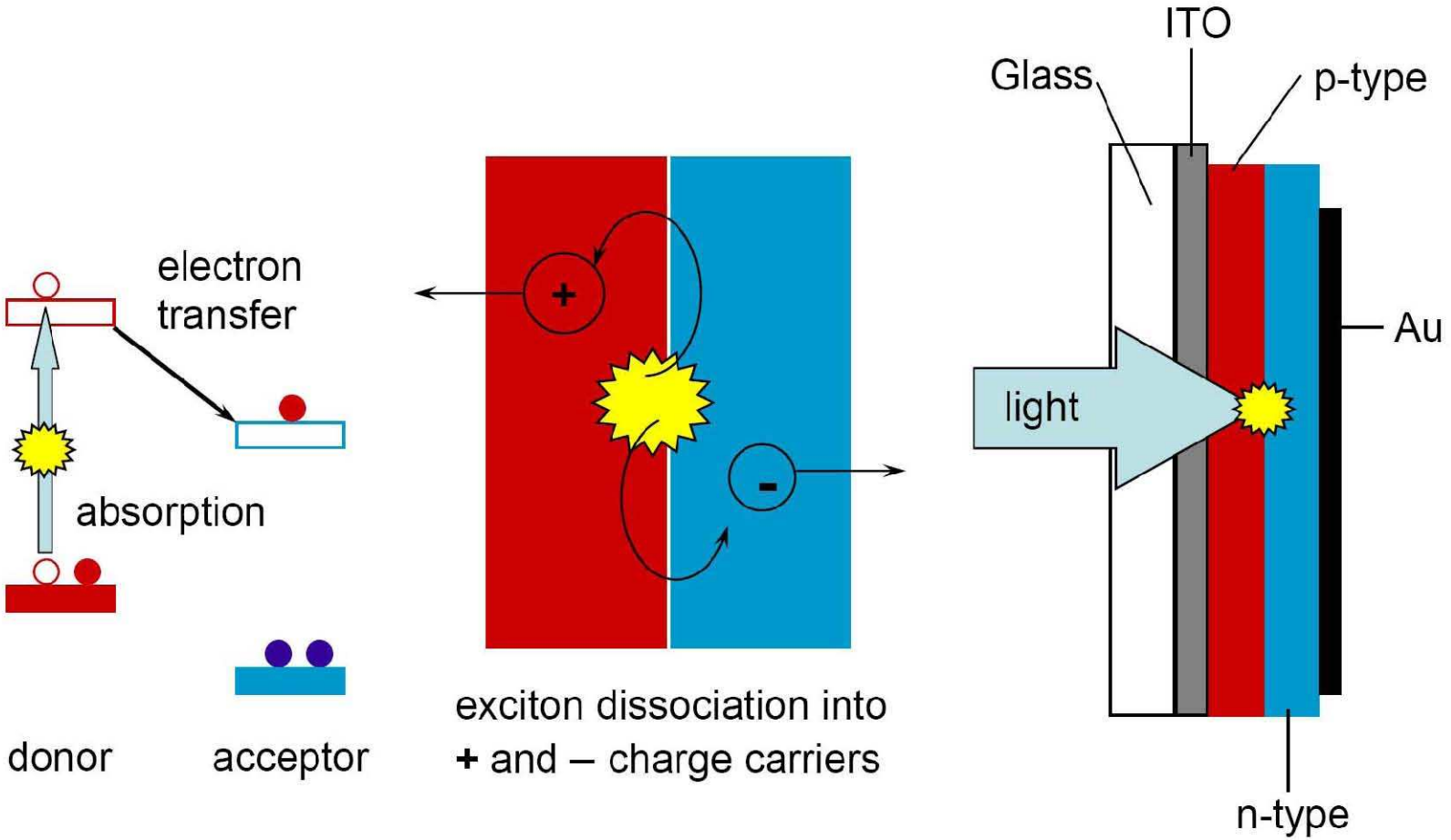
Organic double layer p/n cell

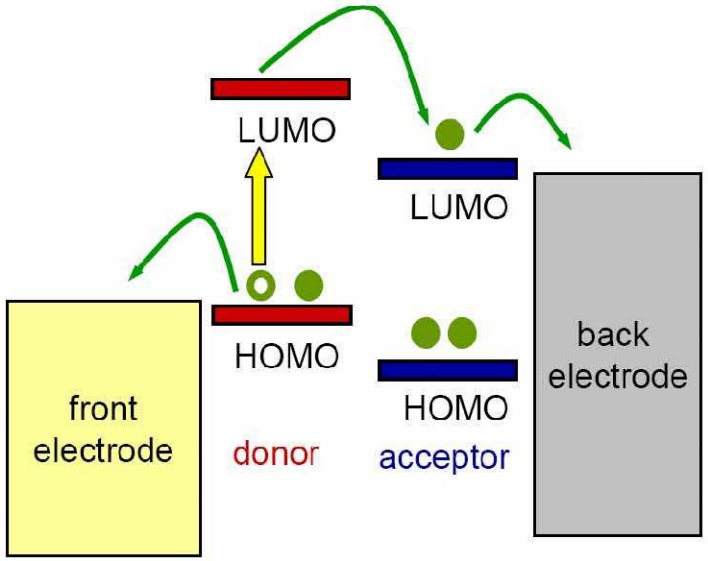


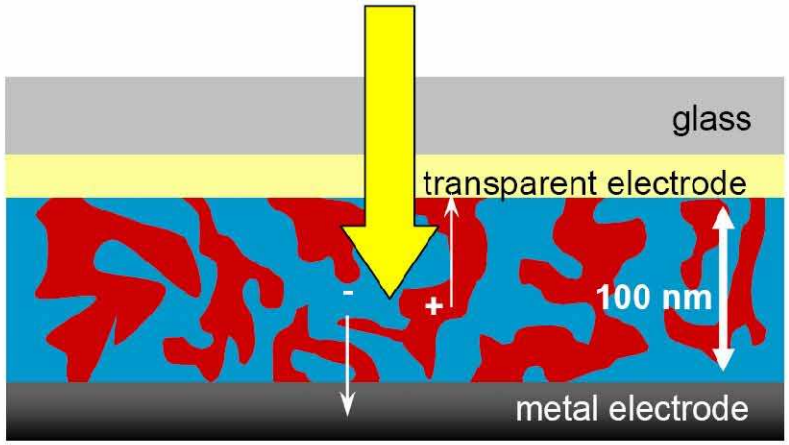
*C. W. Tang, Appl. Phys. Lett. 1985, **48**, 183.*

Copyright 2006 ITRI工業技術研究院

Bulk heterojunction solar cells

Charge separation in nanostructured composite organic semiconductors





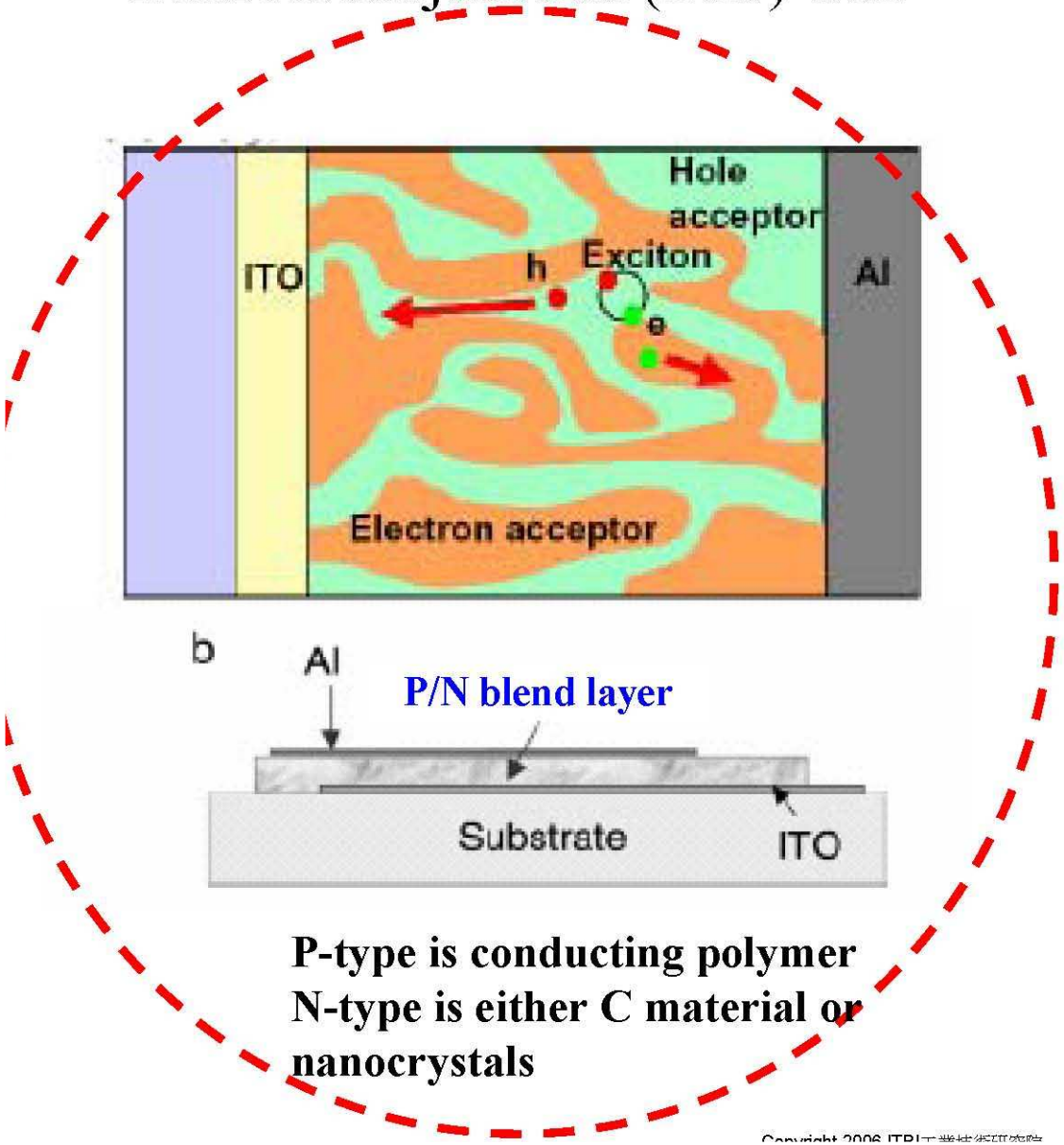
nanoscopic mixing of donor and acceptor to overcome ~10 nm exciton diffusion length

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

Copyright 2006 ITRI工業技術研究院

What & Why Is Organic Solid Phase Photovolta

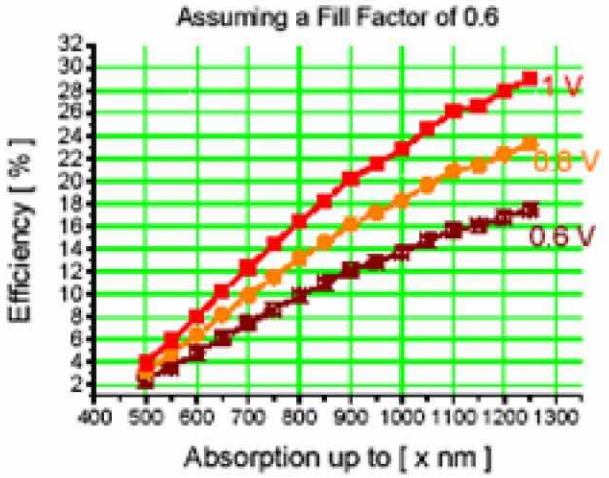
Bulk Heterojunction (BHJ) Cell



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

有機固態太陽光電之優勢：

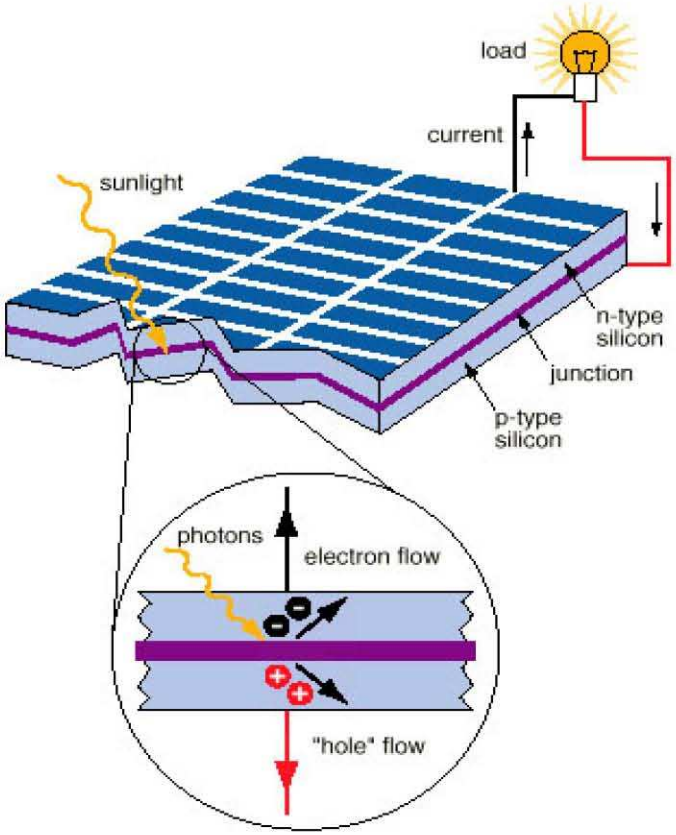
- 理論高效率(可達20%)
- 環保製程（而非只是綠色發電）
- 成本低
- 對光強度敏感度較低(室內光可用)
- 質輕，可撓性



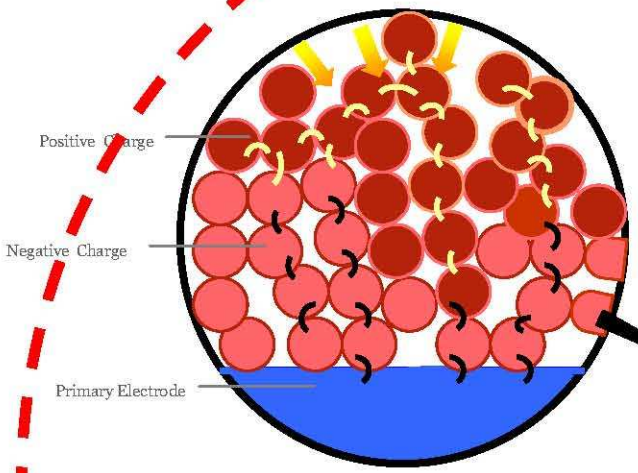
Copyright 2006 ITRI工業技術研究院

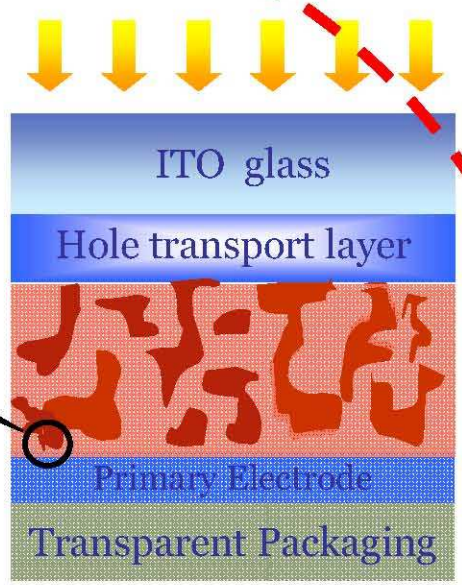
Polymer Based Solar Cell-Active layer

Conventional P-N Junction Cell



Bulk Heterojunction





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

Fullerene/ nanocrystal + Polymer

Polymer Based solar cell (PSC)

Copyright 2006 ITRI工業技術研究院

Light Converting Processes

- Absorption
- Exciton diffusion
- Charge Separation
- Charge Transport

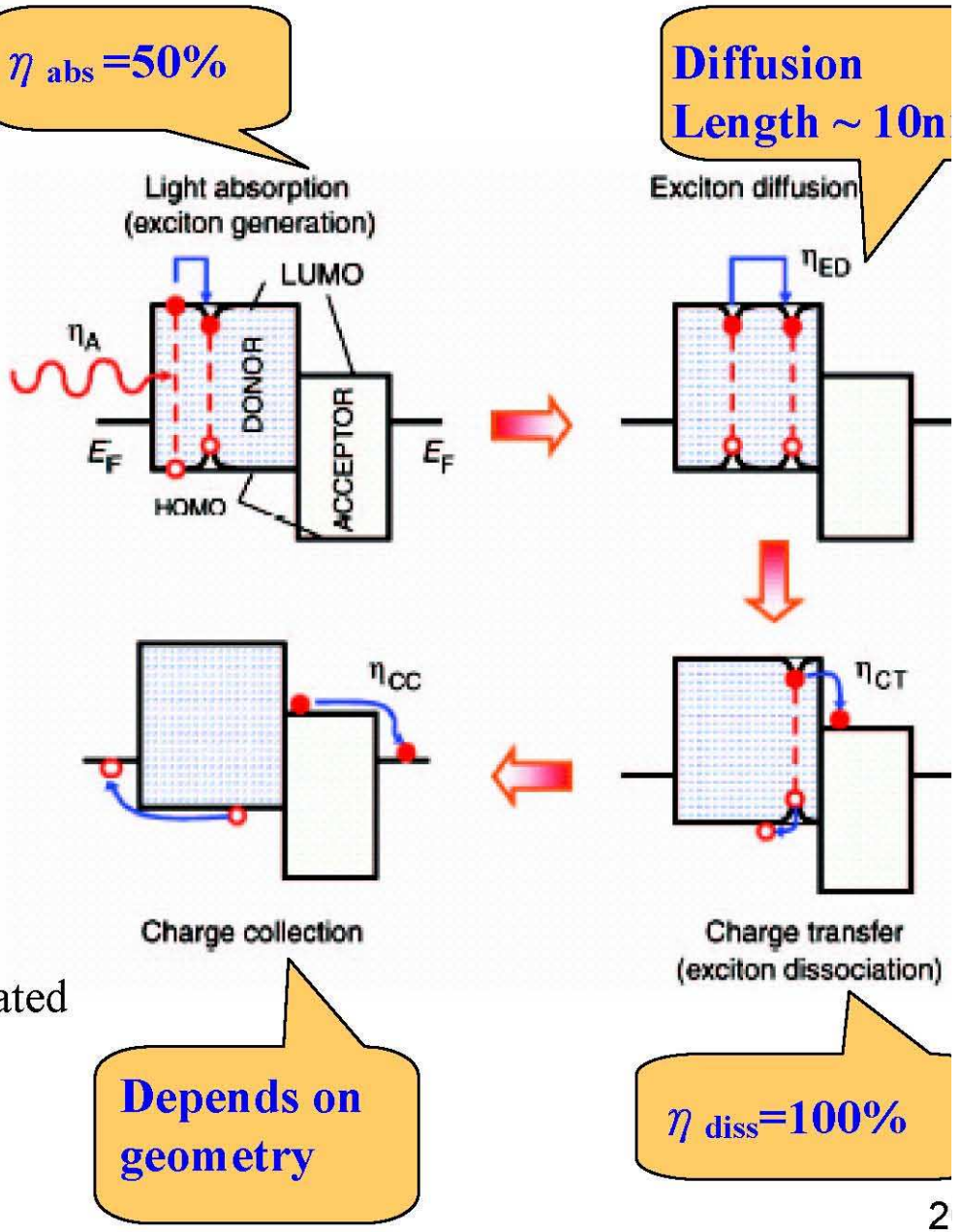
$$\eta_j = \eta_{abs} \times \eta_{diss} \times \eta_{out}$$

overall photocurrent efficiency

$_{abs}$ fraction of photons absorbed

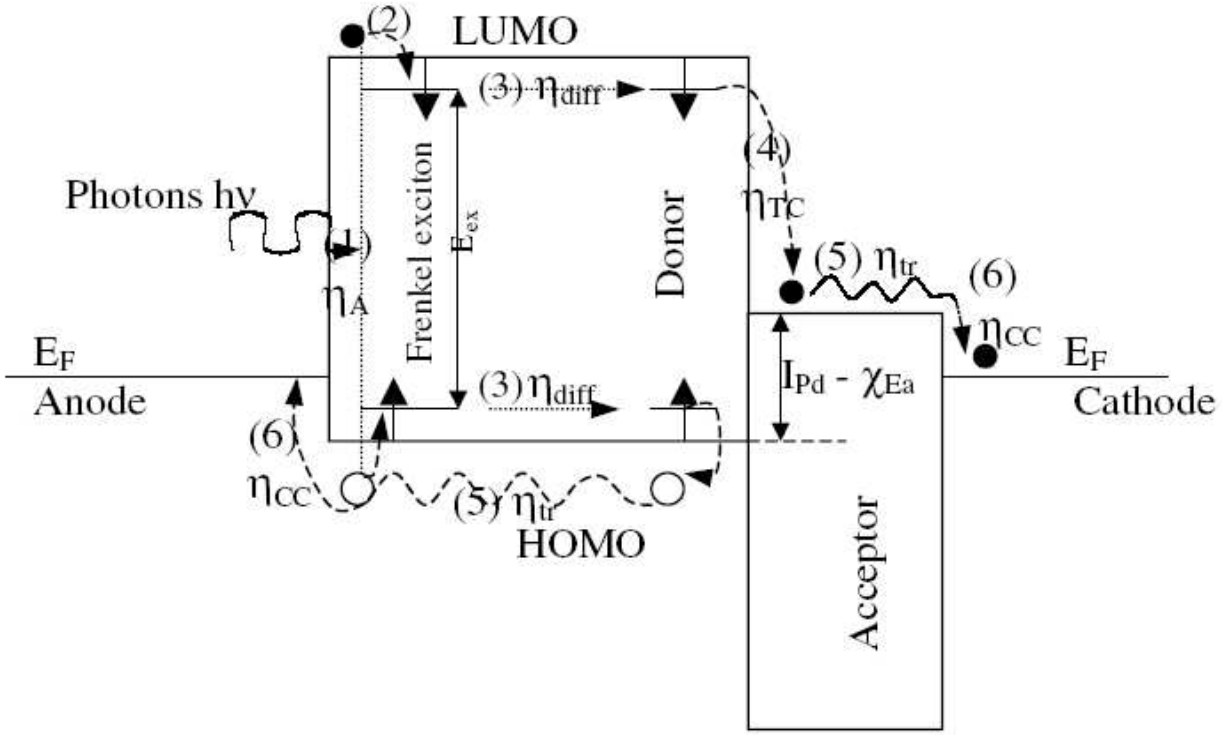
$_{diss}$ fraction of electron-hole pairs that are dissociated

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



Copyright 2006 ITRI工業技術研究院

General Mechanism in Organic Photovoltaic Cells



(1) Photon absoption (η_A)

(2) Generation of excitons

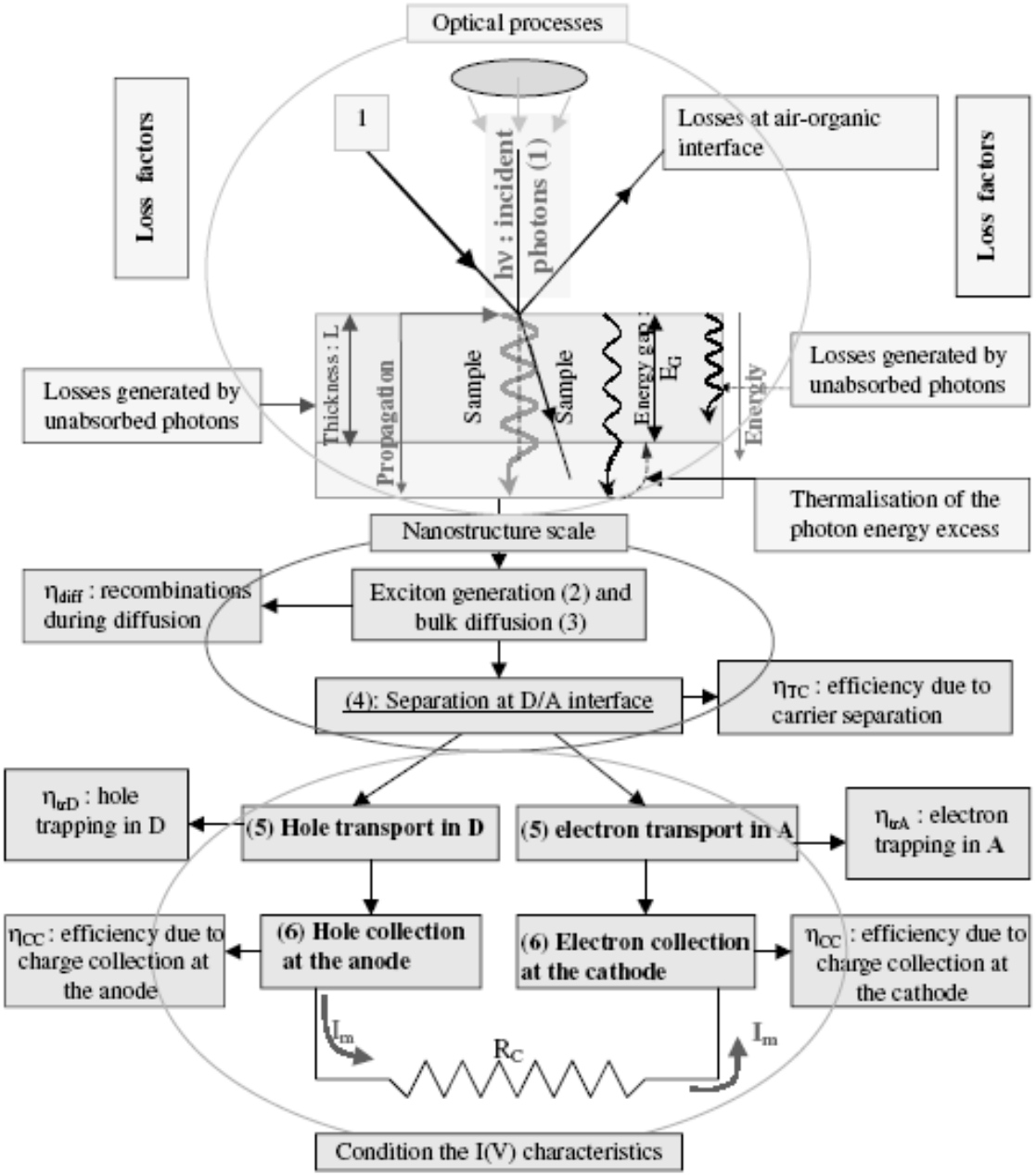
(3) Exciton diffusion (η_{diff})

(4) Hole-electron separation (η_{TC})

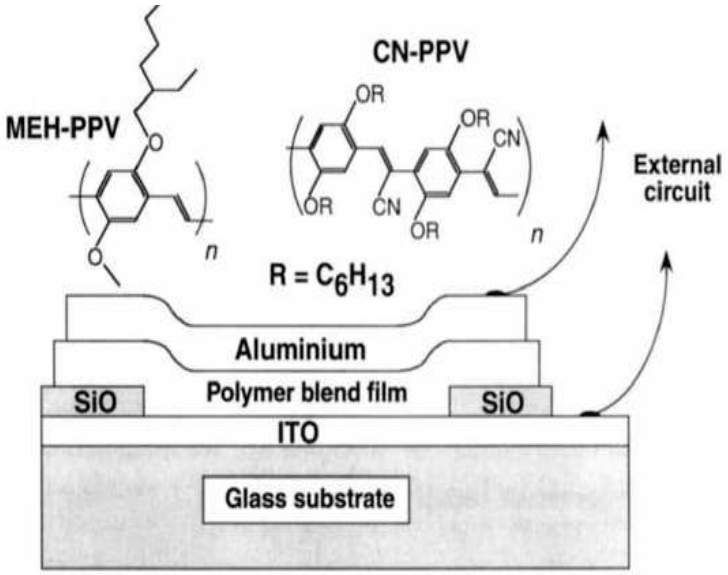
(5) Carrier transport towards the electrode (η_{tr})

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

General Scheme for Organic Photovoltaic Effect

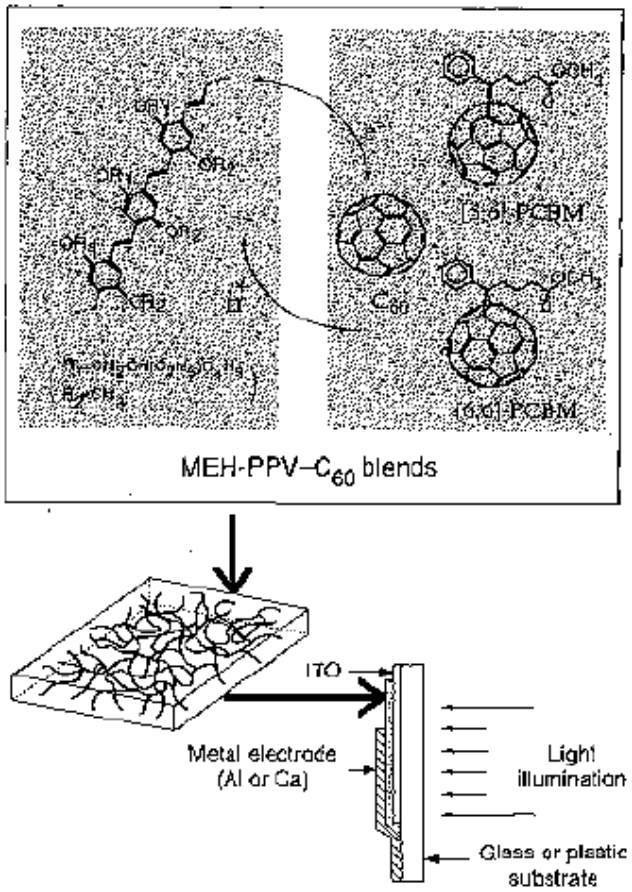


Examples on Polymer Phtovoltaic Devices



First Polymer-Polymer heterojunction PV

NATURE · VOL 376 · 10 AUGUST 1995



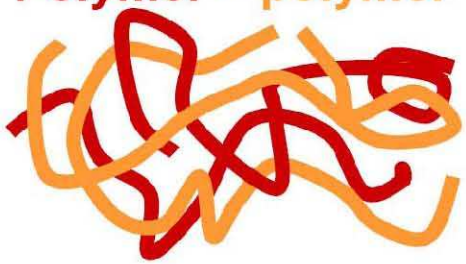
Energy conversion efficiency: 2.9 %

***Science* 1995**

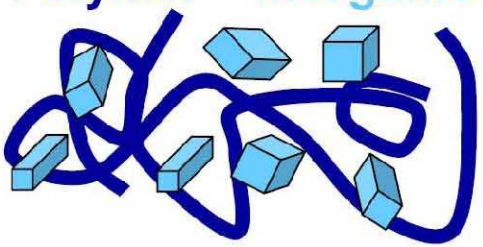
Polymer solution processed cells come in three 'flavors'

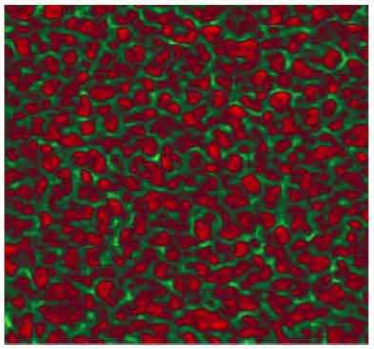
Polymer – fullerene

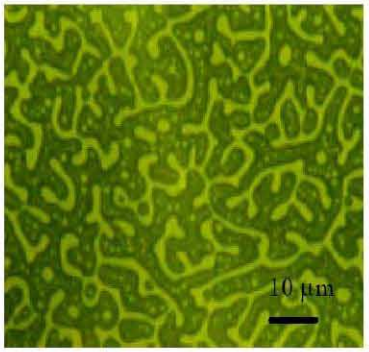
Polymer – polymer

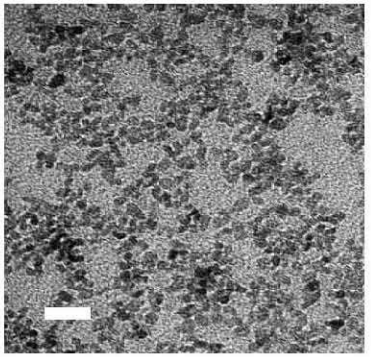


Polymer – inorganic

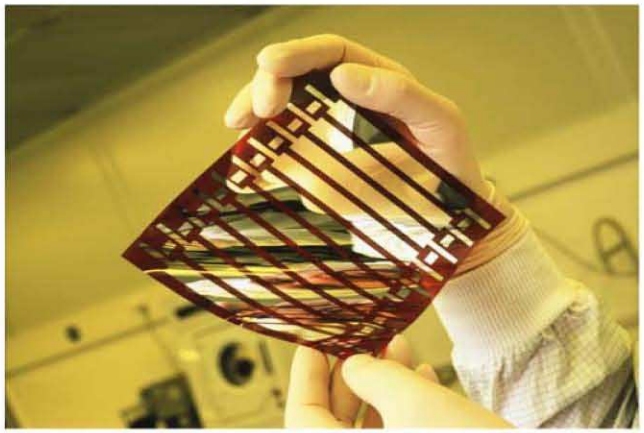


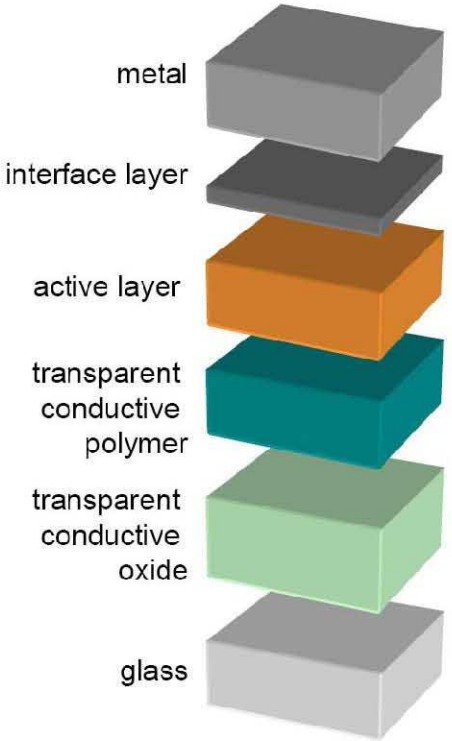






Polymer solar cells





Copyright 2006 ITRI工業技術研究院

太陽電池之 I-V 曲線

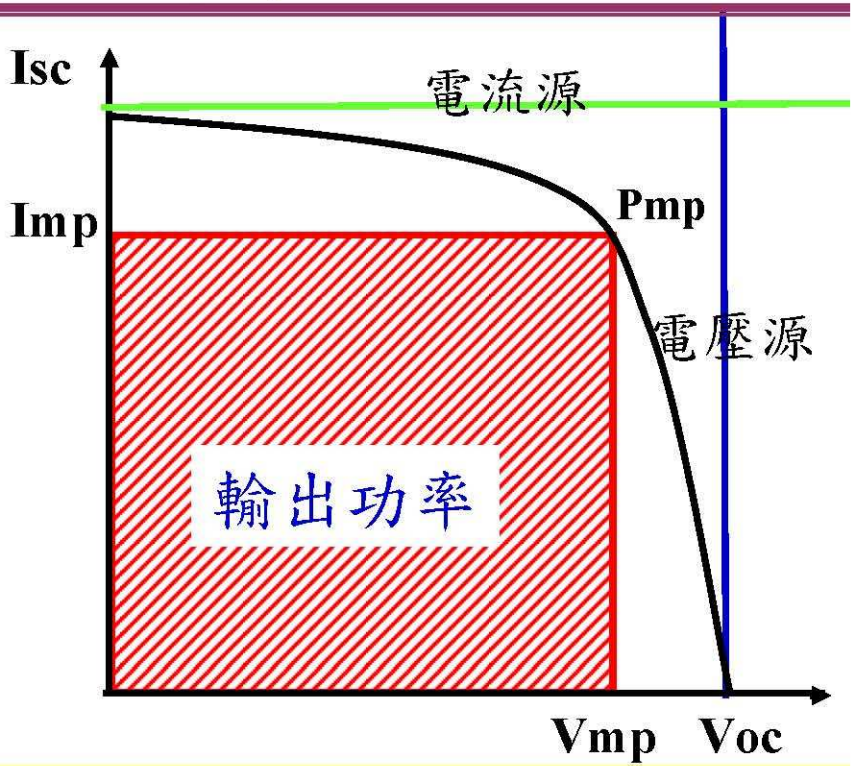
V_{oc}：開路電壓(V)

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%

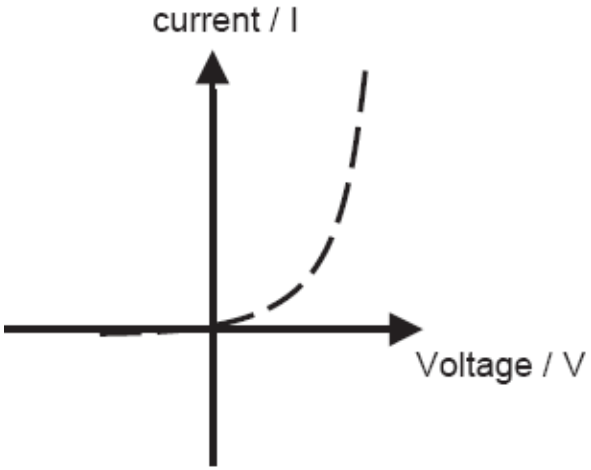
輸入日照功率(W)=太陽電池面積(m^2)×日照強度(W/ m^2)

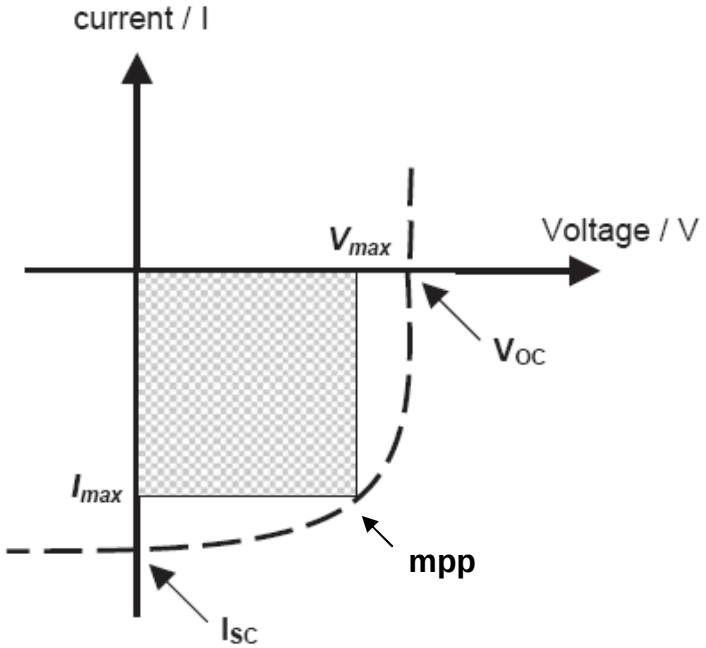
日照強度為1000 W/ m^2之最大輸出功率即為Wp

太陽電池開路、短路時皆不會燒燬

Copyright 2006 ITRI工業技術研究院

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

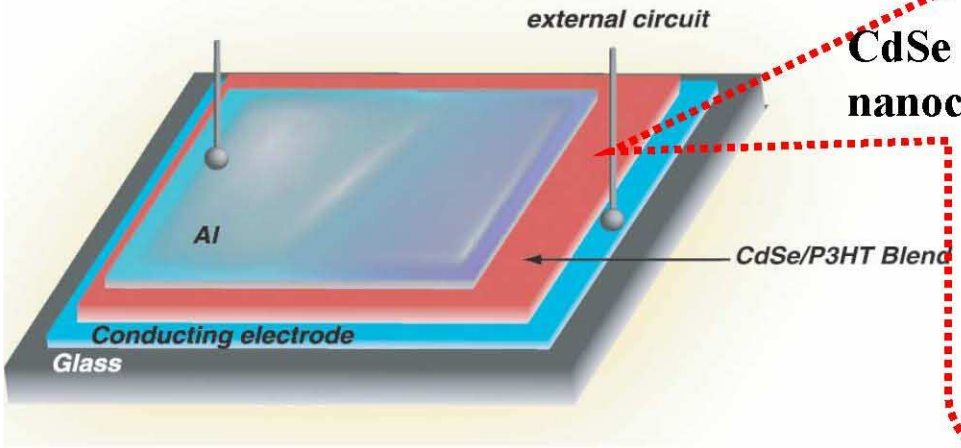
Power conversion efficiency (PCE) $$\eta_e = \frac{I_{\mathrm{mpp}} V_{\mathrm{mpp}}}{P_{\mathrm{in}}} = \frac{I_{\mathrm{sc}} V_{\mathrm{oc}} \mathrm{FF}}{P_{\mathrm{in}}}$$

國際發展比較-有機固態太陽光電

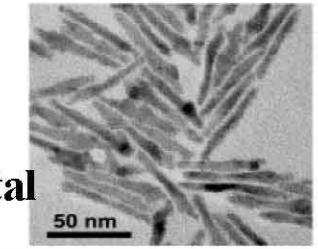
高分子-碳材太陽光電池技術		
Authors/Institutes	**Compositions**	**Efficiency (%)**
David L. Carroll/Wake Forest University, USA/Kyungkon Kim/ KIST, Korea	ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al	6.1
C. J. Brabec /Siemens (Konarka) AU/A. Heeger/Konarka USA	ITO/PEDOT:PSS/P3HT:PCBM/Al	5.68
Kwanghee Lee /Pusan U., Korea/ A. Heeger	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

Copyright 2006 ITRI工業技術研究院

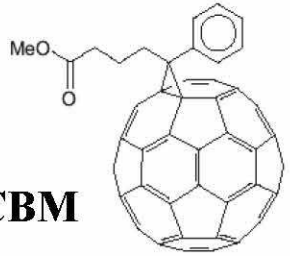
Polymer Photovoltaic Structure



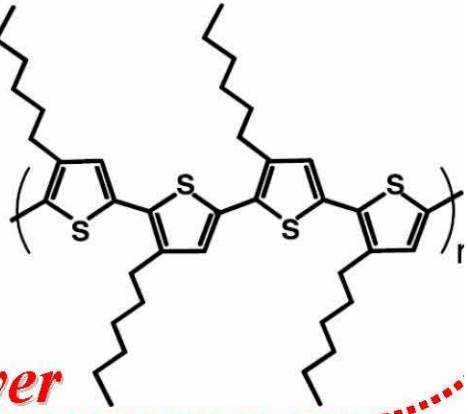
CdSe nanocrystal



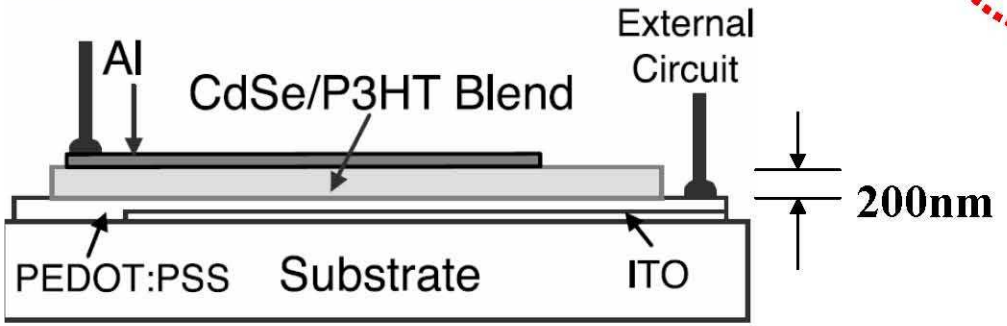
PCBM



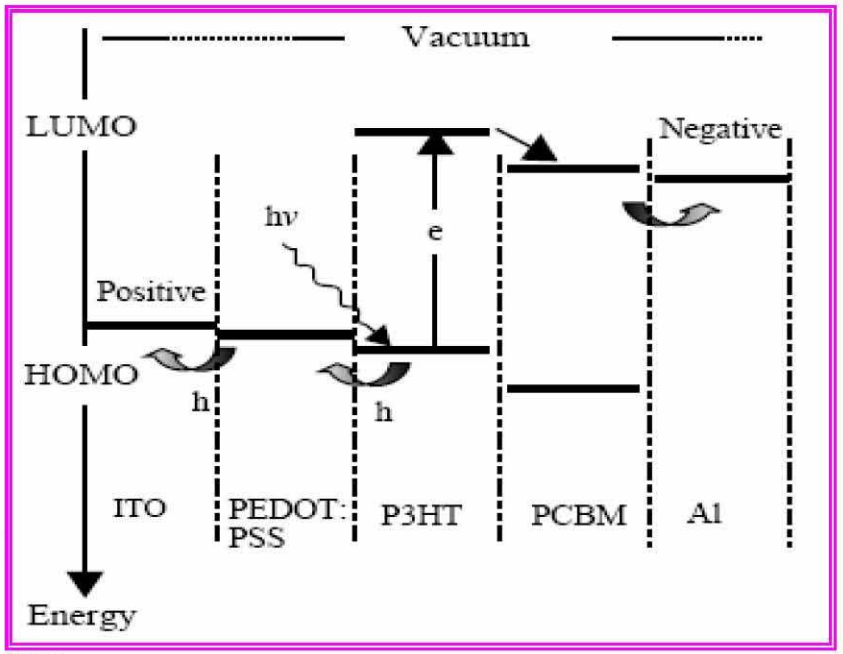
(poly(3-hexylthiophene))
Regioregular P3HT



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)

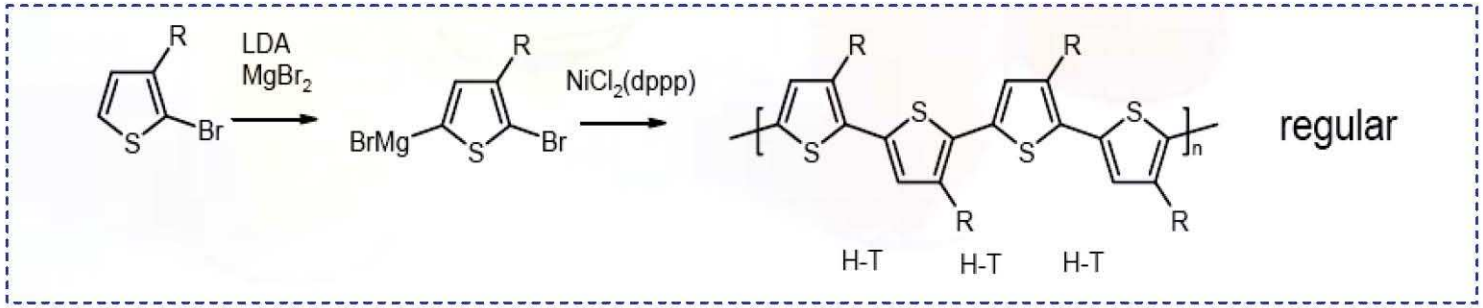
Appl. Phys. Lett. 90, 163511 (2007)

Copyright 2006 ITRI工業技術研究院

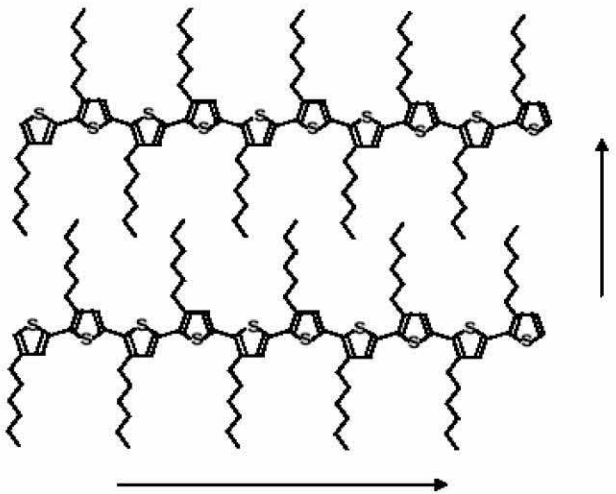
Some of the Approaches in MCL

1. Better packing conducting polymer

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



— Tightly-packing conducting polymer but still maintain its processbility

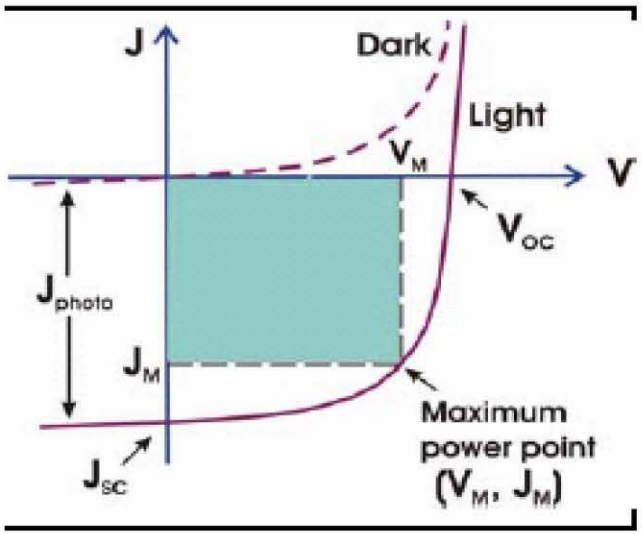


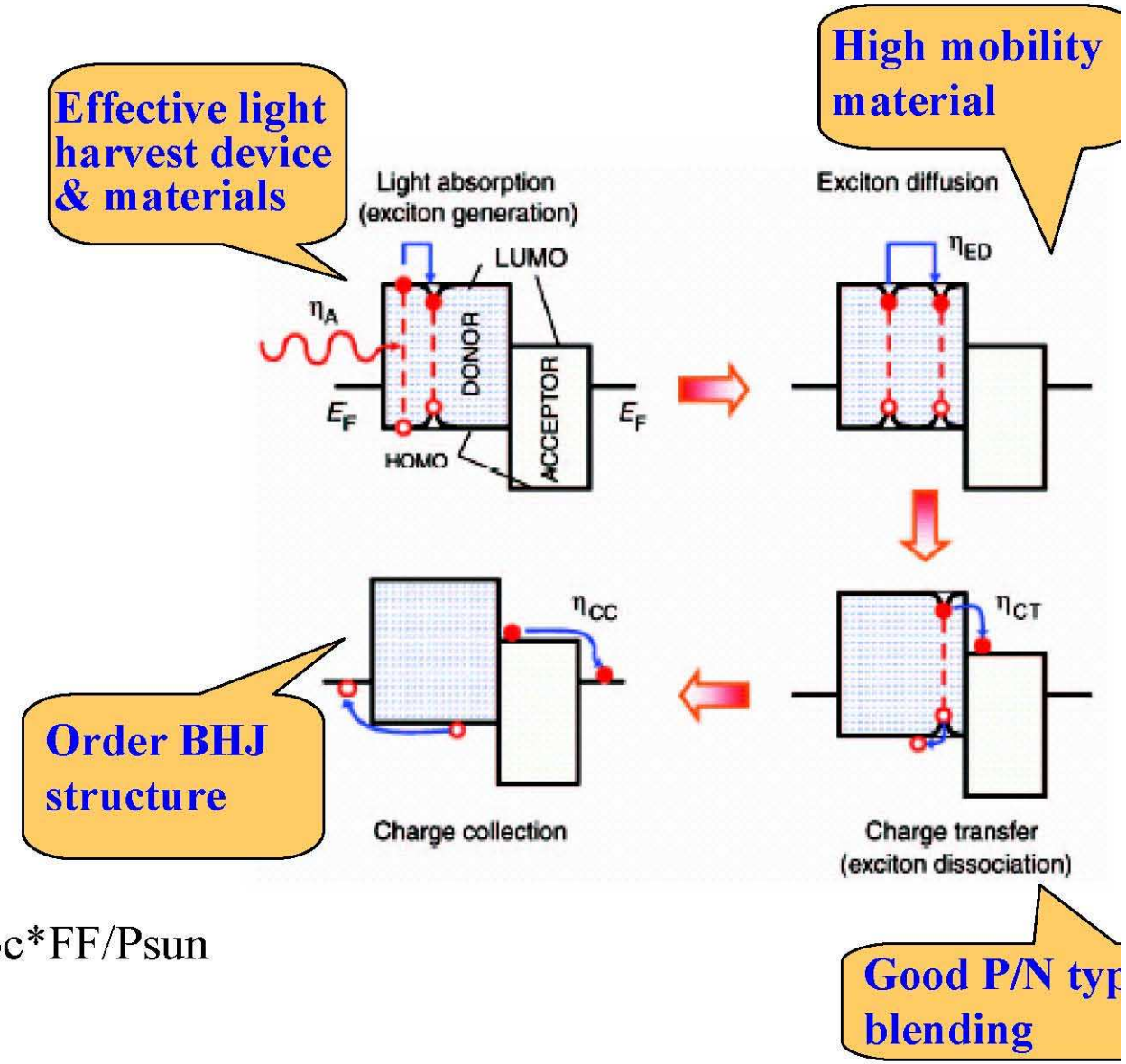
— High mobility conducting polymer design with good solubility

Copyright 2006 ITRI工業技術研究院

關鍵技術分析

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





FF = JmVm/JscVoc

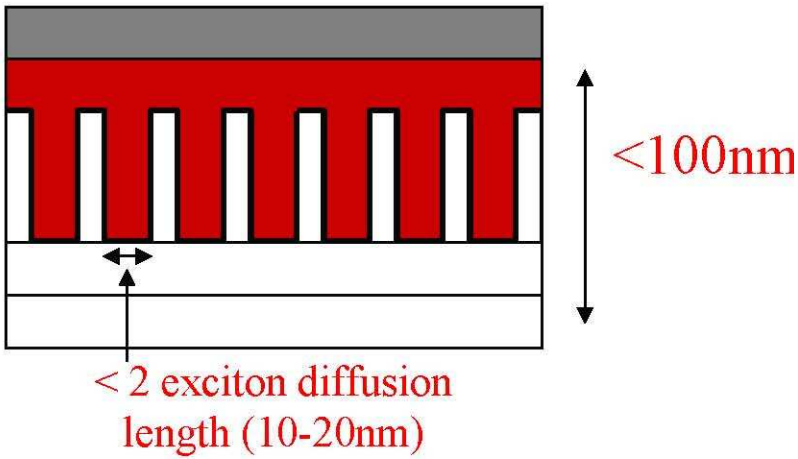
η = JmVm/Psun = 100*Jsc*Voc*FF/Psun

Copyright 2006 ITRI工業技術研究院

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



Copyright 2006 ITRI工業技術研究院

Current Challenges

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

New device designs: Ordered Bulk Heterojuctions

- **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

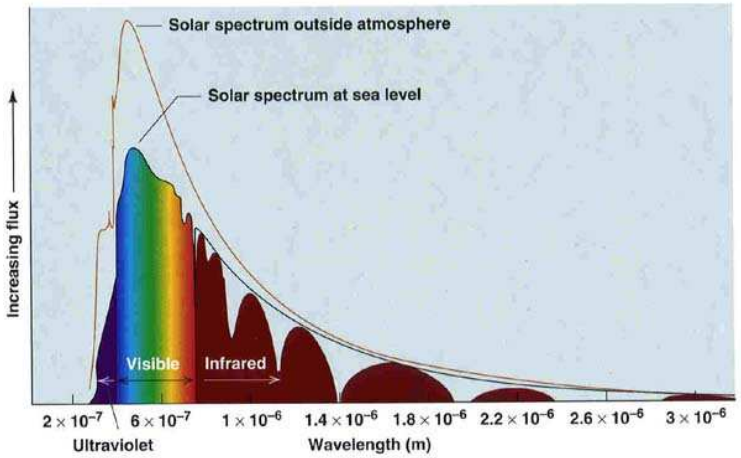
- **Addressing manufacturing issue and improving stability**

By encapsulating cells and more stable materials

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

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

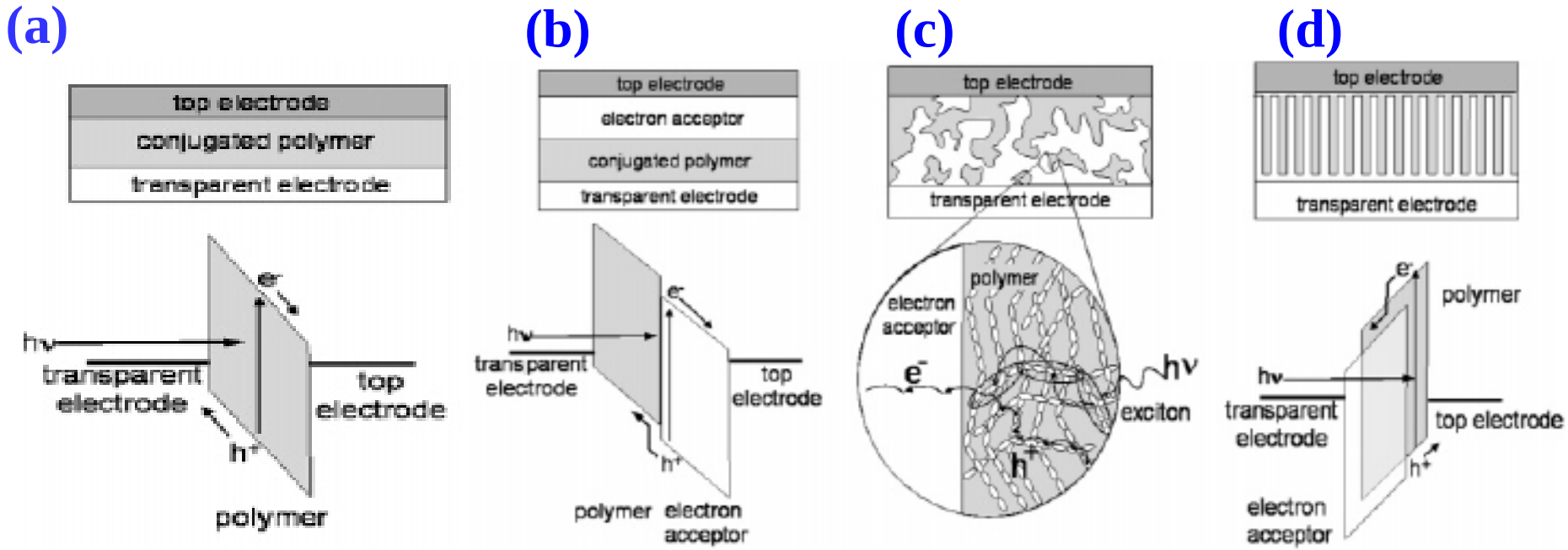
- 1. New device designs: Ordered Bulk Heterojuctions
- Approach: Polymer Semiconductor/acceptor Order Heterojuction Structure
- 2. The high light-absorbing capabilities:
- Conjugated polymer and electron acceptor with lower band gap: 350-900 nm (3.5~1.4eV)
- Approach: Low Eg Polymer



- 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

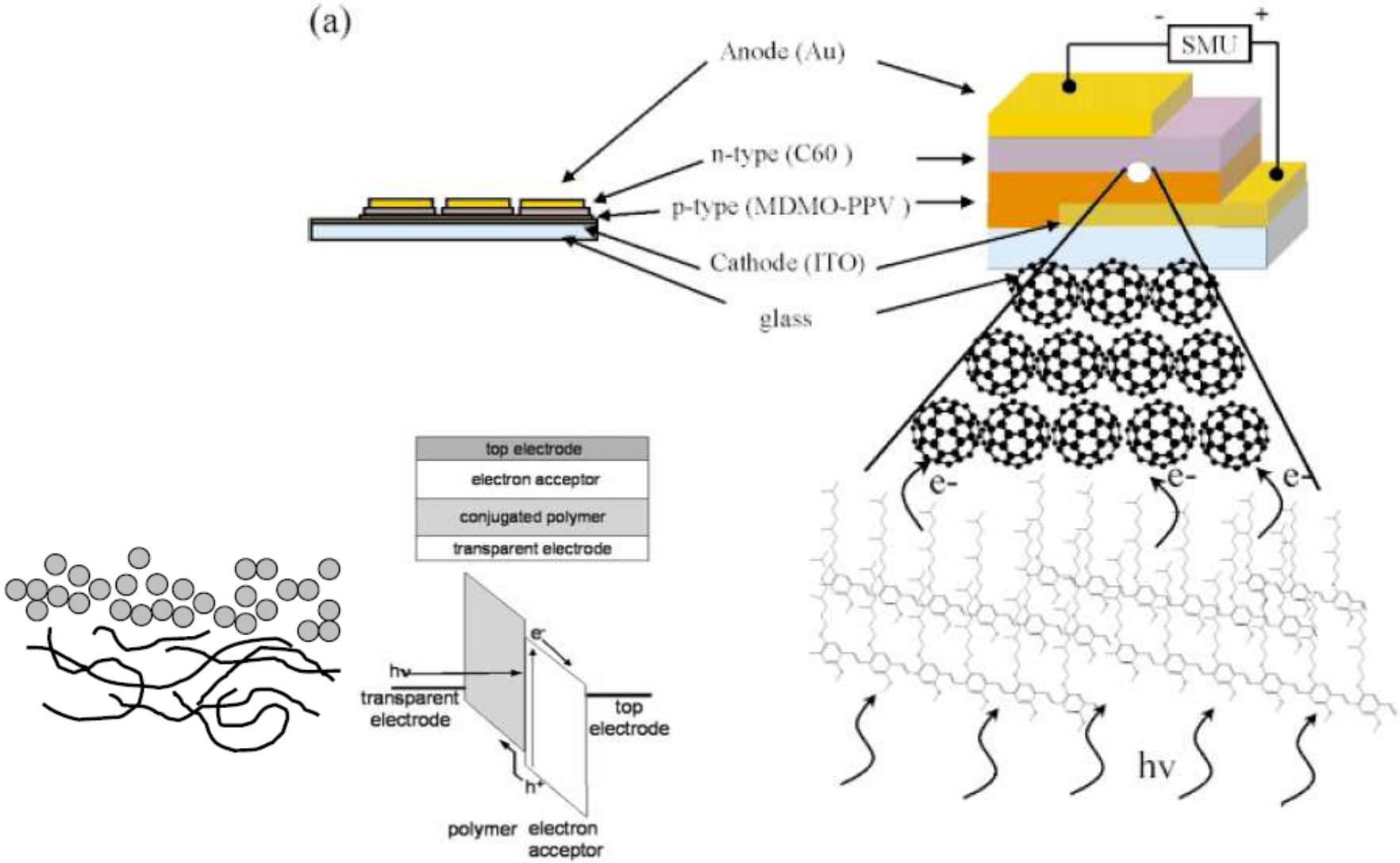


- Single Layer(a): Low EQE(0.1~1%) due to exciton recombination; low carrier mobility
- Bilayers (b) : PA-PPV/TiO_2 25% EQE, 3.9 % power efficiency (435 nm);
  PPV/BBL 66%% EQE, 2% power efficiency
- Bulk heterojunction (c) (d):
  - **PPV/C60 Derivatives 70% EQE, 3.5% power efficiency**

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

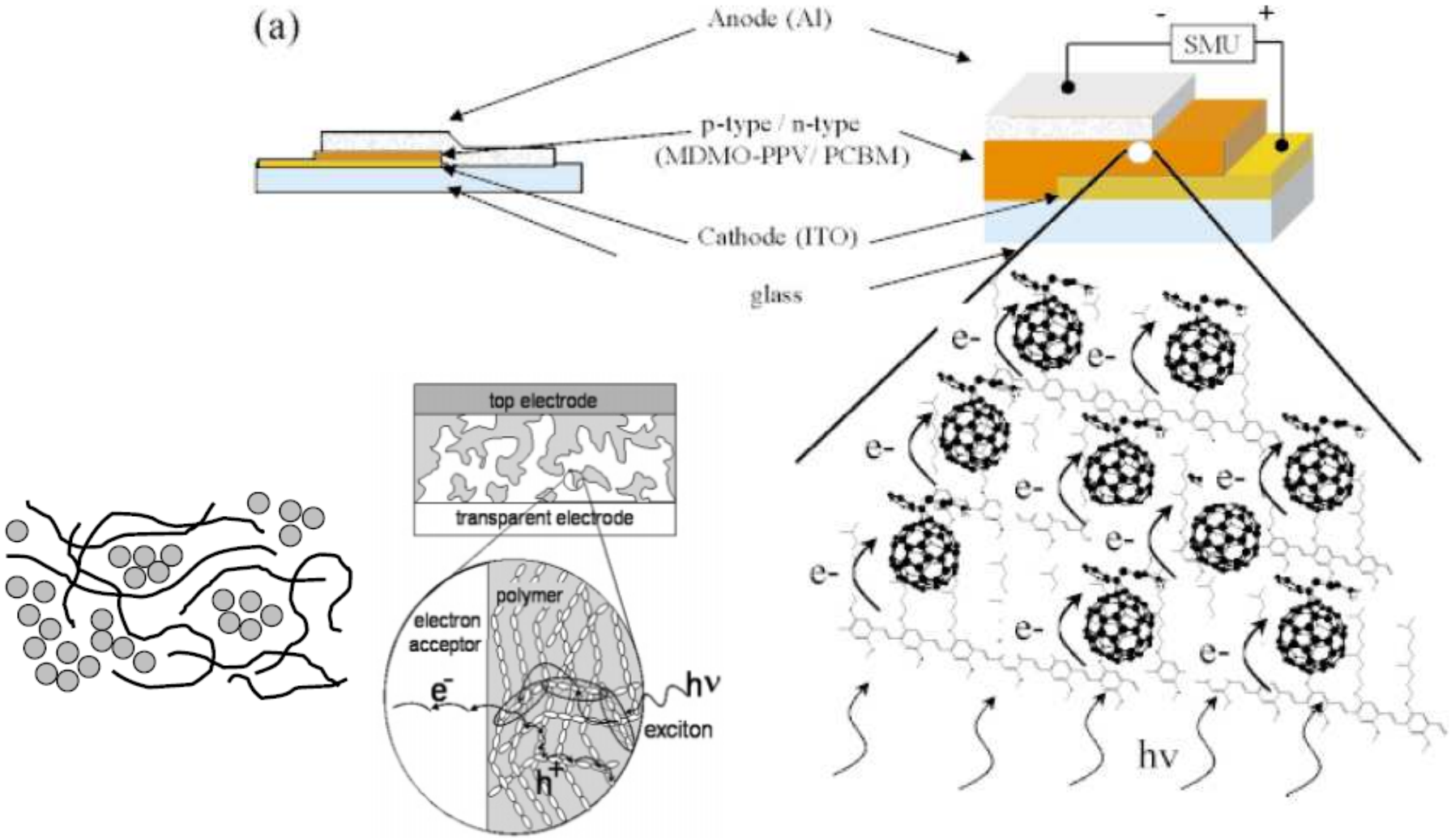
Organic Photovoltaic Device Architectures

Bilayer Devices



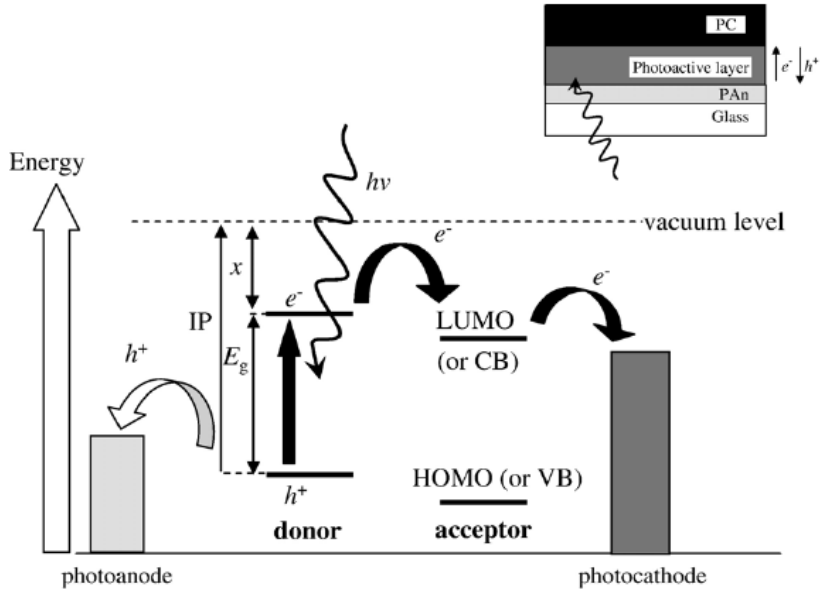
Organic Photovoltaic Device Architectures

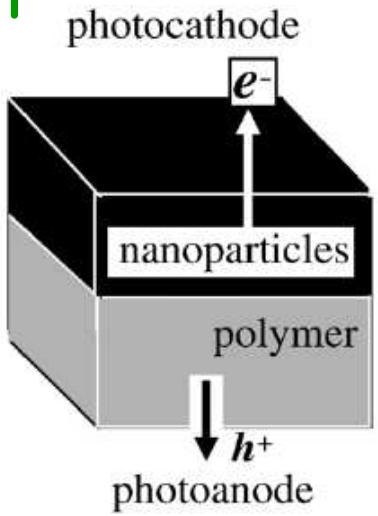
Bulk Heterojunction Devices



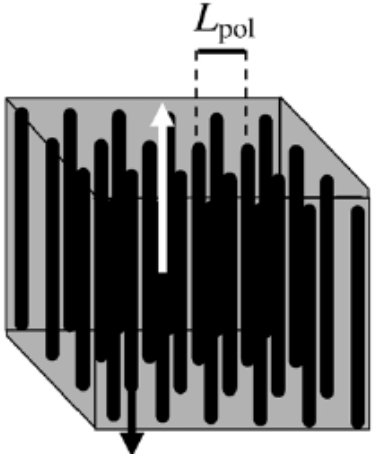
Concept of Polymer/Acceptor Photovoltaic Device

Energy levels and harvesting of energy from D/A interface within a PV cell





Bilayer cell due to complete phase separation : polymer domain size >> exciton diffusion length



Vertical aligned Acceptor: polymer domain size <exciton diffusion length

General rules for preparing efficient polymer-acceptor solar cells

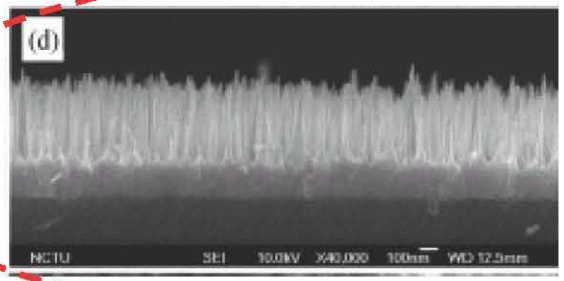
- **High balanced electron and hole mobility and large interfacial area of the bulk heterojunction .**
- **High extinction coefficient and absorb light from much of solar spectrum.**
- **Optimization of energy levels to promote charge separation and transfer.**
- **Form interconnected bicontinous solid dipersion and vertically aligned structure with polymer domain size <exciton diffusion length**

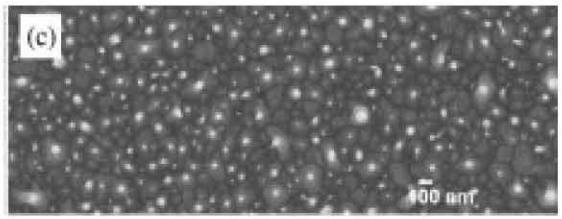
Adv. Colloid Interface Sci. 2008, 138, 1

2. Defined transport path

From Polymer:

From Nanocrystal:

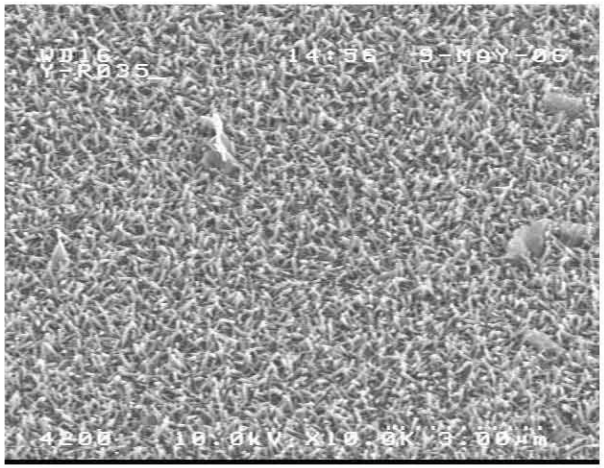


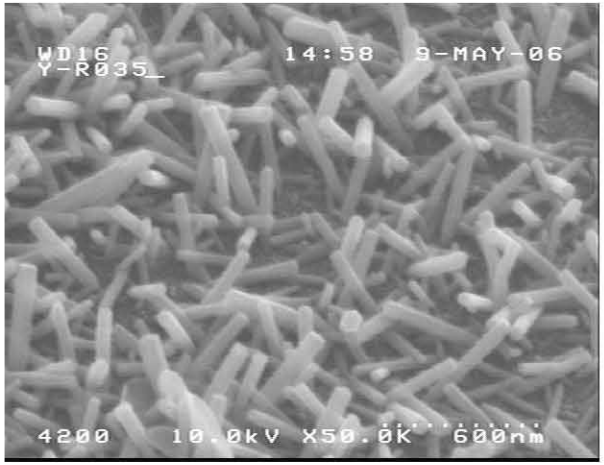


Copyright 2006 ITRI工業技術研究院

Control of Surface Grown ZnO

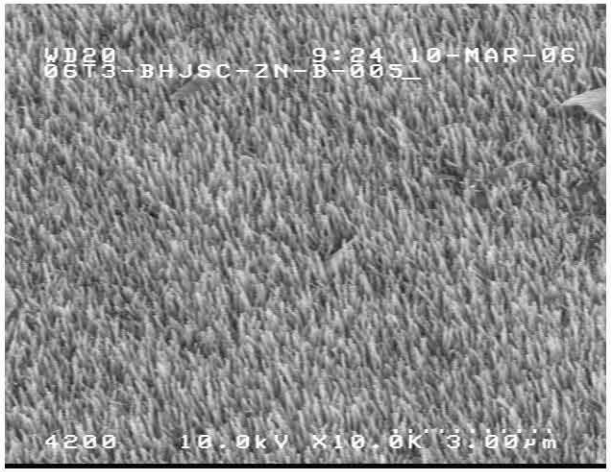
Spin-coating
LD ZnO

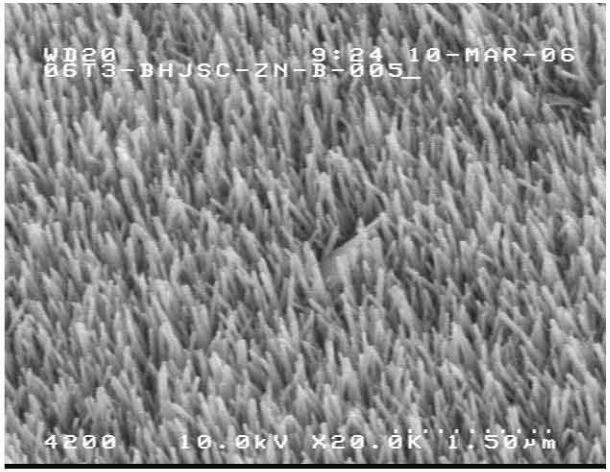




Surface unmodified

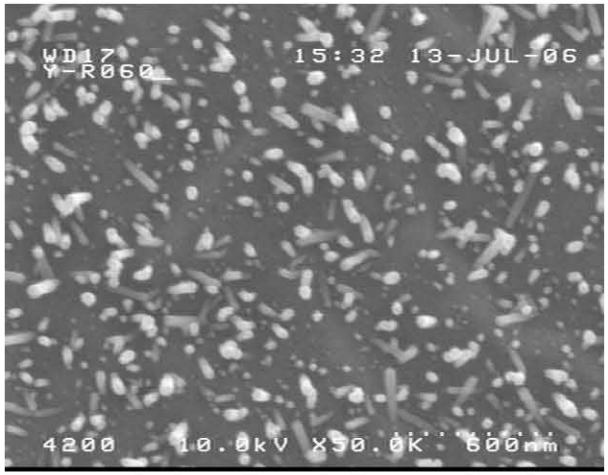
Dip-coating
HD ZnO

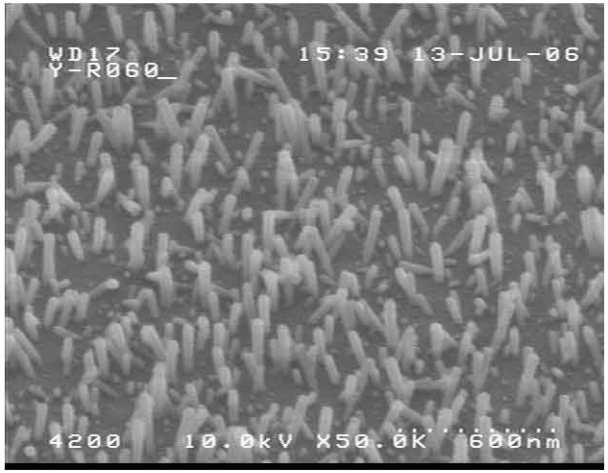




Surface unmodified

Spin-coating
LD ZnO

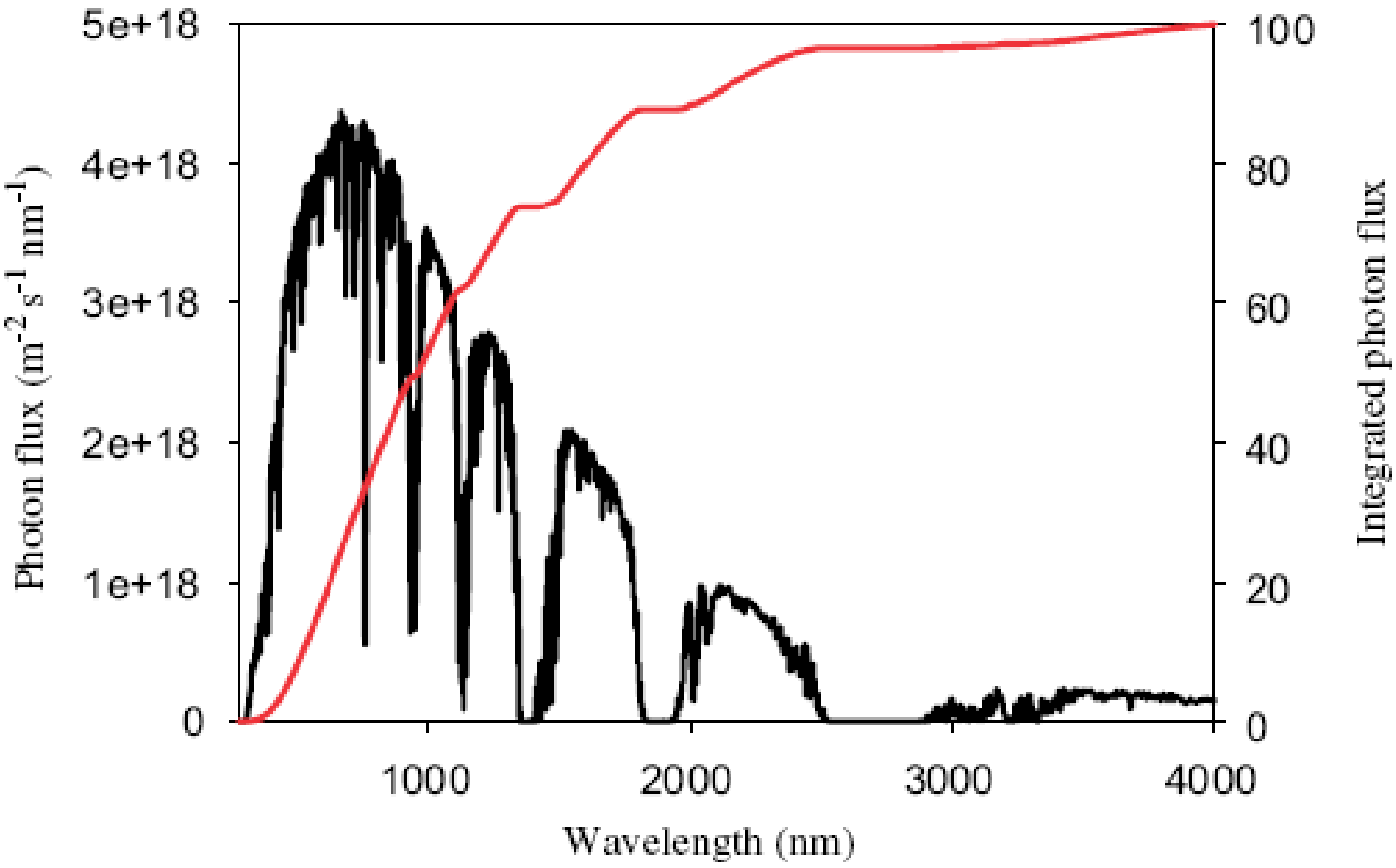




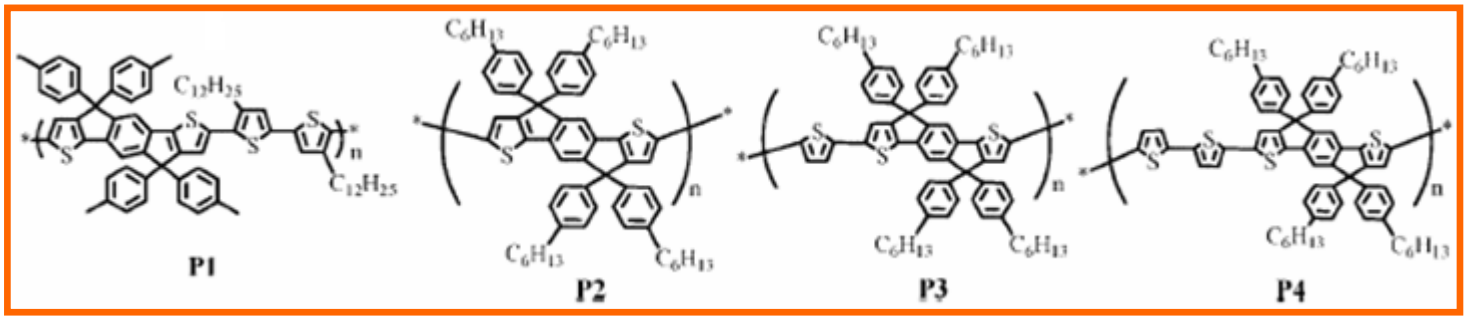
Surface modified

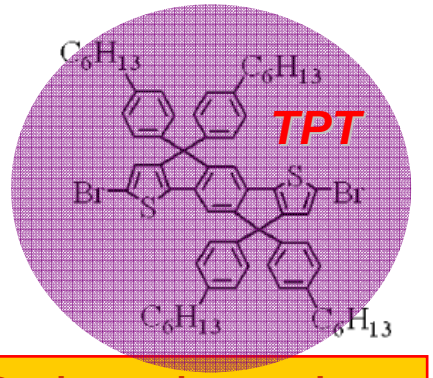
Copyright 2006 ITRI工業技術研究院

Absorption Spectrum of Organic Materials



Photon reflux from the sun (AM 1.5)





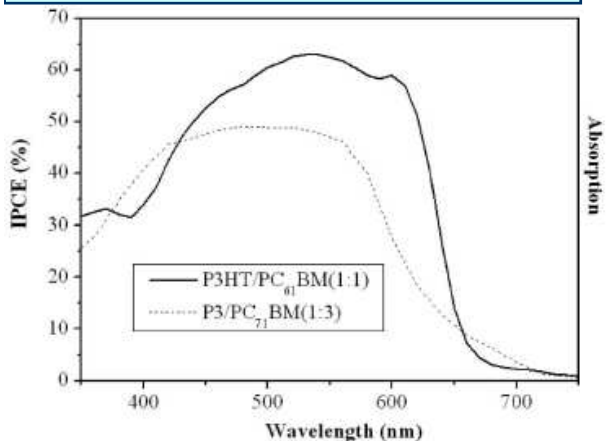
Coplanar chromophore

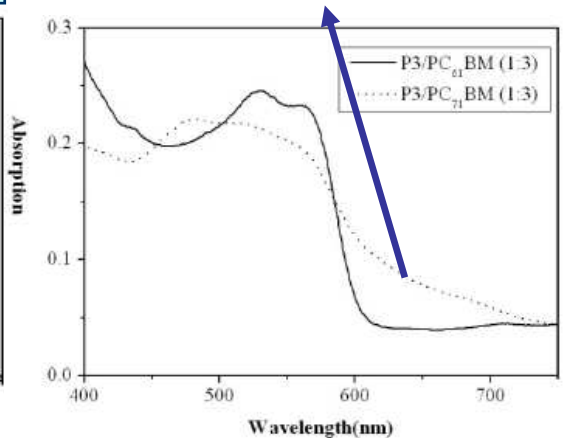
Max. IPCE:

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/cm²)	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

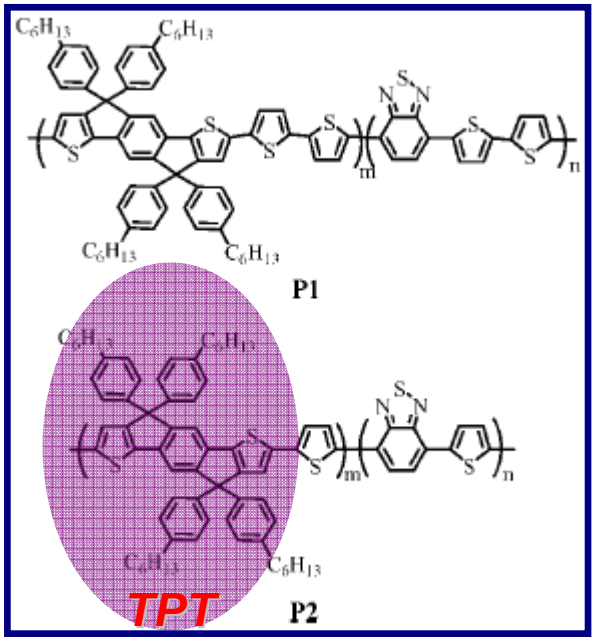
Table 1. Molecular Weights, FET Mobility, and Optical and Electrochemical Properties of Various Polymers

	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

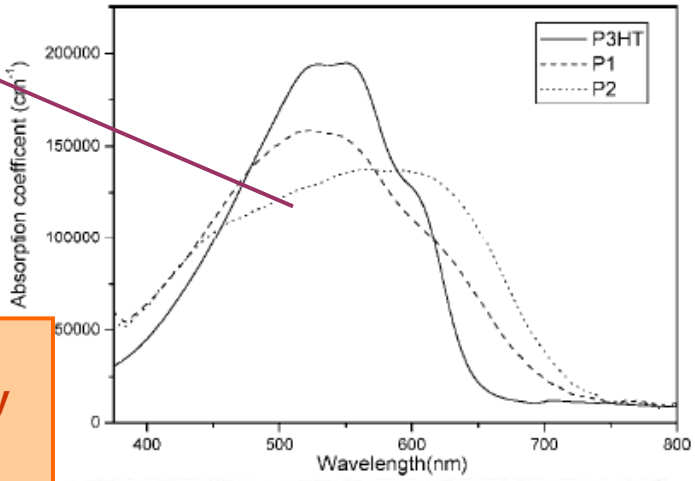
[a] Absorption coefficient was determined at λ_{max} in THF. [b] E_{ox} is the onset potential of oxidation of polymer. [c] Thin-film FETs were fabricated from 1 wt % *o*-DCB solutions. [d] $CHCl_3$ solvent was used instead of *o*-DCB.

High absorption coefficient in comparison to P3HT

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

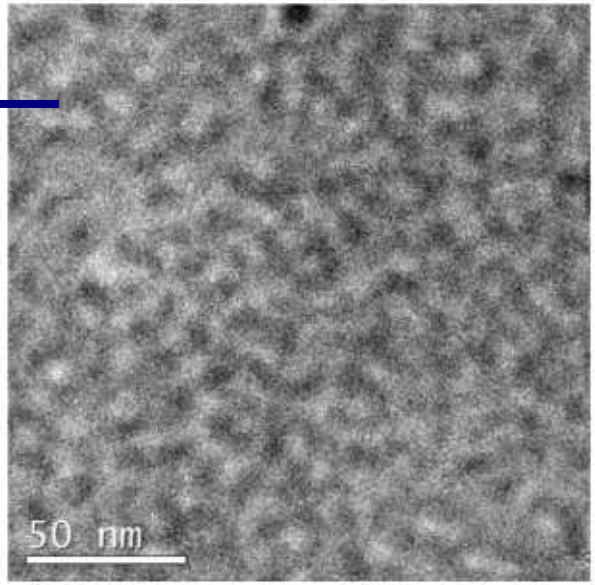


The **broad absorption** feature possibly due to the **random copolymer** structure of **P2** which combine the absorbance of **TPT** rich and **BT** rich structures



■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}^{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 strategy for low band gap: Donor-Acceptor polymers

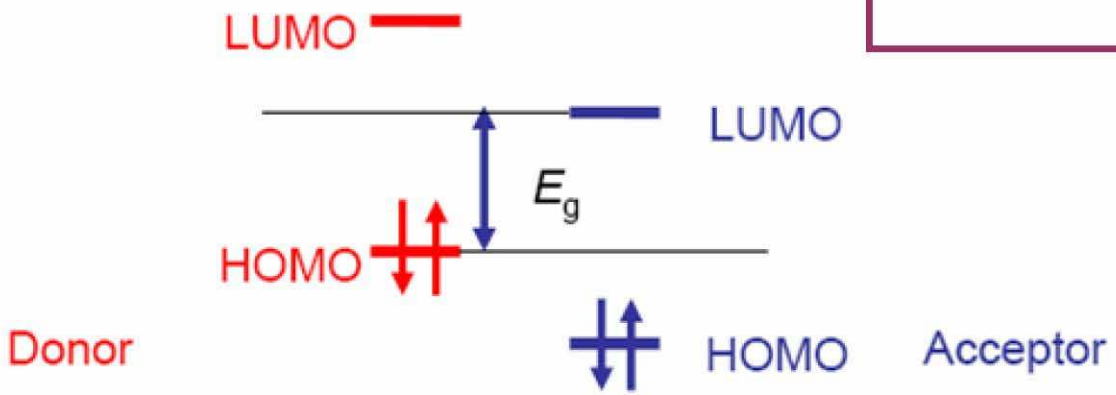
increase the double bond character of the single bonds:

–D–A–D–A–D–A– ⟷ $-D^{+}=A^{-}-D^{+}=A^{-}-D^{+}=A^{-}-$

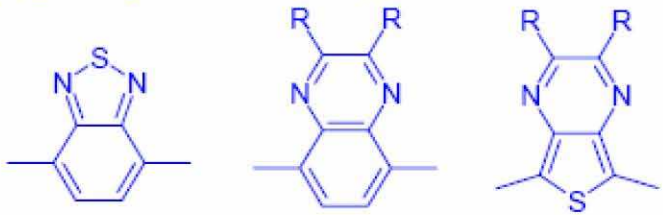
alignment of transition dipoles along the chain

$\overrightarrow{-D-A-D-A-D-A-}$

absorption from HOMO donor to LUMO acceptor



常見acceptor之化學結構：

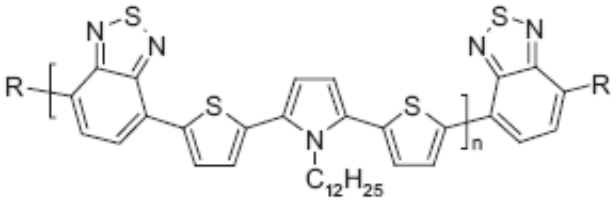


Acceptors

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

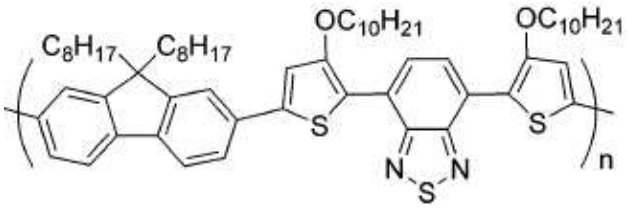
Copyright 2006 ITRI工業技術研究院

D-A Conjugated Alternating Polymers:PCBM Solar Cells



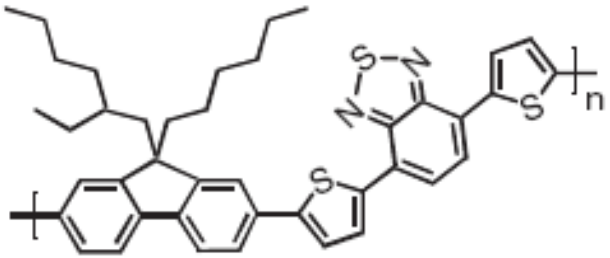
V_{oc} = 0.72 V FF = 0.37

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



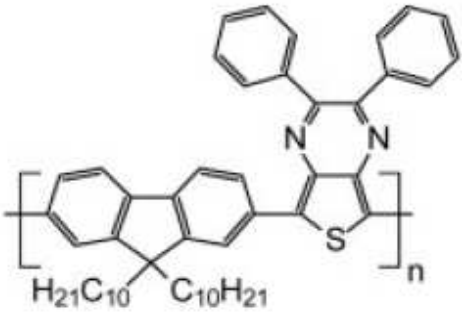
V_{oc} = 0.76 V FF = 0.49

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



V_{oc} = 0.72 V FF = 0.46

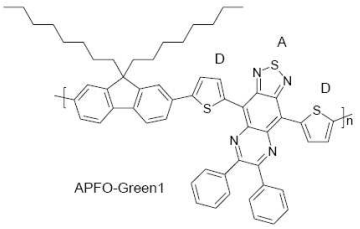
I_{sc} = 4.66 mA/cm^2 PCE = 2.2 %



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



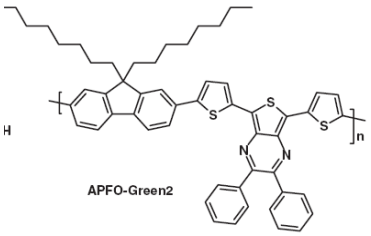
:PCBM

V_{oc} = 0.54 V

I_{sc} = 1.76 mA/cm^2

FF = 0.46

PCE = 0.3 %



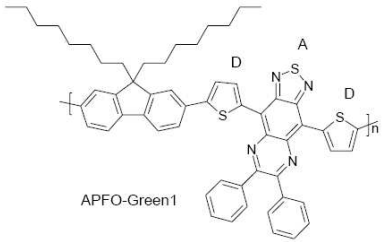
:PCBM

V_{oc} = 0.78 V

I_{sc} = 3 mA/cm^2

FF = N/A

PCE = 0.9 %



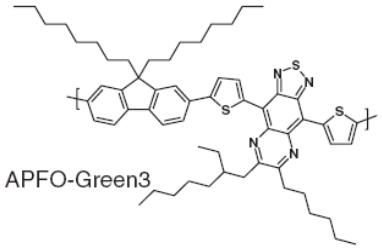
:C_{70}

V_{oc} = 0.58 V

I_{sc} = 3.4 mA/cm^2

FF = 0.35

PCE = 0.7 %



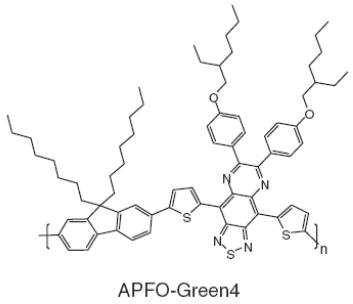
:C_{70}

V_{oc} = 0.61 V

I_{sc} = 2.4 mA/cm^2

FF = 0.40

PCE = 0.59 %



:C_{70}

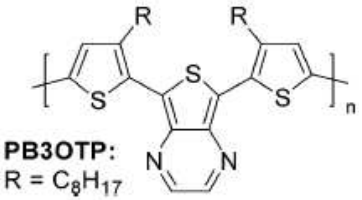
V_{oc} = 0.56 V

I_{sc} = 2.1 mA/cm^2

FF = 0.32

PCE = 0.37 %

D-A Conjugated Alternating Polymers:PCBM Solar Cells

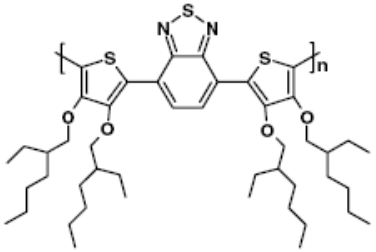


V_{oc} = 0.72 V

I_{sc} = 3.1 mA/cm^2

FF = 0.37

PCE = 1 %

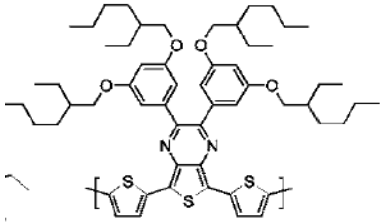


V_{oc} = 0.77 V

I_{sc} = 3.4 mA/cm^2

FF = 0.42

PCE = 0.2 %

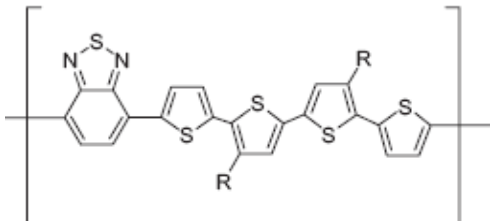


V_{oc} = 0.56 V

I_{sc} = 3.5 mA/cm^2

FF = 0.58

PCE = 1.1 %

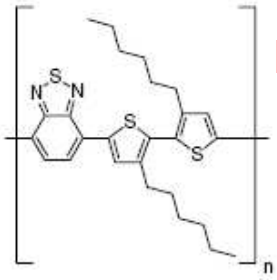


V_{oc} = 0.59 V

I_{sc} = 2.6 mA/cm^2

FF = 0.39

PCE = 0.6 %



V_{oc} = 0.61 V

I_{sc} = 0.2 mA/cm^2

FF = 0.24

PCE = 0.02 %

If the Eg is too small, it would induce the electron/hole recombination and lower PCE. Also, the HOMO/LUMO energy level matching is also important.

Importance of Polymer Morphology on Photovoltaic Efficiency

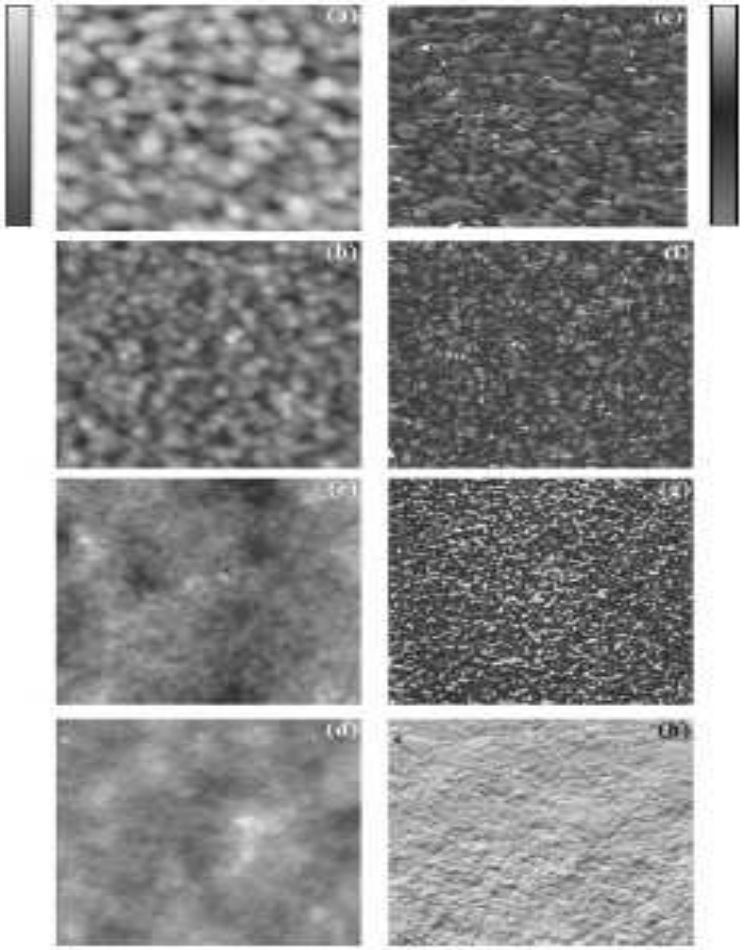
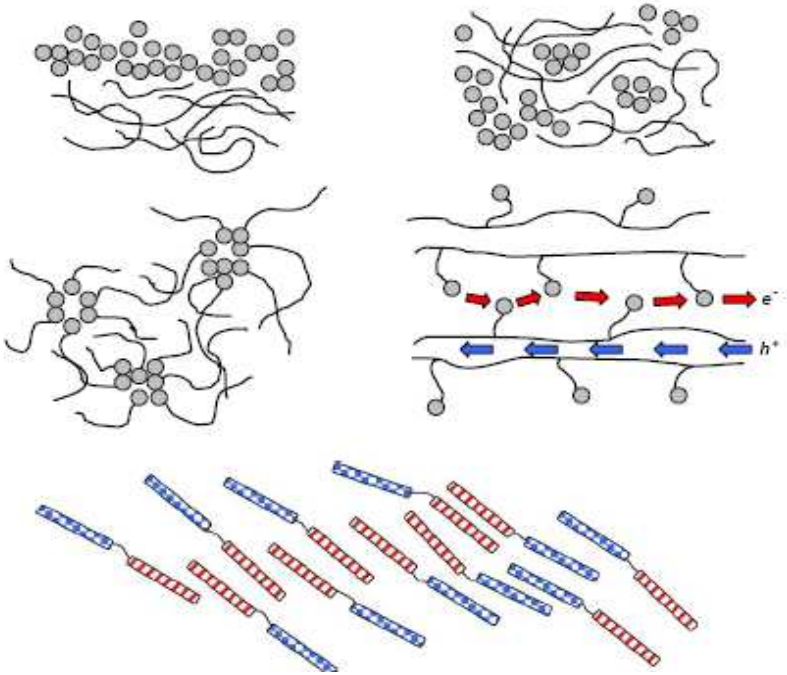


Figure 2. The AFM height (a–d) and simultaneously taken phase (e–h) images of the MDMO-PPV/PCBM composite films of 90 (a,e), 80 (b,f), 67 (c,g), and 50 wt.-% PCBM (d,h). Height bar (maximum peak-to-valley) represents 20 nm (a), 10 nm (b), 3 nm (c), and 3 nm (d). The size of the images is 2.0 μm × 2.0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



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*

Postproduction induced P3HT:PCBM solar cells

P3HT:PCBM solar cells

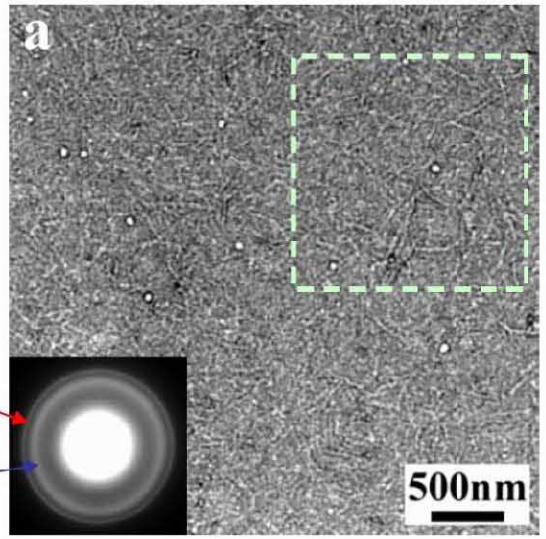
AM1.5 performance

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

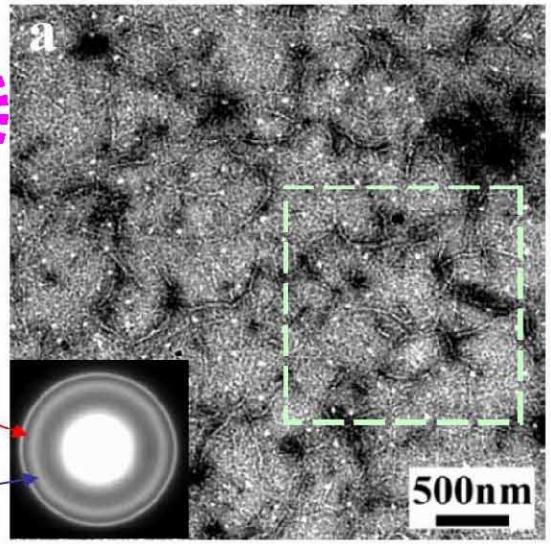
* measured at 80 mW/cm^2; ** at 85 mW/cm^2

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

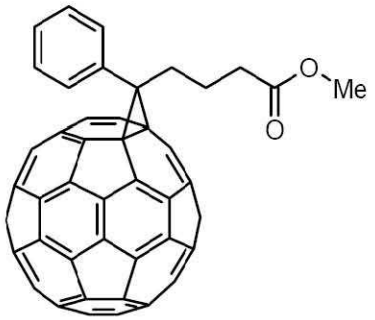


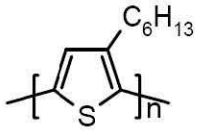
110 °C for
60 min



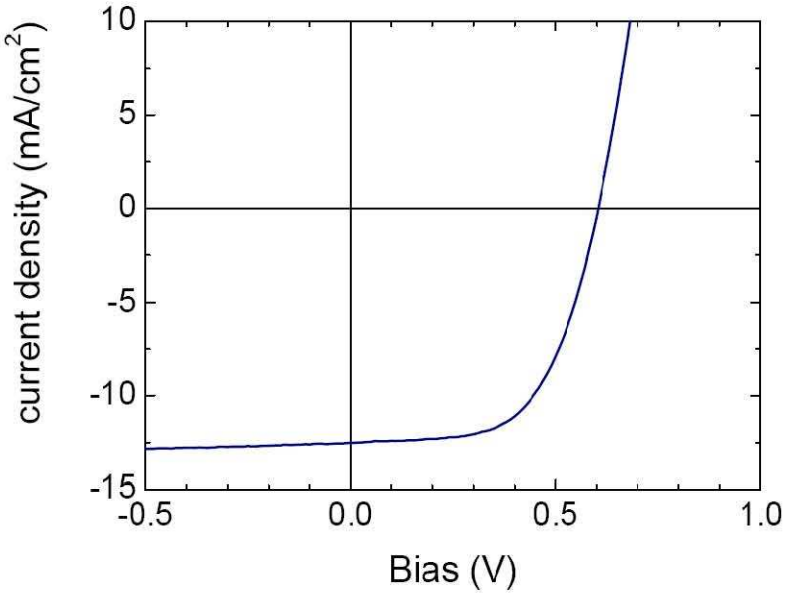
Copyright 2006 ITRI工業技術研究院

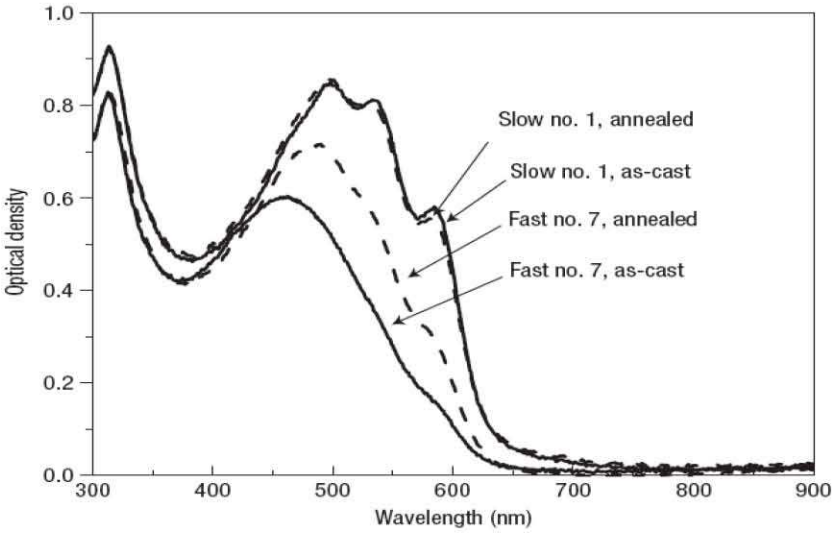
P3HT:PCBM solar cells via slow drying process

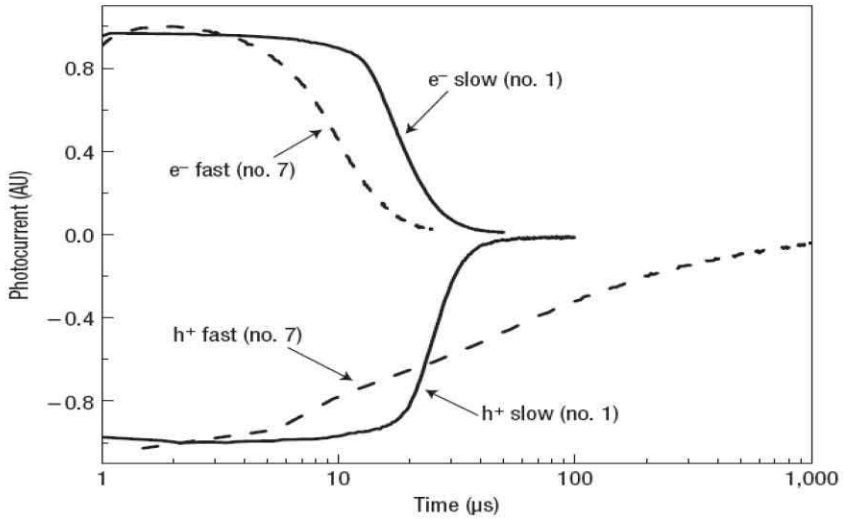




J_{SC}	V_{OC}	FF	EQE	η
12.50	0.604	0.594	66	4.5%



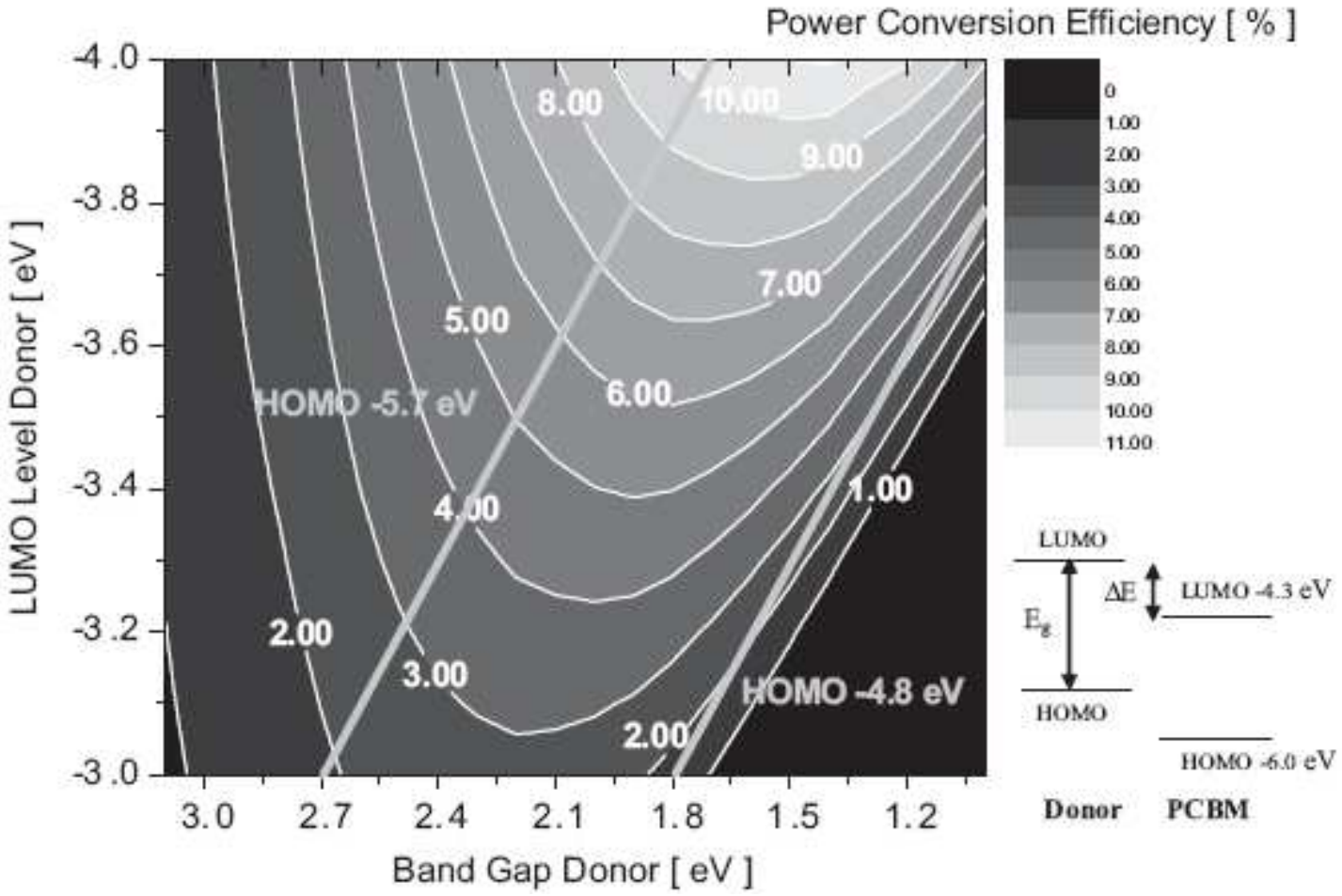




Yang Yang et al. Nature Mater. 2005, 4, 864.

Copyright 2006 ITRI工業技術研究院

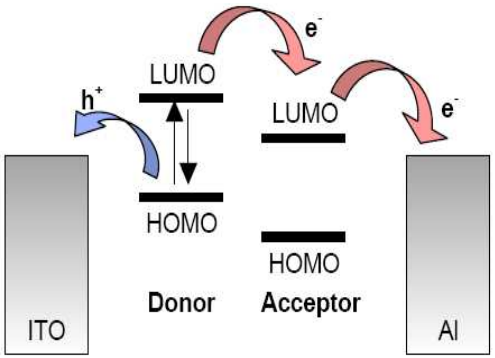
Design Rules for Donors in Solar Cell –Towards 10 % PCE

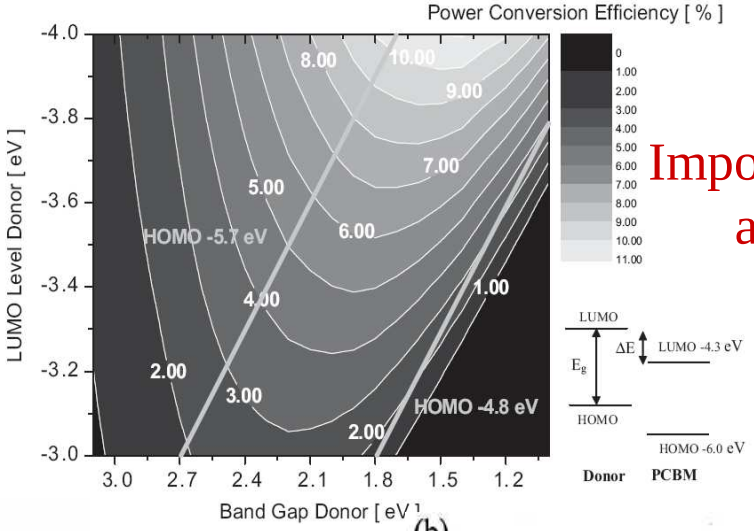


To get PCE >10%

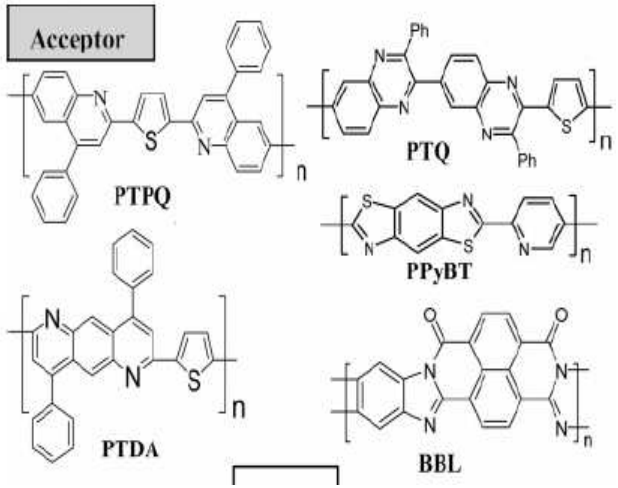
Bandgap of donor polymer < 1.74 eV & LUMO < -3.92 eV

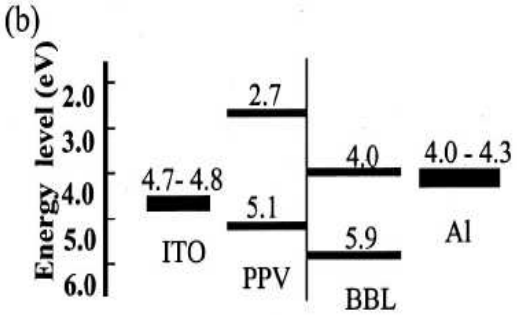
The importance of HOMO/LUMO level on the Photovoltaic Devices

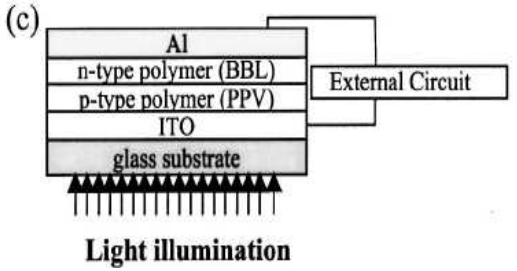




Importance of donor HOMO and acceptor LUMO

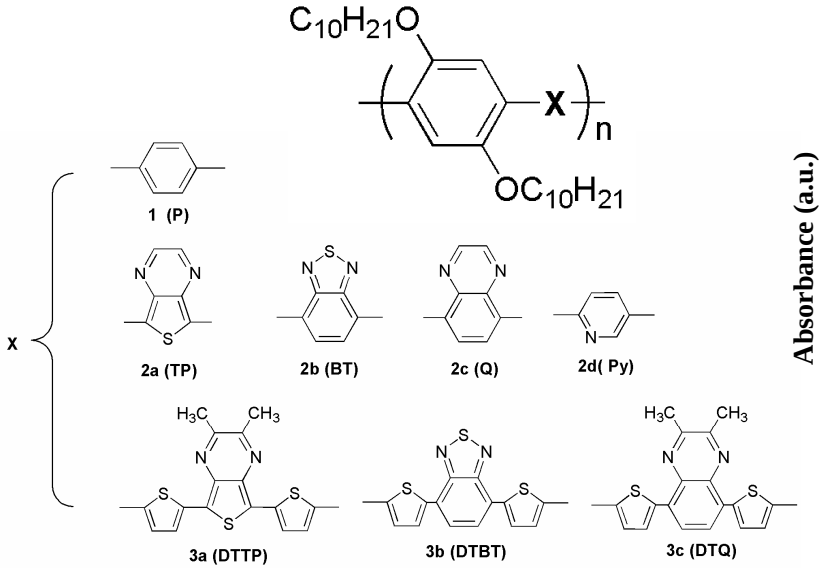


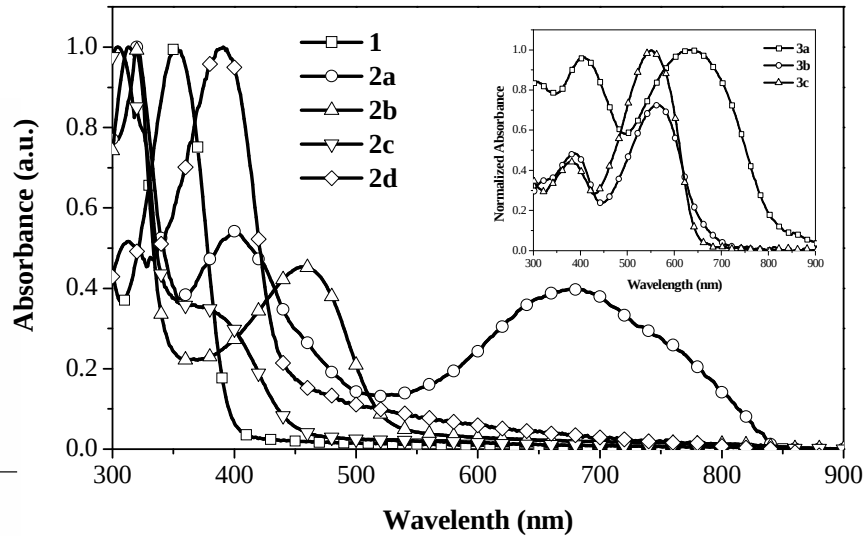




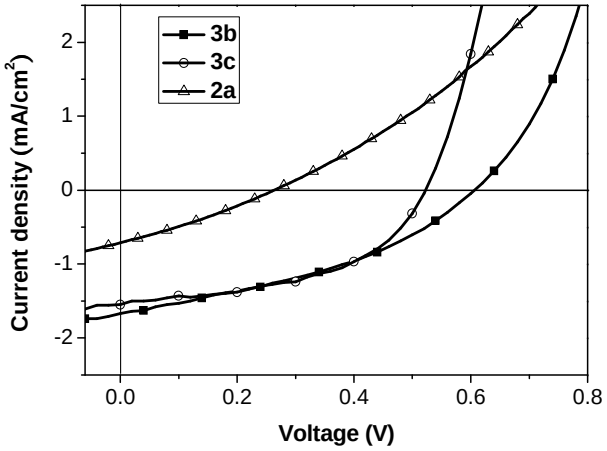
The EA of the PTPQ, PTQ, PPyBT, and PTDA: 2.7~3.0 eV, mismatch with Al→ poor PV efficiency

Didecyloxyphenylene-Acceptor Alternating Conjugated Polymers (solar cell eff.~0.4%)





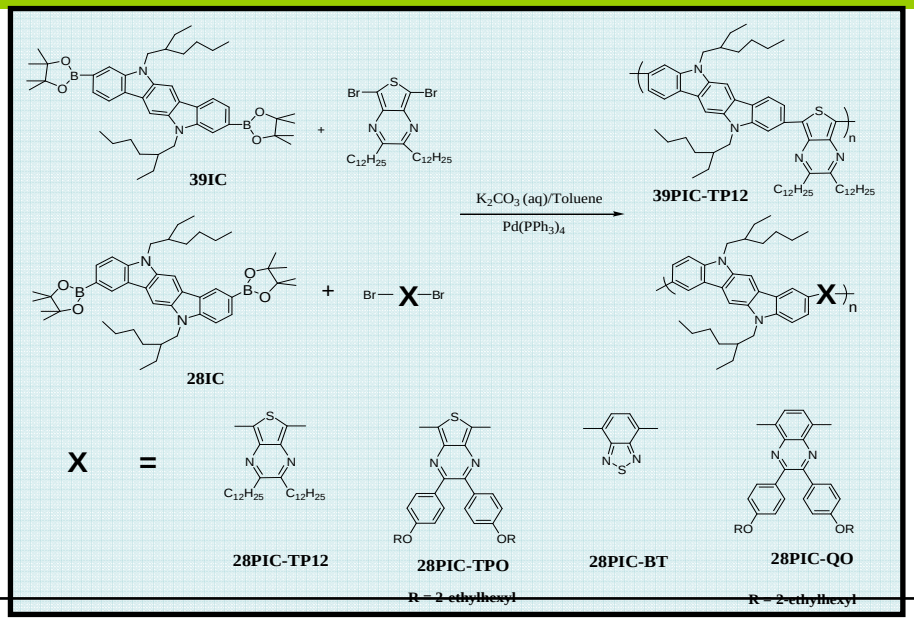
Order of Eg : POC10-P < POC10-Q < POC10-Py < POC10-BT < POC10-TP (intramolecular charge transfer), 3b> 2b, 3c>2c: backbone planarity



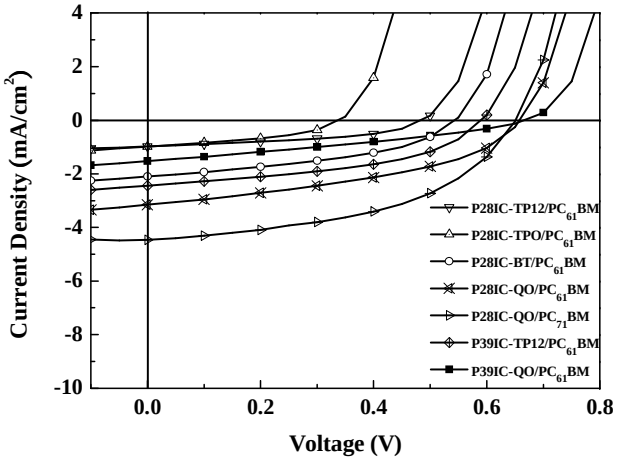
Polymers	$\lambda_{max}^{abs,\ film}$ (nm)	Mobility ($cm^2V^{-1}s^{-1}$)	On/off
DP/TP	401,678	1.89×10^{-3}	82
DP/DTTP	410, 638	1.41×10^{-5}	36
DP/DTBT	413, 618	1.92×10^{-4}	604
DP/DTQ	381, 549	2.10×10^{-3}	3600

Chen and Jenekhe, *Macromolecules*, 2008

Indolocarbazole-Acceptor Alternating Conjugated Polymers (Solar Cell Eff.~1.40%)



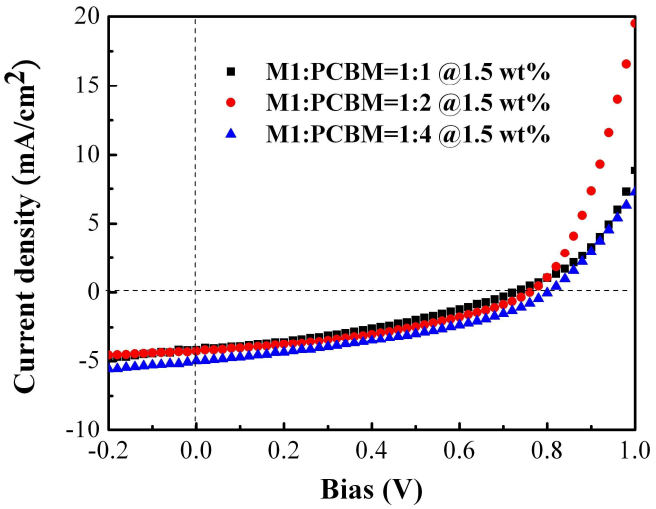
Macromolecules 2009, vol.42, 1897.



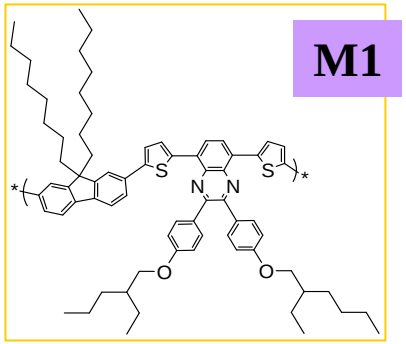
	TFT-**Pristine polymer**		Solar Cell-**Polymer/PCBM (1:4)**			
polymer	**Mobility** ($cm^2V^{-1}s^{-1}$)	**On/Off** (–)	**Jsc** (mA/cm^2)	***Voc*** (V)	**FF** (%)	**PCE[b]** (%)
P28IC-TP12	**$4.04x10^{-4}$**	**236**	**0.98**	**0.49**	**0.45**	**0.22**
P28IC-TPO	**$5.50x10^{-5}$**	**40**	**0.98**	**0.35**	**0.41**	**0.14**
P28IC-BT	**$1.93x10^{-4}$**	**30900**	**2.11**	**0.55**	**0.42**	**0.49**
P28IC-QO	**$1.89x10^{-4}$**	**46900**	**3.15 (4.46)[a]**	**0.66 (0.65)[a]**	**0.42 (0.48)[a]**	**0.87 (1.40)[a]**
P39IC-TP12	**$2.42x10^{-4}$**	**1180**	**2.45**	**0.60**	**0.45**	**0.66**
P39IC-QO	**$1.66x10^{-5}$**	**50**	**1.53**	**0.67**	**0.32**	**0.32**

NewQuinoxaline based Donor-Acceptor Conjugated PolymersFor Optoelectronic Applications

Highest Solar Cell PCE :1.76%

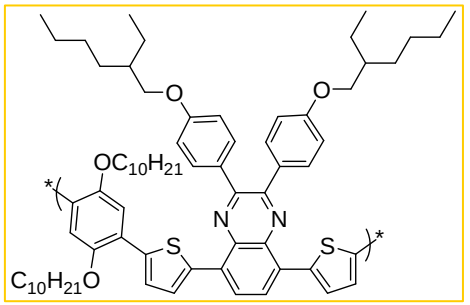


J. Polym. Sci. Polym. Chem. **2009**,
Through the collaboration of
W. C. Chen and F. C. Chen



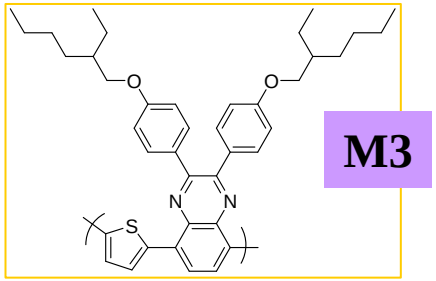
M_n=22308 PDI=2.38

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



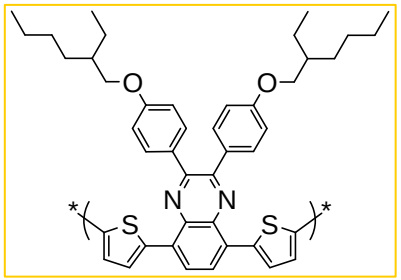
M_n=8590 PDI=1.67

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

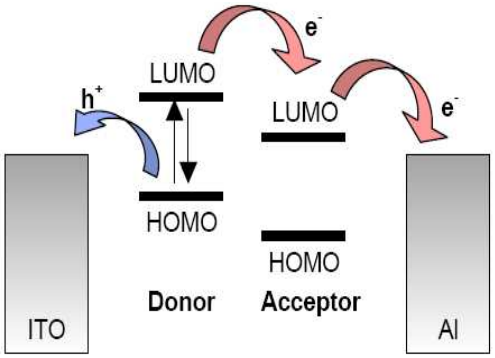
HOMO= -5.06 eV
LUMO= -3.36 eV
Mobility 9.25×10^{-4}
On/off 2.3×10^{4}

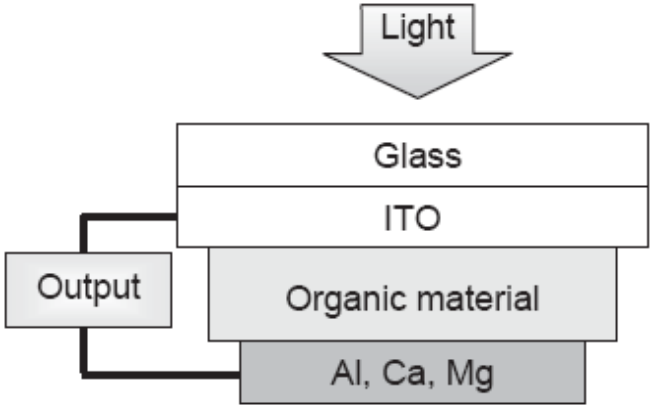


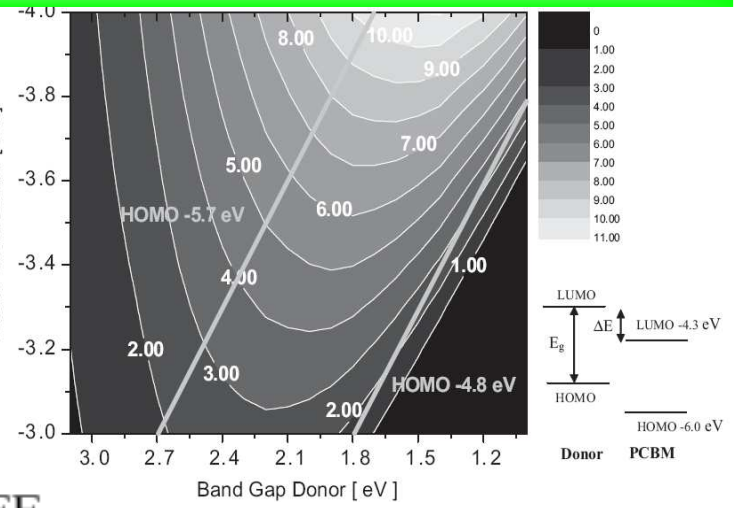
Mn=8450 PDI=1.76

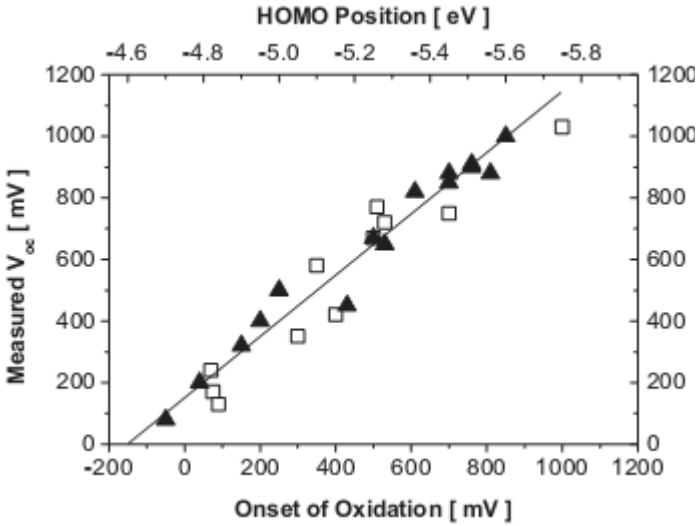
HOMO= -5.06 eV
LUMO= -3.19 eV
Mobility 2.52×10^{-4}
On/off 2.00×10^{4}

The importance of HOMO/LUMO level on the Photovoltaic Devices

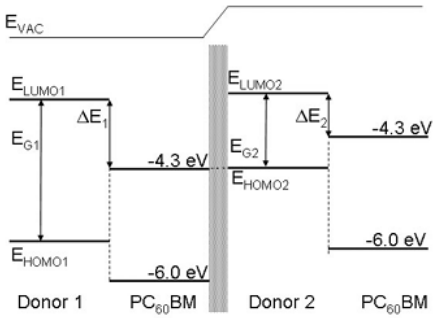




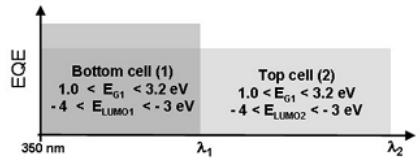




$$\eta_e = \frac{I_{mpp} V_{mpp}}{P_{in}} = \frac{I_{sc} V_{oc} FF}{P_{in}}$$



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



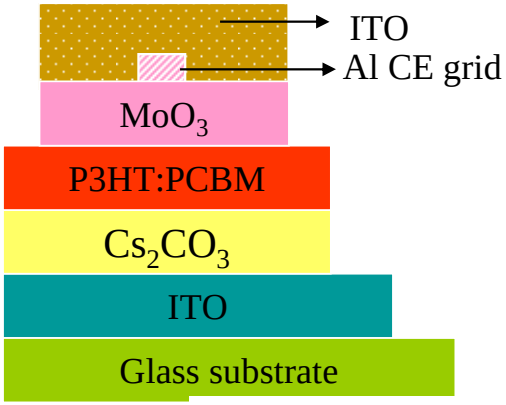
Scharber et al., Adv. Mater. 2006, 18, 789

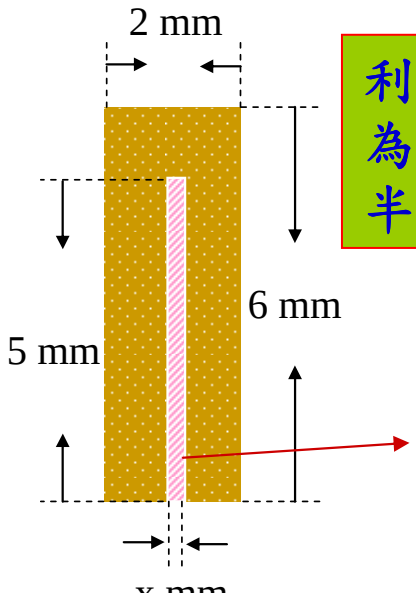
Theoretical PCE ~10% in a single

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**

Inverted semi-tranparent OPVs

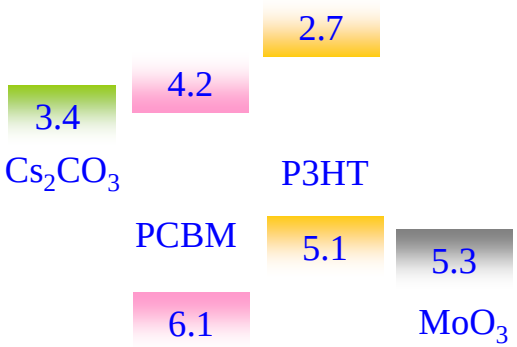




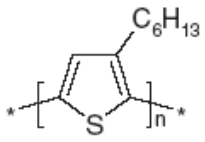
利用 ITO/Cs_2CO_3 以及 MoO_3/ITO 作為透明電極，發展高效率之倒置式半透明元件

Shadow fraction:

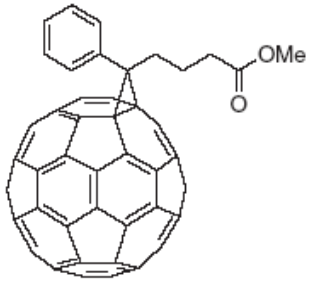
5%, 10%, 15%



Energy levels



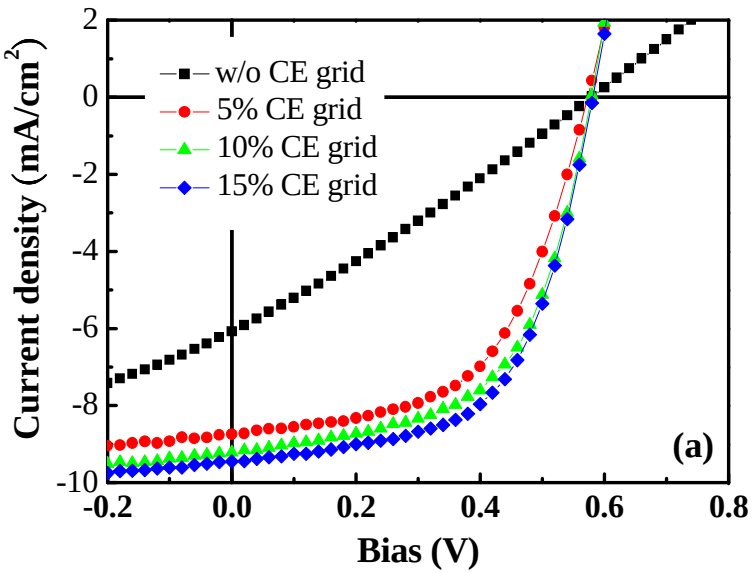
P3HT

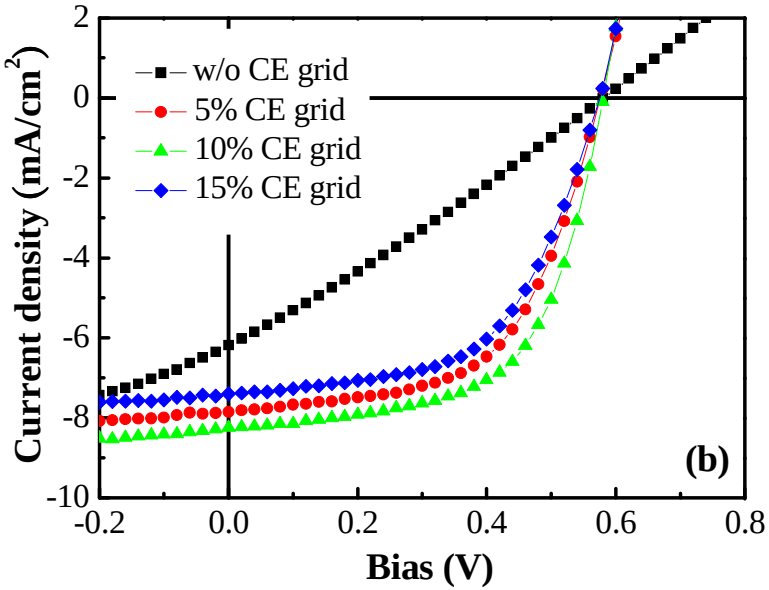


PCBM

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

J-V characteristics





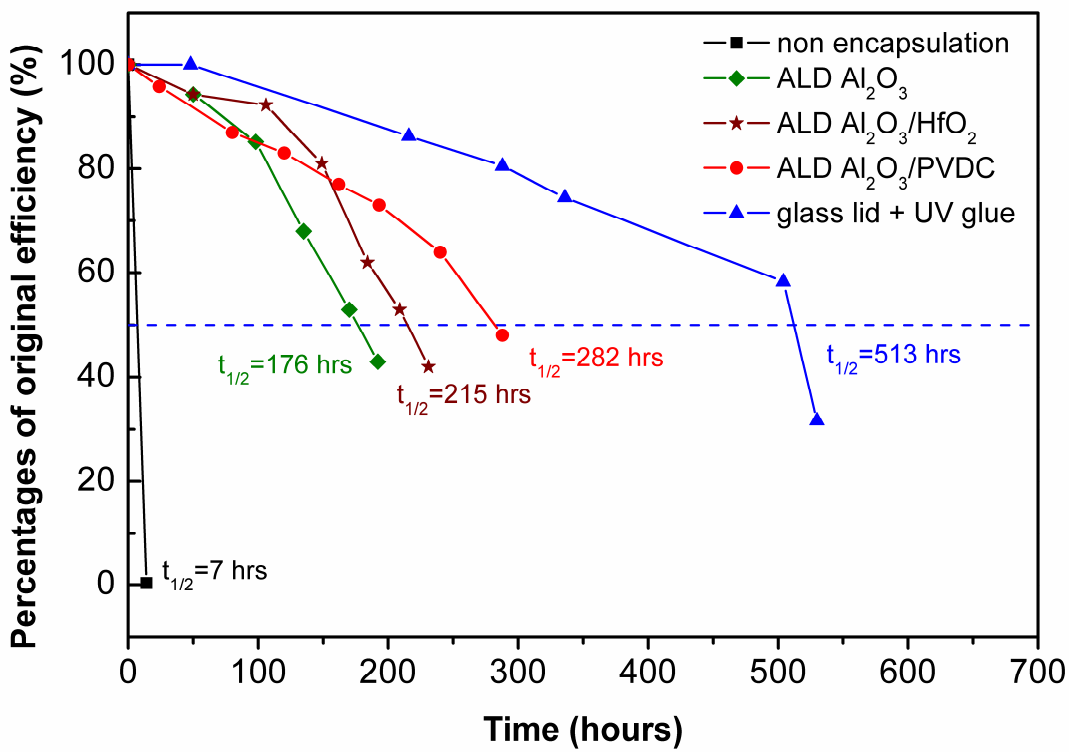
Bottom-illuminated

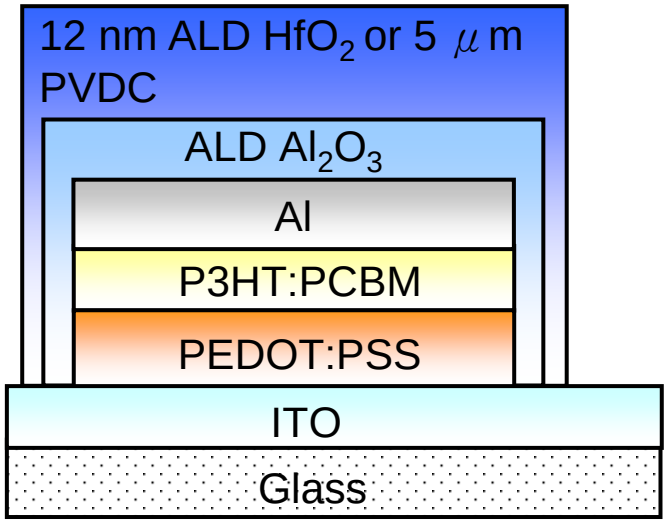
Top-illuminated

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**