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SENSING DEVICES BASED ON METALLOPHTHALOCYANINES AND METALLOPHTHALOCYANINE/NANOCARBONS HYBRID MATERIALS: APPLICATION TO AROMATIC HYDROCARBONS DETECTION

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Scientific context and objectives

Motivations ?

Hazardous effects of VOCs on health and environment

⇨ **direct impacts** ⇨ **precursors of secondary pollutants**

French context ?

Necessity to decrease VOCs emissions

Special focus on Benzene and PAH

Action 7: toward a better identification of indoor pollution sources

Action 9: better management of AQ in public areas

Action 12: to strengthen the measurement of occupational exposures

Our action ?

Coordinator of the French National project CAPBTX (2010-2013)

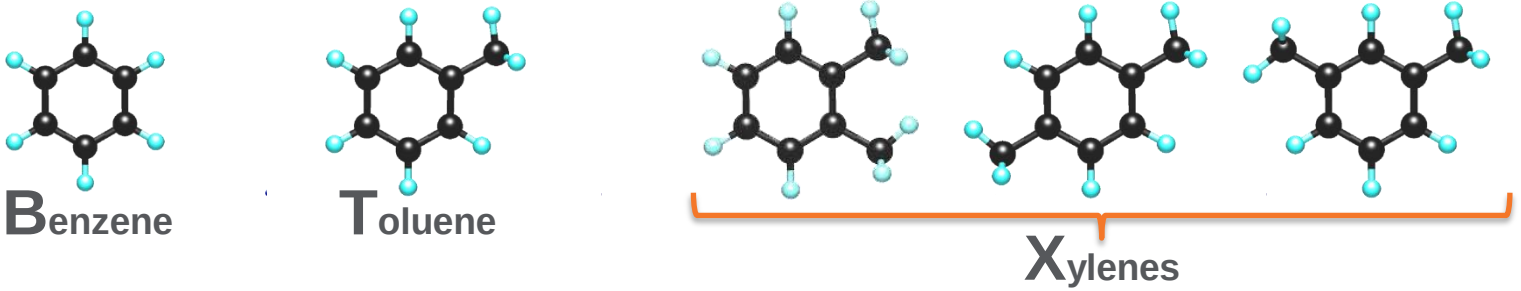
Agence Nationale de la Recherche
ANR

cost
EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

Scientific context and objectives

Target pollutants ?

Aromatic hydrocarbons



Guidelines for BTX

	Non-occupational			Occupational
	ATSDR	EPA	World Health Organization	OSHA
Benzene	3-6 ppb	9-10 ppb	≈ 1.55 ppb	10 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*

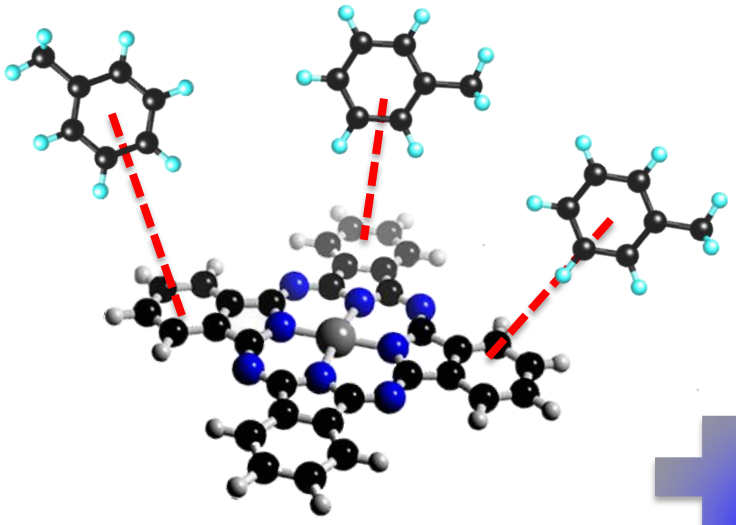
Objectives of CAP-BTX project ?

Development of sensor-system based on hybrid materials devoted to the measurement of BTX

Scientific strategies for BTX detection (1)

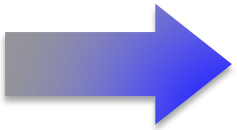
To take advantage of interactions between aromatic groups

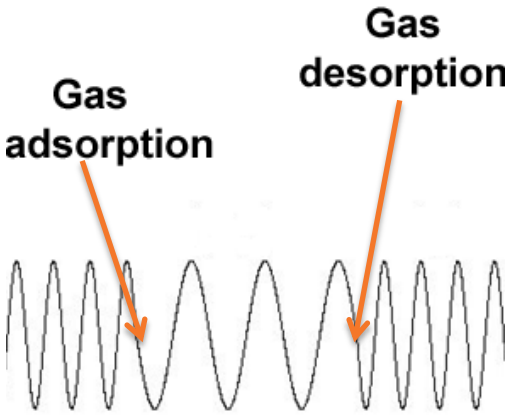
π-stacking ⇨ reversible gas adsorption



Sensitive material

Transducer





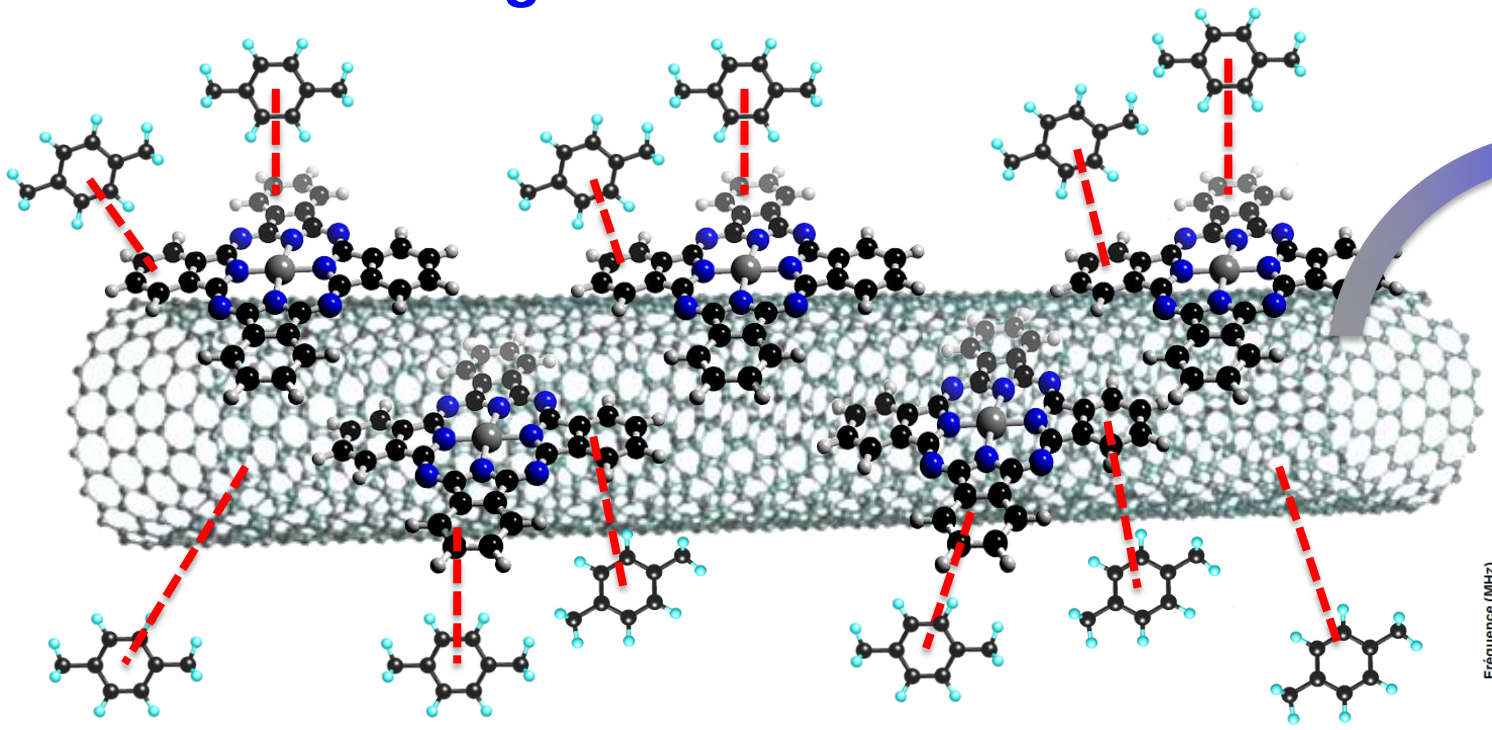
Expected performances ?

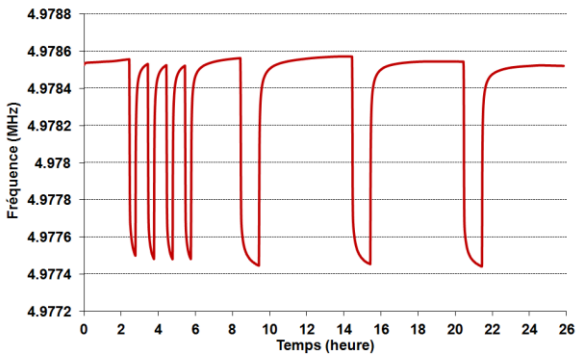
Sensitivity, reversibility & low response time

Scientific strategies for BTX detection (2)

To take advantage of interactions between aromatic groups

π-stacking ⇨ non-covalent functionalization of CNTs





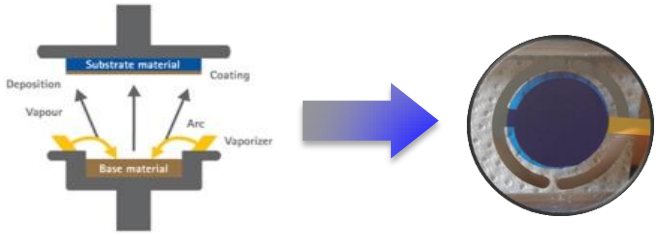
Expected enhancement ?

Higher sensitivity due to high SSA

Sensor development and calibration

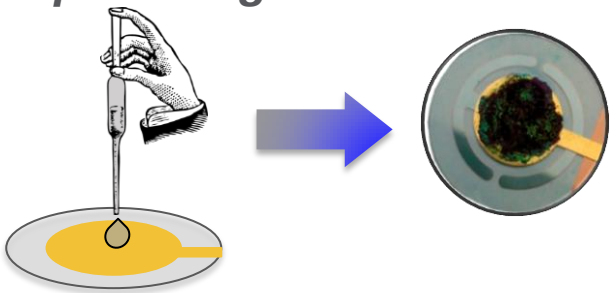
❶ Metallophthalocyanines (MPc)

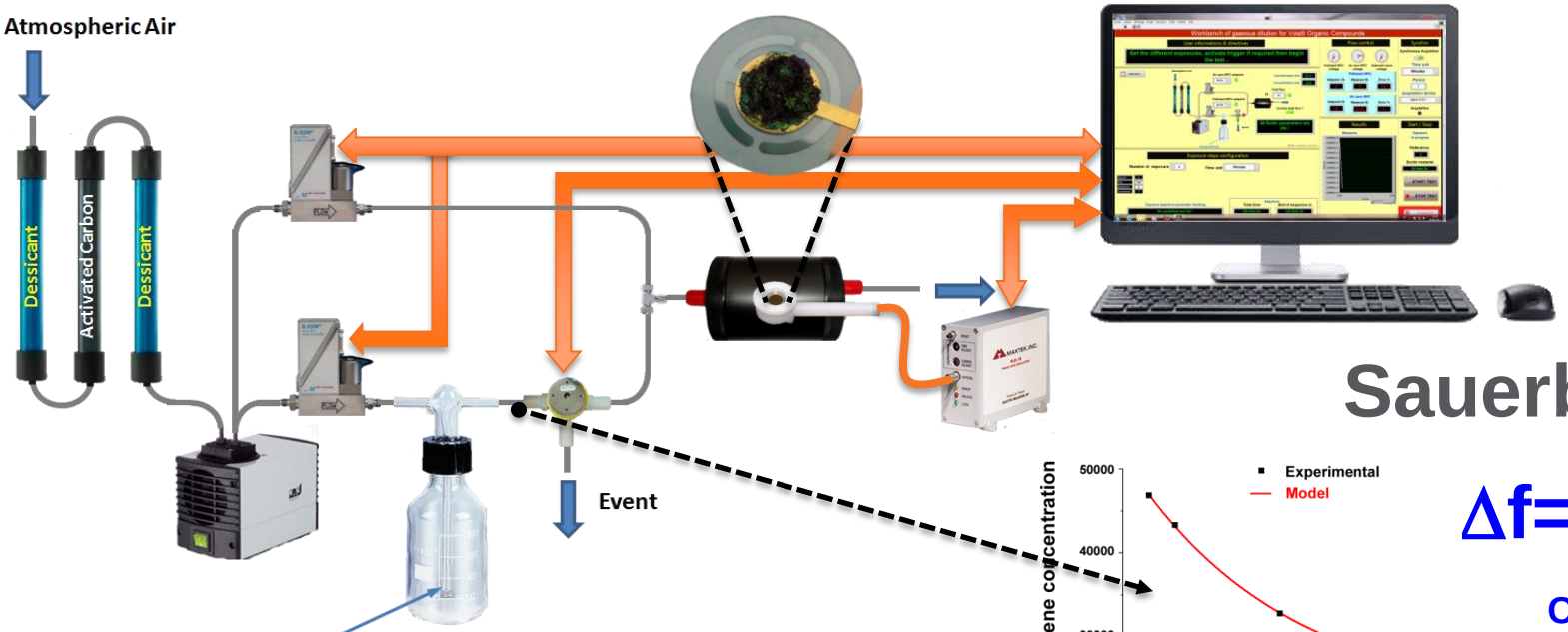
Thermal evaporation



❷ Hybrid materials (MPc/CNTs)

Drop-casting





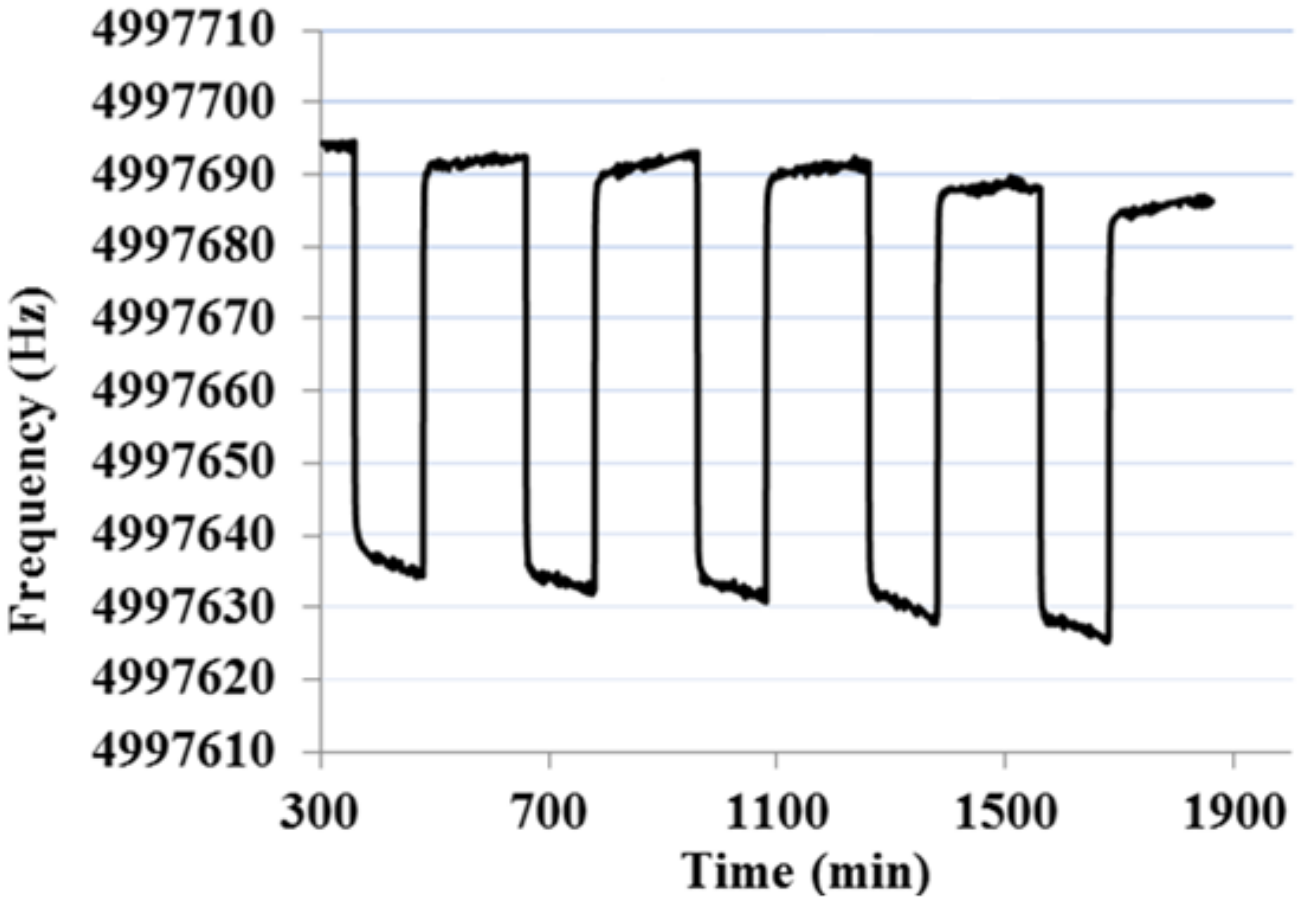
Sauerbrey Equation

$$\Delta f = - C_f \times \Delta m$$

C_f : sensitivity
= 0.056 Hz/ng/cm^2 (@ 5 MHz)

❶ Response of ttb-CuPc QCM sensor (1)

[C_7H_8] = 500 ppm Flow = 0.75 l/min T° = RT Thickness$_{ttb\text{-}CuPc}$ = 400 nm



Performances?

Sensitive

Repeatable

Reversible

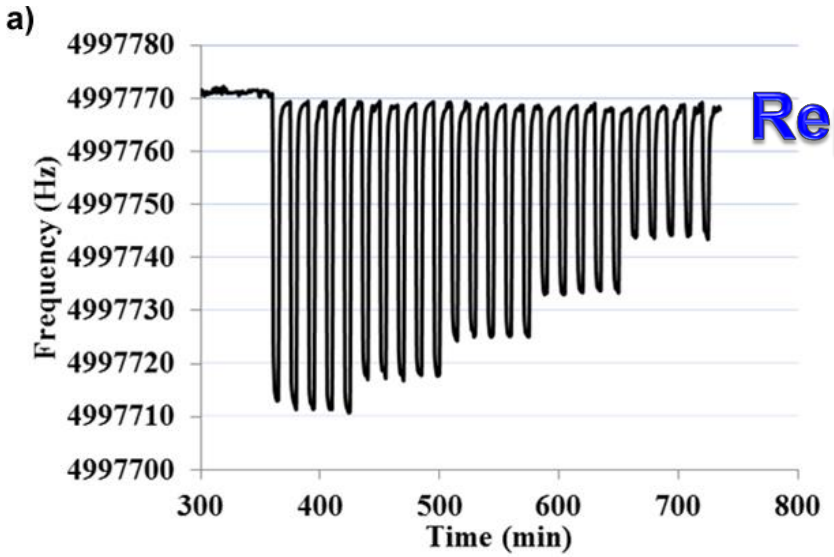
Low recovery time

Low response time

90 % of frequency shift

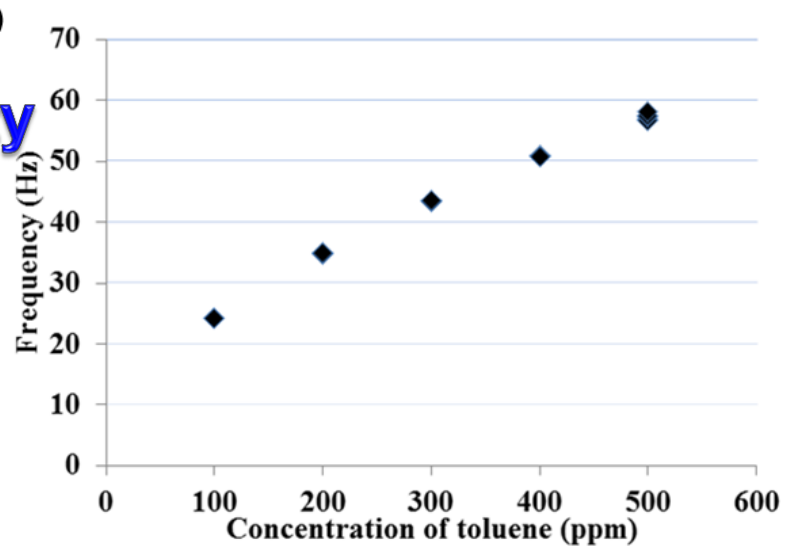
in 3 minutes

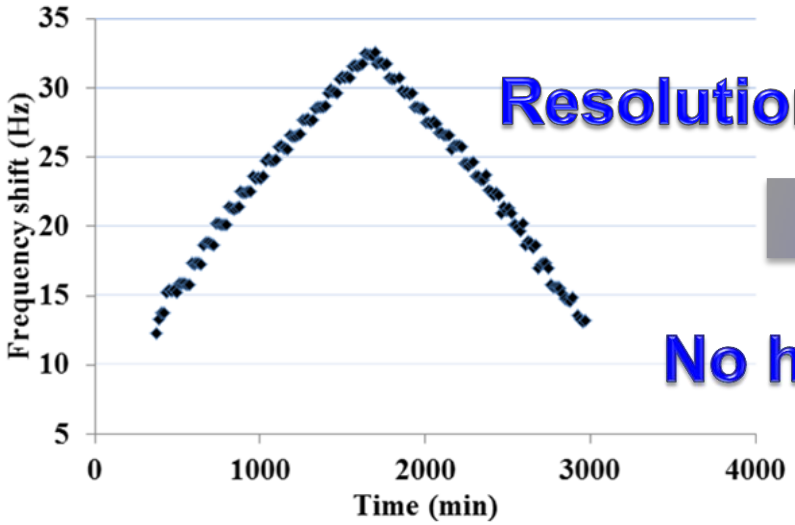
❶ Response of ttb-CuPc QCM sensor (2)



Reproducibility

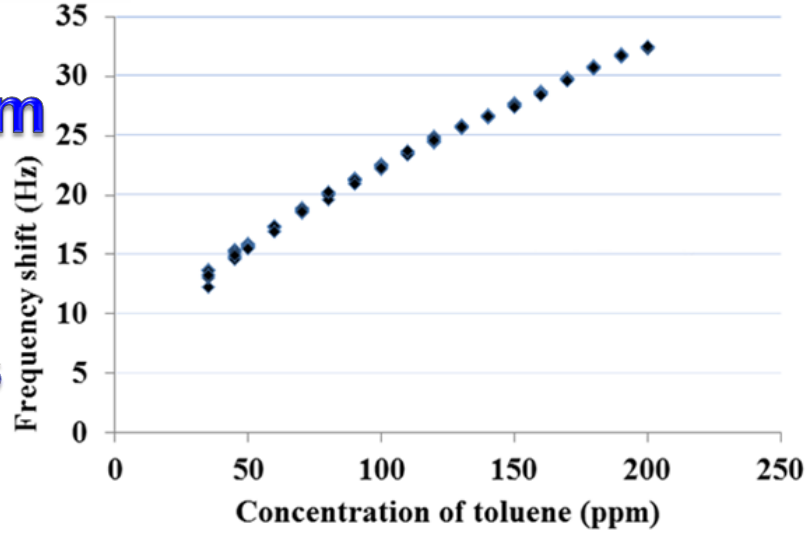
Stability





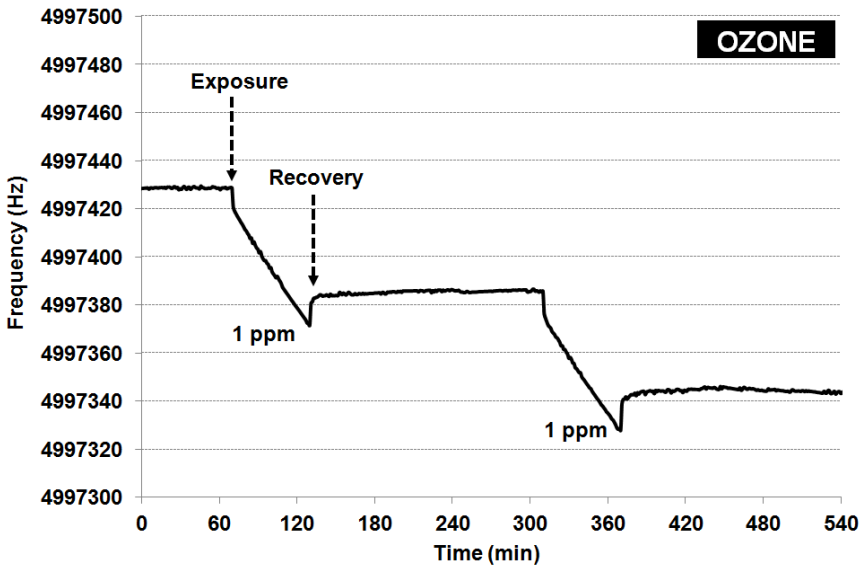
Resolution = 10 ppm

No hysteresis

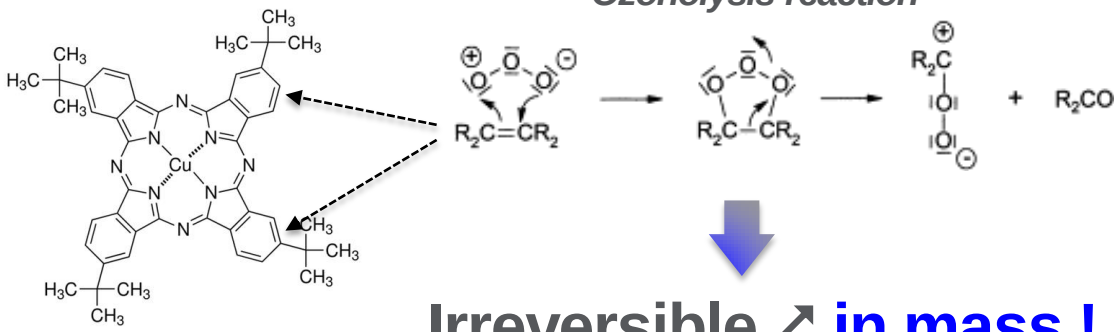


Selectivity of ttb-CuPc QCM sensor ?

No significant response toward CO, H_2S and NO_2 !



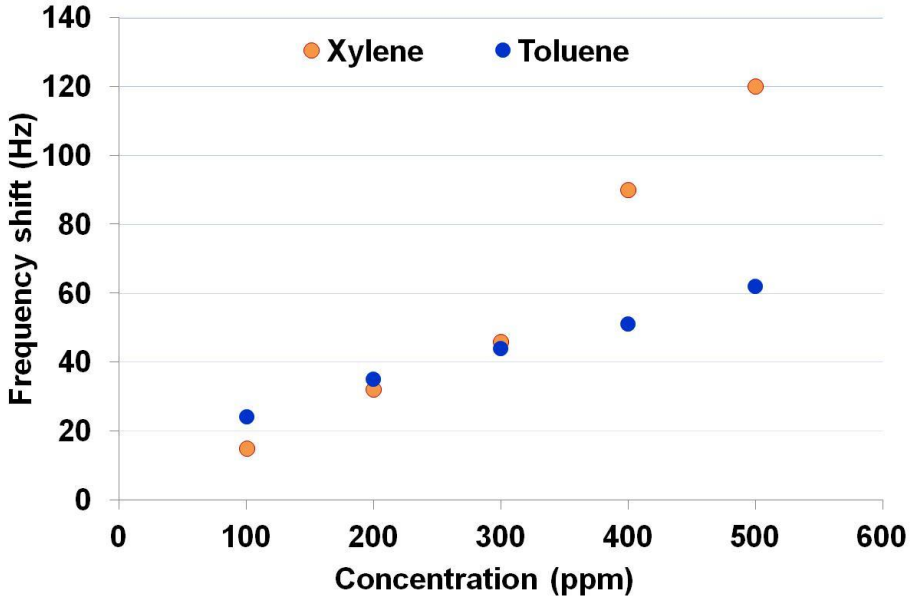
Ozonolysis reaction



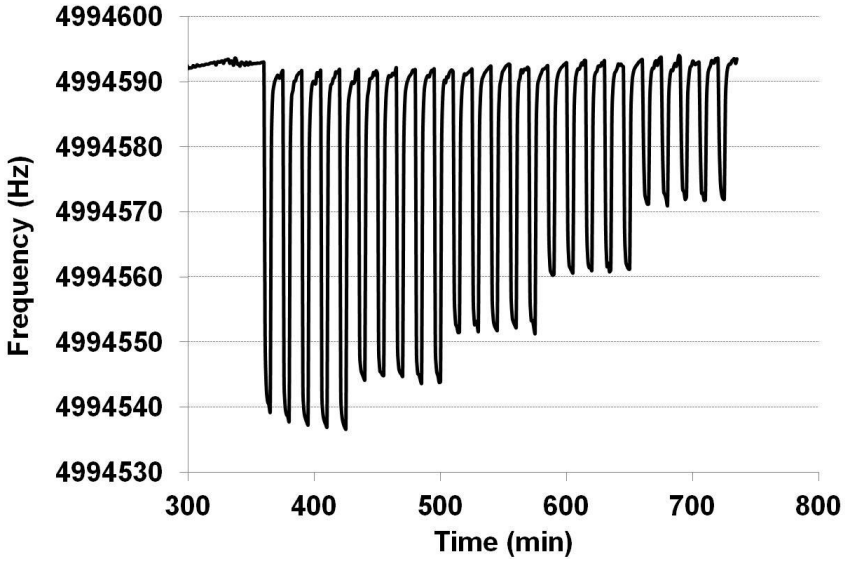
Irreversible ↗ in mass !

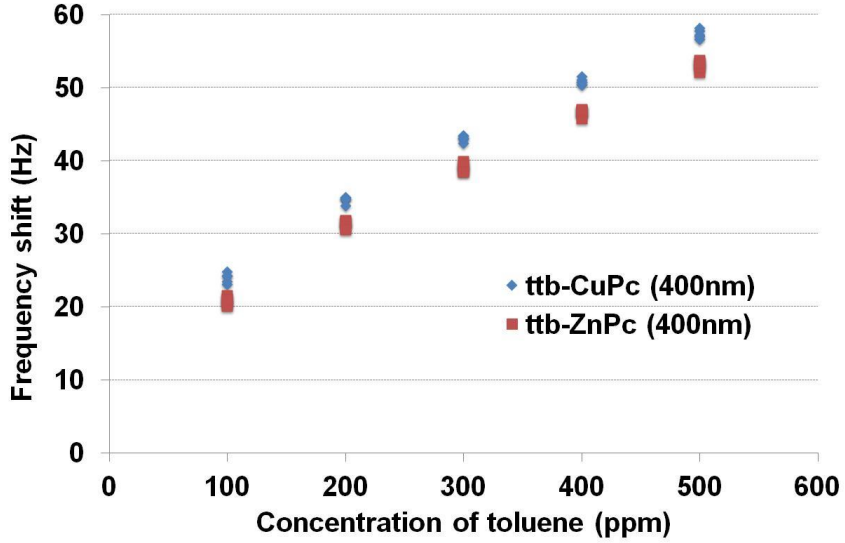
High responses to aromatic hydrocarbons

Partial selectivity in the context of AQC



Response of ttb-ZnPc QCM sensor





No influence of the central metal atom of MPc on gas sensitivity

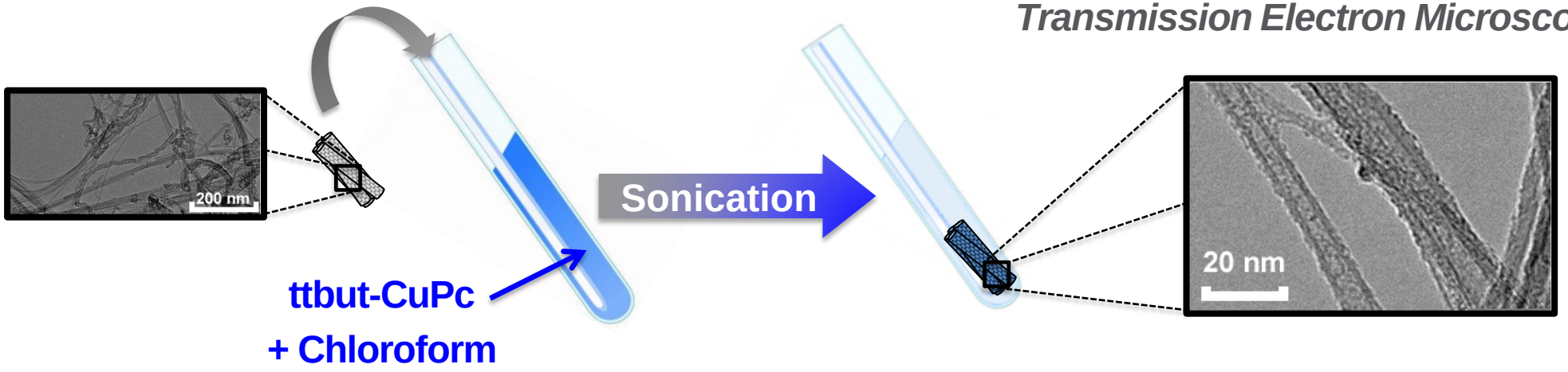
Enhanced adsorption due to tert-butyl groups

⇨ π-stacking interactions strengthened by tert-butyl groups

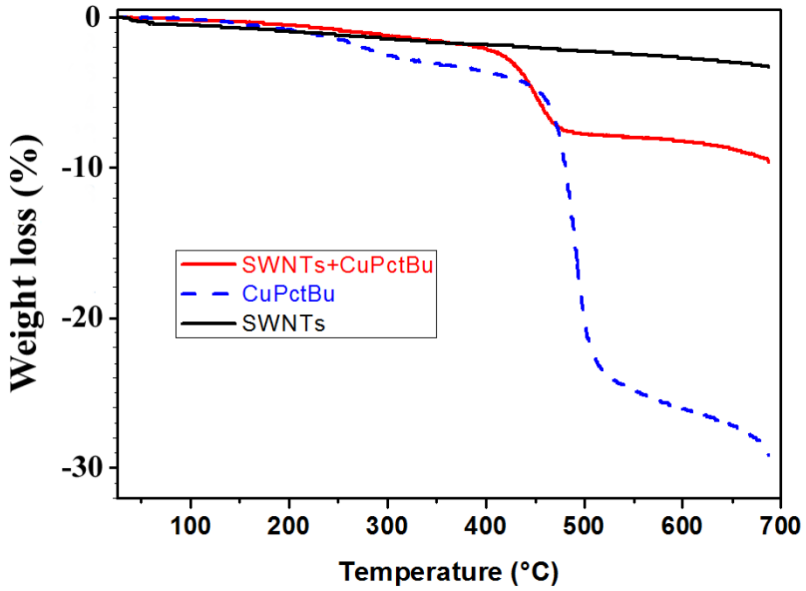
Formalization of gas/material interactions still in progress....

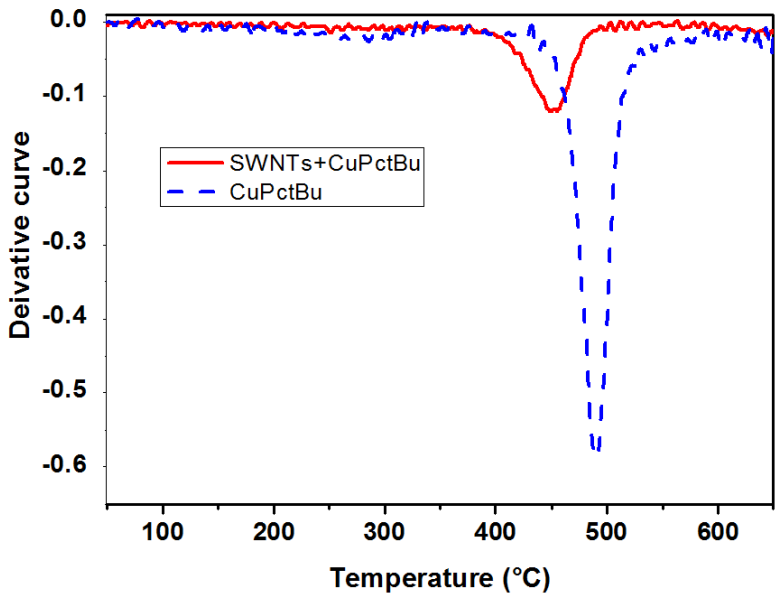
❷ Characterization of hybrid materials

Transmission Electron Microscopy



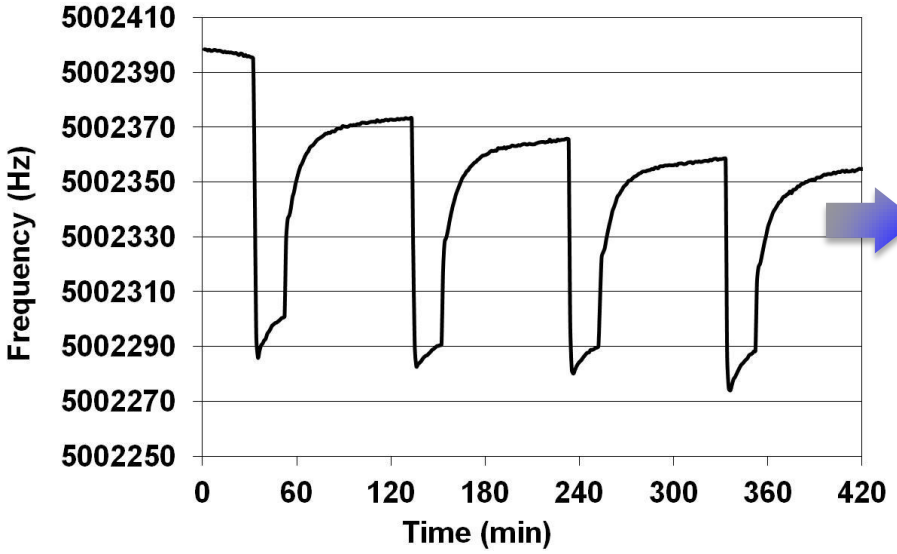
Thermogravimetric analysis





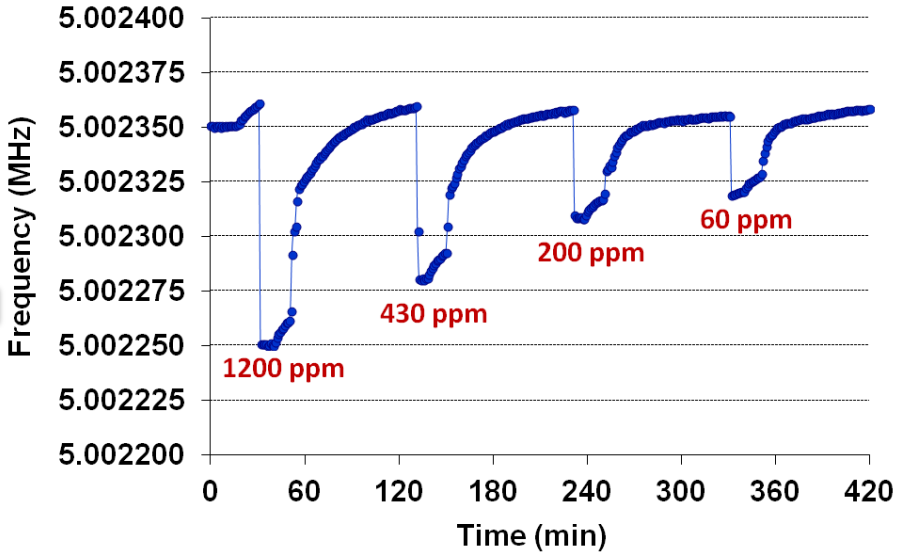
❷ Response of ttb-CuPc/SWCNTs QCM sensors (1)

Gas = Toluene [C_7H_8] = 390 ppm Flow = 0. 5 l/min T° = RT



- Reversible adsorption
- Reproducible response
- **Preconditioning required**

- Fast response time
- Low working temperature
- **Critical point: solvent**



❷ Response of ttb-CuPc/SWCNTs QCM sensors (2)

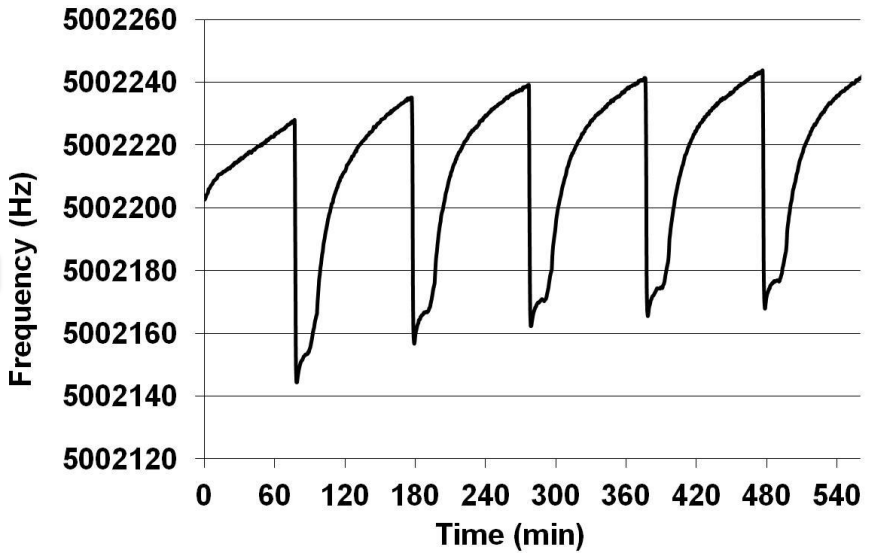
Influence of functional groups

Response in Hz/ng of deposited material	60 ppm	150 ppm	430 ppm	1200 ppm
SWCNTs	Noisy	Noisy	Noisy	Noisy
SWCNTs/$OEPH_2$	1.3×10^{-3}	1.6×10^{-3}	3.0×10^{-3}	4.0×10^{-3}
SWCNTs/$TTPH_2$	1.3×10^{-3}	1.4×10^{-3}	2.5×10^{-3}	3.7×10^{-3}
SWCNTs/ttb-CuPc	1.5×10^{-3}	2.1×10^{-3}	3.5×10^{-3}	4.5×10^{-3}

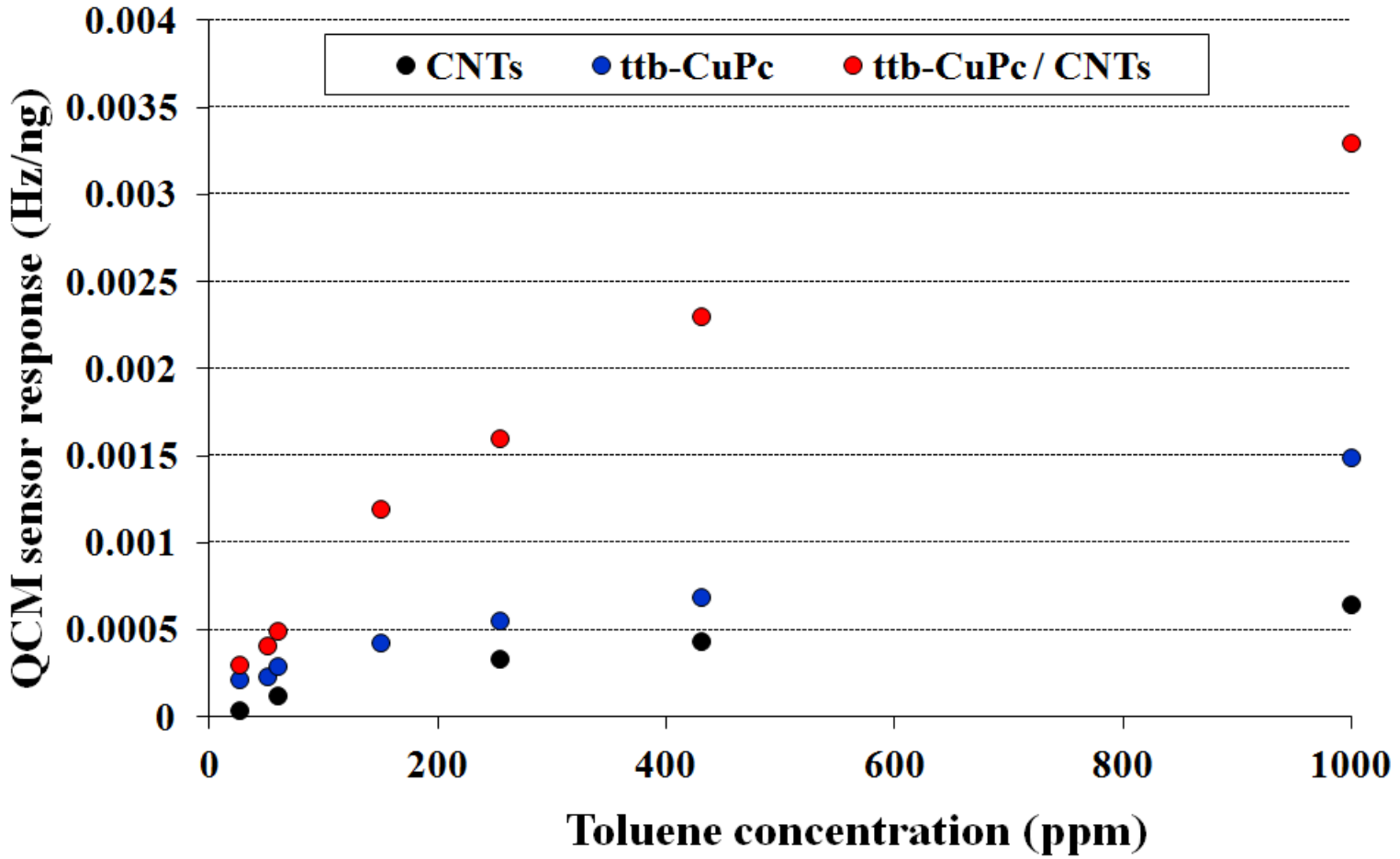
Gas = Xylene $[C_8H_{10}]$ = 110 ppm Flow = 0. 5 l/min T° = RT

Identical behaviour toward xylenes

Discrimination ? a challenge !



ttb-CuPc/SWCNTs vs ttb-CuPc QCM sensors



Higher responses for hybrid materials

Reproducibility of sensors

SAW-based sensors: first results…

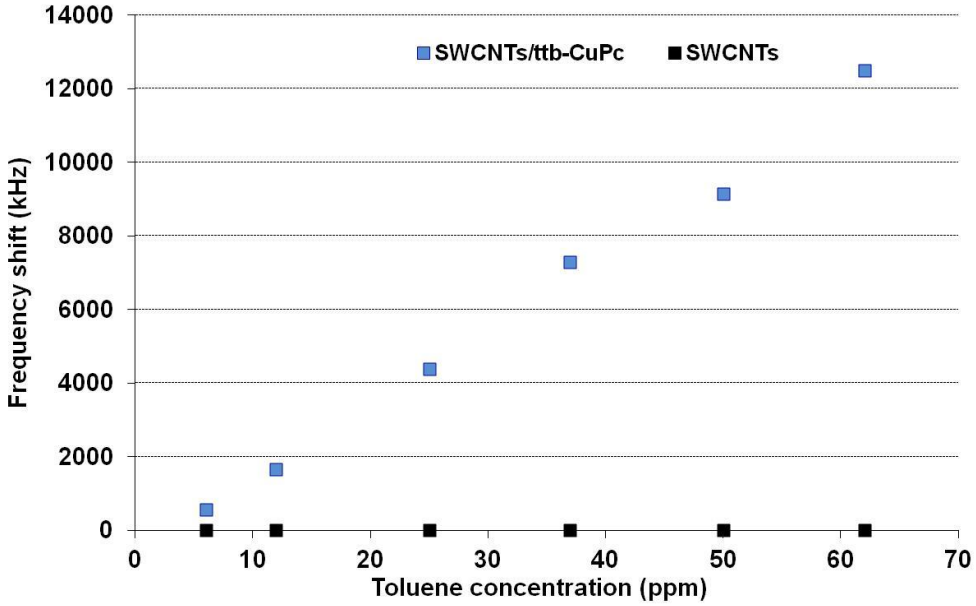
INSTITUT PASCAL
sciences de l'ingénierie et des systèmes

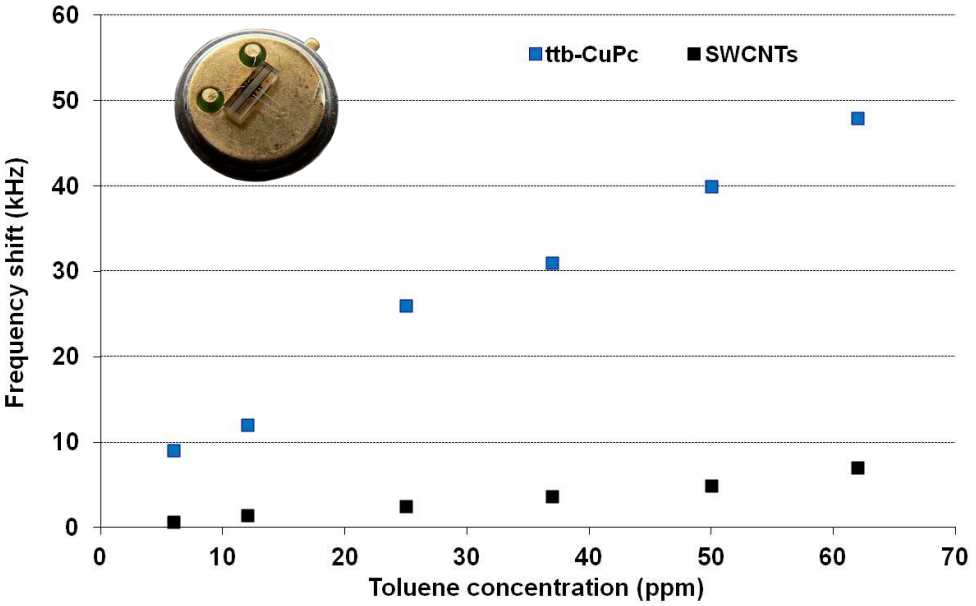
STSM

ENEA

ttb-MPc rings

predominant adsorption sites





ttb-MPc / SWCNTs

Increase in sensitivity

No response to CO, NO_2 and H_2S

Elaboration process to improve !

cost
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Conclusions

- Benzene moieties on MPc ⇨ π-stacking interactions
  ⇨ sensitivity to aromatic hydrocarbons
  ⇨ non-covalent functionalization of CNTs
- Peripheral tert-butyl group ⇨ ↗ solubility into solvent
  ⇨ key-point for BTX detection
- ttb-MPc/SWCNTs hybrid materials ⇨ sensitivity improvement

Open problems and ongoing activities

Investigations on involved gas/materials interactions

Enhancement of performances (threshold, resolution)

Discrimination between aromatic hydrocarbons

Acknowledgments...

My co-workers...

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Short Term Scientific Mission

And you for your attention...


obrigado
Dank U
Merci
mahalo
Köszi
спасибо
Grazie
Thank you
mauruuru
Takk
Gracias
Dziękuję
Děkuju
danke
Kiitos