Metal Complex Spread on Liquid Surface Studied by Polarization-dependent X-ray Absorption Spectroscopy

Recent advances in a total-reflection X-ray absorption fine structure (TR-XAFS) method allow us to investigate the solvation structure of ions at the air-water interface [1-3]. There is very little information on this phenomenon due to the lack of a suitable experimental technique; however, such information is important for colloid and solution chemistry. Further progress in the TR-XAFS method with linearly polarized X-rays described here has been achieved by introducing an X-ray phase retarder to the undulator beamline [4].

Experiments were carried out at the undulator beamlines **BL39XU** and **BL37XU**. The linearly polarized X-ray on the horizontal plane from the undulator was converted to a vertically polarized one using a diamond crystal phase retarder. The degree of linear polarization, P_L, is defined by the following equation: $P_L = (I_h - I_v) / (I_h + I_v)$, where I_h and I_v are the intensities of the polarized X-rays. P_L = -1 corresponds to a perfect linear polarization on the vertical plane. In the present setup, the P_L value was estimated to be approximately – 0.9 for the vertically polarized X-ray.

Various metalloporphyrins have been applied to photoenergy conversion systems as well as to supramolecular structures involving self-assembly features that could further improve the functionality of porphyrin-containing thin films organized by interfacial processes. In this work, we applied the polarized TR-XAFS method to a monolayer of planar zinc(II) porphyrin, *meso*-tetrakis(4-carboxyphenyl) porphyrinato zinc(II) (ZnTPPC), at the air-water interface in order to determine the coordination structure around zinc and the molecular orientation. Under the present acidic condition, four carboxyl groups of ZnTPPC are not dissociated, and consequently, the neutral form of ZnTPPC does not dissolve into the aqueous subphase.

The X-ray absorption near-edge structure (XANES) spectra at the Zn *K*-edge for ZnTPPC are displayed in Fig. 1. A XANES spectrum with a horizontally polarized X-ray (a) is different from that with a vertically polarized one (b); the most striking difference is the appearance of a very strong first peak at 9662 eV in Fig. 1(b), which must correspond to the shoulder structure of the powder sample (d) at the same energy, but is absent in the horizontal spectrum (a). The strong pre-edge or shoulder peak in the XANES spectrum at the Zn *K*-edge must be associated with the $1s$ - $4p_z$ transition in the absence of the axial coordination for zinc atoms, since the assignment of such a peak has been well established for square planar complexes [5]. The polarization dependence of the XANES spectrum indicates that the plane of the ZnTPPC molecule is unambiguously oriented parallel to the air-water interface and there is no coordination to the axial sites of the zinc atoms. On the other hand, the absence of any pre-edge peak in the spectrum for ethyl acetate solution in Fig. 1(c) suggests that the solvent molecules are coordinated to the axial sites of a zinc atom in ethyl acetate (Fig. 2).

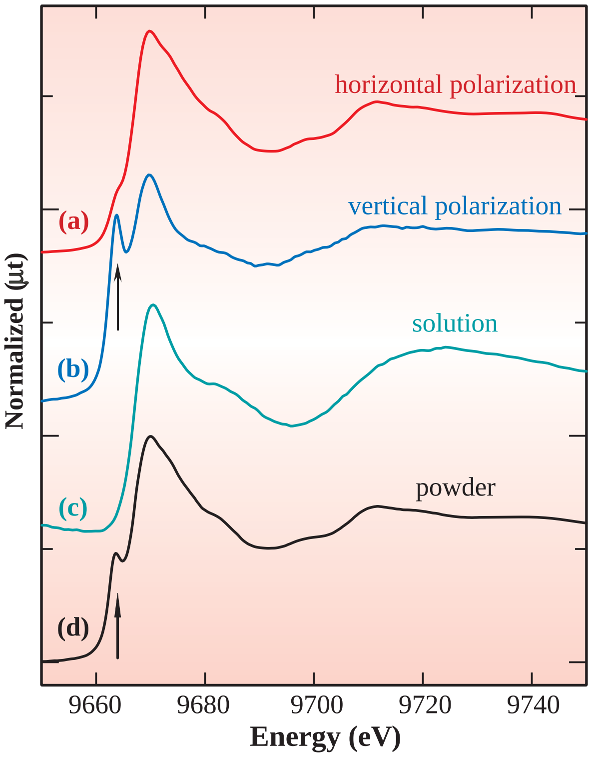

Fig. 1. XANES spectra at the Zn *K*-edge for ZnTPPC spread as a monolayer in the acidic aqueous solution taken with **(a)** horizontal and **(b)** vertical polarization by the TR-XAFS method, **(c)** in the ethyl acetate solution by the fluorescence mode, and **(d)** in the solid powder by the transmission mode.

XAFS is a powerful technique for clarifying the coordination structure in a complex around a metal center. The present results clearly demonstrate that the TR-XAFS method enable the determination of the orientation of a planar complex at the air-water interface in a very simple manner by introducing polarized X-rays. Furthermore, EXAFS analysis would allow us to characterize the molecular structure of metal complex at the interface within the horizontal or the vertical plane separately, e.g., solvation and coordination distances between metal and ligands involved in the self-assembled monolayer, or the Langmuir-Blodgett film formed or in process.

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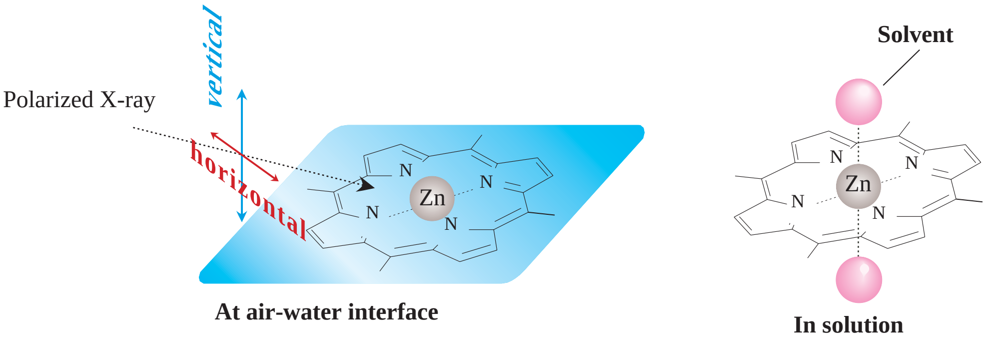

Fig. 2. Schematic drawing of the predicted molecular orientation of ZnTPPC at the air-water interface and the solvation structure in the solution.

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