Pd containing organometallic oligomers films at metal interfaces: model systems studied by EXAFS

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Introduction

Self-assembled monolayers (SAM) containing molecules with functionalised tail-groups, suitable for mediating the binding at the surface of particular molecules, are good candidates for different applications, such as active layers in sensors or molecular electronic devices [1,2]. In the framework of sensors devices and NLO, our general research program concerns the investigation of novel nanostructured organometallic systems, deposited as thin films on metal surfaces. Among others, the recently synthesised sulfur-containing organometallic poly-ynes, whose molecular structure is reported in Figure 1, are expected to show enhanced self assembling properties when deposited as thin films on metal surfaces. The main objective of the performed experiment was to establish a relationship between chemical, geometrical and electronic structure and electro-optical properties of these sulphur containing systems.

First reflEXAFS and EXAFS results have been published on Pt-DEBP and Pd-DEBP polymers [3,4]. Simpler related molecules synthesized on purpose, to have model systems whose structural characterization would be crucial in this context, have been studied by XPS and EXAFS evidencing a square planar structure around the metal, a *cis/trans* isomerization and a charge transfer interaction between units [5]. The systems functionalized with thiolate groups, however, are completely new.

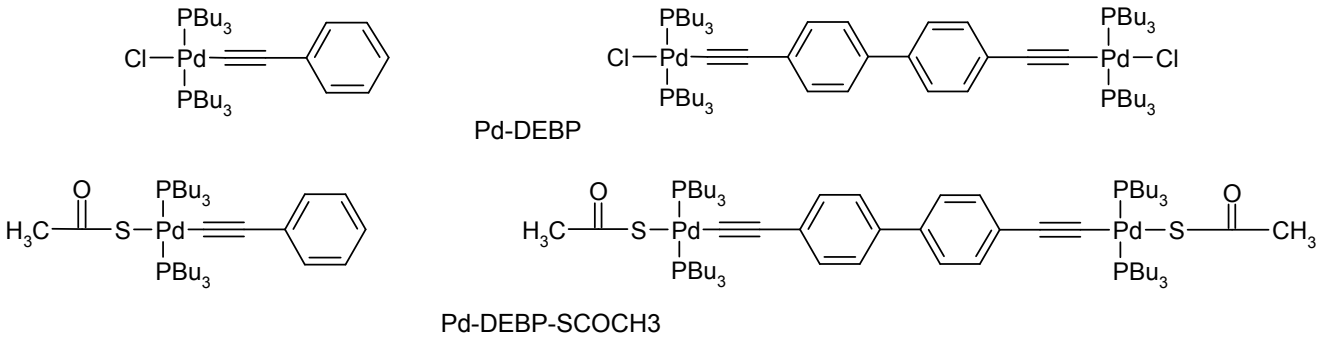

Figure 1 – molecular structure of Pd-DEBP-SR

Experiment:

We performed EXAFS measurements on pellets of organometallic oligomers of Pd-DEBP (Pd-diethynylbiphenyl) and Pd-DEBP-$SCOCH_3$ (Pd-diethynylbiphenyl-thiolate) (see fig. 1), at Pd k-edge (24350 eV) in transmission mode.

Results:

Preliminary data analysis results confirm the hypothesized square planar *trans* configuration of phosphine units around the Pd center. The Fourier Transformate of EXAFS signal is reported in Figure 2 for Pd-DEBP and Pd-DEBP-SR model molecules, showing some difference in the atomic distances of the two Pd clusters due to the different terminal groups (S-$COCH_3$ or Cl).

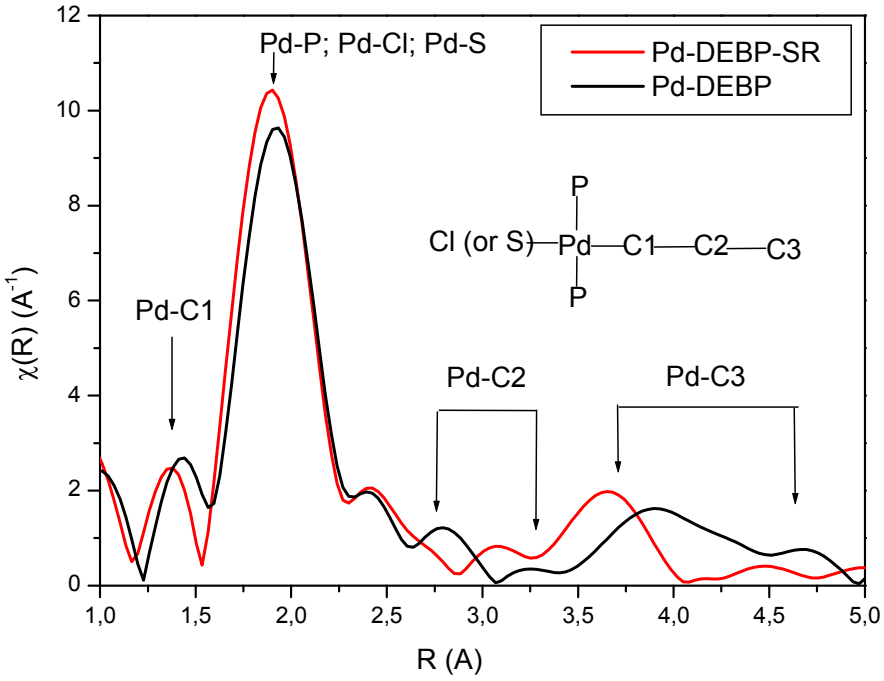

Figure 2 – FT of EXAFS spectra (R space) of Pd-DEBP-$SCOCH_3$ (black) and Pd-DEBP (red).

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Publications:

two congress communications

1) European Polymer Congress 2007, July 2-6, 2007, Portorož - Portorose, Slovenia. Session: Polymers for advanced applications
2) VI CONVEGNO NAZIONALE SULLA SCIENZA E TECNOLOGIA DEI MATERIALI, 12-15 giugno 2007, Perugina, Italia. Sezione Tematica INSTM: 3. Superfici, strati sottili ed interfasi.

Proposal number of the experiment: 08-01-707