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

MSDI HETEROJUNCTIONS, FROM IMPEDANCE AND CHEMO-SENSING STUDIES TO GAS SENSORS IN TRUE ATMOSPHERE

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Scientific context and objectives in the Action

- **Background / Problem statement:** Guidelines for Best Coupling Air-Pollutant and Transducer (SIG 3)

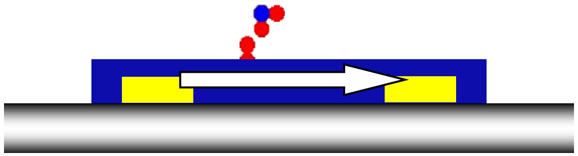
- **Objective:** To operate a same conductometric device in different ways to achieve a better selectivity ?

- **Outline:** - Presentation of the device

  - Current = f(t)

  - Impedance = f(frequency)

Conductometric Gas Sensors



Resistor

Conductivity: $\sigma = n\ e\ \mu$

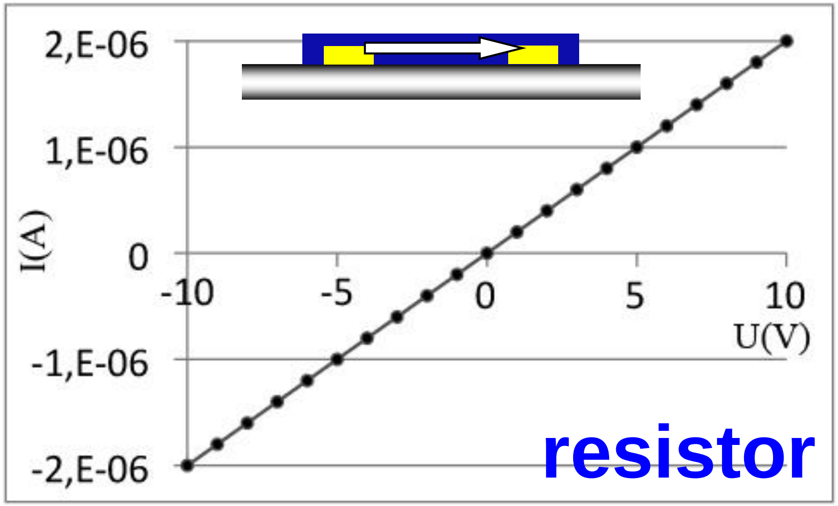
For redox active species, variation of n by doping or neutralization of charge carriers: $\Delta[\text{Gas}] \Rightarrow \Delta n \Rightarrow \Delta\sigma$

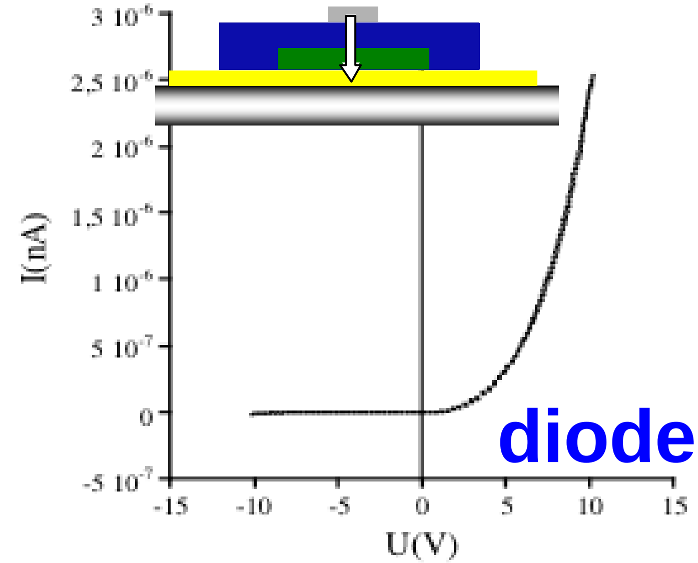
Thus, in a p-type material, a donating species like NH_3 can give 1 electron to the material, neutralizing the positive charge carriers, leading to a decrease of σ.

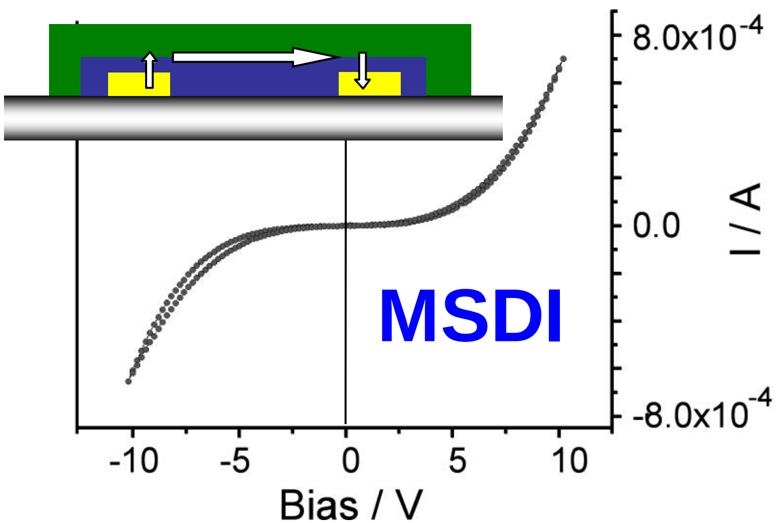
But for non redox active species, variation of μ due to the variation of the dielectric constant of the sensing material: $\Delta[\text{Gas}] \Rightarrow \Delta\varepsilon \Rightarrow \Delta\mu \Rightarrow \Delta\sigma$

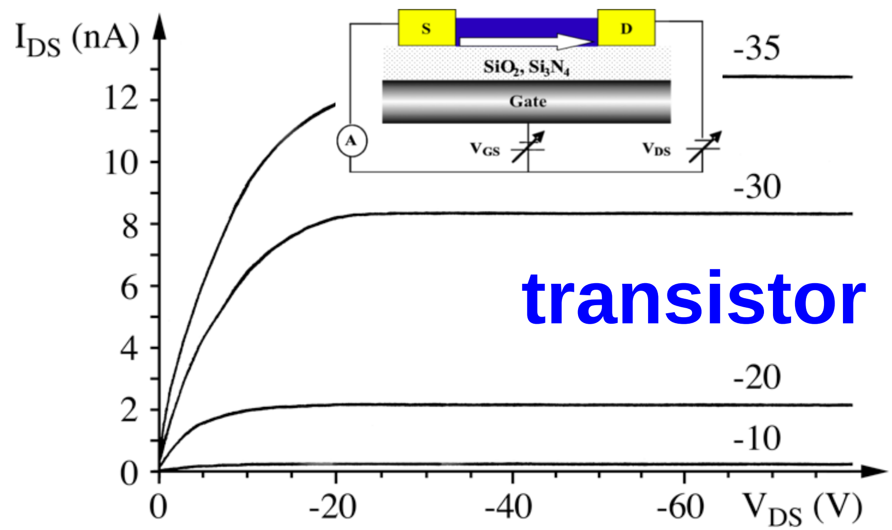
M. Bouvet, A. Pauly, "Molecular Semiconductor - Based Gas Sensors" in The Encyclopedia of Sensors, ed. by C.A. Grimes, E.C. Dickey, M. V. Pishko, American Scientific Publishers, vol 6, 2006, pp 227-270.

Conductometric Gas Sensors

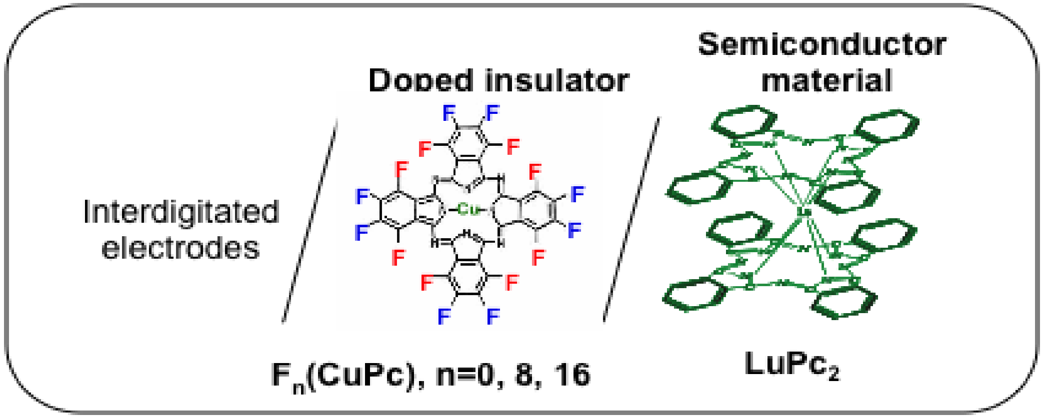


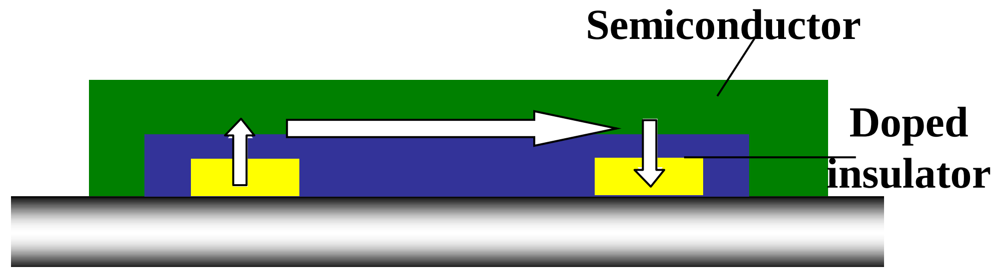


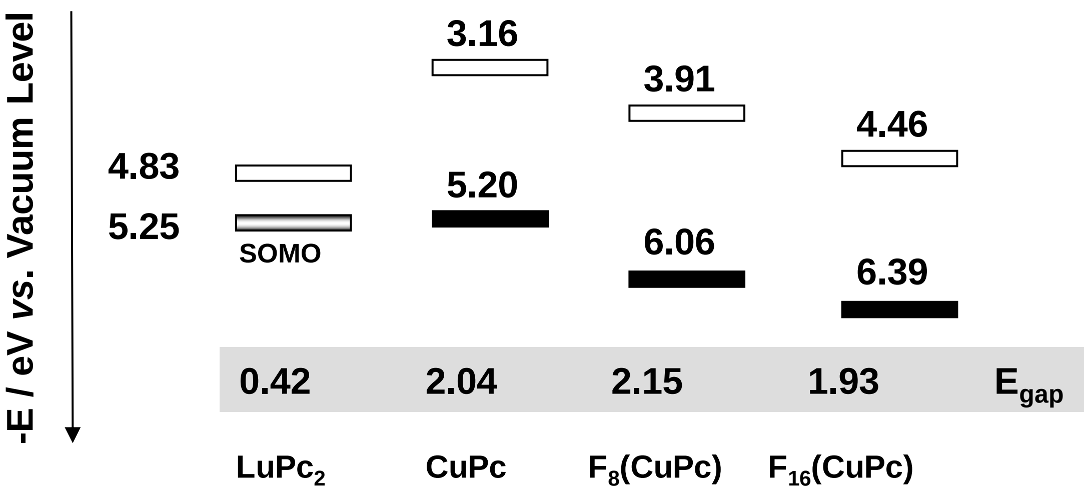


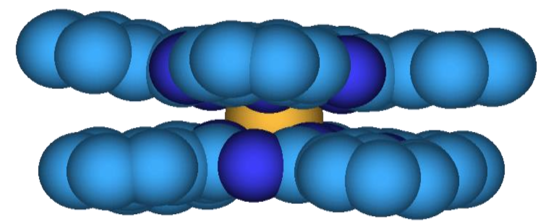


Molecular Semiconductor - Doped Insulator heterojunctions (MSDI)





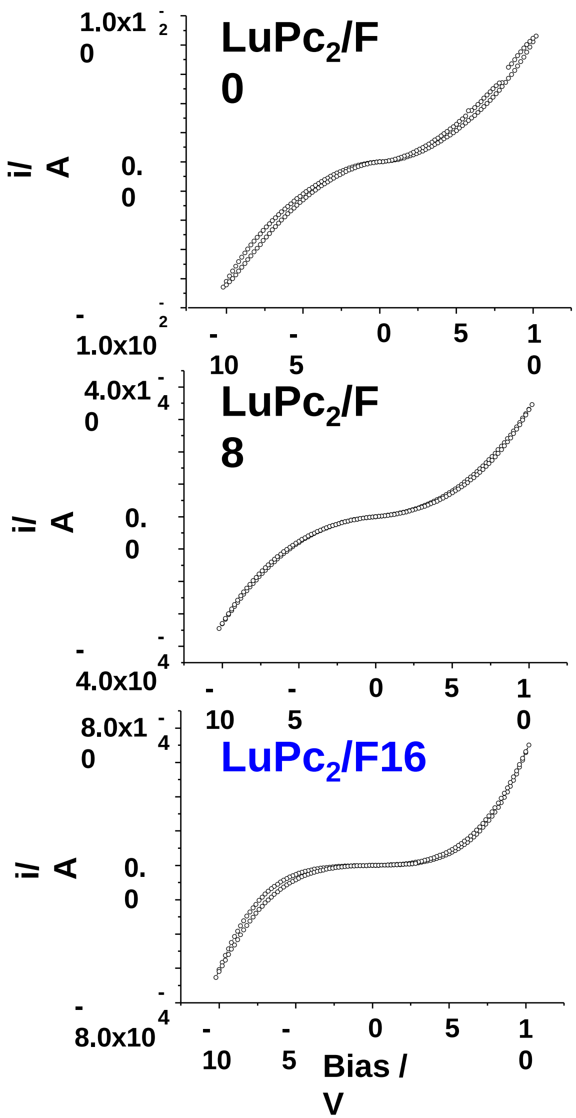


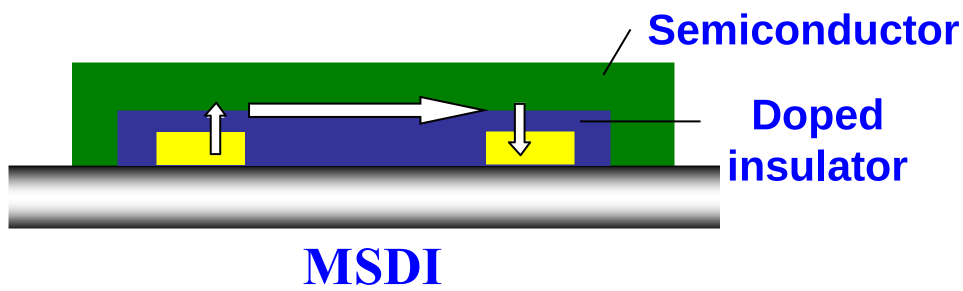


$LuPc_2$ E_{ox}-E_{red} = 0.48 V

V. Parra, J. Brunet, A. Pauly, M. Bouvet, "Molecular semiconductor - doped insulator (MSDI) heterojunctions: An alternative transducer for gas chemosensing", *Analyst*, 134, 1776-1778, 2009.

MSDI heterojunctions



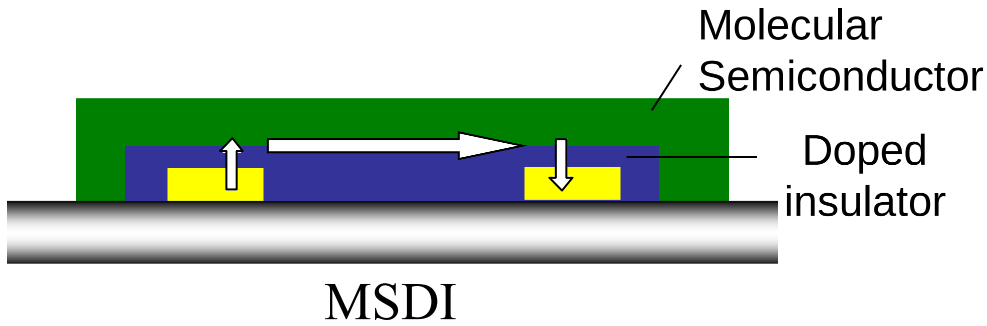


The energy barrier increases from F0 (p-type) to F16 (n-type) since LuPc$_2$ is of p-type in air,

M. Bouvet, V. Parra, Patent Application n° 07/07209, filed on 15/10/2007 by UPMC and CNRS; and PCT 2008/001325, 24/09/2008.

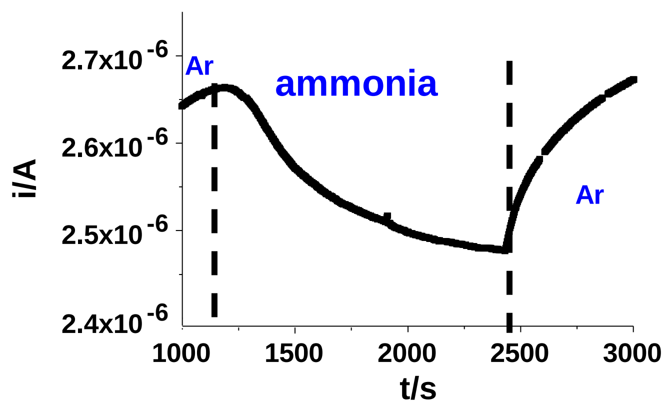
V. Parra, J. Brunet, A. Pauly, M. Bouvet*, "Molecular semiconductor - doped insulator (MSDI) heterojunctions, an alternative transducer for gas chemosensing", *Analyst*, 134, 1776-1778, 2009

Sensitivity to Ammonia of p- and n-MSDIs

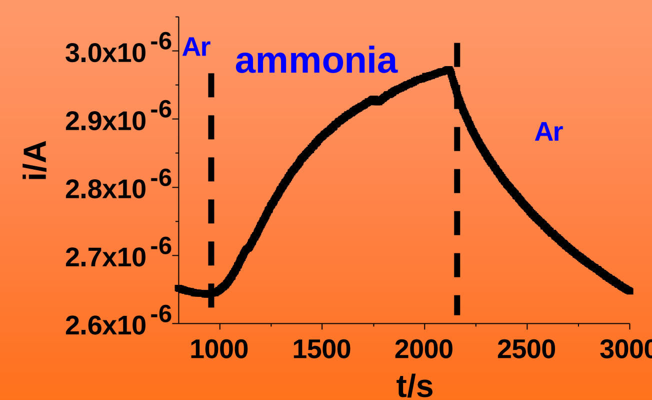


An energy barrier E_{p-n} exists at the interface between the two layers

p-MSDI, $[LuPc_2^+]$ ↘ and I ↘



n-MSDI, E_{p-n} ↘ and I ↗



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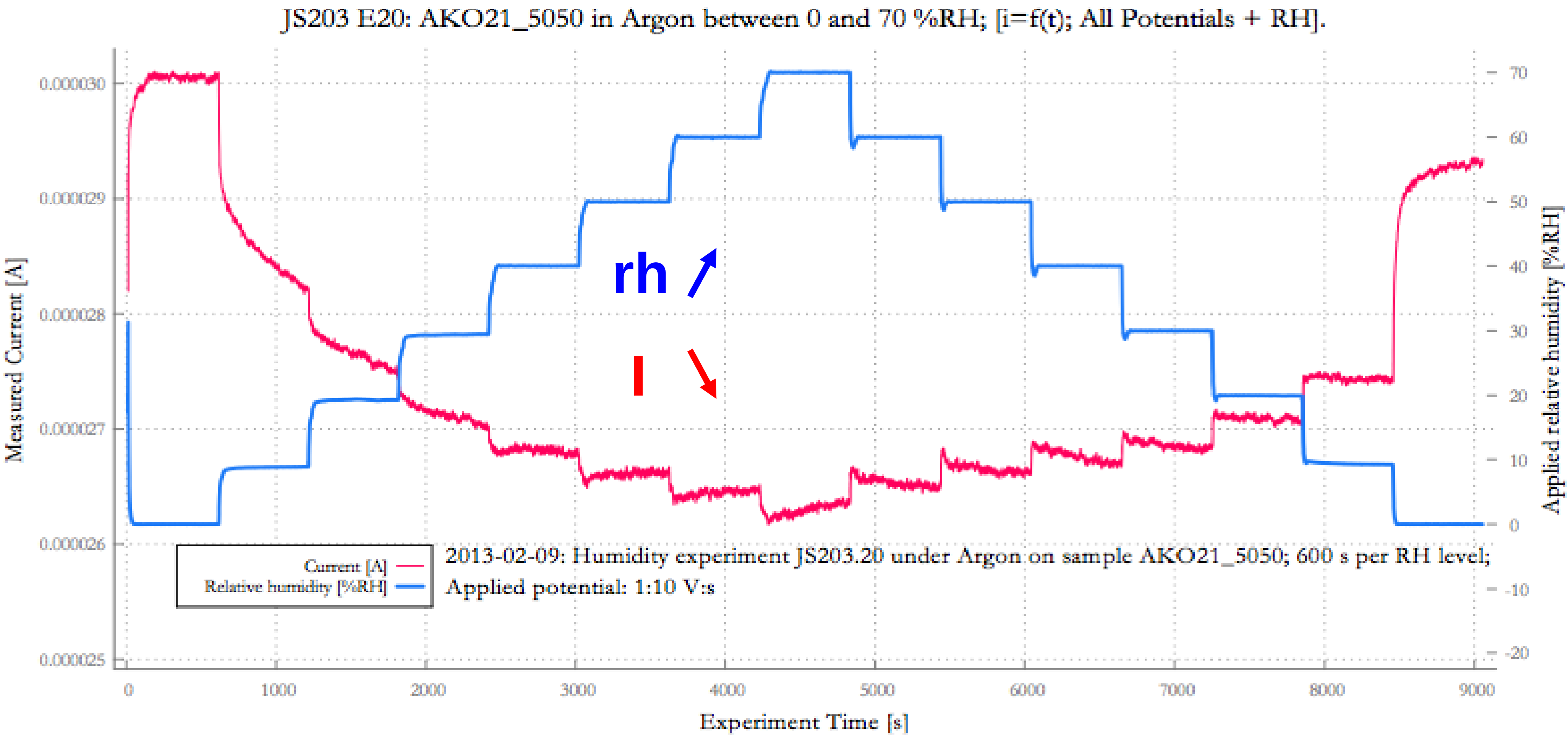
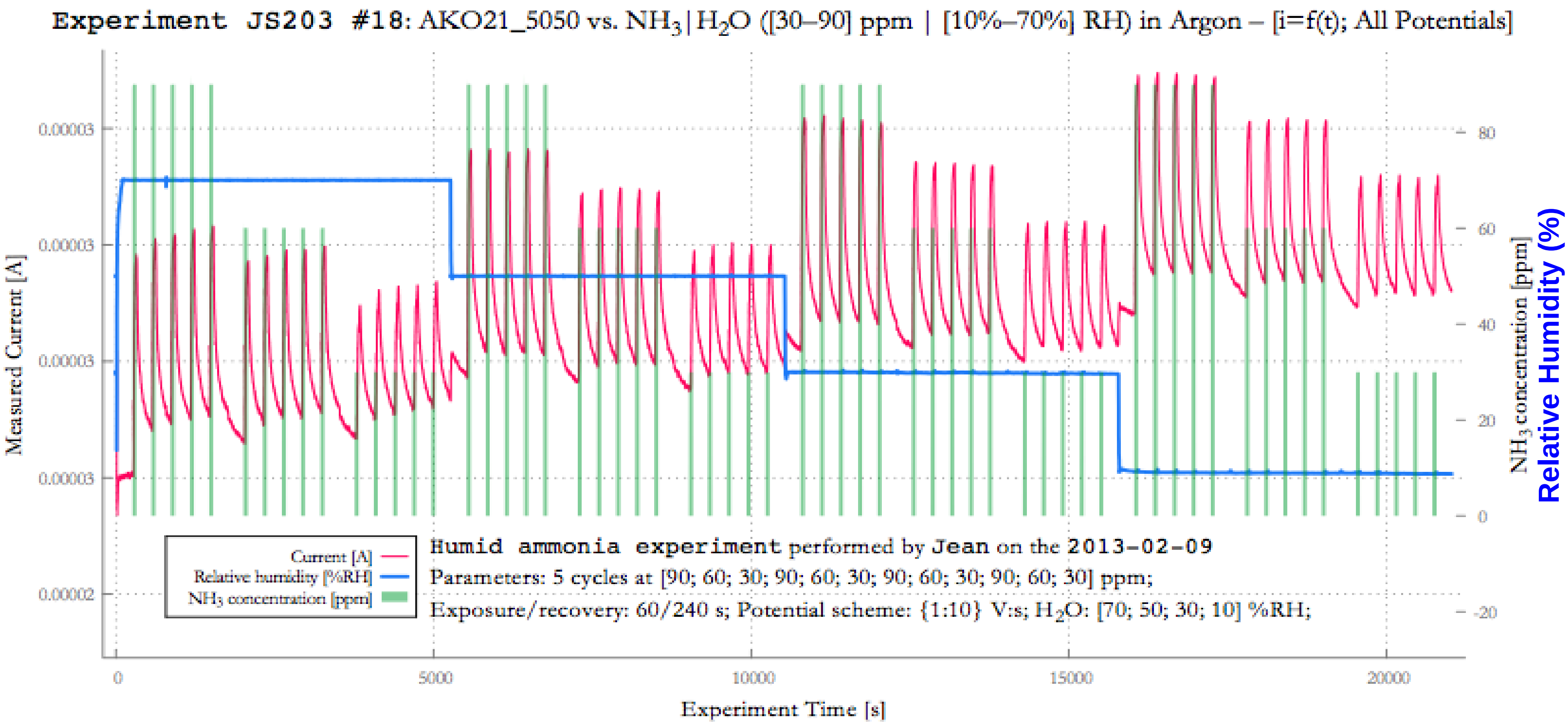
Sensitivity to Humidity of n-MSDIs



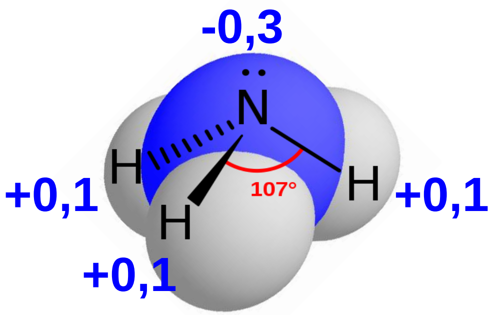
H_2O is a donating species But σ ↘ like NH_3

Sensitivity to Ammonia of n-MSDIs

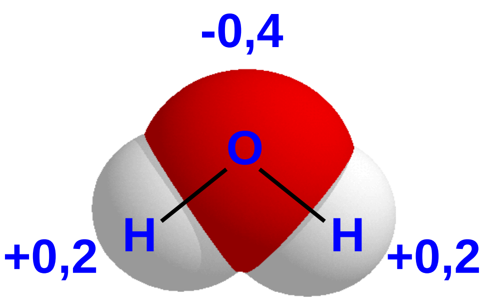


NH_3: σ ↗ **H_2O : σ ↘**

Discrimination between NH_3 and H_2O

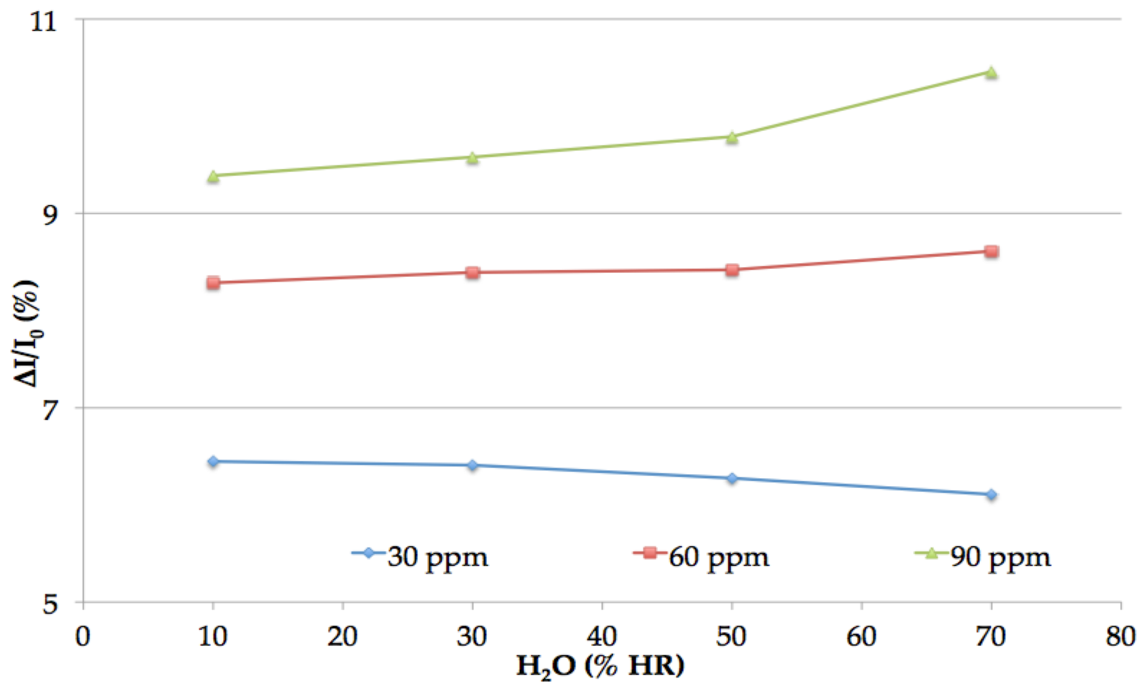


μ = 1,49 D
ε = 22



μ = 1,85 D
ε = 80

Relative response: $\Delta I/I_0 = (I - I_0)/I_0$ =f(Relative Humidity)

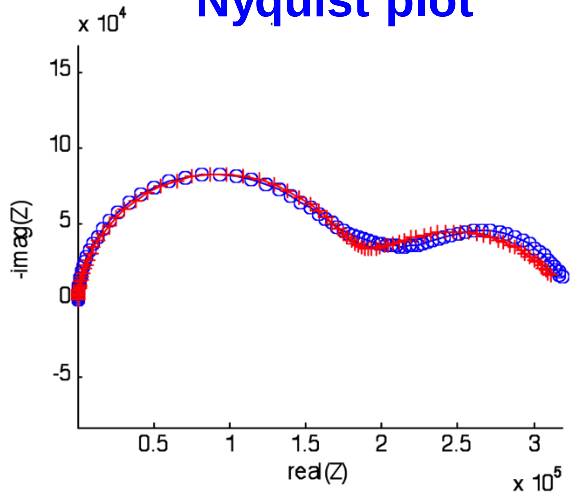


⇒ Good discrimination of NH_3 concentrations whatever the RH in the 10-70 % range

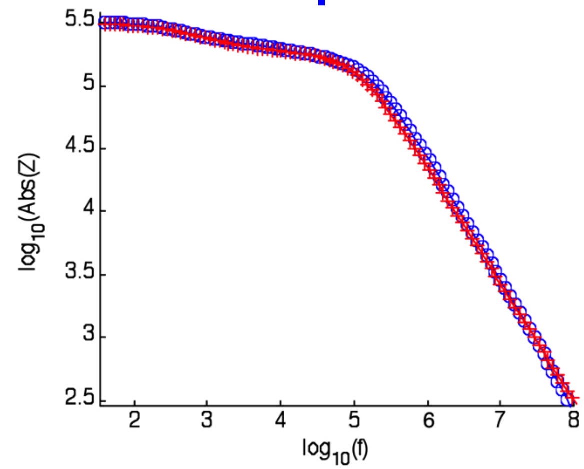
Impedance = f(frequency)

n-MSDI

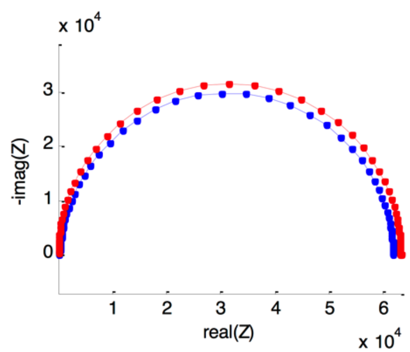
Nyquist plot

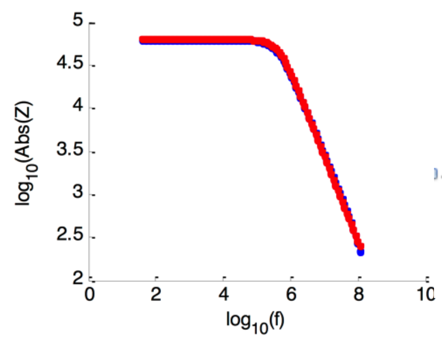


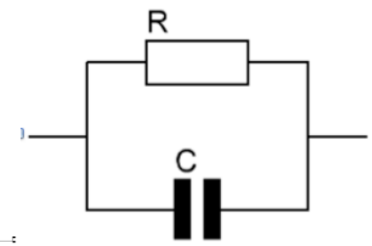
Bode plot



$LuPc_2$ resistor

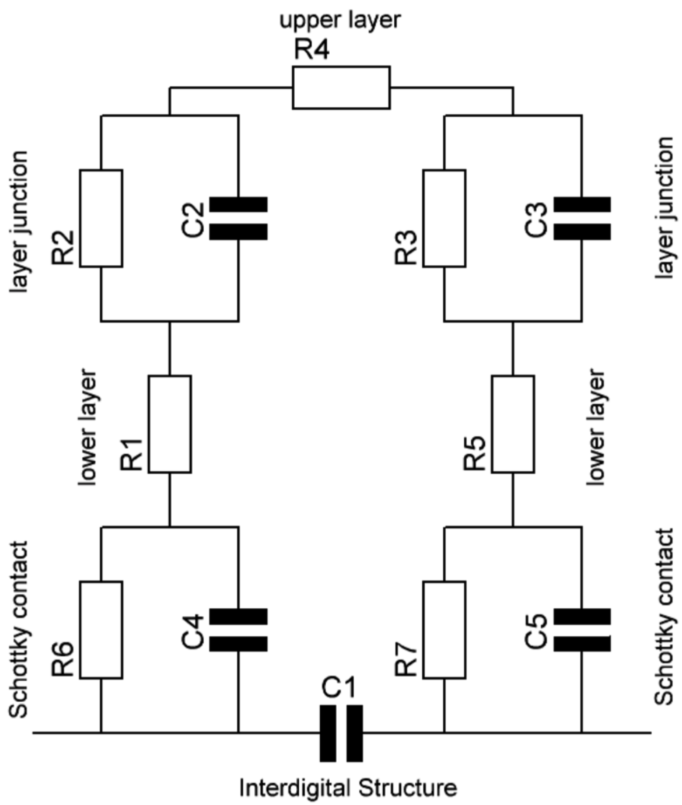


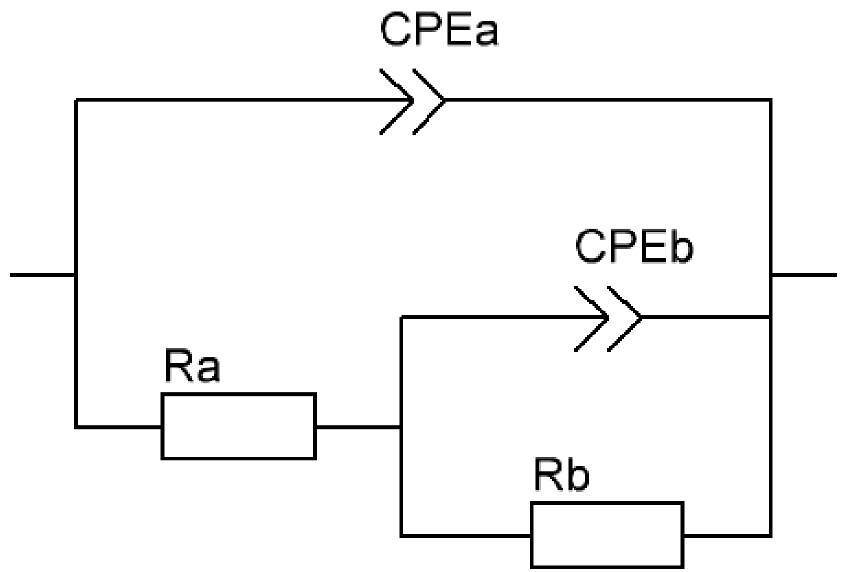




M. Bouvet*, P. Gaudillat, A. Kumar, T. Sauerwald, M. Schüler, A. Schütze*, J.-M. Suisse, "Revisiting the electronic properties of Molecular Semiconductor – Doped Insulator (MSDI) heterojunctions through impedance and chemosensing studies", Org. Electron., 26 (2015), 345-354.

Equivalent circuit



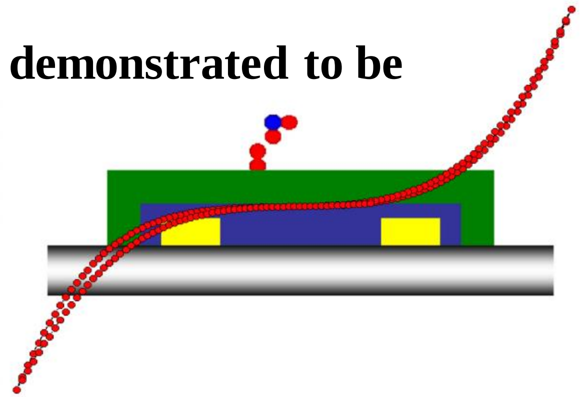


$Z_{CPE} = 1/(Q\ .\ (j\omega)^{\alpha})$
with $\omega = 2\pi f$, where Q is the capacity, f the frequency and α a coefficient.
For the special case of $\alpha = 1$, a CPE equals an ideal capacitor with Q = C.
It can also represent a normal resistor ($\alpha = 0$), or a so-called Warburg element ($\alpha = 0.5$).

M. Bouvet*, P. Gaudillat, A. Kumar, T. Sauerwald, M. Schüler, A. Schütze*, J.-M. Suisse, "Revisiting the electronic properties of Molecular Semiconductor – Doped Insulator (MSDI) heterojunctions through impedance and chemosensing studies", Org. Electron., 26 (2015), 345-354.

Conclusion

MSDIs: New heterojunctions based on molecular materials were demonstrated to be promising transducers for gas chemosensing
(Ex.: For O_3 in the ppb range and for NH_3 in the ppm range)



MSDIs are a new conductometric transducer; they can be operated in different ways :

- **Current = f(t): simple**
- **Impedance = f(frequency): more powerful because more data, but requires more data treatment**

$LuPc_2$/Cu(F_{16}Pc) n-type MSDI exhibits a very good stability of the response to NH_3 over a broad range of RH.

Research directions: To tune the electrode-sublayer interface, by chemical or electrochemical modifications, and study it by impedance spectroscopy

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