Plastic Solar Cells

Lightweight, flexible and rugged!
“Plastic” Solar Cells

The ultrafast electron transfer in polymer BHJ Materials and in small molecule BHJ Materials is enabled by the Uncertainty Principle.
The Initial Discovery (1992): Ultrafast Photo-induced electron transfer

B. Kraabel, C.H. Lee, D. McBranch, D. Moses, N. S. Sariciftci and AJH
Chem. Phys. Lett. 1993, 213, 389 --- <100 fs

Electron Acceptor

Electron Donor

hν

610 nm

Phase separation morphology is critical to OPV solar cell performance

- Need connected pathways
- Need relatively high mobility to get charges out prior to recombination
- Need self-assembly to form phase separated morphology at the 10 – 20 nm length scale
- Ultrafast carrier generation does not suffer the recombination losses expected from regions of low phase purity (e.g. intermixed systems or intercalated systems).

Why phase separation?

- Polymers always want to phase separate --- no entropy of mixing for high polymers
- Crystallinity: Strong driver of phase separation
Time Resolved Charge Transfer
Photo-induced absorption measurements in the sub-ps to sub-ns time regime.

But first, in order to understand the importance of the ultrafast electron transfer, we must understand the morphology.
P3HT:PCBM
Cross-section TEM: “Column-like” Morphology “slice” with Focused Ion Beam

Jisun Moon et al Nano-Letters 2009
“Good” morphology --- relatively direct pathways to the electrodes
Nano-scale solar cells: ALL CONNECTED IN PARALLEL!
Autocorrelation function

\[ ACR(x) = \frac{1}{L_x} \int_0^{L_x} I(x)I(x-x')dx \]

“Period” --- 20 - 25 nm
(Ave. Domain size)
TEM Tomography

1:2 Polymer:PC$_{70}$BM ($\eta=6.0\%$)

Polymer

James Rogers
Ed Kramer
UCSB

100 nm
New Material

Organic Nano-photovoltaics

Concept

Reality

100 nm
Time Resolved Charge Transfer

Photo-induced absorption measurements in the sub-ps to sub-ns time regime.

Excited state and charge transfer

Interfacial traps and interfacial excitons

Mobile carrier sweep out by the internal voltage (built-in electric field)

Energy out ns - μs

Recombination --- mostly bimolecular

Ground state

hν

Photoinduced charge transfer over approx. 20 nm in 50 fs!
Current “conventional wisdom” describes the charge transfer process as occurring in four steps:

- Photo-generation of Frenkel excitons
- Exciton migration to a donor-acceptor interface
- Interfacial charge transfer into a “bound state” (charge transfer (CT) exciton) at the donor-acceptor interface
- Field induced dissociation of the CT exciton

50 fs much too fast for exciton diffusion to interface — of order 100 – 500 ps would be required!
Design and synthesis by Bazan and Welch

Design and synthesis by Mario Leclerc
U of Laval

ESIGN
and synthesis by Bazan and Welch

\[ p\text{-DTS(PTTh}_2\text{)}_2 \]

5,5'-bis((4-(7-hexylthiophen-2-y1)thiophen-2-y1)thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-c]pyridine-3,3'-di-2-ethylhexylsilylene-2,2'-bithiophene

PCDTBT

poly[N-9''-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di2-thienyl-2',1',3'-benzothiadiazole]

PC\textsubscript{70}BM

[6,6]-phenyl C\textsubscript{70}-butyric acid methyl ester

\[ \text{Absorbance} \]

\[ \Delta \text{A (au)} \]

\[ \text{wavelength (nm)} \]

\[ \text{PCDTBT:PC}\textsubscript{70}BM \]

\[ \Delta \text{A (au)} \]

\[ \text{wavelength (nm)} \]
BHJ solar Cells fabricated from small Molecules

Design and synthesis:
G. Bazan and G. Welch

Performance of solar cells with a DTS(PTTh$_2$)$_2$:\textsc{pc}$70$BM active layer as a function of DIO content (as processing additive)

G24:PC$_{70}$BM ($\eta=6.7\%$)

Note: Ratio only 70:30
30% Fullerene

Top View

100 nm

SideView

James Rogers
Ed Kramer
DTS(PTTh$_2$)$_2$ BHJ on MoOx (no DIO)
(163 nm per side)

**False Color**

**Raw Image**

In-plane stacking of DTS(PTTh$_2$)$_2$ at 0.31 Å$^{-1}$.
(approx. 2 nm d-spacing)

Regions of solid color indicate the spatial extent and direction of the crystal lattice fringes.

TEM: Chris Takacs
Fabricated with 0.25% DIO additive (Optimum)

Crystallinity remains very high; crystallite size decreases
p-DTS(PTTh$_2$)$_2$:PC$_{70}$BM

Ultrafast charge separation is enhanced by DIO additive

Loren Kaake

Ultrafast Electron Transfer in Bulk Heterojunction Solar Cells: The Mechanism

DTS(PTTh₂)₂ : PC₇₀BM

PCDTBT:PC₇₀BM

Ultrafast component is linear in the pump intensity. Ultrafast charge transfer is observed at all pump power levels.
At lower pump powers, when the excitation density is close to that of one sun, the carrier density decreases to the point where the bimolecular decay is no longer observable.

Under these conditions, a slow increase emerges over much longer time scales!
The two very different characteristics of the charge transfer dynamics unambiguously imply two mechanisms:

• One consistent with ultrafast charge transfer via delocalized states,

and

• A second, slower contribution from excitons diffusing to a donor-acceptor interface.
No change in dynamics when pump power decreased by another factor of two where excitation densities are comparable to those generated under illumination by 1 sun.

The exciton diffusion contribution to the charge transfer contributes approx. 30% of the mobile charges. The Ultrafast contribution contributes approx. 70%.
The Charge Transfer Exciton

- If the CT exciton is a bound state, it serves as the pathway for recombination (both radiant and non-radiant).

- If the conditions are such that the CT exciton is a bound state, it will serve as a principal route for bimolecular recombination.
Dynamics and Time Scales

Excited state and charge transfer

Interfacial traps and Interfacial excitons

Mobile carrier sweep out by the internal voltage (built-in electric field)

Ground state

Recombination to ground state – mostly bimolecular

Bimolecular Recombination and radiative recombination if the CT exciton is a bound state

Energy out ns - μs

$t < 50 \text{ fs}$

$t \sim 100 – 500 \text{ ps}$
Carrier generation in pure $\rho$-DTS(PTTh$_2$)$_2$

Photoconductive response tracks the absorptance across the entire spectrum despite the fact that the initial absorption is that of an intra-molecular Frenkel exciton.

Polarization anisotropy measurements:

Photo-generated carriers are produced immediately, delocalize and move along the $\pi$-$\pi$ stacking direction) in $\rho$-DTS(PTTh$_2$)$_2$
One cannot know the location of the photoexcitation to an accuracy greater than about $\lambda/4 > 30$ nm.

This coherent state (intramolecular excitations plus delocalized carriers) can yield ultrafast electron transfer to a nearby fullerene domain and, after decoherence, produce localized excitons that diffuse incoherently toward a donor/acceptor interface.

The ultrafast electron transfer in polymer BHJ Materials and in small molecule BHJ Materials is enabled by the Uncertainty Principle.
Origin of $V_{oc}$ and the Built-in Potential

$$V_{oc} \approx E_{\text{fullerene}}(\text{LUMO}) - E_{\text{polymer}}(\text{HOMO}) + \frac{k_B}{e}\{\ln \left(n_e n_h / N_c^2\right)\}$$

Conclusion: Need Deep HOMO for donor material.
COMPETITION between SWEEP–OUT and RECOMBINATION

Mobile carrier sweep out by the internal voltage (built-in electric field)

Ground state

Interfacial traps and Interfacial excitons

Recombination
Time scale ???

When sweep-out is faster than recombination --- high efficiency.

Cowan, Street, Cho and AJH
Phys. RevB 83, 35205
Transient photocurrent in operating solar cell: Competition between Sweep-out and Recombination

Photoconductance = Current / Internal voltage

\[ V_{int} = V_{BI} - V \]

When sweep-out is faster than recombination --- high efficiency.
Caution: Generation of impurity during synthesis

Typically less than 1% impurity

- Remove impurity via extraction with hexanes and column chromatography
- Can avoid methyl transfer by lowering reaction temperature
Earlier work on controlled introduction of impurities:

**PC$_{84}$BM Traps in PCDTBT:PC$_{84}$BM**
- Introduce first-order (monomolecular) recombination and decrease $V_{OC}$
- Reduce mobility
- Reduce $j_{SC}$ and prevent fast sweep out

Result: All parameters adversely affected: $V_{OC}$, $j_{SC}$, FF
What is needed to achieve the predicted high efficiencies?

- **Bandgap** $\approx 1000 \text{ nm}$
- High $V_{oc}$
- Higher mobility and column-like morphology across the thickness of the film.

Sweep-out prior to Recombination!
"Plastic" Solar Cells

Time evolution of efficiency of "plastic" solar cells

Efficiency (%)

1995 2000 2005 2010

Year

0 4 8 12 16 20

Efficiency (%)
**“Plastic” Solar Cells**

**Low $ cost manufacturing**

**Low energy cost manufacturing**

**Low carbon “footprint” manufacturing**

<table>
<thead>
<tr>
<th>Technology</th>
<th>Energy for production (MJ.Wp⁻¹)</th>
<th>CO₂ footprint (gr.CO₂-equ.Wp⁻¹)</th>
<th>Energy payback time (years)</th>
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<tr>
<td>mc-Si</td>
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<td>CdTe</td>
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QUESTIONS?

AJH
Polarization Anisotropy Measurements

Assuming carrier generation along the direction of $\pi-\pi$ stacking, predictions for the anisotropy at vanishing timescales are:

$$ r^0_{\text{band}}(790 \text{ nm}) = 0.21 $$
\[ r^0_{\text{band}}(395 \text{ nm}) = -0.20 \]

Results:

$$ r^0_{\text{exp}}(790 \text{ nm}) = 0.16 \pm 0.3 $$
\[ r^0_{\text{exp}}(395 \text{ nm}) = -0.18 \pm 0.1 \]

Consistent with band formation along the $\pi-\pi$ stacking direction.
No change in dynamics when pump power decreased by another factor of two.
Dynamics and Time Scales

Excited state and charge transfer

Ground state

Interfacial traps and Interfacial excitons

Mobile carrier sweep out by the internal voltage (built-in electric field)

$E_{\text{out}} \approx \mu s$

Recombination to ground state – mostly bimolecular

Geminate Recombination if the CT exciton is a bound state

Exciton diffusion to interface does contribute to the charge transfer, but relatively small amount. If the CT exciton is truly a bound state, then major source of bimolecular recombination.
The "Idea" ----

Typical length scale: $\sim 20$ nm
Localization length in disordered semiconducting polymers

Self-Assembly of “Bulk Heterojunction” nano-material by Spontaneous Phase Separation

Minimum LUMO-LUMO offset $\sim 0.1$ eV
Gong, X. et al.
“Plastic” Solar Cells

Efficiency

Time evolution of efficiency of “plastic” solar cells

- 13% Mitsubishi Japan
- 9.2% SCUT China
**“Plastic” Solar Cells**

- Low $ cost manufacturing
- Low energy cost manufacturing
- Low carbon “footprint” manufacturing

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Lightweight, flexible and rugged!
Semi-transparent “Plastic” OPV: Light for greenhouse plants and Power the fans, Pump the water
Roof of Bus Shelter

- San Francisco, USA
TEM Phase Contrast Imaging

Useful method for exploring morphology in low contrast materials
Cross-section --- Spontaneous Phase Separation

(a) Cross-section diagram showing layers: Al, P3HT, PEDOT:PSS, PCBM, PEDOT:PSS, P3HT:PCBM conventional BHJ, PEDOT:PSS, SiO₂.

(b) Focused image showing layers with a scale of 100 nm.

(c) Defocused image showing layers at 10 μm.

(d) Defocused image showing layers at 30 μm.

Al
P3HT
PEDOT:PSS
PCBM
PEDOT:PSS
P3HT:PCBM conventional BHJ
PEDOT:PSS
SiO₂
DTS(PTTh$_2$)$_2$ BHJ on MoOx (no DIO)
(163 nm per side)

In-plane stacking of DTS(PTTh$_2$)$_2$ at 0.31 Å$^{-1}$
(approx. 2 nm d-spacing)

Regions of solid color indicate the spatial extent and direction of the crystal lattice fringes.

TEM: Chris Takacs
Intensity dependent dynamics

At short circuit:

Sweep – out of photogenerated carriers by internal field ($V_{bi}$)

Efficient collection of photo-generated carriers

At open circuit: Recombination only

$n_{oc}/n_{sc} \sim 50 - 100$

$n = p \sim I^{1/2}$ and $np \sim I$

Band-to-band bimolecular recombination

$R_{Bimolecular} \propto np$
Intensity dependence of $V_{oc}$ probes bimolecular recombination

$$V_{oc} = \frac{1}{e} \left( E_{LUMO}^{Fullerene} - E_{HOMO}^{Polymer} - \Delta \right) - \frac{k_BT}{e} \ln \left( \frac{n_e n_h}{N_c^2} \right)$$

where $N_c$ = density of states in the band tails

Slope = 1

Bimolecular --- $s = 1$  
$(n_p \sim I)$

Monomolecular --- $s = 2$  
$(n_p \sim I^2)$
Temperature / intensity dependence probes the HOMO-LUMO difference

\[ V_{oc} = \frac{1}{e} \left( E_{\text{LUMO}}^{\text{Fullerene}} - E_{\text{HOMO}}^{\text{Polymer}} - \Delta \right) - \frac{k_B T}{e} \ln \left( \frac{n_e n_h}{N_c^2} \right) \]

\( V_{oc} \) reduced by \( \sim 0.3 \) V

\( (k_B T/e) \ln(I) \)

Fermi statistics:

T-dependence of \( E_F \)

Universal dependence

Five different

Semiconducting polymers
Introduce PC$_{84}$BM Traps

RECOMBINATION VIA INTENTIONALLY INTRODUCED TRAPS
Trap-assisted recombination

- Recombination via the trap state

\[ \delta V_{oc} = s \frac{kT}{e} \ln(I) \]

First-order (monomolecular) 
\[ s = 2 \]
Traps:

- Introduce first-order (monomolecular) recombination and decrease $V_{OC}$
- Reduce mobility
- Reduce $j_{SC}$ and prevent fast sweep out

Result: All parameters adversely affected: $V_{OC}$, $j_{SC}$, FF
Mobile carriers are swept out by the internal field

\[ V_{\text{int}} = V_{\text{bi}} - V \]

\[ v_{\text{drift}} \approx \mu E_{\text{int}} \approx \mu V_{\text{int}}/d \]

\[ \tau_{\text{sw}} = d^2/2\mu V_{\text{int}} \]

\[ \tau_{\text{sw}} \approx 10^{-7} \text{ s} \]

with \( \mu \approx 10^{-3} \text{ cm}^2/\text{Vs} \)
**Transient photocurrent in operating solar cell:**

**Competition between Sweep-out and Recombination**

\[
\text{Photoconductance} = \frac{\text{Current}}{\text{Internal voltage}}
\]

\[
V_{int} = V_{BI} - V
\]

When sweep-out is faster than recombination

--- high efficiency.
Internal field is well-defined even in the complex BHJ material

Photocurrent normalization by $V_{int} = V_{BI} - V$

Charge transport via drift.

PCDTBT:PC$_{70}$BM
Comparing lineshapes from 2 ps and 2 ms.

(a) Transient absorption spectra of a p-DTS(PTTh$_2$)$_2$:PC$_{70}$BM film. (b) Transient absorption spectra of a PCDTBT:PC$_{70}$BM film.

Left axis belongs to 2 ms measurements, (blue squares). Right axis belongs to 2 ps measurements, (red line).

Polaron lifetime can be very long when there are no electrodes and no sweep-out.
Selected area electron diffraction from a 200 nm area of neat $p$-DTS(PTTh$_2$)$_2$. 1$^{\text{st}}$ and 2$^{\text{nd}}$ order scattering $\pi$-$\pi$ peaks are Visible.

$\pi$ - $\pi$ Stacking (d = 3.48 A) with good inter-molecular overlap.

Formation of $\pi$ - and $\pi^*$- bands. Transport dominated by these $\pi$- bands. Excellent photoconductor.