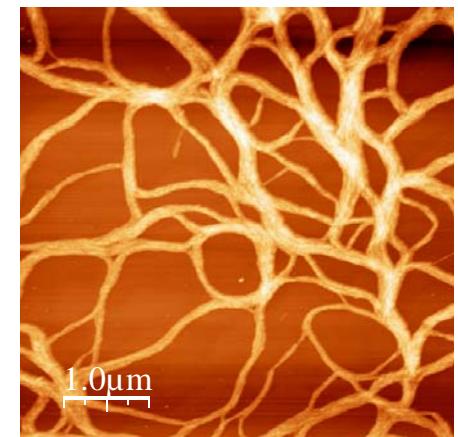


# Nanostructured Polymers and Composites for Applications in Organic Photovoltaic Devices



Renaud Demadrille



## Outline

---

### Introduction and objectives

#### 1-Design of new electron donors for BHJ solar cells

- . Synthesis of the oligomers and copolymers
- . Self-organisation properties
- . Optical and electrochemical properties
- . Photovoltaic properties

#### 2-Nano-structuration of P3HT

- . Formation of nanofibers with P3HT
- . Nanostructured layers and photovoltaic properties

#### 3-Organic-Inorganic hybrid composites for solar cells

- . Preparation of nanocrystals-polymer composites
- . Nanostructured hybrid composites
- . Self-assembly approach : control of the morphology

### Conclusions

# Introduction

## Bulk-heterojunction solar cells (p-n)

- 2 Interpenetrated percolating networks
- Optimal phase segregation (10-20nm)

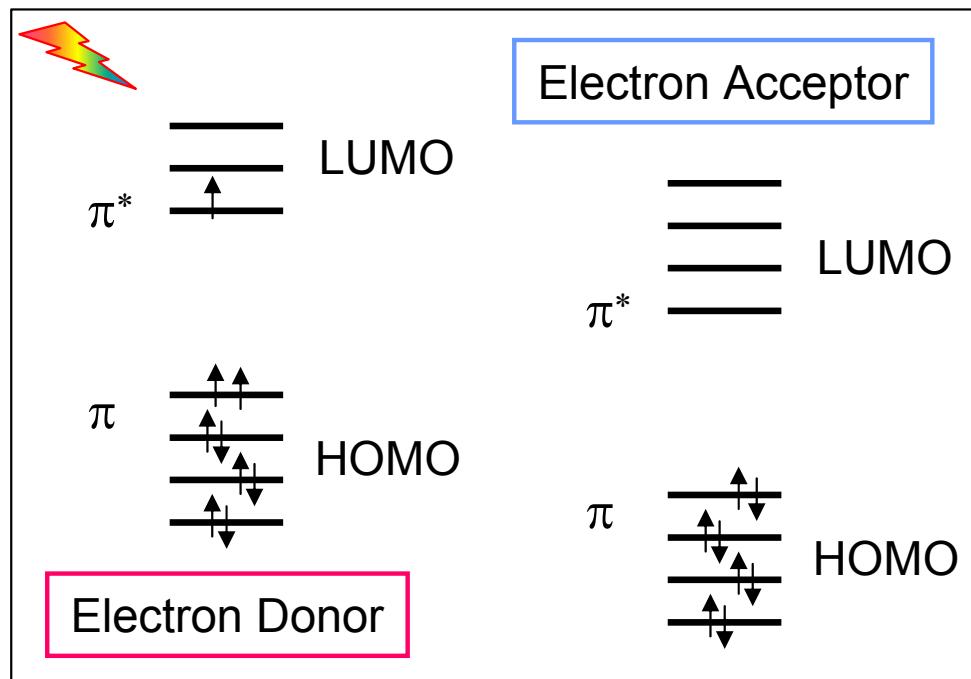
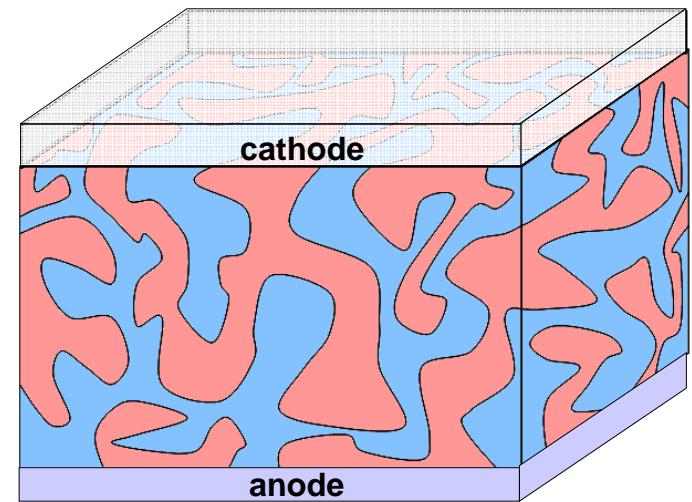
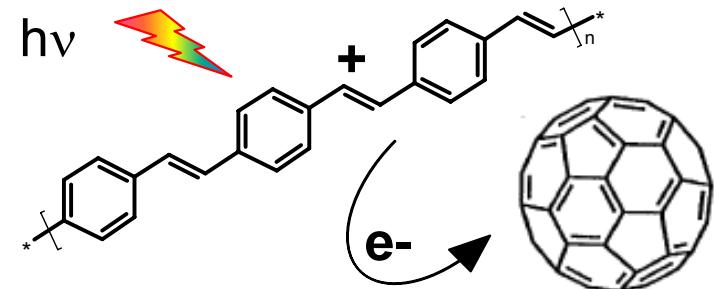


Photo-induced charge transfert



Heeger et al., *Science*, 1992, 258, 1474.

Photo-induced charge transfer <  $10^{-12}$  s



# Introduction

Best performances :

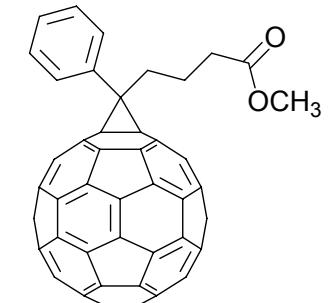
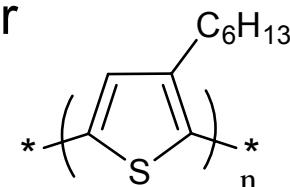
5 % obtained with P3HT-PCBM active layer

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.



# Introduction

Best performances :

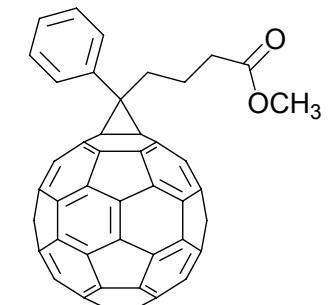
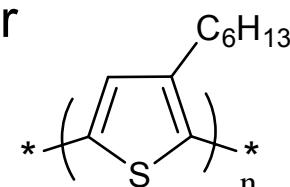
5 % obtained with P3HT-PCBM active layer

M. Reyes-Reyes et al., *Appl. Phys. Lett.*, **2005**, 87, 083506.

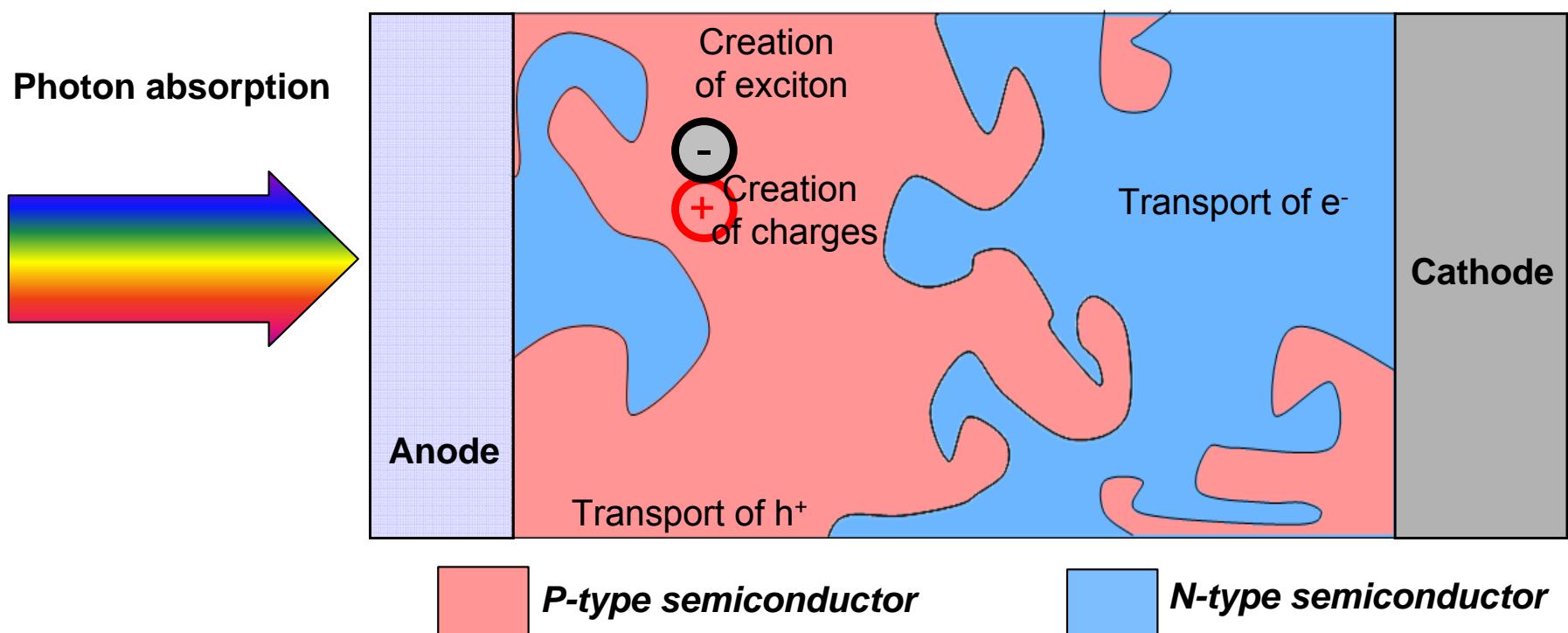
W. Ma et al., *Adv. Funct. Mater.*, **2005**, 15, 1617.

G. Li et al., *Nature Mater.*, **2005**, 4, 864.

Y. Kim et al., *Nature Mater.*, **2006**, 5, 197.



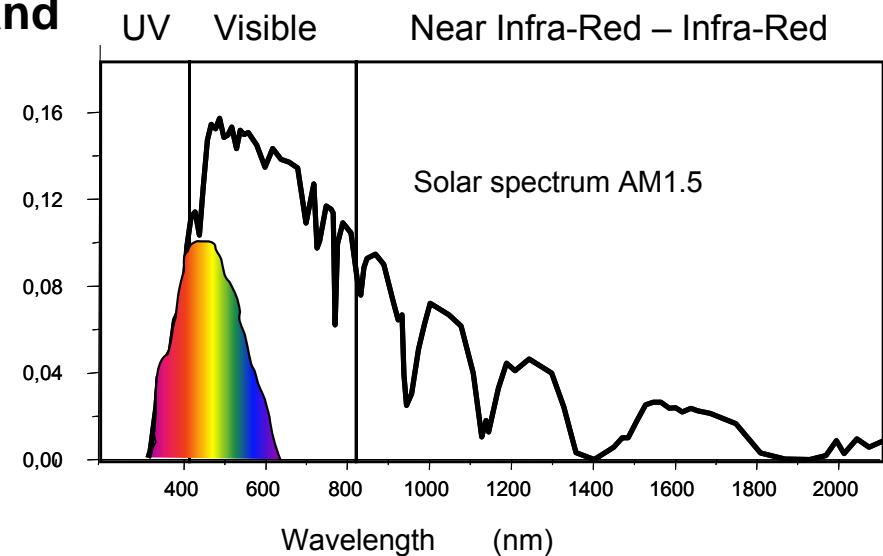
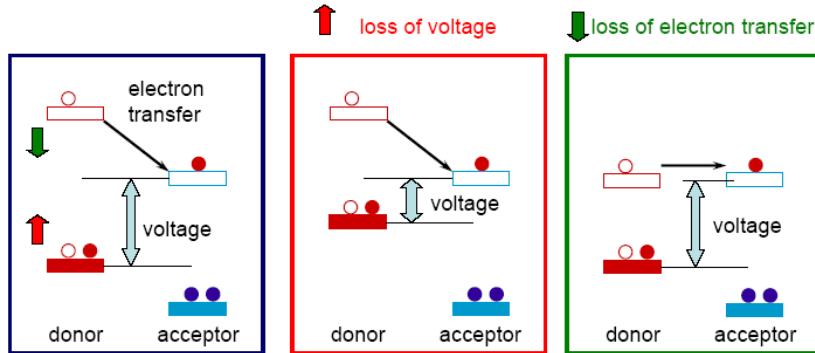
## Photo-induced charge transfert



# Objectives

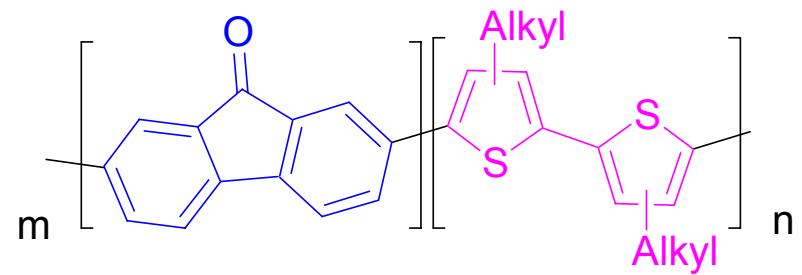
**1-Design and synthesize new oligomers and polymers showing large absorption spectral range.**

**2-The energy levels must be precisely tuned**

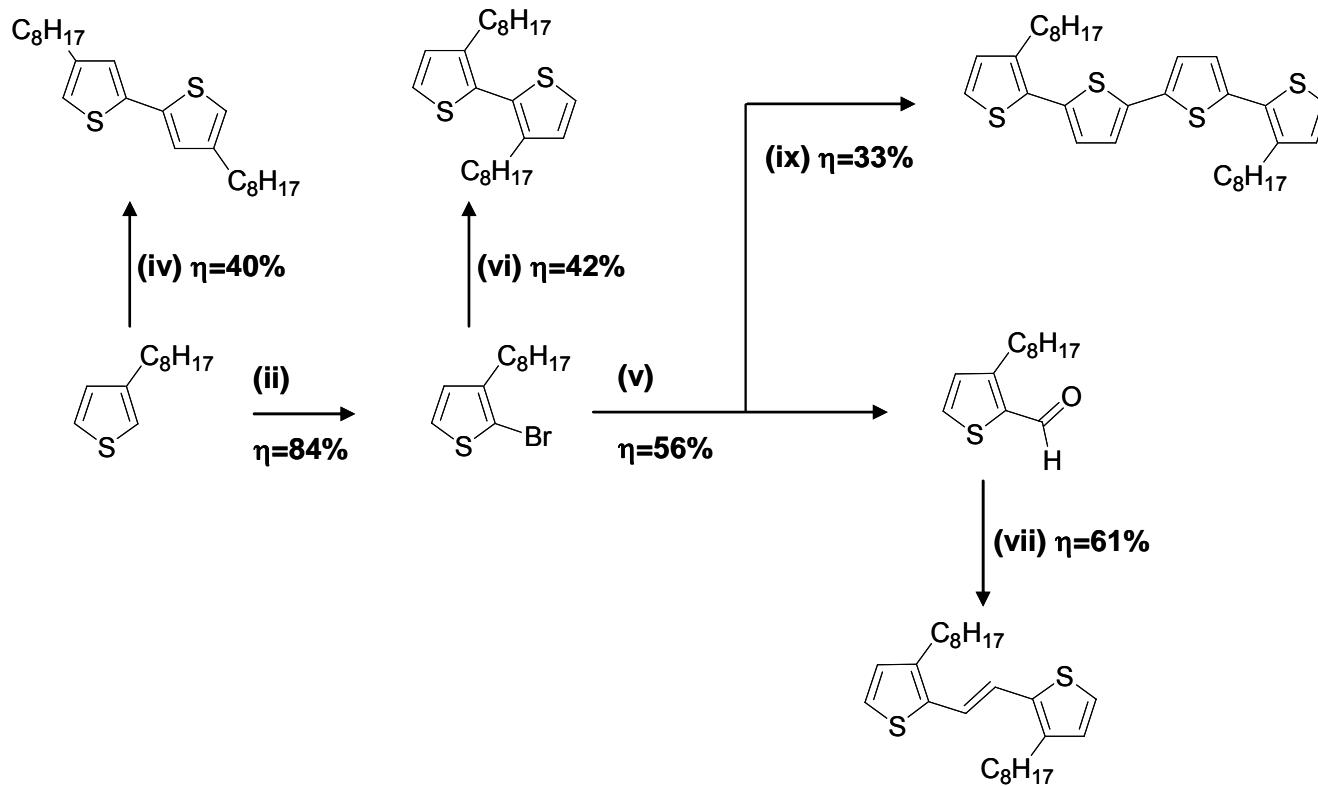


**3-Optimization of the chemical structures to facilitate the self-organization**

Strategy : **Acceptor-Donor**  
Alternate regioregular copolymers



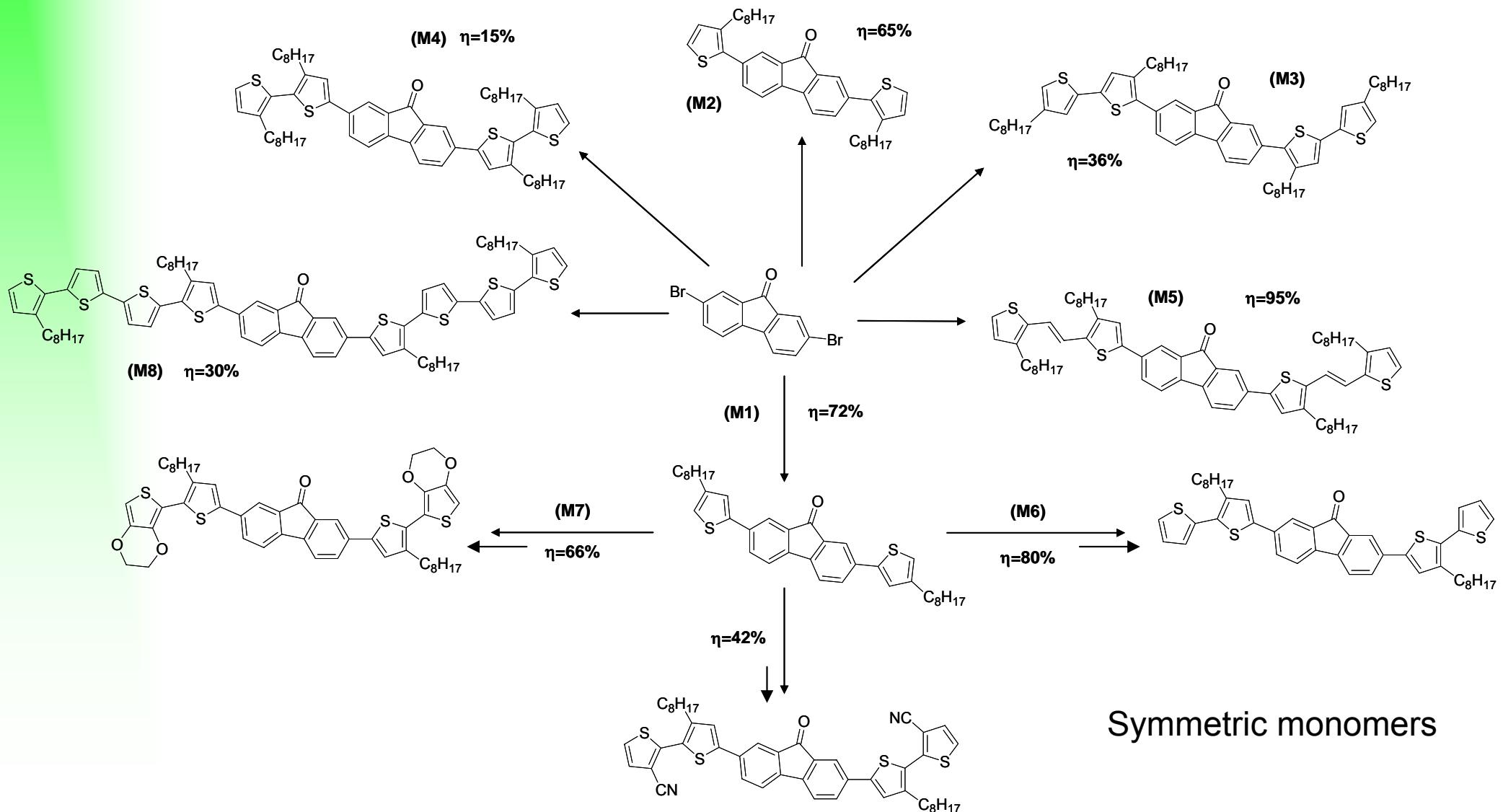
# Synthesis of the thiophene-based precursors


**Conditions:**

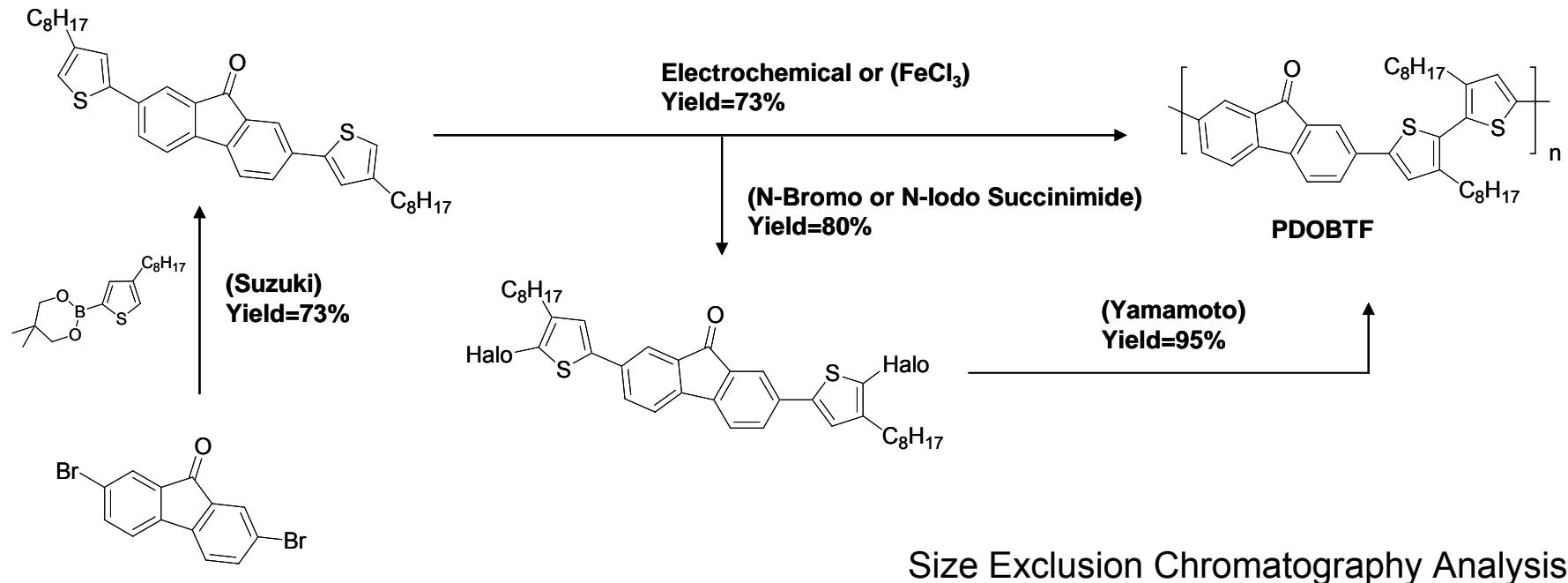
- (i) BuLi, THF,  $B(OBu)_3$ , HCl, Propanediol, (ii) NBS, DMF, (iii) Mg, THF,  $B(OBu)_3$ , HCl, Propanediol, (iv) BuLi, THF,  $CuCl_2$ , (v) Mg, THF, DMF, (vi) (B2),  $Pd(PPh_3)_4$ ,  $K_3PO_4$ , DMF, (vii)  $TiCl_4$ , Zn, THF, (viii) BuLi, THF,  $ClSn(Me)_3$ , (ix) NBS (2.5eq), Chloroform, (x)  $FeCl_3$ , Nitromethane-Chloroform, (xi)  $Ni(COD)_2$ , COD, Bipy, THF-DMF
- (xii)  $Pd(PPh_3)_4$ ,  $K_3PO_4$ , DMF, (B1- B5)

# Synthesis of the fluorenone-based precursors

**Suzuki, Stille coupling conditions**



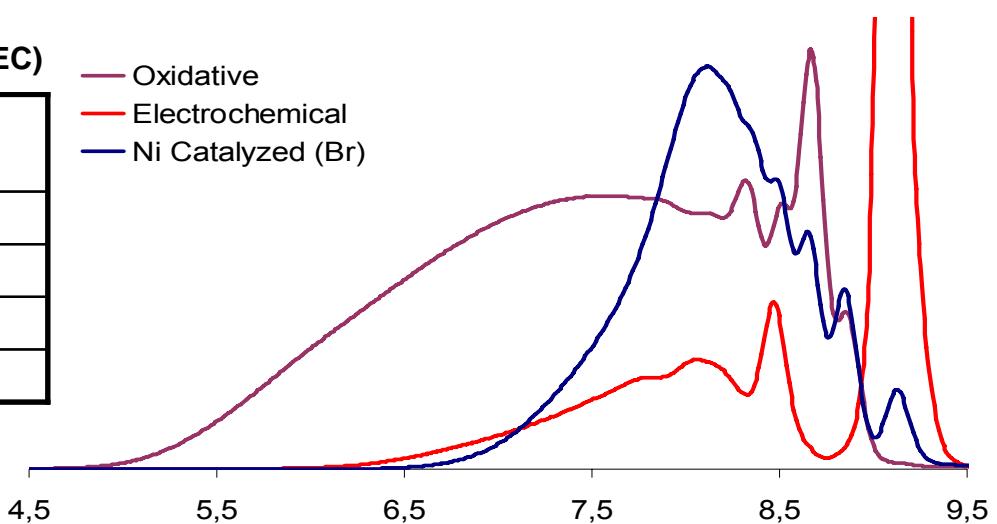
# Synthesis of the fluorenone-based copolymers



Size Exclusion Chromatography Analysis

Molecular Weight and Polydispersity (SEC)

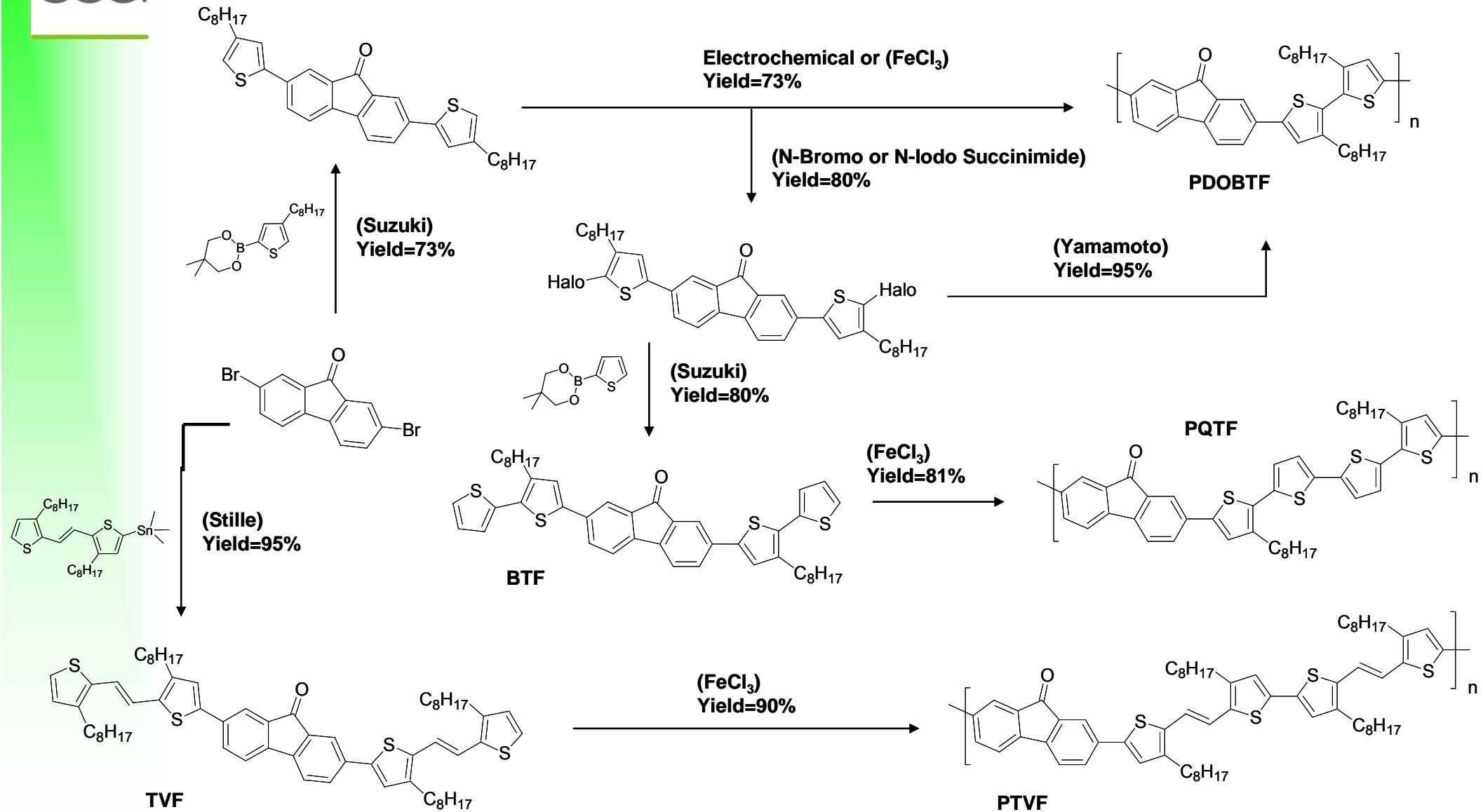
Polymerization method	Mn (Da eq PS)	Mw (Da eq PS)	Mw/Mn PDI
Oxidative ( $\text{FeCl}_3$ )	4990	31550	6.33
Electrochemical	5890	12820	2.18
Ni catalyzed (Br)	3010	8650	2.87
Ni catalyzed from (I)	1920	4620	2.41



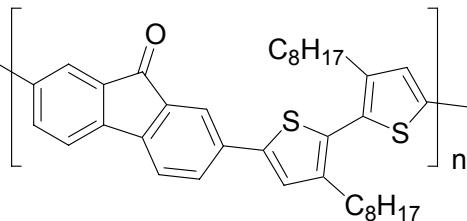
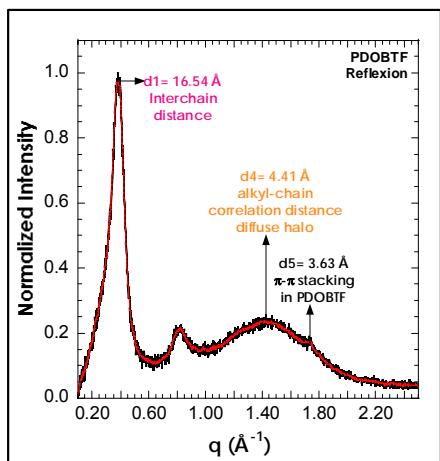
$M_w$  (Highest) = 74kDa and PDI=1.8

Demadrille et al. *Macromolecules*, 2003, 36, 7045.

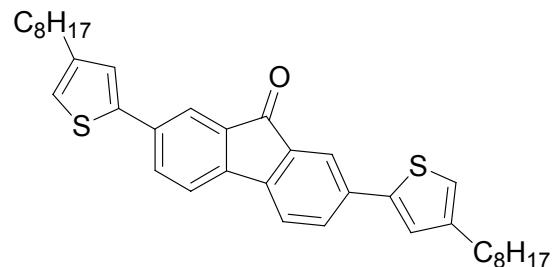
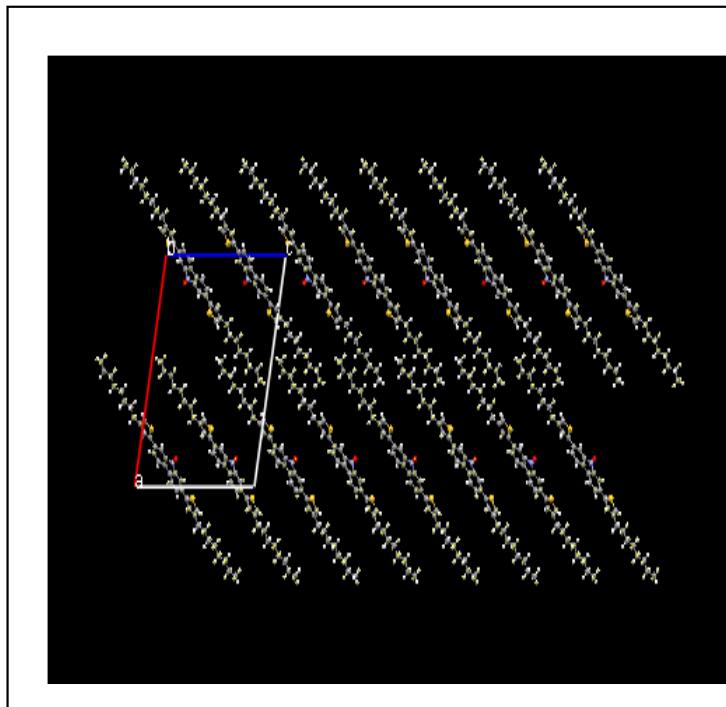
# Synthesis of the fluorenone-based copolymers



# Self-organization properties

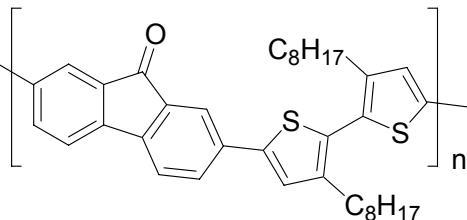
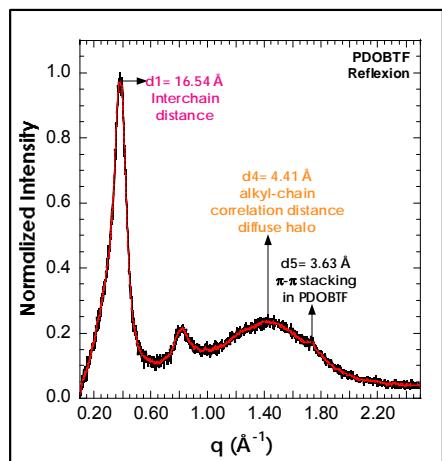


3D Self-organisation of fluorenone-based polymer PDOBTF  
: lamellar type system.

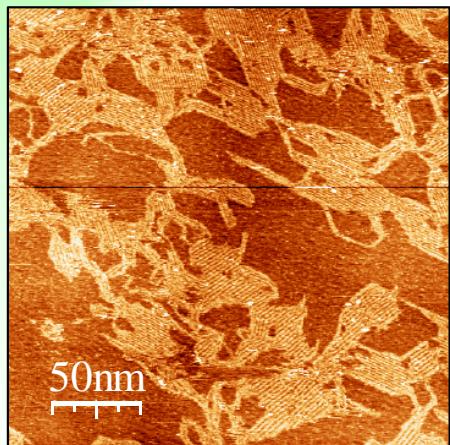


Planar molecule  
Lamellar organization  
in bulk-crystal

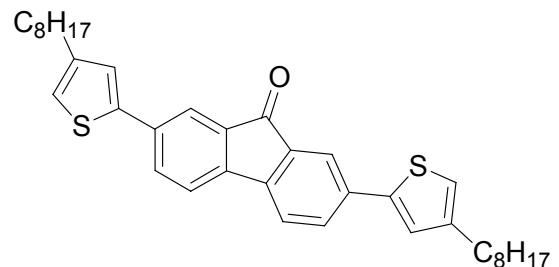
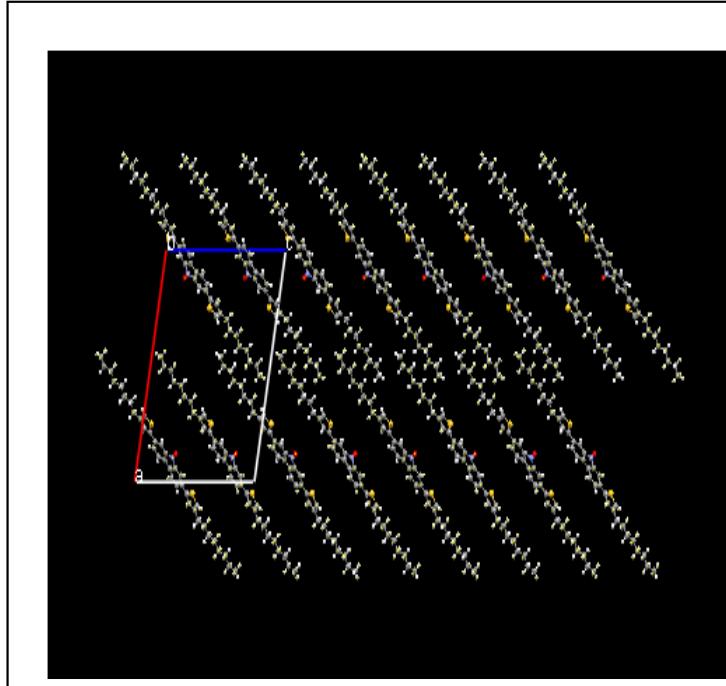
# Self-organization properties



3D Self-organisation of fluorenone-based polymer PDOBTF  
: lamellar type system.

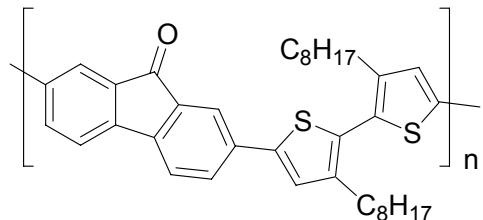


2D monolayer  
on HOPG  
STM study

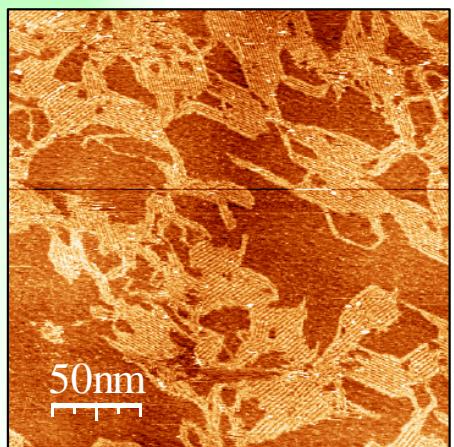


Planar molecule  
Lamellar organization  
in bulk-crystal

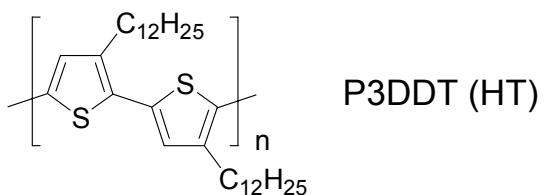
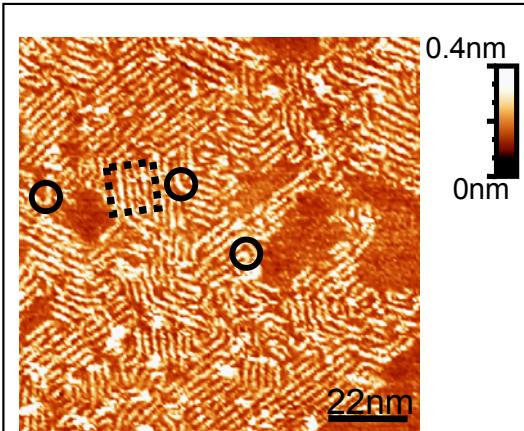
# Self-organization properties



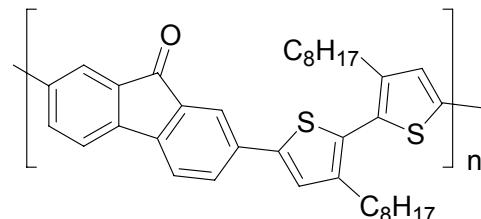
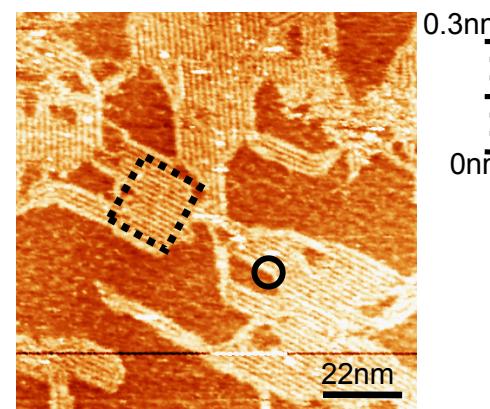
Brun et al. *Adv. Mater.*, 2004, 16, 2087.



2D monolayer  
on HOPG  
STM study



- Three different types of chains folds (60°, 120°, 180°)
- Size of the monodomains < chains length (~18nm)

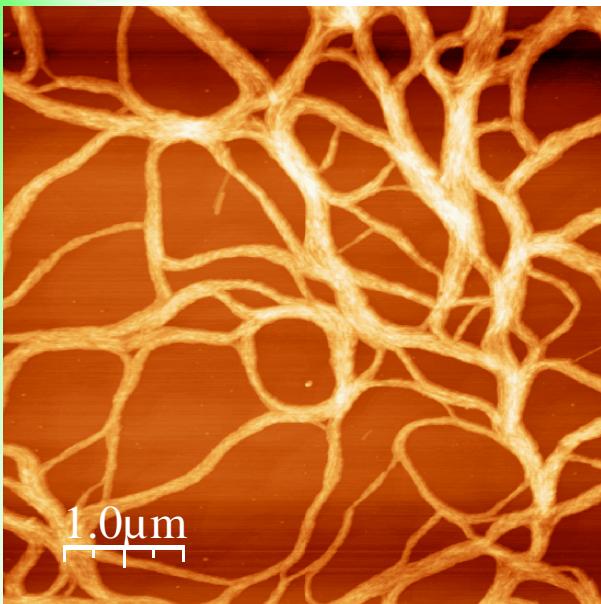
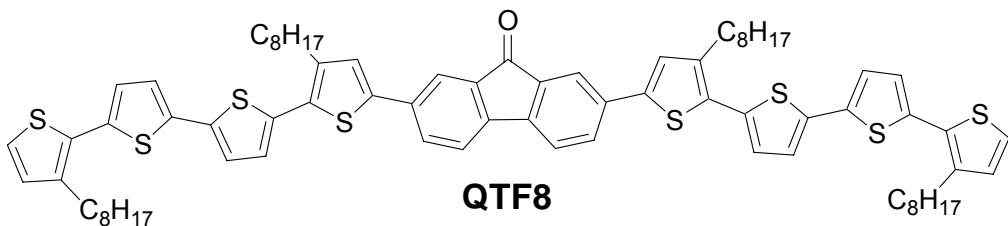


PDOBTf

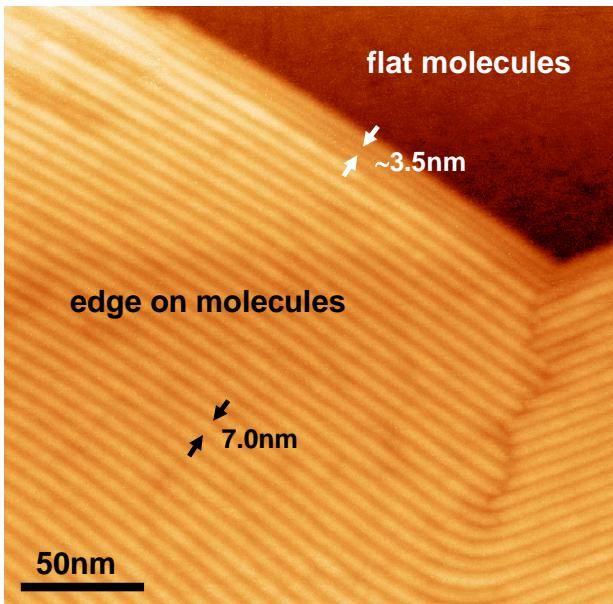
- Only one type of chain folds (120°)
- Size of the monodomains ~ Chains length (~17nm)

Polymer rigid: better 2D self-organization

# Self-organization properties

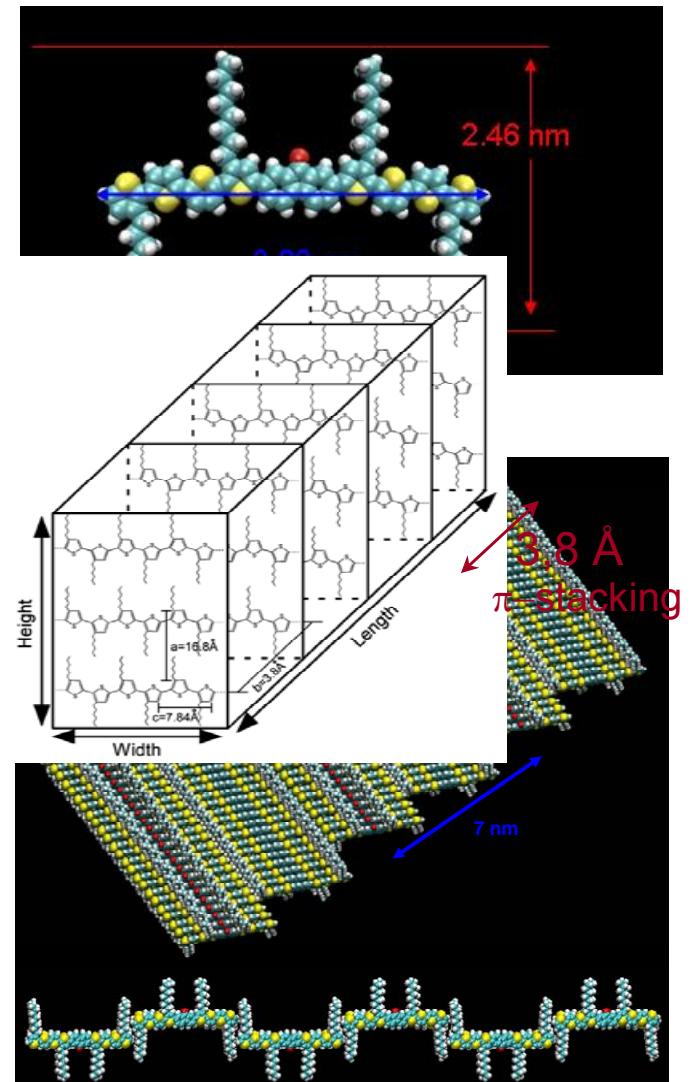


QTF8 on Al<sub>2</sub>O<sub>3</sub>, AM-AFM image.



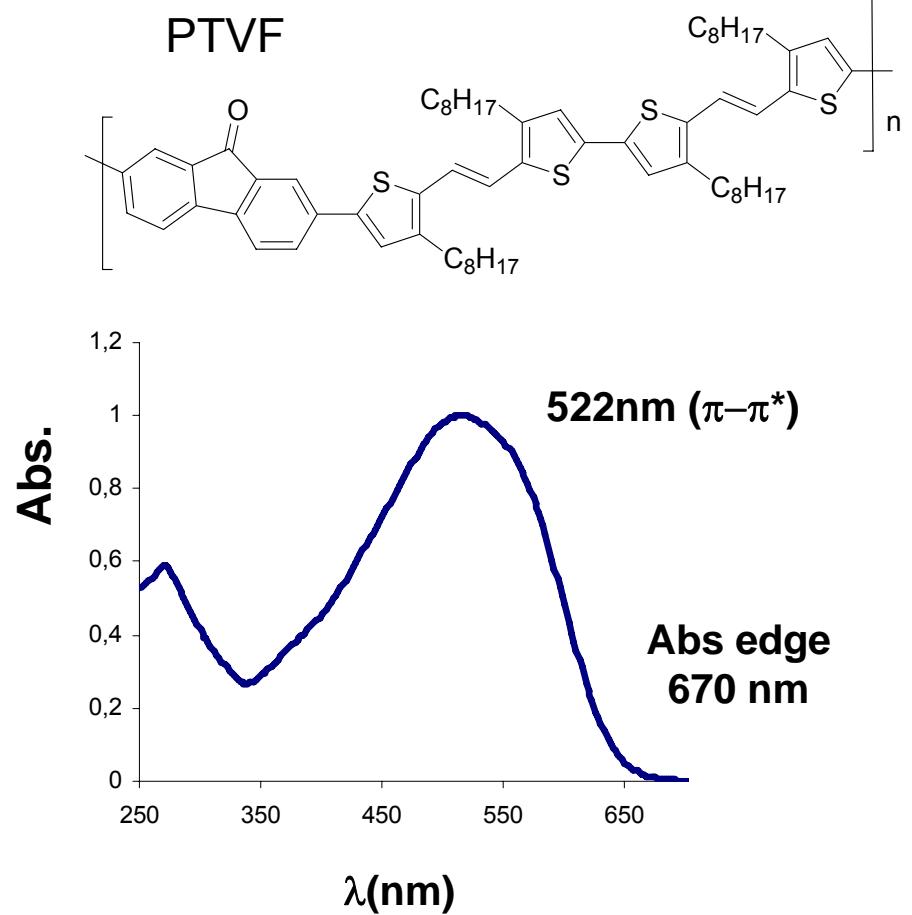
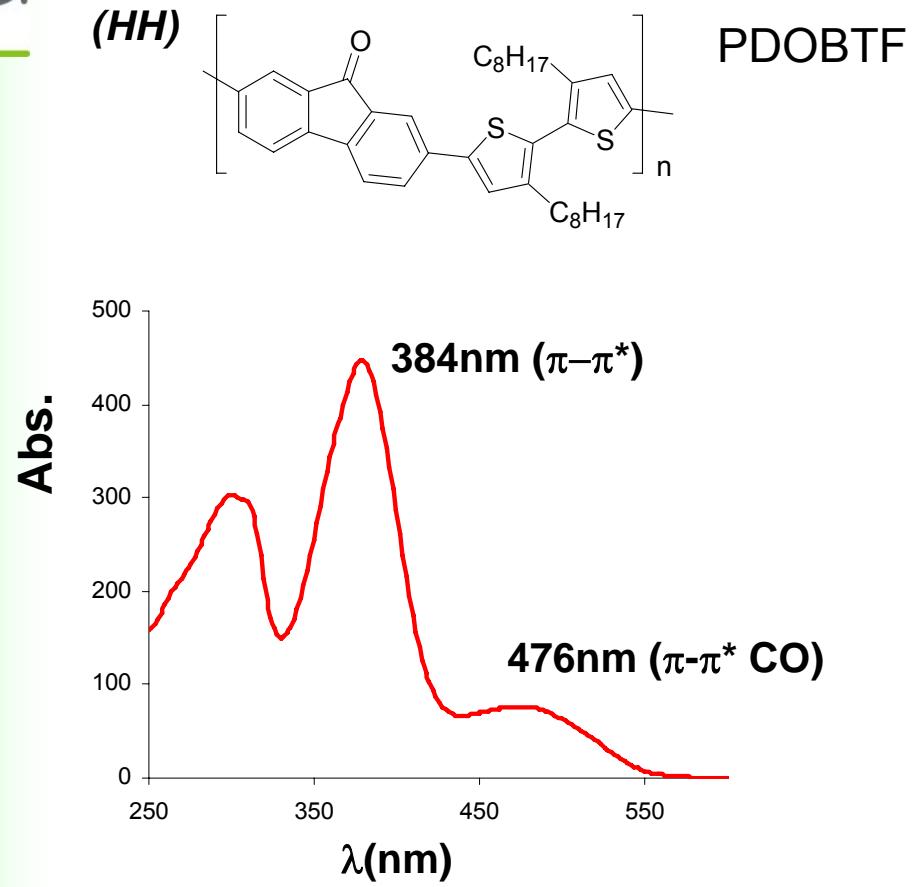
QTF8 on HOPG, NC-AFM image.

P.Leclère, B.Grévin and M.Linares



Nanofibers and molecular wires are made of packed oligomers stabilized by pi-pi interactions

# Optical properties



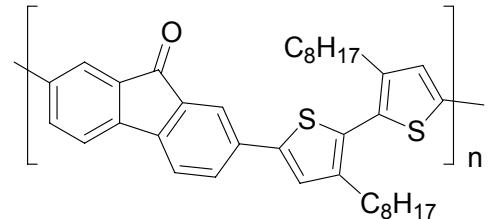
Molecular coefficient of absorption

$$35000 < \varepsilon \text{ (UV)} < 89000 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$$

$$6000 < \varepsilon \text{ (Vis)} < 24000 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$$

## Optical properties

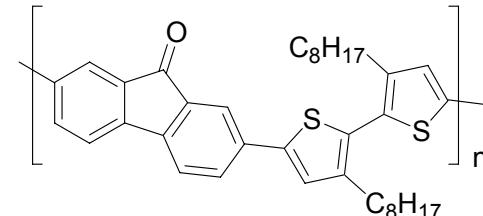
(HH)



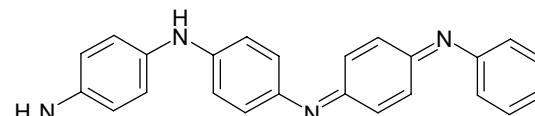
PDOBTF

# Extension of the spectral absorption range

(HH)



Post polymerisation reaction

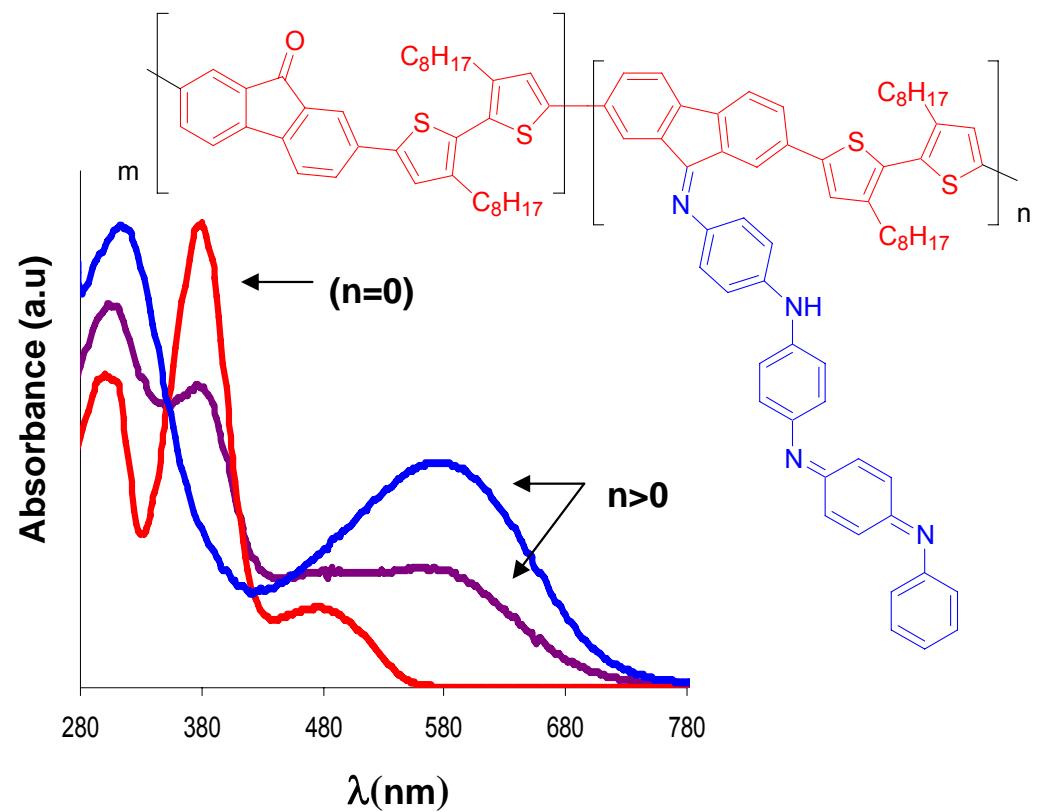


Tuning of the spectrum by changing the grafting level

Shift of the  $\lambda_{\max}$  from 484 nm to 572nm  
(+88nm)

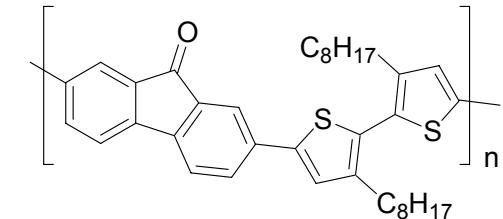
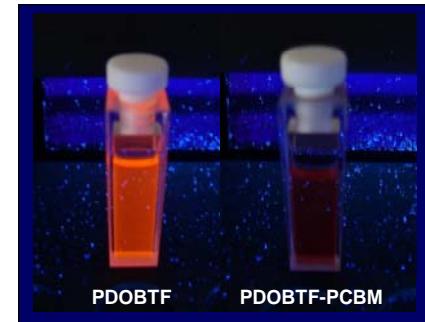
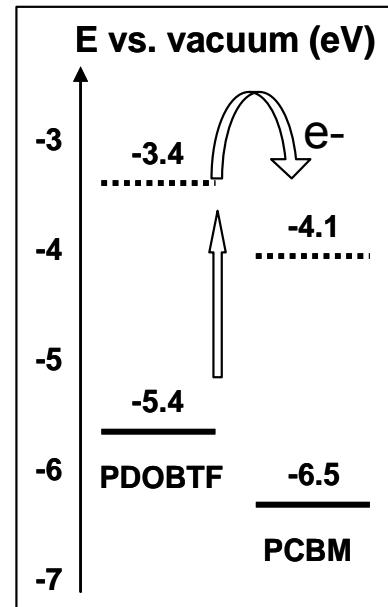
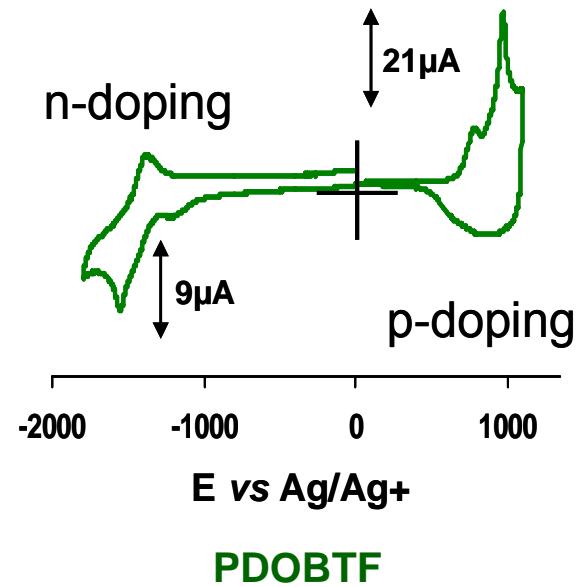
Absorption extended to 750nm  
Highest grafting level : 73%  
Poor solubility

Demadrille et al. *Macromolecules*, 2003, 36, 7045.  
Buga et al *Macromolecules*, 2004, 37, 769.



# Electrochemical properties

Electrochemical study by cyclic voltammetry

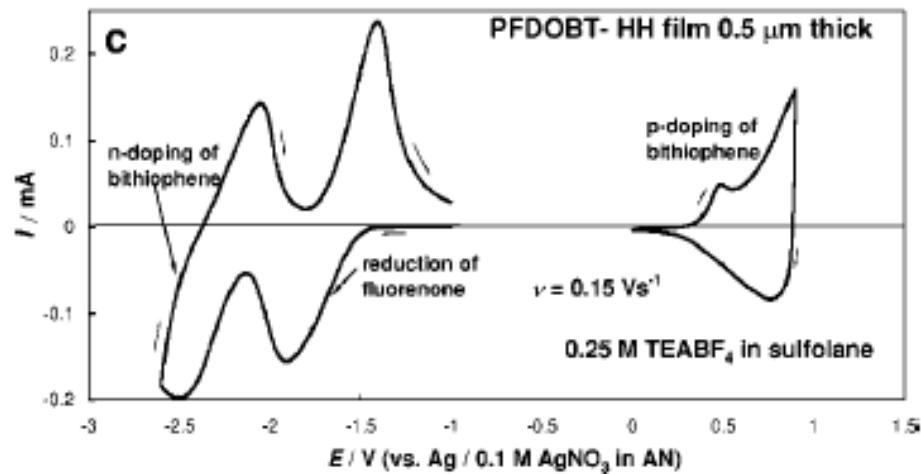


Evidence of the sequential n and p doping

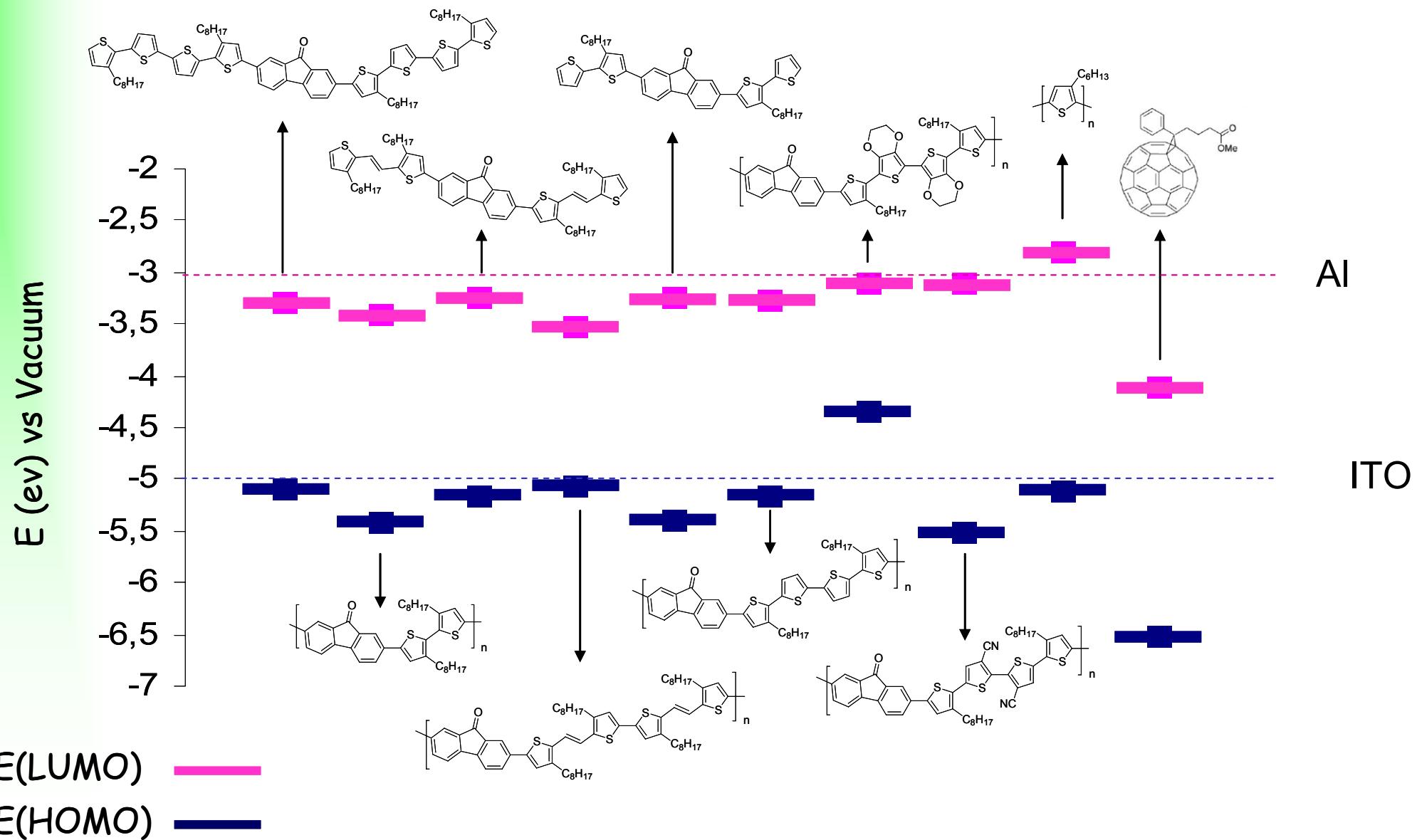
Demadrille et al. *New.J.Chem.*, **2003**, 27, 1479.

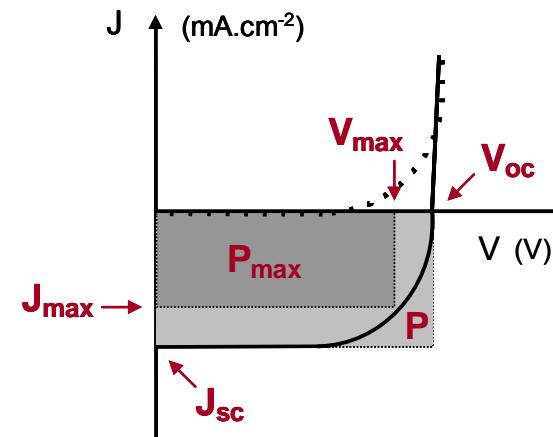
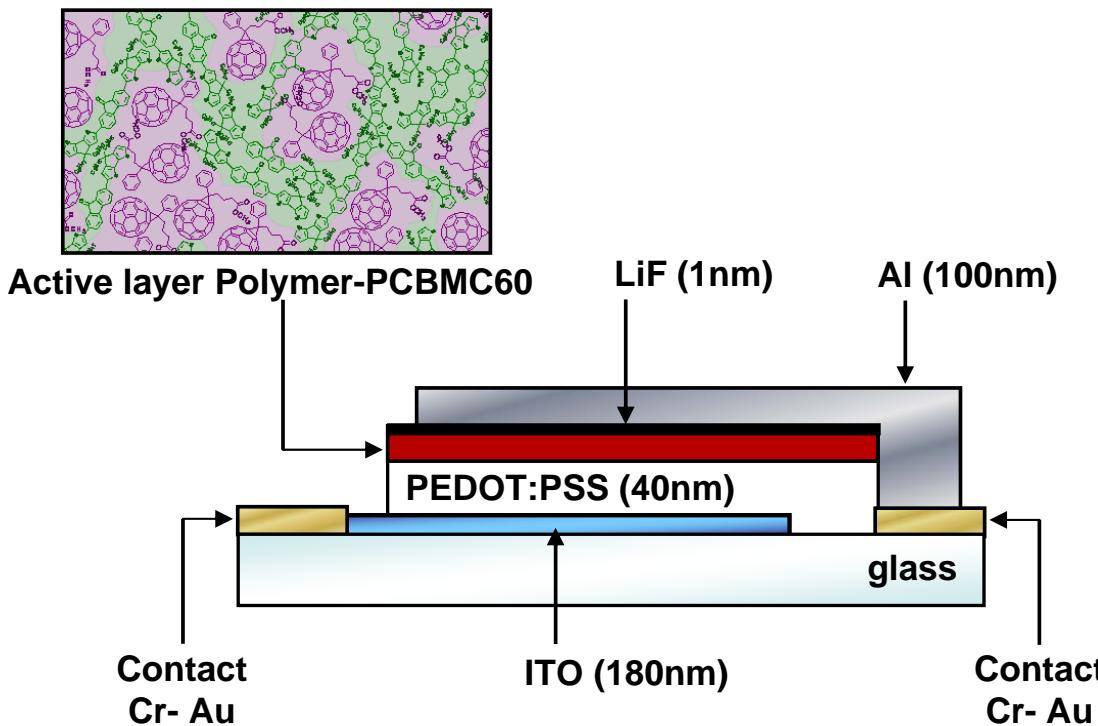
Demadrille et al. *Electrochimica Acta*, **2005**, 50, 1597.

Levi et al. *J.Solid.State.Electrochem.* **2007**, 11, 1051.



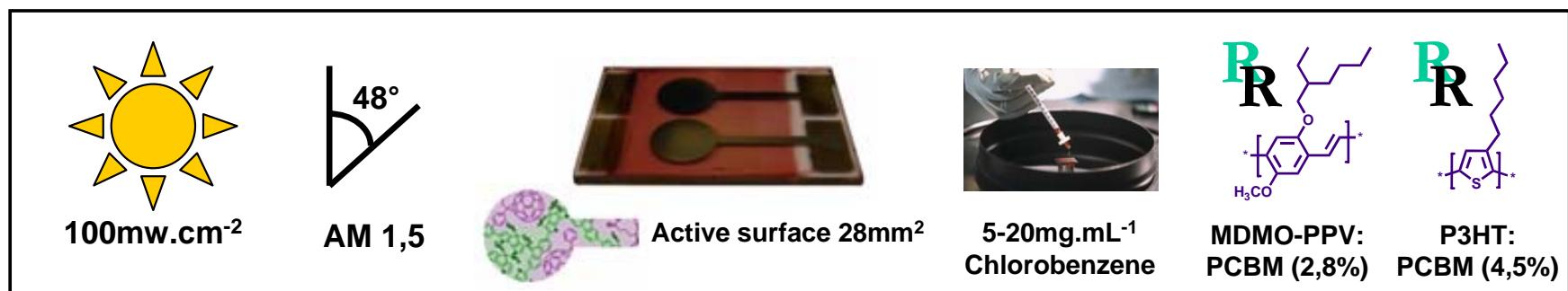
# Electrochemical properties

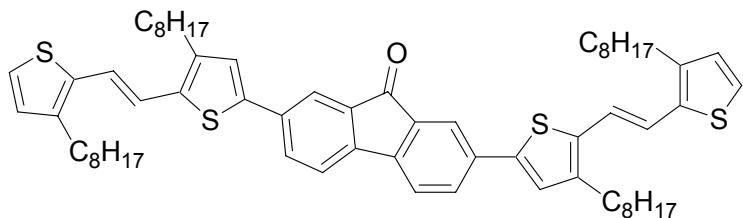




$$\eta (\%) = \frac{FF * V_{OC} * I_{SC}}{P_{irr}}$$

FF = Fill Factor  
 $FF = (V_{max} \times I_{max}) / (V_{OC} \times I_{SC})$





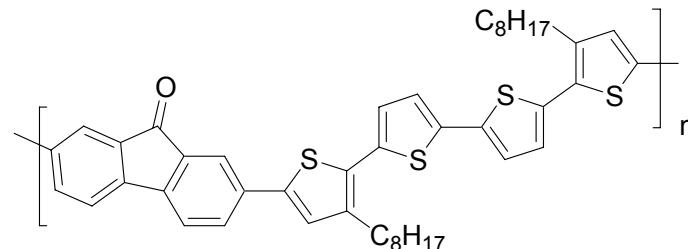
**J<sub>sc</sub> = 3.20mA/cm<sup>2</sup>**

**V<sub>oc</sub> = 0.45V**

**FF = 0.34**

**η = 0.58%**

TVF



**PQTF**

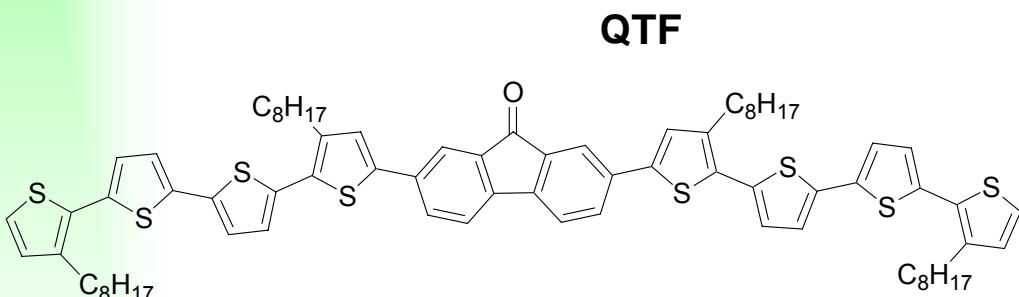
**J<sub>sc</sub> = 5.93mA/cm<sup>2</sup>**

**V<sub>oc</sub> = 0.57V**

**FF = 0.43**

**η = 1.45%**

Mw > 2,3 kDa



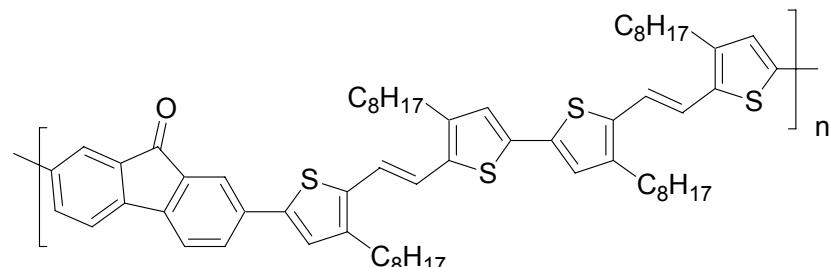
**QTF**

**J<sub>sc</sub> = 3.61mA/cm<sup>2</sup>**

**V<sub>oc</sub> = 0.82V**

**FF = 0.4**

**η = 1.19%**



**PTVF**

**J<sub>sc</sub> = 6.02mA/cm<sup>2</sup>**

**V<sub>oc</sub> = 0.45V**

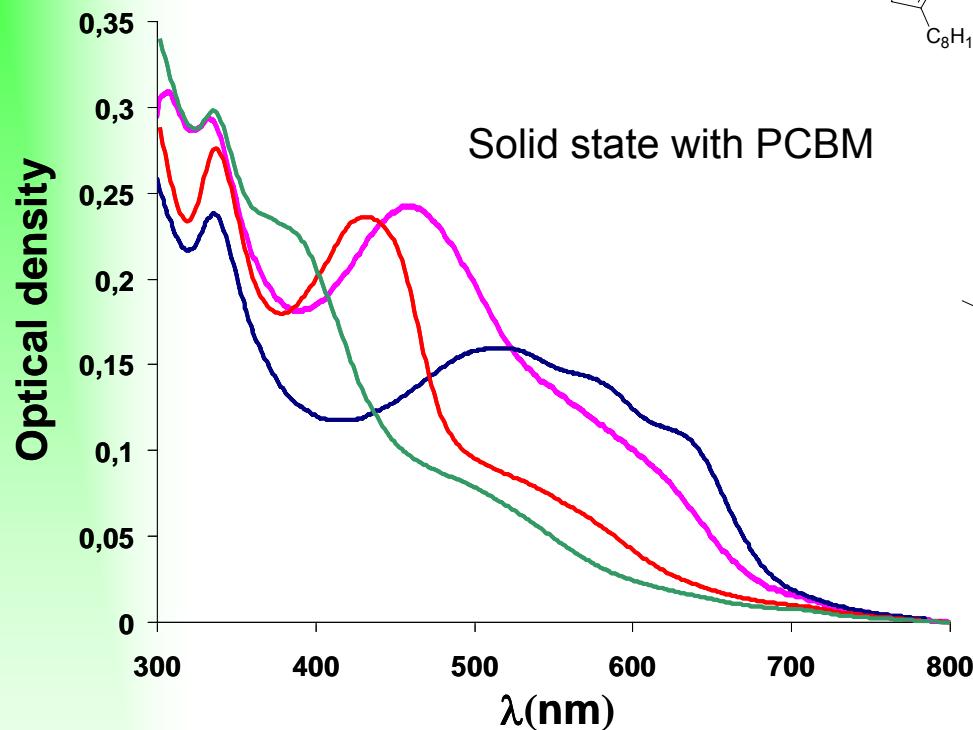
**FF = 0.44**

**η = 1.20%**

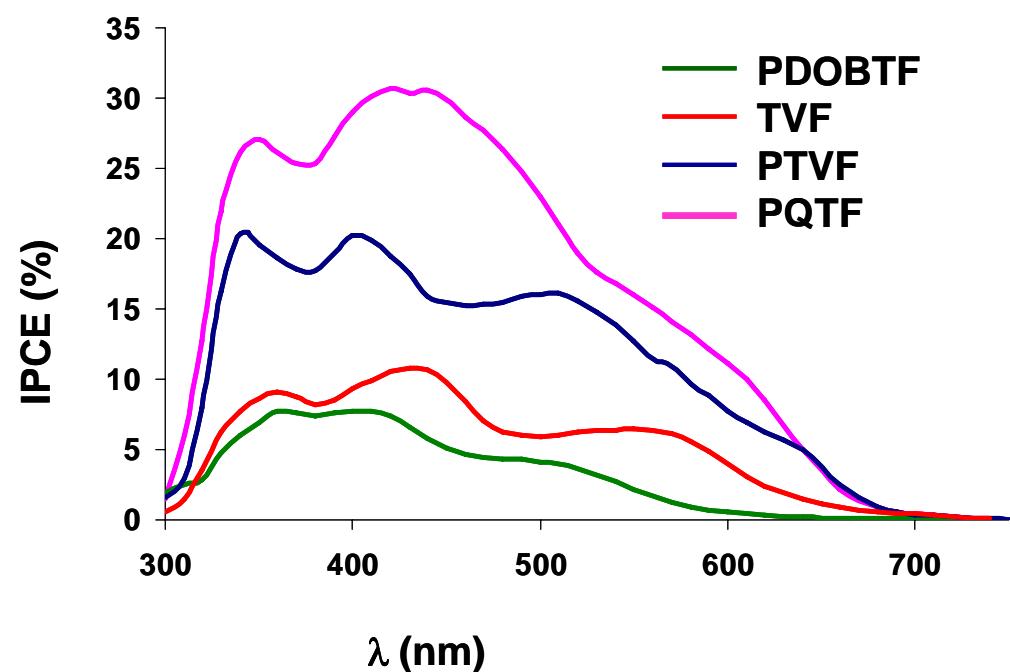
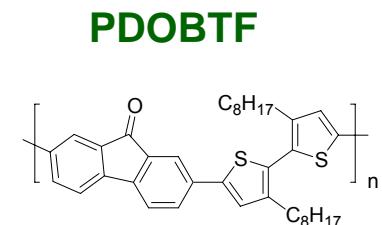
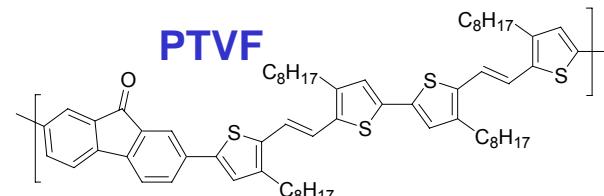
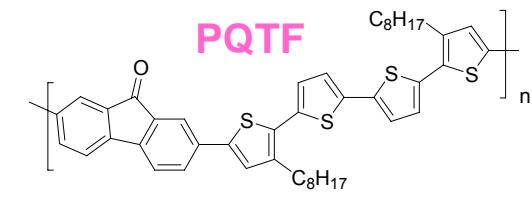
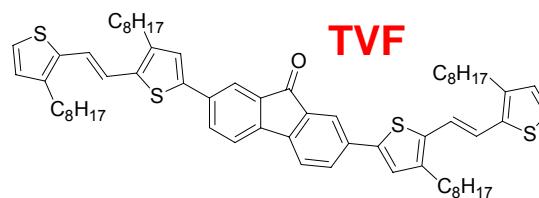
Mw > 3kDa

Demadrille et al. *J.Mater.Chem.*, **2007**, 17, 4661.

Lincker et al. *Adv.Funct.Mat.*, **2008**, under press.



Solid state with PCBM



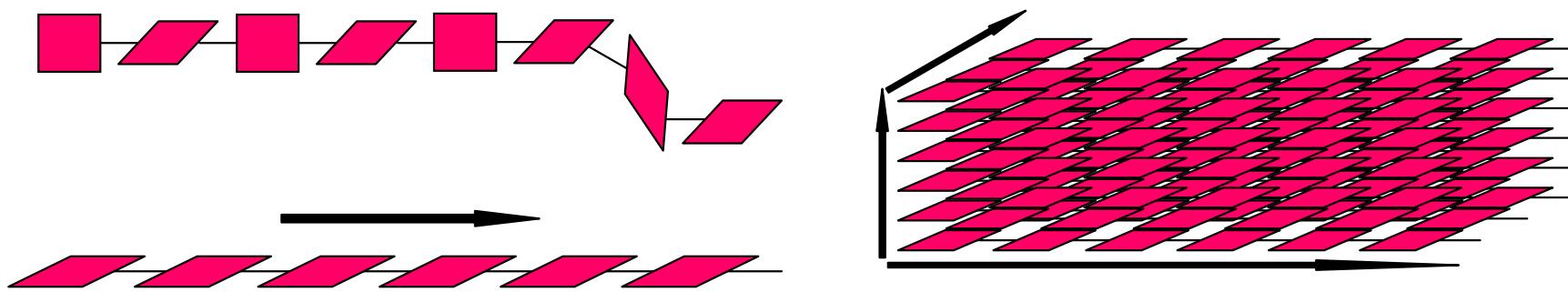
Photons collected by the fluorenones  
are efficiently converted into electrons

Demadrille et al. *Adv.Funct.Mat.*, 2005, 15, 1547.

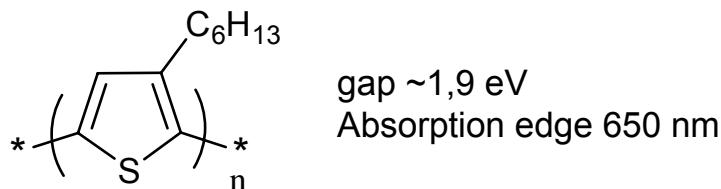
Demadrille et al. *J.Mater.Chem.*, 2007, 17, 4661.

## Nano-structuration of the polymers (S.Berson and coll.)

Goal: to develop a fabrication technique for controlling the morphology of the active layer and by consequence for improving the charge carriers mobility



Nano-structuration of active layers influences Jsc and FF

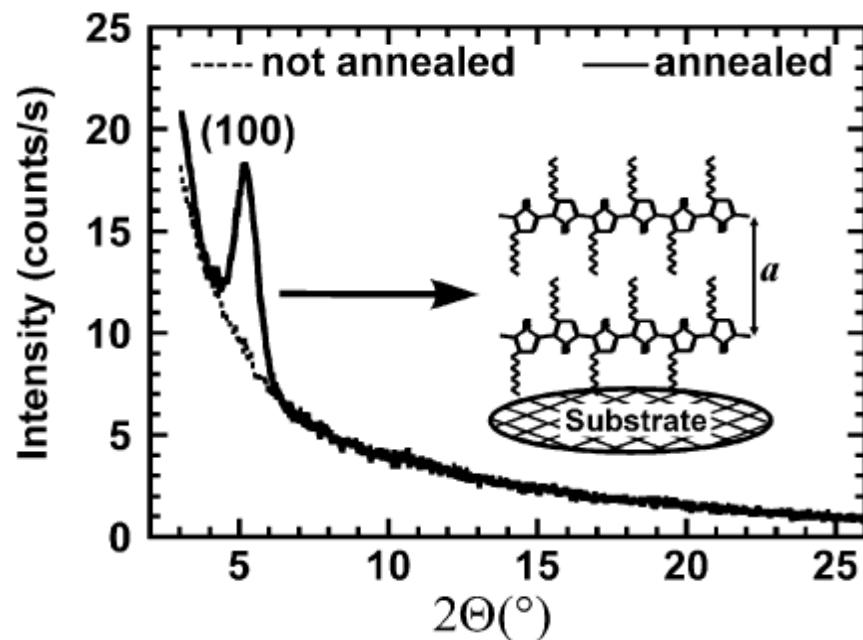


Best performances of P3HT:PCBM solar cells 5% **BUT** after post annealing treatment 5-30 min at 100-150°C

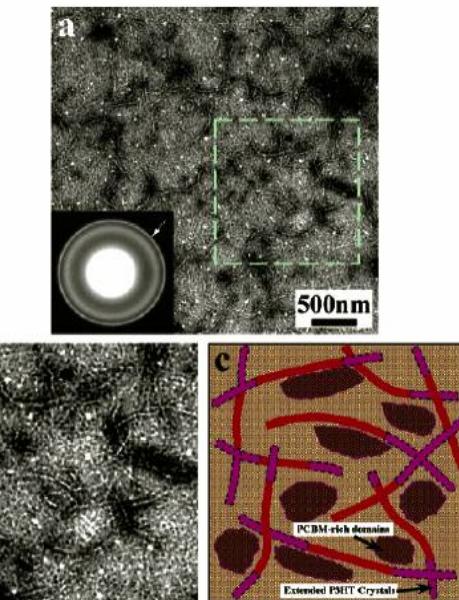
This type of treatment is not compatible with flexible substrates

# Photovoltaic properties of copolymers

After annealing crystalline domains are formed



U. Zhokhavets *et al.*, *Thin Solid Films* **2006**, 496, 679.



R. A. J. Janssen *et coll.*, *Nanoletters*, **2005**, 5, 579.

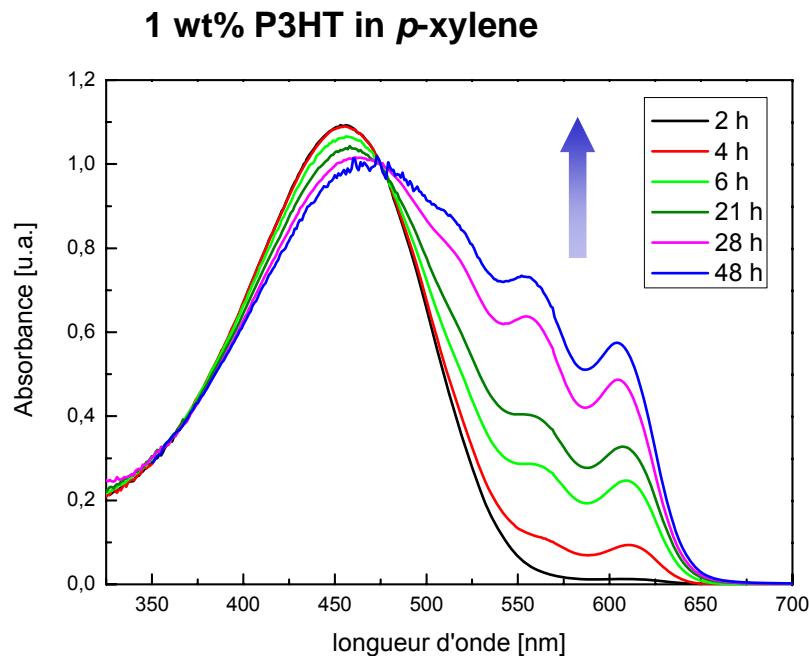
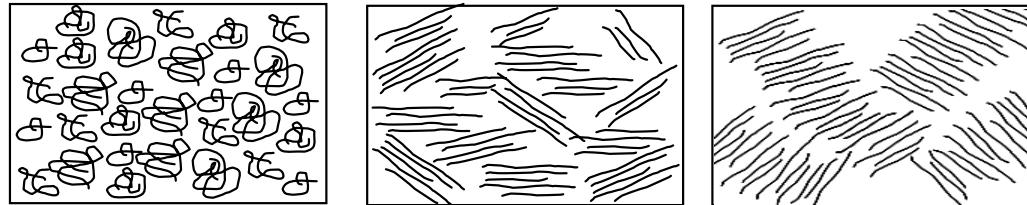
→ Structuration of P3HT : formation of fibrillar-type network

Fibrillar Structures of P3HT can be obtained by a modification of solution processing

K. J. Ihn *et al.*, *J. Polym. Sci. : Part B : Polym. Phys.*, **1993**, 31, 735.

# Elaboration of the nano fibers in solution

- Complete dissolution of the polymer (hot solution)
- Cooling to room temperature (slowly)
- Maturation of the fibers



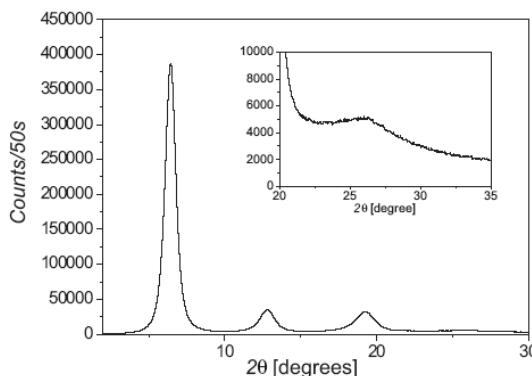
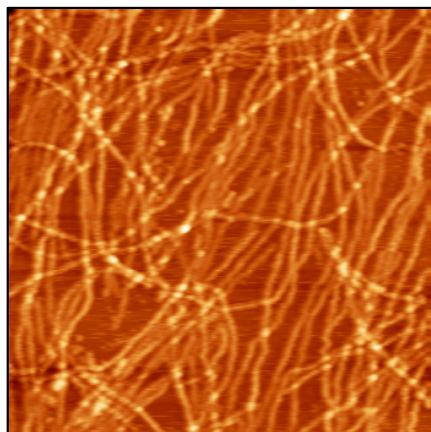
Solution of polymer (2 h)



Stable dispersion of fibers (48 h)

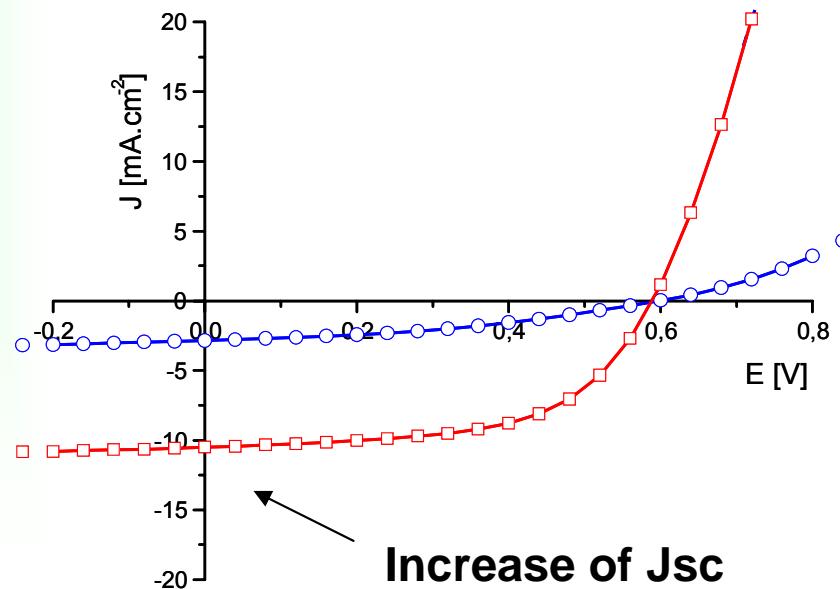
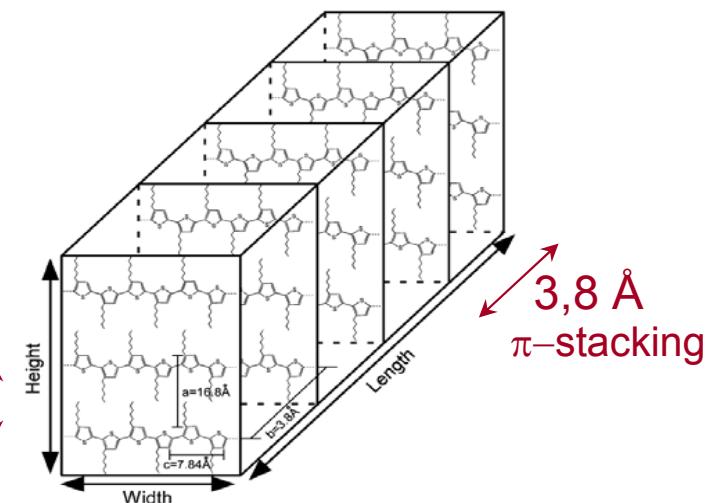


Preparation of concentrated dispersions (2 wt%)

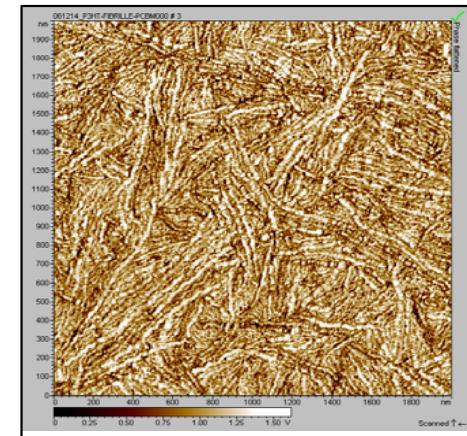


Thickness = 5 - 15 nm  
Width = 30 - 50 nm  
Length = 0,5 - 5  $\mu$ m

Merlo, Frisbie, *J. Phys. Chem. B*, **2004**, 108, 19169



$\eta = 3.6\%$   
Without annealing

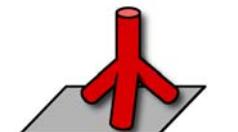
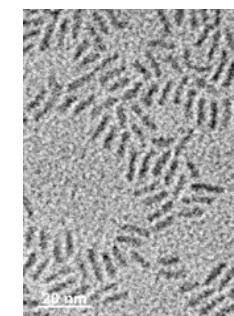
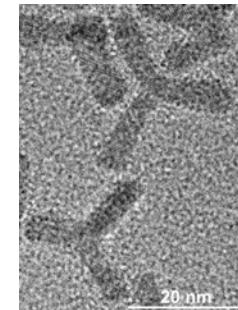


S. Berson et al., *Adv. Funct. Mater.*, **2007**, 13, 1377

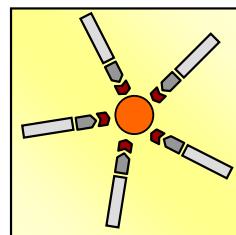
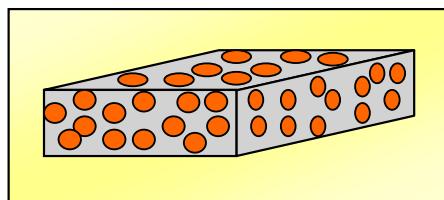
Dispersion of **semiconductor nanocrystals** in a conjugated polymer matrix

Advantages of nanocrystals used as electron acceptors:

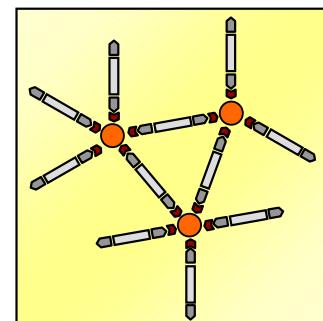
- Large and modulable absorption spectrum
- Electron affinity can be tuned (size, material)
- Percolation and electron transport improved by anisotropic nanocrystals (e.g. nanorods, tetrapods)



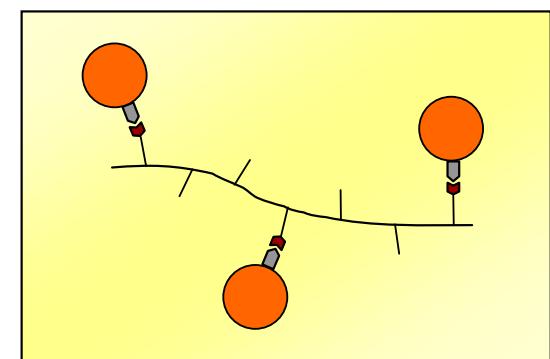
Nanocrystals blended  
in a polymer matrix



Functional oligomers

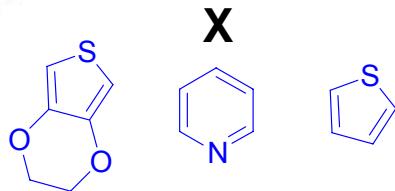
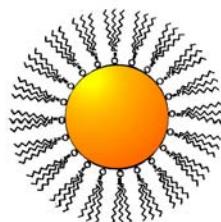
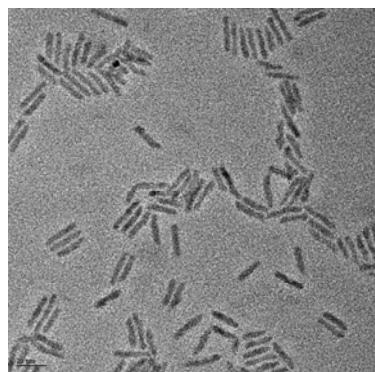


Functional polymer



# Hybrid preparation: blend approach (F.Chandezon and coll.)

N.C. Greenham et al.  
PRB 54 (1996) 17628

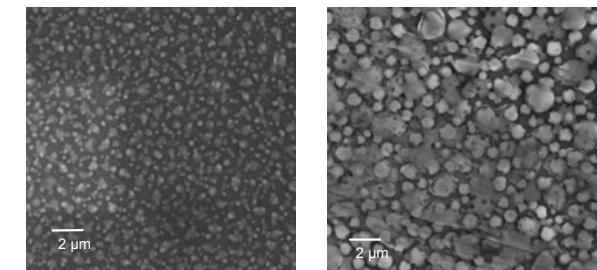
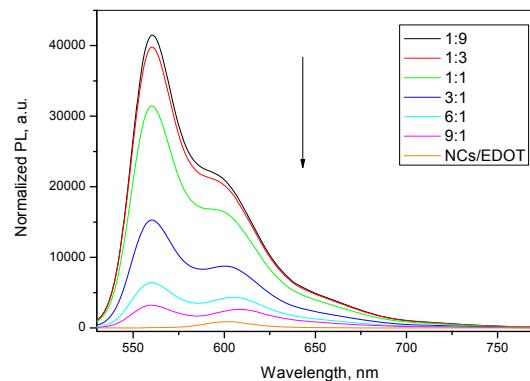
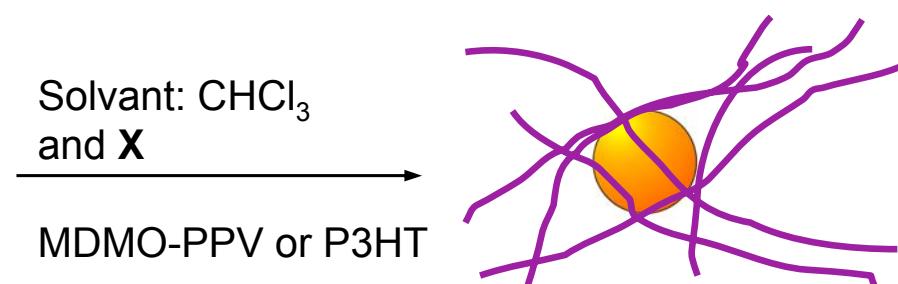


PL quenching in blends of  
EDOT-coated nanorods and MDMO-PPV

CdSe nanocrystals (nanorods)/P3HT PCE = 1,7%  
Huynh et al. *Science* **2002**, 295, 2425

ZnO nanocrystals in MDMO-PPV PCE = 1,6%  
Beek et al. *Adv. Mater.* **2004**, 16, 1009

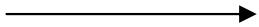
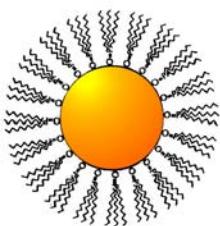
CdSe nanocrystals (tetrapods)/MDMO-PPV PCE = 2,8%  
Sun et al. *J. Appl. Phys.* **2005**, 97 014914



CdSe/EDOT: MDMO-PPV

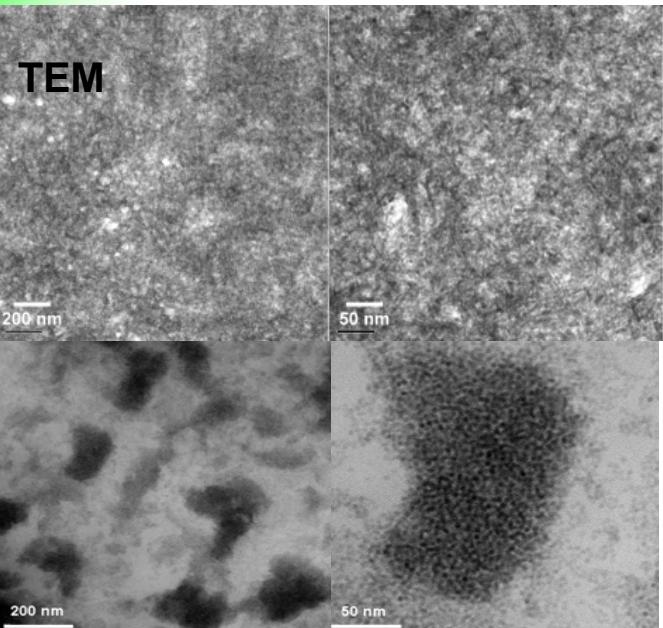
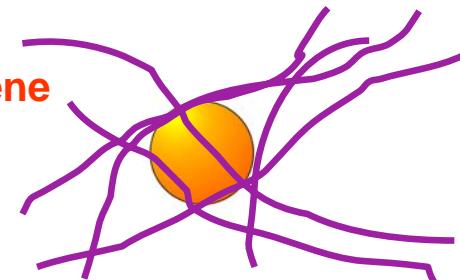
Low power conversion efficiencies due to a lack of morphology control <0.3%

# Hybrid preparation: blend approach

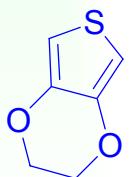
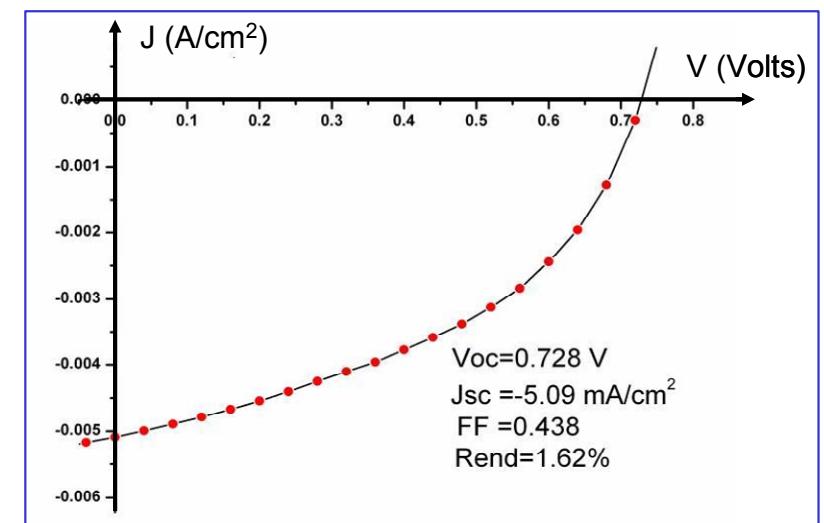


Solvant: **Chlorobenzene**  
and **ligand**

P3HT



CdSe-Pyr: P3HT 9:1 (90 % w/w)



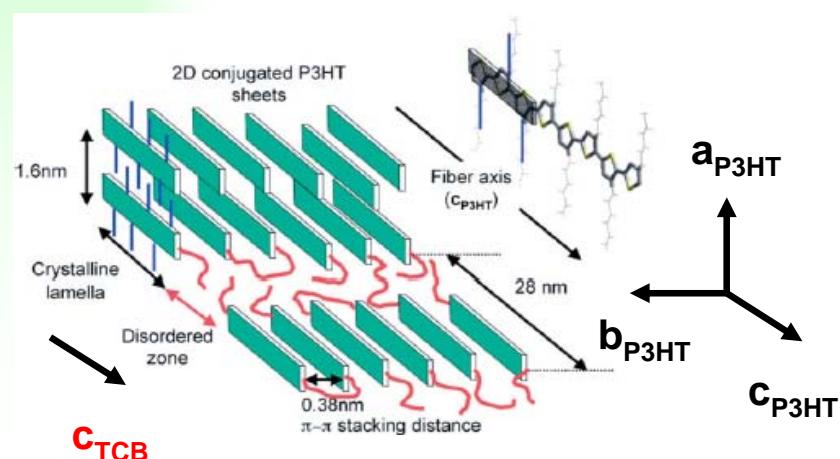
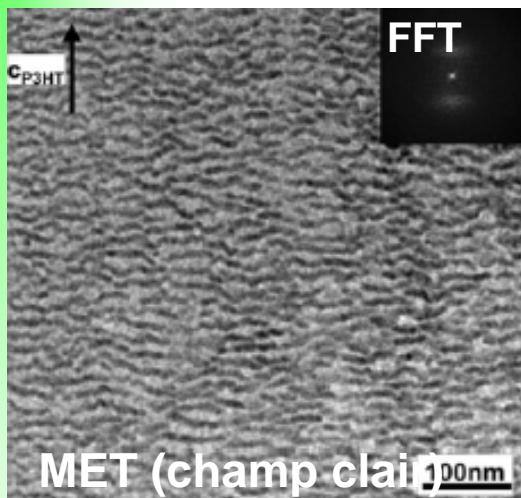
CdSe-EDOT: P3HT 3:1 (75 % w/w)

$\eta \approx 0,01 \%$

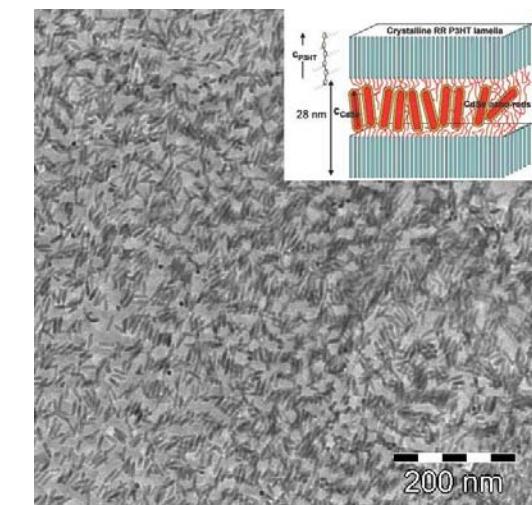
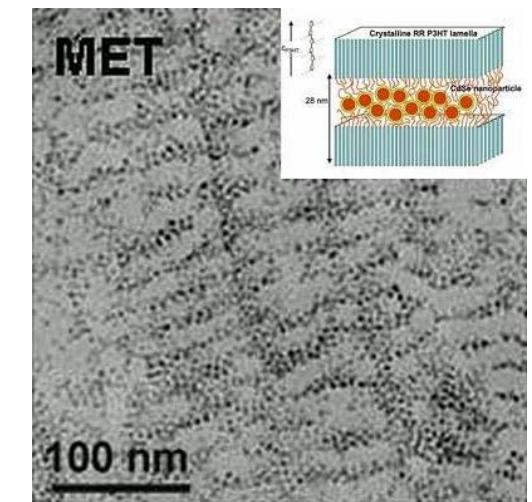
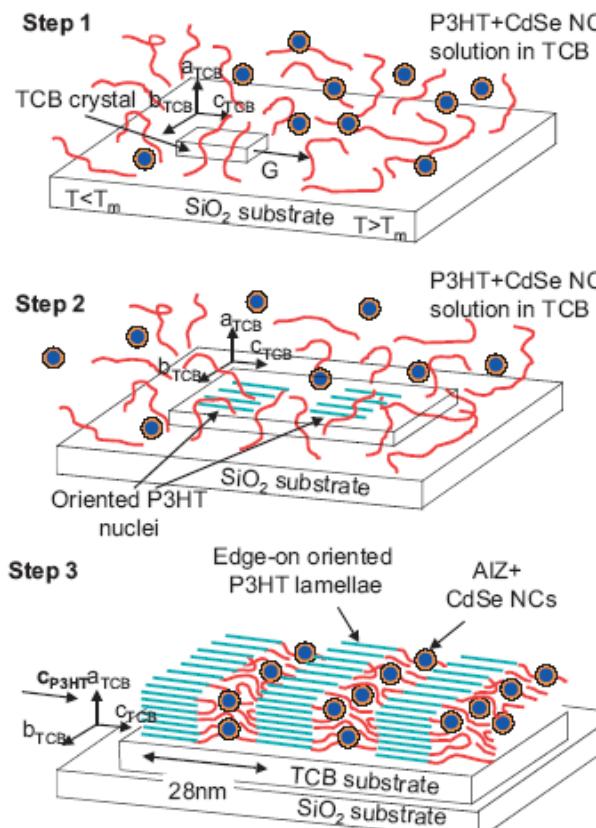
Higher power conversion efficiencies due to better morphology control 1.6%

# Hybrid preparation: nanostructured polymer matrix

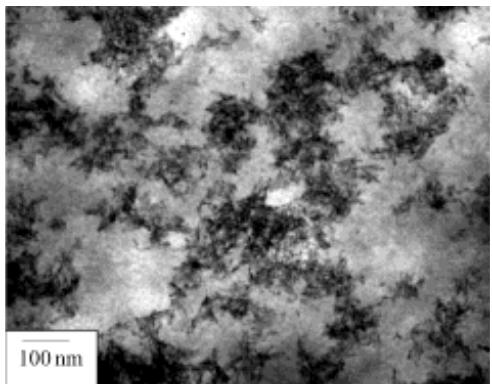
Directional epitaxial solidification of the polymer in a crystallizable solvent.  
Preparation of thin films (100 nm) nanostructured and oriented P3HT : alternating  
crystalline lamellae and amorphous zones



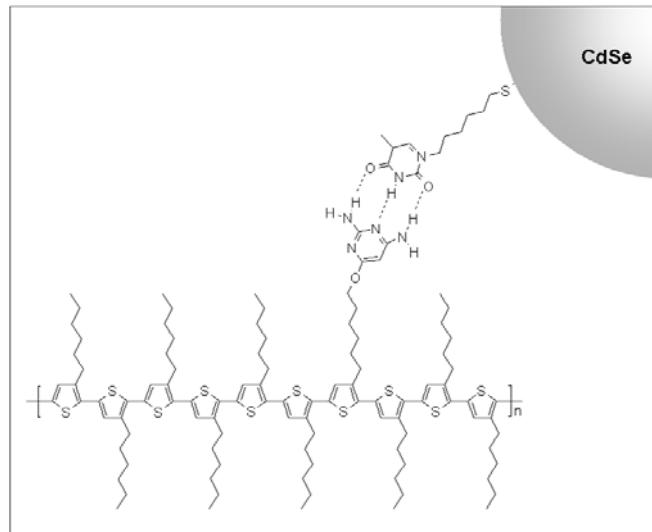
Cristallisation of  $c_{P3HT} \approx 2 \times c_{TBC}$



# Hybrid preparation: bio-inspired self-assembly approach

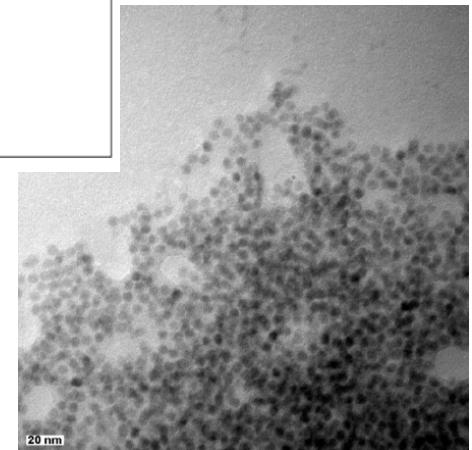


“Traditional” blend P3HT-CdSe

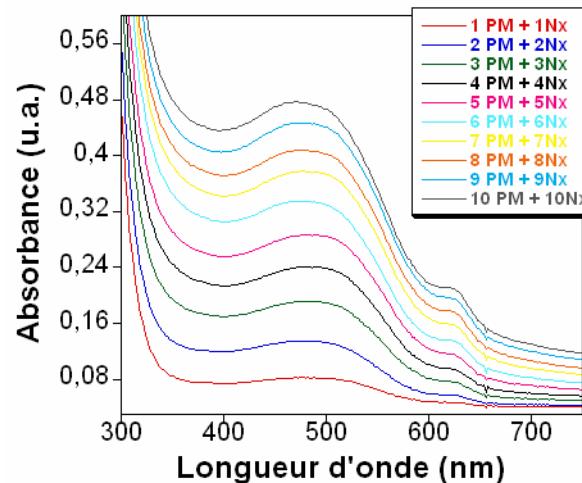
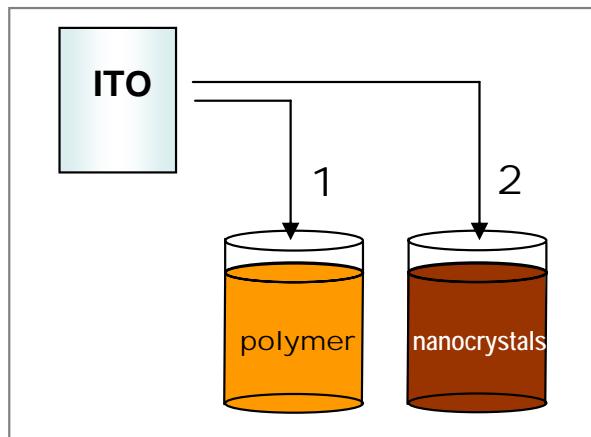


Molecular recognition between  
a diaminopyrimidine-functionalized P3HT  
and thymine-functionalized nanocrystals via triple hydrogen bonding

De Girolamo *et al.*, *J.Phys.Chem.B.*, 2007



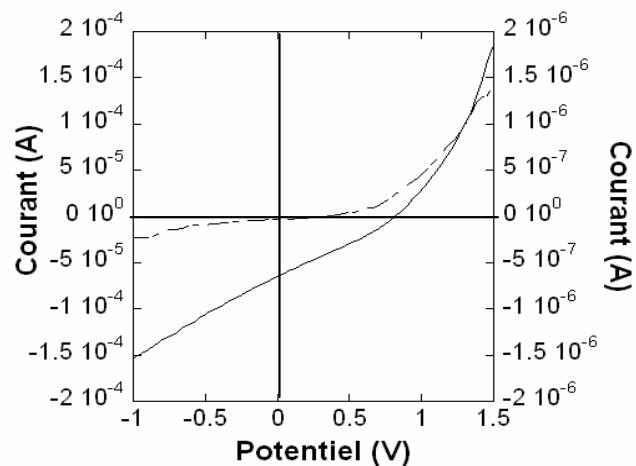
Synthesis of specific ligands for the surface modification of the nanocrystals  
Synthesis of regioregular polythiophene with complementary functional groups



### UV-vis absorption monitoring

in each step the same quantity of polymer and nanocrystals is deposited.

- Morphology control (avoiding undesirable aggregates)
- Simple process, large area, flexible substrates, low consumption of materials
- Interpenetrated network (appropriate morphology)



### Proof of concept : measured photovoltaic effect

## Summary:

---

- We have developed synthetic and processing strategies to fabricate BHJ solar cells
- We have new materials which can be used to fabricate organic solar cells (PCE : 1,5%)
- New processing technique: nanostructuration of P3HT without annealing (PCE of 3.6%)
- New hybrid materials and original processing strategy based self-organization properties of P3HT and on molecular recognition.

## Fundamental Research Department

Frédéric Lincker  
Solenn Berson  
Nicolas Delbosc  
Yann Kervella  
Patrice Rannou  
Benjamin Grévin  
Adam Pron  
Julia de Girolamo  
Peter Reiss  
Tongang Jiu  
Dmitrii Aldakov  
Frédéric Chandezon

## Technological Research Department

Rémi De Bettiginies  
Muriel Firon  
Stéphane Guillerez  
Séverine Baily



## Collaborations

Mikhael Levi (Univ Bar-Ilan Israël)  
Doron Aurbach (Univ Bar-Ilan Israël)  
Philippe Leclère (Univ Mons Hainault Belgium)  
Roberto Lazaroni (Univ Mons Hainault Belgium)  
Mathieu Linares (Univ Mons Hainault Belgium)  
Martin Brinkmann (Institut Charles Sadron, Strasbourg)

## Financial supports

CEA (RTB program)  
ADEME (CSPVP program)  
ANR (Nanorgysol Project)  
ANR (Conaposol Project)  
Programme Energie CNRS (Celasol)



**Thank you for your attention**