

The Study of the Heme Electronic Structure by Soft X-ray Emission Spectroscopy

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The iron(III) porphyrin have attracted much attention because of it's relevance to the naturally occurring hemeproteins. In connection with the catalytic activation mechanisms, it is important to clarify the electronic structure of the complexes carrying the diatomic molecules such as myoglobin, hemoglobin, cytochrome P450, hemeoxygenase, catalase, peroxydase, and so on.^[1,2] Since the nature of the chemical bonds around the iron(III) center greatly affect on the electronic structure of these hemeproteins, the studies on the $d\pi$ - $p\pi$ interactions such as σ - and π - interactions among iron(III) d-orbitals, frontier orbitals of porphyrin ring and axial ligands have been carried out actively by many groups^[3-6]. The tools to clarify the electronic structure have been mainly depends on the combined analyses of the theoretical methods and spectroscopic methods such as NMR, EPR, Mössbauer, resonance Raman, XAS, etc. These combined analyses are sophisticated, but it sometime requires so many methods to obtain the information about the electronic structure and is very time-consuming. So, the development of the simple and direct observation methods for the determination of the electronic structure should be eagerly anticipated.

Thus, it is quite important to investigate the electronic structure of model heme complexes using the recently developed technique of resonant x-ray emission spectroscopy (RXES)^[7] because the method gives the valence- and spin-specific characteristics of ligand-metal binding in terms of the Fe 3d and ligand energy levels. In addition, recent progress of the synchrotron techniques makes it possible to get the information about the intra-atomic d-d transitions, inter-atomic charge transfer, etc. by the high resolution RXES experiment. So, we carried out the RXES experiment to obtain the detailed information about the electronic structure of the model heme complexes.

Samples were prepared as thin layer film coated on the silicon wafer by the Electron Spray Deposition (ESD) method. The samples have basically uniform surfaces, but some samples have rough surfaces that it is quite difficult to measure with the scanning method in order to avoid the damage of the samples. As expected, the reduction of the iron in the model heme complex at the sample surface were occurred, the samples were intentionally moved to the defocused position and measured as fast as we can. XAS spectra were measured at Fe L edge

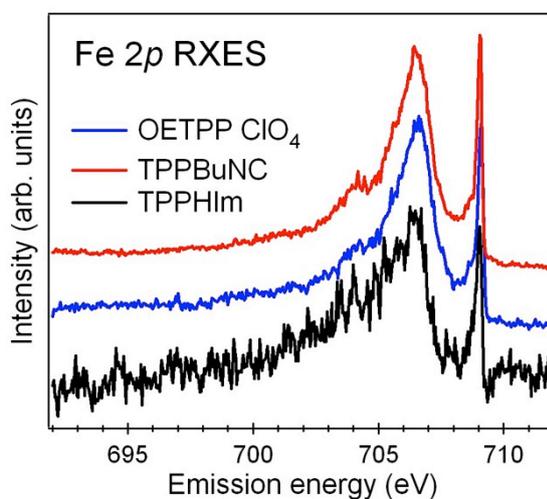


Fig. 1. Fe L3 edge-resonant soft x-ray emission spectra of $\text{Fe}(\text{OETPP})\text{ClO}_4$, $[\text{Fe}(\text{TPP})(\text{BuNC})_2]^+$, and $[\text{Fe}(\text{TPP})(\text{HIm})]$.

(~710eV), and the RXES experiments were carried out at Fe L3 edge. Since d-d excitation energies do not strongly depend on the excitation energy while relative intensity depends on the character of the core-excited states, excitation energy was tuned to 2 eV above the Fe 2p_{3/2} ionization threshold to reduce the area of overlap of an intense elastic line with the d-d excitation spectra.

Fig. 1 shows Fe L3 edge-resonant soft x-ray emission spectra of Fe(OETPP)ClO₄, [Fe(TPP)(^tBuNC)₂]⁺, and [Fe(TPP)(HIm)₂]⁺.^[8] The sharp elastic peak was found at 709 eV, and the resonant x-ray emission including d-d excitation peaks were found as shoulder peak at 708.5 eV and as wide band below 707eV. These wide band structures exhibit strong hybridization with the ligands in these complexes. Since the relative intensity of the resonant emission against the elastic peak shows the degree of the localization of the excited state, the obtained spectra suggests that the delocalization was strengthened in the [Fe(TPP)(HIm)₂]⁺ complex. As shown in Fig. 2., this tendency was more apparent when the excitation energy was varied in RXES measurements. In this experiment we could obtain the informative initial data, which is the first step to get the full picture of the heme electronic structure by the XAS, RXES methods. More detailed data should be obtained by the additional experiments at the BL07LSU beamline. Further investigation is now in progress.

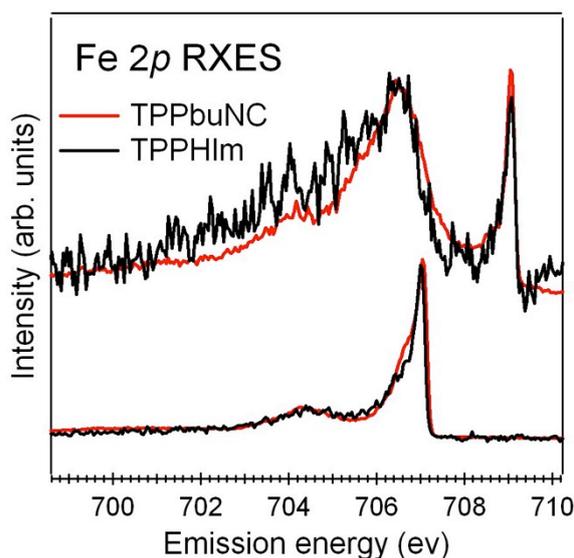


Fig. 2. Excitation energy dependence of the RXES of [Fe(TPP)(^tBuNC)₂]⁺, and [Fe(TPP)(HIm)₂]⁺.

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- [8] Abbreviations: TPP, OETPP: dianions of 5,10,15,20-tetraphenylporphyrin, and 2,3,7,8,12,13,16,17-octaethyl-5,10,15,20-tetraphenylporphyrin, respectively. ^tBuNC: tert-butylisocyanide, HIm: Imidazole.