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

Hybrid materials for the development of acoustic wave chemical sensors dedicated to BTEX detection

Dr. Jérôme BRUNET

French MC Member,

involved in WG2, SIG 1 & 3, STSM

Institut Pascal – University Blaise Pascal

Clermont-Ferrand - FRANCE

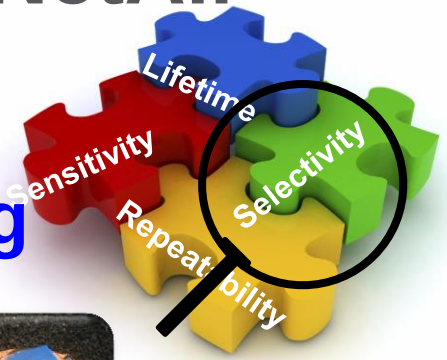
brunet@univ-bpclermont.fr

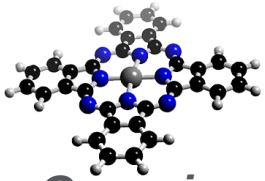
COST is supported by the EU Framework Programme

ESF provides the COST Office through a European Commission contract

Scientific activities linked to EuNetAir

Sensitive and selective sensor-systems for gaseous outdoor pollutants monitoring





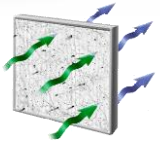
Organic

Mineral

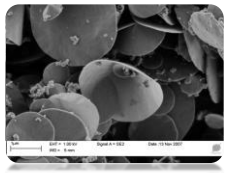
Acoustic

Microwave
(ICB-Dijon)

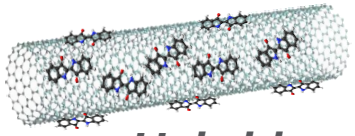
Sensors



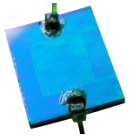
Chemical filters



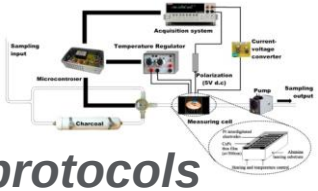
Nanocarbons



Hybrid



Conductimetric



Working protocols

Materials **Transducers** **Sensor-systems**

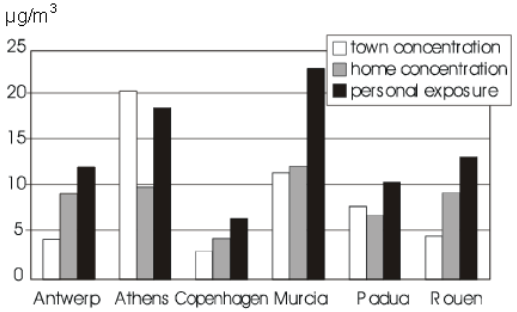
⇨ Functionalized nanostructures for enhanced gas detection at ppb level, stability and selectivity (**WG1 objective**)

⇨ Relevant sensitive material/transducer association (**SIG3 objective**)

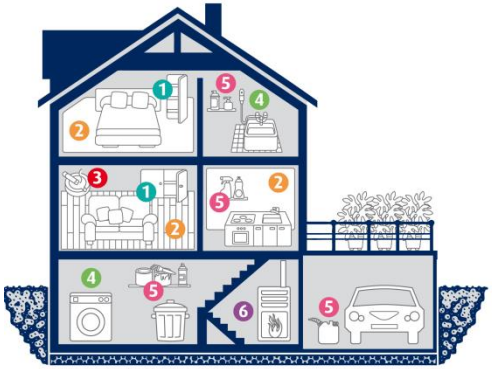
Involved in WG2, SIG1, SIG3 and STSM committee

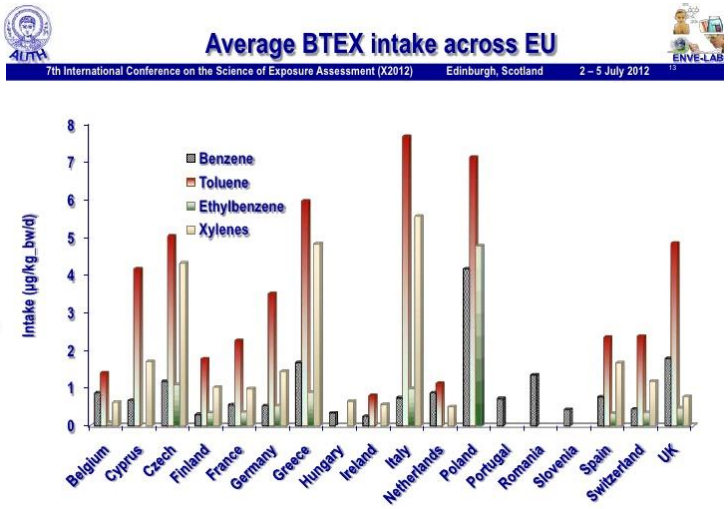
Motivations for BTEX detection

➢Ubiquitous pollutants



MACBETH project (1999)





➢Hazardous for human health

International Agency for Research on Cancer

World Health Organization

Benzene	Group 1	Carcinogenic to humans
Ethyl-benzene	Group 2B	Possibly carcinogenic to humans
Toluene	Group 3	Not classifiable as carcinogenic to humans
Xylenes	Group 3	

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

	Outdoor LCR	Indoor LCR
Industry	2,99E-05	2,01E-04
Urban	6,83E-06	3,57E-05
Semi-rural	3,81E-06	3,50E-05
Residential	3,39E-06	3,46E-05

Indoor–Outdoor Distribution and Risk Assessment of Volatile Organic Compounds in the Atmosphere of Industrial and Urban Areas

Environmental Toxicology DOI 10.1002/tox

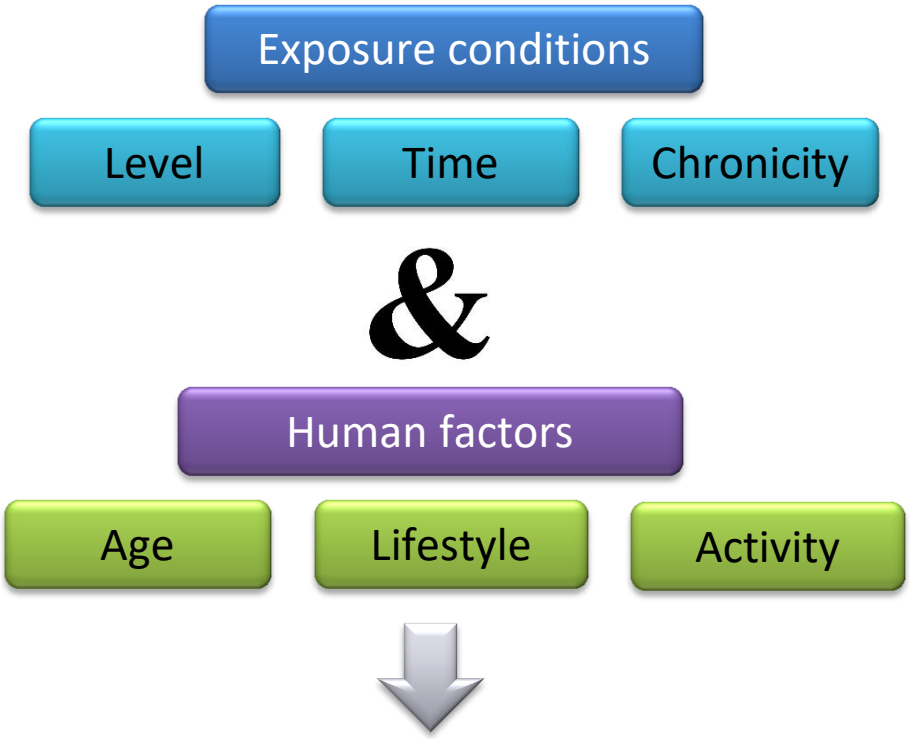
Sensors dedicated to BTEX monitoring

➢Air quality monitoring

	Organism	Note	Benzene	Toluene	Ethyl benzene	Xylene
Occupationnal environments (ppm)	ACGIH	TLV 8h-TWA	0.5	20	20	100
	OSHA	PEL 8h-TWA	1	200	100	100
	NIOSH	REL 8h-TWA	0.1	10	100	100
	Saiosh	PEL 8h-TWA	0.5	47	/	100
		REL 8h-TWA	< 1	50 (8h)	100	50 (8h)
Urban and rural environments (ppb)	World Health Organization	REL	0	70 (8 days)	5000 (annual)	110 (24h)
	Environment Canada	/	9 (1h)	100 (24h)	/	160 (24h)
		TLV	1.5 (annual)	/	/	/
	defra	Annual limit	1.5	500	1000	1000

➢Personal exposure assessment

Health troubles depend from:

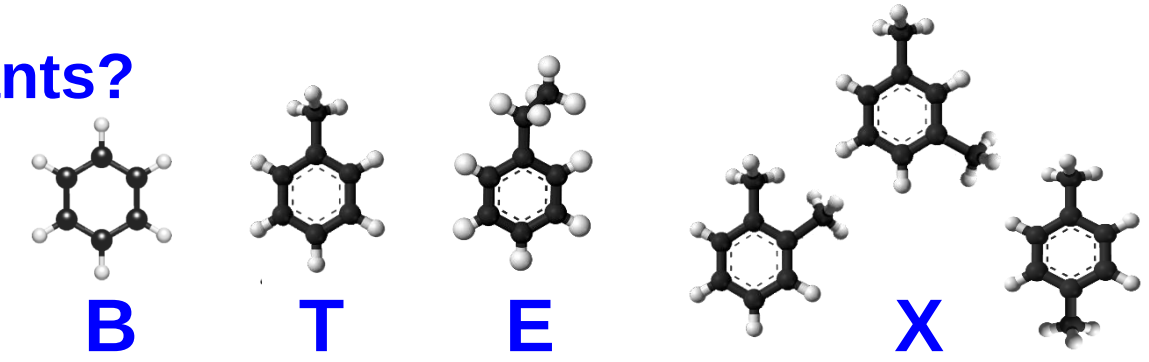


Small and low-power consumption gas sensors for health prevention

Sensing strategy for BTEX detection

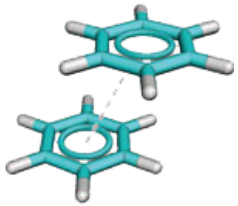
Properties of target pollutants?

- Aromatic compounds



Sensing material?

- Aromatic macromolecules



pi-stacking interactions

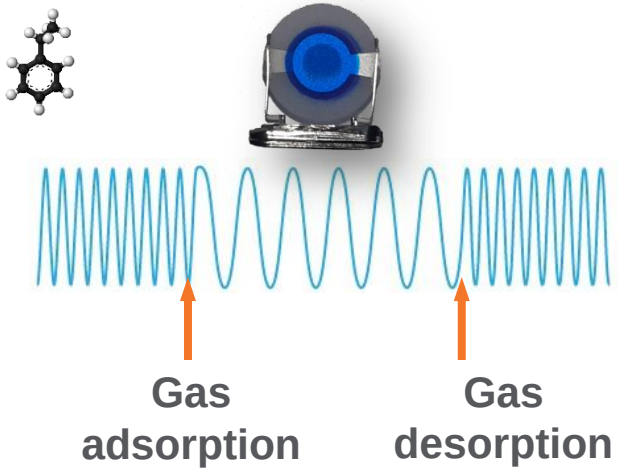
Adsorption sites for BTEX

Weak interaction forces → reversibility

Transducer?

No charge transfer gas ↔ material

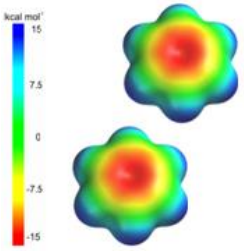
Weak interaction forces



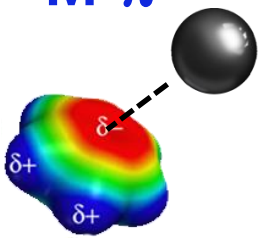
Suitability of phthalocyanine as sensing material

Non-covalent interactions with aromatic hydrocarbons

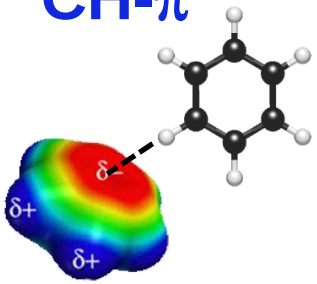
π-π



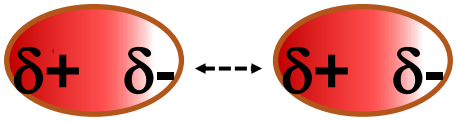
M-π

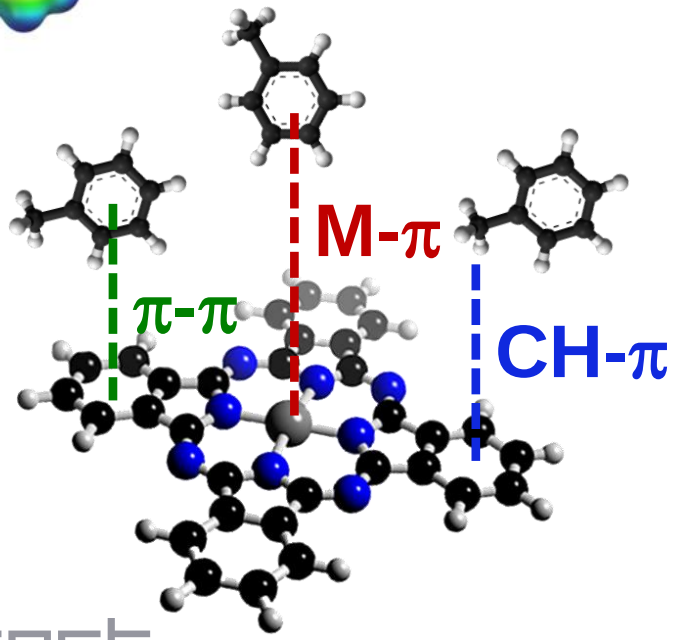


CH-π



Dispersion forces





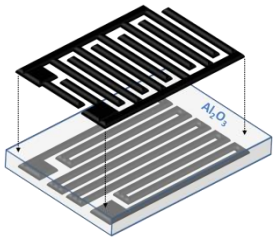
Aromatic interactions

Sensitivity to BTEX

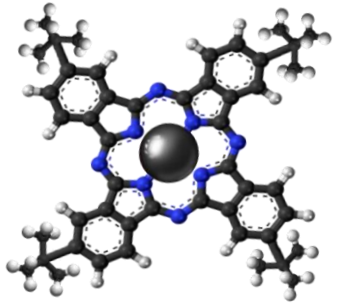
Reversibility

Non-covalent functionalization

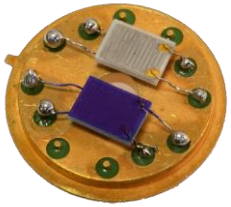
Key role of transducing mode

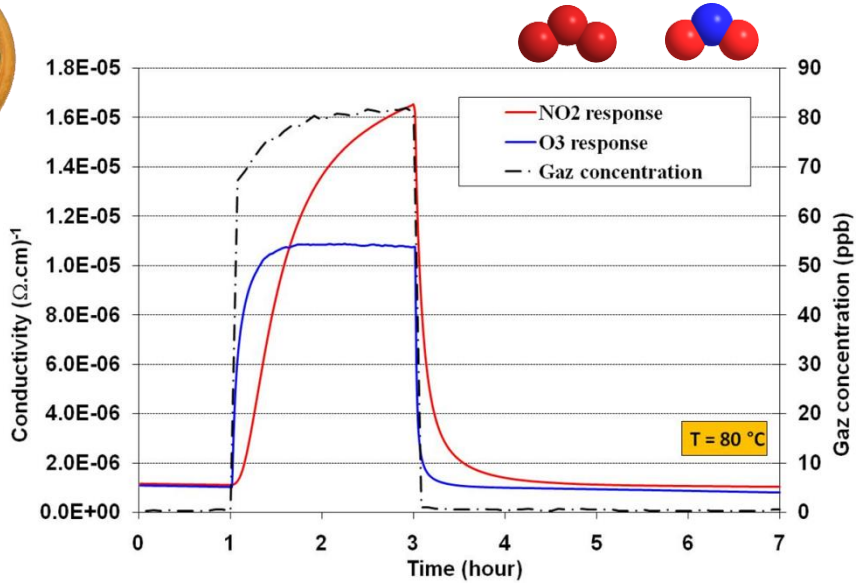


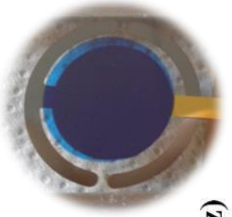
Chemoresistor

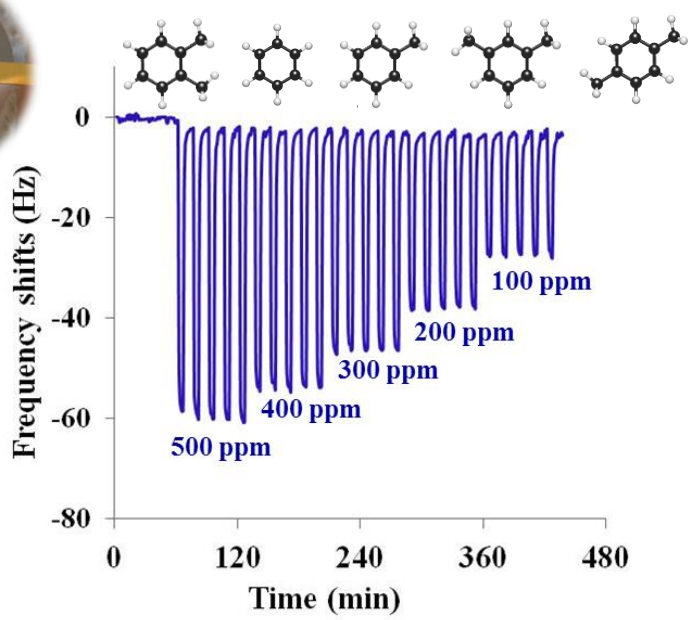


Quartz Crystal Microbalance







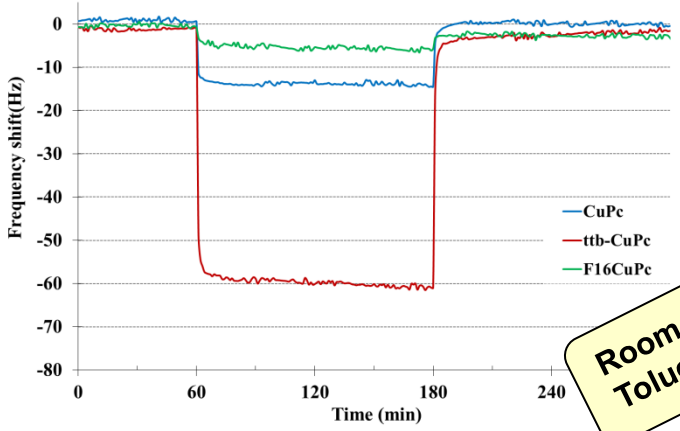


- Modulation of electronic conductivity
  - Partial selectivity / NO_2 and O_3

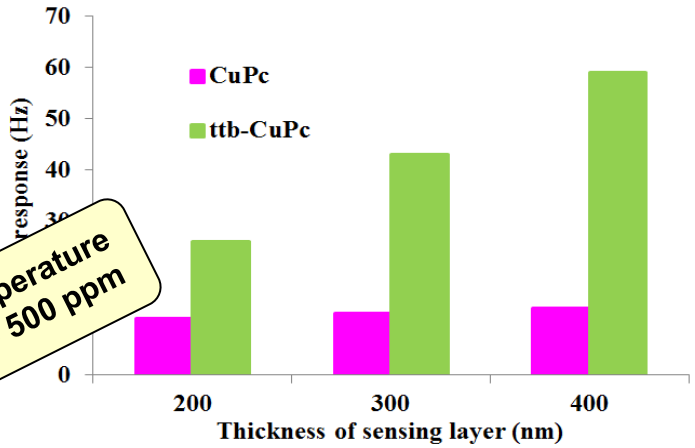
- Modulation of mass
  - Partial selectivity / BTEX

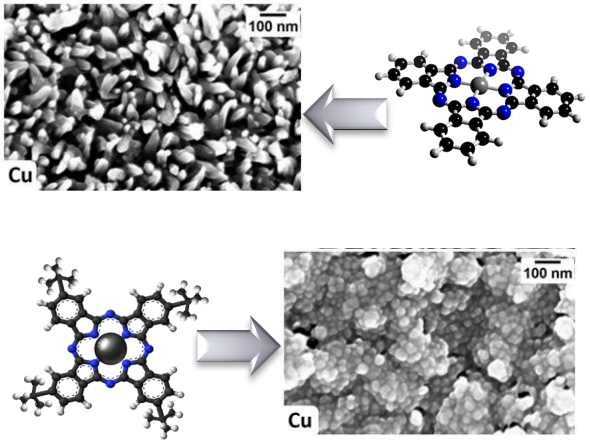
Previous results on phthalocyanine-based sensor

➢Effect of peripheral groups on sensitivity

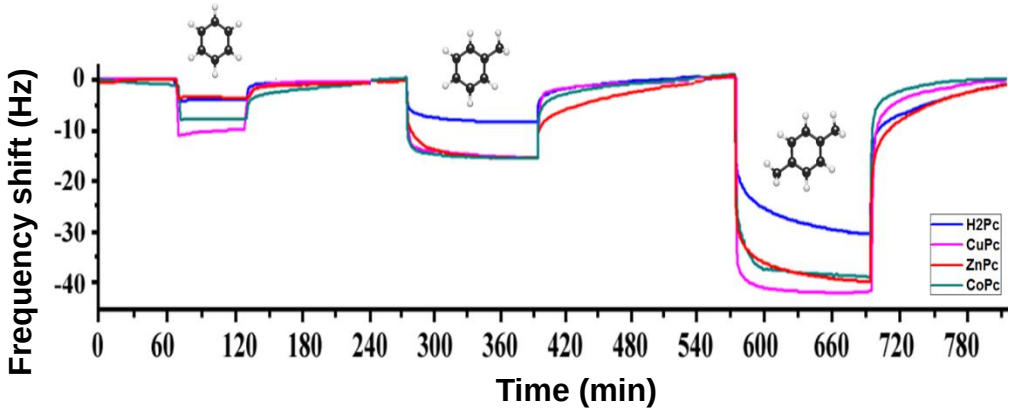


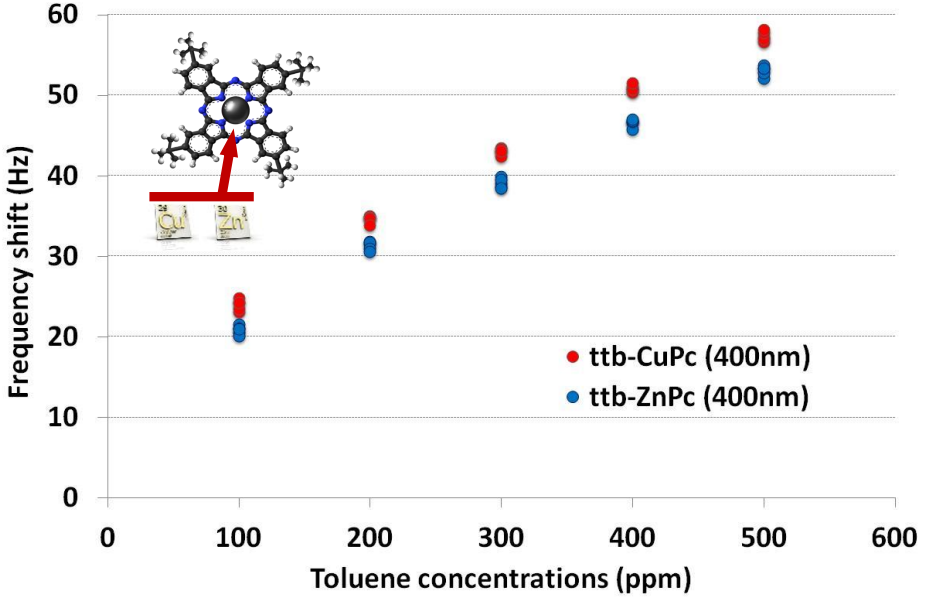
Room Temperature
Toluene = 500 ppm





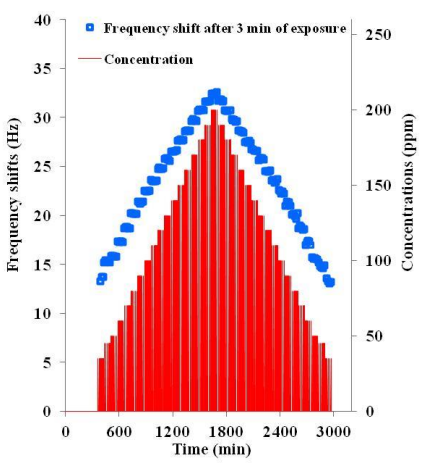
➢No significant influence from central atom

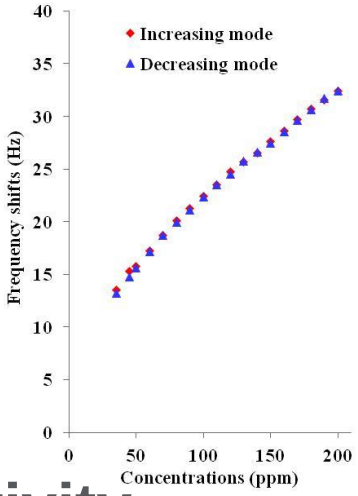




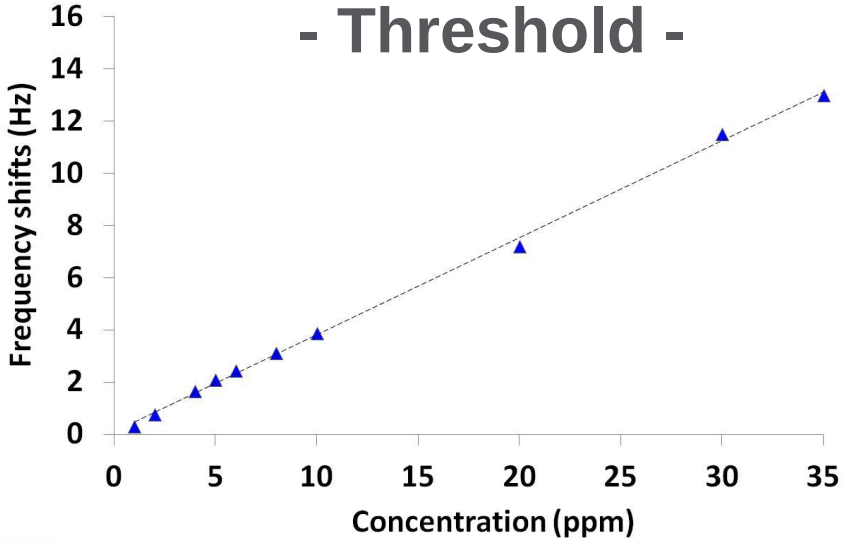
Sensing performances of ttb-CuPc

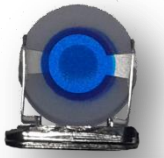
- Resolution -

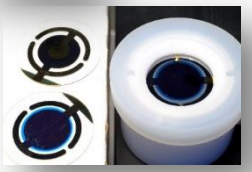




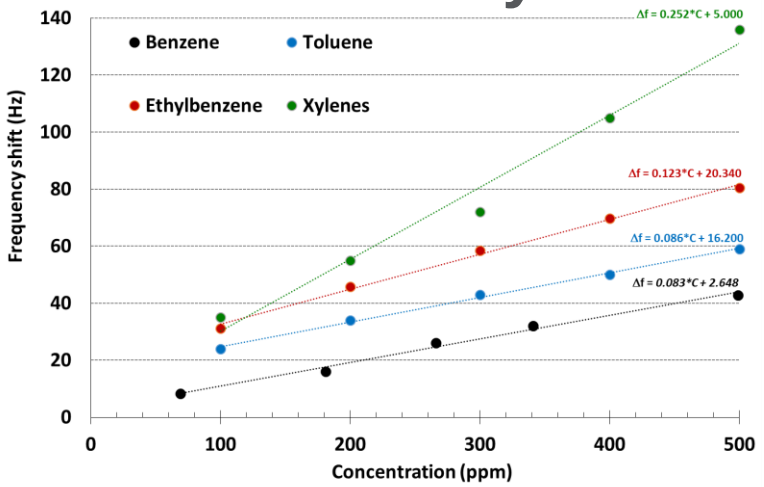
- Threshold -



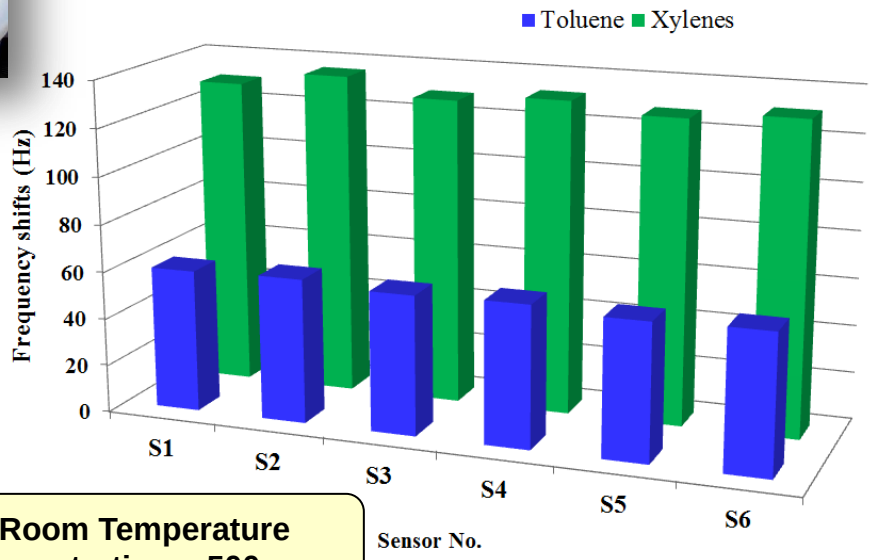




- Selectivity -



- Reproducility -

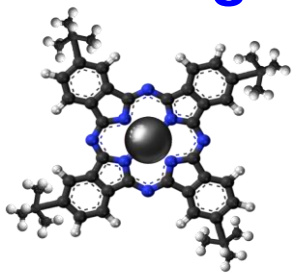


➢ **No response to CO, NO, H_2S and NO_2**

Room Temperature
Concentration = 500 ppm

Interest of hybrid materials

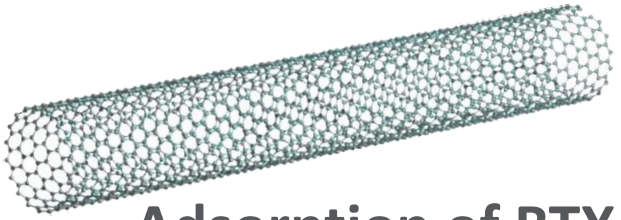
Functional groups



High aromaticity

Adsorption of BTX

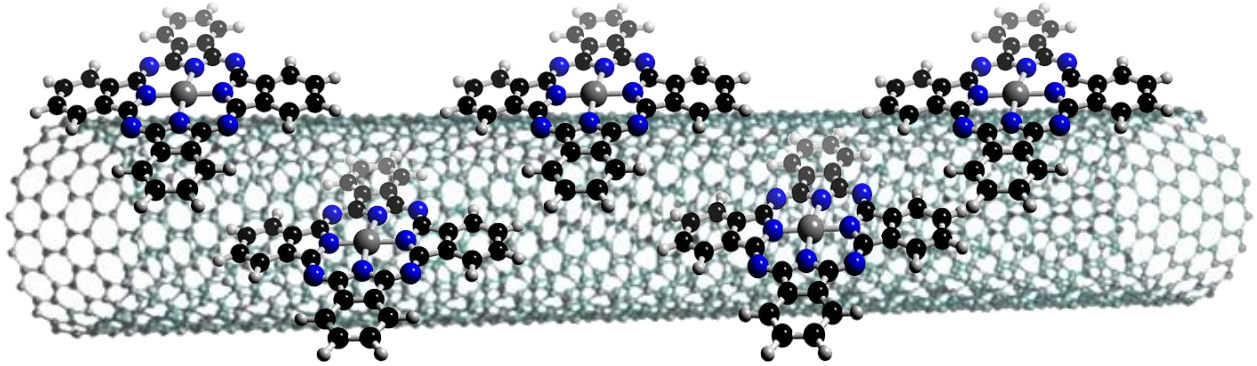
Carbonaceous matrix



Adsorption of BTX

High level of functionalization

High SSA

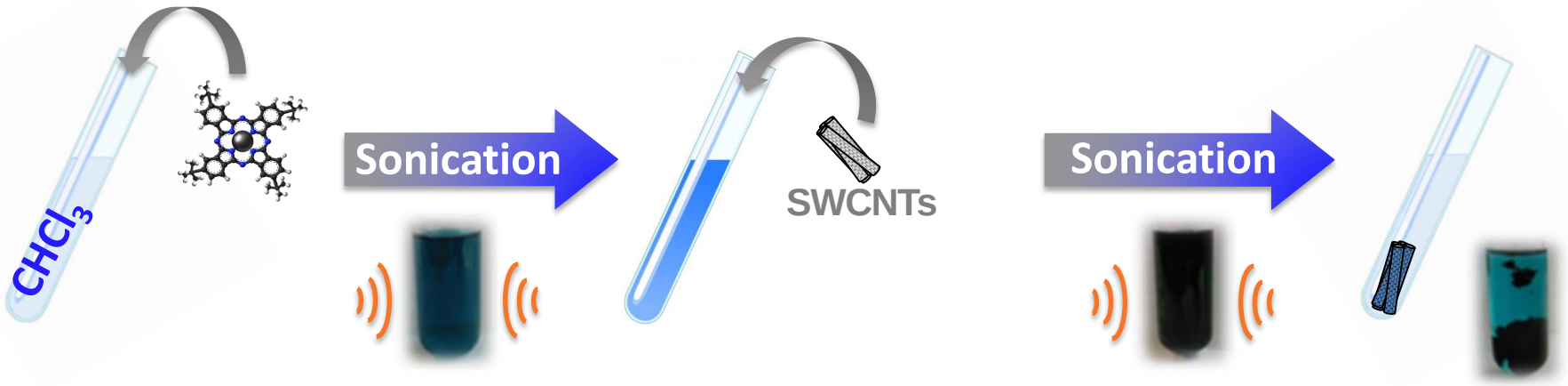


- High surface/volume ratio of active sites available for gas adsorption

- **Higher sensitivity, better resolution and low threshold expected !**

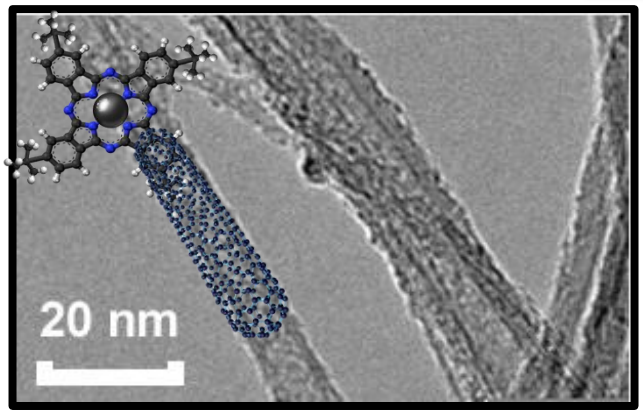
Development and coating of hybrid materials

Elaboration process

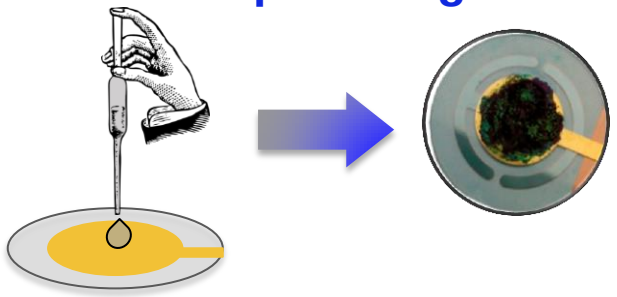


Benzene ring of macrocycles → **π-stacking with nanocarbons**

→ **Non-covalent functionalization**

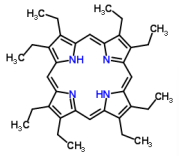


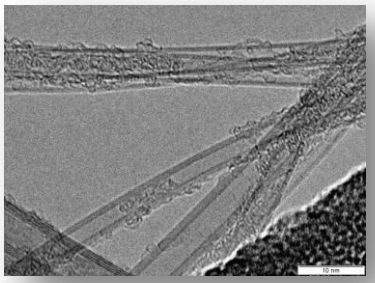
Drop-casting

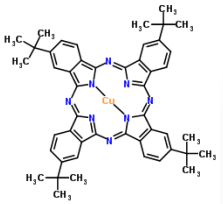


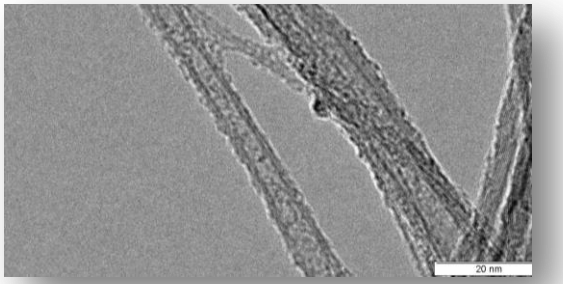
Characterization of hybrid materials

TEM pictures



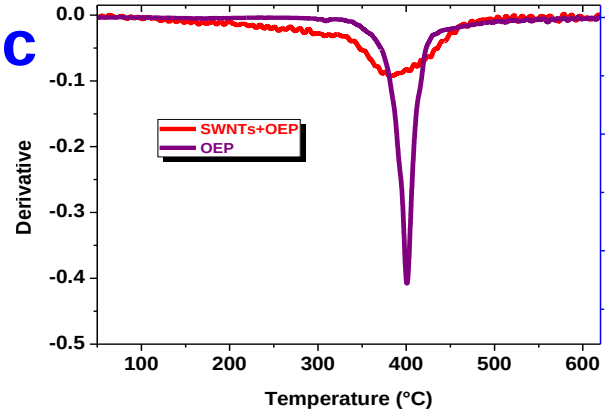


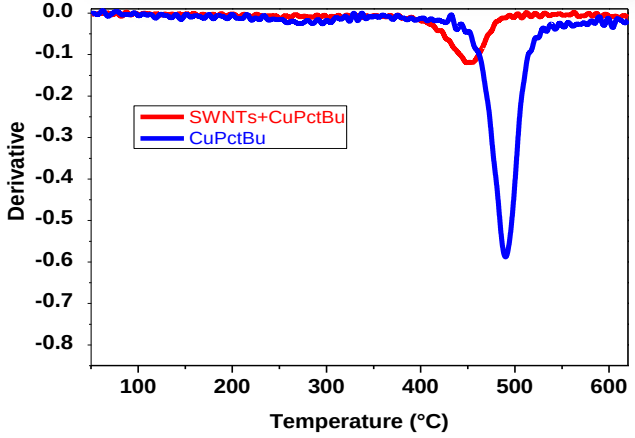




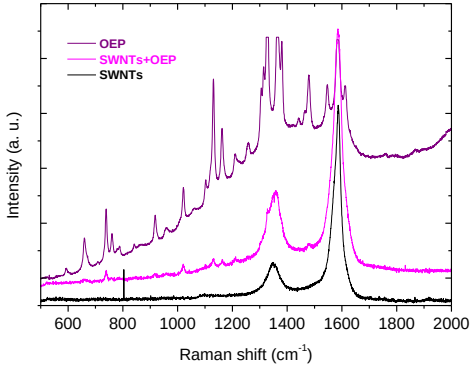
Thermogravimetric analysis

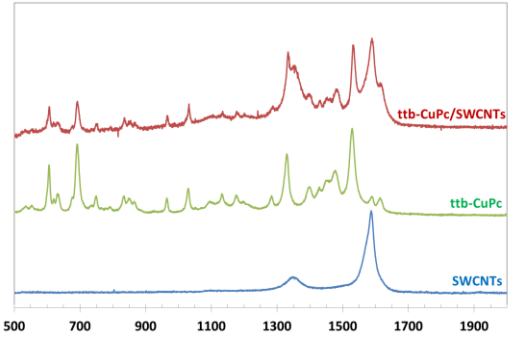
	SWNTs + ttb-CuPc	SWNTs + OEP
Δm (%)	24.4	15.8



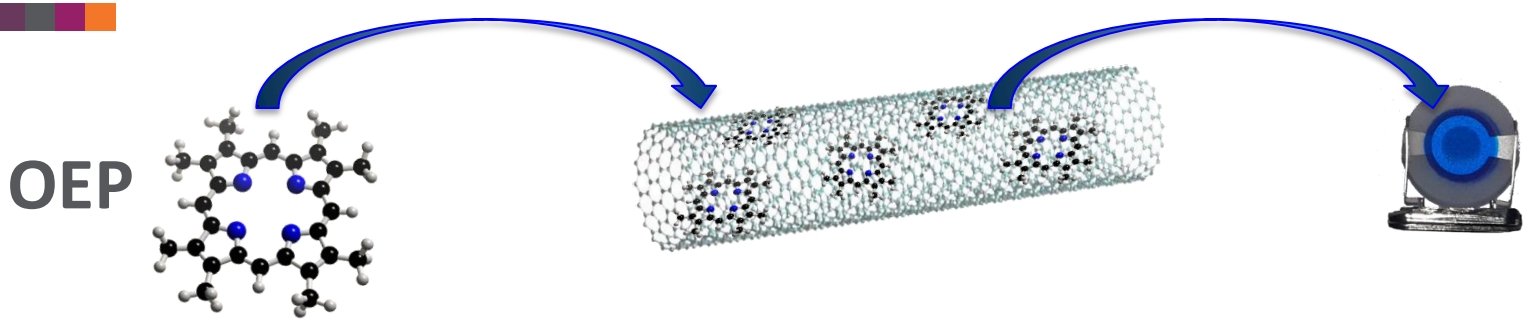


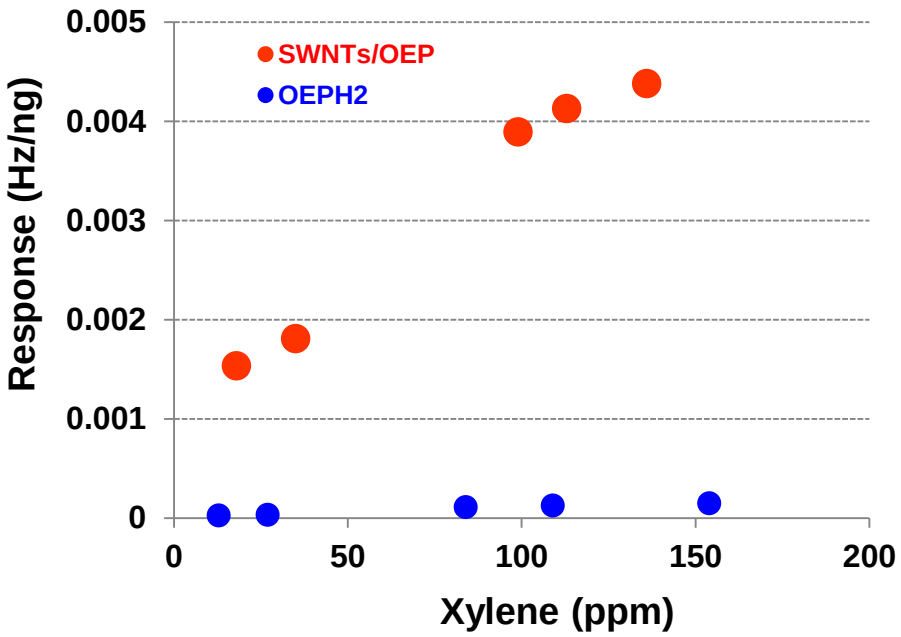
Raman spectroscopy

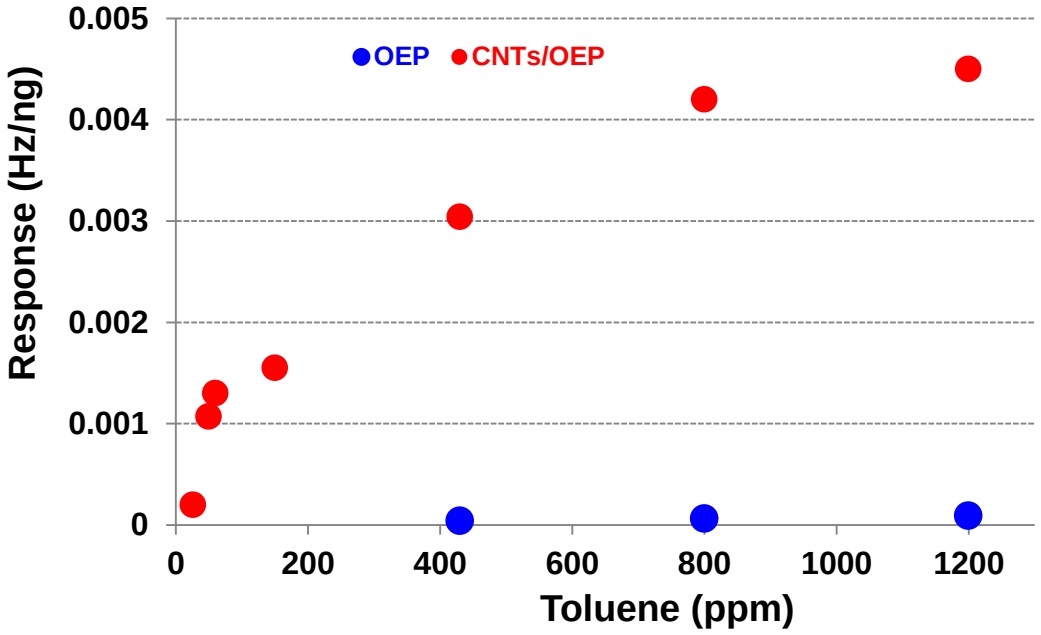




Sensing performances on QCM devices



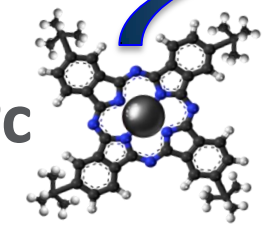


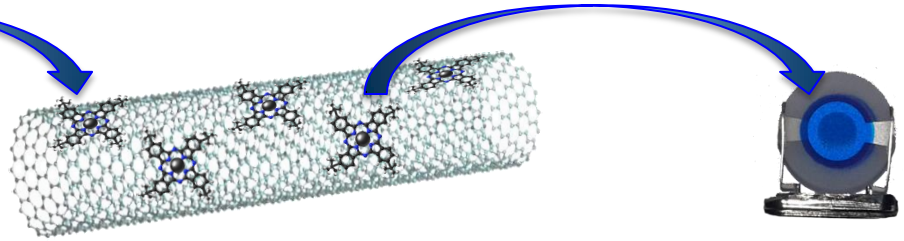


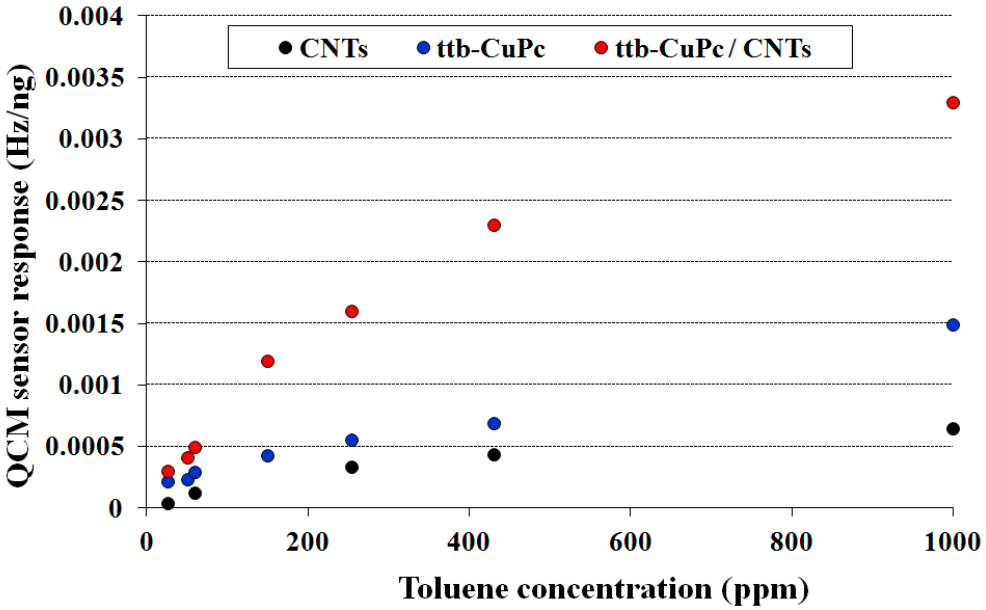
- Higher sensor responses on hybrid material
- Higher sensitivity / xylene
- Response time = few seconds; Recovery time < 10 min @RT

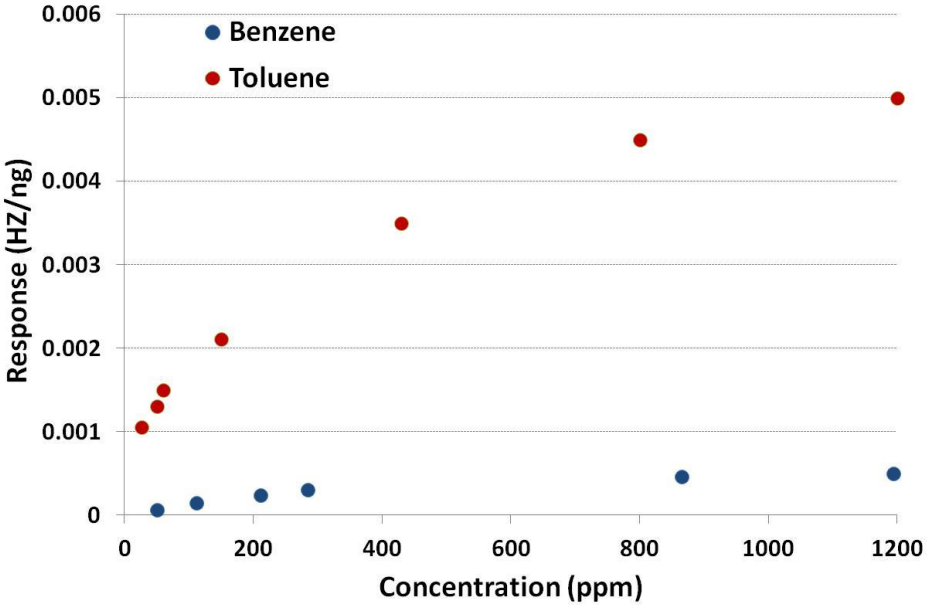
Sensing performances on QCM devices

ttb-CuPc









➢ Higher response / individual materials

Materials	ttb-CuPc	ttb-CuPc/SWCNTs
SSA (m^2/g)	70	260

➢ Discriminated responses

➢ Selectivity ?

Sensing performances on SAW devices

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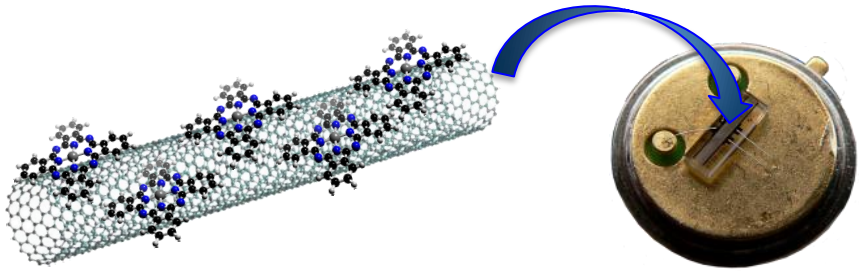
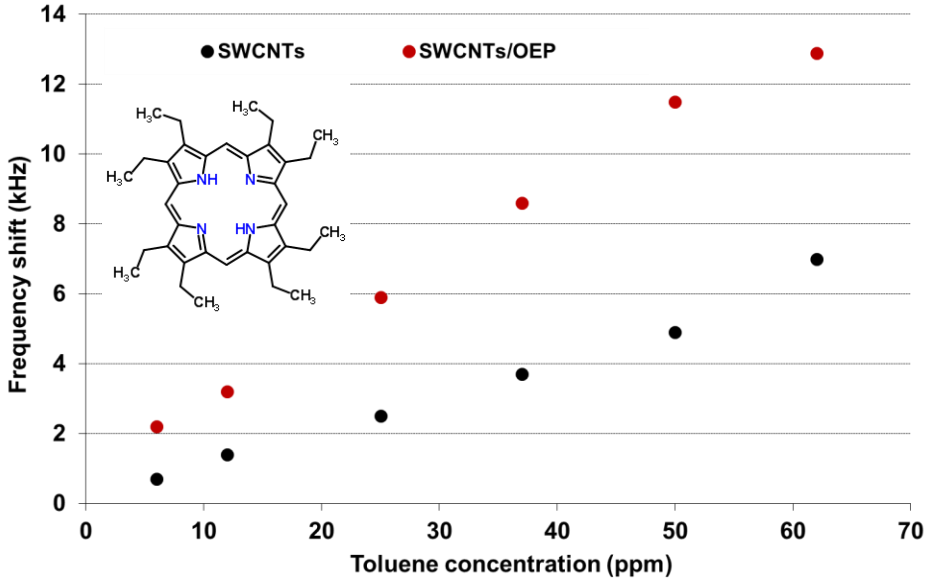
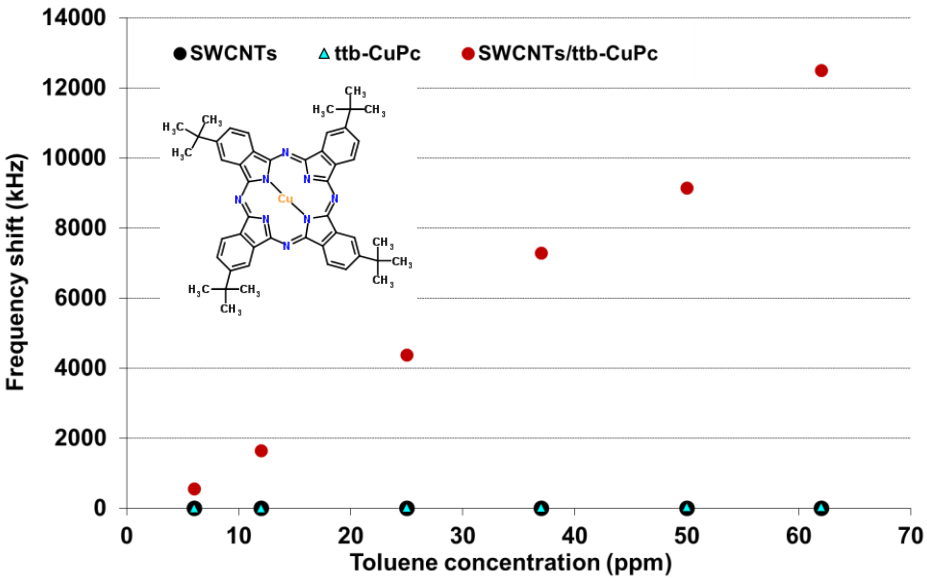




OEP / SWCNTs

Low increase in sensitivity



ttb-CuPc / SWCNTs

High sensitivity enhancement

No response to CO, NO_2 and H_2S

cost
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Conclusion & ongoing activities

- Key role of transducing mode (SIG 3)
- Sensing performances improved for hybrid materials
  - Established on QCM-based sensor
  - Confirmed on SAW-based devices
- Benefit from STSMs

  Valued by 1 joint publication, 1 oral talk, 2 posters & 1 joint seminar

- Toward selective measurement of BTEX
  - ASTHMAA project - granted by cnrs
- VOCs detection by a multi-transducers approach
  - PhD position starting in october 2016
  - Collaborations with EuNetAir partners

Time for questions ?