ESRF	**Experiment title:** Nanostructured Self Assembling Monolayers of newly synthesised Pd-containing organometallic thiolates on gold: molecular structure and thermal and chemical stability studied by EXAFS	**Experiment number**: 08-01 803
Beamline: BM08	**Date of experiment**: from: 26/02/2008 to: 03/03/2008	**Date of report**: 19/03/2009
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Report:

Introduction:

The spontaneous assembly of functionalised molecules on a metal surface provides a useful means to control surface properties at a molecular level. Given a particular substrate, the structure of the resulting Self-Assembled Monolayer (SAM) is governed by the molecular structure of the adsorbates, through their interaction with each other and the substrate, and, as a consequence, the physical properties of the assembly are determined by a combination of the molecular and the SAMs structure and can thus be tailored simply by modifying the chemical structure of the adsorbed molecules [1]. In the past, the majority of related studies have been carried out for thiol-based SAMs with aliphatic backbones such as alkanethiols which can be prepared easily on gold surfaces in a single step [2] by using several different techniques such as immersion [3], spotting [4], soft lithography [5,6] or scanning probe lithography [7]. More recently, aromatic SAMs have become the focus of interest due to their potential applications in lithography, charge transfer, and electronic functionality [8]. Among others, molecules with extended π – conjugation have received special attention, because they are expected to show efficient charge transport and have been considered as potential molecular wires [9]. 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 [10,11]. 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 [12]. Although numerous studies have been reported on SAMs of aliphatic and aromatic thiols on gold [2,9], there is doubtless a need for information on both the structures and properties of SAMs formed from rigid-rod π-conjugated organometallic thiols. Due to the high complexity of these materials, a useful approach in their study is to synthesize simpler related model molecules, to have model systems whose characterization would be crucial for the interpretation of the chemical physical properties of the polymers.

Experiment:

Pd-based mononuclear complexes *trans*-[HS-Pd(PBu_3)$_2$-SH], *trans*-[HS-Pd(PBu_3)$_2$(-C≡C-C_6H_5)] and the binuclear *trans,trans*-[HS-Pd(PBu_3)$_2$(-C≡C-C_6H_4-C_6H_4-C≡C-Pd(PBu_3)$_2$-SH], whose molecular structures are reported in **Figure1**, have been synthesized and deposited on gold surfaces. SAMs have been obtained by following an already tested procedure, i.e. by rinsing the thick films with appropriate solvents, and investigated by reflEXAFS Spectroscopy at Pd K-edge (24350 eV) in fluorescence mode, to study the molecular structure. Temperature-dependent measurements have been carried out in order to collect information about the thermal and chemical stability of the organometallic thiols.

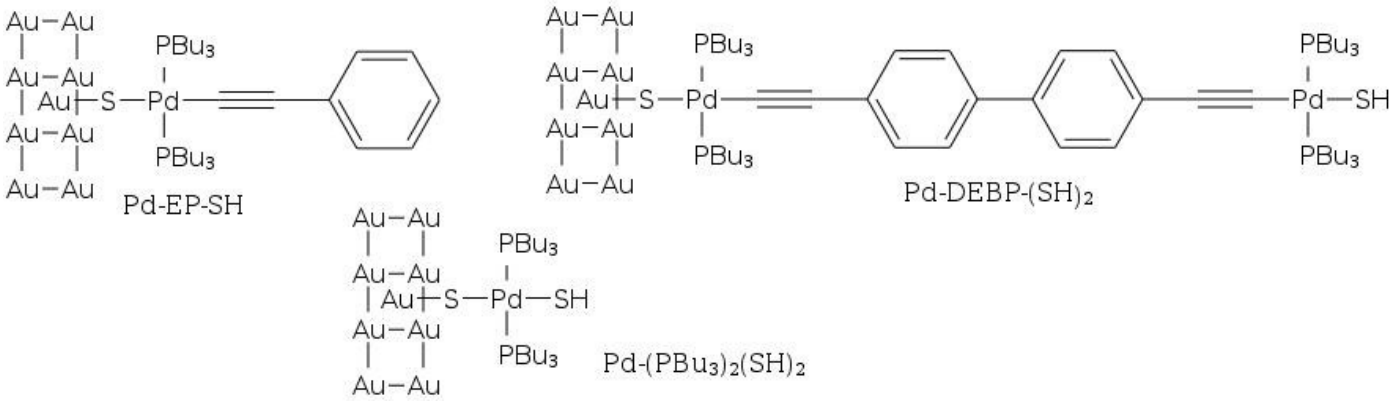

Figure 1: chemical structure of Pd-based complexes *trans*-[HS-Pd(PBu_3)$_2$-SH], *trans*-[HS-Pd(PBu_3)$_2$(-C≡C-C_6H_5)] and *trans,trans*-[HS-Pd(PBu_3)$_2$(-C≡C-C_6H_4-C_6H_4-C≡C-Pd(PBu_3)$_2$-SH].

To characterize the thermal and chemical stability of our samples, measurements after heatin at increasing temperature were performed. The sample was held at the chosen temperature for ten minutes, after a slow heating (about 30 minuter for 10 degrees) in an appropriate oven, then reflEXAFS spectra were recorded. Measurements were carried out from room temperature up to 80° on all the organometallic thiol monolayer films.

Results:

The collected spectra were compared to the reference spectra collected on the SAMs at room temperature, evidencing some differences that are currently under analysis. At about 70° sample degradation occurred, as evidenced by the sudden change in sample color (from dark yellow to red) and in the dramatically modification of the XAS signal.

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