

OPEL International Symposium 2012

Approaches to Achieve High Efficiency and Long-term Stability of Polymer Solar Cells

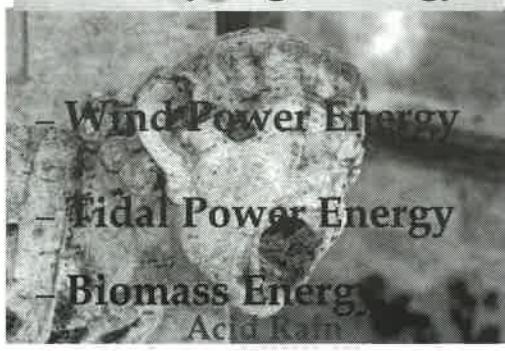
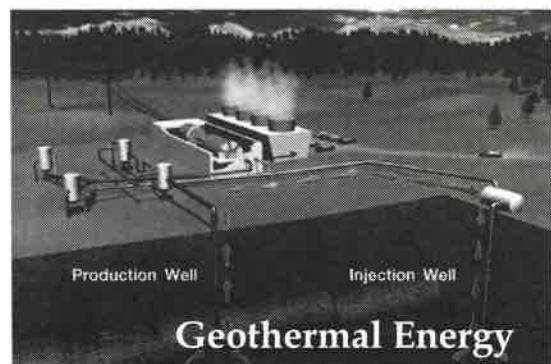
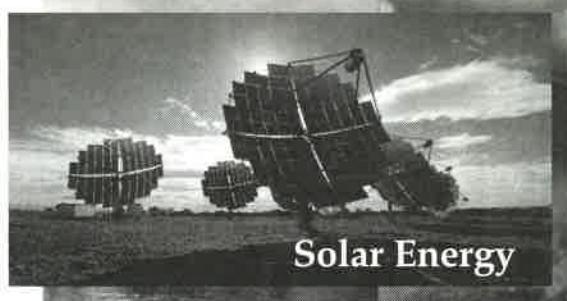
Won Ho Jo

*Department of Materials Science and Engineering
Seoul National University*

January 26, 2012

Why is the Solar Cell for Future?

Renewable Energy Resources



World Energy Consumption:

2010: 13 TW → 2050: more than 30 TW

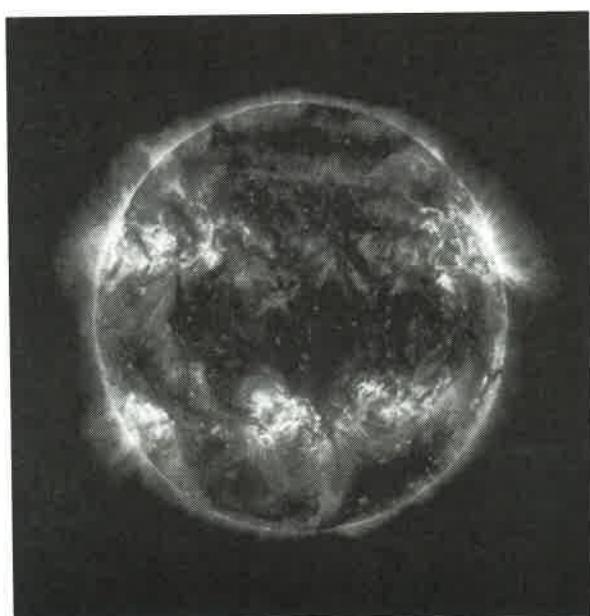


Seoul, Korea

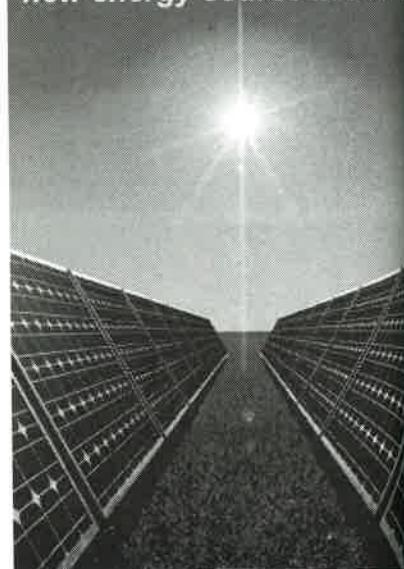
World Energy Consumption:

2010: 13 TW → 2050: more than 30 TW

Solar Energy: more than 120,000 TW



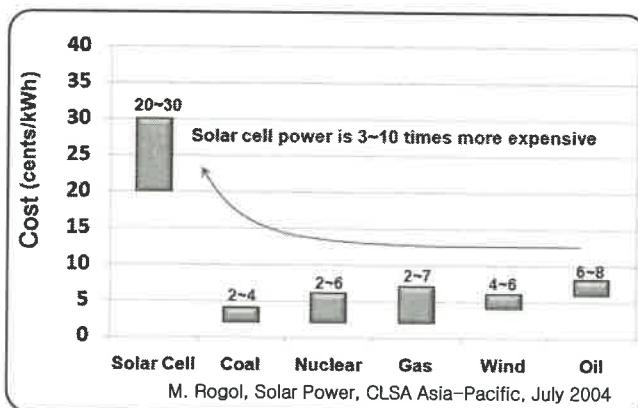
new energy source in future



Silicon or Inorganic-based Solar Cells

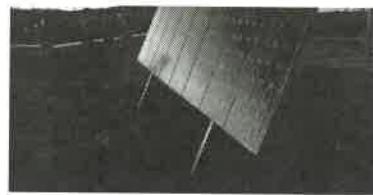
✓ Advantages

- Totally silent at work
- Long lifetime
- Little maintenance
- Low operating costs
- High conversion efficiency



✓ Disadvantages

- High cost of production
- Difficulty in processing
- Limitation of mass production

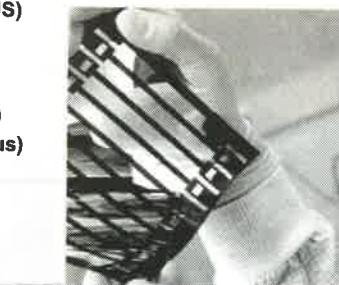


Polymer-based Solar Cell

✓ Advantages

- Inexpensive
- Large area coating

Classification	World's best efficiency	Module price	Best efficiency (Maker)	SS
Single crystal Si	24.7%	3.0 \$/W	UNSW (Aus.) BP, SunPower	modules
Amorphous Si	13.0%	2.0 \$/W	Astro Power (US) Kaneka (JP)	
Dye-Sensitized	11.0%	0.8 \$/W	EPFL (Swiss) Toyoda, STI (Aus)	
Polymer	8.4%	0.5 \$/W	U. Chicago/ UCLA (US)	



✓ Disadvantages

- []
- []
- []

Stability/Durability

- Thermal stability
- Chemical stability
- Photo stability

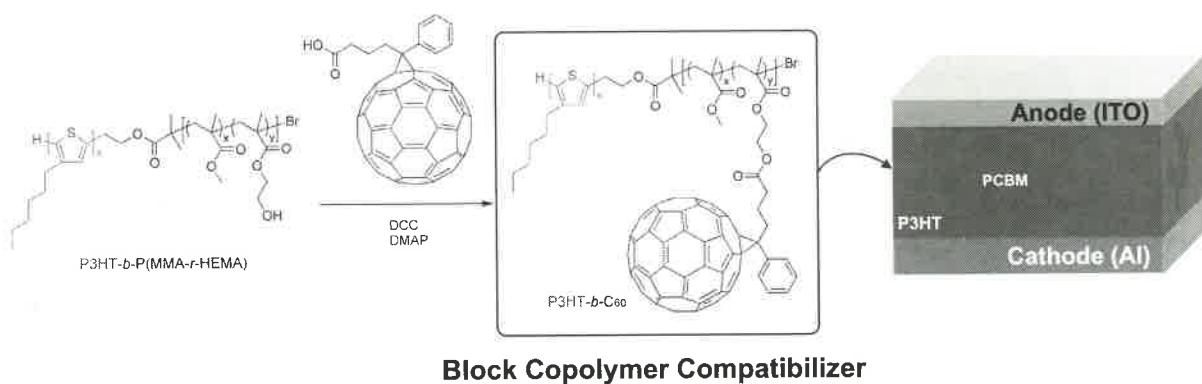
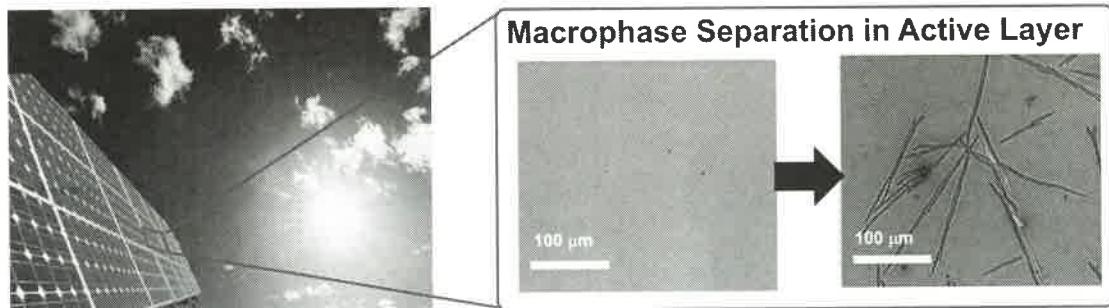
J. Mater. Chem. **2009**, *19*, 1483
Nanotechnology **2010**, *21*, 105201
J. Mater. Chem. **2010**, *20*, 3287
J. Mater. Chem. **2011**, *21*, 17209

Efficiency

- Low bandgap polymer
- Control of HOMO/LUMO levels
- Morphology control
- Interface engineering
- Fabrication method

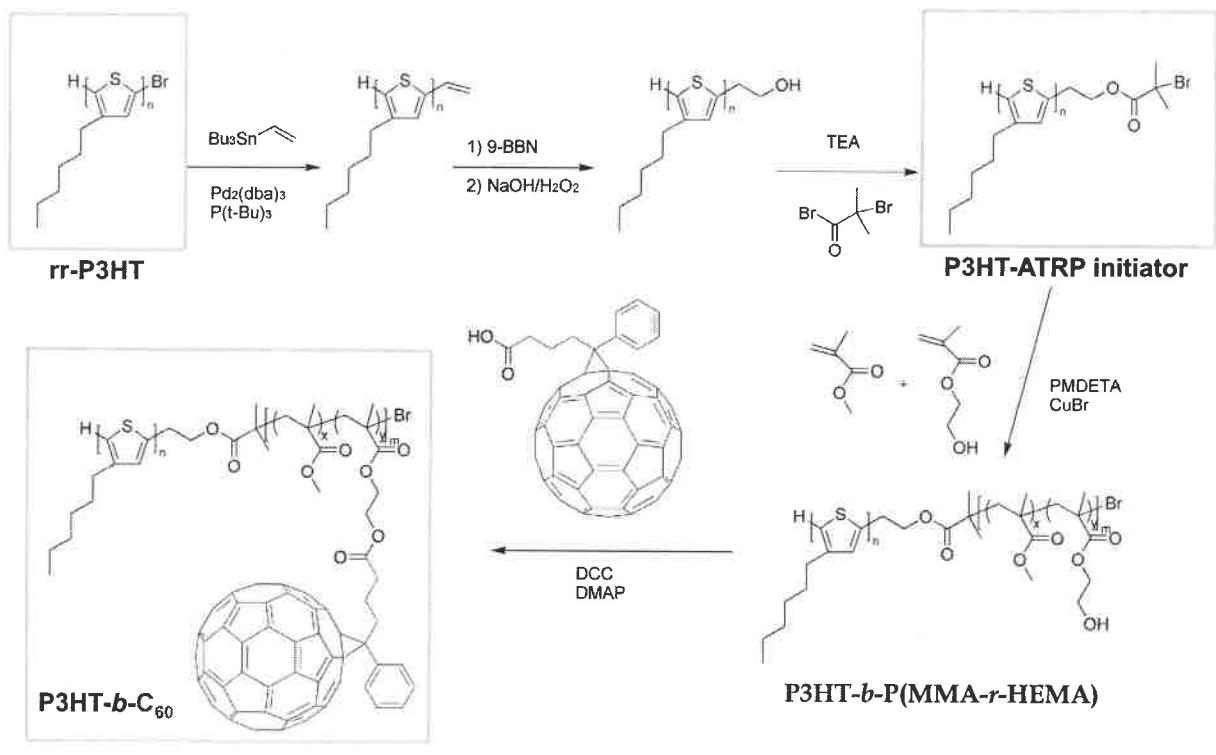
Adv. Funct. Mater. **2010**, *20*, 3287
J. Phys. Chem. C **2010**, *114*, 633
Sol Ener. Mater. Sol Cell. **2010**, *94*, 1118
J. Mater. Chem. **2011**, *21*, 8583
Adv. Mater. **2011**, *23*, 1782

Stability of Polymer Solar Cells



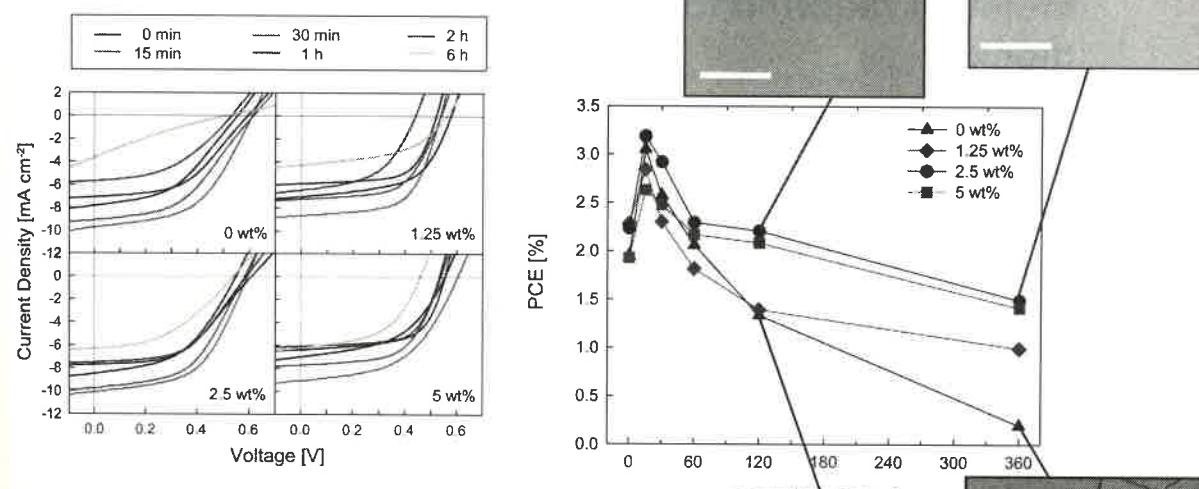
Synthesis of P3HT-*b*-C₆₀ Diblock Copolymer

J. Mater. Chem. 2009, 19, 1483.



Long-term Thermal Stability

Power Conversion Efficiency

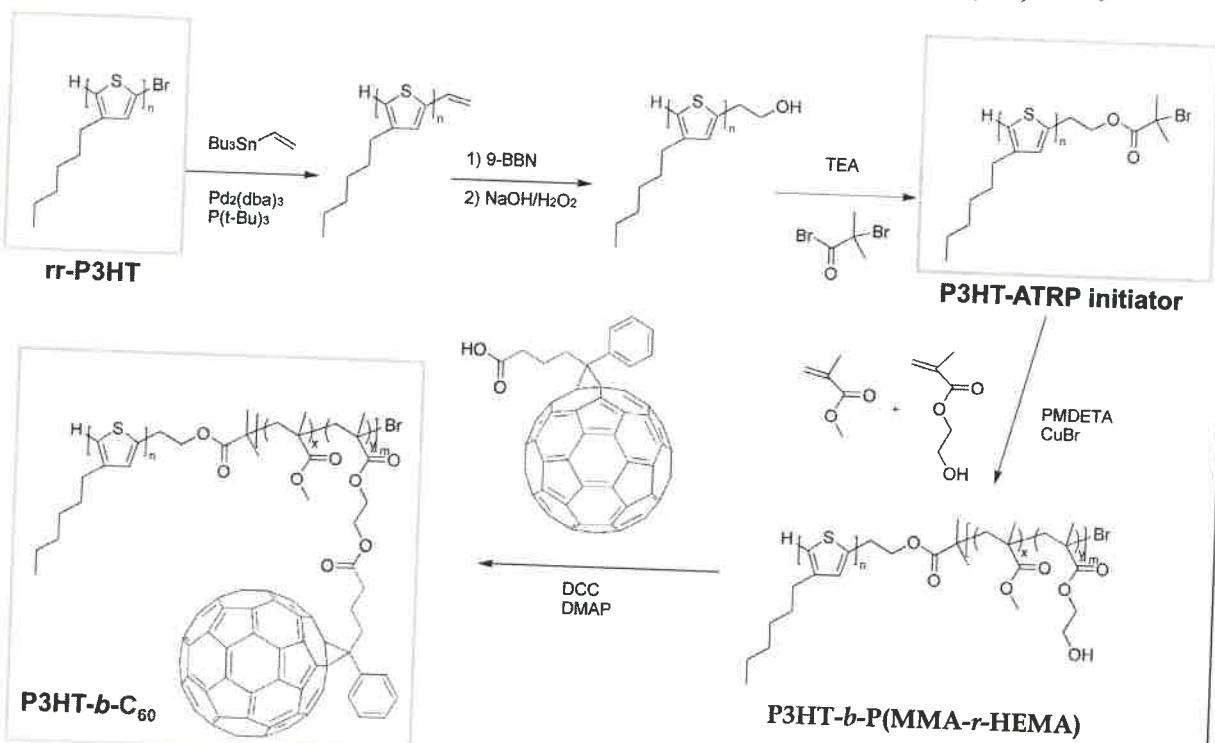


Experimental Conditions:

- P3HT:PCBM blend ratio = 1:1
- Active layer thickness = 150 nm
- Annealing Temperature = 150 °C

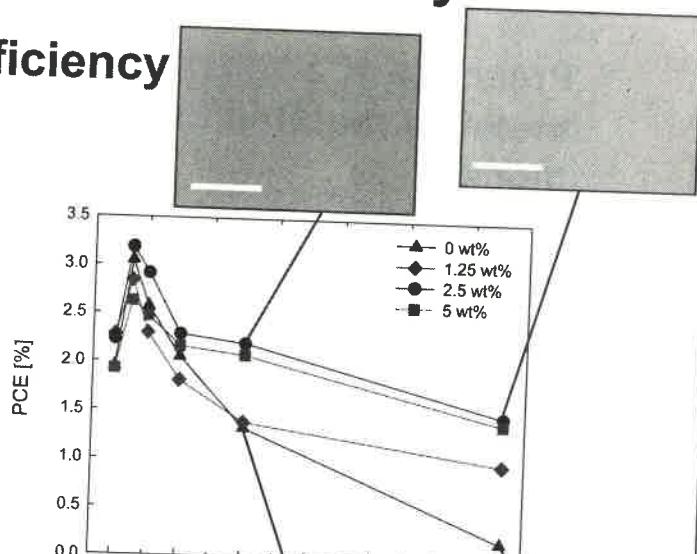
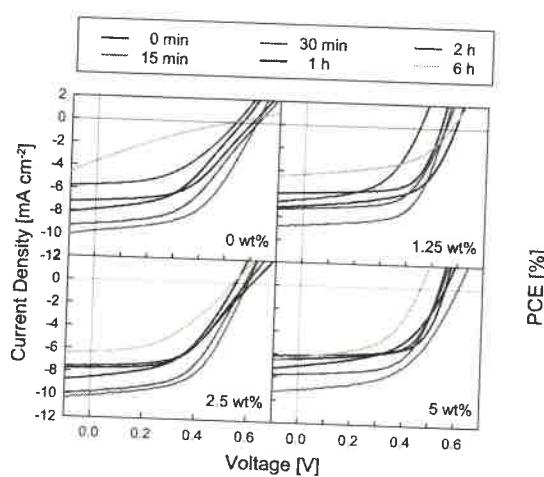
Synthesis of P3HT-*b*-C₆₀ Diblock Copolymer

J. Mater. Chem. 2009, 19, 1483.



Long-term Thermal Stability

Power Conversion Efficiency



Experimental Conditions:

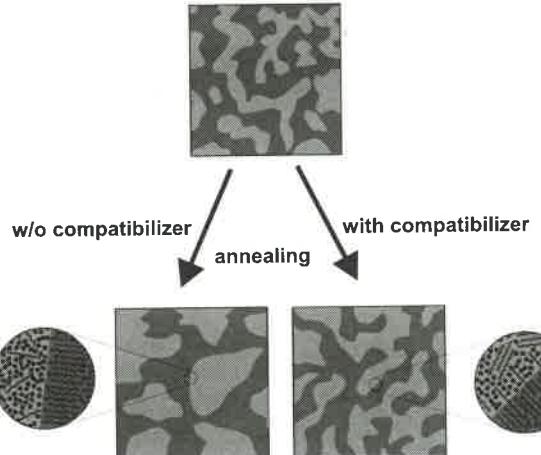
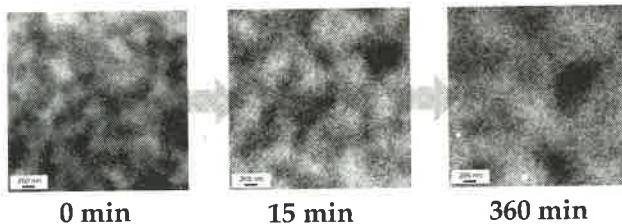
- P3HT:PCBM blend ratio = 1:1
- Active layer thickness = 150 nm
- Annealing Temperature = 150 °C

Block Copolymer as Compatibilizer

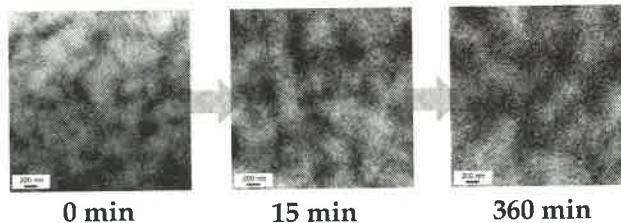
Nanotechnology 2010, 21, 105201.

Morphology of Active Layer

P3HT/PCBM



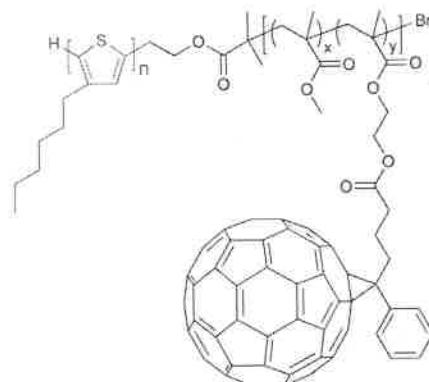
P3HT/PCBM/P3HT-*b*-C₆₀(2.5 wt%)



- Development of nanometer scale phase separation of active layer
- Enhancement of long-term stability of solar cell performance

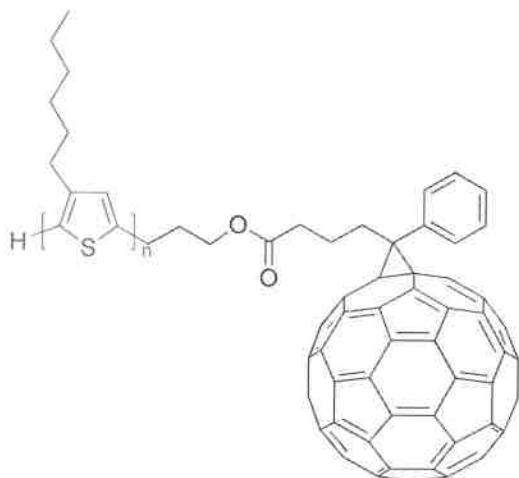
Problems of Block Copolymer Compatibilizer

- Presence of a substantial amount of insulating moieties required for introducing C₆₀ in the second block
- Synthetic difficulty due to the multiple post-polymerization steps



New strategy: Synthesis of C₆₀-end capped P3HT

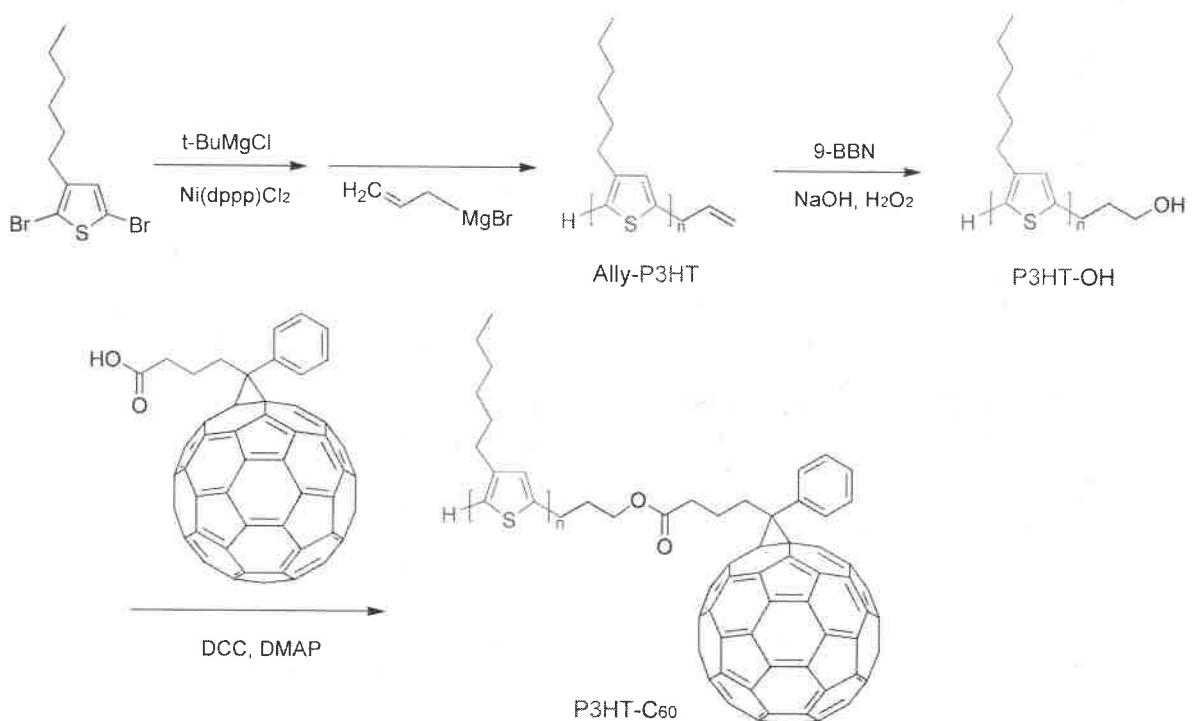
P3HT as the electron donor



Fullerene as the electron acceptor

Synthesis of C₆₀-end Capped P3HT

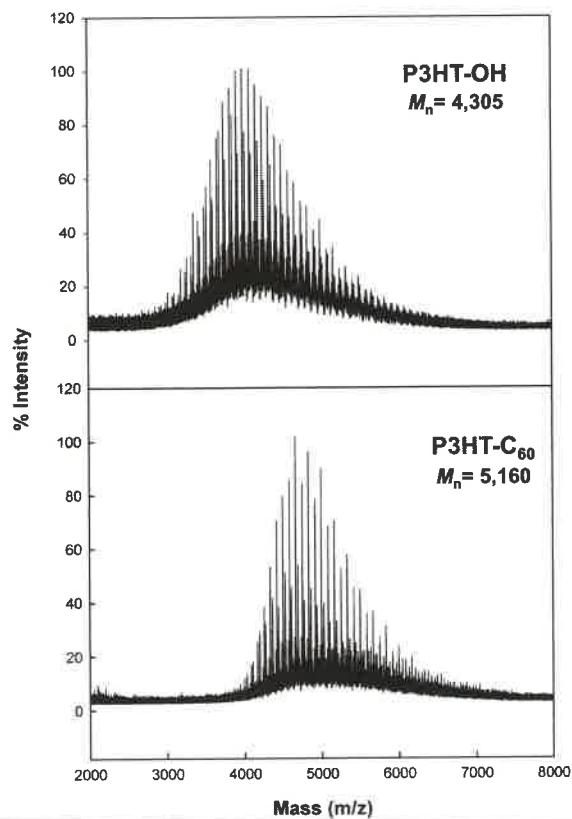
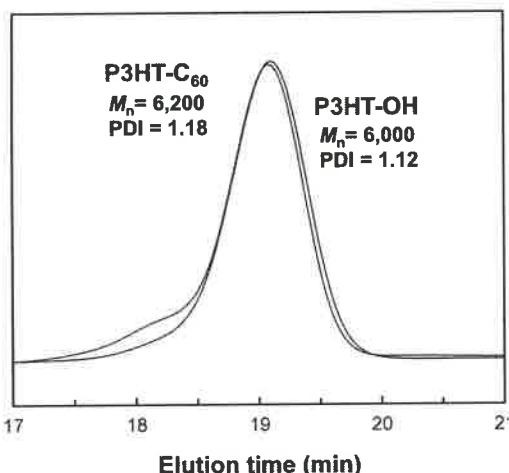
J. Mater. Chem. **2010**, *20*, 3287.



Synthesis of C₆₀-end capped P3HT

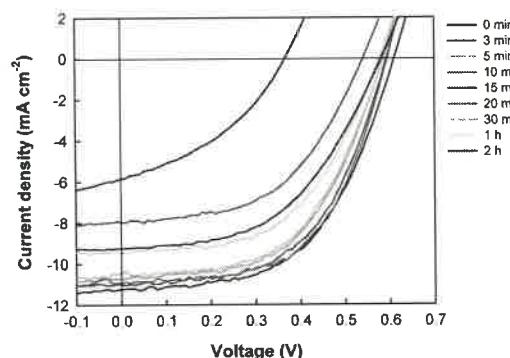
GPC/Mass Analysis

Detector response (a.u.)



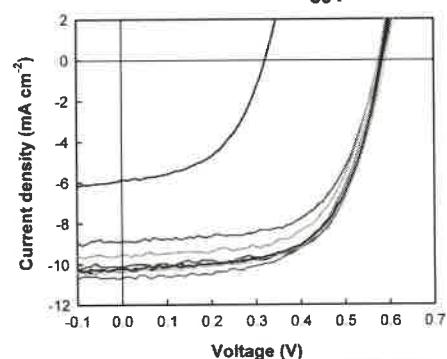
Device Performance and Stability

P3HT/PCBM



Annealing time (min)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	η (%)
0	0.37	5.85	0.38	0.83
3	0.54	7.96	0.51	2.19
5	0.59	10.73	0.54	3.42
10	0.59	11.00	0.55	3.57
15	0.61	11.25	0.56	3.88
20	0.60	10.92	0.56	3.67
30	0.59	10.45	0.54	3.30
60	0.58	9.44	0.52	2.85
120	0.58	9.24	0.50	2.68

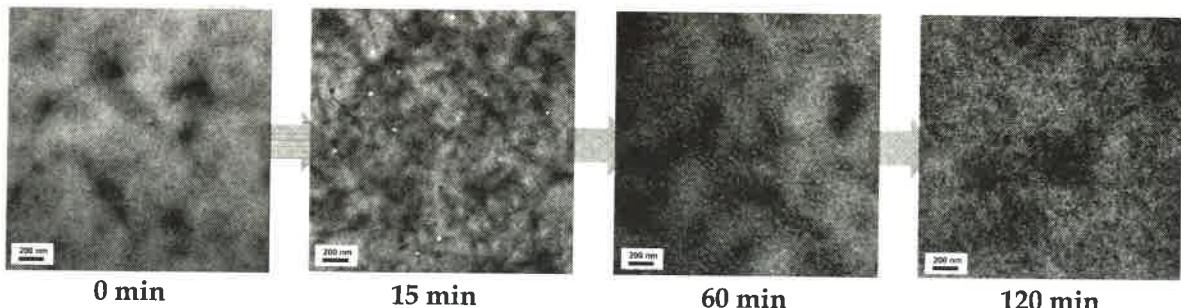
P3HT/PCBM/P3HT-C₆₀(2.5 wt%)



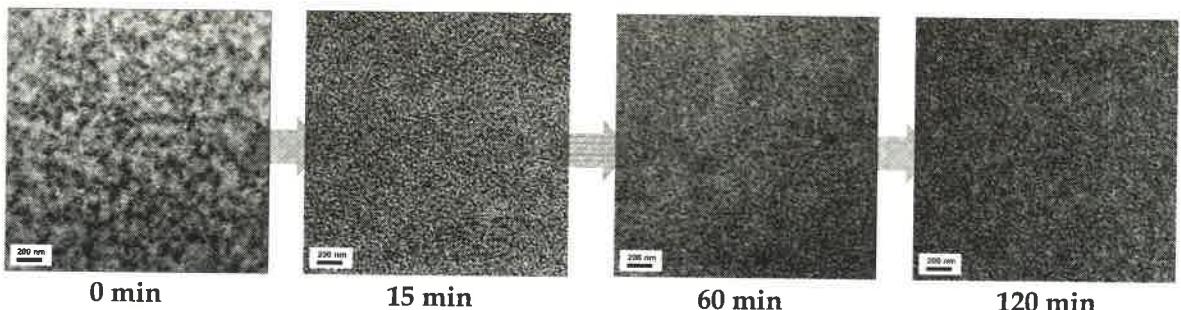
Annealing time (min)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	η (%)
0	0.32	5.85	0.51	0.95
3	0.58	8.87	0.61	3.14
5	0.58	9.53	0.61	3.37
10	0.58	10.12	0.64	3.76
15	0.58	10.25	0.61	3.63
20	0.59	10.66	0.59	3.71
30	0.59	10.39	0.61	3.74
60	0.58	10.26	0.62	3.69
120	0.58	10.18	0.61	3.60

Morphology TEM Image

P3HT/PCBM



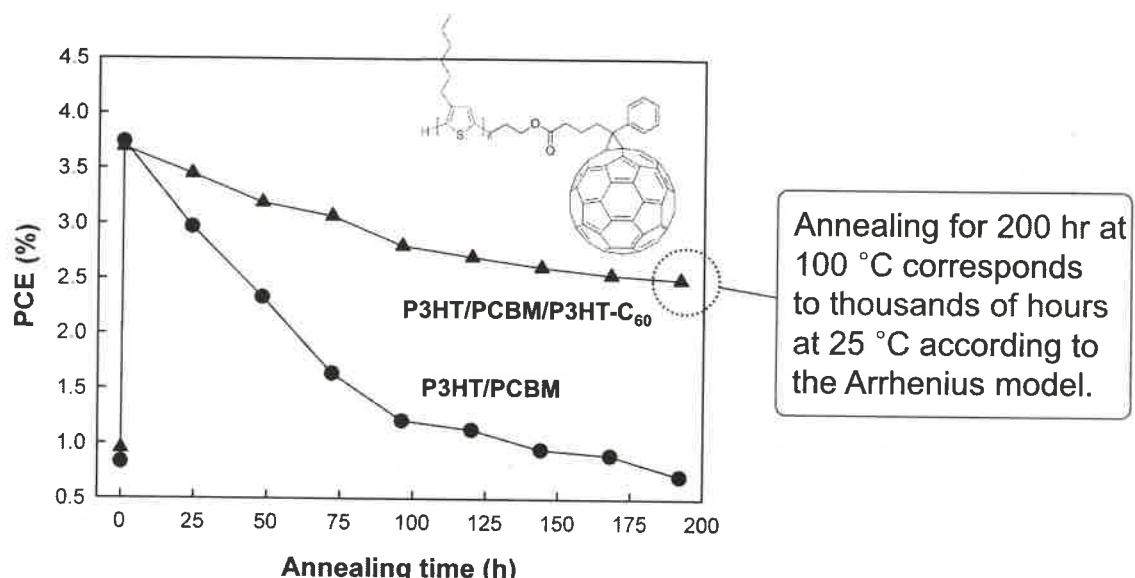
P3HT/PCBM/P3HT-C₆₀(2.5 wt%)



Long-term Thermal Stability

Accelerated Lifetime Measurements

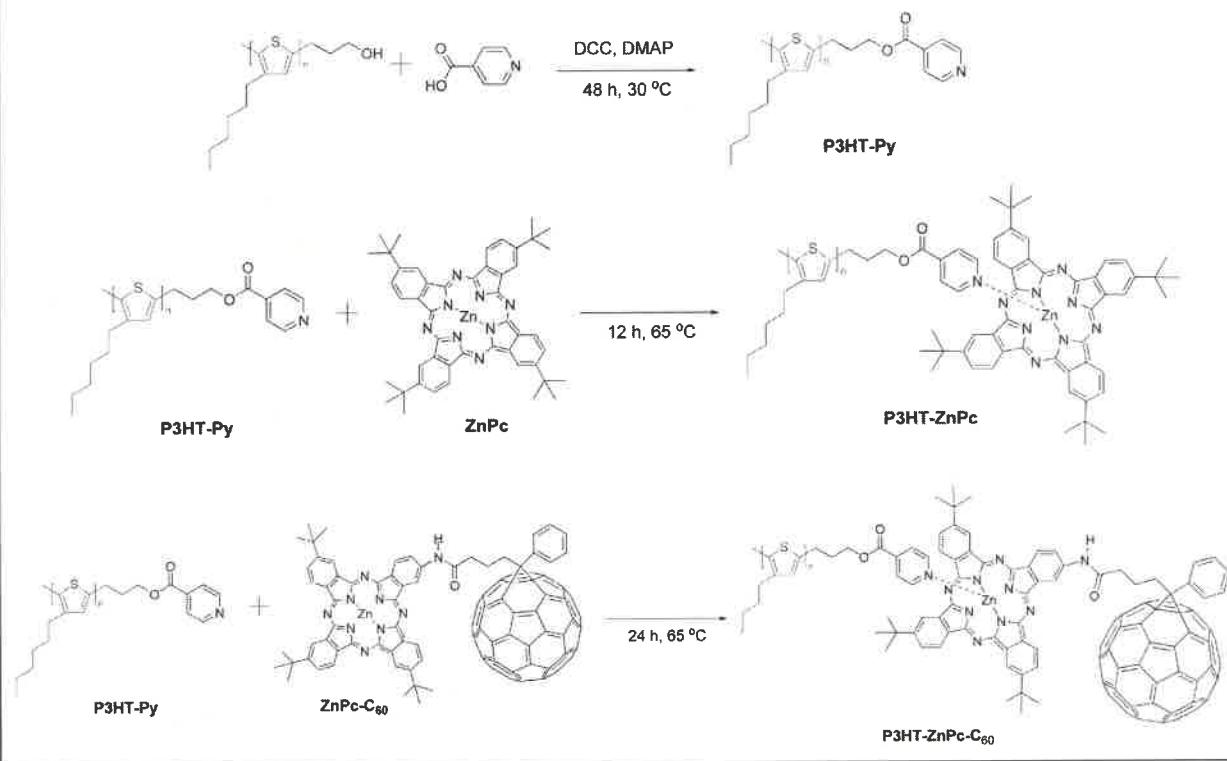
Annealing Temperature: 100 °C



J. Mater. Chem. 2010, 20, 3287.

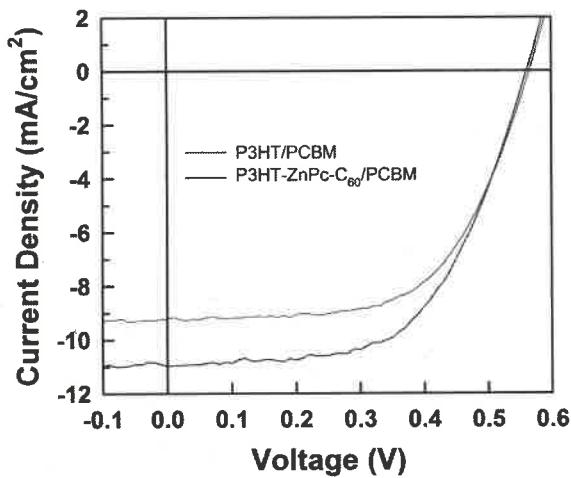
P3HT-Dye-C₆₀

J. Mater. Chem. **2011**, *21*, 17209.

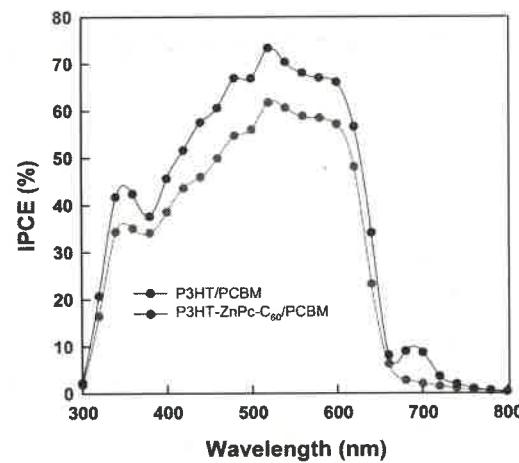


Morphology Control and Device Optimization

J-V Curves



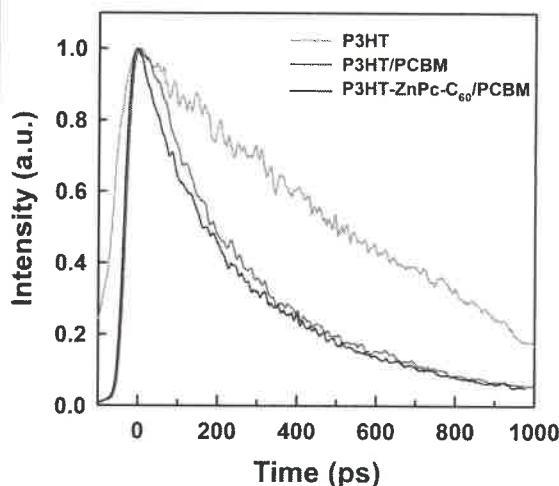
IPCE Spectra



Device	Voc (V)	Jsc (mA/cm ²)	FF (%)	PCE (%)
P3HT/PCBM	0.56	9.22	0.61	3.15
P3HT-ZnPc-C ₆₀ /PCBM	0.56	10.96	0.58	3.56

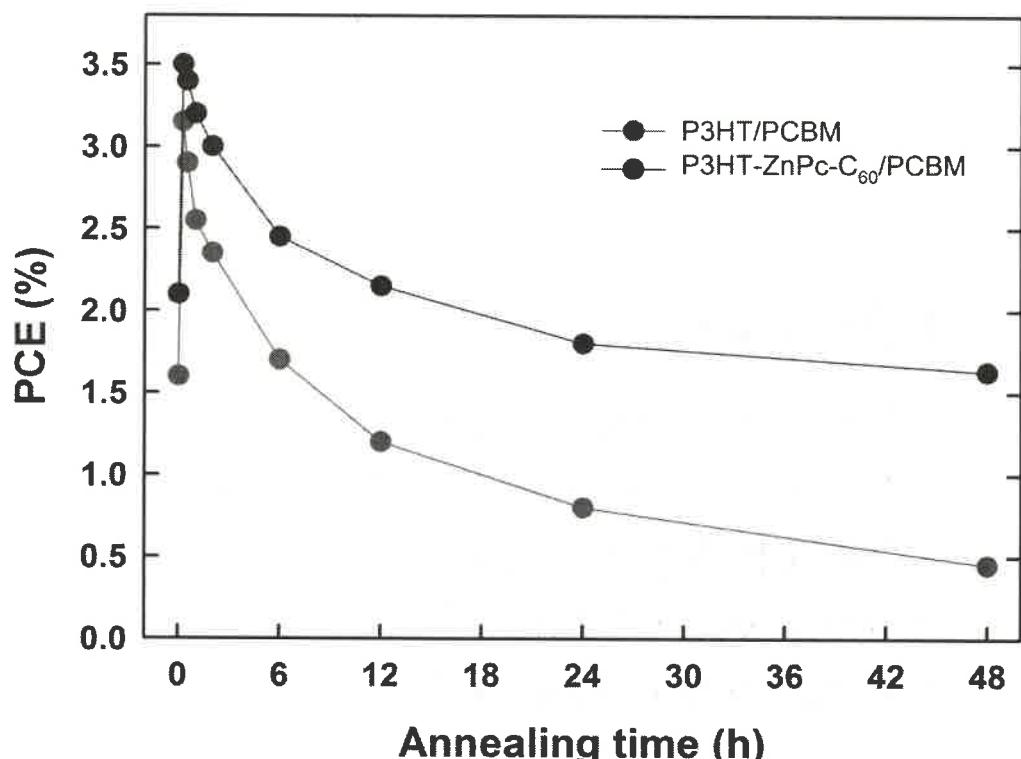
Morphology Control and Performance

Time-resolved Photoluminescence Spectra



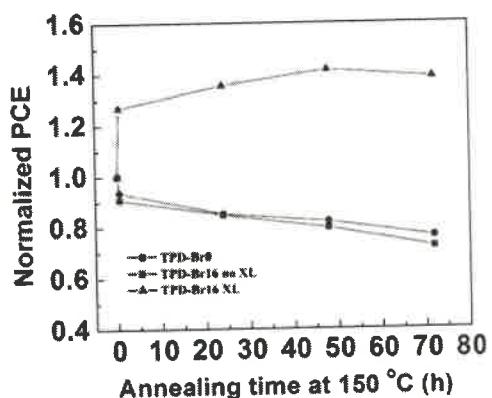
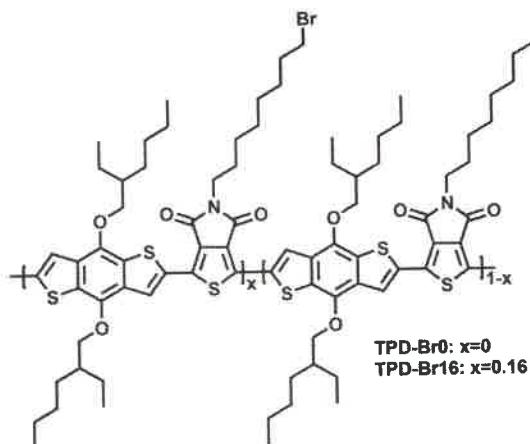
Sample	λ_{ex} (nm)	λ_{em} (nm)	Decay time (ps)
P3HT			700
P3HT/PCBM	532	650	190/450
P3HT-ZnPc-C ₆₀ /PCBM			140/430

Long-term Thermal Stability



Stability by Crosslinking

Fréchet *et al.*, *Adv. Mater.*, 2011, 23, 1660



	Annealing time (h)	J_{SC} (mA/cm ²)	V_{OC} (V)	FF (%)	PCE (%)
TPD-Br0	0	10.6	0.76	64	5.2
TPD-Br0	72	8.2	0.87	55	3.9
TPD-Br16	0	10.0	0.73	45	3.3
TPD-Br16	72	10.1	0.85	53	4.6

Stability/Durability

- Thermal stability
- Chemical stability
- Photo stability

Efficiency

- Low bandgap polymer
- Control of HOMO/LUMO levels
- Morphology control
- Interface engineering
- Fabrication method

Factors affecting J_{sc}

- Absorption of photons – bandgap
- Charge separation – LUMO levels offset of donor and acceptor
- Charge carrier mobility
- Morphology – domain size and connectivity

Factors governing V_{oc}

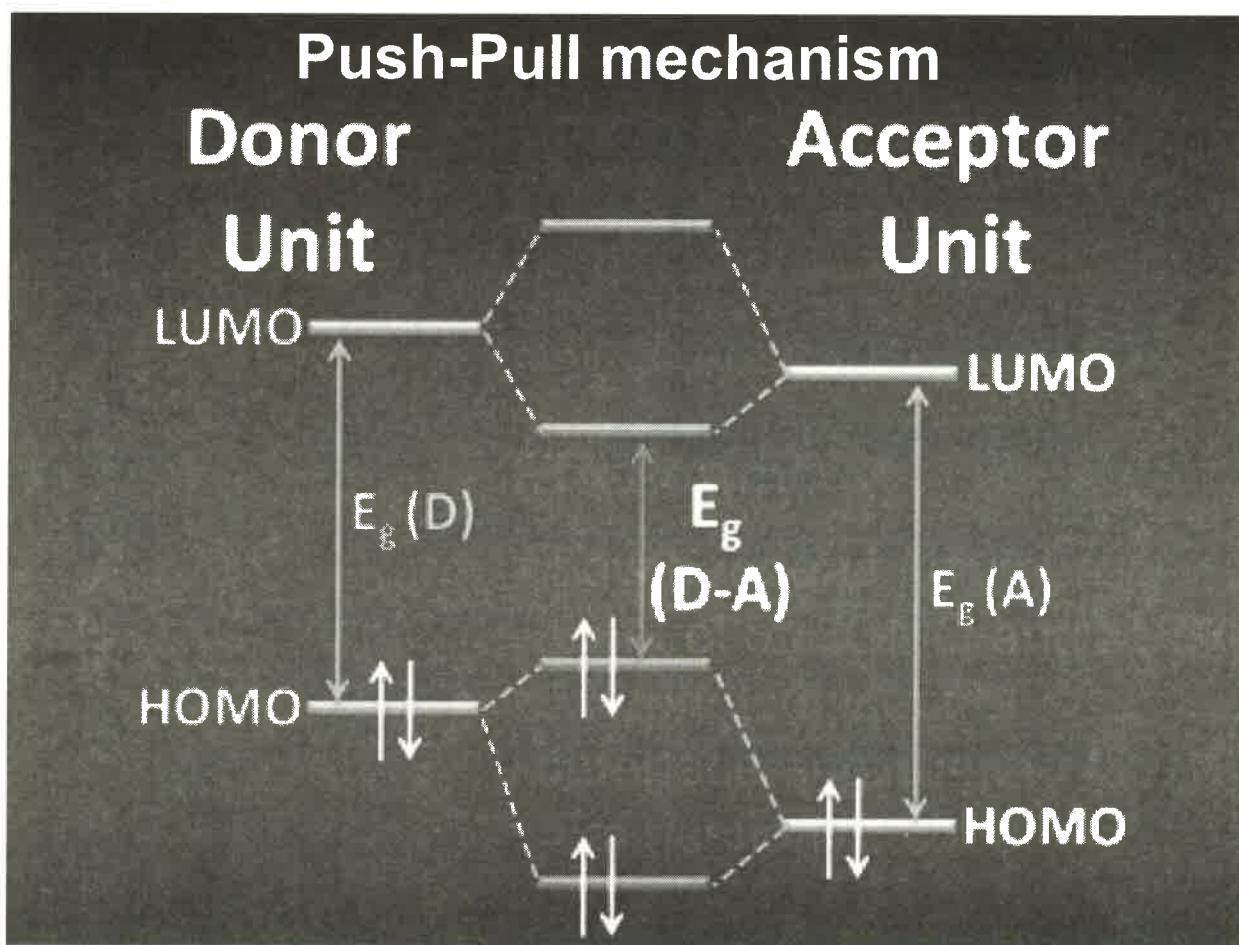
- Energy difference between HOMO of donor and LUMO of acceptor
- Work function difference between anode and cathode
- Formation and recombination of CT states

Factors influencing fill factor

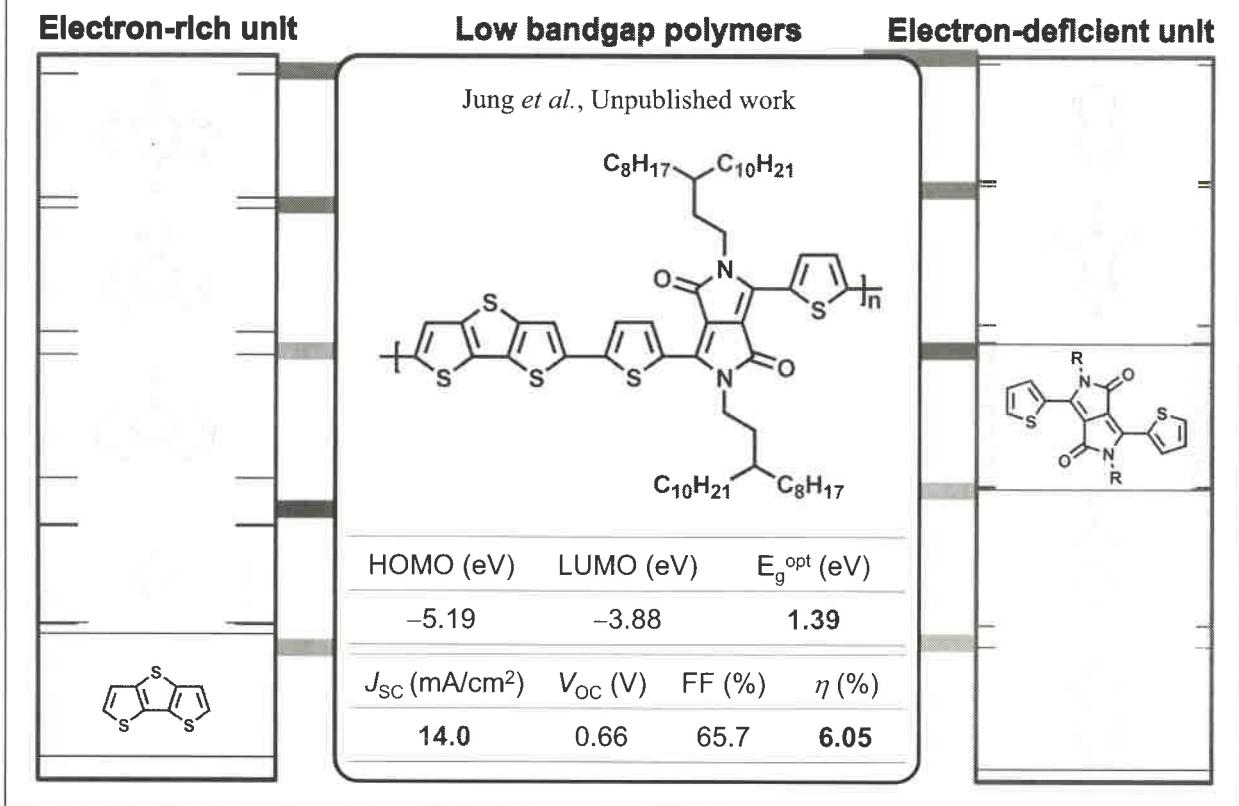
- Balance between hole and electron mobility
- Series and shunt resistances

Factors controlling the HOMO/LUMO levels of conjugated polymers

- Molecular weight
- Intramolecular charge transfer
- Planarity of chain backbone
- Substituents



Alternating Conjugated Copolymers



Stability/Durability

- Thermal stability
- Chemical stability
- Photo stability

Efficiency

- Low bandgap polymer
- Control of HOMO and LUMO levels
- Morphology control
- Interface engineering
- Fabrication method

Processing for Morphology Evolution of Active Layer

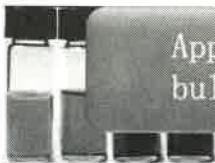
thermal annealing



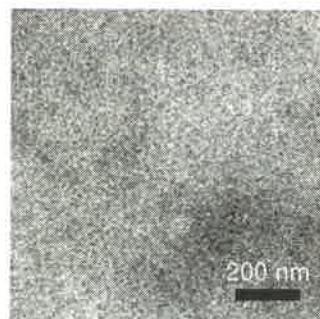
solvent annealing



solvent mixture

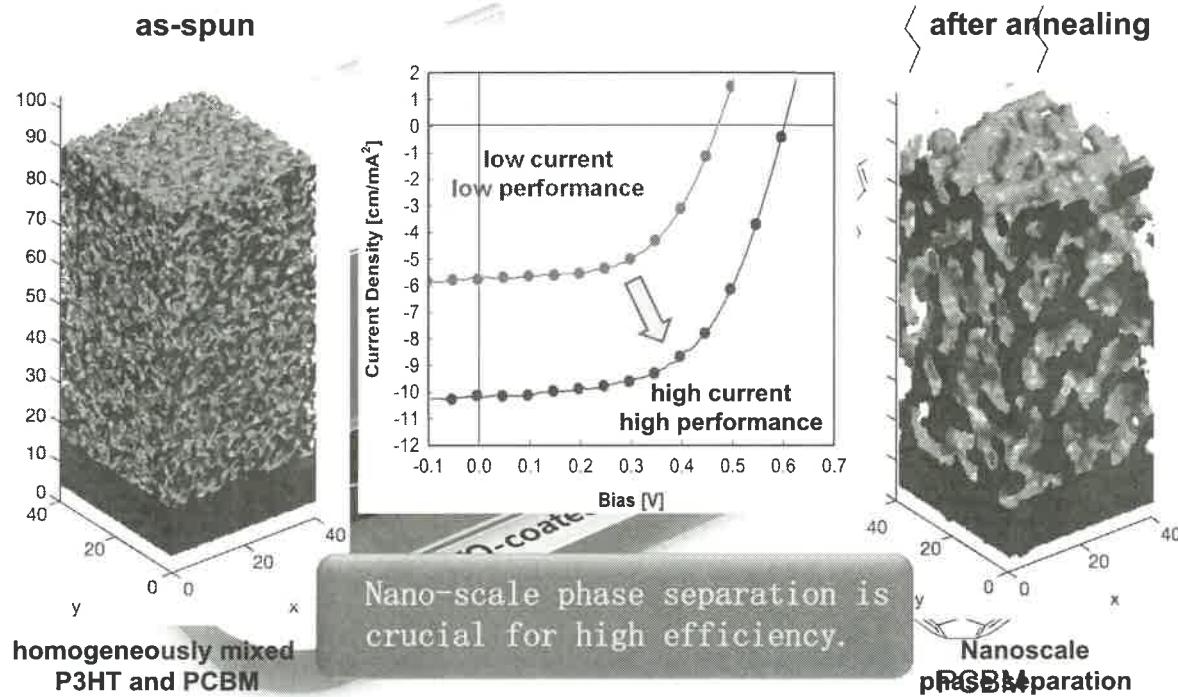


Nano-scale
Phase
Separation



Appropriate processing renders ideal lateral bulk heterojunction morphology.

Morphology of Polymer Solar Cell



Vertical Morphology

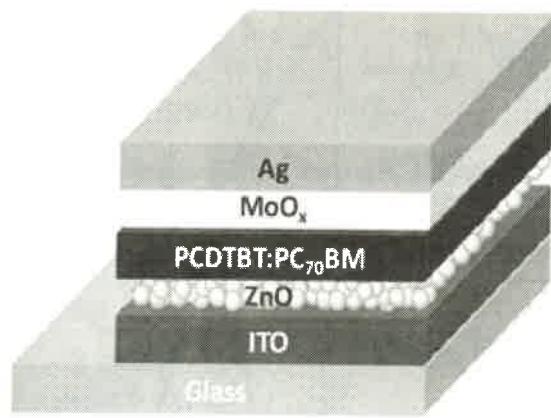
- Imbalanced surface energy: P3HT (26.9 mJ/m²), PCBM (37.8 mJ/m²)
- P3HT accumulates at the surface of the active layer.
- Non-ideal vertical distribution in active layer hinders efficient charge transport.



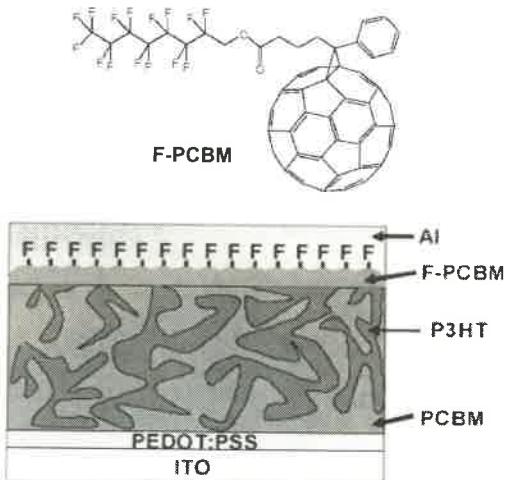
Ideal vertical morphology of active layer will be required for high

Previous Efforts for Ideal Vertical Morphology

Inverted-structure Solar Cell



Fluorinated PCBM

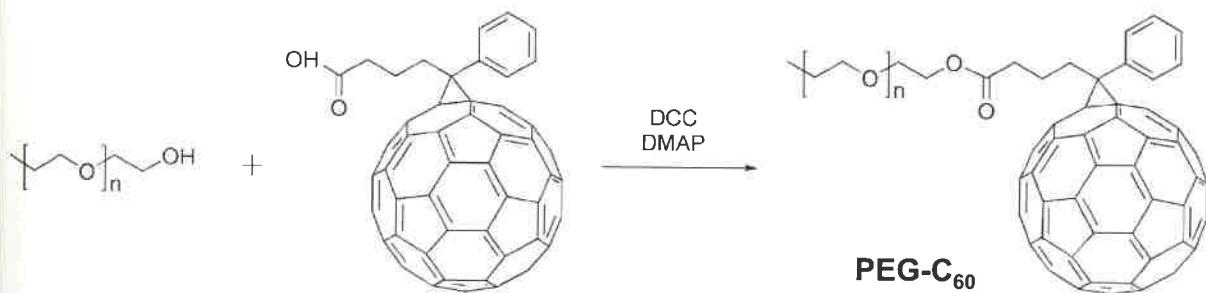


Yang et al., *Adv. Funct. Mater.*, 2009, 19, 1227.

Hashimoto et al., *Adv. Mater.*, 2009, 20, 2250.

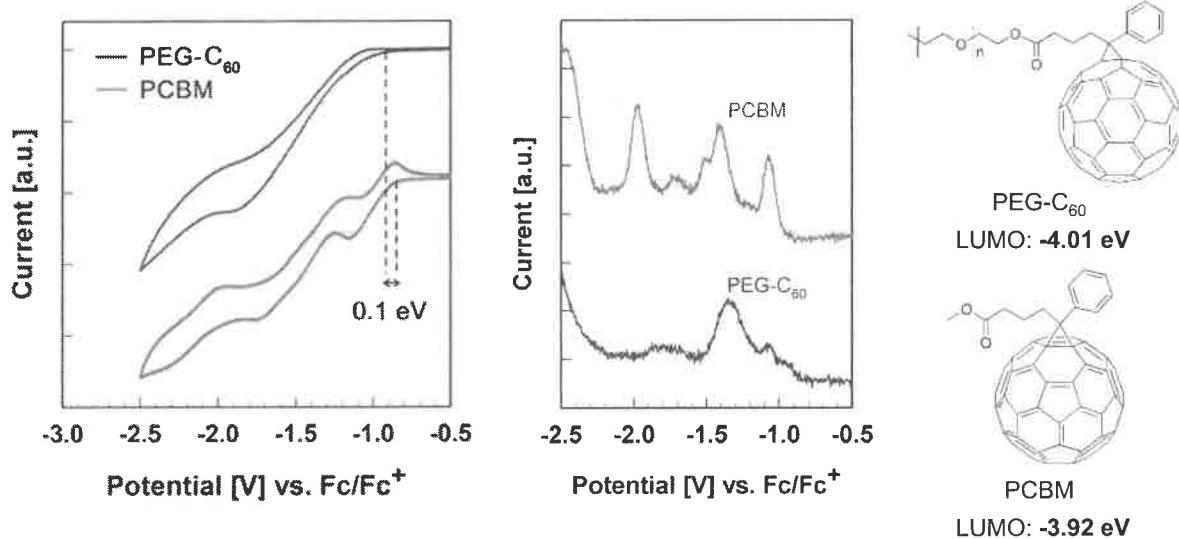
Easy and simple method for an ideal vertical morphology should be developed

Synthesis of Fullerene-End Capped Poly(ethylene glycol)



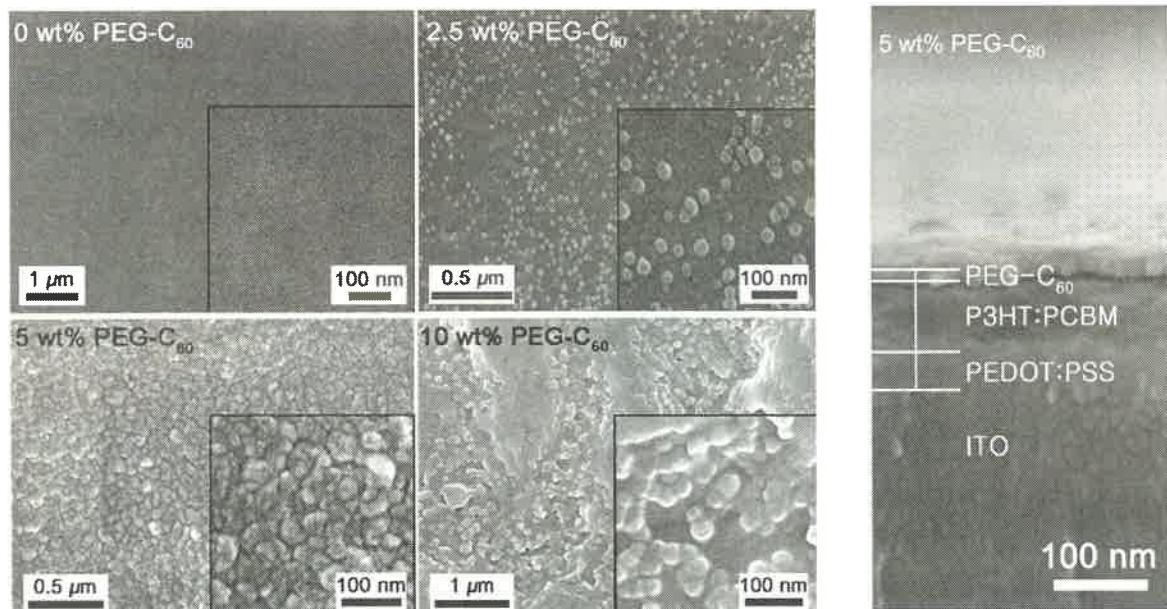
1. Formation of PEG thin layer on the top of P3HT/PCBM
→ Induce the ideal vertical composition gradient.
2. Induction of interfacial dipole due to high dielectric constant of PEG: $\epsilon(\text{PEG})=13.0$ vs. $\epsilon(\text{P3HT})=2.6$, $\epsilon(\text{PCBM})=3.9$.
→ Increase the V_{oc} due to the raise of vacuum level of metal cathode.

Electrochemical characteristics



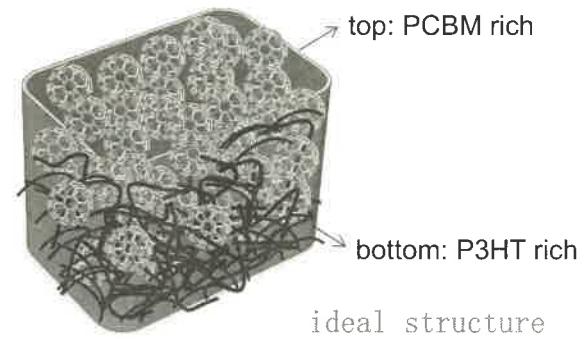
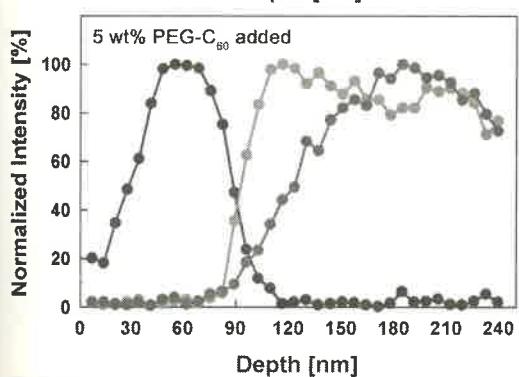
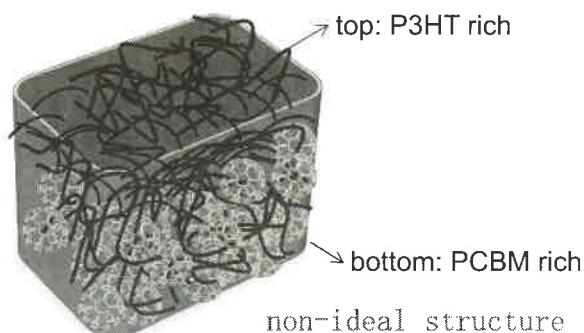
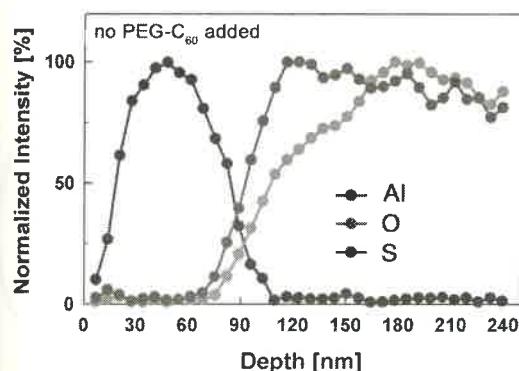
In spite of the insulating property of PEG, PEG-C₆₀ has a similar LUMO level to C₆₀, and thus accept and transport electrons to Al

SEM images: self-assembled buffer layer



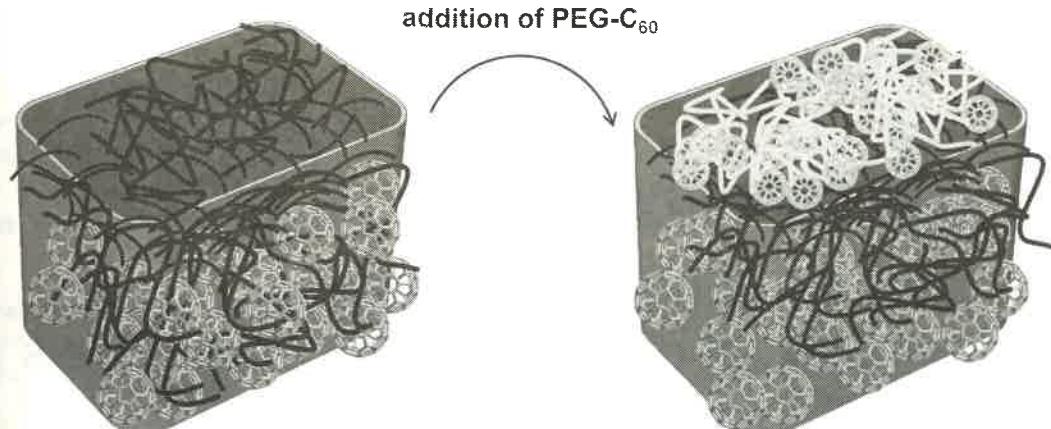
Adv. Mater. 2011, 23, 1782

XPS depth profile: vertical morphology



Development of Ideal Vertical Morphology

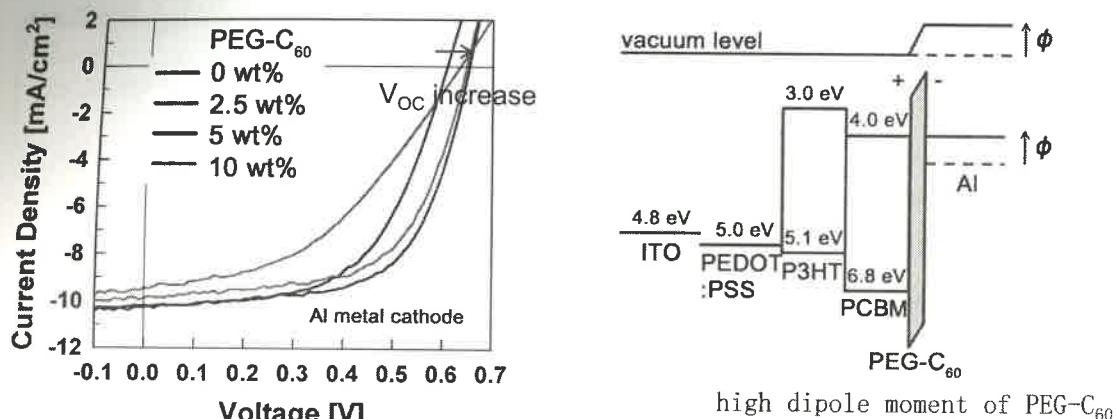
conventional bulk heterojunction PEG-C₆₀ added bulk heterojunction



C₆₀ in PEG-C₆₀ induces PCBM at the surface of the bulk heterojunction film

Enhanced Performance of Polymer Solar Cells

Adv. Mater. 2011, 23, 1782



Amount of PEG-C ₆₀	V _{OC} [V]	FF	J _{SC} [mA/cm ²]	PCE [%]	R _S [Ω·cm ²]
0	0.61	0.58	10.17	3.60	13.25
2.5	0.65	0.60	9.87	3.85	9.47
5	0.66	0.65	10.27	4.41	5.51
10	0.63	0.42	9.45	2.50	48.63

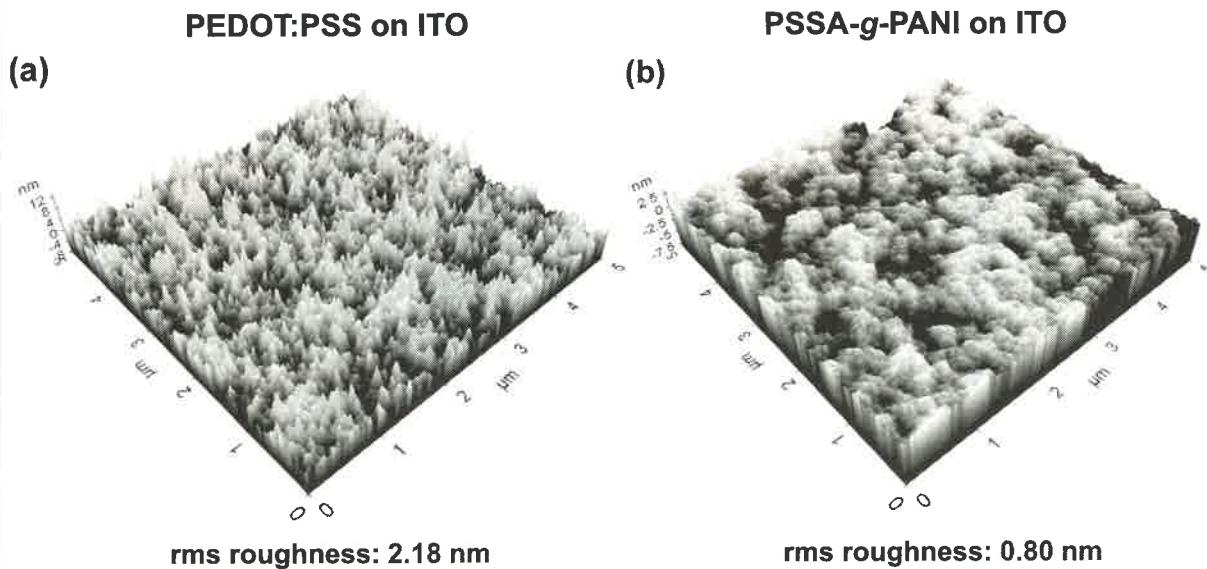
Stability/Durability

- Thermal stability
- Chemical stability
- Photo stability

Efficiency

- Low bandgap polymer
- Control of HOMO and LUMO levels
- Morphology control
- Interface engineering
- Fabrication method

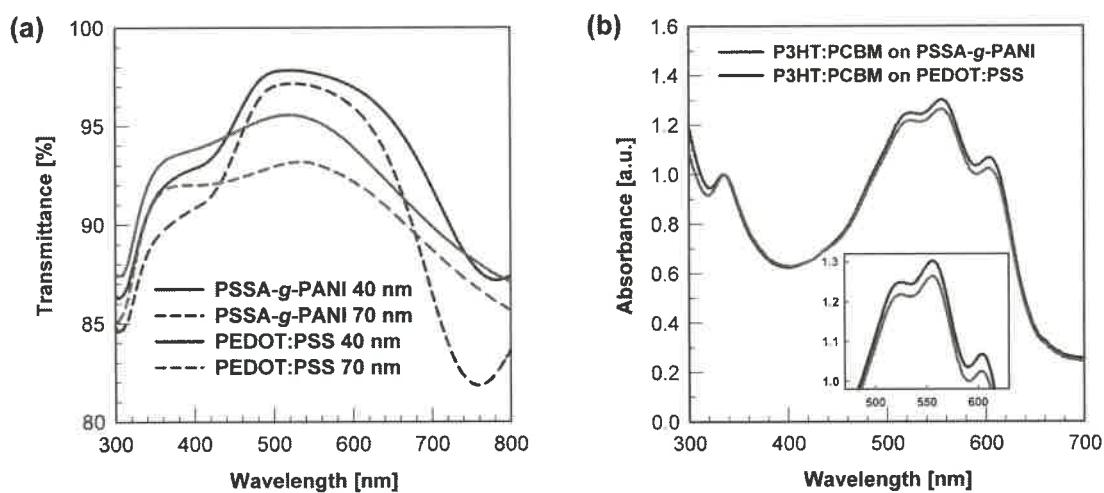
Surface Morphology of PSSA-g-PANI



- **Much smoother surface of PSSA-g-PANI than PEDOT:PSS**

The covalently grafted PANI is more miscible with PSSA than PEDOT with PSSA, and therefore PSSA-g-PANI effectively decreases the roughness of ITO.

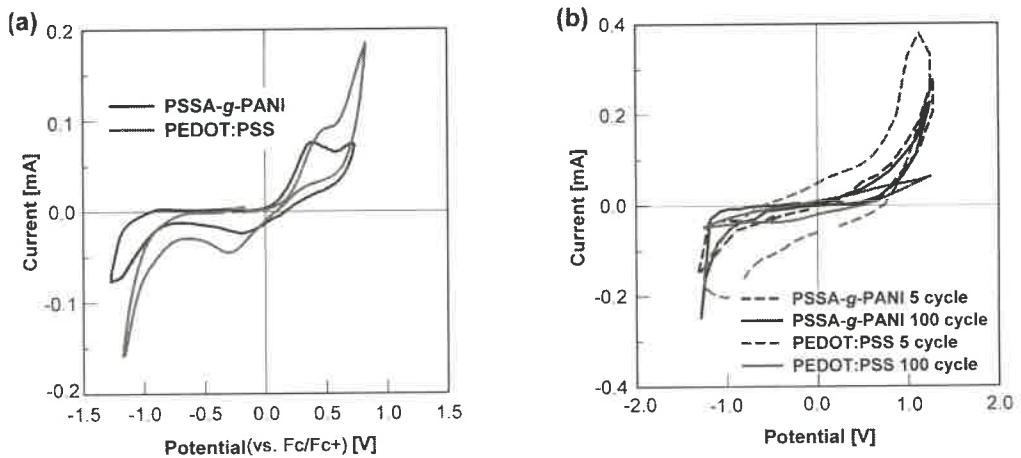
Optical Characteristics of PSSA-g-PANI



- **High transparency in 450–650 nm wavelength of PSSA-g-PANI**

Highly transparent PSSA-g-PANI results in enhanced light absorption in range of 450–650 nm.

Cyclic Voltammetry Measurements



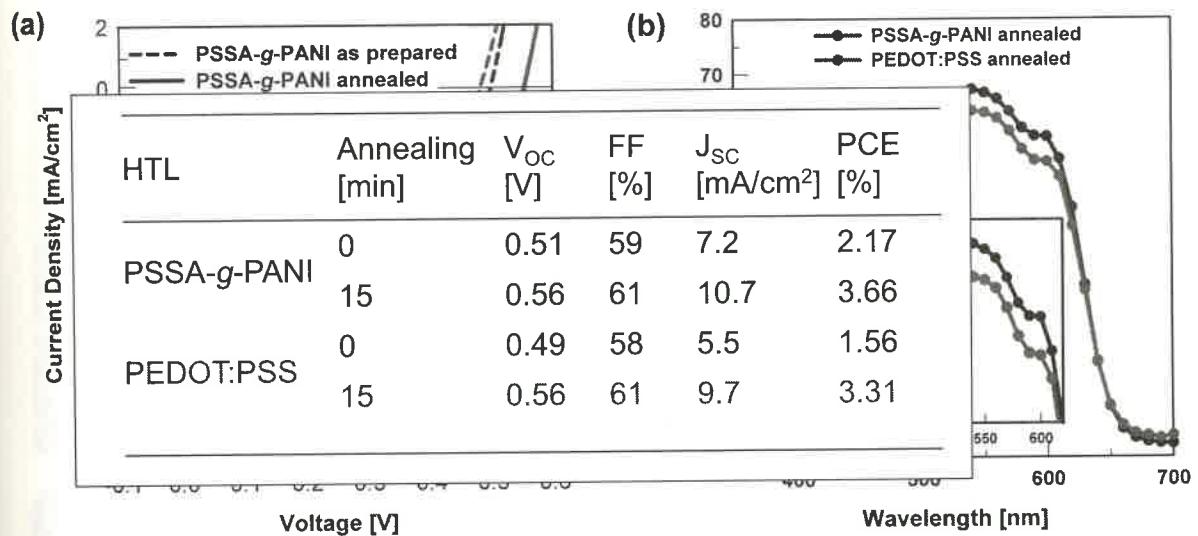
- Nearly equal HOMO level of PSSA-g-PANI and PEDOT:PSS**

Good match to both the work function of ITO (4.7–4.8 eV in air) and the HOMO level of P3HT (5.0–5.1 eV) for efficient hole transport

- High electrochemical stability of PSSA-g-PANI than PEDOT:PSS**

Almost the same oxidation and reduction potential after 100 cycles

Device Performance



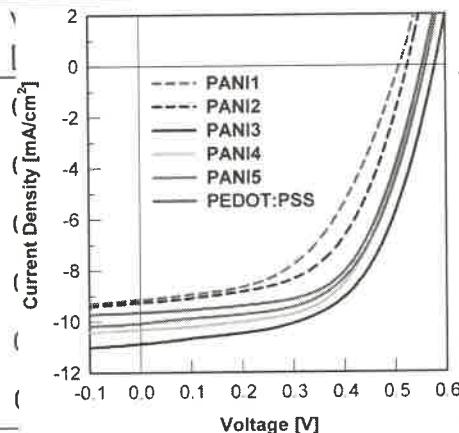
- The device with PSSA-g-PANI shows higher performance than that with PEDOT:PSS**

The higher J_{SC} is attributed to higher transparency and higher conductivity of PSSA-g-PANI than PEDOT:PSS.

Optimized Device Performance

J. Phys. Chem. C 2010, 114, 633.

HTL	Molar ratio of ANI/SSA	Conductivity [$\Omega^{-1}\text{cm}^{-1}$]
PANI1	0.05	0.0005
PANI2	0.07	0.005
PANI3	0.20	0.85
PANI4	0.29	0.10
PANI5	0.40	0.05
PEDOT:PSS	—	0.007



- By changing the molar ratio of ANI/SSA, various PSSA-g-PANIs with different electrical conductivity can be synthesized.
- By using highly conductive PSSA-g-PANI as HTL, high power conversion efficiency about 4% was achieved which is 20% higher than that of the device with PEDOT:PSS.

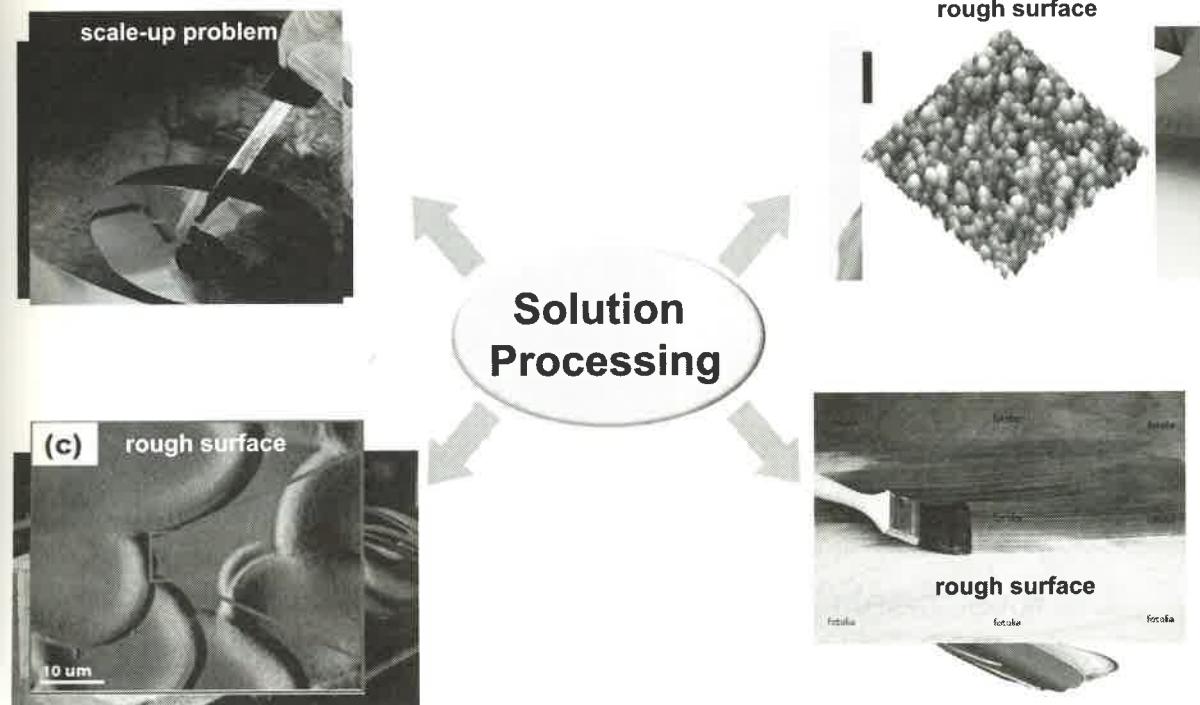
Stability/Durability

- Thermal stability
- Chemical stability
- Photo stability

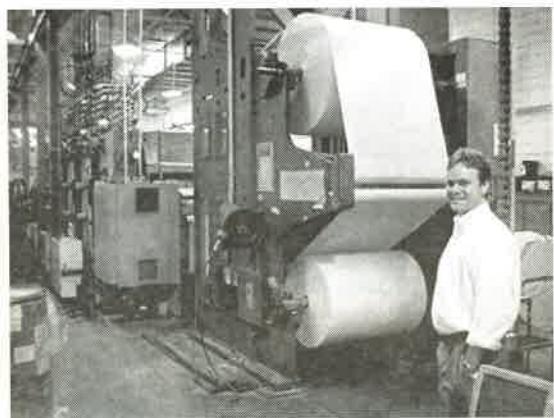
Efficiency

- Low bandgap polymer
- Control of HOMO and LUMO levels
- Morphology control
- Interface engineering
- Fabrication method

Conventional Processing for Polymer Solar Cells



Roll-to-roll processing for solar cells?



- Low-cost and high-throughput
- Suitable for light and flexible solar cell
- No waste of materials for processing

- No fundamental study
- Realistic possibility



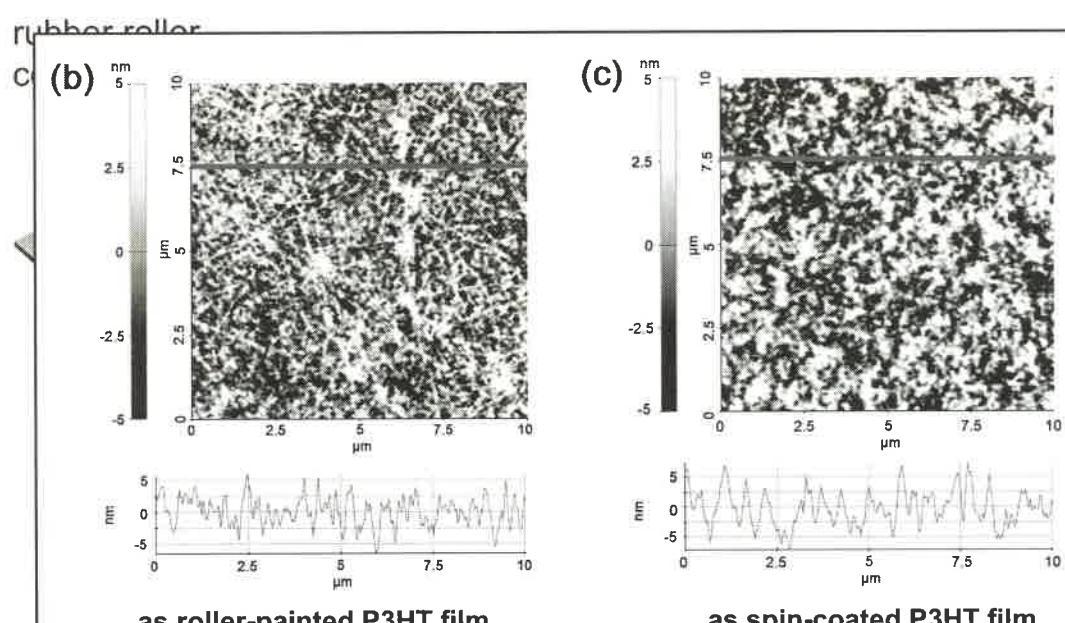
Roller Painting for Solar Cells

If we coat polymeric semiconductor on the wall using the roller painting, ...

Roller painting can be a promising process for organic electronics.



The roller painting process can be a model study for the R2R process of fabricating organic electronics.



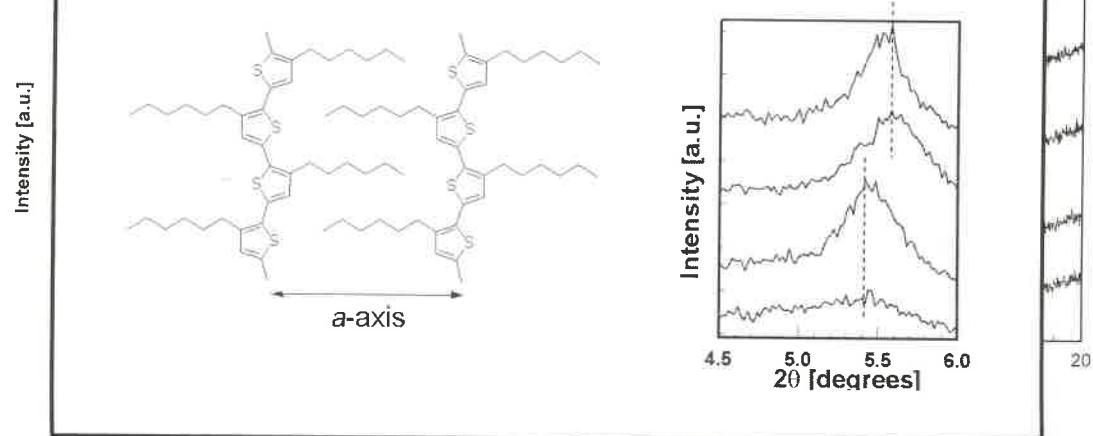
Roller painting affords highly crystalline fibril P3HT.

organic solar cells

Enhanced crystallinity of roller painted film

P3HT films

(a)

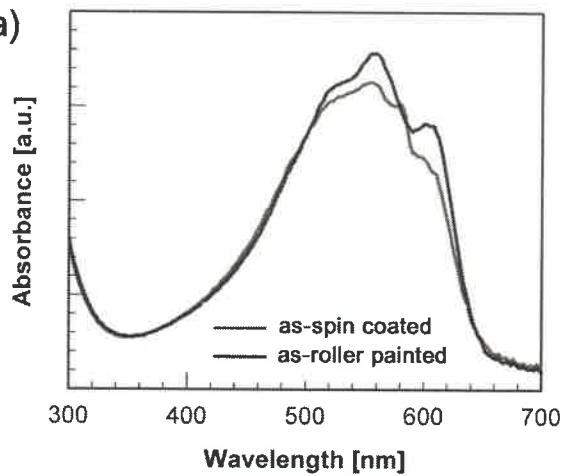


P3HT:PCBM films

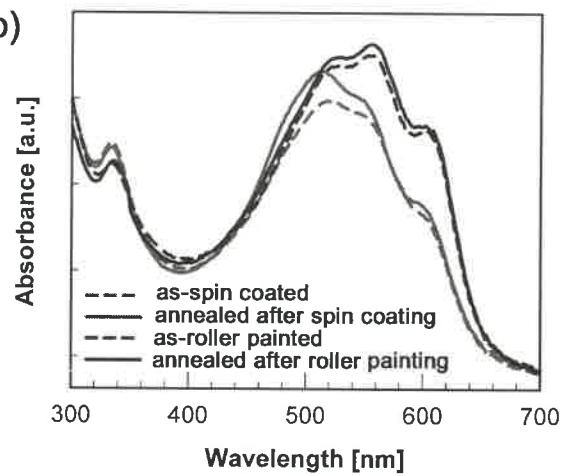
- ✓ Both normal and shear stress, and slow drying during roller painting induce high crystallinity of P3HT.

Effect of roller painting on chain packing of P3HT

(a)



(b)



- ✓ In roller painted film, there was no significant change of crystallinity of P3HT after thermal annealing treatment.

Photovoltaic Performance

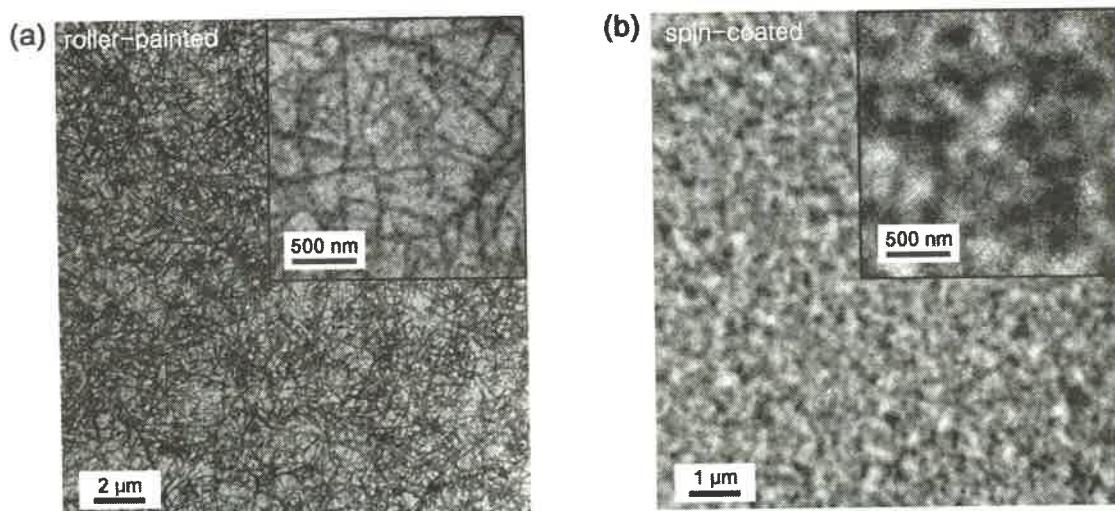
Process	Annealing* [min]	V _{oc} [V]	FF	J _{sc} [mA/cm ²]	PCE [%]
Roller Painting [245 nm]	0	0.57	0.56	7.5	2.4
	8	0.63	0.64	11.3	4.6
Spin Coating [230 nm]	0	0.56	0.52	6.6	1.9
	15	0.61	0.58	11.1	3.9

*Annealing temperature: 150 °C

- ✓ 245 nm thick roller painted device yielded over 4.6% efficiency after optimized thermal annealing process.

Roller Painting Process with Additives

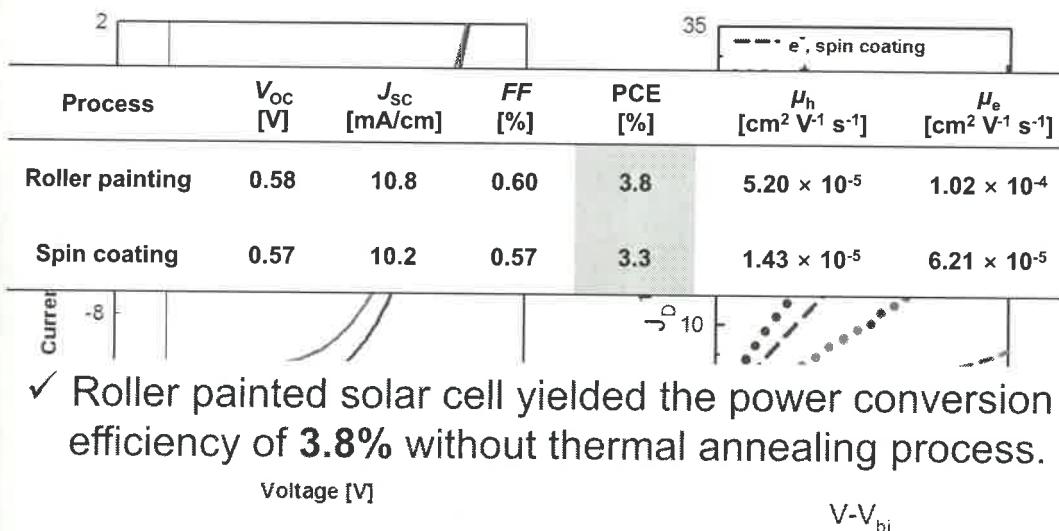
5 wt% 1,8-octanedithiol added film



- ✓ Addition of additives without thermal annealing induces development of PCBM nanocrystals with P3HT nanofibrils.

Photovoltaic Performance

5 wt% 1,8-octanedithiol added film without annealing



Conclusions

- Stability and durability of polymer solar cells was improved by the use of compatibilizer.
- The efficiency of polymer solar cells has recently been improved by various methods toward a PCE over 10%.
- The combination of several potential methods may pave a new avenue to achieve high performance polymer solar cells.

Acknowledgements

Professor T. P. Russell

Professor T. Emrick

Dr. J. U. Lee

Dr. W. J. Bae

Dr. J. Y. Kim

Mr. J. W. Jung Mr. J. W. Jo

Mr. Y. Lee Mr. Y. M. Nam

Mr. K. T. Kim Mr. Y. S. Choi

Mr. S. H. Bae Mr. E. H. Jung

Ms. H. J. Park Mr. J. W. Lee

Sponsored by the Korea
Research Foundation,
Ministry of Education,
Science and Technology,
Korea.



Thank you for your attention!



<http://mse.snu.ac.kr>

College of
ENGINEERING
SEOUL
NATIONAL
UNIVERSITY