

Molecular arrangement and electronic structure for metalloporphyrin bridging dinuclear Pt and Pd complexes as investigated by NEXAFS

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Introduction

Nanostructured materials originating from transition metal coordination complexes and organic aromatic moieties are appealing for applications ranging from chemical sensors to optical devices and catalysts. In fact, an high surface area, typical of a nanostructured material, usually translate into high performance devices. Porphyrins and multiporphyrins are peculiar materials of specific interest, due to their properties appropriate for applications as active layers in optical sensors, optical switches and energy conversion devices. Furthermore, tetrapyrrolic molecules are usually talented to give rise to morphologically organized nanostructures. Recently, a significant endeavour has been applied to the improvement of new chromophores based on multiporphyrinic polymers suitable for constructing optoelectronic devices; in this framework, organometallic assemblies containing Zn-diethynylporphyrin (ZnDEP) coordinated to terminal -Pt(PBu₃)₂Cl and -Pd(PBu₃)₂(C≡CPh) tethers were synthesised and the study of their molecular and electronic structure by means of Near Edge X-ray Absorption Fine Structure spectroscopy (NEXAFS) will be here reported. N K-edge spectra collected on the two macromolecular arrays have been compared to the same measurements already performed on precursors ZnDEP and diethynylporphyrin (DEP), with the aim to investigate the influence of the transition metal tethers on the electronic structure of the macromolecular system.

Methods and Materials

Pt-ZnDEP and Pd-ZnDEP binuclear compounds (Fig.1a) have been synthesised following a procedure that involves the condensation of 2,8,12,18-tetraethyl-5,15-diethynyl-3,7,13,17-tetramethylporphyrinato-Zn (II) with Pt(PBu₃)₂Cl₂ and Pd(PBu₃)₂(C≡C-Ph)Cl respectively. Synchrotron induced NEXAFS measurements on Pt-ZnDEP thin film deposited from a toluene diluted solution onto Au/Si(111) as substrate were carried out at ELETTRA storage ring using the SuperESCA beamline and relative experimental station. The beamline has a multichannel plate detector with an instrumental resolution of $\Delta E/E = 10^{-4}$. NEXAFS experiments on Pd-ZnDEP samples spin deposited on Au/Si(111) were performed at the same storage ring at the BEAR (Bending Magnet for Emission Absorption and Reflectivity) beam-line. In both cases the photon energy scale had been previously calibrated with gas phase nitrogen at the K-edge absorption.

Results

With the aim to investigate the electronic structure of M-ZnDEP assemblies (M = Pt, Pd), NEXAFS N K-edge spectra have been acquired and carefully compared with the same measurements already performed and discussed on Zn-diethynylporphyrin (ZnDEP) and diethynylporphyrin (DEP)

[1,2]. Pt-ZnDEP and Pd-ZnDEP N K-edge spectra have been superimposed and the resulting outline is reported in Fig.1b. The features energy positions are identical for the two molecules in both π^* and σ^* regions, the only difference being the presence of -N-H π^* resonances in Pd-ZnDEP spectrum, assigned by comparison with DEP N K-edge spectrum, and probably due to partially non metallated sample. The different intensity of the σ^* features for Pd and Pt molecules is attributed to the contribution of the two terminal phenyl groups in Pd-ZnDEP. The DEP and ZnDEP N K-edge spectra have been deeply investigated in [1,2] and the N features assignment was made on the basis of the results obtained by the Static Exchange Potentials (STEX) method. By comparing NEXAFS N K-edge spectra of Pt-ZnDEP and Pd-ZnDEP to DEP and ZnDEP spectra, an overall shift at higher photon energy values of about 0.5 eV is detected, leading to the conclusion that charge transfer occurs from the tetrapyrrolic macrocycle to the transition metals terminal groups in both Pt and Pd containing materials.

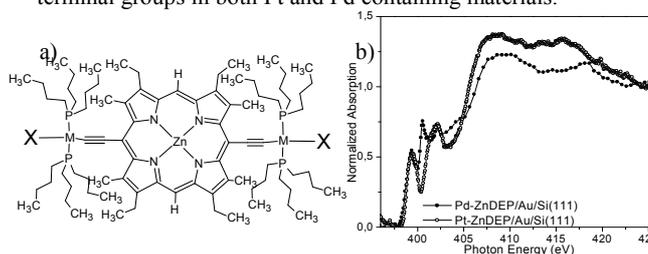


Fig.1: a) Chemical structure of M-ZnDEP (M = Pt, X = Cl; M = Pd, X = C≡C-Ph); b) Pt-ZnDEP and Pd-ZnDEP NEXAFS N K-edge spectra

Discussion

The comparison between the NEXAFS N K-edge spectra collected on Pd-ZnDEP, Pt-ZnDEP and the same measurements already carried out on ZnDEP and DEP has been performed. The observed energy shift at higher photon energy values indicates, in our opinion, that the π conjugated ring acts as electron-donor towards the metal centres. The aromatic system electrons are delocalised on the organometallic chain, and the conjugation involves the metal orbitals, as already observed and reported by some of the authors for Pt poly-ynes containing small diethynyl-aromatic rings as organic moieties [3].

References

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