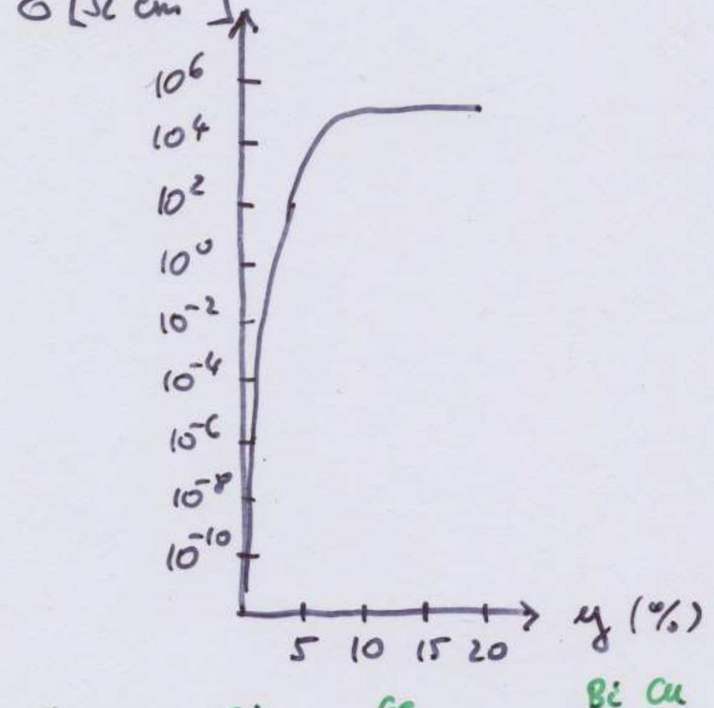
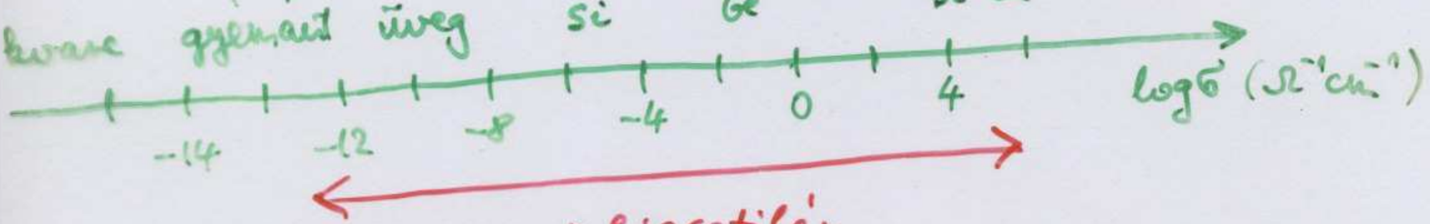
FÉLVEZETŐ → FÉM ÁTMENET

DÓPOLÁS (INTERKALÁLÁS) HATÁSÁRA

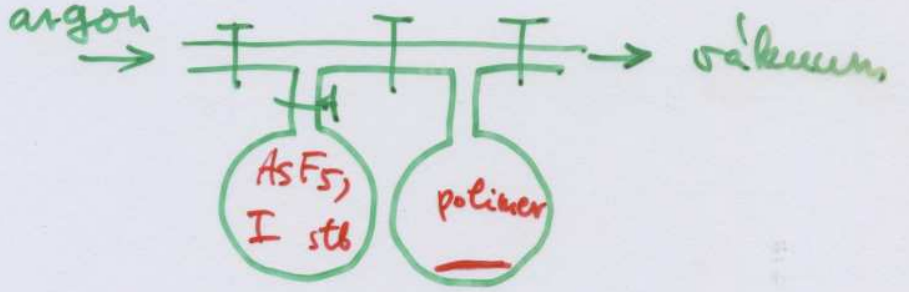
$(CH\,I_y)_x$, $(CH\,Br_y)_x$ $[CH(AsF_5)_y]_x$ stb



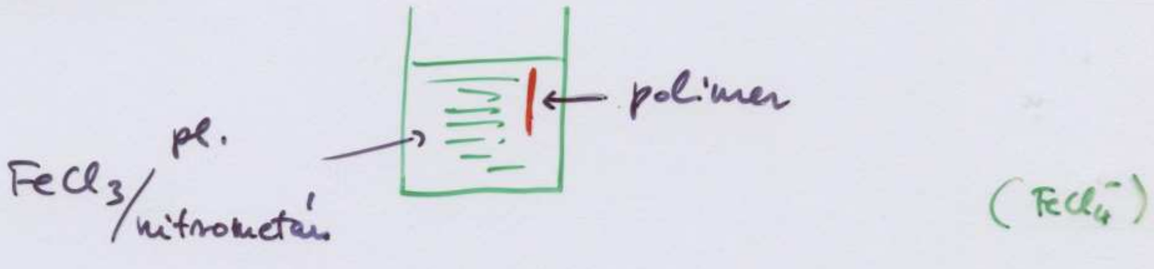


DÓPOLÁS

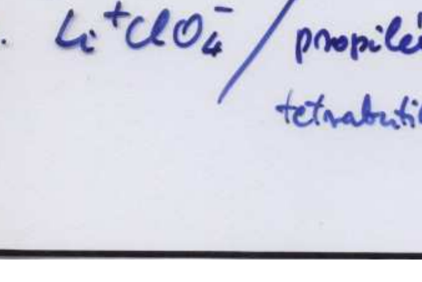
a) Gázfázisból

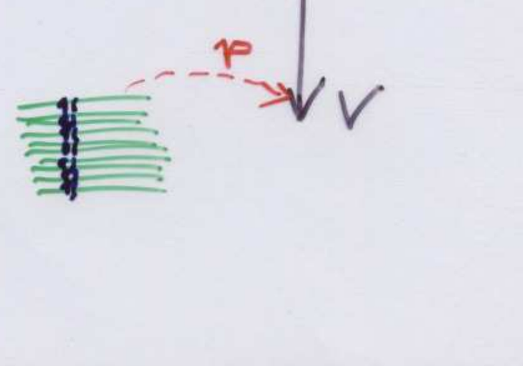


b) Folyadék fázisból



c) Elektrokémiai dópolás





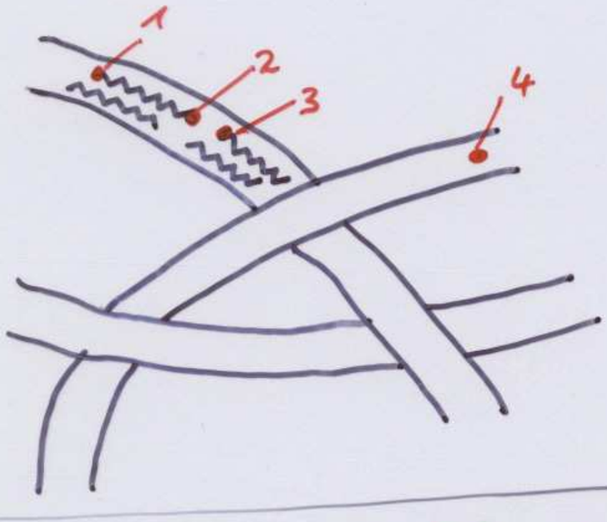
pl. $Li^+ClO_4^-$ / propilén-karbonát (n)
tetrabutil-ammónium (p)

Dópolt polimer : „piszkos fém"

T csökken → σ csökken

$\sigma(T) = \sigma_0 e^{-\left(T_0 + \frac{T_1}{T}\right)}$

(She

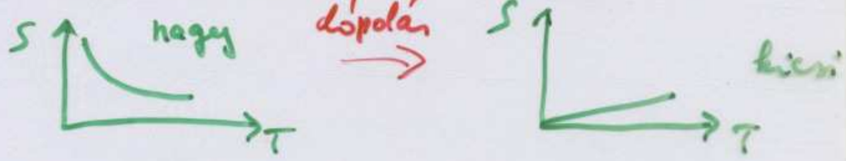


1-2 láncon belüli

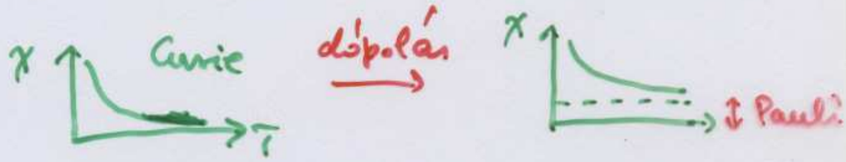
2-3 láncok közötti

3-4 fibrillák közötti

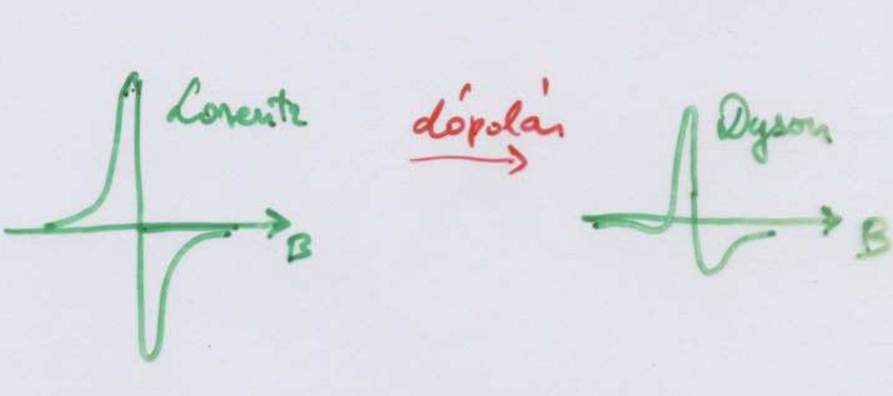
- Termoelektromos erő (S)



- Mágneses szuszceptibilitás (χ)

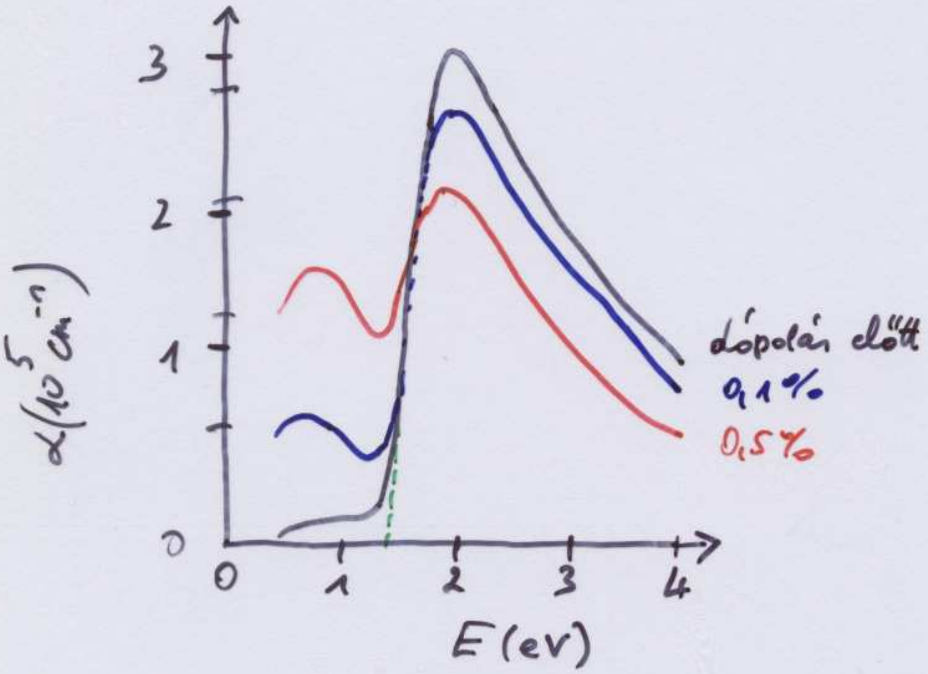


- ESR



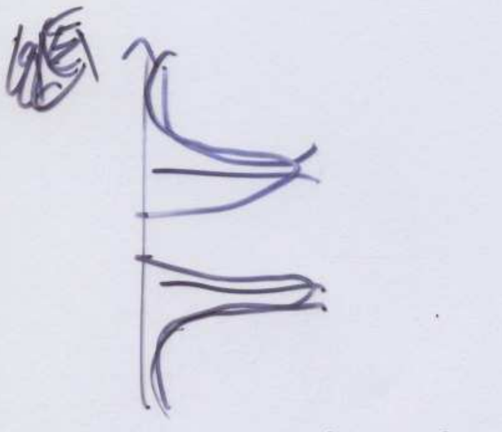
Az optikai abszorpció változása dópolás hatására

$I \sim e^{-\alpha r}$



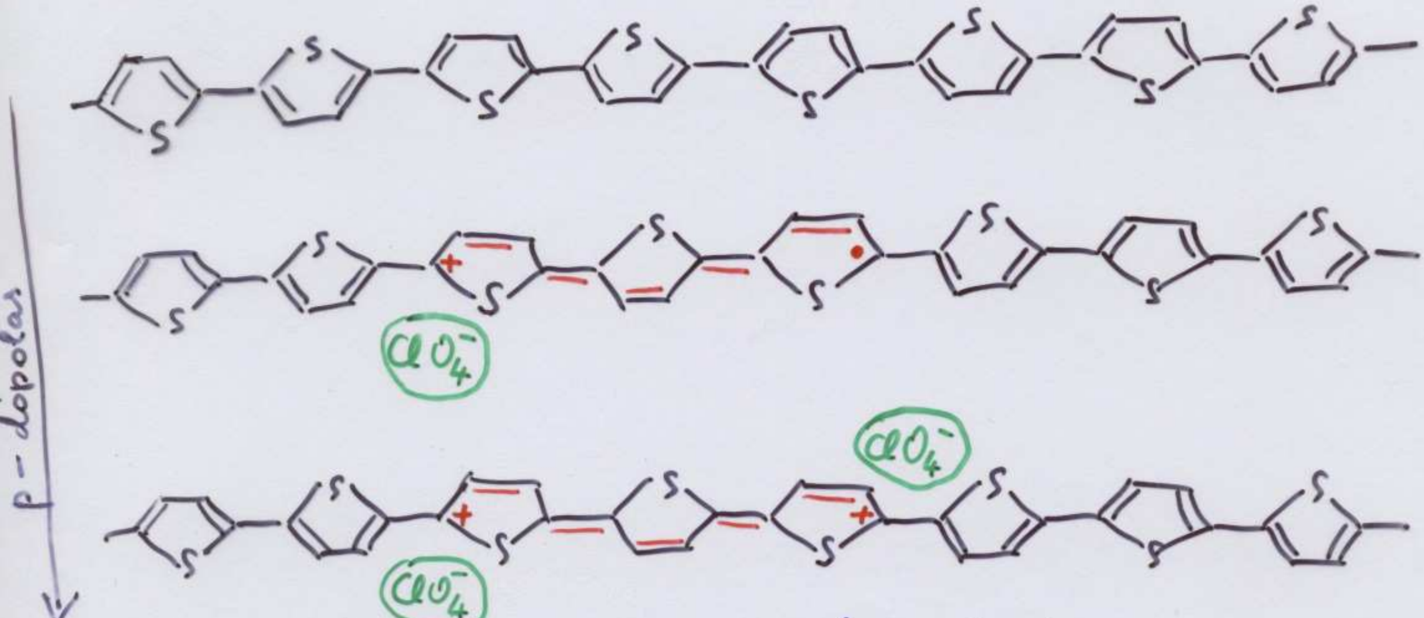
trans-$(CH)_x$

(Suruh

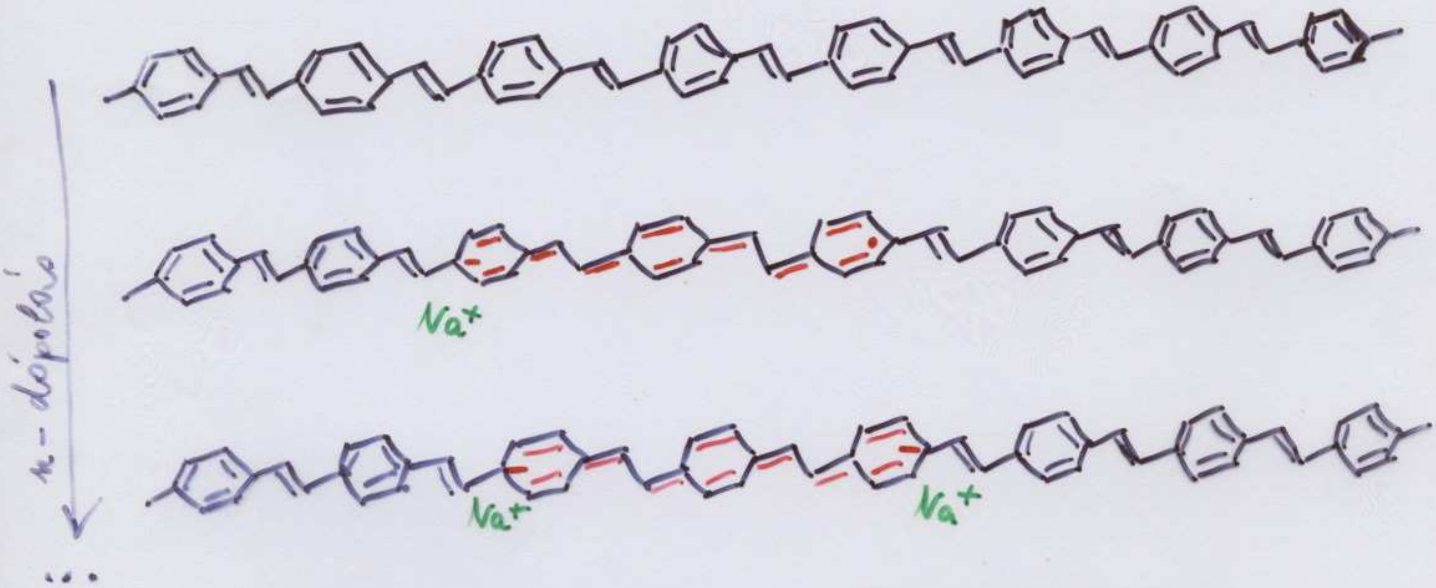


POLARONOK, BIPOLARONOK ...

(gyök-ionok)

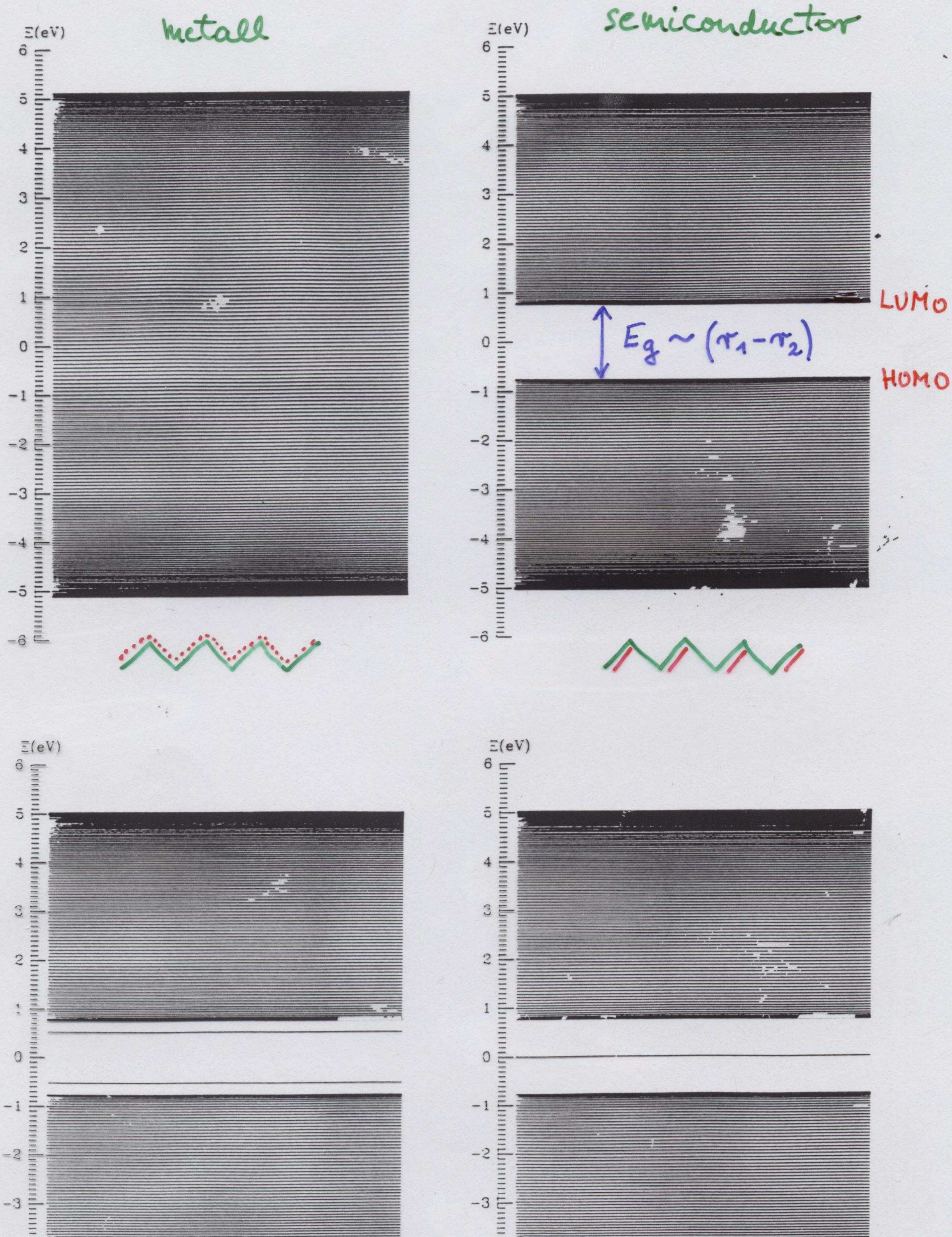


politiofén (PT)



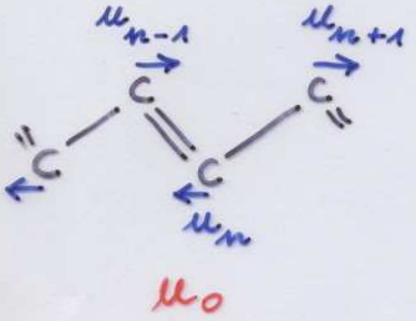
poli-parafenilén-vinilén (PPV)

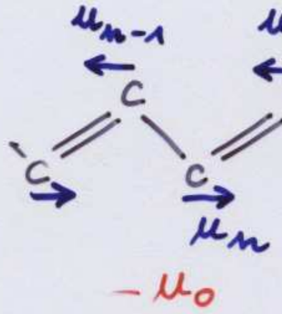
C_{200}



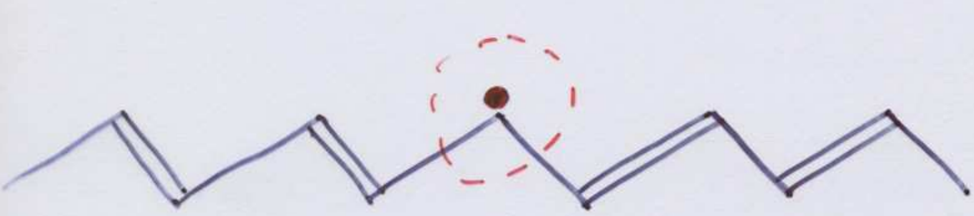
The energy levels for a linear chain of 200 C-atoms, calculated by LHS - model.

SZOLITON (transz-poliacetilénben)



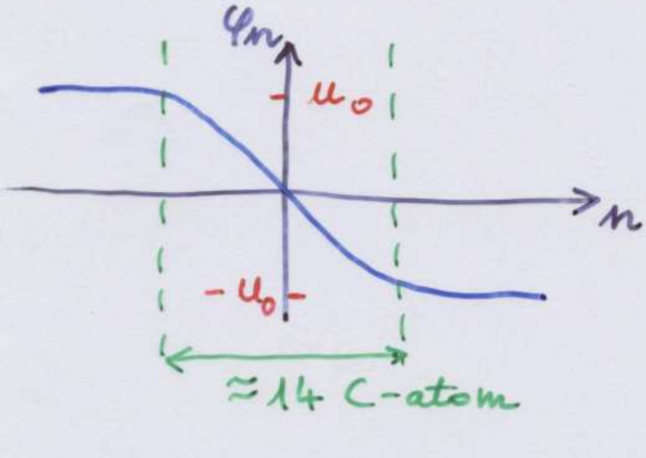


degenerált alapállapot!

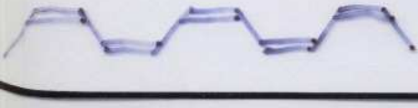


(semleges) szoliton

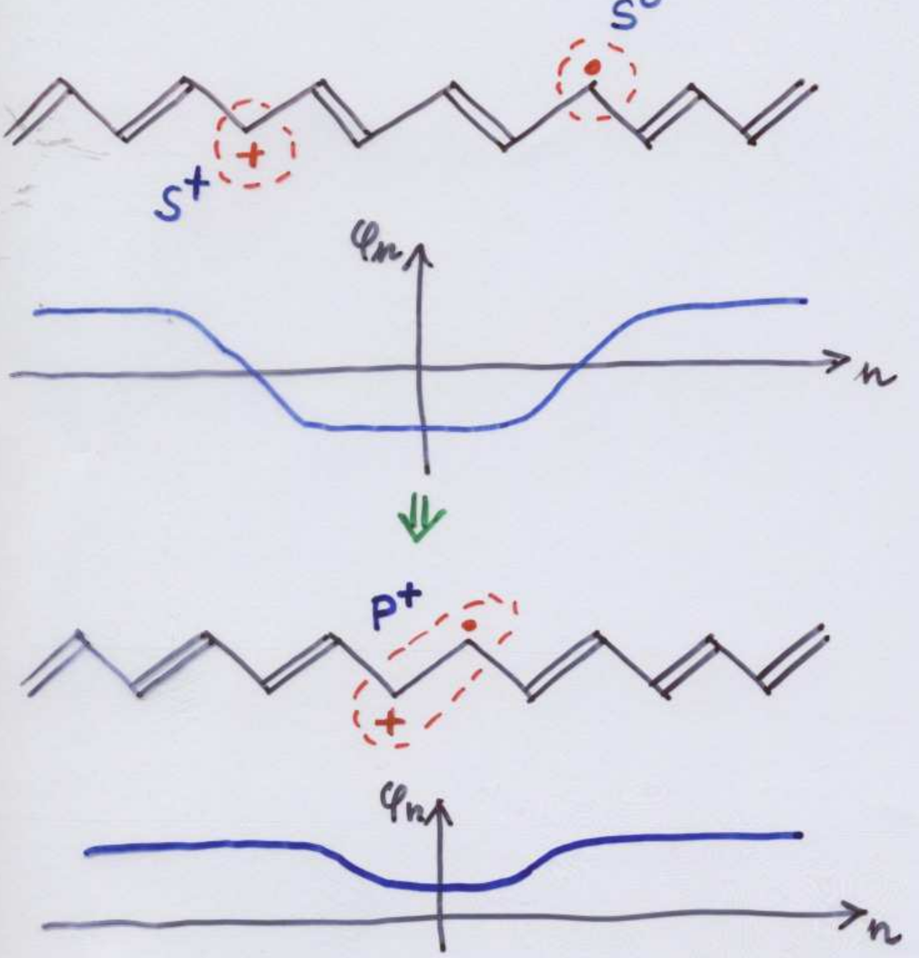
rendparaméter: $\varphi_n = (-1)^n \cdot u_n$



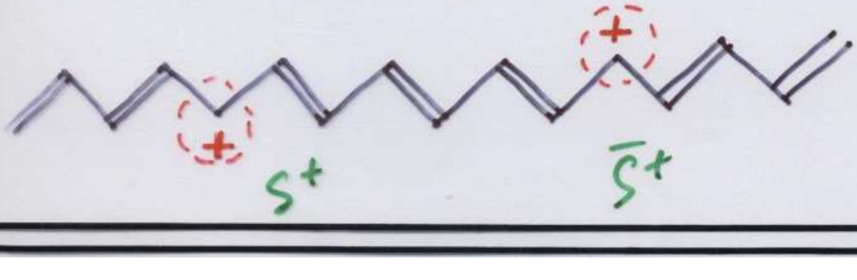
$E_{c-t} < E_{t-c}$



cisz-poliacetilé
nem degenerált!

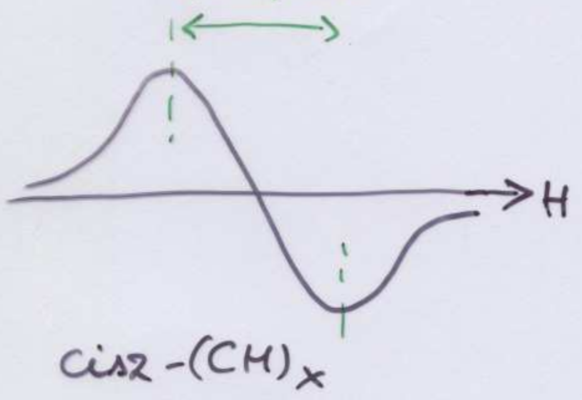


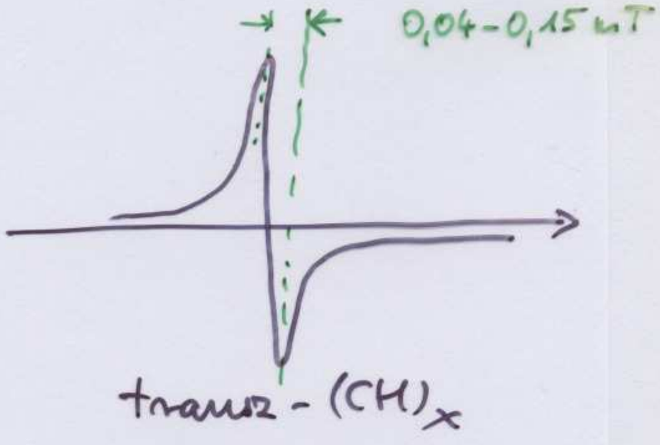
$S^+ + \bar{S}^0 \to P^+$



$P^+ + P^+ \to S^+ + \bar{S}^+$

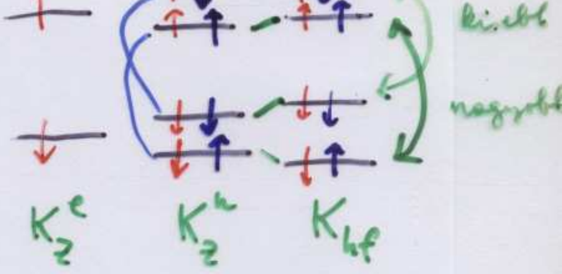
Szolitonok $(CH)_x$ -ben , ESR

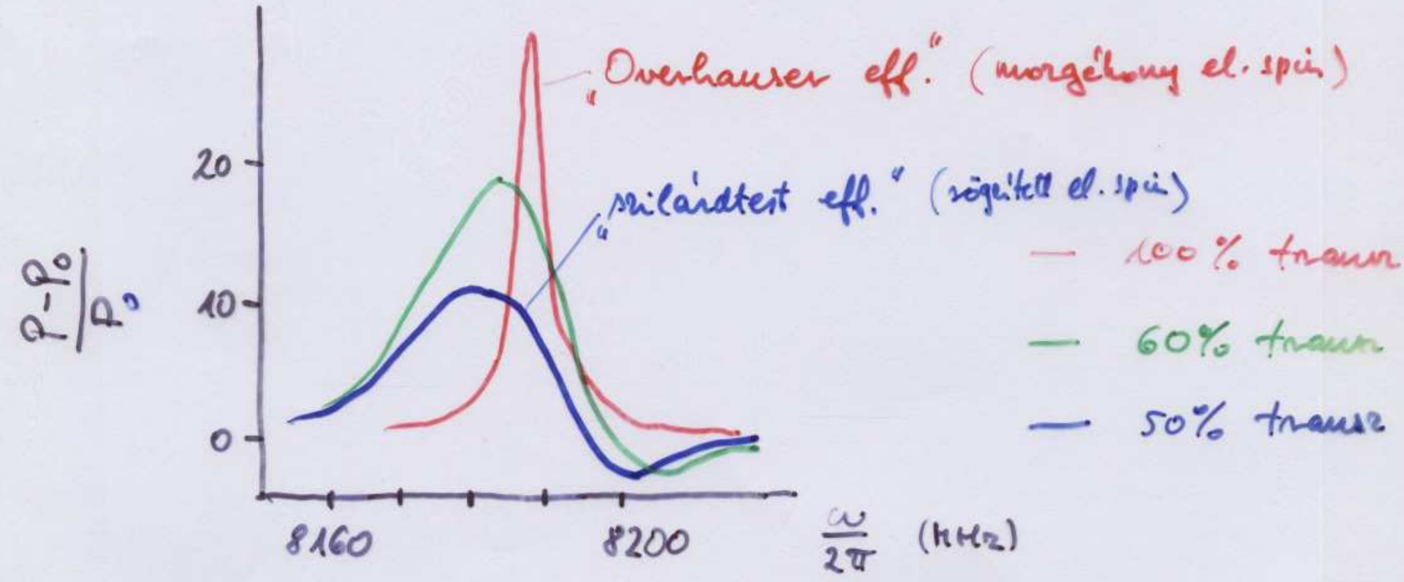




Dynamic Nuclear Polarization

ESR-jel telítése → NMR intenzitás változása



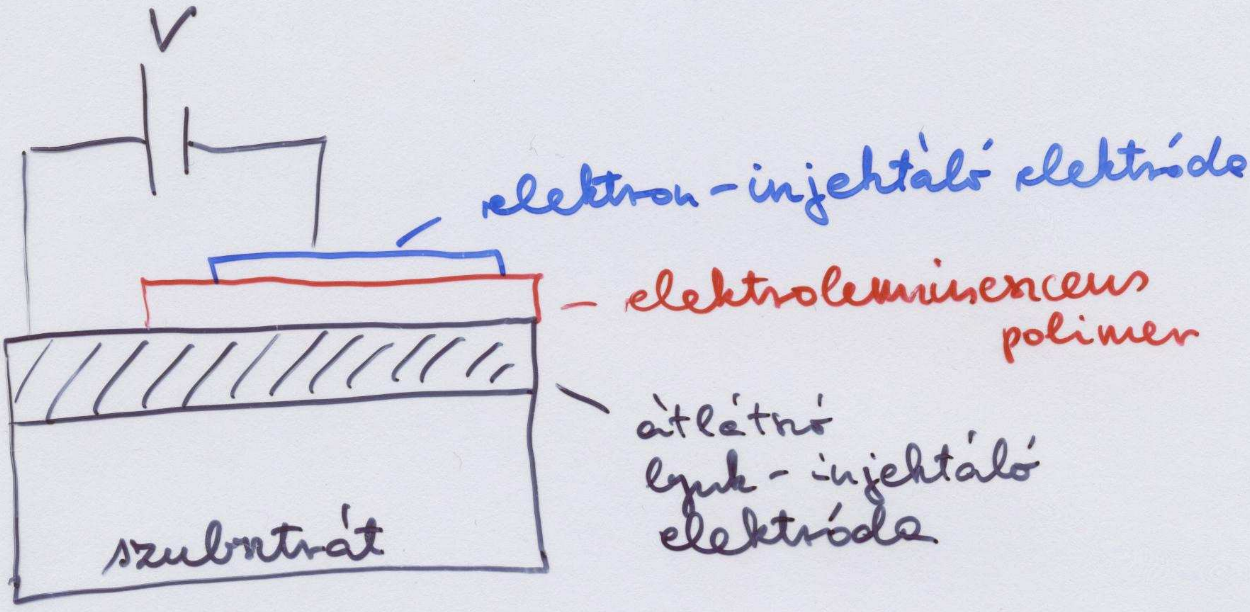


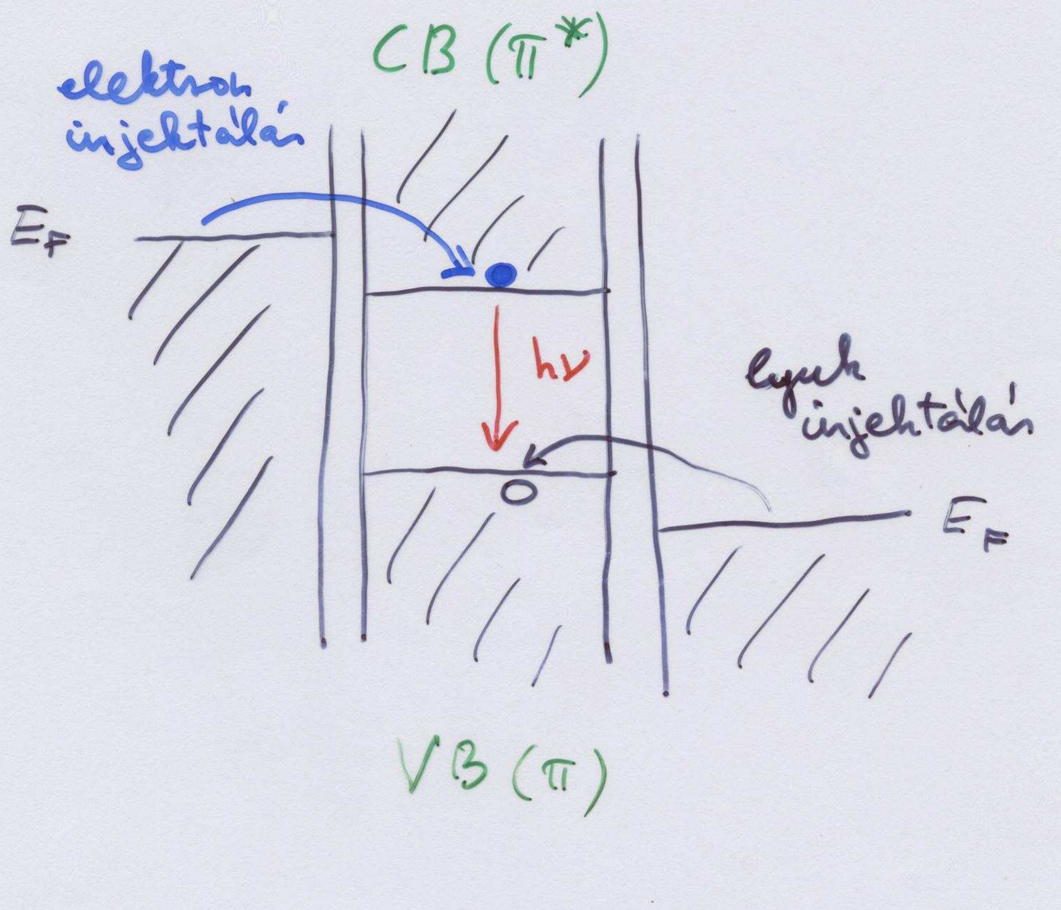
Konjugált polimerek alkalmazási lehetőségei

- elektromos (hajlékony vezető, antisztatikus fólia ... MISFET ...)
- elektrokémiai (gomb-akku)
- optikai (termokróm, LED ...)
- nemlineáris optikai („fotonika", hiperpolarizálhatóság ...)
- „egzotikus" pl. molekuláris elektronikai

O - L E D

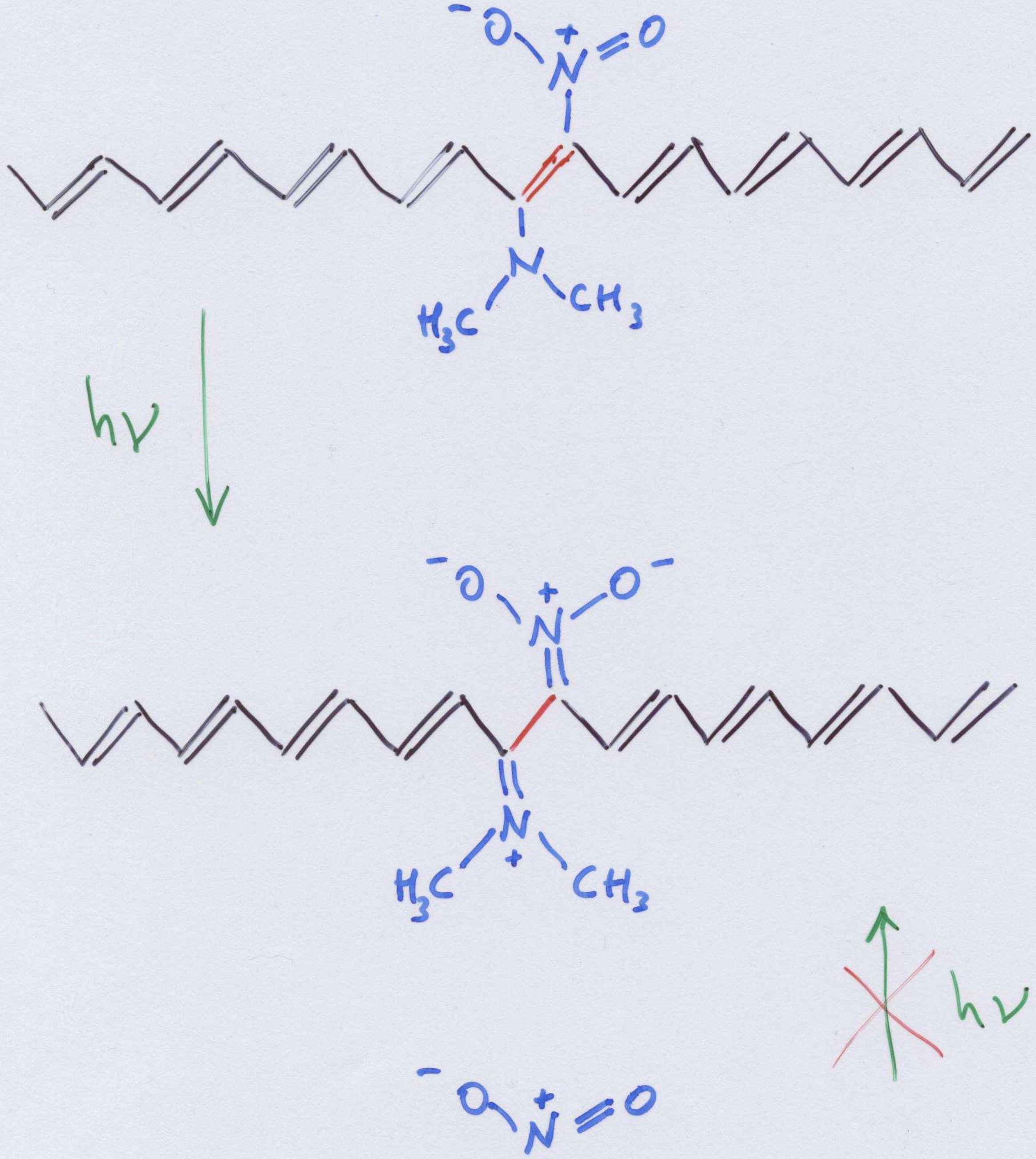
Organic Light Emitting Device



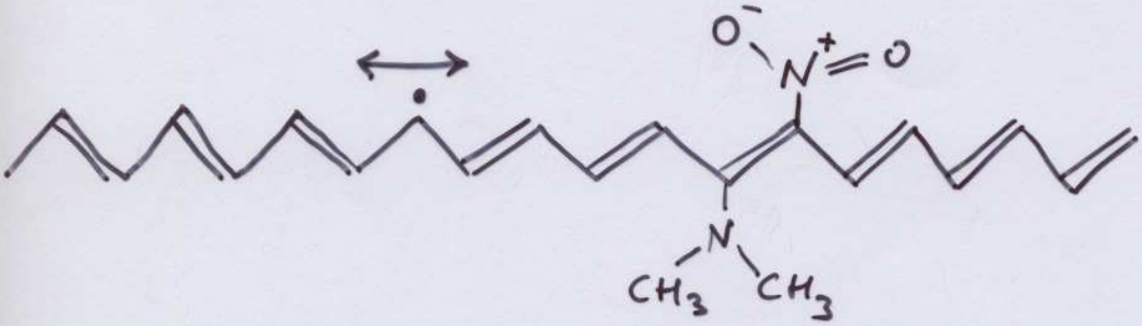


„Molekuláris elektronikai álmok"

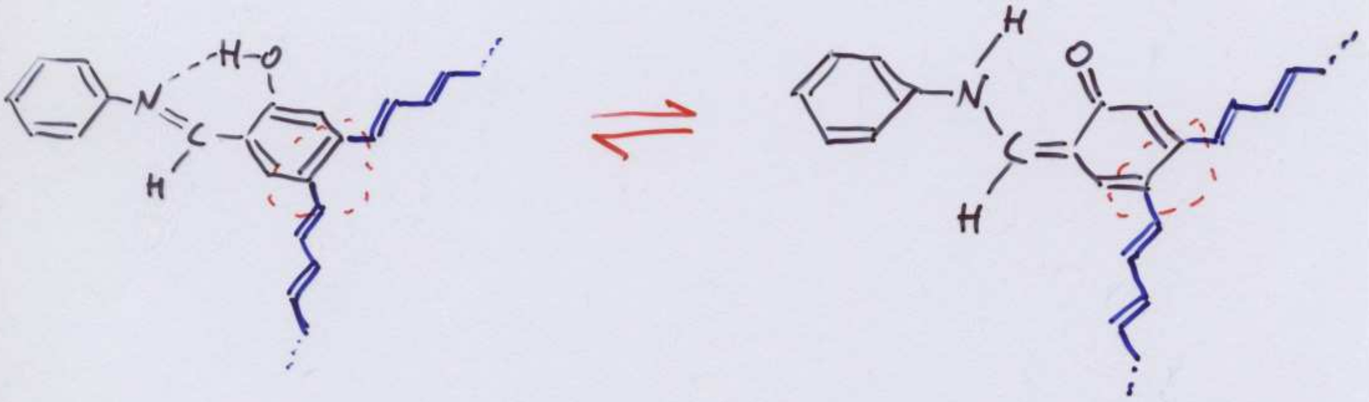
F.L. Carter, 1982



„Molekuláris elektronikai álmok"



Carter, 198



N- salicyliden
fotokrom átmenete

Sixl, Higelin, 198

Langmuir – Blodgett technika   LB – filmek

31. Addition of 1 weight % core material to a mantle source will have no effect on the isotopes of Sr, Nd, Pb, and oxygen, which are well correlated with Os isotopes in most OIBs [for example, Hawaii (*18*, *19*)]. Core-mantle interaction would also buffer the f_{O_2} of OIBs to the iron-wustite buffer, which is three to four orders of magnitude lower than f_{O_2}'s actually measured in OIBs [*Basaltic Volcanism Study Project* (Pergamon Press, New York, 1981)].
32. K. Righter, M. J. Drake, G. Yaxley, *Phys. Earth Planet. Int.* **100**, 115 (1997).
33. J. Myers and H. Eugster, *Contrib. Mineral. Petrol.* **82**, 75 (1983).
34. T. Meisel, R. J. Walker, J. W. Morgan, *Nature* **383**, 517 (1996); H. K. Brueckner *et al.*, *J. Geophys. Res.* **100**, 22283 (1995); L. Reisberg and J.-P. Lorand, *Nature* **376**, 159 (1995); J. W. Morgan, G. A. Wandless, R. K. Petrie, A. J. Irving, *Tectonophysics* **75**, 47 (1981).
35. T. H. Green, *Chem. Geol.* **117**, 1 (1994).

36. We thank C. J. Capobianco, J. Chesley, M. J. Drake, S. Shirey, and P. Warren for discussions; P. Liermann and J. Ganguly for providing samples of Buell Park garnet; and J. Wang for expert assistance with the ion microprobe. This research is supported by NSF grants EAR-9706024 and EAR-9628092.

24 March 1998; accepted 29 April 1998

Integrated Optoelectronic Devices Based on Conjugated Polymers

Henning Sirringhaus,* Nir Tessler, Richard H. Friend*

An all-polymer semiconductor integrated device is demonstrated with a high-mobility conjugated polymer field-effect transistor (FET) driving a polymer light-emitting diode (LED) of similar size. The FET uses regioregular poly(hexylthiophene). Its performance approaches that of inorganic amorphous silicon FETs, with field-effect mobilities of 0.05 to 0.1 square centimeters per volt second and ON-OFF current ratios of >10⁶. The high mobility is attributed to the formation of extended polaron states as a result of local self-organization, in contrast to the variable-range hopping of self-localized polarons found in more disordered polymers. The FET-LED device represents a step toward all-polymer optoelectronic integrated circuits such as active-matrix polymer LED displays.

Solution-processible conjugated polymers are among the most promising candidates for a cheap electronic and optoelectronic technology on plastic substrates. Polymer LEDs exceeding peak brightnesses of 10^6 cd m^{-2} (*1*) and high-resolution video polymer LED displays (*2*) have been demonstrated. One of the main obstacles to all-polymer optoelectronic circuits is the lack of a polymer FET with sufficiently high mobility and ON-OFF ratio to achieve reasonable switching speeds in logic circuits (*3*) and to drive polymer LEDs.

Conjugated polymer FETs (*4*) typically show field-effect mobilities of μ_{FET} = 10^{-6} to 10^{-4} cm^2 V^{-1} s^{-1}, limited by variable-range hopping between disordered polymer chains and ON-OFF current ratios of $<10^4$ (*5*). This is much too low for logic and display applications, and therefore all previous approaches to drive polymer LEDs have used polycrystalline (*2*) or amorphous silicon (a-Si) (*6*) technology. Recently, a polymer FET with a mobility of 0.01 to 0.04 cm^2 V^{-1} s^{-1} and an ON-OFF ratio of 10^2 to 10^4 using regioregular poly(hexylthiophene) (P3HT) was described (*7*). The high mobility is related to structural order in the polymer film induced by the regioregular head-to-tail (HT) coupling of the hexyl side chains. However, a clear understanding of the transport mechanism giving rise to the relatively high mobilities is still lacking.

Here, we report a considerably improved P3HT FET reaching mobilities of 0.05 to 0.1 cm^2 V^{-1} s^{-1} and ON-OFF ratios of $>10^6$, the performance of which starts to rival that of inorganic a-Si FETs and enables us to demonstrate integrated optoelectronic polymer devices. As an example, we have chosen a simple pixel-like configuration in which the FET supplies the current to a polymer LED. This allows us to assess the prospects of active-matrix addressing in all-polymer LED displays.

To construct the multilayer device (Fig. 1A), we first fabricated the FET by spin-coating a film of P3HT (500 to 700 Å) (*8*) onto a highly doped n$^+$-Si wafer with a 2300 Å SiO$_2$ gate oxide (capacitance C_i = 15 nF cm^{-2}). Au source-drain contacts were deposited onto the P3HT through a shadow mask. Then, a layer of SiO$_x$ was thermally evaporated through another, mechanically aligned, shadow mask to define the active LED area on the finger-shaped Au FET drain electrode acting as the hole-injecting anode of the LED. A single layer of poly[2-methoxy-5-(2′-ethyl-hexyloxy)-*p*-phenylene-vinylene] (MEH-PPV) was spin-coated on top. Evaporation of a semitransparent Ca-Ag cathode completed the device. No photolithographic steps were involved. The device

Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 0HE, UK.

---

*To whom correspondence should be addressed.

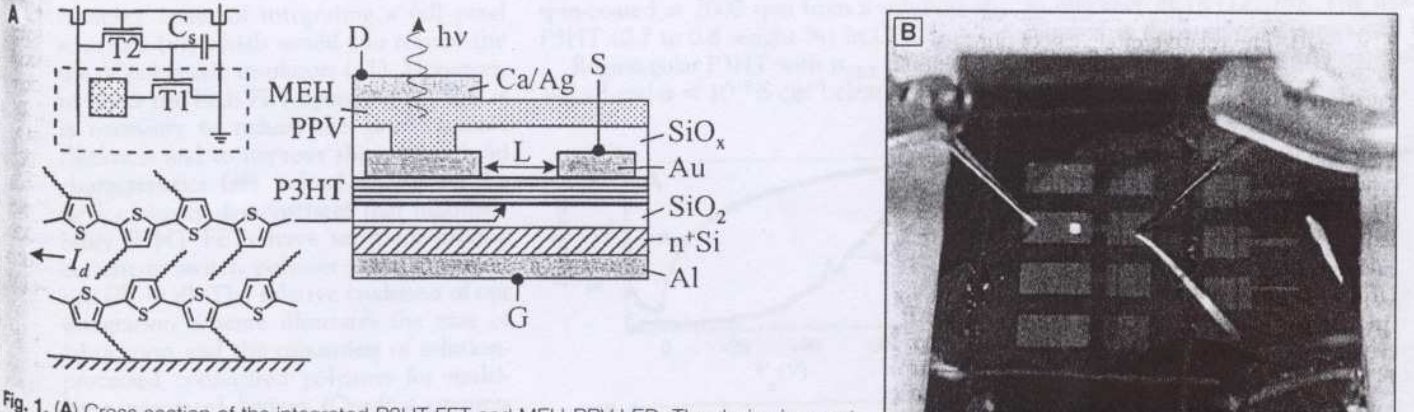


Fig. 1. (**A**) Cross section of the integrated P3HT FET and MEH-PPV LED. The device is a part (shown inside the dashed area in the top left corner) of a full active-matrix polymer LED pixel. The lamellar structure of the regioregular P3HT and its orientation relative to the SiO$_2$ substrate and the direction of the in-plane FET current I_d are shown schematically. (**B**) Photograph of a FET-LED with one of the four "pixels" switched on. The MEH-PPV layer (orange) was made to cover the substrate only partially in order to make the underlying (blueish) P3HT layer visible.

OLED Display Technology

Solution Processed OLED Technology

- Our core technology and expertise is in the development of solution processed P-OLED materials with high performance
- Materials are compatible for large area patterning techniques
- Polymer OLED materials can be printed successfully and reproducibly, producing RGB colours and the high performance required for colour displays

Image courtesy of Panasonic Corp.

P-OLED Device Test Cell Performance Summary

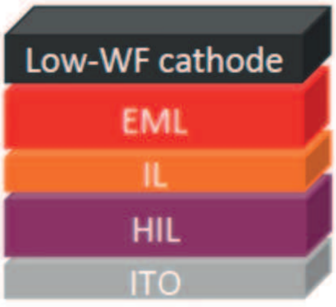
Spin/BE data @1000Cd/m^2	RED			GREEN			BLUE		
Efficiency [cd/A]	**31**	**24**	**18**	**85**	**72**	**61**	**12**	**11**	**9.5**
Colour (C.I.E. x,y)	x=0.62 y=0.38	x=0.66 y=0.34	x=0.65 y=0.35	x=0.32 y=0.63	x=0.32 y=0.63	x=0.32 y=0.63	x=0.14 y=0.12	x=0.14 y=0.12	x=0.14 y=0.13
T50 lifetime [hrs]	**350k**	**200k**	**200k**	**80k**	**350k**	**>300k**	**>10k**	**-**	**-**
T95 lifetime [hrs]	**-**	**2000**	**2400**	**1000**	**2600**	**4400**	**-**	**230**	**700**
Vd [V]	**4.2**	**3.3**	**3.2**	**3.9**	**4.7**	**5.0**	**3.7**	**4.0**	**4.0**

Device structure: ITO (45nm) / HIL (30-65nm) / Interlayer (20nm) / LEP (60-75nm) / Low WF cathode

- Hole injection, interlayer and emitter are all processed from solution
- R, G, B common and simple layer structure
- Devices fabricated by spin coating processes

*Lifetime estimated from luminance acceleration test.

*No electrical ageing applied before lifetime test.



Non-cavity device

EML = emissive layer (R, G, B)

IL = interlayer

HIL = hole injection layer

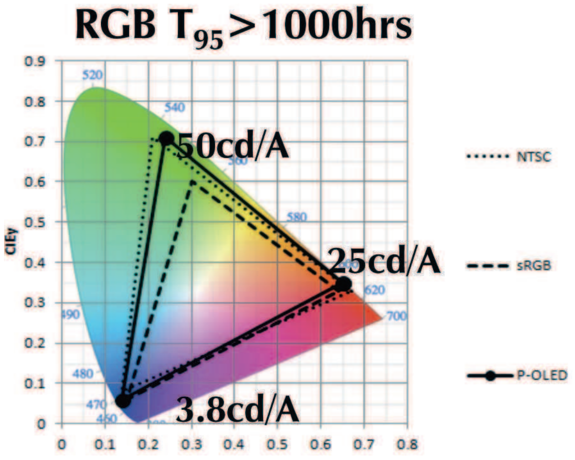
Key Areas of our Expertise in P-OLED Development:

- CDT and Sumitomo Chemical have extensive technical expertise in materials chemistry and device physics to realise high performance materials for high end display and lighting applications
- Our expertise covers a fundamental understanding of materials and devices through to complex understanding of the interplay between ink formulation, print process science and fabrication engineering for realising high performance printed displays

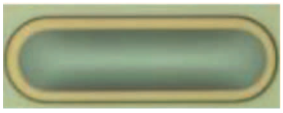
OLED Display Technology

Expertise in Materials, Formulation and Process Development:

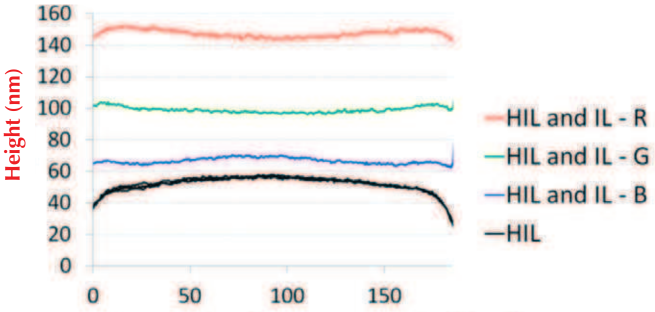
- Expertise across the breadth of the development chain to ensure the printed layers provide exceptional performance
- Utilising our fundamental understanding of device physics, we have developed a combined hole-injection layer and interlayer (hole-transport layer) stack to realise uniform film thickness profiles, providing uniform emission across inkjet printed pixels
- Required film thickness and uniformity can be achieved by inkjet printing, with the HIL and IL printed at high speed with single pass printing for RGB, and with a large process window to allow for large scale manufacturing tolerances
- Uniform emission inkjet printed P-OLED devices do not suffer from any additional initial degradation mechanism. With carefully selected materials, inks and processes, long T95 lifetimes (greater than 1000 hours) are achieved with inkjet printed devices



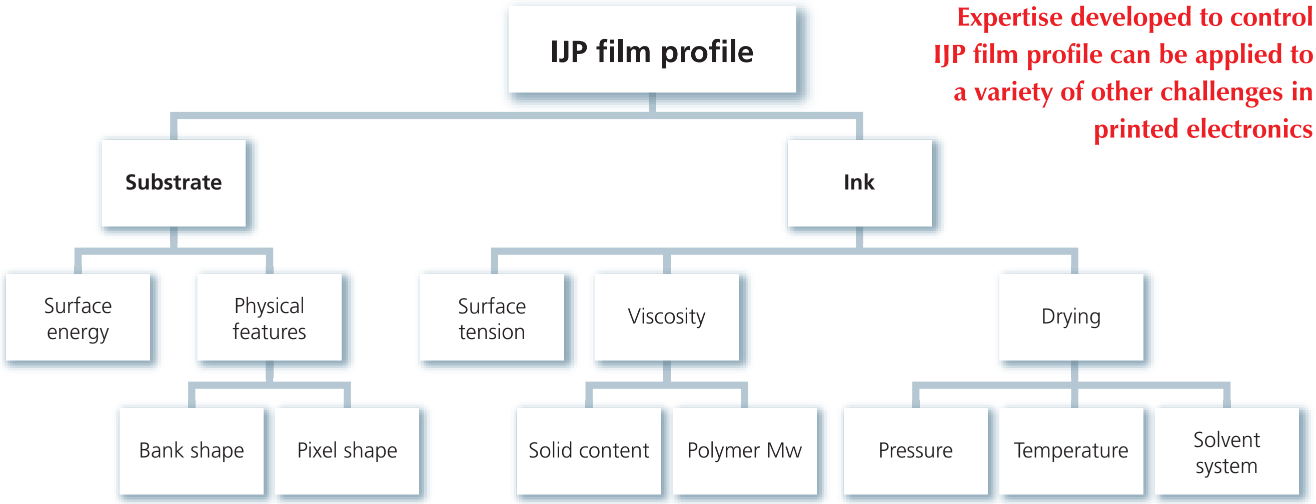
Performance based on films printed into cavity devices



Printed pixel plan view and cross section line



Distance lengthwise across pixel (μm)



- IJP film profile
  - Substrate
    - Surface energy
    - Physical features
      - Bank shape
      - Pixel shape
  - Ink
    - Surface tension
    - Viscosity
      - Solid content
      - Polymer Mw
    - Drying
      - Pressure
      - Temperature
      - Solvent system

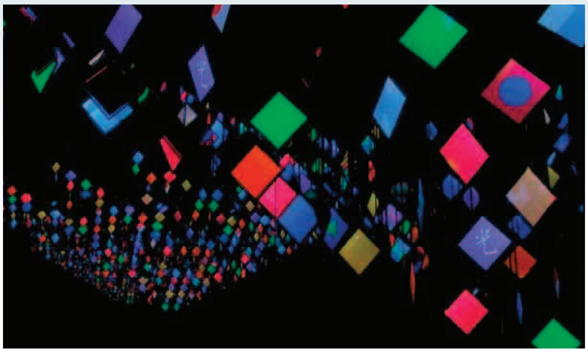
Expertise developed to control IJP film profile can be applied to a variety of other challenges in printed electronics

Head Office: Cambridge Display Technology Ltd, Units 8, 11 and 12 Cardinal Business Park, Godmanchester, Cambridgeshire, PE29 2XG, UK
Contact us: **Tel:** +44 (0)1480 387300 **Fax:** +44 (0)1480 387342 **Email:** displays-info@cdtltd.co.uk **Web:** www.cdtltd.co.uk

Large Area and Decorative OLED Lighting

OLED Lighting Technology

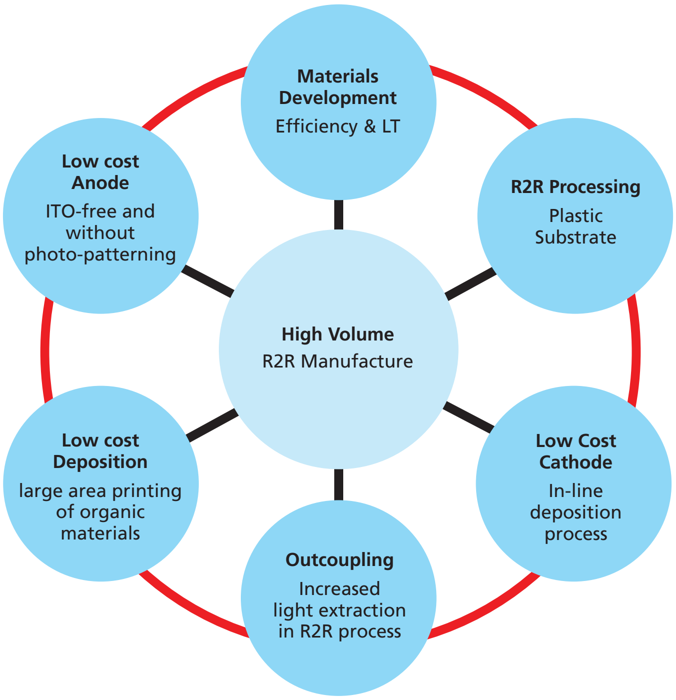
- OLEDs have great potential for creating large area, diffuse light sources.
- Global market for OLED lighting set to take off. Projection for 2018 is US$150M revenue (IDTechEx, 2013).
- CDT and Sumitomo developing materials and manufacturing capability for low cost, large area OLED lighting.



Technology Demonstration

150mm (6inch)
Concept Installation

150mm (6inch)
with printed
emissive layer



Materials Development
Efficiency & LT

R2R Processing
Plastic Substrate

Low Cost Cathode
In-line deposition process

Outcoupling
Increased light extraction in R2R process

Low cost Deposition
large area printing of organic materials

Low cost Anode
ITO-free and without photo-patterning

High Volume
R2R Manufacture

Key OLED Lighting Technology Challenges

- Materials development focussed on colour and improving efficiency and lifetime.
  - 2800K and 3500K White with high CRI. >50Lm/W and 10k hrs LT70.
- Low cost structure and manufacturing: plastic substrate and ITO-free anode.
- Develop scalable process for in-line large printing & drying of all organic layers:
  - Slot Die Coating and Ink Jet Printing.
- Higher efficiency enabled by R2R compatible optical outcoupling technologies.

Performance Parameters

	TECHNICAL SPECIFICATIONS									
White	CIE x	CIE y	CR1	CCT	Duv	EQE	Lm/W	Cd/A	V	I
	0.458	0.461	72	3100	0.018	32	56	80	4.4	18

* Measurement at $1000 cd/m^2$ in integrating sphere with external outcoupling.

C|D|T Cambridge Display Technology

Large Area and Decorative OLED Lighting

Decorative OLED Lighting

- Customized single and dual coloured tiles available → may be patterned.
- OLEDs can be made on plastic, giving flexible form factor & shape variations on very thin substrates.
- Gently diffused light – emits no harsh glare nor UV rays.
- Applications include room and car interiors, displays in hospitality and restaurants and niche lighting for sensitive objects in museums and phototherapy.

Technology Demonstration

50mm (2inch) Colored Tiles (CDT)

OLED Cosmos (Sumitomo)

50mm (2inch) inkjet printed on a flexible/conformable substrate

Shown at the 2013 Automotive Engineering Exposition

Technology Development

- Demonstrators can be supplied for interested customers and end-users.
- Colour and design of tiles is on-demand. Current active area is 94x94mm.
- Lower cost and simpler production process can be achieved with lower efficiency and/or lifetime requirements.
- OLED Cosmos tiles for sale by Sumitomo: prices available on request
- Large range of potential applications, complementary to incumbent lighting technologies.

Head Office: Cambridge Display Technology Ltd, Units 8, 11 and 12 Cardinal Business Park, Godmanchester, Cambridgeshire, PE29 2XG, UK
Contact us: **Tel:** +44 (0)1480 387300 **Fax:** +44 (0)1480 387342 **Email:** lighting-info@cdtltd.co.uk **Web:** www.cdtltd.co.uk

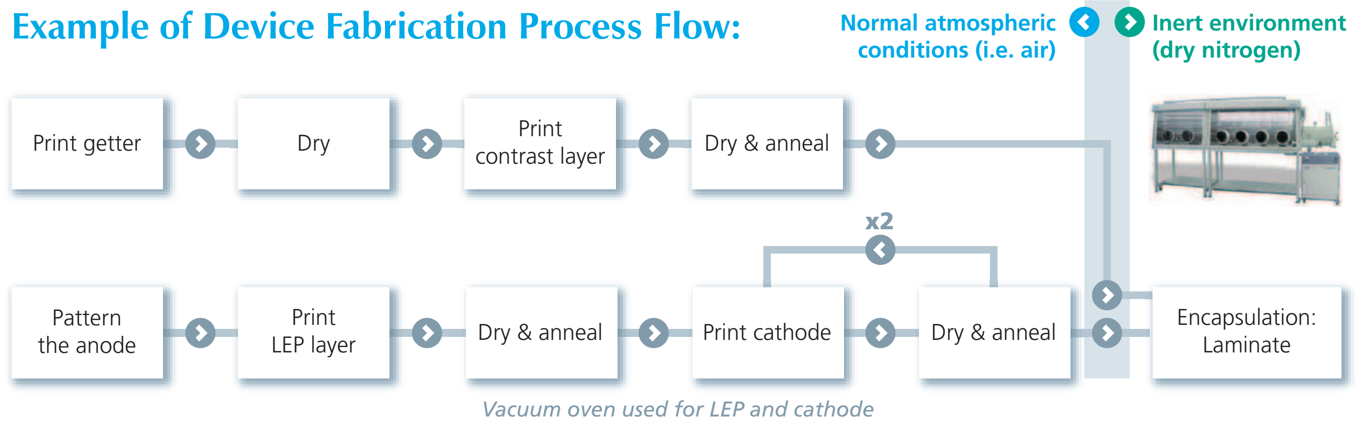
Cambridge DisplayTechnology Limited is a wholly owned subsidiary of Sumitomo Chemical
SUMITOMO CHEMICAL
Cambridge Display Technology Ltd (Company Number 02672530)

Printed Flexible OLED Displays

All-printed, Flexible OLED Displays:

- Technology services for printed displays in a myriad of low cost, low information content devices
- Simpler device structure with fewer device processing steps compared with conventional OLED device fabrication technology
- Device film deposition steps conducted in air

Example of Device Fabrication Process Flow:



Normal atmospheric conditions (i.e. air)

Inert environment (dry nitrogen)

Print getter → Dry → Print contrast layer → Dry & anneal →

Pattern the anode → Print LEP layer → Dry & anneal → Print cathode → Dry & anneal → Encapsulation: Laminate

x2

Vacuum oven used for LEP and cathode

Examples of Exciting Application Areas:

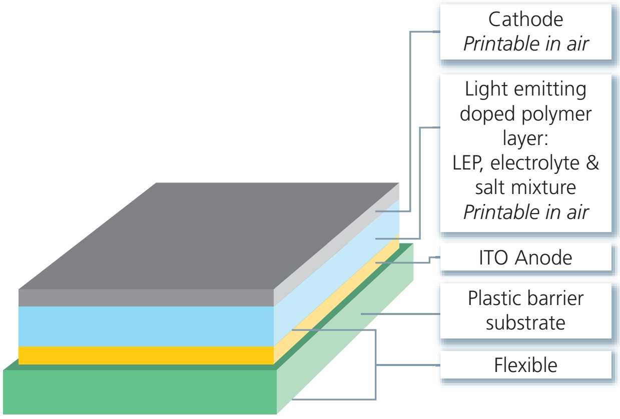
Toys & Games

Hand-held Medical Devices

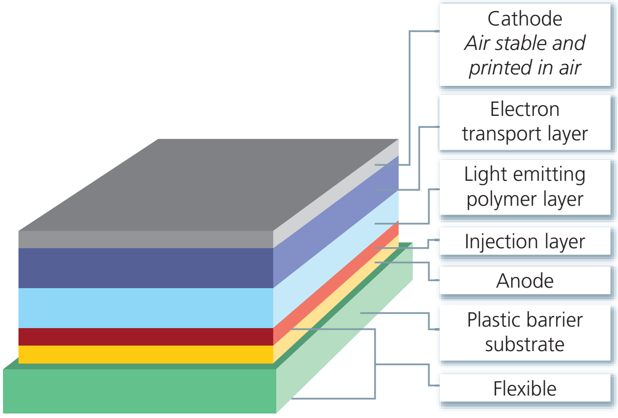
Wearable Devices

Printed Flexible OLED Displays

Current Device Structure



Structure in Development



CURRENT DEVICE STRUCTURE	
Demonstrator technical specifications	
Luminance turn-on	< 1 s
Max operating voltage	24 V
Luminance	~75 (red) to 100 (green) cd/m^2
Operating lifetime	~150 hrs
Drive current density	5 mA/cm^2
Average operating voltage	~16 V
Shelf life	~2 years
Colour range	White; intrinsic Red, Green and Sky Blue

STRUCTURE IN DEVELOPMENT	
Test cell April 2014	**Target demos Dec. 2014**
< 20 msec	< 20 msec
12V	12V
~200cd/m^2	100-200cd/m^2
tbc	200 hrs
2 mA/cm^2	2-3 mA/cm^2
12V	12V
tbc	~2 years
Green	Red, green, blue, white

Key Technology Points and Future Developments:

- Reduced complexity device structure in comparison with conventional OLED devices
  - Layers required for printing: Emitter and cathode layers with getter and contrast layers for final device fabrication completion
- Printed electronics technology opens up many possibilities for low cost devices based on printing techniques such as screen printing and gravure

Head Office: Cambridge Display Technology Ltd, Units 8, 11 and 12 Cardinal Business Park, Godmanchester, Cambridgeshire, PE29 2XG, UK
Contact us: **Tel:** +44 (0)1480 387300 **Fax:** +44 (0)1480 387342 **Email:** printoled-info@cdtltd.co.uk **Web:** www.cdtltd.co.uk

Cambridge DisplayTechnology Limited is a wholly owned subsidiary of Sumitomo Chemical
SUMITOMO CHEMICAL
Cambridge Display Technology Ltd (Company Number 02672530)