

# MASTER REST&STEEM : Polymers for Photovoltaics



## Processing techniques and degradation issues in polymer solar cells

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**01 69 33 43 86 (wing 408)**

# OUTLINE

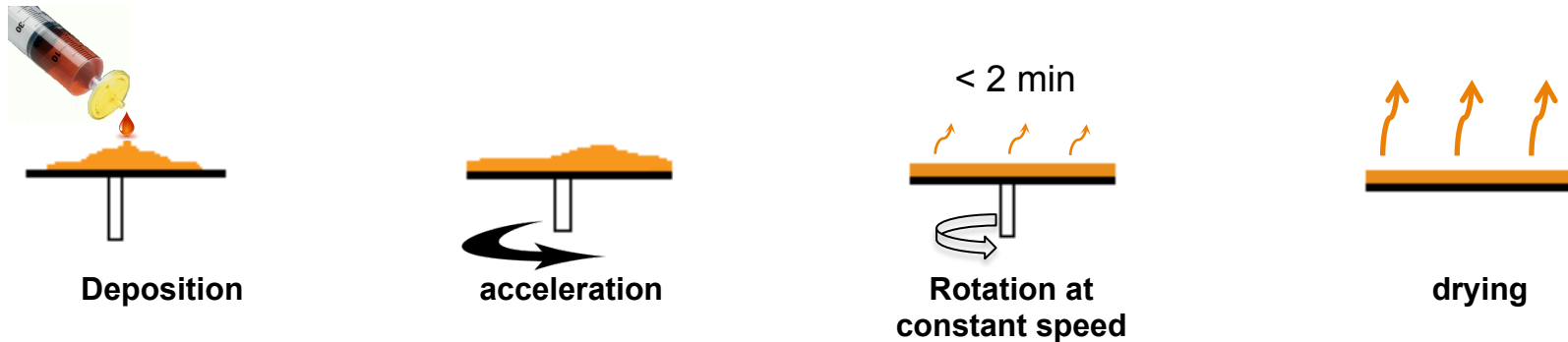
## **I- PROCESSING TECHNIQUES**

- Solution processing
- Film Morphology
- Morphology / properties Relationship

## **II- Degradation mechanism in polymer solar cells**

- Sources of degradation
- Types of degradation
- Some ways to improve Polymer Solar Cells stability

# Spin coating



## Procedure

- Dissolve the material.
- Cast the solution onto the substrate.
- Spin the substrate at 1000 to 6000 revolutions per minute.

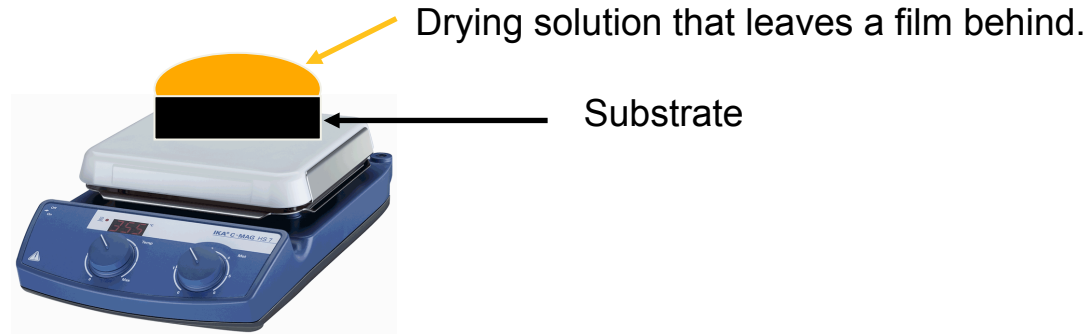
## Advantages:

- high-quality thin films are left behind (uniform thickness until a few hundreds of nm).
- control of the film thickness: the thickness of the films goes up with increasing solution concentration and down with increasing spin speed. Polymers with larger molecular weights tend to result in more viscous solutions, which yield thicker films.
- Cheap technique

## Drawbacks:

- Most (~ 99 %) of the solution is flung off of the substrate
- the whole surface is covered

# Drop casting



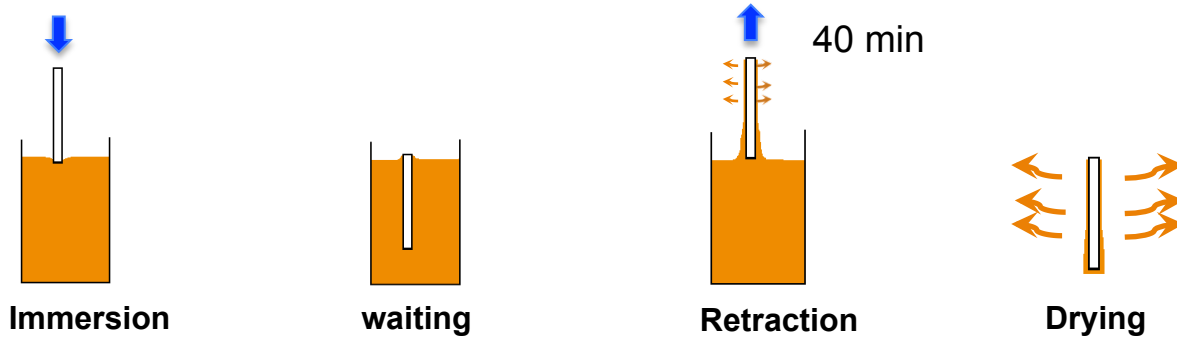
## Advantages:

- Film thickness can be far greater than 1  $\mu\text{m}$ .
- Since the solvent evaporates slowly, the material can crystallize or aggregate into fairly well ordered structures
- This method is very inexpensive.
- In many cases the film can be removed from the substrate by peeling or by dissolving the substrate (which would be NaCl or KBr).

## Disadvantages:

- The film thickness is difficult to control and is not very uniform.
- Very thin films are difficult to prepare.
- The material must be soluble.

## Dip-coating



### Advantages:

- Depending on the speed the work object is raised
- Film thickness can be controlled based on the relationship between the solution viscosity and gravity causing adhered liquid to fall
- A uniformly thin film is formed after eliminating excess solution from the object by drying

### Drawbacks:

- the whole substrate is covered

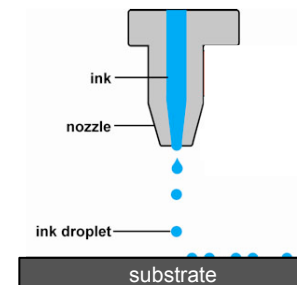
## Ink-jet printing

### Advantages:

- Patterning with resolution approaching 5-10  $\mu\text{m}$  is possible.
- No material is wasted.
- Cost can be extremely low

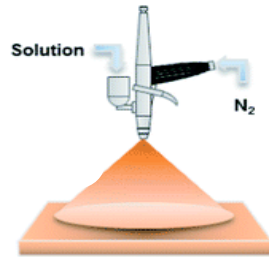
### Disadvantages:

- Controlling film thickness is difficult.



Other techniques are available:

## Spray coating



## Roll-to-roll

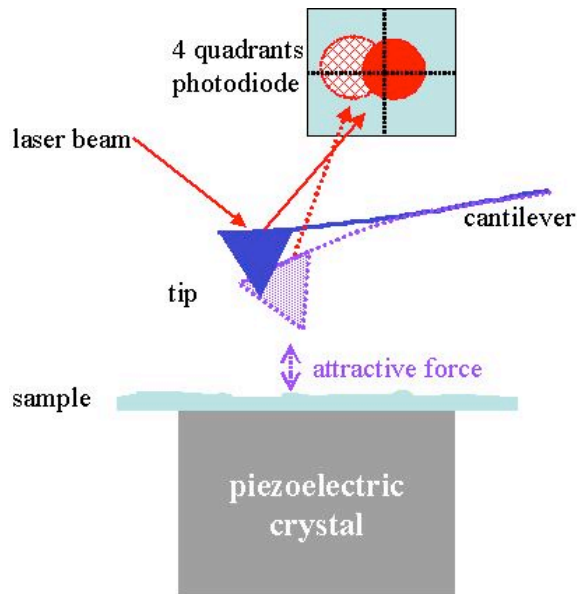


Roll to roll manufacturing on polymer foil or stainless steel substrate

# MORPHOLOGY OF THIN FILMS

Investigated by Atomic Force Microscopy (AFM)

Principle of the measurement:

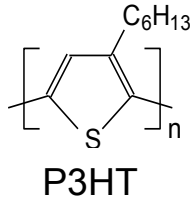


- The piezoelectric crystal is used to move the sample in the 3 directions

- The force between the tip and the sample induces a deflection of the cantilever which is recorded using the optical lever guide: a laser beam is reflected on the cantilever and its position is detected using a 4 quadrants photodiode

**Information :** AFM images the topography of a sample surface

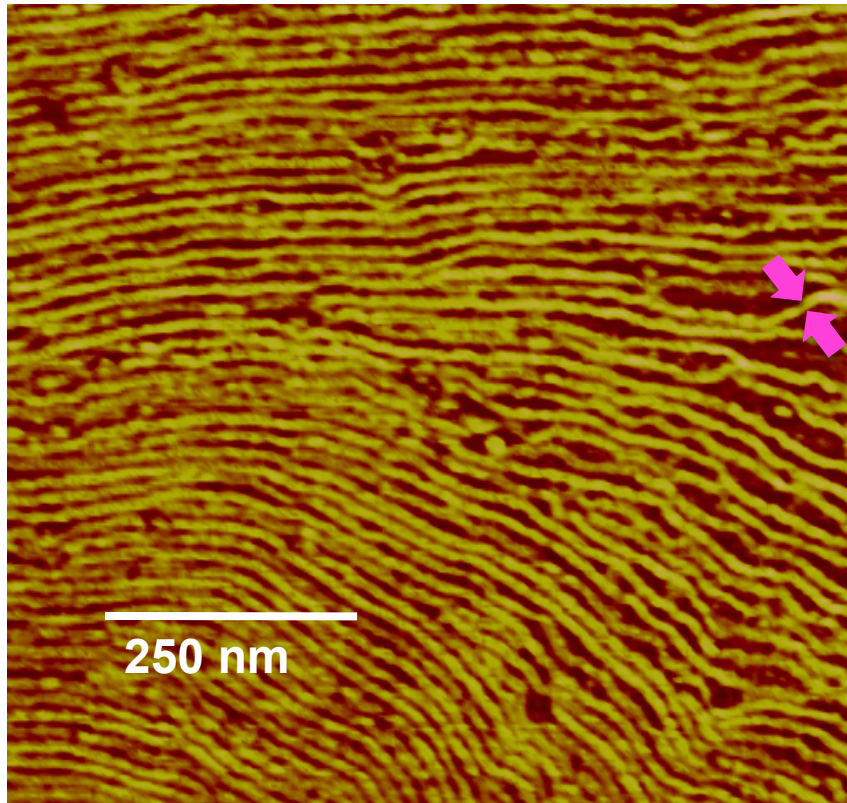
# STUDY OF THE MORPHOLOGY BY AFM



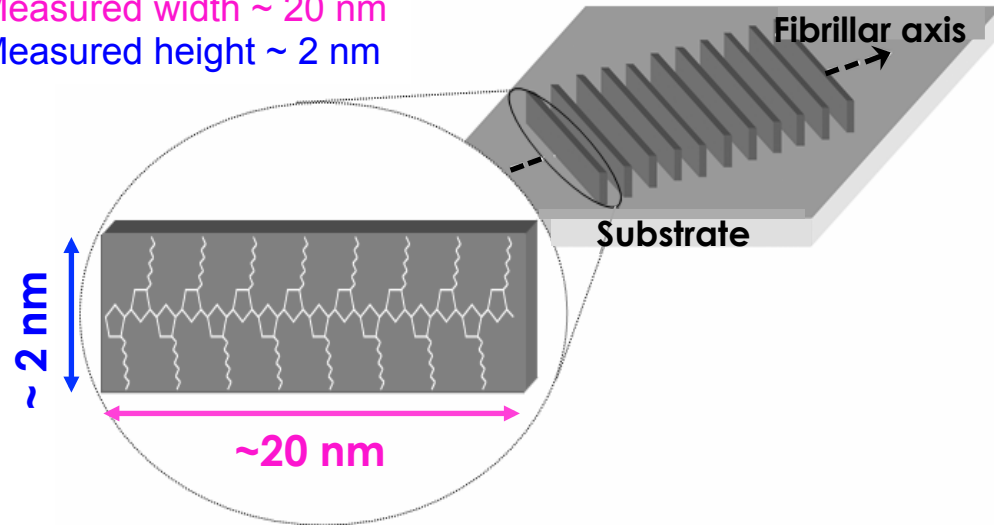
Degree of polymerization (DP): ~ 40 units



Expected chain length ~ 20 nm



Measured width ~ 20 nm  
Measured height ~ 2 nm

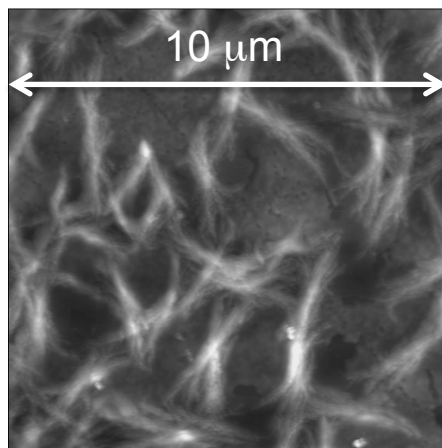
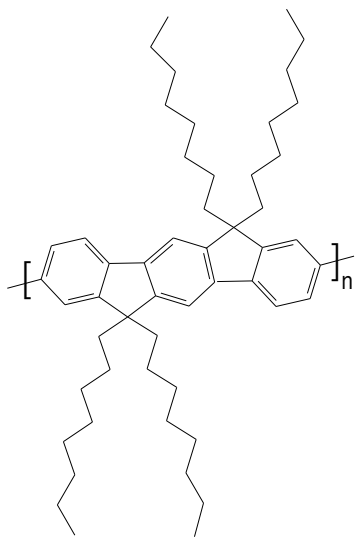


Conjugated chains pack parallel to each other  
→ **Nanofibers** as  $\pi$ -stacks of conjugated chains



# INFLUENCE OF SUBSTITUTION ON THE MORPHOLOGY(I)

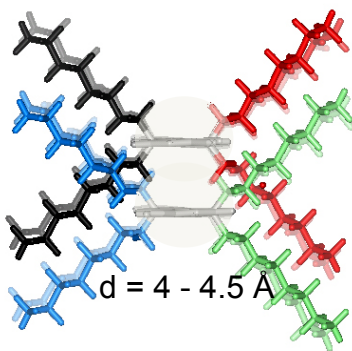
Poly(octylindenofluorene)



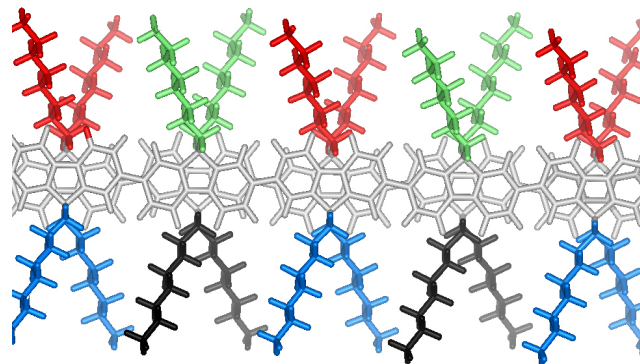
Fibrillar morphology

*Chem. Mater.* **2004**, 16,994

Front view



Top view



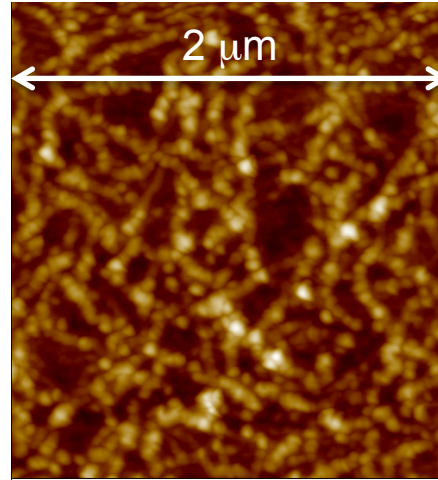
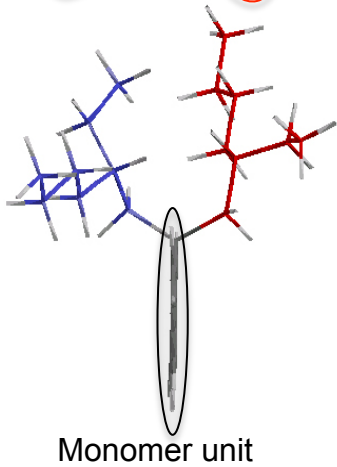
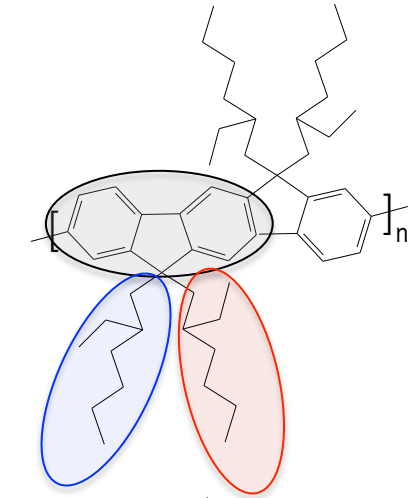
- Conjugated chains pack parallel to each other
- $\pi$ -stacking is maintained

Fibrillar assembly

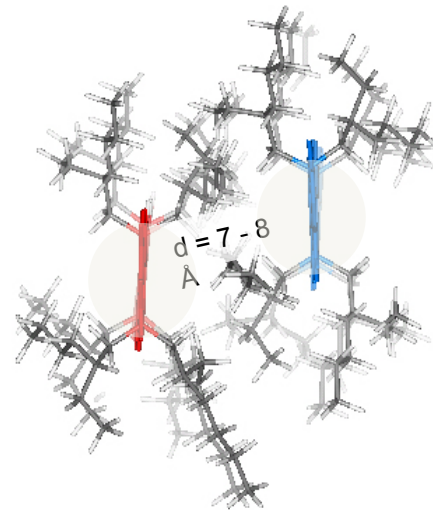
# INFLUENCE OF SUBSTITUTION ON THE MORPHOLOGY(II)

Modifying the nature of the side groups

Poly(octylindenofluorene)



Granular morphology

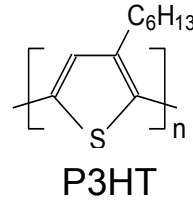


2 units

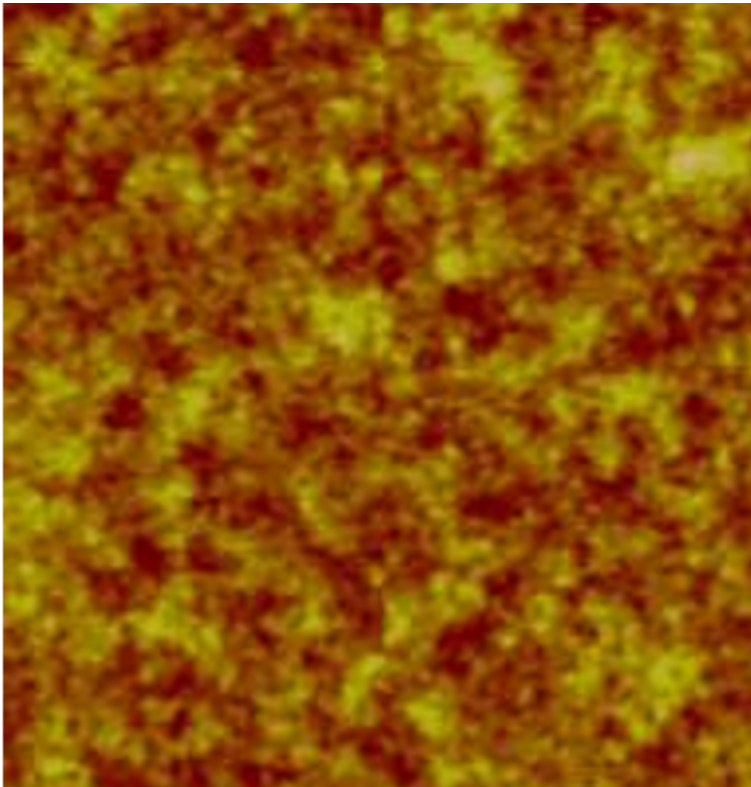
- Bulky side groups
- Steric hindrance suppresses the  $\pi$ -interactions between the conjugated chains

no fibrillar assembly

# INFLUENCE OF DEPOSITION CONDITIONS ON THE MORPHOLOGY

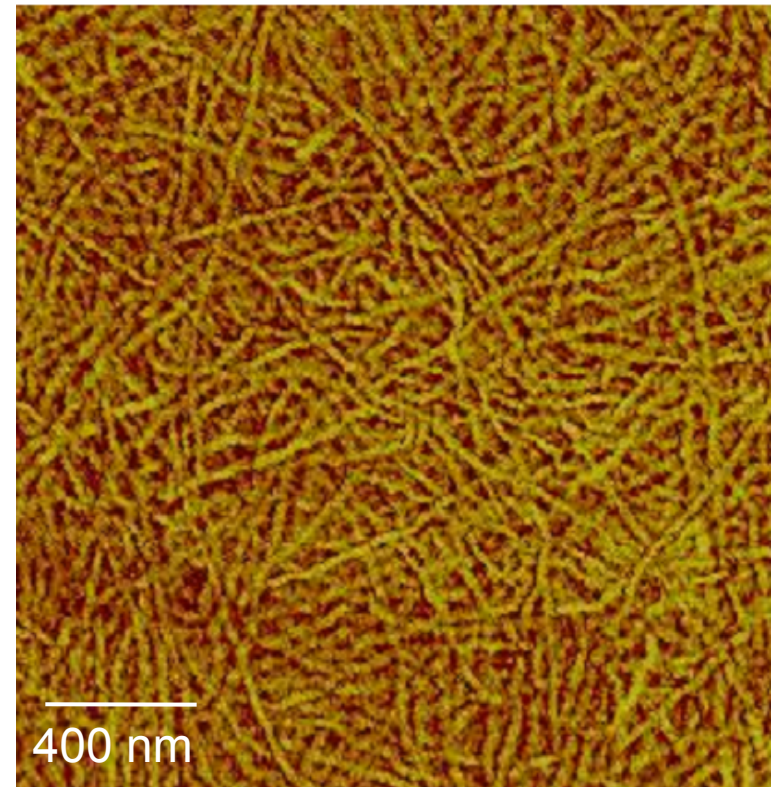


From solution in  
a **good** solvent



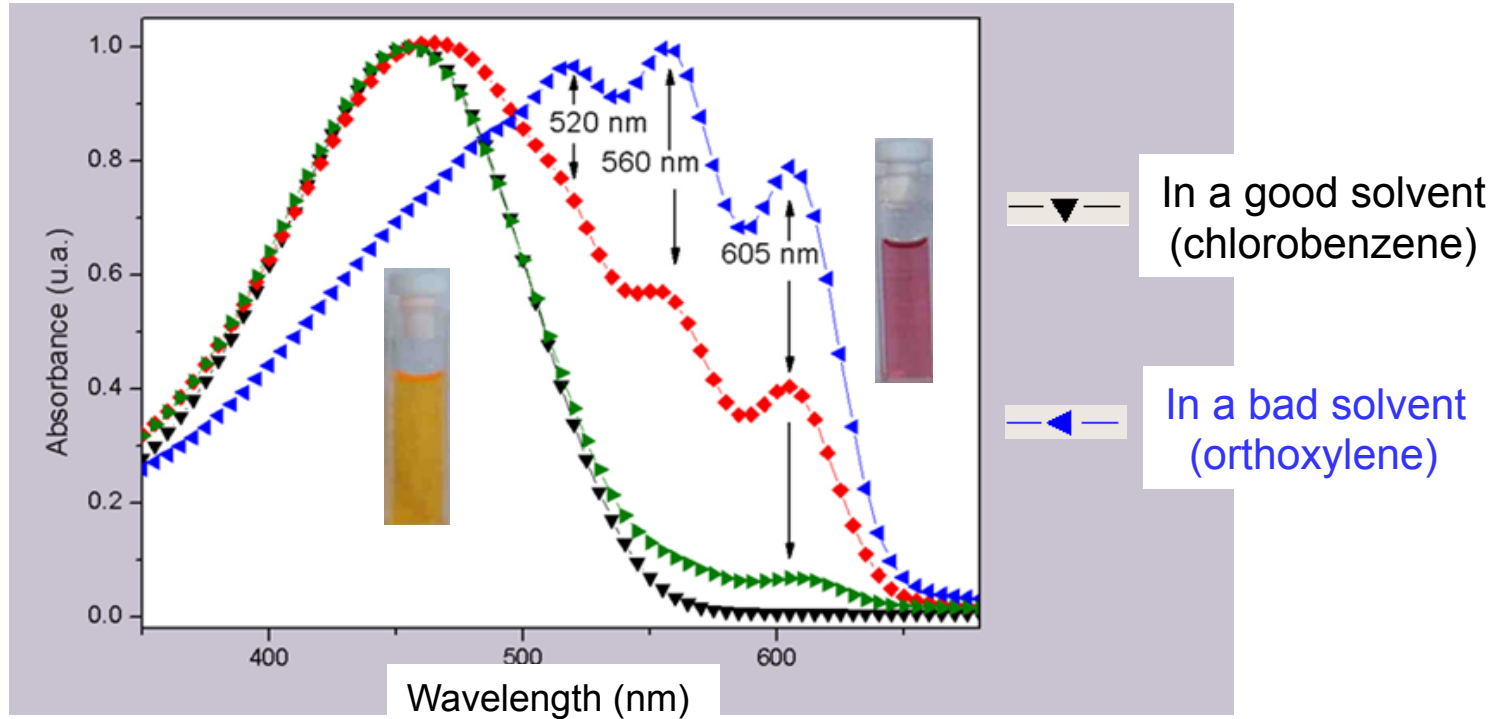
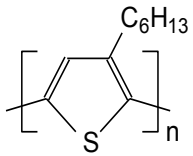
Untextured morphology

From solution in  
a **bad** solvent



Fibrillar morphology

# INFLUENCE OF THE DEPOSITION CONDITIONS ON THE OPTICAL PROPERTIES (I)



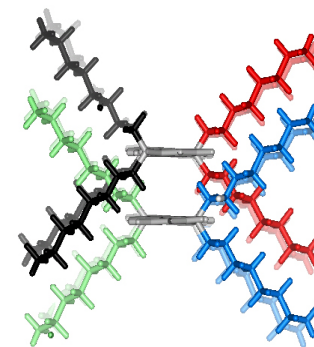
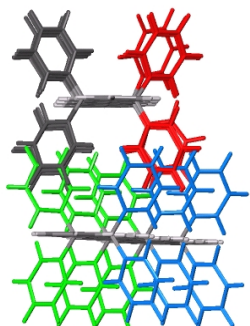
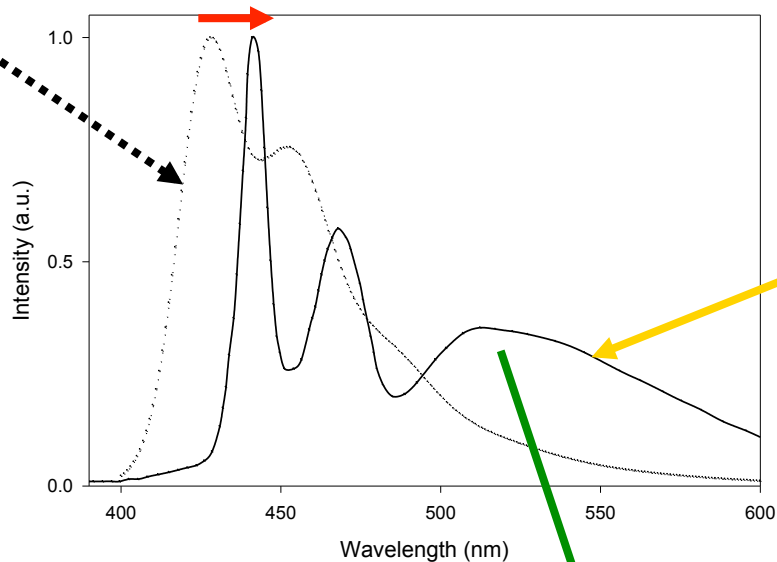
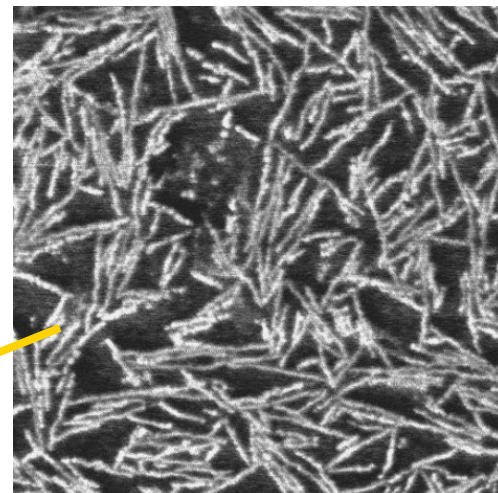
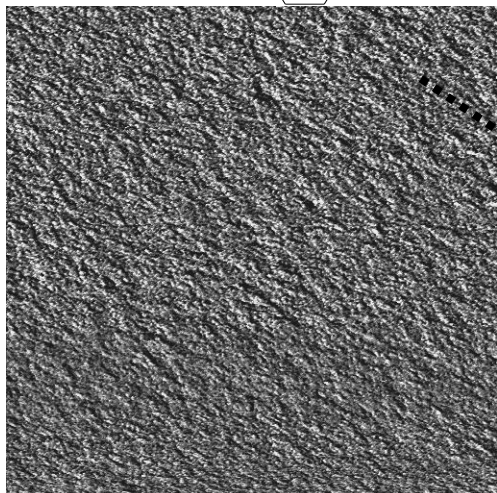
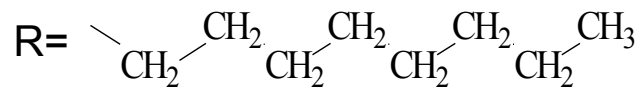
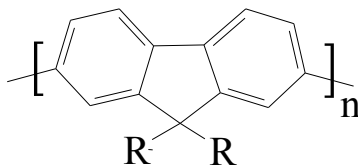
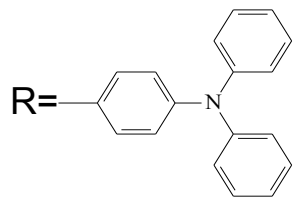
In a good solvent, chains are coiled : broad absorption around 450 nm

In a bad solvent, chains are straight, flat and aggregated : red shift + vibronic structure

Self-assembly of P3HT chains in solution

# INFLUENCE OF DEPOSITION CONDITIONS ON THE OPTICAL PROPERTIES (I)

2 polymers for which luminescence in solution is the same

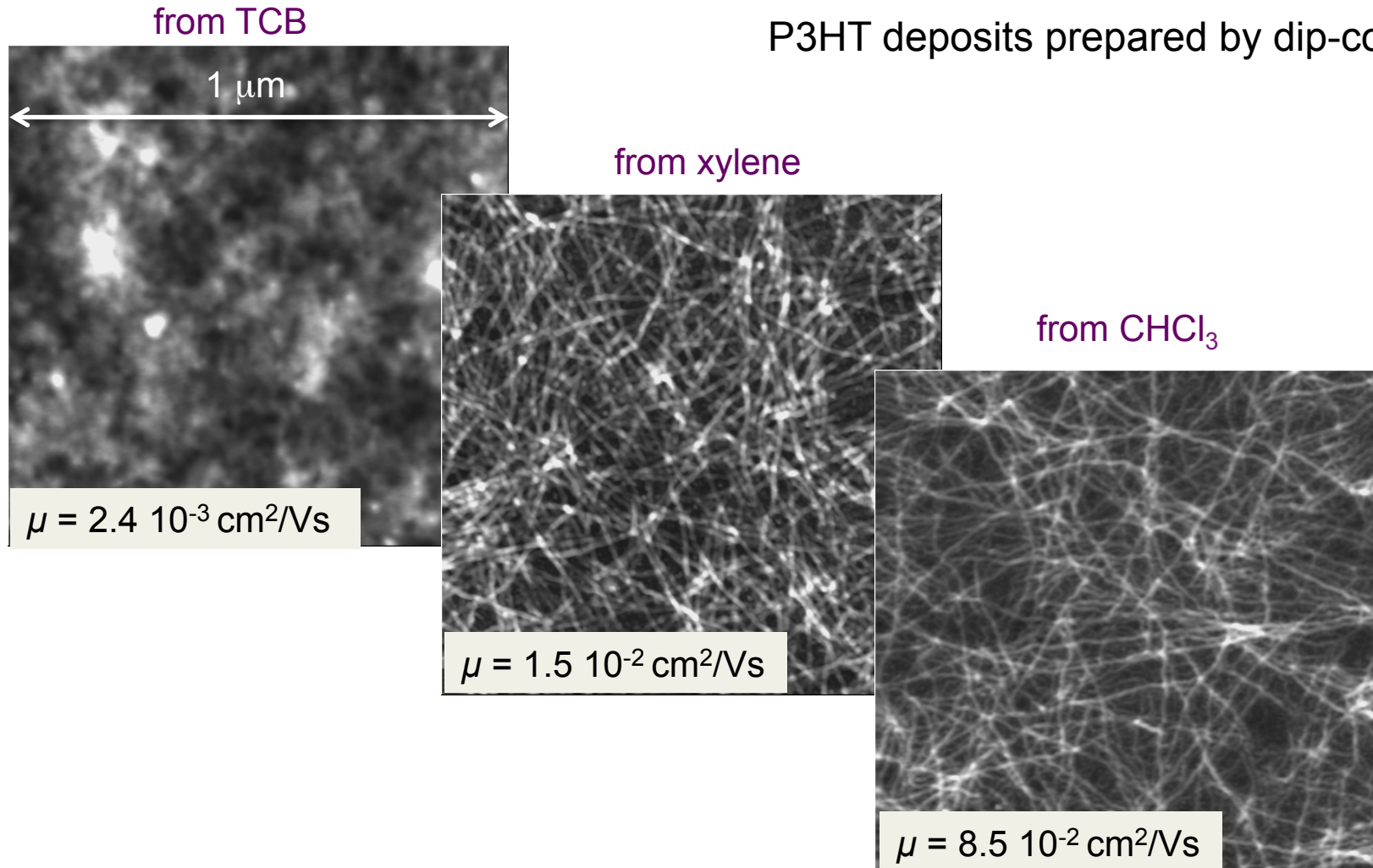


red-shift + broad band in the green region

Change in the emission color

# Morphology-mobility relationship (I)

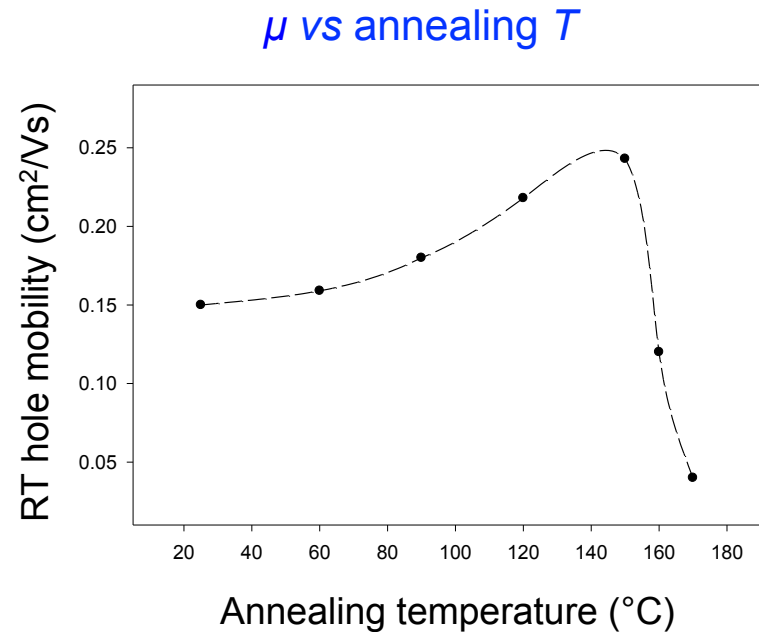
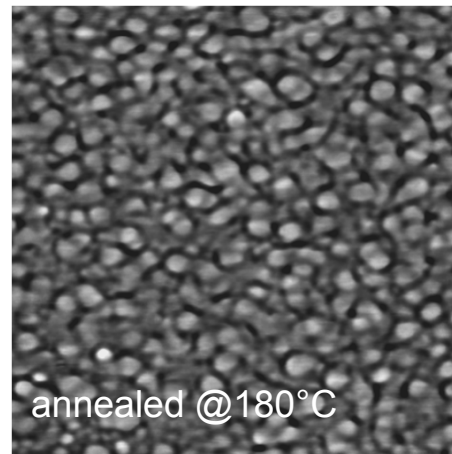
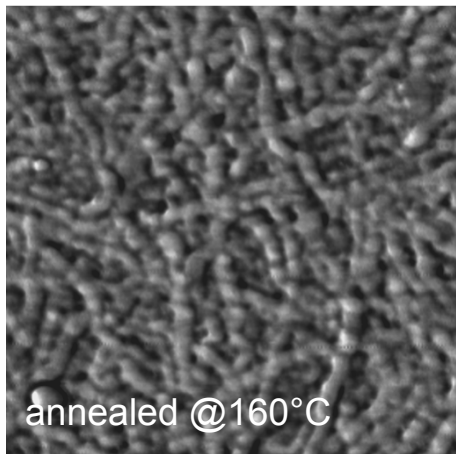
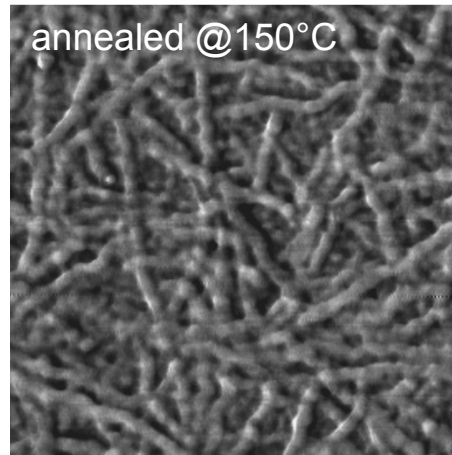
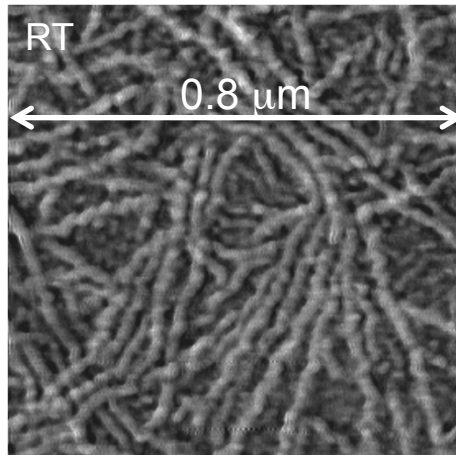
P3HT deposits prepared by dip-coating



Higher mobility for fibrillar morphology than for untextured films: **organization**

# Morphology-mobility relationship (II)

P3HT dip-coated films from  $\text{CHCl}_3$



Morphological transition from a fibrillar to a granular morphology at 155°C:  
**Charge mobility is strongly reduced**

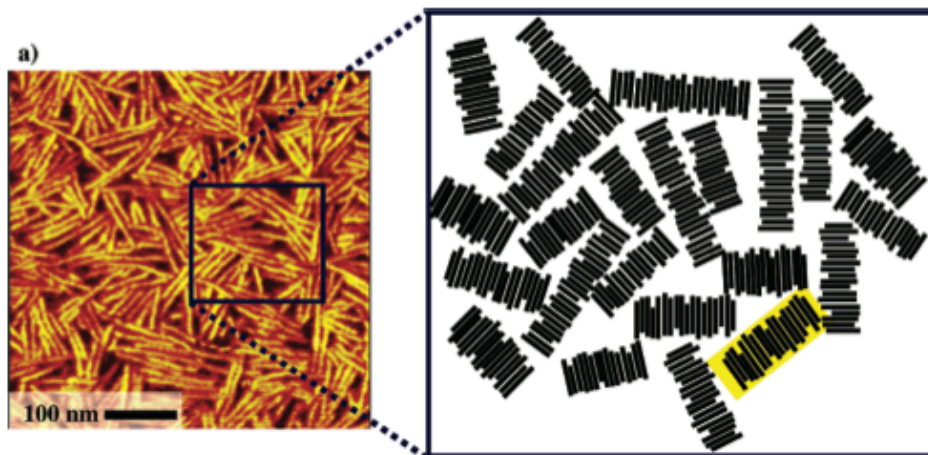
**Higher performance for a fibrillar morphology than for an untextured film**

*J. Appl. Phys.* 2006, 100, 033712

# Molecular Weight-Morphology-Mobility Relationship

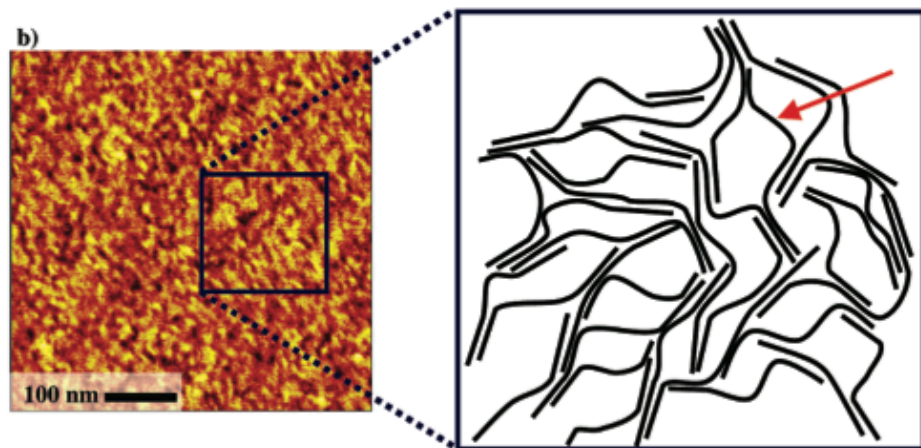
## Influence of $M_n$ on the mobility

Regioregular Poly(3-hexylthiophene) (*rrP3HT*):  $\mu = 1.7 \cdot 10^{-6} \text{ cm}^2/\text{V.s}$  ( $M_n = 3.2\text{K}$ ) ?  
 $\mu = 9.4 \cdot 10^{-3} \text{ cm}^2/\text{V.s}$  ( $M_n = 36.5\text{K}$ ) ?



Low MW:  
more crystalline, but more grain boundaries that limit the mobility

Charge carriers are trapped on nanorods



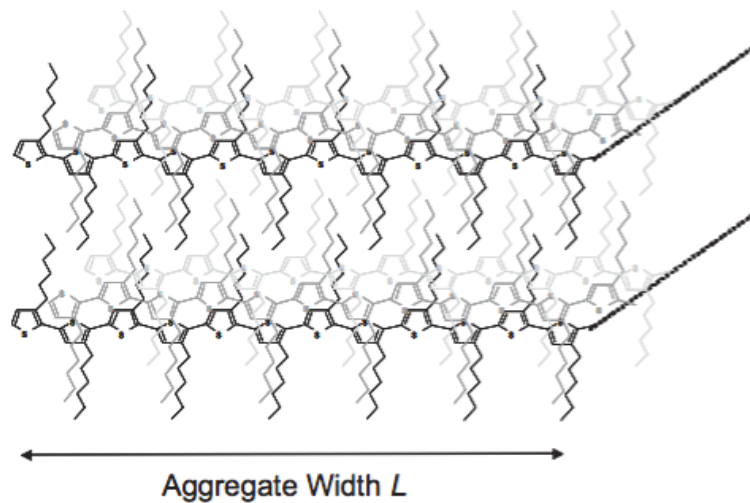
High MW:  
Less crystalline

Long chains in high-MW films bridge the ordered regions and soften the boundaries

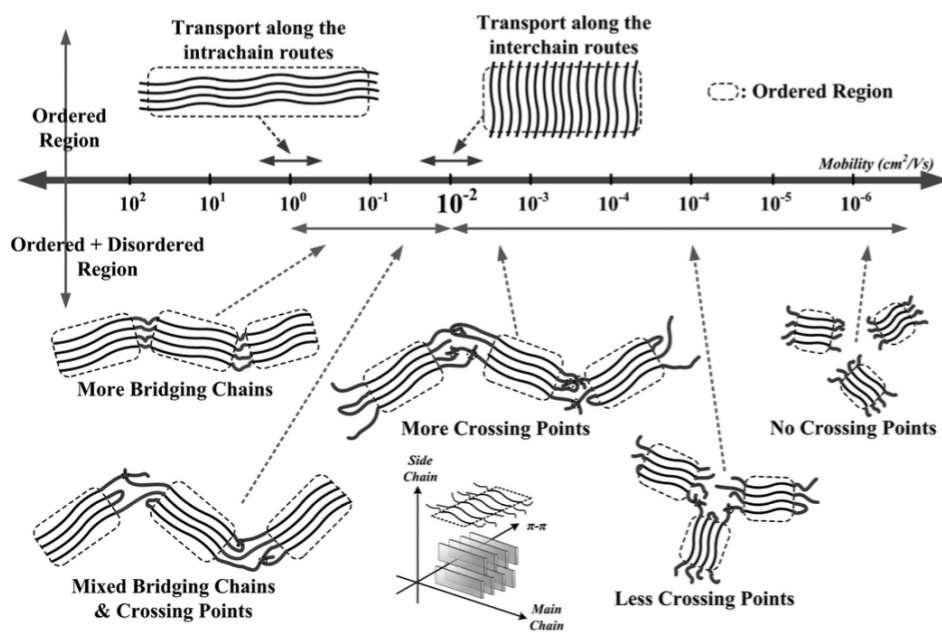
*Macromolecules* **2005**, 38, 3312-3319



# Mobility as a function of molecular arrangement



*Adv. Funct. Mater.* **2010**, *20*, 2286



*J. Phys. Chem. B* **2009**, *113*, 14555

# Degradation mechanisms in Polymer Solar Cells

# WHY ARE ORGANIC SOLAR CELLS NOT STABLE?

## (Un)stability of organic materials (active & buffer layers):

Polymer materials are dynamic and reactive, and prone to attack by a range of agents.

Parameters influencing the stability:

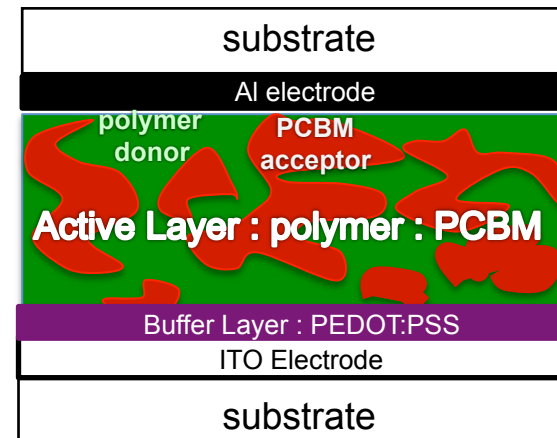
- Heat
- Oxygen
- Water
- Light (UV)

Type of degradation:

Chemical degradation

Morphological degradation

- Mechanical stress
- Metastable morphology



## (Un)stability of the electrodes:

Chemical degradation of the **metallic electrodes** with oxygen (corrosion)

→ Many sources of degradation

# METASTABLE MORPHOLOGY OF THE ACTIVE LAYER

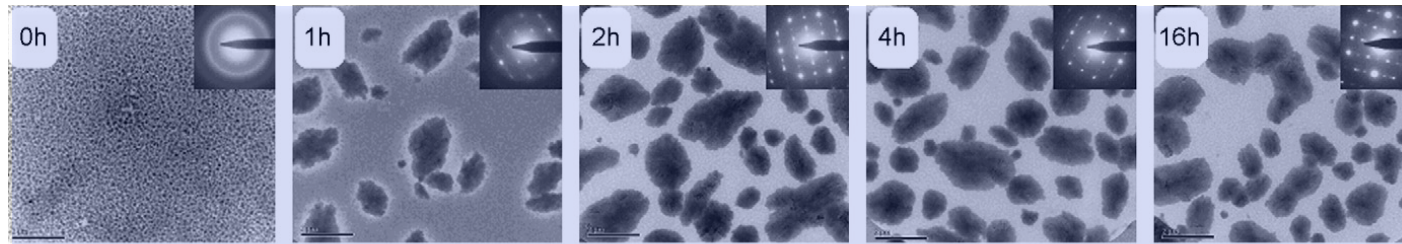
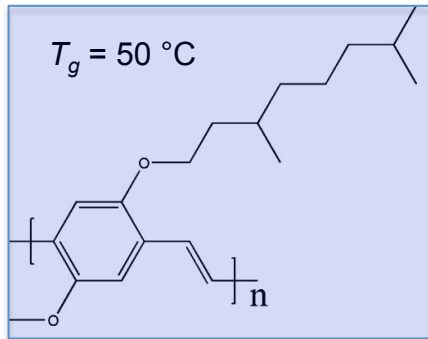
The bulk heterojunction with an initial specific morphology of interconnected domains do not necessarily represent the most thermodynamically stable configuration and growth of PCBM acceptor crystallites altering the optimal morphology has been observed.

During illumination the active layer may reach temperatures high enough to initiate further phase separation

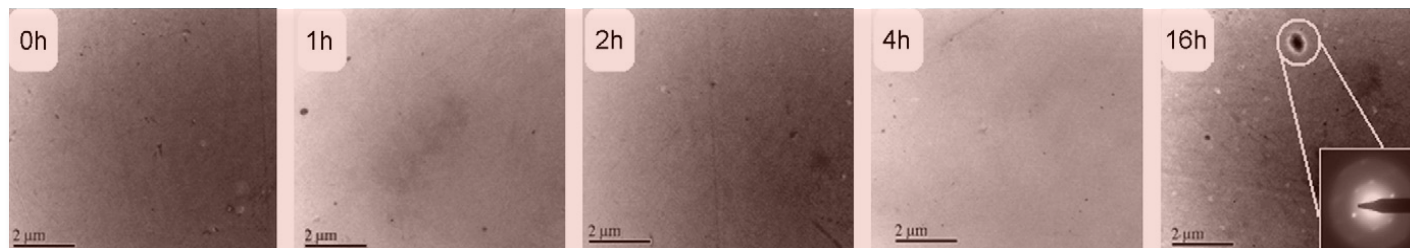
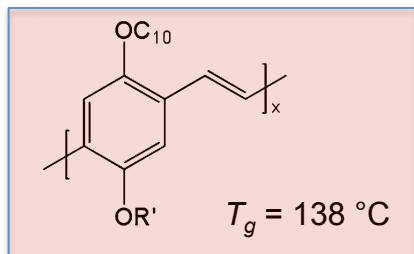
- larger domains, less effective exciton dissociation and smaller photocurrent.
- growth of large, micrometer-sized PCBM crystals that will hamper the solar cell performance considerably

# INCREASING $T_g$ TO STABILIZE THE MORPHOLOGY

Active layer : Polymer + PCBM annealed at 110°C



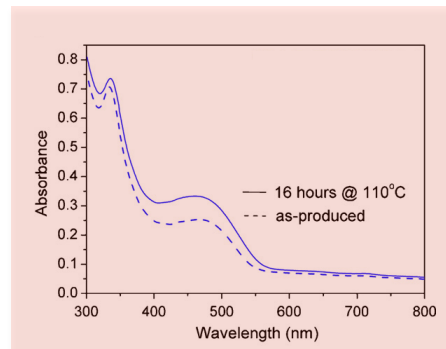
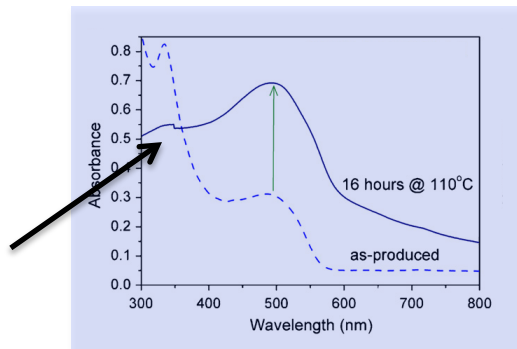
The active layer based on **MDMO-PPV** show a rapid formation of PCBM-clusters upon annealing  
 → decrease in the D/A interfacial area.



The morphology changes are strongly suppressed in the '**High  $T_g$  PPV**' active layers thanks to a firmer matrix which restricts the possible migration and segregation of the PCBM molecules  
 → more stable active layer

Absorption of the Active Layer :

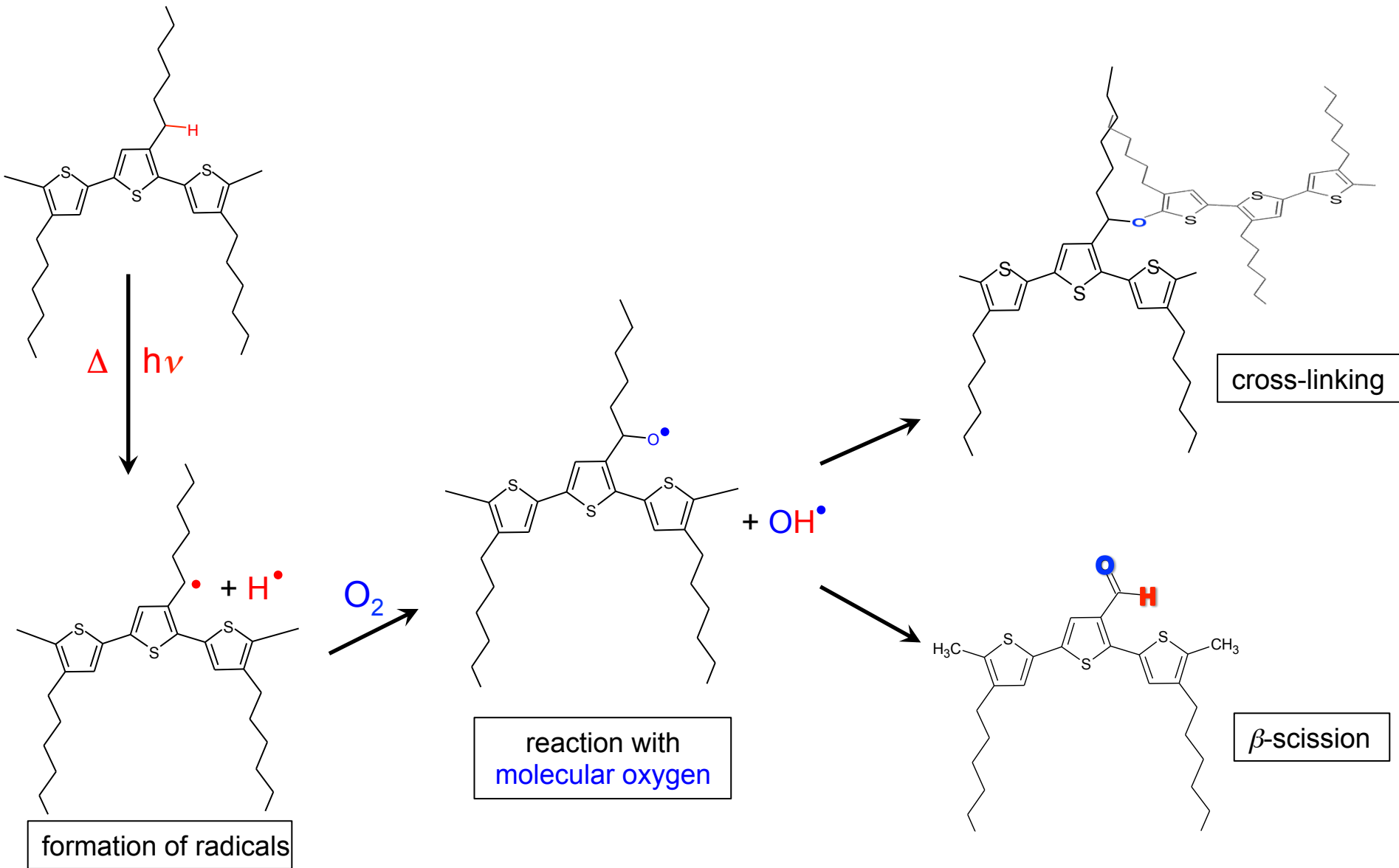
Disappearance of PCBM absorption



*Solar Energy Materials & Solar Cells* 2008, 92, 753–760

# Photo-oxidation of P3HT

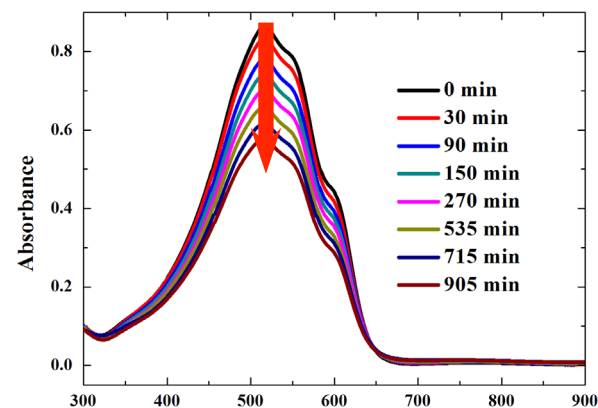
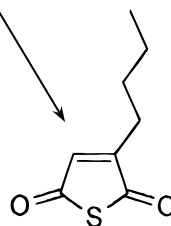
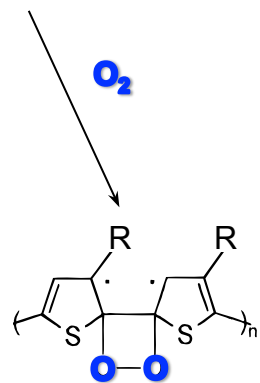
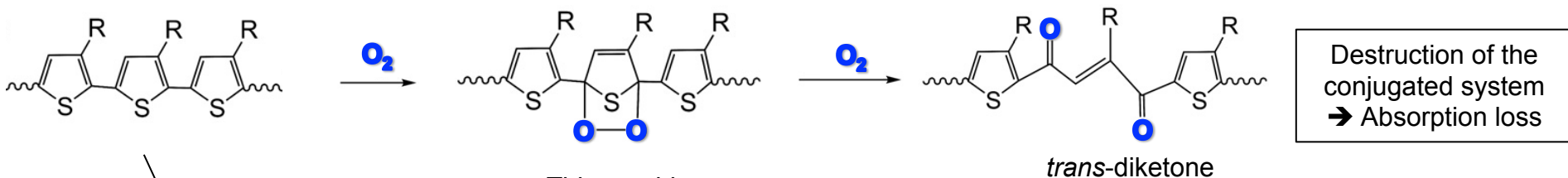
Degradation of the side chains:



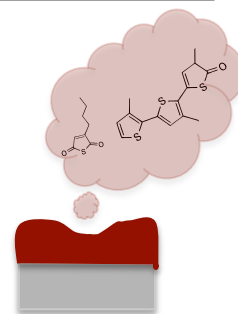
# Photo-oxidation of P3HT

## Degradation of the backbone:

Addition of  $O_2$  to thienyl units



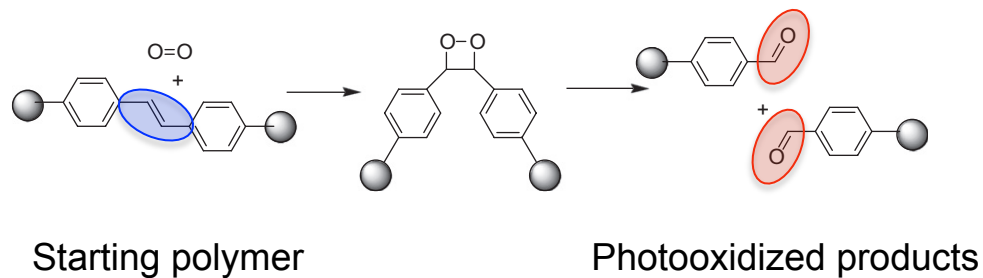
*Sol. Ener. Mater. Sol. Cells* **2014**, 123, 150–158



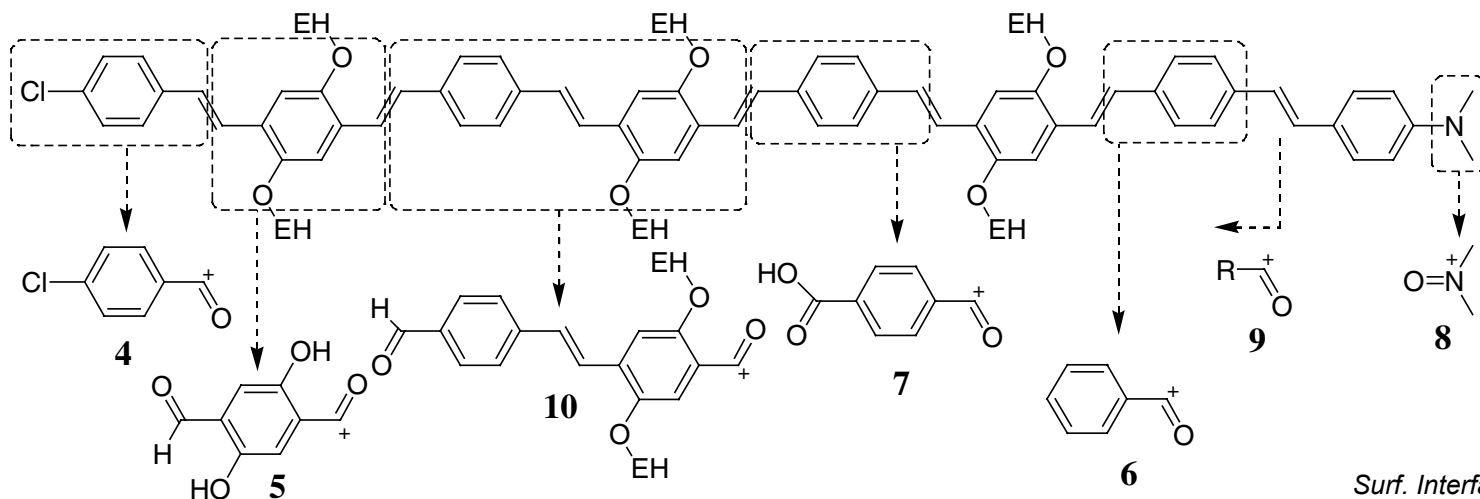
# Photochemistry of PPVs: photo-oxidation

## Fragmentation of the conjugated backbone:

- Photoexcited polymer transfers energy to  $O_2$
- Singlet oxygen reacts with the vinylene group
- Formation of an intermediate product that breaks down by chain scission:



Characterization by IR spectroscopy: simultaneous diminution of the peaks due to the **vinylene** groups and appearance of a broad **carbonyl** peak



*Surf. Interface Anal.* **2006**, 38, 1302–1310

- Identification of the fragments by mass spectrometry
- Fragmentation of the whole polymer chains in small photo-oxidation products

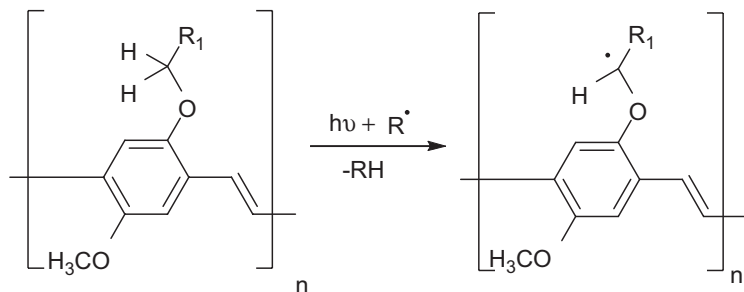


# Photochemistry of PPVs: photo-oxidation

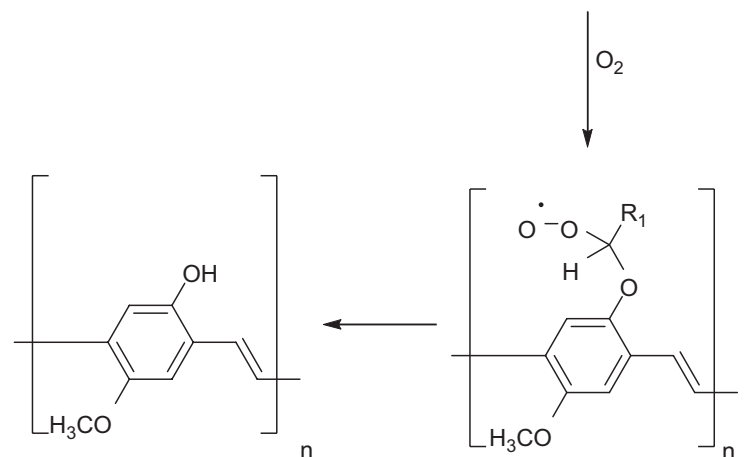
## Fragmentation of the ether side chains:

### MDMO-PPV

Oxidation of the ether side chains



Radical-initiated oxidation ( $\text{R}^\bullet$ )



- When MDMO-PPV +  $\text{C}_{60}$ : degradation was retarded by a factor of 10:

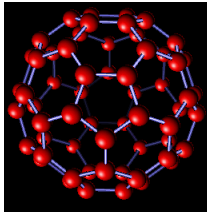
$\text{C}_{60}$  acts as a radical scavenger

- In absence of  $\text{O}_2$ , degradation 1000 times slower

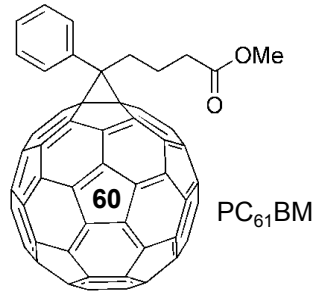
*J. Polym. Sci A Polym. Chem.* **2007**, 45, 317 – 331

# Fullerenes as acceptors : PC<sub>60</sub>BM

Fullerene C60



« footbalene »



Discovered in 1985 (*Nature* **1985**, 318, 162-163)  
Nobel Prize to H. Kroto, R. Smalley, R. Curl in 1996

## Advantages:

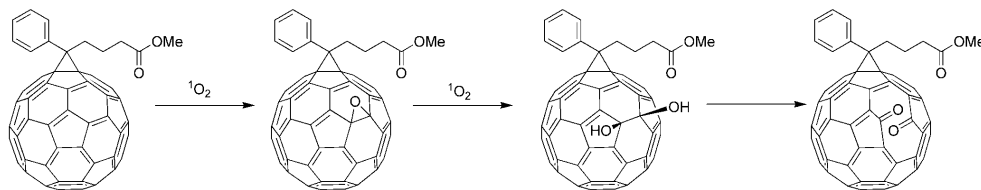
- Surface energy compatible with those of polymer
- High electron mobility (up to 1 cm<sup>2</sup>/V.s, long exciton diffusion length ≈ 40 nm)
- Large electron affinity : LUMO: -3.7/-4.3 eV:
- Well soluble in organic solvents
- Size of domaines D/A similar to exciton diffusion length
- Isotropic Charge transport: 3D compatible with polymers
- Good thermal stability (> 250°C)
- 5000 \$/g in 1990; 120\$/g in 2017 !!! Industrially used



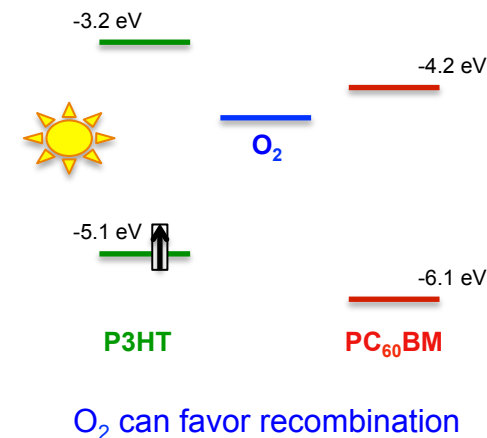
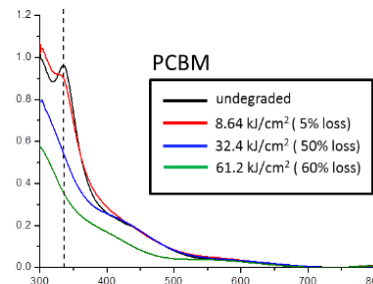
« polymer/fullerene blend »

## Drawbacks:

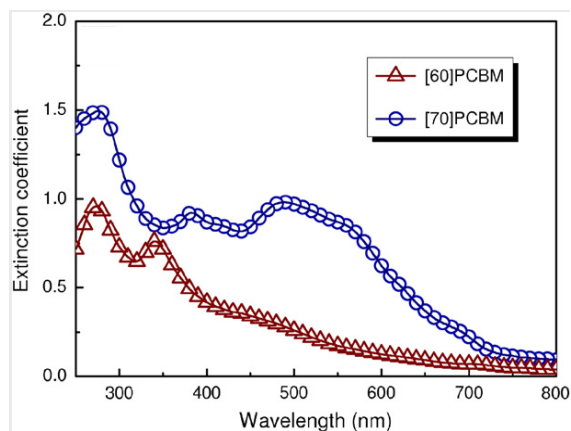
- No green synthesis
- Aggregation in operating conditions
- Limited tunability of the energy levels
- Low visible absorption
- Photo-oxidation was evidenced:



J. Am. Chem. Soc. **2007**, 129, 16149-16162  
Chem. Commun. **2012**, 48, 3878-3880



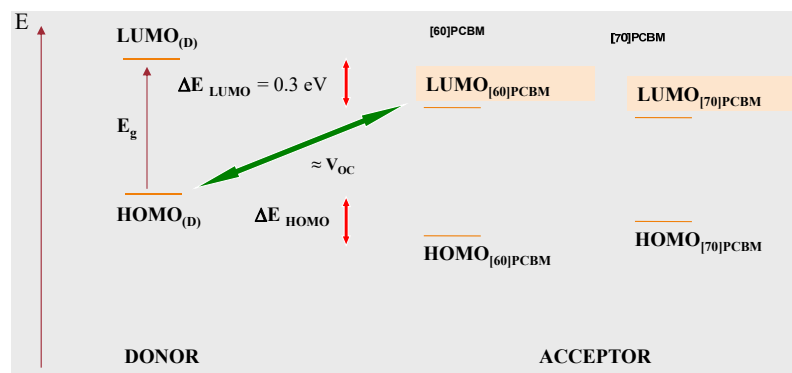
→ PC<sub>61</sub>BM replaced by PC<sub>71</sub>BM



- **PC<sub>70</sub>BM** most absorbant in the visible range
- Better photochemical stability

But...

As for PC<sub>60</sub>BM, the low-lying LUMO level limits the  $V_{OC}$

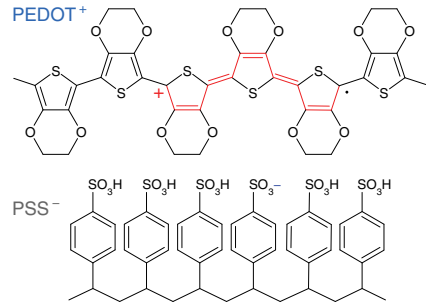


*J. Mater. Chem.* **2010**, *20*, 2934

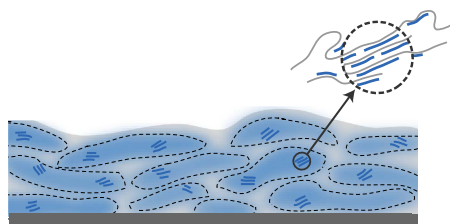
**PC<sub>70</sub>BM** is expensive (> 600 €/g) and no-green synthesis

# Photo-oxidation of PEDOT:PSS

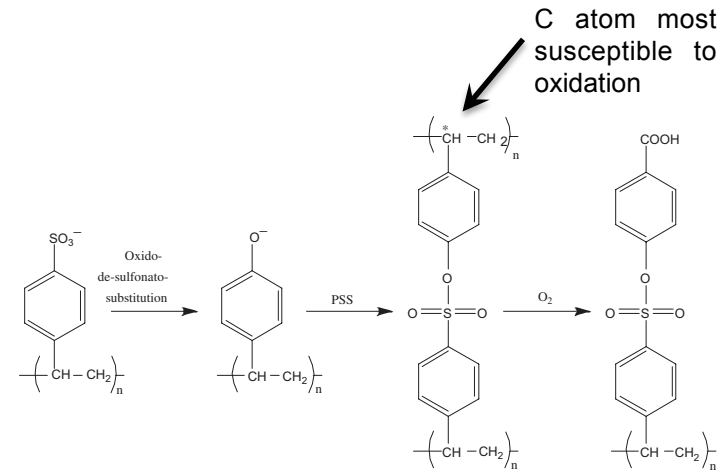
**Poly(3,4-ethylenedioxythiophene)** polystyrene sulfonate (PEDOT:PSS) : smoothes the electrode surface and acts as a hole transporting layer



Aggregates/crystallites :  
enhanced electronic transport



*Nature Commun.* **2016**, 7, 11287



Oxidative degradation of PSS in PEDOT:PSS.

Also, PEDOT:PSS is very acidic (pH = 1-3)

- ➔ Corrosion of the adjacent metallic electrode (with water)
- ➔ Etching of ITO

PEDOT:PSS is found as one of the main sources of device degradation

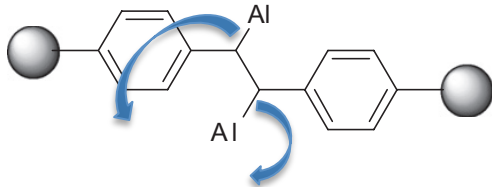
# Chemical degradation of the electrodes

## Metal electrodes (anode):

Al and Ca are attractive metals used as negative electrodes in OPV devices because of their low work function, high electrical conductivity, and their ability to be deposited as thin layers.

But: they are in consequence highly reducing

- Oxidation at the metal/polymer interface and/or at the upper surface of the metal layer
  - formation of an insulating layer of metal oxide (barrier to charge extraction)
- Water diffuses through the device *via* the Al grains and leads to degradation at all the interfaces
- Oxygen diffuses mainly through the pin-holes in the aluminum film causing localized or inhomogeneous degradation
- Al species diffuse through the device and form organo-metallic compounds with the active layer



C-Al bond reacts with  $H^+$  ( $H_2O$ ) or  $O_2$

*J. Chem. Phys.* **1994**, *101*, 4357

## ITO (cathode: transparent as thin film and conductive): $In_2O_3$ doped with $SnO_2$

→ Indium was found in the PEDOT:PSS layer

→ Hygroscopic nature of PSS facilitates absorption of water that leads to etching of the ITO layer

*Chem. Phys. Lett.* 2015, *640*, 201–214

# How to increase the stability of Polymer Solar Cells?

# Increasing the stability of Polymer Solar Cells : active layer improvement (1)

Improving properties of the active materials :

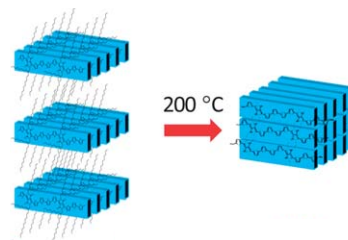
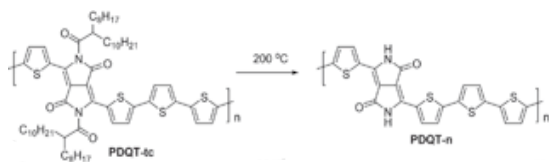
→ appropriate tuning of their **electronic levels** :

→ HOMO level cannot be more positive than 5.2 eV (oxidation threshold of air)

→ HOMO of the donor should be reasonably low to achieve high  $V_{OC}$

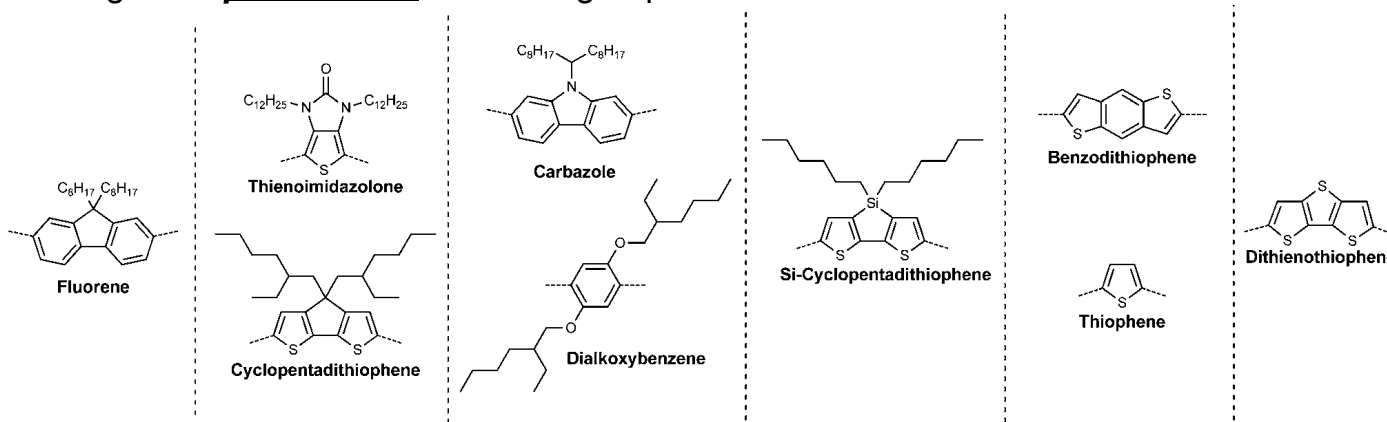
→ tuning of their **glass-transition** temperature (cross-linking)

→ using **thermo-cleavable side chains** : side chains are eliminated post deposition, making otherwise unprocessable but stable materials available



*J. Mater. Chem.*, 2012, 22, 18950–18955

→ Using more **photostable** chemical groups



**Stability**

*J. Mater. Chem.* 2011, 21, 4132–4141

## Increasing the stability of Polymer Solar Cells : active layer improvement (2)

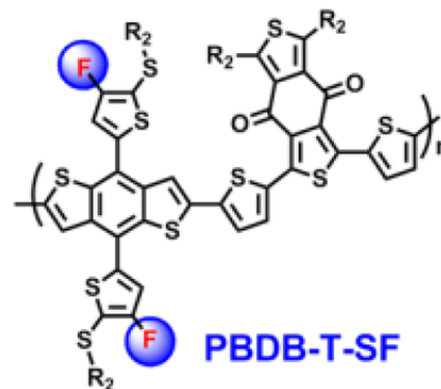
Fullerene derivatives : « universal » electron acceptors but : limited tunability of energy levels, poor light absorption ability, weak endurance against thermal, photo and morphological stresses.

### Designing Non Fullerenes Acceptors (NFA)

Fluorinated molecules:



Acceptor



Donor

Structure of the device : ITO / PBDB-T-SF:IT-4F / MoO<sub>3</sub> / Al

PCE = 13.1 %

Increase in device efficiency due to:

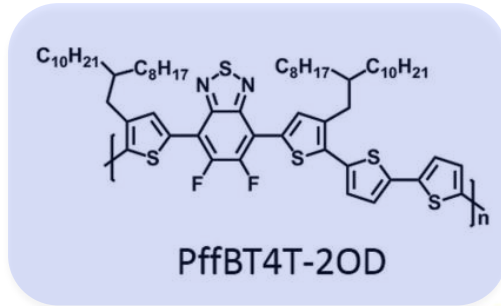
- better crystallinity (F...H; F...S; F... $\pi$  non covalent interactions)
- improve charge transport
- absorption shifted to the red

*J. Am. Chem. Soc.* **2017**, *139*, 7148–7151



# Non Fullerenes Acceptors (NFA)

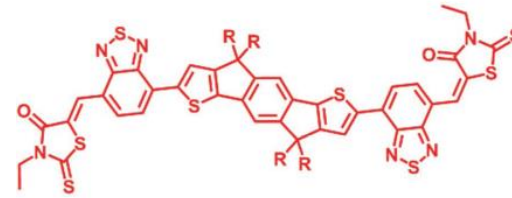
Donor



$$E_{LUMO} = -3.69 \text{ eV}$$

$$E_{HOMO} = -5.34 \text{ eV}$$

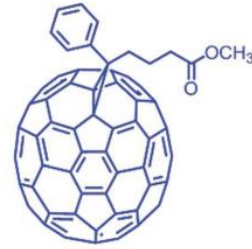
Acceptors



EH-IDTBR (R=Ethylhexyl)

$$E_{LUMO} = -3.90 \text{ eV}$$

$$E_{HOMO} = -5.58 \text{ eV}$$

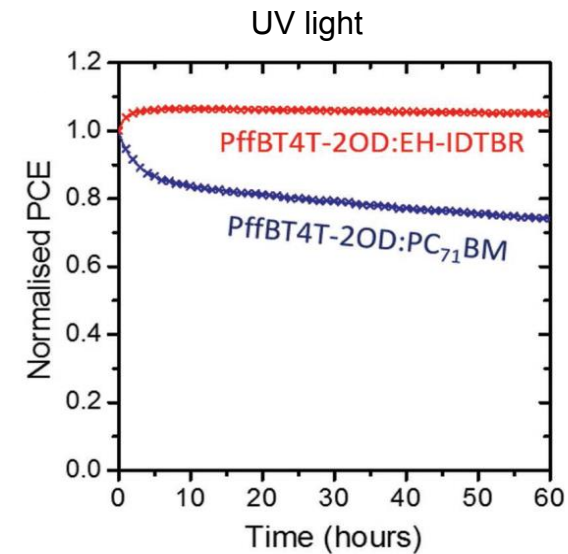
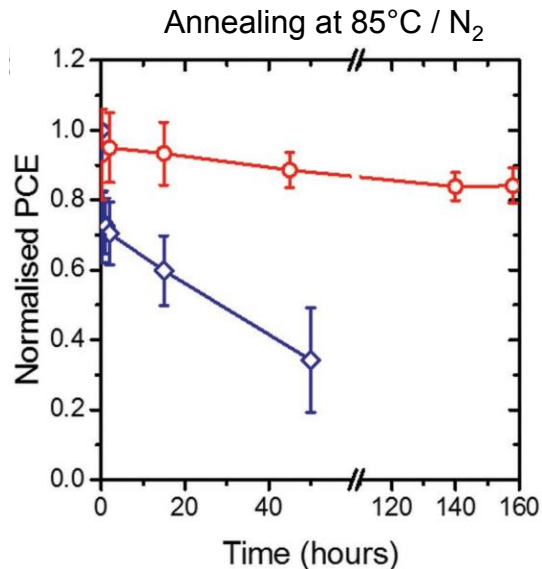
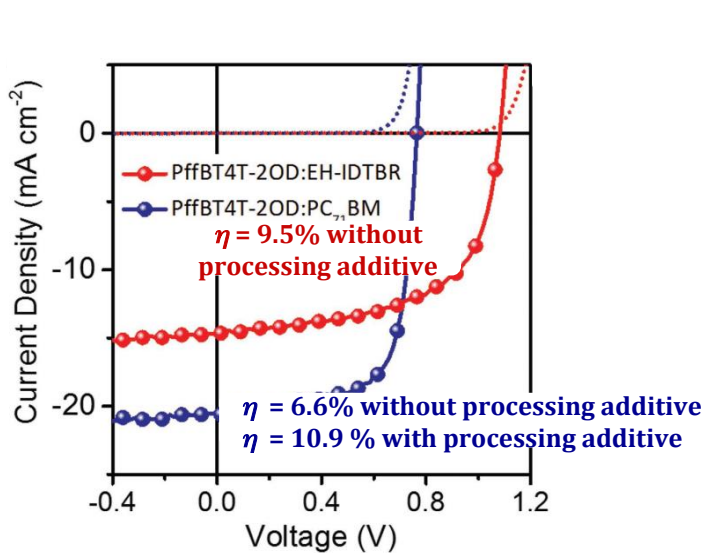


PC<sub>71</sub>BM

$$E_{LUMO} = -4.10 \text{ eV}$$

$$E_{HOMO} = -6.10 \text{ eV}$$

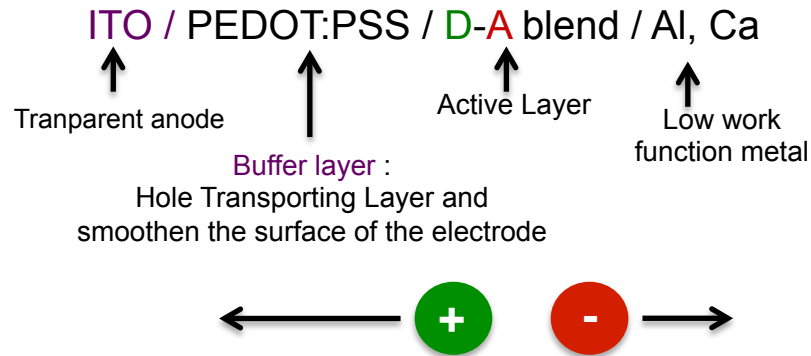
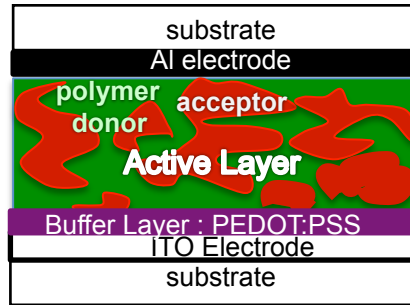
Structure of the device (inverted configuration) : Ag / MoO<sub>3</sub> (HTL) / Donor + acceptor / ZnO (ETL) / ITO



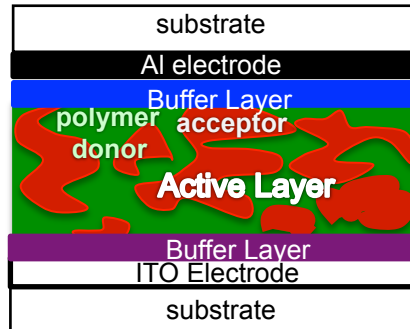
NFA: device more resistant to UV, heat, higher  $V_{OC}$  due to highest LUMO level

# Increasing the stability of Polymer Solar Cells : structure of the device

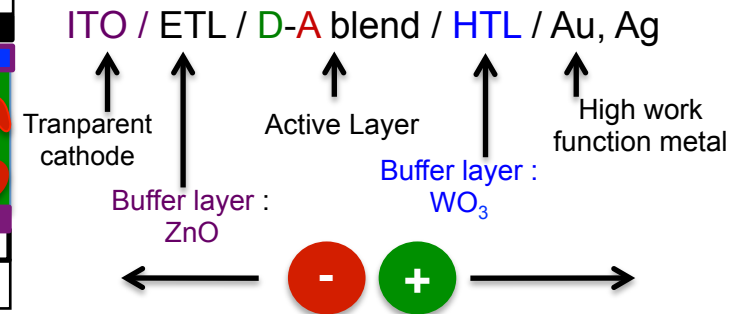
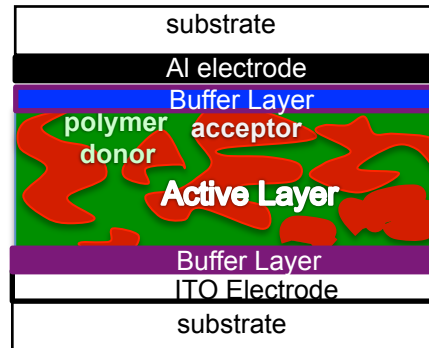
## Conventional structure :



## Improved conventional structure :



## Inverted structure :



- LiF as a cathode buffer layer:
  - prevents diffusion of cathode elements to the AL
  - acts as an Electron Transport Layer (ETL)
- Replace acidic PEDOT:PSS by more stable materials such as MoO<sub>3</sub>

Encapsulation of the device: encapsulant material must be capable of reducing the ingress of moisture and oxygen as well as remaining resistant to UV radiation. It also protects the device against scratch and improves mechanical flexibility.

Some encapsulants: poly(ethylene naphthalate), polyurethane, alternate coatings of polyacrylate/Al<sub>2</sub>O<sub>3</sub>.

# General Conclusion : Polymer Solar Cells

- Suitable for Embarked electronics :

→ mechanical flexibility of the materials and devices



- Record efficiency > 13%

→ possibility to tune energy levels (chemistry), improve morphology (donor/acceptor interface)

- Lifetime : >1 year (7 years at optimal orientation / 10 years in vertical conditions have recently been reported  
*Adv. Energy Mater.* **2017**, 7, 1701201)

- Low-cost devices and large area: solution processing

3 points to mature to the market :

- processing
- stability
- efficiency