Triplet state diffusion in organometallic and organic semiconductors

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From materials properties

To device applications

Organic semiconductors allow for attractive displays ...

OLED display by Sony

... and lighting producs and solar cells

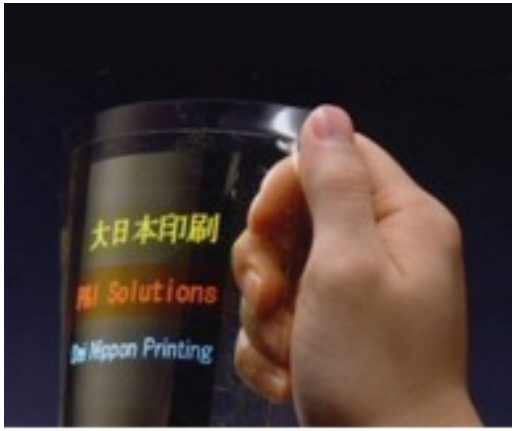
Lighting windows
by Osram

Flexible solar cells
on fabric

...and electronic reader devices ...

The E-ink reader by Plastic Logic, fabricated in Dresden

What makes organic semiconductors so attractive ?



Opto-electronic properties of semiconductors

+

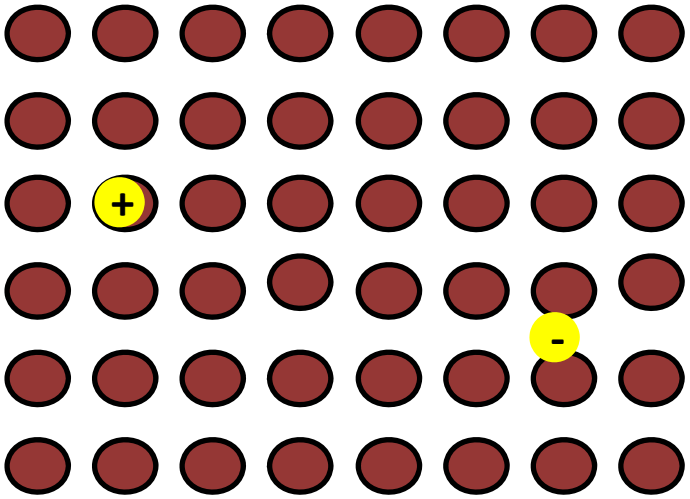
Mechanical properties of plastic

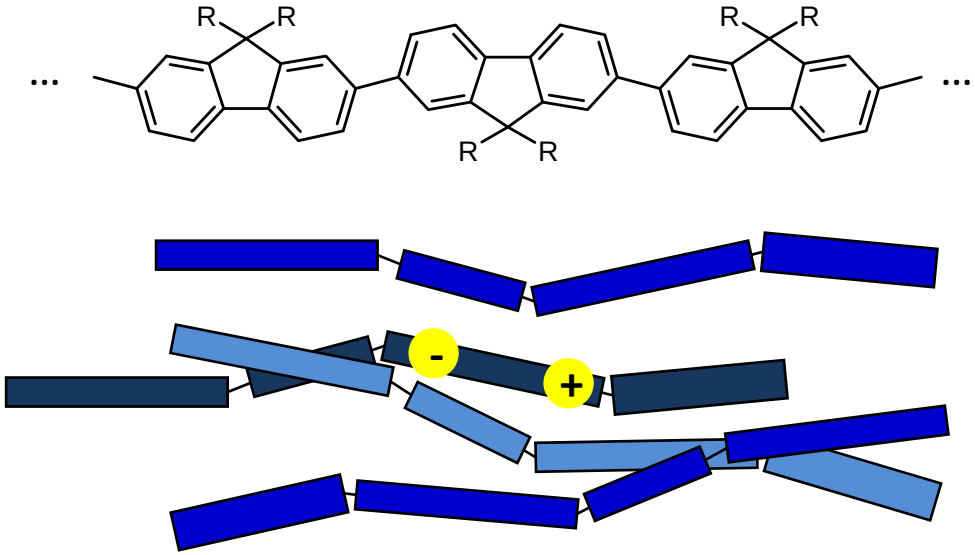
conduction → transistors,
absorption solar cells,
emission light emitting diodes

flexible
robust → novel products
light-weight

soluble → new fabrication technologies

The different physics of organic semiconductors I - Energetics





Inorganic crystal

strong coupling :
bands

high dielectric constant:
large e-h distance
weak binding
weak exchange energy

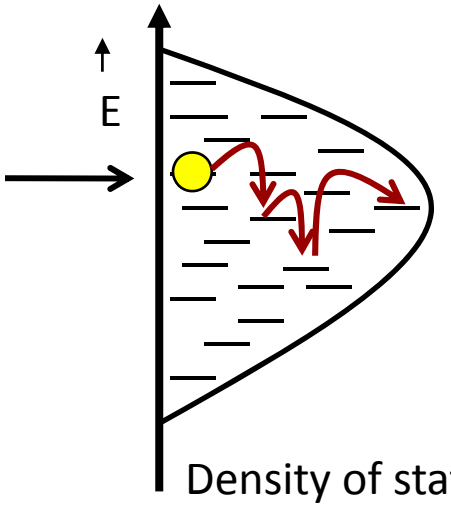
amorphous organic film

weak coupling :
localised states

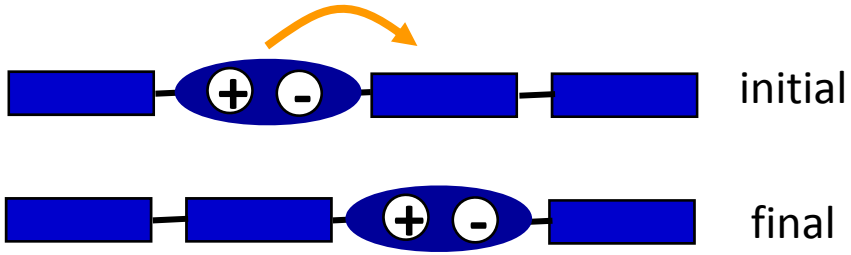
low dielectric constant :
small e-h distance (≈0.3 nm)
strong binding (≈0.4 eV)
high exchange energy (≈0.7 eV)

The different physics of organic semiconductors II - Dynamics

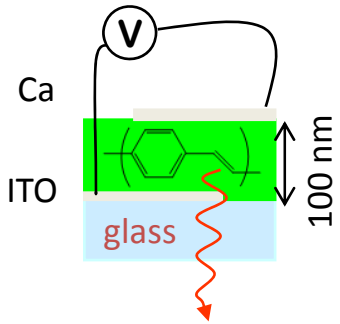
Energetic disorder



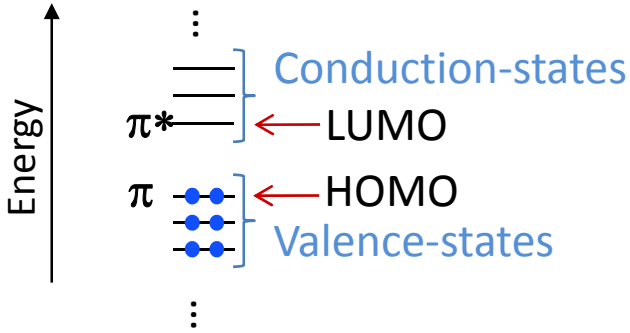
Electron phonon coupling



What happens in an organic LED ?

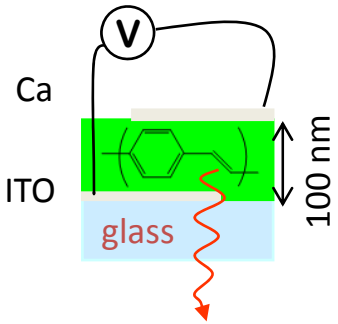


Operate LED

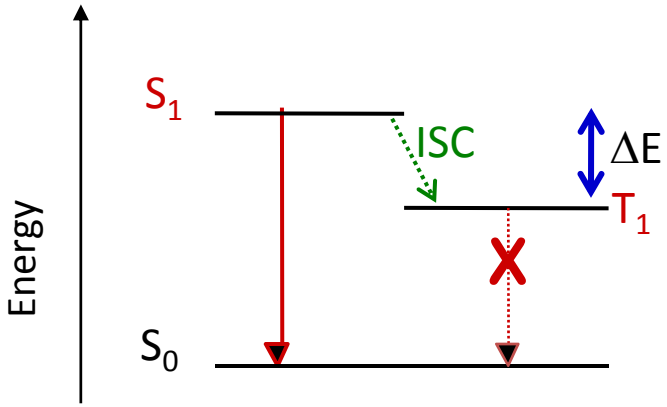


Place spin 1/2 electrons and spin 1/2 holes in π and π* orbitals

What happens in an organic LED ?



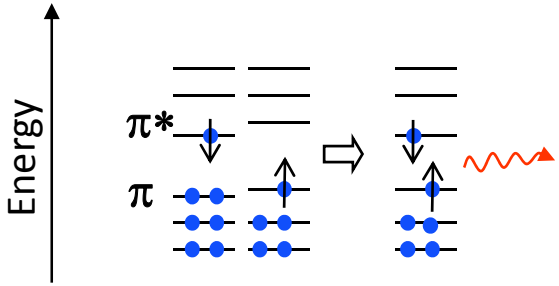
Operate LED



They form two types of states

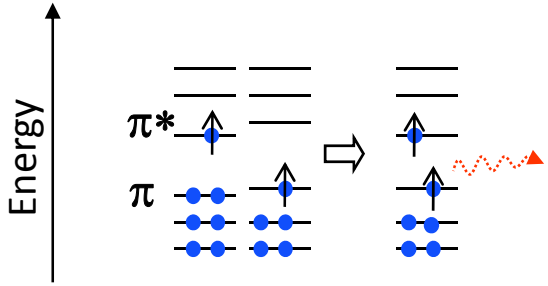
1 spin = 0 :
Singlet state
emission allowed
(fluorescence)

3 spin = 1 :
Triplet state
emission forbidden
(phosphorescence)



Singlet S_1

OR



Triplet T_1

Place spin 1/2 electrons and spin 1/2 holes in π and π* orbitals

Triplet state photophysics

For OLEDs with phosphorescent host-guest-systems

Y.Sun + S. Forrest, Nature 2006
QE_{ext}=19 % , 30 lm/W for white OLED

For solar cells using triplet excitons (W.Y. Wong, Macromol. Chem. Phys. 2008)

➡ We need to know:

- **Energetics**: How big is the exchange energy, and how can we modify it?
- **Dynamics**: How is triplet state energy transferred and what controls it?

What do we know about the exchange energy

It depends on the electron-hole wavefunction overlap

- In π-conjugated polymers with π-π^* transition, it is 0.7 eV
  In associated shorter oligomers, it raises up to 1.3 eV

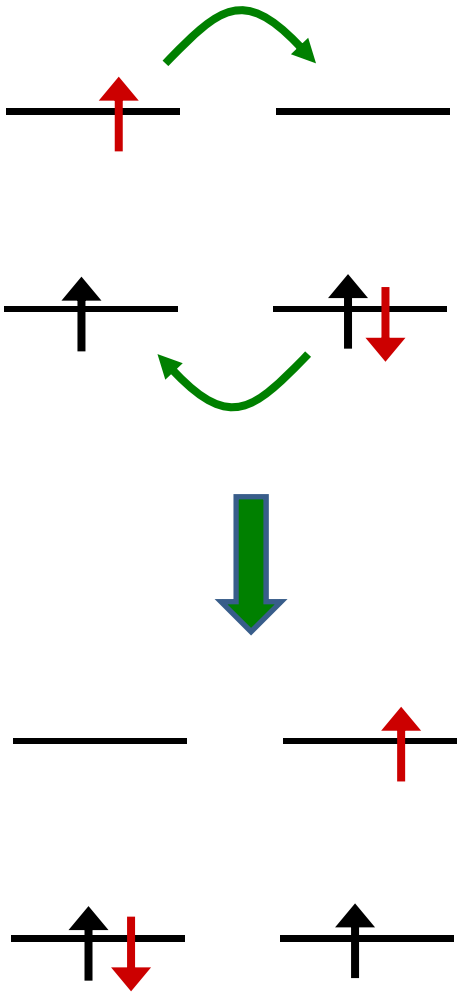
A. Köhler, AFM 2004

To reduce the exchange energy, spatially separate electron and hole

- use n-π^* transitions and non-conjugated linkages
  use charge-transfer states

Brunner, Van Dijken, JACS 2004
Zhang, Köhler JCP 2006 p. 244701 06

Triplet state energy transfer

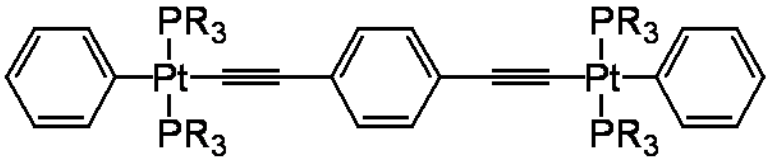


Triplet diffuses via exchange interaction

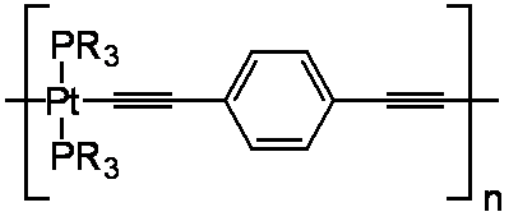
Simultaneous transfer of two electrons

- Depends on wavefunction overlap
  Along a chain or between chains?
- Depends on electron-phonon coupling
  Chain length dependence?
- Depends on Donor-Acceptor energies
  Dependence on energetic disorder?

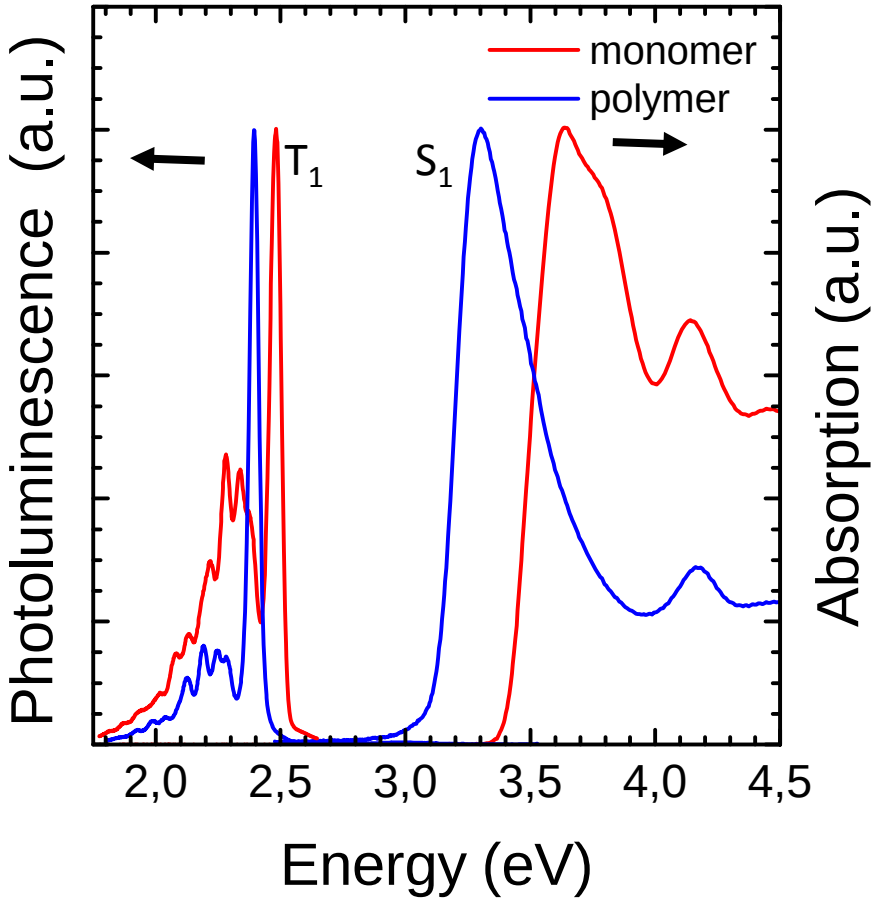
Our workhorse: Pt-containing model systems

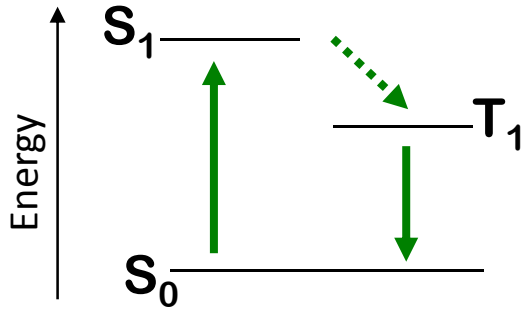


Monomer



Polymer



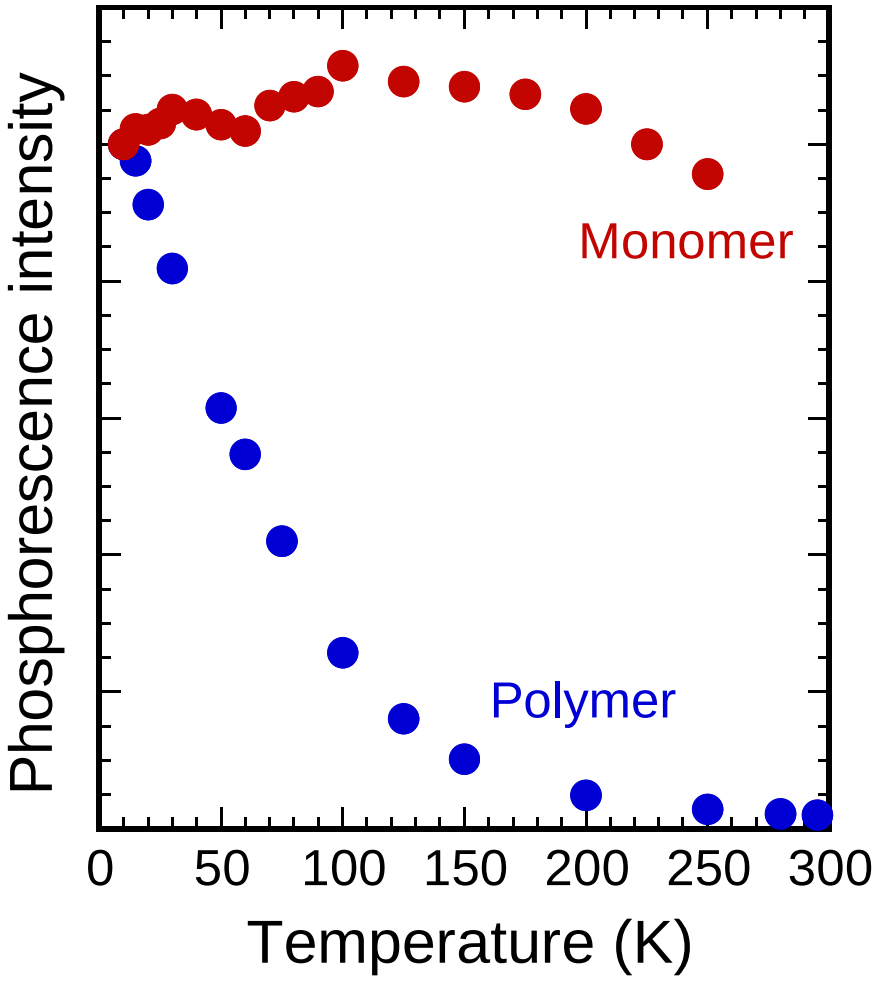


- Strong Spin-orbit coupling

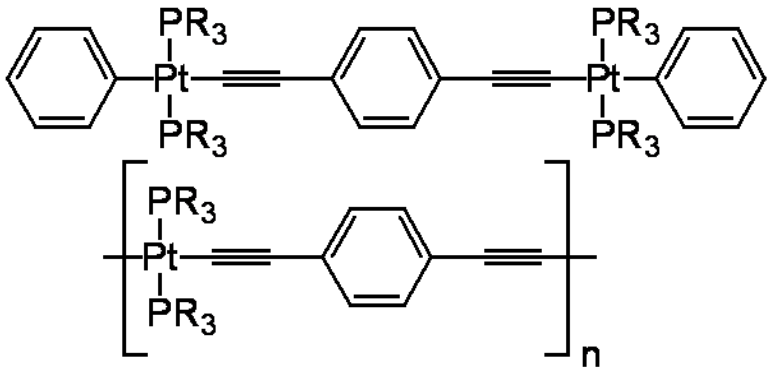
→ strong phosphorescence

- Some conjugation is preserved along the chain

Temperature dependence of phosphorescence intensity

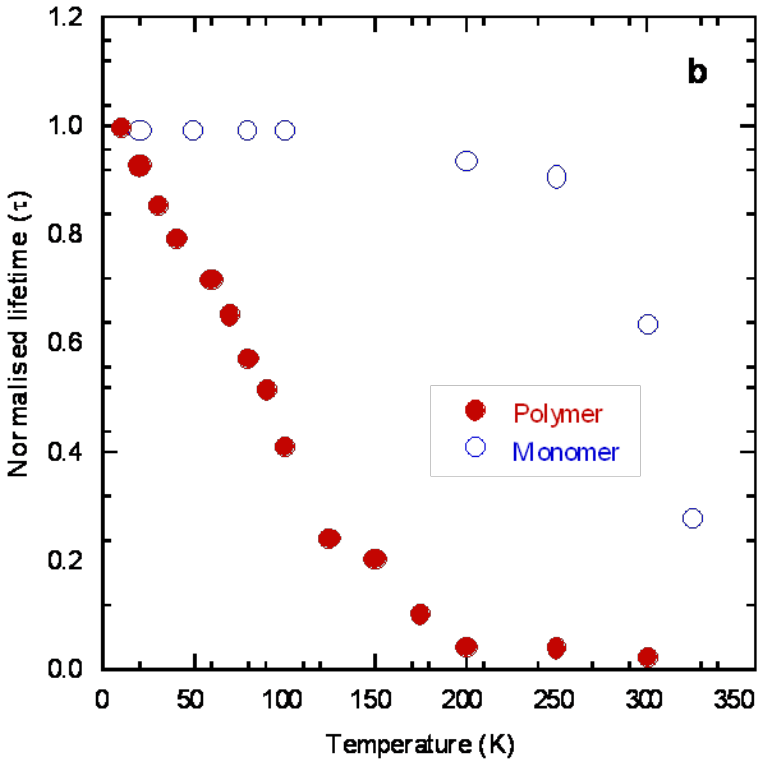


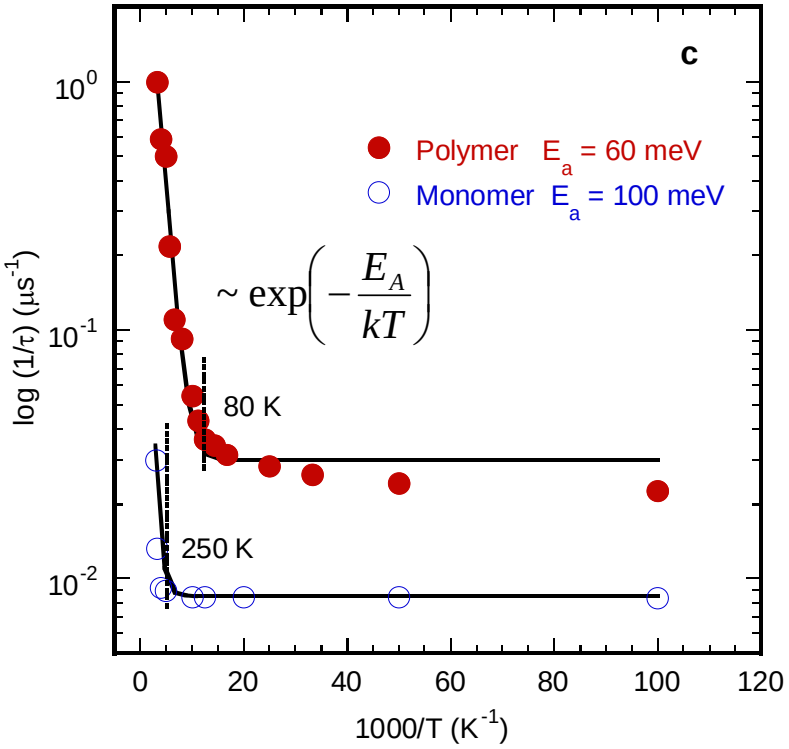
- Different temperature dependence for polymer and monomer
- not due to internal conversion (Wilson, Köhler et al. JACS (2001))



→ Triplet exciton mobility is increased in polymer

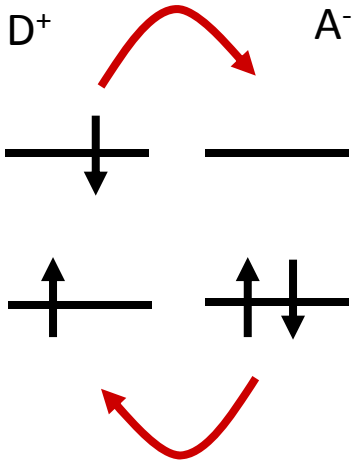
Temperature dependence of phosphorescence lifetime





There is a temperature activated high-energy branch, and a transition temperature below which the thermal activation changes (consistent with the **Holstein Small Polaron** model)

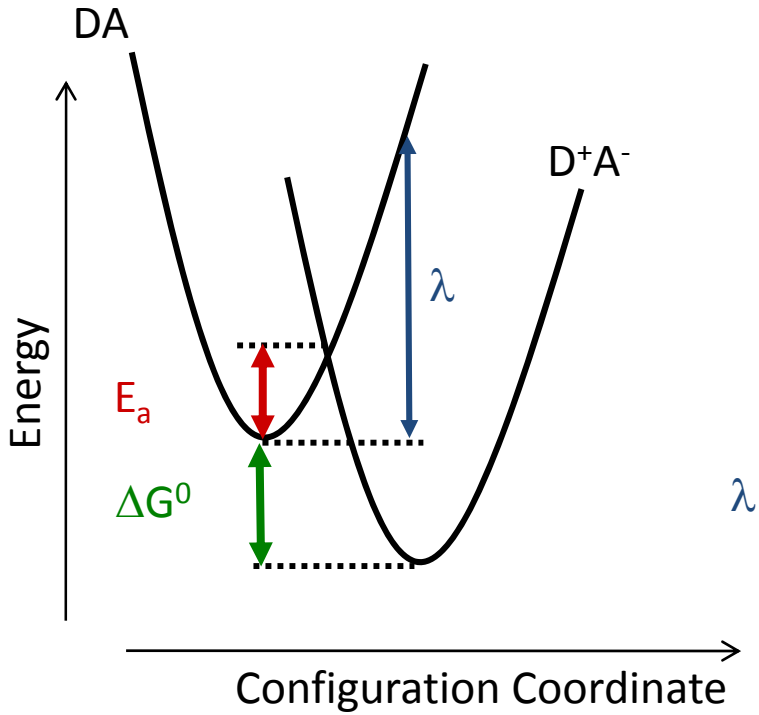
Where does this temperature dependence come from



Consider exchange transfer as a double electron transfer

Markus theory describes electron transfer (at high temp)

The transfer rate is given by:



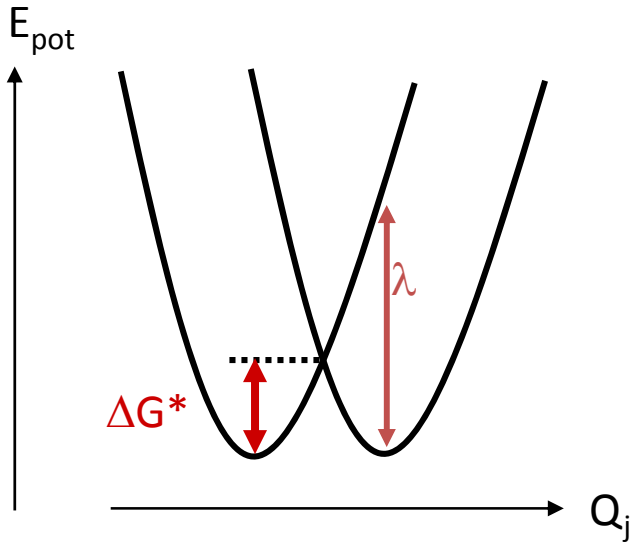
$$W_{if} \propto \left|J_{if}\right|^2 \exp\left(\frac{-E_a}{kT}\right) \qquad E_a = \frac{\lambda}{4}\left[1+\frac{\Delta G^0}{\lambda}\right]^2$$

Activation energy

λ = the reorganisation energy (electron-phonon coupling)

Triplets and Marcus theory

For a self-reaction, $\Delta G^0=0$ (neglecting energetic disorder)



$$W_{if} \propto \left|J_{if}\right|^2 \exp\left(\frac{-E_a}{kT}\right)$$

$$E_a = \frac{\lambda}{4}\left[1+\frac{\Delta G^0}{\lambda}\right]^2$$

$\Delta G^0=0$

$$W_{if} \propto \left|J_{if}\right|^2 \exp\left(\frac{-\lambda}{4kT}\right)$$

$$E_a = \frac{\lambda}{4}$$

The rate of electron transfer k_{if} depends on
the coupling between two sites V_{if}
the reorganisation energy λ.

Triplets and Marcus theory

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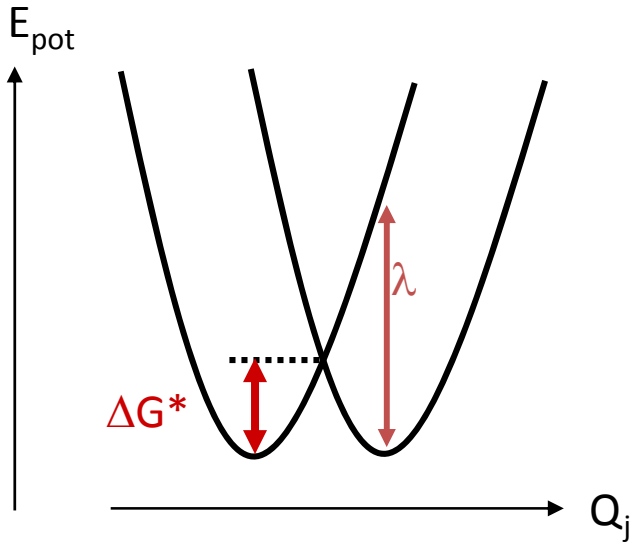

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$\Delta G^0=0$

$$W_{if} \propto \left|J_{if}\right|^2 \exp\left(\frac{-\lambda}{4kT}\right)$$

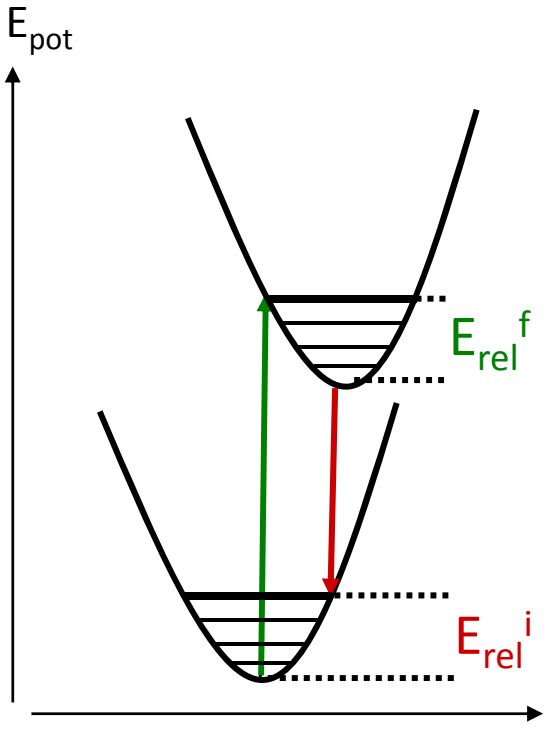
$$E_a = \frac{\lambda}{4}$$

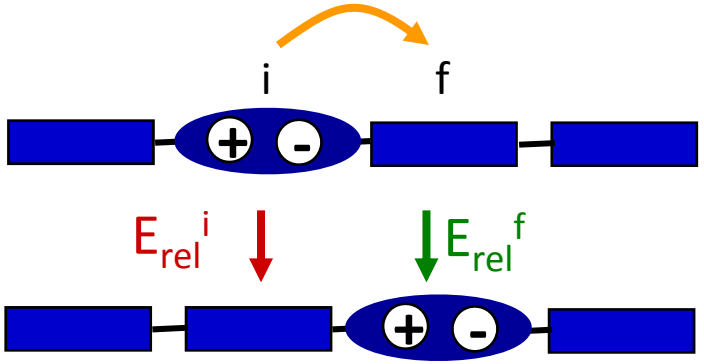
Wavefunction overlap, good along chain

The rate of electron transfer k_{if} depends on
the coupling between two sites V_{if}
the reorganisation energy λ.

The reorganization energy

Can we experimentally determine the reorganisation energy?





$$\lambda = E_{rel}{}^{i} + E_{rel}{}^{f} = 2E_{rel}$$

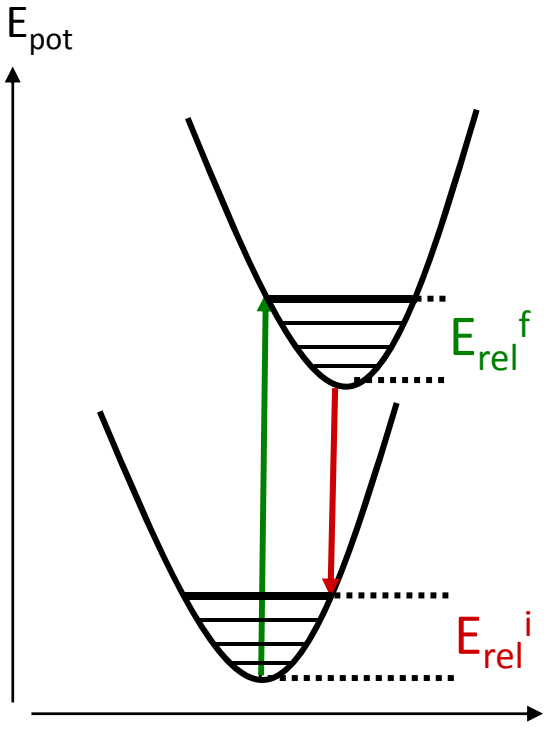
The reorganisation energy λ for the triplet transfer relates to the geometric relaxation energy associated with optical transitions

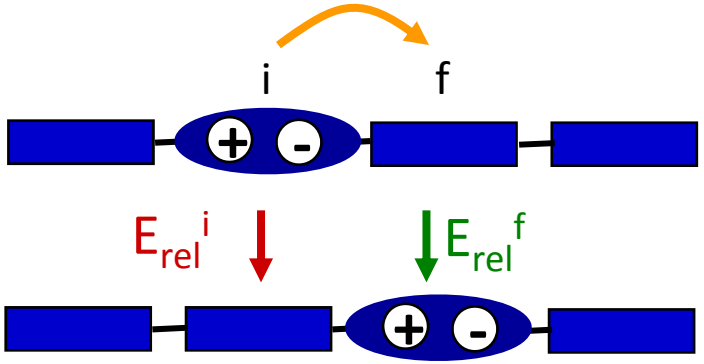
→ We can derive the activation energy for energy transfer just by analysing the absorpton and emission spectra !

Brédas et al, Chem. Rev. 2004, 104, 4971; Markvart & Greef, JCP, 2004, 121, 6401

The reorganization energy

Can we experimentally determine the reorganisation energy?





$$\lambda = E_{rel}{}^{i} + E_{rel}{}^{f} = 2E_{rel}$$

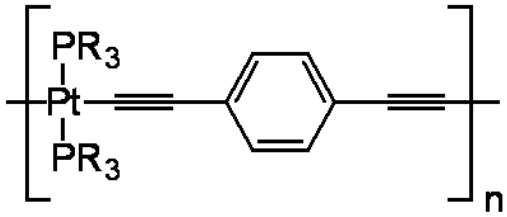
For optical transitions

$$E_{rel} = \sum_j E_{rel,j} = \sum_j \hbar\omega_j S_j$$

S= Huang-Rhys parameter

$$I_{0-n} = \frac{S^n e^{-S}}{n!}$$

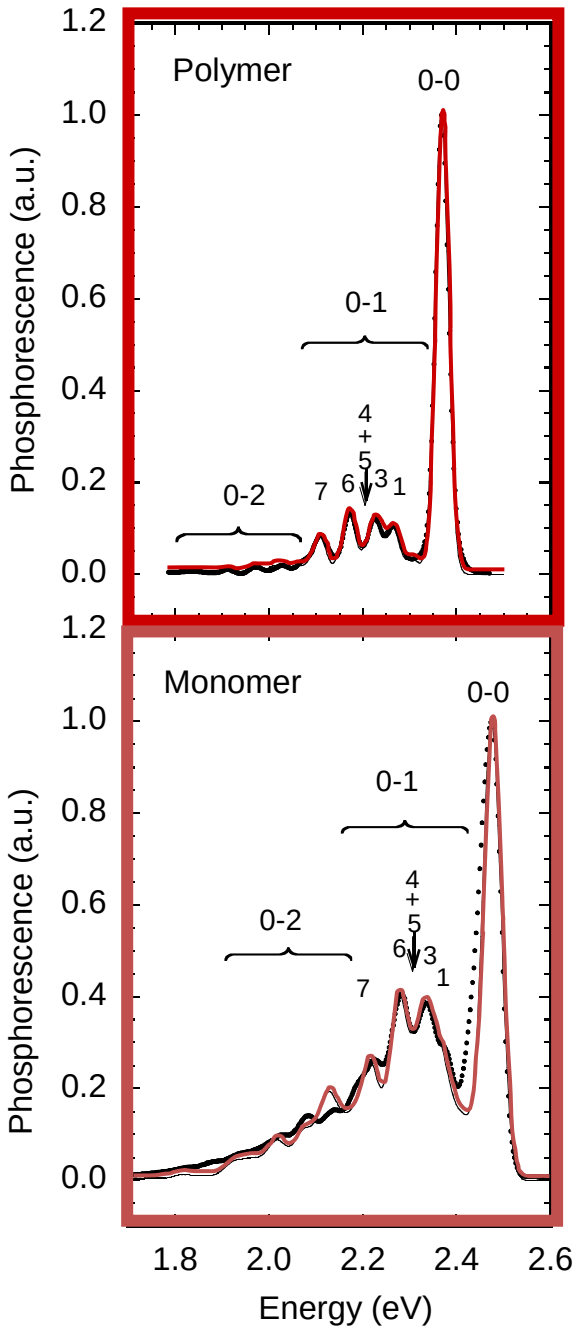
Brédas et al, Chem. Rev. 2004, 104, 4971; Markvart & Greef, JCP, 2004, 121, 6401



mode	$\hbar\omega_j$	S_j	$E_{rel\,j}$
1	61	0.03	2
2	104	0.12	13
3	136	0.03	4
4	145	0.06	9
5	152	0.06	9
6	198	0.18	36
7	261	0.11	29

$$W_{if} \propto \left|J_{if}\right|^2 \exp\left(\frac{-E_a}{kT}\right)$$

$$E_a = \frac{E_{rel}}{2}$$



Polymer

$$E_{rel} = \sum_j S_j \hbar\omega_j = 100 \text{ meV}$$

→ E_a=50 meV

Monomer:

$$E_{rel} = \sum_j S_j \hbar\omega_j = 180 \text{ meV}$$

→ E_a=90 meV

The activation energy for triplet diffusion

From Analysis of optical spectra

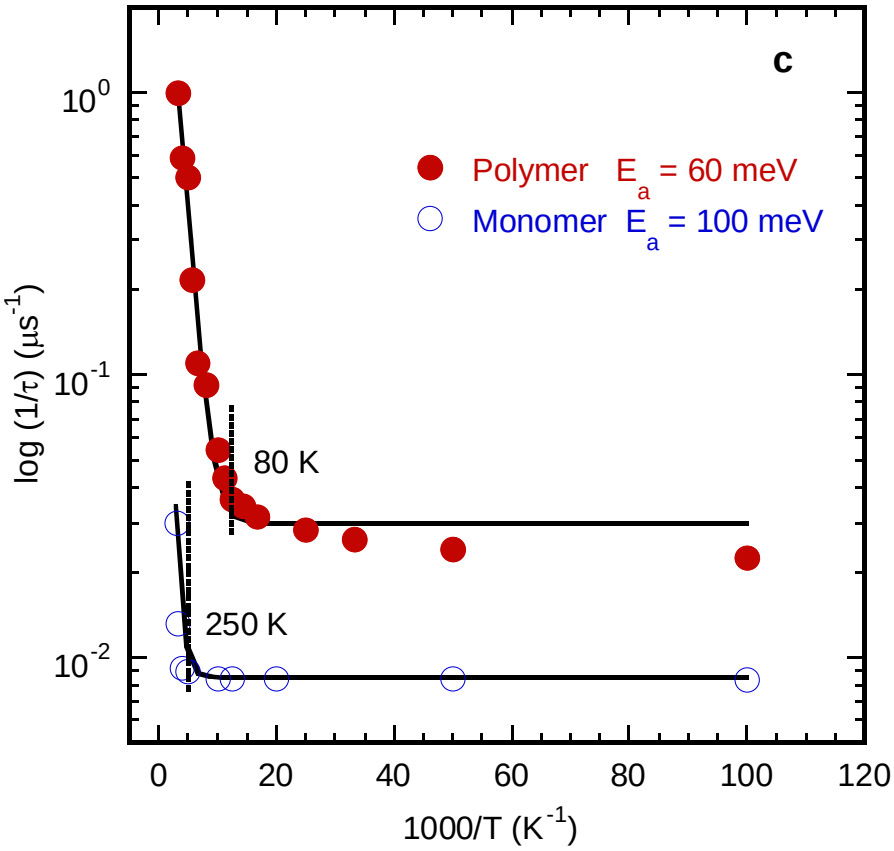
50 meV Polymer

90 meV Monomer

from temp. dep. of phosporescence

60 meV Polymer

~100 meV Monomer

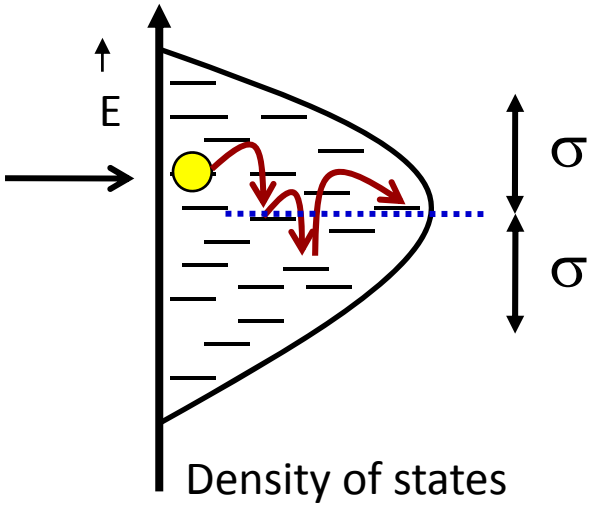


$$E_a = \frac{E_{rel}}{2}$$

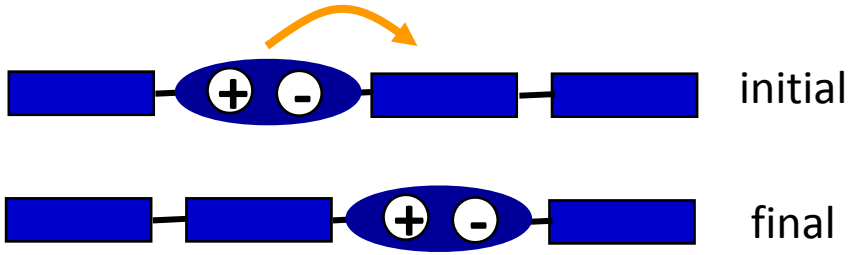
$$W_{if} \propto \left| J_{if} \right|^2 \exp\left(\frac{-E_a}{kT} \right)$$

The different physics of organic semiconductors II - Dynamics

Energetic disorder



Electron phonon coupling



How to consider the effect of disorder on the transport

Holstein small polaron theory, modified by Emin,
+ effective medium approximation

D. Emin, Adv. Phys. 24, 305, (1975)

I. I. Fishchuk et al., PRB 67, 224303 (2003)

I. I. Fishchuk et al., PRB (2008)

High Temperature

$$W_{ij} \sim \exp\left[-\frac{E_a}{k_B T}-\frac{\varepsilon_j-\varepsilon_i}{2k_B T}-\frac{(\varepsilon_j-\varepsilon_i)^2}{16E_a k_B T}\right] \rightarrow W_e \sim \exp\left[-\frac{E_a}{k_B T}-\frac{1}{8}\left(\frac{\sigma}{k_B T}\right)^2\right]$$

Multiphonon hopping

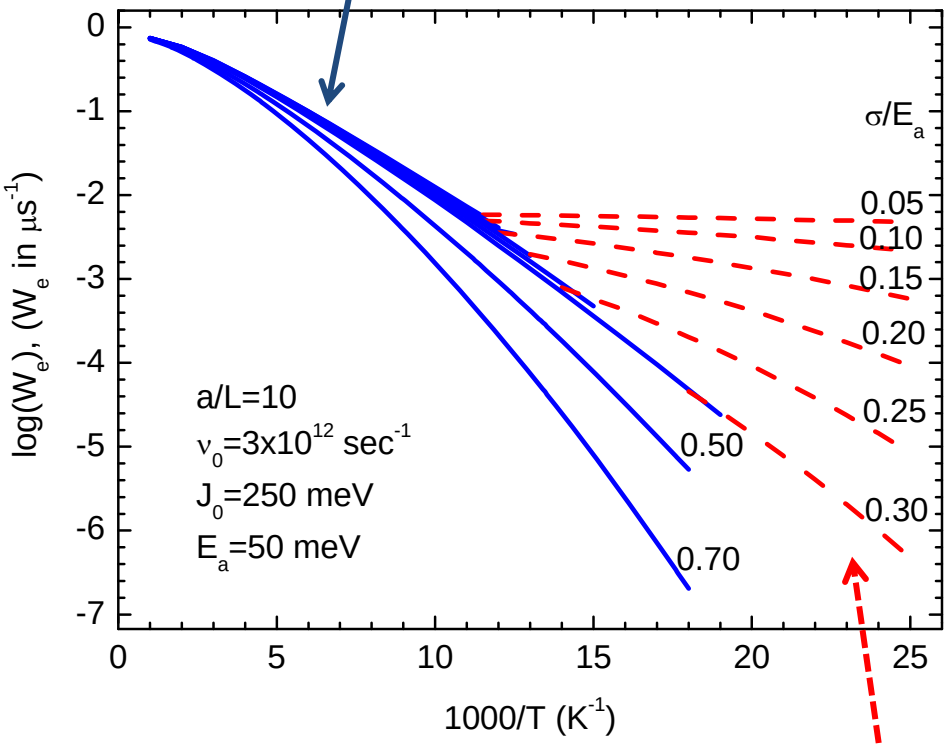
Low Temperature

$$W_{ij} \sim \exp\left(-\frac{|\varepsilon_j-\varepsilon_i|+(\varepsilon_j-\varepsilon_i)}{2k_B T}\right) \rightarrow W_e \sim \exp\left[-\frac{1}{2}\left(\frac{\sigma}{k_B T}\right)^2\right]$$

Phonon-assisted tunneling

And what happens if we increase the energetic disorder?

$$W_e \sim \exp\left[-\frac{E_a}{k_B T} - \frac{1}{8}\left(\frac{\sigma}{k_B T}\right)^2\right]$$



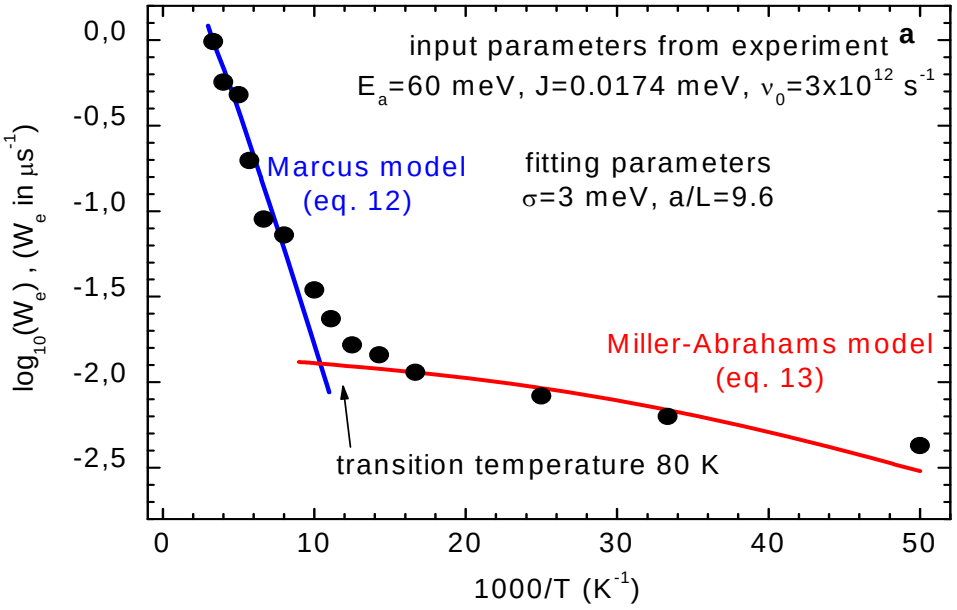
$$W_e \sim \exp\left[-\frac{1}{2}\left(\frac{\sigma}{k_B T}\right)^2\right]$$

The two regimes, multiphonon hopping and phonon-assisted tunneling, are no longer distinct!

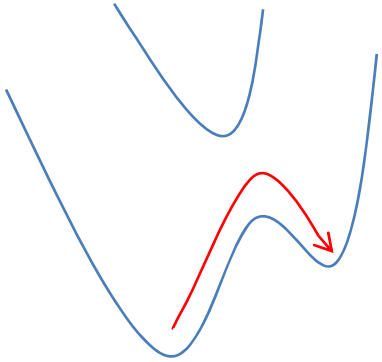
The exp ($-1/T^2$) dependence dominates the energy transfer

I. I. Fishchuk et al., PRB 2008

Test against experimental data

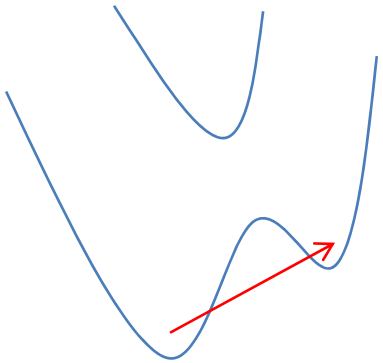


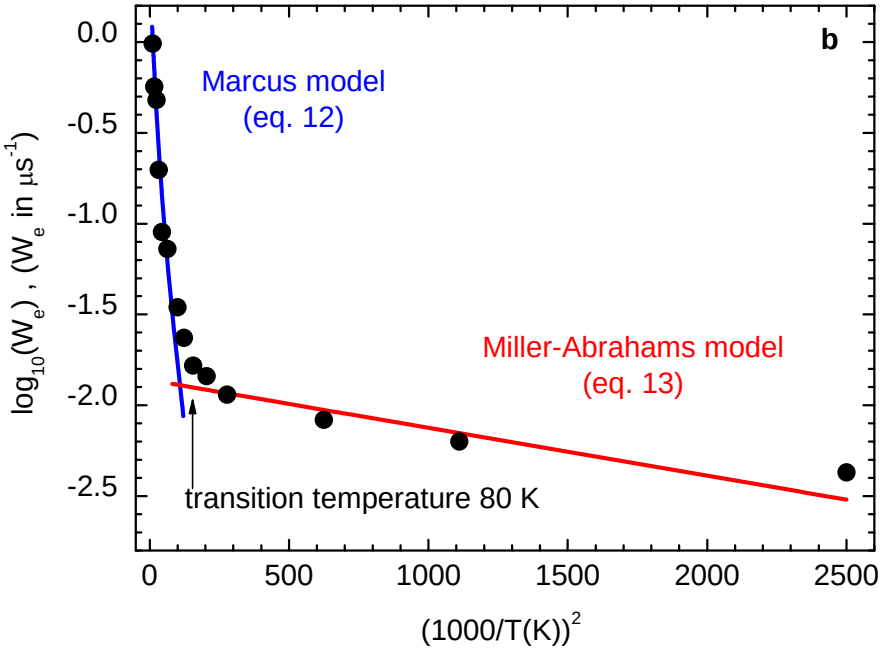
High Temp.:
Multiphonon
hopping

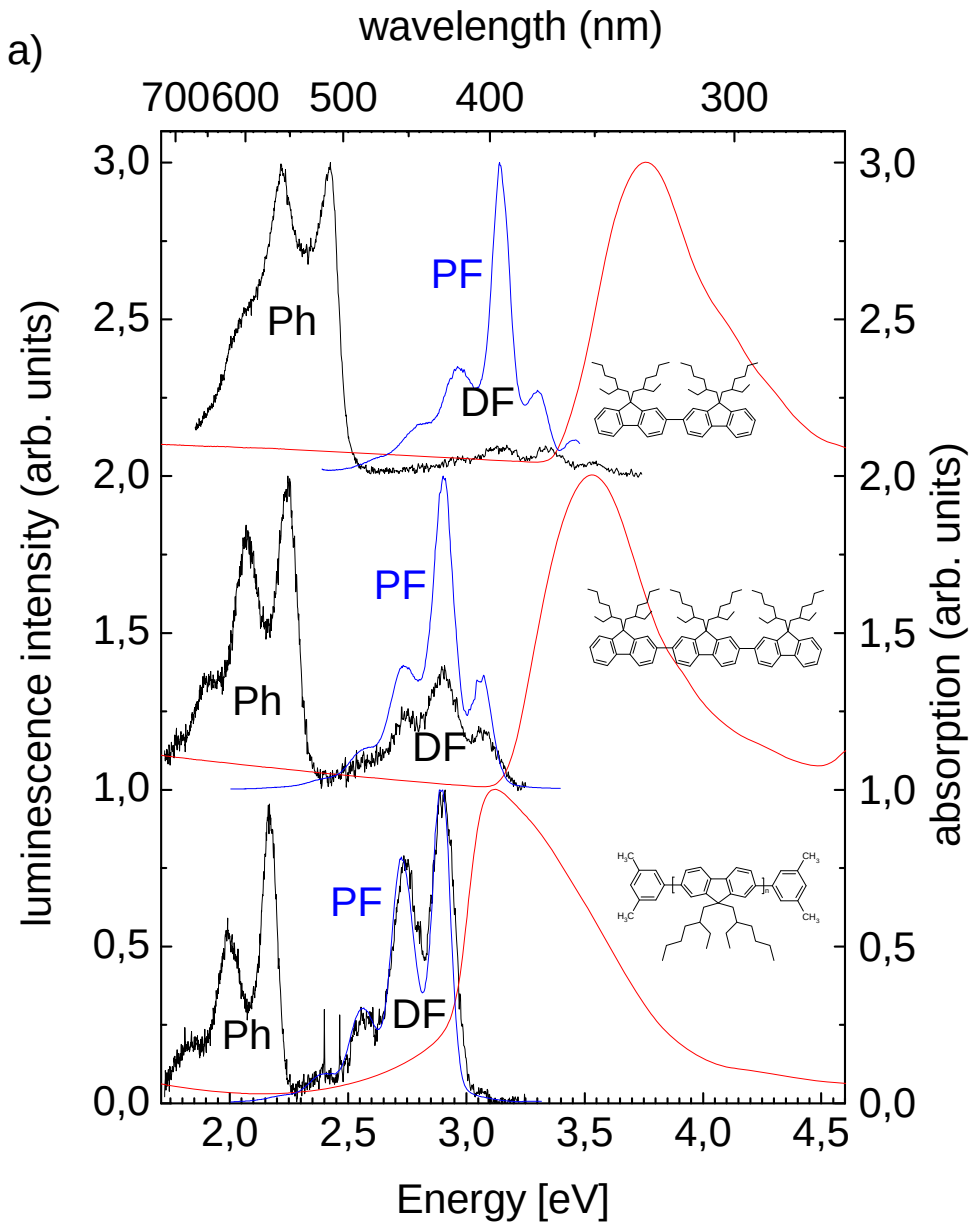


Adiabatic,
multiphonon hopping

Low Temp.:
Phonon-assisted
tunneling



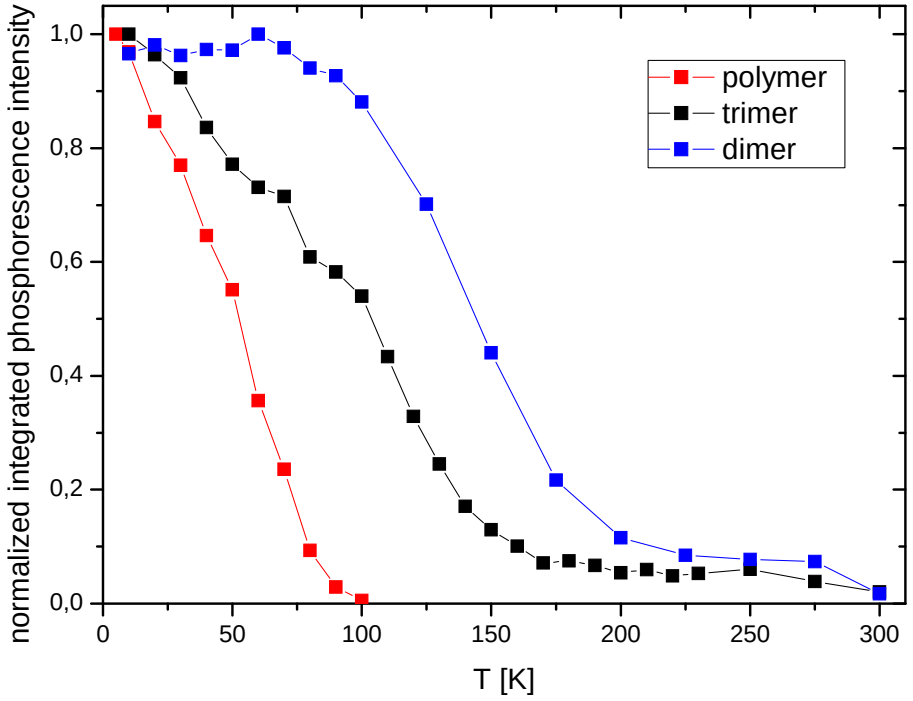


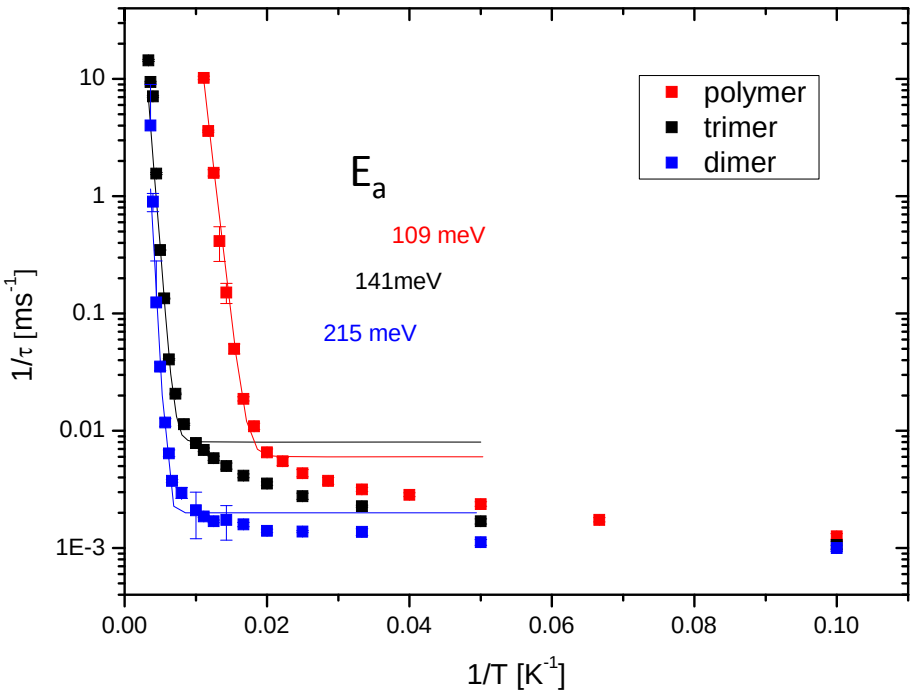


Does our model for triplet diffusion also apply to organic polymers?

Organic model compound:
Polyfluorene
polymer, trimer and dimer

Yes, it does apply!





Summary and Conclusion

How is triplet state energy transferred and what controls it?

- It is transferred via a multiphonon hopping process above T_T and a single-phonon tunneling process below T_T
- It is controlled by wavefunction overlap, the amount of geometric reorganization energy and energetic disorder
- Triplets diffuse faster along polymer chains than between them
  Triplets diffuse much faster in polymers than in oligomers

Acknowledgements

Experimental Physics:
Lekshmi Sudha Devi
Sebastian Hoffmann
Jo Wilson
Ning Zhang

Synthetic chemistry:
Muhammad Khan, Oman + students
Ullrich Scherf, Wuppertal + students
Peter Strohriegel, Bayreuth+ students

Discussions:
Richard Friend, UK
Heinz Bässler, Marburg

Theoretical calculations:
Ivan Fishchuk, Kiev
Andrey Kadashuck, Kiev