POLITECNICO DI MILANO
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Advanced Course on

ORGANIC ELECRONICS
Principles, devices and applications

BASIC CONCEPTS on ORGANIC SEMICONDUCTORS

Marco Sampietro

COURSE OVERVIEW

- How the organic semiconductor “material” is made ?
- How charge transport takes place ?
- How is the interaction with the “external” world ?
  - photons
  - metal contacts
  - defects
- Which devices have been built ?
- Which are the technologies involved ?
- Which are the challenges of the present/future ?

CARBON ATOM

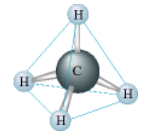
PERIODIC CHART OF THE ELEMENTS

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	INERT GASES
1 H 1.00797																1 H 1.00797	2 He 4.0026
3 Li 6.939	4 Be 9.0122											5 B 10.811	6 C 12.0112	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.183
11 Na 22.9898	12 Mg 24.312											13 Al 26.9815	14 Si 28.086	15 P 30.9738	16 S 32.064	17 Cl 35.453	18 Ar 39.948
19 K 39.102	20 Ca 40.08	21 Sc 44.956	22 Ti 47.90	23 V 50.942	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.9216	34 Se 78.96	35 Br 79.909	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.905	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc [99]	44 Ru 101.07	45 Rh 102.905	46 Pd 106.4	47 Ag 107.870	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.904	54 Xe 131.30
55 Cs 132.905	56 Ba 137.34	*57 La 138.91	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 196.967	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.980	84 Po [210]	85 At [210]	86 Rn [222]
87 Fr [223]	88 Ra [226]	‡89 Ac [227]	104 Rf [261]	105 Db [262]	106 Sg [266]	107 Bh [262]	108 Hs [265]	109 Mt [266]	110 ? [271]	111 ? [272]	112 ? [277]						

- C^6 : 6 electrons , $1s^2 2s^2 2p^2$ — 4 electrons in the external shell
- Medium electronegativity (tendency to "share" electrons rather than to "catch" or "give")

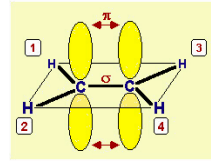
BONDs with CARBON ATOMS

Ibridizza: sp^3

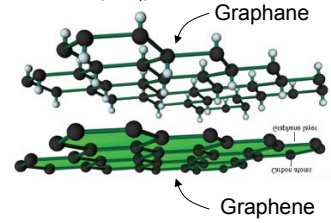


Diamond, Metano (CH_4)

sp^2

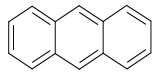


etilene

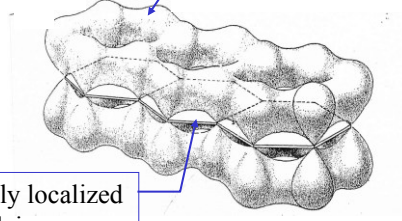


Can form planar structures with σ bonds (strong) on plane and π bonds (lousy) out of plane

π - CONJUGATED MOLECULES

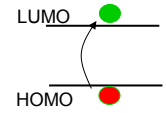


antracene



π electrons laying in the molecular orbitals having higher energy (HOMO)

Easy to be excited to an higher level (LUMO)



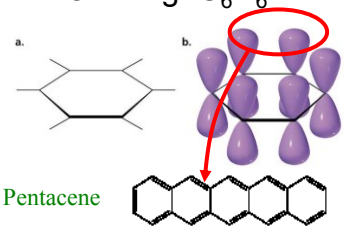
Electrons strongly localized within the C nuclei

Easy CONDUCTION in the molecular plane (delocalisation)

This afternoon
Beatrice Saglio

MOLECULES … and…. POLYMERS

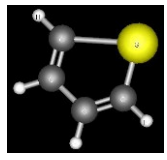
Phenil ring C_6H_6

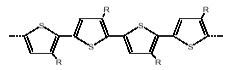


Pentacene

Today and tomorrow
Beatrice Saglio

Tiophene ring SC_4H_4

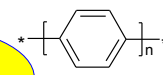




Polytiophene

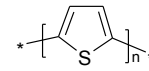
Poly para phenilene

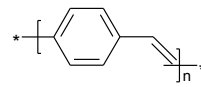
PPP



Poly tiophene

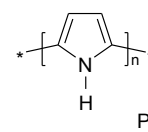
PT





PPV

Poly para phenilene vinilene



PPy

Poly pirrolo

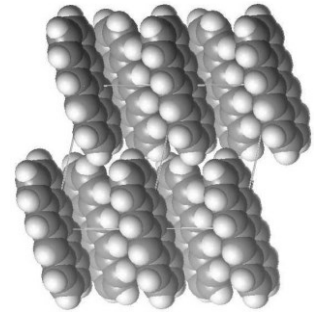
Powder, soluble in solvents

ORGANIZATION IN SPACE

Molecular crystal

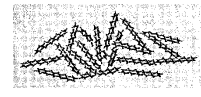
strong superposition of p_z orbitals

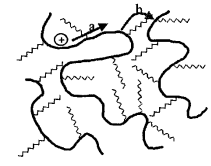
delocalisation of electrons over "the full crystal"



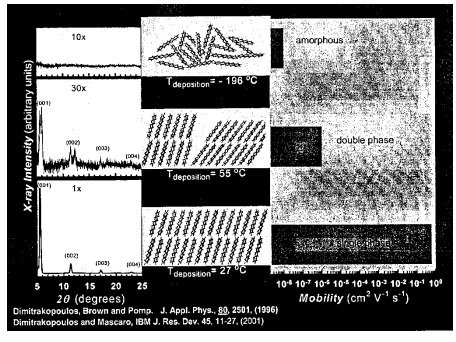
Amorphous Film

Molecules are feeling weak Van der Wals forces

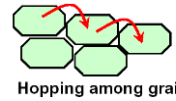




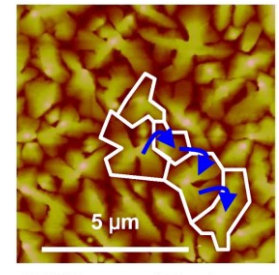
TRANSPORT of CHARGE : HOPPING



Dimitrakopoulos, Brown and Pomp. J. Appl. Phys., 80, 2501, (1996)
Dimitrakopoulos and Mascaro, IBM J. Res. Dev. 45, 11-27, (2001)



Hopping among grains

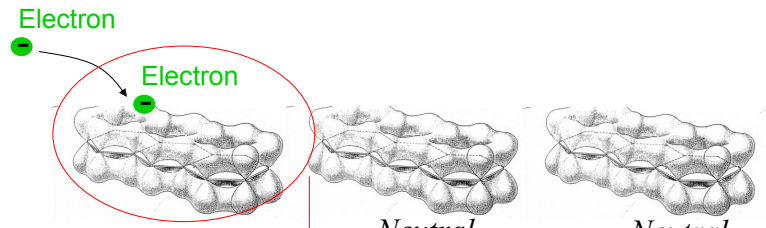


AFM image of Pentacene

Low carrier mobility, set by the slowest step

Tuesday afternoon
Dario Natali

CONDITIONS for CHARGE TRANSPORT



Molecule "charged" negatively (Reduction)

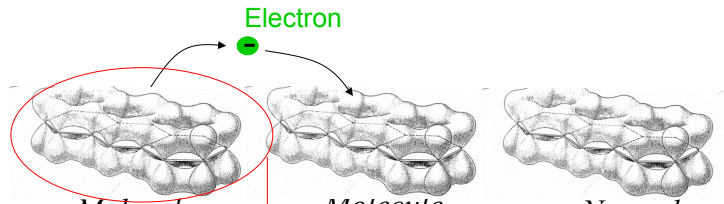
Neutral molecule

Neutral molecule

POLARON
because the charge distribution on the molecule is modified

Reduced molecules should NOT react chemically or modify their structure !

CONDITIONS for CHARGE TRANSPORT



Molecule returns neutral

Molecule "charged" (Reduced)

Neutral molecule

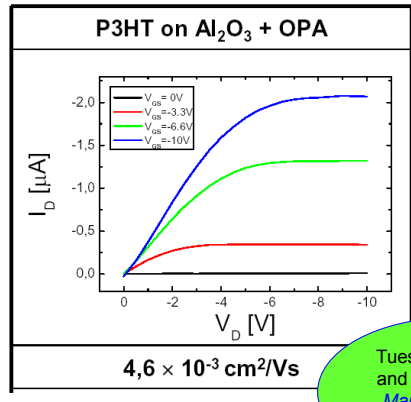
Molecule should go back to exactly the same initial state

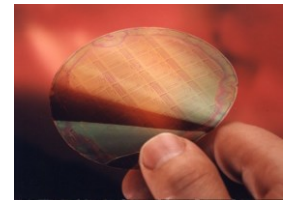
REVERSIBLE REDUCTION

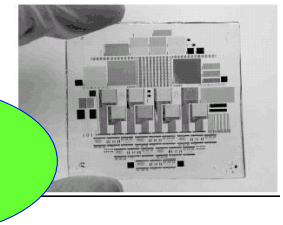
Thursday morning
Paolo Vacca

TRANSISTORS

6 μm channel TFT





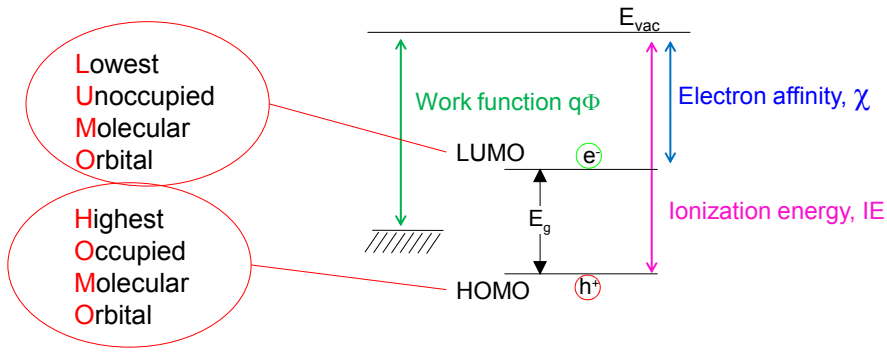


Tuesday afternoon
and following days
Marco Sampietro
Dario Natali
Mario Caironi

MOLECULES and BANDS !

Molecule → molecular energetic levels

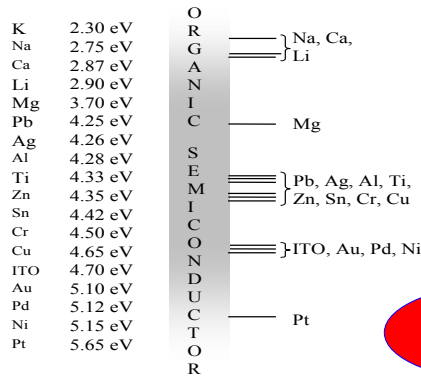
↳ Take origin from the atoms (in finite number) in the molecule

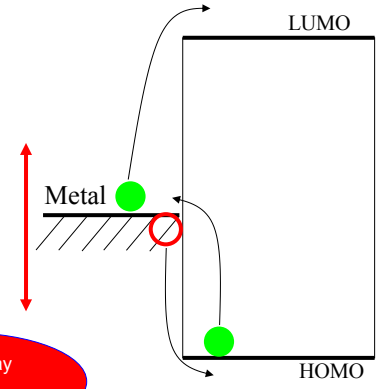


For most materials the "gap" is in the visible !!

METAL-SEMICONDUCTOR CONTACTS

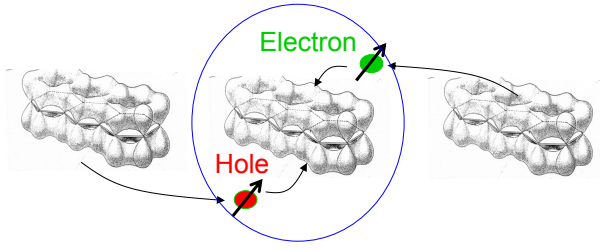
Organic semiconductors “can not” be doped substitutionally



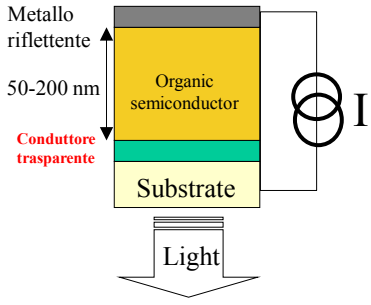


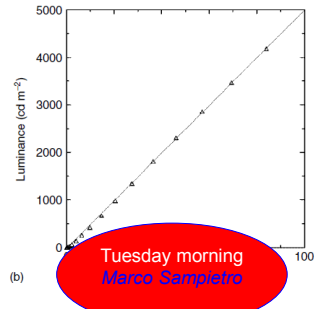
Wednesday morning
Dario Natali

RADIATIVE RECOMBINATION : LED

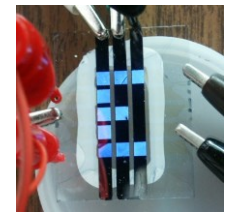


EXCITON
neutral excited molecule
(presence of e^- - h^+ couple)



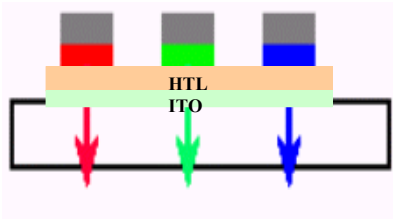


Tuesday morning
Marco Sampietro

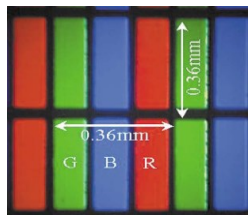


Collaborazione TESEO
(~2002)

From OLED to SCREEN



R G B



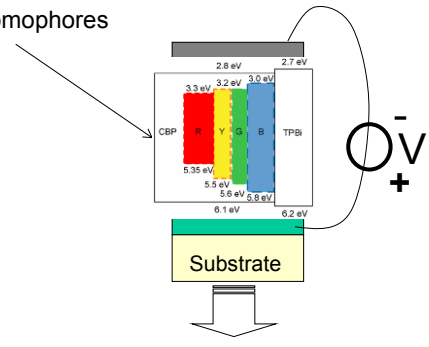
By LG

Thursday
afternoon
Marco Sampietro

WHITE OLED (WOLED)

No single molecule emitting over the entire spectrum !

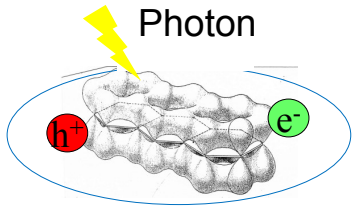
Blend of different
chromophores



Wednesday
afternoon
Marco Sampietro

Wednesday
afternoon
TCI

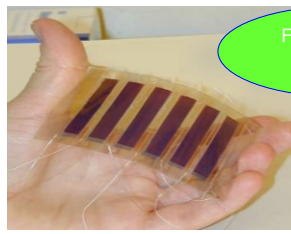
CHARGE PHOTOGENERATION & SOLAR CELLS



- Exciton binding energies are 50meV÷1eV >> k*T*
  ⇒ *thermal dissociation is inefficient*
  ⇒ *external Electric field needed*
  or other tricks !!

Wednesday morning & Thursday afternoon
Maddalena Binda

High performance Solar Cells



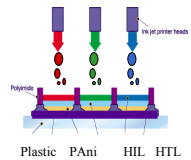
Friday morning
Annamaria Petrozza

Thursday afternoon
Antonio Iacchetti

INK-JET or ROL-to-ROLL or …

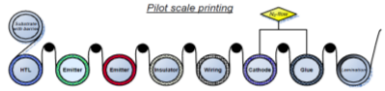
Organic molecules can be deposited from solution ..

Tuesday morning
Andrea Grimoldi



jetlab®4 Table-Top

FUJIFILM DIMATIX



Thickness 50-150nm ±2%. Foils processed at 3-30m/min.

Tuesday afternoon
Mario Caironi

Other applications ….

"Generation of electronic components that promise to be as easily manufactured as colorful magasines and newspapers"

LASERS

Thursday morning
Margherita Zavelani Rossi

WEARABLE DEVICES

Friday morning
Annalisa Bonfiglio

BIO APPLICATIONS

Wednesday & Friday morning
Maria Rosa Antoniazza

INVITED PAPER

Flexible Electronics: The Next Ubiquitous Platform

This paper reviews thin-film materials and technologies for flexible electronics and considers future applications in healthcare, the automotive industry, human–machine interfaces, mobile devices, and other environments.

By Arokia Nathan, *Fellow IEEE*, Arman Ahnood, Matthew T. Cole, Sungsik Lee, *Member IEEE*, Yuji Suzuki, Pritesh Hiralal, Francesco Bonaccorso, Tawfique Hasan, Luis Garcia-Gancedo, Andriy Dyadyusha, Samiul Haque, Piers Andrew, Stephan Hofmann, James Moultrie, Daping Chu, Andrew J. Flewitt, Andrea C. Ferrari, Michael J. Kelly, John Robertson, *Fellow IEEE*, Gehan A. J. Amaratunga, and William I. Milne

Proceedings of the IEEE, Vol. 100, May 13th, 2012, pp.1486-1516
DOI: 10.1109/JPROC.2012.2190168

A ROAD paved of SUCCESS

Patents up to 2011 : raw material (15,696), devices (33,831), equipment(27,685), drive circuit (13,512), packaging technique (9183) and application (4617).