ESRF	**Experiment title:** Gas sensitive Pd containing organometallic macromolecules with functionalised end groups: metal-gas interaction studied by EXAFS	**Experiment number**: **08-01- 838**
Beamline: BM08	**Date of experiment**: from: 07/ 05/ 2010 to: 13/05/2010	**Date of report**: 11/02/2011 *Received at ESRF:*
Shifts: 15	**Local contact(s)**: Dr. Chiara Maurizio	

Names and affiliations of applicants (* indicates experimentalists):

C. Battocchio[1*], G. Polzonetti[1], I. Fratoddi[2*], M. V. Russo[2].

[1] University of “Roma Tre”, Dept. of Physics, Via della Vasca Navale 84, 00146, Rome

[2] University “La Sapienza”, Dept. of Chemistry, P.le A. Moro 5, 00185, Rome

Report:

Introduction:

In the framework of sensors devices, our research program concerns the EXAFS investigation of novel nanostructured and single-molecule organometallic systems, and the study of their interaction with small gaseous molecules.

Since the last decade, great attention has been paid by the scientific community to the synthesis and characterization of polymeric conjugated systems containing transition metal centers σ- or π-bonded to the organic main chain [1]. In this field, the charge transport in model Pt and Pd acetylides was investigated [2] in view of applications for molecular electronics. In fact, rigid-rod π-conjugated transition metal oligomers constitute a potentially new class of molecular wires and there are several studies regarding the electron transfer in α,ω-dithiol, thioacetyl, or α,ω-dithioacetyl endgroups, necessary for the formation of self-assembled monolayers (SAMs) or covalent connections between gold electrodes [3].

The chemical and electronic structure of polymetallyynes, i.e. Pt and Pd-containing *rod-like*organometallic polymers with diethynyl organic spacers [4] that are the building blocks of these materials, have been thoroughly investigated by means of SR-XPS, NEXAFS [5], reflEXAFS and EXAFS [6]. Simpler related model molecules have been recently synthesized to have model systems whose characterization would be crucial for the interpretation of the chemical physical properties of the polymers. In this framework, Pt and Pd based binuclear complexes Pt_2-DEBP-Cl_2, Pd_2-DEBP-Cl_2 and Pd_2-DEBP-SR have been investigated by means of X-ray Photoemission (XPS) and X-ray Absorption (EXAFS) spectroscopies, and molecular and electronic properties such as the square planar structure around the transition metal, charge transfer interaction between units [7,8] have been assessed. Furthermore, Pd_2-DEBP-SR molecules have been successfully anchored on gold nanoparticles and exposed to NO, showing an interesting gas-sensitivity [9].

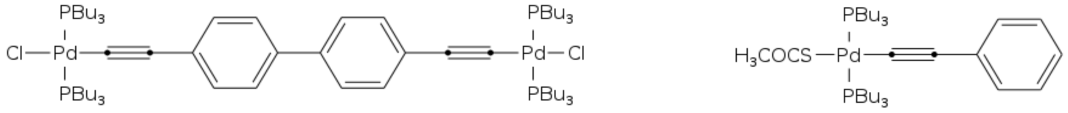
The main objective of this project was to correlate the chemical, geometrical and electronic structure of small Pd containing organometallic systems with different terminal groups (chlorine or thiolate) and their sensitivity and selectivity with regard to gaseous molecules containing sulfur, such as H_2S and SO_2. During the previous experiment **08-01-767**, X-ray Absorption measurements were successfully performed on Pt poly-ynes exposed to H_2S; EXAFS data analysis evidenced an interaction between the metal, covalently bonded to the diethynyl-macromolecule, and H_2S molecules, inducing structural modifications at the Pt coordination centre [10].

To develop the study started in experiment **08-01-767**, our investigation has been extended to the interaction between Pd-diethynylbiphenyl-Cl_2 systems and the corresponding thiolates (Pd-diethynylbiphenyl-S-$COCH_3$) and H_2S, SO_2. The use of thiolate derivatives open new perspective in view of the use of this class of compounds as self assembled monolayers on gold surfaces.

Experiment:

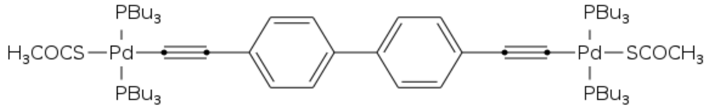
The experiment aimed at achieving information about the interaction occurring between sulfur containing gaseous molecules (H_2S and SO_2) and the transition metal dialkynyl bridged Pd(II) complexes trans-Pd-DEBP$_2$-Cl$_2$, trans-Pd-DEBP$_2$-(SCOCH$_3$)$_2$, trans-Pd-EP-SCOCH$_3$ and trans-Pd-(PBu$_3$)$_2$-(SCOCH$_3$)$_2$. EXAFS spectroscopy measurements were carried out on pellet samples, both in low vacuum conditions ($P = 10^{-5}$ mBar) and in presence of H_2S or SO_2 gas ($P = 100$ mBar maximum). Detection of the transmission signal was done at the Pd K-edge (24350 eV). More in detail:

As a start, we performed EXAFS measurements on the pristine sample pellet ($P = 10^{-5}$ mBar). Then, we filled up the GILDA's chemical cell with sulfur-containing gas (H_2S or SO_2, partial pressure of about 100 mBar), then we performed the same structural characterization. This was done for the four proposed samples. *In situ* treatments were made possible at GILDA by a small chemical chamber equipped with input and output gas lines, that allows to perform EXAFS measurements on samples in controlled chemical environment [11].



trans-Pd-DEBP2-Cl2

trans-Pd-EP-SCOCH3



trans-Pd-DEBP2-(SCOCH3)2

trans-Pd-(PBu3)2-(SCOCH3)2

Fig.1: Molecular Structure of trans-Pd-DEBP$_2$-Cl$_2$, trans-Pd-DEBP$_2$-(SCOCH$_3$)$_2$, trans-Pd-EP-SCOCH$_3$ and trans-Pd-(PBu$_3$)$_2$-(SCOCH$_3$)$_2$

Results:

The hypothesized chemical interaction occurring between Pd(II) and sulfur-containing chemical species was verified and investigated. We believe that this chemical interaction is responsible for the high sensitivity and selectivity of Pd-DEBPn polymers based mass sensor devices towards sulfur-containing compounds [12]. Furthermore, the structural order of the first neighbors surrounding the absorbing metal species in H_2S, SO_2 environment were investigated, and EXAFS data analysis suggested a square-pyramidal geometry around the transition metal with the gas molecule in the apical position for the pentacoordinated palladium center, as already observed and reported by some of us for the analogous Pt(II) containing materials [10].

References

[1] R. P. Kingsborough, T. M. Swager, *In Progress in Inorganic Chemistry*; K. D. Karlin Ed.; Wiley: New York, 1999; Vol. 48, pp 123;

[2] T. H. Shull, J. G. Kushmerick, C. H. Patterson, C. George, M. H. Moore, S. K. Pollack, R. Shashidahr, *J.Am.Chem.Soc.* 125 (2003) 3202;

[3] J.M. Tour, *J. Org. Chem*, 72, (2007) 7477;

[4] I. Fratoddi, A. La Groia, C. Battocchio, M. V. Russo, *Journal of Polymer Science Part A: Polymer Chemistry,* 45 (15) (2007) 3311;

[5] C. Battocchio, I. Fratoddi, M. V. Russo, G. Polzonetti *Chem. Phys. Lett.* 400 (2004) 290;

[6] C. Battocchio, F. D'Acapito, G. Smolentsev, A.V. Soldatov, I. Fratoddi, G. Contini, I. Davoli, G. Polzonetti, S. Mobilio *Chemical Physics* 325 (2006) 422;

[7] C. Battocchio, F. D'Acapito, I. Fratoddi, A. La Groia, G. Polzonetti, G. Roviello, M. V. Russo, *Chemical Physics* 328 (1-3) (2006) 269;

[8] C. Battocchio, I. Fratoddi, R. Vitaliano, M. V. Russo, G. Polzonetti, *Solid State Sciences* 12(11) (2010) 1881

[9] F. Vitale, R. Vitaliano, C. Battocchio, I. Fratoddi, C. Giannini, E. Piscopiello, A. Guagliardi, A. Cervellino, G. Polzonetti, M. V. Russo, L. Tapfer, *Nanoscale Research Letters,* 3 (2008) 461

[10] C. Battocchio, I. Fratoddi, M. V. Russo, G. Polzonetti *J. Phys. Chem. A*, 112 (2008) 7365

[11] A. Longo, A. Balerna, F. d'Acapito, F. D'Anca, F. Giannici, L. F. Liotta, G. Pantaleo, A. Martorana, J. Synchrotron Rad. 12 (2005) 499

[12] M. Penza, G. Cassano, A. Sergi, C. Lo Sterzo, M.V. Russo, Sensors and Actuators B 81 (2001) 88