Correlations of electronic and molecular structures of conducting polymers with device efficiencies in BHJ solar cells

Lin X. Chen
Chemical Sciences and Engineering Division, Argonne National Laboratory
Department of Chemistry, Northwestern University

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Jodi Szarko, Brian Rolczynski, Sylvia Lou, Jianchang Guo, Sung Cho, Nicholas Jackson, Northwestern University/Argonne; Joseph Strzalka, APS, Argonne National Lab. Luping Yu Group; University of Chicago: Tobin Marks, Robert Chang, Mark Ratner Groups; Northwestern University and ANSER Center.
Outline

- Introduction
- Exciton and charge separation dynamics in isolated charge transfer (e.g., PTBF) polymers in solution: implication of materials design
- Exciton and charge separation dynamics in BHJ OPV films (made from charge transfer polymers)
- Morphology requirements for high PCE and the role of DIO additives
- Some challenges and concerns
Conjugated Donor-acceptor Copolymers in BHJ Materials

“Dyad”

“Triad”

Higher electron affinity

Lower electron affinity
Electron Donor-Acceptor Characters in the Copolymers

Small structural tuning, big PCE difference

PTB2 (PTBF0)
PTB2: $R_1 = \text{2-ethylhexyl}, R_2 = \text{n-C}_8\text{H}_{17}$
PTB7: $R_1 = R_2 = \text{2-ethylhexyl}$

PTBF1 (PTB7)

PTBF2
PTBF2: $R_1 = R_2 = \text{2-ethylhexyl}$

PTBF3
PTBF3: $R_1 = R_2 = \text{2-butyloctyl}$

Yu, U. Chicago

Liang et al. JACS (2009), 131, 7792-7799;
Son et al. JACS (2011), 133, 1885-1894.
**Electron Donor-Acceptor Characters in the Copolymers**

Small structural tuning, big PCE difference

<table>
<thead>
<tr>
<th>Material</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTB2(F0)</td>
<td>0.60</td>
<td>12.8</td>
<td>66.3</td>
<td>5.1</td>
</tr>
<tr>
<td>PTB7(F1)</td>
<td>0.74</td>
<td>14.5</td>
<td>69.0</td>
<td>7.4</td>
</tr>
<tr>
<td>PTBF2</td>
<td>0.68</td>
<td>11.1</td>
<td>42.2</td>
<td>3.2</td>
</tr>
<tr>
<td>PTBF3</td>
<td>0.68</td>
<td>8.8</td>
<td>39.0</td>
<td>2.3</td>
</tr>
</tbody>
</table>

Son et al. JACS (2011), 133, 1885-1894.

PTB7 or PTBF1 → promising materials for OPVs with PCE ~8.5% in single junction devices (Solamer).
Fundamental Photophysical Processes in OPV Materials

Detecting transient optical signatures of different species as function of the time delay after the fs laser pulse excitation.

Free charge carriers

ΔG_CS

Intra-molecular and intermolecular processes

Exciton

Pseudo Charge transfer or bound radical pair

Charge separated state
When isolated polymers in solution is excited in the absence of PCBM, PCT (or CT) and CS species are generated within 150 fs of the excitation, with varying relative concentrations.

Where is CS (in < 150 fs) from in a single isolated polymer chain?

A Surprising Correlations of Intramolecular Initial CS/PCT in Isolated PTBFSx with Device Performance

\[ RBR = \frac{\Delta OD_{CS}(0)}{\Delta OD_{PCT}(0)} \propto \frac{[CS]}{[PCT]} \]

- Larger local polarity (local dipole) \(\rightarrow\) More polar exciton \(\rightarrow\) Higher CS efficiency;
- Intramolecular CS defrays some exciton binding energy;
- Intramolecular interactions can be propagated to device performance;
- Stronger pulling of electron density towards thienothiophene could further increase device PCE.

Exciton Splitting Dynamics in Isolated Polymers in Solution

A “tug of war” in local electron density

The local polarity favors the CS state generation and lowers CT state population.
Total electron density vs. no. F

\[ r_c = \frac{e^2}{4\pi \varepsilon_r \varepsilon_0 k_B T} \]
A Surprising Correlation of Intramolecular Initial CS/PCT in Isolated PTBFX with Device Performance

The local dipole creates a polar environment that favors a polarized exciton where a part of binding energy or $\Delta G_{cs}$ has been defrayed by the “pre-charge separation”.

How much local polarity is optimal?
What are D and A in isolated polymers?
What is the exciton diffusion dynamics?

$$r_c = \frac{e^2}{4\pi\varepsilon_r\varepsilon_0 k_B T}$$
A Surprising Correlation of Intrinsic local dipole change and device PCE

\[ \Delta \mu_{ge} = \left[ (\mu_{gx} - \mu_{ex})^2 + (\mu_{gy} - \mu_{ey})^2 + (\mu_{gz} - \mu_{ez})^2 \right]^{1/2} \]

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( \Delta \mu_{ge} ) (D)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTB2</td>
<td>2.96</td>
<td>5.10</td>
</tr>
<tr>
<td>PTBF1</td>
<td>3.92</td>
<td>7.40</td>
</tr>
<tr>
<td>PTBF2</td>
<td>2.41</td>
<td>3.20</td>
</tr>
<tr>
<td>PBB3</td>
<td>0.47</td>
<td>1.44</td>
</tr>
</tbody>
</table>

Equation: \( y = a + b \times x \)

Weight:
- No Weight

Residual Sum of Squares: 1.68478

Pearson's r: 0.95614

Adj. R-Square: 0.87132

<table>
<thead>
<tr>
<th>Value</th>
<th>Standard Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>b</td>
<td>0.179</td>
</tr>
<tr>
<td>b</td>
<td>1.00066</td>
</tr>
<tr>
<td>b</td>
<td>1.682</td>
</tr>
<tr>
<td>b</td>
<td>0.36444</td>
</tr>
</tbody>
</table>

Exciton and Charge Separation Dynamics in Bulk Heterojunction OPV Films

Rolczynski, Szarko, Son, Liang, Yu, Chen, *to be submitted*, Szarko, Rolczynski et al., *to be submitted.*
Dynamics of CT Detrapping in BHJ Films: a Probe for h – e Separation (PTBF1:PC\textsubscript{71}BM)

Excess excitation energy helps detrapping of CT state and sustaining CS population.

Rolczynski, Szarko, Son, Liang, Yu, Chen, \textit{to be submitted}, Szarko, Rolczynski et al., \textit{to be submitted}. 

\[ r_{cs} = \frac{e^2}{4\pi\varepsilon_r\varepsilon_0 k_B T} \]

Excitation 695 nm

Excitation 600 nm

Depth of the trap?
Exciton Dynamics Studies: Summary

- Ultrafast dynamics for EX, PCT (CT) and CS states are measured for PTBF polymer series, and the RBR (CS/CT) varies and linearly correlated with PCE in solution, neat films and BHJ films;

- Larger local dipole changes \( \Delta \mu_{gel} = [(\mu_{gel} - \mu_{ex})^2 + (\mu_{gy} - \mu_{ey})^2 + (\mu_{gz} - \mu_{ez})^2]^{1/2} \)
along the polymer backbone can facilitate polarized excitons, and defrays a part of the EX binding energy in isolated polymers and in BHJ films, leading to high device PCE, but this phenomenological model needs to be evaluated in a longer segment;

- The detrapping of CT state is observed in BHJ films with a trap energy of \(~kT\) for PTBF1 while traps are deeper for poorly performing polymers;

- Ultrafast excitation delocalization and coherent coupling dynamics and long time scale CS/CT dynamics need to be measured in the future.
Correlation of Interfacial $\pi$-stacking and Device Performance, and the Role of DIO
An Interfacial Orientation Favoring Charge Collection

GIWAXS: $\pi$-$\pi$ stacking

$$q = \frac{2\pi}{d}$$

The \( \pi \)-stack Spacing vs. The Device Fill Factor

Better \( \pi \)-stacking at the electrode surface enhances charge collection efficiency,

Effects of additive on the active layer solution

How does the addition of DIO affect the PTB7:PCBM blend in solution?

<table>
<thead>
<tr>
<th></th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>Eff. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTB7:PC$_{71}$BM without DIO</td>
<td>0.76</td>
<td>10.20</td>
<td>50.52</td>
<td>3.92</td>
</tr>
<tr>
<td>PTB7:PC$_{71}$BM with DIO</td>
<td>0.74</td>
<td>14.50</td>
<td>68.97</td>
<td>7.4</td>
</tr>
</tbody>
</table>
Solution small angle x-ray scattering traces of A) PTB7, B) PC$_{71}$BM and C) PTB7:PC$_{71}$BM (1:1.5 w/w) in chlorobenzene solution with and without 3% DIO. Aggregate size of active layer materials determined by small angle scattering equation.

Lou, Szarko, Xu, Yu, Marks, Chen, JACS, 133 20468 (2011);
What else are special about PTBX polymers?

- Media independent UV-vis absorption;
- Face down $\pi$-stacking at the electrode interface;
- Annealing reduces cation initial population, speeds up its formation, but did not change the longer time kinetics.

Some Challenges and Concerns

Photophysics of exciton formation, delocalization, coherence (size of excitons) and splitting mechanisms – are these important to device performance?

The propagation of intrinsic/molecular properties to device performance – from theoretical calculation to molecular design;

Mechanisms of reducing charge germinate and bimolecular recombination – h-e distance control;

Material dependent optimized morphology: anneal or not anneal; amorphous vs. crystalline – one morphology does not fit all;

Re-evaluate/not reinvent conventional wisdom of OPV materials/devices fabrication (domain size vs. exciton diffusion; charge transfer rate vs. h-e distance; NIR light harvesting vs. Voc; exciton polarity vs. oscillator strength; CS driving force vs. band gap, etc.)
Thank you.