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

COST Action TD1105

Final Meeting at PRAGUE (CZ), 5-7 October 2016

New Sensing Technologies for Air Quality Monitoring

Action Start date: 01/07/2012 - Action End date: 15/11/2016 - EXTENSION: 15/11/2016

Emerging Sensing Materials for Air Quality Monitoring

Marcel BOUVET

Sub-WG 1.3 leader, MC member

Univ. Bourgogne Franche-Comté

Dijon / France

COST is supported by the EU Framework Programme

ESF provides the COST Office through a European Commission contract

Plan

- Scientific context and objectives in the Action

- Research facilities available in ICMUB

- Current research activities in ICMUB

- Molecular materials:
    - Cavitands: Selective or not?
    - Solution processing: The example of phthalocyanines

- Polymers:
    - Dielectric materials
    - Conducting polymers

- Suggested R&I Needs for future research

Scientific context and objectives in the Action

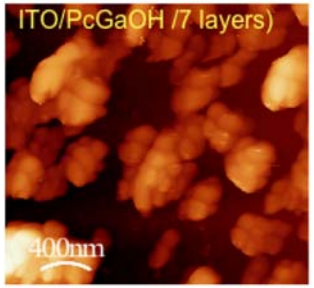
Sub-WG 1.3: Emerging sensor materials for air-pollution detection
molecular materials, organic/inorganic, hybrid, nanocomposites, polymers …

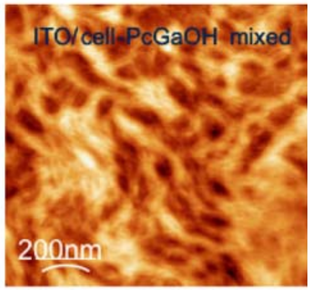
- **Background / Problem statement:**

- Interest: The tuning of properties by molecular engineering

morphology, roughness and specific surface, hydrophilicity or hydrophobicity, processability, electrical properties

- One way: to combine materials for improving chemosensing





AFM images (1 mm x 1 mm) of a pure HOGaPc film (left) and a hybrid film cellulose/HOGaPc film;

Langmuir 23 (2007) 3712-3722

- **Brief reminder of MoU objectives:**

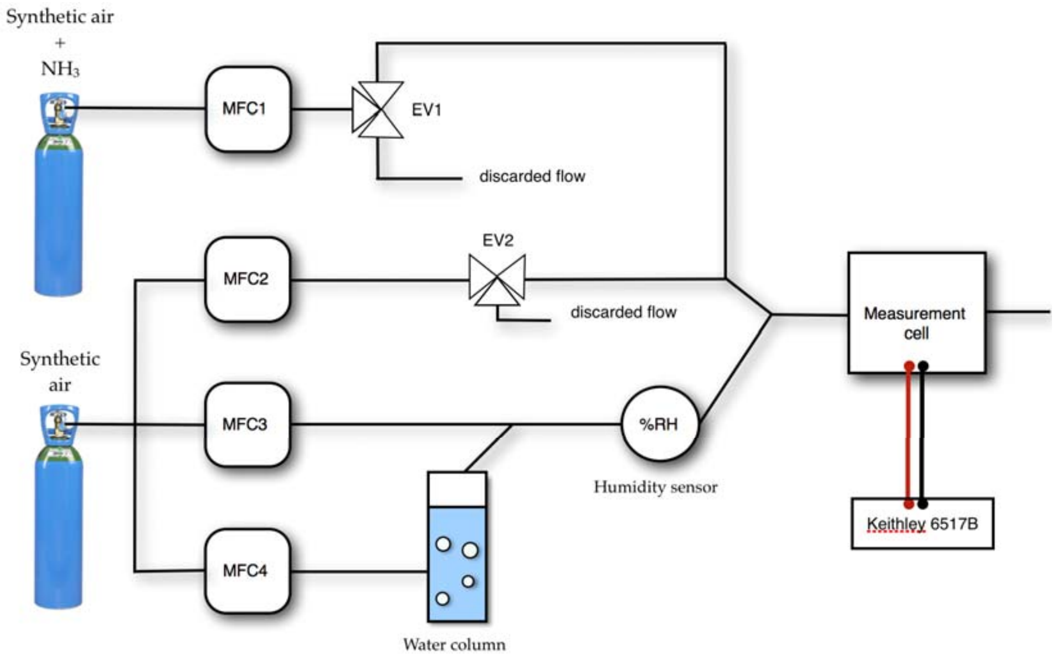
selectivity, low-cost: solution processing (e.g. printing techniques …), low-power consumption (can operate at room temperature)

Research Facilities available in ICMUB

- **Research Facilities:**
- Synthesis
- Solution processing and secondary vacuum chamber
- Electrical and electrochemical measurement set-ups
- Workbenches: O_3 (generator/analyser, ppb range), NH_3 (ppm range),

  BTX (ppm range), humidity

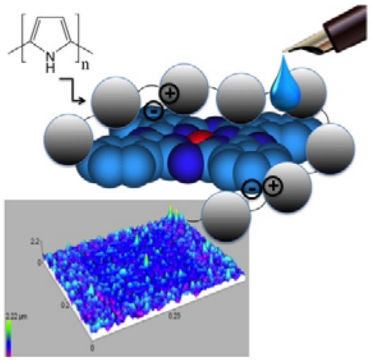
Chemistry
Electrochemistry
Electronics



Current research activities in ICMUB

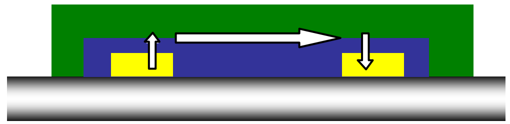
- **Current research topics at the ICMUB:**

  - New materials

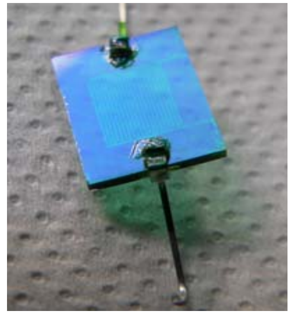


J. Mater. Chem. 2012

  - New transducers



MSDI Org. Electron., 26, 2015



- **Brief list of ongoing research topics of the ICMUB:**

  - Humidity-insensitive ammonia sensors
  - Molecular Semiconductor- Doped Insulator (MSDI) heterojunctions as new conductometric transducers
  - New polymer/macrocycle hybrid materials
  - Electrochemical modification of electrodes

Molecular materials

Weak intermolecular interactions play a key role:

-**From molecules to materials** (structure and morphologies depend on these interactions)

-**Between sensing materials and target gaseous species**

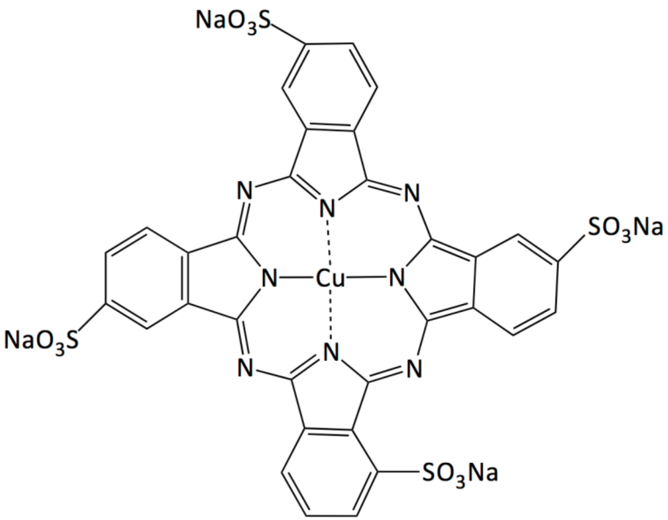
They are Van der Waals, $\pi-\pi$, dipole-dipole, H-bonds, …

Struture and morphology are highly related to the processing techniques

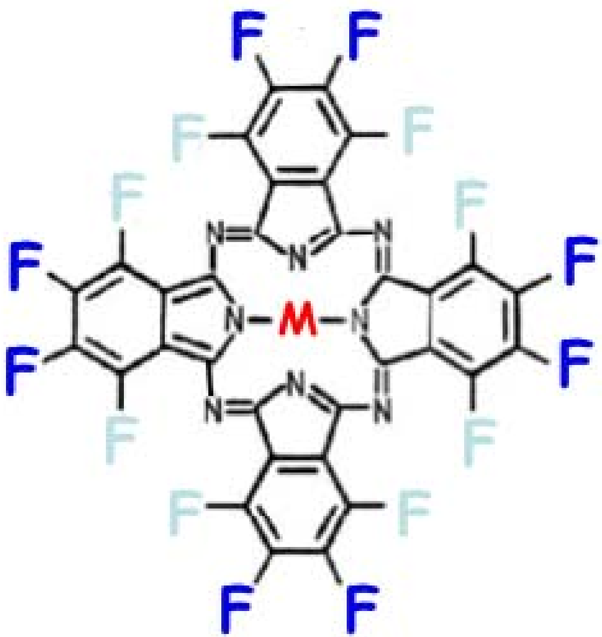
Adsorption and desorption can occur at RT.

Molecular engineering

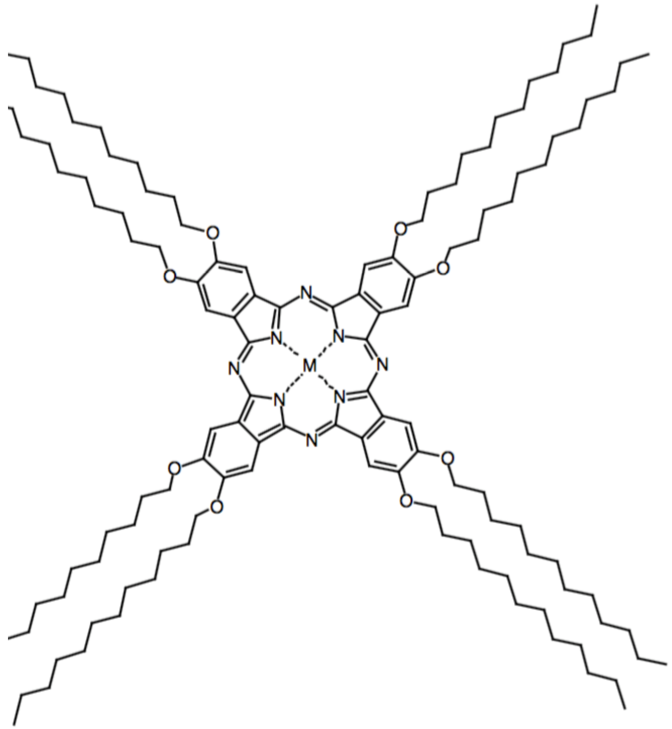
Ionic substituents
→ solubility in water



Withdrawing substituents
→ n-type materials



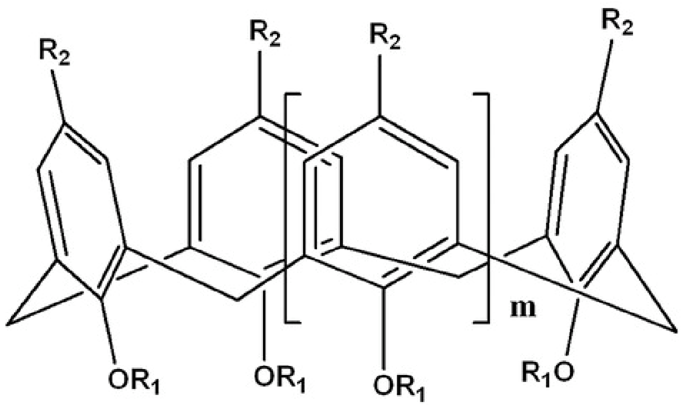
Long alkyl substituents
→ solubility in organic solvents



Cavitands

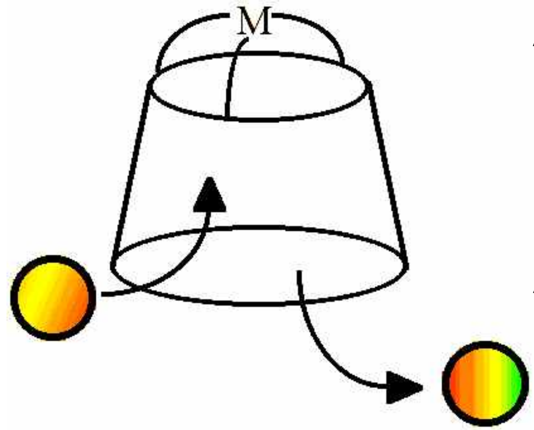
Selectivity?

based on size,
hydrophoby of the cavity,
specific host-guest interactions



$m = 1; 2; 3; 4; 5; 6$

Calixarenes



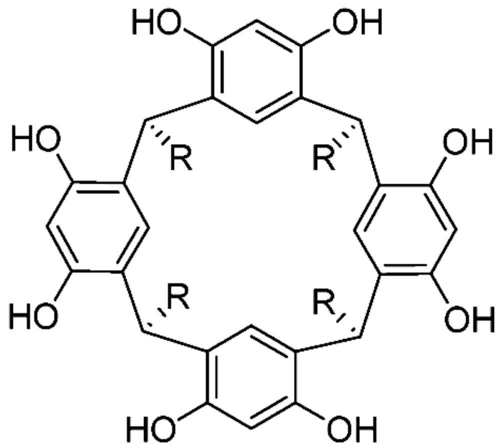
Selectivity?

Actually, in the case of BTX,
R is correlated with the $P_{sat.}$

$P_{sat.}(X) < P_{sat.}(T) < P_{sat.}(B)$

$R(X) > R(T) > R(B)$

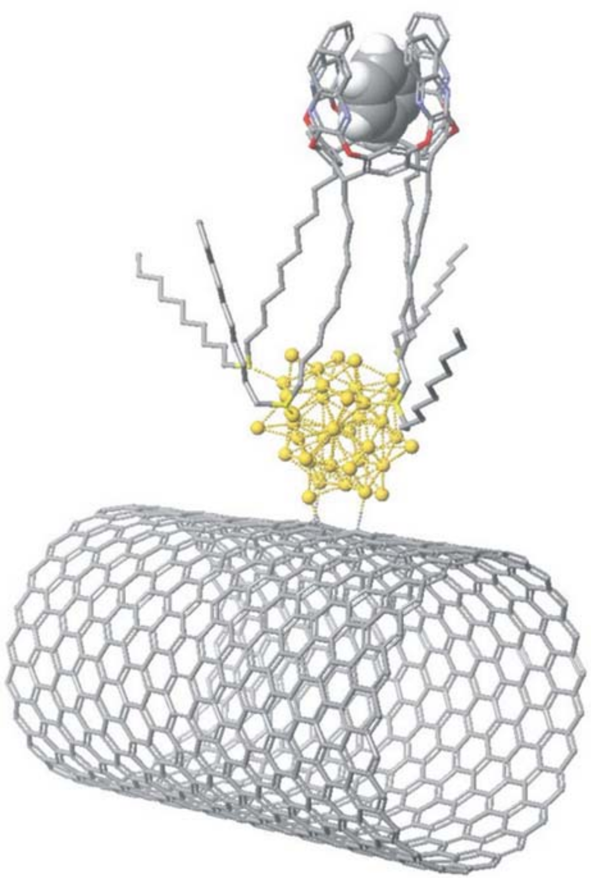
A.V. Nabok et al., Sensors & Actuators: B. 1997

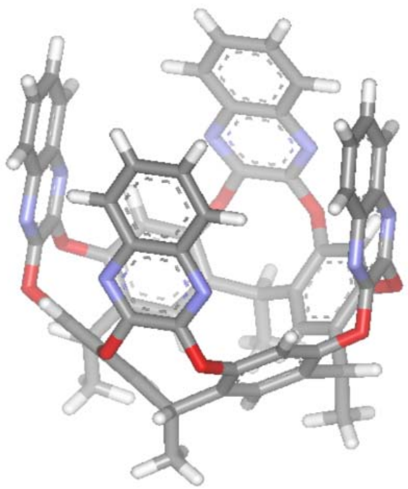


Resorcinarenes

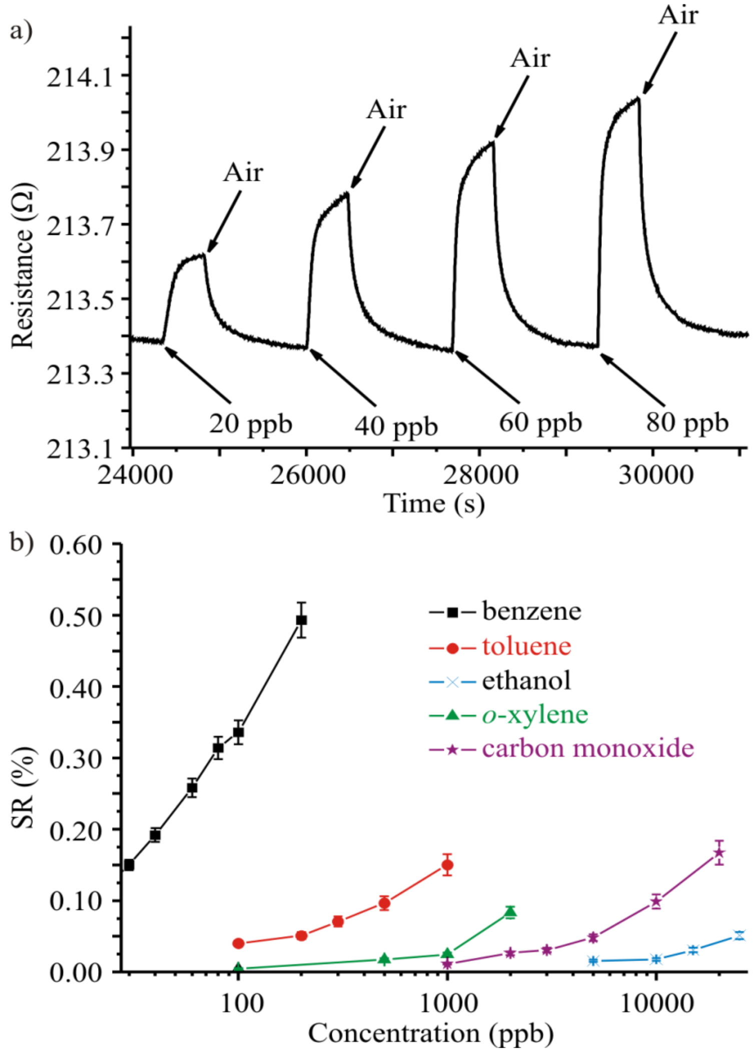
Cavitands

Covalently attached **quinoxaline-bridged resorcin[4]-arene** cavitands to gold nanoparticles anchored on oxygen plasma treated carbon nanotubes



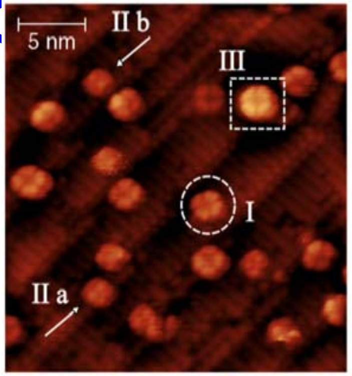


Selectivity towards benzene



E. Llobet, et al., Adv. Funct. Mater., 2015

Solution Processing versus Vacuum evaporation

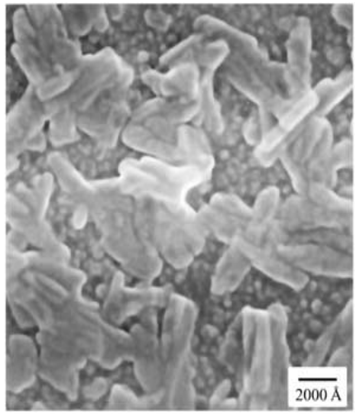


STM image of $LuPc_2$ on vicinal Si
Different molecular orientations and adsorption geometries are pointed out

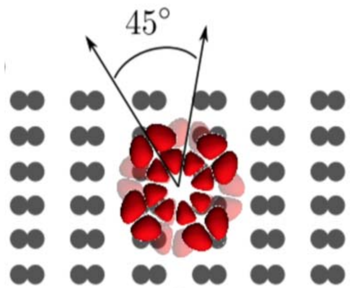
Vacuum Evaporation

Submonolayer
Interaction with the substrate

Thick film
Intermolecular interactions

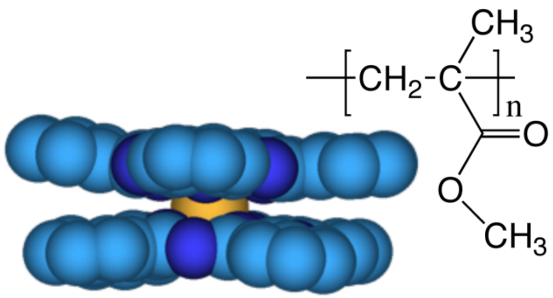


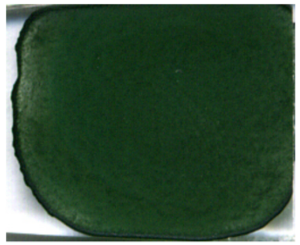
STM
evaporated $LuPc_2$ film, thickness = 1400 Å



A sketch of the proposed adsorption geometry of type I molecule

Solution Processing



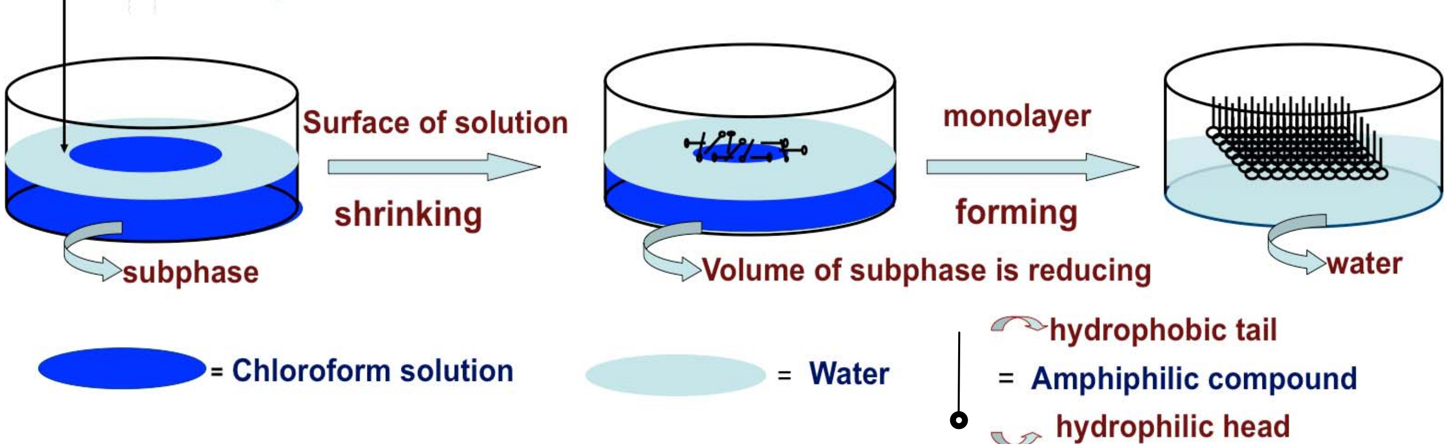


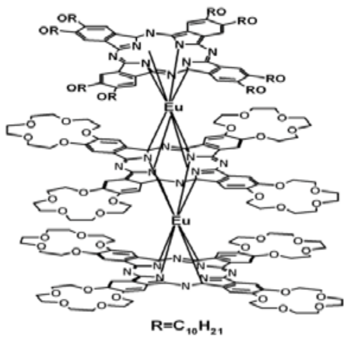
$LuPc_2$ / PMMA (80/20 w/w) (polymethylmetacrylate): by solvent-cast or spin-coating

N. Witkowski et al., Experimental and theoretical study of electronic structure of lutetium bi-phthalocyanine, J. Chem. Phys., 138, 234701, 2013;
V. Parra et al., Electrical transduction in phthalocyanine-based gas sensors: from classical resistors to new functional structures, J. Porphyrins and Phthalocyanines, 13(1), 84-86, 2009.

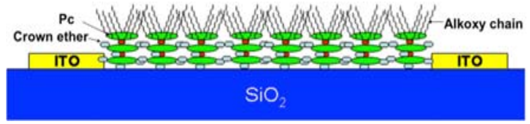
The quasi-Langmuir-Shäfer Technique

Scheme 1. Schematic procedures for the quasi-Langmuir film of amphilic compound.

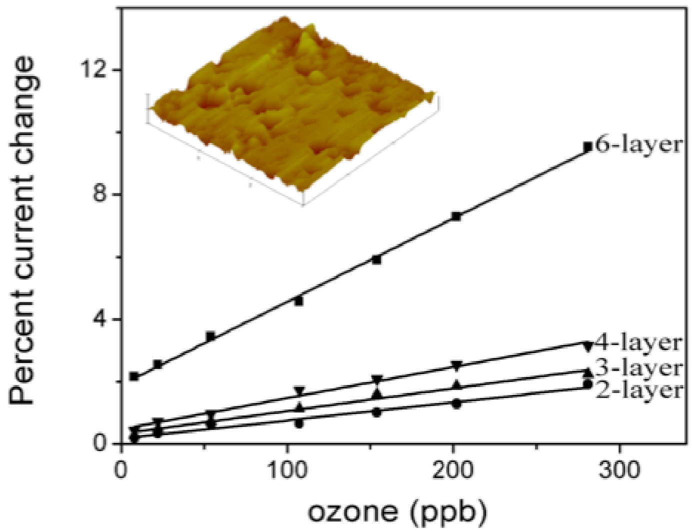




Eu_2Pc_3



resistor



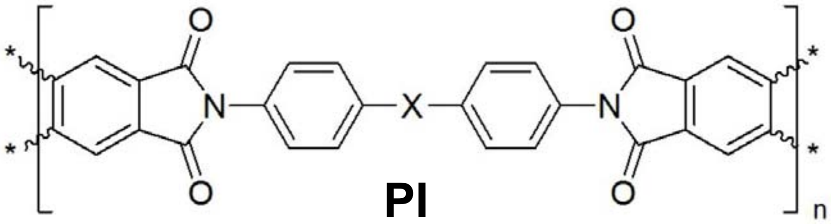
Current increases under ozone

Y. Chen, M. Bouvet*, T. Sizun, Y. Gao, C. Plassard, E. Lesniewska, J. Jiang,
Facile approaches to built ordered amphiphilic tris(phthalocyaninato) europium Triple-decker complex thin films and their comparative performances in ozone sensing, Phys. Chem. Chem. Phys., 12, 12851-12861, 2010. (Hot paper)

Dielectric polymers

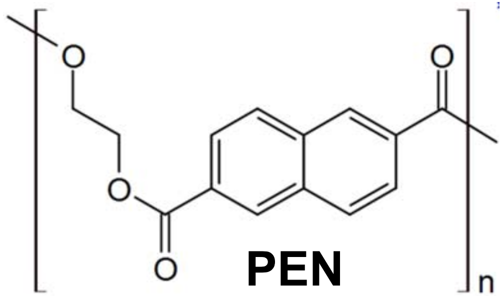
Associated to capacitive or acoustic transducers, their response = f(dielectric constant)

- **Polyimide (PI)**, cellulose acetate, polycellulose acetate butyrate, polymethylmethacrylate and polyvinylpyrrolidone, **polyethylene-naphthalate (PEN)**



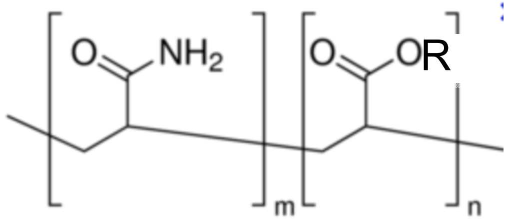
PI

Sensitive to relative humidity



PEN

- **Acrylamide-isooctylacrylate copolymers** are prefered for CO_2 sensing



Specific effects:

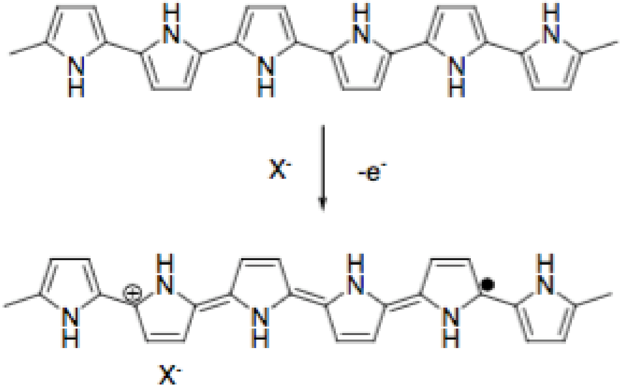
- **swelling**
- **temperature** induces an increase of the motion of polymer chains segments, above T_g (or for low T_g polymers) diffusion of gases is higher

The interaction of polymers with VOCs can be described using **linear solvation energy relationship** (LSER) that takes into account dispersion, polarizability, dipolarity, basicity, acidity and hydrogen bonding interactions.

U. Altenberend, A. Oprea, N. Barsan, U. Weimar, Contribution of polymeric swelling to the overall response of capacitive gas sensors, *Anal. Bioanal. Chem.*, 2013, 405, 6445–6452; J.W. Grate, Hydrogen-Bond Acidic Polymers for Chemical Vapor Sensing, Chem. Rev. 108 (2008) 726–745

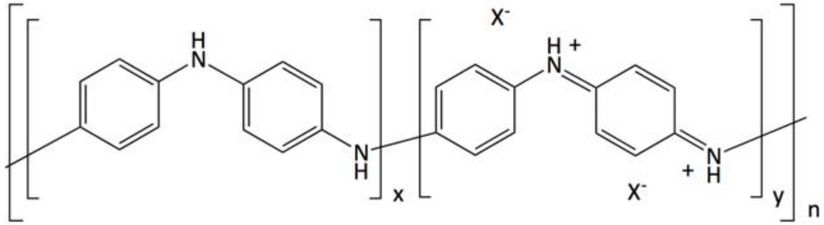
Conducting polymers

Polypyrrole



Partially oxidized = conductive form

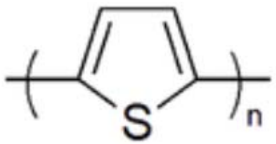
Partially oxidized **Polyaniline**



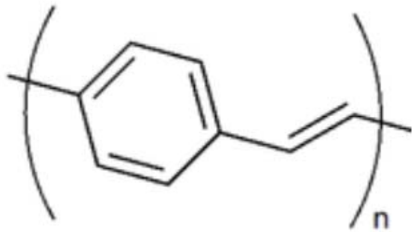
- Generally associated with conductometric transducers;
- Sensitive to redox active species, e.g. NO_x and NH_3

R.A. Potyrailo, C. Surman, N. Nagrajand and A. Burns, Materials and Transducers Toward Selective Wireless Gas Sensing, *Chem. Rev.*, 2011, 111, 7315–7354; D. T. McQuade, A. E. Pullen, T. M. Swager, Conjugated Polymer-Based Chemical Sensors, *Chem. Rev.*, 2000, 100, 2537−2574

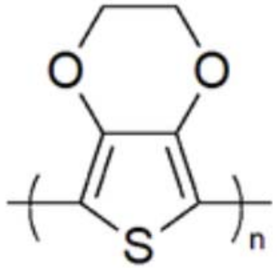
Other conducting polymers



Polythiophene



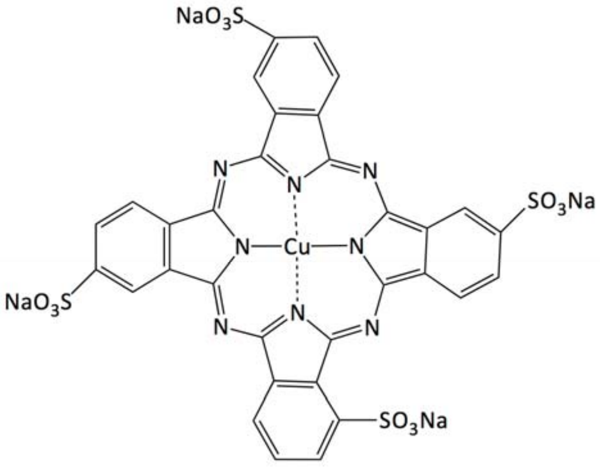
Poly(p-phenylene vinylene)



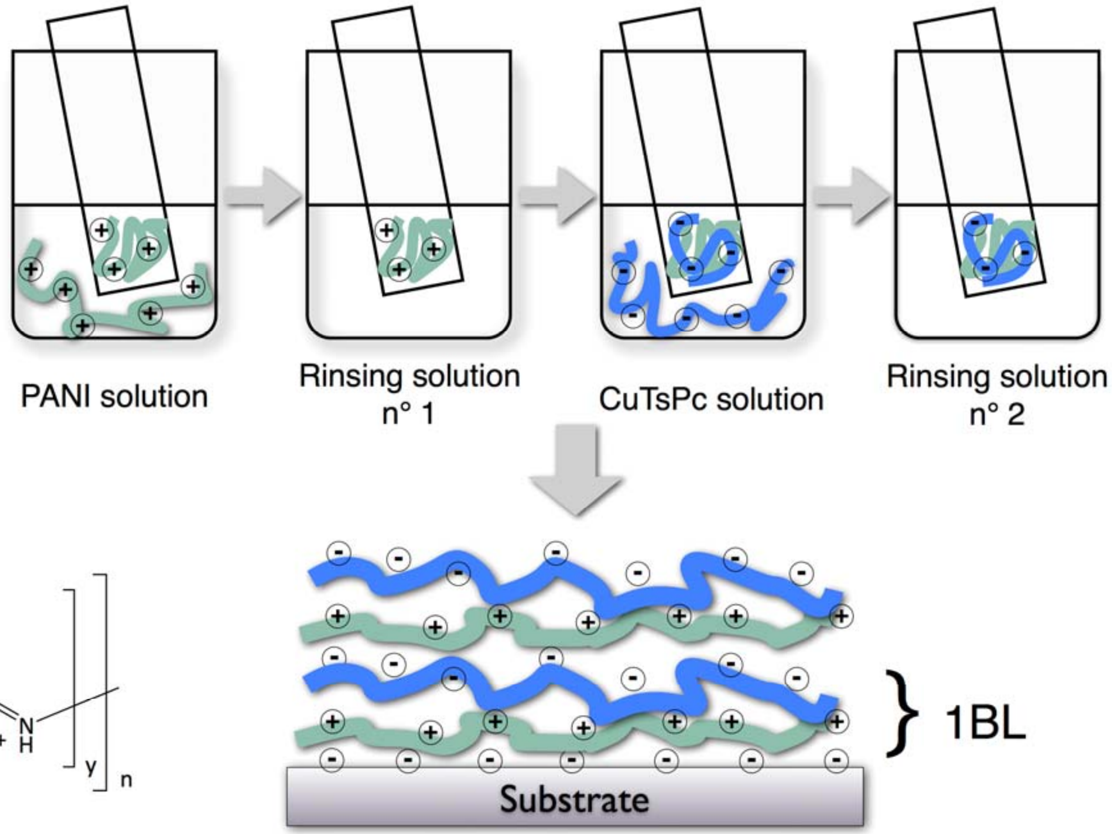
PEDOT

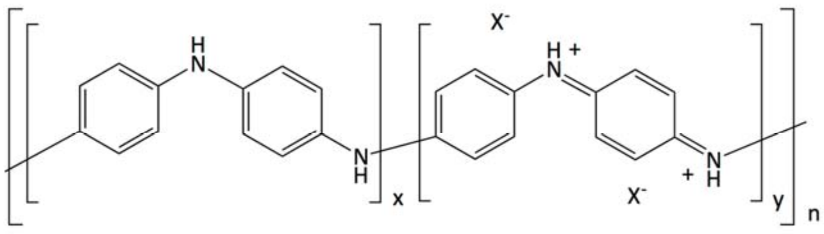
Layer by Layer Deposition of Conducting Polymers – Phthalocyanine Hybrid Materials

Cationic and anionic **polyelectrolytes**



TsCuPc





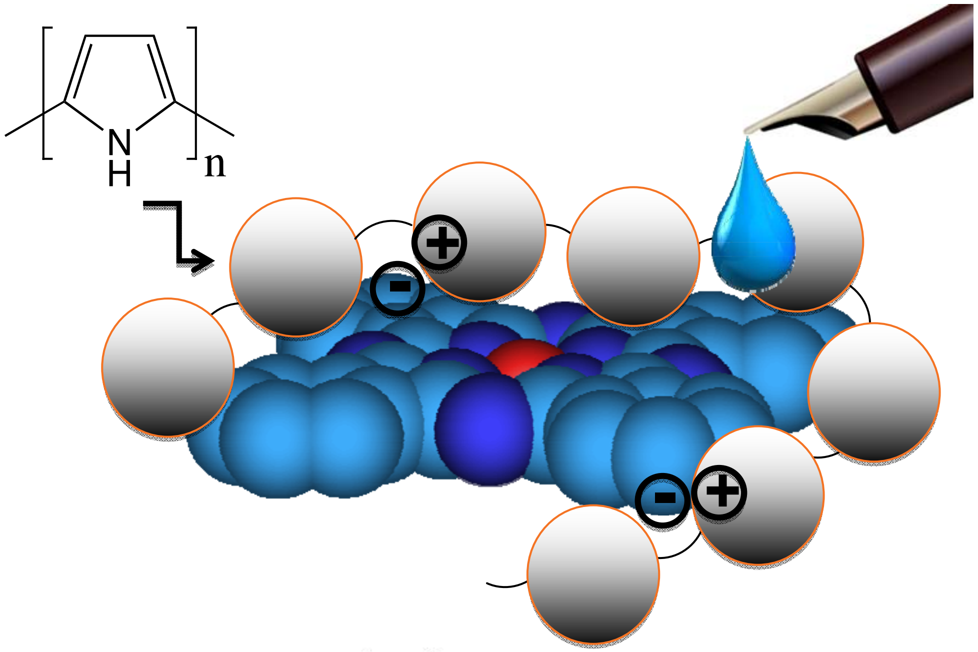
PANI

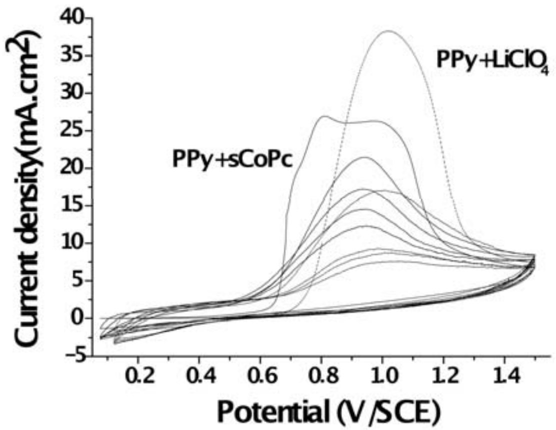
P. Gaudillat, F. Jurin, B. Lakard, C. Buron*, J.-M. Suisse, M. Bouvet*, "Water-stable Polyaniline-Phthalocyanine hybrid material for ammonia sensing in high humidity atmosphere", *Sensors*, 14(8), 13476-13495, **2014**.

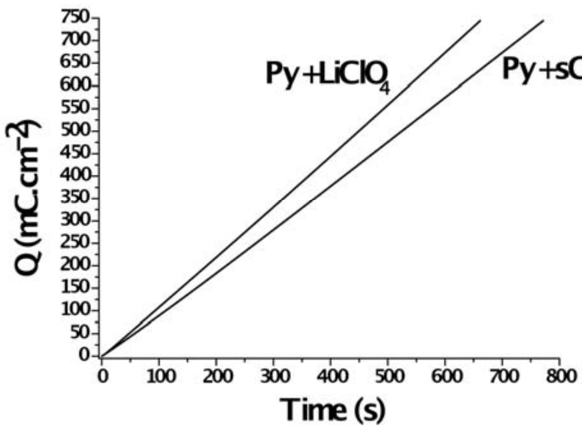
EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

Electrodeposited Polypyrrole-phthalocyanine hybrid materials

Electrooxidation of Pyrrole in the presence of sulfonated CoPc



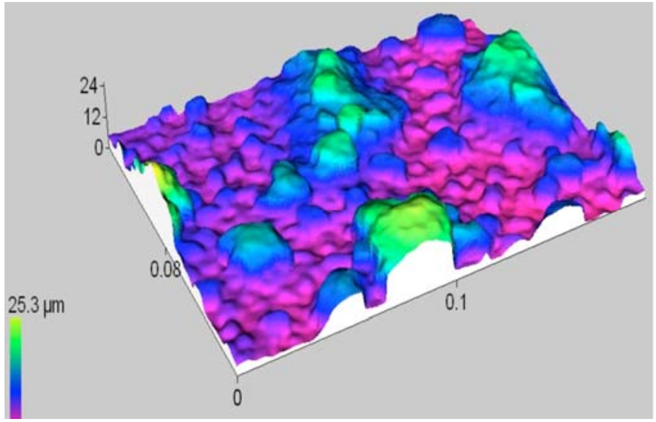


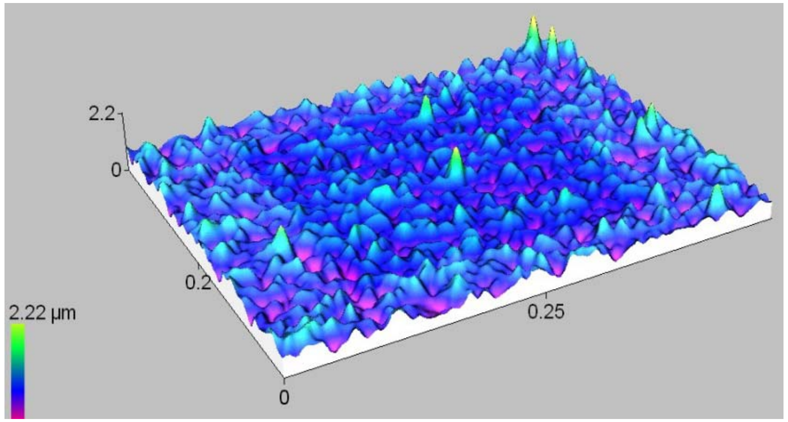


T. Sizun, T. Patois, M. Bouvet*, B. Lakard*, "Microstructured electrodeposited polypyrrole-phthalocyanine hybrid material, from morphology to ammonia sensing", J. Mater. Chem., 22, 25246-25253, **2012**

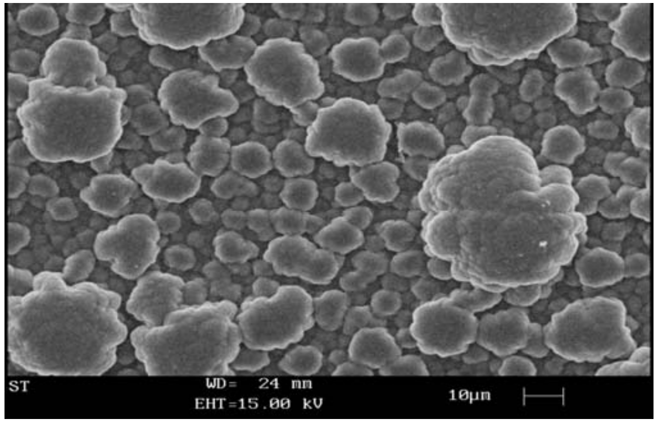
PPy-sCoPc Hybrid materials

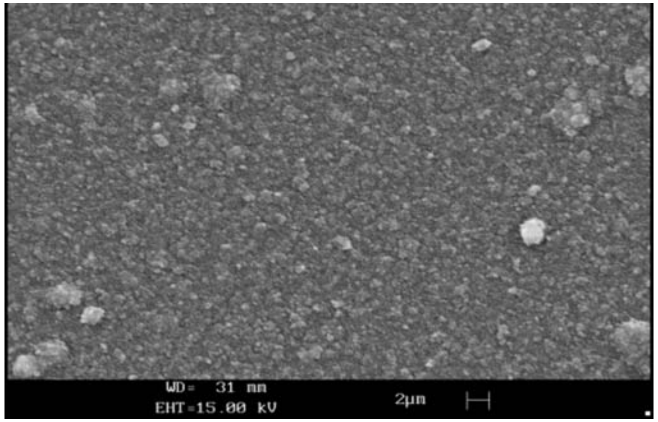
PPy-LiClO$_4$ | **PPy-sCoPc**





Optical topomicroscopy

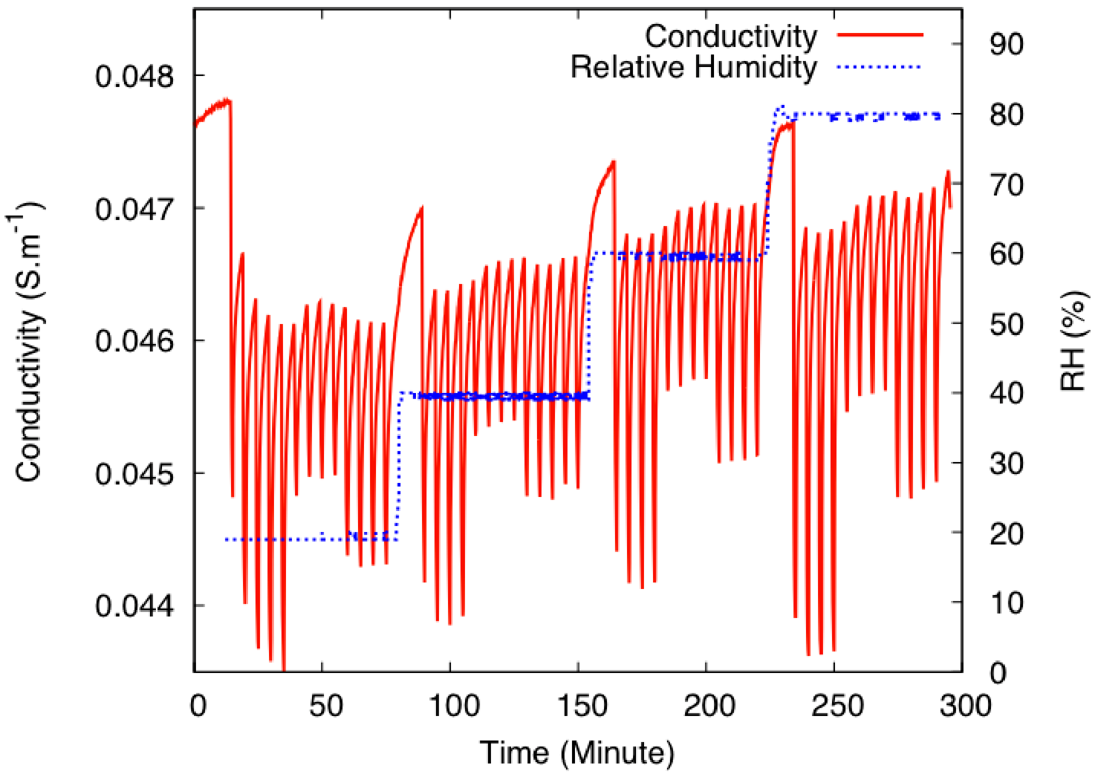




Scanning electron microscopy

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**

Ammonia effect on PPy-sCoPc



Higher sensitivity to NH_3 of the hybrid material, with a weak effect of rh in the 20-80% rh range

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**

Suggested R&I Needs for future research

- **Research directions as R&I NEEDS:**

  - to focus on the **structure and morphology** of sensing materials for a higher stability of the response of sensors (they depend on the processing techniques)

  - to study the compatibility with **humidity** (a key issue in AQM)
  The effect of rh on the response of sensors must be studied, not only at one particular value, but also in a broad rh range
  At RT, 100% rh ≈ 22 000 ppm,
  but 100% rh at 20°C correspond to 73% rh at 25°C.

Acknowlegments

ICMUB, EMMD, Univ. Bourgogne Franche-Comté, Dijon

Dr Thibaut Sizun and Dr Pierre Gaudillat,
Amélie Wannebroucq, Mickael Mateos, Ph. D students,
Dr Abhishek Kumar (Master 3, Delhi University, India)
Dr Rita Meunier-Prest, Dr Jean-Moïse Suisse

France

Prof. Boris Lakard, Dr Cédric Buron and Florian Julin, PhD student,
Univ. Bourgogne de Franche-Comté (Besançon),

Abroad

Dr Vicente Parra, Post-doctorant, DC Wafers then PV Silicon Advisor (Spain)
Prof. Yanli Chen, China University of Petroleum (Qingdao, China)
Dr Inta Muzikante†, Institute of Solid State Physics (Riga, Latvia)
Prof. Naoki Sato, and Dr Richard Murdey, Kyoto University (Japan)

Financial supports:

- The Agence Nationale de la Recherche (ANR)
  CAP-BTX 2010 and OUTSMART 2015
- The Conseil Régional de Bourgogne
- The Heiwa Nakajima Foundation (Japan)

COST Action TD1105