Understanding Morphology:
How measurement affects perception

Scott A. Mauger, John Roehling, Lilian Chang, Stephan Friedrich, Christopher W. Rochester, David M. Huang, Peng Wang, Jaroslaw Majewski, and Adam J. Moulé

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How does it work?

Glass ITO Substrate

PEDOT:PSS

P3HT:PCBM Mixture

Al Electrode

Electron Donor

Electron Acceptor

P3HT

PCBM
How does it work? - Excitation

Glass ITO Substrate

PEDOT:PSS

P3HT:PCBM Mixture

Al Electrode

hv

$D^*\quad A$

$\delta + \delta$

Exciton

$D^+ \quad A^-$

Free Charges

$\rightarrow$

$h v$

Recombination

$\rightarrow$

$D^+ \quad A^-$

Geminate Pair

$E, T$

$\rightarrow$

Photocurrent

$S^0$

$S^1$

$T^1$

CT

CS
How does it work? – Charge transfer

Glass ITO Substrate

PEDOT:PSS

P3HT:PCBM Mixture

Al Electrode

\[
\begin{align*}
D^+ & \quad A^- \\
\delta & + \delta \\
\text{Exciton} & \\
\rightarrow & \\
\text{Free charges} & \\
\rightarrow & \\
\text{Photocurrent} & \\
\end{align*}
\]

\[
\begin{align*}
D & \quad A \\
\rightarrow & \\
\text{Recombination} & \\
\end{align*}
\]

\[
\begin{align*}
D^+ & \quad A^- \\
\rightarrow & \\
\text{Geminate pair} & \\
\end{align*}
\]
How does it work? - photocurrent

- **Glass ITO Substrate**
- **PEDOT:PSS**
- **P3HT:PCBM Mixture**
- **Al Electrode**

**Diagram:**
- **Exciton** (δ+δ)
- **Free Charges** (D⁺ A⁻)
- **Recombination**
- **Geminate Pair** (D⁺ A⁻)
- **Photocurrent**

**Energy Levels:**
- **S¹**
- **T¹**
- **CT**
- **CS**
- **S⁰**
How does it work? - recombination

Chemical Physics Letters 2011, 513, 77
So, can this picture explain OPV device function
So, can this picture explain OPV device function?

Almost

What about Morphology?
1) Domain sizes are <50 nm and so cannot be seen with light
2) There is little scatter contrast between carbon containing materials, SAXS and GWAXS have low signal
3) The materials are semi-crystalline so much of sample is invisible to bragg scattering
4) Surface properties cannot be assumed to be uniform throughout the film so surface techniques give misleading results
5) The sample is highly sensitive to processing conditions, So it is difficult to get a generalizable result.
6) Most spectroscopy is performed on samples that were not produced under the same conditions as a device – no metal and no electrodes
TEM vs. STEM

Depth of Field

Small CL aperture

Large CL aperture

TEM

STEM
Creating Contrast

Lu$_3$N-PC$_{80}$BEH  Lu$_3$N-PC$_{80}$BM

3D-Morphology of P3HT/Lu$_3$N-PC$_{80}$BEH

<table>
<thead>
<tr>
<th>Full</th>
<th>Mixed</th>
<th>Fullerene</th>
<th>P3HT</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
</tr>
<tr>
<td>As-cast</td>
<td>Solvent Anneal</td>
<td>Thermal Anneal</td>
<td></td>
</tr>
</tbody>
</table>

3D P3HT Domains
Morphology of P3HT/Lu₃N-PC₈₀BM

As-cast

Thermal Anneal

Quantifying Morphology

Why are they so different?

Crystallinity is bad!

SA – P3HT/Lu$_3$-PC$_{80}$BEH

SA – P3HT/Lu$_3$-PC$_{80}$BM

Neutron Reflectometry

Scott A. Mauger, Lilian Chang, Stephan Friedrich, Christopher W. Rochester, David M. Huang, Peng Wang and Adam J. Moulé,
Published on-line in Adv. Funct. Mater.
Vertical Segregation in a device

Why does vertical segregation occur?

P3HT and PCBM rearrange upon annealing because of

1) Surface energy effects
2) Charging from interfaces (metals or PEDOT:PSS)
3) Choice of solvents and solvent additives
Why should you care?

These Images
1) Have the highest resolution of any image ever taken of a BHJ layer 1.4x1.4x1.4 nm = 5x10^7 voxels
2) Prove that a three phase diagram is necessary to describe the morphology
3) Quantify concentration at the nanoscale for the first time
4) With NR quantify the vertical and lateral phase segregation for the first time
5) Give us the ability to relate real nanostructure to optical and electrical properties.
Credits

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Thank you for your attention