



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

COST Action TD1105

**4th International Workshop *EuNetAir* on
*Innovations and Challenges for Air Quality Control Sensors***

FFG - Austrian Research Promotion Agency - Austrian COST Association

Vienna, Austria, 25 - 26 February 2016

**FUNCTIONALIZATION OF CARBON NANOMATERIALS:
TOWARDS DEVICES FOR THE MOLECULAR RECOGNITION
OF AROMATIC COMPOUNDS IN THE ENVIRONMENT**



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- Towards molecular recognition
 - Functionalization of CNTs with:
 - Deep cavitands
 - Long-chain mercaptans
- Sensor preparation
- Results on the detection of aromatic and non-aromatic VOCs
- Conclusions and outlook

Towards molecular recognition



Carbon nanomaterials (CNMats) exhibit largely unspecific interactions with gas molecules

But also...

reversible conductivity changes upon gas exposure, even when operated at room temperature

***Strategy:* Use CNMats as ‘transducer’ element and leave the recognition part to complex molecules grafted to their surface.**

Towards molecular recognition

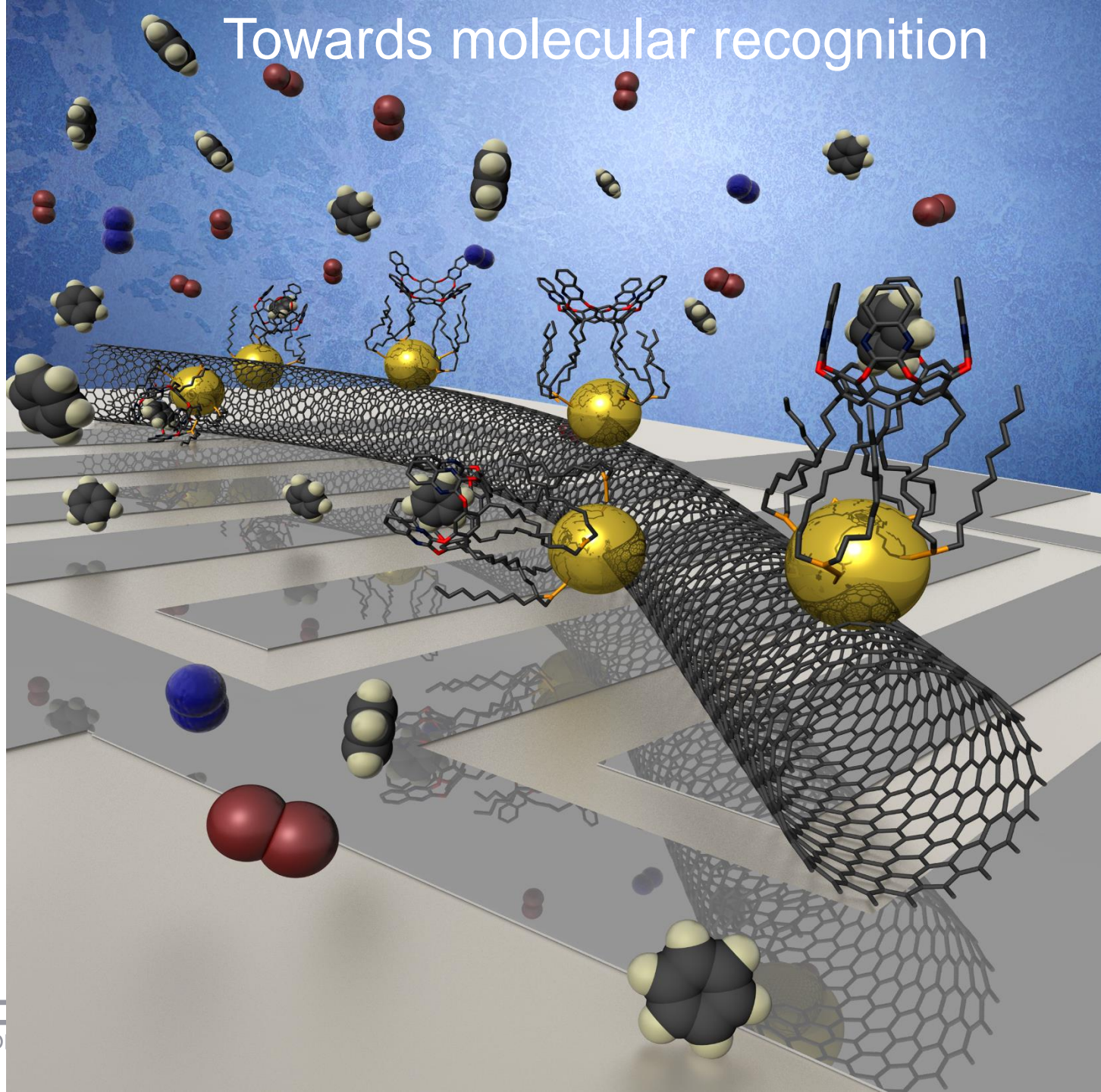


Functionalization of CNTs with:

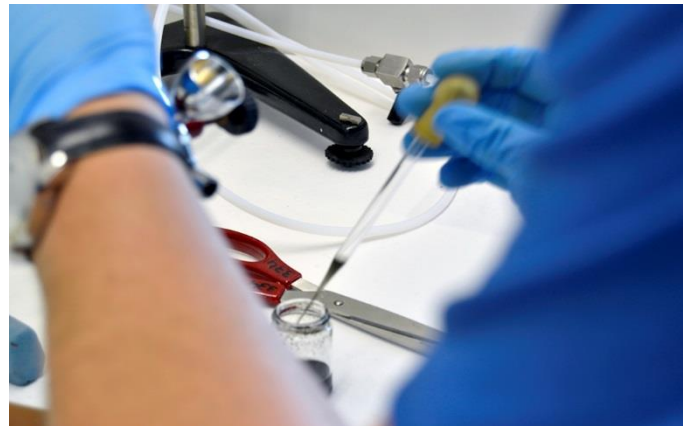
- Quinoxaline walled, deep cavitands (which have been reported as absorbents for aromatics)
- Long-chain mercaptans with terminal carboxyl (hydrophilic) or alkyl (hydrophobic) groups.

In our case we implement this via a SAM technique

Towards molecular recognition



Sensor preparation



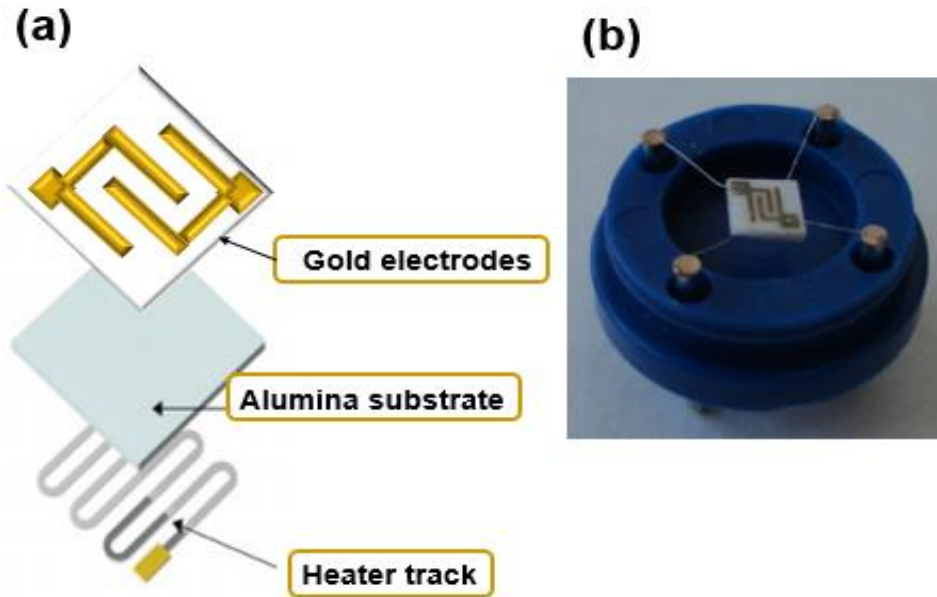
Air-brushing of CNTs dispersed on a suitable solvent onto a heated substrate. Film resistance monitored for reproducibility

P. Clément, E. Llobet, et al.
Sensors and Actuators B
182 (2013) 344- 350

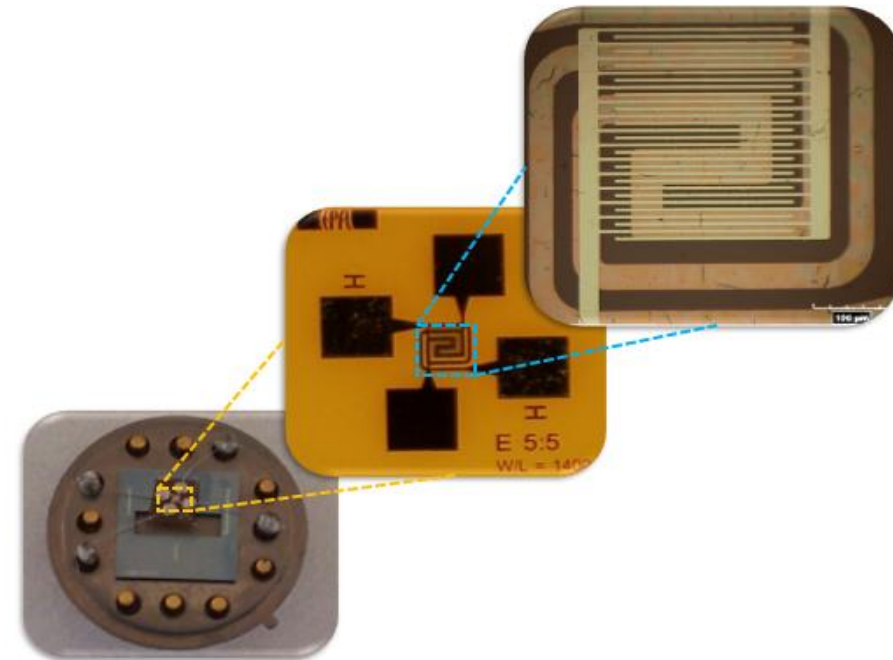
CARBON 78 (2014) 510-
520

Sensor preparation

Ceramic

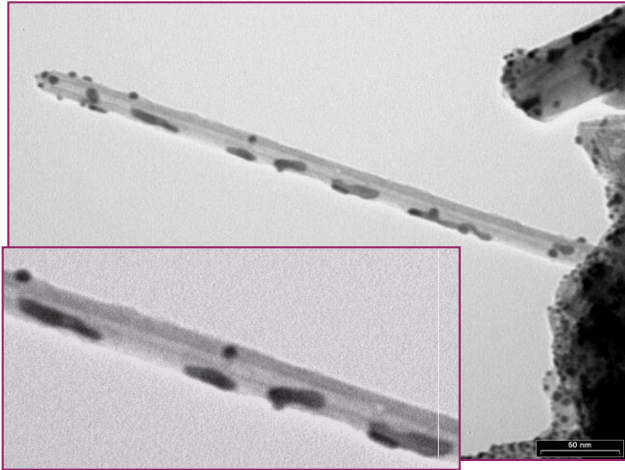


Polymeric

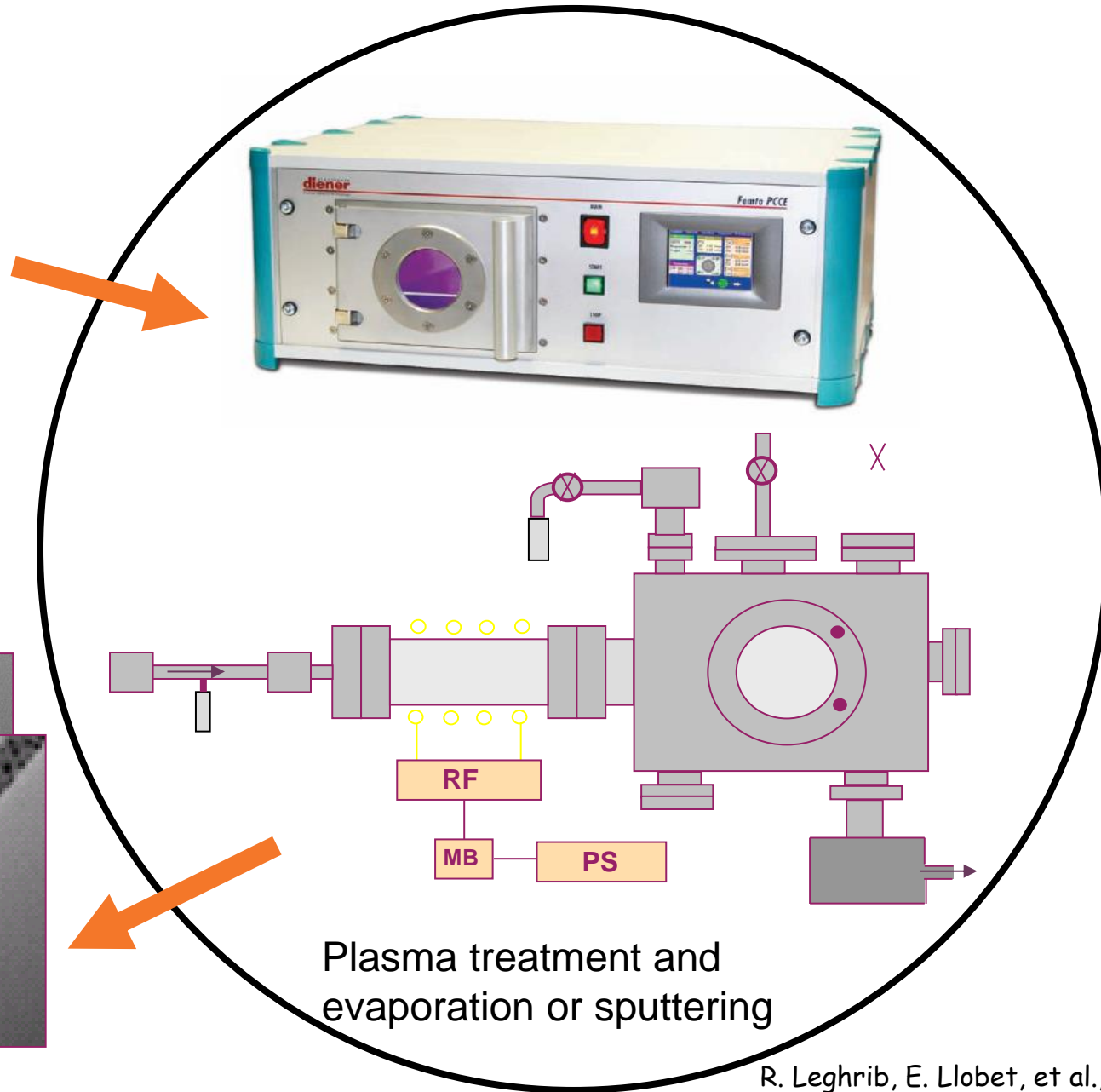
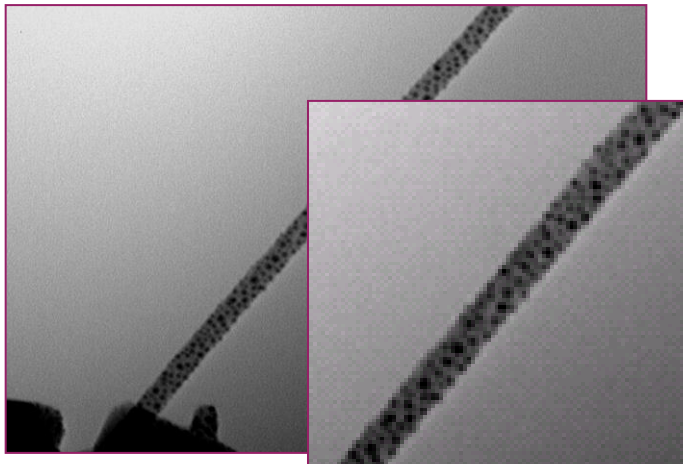


Sensor preparation

as grown MWCNTs



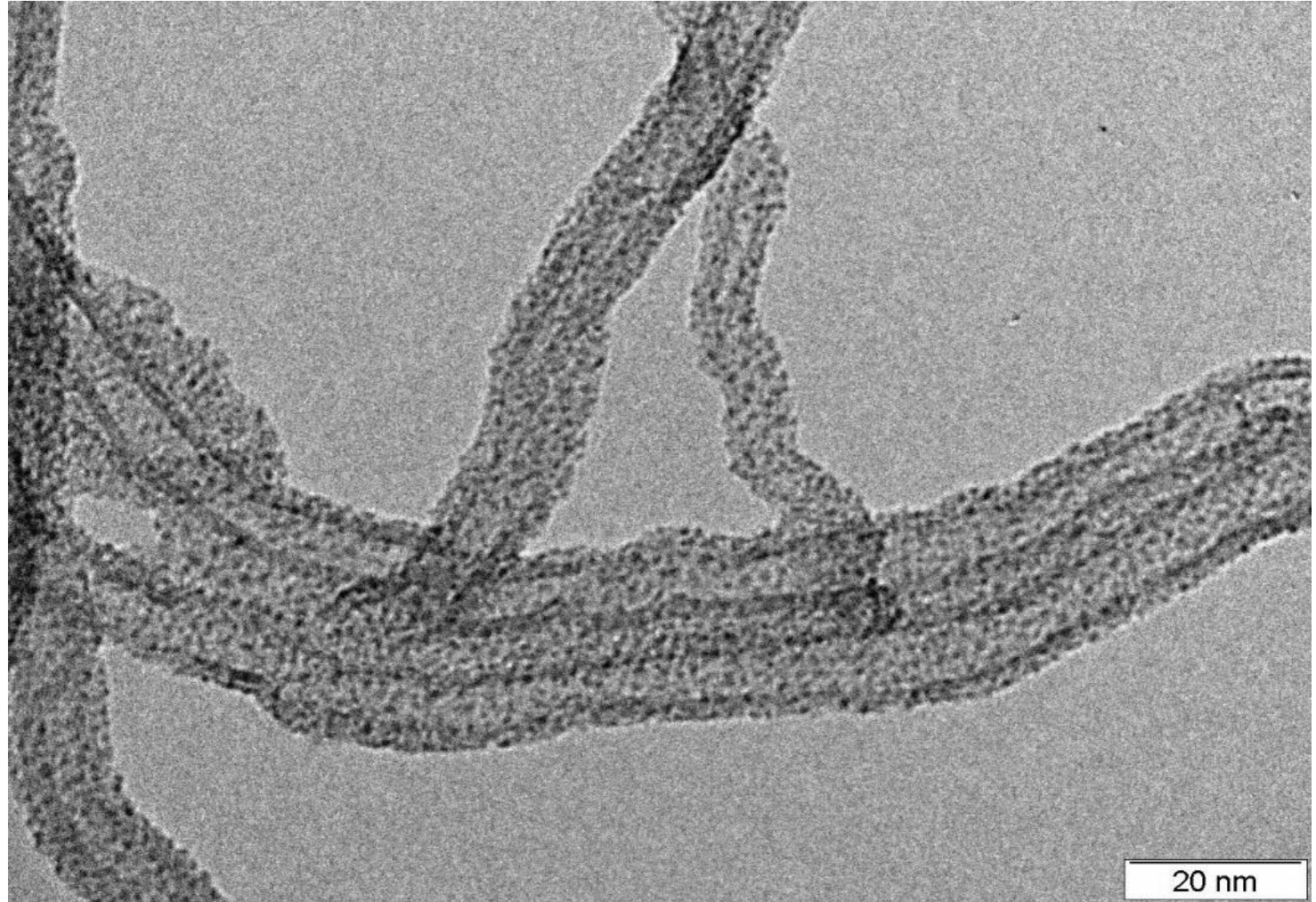
O₂



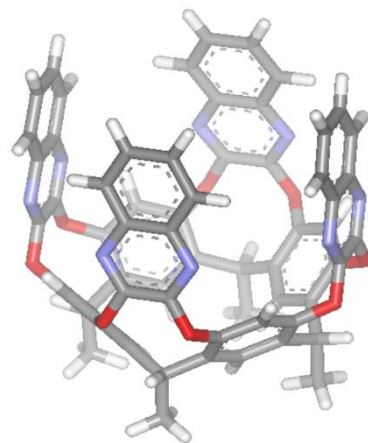
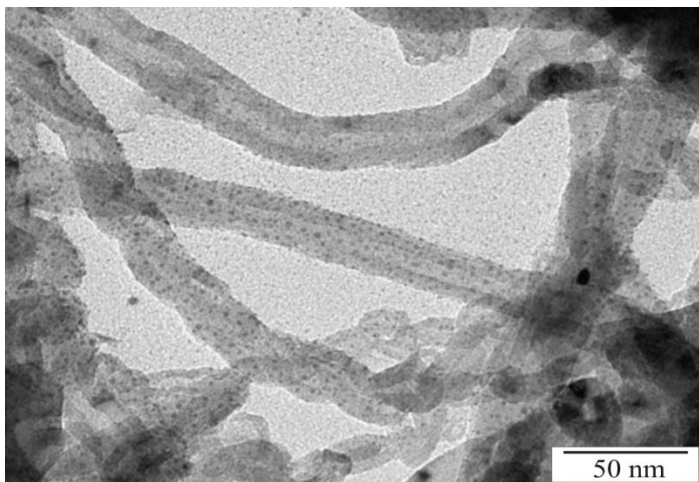
Plasma treatment and
evaporation or sputtering

Sensor preparation

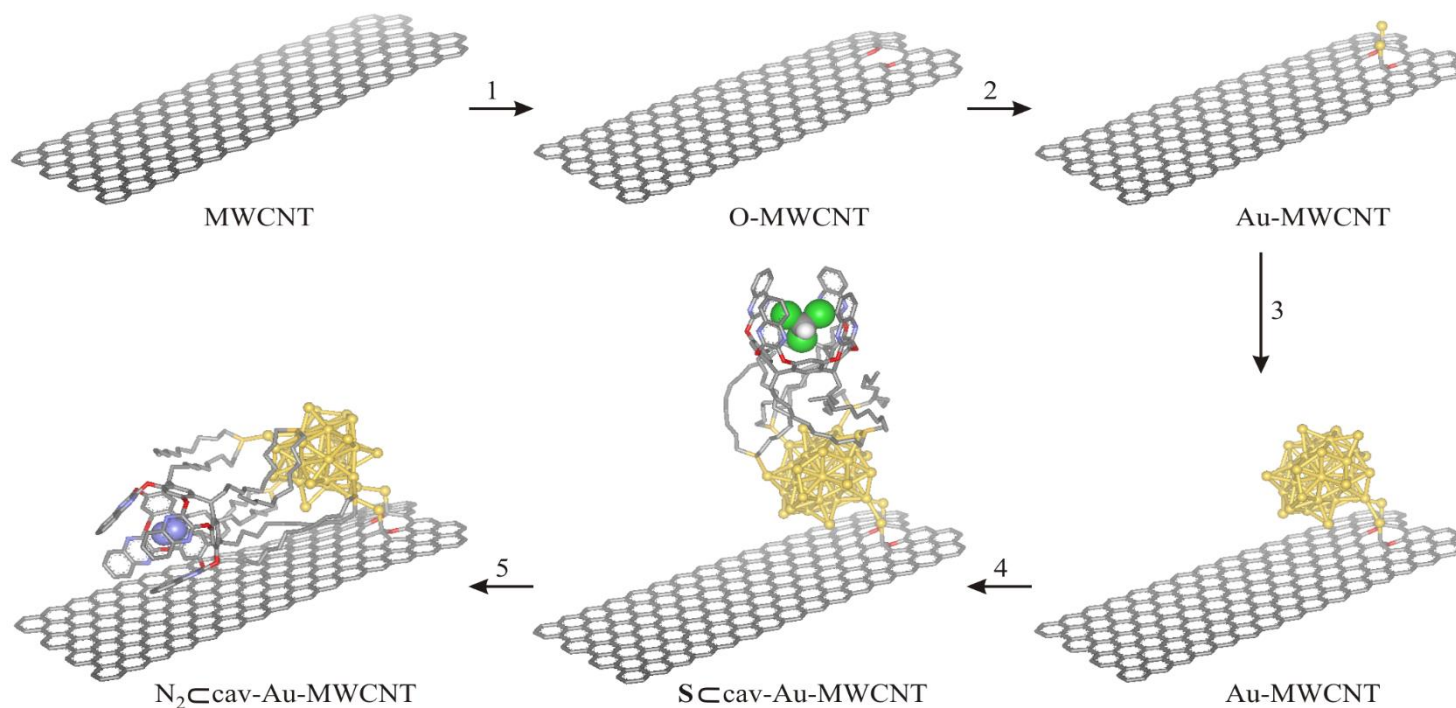
Au-CNT



Functionalisation with deep-cavitands



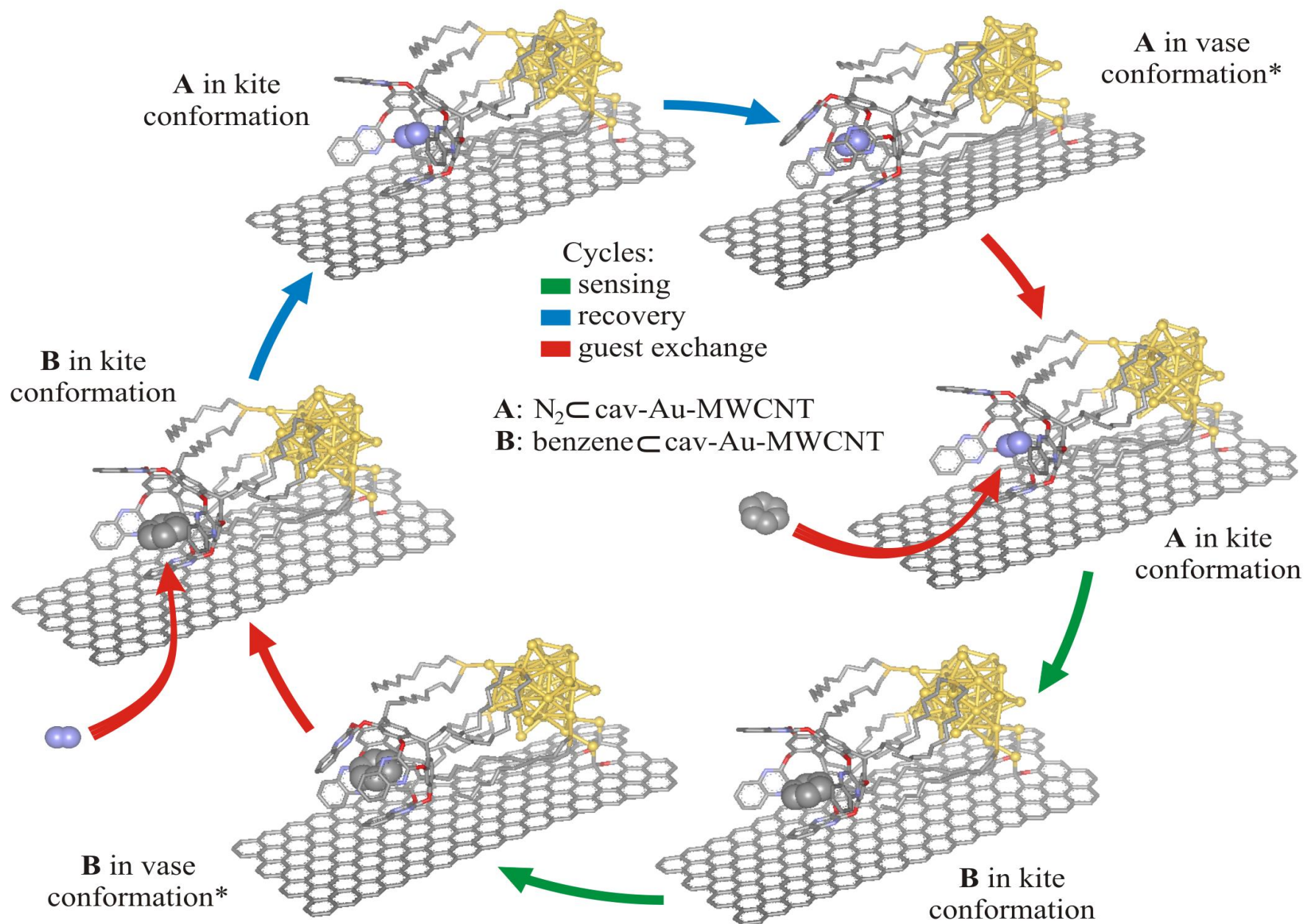
SAM of a
quinoxaline-walled
thioether-legged
cavitand



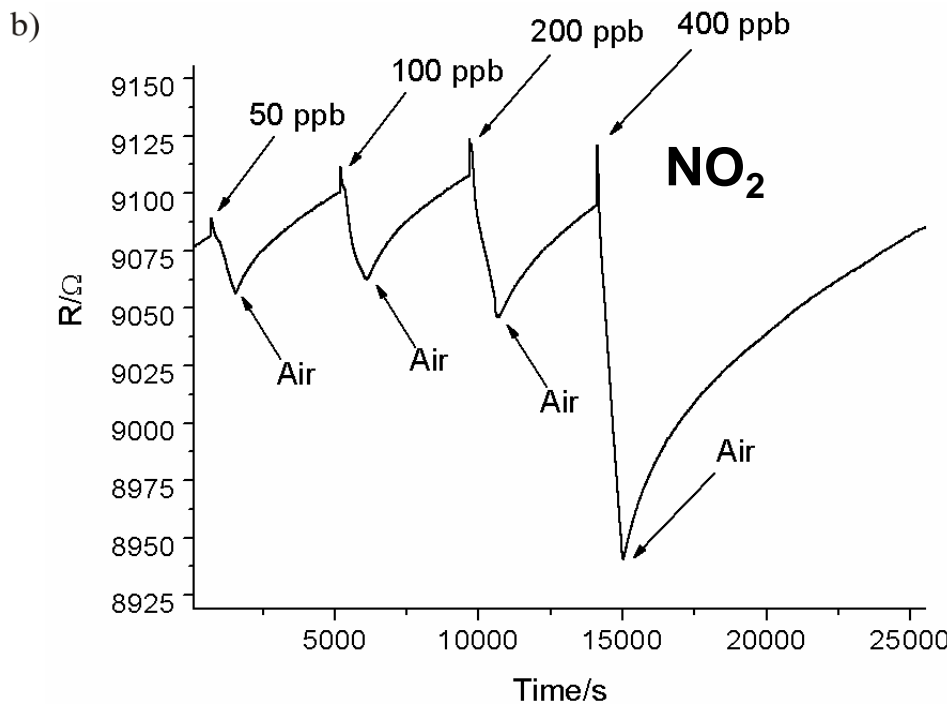
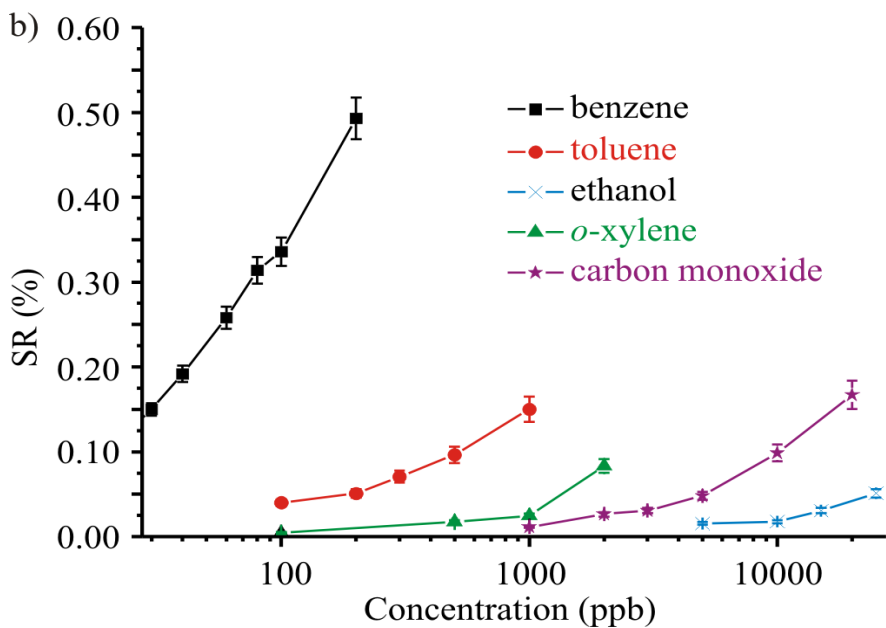
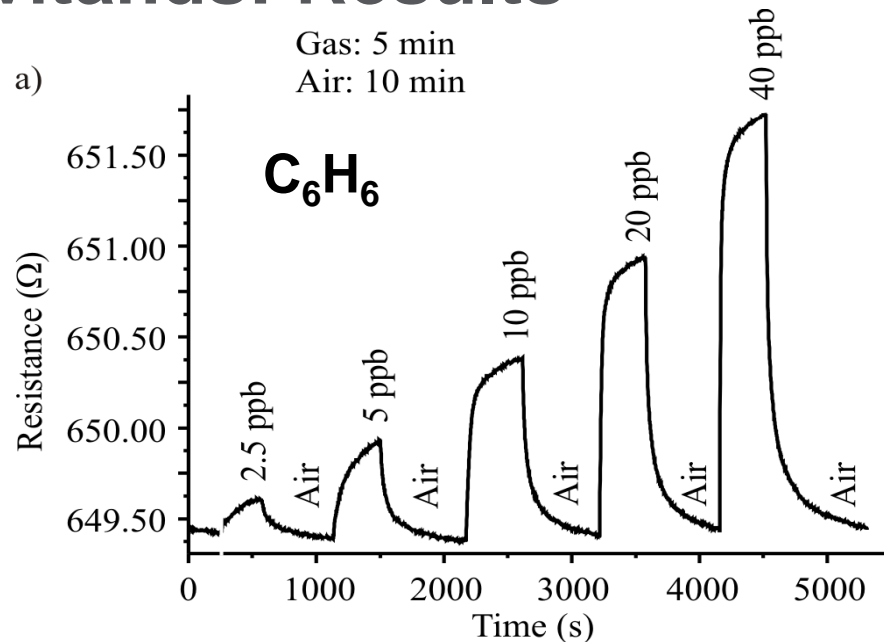
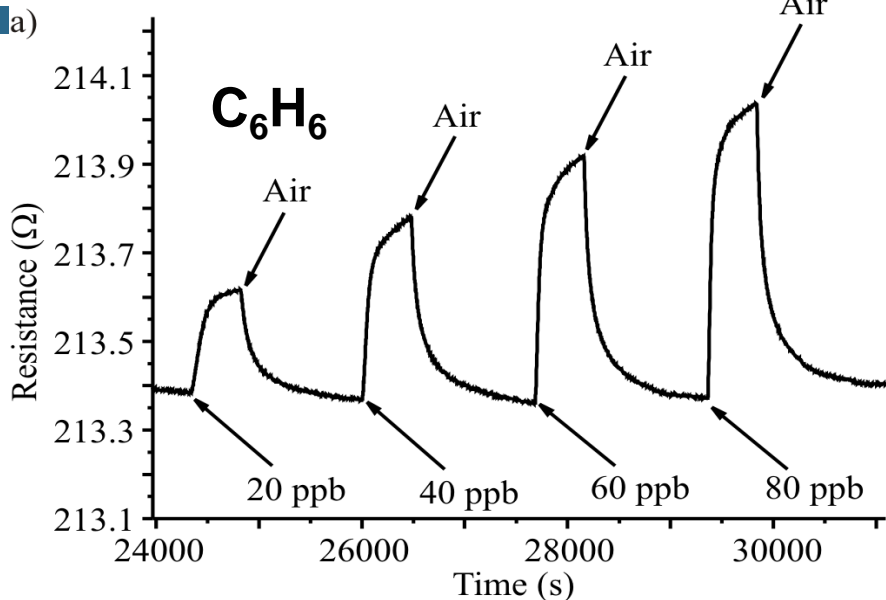
P. Clément, E.J. Parra..., E. Llobet. *Advanced Functional Materials* 25, **2015**, 4011-4020.

Patent filed
PCT/ES2015/070818, Nov.
2015

Functionalisation with deep-cavitands

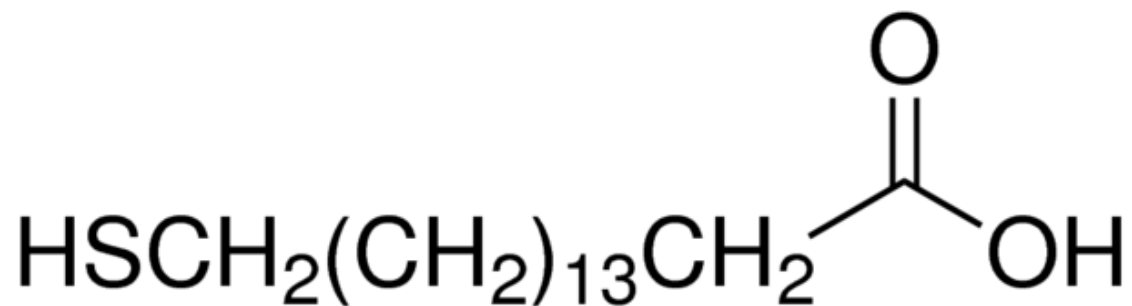


Functionalisation with deep-cavitands: Results

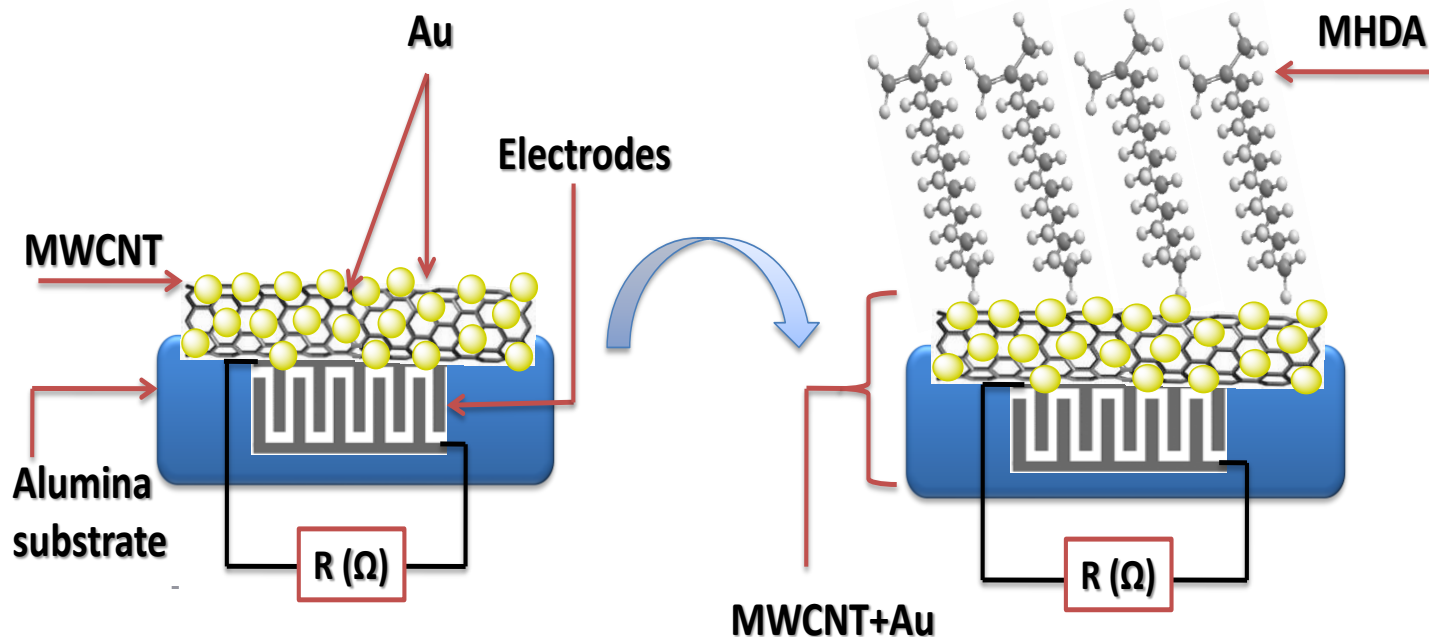


Functionalisation with long-chain mercaptans

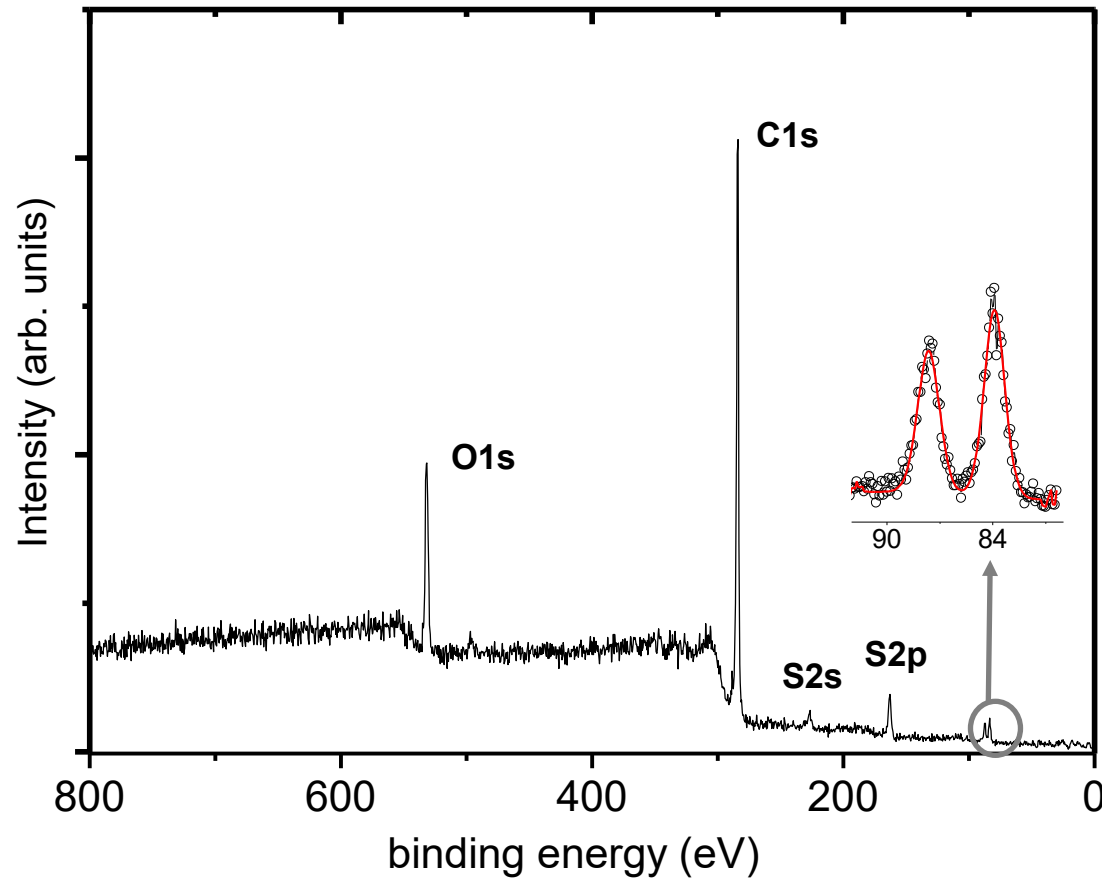
A. Thamri, E. Llobet. et al.,
Submitted, 2016.



16 Mercaptohexadecanoic acid (MHDA)

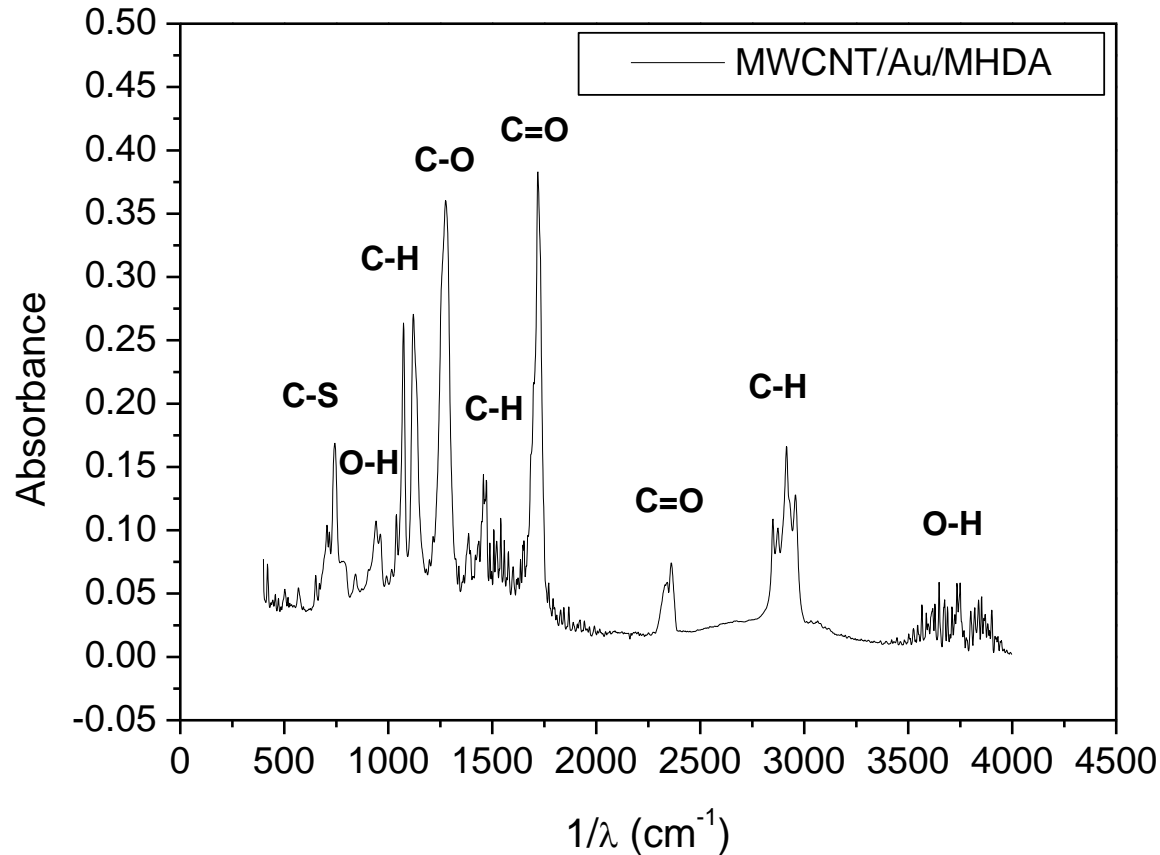


Functionalisation with long-chain mercaptans



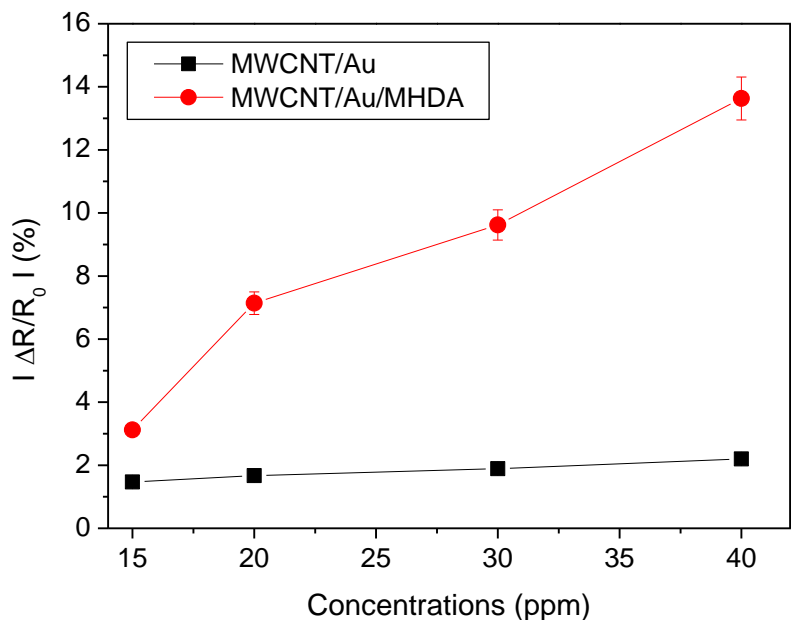
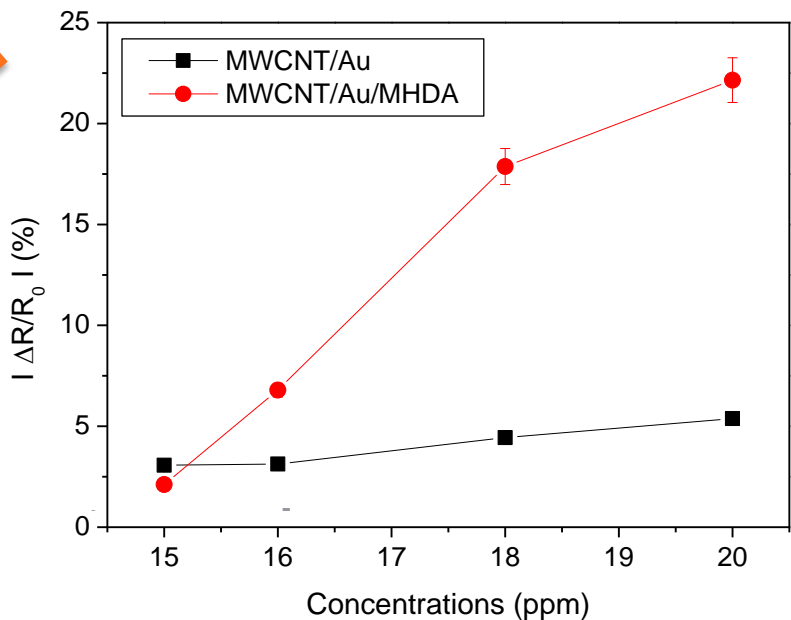
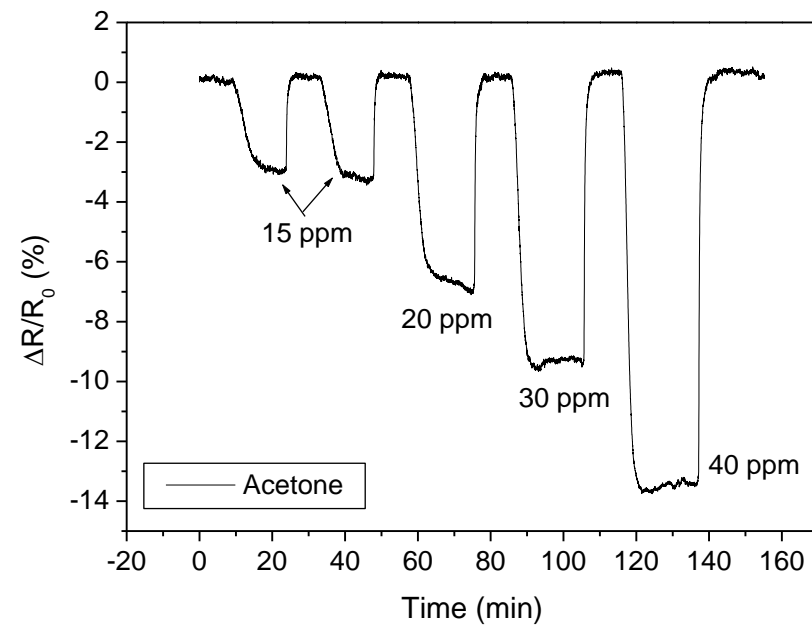
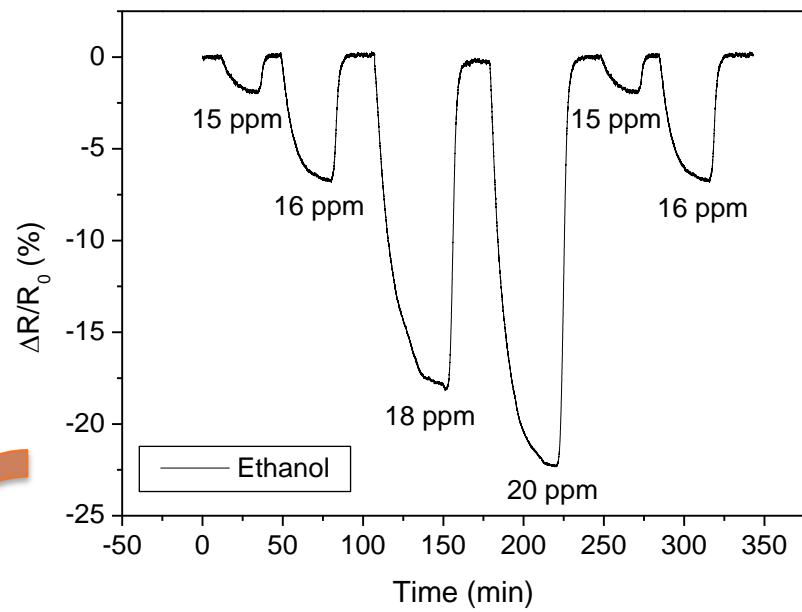
XPS: Survey spectrum of the MWCNT/Au/MHDA gas-sensitive nanomaterial

Functionalisation with long-chain mercaptans

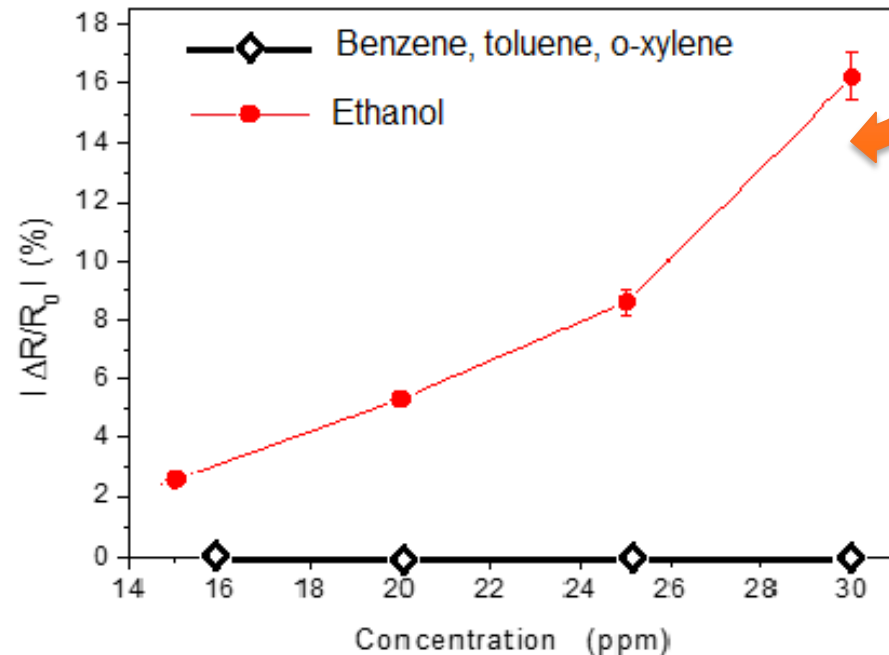
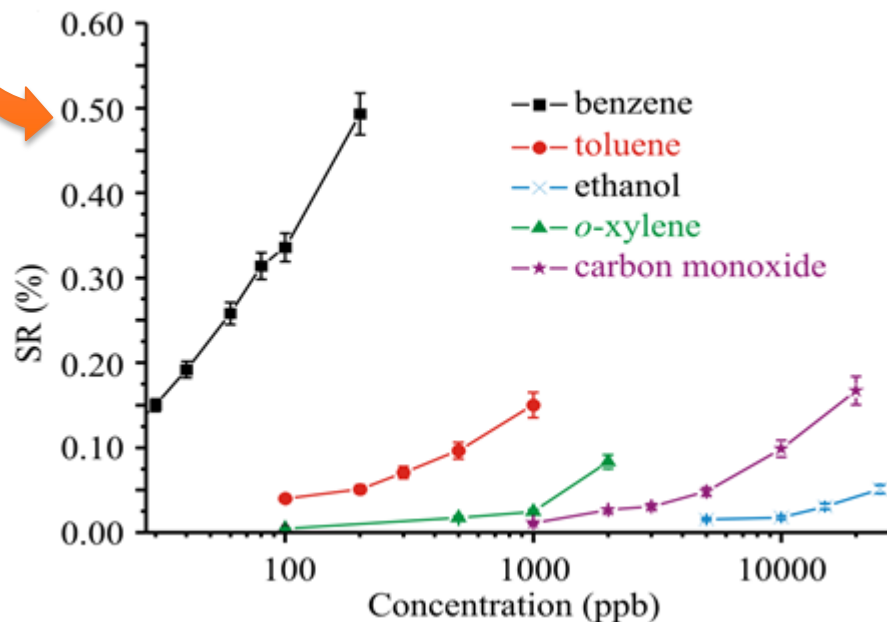
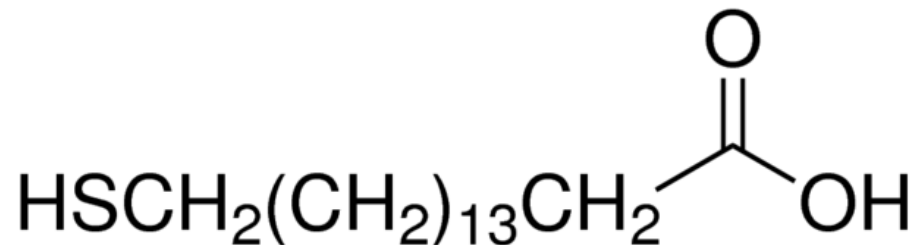
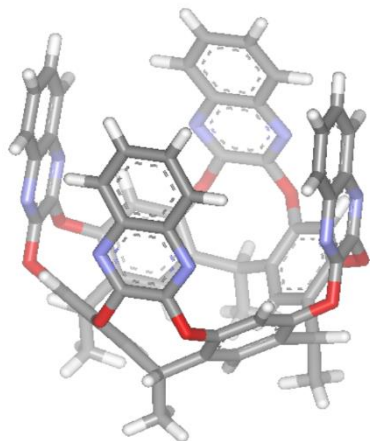


FT-IR spectrum of a film consisting of 16-mercaptohexadecanoic acid deposited on MWCNTs/Au.

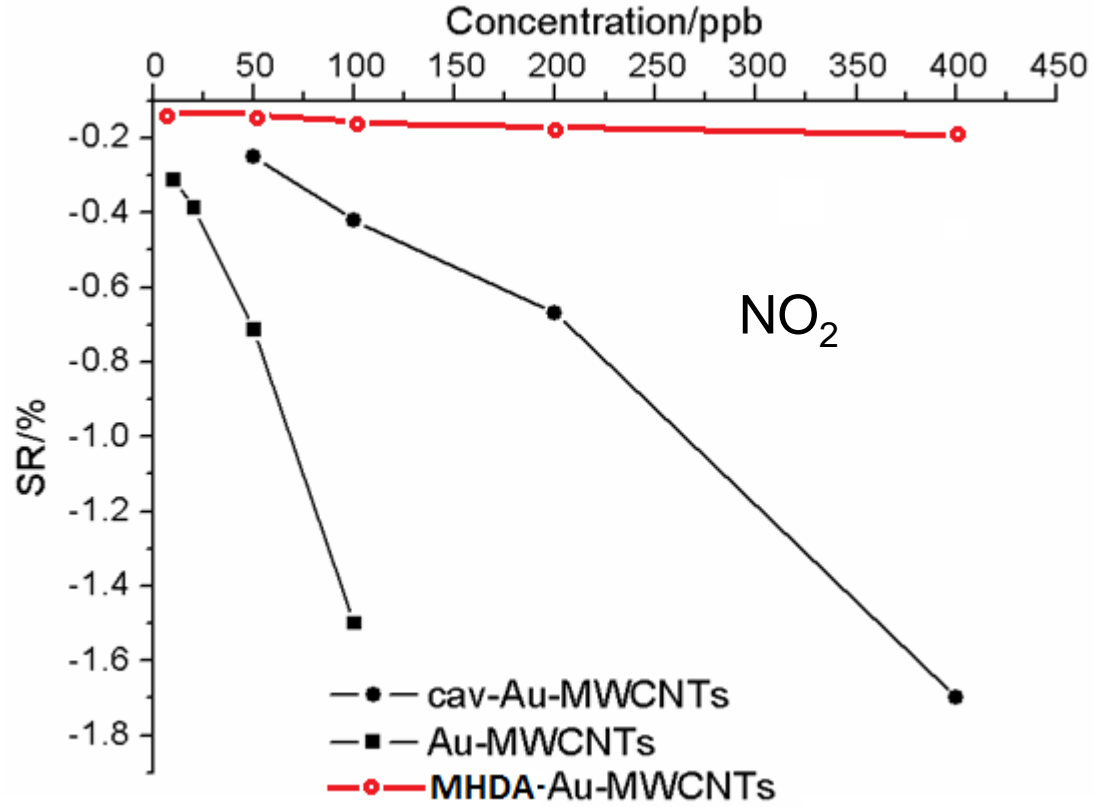
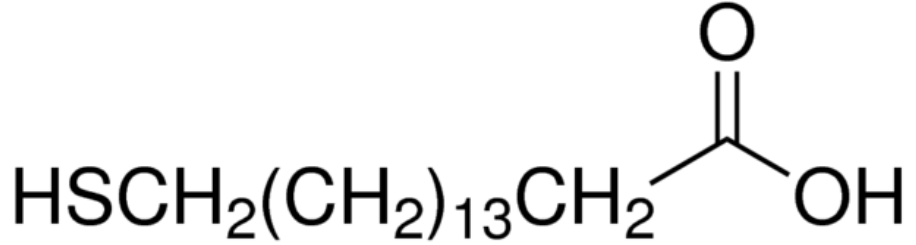
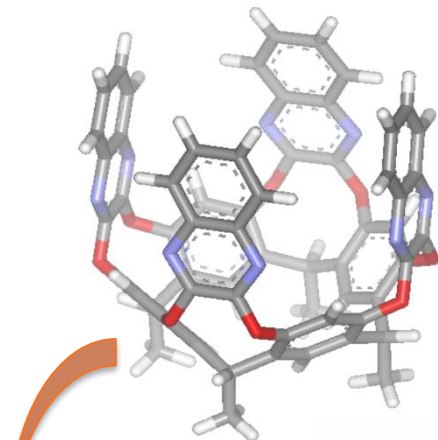
Functionalisation with long-chain mercaptans: Results



Detection results: deep cavitands vs. MHDA



Detection results: deep cavitands vs. MHDA



Conclusions and outlook



- CNTs enable the detection of a-VOCs with sensors that can be fully operated at room temperature.
- Functionalisation with SAMs of macromolecules helps dramatically increasing sensitivity and promotes selectivity.
- Changing the length of the chain molecule and the nature of the terminal functional group (hydrophilic/ hydrophobic) should bring about new functionalities to the nanohybrid material.

Acknowledgements

P. Ballester, ICIQ, Spain
A. Abdelghani, INSAT, Tunisia
C. Bittencourt, UMONS, Belgium
P. Umek, JSI, Slovenia
C. Cané, I. Gràcia, IMB-CNM-CSIC, Spain
D. Briand, N. de Rooij, EPFL, Switzerland

Funded by:

- **ICREA Academia Award**
- **MINECO grant no. TEC2012-32420**
- **NATO under the Science for Peace Programme grant no. SPS 984511**
- **Autonomous Government of Catalonia grant no. 2014 SGR 1267.**
- **European Science Foundation grant COST TD-1105 ‘EuNetAir’**
- **European Commission, H2020 Project ‘TROPSENSE’**

