ESRF	**Experiment title:** hybrid systems of silver nanoclusters and organometallic thiols investigated by EXAFS	**Experiment number:** **CH-3057**
Beamline: BM08	**Date of experiment:** from: 13/ 05/ 2010 to: 18/05/2010	**Date of report:** 13/02/2011
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Report:

Introduction:

The development of new strategies for the chemical stabilization of metallic nanoparticles (MNPs) 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 MNPs 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. Concerning to macromolecular functional systems, organometallic rigid rod polymers and oligomers, opportunely functionalized with thiol ending groups, can be used as ligands to obtain promising MNPs/polymer hybrids [2,3]. Pristine metal poly-ynes containing Pt(II) or Pd(II) square planar complexes in the main chain, between organic spacers as diethynylbiphenyl (DEBP), diethynylthiophene (DET) or diethynyl-Zn-porphyrin (Zn-DEP) have already been synthesized and characterized in our group [4,5]. Our systems have been successfully used in sensors and optical devices [6,7]. ReflEXAFS and EXAFS results have also been published on similar systems [8,9], as well as on the simpler related molecules synthesized on purpose, to have model systems of the more complicated polymers, 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 silver NPs/organic and organometallic thiol hybrids. As a start, we considered AgNPs capped by organic molecules of very simple molecular structure (AM = allyl mercaptane): then we switched to the more complex AgNPs/ PdDEBP, AgNPs/PtDEBP hybrid systems.

Experiment:

The experiments were carried out by EXAFS measurements on AgNPs/AM (four samples of different size) and AgNPs/PdDEBP, AgNPs/PtDEBP hybrid systems (one sample each). Detection of the fluorescence signal was done at the Ag K-edge (25514 eV) and Pd K-edge (24350 eV) (for AgNPs/PdDEBP). The 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.

Results:

EXAFS data collected on AgNPs/AM hybrids of different sizes showed a correlation between the nanoparticles dimensions (controlled through the synthesis procedure, by varying the Ag/thiol stoichiometry) and the amount of Ag-S like species; as illustrated in the following Figure 1a, by increasing the capped

nanoparticles size the contribution of non-metallic silver in the XANES signal becomes more important. Ag-Ag and Ag-S distances were estimated by EXAFS data analysis (preliminary fits of the experimental data, in both R and k space, are reported in Fugure 1b), and the observed results are in good agreement with literature data. AgNPs capped with organometallic thiols were also investigated, and the Ag k-edge EXAFS data analysis confirmed the expected Ag-S interaction. Moreover, by analyzing the EXAFS spectrum collected at Pd k-edge for AgNPs/PdDEBP sample, a square-planar organization of the first shell of neighbors around the Pd center was assessed, indicating that the organometallic complex molecular structure is preserved in the silver nanoparticles capped by rod-like compounds.

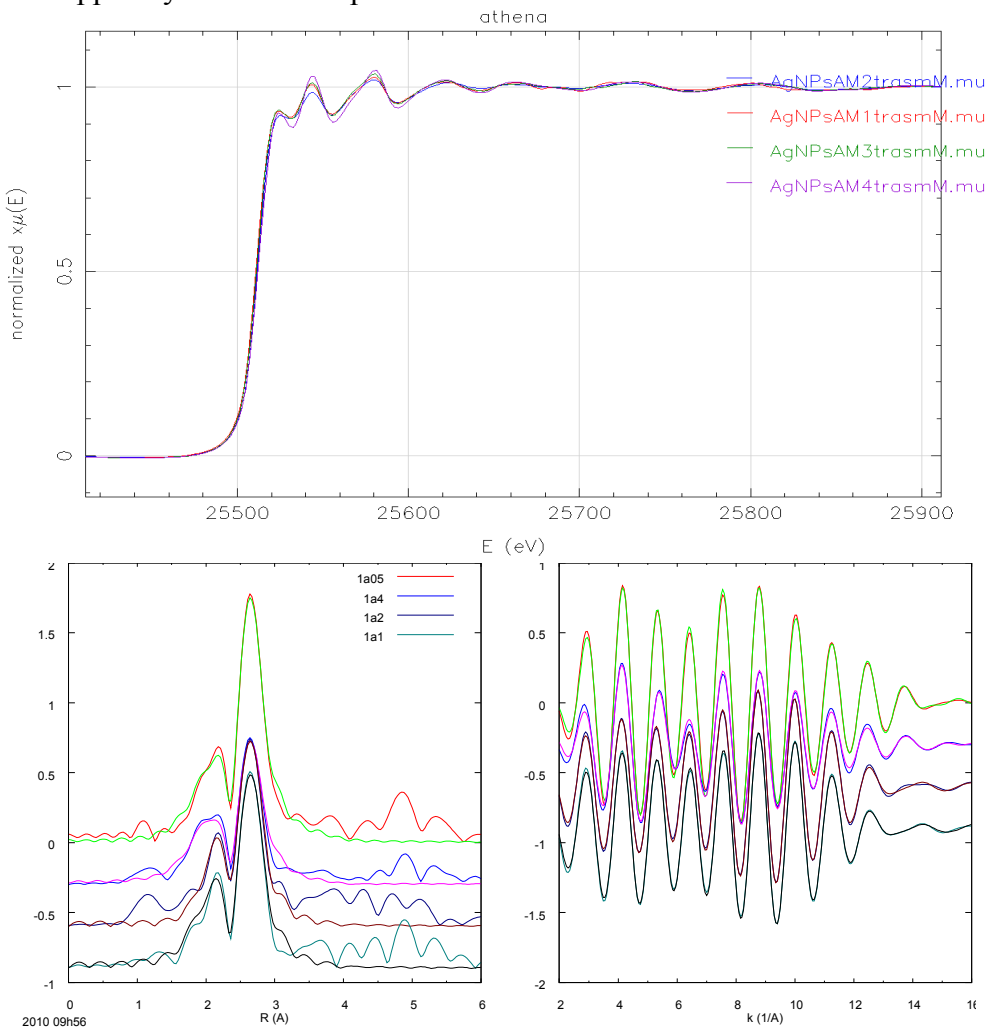

Figure 1: a) EXAFS data for AgNPs/AM 02, 01, 03 and 04 (Ag/thiol stoichiometry increases from 0.25/1 to 2/1); b) Ag k-edge EXAFS data analysis: fits of the experimental data are reported in both R and k space.

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