Organic/Hybrid Photovoltaics Systems: Recent progress and stimulating future challenges

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Outline

• Cyprus University and Technology
• Why Organic/Hybrid Photovoltaics?
• Organic/Hybrid OPV Materials and Operation Principles
• Device Structure and Processing flow
• Towards a product (Efficiency, Lifetime, Cost)
• Future Directions
• Summary
Cyprus
Cyprus University of Technology
Molecular (Organic) Electronics and Photonics Research Unit
at Cyprus University of Technology

Molecular Electronic and Photonic (MEP) Research Unit
Proposal Rank 1st on Technology.
MEP Coordinator: Assoc. Prof S. Choulis
Outreach Coordinator: Prof A. Anayiotos
Budget: 2 Million Euros (Cyprus Research Promotion Foundation)
Duration: 4 years
Why Solution based Organic/Hybrid Photovoltaics?
Solution Process Electronic Materials

• Molecular- Organic materials:
  - Semiconducting polymers (P3HT, PPV, PFO….)
  - Small molecules (pentacene, AlQ3…)

• Buckyball, C60 based materials
  - Fullerenes (PCBM)
  - Carbon nano-tubes

• Inorganic materials
  - Nanoparticles of many type and shapes (Au, Ag, Si or CdTe nanorods)
  - Metal Oxides (TiOx, ZnO)

• Hybrid materials
  - Use a combination of different classes of materials and device structures to optimise device performance.
Why Organic Electronics and Photonics?

An Interdisciplinary and Innovative Research Field with Many Materials Systems and Application Areas. Strong interactions between Academic Institutions and Industry:

- Lasers
- Sensors
- TFTs
- Displays
- Polymers
- Metal Films
- Blends
- Dyes
- Biomolecules
- Molecular s/c
- Nanoparticles
- Lighting
- Molecular Photovoltaics

First MEP Product.
Target Application.

D. D. C. Bradley, IC talk 2004
First Products of Organic Electronics and Photonics (Displays)

The Polymer based Display Technology is based on the discovery of conjugated polymer electroluminescence *


In recent years the myths surrounding the molecular (organic) semiconductors have been dissolved:
Transport was low and only uni-polar¹.
Low injection efficiencies².
Degradation and low stability³.


Now Polymer and Small Molecule based Displays are on the Market
Towards new Electronic Device Products: Solar Energy Applications

- Radiant power at Earth’s surface ~ 100000 TW

~ 14 TW additional Carbon-free energy is needed by 2050!

Observations of recent climate change (Carbon Trust UK)

J. Nelson IC talk 2008

Big expectations for Photovoltaic applications.......but the use of Inorganic PV Technologies - Today is limited by cost.

Can we reduce the PV cost?
Market Shares of Inorganic PV Technologies - Today

- Polycrystalline Si: 51.6%
- Single Crystal Si: 36.4%
- Amorphous Si: 6.4%
- Other Technologies: 4.7%
- CdT: 0.9%

Organic Photovoltaics (OPV) is the most recent technology. Have the lowest efficiency up to now and concerns for long term stability. Why OPVs is a promising technology?
Towards a New Application: Organic Photovoltaics

Supply of clean energy ....... demands low cost Photovoltaics (PVs).

How can we reduce the cost of PVs?

New Materials

Lab Processing

Large Scale Processing

Molecular (Organic) materials can be processed by solution at low temperatures - Low Cost Flexible Organic PVs (OPVs)!

Choulis, Invited Talk, PIRA PVs Summit Europe (Italy, 2009)
Organic OPV Materials and Operation Principles
Photons in, electrons out

- Photovoltaic energy conversion requires:
  - photon absorption across an energy gap
  - charge separation
  - charge transport
Conventional photovoltaics

- **Semiconductor p-n junction:**
  - Light produces free electron-hole pairs throughout semiconductor.
  - Charges separate in the depletion region.

\[
\text{Light} \Rightarrow \text{photovoltage} \times \text{photocurrent} \Rightarrow \text{electric power}
\]
Polymer and Small Molecules with semiconductor properties

Molecular materials can have Semiconducting properties

Exciton binding energy (Eg) ~200-500 meV (exciton diffusion (LD) length~ 1-20 nm).
Solar Cells: Convert Light to Electricity

- Photovoltaic energy conversion requires:
  - photon absorption across an energy gap
  - charge separation
  - charge transport

- Organic Solar Cell energy conversion require two materials. The electron donor and the electron Acceptor.

If excitons recombine and electron hole pairs do not separate, how we convert photons to Charges?
Conjugated Polymers and Fullerenes: An Ideal Composite for Photo-Charge Generation

Ultrafast Charge Separation (fs) combined with slow charge recombination (μs)
One more Fundamental Problem

- Exciton binding energy \( (E_g) \sim 200-500 \text{ meV} \).
- Exciton diffusion \( (L_D) \) length \sim 10-20 \text{ nm}.
- Since \( L_D \ll 1/\alpha \rightarrow \) ultra-thin active layers to maximize exciton collection \( \rightarrow \) while maximising absorption (relevant thick layers).

Double Heterojunction OPV

Problem: How we can absorb enough light in 20 nm thick Layer?

Solution

Bulk Heterojunction OPV

Length scale of heterojunctions within blend \( \sim \) exciton diffusion length.

Thickness of the active layer can be now more than 200 nm.
Organic bilayer structures

- Exciton dissociation at donor-acceptor interface.
- Performance limited by ultra-thin layers → PCE = 1 %.
- Improvement by light trapping structures → PCE = 2.4 %.
Organic Distributed Heterojunctions

- Hole donating /Electron accepting material blend.

- Length scale of heterojunctions within blend ~ exciton diffusion length.

- Efficient charge separation at D-A distributed interface.

- Continuous paths for electron and hole transport to respective electrodes.
BULK HETEROJUNCTION SOLAR CELLS:

- Efficient charge separation
- Maximise the number of donor/acceptor interfaces

![Diagram of bulk heterojunction solar cell]

Self-assembled nanoscale materials with charge-separating junctions everywhere!
Morphology of the blend

- Dimension of the donor and acceptor blend morphology in the nm scale is essential. Can be control by the choice of solvents, annealing temperature, concentrations.
Device Structure and Processing Flow
Bulk heterojunction solar cells

Negative Electrode
(LiF-Al)

p-type / n-type
(MDMO-PPV: PCBM)
Blend

Positive Electrode
(ITO / PEDOT)

Substrate (glass)

MDMO-PPV: PCBM
(1:4) (w:w)
PCE ~ 2.5%

Electrodes: Use two different materials with different work functions.

Electrons will automatically go toward lower work function contact and holes toward higher work function contact.
Towards the Product
Product requirements for any PV technology

- 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, can also play a role.

Applications is defined relevant to the above OPV parameters

Roadmap for Future OPV Applications

**Roadmap for Future OPV Applications**

- **Flexible**
  - Siemens/Konarka OPV Prototype
- **Low cost**
- **Lightweight**
- **Printing production**

**OPV Targeted Markets**

- Initial applications
- 10-50 MW
- 10-30 MW
- 100 MW
- 10,000 MW

**Efficiency (%)**

- 0%
- 4%
- 8%
- 12%
- 16%
- 20%

**Year**

- 1998
- 2003
- 2008
- 2013

**Total Accessible Market**

- in megawatts (MW)

**Create a World without wires**

- Consumer
  - 10-50 MW
  - 10-30 MW
  - 100 MW
  - 10,000 MW

**Initial applications**

- UCSB
- U. Linz
- Konarka
- Siemens

**OPV single junction**

- OPV multiple junction

**Brabec, MRS Bulletin (2005),**
**Brabec & Durrant, MRS Bulletin (2008)**
**Gaudiana & Brabec, Nature Photonics (2008).**
**Organic PV State of the Art**

Proven low cost processing
*Choulis* et al., Adv Mat 2007 & Nanoletters 2008

NREL Certified PCE at 6.1 % for non commercially available materials *Heeger* et al., Nat Phot, 2009

*Heeger* et al., Nat Phot, 2009

Effect of Chemical Structure on Morphology

**OPV State of the Art**
6-7.5 % Efficiency (PCE), Over 1 year outdoor lifetime (LT), morphology critical for high PCE, OPVs can be printed.
Efficiency
Material and Device development

$$\eta = i_{sc} \cdot V_{oc} \cdot FF$$

Understanding of all three parameters necessary.
Conjugated Polymers and Fullerenes: An Ideal Composite for Photo-Charge

**RR-P3HT**
- $E_\alpha = 3.0$ eV, $I_p = 4.9$ eV
- $E_g = 1.9$ eV
  (donor)

**MDMO-PPV**
- $E_\alpha = 2.9$ eV, $I_p = 5.0$ eV
- $E_g = 2.1$ eV
  (donor)

**PCBM:**
- $E_\alpha = 3.7$ eV, $I_p = 6.1$ eV
  (acceptor)

**Why PCBM?**
- Ultrafast electron transfer from polymer to fullerene.
- High solubility
- Excellent transport properties
Device Working principle of a bulk heterojunction

1. Incoming photons are absorbed => Creation of excitons on the Donor / Acceptor
2. Exciton is separated at the donor / acceptor interface => Creation of charge carriers
3. splitting of carriers => Creation of open circuit voltage $V_{OC}$
4. Charge carriers within drift distance reach electrodes => Creation of short circuit current $I_{SC}$
5. Good Charge transport properties=>High Fill factor and no recombination losses.

$PCE=V_{OC} \times I_{SC} \times FF$

C. Brabec, OPV tutorial slide 2006
Device Performance

**Short circuit current density** limited by:
- light harvesting
- charge separation and transport

**Fill factor** limited by:
- charge transport
- recombination

**Open circuit voltage** limited by:
- recombination
- donor/acceptor energy levels.

\[ P_{\text{m}} = J_{\text{sc}} \times V_{\text{oc}} \]

**Voltage**

**Current density**

**PCE** = FF × J_{sc} × V_{oc} / P_{inc} (100 mW/cm²)

FF = P_{m} / J_{sc} × V_{oc}

J. Nelson, OPV tutorial slide 2004
Towards high efficiency organic solar cells

Challenges

Maximise light harvesting

Maximise charge separation/
Minimise recombination

Maximise charge transport
Challenges: Maximise light harvesting

Improve overlap of solar spectrum with polymer absorption spectrum: Use lower energy gap polymers.

![Graph showing solar spectrum and polymer absorption spectra with MDMO-PPV and P3HT polymers.]

- MDMO-PPV: \( E_g = 2.1 \text{ eV} \)
- P3HT: \( E_g = 1.9 \text{ eV} \)
Challenges: Maximise charge separation, Minimise recombination

- Control morphology and energy levels:
  
  - Polymer blend morphology controlled by solvent, annealing and processing conditions

  - Optimise D and A energy levels.

Understand charge recombination with fundamental studies.
Challenges: Maximise charge transport

• Improve mobility:
  • reduce deep charge traps
  • improve morphology
  • balance electron and hole transport
    (minimise space charge and recombination)

• Understand charge transport with fundamental studies
Recombination dynamics in polymer/fullerene blends:

**Experimental approach:**
- 100 nm blend of MDMO-PPV and PCBM spin coated on glass slide
- Sample maintained under argon atmosphere
- Optical excitation of MDMO-PPV at $\lambda = 500$ nm
- Monitor photoinduced absorption of positive MDMO-PPV polarons at $\lambda = 900$ nm.
Recombination dynamics on MDMO-PPV:PCBM blends

Observations

→ Intensity dependent fast phase
→ Intensity independent slow phase
→ Insensitive to PCBM %.

Conclusion- Charges sufficiently long lived after charge separation
Summary of TAS measurements and theoretical simulations

$PPV^+$ $g(E)$

μs-ms power law recombination dynamics limited by localised $PPV^+$ polarons

Mobility edge

< 100 ns decay dynamics of $PPV^+$ polarons

Tail of localised states $\sim 10^{17} \text{cm}^{-3}$

Charge transport: Time of Flight technique

Laser pulse

$E = \frac{V}{d}$

$\mu = \frac{d}{E \cdot t_{tr}}$
Hole mobilities increased by filling the trap states.

At low concentrations PCBM (15 %) impedes hole transport within the blend.

At high PCBM fractions → interpenetrating network developed → electron and hole mobility increased.

Electron mobilities faster than hole mobilities → photocurrent dominated by electron transfer in MDMO-PPV:PCBM solar cell.

Summary for MDMO-PPV:PCBM solar cells:

• **Slow charge recombination in MDMO-PPV:PCBM blends is due to hole trapping in polymer.**

• **Unbalanced transport (Electron mobility >> hole mobility)**

• **For better devices need to remove deep traps and achieve balance mobility.**

• **A better hole transporting polymer will improve device performance.**

Comparison of absorption spectra between P3HT and MDMOPPV

Improve overlap of solar spectrum with polymer absorption spectrum: Use lower energy gap polymers.
Comparison of charge transport on Pristine materials

- Transport faster in P3HT compared to PPVs, faster recombination?
Comparison of charge recombination

- TAS measurements → Recombination dynamics in polymer/fullerene blends
- Recombination in P3HT:PCBM faster, but...
Comparison of charge recombination

- Recombination on P3HT:PCBM faster, but now sensitive to composition and morphology
Effect of annealing on Transport properties RR-P3HT:PCBM blends

- Balanced and faster transport properties in P3HT:PCBM compared to MDMO-PPV:PCBM based solar cells.
- P3HT:PCBM Annealing increases hole transport in the blend
Comparison of solar cells

**Material system**

<table>
<thead>
<tr>
<th>Material system</th>
<th>Ionisation potential (eV)</th>
<th>Optical gap (eV)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>Voc (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MDMO-PPV:PCBM</td>
<td>5.0</td>
<td>2.1</td>
<td>5.25$^{[2]}$</td>
<td>0.825$^{[2]}$</td>
</tr>
<tr>
<td>RR-P3HT:PCBM</td>
<td>4.9</td>
<td>1.9</td>
<td>9.4</td>
<td>0.6</td>
</tr>
</tbody>
</table>

$J_{sc}$ due to optical gap, polymer packing and transport

$V_{oc}$ due to lower HOMO level of P3HT and recombination

Organic OPVs with 4.5 % PCE RR-P3HT:PCBM Solar Cells

• Annealing promote packing in RR-P3HT:PCBM blends:
  • Red shift absorption of RR-P3HT
  • increase mobility within the blend
  • Slows down recombination
  • Chemical properties of P3HT also of high importance for high PCE.

Metal Oxides can be used to provide a highly selective electron contact in the inverted device structures of OPVs.

Interface modification for highly efficient inverted organic photovoltaics

The incorporation of a polyoxyethylene tridecyl ether (PTE) interfacial layer between ITO and solution-processed titanium oxide TiOx raised the power conversion efficiency of inverted organic photovoltaics to 3.6%

R. Steim et al., APPLIED PHYSICS LETTERS 92, 093303 2008
Towards 10 % OPV Efficiency

(Material Synthesis)

- Bandgap: 1.2-2.0 eV
- HOMO: 5.2-5.5 eV
- Mobilities: >10^{-3} \text{ cm}^2/\text{Vsec}

Identify methods to control the morphology within the polymer: fullerene blend photoactive layer.

Materials and Device Structures for High Efficiency solar cells: Identify non conventional methods to manipulate the Morphology

PCPDT-BT
Poly(cyclopentadithiophene-alt-benzothiadiazole)

PCE = 5.5 %

Bazan et. al. *Nature Materials* 2007, 6, 497
New Materials

The best PCE of the System

\[ V_{OC} = 0.88 \text{ V} \]
\[ J_{SC} = 10.8 \text{ mA cm}^{-2} \]
\[ FF = 0.66 \% \]
\[ PCE = 6.1\% \]

The Certified PCE recorded in NREL

Record Published OPV power conversion efficiency today

based on alternating ester substituted thieno[3,4-b]thiophene and benzodithiophene units. These polymers exhibit a synergistic combination of properties that lead to an excellent photovoltaic

PCE 7.4-7.9 %
V_{oc} = 0.87 V \quad J_{sc} = 9.6 \text{ mA/cm}^2 \quad \text{FF} = 64\%

NREL Certified Efficiency = 5.21\% (2007), 6.5\% (2009)
Lifetime Performance
Parameters affecting the Lifetime of Organic Solar Cells

Focused testing

- High T storage at 65 °C in the dark
- Environmental stability (65 °C, 85 rh)*
- Light soaking (65 °C, 1 sun)
- Mechanical stability of flexible devices

Device lifetime: less than 20% losses in PCE compared to 0 time performance.
Outdoor Roof Testing of Flexible OPVs at Konarka

Konarka Flexible Organic Solar Cells with more than 1 Year Outdoor Lifetime.

Long lived outdoor lifetimes needed for On-grid applications.
Lifetime- Large Area flex cells from Konarka

OPV flex cells
Towards 5 Year OPV Lifetime (LT)

For Long Lifetime you need to:
1. Identify Limitations of State of the art materials and devices.
2. Design of new Electrodes and **Interfaces**.
3. Design Materials with stable **bulk properties**
4. Protect from water and oxygen using low cost **packaging**.
Cost: *Printed and flexible*
From Lab Cells to Mass Production

Roll to roll processing of organic photovoltaics:

- flexible and light weight
- low cost
- scalable production process
- high volume
Printing Technology

Thin films can be obtained by *printing techniques*.

- Reformulation of solution (organic solvents) necessary
- Temperature control of substrate due to table heating
- Drop on demand – defined structures
- Compatibility with roll to roll production technology
Lab Inkjet tool at Konarka and CUT

Lab inkjet tool

Roll to roll processing of organic photovoltaics:
- low cost
- high volume
- scalable production process
2 solutions were prepared comprising the P3HT:PCBM blend materials:

1) pristine solvent: Tetrahydronaphthalene (Tetralene)

2) two-component solvent system:

68 % ortho-Dichlorobenzene (oDCB)

32 % 1,3,5-Trimethylbenzene (Mesitylene)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Vapor Pressure at 20°C [mm Hg]</th>
<th>Boiling Point [°C]</th>
<th>Surface Tension [dynes/cm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetralene</td>
<td>0.18</td>
<td>207</td>
<td>34.9</td>
</tr>
<tr>
<td>ortho-Dichlorobenzene</td>
<td>1.20</td>
<td>180</td>
<td>37.0</td>
</tr>
<tr>
<td>Mesitylene</td>
<td>1.86</td>
<td>165</td>
<td>28.8</td>
</tr>
</tbody>
</table>

* C. N. Hoth et al., Advanced Materials, 2007, 19, 3973-3978
Inkjet Printing – Morphology and Surface Profile

- Tetralene IJP
  - Scale: 200 nm
  - Roughness: 21 nm

- Tetralene DB
  - Scale: 20 nm
  - Roughness: 1.8 nm

- Tetralene IJP
  - Scale: 50 nm
  - Roughness: 2.6 nm

- oDCB/Mesitylene IJP
  - Scale: 50 nm
  - Roughness: 2.4 nm

- oDCB/Mesitylene DB
  - Scale: 50 nm
  - Roughness: 2.4 nm
Results (Effect of Solvents)–Device Performance

<table>
<thead>
<tr>
<th></th>
<th>Jsc [mA/cm²]</th>
<th>Voc [V]</th>
<th>FF</th>
<th>PCE [%]</th>
<th>rms [nm]</th>
<th>ideality n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetralene IJP</td>
<td>4.7</td>
<td>0.45</td>
<td>0.63</td>
<td>1.29</td>
<td>21.0</td>
<td>1.34</td>
</tr>
<tr>
<td>Tetralene DB</td>
<td>7.9</td>
<td>0.60</td>
<td>0.68</td>
<td>3.30</td>
<td>1.8</td>
<td>1.65</td>
</tr>
<tr>
<td>oDCB/Mesitylene IJP</td>
<td>8.4</td>
<td>0.54</td>
<td>0.64</td>
<td>2.90</td>
<td>2.6</td>
<td>1.55</td>
</tr>
<tr>
<td>oDCB/Mesitylene DB</td>
<td>10.4</td>
<td>0.58</td>
<td>0.67</td>
<td>3.98</td>
<td>2.4</td>
<td>1.55</td>
</tr>
</tbody>
</table>

AM 1.5G spectra at 100 mW/cm²; all PCE values are within a tolerance of 10%.
Optimising the RR of P3HT for inkjet trials

Effect of Gelation:
Viscosity increase due to accumulation of P3HT domains
Creation of particles

Gelation can be controlled by altering the Chemical Properties of RR-P3HT
3.5 % energy efficient inkjet printing organic solar cell with conventional P3HT:PCBM

• 3.5 % ink jet printed solar cell has been demonstrated with 4 orders of magnitude higher PCE than previous published data.

• New proposed solvent mixture controls the phase separation- and RR optimization for inkjet printing trials increase gelation time resolving limitations. Performance still lower for optimized cells process by spin coated or blading process.

Spray Coating vs. Inkjet Printing

<table>
<thead>
<tr>
<th></th>
<th>Spray Coating</th>
<th>Inkjet Printing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Voc [mV]</td>
<td>606</td>
<td>535</td>
</tr>
<tr>
<td>Jsc [mA/cm²]</td>
<td>8.9</td>
<td>8.4</td>
</tr>
<tr>
<td>FF</td>
<td>0.54</td>
<td>0.64</td>
</tr>
<tr>
<td>PCE [%]</td>
<td>2.9</td>
<td>2.9</td>
</tr>
<tr>
<td>rms [nm]</td>
<td>13.0</td>
<td>2.6</td>
</tr>
<tr>
<td>Rs [Ohm]</td>
<td>4.0</td>
<td>2.2</td>
</tr>
<tr>
<td>ideality</td>
<td>1.72</td>
<td>1.55</td>
</tr>
</tbody>
</table>

C. Hoth et al, Organic Electronics 2008
OPV Manufacturing

Production technology

AkzoNobel’s R2R pilot facility for Flexible solar cells

Examples of Roll-to-roll processing

VTT’s R2R ‘Pico’ pilot facility for plastic electronics
Flexible, printed modules from Konarka Technologies

_innovation in very low-cost, light-weight, flexible, polymer photovoltaic materials manufactured roll-to-roll._
Summary

• OPV shows a promising technological development – efficiencies at 6-8 % level.

• Outdoor LT of over 1 year.

• Proof of concept for the printing manufacturing process has been achieved.

• In comparison to conventional inorganic technologies performance of OPVs must be further improved.

• Deep understanding of the device Physics → Development of new materials and application of printed technology is needed to prove the full potential of these novel materials for advanced electronic applications.
Achowlegements

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Prof Jenny Nelson, Prof J. Durrant.

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