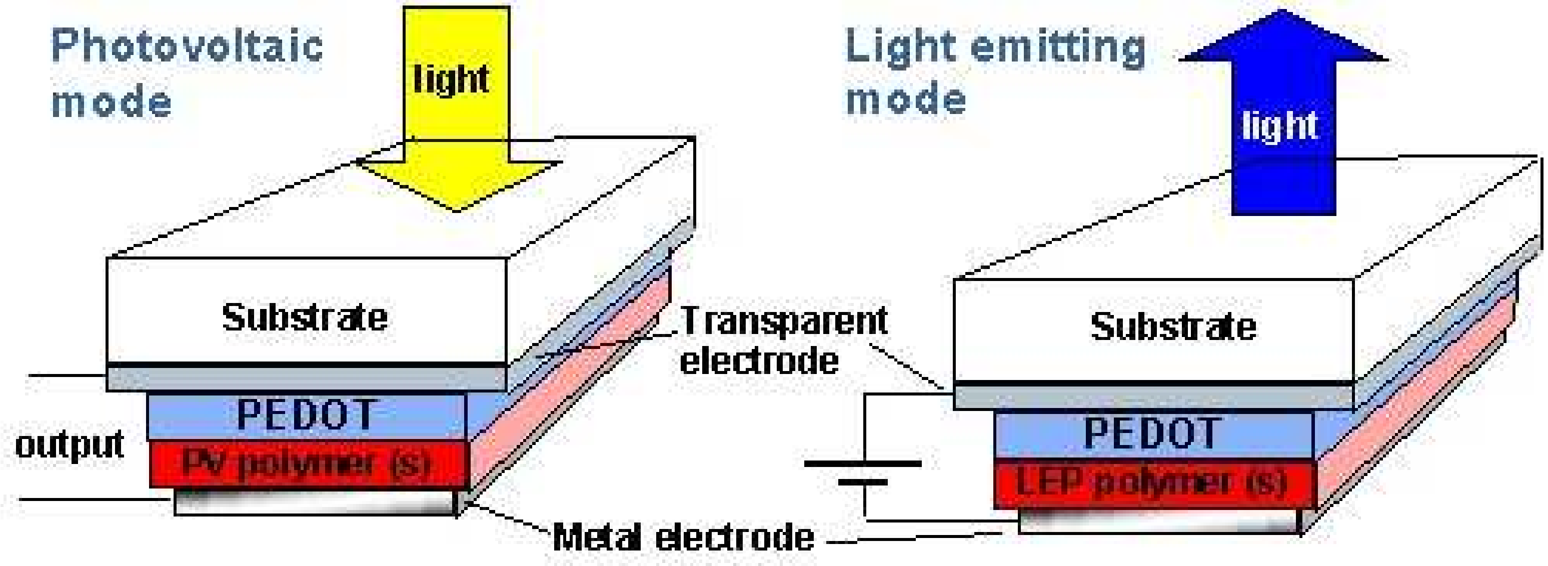
Outlines

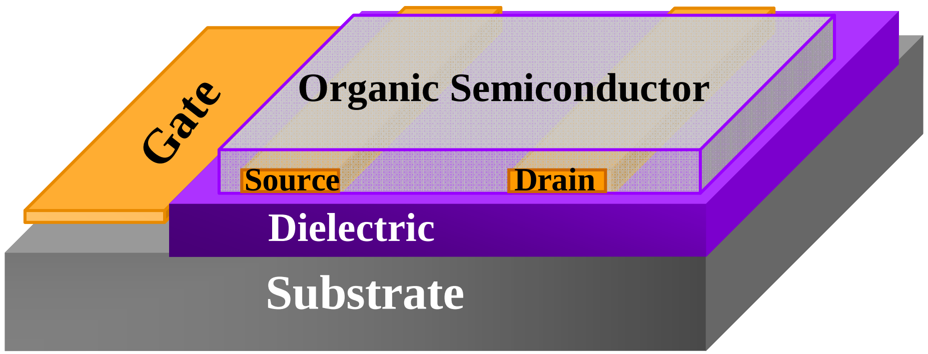
- **History of Conjugated Polymers**
- **Electronic Structures of Conjugated Polymers**
- **Polymer Light-emitting Diodes**
- **Polymer-based Thin Film Transistors**
- **Polymer-based Photovoltaics**
- **Polymers for Memory devices**

Device Applications of Donor-Acceptor Conjugated Polymers in My Group

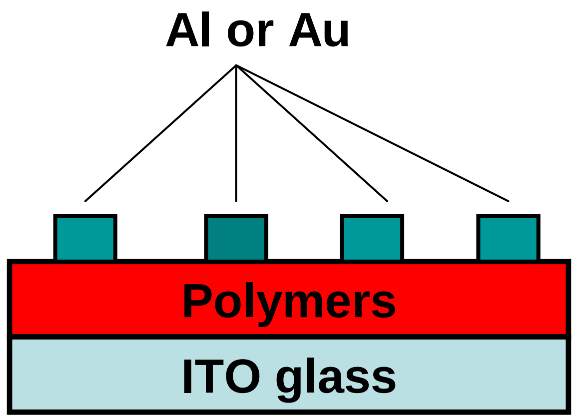
Polymer Solar Cells

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**

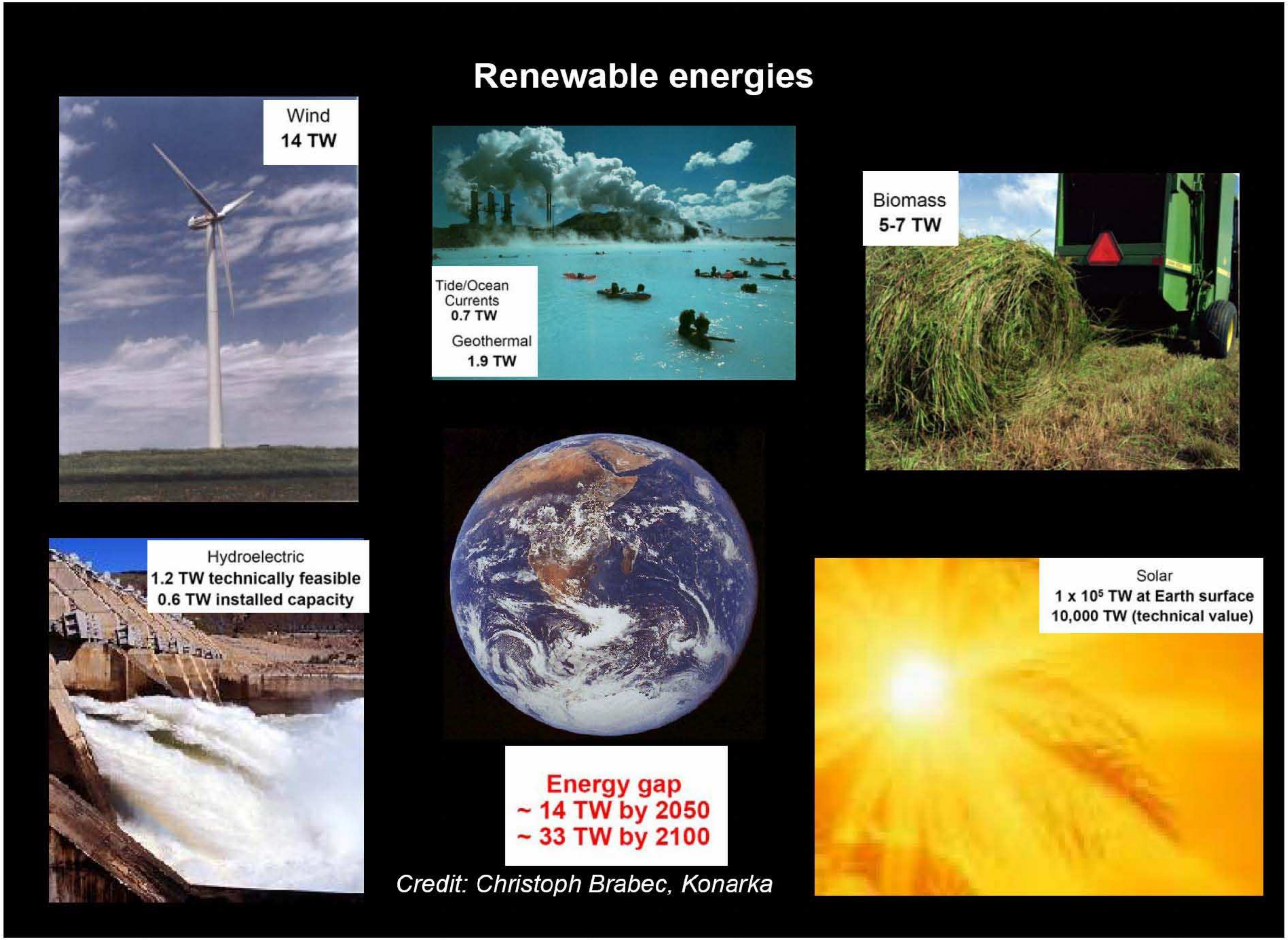
Source: Richard Smalley, Energy & Nanotechnology Conference, Houston; Christoph Brabec; Konarka .

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)

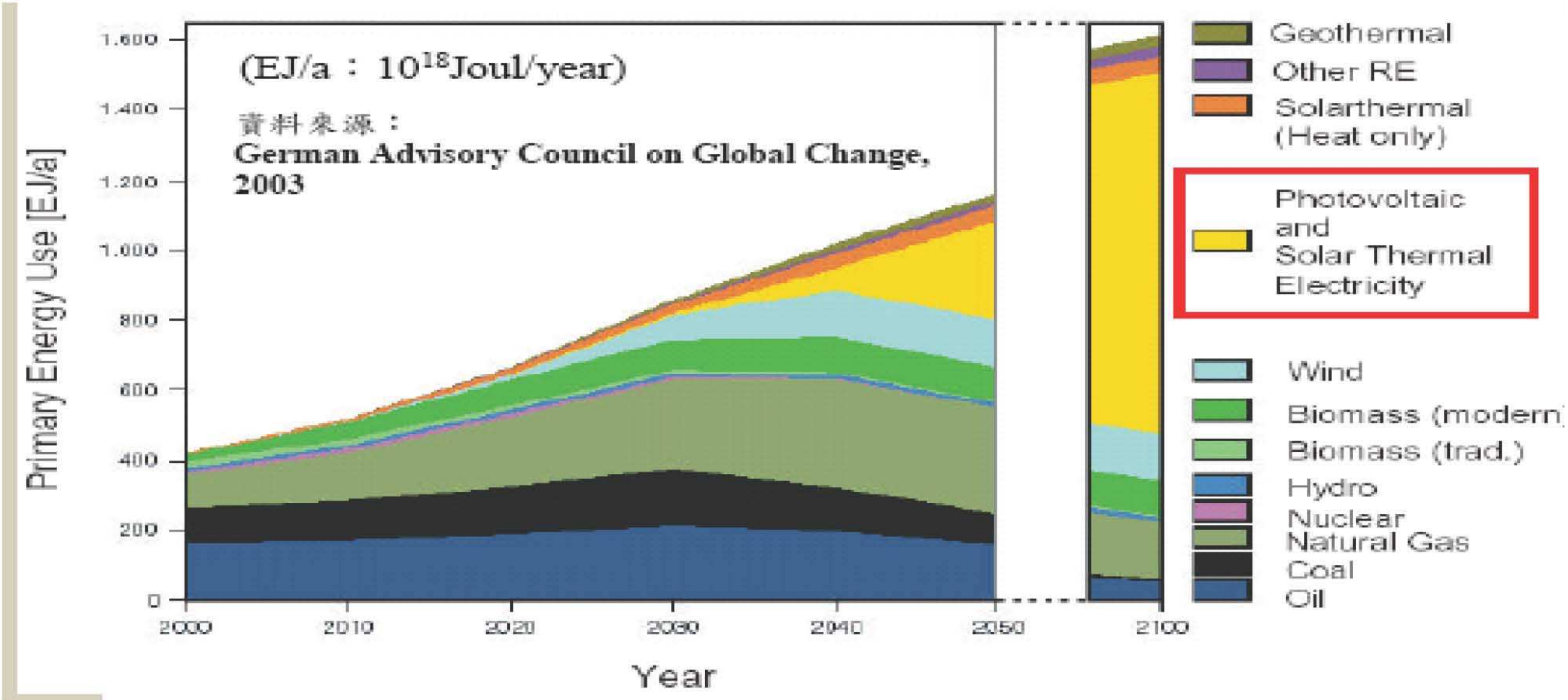

Renewable energies
Wind
14 TW
Tide/Ocean Currents
0.7 TW
Geothermal
1.9 TW
Biomass
5-7 TW
Hydroelectric
1.2 TW technically feasible
0.6 TW installed capacity
Solar
1 x 10⁵ TW at Earth surface
10,000 TW (technical value)
Energy gap
~ 14 TW by 2050
~ 33 TW by 2100
Credit: Christoph Brabec, Konarka

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)

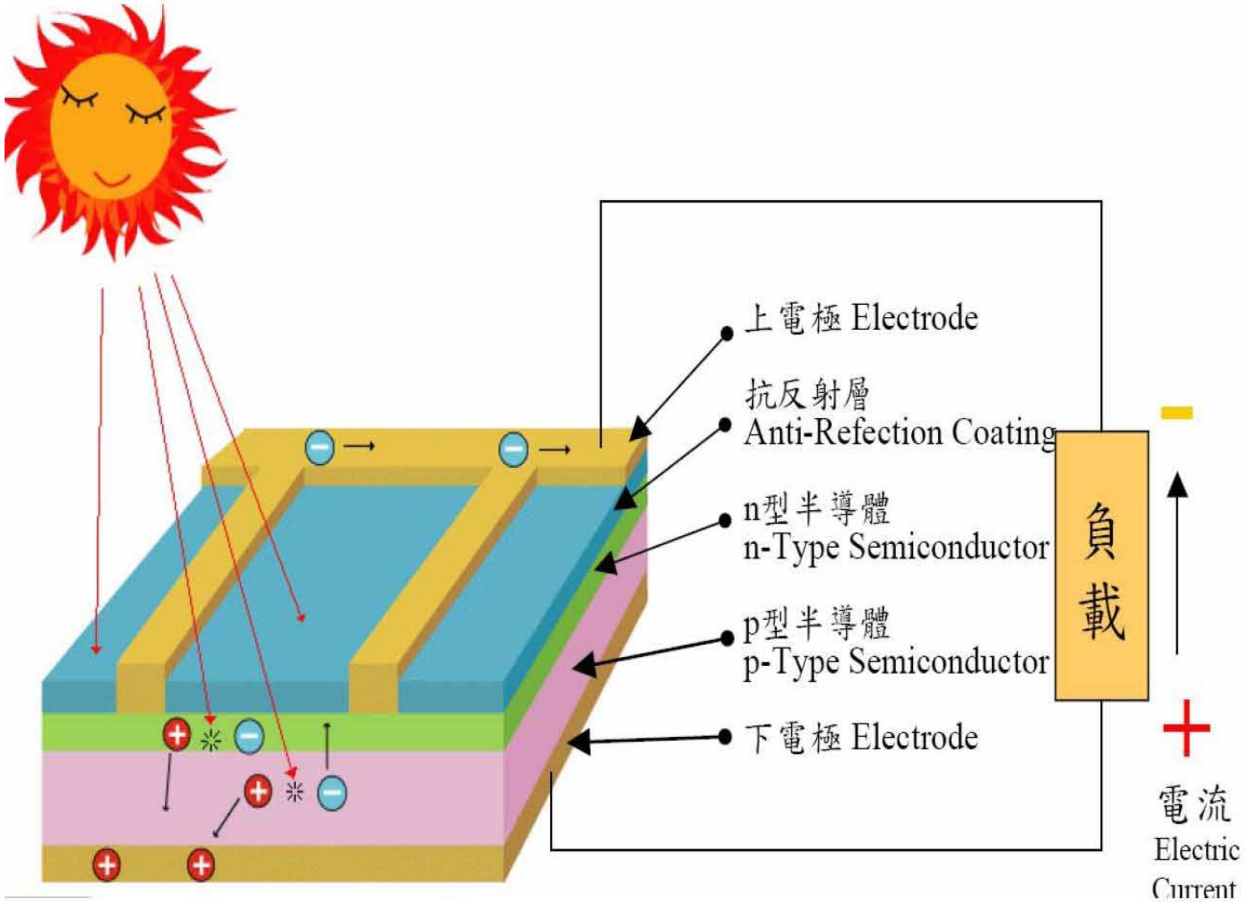
History of Organic Solar Cells

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

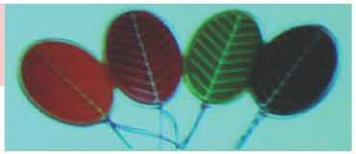
- Solar Cells
  - Silicon
    - Bulk
      - Single Crystalline
      - Multi Crystalline
    - Thin Film (a-Si; uc-Si)
  - Compound
    - GaAs
    - CdSe, CdTe, $CuInGaSe_2$
  - Organic
    - Conducting Polymer
    - Small molecules
    - Dye Sensitized

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)



Technology Push

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

Highest Solar Cell Efficiency Tables until 2006. 04

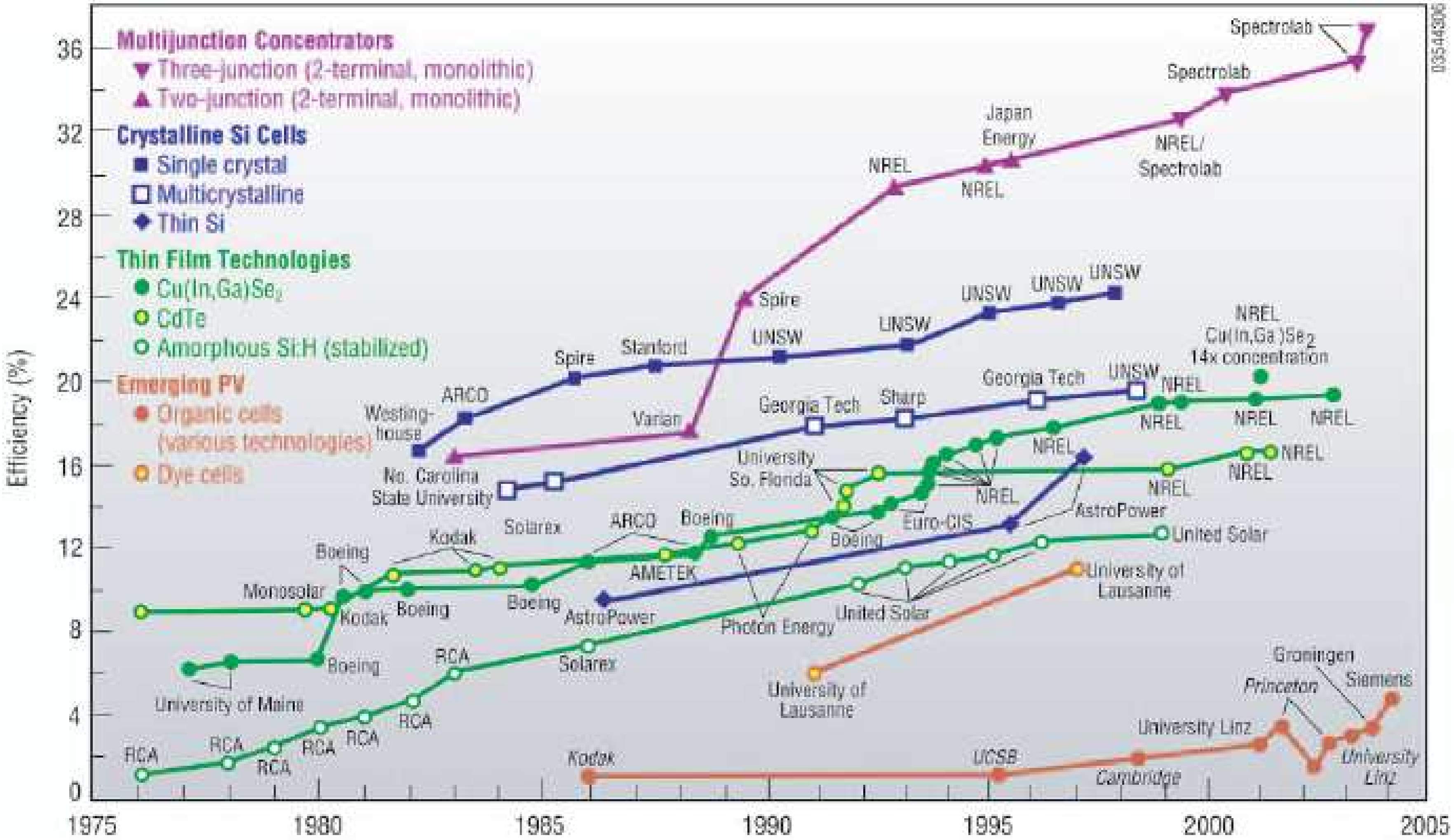
Table I. Confirmed terrestrial cell and submodule efficiencies measured under the global AM1.5 spectrum (1000 $W m^{-2}$) at 25°C

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

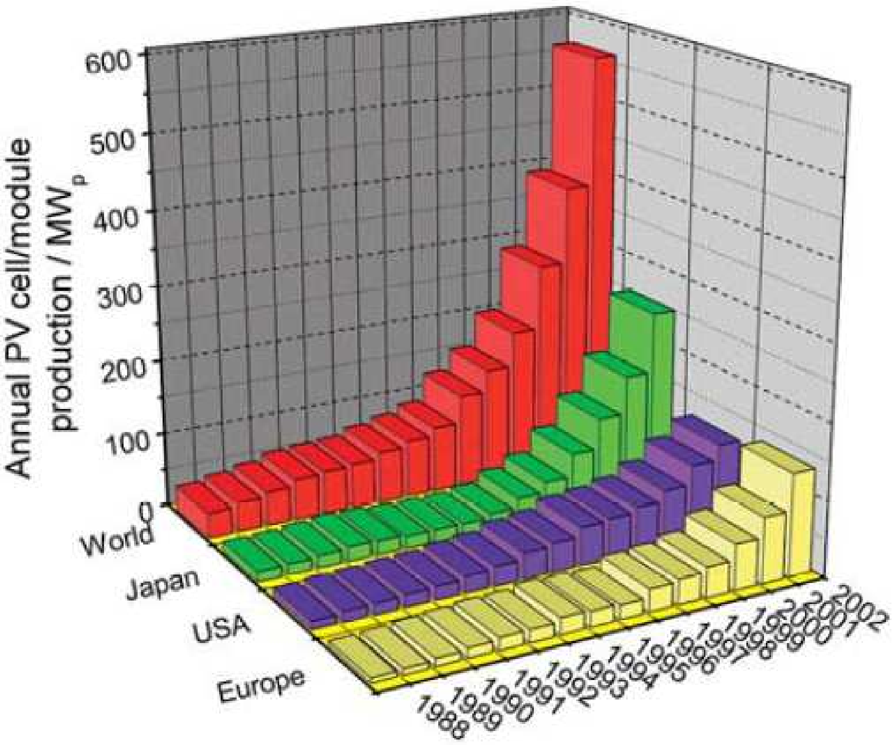
Efficiency of Photovoltaic Devices

Measured Solar Cell Efficiency from 1975 to the present

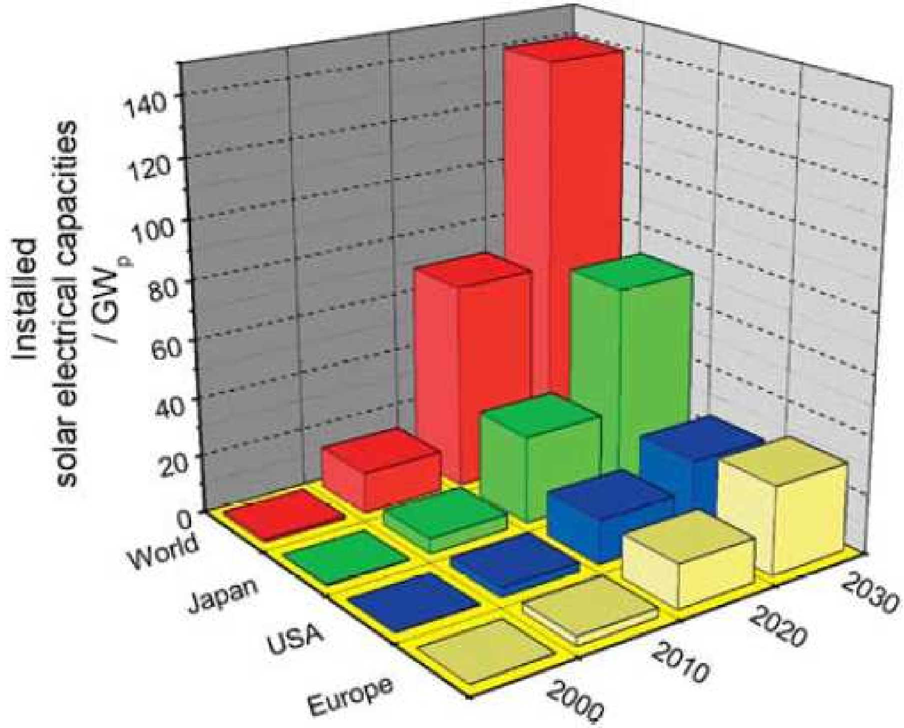


From NREL, USA

Requirement Trends of the Photovoltaic Industry



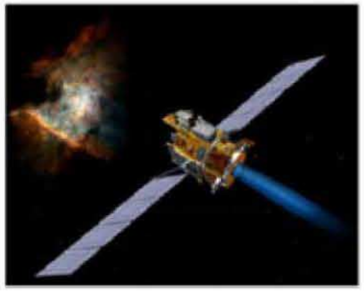
Annual PV cell/module production



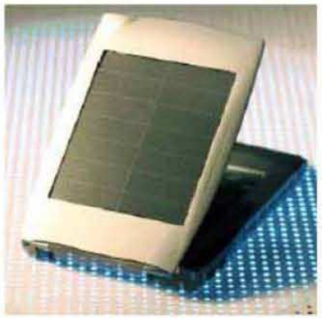
Estimation of present and future installed solar capacities

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
- 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)
- 緊急防災用電力系統
- 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

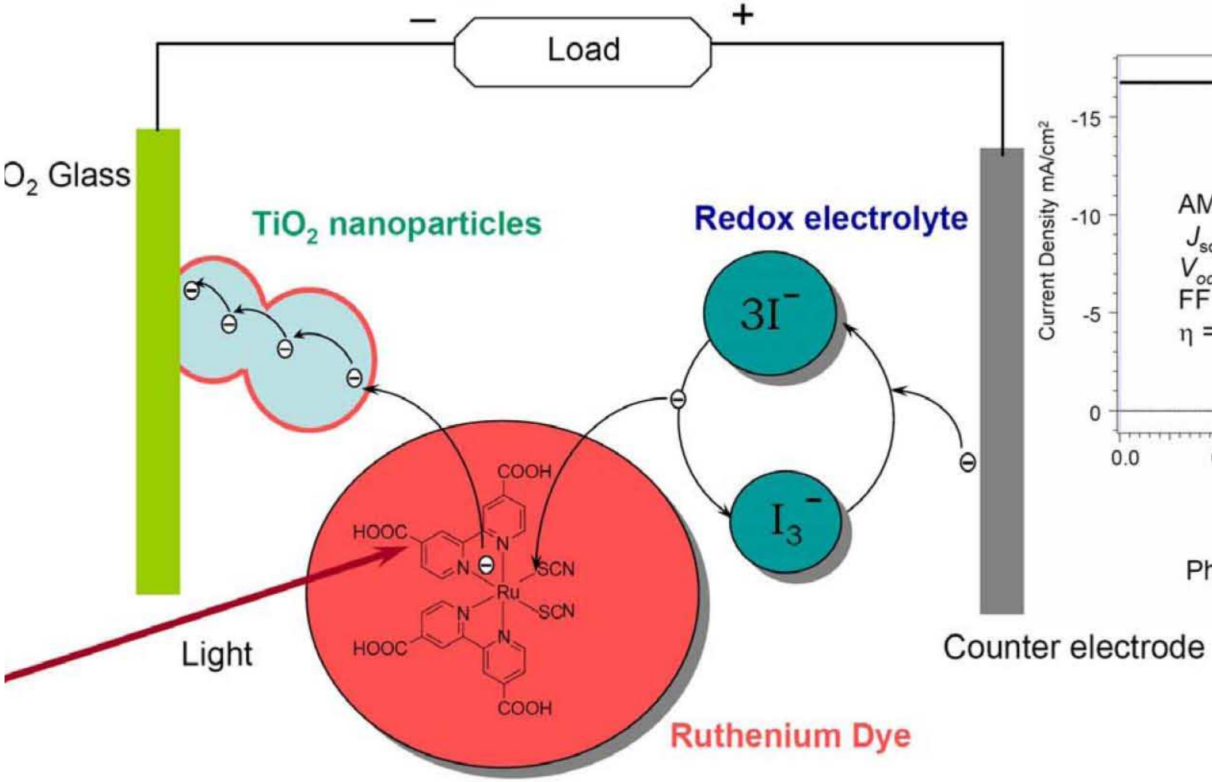
- Dye sensitized solar cells: Electrochemical cells
- Small molecule organic solar cells: Made by vacuum deposition
- Polymer solar cells: Made by solution, low temperature processing

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

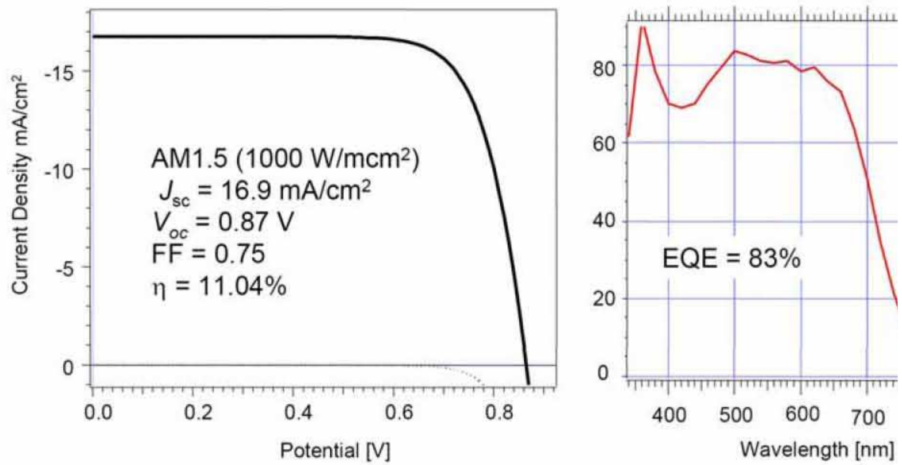
Physical cell !!

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

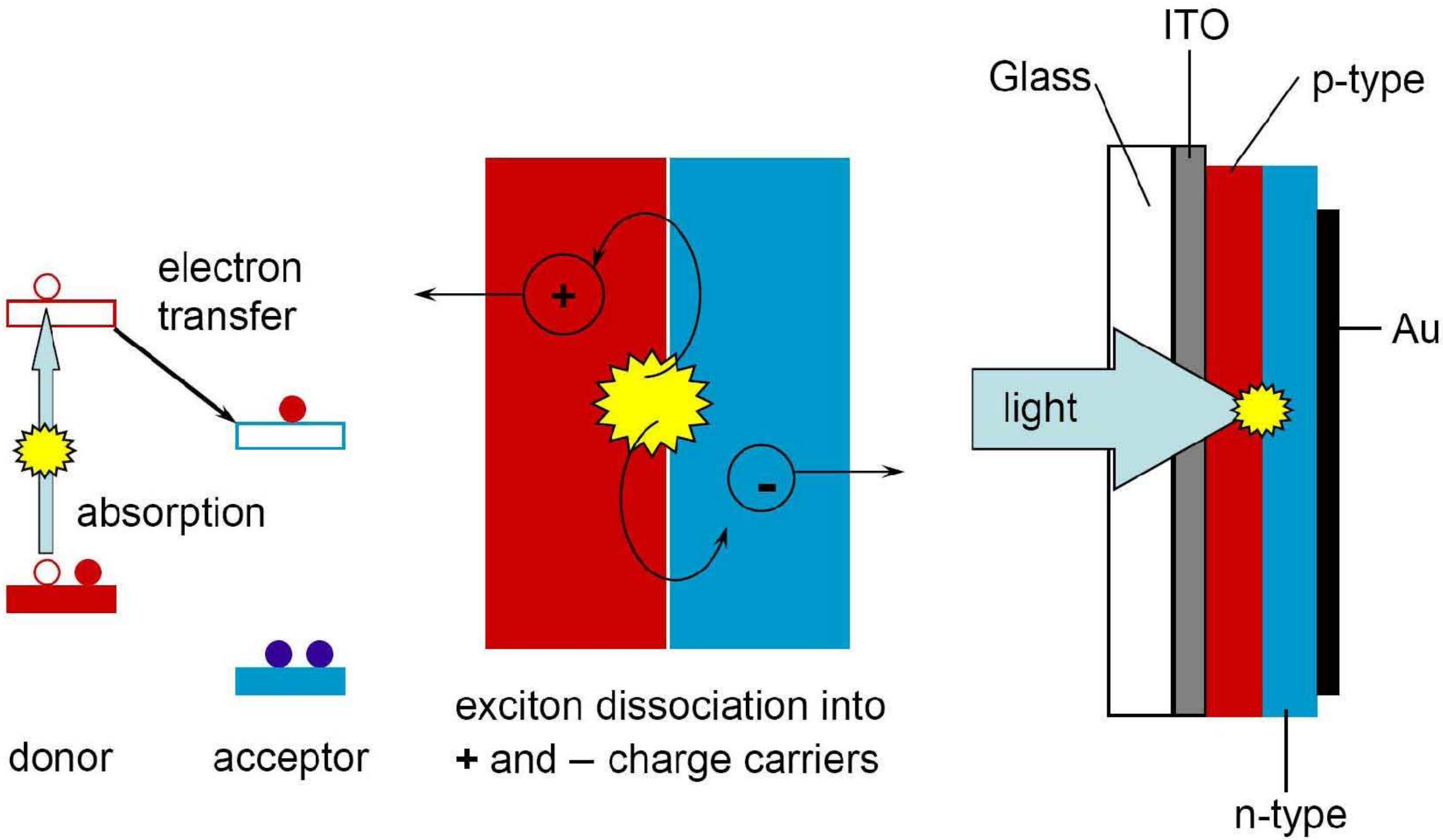


Photocurrent action spectrum obtained with the N719 dye attached to 16 + 4 μm nanocrystalline TiO2 film

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:	$e^-(Pt) + h\nu \rightarrow e^-(TiO_2)$	

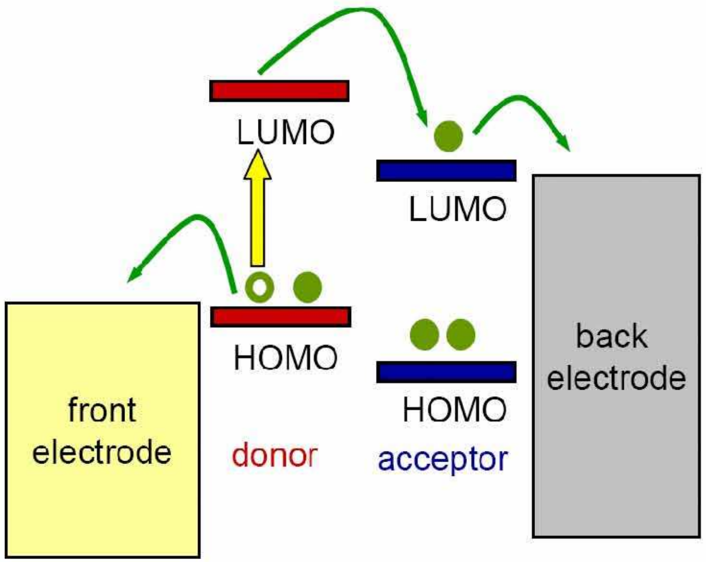
Organic double layer p/n cell

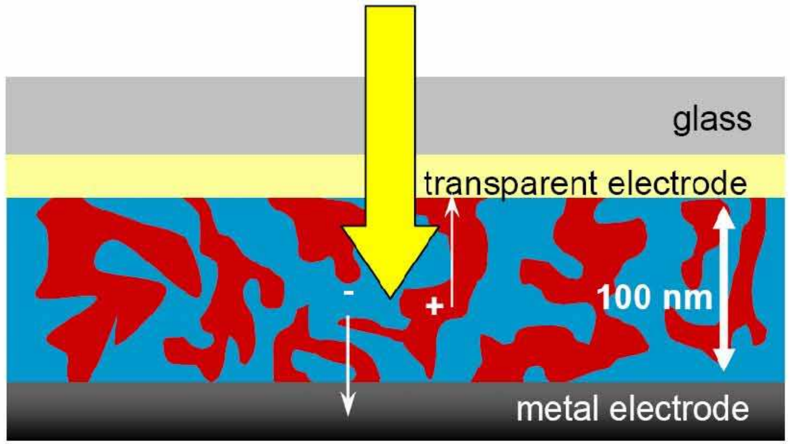


C. W. Tang, *Appl. Phys. Lett.* 1985, **48**, 183.

Bulk heterojunction solar cells

Charge separation in nanostructured composite organic semiconductors

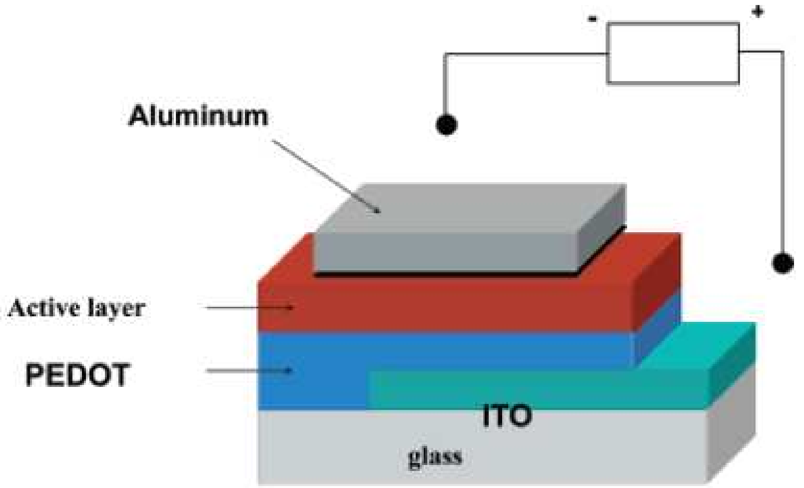


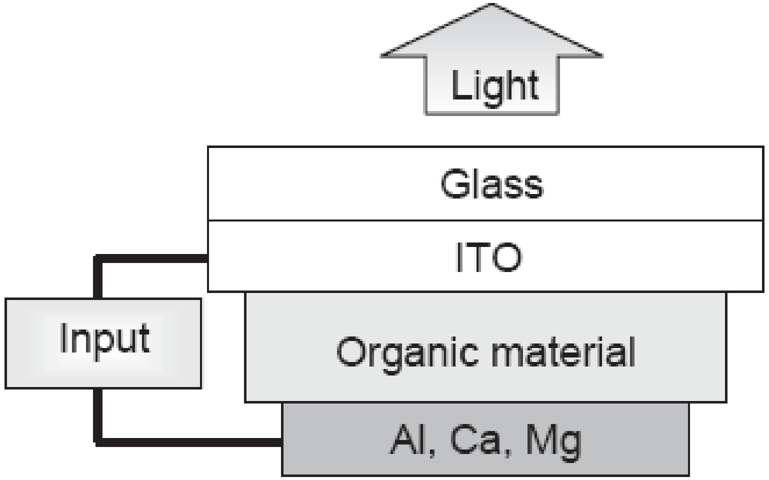


nanoscopic mixing of donor and acceptor to
overcome ~10 nm exciton diffusion length

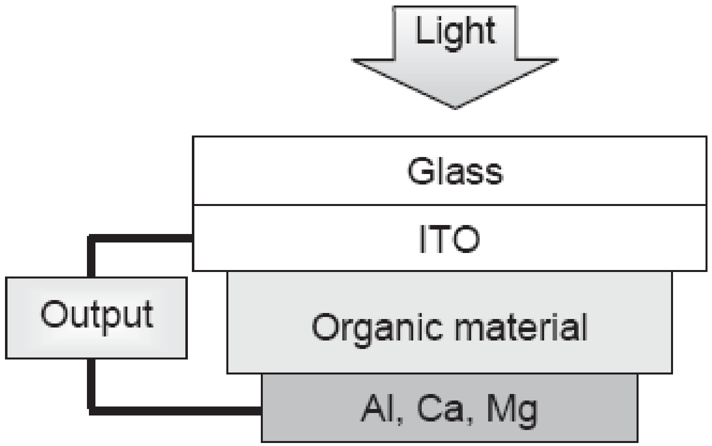
*R. H. Friend et al., Nature 1995, **376**, 498*
*A. J. Heeger et al., Science 1995, **270**, 1789*

Structures and Principles of LED & Photovoltaic mode





LED mode

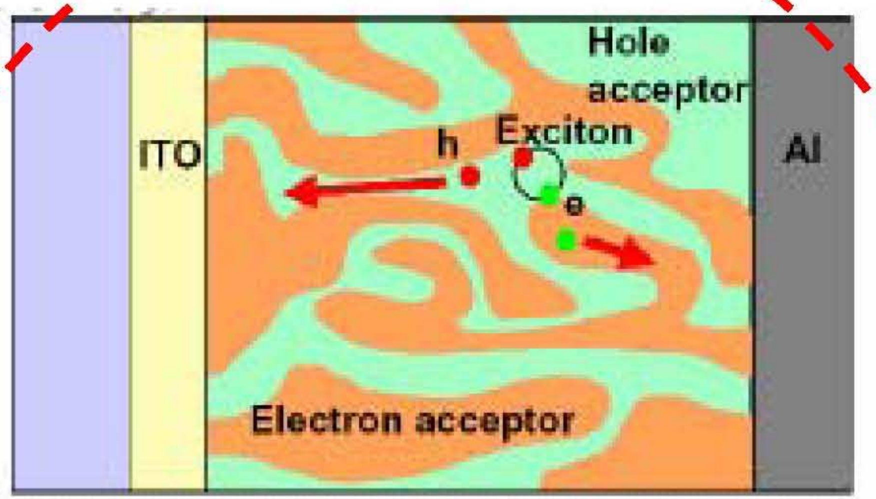


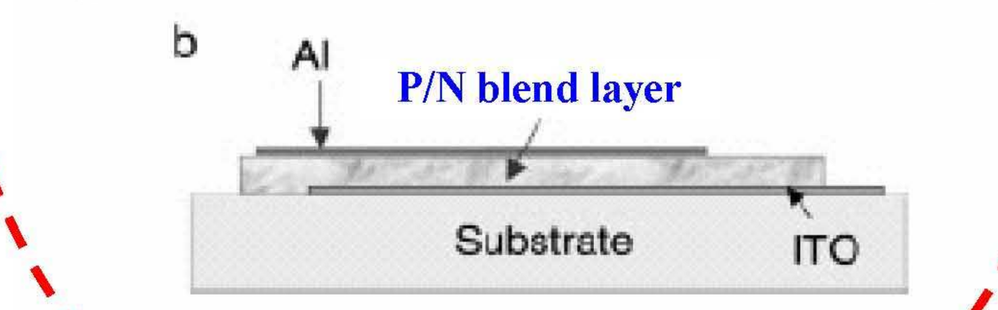
Photovoltaic mode

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

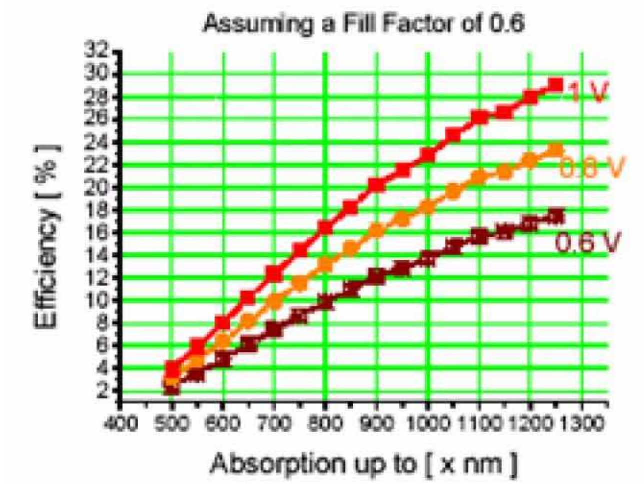




P-type is conducting polymer
N-type is either C material or nanocrystals

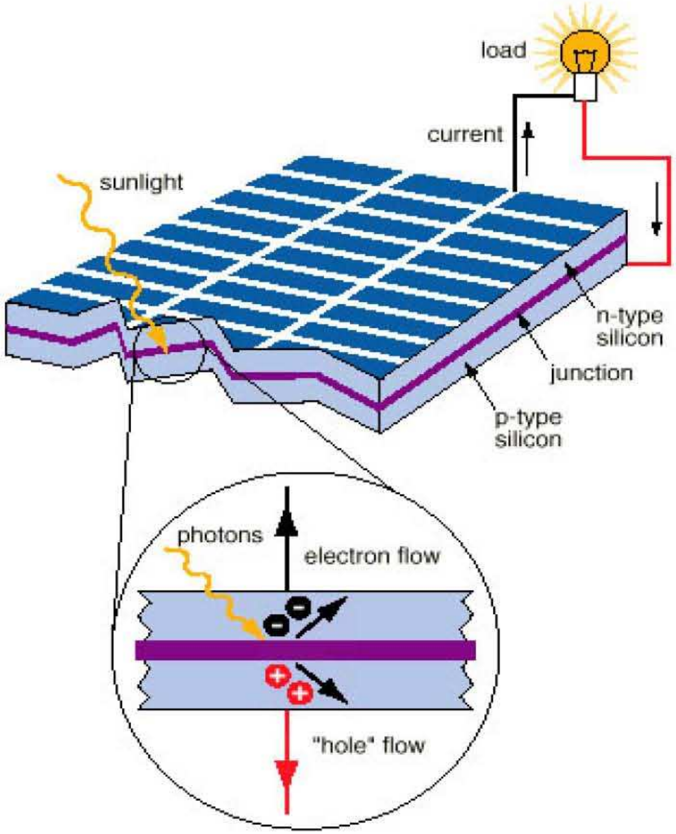
有機固態太陽光電之優勢：

- 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

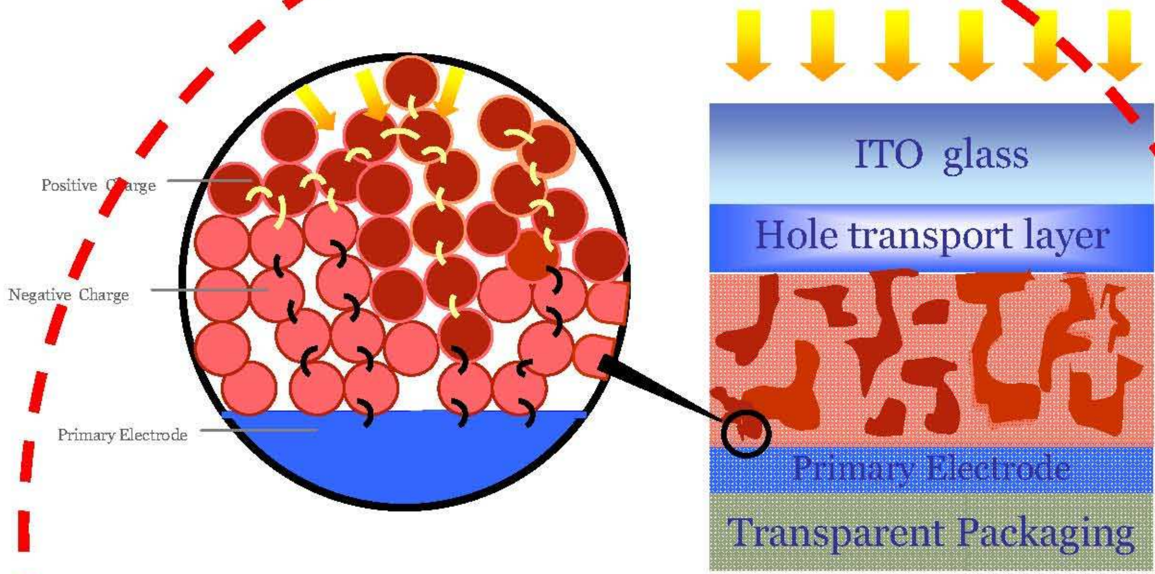


Polymer Based Solar Cell-Active layer

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

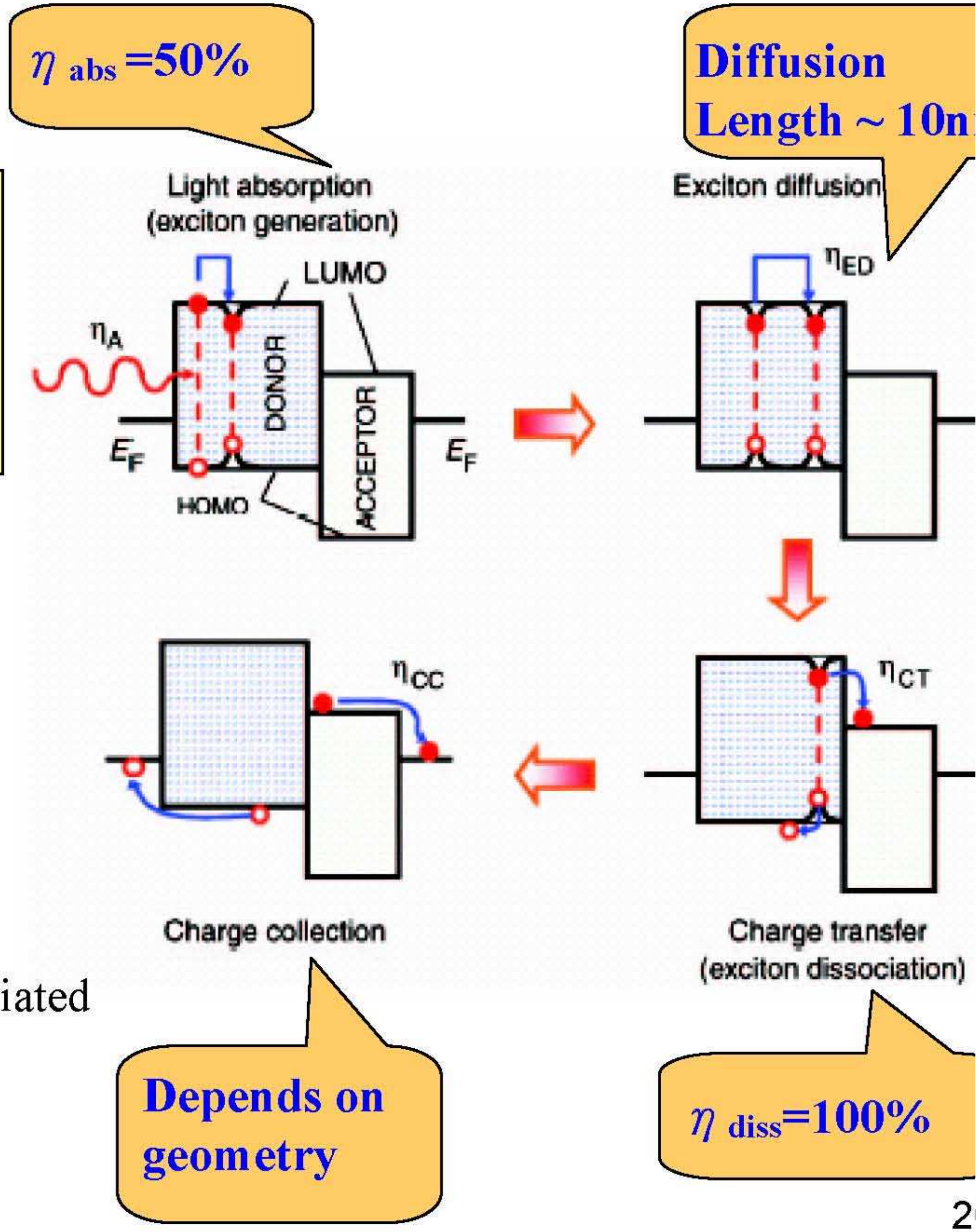
$$\eta_j = \eta_{abs} \times \eta_{diss} \times \eta_{out}$$

overall photocurrent efficiency

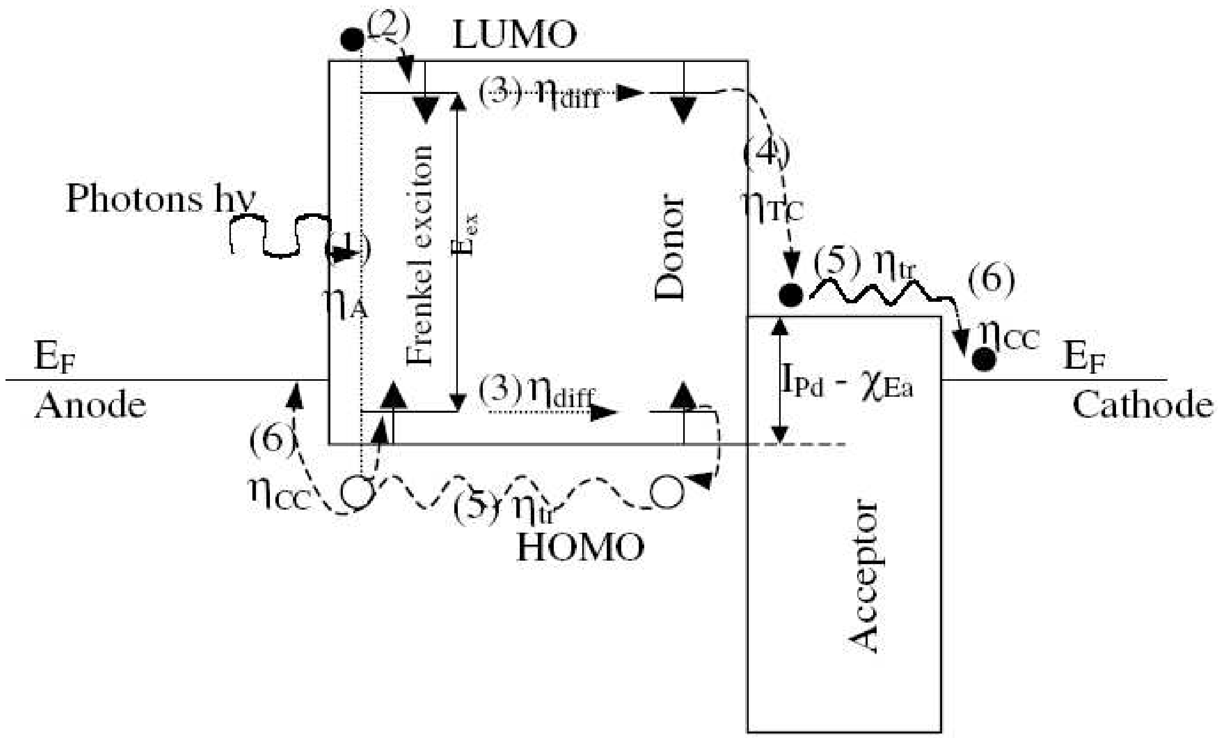
$_{abs}$ fraction of photons absorbed

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

$_{out}$ fraction of charges that reach the electrodes



General Mechanism in Organic Photovoltaic Cells



(1) Photon absoption (η_A)

(2) Generation of excitons

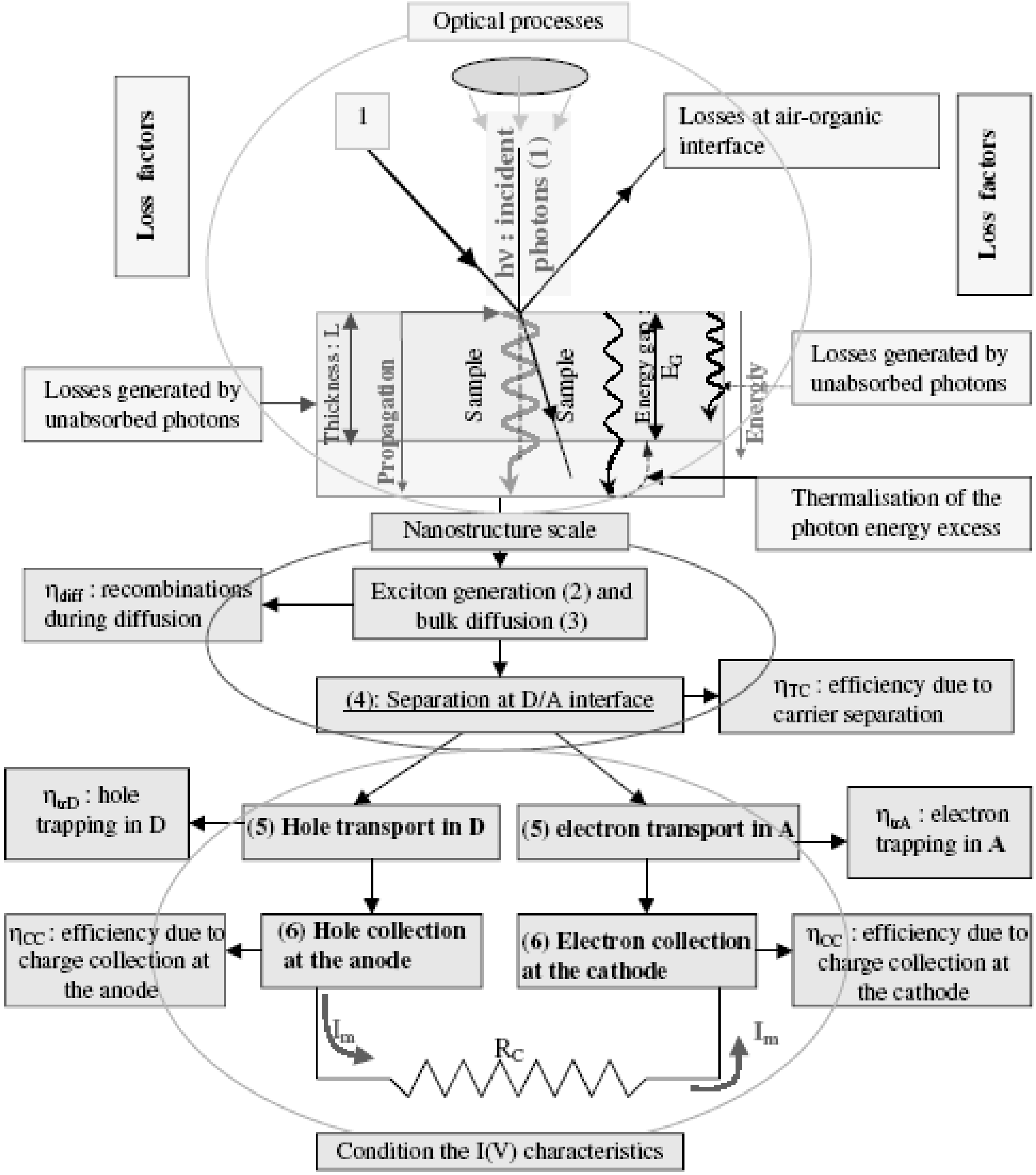
(3) Exciton diffusion (η_{diff})

(4) Hole-electron separation (η_{TC})

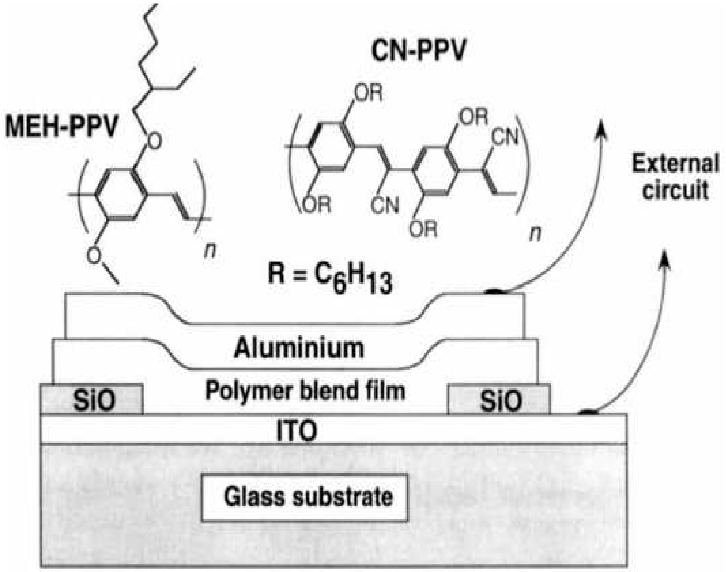
(5) Carrier transport towards the electrode (η_{tr})

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

General Scheme for Organic Photovoltaic Effect

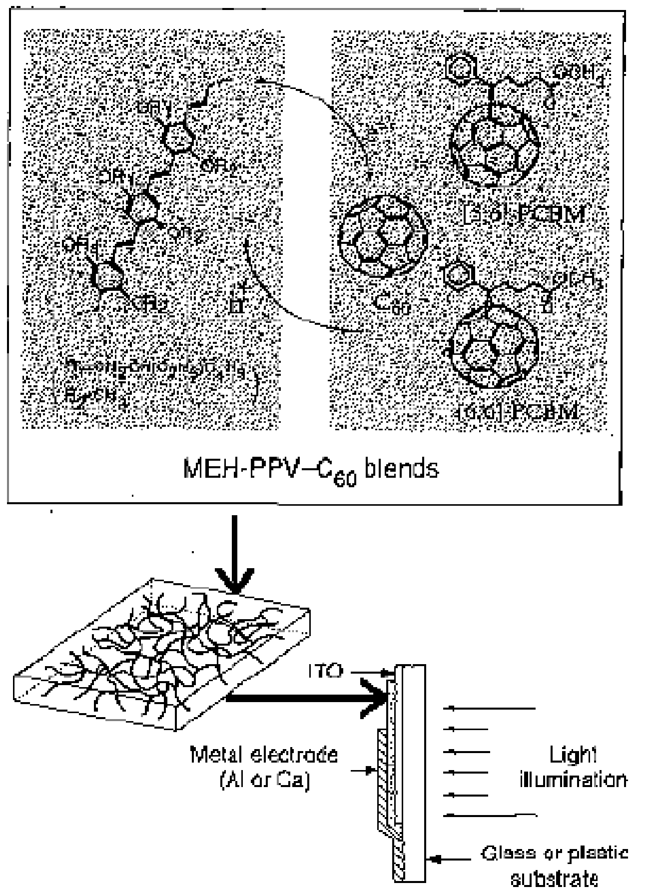


Examples on Polymer Phtovoltaic Devices



First Polymer-Polymer heterojunction PV

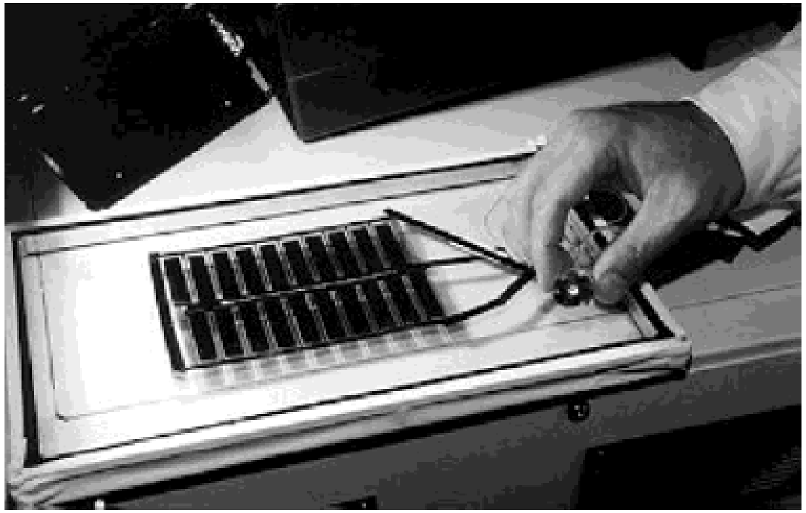
NATURE · VOL 376 · 10 AUGUST 1995



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

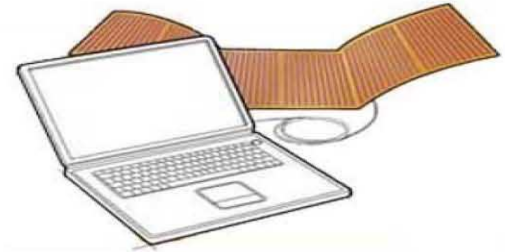
Power generation systems.

Organic solid Photovoltaics

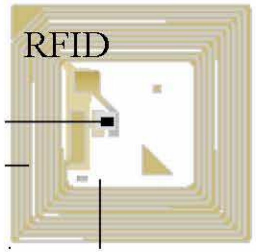
Leisure, tents, remote equipment

Building integrated PV.

Portable and mobile systems



Small electronic devices



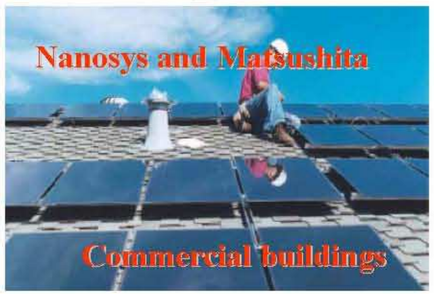
Application Roadmap

2010

2015

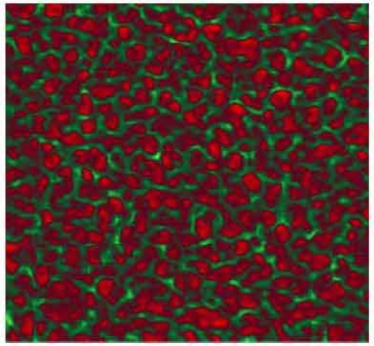
2020

Organic solid photovoltaics

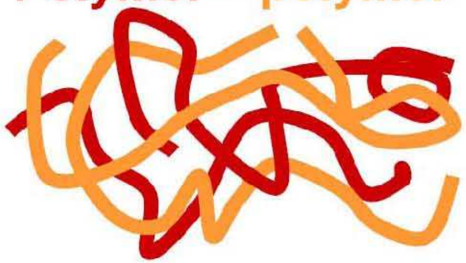


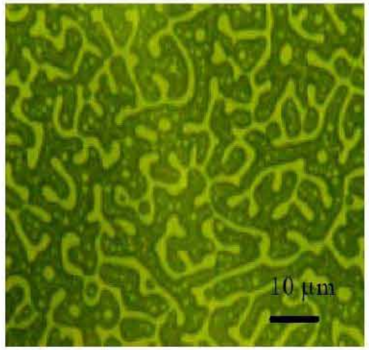
Polymer solution processed cells come in three 'flavors'

Polymer – fullerene

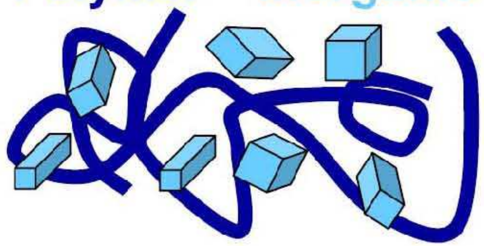


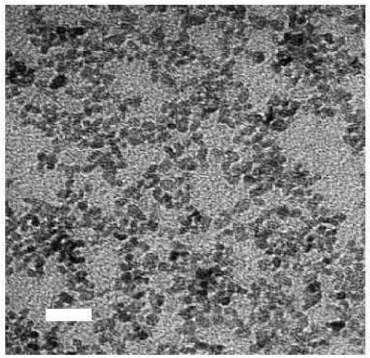
Polymer – polymer



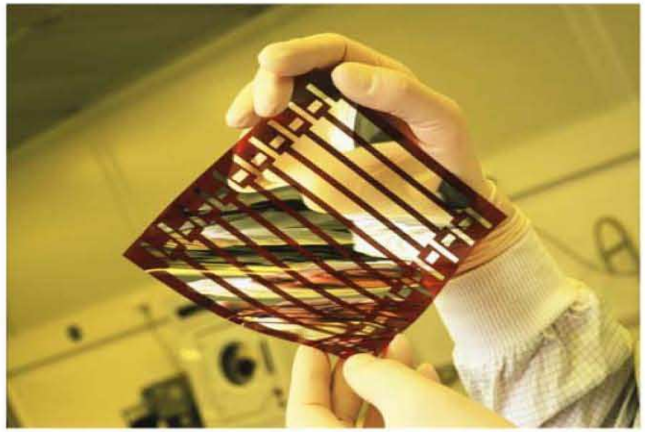


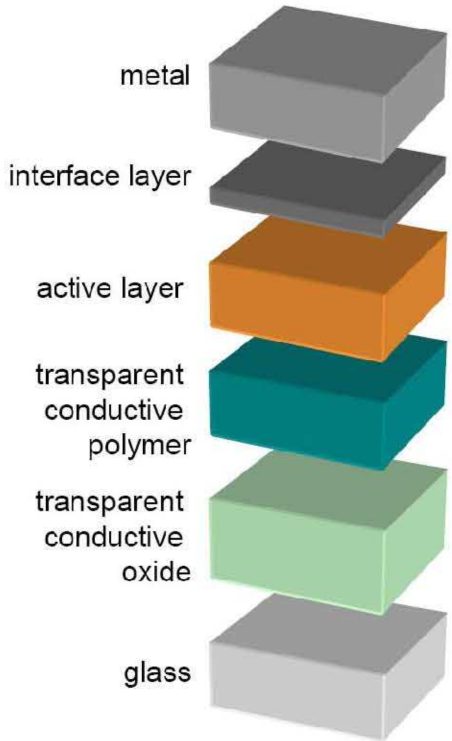
Polymer – inorganic





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

微影 lithography

Plasma cleaner

曝光機

塗佈 coating

PEDOT:PSS

active layer

蒸鍍 evaporated

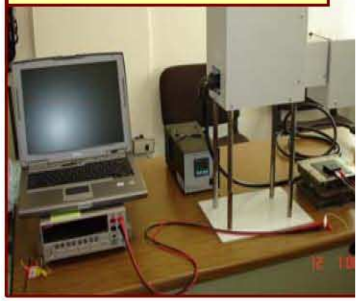
蒸鍍機

封裝 encapsulation

UV curing

測試 test

Solar simulator

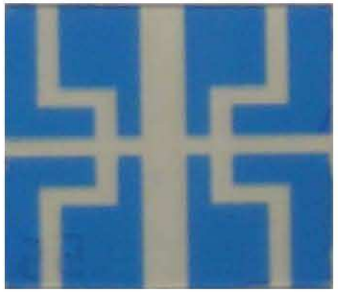


標準元件製作流程

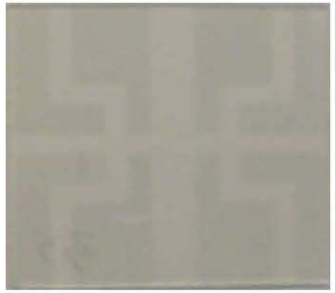
Procedure:

ITO glass

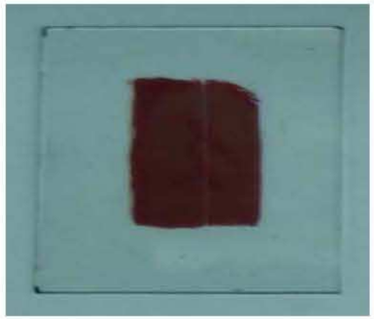
Exposure



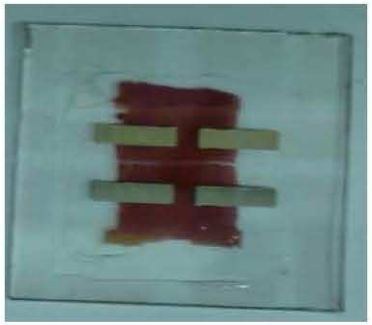
Development



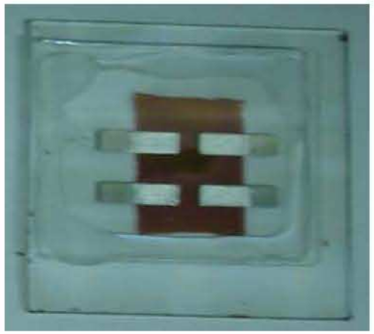
Etching



Polymer Coating



Top Electrode



Encapsulation

太陽電池之I-V曲線

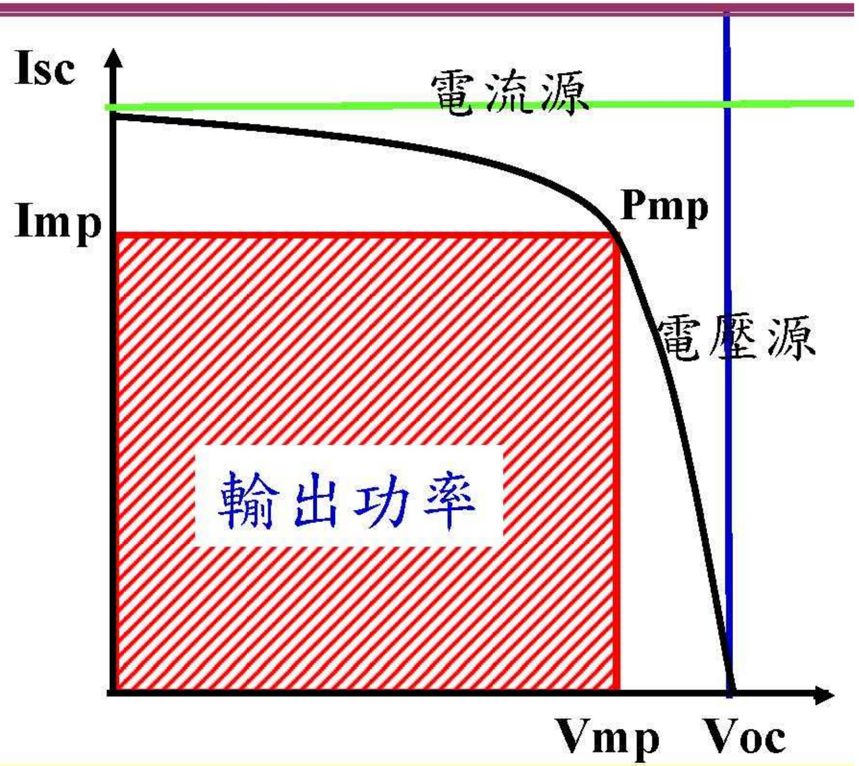
V_{oc}：開路電壓(V)

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%

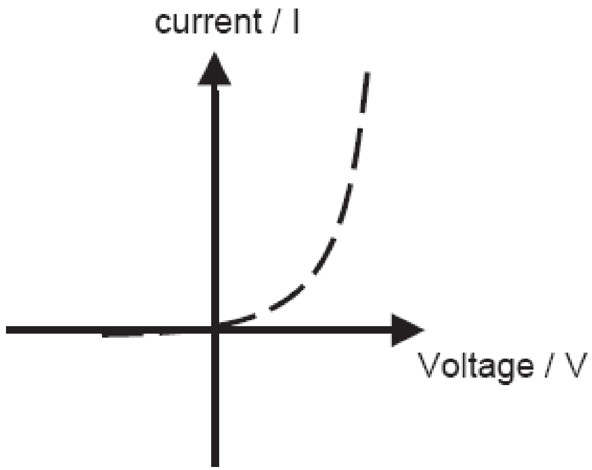
太陽電池效率(Efficiency；η) = (I_{sc} x V_{oc} x FF / 輸入日照功率) x 100%

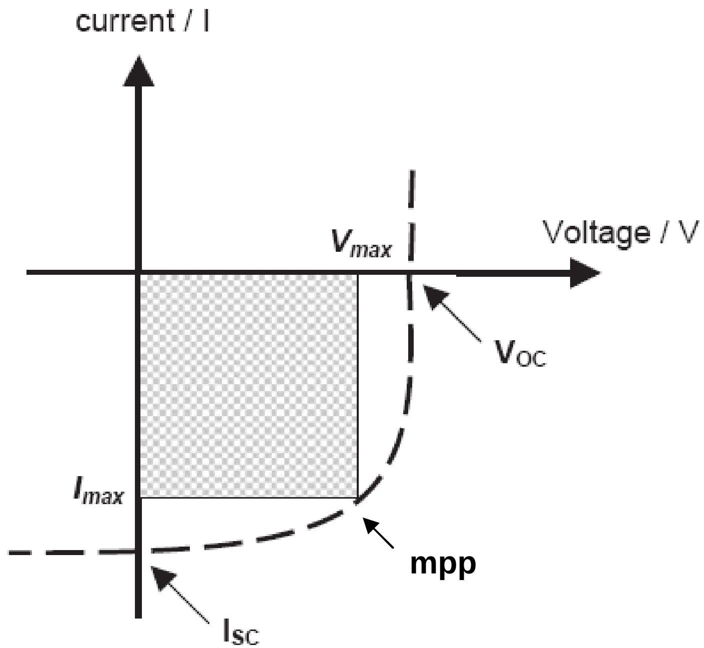
輸入日照功率(W)=太陽電池面積(m^2) × 日照強度(W/ m^2)

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.**

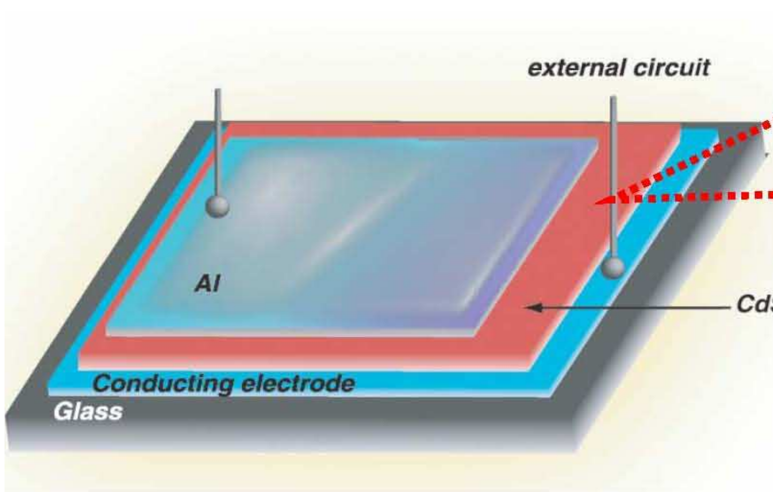
Short circuit voltage (I_{sc}) **Current flows through an solar cell when there is no external resistance.**

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

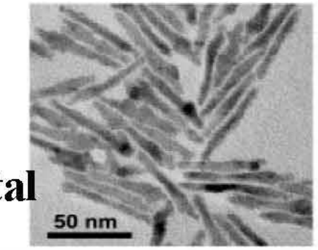
Fill Factor (FF) $$\mathrm{FF} = \frac{I_{\mathrm{mpp}} V_{\mathrm{mpp}}}{I_{\mathrm{sc}} V_{\mathrm{oc}}}$$

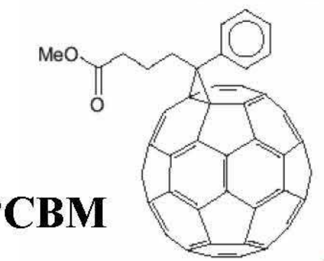
Power conversion efficiency (PCE) $$\eta_e = \frac{I_{\mathrm{mpp}} V_{\mathrm{mpp}}}{P_{\mathrm{in}}} = \frac{I_{\mathrm{sc}} V_{\mathrm{oc}} \mathrm{FF}}{P_{\mathrm{in}}}$$

Polymer Photovoltaic Structure



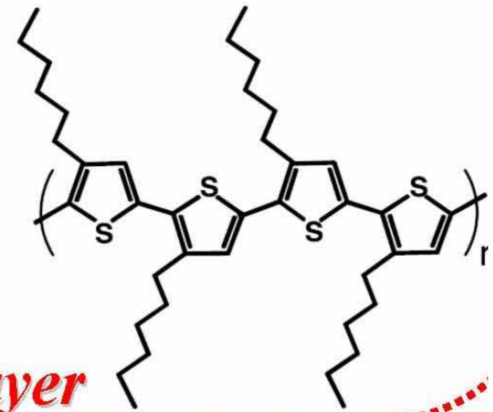
CdSe nanocrystal



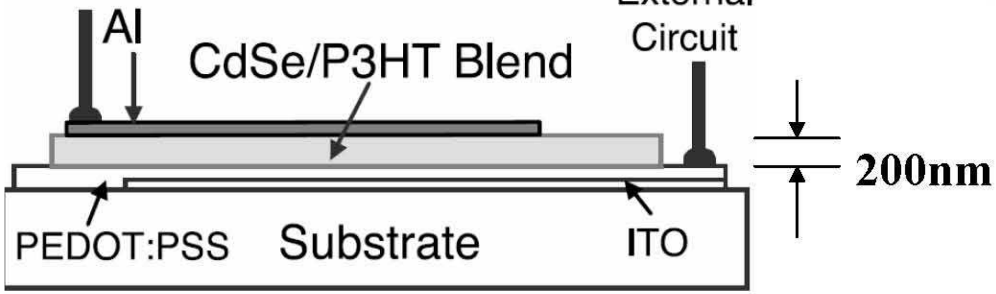


PCBM

(poly(3-hexylthiophene))
Regioregular P3HT



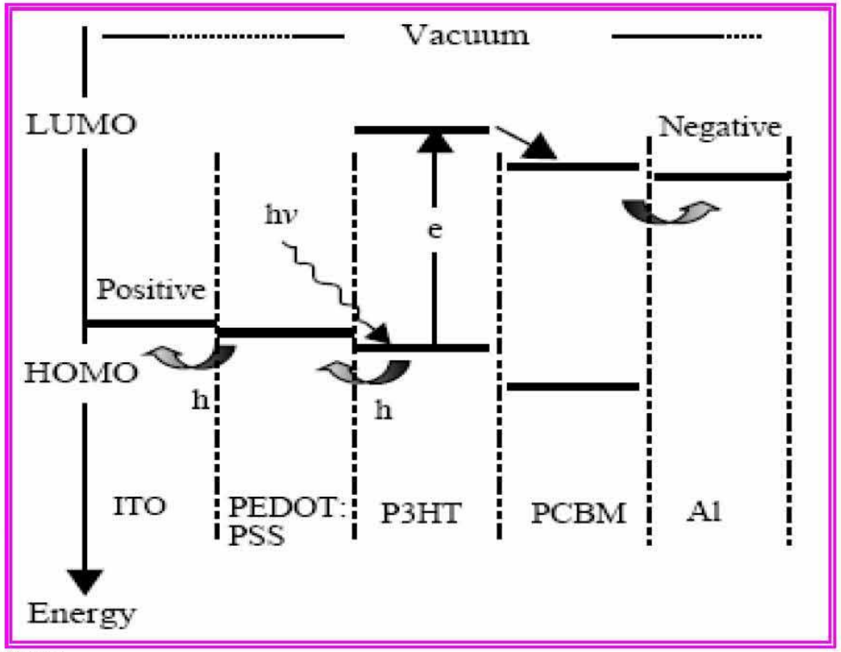
Active layer



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

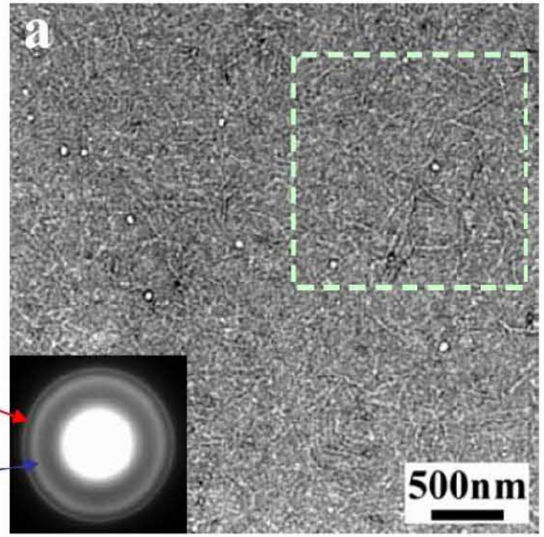
AM1.5 performance

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

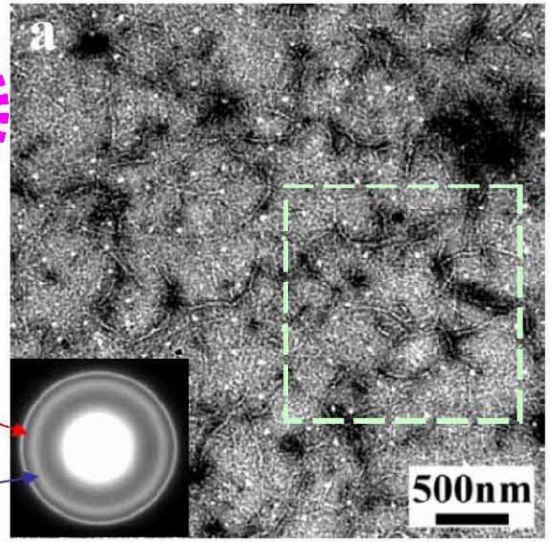
*P. Schilinsky et al., Appl. Phys. Lett. 2002, **81**, 3885.*
*F. Padinger et al., Adv. Funct. Mater 2003, **13**, 85.*
*Y. Kim et al., Appl. Phys. Lett. 2005, **86**, 063502.*
*X. Yang et al., Nano Lett. 2005, **5**, 579.*
*M. Reyes-Reyes et al., Appl. Phys. Lett. 2005 **87**, 083506*
*W. Ma et al.,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



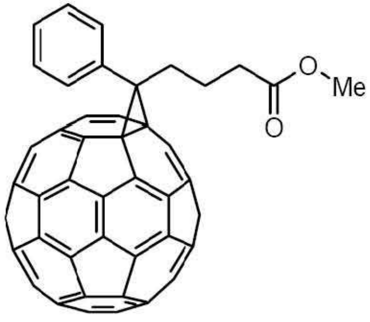
P3HT
0.39 nm*
PCBM
0.46 nm

110 °C for
60 min

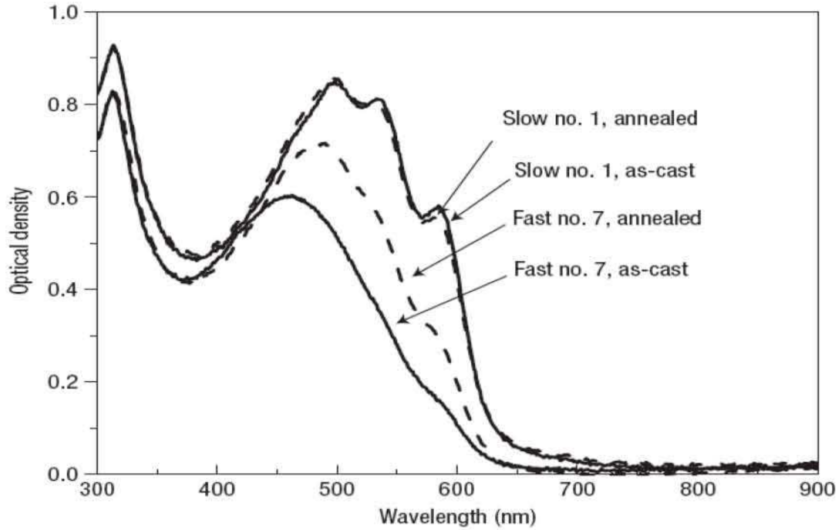


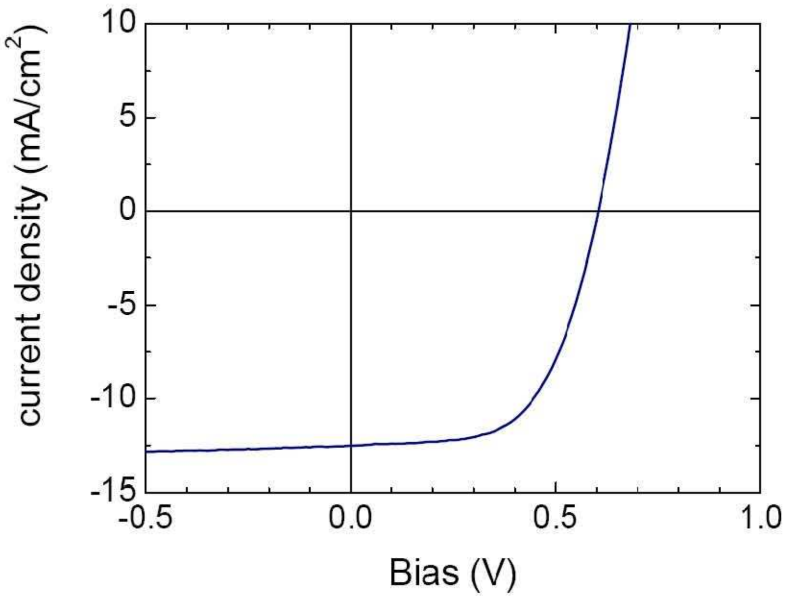
P3HT
0.39 nm*
PCBM
0.46 nm

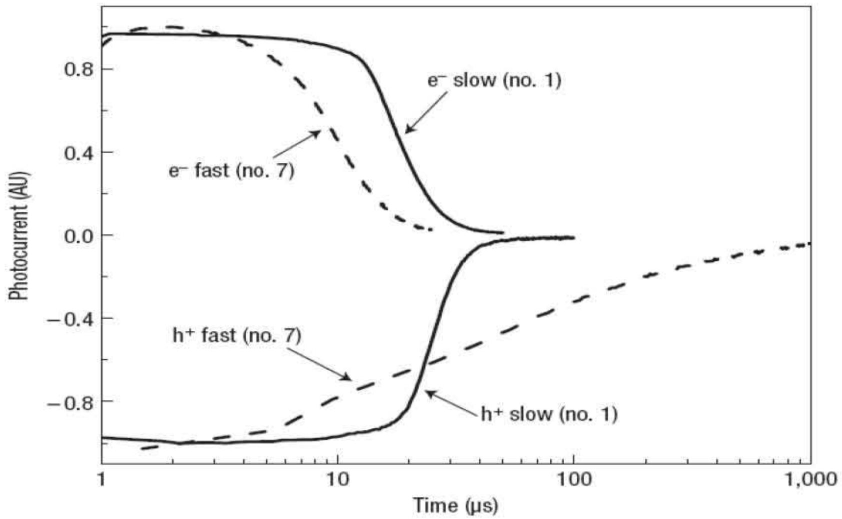
P3HT:PCBM solar cells via slow drying process



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





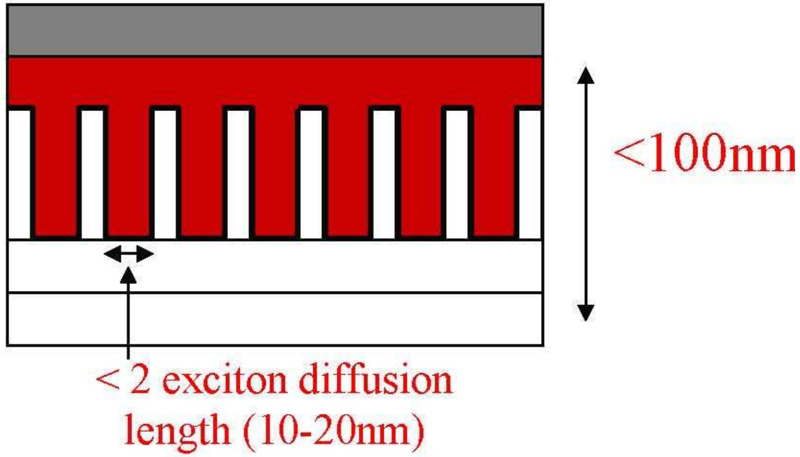


Yang Yang et al. Nature Mater. ***2005****, 4, 864.*

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

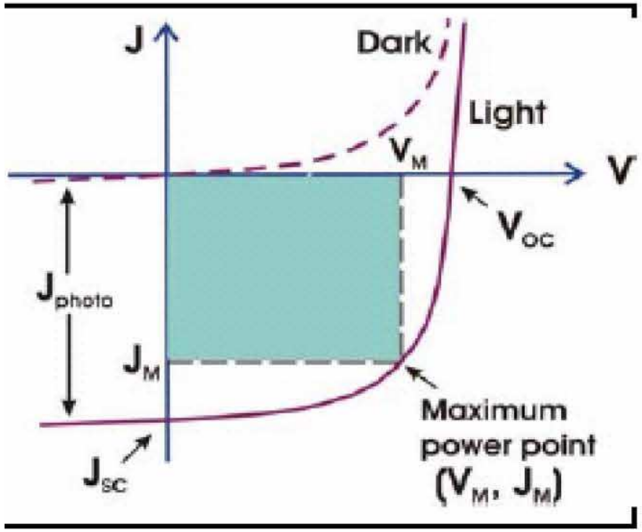
- **Understanding device function and limits to performance**

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

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

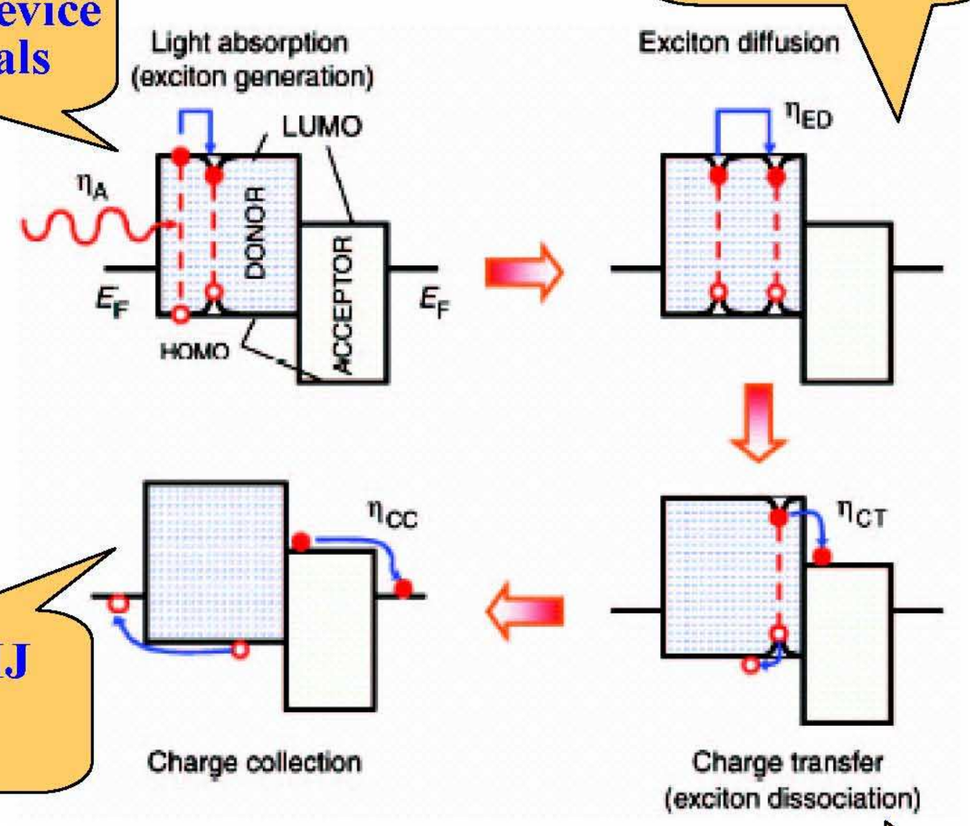


FF = JmVm/JscVoc

η = JmVm/Psun = 100*Jsc*Voc*FF/Psun

Effective light harvest device & materials

High mobility material



Order BHJ structure

Good P/N typ[e] blending

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

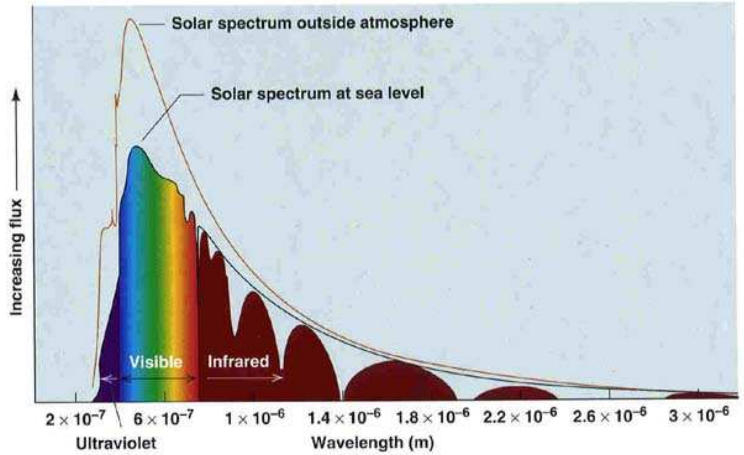
– **1. New device designs: Ordered Bulk Heterojuctions**

– **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**



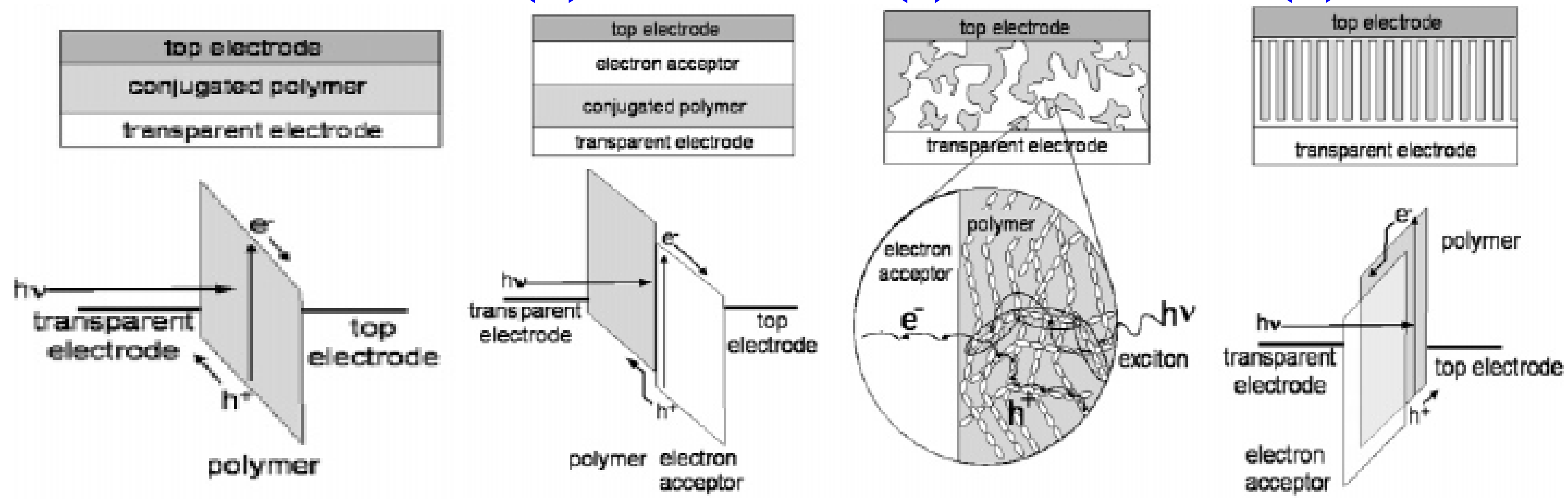
– 3. **Higher carrier mobilities:**

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

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

Four device architectures of conjugated polymer–based PV cells

(a) (b) (c) (d)



- 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);

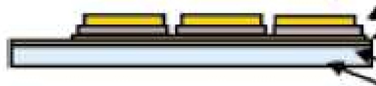
  PPV/BBL 66%% EQE, 2% power efficiency
- Bulk heterojunction (c) (d):
  - **PPV/C60 Derivatives 70% EQE, 3.5% power efficiency**

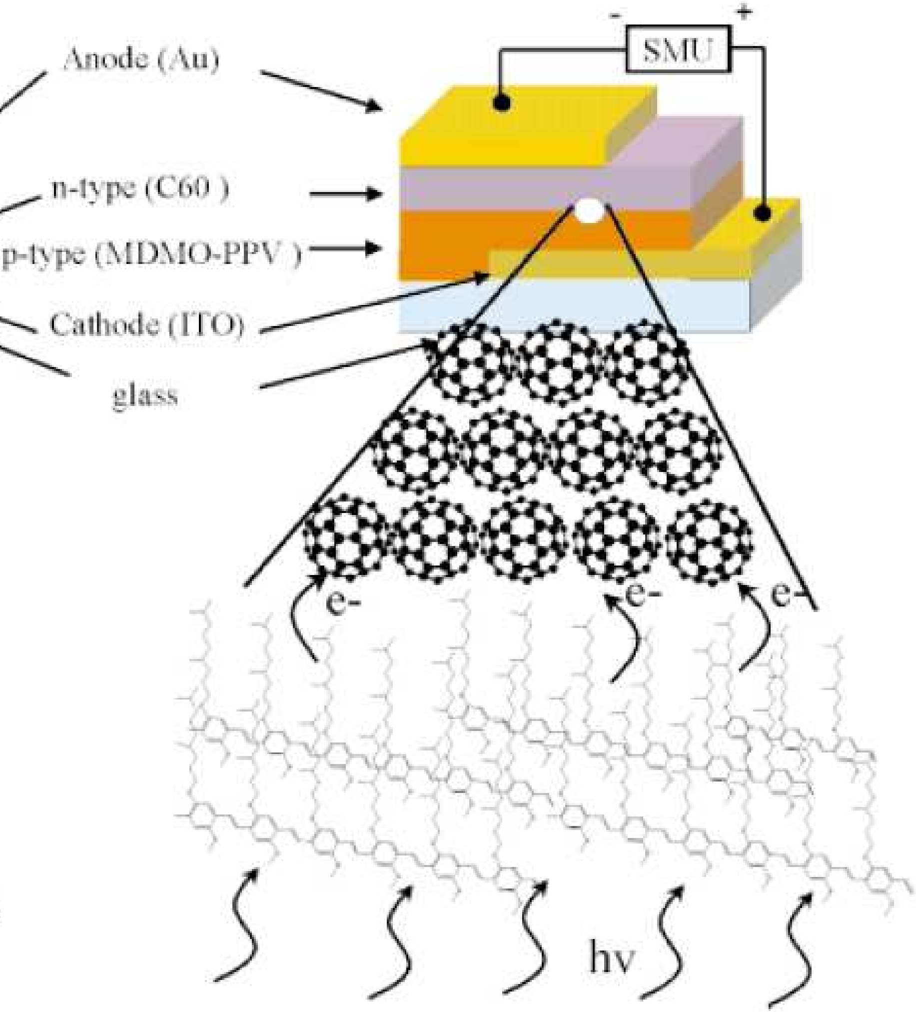
Chem. Mater. **2004**, *16*, 4533

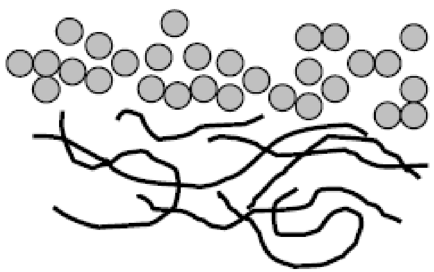
Organic Photovoltaic Device Architectures

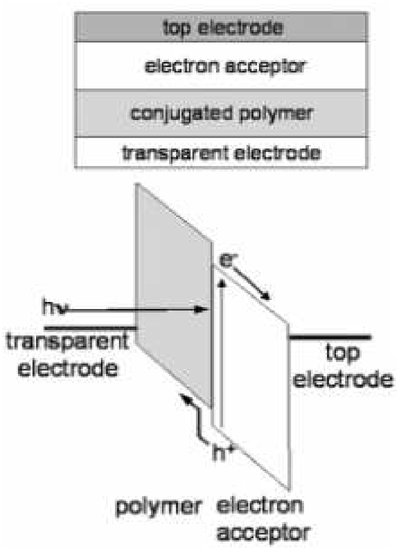
Bilayer Devices

(a)



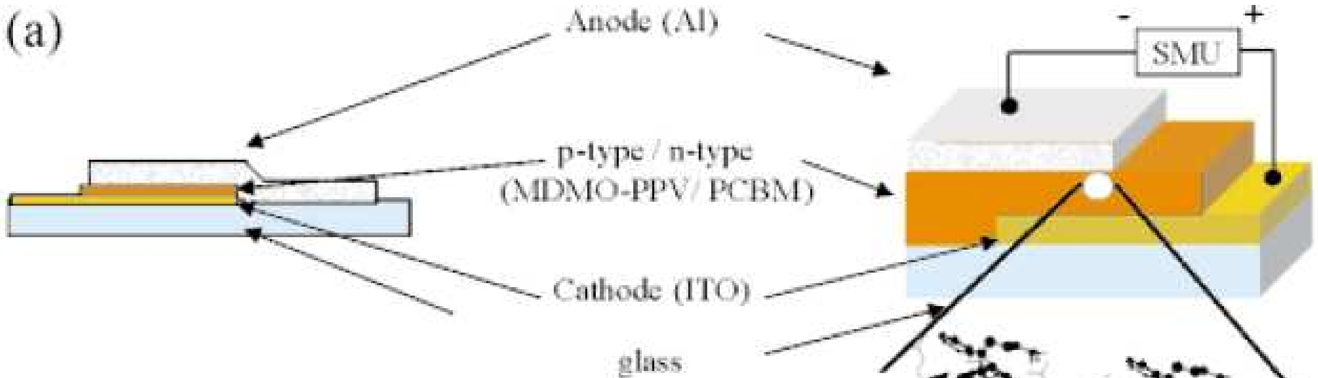


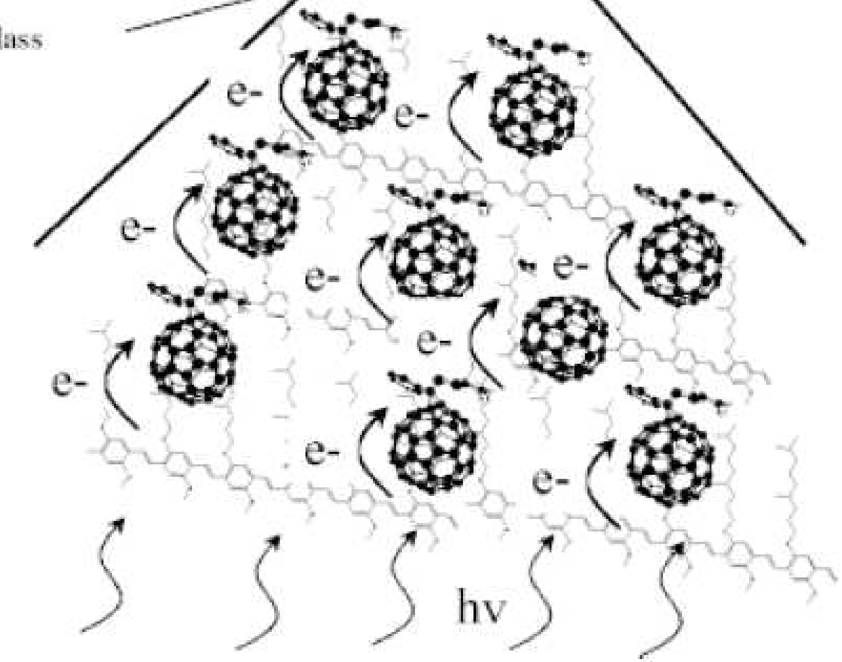


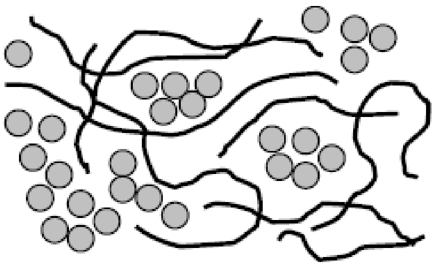


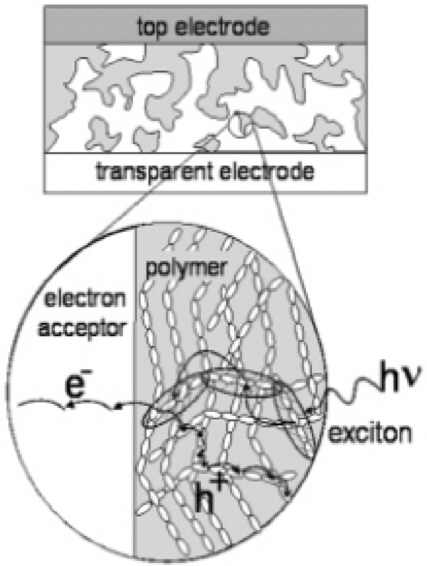
Organic Photovoltaic Device Architectures

Bulk Heterojunction Devices

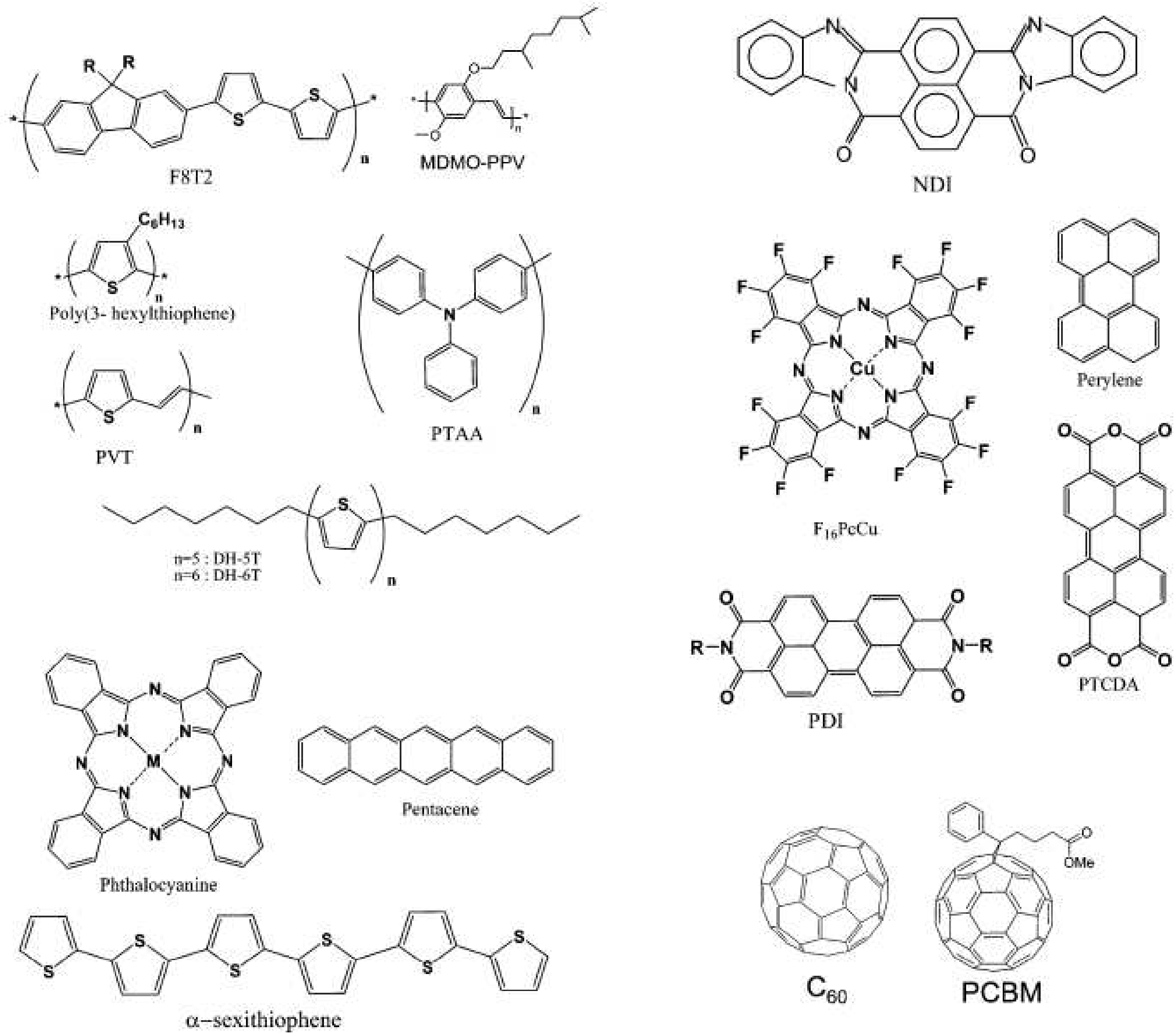








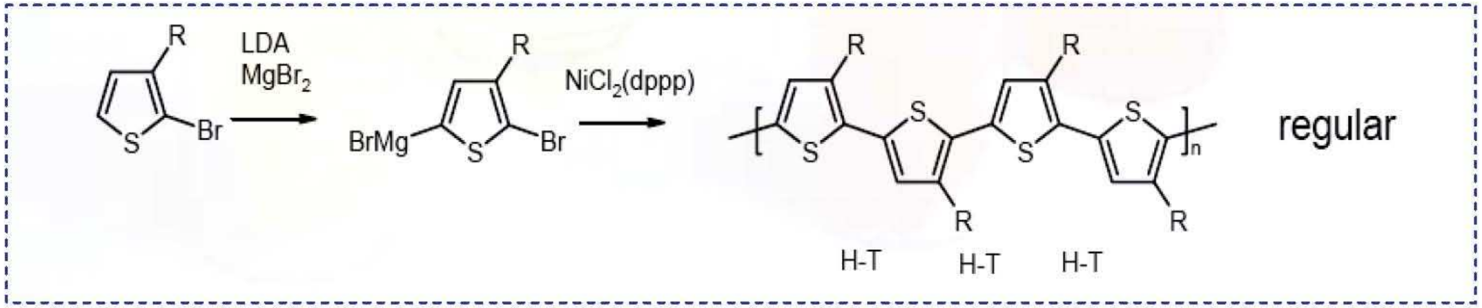
Organic Semiconductors Used in Solar Cells



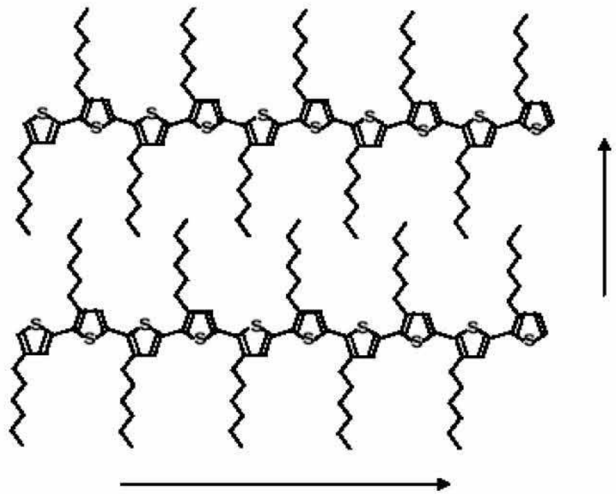
Some of the Approaches in MCL

1. Better packing conducting polymer

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

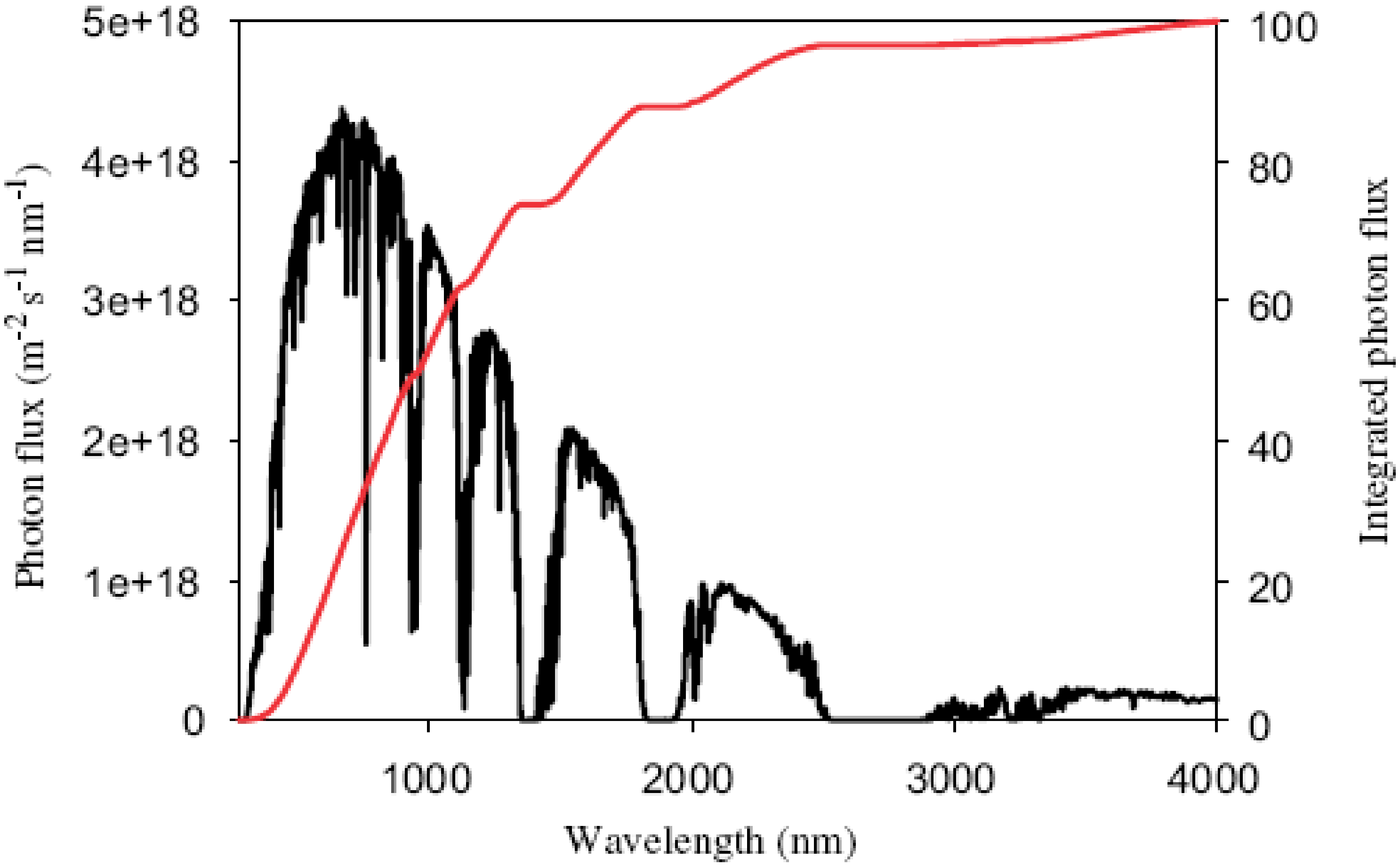


— Tightly-packing conducting polymer but still maintain its processbility



— High mobility conducting polymer design with good solubility

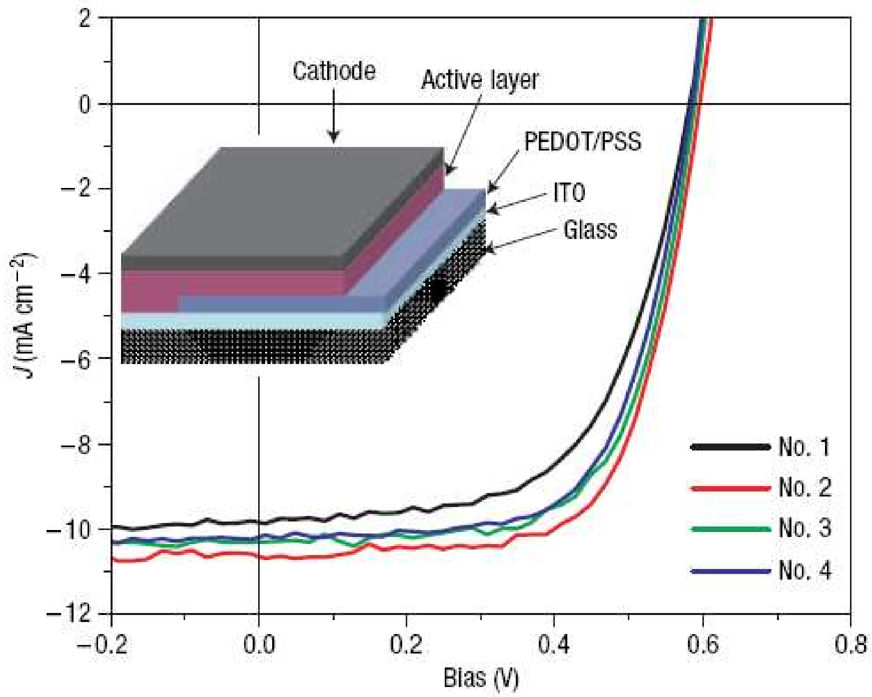
Absorption Spectrum of Organic Materials



Photon reflux from the sun (AM 1.5)

P3HT:PCBM Solar Cells

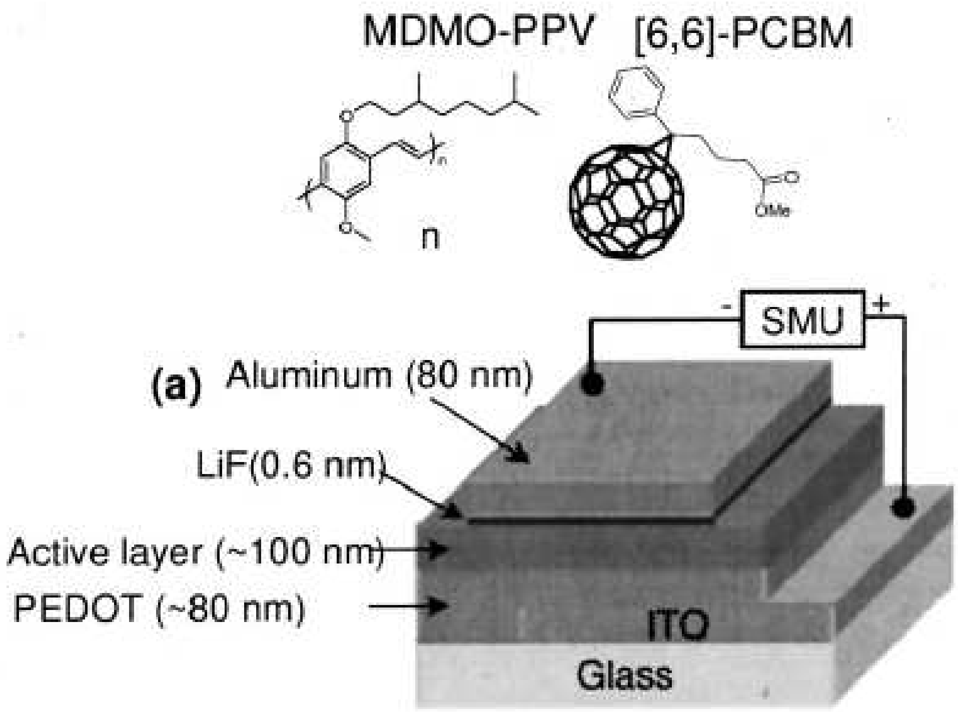
Different annealing time

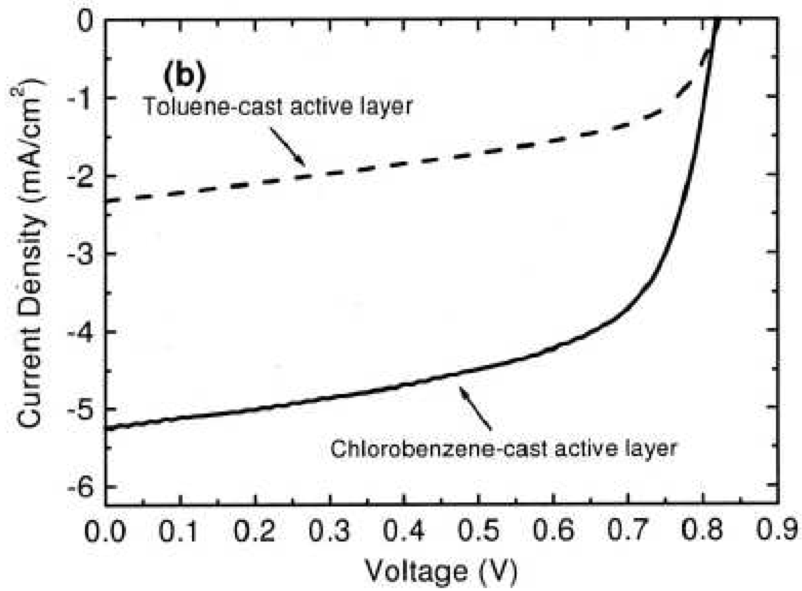


V_{oc} = 0.61 V **FF = 0.67**

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/cm^2

PCE = 2.5 %

APL 2001, 78, 841

Design strategy for low band gap: Donor-Acceptor polymers

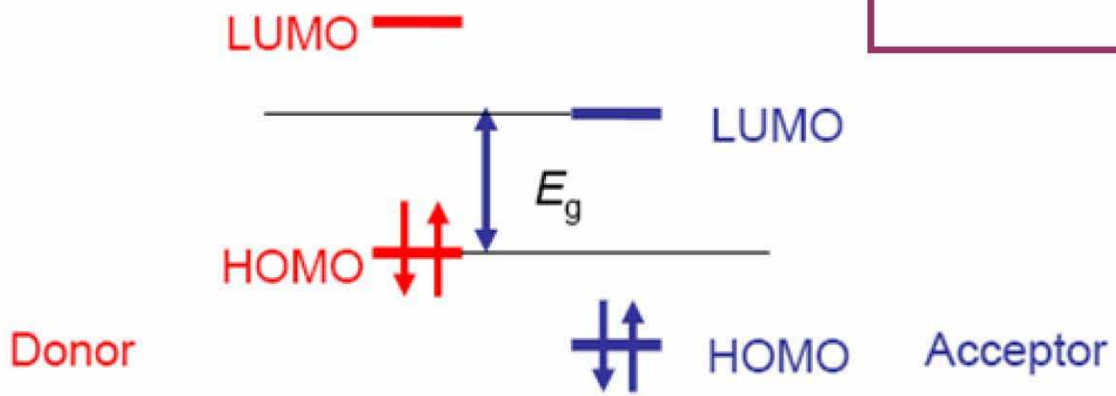
increase the double bond character of the single bonds:

–D–A–D–A–D–A– ⟷ –D^+=A^-–D^+=A^-–D^+=A^-–

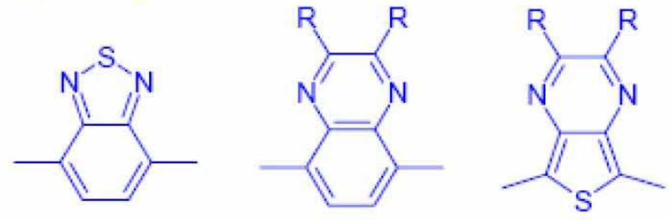
alignment of transition dipoles along the chain

–$\vec{D}$–A–$\vec{D}$–A–$\vec{D}$–A–

absorption from HOMO donor to LUMO acceptor



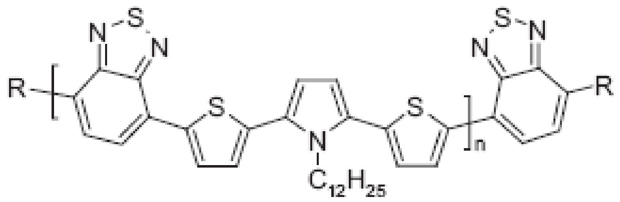
常見acceptor之化學結構：



Acceptors

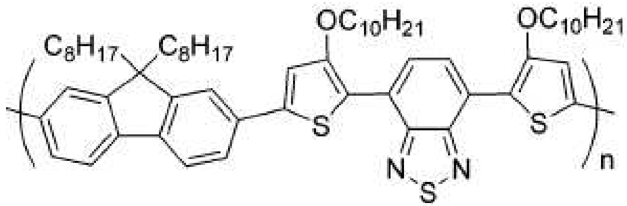
E. E. Havinga, et al. *Polym. Bull.* **1992**, 29, 119.
J. Roncali, *Chem. Rev.* **1997**, 97, 173.

D-A Conjugated Alternating Polymers:PCBM Solar Cells



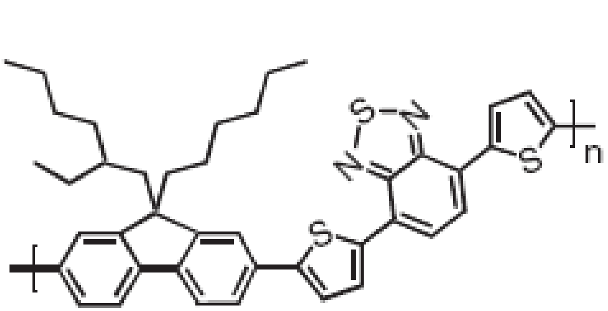
V_{oc} = 0.72 V   FF = 0.37

I_{sc} = 3.1 mA/cm²   PCE = 1 %



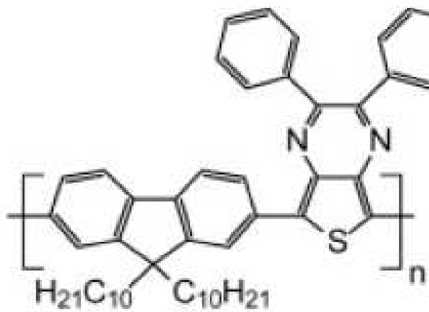
V_{oc} = 0.76 V   FF = 0.49

I_{sc} = 4.31 mA/cm²   PCE = 1.6 %



V_{oc} = 0.72 V   FF = 0.46

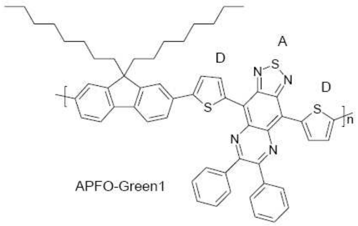
I_{sc} = 4.66 mA/cm²   PCE = 2.2 %



V_{oc} = 0.56 V   FF = 0.49

I_{sc} = 3.6 mA/cm²   PCE = 0.51 %

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



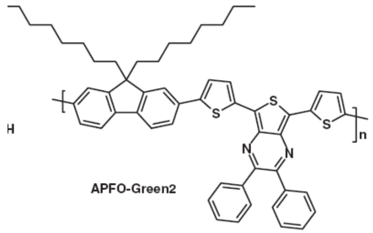
:PCBM

V_{oc} = 0.54 V

I_{sc} = 1.76 mA/cm^2

FF = 0.46

PCE = 0.3 %



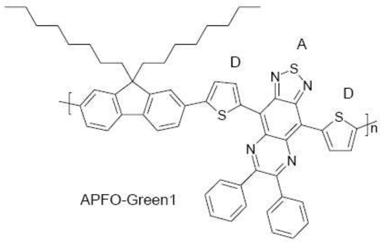
:PCBM

V_{oc} = 0.78 V

I_{sc} = 3 mA/cm^2

FF = N/A

PCE = 0.9 %



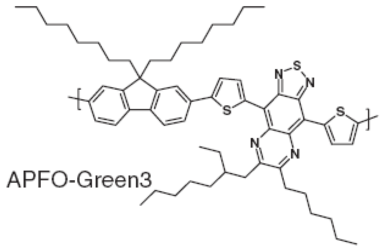
:C_{70}

V_{oc} = 0.58 V

I_{sc} = 3.4 mA/cm^2

FF = 0.35

PCE = 0.7 %



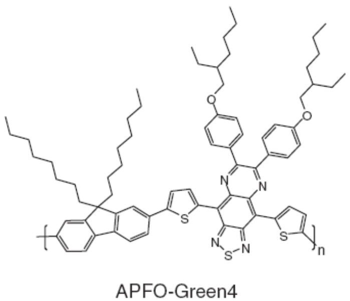
:C_{70}

V_{oc} = 0.61 V

I_{sc} = 2.4 mA/cm^2

FF = 0.40

PCE = 0.59 %



:C_{70}

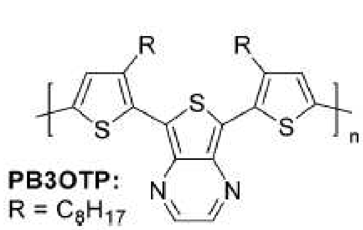
V_{oc} = 0.56 V

I_{sc} = 2.1 mA/cm^2

FF = 0.32

PCE = 0.37 %

D-A Conjugated Alternating Polymers:PCBM Solar Cells

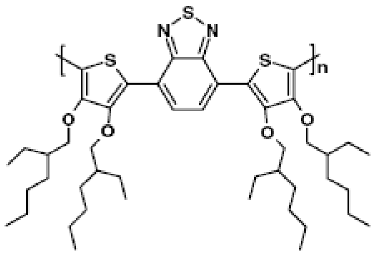


V_{oc} = 0.72 V

I_{sc} = 3.1 mA/cm^2

FF = 0.37

PCE = 1 %

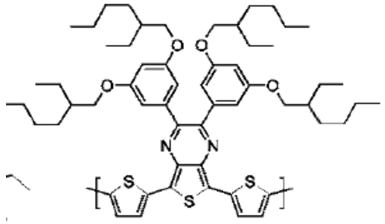


V_{oc} = 0.77 V

I_{sc} = 3.4 mA/cm^2

FF = 0.42

PCE = 0.2 %

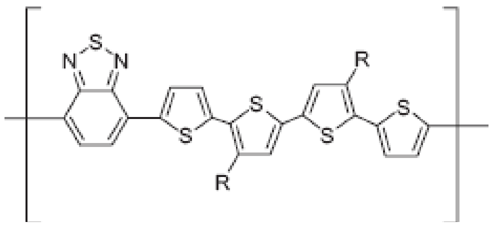


V_{oc} = 0.56 V

I_{sc} = 3.5 mA/cm^2

FF = 0.58

PCE = 1.1 %

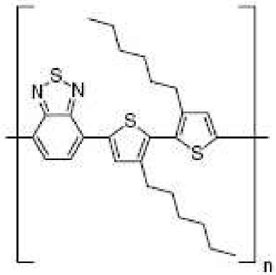


V_{oc} = 0.59 V

FF = 0.39

I_{sc} = 2.6 mA/cm^2

PCE = 0.6 %

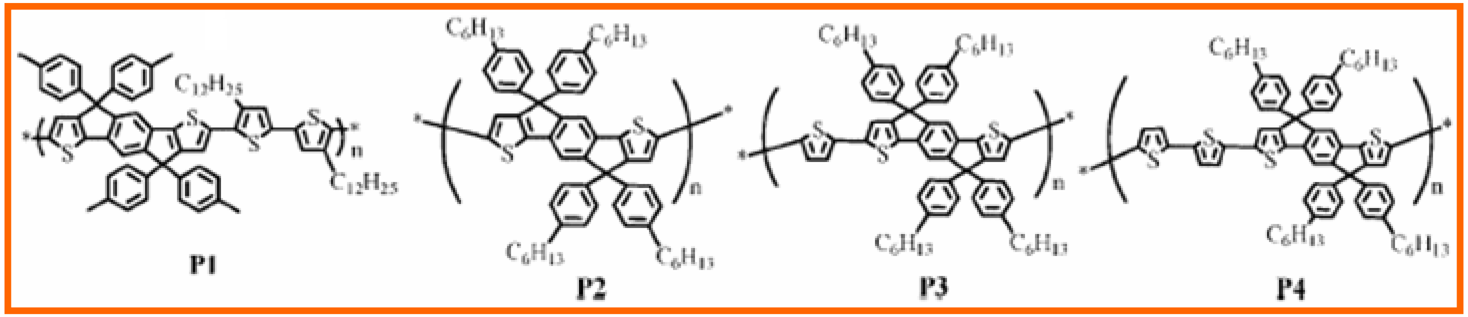


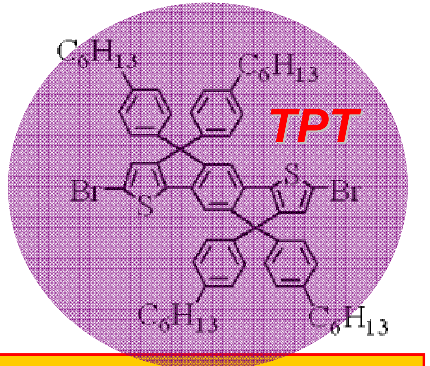
V_{oc} = 0.61 V

FF = 0.24

I_{sc} = 0.2 mA/cm^2

PCE = 0.02 %



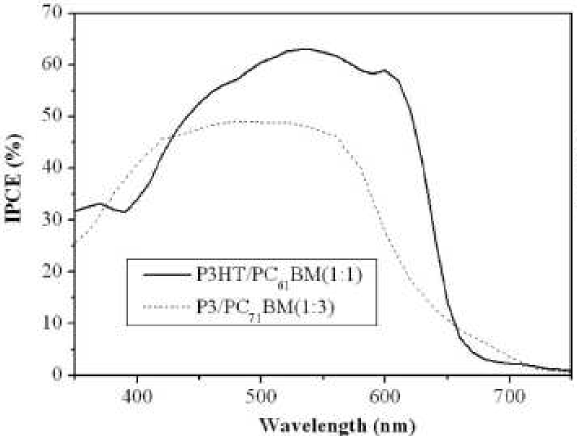


Coplanar chromophore

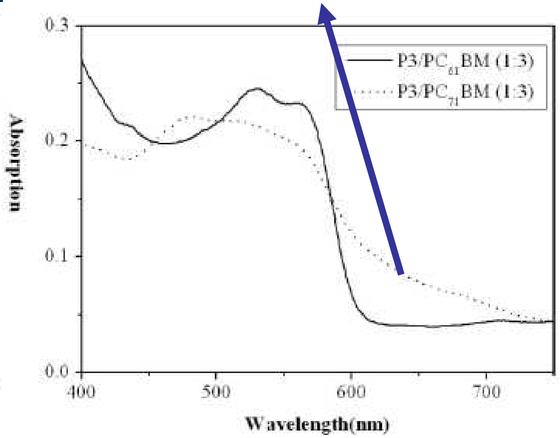
<u>Max. IPCE:</u>

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

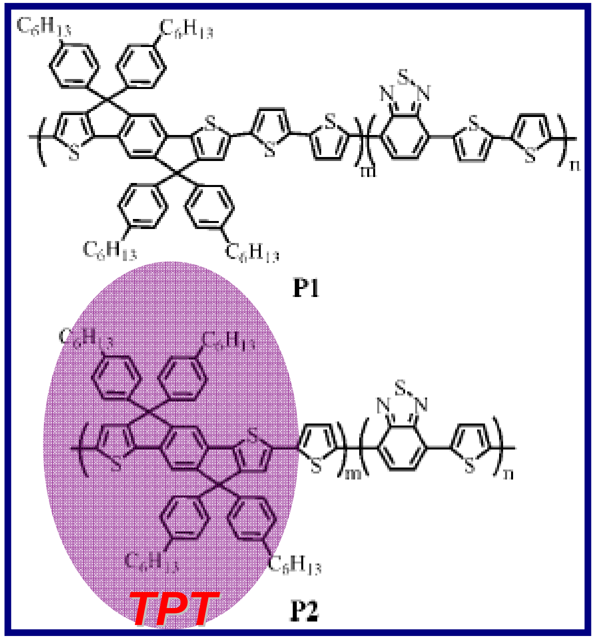
Table 1. Molecular Weights, FET Mobility, and Optical and Electrochemical Properties of Various Polymers

	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} $(9.9 \times 10^{-4})^d$	1.3×10^6 $(6.5 \times 10^5)^d$
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

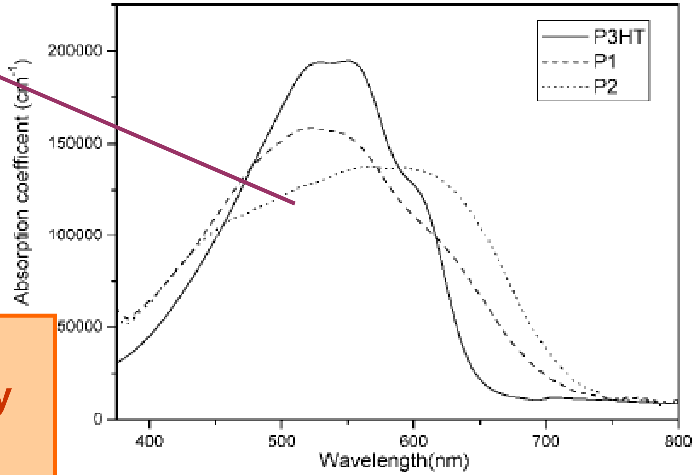
[a] Absorption coefficient was determined at λ_{max} in THF. [b] E_{ox} is the onset potential of oxidation of polymer. [c] Thin-film FETs were fabricated from 1 wt % *o*-DCB solutions. [d] $CHCl_3$ solvent was used instead of *o*-DCB.

High absorption coefficient in comparison to P3HT

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

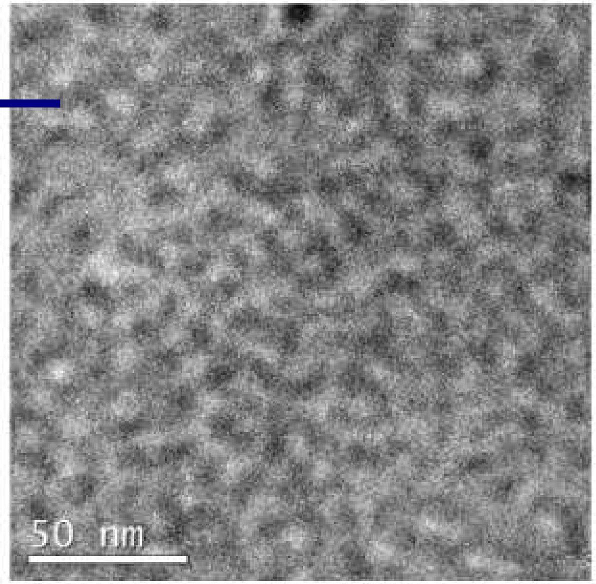


The **broad absorption** feature possibly due to the **random copolymer** structure of **P2** which combine the absorbance of **TPT** rich and **BT** rich structures



- The PCBM domains (dark) are around **10nm** and **homogeneously** distributed in the matrix

- The **nanoscale phase separation** between electron donor and acceptor allowing large areas of interface for better photogenerated charges



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

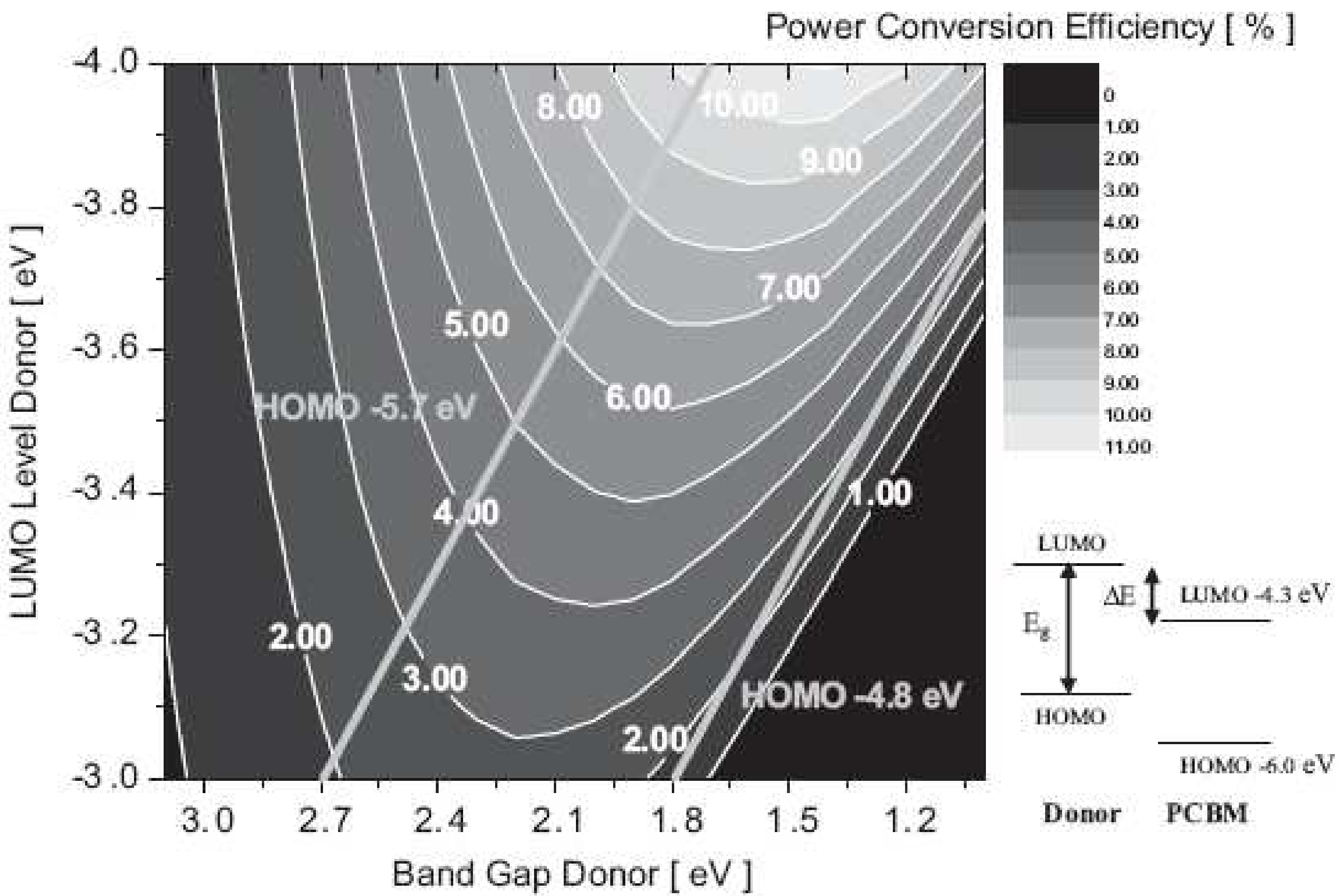
	polymer/PCBM(w/wratio)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η (%)[d]
P3HT[a]	1:1[b]	9.9	0.64	0.62	3.9
P3HT[a]	1:1[c]	7.7	0.65	0.68	3.4
P1	1:3[b]	5.4	0.80	0.47	2.0
P1	1:3[c]	8.7	0.84	0.53	3.9
P2	1:3[b]	6.2	0.80	0.51	2.5
P2	1:3[c]	10.1	0.80	0.53	4.3

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}^{a} (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

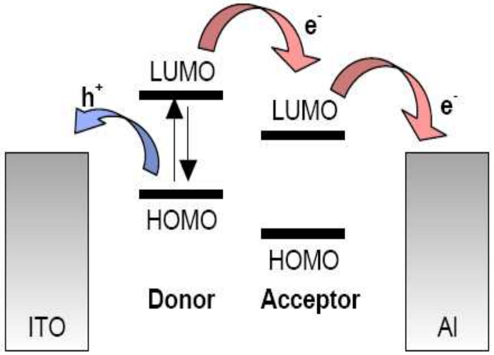
Design Rules for Donors in Solar Cell –Towards 10 % PCE

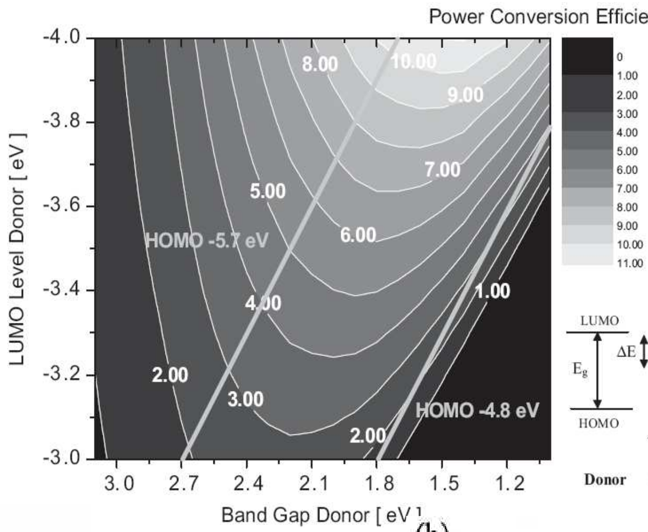


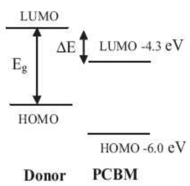
To get PCE >10%

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

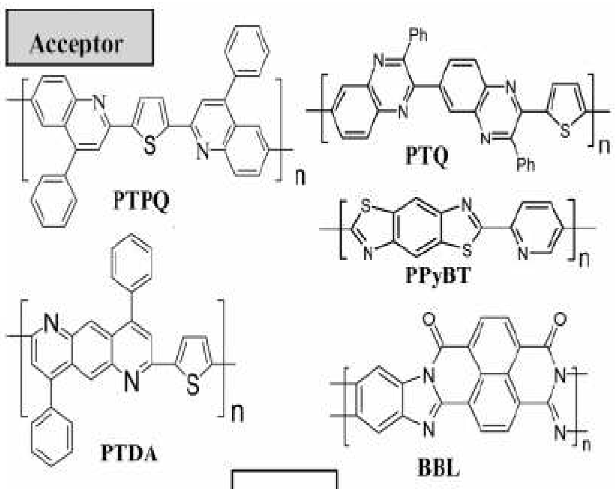
The importance of HOMO/LUMO level on the Photovoltaic Devices

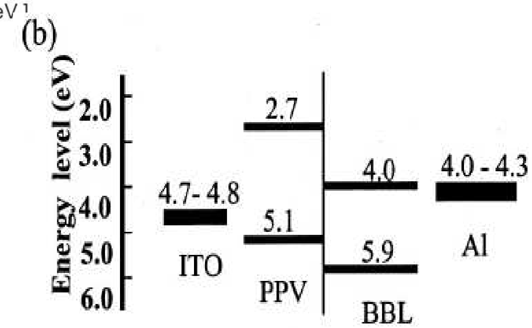


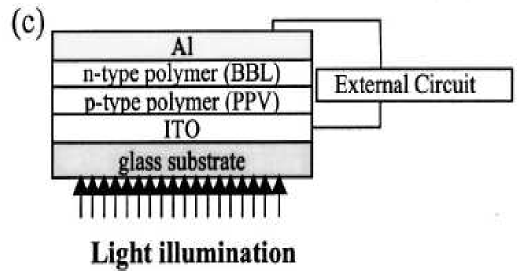




Importance of donor HOMO and acceptor LUMO

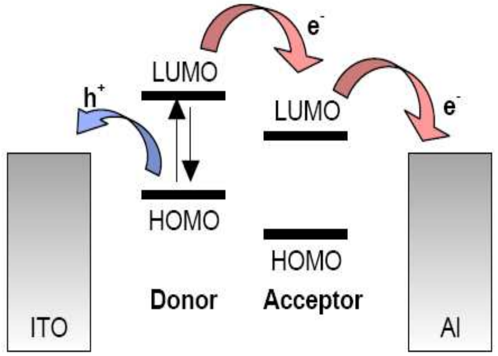


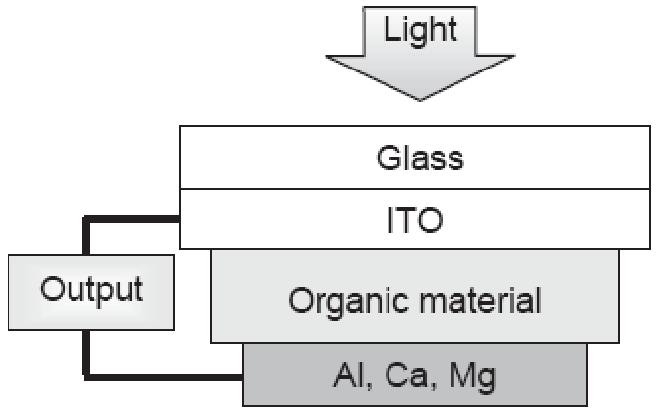


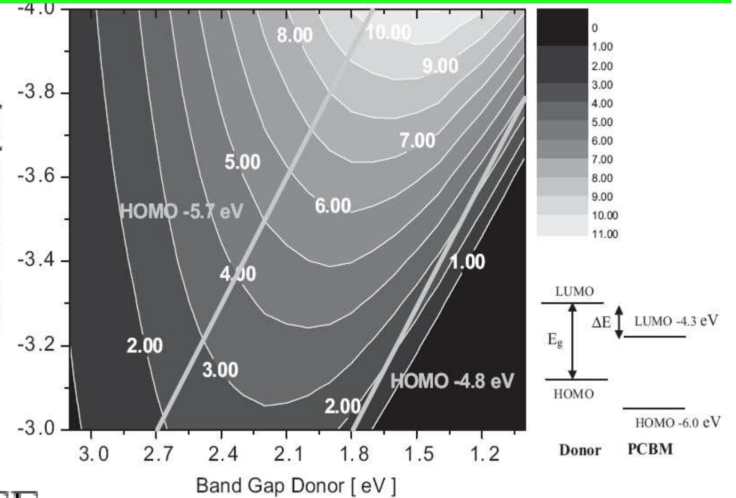


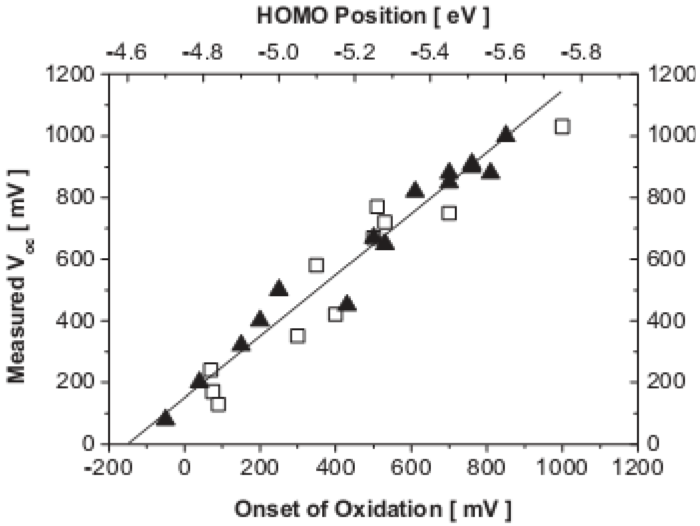
The EA of the PTPQ, PTQ, PPyBT, and PTDA: 2.7~3.0 eV, mismatch with Al→ poor PV efficiency

The importance of HOMO/LUMO level on the Photovoltaic Devices

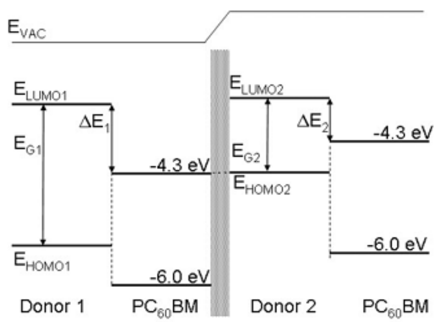




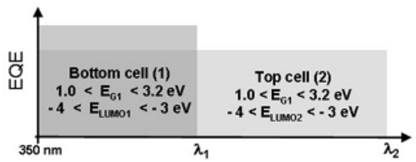




$$\eta_e = \frac{I_{mpp} V_{mpp}}{P_{in}} = \frac{I_{sc} V_{oc} FF}{P_{in}}$$



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



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**

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

Importance of Polymer Morphology on Photovoltaic Efficiency

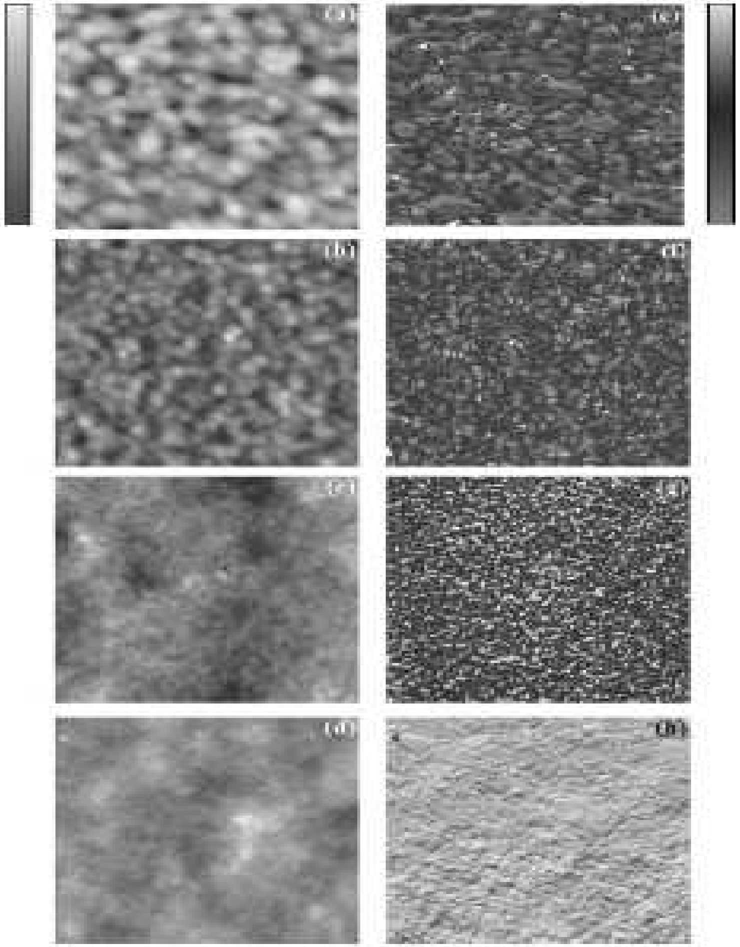
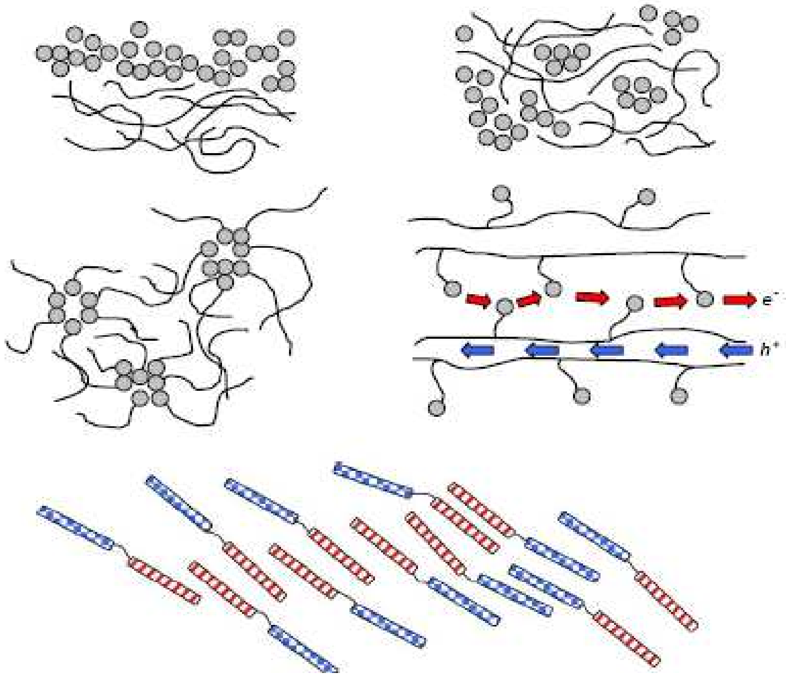


Figure 2. The AFM height (a–d) and simultaneously taken phase (e–h) images of the MDMO-PPV/PCBM composite films of 90 (a,e), 80 (b,f), 67 (c,g), and 50 wt.-% PCBM (d,h). Height bar (maximum peak-to-valley) represents 20 nm (a), 10 nm (b), 3 nm (c), and 3 nm (d). The size of the images is 2.0 μm × 2.0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



<u>Morphology determining parameters:</u>

The spin casting solvent

The composition between polymer and fullerene

The solution concentration

The controlled phase separation and crystallization induced by thermal annealing

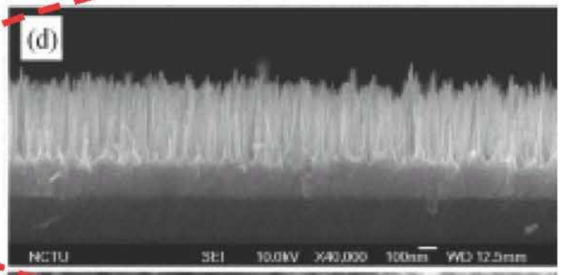
The chemical structure of the materials

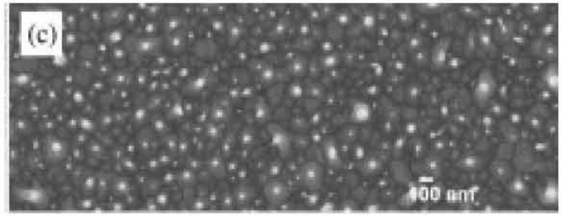
Adv. Funct. Mater. 2004, 14, No. 5, May   J. Mater. Chem., 2006, 16, 45–61   H. Spanggaard, F.C. Krebs / Solar Energy Materials & Solar Cells 83 (2004) 125–146

2. Defined transport path

From Polymer:

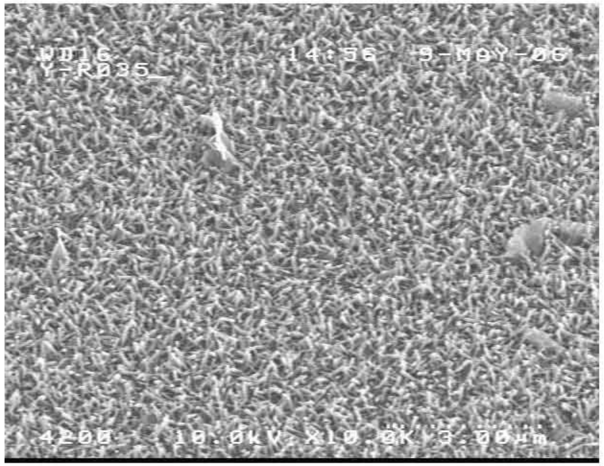
From Nanocrystal:





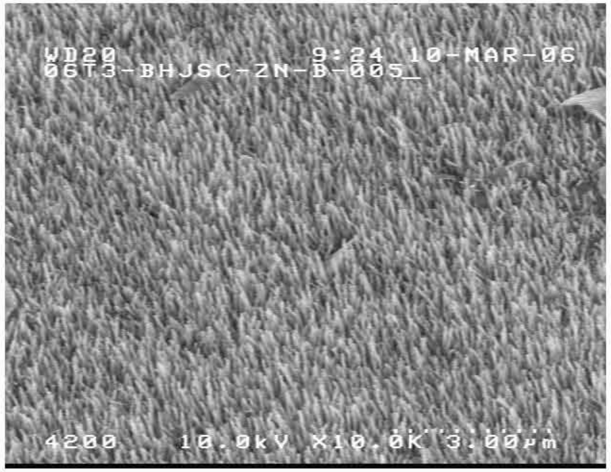
Control of Surface Grown ZnO

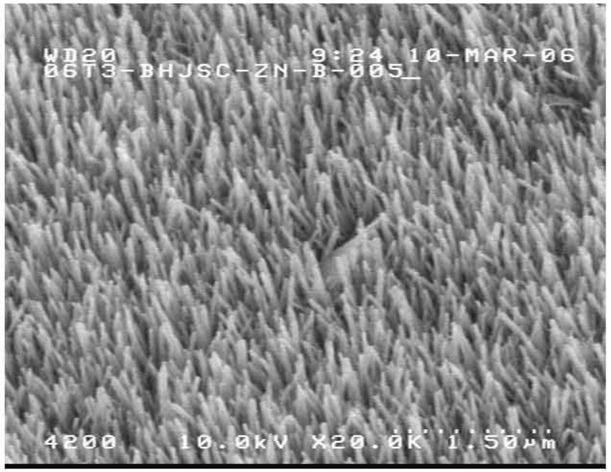
Spin-coating
LD ZnO



Surface unmodified

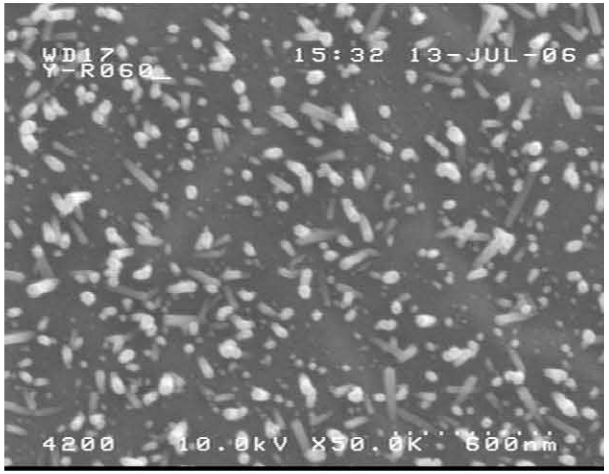
Dip-coating
HD ZnO

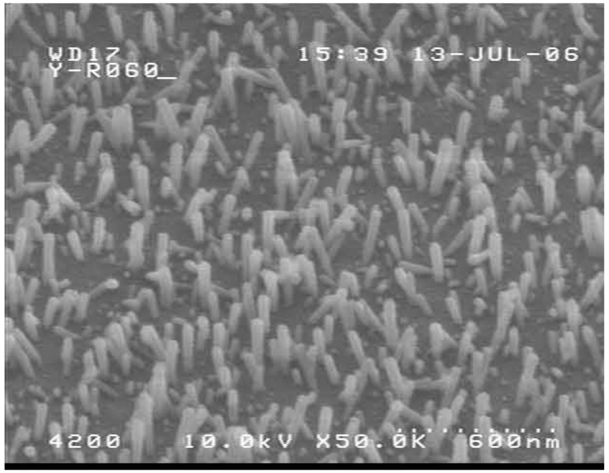




Surface unmodified

Spin-coating
LD ZnO





Surface modified