European Network on New Sensing Technologies for Air Pollution Control and Environmental Sustainability - *EuNetAir*

COST Action TD1105

1ST International Workshop as Open Satellite to *Transducers 2013* on

New Sensing Technologies and Transducers for Air Quality Monitoring

Barcelona International Convention Centre, Barcelona, Spain, 20 June 2013

Emerging Hybrid Materials For Air-pollution Microsensors

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Plan

- The tuning of physical properties to improve chemosensing
- Phthalocyanine-Carbon Nanotubes hybrid materials
- Polymer-Phthalocyanine hybrid materials

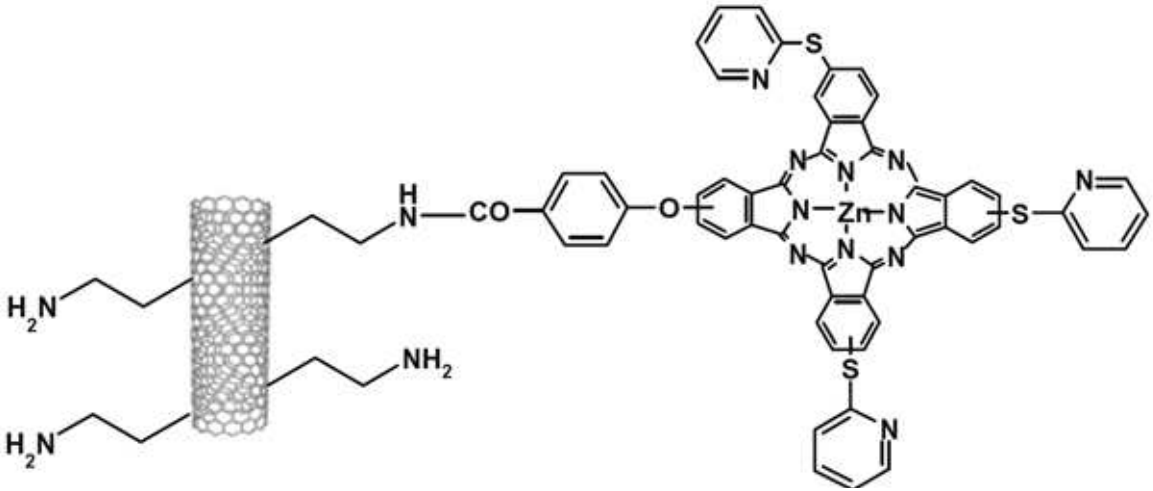
The tuning of physical properties to improve chemosensing

- To make possible the solution processing of sensing materials
- To modify their hydrophily/hydrophoby
- To modify their structure and morphology
- To tune their conductivity
- To increase their selectivity

Bouvet M., Gaudillat P., Suisse J.-M. *J. Porphyrins and Phthalocyanines* 2013 accepted.

Phthalocyanine-CNT hybrid materials

- Covalent bonding to SWCNT



View of ZnPc chemically linked to SWCNT obtained by reaction of a carboxyphenoxy-substituted ZnPc with a amine functionalized SWCNT

Usefull in conductimetric transducers, but also for electrochemical measurements

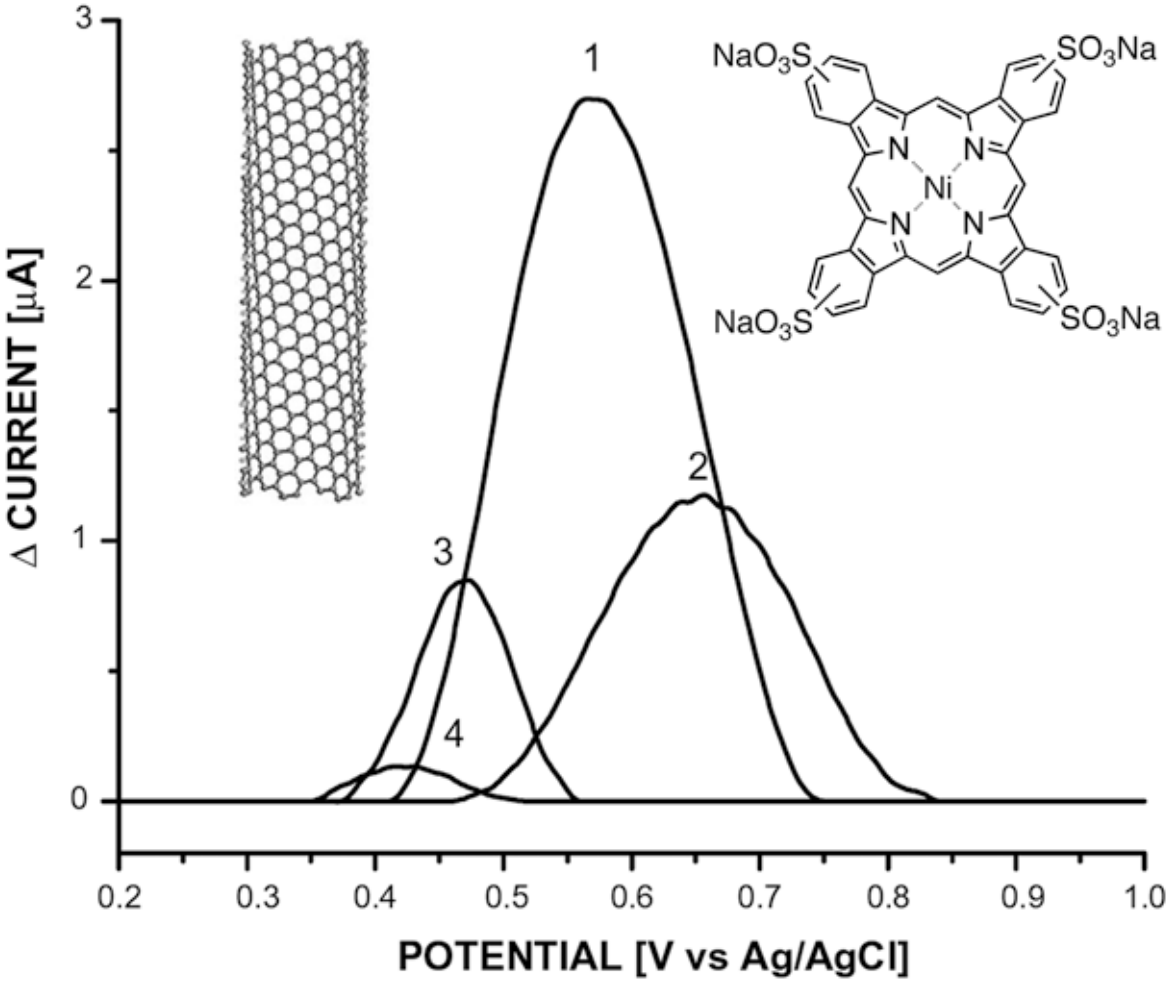
Chidawanyika W and Nyokong T *Carbon* 2010; 48: 2831–2838.

Phthalocyanine-CNT hybrid materials

- Non covalent bonding

Curve 1: GC/SWCNT-NiTSPc;
curve 2: GC/NiTSPc;
curve 3: GC/SWCNT
curve 4: unmodified GC.
All electrodes were cast with an outermost external layer of nafion®.

Cyclic voltammetry peaks of 0.1 mM NO in aerated phosphate buffer solution (pH 7.4) at different composite electrodes.

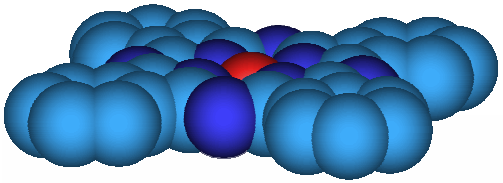


Cruz Moraes F, Golineli D, Mascaro L and Machado SAS *Sens. Actuators B* 2010; 148: 492–497

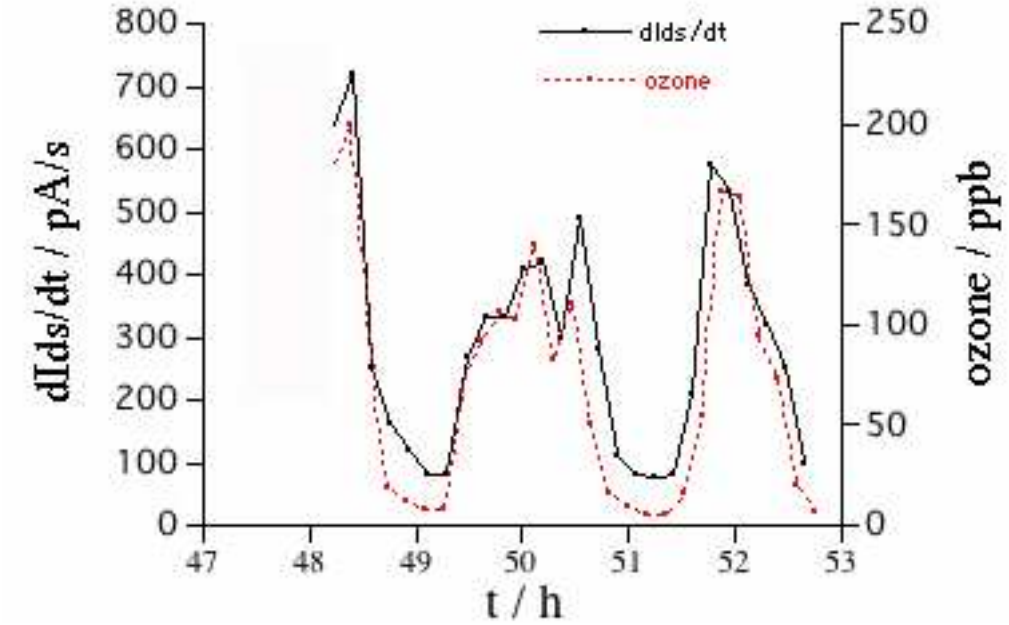
Penza M, Rossi R, Alvisi M, Signore MA, Serra E, Paolesse R, D'Amico A and Di Natale C *Sens. Actuators B* 2010, *144* (2), 387–394.

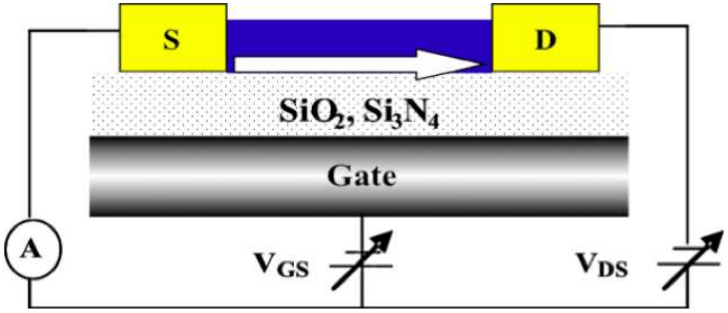
Molecular sensing materials for ozone detection

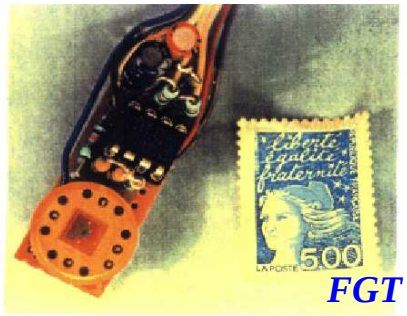
- The example of phthalocyanine-based OFETs:



$Pc^{2-}M^{2+}$





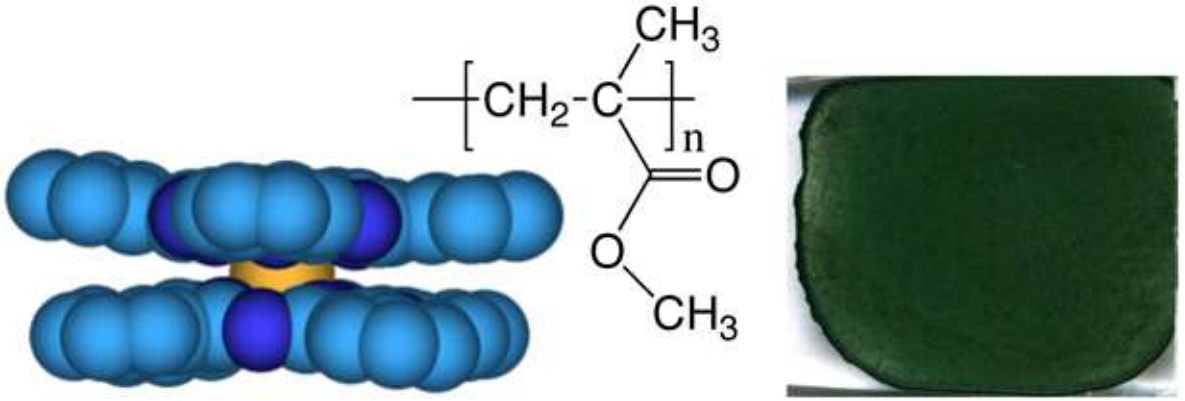


Used to measure the ozone concentration in Paris (AIRPARIF).

M. Bouvet et al. Sensors and Actuators B, 72, 86-93, 2001 ;
M. Bouvet Anal. Bioanal. Chem. 384, 366-373, 2006.

Phthalocyanine-polymer hybrid materials

- Solution processing by a simple incorporation in a polymer:

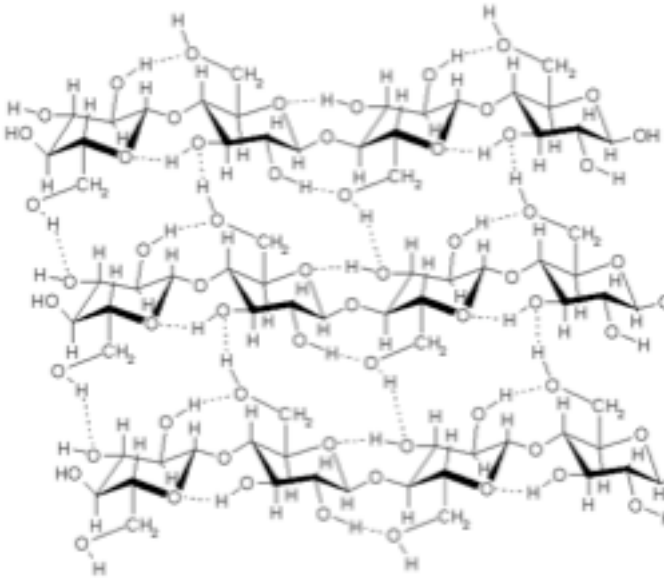


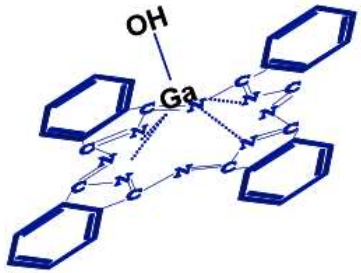
$LuPc_2$ / PMMA (80/20 w/w) as deposited by spin-coating, for the detection of ozone in the ppb range

Bouvet M, Parra V, Locatelli C and Xiong H *J. Porphyrins Phthalocyanines* 2009; 13: 84–86.

Cellulose/HOGaPc hybrid materials

- Via a chemically modified polymer





Trimethylsilylcellulose (TMSC)
0.5 gL^{-1} in THF

Spin-coating over
GaAs and ITO/glass substrates
2000 rpm; 400 $rpm.s^{-1}$; 60"

CELL-Si

ITO/glass
or GaAs (100)

Regeneration of cellulose by vapor hydrolysis, using HCl 35%, during 30"

H_3O^+ (v)

CELL-R

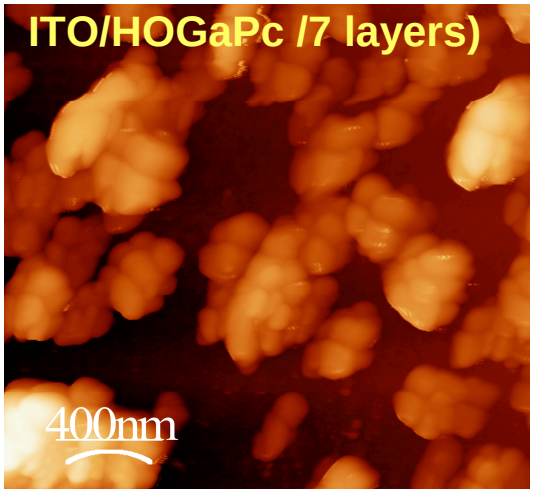
Spin-coating of a HOGaPc solution (10^{-3} M in $CHCl_3$)

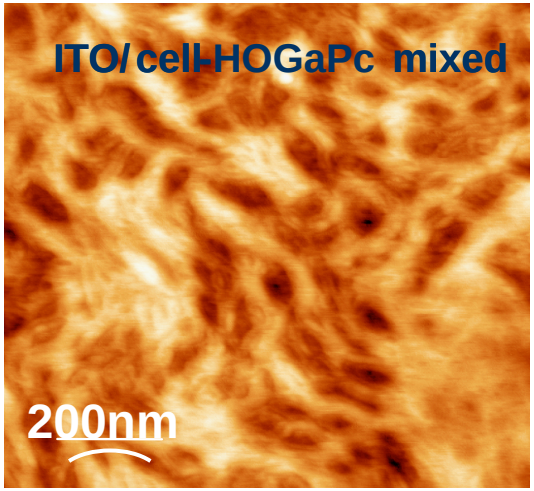
HOGaPc

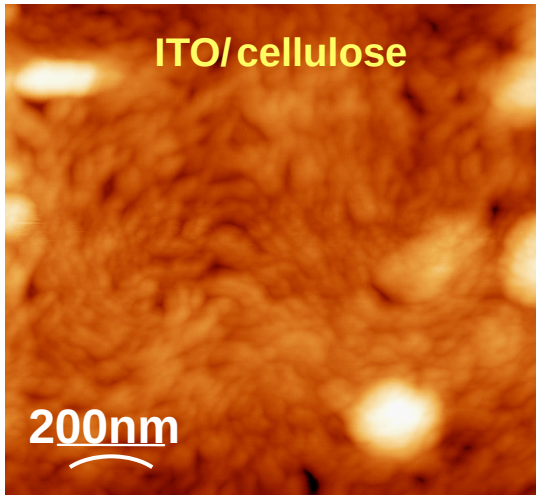
V. Parra et al. "New Hybrid Films Based on Cellulose and Hydroxygallium Phthalocyanine. Synergetic Effects in the Structure and Properties" Langmuir, 23, 3712-3722, 2007.

Cellulose/HOGaPc hybrid materials

- AFM pictures of the hybrid material compared to pure compounds





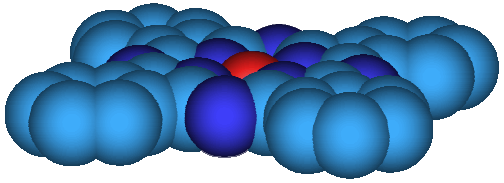


- The sensitivity of the cellulose/HOGaPc hybrid film to O_3 is higher.
- The synergetic behavior between the film-forming materials allows a fast and sensible change in surface potential after cyclic exposures to ozone.

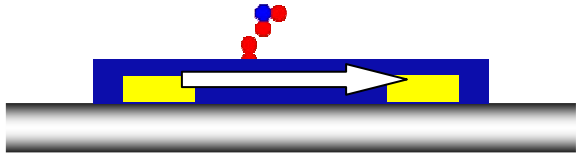
V. Parra et al. "New Hybrid Films Based on Cellulose and Hydroxygallium Phthalocyanine. Synergetic Effects in the Structure and Properties" Langmuir, 23, 3712-3722, 2007.

Sensitivity of p- and n-type materials to NH_3

- Conductimetric transducers

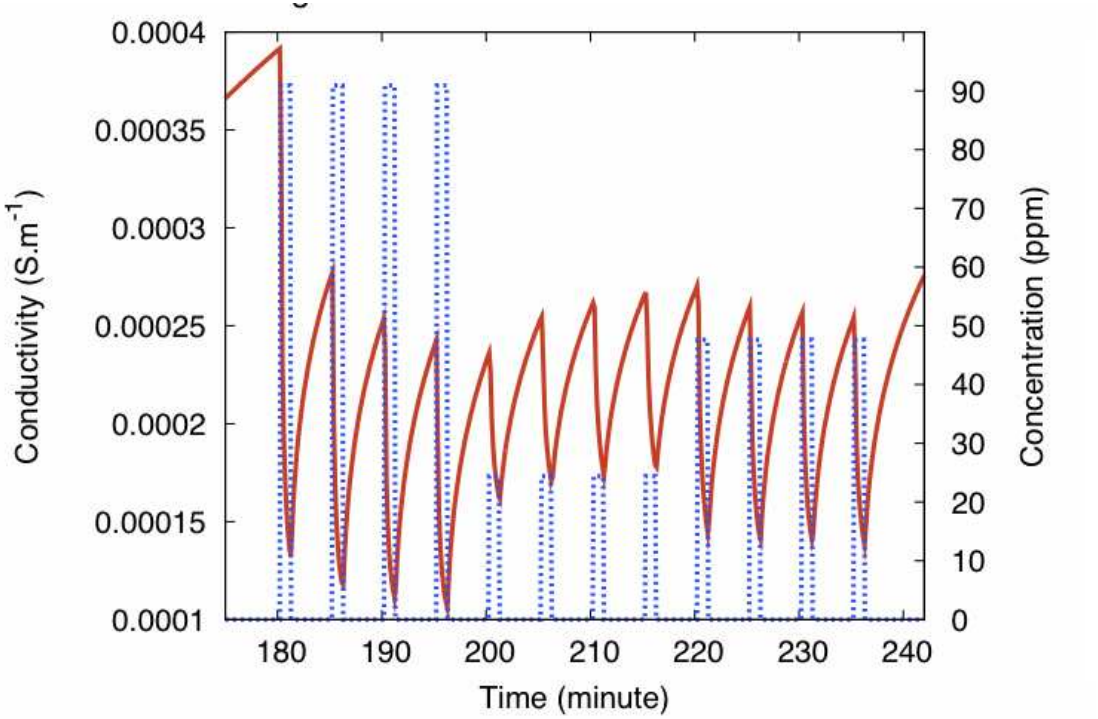


$Pc^{2-}M^{2+}$

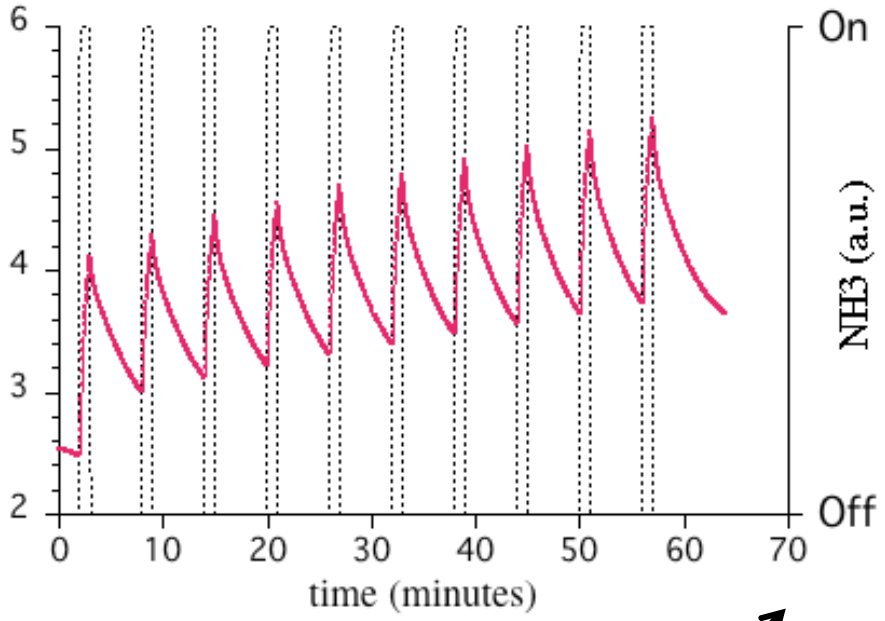


$\sigma = p\ e\ \mu$

$\sigma = n\ e\ \mu$



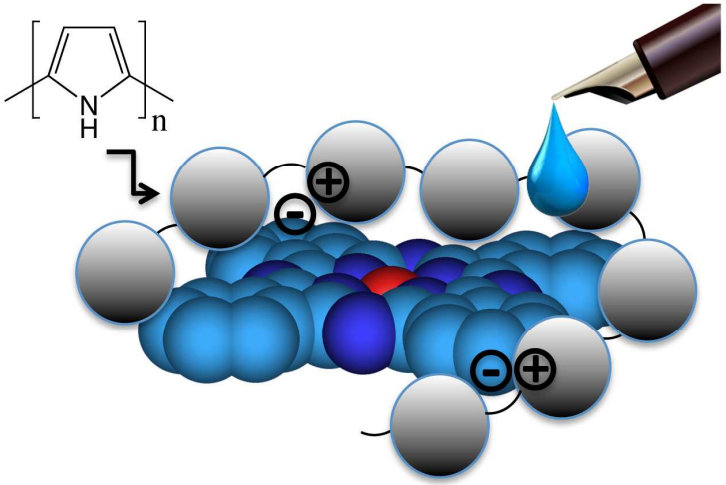
CoPc : p-type **p**

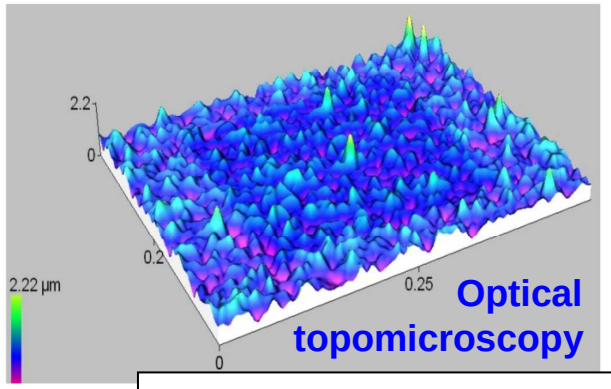


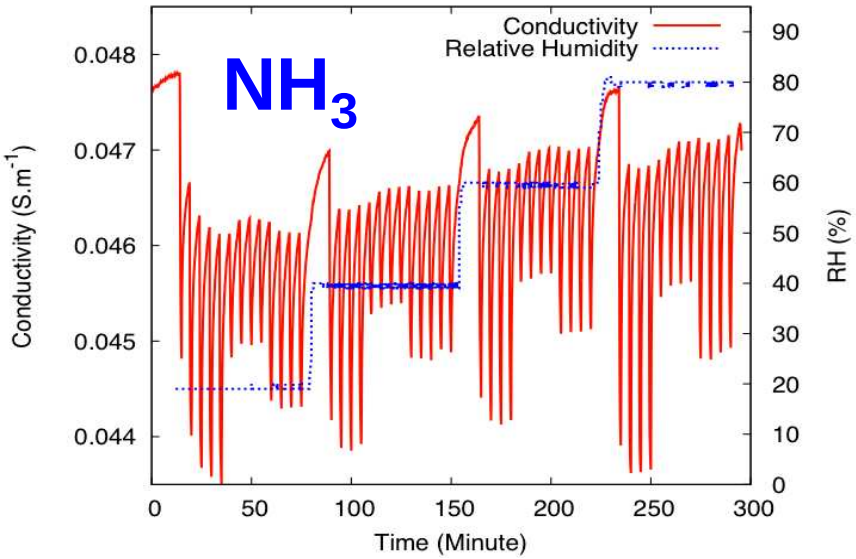
$(F_{16}Pc)$ Cu : n-type **n**

Bouvet M and Pauly A in The Encyclopedia of Sensors, Vol. 6, Grimes CA, Dickey EC and Pishko MV (Eds.), American Scientific Publishers, 2006; 227–270

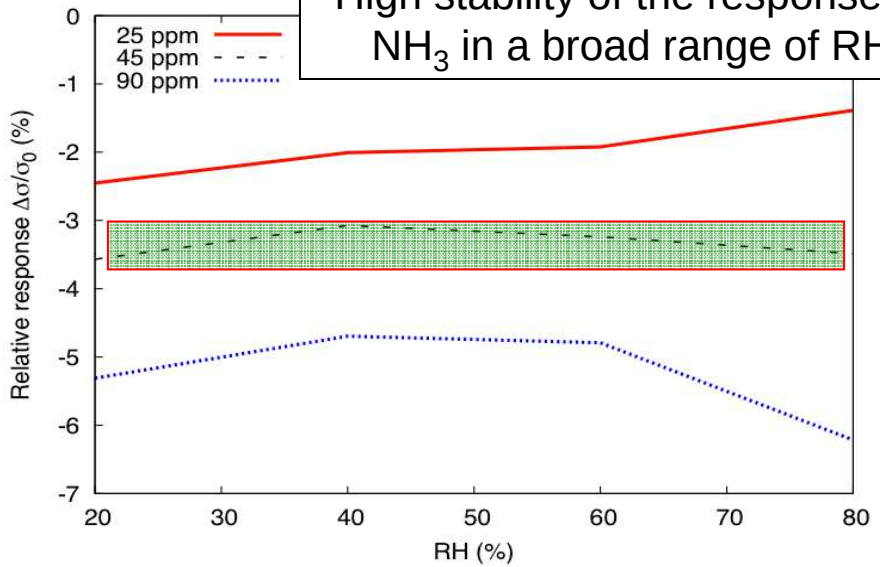
Electrodeposited Ppy-sCoPc hybrid material







High stability of the response to NH_3 in a broad range of RH



T. Sizun, T. Patois, M. Bouvet*, B. Lakard*, "Microstructured electrodeposited polypyrrole-phthalocyanine hybrid material, from morphology to ammonia sensing", J. Mater. Chem., 22, 25246-25253, 2012

CONCLUSIONS

- CNTs can be covalently (or not) bonded to molecules:
  - Solution processing
  - Synergetic effect between CNTs and phthalocyanines
- Incorporation in polymers:
  - Simple mixing in solution
  - Electrodeposition
- Main *achievements:*
  - Selectivity improvement
  - *Stability of the response in a broad range of humidity*
- Applications:
  - Detection of ozone in air
  - Detection of ammonia in real atmospheres

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