BL-13A/2022G522

Fe–O Bond Character of a μ-Oxo-Bridged Iron Phthalocyanine Dimer Investigated by O K-Edge X-Ray Absorption Spectroscopy

Yasuyuki YAMADA[1, *], Fumitoshi KUMAKI[2], Kaisei SUGIHARA[3], Narumi ITO[4], Jun-ichi ADACHI[2, 5], Masanari NAGASAKA[6, 7], Quan Manh PHUNG[3, 8], Kentaro TANAKA[3, 9]

[1]Department of Biotechnology & Chemistry, Faculty of Engineering, Kindai University, Takayaumenobe, Higashihiroshima, Hiroshima 739-2116, Japan
[2]Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization, Tsukuba, Ibaraki 305-0801, Japan
[3]Department of Chemistry, Graduate School of Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Aichi 464-8602, Japan
[4]Research Center for Materials Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Aichi 464-8602, Japan
[5]Graduate Institute for Advanced Studies, SOKENDAI, Tsukuba, Ibaraki 305-0801, Japan
[6]Institute for Molecular Science, Myodaiji, Okazaki, Aichi 444-8585, Japan
[7]Graduate Institute for Advanced Studies, SOKENDAI, Myodaiji, Okazaki, Aichi 444-8585, Japan;
[8]Institute of Transformative Bio-Molecules(WPI-ITbM), Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Aichi 464-8602, Japan
[9]Research Center for Quantum and Chemical Innovation, Institute of Innovation for Future Society, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Aichi 464-8602, Japan

1 Introduction

μ-Oxo-bridged iron phthalocyanine dimers are functional metallophthalocyanines used in oxidation catalysis, sensing, nonlinear optics, and electrocatalysis [1]. Their Fe–O–Fe cores may adopt bent or quasi-linear structures, and their electronic and magnetic states are sensitive to solvents, peripheral substituents, and axial ligands. Although these compounds have been studied by diffraction, magnetic, optical, Mössbauer, and hard X-ray techniques, the electronic structure of the bridging oxygen has remained less directly characterized.

Soft X-ray absorption spectroscopy (XAS) provides element-selective information because the region below 1 keV contains both the O K-edge and Fe $L_{2,3}$-edges [2]. However, μ-oxo iron porphyrinoids had not previously been examined by soft XAS. We therefore investigated the soluble *tert*-butyl-substituted dimer **$(Fe^{III}Pc{t}Bu_4)_2O$** and compared it with monomeric **$ClFe^{III}Pc{t}Bu_4$** and double-bonded oxotitanium phthalocyanine (**$OTi^{IV}Pc$**). The aim was to determine how the formally single Fe–O bonds of the bridge are expressed in the O K-edge spectrum.

2 Experiment

$(Fe^{III}Pc{t}Bu_4)_2O$ was prepared from **$Fe^{II}Pc{t}Bu_4$** using aqueous NaOH and purified by gel permeation chromatography; **$ClFe^{III}Pc{t}Bu_4$** was obtained by acid cleavage of the dimer. The products were characterized by MALDI-TOF mass spectrometry, UV-visible spectroscopy, and elemental analysis. Solid films were prepared by drop-casting 40 μL of 10 mM CH_2Cl_2 solutions onto 100-nm Si_3N_4 membranes and drying them under vacuum.

Transmission-mode O K-edge and Fe $L_{2,3}$-edge XAS spectra were recorded at KEK-PF BL-13A at room temperature under helium [3]. The transmitted intensity through each sample was normalized to that through a bare Si_3N_4 membrane. A 400-nm-thick Ni filter suppressed higher-order light, and the O K-edge energy was calibrated with a polymer membrane. TD-DFT calculations were carried out with ORCA 6.0.1; core-level excitations and natural transition orbitals were used to identify the acceptor-orbital character.

3 Results and Discussion

The Fe L_3-edge maximum of **$(Fe^{III}Pc{t}Bu_4)_2O$** (709.3 eV) was nearly identical to that of **$ClFe^{III}Pc{t}Bu_4$** (709.5 eV), and their L_2-edge maxima were likewise comparable (722.0 and 721.7 eV). These results indicate that both complexes contain Fe(III) center(s).

At the O K-edge, **$ClFe^{III}Pc{t}Bu_4$** showed no feature from 520 to 550 eV, whereas the μ-oxo dimer displayed a sharp peak at 529.1 eV. This energy is substantially lower than the >534 eV region typical of single-bonded oxygen, and is close to the 530.6 eV peak of **$OTi^{IV}Pc$**, even though the Fe-O bonds in the dimer formally have single-bond character.

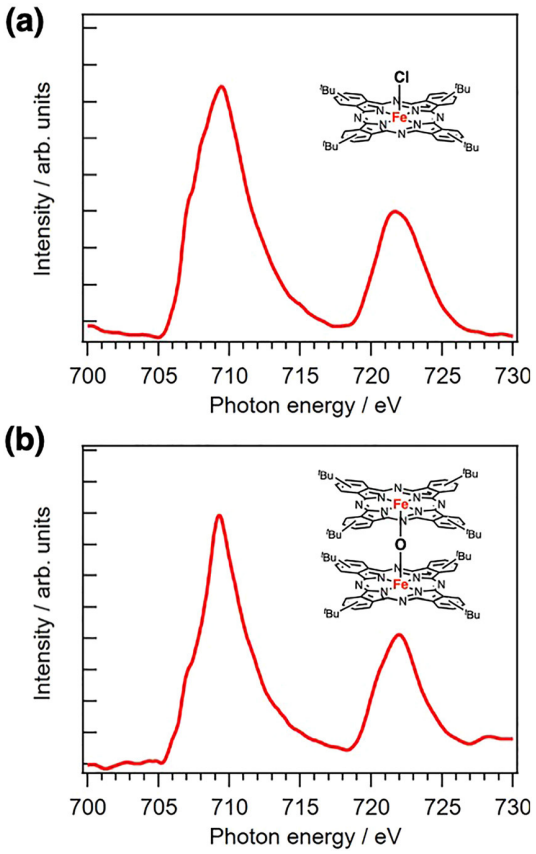

Fig. 1: Fe $L_{2,3}$-edge XAS spectra of (a) **ClFe^{III}Pc*t*Bu$_4$** and (b) **(Fe^{III}Pc*t*Bu$_4$)$_2$O**.

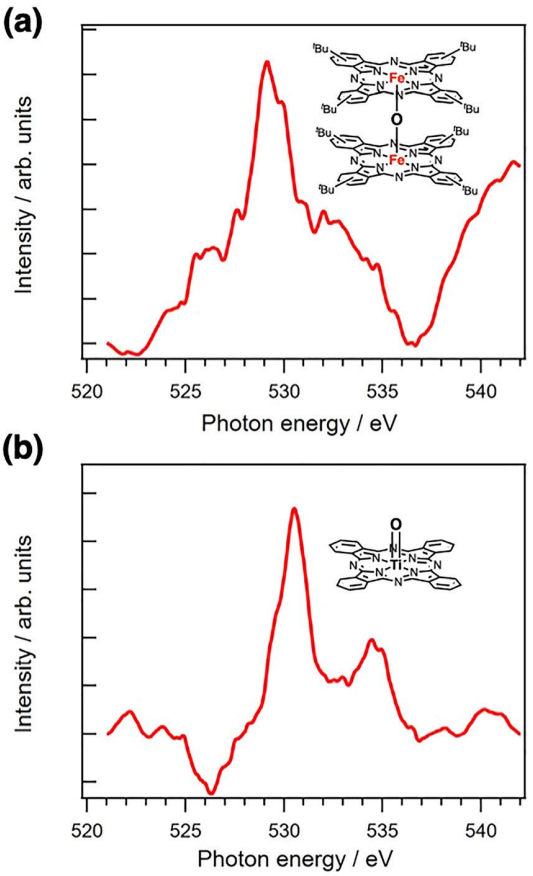

Fig. 2: O K-edge XAS spectra of (a) **(Fe^{III}Pc*t*Bu$_4$)$_2$O** and (b) **OTi^{IV}Pc**.

The comparison in Fig. 2 is notable because molecules containing single-bonded oxygen, such as H_2O, generally absorb above 534 eV, whereas multiple-bonded oxygen gives lower-energy features. Thus, a direct interpretation based only on formal bond order would incorrectly suggest double-bond character for the μ-oxo bridge.

TD-DFT reproduced the experimental energy trends without an empirical shift. For the high-spin, antiferromagnetically coupled dimer, the first calculated feature near 530 eV arose mainly from O 1s → π*(Fe $3d_{xz}$-O p_x) and O 1s → π*(Fe $3d_{yz}$-O p_y) excitations, with a weaker σ*(Fe $3d_{z2}$-O p_z) contribution. The corresponding natural transition orbitals are concentrated along the Fe–O–Fe axis. Removing the peripheral *tert*-butyl groups or changing the Fe–O–Fe angle had little effect on the first peak, confirming that the excitation is localized in the μ-oxo unit.

Calculations for coordinated H_2O and OH species placed their dominant O K-edge features at higher energies and further supported the assignment. The unusually low energy of the dimer peak is therefore governed by the energies of metal-oxygen antibonding acceptor orbitals, rather than by a simple single- versus double-bond classification.

4 Conclusion

Transmission soft XAS directly detected the bridging oxygen of a μ-oxo iron phthalocyanine dimer. The 529.1 eV peak was assigned to transitions from O 1s into Fe–O antibonding orbitals by TD-DFT. This combined spectroscopic and computational approach provides an element-specific description of the Fe–O–Fe core and should be applicable to other μ-oxo iron porphyrinoids, including future measurements in solution.

Acknowledgement

This work was supported by JSPS KAKENHI (25K22271, 25K01843, 24H01844, 26H00874, 25K03396, 24K17694, and 26K08384) and the Toyoaki Foundation. XAS measurements were performed with approval of the Photon Factory Program Advisory Committee (No. 2022G522).

References

[1] A. B. Sorokin et al., *Coord. Chem. Rev.* **28**, 19283-19289 (2026).

[2] M. Nagasaka, S. Tsuru and Y. Yamada, *Phys. Chem. Chem. Phys.* **26**, 23636-23645 (2024).

[3] A. Toyoshima et al., *J. Phys.: Conf. Ser.* **425**, 152019 (2013).

Research Achievements

Publication: Y. Yamada et al., “Fe–O bond character of a μ-oxo-bridged iron phthalocyanine dimer investigated by O K-edge X-ray absorption spectroscopy,” *Phys. Chem. Chem. Phys. 28*, 19283-19289 (2026), DOI: 10.1039/D6CP01650B.

* yy@hiro.kindai.ac.jp