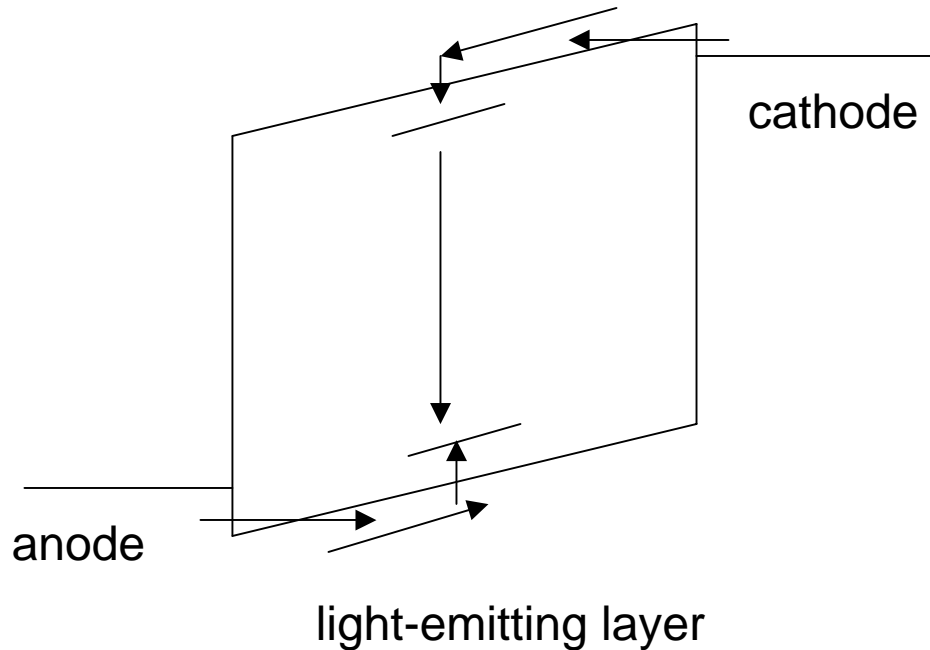


Making OLEDs efficient



$$\eta_{EL} = \gamma_{st} \eta_{PL} k$$

External Efficiency – Outcoupling

Internal efficiency of LEDs

$$\eta_{EL} = \gamma r_{st} \eta_{PL} k$$

γ = excitons formed per charge flowing in the circuit (1 in a device with carrier balance)

r_{st} = singlets per exciton formed

η_{PL} = photoluminescence efficiency

k = miscellaneous factor (e.g. reduction in efficiency due to metal electrodes)

Achieving high quantum efficiencies

To get efficient radiative recombination, we must avoid

- energy migration to non-emissive trap states (e.g. carbonyl defects)
- coupling to nuclear motion
- quenching by the metal electrodes.

We must also avoid processes that slow down the rate of radiative decay, such as

- excimer formation
- mirror effects

Selecting metals for cathodes

An important property of the cathode is its work function. It's ability to dope the polymer also appears to be important.

Element	Work function	
Cs	2.14	
K	2.30	
Ba	2.70	} popular cathode materials
Na	2.75	
Ca	2.87	
Li	2.90	
Mg	3.66	
In	4.12	
Ag	4.26	
Al	4.28	
Nb	4.30	
Cr	4.50	
Cu	4.65	
Si	4.85	
Au	5.10	
Pt	5.60	

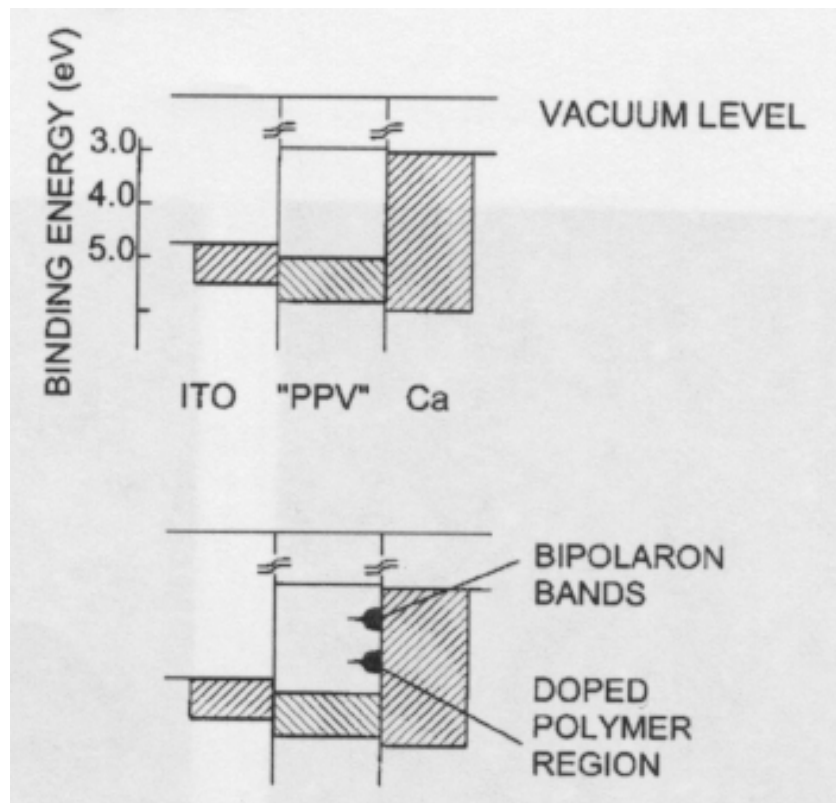
Calcium dopes the polymer

W.R. Salaneck et al. have used photoelectron spectroscopy to show that calcium dopes the polymer interface.

Yang Yang et al. have shown that 2 Å of Ca capped with Al is as good as a full Ca electrode.

J.R. Sheets et al. have shown that ZrC, which does not react with the polymer, is not a good electrode despite its low work function.

Summary: Doping may fill traps and help carriers to get away from the electrode before they hop back onto it.



See *Acc. Chem. Res.* Vol 32, 1999
p. 193-200 and 225-234 and references
within.

Anodes

Indium tin oxide (ITO) was almost always chosen as the anode in early studies of polymer LEDs because:

- it has a work function of 4.5 - 5.0 eV, which is good for injecting holes
- it is transparent
- it is sufficiently conductive
- it is readily available.

ITO is non-stoichiometric. Its conductivity, transparency, and work function depend on the number of oxygen vacancies.

Hydrogen and oxygen plasma treatments can be used to vary the oxygen concentration, which fine tunes the work function of ITO.

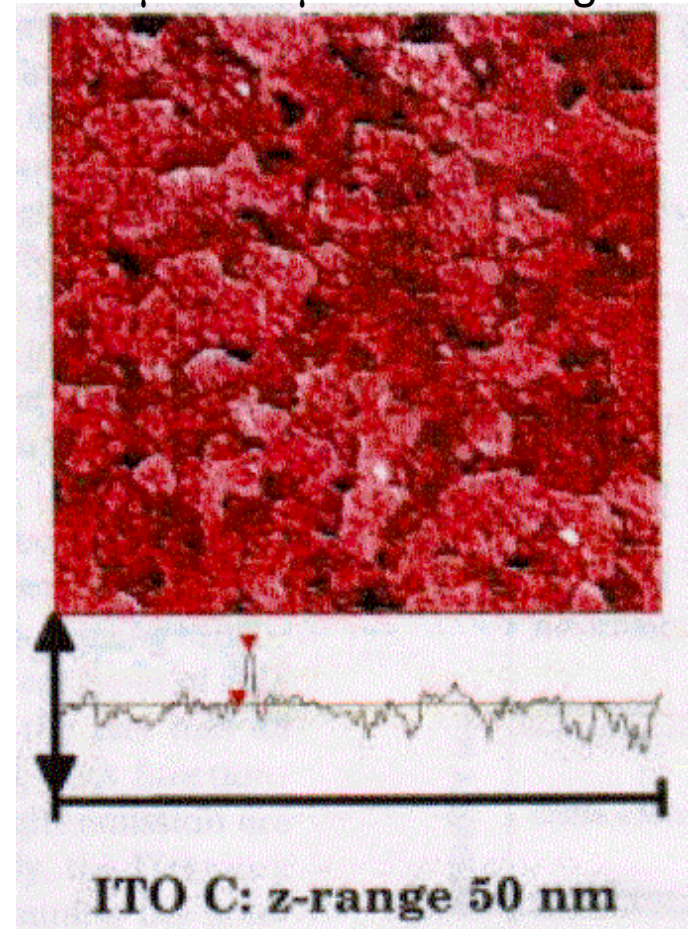
Problems with ITO

ITO tends to have a rough surface.

If the thickness of an LED is not constant, the electric field varies. Consequently the current and brightness vary.

An ITO spike can short a thin device.

1 μm x 1 μm AFM image



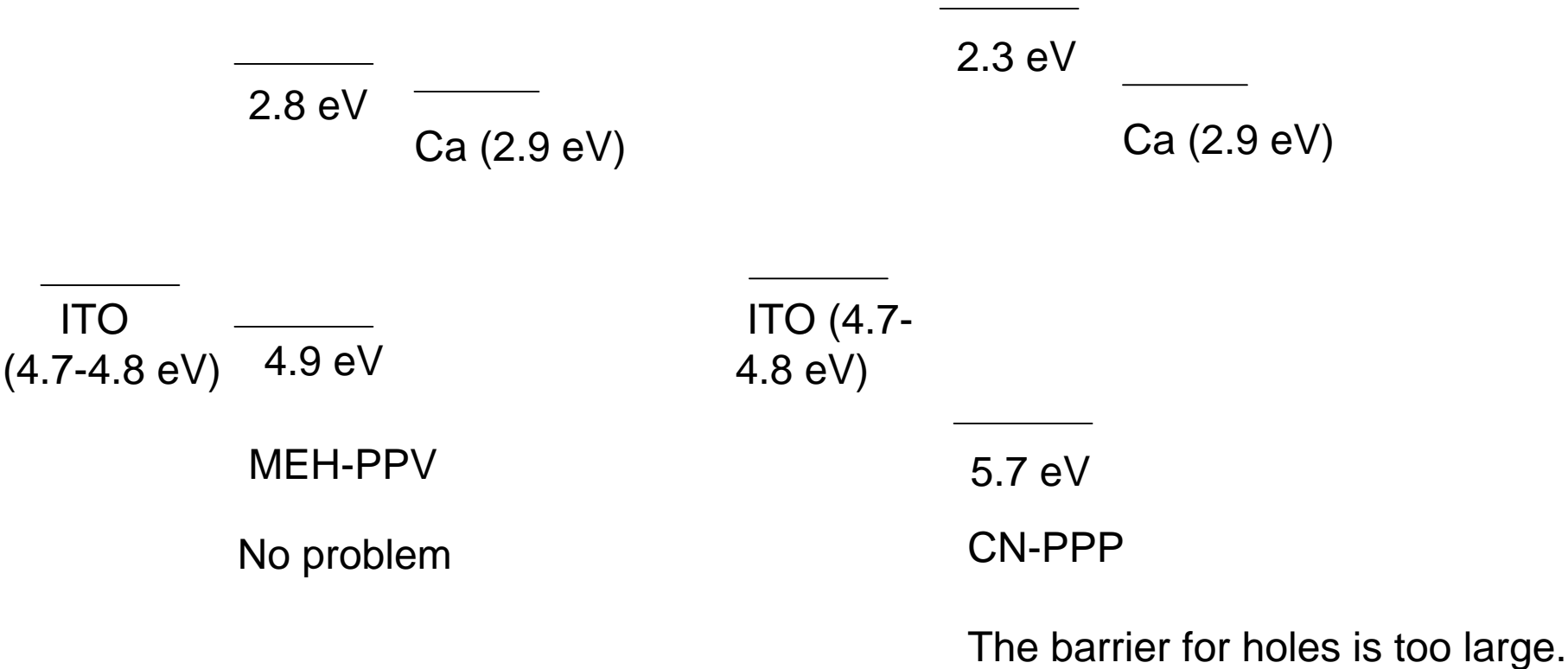
ITO causes device degradation

ITO can introduce oxygen into the polymer, which leads to the creation of carbonyl defects.

Because of the intense electric field, indium ions can diffuse from the ITO all the way through the polymer film. This has been observed with time-of-flight secondary ion mass spectrometry.

ITO work function

ITO's work function is good for injecting holes into most green- and red-emitting organic semiconductors, but it is not high enough for injecting holes into most blue-emitting organic semiconductors.



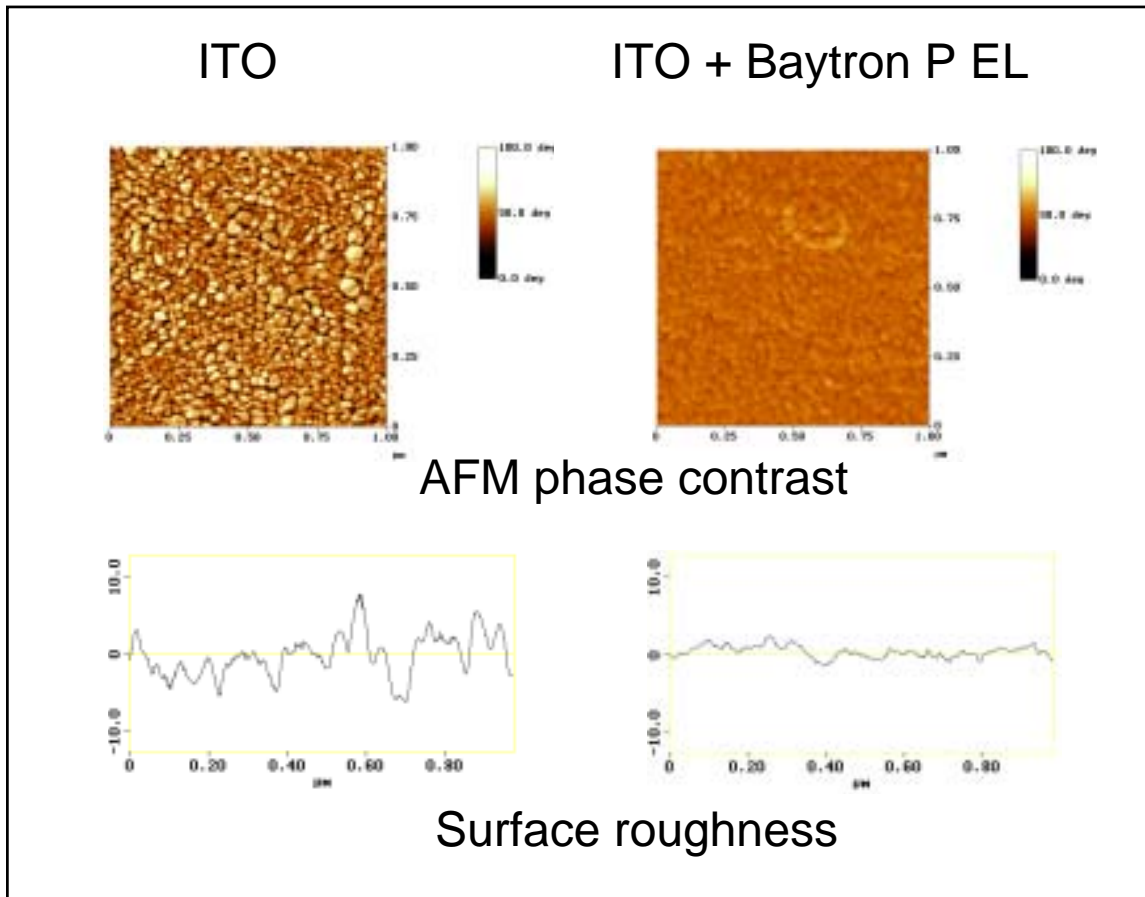
Using conducting polymers as anodes

Spin coatable conducting polymers aren't sufficiently conductive to carry current across a substrate, but they can be used to coat an ITO electrode.

Spinning polymers like doped polyaniline and PEDOT over ITO

- makes the anode smoother
- separates the ITO from the light-emitting polymer to prevent degradation
- optimizes the work function to improve hole injection.

Smoothness of PEDOT: PSS (Baytron P EL)



Preparation:

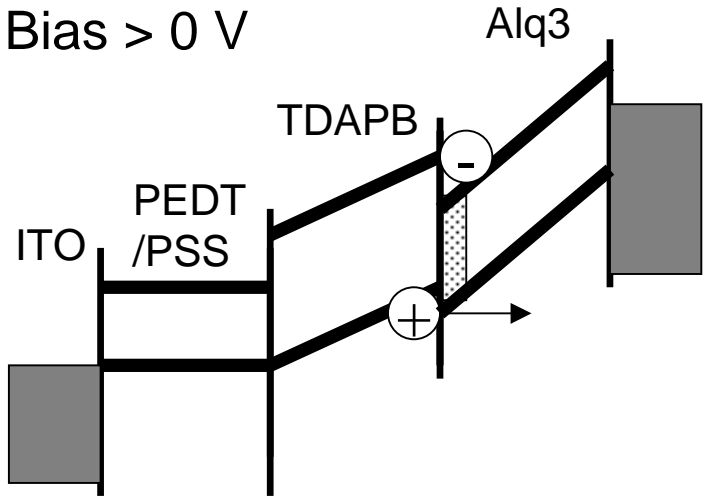
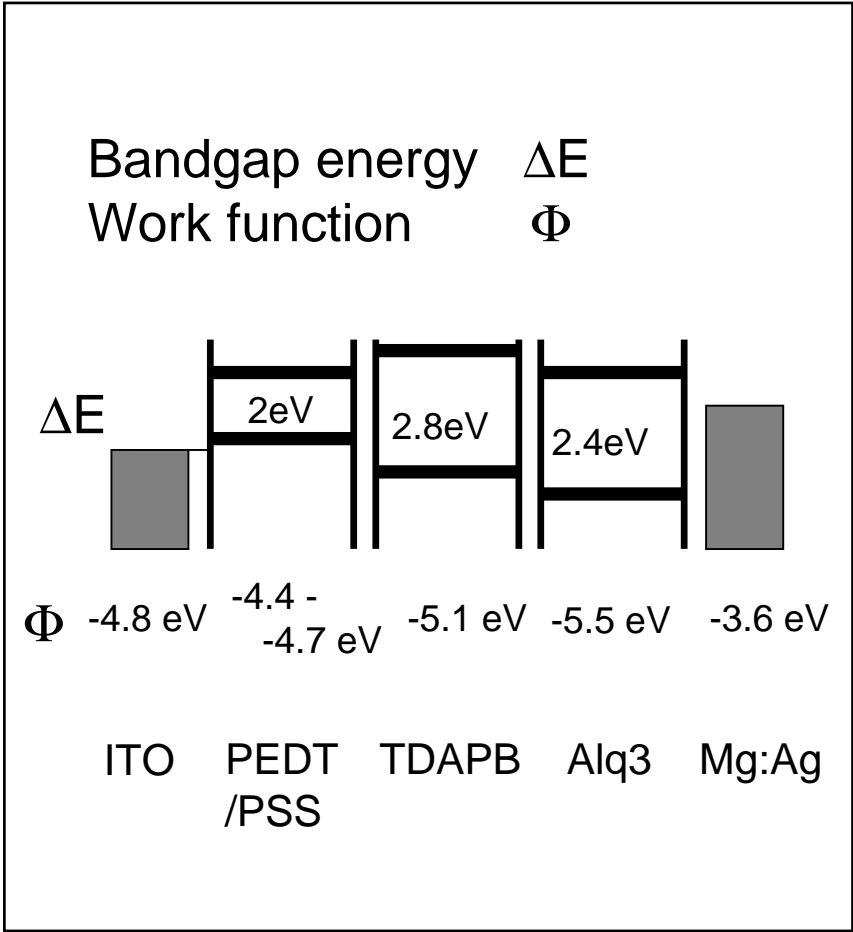
A 50 nm **BAYTRON P VP AI 4083** layer is spin-coated onto precleaned ITO substrate in ambient air.

The **BAYTRON P VP AI 4083** layer reduces the surface roughness:

$R_a = 1.8$ nm (ITO alone)

$R_a = 0.8$ nm (ITO + **BAYTRON**)

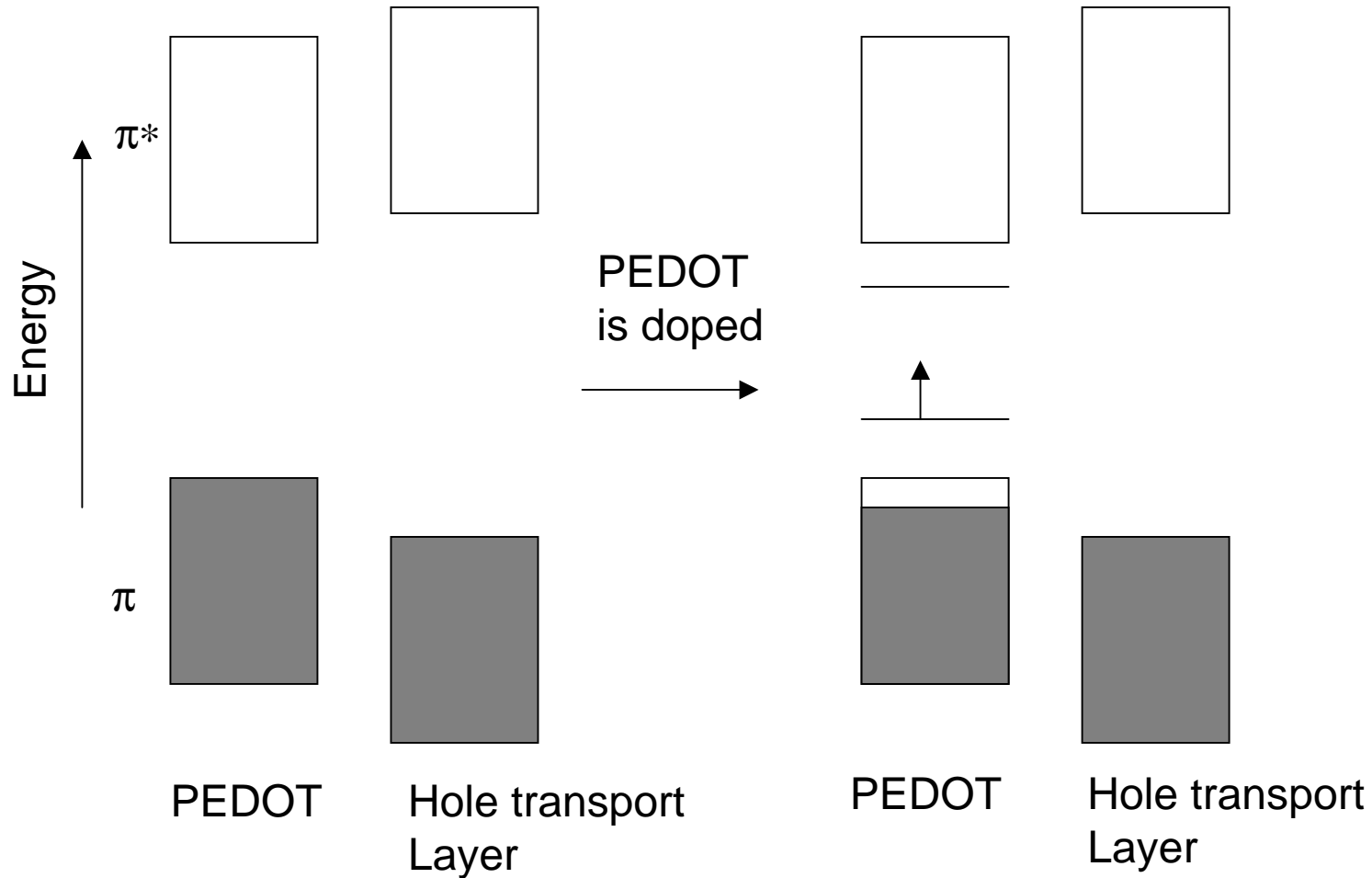
Energy level diagram for an OLED with a conducting polymer anode



Since the electric field is small near the ITO, In^{3+} doesn't migrate through the polymer.

Oxygen from the ITO doesn't degrade the light-emitting material.

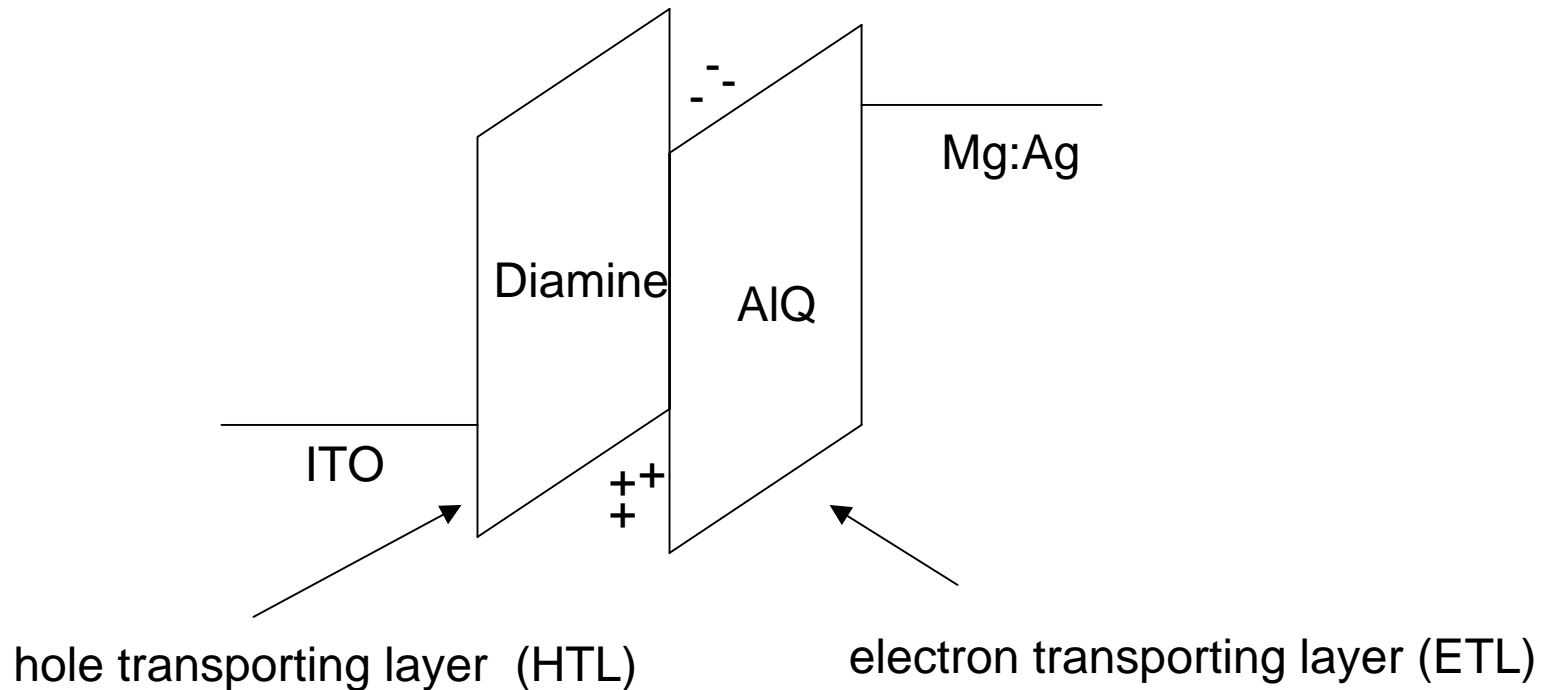
Work function optimization



As the PEDOT (or a similar conducting polymer) is doped, the barrier for hole injection is reduced. One can fine tune the barrier by optimizing the doping level.

Carrier balance

Ideally, there will be ohmic contacts at the cathode and anode and equal numbers of electrons and holes will be injected. If this cannot be achieved, a multilayer design can be used to confine charge and promote recombination.



Fluorescence and phosphorescence

Allowed singlet emission is called fluorescence. For most organic lumophores, **fluorescence** occurs on a time scale of 0.2-10 ns.

Forbidden triplet emission is called **phosphorescence**. It typically has a time constant of 1-1000 μ s.

Importance of singlets and triplets

The ground state of all molecules is a singlet.

If angular momentum is not conserved, then the matrix element is zero and the transition is forbidden.

Absorption of light always creates singlets. They can all fluoresce.

In LEDs, triplets can form. The triplets almost always decay nonradiatively.

Singlet and triplet excitons

There are 3 symmetric spin states, known as triplets, with an angular momentum of 1.

$$S = | \uparrow \uparrow \rangle$$

$$S = \frac{1}{\sqrt{2}} (| \uparrow \downarrow \rangle + | \downarrow \uparrow \rangle)$$

$$S = | \downarrow \downarrow \rangle$$

There is one antisymmetric spin state, known as a singlet, with an angular momentum of 0.

$$S = \frac{1}{\sqrt{2}} (| \uparrow \downarrow \rangle - | \downarrow \uparrow \rangle)$$

Limits to EL efficiency

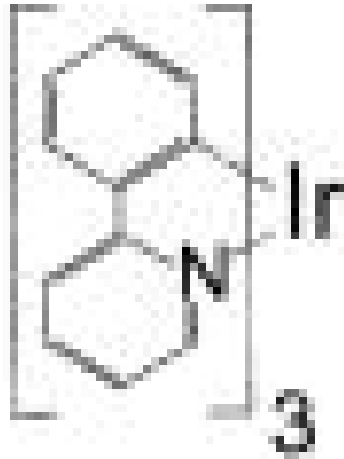
For many years everyone assumed that 1/4 of the excitons formed in an LED were singlets and 3/4 were triplets.

Consequently, many people thought that η_{EL} could not be greater than 25 % of η_{PL} .

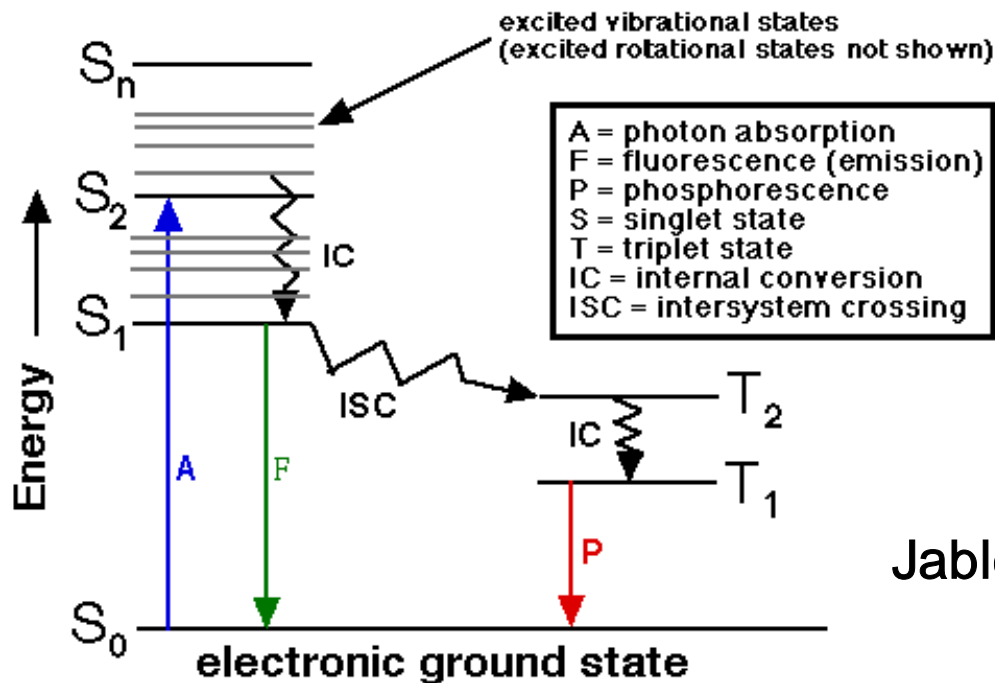
Forrest and Thompson developed phosphorescent complexes that have relatively short radiative lifetimes by using heavy elements to increase spin orbit coupling, which makes triplets more like singlets and singlets more like triplets.

Yong Cao et al. made a polymer LED with $\eta_{\text{EL}} = 0.5 \eta_{\text{PL}}$. This suggested that more than 1/4 of the excitons are singlets. [*Nature*, **397** (1999) p. 414.]

Phosphorescent molecules



- Previously we saw that the radiative rate of recombination for singlets is fast, while that for triplets is slow.
- When heavy elements are incorporated into complexes, spin-orbit coupling makes the triplet state more like a singlet state (and vice versa). The phosphorescence decay time can be less than $1 \mu\text{s}$. These complexes can phosphoresce efficiently.



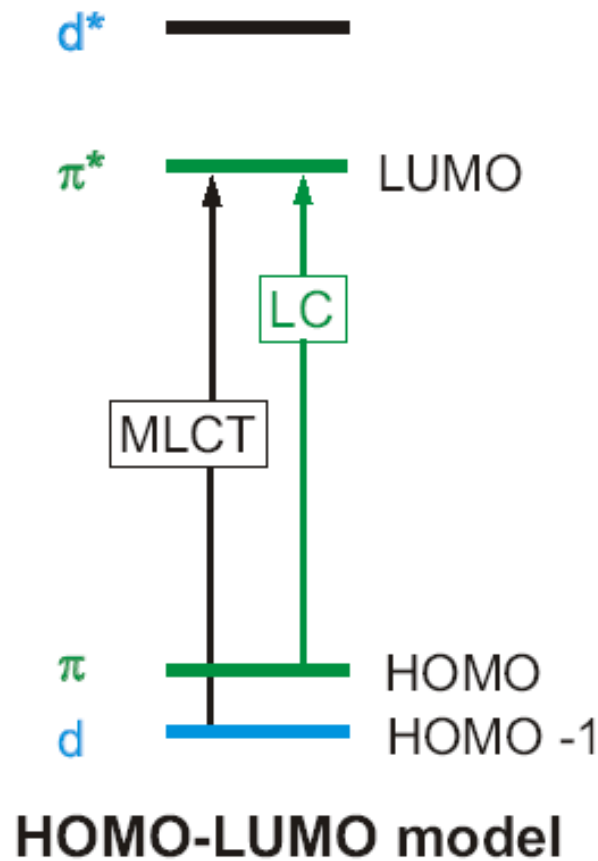
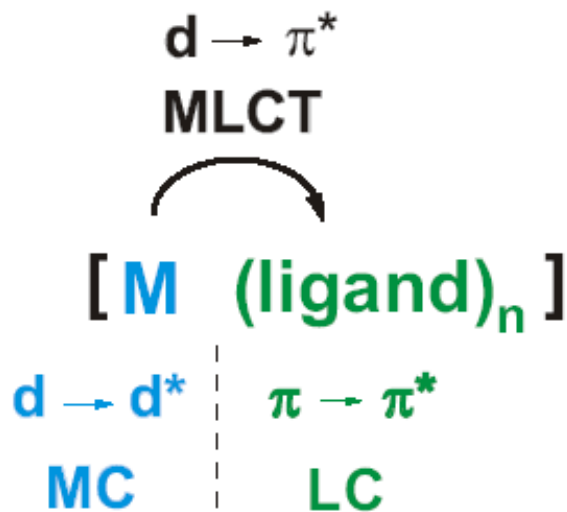
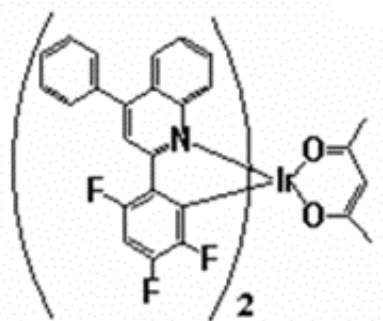
Jablonski Energy Diagram

Three radiationless processes

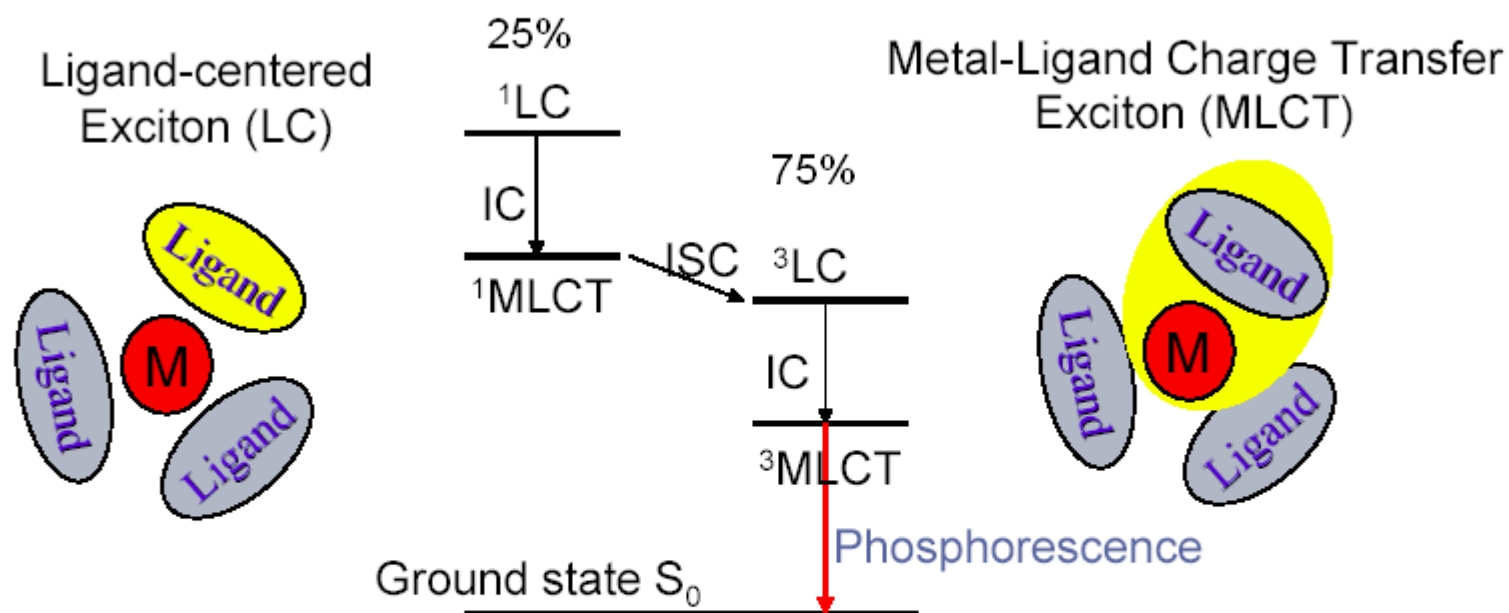
- **Internal conversion(IC)**: transition between energy states of the same spin state (compare with fluorescence - a radiative process).
- **Intersystem crossing(ISC)**: transition between different spin states (compare to phosphorescence).
- **Vibrational relaxation**: in the form of vibrations and rotations, enhanced by physical contact of an excited molecule with other particles, occurs very quickly ($< 1 \times 10^{-12}$ seconds)

Transition metal complexes

Example:

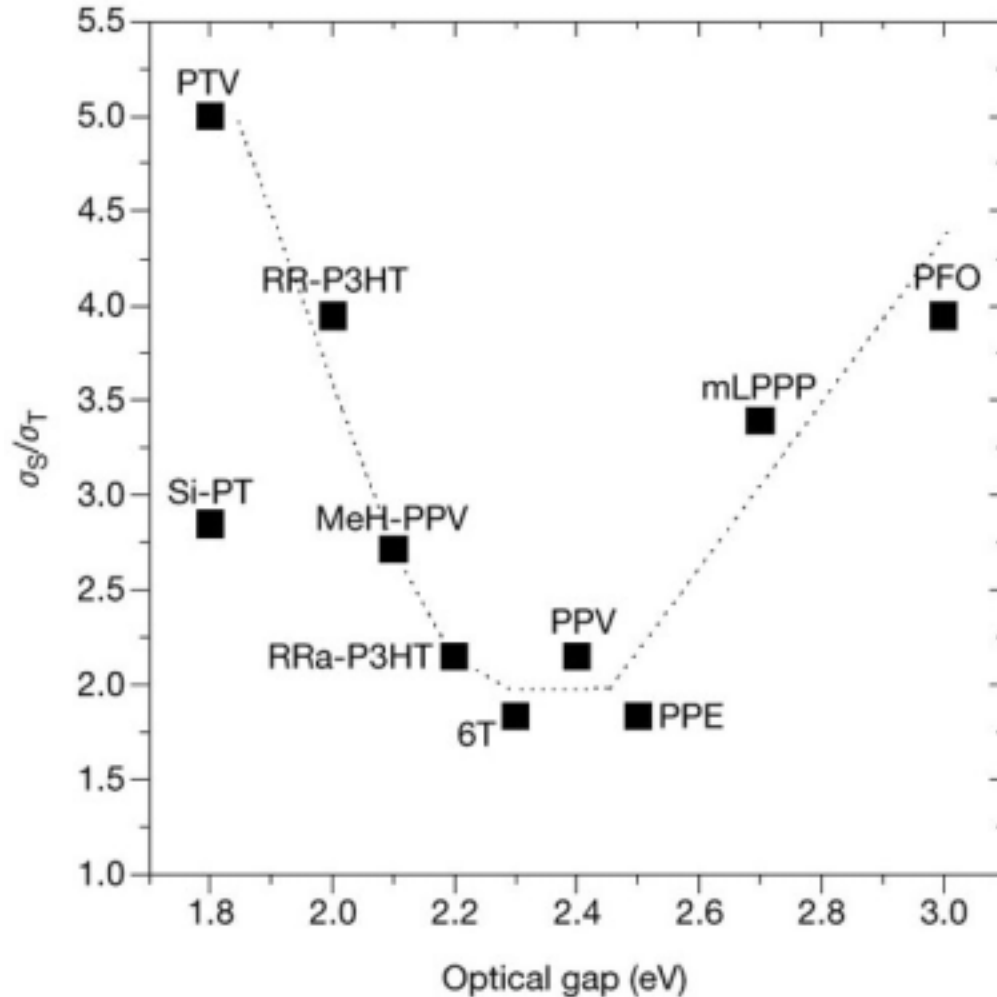


Phosphorescence



- The emissive state is a mixture of a LC exciton and a MLCT exciton
- The MLCT state has stronger singlet - triplet mixing, due to the overlap with the heavy - metal atom.
- For strong spin-orbit coupling, the IC and ISC rates are very fast.

Formation cross-sections of singlets and triplets



Recently photoinduced absorption magnetic resonance spectroscopy was used to measure the ratio of singlets to triplets that form in a variety of polymers.

Singlets form much more readily than triplets.

For RR-P3HT, the ratio of singlets to triplets would be

$$(4.0 \times 1) / (1 \times 3) = 1.33,$$

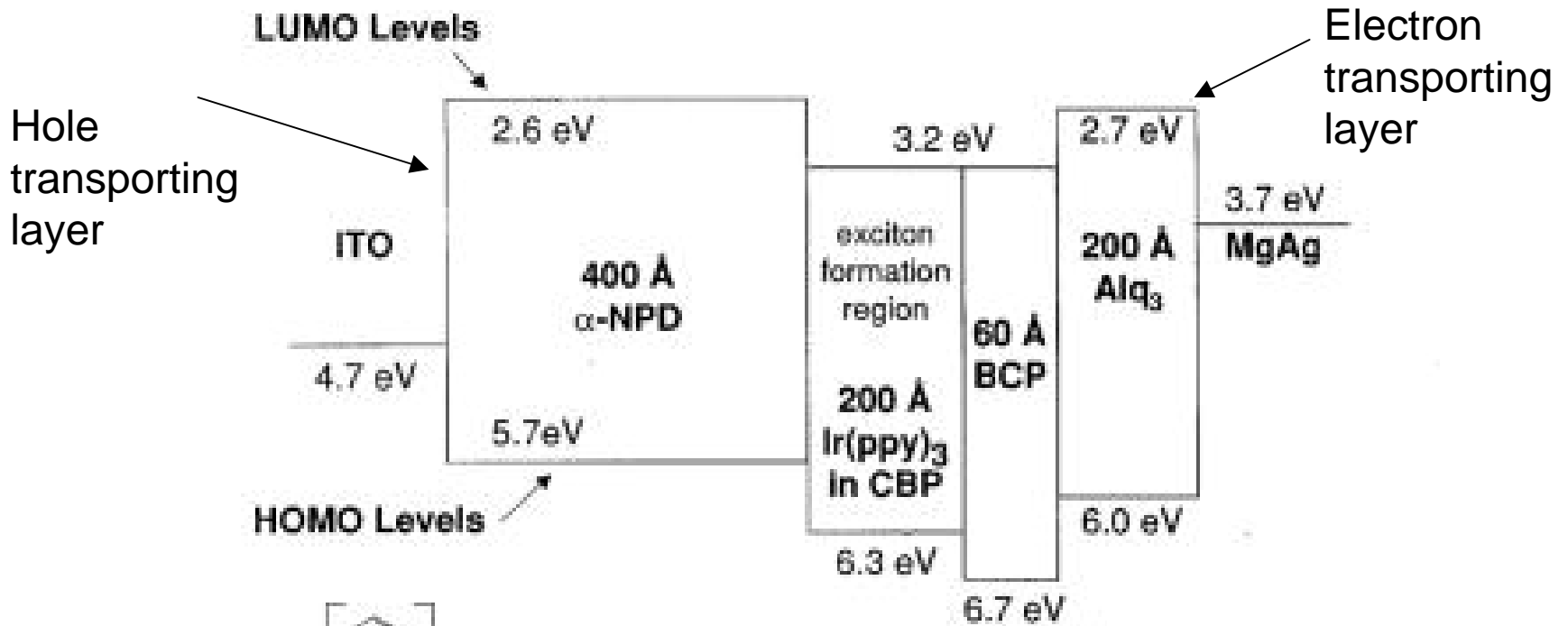
which is much higher than 0.33.

Theory of exciton formation

See Z.V. Vardeny et al. *Phys. Rev. Lett.* **88** 197401 (2002) for the latest explanation of why the singlet cross section is higher than the triplet cross section.

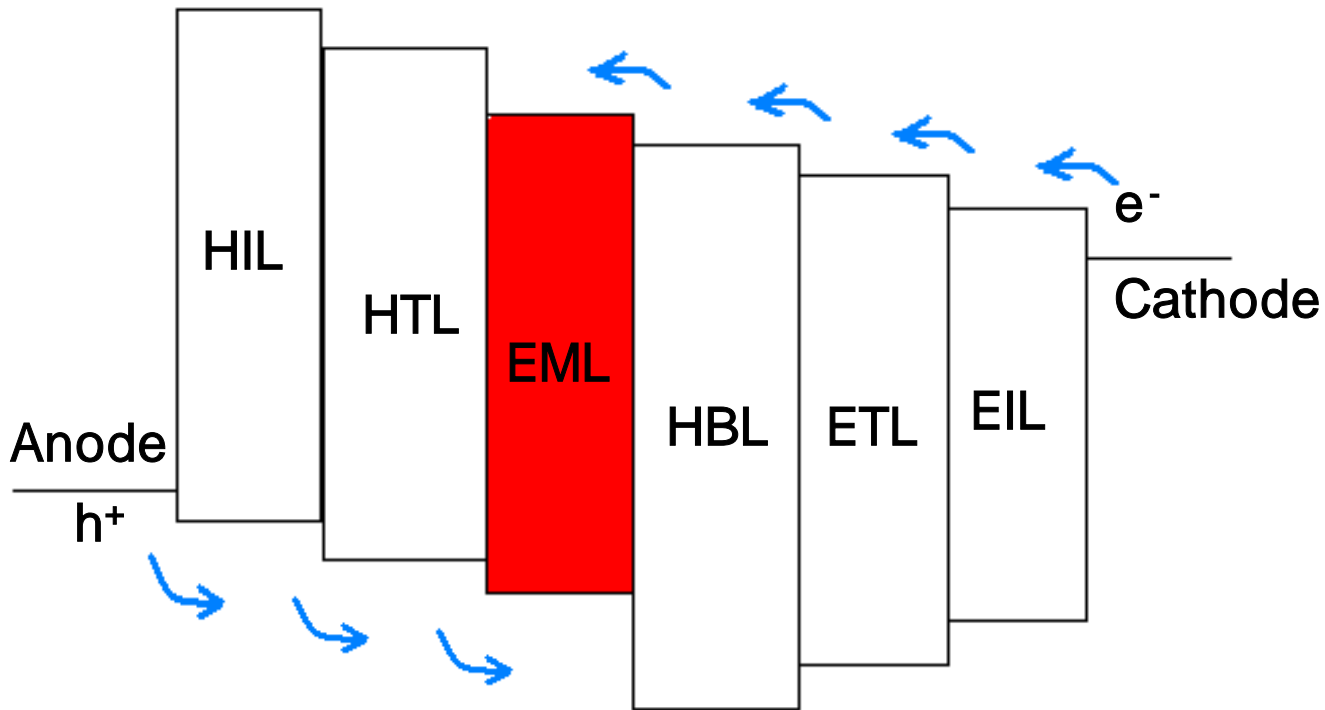
This subject is currently very controversial.

Electrophosphorescence

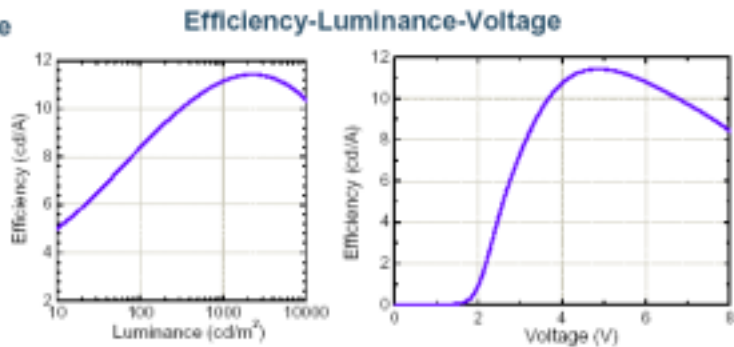
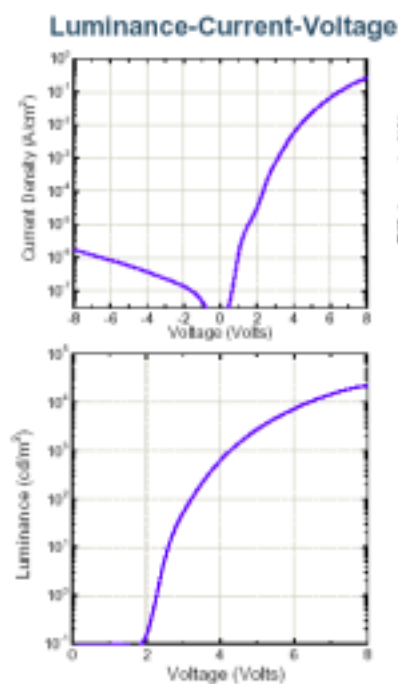
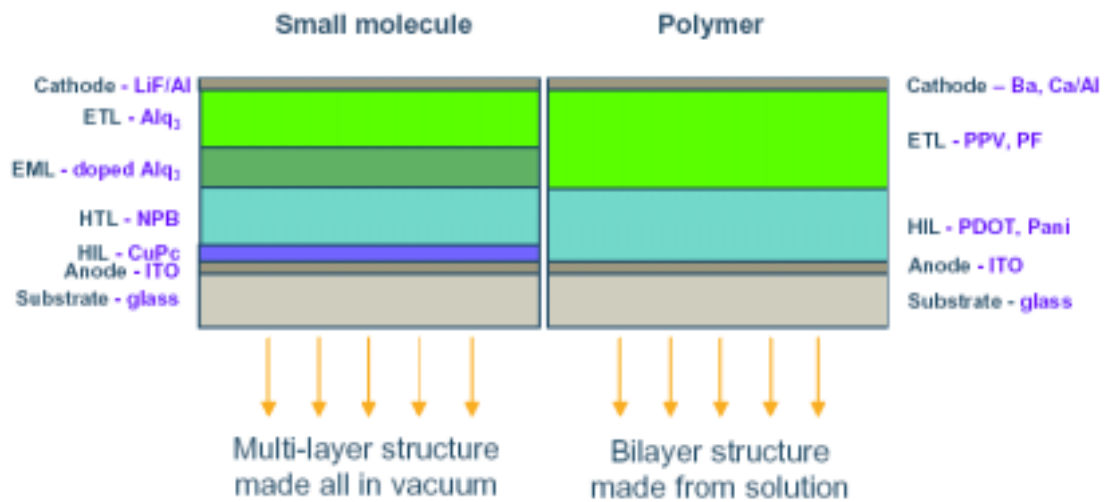


At a brightness of 100 cd/m², the quantum efficiency is 7.5 %. This high value is achieved because the singlets and triplets are harnessed.

This BCP hole blocking-layer keeps both holes and excitons from migrating over to the MgAg.



Anode: (large work function), 가 , ITO, IZO .
 HIL: PEDOT+PSS
 HTL: , IP(HIL EML), EA(EML e⁻ 가).
 EML: , PPP, PPV, PF, / energy transfer .
 HBL: EA (ETL EML), IP가 EML ~0.5ev (EML h⁻ 가).
 ETL: , IP EA, Alq3가 .
 EIL: ETL Cathode LiF .
 Cathode: (low work function: Ca, Li, Mg, Cs) / (Al, Cu, Ag)
 , HBL, ETL, EIL .



LUMINANCE is the luminous intensity per unit area projected in a given direction

The SI unit is the candela per square meter (**cd/m²**), which is still sometimes called a **nit**

The **footlambert (fL)** is also in common use:
1 fL = 3.426 cd/m²

<http://www.resuba.com/wa3dsp/light/lumin.html>

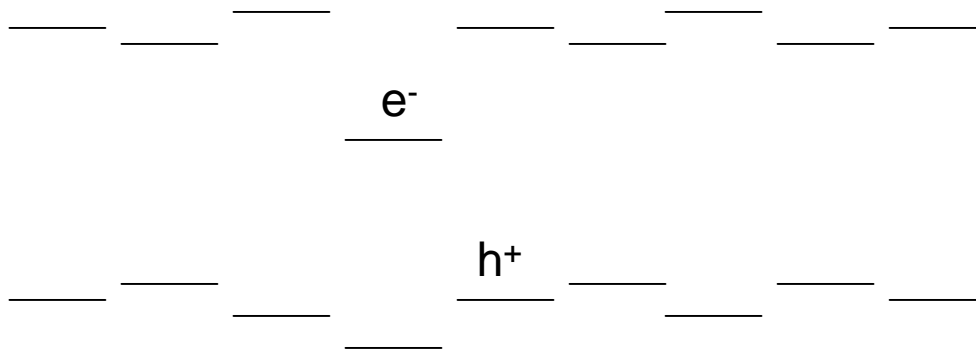
Achieving high η_{PL}

To get efficient radiative recombination, we must avoid

- energy migration to non-emissive trap states (e.g. carbonyl defects)
- coupling to nuclear motion

We must also avoid processes that slow down the rate of radiative decay, such as excimer formation (concentration quenching)

Non-emissive traps

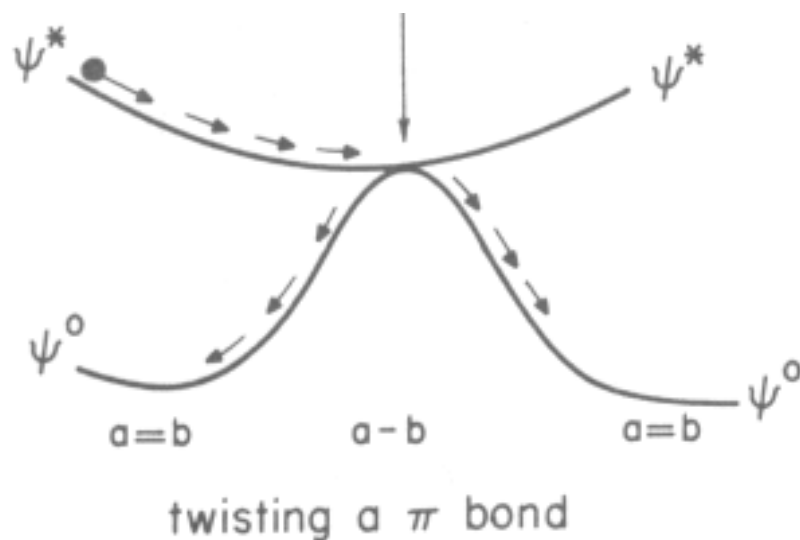


An exciton lives for approximately 1 ns and can diffuse over approximately 10 nm. Consequently, just one non-emissive trap state (e.g. a carbonyl defect) can eliminate luminescence from a relatively large region of material.

To avoid this problem, people reduce the number of non-emissive traps or make emissive traps.

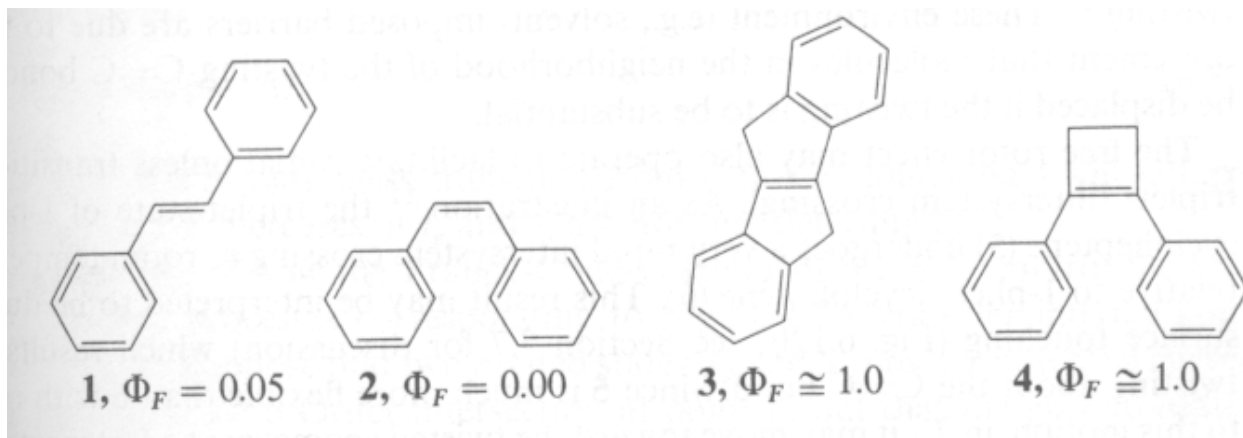
Another way to reduce k_{nr} is to cool the sample to slow the diffusion down.

Radiationless transitions due to stretching and twisting



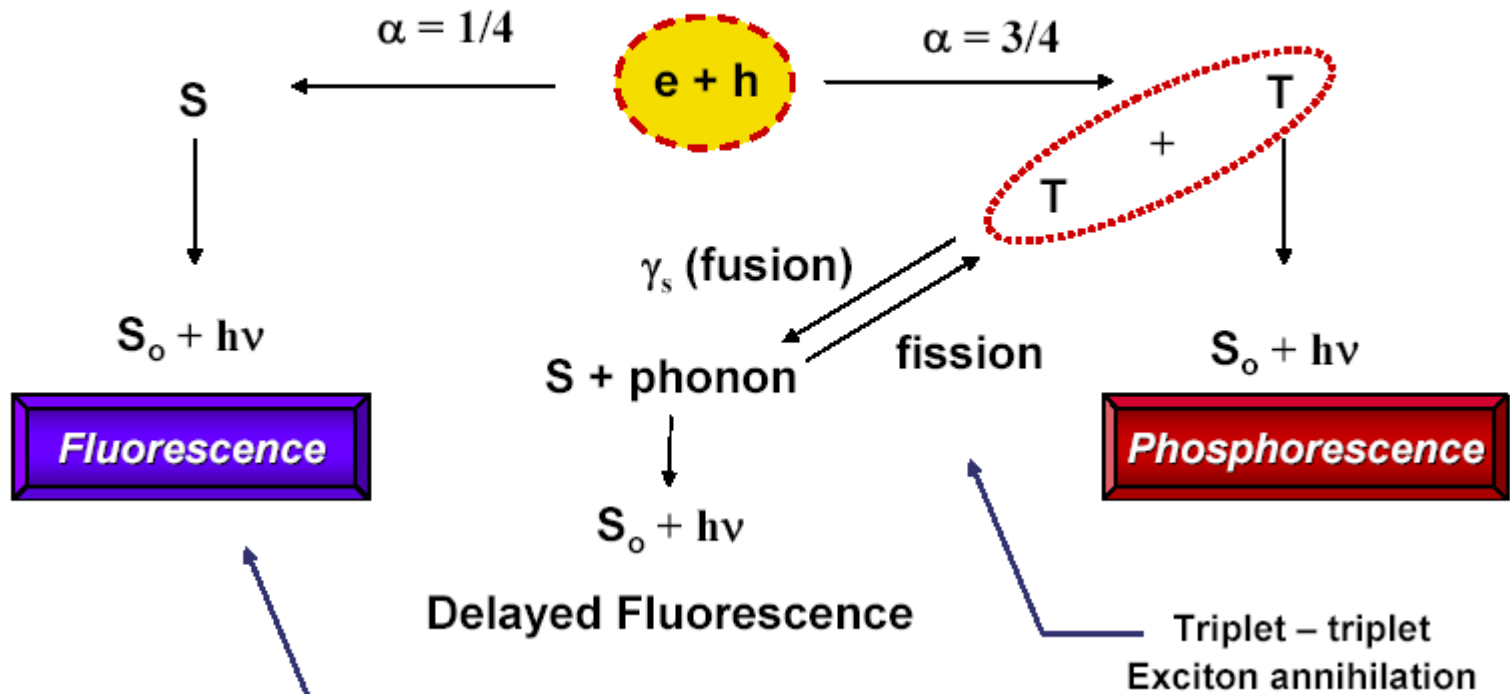
This type of nonradiative decay can be prevented by making the chromophores rigid.

In some cases cooling the sample will keep the molecule from flopping its way over an activation barrier and down to the ground state.



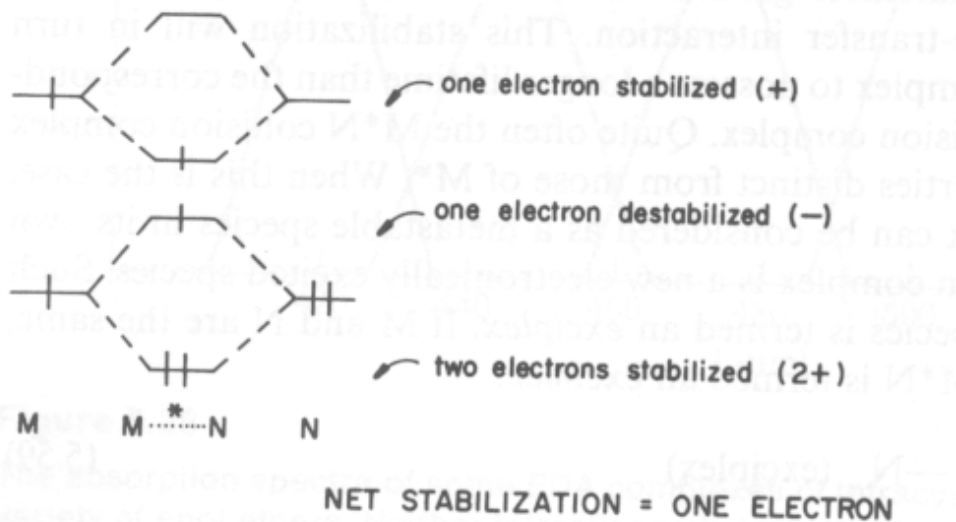
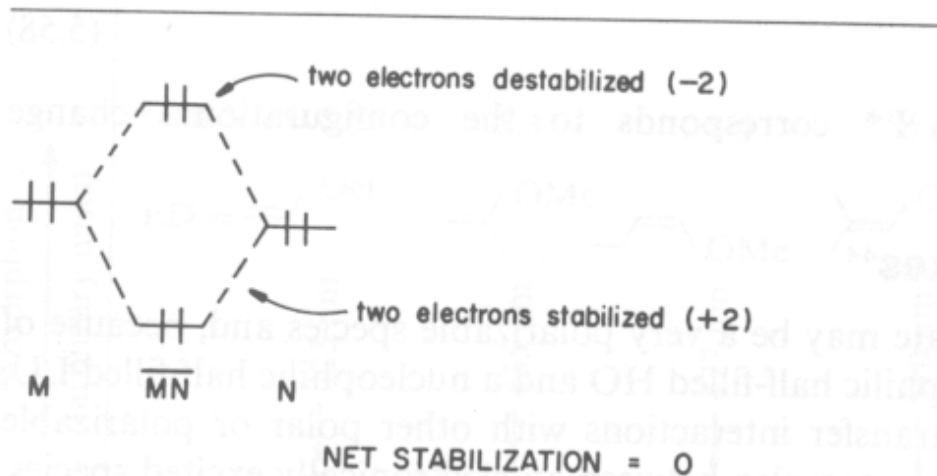
Quenching Problems

Exciton interactions



Excimer:
Concentration quenching

Excimers



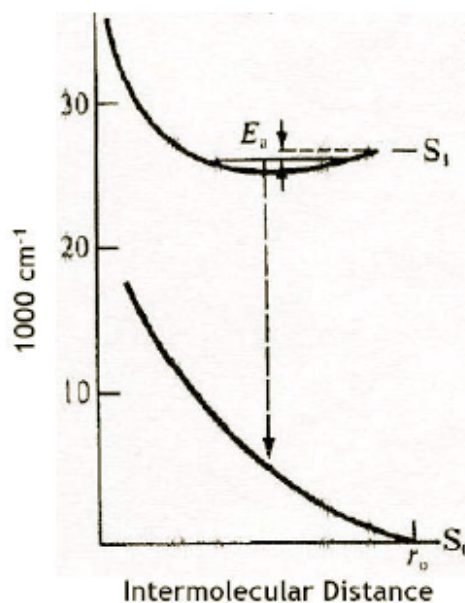
An excimer is a bound state between an excited molecule and a ground state molecule that would not form if both molecules were in the ground state.

Absorption spectrum is unchanged. Emission spectrum is red-shifted. If there are many ways that the two molecules can come together, the splitting of the levels will vary and the spectra will be smeared out.

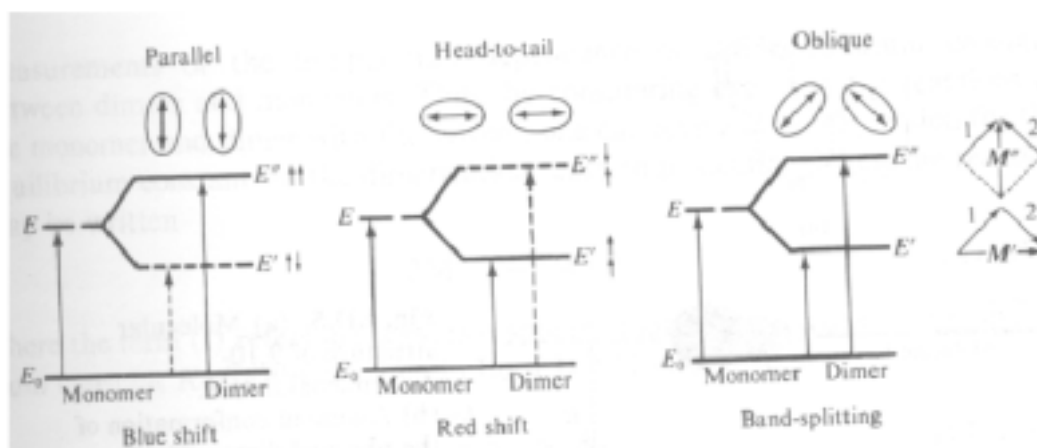
Excimer

● A class of compounds that exhibits the optical absorption characteristic of a monomer, but their luminescence is characteristic of a physical dimer.

- In excited state – dimer exists
- Ground state – is dissociative
- Excimer : $M + M^*$
- Exciplex : $D + A^*$ or $D^* + A$
- Red shift
- Broad peak with no vibronic structure



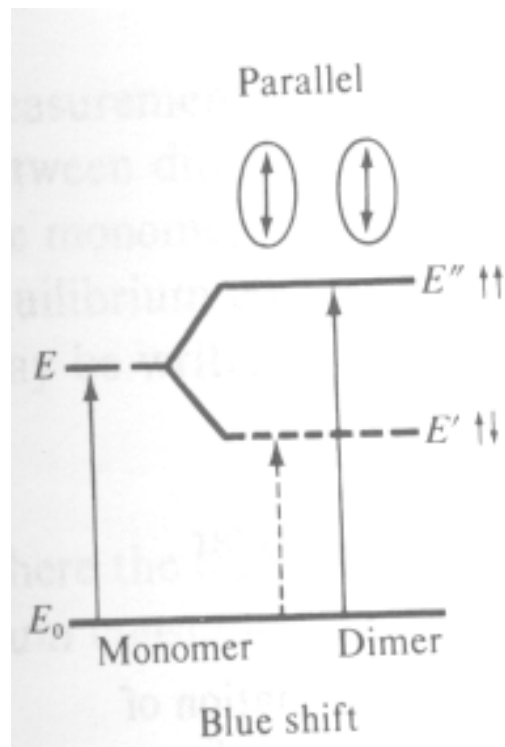
Radiation rates of excimers



For the dotted line transitions, The wavefunction on neighboring molecules oscillates out of phase. This eliminates the dipole and makes radiation a forbidden process.

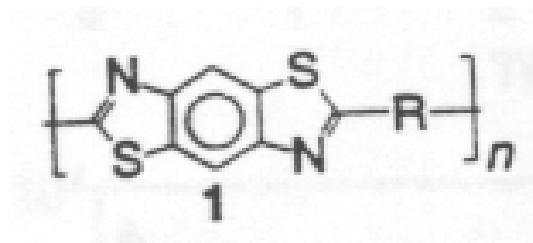
Pope and Swenberg, *Electronic Processes in Organic Crystals and Polymers*

Radiation rates of excimers



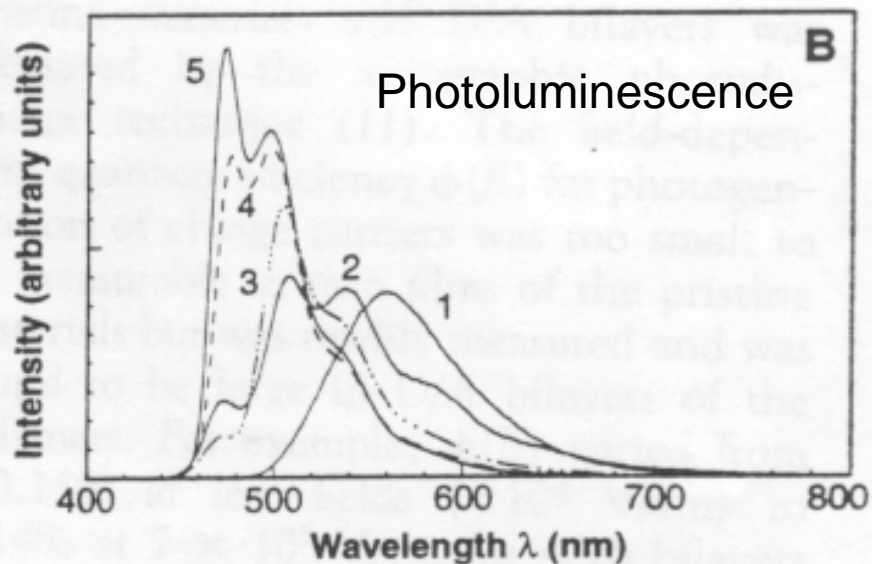
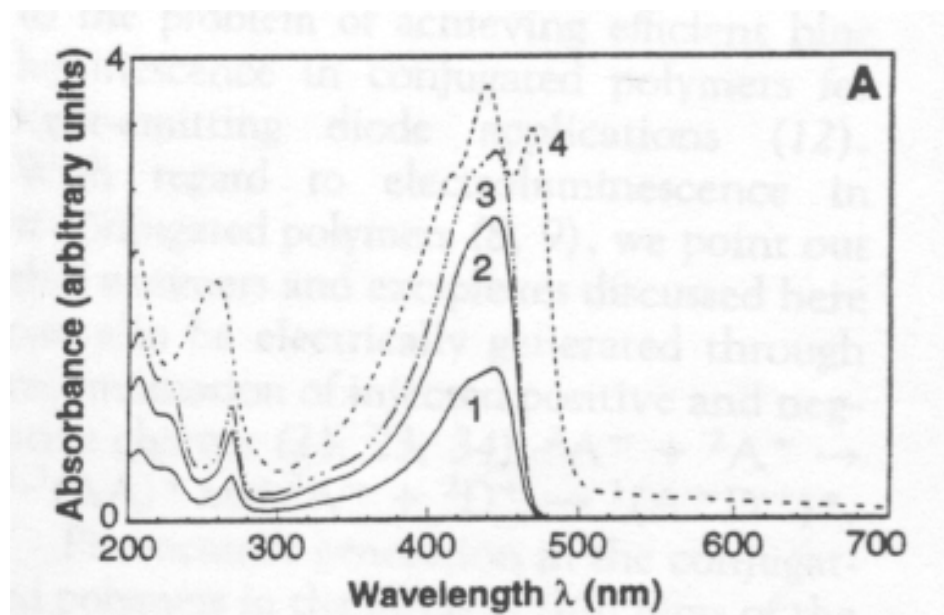
For the dotted line transition, the wavefunction on neighboring molecules oscillates out of phase. This eliminates the dipole and makes radiation a forbidden process. Since the lower energy excimer state is the one that gets occupied, the rate of emission is very low. At room temperature, nonradiative recombination tends to be much faster.

Excimer spectra



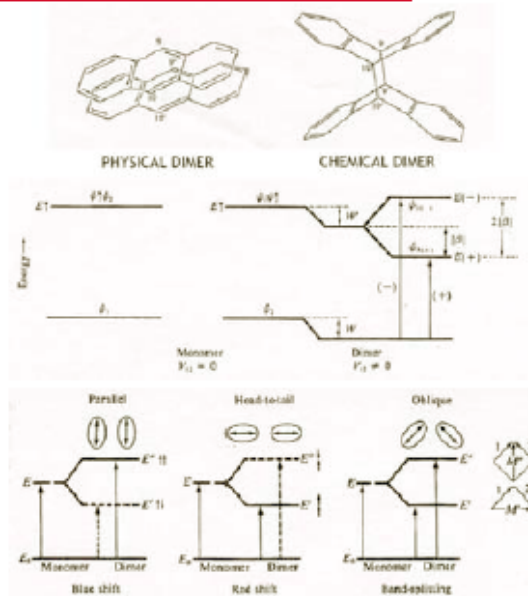
1-3 solutions
4 solid film

- 1** thin film
- 2** 5×10^{-3} M solution
- 3** 1×10^{-4} M solution
- 4** 1.4×10^{-5} M solution
- 5** 3.6×10^{-6} M solution



Dimers

- All dimer maxima lie at a lower energy than the corresponding maxima of the monomer spectrum
- The Franck-Condon maximum of the dimer is represented by the $0 \rightarrow 1$ transition, as compared to the $0 \rightarrow 0$ transition in the monomer.
(There is typically greater nuclear displacement in the dimer)
- The dimer spectrum is broader and less well defined as compared to the monomer spectrum due to the presence of new vibrational modes associated with the dimer
- There is a decrease in dimer luminescence intensity as compared to the luminescence of monomers



Exciton band splitting and energy shift for a physical dimer

Absorption spectra of dimer

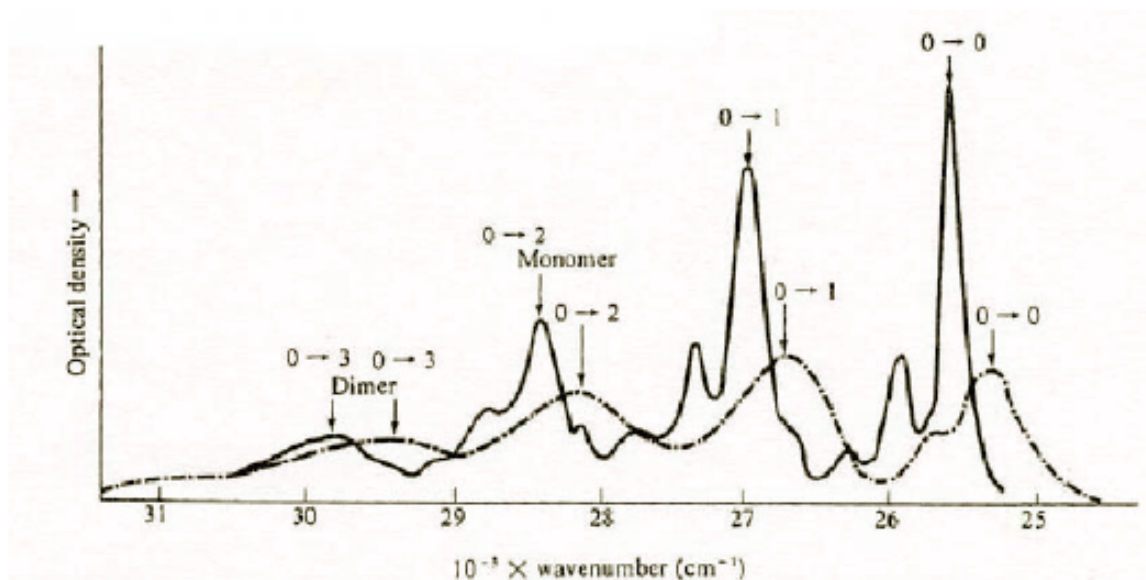


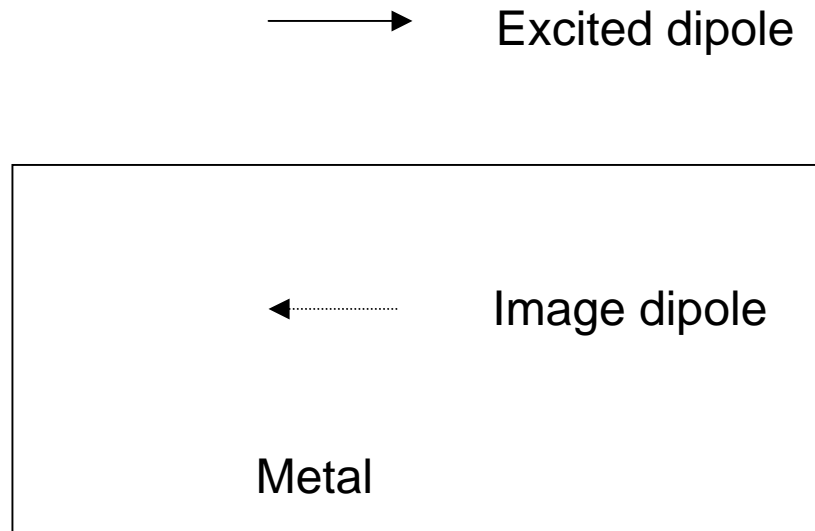
Fig. 1.D.6. Absorption spectra of the sandwich dimer (dashed line) and monomer (solid line) of 9-chloroanthracene in methyl cyclohexane glass. The 1400-cm^{-1} vibrational mode progression is labeled $0 \rightarrow n$. Additional structure in the spectrum is due to other intramolecular vibrational modes. (Chandross and Ferguson 1966)

Avoiding excimer formation (concentration quenching)

Dilute the chromophore. If one transfers energy from a host to a guest, high excitation densities can still be achieved.

Design the molecules so they cannot pack on each other (e.g. by using appropriate nonconjugated side chains).

Quenching by metal electrodes

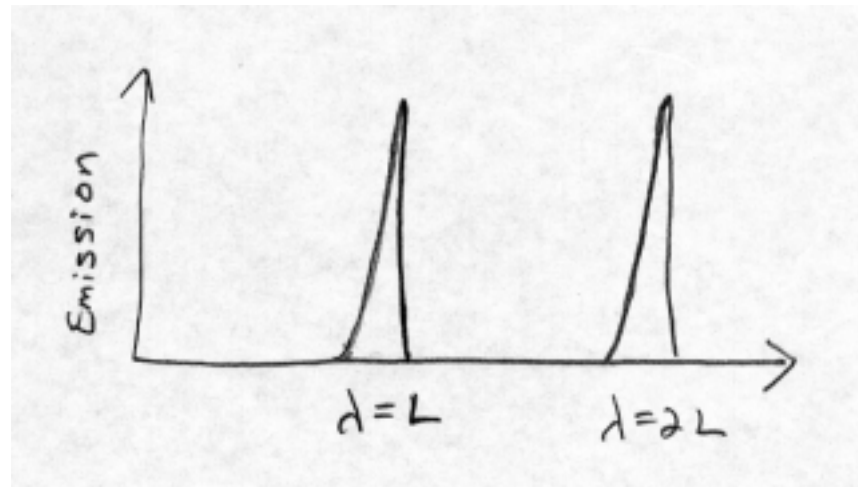
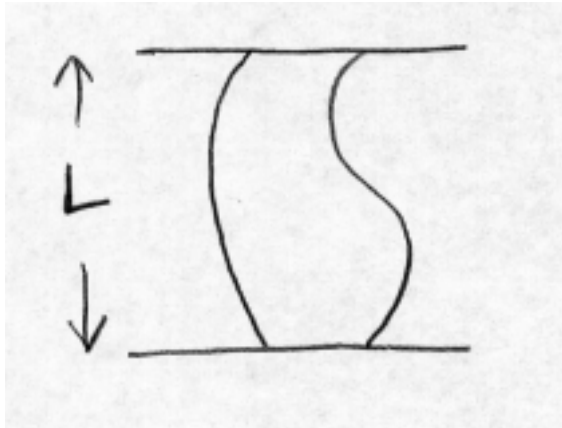


An exciton can excite a plasmon in the metal electrode if it is formed within about 10 nm of the metal. This energy is dissipated as heat.

How can we avoid quenching by the electrodes?

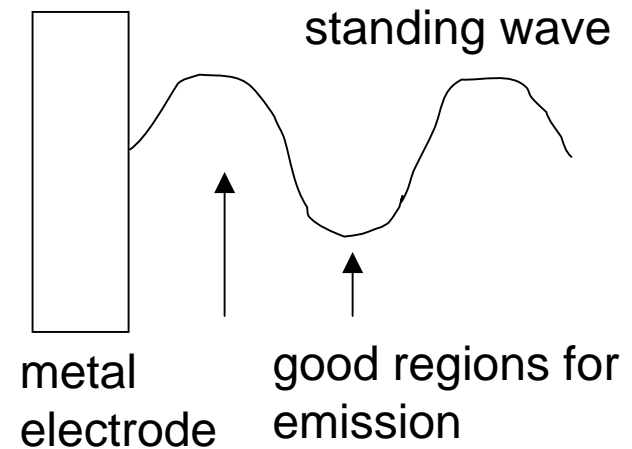
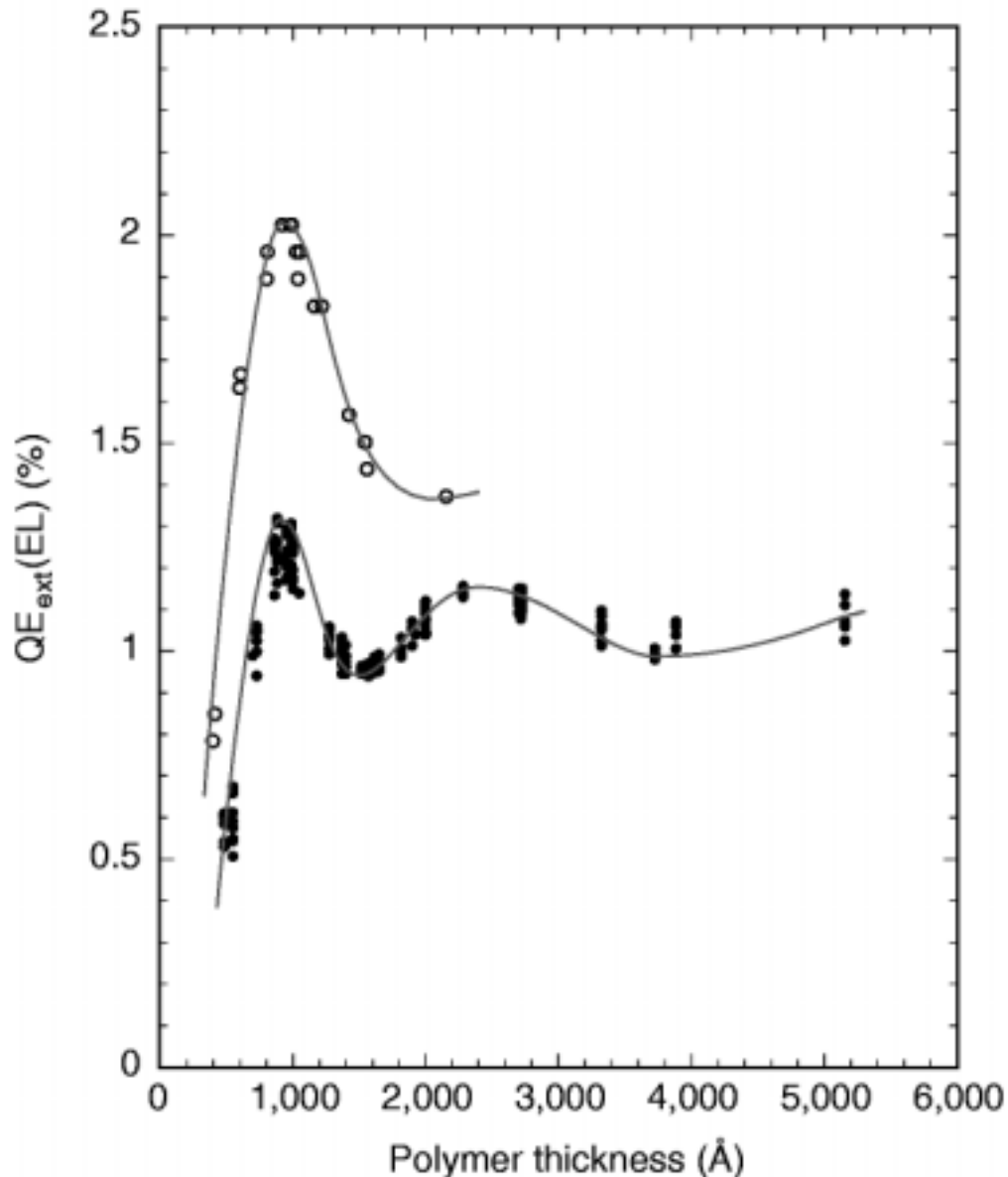
Spontaneous emission in a microcavity

A cavity made with two mirrors only has optical modes that satisfy $m\lambda/2 = L$, where m is an integer. Consequently, a light-emitting material inside the cavity only emits at those resonant wavelengths, even though that material would have a broad spectrum outside of the cavity.



A molecule located at the node of one of the modes cannot emit into that mode.

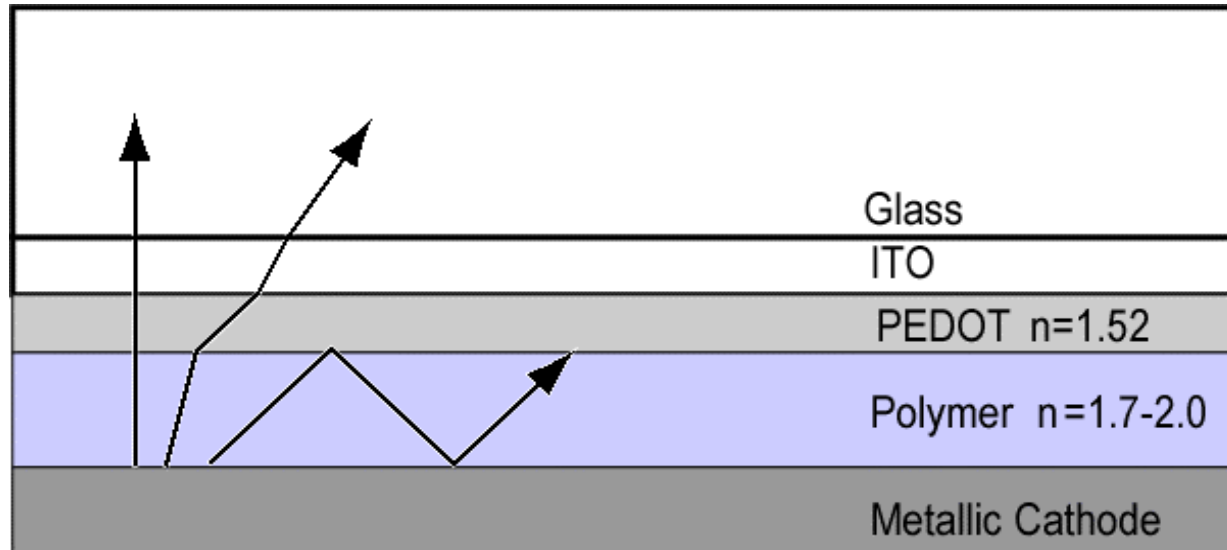
LED efficiency versus film thickness



In an LED with one reflective electrode, the best spots for emission are at a distance of $\lambda/4$ and $3\lambda/4$ from the electrode. It is for this reason that most LEDs are approximately 1000 Å thick.

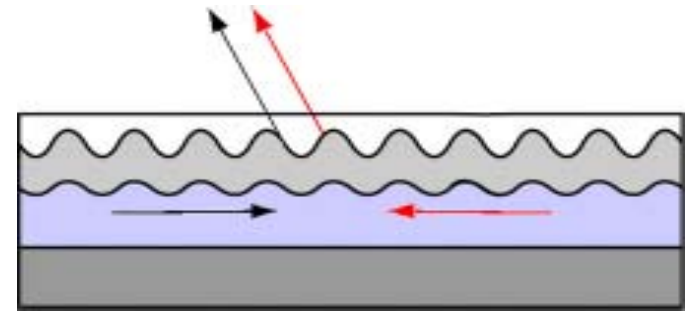
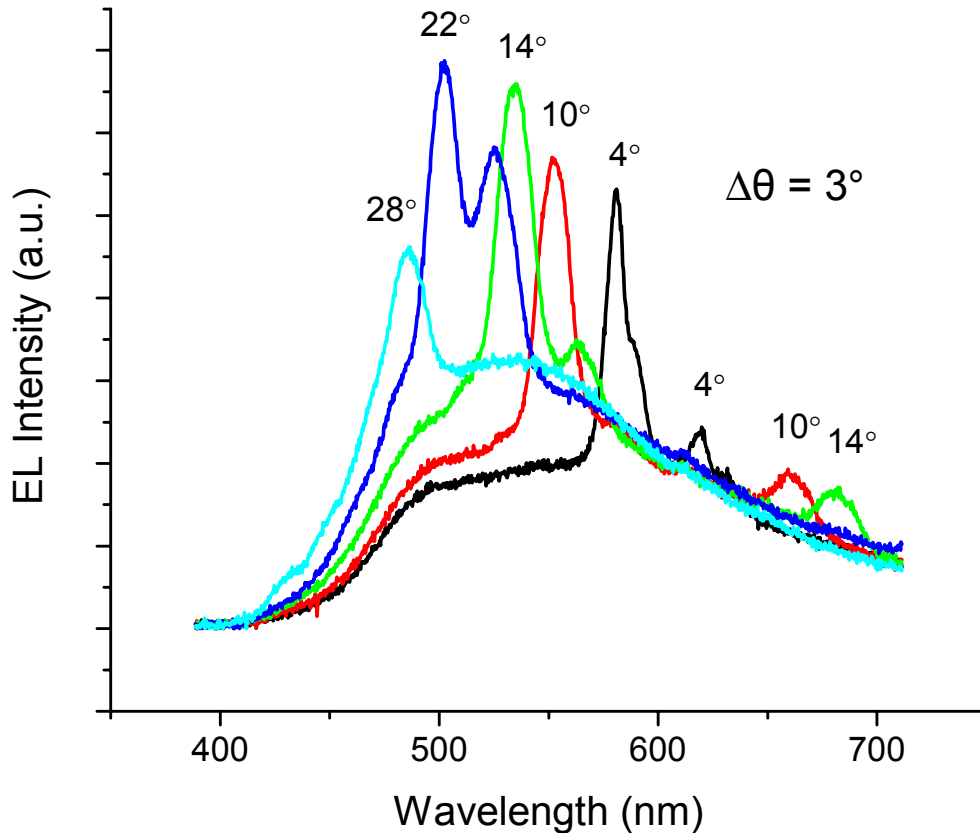
Extracting light from organic LEDs

If the emission is isotropic, only $1/2n^2$ escapes.



Blue LED with a grating

- Grating increases light output.
- The peak wavelength changes as the angle is varied.
- Approximately twice as much light escapes the LED



What remains to be done?

- Full color patterning by inexpensive methods such as ink jet printing and screen printing must be improved.
- Lifetimes for blue LEDs are 2000-5000 hours. At least a 10x improvement is needed.
- Light extraction needs to be improved to get a 2-5 x improvement in efficiency.
- A 2-3x improvement in efficiency along with a boost in lifetime would open up the lighting market.
- High-quality transparent flexible substrates need to be produced at low cost.
- Processing methods for large substrates need to be developed.
- Will device operation ever be completely understood?