

Week 1-7

Optical Properties 4

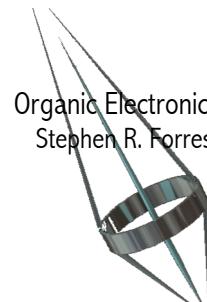
Energy transfer (cont'd)

Exciton diffusion

Exciton recombination and annihilation

Chapter 3.8.2 – 3.10

Organic Electronics
Stephen R. Forrest



Using Energy Transfer to Achieve High Efficiency Emission: Phosphor sensitized fluorescence

1. Triplet-singlet exchange transfer is disallowed
2. Triplet-singlet Förster transfer permitted if triplet relaxation on donor is allowed
i.e. triplet-singlet transfer is possible from a phosphorescent donor

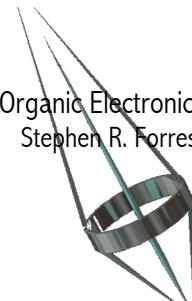
Predicted by Förster in 1959 (†)

Observed by Ermolaev and Sveshnikova in 1963 (§)

e.g. for triphenylamine as the donor and chrysoidine as the acceptor, in rigid media at 77K or 90K the interaction length is 52Å

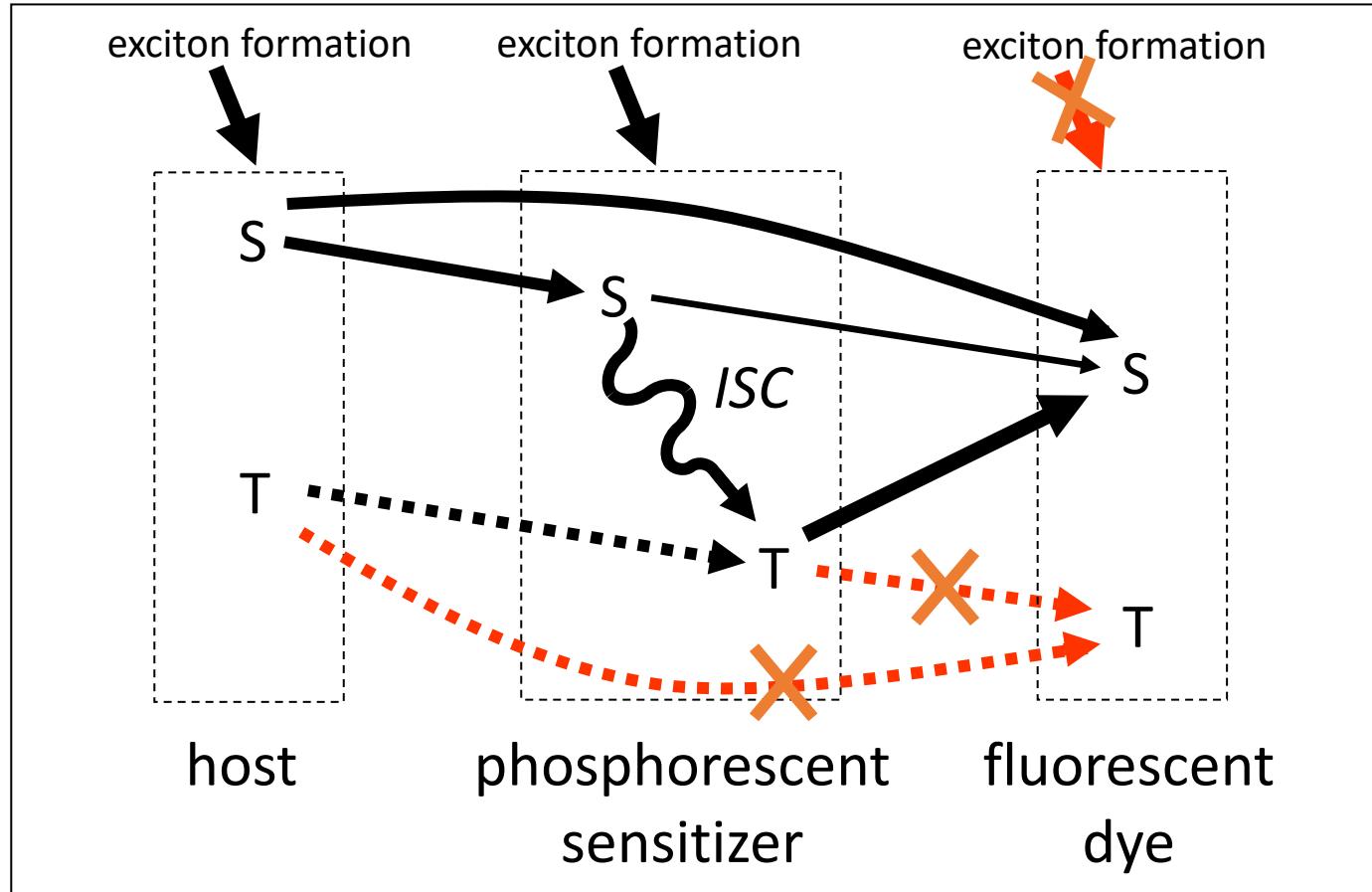
(†) Förster, Th. *Discussions of the Faraday Society* **27**, 7-17 (1959).

(§) Ermolaev, V.L. & Sveshnikova, E.B. *Doklady Akademii Nauk SSSR* **149**, 1295-1298 (1963).

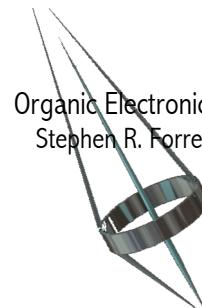


Phosphor sensitized fluorescence

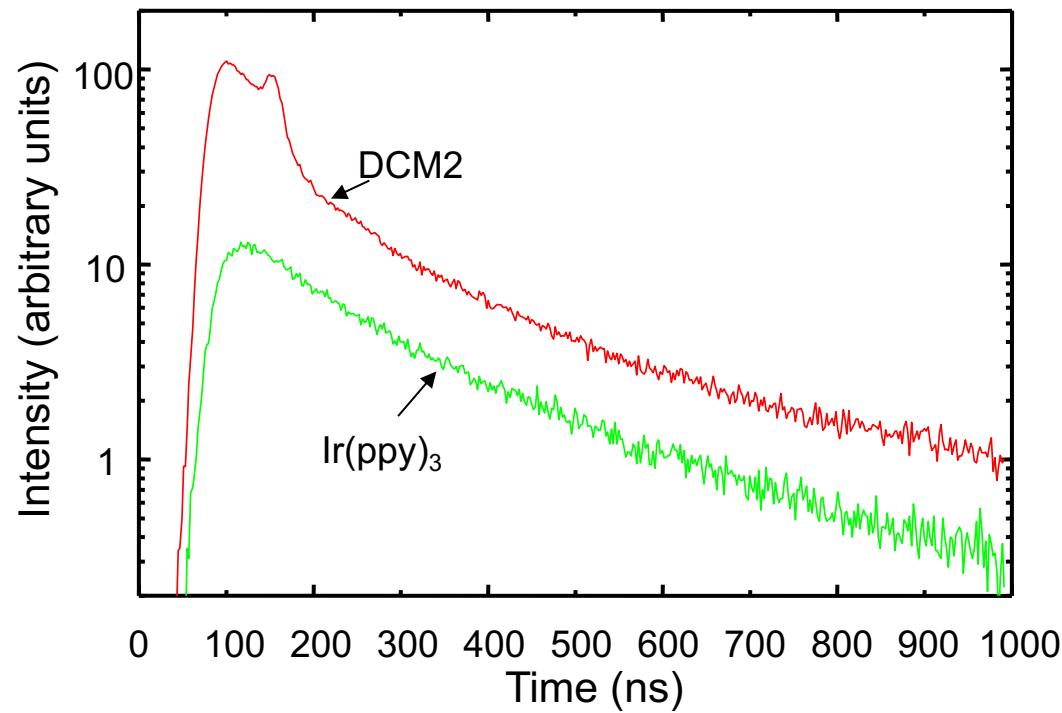
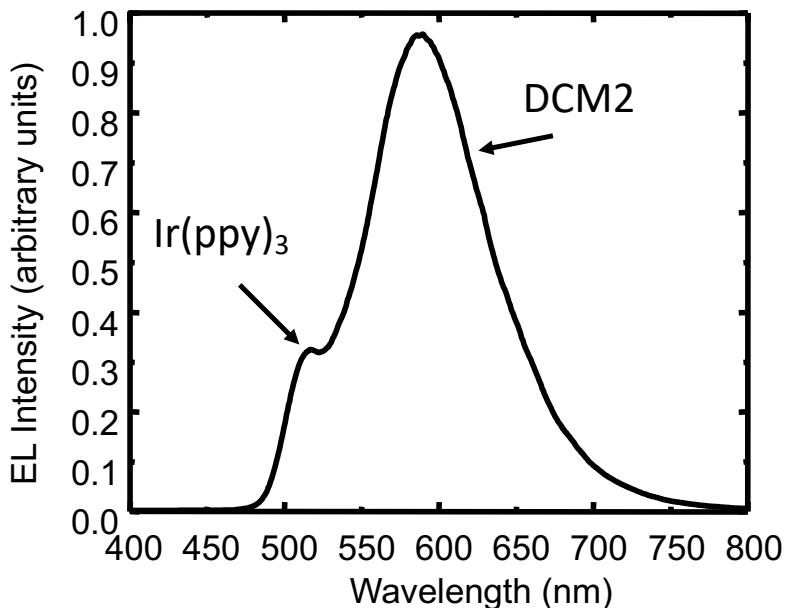
Mechanisms in guest-host systems



- ◆ Phosphorescent donor and fluorescent acceptor must be separated to prevent direct Dexter transfer to fluorescent triplet state
- ◆ Transfer possible for radiative triplet states



Red DCM2 Fluorophore sensitized by co-doping with green $\text{Ir}(\text{ppy})_3$ phosphor in an OLED

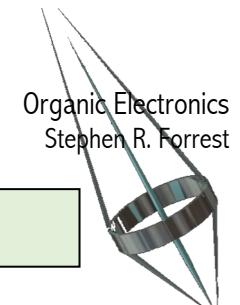


Nearly complete energy transfer
from $\text{Ir}(\text{ppy})_3$ to DCM2

Examine transient response of different spectral components of OLED luminescence.

Natural lifetime of DCM2 only $\sim 1\text{ ns}$.

Delayed DCM2 fluorescence confirms sensitizing action of $\text{Ir}(\text{ppy})_3$



The Far Field: Radiative (Trivial) Energy Transfer

- Involves the isotropic emission of a photon by a donor followed by absorption from a distant acceptor
- $R_{DA} > 50 \text{ \AA}$ such that FRET inactive
- No spin selection rules
- Two step process:

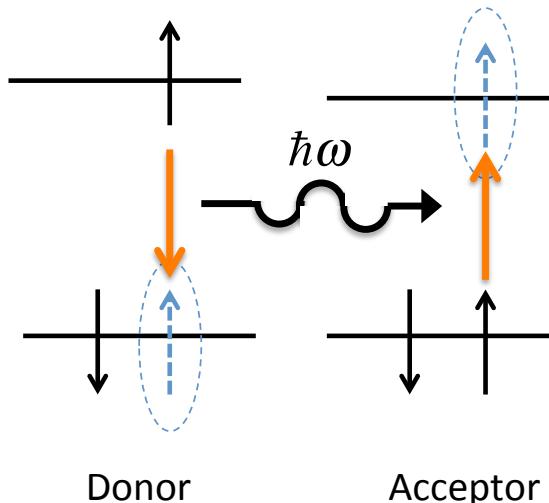


- There is an orientation dependence due to dipole coupling

$$k_{ET} = \frac{9\kappa_{rad}^2 \Phi_D}{8\pi n_r \tau_D R_{DA}^2} \int f_D(\omega) \sigma_A(\omega) \exp(-\sigma_A(\omega) \rho_{NA} R_{DA}) d\omega$$

$\kappa_{rad}^2 = (\cos \theta_{DA} - \cos \theta_D \cos \theta_A)^2$: Geometric factor (dipoles couple when aligned)

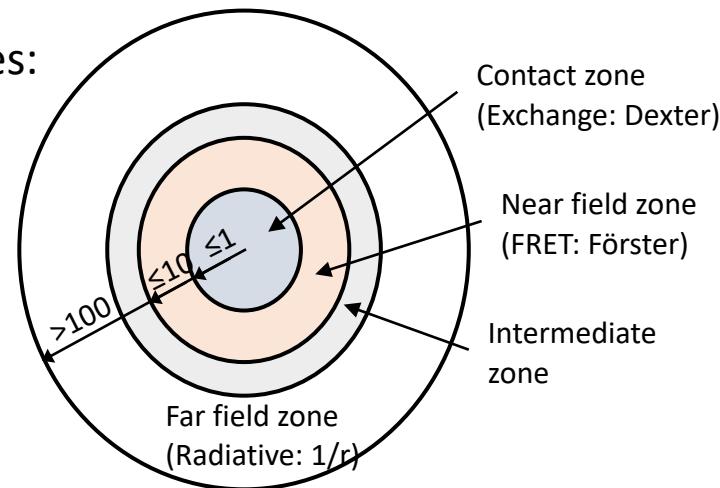
$\alpha_A(\omega) = N_A \rho_{MA} \sigma_A(\omega) / M_{wA} = \sigma_A(\omega) \rho_{NA}$: Absorption coefficient



Summarizing our discussion on energy transfer

The total rate is equal to the sum of the individual rates:

$$k_{ET,tot} = k_{ET,exch} + k_{ET,FRET} + k_{ET,rad}$$

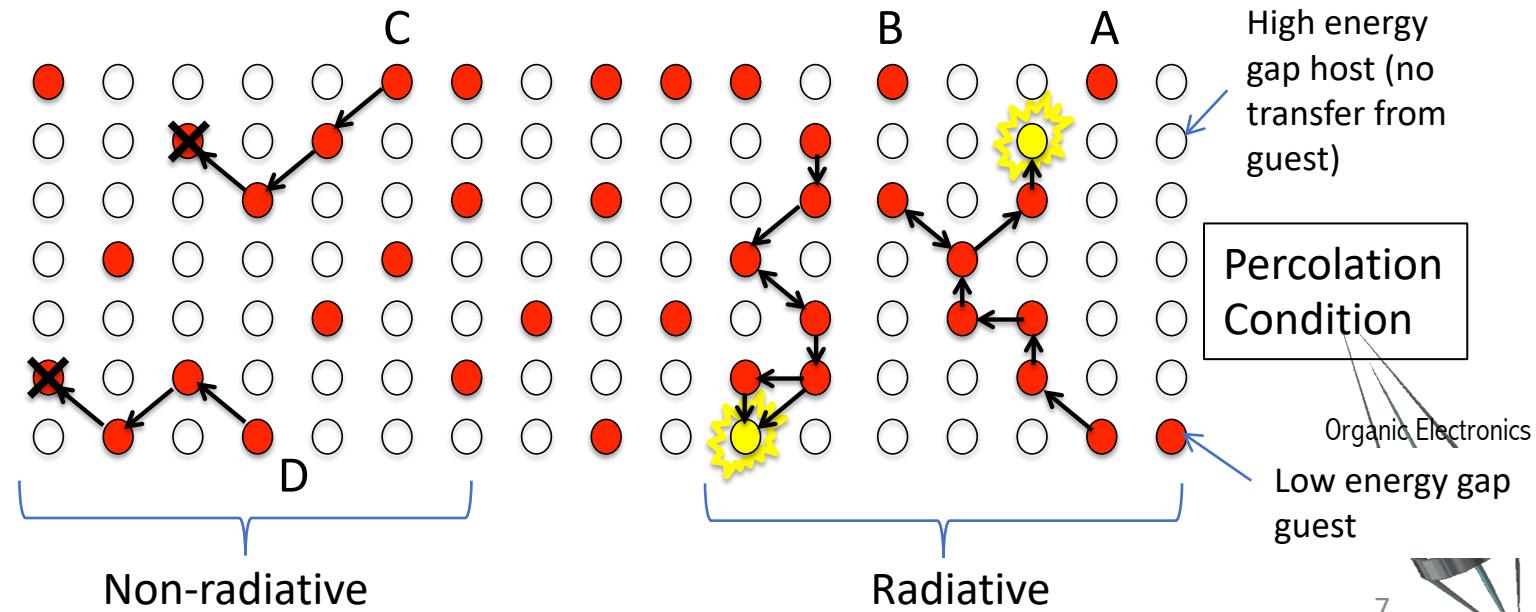


Process	Transfer rate	Distance Dependence	Zone	Characteristic transfer distance
Exchange (Dexter)	$k_{ET,exch}$	$\frac{1}{R_{DA}^2} \exp(-2R_{DA}/L)$	Contact	<1 nm
FRET	$k_{ET,FRET}$	$\frac{1}{R_{DA}^6}$	Near	<10 nm
Radiative	$k_{ET,rad}$	$\frac{1}{R_{DA}^2} \exp(-\alpha_A R_{DA})$	Far	>100 nm

Exciton Diffusion

- The macroscopic transfer of energy resulting from a series of exciton transfers between molecules
 - Process is random
 - Duration of process determined by lifetime τ_D of the exciton
 - Mean distance travelled known as diffusion length, L_D
 - Diffusion constant: $L_D^2 = D\tau_D$

Donor-Acceptor Transfer



Capture of excitons by acceptors

Diffusion over large distances occurs by a series of random transfer steps from donor to acceptor

⇒ Relationship between capture rate, k_c , and the diffusion constant is obtained using the diffusion equation

⇒ Assume probability for capture is unity when the exciton arrives within a distance R_c from the acceptor. (R_c = exciton *capture radius*.)

$$k_c \approx 4\pi DR_c$$

Chandrasekhar, S. 1943. *Rev. Modern Phys.*, 15, 1.

If diffusion occurs by individual FRET steps, then the relationship between L_D and the Förster radius is:

$$L_{D,FRET} = \frac{1}{\sqrt{6}} \frac{R_0^3}{a^2}$$

- Assumes molecules on a 3D cubic lattice, lattice constant a .
- Analogous relationship holds for Dexter transfer

Diffusion Equation

$$D\nabla^2 n(\mathbf{r}, \lambda, t) - \frac{n(\mathbf{r}, \lambda, t)}{\tau_D} + G(\mathbf{r}, \lambda, t) = \frac{\partial n(\mathbf{r}, \lambda, t)}{\partial t}$$

Diffusion from point of origin Generation due to incident light, etc.
Loss due to recombination

n = exciton density
 τ_D = exciton natural lifetime
 G = Generation rate

All variables functions of position, wavelength and time

Fick's Law: In steady state, the flux is given by: $J = -D\nabla n$

That is, flux is driven by a gradient in the concentration of n .

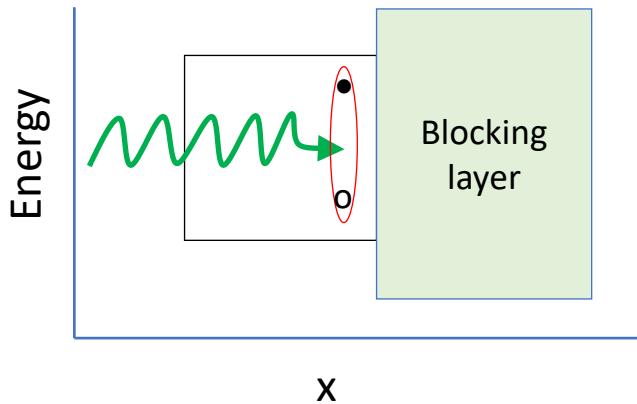
But energy conservation (no losses or sources) gives: $\nabla J = -\frac{\partial n}{\partial t}$

Which leads to Fick's 2nd Law and the diffusion equation: $D\nabla^2 n = \frac{\partial n}{\partial t}$

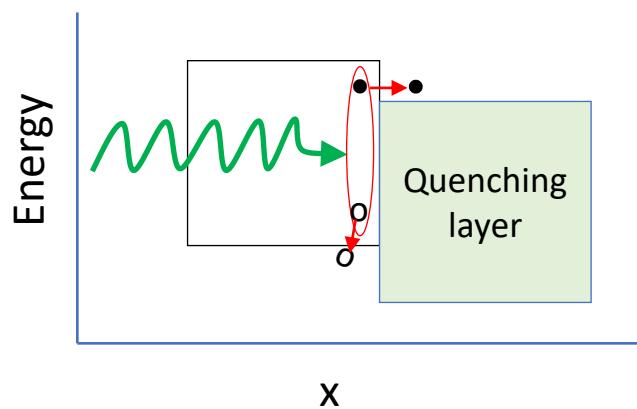
Measuring Exciton Diffusion Boundary Conditions and Solutions

Set up two experiments: one with a blocking and the other with a quenching layer on the material under test

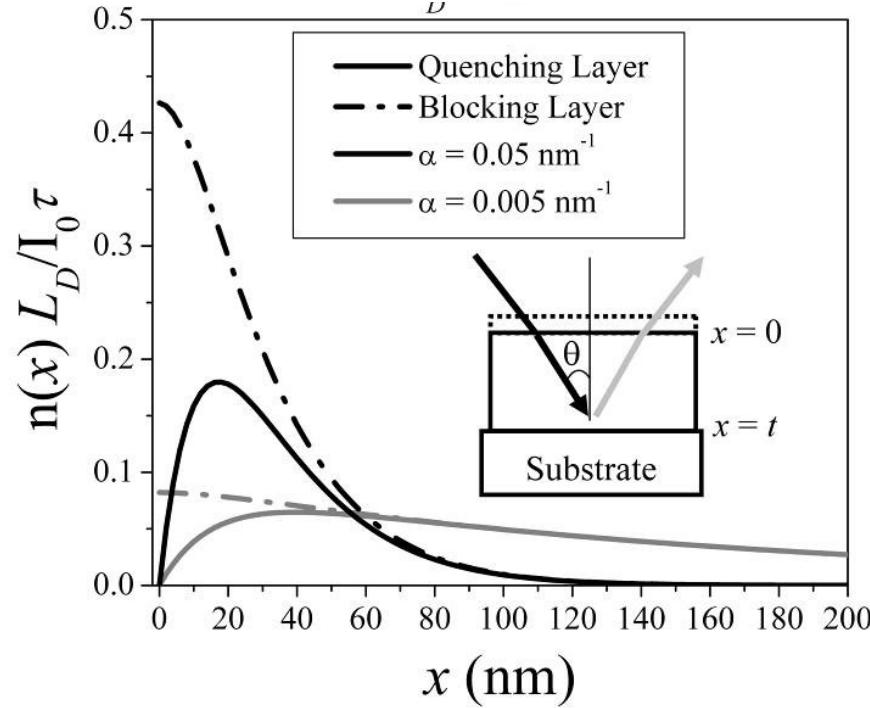
Blocking: $\frac{\partial n}{\partial x} = 0$



Quenching: $n=0$



Spectrally resolved luminescent quenching (SR-PLQ)



$$G(x, \lambda, t) = I_0(\lambda, t) \exp[-\alpha(\lambda)x]$$

Generation follows Beer-Lambert Law

Lunt, R. R., et al. *J. Appl. Phys.*, 105, 053711.

Diffusion Length Measurement by SR-PLQ

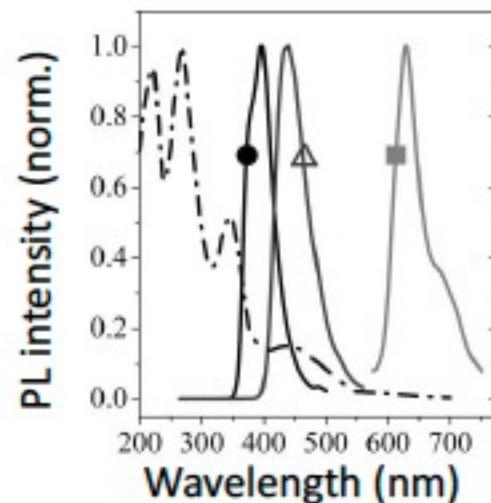
PL efficiency in the presence of a blocking (B) or quenching (Q) layer is a function of wavelength

$$\eta(\alpha) = \frac{PL_B(\alpha)}{PL_Q(\alpha)} = \frac{\int_0^{\infty} n_B(x, \alpha) dx}{\int_0^{\infty} n_Q(x, \alpha) dx}.$$

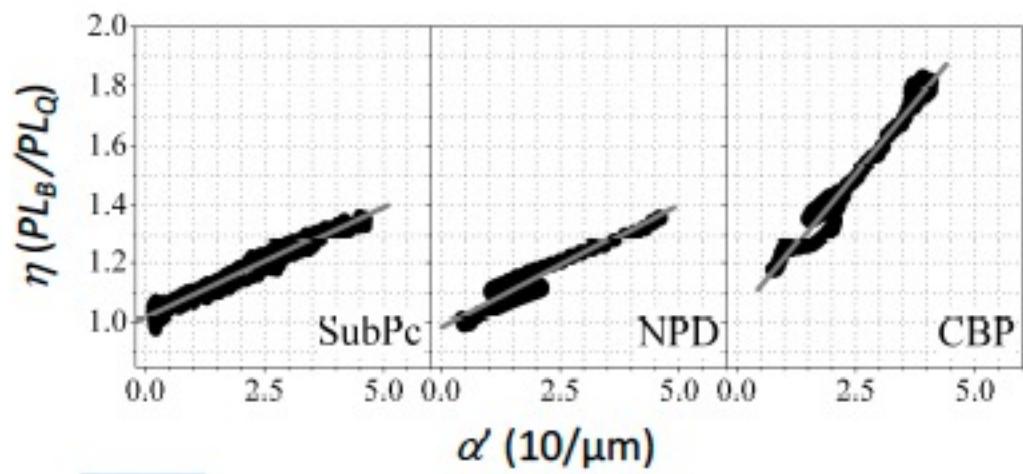
Plot of their ratio gives a straight line with slope $\propto L_D$

$$\eta(\alpha) = \frac{\alpha(\lambda)L_D}{\cos\theta} + 1 = \alpha'(\lambda)L_D + 1$$

(a)



(b)



Measured Diffusion Lengths

Table 3.6: Measured diffusion lengths (L_D) for singlet (S) and triplet (T) excitons of crystalline (C.) and amorphous (A.) films measured by spectrally resolved photoluminescence quenching.

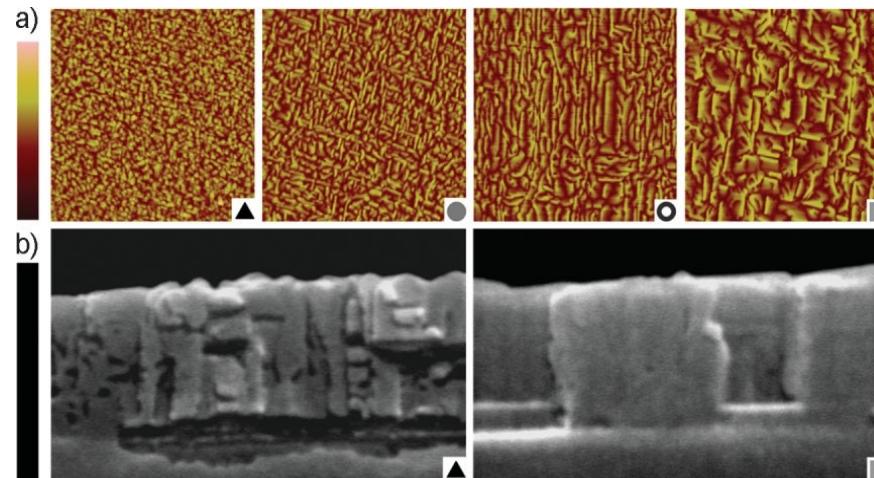
Material ^{a,b}	Exciton	Morphology ^c	Quenching/Blocking Layer ^b	L_D (nm)	D (10^{-4} cm 2 /s)
NPD	S	A.	C ₆₀ /BCP	5.1 (± 1.0)	0.7 (± 0.2)
CBP	S	A.	C ₆₀ (or NTCDA)/Free	16.8 (± 0.8)	40 (± 12)
SubPc	S	A.	C ₆₀ /Bare	8.0 (± 0.3)	≥ 6.4
PTCDA	S	C. - 55nm (flat)	C ₆₀ (or NPD)/NTCDA	10.4 (± 1.0)	3.4 (± 0.9)
DIP	S	C. - >150nm (up)	C ₆₀ / Free	16.5 (± 0.4)	15 (± 4)
DIP	S	C. - 30nm (flat)	C ₆₀ / Free	21.8 (± 0.6)	26 (± 7)
C ₆₀	S	A.	NPD/BPhen	34 (± 3)	20 (± 4)
C ₇₀	S	A.	NPD/BPhen	10 (± 2)	
PtOEP	T - Mon.	C. - >150nm (up)	C ₆₀ /BCP	18.0 (± 0.6)	0.041 (± 0.003)
PtOEP	T – Dim.	C. - >150nm (up)	C ₆₀ /BCP	13.1 (± 0.5)	0.00061 (± 0.0001)

^aAll data are from (Lunt et al., 2009) except for C₆₀ and C₇₀ from (Bergemann et al., 2015). The larger error bars for L_D for C₆₀ and C₇₀ is due to their comparatively weak luminescence.

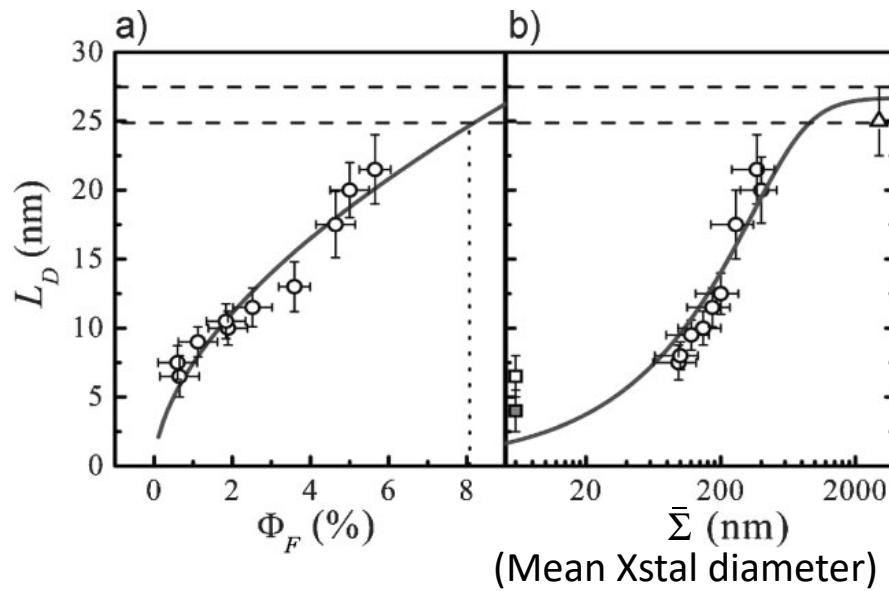
^b Materials used: NPD= N,N'-diphenyl-N,N'-bis(1-naphthyl)-1,1'biphenyl-4,4'diamine; CBP=4'-bis(9-carbazolyl)-2,2'-biphenyl; PTCDA=3,4,9,10-perylenetetracarboxylic dianhydride; NTCDA=3,4,7,8 naphthalenetetracarboxylic dianhydride; SubPc= boron subphthalocyanine chloride; DIP= diindenoperylene; PtOEP=Pt octaethylporphyrin; BCP=bathocuproine; BPhen=bathophenanthroline; Free=no layer.

^c Up/flat refers to whether the molecular plane is perpendicular/parallel to the substrate.

Diffusion Length Increases with Order



PTCDA grain size
varied by OVPD
growth conditions



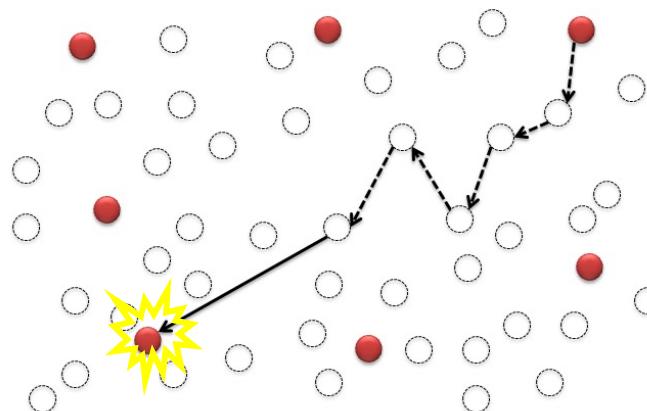
Why does the crystallite grain size have to be $\sim 10 \cdot L_D$ to realize the full L_D of the material?

Annihilation!

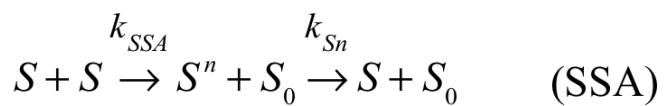
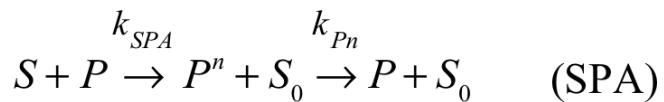
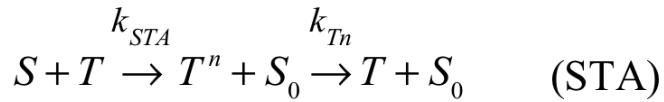
When excitons collide at a single molecular site, they can combine to form a single exciton and a ground state molecule: Exciton-exciton annihilation

Spin multiplicity can determine annihilation efficiency (Dexter vs FRET). Annihilation leads to losses, and phenomena like delayed fluorescence.

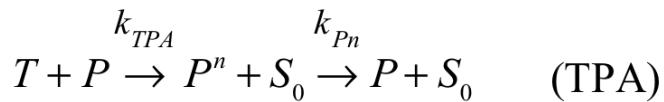
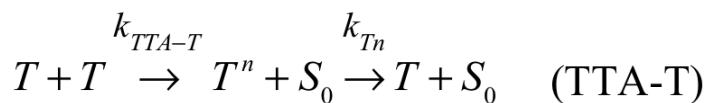
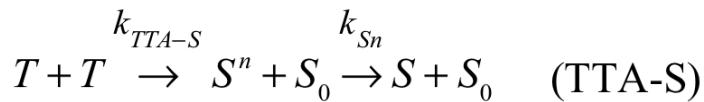
When excitons collide with charges, the charge can be excited, losing the exciton: Exciton-polaron annihilation



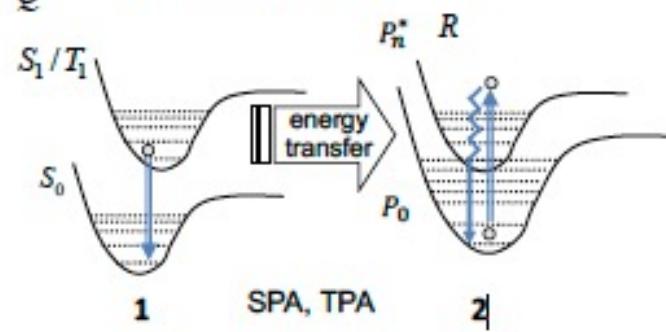
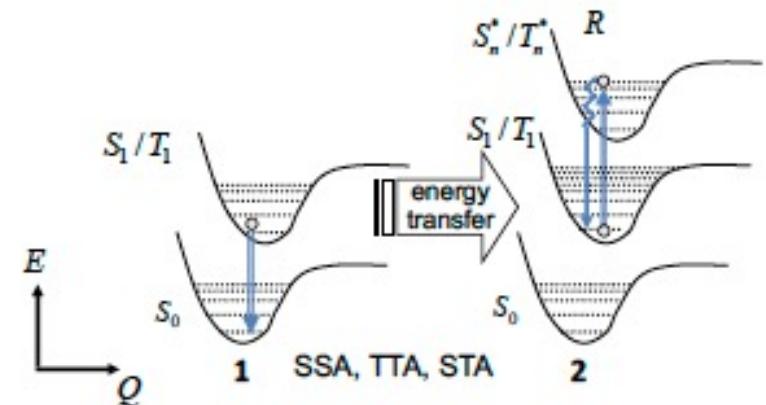
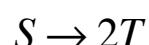
Bad things happen to good excitons



Delayed fluorescence
Triplet fusion



Singlet fission when
 $E_S \geq 2E_T$



Rate Equations for Annihilation

Including all processes, we get two coupled rate equations:

$$\frac{dS}{dt} = G_S - k_S S - \frac{1}{2} k_{SSA} S^2 - k_{STA} ST - k_{SPA} SP + k_{TTA-S} T^2$$

Exciton generation rates

$$\frac{dT}{dt} = G_T - k_T T - 2k_{TTA-S} T^2 - \frac{1}{2} k_{TTA-T} T^2 - k_{TPA} TP$$

Example: Exciton generation by current (J) injection:

$$G_{T,S}(J) = \chi_{T,S} \eta_J j / qd$$

electron-to-exciton conversion ratio

Probability for forming triplet or singlet: $\chi_T = \frac{3}{4}$; $\chi_S = \frac{1}{4}$ (spin formation statistics)

Layer thickness

But j is due to the injection of polarons, introducing rate equation #3:

$$\frac{dP}{dt} = \frac{j(t)}{qd} - k_{rec} P^2$$

Langevin recombination

Bimolecular process when an electron and hole collide

Random polaron collisions: $P_e + P_h \rightarrow \hbar\Omega$ (heat, or possibly S or T)

Langevin recombination rate: $k_{rec} = \frac{q}{\varepsilon_r \varepsilon_0} (\mu_h + \mu_e)$

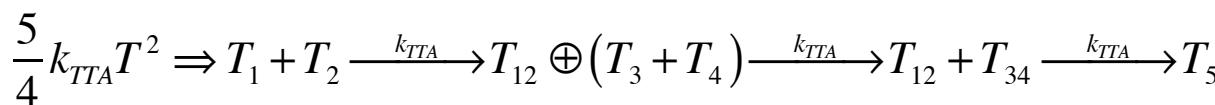
Giving two new rate equations:

$$\frac{dT}{dt} = \frac{3}{4} k_{rec} P^2 - k_T T - \frac{5}{4} k_{TTA} T^2 - k_{TPA} TP$$

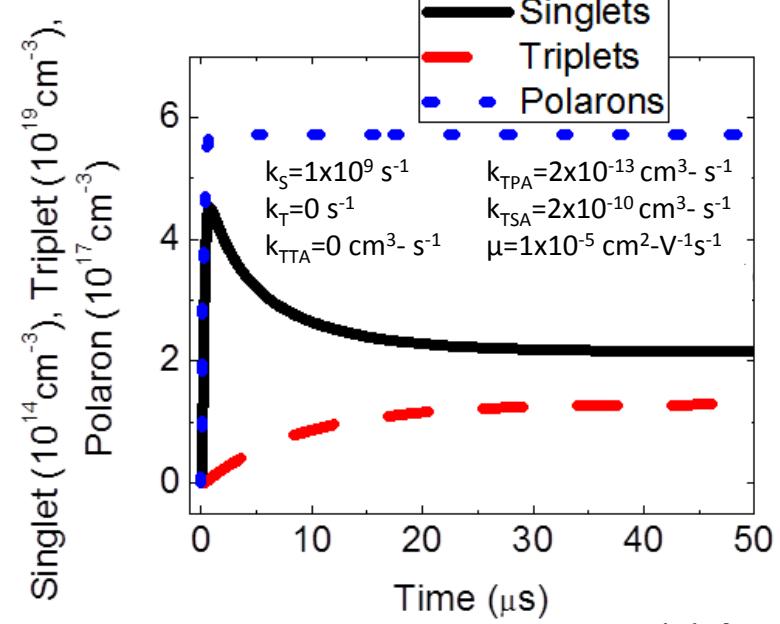
$$\frac{dS}{dt} = \frac{1}{4} k_{rec} P^2 - k_S S + \frac{1}{4} k_{TTA} T^2 - k_{STA} ST$$

The fractions come from spin statistics:

Ex.



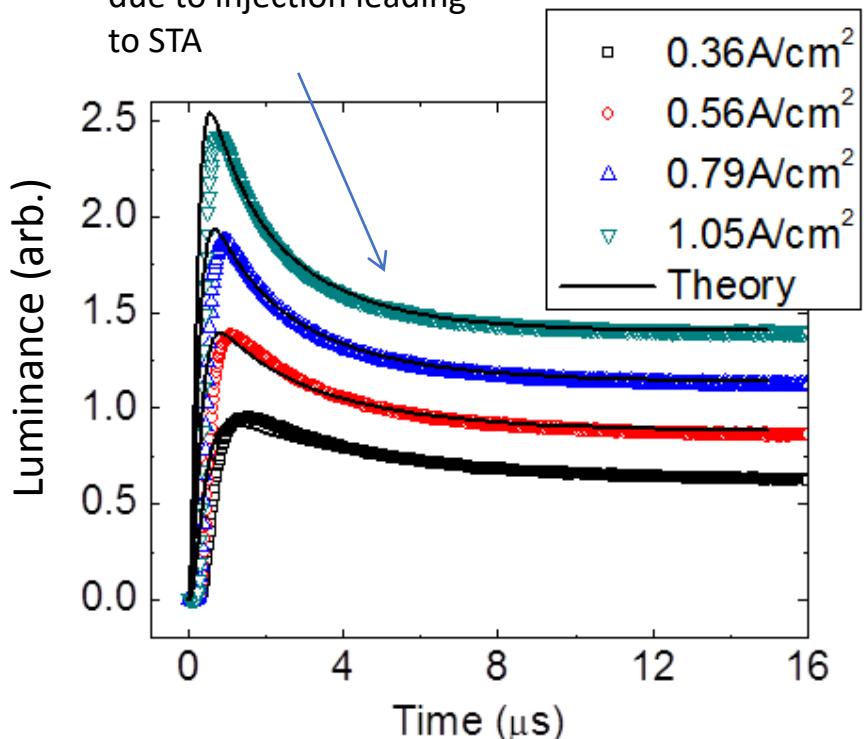
Transient response in a material with triplets, singlets & polarons



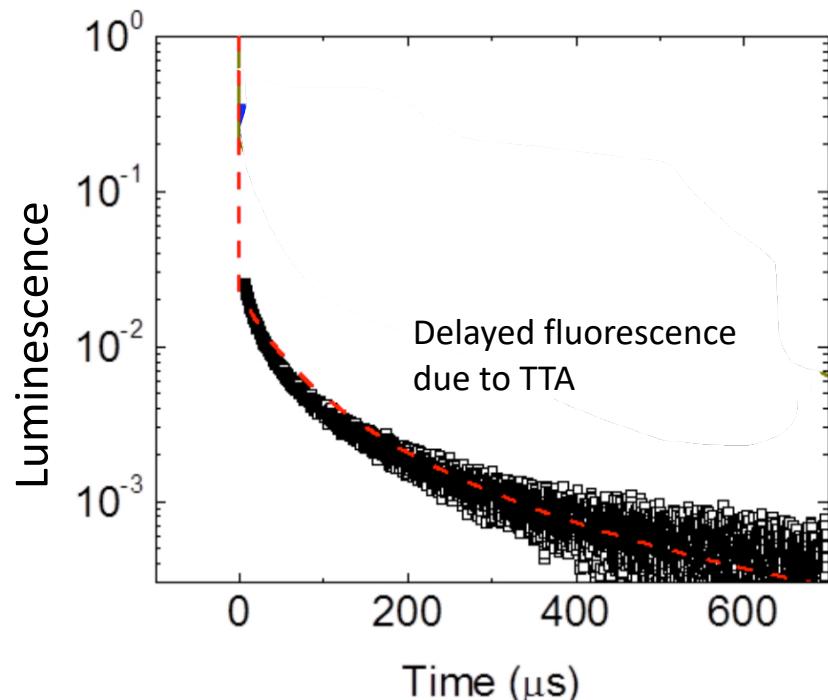
Zhang et al., Chem. Phys. Lett., 495, 161 (2010)

DCM2:Alq₃ Fluorescent OLEDs

Accumulation of triplets
due to injection leading
to STA



Turn –on transient



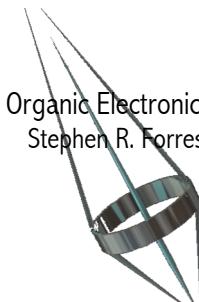
Turn –off transient

Fits to rate equations shown by lines

What we learned

- The concepts leading to our understanding of individual molecular spectra
 - Born-Oppenheimer, Franck-Condon, Pauli Exclusion
 - Molecular orbitals
- Understanding molecular spectra
 - Excitons
 - Fermi's Golden Rule
 - Selection rules
 - Spin: Fluorescence, phosphorescence, delayed fluorescence
- Building up to a solid
 - Dimers, excimers, exciplexes
 - Polarization effects in solution and the solid state
- Exciton diffusion and annihilation

The next step: Charge transport in solids



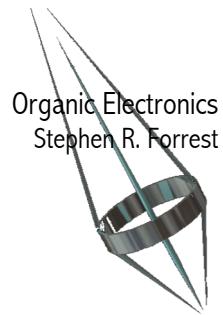
Electronic Properties of Organic Semiconductors

Electronic Properties 1

Energy Bands

Chapter 4.1

Organic Electronics
Stephen R. Forrest



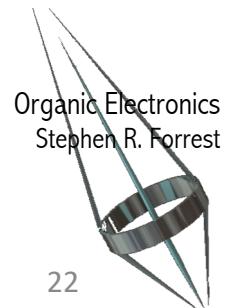
Organic & Inorganic Semiconductor Properties: A Reminder

Property	Organics	Inorganics
Bonding	van der Waals	Covalent/Ionic
Charge Transport	Polaron Hopping	Band Transport
Mobility	$<0.1 \text{ cm}^2/\text{V}\cdot\text{s}$	$\sim 1000 \text{ cm}^2/\text{V}\cdot\text{s}$
Absorption	$10^5\text{-}10^6 \text{ cm}^{-1}$	$10^4\text{-}10^5 \text{ cm}^{-1}$
Excitons	Frenkel	Wannier-Mott
Binding Energy	$\sim 500\text{-}800 \text{ meV}$	$\sim 10\text{-}100 \text{ meV}$
Exciton Radius	$\sim 10 \text{ \AA}$	$\sim 100 \text{ \AA}$

Objectives: Electronic Properties

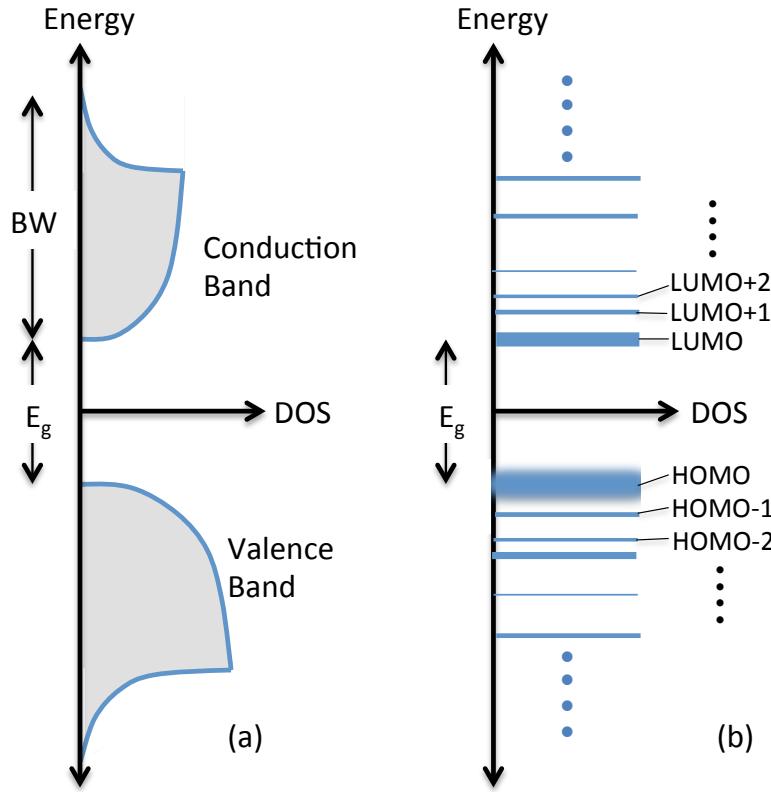
“When talking about semiconductors, if you can’t draw a band diagram then you don’t know what you’re talking about”, ‘Kroemer’s Lemma’, Herbert Kroemer, ca. 1990.

- Organic electronic devices can only be understood in the context of the conductive properties of materials
- In this discussion we introduce
 - Origins of electronic band structure
 - Concept of polarons (large and small)
 - Charge transfer
 - Conductivity, effective mass and mobility
 - Injection
 - Charge trapping
- At the end of this discussion, you will have learned about structure, optical and electronic properties: all the tools needed to fully understand and analyze all OE devices and phenomena



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From energy levels to energy bands

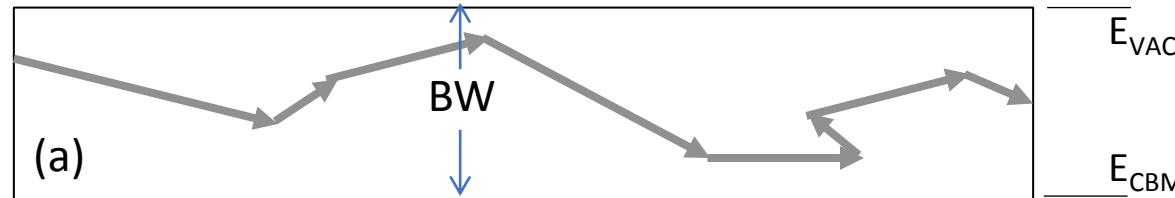


Due to limited orbital overlap between adjacent molecules, energy bandwidths are small:

- Large effective mass
- Low charge velocity (and hence mobility)
- Low conductivity
- Band conduction is replaced by charge hopping

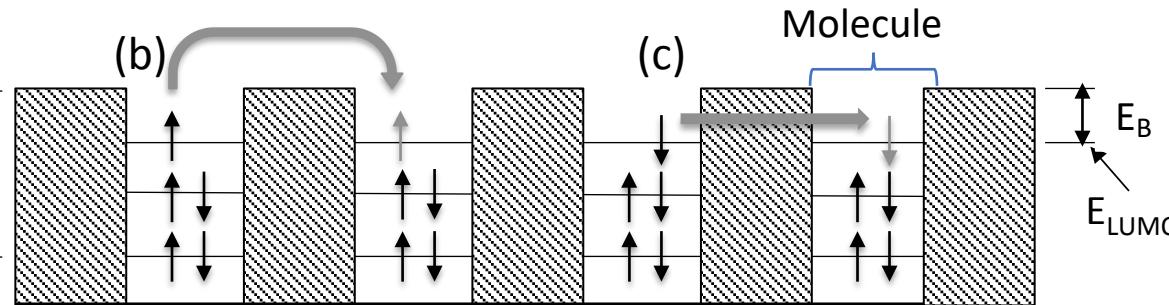
Modes of Conduction

Band transport



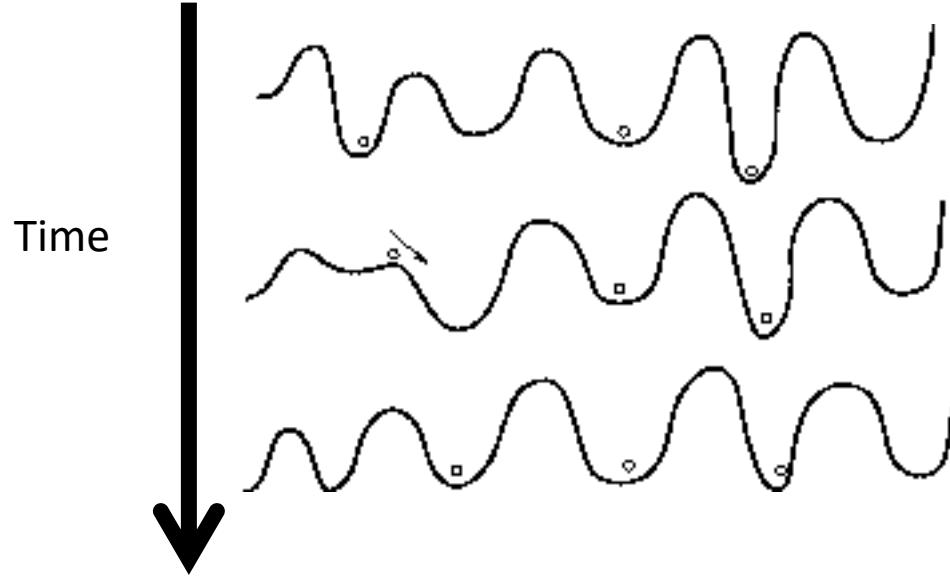
- Coherent
- Charge mean free path $\lambda \gg a$
- $BW > k_B T, \hbar\omega_0$

Hopping and tunneling transport



- Incoherent (each step independent of previous)
- Charge mean free path $\lambda \sim a$
- Tunneling between states of equal energy is band-like
- $BW < k_B T, \hbar\omega_0$

Hopping



When there is strong electron-phonon (small polaron) coupling, we get another condition for band transport:

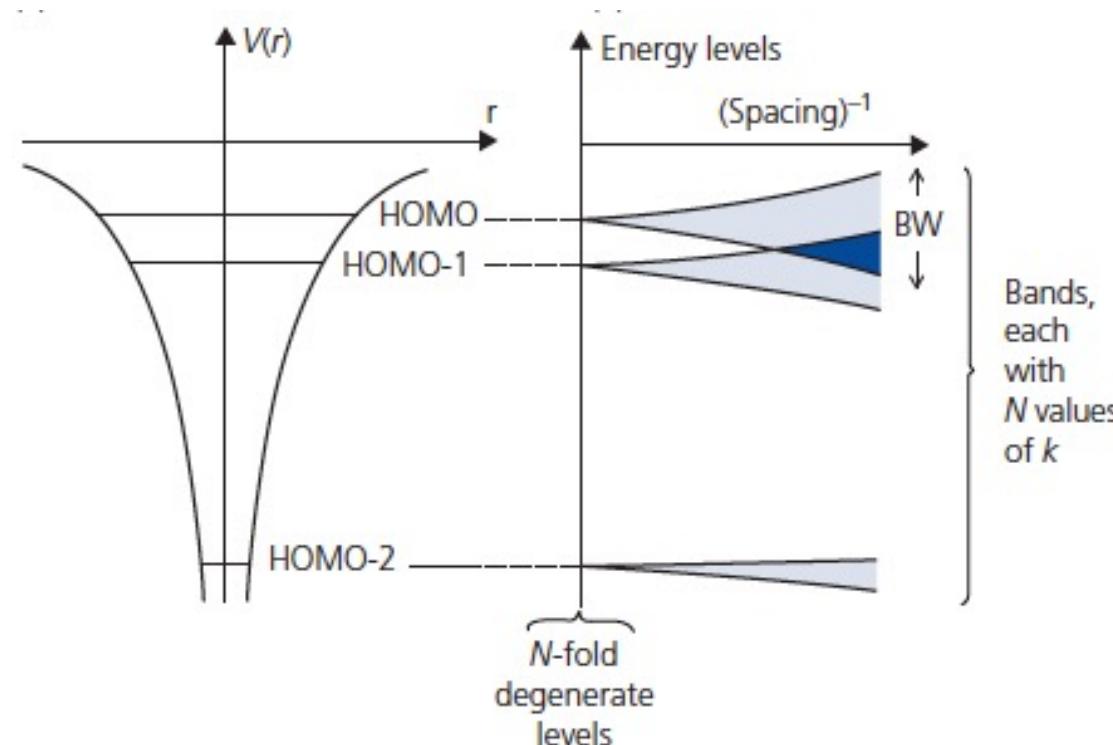
$$\mu > \frac{qa^2}{\hbar} \left(\frac{\hbar\omega_0}{k_B T} \right)$$

Optical phonon energy
(typ. ~ 100 meV)

$\mu \sim 20 \text{ cm}^2/\text{V-s}$ at room temperature...very high (and probably unrealistic)!

Transport Bands in Organics

- **Tight binding** approximation is useful due to importance of only nearest neighbor interactions
- Recall case of dimers and larger aggregates on exciton spectrum. Close proximity of neighbors results in:
 - Coulomb repulsion
 - Pauli exclusion➤ Splitting leads to broadening of discrete energies into bands



Tight Binding Approximation

Calculating organic band structure

- Start with the unperturbed molecular orbitals of HOMO, HOMO-1, HOMO-2..., and LUMO, LUMO+1... These will diverge into separate bands as molecules approach
- The total Hamiltonian consists of the individual molecular component and the interaction between neighbors:

$$H_{tot} = H_{mol} + H_{int}$$

- $H_{int} = U(\mathbf{r})$ that must be consistent with Bloch's Theorem: $U(\mathbf{r} + \mathbf{R}) = U(\mathbf{r})$
 - \mathbf{R} = lattice spacing
- From LCAO, for the n^{th} orbital, over N lattice sites, for wavevector \mathbf{k} :

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \sum_i^N c_{\mathbf{k}i} \psi_n(\mathbf{r} - \mathbf{R}_i)$$

↑
Contribution from i^{th} molecule

- This must have translational invariance of $\psi_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}} \psi_{\mathbf{k}}(\mathbf{r})$ (Bloch Theorm)

Tight Binding Approximation-cont'd

- Schrodinger's Eq. is now:

$$H_{tot}\psi_{\mathbf{k}}(\mathbf{r}) = (H_{mol} + H_{int})\psi_{\mathbf{k}}(\mathbf{r}) = E(\mathbf{k})\psi_{\mathbf{k}}(\mathbf{r})$$

- It follows that:

$$\langle \psi_m(\mathbf{r}) | H_{tot} | \psi_{\mathbf{k}}(\mathbf{r}) \rangle = \langle \psi_m(\mathbf{r}) | (H_{mol} + H_{int}) | \psi_{\mathbf{k}}(\mathbf{r}) \rangle = E(\mathbf{k}) \langle \psi_m(\mathbf{r}) | \psi_{\mathbf{k}}(\mathbf{r}) \rangle$$

Starting orbital wavefunction

- Solving, and since the eigenvalues of H_{mol} are E_m of the original molecules:

$$(E(\mathbf{k}) - E_m) \langle \psi_m(\mathbf{r}) | \psi_{\mathbf{k}}(\mathbf{r}) \rangle = \langle \psi_m(\mathbf{r}) | H_{int} | \psi_{\mathbf{k}}(\mathbf{r}) \rangle$$

Since $\psi_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}} \psi_{\mathbf{k}}(\mathbf{r})$

And solving this for an s-like HOMO level this equation has solution:

$$E(\mathbf{k}) - E_{HOMO} = -(E(\mathbf{k}) - E_{HOMO}) \sum_i^N \alpha(\mathbf{R}_i) e^{i\mathbf{k}\cdot\mathbf{R}_i} - \beta \left[\sum_i^N J(\mathbf{R}_i) e^{i\mathbf{k}\cdot\mathbf{R}_i} \right] : \text{overlap}$$

(higher symmetry orbitals have multiple solutions but we'll keep it simple!)

Solutions yield these coefficients

$$\alpha(\mathbf{R}_i) = \int \phi^*(\mathbf{r}) \phi(\mathbf{r} - \mathbf{R}_i) d^3\mathbf{r} = \langle \phi(\mathbf{r}) | \phi(\mathbf{r} - \mathbf{R}_i) \rangle$$

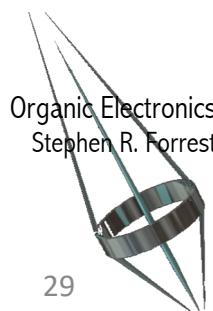
$$\beta = \langle \phi(\mathbf{r}) | H_{\text{int}} | \phi(\mathbf{r}) \rangle$$

$$J(\mathbf{R}_i) = -\langle \phi(\mathbf{r}) | H_{\text{int}} | \phi(\mathbf{r} - \mathbf{R}_i) \rangle.$$

Where perturbed orbitals are a linear combination of initial orbitals

$$\phi(\mathbf{r}) = \sum_n a_n \psi_n(\mathbf{r})$$

- All coefficients must be small for this to be a perturbation.
- J is the most important: it is the overlap integral, and gives the bandwidth (BW) of the particular orbital
- All coefficients must possess the same symmetry as the lattice



Tight Binding Approximation-cont'd.

- Now all the coefficients are small (this is only a perturbation), so the simple solution to $E(\mathbf{k})$ is just:

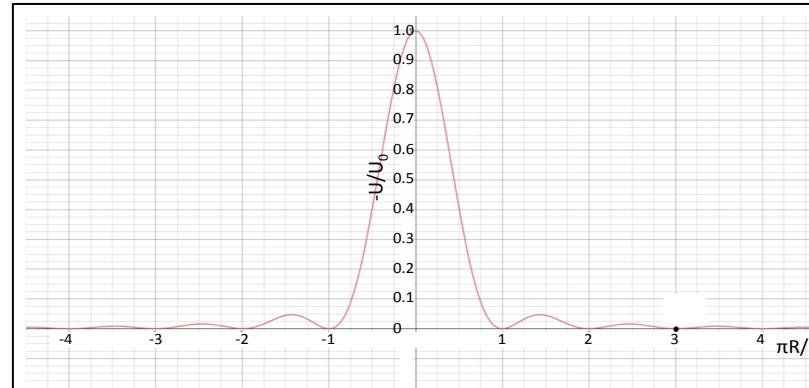
$$E(\mathbf{k}) \sim \Delta E' + 2E_w \cos(\mathbf{k} \cdot \mathbf{R})$$

$$BW = 4E_w$$

Sum of E_{HOMO} & excited monomer energies

- And $BW \sim \langle \psi_m(\mathbf{r}) | H_{\text{int}} | \psi_k(\mathbf{r} - \mathbf{R}_{n.n.}) \rangle$, the overlap between the perturbed and initial wavefunctions
- To solve this, we actually need a potential $U(\mathbf{R})$ that should be large when the overlap is small, and small when the overlap is big so as not to perturb the system too much.

$$U(\mathbf{r}) = -U_0 \frac{\sin^2(\pi \mathbf{R}/a)}{(\pi \mathbf{R}/a)^2}$$



Simple Example of the TBA: fcc lattice

- First, assume $\alpha \ll 1 \Rightarrow$ in absence of interaction, overlap very small

$$E(\mathbf{k}) - E_{HOMO} = -\beta - \sum_{i=1}^{12} J(\mathbf{R}_i) \cos(\mathbf{k} \cdot \mathbf{R}_i)$$

- Now in fcc lattice, molecules at all 12 positions at $\frac{1}{2}a$ from origin
- J has form: $J(\mathbf{R}_i) = J_{fcc} \sim -\langle \phi(\mathbf{r}) | H_{int}(\mathbf{r}) | \phi\left(x - \frac{a}{2}, y - \frac{a}{2}, z\right) \rangle$
- Total solution is cosine-like with $BW = 8J_{fcc}$:
$$E(\mathbf{k}) - E_{HOMO} = -\beta - 4J_{fcc} \{ \cos\left(\frac{1}{2}k_x a\right) \cos\left(\frac{1}{2}k_y a\right) + \cos\left(\frac{1}{2}k_x a\right) \cos\left(\frac{1}{2}k_z a\right) + \cos\left(\frac{1}{2}k_y a\right) \cos\left(\frac{1}{2}k_z a\right) \}$$
- Near zone center, $\frac{1}{2}ka$ is small.

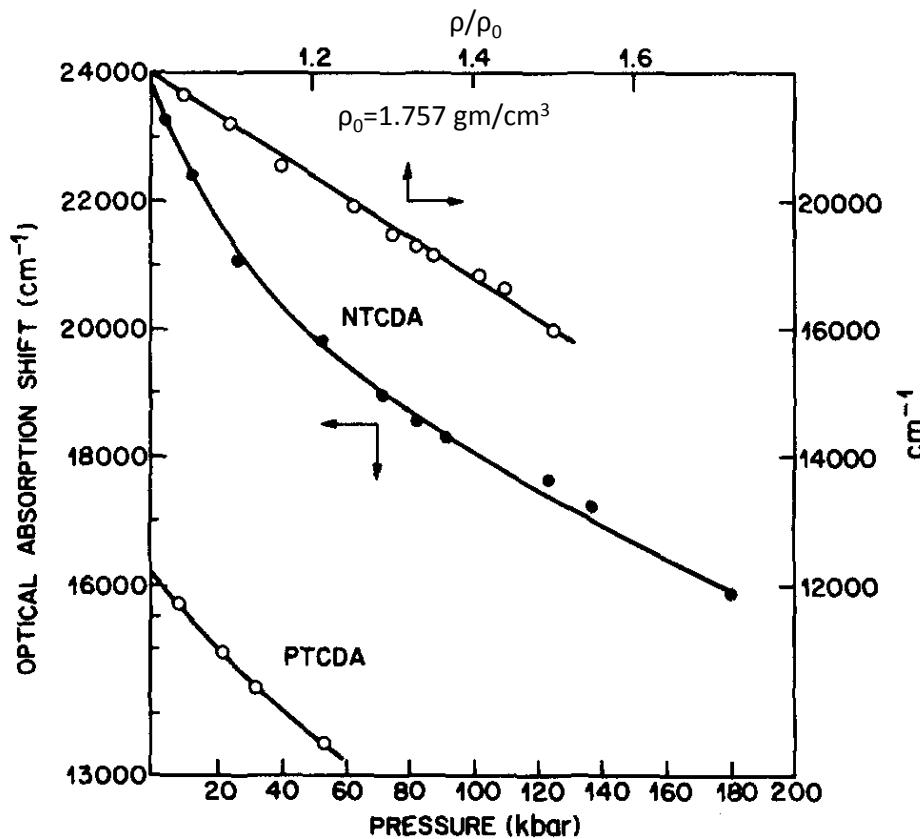
From energy dispersion relation, we obtain group velocity and mass

$$v_x(k) = \frac{2J_{fcc}k_x a^2}{\hbar} \quad m_x^* = \frac{\hbar^2}{2J_{fcc}a^2}$$

(same along y, z in cubic lattice)

Can we count on such a simple theory?

- Weak binding makes this approach plausible
- Nearest neighbor interactions (e.g. due to vdW forces) makes the solutions tractable.
- What does it predict?



Molecules under hydrostatic pressure have a decreasing energy gap.