

Excitation Dynamics in Real Systems

Papers handed:

Synth. Met. 78 (1996) 289-293.

Chem Phys. Lett. 119 (1985) 377-382

Adv. Mat., 11, (1999) 285-288

Other references:

1. Electronic properties of polymers, Wiley, 1982.

In this lecture we aim to illustrate that knowing the basic processes that may occur in an organic semiconductor (as those discussed in the previous lecture) makes it possible to design experiment that can be used to extract important physical parameters.

Units etc.

ϵ_A is the molar decadic extinction coefficient which is related to the absorption cross section (A) through the following relations:

$$\frac{I}{I_0} = \exp(-\alpha L) = \exp(-AnL) \quad \text{Here } n \text{ is the concentration in cm}^{-3} \text{ and } L \text{ is the}$$

length (cm).

$$\frac{I}{I_0} = 10^{-\epsilon_A CL} \quad \text{Here } C \text{ is the concentration in mole/litre } (C=n*1000/6e23) \text{ [}\epsilon_A CL$$

is also known as the optical density (OD) of the film].

$$\text{And finally } \epsilon_A = \frac{A * N_A}{1000 * \ln(10)} \text{ [litre/(mole * cm)]}$$

[We note that the packing density of a polymer film and the concentration of conjugated sites is not as straight forward evaluation as the calculation of the concentration of molecules in solution.]

The exciton energy-transfer lifetime (paper 2 – stretched exponential)

We consider an exciton located at $r=(0,0,0)$ which can couple through dipole-dipole interactions with a large number of sites which are randomly distributed in the film and located at r_j . The energy transfer rate or the inverse lifetime of a single transfer between $(0,0,0)$ and r_j follows the Förster formula:

$$W(r_j) = ar_j^{-6} \equiv \tau_0^{-1} \left(\frac{r_0}{r_j} \right)^6$$

Here τ_0 is the decay rate in the absence of Förster

transfer mechanisms and r_0 is the critical length beyond which the Förster rate is not significant with respect to $1/\tau_0$.

This will result in a relaxation of the excited state according to:

$$f(t, r_j) = \exp[-tW(r_j)]$$

If we let p to be the probability of having a defect at site j then the relaxation becomes:

$$\phi(t, r_j) = (1 - p) + pf(t, r_j)$$

which express' the idea that only a fraction p will couple to sites at distance r_j and what is not coupled does not decay with time (we neglected in this formula other types of relaxation).

To account for all distances r we have:

$$\phi(t) = \prod_{r_j} [(1 - p) + pf(t, r_j)]$$

using the above framework and a few mathematical manipulations (see paper 2) one can arrive at the formula:

$$\phi(t) = f_0(t) \exp \left(-k \left(\frac{t}{\tau_0} \right)^{0.5} \right)$$

where f_0 is the decay in the absence of any Förster

transfer and many times takes the form of $f_0 = \exp \left(-\frac{t}{\tau_0} \right)$ and $k = \frac{C_A}{C_A^0}$. C_A is the

acceptor concentration and C_A^0 is the critical concentration which is related to r_0 .

$$C_A^0 = \frac{1.5}{\pi^{3/2} r_0^3} [\text{cm}^{-3}] = \frac{1500}{N_A \pi^{3/2} r_0^3} [\text{mole/litre}]$$

$$r_0^6 = \frac{9000F^2 \ln(10)}{128\pi^5 n^4 N_A} \eta_D \Omega$$

$$\Omega = \int_0^\infty \overline{I_D} \epsilon_A \frac{d\nu}{\nu^4}$$

F^2 is the orientation factor (0.6 in random oriented systems), η_D is the donor efficiency, N_A is the Avogadro constant, which is $6.022 \times 10^{23} \text{mole}^{-1}$, and ϵ_A is the molar decadic extinction coefficient.

Finally we are at a position to use a decay rate curves (as in ref 1) to check for the existence of a Förster process and evaluate the Förster radius.

The decay curve is first measured for a film containing only donor molecules or the pristine film, this curve defines the function f_0 .

Then the decay curves are measured as a function of acceptor concentration and the formula for $\phi(t)$ is fitted to extract k as a function of concentration. If one finds good fits and a linear dependence of k on the concentration then it is most likely a Förster process. If ϵ_A is known (literature/measurement in solution/assuming a density in a solid pristine film of 10^{21}cm^{-3}) then C_A^0 can be evaluated and r_0 deduced from it.

The triplet diffusion length (paper 3-4)

The triplet density following an excitation is governed by the equation:

$$\frac{\partial n}{\partial t} = I - \beta n - \gamma n^2 + D \frac{\partial^2 n}{\partial x^2}$$

Here I is the generation term β is the triplet mono molecular decay rate, γ is the bimolecular decay rate, and D is the triplet diffusion coefficient. As we saw in the last lecture a fraction (f) of the bimolecular recombination will result in generation of singlets and the phenomena of delayed fluorescence. If n is small so that $\beta \gg \gamma n$ then the bimolecular recombination has no effect on the triplet dynamics and the delayed fluorescence can be regarded as a probe for the triplet density. If the excitation is spatially confined one then the diffusion will broaden the triplet distribution which will also result in a reduced delayed fluorescence. If we compare excitation of a small spot with a uniform excitation (diffusion has no effect on the density) then the diffusion constant can be extracted. As it turns out, the time dependence of the difference between the two normalised responses is very sensitive to the triplet diffusion constant.

An alternative way of probing the triplets in a given material (polymer film) would be to use a methodology somewhat similar to the singlet case described above. In other words, to blend into the film molecules which are capable of receiving the triplet energy from the polymer (host) and of converting it into light. This would be the case of a molecule which can emit in the triplet state due to the presence of a heavy atom which is promoting the spin-orbit coupling.

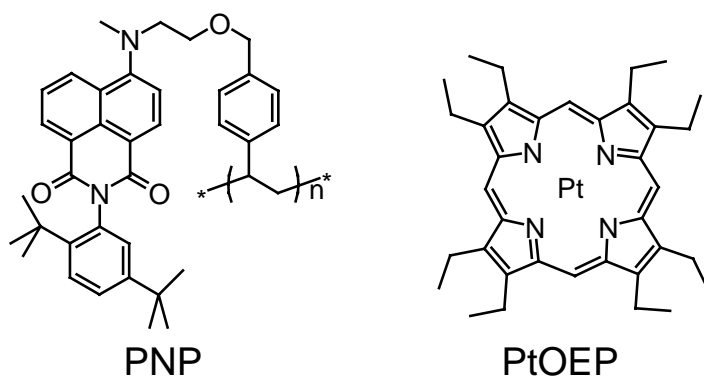


Figure 1. Molecular structure of the host polymer PNP and of the triplet emitting molecule PtOEP.

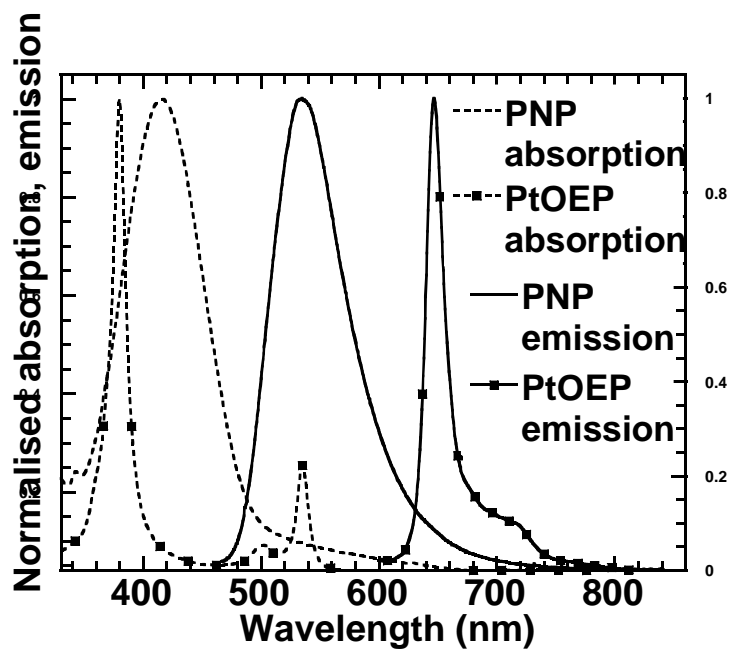


Figure 2. Emission and absorption → Förster is likely to happen

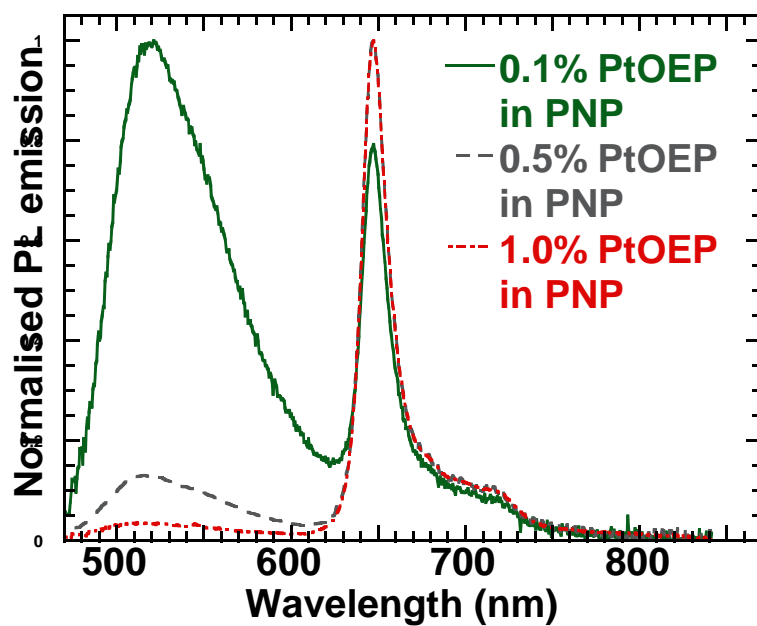


Figure 3. PL of blends

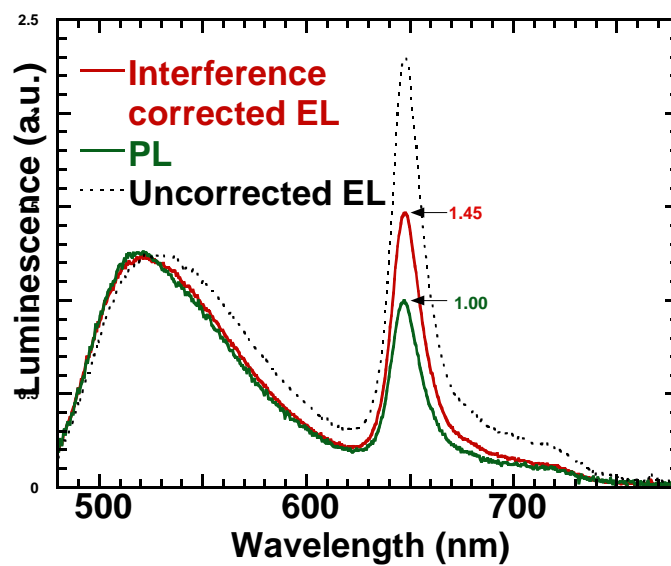


Figure 4.

We note that in the LED there is an additional input source for the PtOEP \rightarrow the PNP triplets. Without accounting for interference due to the metal \rightarrow over estimate the extra channel (triplets in PNP).

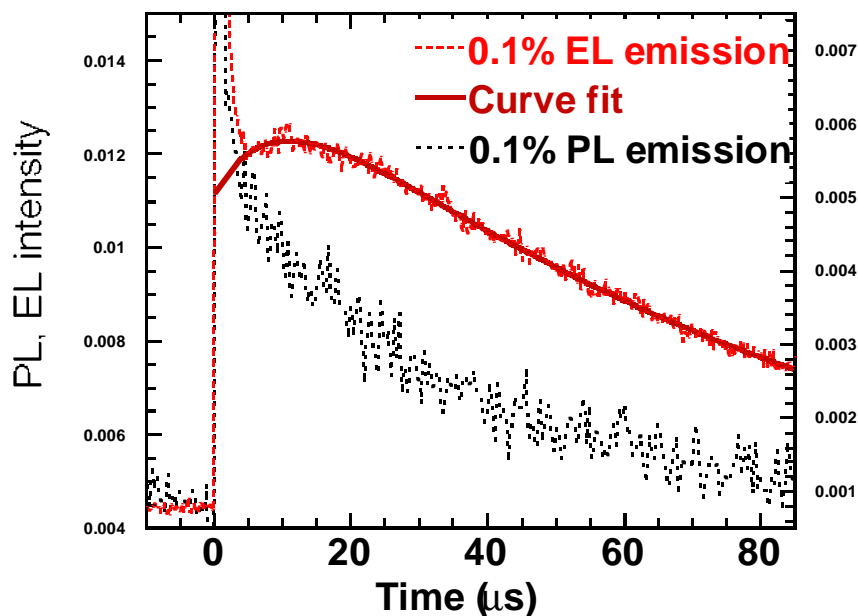


Figure 5. Time resolved emission of the PtOEP in a PtOEP-PNP blend using two excitation schemes (work by V. Cleave et. al.).

To analyse such an experiment we write down the set of equations:

$$\frac{dT^{Pn}}{dt} = -(k_{Tpn} + k_{Tr})T^{Pn} \quad \text{Triplet in PNP}$$

$$\frac{dT^{Pt}}{dt} = k_{Tr}T^{Pn} - k_{pt}T^{Pt} \quad \text{Triplets in PtOEP}$$

$$T^{Pn}(0) = T_0^{Pn}, T^{Pt}(0) = T_0^{Pt} \quad \text{Initial conditions}$$

$$T^{Pn} = T_0^{Pn} \exp(-[k_{Tpn} + k_{Tr}]t)$$

$$\frac{dT^{Pt}}{dt} = k_{Tr}T^{Pn} - k_{pt}T^{Pt} = k_{Tr}T_0^{Pn} \exp(-[k_{Tpn} + k_{Tr}]t) - k_{pt}T^{Pt}$$

$$\frac{dT^{Pt}}{dt} + k_{pt}T^{Pt} = k_{Tr}T_0^{Pn} \exp(-[k_{Tpn} + k_{Tr}]t)$$

$$\frac{dT^{Pt}}{dt} \exp(k_{Pt}t) + k_{Pt}T^{Pt} \exp(k_{Pt}t) = k_{Tr}T_0^{Pn} \exp(-[k_{Tpn} + k_{Tr} - k_{Pt}]t)$$

$$\frac{d}{dt} [T^{Pt} \exp(k_{Pt}t)] = k_{Tr}T_0^{Pn} \exp(-[k_{Tpn} + k_{Tr} - k_{Pt}]t)$$

$$[T^{Pt} \exp(k_{Pt}t)] = -\frac{k_{Tr}T_0^{Pn}}{[k_{Tpn} + k_{Tr} - k_{Pt}]} \exp(-[k_{Tpn} + k_{Tr} - k_{Pt}]t) + C$$

$T^{Pt}(0) = T_0^{Pt}$ Generated either directly or Förster transfer.

$$C = T_0^{Pt} + \frac{k_{Tr}T_0^{Pn}}{k_{Tpn} + k_{Tr} - k_{Pt}}$$

$$T^{Pt} = T_0^{Pt} \exp(-k_{Pt}t) + \frac{k_{Tr}T_0^{Pn}}{[k_{Tpn} + k_{Tr} - k_{Pt}]} [\exp(-k_{Pt}t) - \exp(-[k_{Tpn} + k_{Tr}]t)]$$

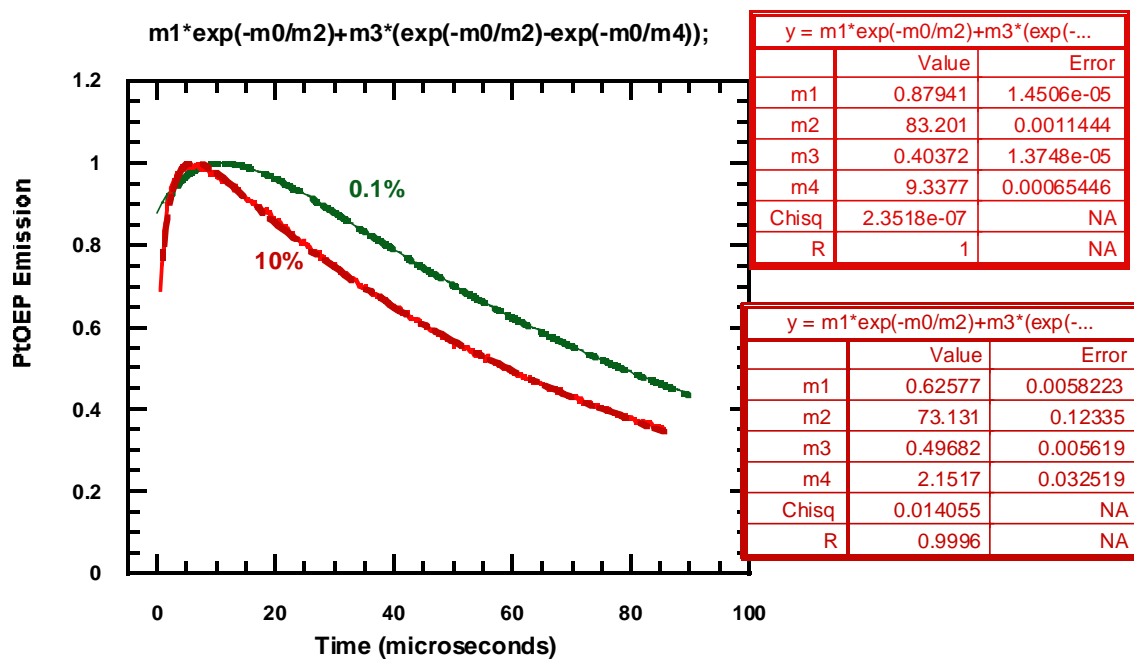


Figure 6.

Fitting these curves to equation to the traces in Figure 6 results in:

$$1. \frac{k_{Tr}}{[k_{Tpn} + k_{Tr} - k_{Pt}]} \frac{T_0^{Pn}}{T_o^{Pt}} = 0.44$$

2. $[k_{Tpn} + k_{Tr}]$ being equal to $1/9\mu\text{s}^{-1}$ and $1/2\mu\text{s}^{-1}$ for the 0.1% and 10% respectively.

3. Neglecting k_{Tpn} we get for the 0.1% blend $\frac{T_0^{Pn}}{T_o^{Pt}} = 0.40$ and for the 10% blend

$$\frac{T_0^{Pn}}{T_o^{Pt}} = 0.77$$

What is not shown here is that the two curves are also voltage dependent and hence a direct comparison, as the one suggested above, should be taken with a pinch of salt.

In the previous discussion we assumed a pulsed (delta function) excitation which served as a source for the initial conditions and we solved for the transient response.

$$\frac{dT^{Pn}}{dt} = -(k_{Tpn} + k_{Tr})T^{Pn} \quad \text{Triplet in PNP}$$

$$\frac{dT^{Pt}}{dt} = k_{Tr}T^{Pn} - k_{pt}T^{Pt} \quad \text{Triplets in PtOEP}$$

$$T^{Pn}(0) = T_0^{Pn}, T^{Pt}(0) = T_0^{Pt} \quad \text{Initial conditions}$$

Now we assume a sinusoidal excitation and we solve for the frequency response. The excitation source now appears explicitly in the equations:

$$\frac{dT^{Pn}}{dt} = I^{Pn} - (k_{Tpn} + k_{Tr})T^{Pn} \quad \text{Triplet in PNP}$$

$$\frac{dT^{Pt}}{dt} = I^{Pt} + k_{Tr}T^{Pn} - k_{pt}T^{Pt} \quad \text{Triplets in PtOEP}$$

Here I^{Pn} and I^{Pt} are direct excitation of the two triplet levels (as in optical absorption). We assume the excitation is sinusoidal of the form $Ie^{i\omega t}$ and we look for the response of the system at this frequency $T \rightarrow Te^{i\omega t}$

$$\frac{d[T_o^{Pn} \exp(i\omega t)]}{dt} = I_o^{Pn} \exp(i\omega t) - (k_{Tpn} + k_{Tr})[T_o^{Pn} \exp(i\omega t)] \quad \text{PNP}$$

$$\frac{d[T_o^{Pt} \exp(i\omega t)]}{dt} = I_o^{Pt} \exp(i\omega t) + k_{Tr}T_o^{Pn} \exp(i\omega t) - k_{pt}T_o^{Pt} \exp(i\omega t) \quad \text{PtOEP}$$

$$i\omega T_o^{Pn} \exp(i\omega t) = I_o^{Pn} \exp(i\omega t) - (k_{Tpn} + k_{Tr})[T_o^{Pn} \exp(i\omega t)]$$

$$i\omega T_o^{Pt} \exp(i\omega t) = I_o^{Pt} \exp(i\omega t) + k_{Tr}T_o^{Pn} \exp(i\omega t) - k_{pt}T_o^{Pt} \exp(i\omega t)$$

We noticed that effectively $d/dt \rightarrow i\omega$. And we now divide by $\exp(i\omega t)$

$$i\omega T_o^{Pn} = I_o^{Pn} - (k_{Tpn} + k_{Tr})T_o^{Pn}$$

$$i\omega T_o^{Pt} = I_o^{Pt} + k_{Tr}T_o^{Pn} - k_{pt}T_o^{Pt}$$

$$T_o^{Pn} = \frac{I_0^{Pn}}{i\omega + (k_{Tpn} + k_{Tr})}$$

$$T_o^{Pt} = \frac{I_0^{Pt} + \frac{k_{Tr} I_0^{Pn}}{i\omega + (k_{Tpn} + k_{Tr})}}{i\omega + k_{pt}}$$

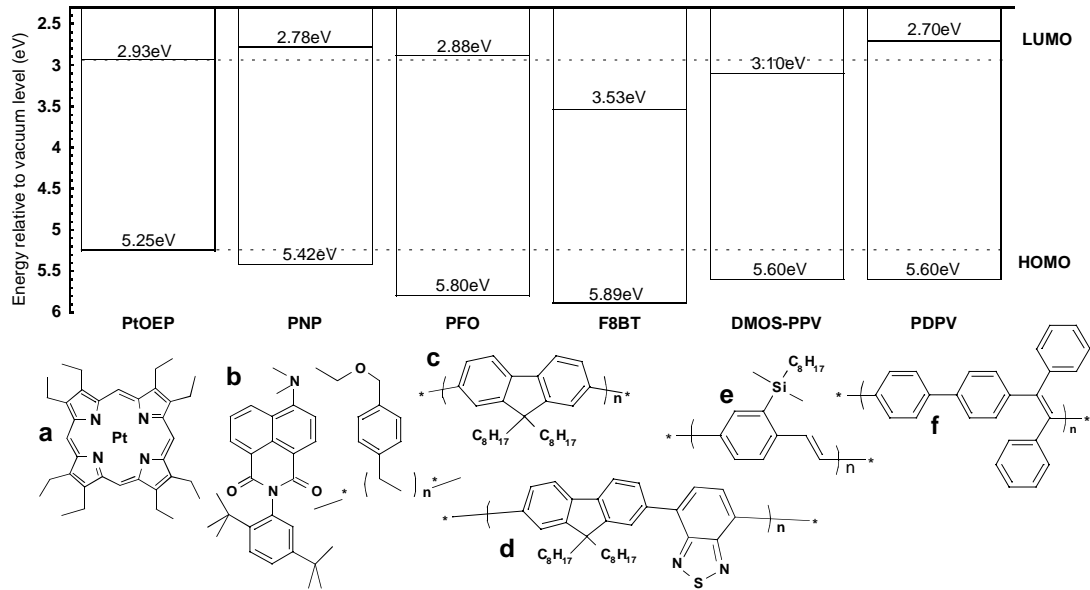


Figure 7. The band-gap → more things to consider!!

I thank Vicki Cleave for making her work and figures available for this lecture.