

Beamline: ID1	Date of experiment: from: 16.6.2004 to: 21.6.2004	Date of report: 28.2.2005
Shifts: 21	Local contact(s): Bruno Jean	<i>Received at ESRF:</i>
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Report:

Poly(2,5-pyridine diyl) (PPY) is a much studied conjugated polymer for its potential use in polymer based electronics. We have noted that *purified* PPY undergoes smectic organization in the direction of the polymer chain which we have previously observed in sulphonic acid complexes with PPY [1]. This affords multilevel hierarchial assembly of the polymer. We investigated this behaviour using anomalous x-ray scattering.

Solid PPY is for the most part crystalline (crystallinity >90 %) and the chains are assumed to be coplanar [2]. Strict crystal structure remains unresolved since at wide angles PPY shows mainly two intense but broad reflections, interpreted to result from lateral and π - π -stacking (see Fig.1).

Both pure PPY and PPY complexed with camphorsulphonic acid (CSA) were measured. The experiments were made close to the Br K-edge (13474 eV) at the beam line ID1. The optics comprised two bent Si-coated mirrors, between which a sagittally focussing double crystal Si₁₁₁ monochromator provides fixed exit beam with energy resolution of about 1 eV. The beam size at the sample was 0.2×0.2 mm². The scattering intensities were measured with CCD detector at the distance 0.553 m. Acquisition times for single frames varied between 3-60 s so as to keep the maximum counts per pixel well below the saturation limit. Several (typically three) frames were taken for each energy to improve statistical accuracy and to check for radiation damage (which there never was any). Dark current and flood field corrections were applied to the data and the frames were normalized and averaged into 1-D intensity curves using in-house software.

short EXAFS scans of the samples were routinely made between the experiments to monitor the position of the K-edge. There was a steady increase in the x-ray energy (about 3.5 eV, in total) during the experiment. From the EXAFS scans and from observed increase in x-ray fluorescence (Fig. 1) the correctness of the x-ray energy relative to the K-edge could be verified with sufficient precision.

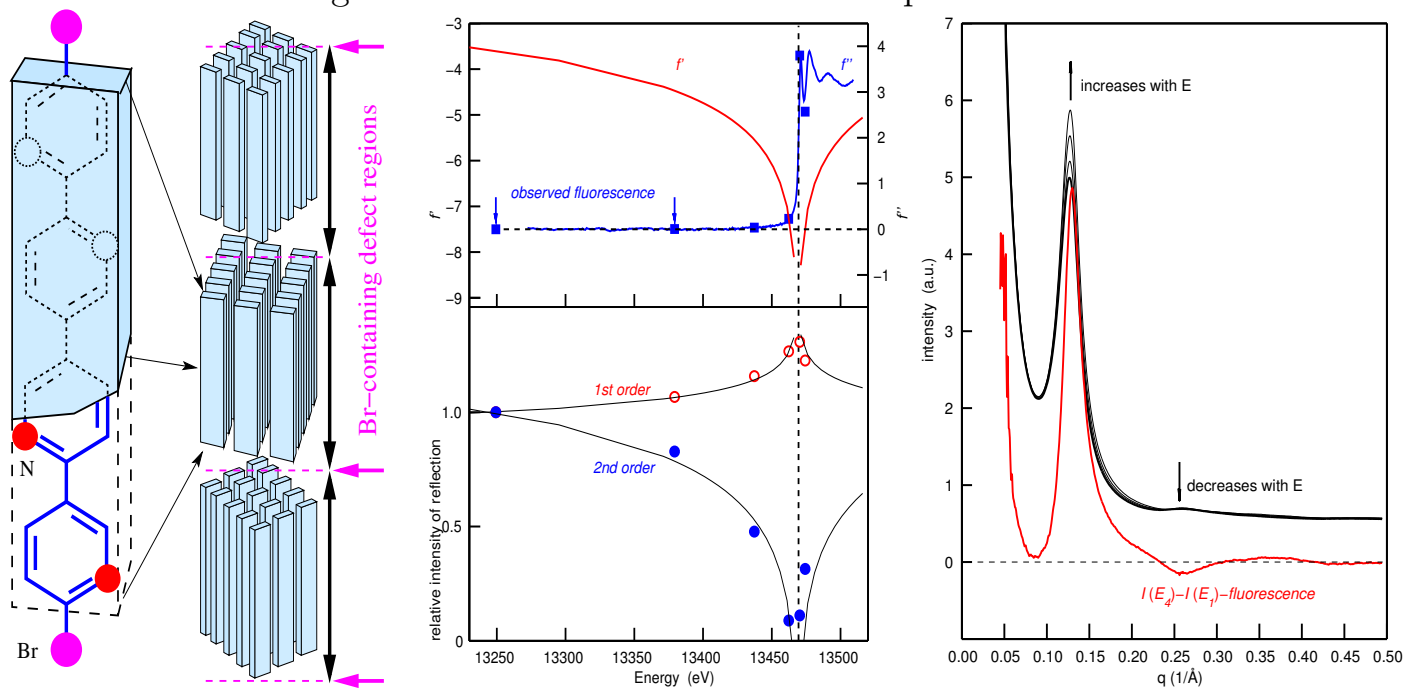


Figure 1. *Left:* Proposed smectic ordering in PPY. *Center:* Dispersion terms f' and f'' (K-shell electrons only) near Br K-edge. f'' is calculated directly from one of the EXAFS scans. f' is obtained from the program by Brennan and Cowan [3] which does not account for the effects of neighboring atoms. The markers denote energies at which the scattering measurements were made. In the useful energy range below the K-edge, the scattering factor typically changes by 3-4 electrons. The lower panel shows relative intensities of the first and second order reflections. *Right:* Intensity curves for one the pure PPY samples. The difference in intensities between the first and fourth energy (corrected for constant fluorescence and multiplied by 15) is shown in red.

The results support the original hypothesis of PPY organization as shown in Fig 1 where the intensity of the first diffraction peak is seen to depend on the energy. While the Br-content is only 3-4 %, the samples give relatively large anomalous scattering contribution since the total structure factor of the extended chain is small in intensity. The Bromine atoms reside at the chain ends which tend to migrate to form distinct layers between crystalline layers. The changes in intensity with E are fairly well represented by linear dependence with f_{Br} .

References:

- [1] M. Knaapila et al. *J. Appl. Cryst.* 36 (2003) 702-707.
- [2] E. J. Samuelsen et al. *Synthetic Metals* 124 (2001) 393-398.
- [3] S. Brennan et al. *Rev. Sci. Instrum.* (1992) 63, 850-853.