Plastic Electronics

Joaquim Puigdollers

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Origins…

Since the discovery that the conductivity of *trans*-polyacetylene increases seven orders of magnitude upon oxidation with iodine …

J.C.S. CHEM. COMM., 1977, 578-580

Synthesis of Electrically Conducting Organic Polymers: Halogen Derivatives of Polyacetylene, $(CH)_x$

By HIDEKI SHIRAKAWA, EDWIN J. LOUIS, ALAN G. MACDIARMID,* CHWAN K. CHIANG, and ALAN J. HEEGER
(Department of Chemistry and Department of Physics, Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia 19104)

Summary When silvery films of the semiconducting polymer, *trans* 'polyacetylene', $(CH)_x$ are exposed to chlorine, bromine, or iodine vapour, uptake of halogen occurs, and the conductivity increases markedly (over seven orders of magnitude in the case of iodine) to give, depending on the extent of halogenation, silvery or silvery-black films, some of which have a remarkably high conductivity at room temperature.


A.J. Heeger


A.G. MacDiarmid


H. Shirakawa

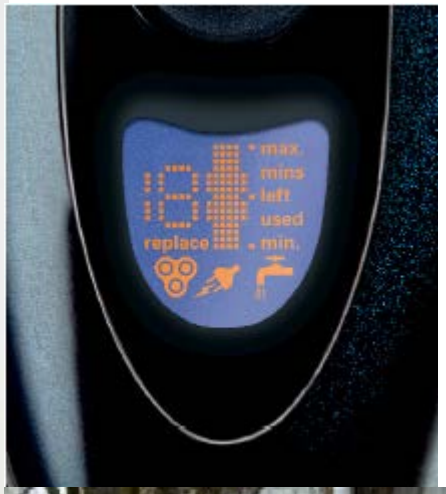
Nobel Prize Chemistry 2000

Technological Interest

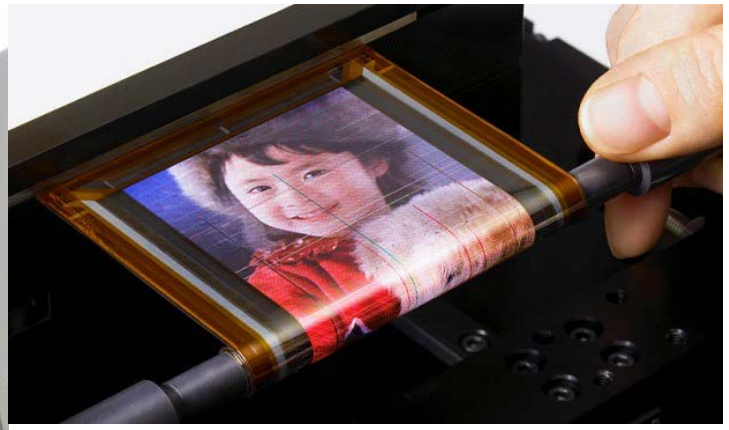
First products..

PHILIPS

MONOCROMATIC



Today…Future

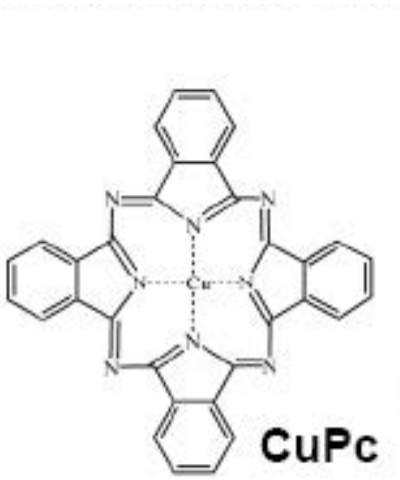


Technological interest

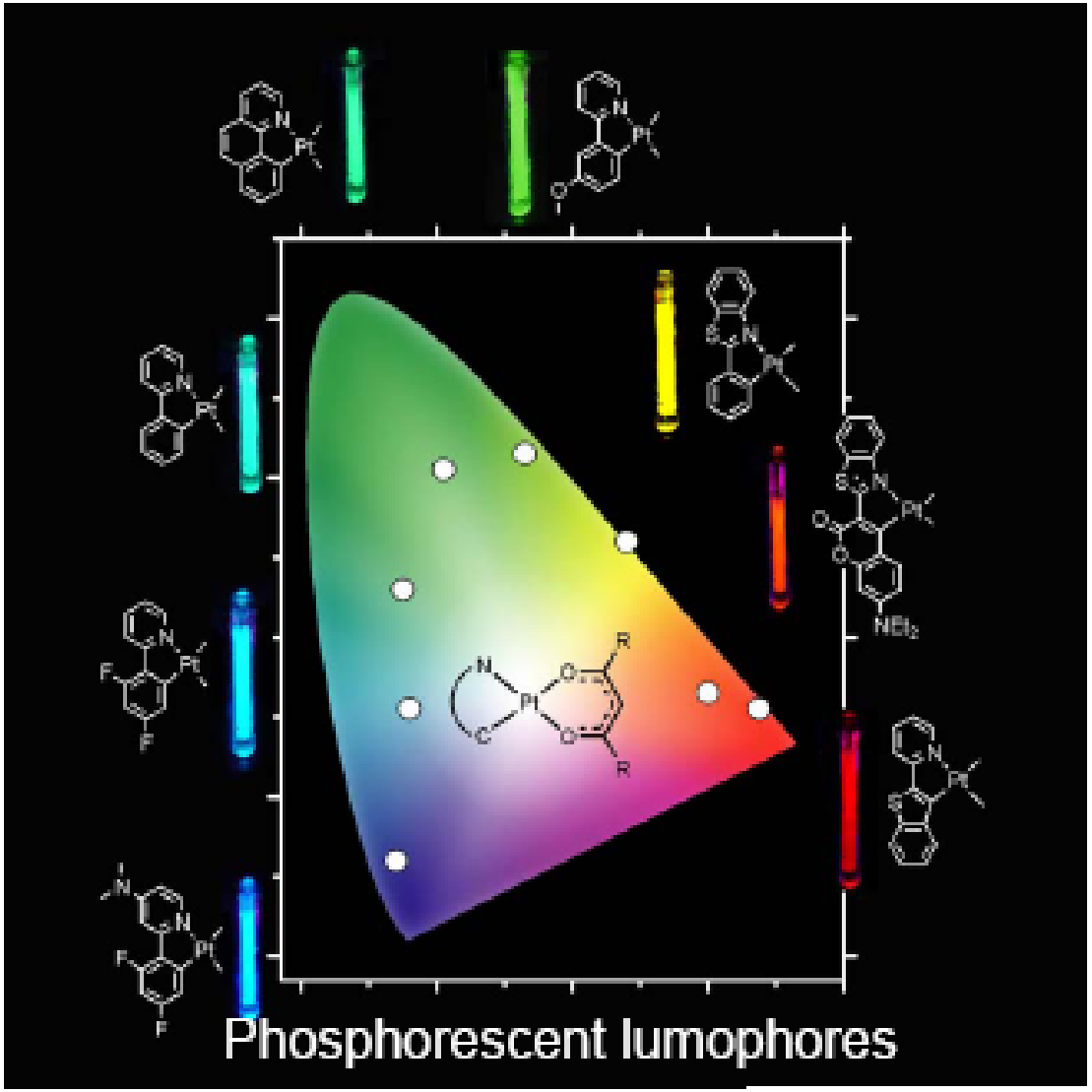
Low processing T (< 200ºC)
Flexible
Huge variety of polymers / organic molecules

Dyes

Pigments: stables, small-molecule, visible optical absorption

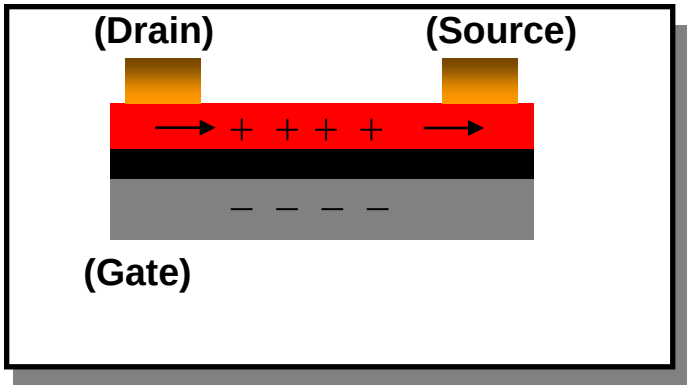


Molecules with adjustable properties



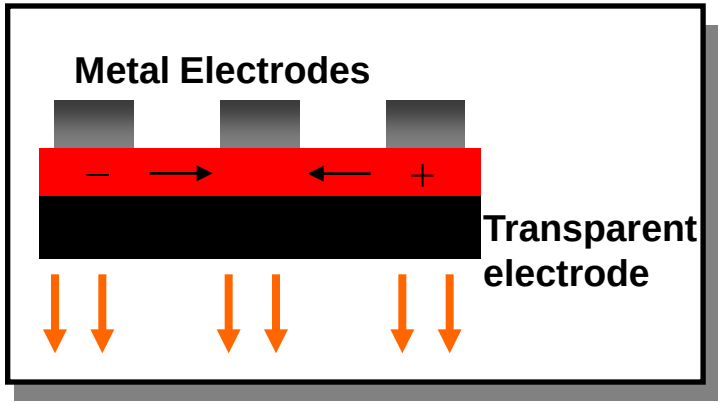
Organic Devices

Thin-film transistor (TFT)

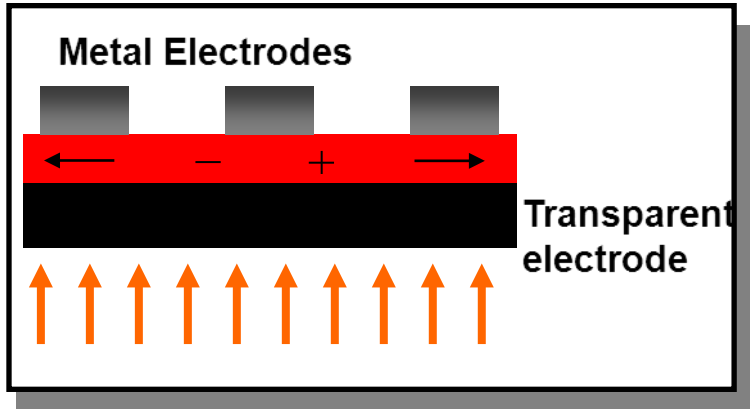


Thin-Film

Light emitter diode (OLED)



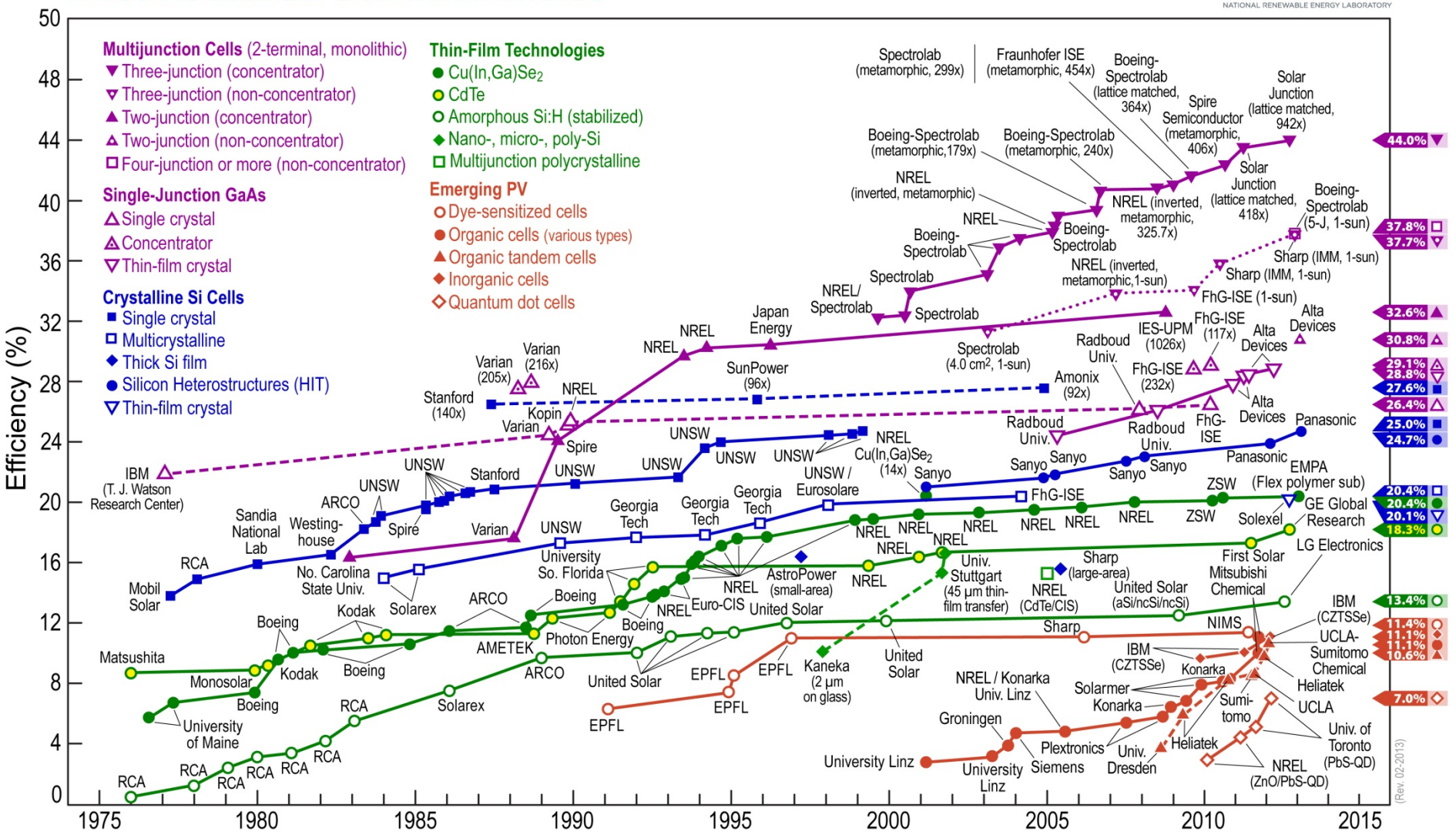
Solar cell

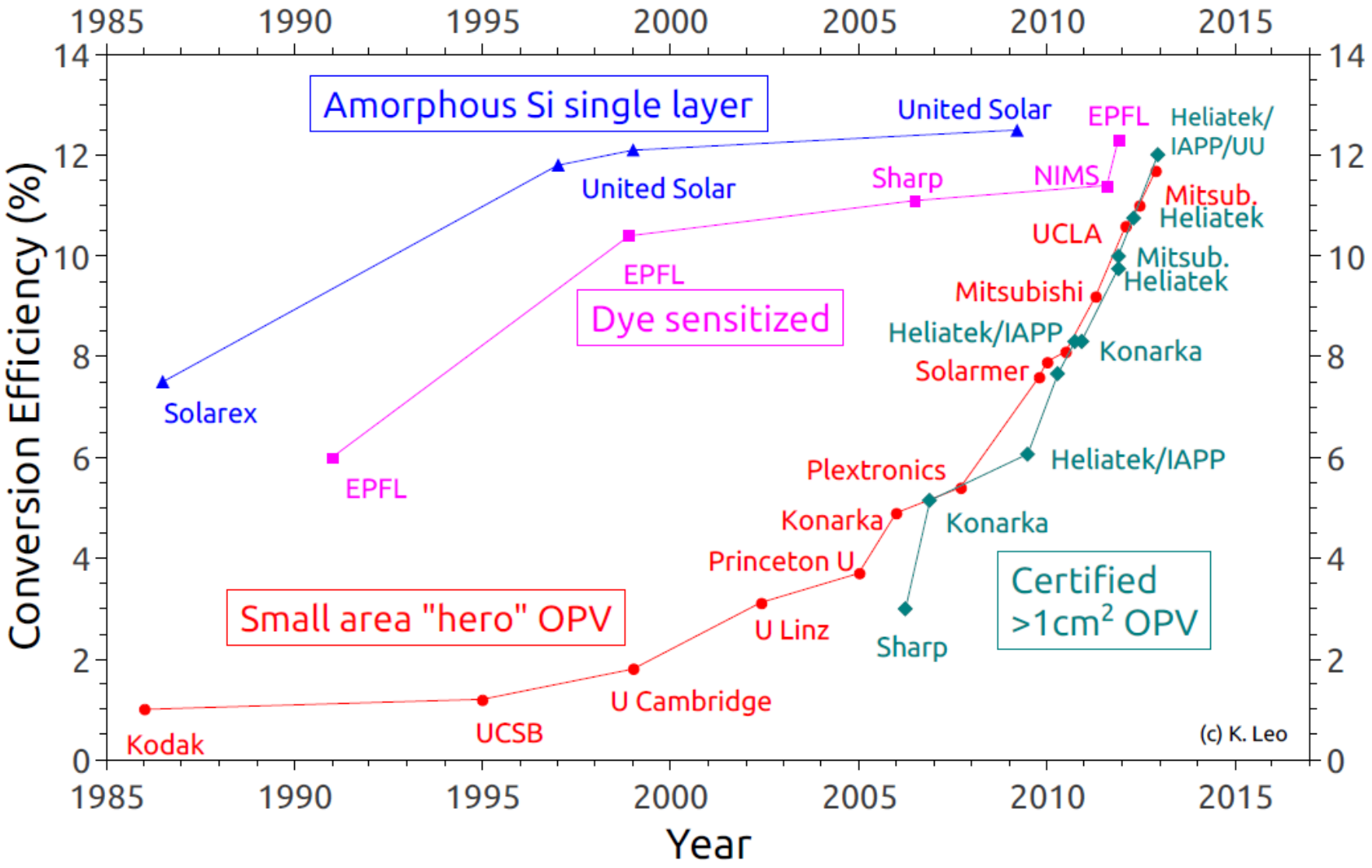


Organic Solar Cells

Best Research-Cell Efficiencies

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

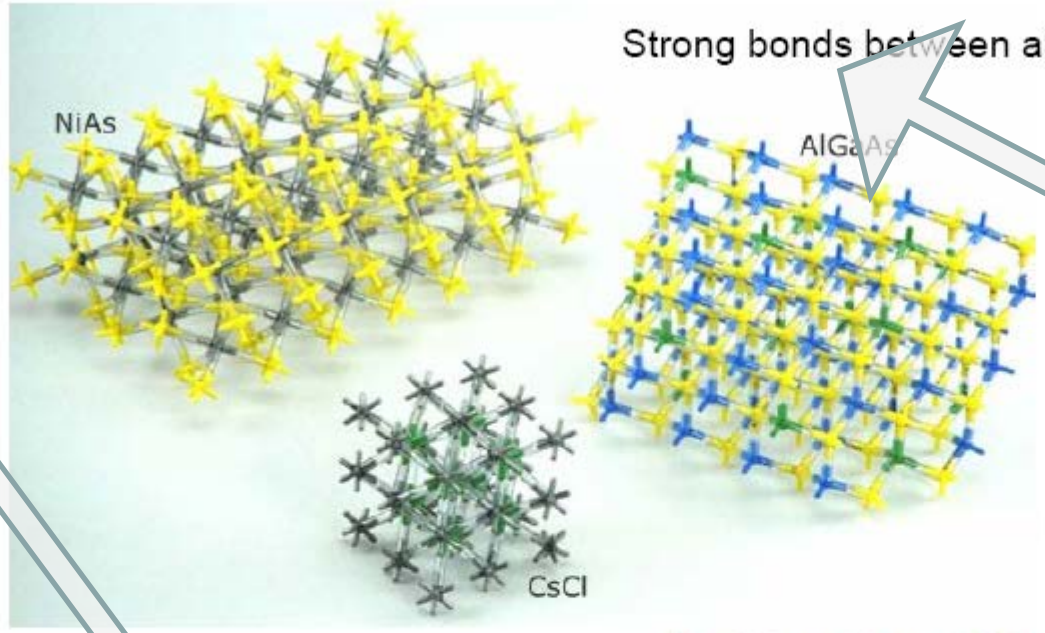



Amorphous Si single layer
United Solar
United Solar
Solarex
Dye sensitized
EPFL
Sharp
NIMS
EPFL
Heliatek/
IAPP/UU
Mitsub.
Heliatek
UCLA
Mitsub.
Heliatek
Mitsubishi
Heliatek/IAPP
Konarka
Solarmer
EPFL
Plextronics
Heliatek/IAPP
Konarka
Konarka
Princeton U
Small area "hero" OPV
U Linz
Sharp
Certified
>1cm² OPV
U Cambridge
UCSB
Kodak
(c) K. Leo
Conversion Efficiency (%)
Year
1985
1990
1995
2000
2005
2010
2015
0
2
4
6
8
10
12
14

Organic material
(or molecular material) ?

Organic material (or molecular material) ?

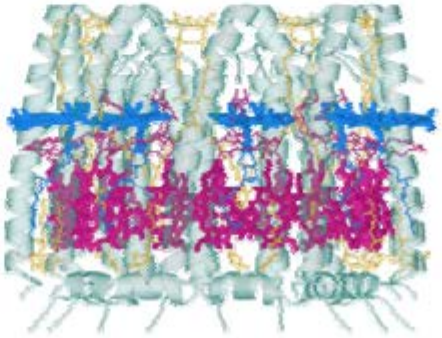
Covalent, Ionic and Metallic Solids

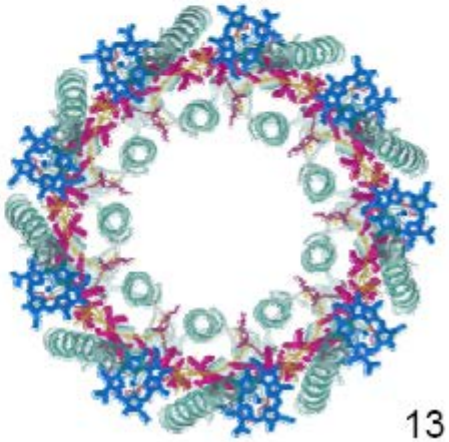


Strong bonds between all atoms

Molecular "Solid"

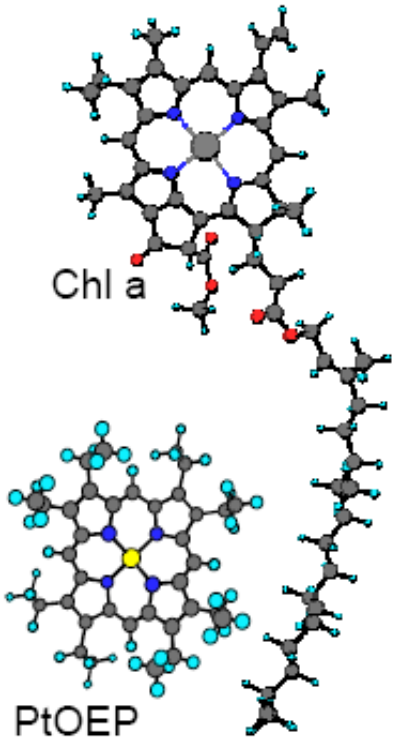
Aggregates of atoms (molecules) that are strongly bonded are held together via weaker intermolecular forces

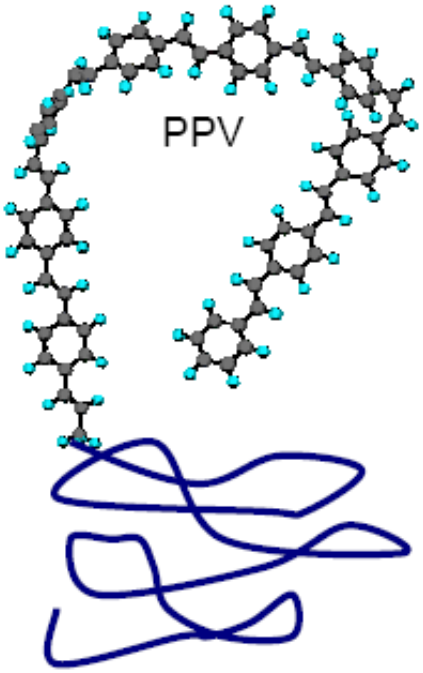


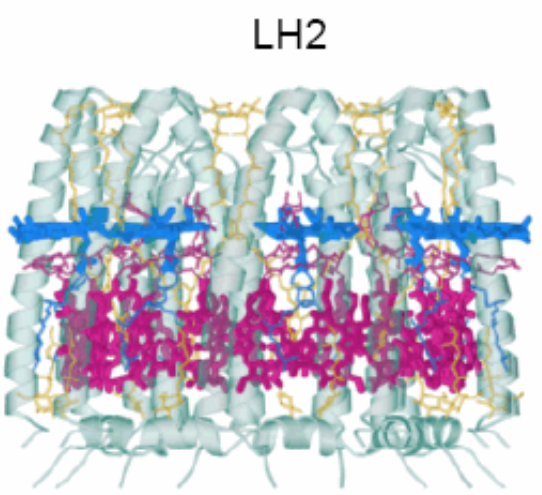


http://peumans-pc.stanford.edu/teaching/ee322-wtr-06

Polymer vs small molecule







Monomers **Polymers** **Biological Molecules**

Complexity

Organic Solar Cells

Two approach

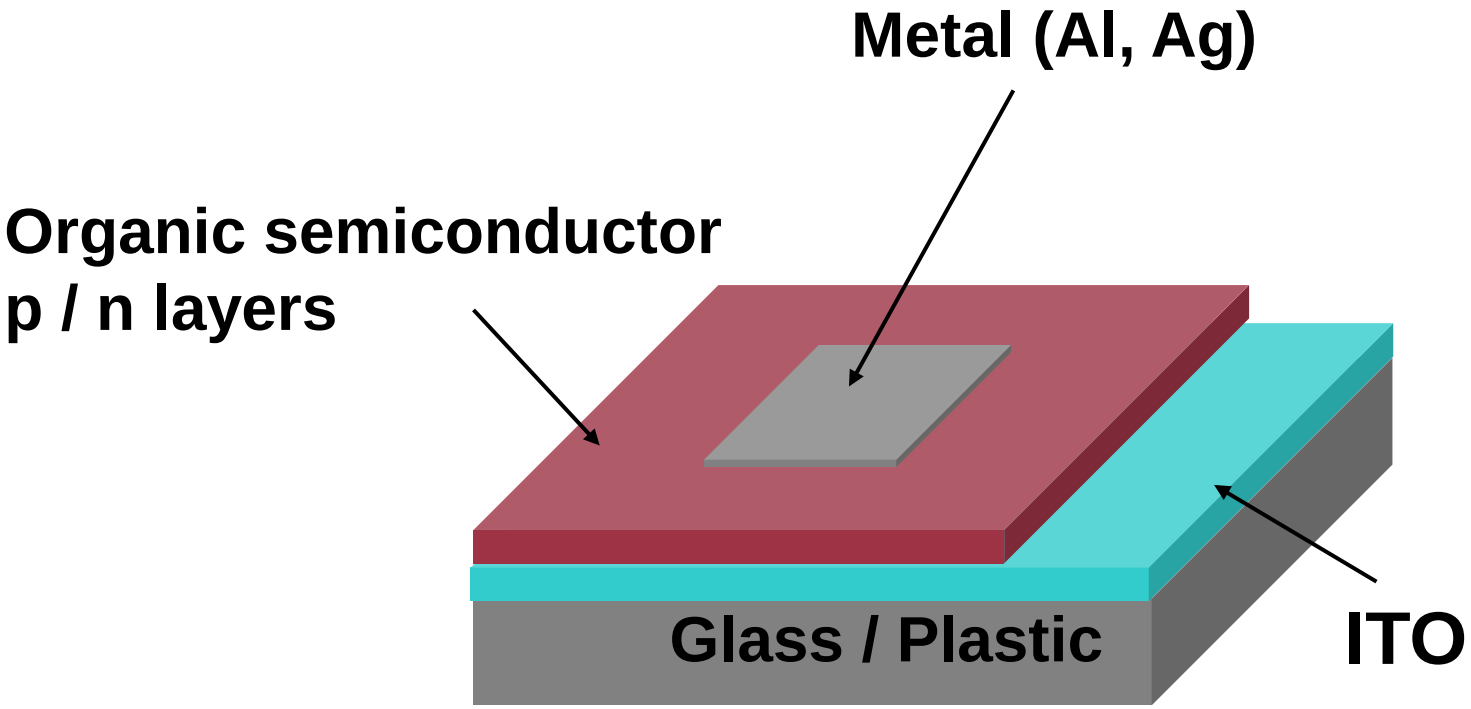
Polymer

Solution
spin coating

Small molecule

Thermal evaporation
(sublimation) in high-vacuum

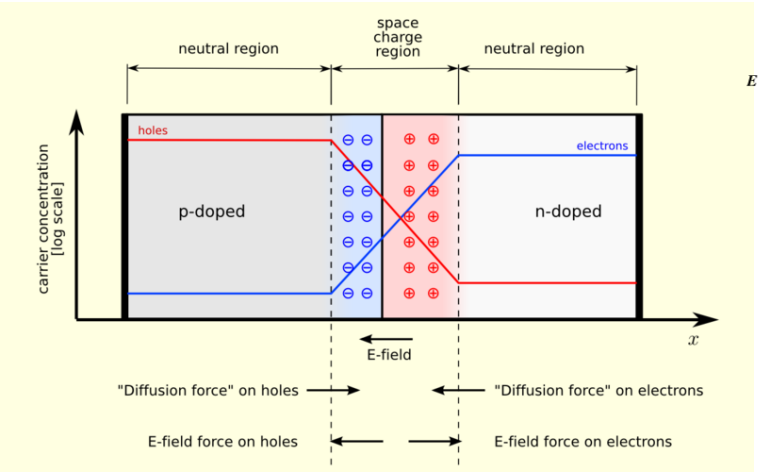
Basic structure

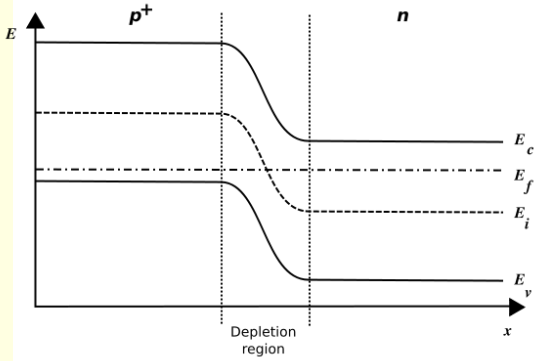


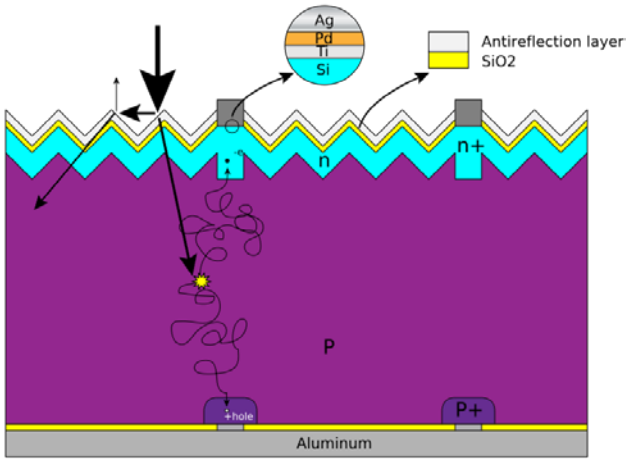
ITO: Indium Tin Oxide / Conductor and transparent

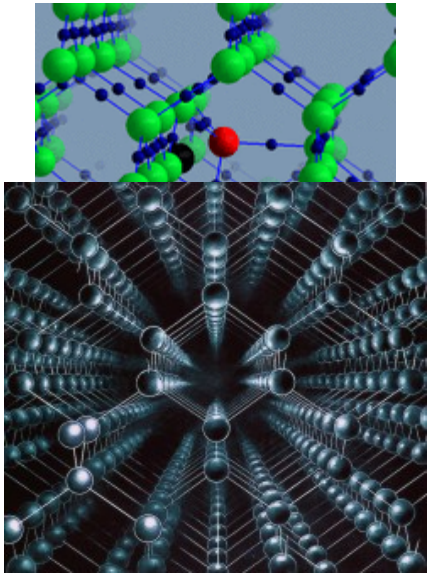
Usually deposited by Sputtering

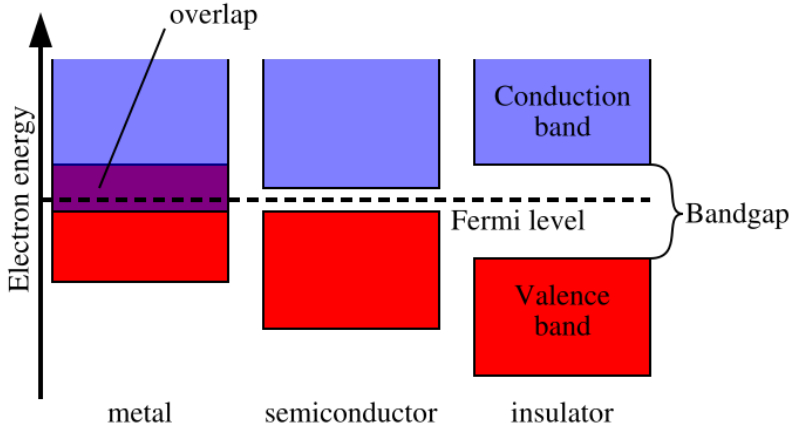
Inorganic Solar cell (Crystalline silicon)

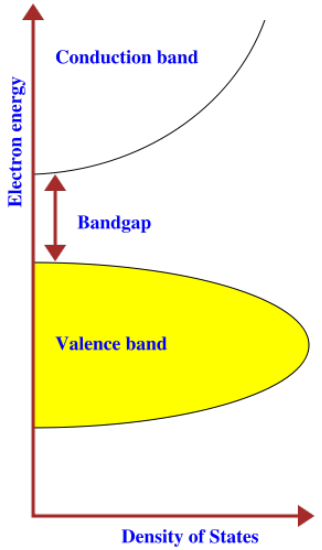








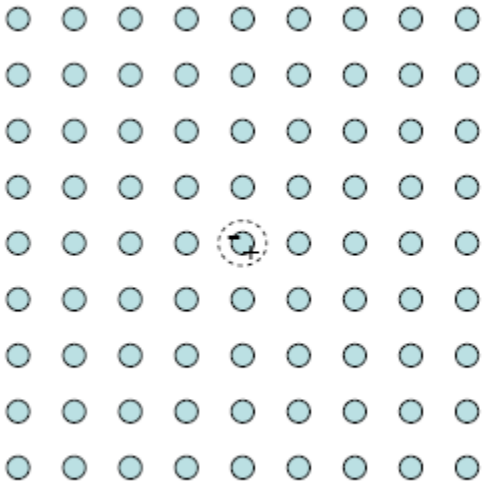




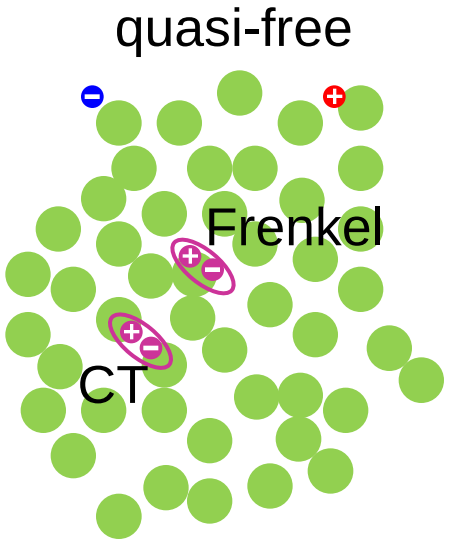
http://britneyspears.ac/physics/basics/basics.htm

Exciton

Exciton: electron - hole pair
(molecular or Frenkel exciton)



Frenkel exciton



$$F = - e^2 / 4 \pi \varepsilon\varepsilon_0 r^2$$

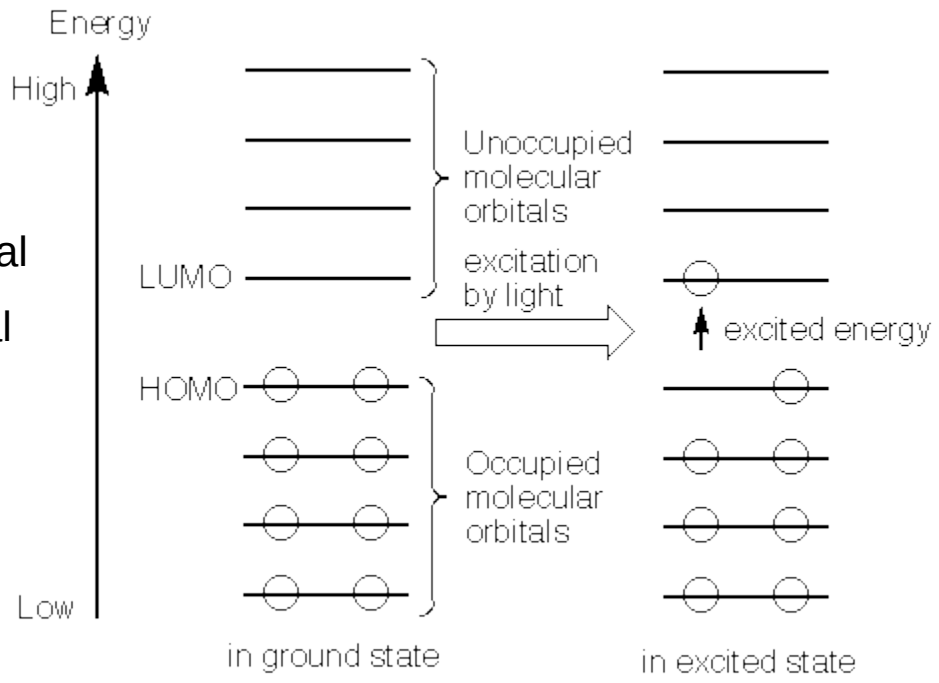
Large binding energy (>> kT) due to the low dielectric constant

- Quasi-free charge carriers
- Frenkel exciton
- Charge-transfer (CT) exciton

HOMO LUMO levels

LUMO Low Unocupied Molecular Orbital

HOMO High Occupied Molecular Orbital



LUMO similar to conduction band

HOMO similar to valence band

IP Ionization Potential [remove electron]

EA Electron affinity [energy gained when an electron is added].

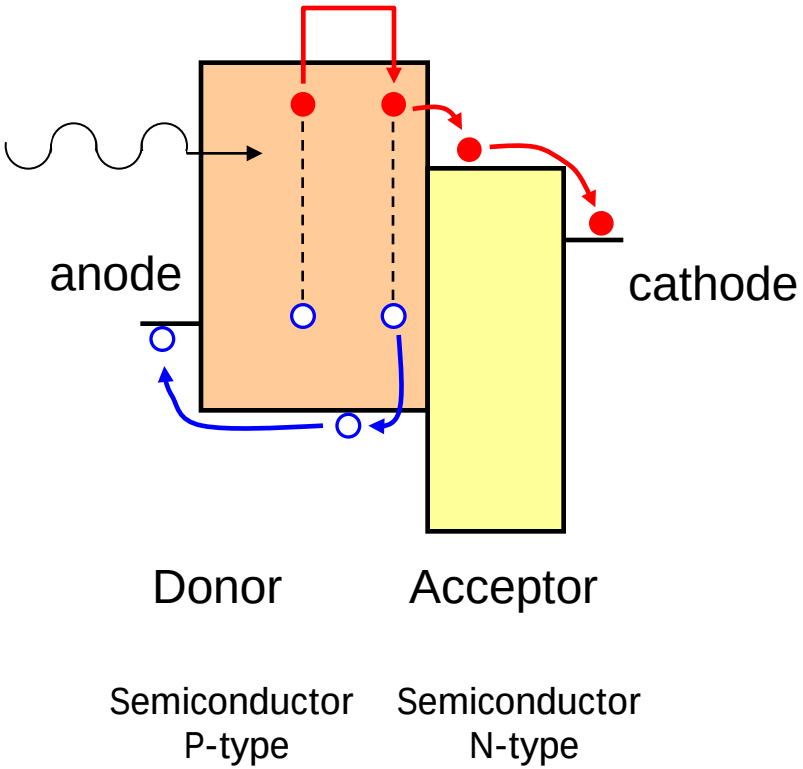
Photocurrent generation

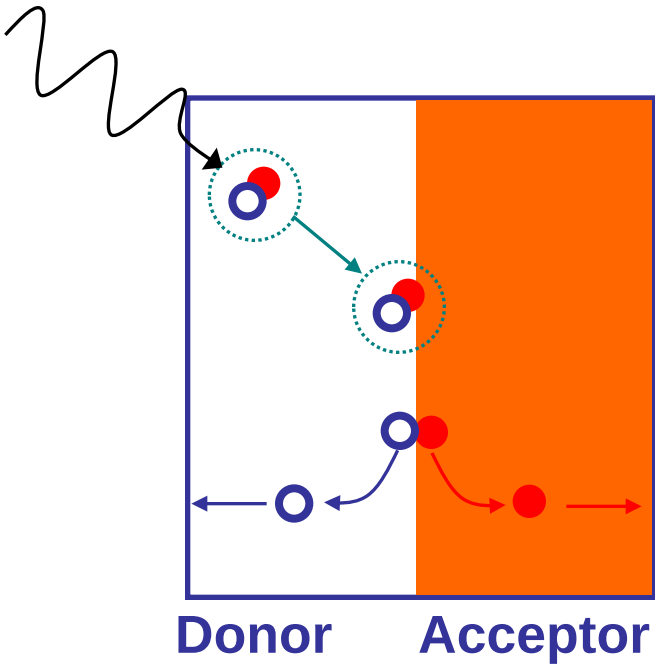
1 Photon absorption and exciton generation

2 Exciton diffusion

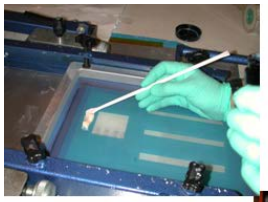
3 Charge Transfer

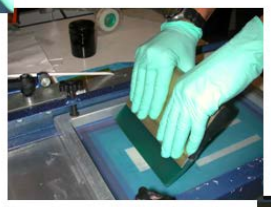
4 Carrier collection

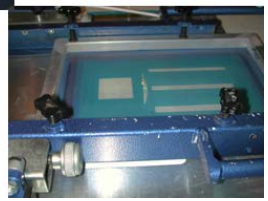




Polymer solar cell

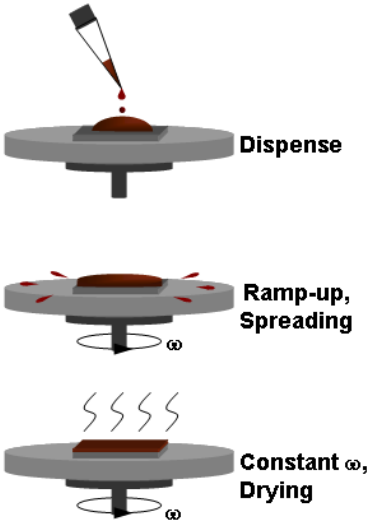






Dr Blade technique

Spin coating



Semiconductor

↓

Dissolution (different solvent)

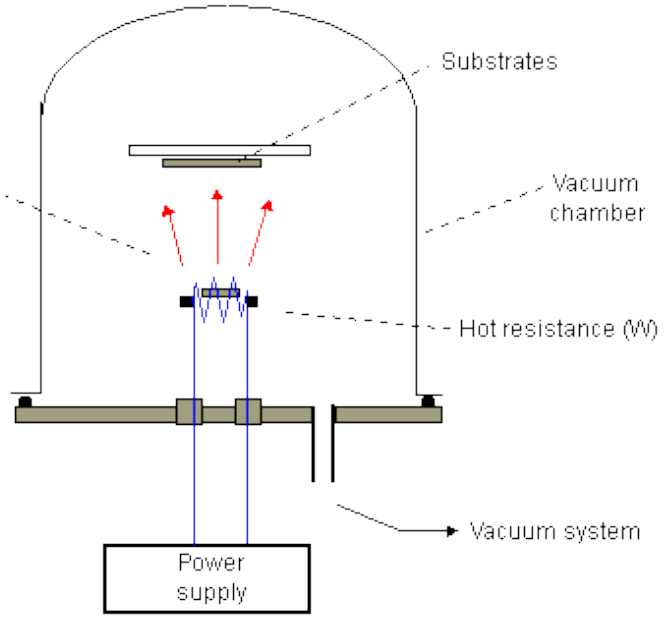
↓

Liquid distribution (spin-coating, or Dr Blade technique)

Small molecule solar cell

Semiconductor (powder)

Thermal evaporation in high vacuum



GloveBox

Our research activities at UPC on Organic Solar cells

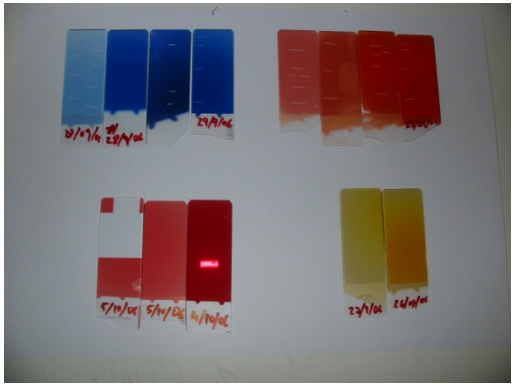
Evolution

Year 2002

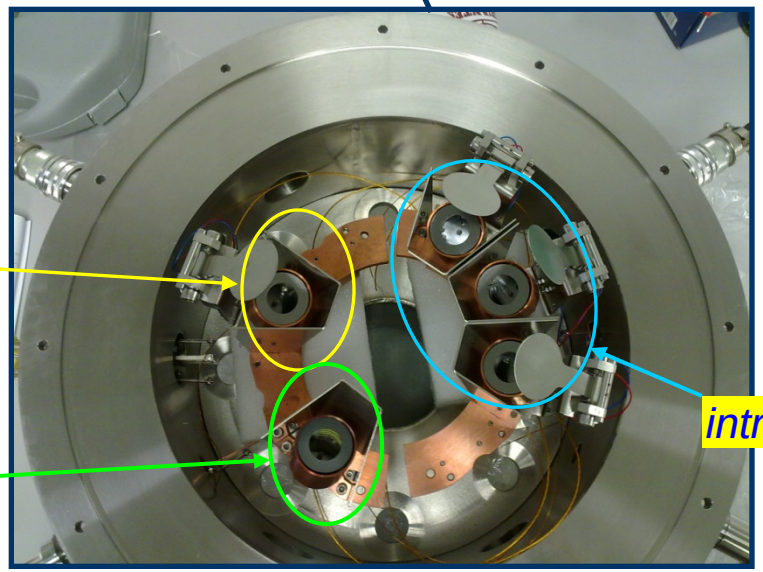
Year 2006

Year 2011

Thermal evaporation

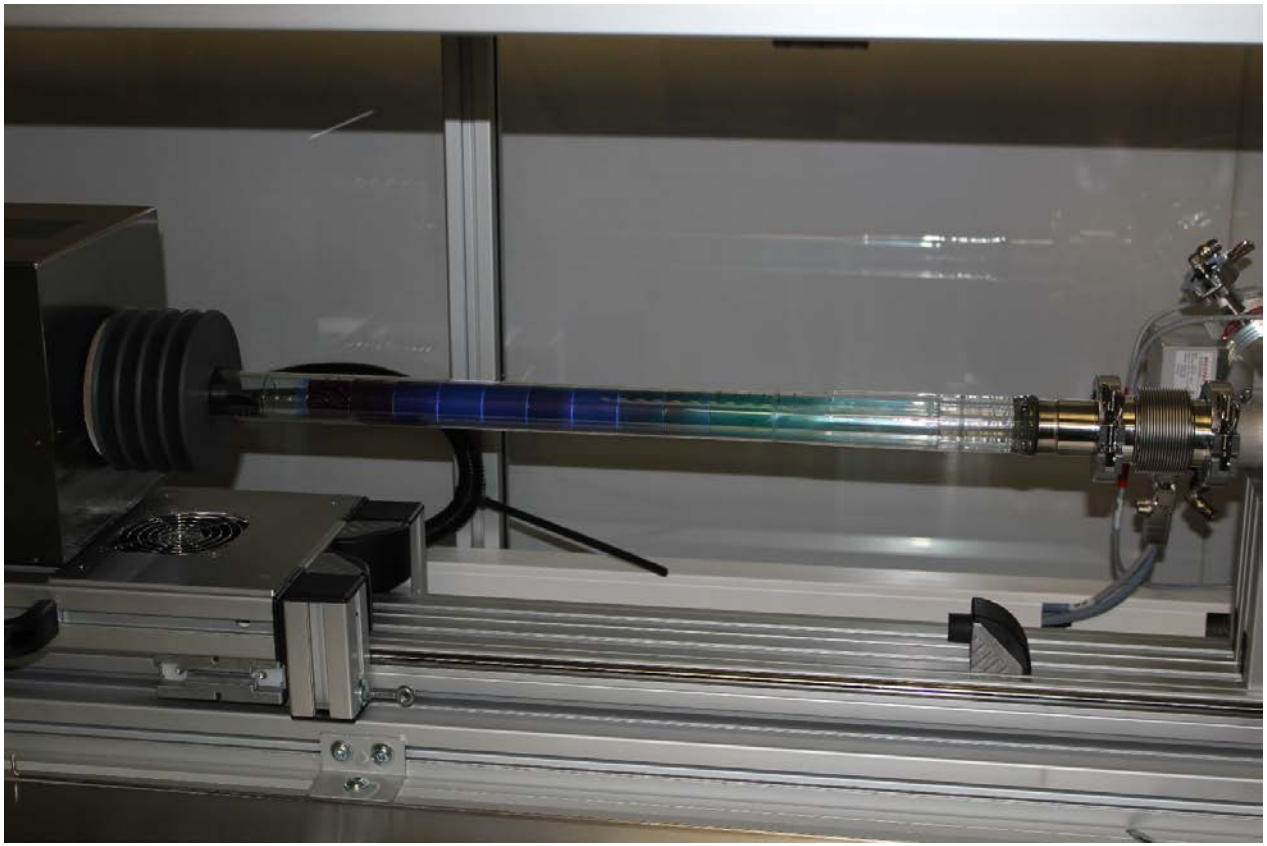


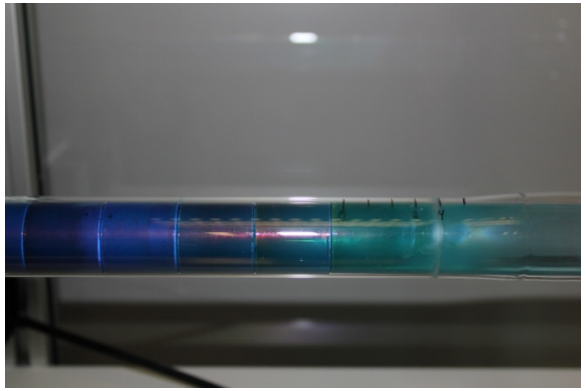
Metal evaporation

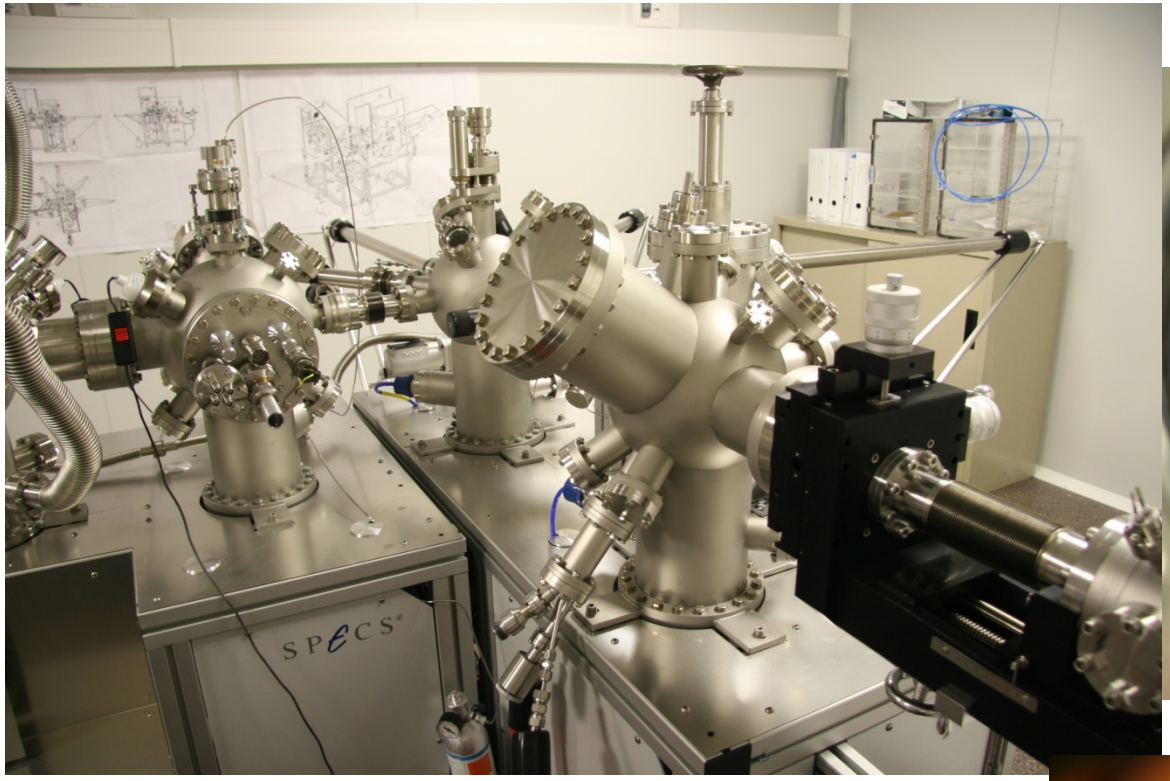


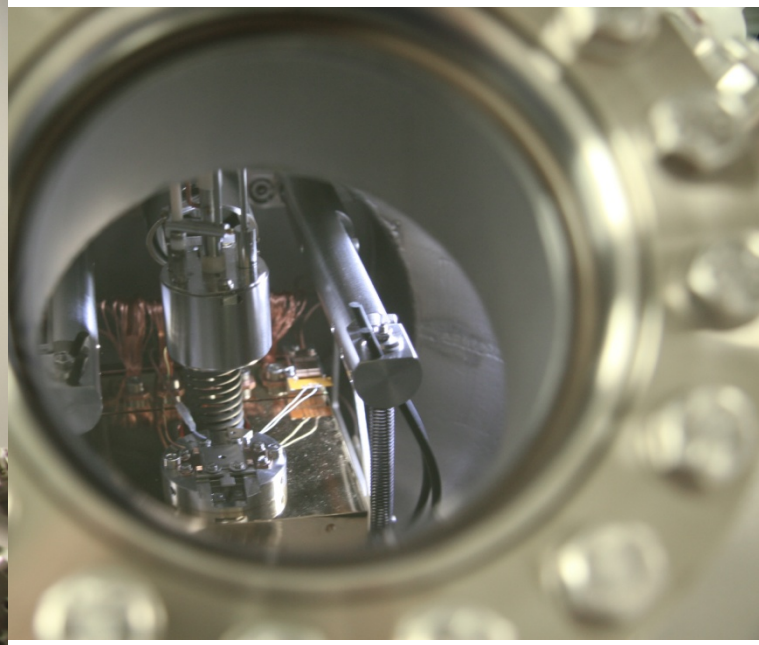
Organic evaporation

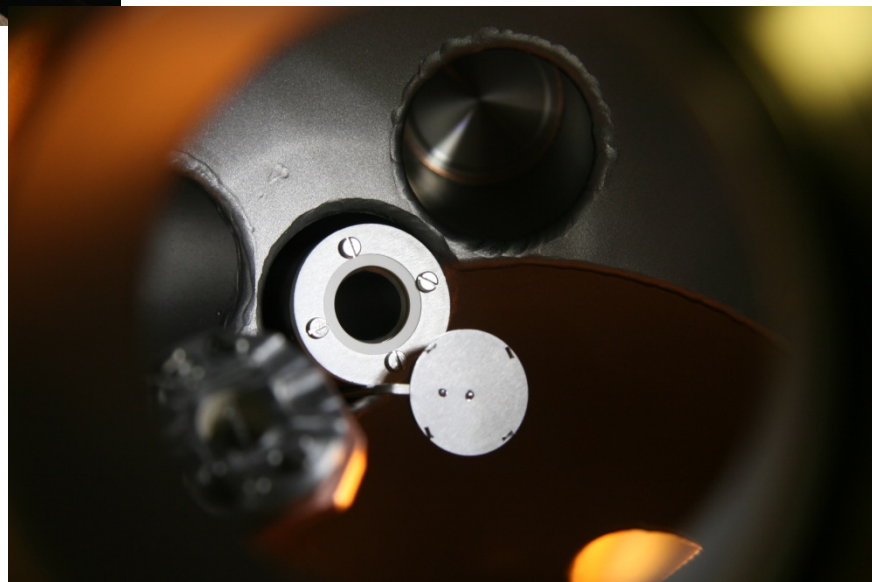
Organic semiconductor purification by gradient thermal sublimation





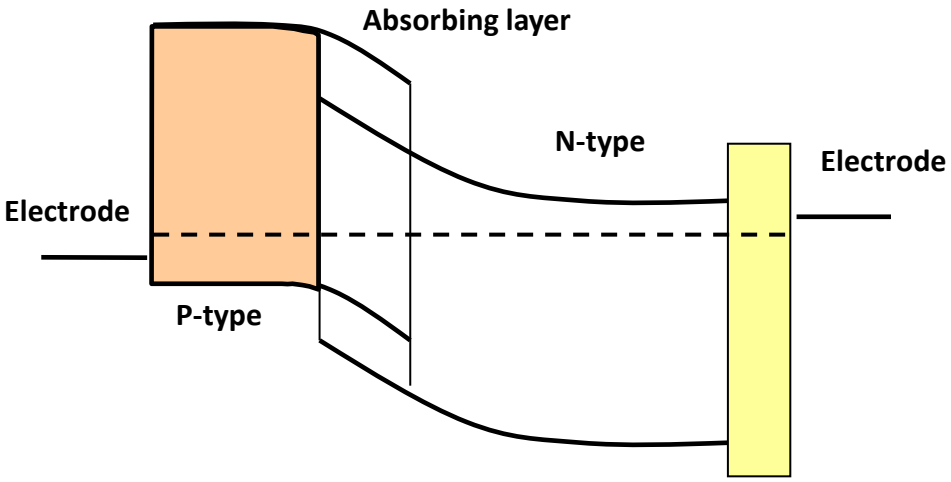


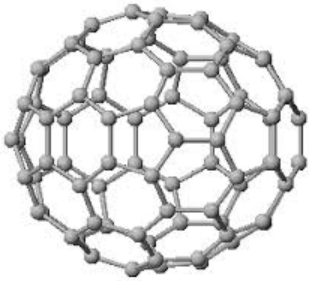


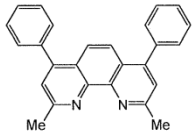


AFM and STM microscope UHV.
Small-molecule thermal deposition

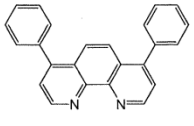
Our solar cell p-i-n



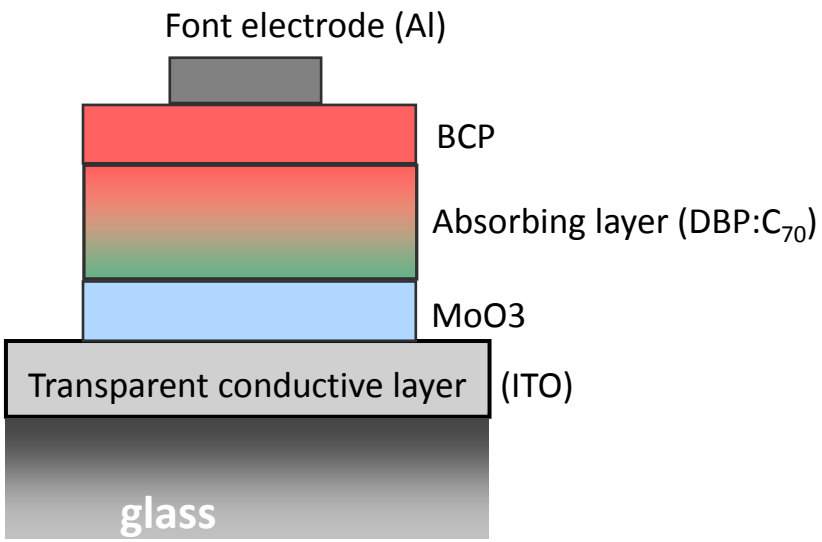


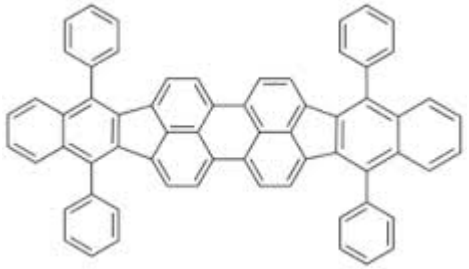


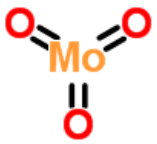
BCP



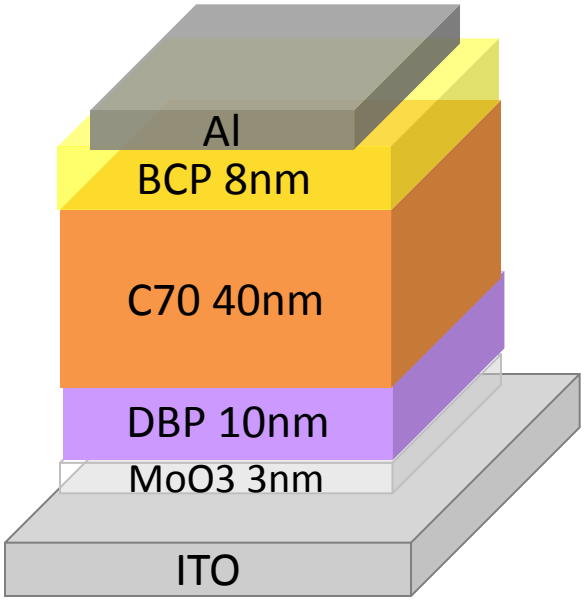
BPhen

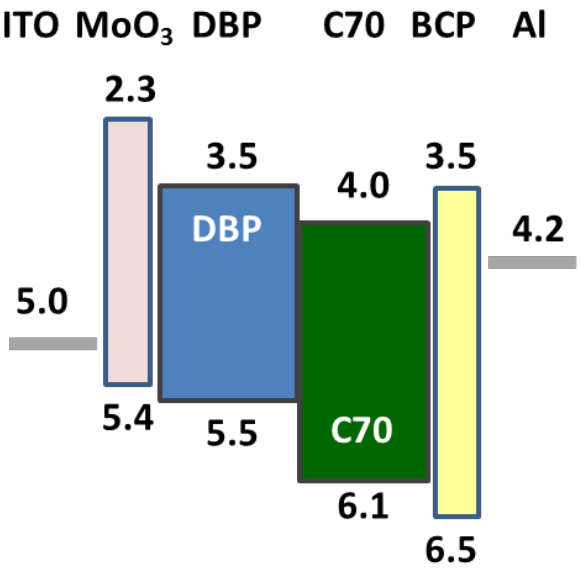


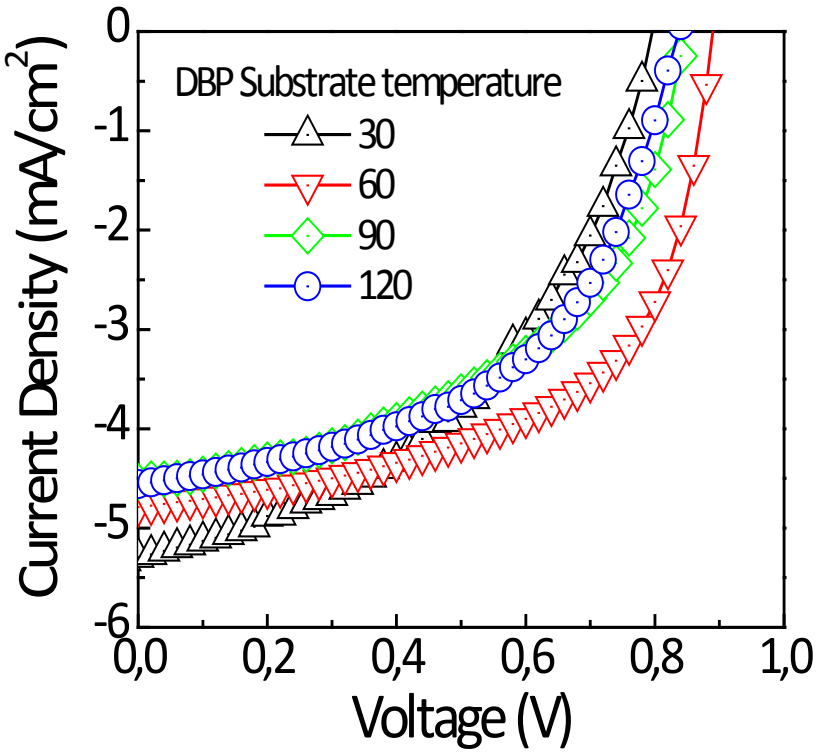




Bilayer solar cell

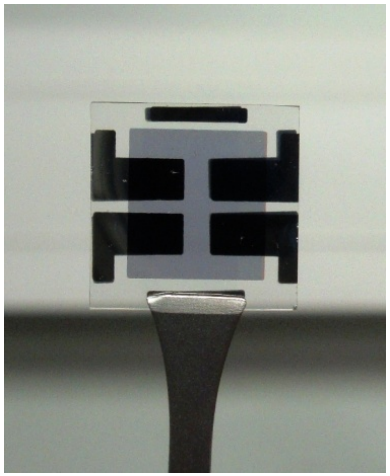


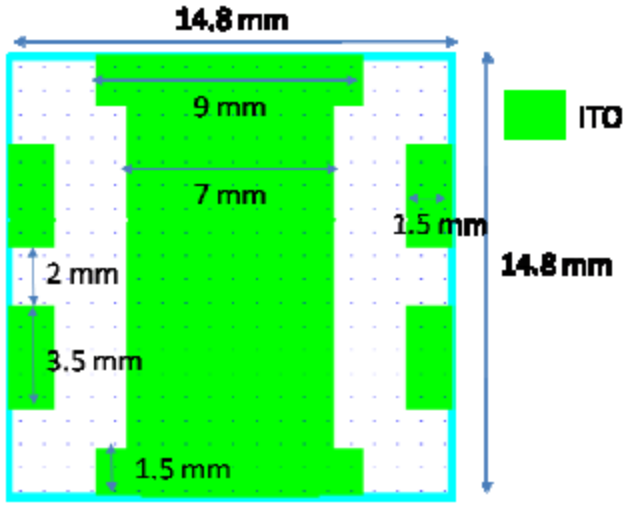


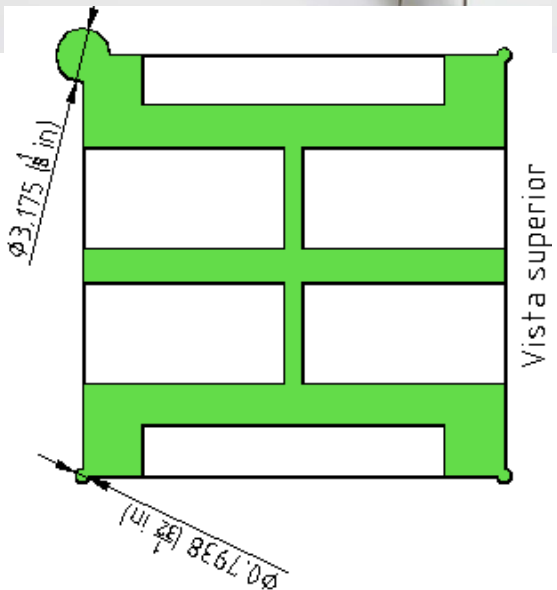


Temp (C)	PCE (%)	Voc (V)	J_{sc} (mA/cm²)	FF
30	1.92	0.79	-5.29	0.46
60	2.48	0.89	-4.79	0.58
90	1.96	0.85	-4.53	0.51
120	1.98	0.83	-4.56	0.52

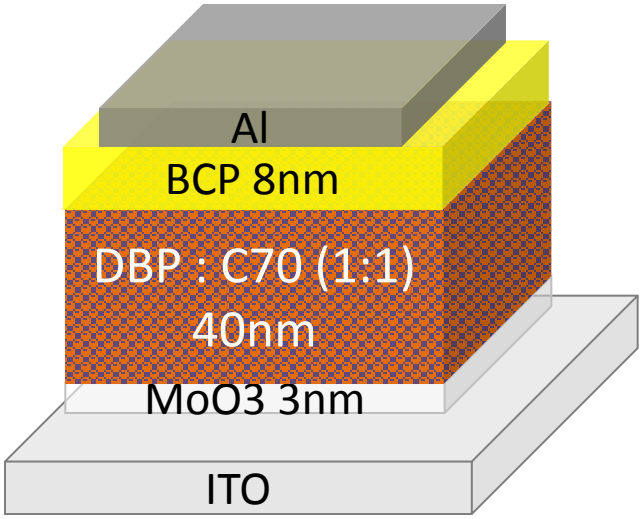
Facilities




14.8 mm
9 mm
7 mm
1.5 mm
2 mm
14.8 mm
3.5 mm
1.5 mm
ITO

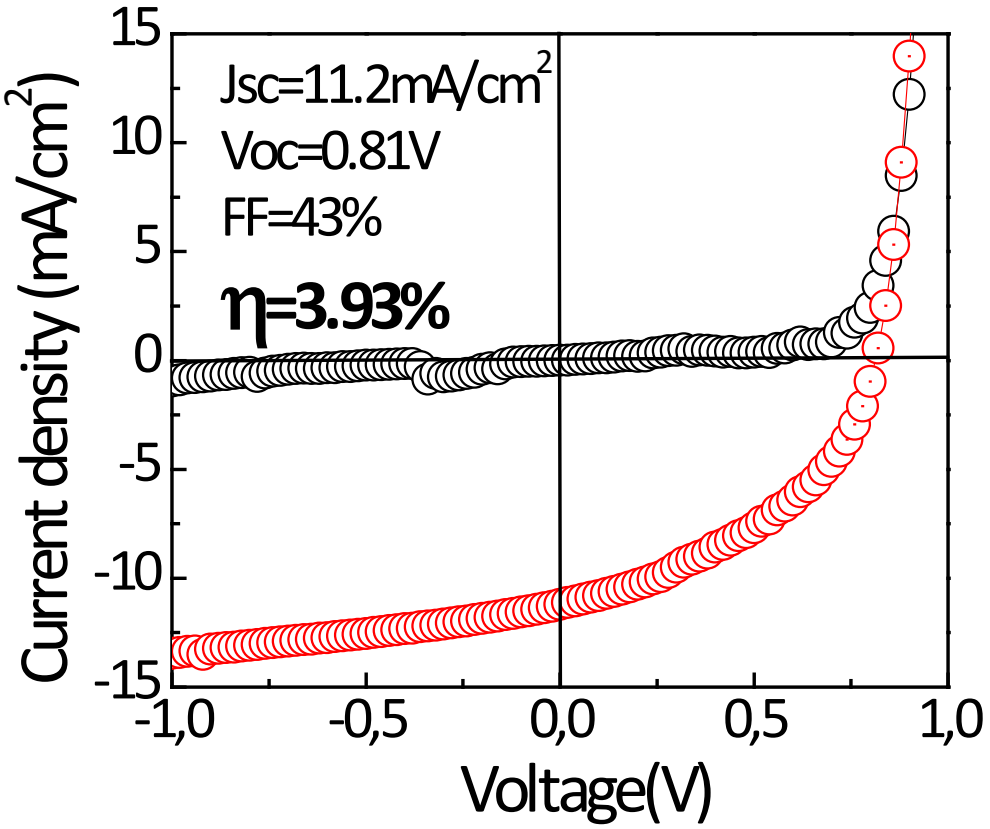

Ø3.175 (⅛ in)
Ø0.7938 (32 in)
Vista superior

Coevaporated solar cell



T_{SUBS} = 60 °C

Coevaporated ~ 4%

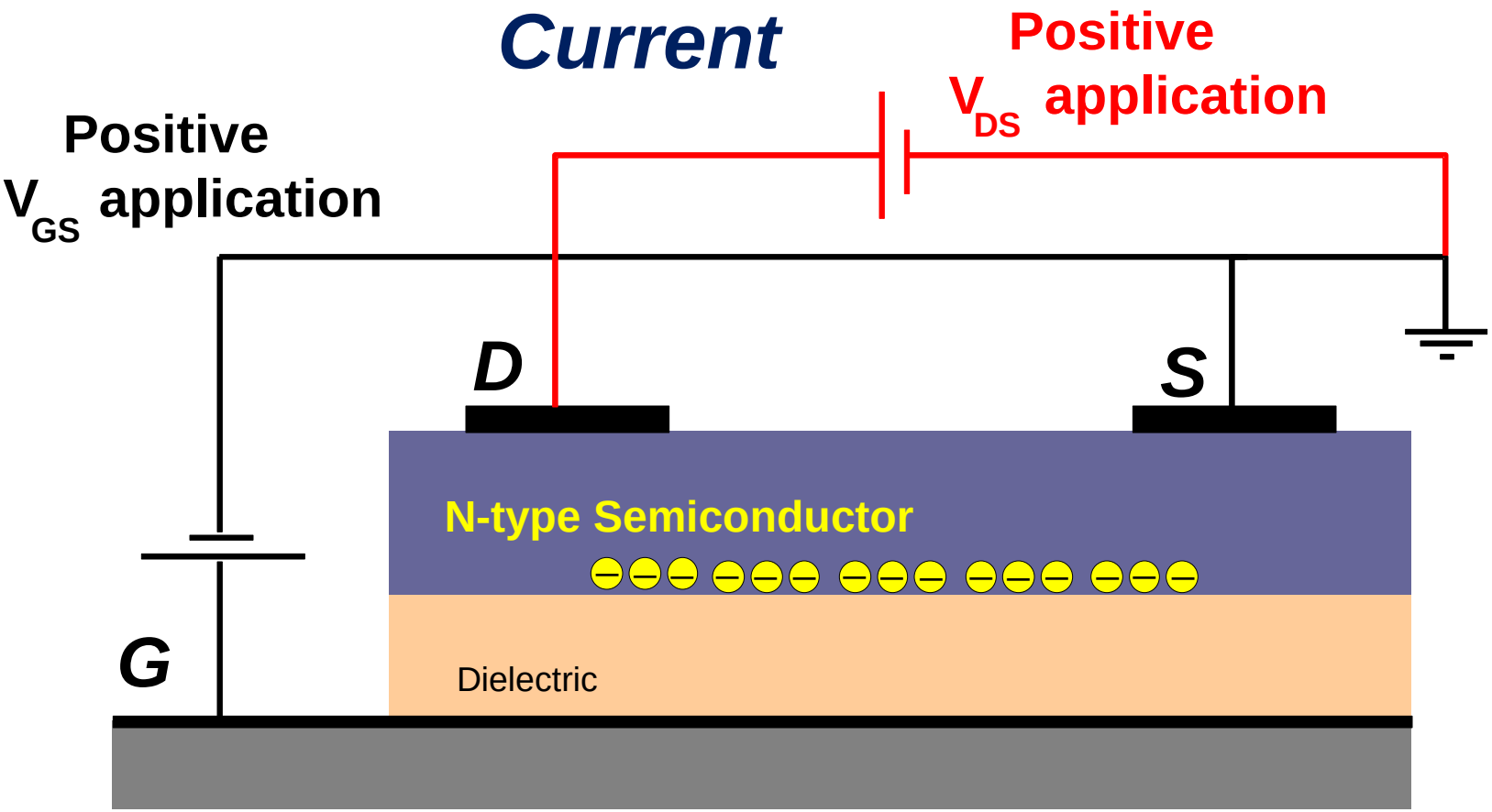


Macko J.A., Lunt R.R., Osedach T.P., Brown P.R., Barr M.C., Gleason K.K., Bulovic V., Phys. Chem. Chem. Phys. 14, 14548–14553 (2012)

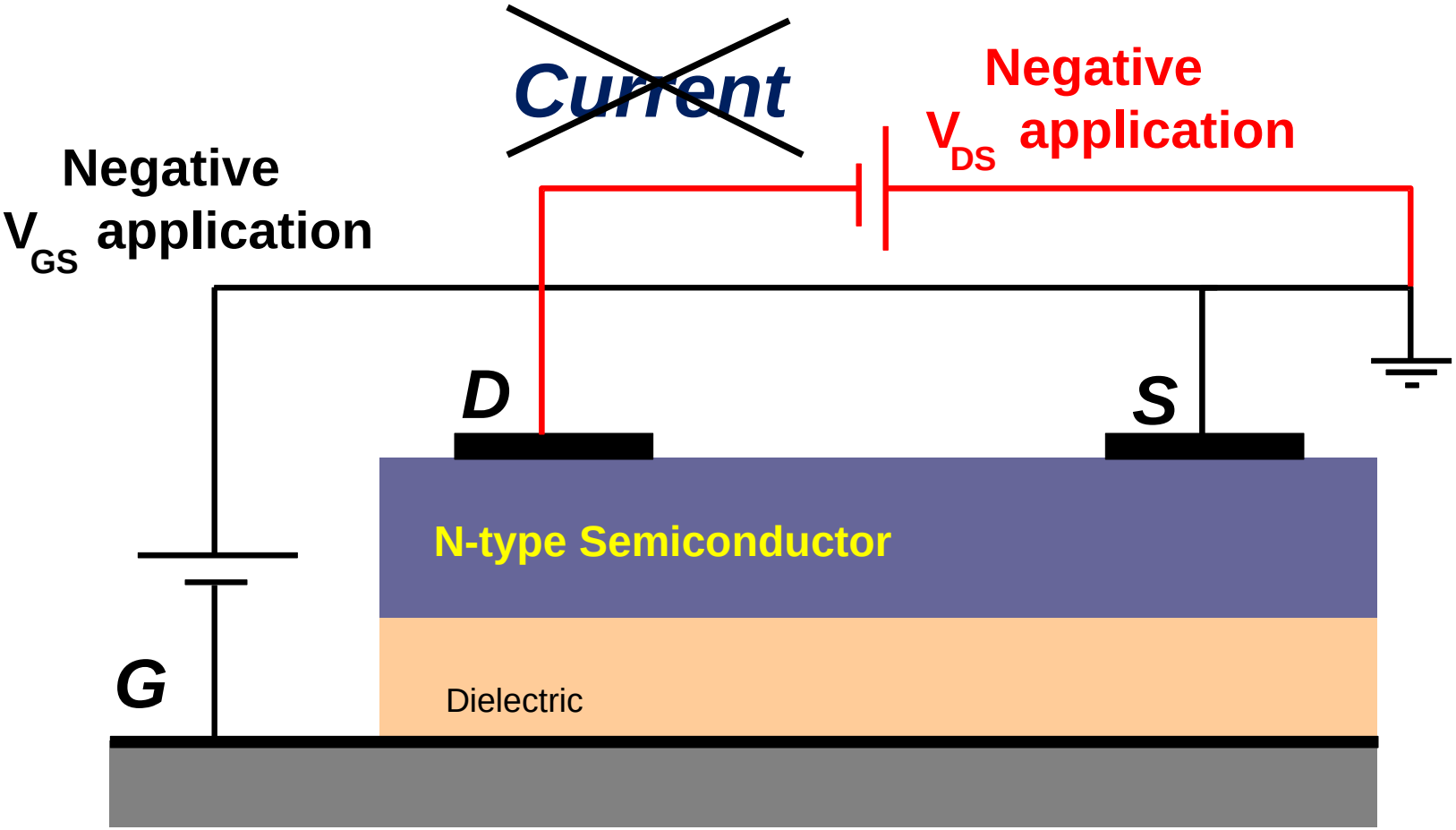
X. Xiao, J. D. Zimmerman, B. E. Lassiter, K. J. Bergemann, S. R. Forrest, Appl. Phys. Lett. 102, 073302 (2013)

Organic Thin-Film Transistors (OTFTs)

Working principle TFTs

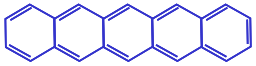


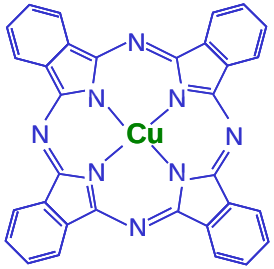
Working principle TFTs



OTFTs allows to determine field-effect mobility (μ)

- μ is an important parameter in organic solar cells
- OTFTs allow to optimize technological parameters



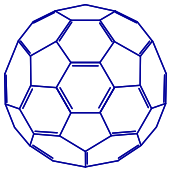


P-type

pentacene
CuPc
Carbazole
Picene

TTF-TCNQ

N-type

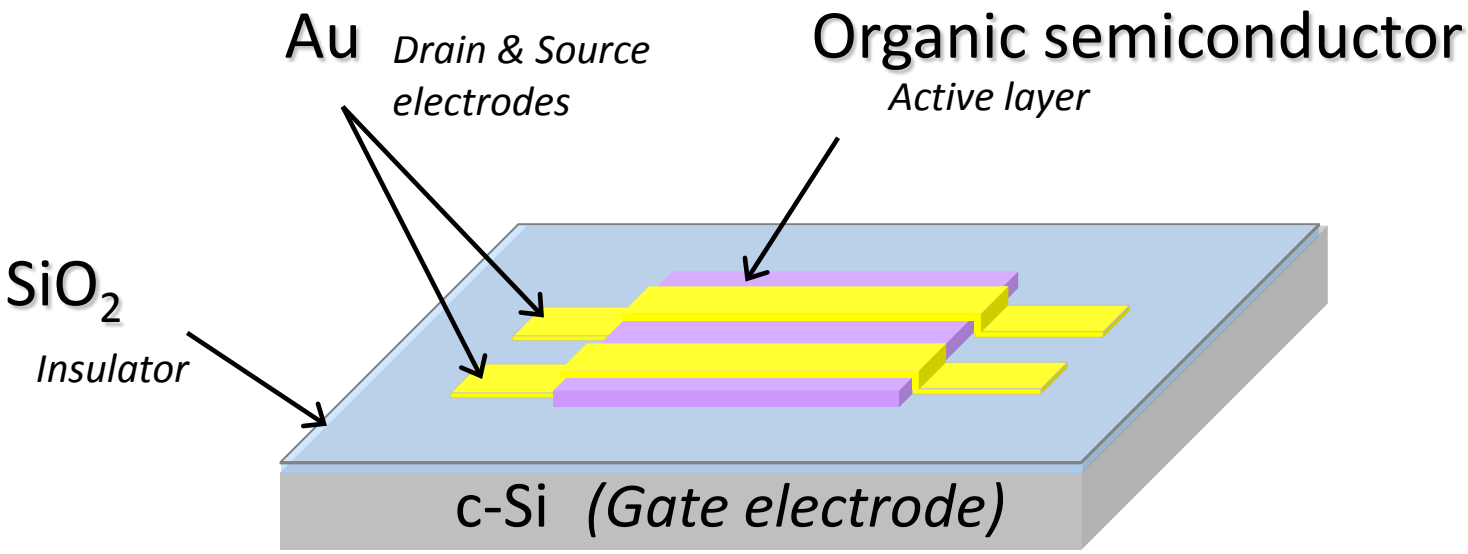


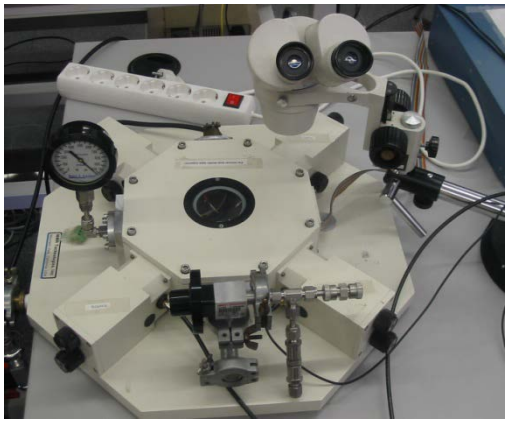
fullerene (C_{60})

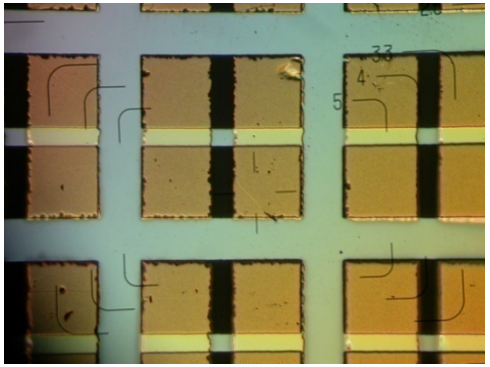
DP-PTCDI
F16CuPc
PTCDI-C_{13}

PTCDI-C13

TFTs Structure

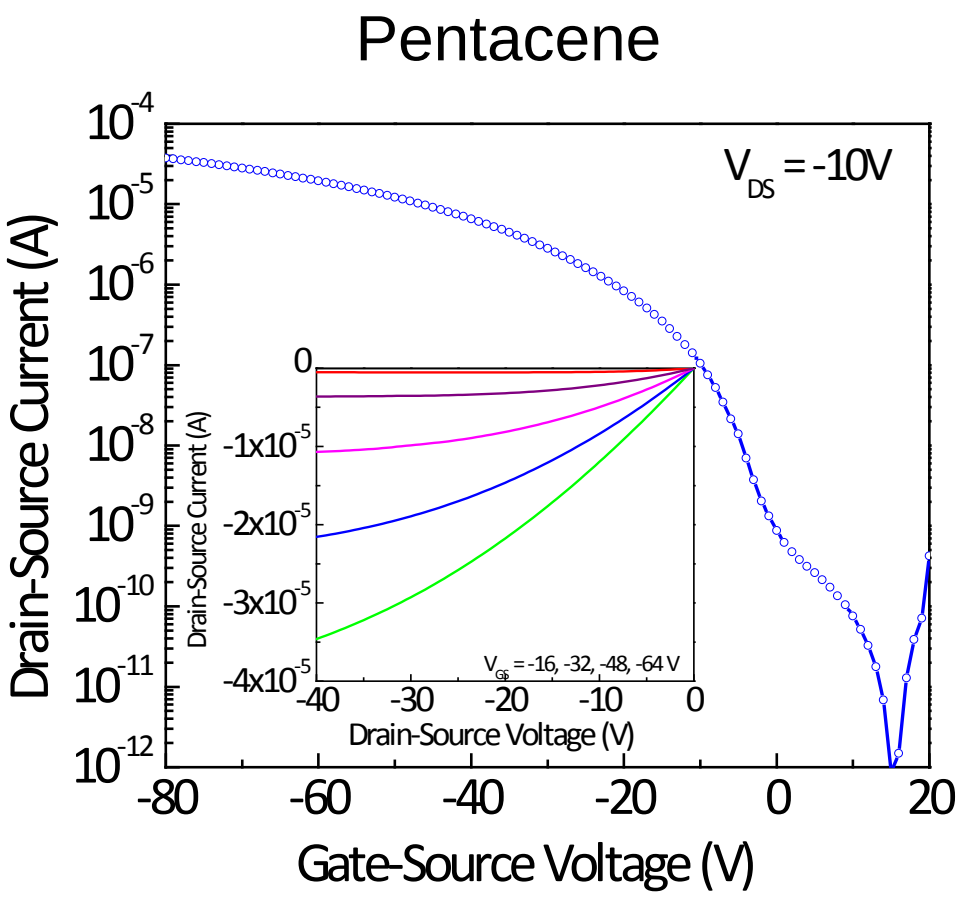


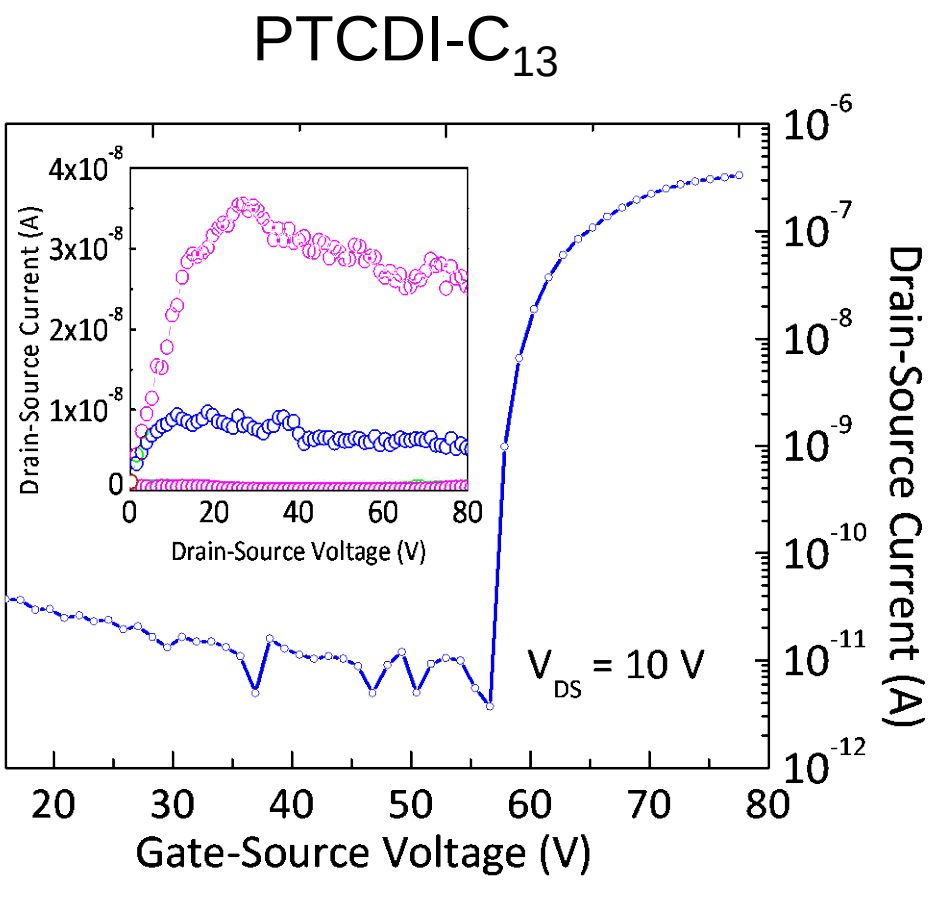




UPC

Individual TFT characteristics

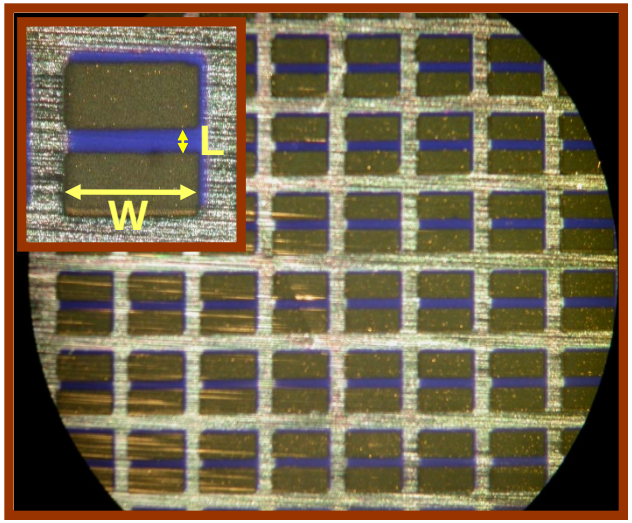




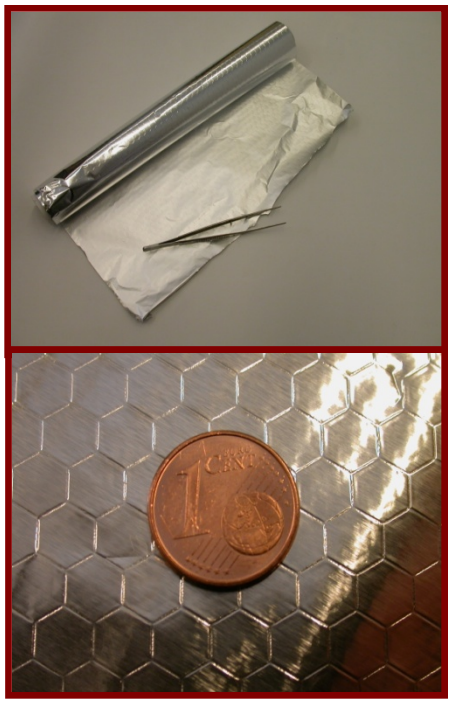
μ = 0.5 $cm^2/V \cdot s$
V_T = 15.6 V

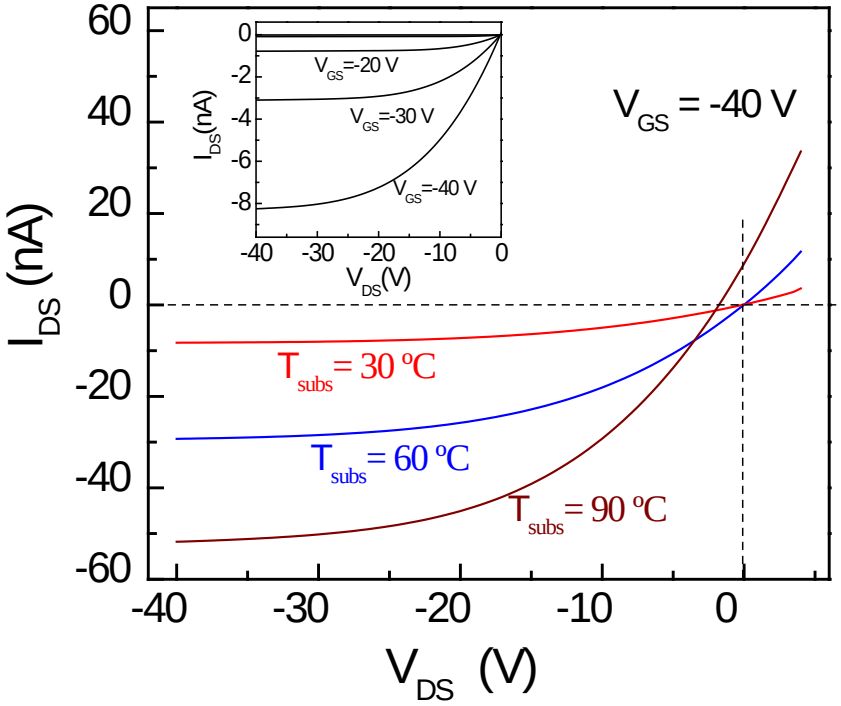
μ = 0.036 $cm^2/V \cdot s$
V_T = 61.7V

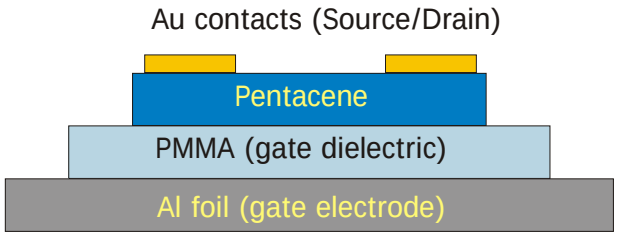
OTFTs on alumnium foil



Dielectric PMMA



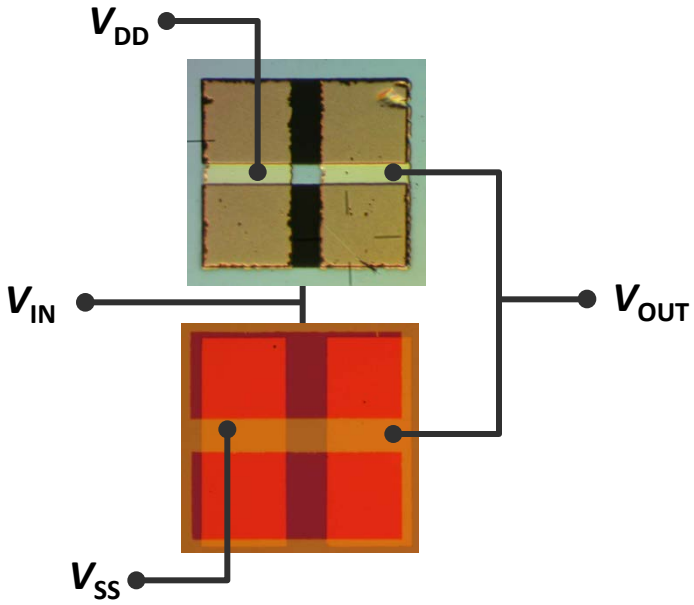


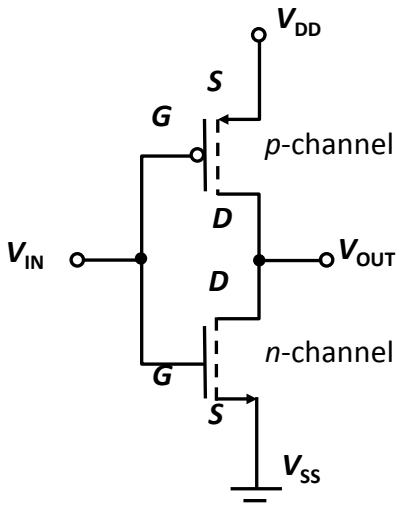


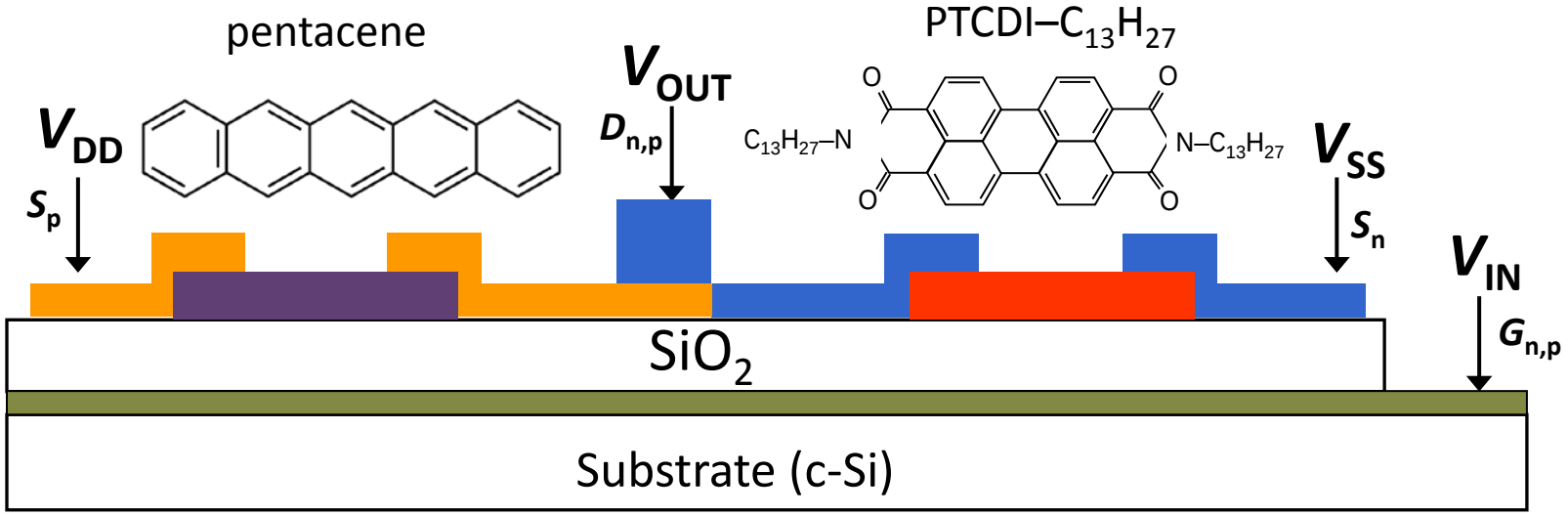
UPC

J. Puigdollers et al., presented at MRS Spring Meeting 2005

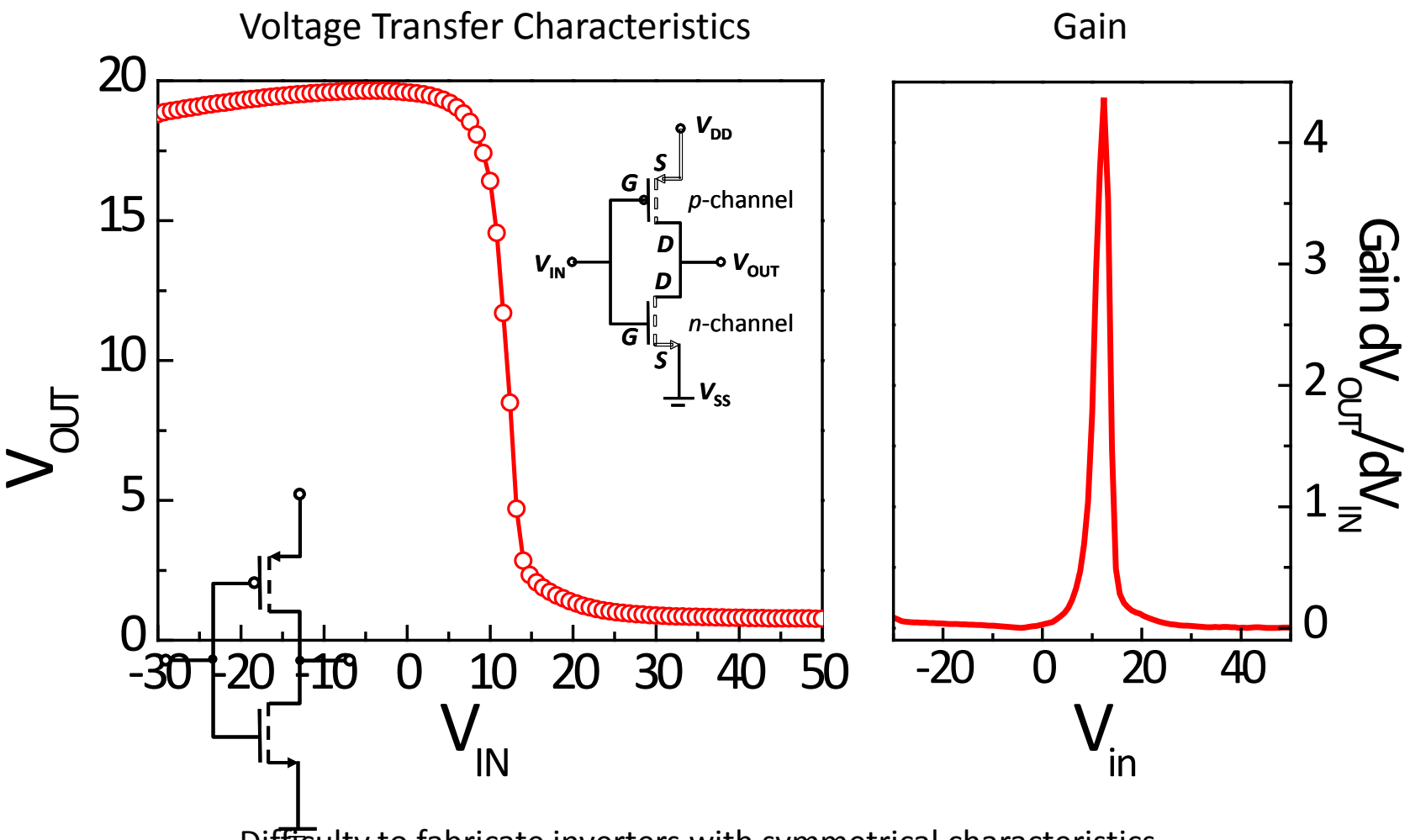
Complementary Inverter





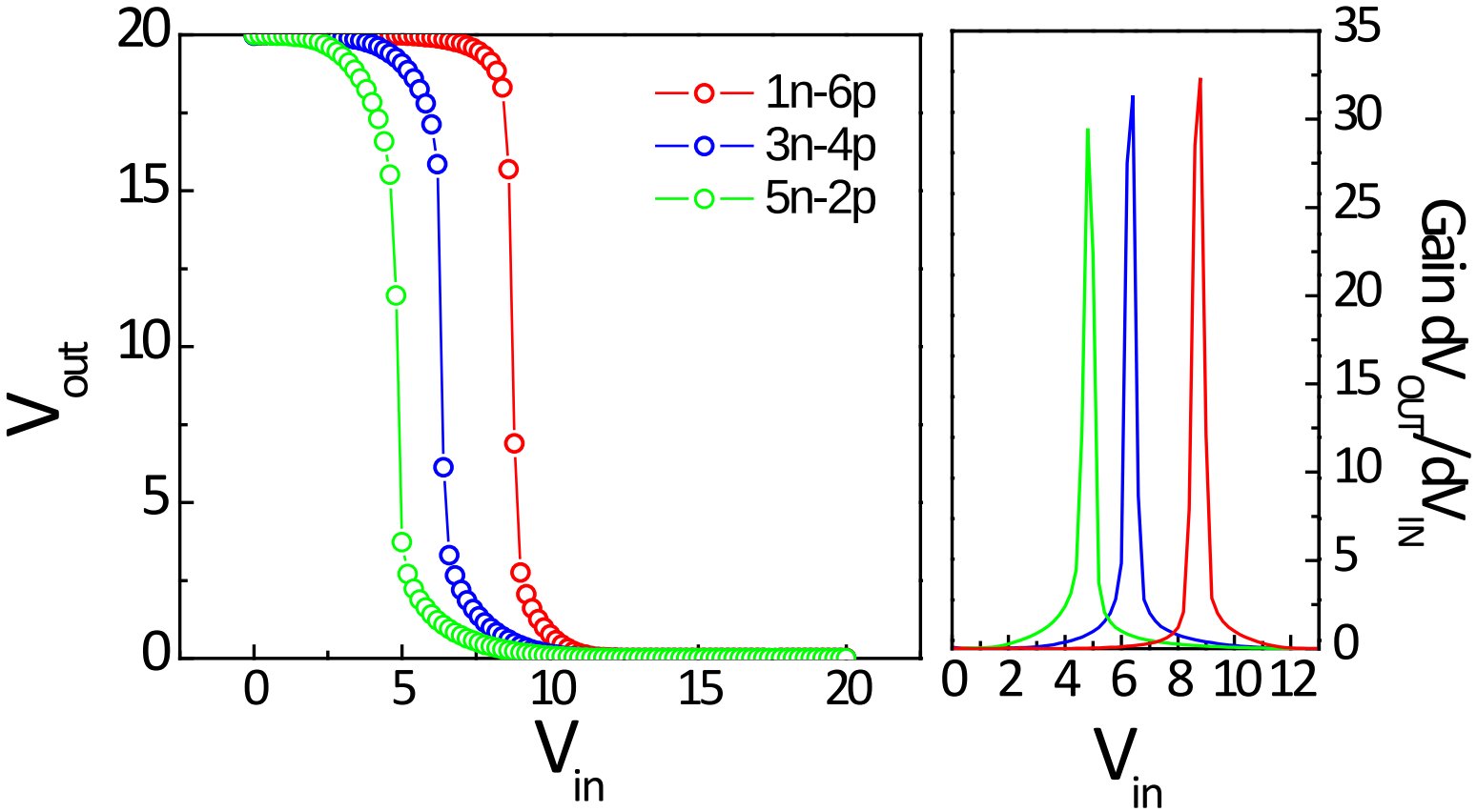


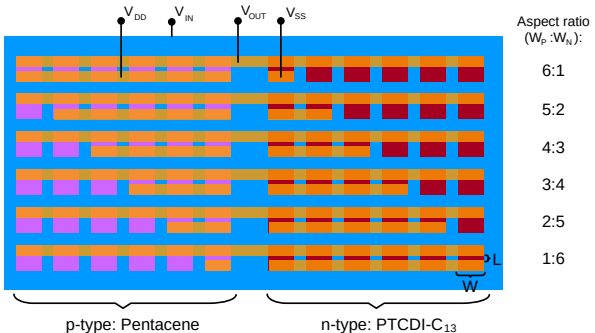
Voltage transfer characteristics

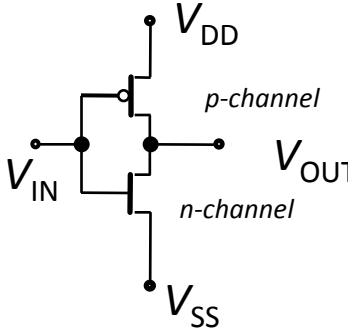


Difficulty to fabricate inverters with symmetrical characteristics

Complementary organic inverters (different W/L)







Thank you