

Surface Characterization of Polycrystalline Hemin

Hiromi IKEURA-SEKIGUCHI^{1,*} and Tetsuhiro SEKIGUCHI²¹ Research Institute for Measurement and Analytical Instrumentation (RIMA),
National Metrology Institute of Japan (NMIJ),National Institute of Advanced Industrial Science and Technology (AIST),
1-1-1 Umezono, Tsukuba, Ibaraki, 305-8568, Japan²Japan Atomic Energy Agency (JAEA), Tokai-mura, Naka-gun, Ibaraki 319-1195, Japan

1 Introduction

Hemin, iron(III) protoporphyrin IX, is one of metal porphyrin complexes which are naturally occurring molecules and found in a variety of important biological processes such as oxygen transport and photosynthesis. Metalloporphyrin ring is composed of four pyrrole units conjugated through methine bridges, with this highly conjugated structure (Fig. 1) giving electron or charge delocalization over a whole molecule. In order to understand electron and energy transfer processes, partial density of unoccupied states was measured using X-ray absorption spectroscopy (XAS) monitored by total electron yield (TEY) for bulk and Auger electron yield (AEY) for surface.

2 Experiment

Experiments were performed at beamline BL-27A with an InSb(111) double-crystal monochromator with an energy resolution of ca. 0.9 eV around Cl *K*-edge. The XAS spectra of polycrystalline hemin were measured in the TEY mode as monitoring sample drain current and the AEY mode as monitoring Cl *KLL* Auger electrons near the Cl *K*-edge (2815–2870 eV) and normalized to the incident flux with thin aluminum films. Such energies were chosen to excite the Cl 1s core electron to 3*p* and 4*p* unoccupied orbitals.

3 Results and Discussion

Fig. 1 shows Cl *K*-edge XAS spectra of polycrystalline hemin measured in the TEY and the AEY modes. XAS has the highest surface sensitivity in the AEY mode with the probing depth of ~7.5 nm at Auger electron energy of ~2.3 keV, which is about three times larger than the Inelastic Mean-Free Path (IMFP). Although the TEY is known as surface sensitive analysis, the probing depth of the TEY is estimated to more than ~70 nm [1] in the excitation energy regions of deep core levels.

Based on the previous study of metal chloride [2], pre-edge peak A is assigned to Cl 1s → Fe 3*d* hybridized with Cl 3*p* orbital. Peak B is assigned to Cl 1s → 3*p* orbital. We found that surface states of polycrystalline hemin are higher in energy (~0.8 eV) than bulk ones as shown in peak A. Peak B also shifts to higher energy state. Similar energy shifts have been observed in N *K*-edge XAS among hemin monomer, dimer, and solid states [3]. Considering the previous study [3], the shifts suggest that “dimer-like” layers with less intermolecular hemin-hemin interactions could be produced near surface regions. In

contrast, stronger hemin-hemin interactions could be caused partly by hydrogen interactions of side groups.

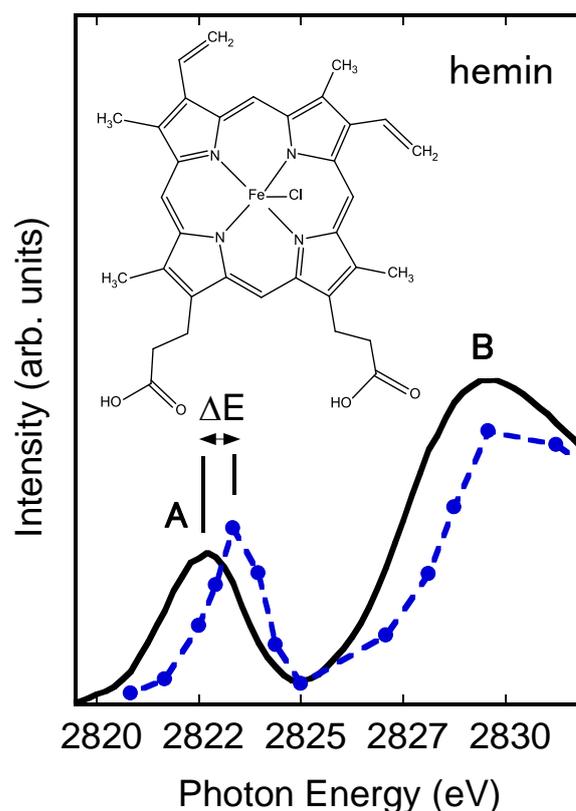


Fig. 1: Comparison of bulk- and surface-sensitive Cl *K*-edge XAS spectra of polycrystalline hemin measured by the TEY (black line) and the AEY (blue dot line).

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References

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*ikeura-sekiguchi@aist.go.jp