Optimization of Conjugated-Polymer-Based Bulk Heterojunctions

J.C. (Kees) Hummelen

Molecular Electronics
Materials Science Centre Plus
University of Groningen, The Netherlands

GCEP Solar Energy Workshop
Oct. 18 – 18, 2004  Stanford University
Introduction, Morphology, Mobilities, Improving $V_{oc}$, Improving $I_{sc}$,

Opening the *box of Pandora*: from bilayer to mixture

Basic processes *in a PV cell*
Commonly used PPVs

- **EH**
- **MDMO-PPV**
- **MEH-PPV**
- **MDMO-PPV (OC$_1$C$_{10}$PPV)**
The standard fullerene acceptor

A highly processable methanofullerene
(50-80 weight % of the D:A blend!)

Available from Nano-C Inc. (Westwood, Mass)
nano-c.com
PCBM (PhCl) crystal structure

Fullerene moieties at < 10 Å in THREE dimensions
Spheres: orientation always OK!

Charge carrier mobility in PCBM

- (MDMO-PPV: holes \( \mu_h = 5 \times 10^{-7} \text{ cm}^2/\text{Vs} \))
- PCBM: electrons \( \mu_e = 2 \times 10^{-3} \text{ cm}^2/\text{Vs} \)
  (C\(_{60}\) films: \(8 \times 10^{-2} \text{ cm}^2/\text{Vs}\); C\(_{60}\) single crystals: 0.5 cm\(^2/\text{Vs}\))

i.e. PCBM does 4000 times better than MDMO-PPV!

Average hopping distance in PCBM \(\sim 3\) nm!

Charge carrier mobility in blend

- enhanced intermolecular interaction by adding PCBM.

- electron mobility increases due to the increase number of percolated pathways.

- more balanced transport: $\mu_e \approx 10 \times \mu_h$.

C. Melzer et al., Adv. Funct. Mat., (accepted)
M. Kemerink et al., Nano Lett., 2003, 3, 1191
Morphology: influence of spin cast solvent:

MDMO-PPV:PCBM

from toluene

from chlorobenzene
Morphology: influence of spin cast solvent:

Morphology control: compatibilizing with the PCBX series
Dropcasting using different acceptors

Gilch-PPV/PCBM
Toluene 1:4

Gilch-PPV/PCBDMO
Toluene 1:4

TEM Unfiltered

T. Martens, Z. Beelen, J. D’Haen, J. Manca, IMEC

GCEP2004
Dropcasting using different acceptors

**Gilch-PPV/PCBM**

Chlorobenzene 1:4

**Gilch-PPV/PCBDMO**

Chlorobenzene 1:4

T. Martens, Z. Beelen, J. D’Haen, J. Manca, IMEC

TEM Unfiltered
The photoinduced LUMO-LUMO electron transfer process (from excited donor)
Improving $V_{oc}$

is there some truth in this picture?
Soluble fullerene derivatives with varying acceptor strength

PCBM-[6,6]  EHO-Azafulleroid-[5,6]  EHO-Ketolactam
PCBM $E_{\text{red}}$ tuning

Joop Knol, Floris Kooistra

GCEP 2004
$V_{oc}$ versus $E_{\text{red}}$ acceptor in MDMO-PPV/acceptor cells (CB)
Higher fullerences: [70]PCBM

The photoinduced HOMO-HOMO electron transfer process (to excited acceptor)

~ ‘hole transfer’
IPR Fullerenes $C_{60}-C_{80}$ (calculated)
UV-Vis spectrum of [60]PCBM
Synthesis of [70]PCBM

85% (chiral)

15%
UV-Vis spectra of [60]PCBM and [70]PCBM

[60]PCBM:MDMO-PPV (4:1, w/w) and [70]PCBM:MDMO-PPV (4:1, w/w) (normalized)
All in toluene
PL decay of the fullerene emission at 720 nm of [70]PCBM:MDMO-PPV (4:1 w/w) films

Spun from chlorobenzene, o-xylene, and ODCB.
Yellow: pristine [70]PCBM film

PL quenching: 0, 30, 60, 95 %
AFM tapping mode height images

[70]PCBM:MDMO-PPV (4:1 w/w) films on glass

**CB**
- z-range = 86 nm
- rms roughness = 12 nm

**o-xylene**
- z-range = 37 nm
- rms roughness = 7 nm

**ODCB**
- z-range = 8.2 nm
- rms roughness = 1.0 nm
Spectral response (EQE) of ITO/PEDOT-PSS/fullerene:MDMO-PPV/LiF/Al cells

[70]PCBM:MDMO-PPV cells, spun from CB and ODCB
[60]PCBM: MDMO-PPV cell spun from CB; active areas = 0.1 cm²
I / V characteristics of [70]PCBM:MDMO-PPV devices

\[
\begin{align*}
V_{OC} &= 0.77 \text{ V} \\
I_{SC} &= 7.6 \text{ mA/cm}^2 \\
FF &= 0.51 \\
\eta &= 3.0 \% 
\end{align*}
\]


[70]PCBM Available from Nano-C Inc. (Westwood, Mass) nano-c.com
Morphology of the bulk heterojunction

- **Formation**
  phases, domain sizes, percolation, wetting, processing, annealing, thickness

- **Efficiency**
  exciton diffusion, charge separation, charge recombination, (balanced) mobilities

- **Stability**
  phase separation (crystallization), (photo-)chemistry
Some provoking remarks

- No theoretical grounds for inferior efficiency of molecular devices
- Higher efficiency $\Rightarrow$ improved stability
- Molecular materials offer infinite architectural opportunities (even for 3rd generation tricks)
- General: 225M$ is very attractive! Beware of groups that not have a real focus on sustainable energy? (PV in this case)
Acknowledgments

- Joop Knol
- Minze T. Rispens
- Floris Kooistra
- Luis Sanchez
- Jan Alma
- Patrick van ‘t Hof
- Valentin Mihailetechi
- Paul Blom (RuG)
- Paul van Hal
- René Janssen (TU/e)
- Jan M. Kroon
- Wiljan Verhees
- Martijn Wienk (ECN)
- Christoph Brabec (now Siemens/Konarka)
- Serdar Sariciftci (Uni Linz)
- David Kronholm
- Henning Richter (Nano-C)