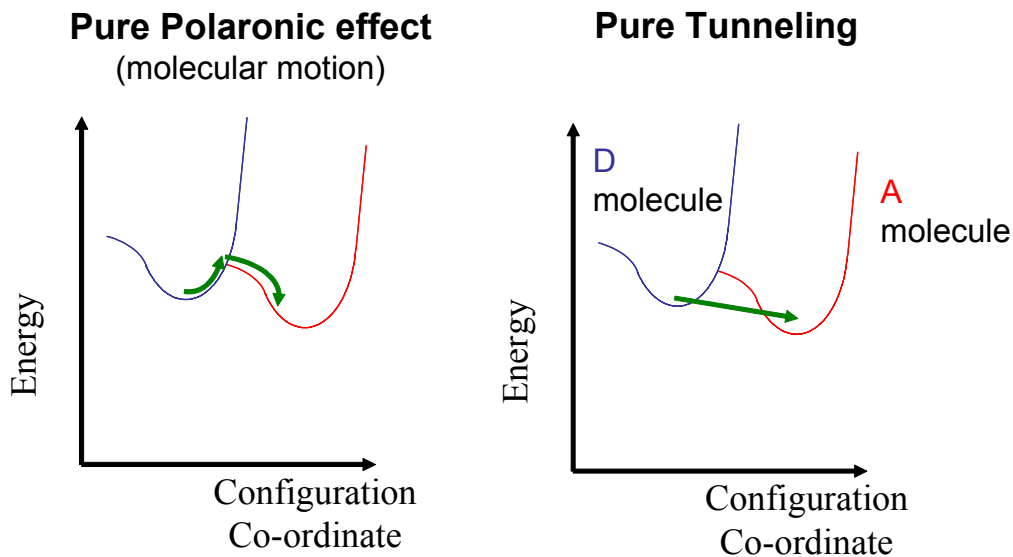


How does a polymer LED OPERATE?

Now that we have covered many basic issues we can try and put together a few concepts as they appear in a working device. We start with an LED:

1. **Charge injection**
 - a. Hole injection = oxidation of a molecule at the interface
 - b. Electron injection = reduction of a molecule at the interface
2. **Hopping** under an applied electric field towards the opposite electrode.
 - a. Hopping is oxidation-reduction reaction (i.e. chemistry, lifetime,...)
 - b. The oxidation-reduction can be described with the Marcus Theory taking into account the polaronic nature of the molecules and the notion of configuration coordinates
 - c. Hopping can also be described as a tunneling process which is a special case in the Marcus theory.



3. **Attraction** of negative and positive excitation **towards a recombination** event. The process is described as a Langevin type recombination which is a random motion in the attractive potential. Namely, the recombination rate depends on the charge mobility.

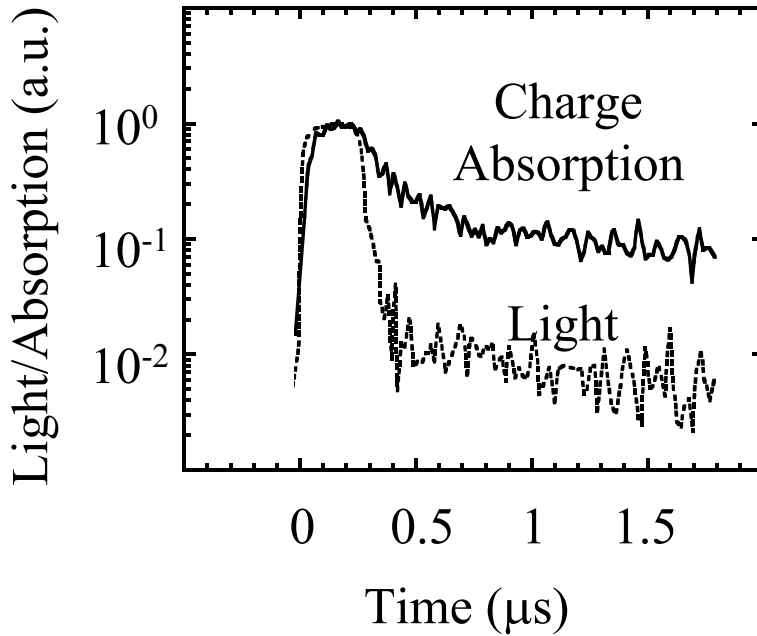
The capture radius is: $r_c = \frac{q^2}{4\pi\epsilon_r\epsilon_0 kT} = 185 \text{ \AA}$ (T=300K, $\epsilon_r=3$)

The bimolecular coefficient is: $B = \frac{q}{\epsilon_r\epsilon_0} (\mu_n + \mu_p)$

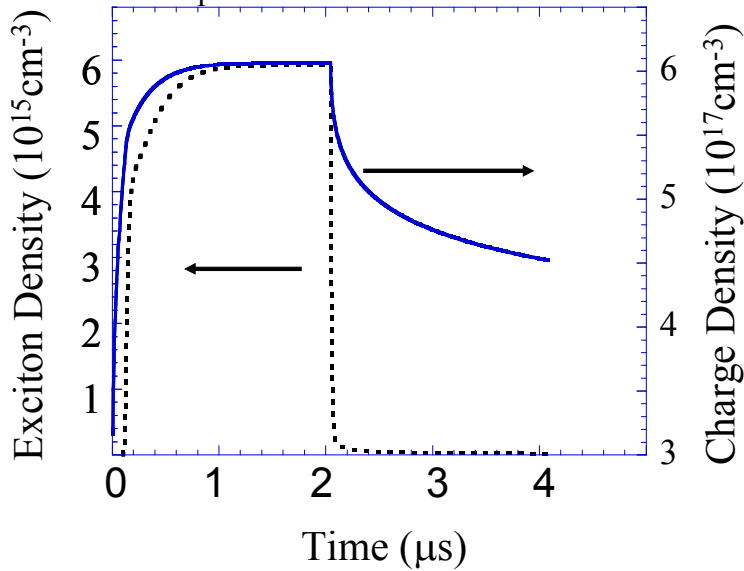
The capture (recombination) rate is: $R = BNP$

This model seems to extend also for the case when the charges are accelerated in electric fields and the effective recombination rate depends on the field-dependent mobility^[1,2].

The direct proof for the role of the field dependent mobility in the recombination rate was given experimentally^{[3]i}



and was also reproduced in a numerical simulation:



ⁱ Some authors insist on using $\mu(E=0)$ in the Langevin rate. It could be that the validity having $\mu(E)$ in the Langevin rate is morphology dependent and that in some cases one should use $\mu(E=0)$. However, we couldn't reproduced the above two figures without it (for PPVs and polyfluorenes).

The nature of the recombination (it be langevin) was used by Pinner to evaluate internal parameters^[1]:

In an LED the space charge that builds up throughout the charge injection process induces an electric field distribution, $F_{SC}(z)$, such that $F_{int}(z)=F_{app}+F_{bi}+F_{SC}(z)$, where $F_{app}=V_{app}/l$, $F_{bi}=V_{bi}/l$ and $F_{int}(z)$ is the total internal electric field.

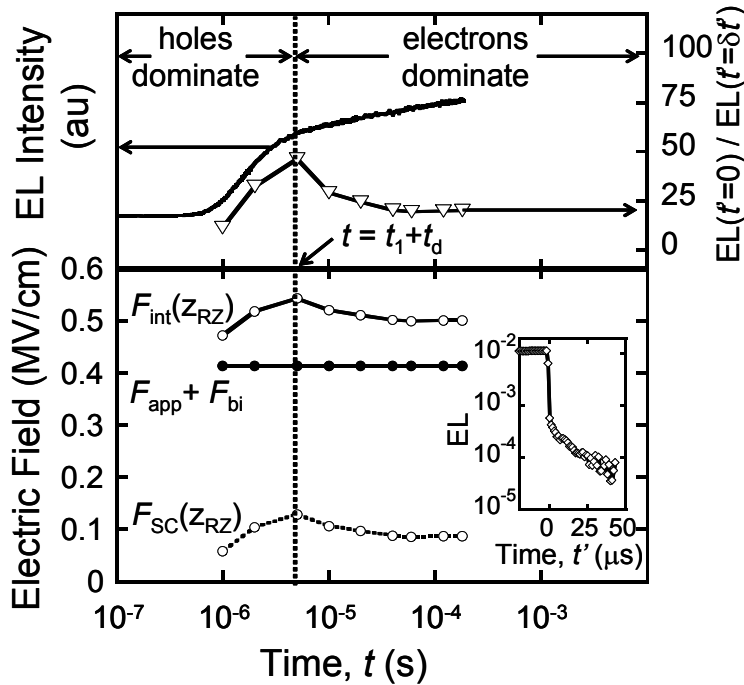
At the end of a step function in the applied voltage the internal field changes abruptly from $F_{int}(z)=F_{app}+F_{bi}+F_{SC}(z)$ to $F_{int}(z)=F_{bi}+F_{SC}(z)$ at $t=t_{OFF}$

The langevin recombination rate $[R(z)=B\mu_{eff}(z)n(z)p(z)]$ depends on the internal electric field through the mobility $\mu_h(z)=\mu_{h,0}\exp\left(-\frac{\Delta}{kT}\right)\exp\left(\gamma\sqrt{F_{int}(z)}\right)$.

Since the EL intensity is proportional to the recombination rate, R, we can we write down the ratio of the EL immediately before and after turn-off:

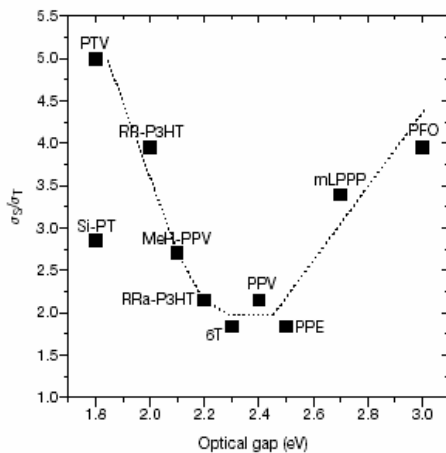
$$\frac{EL(t'=0)}{EL(t' \cong 1ns)} = \frac{\exp\gamma\left(F_{app} + F_{sc}(z_{RZ}) + F_{bi}\right)^{1/2}}{\exp\gamma\left(F_{sc}(z_{RZ}) + F_{bi}\right)^{1/2}}$$

The above equation can be used to calculate $F_{SC}(z_{RZ})$, the value of the space charge-induced electric field at the position of the recombination zone. By doing this for a series of pulses of different widths, we may then determine both the time evolution of the space charge-induced electric field and the overall net internal electric field at the position of the recombination zone as a function of time *during* the applied pulse.



4. **Recombination** – negatively charged molecule and positively charged molecule transform into a neutral excited-state (since in our case it can also move it is an exciton).

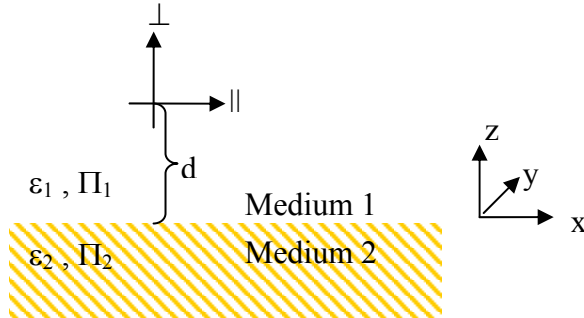
Since the final state is an exciton it may assume two different orientations: Singlet exciton and Triplet exciton. As mentioned in the lecture about excitons (“triplet state of any particular energy level to be stabilised with respect to the corresponding singlet state by a quantity known as the *exchange energy*”) the energy of the two differ and as a consequence their spatial extent and wave functions are different. Namely, one would expect that the overlap integral between a charged-state and an exciton will depend on the exciton being singlet or triplet. This has been calculated and measured for some compounds and it seems that it is easier to couple to the spatially more spread singlet exciton.^[4, 5] The ratio between the formation cross sections for singlet (σ_S) and triplet (σ_T) was measured by Wohlgenannt and colleagues^[5] for a range of materials:



As we often see, the ratio is material or chemical-structure dependent.

5. **Emission of radiation.**

In the **quasi-static** approximation (i.e. at short distances from an interface or metal where $k_1 d < 0.1$, typically up to about 5-10nm)



the radiation rate is given by:

$$\hat{b} = 1 + \frac{3}{16} \frac{q}{\pi} \frac{\Delta}{k_1^3 d^3} \text{Im}(\gamma)$$

$\Delta=1$ for parallel dipole and $\Delta=2$ for perpendicular. q is the free-space quantum efficiency.

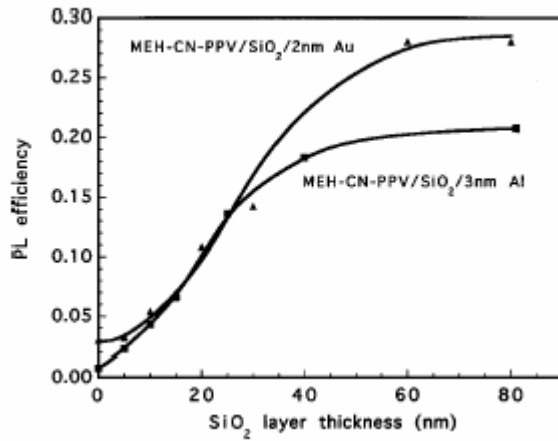
$$\gamma = \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + \varepsilon_1};$$

$$\varepsilon_2 = \varepsilon_2' + i\alpha \quad \text{Im}(\gamma) = \frac{2\alpha\varepsilon_1}{(\varepsilon_2' + \varepsilon_1)^2 + \alpha^2}$$

$$\boxed{\hat{b} = 1 + \frac{3}{16} \frac{q}{\pi} \frac{\Delta}{k_1^3 d^3} \frac{2\alpha\varepsilon_1}{(\varepsilon_2' + \varepsilon_1)^2 + \alpha^2}}$$

This expression is in the quasi-static approximation and hence it does not include waves that will propagate long distance and reach any practical detector. Namely, this is a non-radiative rate that is induced by the metal (quenching).

This effect have been measured^[6] by examining the quantum efficiency of a 15–20-nm-thick MEH-CNPPV film on a SiO₂ spacer layer on 2 nm of gold or 3 nm of aluminum as a function of the SiO₂ thickness.ⁱⁱ



For the **quasi optic** (radiation measured far away) case we have only the parallel dipole ($k_1 d > 2$, typically beyond 80-100nm):

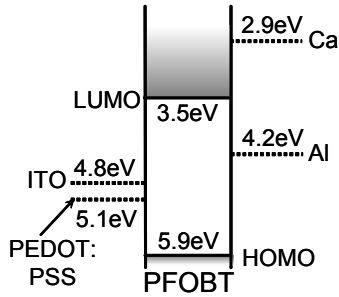
$$\hat{b} = 1 + \frac{3q}{16\pi} \frac{1}{k_1 d} \frac{1}{\underbrace{(|n_1|^2 - |n_2|^2) \sin(2k_1 d) - 2n_1 n_2 \cos(2k_1 d)}_f \underbrace{|n_1 + n_2|^2}_f}$$

where $n_2 = n'_2 + i n''_2$.

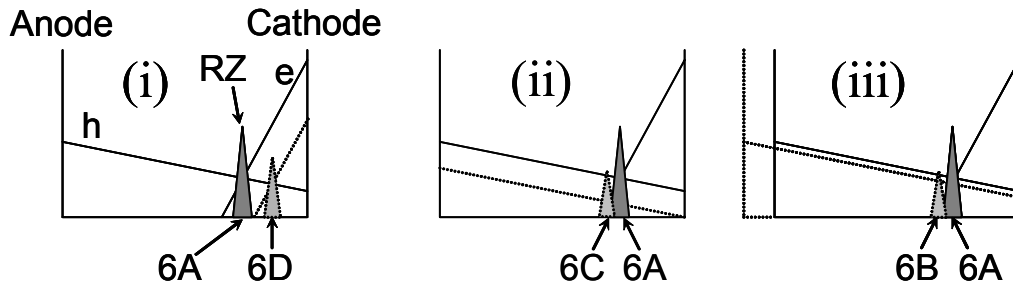
The effect seen in the quasi-optic case is that of interference between the wave emitted from the dipole towards the observer and the wave emitted towards the mirror and is reflected back towards the observer. Since it depends on $k = \frac{2\pi n}{\lambda}$ there will often be modifications to the emission spectrum.

ⁱⁱ These results were taken from Helmut Becker and Seamus Burns PhD work.

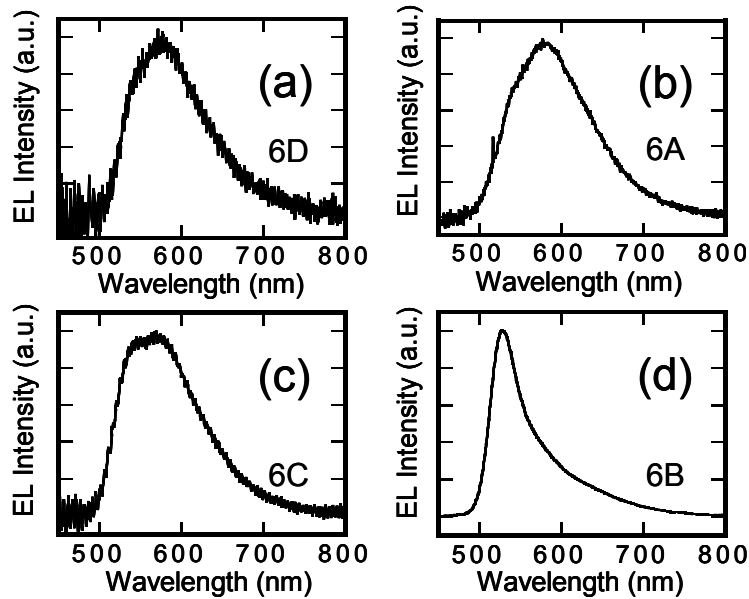
For example in an LED the position of the recombination zone may vary depending on the contacts used and the length of the polymer layerⁱⁱⁱ.



The way one can use different electrodes and polymer thickness to shift the position of the recombination zone relative to the mirror-electrode (Ca or Al) is shown schematically below.



This effect was used to fabricate several LED structures that demonstrated the role of the contacts in positioning the recombination zone and the resulting role of interference in determining the measured emission spectrum.

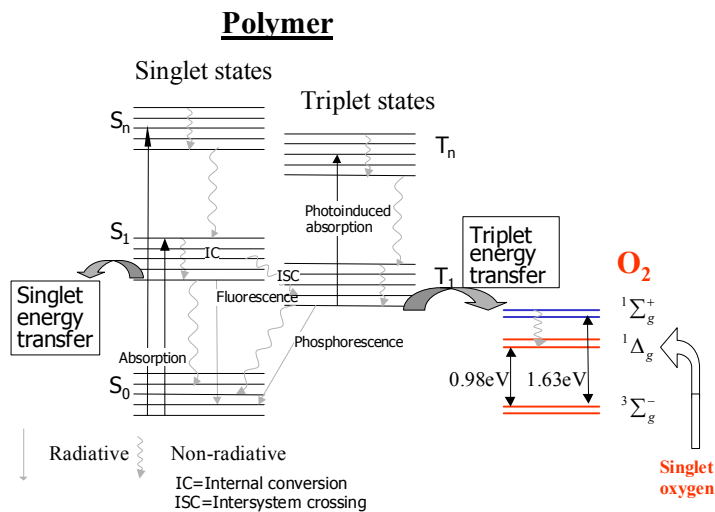


ⁱⁱⁱ These results were taken from the PhD thesis of Dickon J. Pinner.

6. **Stability**

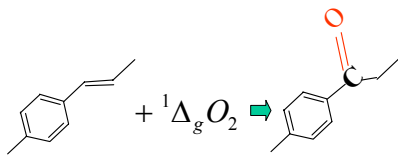
a. Environmental stability of the chemical structure

**Singlet Oxygen Sensitization Via the polymer
Triplet state**



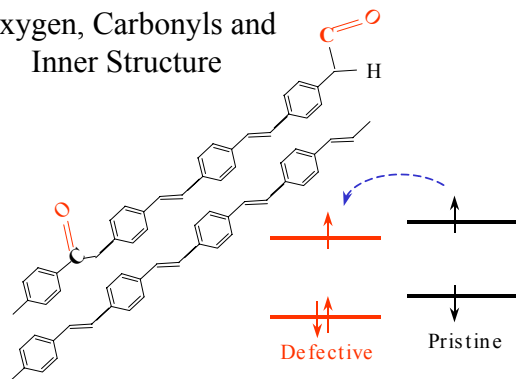
See also: B. H. Cumpston and K. F. Jensen, *Synthetic Metals* **73** (3), 195 (1995); B. H. Cumpston, I. D. Parker, and K. F. Jensen, *Journal of Applied Physics* **81** (8 Pt1), 3716 (1997)

Formation of carbonyl groups



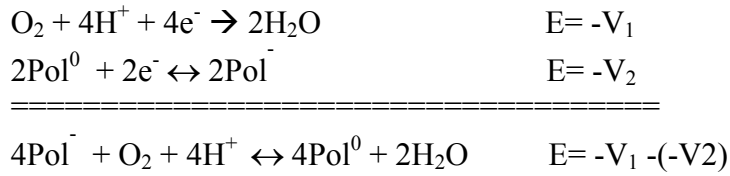
Chemical defects = dissociation centers, traps^[7, 8]

Oxygen, Carbonyls and Inner Structure

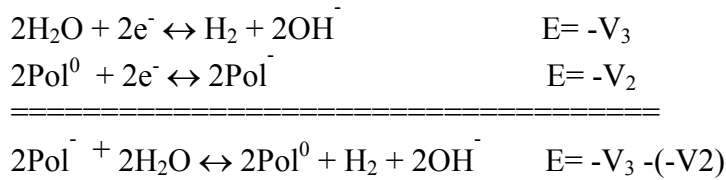


L.J. Rothberg

- b. Environmental stability of electronic conductivity (doping)^[9]
Instability of N type towards oxygen (or tendency of intrinsic to become P type)



Instability of N type towards water (or tendency of intrinsic to become P type)



The value of V_2 depends on the specific polymer however, for most (all?) polymers it is such that N type is not chemically stable. \Rightarrow Encapsulate devices. [a dense material that does not allow penetration (diffusion) of oxygen and water will show better stability but probably still require encapsulation to be truly stable]

7.

REFERENCES

- [1] D. J. Pinner, R. H. Friend, N. Tessler, *Appl. Phys. Lett.* **2000**, *76*, 1137.
- [2] U. Albrecht, H. Bassler, *Phys. Stat. Solidi B - Basic Research* **1995**, *191*, 455.
- [3] N. Tessler, D. J. Pinner, V. Cleave, D. S. Thomas, G. Yahiolu, P. Lebarney, R. H. Friend, *Appl. Phys. Lett.* **1999**, *74*, 2764.
- [4] Z. Shuai, D. Beljonne, R. J. Silbey, J. L. Bredas, *Phys. Rev. Lett.* **2000**, *84*, 131.
- [5] M. Wohlgenannt, K. Tandon, S. Mazumdar, S. Ramasesha, Z. V. Vardeny, *Nature* **2001**, *411*, 617.
- [6] H. Becker, S. E. Burns, R. H. Friend, *Phys. Rev. B* **1997**, *56*, 1893.
- [7] L. J. Rothberg, M. Yan, F. Papadimitrakopoulos, M. E. Galvin, E. W. Kwock, T. M. Miller, *Synth. Met.* **1996**, *80*, 41.
- [8] L. J. Rothberg, M. Yan, S. Son, M. E. Galvin, E. W. Kwock, T. M. Miller, H. E. Katz, R. C. Haddon, F. Papadimitrakopoulos, *Synth. Met.* **1996**, *78*, 231.
- [9] D. M. deLeeuw, M. M. J. Simenon, A. R. Brown, R. E. F. Einerhand, *Synthetic Metals* **1997**, *87*, 53.