PCBM-solvent Condensed Phase

Speaker: Chun I Wang (王俊壹)

2013.11.25 & 12.09
Introduction

[6,6]-phenyl-C61-butyric acid methyl ester
PCBM

melting point: 560K

Fullerene
C_{60}

sublimation point: 873K
Introduction

Organic solar cells

PCBM solid phase

Amorphous?
Crystalline?

PCBM-solvent condensed phase

Quenching

Solution state

PCBM

Solvents
Outline

- Co-crystals of PCBM with remnant solvent
- Thermal history-dependent structure of PCBM
- Electron mobility for various PCBM packing motifs
- Anisotropic molecular packing of PCBM
- Conclusion
Co-crystals of PCBM with remnant solvent

**Chloroform (CF)**
- Monoclinic crystal (2D layer structure)
- Four CF and four PCBM

**ortho-dichlorobenzene (oDCB)**
- Monoclinic crystal (2D layer structure)
- Four oDCB and four PCBM

**Chlorobenzene (CB)**
- Triclinic crystal (3D network)
- Two CB and four PCBM

---

**Table 1: Photovoltaic parameters of MDMO-PPV : PCBM (1 : 4) devices**

<table>
<thead>
<tr>
<th>% MDMO-PPV</th>
<th>$V_{oc}$/mV</th>
<th>$I_{sc}$/mA cm$^{-2}$</th>
<th>FF</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ODCB</td>
<td>796</td>
<td>4.46</td>
<td>0.5171</td>
<td>2.294</td>
</tr>
<tr>
<td>CB</td>
<td>802</td>
<td>5.37</td>
<td>0.5628</td>
<td>3.034</td>
</tr>
<tr>
<td>Xylenes</td>
<td>816</td>
<td>4.16</td>
<td>0.4922</td>
<td>2.09</td>
</tr>
</tbody>
</table>

$I$ at $-2$ V/mA cm$^{-2}$, $I$ at $+2$ V/mA cm$^{-2}$, Area/mm$^2$.
Thermal history-dependent structure of PCBM

oDCB-PCBM co-crystal
(2D layer structure)

CB-PCBM co-crystal
(3D network)

The melting point for pure PCBM is around 560 K.

Orientational time-correlation functions

PCBM

oDCB

PCBM

CB
Thermal history-dependent structure of PCBM

**oDCB-PCBM co-crystal**
(2D layer structure)

**CB-PCBM co-crystal**
(3D network)

oDCB molecules represent a element of the co-crystal scaffold.

CB molecules occupy the voids left within a well interconnected and inherently stable PCBM-only framework.
Thermal history-dependent structure of PCBM

- oDCB-PCBM co-crystals (2D layer structure)
- Solvent-free crystal structure (n-PCBM) (3D network)

Solvent evaporation

Thermal annealing
Electron mobility for various PCBM packing motifs

- oDCB-PCBM co-crystal (2D layer structure)
- CB-PCBM co-crystal (3D network)

![Graph showing mobility for different crystal structures](image)

- Triclinic
  - (CB)
  - (No solvent)
- Monoclinic
  - (oDCB)
  - (No solvent)
- Amorphous

Axes: X, Y, Z
Anisotropic molecular packing of PCBM in hexagonal nanocrystals obtained by solvent vapor annealing

PCBM crystalline aggregates

Deposited and annealed with chloroform

PCBM molecules can aggregate in a highly **anisotropic lattice** with a well-defined stacking of pairs of C$_{60}$ layers separated by a layer of solvent molecules.
Conclusion

Two type of PCBM crystals were illustrate: 2D layer structure and 3D network. The choice of solvent and evaporating process significantly influences the formation of the crystalline.

The choice of solvent, and the presence of remnant solvent molecules post deposition, can promote a lowering of the temperature required to rearrange the PCBM molecules in the solid state.

Tuning the microphases of polymer and fullerene might improve the electronic process. However, it deeply depends on what depth of understanding we could reach for these diverse systems.
References

- Influence of the solvent on the crystal structure of PCBM and the efficiency of MDMO-PPV:PCBM ‘plastic’ solar cells

- Molecular dynamics simulations of the solvent- and thermal history-dependent structure of the PCBM fullerene derivative

- Anisotropic molecular packing of soluble C₆₀ fullerenes in hexagonal nanocrystals obtained by solvent vapor annealing
  R. Colle et al, Carbon 50, 2012, 1332-1337

- Materials-scale implications of solvent and temperature on [6,6]-Phenyl-C₆₁-butyric acid methyl ester (PCBM): a theoretical perspective

- Solvent-free phenyl-C₆₁-butyric acid methyl ester (PCBM) from clathrates: insights for organic photovoltaics from crystal structures and molecular dynamics

- Effect of packing on the cohesive and electronic properties of methanofullerene crystals