ESRF	**Experiment title: Gold nanoparticles chemically stabilized by innovative fluorescent thiols: local chemistry and chemical structure investigated by EXAFS**	**Experiment number**: **CH-3777**
Beamline: BM25-A	**Date of experiment**: from: 19 June 2013 to: 24 June 2013	**Date of report**:
Shifts: 15	**Local contact(s)**: Alvaro Munoz-noval	*Received at ESRF:*

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Report:

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]. Capped noble metal nanoparticles have been exstensively investigated by some of us by means of SR-XPS, NEXAFS and EXAFS; in a recent work, a joint SR-XPS and EXAFS analysis carried out on AgNPs stabilized by simple organic thiols (AM) allowed to probe the local structure at the NP-ligand interface, providing extremely useful information about the chemical structure and stability of these innovative materials [6].

The main objective of this project was to investigate the correlation between chemical and geometrical structure of a series of AuNPs/organic thiols hybrids of different molecular structure and NPs size; in particular, the aromatic ligands have been selected for their peculiar optical properties (fluorene-based species, Iodine or Bromine-containing-aromatic molecules).

Experiment:

The experiments were carried out by EXAFS measurements on AuNPs/SFL (three samples of different NPs size), AuNPs/A-Ar-Br (three samples of different NPs size) and AuNPs/S-Ar-I copolymer core shell (three samples of different NPs size) hybrid systems. Detection of the fluorescence signal has been done at the Au L_{III}-edge (11919 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 SFL, then switched to AuNPs/S-Ar-Br and, finally, AuNPs/ S-Ar-I hybrids.

Results:

Detection of the EXAFS signal was carried out at Au L_{III}-edge (11919 eV) in fluorescence mode for all the proposed samples, obtaining data of satisfactory quality even for highly diluted samples. As an example, the rough EXAFS spectrum of AuNps/SFL hybrid obtained with Au/S atomic ratio = 1/1 is reported in Figure 1.
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 is expected for the AuNPs capped by fluorescent thiols investigated in this experiment CH3777.
Good quality spectra have also been acquired for AuNPs/S-Ar-Br and AuNPs/S-Ar-I systems.
EXAFS data analysis will lead to determine Au-Au and Au-S distances and coordination numbers for all the investigated systems, as in the previous CH3057 experiment [6].

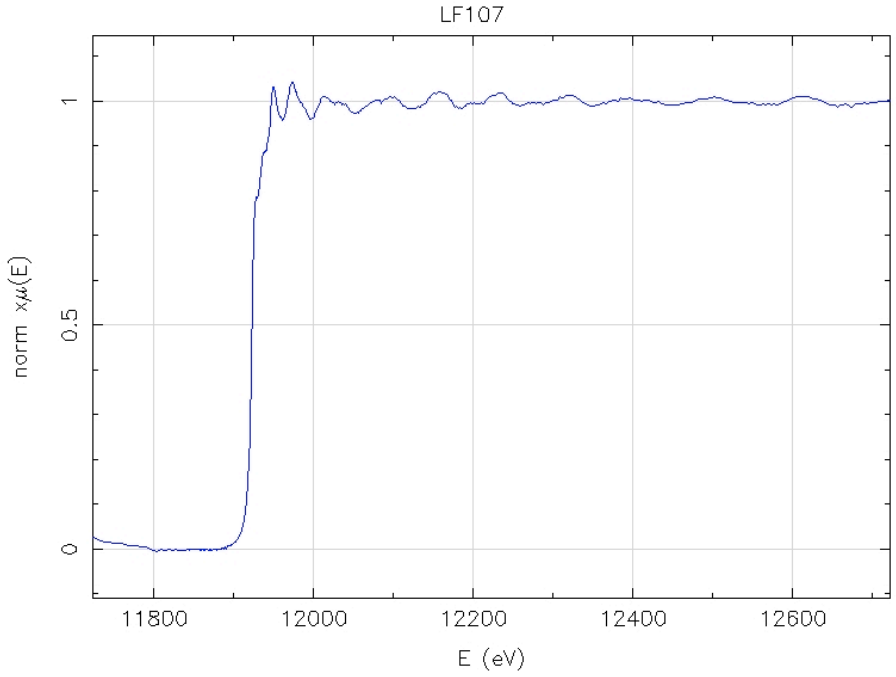

Figure 1: Raw EXAFS data for AuNPs/SFL sample.

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