



COUPLING ELECTROCHEMISTRY WITH X-RAY ABSORPTION SPECTROSCOPY TO STUDY POLYMERS

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The field of chemically modified electrodes has seen an important growth in the two last decades, especially conjugated polymers including redox-active transition metal centers for their potential applications in electrocatalysis, sensor or electronic devices. However, there is limited information on the structure of these layers. On the other hand, x-ray absorption spectroscopy represents a highly sensitive tool to study atomic and molecular details of non-crystalline materials. Thus, EXAFS measurements on chemically modified electrodes under different controlled potentials can provide information about interactions between redox active metal centers and the conjugated structure, i.e. about the degree of electronic communication between them.

By using thiophene or pyrrole derivatives bearing functionalities (a metal ion binding site, an anionic or cationic site) as monomers for electropolymerisation, electrodes can be modified with a conductive matrix containing these groups and thus can be useful in electrocatalysis, sensor or electrochromic devices. A few years ago, G. Bidan (CEA-Grenoble), J.-P. Sauvage (Univ. of Strasbourg) and co-workers have used electropolymerisation of pyrrole-bearing 1,10-phenanthroline tetrahedral complexes of transition metals to modify electrodes, leading to sites rigidly anchored within the polymer matrix and then to stabilisation of unusual oxidation states. More recently, related works, with polythiophene, have been published by us [1] and others, in an effort for a more direct electronic coupling

between the receptor site and the conjugated polymer backbone and for a better control of the structure.

By combining the phenanthroline containing macrocycle **2** with the key ligand bearing two pendant bithiophene units **1** (Figure 1) via the templating copper (I) ion, rotaxane complex was obtained and then electropolymerised to afford a coordinating polyrotaxane with a conjugated backbone alternating quaterthiophene moieties and phenanthroline complexes with threaded cyclic units. By testing this system for transition metal ion sensing ability, we discovered an original structural effect: as shown in Figure 2, the Cu(I) template used to assemble the fragments of the precursor could be removed but, interestingly, subsequent

remetallation was only possible if lithium was present during demetallation. The function of lithium is assumed to be that of an ionic scaffolding, maintaining the topography of the coordination site after copper removal, though forming a labile complex. XAS studies at the Cu K-edge have been undertaken on this conjugated polyrotaxane at the ESRF, on the CRG-IF BM32 beamline, in order to obtain 1) information about interactions between redox active copper centers and the conjugated structure at different controlled potentials and 2) additionally proof of the high reversibility of copper(I) binding when lithium is present. The high flux available at the ESRF allows short acquisition time and due to the high dilution of metallic sites in our samples, data were collected with a highly sensitive

Fig. 1: The monomers.

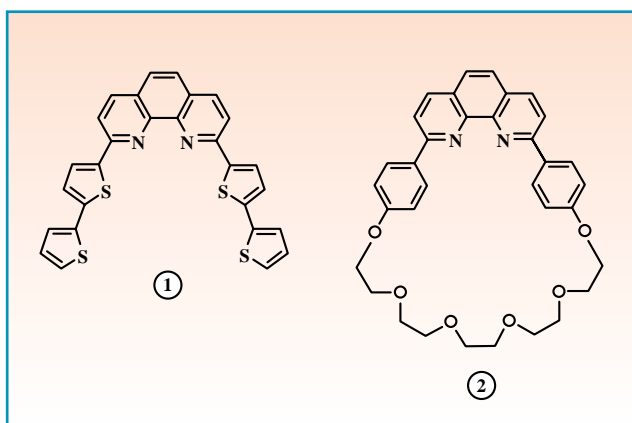
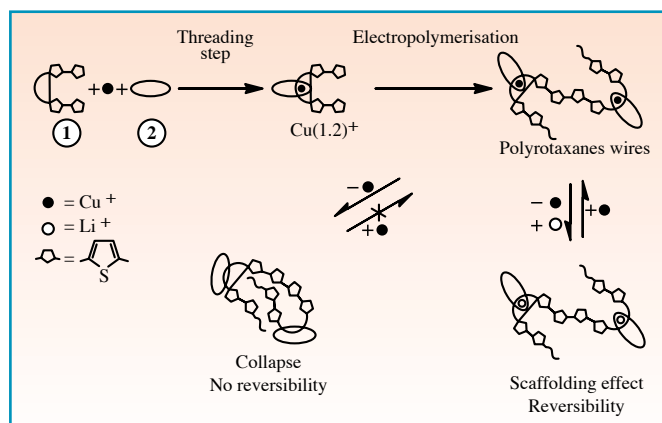


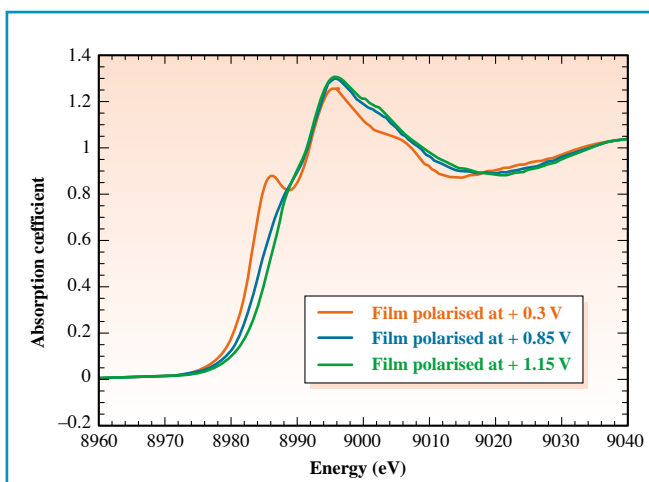
Fig. 2: Schematic representation of the synthetic strategy used and of the scaffolding effect.





fluorescent detector. We have recorded spectra of the films of polyrotaxane electropolymerised onto a carbon electrode and in contact with a dichloromethane / 0.2M tetra-n-butyl ammonium hexafluorophosphate solution at different controlled potentials. As shown in Figure 3, changes in oxidation state of the copper centers are evidenced by the shift (by about 2.5 eV) in the position of the edge upon oxidation of the polymer film from Cu(I) (+ 0.3 V) to Cu(II) (+1.15 V). Furthermore, no increase in the coordination number seems to occur (via a counterion in electrolyte solution) when passing from Cu(I) to Cu(II), contrary to what is observed with monomeric model compounds. Upon fitting of the data with MC Kale functions, further evidence is obtained for an unchanged coordination with 4 donor nitrogen ligands when passing from + 0.3 V to + 1.15 V. Nevertheless, a considerable change in geometry occurs upon oxidation of the film: at + 0.3 V the geometry around Cu(I) is best described as

Fig. 3: A shift in the position of the edge shows the oxidation state of the copper centers.



distorted tetrahedral with 2 Cu-N distances at 2.08 Å and 1.96 Å approximately, while at + 1.15 V, the geometry around Cu(II) is flattened tetrahedral with an average Cu-N distance of 2.01 Å. Comparison between spectra recorded with freshly-prepared and remetalated via lithium/copper exchange films reveals no evident change

in geometry and distances around Cu(I) centers, thus confirming the high reversibility of copper binding. ■

REFERENCE

[1] P.L. Vidal, M. Billon, B. Divisia-Blohorn, G. Bidan, J.M. Kern and J.P. Sauvage, *Chem. Commun.*, 629 (1998).