Polymer-Fullerene Bulk Heterojunction Solar Cells

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1. The Need for Bulk Heterojunction

- In organic polymer-based photovoltaic devices, the primary effect upon exposure to solar light is **a photoinduced electron** transfer between donor- and acceptor-type semiconducting polymers or molecules

⇒ boosts **the photogeneration** of free charge carriers

• In combining electron-donating (*p*-type) and electron-accepting (*n*-type) materials in the active layer of a solar cell, care must be taken that **excitons** created in either material can diffuse to the interface, **to enable charge separation**.

1. The Need for Bulk Heterojunction

- Due to their **short lifetime** and **low mobility**,
  the diffusion length of excitons in organic semiconductors is limited to about 10 nm only.

  ⇒ important condition on efficient charge generation

- A 20 nm double layer of donor and acceptor materials would not be optically dense, allowing most photons to pass freely.

- Solution

Mix the *p* and *n*-type materials and rely on the intrinsic tendency of polymer materials to phase-separate on a nanometer
→ junctions throughout the bulk of the material are created

1. The Need for Bulk Heterojunction

- Photogenerated charges must be able to migrate to the collecting electrodes through this intimately mixed blend.

- These materials should be preferably mixed into a bicontinuous, interpenetrating network.

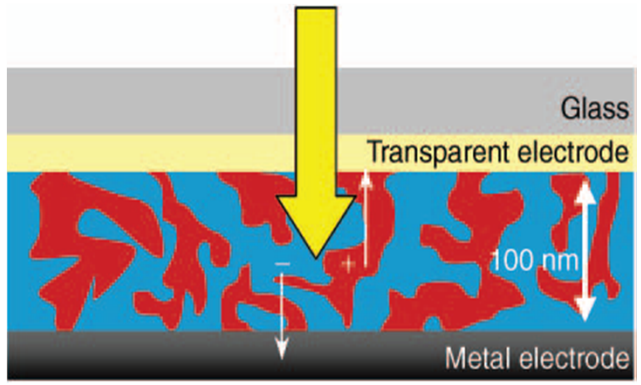
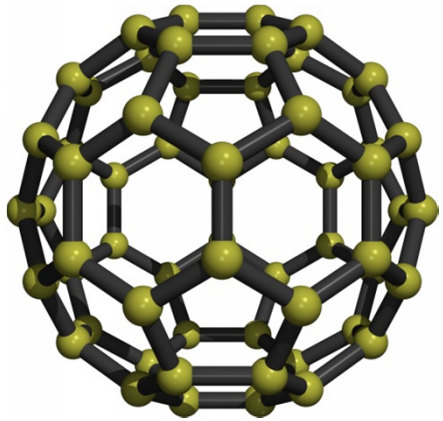


Figure 1. Schematic representation of a bulk heterojunction solar cell, showing the phase separation between donor(red) and acceptor (blue) materials.

2. Semiconducting Polymer-Fullerene Blends

- One of the most promising combinations of materials is a blend **of a semiconducting polymer as a donor and a fullerene (C60 rivative) as acceptor.**



[C 60]

• The **lifetime** of the resulting charge separated state in these blends **extends into the millisecond time domain**.

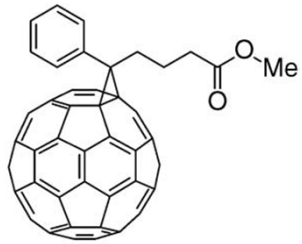
⇒ the photogenerated charge carriers to diffuse away from the interface, to be collected in an external circuit at the electrodes.

2. Semiconducting Polymer-Fullerene Blends

- A breakthrough to truly appealing power conversion efficiencies exceeding 2.5% under simulated AM 1.5 illumination

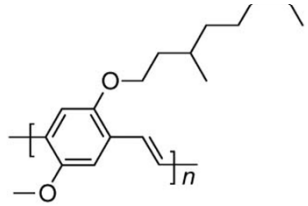
  ⇒ **bulk heterojunction solar cell**

  (MDMO-PPV as a donor / PCBM as an acceptor)



PCBM

- In PCBM, the fullerene cage carries a substituent that prevents extensive crystallization upon mixing with the conjugated polymer and enhances the miscibility.



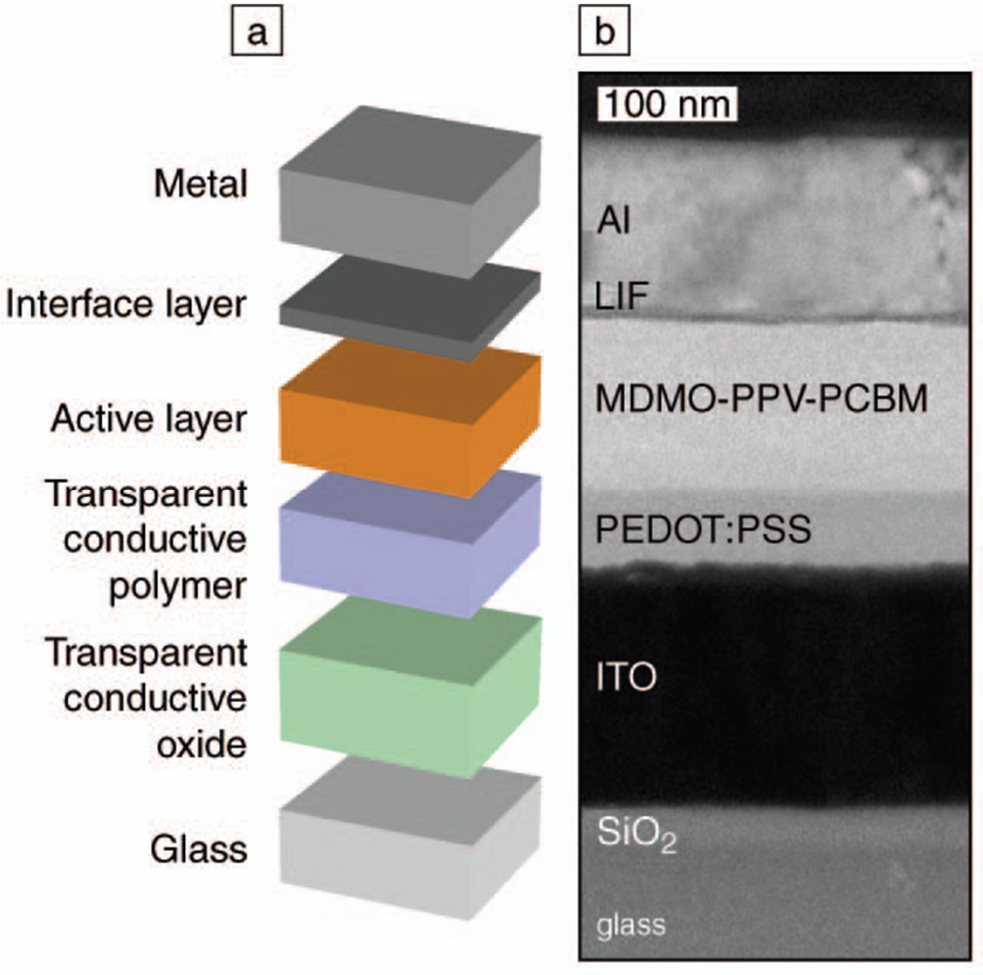
MDMO-PPV

- In these 2.5% efficiency cells,
  the photoactive composite layer is sandwiched between two electrodes with different work functions.

2. Semiconducting Polymer-Fullerene Blends

(a) Schematic layout of the device architecture of a polymer–fullerene bulk heterojunction solar cell.

(b) Transmission electron microscopy (TEM) image of a thin slab of an actual device, showing the individual layers: glass, SiO2, indium tin oxide (ITO), PEDOT:PSS, MDMO-PPV:PCBM (1:4 by wt), LiF, and Al layers.

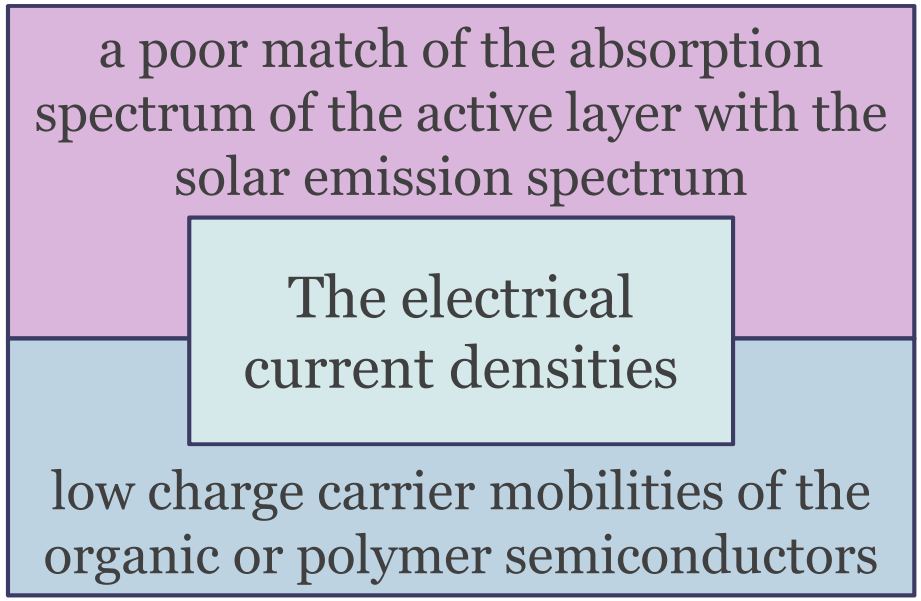


2. Semiconducting Polymer-Fullerene Blends

- The crucial step that **improved the performance** came from **using a special solvent in the spin coating of the active layer**

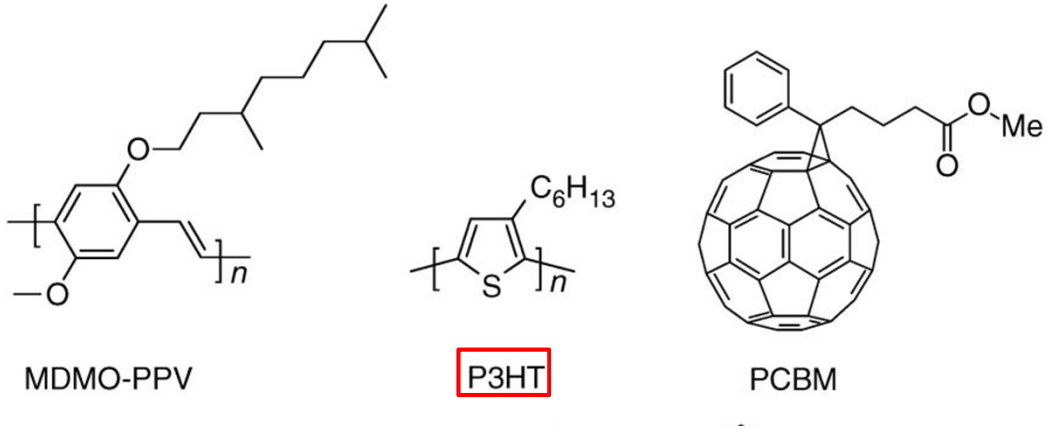
  ⇒ improve the nanoscale morphology for charge generation and transport.

3. Recent Advances in Performance



- the use of P3HT, which is known to have a high charge carrier mobility and reduced bandgap, as compared with MDMO-PPV, has been considered for use in solar cells in combination with PCBM.

3. Recent Advances in Performance



MDMO-PPV P3HT PCBM

➢ P3HT/PCBM blends indeed provide an increased performance, compared with MDMO-PPV.

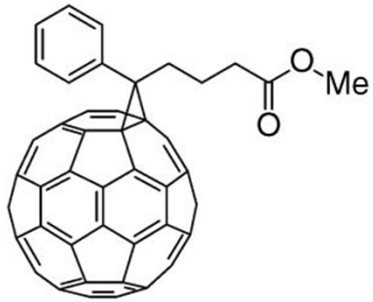
- After spin coating of the active layer and deposition of the aluminum top electrode

⇒ treating P3HT/PCBM solar cells with a potential higher than the open-circuit voltage and a temperature higher than the glass-transition temperature *T*g led to an improved overall efficiency.

3. Recent Advances in Performance

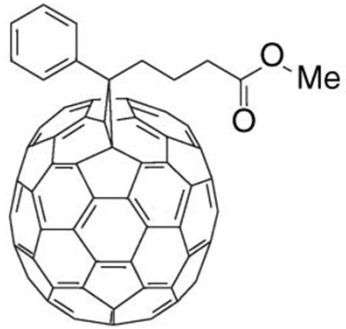
- It is important to note that PCBM-which may amount to as much as 75% of the weight of the photoactive layer-has a very low absorption coefficient in the visible region of the spectrum and, hence, provides a relatively small contribution to the photocurrent.

• The **low absorption of C60** derivatives is due to their **high degree of symmetry.**
⇒ which makes many of **the low-energy transitions forbidden** and hence of **low intensity**.



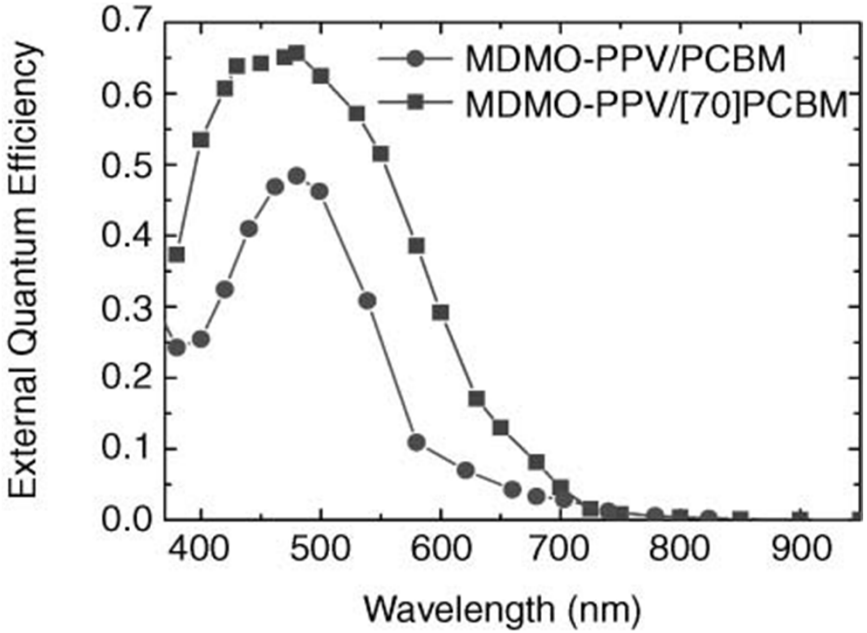
PCBM

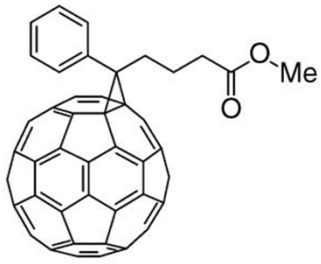
• When the C_{60} moiety is replaced by a less symmetrical fullerene, such as C_{70}
⇒ dramatic increase in light absorption can be expected.



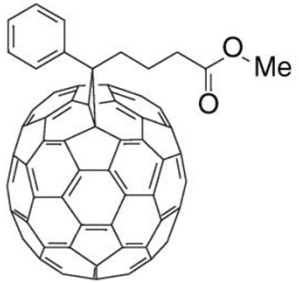
[70]PCBM

3. Recent Advances in Performance

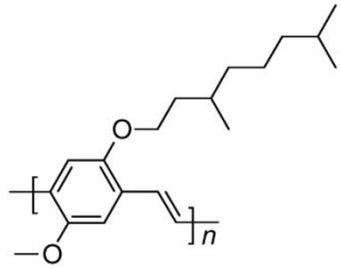




PCBM



[70]PCBM



MDMO-PPV

- when [70]PCBM was used in combination with MDMO-PPV instead of PCBM

⇒ the external quantum efficiency increased from 50% to 65%,
the current density of the solar cell increased by 50%,
power conversion efficiency increased to 3.0%.

4. Future Directions for Improving Efficiencies

- New combinations of materials being developed in various laboratories focus on improving the three parameters that determine the energy conversion efficiency of a solar cell.

1. Open-circuit voltage (*V*oc)
2. Short-circuit current (*J*sc)
3. Fill factor

4. Future Directions for Improving Efficiencies

1. Open-circuit voltage (*Voc*)

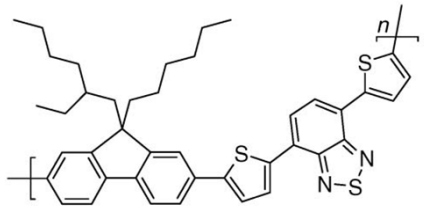
- The open-circuit voltage of bulk heterojunction polymer photovoltaic cells

  ⇒ The Highest occupied molecular orbital (HOMO)
  the lowest unoccupied molecular orbital (LUMO)

- In most polymer/fullerene solar cells, the positioning of these band levels of donor and acceptor is such that up to 0.4–0.8 eV is lost in the electron transfer reaction.

⇒ *PFDTBT*

*V*oc 1.04 V in combination with PCBM, as compared with 0.8–0.9 V for MDMO-PPV and 0.5-0.6 V for P3HT



PFDTBT

4. Future Directions for Improving Efficiencies

2. Short-circuit current (*Jsc*)

- the absorption of more photons.

⇒ By increasing the layer thickness and by shifting the absorption spectrum of the active layer to longer wavelengths.

- The use of polymers such as P3HT

⇒ increase in film thickness from the usual 100 nm to well above 500 nm, without a loss of current.

- Because the open circuit voltage of bulk heterojunction solar cells is governed by the HOMO of the donor and the LUMO levels of the acceptor, the most promising strategy seems to be to lower the bandgap by adjusting the other two levels

4. Future Directions for Improving Efficiencies

3. Fill factor

- a high fill factor can be obtained when the charge mobility of both charges is high.

- Currently, the fill factor is limited to about 60% in the best devices, but values of up to 70% have been achieved recently.

5. Conclusion

- Even more important for the future is that a vibrant community of industrial and university scientists and engineers has assembled in this area to actively pursue the quest for new materials and device architectures, aiming at increasing the efficiency to 8-10%.

Thank you