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 ~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 $\pi$-molecular orbitals: energy gap between filled $\pi$-bonding states and empty $\pi^*$ 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(\text{para-phenylene})

6 electrons into $\pi$ bonding orbitals

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

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

Recall for inorganic semiconductors:
• optical excitation can produce a bound electron-hole state

\[ E_{\text{binding}} = \frac{e^4 \mu}{2(4\pi\epsilon\epsilon_0\hbar)^2} = \frac{\mu/m}{\epsilon^2} \times 13.6 \text{eV} \]

where \( \mu \) is the reduced mass for the e-h system:

\[ \frac{1}{\mu} = \frac{1}{m_e^*} + \frac{1}{m_h^*} \]

• 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
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:

\[ E_{\text{exciton}} < \Delta I_p, \Delta E_A \]

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)
Description of coupled electronic-vibronic transitions:

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.

\[
\left|\langle \chi_0 | \chi_n \rangle \right|^2 = e^{-S} \frac{S^n}{n!}
\]

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

\[
S = \frac{M\omega}{2h} (\Delta Q)^2
\]

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,
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:

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

$F_D$ is donor emission rate, $\varepsilon$ is molar absorption coefficient

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

$\phi_D$ is the quantum efficiency of luminescence of the donor, and $\tau_D$ its lifetime, $N_A$ Avogadro’s number, $k_{DA}$ 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:

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

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

NB. no photon is actually emitted and reabsorbed

Transporting excitons to a heterojunction
Exciton diffusion

• Exciton lifetime ~ 1ns
• 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

Polymer/C$_{60}$ photovoltaics – efficiencies up to 5%

- polythiophene – absorbs from 600 nm
- PCBM not very absorbing but a good electron-acceptor
Electron transfer at the heterojunction – want fast transfer (~ps), slow recombination (~μs):

- Isoenergetic electron transfer requires thermal excitation to crossing point
- Activation barrier:
  \[ \Delta G^\dagger = \left( \Delta G^0 + \lambda \right)^2 / 4\lambda \]
  where \( \lambda \) is the ‘reorganisation energy’, the energy change associated with molecular rearrangements such that \( 1^D*A \) takes up the equilibrium geometry of \( D^+A^- \).

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

\[ V_{\text{tunnelling}}^2 \propto \langle \psi_{1D^*} | \psi_A \rangle^2 \propto \exp \left( \frac{-2r\sqrt{2mV}}{\hbar} \right) = \exp(-\beta r) \]
Dependence of transfer rate on $\Delta G$

$\lambda$ depends on solvent environment $\sim 1.5$ eV in water, $\leq 1$ eV in non-polar solvents ($1$ eV $= 1.6 \times 10^{-19}$ J, equivalent to $96$ kJmol$^{-1}$)

Photosynthetic reaction centres evolved such that:
- Non-polar interior ($\lambda \leq 1$ 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

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

- 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