

Materials, Electronics and Renewable Energy

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- Molecular semiconductors
- Organic photovoltaics

Cost of solar energy

- Current module cost around $\$5/W_p$
- Need $<1\$/W_p$ for parity with current grid cost per kWh
- Improve efficiency, or reduce cost
- Fundamental change in materials technology required

Can we trade efficiency against cost?

- In principle yes, but balance of systems cost (especially mounting of modules) is $\sim 50\%$ of current total system cost, and scales largely with device area.
- So, best to be cheap and efficient...

Why organics?

- Thin films
- Strongly absorbing
- Flexible

Process from solution

- printing (especially for polymers)

(vacuum evaporation can be used for processing small molecules)

No dangling bonds at surface of an organic semiconductor



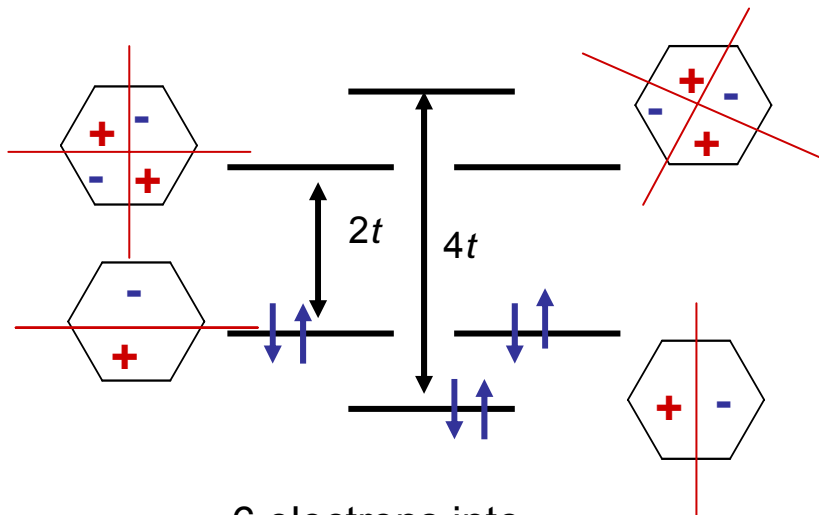
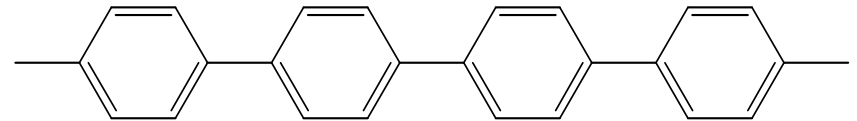
Electronic structure

Molecules or polymer chains with extended π -molecular orbitals: energy gap between filled π -bonding states and empty π^* antibonding states can be selected to lie in the visible part of the spectrum.

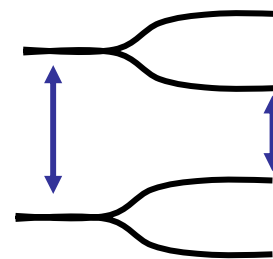
Benzene:

$$E(k) = E_{\text{atomic}} - 2t \cos(ka) - B$$

Poly(*para*-phenylene)



6 electrons into π bonding orbitals



benzene MOs broaden to form bands.
Energy gap falls from near 6 eV to around 3 eV

switch on inter-ring transfer contact, transfer integral t'

Excitons

Recall for inorganic semiconductors:

- optical excitation can produce a bound electron-hole state

$$E_{binding} = \frac{e^4 \mu}{2(4\pi\epsilon\epsilon_0\hbar)^2} = \frac{\mu/m}{\epsilon^2} \times 13.6 \text{ eV} \quad \text{where } \mu \text{ is the reduced mass for the e-h system:} \quad \frac{1}{\mu} = \frac{1}{m_e^*} + \frac{1}{m_h^*}$$

- Typical energies 2-40 meV
- Exciton radii: a few nm (many atomic sites)

Organics:

- Dielectric constant much lower ($\epsilon_r \sim 3 - 4$)
- Mott-Wannier model above ($m_e^* = m_h^* = m_e$) gives $E_b \sim 0.75 \text{ eV}$, $r \sim 0.3 \text{ nm}$
- Localised on one molecule – “Frenkel exciton”
- Localisation of the exciton to relatively few bonds causes significant coupling of the molecular geometry to the electronic configuration.

Difficult to generate free electrons and holes, even at room temperature

Organic Photovoltaics: Heterojunctions are needed!

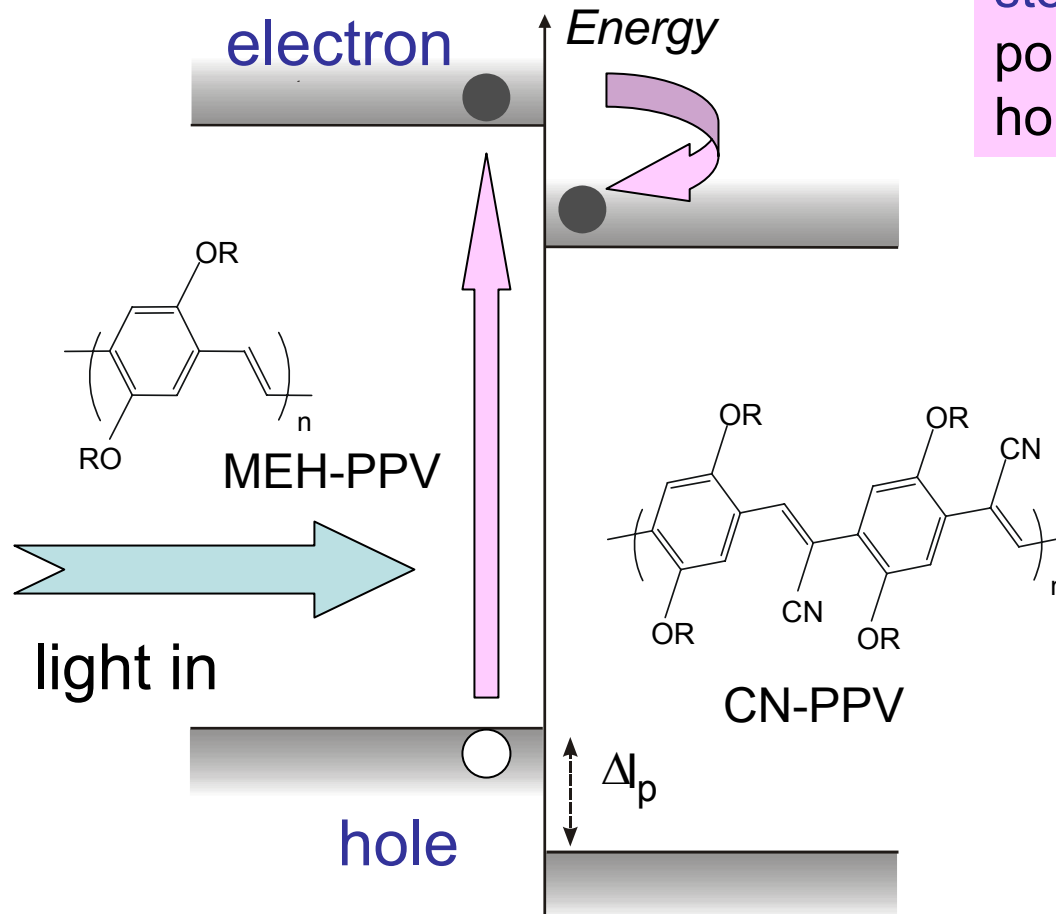
Charge separation at a
'heterojunction' between different
organic semiconductors

step 1 photon absorbed in
polymer creates electron and
hole on same polymer chain

step 2 electron drops
down to lower energy
site on the other
polymer chain

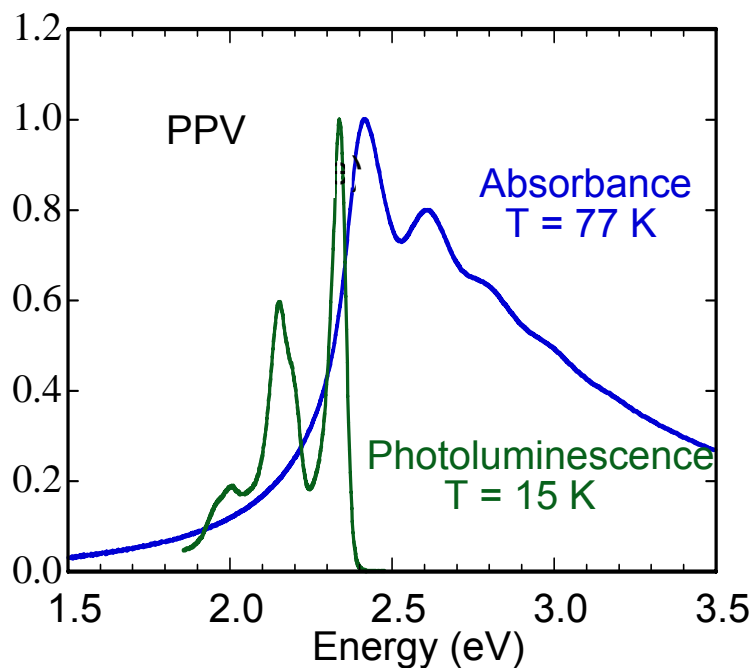
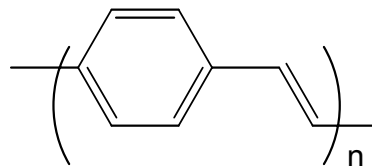
Outcome of exciton at
heterojunction =
charge transfer when:
criterion for charge
transfer:

$$E_{\text{exciton}} < \Delta I_p, \Delta E_A$$



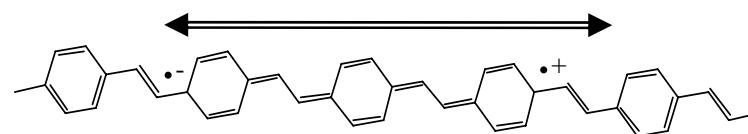
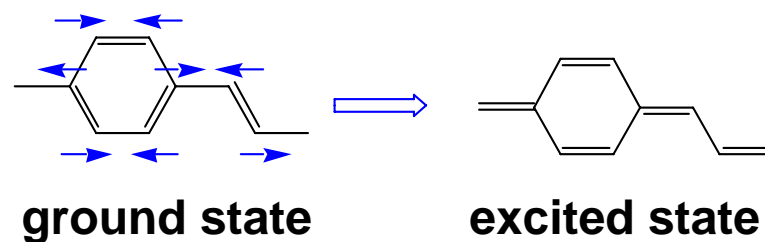
Halls, Cornil, Silbey et al. Phys.
Rev. B **60** 5721, (1999)

Optical Properties of PPV:



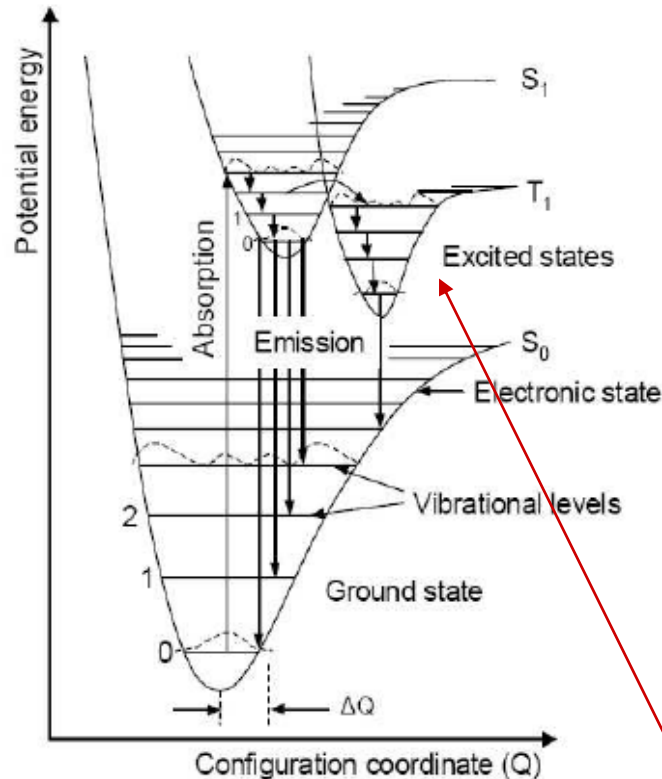
Creation of, and emission from singlet excitons

- intra-chain
- vibronic side-bands evident in absorption and emission (vibrational frequency about 1600 cm^{-1} , 0.18 eV)



exciton

Description of coupled electronic-vibronic transitions:



configuration coordinate – a multi-dimensional space! but shown here as a single variable (such as the bond dimerisation amplitude for PPV)

Coupling of vibrational transitions to electronic transitions:

Matrix element between different initial and final vibrational wavefunctions (the Frank-Condon factor) is zero if 'configuration coordinate' is same, but non-zero if the initial and final state geometries are different.

$$|\langle \chi_0 | \chi_n \rangle|^2 = e^{-S} \frac{S^n}{n!}$$

where S (the Huang-Rees parameter) is given by

$$S = \frac{M\omega}{2\hbar} (\Delta Q)^2$$

and is equal to the amplitude of the displacement in geometry between ground and excited state in units of the phonon quantum

Note spin-triplet excited states can be formed – generally between 0.5 and 1 eV lower energy than singlet excited states – give rise to 'phosphorescence'

Intermolecular Interactions:

three-dimensional energy bands?

Characterise the inter-molecular p-electron contact by an 'intermolecular' transfer integral, t

This can be as large as 0.1 eV for the contact between planar molecules,

Sufficient for inter-molecular charge transport (though carrier mobilities are much lower than as found in inorganic semiconductors)

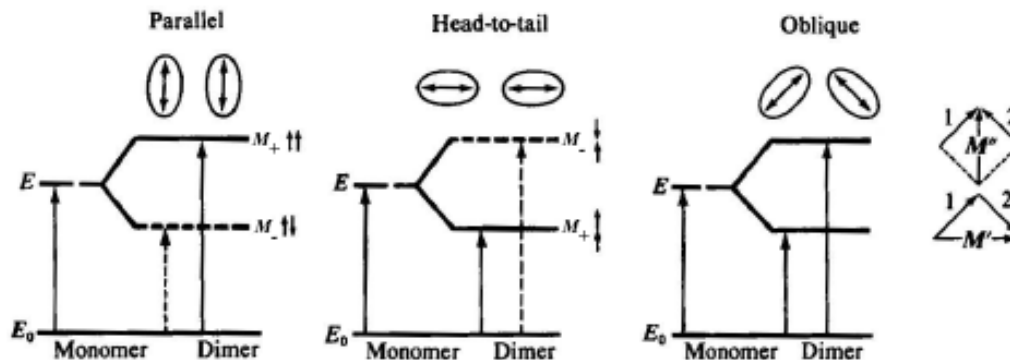
Dimers, or 'aggregates' can show significantly red-shifted bandgaps.

Excitonic interactions:

Usual treatment is by consideration of the effect of the transition dipole generated at one site at a distant site. Usual to treat this as a point dipole.

short range:

dipole-dipole interaction splits exciton states, e.g. for a dimer,



Transporting excitons to a heterojunction

Weak interactions. Transfer is slow compared with coherence time: Förster Resonance Energy Transfer (FRET)

Dipole field falls as $1/R^3$. Induced (oscillating) dipole on nearby molecule scales as $1/R^3$. Interaction (coupling) between the two dipoles leads to energy transfer with rate scaling as $1/R^6$ (cf. van der Waals interaction).

Must conserve energy: Forster transfer rate, k_{DA} depends on the overlap of the emission spectrum of the emitter and the absorption spectrum of the receiving site:

$$I_{DA} \propto \int_0^\infty \frac{F_D(\nu)\varepsilon(\nu)}{\nu^4} d\nu$$

F_D is donor emission rate, ε is molar absorption coefficient

$$k_{DA} = \frac{1}{\tau_D} \frac{9000 \ln(10) \phi_D}{128 \pi^5 N_A n_{solv}^4} I_{DA} \kappa_{DA} \frac{1}{R_{DA}^6}$$

NB. no photon is actually emitted and reabsorbed

ϕ_D is the quantum efficiency of luminescence of the donor, and τ_D its lifetime, N_A Avogadro's number, κ_{DA} an orientational factor for the dipole, n_{solv} the refractive index in the medium, R_{DA} the donor-acceptor separation

expressing this in terms of a Forster Radius, R_F as:

$$\kappa_{DA}(R) = \frac{1}{\tau} \left(\frac{R_F}{R_{DA}} \right)^6$$

values of the Forster radius are in the range 2-4 nm.

Exciton diffusion

- Exciton lifetime ~ 1 ns
- Hops between many sites (by Förster transfer)
- Typical diffusion range 5 – 10 nm

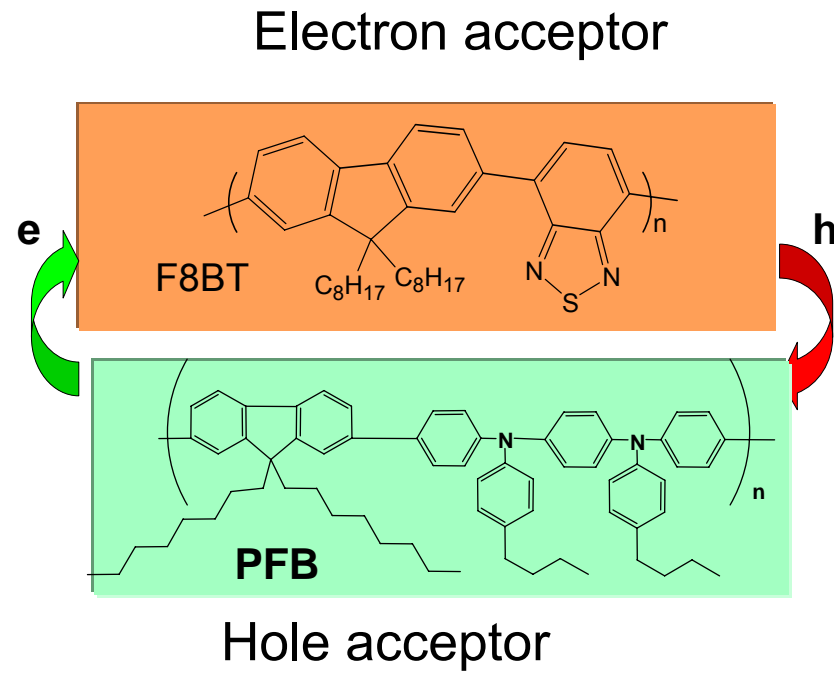
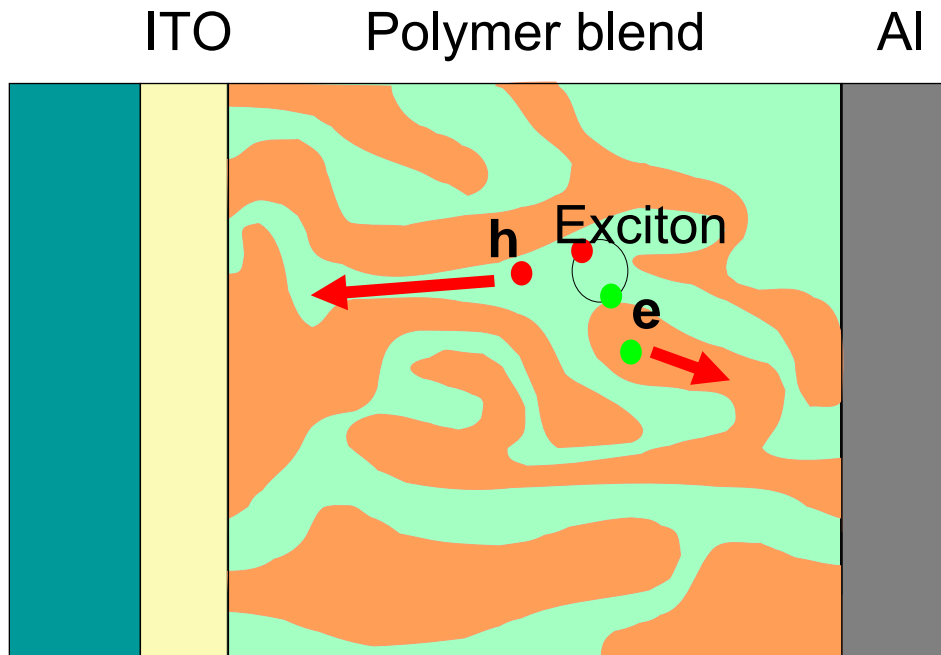


- For efficient PV operation, must find interface within 5 – 10 nm
- But, absorption depth still ~ 100 nm

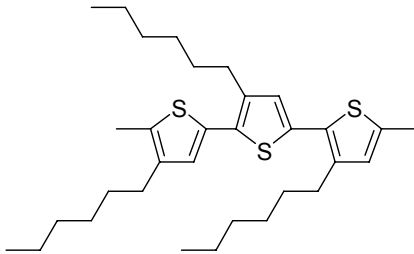
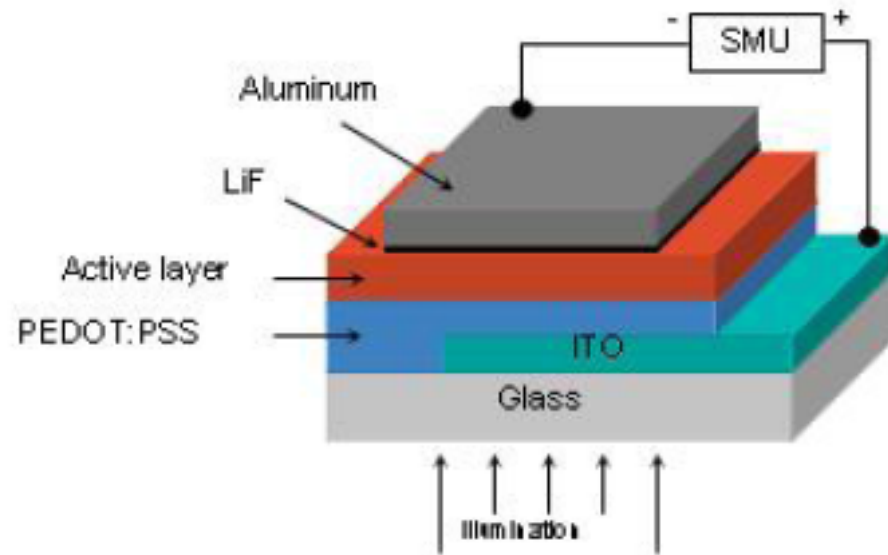
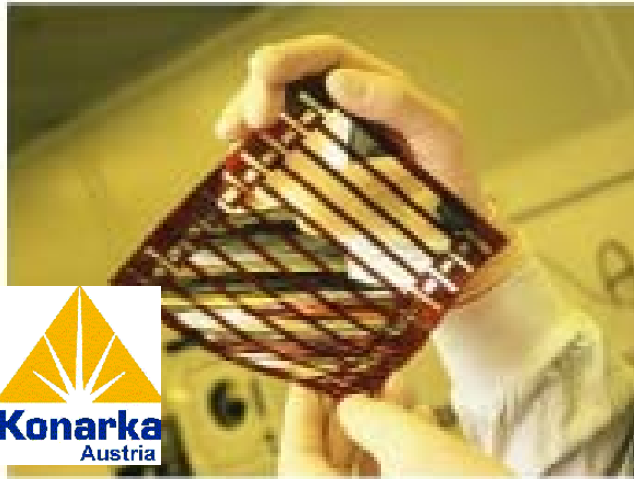
'Dispersed Interface' Photovoltaics

'mixed' polymers generally phase-separate due to low entropy of mixing – **spinodal decomposition**

Halls et al. Nature **376**, 498 (1995),
Yu et al. Science **270**, 1789 (1995)

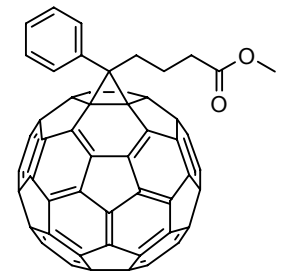


Polymer/C₆₀ photovoltaics – efficiencies up to 5%



P3HT

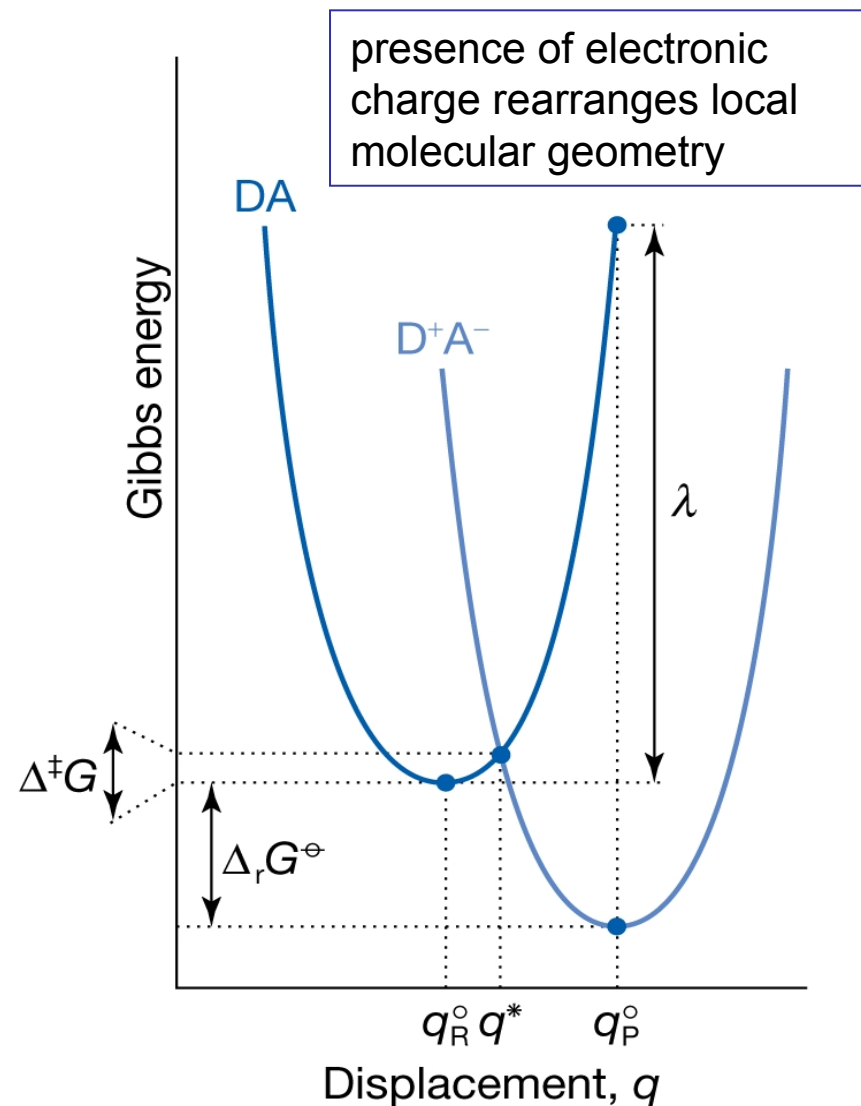
- polythiophene – absorbs from 600 nm
- PCBM not very absorbing but a good electron-acceptor



PCBM

Electron transfer at the heterojunction – want fast transfer (\sim ps), slow recombination (\sim μ s):

Marcus theory (chemists),
Polaron hopping (physicists)



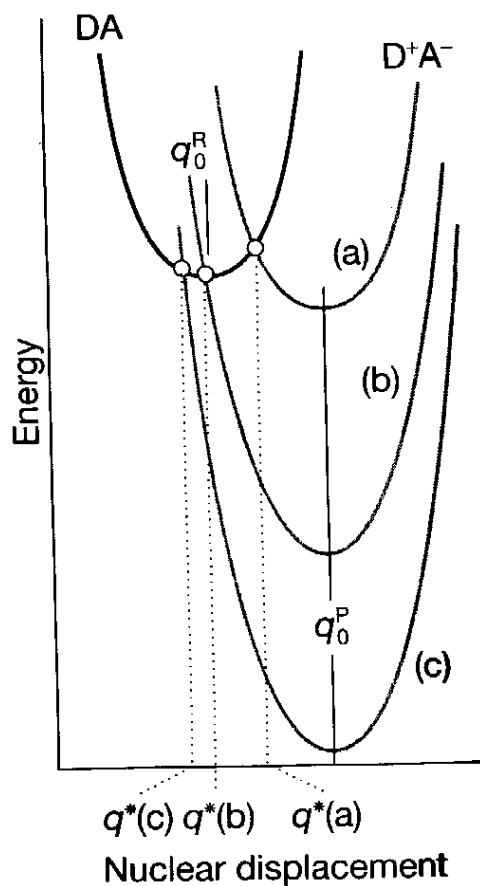
- Isoenergetic electron transfer requires thermal excitation to crossing point
- Activation barrier:

$$\Delta G^\ddagger = (\Delta G^0 + \lambda)^2 / 4\lambda$$
 where λ is the 'reorganisation energy', the energy change associated with molecular rearrangements such that ${}^1D^*A$ takes up the equilibrium geometry of D^+A^- .

$$k_{transfer \ rate} \propto V_{tunnelling}^2 e^{-\left(\frac{(\Delta G^0 + \lambda)^2}{4\lambda k_B T}\right)}$$

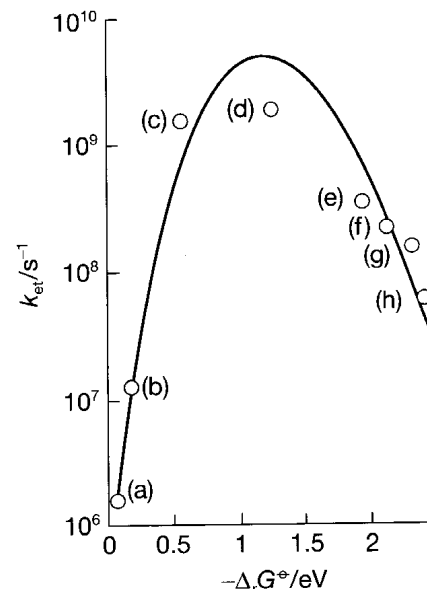
$$V_{tunnelling}^2 \propto \langle \psi_{1D^*} | \psi_A \rangle^2 \propto \exp\left(\frac{-2r\sqrt{2mV}}{\hbar}\right) = \exp(-\beta r)$$

Dependence of transfer rate on ΔG



$$k_{\text{transfer rate}} \propto V_{\text{tunnelling}}^2 e^{-\left(\frac{(\Delta G^0 + \lambda)^2}{4\lambda k_B T}\right)}$$

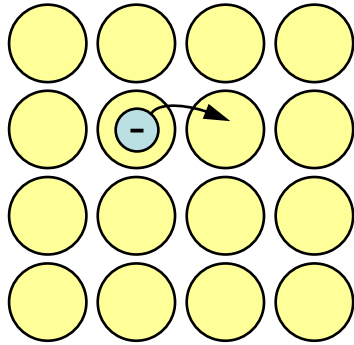
- $\Delta G^0 < 0$ for downhill electron transfer
- as ΔG^0 is reduced, at some point $|\Delta G^0| = \lambda$ and 'Boltzmann factor' = 1.
- 'Activationless' electron transfer!
- For given V_{eltr} , rate is maximal.
- As $|\Delta G^0| > \lambda$, the Boltzmann factor becomes < 1 and rate slows: the 'inverted Marcus regime'



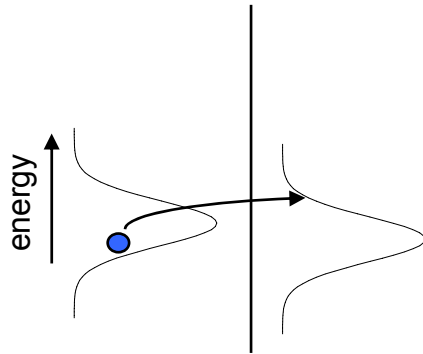
Data for covalently attached D/A pair

- λ depends on solvent environment ~ 1.5 eV in water, ≤ 1 eV in non-polar solvents ($1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$, equivalent to 96 kJmol^{-1})
- Photosynthetic reaction centres evolved such that:
 - Non-polar interior ($\lambda \leq 1 \text{ eV}$)
 - Forward reactions activationless: $|\Delta G^0| = \lambda$: fast
 - Reverse reactions in inverted region: $|\Delta G^0| > \lambda$: slow

Charge transport in disordered systems



- Hopping transport
- Individual hopping rates given by Marcus theory
- But all the sites have slightly different energies (due to different environments/conformations)
- Also disorder in hopping distances



$$\mu = \mu_0 e^{-\beta r} f(E, n)$$

\uparrow
 $e^{\gamma\sqrt{E}}$

- Mobility increases with field
 - more sites available to hop to without going uphill in energy
- Mobility increases with carrier density
 - higher energy sites occupied

Summary for organic photovoltaics so far

- Absorb light
 - 100-200 nm required
- Exciton diffuses to heterojunction
 - only goes 5-10 nm
 - fine control of morphology required
- Charge transfer takes place
 - fast
 - try not to lose too much energy in this step
- Charges separate further
 - initially still coulombically bound
 - hope recombination across interface is slow
- Transport charges out of device
 - difficult in fine blend
 - avoid bimolecular recombination