NATIONAL INSTITUTE FOR RESEARCH AND DEVELOPMENT
OF ISOTOPIC AND MOLECULAR TECHNOLOGIES
CLUJ-NAPOCA ROMANIA

FROM COMPUTATIONAL DESIGN TO MOLECULAR ELECTRONICS ON NANOPATTERNED SURFACES

LUIZA BUIMAGA-IARINCA, DANIEL MARCONI,
ALIA COLNIȚĂ, CRISTIAN MORARI, IOAN TURCU

The 16th edition of the National Seminar of Nanoscience and Nanotechnology
Bucharest, Library of the Romanian Academy, June 6th 2017

Outline

- ✓Starting the nano-device construction:
  - ✓construct the surface,
  - ✓construct the active layer,
  - ✓evaluate their properties
- ✓Assessing the device electronic properties:
  - ✓DFT calculations
- ✓Real case: hybrid organic – inorganic diode based on ZnO/FePc junction

http://www.itim-cj.ro/en/department-molecular-and-biomolecular-physics

SPM-MBE facility at NIRDIMT Cluj

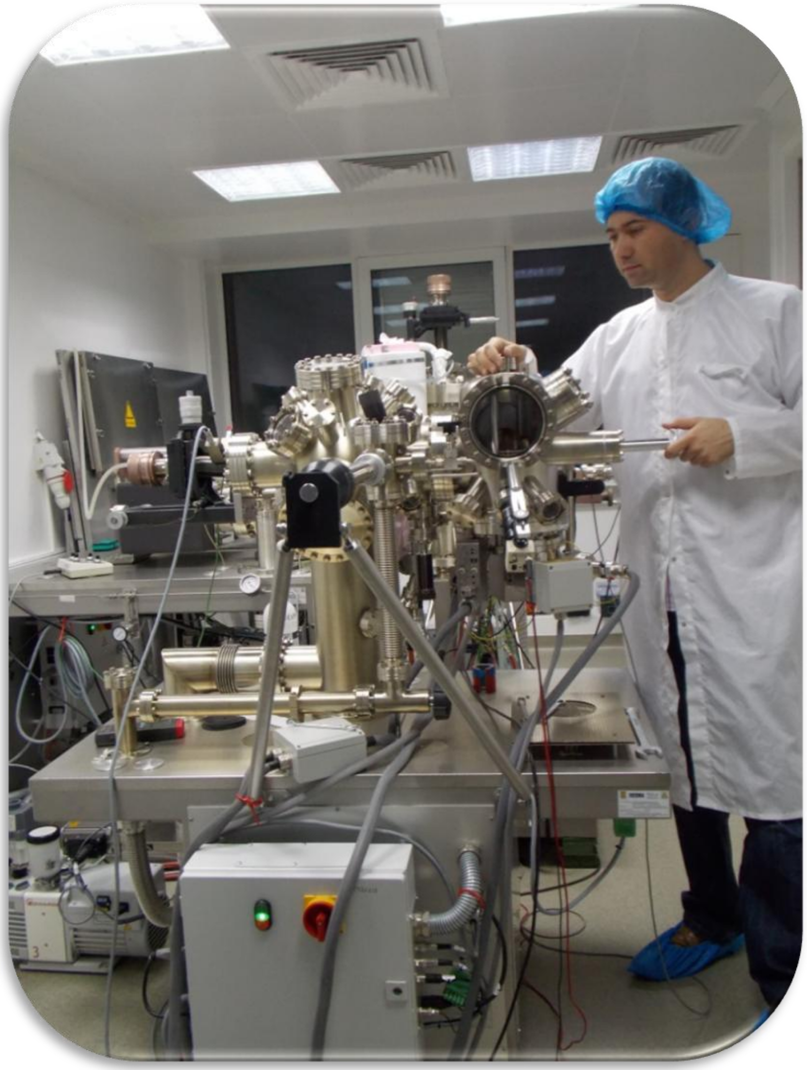
http://grid.itim-cj.ro/
https://erris.gov.ro/INGRID---GRID-System-1

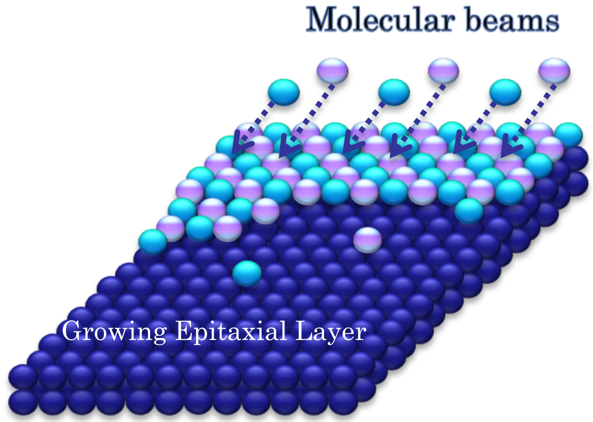
https://erris.gov.ro/MOL-BIO-MOLecular-and-BIOmol-1

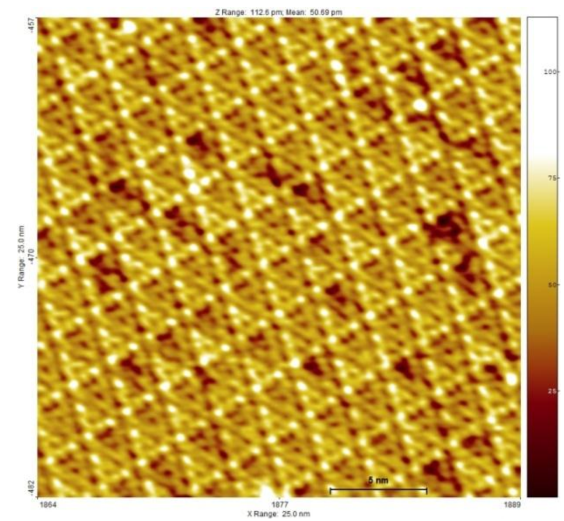
Experiment: how to build a molecular layer on a surface?

- surface preparation
- molecule deposition
- characterization via STM images

Examples: Fabrication of nanostructured, ultra-flat thin films as promising substrates for molecular electronics[1,2]



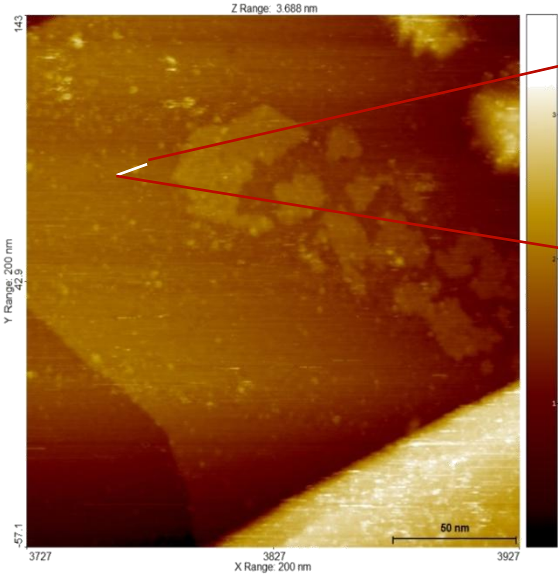




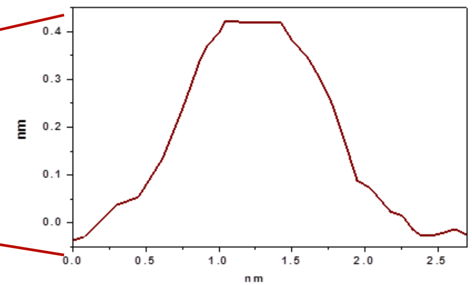
Reconstructed 7×7 Si(111) substrate

[1]D. Marconi, A. Ungurean, Appl. Surf. Sci. 288 (2014) 166.
[2]D. Marconi, A. Colniță and I. Turcu, Anal. Lett. 49 (2016) 400.

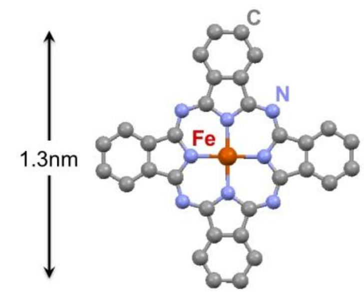
Sub-monolayer molecular deposition: FePc on Au(111) *case study*



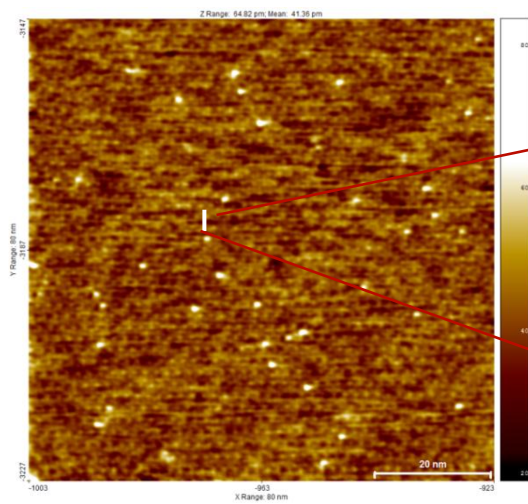
2D-STM image for sub-monolayer FePc/Au(111)

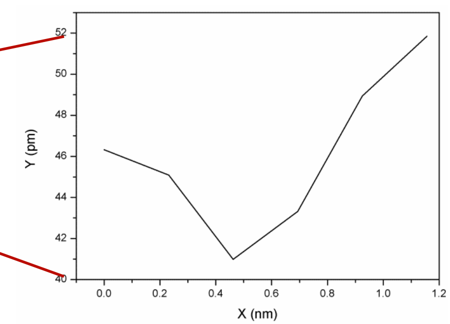


2D-STM image for 200 nm thickness of FePc/Au(111)

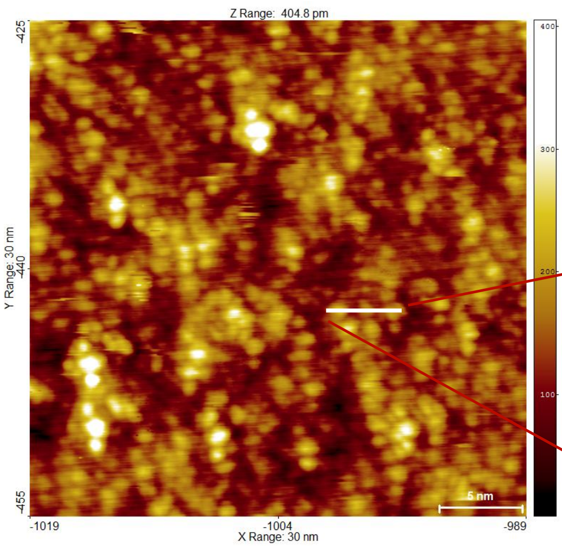


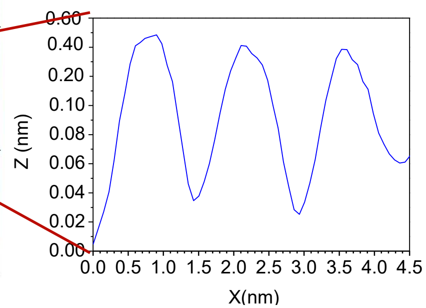
Phtalocyanine (Pc) molecule





2D-STM image of Au(111) surface with atomic defects

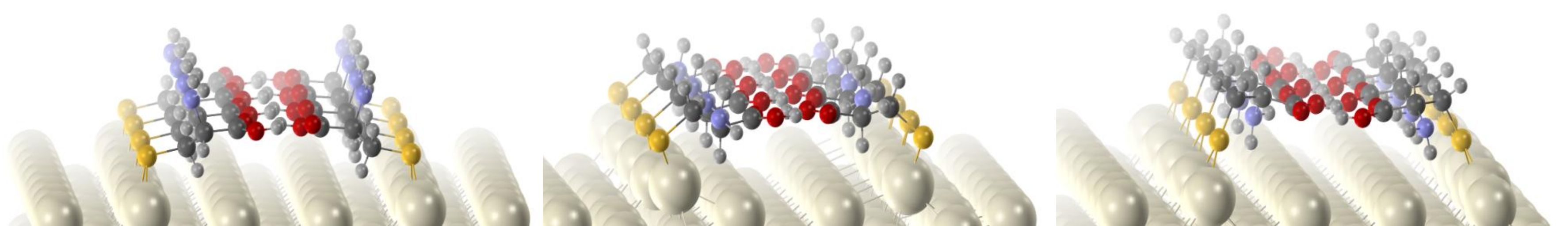




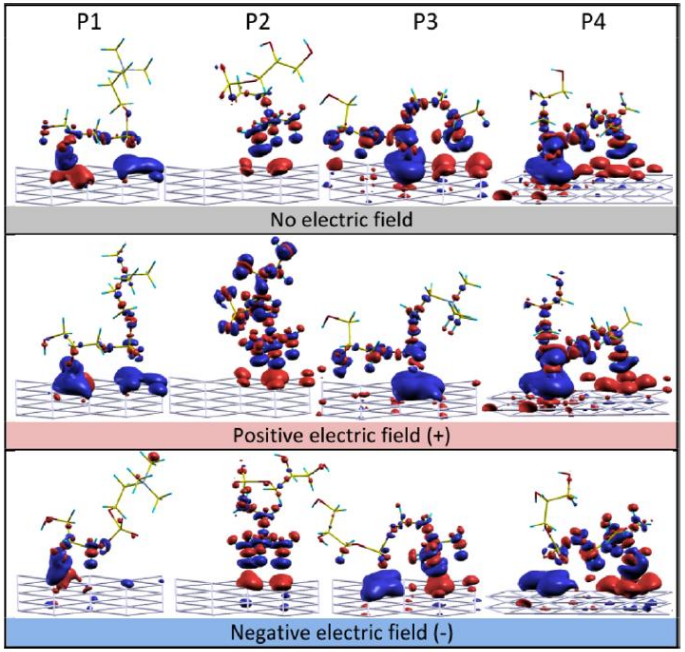
Roughness RMS=0.32 nm

Theory: how to design the properties of molecular devices

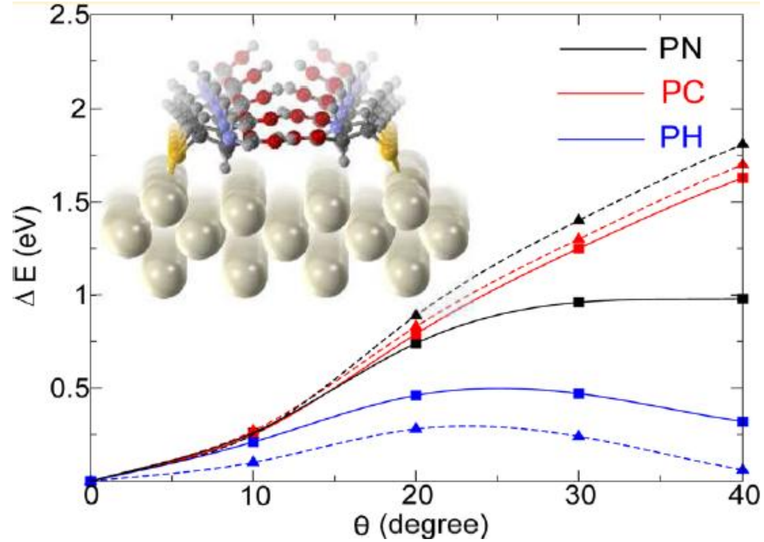
- periodic structure calculations (slab model)
- computational technique: DFT
  - ✓ charge transfer
  - ✓ density of states
  - ✓ molecule-substrate interaction geometry



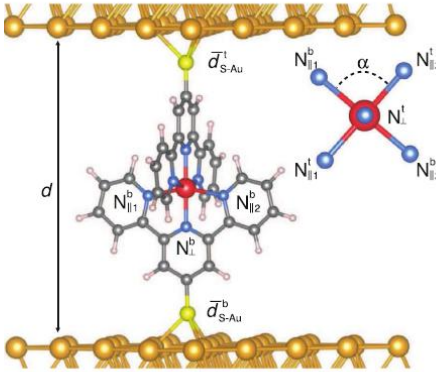
Examples: molecules on surfaces



σ-bonded molecule (alpha glycerophosphocholine) in interaction with Au surface; positive and negative electric charge effect[1].



Molecular self-assembly on metallic surface (cysteine on gold)[2]

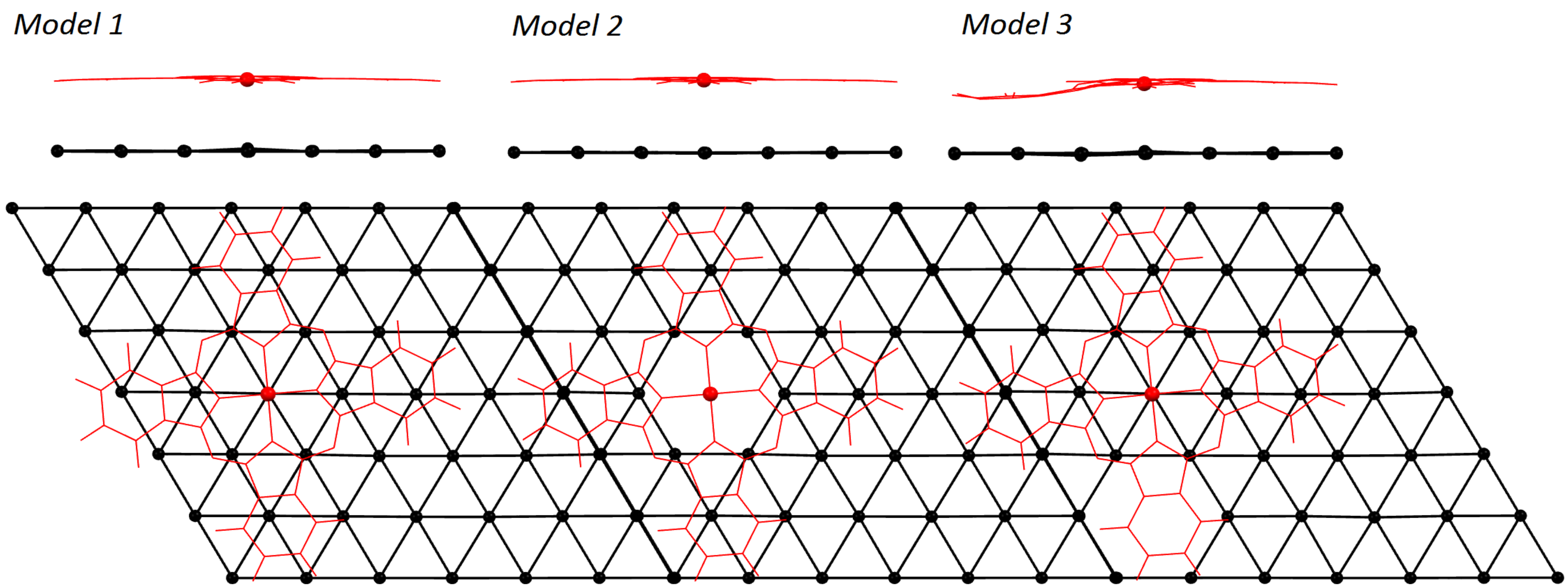


Calculation of unimolecular device properties (rutenium-di-terpyridine sandwiched between two gold electrodes)[3]

[1]L. Buimaga-Iarinca, C. Morari et al, J.Phys.Chem. C, 120 (18), 9740–9749 (2016)
[2]L. Buimaga-Iarinca, C. Morari, J. Phys. Chem. C 117(39) 20351 (2013)
[3]C. Morari, L. Buimaga-Iarinca et al, Nature Scientific Reports 6, 31856 (2016)

Practical approach for FePc on Au(111) *case study*

Main idea: the molecular structure and parameters have to be stable in the adsorption state when structural deformation occurs on the surface (i.e. lab-made/ cheap surfaces)



Computational details:
Molecule (FePc) – 57 atoms; Au(111) surface – 7x7x3 atoms; lattice parameter 4.08 Ang.
The **molecule and first Au layer** set free to relax their position
Relaxed until a gradient < 0.03 eV/Ang;
Spin-polarized calculations
We used the SIESTA code in VdW setup, with the BH* functionals.

*BH: vdW-DF functional of Dion et al (same as DRSLL) with exchange modified by K. Berland and P. Hyldgaard, Phys. Rev. B 89, 035412 (2014)

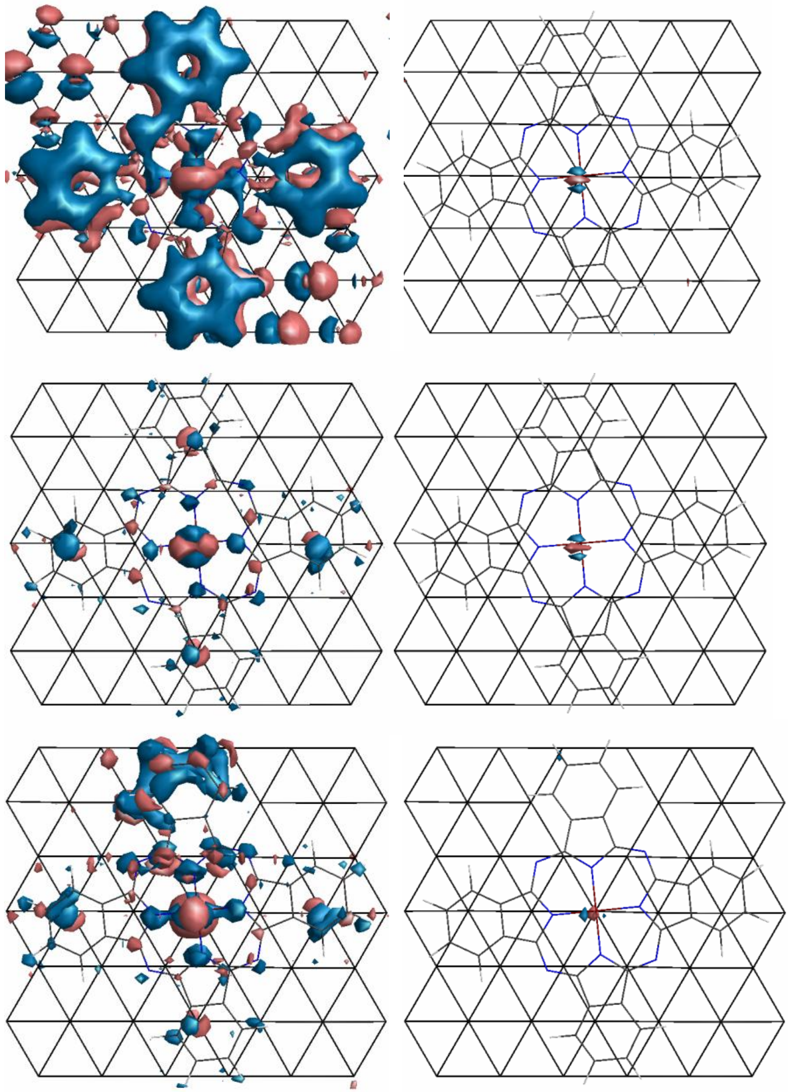
Charge transfer between FePc and Au substrate

$\Delta\rho$=0.001 Å/B^3 | $\Delta\rho$=0.01 Å/B^3

Model 1

Model 2

Model 3



CONCLUSION

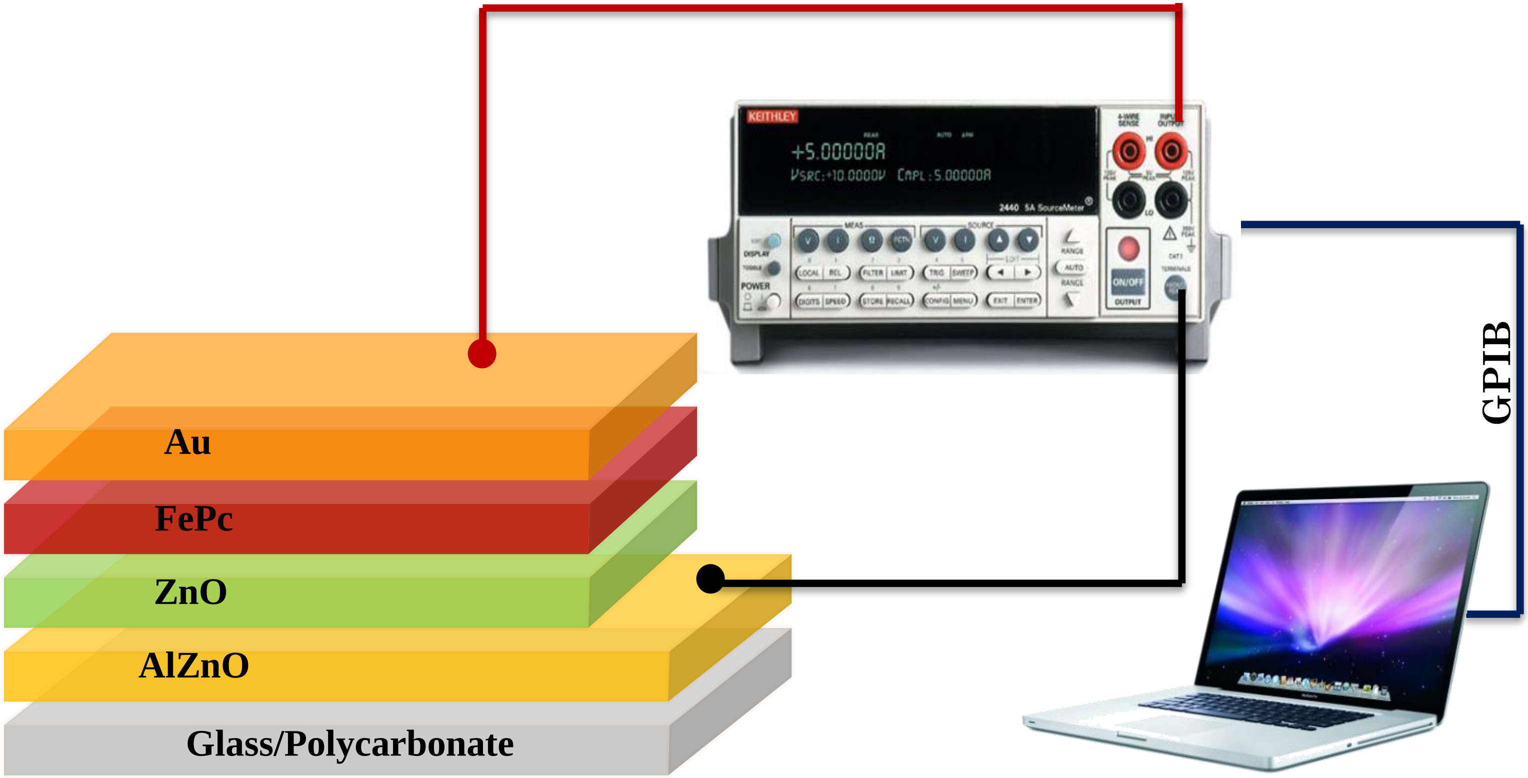
Charge transfer between molecule and surface differ for each case (left images)

BUT
is small - little or no difference for the Fe atom (right images)

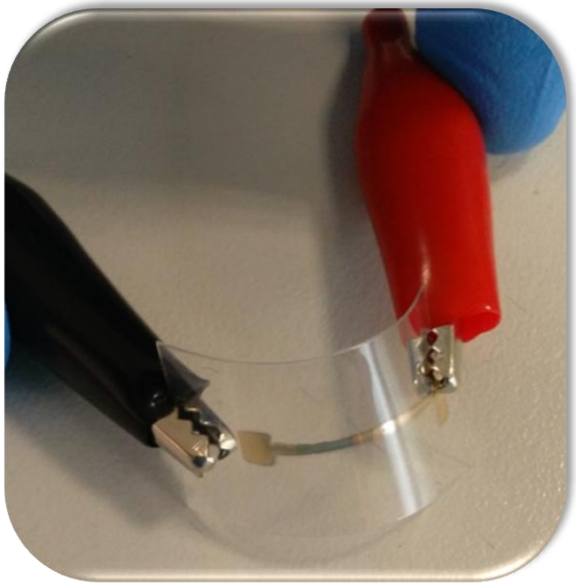
SO
It may be possible to build devices using 'lab-made' surfaces

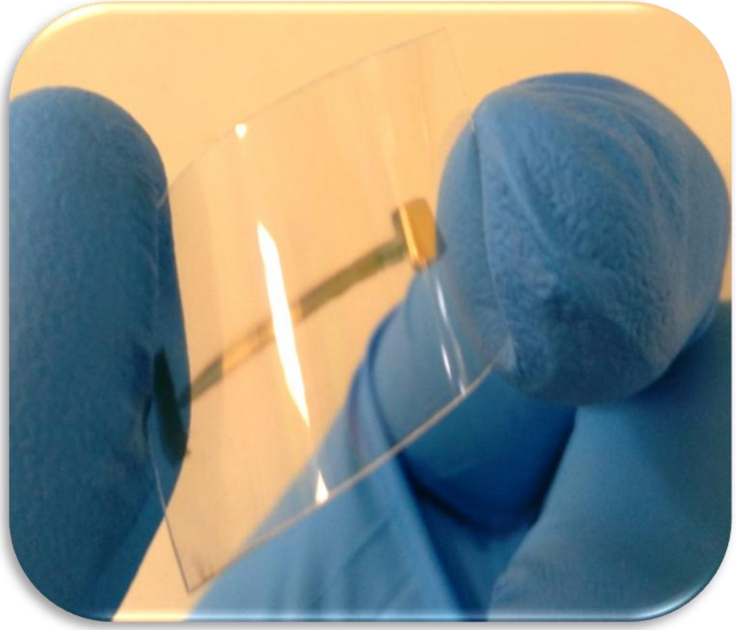
Red – FePC accept charge from the surface; Blue – FePC loose charge to the surface

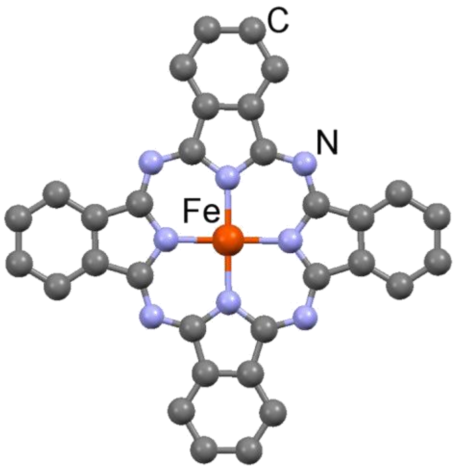
EXPERIMENTAL IMPLEMENTATION: HYBRID ZnO/FePc NANO-DIODE



Organic-inorganic hybrid diode

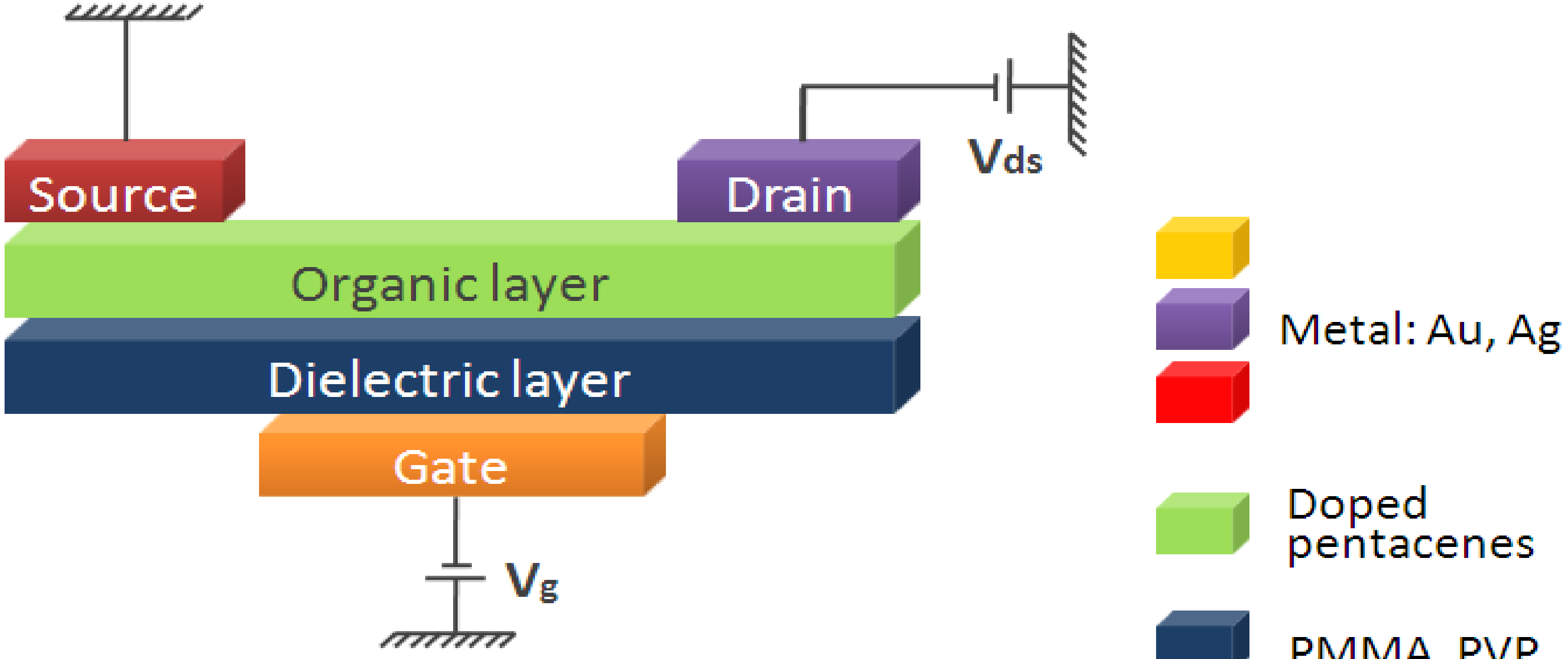






In the near-future:

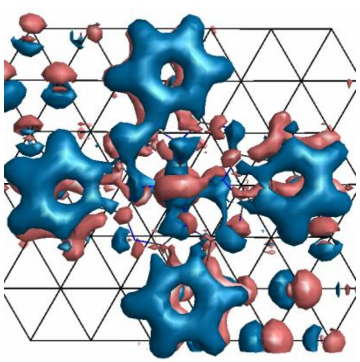
Thin-film MOLECULAR TRANSISTOR on transparent and flexible substrate

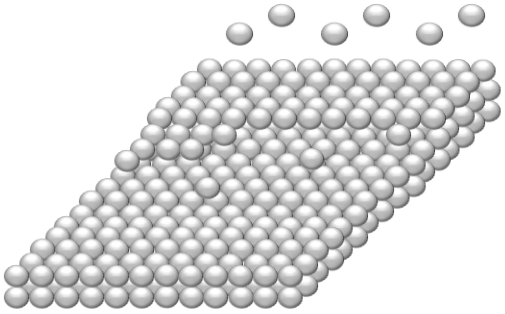


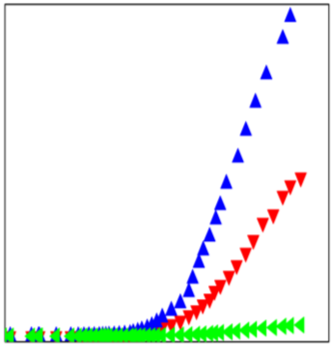
CONCLUSIONS

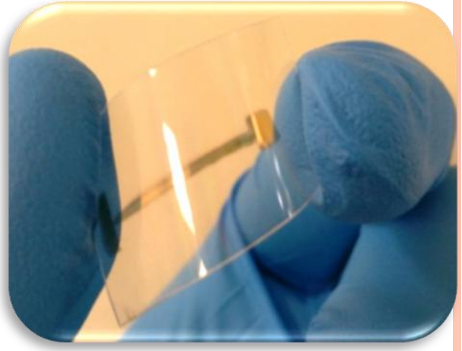
We construct the surface by MBE → design and assess the device properties by DFT → construct the molecular device components → assemble the device → perform complete measurements and characterizations.

From design to proof-of-concept: calculations, fabrication and characterization – we integrate all the steps to produce nanometric-scale organo-metallic flexible devices.









Dr. Ioan Turcu
Head of Department

Dr. Cristian Morari
Dr. Luiza Buimaga
Computational Group

Dr. Daniel Marconi
Dr. Alia Colniță
Experimental Group

ioan.turcu@itim-cj.ro
cristian.morari@itim-cj.ro
luiza.iarinca@itim-cj.ro
daniel.marconi@itim-cj.ro
alia.ungurean@itim-cj.ro

Financial support is gratefully acknowledged from

UEFISCDI, CAPACITIES – Module I – Large investment projects for 2PM/I/07.10.2008
UEFISCDI, for PN-II-ID-PCCE-2011-2-0027
ANCSI, Core Programme for Project PN16-30 02 01