

Extended X-ray Absorption Fine Structure of Copper(II) Complexes at the Air-Water Interface by a Polarized Total-Reflection X-ray Absorption Technique

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Copper(II) complexes spread on an aqueous solution surface were studied by a polarized total-reflection X-ray absorption fine structure (TR-XAFS) technique. The polarized TR-XAFS spectra at the Cu-K edge for copper(II) porphyrins and copper(II) chlorophyllin in a monolayer were measured *in situ* at the air-water interface. The polarization dependences of X-ray absorption near-edge structure (XANES) involving a $1s \rightarrow 4p_z$ transition allowed us to estimate the molecular orientation and the local coordination structure around the copper(II) atom in the polarization plane selectively. The extended X-ray absorption fine structure (EXAFS) region of the polarized TR-XAFS spectra for the metal complexes present at the air-water interface was successfully analyzed for the first time. The relative coordination number for the copper center evaluated from the EXAFS analysis indicated larger values in the vertical polarization than in the horizontal one, in agreement with the standing-up molecular orientation at the air-water interface estimated from the XANES region.

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Introduction

The interfacial species at the air-water interface have been characterized by means of infrared reflection absorption spectroscopy^{1,2} and nonlinear spectroscopy.^{3,4} The molecular orientation and conformation in monolayers at the air-water interface have been analyzed *in situ* by the polarization dependence of spectral data. Grazing incidence X-ray/neutron diffraction techniques can also provide structural information on the surface layer at the atomic level.^{5,6} Nevertheless, the coordination structure of the metal complex at the air-water interface has not been revealed in detail by those methods. The X-ray absorption fine structure (XAFS) method is a powerful tool to study the coordination structure of metal complexes.⁷ Total-reflection XAFS (TR-XAFS) techniques have been applied to investigate the coordination structure of the surface species on solids^{8,9} and solution surfaces.¹⁰ The local structure around metal ions electrostatically attracted from the bulk solution phase to a Langmuir monolayer at the air-water interface was revealed in detail by analyzing the extended X-ray absorption fine structure (EXAFS) through the total-conversion helium ion yield^{11,12} or fluorescence modes.¹³

For a solid surface, the polarization-dependent XAFS technique has been utilized to elucidate a well-organized structure such as thin-layer materials and coordination sites of adatoms on crystals.¹⁴⁻¹⁸ Recent applications of the polarized

TR-XAFS method have revealed the specific solvation structure of zinc(II) porphyrins at the air-water interface,^{19,20} in which the X-ray absorption near edge structure (XANES) exhibited a significant difference depending on the polarization of X-rays. A pre-edge peak, which is known to correspond to the $1s \rightarrow 4p_z$ transition for a square-planar metal complex without axial coordination, was observed at the Zn K-edge, and it was concluded that the axial coordination sites of the zinc porphyrin molecules examined were not fully hydrated at the air-water interface. The molecular orientation of zinc(II) porphyrins was also estimated by analyzing the dichroic ratio of the $1s \rightarrow 4p_z$ transition peak. The planar molecules of *meso*-substituted porphyrin derivatives, 5,10,15,20-tetraphenylporphyrinato zinc(II) (ZnTPP) and 5,10,15,20-tetrakis(4-carboxyphenyl)-porphyrinato zinc(II) (ZnTPPC) were found to orient roughly parallel to the solution surface.^{19,20} On the other hand, zinc(II) protoporphyrin IX (ZnPP) with hydrophilic carboxyl groups at one side of the molecule was standing-up with respect to the solution surface.²⁰

The axial coordination behavior of the metalloporphyrin plays an important role in the molecular recognition properties in sensor applications,²¹⁻²³ the self-assembling of supramolecular structures²⁴⁻²⁶ and monolayer formations at the air-water interface.^{27,28} The surface concentration of bulky metal complexes well-oriented at the air-water interface without self-aggregation or multilayer formation is generally much lower than the metal ions attracted to a condensed surfactant layer. Thus, an EXAFS analysis, which provides detailed structural information such as coordination distance and number, has not yet been achieved for the monolayer of a metal complex

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including metalloporphyrin at the air-water interface.

In this work, monolayers of copper(II) porphyrins and copper(II) chlorophyllin with hydrophilic carboxyl groups at the air-water interface were investigated by the polarized TR-XAFS technique. Significant spectral differences in the TR-XAFS spectra taken with horizontal and vertical polarizations were observed in both the XANES and EXAFS regions. An EXAFS analysis of the polarized TR-XAFS spectrum was successfully achieved for the first time at an air-water interface and discussed in comparison with solid powder and bulk solution species.

Experimental

Reagents

Copper(II) complexes of protoporphyrin IX (CuPP) and 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (CuTPPC) (Frontier Scientific/Porphyrin Products) were used as received. Copper(II) chlorophyllin (CuChl) was prepared from the recrystallization of CuChl trisodium salt (Nacalai Tesque EP) in 0.10 mol dm⁻³ hydrochloric acid. The copper complexes shown in Fig. 1 were dissolved in chloroform/*N,N*-dimethylformamide (DMF) (9:1 v/v for CuPP and CuChl, 8:2 v/v for CuTPPC), and were carefully spread onto an acidic aqueous solution of 1.0 × 10⁻² mol dm⁻³ hydrochloric acid. The concentrations of the spreading solutions were 9.3 × 10⁻⁵ mol dm⁻³ for CuPP, 1.0 × 10⁻⁴ mol dm⁻³ for CuChl, and 9.4 × 10⁻⁵ mol dm⁻³ for CuTPPC, respectively. The carboxyl groups of porphyrins and chlorophyllin did not dissociate in the present acidic condition, and the copper(II) complexes remained electrically neutral on the aqueous solution surface. The aqueous solutions were prepared with highly purified water by a Milli-Q system (Millipore Milli-Q Plus with Elix 5). All other reagents were of analytical or higher grade.

Polarized TR-XAFS

All of the XAFS measurements were carried out at the undulator beamline BL39XU at SPring-8, Hyogo, Japan. The linear polarization of the X-ray beam, which was originally polarized in the horizontal plane, was converted to vertical polarization by a double-crystal X-ray phase retarder (XPR). The degree of linear polarization (P_L), in which $P_L = -1$ corresponds to perfect linear polarization in the vertical plane, was -0.9 by using a couple of 0.73 mm thick diamond(111) XPR crystals.²⁹ The monochromatized X-ray beam was introduced onto the aqueous solution surface under the total-reflection condition. The surface area (S) of the aqueous solution was controlled from 220 × 180 to 220 × 60 mm (396 cm² ≥ S ≥ 132 cm²) by a Langmuir trough made of PTFE thermostated at 288 K. The angle of incidence of the X-ray beam (0.050 mm (height); 1.0 mm (width)) was smaller than 1.2 mrad in all measurements, and the footprint of X-rays on the solution surface was *ca.* 42 × 1 mm. The TR-XAFS spectra at the Cu K-edge were measured in a fluorescence mode by using a 19-element Ge solid state detector (SSD) (Canberra). A Ni filter (EXAFS Company) and a solar slit were placed in front of the SSD to improve the S/N ratio. Further details of an analogous optical setup are described elsewhere.²⁰

The XAFS spectra for the copper complexes dissolved in DMF and the solid powder sample pressed as boron nitride pellets containing 5 wt% copper complex were also measured in the fluorescence mode without controlling the polarization. The concentrations of the bulk solution samples were 9.3 × 10⁻⁴ mol dm⁻³ for CuPP, 1.0 × 10⁻³ mol dm⁻³ for CuChl, and 1.1 × 10⁻³ mol dm⁻³ for CuTPPC, respectively.

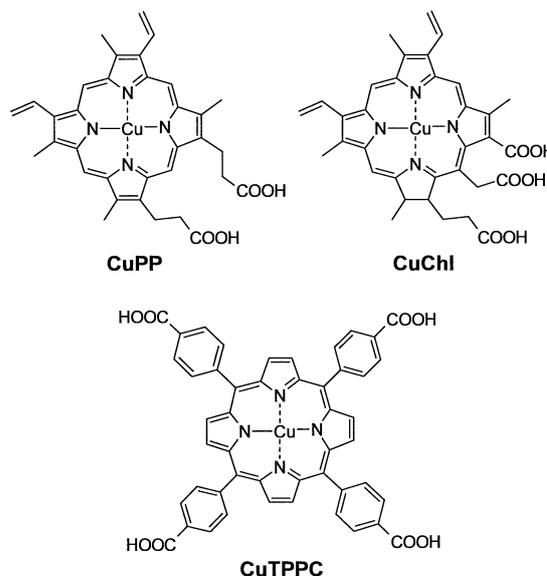


Fig. 1 Molecular structures of copper(II) porphyrins and copper(II) chlorophyllin.

EXAFS analysis

The data analysis was carried out by using the program REX2000 (Rigaku Ver. 2.5.9).³⁰ The Cu K-edge XAFS was extracted from the fluorescence intensity raw data by subtracting the background intensity estimated by applying the Victoreen equation to the pre-edge data. The μ_0 data, the hypothetical absorption coefficient of an isolated atom, was estimated from the data over the post-edge region by Cook-Sayers spline smoothing.³¹ An EXAFS analysis was performed in the k -space range from 2.3 to 9.0 Å⁻¹, where k is the photoelectron wave vector. The k -space data of the EXAFS oscillation were converted to r -space data associated with the distance between the copper center and scattering atoms by a Fourier-transformation (FT) with a Hanning window function. Nonlinear curve-fitting with the standard EXAFS equation was carried out by an inverse Fourier-transformation for a first-shell region of the r -space data. The theoretical EXAFS for the molecular structure, which was optimized by a Molecular Mechanics (MM) calculation, was evaluated *ab initio* using FEFF8 (Ver. 8.20).³² The values for the Debye-Waller factor (σ) were determined by analyzing EXAFS for the solid powder with the first coordination shell defined strictly as four equatorial nitrogen atoms, *i.e.*, the coordination number fixed as 4. The coordination number for the solution and the interfacial species was estimated as the relative coordination number (n') by taking the same σ value as that for the solid powder species.

Surface pressure measurements

The surface pressure (Π)-molecular area (A) isotherms were measured by the Wilhelmy method with the Langmuir trough for TR-XAFS prior to the X-ray measurement. A ground glass plate of 0.30 mm (thickness) × 23.85 mm (width) was used as a Wilhelmy plate. The porphyrin solution was spread on an aqueous subphase thermostated at 298 ± 2 K. The surface layer formed at the air-water interface was compressed at a rate of 24 mm min⁻¹ by a PTFE surface barrier.

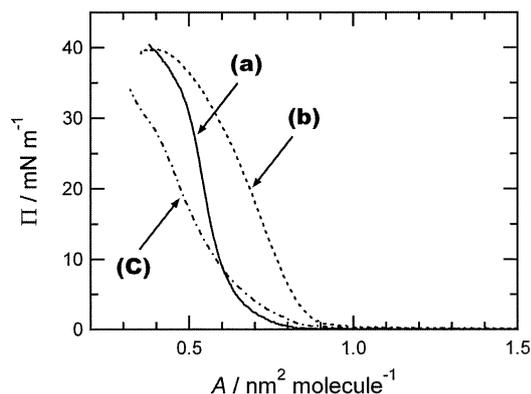


Fig. 2 Π - A isotherms for (a) CuPP, (b) CuChl and (c) CuTPPC on a 1.0×10^{-2} mol dm^{-3} hydrochloric acid solution at 298 K.

Table 1 Molecular limiting areas ($A^{\Pi \rightarrow 0}$) and tilting angles (Φ) of the $1s \rightarrow 4p_z$ transition moment

	$A^{\Pi \rightarrow 0}/\text{nm}^2 \text{ molecule}^{-1}$	Φ/degree
CuPP	0.63	29 ± 1
CuChl	0.85	34 ± 1
CuTPPC	0.68	

Results and Discussion

Π - A isotherms and polarized TR-XAFS spectra at the air-water interface

The copper complexes were effectively prevented from dissolution into the bulk phase by adding hydrochloric acid at a concentration of $0.010 \text{ mol dm}^{-3}$ to the aqueous subphase. Π - A isotherms of the copper(II) complex monolayers are shown in Fig. 2. Both CuPP and CuChl formed a stable monolayer when spread on the aqueous solution surface. The molecular limiting areas ($A^{\Pi \rightarrow 0}$) listed in Table 1 were determined from extrapolation of the Π - A data in the condensed region of the isotherms. CuPP and CuChl had $A^{\Pi \rightarrow 0}$ values of 0.63 and $0.85 \text{ nm}^2 \text{ molecules}^{-1}$, respectively. The surface area occupied by a molecule in the case of the porphyrin plane lying parallel to the air-water interface (A_{calc}) could be evaluated, respectively, as 1.80 nm^2 for CuPP and 1.68 nm^2 for CuChl by MM calculations. For both copper complexes, the smaller value of $A^{\Pi \rightarrow 0}$ must be associated with a favorable standing-up orientation of the porphyrin plane to the air-water interface in the monolayer.^{20,33} CuTPPC also has a small $A^{\Pi \rightarrow 0}$ value of $0.68 \text{ nm}^2 \text{ molecule}^{-1}$ compared with A_{calc} of 2.28 nm^2 . In the CuTPPC system, a gradual increase in the surface pressure with a decrease in the surface area is possibly due to spontaneous multilayer formation in analogy with the symmetrically *meso*-substituted metalloporphyrin, ZnTPP.²⁰ In fact, the CuTPPC surface layer was not stable enough, and some inhomogeneous condensed structures, which enhance the baseline drift and sudden spike noises, were observed on the solution surface during TR-XAFS experiments. Therefore, the TR-XAFS spectra for CuTPPC at the air-water interface were poorly reproducible and were excluded from the detailed analysis.

The Cu K-edge XANES spectra for DMF solutions of copper(II) porphyrin derivatives are displayed in Fig. 3. The characteristic shoulder peak associated with the $1s \rightarrow 4p_z$ transition along the z -axis of a square-planar metal complex was

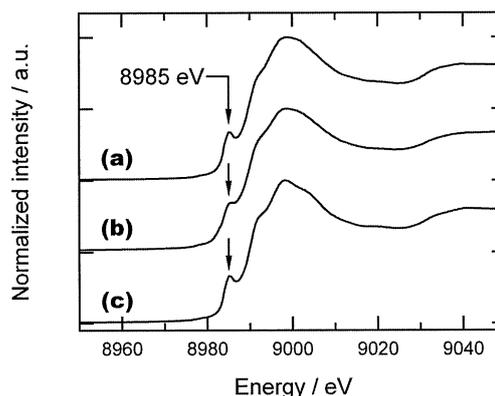


Fig. 3 XANES spectra at the Cu K-edge for (a) CuPP, (b) CuChl and (c) CuTPPC in DMF. The concentrations were (a) 9.3×10^{-4} , (b) 1.0×10^{-3} , and (c) $1.1 \times 10^{-3} \text{ mol dm}^{-3}$, respectively.

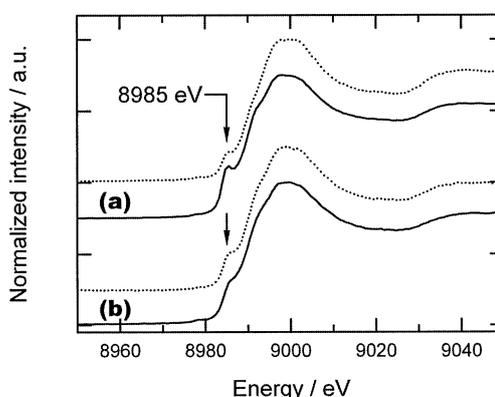


Fig. 4 Typical XANES spectra at the Cu K-edge for (a) CuPP and (b) CuChl spread on a $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ hydrochloric acid solution by the polarized TR-XAFS method. The surface concentrations were (a) 3.7×10^{-10} and (b) $4.0 \times 10^{-10} \text{ mol cm}^{-2}$, respectively. The solid and dashed lines refer to the XANES spectra taken with horizontal and vertical polarizations, respectively.

observed at 8985 eV prior to the white line.³⁴⁻³⁶ This $1s \rightarrow 4p_z$ transition peak is known to be attenuated or to disappear when the axial site(s) is (are) coordinated by ligand(s) such as in a square-pyramidal or octahedral coordination geometry. In the case of zinc(II) porphyrins, for instance, the peak at the Zn K-edge disappears when they are dissolved in ethyl acetate owing to an effective axial coordination of solvent molecules to the zinc center.^{19,20} On the other hand, one can observe a weak peak at 8985 eV in the XANES spectra for solutions of copper(II) porphyrin derivatives, indicating the presence of weak axial coordination of the solvent molecules.

Polarized TR-XAFS measurements for CuPP and CuChl were carried out at several surface concentrations. Typical XANES spectra for CuPP and CuChl at the air-water interface measured by the polarized TR-XAFS technique are displayed in Fig. 4. The fluorescent X-ray intensity was found to be roughly proportional to the surface concentration of the copper(II) complex spread on a $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ hydrochloric acid solution. In both the CuPP and CuChl systems, the $1s \rightarrow 4p_z$ peak was observed at 8985 eV similar to that of the bulk solution samples. Its relative intensity depends on the polarization of X-rays, *i.e.* horizontally polarized X-rays give a stronger peak than the vertical ones. The polarization

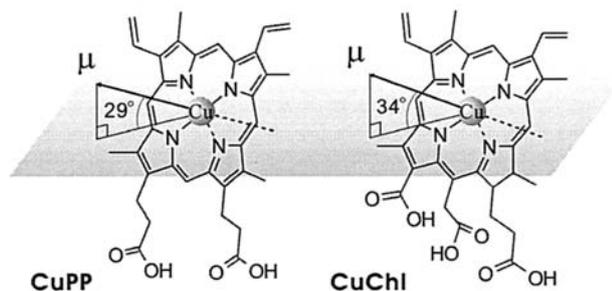


Fig. 5 Schematic drawing for the molecular orientations of CuPP and CuChl at the air-water interface. The tilting angles for the $1s \rightarrow 4p_z$ transition dipole moment (μ) were evaluated to be $29 \pm 1^\circ$ for CuPP and $34 \pm 1^\circ$ for CuChl, respectively, with respect to the solution surface.

dependence of XANES spectra suggests that neither CuPP nor CuChl lies down on the solution surface. The molecular orientation of metalloporphyrin can be roughly evaluated through the dichroic ratio ($D_{\text{v/h}}$) for the $1s \rightarrow 4p_z$ transition peak.^{20,27} Assuming a narrow distribution of the molecular orientation, the dichroic ratio is described as a function of the angle Φ of the $1s \rightarrow 4p_z$ transition moment with respect to the solution surface by the following equation:³⁷

$$D_{\text{v/h}} = \sin^2 \alpha + 2 \tan^2 \Phi \cos^2 \alpha \quad (1)$$

where α is the incidence angle of X-rays onto the solution surface. Polarized TR-XAFS measurements were successfully carried out in a surface concentration range from 9×10^{-11} to 8.3×10^{-10} mol cm^{-2} for CuPP ($1.80 \text{ nm}^2 \geq A_{\text{CuPP}} \geq 0.20 \text{ nm}^2$) and from 2.0×10^{-10} to 8.9×10^{-10} mol cm^{-2} for CuChl ($0.84 \text{ nm}^2 \geq A_{\text{CuChl}} \geq 0.19 \text{ nm}^2$), respectively. The molecular orientations of CuPP and CuChl were found to be approximately constant irrespective of the surface concentration examined. As summarized in Table 1, the tilting angles of the $1s \rightarrow 4p_z$ transition moment normal to the porphyrin (or chlorin) ring were $29 \pm 1^\circ$ for CuPP and $34 \pm 1^\circ$ for CuChl, respectively, with respect to the solution surface. The smaller Φ value for CuPP is consistent with the smaller molecular limiting area for CuPP, indicating that the CuPP molecules stand up straighter than CuChl (Fig. 5). In previous work, the Φ value for ZnPP was reported to be within $46^\circ \geq \Phi_{\text{ZnPP}} \geq 33^\circ$, depending on the surface concentration.²⁰ The molecular orientation of ZnPP could be influenced by the hydration/dehydration behavior to the zinc atoms and the lateral interaction between porphyrin molecules in the monolayer. In contrast, the constant Φ values for CuPP and CuChl indicate that the weak axial-hydration to the copper center could not affect the molecular orientation at the air-water interface within the surface concentration examined. The molecular structure of the ligand moiety seems to play a more important role in the interfacial behavior of copper(II) porphyrin derivatives.

EXAFS analysis for copper(II) porphyrin derivatives at the air-water interface

The $k^3\chi(k)$ data extracted from the polarized TR-XAFS spectra for CuPP and CuChl at the air-water interface could be obtained at surface concentrations higher than 1.8×10^{-10} mol cm^{-2} for CuPP ($A_{\text{CuPP}} \leq 0.90 \text{ nm}^2 \text{ molecule}^{-1}$) and 3.0×10^{-10} mol cm^{-2} for CuChl ($A_{\text{CuChl}} \leq 0.56 \text{ nm}^2 \text{ molecule}^{-1}$), respectively. The $k^3\chi(k)$ spectra for CuPP and CuChl at the air-water interface are similar to those for the bulk solutions as displayed in Figs. 6 and 7. It should be noted that the $k^3\chi(k)$ spectra taken with vertically

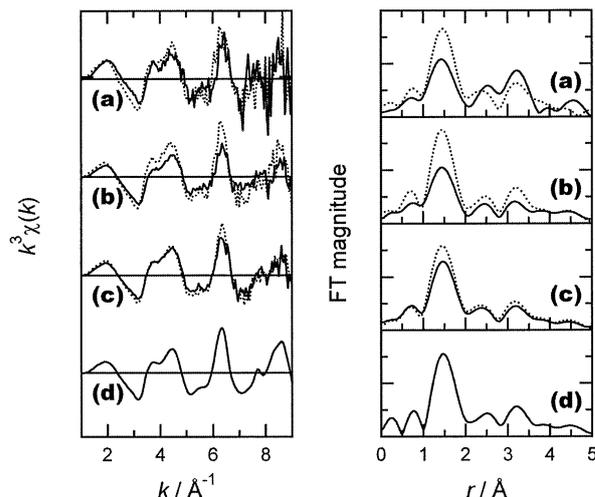


Fig. 6 $k^3\chi(k)$ and FT spectra for CuPP (a – c) at an air-water interface and (d) in bulk solution. The surface concentrations were (a) 1.8×10^{-10} , (b) 3.7×10^{-10} , and (c) 5.5×10^{-10} mol cm^{-2} , respectively. The solid and dashed lines refer to the horizontal and vertical polarizations of X-rays, respectively. (d) The concentration of CuPP in DMF was 9.3×10^{-4} mol dm^{-3} .

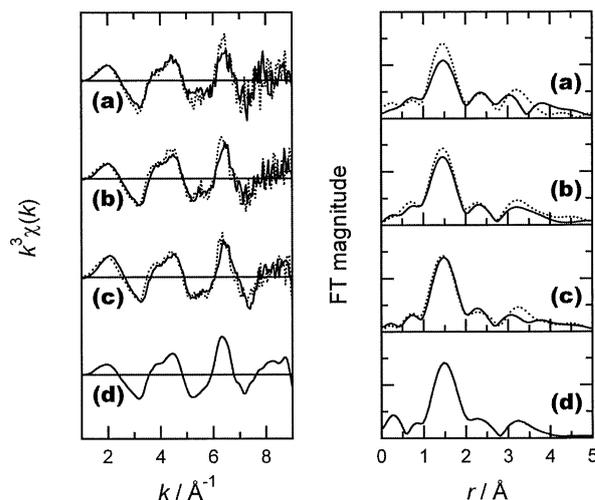


Fig. 7 $k^3\chi(k)$ and FT spectra for CuChl (a – c) at an air-water interface and (d) in bulk solution. The surface concentrations were (a) 3.0×10^{-10} , (b) 4.0×10^{-10} , and (c) 5.9×10^{-10} mol cm^{-2} , respectively. The solid and dashed lines refer to the horizontal and vertical polarizations of X-rays, respectively. (d) The concentration of CuChl in DMF was 1.0×10^{-3} mol dm^{-3} .

polarized X-rays for both CuPP and CuChl exhibit a relatively larger oscillation amplitude than those with the horizontal one in every surface concentration. The polarization dependence is explicitly elicited from the conversion of $k^3\chi(k)$ to the r -space data (i.e., FT spectrum). The FT magnitude is correlated with the coordination number, and larger magnitudes are always obtained with vertically polarized X-rays than with horizontally polarized ones. The FT spectra express an intense peak around 1.5 \AA , which is attributed to the coordination characteristic of a first coordination shell (Cu-N). Additional polarization-dependent components in the FT spectra are also observed at a larger r -range than 2 \AA relevant to carbon atoms in the porphyrin (or chlorin) ring and an axial coordination feature. For CuPP at

Table 2 Structural parameters determined by EXAFS analysis^a

	$\Gamma_s /$ mol cm ⁻²	$A /$ nm ² molecule ⁻¹	Polarization	n'	$R / \text{\AA}$	$\sigma / \text{\AA}$
CuPP	1.8×10^{-10}	0.90	v	4.7	1.96	
			h	3.0	1.95	
	3.7×10^{-10}	0.45	v	4.9	1.96	
			h	2.9	1.96	
	5.5×10^{-10}	0.30	v	4.5	1.96	
			h	3.7	1.97	
In soln. Powder				4.4	1.98	
CuChl	3.0×10^{-10}	0.56	v	4.3	1.97	0.069
			h	3.4	1.97	
	4.0×10^{-10}	0.42	v	4.4	1.96	
			h	3.9	1.96	
	5.9×10^{-10}	0.28	v	4.4	1.96	
			h	4.3	1.97	
In soln. Powder				4.5	1.98	
CuTPPC	In soln. Powder			4	1.96	0.081
				4	1.97	
				4	1.97	0.069

a. A is the surface area occupied by a molecule at the corresponding surface concentration (Γ_s). The polarizations v and h denote vertical and horizontal polarizations of the incident X-ray with respect to the solution surface. n' and R relate to the relative coordination number and the coordination distance, respectively. The Debye-Waller factor (σ) was determined by analyzing the powder sample with n' fixed as 4 and used for the solution and the interfacial species.

1.8×10^{-10} mol cm⁻² (Fig. 6(a)), a lower surface concentration than the monolayer formation, the peaks at $2.3 \text{ \AA} < r < 3.5 \text{ \AA}$ exhibit a reverse polarization dependence compared to other surface conditions. Although the spectral profiles of the XANES region are little affected by the surface concentration, the unique dichroism of the FT spectrum at 1.8×10^{-10} mol cm⁻² might reflect a certain difference in the axial-hydration structure depending on the surface concentration.

The r -space data were analyzed while taking into account the backscattering amplitude and the phase shift evaluated by the FEFF8 calculation. The structural parameters were obtained through a nonlinear least-squares curve-fitting with a single-shell model consisting of four nitrogen scattering atoms (Cu-N). A two-shell model, in which the possible two axial hydrations to the copper atom (Cu-O) are additionally considered, was also examined to analyze the EXAFS data. An appropriate convergence of the fitting parameters, however, was not achieved by the two-shell model, even for the case of bulk solution systems. As discussed in the previous section, the pre-edge transition peak indicates weak axial coordination for the square-planar copper(II) porphyrin derivatives. In the present system, therefore, the single-shell model is reliable to analyze the EXAFS data. The structural parameters determined by the EXAFS analysis are summarized in Table 2. The coordination distance (R) is associated with the interatomic distance between the copper atom and the equatorial nitrogen atoms. Almost the same R values for copper complexes (1.97 ± 0.01 nm) indicate that the square-planar coordination structure at the air-water interface is hardly modified from the bulk solution or the solid powder species. The relative coordination number (n') for the solution and the interfacial species was analyzed by taking a fixed parameter, σ , determined for the solid powder species. The same σ value was used instead of adjusting its value during the fitting calculation, because the polarized TR-XAFS gave

relatively noisy data, and it was well assumed that the metalloporphyrin moiety should be preserved wherever the complex exists. The n' value of 4.4 obtained for CuPP in the bulk solution is equivalent to 4.5 for CuChl and CuTPPC in the bulk solution. The proximal coordination to the copper center is fixed by four equatorial nitrogen atoms (*i.e.*, $n' = 4$) in each copper(II) porphyrin derivative. The relatively large n' values estimated for the solution species could be associated with a partial axial solvation of DMF molecules. In the solution, therefore, the coordination structure of the copper center was essentially the same for all of the copper complexes examined.

For the case of copper complexes at the air-water interface, it is noteworthy that the n' values measured in the vertical polarization (n'_v) were larger than the horizontal ones (n'_h) under all of the analyzable conditions. The n' value determined by polarized TR-XAFS at the air-water interface reflects the number of photoelectron back scattering atoms located in the plane of the linear polarization similar to that for oriented materials on a single crystal substrate.^{7,38} In principle, the K-edge EXAFS oscillation of the well-organized species depends on the X-ray polarization, and the effective coordination number (N^*) can be described as:^{7,39}

$$N^* = 3 \sum_i \cos^2 \theta_i \quad (2)$$

where θ_i is the angle between the i th bond and the electric field vector. In the present system, the n' value is predominantly associated with the proximal coordination of four equatorial nitrogen atoms. For instance, assuming that the porphyrin (or chlorin) ring is strictly oriented parallel to the air-water interface, four equatorial nitrogen atoms should exist in a horizontal polarization plane and, then, the n'_v will have a negligibly small value under the present experimental condition with a small incident angle (*i.e.*, $\alpha \leq 1.2$ mrad). The EXAFS dichroism obtained in this study ($n'_v > n'_h$) demonstrates that the scattering atoms exist more densely in the vertical polarization plane, in agreement with the standing-up molecular orientation evaluated from the $1s \rightarrow 4p_z$ transition peak.

Conclusions

In the present study, an EXAFS analysis for the copper(II) complex at the air-water interface could be achieved for the first time at a monolayer level by using the polarized TR-XAFS technique in the fluorescence mode. The local coordination structures of CuPP and CuChl are characterized in the respective polarization plane. The coordination distance between copper and nitrogen atoms in the square-planar coordination at the air-water interface is analogous to that of the bulk solution species. For CuPP and CuChl, the relative coordination numbers for the copper center are found to be larger in the vertical polarization than in the horizontal polarization. The EXAFS dichroism agrees with the standing-up molecular orientation concluded from a XANES analysis and $A^{\pi \rightarrow 0}$ estimated from the I/I_0 isotherm. The EXAFS analysis with polarized TR-XAFS at the air-water interface will allow us to elucidate the metal-ligand interaction in a monolayer, 2-D supramolecular structure, and the molecular structure of interfacial species formed only at an air-water interface.

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