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Optical and ESR Studies on the Micellar Formation with Surfactant Cu(II)–Porphyrin

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Synopsis. A new surface-active porphyrin, 1-dodecyl-4-(10,15,20-triphenyl-5-porphinyl)pyridinium bromide, and its copper complex (Cu(II)DPyTPP) were synthesized. In toluene, chloroform and ethanol, a typical ESR hyperfine structure (hfs) ascribable to monomeric Cu(II) porphyrin was observed. In ethanol containing a buffer of pH=7.4, a reversible formation of the micellar colloid which is strongly dependent on the water/ethanol mixing ratio, was confirmed based on mearsurements of ESR line broadening and the splitting of the Soret band.

As a simple model for naturally occuring Hemeproteins, micellar vesicles which contain surface-active porphyrins have already been reported.[1,2] Yamamura synthesized Cu(II)-4,4′,4″,4‴-(5,10,15,20-porphyneteayl)-tetrakis{1-octadecylpyridinium}tetraiodide, whose ESR spectra revealed a broadened ESR line width, related to strong paramagnetic interactions between the metal active sites in the reversed micellar visicles.[3] On the other hand, Katagi *et al*, found that the Soret band (426 nm) of magnesium porphyrins showed a red shift when it was incorporated into liposome vesicles.[4] A concomitant decrease of the absorption intensity was also observed.

To our present knowledge, there have been a few investigations of the Cu(II) porphyrin systems incorporated in the micellar vesicles, in which the ESR and optical spectrographic data were combined in order to understand the physicochemical properties of the metallo-porphyrins systems. We now report on the preparation of a new surface active porphyrin copper complex, Cu(II)DPyTPP, which bears both the hydrophilic pyridinium group and the hydrophobic alkyl group (Fig. 1). At a critical value in the water–ethanol mixing ratio, a reversible formation of micelles was clearly demonstrated based on measurements of the line broadening of the ESR hfs and the anomalous splitting in the Soret band of the Cu(II)-DPyTPP complex.

Experimental

Preparation: DPyTPPH$_2$ was prepared by the N-alkylation of the free base, PyTPPH$_2$, which was obtained from the usual mixed aldehyde method.[5] The N-alkylation of PyTPPH$_2$ was carried out in a refluxing DMF[6] in the presence of a 50-fold excess of dodecyl bromide; yield 70 (%).

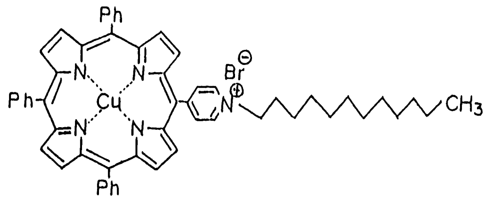

Fig. 1. Molecular structure of Cu(II)DPyTPP.

Found (%): C, 76.37; H, 6.29; N, 8.10; Br, 9.24. Calcd (%) for C$_{55}$H$_{54}$N$_5$Br: C, 76.38; H, 6.41; N, 8.03; Br, 9.34. Cu(II)-DPyTPP was prepared by the ordinary method; the 40% excess of dry CuBr$_2$ and DPyTPPH$_2$ were treated in refluxing ethanol for 1 hour under a nitrogen atomsphere.

Found (%): C, 70.84; H, 5.86; N, 7.76; Br, 8.82. Calcd (%) for C$_{55}$H$_{52}$N$_5$BrCu: C, 71.13; H, 5.87; N, 7.54; Br, 8.69.

Measurments: ESR measurments were carried out while changing the solvent mixing ratio, r=water/ethanol, 0/10 to 9/1. The final concentration of the copper complex kept in 2×10^{-5} M (1 M=1 mol dm^{-3}), and the pH was adjusted to 7.4 with 2×10^{-3} M Tris-Cl. ESR spectra at 77 K were recorded with a JEOL-FE-2XG X-band spectrometer with a 100 KHz modulation. The magnetic field was calibrated by the splitting of Mn(II) in MgO (Δ_{3-4}=8.69 mT) and the g-values were standardized using Li–TCNQ (g=2.00252) as a reference. The optical spectra were recorded with a JASCO UVDEC-1 spectrometer at room temperature. All the measurements were performed at the Advanced Instrumental Center for Chemical Analysis, Ehime University.

Results and Discussion

The optical spectrum of Cu(II)DPyTPP measured in ethanol was identical with that reported previously (Soret band λ_{max}=426 nm, $\varepsilon=2.31\times10^5$, α-band; λ_{max}=548 nm, $\varepsilon=22\times10^3$, β-band; λ_{max}=578 nm, $\varepsilon=3\times10^3$).[7] When the buffer solution was added to the ethanol solution, the intensity of the Soret band decreased depending on the solvent composition, but no significant shift of λ_{max} was observed in both the Soret band and α-band until r=4/6, as shown in Fig. 2. When the r-value became about 7/3, a drastic spectral change was observed involving an abrupt decrease of the Soret band and a splitting of the Soret band into two different absorption maxima, (λ_{max}=440 nm, $\varepsilon=4.96\times10^4$ and λ_{max}=392 nm, $\varepsilon=2.6\times10^4$) (Fig. 2). A concomitant red shift was also noted in the α-band from 540 nm to 553 nm. With higher r-values than 7/3, the sparated maxima in the Soret band began to merge into a single peak with an increased ε-value and the α-band blue shifted, (Fig. 2). The observed trend in the visible absorption spectra is consistent with a spectral change reported for a surfactant Mg(II) porphyrin incorporated into liposome vesicles.[4] The formation of micelles with our surfactant Cu(II)porphyrin, therefore, was suggested. In order to understand the mechanism of this surfactant porphyrin in detail, studies were made with the aid of ESR spectrometry. As shown in Fig. 3-a, a well resolved hfs of the monomeric Cu(II)DPyTPP was ovserved in ethanol. The observed ESR parameters were actually identical with those measured in toluene and chloroform, ($g_{/\!/}$=2.196, $g_\perp$=2.067, $A_\perp$=203.8×10^{-4} cm^{-1}).[8] When a buffer solution was added to the ethanol, a slight decrease in the ESR line intensity ascribed to the ligand N hyperfine was ob-

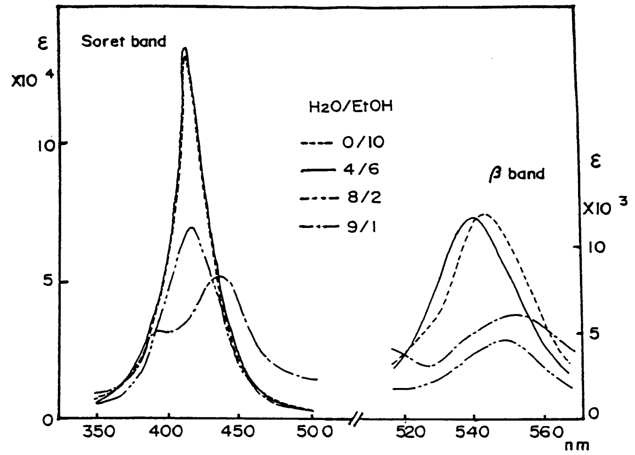

Fig. 2. Absorption spectra of Cu(II)DPyTPP (2×10^{-5} M), with various mixing ratio of ethanol and water, where the pH was adjusted to 7.4 by Tris-Cl (2×10^{-3}M).

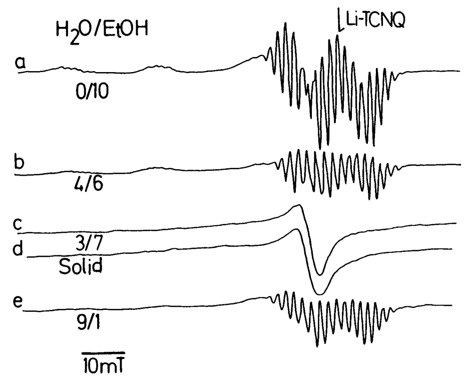

Fig. 3. ESR spectra of Cu(II)DPyTPP (2×10^{-5}M) at 77K, with various mixing ratio of ethanol and water, where the pH adjusted to 7.4 by Tris-Cl (2×10^{-3}M).

served. However, the mangitude of the hfs for both copper and the ligand N atoms showed no significant changes unitil $r=4/6$, as shown in Fig. 3-b. An abrupt decrease in the net ESR line intensity and anomalous line broadening occures at the r-value 7/3, where hyperfine splittings for ligand N and copper atoms were smeared out except for the hfs due to the g-anisotropy. It is notewothy that the ESR line shape of Fig. 3-c was analogous to that measuerd for a powdered Cu(II)DPyTPP complex, Fig. 3-d. A similar line broadening due to a clustering of the copper tetra-alyl porphyrin has been described for copper complexes involving the surfactant active porphyrins upon the micellar formation.[3] The central copper ions interact magnetically in such a way as to smear out the copper nuclear hyperfine interaction. The ESR spectra of the dimer Cu(II) obtained from the proto-porphyrin derivatives have already been reported, and the internuclear distance between the copper ions were found to lie in a range from 3.5 to 4 Å.[9] Many trials were made to detect the formation of the triplet species in the ESR spectra. In the persent case, however, positive evidence for the dimer formation was hardly obtained everywhere. With a further addition of the buffer solution, 9/1, the ESR signal again revealed a well resolved hfs due to the monomeric Cu(II) and ligand N was clearly detected as shown in Fig. 3-e, ($g_{\parallel}=2.202$, $g_{\perp}=2.064$, $A_{\parallel}=195\times10^{-4}\,\mathrm{cm}^{-1}$). In comparision with the values measured in a weak polar solvent, such as chloroform and toluene, the observed $g_{\parallel}$-value was slightly higher and the $A_{\parallel}$-value was, conversely, reduced. On the bases of the observation of the optical and ESR spectra, some important notions on micelle formation with a surfactant metallo-porphyrin can be deduced. For lower contents of water (0/10 to 4/6) the spectroscopic data suggest that a relatively small intermolecular interaction exists between each chromophore. The decrease in the magnitude of the ESR line intensity and the disappearance of the ligand N hyperfine observed in the medium water content, 4/6 to 7/3, might be attributed to an electron spin-spin interaction among the metal sites, which can be accessible together by the hydrophobic interaction between the long alkyl chains. The splittings of the Soret band supported the evidence that the metalloporphyrin actually formed the micellar vesicles. For r-values greater than 9/1, the reappearance of a well resolved ESR hfs and the collapes of the splittings in the Soret band were observed. These findings suggest that a molecular rearrangement on metalloporphyrin array occurs in the micell vesicles, in which the interaction between the active sites is reduced. Such a rearrangement of metallo-porphyrin is probably due to the hydration of the metal chrmophore, where the hydration would be greatly accelerated by the hydrophilic pyridinium group involved in the surfactant porphyrin. In this situation, the solvation of the water molecule causes a distortion of the copper porphyrin, as judged from the trend in the observed ESR parameter. This trend indicates that the $g_{\parallel}$-value shows a slight increase while the $A_{\parallel}$- value is reduced.[10] The results herein may provide not only a model for metalloporphyrin containing proteins but also a useful tool for understanding the orientation of the metalloporphyrin moiety in proteins.

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