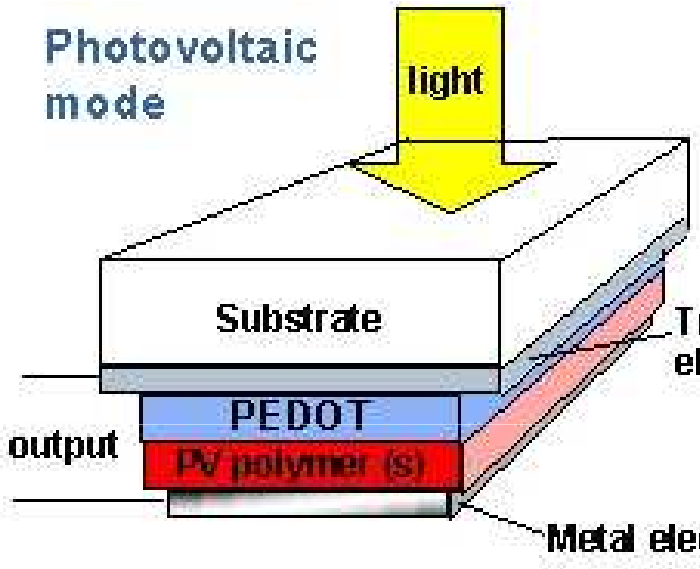
Outlines

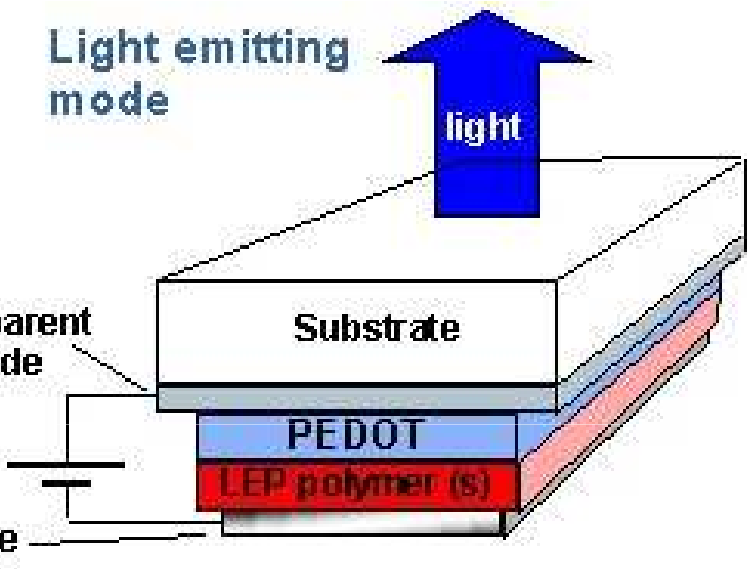
- **History of Conjugated Polymers**
- **Electronic Structures of Conjugated Polymers**
- **Polymer Light-emitting Diodes**
- **Polymer-based Thin Film Transistors**
- **Polymer-based Photovoltaics**
- **Polymers for Memory devices**

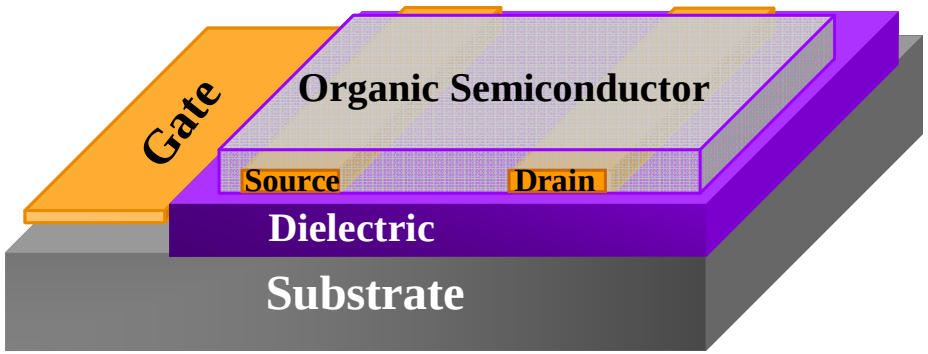
Device Applications of Donor-Acceptor Conjugated Polymers in My Group

Polymer Solar Cells

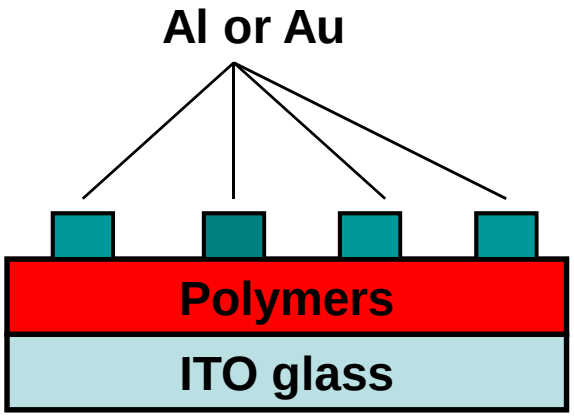


Polymer Light-emitting Diodes





Polymer Thin Film Transistors



Polymer Memory Devices

Humanity's core problems in 2050

1. ENERGY
2. WATER
3. FOOD
4. ENVIRONMENT
5. POVERTY
6. TERRORISM & WAR
7. DISEASE
8. EDUCATION
9. DEMOCRACY
10. POPULATION

2003 6.3 Billion People
2050 8-10 Billion People

Source: Richard Smalley, Energy & Nanotechnology Conference, Houston; Christoph Brabec; Konarka .

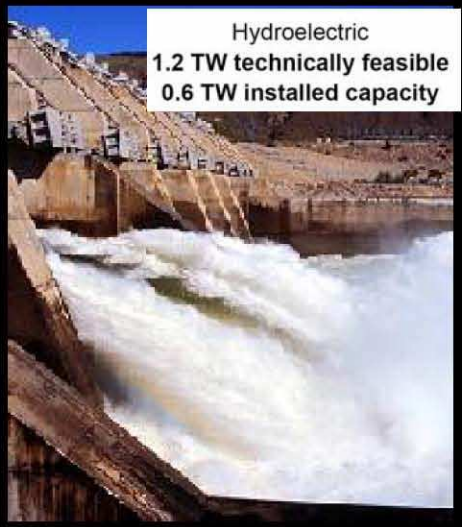
能源之種類

- 傳統能源：
  - 石化燃料(煤[230]、石油[45]、天然氣[60])
  - 火力
  - 核能[鈾：75]

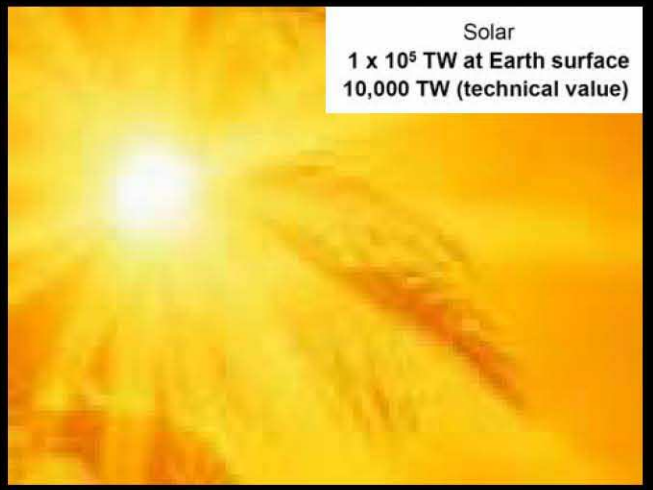
註：[ ] 為預估使用年限，單位--年

- 再生能源：
  - 太陽能(太陽光發電、太陽熱能)
  - 風力發電
  - 生質能(廢棄物發電、沼氣發電、生質物轉化、生質物汽化發電.....)
  - 地熱發電
  - 小水力發電
  - 海洋能(波浪發電、潮汐發電、海洋溫差)

Renewable energies



Energy gap
~ 14 TW by 2050
~ 33 TW by 2100



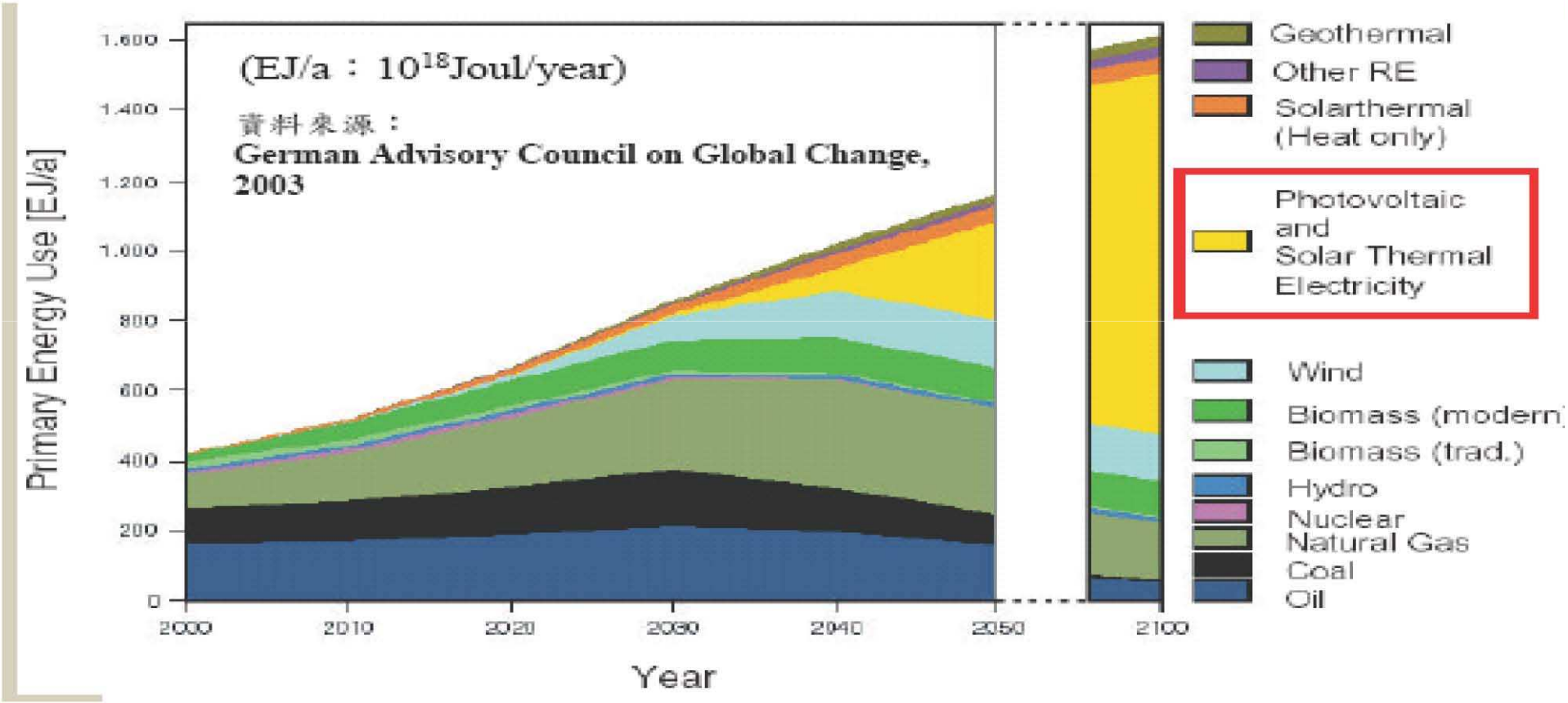
Credit: Christoph Brabec, Konarka

太陽光發電(光伏發電, Photovoltaic, PV)之特點

1. 太陽電池通常為一種固態半導體元件，將光能直接轉換為(直流)電能，但本身不儲存能量。
2. 太陽電池使用方便、無廢棄物、無污染、無轉動部份、無噪音、可阻隔輻射熱、或可設計為半透光。
3. 太陽電池模板壽命長久，可達二十年以上 。
4. 太陽電池外型尺寸可隨意變化，應用廣泛(小至消費性產品--如計算機，大至發電廠皆實用)。
5. 太陽電池未來與建築物結合，將可普及化。
6. 太陽能是免費、取之不盡、用之不竭之潔淨能源，但必須找到使用之方法。

Future Trend-- Renewable Energy

太陽光熱發電將是未來電源供應主力



Source： German Advisory Council on Global Change, 2003

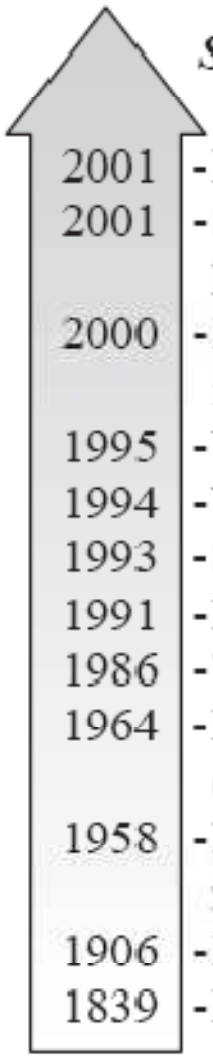
太陽每天照射到地表的能量，超過全人類30年能源需求！

太陽能發電之重要發展歷史

- 1954年Bell Labs發展出矽太陽電池
  (Chapin等人，轉換效率約6%)
- 1958年開始太空應用(GaAs)

- 1970年開始太陽光發電系統地面應用(Si) (能源危機)
- 1976年Carlson製作出第一個非晶薄膜太陽電池
- 1980年消費性薄膜太陽電池應用(a-Si, CdS/CdTe)
- 1990年與公用電力併聯之太陽光發電系統技術成熟
  (Grid-Connected PV System, Si) (電力電子技術)
- 1992年起歐美、日各國推動PV補助獎勵
- 2000年建材一體型太陽電池應用(BIPV)

History of Organic Solar Cells



Some important milestones in the development of organic solar cells

2001 - Ramos used *double-cable* polymers in PV cells.

2001 - Schmidt-Mende made a self-organised liquid crystalline solar cell of hexabenzocoronene and perylene.

2000 - Peters / van Hal used oligomer-C_{60} dyads/triads as the active material in PV cells.

1995 - Yu / Hall made the first bulk polymer/polymer heterojunction PV.

1994 - Yu made the first bulk polymer/C_{60} heterojunction PV.

1993 - Sariciftci made the first polymer/C_{60} heterojunction device.

1991 - Hiramoto made the first dye/dye bulk heterojunction PV by co-sublimation.

1986 - Tang published the first heterojunction PV device.

1964 - Delacote observed a rectifying effect when magnesium phthalocyanines (CuPh) was placed between two different metalelectrodes.

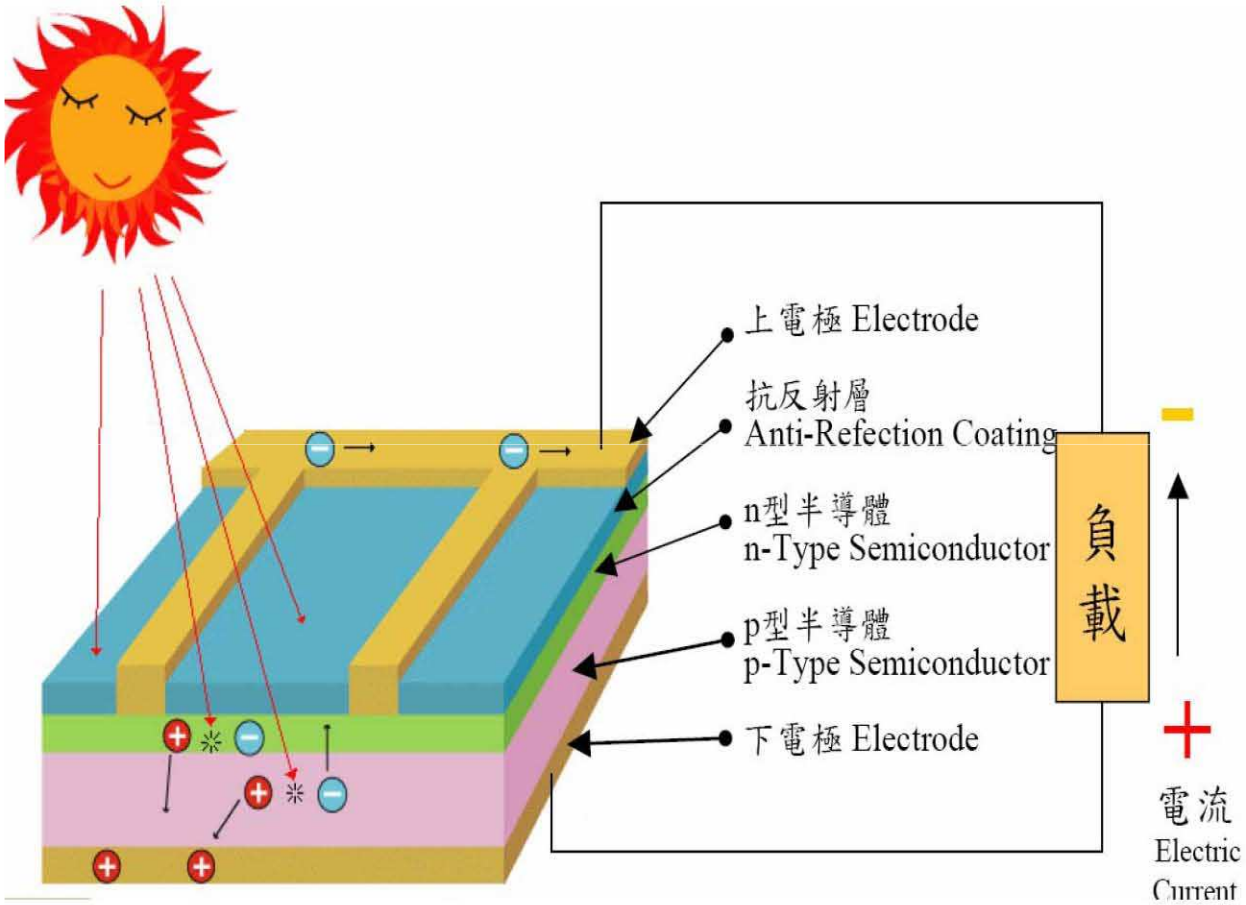
1958 - Kearns and Calvin worked with magnesium phthalocyanines (MgPh), measuring a photovoltage of 200 mV.

1906 - Pochettino studied the photoconductivity of anthracene.

1839 - Becquerel observed the photoelectrochemical process.

Solar Energy Materials & Solar Cells 2004, 83, 125

太陽能發電(Photovoltaic)原理



- 太陽電池是以P 型與N型半導體材料接合構成的裝置。
- 當陽光照射太陽電池時，半導體材料吸收光子會產生電子-電洞對。
- 分離正電荷(Hole)、負電荷(Electron)會分別往正(P型)、負(N型)極方向移動並且聚集。
- 正、負極接上負載時，將有電流流出，可以對負載作功(燈泡會亮、馬達會轉)。

太陽能電池種類

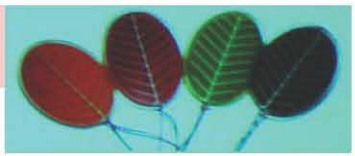
- Solar Cells
  - Silicon
    - Bulk
      - Single Crystalline
      - Multi Crystalline
    - Thin Film (a-Si; uc-Si)
  - Compound
    - GaAs
    - CdSe, CdTe, $CuInGaSe_2$
  - Organic
    - Conducting Polymer
    - Small molecules
    - Dye Sensitized

η :12~20%

η :10~18%

η : 6~8%，應用消費性產品、玩具等

η : 18-30 % (應用於太空或聚光型 PV 系統)



otential high efficiency
ow cost
ght weight to be portable
exible is highly feasible
rge area
een process

Technology Push

Highest Solar Cell Efficiency Tables until 2006. 04

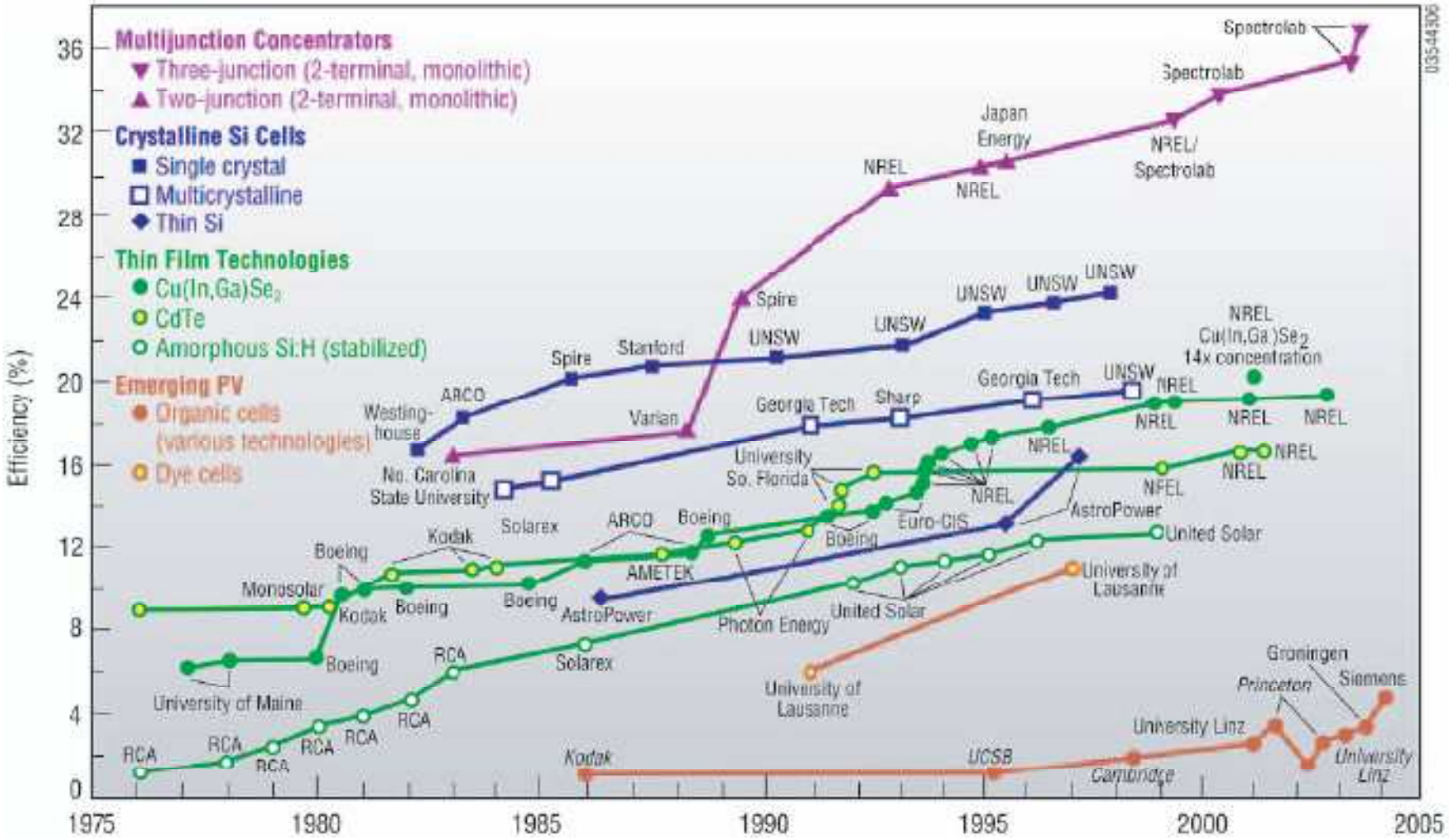
Table I. Confirmed terrestrial cell and submodule efficiencies measured under the global AM1.5 spectrum (1000 Wm^{-2}) at 25°C

Classification[a]	Effic.[b] (%)	Area[c] (cm2)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF[d] (%)	Test Centre[e] (and Date)	Description
Silicon							
Si (crystalline)	24.7 ± 0.5	4.00 (da)	0.706	42.2	82.8	Sandia (3/99)	UNSW PERL[14]
Si (multicrystalline)	20.3 ± 0.5	1.002 (ap)	0.664	37.7	80.9	NREL (5/04)	FhG-ISE[15]
Si (thin film transfer)	16.6 ± 0.4	4.017 (ap)	0.645	32.8	78.2	FhG-ISE (7/01)	U. Stuttgart (45 μm thick)[16]
Si (thin film submodule)	**9.4 ± 0.3**	**94.9 (ap)**	**0.493[f]**	**26.0[f]**	**73.1**	**Sandia (4/06)**	**CSG Solar (1–2 μm on glass; 20 cells)[5]**
III–V Cells							
GaAs (crystalline)	25.1 ± 0.8	3.91 (t)	1.022	28.2	87.1	NREL (3/90)	Kopin, AlGaAs window[17]
GaAs (thin film)	24.5 ± 0.5	1.002 (t)	1.029	28.8	82.5	FhG-ISE (5/05)	Radboud U., NL[18]
GaAs (multicrystalline)	18.2 ± 0.5	4.011 (t)	0.994	23.0	79.7	NREL (11/95)	RTI, Ge substrate[19]
InP (crystalline)	21.9 ± 0.7	4.02 (t)	0.878	29.3	85.4	NREL (4/90)	Spire, epitaxial[20]
Thin Film Chalcogenide							
CIGS (cell)	18.4 ± 0.5[g]	1.04 (ap)	0.669	35.7	77.0	NREL (2/01)	NREL, CIGS on glass[21]
CIGS (submodule)	16.6 ± 0.4	16.0 (ap)	0.661[f]	33.4[f]	75.1	FhG-ISE (3/00)	U. Uppsala, 4 serial cells[22]
CdTe (cell)	16.5 ± 0.5[g]	1.032 (ap)	0.845	25.9	75.5	NREL (9/01)	NREL, mesa on glass[23]
Amorphous/Nanocrystalline Si							
Si (amorphous)[h]	9.5 ± 0.3	1.070 (ap)	0.859	17.5	63.0	NREL (4/03)	U. Neuchatel[24]
Si (nanocrystalline)	10.1 ± 0.2	1.199 (ap)	0.539	24.4	76.6	JQA (12/97)	Kaneka (2 μm on glass)[25]
Photochemical							
Dye sensitised	10.4 ± 0.3	1.004 (ap)	0.729	21.8	65.2	AIST (8/05)	Sharp[26]
Dye sensitised (submodule)	**6.3 ± 0.2**	**26.5 (ap)**	**6.145**	**1.70**	**60.4**	**AIST (8/05)**	**Sharp[6]**
Organic							
Organic polymer[i]	**3.0 ± 0.1**	**1.001 (ap)**	**0.538**	**9.68**	**52.4**	**AIST (3/06)**	**Sharp, fullerene derivative[7]**
Multijunction Devices							
GaInP/GaAs/Ge	32.0 ± 1.5	3.989 (t)	2.622	14.37	85.0	NREL (1/03)	Spectrolab (monolithic)
GaInP/GaAs	30.3	4.0 (t)	2.488	14.22	85.6	JQA (4/96)	Japan Energy (monolithic)[27]
GaAs/CIS (thin film)	25.8 ± 1.3	4.00 (t)	—	—	—	NREL (11/89)	Kopin/Boeing (4 terminal)[28]
a-Si/μc-Si (thin submodule)[j]	11.7 ± 0.4	14.23 (ap)	5.462	2.99	71.3	AIST (9/04)	Kaneka (thin film)[29]

Prog. Photovolt: Res. Appl. 2006; 14:455–461

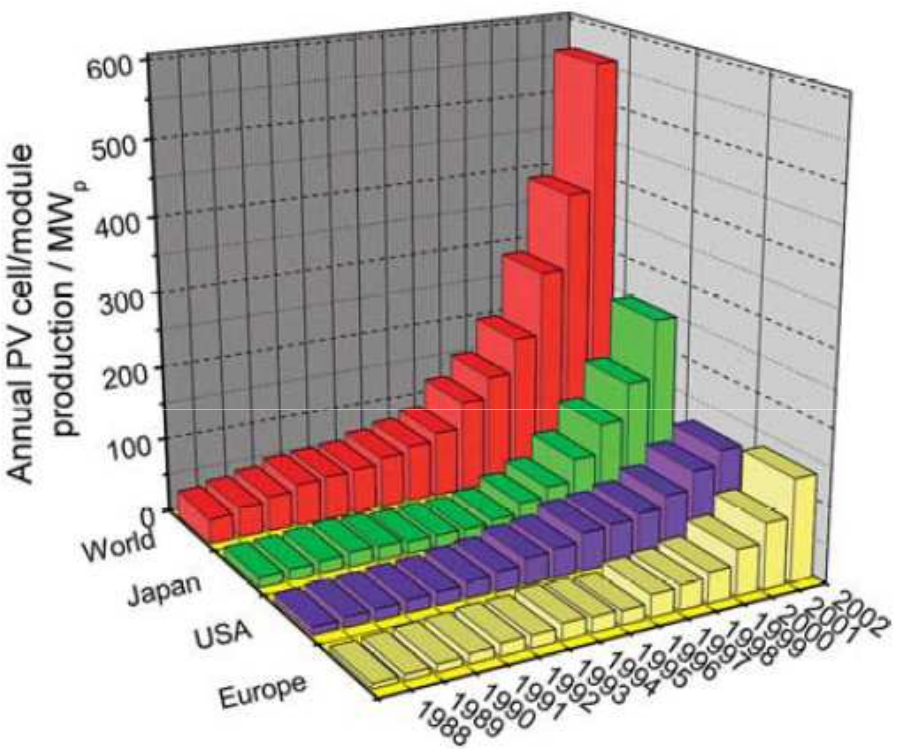
Efficiency of Photovoltaic Devices

Measured Solar Cell Efficiency from 1975 to the present

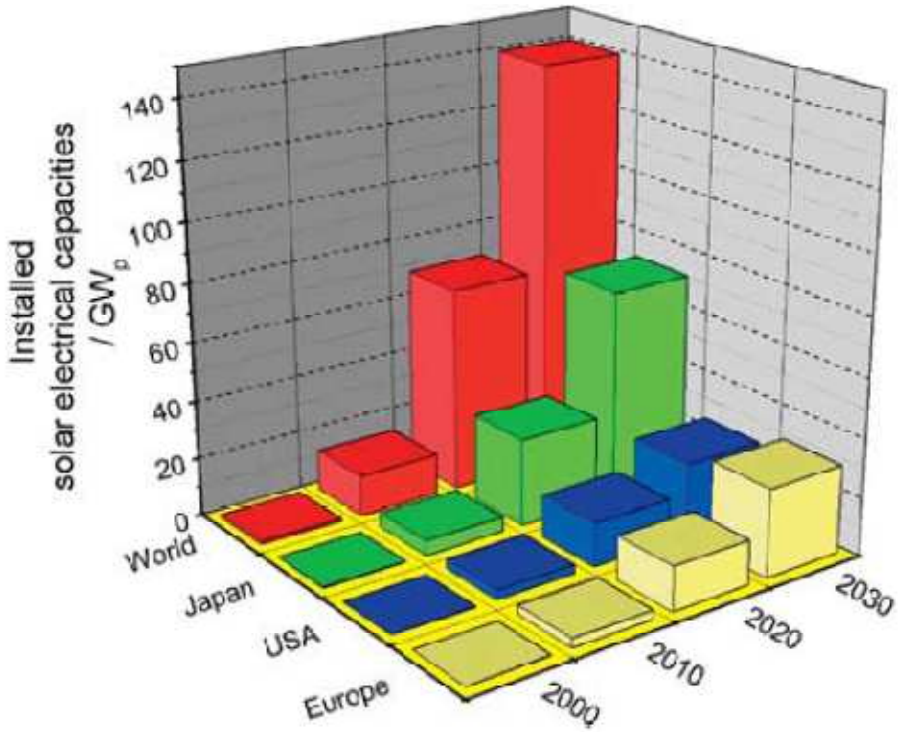


From NREL, USA

Requirement Trends of the Photovoltaic Industry



Annual PV cell/module production

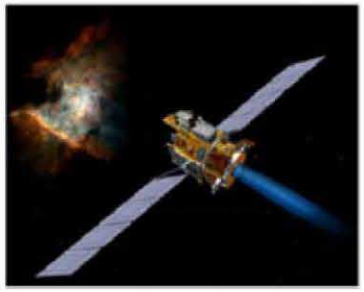


Estimation of present and future installed solar capacities

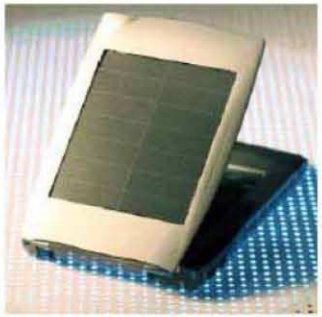
Proceeding of the IEEE 2005, 93, 1429

太陽光發電之應用領域

- 太空用發電系統



- 偏遠地區發電系統
  (山區、離島、....)
- 交通工具之電源(車、船、飛機、飛行船....)
- 交通標誌、號誌之電源



- 攜帶式電源
- 住宅用電力系統
- 產業工商用電力系統
- 緊急防災用電力系統
- 消費性電子產品之電源(手錶、時鐘、電子計算機、充電器、燈、玩具)
- 發電廠

Solid State Organic Solar Cells

Photovoltaics

- **Optical power ⇒ electrical power**
- FIGURES OF MERRIT:
  - Power conversion efficiency
  - Full solar intensities
  - Reliability

High absorption in the visible spectrum

Have relaxed deposition requirements

can be manufactured in a low cost process

can be grown on thin and flexible substrate

can add value to existing product

Challenge!

Current power conversion efficiencies are too low for commercial implementation

有機太陽光電技術

Organic solar cells : three types

- Dye sensitized solar cells: Electrochemical cells

- Small molecule organic solar cells: Made by vacuum deposition

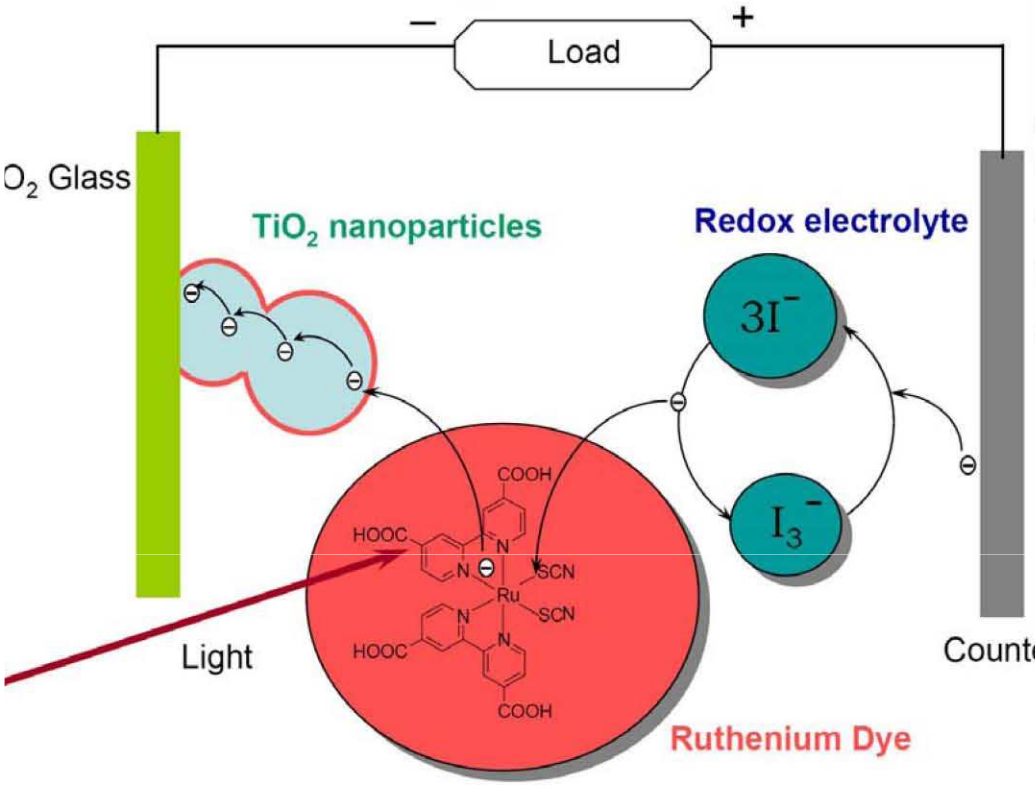
- Polymer solar cells: Made by solution, low temperature processing

Each of these cells face more or less the same challenges:

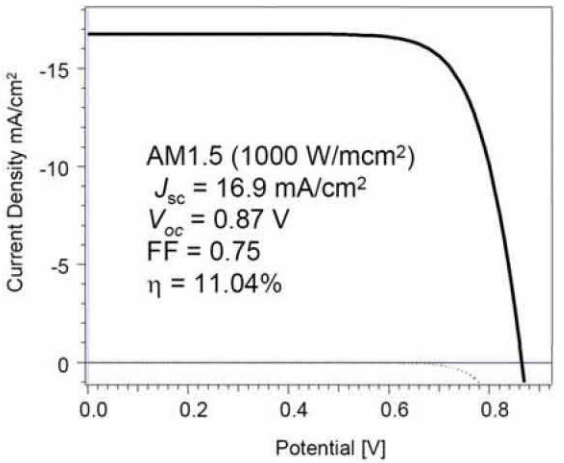
Physical cell !!

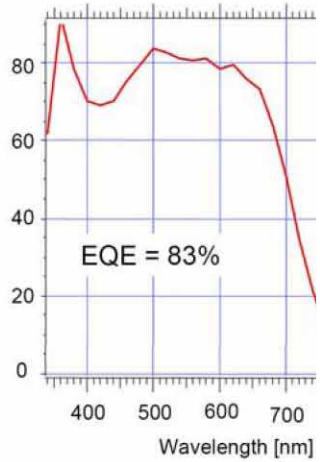
1. Increase power conversion efficiency
2. Increase stability
3. Develop a technology for large areas

Dye-sensitized TiO_2 solar cell operation principle



Best performance for a single cell so far



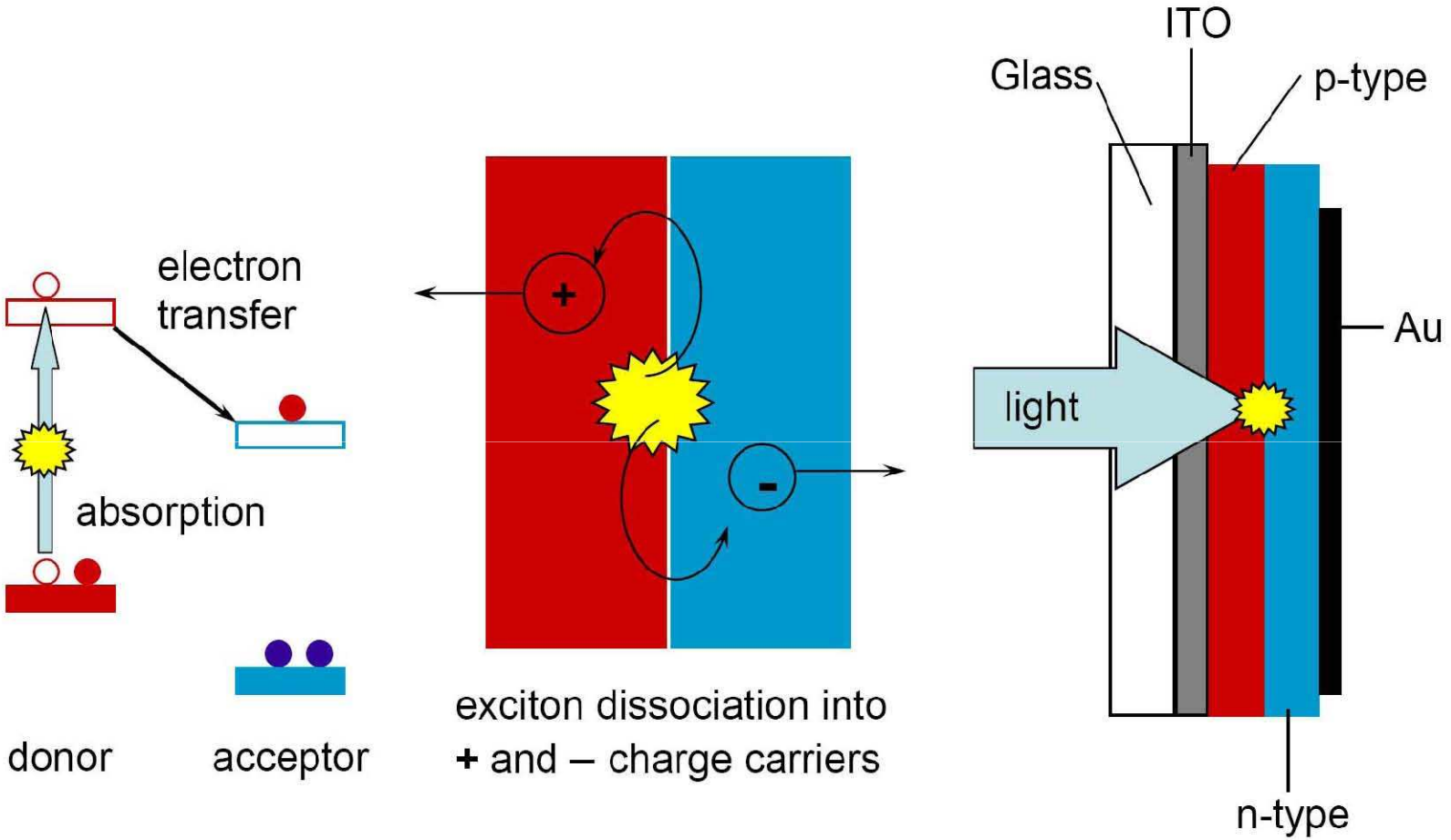


Photocurrent action spectrum obtained with the N719 dye attached to 16 + 4 μm nanocrystalline TiO2 film

M. Grätzel, Nature 1991, ***353,*** *737.*

Anode:	$S + h\nu \rightarrow S^*$	*Absorption*
	$S^* \rightarrow S^+ + e^-(TiO_2)$	*Electron injection*
	$2S^+ + 3I^- \rightarrow 2S + I_3^-$	*Regeneration*
Cathode:	$I_3^- + 2e^-(Pt) \rightarrow 3I^-$	
Cell:	$e^-(Pt) + h\nu \rightarrow e^-(TiO_2)$	

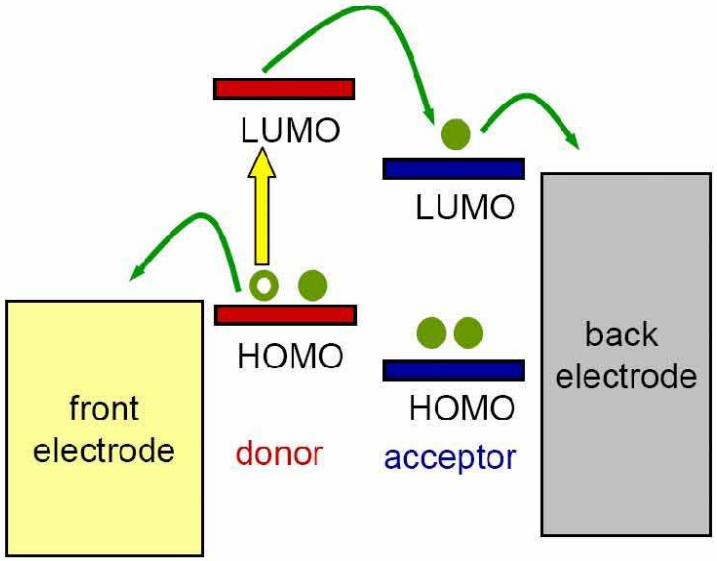
Organic double layer p/n cell

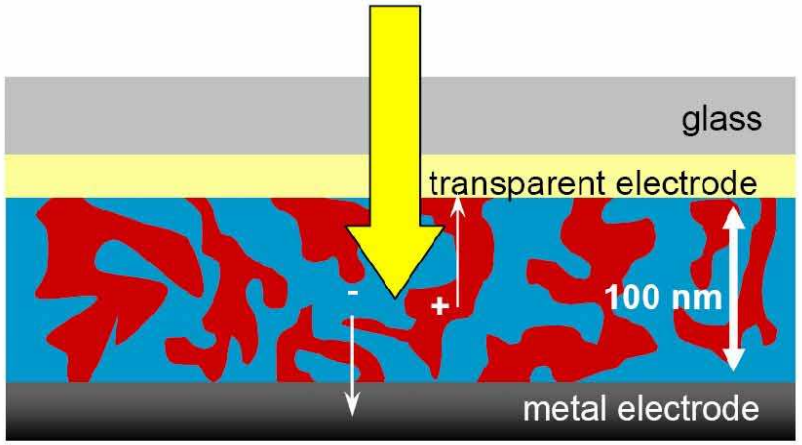


*C. W. Tang, Appl. Phys. Lett. 1985, **48**, 183.*

Bulk heterojunction solar cells

Charge separation in nanostructured composite organic semiconductors

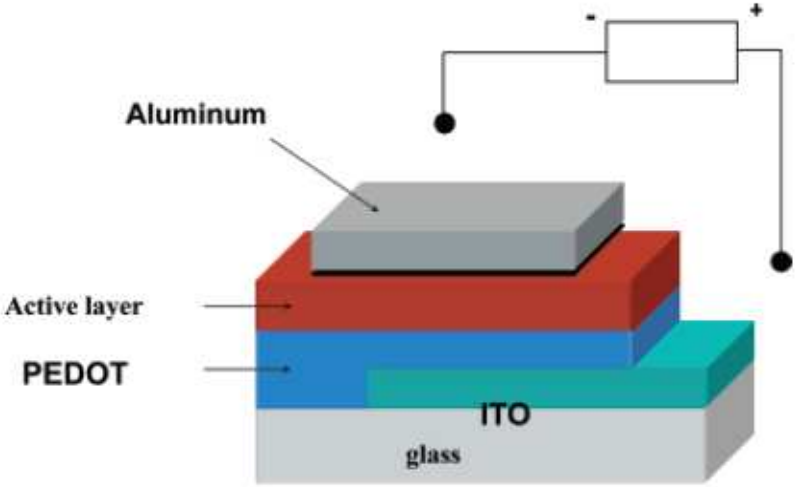


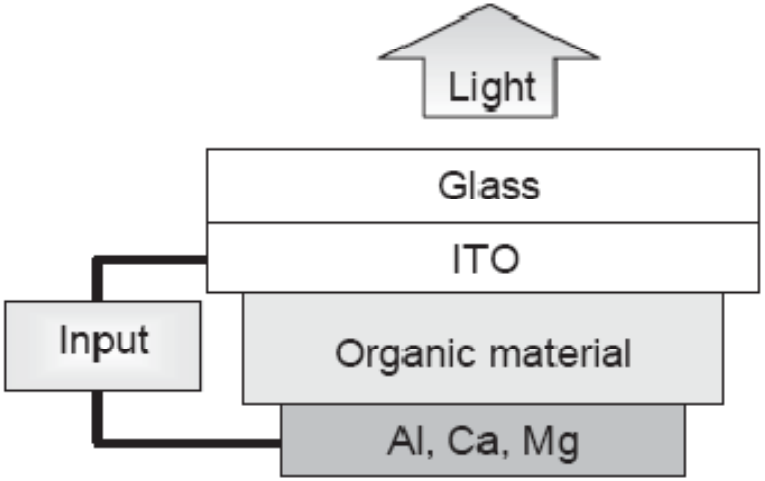


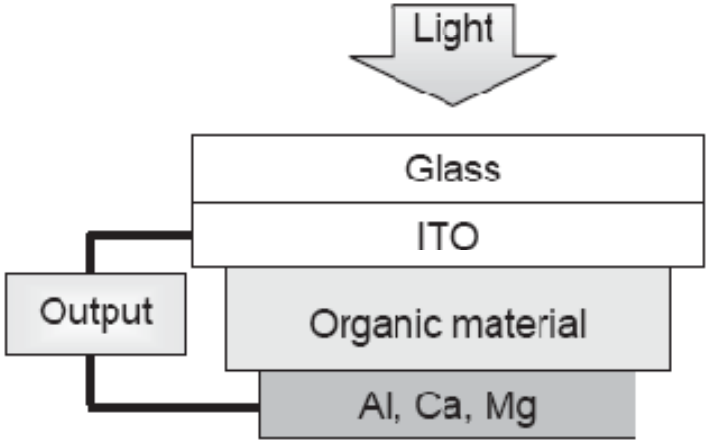
nanoscopic mixing of donor and acceptor to overcome ~10 nm exciton diffusion length

R. H. Friend et al., Nature 1995, ***376****, 498*
A. J. Heeger et al., Science 1995, ***270****, 1789*

Structures and Principles of LED & Photovoltaic mode





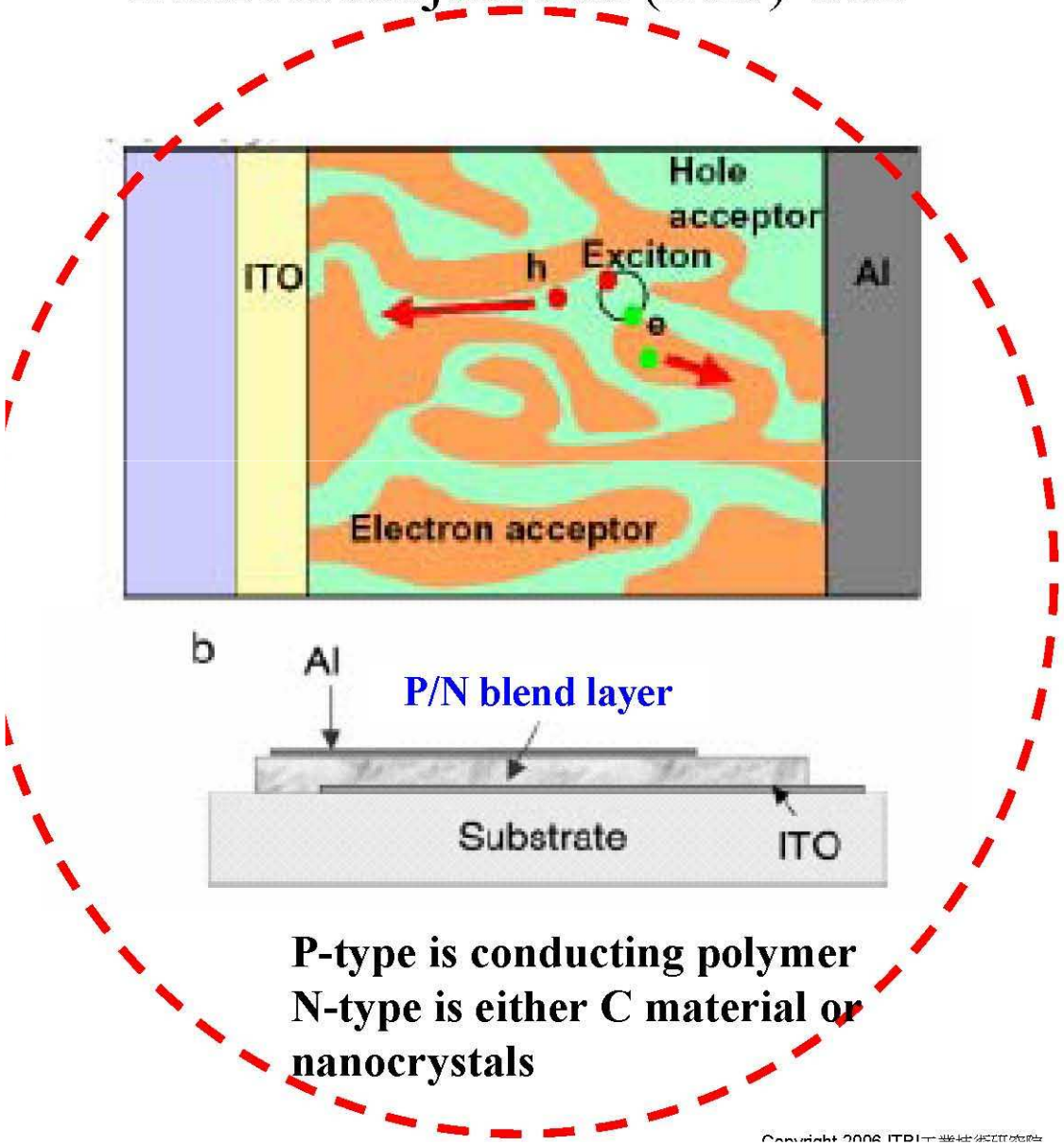


LED mode **Photovoltaic mode**

A PV mode is the reverse of a LED. In PVs electrons are collected at the metal electrode and holes are collected at the ITO electrode.

What & Why Is Organic Solid Phase Photovolta

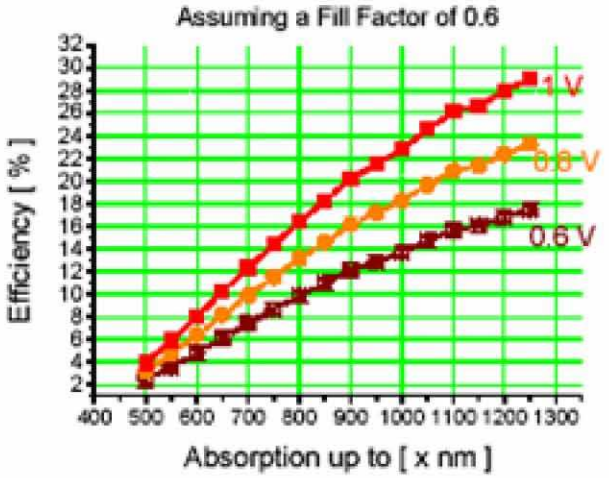
Bulk Heterojunction (BHJ) Cell



P-type is conducting polymer
N-type is either C material or nanocrystals

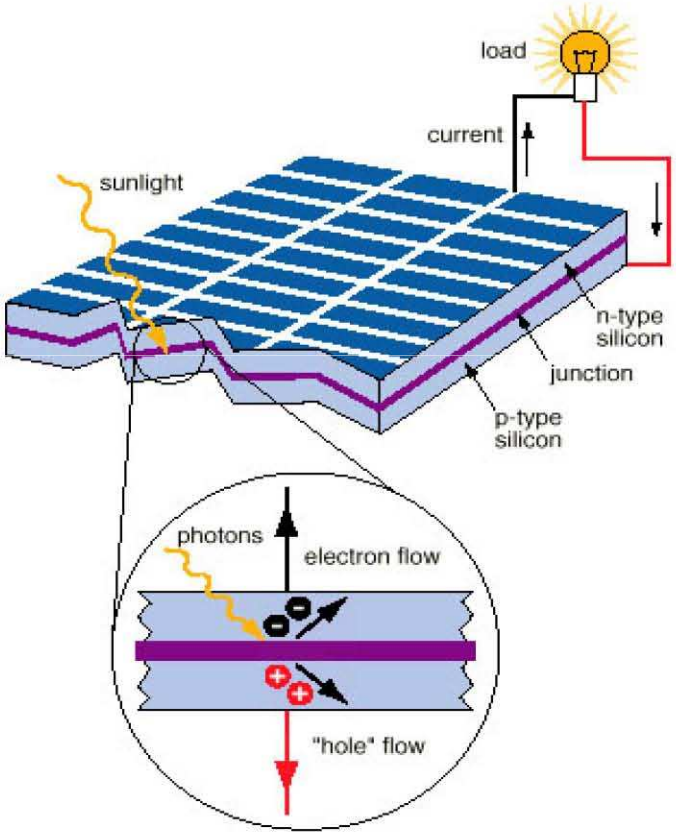
有機固態太陽光電之優勢：

- 理論高效率(可達20%)
- 環保製程（而非只是綠色發電）
- 成本低
- 對光強度敏感度較低(室內光可用)
- 質輕，可撓性

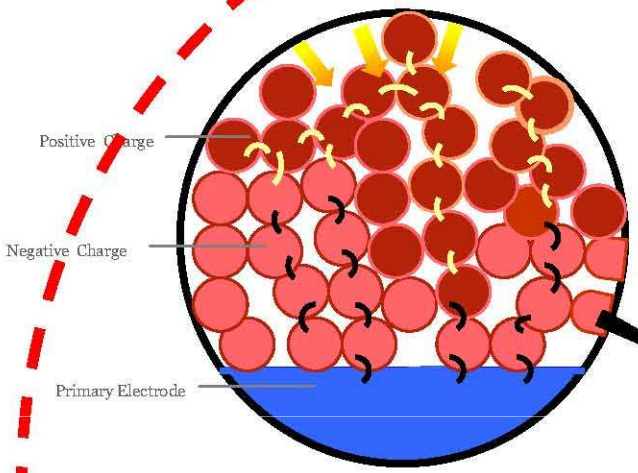


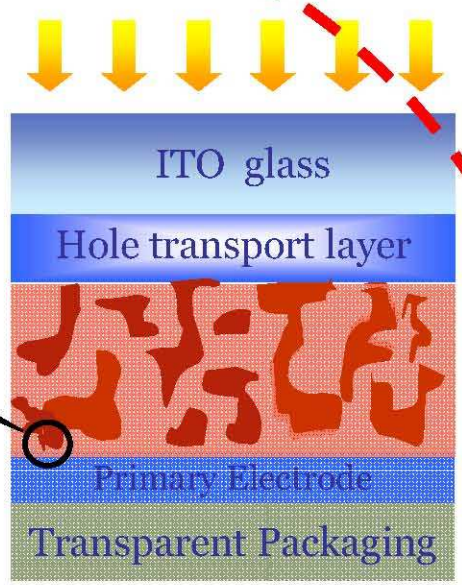
Polymer Based Solar Cell-Active layer

Conventional P-N Junction Cell



Bulk Heterojunction





Three Active Composition → *e⁻ transporter* + *absorber* + *h⁺ transport*

Fullerene/ nanocrystal + Polymer

Polymer Based solar cell (PSC)

Light Converting Processes

- Absorption
- Exciton diffusion
- Charge Separation
- Charge Transport

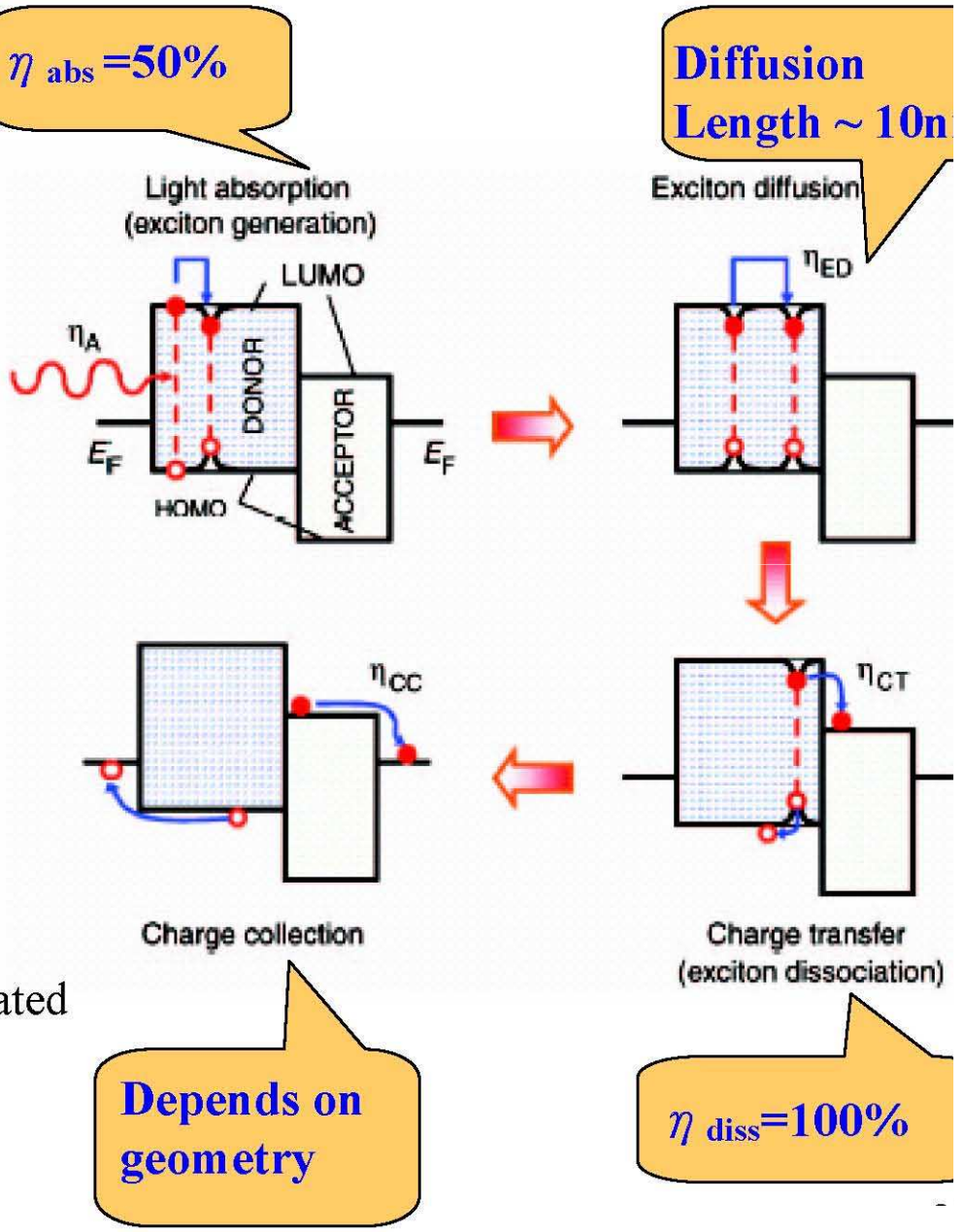
$$\eta_j = \eta_{abs} \times \eta_{diss} \times \eta_{out}$$

overall photocurrent efficiency

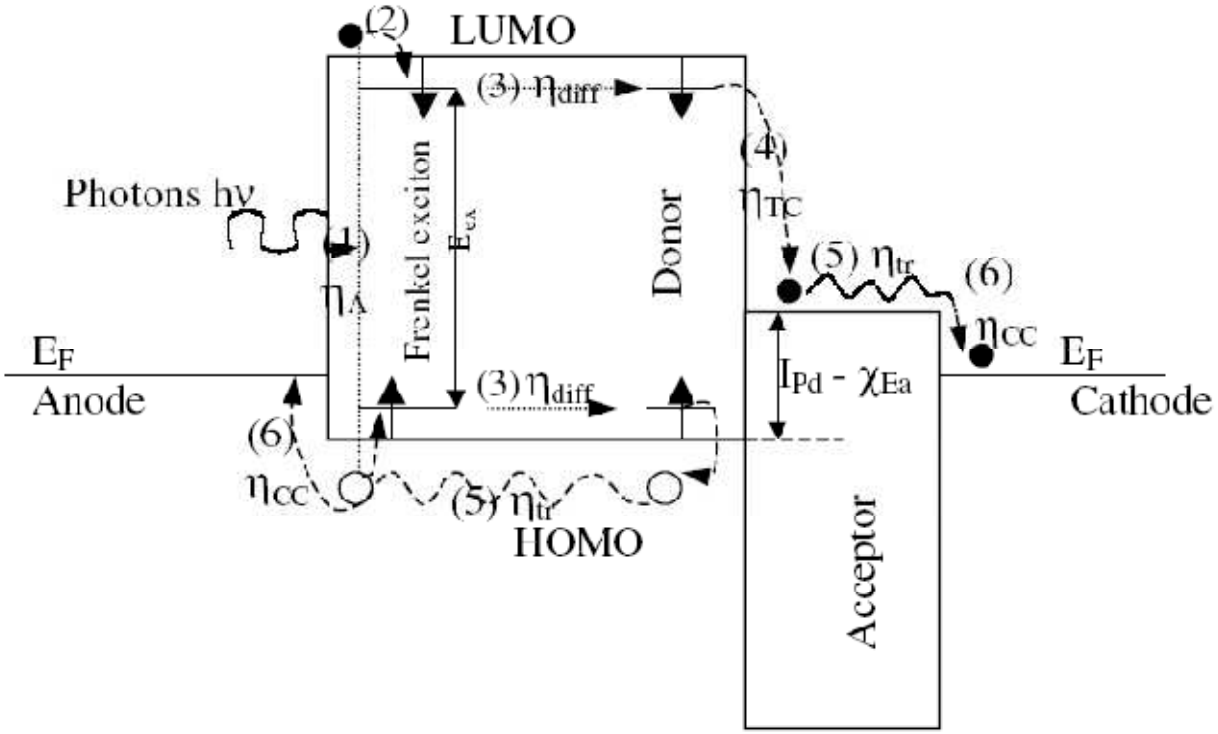
η_{abs} fraction of photons absorbed

η_{diss} fraction of electron-hole pairs that are dissociated

η_{out} fraction of charges that reach the electrodes



General Mechanism in Organic Photovoltaic Cells



(1) Photon absoption (η_A)

(2) Generation of excitons

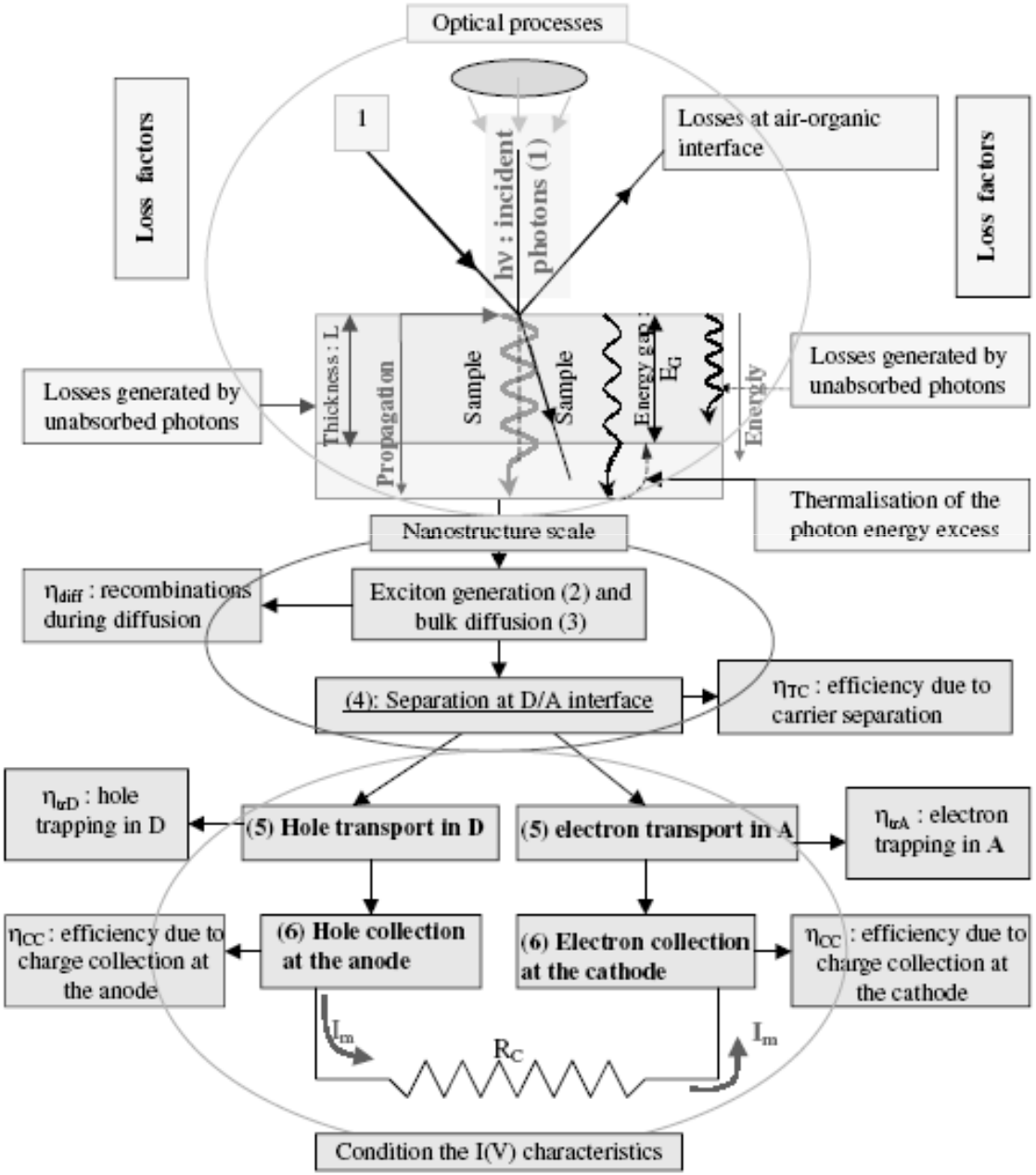
(3) Exciton diffusion (η_{diff})

(4) Hole-electron separation (η_{TC})

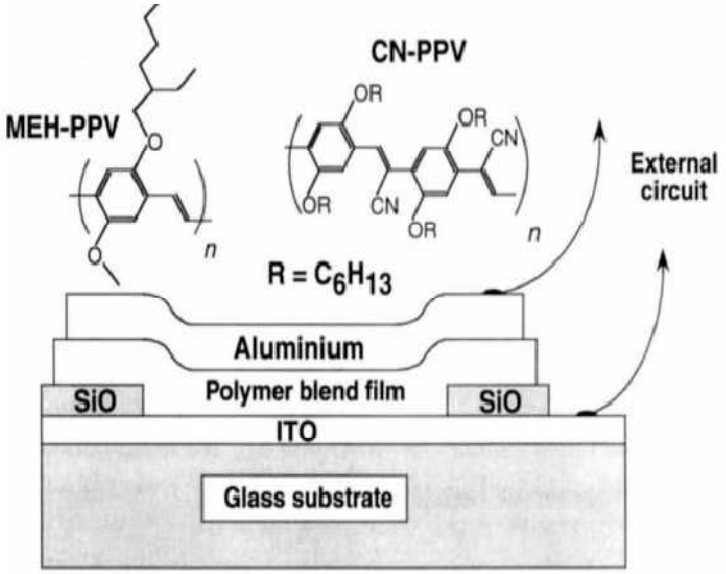
(5) Carrier transport towards the electrode (η_{tr})

(6) Charge collection at the respective electrode(η_{CC})

General Scheme for Organic Photovoltaic Effect

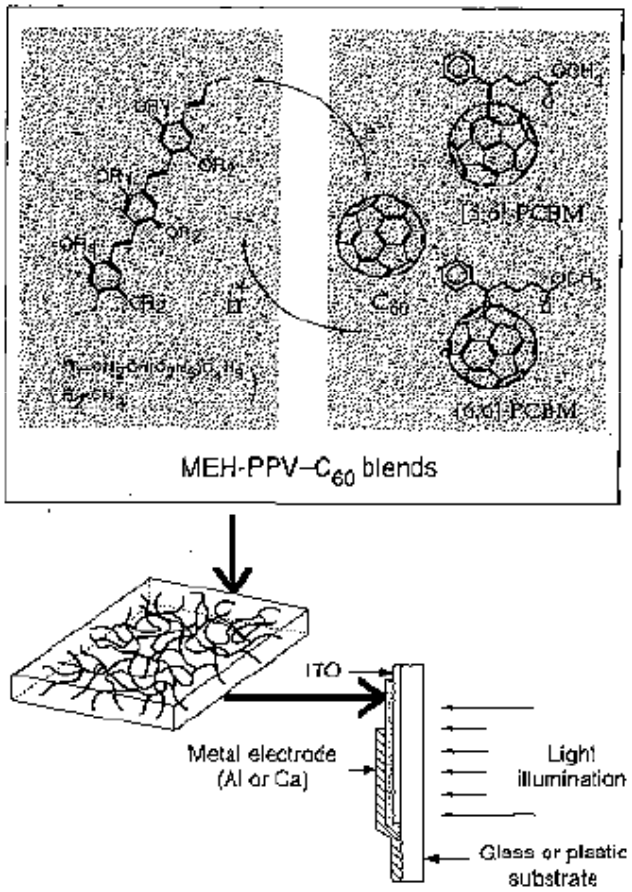


Examples on Polymer Phtovoltaic Devices



First Polymer-Polymer heterojunction PV

NATURE · VOL 376 · 10 AUGUST 1995

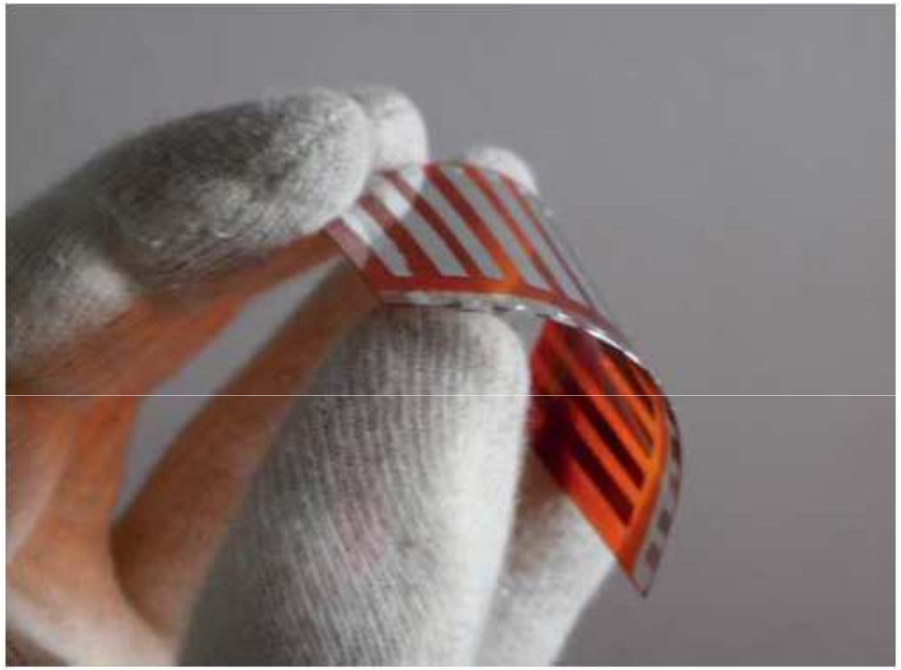


Energy conversion efficiency: 2.9 %

***Science* 1995**

Plastic Solar Cells

A large area plastic solar cell running a small motor



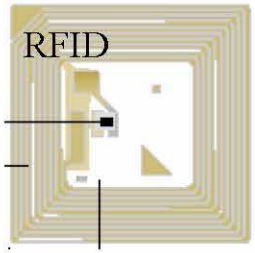
MDMO-PPV:PCBM solar cell realized on a PET substrate

Applications

Ultra-low-margin products

Leisure, tents, remote equipment

Small electronic devices

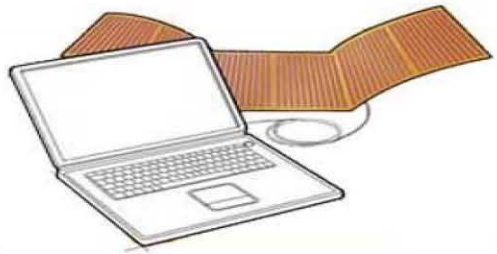


Organic solid Photovoltaics

Power generation systems.

Building integrated PV.

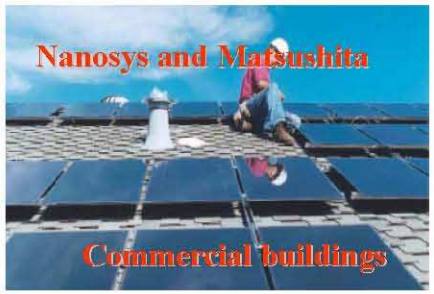
Portable and mobile systems



Application Roadmap

2010 | 2015 | 2020

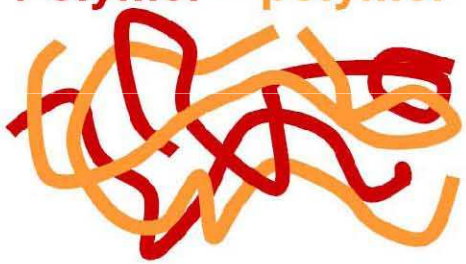
Organic solid photovoltaics



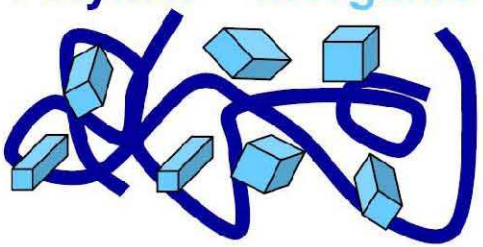
Polymer solution processed cells come in three 'flavors'

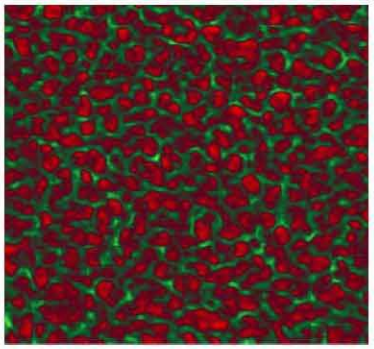
Polymer – fullerene

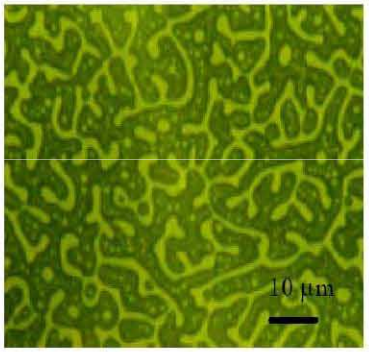
Polymer – polymer

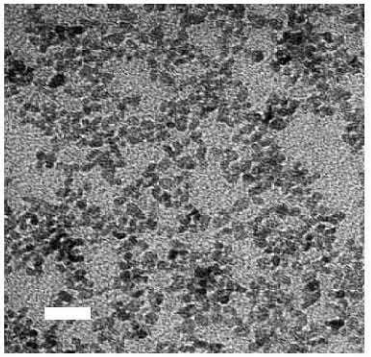


Polymer – inorganic

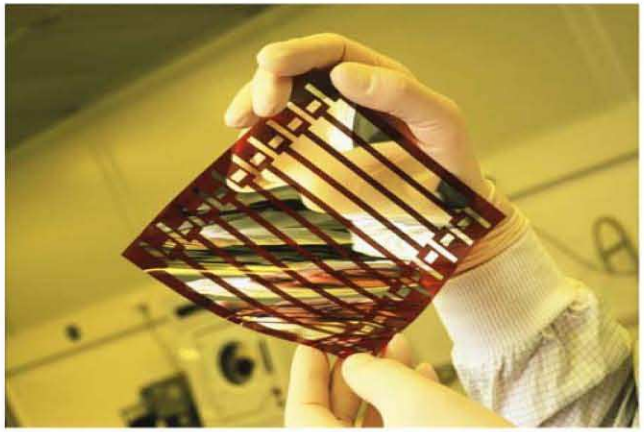


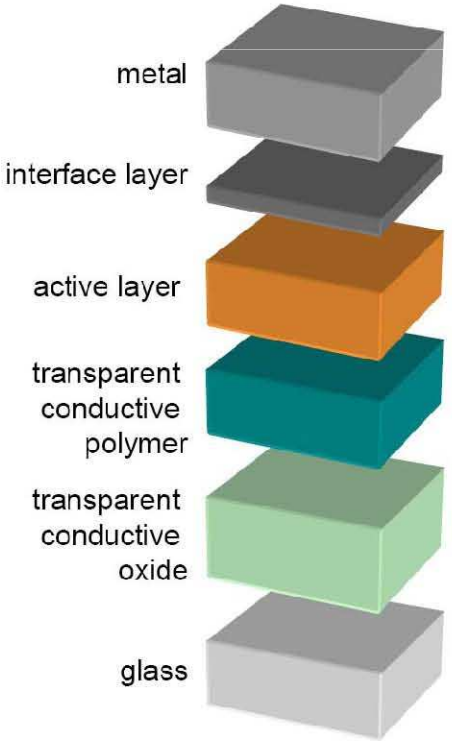






Polymer solar cells





建構高分子太陽能電池元件製程平台

微影 lithography → 塗佈 coating → 蒸鍍 evaporated → 封裝 encapsulation → 測試 test

Plasma cleaner

曝光機

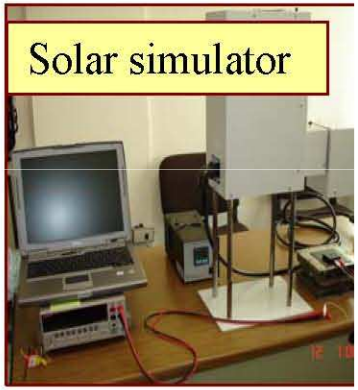
PEDOT:PSS

active layer

蒸鍍機

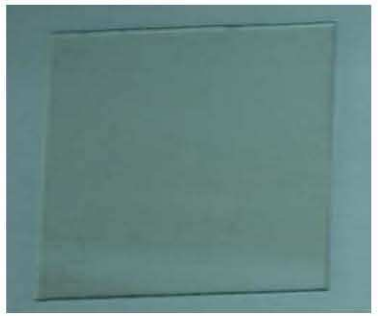
UV curing

Solar simulator



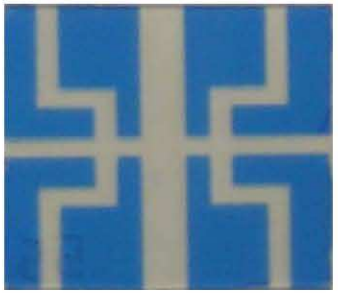
標準元件製作流程

Procedure:

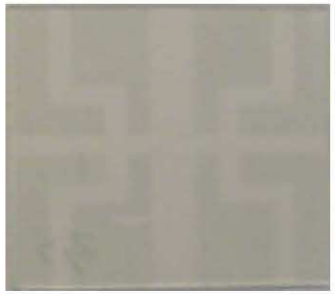


ITO glass

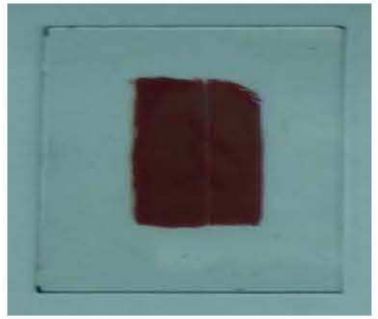
Exposure



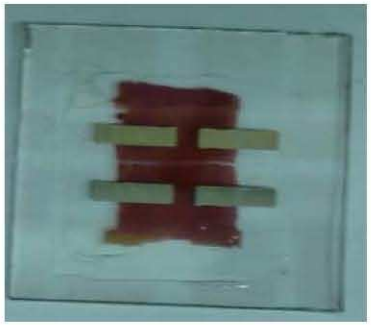
Development



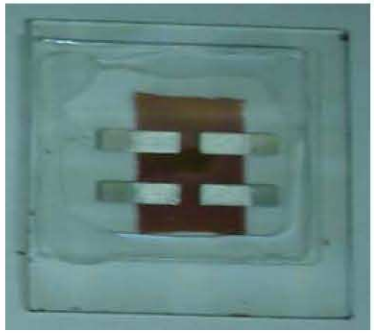
Etching



Polymer Coating



Top Electrode



Encapsulation

太陽電池之 I-V 曲線

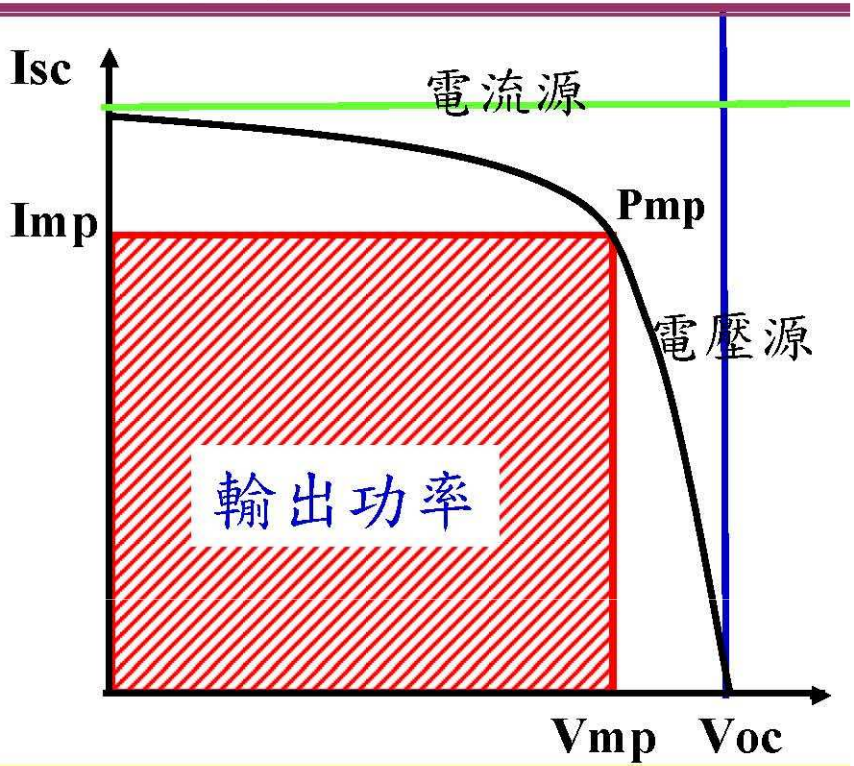
V_{oc}：開路電壓(V)

I_{sc}：短路電流(A)

P_{mp}：最大輸出功率值(W)

V_{mp}：最大輸出功率時之電壓(V)

I_{mp}：最大輸出功率時之電流(A)



ill Factor (F.F.) = (V_{mp} x I_{mp} / V_{oc} x I_{sc}) x 100%

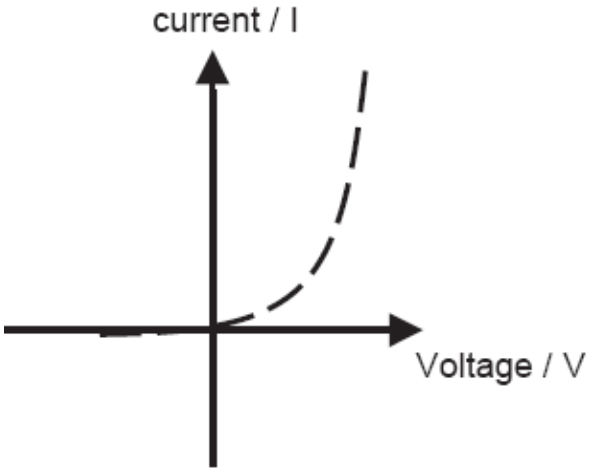
太陽電池效率(Efficiency；η) = (I_{sc} x V_{oc} x FF / 輸入日照功率) x 100%

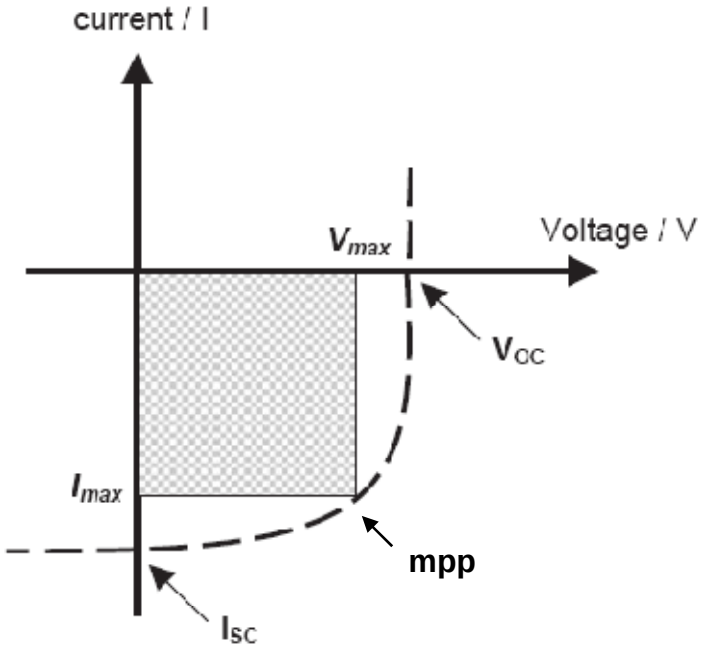
輸入日照功率(W)=太陽電池面積(m^2)×日照強度(W/ m^2)

日照強度為1000 W/ m^2之最大輸出功率即為Wp

太陽電池開路、短路時皆不會燒燬

Characteristics of Solar Cells





Air Mass (AM)- A measure of how much atmosphere sunlight must travel through to reach surface. The intensity is fixed at 100W/cm^2.

Open circuit voltage (V_{oc}) Voltage across the cell in sunlight when no current is flowing.

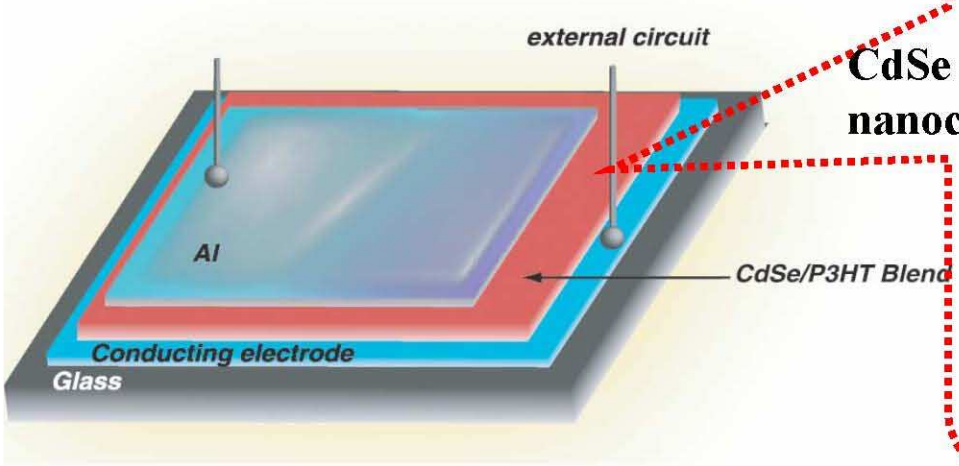
Short circuit voltage (I_{sc}) Current flows through an solar cell when there is no external resistance.

Maximum power point (mpp) The maximum power is produced.

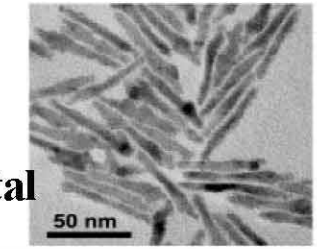
Fill Factor (FF) $$\mathrm{FF} = \frac{I_{\mathrm{mpp}} V_{\mathrm{mpp}}}{I_{\mathrm{sc}} V_{\mathrm{oc}}}$$

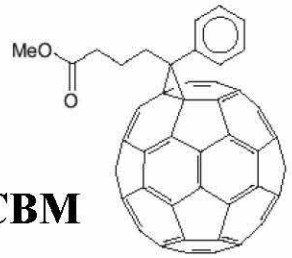
Power conversion efficiency (PCE) $$\eta_e - \frac{I_{\mathrm{mpp}} V_{\mathrm{mpp}}}{P_{\mathrm{in}}} - \frac{I_{\mathrm{sc}} V_{\mathrm{oc}} \mathrm{FF}}{P_{\mathrm{in}}}$$

Polymer Photovoltaic Structure



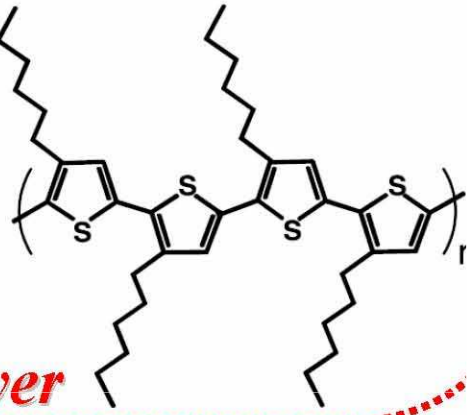
CdSe nanocrystal



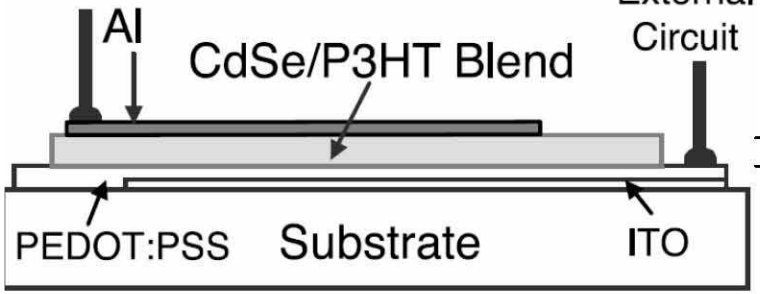


PCBM

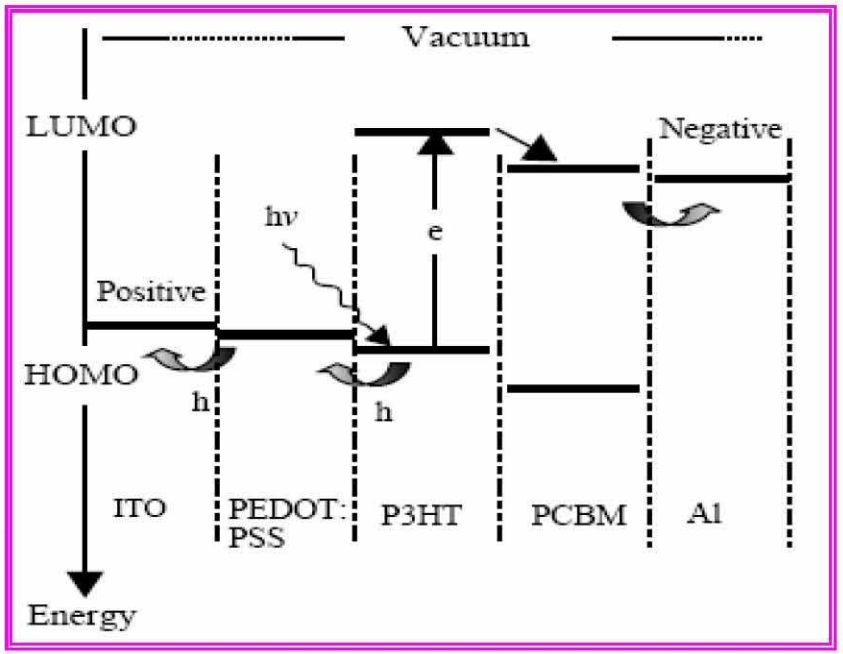
(poly(3-hexylthiophene))
Regioregular P3HT



Active layer



Active Area：0.03cm^2



光電轉換效率2.4% (CdSe)
J. Appl.Phys. 2005, 97, 014914

光電轉換效率6.1% (PCBM)
Appl. Phys. Lett. 90, 163511 (2007)

Postproduction induced P3HT:PCBM solar cells

P3HT:PCBM solar cells

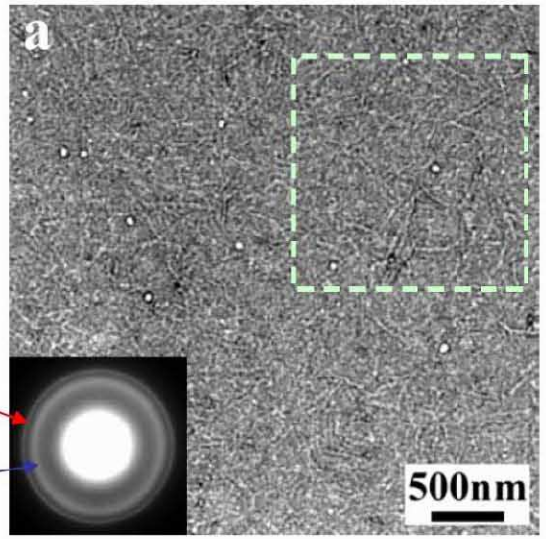
AM1.5 performance

J_{sc}	V_{oc}	FF	EQE	η
8.7	0.58	0.55	70	2.8
8.5*	0.55	0.60	70	3.5
9.4	0.61	0.53	58	3.0
7.2	0.62	0.62	58	2.7
11.1*	0.65	0.54	-	4.9
9.5*	0.63	0.68	-	5.0
10.6	0.61	0.67	63	4.4
> 10**	~0.60	-	73	4.4

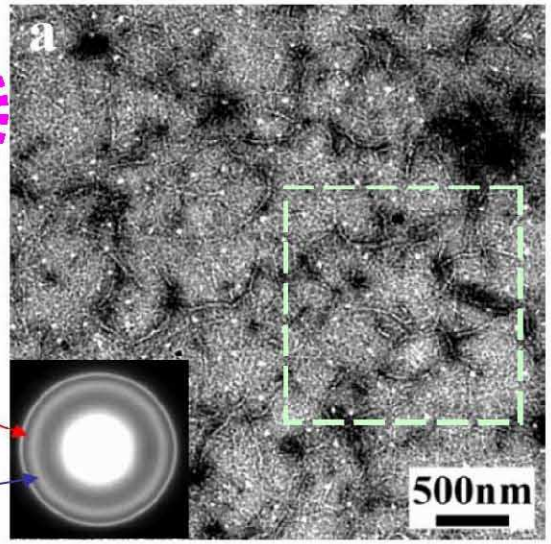
* measured at 80 mW/cm^2; ** at 85 mW/cm^2

P. Schilinsky et al., Appl. Phys. Lett. 2002, ***81****, 3885.*
F. Padinger et al., Adv. Funct. Mater 2003, ***13****, 85.*
Y. Kim et al., Appl. Phys. Lett. 2005, ***86****, 063502.*
X. Yang et al., Nano Lett. 2005, ***5****, 579.*
M. Reyes-Reyes et al., Appl. Phys. Lett. 2005 ***87****, 083506*
W. Ma et al., Adv. Funct. Mater., 2005, ***15****, 1617.*
G. Li et al.,Nature Mater. 2005, ***4****, 864.*
Y. Kim et al., Nature Mater. 2006, ***5****, 197.*

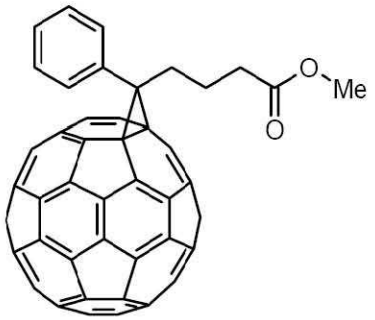
spin coating
chlorobenzene

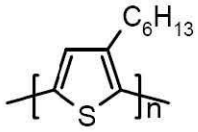


110 °C for
60 min

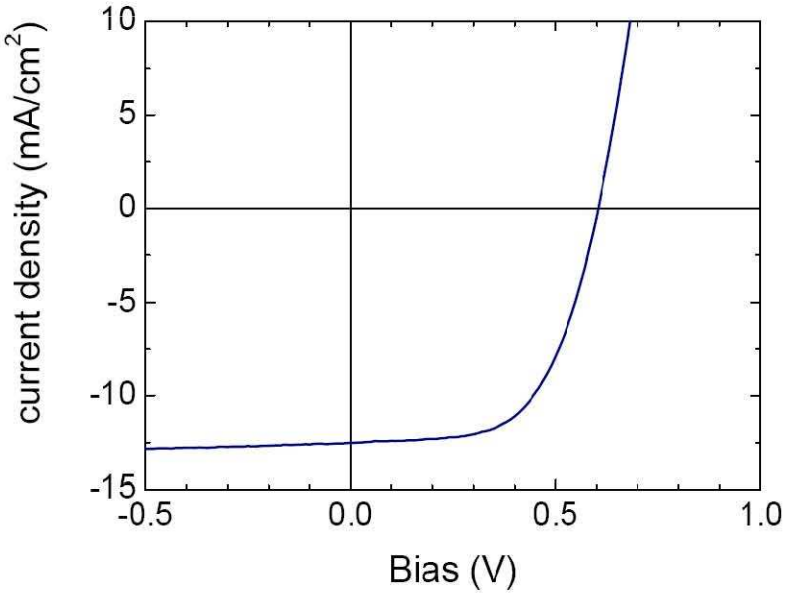


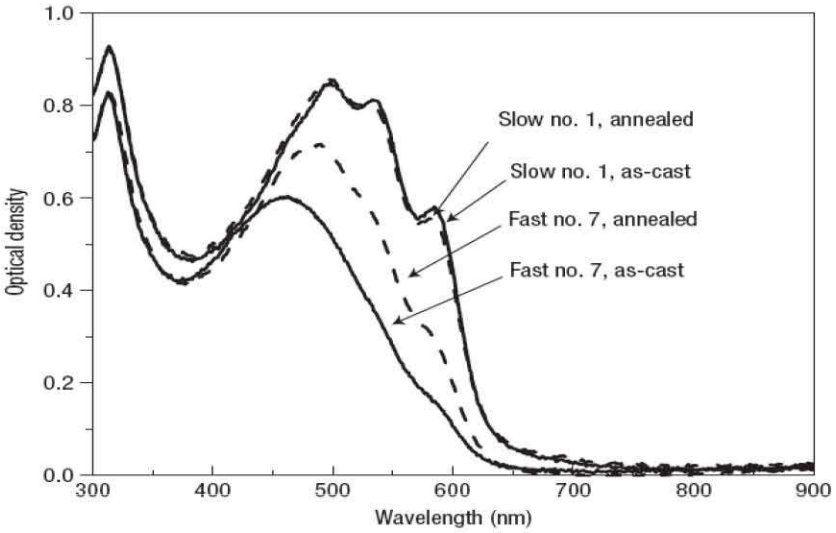
P3HT:PCBM solar cells via slow drying process

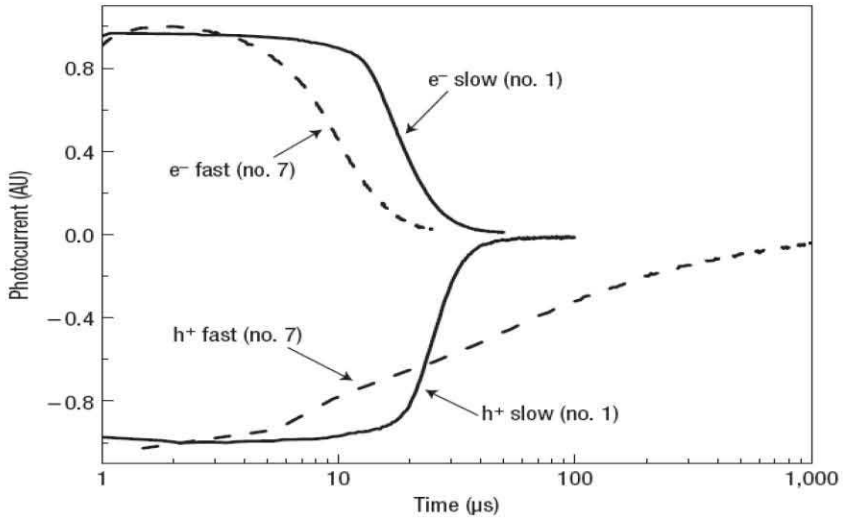




J_{SC}	V_{OC}	FF	EQE	η
12.50	0.604	0.594	66	4.5%





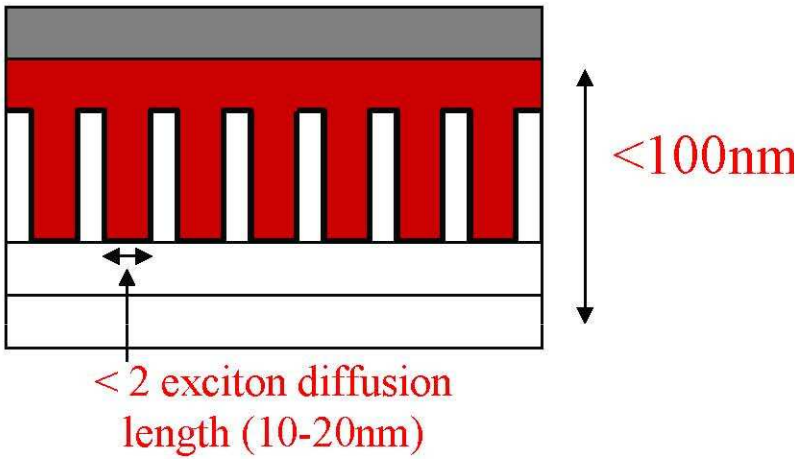


Yang Yang et al. Nature Mater. 2005, 4, 864.

R&D Focuses to Tackle Critical Issues

- New polymer design to enhance mobility & light harvesting
- Ordered BHJ structure with well-defined paths and limited width
- New device design to enhance Jsc or Voc
- Life time issues

Ordered BHJ



Current Challenges

The lower photocurrent is due to poor light absorption, generation and transport. The fill factor is due to poor transport and recombination.

- **Improving light harvesting**

Small band gap polymer, dye-sensitized materials, light-trapping structures

- **Improving charge transport**

Carrier mobility (10^{-2}~10^{-5} cm^2/VS) is low

- **Control morphology**

Processing condition, self organization, synthesis of D-A block copolymer, use of porous films as template

- **Addressing manufacturing issue and improving stability**

By encapsulating cells and more stable materials

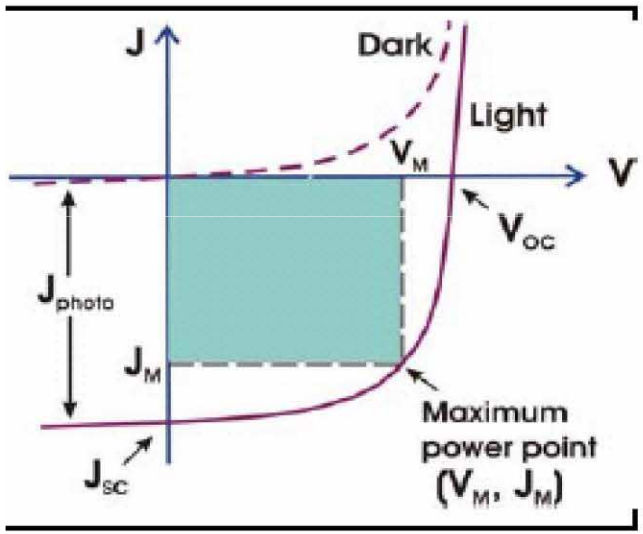
- **Understanding device function and limits to performance**

國際發展比較-有機固態太陽光電

高分子-碳材太陽光電池技術		
Authors/Institutes	**Compositions**	**Efficiency (%)**
David L. Carroll/Wake Forest University, USA/Kyungkon Kim/ KIST, Korea	ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al	6.1
C. J. Brabec /Siemens (Konarka) AU/A. Heeger/Konarka USA	ITO/PEDOT:PSS/P3HT:PCBM/Al	5.68
Kwanghee Lee /Pusan U., Korea/ A. Heeger	ITO/PEDOT:PSS/P3HT:PCBM/TiO2/Al	5.8
A. Heeger/UC Santa Barbara , USA	ITO/PEDOT:PSS/P3HT:PCBM/Al	4.8-5.1/100 samples
N. S. Sariciftci /Linz Austria	ITO/PEDOT:PSS/MDMO-PPV:PCBM/LiF/Al	3.5
Y. Yang /UCLA ,USA	ITO/PEDOT:PSS/P3HT:PCBM/Al	4.4/3.8
R. A. J. Janssen/ECN Netherlands	ITO/PEDOT:PSS/MDMO-PPV:[70]PCBM/LiF/Al	3.0
ITRI	ITO/PEDOT:PSS/P3HT:PCBM/Ca:Al	5.4

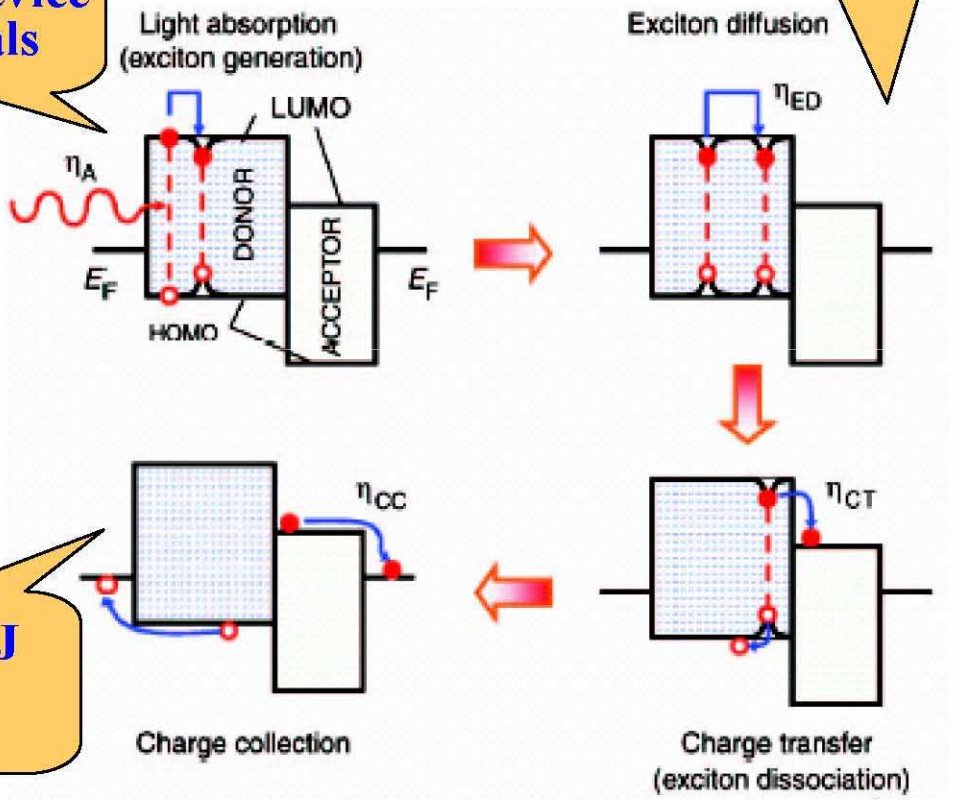
關鍵技術分析

$$\eta_j = \eta_{abs} \times \eta_{diss} \times \eta_{out}$$



Effective light harvest device & materials

High mobility material



Order BHJ structure

Good P/N typ blending

FF = JmVm/JscVoc

η = JmVm/Psun = 100*Jsc*Voc*FF/Psun

Prospects for high-efficiency (>10%) Polymer PV cells

1. New device designs: Ordered Bulk Heterojuctions

– Approach: Polymer Semiconductor/acceptor Order Heterojuction Structure

2. The high light-absorbing capabilities: Conjugated polymer and electron acceptor with lower band gap: 350-900 nm (3.5~1.4eV)

- Approach: Low Eg Polymer with a broad absorption

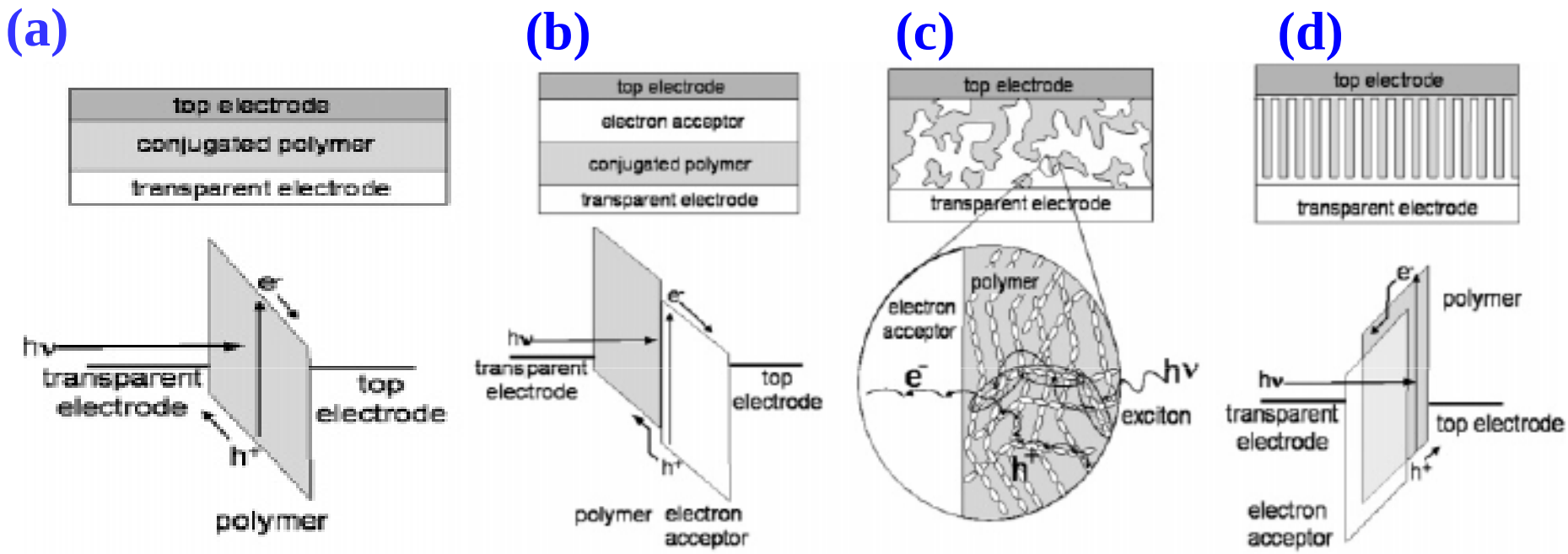
3. Suitable energy level for high Voc: Low HOMO level

4. Higher carrier mobilities:

Approach : 高分子mobilities > 0.01 cm^2/Vs and Morphology control

5. Optimized Processing Conditions: coating/drying/additives

Four device architectures of conjugated polymer–based PV cells

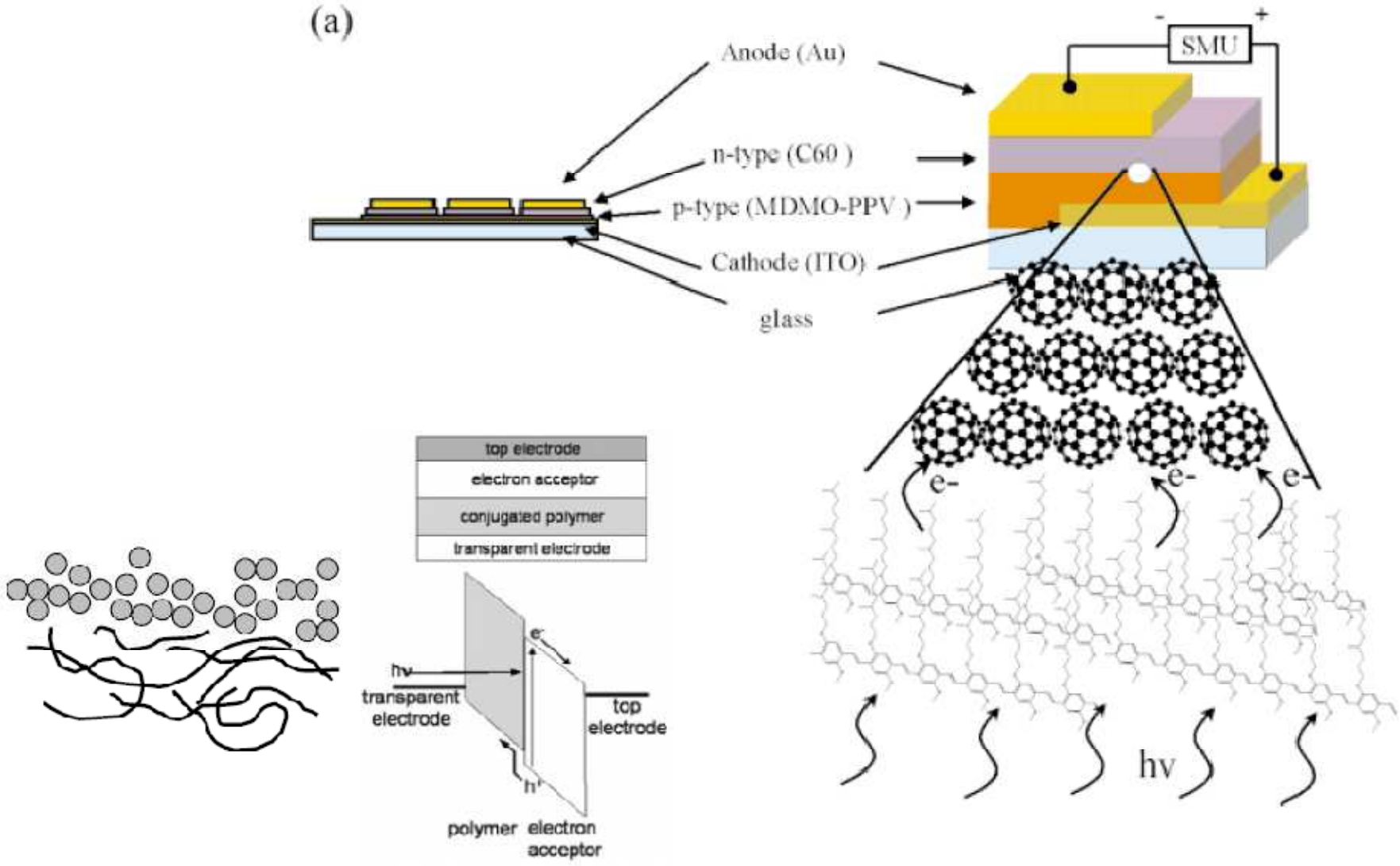


- Single Layer(a): Low EQE(0.1~1%) due to exciton recombination; low carrier mobility
- Bilayers (b) : PA-PPV/TiO_2 25% EQE, 3.9 % power efficiency (435 nm);
  PPV/BBL 66%% EQE, 2% power efficiency
- Bulk heterojunction (c) (d):
  - **PPV/C60 Derivatives 70% EQE, 3.5% power efficiency**

Chem. Mater. **2004**, *16*, 4533

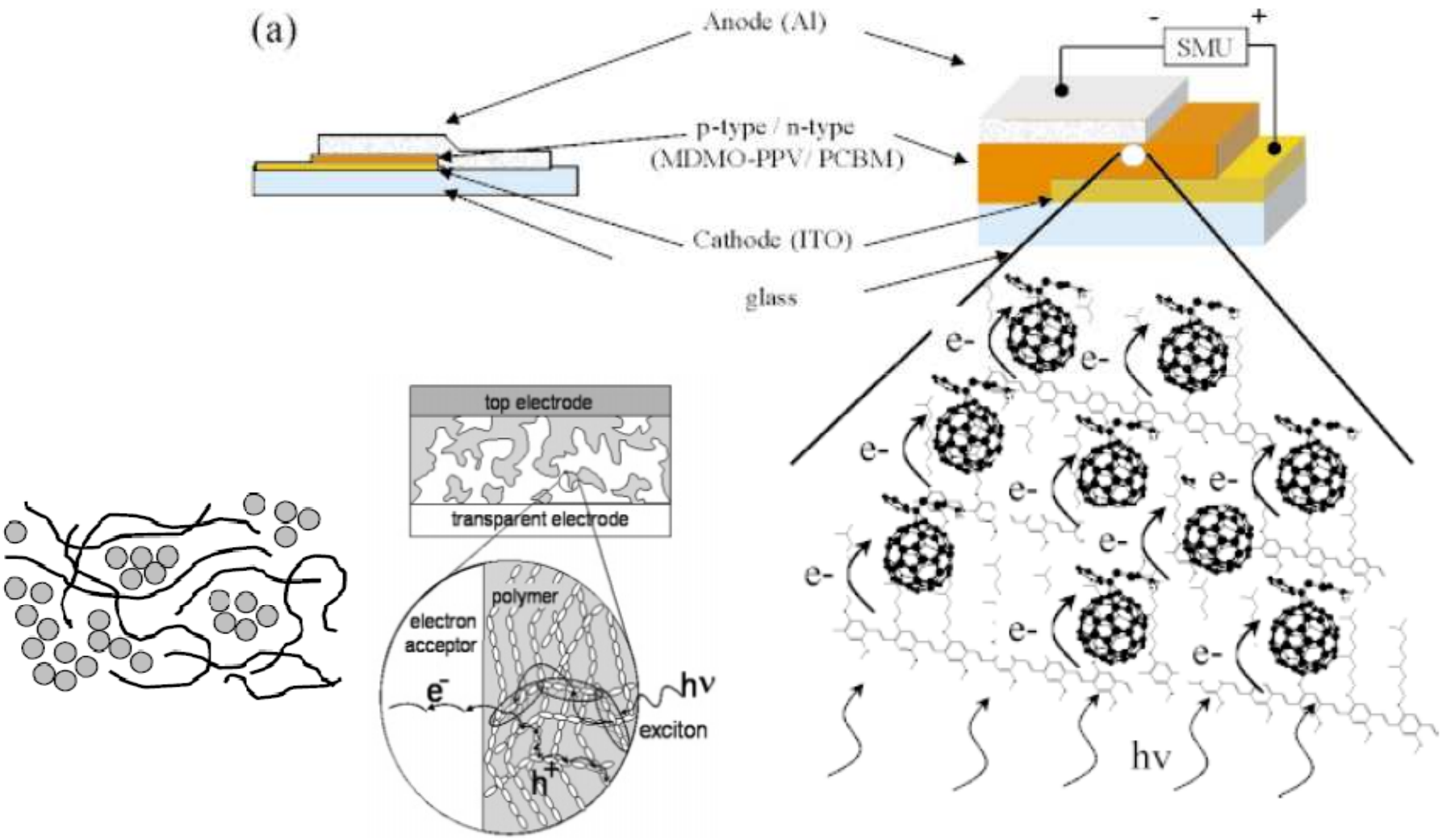
Organic Photovoltaic Device Architectures

Bilayer Devices

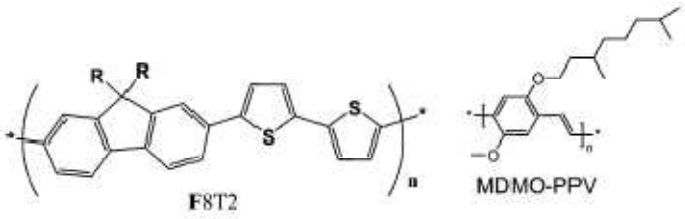


Organic Photovoltaic Device Architectures

Bulk Heterojunction Devices

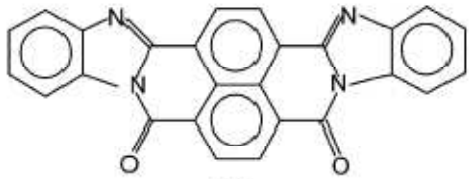


Organic Semiconductors Used in Solar Cells

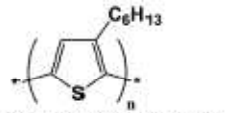


F8T2

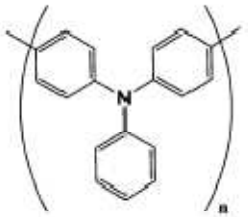
MDMO-PPV



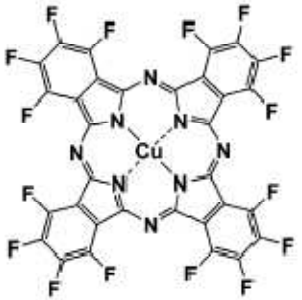
NDI



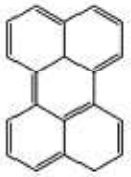
Poly(3- hexylthiophene)



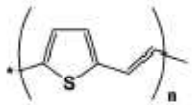
PTAA



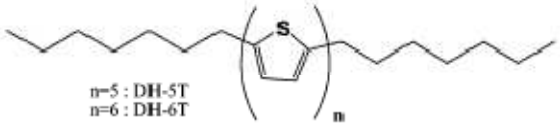
$F_{16}PcCu$



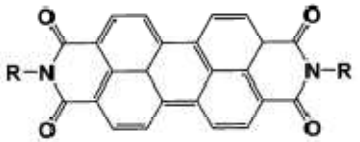
Perylene



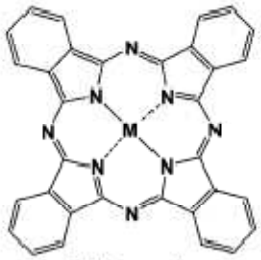
PVT



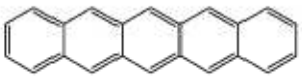
PTCDA



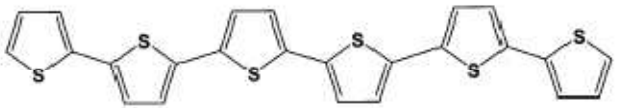
PDI



Phthalocyanine

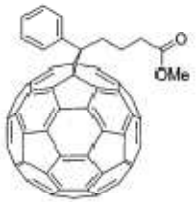


Pentacene



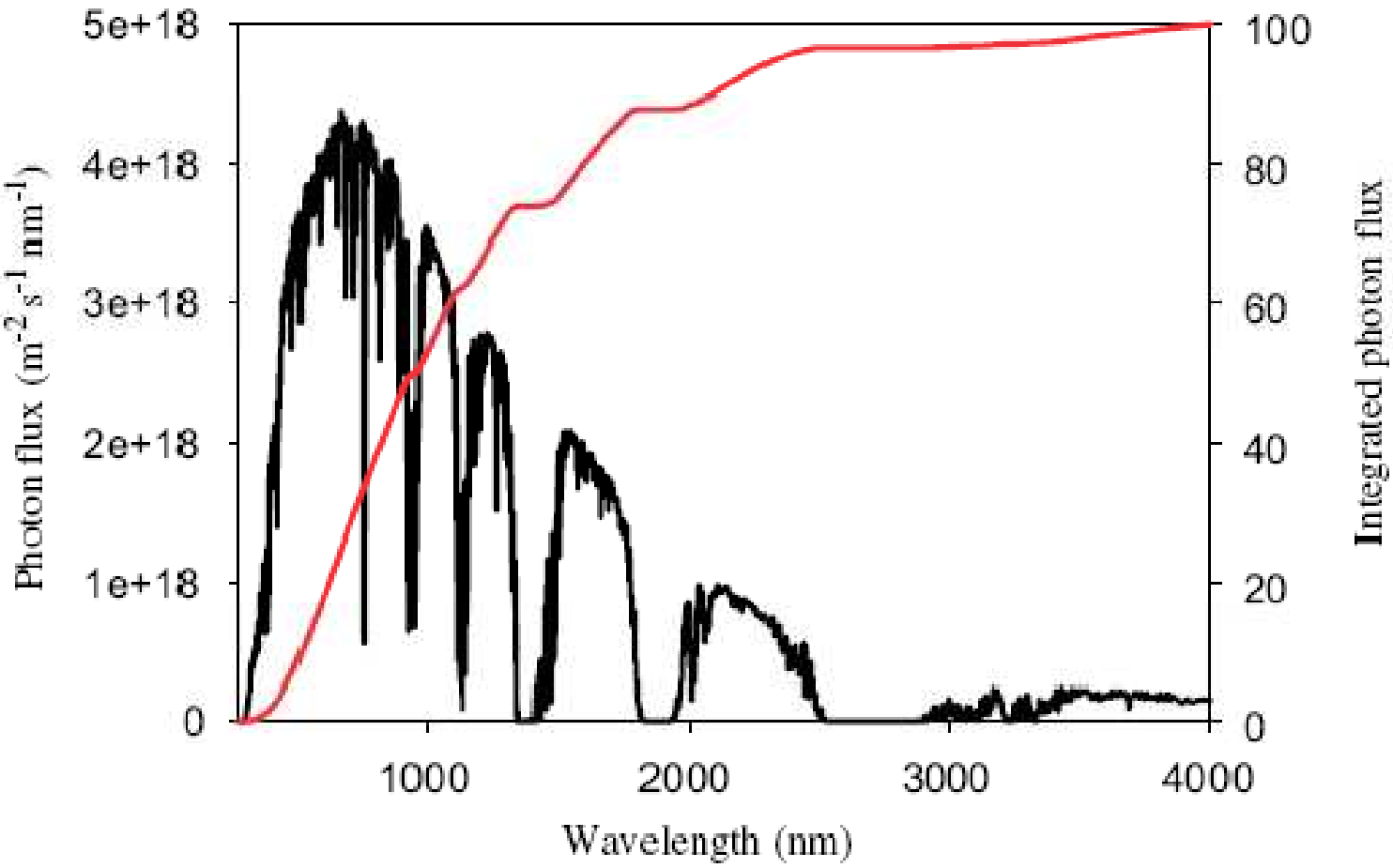
α–sexithiophene

C_{60}



PCBM

Absorption Spectrum of Organic Materials



Photon reflux from the sun (AM 1.5)

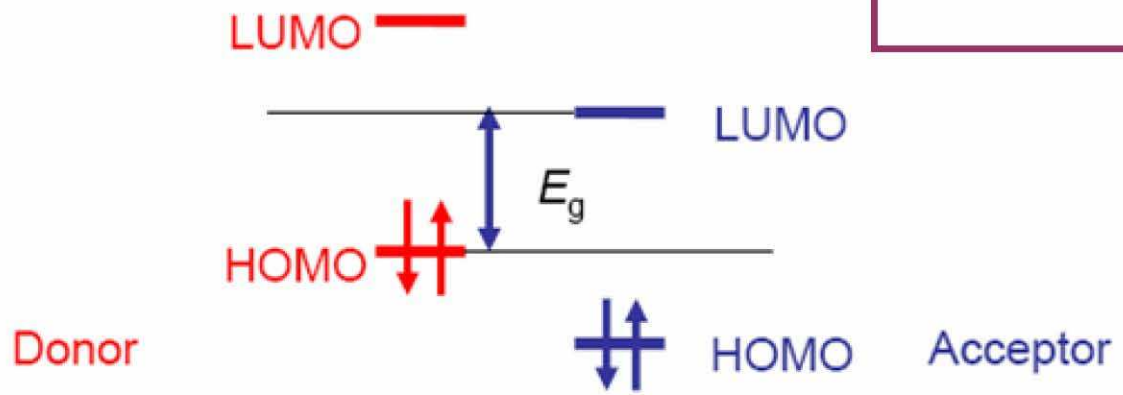
Design strategy for low band gap: Donor-Acceptor polymers

increase the double bond character of the single bonds:

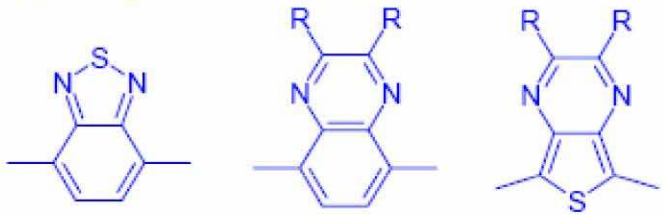
–D–A–D–A–D–A– ⟷ –D⁺=A⁻–D⁺=A⁻–D⁺=A⁻–

alignment of transition dipoles along the chain

absorption from HOMO donor to LUMO acceptor



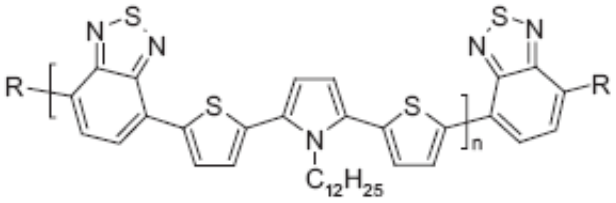
常見acceptor之化學結構：



Acceptors

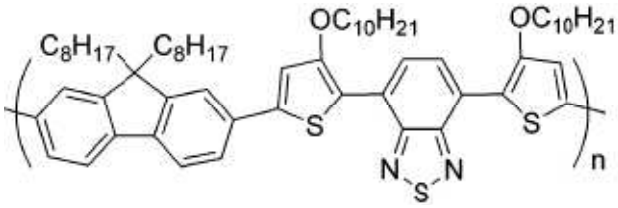
E. E. Havinga, et al. Polym. Bull. ***1992****, 29, 119.*
J. Roncali, Chem. Rev. ***1997****, 97, 173.*

D-A Conjugated Alternating Polymers:PCBM Solar Cells



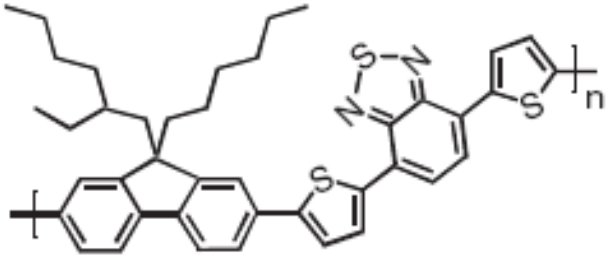
V_{oc} = 0.72 V FF = 0.37

I_{sc} = 3.1 mA/cm^2 PCE = 1 %



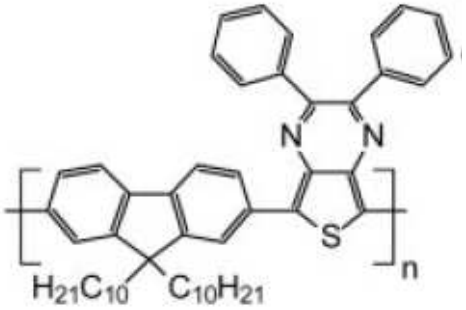
V_{oc} = 0.76 V FF = 0.49

I_{sc} = 4.31 mA/cm^2 PCE = 1.6 %



V_{oc} = 0.72 V FF = 0.46

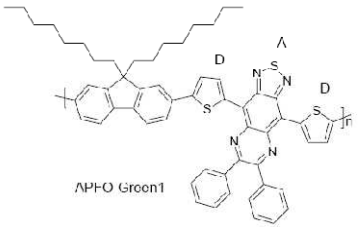
I_{sc} = 4.66 mA/cm^2 PCE = 2.2 %



V_{oc} = 0.56 V FF = 0.49

I_{sc} = 3.6 mA/cm^2 PCE = 0.51 %

D-A Conjugated Alternating Polymers:PCBM or C_{70} Solar Cells



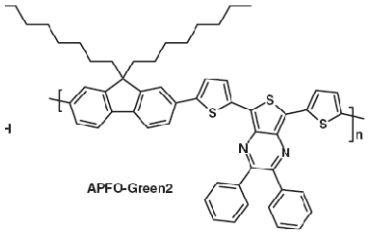
:PCBM

V_{oc} = 0.54 V

I_{sc} = 1.76 mA/cm^2

FF = 0.46

PCE = 0.3 %



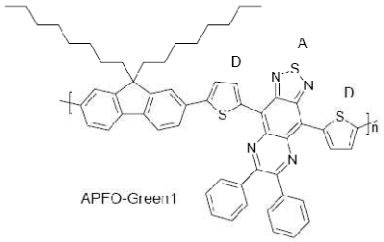
:PCBM

V_{oc} = 0.78 V

I_{sc} = 3 mA/cm^2

FF = N/A

PCE = 0.9 %



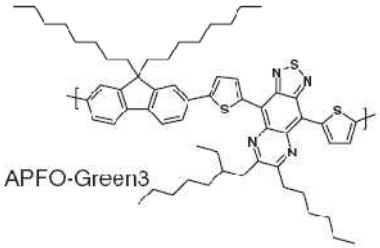
:C_{70}

V_{oc} = 0.58 V

I_{sc} = 3.4 mA/cm^2

FF = 0.35

PCE = 0.7 %



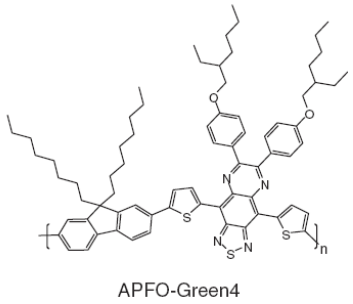
:C_{70}

V_{oc} = 0.61 V

I_{sc} = 2.4 mA/cm^2

FF = 0.40

PCE = 0.59 %



:C_{70}

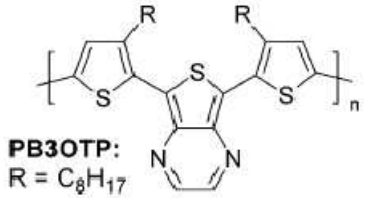
V_{oc} = 0.56 V

I_{sc} = 2.1 mA/cm^2

FF = 0.32

PCE = 0.37 %

D-A Conjugated Alternating Polymers:PCBM Solar Cells

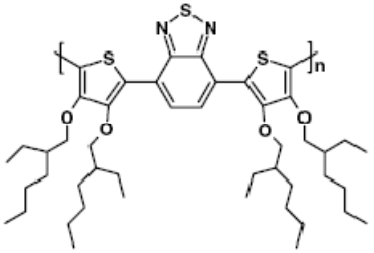


V_{oc} = 0.72 V

I_{sc} = 3.1 mA/cm^2

FF = 0.37

PCE = 1 %

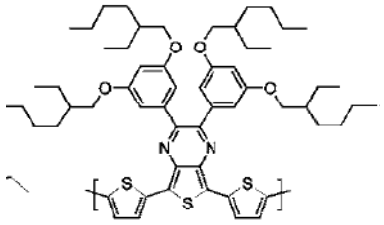


V_{oc} = 0.77 V

I_{sc} = 3.4 mA/cm^2

FF = 0.42

PCE = 0.2 %

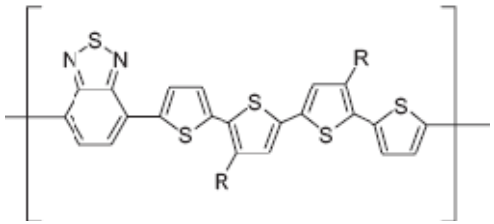


V_{oc} = 0.56 V

I_{sc} = 3.5 mA/cm^2

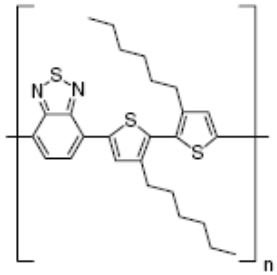
FF = 0.58

PCE = 1.1 %



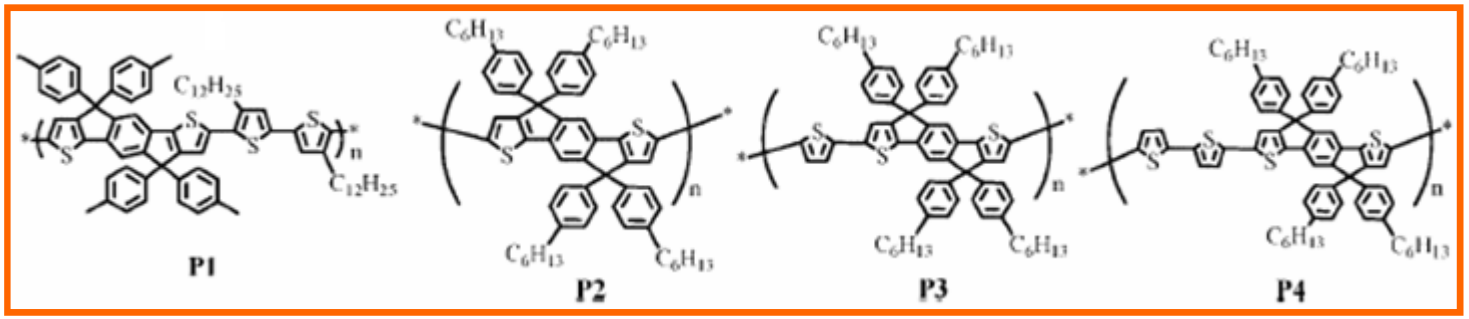
V_{oc} = 0.59 V FF = 0.39

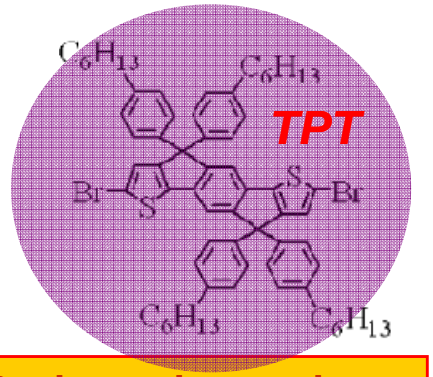
I_{sc} = 2.6 mA/cm^2 PCE = 0.6 %



V_{oc} = 0.61 V FF = 0.24

I_{sc} = 0.2 mA/cm^2 PCE = 0.02 %





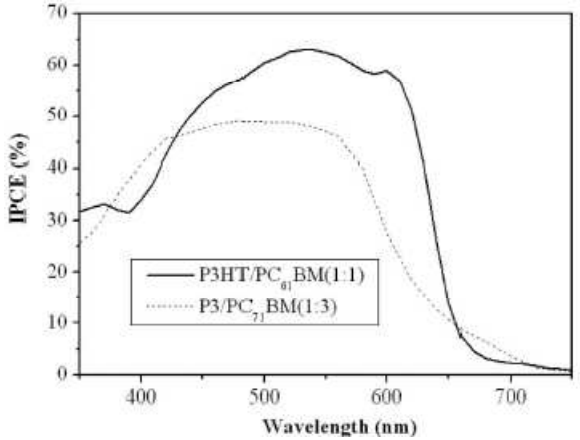
Coplanar chromophore

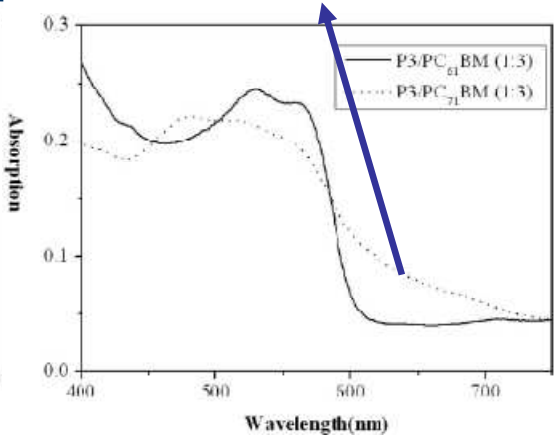
Max. IPCE:

P3HT/$PC_{61}BM$-63% at 540 nm

P3/$PC_{71}BM$-49% at 500nm

The presence of $PC_{71}BM$ can provide more photon current because it can absorb the photon beyond wavelength of 600nm





b-$PC_{61}BM$; c-$PC_{71}BM$

	polymer/PCBM (w/w ratio)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η (%)
P3HT[a]	1:1[b]	9.9	0.64	0.62	3.9
P1	1:3[b]	3.5	0.79	0.39	1.1
P2	1:3[b]	1.4	0.76	0.54	0.6
P3	1:2[b]	4.8	0.79	0.53	2.0
P3	1:3[b]	5.3	0.77	0.53	2.2
P3	1:3[c]	7.6	0.80	0.54	3.3
P4	1:2[b]	4.1	0.75	0.45	1.4
P4	1:3[b]	4.6	0.76	0.49	1.7
P4	1:3[c]	7.0	0.79	0.49	2.7

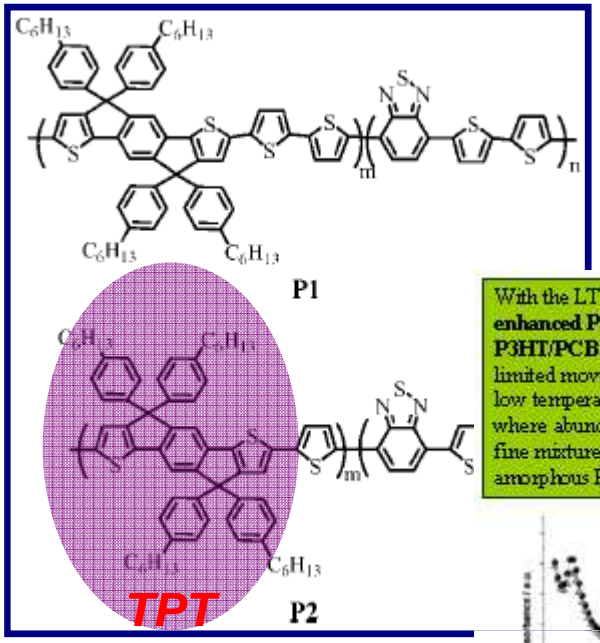
Table 1. Molecular Weights, FET Mobility, and Optical and Electrochemical Properties of Various Polymers

	M_w (PDI)	λ_{max} (film)	α[a] (cm^{-1})	E_g^{opt} (eV)	E_{ox} (V)[b]	IP (eV) (HOMO)	EA (eV) (LUMO)	μ_h[c] (cm^2/(V s))	on/off[c]
P1	25200 (1.52)	490	6.3 × 10^5	2.10	0.71	5.17	3.07	3.7 × 10^{-4}	5.2 × 10^3
P2	21800 (1.97)	510	3.0 × 10^5	2.10	0.72	5.18	3.08	1.5 × 10^{-4}	1.4 × 10^4
P3	48700 (2.19)	510	9.9 × 10^5	2.08	0.64	5.1	3.02	8.3 × 10^{-4}	9.1 × 10^4
P4	29300 (1.87)	508	9.4 × 10^5	2.11	0.72	5.18	3.07	3.0 × 10^{-3} (9.9 × 10^{-4})[d]	1.3 × 10^6 (6.5 × 10^5)[d]
P3HT	47000 (2.45)	552	1.2 × 10^6	1.90	0.74	5.20	3.30	6.5 × 10^{-2}	1.3 × 10^3

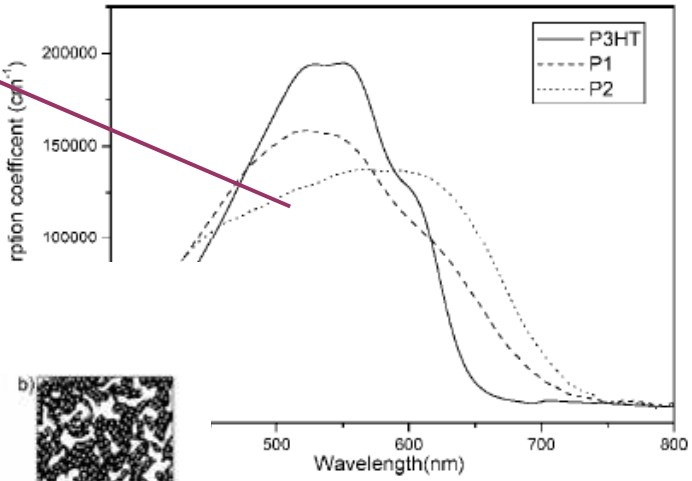
[a] Absorption coefficient was determined at λ_{max} in THF. [b] E_{ox} is the onset potential of oxidation of polymer. [c] Thin-film FETs were fabricated from 1 wt % *o*-DCB solutions. [d] $CHCl_3$ solvent was used instead of *o*-DCB.

High absorption coefficient in comparison to P3HT

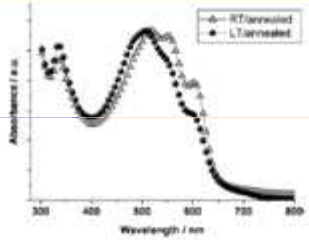
Ko et al., Macromolecules **2008**, 41, 5519



The **broad absorption** feature possibly due to the **random copolymer** structure of **P2** which combine the absorbance of **TPT** rich and **BT** rich structures



With the LT process, the low drying temperature **enhanced P3HT nucleation,** but **restricted P3HT/PCBM phase separation** (due to the limited movements of the molecules under the low temperature), resulting in a morphology where abundant P3HT nuclei dispersed within a fine mixture of PCBM-rich domains and amorphous P3HT-rich domains.



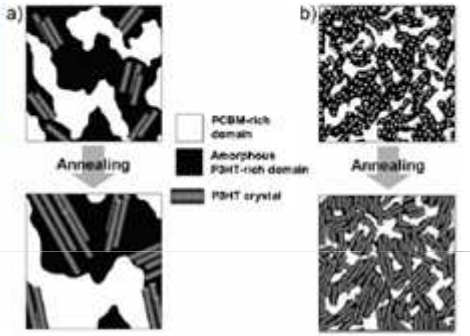


Figure 7. Schematic representations illustrating the morphology of the active layer upon drying (top) and annealing (bottom): a) the RT and b) LT layers.

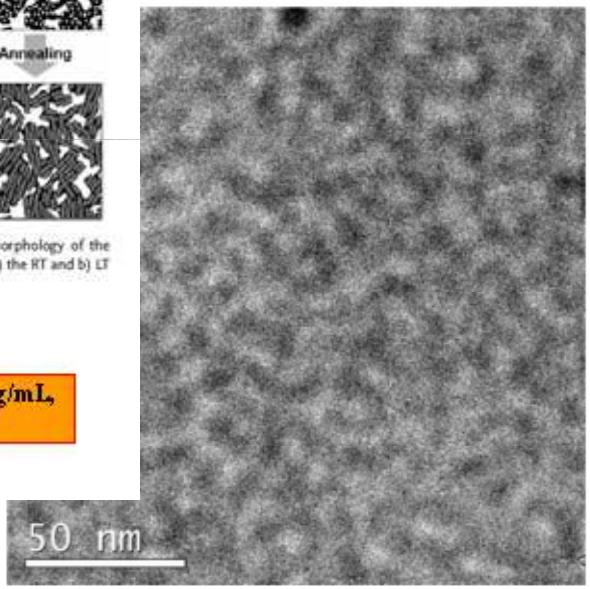
b-$PC_{61}BM$; c-$PC_{71}BM$

	polymer/PCBM(w/wratio)	J_{sc}
P3HT[a]	1:1[b]	9
P3HT[a]	1:1[c]	7
P1	1:3[b]	5
P1	1:3[c]	8
P2	1:3[b]	6
P2	1:3[c]	10.1

Process	Annealing	J_{sc} [mA cm^{-2}]	V_{oc} [mV]	FF [%]	PCE [%]
RT	None	9.42 ± 0.54	534 ± 18	63.7 ± 1.6	3.20 ± 0.14
RT	2 min/190 °C	8.41 ± 0.46	587 ± 16	65.4 ± 1.3	3.23 ± 0.18
RT	30 min/190 °C	8.25 ± 0.39	566 ± 14	53.3 ± 4.6	2.49 ± 0.18
RT	8 h/100 °C	1.72 ± 0.28	545 ± 7	39.0 ± 2.1	0.36 ± 0.05
RT	1368 h/65 °C [a]	2.48 ± 0.29	487 ± 14	37.2 ± 2.3	0.45 ± 0.07
LT (~5 °C)	None	1.40 ± 0.47	418 ± 15	33.9 ± 0.9	0.20 ± 0.06
LT (~5 °C)	2 min/190 °C	11.50 ± 0.73	615 ± 11	62.8 ± 2.4	4.43 ± 0.31

P3HT/PCBM (21mg/mL, 1:1, 600rpm 50sec)

Best PCE~4.7%



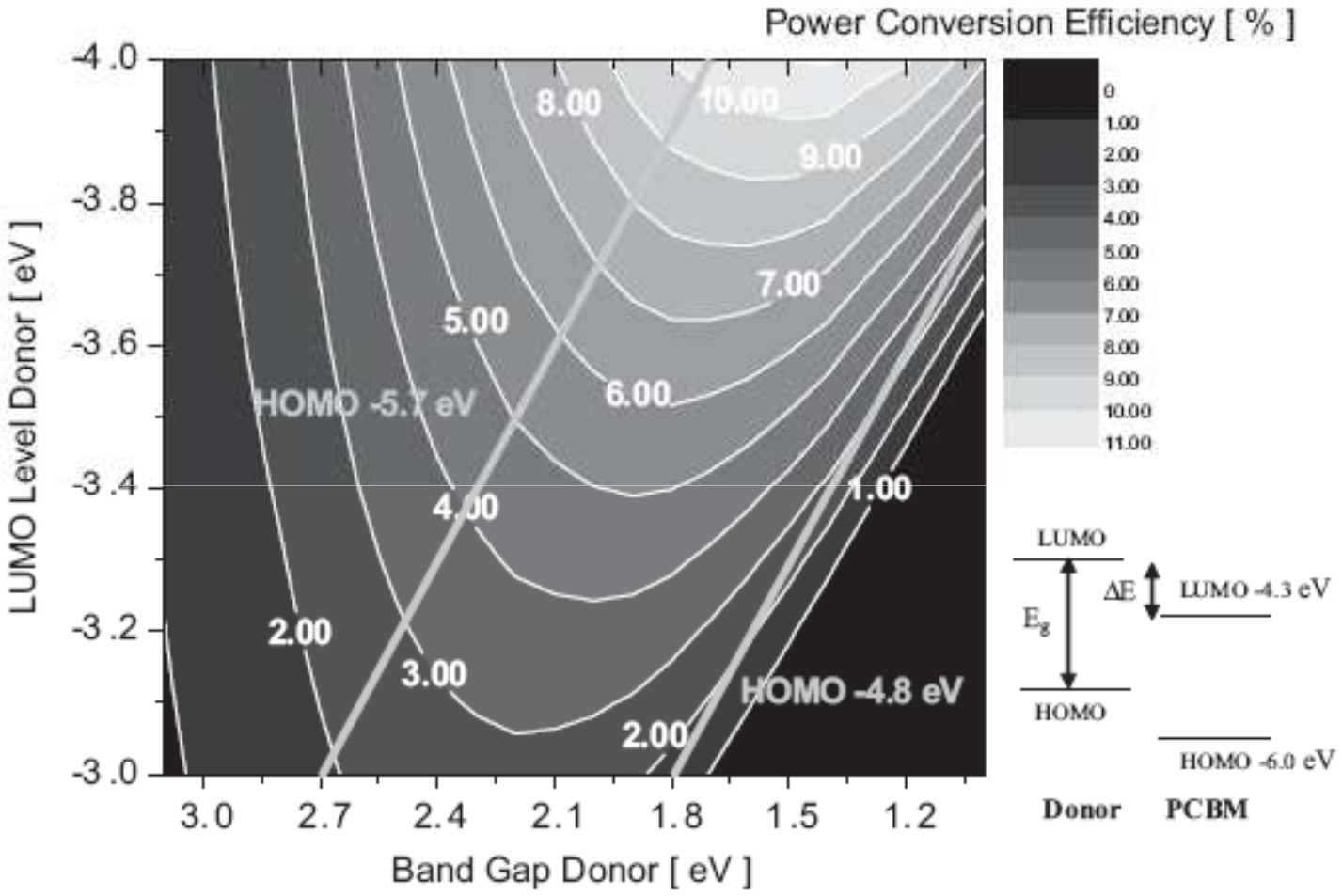
0.80 0.53 4.3

Table 1. Molecular Weights, OTFT Mobility, Optical and Redox Properties of Various Polymers

	M_w (PDI)	λ_{max} (film)	α ($\times 10^5$ cm^{-1})	E_g^{opt} (eV)	E_{ox}^{c} (V)	HOMO (eV)	LUMO (eV)	μ_h (cm^2/Vs)	on/off
P1	26300 (1.55)	520	11[a] (1.6)[b]	1.76	1.00	−5.46	−3.56	7.0×10^{-4}	1.3×10^5
P2	38600 (1.74)	590	7.7[a] (1.4)[b]	1.70	0.97	−5.43	−3.66	3.4×10^{-3}	5.6×10^6

Ko et al, J. Am. Chem. Soc. **2008**, in press

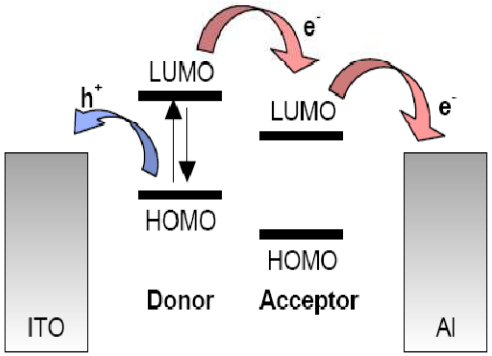
Design Rules for Donors in Solar Cell –Towards 10 % PCE

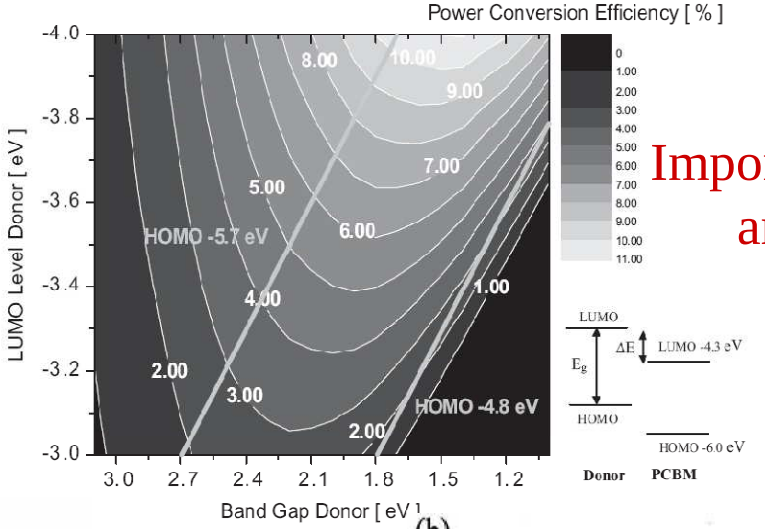


To get PCE >10% **The highest PCE of polymer solar cell up to now : 7.9%**

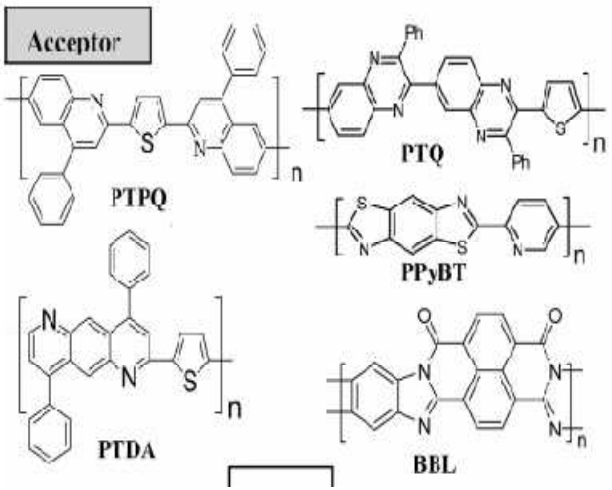
Bandgap of donor polymer < 1.74 eV & LUMO < -3.92 eV

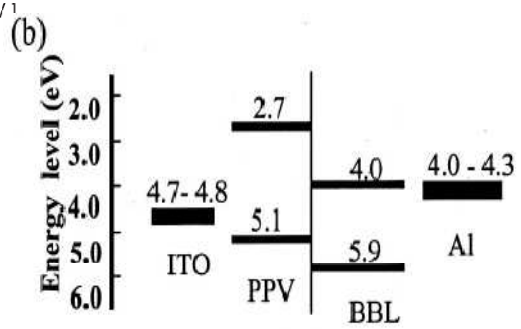
The importance of HOMO/LUMO level on the Photovoltaic Devices

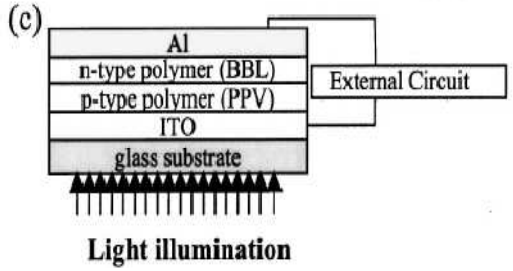




Importance of donor HOMO and acceptor LUMO

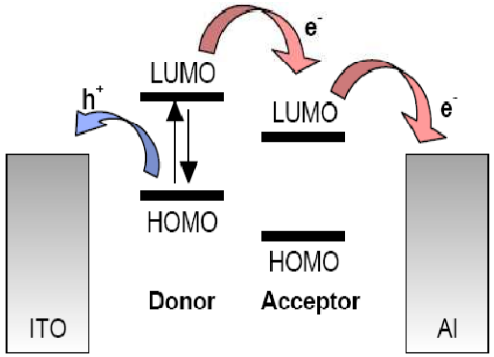


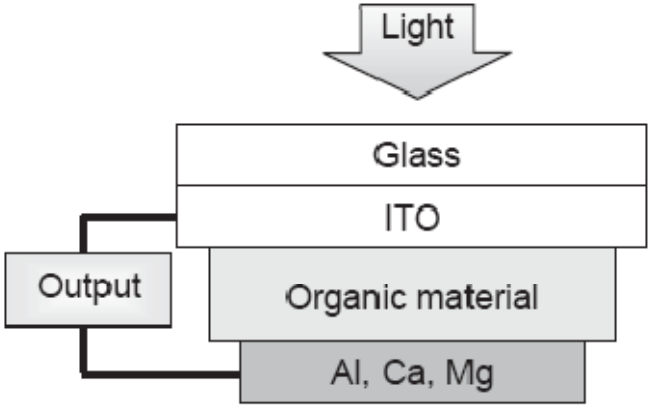


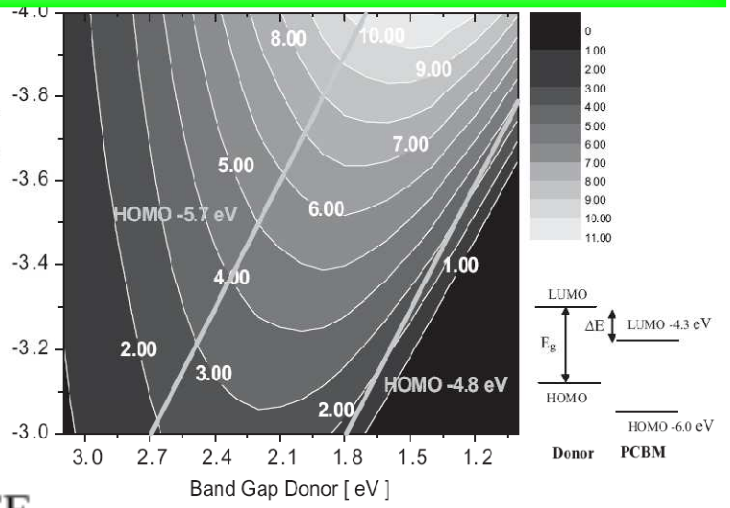


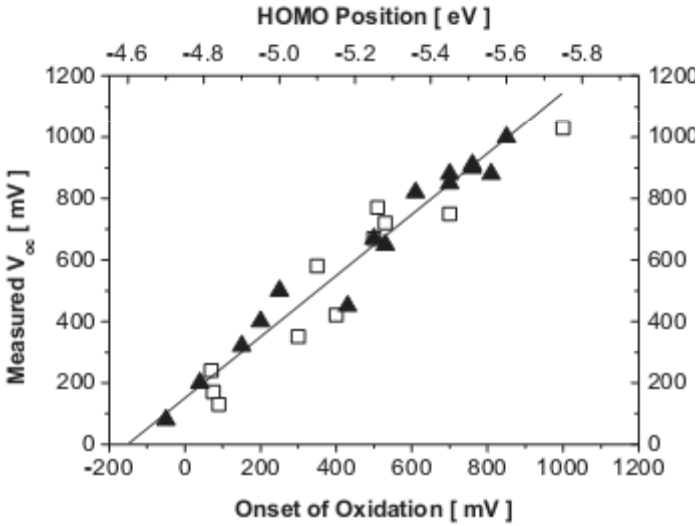
The EA of the PTPQ, PTQ, PPyBT, and PTDA: 2.7~3.0 eV, mismatch with Al→ poor PV efficiency

The importance of HOMO/LUMO level on the Photovoltaic Devices

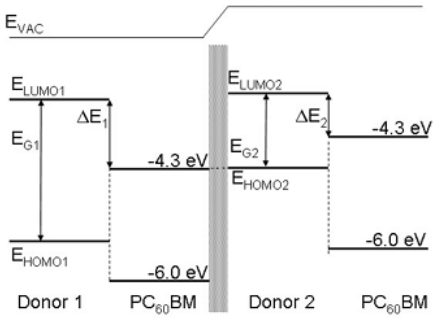




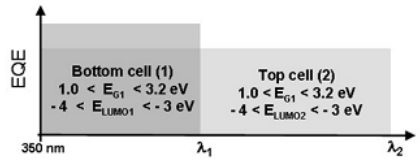




$$\eta_e = \frac{I_{mpp} V_{mpp}}{P_{in}} = \frac{I_{sc} V_{oc} FF}{P_{in}}$$



$$V_{oc} = (1/e)(|E^{Donor}\text{HOMO}| - |E^{PCBM}\text{LUMO}|) - 0.3\ \text{V}$$



Scharber et al., Adv. Mater. 2006, 18, 789

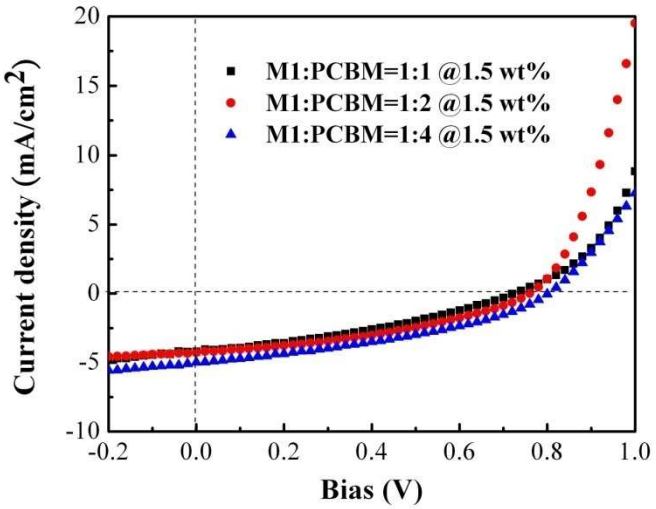
Theoretical PCE ~10% in a single

PV cell: Bandgap of donor polymer < 1.74 eV & LUMO < -3.92 eV using PCBM

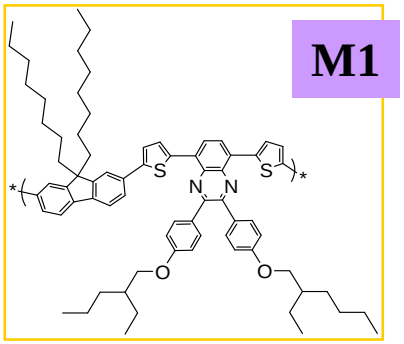
Theoretical PCE up to 15%
By Tandem cell
***Adv. Mater* 2008, *20*, 579-583**

NewQuinoxaline based Donor-Acceptor Conjugated PolymersFor Optoelectronic Applications

Highest Solar Cell PCE :1.76%

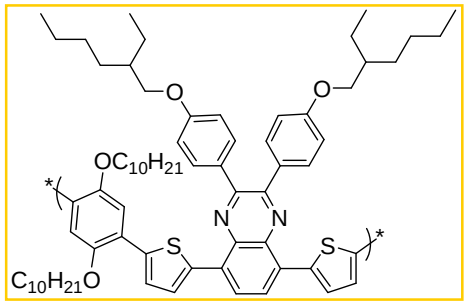


J. Polym. Sci. Polym. Chem. **2009**,
Through the collaboration of
W. C. Chen and F. C. Chen



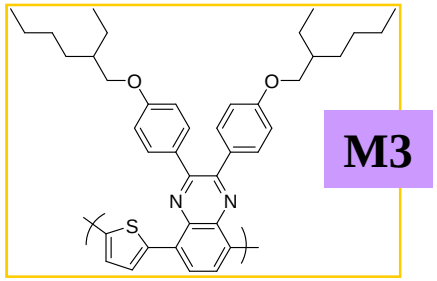
M_n=22308 PDI=2.38

HOMO= -5.18 eV
LUMO= -3.60 eV
Mobility 9.25×10^{-4}
On/off 2.31×10^{4}



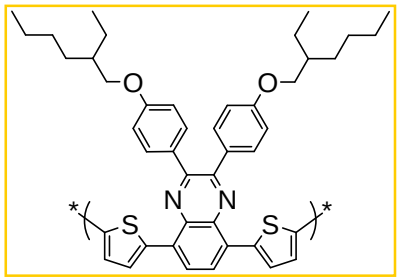
M_n=8590 PDI=1.67

HOMO= -4.91 eV
LUMO= -3.03 eV
Mobility 4.71×10^{-5}
On/off 4.07×10^{3}



M_n=4003 PDI=1.26

HOMO= -5.06 eV
LUMO= -3.36 eV
Mobility 9.25×10^{-4}
On/off 2.3×10^{4}

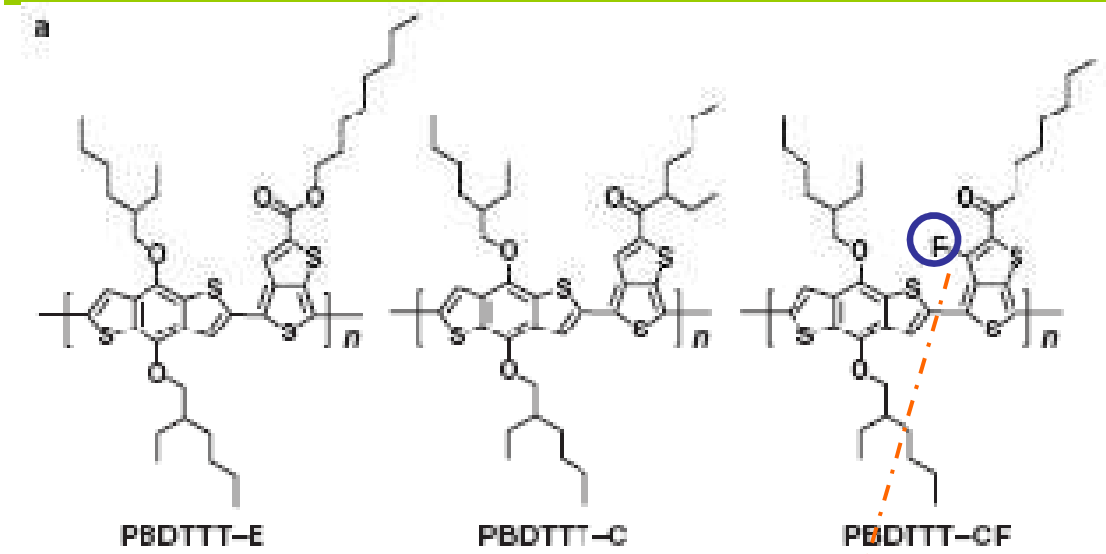


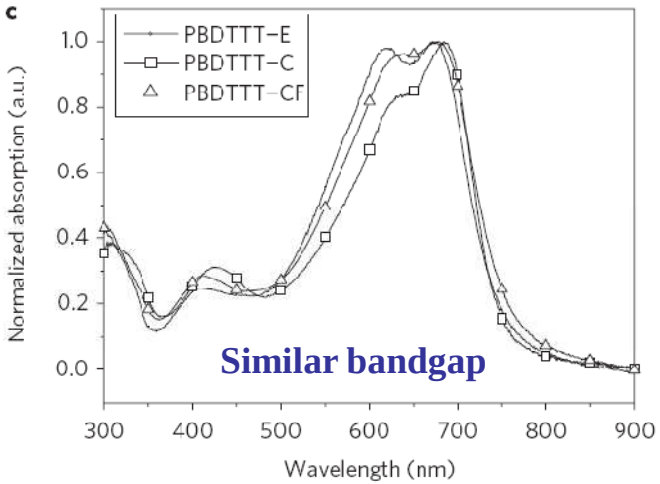
Mn=8450 PDI=1.76

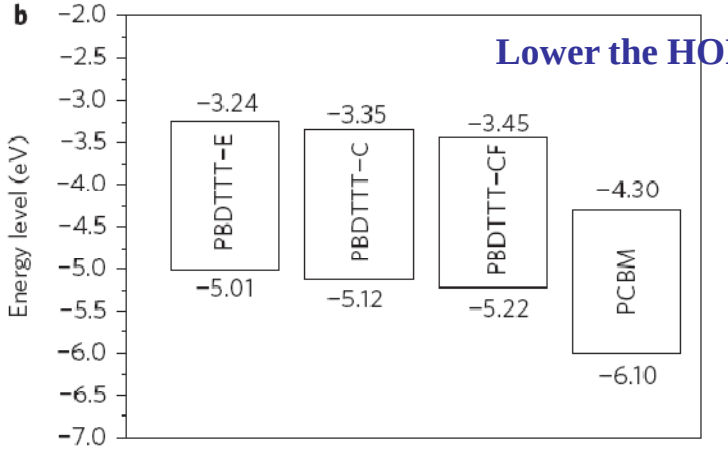
HOMO= -5.06 eV
LUMO= -3.19 eV
Mobility 2.52×10^{-4}
On/off 2.00×10^{4}

Polymer Solar cells with enhanced open-circuit voltage and efficiency

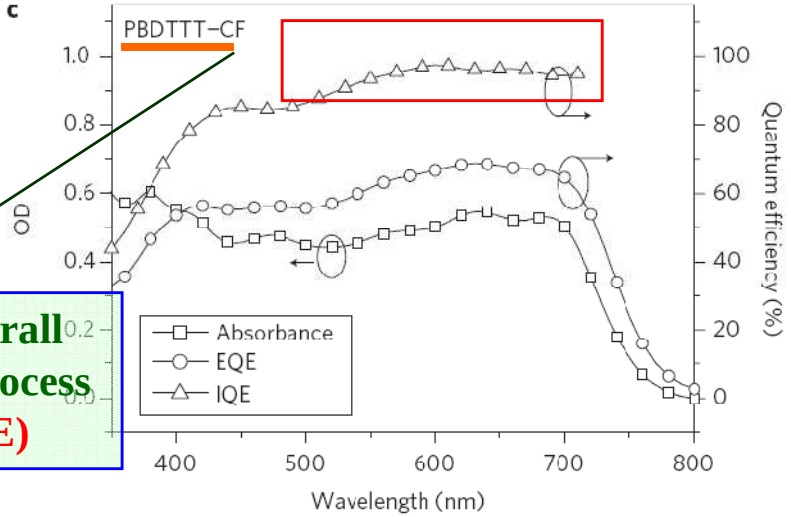
Yu, L. Nat. Photon. **2009**, *3*, 649.







Lower the HOM/LUMO levels



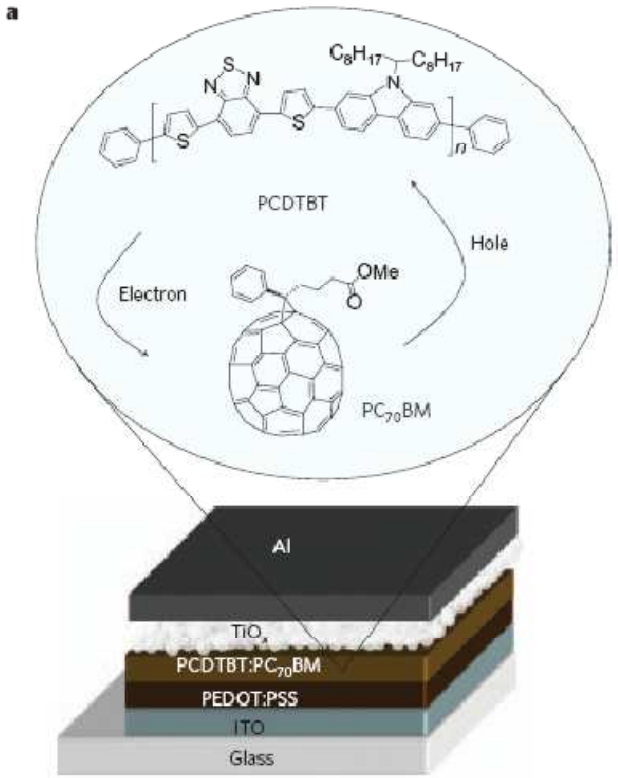
Highly efficient overall photoconversion process in the cell (high IQE)

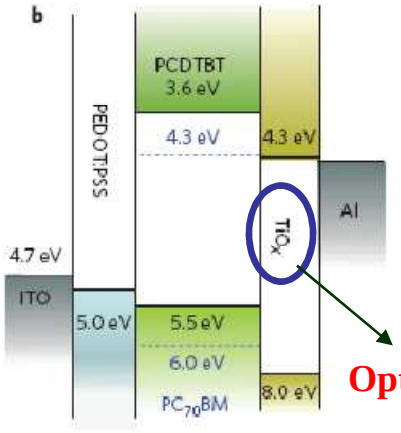
Table 1 | Solar cell parameters of devices based on the three different polymers.

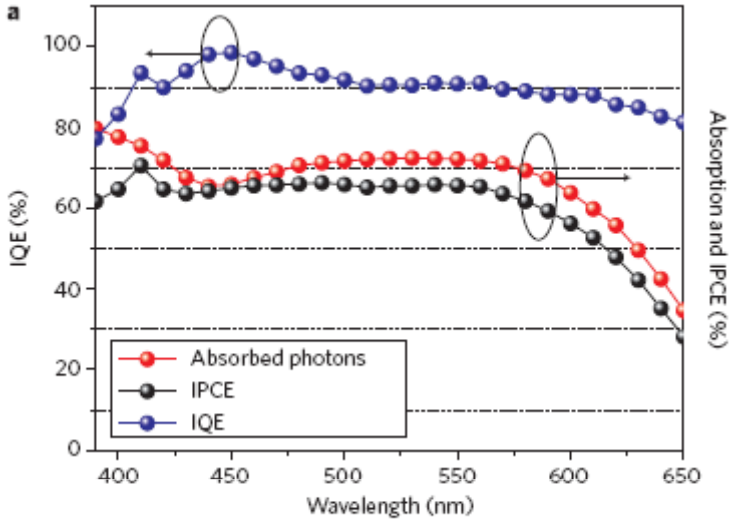
	LUMO	HOMO	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)	
						Best	Ave
PBDTTT-E	−3.24	−5.01	0.62	−13.2	63	5.15	4.8
PBDTTT-C	−3.35	−5.12	0.7	−14.7	64.1	6.58	6.3
PBDTTT-CF	−3.45	−5.22	0.76	−15.2	66.9	7.73	7.4

Bulk heterojunction solar cells with internal quantum efficiency approaching 100%

YU, L. Nat. Photon. **2009**, *3*, 297.



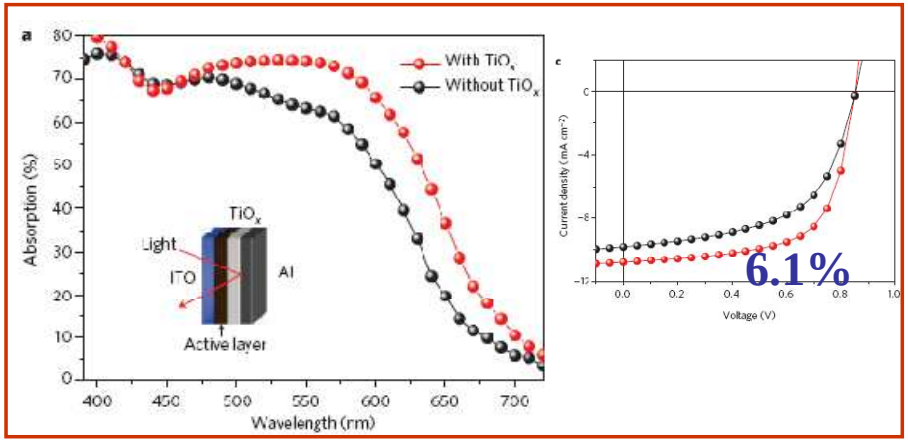




Optical spacer & hole-blocking layer

The TiO_x layer redistributes the light intensity within the BHJ by changing the optical interference between the incident light and the light reflected from the metal electrode. **(opitcal spacer)**

Efficient collection of electrons by hole-blocking feacture of TiO_x

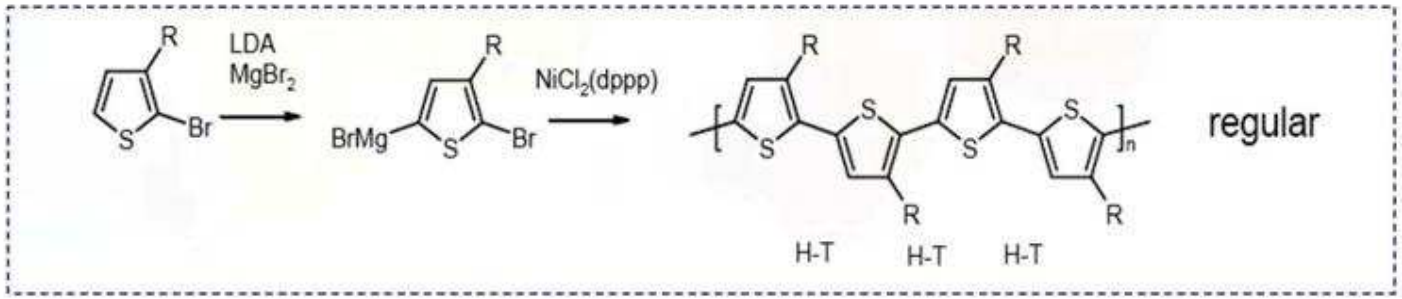


With TiO_x layer, the IQE, EQE, absorption could be enhanced, leading to the best efficiency up to 6.1%

Some of the Approaches in MCL

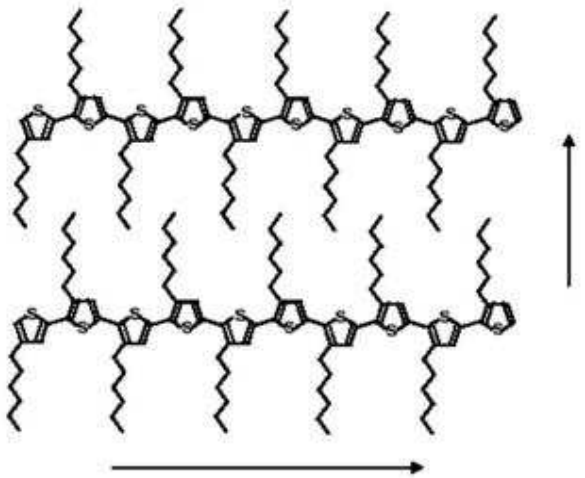
Better packing conducting polymer

— Stereo-regular conducting polymer (no micro-structure defects)



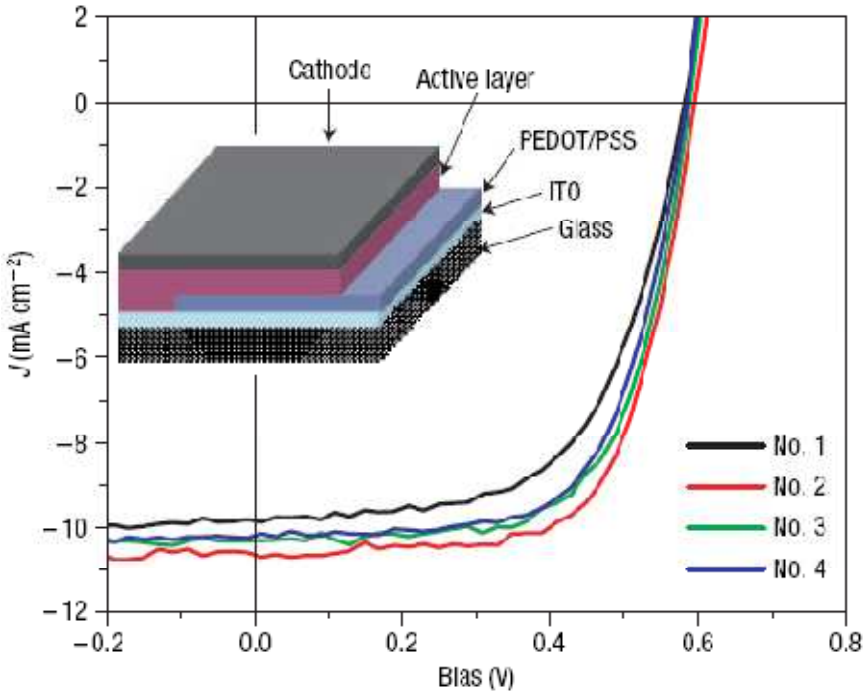
— Tightly-packing conducting polymer but still maintain its processbility

— High mobility conducting polymer design with good solubility



P3HT:PCBM Solar Cells

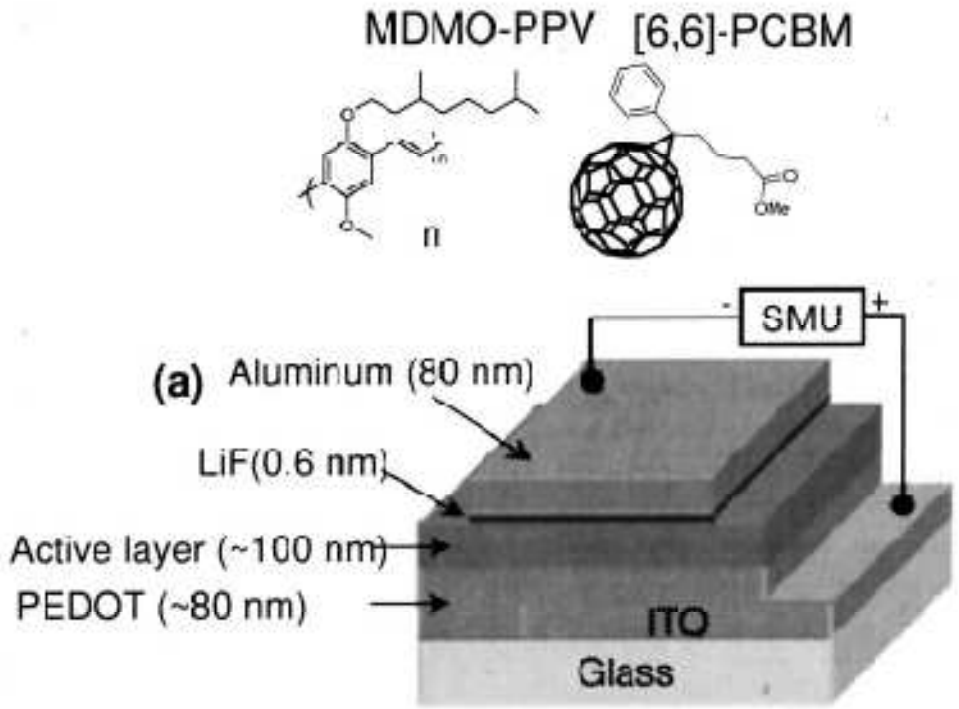
Different annealing time

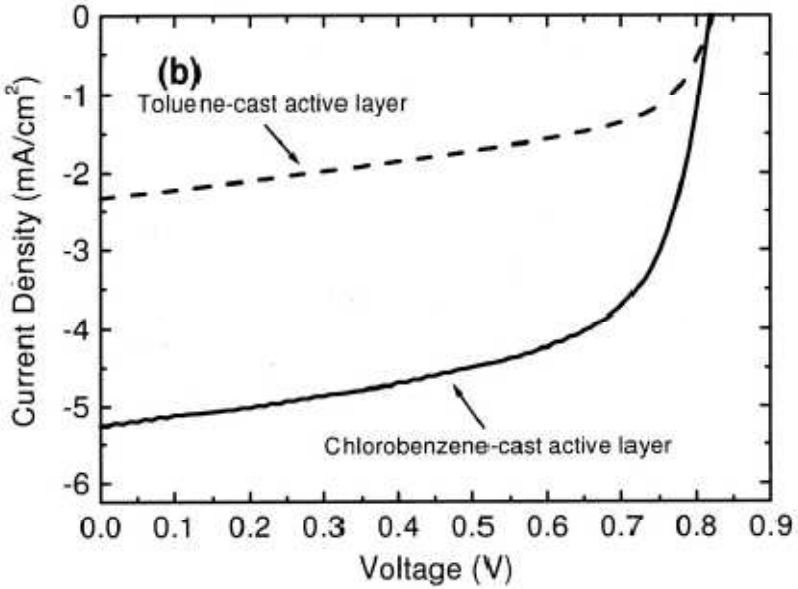


V_{oc} = 0.61 V FF = 0.67

I_{sc} = 10.6 mA/cm^2 PCE = 4.37 %

PPV:PCBM Solar Cells





V_{oc} = 0.82 V **FF = 0.61**

I_{sc} = 5.25 mA/cm² **PCE = 2.5 %**

APL 2001, 78, 841

Importance of Polymer Morphology on Photovoltaic Efficiency

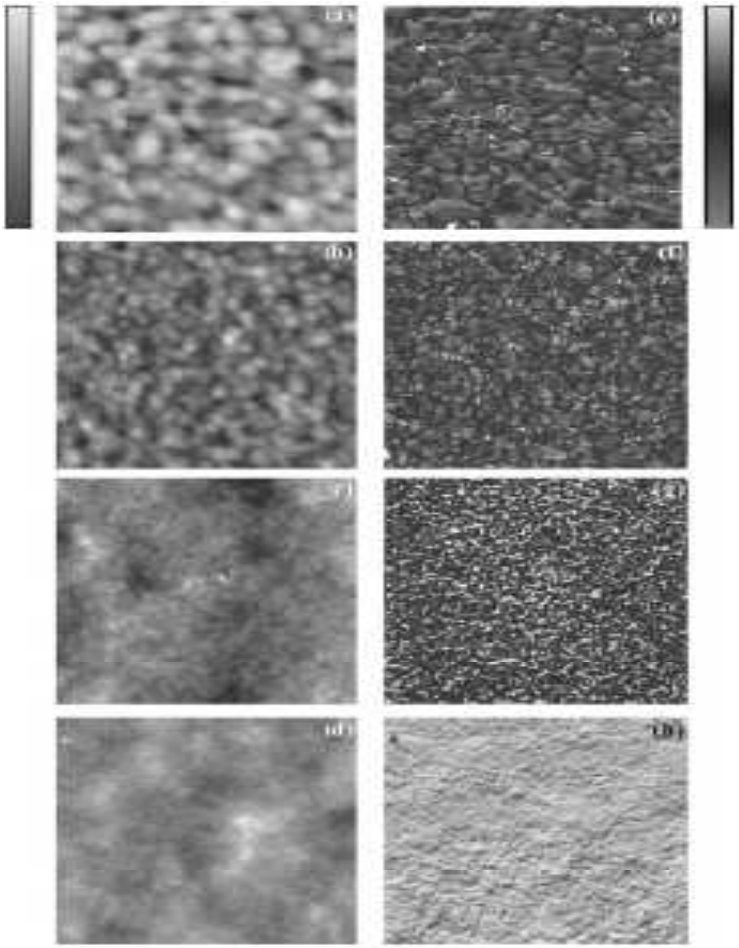
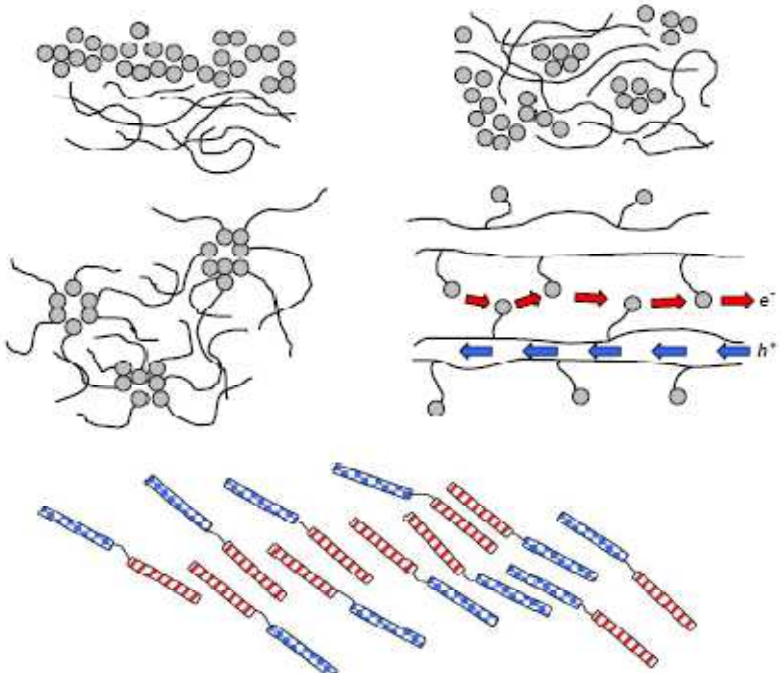


Figure 2. The AFM height (a–d) and simultaneously taken phase (e–h) images of the MDMO-PPV/PCBM composite films of 50 (a,e), 80 (b,f), 67 (c,g), and 90 wt.-% PCBM (d,h). Height bar (maximum peak-to-valley) represents 20 nm (a), 10 nm (b), 3 nm (c), and 3 nm (d). The size of the images is 2.0 μm × 2.0 μm.



Morphology determining parameters:

The spin casting solvent
The composition between polymer and fullerene
The solution concentration
The controlled phase separation and crystallization induced by thermal annealing
The chemical structure of the materials

Adv. Funct. Mater. 2004, 14, No. 5, May *J. Mater. Chem.*, 2006, 16, 45–61 *H. Spanggaard, F.C. Krebs / Solar Energy Materials & Solar Cells 83 (2004) 125–146*

Enhanced thermal stabilitiy and efficiency by Low Temp. Drying

Adv. Funct. Mater. **2010**, *20*, 834

With the LT process, the low drying temperature **enhanced P3HT nucleation**, but **restricted P3HT/PCBM phase separation** (due to the limited movements of the molecules under the low temperature), resulting in a morphology where abundant P3HT nuclei dispersed within a fine mixture of PCBM-rich domains and amorphous P3HT-rich domains.

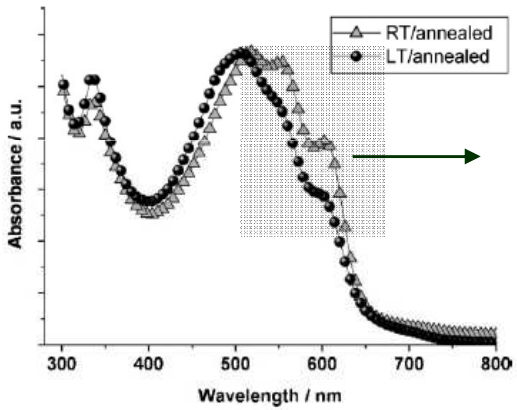


Figure 6. UV–vis spectra of the RT and LT layers (annealed at 190 °C for 2 min).

In **RT**, the larger P3HT crystallite size would result to the higher π- π* interaction

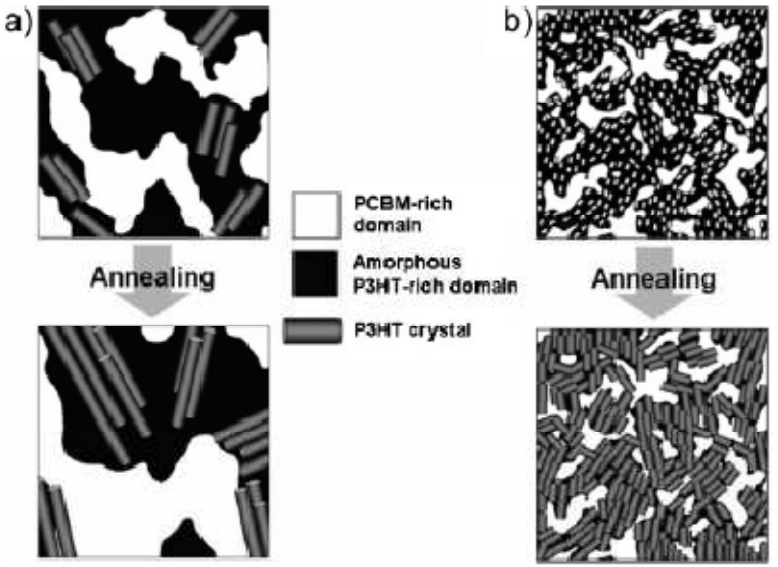


Figure 7. Schematic representations illustrating the morphology of the active layer upon drying (top) and annealing (bottom): a) the RT and b) LT layers.

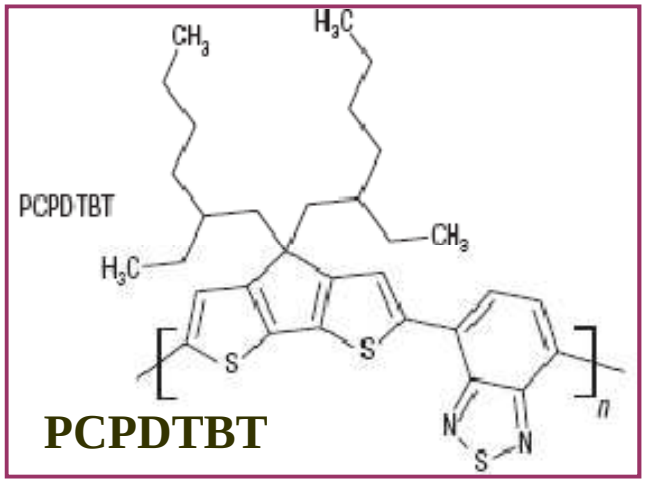
Process	Annealing	J_{sc} [mA cm^{-2}]	V_{oc} [mV]	FF [%]	PCE [%]
RT	None	9.42 ± 0.54	534 ± 18	63.7 ± 1.6	3.20 ± 0.14
RT	2 min/190 °C	8.41 ± 0.46	587 ± 16	65.4 ± 1.3	3.23 ± 0.18
RT	30 min/190 °C	8.25 ± 0.39	566 ± 14	53.3 ± 4.6	2.49 ± 0.18
RT	8 h/100 °C	1.72 ± 0.28	545 ± 7	39.0 ± 2.1	0.36 ± 0.05
RT	1368 h/65 °C [a]	2.48 ± 0.29	487 ± 14	37.2 ± 2.3	0.45 ± 0.07
LT (−5 °C)	None	1.40 ± 0.47	418 ± 15	33.9 ± 0.9	0.20 ± 0.06
LT (−5 °C)	2 min/190 °C	11.50 ± 0.73	615 ± 11	62.8 ± 2.4	4.43 ± 0.31

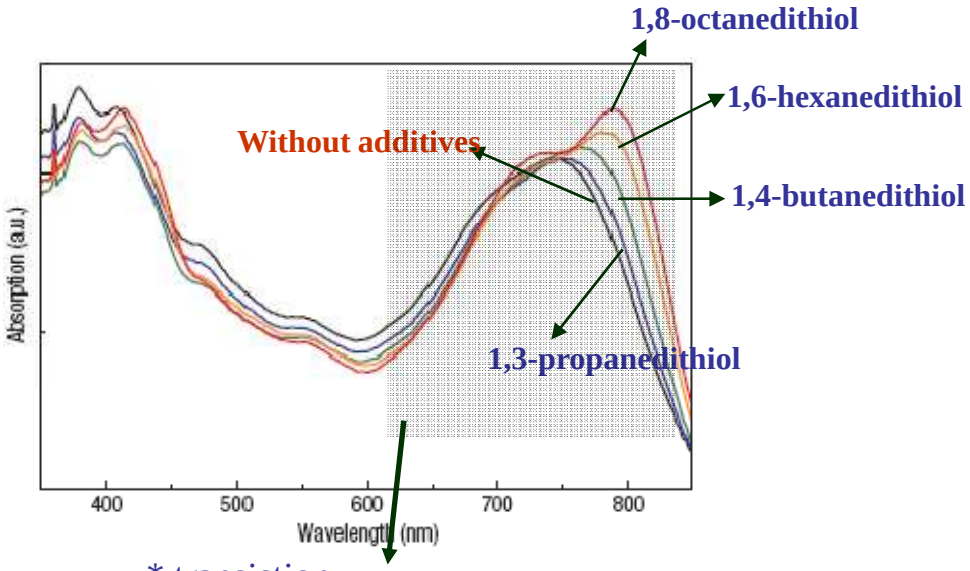
P3HT/PCBM (21mg/mL, 1:1, 600rpm 50sec)

Best PCE~4.7%

Efficiency enhancement in low-bandgap polymer solar cells by processng with alkane dithiols

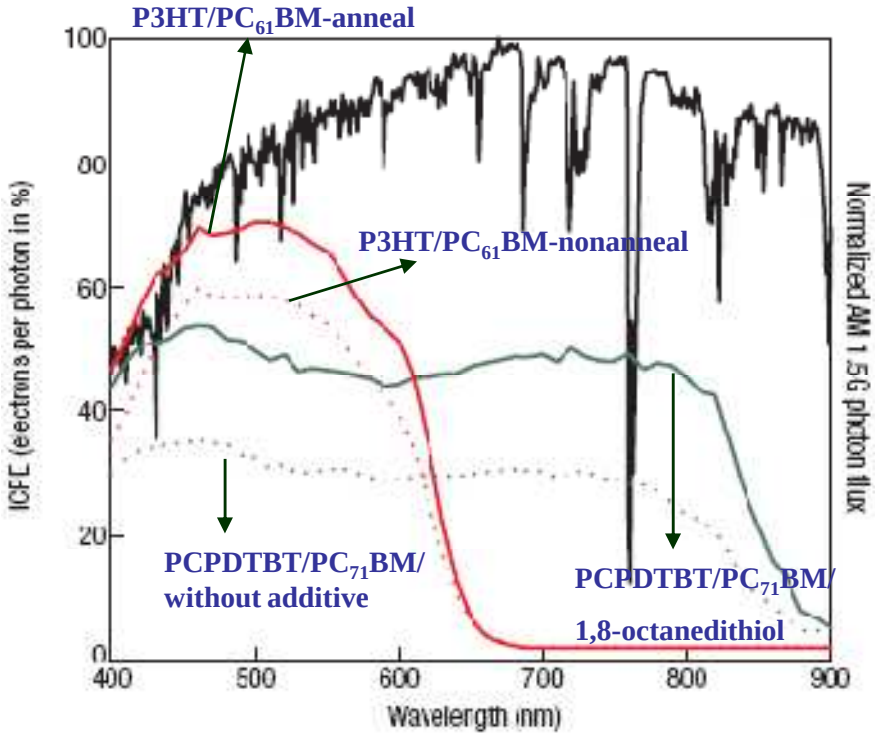
Heeger, Nat. Mater. **2007**, *6*,497.

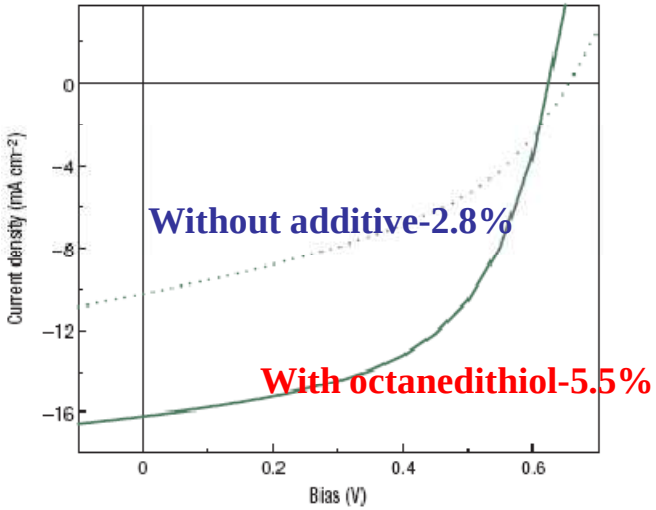




π- π* transistion

It indicates that the PCPDTBT chains interact more strongly and improved local structural order compared with films processed from pure chlorobenzene.

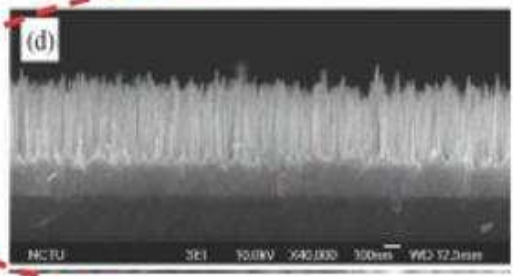


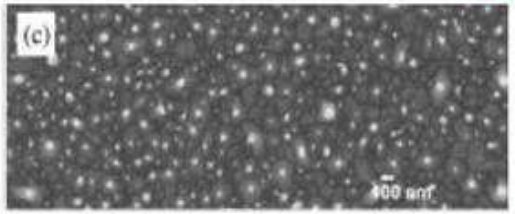


Defined transport path

From Polymer:

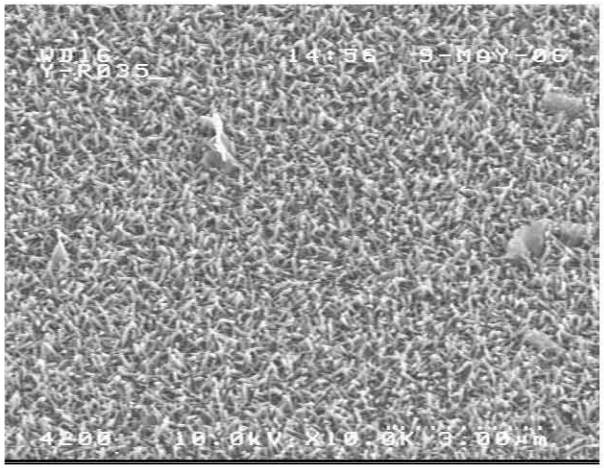
From Nanocrystal:

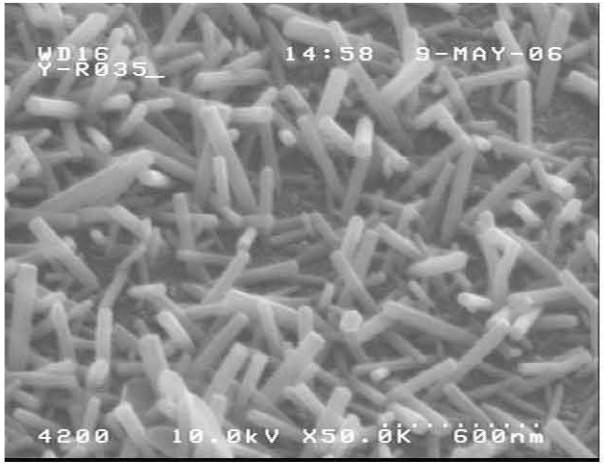




Control of Surface Grown ZnO

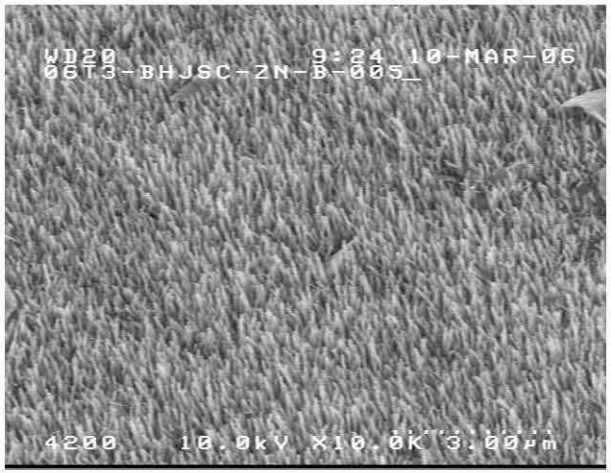
Spin-coating
LD ZnO

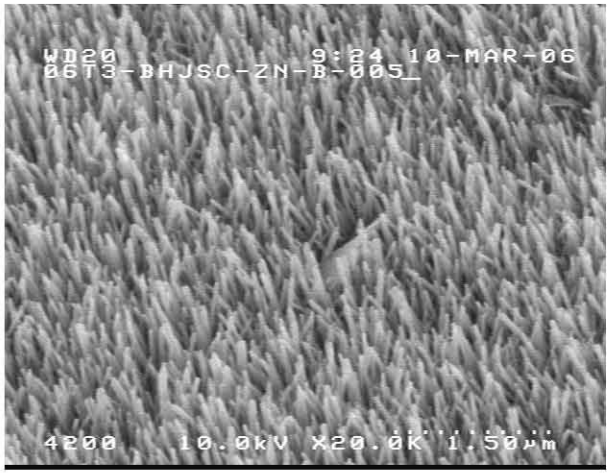




Surface unmodified

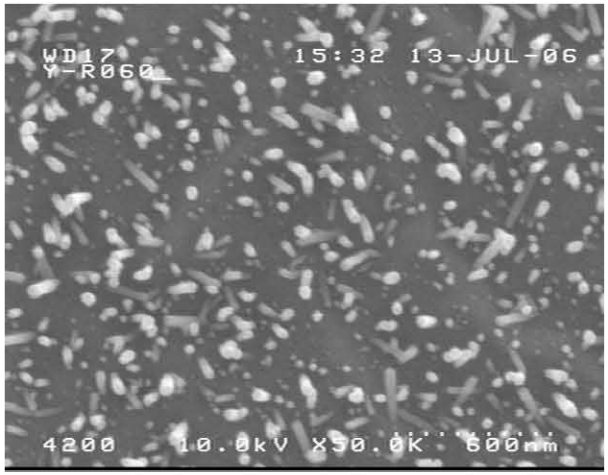
Dip-coating
HD ZnO

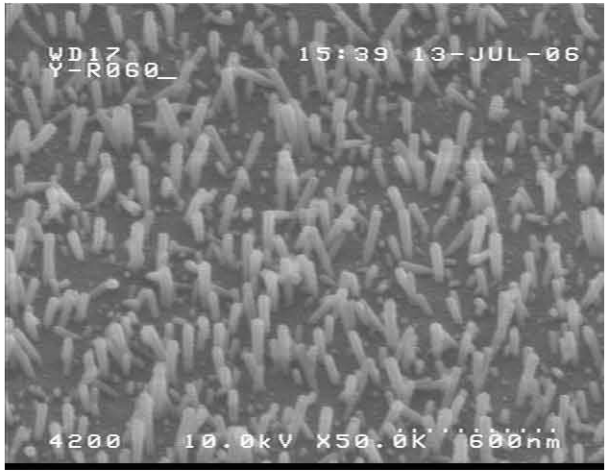




Surface unmodified

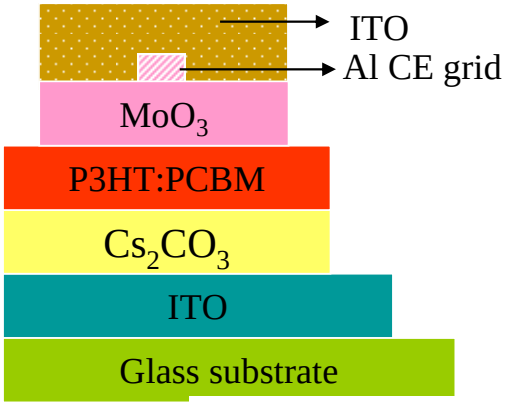
Spin-coating
LD ZnO

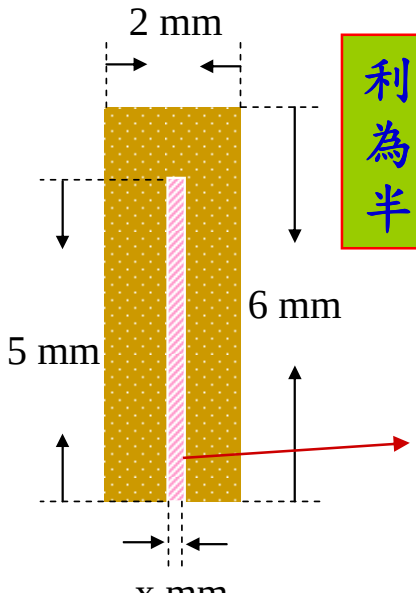




Surface modified

Inverted semi-tranparent OPVs

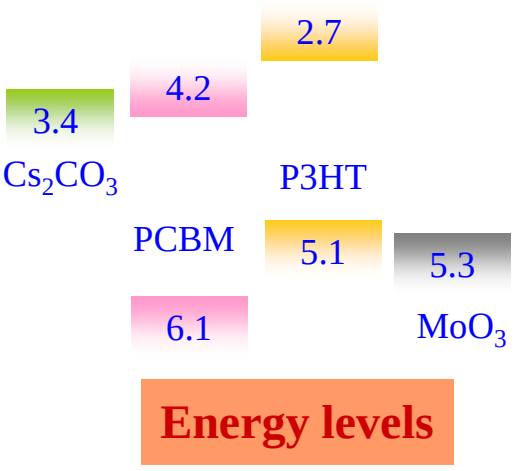




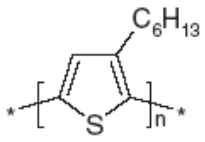
利用 ITO/Cs_2CO_3 以及 MoO_3/ITO 作為透明電極，發展高效率之倒置式半透明元件

Shadow fraction:

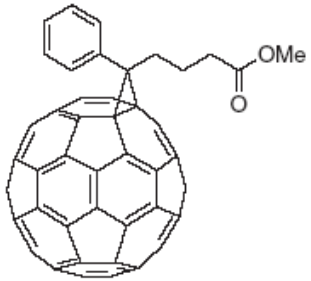
5%, 10%, 15%



Energy levels



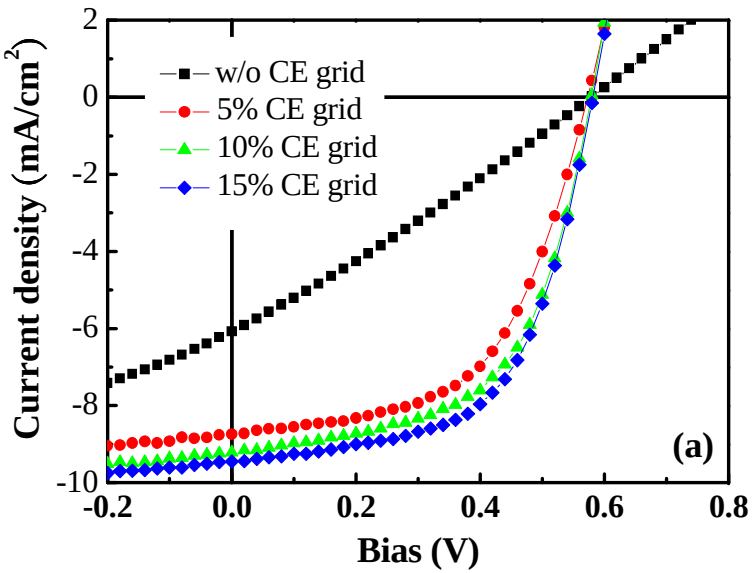
P3HT

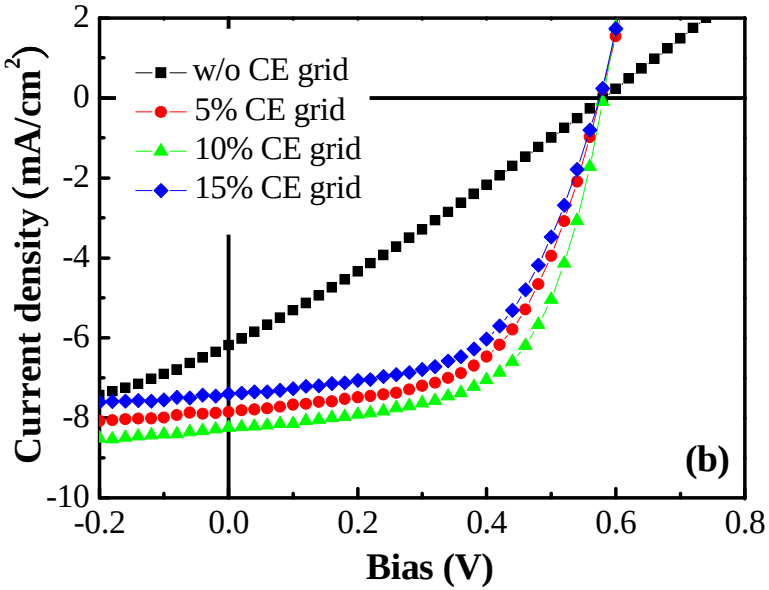


PCBM

F. C. Chen, J. L. Wu, K. H. Hsieh, and W. C. Chen, *Org. Electron*. 2008

J-V characteristics





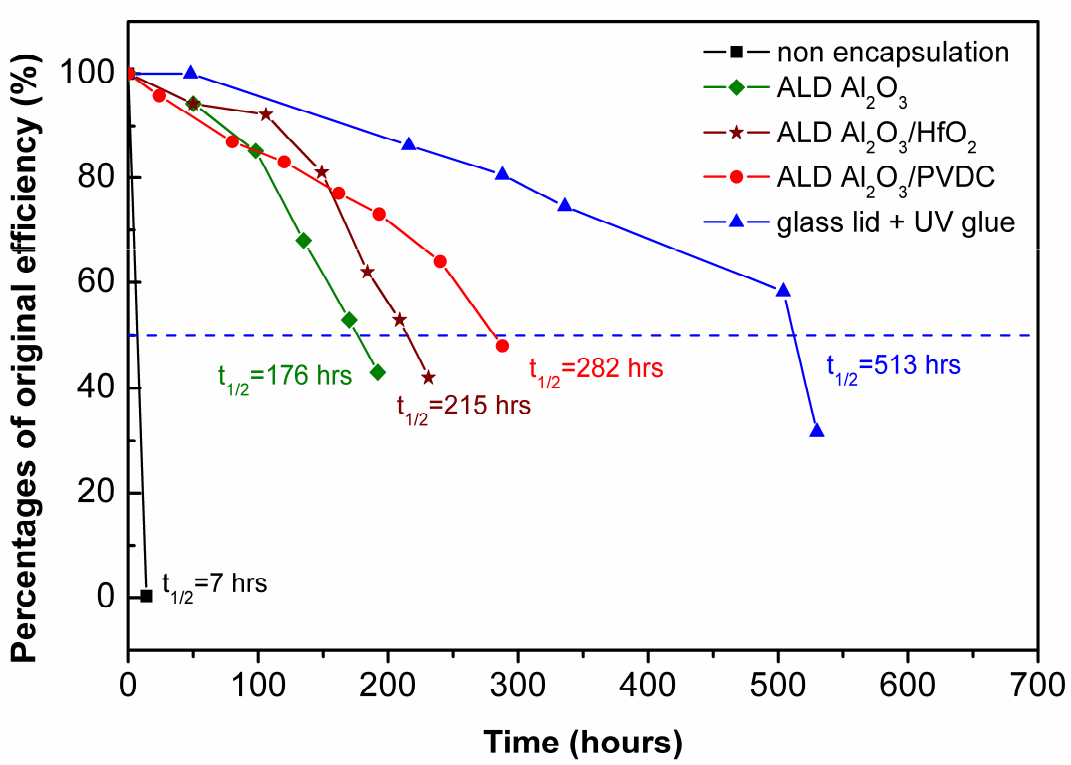
Bottom-illuminated

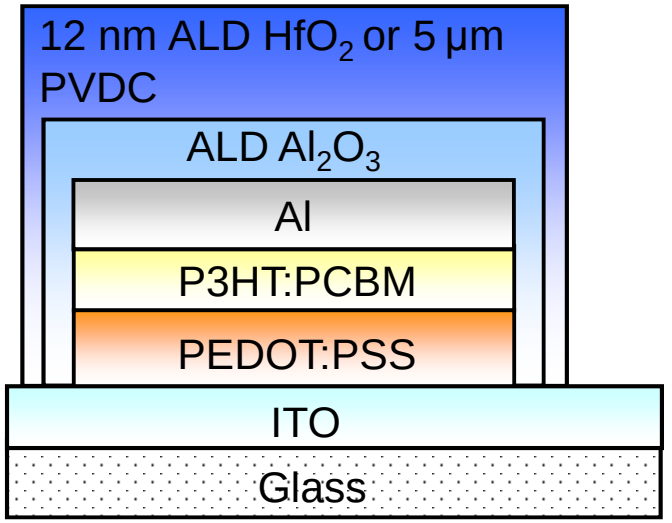
Top-illuminated

Incorporating an Al CE grid of 10% shadow fraction, the semi-transparent OPVs exhibited very similar electrical characteristics whether the device was illuminated from the bottom side (PCE = 3.15%) or from the top side (PCE = 2.8%).

高分子太陽能電池封裝技術之開發

Adding a hydrophobic layer, including a ALD HfO_2 film or a PVDC film, on top of the ALD Al_2O_3 increased the lifetime to up to 282 hrs





	Al_2O_3	Al_2O_3/HfO_2
Water contact angel (deg)	**79**	**98**