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Evolution upon doping of the π^* and σ^* bands of poly-(3-methylthiophene) grafted on Pt electrodes as studied by near-edge x-ray-absorption fine-structure spectroscopy

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With the use of near-edge x-ray-absorption fine structure spectroscopy (NEXAFS), the unoccupied π^* and σ^* bands of poly-(3-methylthiophene) electrochemically grafted on to a Pt surface have been probed. The C K-edge NEXAFS characteristics confirm that (i) the polymeric chain unit is composed of the same structural architecture as the monomer and (ii) the doping proceeds via a narrowing of the band gap with the appearance of metalliclike behavior. The same tendencies are observed by varying the structure of the monomer and the nature of the dopant which evidences a similar conduction mechanism for these poly-five-membered-heterocycles.

Polythiophene and its derivatives have been extensively studied during recent years because of their high stability against oxygen and moisture compared to other organic conducting polymers.[1] Such a property has been put forward for practical applications in the field of catalysis, energy storage, or photovoltaic conversion.[2] Moreover, by varying the structure of the monomer and the nature of the dopant, long-range order[3] and partial crystallization[4] have been obtained. Several theoretical models[5,6] have been proposed to explain the large change in conductivity between the doped and undoped states. Based essentially on the appearance of localized levels in the gap, they involve spinless bipolarons, related to local lattice deformations.[7]

X-ray (XPS) and ultraviolet (UPS) photoemission spectroscopy data[3] have shown that (i) a π-bonding band located at 1.1 eV below the Fermi level is formed during the coupling of the monomeric units, in good agreement with theoretical calculations[8] and (ii) doping proceeds through uniform extraction of π-bonding electrons resulting in a band-gap narrowing. In order to confirm these electronic characteristics, we have probed the unoccupied levels of poly-(3-methylthiophene) (PMeT). We report, in this Rapid Communication, the evolution of the π^* and σ^* bands of thin PMeT films grafted on Pt by using near-edge x-ray-absorption fine-structure (NEXAFS) spectroscopy around the C K edge as a function of the doping level.

Films of PMeT were electrochemically deposited on a flat Pt electrode immersed in a CH_3CN-$5\times10^{-1}M$ $LiClO_4$-$5\times10^{-1}M$ 3-methylthiophene electrolytic medium.[9] The electrode was polarized at +1.35 V relative to a saturated calomel electrode (SCE) for obtaining the 30%-ClO_4^- fully doped film. Intermediate-doped (15% and 3%) and fully undoped films were synthesized by changing the potential from +1.35 to +0.8, +0.1 and −0.2 V with respect to SCE, respectively. Film thicknesses were adjusted between 500 and 1000 Å according to the chosen deposition time. Samples were rinsed with acetone, dried in a N_2 stream, and then transferred through a series of interlocks into an ultrahigh-vacuum sample chamber.

NEXAFS experiments were carried out at the electron storage ring BESSY-Berlin using the high-energy TGM2 beam line[10] with a resolution of 0.5 eV at the C K edge. The incident photon beam I_0 is monitored by collecting the total electron yield from a high-transmission metal grid (~90%) freshly coated with copper. The total yield from the sample, I, is then normalized with respect to I_0. The background at the C K edge is estimated from the yield of a clean Pt surface in the C K-edge region.

3-methylthiophene is a planar molecule with a C_{2v} symmetry and a high degree of aromaticity. Incomplete and complete neglect of differential overlap theoretical calculations (INDO, CNDO/S3) performed by Duke, Paton, Salaneck,[8] show that the highest occupied molecular orbital, $1a_2\pi$, and the lowest unoccupied molecular orbital, $3b_1\pi^*$, have pure carbon π character. Upon polymeriza-

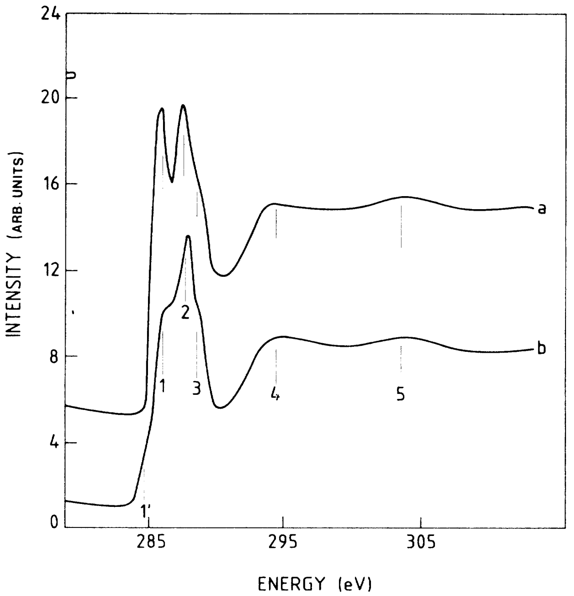

FIG. 1. C *K*-edge NEXAFS spectra of 1000-Å-thick PMeT film grafted on Pt. (a) Undoped form and (b) fully doped state.

tion, the $1a_2\pi$ and $3b_1\pi^*$ orbitals give π-bonding and π^*-antibonding bands, the first one being located 1 eV below the Fermi level E_F.[8] In addition to the π^* band, there are unoccupied levels of σ symmetry from both the C—S and C—C bonds.

The normalized C *K*-edge NEXAFS spectrum [Fig. 1(a)] of a 1000-Å-thick undoped PMeT film grafted on Pt is very similar to those obtained for thiophene in the solid phase[11] which confirms the same structural architecture for the polymeric chains.

Five transitions are observed at 286, 287.7, 289, 294.7, and 304 eV. The first one corresponds to the $1s \rightarrow \pi^*$ bound-state transition (Table I). From XPS measurements of gas-phase thiophene, the C 1*s* levels are split by a 0.3-eV chemical shift between the $C_{2,5}$ and $C_{3,4}$ positions in the ring.[12] From the convolution with the π^* final band states, this splitting is clearly smeared out in a single structure in NEXAFS experiments.

The second transition at 287.7 eV arises from a σ shape resonance due to the C—S bond. Actually, the first and the second transitions exhibit an opposite angular dependence as observed for either chemisorbed thiophene on Pt,[13] or 20-Å-thick PMeT electrochemically grafted on Pt.[14]

The origin of the third transition at 289 eV, observed also in the thiophene gas-phase spectrum is not well understood. Hitchcock, Horsley, and Stohr[11] have assigned this feature to *np* Rydberg transitions because it is not observed in the solid state. We assign this peak as a π resonance arising from the transition of the C 1*s* core electron to the second antibonding π^* band of PMeT. The other one at 294.7 eV is attributed to a σ^*(C—C) shape resonance. Finally, the last feature at 304 eV could correspond to a σ^*(C═C) shape resonance or to a double excitation of π symmetry since no transition is expected at this energy in the multiple-scattering $X\alpha$ calculations.[11]

When PMeT is doped with ClO_4^- [Figs. 1(b) and 2], no energy variations of the σ(C—S) and σ(C—C) shape resonances are observed, suggesting that no modifications in the bond lengths take place during the doping process according to the shape-resonance—bond-length relationship.[15]

However, the π^* antibonding band is greatly affected as evidenced by the continuous decrease in intensity with the doping level. Additionally, a transition appears at low energy whose intensity increases with the doping process: 0% [Fig. 2(a)], 3% [Fig. 2(b)], 15% [Fig. 2(c)] and 30% [Fig. 2(d)]. These empty states created in the band gap are still observed by changing the structure of the monomer (thiophene, pyrrole[16]) and/or the nature of the dopant ($SO_3CF_3^-$,BF_4^-) (Fig. 3). This evidences a similar conduction mechanism for these five-membered heterocycles.

Several models have been suggested to explain the large increase of conductivity during the electrochemical oxidation of these polymers.

(a) Formation of a degenerate semiconductor associated with the extraction of electrons from the π-bonding band and with a shift of the Fermi level below the valence band.[17] Thus if the conducting states of PMeT were those of a degenerate semiconductor, the C 1*s* NEXAFS spectrum would exhibit a peak followed by a sharp threshold 2.2 eV higher in energy (corresponding to the undoped-PMeT-film gap value) due to the onset of transition into the conduction-band states. The intensity of this last transition should be constant in the fully doped state; the den-

TABLE I. Assignment of features in C *K*-edge NEXAFS spectra (in eV).

Undoped		Doped	Transition assignment
1'		~284–284.5	New empty states
1	286	286	$3b_1\pi^*$
2	287.7	287.7	σ^*(C-S)
3	289	289	$2a_2\pi^*$
4	294.7	294.7	σ^*(C-C)
5	304	304	σ^*(C=C) or double excitation
	284.6	284.3	C1*s* ionization energy XPS[a]

[a] Reference 3.

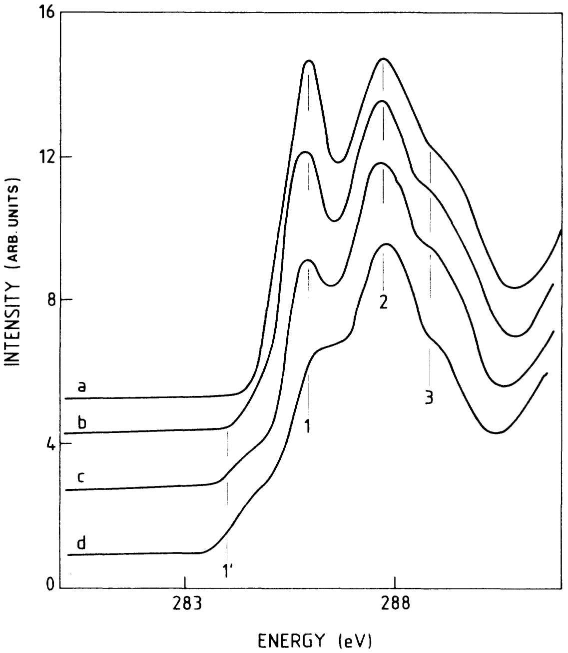

FIG. 2. Evolutions of the C K NEXAFS spectra with the doping level for a 1000-Å-thick PMeT film deposited on Pt. (a) Undoped, (b) 3% ClO_4^- doped, (c) 15% ClO_4^- doped, and (d) 30% ClO_4^- fully doped.

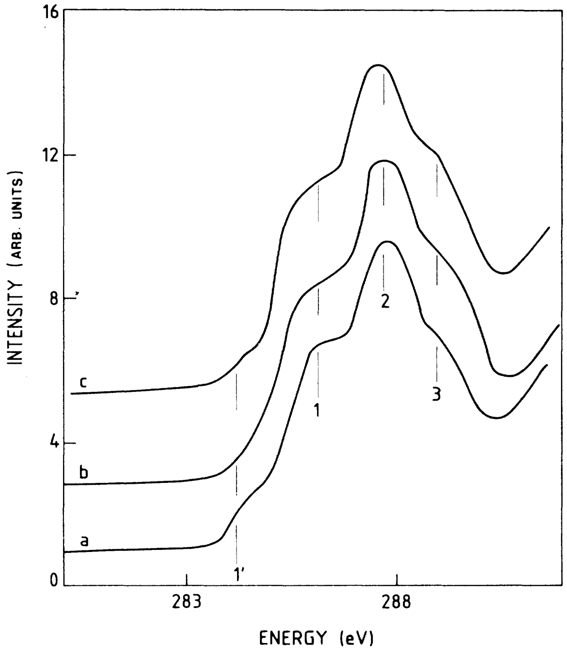

FIG. 3. C K-edge NEXAFS characteristics of 1000-Å fully doped polymer grafted on Pt. (a) PTet-ClO_4^-, (b) PTet-$SO_3CF_3^-$ and (c) polythiophene-$SO_3CF_3^-$.

sity of states of this π^* antibonding band is not affected. Evidently, the C 1s NEXAFS characteristics do not fit with this scheme.

(b) Formation of local distorsions in the polymeric chains around localized charges associated with the transformation of the aromatic structure to the quinoid structure. This leads to the appearance of two localized levels in the band gap which become empty narrow bands when the doping level increases (bipolaron model[7]). These structural modifications would be accompanied with variations in the C—C and C—S bond lengths, this last one increasing from 1.72 to 1.78 Å in the doped state; so a shift to lower energy of the transitions 2 and 4 would be expected. Moreover, the NEXAFS spectra would show two new peaks at low energy, corresponding to the C 1s transition toward the bipolaron narrow bands followed by the sharp initial transition shifted to higher energy due to the increase of the gap value from 2.2 to 2.9 eV.[7] The evolution of the C 1s NEXAFS characteristics combined with the S K-edge extended x-ray-absorption fine-structure results obtained during the doping-undoping cycles which do not reveal any modification in the C—S bond length[18] do not appear to agree with the bipolaron predictions.

(c) Finally, if the doped conducting state corresponds to a metalliclike behavior, a simple steplike absorption edge ~2.2 eV (gap value) below the π^*-antibonding band edge would be observed.[17] In the fully doped state, the strong C 1$s \rightarrow \pi^*$ resonance intensity observed in the undoped form has almost disappeared, and the absorption threshold has been shifted ~2 eV to lower energy. Thus the NEXAFS spectra strongly suggest a closed-gap metallic state. Combining these results with XPS and UPS ones,[3] we conclude that doping proceeds through (i) a uniform extraction of electrons from the π-bonding band and (ii) a progressive narrowing of the π-π^* gap, since new features on the high-energy side of π band and on the low-energy side of π^* band are detected whose intentities increase with the doping level; a small residual gap (~0.3–0.4 eV) in the metallic state has been measured by uv-visible spectroscopy[1] and recently confirmed by inverse photoemission.[19]

A precise description of the nature of the metallic state would involve an accurate calculation of the absorption line shape. It is clearly not the step function expected for a simple metal. Many-body effects[20] as well phonon broadening[21] may be important. However, as opposed to the case for intercalated graphite compounds,[22] the π^*-antibonding-band density of states is greatly altered in fully doped poly-five-membered heterocycles.

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