ESRF	**Experiment title:** Hybrid systems of noble metal nanoclusters (Au, Ag) and organometallic thiols of Pt(II) and Pd(II) investigated by EXAFS	**Experiment number**: **CH- 3174**
Beamline: BM08	**Date of experiment**: from: 10/02/2011 to: 15/02/2011	**Date of report**: 15/02/2011
Shifts: 15	**Local contact(s)**: Dr. Angela Trapananti	*Received at ESRF:*

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Report:

Introduction:

The development of new strategies for the chemical stabilization of metallic nanoparticles by means of capping metallic clusters with appropriate ligands (selected on the basis of the expected behaviour) is the general topic of our research. In this framework, the study and control of the interaction occurring between the capping molecular species and metal nanoparticles synthesized on purpose is of primary importance.

Hybrid systems obtained by chemically bonding properly functionalized molecules to nanometric metal clusters, own peculiar optical, photochemical, electrochemical, catalytic and magnetic properties [1], that can be modulated by appropriate choice of the metal, by changing the cluster dimensions and by modifying the molecular structure and/or chain length of the ligand. When properly stabilized by a shell of ligands such as thiols, amines, ammonium salts and polymers, MNPs display excellent stability toward aggregation, which enables attempts to achieve NPs with different sizes and shapes. In the midst of different materials, thiol stablized MNPs can exhibit desired reactivities due to the variety of functionalizations and the strong M-S bond formation [2]. Concerning to macromolecular functional systems, organometallic rigid rod complexes and oligomers, opportunely functionalized with thiol ending groups, can be used as ligands to obtain promising MNPs/organometallic thiols hybrids [3,4,5]. Pristine rod-like mononuclear or dinuclear organometallic thiols constituted by Pt(II) or Pd(II) square planar complexes between organic spacers as diethynylbiphenyl (DEBP) or with organic end groups as ethynylphenyl (EP), have already been synthesized and characterized in our group, both pristine and anchored on Au surfaces as SAMs [6]. ReflEXAFS and EXAFS results have been published on these systems [7,8], evidencing a square planar structure around the metal, a *cis/trans* isomerization and a charge transfer interaction between units.

The main objective of this project was to investigate the correlation between chemical and geometrical structure of a series of AgNPs/organometallic thiols hybrids of different molecular structure and NPs size.

Experiment:

The experiments were carried out by EXAFS measurements on AgNPs/3MPS (three samples of different NPs size), AgNPs/PtDEBP (three samples of different NPs size) and AgNPs/PA-AA copolymer core shell (three samples of different NPs size) hybrid systems. Detection of the fluorescence signal has been done at the Ag K-edge (25514 eV). Spectra were measured both in the XANES region (at higher resolution) and in the EXAFS region. Our molecular samples showed, as usual, high stability under SR.

We started with AgNPs of different dimensions capped by the charged thiol 3MPS, then switched to AgNPs/PtDEBP and, finally, AgNPs/ PA-AA copolymer hybrids.

Results:

Detection of the EXAFS signal was carried out at Ag K-edge (25514 eV) in fluorescence mode for all the proposed samples, obtaining data of very satisfactory quality even for highly diluted samples. As an example, the rough EXAFS spectra of AgNps/PtDEBP systems of three different NPs sizes are reported in Figure 1a.
In the previous experiment CH3057, EXAFS data collected at Ag K-edge on a series of AgNPs/AM hybrids of different sizes showed a correlation between the NPs dimensions and the amount of Ag-S like species (see experimental report CH3057). An analogous trend has been observed for the AgNPs capped by organometallic Pt(II) based thiols investigated in this experiment CH3174; as shown in Figure 1 b), the contribution of non-metallic silver in the XANES signal varies with the relative Ag/thiol amount.
A similar trend has been observed for AgNP/3MPS systems; AgNPs/ PA-AA copolymer hybrids data have still to be analyzed.
EXAFS data analysis will lead to determine Ag-Ag and Ag-S distances and coordination numbers for all the investigated systems.

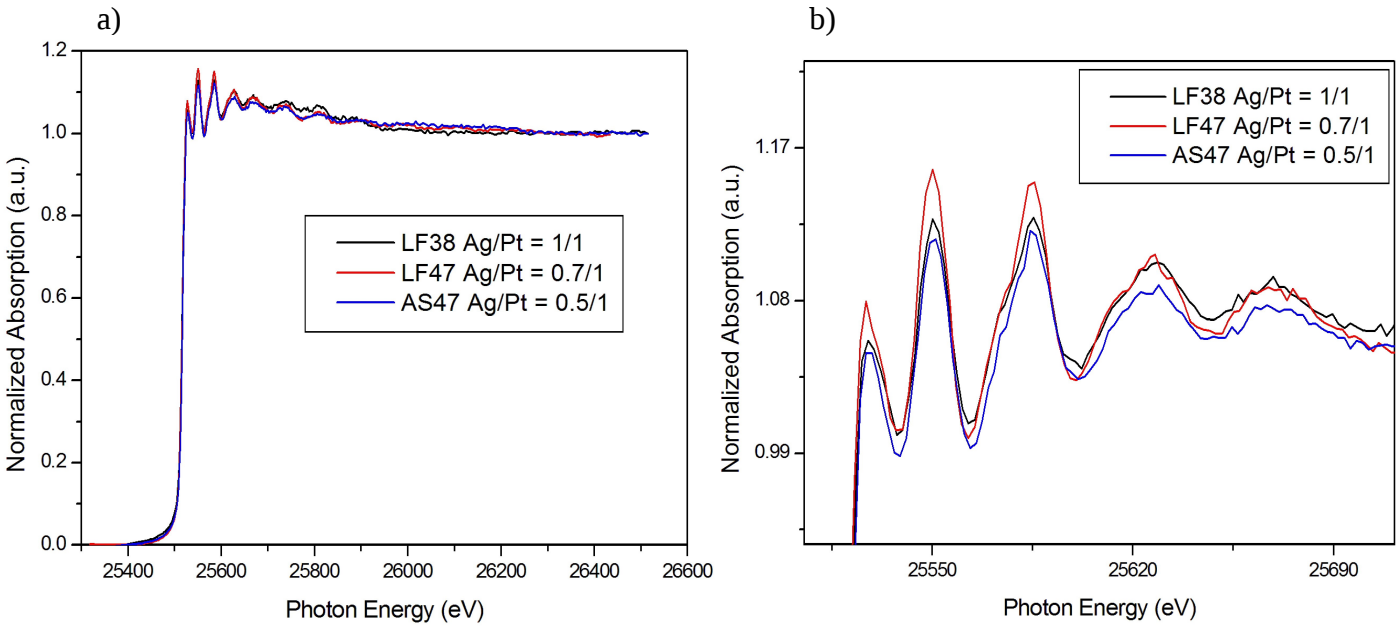

Figure 1: Raw EXAFS data (a), and detail of the XANES region (b) for AgNPs/PtDEBP samples of three different Ag/thiol stoichiometries.

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