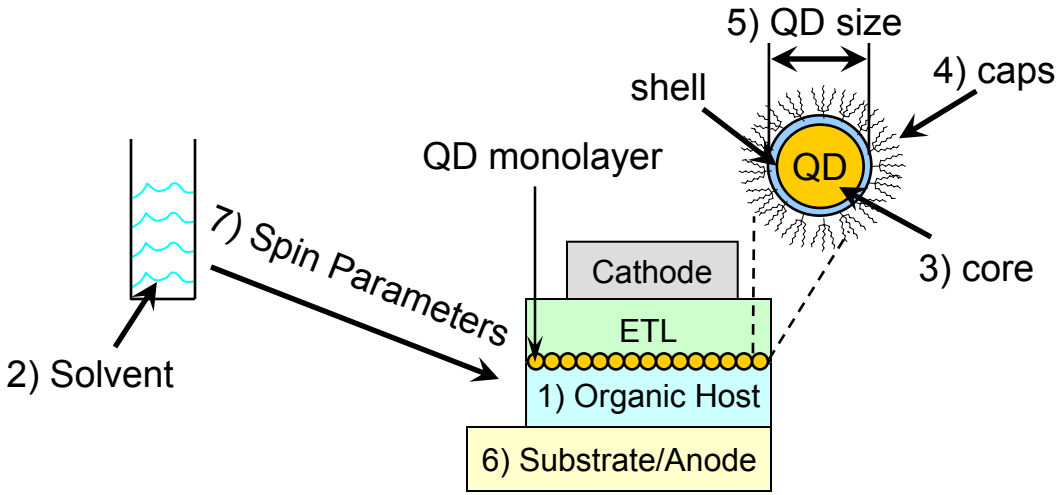
A general method?

Phase segregation occurs for different

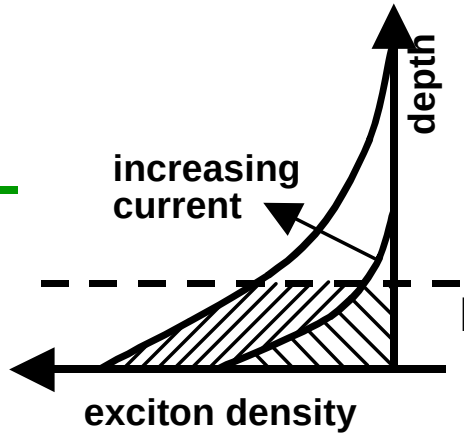
1) organic hosts: TPD, NPD, and poly-TPD.
2) solvents: chloroform, chlorobenzene, and mixtures with toluene.
3) QD core materials: PbSe, CdSe, and CdSe(ZnS).
4) QD capping molecules: oleic acid and TOPO.
5) QD core size: 4-8nm.
6) substrates: Silicon, Glass, ITO.
7) Spin parameters: speed, acceleration and time.

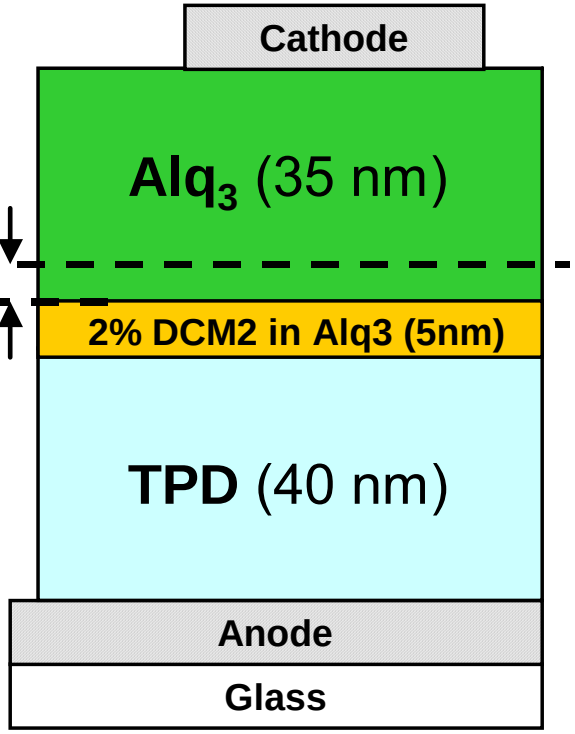
- **This process is robust, but further exploration is needed to broadly generalize these findings.**
- **For the explored materials, consistent description is possible.**
- **We have shown that the process is not dependent on any one material component.**

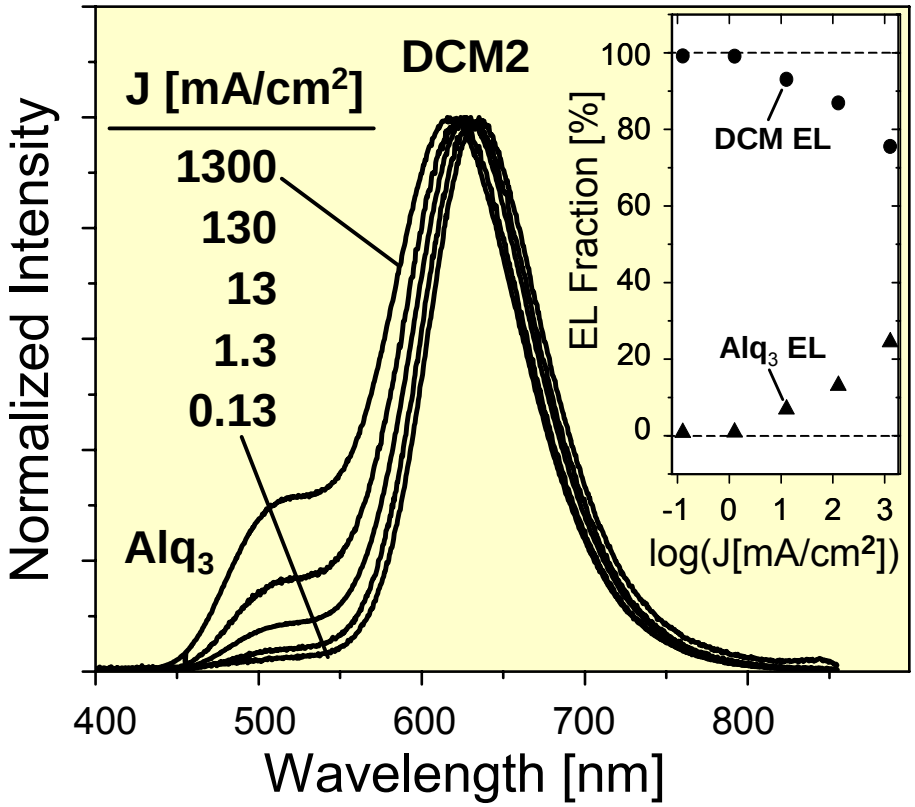
Phase segregation → *QD-LED structures*



EL Recombination Region Dependence on Current

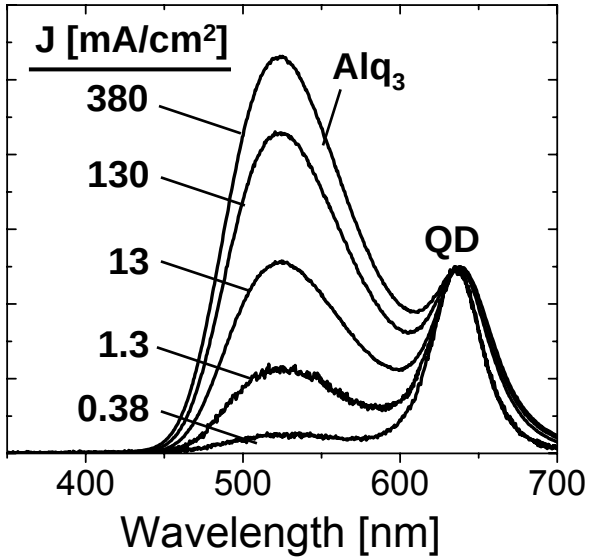




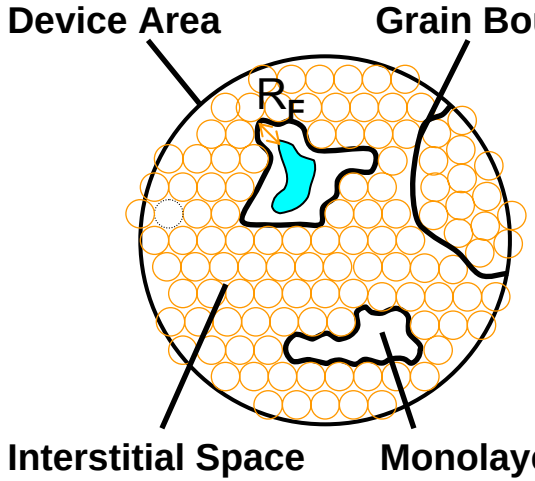


Coe et al., Org. Elect. (2003)

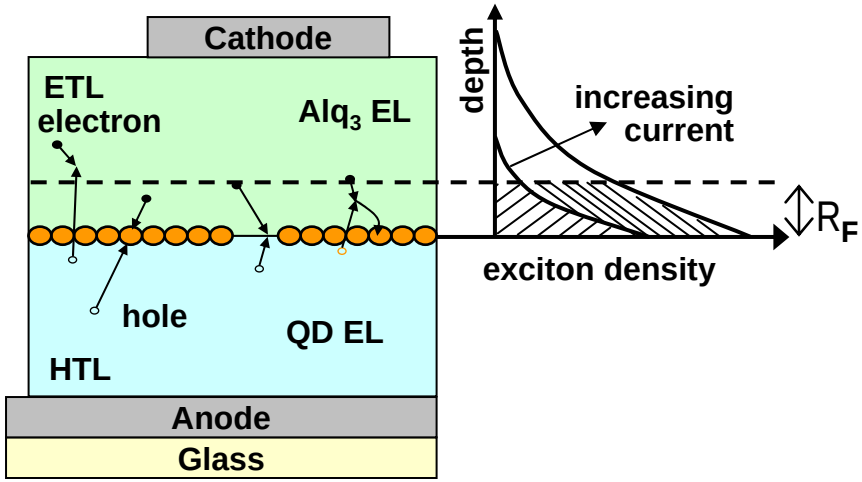
Spectral Dependence on Current Density



TOP DOWN VIEW of the QD MONOLAYER



Exciton recombination width far exceeds the QD monolayer thickness at *high current density*. To achieve true monochrome emission, new exciton confinement techniques are needed.



CROSS-SECTIONAL VIEW of QD-LED

Benefits of Quantum Dots in Organic LEDs

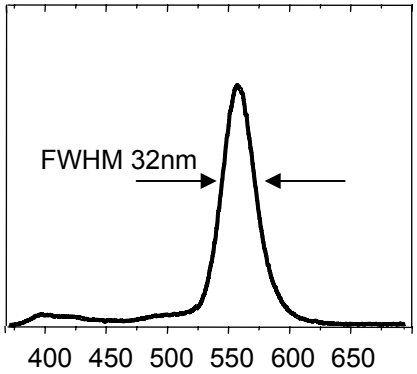
Demonstrated:

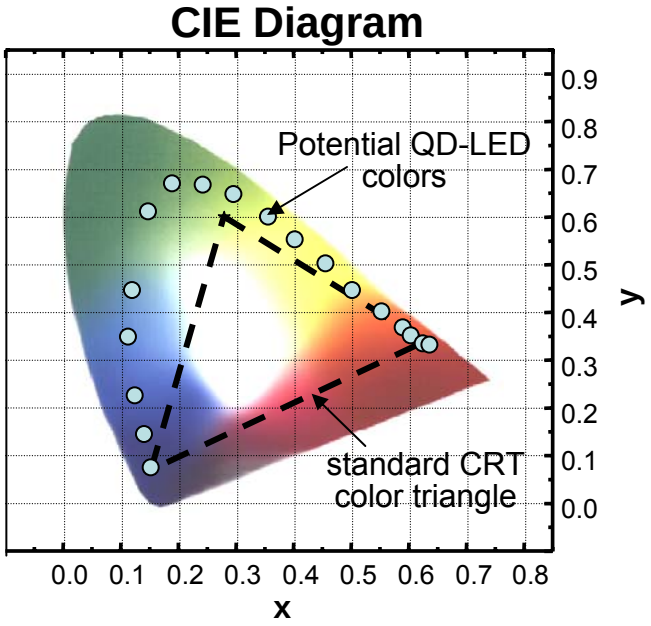
- Spectrally Tunable – single material set can access most of visible range.
- Saturated Color – linewidths of < 35nm Full Width at Half of Maximum.
- Can easily tailor "external" chemistry without affecting emitting core.
- Can generate large area infrared sources.

Potential:

- High luminous efficiency LEDs possible even in red and blue.
- Inorganic – potentially more stable, longer lifetimes.

The ideal dye molecule!





Coe *et al*, Nature **420**, 800 (2002).