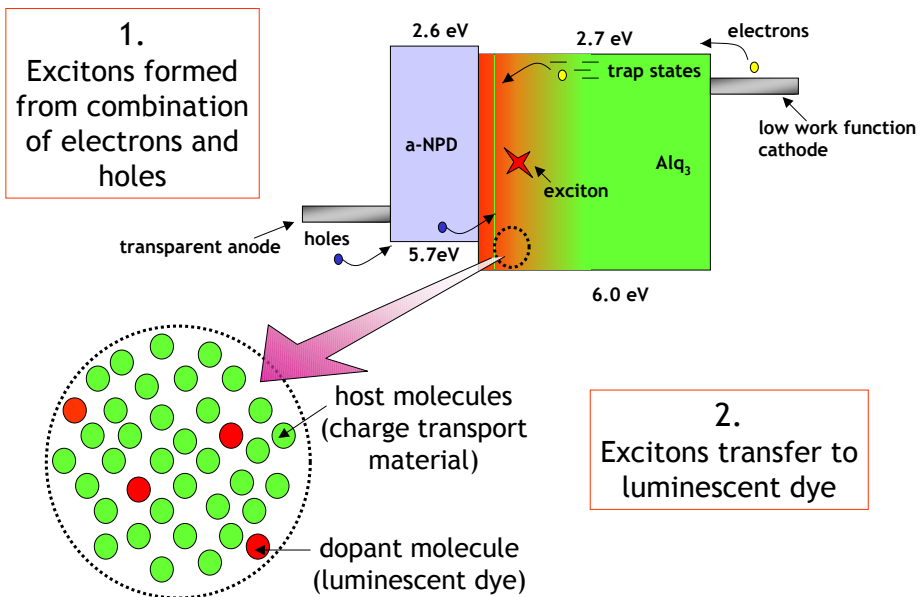# Organic LEDs – part 7

- Solvation Effect - Review

- Solid State Solvation

- Exciton Dynamics in Disordered Organic Thin Films

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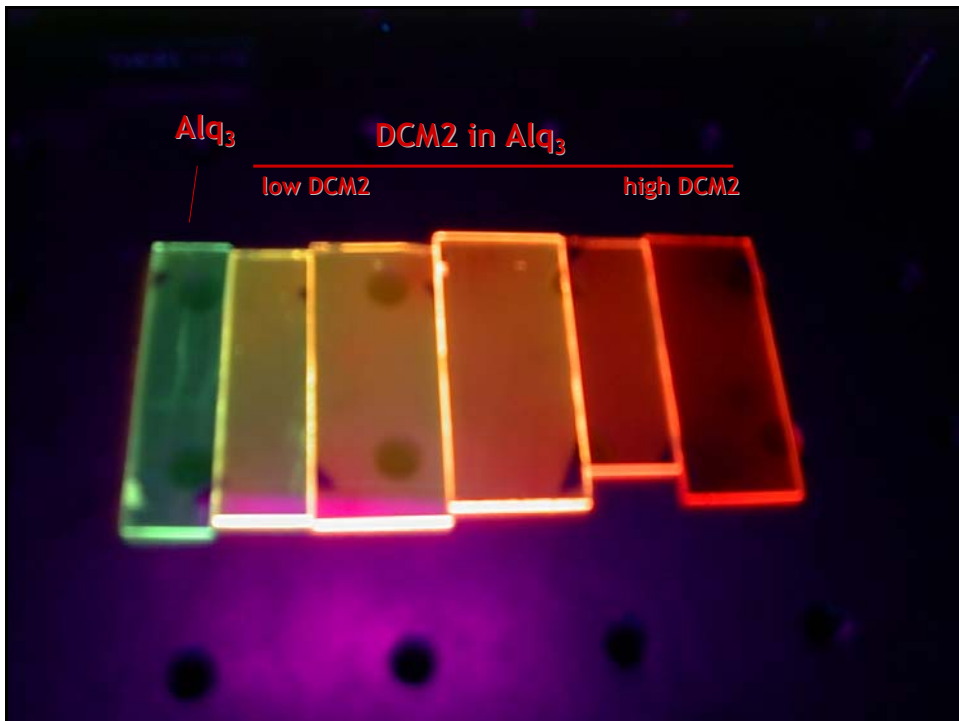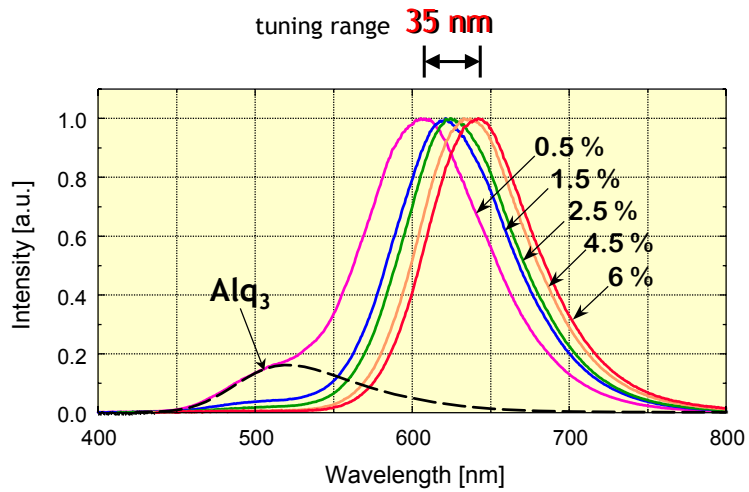
Handout on QD-LEDs: Coe et al., Nature 420, 800 (2002).

looe
@ MIT

Electroluminescence in Doped Organic Films

1.
Excitons formed from combination of electrons and holes

2.6 eV

2.7 eV

electrons

trap states

a-NPD

Alq_3

low work function cathode

exciton

transparent anode

holes

5.7eV

6.0 eV

host molecules (charge transport material)

2.
Excitons transfer to luminescent dye
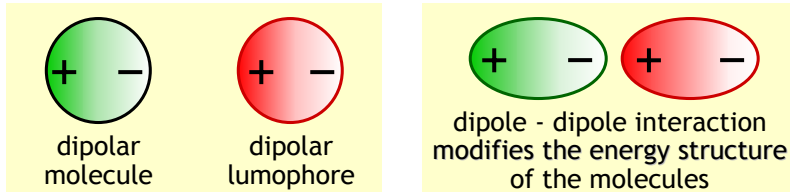
dopant molecule (luminescent dye)

Electroluminescence of **x% DCM2 in Alq₃** OLEDs

SOLVATOCHROMISM

... change in the spectral position of
aborption/luminescence band
due to change in the polarity of the medium

dipolar molecule	dipolar lumophore

dipole - dipole interaction modifies the energy structure of the molecules

⇨ solvation is a physical perturbation of lumophore's molecular states
⇨ isolated molecule (in a gas phase) and solvated molecule
   are in the same chemical state
(**no** solvent induced proton or electron transfer, ionization, complexation, isomerization)

Solid State Solvation (SSS)

$$\Delta E = \Delta \langle \mu \cdot \mathcal{E}_{loc} \rangle$$

$\mathcal{E}_{loc} \sim 10^7$ V/cm
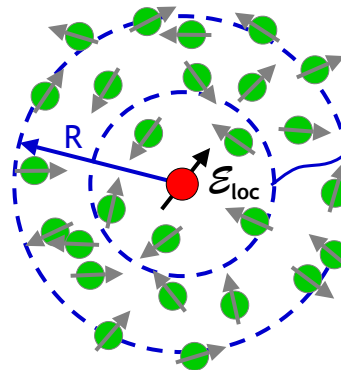
$\langle \mu \rangle > 0$

$\langle \mu \rangle \rightarrow 0$
as R → large

🔴 polar lumophore

🟢 dipolar host with moment μ

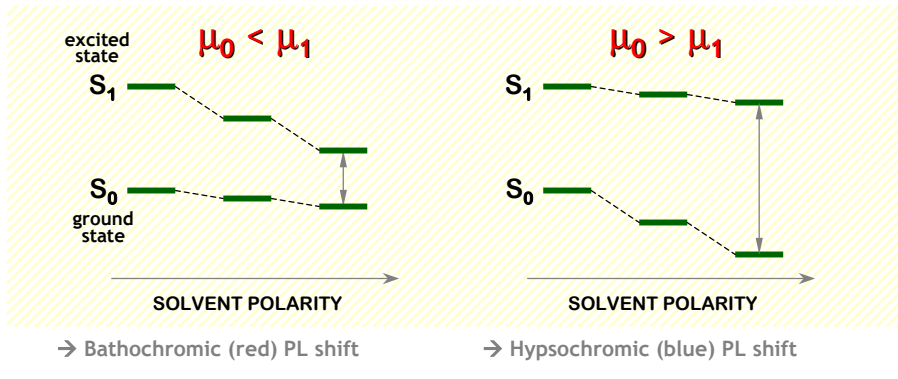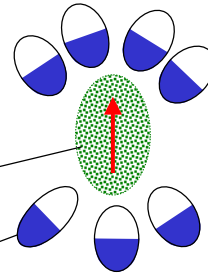"self polarization"
for strongly dipolar lumophores

(aggregation possible for highly polar molecules)

Influence of μ_0 and μ_1 on Chromatic Shift Direction

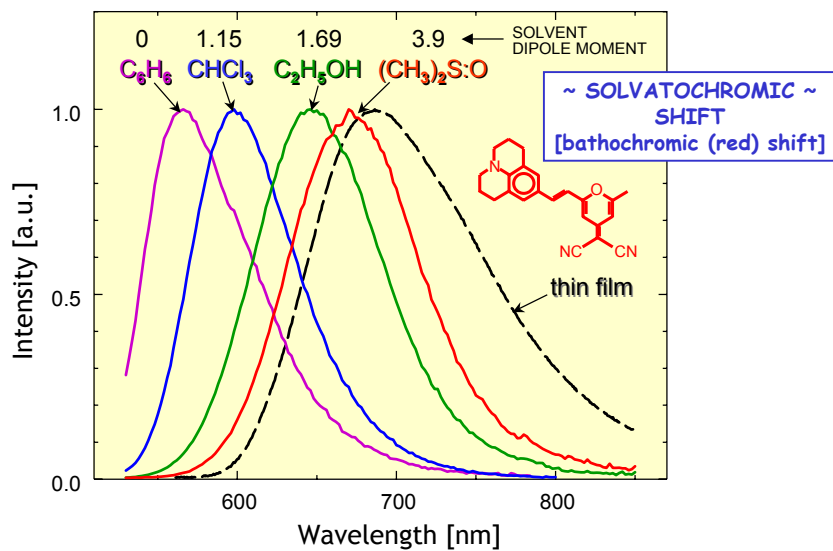$$\Delta E = \Delta \langle \mu \cdot \mathcal{E} \rangle$$

solute (chromophore)
WITH DIPOLE MOMENT μ

solvent

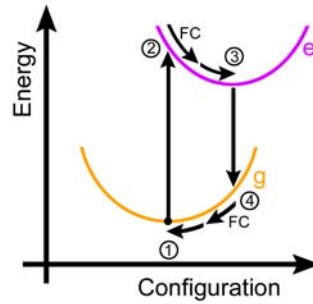$\mu_0 < \mu_1$

excited state
S_1

S_0
ground state

SOLVENT POLARITY

→ Bathochromic (red) PL shift

$\mu_0 > \mu_1$

S_1

S_0

SOLVENT POLARITY

→ Hypsochromic (blue) PL shift

PL of DCM2 Solutions and Thin Film

Bulović et al., *Chem. Phys. Lett.* 287, 455 (1998).

| 0 | 1.15 | 1.69 | 3.9 | ← SOLVENT DIPOLE MOMENT |
| C_6H_6 | $CHCl_3$ | C_2H_5OH | $(CH_3)_2S{:}O$ | |

~ SOLVATOCHROMIC ~
SHIFT
[bathochromic (red) shift]

thin film

Intensity [a.u.]

1.0

0.5

0.0

600   700   800

Wavelength [nm]

Dynamic Relaxation Picture (a.k.a. solvation)

μ_e, $E^*_{g,loc}$
②

Excited State
(non-equilibrium)

μ_e, $E_{e,loc}$
③

Excited State
(equilibrium)

μ_g, $E_{g,loc}$
①

Ground State
(equilibrium)

μ_g, $E^*_{e,loc}$
④

Ground State
(non-equilibrium)

Energy

② FC ③ e

g

① FC ④

Configuration
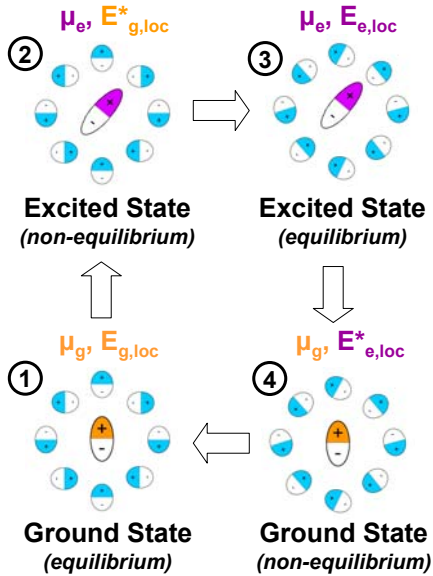
Continuum, Dipole in Spherical Cavity Model:
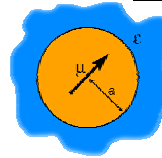
$$\vec{E}_{loc} = \underbrace{\frac{2(\varepsilon-1)}{2\varepsilon+1}}_{\Gamma'''_\varepsilon}\frac{\vec{\mu}}{a^3}$$

Thin Film Photoluminescence

Intensity [a.u.]

635 nm
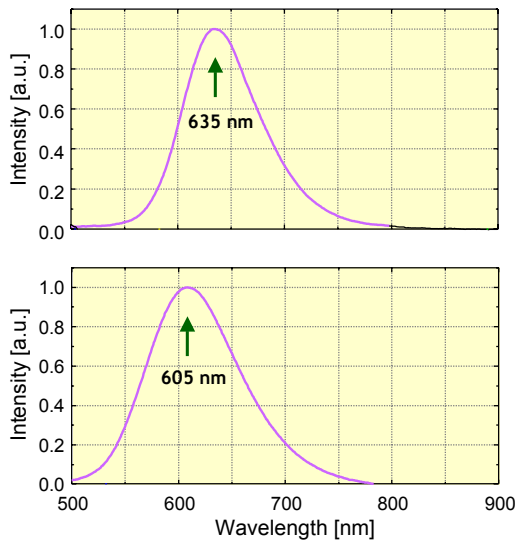
1% DCM2 in Alq$_3$

polar host
$\mu \sim 5.5$ D

Intensity [a.u.]
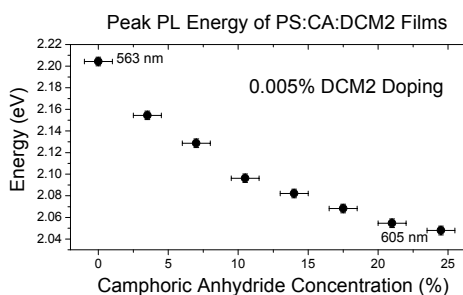
605 nm

1% DCM2 in Zrq$_4$

non-polar host

Wavelength [nm]

A "Cleaner" Experiment

- Employ trace DCM2 so as to effectively eliminate aggregation
- But still appreciably change local medium $\Rightarrow$ use *another* dopant!
   - should be polar and optically inactive (i.e. wide band gap)

DCM2

Camphoric Anhydride (CA)

Polystyrene (PS)

PL Spectra of Different PS:CA:DCM2 Films

CA %: 25%

0%

0.005% DCM2 Doping

Normalized Intensity

Energy (eV)
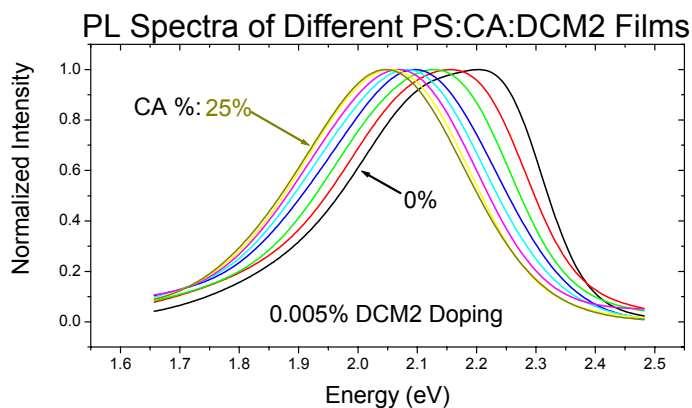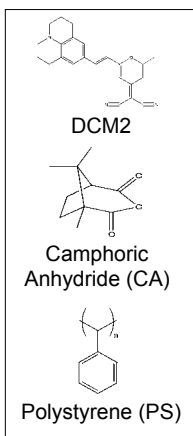
CA Doping and Electronic Susceptibility

Peak PL Energy of PS:CA:DCM2 Films

563 nm

0.005% DCM2 Doping

605 nm

Energy (eV)

Camphoric Anhydride Concentration (%)

Bulk Electronic Susceptibility of PS:CA:DCM2 Films

0.005% DCM2 Doping

$\varepsilon = 2.44 + 0.13 \times (CA\ \%)$

Epsilon (at 100 KHz)

Camphoric Anhydride Concentration (%)

42 nm red shift from 0 to 25% CA

Results unchanged even for 10x higher DCM2 concentration:
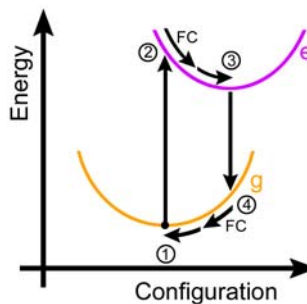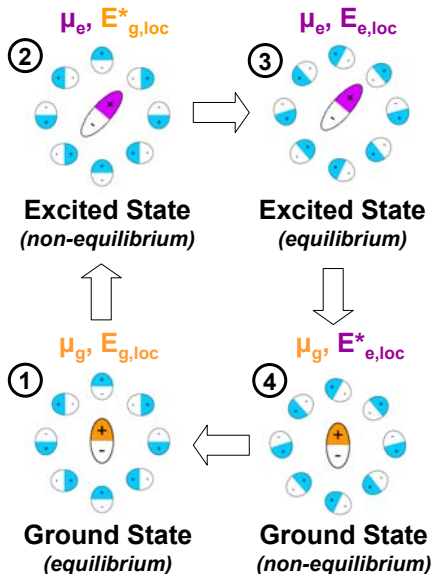
DCM2 aggregation not the answer
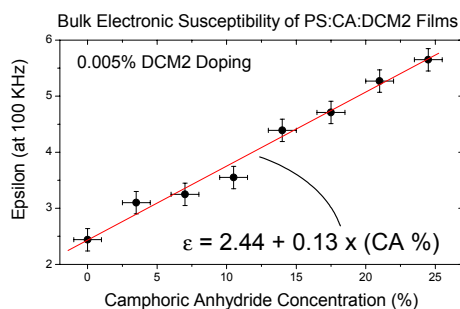
Local fields are responsible for the spectral shifts…

… and dielectric measurements suggest a "solvatochromic" effect.

Solvation Theory

Dynamic Relaxation Picture (a.k.a. solvation)

② μ_e, $E^*_{g,loc}$

③ μ_e, $E_{e,loc}$

Excited State
(non-equilibrium)

Excited State
(equilibrium)

① μ_g, $E_{g,loc}$

④ μ_g, $E^*_{e,loc}$

Ground State
(equilibrium)

Ground State
(non-equilibrium)

Continuum, Dipole in Spherical Cavity Model:

$$\vec{E}_{loc} = \underbrace{\left(\frac{2(\varepsilon - 1)}{2\varepsilon + 1}\right)}_{\Gamma_\varepsilon} \frac{\vec{\mu}}{a^3}$$

Connecting Theory to Experiment

$$E_\downarrow = E_\downarrow^{gas} - \Delta\vec{\mu} \cdot \left(\Gamma_\varepsilon \vec{\mu}_e + \Gamma_{n^2} \vec{\mu}_g\right)/a^3$$
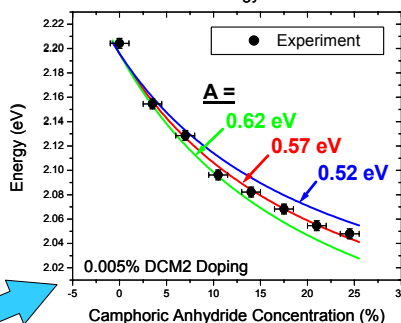
$E_\downarrow^{gas}$ constant with CA%

n nearly constant with CA%
(ranging from ~1.55 to ~1.65)

$$\Delta E_\downarrow \approx -\Gamma_\varepsilon A \quad \text{where} \quad A = \frac{\Delta\vec{\mu} \cdot \vec{\mu}_e}{a^3}$$
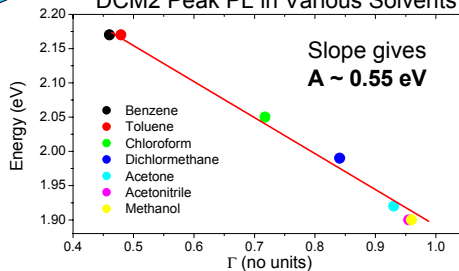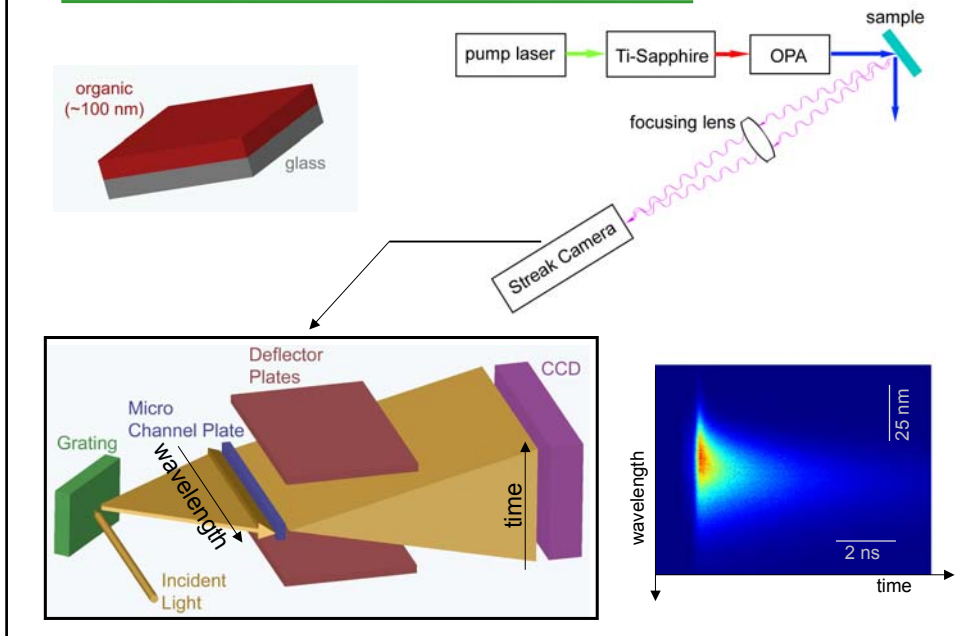
Gamma Functional Shape

$$\left(\Gamma_\varepsilon \equiv \frac{2(\varepsilon - 1)}{2\varepsilon + 1}\right)$$
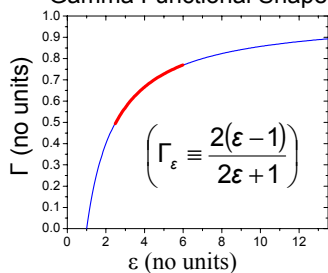
Evolution of Peak PL Energy for PS:CA:DCM2 Films

A =
0.62 eV
0.57 eV
0.52 eV

0.005% DCM2 Doping

Camphoric Anhydride Concentration (%)

DCM2 Peak PL in Various Solvents

Slope gives
A ~ 0.55 eV

Benzene
Toluene
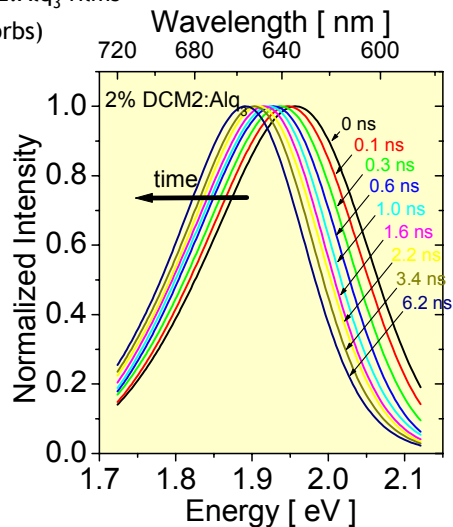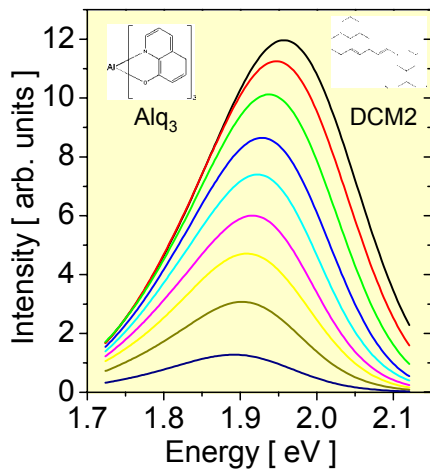Chloroform
Dichlormethane
Acetone
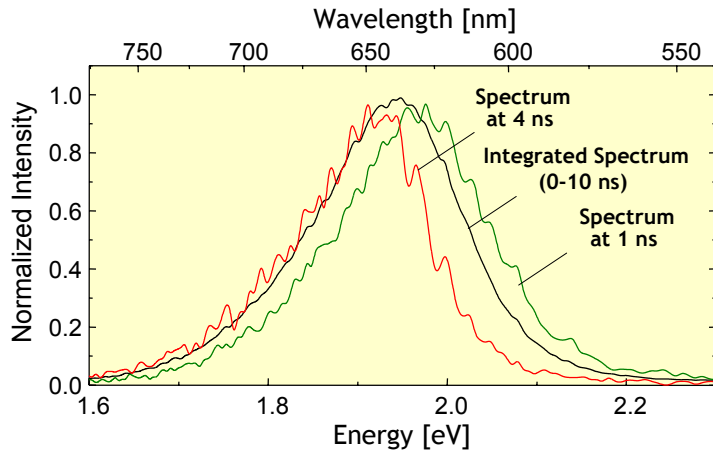Acetonitrile
Methanol

Exciton Dynamics in Time Dependant PL

Dynamic Spectral Shifts of DCM2 in Alq₃

- Measurement performed on doped DCM2:Alq₃ films
- Excitation at λ=490 nm (only DCM2 absorbs)

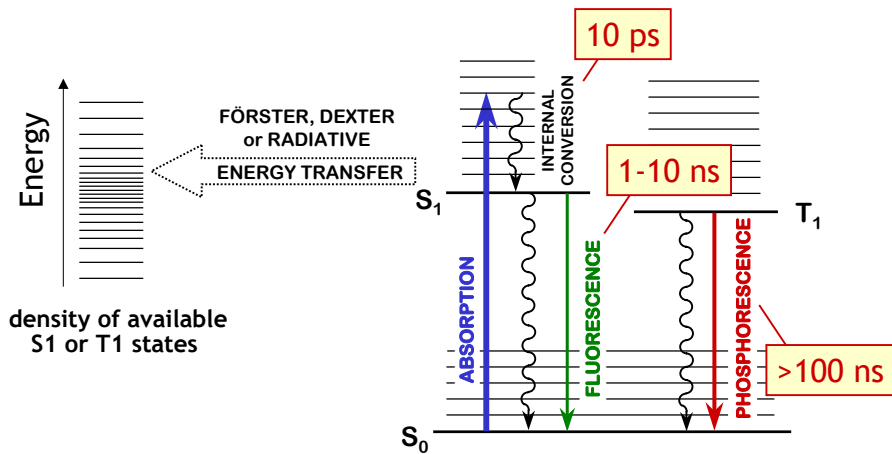~ DCM2 PL red shifts > 20 nm over 6 ns ~

Time Evolution of 4% DCM2 in Alq$_3$ PL Spectrum

Electronic Processes in Molecules

Time Evolution of DCM2 Solution PL Spectra

Benzene

CHCl$_3$

CHCl$_2$

Acetone

CH$_3$CN

DMSO

Energy [eV] / Wavelength [nm] vs Time [ns]
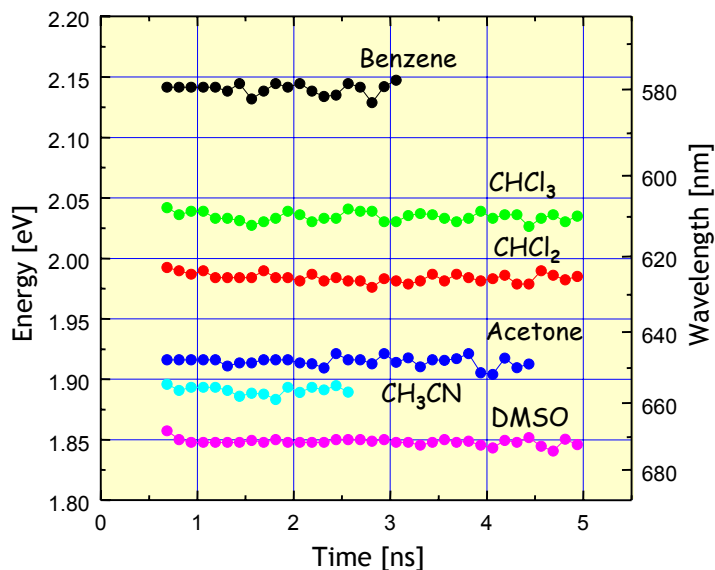
➡ **Spectral Shift due to**

~ Exciton Diffusion ~
~ Intermolecular Solid State Interactions ~

wavelength shift **35 nm**

10% DCM2 in Alq$_3$

Time [ns] vs Wavelength [nm]
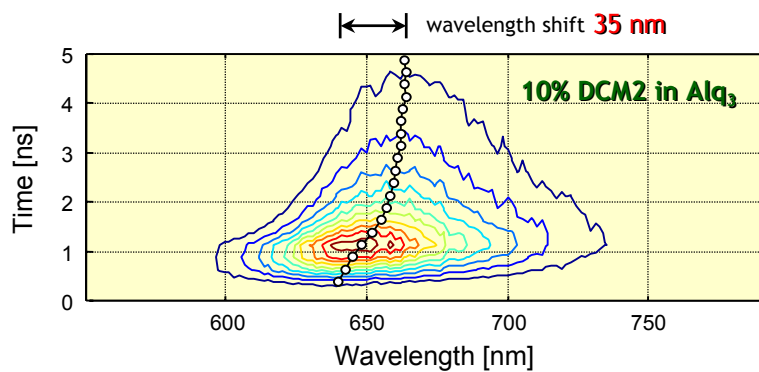
Excitonic Energy Variations
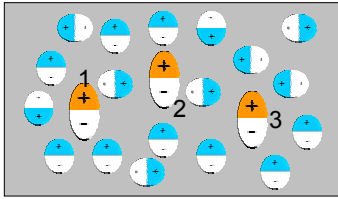
Each dye molecule experiences a different local medium
$\Rightarrow$ variations in excitonic energies

Non-zero width to excitonic density of states

Molecular PL Spectra

Excitonic Density of States
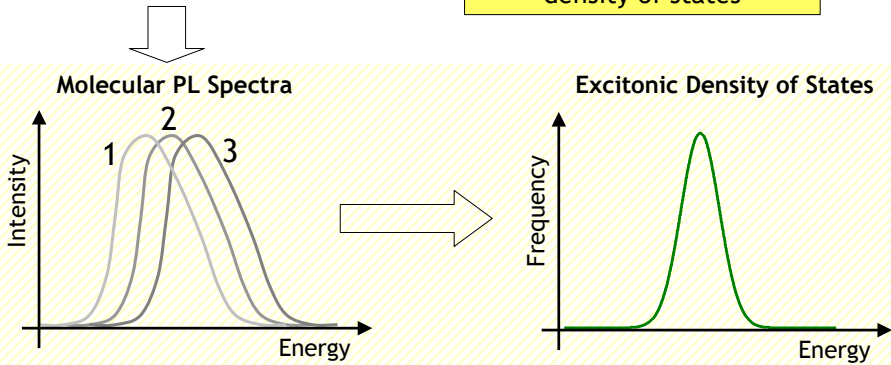
Exciton Distribution in the Excited State (S_1 or T_1)

~ Time Evolved Exciton Thermalization ~

S_1 or T_1 Energy

fwhm

log(Time)

$h\nu$
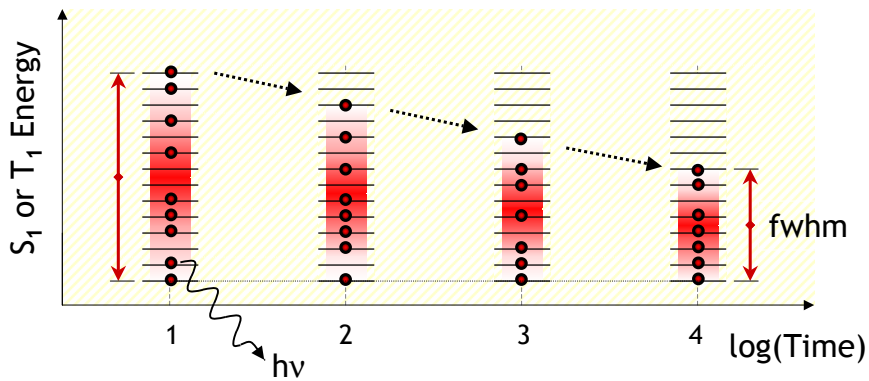
EXCITON DIFFUSION LEADS TO REDUCTION IN FWHM

4% DCM2 in Alq₃ — Energy [eV] vs Time [ns], with High E midpoint, Low E midpoint, T = 15~125 K, and inset showing Low E midpoint, High E midpoint, FWHM, Energy.

x% DCM in Alq₃ — Energy [eV] vs Time [ns], labeled Alq3, 0.2 %, 0.4 %, 0.6 %, 2 %, 4.5 %.

X% DCM in Alq$_3$

Initial Peak PL

Final Peak PL

Energy [eV]

Wavelength [nm]

% of DCM in Alq$_3$

Time Evolution of Peak PL in Neat Thin Films

Energy [eV]

Alq$_3$

Ir(ppy)$_3$

Time [ns]
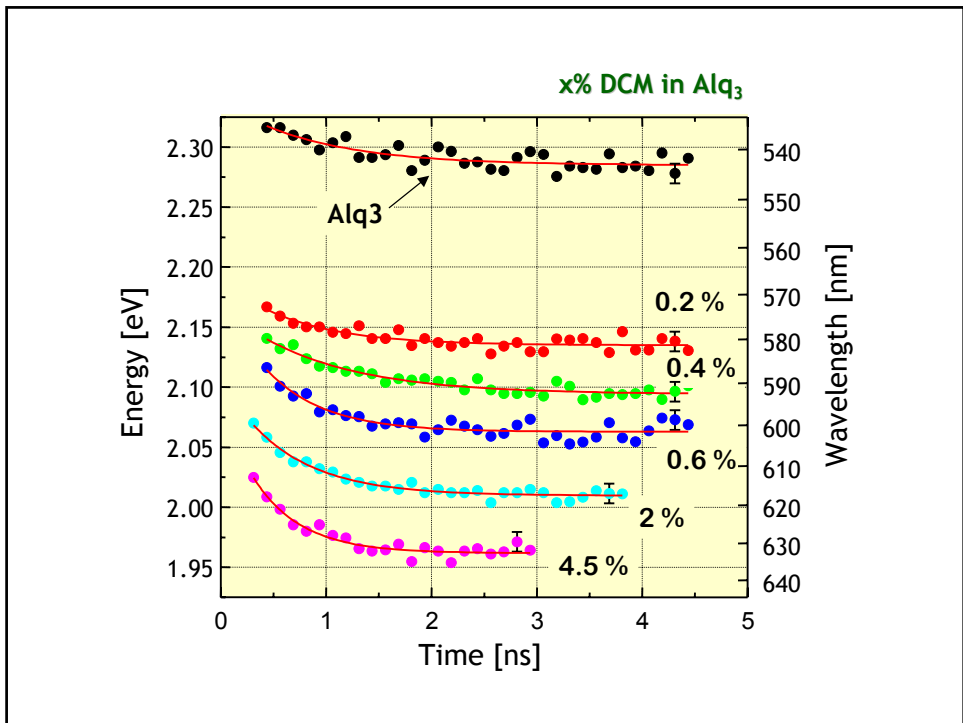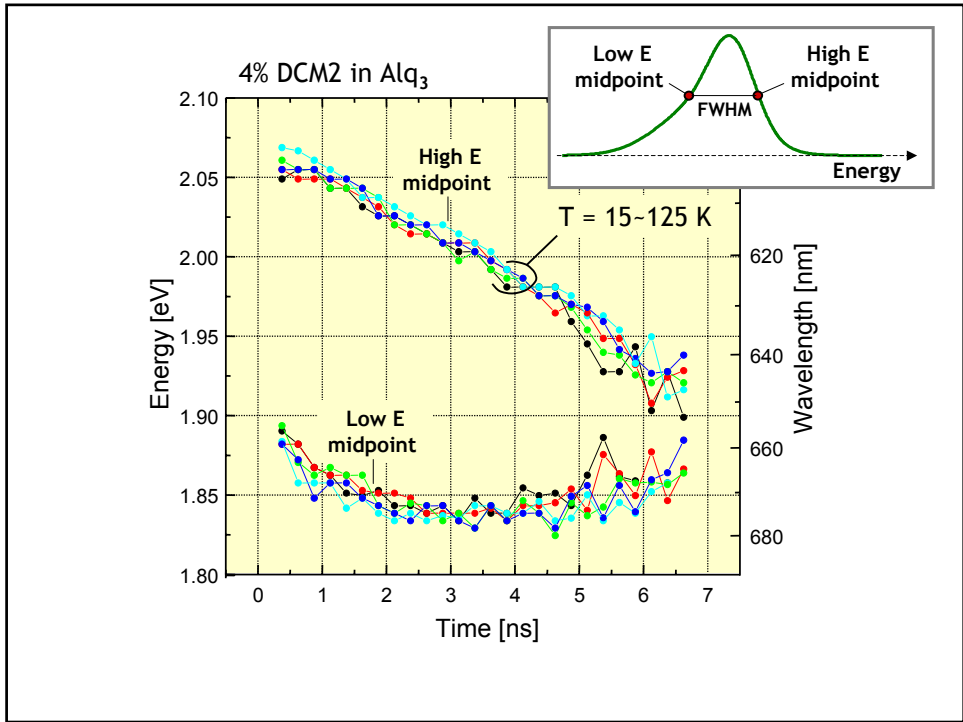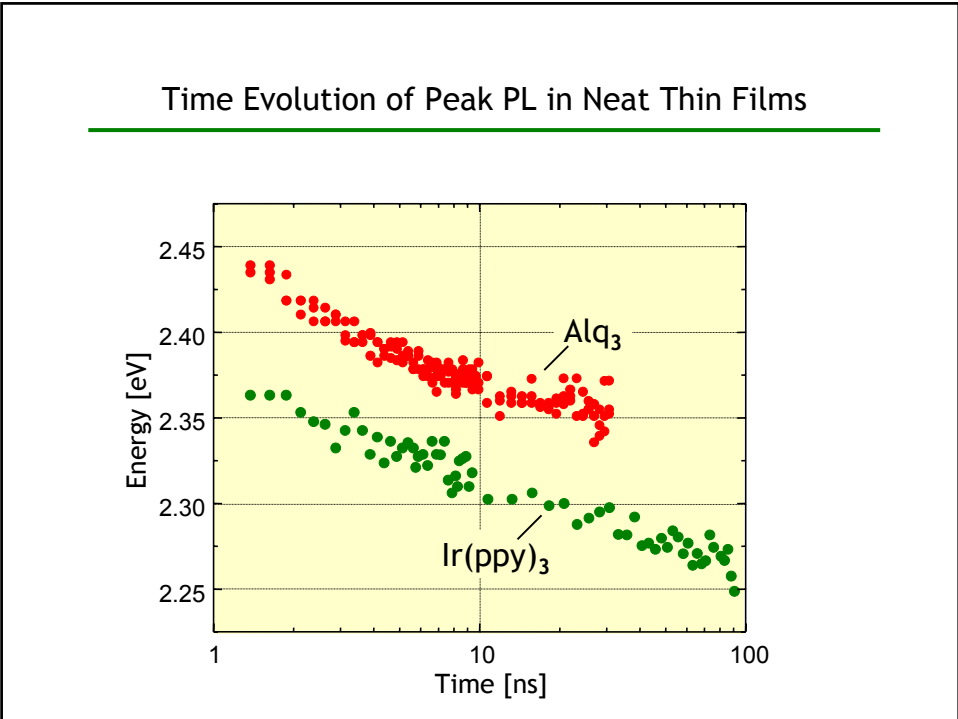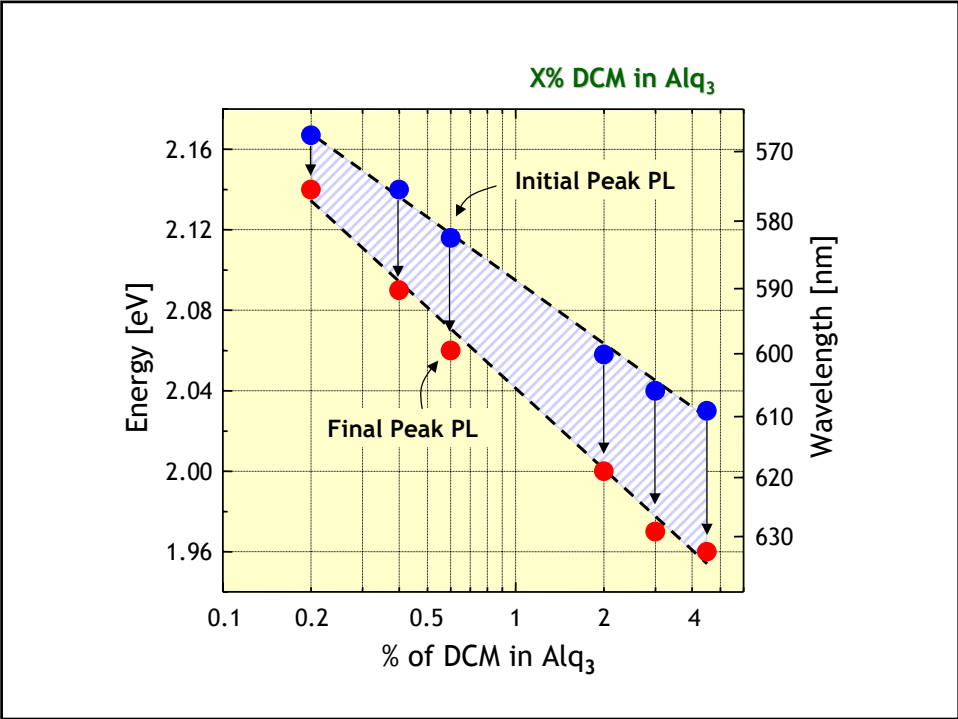
Parameters for Simulating Exciton Diffusion

observed radiative lifetime (τ)

decreasing doping
(5% down to 0.5%)

τ = 3.3 ns

Normalized Integrated Spectral Intensity

Time [ns]
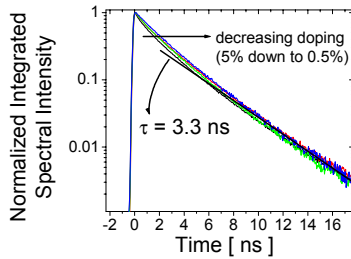
Förster radius (R_F)

► Assign value for *allowed* transfers:

Γ_F

$$\frac{1}{\tau}\left(\frac{R_F}{R}\right)^6$$

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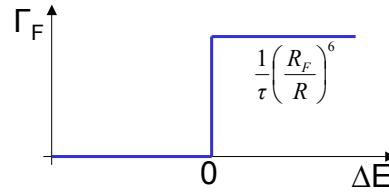
excitonic density of states ($g_{ex}(E)$)

► Assume Gaussian shape of width, w_{DOS}

► Center at peak of initial bulk PL spectrum

► Molecular PL spectrum implied…

Wavelength [nm]

FWHMs
$S_{init}(E)$: 0.27 eV
$S_{mol}(E)$: 0.22 eV
$g_{ex}(E)$: 0.15 eV

Normalized Intensity [arb. units]

Energy [eV]
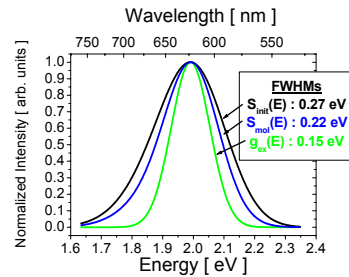
Fitting Simulation to Experiment – Doped Films

R_F=0.88 w_{DOS}=0.185 eV
R_F=0.98 w_{DOS}=0.161 eV
R_F=1.08 w_{DOS}=0.146 eV
R_F=1.18 w_{DOS}=0.136 eV
R_F=1.28 w_{DOS}=0.130 eV

0.5% DCM2:Alq$_3$

Energy [eV]   Wavelength [nm]   Time [ns]

Peak PL of x%
DCM2:Alq$_3$

0.5%
1%
2%
5%

Energy [eV]   Wavelength [nm]   Time [ns]
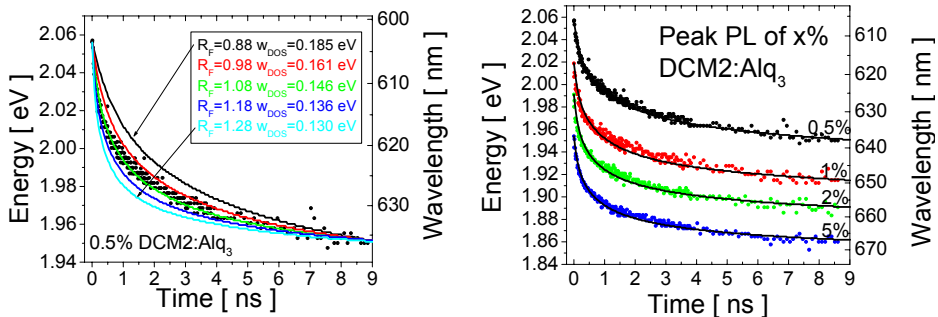
• Good fits possible for all data sets

• 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

Slide 1

Fitting Simulation – Neat Films

Ir(ppy)$_3$
w_{DOS}~0.21 eV

Alq$_3$
w_{DOS}~0.15 eV

NPD
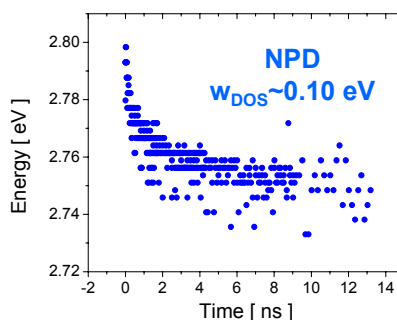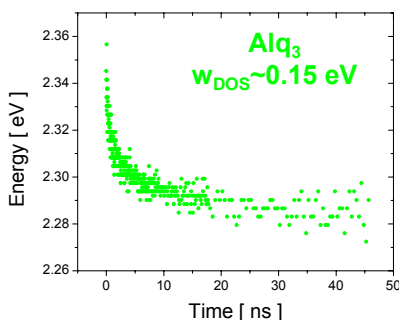w_{DOS}~0.10 eV
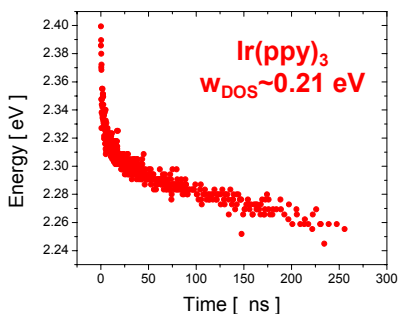
- Spectral shift observed in each material system
- Molecular dipole and w_{DOS} are correllated: **lower dipoles correspond to less dispersion**
- Even with no dipole, some dispersion exists
- Experimental technique **general**, and yields **first measurements** of **excitonic energy dispersion** in amorphous organic solids

Slide 2

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 ~
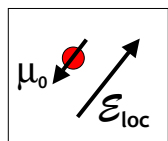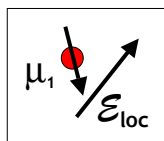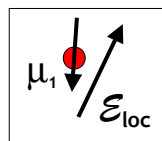
μ_0 μ_1 μ_1
$\mathcal{E}_{loc}$ $\mathcal{E}_{loc}$ $\mathcal{E}_{loc}$
t < 0   t = 0   t ~ 1 ns

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

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
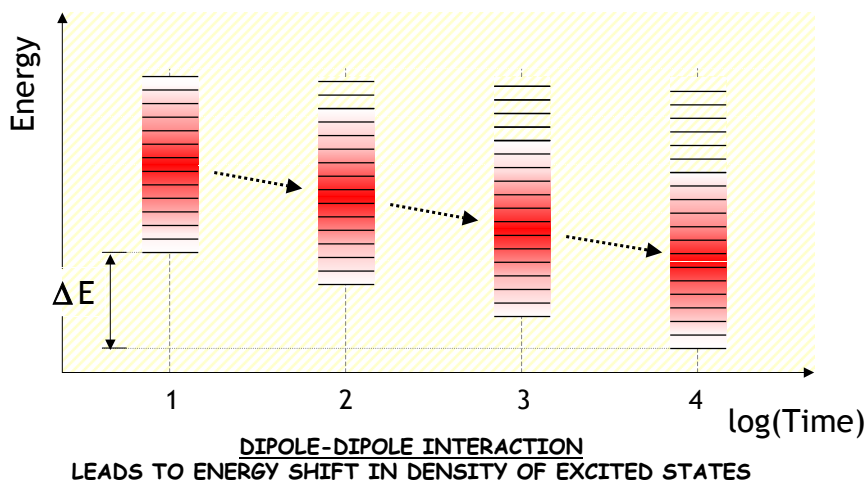
Fusion of Two Material Sets

Efficient

Organic Semiconductors

Flexible

Emissive

Photo by F. Frankel

Tunable

Colloidal QDs
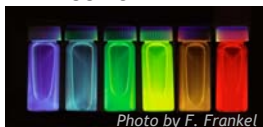
Nanoscale
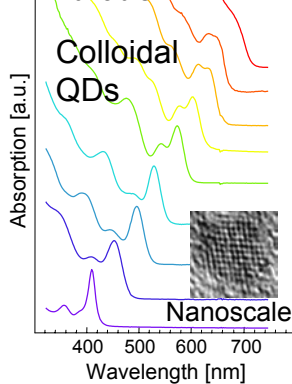
Hybrid devices could enable

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

ZnS
CdSe

E

Lowest allowed energy level

D

Quantum Dot *SIZE*

Photo by F. Frankel

Absorption [a.u.]

D=
120Å
80Å
72Å
55Å
45Å
33Å
29Å
20Å
17Å

400   500   600   700
Wavelength [nm]
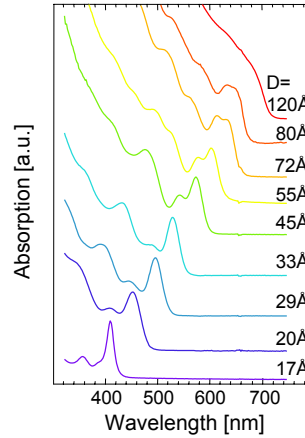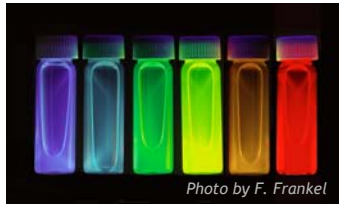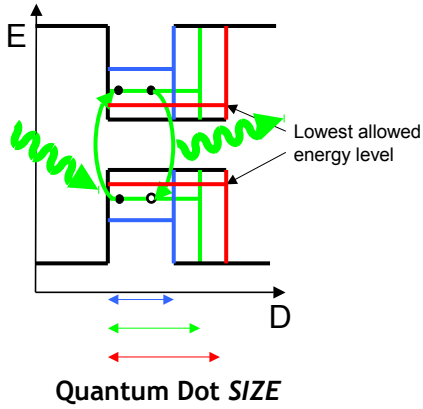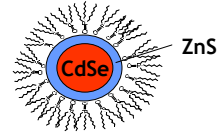
Synthetic route of Murray et al, J. Am. Chem. Soc. **115**, 8706 (1993).

Fusion of Two Material Sets

Quantum Dots

Absorption Spectra

EMISSIVE

NANOSCALE

TUNABLE

CdSe(ZnS)

PbSe

300 400 500 600 700
Wavelength [nm]

0.9 1.2 1.5 1.8 2.1 2.4
Wavelength [µm]
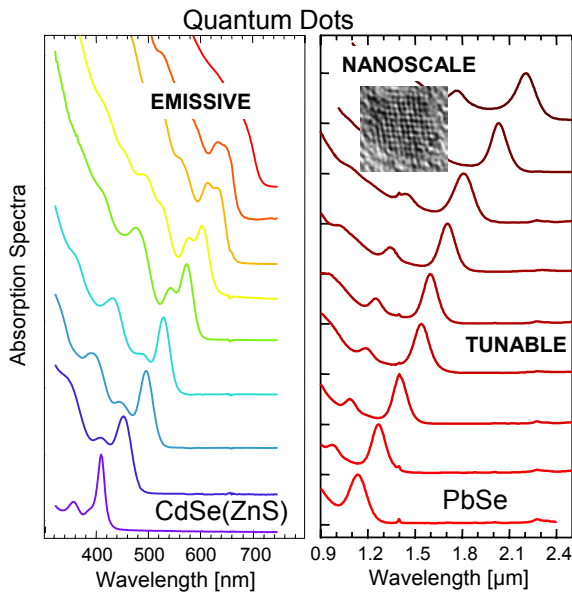
Organic Molecules

Alq_3

TPD
CH_3 H_3C

TAZ

NPD
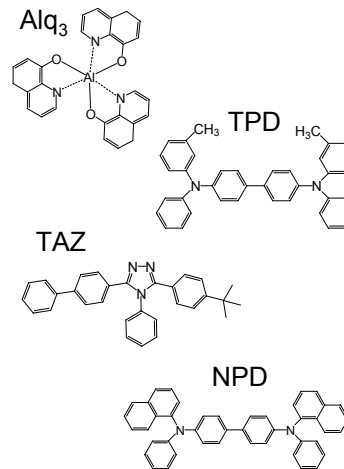
Integration of Nanoscale Materials
Quantum Dots and Organic Semiconductors

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

PbSe or CdSe Core

D = 17-120Å

(~50Å pictured)

Oleic Acid

10Å

Alq₃

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   **poly-TPD**

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

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

Phase Segregation and Self-Assembly

QD Solution   **TPD Solution**

1   2   3   **TPD/solvent**   QDs   4   **close packed QDs**

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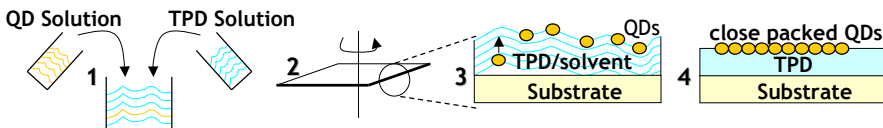
1. A solution of an organic material, QDs, and solvent…
2. is spin-coated onto a clean substrate.
3. During the solvent drying time, the QDs rise to the surface…
4. and self-assemble into grains of hexagonally close packed spheres.

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*.

~8nm PbSe QDs

Flat TPD background
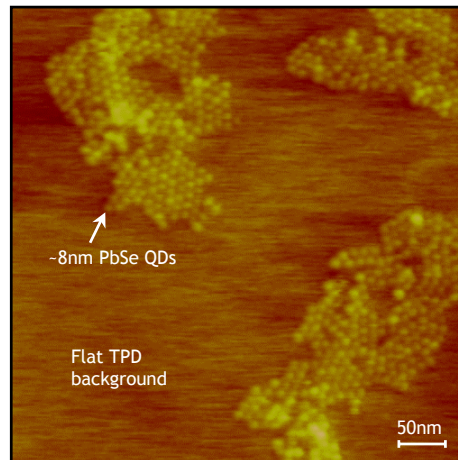
50nm

Monolayer Coverage – QD concentration

QD coverage = 20%   50%   80%

250nm   500nm   500nm

90%   100%

500nm   100nm

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

50nm Ag
50nm Mg:Ag
30nm Alq$_3$
10nm TAZ
40nm TPD
ITO
Glass

Vacuum Level = 0 eV

Electron Energy [eV]

EA=2.1
TPD
QD
EA=3.0   EA=3.1
TAZ   Alq$_3$ E$_F$=3.7
Mg
E$_F$=4.7
ITO
EA=4.6
IE=5.4   CdSe
IE=6.8
IE=6.5   IE=5.8
ZnS
TOPO

Current Density [A cm^{-2}]

10^0
10^{-2}
10^{-4}
10^{-6}
10^{-8}

Control

QD-LED

1   10

Voltage [V]

CdSe(ZnS)/TOPO   PbSe/oleic acid

Normalized counts

400   500   600   1200   1400   1600

Wavelength [nm]

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)

Wavelength (nm)

QDs are poor charge transport materials...

QD

CdSe

ZnS

TOPO caps   QD intersite spacing

But efficient emitters…

Design of Device Structures

QD monolayer

ZnS shell   CdSe core   TOPO caps

QD

50nm Ag
50nm Mg:Ag
30nm Alq₃
10nm TAZ
40nm TPD
ITO
Glass

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.

Vacuum Level = 0 eV

Electron Energy [eV]

$E_F=4.7$ ITO
$EA=2.1$ TPD
$IE=5.4$
QD $EA=4.6$
CdSe $IE=6.8$
ZnS
TOPO
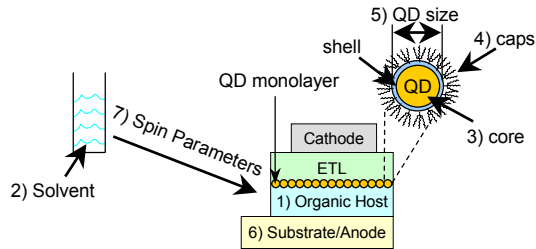$EA=3.0$ TAZ $IE=6.5$
$EA=3.1$ Alq₃ $IE=5.8$
$E_F=3.7$ Mg

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.
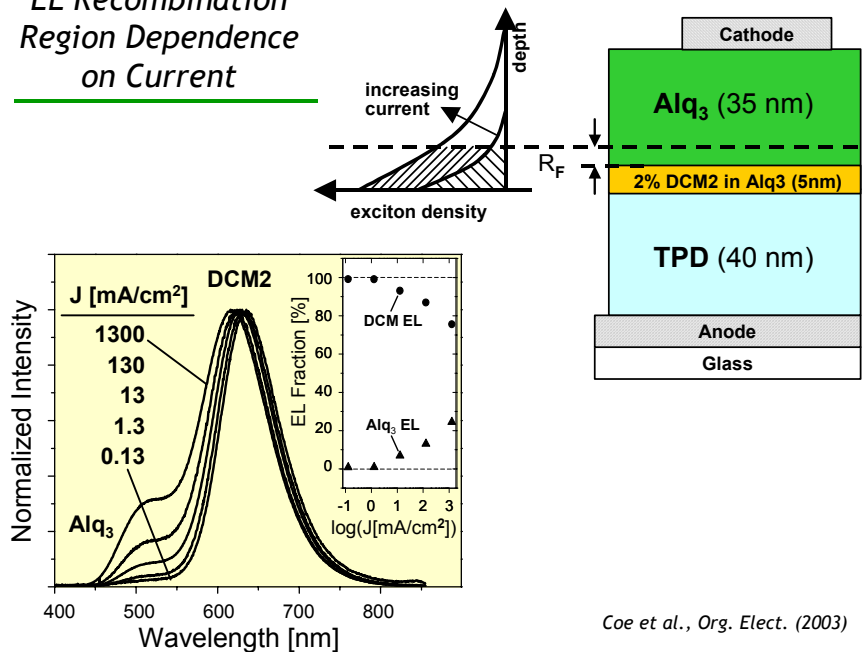
7) Spin parameters: speed, acceleration and time.

- **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.**
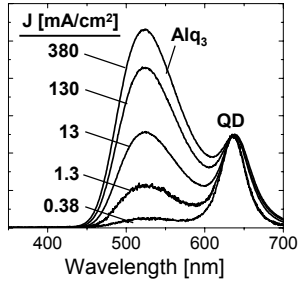
Phase segregation → *QD-LED structures*

5) QD size
shell
4) caps
QD monolayer
QD
3) core
Cathode
ETL
7) Spin Parameters
1) Organic Host
2) Solvent
6) Substrate/Anode

For more details on phase segregation process, come to the talk tomorrow - **P10.7**.

EL Recombination Region Dependence on Current

increasing current
depth
exciton density
R_F

Cathode
Alq$_3$ (35 nm)
2% DCM2 in Alq3 (5nm)
TPD (40 nm)
Anode
Glass

J [mA/cm^2]
DCM2
1300
130
13
1.3
0.13
Alq$_3$

EL Fraction [%]
DCM EL
Alq$_3$ EL
100
80
60
40
20
0
-1 0 1 2 3
log(J[mA/cm^2])

Normalized Intensity
400   500   600   700   800
Wavelength [nm]

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

Spectral Dependence on Current Density

J [mA/cm²]
380
130
13
1.3
0.38

Alq₃

QD

400   500   600   700
Wavelength [nm]

TOP DOWN VIEW of the QD MONOLAYER

Device Area   Grain Boundary

R_F

Interstitial Space   Monolayer Void

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

Cathode

ETL
electron   Alq₃ EL

depth

increasing
current

exciton density R_F

hole   QD EL
HTL

Anode
Glass
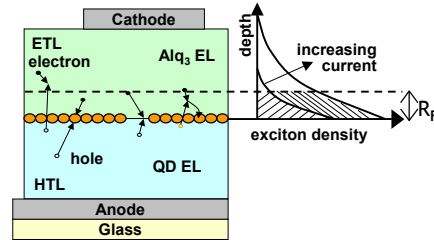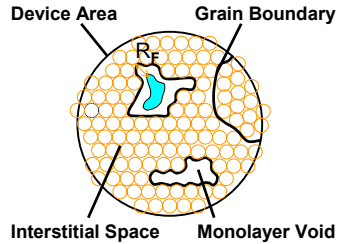
CROSS-SECTIONAL VIEW of QD-LED

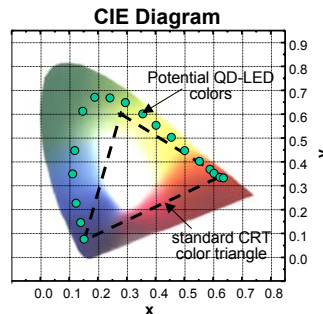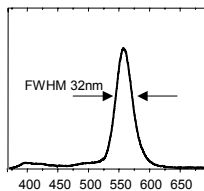## Benefits of Quantum Dots in Organic LEDs

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!

QD

CIE Diagram

Potential QD-LED colors

standard CRT color triangle

0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8
x

y

FWHM 32nm

400 450 500 550 600 650

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