ET-1039: Nanotechnology

UNIVERSITAT JAUME•I

Chapter 4: Applications with organic, inorganic and hybrid materials

4.1 Photocatalysis

4.2 Optoelectronic devices

4.3 Solar cells

4.4 Sensors

4.5 Batteries and supercapacitors

4.6 Other applications

4. Applications with organic, inorganic and hybrid materials

4.1 Photocatalysis

semiconductors

4. Applications with organic, inorganic and hybrid materials

4.3 Electronic and optoelectronic devices

This section starts with the introduction of organic materials with semiconducting properties. Their properties allow producing OFET, transistors, organic solar cells, OLED and electrochromic displays with flexible materials. Then, other technologies in the field of electrochromism are presented, including metal oxides, liquid crystals and other optoactive polarizable molecules

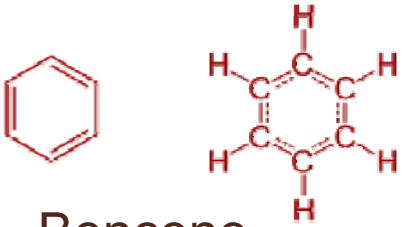
One of the strong tracking forces for the the application of organic materials as semiconductors is the potential for their large scale fabrication using well-known standard polymer technology. Together with the properties of polymers, this allows an enormous flexibility in the design of optoelectronic devices which may be produced at low cost and weight.

Organic semiconductors use the conjugation of molecular orbitals to produce delocalized bands extended along the complete material

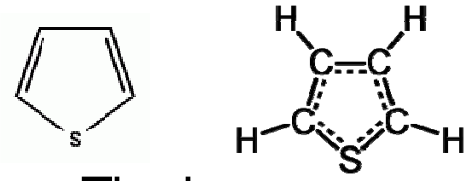
4. Applications with organic, inorganic and hybrid materials

4.3 Electronic and optoelectronic devices

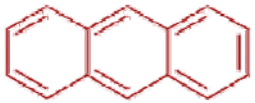
Organic semiconductors: some conductive polymers (and their monomers)



Bencene

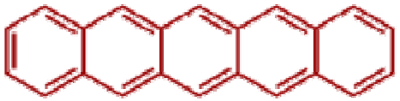


Tiophene

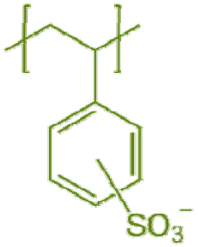


Anthracene

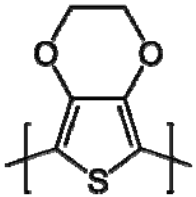
Polytiophene



Pentacene



PSS
Poly(styrene sulfonate)

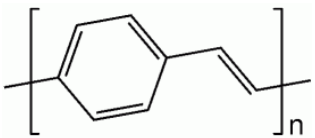


PEDOT
poly(3,4-ethylene dioxythiophene)

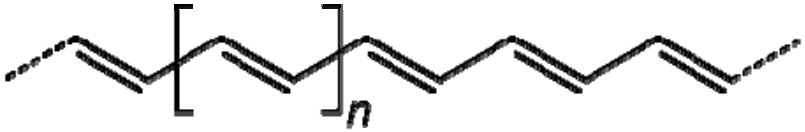
4. Applications with organic, inorganic and hybrid materials

4.3 Electronic and optoelectronic devices

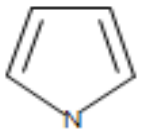
Organic semiconductors: some conductive polymers
(and their monomers)



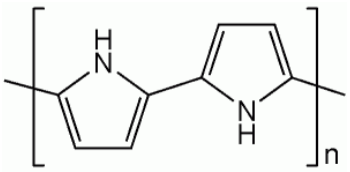
PPV
polyphenylene vinylene



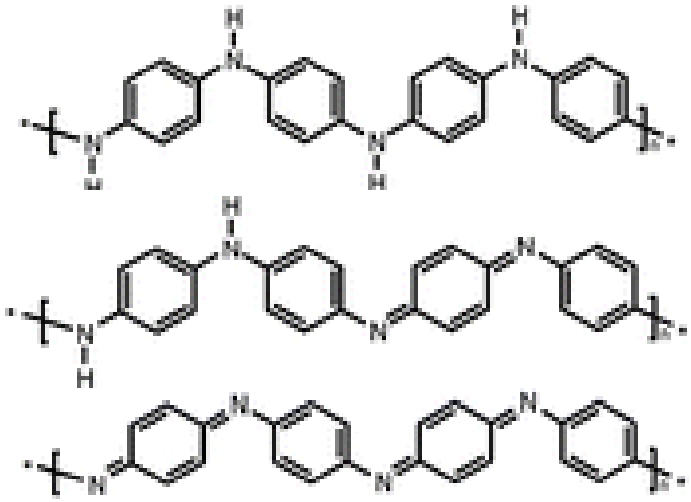
polyacetylene



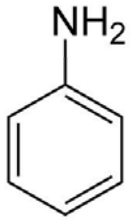
Pyrrol



PPy
polypyrrole



PANI: Polyaniline

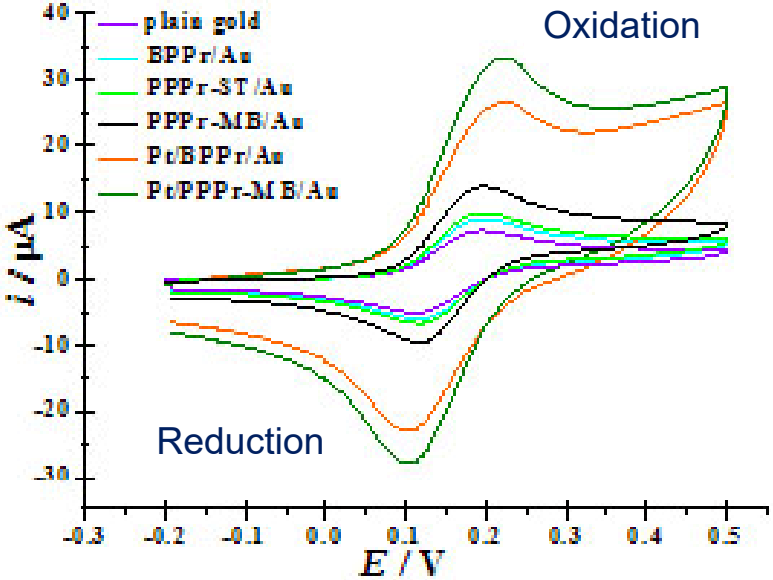


aniline

4. Applications with organic, inorganic and hybrid materials

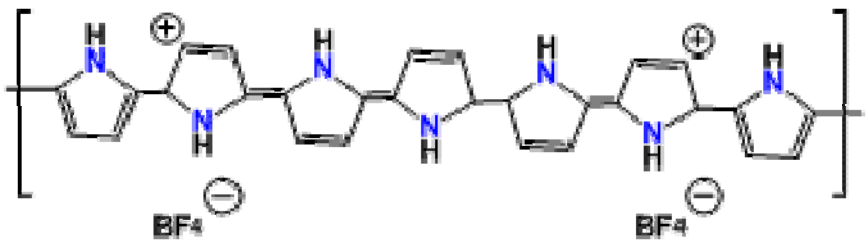
4.3 Electronic and optoelectronic devices

Organic semiconductors
Electrochemical doping

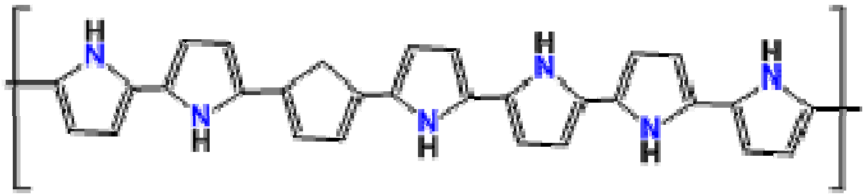


Conductivity: 0.1-100 S·cm^{-2}

Polypyrrole: oxidized form



Oxidation ⇅ Reduction



Polypyrrole: reduced form

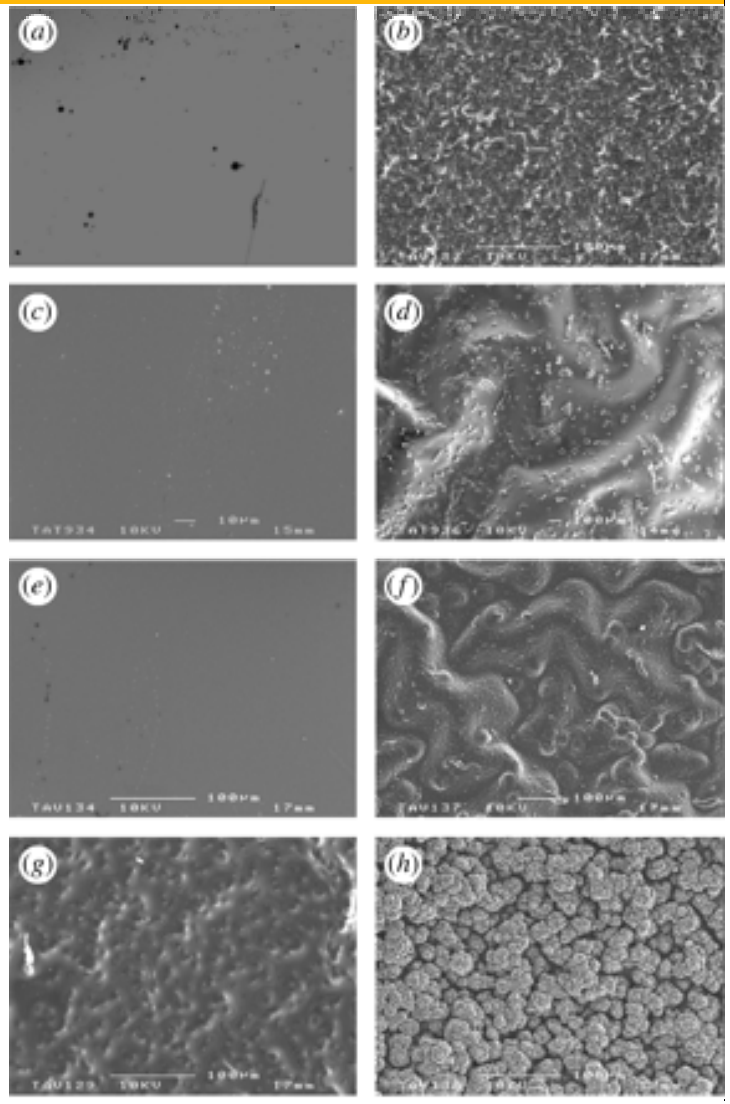
http://www.chemtube3d.com/polymer/_PyrroleF.html
http://www.ceb.cam.ac.uk/research/groups/rg-eme/research/microfuel-cells

4. Applications with organic, inorganic and hybrid materials

4.3 Electronic and optoelectronic devices

Organic semiconductors

Scanning electron microscopy images of polypyrrole (PPy) surface topography generated for different counterions and electropolymerization durations (*a–b*) PPy/chloride, (*c–d*) PPy/polyvinyl sulphate, (*e–f*) PPy/dermatan and (*g–h*) PPy/collagen. The shorter times produced thin films (left column) with none or little surface features whereas at extended times, thicker films with distinct topography are seen (right column). More instances of counterion controlled topography may be found in the literature (Skotheim 1986).



*J. R. Soc. Interface 2006 , **3** (11), 741-752*

4. Applications with organic, inorganic and hybrid materials

4.3 Electronic and optoelectronic devices

Organic semiconductors

Formulation	Conductivity ($mS\ cm^{-1}$)
1.00:0.25:1.60 aniline:APS:DBSA (Example 1)	0.8 ± 0.1
1.0:0.5:1.6 aniline:APS:DBSA	2.2 ± 0.2
1.0:1.0:1.6 aniline:APS:DBSA	32.8 ± 7.4
1.0:0.5:1.2 aniline:APS:DBSA	4.3 ± 0.6

PANI: polyaniline
APS: Ammonium persulfate
DBSA: dodecylbenzenesulfonic acid

Graphene: $1.0 \cdot 10^9$ mS/cm
Sea water 48 mS/cm
Drinking water 0.8 mS/cm

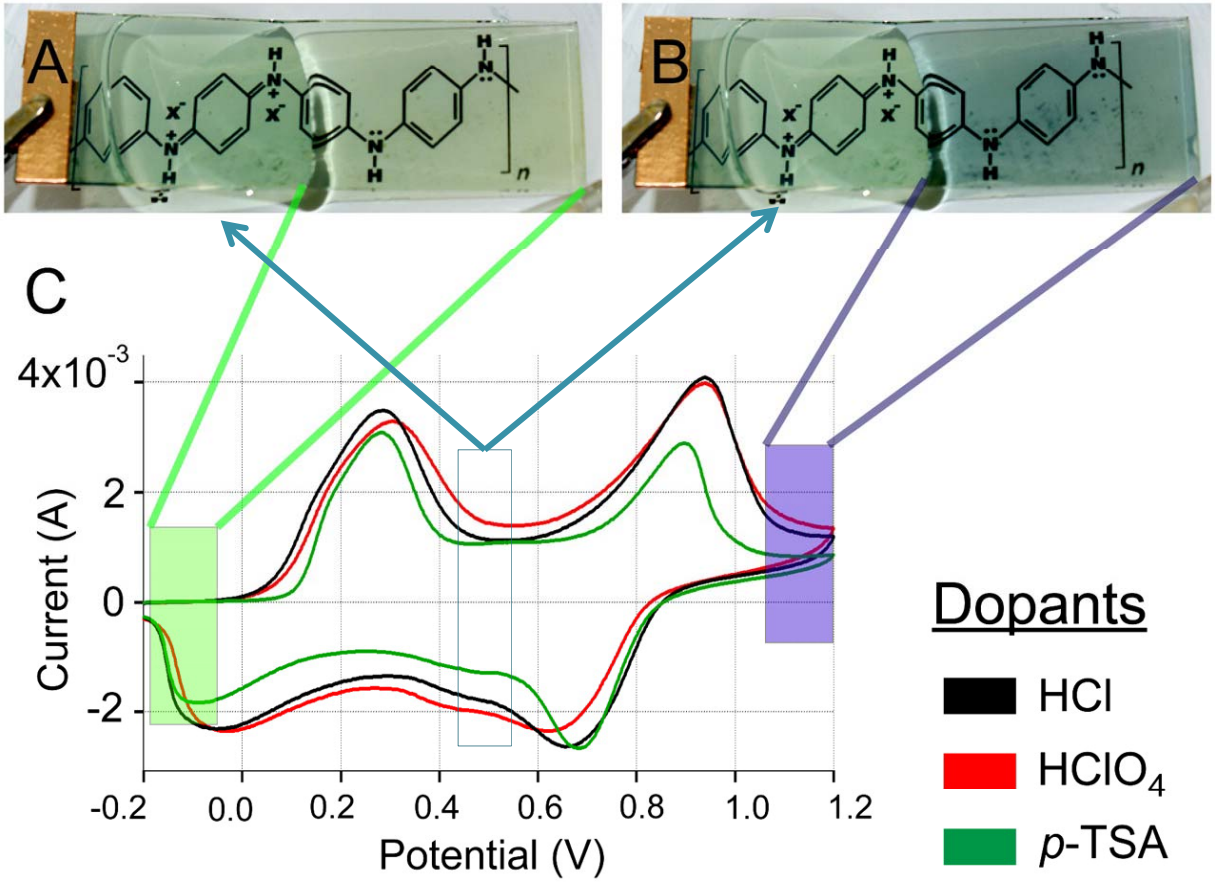
Cu :$6.0 \cdot 10^8$ mS/cm
Ge: 21.7 mS/cm
Si: 0.015 mS/cm

4. Applications with organic, inorganic and hybrid materials

4.3 Electronic and optoelectronic devices

Organic semiconductors

PANI: Polyaniline

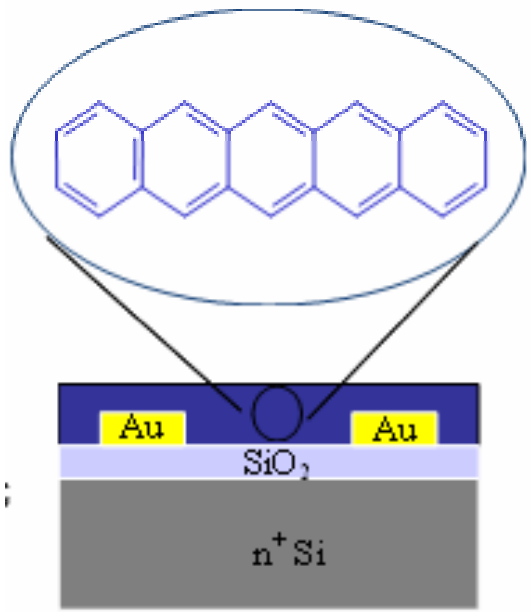


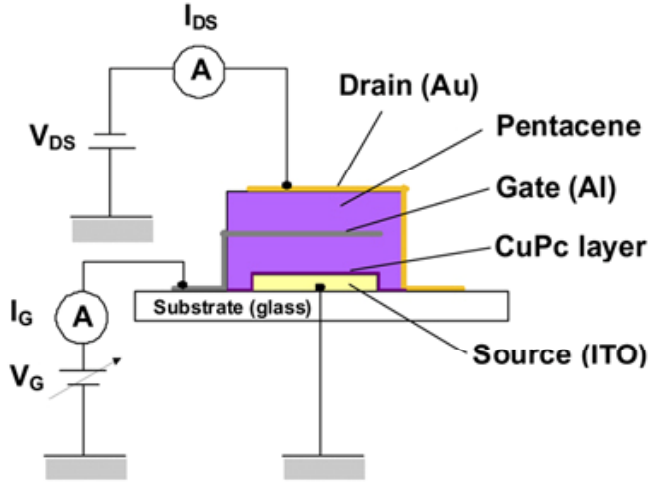
*PNAS 2010, **107**, 19673-19678*

4. Applications with organic, inorganic and hybrid materials

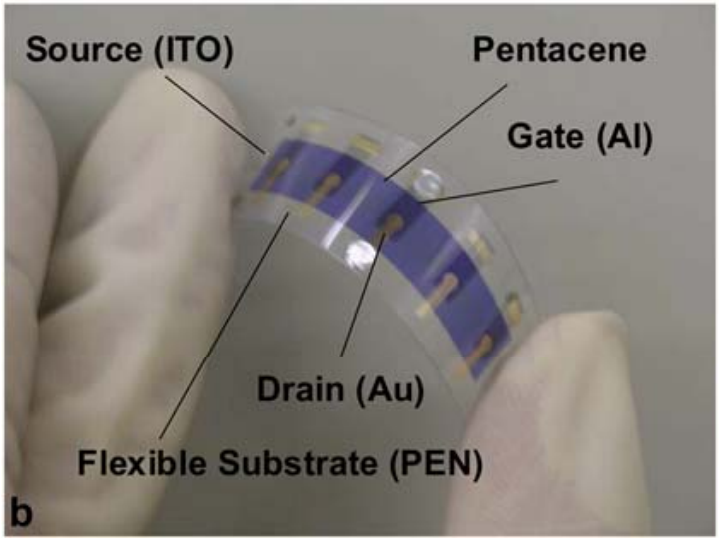
4.3 Electronic and optoelectronic devices

Organic Transistors (OFET)





a



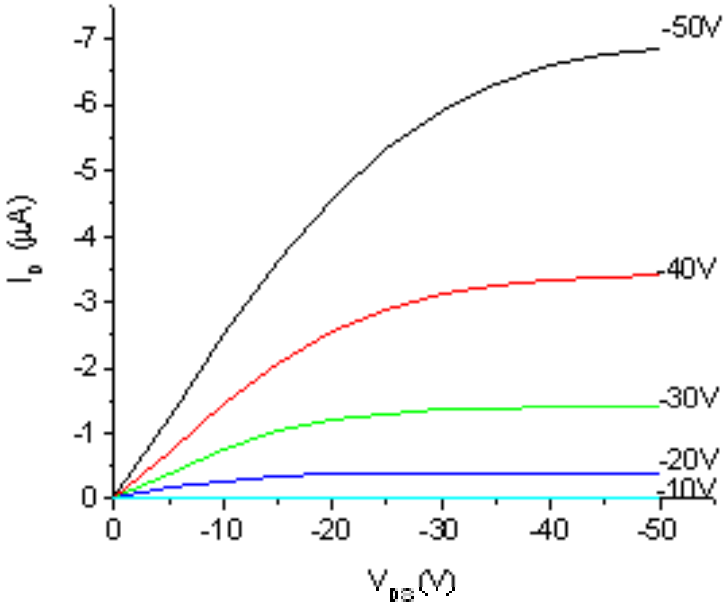
b

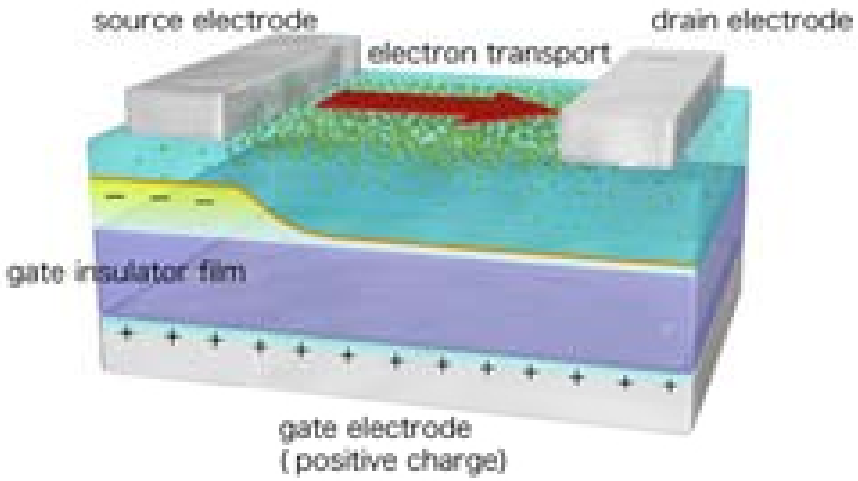
https://spie.org/x36406.xml

4. Applications with organic, inorganic and hybrid materials

4.3 Electronic and optoelectronic devices

Organic Transistors (OFET)





4. Applications with organic, inorganic and hybrid materials

4.3 Electronic and optoelectronic devices

Organic Light Emitting devices (OLED)

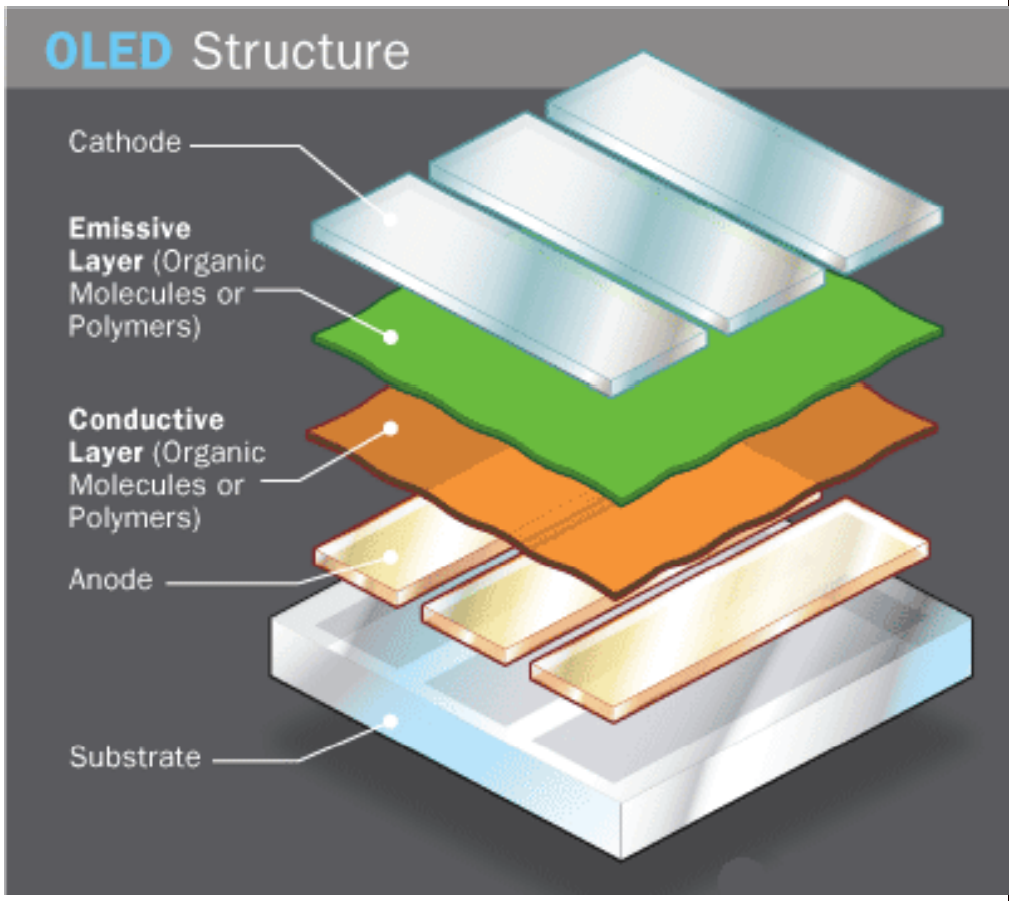
Al, Ca

PPV (polyphenylene vinylene)
PPy (Polypirrole)

PEDOT-PSS

ITO ($In2O_3$+SnO_2)

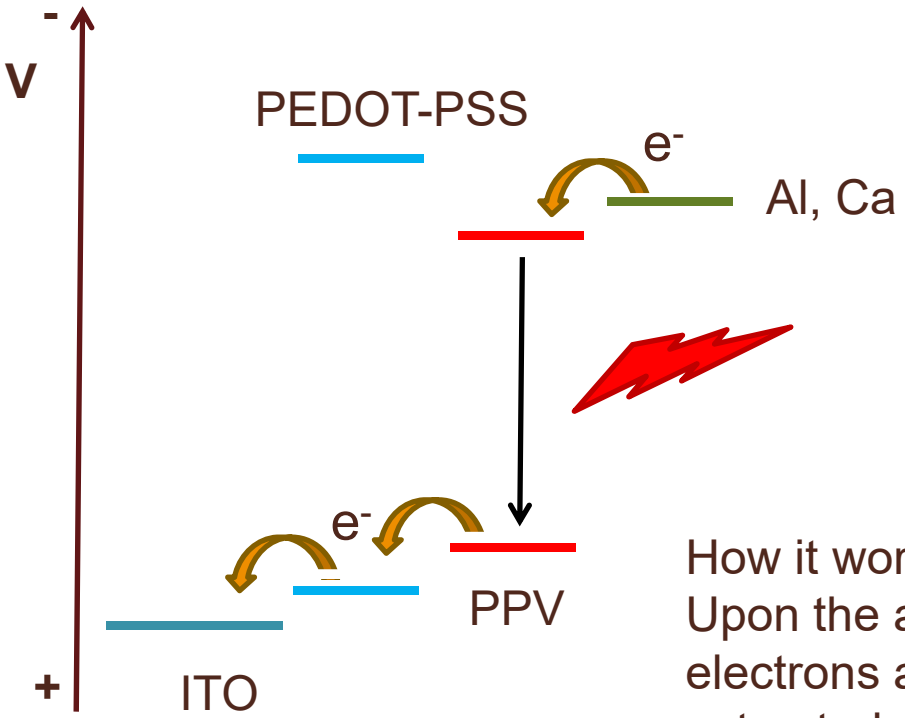
PEN, glass…

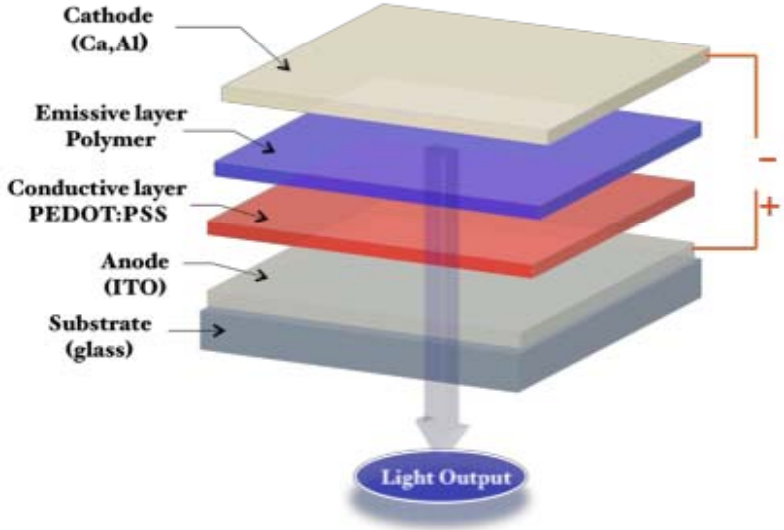


4. Applications with organic, inorganic and hybrid materials

4.3 Electronic and optoelectronic devices

Organic Light Emitting devices (OLED)



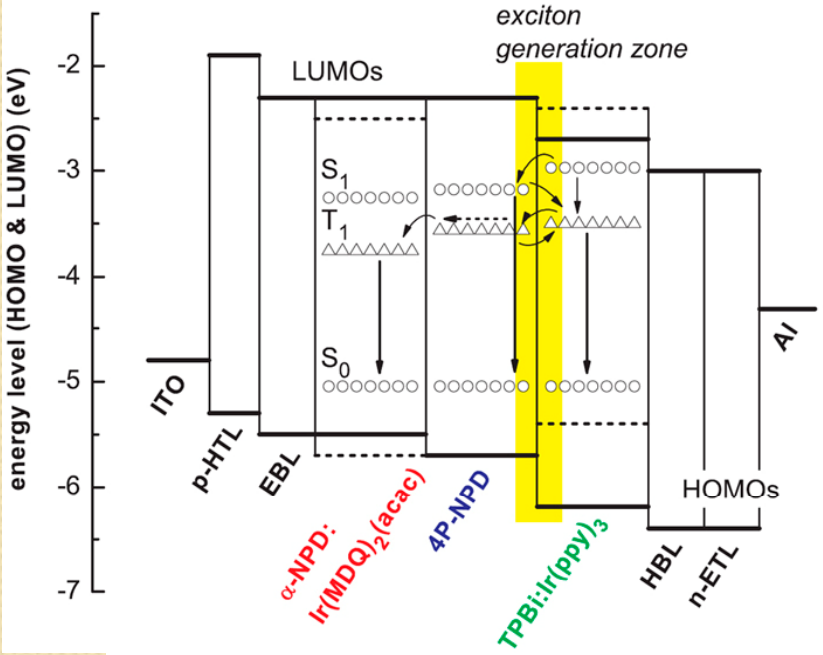


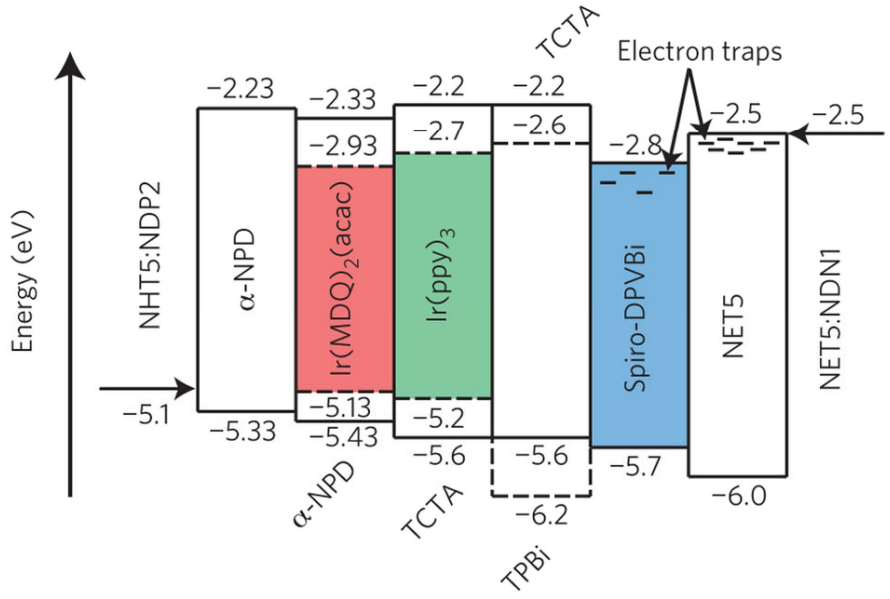
How it works:
Upon the application of a large enough voltage, electrons are injected from the cathode and extracted at the anode side.
This produces an electron in the CB (LUMO) and a hole in the VB (HOMO) of the emissive material that then, may recombine emitting light

4. Applications with organic, inorganic and hybrid materials

4.3 Electronic and optoelectronic devices

Organic Light Emitting devices (OLED)





Initial but incorrect Energetic schemes

https://spie.org/x38277.xml
Nature Materials 12, 652–658 (2013)

4. Applications with organic, inorganic and hybrid materials

4.3 Electronic and optoelectronic devices

Organic Light Emitting devices (OLED)

Advantages:

• Manufacture of OLED is highly economical and more efficient than LCD and flat panel screens.
• Contrast ratio of OLED is very high (high-definition)
• OLED can be watched from an angle close to 90 degrees.
• No backlight is produced by this device and the power consumption is very low for black dots.
• The response time is less than 0.01 ms (vs 1ms in LCD)

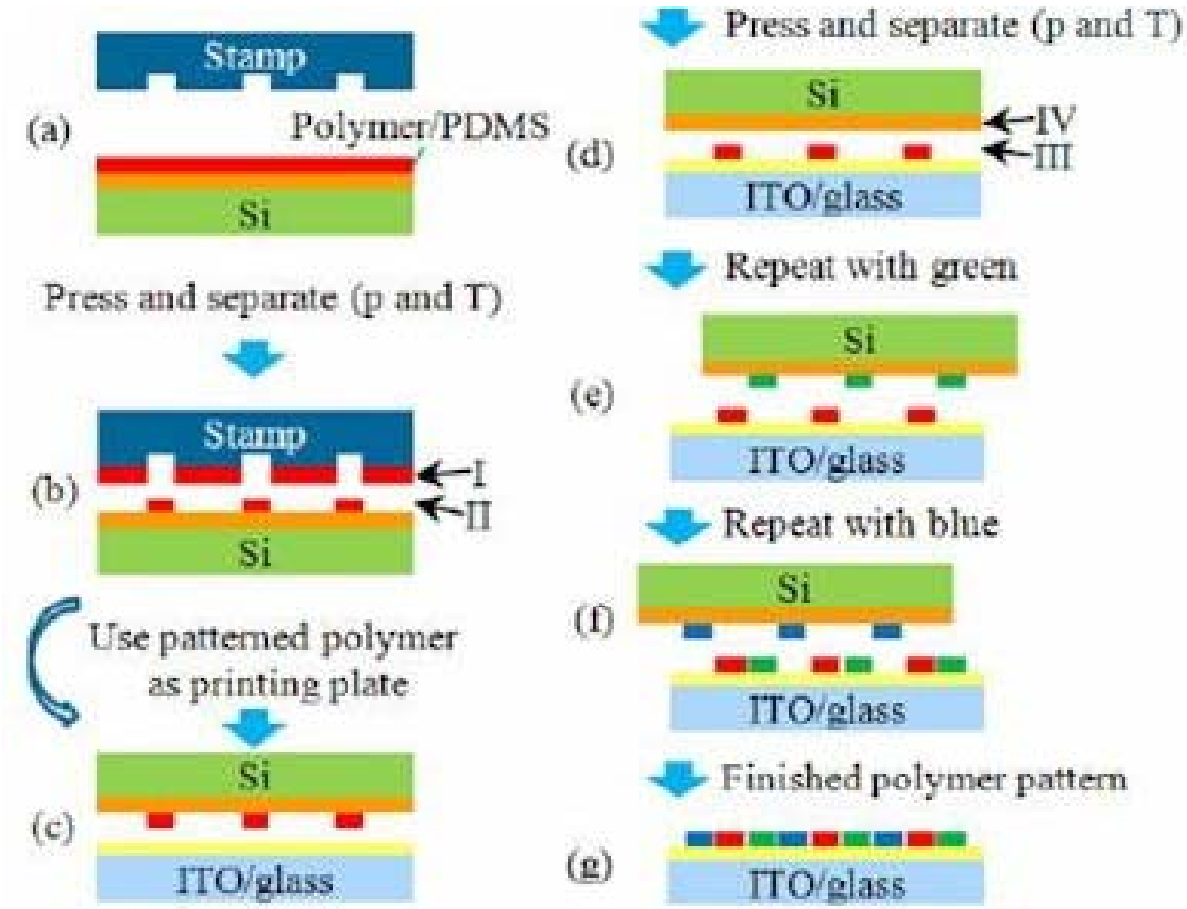
Disadvantages:

• The power consumption of this device depends upon the color with high consumption for bright colors (such white)
• The initial capital cost for production is high.
• Poor reading in bright light surroundings.
• The device is not at all water resistant.
• The lifetime of this device is much lesser when compared with an LCD or LED.

4. Applications with organic, inorganic and hybrid materials

4.3 Electronic and optoelectronic devices

Organic Light Emiting devices (OLED): fabrication

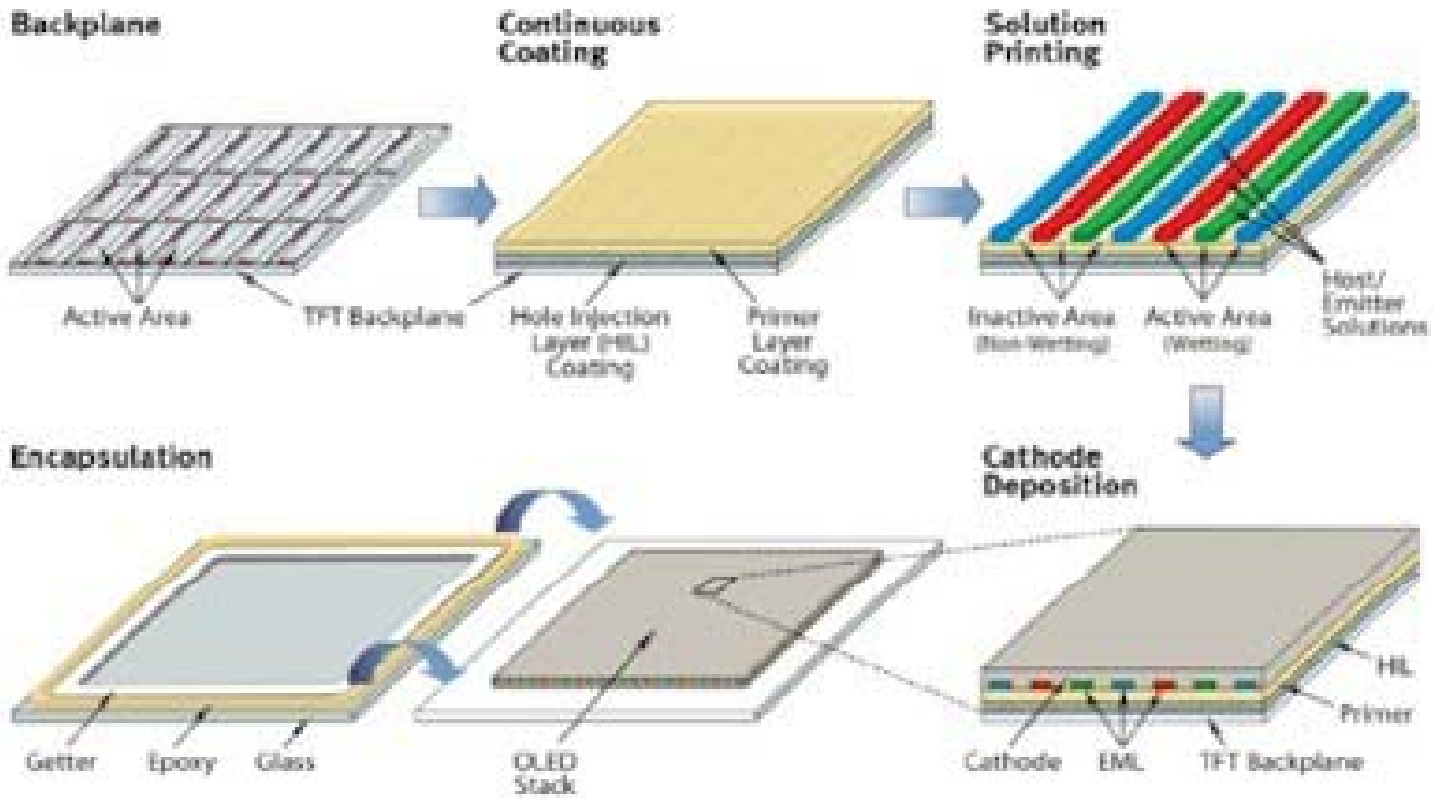


http://www.printedelectronicsworld.com/articles/oled-progress-round-up-from-s-i-d-2009-00001474.asp?sessionid=1

4. Applications with organic, inorganic and hybrid materials

4.3 Electronic and optoelectronic devices

Organic Light Emiting devices (OLED): fabrication

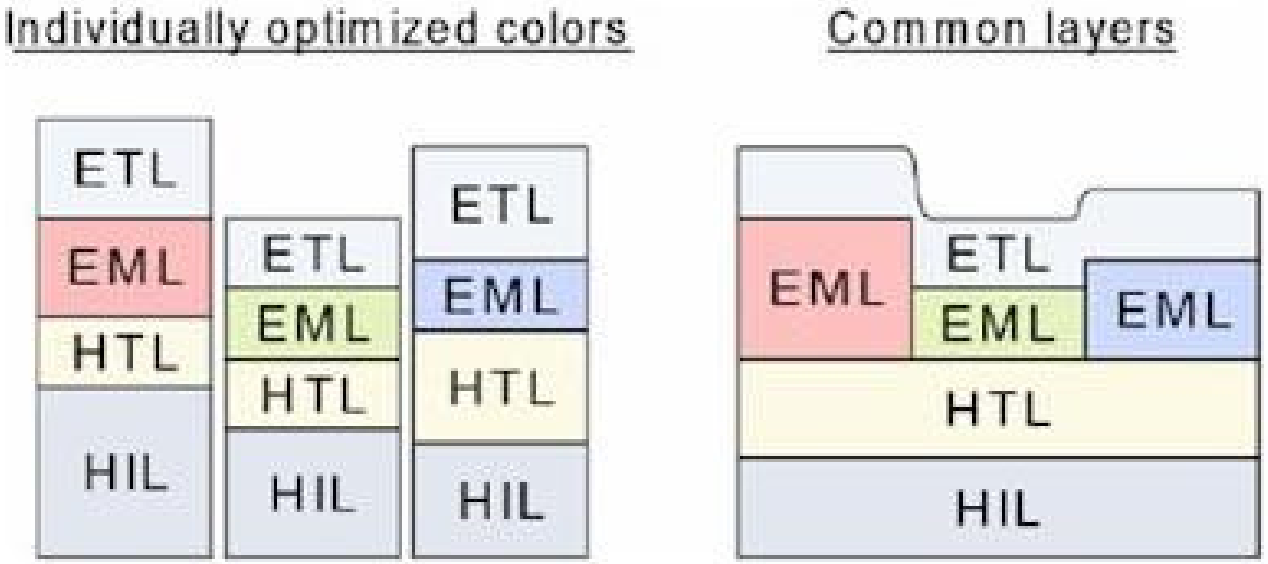


http://www.printedelectronicsworld.com/articles/oled-progress-round-up-from-s-i-d-2009-00001474.asp?sessionid=1
http://www.oled-info.com/introduction

4. Applications with organic, inorganic and hybrid materials

4.3 Electronic and optoelectronic devices

Organic Light Emitting devices (OLED): esquematics



Dupont

ETL: Electron Transport Layer
EML: EMision Layer
HTL: Hole Transport Layer
HIL: Hole Injection Layer

http://www.printedelectronicsworld.com/articles/oled-progress-round-up-from-s-i-d-2009-00001474.asp?sessionid=1

4. Applications with organic, inorganic and hybrid materials

4.3 Electronic and optoelectronic devices

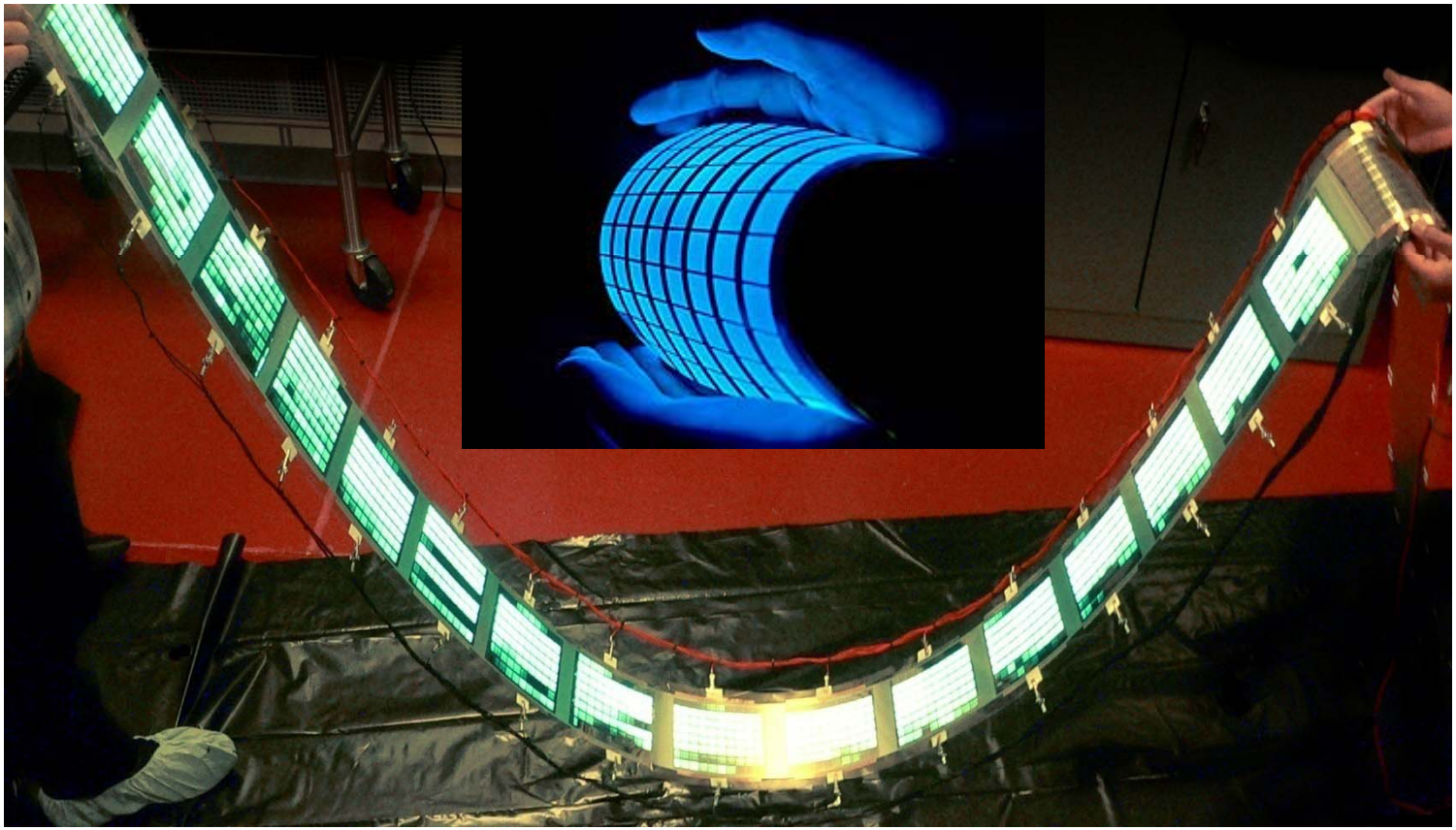
Organic Light Emitting devices (OLED)

http://www.printedelectronicsworld.com/articles/oled-progress-round-up-from-s-i-d-2009-00001474.asp?sessionid=1

4. Applications with organic, inorganic and hybrid materials

4.3 Electronic and optoelectronic devices

Organic Light Emitting devices (OLED)

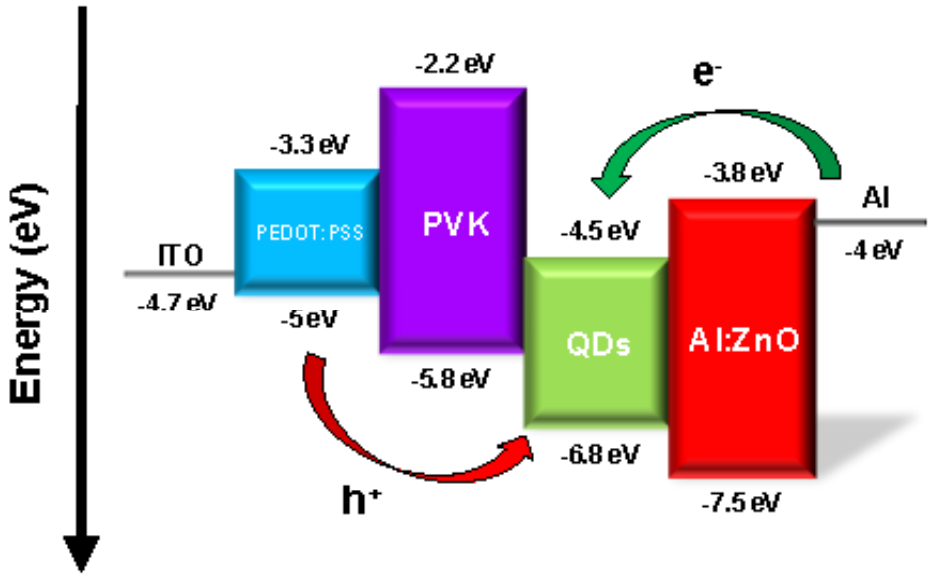


http://tyler.blogware.com/2008/3/11/
https://nice.asu.edu/nano/organic-led-lighting%E2%80%94nonacene

4. Applications with organic, inorganic and hybrid materials

4.3 Electronic and optoelectronic devices

Other configurations for Light Emitting devices: Quantum Dot (QD-LED)



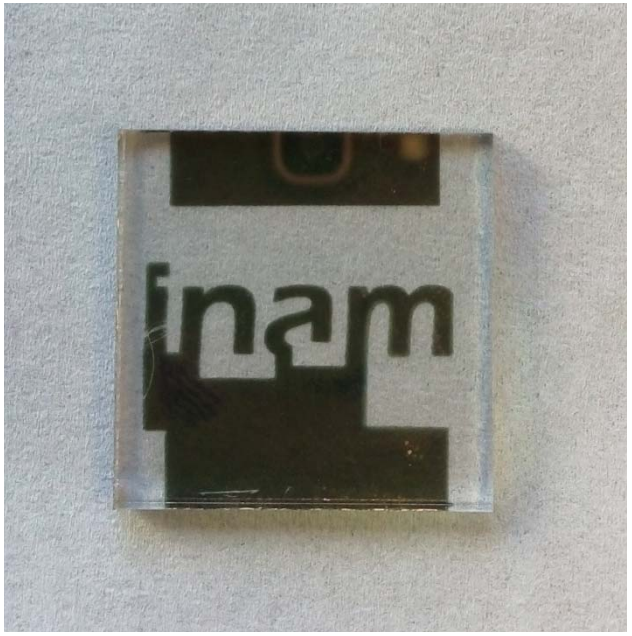
Blue light emitting QDs : CdZnS/ZnS
Green, Orange and Red QDs: CdSe/CdS/ZnS
PVK: poly(9-vinylcarbazole)

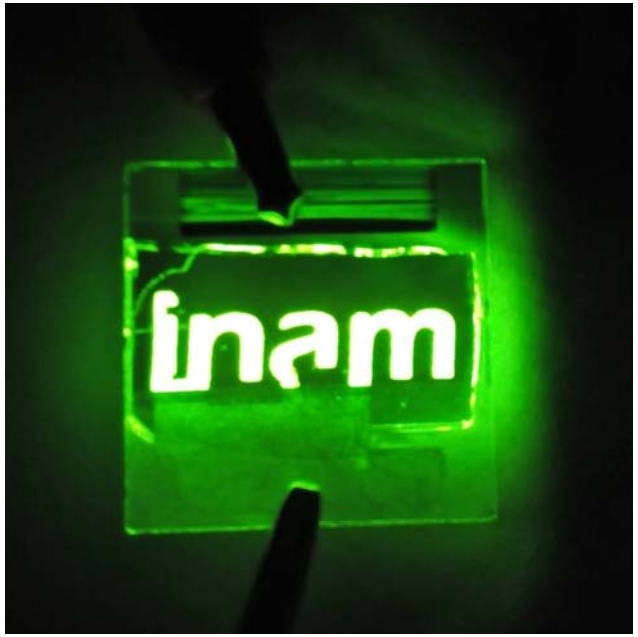
Images from Rafael Sánchez., INAM, UJI

4. Applications with organic, inorganic and hybrid materials

4.3 Electronic and optoelectronic devices

Other configurations for Light Emitting devices: Quantum Dot (QD-LED)





Images from Rafael Sánchez., INAM, UJI

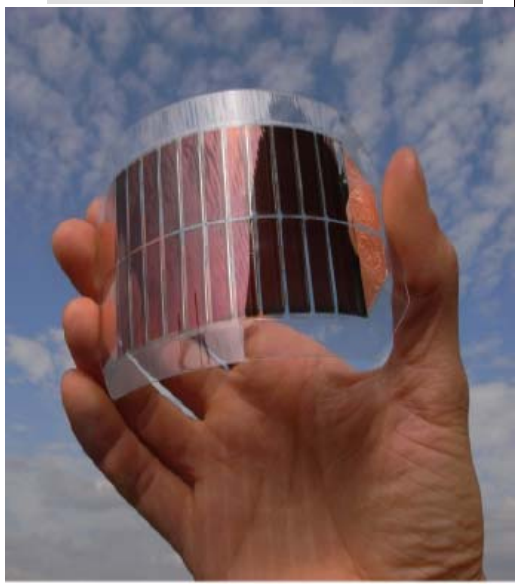
4. Applications with organic, inorganic and hybrid materials

4.3 Electronic and optoelectronic devices

Organic solar cells (OSC)

Advantages:
- Easy process,
- low cost
- Very intense absorption bands

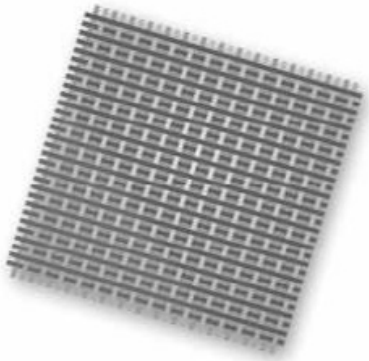
Inconvenients:
- Inestable under O_2 i H_2O
- Exciton diffusion length small (nm)



4. Applications with organic, inorganic and hybrid materials

4.3 Electronic and optoelectronic devices

Organic solar cells (OSC)



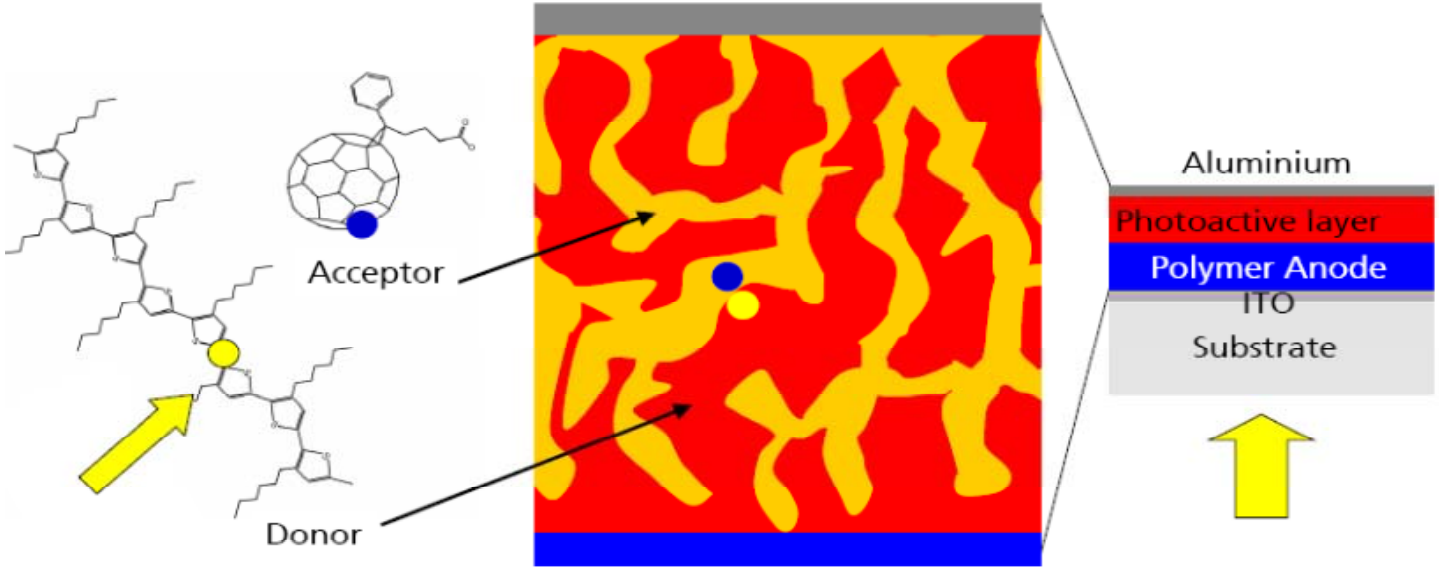
http://www.konarka.com
http://www.plextronics.com

4. Applications with organic, inorganic and hybrid materials

4.3 Electronic and optoelectronic devices

Organic solar cells (OSC): bulk Heterojunction

PCBM: fullerente derivative

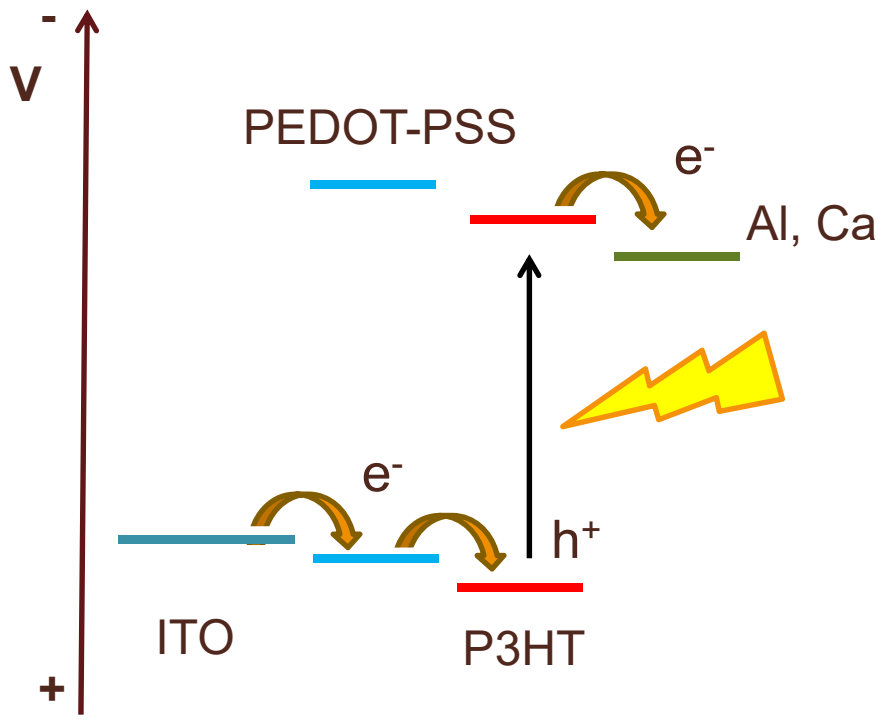


P3HT: Poly(3-hexylthiophene),

4. Applications with organic, inorganic and hybrid materials

4.3 Electronic and optoelectronic devices

Organic solar cells (OSC): bulk Heterojunction



How it works:

Light is absorbed by the photoactive molecule/polymer, generating an electron and a hole.

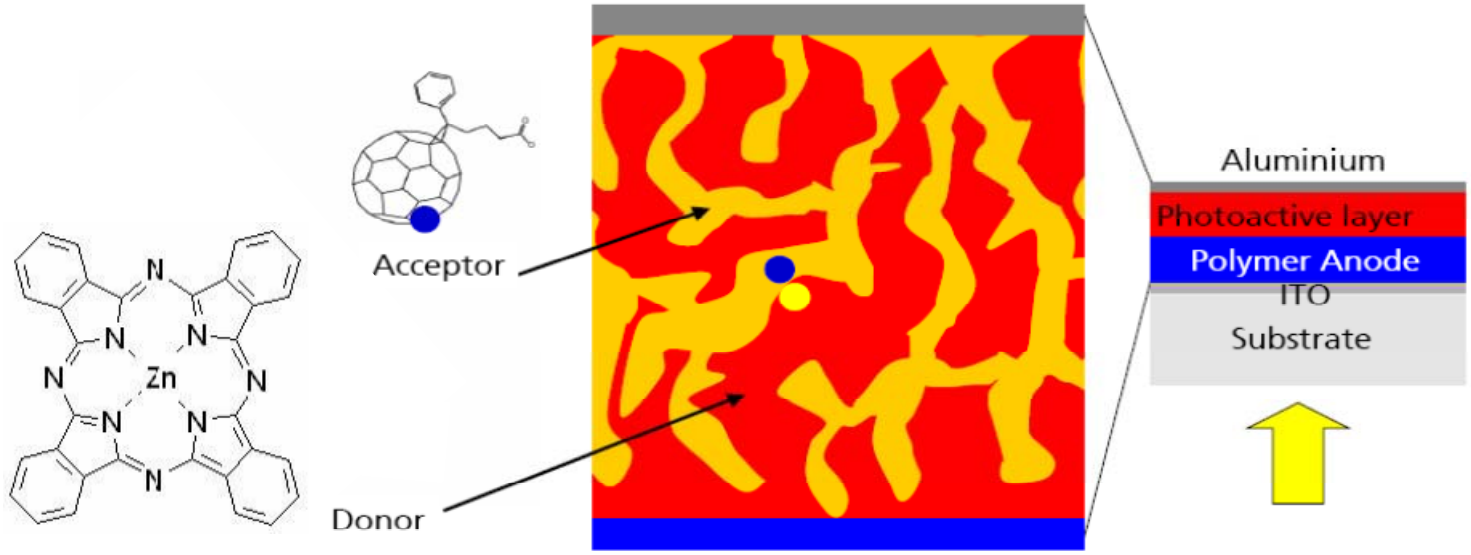
Electrons are extracted at the cathode. The anode, typically transparent (ITO) provides the electrons to the PEDOT-PSS (a hole conductor) that regenerate the absorber. Electron selective material may be introduced between the absorber and the cathode to enhance charge selectivity and thus performance.

4. Applications with organic, inorganic and hybrid materials

4.3 Electronic and optoelectronic devices

Organic solar cells (OSC): Small molecule

PCBM

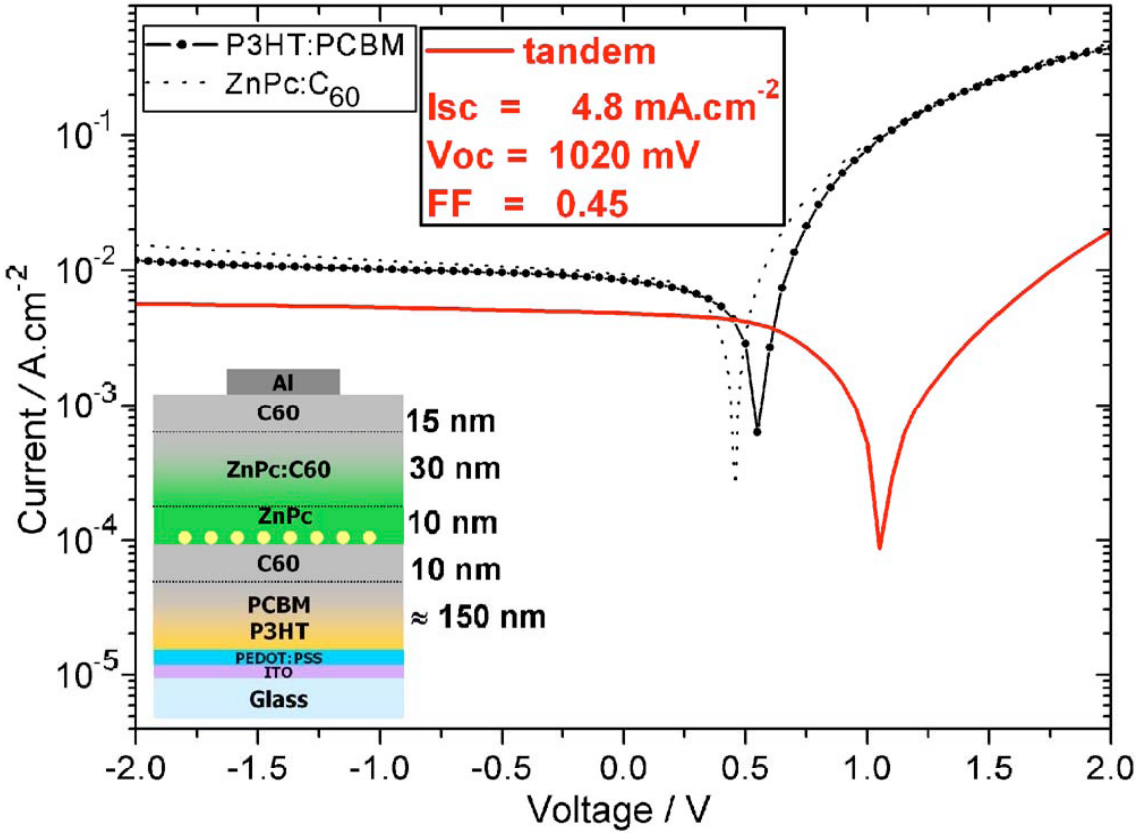


ZnPc: Zinc Phtalocyanine

4. Applications with organic, inorganic and hybrid materials

4.3 Electronic and optoelectronic devices

Organic solar cells (OSC): Tandem

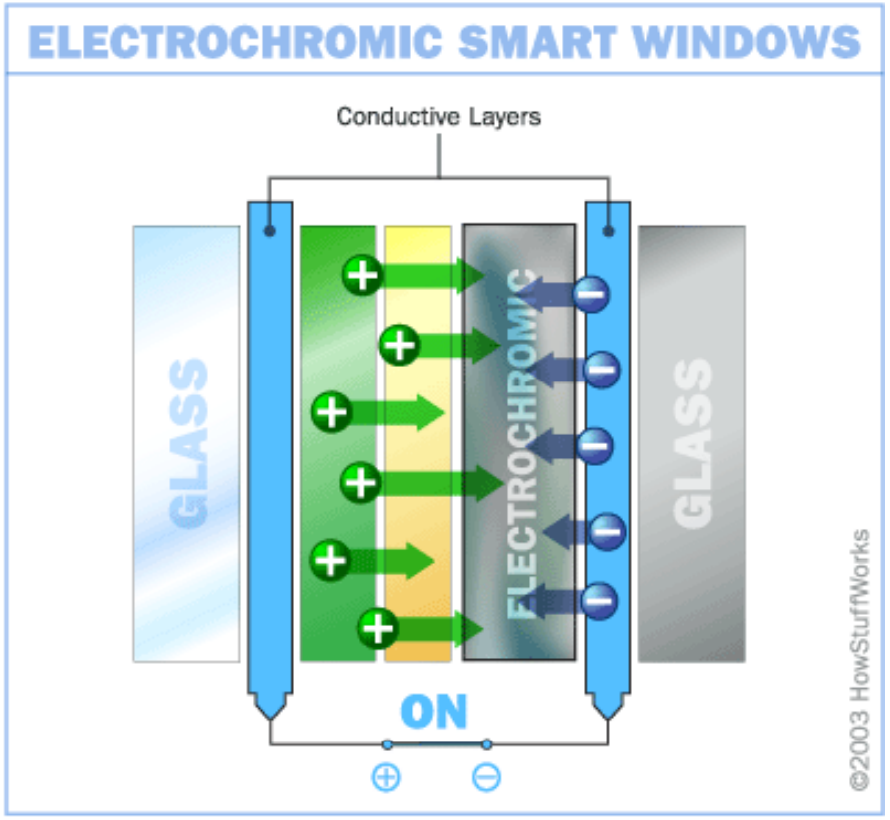


G. Dennler, H.-J. Prall, R. Koeppe, M. Egginger, R. Autengruber, N.S. Sariciftci, APL 89 (2006), 073502-1

4. Applications with organic, inorganic and hybrid materials

4.3 Electronic and optoelectronic devices

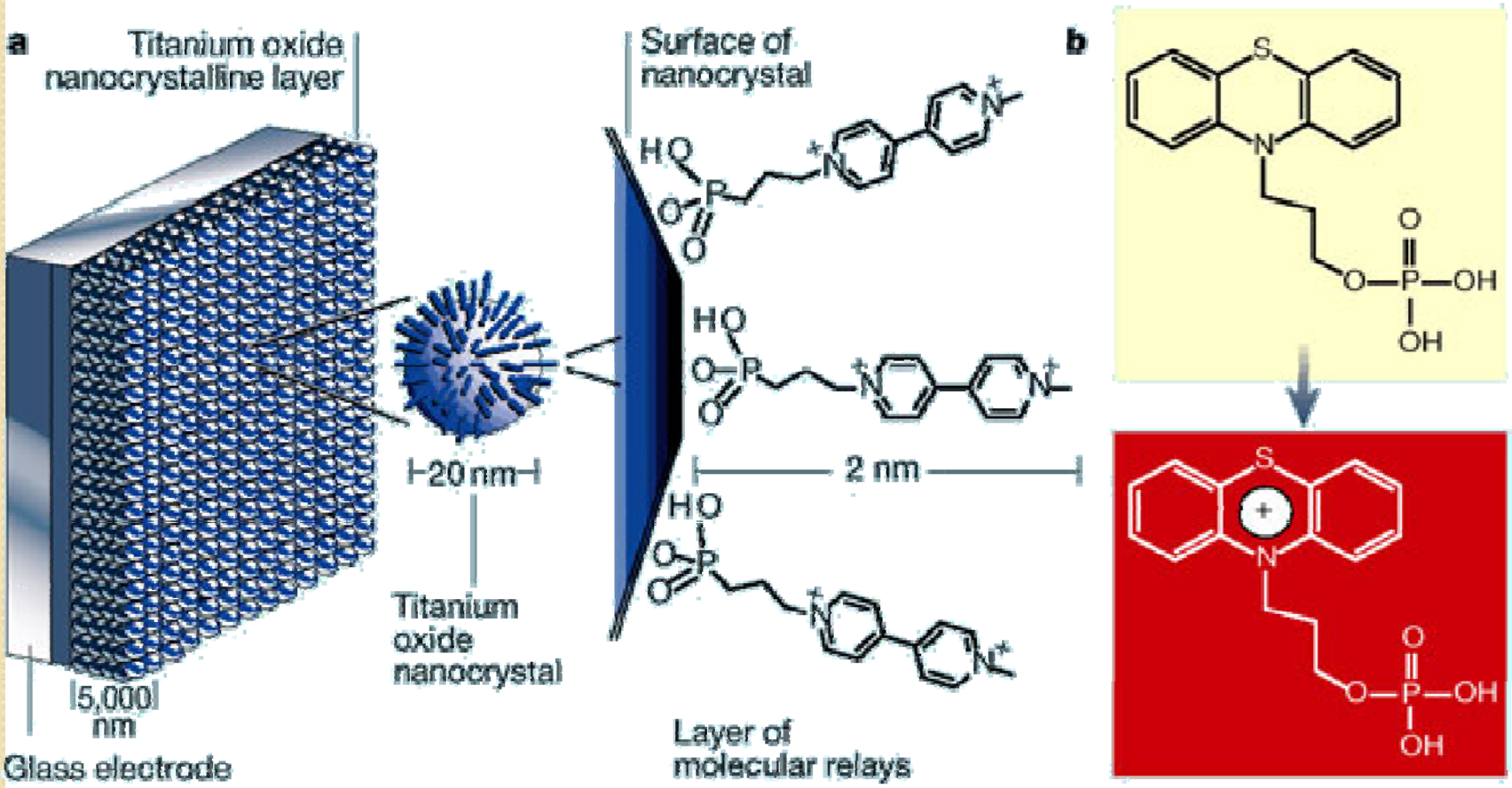
Electrochromic devices



4. Applications with organic, inorganic and hybrid materials

4.3 Electronic and optoelectronic devices

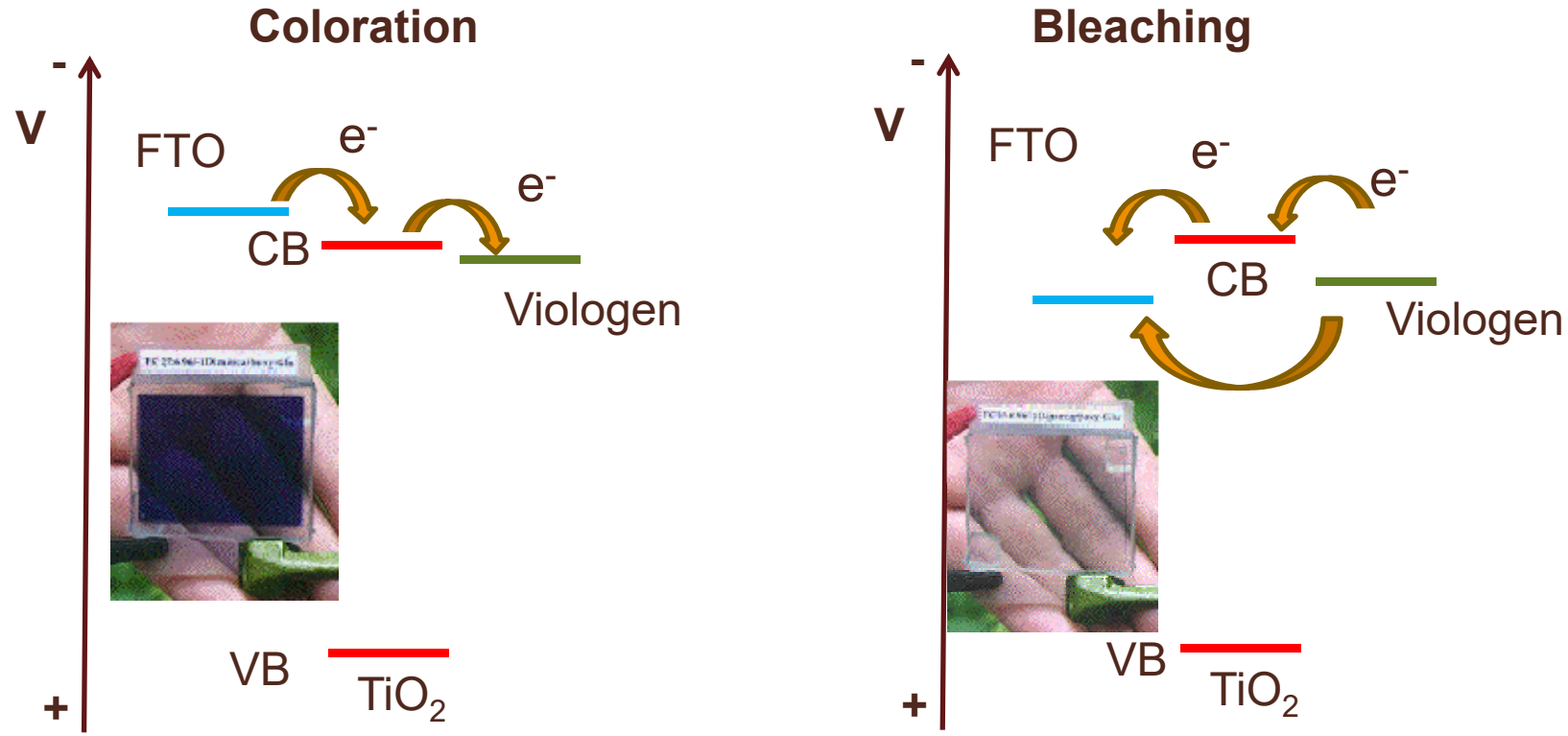
Electrochromic devices



4. Applications with organic, inorganic and hybrid materials

4.3 Electronic and optoelectronic devices

Electrochromic device: Viologen functionalized TiO_2

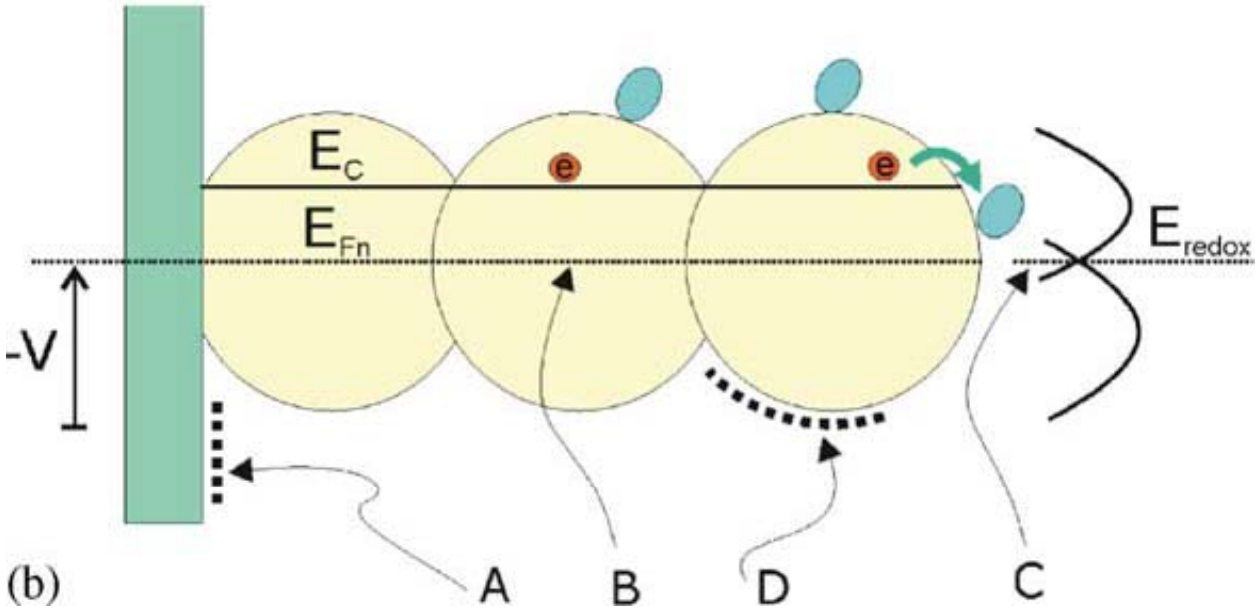


How it works: When negative enough potential is applied, electrons are injected to the TiO_2 that transport them to the viologen which becomes reduced (V^-) and blue.. When the potential is lowered, electrons are extracted and viologen oxidized to its neutral (V^0) transparent state

4. Applications with organic, inorganic and hybrid materials

4.3 Electronic and optoelectronic devices

Electrochromic devices



Electrochimica Acta 49 (2004) 745–752

4. Applications with organic, inorganic and hybrid materials

4.3 Electronic and optoelectronic devices

Electrochromic devices

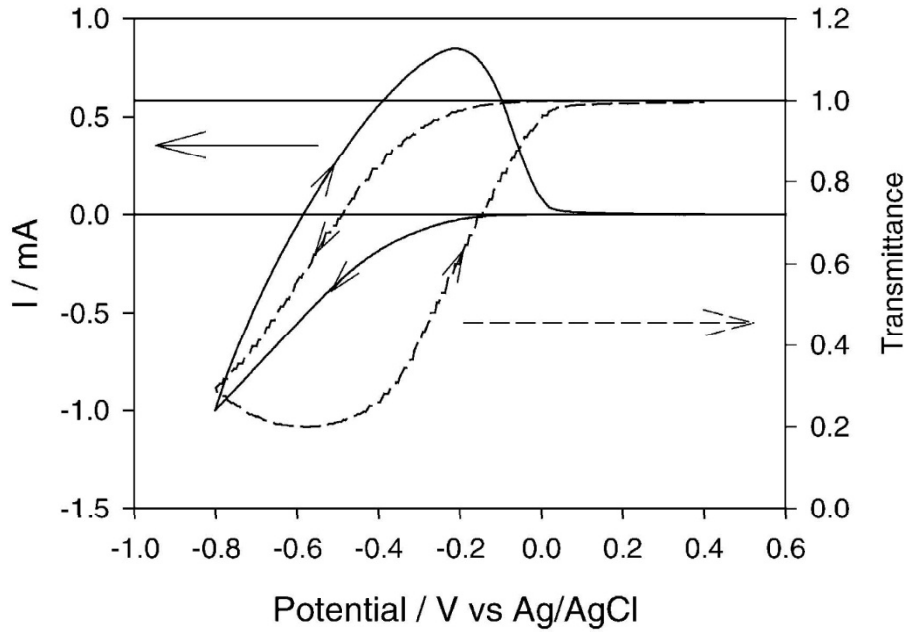
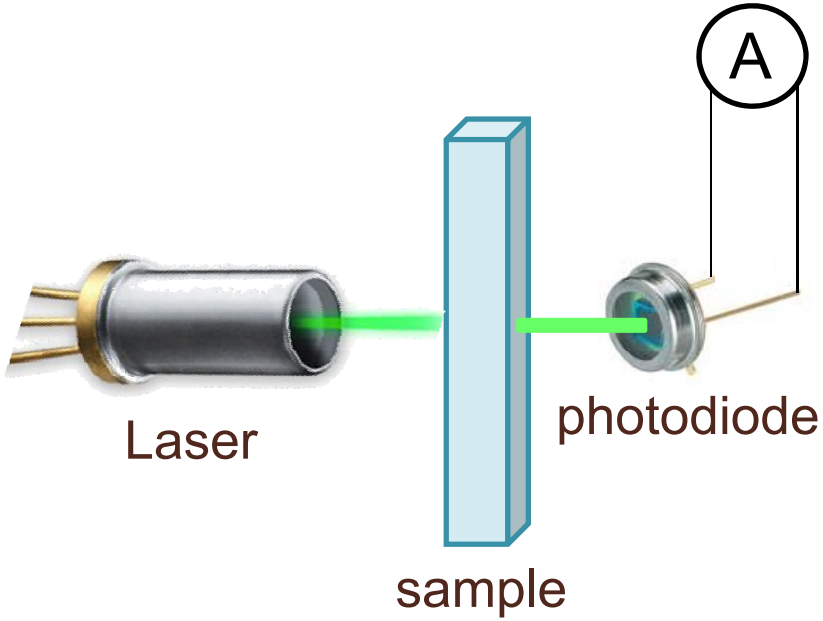


Fig. 7. Comparison of the voltammogram (left axis) taken at a scan rate of 50 mV/s with the transmittance of the film (right axis).



Electrochimica Acta 49 (2004) 745–752

4. Applications with organic, inorganic and hybrid materials

4.3 Electronic and optoelectronic devices

Electrochromic devices

A better way to see the redox process separately is to treat transmittance data taken during voltammetry: considering that any variation in the transmittance of the film, T, is due to the injection of electrons in the viologen, Beer–Lambert law may be written as

$$A = \varepsilon L \frac{c_{\mathrm{red}}}{N_A} \tag{7}$$

where, neglecting reflectance, $A = -\ln(T)$ is the absorbance, ε the molar absorption coefficient of reduced viologen and L the film thickness.

If we derive this expression with respect to the potential and take into account that for cyclic voltammetry $\mathrm{d}V = s\mathrm{d}t$, we obtain

$$\frac{\mathrm{d}A}{\mathrm{d}V} = \frac{\varepsilon L}{N_A}\frac{\mathrm{d}c_{\mathrm{red}}}{\mathrm{d}V} = \frac{\varepsilon L}{sN_A}\frac{\mathrm{d}c_{\mathrm{red}}}{\mathrm{d}t} \tag{8}$$

being $\mathrm{d}c_{\mathrm{red}}/\mathrm{d}t$ the variation of reduced viologens with time or, in other words, the current density, j, that enters viologen molecules divided by the electron charge and the length of the film. Thus Eq. (8) yields [13]

$$s\frac{\mathrm{d}A}{\mathrm{d}V} = \frac{\varepsilon}{F}j \tag{9}$$

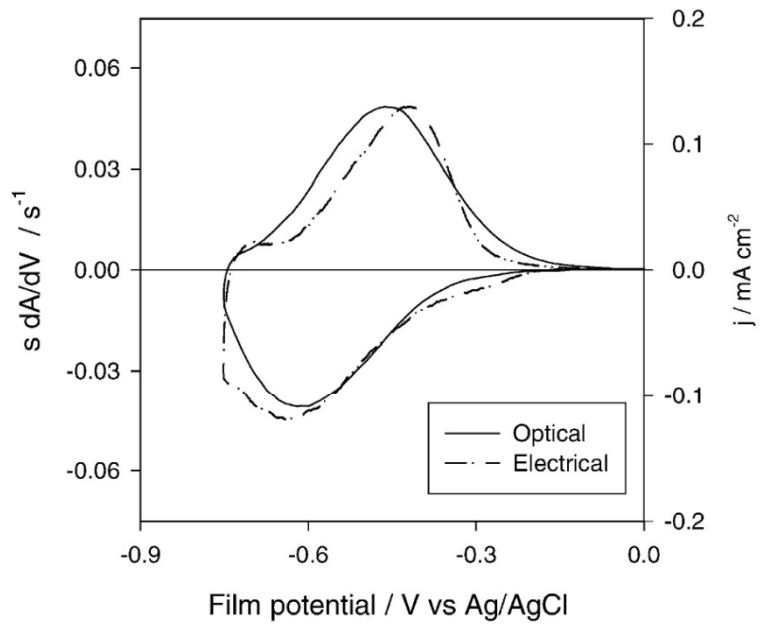


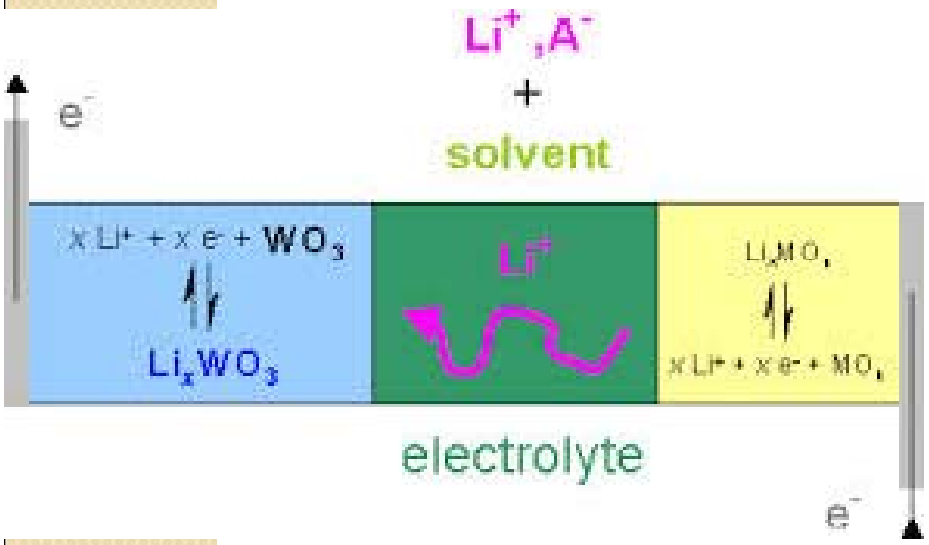
Fig. 10. Comparison of the decoupling of the redox process of viologen by the electrical and optical methods. Right axis: subtracted electrical voltammetry obtained in Fig. 9(b). Left axis: derivate of absorbance times scan rate ($5\,\mathrm{mV\,s^{-1}}$).

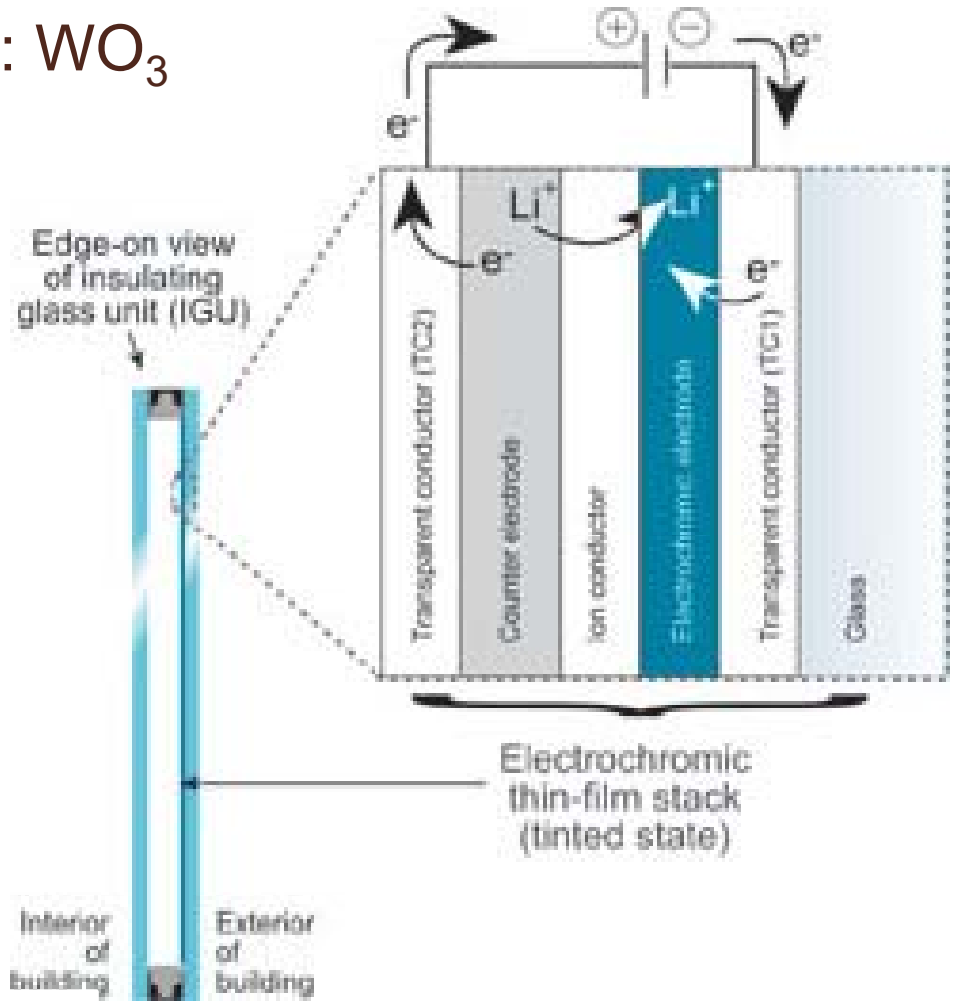
Electrochimica Acta 49 (2004) 745–752

4. Applications with organic, inorganic and hybrid materials

4.3 Electronic and optoelectronic devices

Electrochromic devices: WO_3



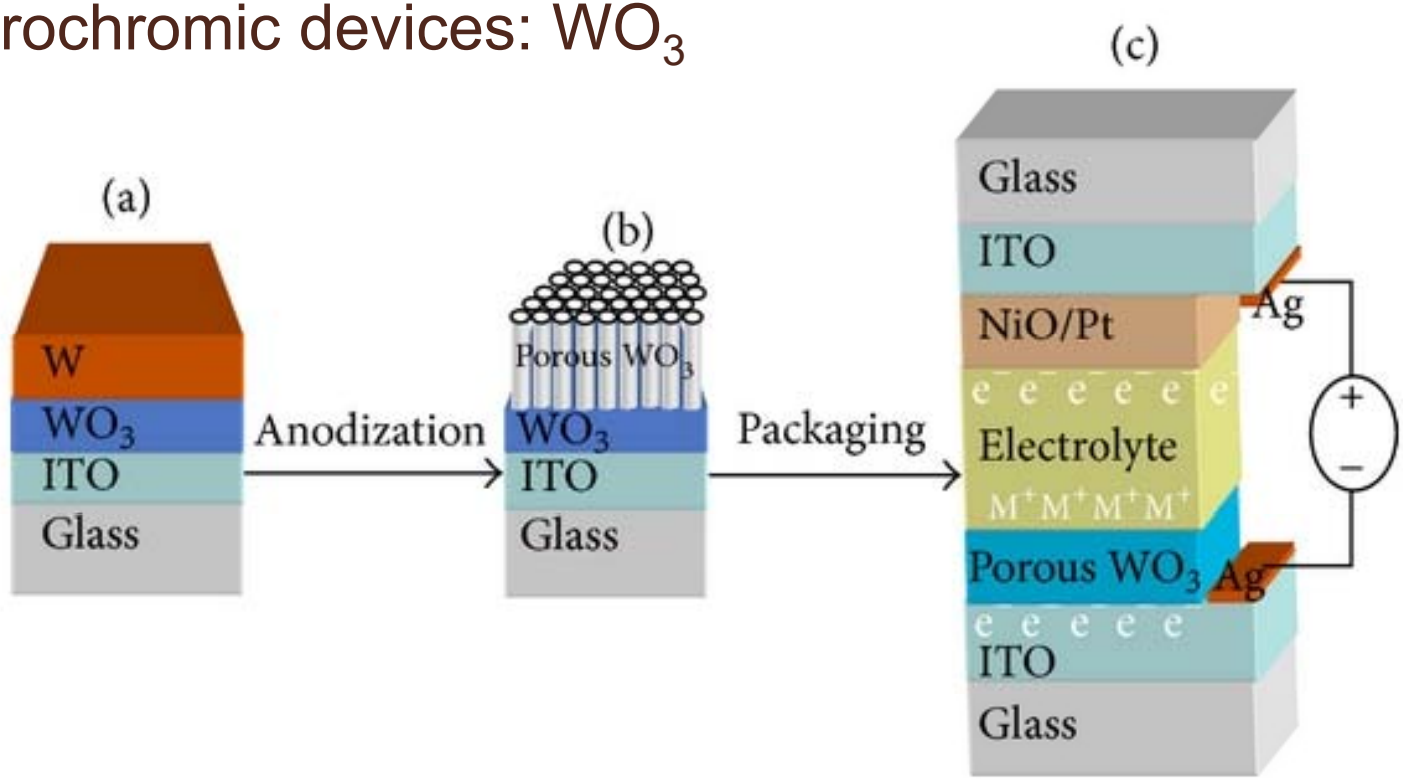


patoo.hope.free.fr
www.ceramicindustry.com

4. Applications with organic, inorganic and hybrid materials

4.3 Electronic and optoelectronic devices

Electrochromic devices: WO_3



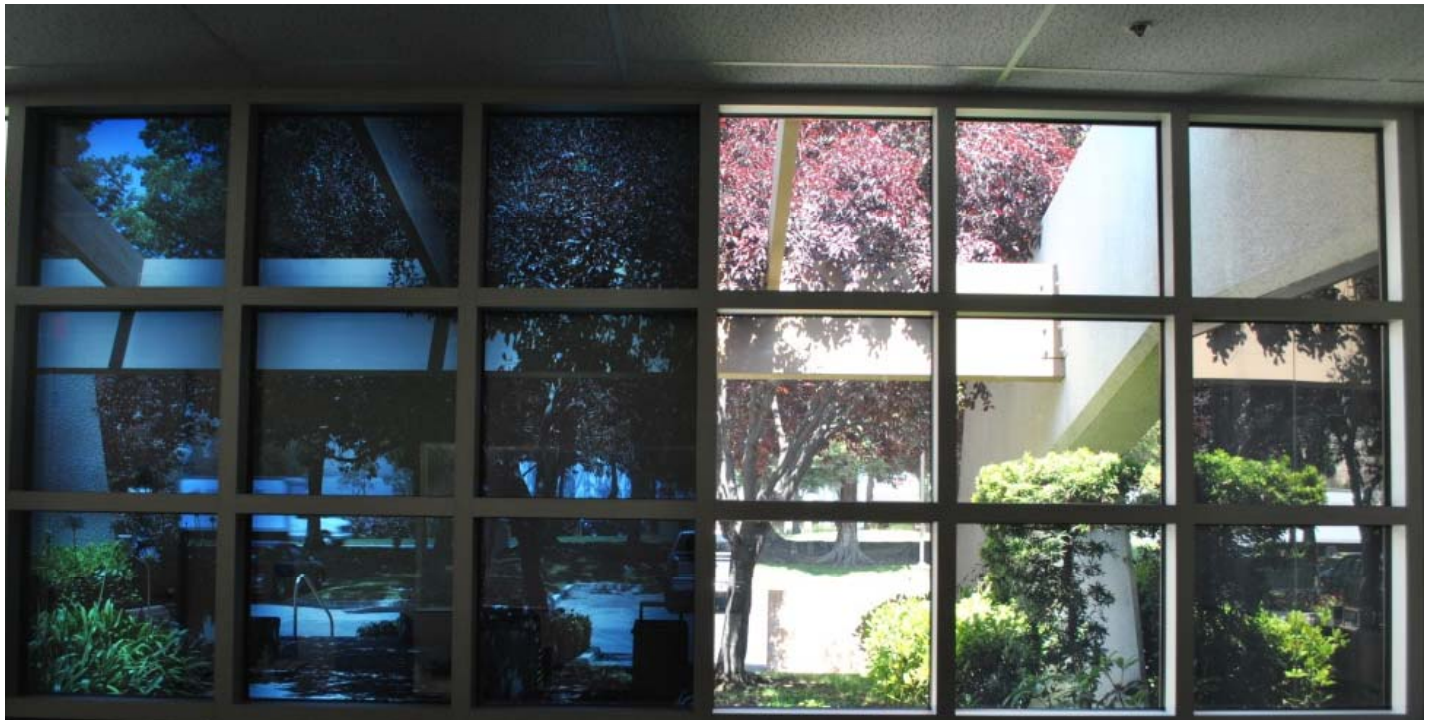
How it works: The application of a negative voltage to the WO_3 anode attracts Li^+ ions from the electrolyte to film surface. Li^+ ions penetrate WO_3 structure and form a blue bronze. When voltage is released, Li^+ ions exit the film that returns to transparent mode

http://www.hindawi.com/journals/jnm/2013/785023/

4. Applications with organic, inorganic and hybrid materials

4.3 Electronic and optoelectronic devices

Electrochromic devices: WO_3

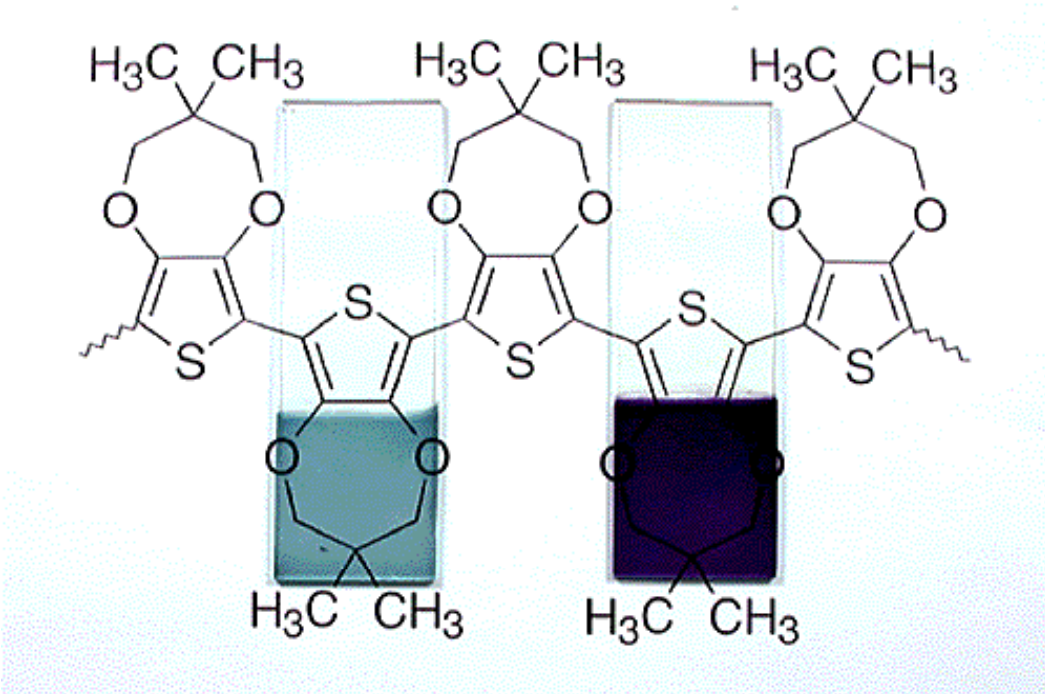


http://www.hindawi.com/journals/jnm/2013/785023/
https://www.youtube.com/watch?v=qC1ivQQumOA
https://www.youtube.com/watch?v=afLGMFUNlfY

4. Applications with organic, inorganic and hybrid materials

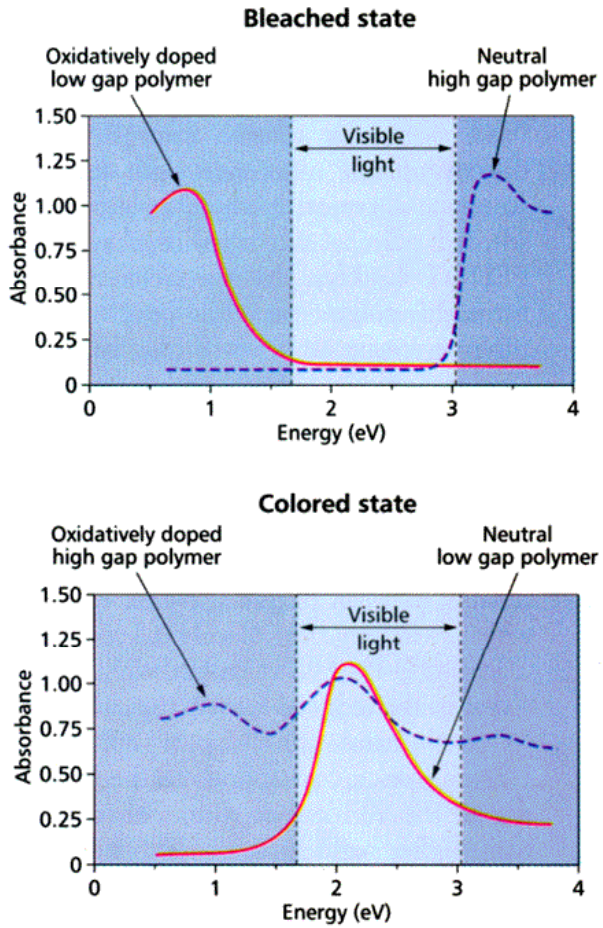
4.3 Electronic and optoelectronic devices

Electrochromic devices: Polymer



PProDOT-Me_2

poly [3,3-dimethyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine]



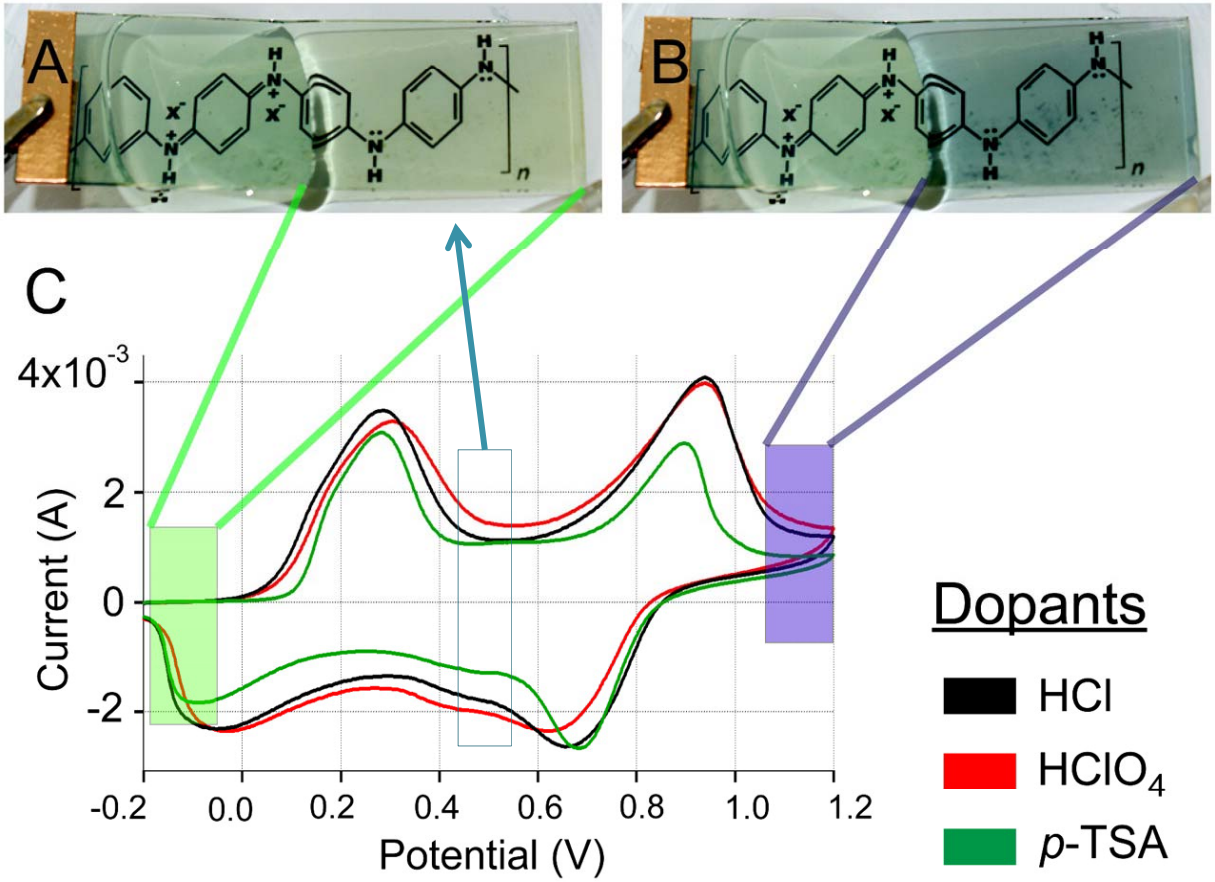
Adv. Mater. **1999**, *11*, 1379.
Macromolecules **2000**, *33*, 1132.

4. Applications with organic, inorganic and hybrid materials

4.3 Electronic and optoelectronic devices

Electrochromic devices: Polymer

PANI: Polyaniline

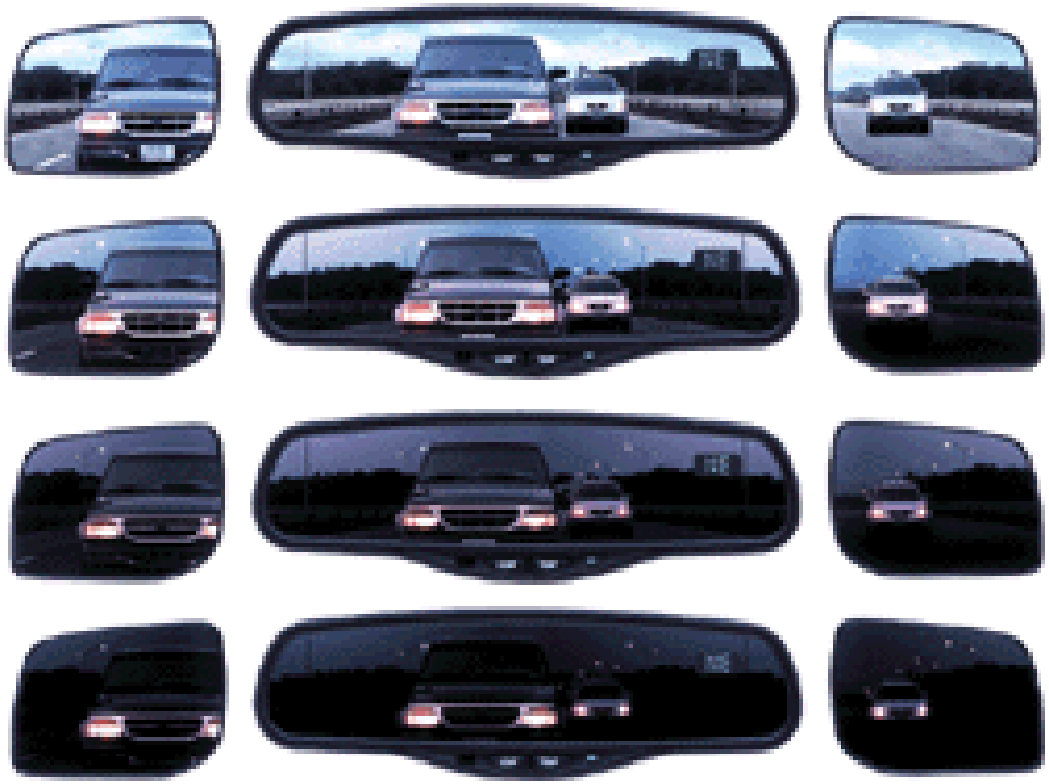


*PNAS 2010, **107**, 19673-19678*

4. Applications with organic, inorganic and hybrid materials

4.3 Electronic and optoelectronic devices

Electrochromic devices:



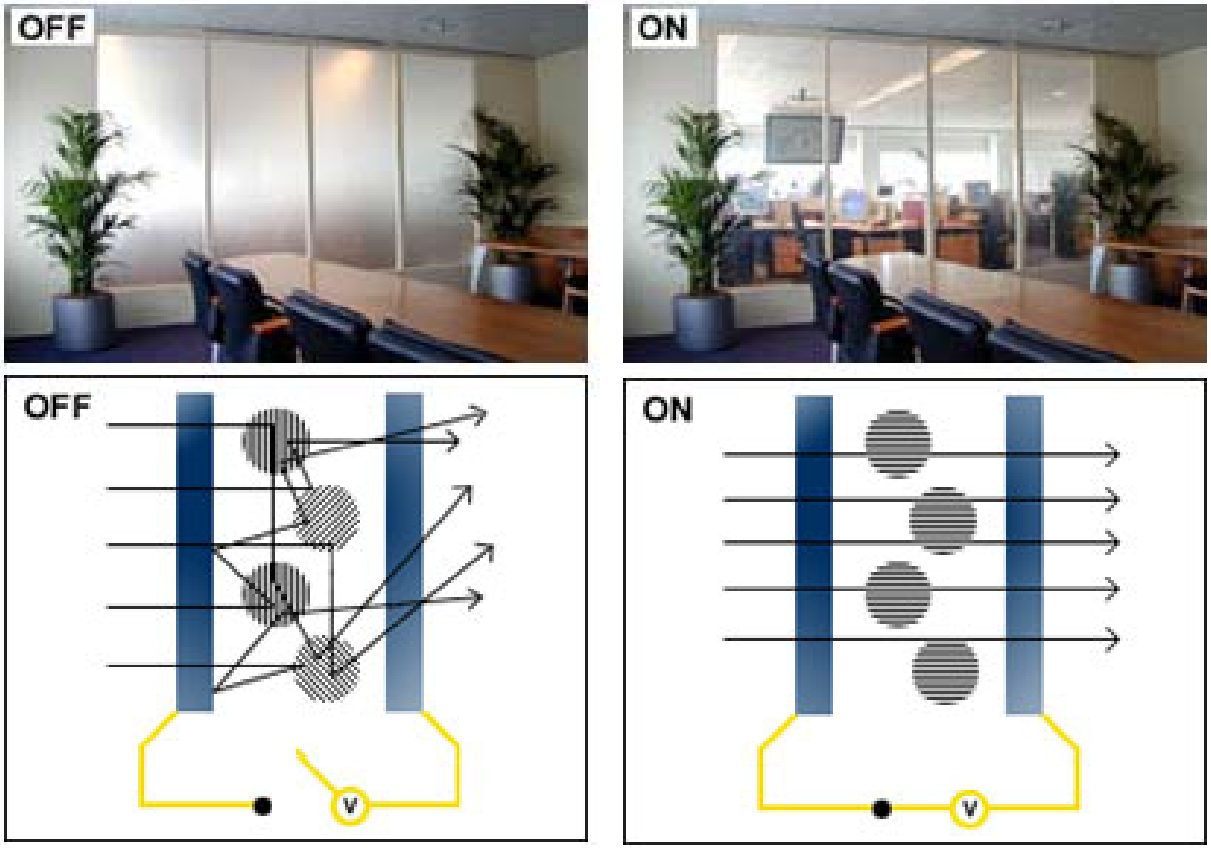
http://www.aandetrading.com/gentex/ebayk3.htm

Cathode: dipyridinium, anode Dihydrophenazine

4. Applications with organic, inorganic and hybrid materials

4.3 Electronic and optoelectronic devices

Electrochromic devices: suspended particle device SPD

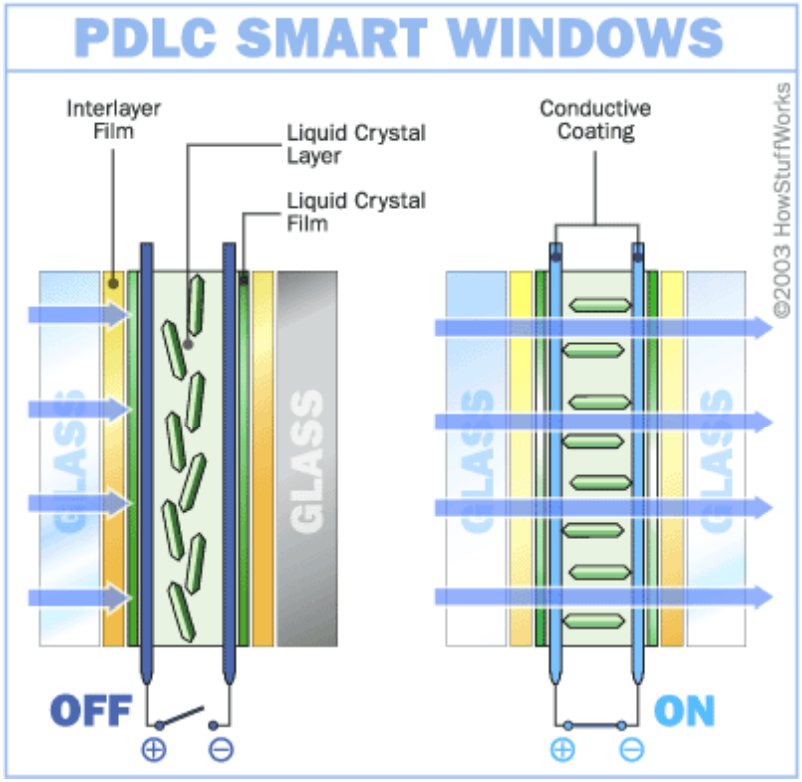


http://inhabitat.com/super-smart-privacy-glass/

4. Applications with organic, inorganic and hybrid materials

4.3 Electronic and optoelectronic devices

Electrochromic devices: Liquid crystal



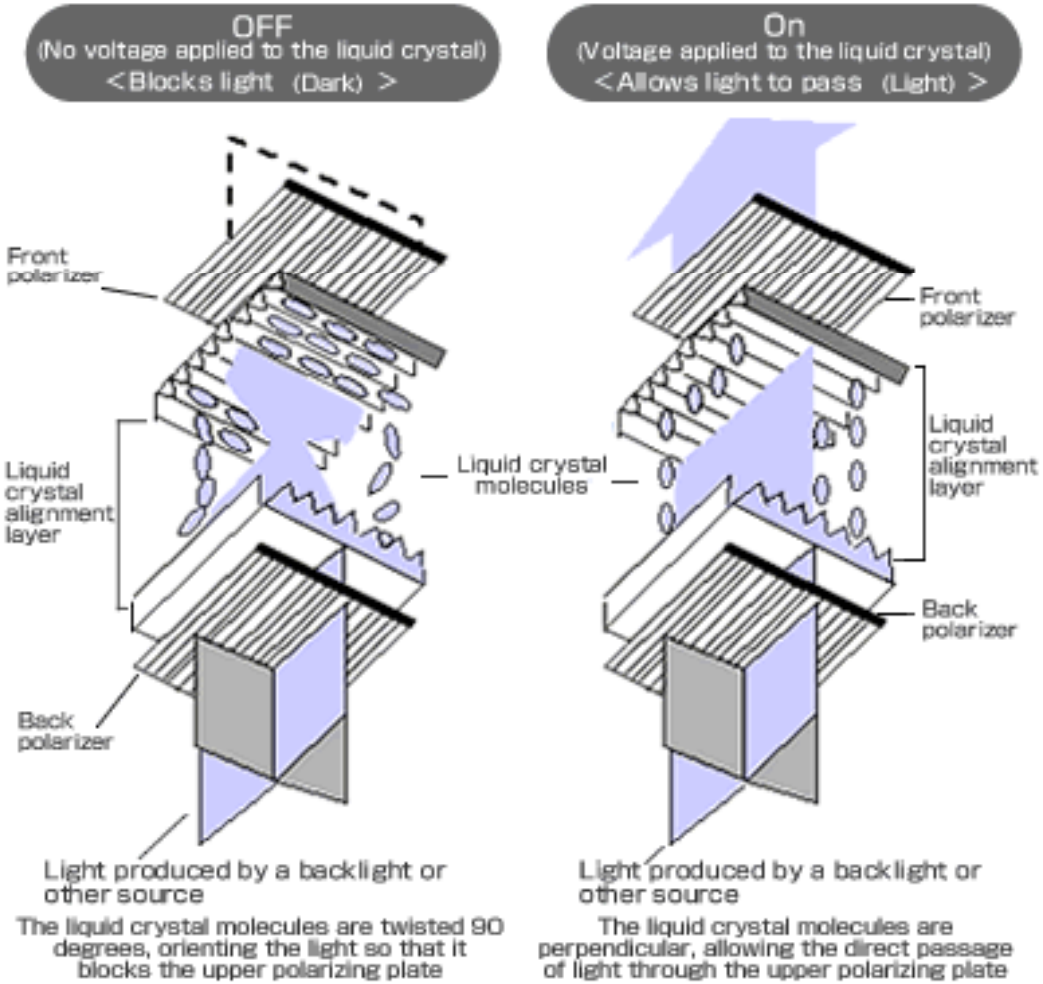
polymer dispersed liquid crystals

https://www.youtube.com/watch?v=RIDN4iH8xr4

4. Applications with organic, inorganic and hybrid materials

4.3 Electronic and optoelectronic devices

Electrochromic devices: Liquid crystal

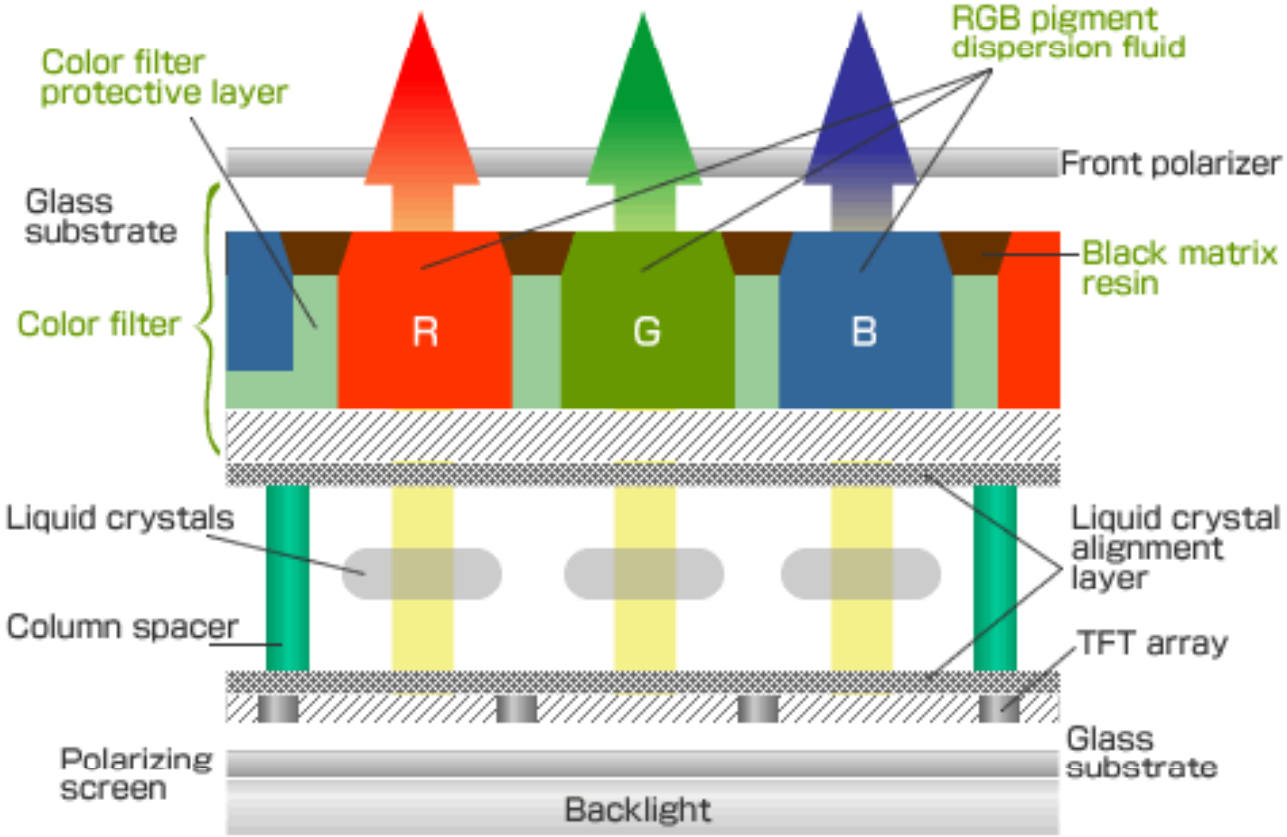


http://www.nof.co.jp/english/business/display/product01.html

4. Applications with organic, inorganic and hybrid materials

4.3 Electronic and optoelectronic devices

Electrochromic devices: Liquid crystal display (LCD)



http://www.nof.co.jp/english/business/display/product01.html