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Electron energy-loss investigation of the electronic structure of a PPP-related ladder polymer

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Abstract

The electronic structure of a ladder polymer of PPP has been investigated by high-energy electron energy-loss spectroscopy (EELS) in transmission. The band gap of the undoped compound is about 0.4 eV smaller compared to PPP. Information on the character of the undoped LPPP as well as on bipolaron states formed upon K doping in the former band gap are obtained from momentum dependent EELS investigations. The extension of the bipolaron is estimated to 20 ±4 Å.

1. INTRODUCTION AND EXPERIMENTAL

The electronic structure of undoped and doped PPP has been investigated some years ago.[1,2] Investigations performed using electron energy-loss spectroscopy in transmission (EELS) resulted in the observation of new bipolaronic states in the former band gap upon doping, which, however, do not overlap with the former π or π^* bands. This was deduced by the lack of a dispersion of the doping-induced interband transition. The interest in producing light emitting diodes [3,4,5] using organic material as active layers has triggered further studies on PPP related materials. As PPP has a rotational degree of freedom in the single bond between the phenyl rings, the degree of intramolecular order may depend on sample preparation conditions. An ordering can be gained by forming a ladder polymer. The species we report on here are described and labeled as l/m-LPPP in the contribution of W. Graupner et al. in this volume.[6]

Thin films of the polymers of about 1000 Å thickness were cast on NaCl crystals,[6] floated off in distilled water, mounted on electron-microscopy grids and transferred to a dedicated EELS spectrometer.[2] Doping has been achieved by evaporation of K from a well degassed SAES getter onto the films in vacuum (base pressure 10^{-9} mbar). The measurements have been performed with an energy resolution of 100 meV and a momentum resolution of 0.05Å^{-1}.

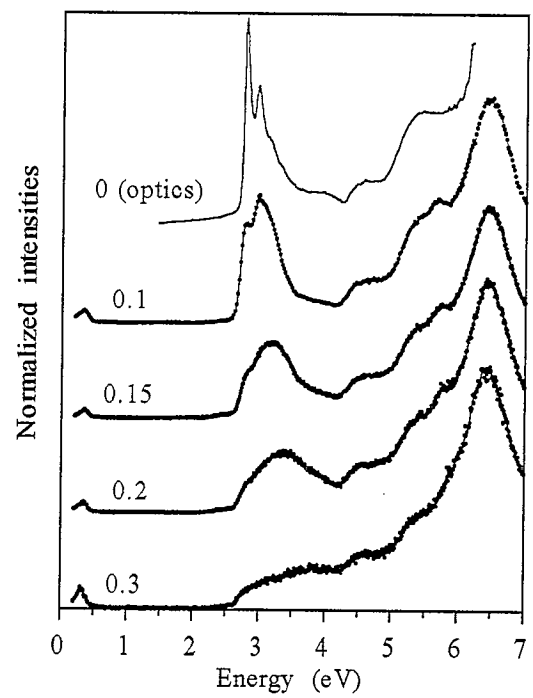

Figure 1. Loss function Im(-1/ε) for LPPP as obtained from UV-VIS absorption measurements (uppermost curve) and as measured by EELS at momentum transfers labeled in Å^{-1}.

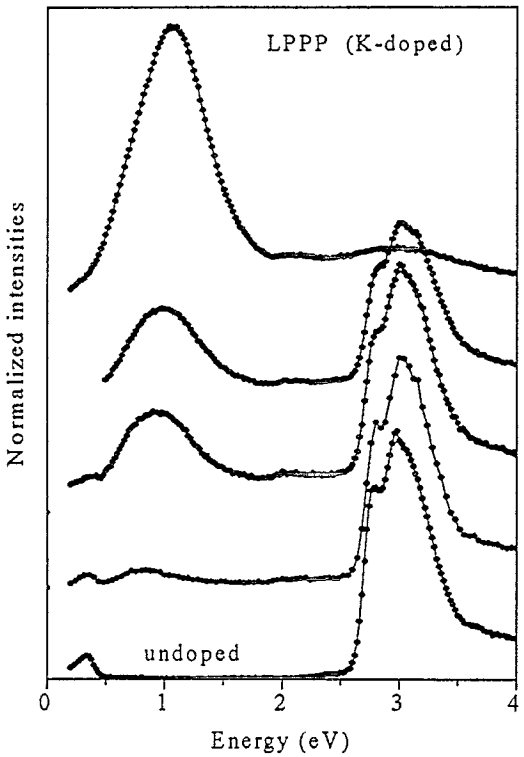

Figure 2. Loss function Im(-1/ε) of K-doped LPPP for various doping levels (the lowest curve is undoped LPPP). The momentum transfer is 0.1 Å^{-1}.

2. RESULTS AND DISCUSSION

Fig. 1 shows the low energy loss function of undoped LPPP obtained from optical measurements,[6] where the momentum transfer is negligible, and from EELS for momentum transfers k of 0.1, 0.15, 0.2 and 0.3 Å^{-1}. For k=0 the zero phonon 0-0 peak at 2.78 eV is dominant, while with increasing k higher transitions (involving phonon excitation) become more and more important. A strong linear dispersion is seen with a dispersion constant of 2.4 eVÅ. Strong damping occurs at higher k. We want to notice, that the second main feature near 6.5 eV shows, as in PPP, no dispersion, and no k-dependent damping.

In all LPPP samples a small structure appears near 0.35 eV, which is assigned to O-related defect states [6]. This feature shows no dispersion, as expected for a localized state. The intensity of this structure varies from sample to sample within about a factor 2.

Upon doping with K, like in PPP, there appears a broad structure in the gap with a maximum below and above 1 eV for low and high doping levels, respectively. Again similar to PPP, a small step-like structure near 2 eV is observed. The two features correspond to transitions from the two bipolaron bands to the conduction band.[1,2] In comparison to doped PPP [1] the energies of these doping induced features are lowered by ~0.2 eV, which corresponds to the observed lower band gap in LPPP.

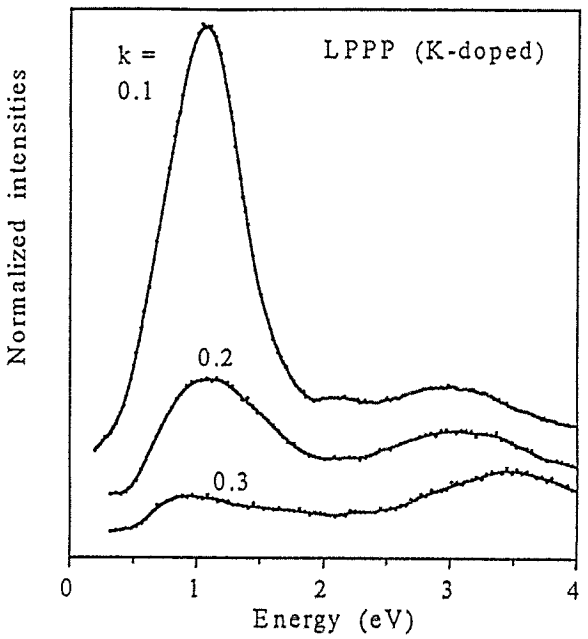

Figure 3. Loss function Im(-1/ε) of highly K-doped LPPP for various momentum transfers labeled in Å^{-1}.

In Figure 3 we show the loss function of the highly doped LPPP sample as a function of k. The remainder of the $\pi \rightarrow \pi^*$ transition near 3 eV shows the dispersion discussed above. The energetic position of the main feature near 1 eV is not changed upon changing the momentum transfer, while the intensity decreases extremely strong. From the half width of this bipolaron-π^* transition in momentum transfer of 0.32 ±0.05 Å^{-1} the extension of the bipolaron can be estimated to 20 ±4 Å.

In conclusion, the electronic structure of undoped and doped LPPP is analoguous to that of PPP, however the higher intramolecular order leads to a decrease of the band gap and the bipolaron-π^* interband transition energies in LPPP.

4. ACKNOWLEDGMENT

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