Total-reflection polarized XAFS of metalloporphyrins spread on the solution surface

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Development of a polarized total-reflection XAFS method (TR-XAFS) for the solution surface using an X-ray phase retarder (XPR) has demonstrated its high potential as a novel tool for the structural study of metal complexes on the solution surface at the monolayer amount. The previous study[1] on symmetrically substituted zinc(II) porphyrins, tetrakis (4-carboxyphenyl) porphyrinato zinc (ZnTPPC) and tetraphenylporphyrinato zinc (ZnTPP), spread on the aqueous solution surface has concluded that their molecular orientations are such as the porphyrin ring is in parallel to the solution surface and that no axial coordinations exist at the zinc center.

Our next target to be reported here was an asymmetrically substituted zinc complex of protoporphyrin IX (ZnPP) spread on the acidic aqueous solution surface.

A layer of ZnPP was formed on a 0.010 mol dm^{-3} hydrochloric acid solution surface by spreading a 5.4×10^{-5} mol dm^{-3} ZnPP ethyl acetate solution. The XAFS spectra at Zn K-edge were obtained in the fluorescence mode by means of a 19-element solid-state detector (SSD) at BL39XU. The polarization dependence was studied by using two linearly polarized X-ray beams, one horizontally polarized and the other vertically polarized by the XPR. The X-ray beam was introduced onto the solution surface at an angle of ca. 1 mrad, under the total-reflection condition.

The XANES spectra for ZnPP on the solution surface exhibited the contrastive behavior in comparison with our previous results[1] for symmetrically substituted zinc porphyrins. The shoulder peak at ca. 9660 eV corresponding to the 1s to $4p_z$ transition appears in both polarization spectra as shown in Fig.1. Since the intensity of the shoulder peak is proportional to $\cos^2(\theta)$, where θ is the angle between the X-ray polarization and the z-axis, the results shown in Fig.1 demonstrate that the ZnPP molecule with hydrophilic functional groups at one-side would rather be tilted at the surface (refer to the illustration inserted in Fig.1.).

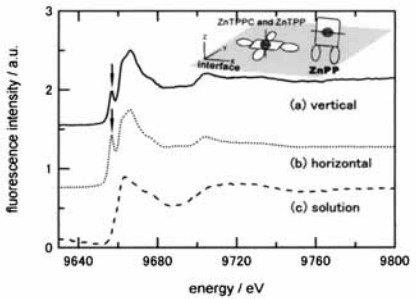

Fig.1. Zn K-edge XANES spectra for ZnPP at the air/aqueous solution interface taken with (a) vertical and (b) horizontal polarizations by TR-XAFS, and (c) for ZnPP ethyl acetate solution by a fluorescence mode.

Reference

(1) H. Tanida, H. Nagatani, I. Watanabe *J. Chem. Phys.*, **118**, 10369 (2003).

Study on the perpendicular magnetic recording media by nanoscale element-specific magnetic imaging using photoelectron emission microscopy (PEEM)

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The research on ultra-high density media has been extensively performed. Among them, perpendicular magnetic media are considered as a good candidate for the next generation hard disk drives (HDDs). The magnetic imaging of perpendicular magnetic media is essentially important for the development. We have performed a hard x-ray magnetic imaging using PEEM (Photoelectron emission microscopy) at the BL39XU of Spring-8 (Fig. 1). The spatial resolution of 40 nm was achieved at the Co K-edge using a nano-fabricated line and space sample. The magnetic imaging of CoCrPt perpendicular magnetic recording media has been performed using circularly poralized x-rays at the Pt L-edge. The magnetic contrast was obtained by the difference between the PEEM images acquired at the x-rays with plus and minus helicity (Fig. 2).

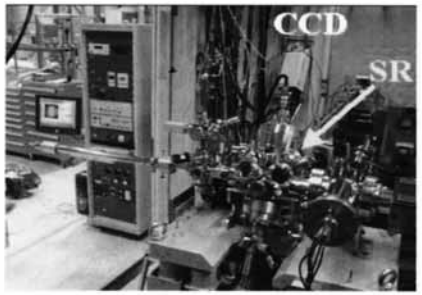

Fig. 1 Photograph of the PEEM system installed at BL39XU

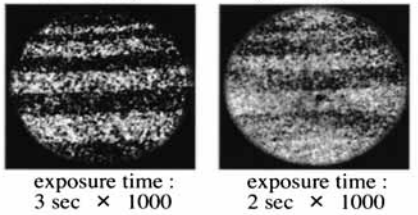

Figure 5 Magnetic imaging of CoCrPt perpendicular recording media (Field of view: 100 μm)