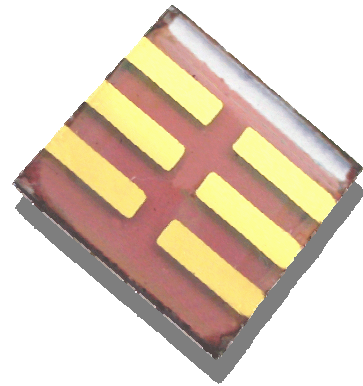


# Cellules Solaires Hybrides à Hétérojonction : Potentialités et récents développements.

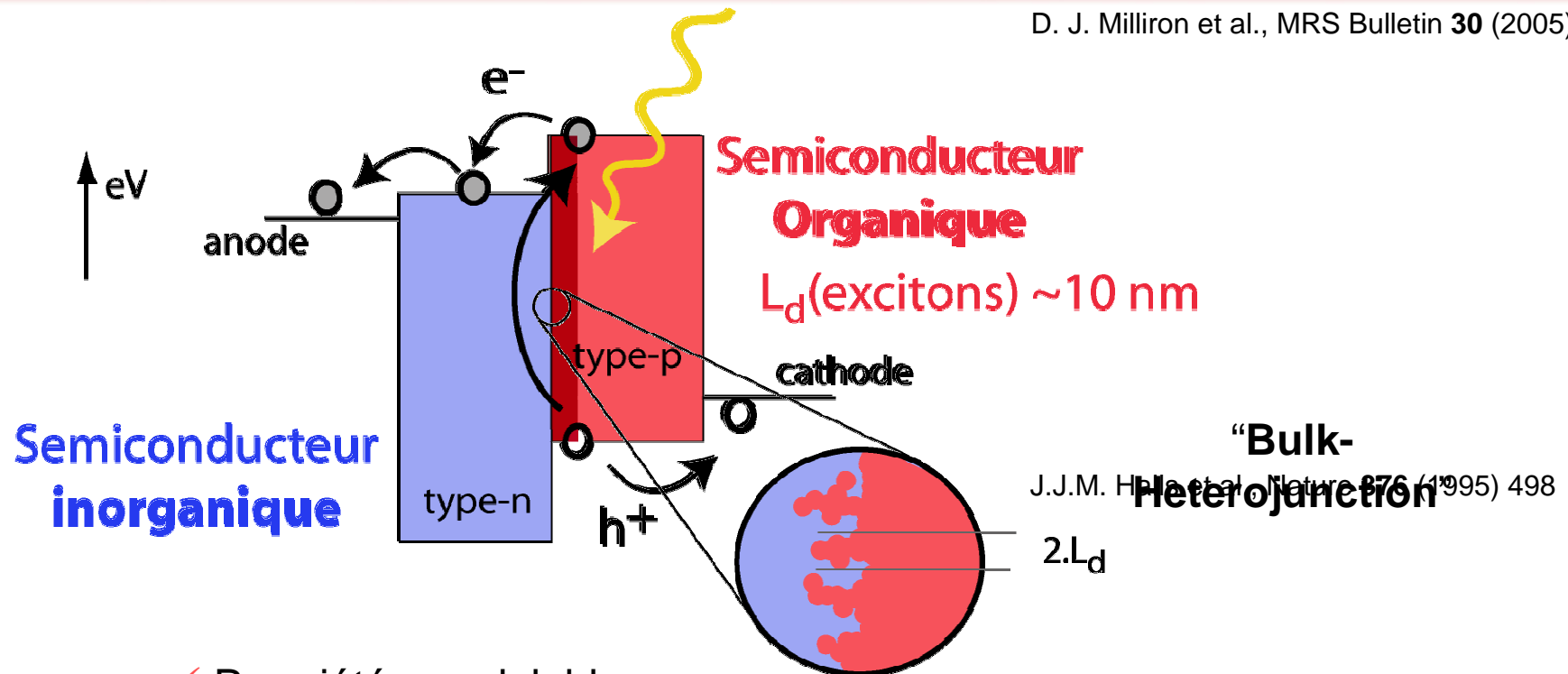


Johann Bouclé  
Optoelectronics Group  
Cavendish Laboratory  
[jb576@cam.ac.uk](mailto:jb576@cam.ac.uk)



# Cellules solaires Hybrides à Hétérojonction

D. J. Milliron et al., MRS Bulletin **30** (2005) 4

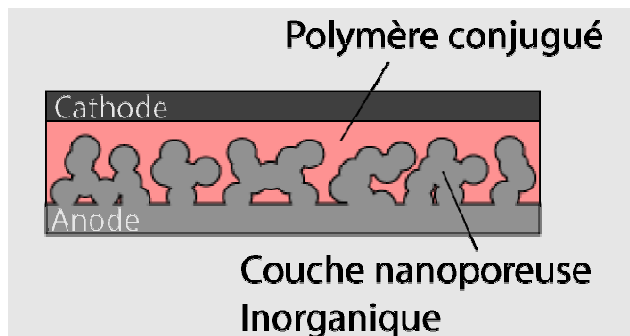


- ✓ Propriétés modulables
- ✓ Bas coûts, Flexibles
- ✓ Fortes mobilités des porteurs de charge ( $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{CdSe}$ , etc...)
- ✓ Morphologie modulable
  - Contrôle de la morphologie à l'échelle nanométrique
  - Élaboration en solution, procédés peu coûteux
  - Stabilité améliorée

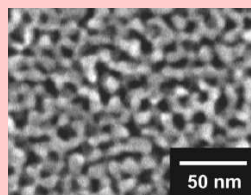
# Électrode Mésoporeuse/Polymère conjugué

C. C. Oey et al., Nanotechnology **17** (2006) 706–713

M. Lira-Cantu et al., Solar Energy Materials & Solar Cells **90** (2006) 2076-2



- ☺ Importante mobilité (TiO<sub>2</sub>, ZnO, etc...)
- ☺ Réseau interconnecté (type-n)  
= Transport efficace des charges



## ☐ TiO<sub>2</sub> mésoporeux (P123) / P3HT

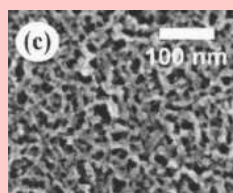
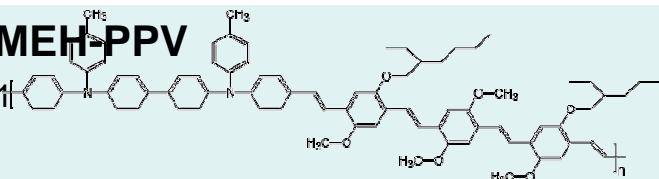
K. M. Coakley et al., Appl. Phys. Lett. **83** (2003) 3380

EQE ~ 10%,  $\eta = 0.45$  %

## ☐ TiO<sub>2</sub> nanocristallin (DSSC) / dérivé du MEH-PPV

P. Ravirajan et al., Appl. Phys. Lett. **86** (2005) 143101

EQE ~ 40%,  $\eta = 0.58$  %



## ☐ TiO<sub>2</sub> mésoporeux (PS-*b*-PEO) / MEH-PPV

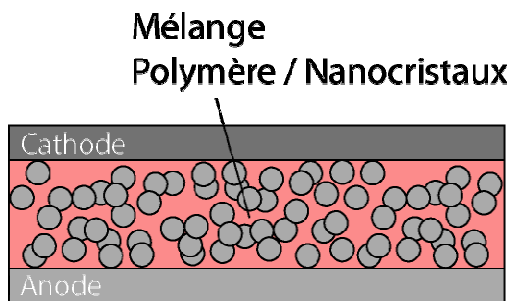
H. Wang et al., Appl. Phys. Lett. **87** (2005) 023507

EQE ~ 34%,  $\eta = 0.71$  %

$\eta < 1\%$  → ☹ Infiltration du Polymère

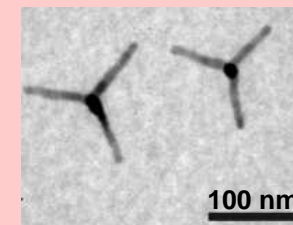
# ❖ Mélanges Nanocristaux / Polymères conjugués

D.J. Milliron et al., MRS Bulletin **30** (2005) K.M. Coakley et al., MRS Bulletin **30** (2005)



- ☺ Grande interface
- ☺ ~~Infiltration du polymère~~
- ☺ Basses températures, bon marché
- ☺ Morphologie variable  
Nanorods = transport amélioré

nc-CdSe:P3HT	$\eta = 1.7\%$	W.U. Huynh, Science <b>295</b> (2002)
nc-ZnO:MDMO-PPV <b>16</b> (2004)		$\eta = 1.6\%$ W.J.E. Beeck, Adv. Mater.
nc-ZnO:P3HT (2006)	$\eta = 0.9\%$	W.J.E. Beeck, Adv. Funct. Mater. <b>16</b>
Tetra-CdSe:OC <sub>1</sub> C <sub>10</sub> PPV	$\eta = 2.1\%$	B. Sun, J. Appl. Phys. <b>97</b> (2005)
Tetra-CdSe:Red-APFO	$\eta = 2.4\%$	P. Wang, Nanoletters <b>6</b> (2006)



## Principales limitations:

- ☹ Obtention d'une morphologie adaptée...
- ☹ **Transport** des charges

✓ Mélanges P3HT / Nanofils de TiO<sub>2</sub> 

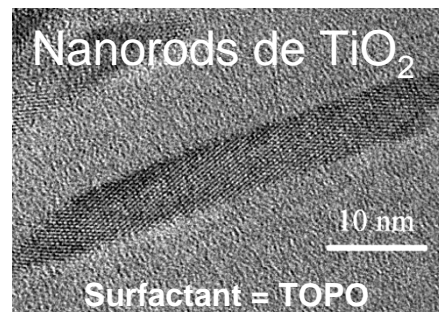
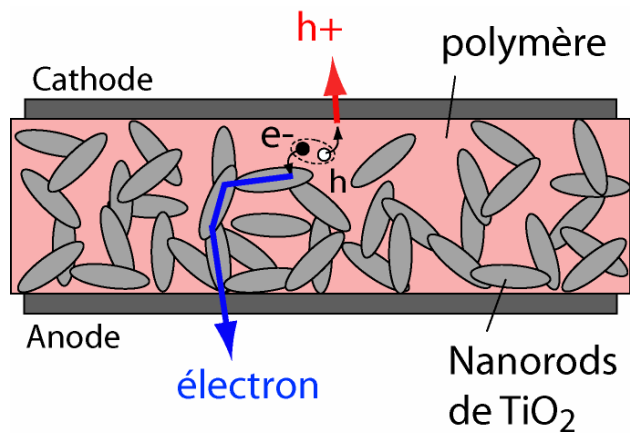
✓ Électrodes nanoporeuses de ZnO élaborées en solution



✓

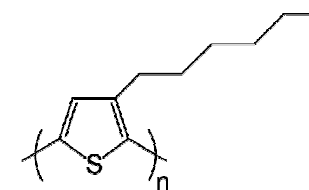
Conclusions

# Mélanges P3HT / « Nanofils » de TiO<sub>2</sub>

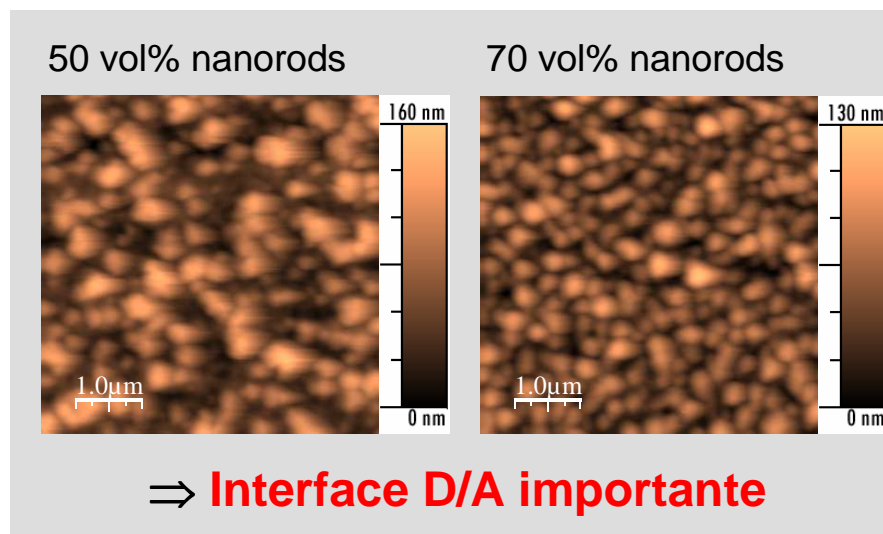
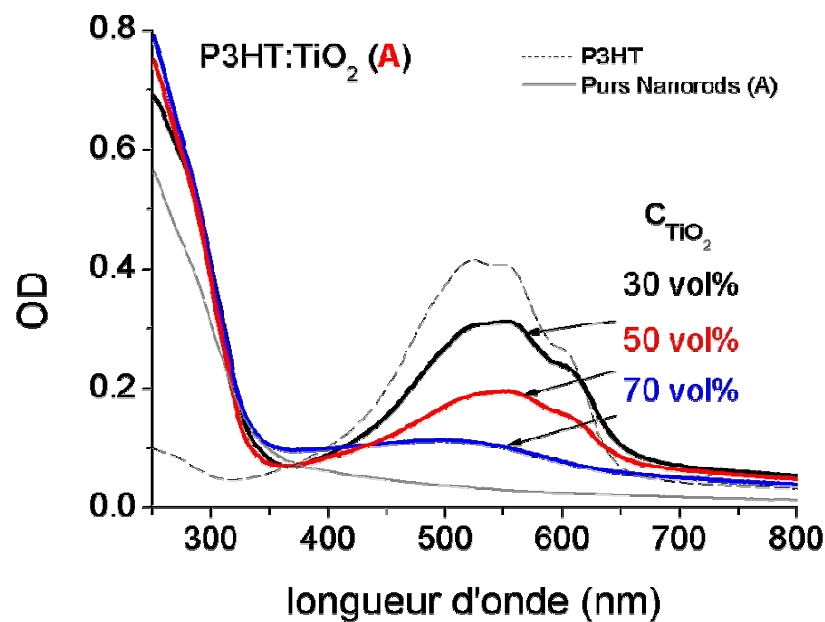


**Poly(3-hexylthiophene) P3HT**

Merck, RR 96.1% , Mn=12.4k, PI = 1.67

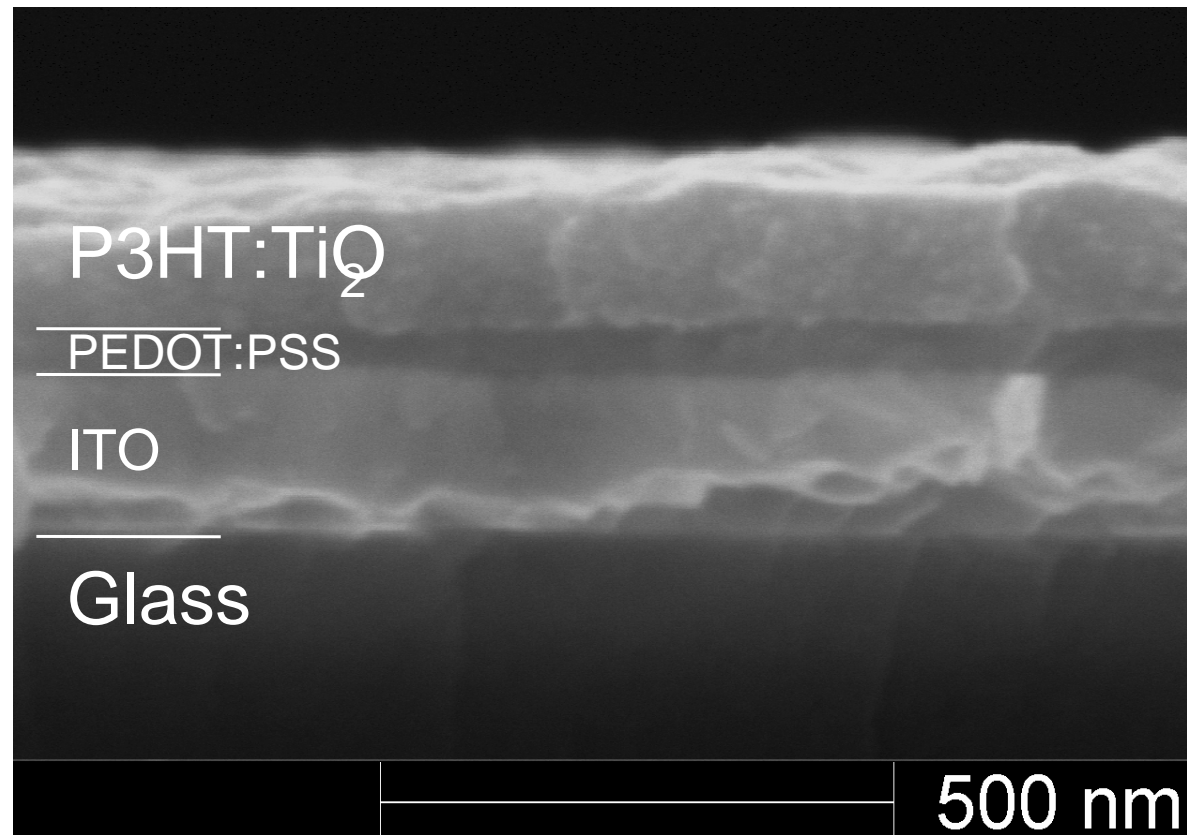


Dr. S. Chyla, Dr. M. S. P. Shaffer  
Dpt. Of Chemistry, Imperial College London





# Morphologie

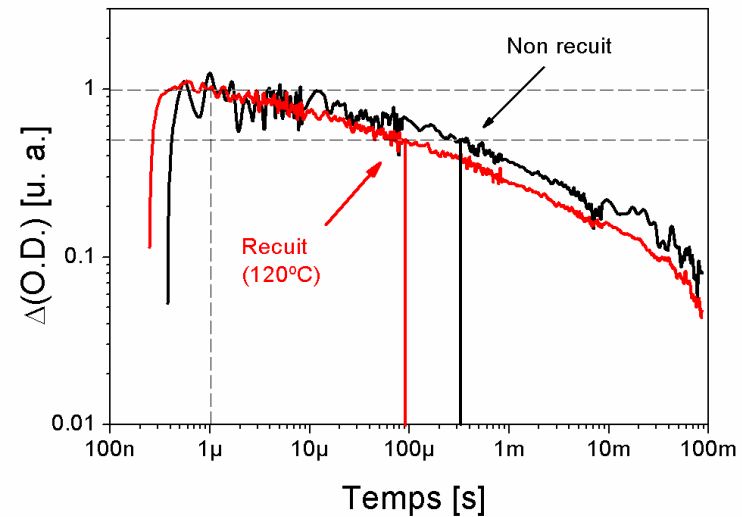
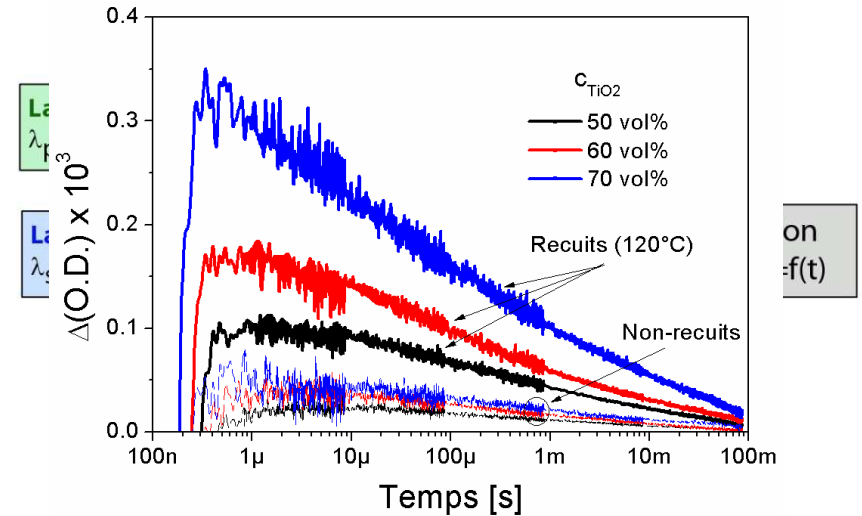
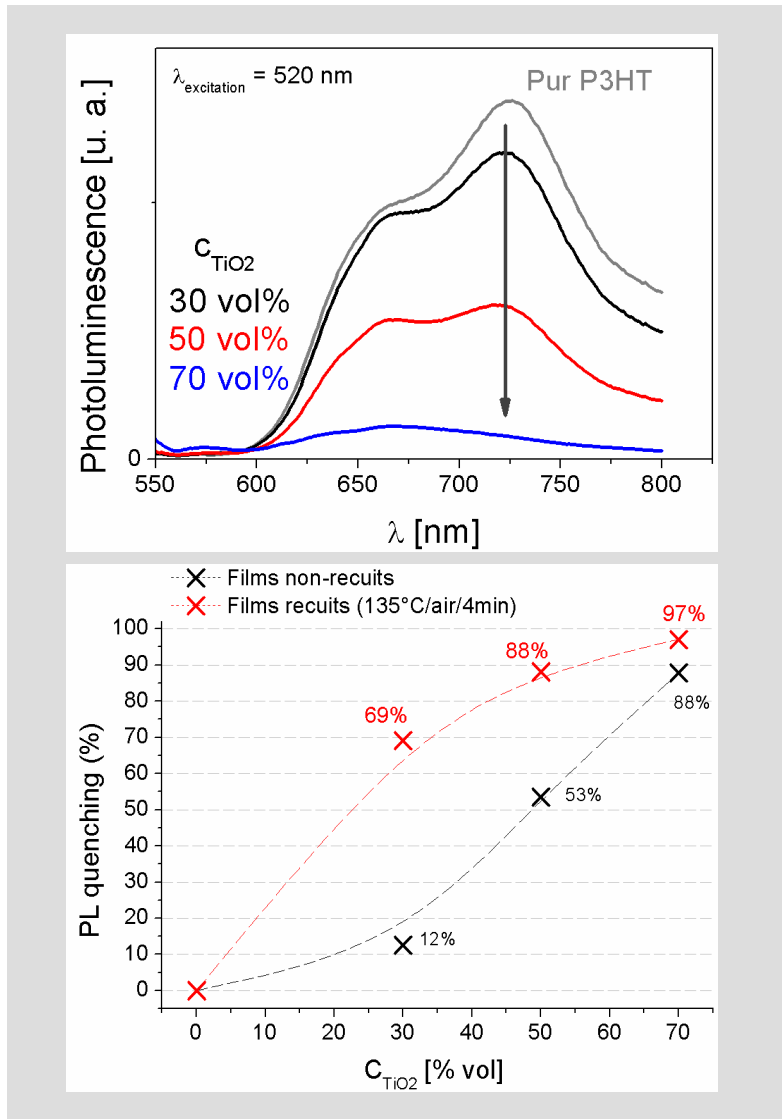


PEDOT:PSS = Poly-(3,4-ethylenedioxythiophene):poly(styrene sulfonate)



# Propriétés de transfert de charges

## ➤ Spectroscopie d'absorption résolue en temps

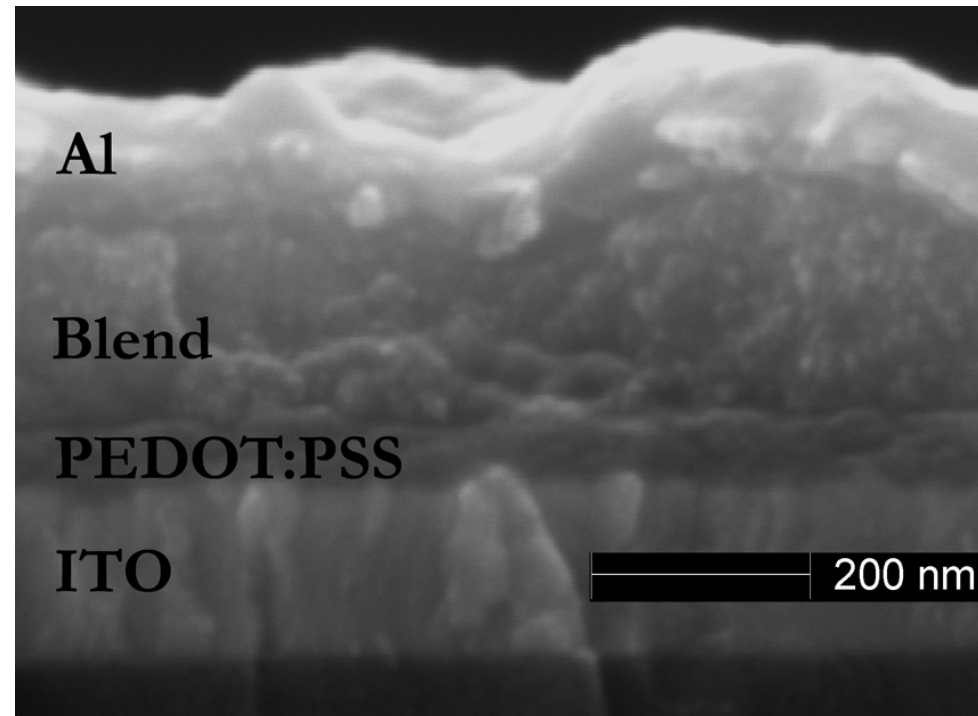
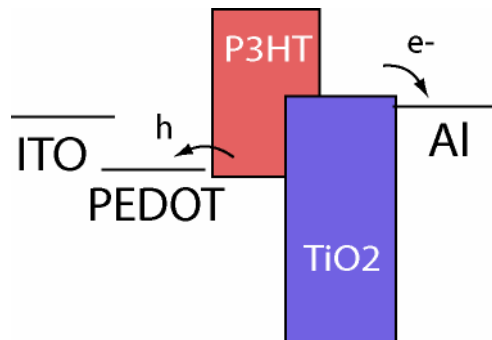
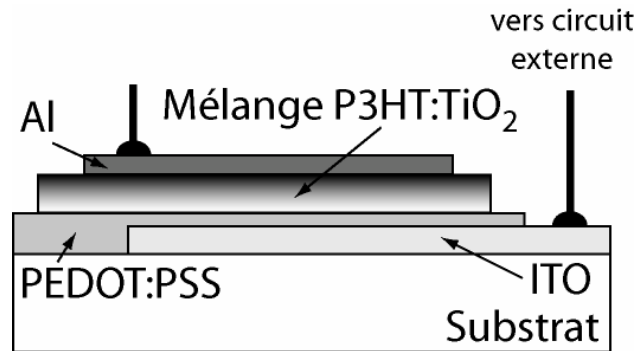


⇒ Charges à longue durée de vie (100  $\mu$ s)

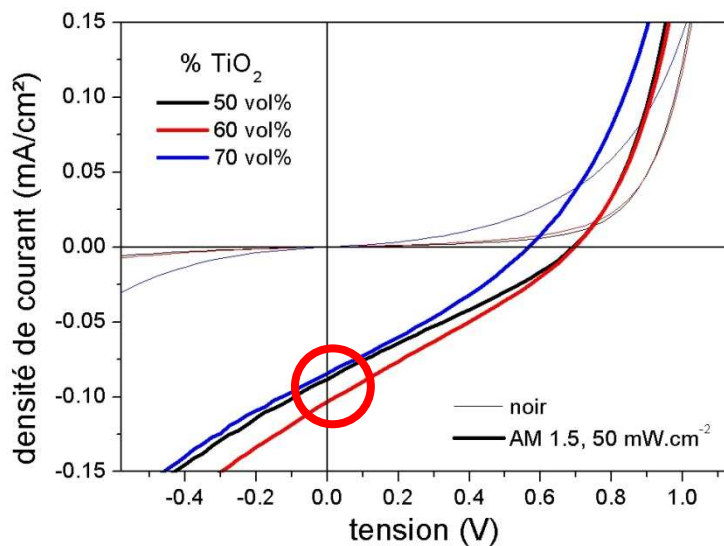
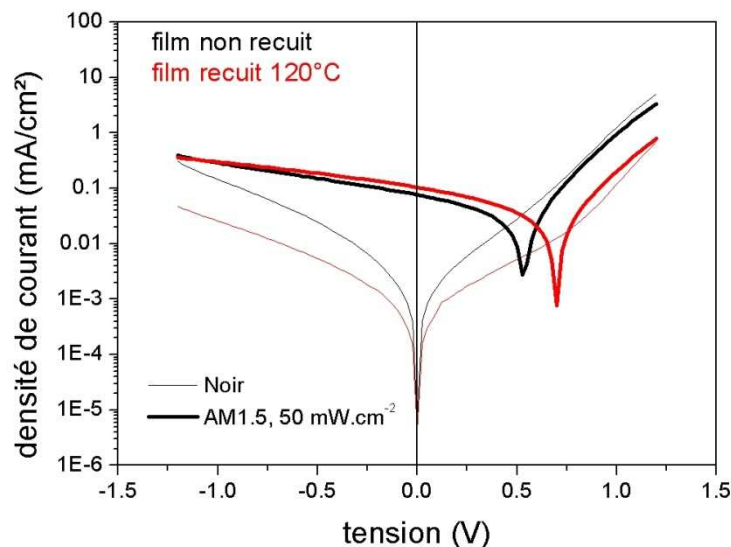
⇒ **Importante séparation de charges**



# Propriétés photovoltaïques



# Propriétés photovoltaïques



⇒ Influence du recuit

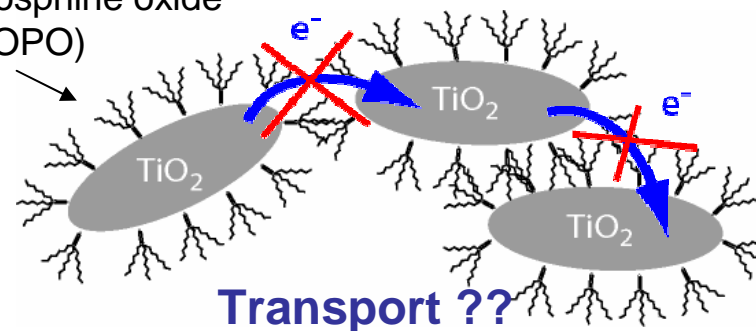
⇒ Influence de la

concentration

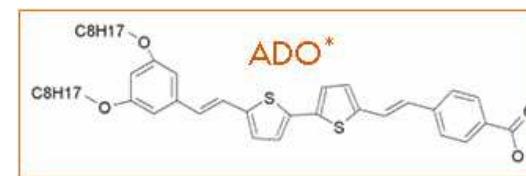
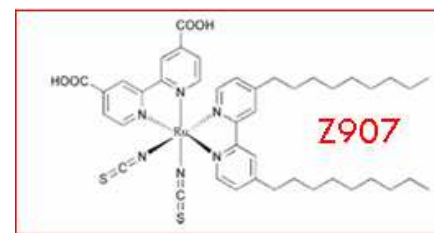
photocourants !!

$$\text{Absorbance} + \text{EQE} = 100\% \Rightarrow 4 \text{ mA.cm}^{-2} !!!$$

Tri-octylphosphine oxide (TOPO)

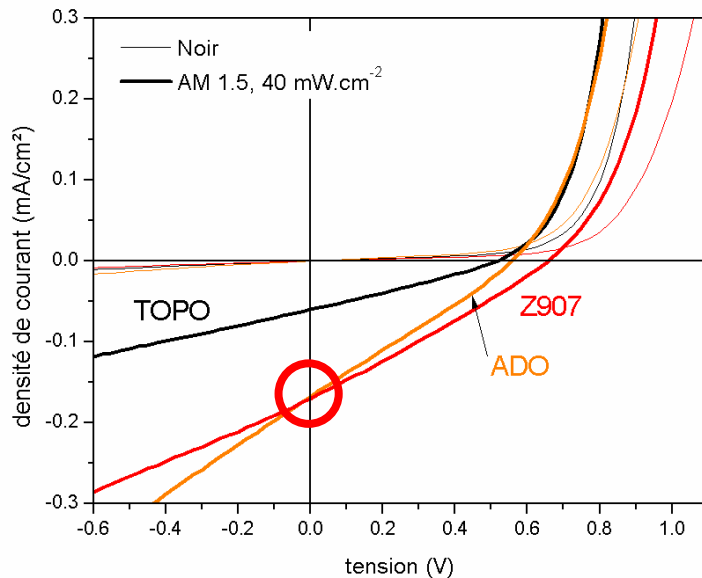
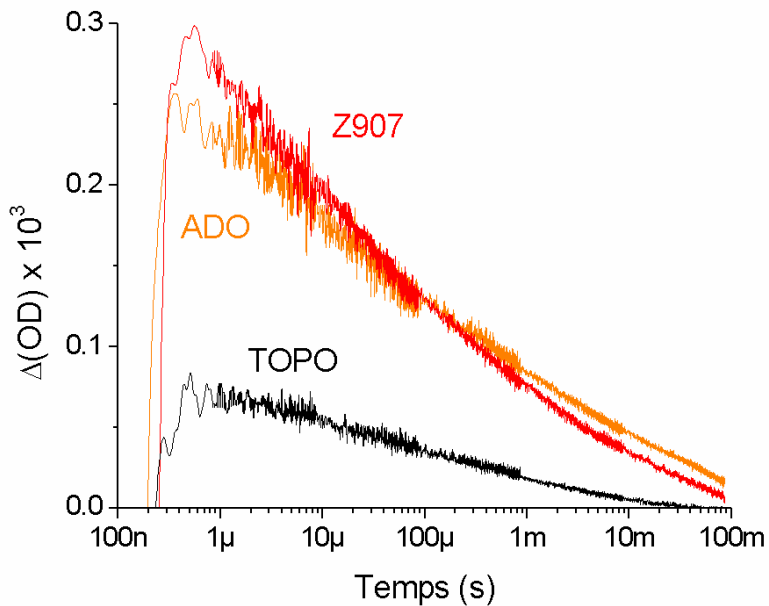


➤ Procédures d'échange de Ligands



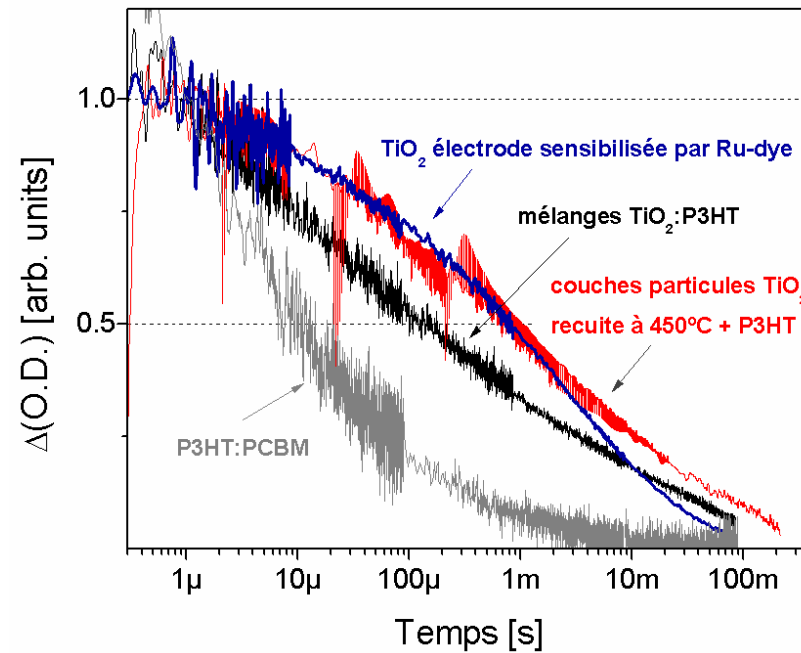
\* Collaboration with J. Ackermann, Université Aix-Marseille II, France

# Échange de ligands – Origine du piégeage de charge



**Faibles Photocourants**

Transport limité par Piégeage de charges



- Piégeage géométrique (TiO<sub>2</sub>, P3HT)
- Piégeage intrinsèque au nanofils de Ti

J. Bouclé, S. Chyla, M. Shaffer, J. Durrant, D. Bradley and J. Nelson, soumis à Adv. Func. Mater., Mars 2007

✓ Mélanges P3HT / Nanofils de TiO<sub>2</sub> Imperial College  
London

✓ Électrodes nanoporeuses de ZnO élaborées en solution



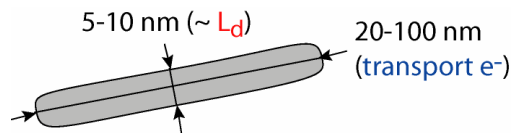
✓

Conclusions

# Électrodes nanoporeuses de ZnO élaborées en so

## ➤ Motivations

$$\mu_e \sim 150 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$$

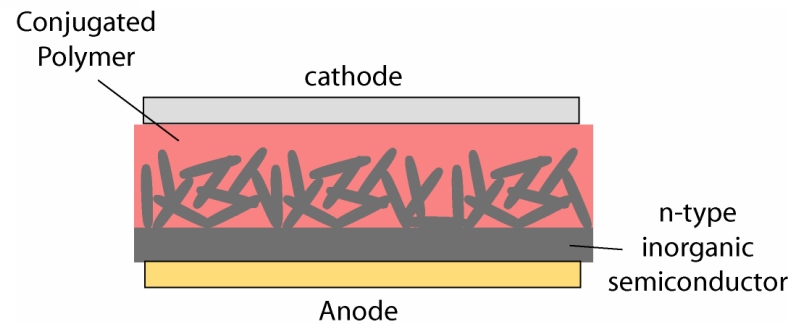


## ➤ Stratégie

A – Synthèse de nanorods de ZnO

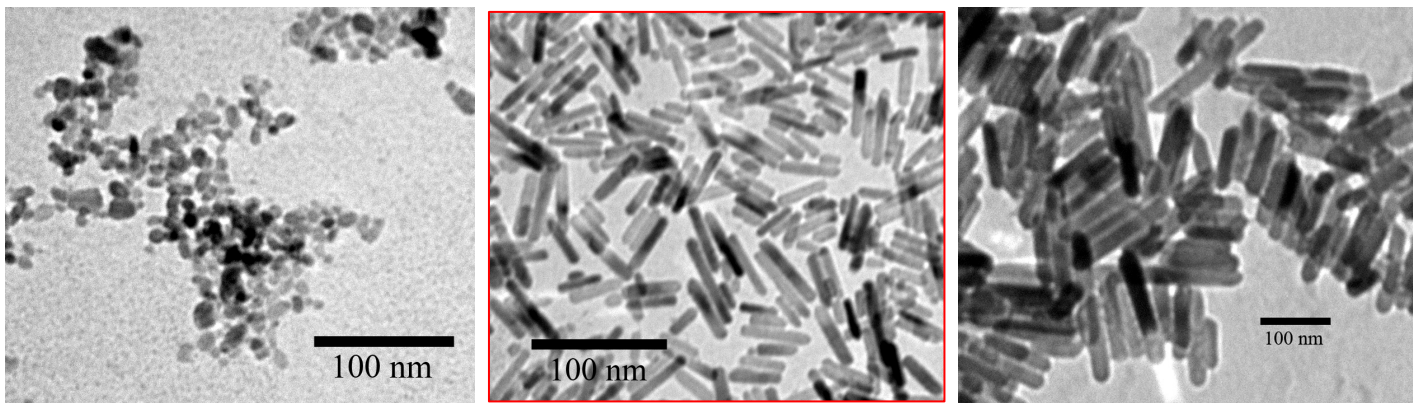
B – Formulation d'une **suspension** ZnO + polym

C – Dépôt de **films minces** + **recuits adaptés**



## A. Synthèse des nanorods de ZnO B. Sun, Nano Letters 5 (2005)

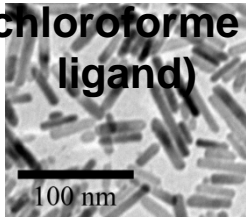
Hydrolyse/condensation [Zn-acetate]:2H<sub>2</sub>O par KOH (méthanol)



# Électrodes nanoporeuses de ZnO élaborées en so

## B. Formulation d'une suspension précurseur de Z C. Dépôt de films minces

Colloïde de  
**Nanorods**  
(chloroforme +  
ligand)



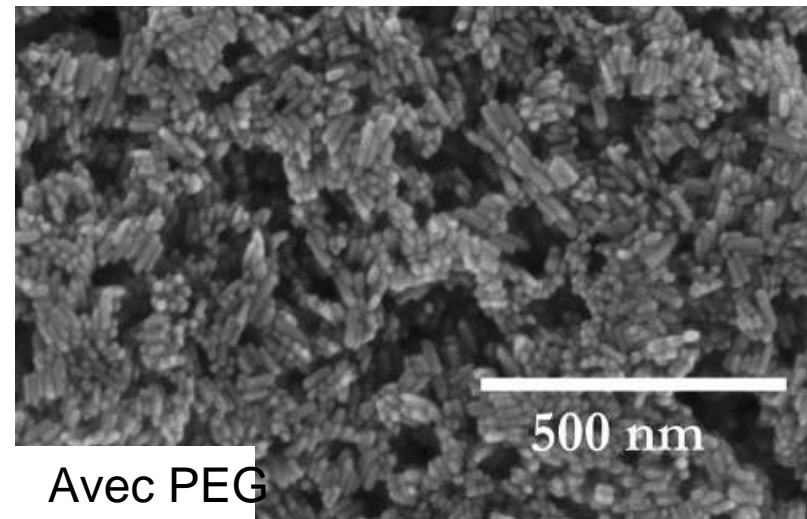
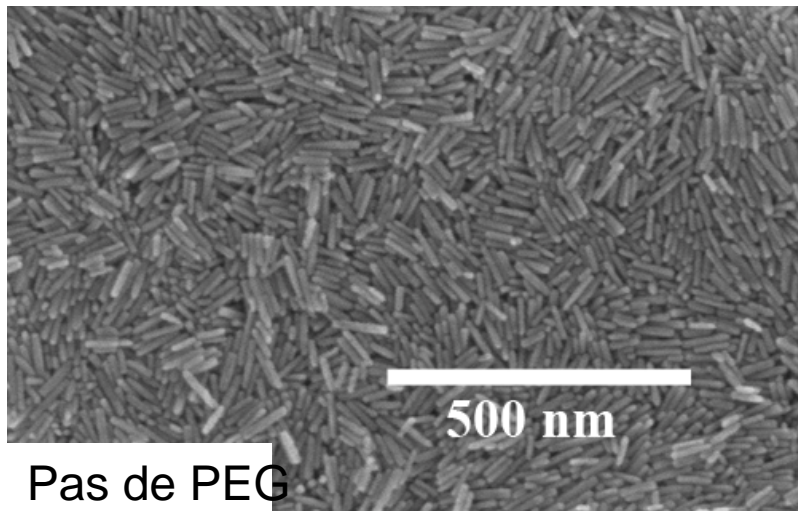
+

Poly-(ethylene glycol)  
**PEG**  
(liant)



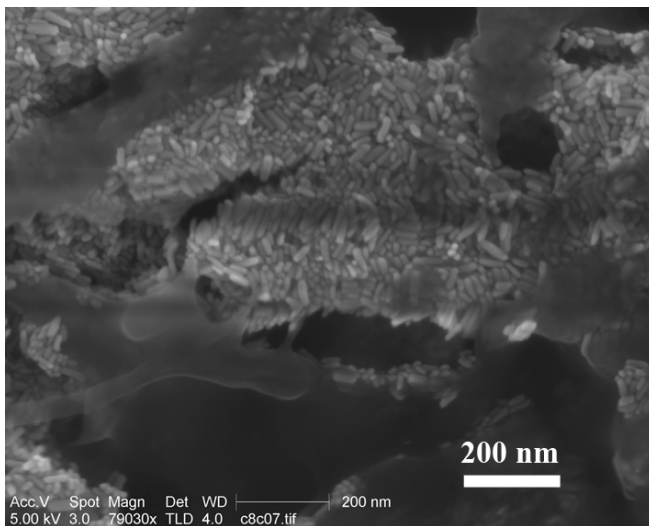
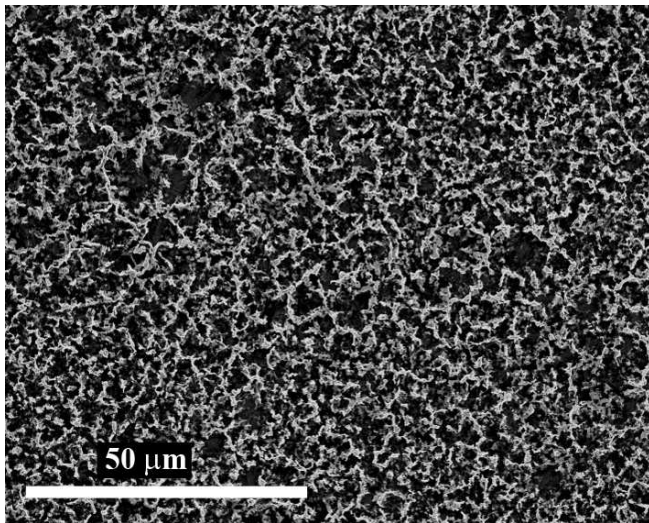
- ✓ Spin-coating (50 – 500 nm)
- ✓ Recuit à 250-500°C sous air

### □ Morphologie des films

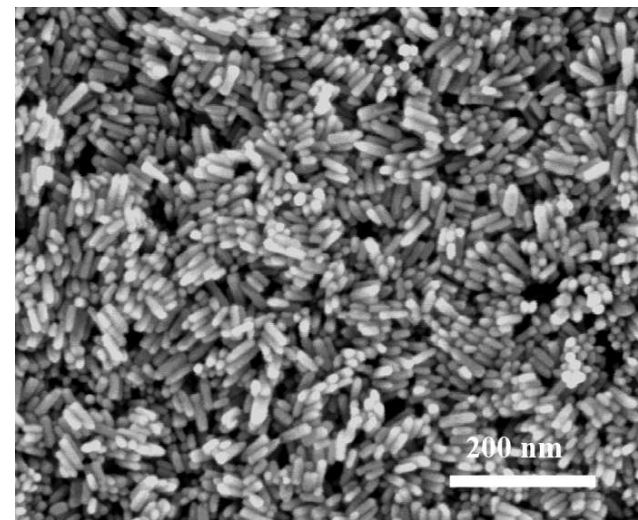
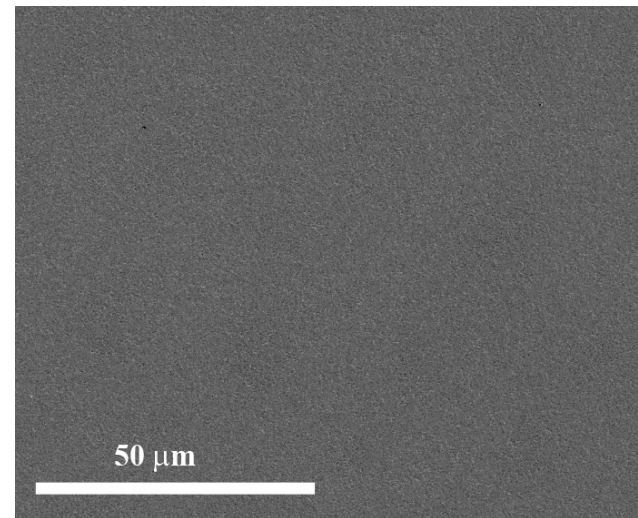


# Influence du ligand

n-Octylamine  
 $C_8H_{17}-NH_2$

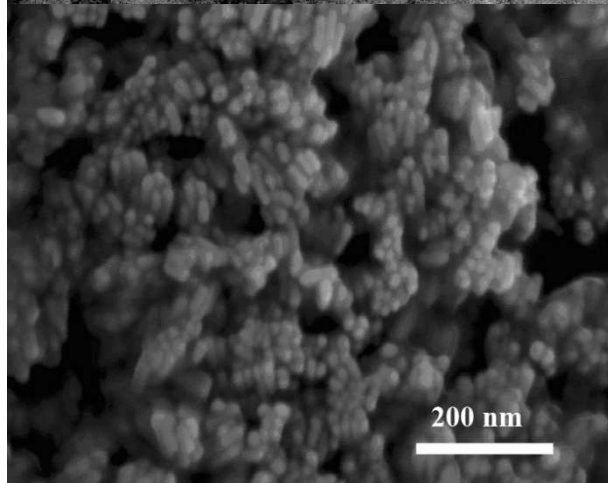
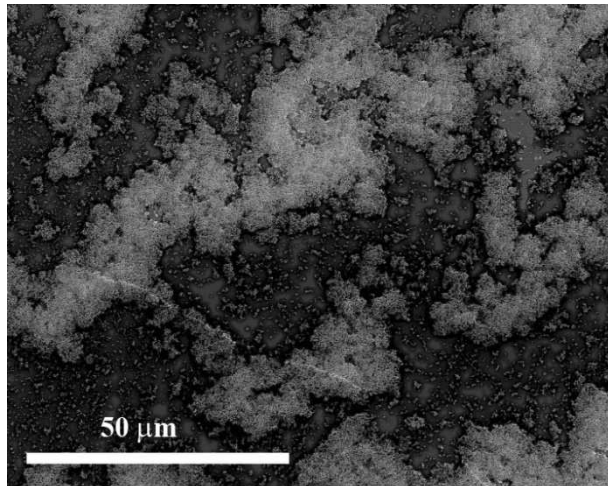


n-Butylamine  
 $C_4H_9-NH_2$

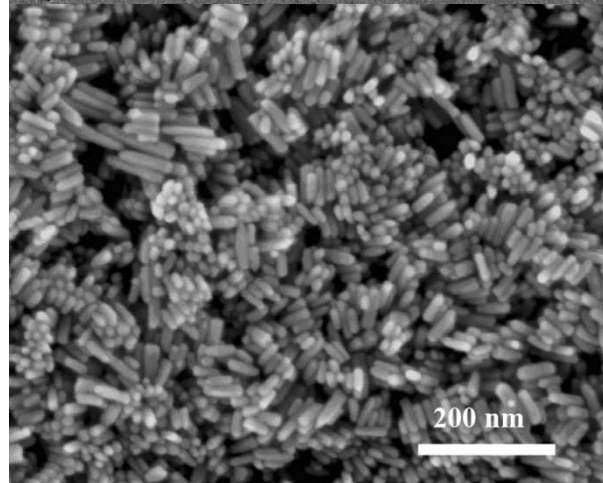
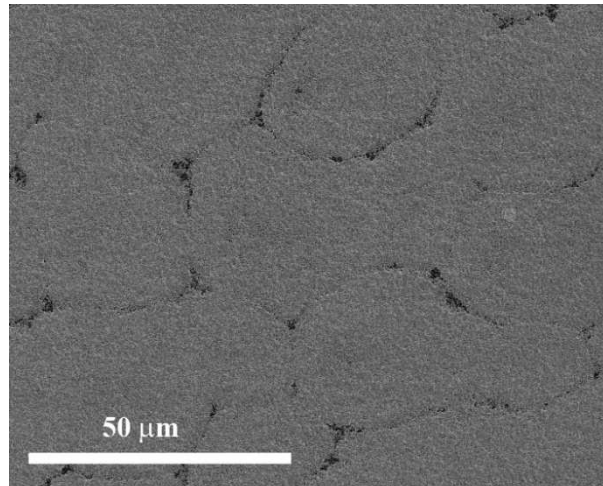


# 🏗 Influence de la composition (ZnO:PEG masse)

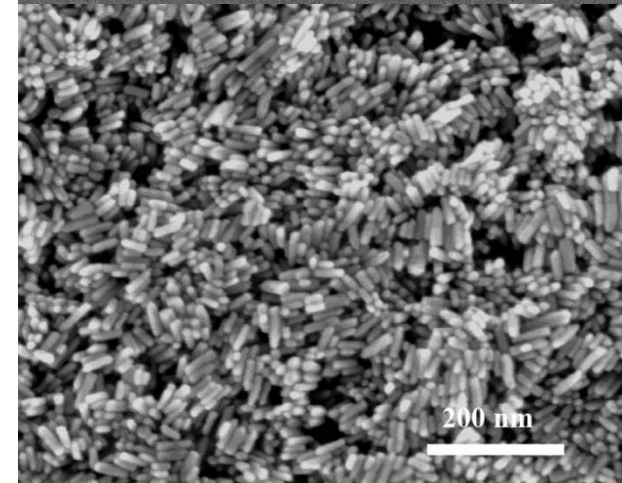
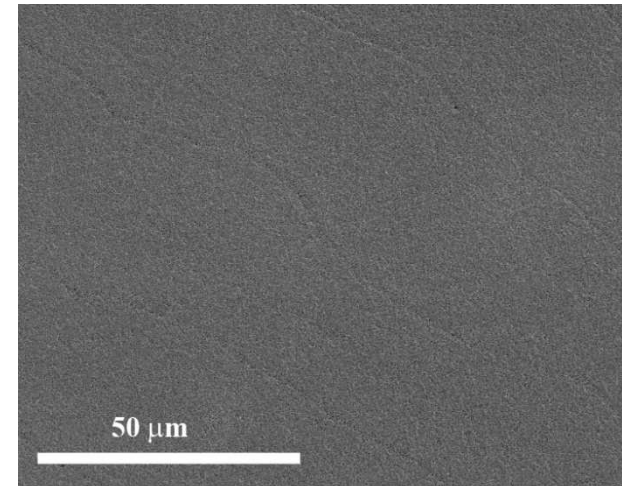
1:1



3:1



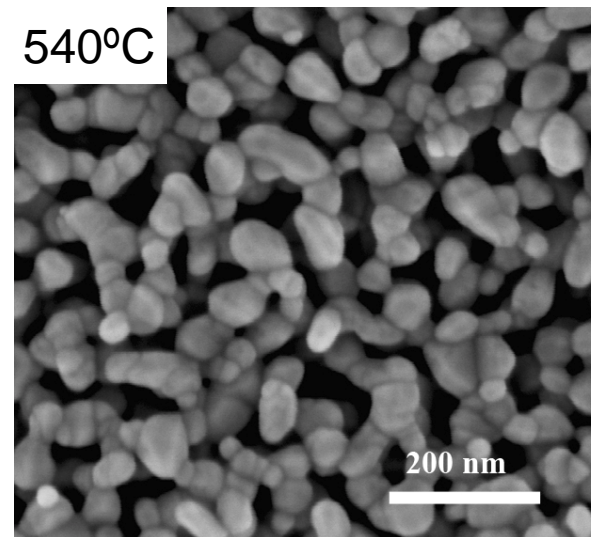
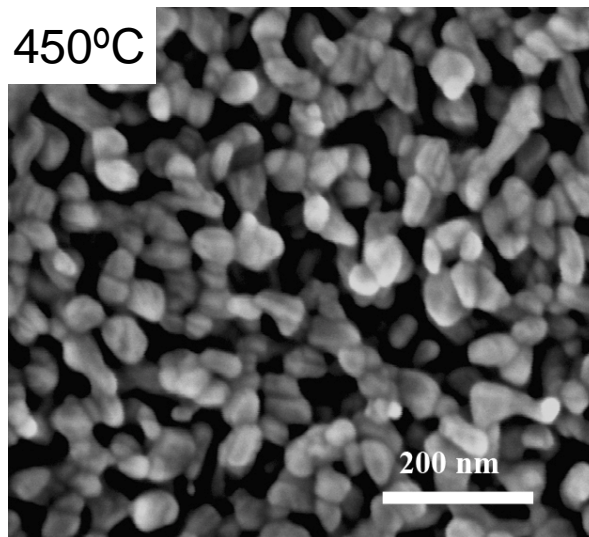
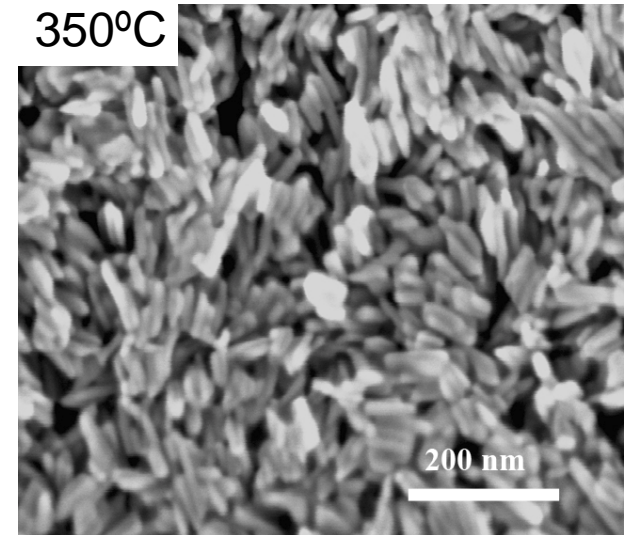
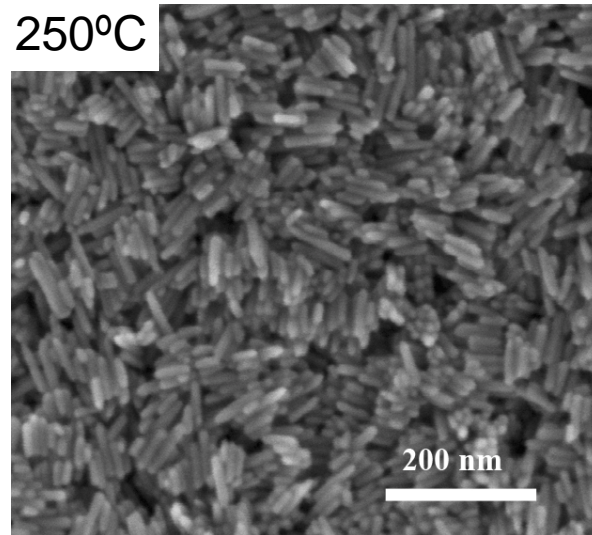
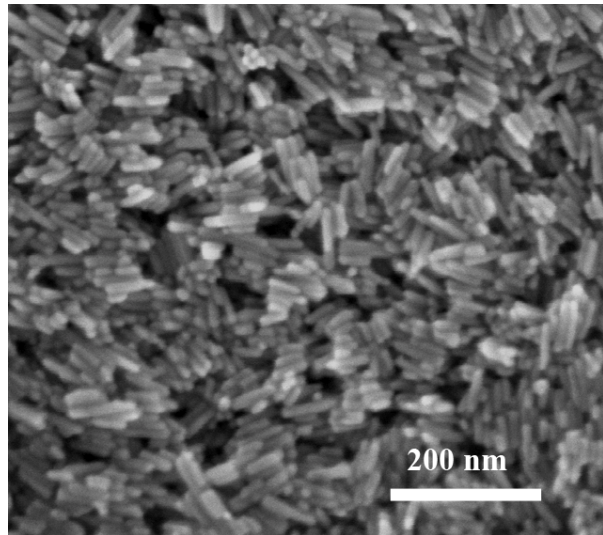
5:1



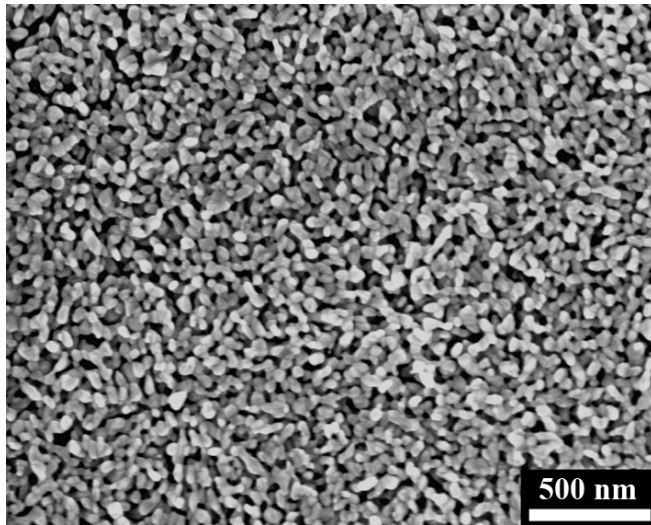
⇒ Contrôle de la **porosité** des films



# Influence du recuit sous air



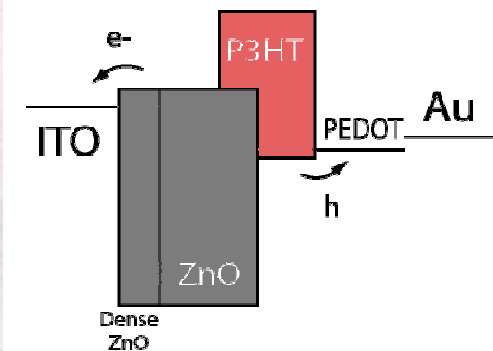
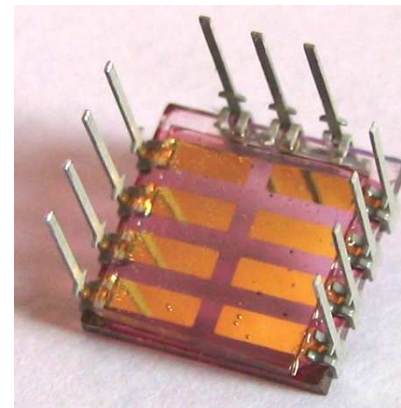
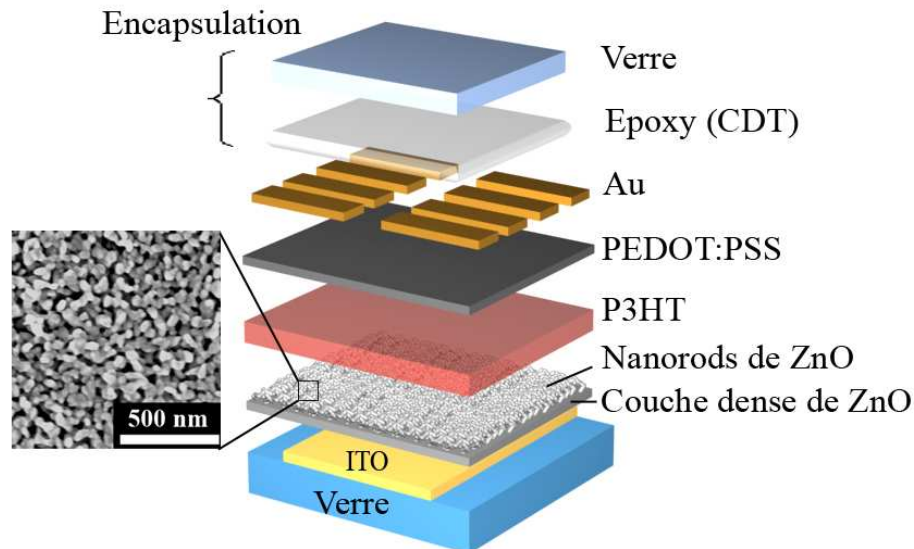
# Électrodes nanoporeuses de ZnO élaborées en so



- ✓ Coalescence des grains
- ✓ Élimination du ligand
- ✓ Connectivité entre particules
- ✓  $10 \text{ nm} < \text{Pores} < 80 \text{ nm}$

⇒ **Bon candidat** pour cellules solaires hybrides à hétérojonction

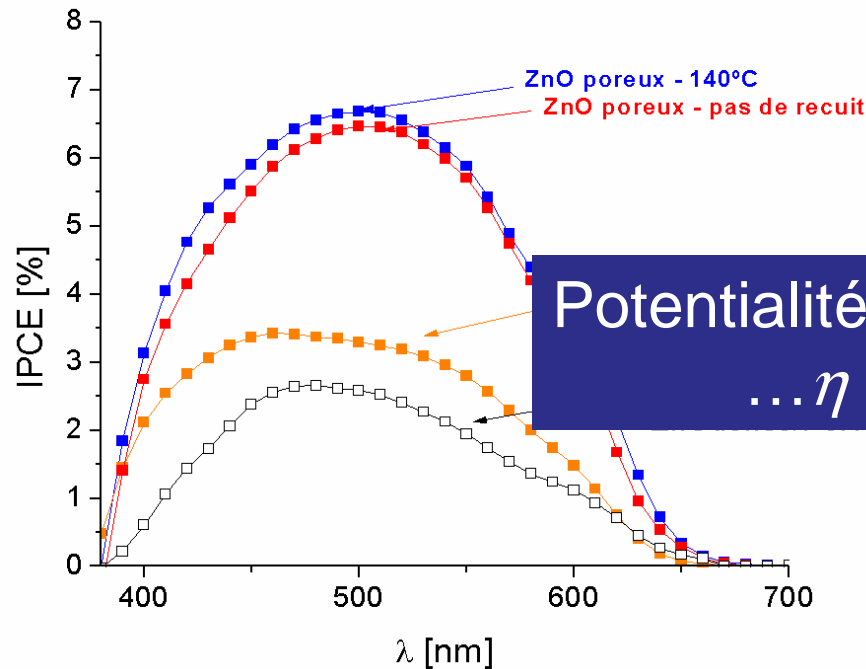
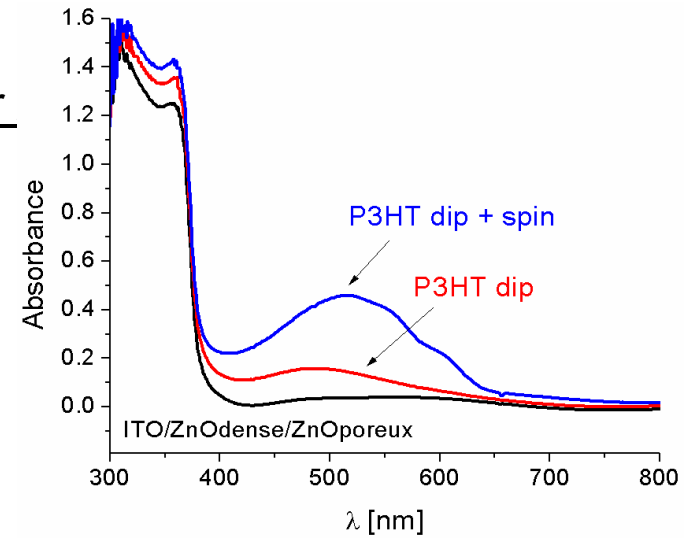
## □ Premières cellules solaires



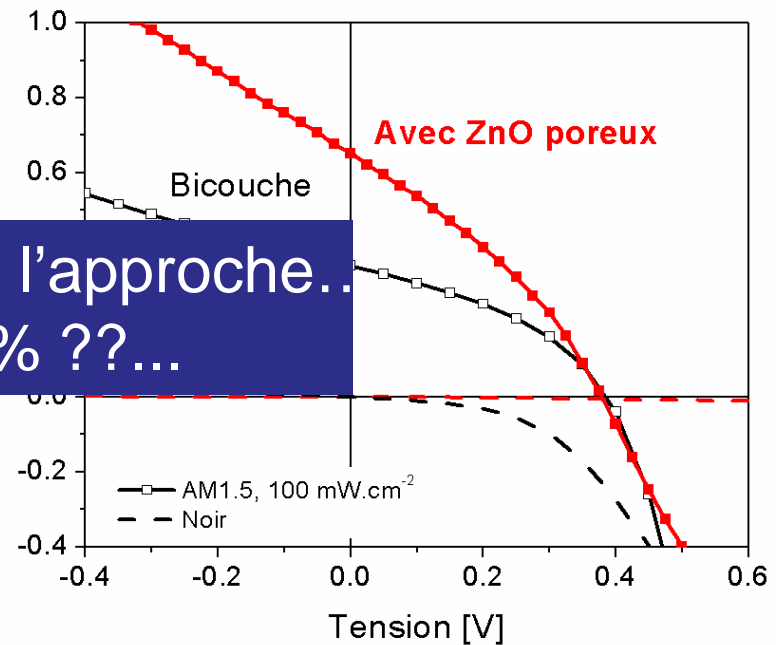
# ❖ Résultats (très) préliminaires...

## Sensibilisation de l'électrode de ZnO (150 nm) par

- Électrode dans P3HT (1 mg/ml, 110°C, 15h)
- Spin-coat P3HT (150 nm)
- Différents recuits (sous N<sub>2</sub>)



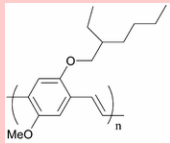
Potentialités de l'approche...  
... $\eta = 1\%$  ??...





# Conclusions – Systèmes Optoélectroniques Hybrides

## Semiconducteurs organiques



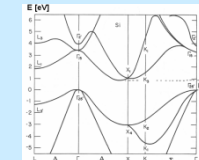
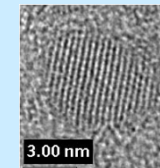
Flexibilité  
Bon marché  
Procédés simples  
Propriétés "ajustables"  
(stabilité ?)



## Systèmes Optoélectroniques Organiques et Hybrides

## Semiconducteurs Inorganiques

Propriétés ajustables  
Non toxiques (TiO<sub>2</sub>, ZnO, etc.)  
Stables  
Bon marché

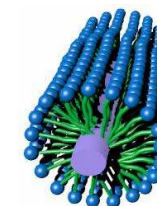
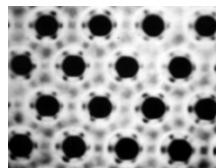


## Organisation de la matière à l'échelle nanométrique

(auto-assemblage, sol-gel, etc.)

+ effets aux interfaces

(transfert de charges, polarisation, etc.)



Systèmes fonctionnels, Composants actifs compétitifs à moindre coût

Cellules solaires, OLED, OFET, ONL, etc.



# Remerciements

Physics

**Prof. J. Nelson**, Prof. D.D.C. Bradley  
Dr. P. Ravirajan, Mrs. T. Ishwara

Chemistry

**Prof. J. R. Durrant**, Dr. B. O'Regan  
Dr. M. S. P. Shaffer, Dr. S. Chyla

Molycell Project  
Supergen Project

**Imperial College  
London**

Optoelectronics Group

**Dr. N. C. Greenham**,  
Dr. H. Snaith, Dr. B. Sun,  
Mr. H. Wong



**UNIVERSITY OF  
CAMBRIDGE**

Naimo Project