ESRF	**Experiment title:** Gold nanoparticles/organic thiols hybrid systems for fuel ce applications investigated by EXAFS	**Experiment number**: **08-01-944**
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Names and affiliations of applicants (* indicates experimentalists):

C. Battocchio[1*], F. Porcaro, 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:

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 AuNPs/organometallic thiols hybrids of different molecular structure and NPs size.

Experiment:

The experiments were carried out by EXAFS measurements on AuNPs/3MPS (three samples of different NPs size), AuNPs/SFL (three samples of different NPs size) and AuNPs/SFLPt (three samples of different NPs size) hybrid systems. Detection of the fluorescence signal has been done at the Au L_{III}-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 AuNPs of different dimensions capped by the charged thiol 3MPS, then switched to AuNPs/SFL and, finally, AuNPs/SFLPt copolymer hybrids.

Results:

Detection of the EXAFS signal was carried out at Au L_{III}-edge in fluorescence mode for all the proposed samples, obtaining data of very satisfactory quality even for highly diluted samples. The data analysis results are in excellent agreement with a trend already observed on analogous systems, based on Ag nanoparticles functionalized with small organic thiols and more complicated bifunctional organometallic ligands. In fact, in the previous experiments CH3057 and CH3174, EXAFS data collected at Ag K-edge on a series of AgNPs/AM and respectively AgNPs/PtDEBP$(SH)_2$ hybrids of different sizes showed a correlation between the NPs dimensions and the Ag/thiol atomic ratio used in the synthesis procedure (see experimental reports CH3057, CH3174). An analogous trend has been observed for the AuNPs capped by SFL fluorine-based thiols investigated in this experiment 08 01-944. The obtained results have also been confirmed by semiquantitative X-ray photoelectron spectroscopy data analysis, and are in very well agreement with the hybrid NPs mean sizes observed in HR-TEM images.
A similar trend has been observed for AuNPs/SFLPt hybrids; the data collected on AuNPs/3MPS are currently under analysis. EXAFS data analysis will lead to determine Au-Au and Au-S distances and coordination numbers for all the investigated systems.

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