The Organic Electronics Story

Condensed Matter Physics in One Dimension

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ADVANCES IN PHYSICAL SCIENCES:
meeting in honour of Professor A. L. Leite Videira

September 5 to 7, 2005

Meaning

Organic Electronics

Multidisciplinary science and technology related to a class of organic materials, both single molecules and polymers which are emerging as the basis for a new technological paradigm, which aims at ultralow-cost, lightweight and flexible electronic devices for displays, circuits and memories that can be printed on anything and placed anywhere.

OUTLINE

- **INTRODUCTION**
- **THE INTERESTING PHYSICS — 1D INSTABILITIES**
- **THE PHYSICS OF CONDUCTING POLYMERS**
- **APPLICATIONS**
  - **THE NEED FOR A NEW PARADIGM IN MICROELECTRONICS**
  - **MATERIALS, DEVICES AND SYSTEMS**
  - **LUMINESCENCE — OLEDS**
  - **MOBILITY — OTFTS**
  - **PROCESSING TECHNOLOGIES**

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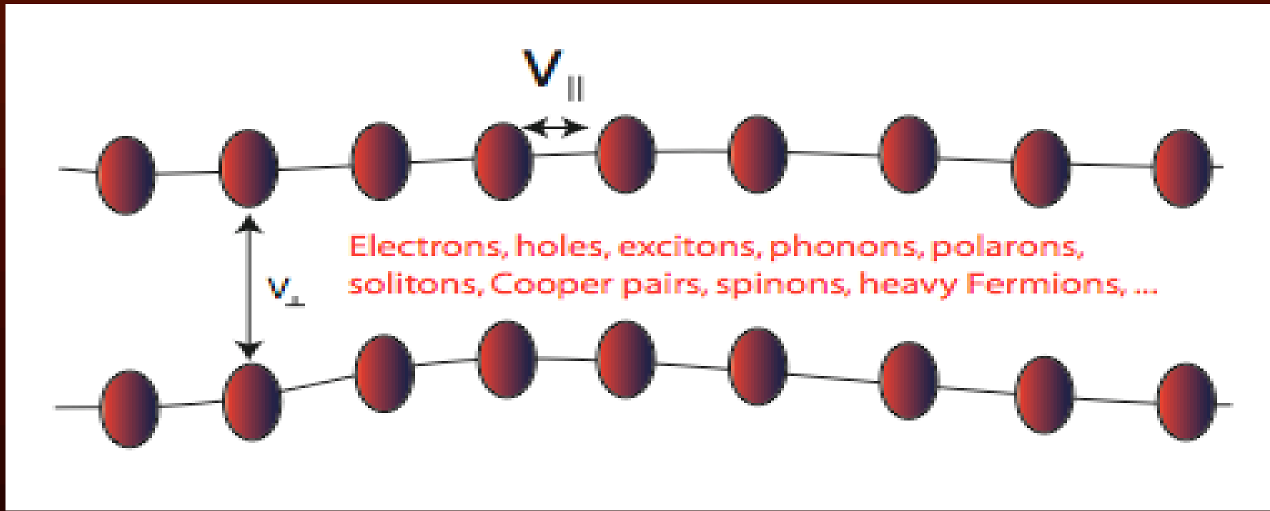


Linear chains of atoms or molecules

In 1D, *fluctuations* destroy all long-range order — problem of connectivity.

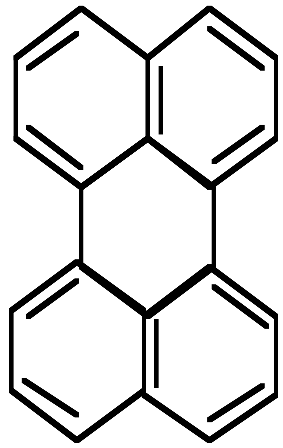
The only way one end of a one-dimensional sytem knows what is going on in the other end is via information transmitted directly along the chain. For an infinitely long system, any fluctuation cuts the flow of information and hence the order.

Since there are always fluctuations at any finite temperature, **a one-dimensional system cannot be ordered except at zero temperature.**

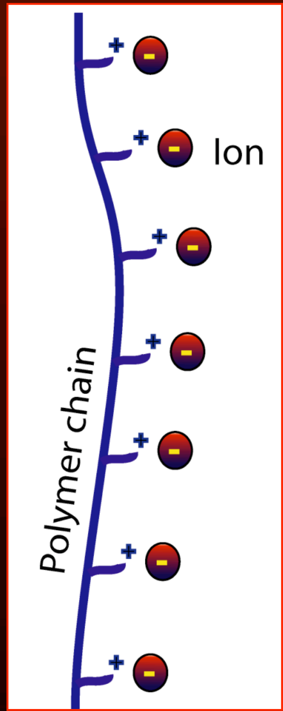
This is what makes the *1D* **real** systems interesting — they are not strictly 1D and they exhibit many interesting kinds of *fluctuations, instabilities and phase transitions.*

- The first organic conductor to be reported was a perylene-bromine complex, in 1954, by H. Akamatu, H. Inokuchi and Y. Matsunaga

  Nature 173 (1954)168.

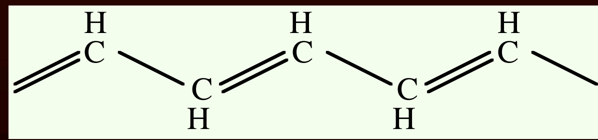


Perylene



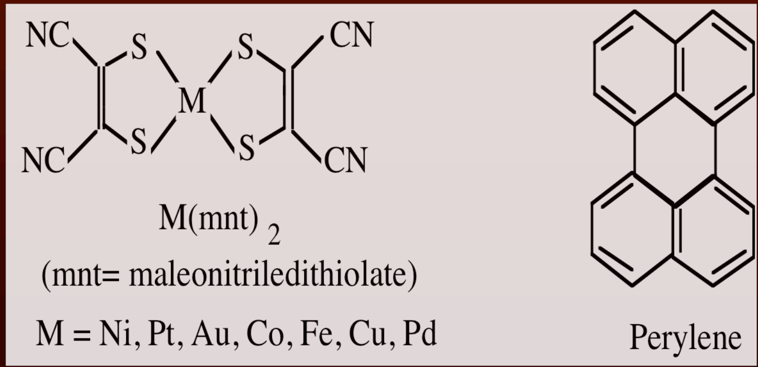
W.A.Little
Possibility of Synthesizing an Organic Superconductor
Physical Review 134A(1964) 1416

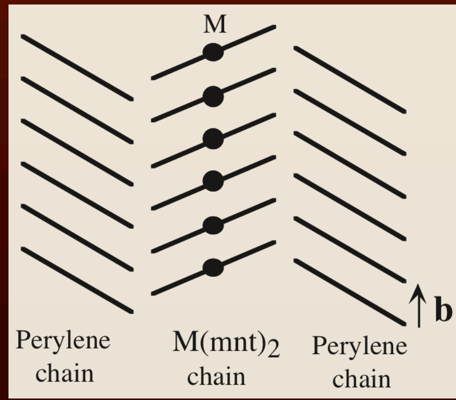
e.g., polyacetylene

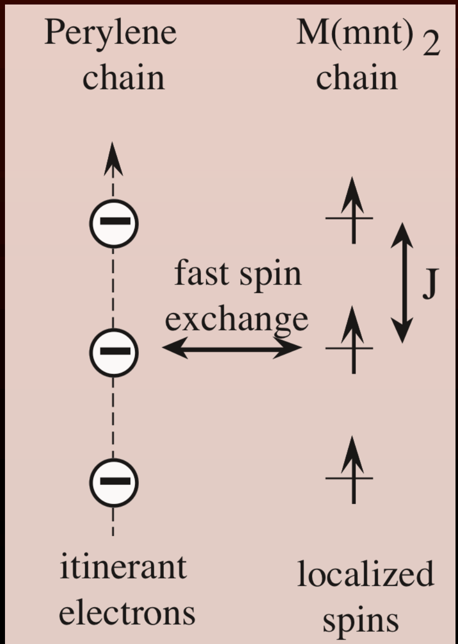


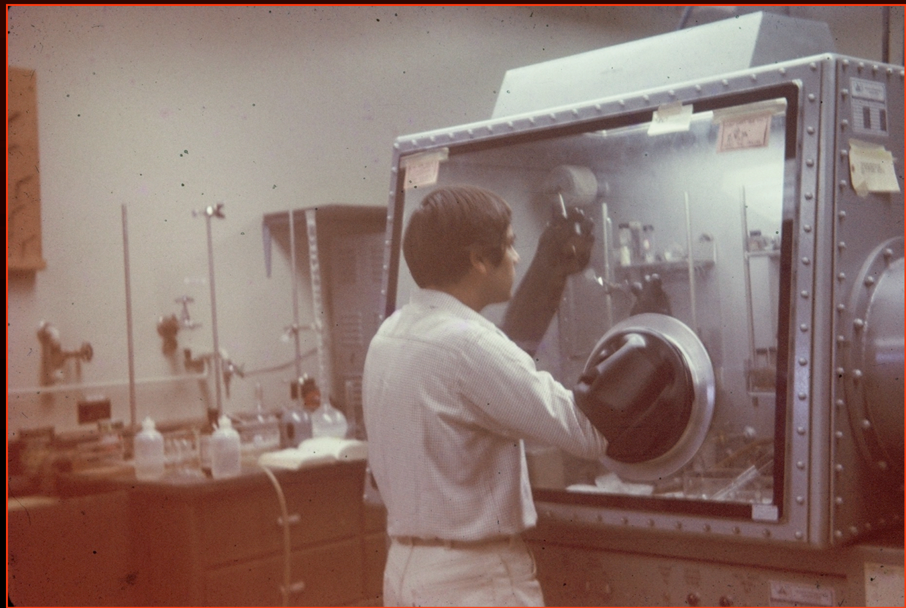
"Little's concept involved replacing the phonons (from BCS theory) with excitons, with much higher characteristic energies. If excitons were to become the electron-pairing `glue', superconductors with Tc's as high as 500 K might be possible. Little proposed a possible realization of the idea: a structure composed of a conjugated polymer chain dressed with highly polarizable molecule as side groups. The polymer chain would be a **one-dimensional metal** with a single mobile electron per C-H unit; electrons on separate units would be paired by interacting with the exciton field on the polarizable side groups."

Coincidence? "One-Dimensional Man", Herbert Marcuse, 1964







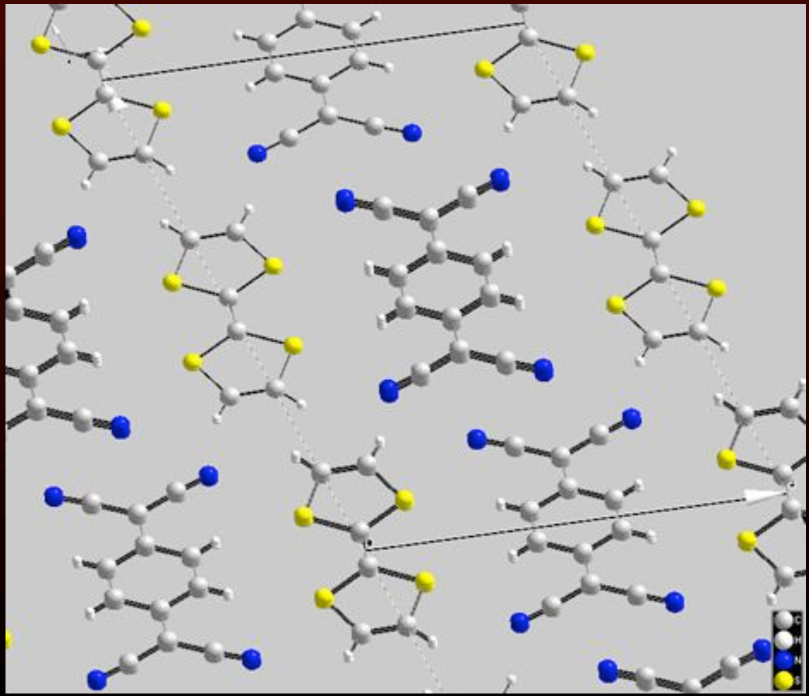


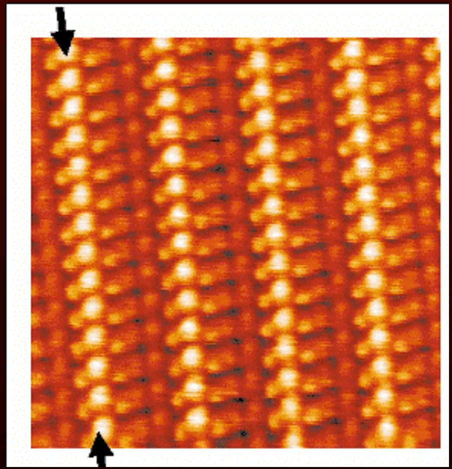
Making Per2-Ni(mnt)2 for the first time (1969)

Desperately trying to tune the ESR machine

L. Alcácer e A. H. Maki, "Electrically conducting metal dithiolate-perylene complexes" *Journal of. Physical Chemistry* **78** (1974) 215

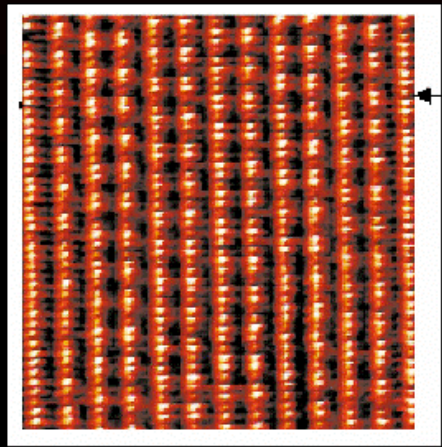
- **In the meanwhile** **TTF-TCNQ**





STM IMAGES

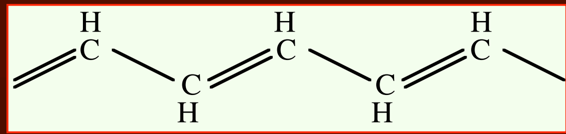
$T_{CDW}=53$ K



L. B. Coleman, M. J. Cohen, D. J. Sandman, F. J. Yamagishi, A. F. Garito e A. J. Heeger, “Superconducting fluctuations and Peierls instability in an organic solid”, *Solid State Communications* **12** (1973)1125.

Conducting Polymers

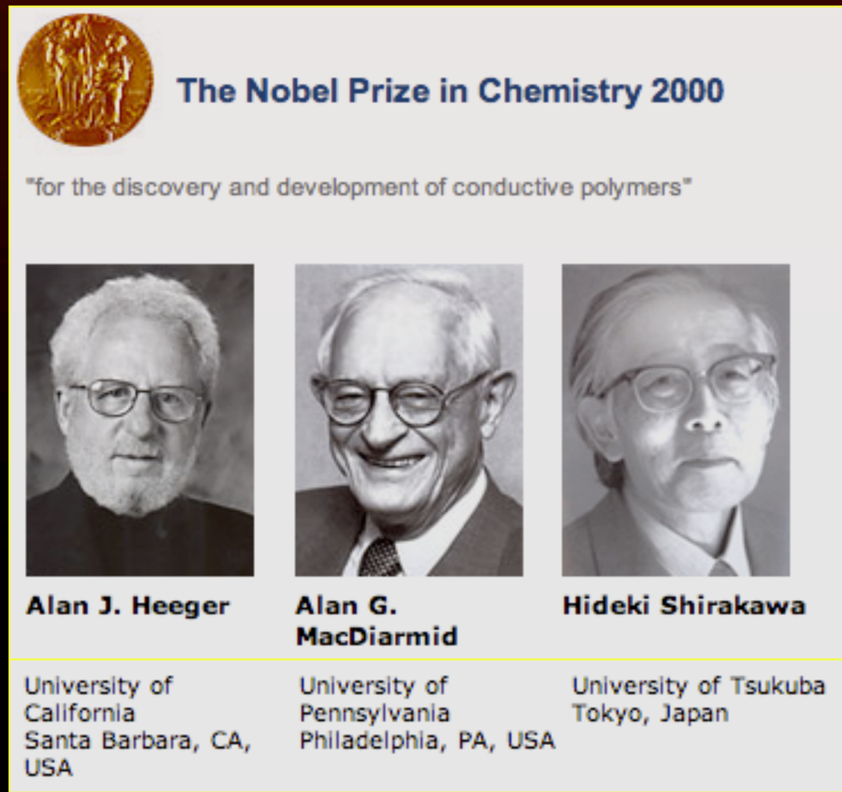
The story of Polyacetylene



- In Japan, in 1967, a group of scientists were studying the polymerization of acetylene into plastics.... One day a visiting researcher in the laboratory, the story goes, added more catalyst than written in the recipe: actually one thousand times too much! ... The result was a surprise also to the scientists. Instead of the expected black polyacetylene powder that normally was obtained, and that was of no use, a beautifully lustrous silver colored film resulted. It was, however, only its appearance that was metallic.

The material did not conduct electricity. The breakthrough was not made until ten years later in collaboration between physicist Alan Heeger and chemists Alan MacDiarmid and Hideki Shirakawa, continuing the experiments with the silver colored film. They tried to oxidize the film using iodine vapor, and - Bingo! The conductivity of the plastic increased by as much as ten million-fold; it had become conductive like a metal, comparable to copper.

Your serendipitous discovery of how polyacetylene could be made electrically conductive has led to the prolific development of a research field of great theoretical and experimental importance.



From the Nobel 2000 speach

The big thing in the early 1980s was the **theoretical work on solitons** etc., and then the synthesis of a range of new materials that really began to lead to the promise that we would have soluble, processable polymers that would still have the optical properties of metals and semiconductors.
At the beginning of the 1990s, a couple of things happened. First, the field matured to the point that we knew enough about polymers to synthesize stable polymers with specific energy gaps.
Around 1990 this led to the discovery of LEDs, the application that was discovered in Cambridge by Richard Friend and his collaborators and that created one focus of much of the work in the 1990s.

From an interview with Alan Heeger

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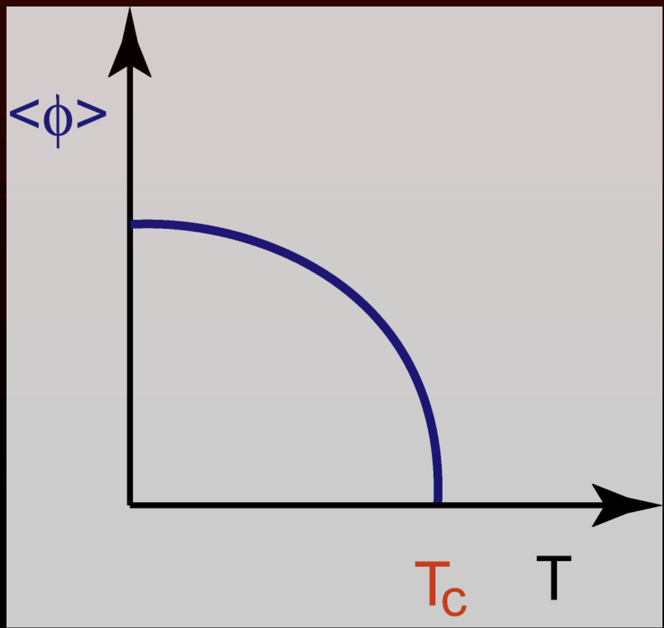
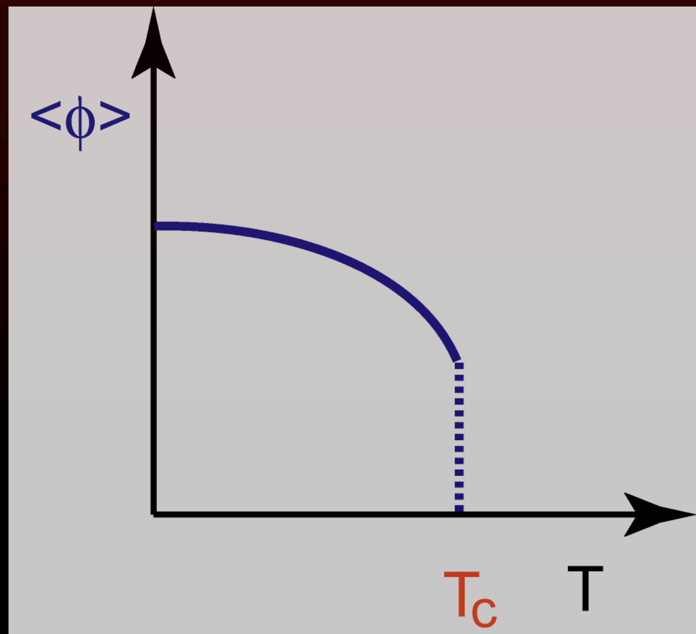
4 instabilities in 1 D:

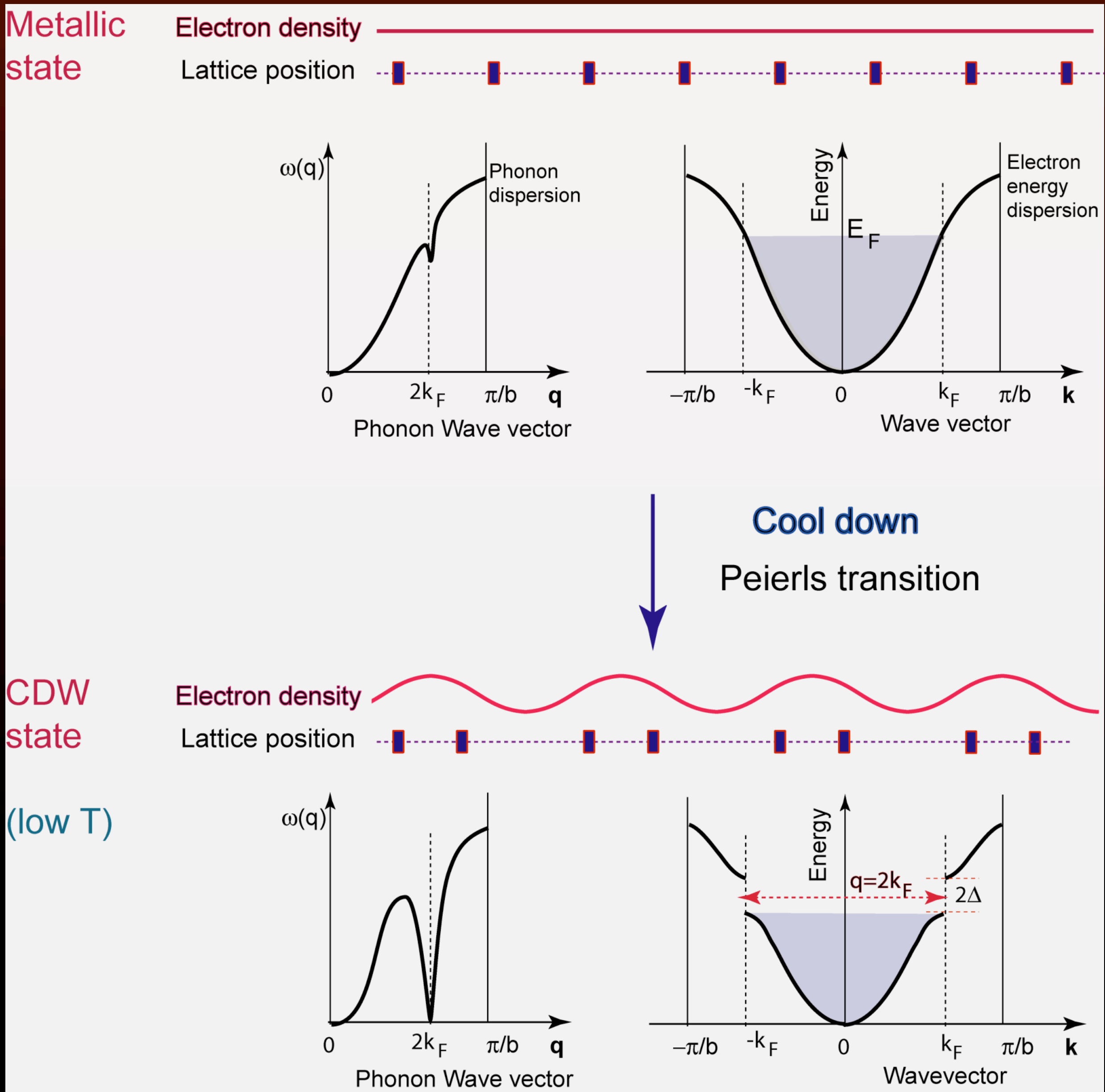
- Charge Density Wave, CDW (Peierls)
- Spin Density Wave, SDW
- Spin-Peierls, S-P
- Superconductivity, Sc





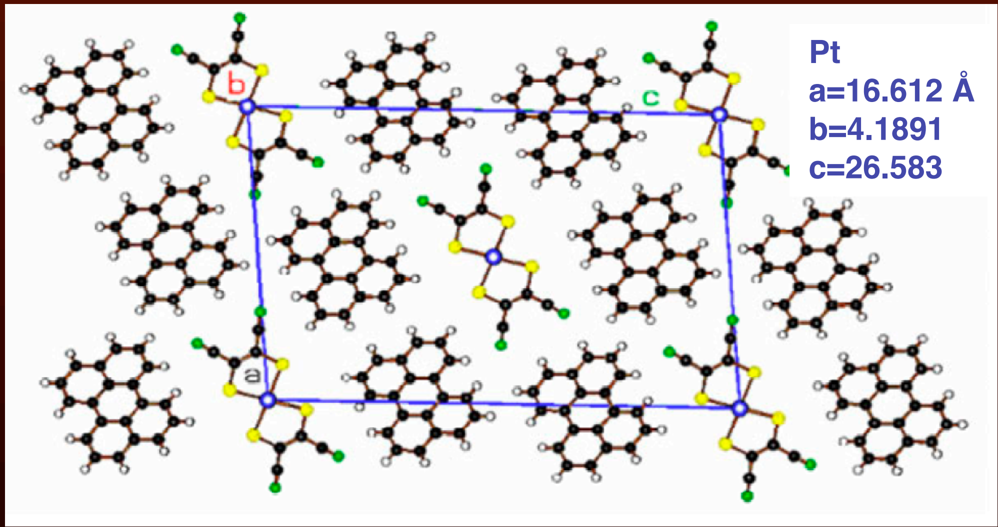
Order parameter as a function of temperature for a second order and for a first order transition

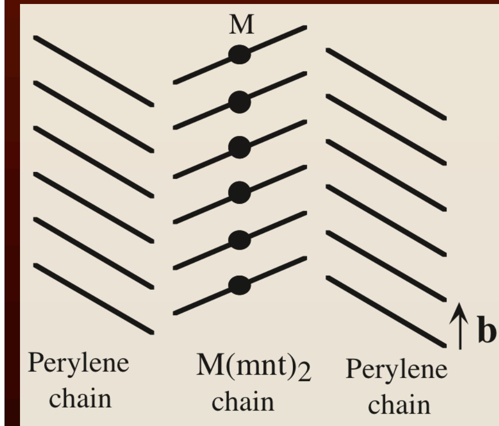
Formation of the energy gap



- **A CDW forms due to electron-phonon interaction**
- **Creates energy gaps at E_F**
- **Has wavelenght $\lambda = \pi/k_F$ and wave vector $q=2k_F$**

In quasi-1D metals, at low T, the elastic energy cost to modulate the lattice is less than the gain in conduction electron energy, so the CDW state is the ground state





t_b = -150 meV

t_a = 2 meV

t_c < 0.2 meV

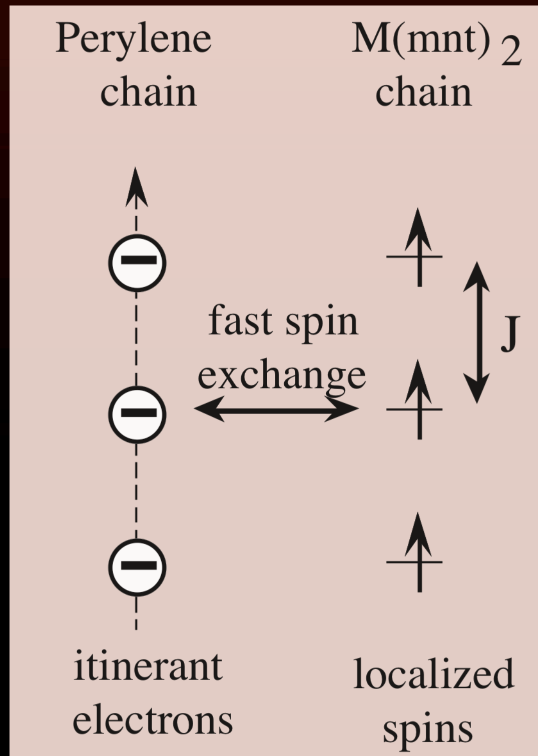
(Per)2M(mnt)2

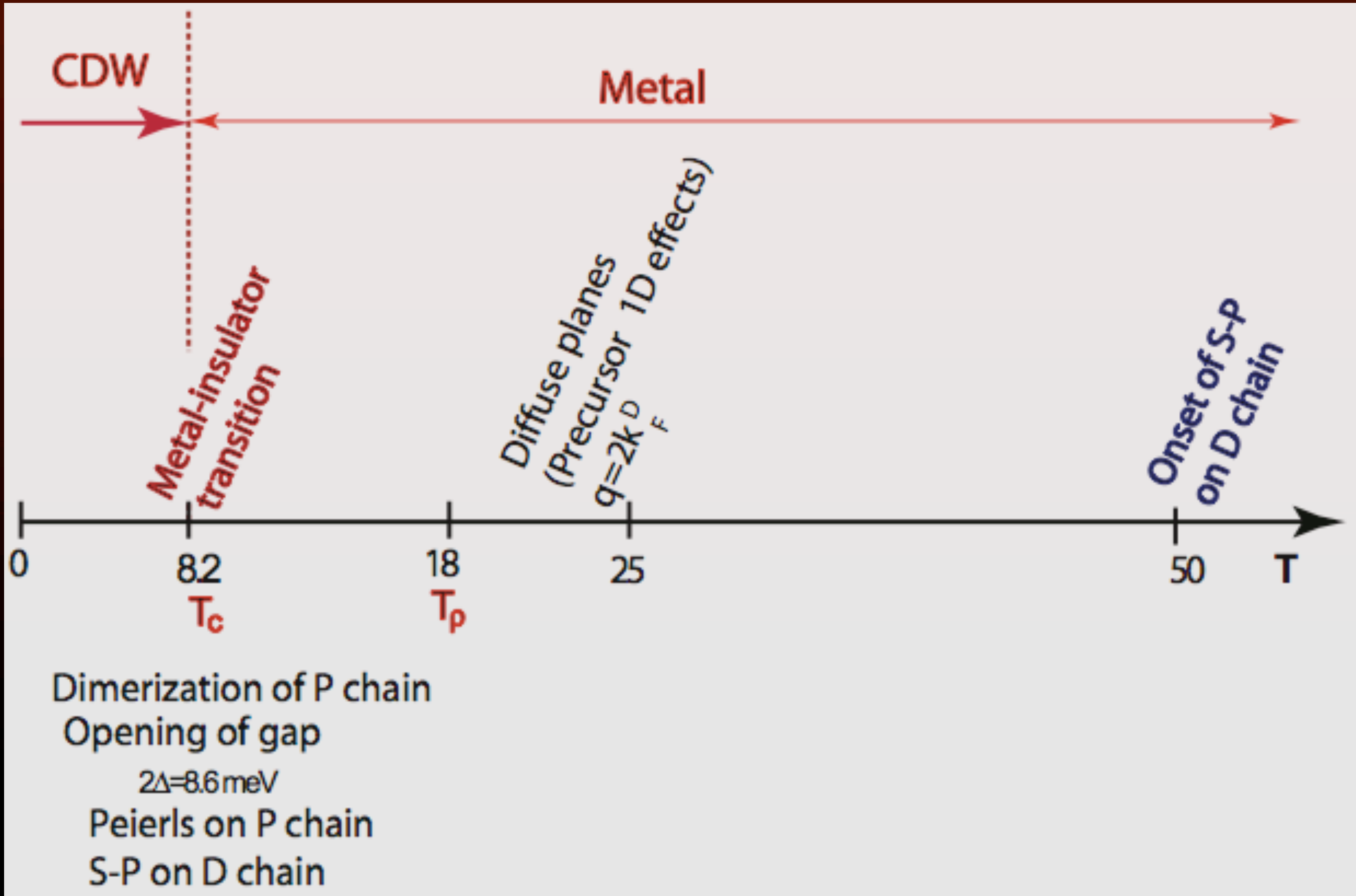
M =Au, Pt, Pd, Ni, Cu, Co, Fe

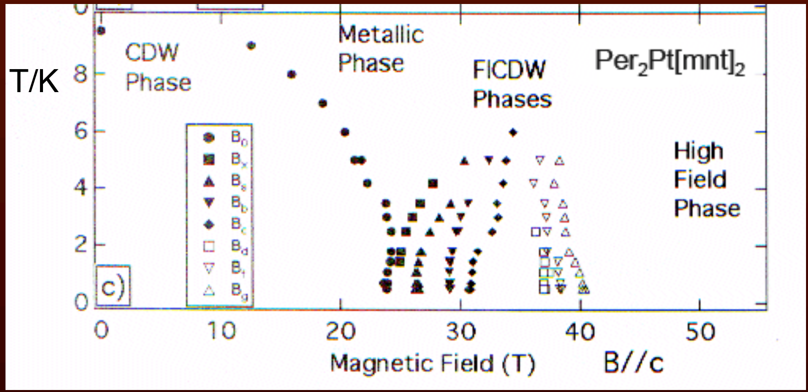
It has been proposed that the antiferromagnetic coupling between the M(mnt)−2 paramagnetic units is mediated by the conduction electrons in the perylene chains through a RKKY type mechanism

the full details of the field induced transitions, which are expected to be sensitive to Fermi surface topology only become visible below 2 K.

L. Alcácer, H. Novais, F. Pedroso, S. Flandrois, C. Coulon, D. Chasseau, J. Gaultier, Solid State Commun. **35**, 945 (1980)




CDW
Metal
Metal-insulator transition
Diffuse planes (Precursor 1D effects) $q=2k_F^D$
Onset of S-P on D chain
0
8.2
T_c
18
T_p
25
50
T
Dimerization of P chain
Opening of gap
2Δ=8.6 meV
Peierls on P chain
S-P on D chain



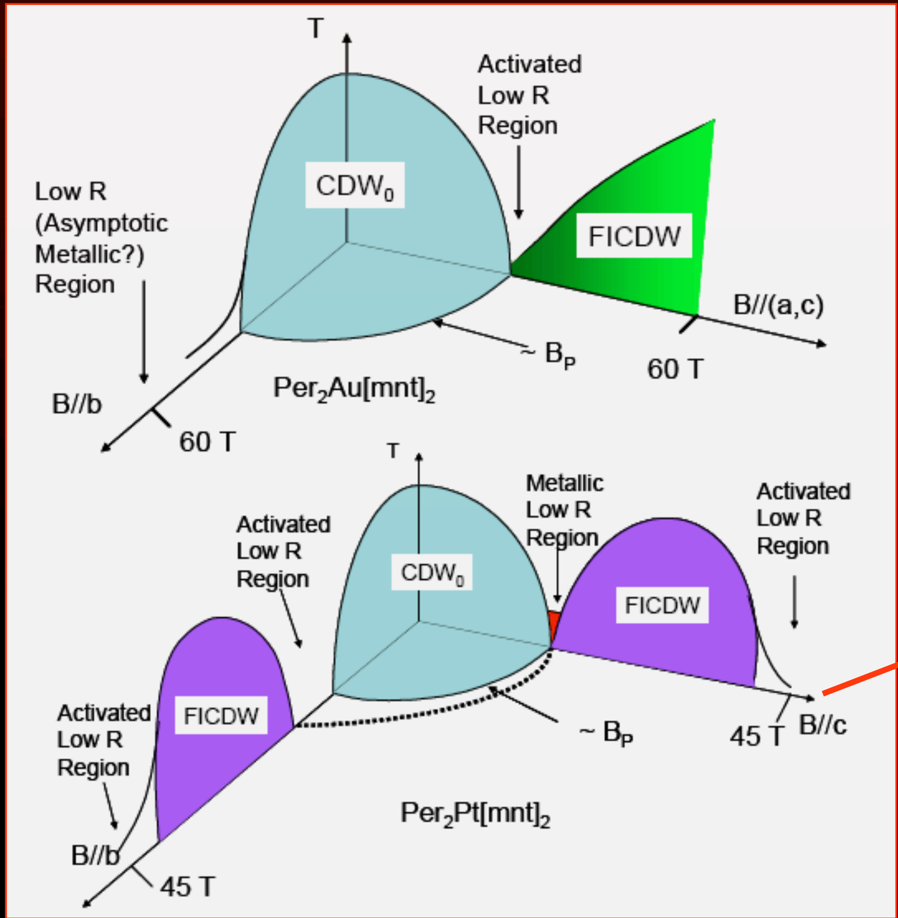
Cascade of transitions

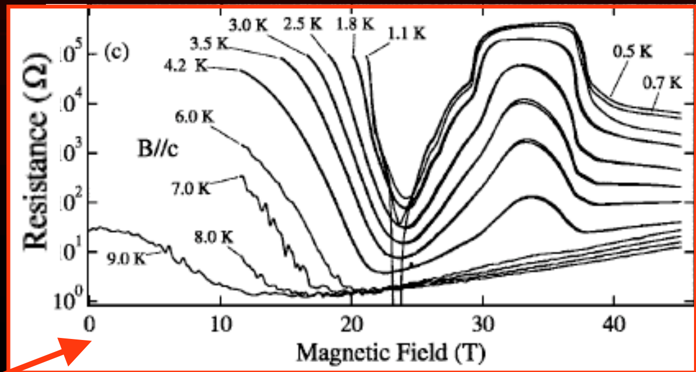
High field behavior of the CDW ground state in

a) $(Per)_2Pt[mnt]_2$

b)$(Per)_2Au[mnt]_2$

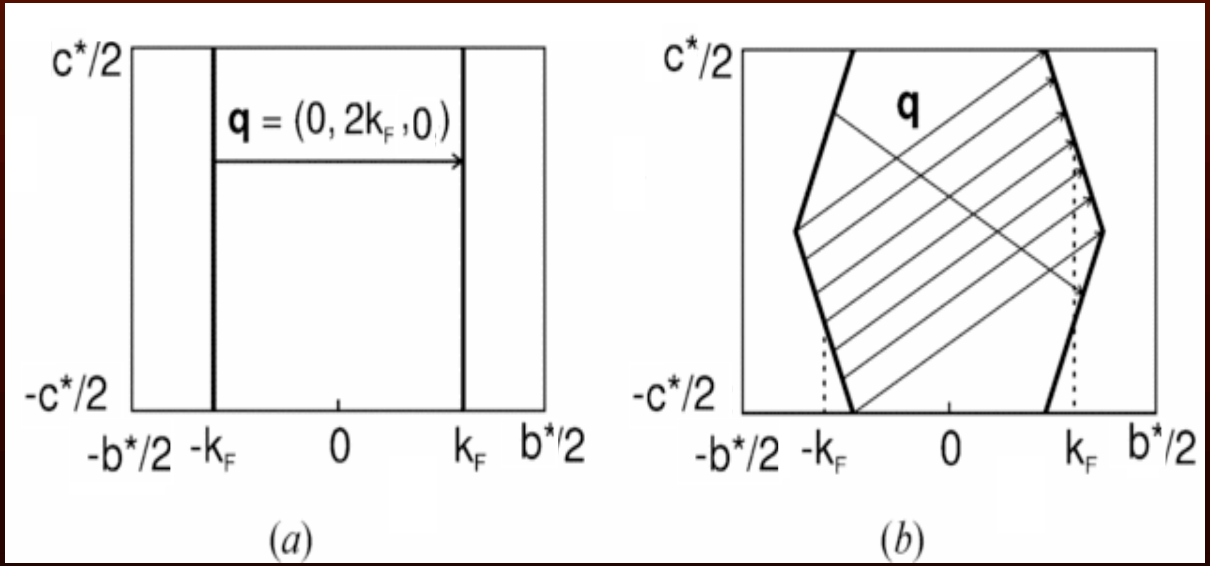
for B//c and B//b





From:
J.S. Brooks, D. Graf, E.S. Choi, M. Almeida, J.C. Dias, R.T. Henriques, M.Matos; Phys. Rev. B 69 (2004) +…

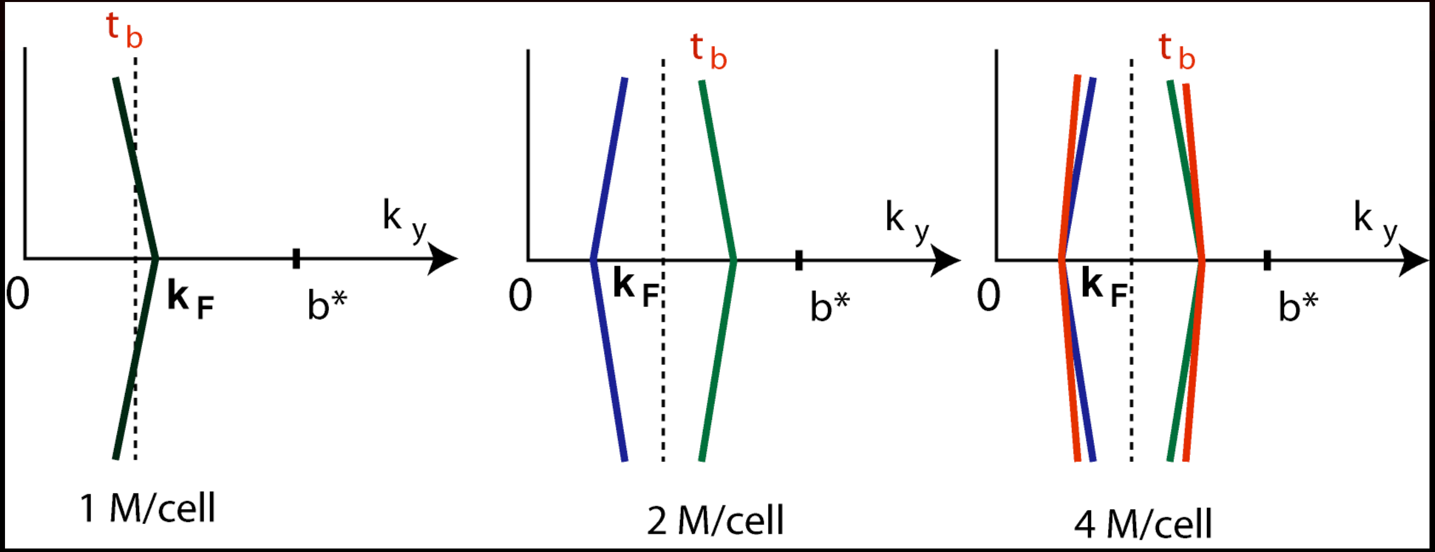
Work done at NHMFL-Tallahasse (USA) and ITN - Sacavem (Portugal)

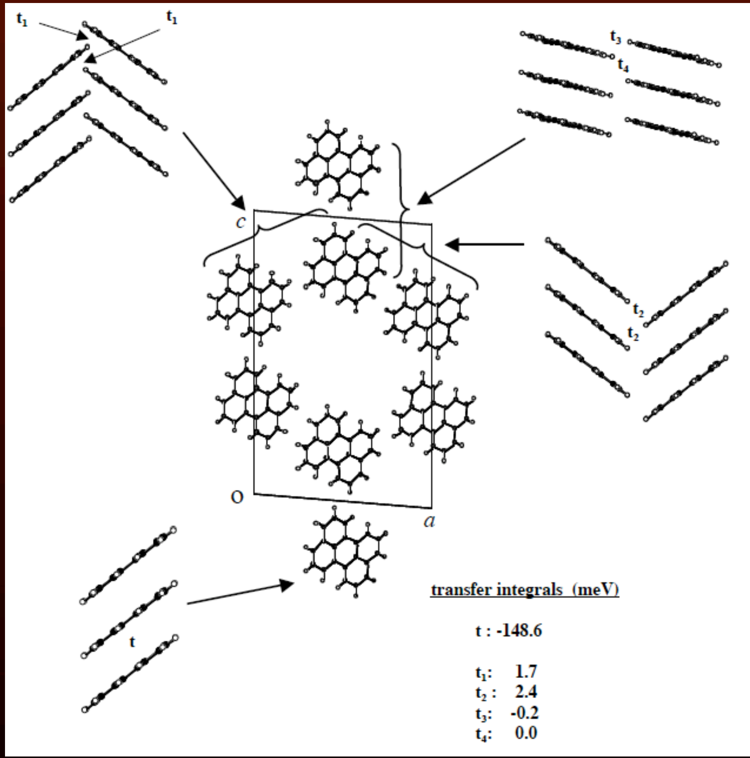


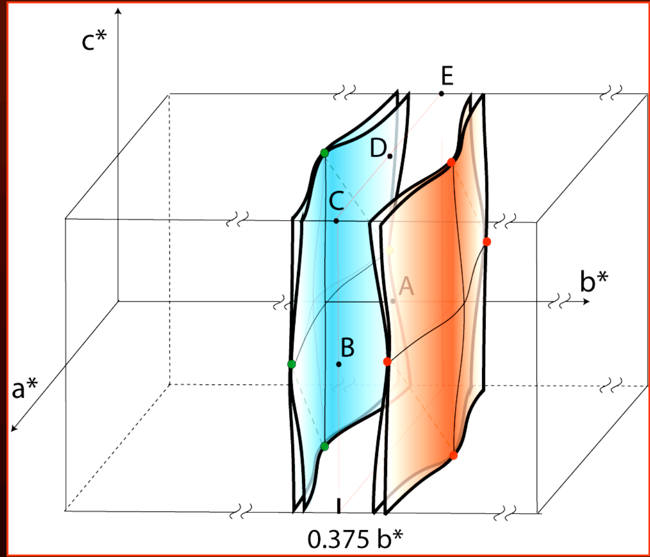
2D Sections of the Fermi surfaces of quasi-one-dimensional crystals.

(a) Non-interacting metallic chains parallel to [0 1 0]

(b) Weakly interacting metallic chains resulting in a warping of the Fermi surface. Perfect nesting is obtained for **q**=(0, q_2,1/2), where q_2 assumes the value such that **q** fulfills the nesting condition.



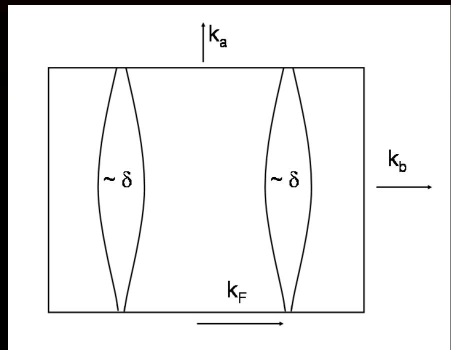




warping of the sheets can be of the order of 2 meV

Without the transverse interactions t_1, t_2, t_3 and t_4, the Fermi surface would be the superposition of four planes at $\mathbf{k_b}$ = ±0.375, but because of these transverseinteractions, the Fermi surface splits into four pairs of sheets with some warping.

The band structure of $(Per)_2M(mnt)_2$, leads to a description of these materials as nearly perfectly one dimensional conductors.



Simplified Fermi surface topology for $(Per)_2Pt(mnt)_2$ in the a-b plane (δ~0.001–0.002),

High magnetic field experiments suggest orbital coupling of the magnetic field to the electronic structure, indicating a finite interchain bandwidth

Calculations by Enric Canadell
(Institut de Ciència de Materials de Barcelona)

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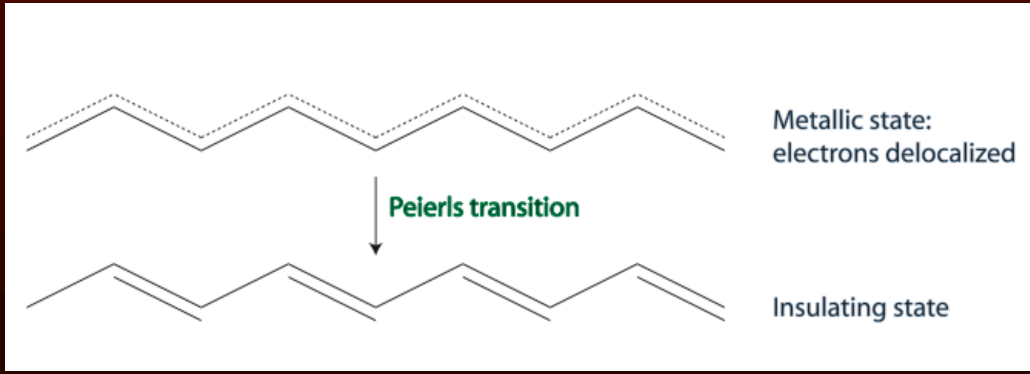
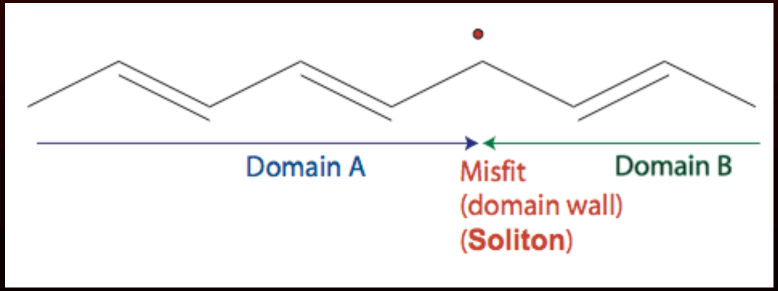
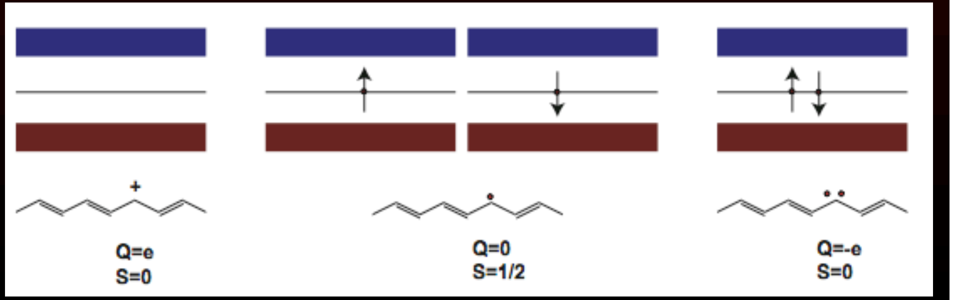
Physics of conjugated double bonds

Features of the electronic structure

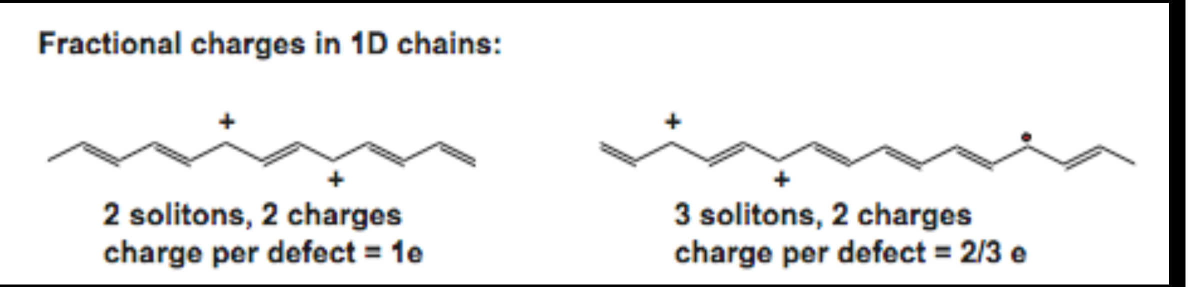
Degenerate polymers (e.g., polyacetylene)

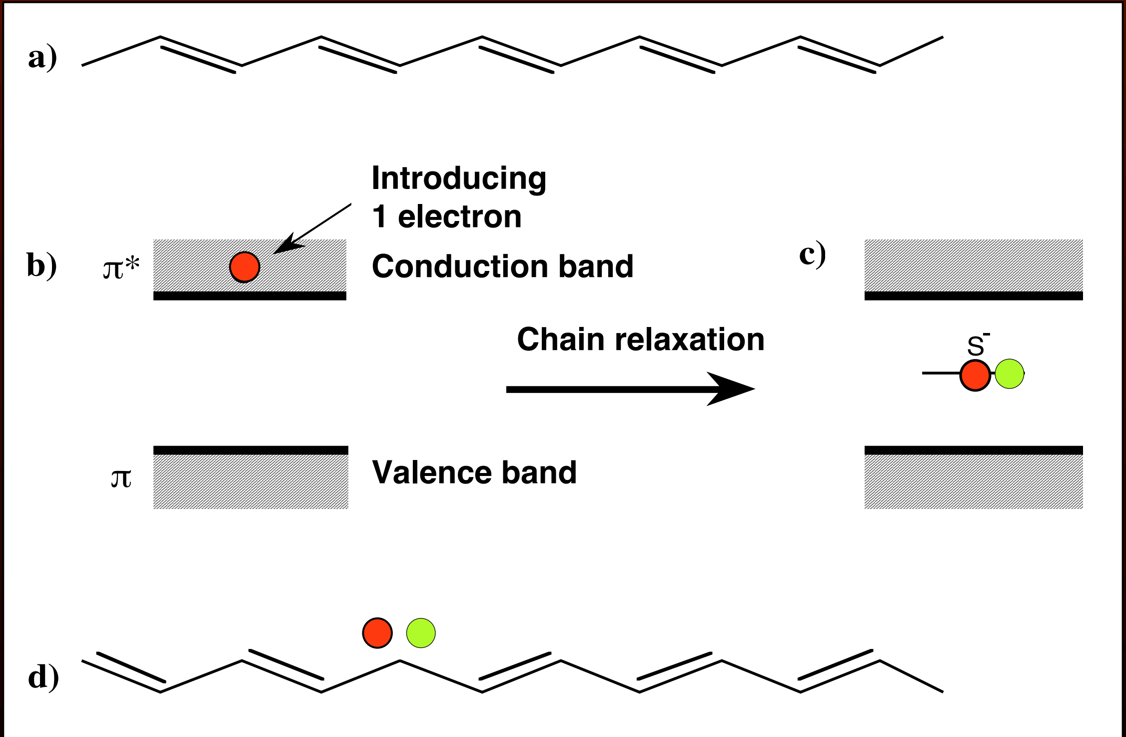






Solitons are delocalized over 10 - 15 carbon atoms

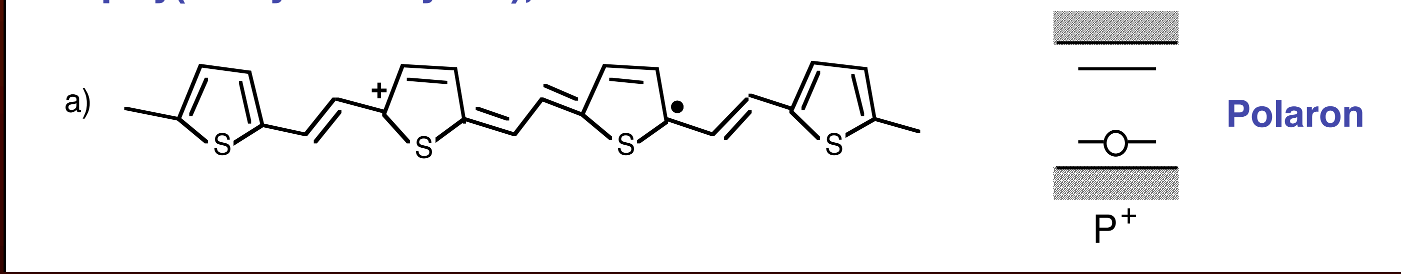


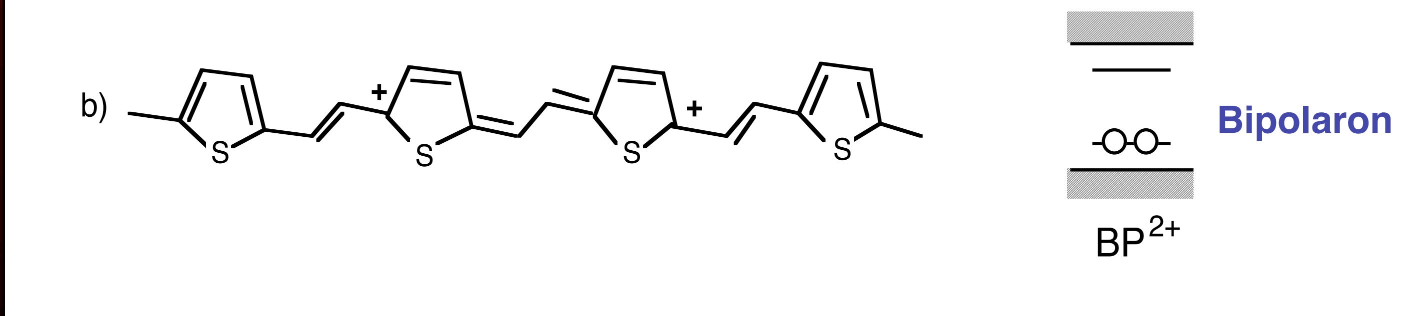


Soliton formation in polyacetylene.
a) Undistorted chain
b) Energy bands.

If 1 electron is introduced in the chain, it goes first to the conduction band, then the chain relaxes to accommodate the charge in a nonbonding p_z orbital in the midle of the gap (c). This midgap level has two electrons, one introduced through the conduction band and another one which was already in the carbon p_z orbital. The two electrons in this nonbonding orbital together with the deformation of the chain is a negative soliton. This soliton transports a negative charge.

poly(thienylene vinylene), PTV





a) Positive polaron (P^+), formed by removing one electron. This leaves one positive charge and one unpaired electron which separate through relaxation.

b) Positive bipolaron (BP^{2+}) formed by removing a second electron. This leaves two positive charges.

The energy bands are represented on the wright. In the picture the bonding level in the gap is normally full and only the *holes* are shown.

TRANSPORT PROPERTIES

Conjugated polymers are semiconductors in consequence of the gap

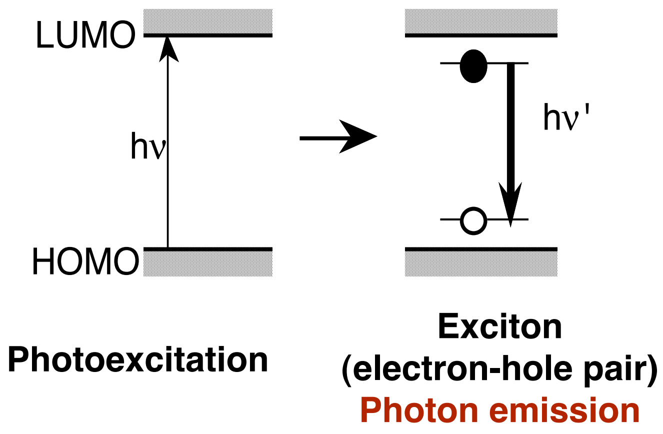
Doping induces the creation of solitons or polarons/bipolarons

Some, when highly doped exhibit high conductivities

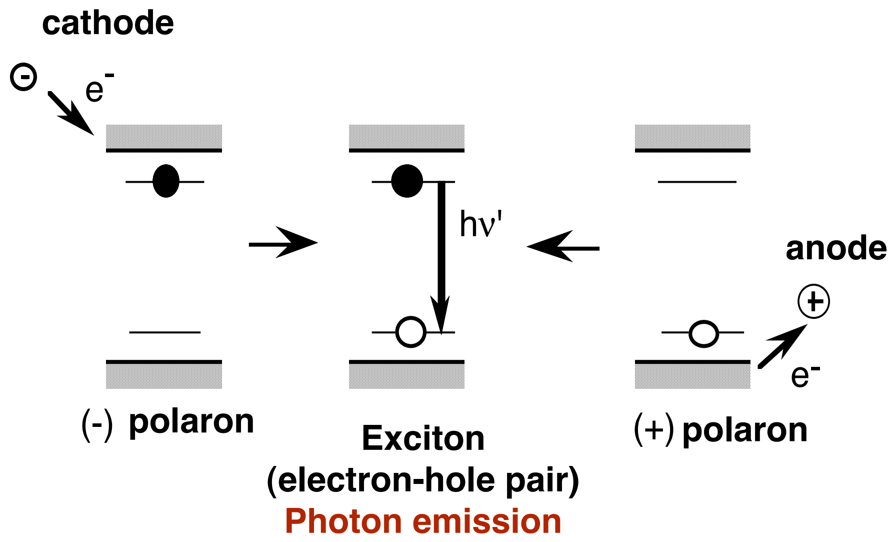
The theoretiacal conductivity of polyacetylene is estimated to be of the order of $2x10^9$ Sm^{-1} (30 x the conductivity of copper). Real conductivities are, however lower

Many mechanisms are proposed.
A common model is the variable range hopping (Mott). The charge carriers (electrons or holes) associated to solitons, polarons/bipolarons move along the chains. There is also some transport between chains.

OPTICAL PROPERTIES



a) Photolumiscence



b) Electrolumiscence

Device processes

- Charge carrier injection and transport — Transistors
- Recombination — Light emitting diodes, LEDs
- Exiton decay — LEDs

MOBILITIES ARE VERY LOW!

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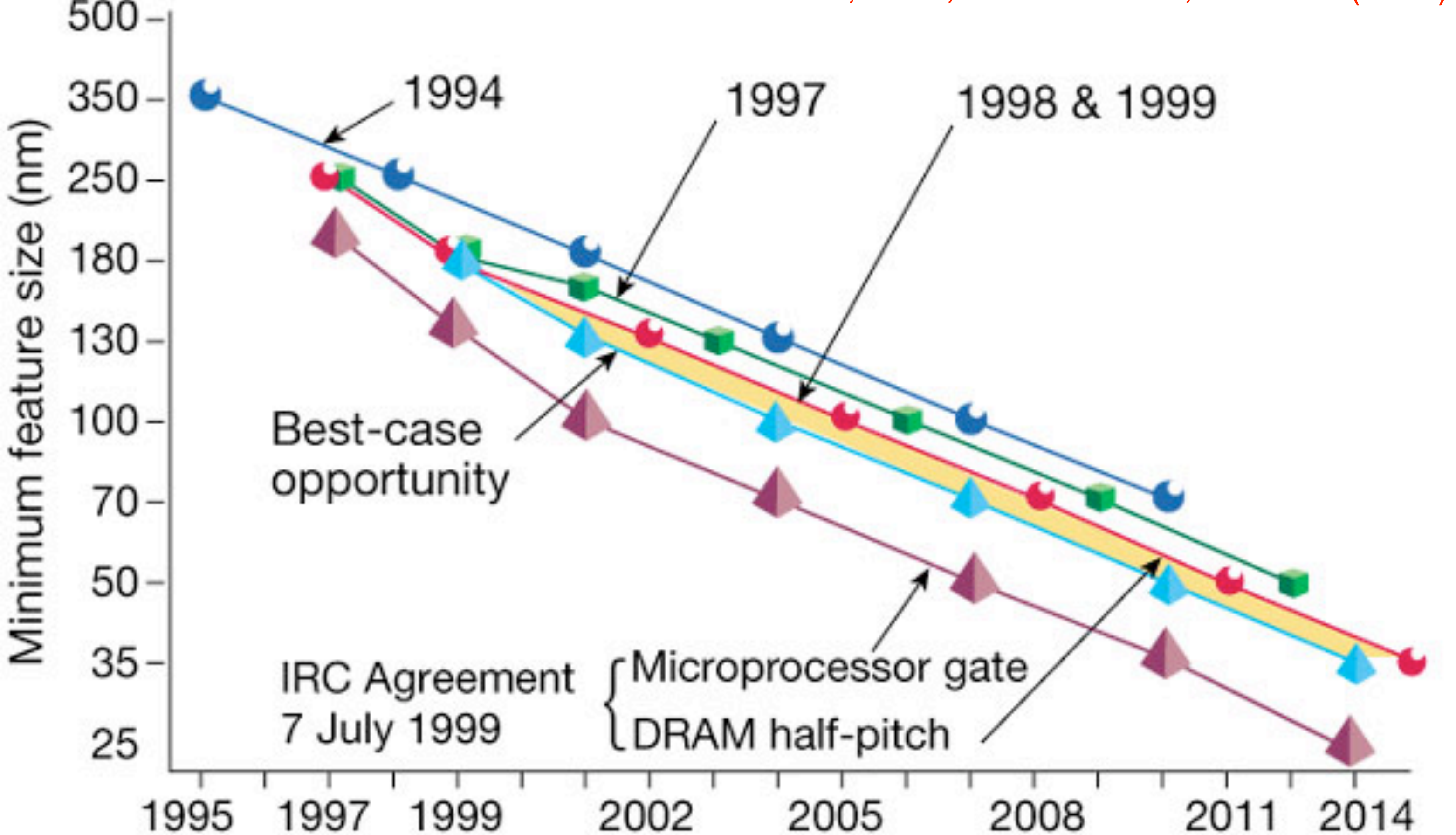
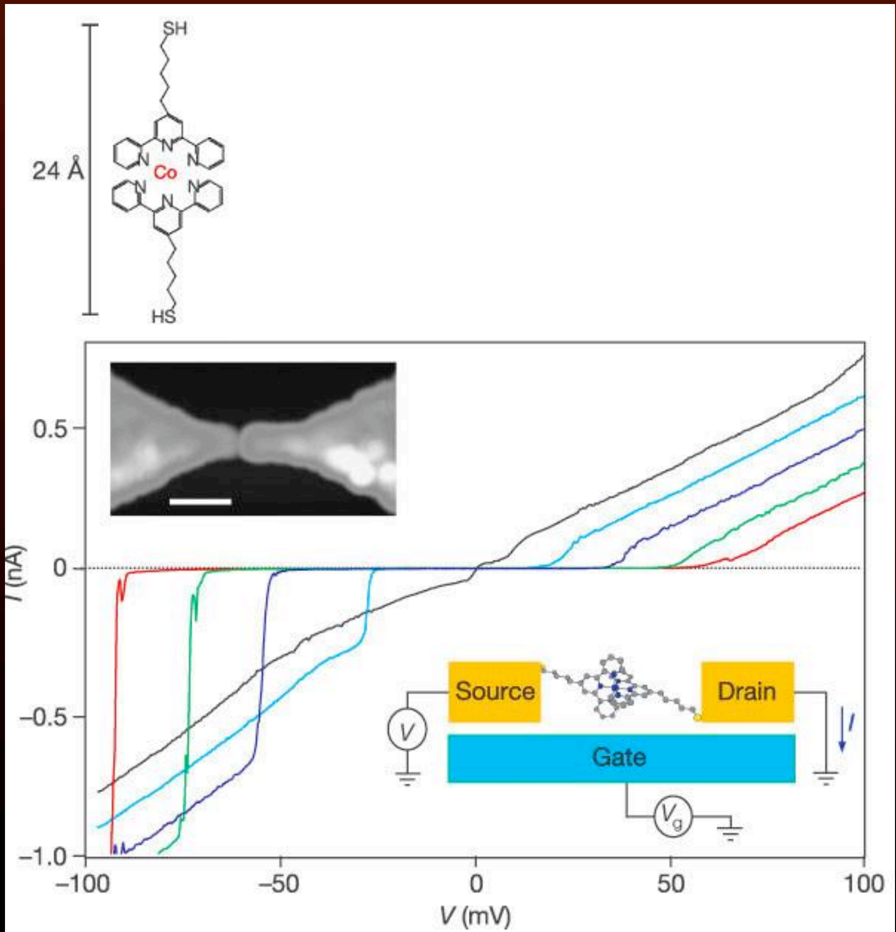
The need to downsize — Moore's law

Moore, G. E., Electronics 38, 114–116 (1965)



Moore's law predicts that the number of components per chip doubles every 18 months.

NATURE, VOL 406, 31 AUGUST 2000



Single atom transistor

Single-electron transistor

[Co(tpy-(CH2)5-SH)2]2

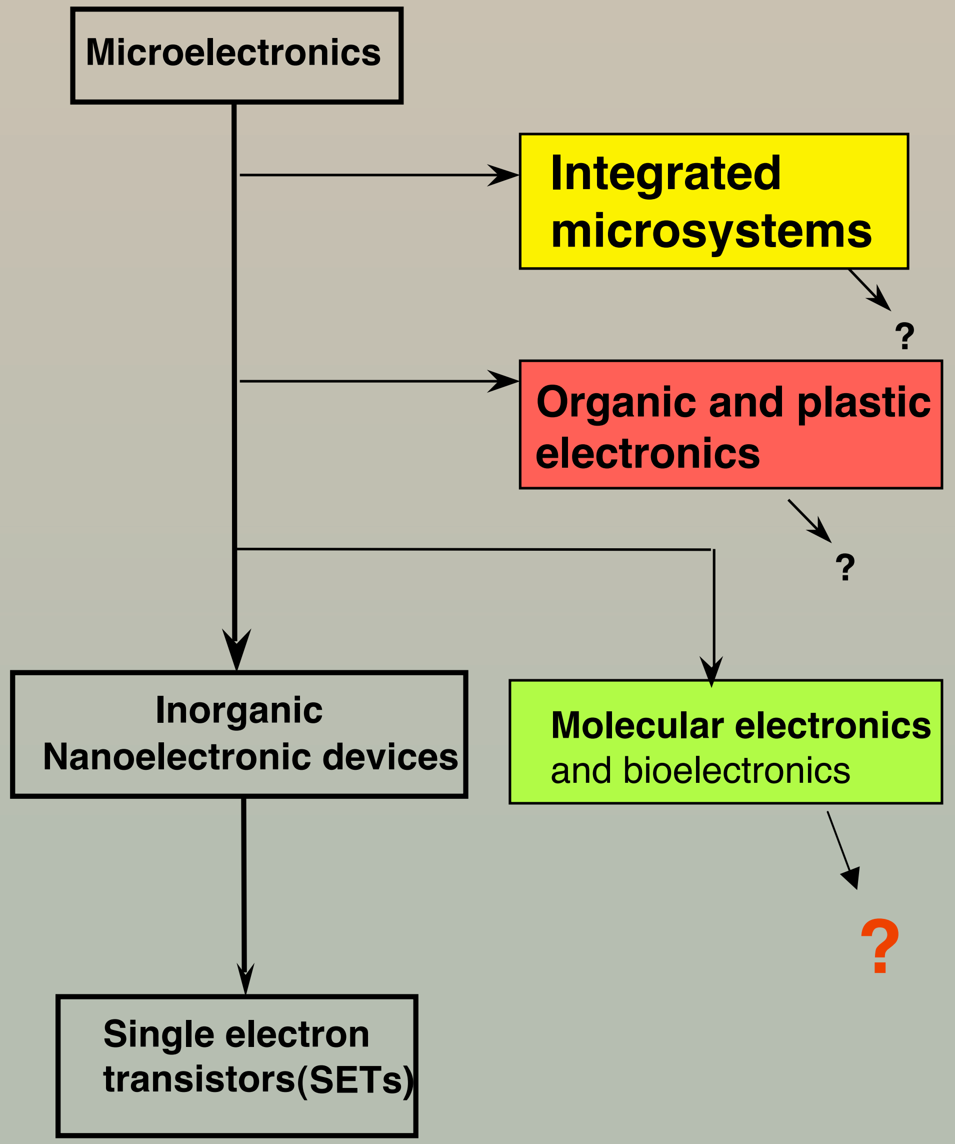
Upper inset, AFM image of the electrodes with a gap (scale bar, 100 nm).

Lower inset, diagram of the device.

Transfer of one electron by changing the oxidation state of the Co atom!

Jiwoong Park, et al
NATURE VOL 417 13 JUNE 2002, 723

THE NEAR FUTURE



Taxonomy of electronic devices as they tend to evolve.

Future Solutions in Optoelectronics

Systems

- Flexible Displays
- Smart Cards
- Smart Labels (RFIDs)
- Smart Sensors
- …

Devices

- Light Emitting Devices (LEDs)
- Transistors (TFTs)
- Sensors
- New Devices

New Materials

- **Organic Semiconductors**
- Hybrids
- …

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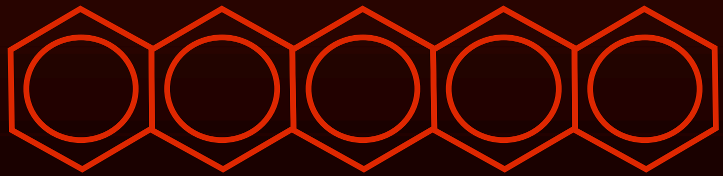
Materials

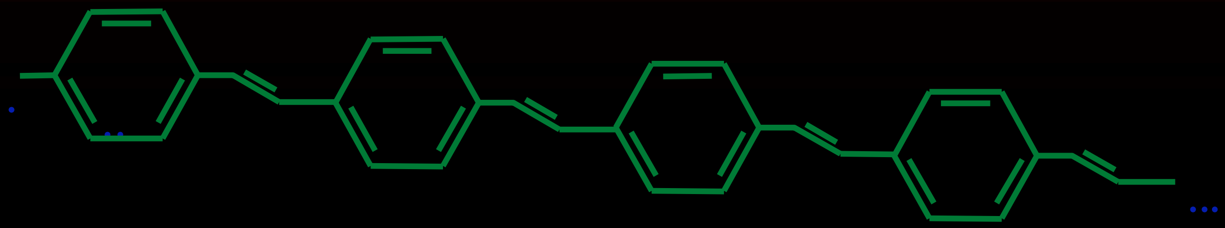
Common feature: Conjugated bonds

Small molecules, e.g., pentacene



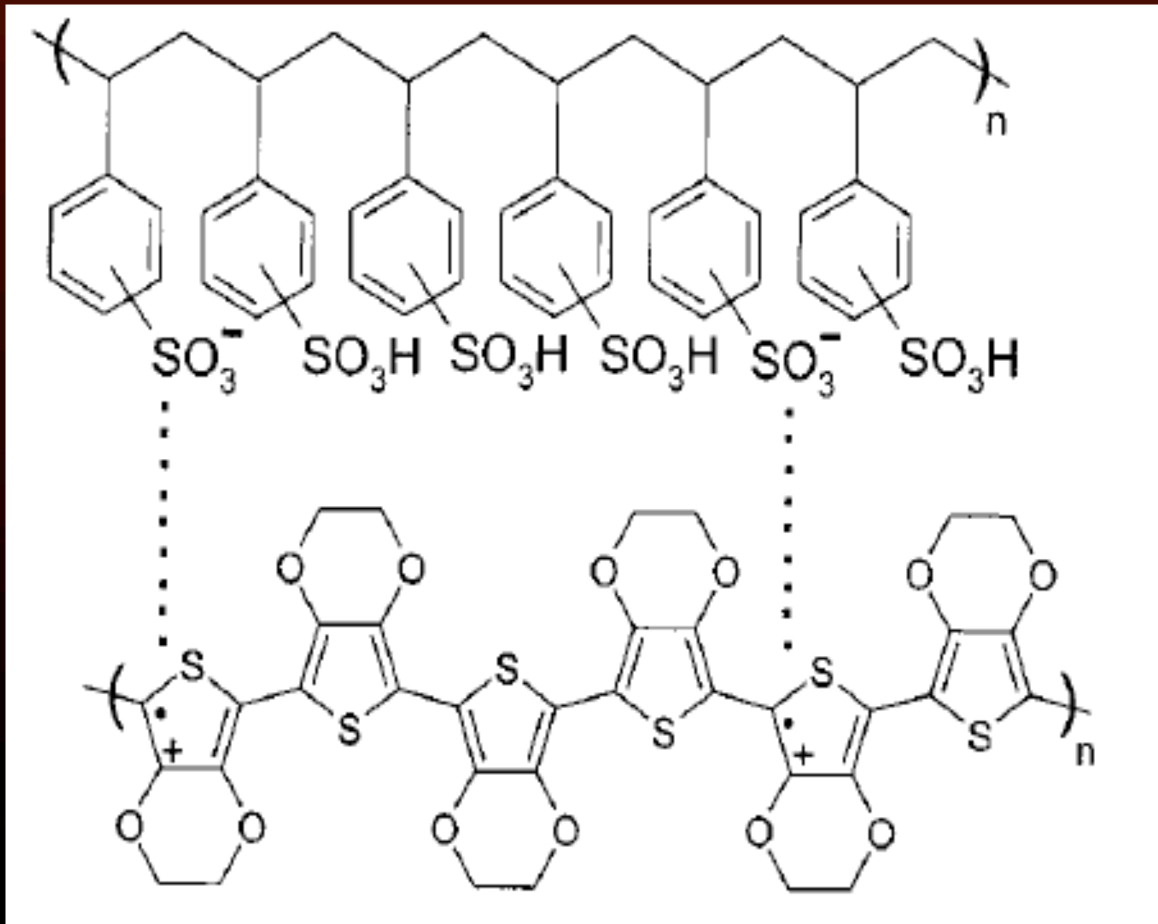
Conjugated polymers

e.g.,



Poly(p-phenylene vinylene) (PPV)

PEDOT/PSS



300 S/m

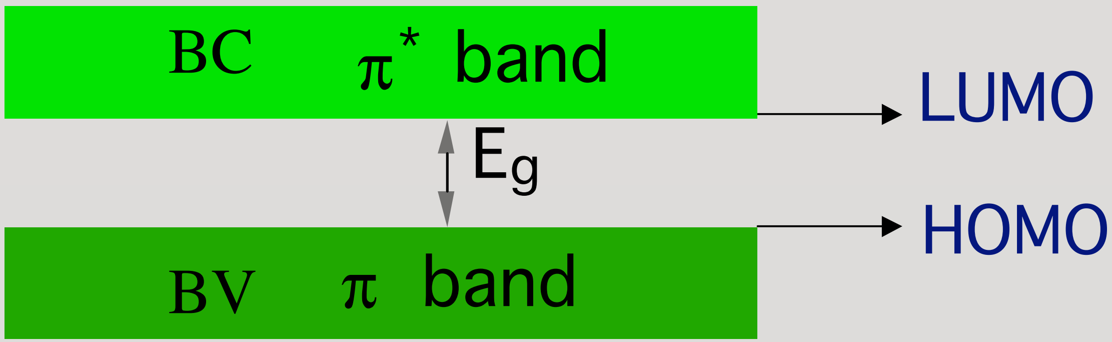
Hole conductor

Bandgap: 1.6 - 1.7 eV controlable

Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) aqueous dispersion

Baytron® P

Electronic Structure



Semiconductor !

- Optoelectronics

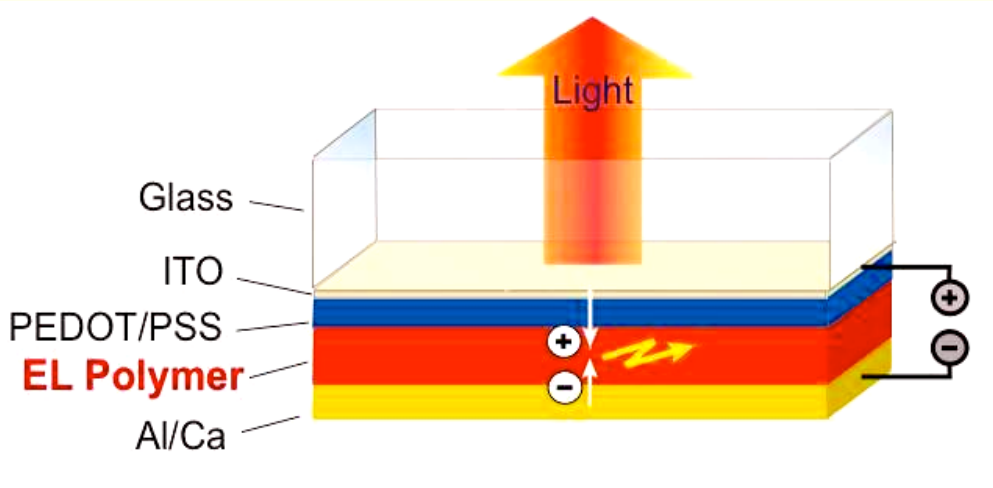
- Doping

DEVICES AND SYSTEMS

LUMINESCENCE — OLEDs → **Displays**

MOBILITY — OTFTs → **Integrated circuits**

LUMINESCENCE — OLEDs



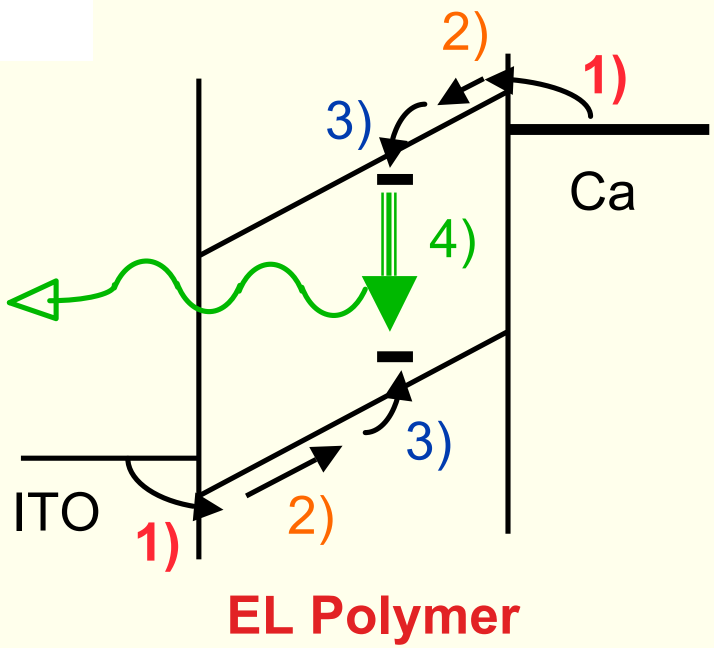
Processes in electroluminescence

1) Charge injection (electrons and holes)

2) Charge transport

3) Capture — exciton creation

4) Emission



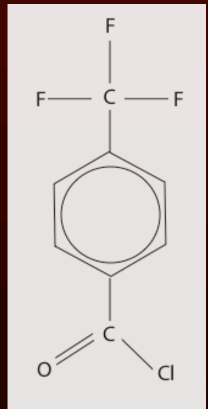
Displays

The world's first 40-inch full-color OLED display, built by EPSON, using TFT substrates and ink-jet printed OLEDs

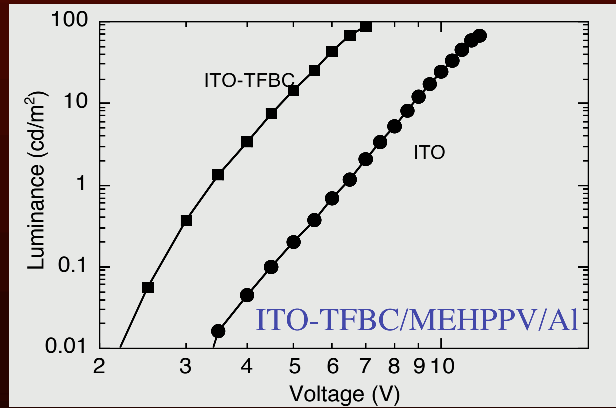
Conceptual view of OLED flexible display, which can be roled into a pen-like device containing computational and wireless comunication electronics. Images of Universal Display Corp.

What we do:

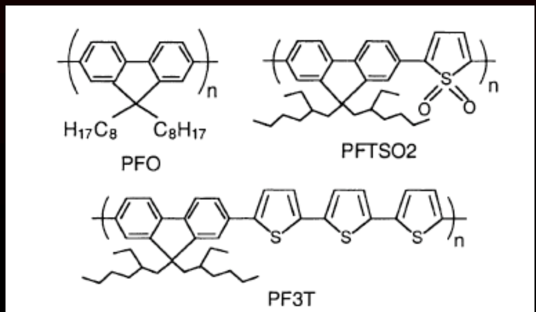
- Surface engineering (self-assembly)

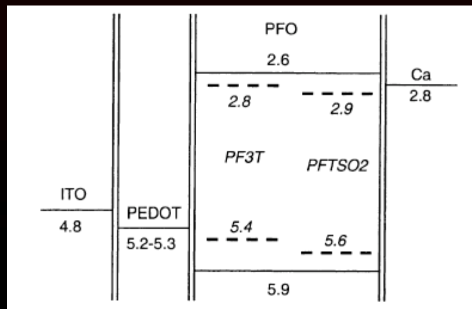


TFBC
=
4-(trifluoromethyl) benzoyl chloride



- Polymer blends





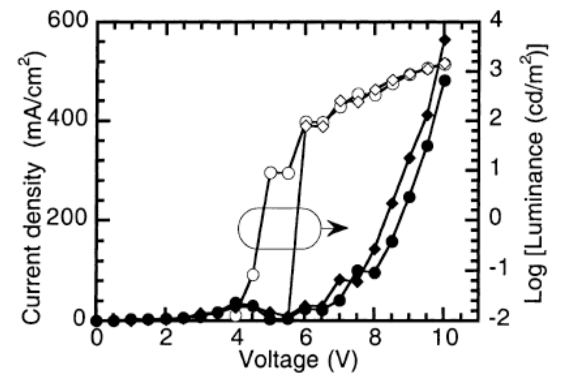


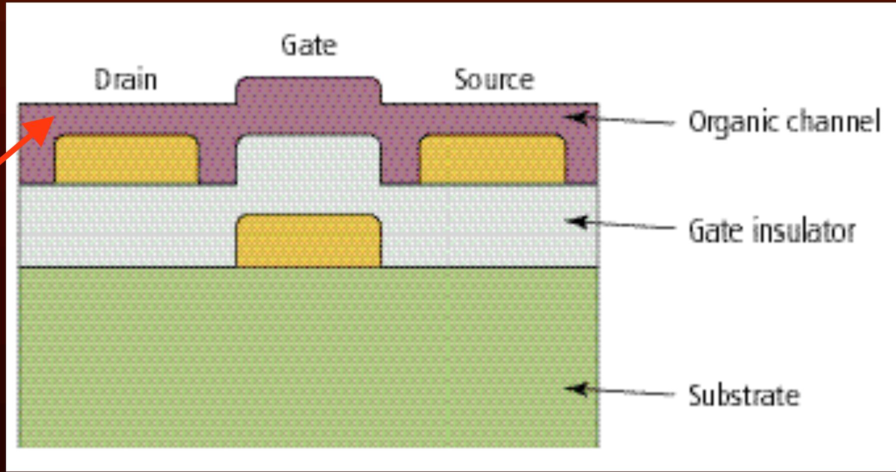
Fig. 3. Current density (filled symbols) and luminance as a function of the voltage for ITO/PEDOT/PFO:PF3T(95 nm thick)/Ca, circles, and ITO/PEDOT/PFO:PFTSO2(80 nm thick)/Ca, diamonds, LEDs.

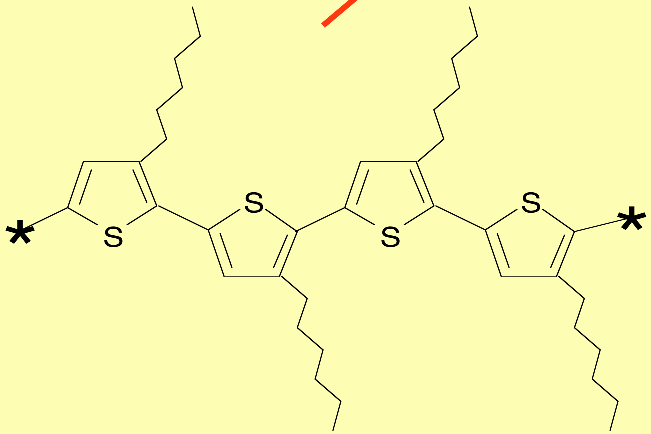
ITO/PEDOT/PFO:PFTSO2/Ca
Vonset= 4V; Max L=1500 cd/m2; max quantum ef.: 0.14.

A. Charas et al., *Synth. Met.* **137 (1-3),** 1039 (2003).

• Mobility — OTFTs

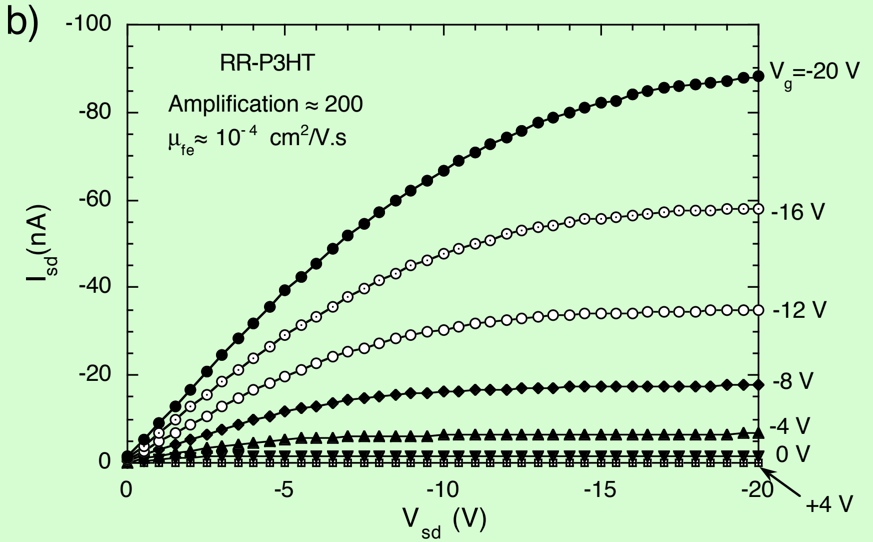
Polymer (plastic) FET



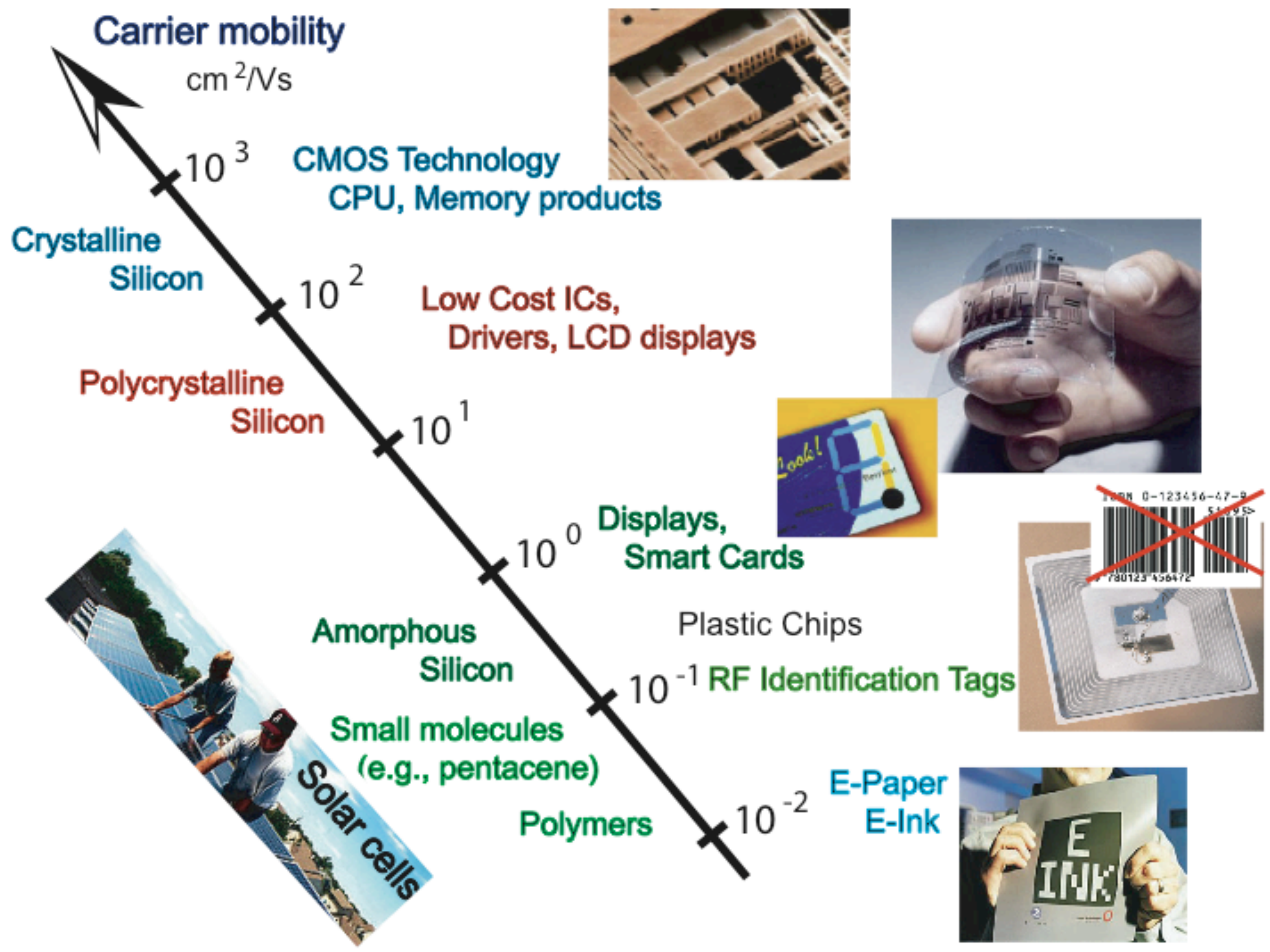


RR-P3HT

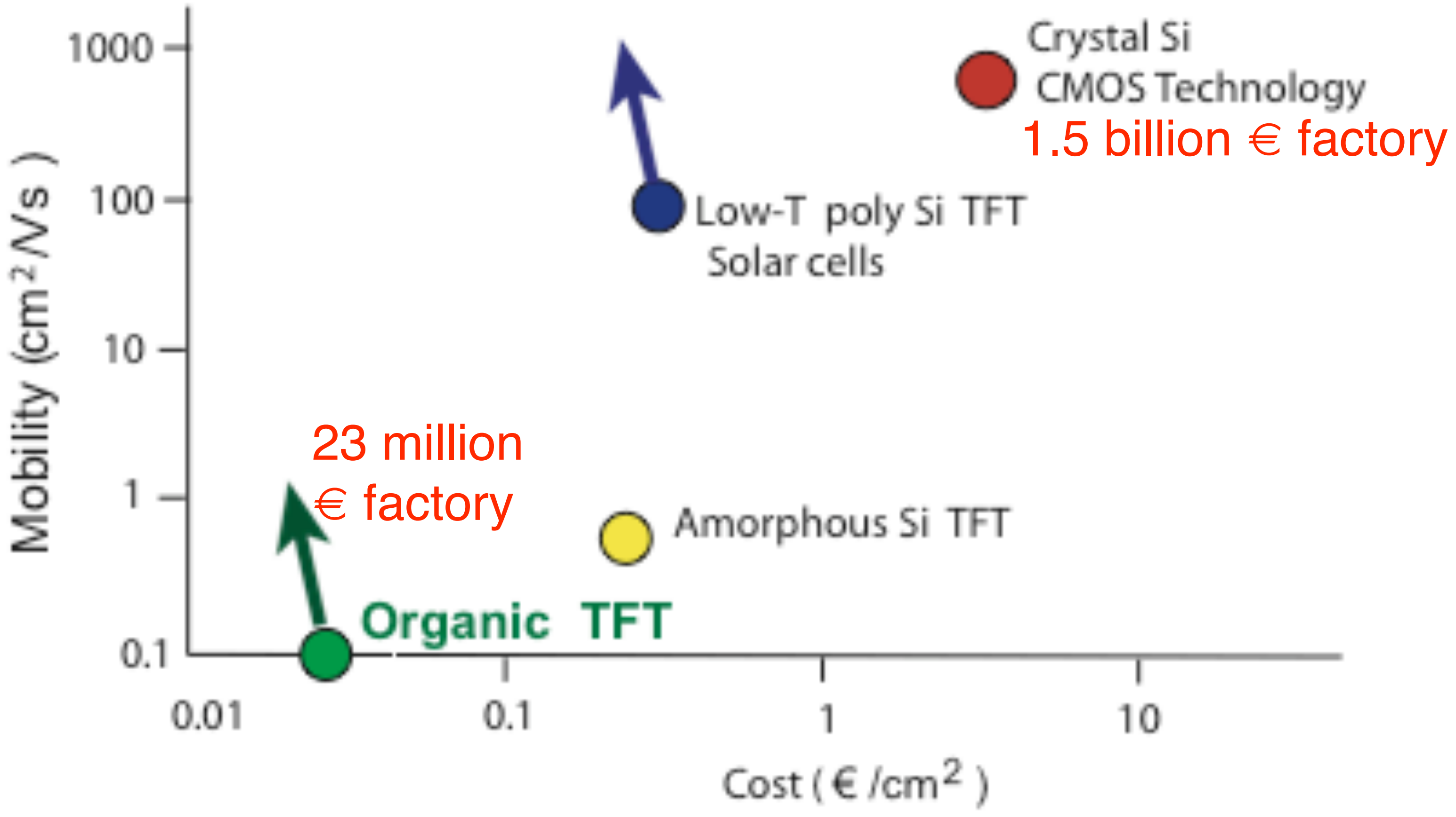
Regioregular poly(3-hexyl)thiophene



Channel: W= 3mm; L=20 µm
polymer film thickness ≈35 nm
Insulating gate: 200 nm, SiO_2


Carrier mobility
cm 2/Vs
10 3
CMOS Technology
CPU, Memory products
Crystalline
Silicon
10 2
Low Cost ICs,
Drivers, LCD displays
Polycrystalline
Silicon
10 1
10 0
Displays,
Smart Cards
Plastic Chips
Amorphous
Silicon
10 -1
RF Identification Tags
Small molecules
(e.g., pentacene)
Polymers
10 -2
E-Paper
E-Ink
Solar cells

PERFORMANCE Vs COST



News print: 0.0001 € /cm²

Source: Cambridge Research Laboratory of Epson

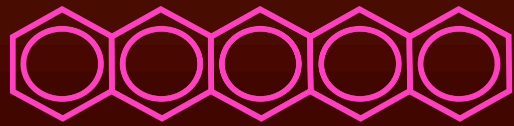
Processing Technologies

- Thermal evaporation
- Solution processing (polymers or small molecules precursor)
  - Ink-jet printing (with pre-patterning)
  - Stamping (direct patterning)
  - Roll-to-roll sheet vs batch processing (printing technology)
  - Spin-coating + Uv light patterning through mask or direct writing

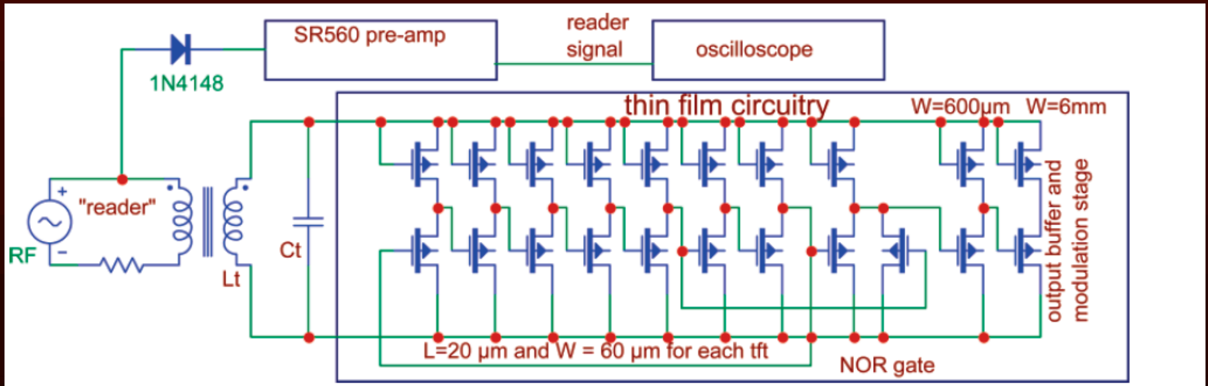
Review: NATURE VOL 428 29 APRIL 2004

- # Technology: Integrated Circuits

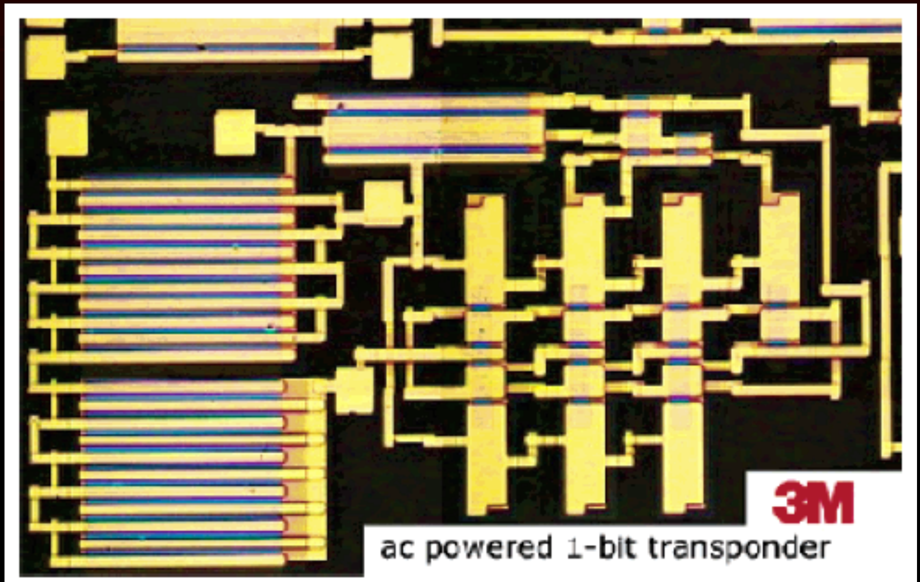
Pentacene



Mobility: >1 cm^2/Vs



Circuit diagram of one-bit rf transponder



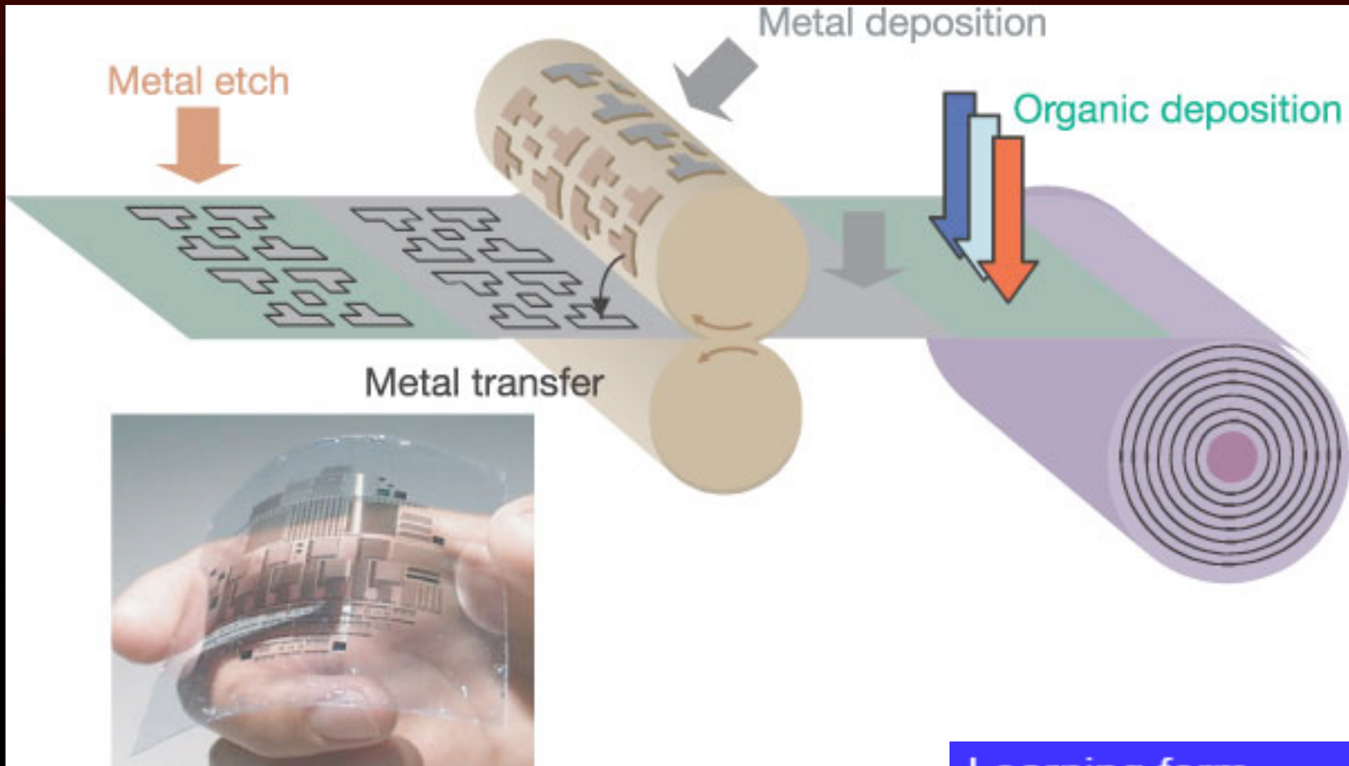
Completed pentacene-based one-bit RFID tag with 7 stage-ring oscillator,
An NOR gate and two output inverters. The gate is Ti/Au and the dielectric
Al_2O_3

Chem. Mater. **2004**, *16*, 4413−4422

- **Processing Technologies The future**

Solution processing

- **Roll-to-roll sheet vs batch processing (printing technology**



Learning form
Printing Processes

From NATURE VOL 428 29 APRIL 2004

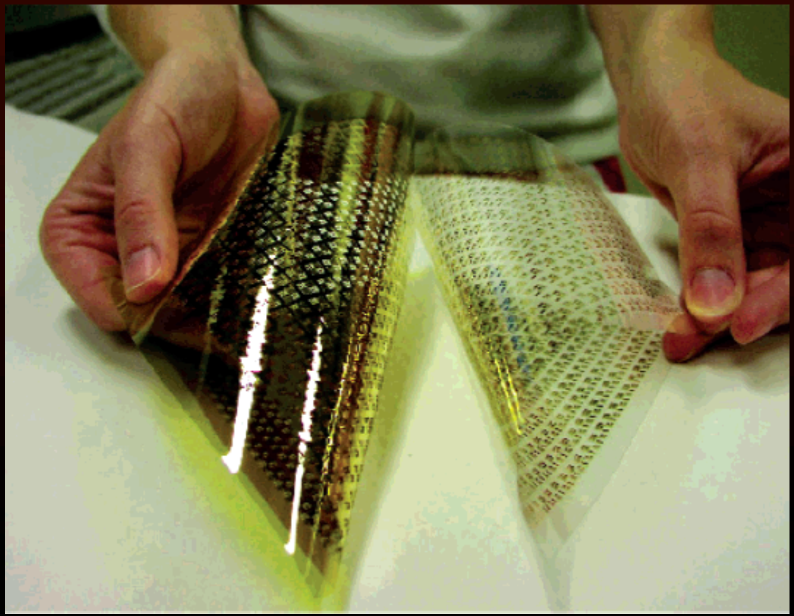
Processing Technologies

Solution processing

- Spin-coating + Uv light patterning

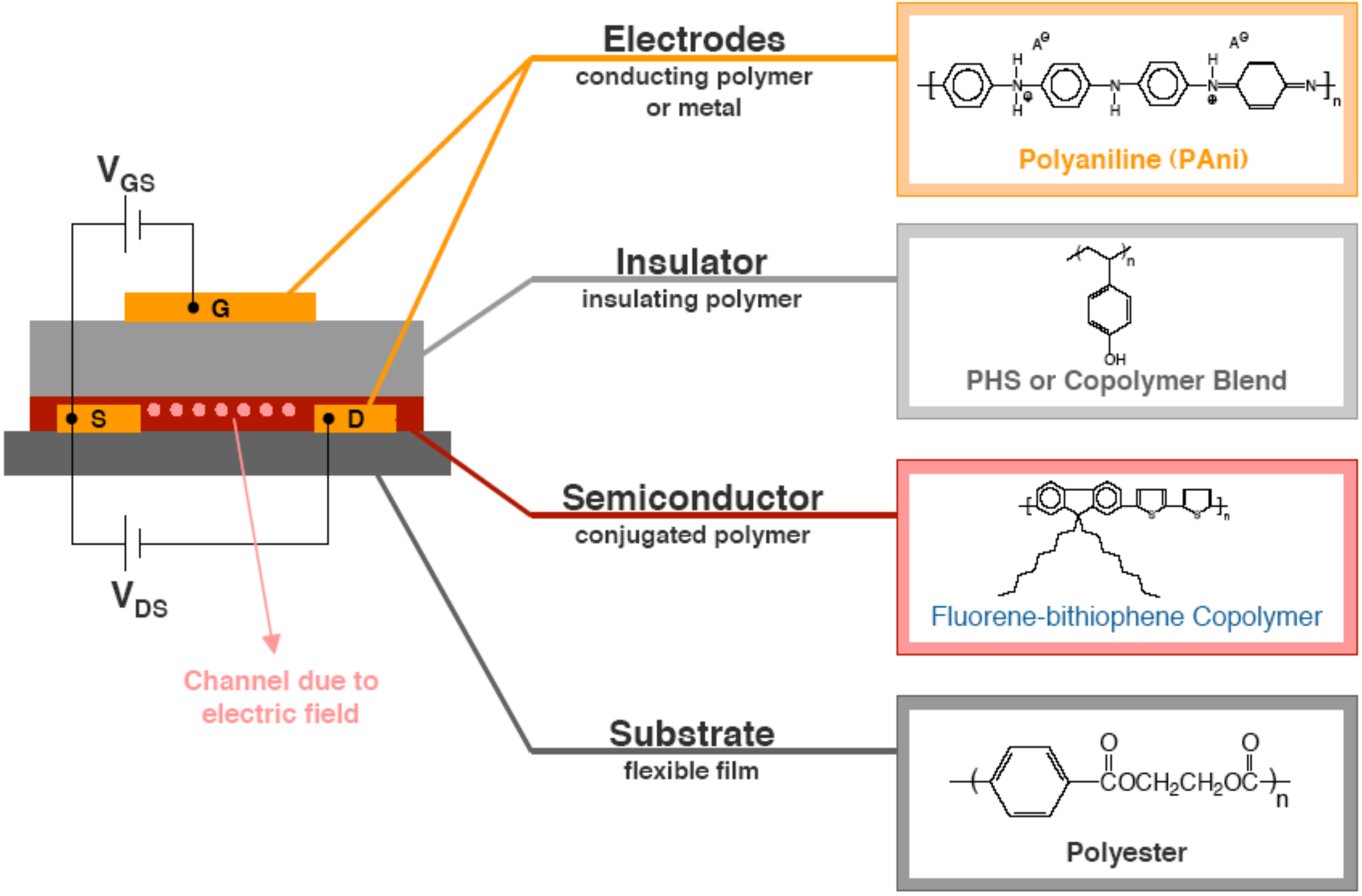
  - Through shadow mask

6 in x 6 in RFID circuit array (right) fabricated on polymeric substrate, via the polymeric shadow mask shown at left.



  - Direct writing

All organic field effect transistor

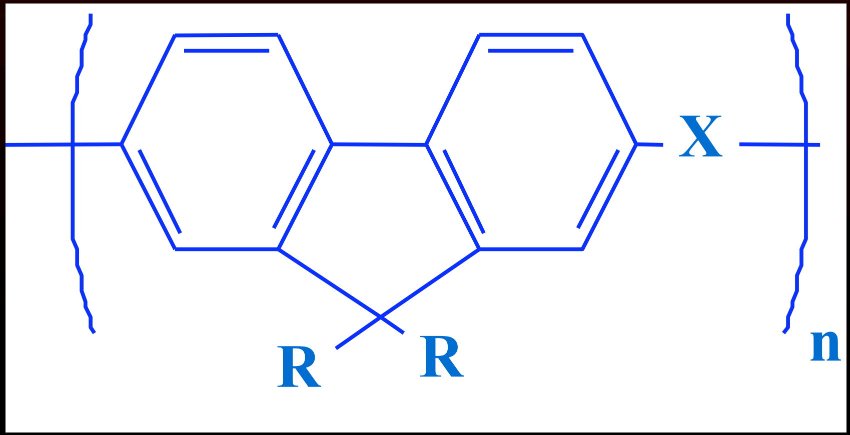


- What we do

Suitable for solution processing
Spin-coating+ UV light patterning

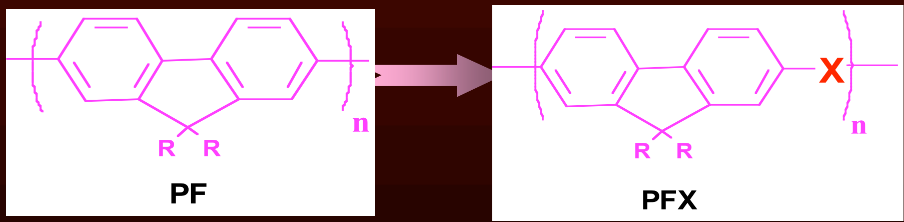
POLYFLUORENES:

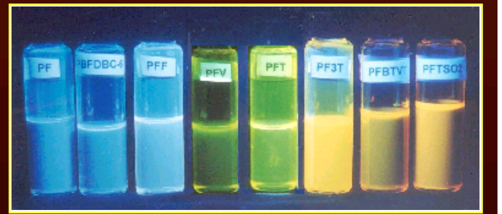
- Versatile,
- Electroluminescent



Polyfluorenes: versatility synthesis ⇔ properties:

1) COPOLYMERISATION

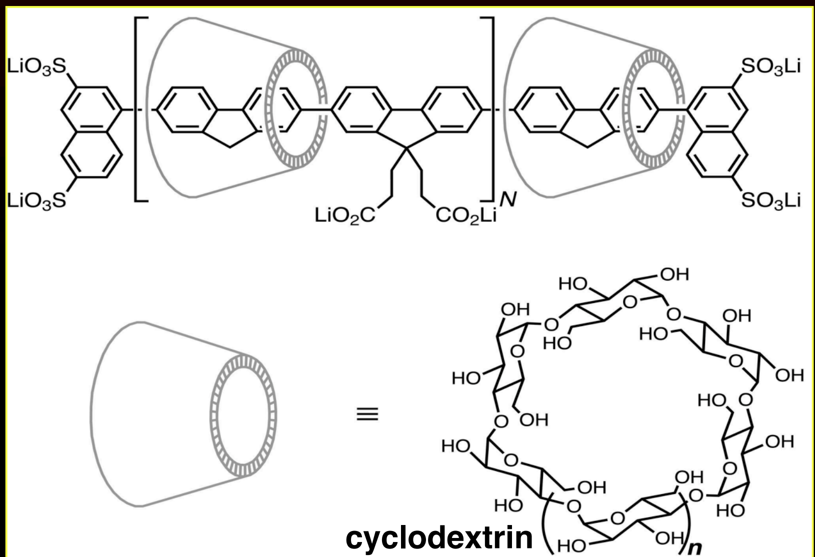




Control of

- Emission colour
  Multicolour displays
- HOMO & LUMO positions
  Charge injection
- Solubility
  Multilayers (spincoating)
  Nanometer size patterning

2) ENCAPSULATION

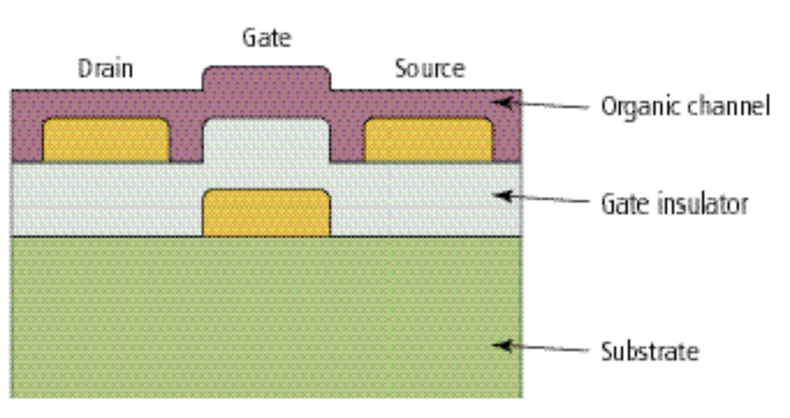


CONTROL OF INTERCHAIN INTERACTIONS (SOLID FILM)

OPTIMISATION OF LUMINESCENCE EFFICIENCY

Our New Projects

Fully pattern all components of all *plastic* integrated circuits: source, drain, gate, dielectric, polymer channel.



Materials:

Solution processable polymers by themselves or upon addition of reactive additives (e.g., photoacid), are converted into insoluble forms (by crosslinking) upon UV illumination

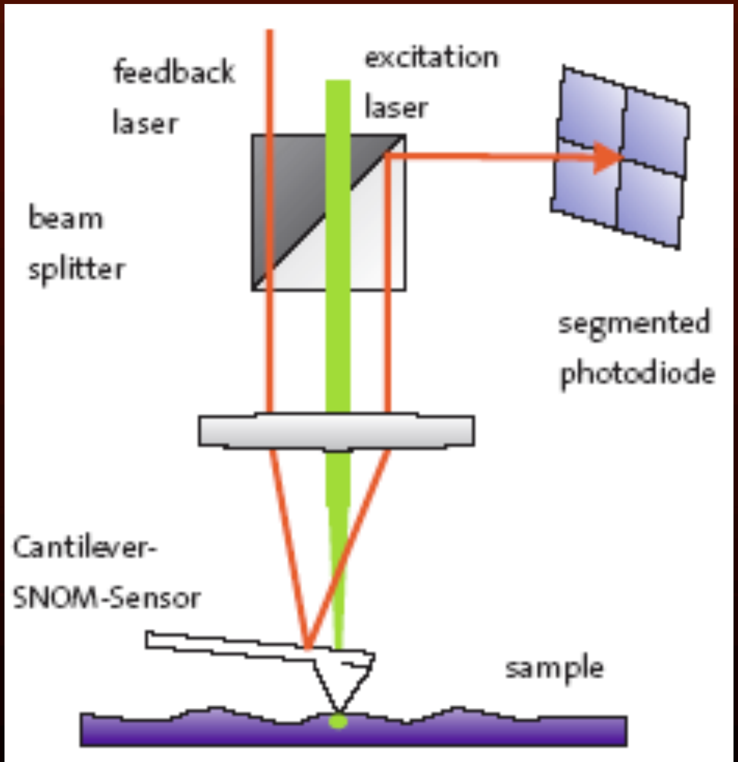
Micrometer scale features: photomask.

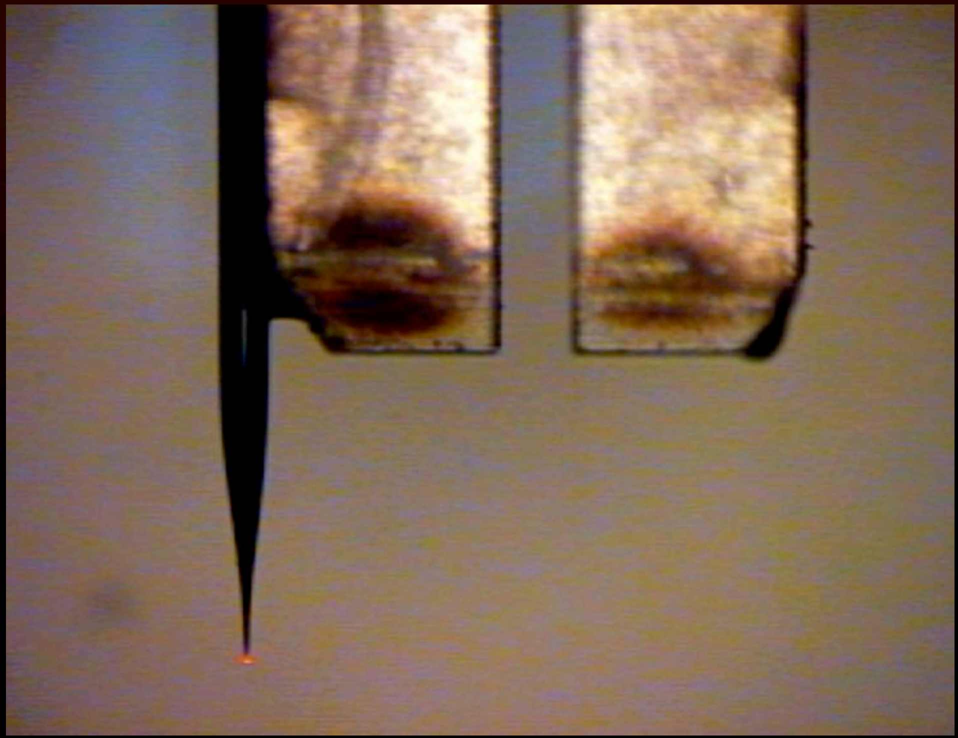
The non-illuminated parts remain soluble and are removed upon washing with appropriate solvents.

Direct writing at nanometer scale

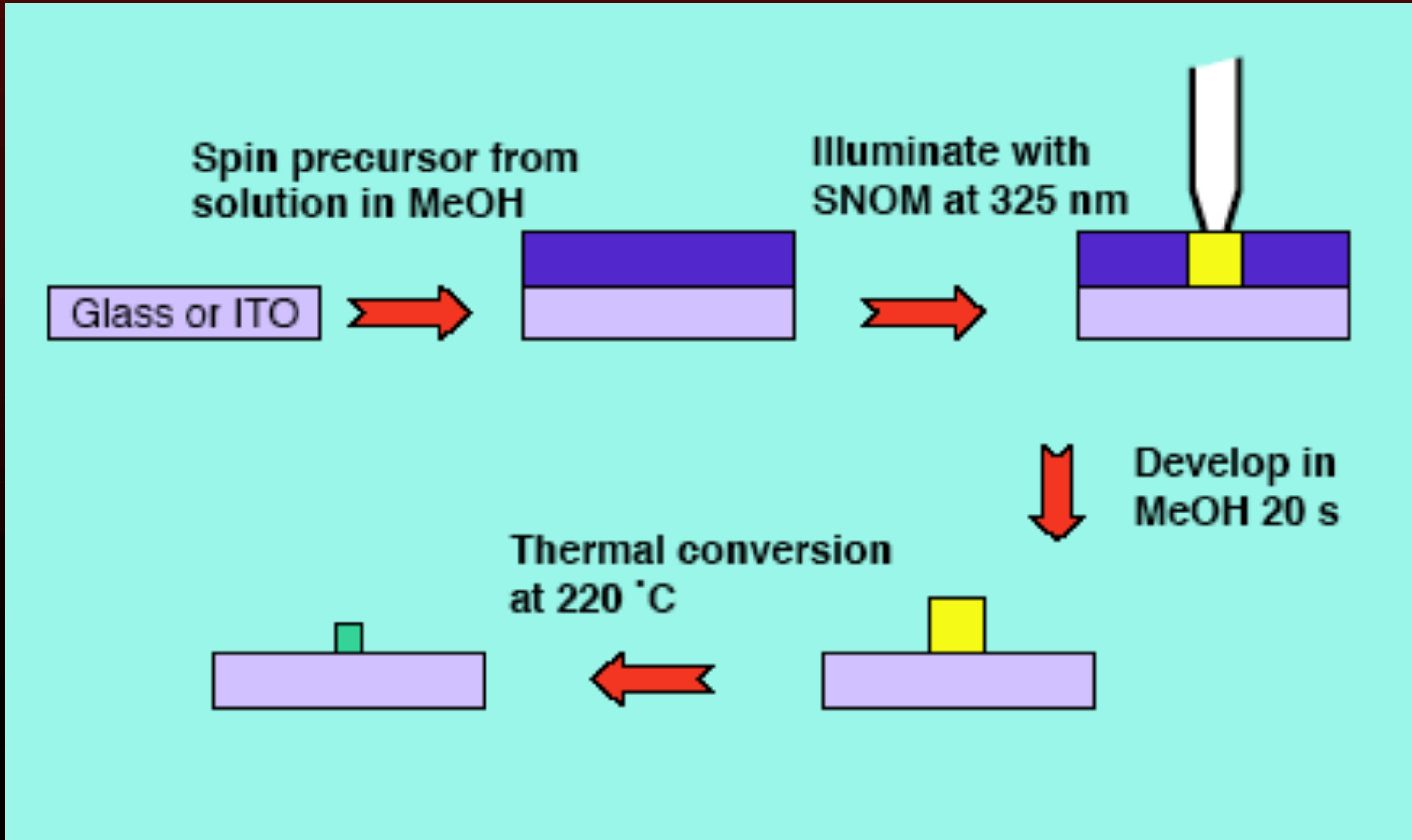
Using a Scanning Near-Field Optical Microscope (SNOM).

"Nanopatterning" of conjugated polymers


feedback
laser
excitation
laser
beam
splitter
segmented
photodiode
Cantilever-
SNOM-Sensor
sample

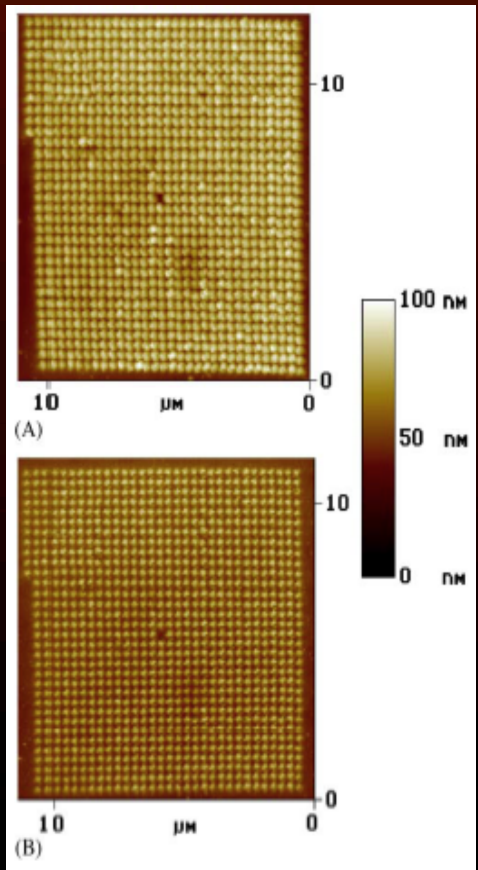


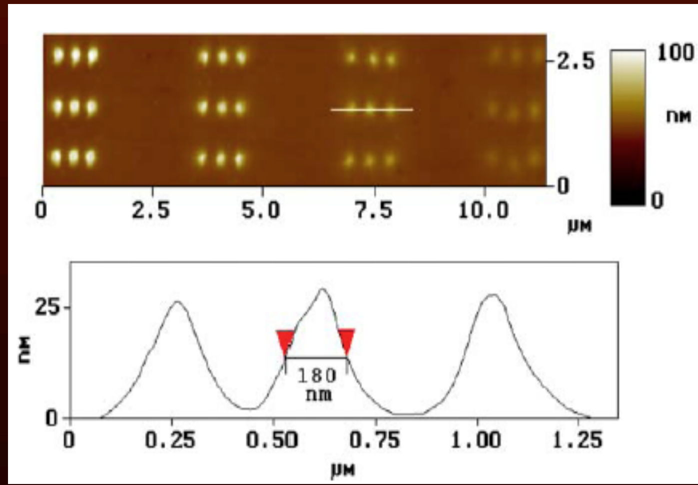
- # Direct writing



Schematic representation of lithographic route

PPV Pattern - via precursor





Top: AFM image of patterned features written in a PPV precursor film.
Exposure times: 0.4 - 0.1 s.
Probe aperture: 50 nm
Bottom: section along white line in top panel.

AFM images of a 2.dimensional photonic structure with a 333 nm square lattice before (A) and after(B) thermal conversion (220 °C, 5 h, 10^{-5} mbar).
The pattern was written with the 325 nm line of a HeCd laser. The power coupled into the fiber was less than 0.2 mW.

R. Riehn, A. Charas, J. Morgado and F. Cacialli, App. Phys. Lett, 82, 4,(2003) 526

Acknowledgements and credits

Main activity areas

Plastic Electronics and Molecular Electronics

The people

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- M. Matos
- L. Alcácer

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- University College London- Franco Cacialli
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- Universidade de Wuppertal - U. Scherf

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INSTITUTO SUPERIOR TÉCNICO

itn

FCT projects

FCT