# NDIP 2011

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# Organic Photodetectors

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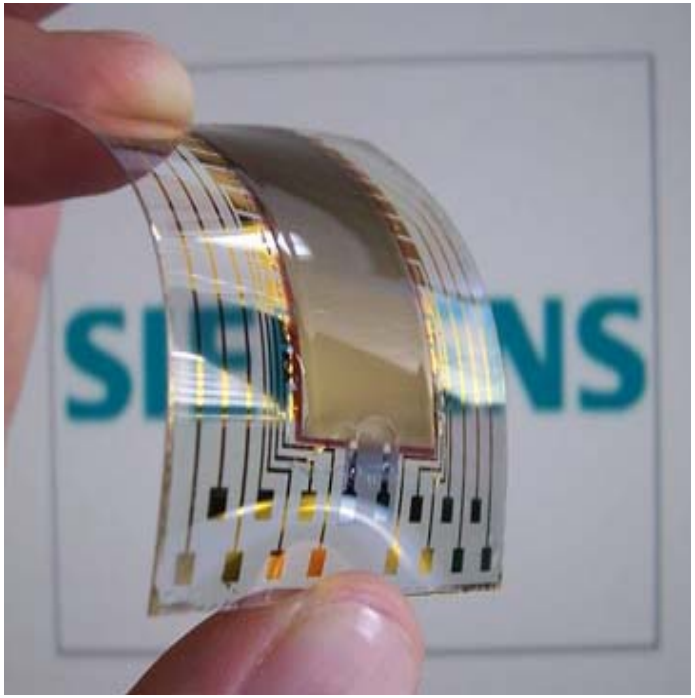
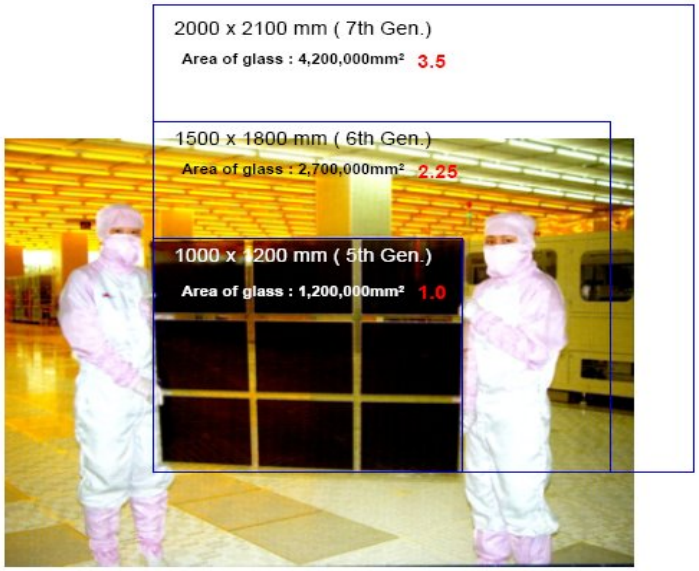
- Introduction
- Organic semiconductor
- Organic device
- Organic photodetector
- Conclusion



# Introduction

## Large Area Electronics

*Thin film Electronics made on m² substrate*

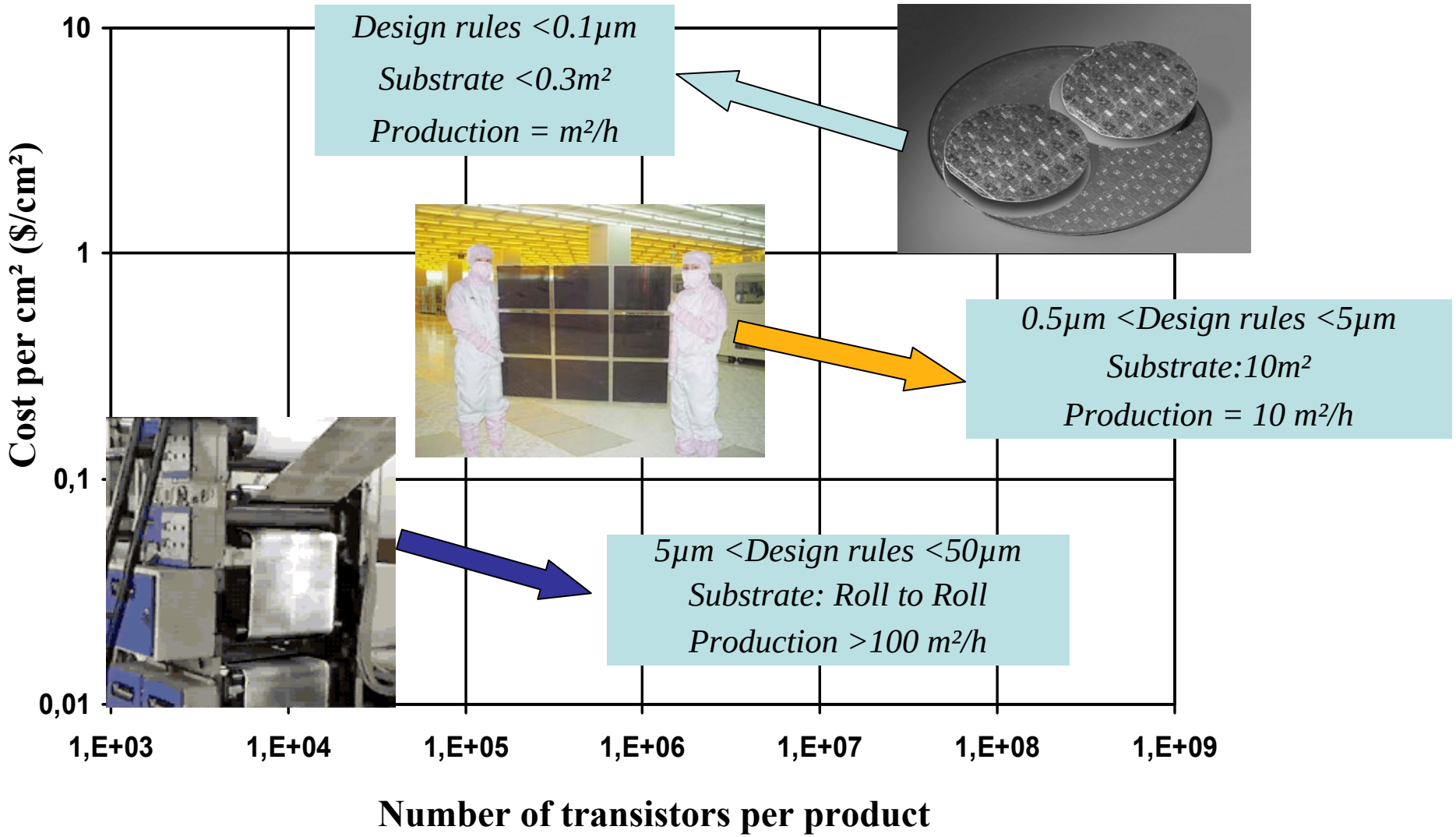



## Flexible Electronics

*Non-flat and rectangular substrates: conformable, flexible, foldable*

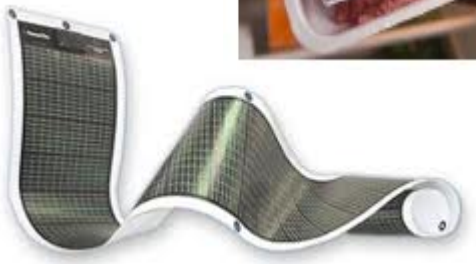
## Organic Electronics

*Active elements are plastic (carbon chemistry)*


Design rules <0.1µm
Substrate <0.3m²
Production = m²/h
0.5µm <Design rules <5µm
Substrate:10m²
Production = 10 m²/h
5µm <Design rules <50µm
Substrate: Roll to Roll
Production >100 m²/h
Cost per cm² ($/cm²)
10
1
0,1
0,01
1,E+03
1,E+04
1,E+05
1,E+06
1,E+07
1,E+08
1,E+09
Number of transistors per product

**Flexible displays**

**Flexible sensors**



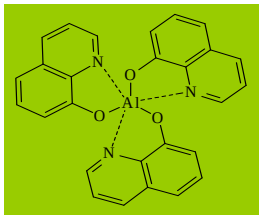
**Flexible solar cells**

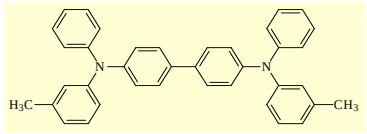
**Flexible light**

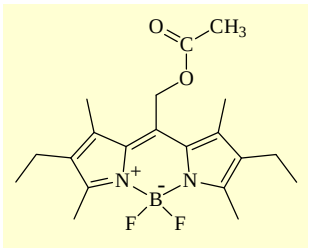
# Organic Semiconductor

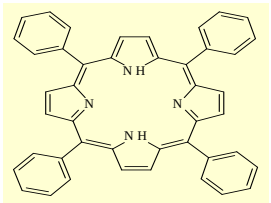
# Two different family

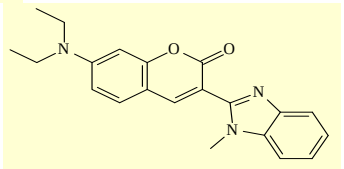
## ‘Small molecules’ M ~ <800





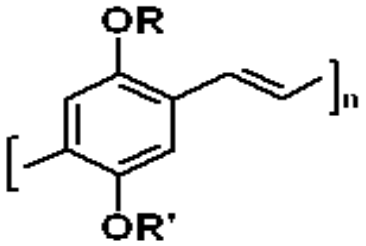


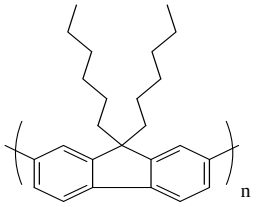




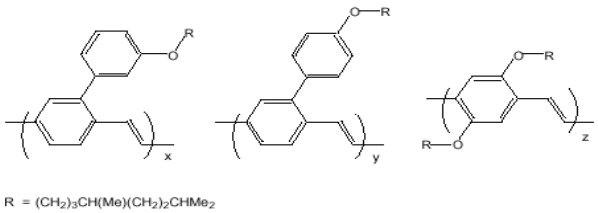
**Vacum deposition**

## Polymers




POLYFLUORENE




Covion PPV co-polymers

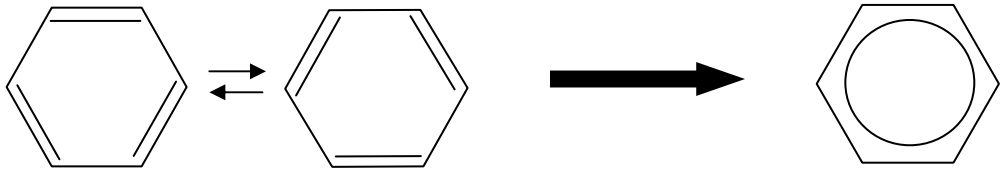
**Liquid deposition**

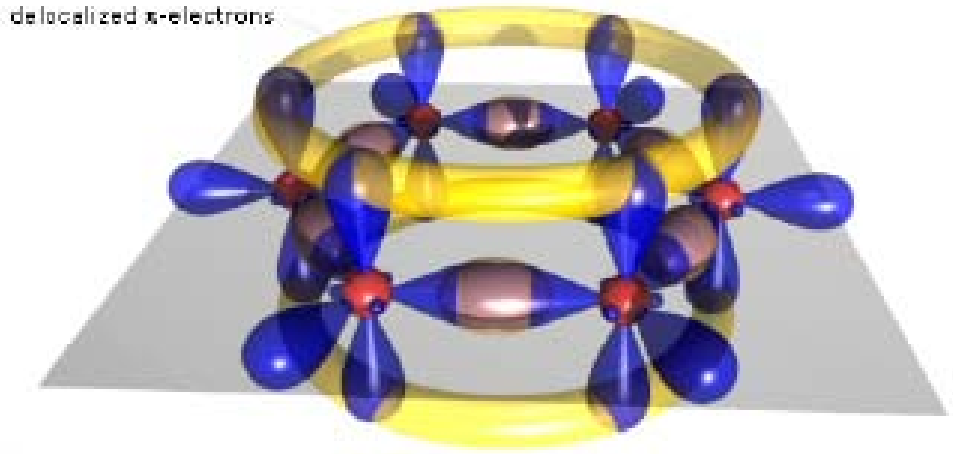
## Conjugate Molecule (1)

**Conjugation = alternating single and double bonds**

**Double bonds: hybridizing $sp^2$ (orbital's superposition s & $p_z$)**

**Benzene: $C_6H_6$**

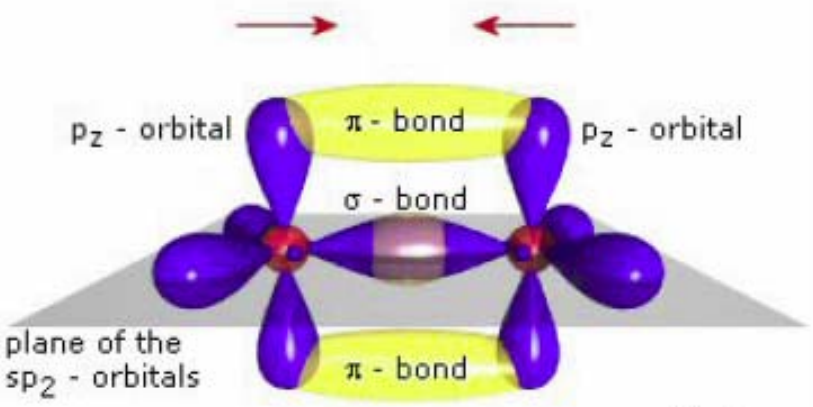


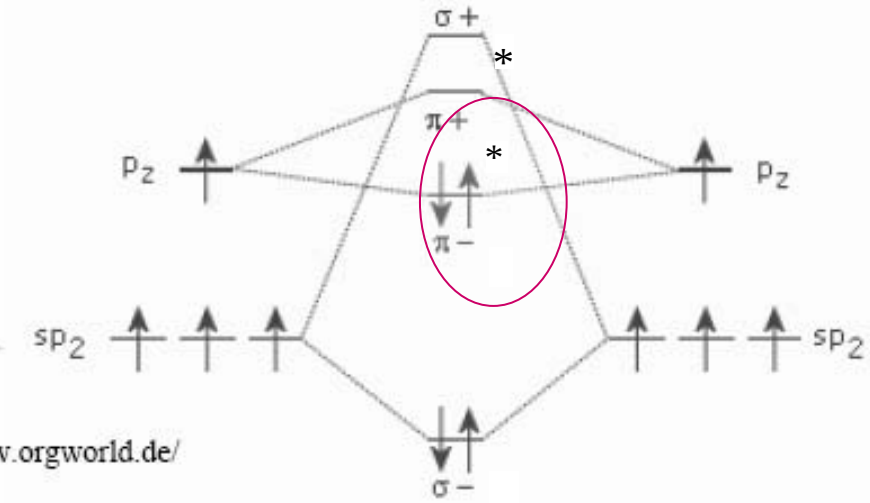



6 electrons delocalized over the entire molecule

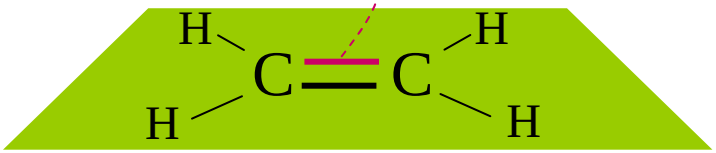
# Conjugate Molecule (2)

## σ bond & π bond




http://www.orgworld.de/

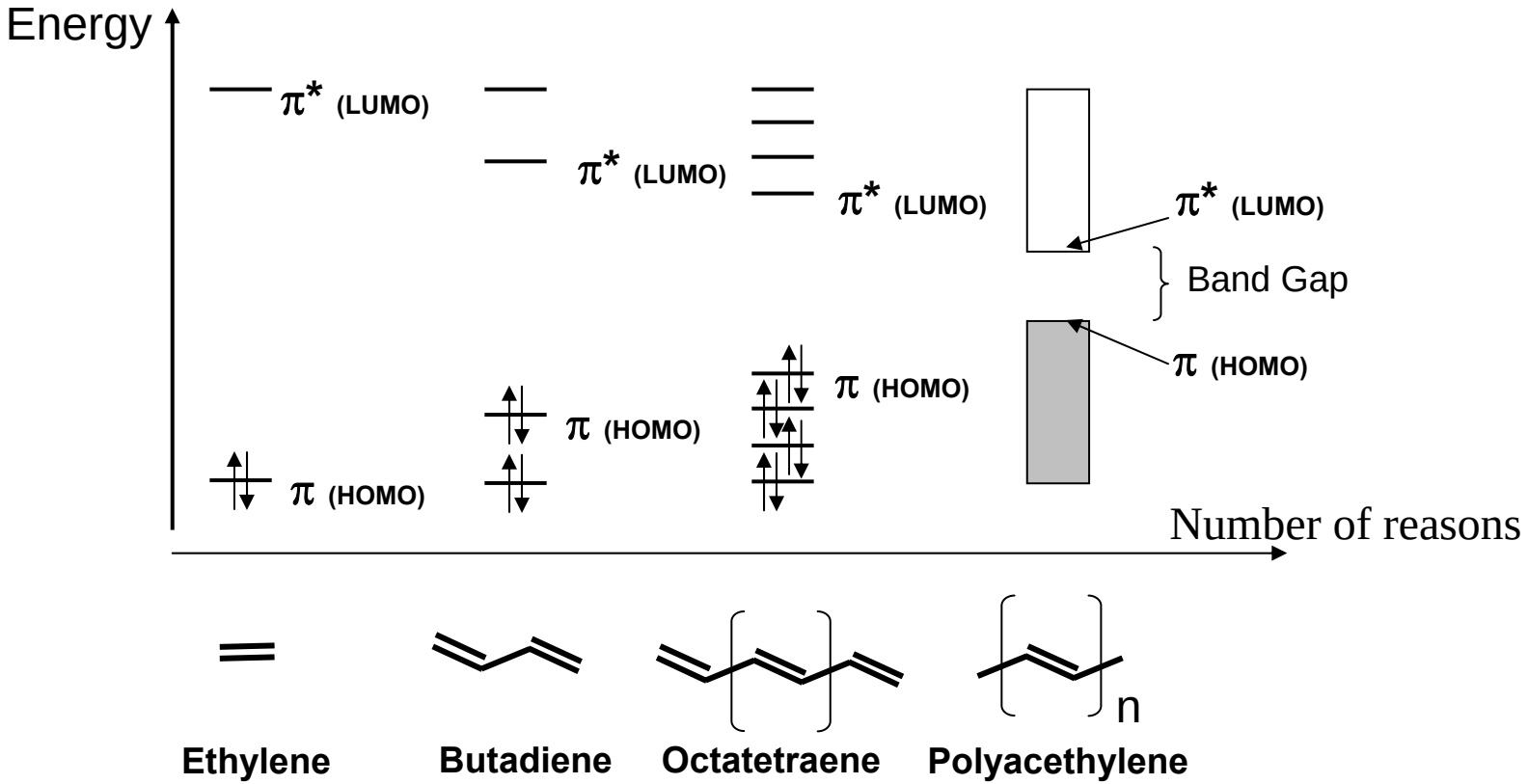



**Ethylene: $C_2H_4$**

**σ bond** ⇒ link the maintenance of the molecule

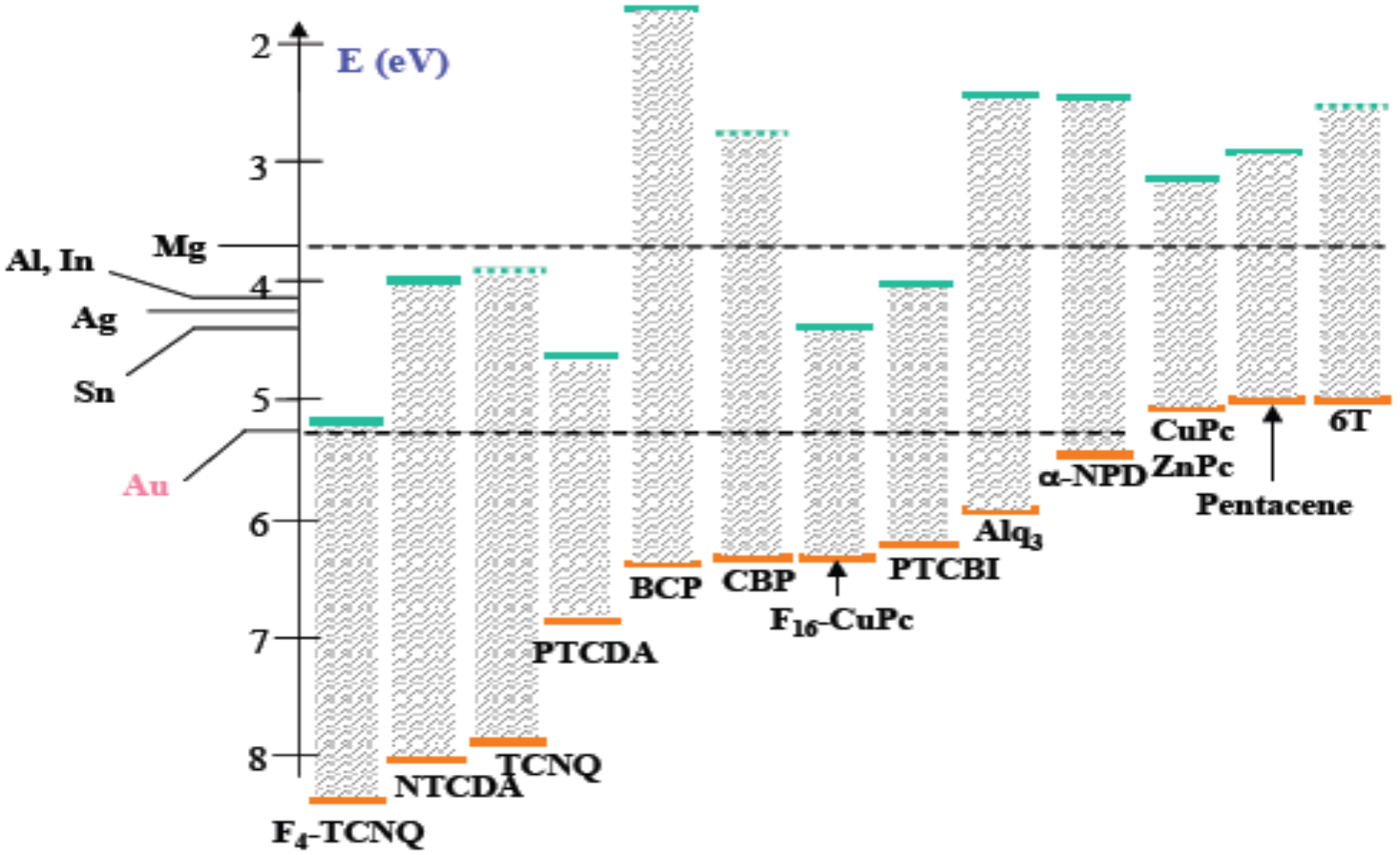
**π bond** ⇒ electronic properties

## HOMO & LUMO levels




**HOMO**: Highest Occupied Molecular Orbital
**LUMO**: Lowest Unoccupied Molecular Orbital

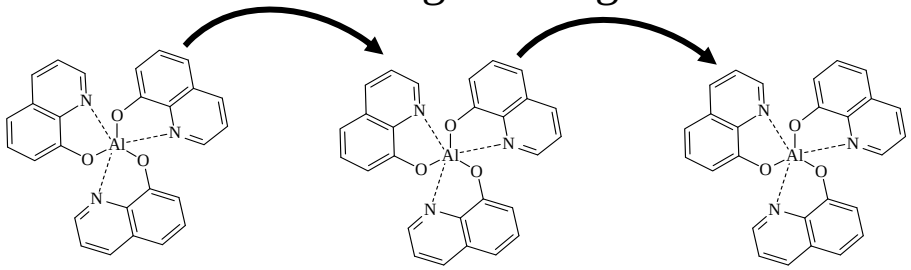
## Band gap samples




N. Koch et al., Appl. Surf. Sci. 2003, 82, 70

## Charge transport in small molecules

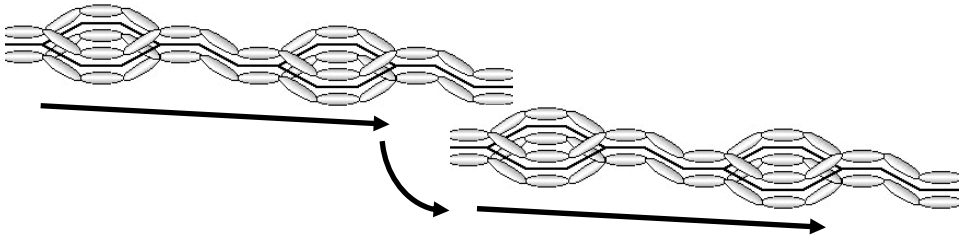
Charge transport in small molecules is via hopping, i.e. the charges have to jump from one molecule to the neighbouring one to be transported.



## Charge transport in conjugated polymers

In conjugated polymers the charges are partially transported via delocalisation along the HOMO and LUMO levels.

Transport properties are usually determined by defects in the 1D-chains (intra molecular) or by hopping from chain to chain (inter molecular)

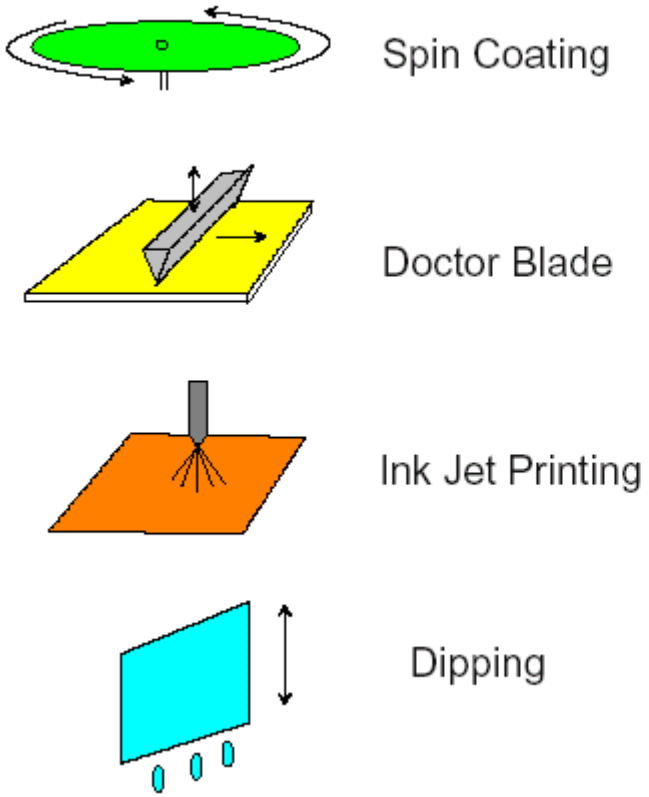


## Charge carrier mobilities of organic thin films

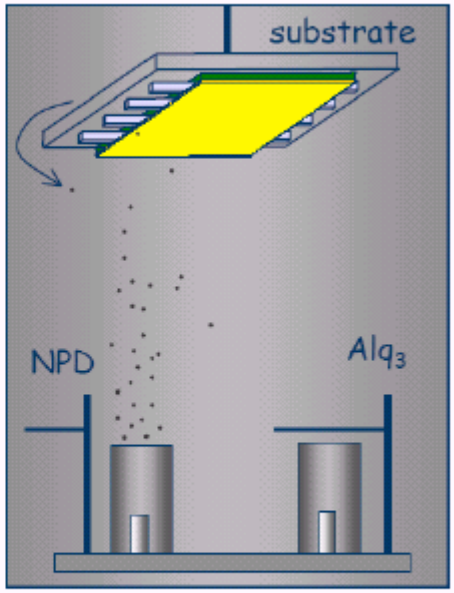
| Material | Electron (e) or hole (h) mobilities ($cm^2/(Vs)$) | Reference |
|---|---|---|
| **Organic** | | |
| Polythiophene (spin-coated films) | $10^{-4} - 10^{-2}$ (h) | [21] |
| Polythiophene (aligned by drawing method) | | |
| parallel to the alignment direction | $0.9 * 10^{-4}$ (h) | [22] |
| perpendicular to the alignment direction | $7.4 * 10^{-4}$ (h) | [22] |
| Polythiophene (printed) | 0.1 (h) | [20] |
| MDMO-PPV/PCBM (spin-coated films) | $2 * 10^{-7} - 5 * 10^{-6}$ (h), | [23] |
| | $2 * 10^{-5} - 4 * 10^{-4}$ (e) | [23] |
| Oligothiophene | $0.1 - 0.5$ (h) | [24] |
| Pentacene (polycrystalline) | $0.3 - 1.0$ (h) | [25] |
| Pentacene (single crystal) | 2.0 (h) | [26] |
| **Anorganic** | | |
| c-Si | 1400 (e), 480 (h) | [27] |
| c-GaAs | 8000 (e), 400 (h) | [28] |

# Organic Semiconductors: Processing

## Solution processing (polymers):




## Evaporation (small molecules):

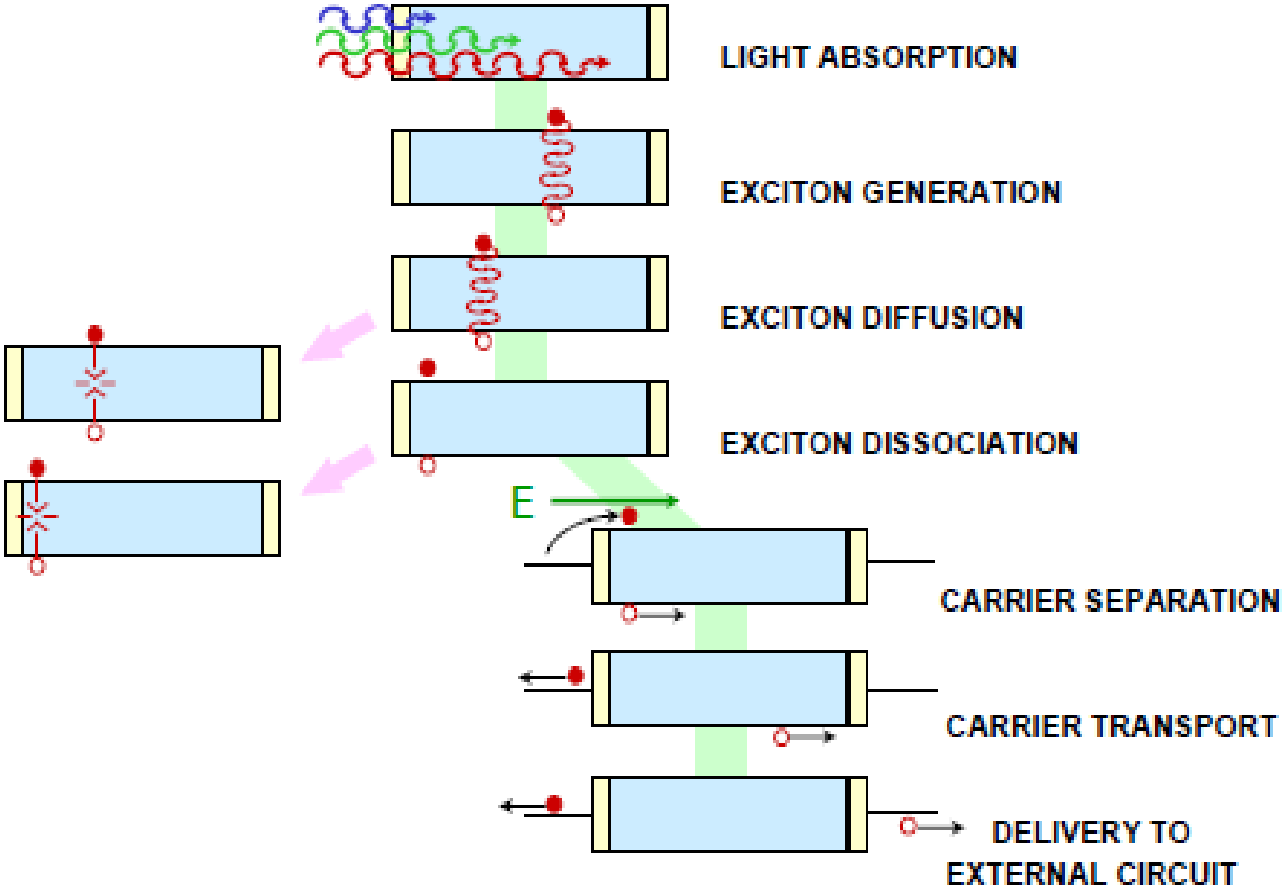



Small molecules are thermally evaporated in vacuum

# Organic device

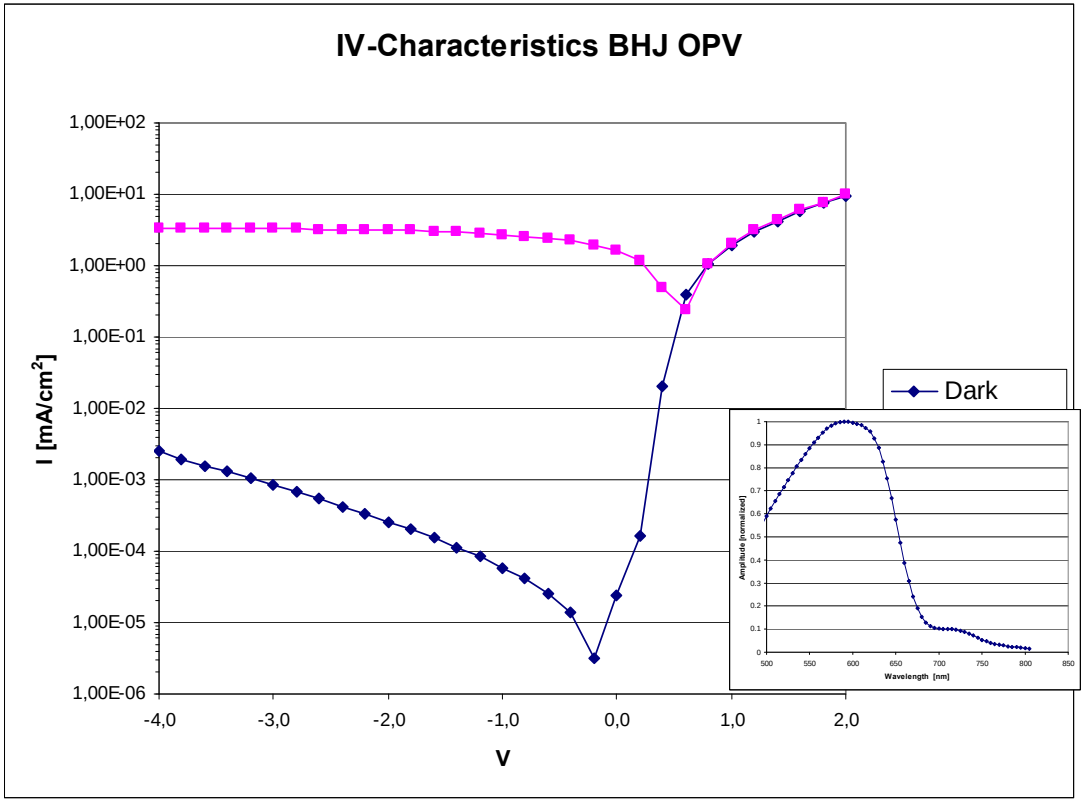
# Photodetector: operating principle

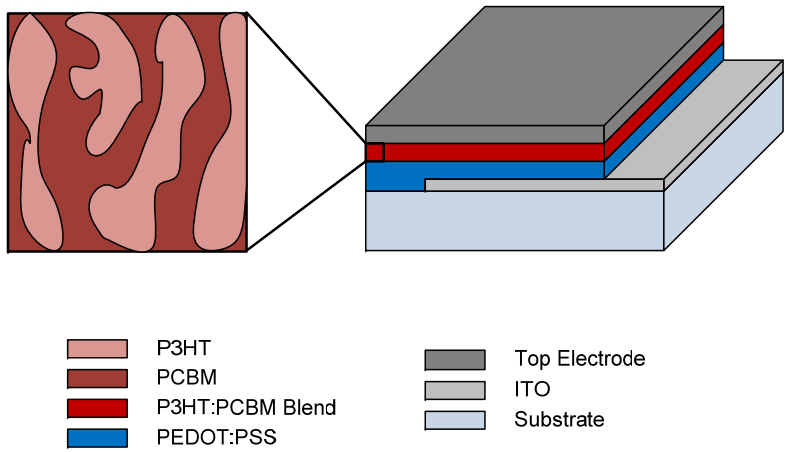
**photon absorption, creating excitons**



# Organic Photodetectors on glass

## Bulk heterojunction photodetector




ITO/PEDOT:PSS/P3HT:PCBM/LiF/AL

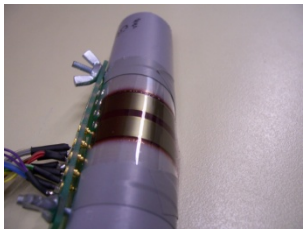
0.6 nm LiF, 100 nm Al

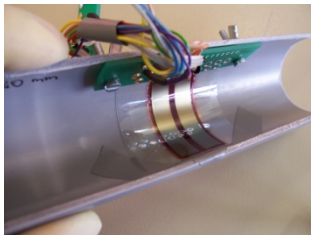
140 nm P3HT:PCBM (1:1)

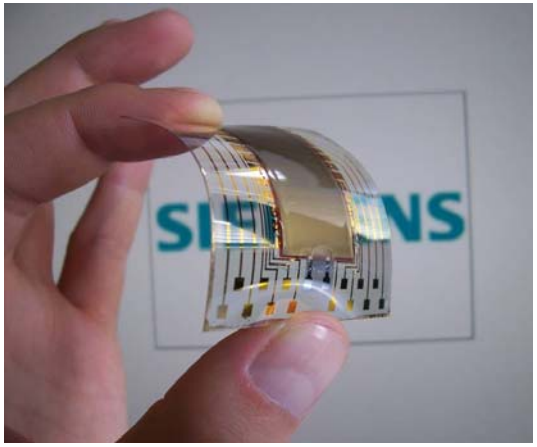
- OPD with on/off ratio of more than $10^4$ @ -1 V

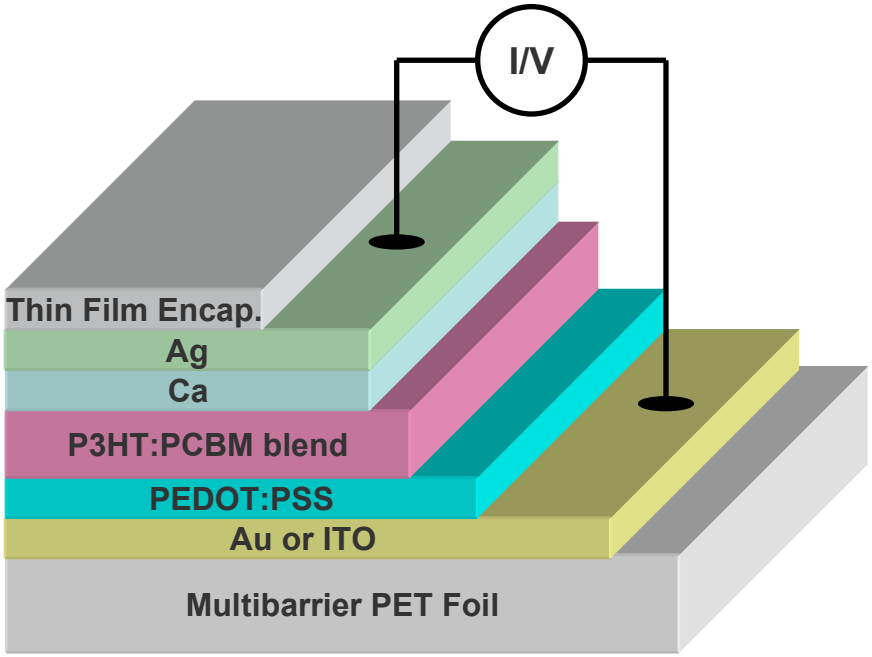
S. Tedde *et al.*, *Fully Spray Coated Organic Photodiodes*, Nano Letters 9 (3), 980 (2009)

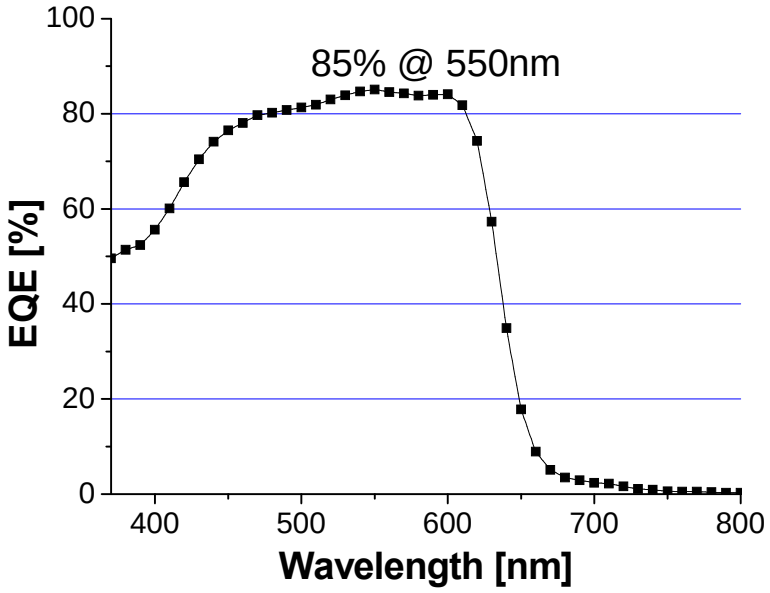
# Organic Photodetectors on plastic










SIEMENS

# Organic Photodetectors

## NIR Photodetector structure

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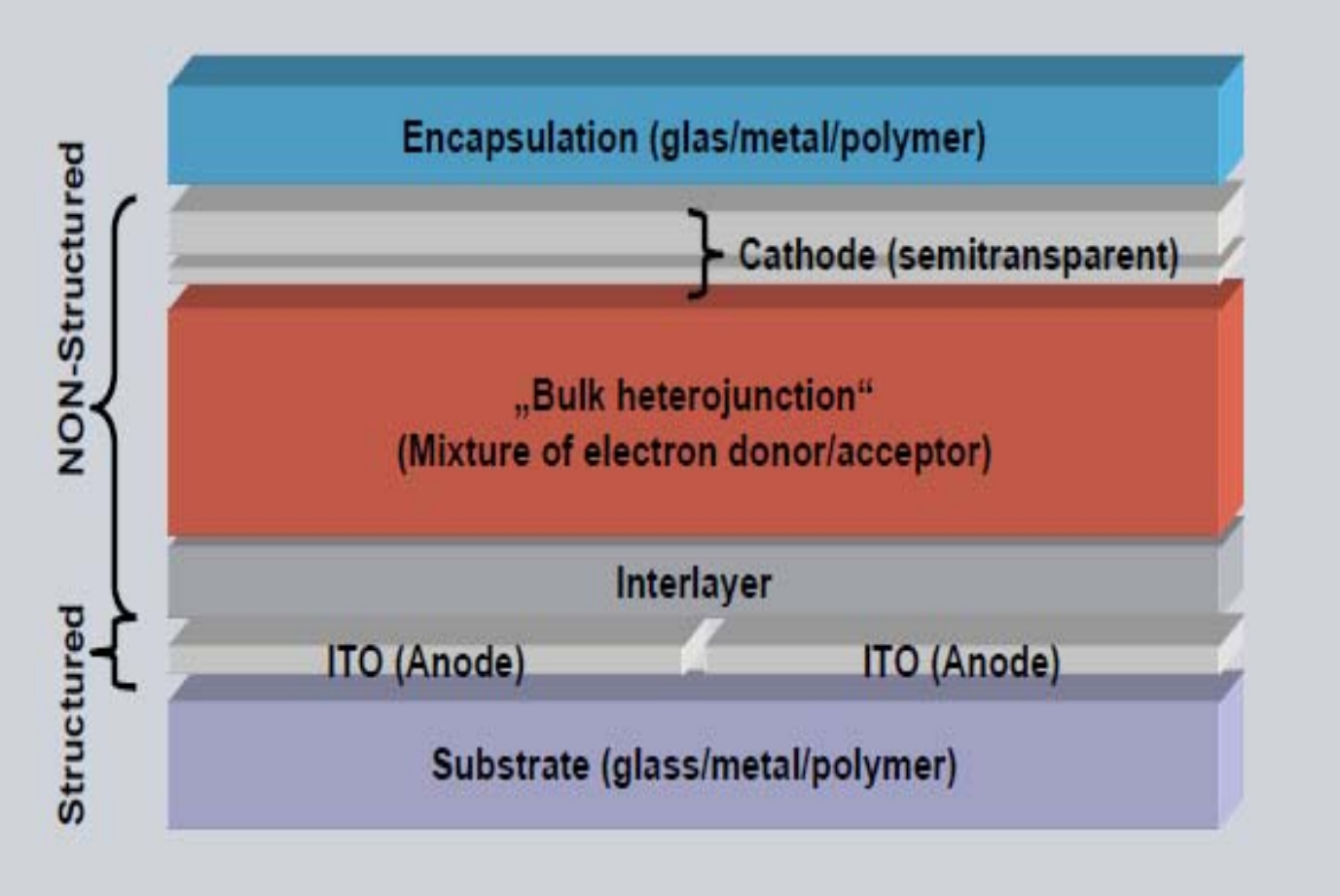
Near to market product (end 2011)



## Current voltage characteristics

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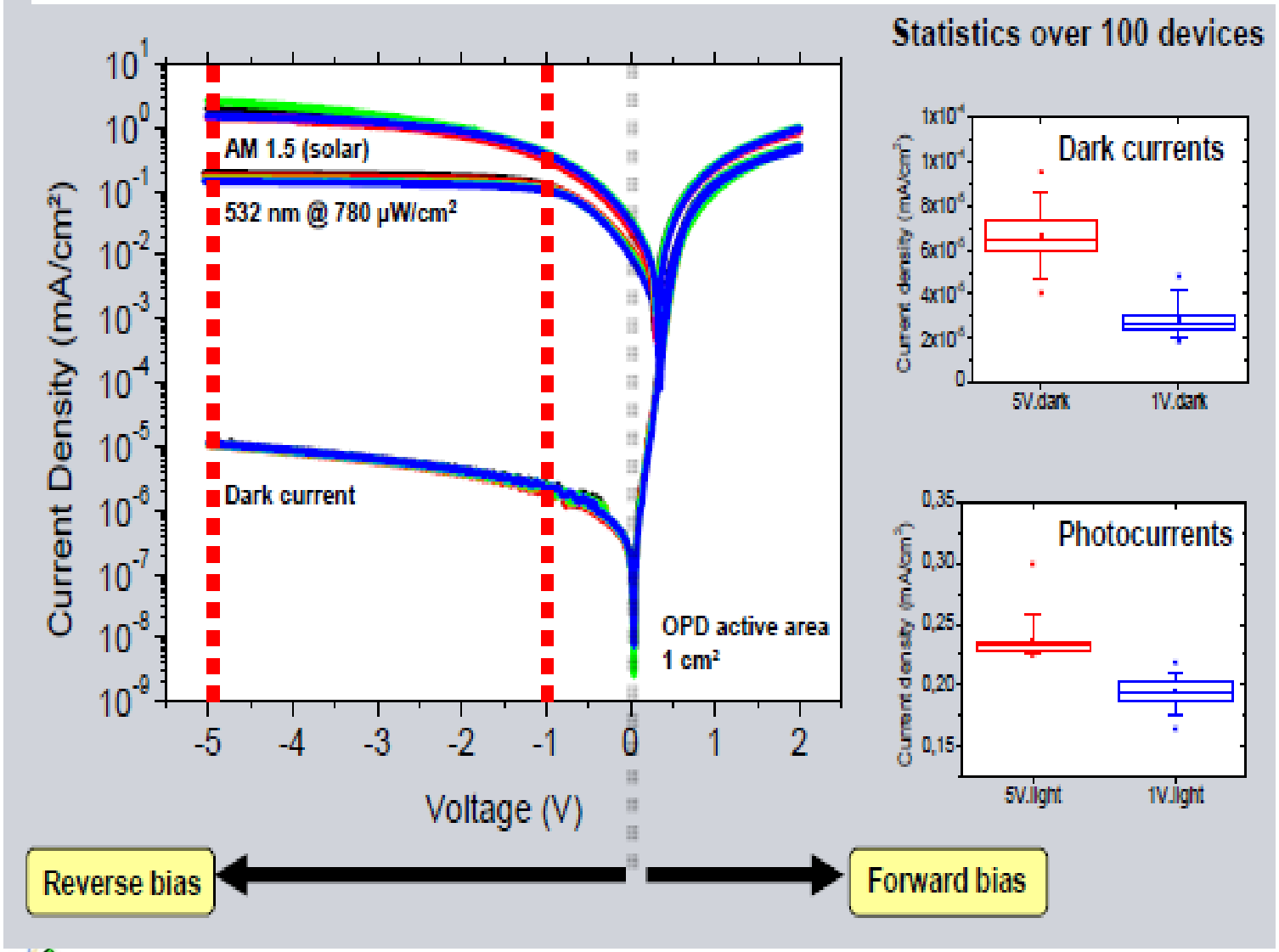

## VIS to NIR spectra sensitivity

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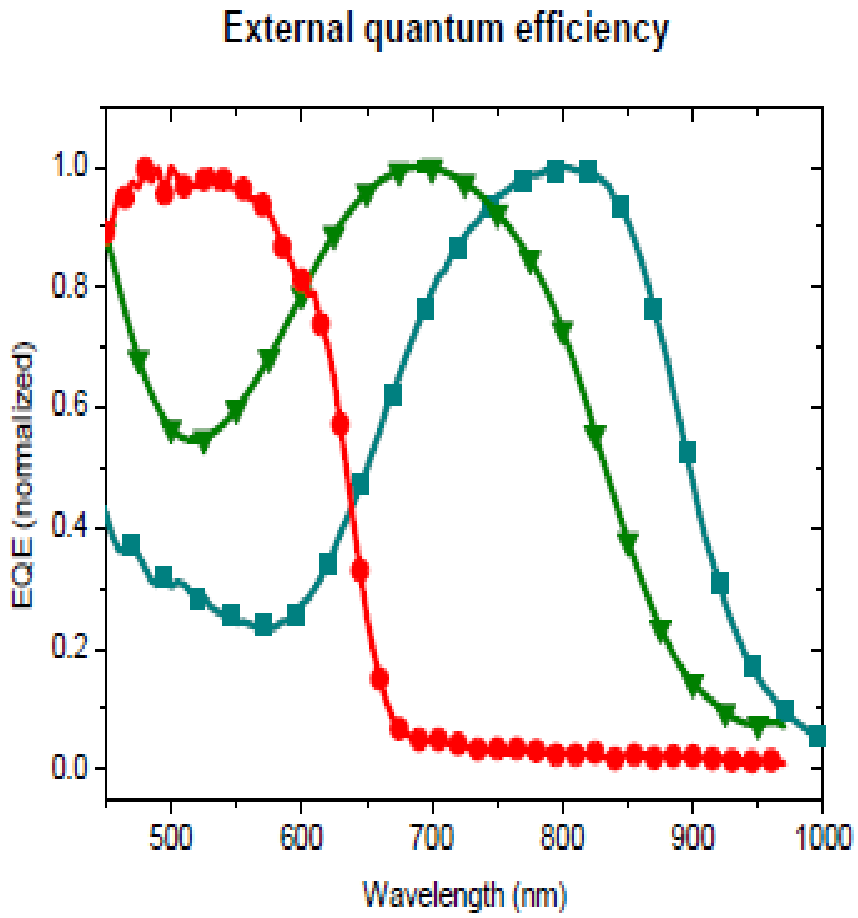


$$EQE \sim \frac{Electrons}{Photon}(\%)$$

Tailored absorption spectra with different organic semiconductors in a BHJ covering the VIS-NIR range

## Dynamic response

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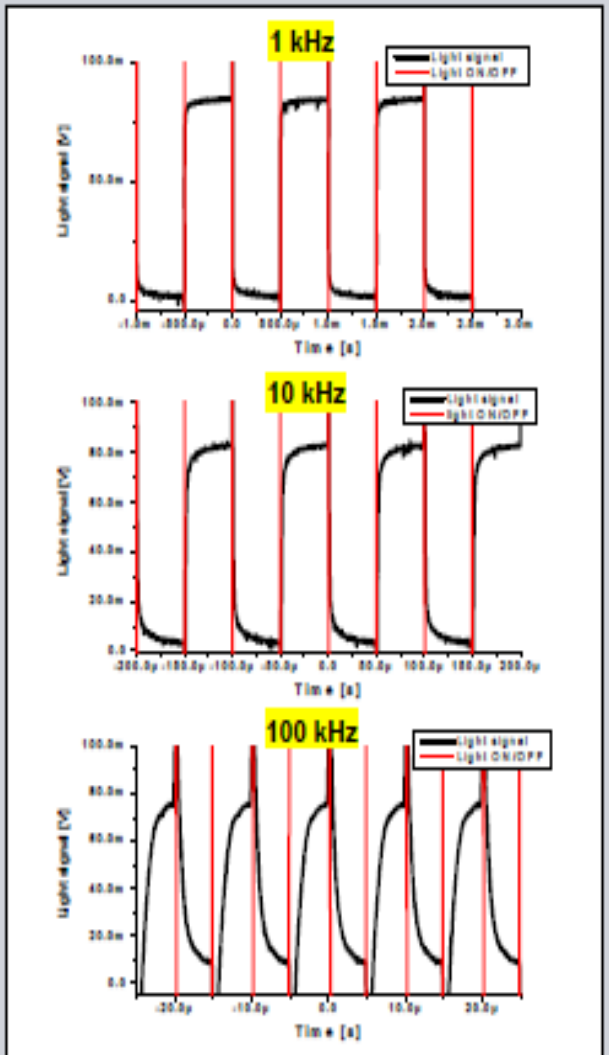
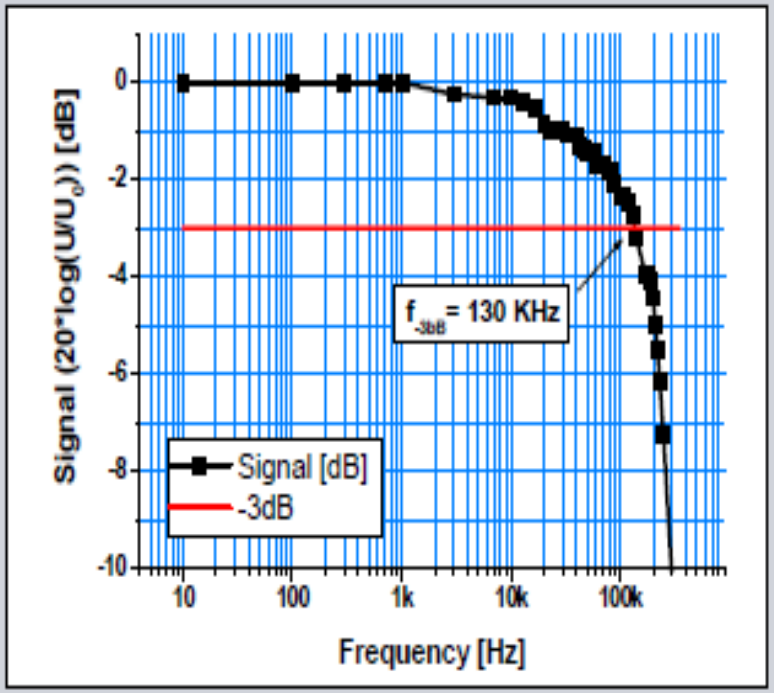
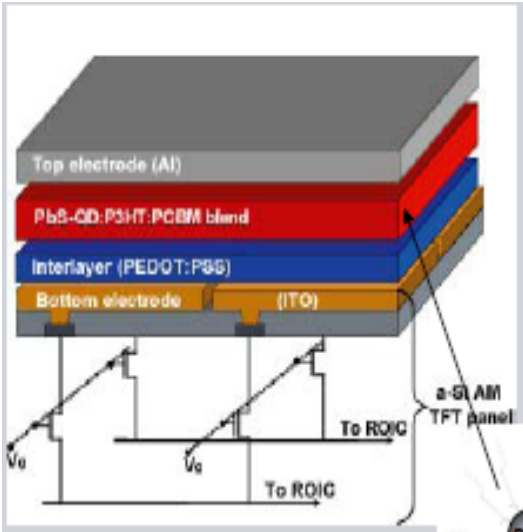


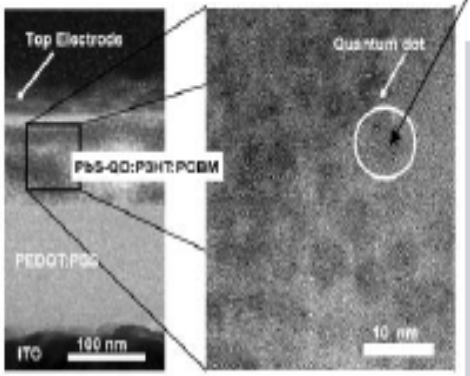



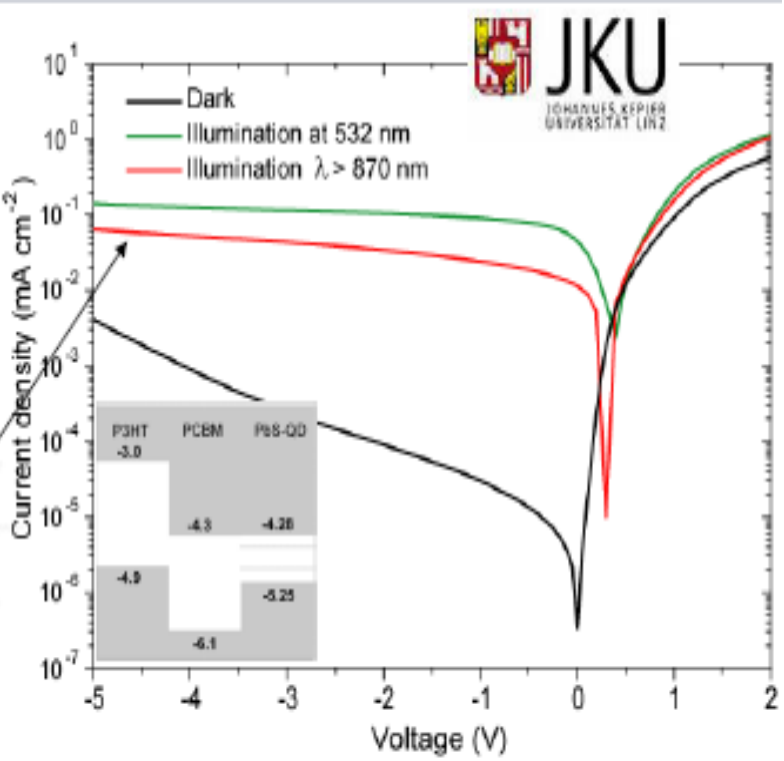

Active area: 0.7 cm²

Light source: - 1 KingBright SMD Chip LED KPL-3015SRC-PRV
(λ peak ~660 nm) super bright red light
- Light intensity ~ 130 µW/cm²

# Quantum Dots in Organic BHJ for NIR Hybrid Photodiodes



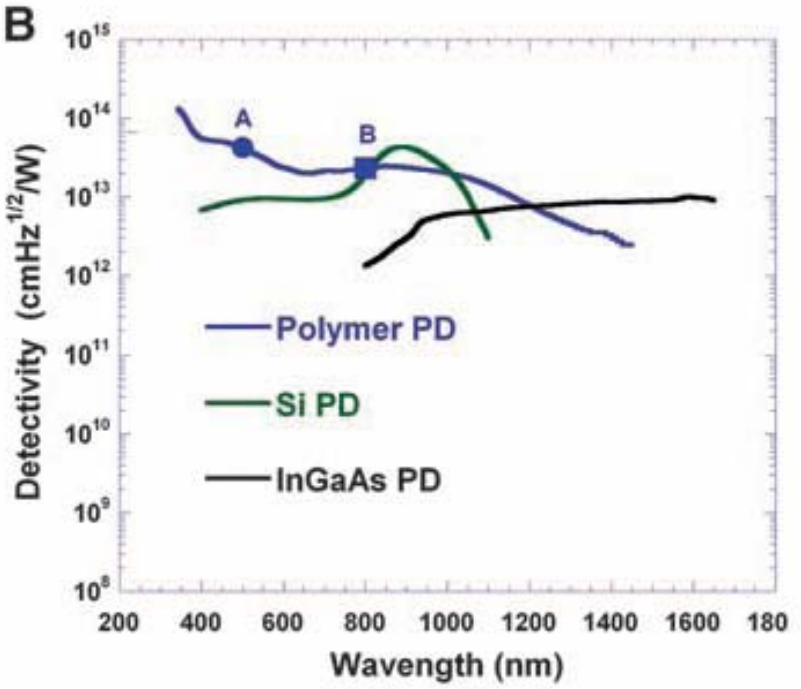

Embedding colloidal PbS-QDs into a bulk-heterojunction:

- Photodiode behavior is retained
- Sensitivity is expanded to the NIR
- Charge transfer to BHJ from PbS-QDs
- Hole/Electron extraction over BHJ (PbS-QD oleic acid capped)

# Conclusion

## Organic advantages

- Metallic and semiconducting properties by doping
- Combination of plastic with electronic properties
- Property engineering
- Solubility in organic solvents, variable processibility
- Use of printing technologies
- No vacuum and no high temperature processes




**Low-cost production**

## Disadvantages

- Low integrated devices and circuits
- Degeneration in $O_2$- and $H_2O$-atmosphere

**Long-term stability is still a critical point**

## Integration with CMOS

The combination of organic semiconductors with a CMOS-chip offers advantages compared with a conventional CMOS-sensor:

- high photosensitivity -> fill factors up to 100 %
- wavelength tunability -> sensors for infrared/ultraviolet region
- inexpensive fabrication
- subwavelength grading for optimized performance and polarization sensitivity

## Requirements for combination CMOS-organic

- work function of the metallization of CMOS chip must be aligned to organic semiconductor energy levels -> e.g. Aluminium
- deposition process of organic semiconductors should be possible on rough/patterned surfaces

# Thanks