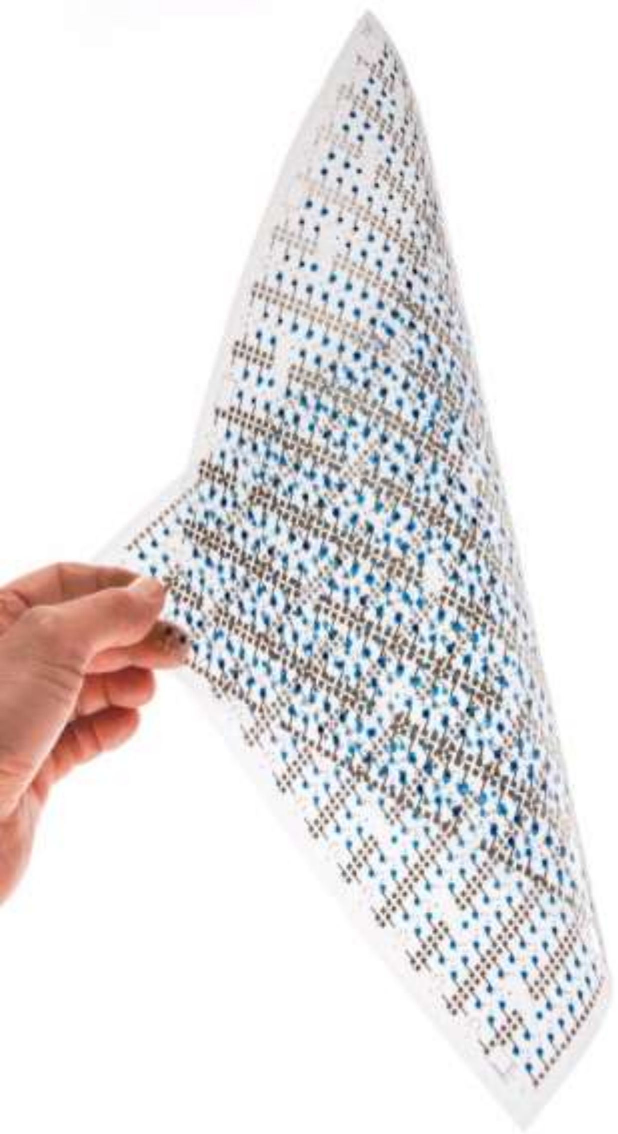
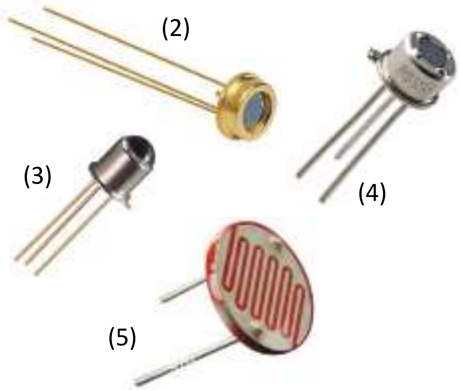


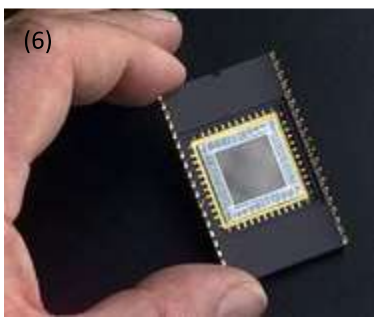
Printed organic photodetectors for large area detection on conformable substrates

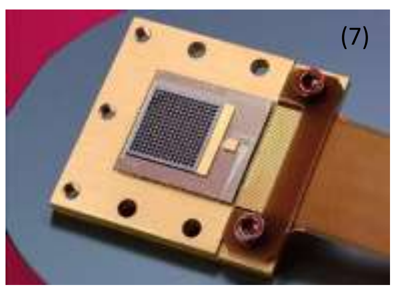
Jean-Marie VERILHAC
verilhacjm@cea.fr
CEA Liten LCOI (Grenoble, France)
(Printed Optoelectronic Components Laboratory)

Photodetecting devices

« Conventional » inorganic photodetectors







(1) Photomultiplier tubes
(2) Si photodiode (p-n; p-i-n)
(3) Phototransistor
(4) Pyroelectric photodetector
(5) Photoresistor
(6) Charge-Coupled Device (CCD)
(7) Bolometer

Organic photodetectors

- ❑ Phototransistors
  K.S. Karayan et al, Appl. Phys. Lett. 79, 1891 (2001)
- ❑ Photoresistors
  D. Natali et al, Proceedings of ESSDERC 2002, Firenze, 2002, 523-526
- ❑ CCD
  C.P. Watson et al, Appl. Phys. Lett. 99, 223304 (2011)
- ❑ Photodiodes
  G. Yu et al, Science 270, 1789 (1995)

Organic vs inorganic: complementary technologies

Inorganic

- ❑ High performances,
- ❑ Robust and reliable devices,
- ❑ Well established technologies and industrial context,

but…

- ❑ Needs for cost effective tools,
- ❑ Long development cycles,
- ❑ Low versatility (difficulties for exotic integration).

Organic

- ❑ Ease for large surface integration,
- ❑ Use of flexible plastic substrates,
- ❑ Compatibility with high throughput printing tools,
- ❑ Short development cycles,
- ❑ Well adapted for non standard designs,
- ❑ Ease of hybridization on existing technologies,

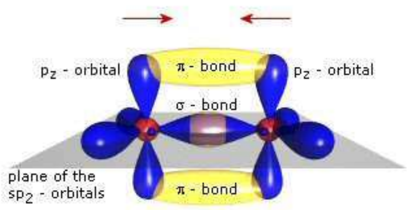
but…

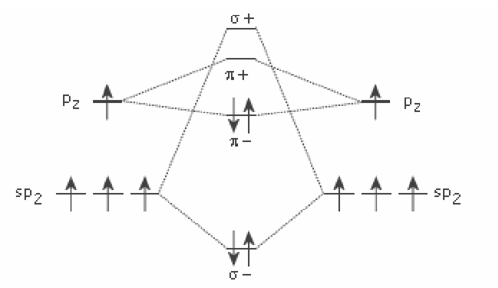
- ❑ Lower performances (still under improvement),
- ❑ Industrial field under construction.

π-conjugated organic materials

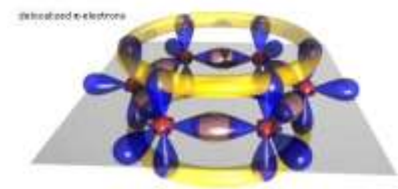
Chem. Commun., p578 (1977)

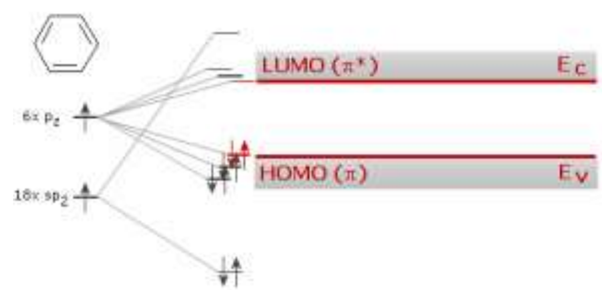
Ethylene



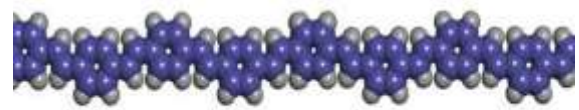


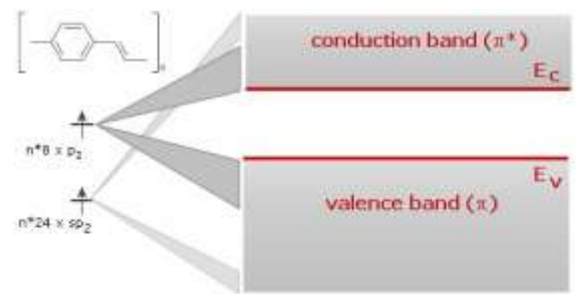
Benzene





Polyparaphenylene vinylene





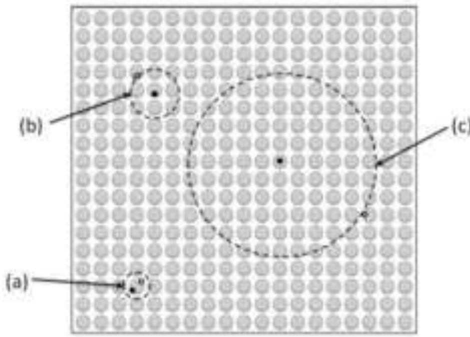
Unique properties:

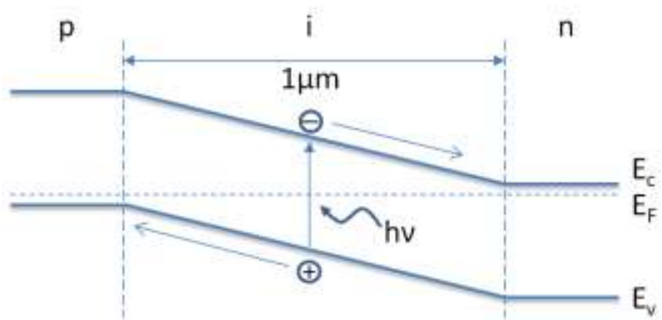
- ❑ Electrical properties of semiconductors and conductors (if doped),
- ❑ High absorption coefficients of organic materials,
- ❑ Mechanical properties of polymers,
- ❑ Ease of process of polymers.

Light harvesting: the role of excitons

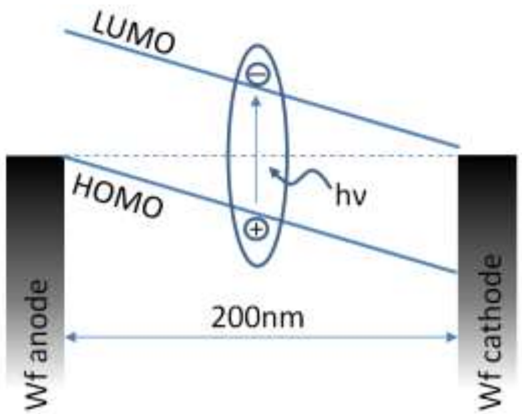
Excitons = bound hole/electron pairs

	Permittivity	Exciton type	Exciton binding energy (eV)
a-Si	12	Wannier-Mott (c)	<0,05eV
Organic materials	3-4	Frenkel (a) or Charge-Transfer (b)	0,1-1eV





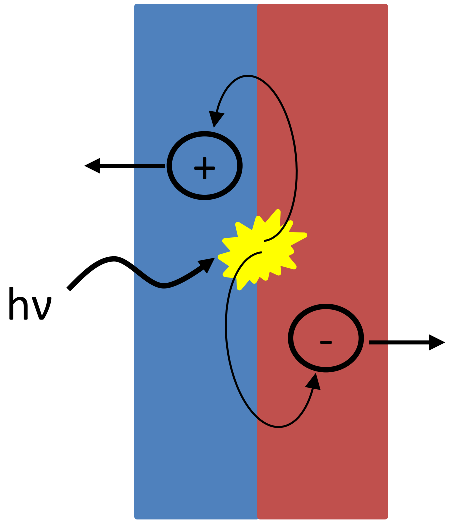
Strong exciton delocalization
EQE>80%



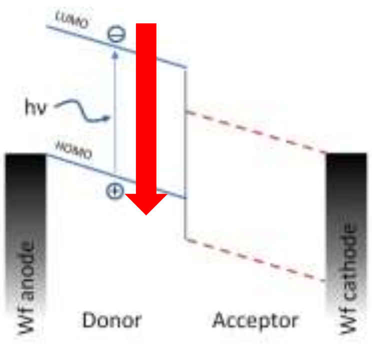
Strong exciton localization
EQE<1%

« Organic devices can not copy inorganic photodiodes structures »

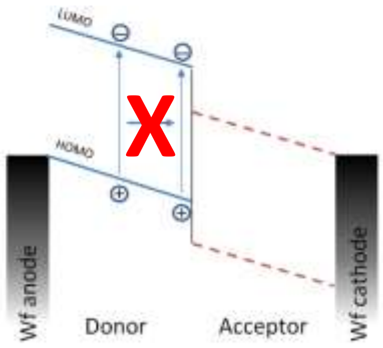
Combination of Donor and Acceptor material



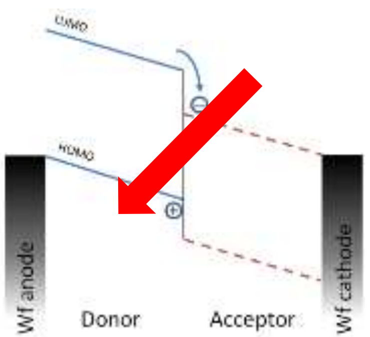
*C.W. Tang, Appl. Phys. Lett. 1985, **48**, 183*



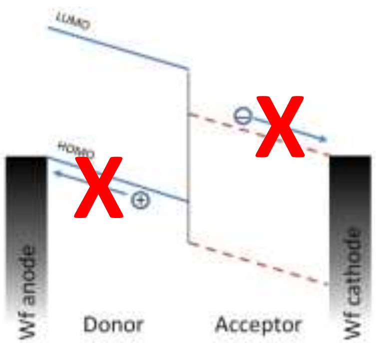
1. Light Absorption - η_{abs}



2. Exciton Diffusion- η_{ED}



3. Exciton Dissociation - η_{CT}

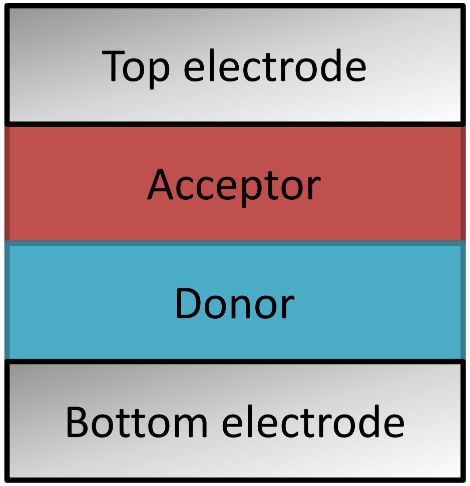


4. Charge Collection- η_{CC}

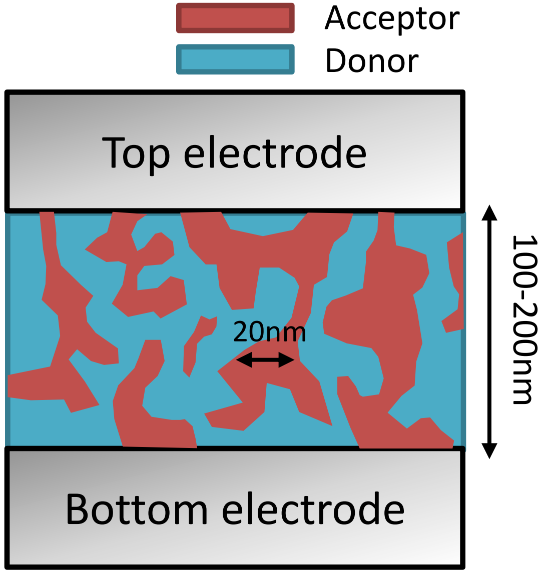
$$\eta_{EQE} = \eta_{abs}\,\eta_{ED}\,\eta_{CT}\,\eta_{CC}$$

Planar heterojunction vs bulk heterojunction

Typical exciton diffusion length in conjugated polymers: L_d~10nm
(Optimum domains length ~$2L_d$)



Bilayer heterojunction
Poorly efficient devices
EQE~1%

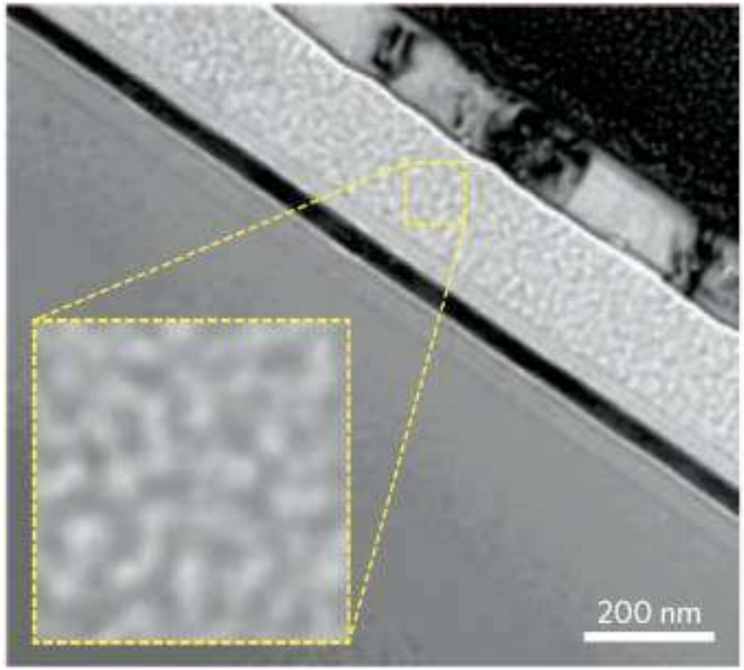


Bulk heterojunction
Highly efficient devices
EQE~50-100%

*R.H. Friend et al., Nature 1995, **376**, 498*
*A.J. Heeger et al., Science 1995, **270**, 1789*

Visualisation of the bulk heterojunction

Transmission Electron Microscopy (TEM)

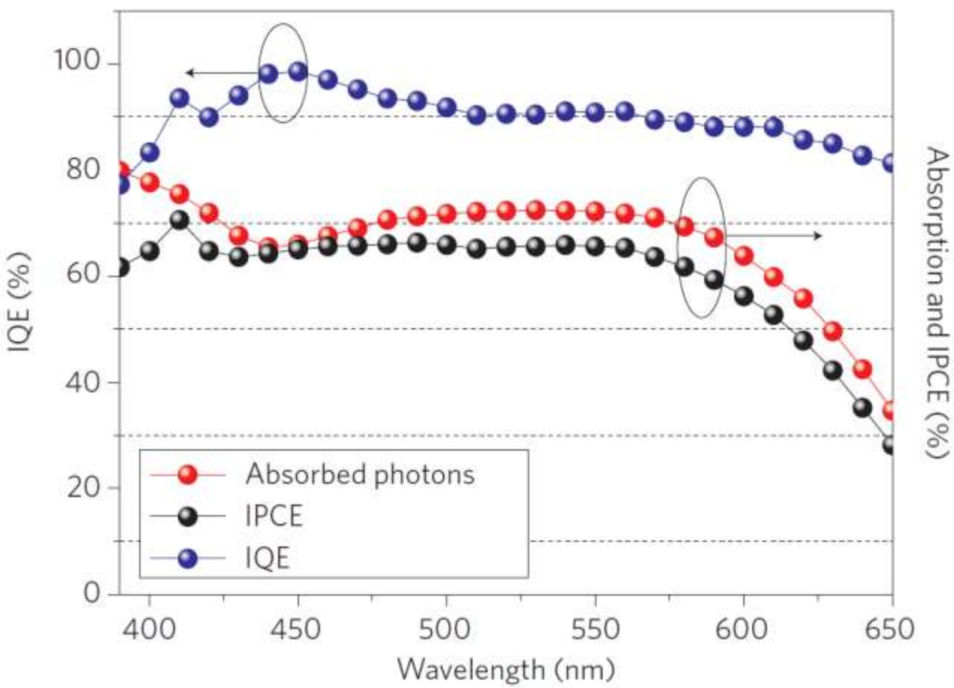


*A.J. Heeger et al., Nano Lett. 2009, **9**, 230*

Quantum Efficiency (1/2)

$$IQE = \frac{J_{bias}/q}{P_{abs}\lambda/hc}$$

P_{abs} absorbed light



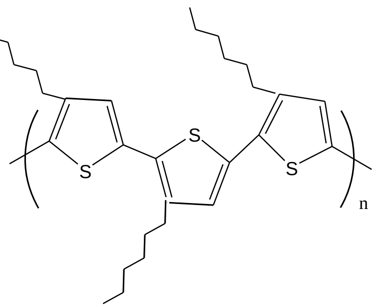
$$EQE\ or\ IPCE = \frac{J_{bias}/q}{P_0\lambda/hc}$$

P_0 incident light

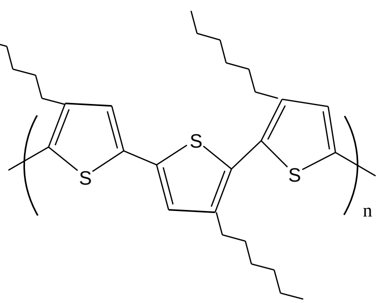
A.J. Heeger et al, Nat. Photonics 3 (2009), 297

Quantum Efficiency (2/2)

"Major impact of materials and blend morphology"

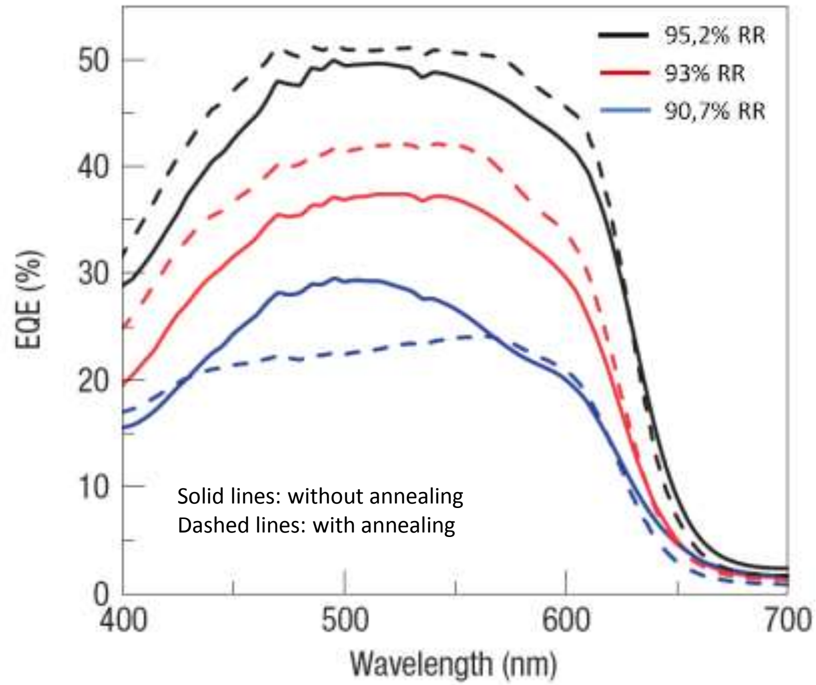


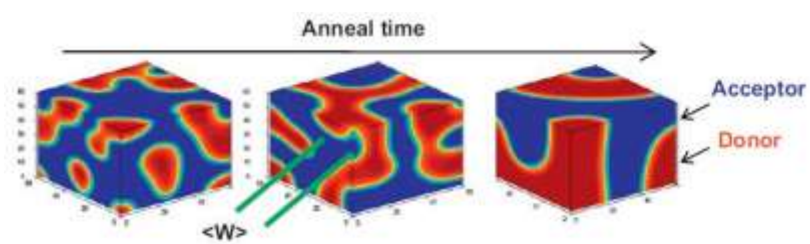
Regioregular P3HT



Amorphous P3HT

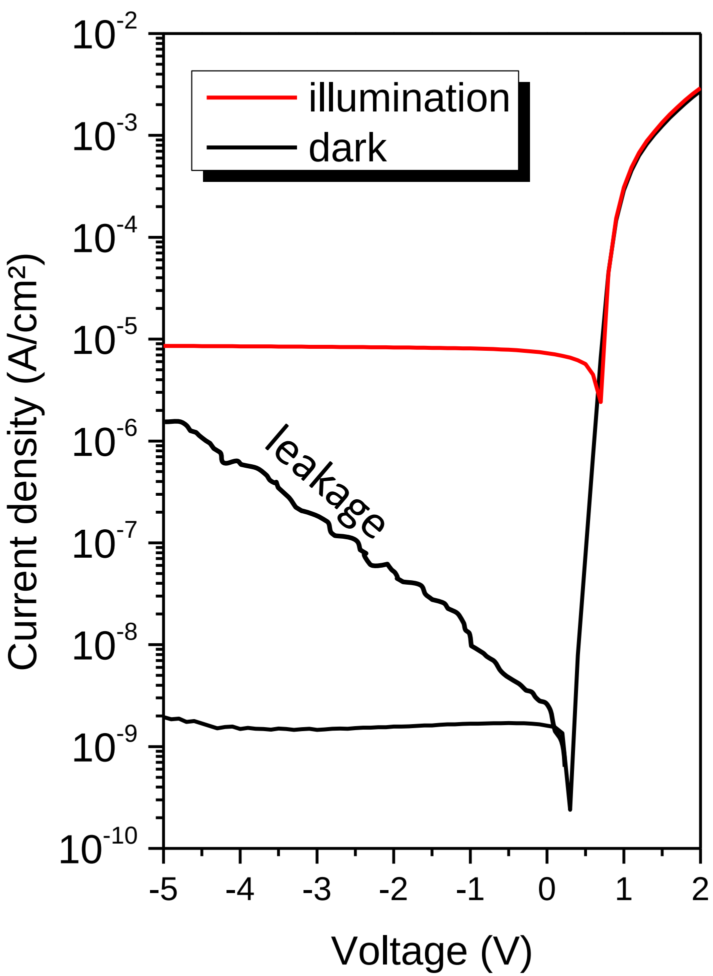
*Y. Kim et al., Nat. Mater., 2006, **5**, 197*



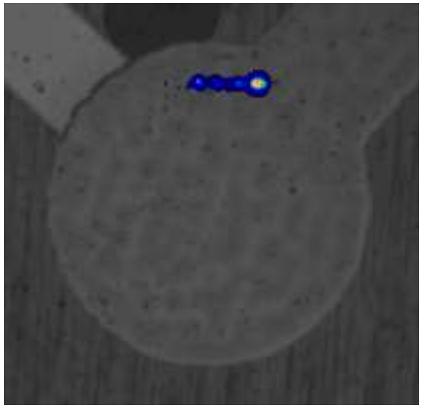


B. Ray et al., Sol. Energ. Mat. Sol. C., 2012, 99, 204

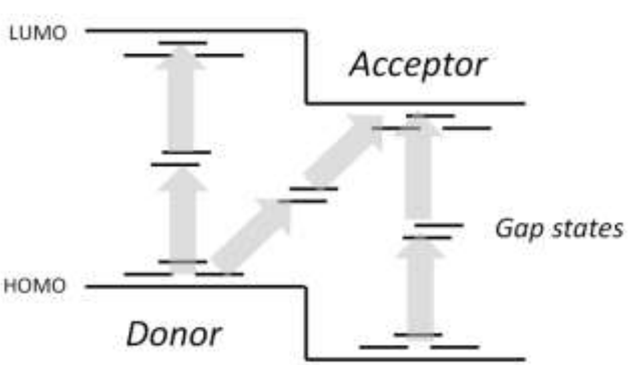
Reverse dark current



- ❑ Topological defects (pinholes, spikes, dusts),
- ❑ Injection from electrodes: barrier height,
- ❑ Gap states (thermal generation, tunneling current),
- ❑ Unintentional doping,
- ❑ Morphology (material percolation),
- ❑ Ground state charge transfer.

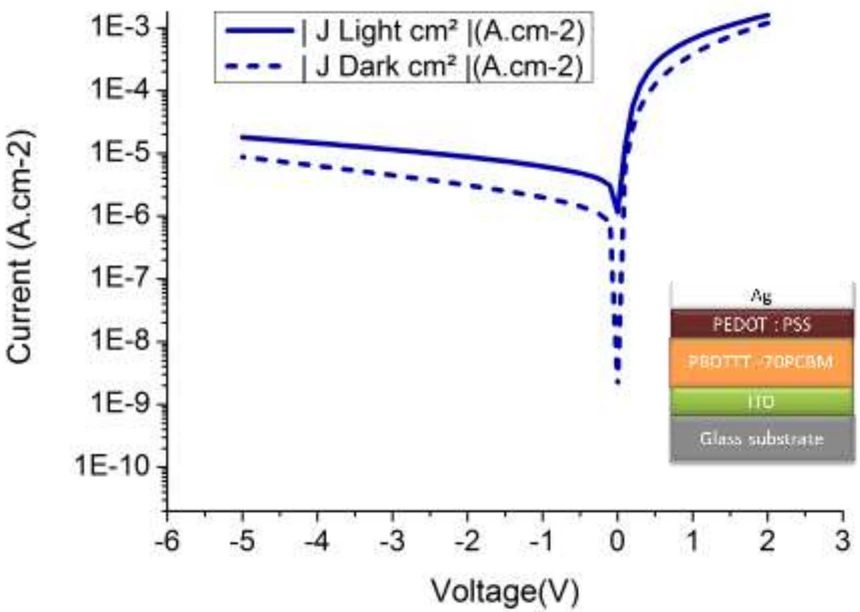


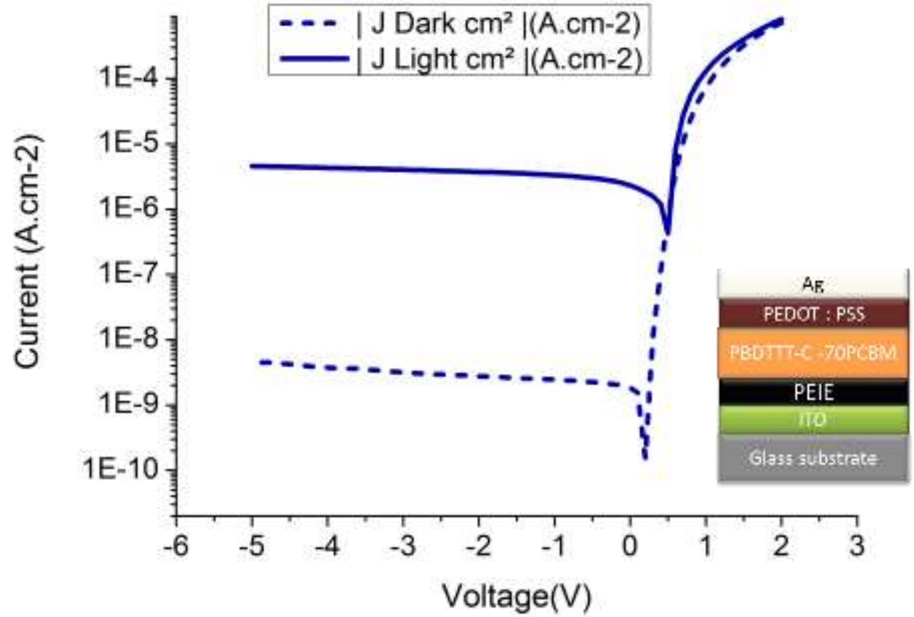
Defects (scratch) revealed by Dark Lock In Thermography

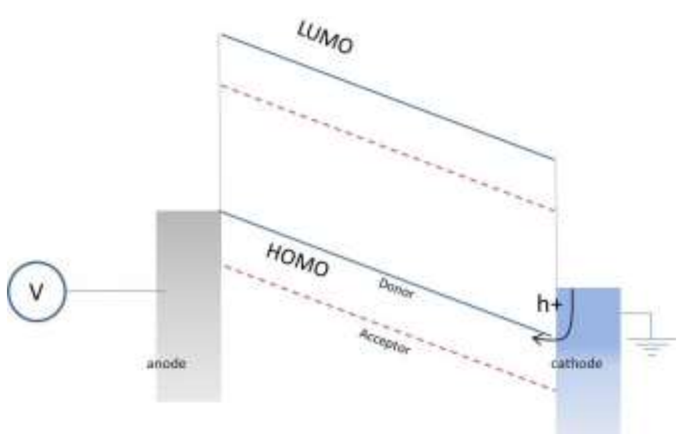


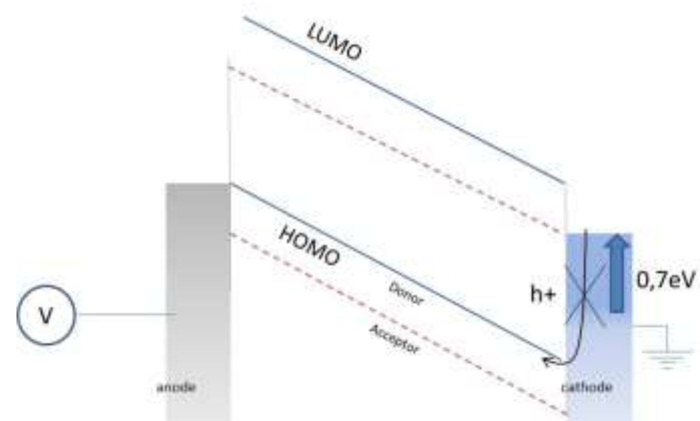
Charge generation through gap states

Reverse dark current: impact of contact barrier height





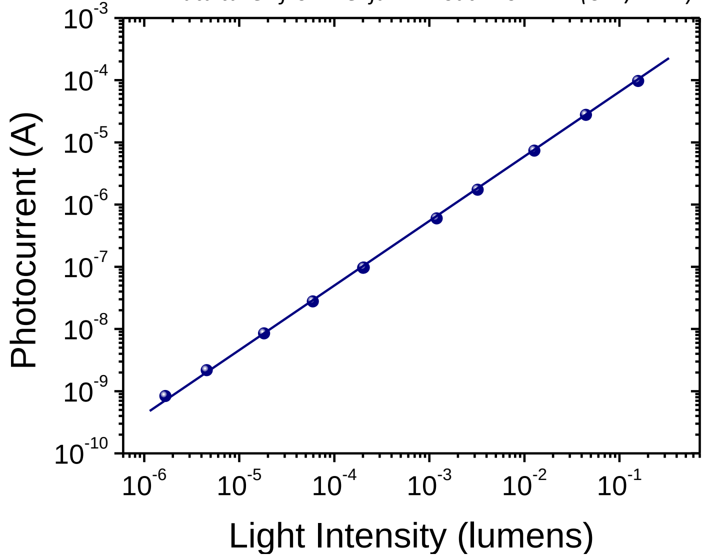




J.M. Verilhac et al., Adv. Mater. 2013, 25, 6534

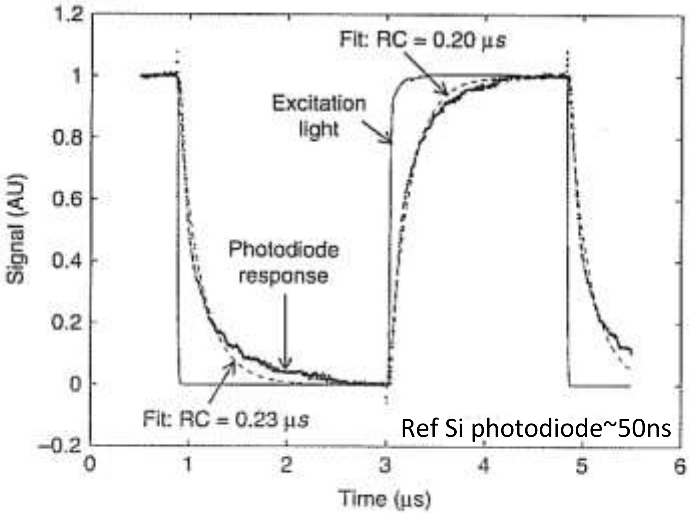
Others figures of merit

Photocurrent linearity



- Low light intensity→ Photocurrent mainly limited by traps,
- High light intensity→ photocurrent limited by Langevin recombination.

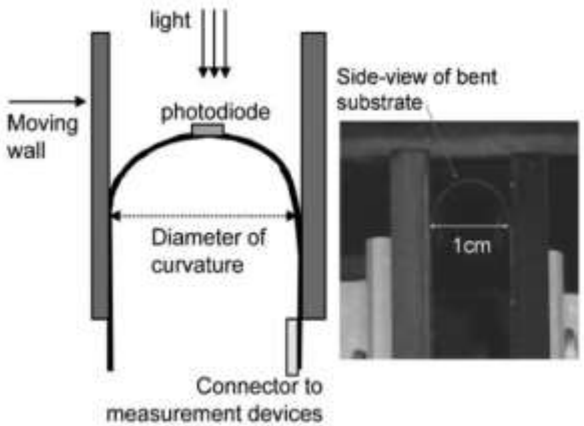
Response time



J. Huang et al., Chapter6, Organic Electronics in Sensors and biotechnology

- Organic slower than Si
- Rooms for optimizations

Mechanical strain: organic vs inorganic photodiodes on plastic substrate



Organic photodiode   a-Si:H photodiode

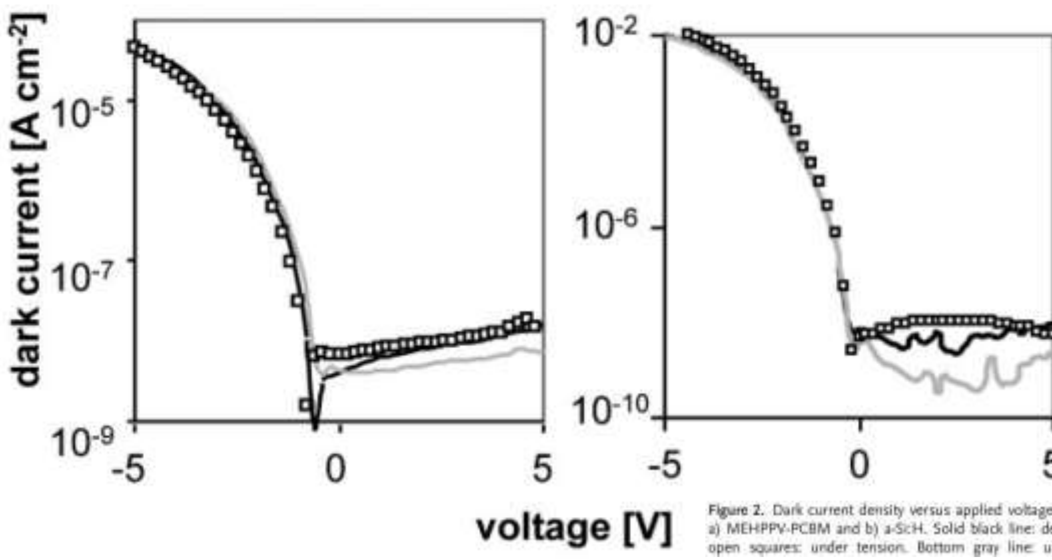


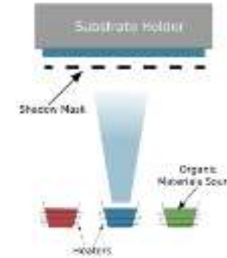
Figure 2. Dark current density versus applied voltage under bending for a) MEHPPV-PCBM and b) a-Si:H. Solid black line: device lying flat. Top open squares: under tension. Bottom gray line: under compression.

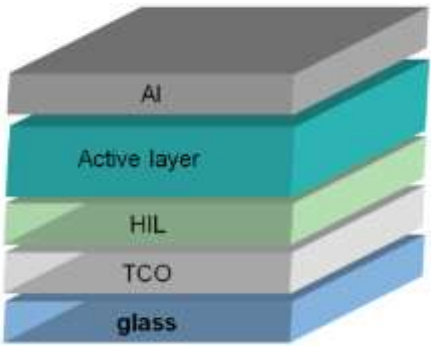
Min radius of curvature under	Organic PD	a-Si:H PD
Tension	7,5mm	20mm
Compression	<2,5mm	12,5mm

"Failure limits of organic photodiodes exceed those of a-Si:H under tension and compression strains"

*T.N Ng et al., Adv. Mater. 2009, **21**, 1855*

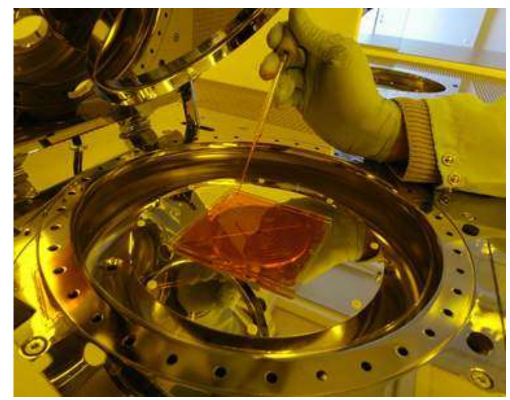
Organic layer for photoconversion





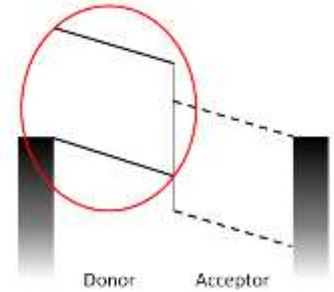
Vacuum evaporation
(small molecules)

Solution-process
(small molecules/polymers)



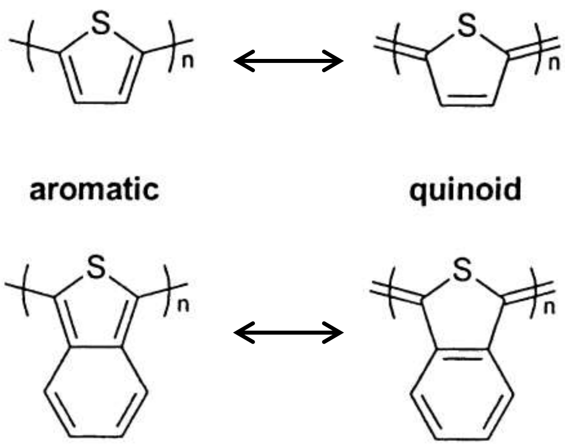
« Infinity of solutions offered by organic chemical synthesis and chemical designs »

Donors polymers: Band Gap tuning



<u>1st strategy</u>:

Planarizing the polymer backbone

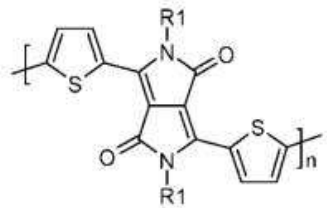


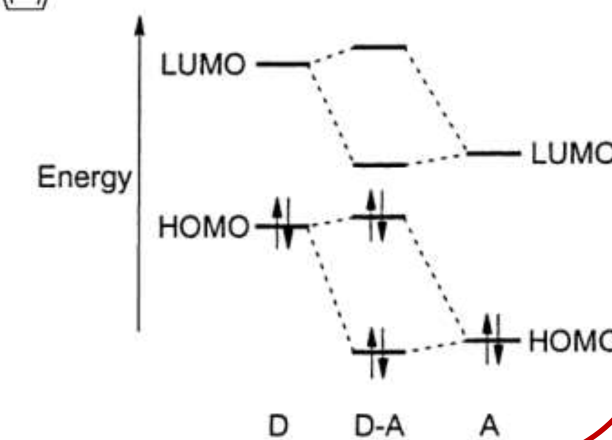
Gap~2eV

Gap~1eV

<u>2nd strategy</u>:

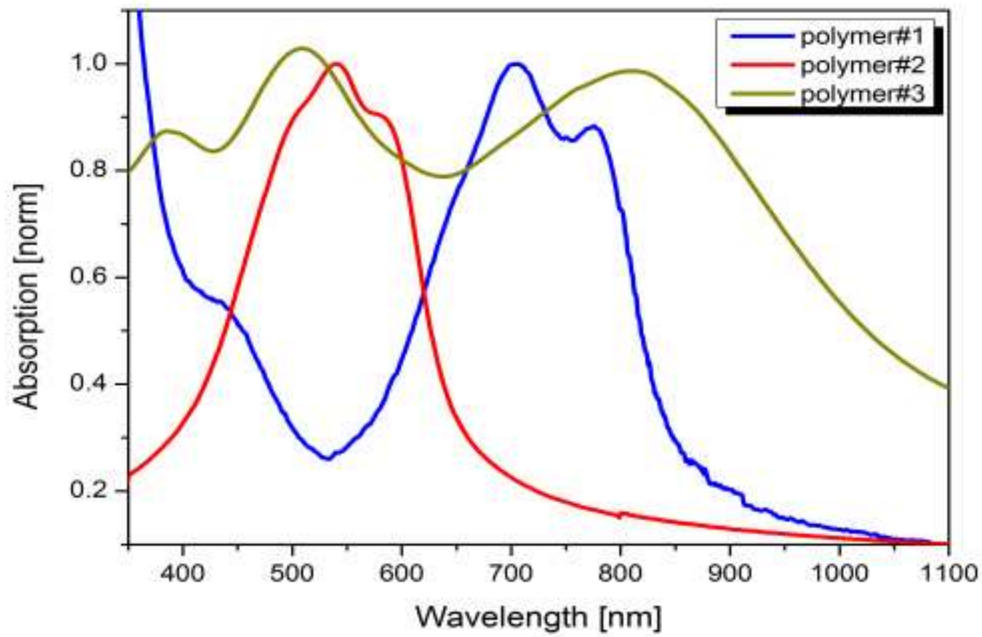
Push-Pull: combination of electron-deficient and electron-rich units

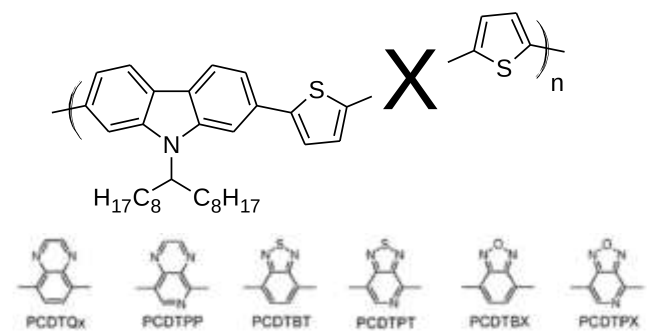




E.W. Meijer et al. Mater. Sci. Eng. R., 2001, ***32****, 1*

Tuning the absorption of polymers



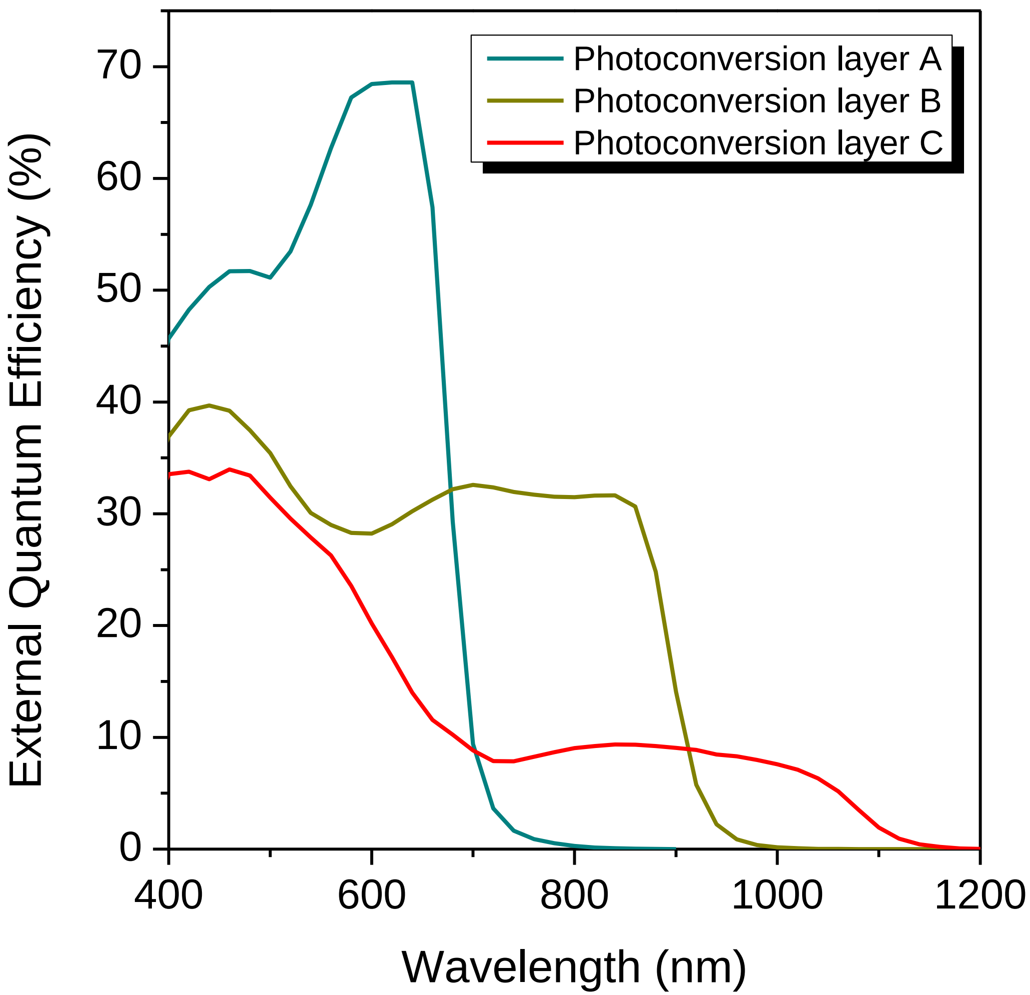


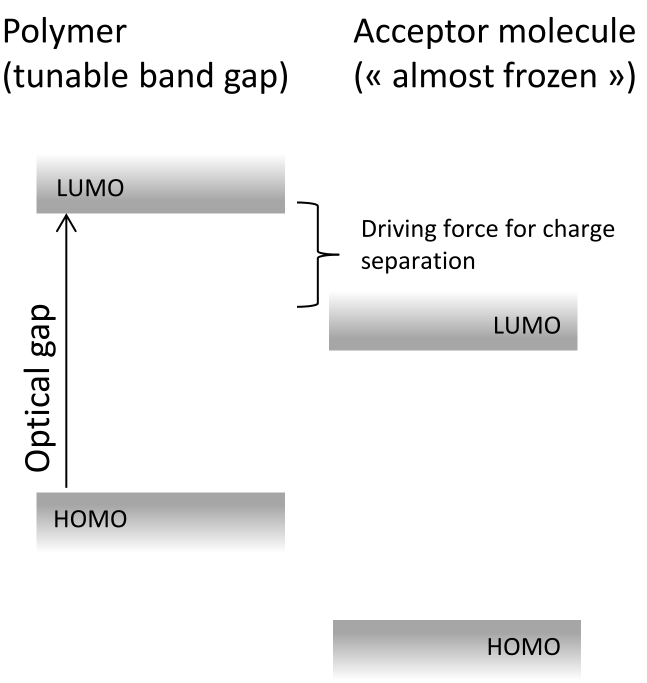
410 nm
(3.0 eV)

1100 nm
(1.1 eV)

*Mario Leclerc et al., Polym. Chem., 2010, **1**, 127*

Photodetection in the near-infrared





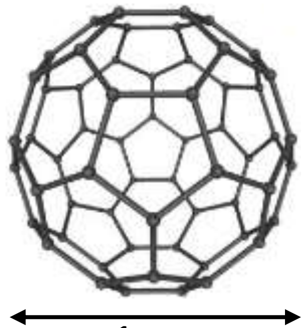
Max light harvesting near 1100nm, due to currently available materials.

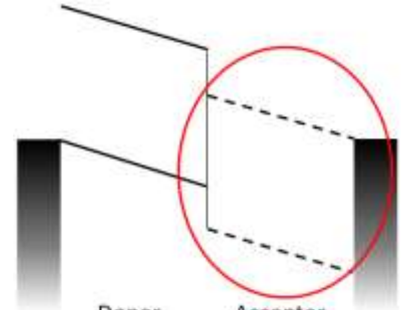
Acceptors: Fulleren derivatives

Robert F. Curl Jr. Sir Harold W. Kroto Richard E. Smalley

The Nobel Prize in Chemistry 1996 was awarded jointly to Robert F. Curl Jr., Sir Harold W. Kroto and Richard E. Smalley *"for their discovery of fullerenes"*.

*H.W. Kroto et al., Nature 1985, **318**, 162*



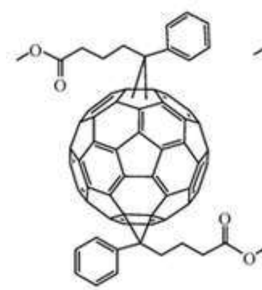


- ❑ Good solubility,
- ❑ Good electron mobility,
- ❑ Low lying LUMO (well matched with conventional polymeric semiconductors),
- ❑ Good miscibility with polymers,
- ❑ Low absorption in the visible.

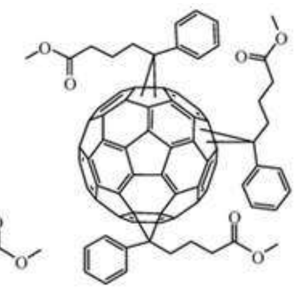
"Current best material choice for organic bulk-heterojunction systems"

Examples of some fulleren derivatives

[60]PCBM

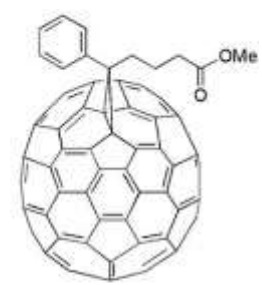


Bis-[60]PCBM



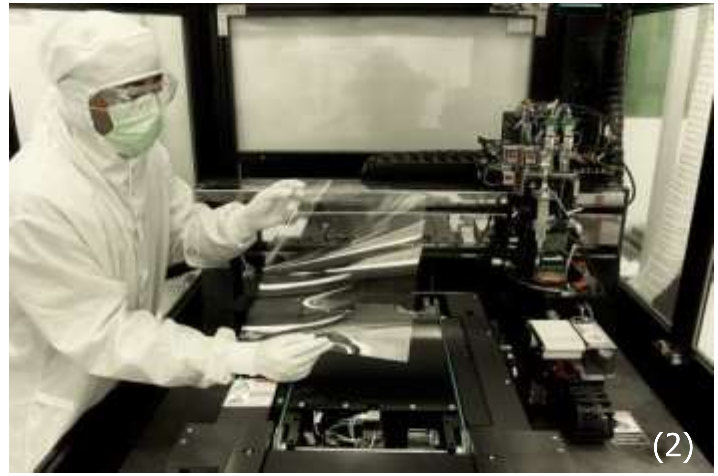
Tris-[60]PCBM

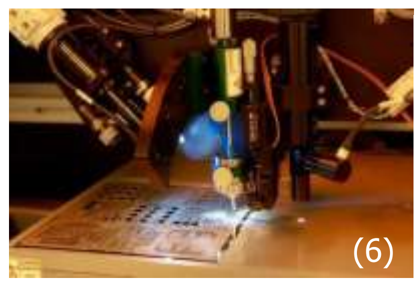
Bis-indene



[70]PCBM

Printing: « the » disruptive technology?





(1) Screen-printing
(2) Inkjet
(3) Spray-coating
(4) Slot-die
(5) Inkjet (lab tool)
(6) Local spray coating
(7) Gravure printing

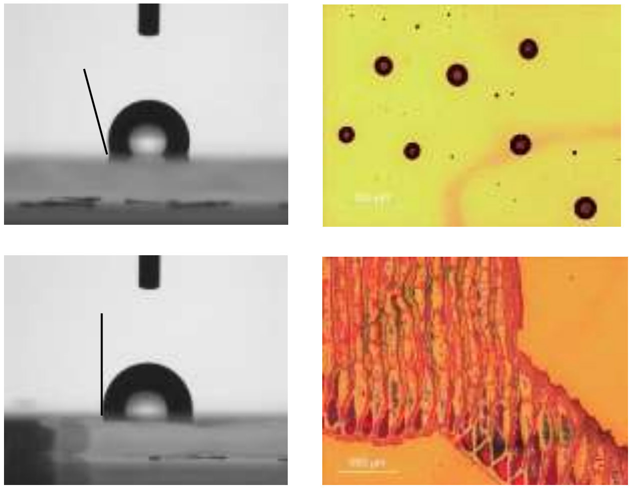
Images taken from CEA PictiC

Graphic art printing techniques well adapted for organic macroelectronic:

- ▶ Thicknesses of printed layer<100nm,
- ▶ Good layer homogeneity,
- ▶ Micrometric resolution and alignment,
- ▶ Sheet to sheet or roll to roll.

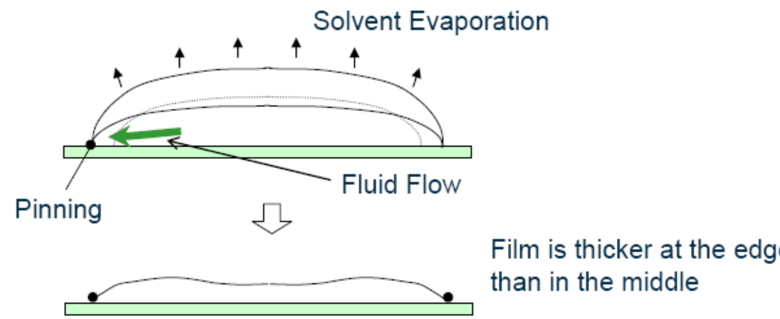
Some challenges about printing

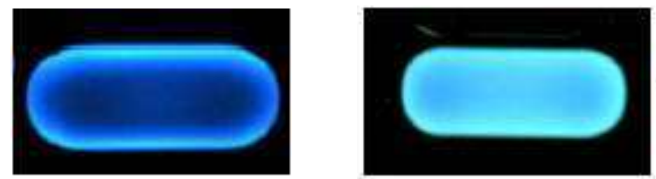
Wetting



$\gamma_{substrate} > \gamma_{ink}$

Edge effect (coffee stain)





with

« Almost » without

Inks formulation

Resolutions (line/space)

Decreasing spacing

Printed OPD devices on large area (Gen1)

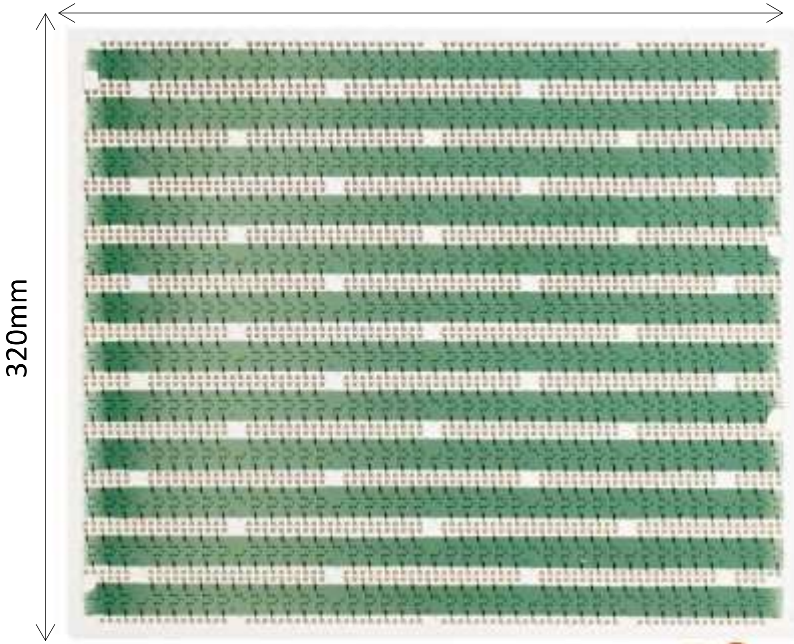


Image from CEA/ISORG

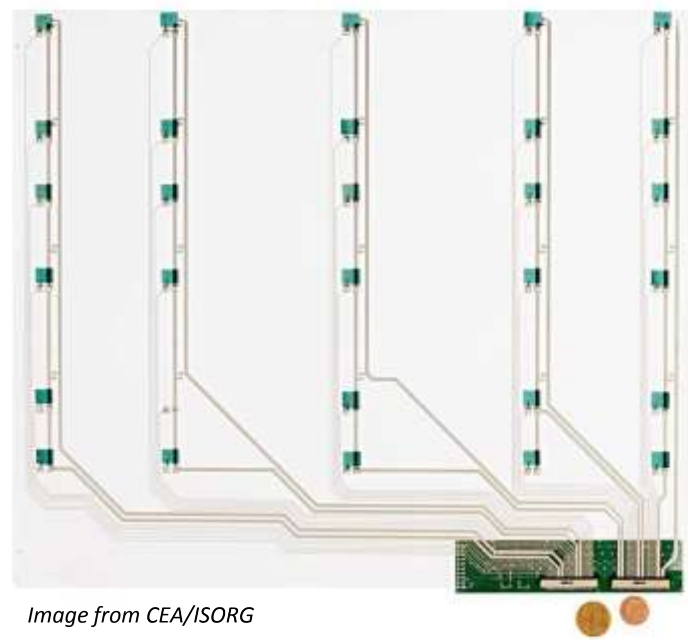


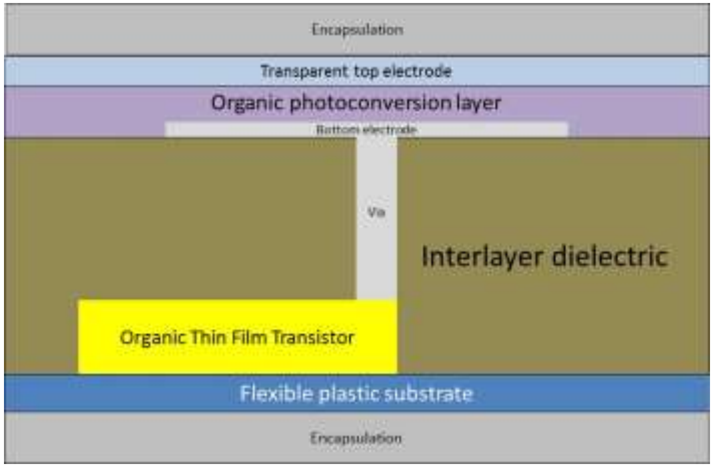
Image from CEA/ISORG

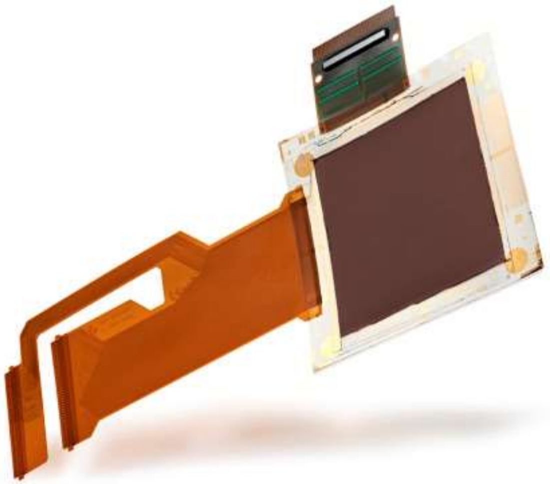
Fully printed OPD devices (>1000/sheet)

Custom printed OPD designs

Organic photodetectors on Active matrix

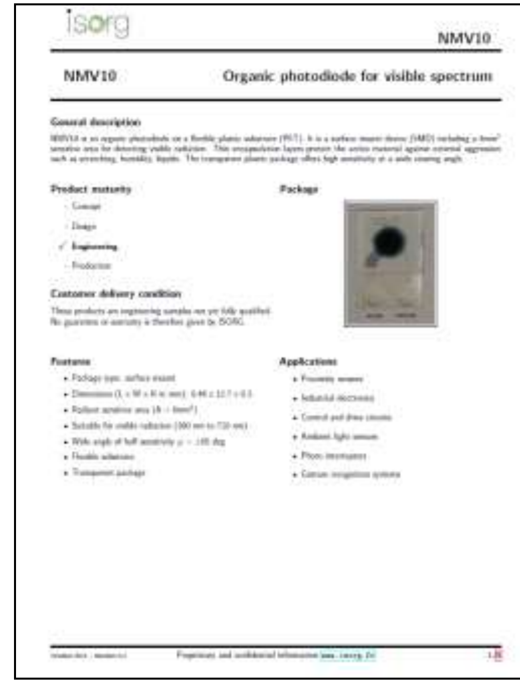
- Fully solution-processed and flexible visible imager (OTFT + OPD),
- Collaboration between CEA/ISORG/plastic Logic (Flexi Award 2014),
- Demo substrate size: 50x50mm,
- 96x96 pixels,
- Pixel size = 175µm,
- Pixels spacing = 200µm (<30µm for next demo),
- Process compatible with large area.





ISORG (Image Sensor ORGanic)

- 21 employees,
- Technological developments supported by CEA,
- Manufacturing plants by mid 2016,
- Customized discrete OPD and imager designs on large area, rigid and flexible substrates,
- Fields of applications: medical, industrial, scientific, security, consumer…
- Contact: laurent.jamet@isorg.fr
- Website: www.isorg.fr


NMV10

NMV10 Organic photodiode for visible spectrum

General description

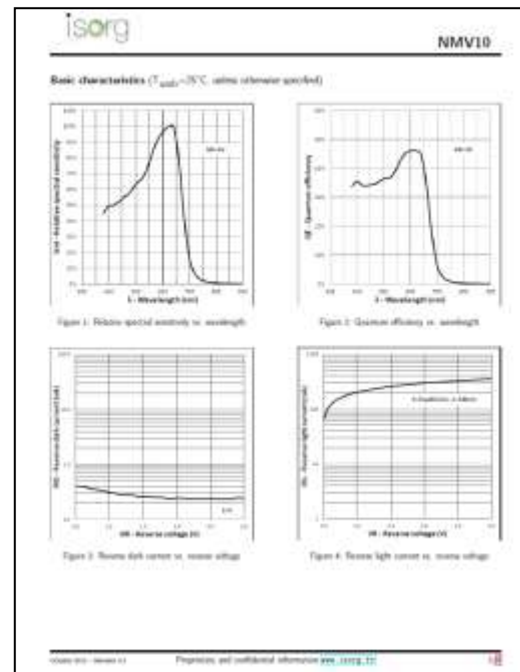
Product maturity

Package

Customer delivery condition

Features

Applications


NMV10

Basic characteristics

OPD data sheet

Conclusions

- Organic photodetectors have gained in maturity in the last ten years, and are now on the way to be commercialized,
- Organic photodetectors take unique advantages of organic materials (opto-electronic properties and processability),
- Photoconversion from UV up to the near infrared,
- Organic photodetectors are compatible with large area and flexible substrates, and could be hybridized on many existing inorganic technologies.

Thank you for your attention