Organic Semiconductor-based Plastic Solar Cells
OPVs
Advantages of Organic PVs (OPVs)
- Processed easily over large area using
  - spin-coating
  - doctor blade techniques (wet-processing)
  - evaporation through a mask (dry processing)
  - printing
- Low cost
- Low weight
- Mechanical flexibility and transparency
- Band gap of organic materials can be easily tuned chemically by incorporation of different functional group
Why OPVs?

The concept of third-generation PV technologies, originally developed by Martin Green of the University of New South Wales.

Cost-efficiency analysis for first-, second-, and third-generation PV technologies (labeled 1, 2, and 3, respectively). Region 3-1 depicts very-high-efficiency devices that require novel mechanisms of device operation. Region 3-2 (the region in which organic PV devices lie) depicts devices with moderate efficiencies and very low costs.
Why OPVs?

- OPV shows a promising technological development – efficiencies at 5% level, no obstacles identified for 10%.
- The usage of reel to reel printing technologies guarantees a favorable cost structure.
- The PV market demands low cost flexible solutions.
- The energy market demands portable, decentralized renewable energies.

OPV is the most promising candidate for a next generation PV.
Why OPVs? (Applications)

Polymer Solar Cells Applications

- The low cost of plastic PV may enable solar power in applications where it was previously un-economic
- Disposable solar powered products become a reality
- Flexible and conformable PVs can be integrated more easily into ‘soft’ or non-planar packaging
- Large-area, flexible solar panels could be used to make solar tents, solar sails, portable solar power modules

Rechargeable mobile products

Portable PV

'smart' packaging

Polymer solar panel

Polymer display

PDA wallet

Cornflakes
Why OPVs? (Applications)
Requirement of OPVs

- The most important parameters of every solar technology are efficiency, lifetimes and costs.
- The actual application defines which parameter or combination of parameters are more or less important.
- Other OPV features like flexibility, weight, transparency are not sufficient to constitute a relevant competitive advantage.

- Applications define relevant OPV parameters.
- In the medium term there is no direct competition with Silicon.
Organic solar cells: three types

- **Dye sensitized solar cells**: Electrochemical cells
- **Small molecule organic solar cells**: Made by vacuum deposition
- **Polymer solar cells**: Made by solution, low temperature processing

Each of these cells face more or less the same challenges:

1. Increase power conversion efficiency
2. Increase stability
3. Develop a technology for large areas
History of OPVs

Some important milestones in the development of organic solar cells

2001 - Ramos used double-cable polymers in PV cells.
2001 - Schmidt-Mende made a self-organised liquid crystalline solar cell of hexabenzocoronene and perylene.
2000 - Peters / van Hal used oligomer-C₆₀ dyads/triads as the active material in PV cells.
1995 - Yu / Hall made the first bulk polymer/polymer heterojunction PV.
1994 - Yu made the first bulk polymer/C₆₀ heterojunction PV.
1993 - Sariciftci made the first polymer/C₆₀ heterojunction device.
1991 - Hiramoto made the first dye/dye bulk heterojunction PV by co-sublimation.
1986 - Tang published the first heterojunction PV device.
1964 - Delacote observed a rectifying effect when magnesium phthalocyanines (CuPh) was placed between two different metalelectrodes.
1958 - Kearns and Calvin worked with magnesium phthalocyanines (MgPh), measuring a photovoltage of 200 mV.
1906 - Pochettino studied the photoconductivity of anthracene.
1839 - Becquerel observed the photoelectrochemical process.
PV effect in conjugated polymer

- Light is absorbed in the polymer layer
- Absorption creates a bound electron-hole pair (exciton)
- Exciton is split into separate charges which are collected at contacts

- Exciton must be separated so that a photocurrent can be collected.
- Excitons dissociated by electron transfer to an acceptor material, or hole transfer to a donor.
- Simplest approach is to make a donor-acceptor heterojunction
Critical Steps in organic Photovoltaics

1. Photon Absorption (Band gaps, e.g. 1.3-2.0 eV on earth).
2. Exciton Diffusion (D/A interface within 10-70nm).
3. Charge separation (orbital offsets)
4. Charge transportation (morphology)
5. Charge collection at electrodes.

Key Losses of OPVs

1. Photon loss (light wavelength/spectra vs Band Gap)
2. Exciton Loss (D/A domain size/morphology/Energy Levels)
3. Carrier Loss (Transport Pathway/Morphology/
   Molecular Packing/Collection at Electrodes).
Key role of the morphology!

**Energy Migration**
Diffusion length $\sim 10$ nm !!!!

**Photoinduced Charge Generation**
Device architecture

- Top electrode
- Active layer
- ITO glass

- Single-layer
- Bilayer
- Bulk heterojunction

Single-layer PV cell
I. Organic or polymer single-layer PVs

Disadvantage
High exciton binding energy
Low mobility

Quantum efficiency < 1 %
Charge transfer can occur between two semiconductors with offset energy levels.

- **Excitons can diffuse approximately 10 nm to an interface. (less than 20 nm)**
- A film thickness of approximately 100 nm is needed to absorb most of the light.
- Polymer bilayer cell showed 1.9 % energy conversion efficiency.
- Small molecule bilayer cell showed 3.6 % power conversion efficiency with 3 layers.
Device geometries

**BILAYER**

- Aluminum
- PEDOT-PSS
- ITO
- Plastic foil
- Light

**MDMO-PPV**

**PCBM**

**BULK HETEROJUNCTION**

- Aluminum
- PEDOT-PSS
- ITO
- Plastic foil
- Light

**MDMO-PPV**

**PCBM**

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**Bilayer Concept**

- HOMO $C_{1s}$
- LUMO $C_{2s}$
- $E_g$

**Bulk Heterojunction Concept**

- HOMO $C_{1s}$
- LUMO $C_{2s}$
- $E_f$

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Electronic levels:

- $E_g$
- $E_f$
- $E_{LUMO}$
- $E_{HOMO}$
- $E_{core}$
- $E_{valence}$

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$Ito$
Limitation of organic or polymer bilayer PVs

Separating photoexcited states

- Exciton must be separated so that a photocurrent can be collected
  - Binding energy ~0.5 eV
- Excitons dissociated by electron transfer to an acceptor material, or hole transfer to a donor
- Simplest approach is to make a donor-acceptor heterojunction
- First done effectively by C W Tang in 1986
- Limited by imbalance between exciton diffusion range (~10 nm) and absorption depth (~100 nm)
  - Not all excitons dissociated
III. Bulk heterojunction (BHJ) PVs

- Solution to the limited exciton diffusion range problem
- Donor and acceptor materials mixed together
- Distribute active interfaces throughout the bulk
- **All excitons are within a diffusion range of an interface**
- Charges travel to respective electrodes
Bulk heterojunction solar cells

Charge separation in nanostructured composite organic semiconductors

nansoscopic mixing of donor and acceptor to overcome ~10 nm exciton diffusion length
Donor-acceptor bulk heterojunction devices

- Al cathode
- Donor-acceptor blend: e.g. polymer/fullerene, polymer/nanocystal, polymer/polymer
- ITO anode
- Glass substrate

- Both components deposited from same solution
Optimization for high efficiency

1. Conjugated polymer with low band gap
   Maximum photon flux of sun = 700 nm
   \( E_g = \frac{1.24}{0.7} = 1.77 \text{ [eV]} \)
   Maximum absorption of photon of sun

2. Bulk heterojunction morphology
   exciton diffusion length of conjugated polymer  = below 20 nm

3. High carrier mobility
   electron and hole mobility of conjugated polymer

\[ \eta = \frac{I_{sc}V_{oc}FF}{P_S} \times 100 \]
# Materials for BHJ organic solar cell

<table>
<thead>
<tr>
<th>donor</th>
<th>acceptor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer</td>
<td>$C_{60}$ derivative</td>
</tr>
<tr>
<td>Polymer</td>
<td>Polymer</td>
</tr>
<tr>
<td>Polymer</td>
<td>CdSe nanocrystal</td>
</tr>
<tr>
<td>Polymer</td>
<td>Metal oxide nanocrystal</td>
</tr>
<tr>
<td>Small molecule</td>
<td>Small molecule</td>
</tr>
</tbody>
</table>

- **MDMO-PPV**
- **P3HT**
- **PFB**
- **CuPc**
- pentacene
- **TiO$_2$ or ZnO nanoparticles**
- **PCBM**
- **F8BT**
- **C$_{60}$**
Polymer/PCBM interpenetrating system

Donor/Acceptor composite solution

MDMO-PPV

PCBM

$V_{oc} = 0.82$ V

$J_{sc} = 5.25$ mA/cm$^2$

FF = 0.61

$\eta_{AM1.5G} = 2.5\%$ (under 80 mW/cm$^2$)
Polymer solution processed cells come in three 'flavors':

1. Polymer – fullerene
2. Polymer – polymer
3. Polymer – inorganic
Production

ITO coated glass of plastic serves as substrate.

- Preparation of ITO-cleaning
- Evaporation of top contact
- Coating of hole conduction layer PEDOT:PSS
- Sealing against oxygen/water
- Coating of active layer
- Device/panel testing
Spin Casting is an easy coating technique for small areas. Material loss is very high.

Doctor Blade Technique was developed for large area coating.

Doctor Blade Technique has no material loss.

FILM THICKNESS IS ~ 100 nm
Film preparation

Large Area Thin Film Production using Doctor/Wire Blading

a) 

b)
Cheap: Roll-to-Roll Processing

1. Substrate preparation
   - Roll-to-roll coater (Applied Films)

2. Organic deposition and metal transfer
   - Chamber size
   - 30 cm
   - M. Shtein, unpublished

3. Metal deposition and metal transfer
   - 1 μm
   - P. Peumans, unpublished

Solar Fiber
- Auxiliary conductor
- Barrier coating
- Photoactive layer
- Nylon core
- Inner conductor
- Outer conductor
Materials issue - matching the solar emission

The flexibility in chemical tailoring is necessary for matching the absorption of the PV material to the solar emission spectrum.
Bandgap engineering

< The parameters determining the bandgap of conjugated polymers >

\[ E_G = E_I + RE + E_{ROT} + E_{SUB} \]

1. Aromatic form shows higher stabilization energy and therefore the higher bandgap.
2. **Resonance energy** leads to an energy stabilization and so to an increased splitting of the HOMO-LUMO energy.
3. **Torsion between the ring** plain interrupts the conjugation and therefore increases the bandgap.
4. **Electron donating groups** raise the HOMO level and **electron withdrawing groups** lower the LUMO.
5. In the solid phase, additional **intermolecular effects** between the chains have to be taken into account, which generally leads to broader bands and a lower bandgap.
What has been achieved and what remains to be done

Efficiencies of 4-5% have been reached
  The performance is an intricate combination of:
  photophysics
  charge transport
  nanoscale morphology
  electrodes and device architecture

What remains to be done:
  new materials to increase voltage and spectral overlap
  increase transport and collection
  establish long lifetimes
  develop a real technology
Summary: optimization

**Materials**
- Up to now, polymers for PVs have largely been taken into account for optimum results and maximum efficiency
- Too much work has been done to develop new polymers optimized to absorb solar radiation
- Materials optimized for electron or hole transport

**Device Architecture**
- Morphology of polymer blend crucial to determining device performance
- Morphology can be controlled through careful processing, surface treatment and materials design
Think green with cheap materials

Thank you for your attention