Conjugated Polymers Based on Benzodithiophene for Organic Solar Cells

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Current Industry Leader: Si Solar Cells

Modules
- 12% efficiency
- $350/m²
- $3/W_p (from manufacturer)
- $6/W_p (installed)

$1/W_p \sim $0.05/kWh
## DOE numbers

Average cost of PV cell electricity (based on single crystal Si): 
$0.27/kWh

Today’s grid electricity: 
$0.06/kWh

$1/W_p \sim 0.05/kWh

<table>
<thead>
<tr>
<th>Materials</th>
<th>Efficiency</th>
<th>Materials Cost</th>
<th>Installed Cost</th>
<th>$/kWh</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly Si</td>
<td>12-14%</td>
<td>Expensive</td>
<td>$4-6/W_p</td>
<td>$0.20-0.30</td>
</tr>
<tr>
<td>CIGS</td>
<td>10-11%</td>
<td>Cheap</td>
<td>$4/W_p</td>
<td>$0.20</td>
</tr>
<tr>
<td>Organic</td>
<td>5-6%</td>
<td>Cheapest</td>
<td>$3/W_p or lower</td>
<td>$0.15 or lower</td>
</tr>
</tbody>
</table>

If the efficiency could be further increased, the $/W_p would be even lower!
Low Cost Alternative: Organic Solar Cells

Advantages of Organic Semiconductor (OSC) Based Photovoltaics Over Inorganic

- Low cost
- Light weight
- Compatible with plastic substrate and can be fabricated using high-throughput printing techniques (large area; flexible)
- High optical absorption coefficients
- Band gap & energy levels can be fine-tuned through molecular design

Konarka
Excitonic Solar Cell: Donor-Acceptor Interface
Fundamental Physical Processes in OPV

It’s All about Exciton!

\[ \eta_{EQE} = \eta_A \times \eta_{ED} \times \eta_{CT} \times \eta_{CC} \]
Bulk Heterojunction (BHJ) Polymer Solar Cells

Brabec, C. & Durrant, J. *MRS Bulletin* **2008**, *33*, 670
Fill factor = $rac{P_{\text{max}}}{J_{\text{sc}} V_{oc}}$

$J_{sc}$ = short circuit current

$J_{sc}$ is determined by how many charge carriers reach the electrodes before recombination occurs.

$V_{oc}$ = open circuit voltage

$V_{oc}$ is determined primarily by the energy levels in the system.
Efficiency Definitions

**External quantum efficiency** \((h_e)\)
- Also known as IPCE (incident photon to converted electron) efficiency
- Electron out/photons on the device

**Internal quantum efficiency** \((h_i)\) = Electrons out/photons absorbed

\(h_i\) can be very high in a thin device because the electric field is high and the charge carriers don’t have far to go, but \(h_e\) is low because not many photons are absorbed.

**Energy conversion efficiency**
\[
\text{Energy conversion efficiency} = \frac{\text{electrical power generated}}{\text{incident optical power}}
\]
\[
= \frac{V_{oc} J_{sc} FF}{P_{in}}
\]
State-of-the-art P3HT/PCBM

\( J_{sc} > 10 \text{ mA/cm}^2 \)
\( V_{oc} > 0.6 \text{ V} \)
\( FF > 65\% \)
Efficiency \( \sim 5\% \)

A Bandgap Challenge

Table 1
The integrated photon flux and maximum current density available for a PV that harvest light from 280 nm up to the wavelength quoted assuming that every photon is converted into one electron in the external circuit.

<table>
<thead>
<tr>
<th>Wavelength</th>
<th>Max. % harvested (280 nm →)</th>
<th>Current density (mA cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>8.0</td>
<td>5.1</td>
</tr>
<tr>
<td>600</td>
<td>17.3</td>
<td>11.1</td>
</tr>
<tr>
<td>650</td>
<td>22.4</td>
<td>14.3</td>
</tr>
<tr>
<td>700</td>
<td>27.6</td>
<td>17.6</td>
</tr>
<tr>
<td>750</td>
<td>35.6</td>
<td>20.8</td>
</tr>
<tr>
<td>800</td>
<td>37.3</td>
<td>23.8</td>
</tr>
<tr>
<td>900</td>
<td>46.7</td>
<td>29.8</td>
</tr>
<tr>
<td>1000</td>
<td>53.0</td>
<td>33.9</td>
</tr>
<tr>
<td>1250</td>
<td>68.7</td>
<td>43.9</td>
</tr>
<tr>
<td>1500</td>
<td>75.0</td>
<td>47.9</td>
</tr>
</tbody>
</table>

The current density may increase if the polymer is applied in a bulk heterojunction device, due to the absorption of the acceptor beyond the band gap of the donor.

**Factors:**
- Band gap
- HOMO, LUMO energy level
- Morphology

1. *Alternating D-A in conjugated backbone*

- **D** - **A** - **D** - **A**
- **D** - **A**

2. *Incorporating more stable quinoid resonance structures in the ground state*

- **R**
- **R**
- **R**

Energy (eV):
- -3
- -4
- -5
- -6

Energy ranges:
- 1.7-1.9 eV
- 1.0-1.3 eV
- 0.9-1.0 eV
Different Types of Low Bandgap Polymers

**Type A**

**Type B**

$E_{\text{gap}}$  
$V_{\text{oc}}$
## Best Performing Low Bandgap Polymers

<table>
<thead>
<tr>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>Egap (opt)</th>
<th>$V_{oc}$</th>
<th>$J_{sc}$</th>
<th>FF</th>
<th>$\eta$ %</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>-5.80</td>
<td>-3.5</td>
<td>1.03</td>
<td>6.3</td>
<td>0.43</td>
<td>2.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td><img src="image" alt="APFO-3" /></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Adv. Funct. Mater. 2006, 16, 667; APL 2007, 91, 071108 (3.5%)</td>
</tr>
<tr>
<td>-6.30</td>
<td>-3.6</td>
<td>1.0</td>
<td>6.0</td>
<td>0.63</td>
<td>3.5</td>
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<tr>
<td><img src="image" alt="APFO-B" /></td>
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<td>Adv. Funct. Mater. 2007, 17, 3836 (3.5%)</td>
</tr>
<tr>
<td>-5.5</td>
<td>-3.6</td>
<td>1.88</td>
<td>0.89</td>
<td>6.92</td>
<td>0.63</td>
<td>3.6</td>
<td>Adv. Mater. 2007, 19, 2295. JACS 2008, 130,732. Nat. Photon. 2009, 3, 297 (6%)</td>
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<tr>
<td><img src="image" alt="PCDTBT" /></td>
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</tr>
<tr>
<td>-5.39</td>
<td>1.82</td>
<td>0.90</td>
<td>9.5</td>
<td>0.507</td>
<td>5.4</td>
<td></td>
<td>APL 2008, 92, 033307.</td>
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<tr>
<td><img src="image" alt="PCDTBT" /></td>
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<td></td>
</tr>
<tr>
<td>-5.3</td>
<td>-3.57</td>
<td>1.40</td>
<td>0.7</td>
<td>9</td>
<td>0.47</td>
<td>2.8</td>
<td>Adv. Mater. 2006, 18, 2884. Nat. Mater. 2007, 7, 497. Jsc 16.2, Voc 0.62, FF 0.55, efficiency 5.5%, IPCE over 50%</td>
</tr>
<tr>
<td><img src="image" alt="PCDTBT" /></td>
<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>-5.43</td>
<td>-3.66</td>
<td>1.70</td>
<td>0.80</td>
<td>6.2</td>
<td>0.51</td>
<td>2.5</td>
<td>JACS 2008, 130, 12828.</td>
</tr>
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<td><img src="image" alt="PCDTBT" /></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-5.1</td>
<td>-3.4</td>
<td>1.7 (film)</td>
<td>0.66</td>
<td>9.4</td>
<td>0.47</td>
<td>2.9</td>
<td>Adv. Mater. 2008, 20, 2556.</td>
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<tr>
<td><img src="image" alt="pBBDPP2" /></td>
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<tr>
<td>-5.05</td>
<td>-3.27</td>
<td>1.45</td>
<td>0.68</td>
<td>12.7</td>
<td>0.55</td>
<td>5.1</td>
<td>JACS 2008, 130, 16144.</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-4.90</td>
<td>-3.20</td>
<td>1.62</td>
<td>0.58</td>
<td>12.5</td>
<td>0.654</td>
<td>4.76</td>
<td>JACS 2009, 131, 56. JACS 2009, 131, 7792 (6.1%)</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
"Ideal" Polymer?

- Absorption: Low band gap, Broad absorption
- Energy Level: Low HOMO level, Minimize voltage lost at electrodes
- Morphology: Maximize D/A interface, High mobility & balanced, Biphasic

Weak donor → Strong acceptor

P3HT (3.3 eV) → "Ideal" Polymer (3.9 eV)

Strong acceptor

PCBM (5.2 eV) → "Acceptor" (5.4 eV)

J_{sc} (upper limit)

V_{oc}

J_{sc} (attainable)

FF

Energy (eV)

-6

-5

-4

-3

-2

-1

0

-1
10% Possible?

Fused Thiophenes

• Fused ring: Increased $\pi$ conjugation
• $\pi - \pi$ stacking: mobility
• Tuning HOMO level!
A Case Study of Benzodithiophene Series

HMPQTN

PQTN-BT
Simple Chemistry

\[
\begin{align*}
\text{I₂, PhMe, hr, [O]} & \quad \rightarrow \\
\text{BuLi, THF, -78°C} & \\
\text{I₂, THF} & \\
\end{align*}
\]
More Polymers

C$_{8}H$_{17}C$_{6}H$_{13}C$_{8}H$_{17} + C$_{8}H$_{17}C$_{6}H$_{13}C$_{8}H$_{17} \xrightarrow{\text{Pd(PPh$_3$)$_4$, PhMe, Reflux, Ar, 3 days}} \text{HMPQTN}

C$_{8}H$_{17}C$_{6}H$_{13}C$_{8}H$_{17} + \text{Br-S-S-Br} \xrightarrow{\text{Pd(PPh$_3$)$_4$, PhMe, Reflux, Ar, 24 h}} \text{PQTN-BT}
0.005mg/mL in CHCl₃ at room temperature
Films of polymers from the solutions in PhCl$_3$ at room temperature with thickness around 40-60nm.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>CHCl$_3$ solution</th>
<th>Film</th>
<th>Cyclic Voltammetry</th>
<th>TD-DFT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_{\text{max}}$ [nm]</td>
<td>$\lambda_{\text{onset}}$ [nm]</td>
<td>$E_g$ [eV]</td>
<td>$\lambda_{\text{onset}}$ [nm]</td>
</tr>
<tr>
<td>HMPQTN</td>
<td>573,530</td>
<td>612</td>
<td>2.04</td>
<td>592,545</td>
</tr>
<tr>
<td>PQTN-BT</td>
<td>716,657</td>
<td>770</td>
<td>1.61</td>
<td>714,652</td>
</tr>
</tbody>
</table>
Calculated HOMO/LUMO
What Might Be Achievable?

- FF: 0.65
- IPCE: 65%
**HMPQTN**: PCBM = 1:2, 180 nm thick film

- $V_{oc}$ - 0.76 V
- $J_{sc}$ - 5.02 mA/cm$^2$
- $FF$ - 53.08%
- $\eta$ - 2.03%
**Optimized Devices**

**PQTN-BT**: PCBM = 1:2, 80 nm thick film

- \(V_{oc}\) - 0.72 V
- \(J_{sc}\) - 5.69 mA/cm\(^2\)
- \(FF\) - 50.26%
- \(\eta\) - 2.06%
## Performance vs. Thickness

<table>
<thead>
<tr>
<th>Polymer</th>
<th>PCBM /Polymer</th>
<th>Film Thickness (nm)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_s$ (mA/cm²)</th>
<th>FF</th>
<th>η (%)</th>
<th>Mobility (cm²/V·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HMPQTN</td>
<td>2:1</td>
<td>55</td>
<td>0.60</td>
<td>2.1</td>
<td>36</td>
<td>0.45</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2:1</td>
<td>70</td>
<td>0.76</td>
<td>2.42</td>
<td>41</td>
<td>0.76</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2:1</td>
<td>180</td>
<td>0.76</td>
<td>5.02</td>
<td>53.08</td>
<td>2.03</td>
<td>8.2×10⁻⁵</td>
</tr>
<tr>
<td></td>
<td>2:1</td>
<td>200</td>
<td>0.72</td>
<td>3.7</td>
<td>50.57</td>
<td>1.35</td>
<td></td>
</tr>
<tr>
<td>PQTN-BT</td>
<td>2:1</td>
<td>45</td>
<td>0.72</td>
<td>3.91</td>
<td>49.06</td>
<td>1.38</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2:1</td>
<td>55</td>
<td>0.74</td>
<td>5.97</td>
<td>39.52</td>
<td>1.75</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2:1</td>
<td>80</td>
<td>0.72</td>
<td>5.69</td>
<td>50.26</td>
<td>2.06</td>
<td>1.3×10⁻⁵</td>
</tr>
<tr>
<td></td>
<td>2:1</td>
<td>115</td>
<td>0.60</td>
<td>2.18</td>
<td>37.46</td>
<td>0.49</td>
<td></td>
</tr>
</tbody>
</table>
• “Ideal” polymers require \textbf{low HOMO} level (maximize $V_{oc}$) and \textbf{low bandgap} (maximize $J_{sc}$) (when PCBM is used)

• Combining \textbf{weak donor} and \textbf{strong acceptor} would potentially lead to “ideal” polymers for OSC

• \textbf{Mobility} and \textbf{morphology} are crucial to approach the theoretical efficiency: attainable $J_{sc}$ and $FF$

• Polycyclic, fused aromatic molecules are excellent building blocks for “ideal” polymers
  (a) effectively lower the HOMO
  (b) improved $\pi$-$\pi$ interactions between polymer chains in thin solid films would enhance the charge carrier mobility
Is 10% Really Achievable?

Efficiency = \frac{V_{oc} \times J_{sc} \times FF}{P_{input}}

For example

\begin{align*}
V_{oc} & \quad 0.9 \text{ V} & \quad 1.0 \text{ V} \\
J_{sc} & \quad 12 \text{ mA/cm}^2 & \quad 15 \text{ mA/cm}^2 \\
FF & \quad 0.6 & \quad 0.70
\end{align*}

\eta \quad 6.5\% & \quad 10.5\%

\downarrow

ACHEIVED!
Acknowledgments

The You Group:
Sam Price (4th yr)
Jeremy Niskala (4th yr)
Andrew Stuart (3rd yr)
Huaxing Zhou (3rd yr)
Rycel Uy (2nd yr)
Liqiang Yang (2nd yr)
Sarah Stoneking (undergraduate)
Nabil Kleinhenz (undergraduate)

Dr. Shubin Liu

$$ Support: