ESRF	**Experiment title:** THIN FILMS OF SULFUR-CONTAINING PdPOLY-YNES ON METAL SURFACES: INTERFACE PROPERTIES STUDIED BY REFLEXAFS	**Experiment number**: SI 1592
Beamline: BM08	**Date of experiment**: from: 11/09/2007 to: 16/09/2007	**Date of report**: 29/10/2007
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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

Self-assembled monolayers (SAM) containing molecules with functionalised tail-groups, suitable for mediating the binding at the surface of particular molecules, are good candidates for different applications, such as active layers in sensors or molecular electronic devices [1,2]. In the framework of sensors devices and NLO, our general research program concerns the investigation of novel nanostructured organometallic systems, deposited as thin films on metal surfaces. Among others, the recently synthesized sulfur-containing organometallic poly-ynes, whose molecular structure is reported in Figure 1, are expected to show enhanced self assembling properties when deposited as thin films on metal surfaces. The main objective of the performed experiment was to establish a relationship between chemical, geometrical and electronic structure and electro-optical properties of these sulfur containing systems.

First reflEXAFS and EXAFS results have been published on Pt-DEBP and Pd-DEBP polymers [3,4]. Simpler related molecules synthesized on purpose, to have model systems whose structural characterization would be crucial in this context, have been studied by XPS and EXAFS evidencing a square planar structure around the metal, a *cis/trans* isomerization and a charge transfer interaction between units [5]. The systems functionalized with thiolate groups whose structural analysis is here reported,however, are completely new.

Experiment:

We performed reflEXAFS measurements at Pd k-edge (24350 eV) in transmission mode on thin films of the organometallic molecules Pd-EP-SH (Pd-ethynylphenyl-thiole), Pd-(PBu3)2(SH)2 (Pd-bis-tributylphosphyne-dithiole) and Pd-DEBP-SH2 (Pd-diethynylbiphenyl-dithiole) (see fig. 1) deposited on Au substrates in both monolayer and multilayer regime. Thin films of all samples deposited onto chromium substrates have been investigated as well. Samples in multilayer regime were prepared by dissolving the acetylthiolate precursor of the sample molecules in THF to give a 1nM solution, then immersing the gold substrate in 1-2 mL of this solution under argon, and adding NH_4OH to hydrolyze the acetyl protecting group, as reported in the literature for similar compounds [6]. Samples prepared as described have been measured with reflEXAFS, then rinsed with THF, ethanol and toluene, as to wash the physisorbed layers, in order to obtain the SAMs (self assembled monolayers).

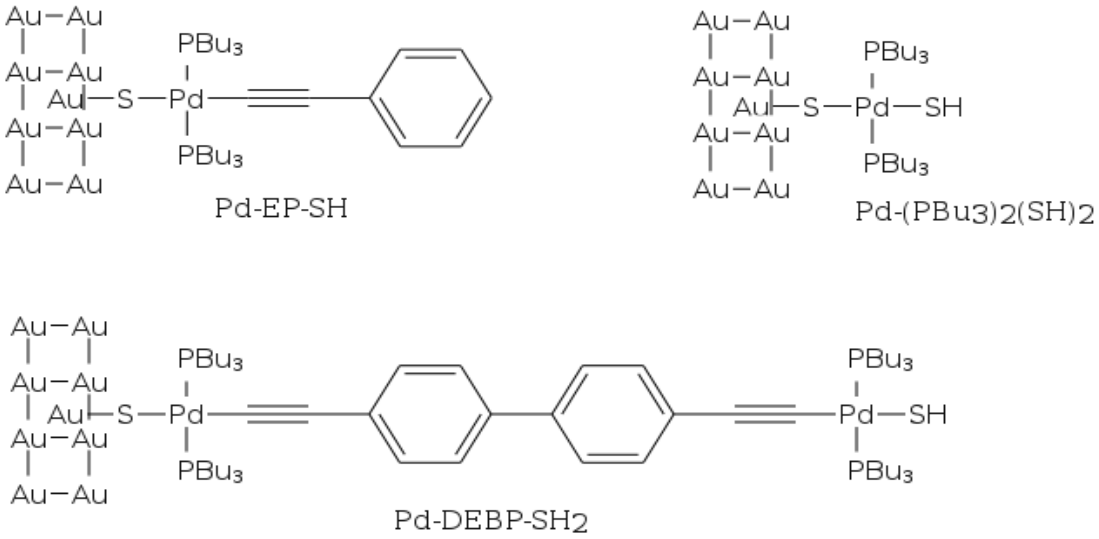

Figure 1 – molecular structure of Pd-EP-SH, Pd-$(PBu_3)_2(SH)_2$ and Pd-DEBP-SH_2 bound to the gold surface

Results:

Preliminary EXAFS data analysis results confirm the hypothesized square planar *trans* configuration of phosphine units around the Pd center, and suggests the Pd-Au bond formation for the monolayers. ReflEXAFS signals achieved on both Pd-DEBP-SH_2 monolayer and multilayer on gold substrate are reported in Figure 2; the observable differences between the two reported Pd K-edge signals have been attributed to the S-Au bond contribution in the monolayer spectrum, that decreases in the multilayer sample. More accurate data analysis is in progress in order to determine Pd-S-Au distances and to estimate the value of the angle between Pd-Au and Pd-S bonds.

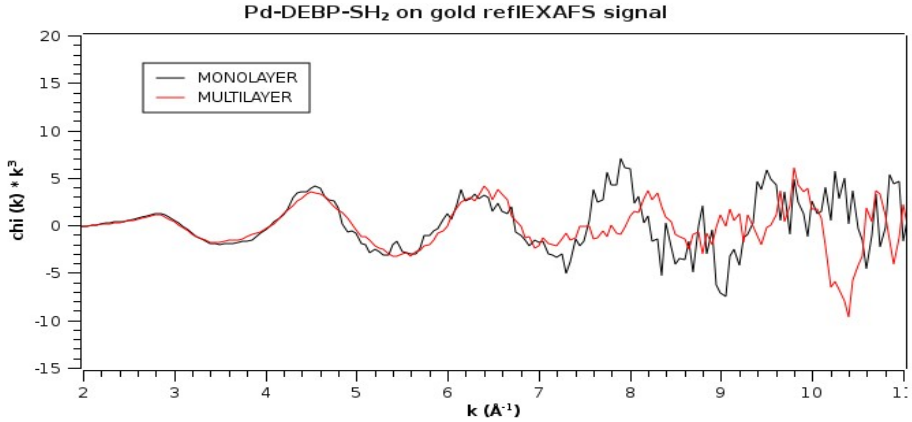

Figure 1 – reflEXAFS signal chi(k) * k^3 of Pd-DEBP-SH_2 multilayer and monolayer on gold substrates.

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