Imperial College London

Computer Simulation of Advanced Materials
International Summer School
Moscow State University
21 July 2012

The Centre for Plastic Electronics

Organic Solar Cells: From Material Design to System Efficiency

Jenny Nelson

Centre for Plastic Electronics, Department of Physics, Imperial College London, London SW7 2AZ, U. K.

EPSRC Engineering and Physical Sciences Research Council

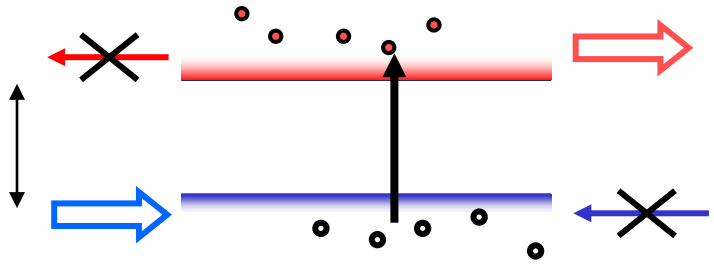
THE ROYAL SOCIETY

Outline

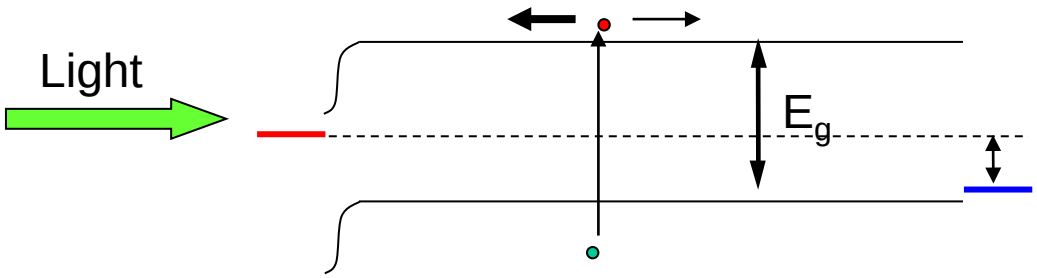
- **Introduction to organic solar cells**
- **Microscopic and macroscopic modelling of organic solar cells**
- **Tools for microscopic modelling**
  - **Case studies of microscopic models of charge transport**
- **Continuum modelling of devices with energetic disorder**
  - **Steady state model**
  - **Tranisent model**
- **Conclusion**

Photovoltaic energy conversion

- Photovoltaic energy conversion requires:
  - photon absorption across an energy gap
  - separation of photogenerated charges
  - asymmetric contacts to an external circuit

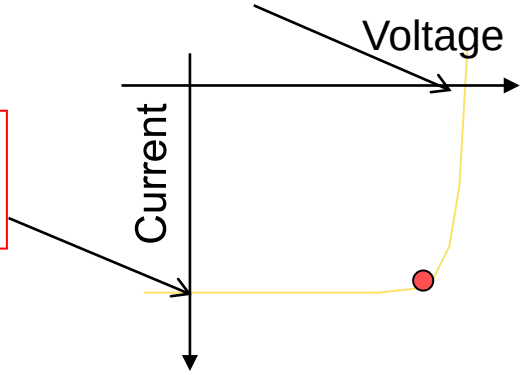


- Usually these functions are achieved with a Si p-n junction

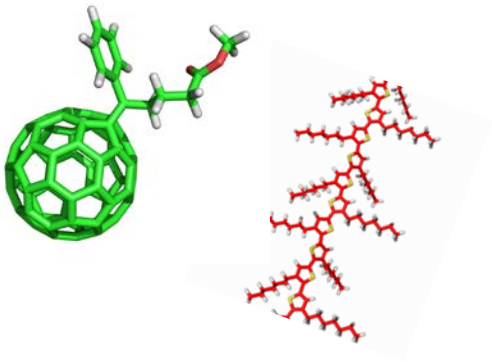


$\Delta E_F = eV_{oc}$

$$e\int_{E_g}^{\infty} b_{inc}(E)Abs(E)dE \geq J_{sc}$$



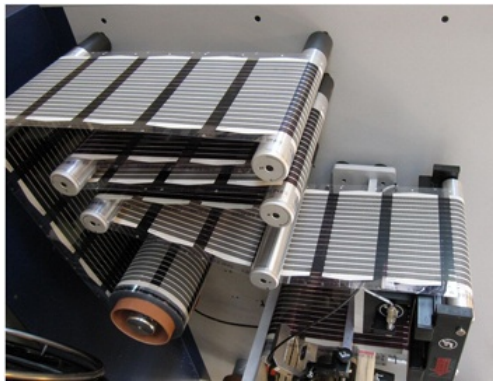
Alternative approach: Organic photovoltaic materials

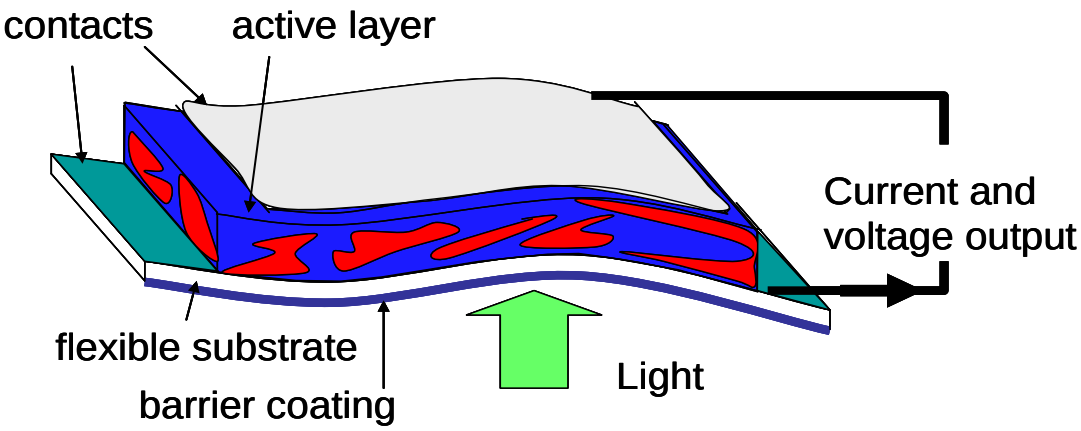


Molecular semiconductors

Solution processable

Manufacture by printing or coating



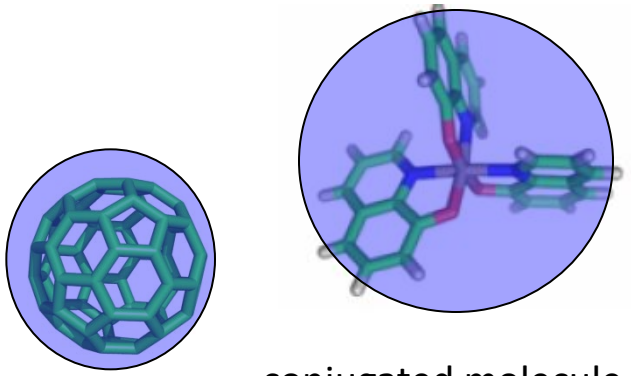


Rapid growth in production capacity possible
Projected cost per W_p << Si PV

Lightweight, flexible solar cell device

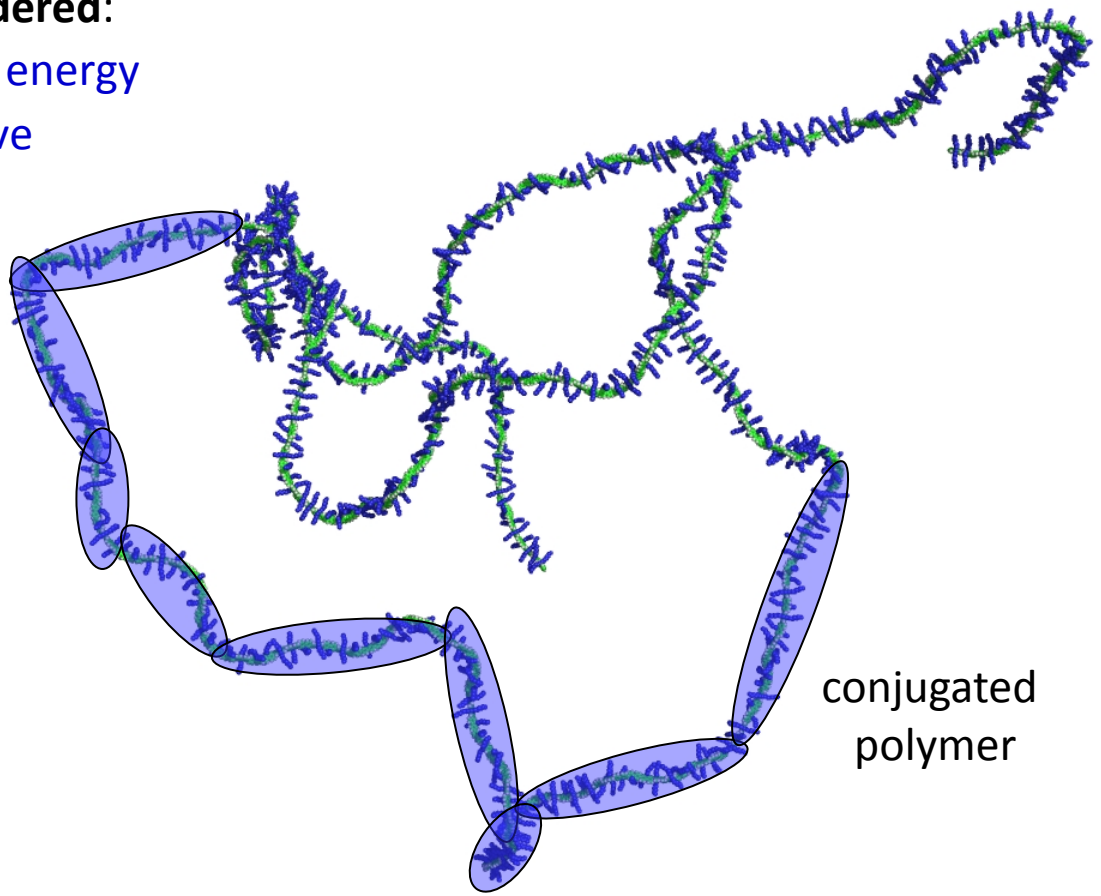
Organic photovoltaic materials

- Electronic states are **localised**:
  - Photo-excited states are localised
  - Charges are localised ⇨ low mobility μ



conjugated molecule

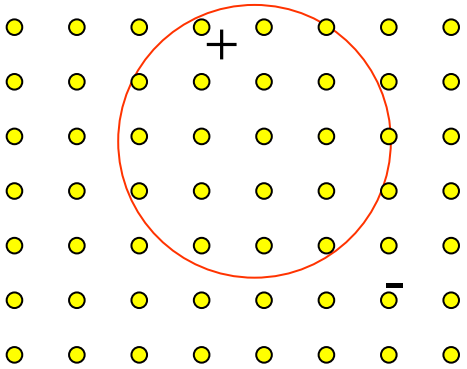
- Electronic states are **disordered**:
  - Charged states vary in energy
  - Dynamics are dispersive



conjugated polymer

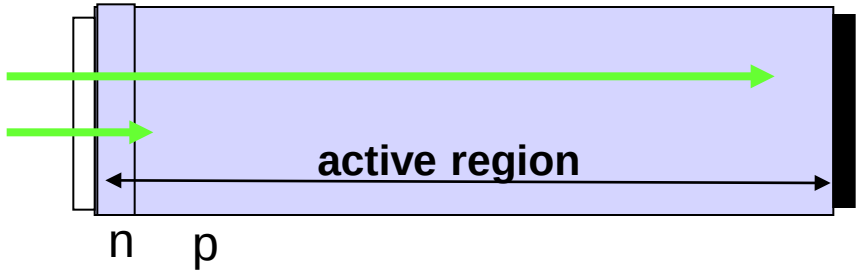
Charge separation in molecular materials

Inorganic semiconductor

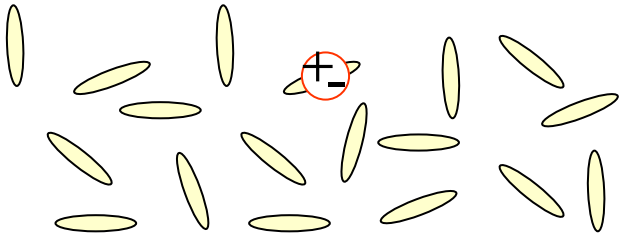


E_B ~ 0.01 eV

Spontaneous charge pair generation



Molecular semiconductor

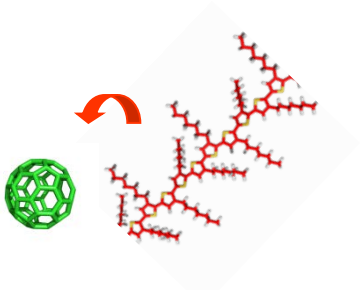


E_B ~ 0. 1- 0.5 eV

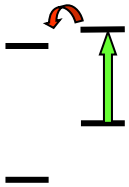
Charges hard to dissociate

Cannot copy inorganic PV device structures!

Donor:acceptor composites for charge separation

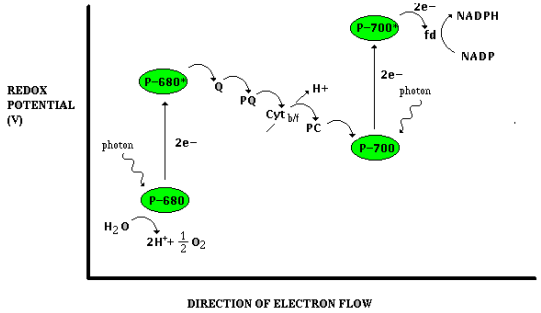


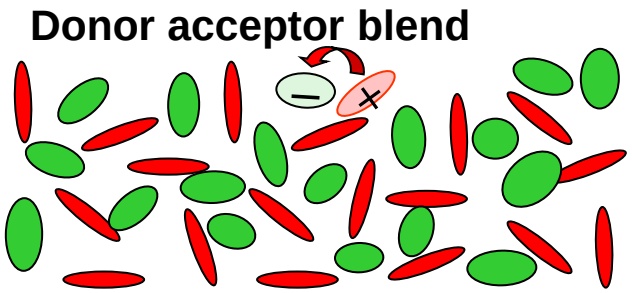
C_{60} Conjugated polymer

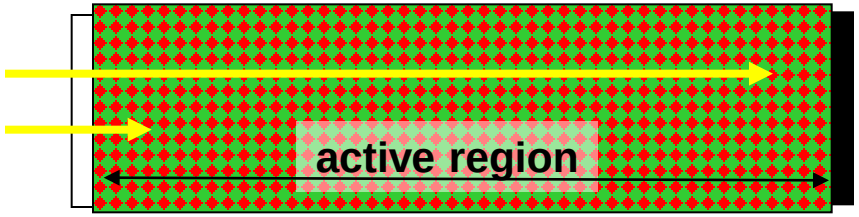


Electron acceptor Electron donor

E_B can be supplied by the energy offset between donor and acceptor molecule

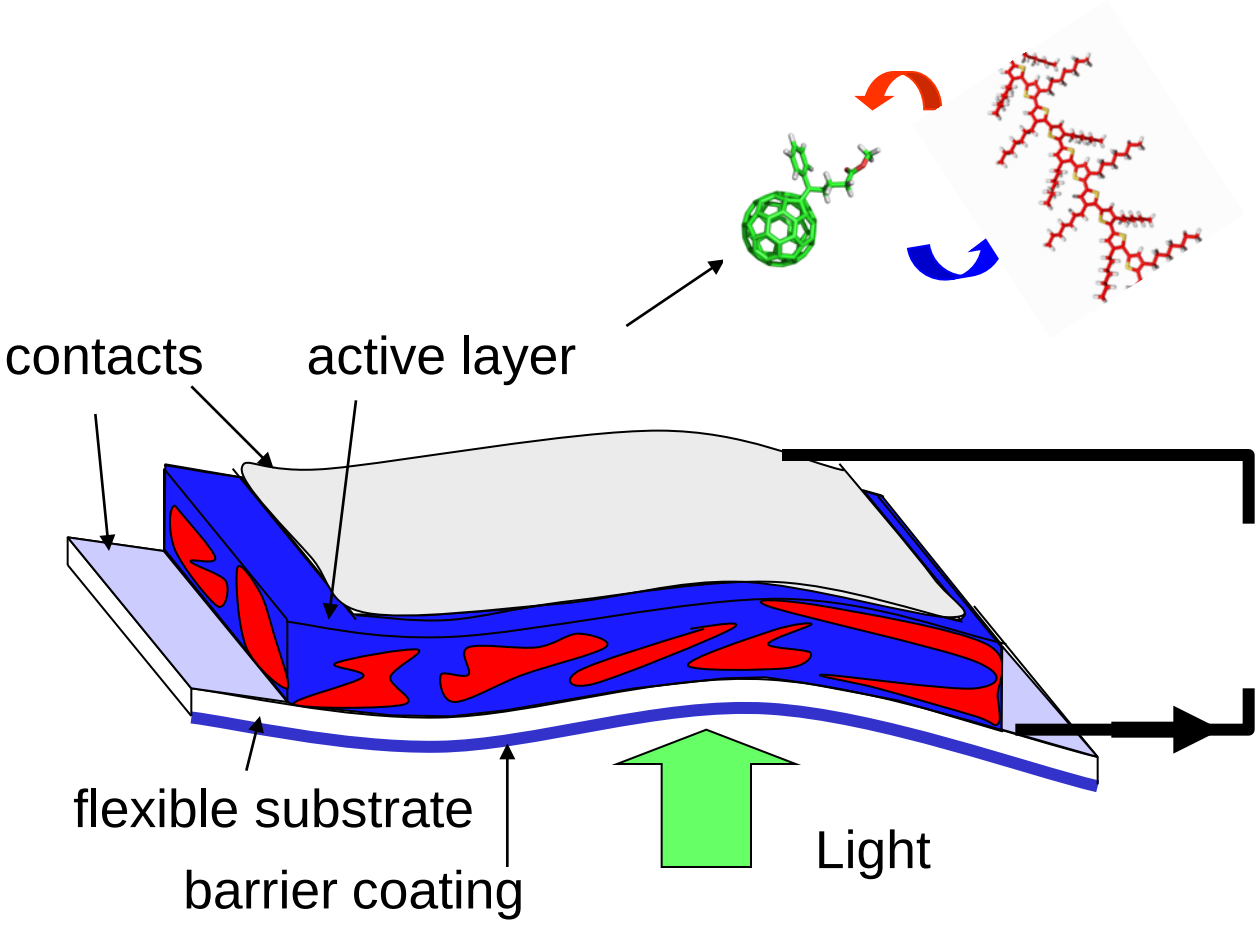






Organic photovoltaic device structure

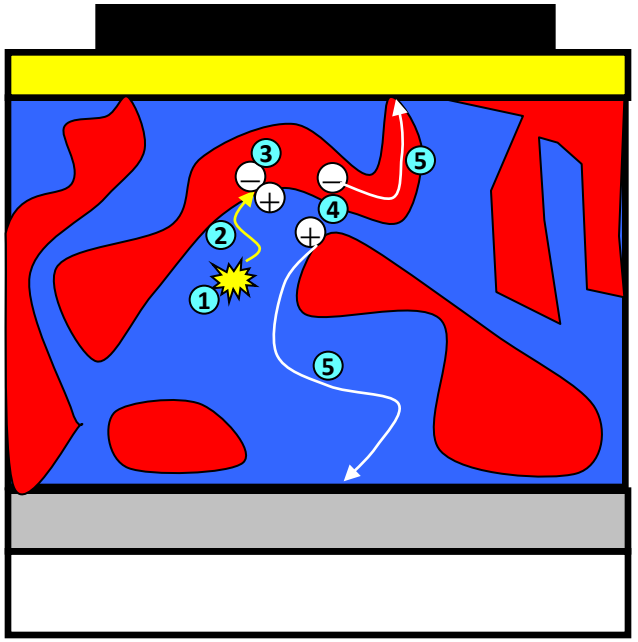
- To separate charges, organic semiconductor is doped with a second semiconductor with strong electron affinity to make a bulk heterojunction



Active layer typically 100s of nm - limited by charge transport

- Active layer and some electrode layers deposited from solution

Key steps in photocurrent generation



1. Photon absorption

2. Exciton diffusion

Exciton decay

3. Exciton dissociation ⇨ geminate charge pair

⇨ Other excited states e.g. triplets

4. Geminate charge pair separation

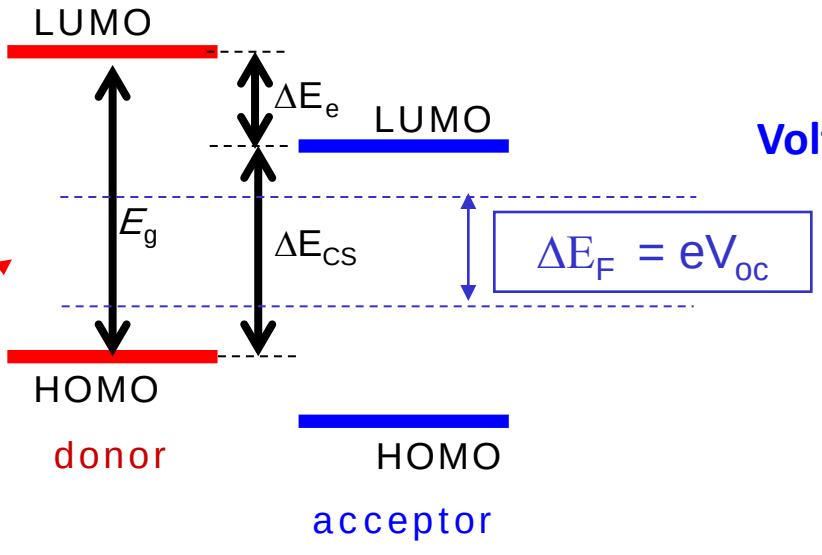
Geminate charge pair recombination

5. Charge transport to contacts

Non-geminate charge pair recombination

Current generation

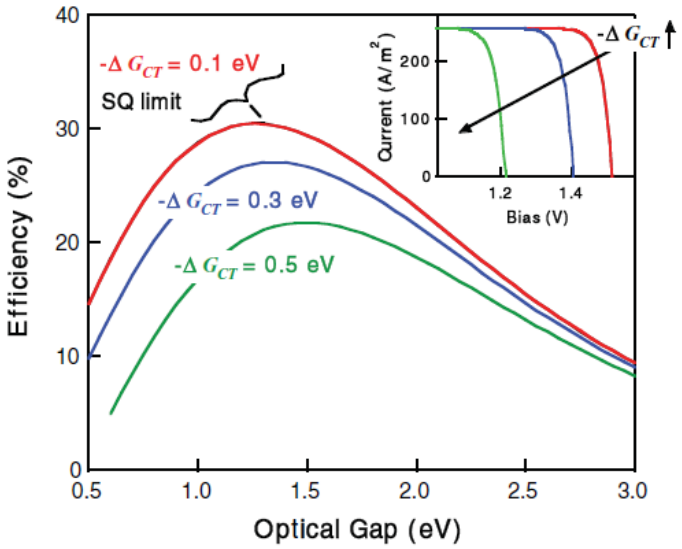
Photovoltaic power conversion efficiency



Voltage determined by electrical gap at heterojunction

$$e\int_{E_g}^{\infty} b_{inc}(E)Abs(E)dE \geq J_{sc}$$

Current determined by lowest optical gap

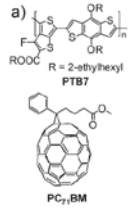


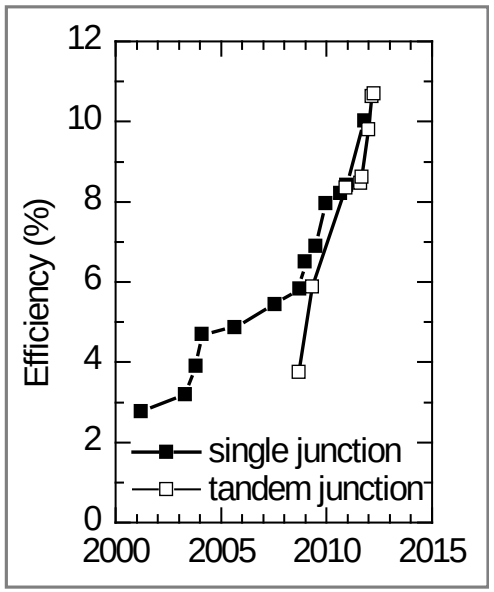
N. Giebike et al. Phys Rev B 83, 195326 (2011)

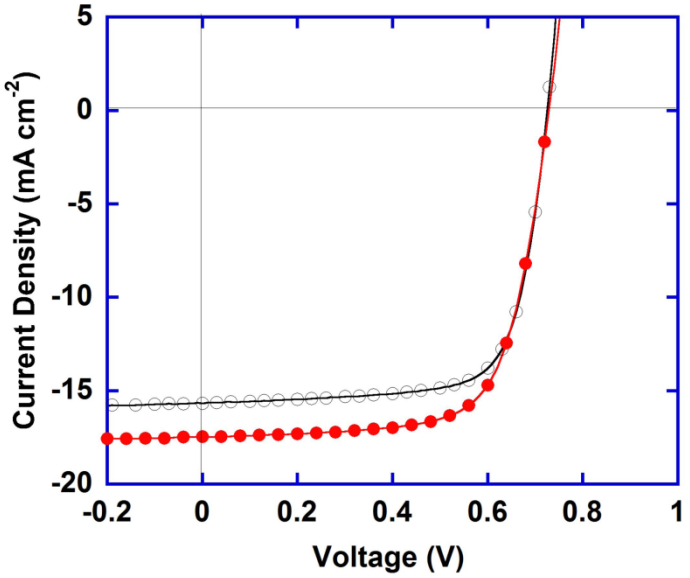
- Energy loss at heterojunction results in lower limiting efficiency and higher optimum E_g than single material limit

State of the Art in Organic Photovoltaics

2001: Efficiency increased from 1 to 2.5%







2012: Efficiency exceeds 10%

8-9% efficient solar cell

There is still room to improve, but many new materials underperform. Simulation methods are needed to relate materials to devices.

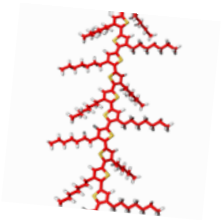
Figure: courtesy Rene Janssen, 2012

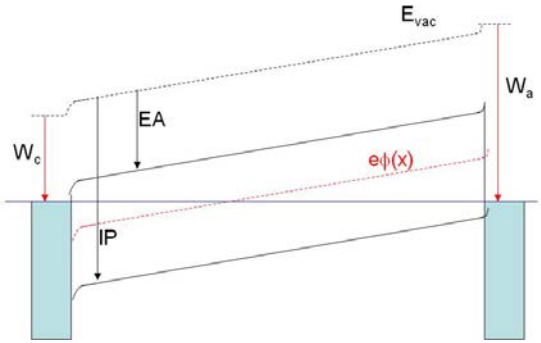
Outline

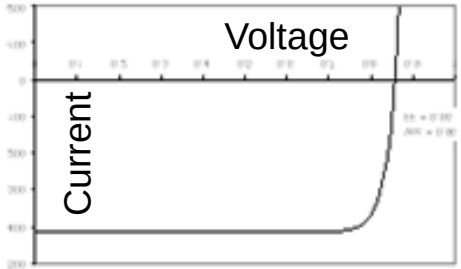
- Introduction to organic solar cells
- **Microscopic and macroscopic modelling of organic solar cells**
- Tools for microscopic modelling
  - Case studies of microscopic models of charge transport
- Continuum modelling of devices with energetic disorder
  - Steady state model
  - Tranisent model
- Conclusion

What we expect from solar cell models

Molecular semiconductors

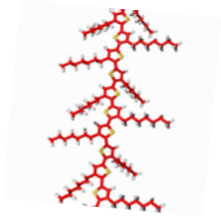




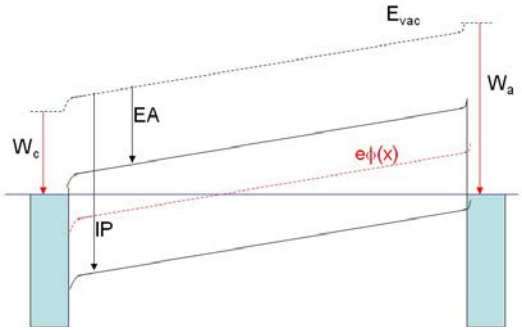


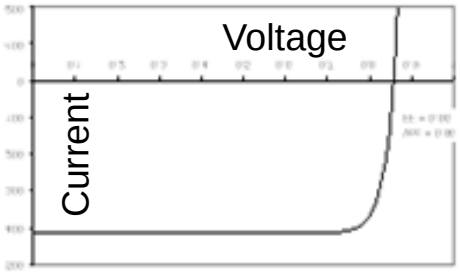
This problem is too difficult.
Part of the problem is disorder in molecular materials.

What we can actually do (sometimes)



→ μ, D, α, k, ..



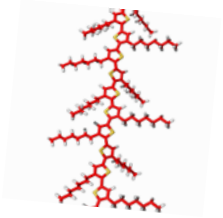


Microscopic simulation

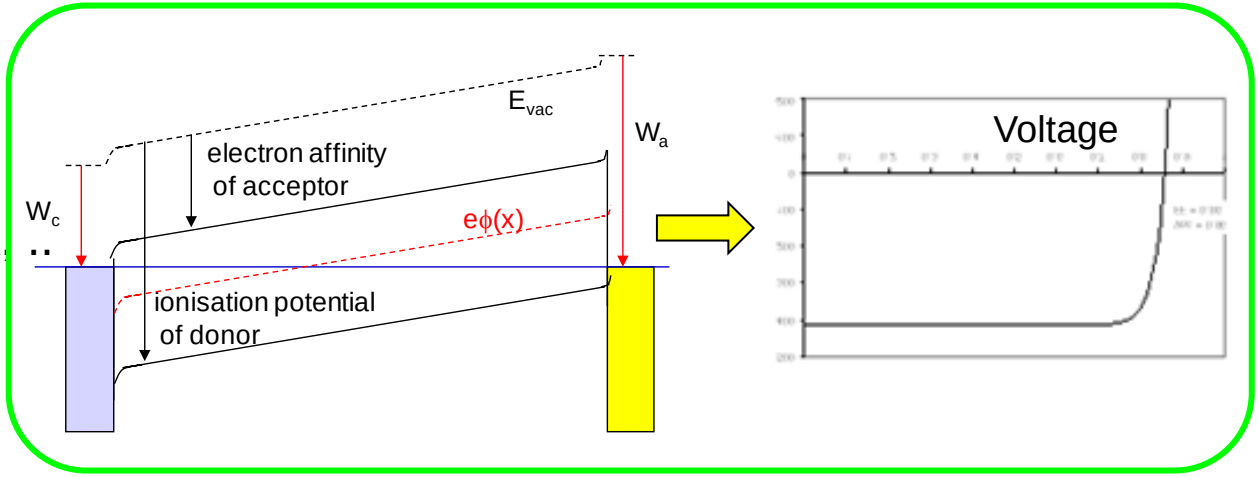
- Quantum chemistry + molecular modelling ⇨ electronic structure
- + kinetic Monte Carlo ⇨ electron dynamics

- BUT:
  - Computationally intensive: limited to 1 – 10 nm
  - Microstructure hard to validate
  - Interfacial processes poorly understood

What we can actually do (sometimes)



μ, D, α, k, ..



$$-\frac{1}{e}\nabla \cdot \mathbf{J}_n = G - R$$

Macroscopic simulation

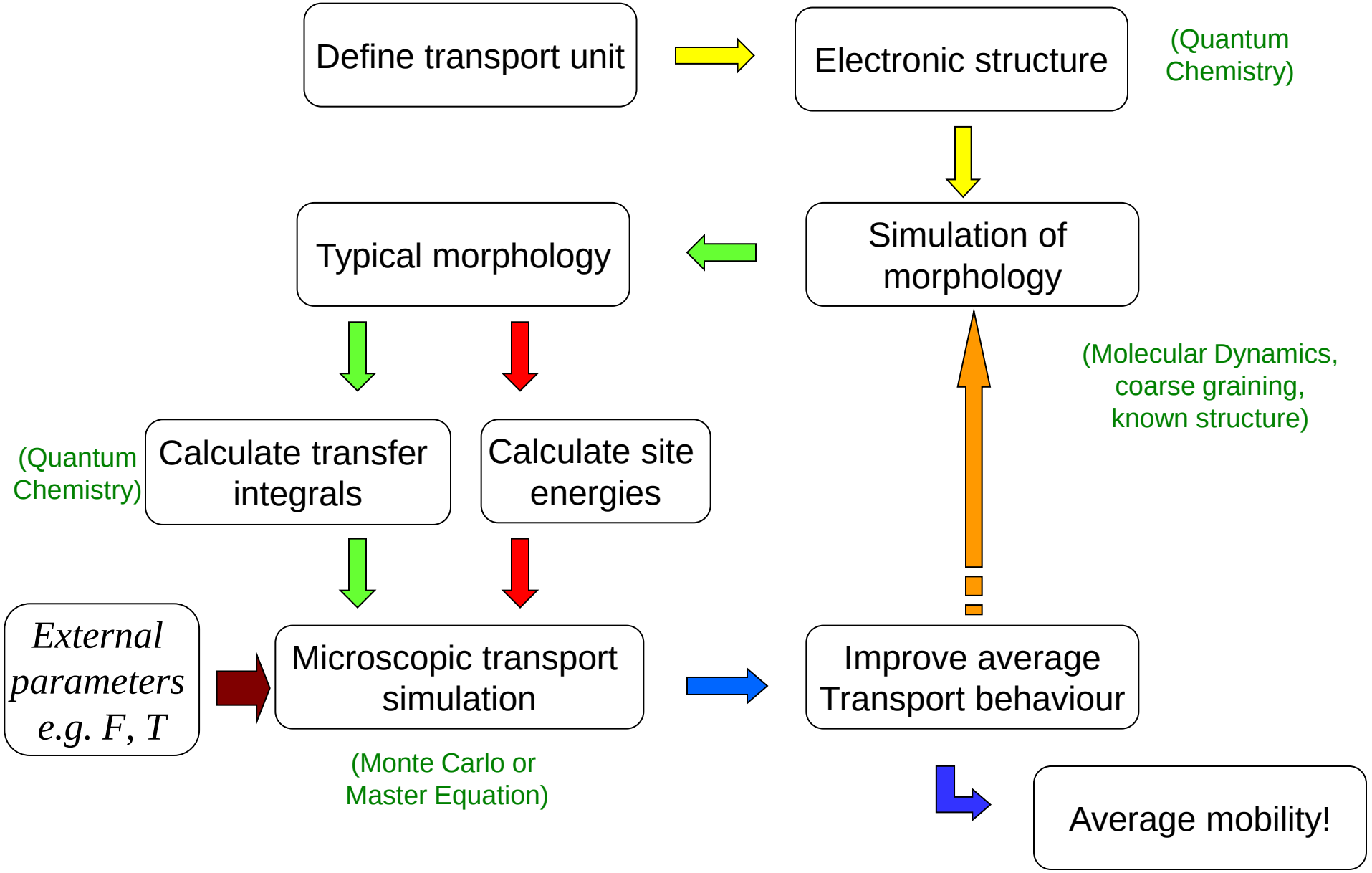
- **D(n), μ(n), n(V)** Energetic disorder
- **G ≠ absorption** Energetic driving force, delocalisation
- **R = k(n) n p** Energetic disorder, phase segregation

- BUT
  - **Terms in DEs not well known,**
  - **Not predictive, not structure specific**

Outline

- Introduction to organic solar cells
- Microscopic and macroscopic modelling of organic solar cells
- Tools for microscopic modelling
  - Case studies of microscopic models of charge transport
- Continuum modelling of devices with energetic disorder
  - Steady state model
  - Tranisent model
- Conclusion

Tools for multi-scale modelling of charge transport

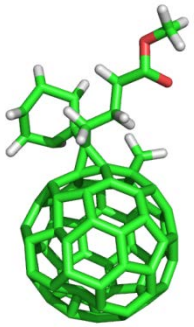


Tools for multi-scale modelling

Define transport unit

Electronic structure

(Quantum Chemistry)



(UFF, AM1, DFT)

HOMO: Highest Occupied Kohn Sham Energy Level (well defined)

LUMO: HOMO+TD-DFT(1st Singlet): TD-DFT 'spectroscopic' calculation

imulation of morphology

(Molecular Dynamics coarse graining, known structure)

(Quantum Chemistry)

Calculate transfer integrals

Calculate site energies

External parameters e.g. F, T

Microscopic transport simulation

(Monte Carlo or Master Equation)

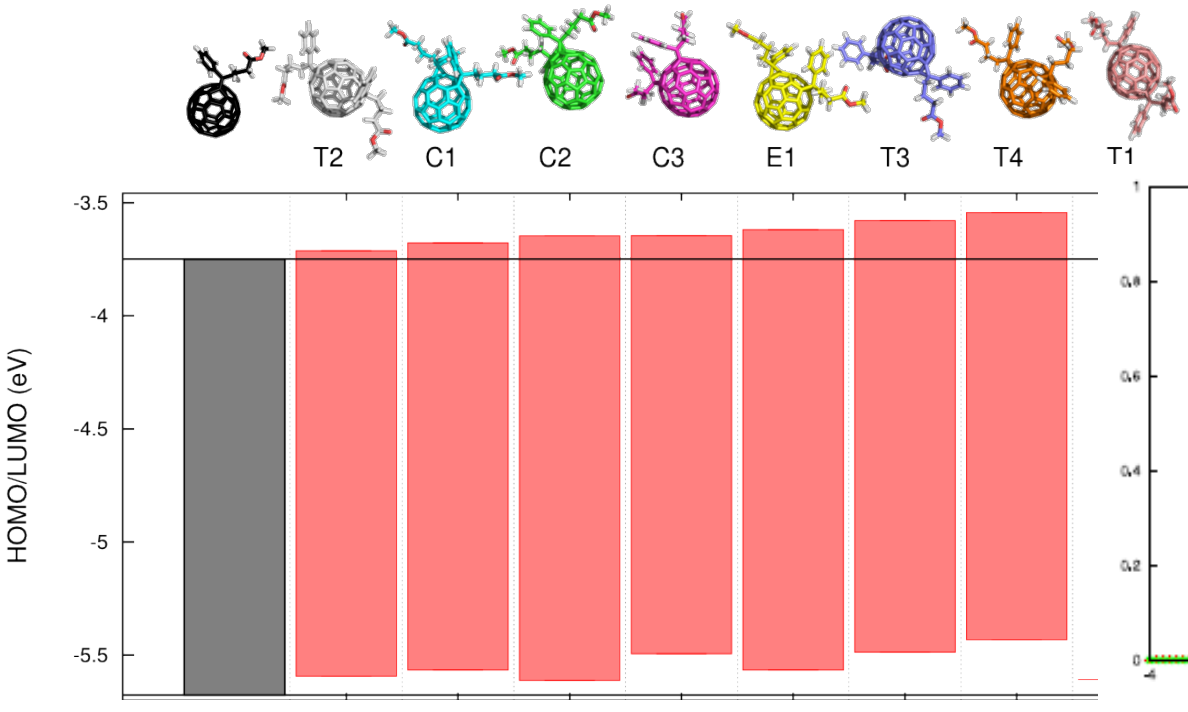
Improve average Transport behaviour

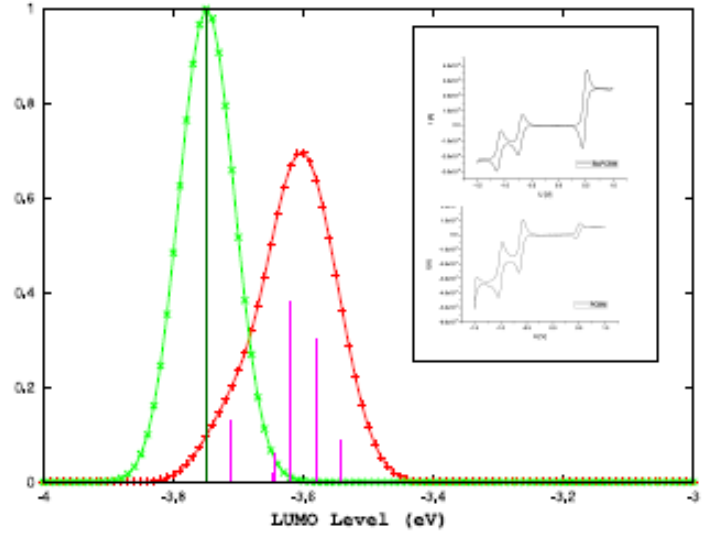
Average mobility!

Jarvist Frost et al., Adv. Matr. (2010)

Calculations of excited states and energies

- Excited states calculated using DFT with B3lyp 6-31g* plus TDDFT singlet at same level. Find energies and oscillator strengths.
- Validate excited state calculations against absorption or electrochemical spectra



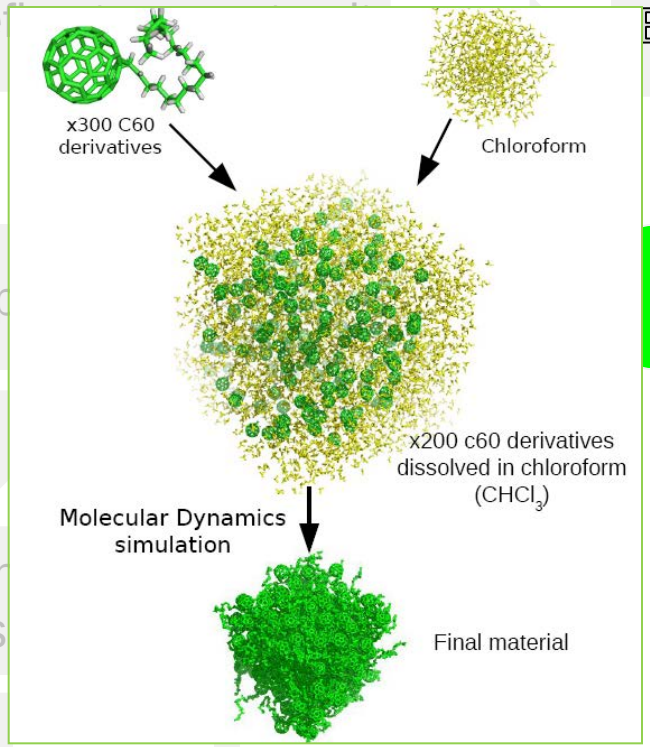


- Use excited state calculations in molecular design

Jarvist Frost

Tools for multi-scale modelling

R. MacKenzieet al., J. Chem. Phys 132, 064904 (2010)



Electronic structure

(Quantum Chemistry)

Simulation of morphology

(Molecular Dynamics, coarse graining, known structure)

Calculate tran… integrals

…uantum …emistry)

External parameters e.g. F, T

Microscopic transport simulation

(Monte Carlo or Master Equation)

Improve average Transport behaviour

Average mobility!

Tools for multi-scale modelling

Define transport unit

Electronic structure

(Quantum Chemistry)

Simulation of morphology

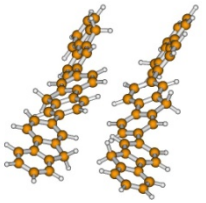
Typical morphology

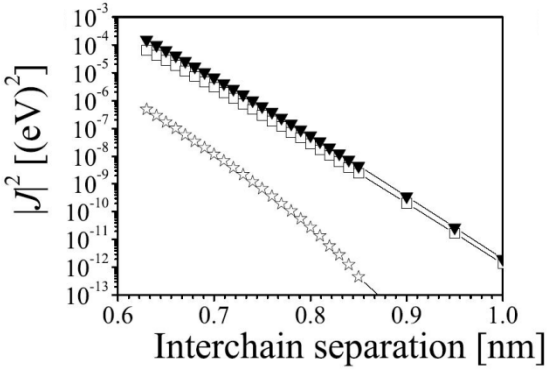
Molecular Dynamics, coarse graining, known structure)

(Quantum Chemistry)

Calculate transfer integrals

$$\Gamma_{ij} = \frac{\left|J_{ij}\right|^2}{\hbar}\sqrt{\frac{\pi}{\lambda kT}}\exp\left(-\frac{\left(E_i - E_j - \lambda\right)^2}{4\lambda kT}\right)$$





External parameters e.g. F, T

Microscopic simulat

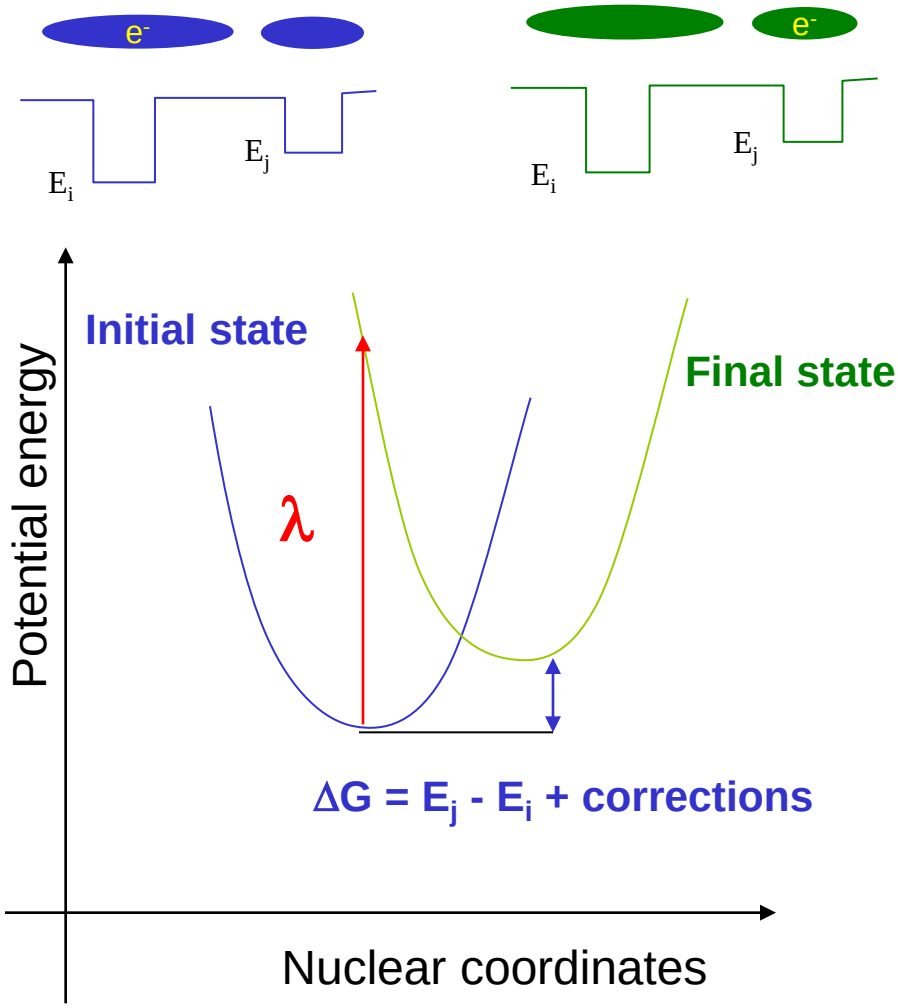
(Monte Carlo or Master Equation)

our

Average mobility!

J. Nelson et al. Acc. Chem. Res. 42, 1768 (2009)

Intermolecular charge transfer



Charge transfer reaction:

$M_i^- + M_j \rightarrow M_i + M_j^-$

Charge transfer rate from non-adiabatic Marcus theory:

$$\Gamma_{ij} = \frac{|J_{ij}|^2}{\hbar}\sqrt{\frac{\pi}{\lambda kT}}\exp\left(-\frac{(E_i - E_j - \lambda)^2}{4\lambda kT}\right)$$

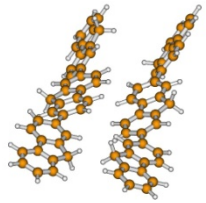
Electronic coupling $J = \langle \psi_i | H_e | \psi_j \rangle$

Site energies E_i, E_j

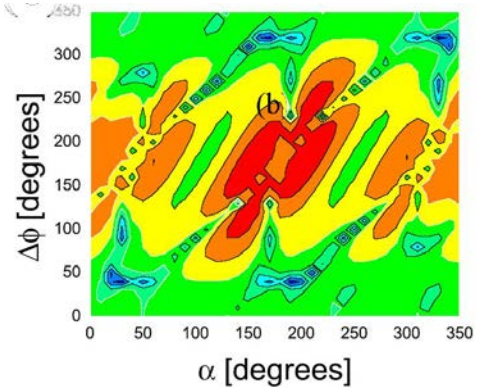
Reorganisation energy λ

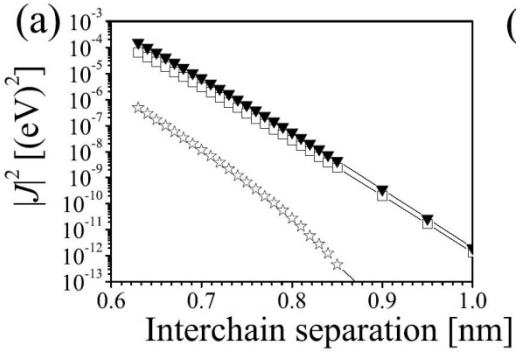
e.g.: V. Corpoceanu et al., Chem. Rev. **2007,** 107, 926-952

Calculation of rate parameters



- J_{ij} depends on
  - chemical structure
  - separation $|J| \sim \exp(-r/r_0)$
  - orientation



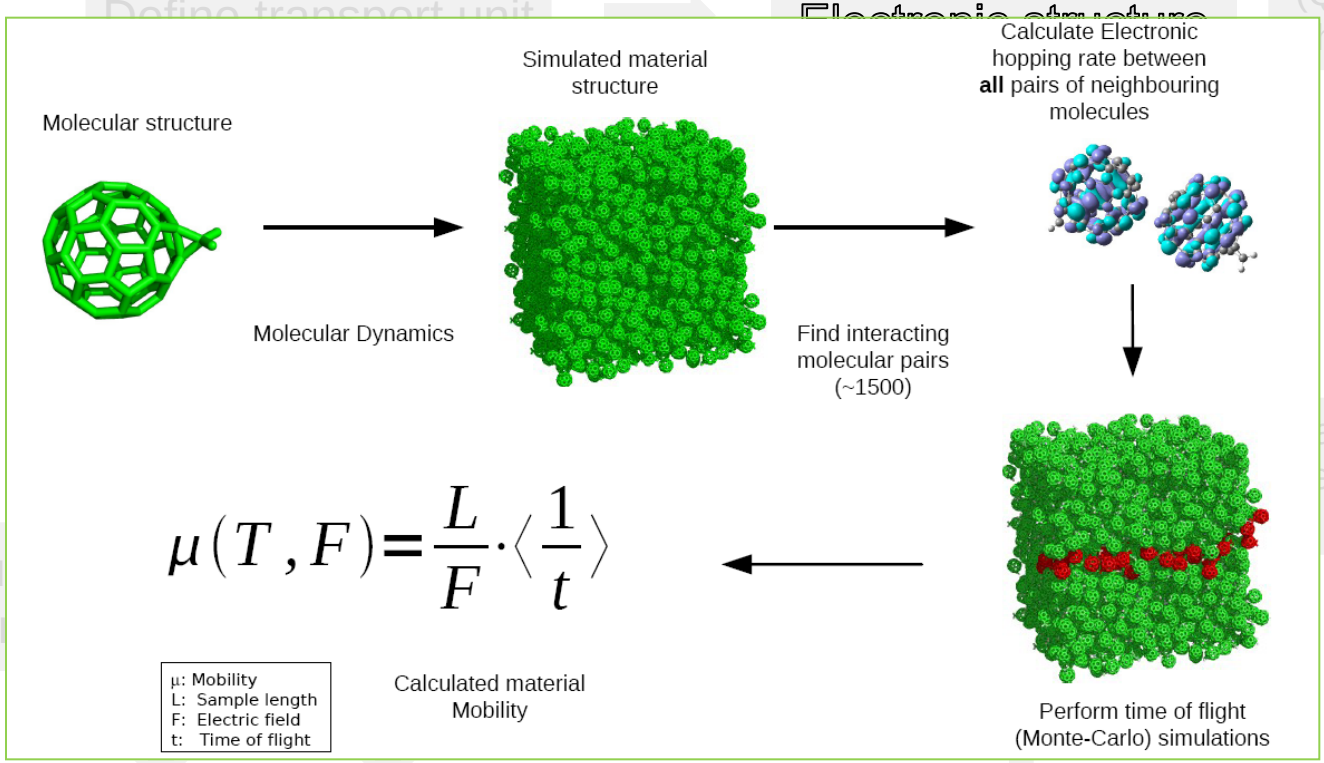


- λ depends on
  - chemical structure
  - dielectric environment

- Site energies depend on
  - chemical structure
  - conformation
  - intermolecular interactions
  - external applied fields

Charge transfer dynamics are extremely sensitive to molecular packing!

Tools for multi-scale modelling



External parameters e.g. F, T

Microscopic transport simulation

(Monte Carlo or Master Equation)

Improve average Transport behaviour

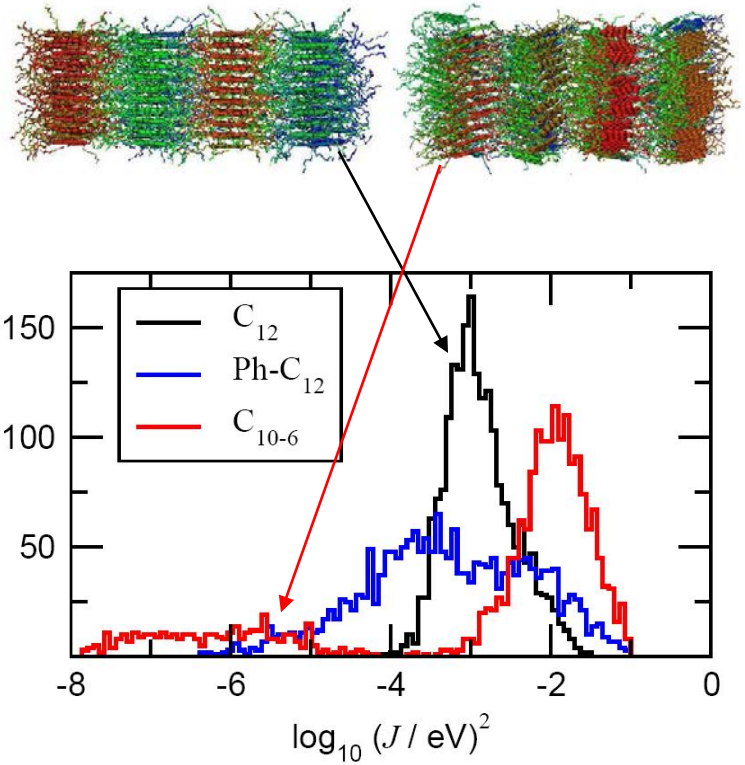
Average mobility!

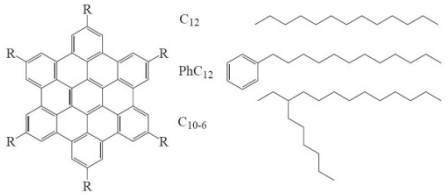
J. Nelson et al. Acc. Chem. Res. 42, 1768 (2009)

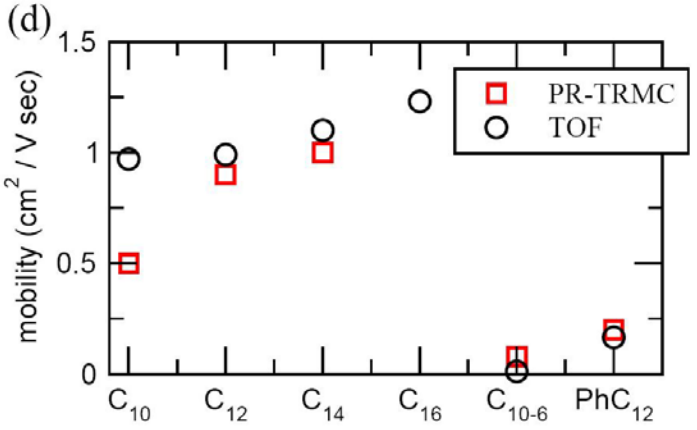
Outline

- Introduction to organic solar cells
- Microscopic and macroscopic modelling of organic solar cells
- Tools for microscopic modelling
  - **Case studies of microscopic models of charge transport**
- Continuum modelling of devices with energetic disorder
  - Steady state model
  - Tranisent model
- Conclusion

Case study: Discotic phases of HBC





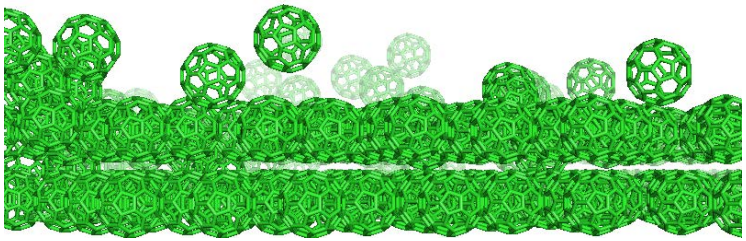


- Branched side chains ⇨
  - more stacking disorder than linear side chains
  - higher probability of very low transfer integral
  - lower mobilities
- Simulations reproduce experimental mobilities with no fitting parameters

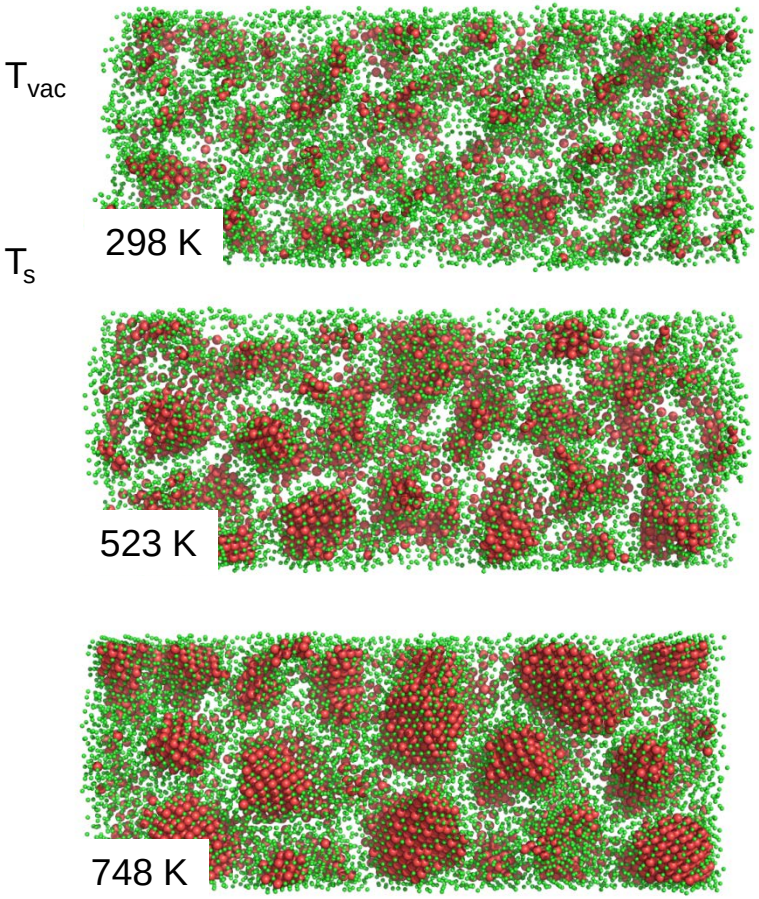
J. Kirkpatrick et al. Phys. Rev. Lett. 98, 227402 (2007)

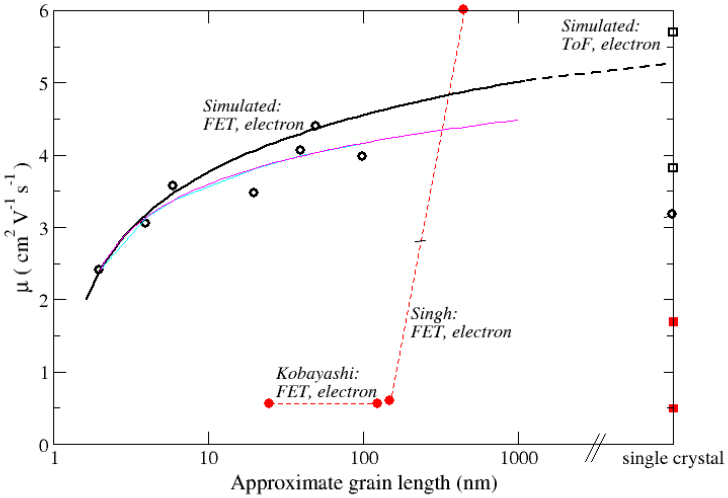
Case study: effect of C60 grain size on mobility

- How does C60 grain size influence FET electron mobilities ?



Model of vacuum deposition. Isotropic force field. T_s determines rate of diffusion hence crystal size.



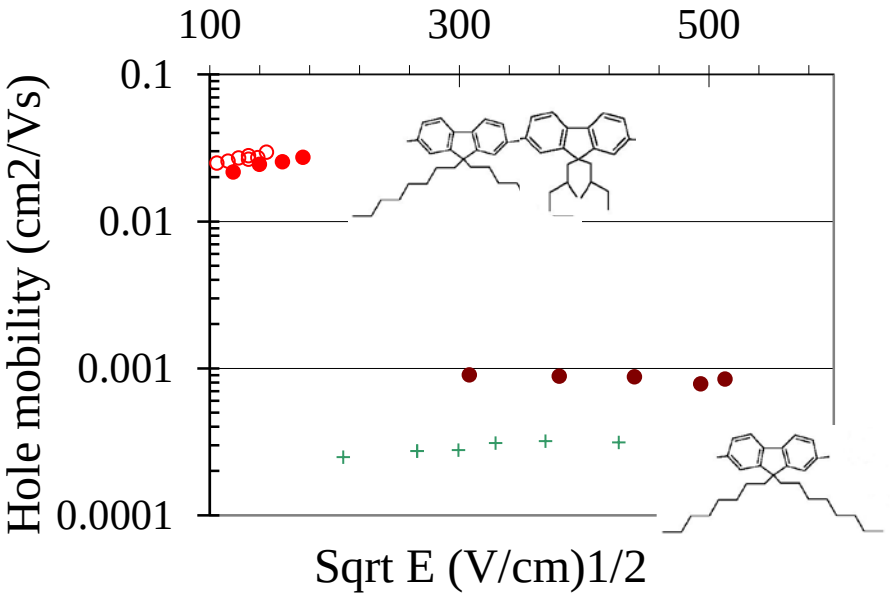


- Simulations explain weak dependence of FET mobility on grain size

J J Kwaitkowski et al., Nano Letters 9, 1085 (2009)

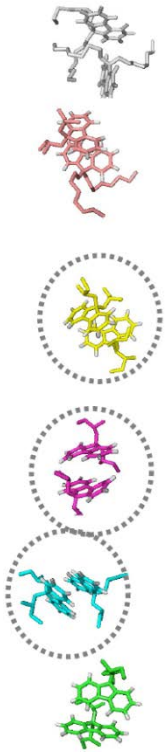
Case Study: charge transport in fluorene polymers

- Why is hole transport in polyfluorenes so sensitive to side chain type?



Yap et al. Nat. Mater. 7, 376 (2008)

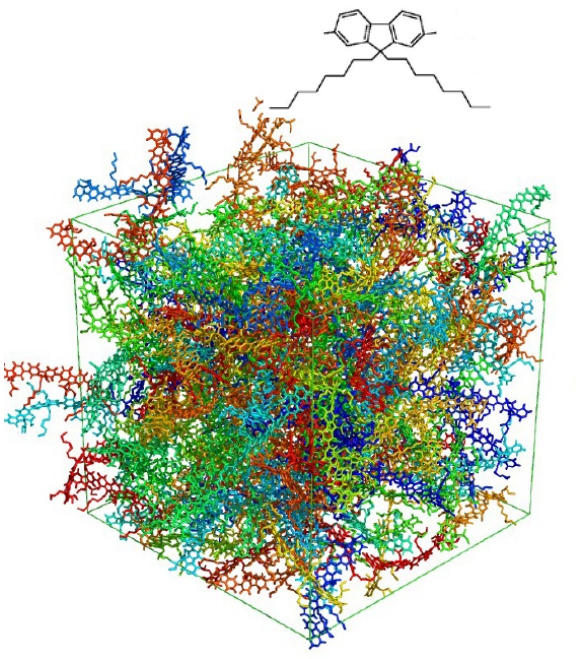
Do short chains lead to hopping hot spots?



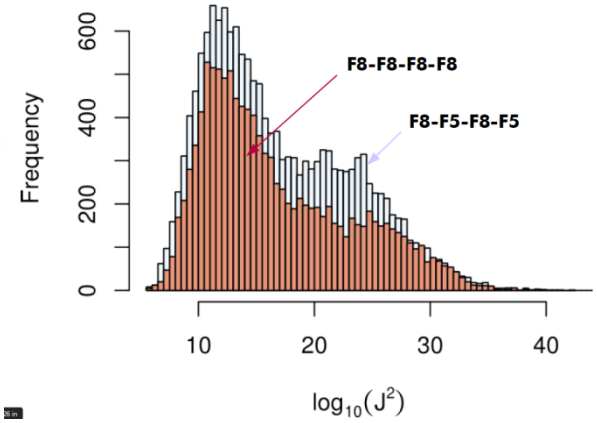
- Simulate packing of fluorene oligomers (tetramers) with different side chain
- Fix relaxed tetramers into positions found by MD.
- Calculate transfer integrals between neighbours

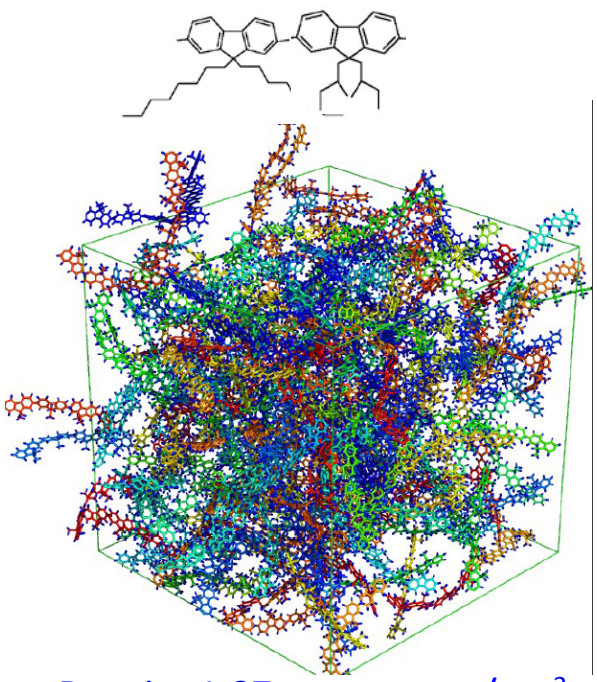
Case Study: charge transport in fluorene polymers

J. M. Frost PhD Thesis, 2011



Density 1.66 monomers /nm^3





Density 1.87 monomers /nm^3

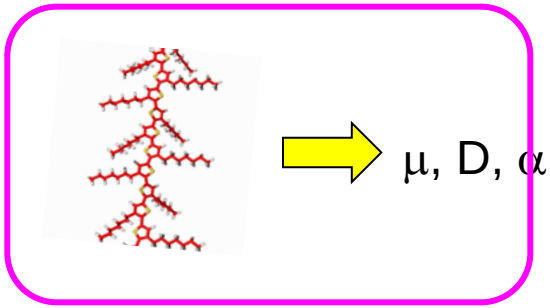
- Simulate charge transport by hopping between tetramers:

Mobility 0.98 cm^2/Vs

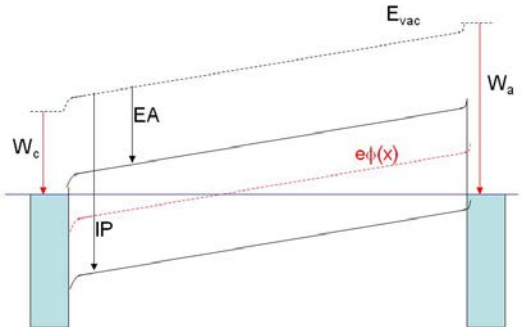
Mobility 1.35 cm^2/Vs

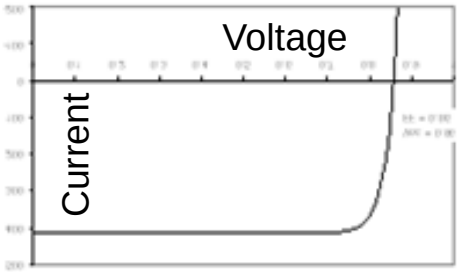
- Mobility is increased for short side chains but not enough
- Packing disorder cannot explain the results
- Currently including disorder in energies of states considering conformational defects

Conclusions from microscopic simulation



μ, D, α, k, ..



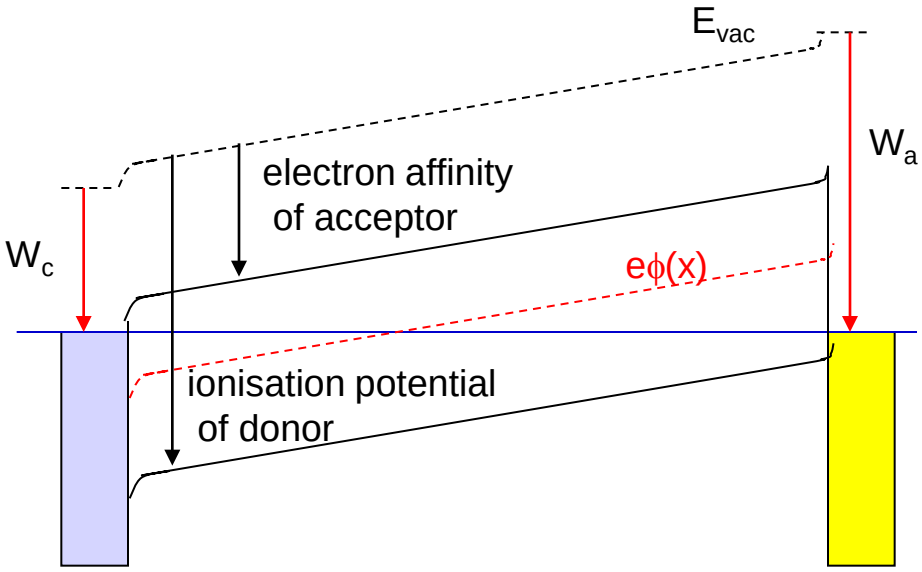


- Have tools to calculate energies and positions of molecules and molecular segments
- Have tools to calculate charge (and exciton) dynamics
- Can rationalise charge mobility for different materials
- Can calculate a density of states
- Problem is in validating the structure simulated

Outline

- Introduction to organic solar cells
- Microscopic and macroscopic modelling of organic solar cells
- Tools for microscopic modelling
  - Case studies of microscopic models of charge transport
- **Continuum modelling of devices with energetic disorder**
  - Steady state model
  - Tranisent model
- Conclusion

One-dimensional model of OPV device



- Active layer is an effective semiconductor medium with conduction band energy at LUMO of acceptor and valence band at HOMO of donor
- Charge dynamics and electrostatics within active layer described by coupled partial differential equations
- Semiconductor – electrode interface described by boundary conditions

One-dimensional model of OPV device

$$j_n(x) = -D_n \frac{dn}{dx} - F\mu_n n \qquad j_p(x) = -D_p \frac{dp}{dx} + F\mu_p n \qquad \frac{dF}{dx} = \frac{e\rho(x)}{\varepsilon\varepsilon_0}$$

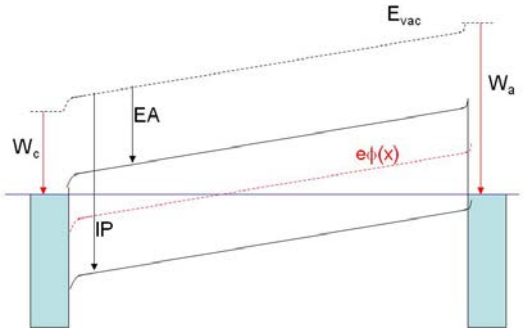
$$\frac{dj_n}{dx} = G(x) - knp \qquad \frac{dj_p}{dx} = G(x) - knp \qquad \frac{d\phi}{dx} = F$$

- In steady state, three coupled second order differential equations describing
  - electron and hole density, electron and hole current, electric potential
- Boundary conditions describe terminal potential difference, and electron and hole flux at boundaries
- Straightforward to solve for semiconductors with linear coefficients
- **In organic semiconductors, k, D and μ are not constants**

Koster et al., Phys.Rev.B 72, 085205 (2006); Lacic et al., J. Appl. Phys. 97, 124901 (2005); Nelson Phys. Rev B 69, 155209 (2003)

Modelling effect of energetic disorder : Steady state

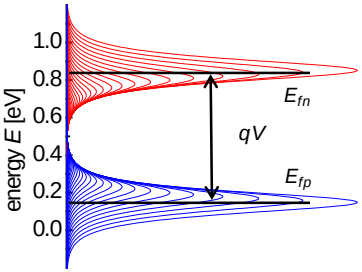
$$-\frac{1}{e}\nabla \cdot \mathbf{J}_n = G - R$$



$\mu(n), D(n)$

$R = k(n, p)np$

Use concept of mobility edge



Mobility: $\mu = \mu_0 \frac{n_{free}}{n} \propto n^{\beta}$

For exponential DoS:

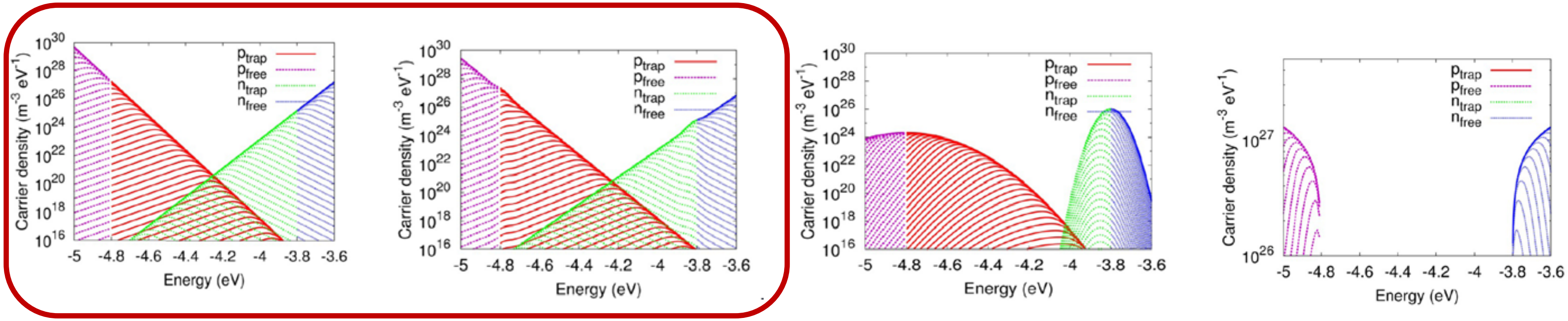
Use modified Langevin Recombination

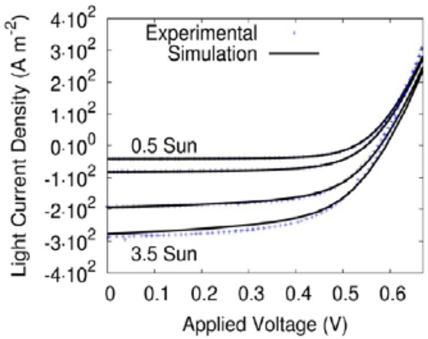
$R \approx k(n)n^2$

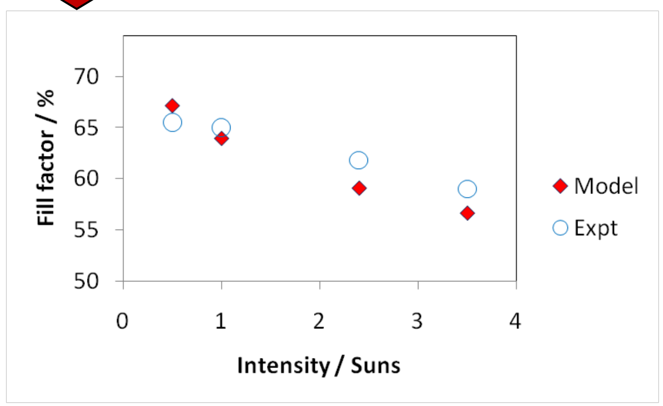
Power law form for exponential DoS

- **Include carrier density dependent mobilities and recombination rate in device model**
- **Can use general form for densities of states**

Including energetic disorder in device simulation





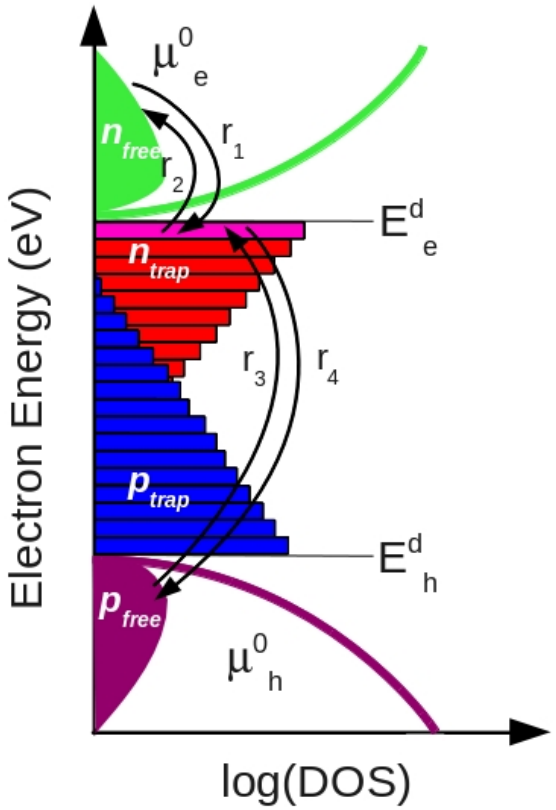


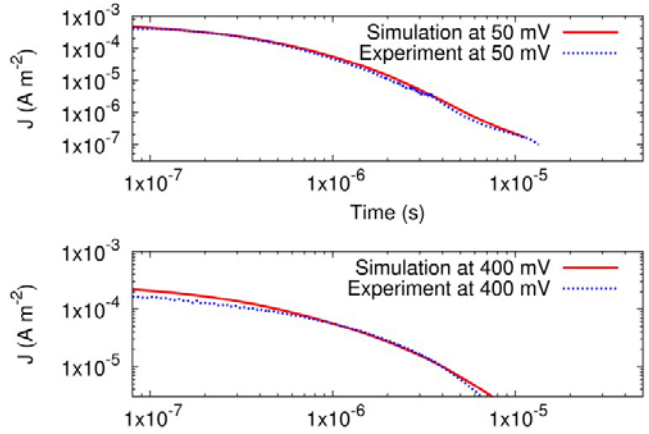
- Comparison of several classes of density of states.
- An exponential tail of states is necessary to reproduce both
  - bimolecular recombination coefficient
  - intensity dependent device J-V

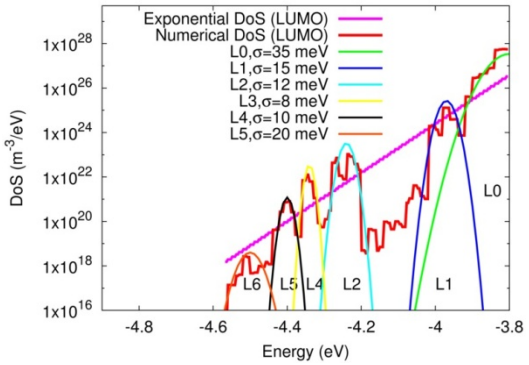
Rod MacKenzie et. al. J. Phys. Chem A (2011)

Determining the shape of the energetic density of states

- How to determine DoS more precisely? Large amplitude transient measurements.
- Discretise the tails and include trapping, detrapping and recombination from each
- Fit several photocurrent transients and device J(V) simultaneously







Extract best DoS as exponential fit or free form fit.
But, many parameters and hard to validate.

Roderick MacKenzie et. Adv. Energy Mater. 10.1002/aenm.201100709 (2012)

Summary and Conclusions

- Simulation of organic solar cells is complicated by disorder and poorly understood mechanisms
- Charge dynamics in organic semiconductors can be modelled by a three level process (MD, Quantum chemistry and kinetic MC)
- In simple cases microscopic models can explain experimental trends in mobility
- Energetic disorder arises from variations in chemical structure and molecular packing, and influences the response of solar cells
- When included in device model, energetic disorder explains trends in device response.
- First step on the way to predictive device simulation!