Charge separation in molecular donor – acceptor heterojunctions

Jenny Nelson, James Kirkpatrick, Jarvist Frost, Panagiotis Keivanidis, Clare Dyer-Smith, Jessica Benson-Smith
Department of Physics, Imperial College London

James Durrant, Tracey Clarke
Department of Chemistry, Imperial College London
Molecular photovoltaic materials

- Easily processable e.g. from solution
- Abundant, non-toxic materials
- Tune properties via chemical design
- Excited states are localised: limited charge and exciton mobility

Konarka Technologies
Device structures

Inorganic semiconductor

EB ~ 0.01 eV
Spontaneous charge pair generation

Molecular semiconductor

EB ~ 0.1 - 0.5 eV
Charges hard to dissociate

Cannot copy inorganic PV device structures!
Donor-acceptor solar energy converters

\[ \text{C}_{60} \quad \text{Conjugated polymer} \]

Electron acceptor  Electron donor

REDOX POTENTIAL (V)

PHOTOHETEROTROPHY

\[ \text{H}_2\text{O} \rightarrow 2\text{H}^+ + \frac{1}{2} \text{O}_2 \]

\[ \text{P-680} \rightarrow \text{P-700} \]

\[ \text{Q} \rightarrow \text{PQ} \]

\[ \text{Cyt b6} \rightarrow \text{PC} \]

\[ \text{NADPH} \rightarrow \text{NADP} \]

DIRECTION OF ELECTRON FLOW
Device structures

- Donor-acceptor bulk heterojunction devices
  - Active layer can be 100s of nm - limited by charge diffusion length
  - Domain size ca. 10 nm. ~ exciton diffusion length

- Both components deposited from same solution
  - Al cathode
  - Donor-Acceptor blend
  - ITO anode
  - Glass substrate

© Imperial College London
Device structures

- Donor-acceptor bulk heterojunction devices

Al cathode

Donor-Acceptor blend

ITO anode

Glass substrate

- Both components deposited from same solution
Key steps in photocurrent generation

1. Photon absorption

2. Exciton diffusion

3. Exciton dissociation $\Rightarrow$ geminate charge pair

$\Rightarrow$ Other excited states e.g. triplets

4. Geminate charge pair separation

Geminate charge pair recombination

5. Charge transport to contacts

Current generation

Non-geminate charge pair recombination
Key challenges

\[ \Delta E_F = eV_{oc} \]

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

\[ \eta = 5\% \]

\[ \eta = 24\% \]
Key challenges

- **LUMO**
- **HOMO**
- **ΔE<sub>e</sub>**
- **ΔE<sub>cs</sub>**
- **ΔE<sub>F</sub> = eV<sub>oc</sub>**

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

**Band Gap [ eV ]**

**LUMO Level Donor [ eV ]**

**Lower donor HOMO level**

**Reduce optical gap**
Reducing the donor optical gap: an example

- Disappointing performance of low gap selenophene polymer related to low efficiency of charge pair generation:

Outline

- Molecular photovoltaic devices
- Process of charge separation
- Factors that influence charge separation
  - competing excited states
  - driving force
  - chemical structure
  - microstructure
- Modelling the process
  - excited states and energies
  - how charge separation can occur
  - escape from bimolecular recombination
  - dynamics of charge separation
Outline

- Molecular photovoltaic devices

- Process of charge separation

- Factors that influence charge separation
  - competing excited states
  - driving force
  - chemical structure
  - microstructure

- Modelling the process
  - excited states and energies
  - how charge separation can occur
  - escape from bimolecular recombination
  - dynamics of charge separation
Process of charge pair generation

\[ \Gamma = \frac{|\mathcal{H}|^2}{\hbar} \sqrt{\frac{\pi}{2kT}} \exp\left[ -\frac{\Delta E + \lambda}{2kT} \right] \]
Measurement of charge generation

Transient optical spectroscopy

pump pulse

Probe light

t

Sample

Detector

ΔO.D (λ, t)

Wavelength (nm)

Relative ΔOD

Time / s

ΔAbsorbance (10⁻³)

Nature of photoexcited state

yield

lifetime
Time scales of events

- Revolution period of the electron in Bohr's model
- Vibrational relaxation of an electronically excited state
- Photo-induced electron transfer reaction
- Fluorescence lifetime
- Geminate (monomolecular) charge recombination
- Energy migration in a polymeric matrix, eg in poly(fluorene)
- Phosphorescence lifetime
- Non geminate (bimolecular) charge recombination
- Charge carrier extraction from an organic PV device
- Molecular (segmental) motion in a polymer matrix

ns – ms TAS

ultrafast fluorescence

not accessible
Outline

- Molecular photovoltaic devices
- Process of charge separation
- Factors that influence charge separation
  - competing excited states
  - driving force
  - chemical structure
  - microstructure
- Modelling the process
  - energies of excited states
  - charge transfer excited states
  - means of charge separation
  - dynamics of charge separation
Influence of $\Delta E_{CS}$ on charge separation

$\Delta E_{CS}$

- 1.5 eV
- 1.6 eV
- 2.1 eV
- 2.2 eV
Influence of $\Delta E_{CS}$ on charge separation

Small $\Delta E_{CS}$ leads to photocurrent generation

Large $\Delta E_{CS}$ leads to appearance of transient PCBM triplet spectrum, small $\Delta E_{CS}$ leads to polarons.
Influence of $\Delta E_{cs}$ on charge separation

$J_{sc} = 0.006 \text{mA/cm}^2$, PCBM triplet

$J_{sc} = 0.7 \text{mA/cm}^2$, no triplet
Influence of $\Delta E_{CS}$ on charge separation

**Small $\Delta E_{CS}$:**
HOMO$_D$ - LUMO$_A$ < $^3$PCBM
Charge pair formation is most favourable

**Large $\Delta E_{CS}$:**
HOMO$_D$ - LUMO$_A$ > $^3$PCBM
PCBM triplet formation is most favourable
Influence of $\Delta E_{CS}$ on charge separation: Transitional case

Red F : PCBM

$\star$ Lowest neutral excited state limits charge pair generation, but influenced by microstructure
Emissive charge transfer (CT) states

- Polyfluorenes blended with F and non F silole acceptors
- Slow red shifted emission assigned to CT state
- Fluorinated silole acceptors show:
  - less CT state emission
Emissive charge transfer (CT) states

- Polyfluorenes blended with F and non F silole acceptors
- Slow red shifted emission assigned to CT state
- Fluorinated silole acceptors show:
  - less CT state emission
  - higher polaron yield
  - higher photocurrent

☆ Emissive CT states are a loss pathway
Outline

- Molecular photovoltaic devices
- Process of charge separation
- Factors that influence charge separation
  - competing excited states
  - driving force
  - chemical structure
  - microstructure
- Modelling the process
  - energies of excited states
  - charge transfer excited states
  - means of charge separation
  - dynamics of charge separation
Influence of $\Delta E_e$ on charge separation

- $\Delta E_e$ needs to exceed Coulombic binding energy of geminate charge pair
- Correlation suggests need large $\Delta E_e$ (> 0.6 eV) for charge generation
Influence of $\Delta E_e$ on charge separation

- $\Delta E_e$ needs to exceed Coulombic binding energy of geminate charge pair
- Correlation suggests need large $\Delta E_e$ (> 0.6 eV) for charge generation

- What about other donor : acceptor combinations?...
Influence of $\Delta E_e$ on charge separation

- Alternative acceptors cause charge generation at lower $\Delta E_e$ than P3HT:PCBM
Influence of $\Delta E_e$ on charge separation

- Alternative acceptors cause charge generation at lower $\Delta E_e$ than P3HT:PCBM
- Alternative donors with D-A character capable of efficient charge generation..

🌟 Charge separation efficiency depends on specific chemical structure at interface
Outline

- Molecular photovoltaic devices
- Process of charge separation
- Factors that influence charge separation
  - competing excited states
  - driving force
  - chemical structure
  - microstructure
- Modelling the process
  - energies of excited states
  - charge transfer excited states
  - means of charge separation
  - dynamics of charge separation
Effect of microstructure on current generation

Photocurrent generation in P3HT:PCBM blends is sensitive to composition and annealing.
Optical absorbance increases on annealing but not by enough to explain $J_{sc}$.
Influence of microstructure on charge separation

Larger PCBM domains, ordered packing: most excitons dissociate, geminate charges able to escape each other

Well dispersed PCBM: excitons dissociate but high probability of prompt charge recombination.

Exciton dissociation inefficient.

Photocurrent generation correlates to charge separation yield

Local microstructure influences efficiency of pair separation.
Effect of microstructure on charge separation

- Charge generation yield (1 us) increases on annealing
  - phase segregation reduces (bimolecular) recombination coefficient
  - molecular ordering increases efficiency of geminate pair separation

Need to study excited state dynamics at shorter times
Questions

- What are the stages and intermediates in charge separation?
- What controls the energies of different excited states?
- How does chemical structure affect the process?
- How do local molecular ordering and phase separation affect the process?
- How do extinction coefficients of excited states evolve?
- How do charges separate anyway?
Outline

- Molecular photovoltaic devices
- Process of charge separation
- Factors that influence charge separation
  - competing excited states
  - driving force
  - chemical structure
  - microstructure
- Modelling the process
  - energies of excited states
  - charge transfer excited states
  - means of charge separation
  - dynamics of charge separation
Calculations of excited states and energies

- Excited states calculated using DFT at B3lyp 6-31g* level plus TDDFT singlet at same level. Good agreement with calculation of anion using SCF.
- Find excited state energies and oscillator strengths
- Identify contributions of MOs to excited states
- Simulate absorption spectrum by broadening each excited state energy

Example: PCBM. Five quasi degenerate HOMOs, three LUMOs
Calculations of excited states and energies

- Validation of excited state calculations against absorption spectra or electrochemical reduction spectra
Calculations of excited states and energies

- Use of excited state calculations in molecular design
Calculations of excited states and energies

- Study of charge transfer excited states in complex of oligo-CPDTBT + PCBM
- CT character appears at very short separations
- Influenced by specific position of acceptor
How can charge separation occur anyway?

Energy

$1D^*$

Energy of $P^+ + \text{PCBM}^-$

0.3 – 1 eV

Spatial separation of $P^+ \text{PCBM}^-$

Nearest neighbour separation (1-2 nm)
How can charge separation occur?

- Coulomb binding energy for point charges at ~ 1 nm separation in medium with $\varepsilon = 3$ is $>> kT$

- What effects could reduce the effective binding energy?
  - Effect of polarisable medium
  - Spatial distribution of charge
  - Entropic contribution

Model system: cubic lattice of isotropically polarizable dipoles. Charge pair placed on this lattice at some separation. Dipoles moved self consistently.

Effect of solvation is to reduce binding at close separations.
Effect of vibrationally hot excited states

james.kirkpatrick99@imperial.ac.uk
Effect of vibrationally hot excited states

Hamiltonian for a three level system:

\[
\begin{pmatrix}
\frac{1}{2} \omega^2 \left( (\Delta + x_1)^2 + x_2^2 + x_3^2 \right) + \varepsilon_1 \\
\text{Conjugate}[J] \\
0
\end{pmatrix}
\]

Transfer integral

\[
\begin{pmatrix}
J \\
0 \\
J
\end{pmatrix}
\]

The diagonal energies correspond to those from the coulomb potential

Classical modes

Introduce dampening:

here we take Random to be a random real uniformly distributed between 0 and 1.

Force operator

\[
F = \left( \begin{pmatrix} \phi \\ \frac{d\phi}{dx} \end{pmatrix} \right) - \gamma \varepsilon + R
\]

Characteristic timescale for dampening

\[
R = \sqrt{2 \times 6 \kappa T} \; \text{(Random - 0.5)}
\]

From fluctuation dissipation theorem

james.kirkpatrick99@imperial.ac.uk
Effect of vibrationally hot excited states

Faster charge separation achieved as a result of slow cooling of the excited pair state

james.kirkpatrick99@imperial.ac.uk
Conclusions

- Photocurrent generation in polymer:fullerene solar cells relies on charge separation at a donor-acceptor interface.

- The efficiency of charge separation depends on:
  - driving force
  - chemical structure
  - microstructure (domain size and order)
  - competing excited states (triplets and CT states)

- No simple guidelines exist to describe the process.

- Need new methods to address:
  - nature and energy of excited states
  - stages involved in charge separation
  - dynamics of charge separation
  - dynamics of excited states during charge separation

Thank you for your attention!