

Cellules solaires organiques : du laboratoire au marché



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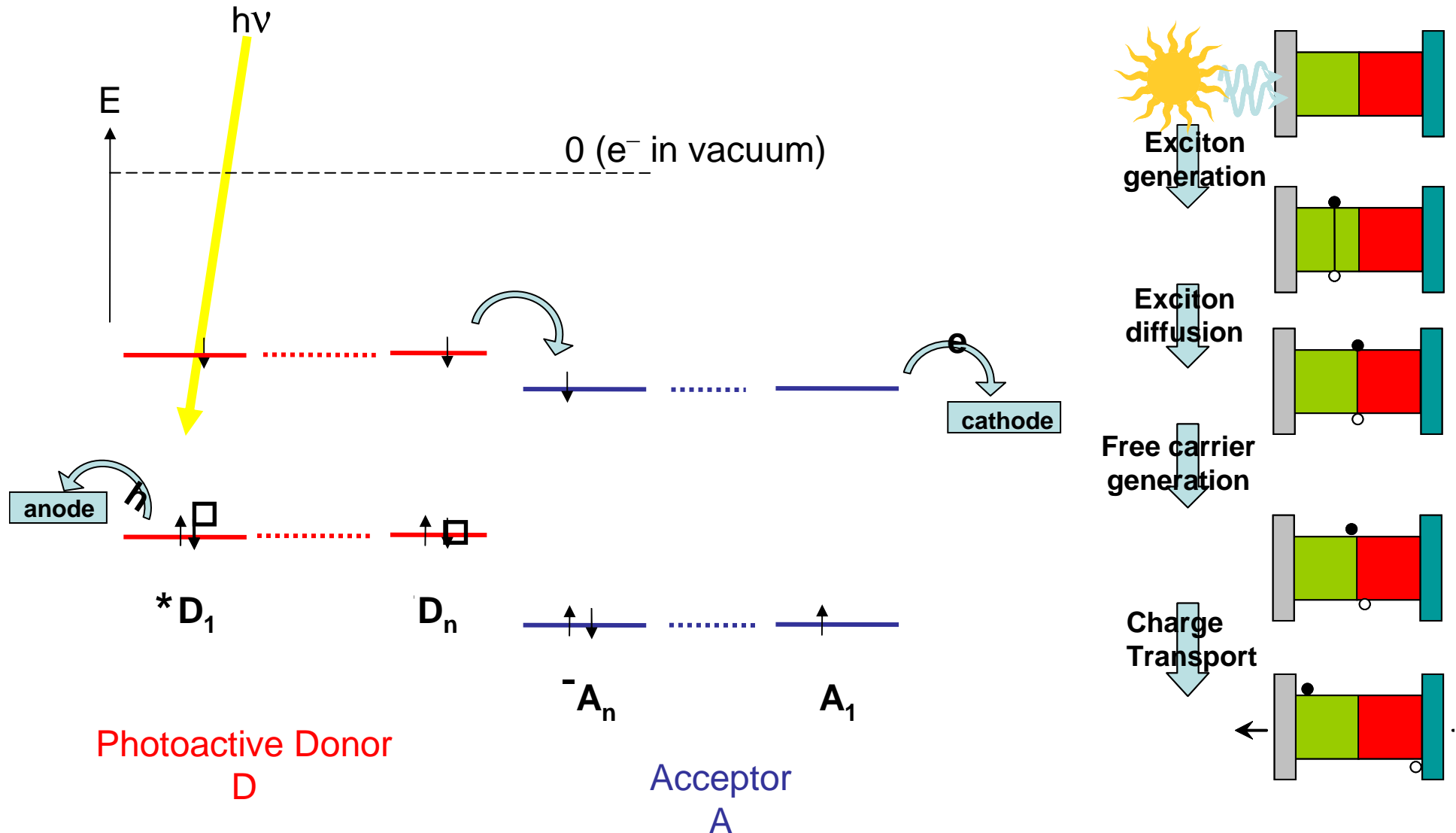
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Conversion photovoltaïque dans les cellules organiques

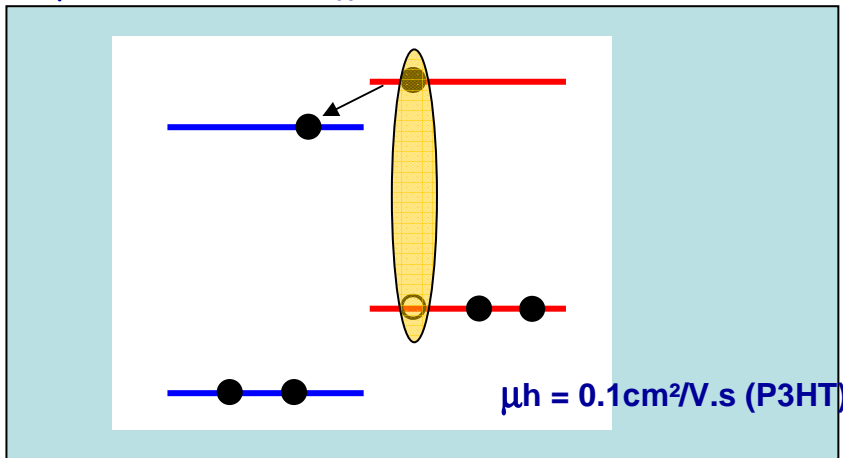
Principe de base: Hétérojonction entre deux matériaux semiconducteurs



Propriétés électroniques des semiconducteurs

Organique

$\mu_e = 0.6 \text{ cm}^2/\text{V.s}$ (C_{60})

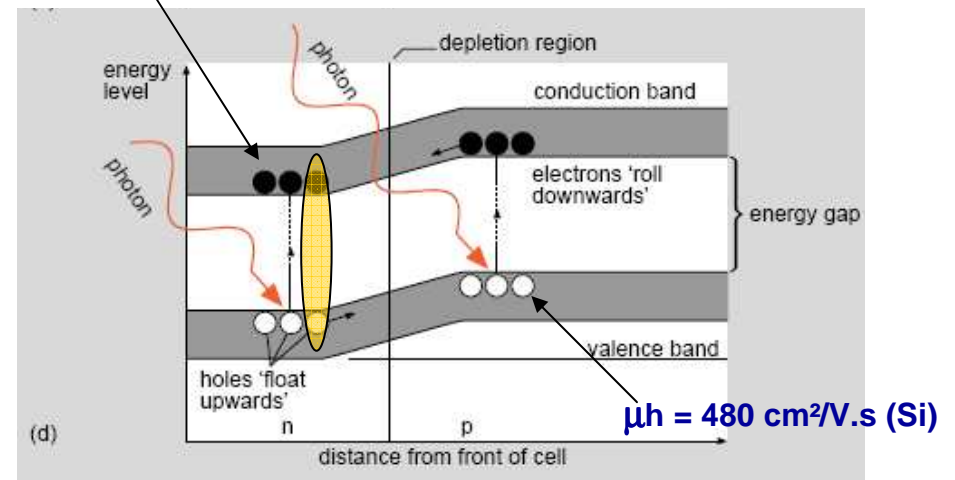


Exciton : $E_f \approx 0.25 \text{ eV}$;
 $L_d \approx 10 \text{ nm}$

VS

Inorganique

$\mu_e = 1450 \text{ cm}^2/\text{V.s}$ (Si)



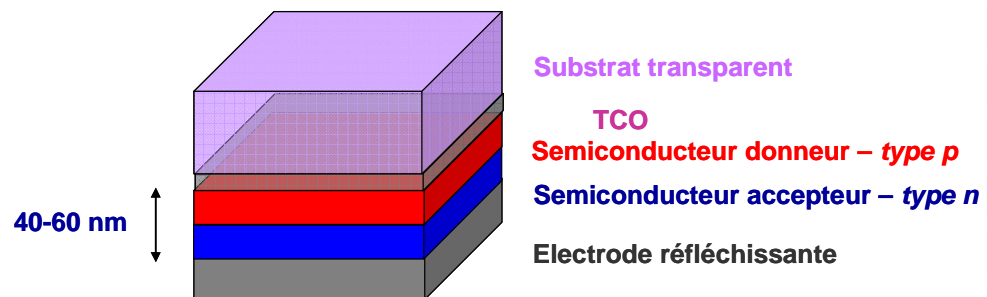
Paire électron-trou : $E_f \approx \text{meV}$ (4 meV pour AsGa)
 $L_d \approx 100 - \text{qqs } 100 \mu\text{m}$

Organique

vs

Inorganique

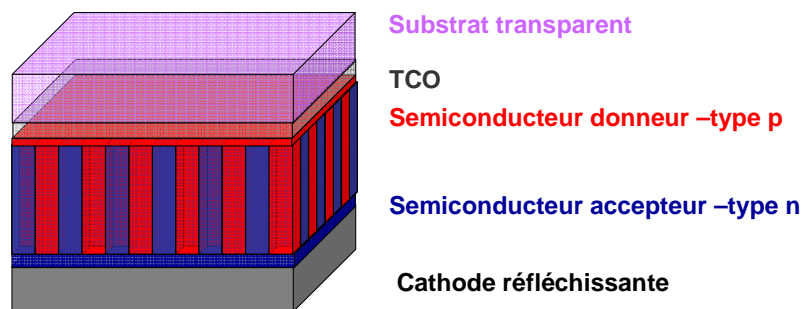
1: structure bi-couches



Epaisseur couche active limitée par

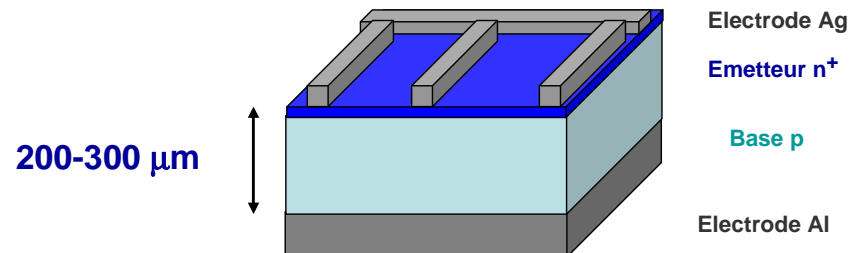
- Longueur diff excitons
- Mobilité des porteurs

2: structure en réseaux interpénétrés



Epaisseur couche active limitée par

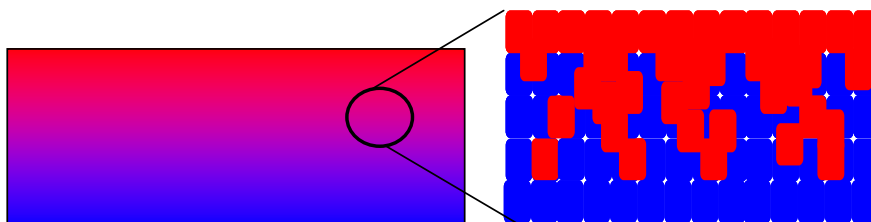
- Mobilité des porteurs



Structures de couches actives

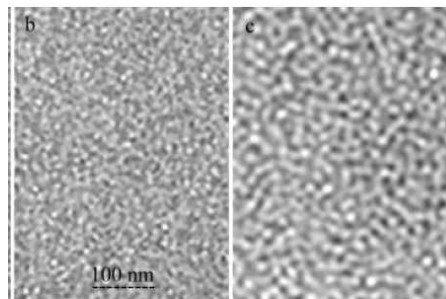
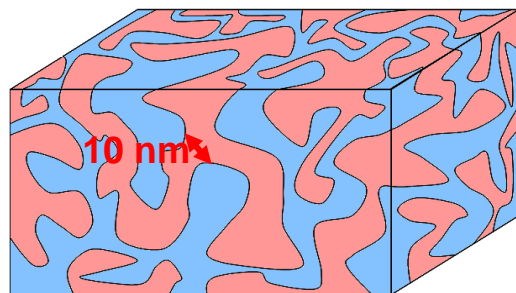
Interface donneur accepteur >> surface géométrique de la cellule

Contrôle des paramètres de dépôt → Développement de l'interface



Dépot PVD
Petites molécules

Séparation de phase spontanée entre matériaux



Dépot en solution
Polymère/petite molécule

TEM images of P3HT/PCBM film morphology after thermal annealing:
b) 150°C for 30 min; c) 150°C for 2h
From Ma et al., Adv. Funct. Mater., 2005, 15, 16717

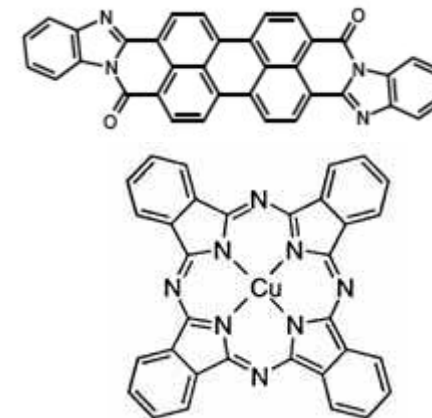
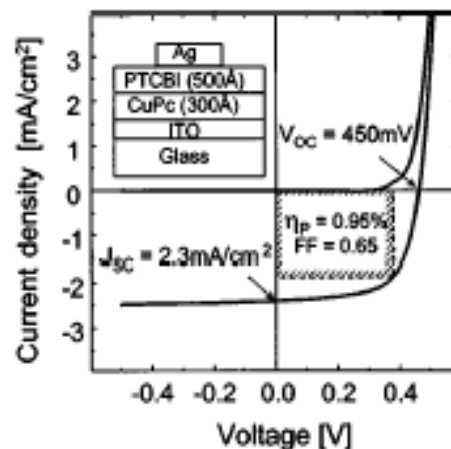


Filière petites molécules : dépôt PVD
Filière polymère : dépôt en solution

Un peu d'histoire

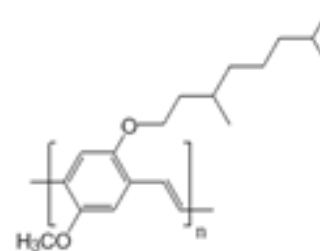
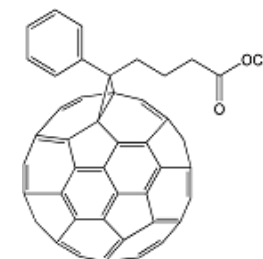
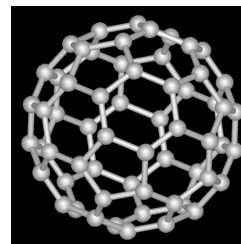
•Tang (Kodak)

1^{ère} cellule organique à hétérojonction
 Cellule bicouche, molécules évaporées
 PCE = 0.95% @ 70 mW/cm²
 Brevet: 1979 – publi : 1986

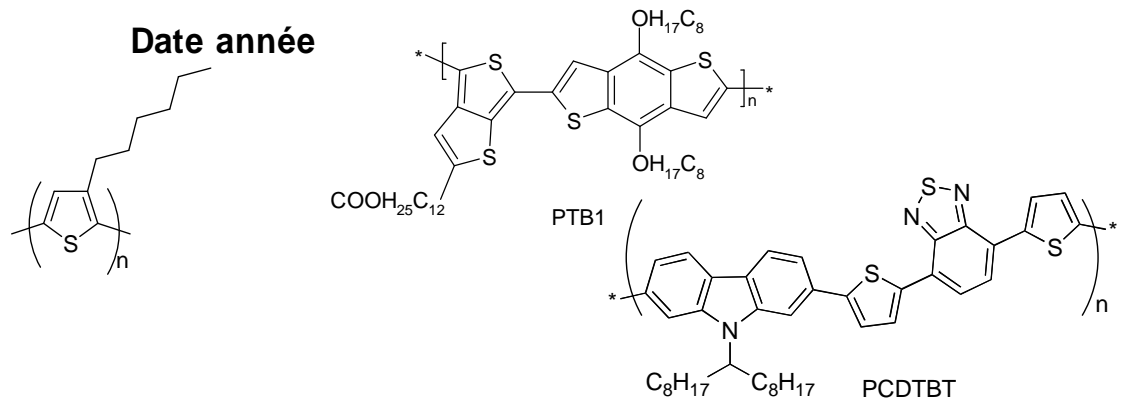
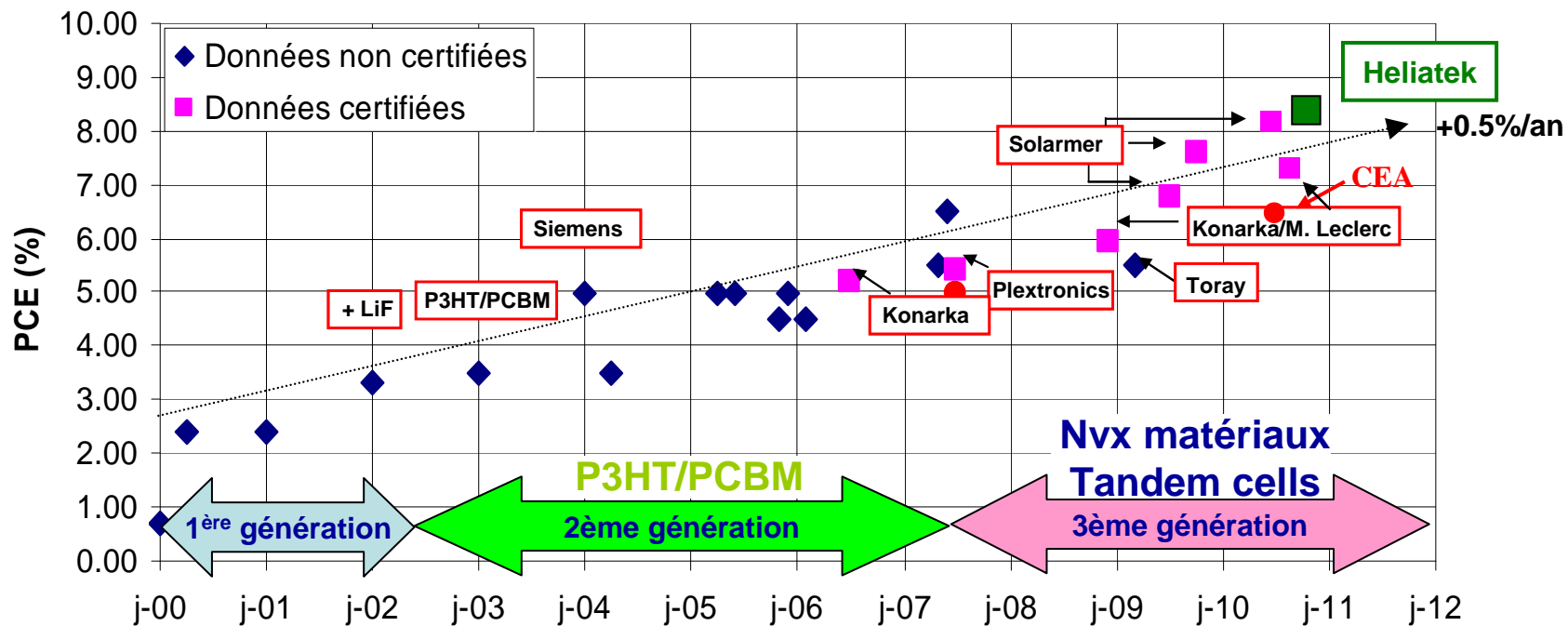


•Cellules polymères

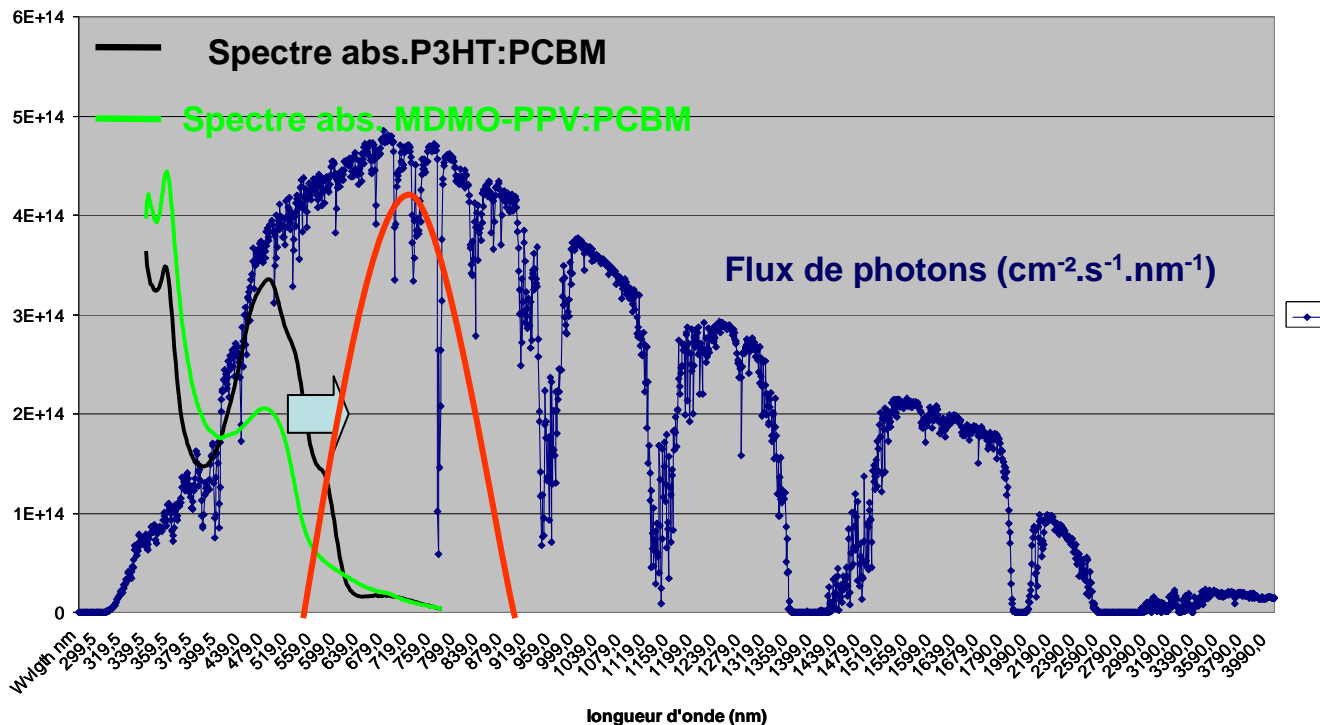
1992: 1^{ère} cellule bicouche polymère/ C60
 Brevet Saricifti et Heeger 1992, publi 1993
1994: 1^{ère} Cellule à hétérojonction en volume
 mélange polymère/fullérène
1995: introduction PCBM



Evolution of performances



Evolution des polymères



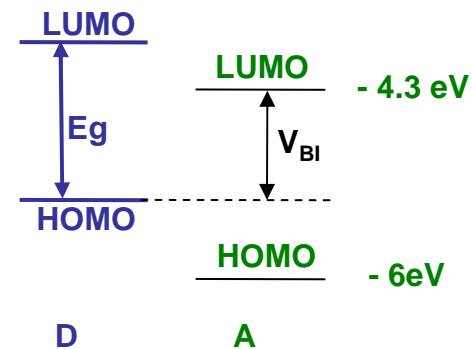
Décalage vers le rouge du spectre d'absorption des matériaux

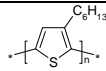
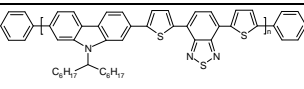
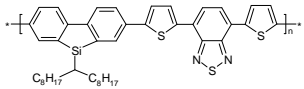
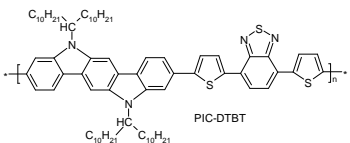
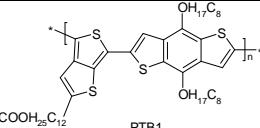
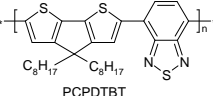
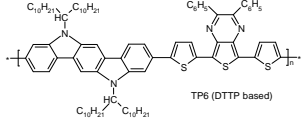
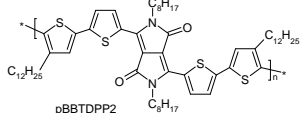
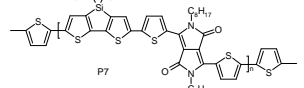


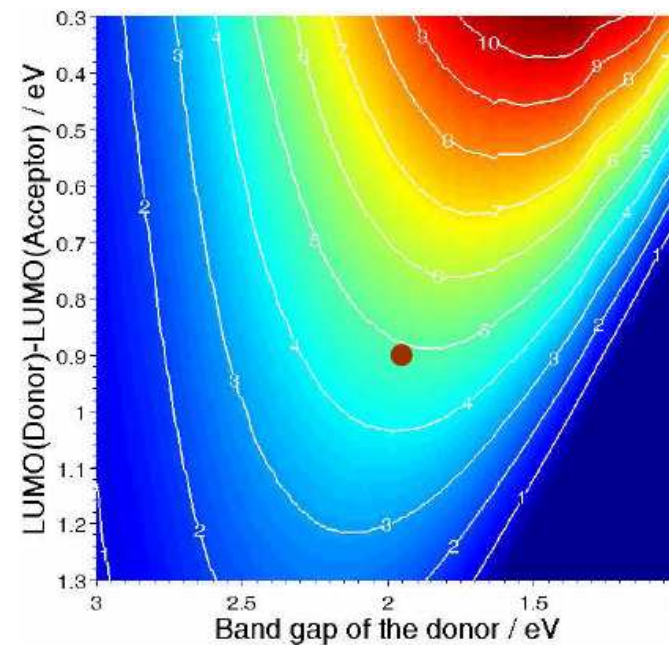
Forme gaussienne spectre d'abs des matériaux organiques

→ 'trou' dans le bleu

Diminution de la Voc



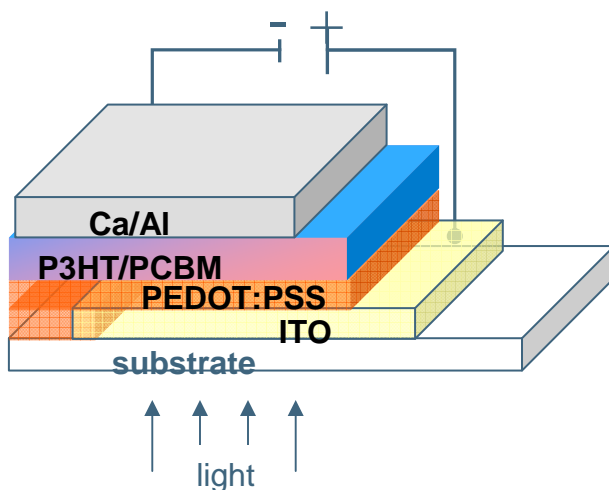
Polymère	Structure	λ_{\max} (nm)	λ_{offset} (nm)	Gap (eV)	LUMO (eV)	HOMO (eV)	PCE (%) *[70]PCBM
HBG							
P3HT		515	650	1.9	3.2	5.1	4-5
PCDTBT		515	650	1.9	3.6	5.5	4.6* 6.1* 7.13*
PSiFDBT		584	680	1.82	3.57	5.39	5.4
PIC-DTBT		398/540	630	1.9	3.55	5.45	1.47
LBG							
PTB1		680	760	1.7	3.2	4.9	7.4*
PCPDTBT		775	890	1.4	3.55	5.3	5.5*
TP6		430/640	725	1.7eV	3.59	5.32	1.27
pBBTDPP2		810	860	1.4	-	-	4*
P7		700	1000	1.24	3.80	5.31	-



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

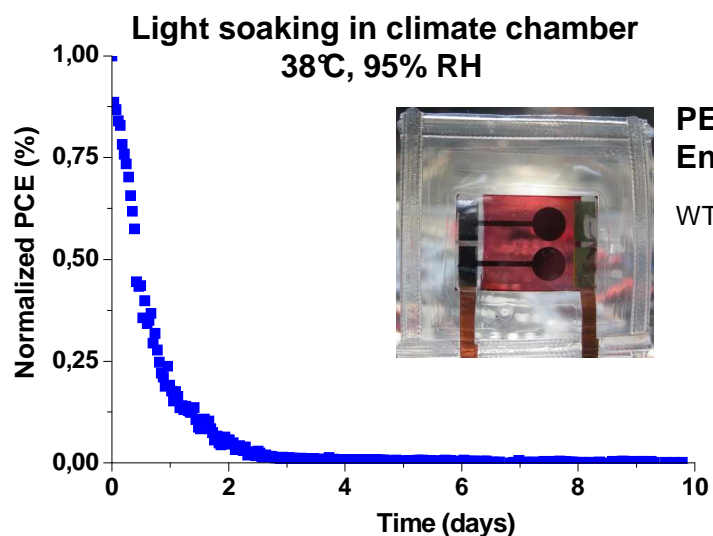
Dispositifs

• Structure 'classique' (historique)



Simple: 3- 4 couches déposées
 Excellent rendement initial (4-5% pour P3HT:PCBM)

Difficile à industrialiser
 Stabilité de la cathode



PET/ITO/PEDOT/P3HT:PCBM/Ca/Al
 Encapsulated with Escal[®]

WTR = $9 \cdot 10^{-3} \text{g.m}^{-2}.\text{d}^{-1}$ OTR = $5 \cdot 10^{-2} \text{cm}^3.\text{m}^{-2}.\text{d}^{-1}$

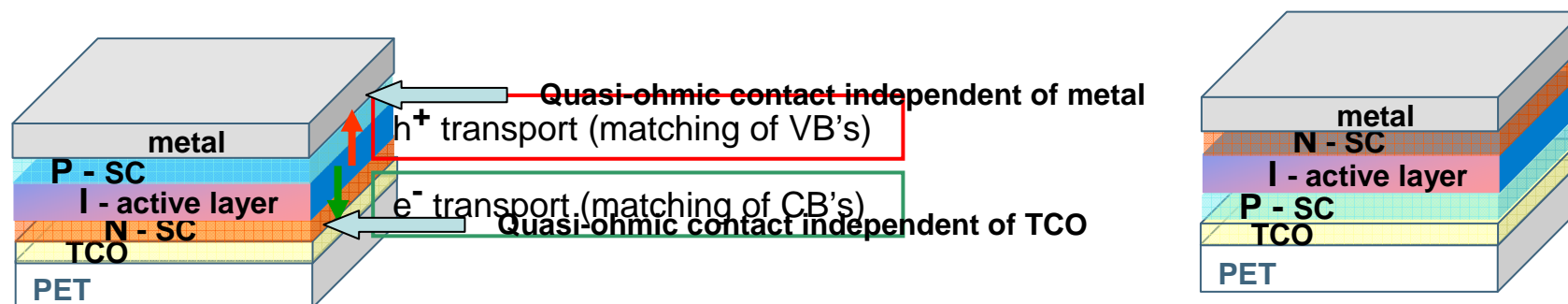
Short lifetime due to cathode's degradation
 No printable electrode materials

•structure PIN

Common use in inorganic PV (suppress recombinations at metal contacts)

Introduced in organic LED's (K. Leo, M. Pfeiffer and coll: 2002)

PV (K. Leo, M. Pfeiffer, S. Sariciftci and coll: 2004 on small molecules,
M. Glathaar et al : 2005 on polymers*)



Use of stable electrode materials



Environmental stability
Printable electrode materials

No contact p-SC/TCO

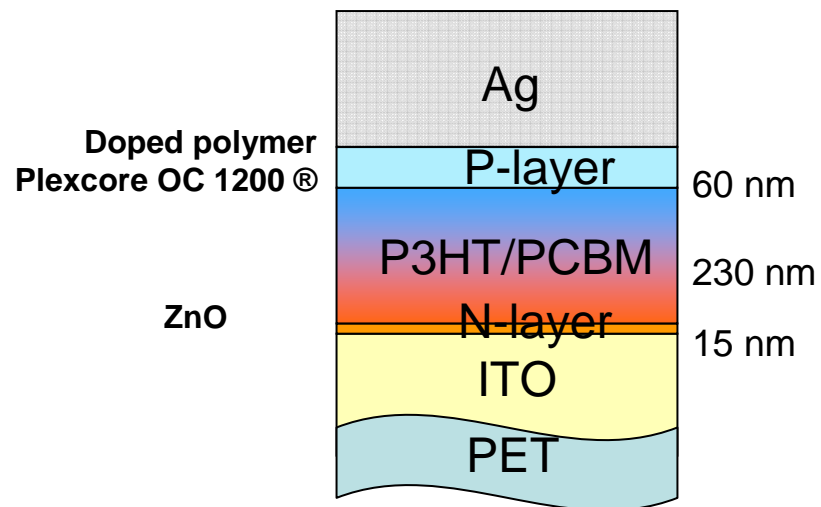


No reaction between PEDOT and ITO (or others)
PEDOT at the back side; less photodegradation

P-type, n-type SC's :

- doped molecular, polymeric SC's
- metal oxides, sulfides, ...

PIN structure on PET

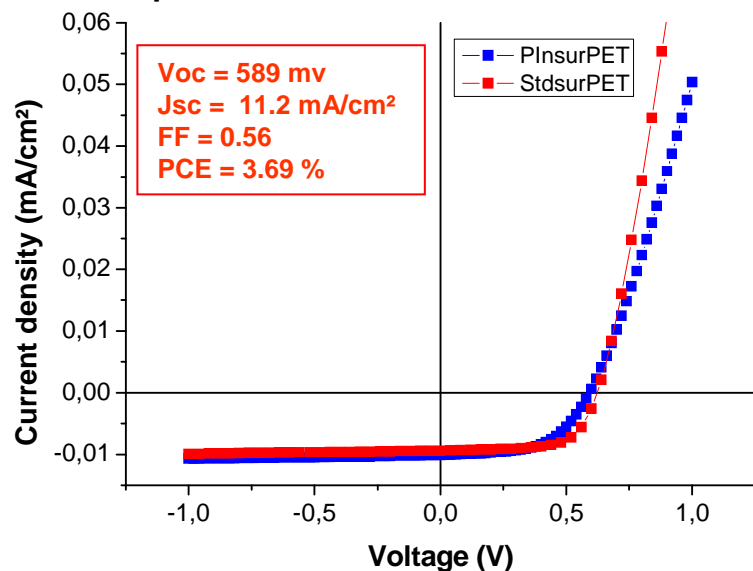


Selection of injection materials

Optimization of processing conditions
(precursor, formulation, 'backing', ...)

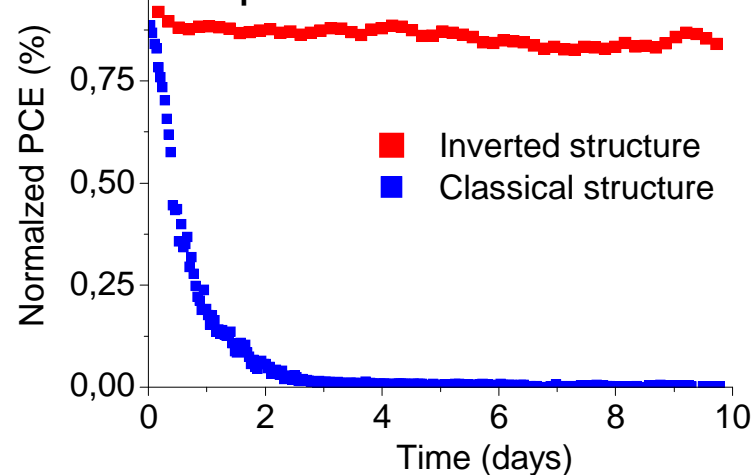
Optimization of layer thickness

Comparison PIN vs STD structure on PET



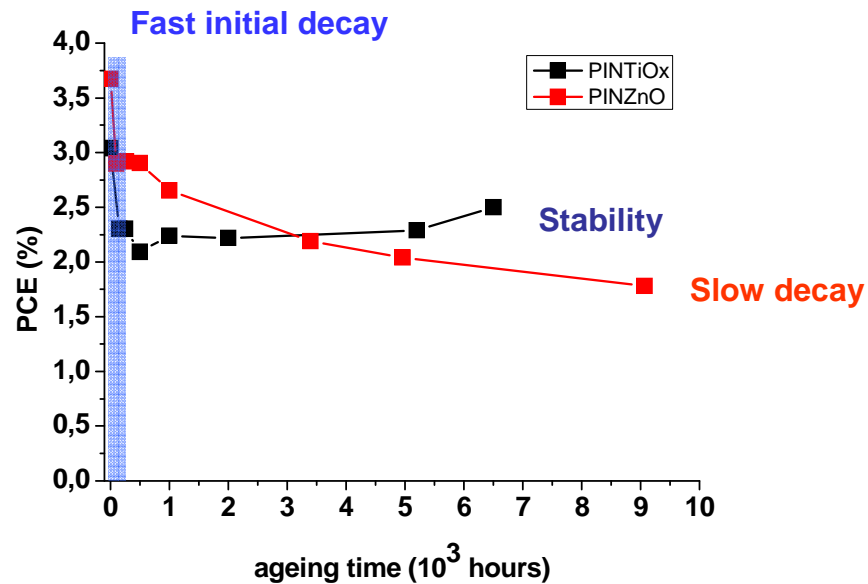
Ageing of flexible solar cell under AM1.5 illumination

Encapsulation with Escal ® barrier films*

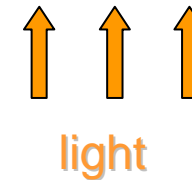
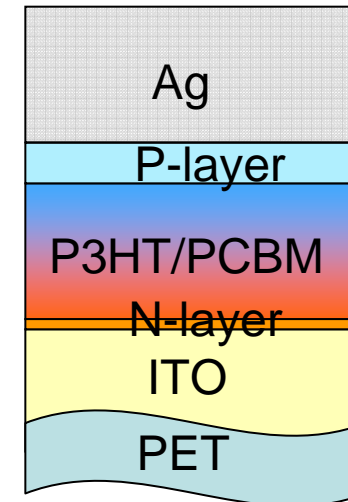


Lifetime study

Ageing of flexible solar cell under AM1.5 illumination.
 Encapsulation with Escal® barrier films



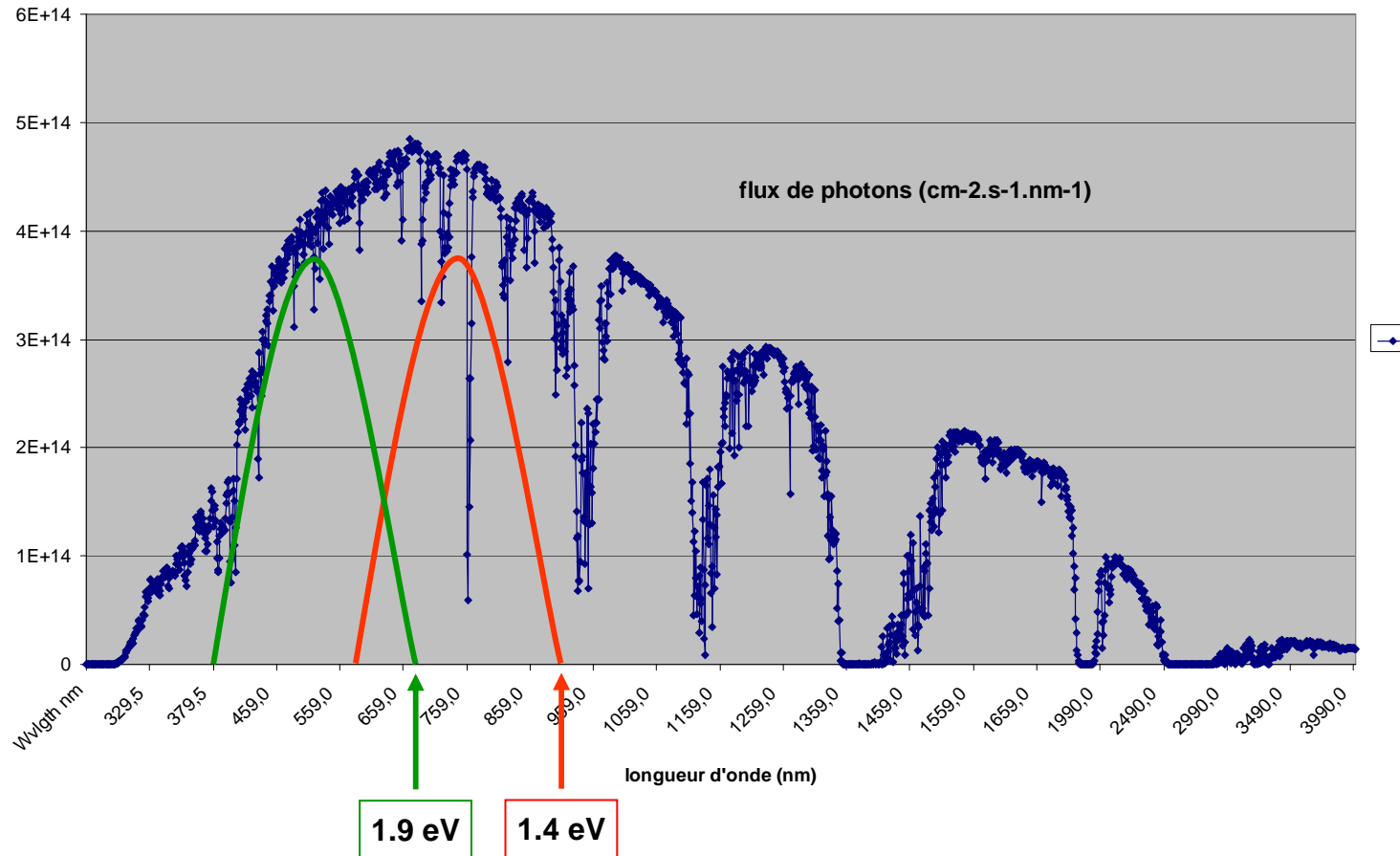
ZnO: 15 nm
 TiOx: 120 nm



- Very good stability for a flexible device after initial stage of burn-in
- Loss of PCE driven by evolution of Jsc
- Filter effect of oxide layer (protection of active layer against UV light?)

PIN structure compatible with full printing on flexible substrates (low temperature process)
Good stability demonstrated
Basic structure for tandem cells: application of injection layers

•structures multi-jonctions

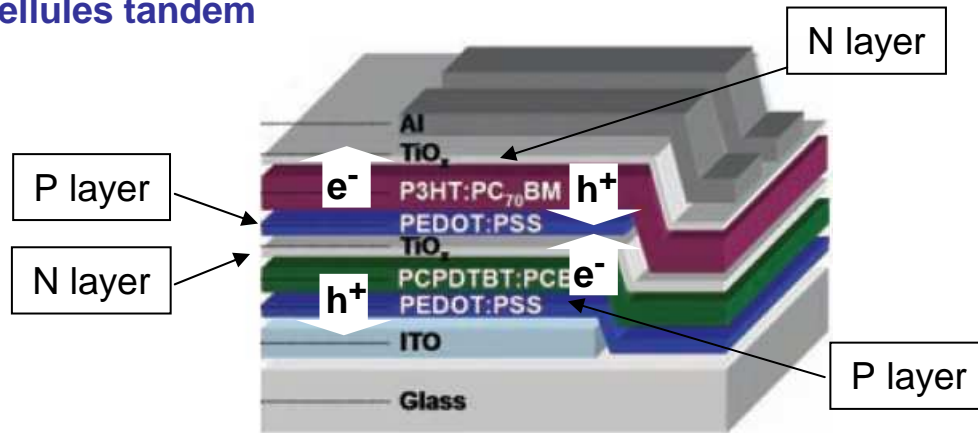


Narrow spectral width of absorption spectrum of organics
(gaussian shape of absorption spectrum)

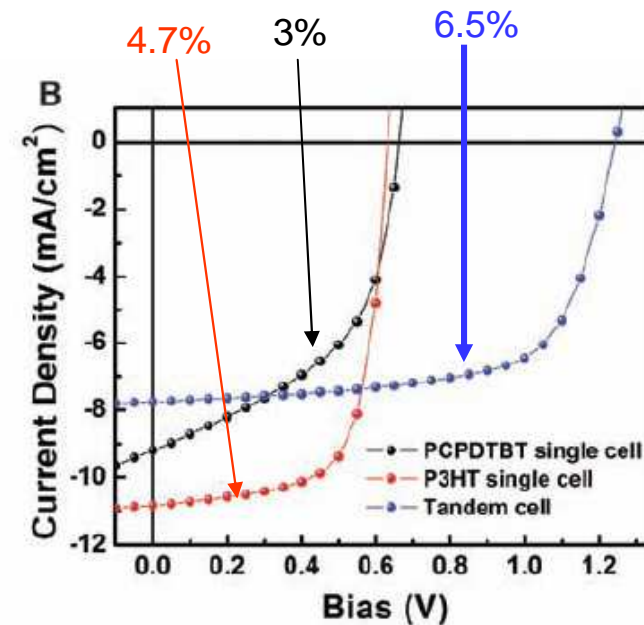
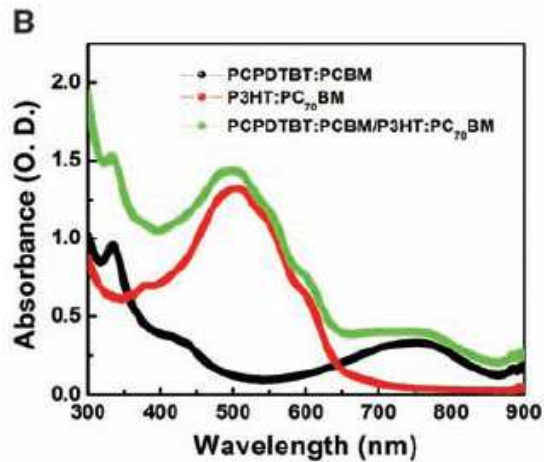


Ideal for combination in tandem cells
(low loss in current expected)

Cellules tandem

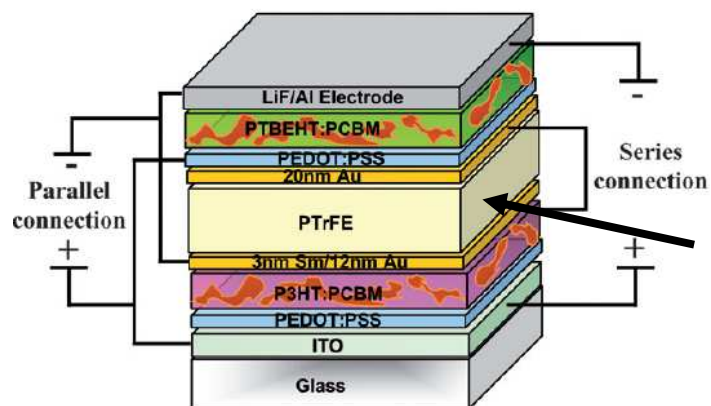


1st organic tandem cell: 6.5%
Kim et al., Science, 317 (2007), 222



Connection en série des sous-cellules
Nécessité d'équilibrer les courants produits dans les sous-cellules
(courant total limité par la plus faible cellule)

Cellules tandems 4 fils



A. Hadipour et al., J. Appl. Phys., 102 (2007), 074506

Espaceur optique

→ optimisation du couplage optique entre cellules

Selection électronique du mode de couplage

→ Série : addition des tensions
→ Parallèle : addition des courants

Conclusion:

Cellules PIN = technologie de référence avec un potentiel de rendement de 8-10% en cellule, une DDV de 10.000 heures

Progrès considérables depuis 2007 sur matériaux actifs

Technologie des cellules tandems adaptée à l'organique – développement à l'échelle labo

Technologies de production des cellules solaires organiques

Petites molécules → Technologies de dépôt sous vide

Polymères → Technologies de dépôt en voie humide

•Filière 'petites molécules'

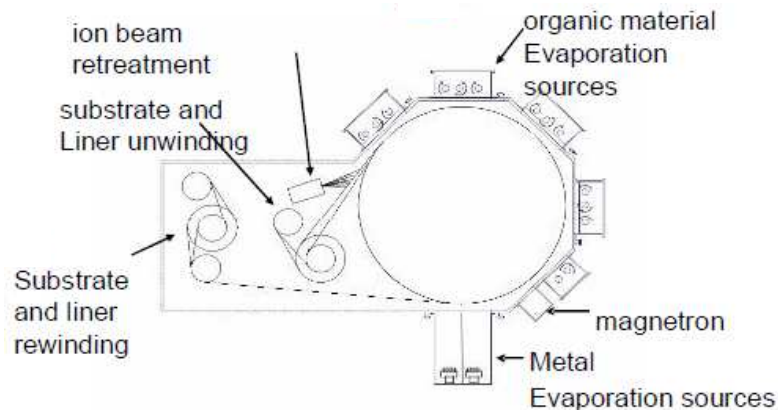
→ Société de référence : Heliatek (Dresden)

Participations de Bosch, RWE, BASF

Coll IAPP, Fh IPMS

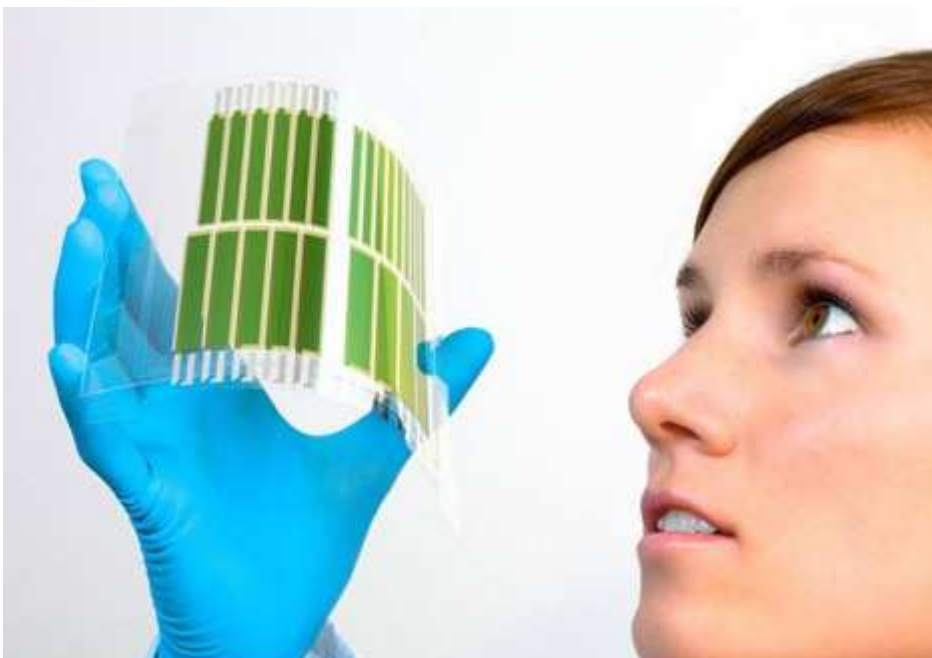
Record mondial de perf à 8.3% (coll. avec IAPP)

Technologie de production au déroulé sur support flexible



Installation de dépôt sous vide en ligne à l'IPMS ; COMEDD II (remerciements: O. Hild)

Page d'accueil du site de Heliatek

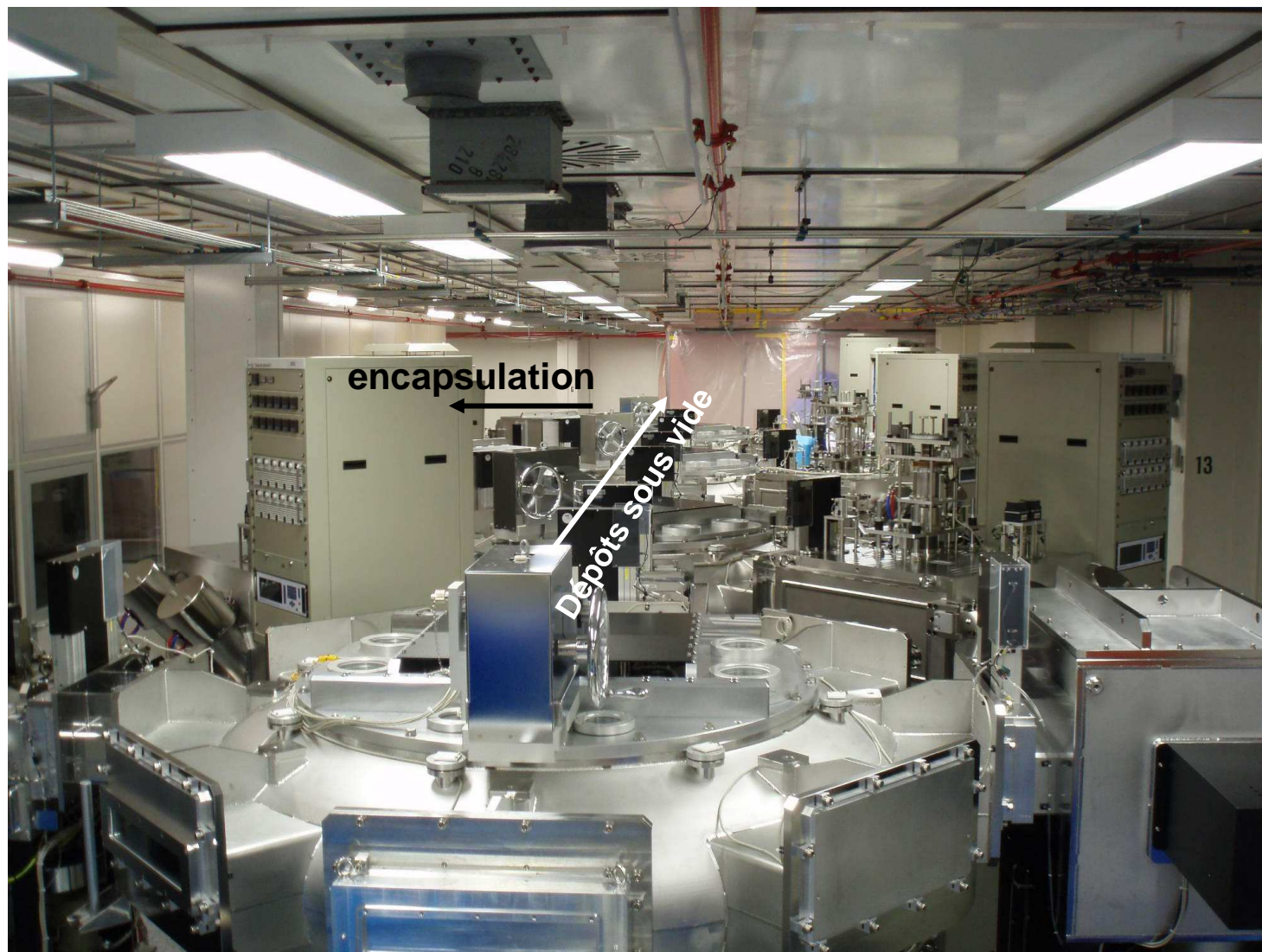


Part of the
solution to both
the world's energy
and environmental
issues

Affordable energy
for emerging
nations

Light-weight,
flexible energy on
the move

Installation de dépôt en ligne de l'IPMS (OLED's)



•Filière 'polymères'

➡ Société de référence : Konarka (Lowell, MA)

4 sites : Lowell, New Bedford, Nuremberg, Linz

>100 pers

Participations de Total (45 M\$), Konica-Minolta (20 M\$), ...

Ligne pilote de 150 mm de large



- Modules monolithiques auto-alignés
- 10 lignes connectées en série (150 mm de large)

Ligne de production

Ligne Polaroid de capacité 10 M.m²/an

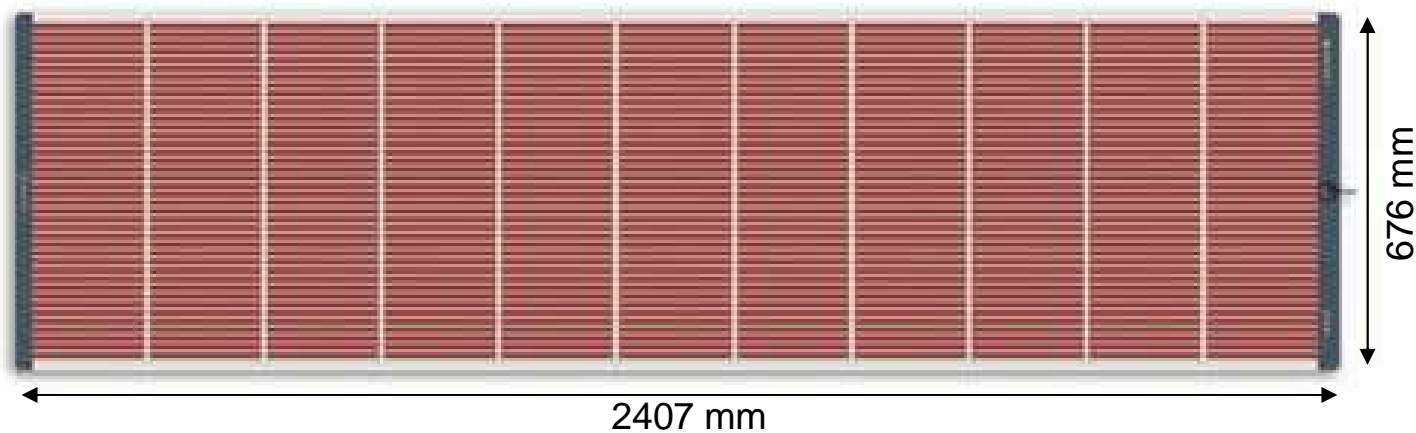


Annonce Konarka 2008

Rdt de 10% module → 1GW/an

Production totale modules PV: 10.7 GW en 2009

Consommation de produits actifs: 2 T /an

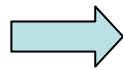


Initiatives industrielles en France (incluant le CEA)

Production de modules OPV: technologie adaptée au marché

Marchés de grand volume

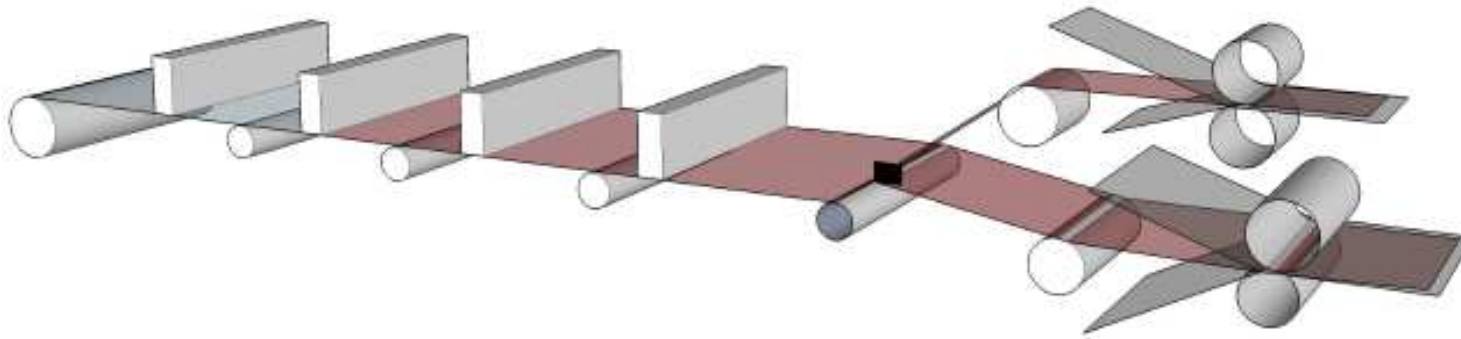
- Produits standardisés
- Design figé



Procédés d'enduction
en continu



Capacité de prod élevée
Prix faible

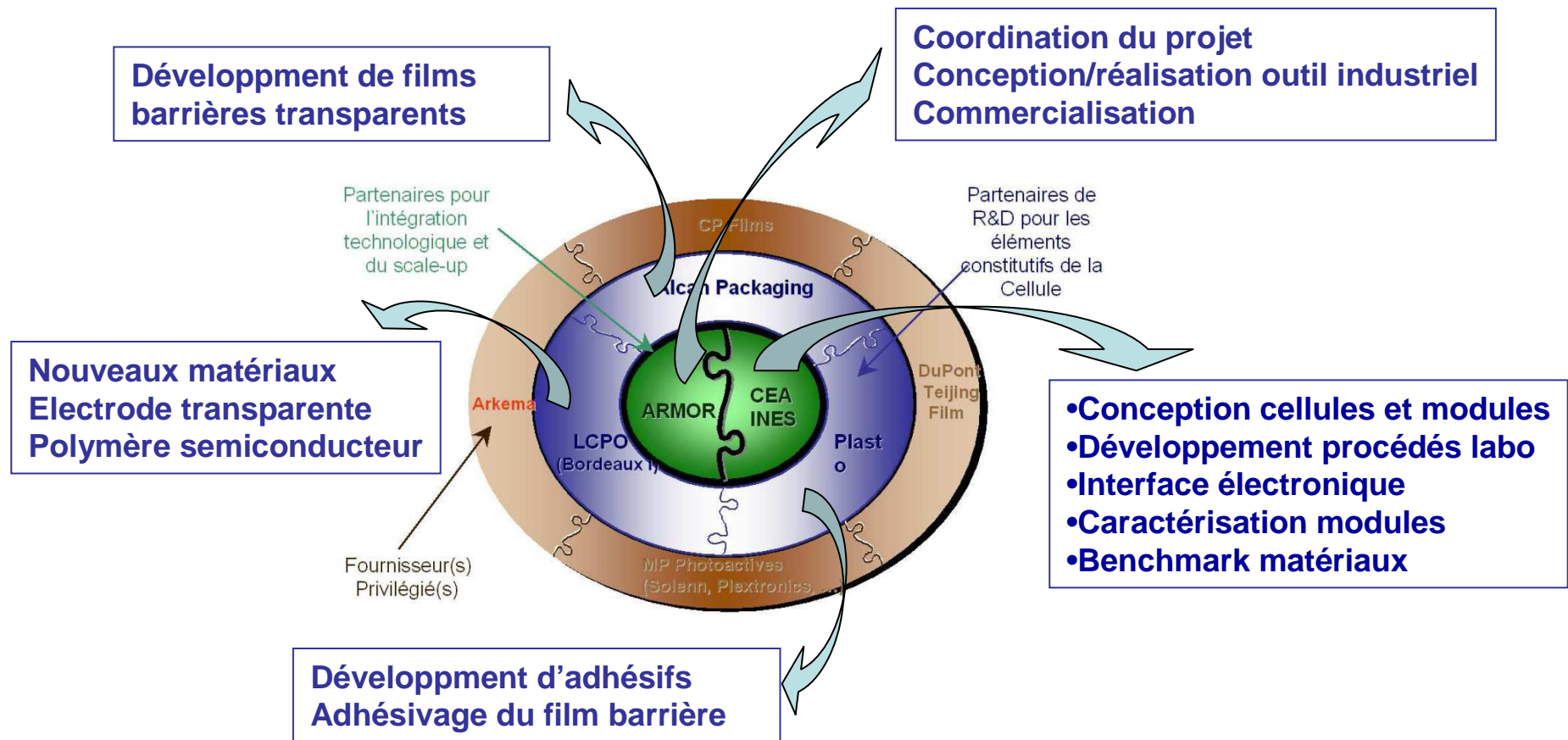


• **Projet OSCAR :**

Partenariat: **ARMOR**, CEA, LCPO, Alcan, Plasto,

Budget total: 16 M€; financement OSEO

Objectif: industrialiser technologie d'ici 4 ans



Marchés de niche

- Produits adaptés à la demande
- Volumes limités (qqs 10^3 pièces)



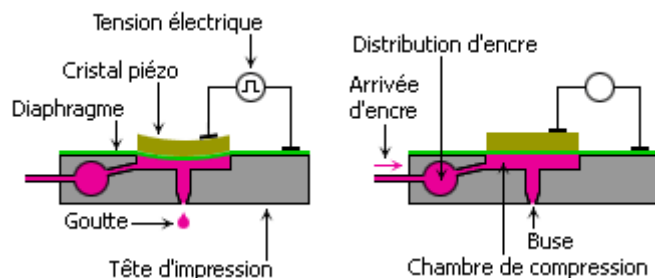
- Procédés d'impression numérique (Jet d'encre, spray, ...)



- Capacité de prod modérée
- Prix moyen
- Coût du changement design faible

Procédé Jet d'encre

Principe de base du jet d'encre



Technologie numérique rapide



Presse jet d'encre Agfa 'the factory'
(900m²/h en 63 cm de laize)

2 projets industriels de la **conception** à la réalisation de **modules OPV « sur-mesure »**

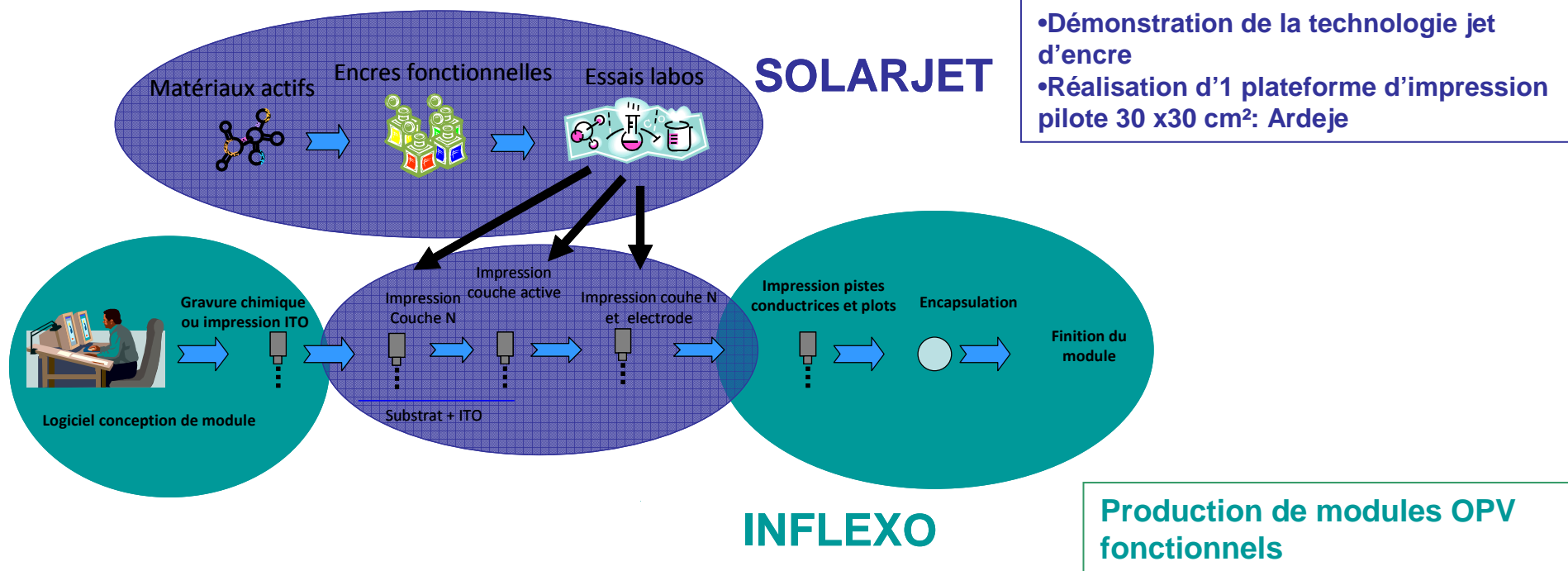
▪ **SOLARJET** : Ardèche, Hutchinson, CEA



Rhône-Alpes Région



▪ **INFLEXO** : DISA, CEA



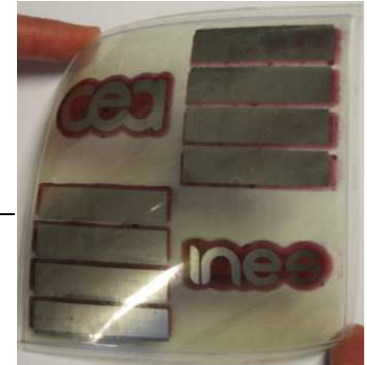
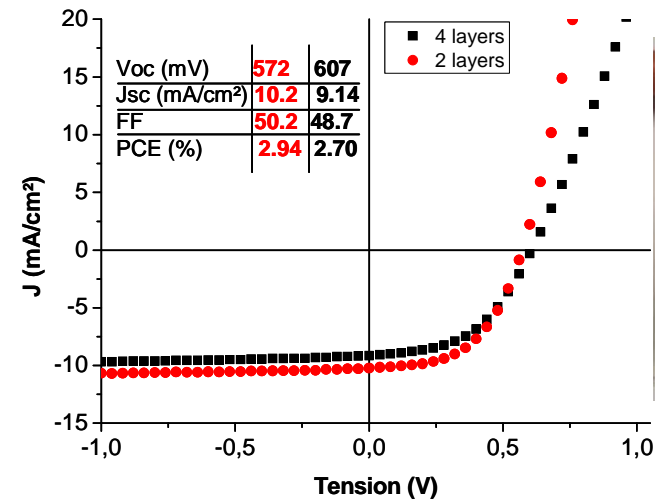
Development at lab-scale



Dimatix DMP 2800



**ZnO + active layer +
HIL on PET/ITO**



Development at pilot-scale



Ardeje 400

4 printing heads, 512 nozzles
 XY position accuracy : < +/- 5 μm
 Printing area: 300 x 300 mm
 Printing speed up to 2500 cm^2/min (1 head)
 Operating under inert gas

Conclusion

Development of PIN architectures on flex

PCE = 3.5 % (max: 3.7)

Extended lifetime: PCE = 2% after 6000 h

Ongoing Industrial projects on printing technologies

Inkjet: small markets, customized products

R2R: large markets, standardized products

Development of barrier film by wet process

WTR = $2 \cdot 10^{-3} \text{ g.m}^{-2}.\text{d}^{-1}$

Structure, process optimization: work under progress

New active materials

Tests and optimization: BP = 6.3% for PIN structure

Lifetime

Test platforms under various conditions

