

## Study of Spin States and Molecular Orientation of Porphyrin Compounds in Films Using NEXAFS

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### Introduction

Sandwich-type metal/insulator/metal (MIM) junctions exhibit various interesting phenomena such as electroluminescence (EL), photovoltaic effects, and anomalous magnetoresistance. Parts of authors have recently fabricated biomolecular light-emitting-diode (BIODE) using hemin, which is a small molecule containing an iron protoporphyrin IX unit (Fig. 1a). Interestingly, this device exhibited anomalous change of the EL spectrum, when we applied the voltages over  $\sim 5$  V. (See Fig. 1b) This voltage-induced transition was irreducible [1].

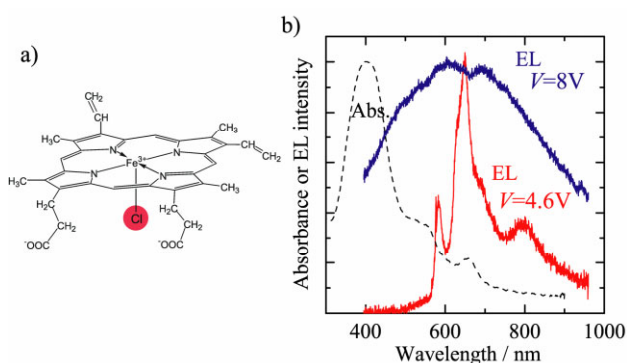


Fig. 1 (a) The molecular structure of hemin. (b) The EL and absorption spectra of hemin.

In the previous paper [1], we have proposed the possibility of high-spin to low-spin transition for this transition. In order to examine this possibility, we have measured Fe  $L$ -edge XANES spectra.

### Results

Figure 2a shows the Fe- $L$  XANES spectra of Fe(TPP)Cl and [Fe(TPP)(Im)<sub>2</sub>]ClO<sub>4</sub>. These compounds have porphyrin skeleton as well as hemin. The former is a high-spin compound, while the latter is a low-spin compound. We selected them as references in both spin state. The peaks at 710 eV and 720 eV are respectively attributable to  $L_{III}$  and  $L_{II}$  peaks associated with 2p-3d transition. The  $L_{II}$  peak in the high-spin Fe[(TPP)Cl] is weaker than that of low-spin [Fe(TPP)(Im)<sub>2</sub>]ClO<sub>4</sub>. A satellite peak at 715 eV appears only in the high-spin Fe[(TPP)Cl]. Similar trends are reported in other compounds. We have also measured the XANES

spectrum of high-spin hemin in the crystalline powder. The obtained spectrum was similar to that of Fe(TPP)Cl.

Figure 2b shows the XANES spectrum of hemin in the ITO/hemin/Al junction. In this measurement, X-ray was incident on the Al electrode. A bias voltage (6 V) was applied to electrodes in the chamber. We measured the XANES spectra of hemin before and after applied the voltage. The background was subtracted in the analysis.

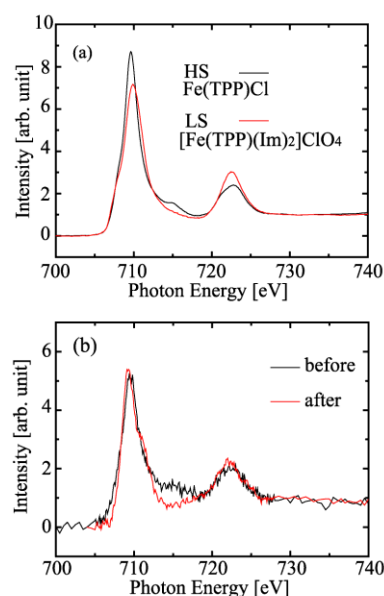


Fig. 2 XANES spectra of (a) Fe(TPP)Cl [powder, high-spin state] and [Fe(TPP)(Im)<sub>2</sub>]ClO<sub>4</sub> [powder, low-spin state]; (b) hemin in ITO/hemin/Al junction before and after a bias voltage (6 V) was applied.

Although the  $L_{II}$  and  $L_{III}$  peaks hardly changed before and after applied voltage, the satellite at 715 eV appeared only in the spectrum before applied the voltage. This suggests that the high-spin to low-spin transition occurred in this system. More detailed analyses are still in progress.

### References

[1] H. Tajima et al, K. Shimatani, T. Komino, M. Matsuda, S. Ikeda, Y. Ando, and H. Akiyama, *Bull. Chem. Soc. Jpn.*, **79**, 549 (2006).

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