

# Spectroscopic observation of polaron-lattice band structure in the conducting polymer polyaniline

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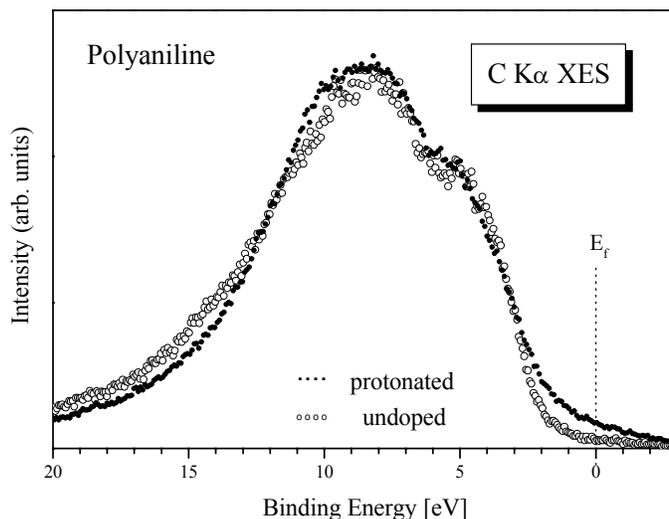
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Interest in polyanilines has been reinforced by the discovery of their high electrical conductivity observed in doped phases, giving rise to a new class of conducting polymers. Polyaniline can be prepared in three major forms that differ in the degree of oxidation  $y$  (the ratio of amine nitrogens over the total number of nitrogen atoms). For the fully reduced leucoemeraldine base (LEB)  $y$  is one, the half-oxidized emeraldine base (EB)  $y$  is 0.5 and for fully oxidized pernigraniline base (PNB)  $y$  is 0. Polyaniline is an insulator in each of these forms with a band gap of 3.6 eV for LEB and EB and about 1.4 eV for PNB. The polymers can also exist in the corresponding protonated (salt) forms but only emeraldine salt (ES) is highly electrically conductive in this case. The largest conductivity reported to date is about 400 S/cm [1], which is 14 orders of magnitude higher than for the insulating emeraldine base form. Protonation does not change the electronic concentration and a local distortion of the chemical bonds is giving rise to conductivity of the polymer. These distortions are commonly referred to as either a polaron (storing the extra positive charge when only one nitrogen is protonated) or a bipolaron (in the case that both imine nitrogens are protonated). In order to explain the conductive state of ES two models have been proposed. A regular distribution of polarons leaves the electronic band half-filled or the random bipolaron structure leads to the formation of extended electronic states at the Fermi energy. There is no direct spectroscopic evidence to date regarding the electronic structure of ES, which is essential for selecting the adequate picture.

We have studied the differences in the electronic structure of protonated and undoped polyemeraldine by means of soft x-ray emission spectroscopy (XES). Our findings support the application of the polaronic-metal model for highly conducting polymers.

The experiments were carried out at Beamlines 7.0 and 8.0.1 at the Advanced Light Source at the Lawrence Berkeley National Laboratory employing the Uppsala University [3] and University of Tennessee at Knoxville [4] endstations. Photons with energies well above the carbon K-edge (300 eV) and well above the nitrogen K-edge (412-430 eV) were delivered to the sample. The X-ray fluorescence spectrometer provides an energy resolution of 0.30 eV and 0.65 eV for the carbon and nitrogen measurements, respectively. For our measurements we have chosen the basic form of undoped and protonated polyemeraldine. The doped samples were prepared by protonation with 60% camphorsulphonic acid (CSA). The protonation with  $H^+$  adds holes to the imine groups around the quinoid ring.

Figure 1 shows carbon  $K\alpha$  emission spectra ( $2p \rightarrow 1s$  transition) of undoped and protonated emeraldine converted to the binding energy scale [5]. The spectra are normalized to the same peak height in the intensity maximum. The intensity of the C  $K\alpha$  emission in the vicinity of the Fermi level  $E_F$  is clearly increased for the protonated emeraldine compared to the undoped sample. This finite density of states at the Fermi level evidences the metallicity of the doped phase. The same tendency of higher spectral intensity in the vicinity of the Fermi level for protonated polyemeraldine with respect to the undoped phase is observed in N  $K\alpha$  XES though these measurements have been performed with less energy resolution (due to the higher emission energy) and lower count rate than the carbon data, the latter being due to the smaller content of nitrogen atoms in polyaniline. Protonating increases the finite density of states near the Fermi level and the origin of the increase is the formation of the polaron band. In the case of the bipolaron band structure no finite density of states is expected near  $E_F$ . Recently, an extremely small finite density of states for protonated emeraldine has been observed in photoemission measurements [6]. The authors do not indicate the level of protonation and in a protonation of too low concentration could lead to such effect.



**Figure 1 Carbon  $K\alpha$  XES of undoped and protonated polyemeraldine displayed on the binding energy scale.**

To summarize, we have observed a finite density of states in protonated emeraldine in the vicinity of the Fermi level using soft X-ray emission measurements. This direct observation is in a full agreement with band structure calculations for the polaron lattice and therefore supports a polaronic-metal model for conducting polymers.

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