L'Electronique Organique, une réalité Industrielle pour les écrans plats OLEDs

TELECOM & JFMMA 2017

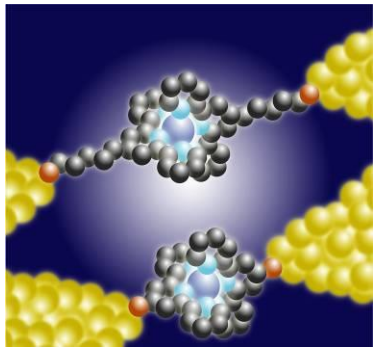
iemn
Institut d'Electronique, de Microélectronique et de Nanotechnologie
UMR CNRS 8520

Kamal LMIMOUNI équipe NCM
kamal.lmimouni@iemn.univ-lille1.fr

cnrs | Université de Lille 1 Sciences et Technologies | Université de Valenciennes et du Hainaut-Cambrésis | ISEN école d'ingénieurs ALL IS DIGITAL LILLE | RENATECH

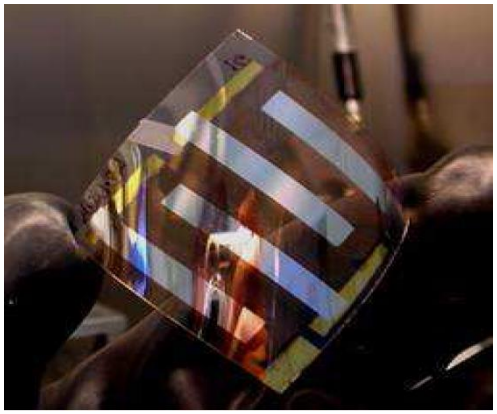
Sommaire

L'électronique organique et moléculaire : définitions



- L'Electronique moléculaire : basée sur des composants actifs constitués d'une ou d'un petit nombre de molécules (couche mono-moléculaire).

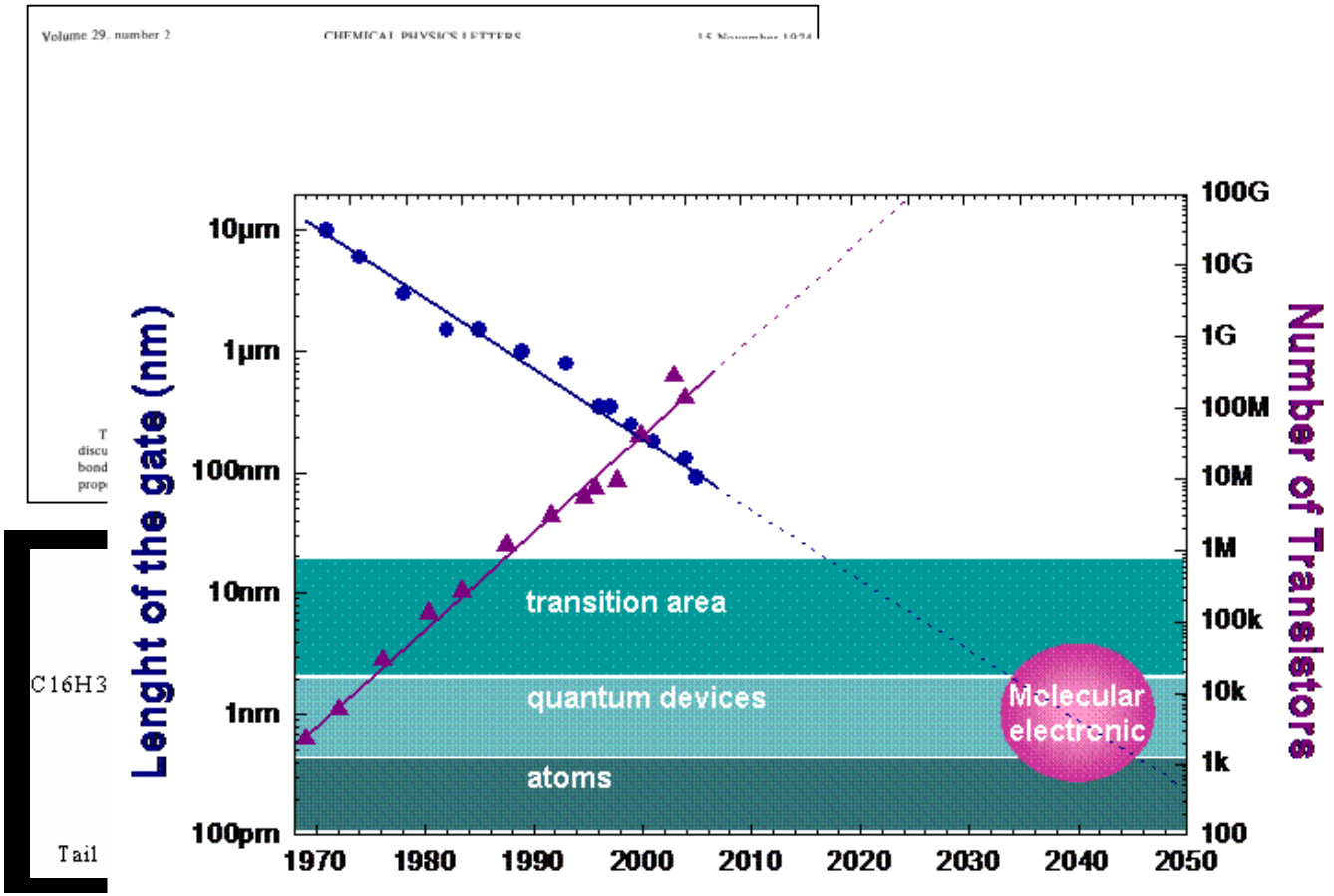
  De la petite molécule à la macro-molécule (polymère) en passant par les oligomères, les fullerène, les NTC …mais aussi des nano-fils inorganiques. [1 à qcq dizaines de nm].



- L'Electronique Organique: basée sur des composants dans lesquels l'élément actif est un matériau constitué d'une grande assemblée de molécules ordonnées ou non.

  Finalité: électronique plastique: i.e souple , pas nécessairement performante en terme de densité d'intégration, mais bas coût et grand public.

Comment augmenter la densité des composants en surface?
… en utilisant 1 composant à 1 molecule !

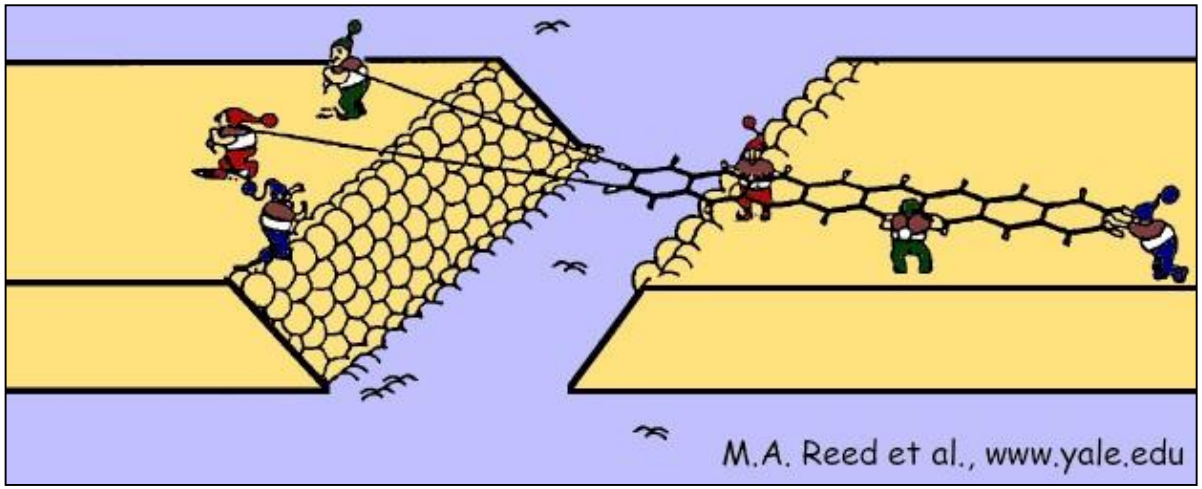


No

Peut-on faire de l'électronique avec des matériaux organiques ?

- **Principale difficulté en électronique moléculaire :**

Connexion électrique de la molécule pour la caractérisation ?



Comportement électrique :

- nature de la molécule / conformation
- les électrodes (travaux de sorties)
- l'interface molécule/metal (liaison covalente, rugosité, …)

Organic Electronics???What is it?

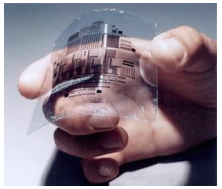
1- OLEDs

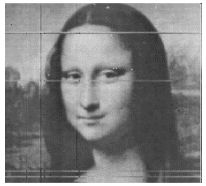
2- Organic Thin Film Transistors OTFTs / Photodetectors.

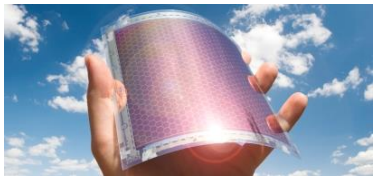
3- Photovoltaic Cells : OPVs

4-Spintronic

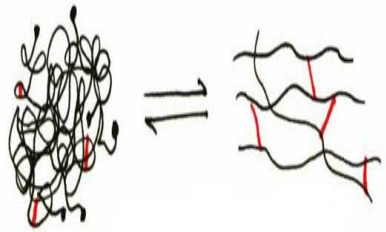
5- Organic bioelectronics

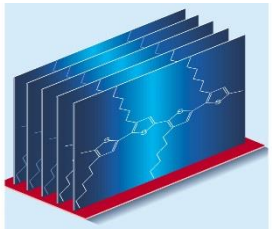


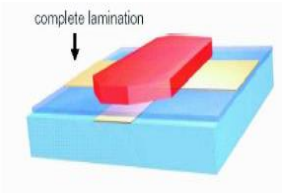


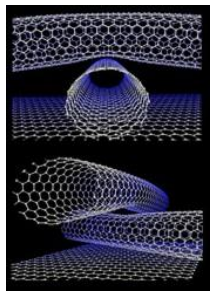


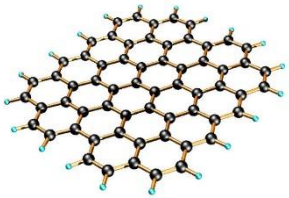
Low cost, OSC diversity (electrical properties versus structure), Flexibility, Consumption, transport properties, …



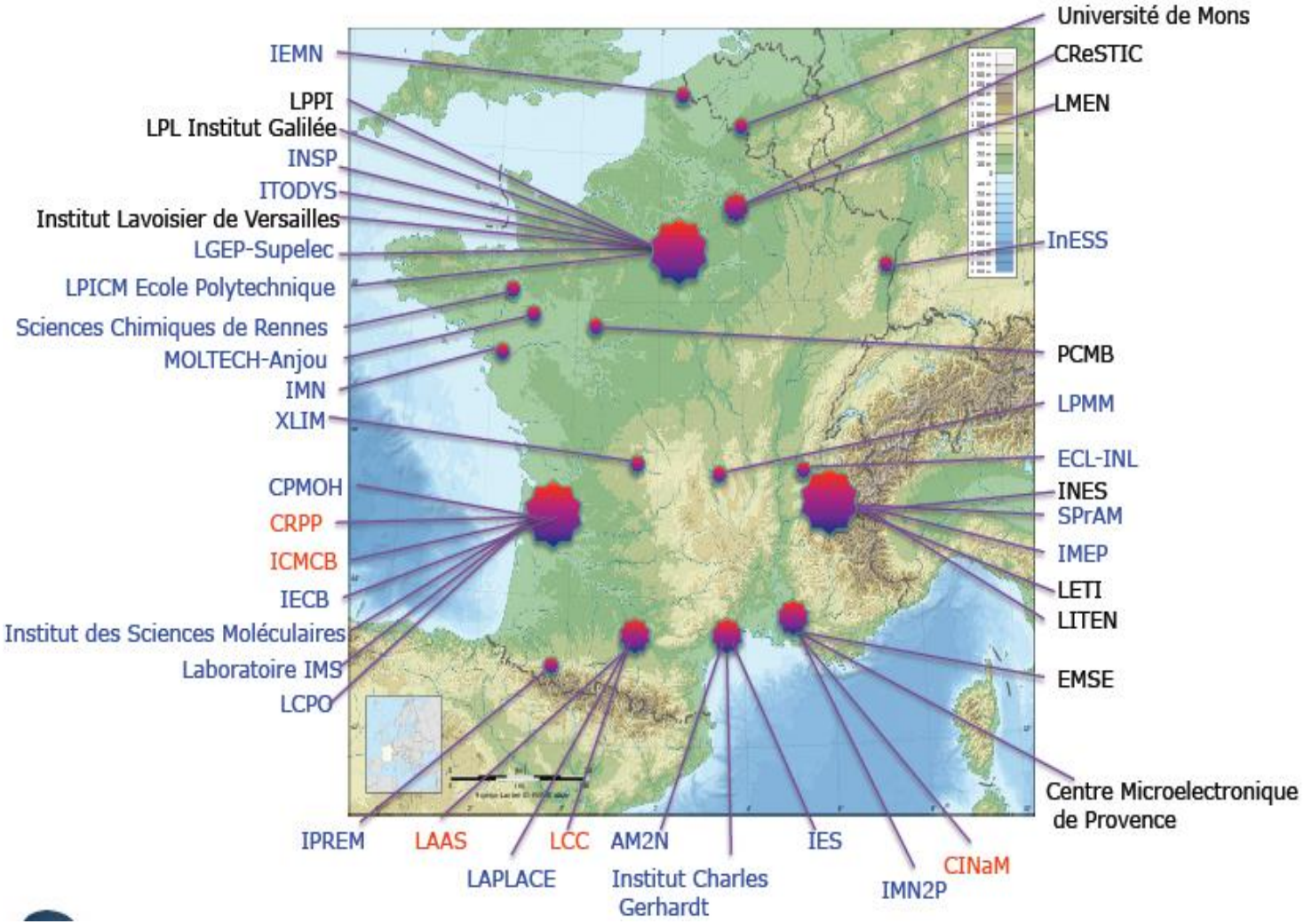








Electronique 0rganique en France …



Source: GDR EO –Bordeaux 2011

Les Oleds….un peu d ’histoire

- **1960 Etude de l ’EL des cristaux organiques**
  - Anthracène, pyrène , tétracène
  - cristaux en monocouches épaisses 10µm à 10mm
  - Rendements 5%, tensions de fonctionnement élevées

- **1977 Découverte des polymères conducteurs**
  - Polyacétylène - dopage
  - instabilité à l ’air


Heeger

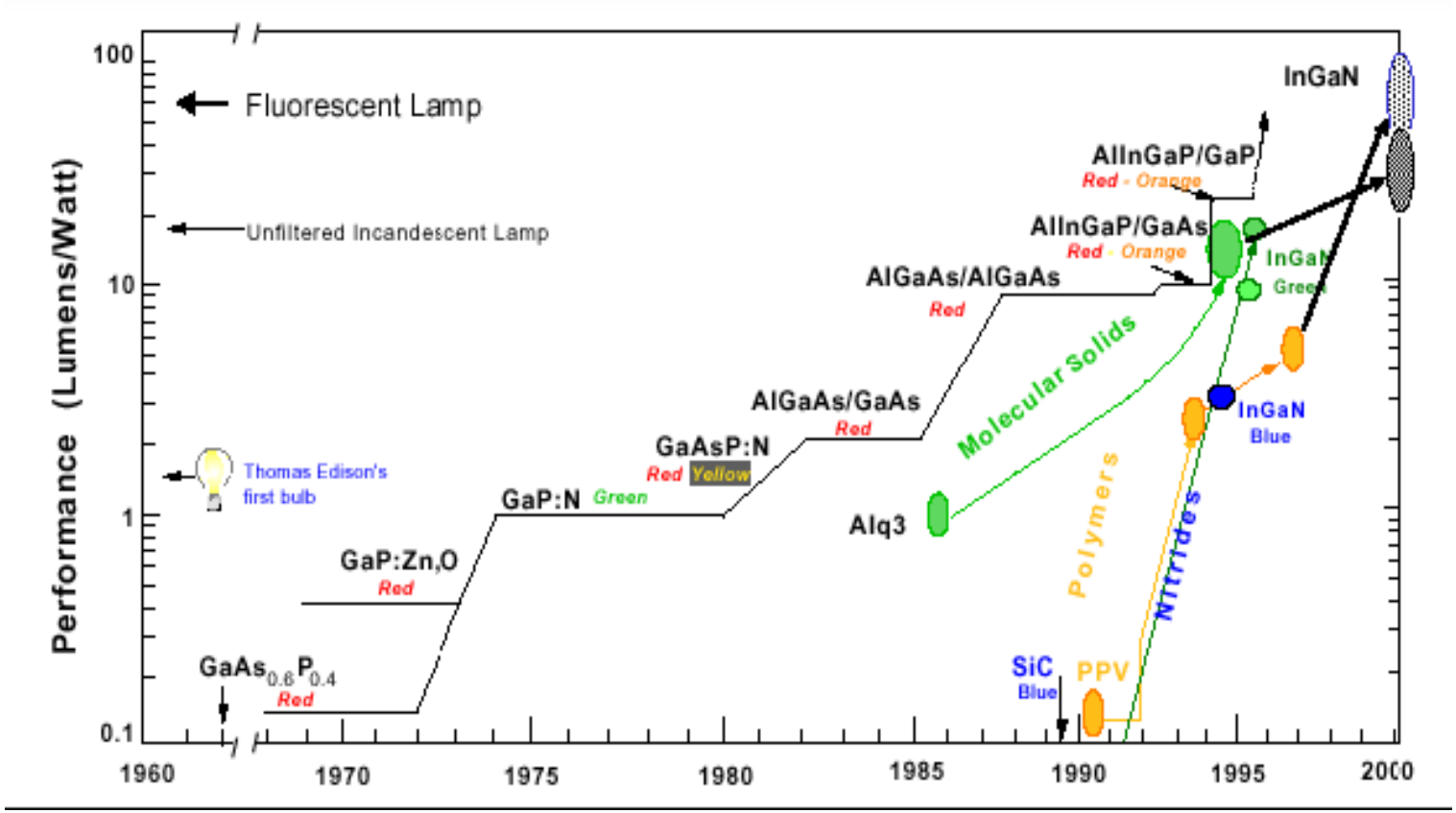

MacDiarmid


Shirakawa

- **1987 Diode à base d ’Alq3**
  - séparation des fonctions de transport et d ’emission
  - Tensions de fonctionnement de l ’ordre de 10V
  - Luminance de 1000cd/m2

- **1990 Diode EL à base de polymères conjugués**
  - Matériau PPV
  - CDT - Uniax
  - Dépôt par spin coating

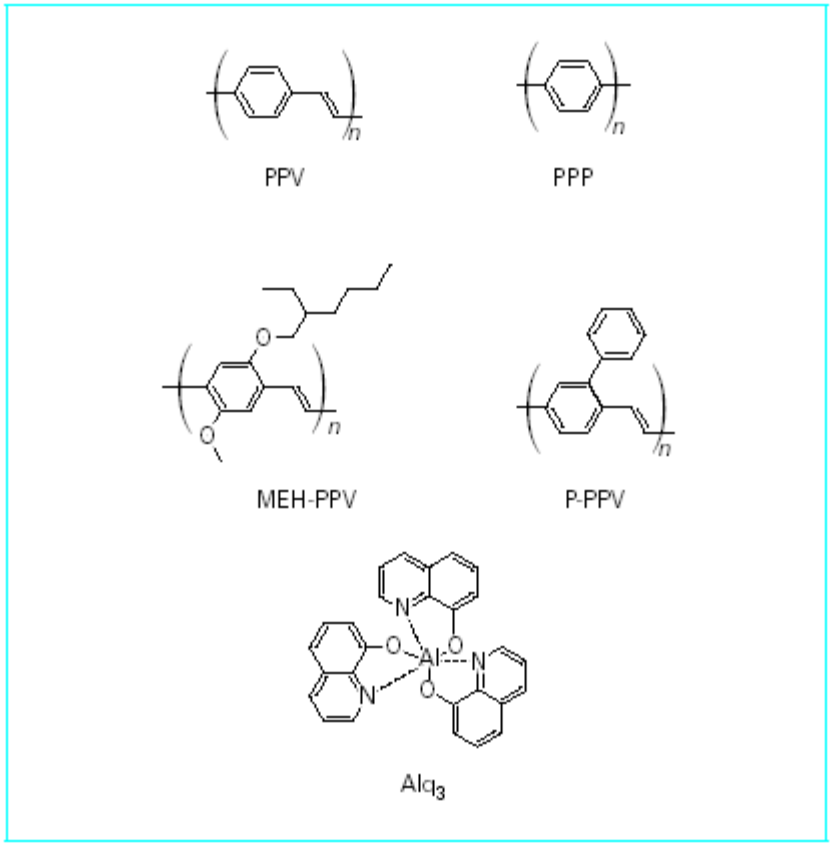
Evolution des technologies



Les matériaux organiques utilisés dans les OLEDs

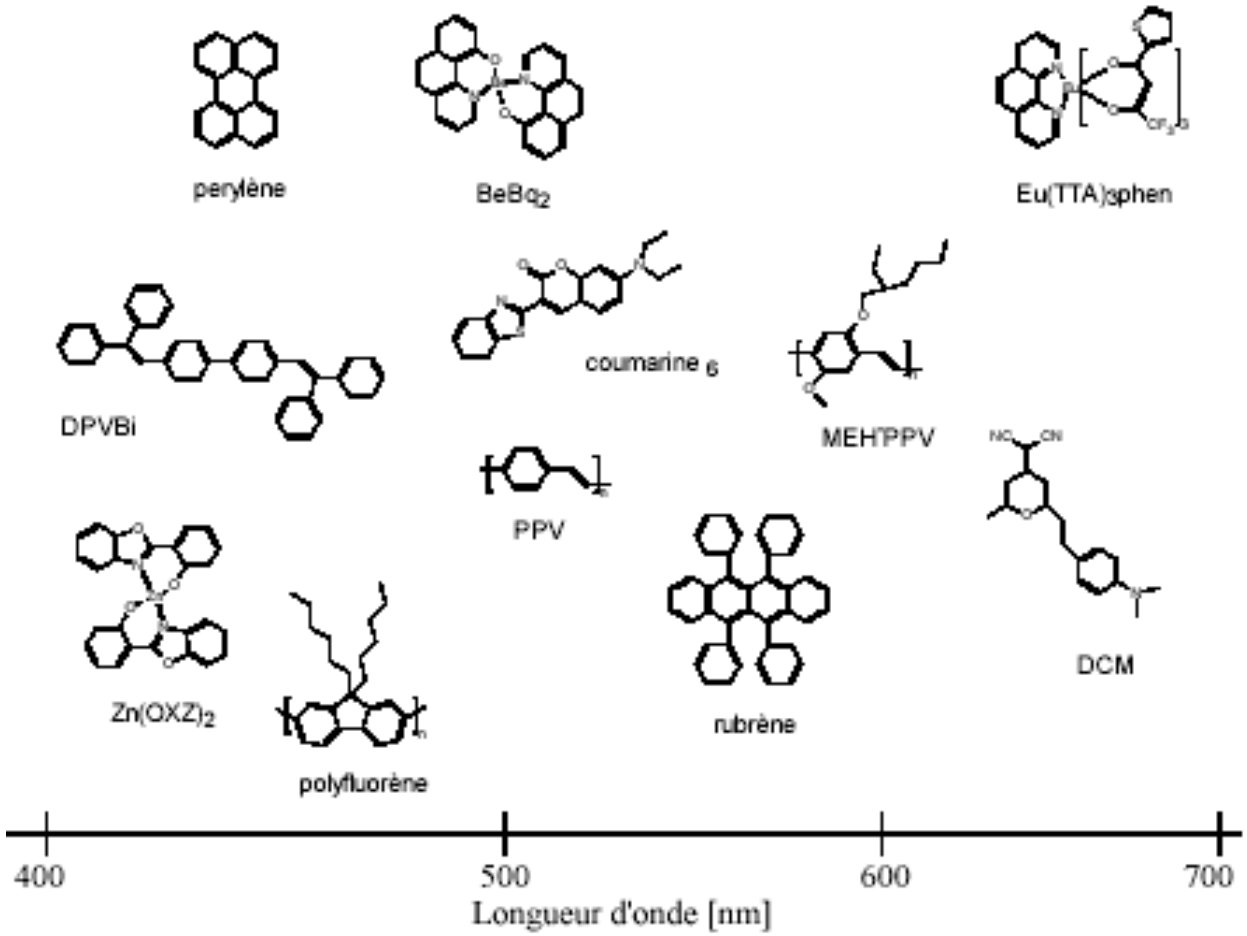
Matériaux organiques: Polymères ou petites molécules ?

Les Polymères conducteurs

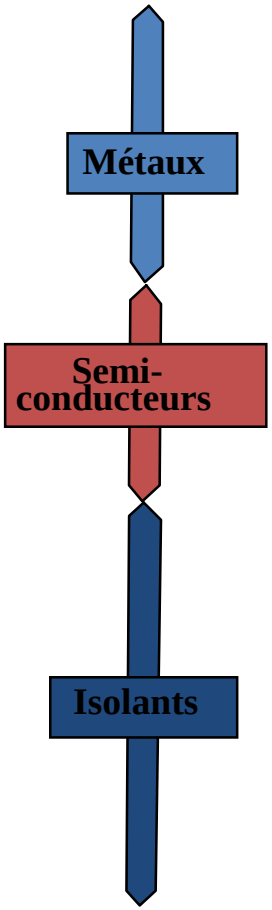


Molécules organiques à petite masse

Matériaux organiques



Polymères , oui mais conjugués…



σ (S/cm)

1E6
1E4
1E2
1
1E-2
1E-4
1E-6
1E-8
1E-10
1E-12
1E-14
1E-16
1E-18

(CH_x)

(PPP)

(PTh)

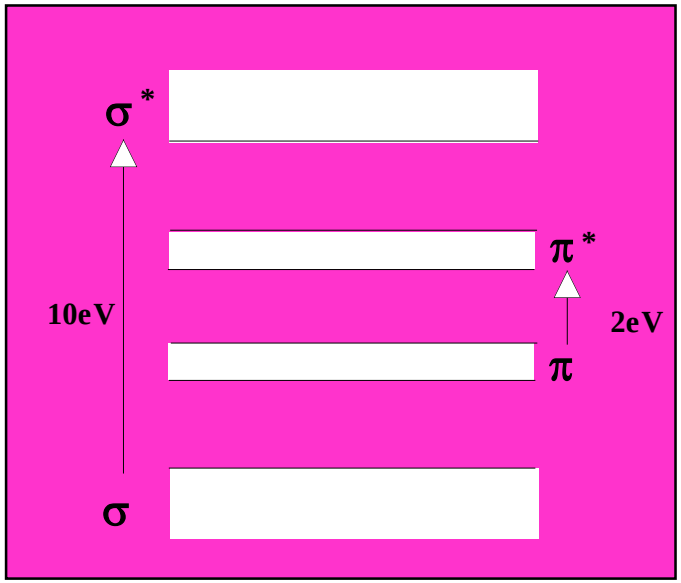
(PPy)

(PANI)

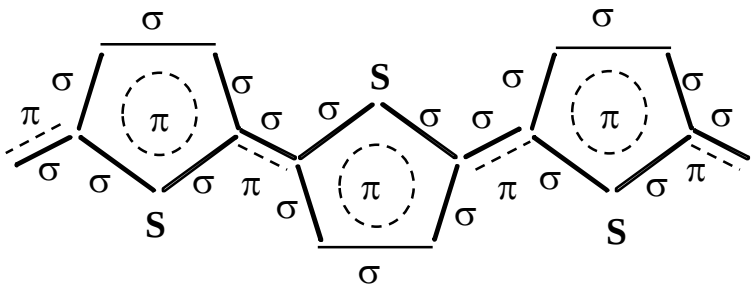
- Synthèse
- Dopage
- Conjugaison

Les Polymères conducteurs conjugués

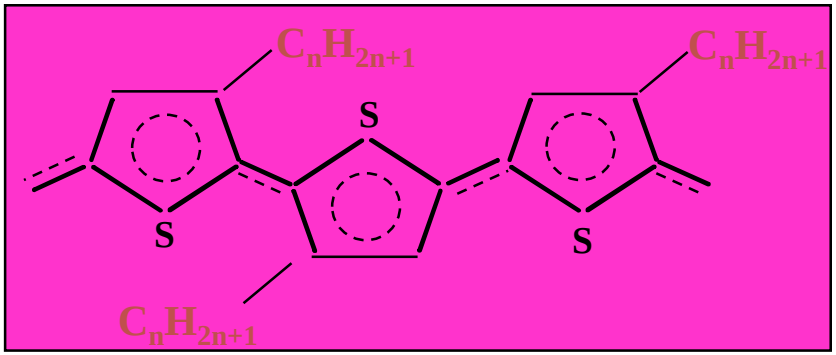
- Propriétés semiconductrices



Exemple du polythiophène

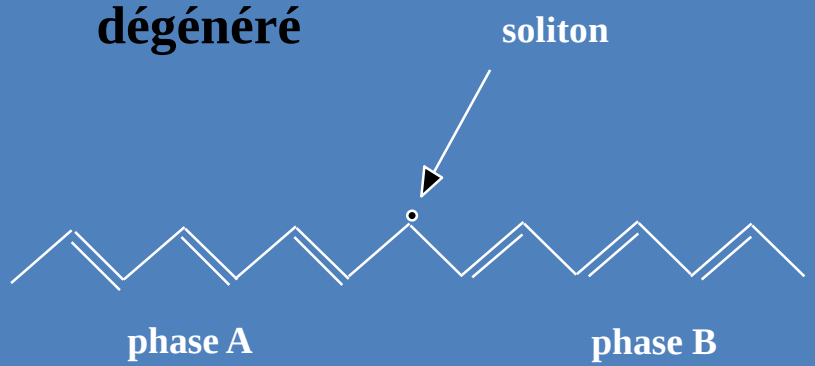


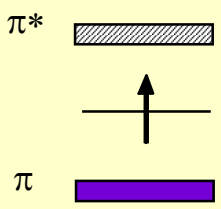
- Propriétés de solubilité



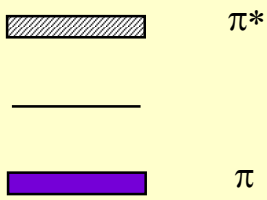
Les Solitons ?? C'est quoi???

Exemple du polyacétylène dégénéré





Spin S=1/2
Charge=0

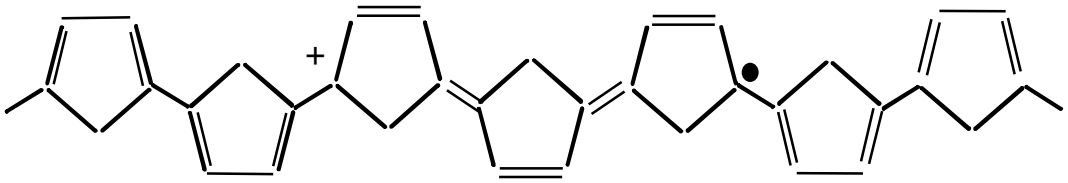


Spin S=0
Charge=+e

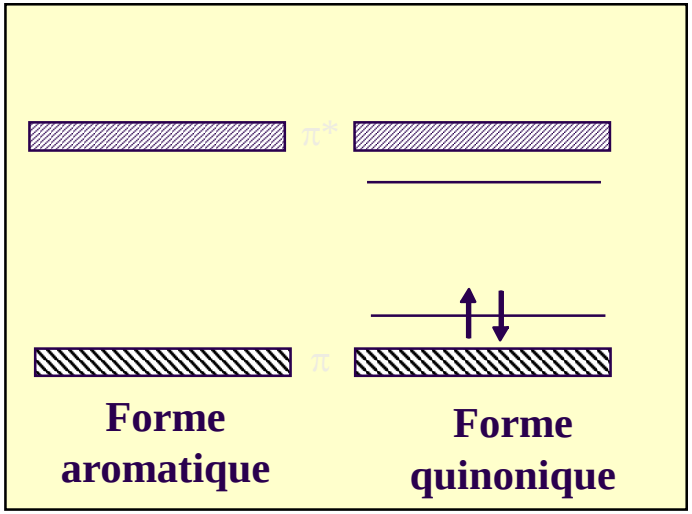
Spin S=0
Charge=-e

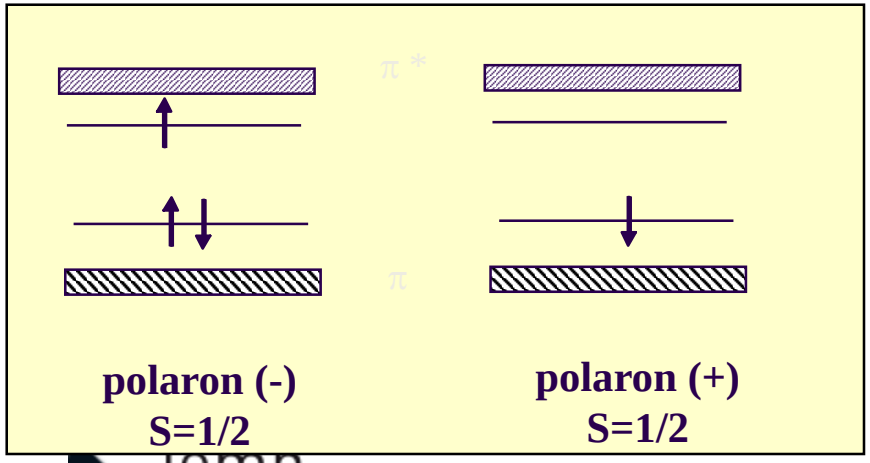
Les Polarons et Bipolarons

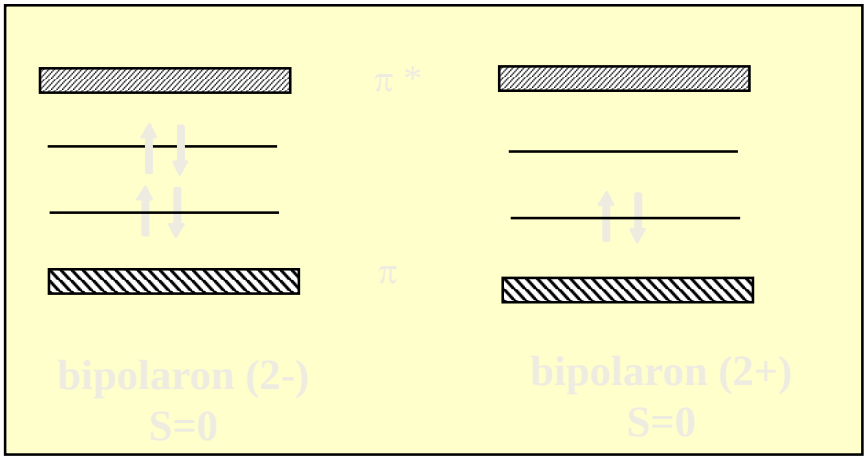
Exemple du polythiophène non dégénéré



Forme aromatique **Forme quinonique** **Forme aromatique**



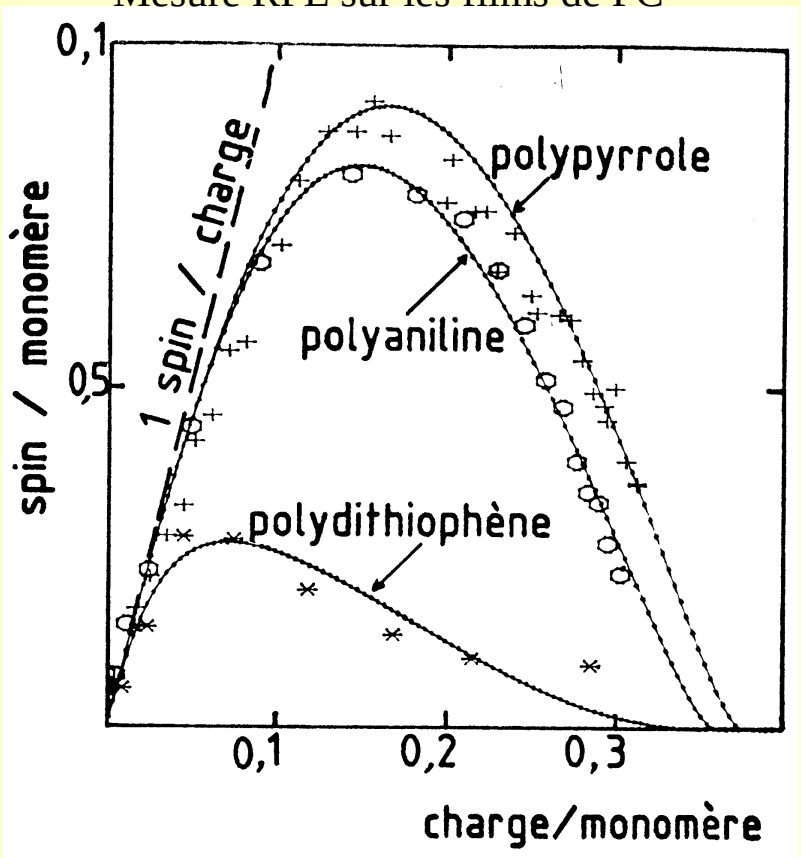




Les Porteurs de charge dans les polymères

- **Polarons spin 1/2**
- **Bipolarons spin 0**

Mesure RPE sur les films de PC*



Conduction

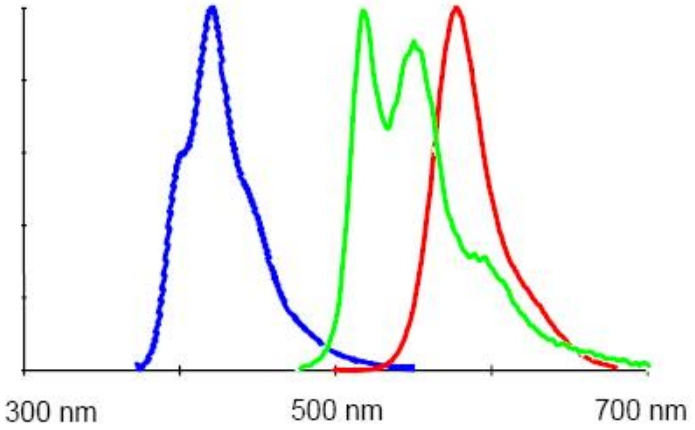
intra-chaîne

et

inter-chaînes

* Groupe Dynamique de Spin, CEA, Grenoble

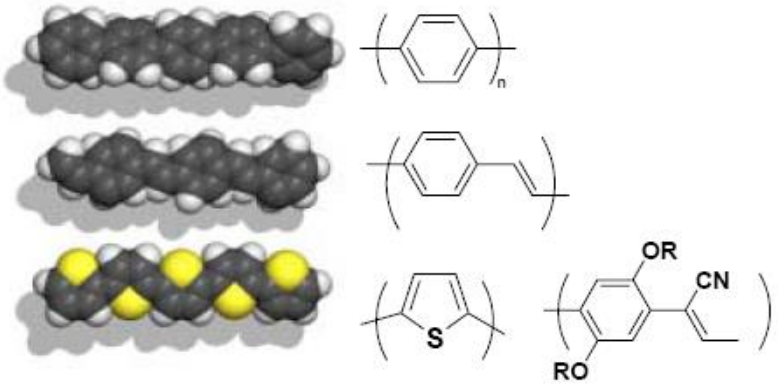
Matériaux organiques: COVION



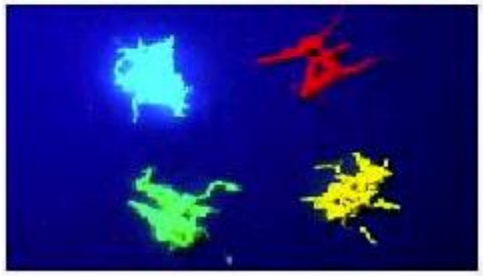
PPP

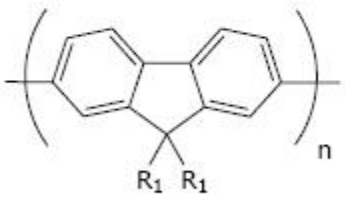
PPV

PT or
CN-PPV



Matériaux organiques: Dow chemical

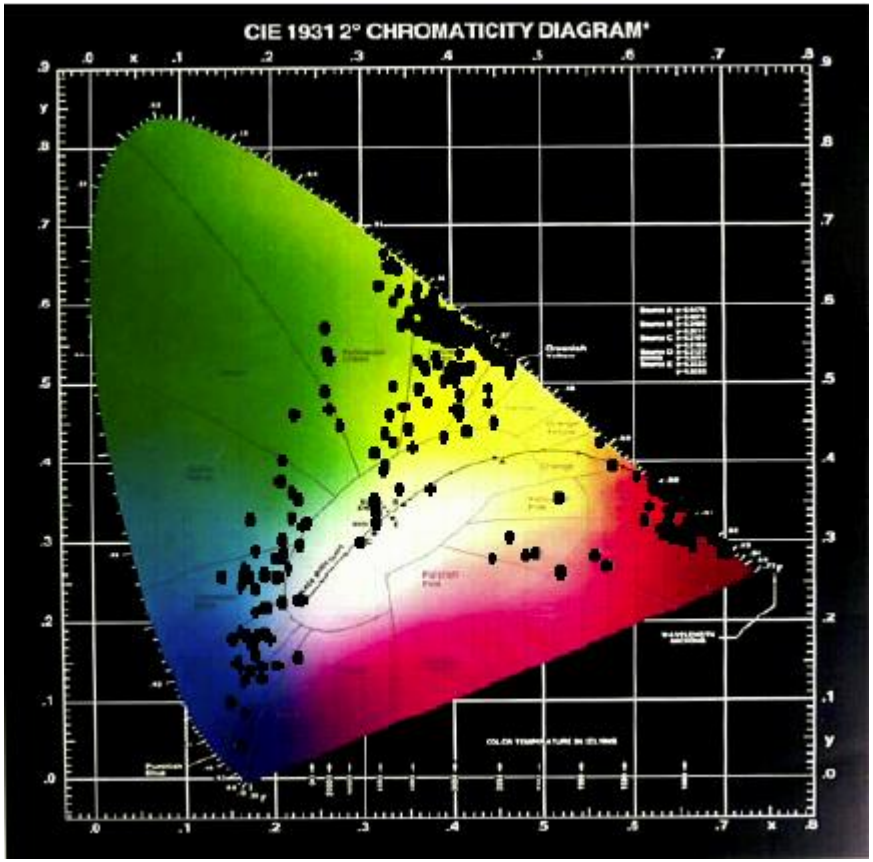




PF

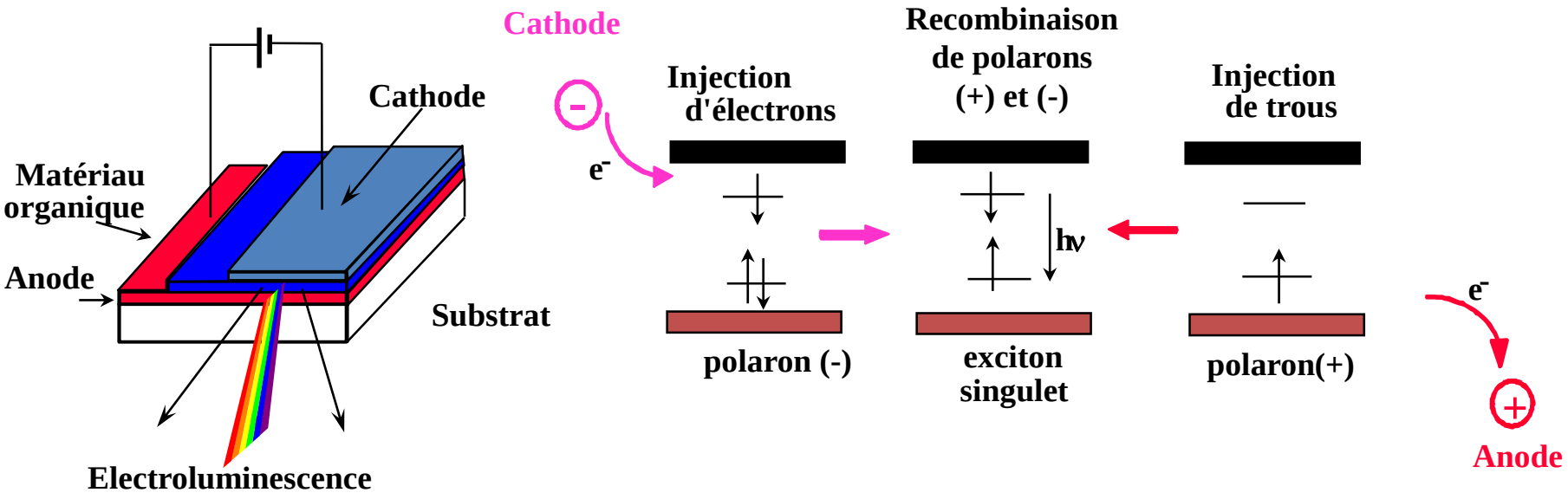
lumation™

DOW

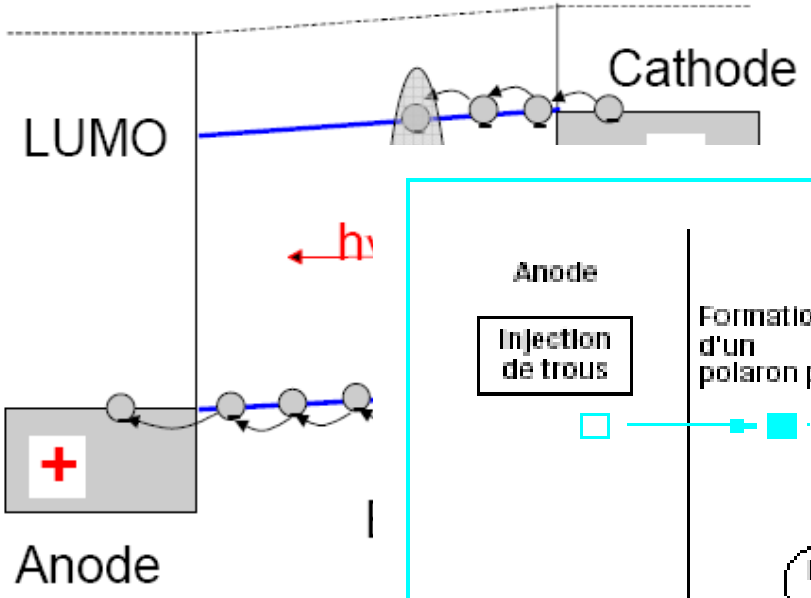


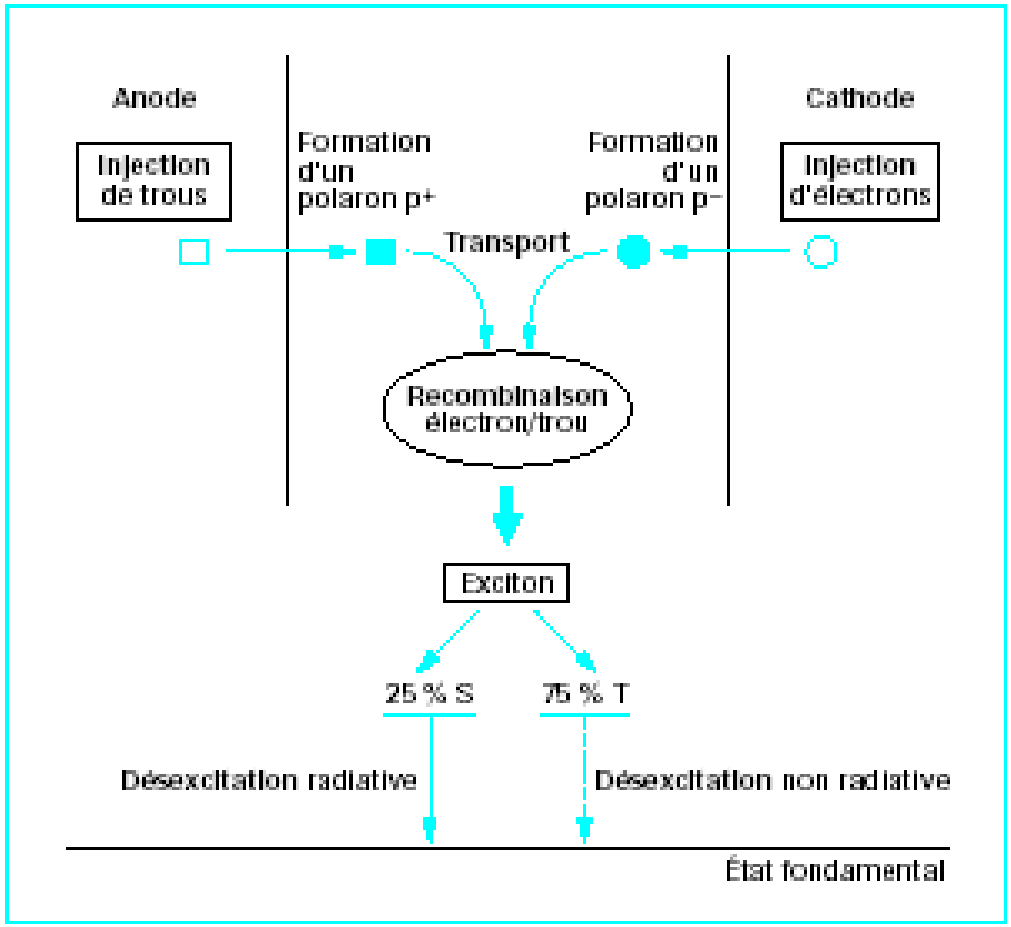
Structure / Principe de fonctionnement / et Technologie des OLEDs

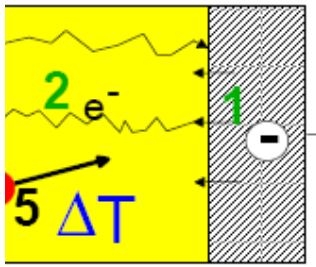
Principe de fonctionnement des OLEDs

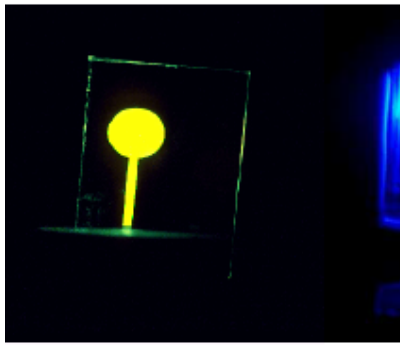


Etapes du processus d 'Electroluminescence





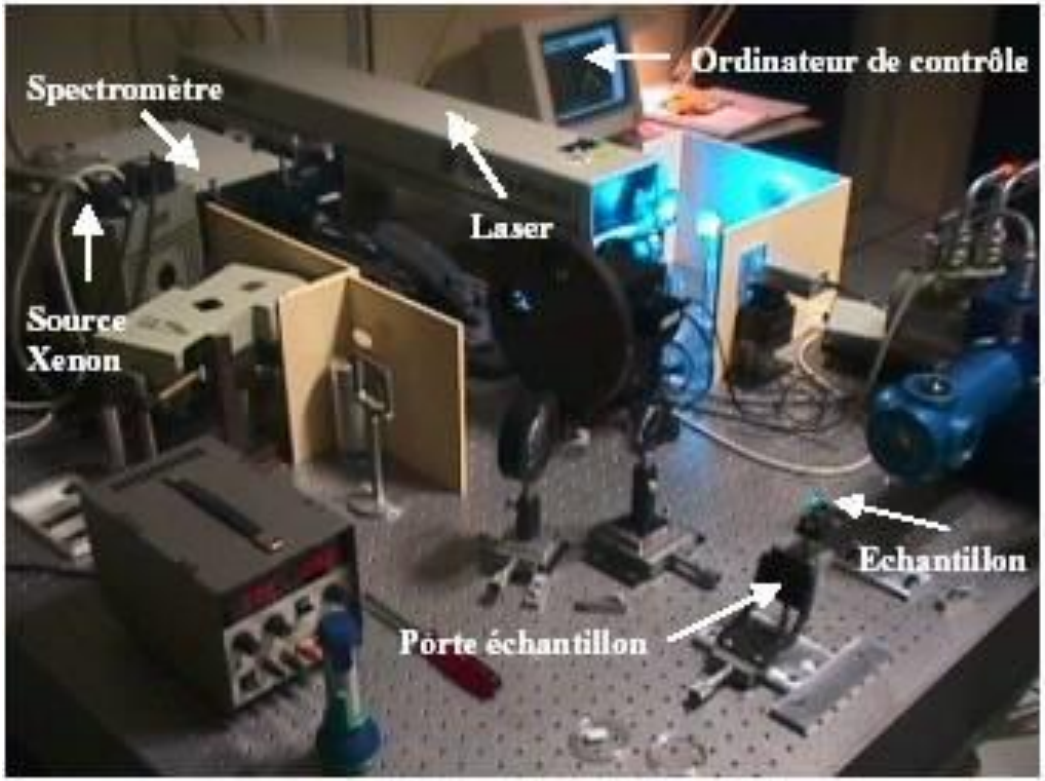


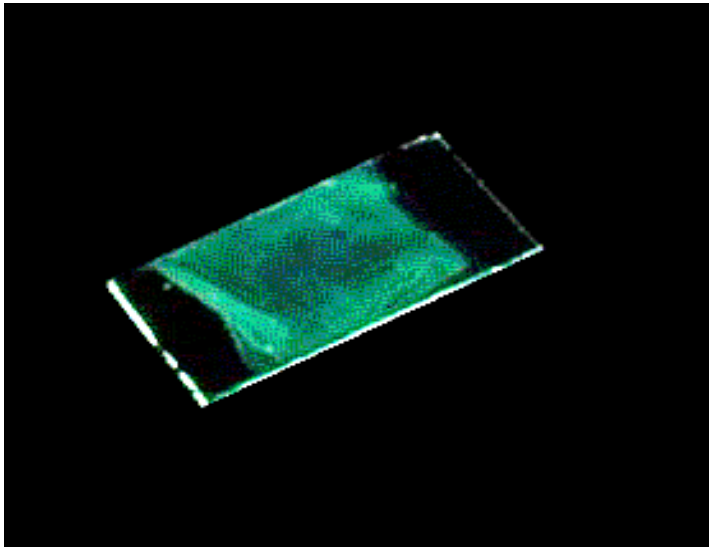


n formation)

noton emission

Experimental set-up

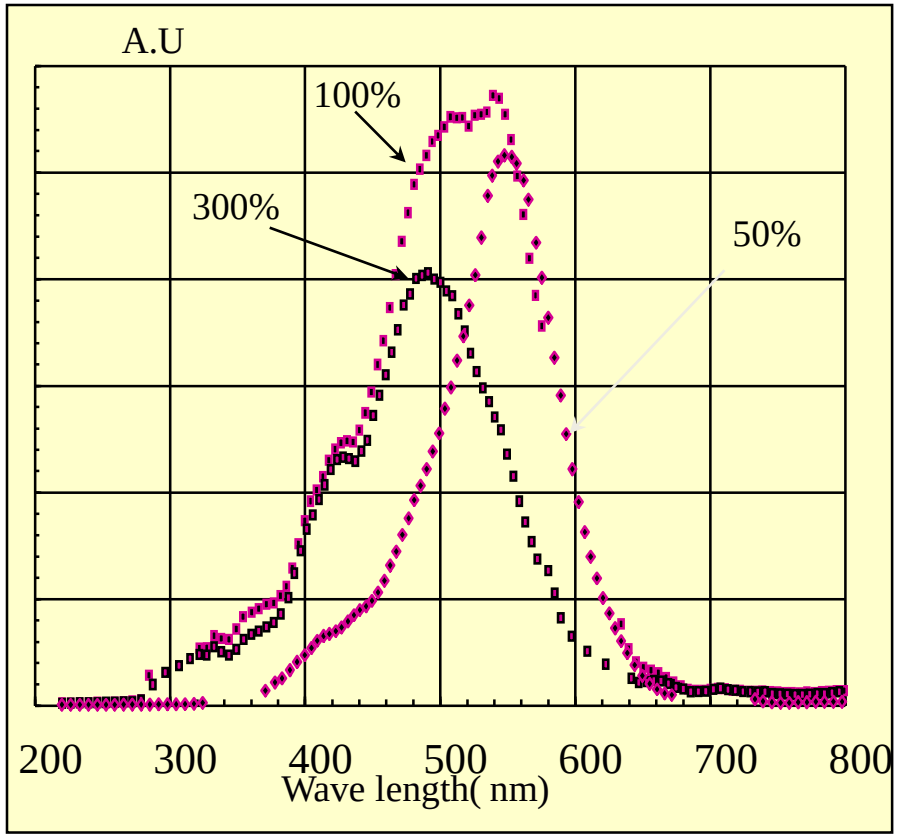




Polymer PL

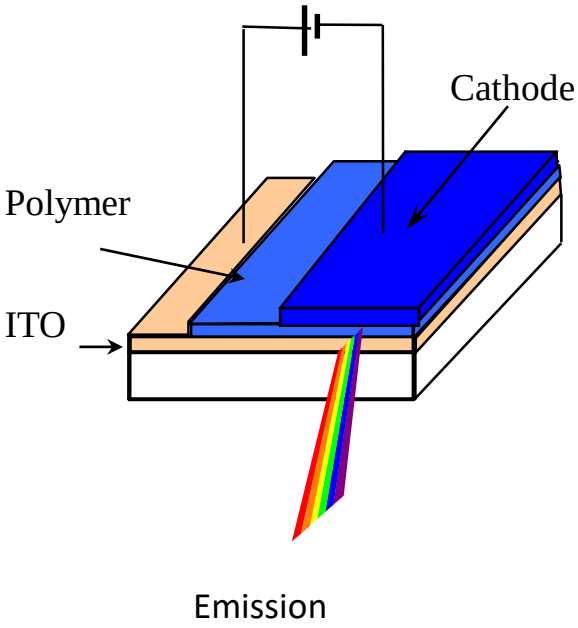
K. Lmimouni et coll, Synth. Met. Vol 126, 241-244 (2002)

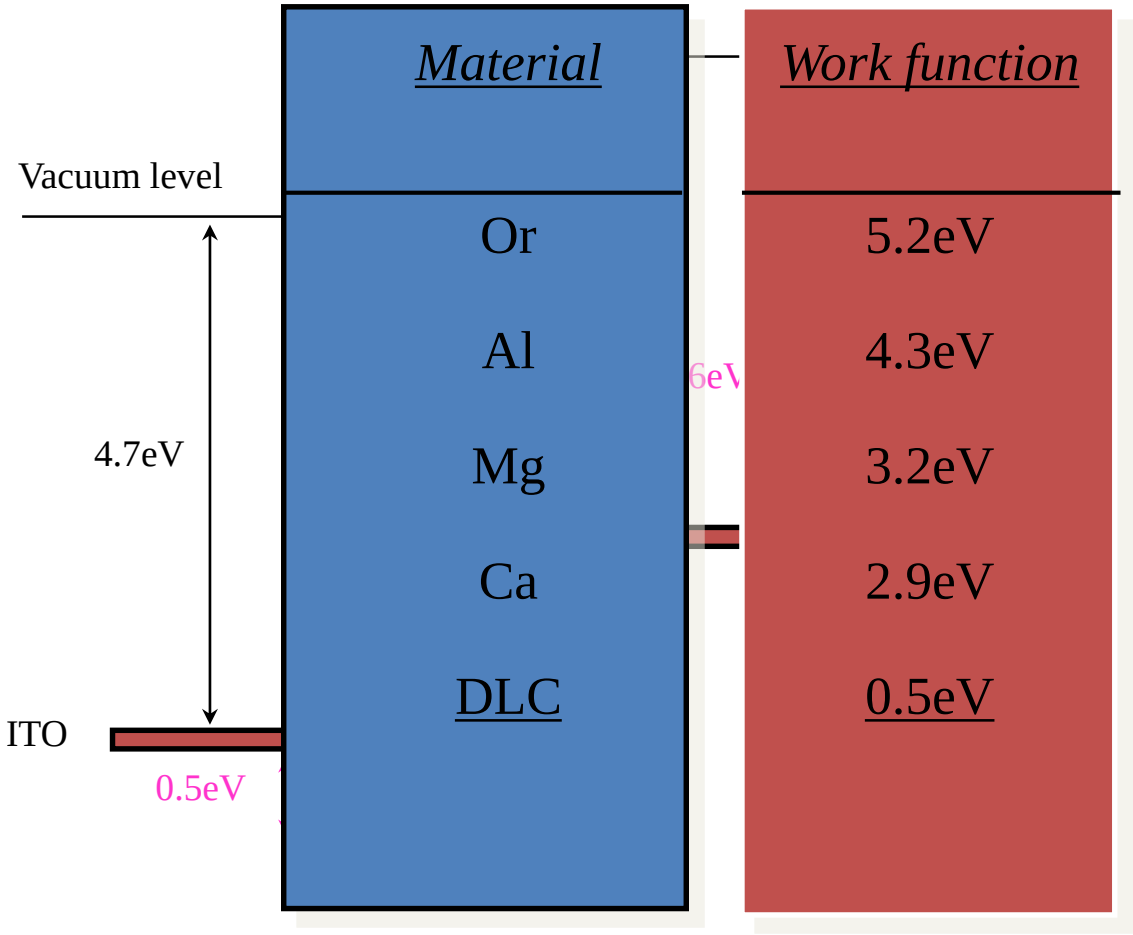
P3OT/PBuC Blend



PL shift

M. Berliocchi, K. Lmimouni, C. Dufour, D. Vuillaume et coll; INFM Meeting Bari, Italie (2002)



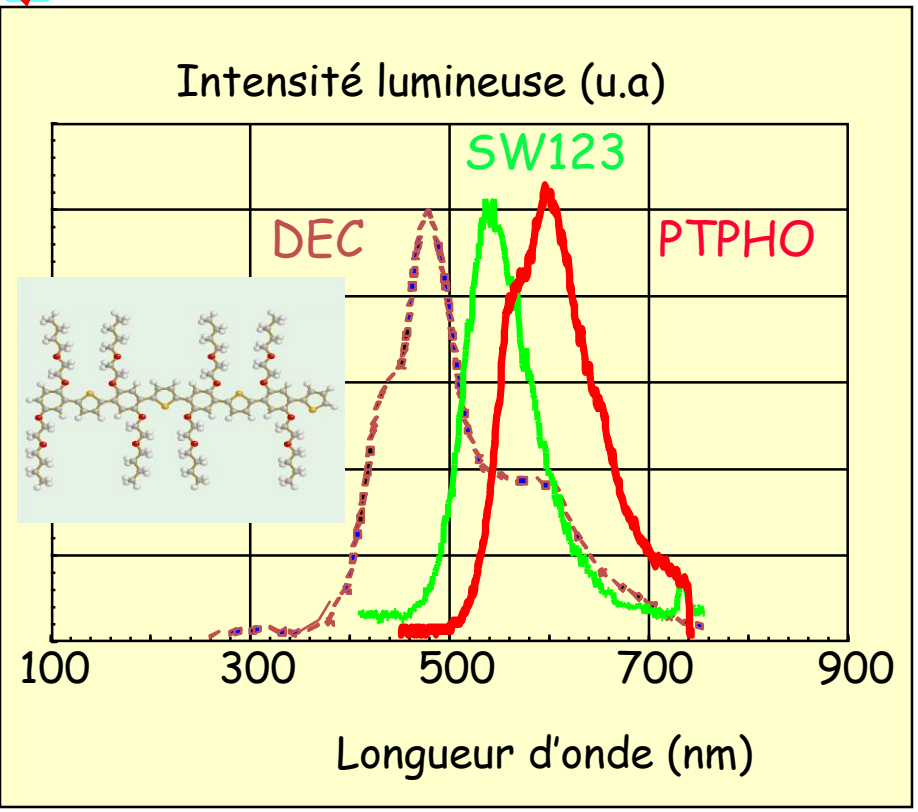


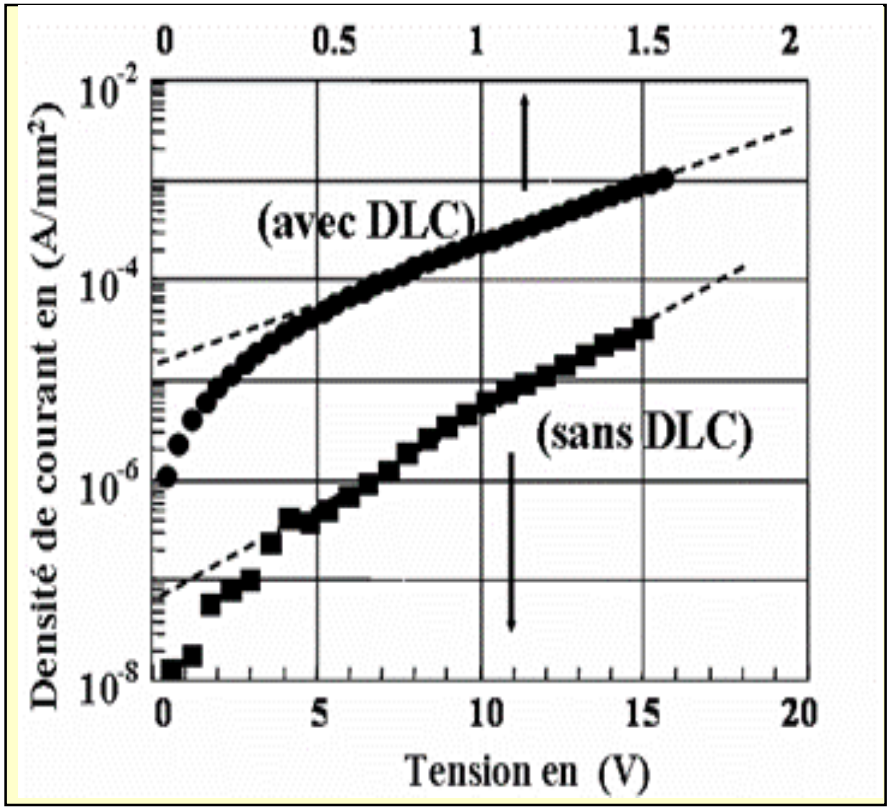
K. Lmimouni, C. Legrand et A. Chapoton. Appl.Phys.Lett. Vol78-N° 17, 2473-2439 (2001)

Collaboration : Mr Belouet : Alcatel Alsthom Recherche

1998-2002

Emission bleue, rouge et verte





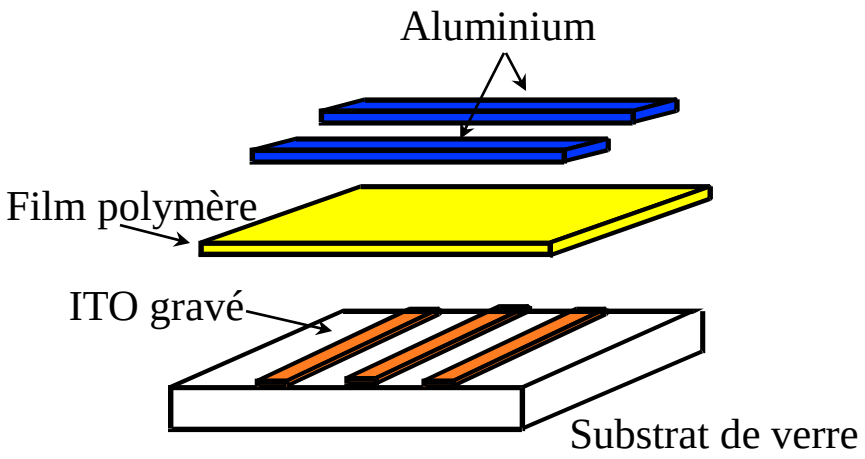
Collaborations: ENSCM / LPPI Cergy Pontoise / Univ Tor Vergata / Alcatel Marcoussis

K. Lmimouni, C. Legrand et A. Chapoton. Appl.Phys.Lett.Vol78-N° 17, 2473-2439 (2001)

K. Lmimouni et coll, Synth. Met.Vol 126, 241-244 (2002)

M. Berliocchi, K. Lmimouni, C. Dufour, D.Vuillaume et coll; INFM Meeting Bari, Italie (2002)

Etapes technologiques de réalisation_Process

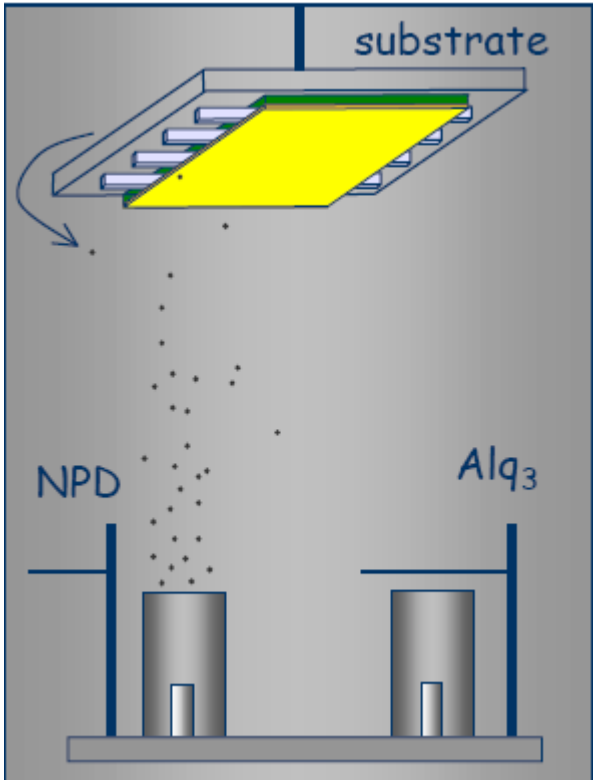


*** Substrat (verre + ITO)**
ITO de résistance 5Ω et d'épaisseur 300nm

***Gravure de l'ITO (pistes de 1mm)**
attaque à l'eau régale ($HCl+HNO_3$)

***Dépôt des films de polymères (30 à 300nm)**
par évaporation sous vide
par centrifugation

***Evaporation sous vide de la cathode (Al, In)**
$P=10^{-6}$ à 10^{-7} Torr
masque mécanique (pistes de 1mm)
surface active $1mm^2$



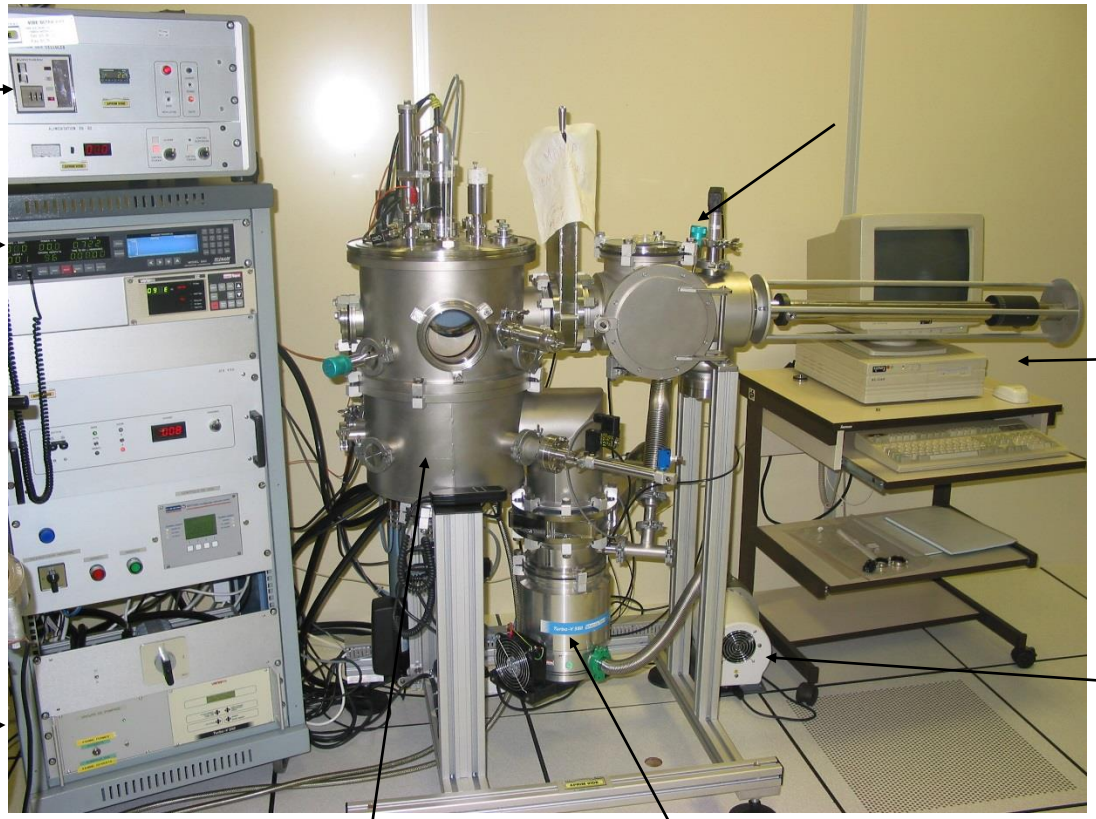
Small molecules are thermally evaporated in vacuum

Soluble materials (polymers)

-solvents : dichloromethane, chloroform,THF,Toluene,Xylene°
-concentration 5 to 20mg/ml,
-speed : 500 à 4000 tr/mn, acc 3000tr/mn/s

Large area

Le dépôt par évaporation sous vide

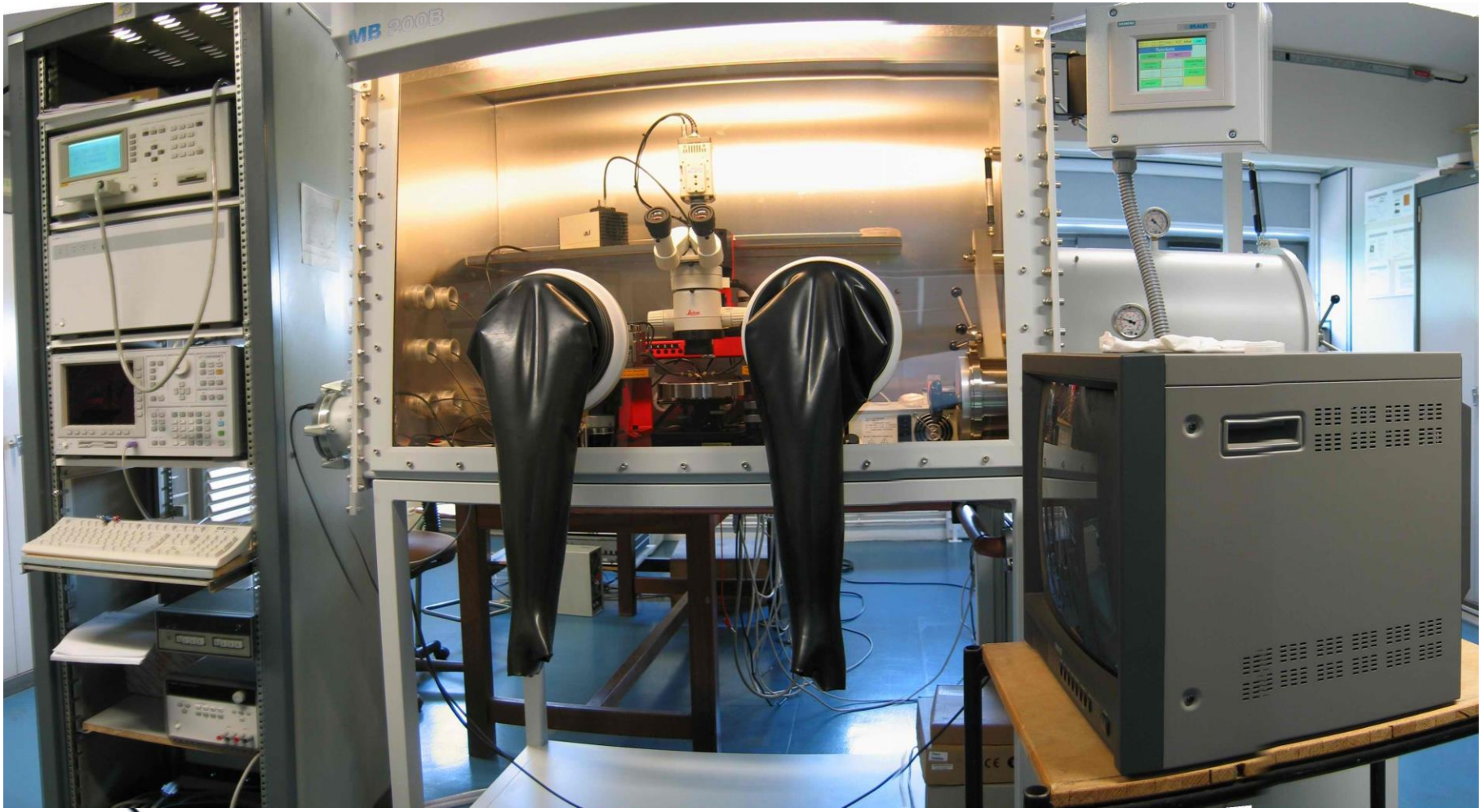


P: 10^{-7} Torr

Vitesse de dépôt <0.1 Å/s

Plateforme d'Electronique organique IEMN

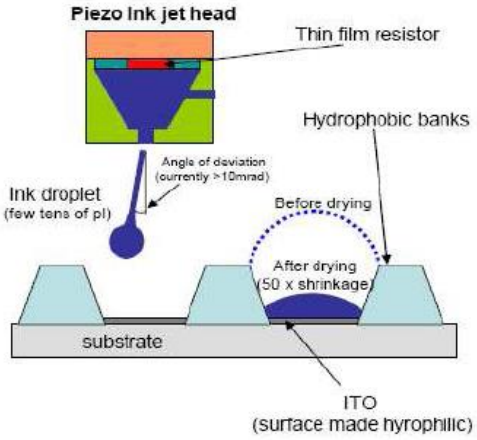
Plateforme d'Electronique organique IEMN



Dépôt par jet d'encre

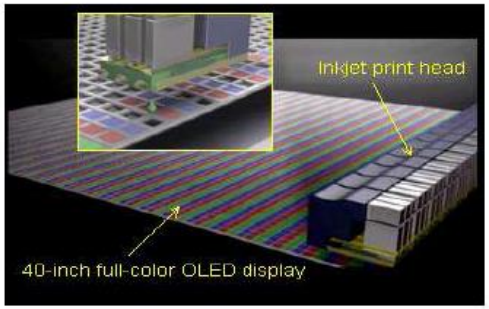
- **Dépôt par jet d'encre**

  - **Pas de perte de matériaux**
  - **Applicable aux grandes surfaces**

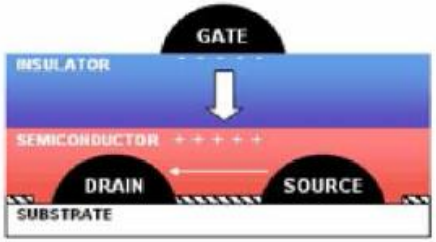


  - **Structure bi/tri couches**
  - **Contrôle dépôt (séchage, homogénéité)**
  - **Structuration substrat (mélange couleurs)**

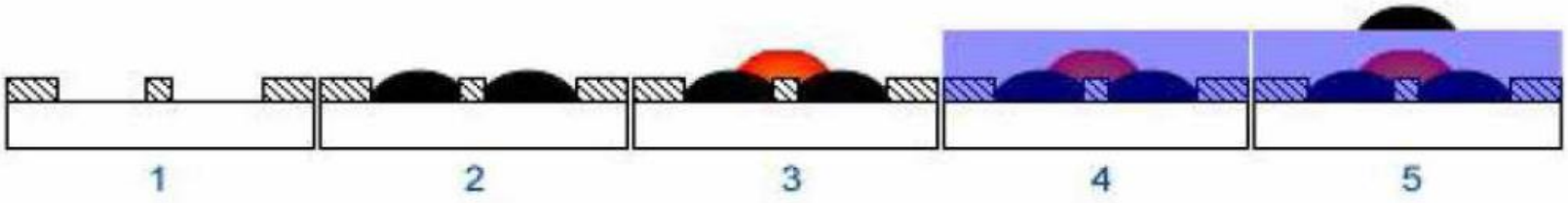
- **Technologie de base pour les polymères (écrans)**
  - **Précision : ± 15 µm**



OFET par jet d'encre



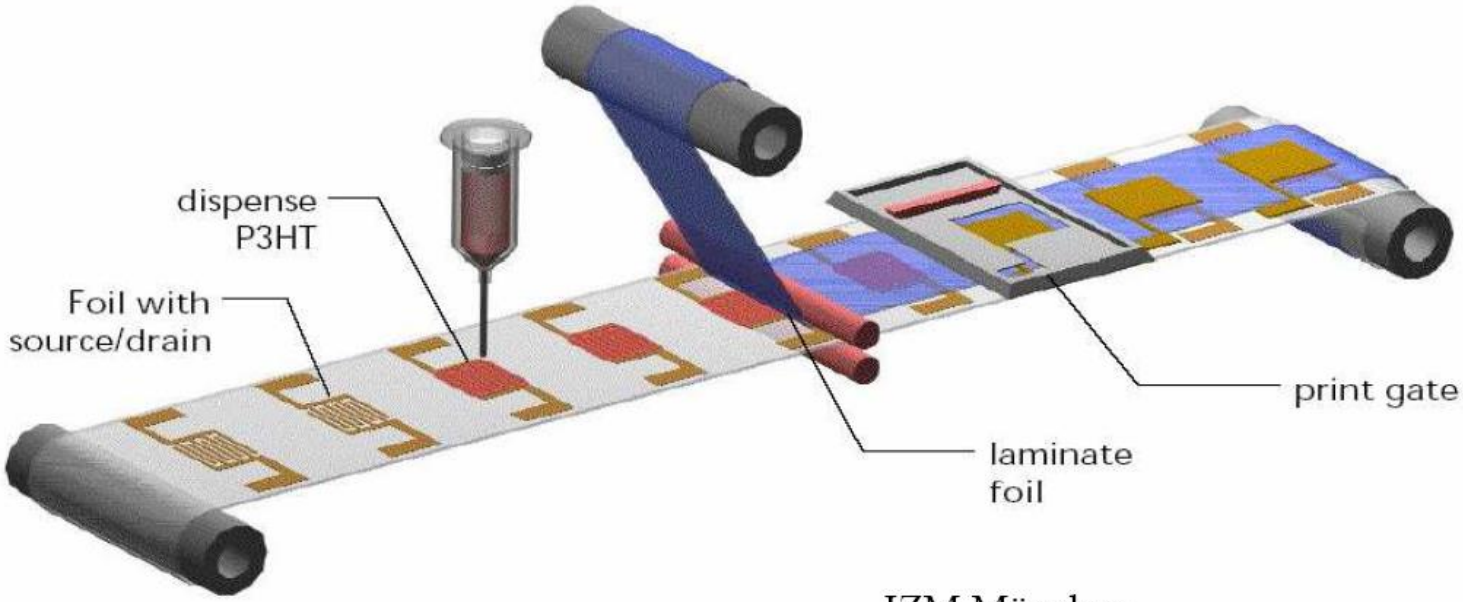

An inkjet printed TFT



TFT realized by Plastic Logic

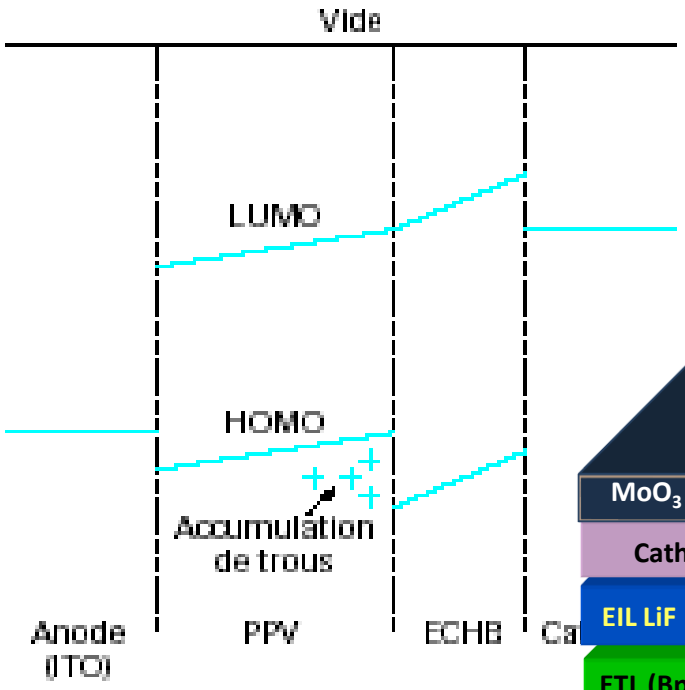
Roll to Roll

Reel-to-Reel Processing of Polymer Transistor

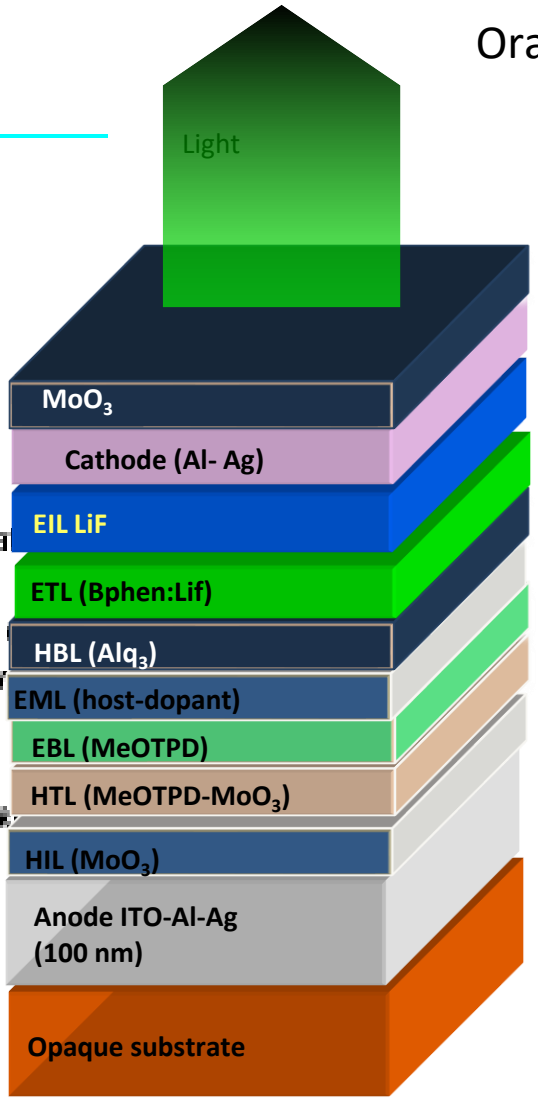


IZM München

Structure Multicouche



LUMO *lowest unoccupied molecular*
HOMO *highest occupied molecular or*
ITO *indium tin oxide*
PPV poly(paraphénylène vinylène)
ECHB *electron conducting/hole block*



Orange: ~18 Cd/A

Blue: ~ 6 Cd/A

Diodes PiN , dopage des ETL et HTL

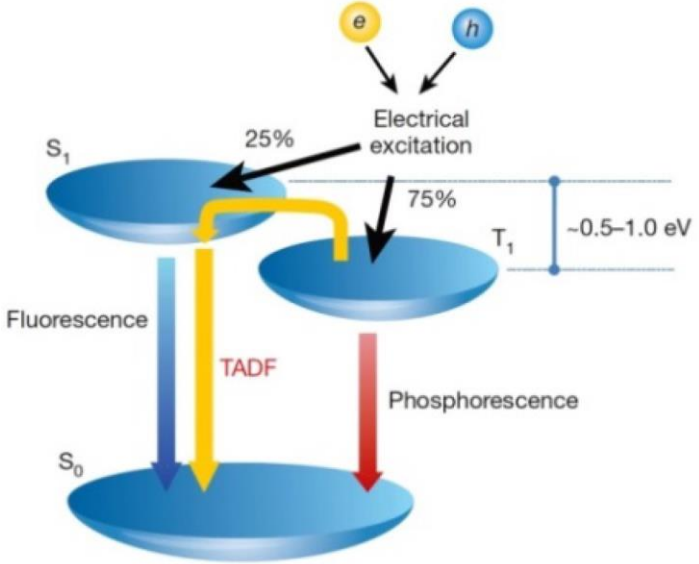
iemn
Institut d'Electronique, de Microélectronique et de Nanotechnologie
UMR CNRS 8520

MateriaNova
MATERIALS R&D CENTER

Fluorescence retardée thermiquement activée
Thermally-Activated Fluorescence TADF

Principe:

Repeuplement des états S des états T Inférieurs



+ Rendement quantique interne proche de 100% et externe 20%

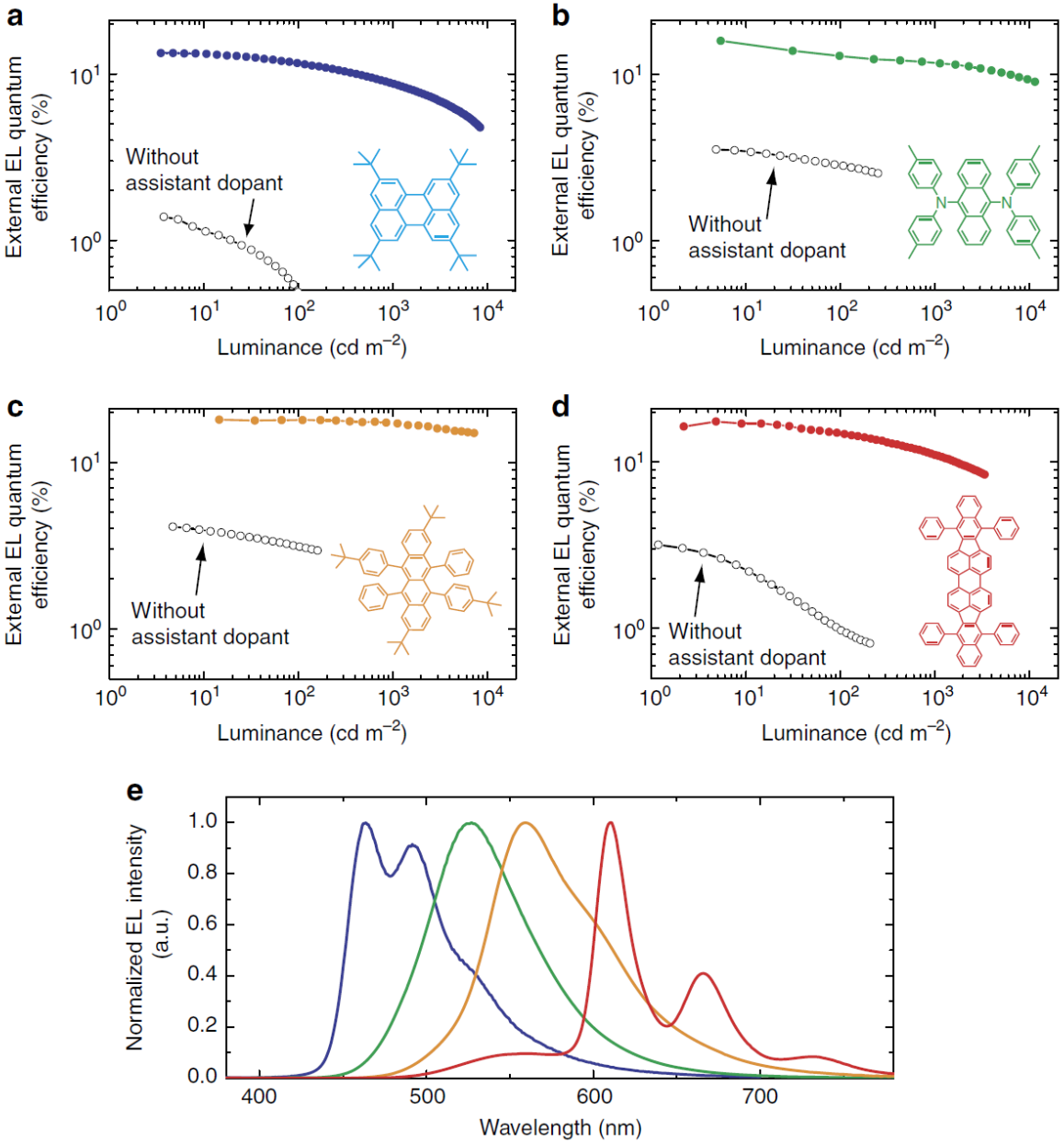
+ Eviter les métaux lourds utilisés dans les systèmes phosphorescents

Déjà dans les AMOLEDs des smartphones ‘’UDC’’

Alternative / Kyulux aux phospohorescents de UDC

	Emetteurs phosphorescents		*Emetteurs TADF*	
Couleur	*Efficacité électrique (cd/A) ; η_{ext} (%)*	*CIE 1931*	*Efficacité électrique (cd/A) ; η_{ext} (%)*	*CIE 1931*
Rouge	30 (20 %)	0.64 ; 0.36	20 (10.9 %)	0.61 ; 0.39
Vert	85 (20 %)	0.31 ; 0.63	38 (11.7 %)	0.29 ; 0.59
Bleu	50 (20 %)	0.18 ; 0.42	18 (8.7 %)	0.17 ; 0.30

C. Adachi et coll, université de Kyushu, Japon. Nature 492, 234 (2012)

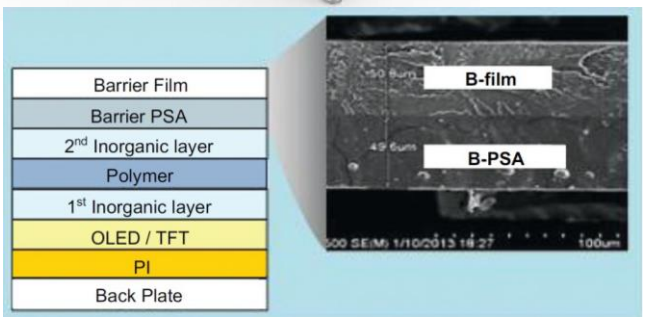

a
External EL quantum efficiency (%)
Without assistant dopant
Luminance (cd m−2)
b
External EL quantum efficiency (%)
Without assistant dopant
Luminance (cd m−2)
c
External EL quantum efficiency (%)
Without assistant dopant
Luminance (cd m−2)
d
External EL quantum efficiency (%)
Without assistant dopant
Luminance (cd m−2)
e
Normalized EL intensity (a.u.)
Wavelength (nm)

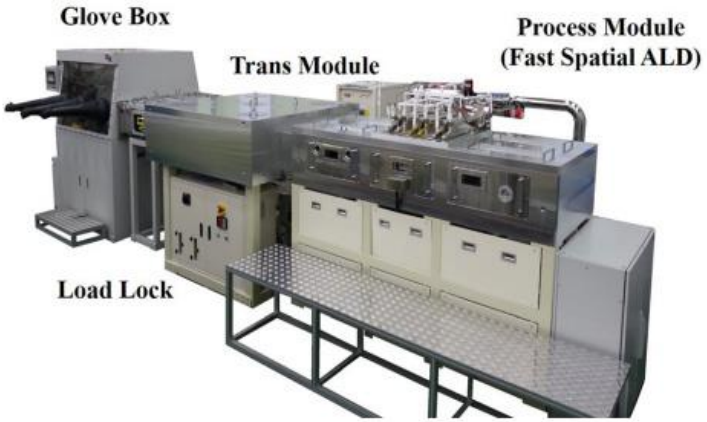
Encapsulation des OLEDs

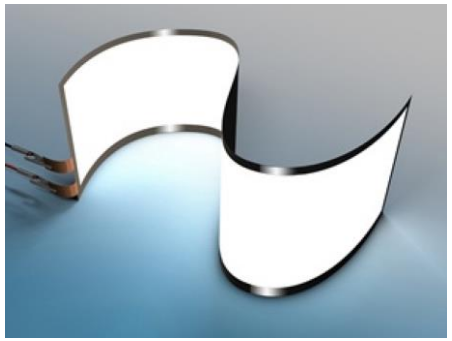
- Vitex System (rachetée par Samsung) AIXTRON

Dépôt PECV mais Plasma

- *Jusung (ALD /Polymère/ALD) LG ALD Infinity 200 Encapsulix (équipt CEA_Leti)*







- *Projet Konfekt (Shott , Tesa , Von Ardenne): verre mince flexible*

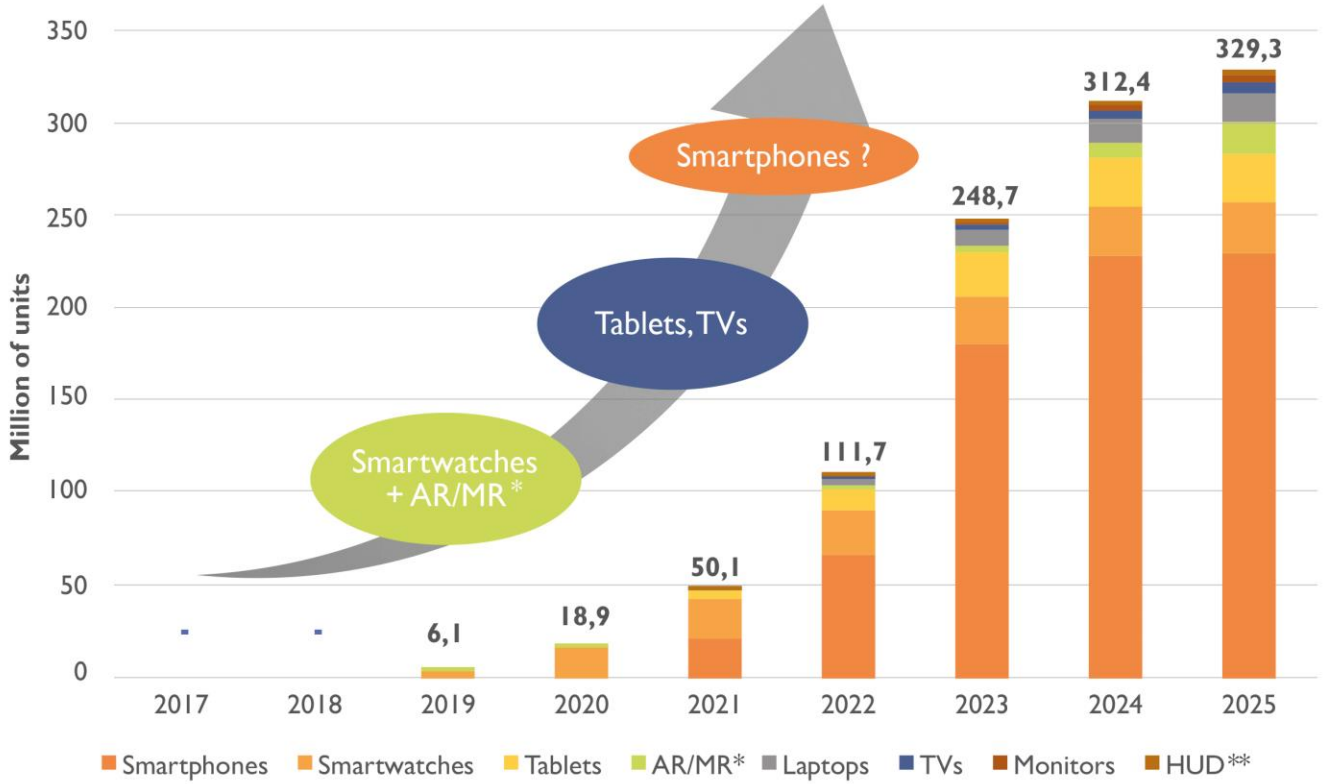
Application aux écrans plats

Avantages des Ecrans OLEDs

- Faible consommation
- Compatibilité aux larges surfaces
- Technologie simple et peu coûteuse
- Ecrans flexibles (substrats souples)
- Faible poids

MicroLED display volume forecast – Aggressive scenario

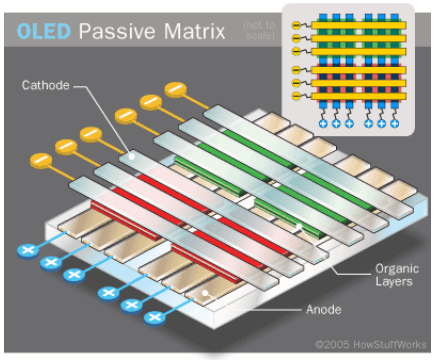
(Source: MicroLED Displays 2017 report, February 2017, Yole Développement)

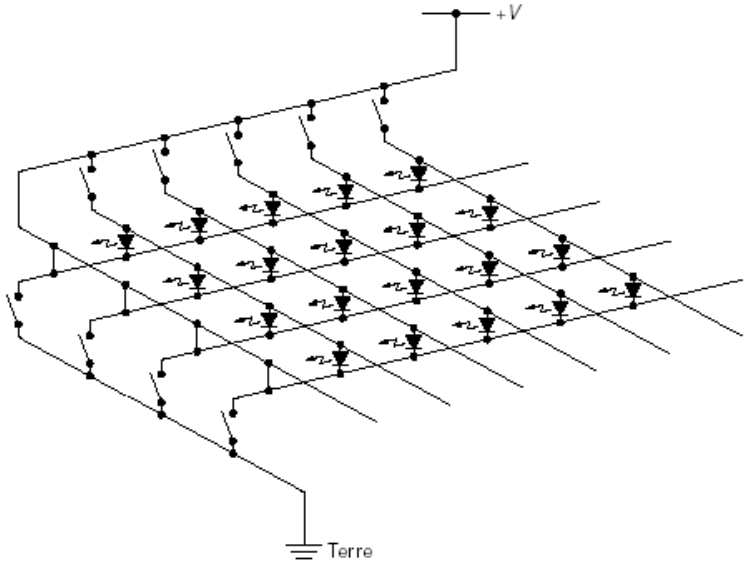


** AR/MR: Augmented Reality/Mixed Reality / ** HUD: Head Up Display*

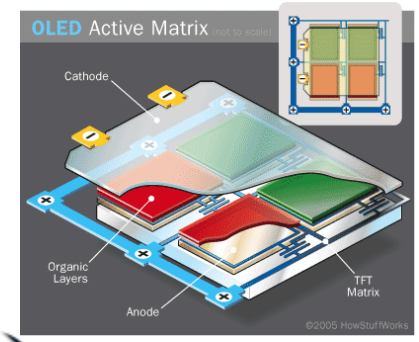
Adressage des écrans OLEDs

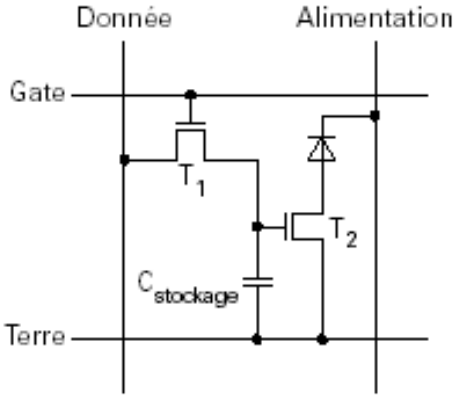
Adressage passif





Adressage actif

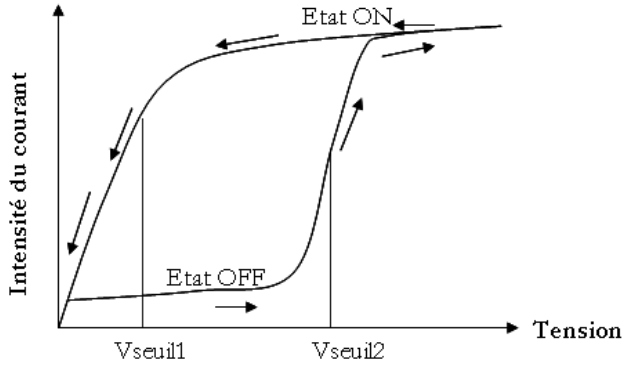




T transistors
C capacité

Adressage par Bistable

Composant bistable



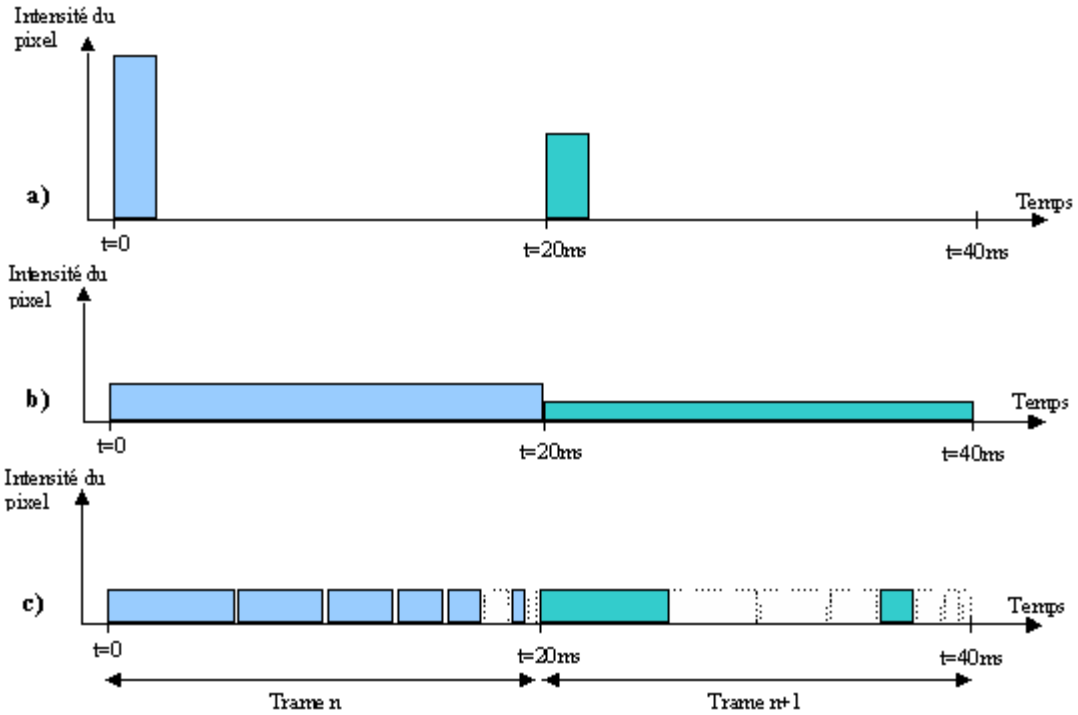
-Rapport $I_{ON}/I_{OFF} > 10^4$
-Temps de commutation< 100ns
-Stabilité jusqu'à 100° C

Collaboration: Thomson Multimédia à Rennes

Passif

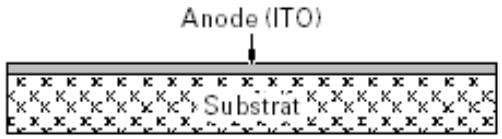
Actif

Bistable

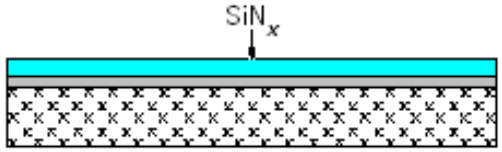


D. Tondelier, K. Lmimouni, D. Vuillaume, Appl. Phys. Lett, Vol85-23, 5763 (2004)

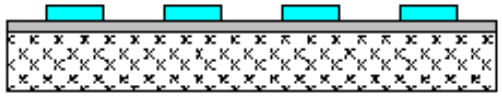
Mise en place d 'un type de pixel monochrome



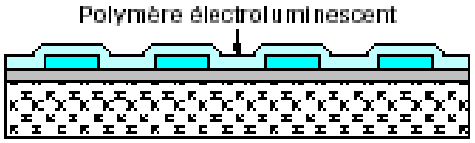
ⓐ substrat recouvert de l'anode



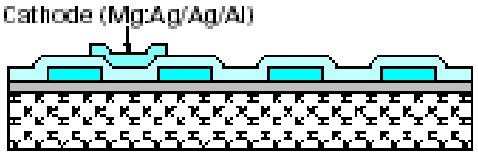
ⓑ dépôt d'une couche mince de nitrure de silicium (isolant) sur l'ITO



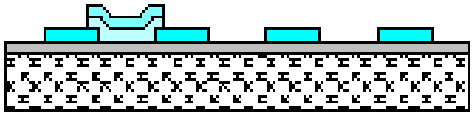
ⓒ gravure de la couche de nitrure par des techniques standards de photolithographie



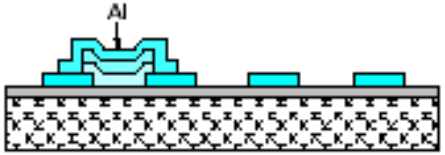
ⓓ *spin-coating* du premier type de polymère électroluminescent



ⓔ évaporation de la cathode (tricouche Mg : Ag, Ag, puis Al) à travers un masque

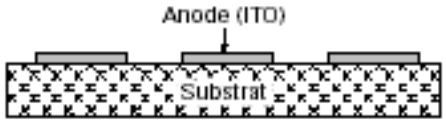


ⓕ gravure par un plasma O_2 du film de polymère non protégé par l'aluminium

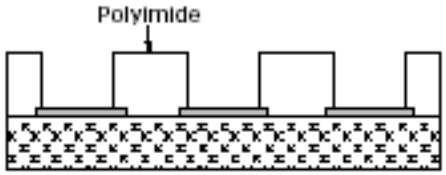


ⓖ encapsulation des pixels ainsi obtenus par un dépôt d'aluminium

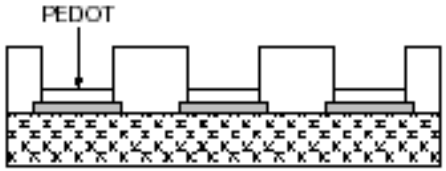
Technologie jet d 'encre CDT-Seiko-Epson



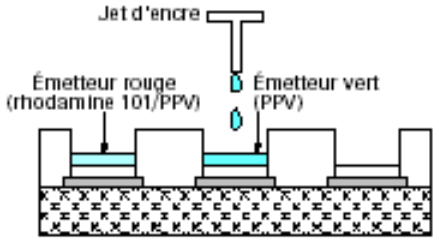
ⓐ gravure de l'ITO



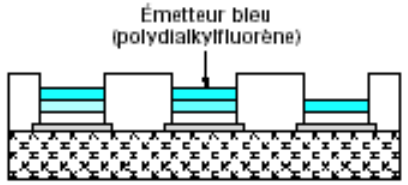
ⓑ dépôt de rubans de polyimide qui servtront à contenir les gouttes de solution de polymère puis traitement de la surface par un plasma O_2 suivi d'un plasma CF_4 afin de modifier la mouillabilité du polyimide



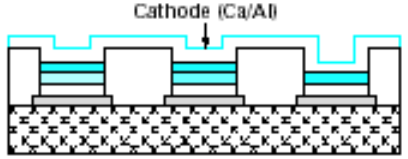
ⓒ *spin-coating* du polymère conducteur PEDOT



ⓓ dépôt par jet d'encre des polymères émetteurs dans le rouge et dans le vert



ⓔ *spin-coating* du polymère émetteur dans le bleu

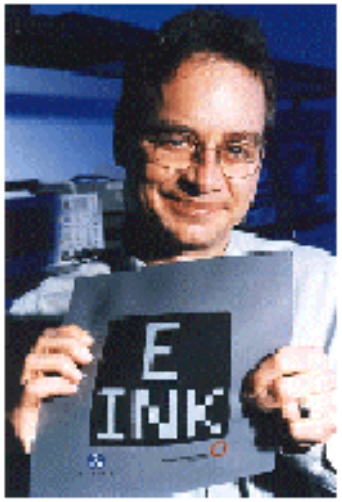


ⓕ évaporation de la cathode (Ca protégé par Al)

Les toutes premières réalisations technologiques

Afficheurs souples sur PET (COVION)

Image 14 : Prototype d'Ecran Flexible Feuille Papier Electronique



(Source: Elnk)

Image 8 : Ecran Organique Electroluminescent à Matrice Passive sur Substrat Flexible de Polyéthylène Téréphtalate

(Source : Universal Display Crop.)

Ecran Epson 40 ' '

40” OLED PROTOTYPE (SAMSUNG)

Info-OLED.com-web site

Produits commerciaux

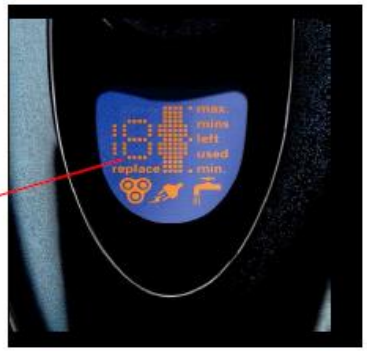
THOMSON

SEL

COVION Organic Semiconductors GmbH

autronic-MELCHERS GmbH

CDT

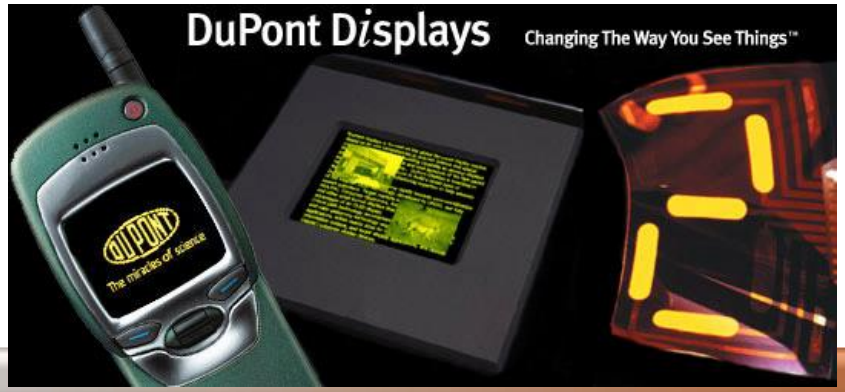


UNIAX
POLYMER ELECTRONICS

ORMECON

PHILIPS

MP3 : ~50% des écrans sont des OLED



iemn
Institut d'Electronique, de Microélectronique et de Nanotechnologie
UMR CNRS 8520

Produits commerciaux…

50% des produits

Samsung Galaxy Note 5.3'', 1280x800, super AMOLED technology

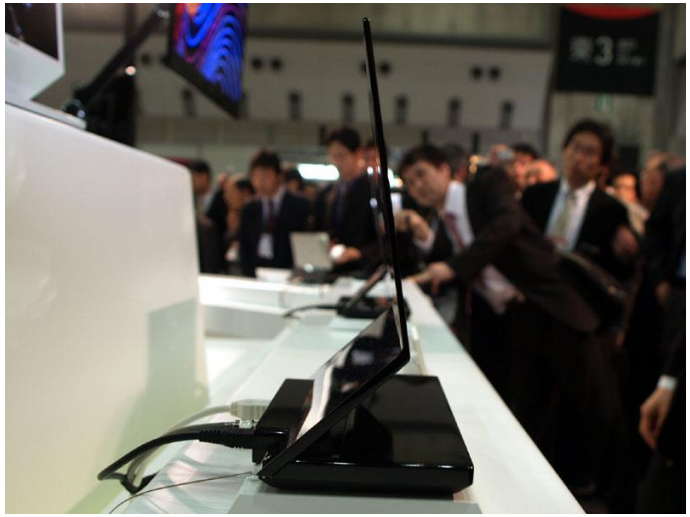
LG 55EM9600 55'' full HD (~**10000$**) - 2012

XEL-1

Sony XEL-1 11'' OLED Digital TV (~ **4000€**) - 2009

Sony Walkman X-series, 3-inch OLED touchscreen (432x340 WQVGA)

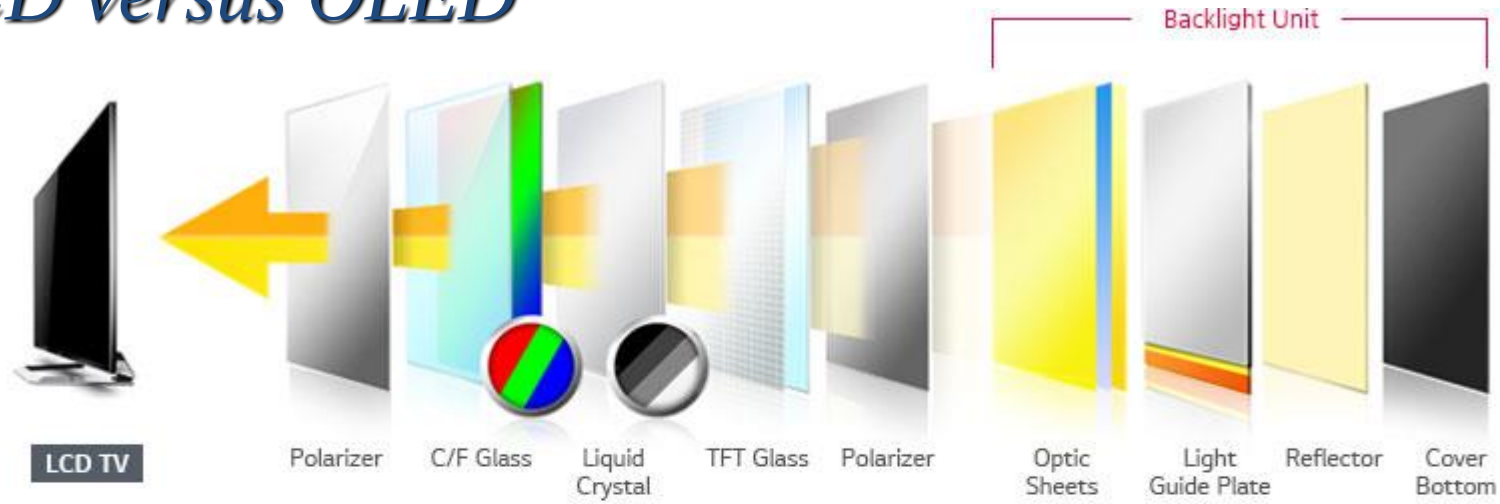
LG 15EL9500 15.1'' OLED Digital TV 1366x768 (~**2000€**) - 2010

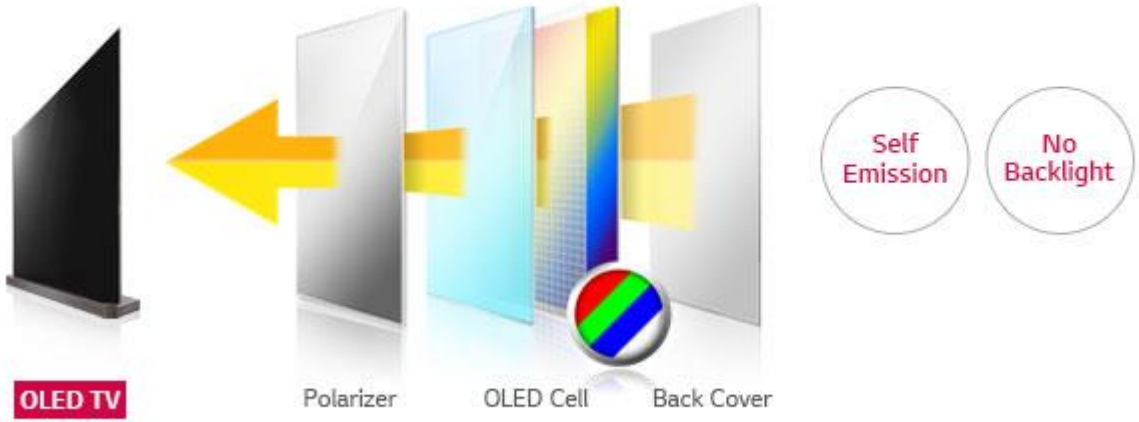


iemn
Institut d'Electronique, de Microélectronique et de Nanotechnologie
UMR CNRS 8520

A suivre .....

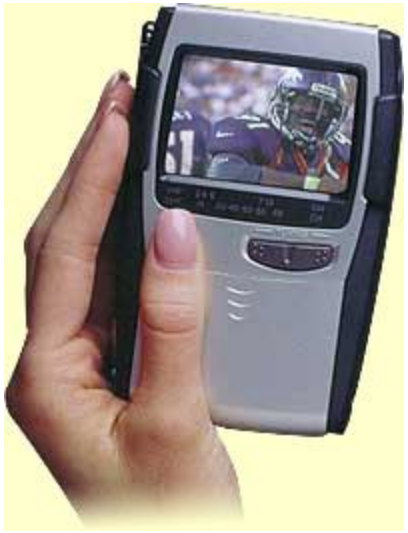
LCD versus OLED





Comparaison de deux écrans : LCD et OLED

OLED



LCD

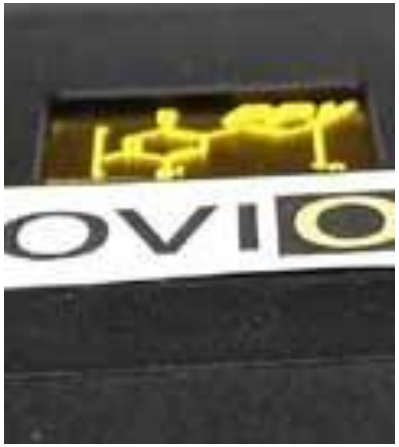
Brightness and Color

A side-by-side comparison reveals the striking contrast, brightness, and color of an OLED screen (left) versus an LCD screen (right).

Différence de luminosité, de contraste et de brillance entre un écran LCD et un écran OLED

Angle d 'ouverture des écrans à OLEDs

6000 Pixcel passive matrix adressed devices produced by UNIAX



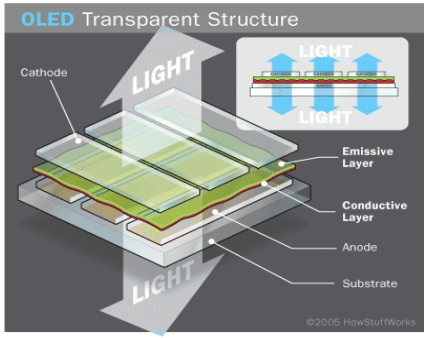
Front view ~45° view~10° view

High brightness and contrast

- Ultra-wide viewing angle
- No backlight required
- Fast response time
- Low power consumption

Ecrans transparents…..

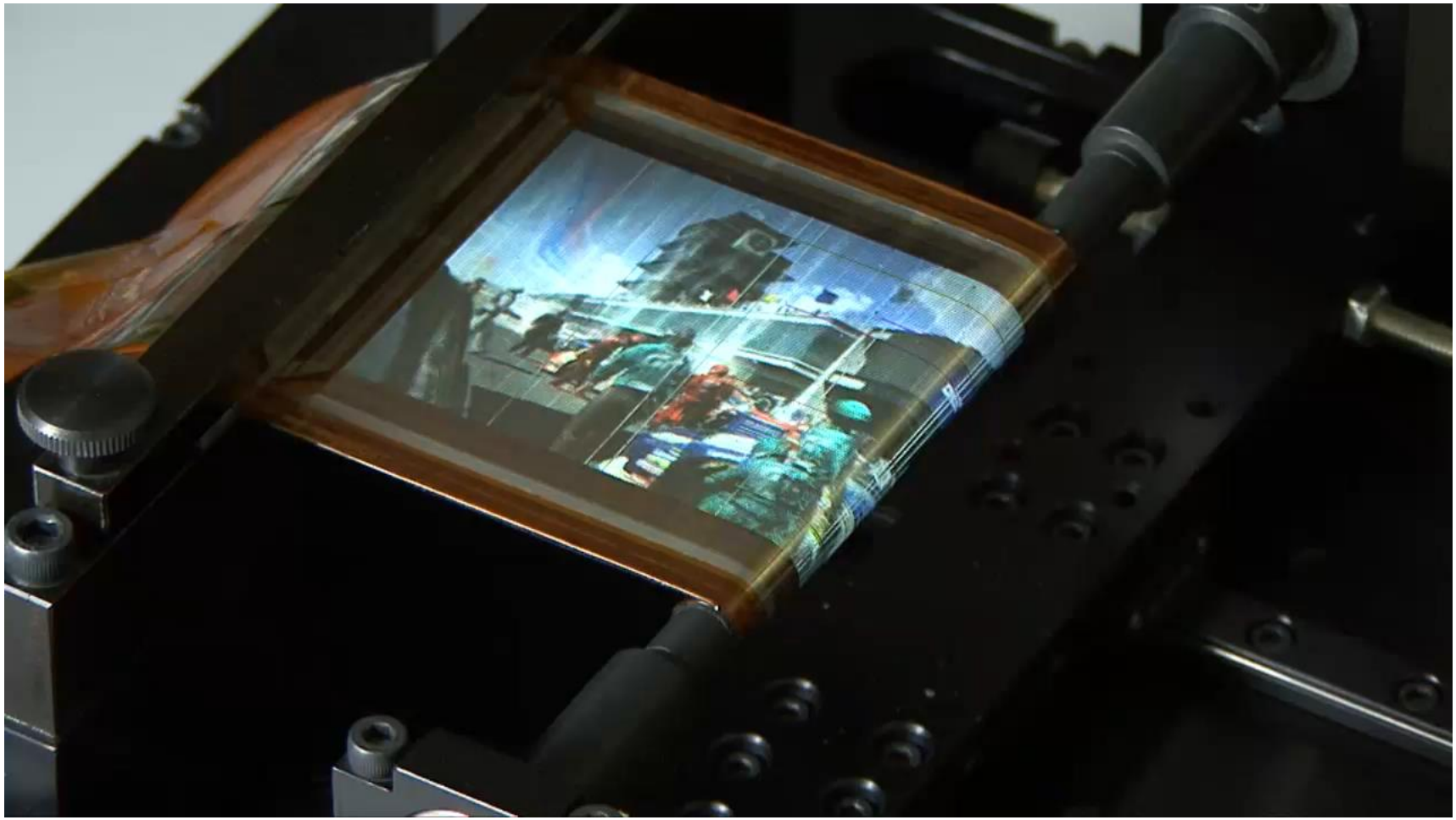
Ecran miroir et transparent de Samsung.
Application cockpit
www.osadirect.com



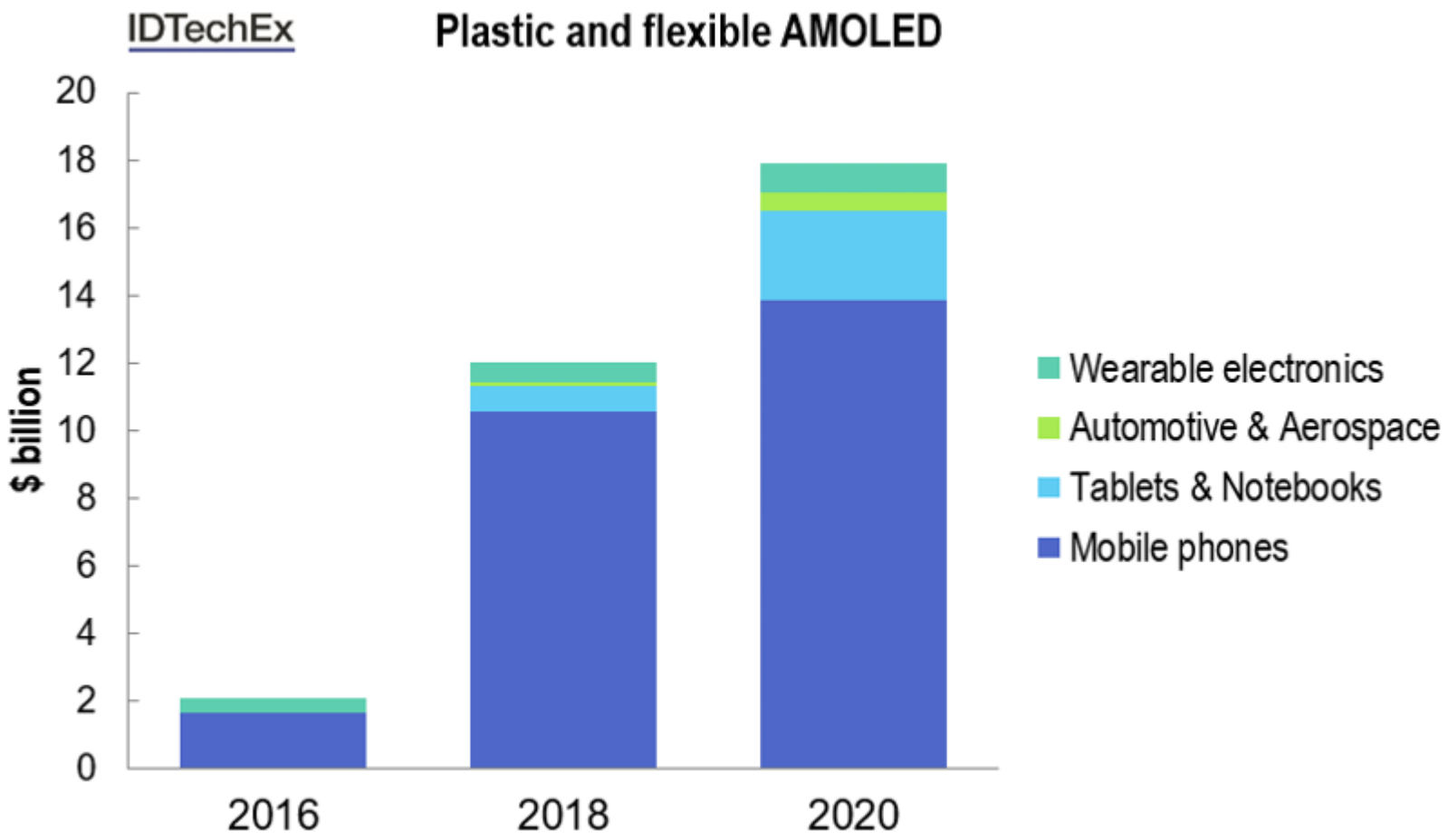
.....et Flexibles

Ecran TV mural mince et flexible de LG Display

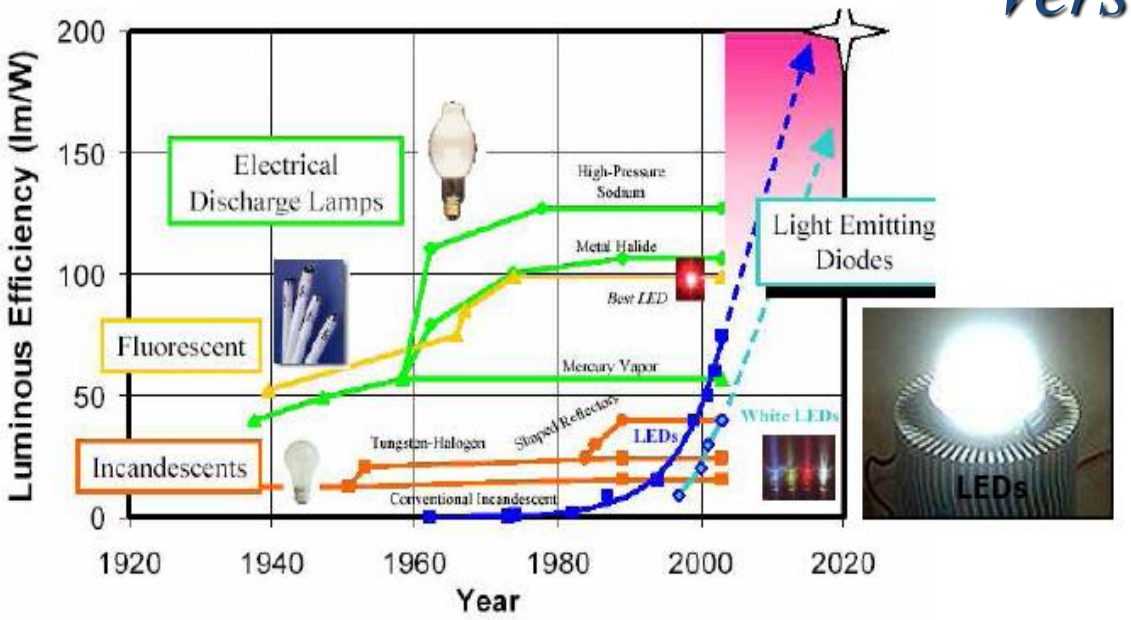
www.osadirect.com



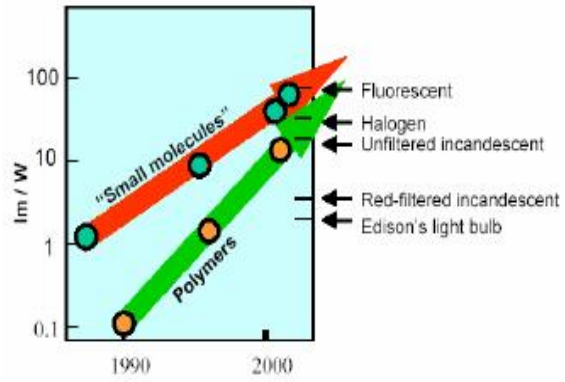
Le Marché…


IDTechEx
Plastic and flexible AMOLED
$ billion
20
18
16
14
12
10
8
6
4
2
0
2016
2018
2020
Wearable electronics
Automotive & Aerospace
Tablets & Notebooks
Mobile phones

Vers l'Eclairage



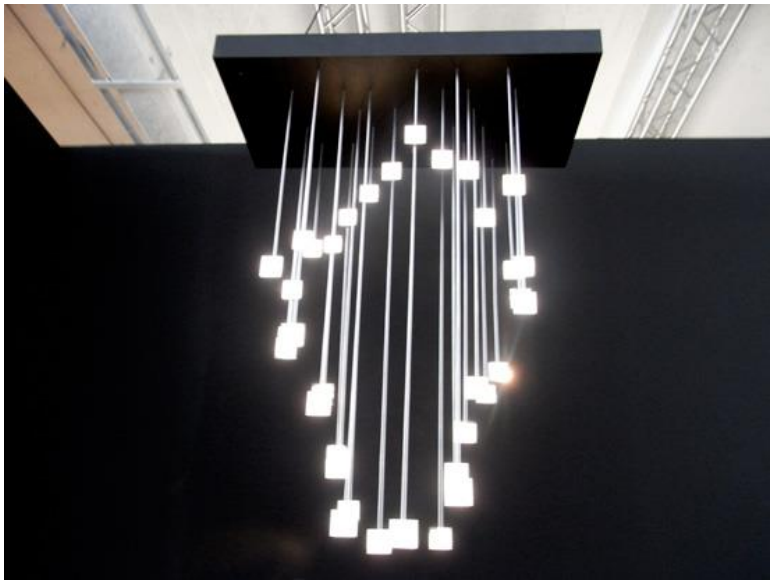
< 20 lm/W <100 lm/W



NOVALED : record du monde

Développement d'une OLED **verte** avec une efficacité de **110 lm/W** à 1000 Cd/m^2

(**PRESS RELEASE,** Dresde, February 16th 2005)



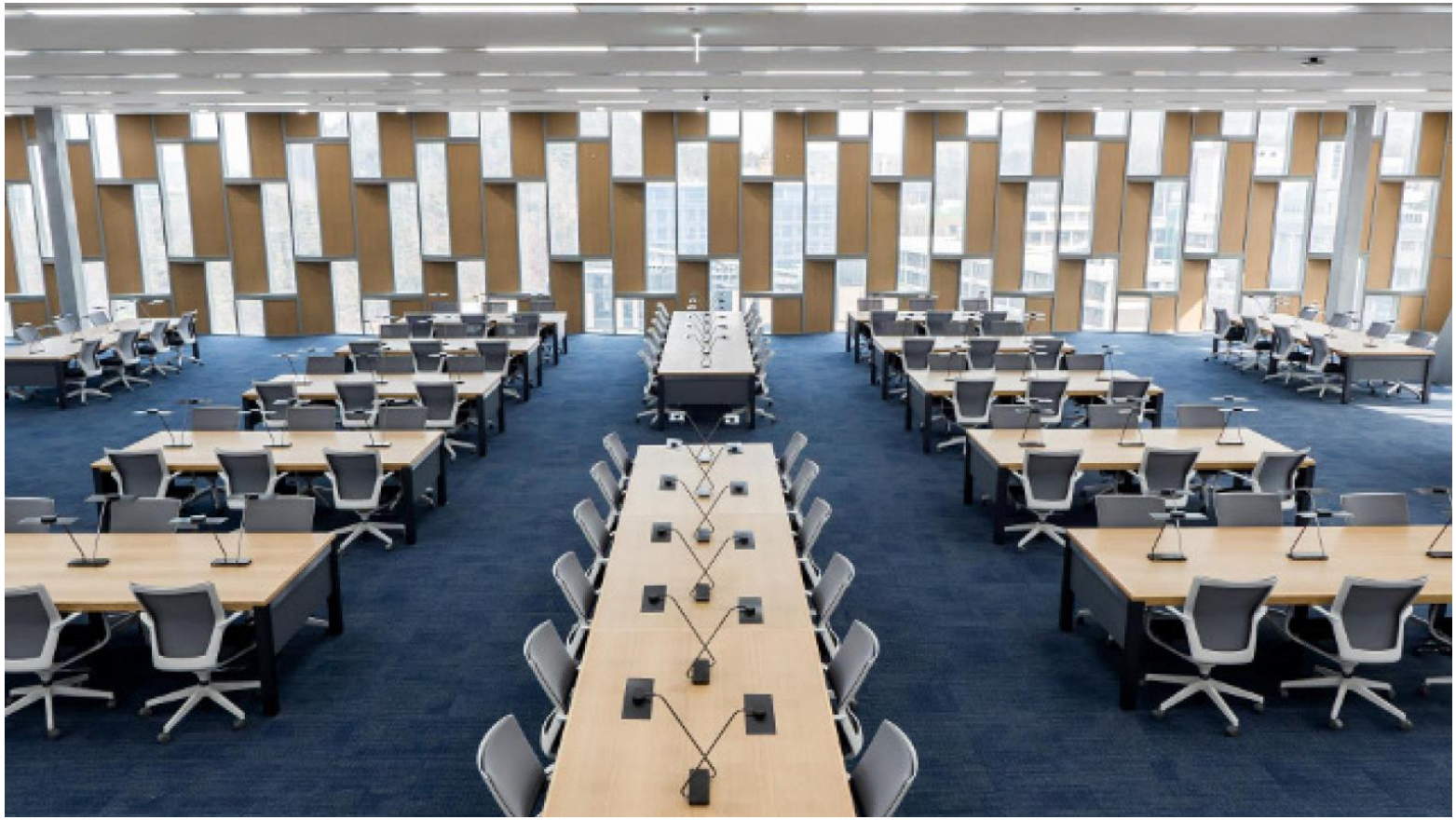
iemn
Institut d'Electronique, de Microélectronique et de Nanotechnologie
UMR CNRS 8520

Le marché automobile: y vas ..n'y va pas. ...y va ?! .....

Puissance insuffisante pour STP et direction/
OK pour signalisation arrière.(Astron FIAMM) Toulouse

(Astron-FIAMM) de Toulouse

AUDI…OLEDS Matrix et BMW …Osram

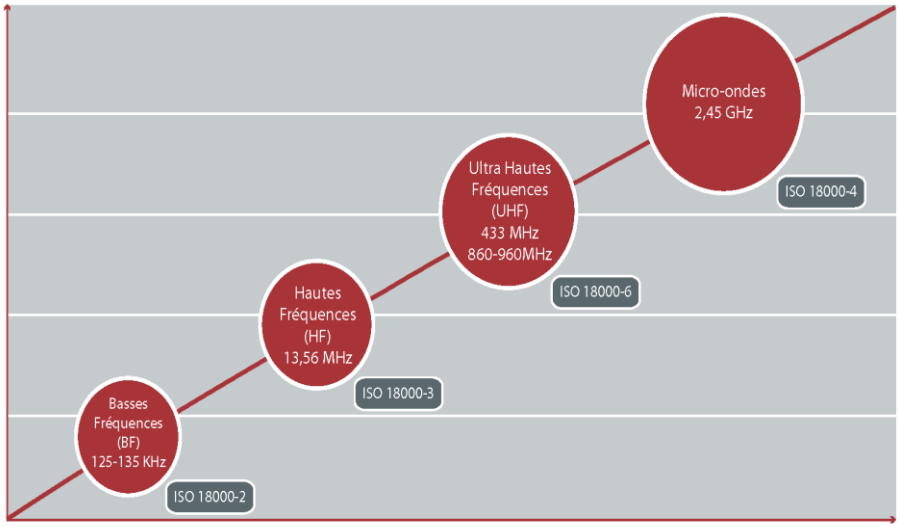


Eclairage de la grande Librairie de l’université de Séoul. LG Display

www.osadirect.com/

http://start.eure.fr/Formation-insertion-professionnelle

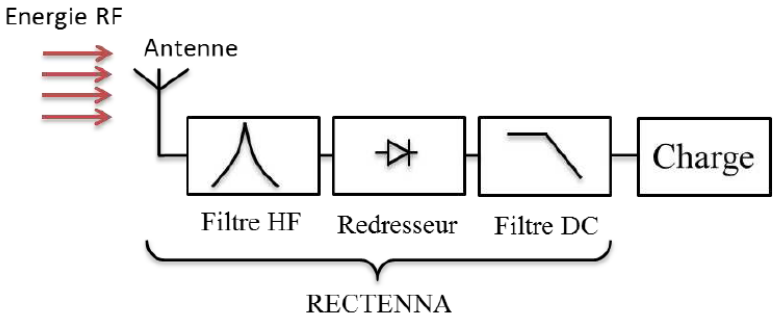
Source: IMEC

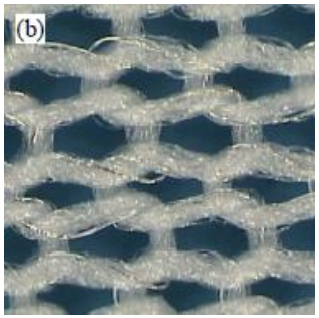


iemn
Institut d'Electronique, de Micro
UMR CNRS 8520

Scavenging Array by Textile Technology for Electromagnetic Energy ????

Basic principle





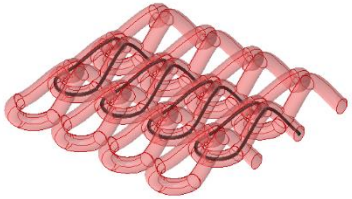
Omega-like metamaterials / knitted fabric

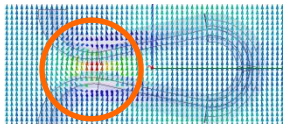
Global System for Mobile Comm. = 850-900 MHz
Personnal Communication Service = 1.8 - 1.9 GHz
Wireless Local-Area Networks = 2.45 GHz

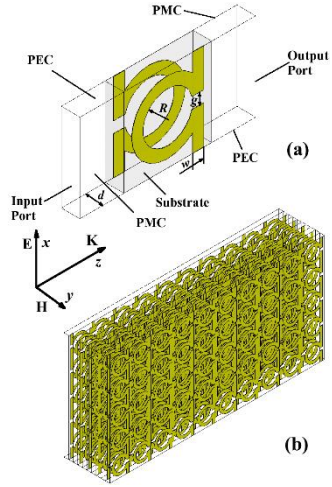
dielectric D=10 µm + Ag D = 2-3 µm

ANR CONTEXT ?

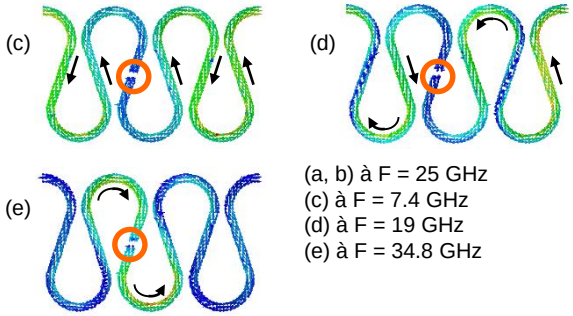
Textile-inspired metamaterial technology
Organic rectification circuit







Concentration of the elecric field in knitted fabric



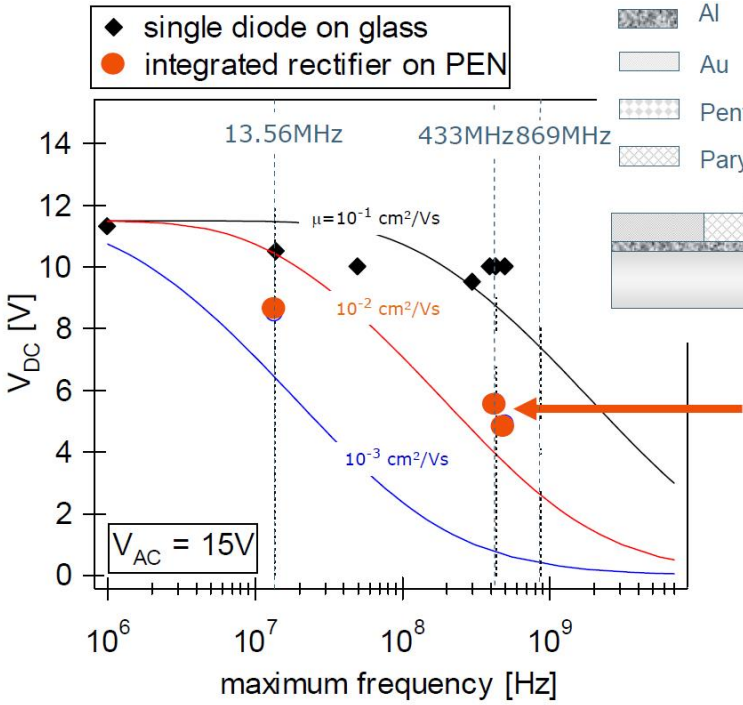
(a, b) à F = 25 GHz
(c) à F = 7.4 GHz
(d) à F = 19 GHz
(e) à F = 34.8 GHz

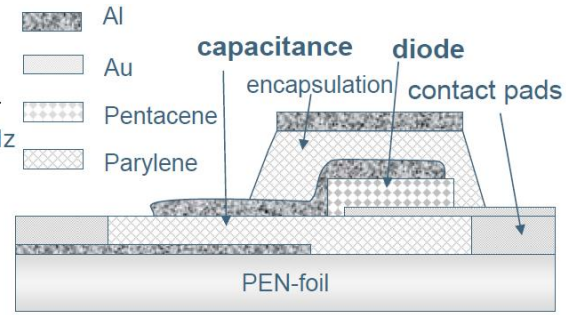
Burgnies et al, J Appl. Phys., 2015

iemn
Institut d'Electronique, de Microélectronique et de Nanotechnologie
UMR CNRS 8520

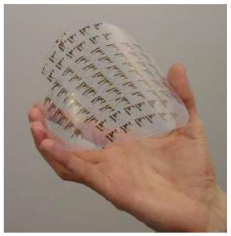
Collaborations: L. Burgnies DOME and F. Raults GEMTEX-ENSAIT

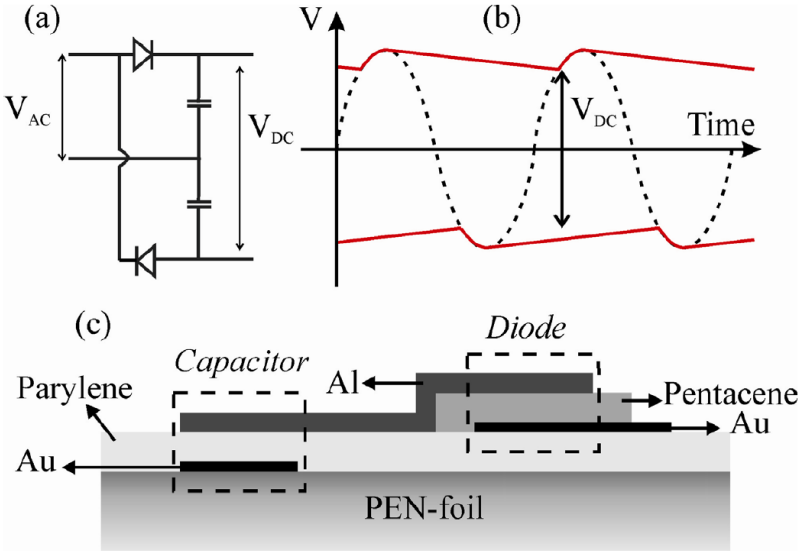
The first UHF integrated rectifier on Flexible substrate





5 V at 433 MHz



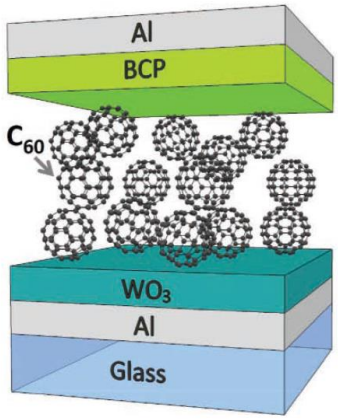


Double half wave rectifier
C: 20pF ; Pentacene 350nm
Parylene 400nm ; Gold 30 nm
Active area of the diode
500x200μm2 ; PEN 200μm

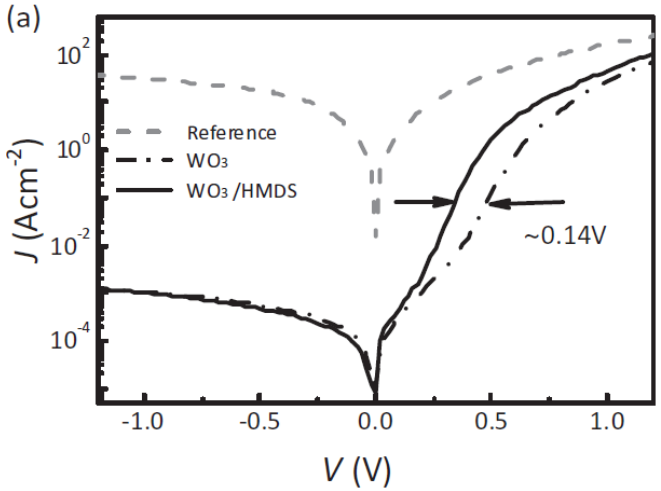
K. Myny *et al*, Appl. Phys. Lett. **93**, 093305 (2008)

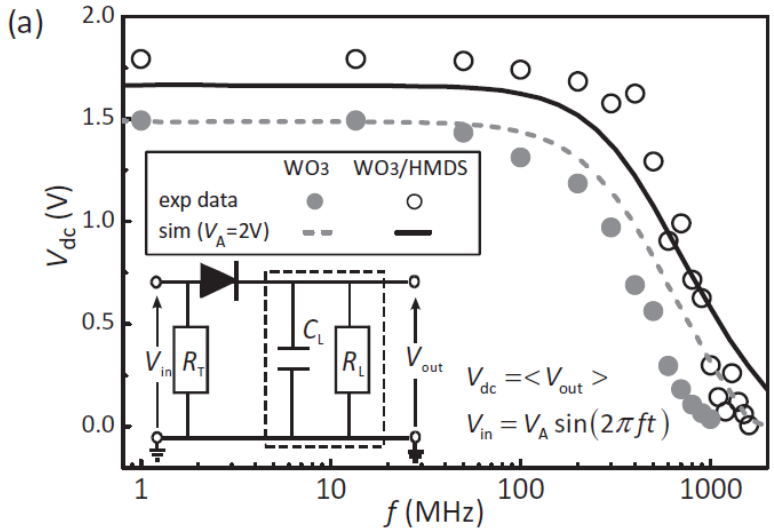
Organic rectification circuit….Towards Gigahertz operation

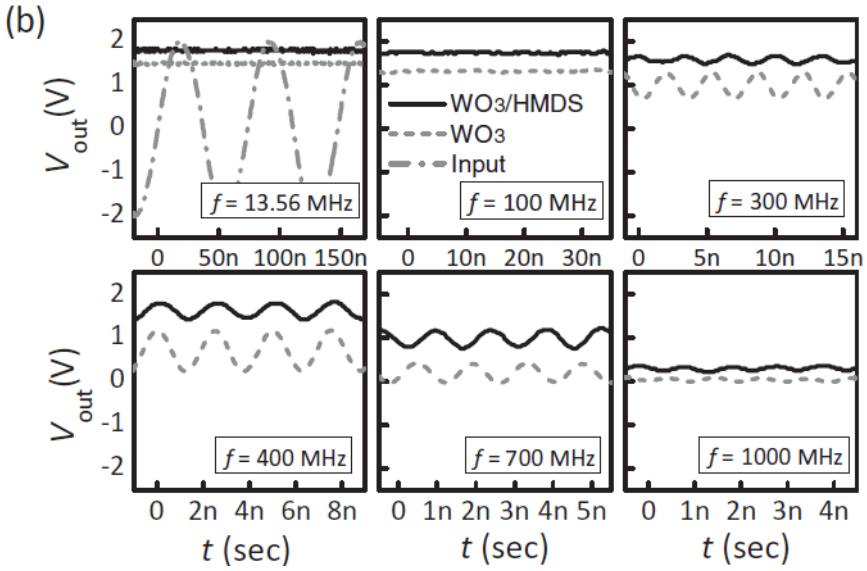
Vertical diode structure



BCP: dimethyl diphenyl phenanthroline (7nm)
HMDS hexamethyldisilazane -WO_3 (20nm)





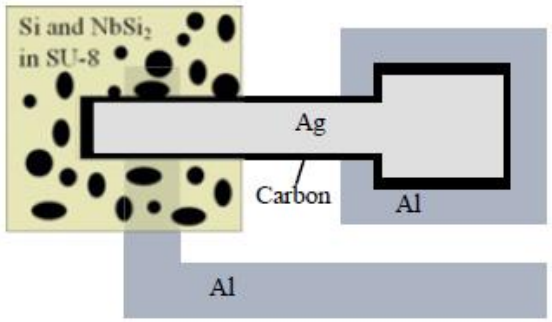


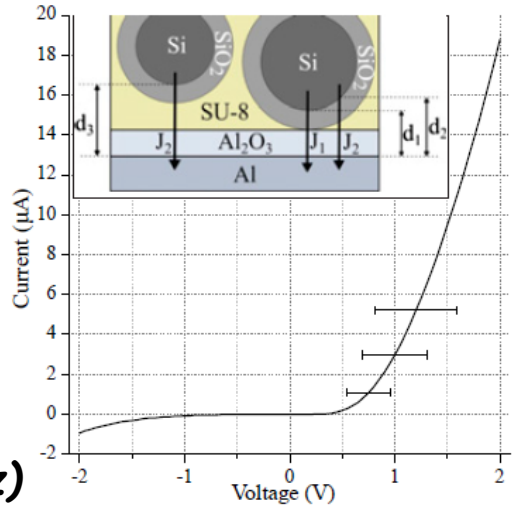
iemn
Institut d'Electronique, de Microélectronique et de Nanotechnologie
UMR CNRS 8520

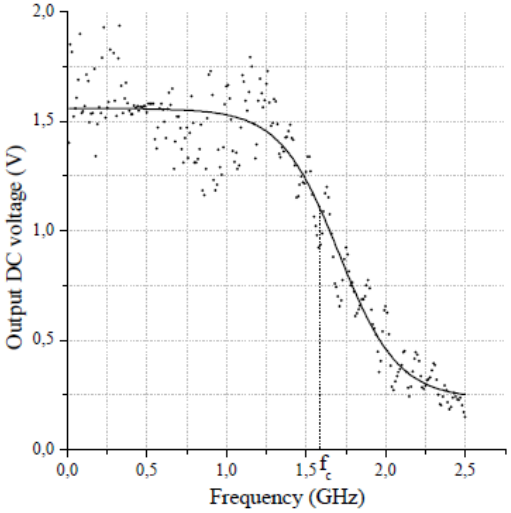
Challenges: High frequency and Low turn-on voltage Vt

D. Im and coll, Adv.Mater. 2011, 23, 644-648

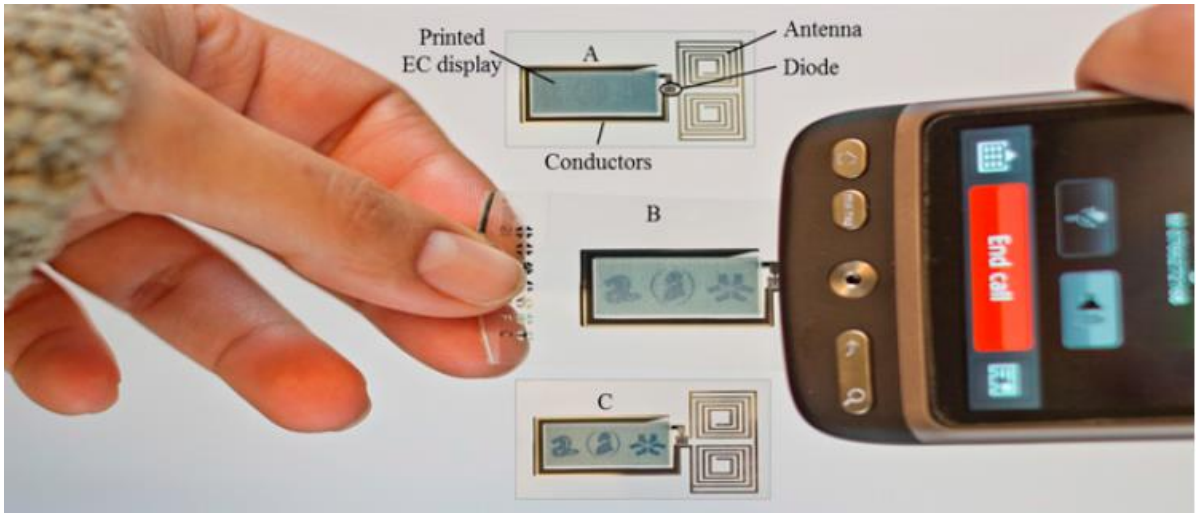
Printed diodes operating at mobile phone frequencies







Rectification factor 100@ 1V
Cutoff frequency 1.6GHz (1.8GHz)
Device turn on within 10s

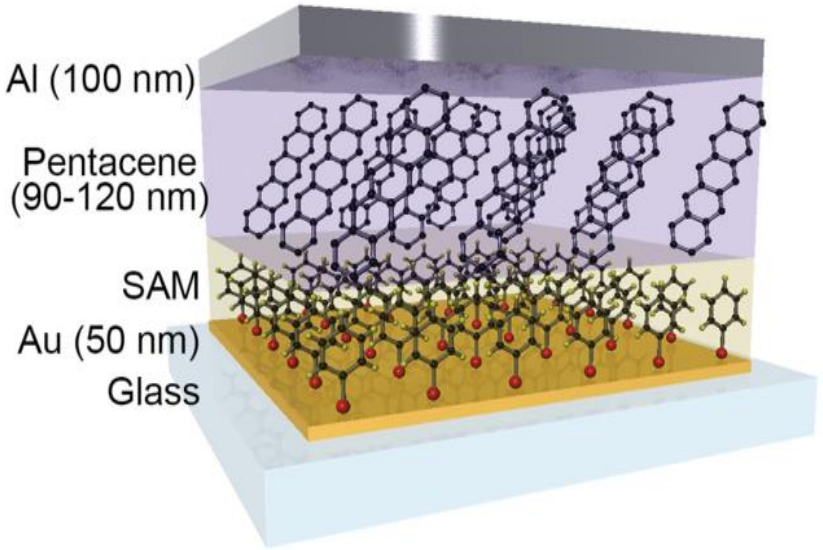


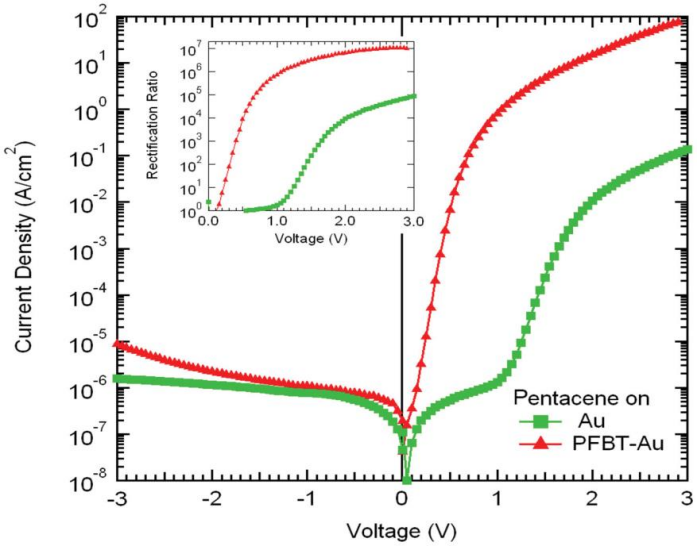
Strategy:
copolymers
DKP-DKP
(diketoPyrrole)

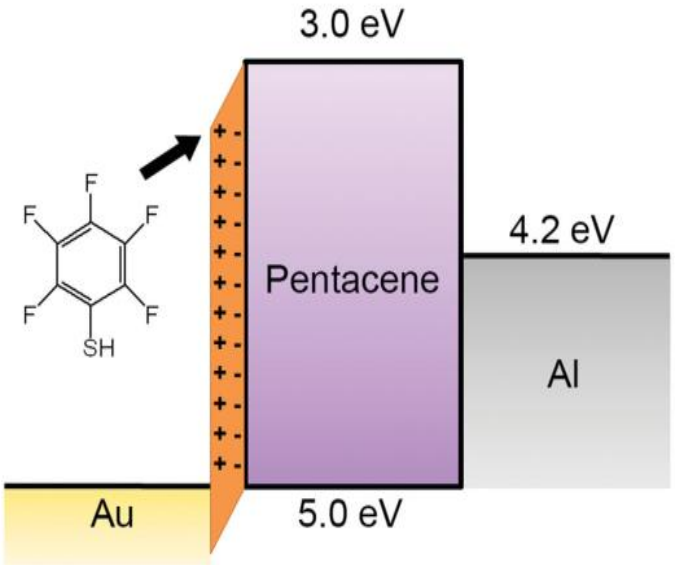
iemn
Institut d'Electronique, de Microélectronique et de Nanotechnologie
UMR CNRS 8520

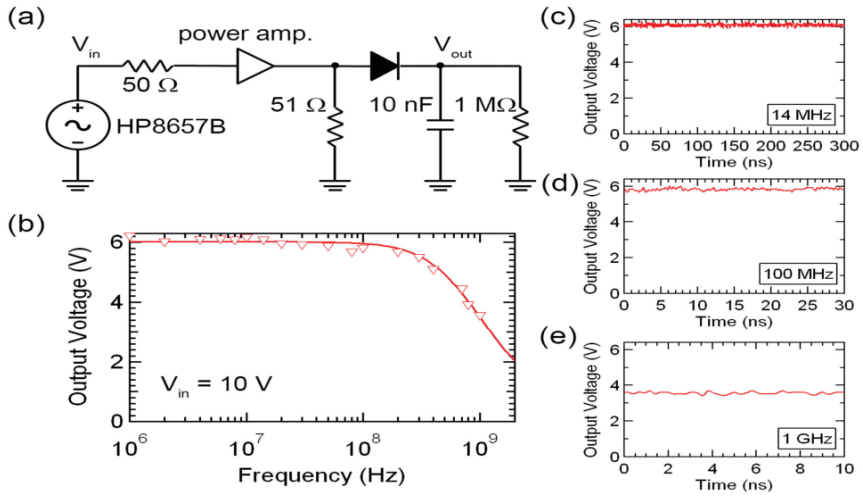
N. Sani et al Proc Natl Acad Sci PNAS USA 111:11943

Traitement de surface SAM



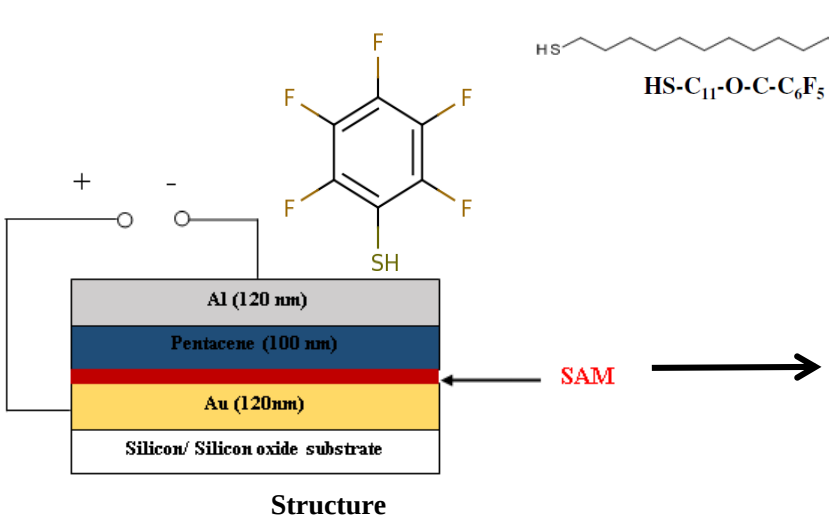




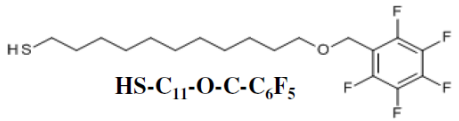


Chan-mo Kang et al, Adv. Electron. Mater, 2 (2016) 1500282.

Jonction PN versus Fonctionnalisation des électrodes

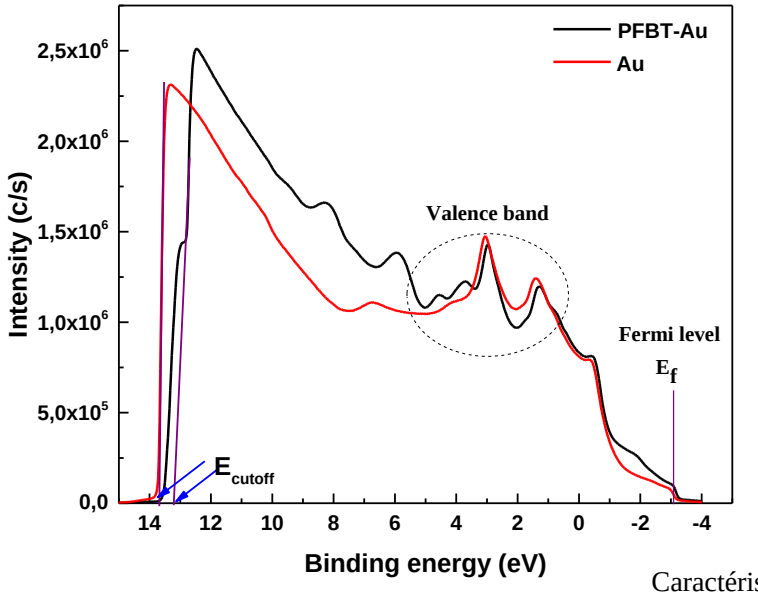


Structure



PFBT

- **Gold** : 120 nm
- **Pentacene** : 26 nm
- **N2200** : 120 nm
- **Silicon (Si ++)** : 350 µm
- **Surface :** 0.01 mm2



Caractérisation UPS

$$\Phi = h\upsilon - (E_{cutoff} - E_f)$$

$h\upsilon = 21.2$ eV

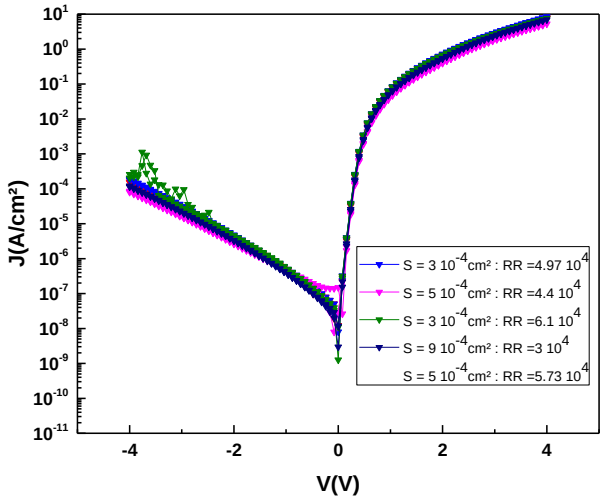
$E_f = 3.07$eV

$$\Phi\,(Au) = 4.49\ eV$$
$$\Phi\,(Au - PFBT) = 4.92\ eV$$

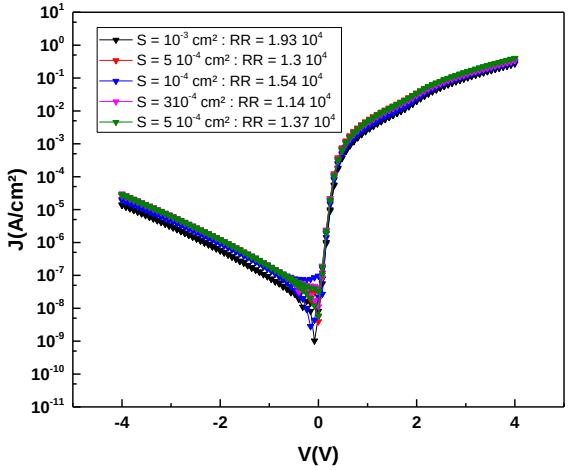
Interreg France-Wallonie-Vlaanderen
UNION EUROPÉENNE EUROPESE UNIE
LUMINOPTEX

Fonctionnalisation des électrodes

Etudes préliminaires: PhD Ferchichi Khaoula :

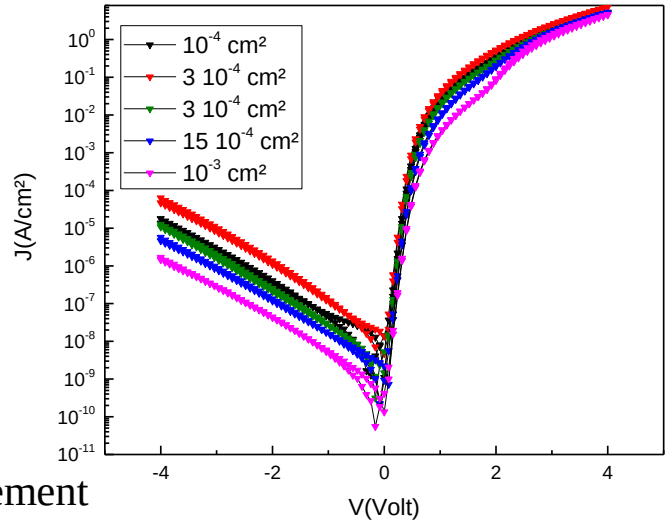


Au sans recuit–Pentacène-Al

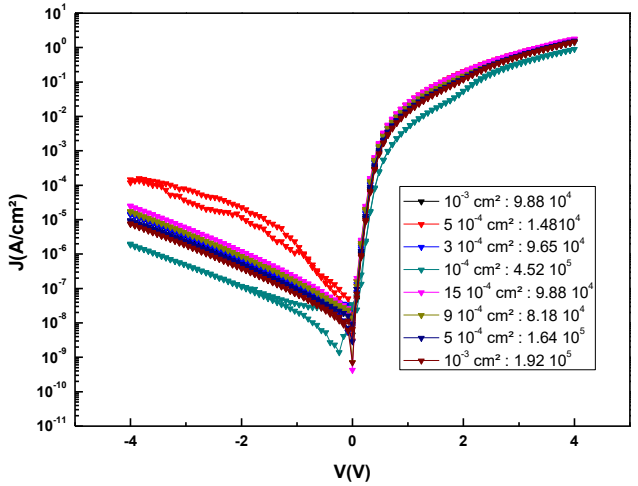


Au -PFBT–Pentacène-Al

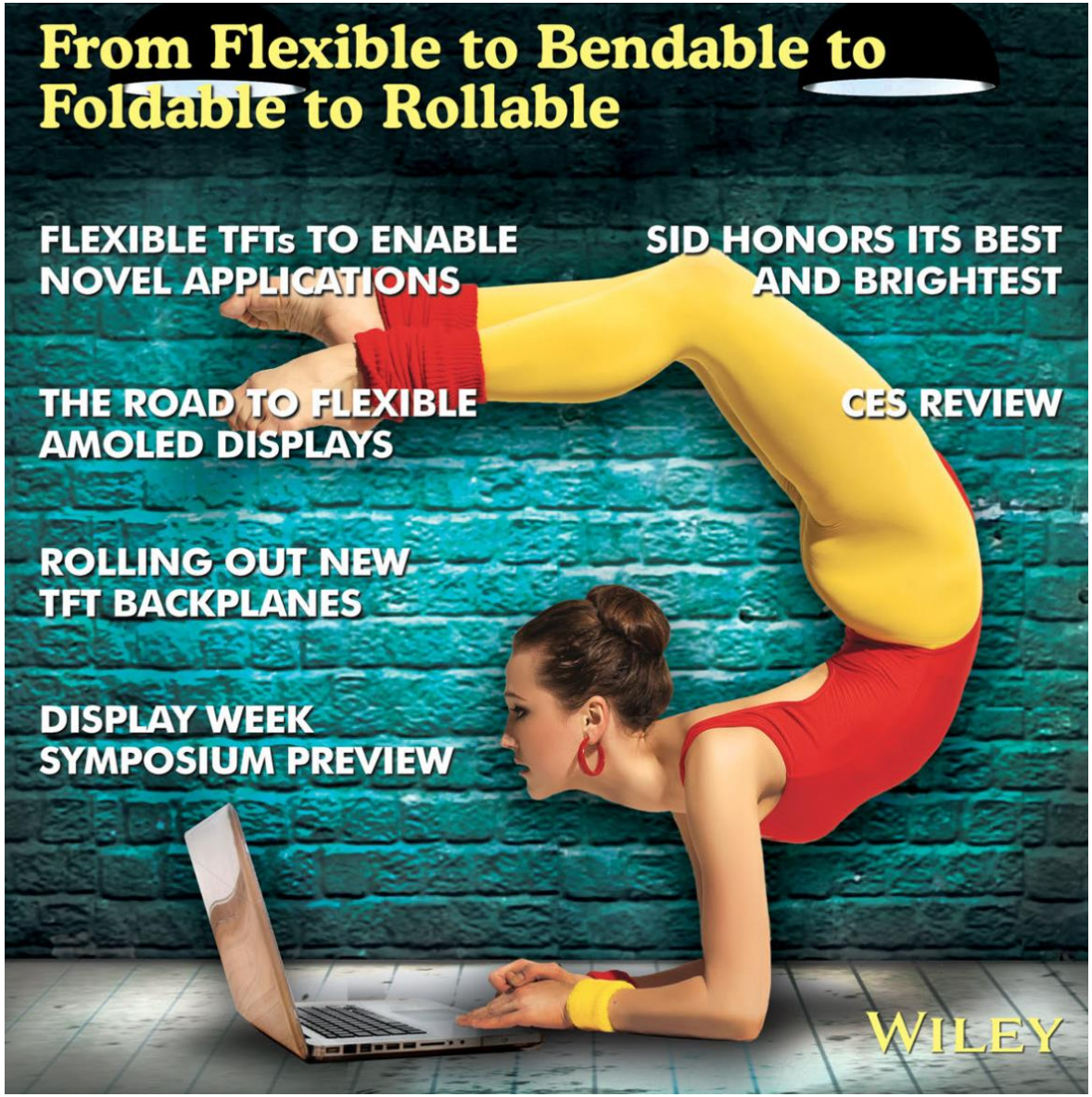
Tension de fonctionnement très faible (60-80 mV).



Au avec recuit –Pentacène-Al



Au-PFBT avec recuit à 80° C



Merci pour votre Attention