Advanced Electron Transport Materials for Application in Organic Photovoltaics (OPV)

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Why Solar?

1 % of land with solar cells could meet our electricity needs

6 Boxes at 3.3 TW Each

- Amount of solar energy in hours, received each day on an optimally tilted surface during the worst month of the year.
Total PV installation: Germany 50%
USA 9%!
Types of Solar Technologies

Lowest cost $/W
Attractive properties:

• Abundant: ~100,000 tons/year
• Mature industry/markets
• Low materials cost: ~$1/g → 15¢/m²
• Low-cost processing: printing
• Excellent stability
• Non-toxic
Organic LEDs for Displays
Organic LEDs for Lighting
New Applications for Organic Solar Cells
Chemistry Nobel Prize Day!
Organic Electronics: Combination of 3 Nobel Prizes!

- 1996 Nobel Prize in Chemistry - Robert F. Curl Jr., Sir Harold Kroto, Richard E. Smalley for their discovery of fullerenes (C60)

- 2000 Nobel Prize in Chemistry - Alan Heeger, Alan G. MacDiarmid, Hideki Shirakawa for their discovery and development of conductive polymers

- 2010 Nobel Prize in Chemistry - Richard F. Heck, Ei-ichi Negishi, Akira Suzuki for palladium-catalyzed cross couplings in organic synthesis
  - C-C bond formation
Motivation for Organic-Based PV

- Lower production cost
  - Roll-to-roll coating
  - Inexpensive active materials
  - Inexpensive processing
  - Lower capital cost

- Lower environmental impact - $/W

<table>
<thead>
<tr>
<th>Material</th>
<th>Energy Payback Time (yrs)</th>
<th>CO₂ Emission in Production (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystalline silicon</td>
<td>2.3</td>
<td>1560</td>
</tr>
<tr>
<td>Thin film (CIGS, CdTe, etc.)</td>
<td>1.2-3.2</td>
<td>900-2560</td>
</tr>
<tr>
<td>Polymer PV (Glass substrate)</td>
<td>1.3</td>
<td>820</td>
</tr>
<tr>
<td>Polymer PV (Plastic substrate)</td>
<td>0.2</td>
<td>130</td>
</tr>
</tbody>
</table>

Roes et al., *Prog. Photovoltaics*. 2009 (17) 372-393
Cost Analysis for Solar Cell Technologies

- **Thin Film**
  - near term/today
  - Efficiency: \$/W basis competitive

- **Crystalline Si**
  - today
  - Efficiency: 14.6% — Pmax 1.46W

- **Organic/Hybrid**
  - future
  - Efficiency: \$/W basis competitive

- **Material and Manufacturing Cost**
  - Paint
  - Ingot
What is an Organic Photovoltaic?

Simplified Working Principle

Progress in Organic Solar Cells

- Solution processes (Polymer, PCBM)
- Vacuum processed

- Similar development for organic solar cells as for amorphous silicon 20 years ago
- Both approaches are reaching nearly similar efficiencies
- Improvements are largely materials discovery based
### Estimated lifetimes of OPVs

<table>
<thead>
<tr>
<th></th>
<th>Burn-in loss</th>
<th>Burn-in time</th>
<th>Lifetime in linear regime*</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT:PCBM</td>
<td>16%</td>
<td>55 days</td>
<td>3.5 years</td>
</tr>
<tr>
<td>PCDTBT:PC70BM</td>
<td>27%</td>
<td>38 days</td>
<td>6.7 years</td>
</tr>
</tbody>
</table>

*Lifetime assumes 5.5 hrs/day of one-sun intensity$^1$

- Heliatek (BASF and Bosch) has achieved 30 year lifetimes with tandem OPVs$^2$

2. www.heliatek.com
**Bulk heterojunction (BHJ) Polymer Solar Cell**

**Advantages:**
- Solution processing (roll-to-roll), increased contact area between active phases,

**Disadvantages:**
- Difficult to achieve optimum morphology, polymers generally less pure than molecules, solvent dependence

**Current world record:**
- 8-10%
- Extrapolated lifetimes >6 years

http://www.solarmer.com/
High-efficiency BHJ solar cells

- Record OPV cells ALL use fullerene derivatives
- Recent development based on donor materials discovery

Liang et al., *Adv. Mat.* 2010 (22) E135-E138

Park et al., *Nat. Phot.* 2009 (3) 297-303

Zhao et al., *Adv. Mat.* 2010 (22) 4355-4358
Drawbacks for fullerenes

**Reduced solar spectrum absorption**

**Lower V_{OC}**

**Difficult synthesis and purification = Higher cost**

PC_{60}BM: $50/g  
CuPc: $1-5/g

Fullerene acceptor – up to 10% of total PV system cost

Roes et al., *Prog. Photovoltaics.* 2009 (17) 372-393
Effect of Production Steps on Cost

- Significant increases (2X) for higher purification
- PC\textsubscript{71}BM approximately 3.4X more expensive than PC\textsubscript{61}BM

Non-fullerene acceptors

- Lower efficiencies due to lower $J_{SC}$ and lower FF
New Acceptors based on Vinazene

- Original applications as high nitrogen containing materials for reduced flammability. Without vinyl groups has been used in the agriculture sector (fertilizers).

- Their highly electron deficient properties make them candidates as acceptor materials in organic electronic applications.

Vinazene
2-vinyl-4,5-dicyanoimidazole

4,5-dicyanoimidazole

Commercially available
Alkylation of 2-Vinyl-4,5-dicyanoimidazole

- Reaction with 1-Butylvinazene (90%)
- Reaction with 1-Hexylvinazene (90%)
- Reaction with 1-Ethylhexylvinazene (56%)

Reagents:
- Acetone, $K_2CO_3$
- DMF, $K_2CO_3$, 70°C
Tunable Synthesis: Heck Chemistry

Optical properties of selected vinazene derivatives

UV spectra of the molecules in toluene

PL spectra of the molecules in toluene

Significant absorption in visible spectrum
Vinazenes used for OPVs

- Solubilizing groups for solution processing
- Conjugated chemical links
- Electron accepting sites

- Can be thermally sublimed as well

HV-BT

EV-BT

Better solubility
Preparation of OPV Devices

- Solution processed active layer

- New Electron Acceptor
- POPT donor polymer
POPT with HV-BT

Voc = 0.62 V, FF = 0.40, PCE = 1.41%

Can we make better acceptors?

Solubilizing groups for solution processing
Conjugated chemical links
Electron accepting sites

• Corresponding electron donor has charge mobility (cm$^2$/V sec) in 10^{-4} range. Is charge transport mis-match a problem?
Improving Organic Acceptor Materials

Accepter Molecule Building Blocks

Current vinazene-based materials: $10^{-5}$ mobility

Symmetric structure: better packing, better mobility, solubility?

OR

Better solubility!
Improved Acceptor Materials?

Symmetric structure: better packing, better mobility, solubility?
Acceptor Materials: Computational Studies

Ground-state geometries

LUMO

HOMO
Synthetic Scheme for PI-BT/NI-BT

PI-BT

\[
\text{Br} \quad \text{Br} + \quad \text{O} \quad \text{Si} \quad \text{O} \quad \text{Si} \quad \text{O} \quad \text{Si} \quad \text{O} \quad \text{O} \quad \text{Si} \quad \text{O} \quad \text{Si} \quad \text{O} \quad \text{O} \\
\text{Si} \quad \text{O} \quad \text{Si} \quad \text{O} \quad \text{Si} \quad \text{O} \quad \text{O} \quad \text{Si} \quad \text{O} \quad \text{Si} \quad \text{O} \quad \text{O} \quad \text{Si} \quad \text{O} \quad \text{Si} \quad \text{O} \quad \text{O} \\
\text{Cy}_{2}\text{NMe} \quad \text{Pd}([\text{P}][\text{Bu}]_{3})_{2} \quad \text{Toluene} \quad 80 \degree \text{C}, 24 \text{ h} \\
\text{Pd}([\text{dba}]_{2}/\text{Lig}, \text{TBAF} \quad \text{Toluene} \quad 80 \degree \text{C}, 2 \text{ days}}
\]

NI-BT

\[
\text{(EtO)}_{3}\text{Si} \quad \text{Br} + \quad \text{O} \quad \text{N} \quad \text{O} \quad \text{N} \quad \text{O} \quad \text{N} \quad \text{O} \quad \text{N} \quad \text{O} \quad \text{N} \quad \text{O} \quad \text{N} \quad \text{O} \quad \text{N} \quad \text{O} \\
\text{O} \quad \text{N} \quad \text{O} \quad \text{N} \quad \text{O} \quad \text{N} \quad \text{O} \quad \text{N} \quad \text{O} \quad \text{N} \quad \text{O} \quad \text{N} \quad \text{O} \quad \text{N} \quad \text{O} \quad \text{N} \quad \text{O} \\
\text{Pd}([\text{dba}]_{2}/\text{Lig.} \quad \text{TBAF} \quad \text{Toluene} \quad 80 \degree \text{C}, 2 \text{ days}}
\]

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New Acceptor Properties

- Peak acceptor absorption is in visible spectrum
- Larger $E_{\text{LUMO,Acc}} - E_{\text{HOMO,Don}}$ than for P3HT:PC$_{60}$BM
- Tunable LUMO – expected higher $V_{oc}$ than fullerenes
• Believed highest efficiency BHJ with non-fullerene acceptor and commercially available P3HT donor

• High voltage as expected with higher-lying LUMO

• Why is the efficiency for NI-BT 10X lower?
EQE Spectra of P3HT:PI-BT Device

- Significant photocurrent generation from acceptor absorption
Twisting of NI-BT molecule due to steric interactions may prevent crystallization in films.
GIXS – Acceptor Crystallization

- More acceptor peaks in PI-BT sample than NI-BT
OPV Conclusions

• Very promising new acceptor materials as potential replacement for fullerene derivatives
  – Synthesized in minimal step/moderate yield reactions
  – Tunable energy levels
  – Anticipated to be much less expensive than fullerenes

• Initial device performance very promising
  – From initial PCE of 0.1% → \( >2.54\% \ PCE_{\text{max}} \), 5 years of R&D, (5-7 total researchers)
  – Close interaction between chemists and device engineers/physicists
Acknowledgements

• Co-PI - Prof. Michael McGehee
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