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

COST Action TD1105

WGs & MC Meeting at SOFIA (BG), 16-18 December 2015

New Sensing Technologies for Indoor Air Quality Monitoring: Trends and Challenges

Action Start date: 01/07/2012 - Action End date: 30/04/2016 - Year 4: 1 July 2015 - 30 April 2016

Suitability of QCM coated with ttb-MPc as sensing device for BTEX monitoring at room temperature

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French MC Member,

involved in WG2, SIG 1 & 3, STSM

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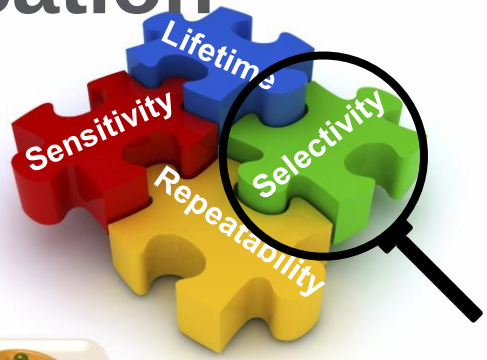
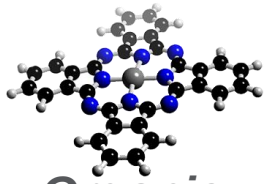
COST is supported by the EU Framework Programme

ESF provides the COST Office through a European Commission contract

Scientific objectives and application

Sensitive and selective sensor-systems for gaseous pollutants monitoring



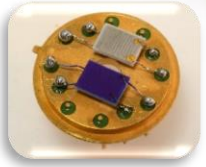


Organic

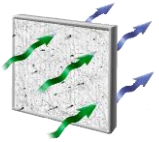
Mineral

Acoustic

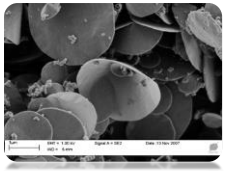
Microwave
(ICB-Dijon)



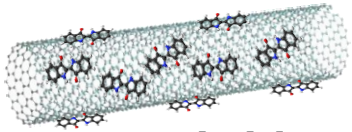
Sensors



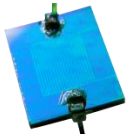
Chemical filters



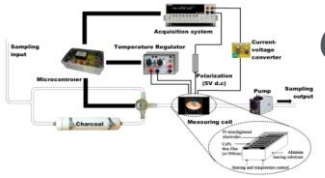
Nanocarbons



Hybrid

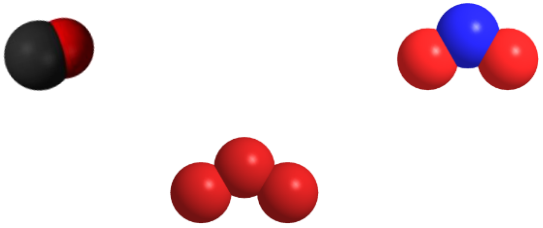


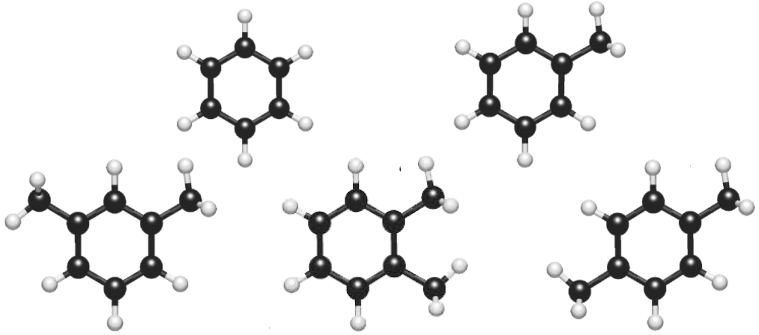
Conductimetric



Working protocols

Target analytes ?





Others…

cost
EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

Special focus on BTX detection

A serious concern for indoor environments

Journal of Environmental Sciences
Volume 20, Issue 9, 2008, Pages 1063–1069

Indoor and outdoor BTX levels in Barcelona City metro… area and Catalan rural areas

E. Gallego[a], F.X. Roca[a], X. Guardino[b], M.G. Rosell[b]

Table 4 Indoor/Outdoor mean rat… …l rural areas

Component	…io	Mean rural areas (±SD)	p-value[a]
Benz…	… ± 1.68	5.95 ± 9.91	0.0001
T…	2.29 ± 3.01	9.26 ± 14.98	0.0001
Su…	3.19 ± 9.40	9.38 ± 13.16	0.0001

[a] Sta… …ical evidence for differences between the distributions and median values was attributed to p-values where $p < 0.05$.

Ubiquitous pollutants

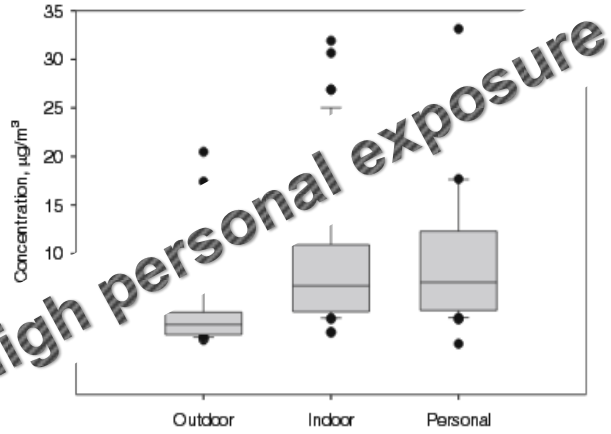
TABLE IV. Children's lifetime cancer risk (LCR) for benzene exposure indoors and outdoors in the different study areas

	Outdoor	Indoor LCR
Industry		2,01E-04
Urban		3,57E-05
Semi-rural	…o	3,50E-05
Residenti…	…9E-06	3,46E-05

Indo… …door Distribution and Risk Asse… …ment of Volatile Organic Compounds in the Atmosphere of Industrial and Urban Areas

Environmental Toxicology DOI 10.1002/tox

Health risks



High personal exposure

Personal, indoor, and outdoor exposure to VOCs in the immediate vicinity of a local airport

Environ Monit Assess (2011) 173:555–567
DOI 10.1007/s10661-010-1404-9

Sensor-systems highly relevant for indoor AQC

2010 2011 2012 2013 2014 2015 2016

CAP-BTX project (ANR)

ENEA Sc. Mission

ASTHMAA project (CNRS)

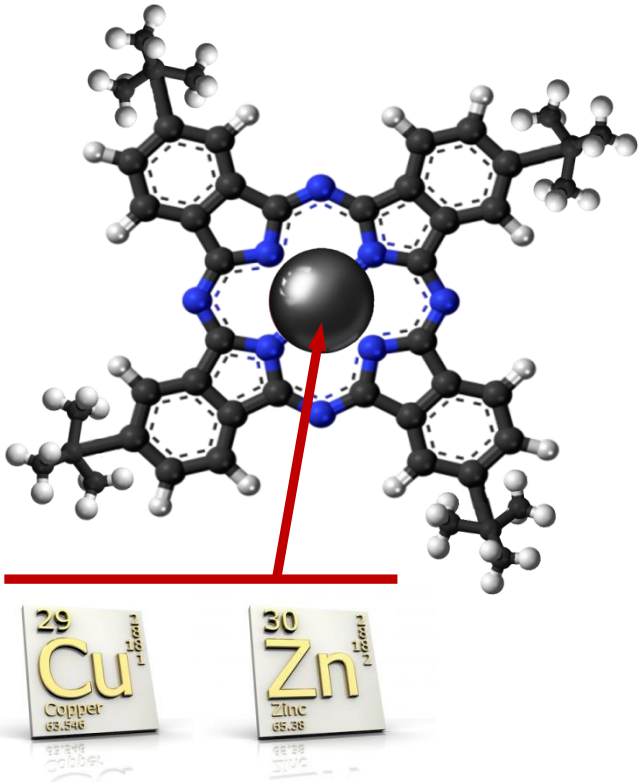
EuNetAir COST Action

ESSC Cluster

Investment on topic?

cost EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

Sensor strategy: sensing material



- Aromatic macromolecules
- High π-electrons delocalization

Aromatic interactions with analytes

Adsorption sites for aromatic gas

Adsorption easily reversible

- Modularity of peripheral groups

Tuning of the sensing properties

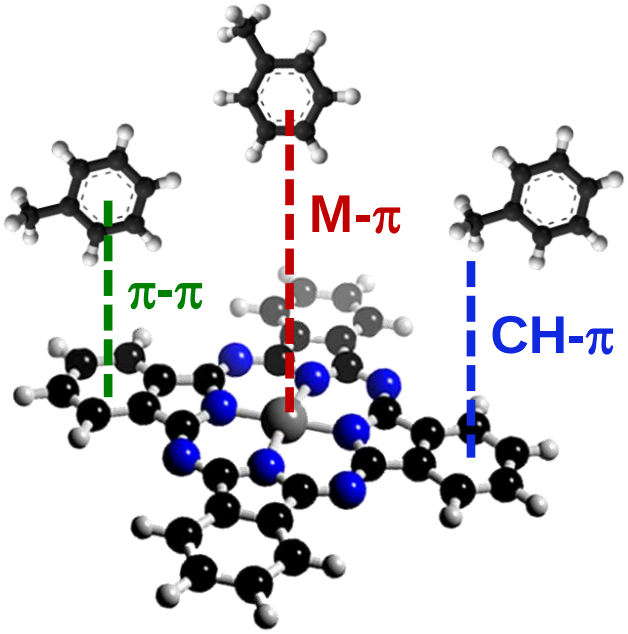
Modulation of sensitivity, selectivity

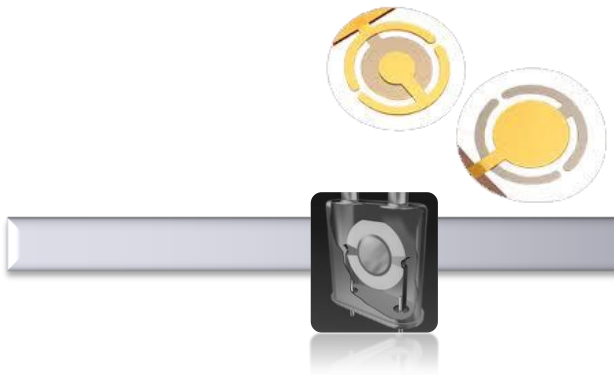
- Peripheral electron-donating groups

Higher solubility

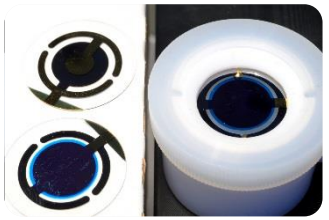
Strengthening of aromatic interactions

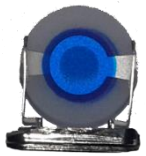
Sensor strategy: transducing mode



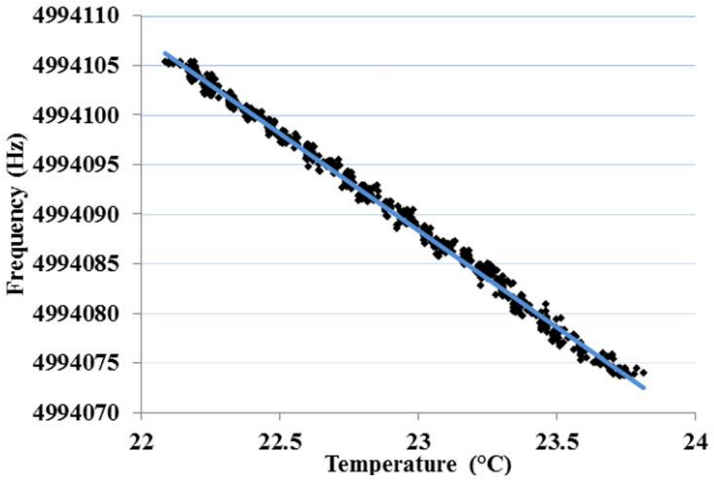


Quartz Crystal Microbalance





Sensing devices



Temperature correction on sensor signal

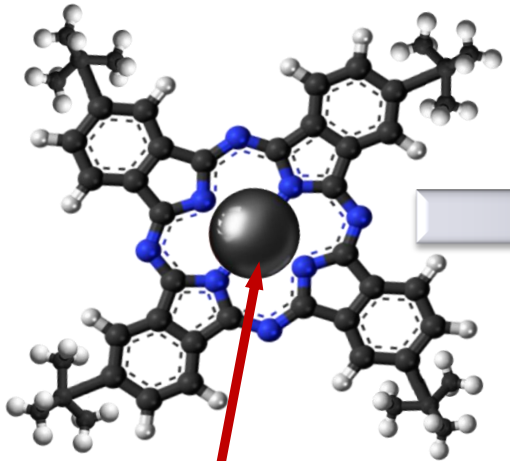
$$F_{corr} = F_{meas} - K \cdot (T_0 - T)$$

K : temperature sensitivity of QCM

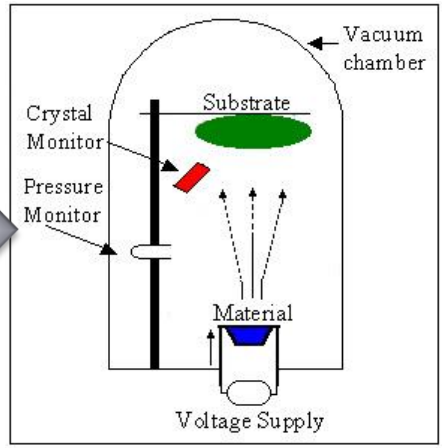
T_0 = 30°C (Zero error)

70% of signal drift removed

Material: coating & characterizations



Thermal evaporation

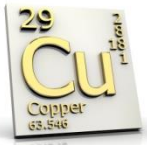


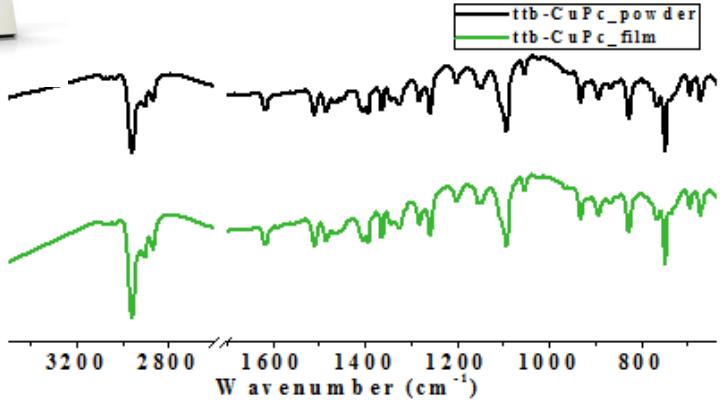
Homogenous layers

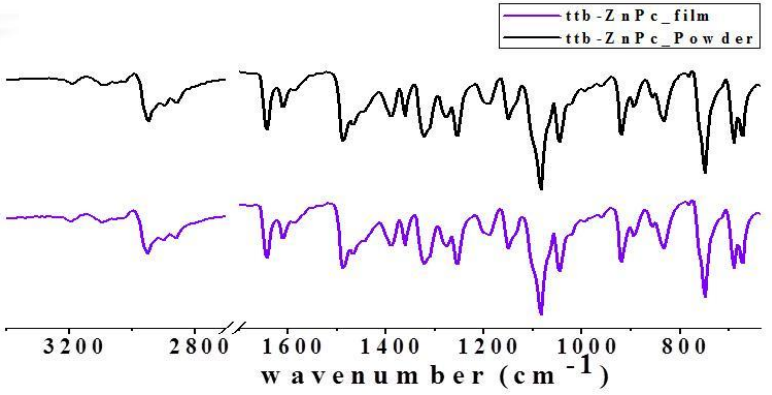
Suitable for non-soluble MPc

Control of thickness and deposition rate

Removal of long-chain groups

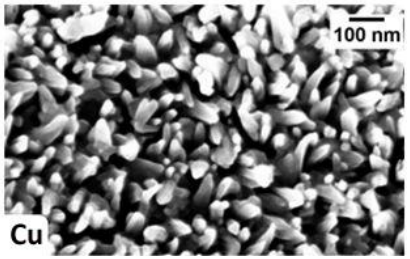


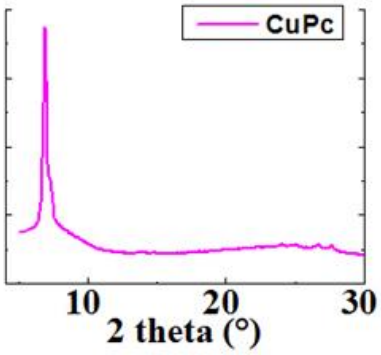




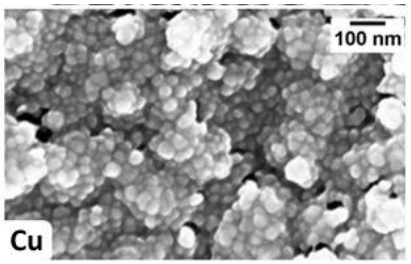
Sensing behaviour: effect of peripheral groups

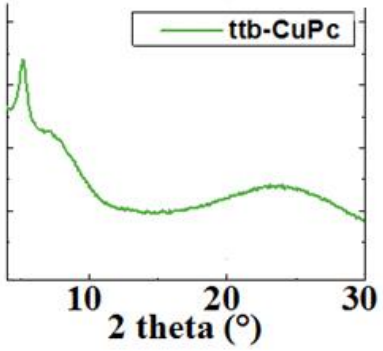
Unsubstituted CuPc



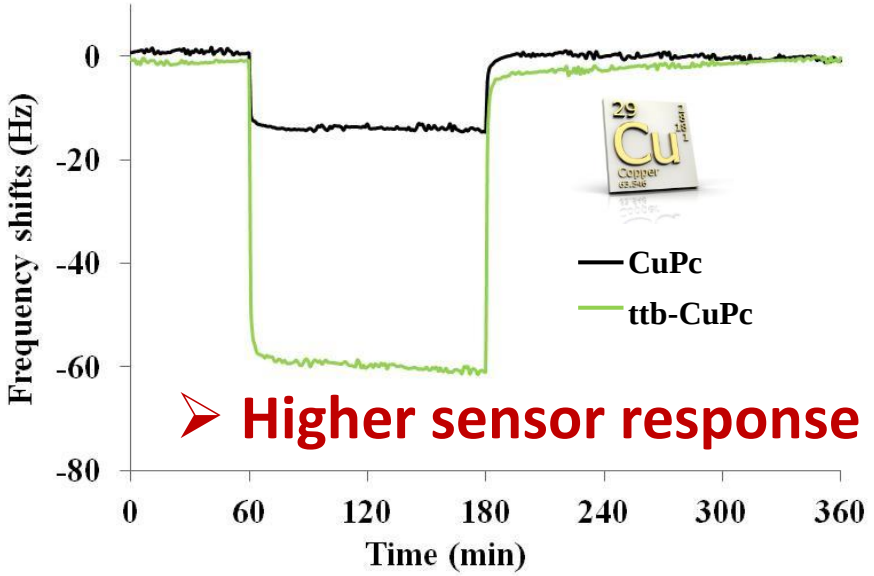


ttb-CuPc

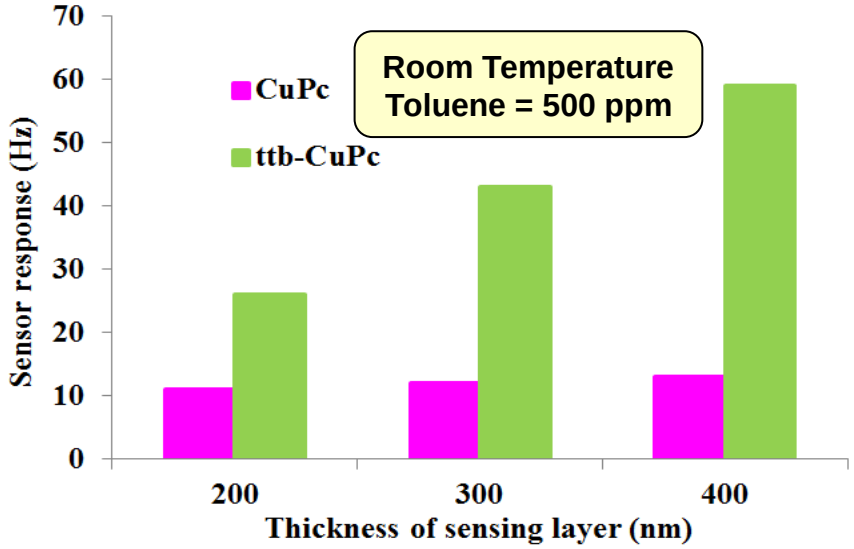




➢ Change on layer morphology

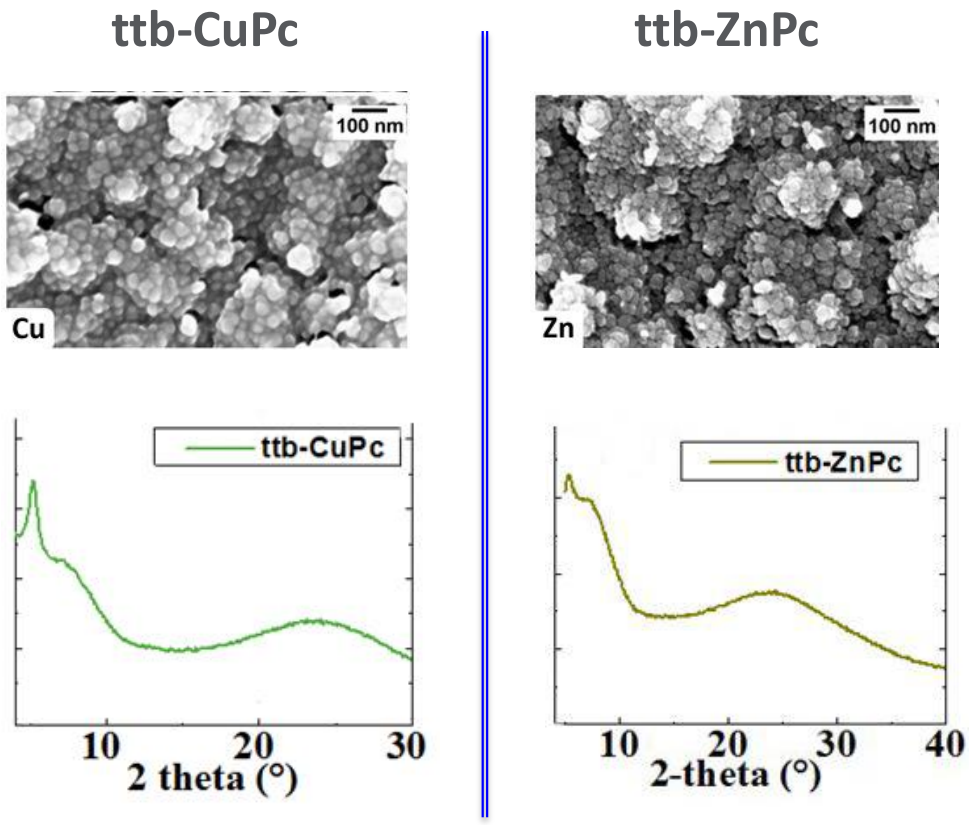


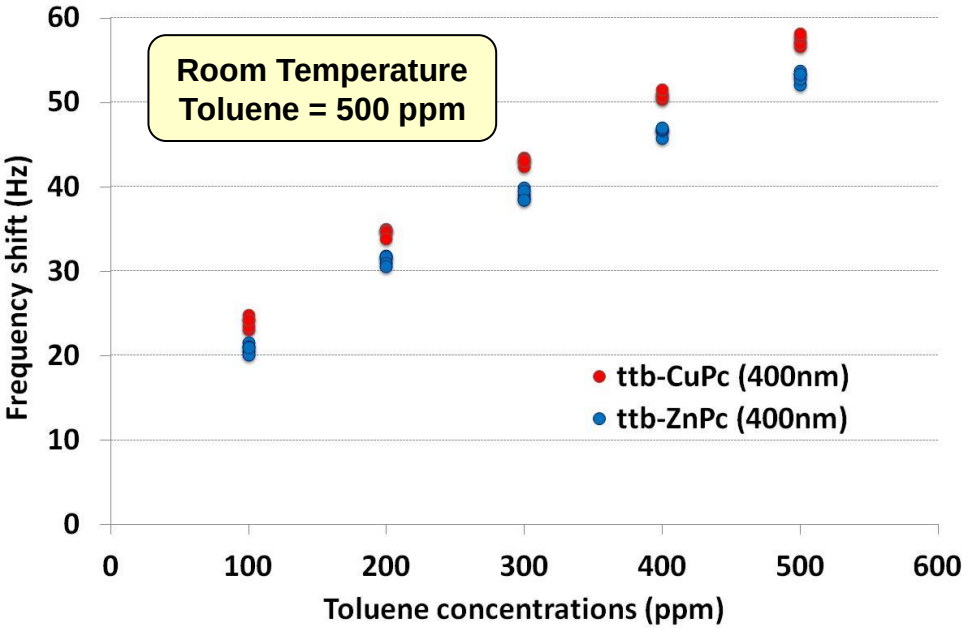
➢ Higher sensor response



➢ Adsorption into the volume

Sensing behaviour: effect of metal





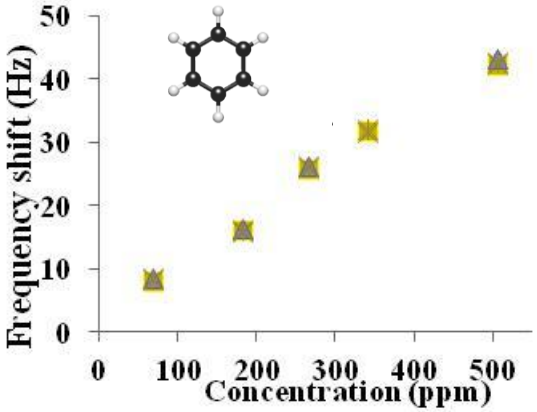
Materials	Frequency shifts / 500 ppm (Hz)	Response time (min)	Recovery time (min)
ttb-CuPc	58	3	3
ttb-ZnPc	53	3	3

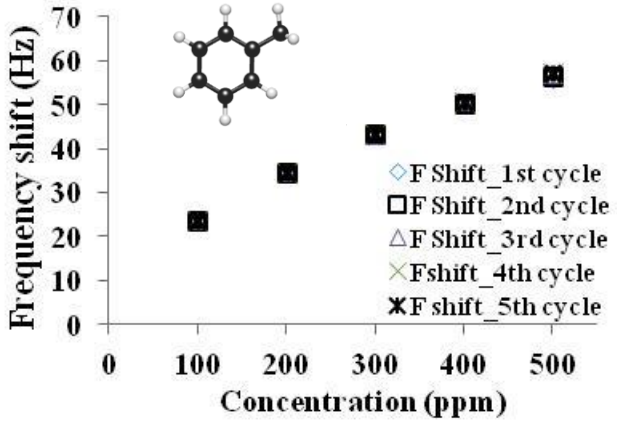
➢ No influence on structural properties

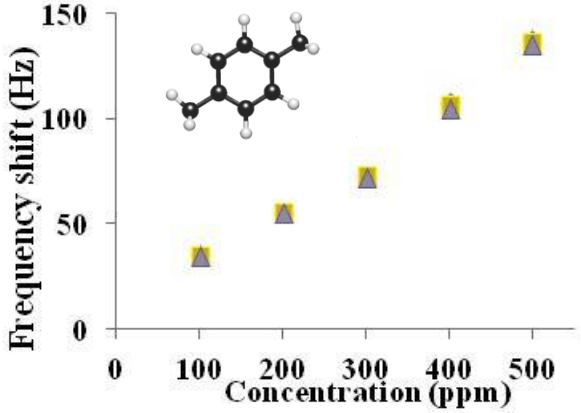
➢ No significant change on sensing characteristics

Performances of ttb-MPc based QCM sensors

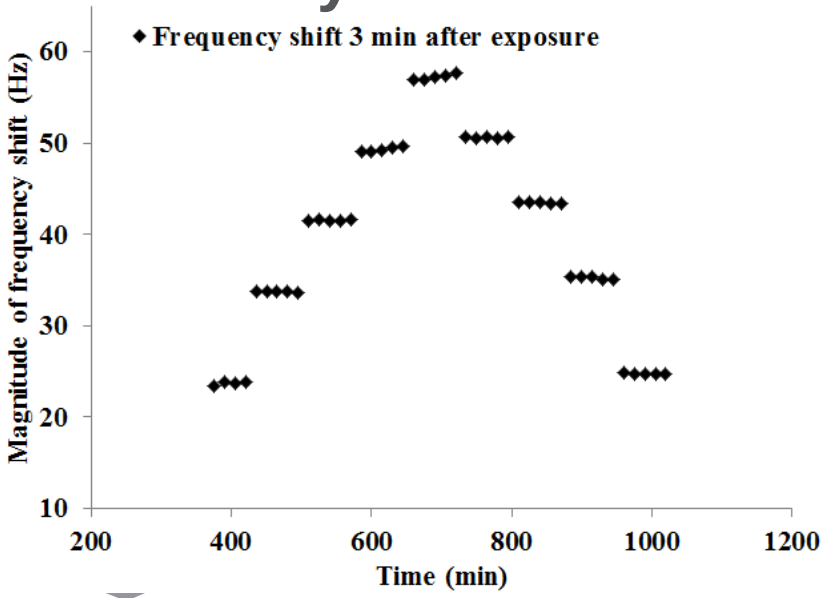
- Repeatability -



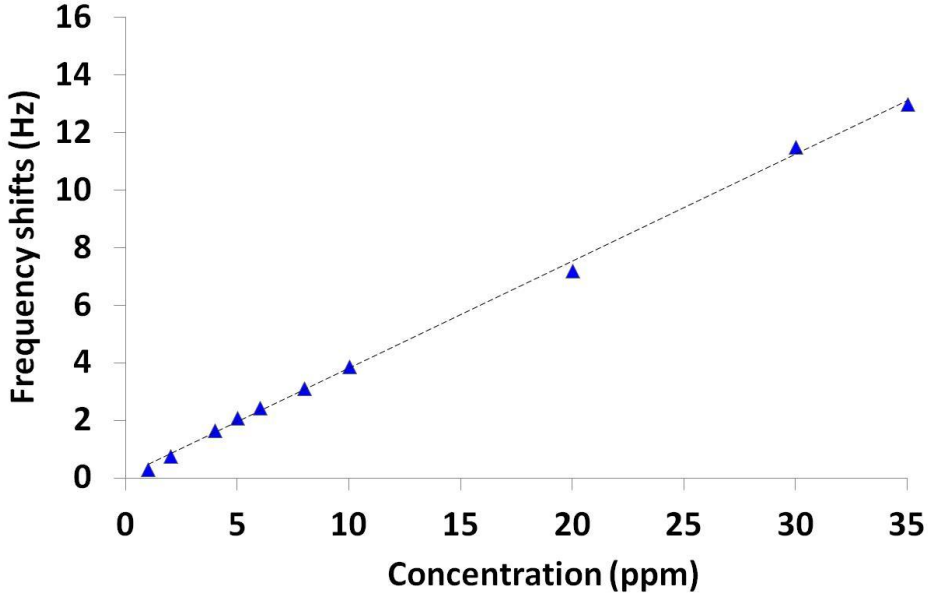




- Hysteresis -

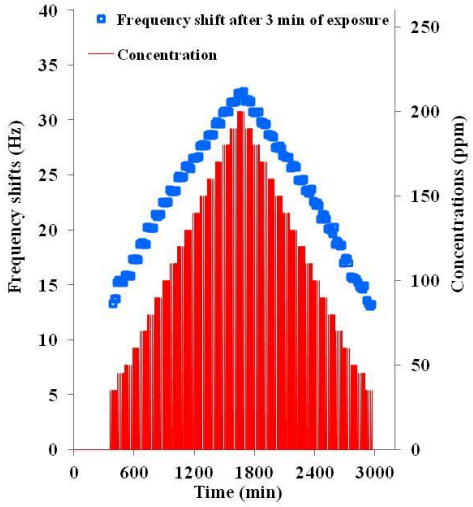


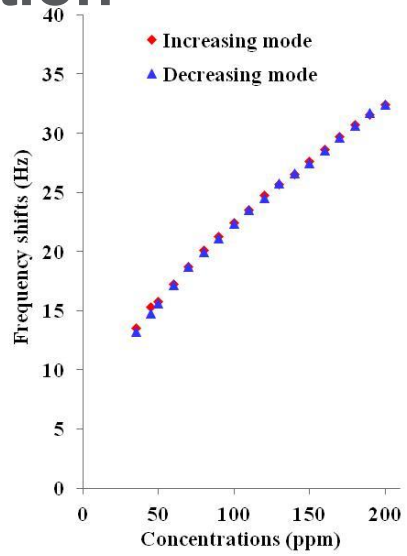
- Linearity -



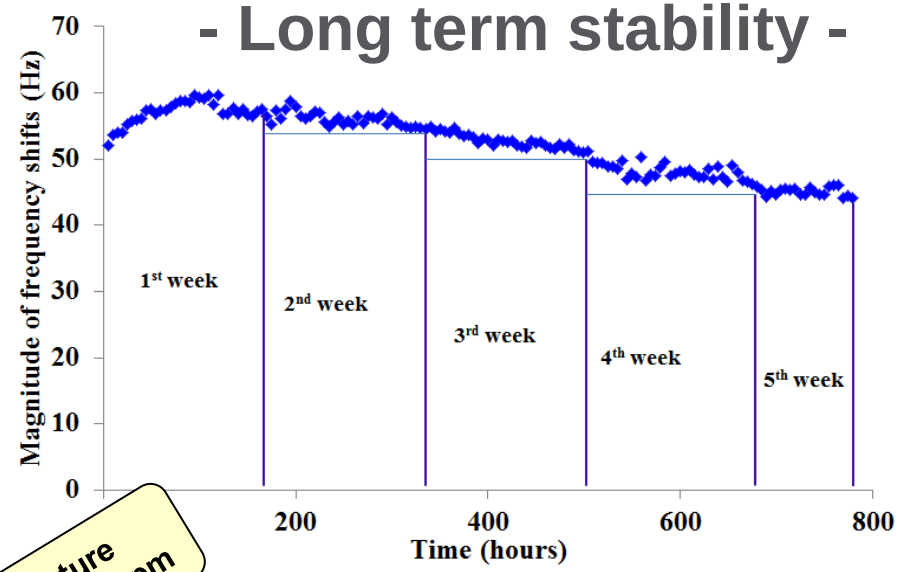
Performances of ttb-MPc based QCM sensors

- Resolution -



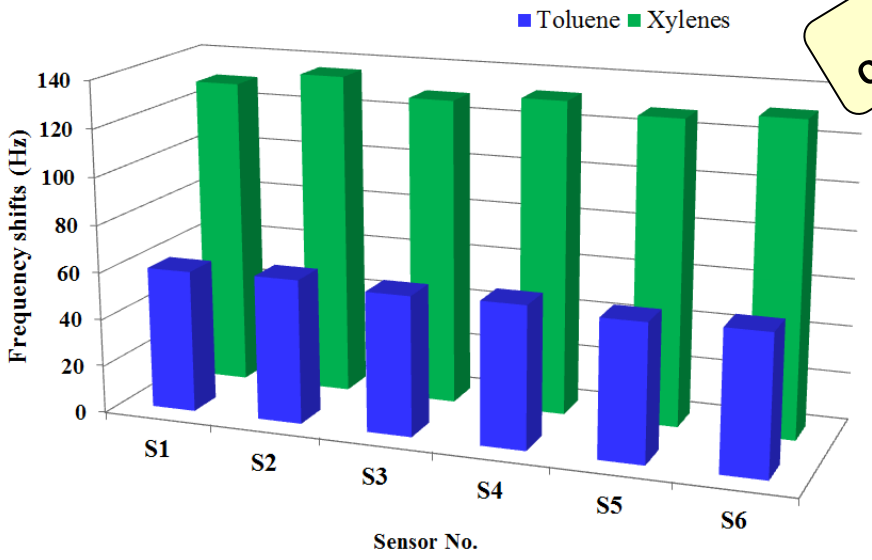


- Long term stability -

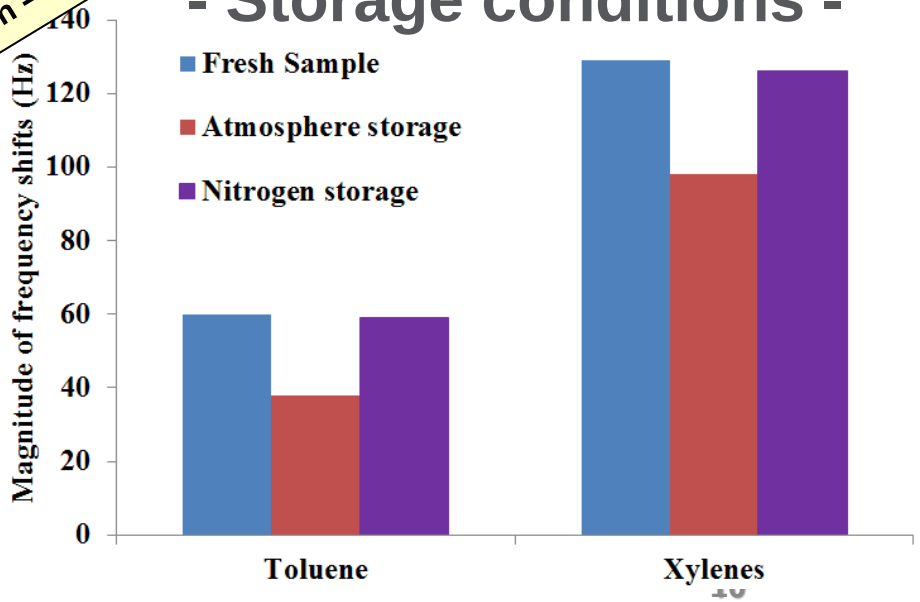


Room Temperature
Concentration = 500 ppm

- Reproducility -



- Storage conditions -



LOGY

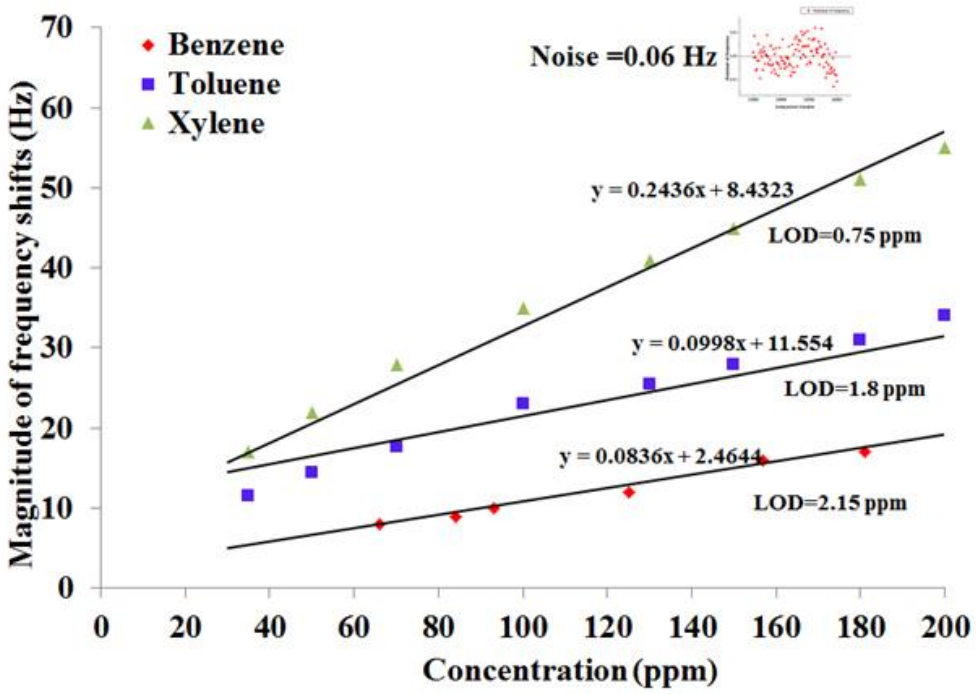
Sensor performances: limits

No significant response toward CO, H_2S and NO_2 !

INSTITUT PASCAL
sciences de l'ingénierie et des systèmes

STSM

ENEA



➢ **Incomplete selectivity**

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Contents lists available at ScienceDirect

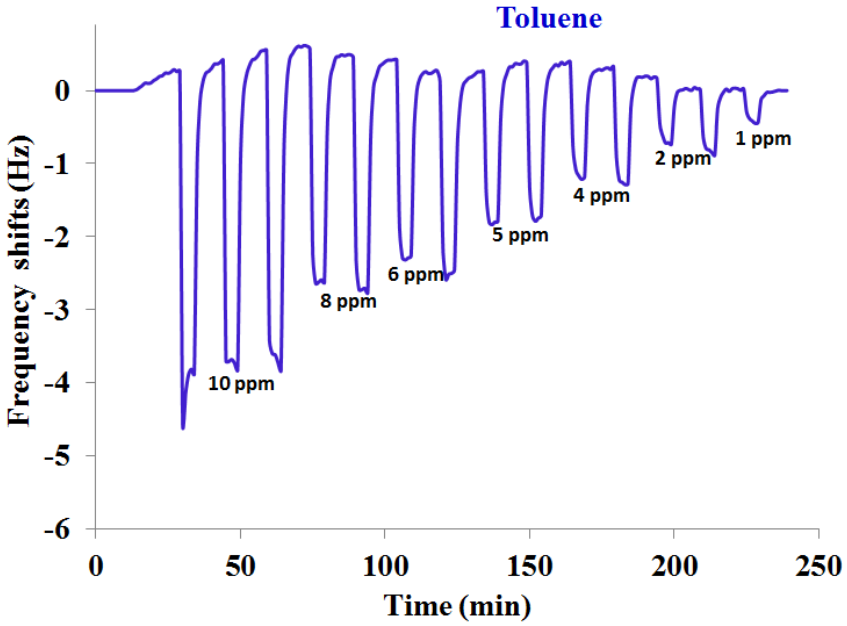
Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

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

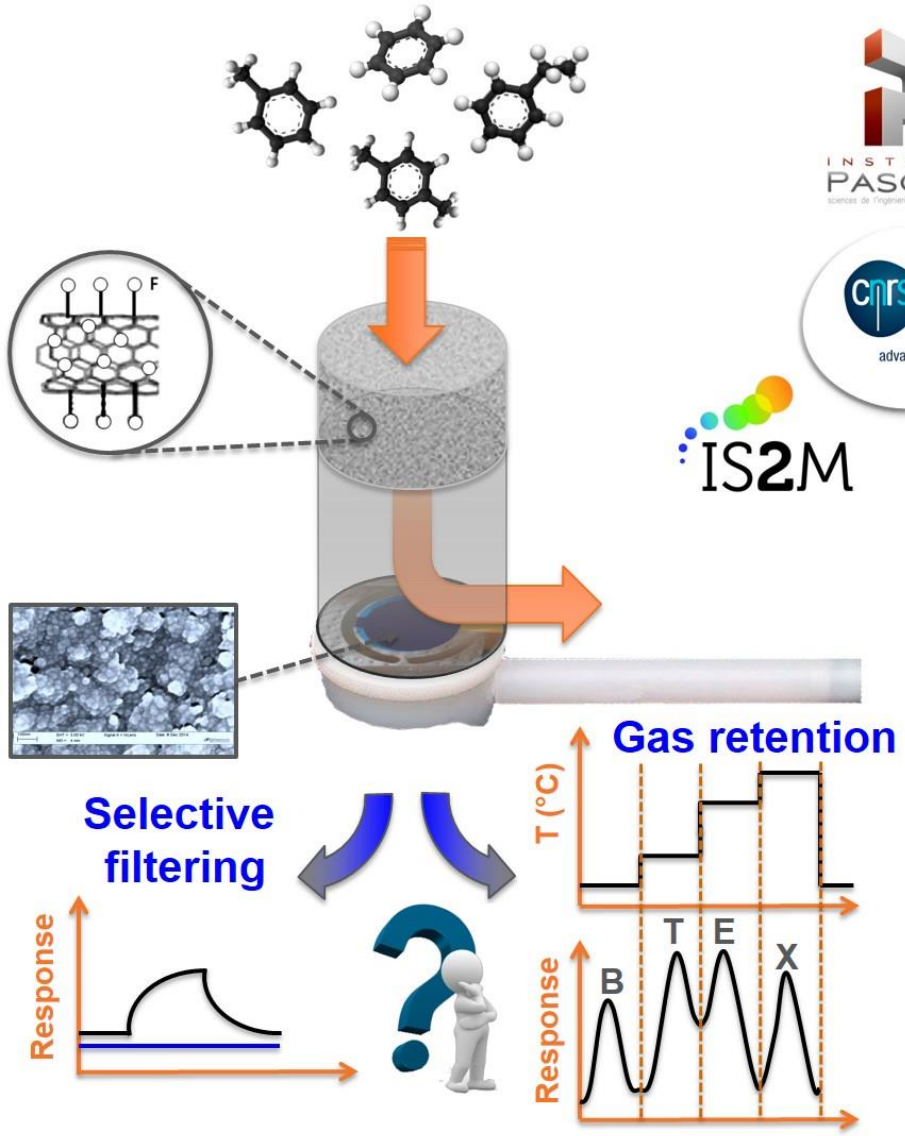
A. Kumar[a,b,*], J. Brunet[a,b], C. Varenne[a,b], A. Ndiaye[a,b], A. Pauly[a,b], M. Penza[c], M. Alvisi[c]

[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] ENEA, Brindisi Technical Unit of Technologies for Materials, PO Box 51-Br4, I-72100 Brindisi, Italy



➢ **Threshold to improve**

ASTHMAA project: objectives & strategy



- **Discriminated measurements of BTEX**
- **Improvement of LOD (preconcentrating effect)**

ASTHMAA project: preliminary results

Investigated nanocarbons

	Material	Origin	SSA (m^2/g)	Vt (cm^3/g)	Vmicro (cm^3/g)	Vmeso (cm^3/g)	Oxygen Groups (mol/g)
Mesoporous Lower SSA	CGL-10	IS2M	720	1.00	0.30	0.70	1.20×10^{-3}
Microporous Higher SSA	CDC	Institut de Chimie de Clermont-Ferrand	2190	0.89	0.66	0.23	1.80×10^{-3}
	CNR-115	Commercial	1880	0.94	0.64	0.30	2.75×10^{-3}

Oxygen groups: - → +

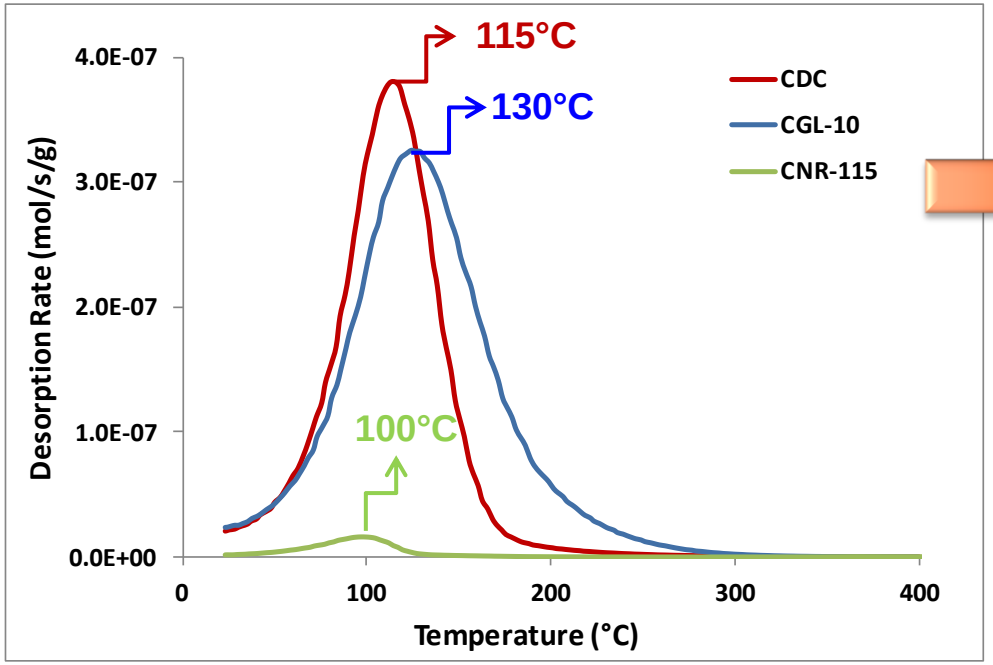
Modulation of surface chemistry → **Treatment by fluorination**

Weakness of adsorption forces → **Lower temperature of desorption**

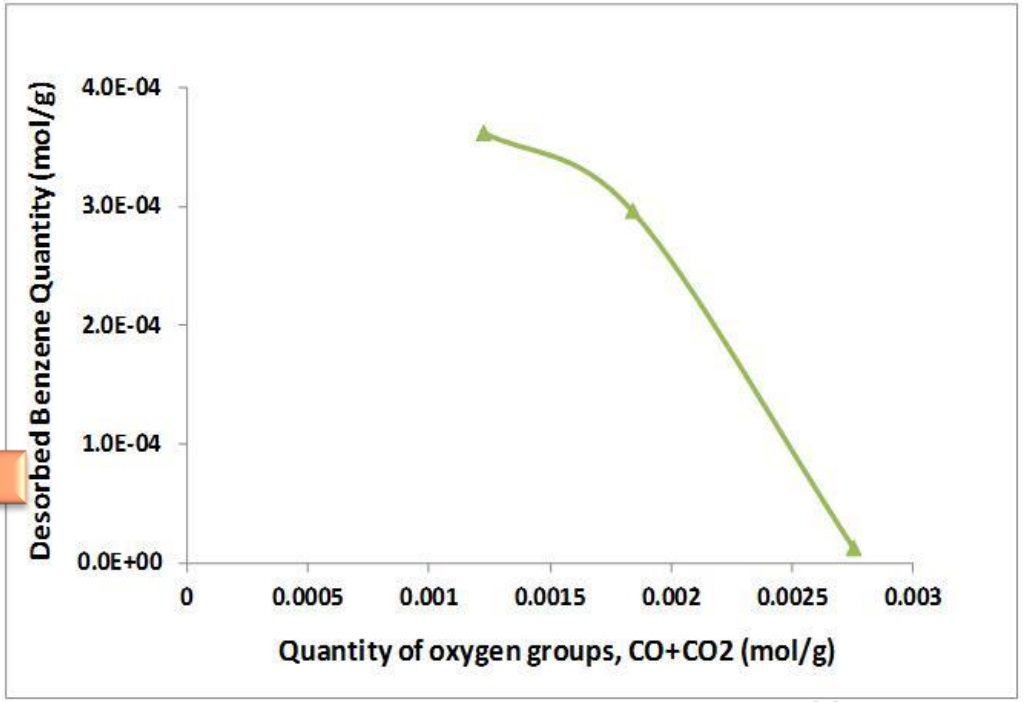
ASTHMAA project: preliminary results

Characterization of benzene adsorption

Temperature Programmed Desorption Mass Spectrometry (TPD-MS)



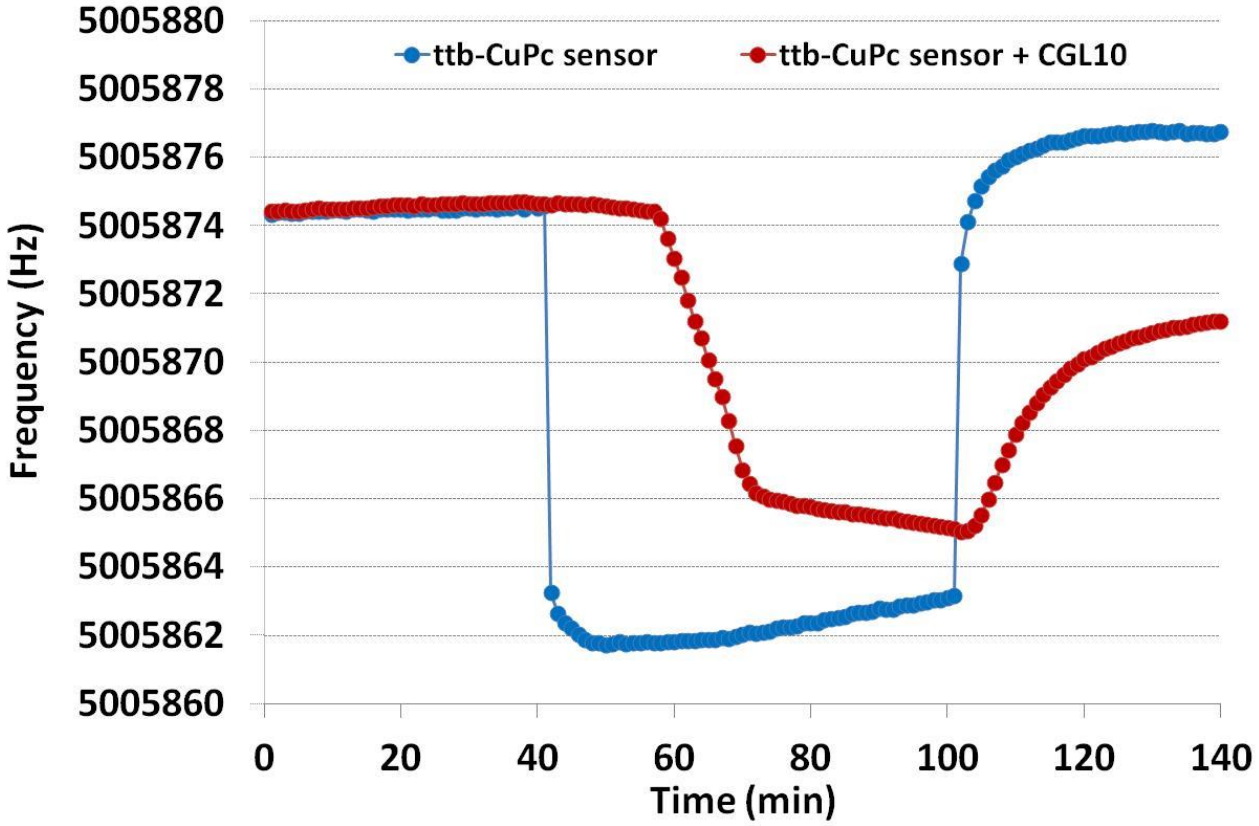
No correlation of adsorption rate with textural properties (SSA, pore size)



Adsorption & desorption temperature correlated with oxygen groups concentration

ASTHMAA project: preliminary results

Response of sensor-system towards benzene



Room Temperature
Concentration = 500 ppm

No response for the lowest concentrations of benzene (< 100 ppm)

Lower kinetics of response and recovery

Delayed response

Material	CGL-10	CDC	CNR-115
Delay (min)	≈ 15	≈ 5	≈ 120

ASTHMAA project: summary

CNR-115 → Lowest desorbed quantity

Lowest desorption temperature

Highest delay of response

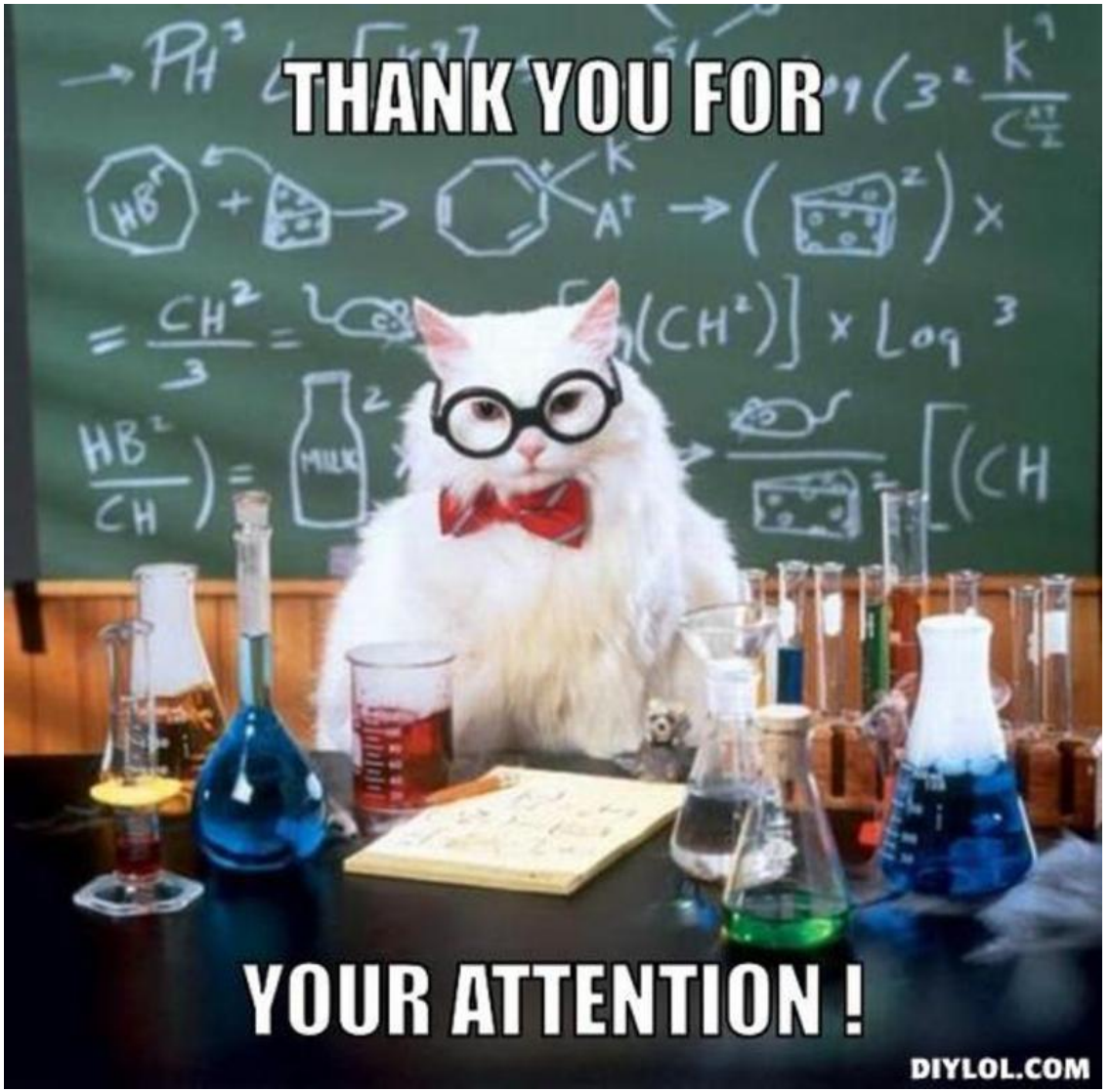
High number of oxygen groups → Weak forces of adsorption → physisorption

CGL-10 → Highest desorbed quantity

Low delay of response

Highest desorption temperature

Low number of oxygen groups → Strong forces of adsorption → Strongest physisorption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