

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

COST Action TD1105

WGs and MC Meeting at LINKOPING, 3 - 5 June 2015

Action Start date: 01/07/2012 - Action End date: 30/06/2016

Year 3: 1 July 2014 - 30 June 2015 (*Ongoing Action*)



Dr. Jérôme BRUNET

French MC Member,

involved in WG2, SIG 1 & 3, STSM

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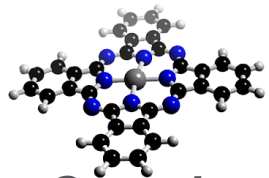
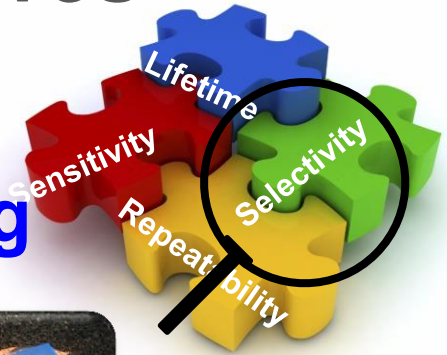
brunet@univ-bpclermont.fr

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Scientific context and objectives

Sensitive and selective sensor-systems for gaseous outdoor pollutants monitoring



Organic



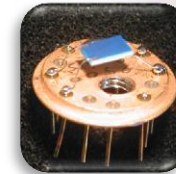
Mineral



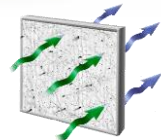
Acoustic



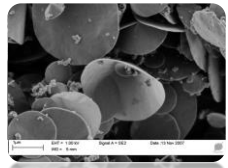
Microwave
(ICB-Dijon)



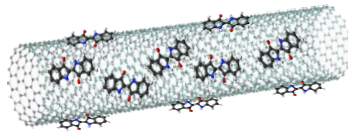
Sensors



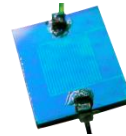
Chemical filters



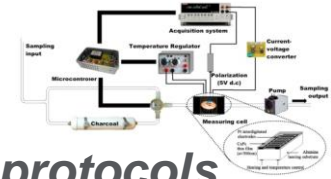
Nanocarbons



Hybrid



Conductimetric



Working protocols

Materials

Transducers

Sensor-systems

- ⇒ Functionalized nanostructures for enhanced gas detection at ppb level, stability and selectivity (WG1 objective)
- ⇒ Relevant sensitive material/transducer association (SIG3 objective)

Skills & expertise

Our team ? **Multidisciplinary !**



System & Microsystem Gas Sensor group



Electronics

1 Professor
1 Associate Professor

Physicist

1 PhD student

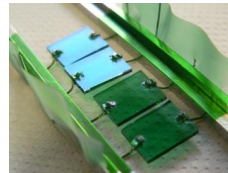
Physical chemist

1 Associate Professor

Chemist

1 Research Engineer

Thin layers realization



Electrical characterizations of semiconductors



Development of electronic units



Sensors & sensor-systems development

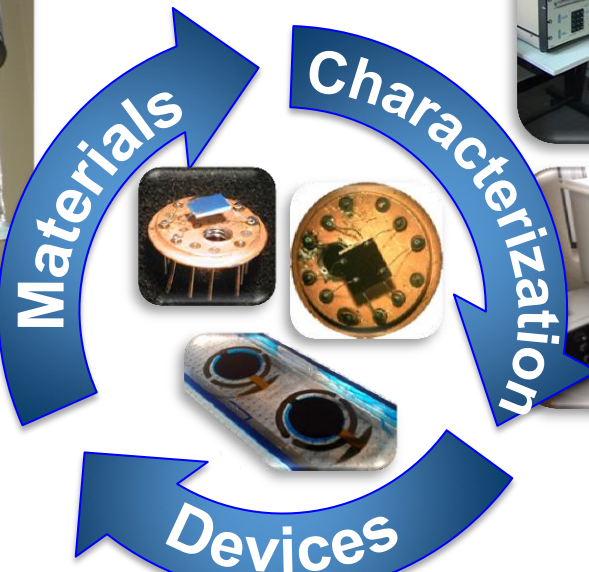


Research facilities for sensor development

Thin film deposition



Electrical measurements



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Measurement of monocyclic hydrocarbons by phthalocyanine-based QCM sensors:

Results and Outlooks

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Societal and scientific context

Outdoor air pollution  **Public health trouble**

2010

223 000 deaths from lung cancer worldwide resulted from air pollution

2012

7 millions premature deaths annually linked to air pollution



World Health Organization

2013

**Outdoor air pollution classified as carcinogenic for humans
at worldwide scale**

2015

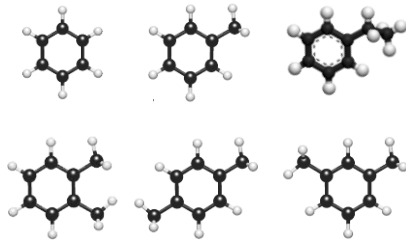
Project call “CANC’AIR”



**Better characterization of air pollutant exposures linked to cancer
Innovative prevention methods**

Special focus on monocyclic hydrocarbons

International Agency for Research on Cancer



Benzene	Group 1	Carcinogenic to humans
Ethyl-benzene	Group 2B	<i>Possibly carcinogenic to humans</i>
Toluene	Group 3	<i>Not classifiable as to its carcinogenicity to humans</i>
Xylenes	Group 3	

Guidelines

	Non-occupational			Occupational
	ATSDR <small>AGENCY FOR TOXIC SUBSTANCES AND DISEASE REGISTRY</small>	EPA <small>ENVIRONMENTAL PROTECTION AGENCY</small>	World Health Organization	OSHA [®]
Benzene	3-6 ppb	9-10 ppb	≈ 1.5 ppb	10 ppm
Ethyl-benzene	0.06-5 ppm	230 ppb	≈ 90 ppb	100 ppm
Toluene	0.08-1.3 ppm	1.3 ppm	≈ 265 ppb	200 ppm
Xylenes	0.05-2 ppm	26.5 ppb	≈ 1 ppm	100 ppm

MRL TWA-8h
RfC
Odor threshold -1/2h
PEL TWA-8h

Ubiquitous pollutants

Daily exposed

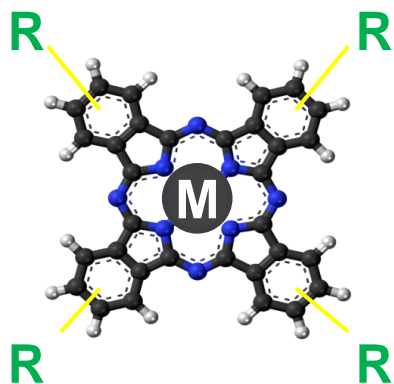


A priority for health prevention



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Scientific approach for sensor development



Metallophthalocyanines

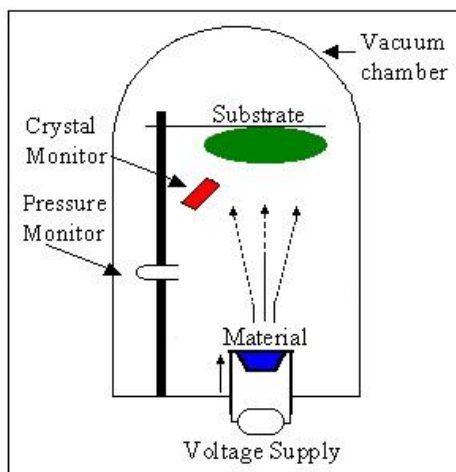
↓
π-electron delocalization High aromaticity Easy functionalization at periphery



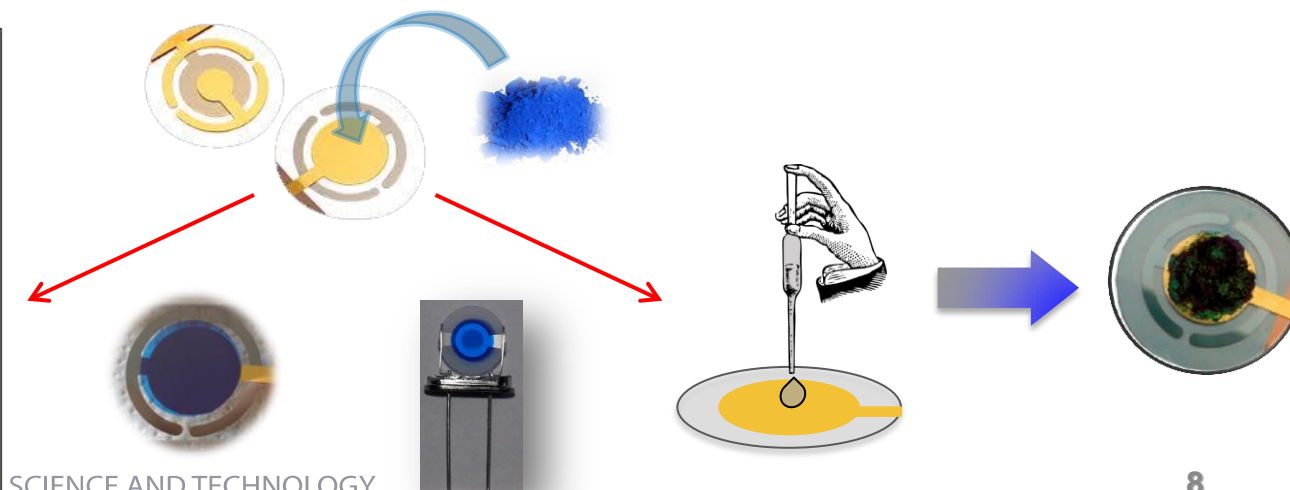
Aromatic properties → pi-stacking interactions with analytes

Processability → Compatible with several transducing modes

Nature of interaction → Quartz Crystal Microbalances

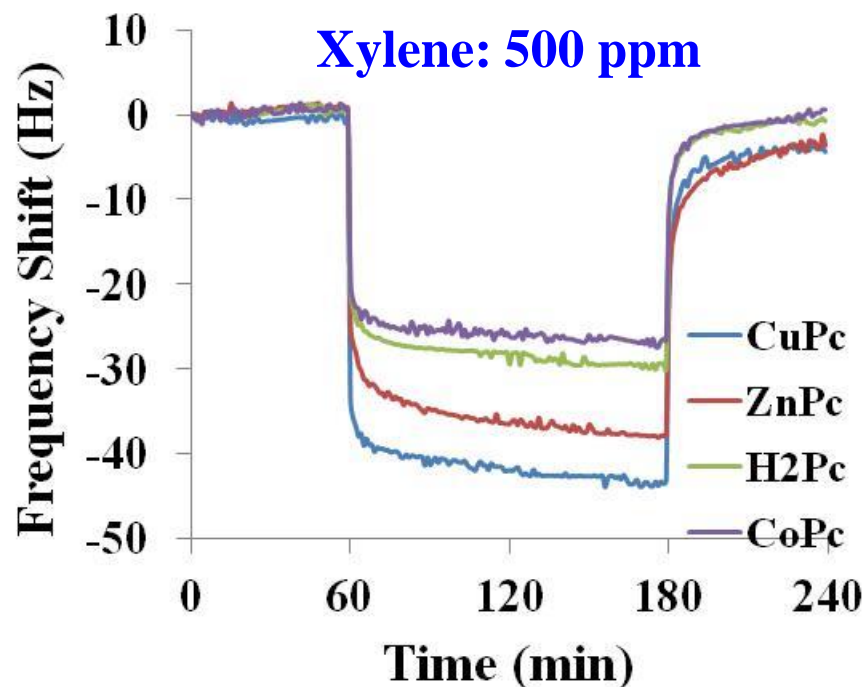
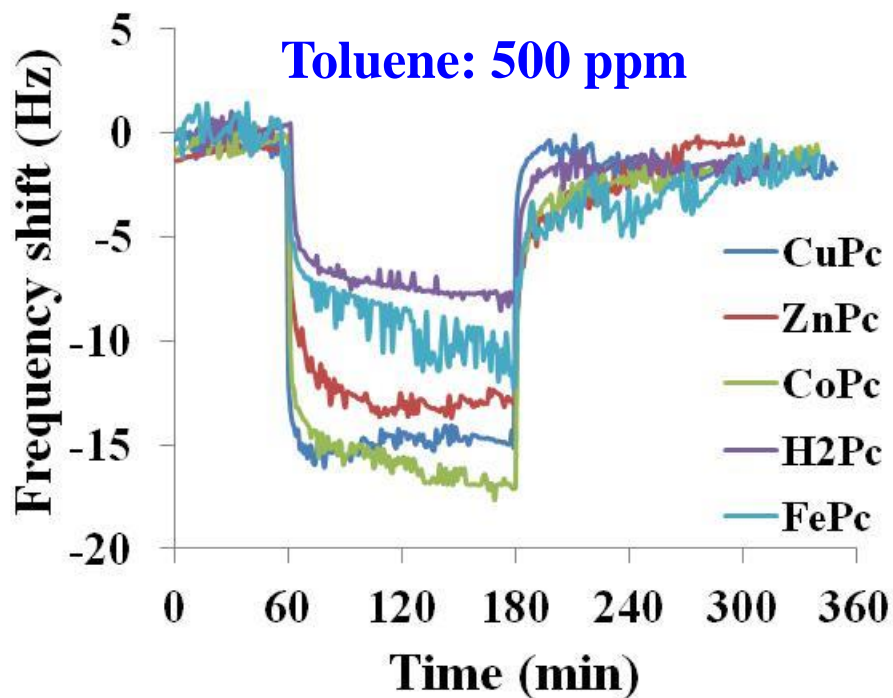


Thermal evaporation



SCIENCE AND TECHNOLOGY

Phthalocyanines: effect of metal



Benzene  Low sensitivity, low signal/noise ratio

Low sensitivity

No significant effect of metal
on sensor response



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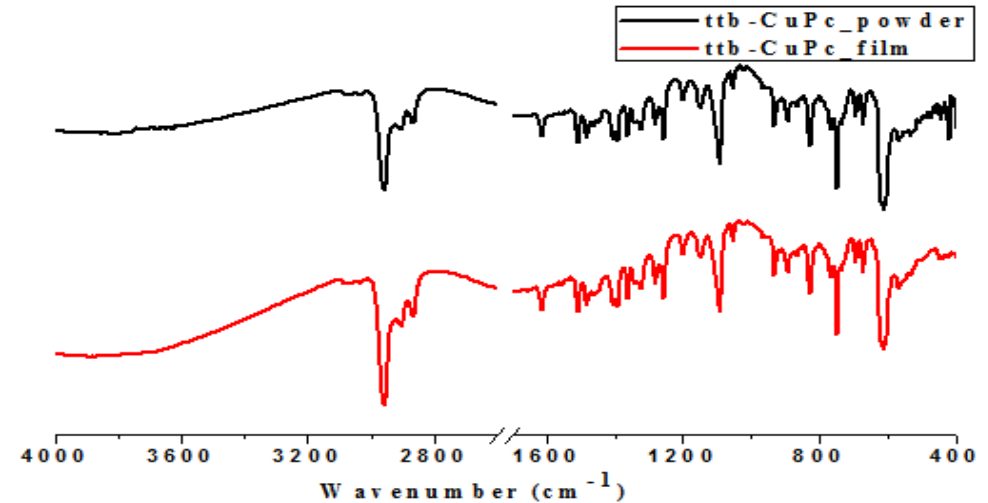
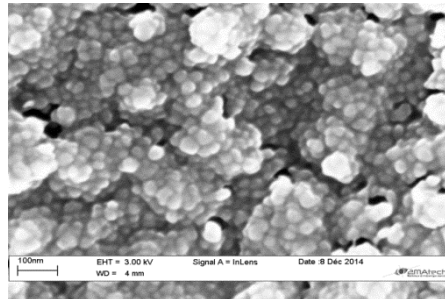
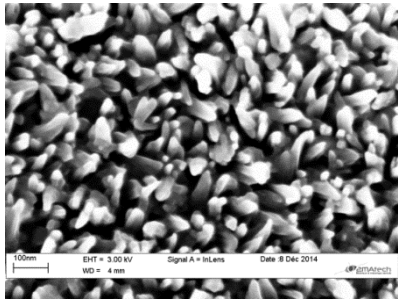
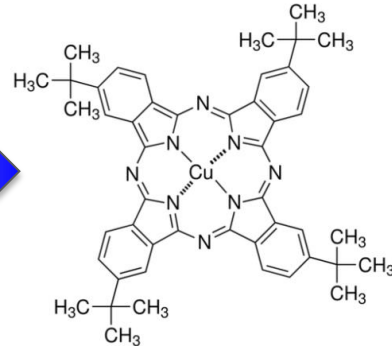
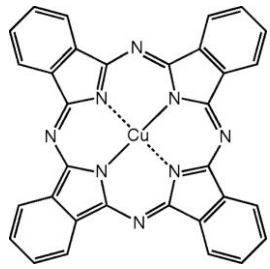


**Electro-donor
peripheral groups**



**pi-stacking interactions
strengthened**

Phthalocyanines: effect of peripheral groups

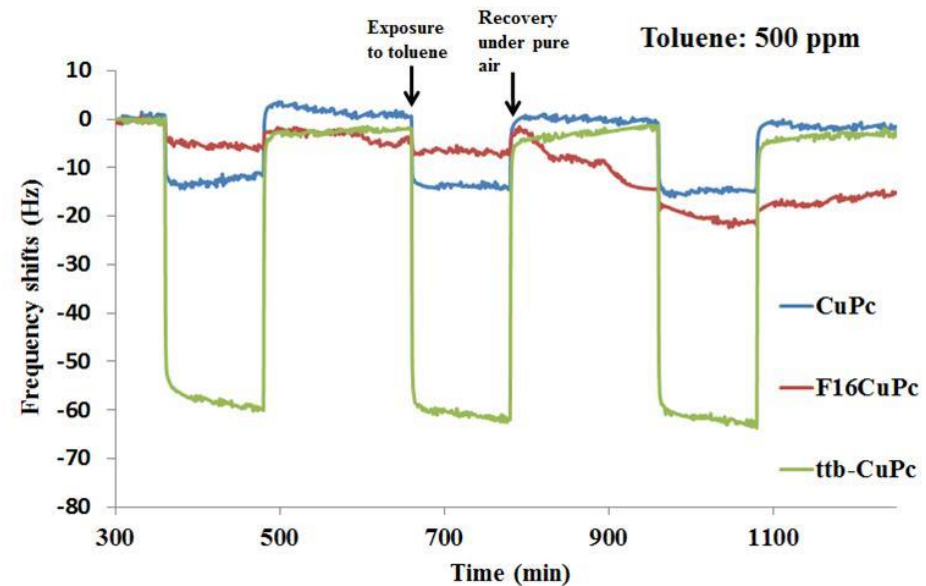


Same results with ttb-ZnPc

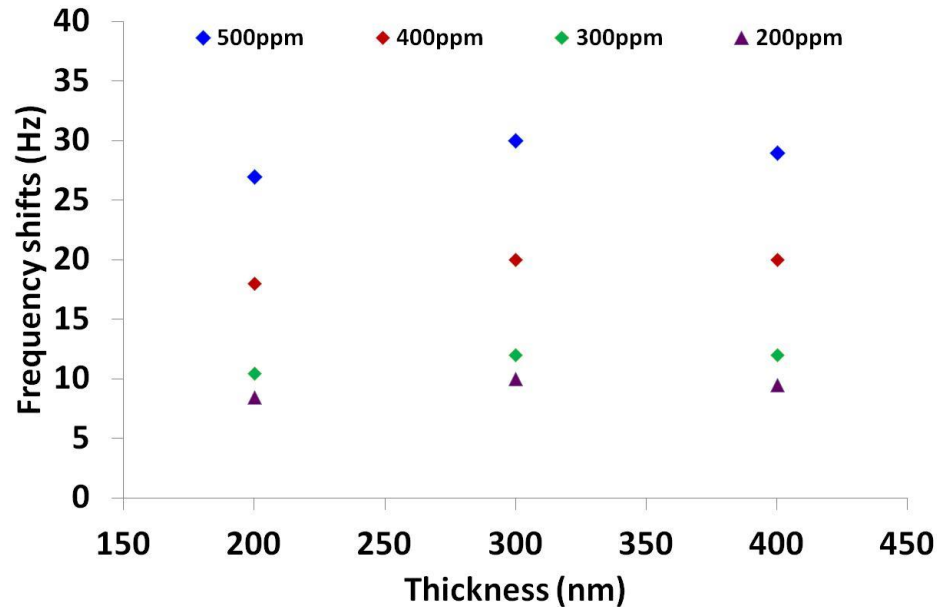
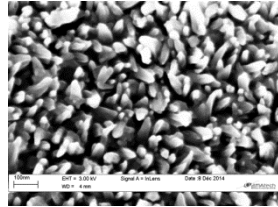
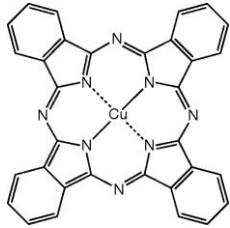
Strong influence of peripheral groups on gas/material interactions



Higher sensitivity to BTX



Effect of layer thickness

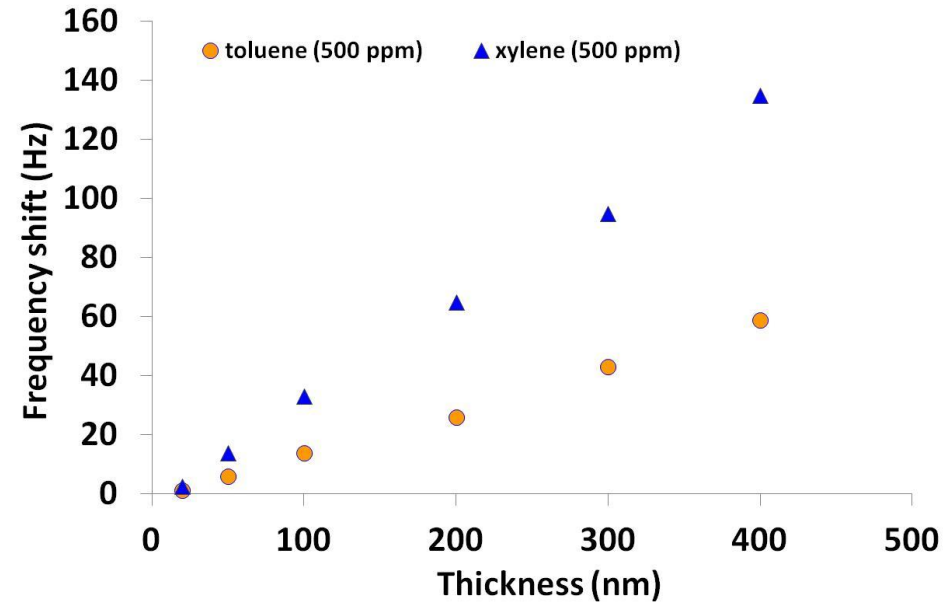
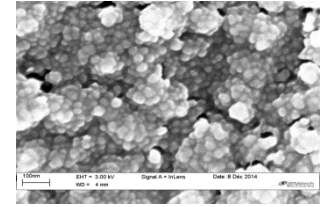
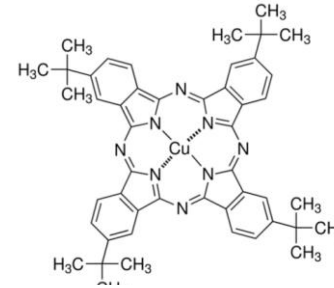


No thickness influence



Adsorption localized

at layer surface
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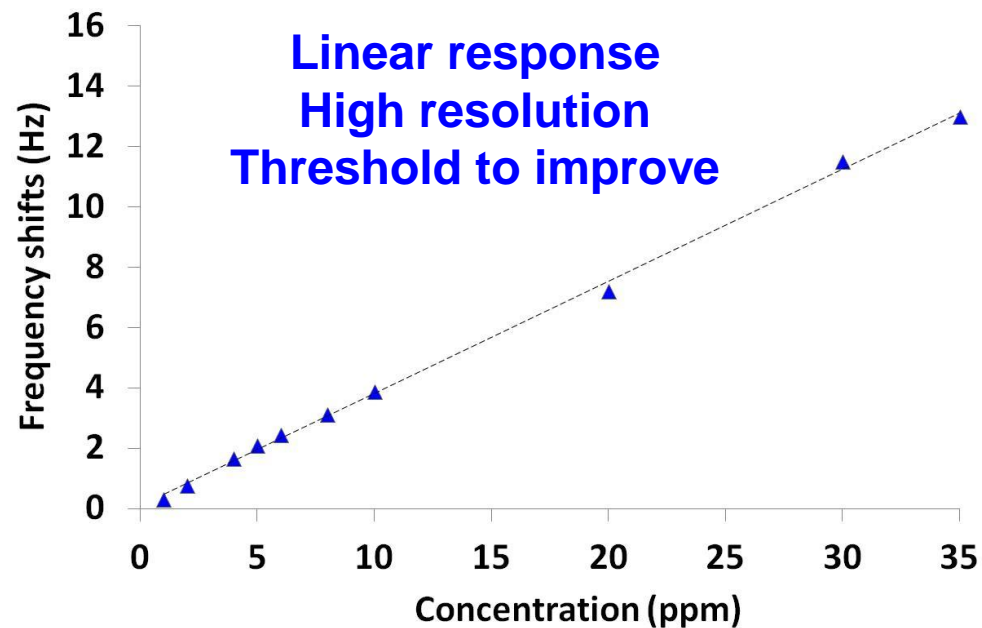
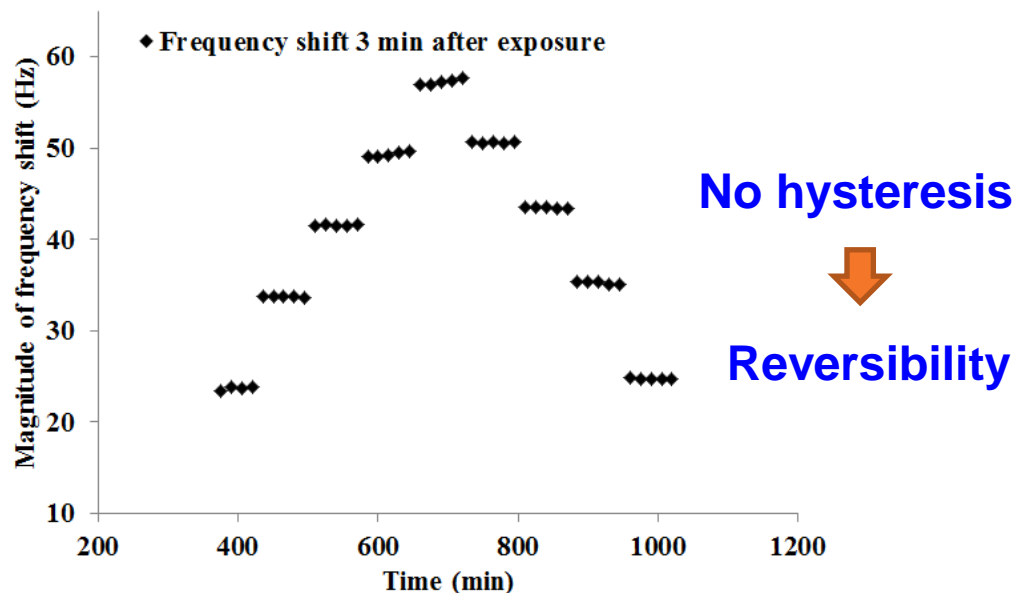
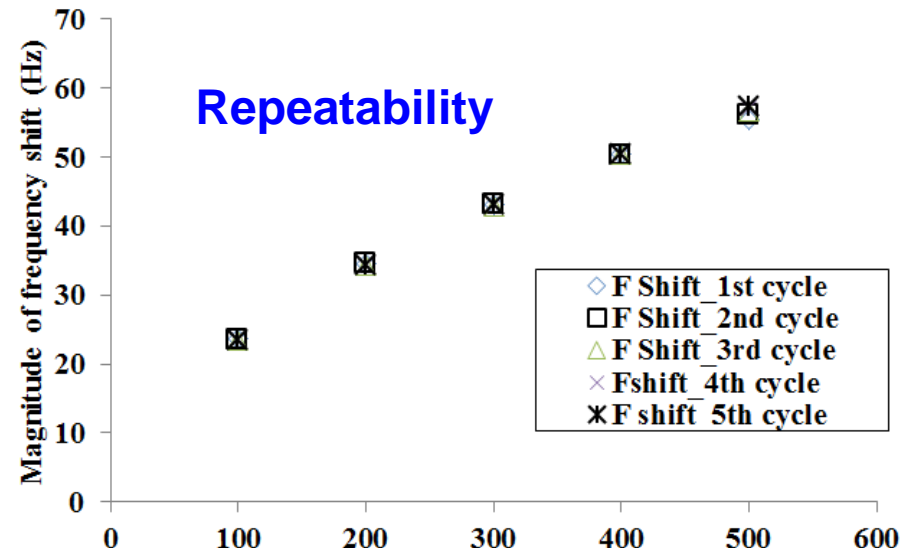
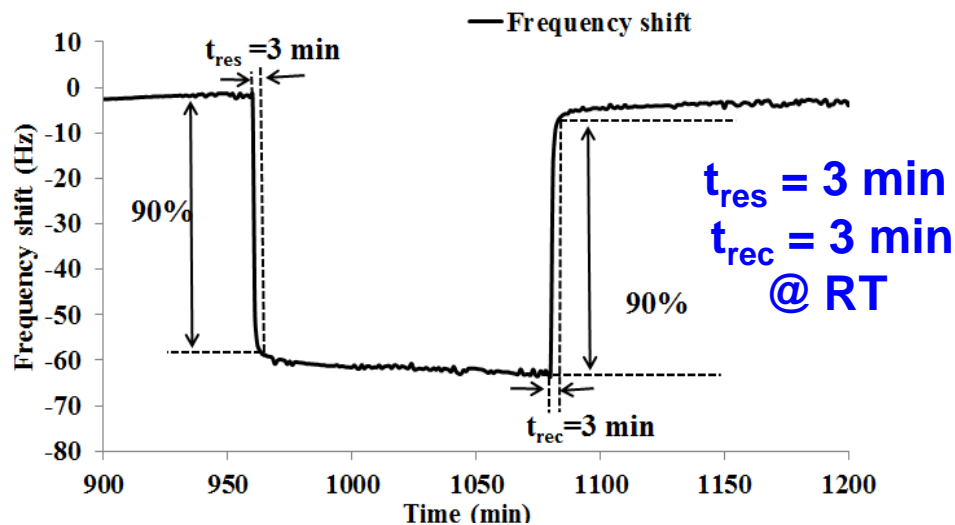


Linear dependence



Interactions distributed
 into the layer volume

Sensing performances



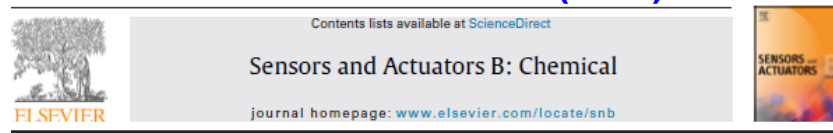
What about the selectivity?

No significant response toward **CO, H₂S and NO₂ !**

Sensor partially selective to **BTX compounds**



Sensors and Actuators B 210 (2015) 398–407



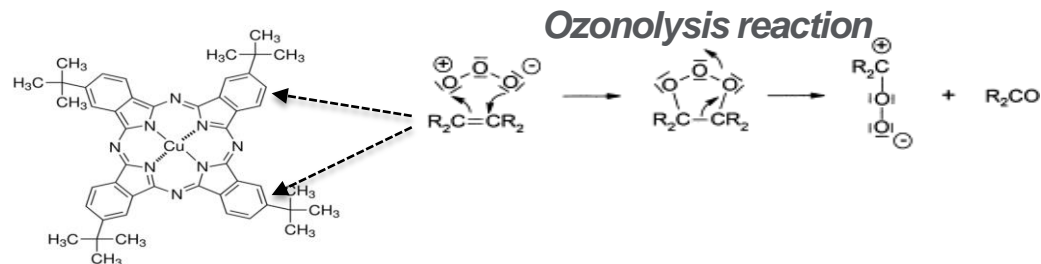
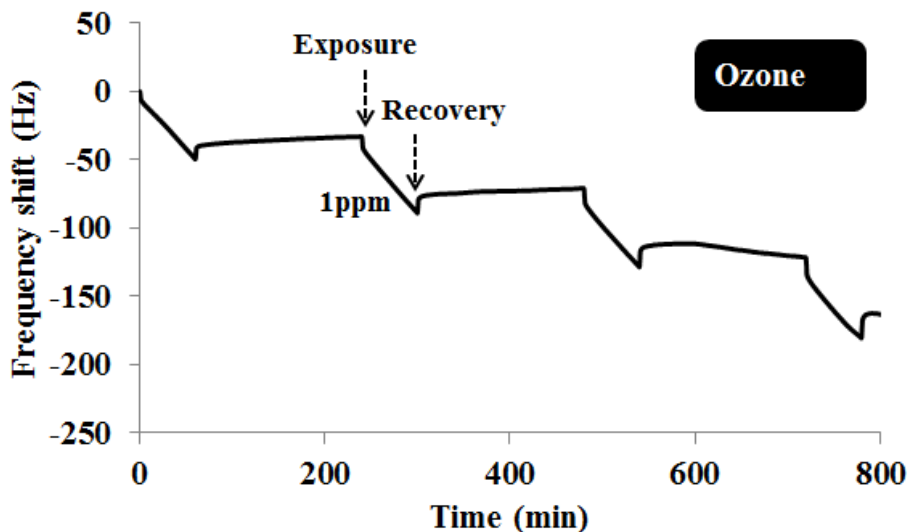
Tetra-tert-butyl copper phthalocyanine-based QCM sensor for toluene detection in air at room temperature

A. Kumar^{a,b,*}, J. Brunet^{a,b}, C. Varenne^{a,b}, A. Ndiaye^{a,b}, A. Pauly^{a,b}, M. Penza^c, M. Alvisi^c

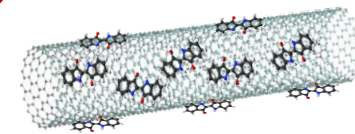
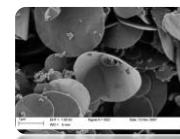
^a Clermont Université, Université Blaise Pascal, Institut Pascal, BP 10448, F-63000 Clermont-Ferrand, France

^b CNRS, UMR 6602, Institut Pascal, F-63171 Aubière, France

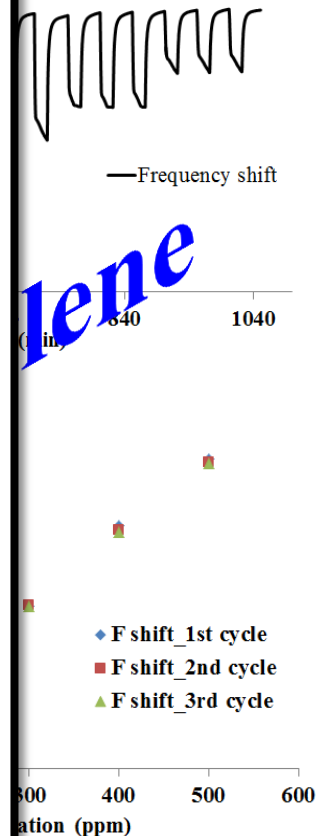
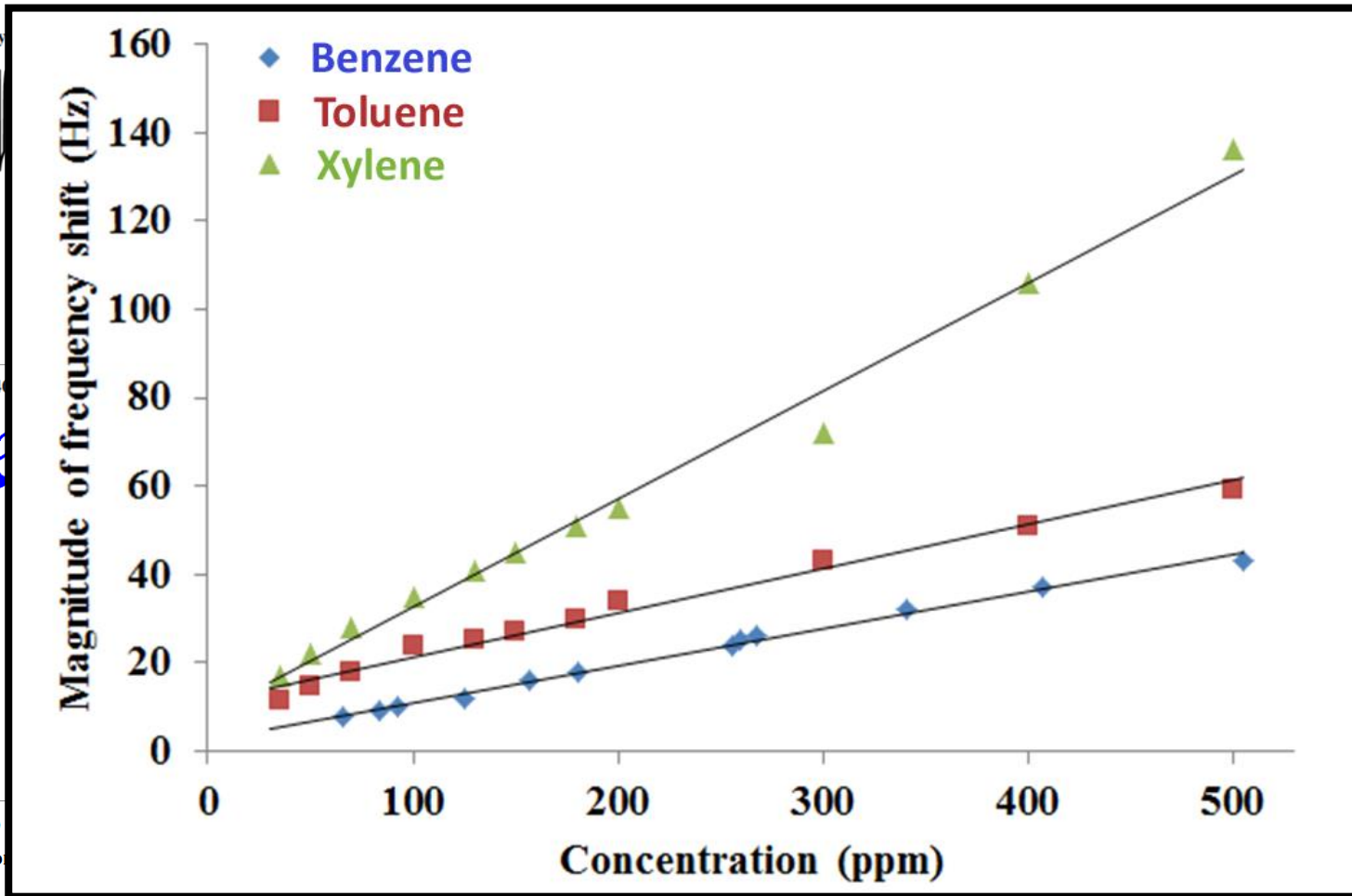
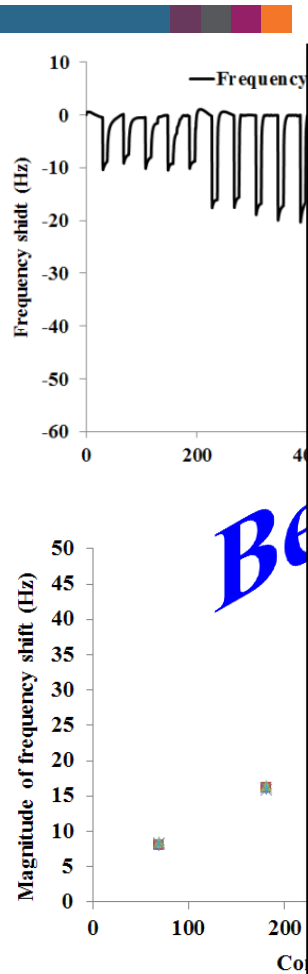
^c ENMA, Brindisi Technical Unit of Technologies for Materials, PO Box 51-Br4, I-72100 Brindisi, Italy



Selective chemical filter for O₃ removal



What about the selectivity?



Challenge ?  Discrimination !

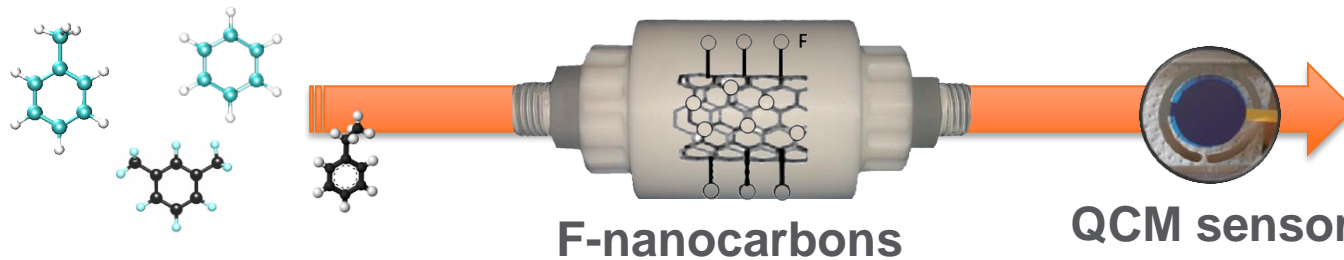
Ongoing research activities

1 Sensor-system for VOCs monitoring

ASTHMAA exploratory project (granted)

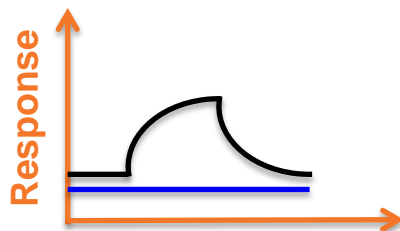


Scientific strategy:

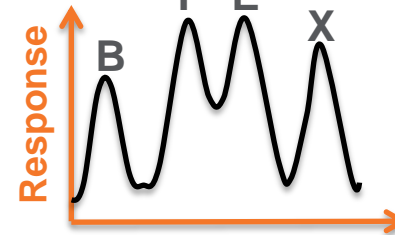
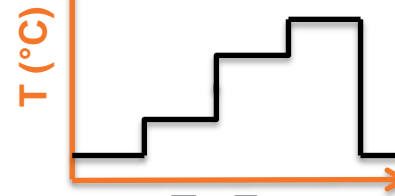


Discriminated responses

Selective filter



TPD

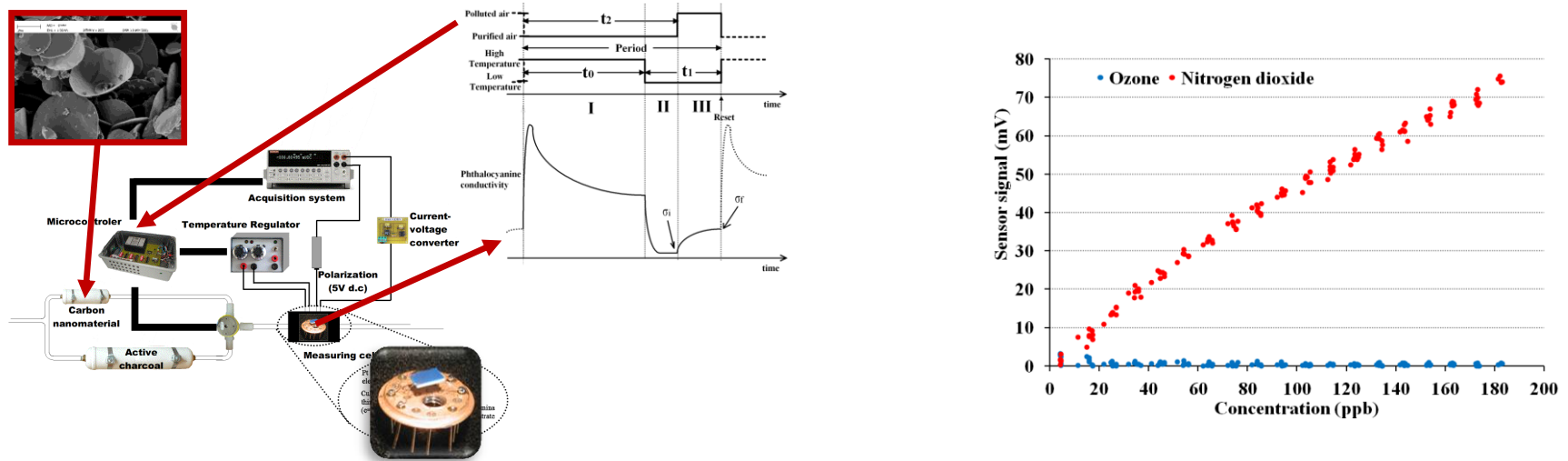


Partners:



Ongoing research activities

② Sensor-system for the selective metrology of NO₂



From patent to...

Use of carbon nanomaterial as a filtration material impervious to O₃

Blaise Pascal University / CNRS

Published as FR2931701, WO2010000956, EP2291230, US2011124112

...transfer of technology



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TRANSFERT DE TECHNOLOGIE



Suggested R&I Needs for future research

R&I needs for sensing devices

- Selectivity, resolution, threshold and stability: high level and in agreement with the target application
- Low-power, low cost and flexible sensors able to be integrated into new technological devices
 - ✓ Integration to mobile phones, clothes or cycles
 - ✓ Citizen contribution to pollution monitoring
 - ✓ Safety working and living conditions
- Environment-friendly materials and technologies
 - ✓ No hazard for environment and health, limited wastes
 - ✓ What about nanomaterials?



Suggested R&I Needs for future research

Innovations in AQC

- Sensor-systems as decision support
 - ✓ Adapted commuting / street air quality
 - ✓ Innovative mobility
- Sensor-systems for real-time personal exposure
 - ✓ Complementary to air monitoring stations
 - ✓ Health prevention
- Making citizens, policymakers and authorities aware of the potential decrease in public health expenses by AQC
 - ✓ Individual actions for health prevention





thank you

