Molecular Organization of Mono(p-hydroquinonyl)porphyrin through Coordinate Bond

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Mono(p-hydroquinonyl)tritolylporphyrin and its magnesium complex were prepared. Molecular organization of the magnesium complex in solution was examined by using ^{1}H-NMR spectroscopy.

Recently, the structure of light-harvesting complex LH2 in photosynthetic bacteria was elucidated by X-ray crystallography at atomic resolution.[1] In the macro-ring structure of bacteriochlorophyll B850, each bacteriochlorophyll a (Bchl a) molecule is partially overlapped with another Bchl a in a slipped cofacial arrangement by coordination of histidine residues from α and β-apoproteins to Mg metals. A similar organized structure through hydroxyl-Mg coordinate bond is also proposed for antenna chlorosomes of green photosynthetic bacteria.[2]

We have been interested in constructing supramolecular systems having partially overlapped porphyrin π-orbitals by using ligand-to-metal coordinate bond of appropriately designed simple porphyrin systems. According to this line, we have already reported a supramolecular organization of bis(imidazolyl) porphyrin Zn complex to a slipped cofacial dimer by mutual coordination from the imidazolyl nitrogen to Zn.[3] When Mg, which allows a hexa-coordination, was introduced as the central metal, growth of the stacking structure through an imidazolyl-Mg-imidazolyl coordination was observed.[4]

Here, we will report another type of molecular organization of porphyrins by using coordination of the hydroxyl group of p-hydroquinone to Mg. For this purpose, we have prepared mono(p-hydroquinonyl)tritolylporphyrin **1**[5-7] and its Mg complex **2**.[8] Studies on ^{1}H-NMR spectroscopy indicated the molecular organization of mono(p-hydroquinonyl) tritolylporphyrin Mg complex through coordinate bond as illustrated in Figure 1.

The ^{1}H-NMR spectra of **1** and **2** in a $CDCl_3$ solution (8 mM, 20 °C) were shown in Figure 2A and B, respectively. The most characteristic changes on Mg insertion to free base porphyrin **1** are as follows: β-Pyrrolic protons appeared at δ 8.9 (8H) split into two doublets at δ 8.68 and 8.47 ppm (2H each) and multiplets at δ 8.84 ppm (4H). Tolyl protons appeared as A_2B_2 at δ 8.1 (6H, H2' and H6') and 7.6 (6H, H3' and H5') ppm now split into two groups, in which two sets of multiplets are observable at δ 8.05, 7.93 ppm and δ 7.49, 7.41 ppm. The shift of protons assigned at the hydroquinone part is more drastic, Ha, Hb and Hc protons being shifted from 7.21, 7.16 and 7.45 ppm, respectively, to 6.58 (2H) and 6.38 (1H) ppm.

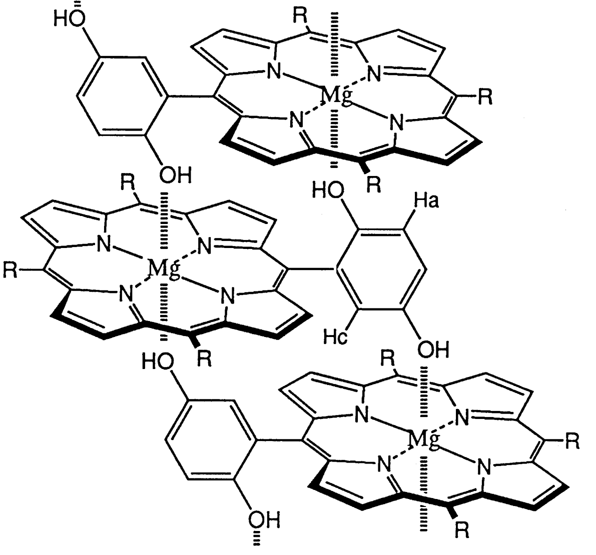

Figure 1. A proposed structure of mono(hydroquinonyl)-porphyrin Mg complex through coordinate bond (R = p-tolyl).

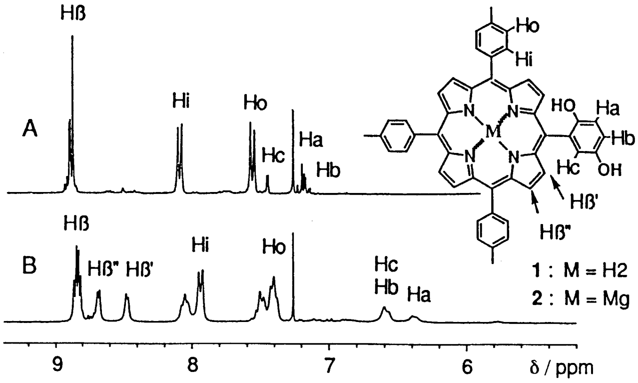

Figure 2. 270 MHz ^{1}H-NMR spectrum of free base **1** (A) and Mg complex **2** (B) in $CDCl_3$ (8 mM, 20 °C).

Since the large shift of the hydroquinone part makes it difficult to correlate explicitly each peak from the spectrum, the concentration dependence of these peaks was first examined. The result was illustrated in Figure 3. The shift-correlation pattern of each hydroquinonyl proton seems possible as connected by dotted lines, since the shift is continuously traced down to the spectrum at the lowest concentration (Figure 3F), which resembles the spectrum of the monomeric free base **1**. Changes of all the other peaks are also monotonous and correlated with each other as shown in Figure 3.

For the sample of 4 mM solution, COSY spectrum was also measured to confirm hydroquinonyl protons Ha, Hb and Hc. Cross-peak correlation was seen between 6.68 (1H) and 6.78 (1H) ppm. This correlation established the ortho disposition of Ha and Hb. Other correlations were also seen between Ho and Hi, and between Hß' and Hß". These correlations and the NMR features clearly suggest the coordination of hydroxyl of hydroquinone to Mg at higher concentrations. By this

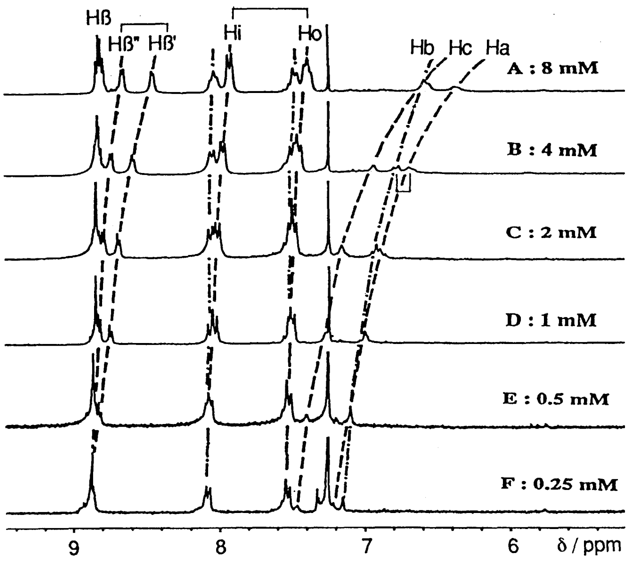

Figure 3. Concentration dependence of ^{1}H-NMR spectra of Mg complex **2** in $CDCl_3$ (measured at 20 °C).

coordination, Ha and Hc protons receive the maximum upfield shifts from the facing porphyrin ring. And also ß-pyrrolic Hß' and Hß" protons receive upfield shift due to ring current as locating just over the slipped cofacial porphyrin plane.

Since such a coordination seems more favorable at lower temperature, the spectrum was measured at temperatures down to -40 °C for the sample of 8 mM in $CDCl_3$. The analysis of the data was summarized in Figure 4.

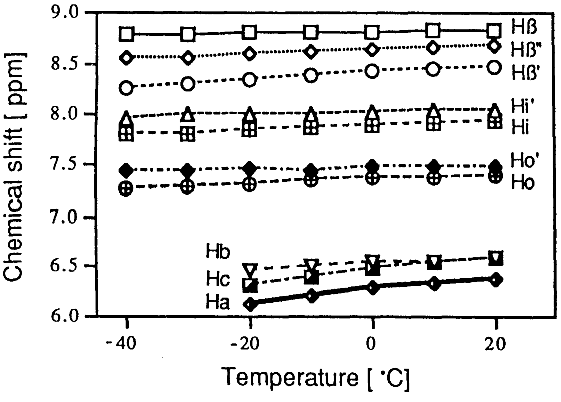

Figure 4. Temperature dependence of ^{1}H-NMR spectra of Mg complex **2** in $CDCl_3$ (measured at 8 mM).

On lowering the temperature, considerable upfield shifts were observed for all protons involved in the order:

Ha ≈ Hc > Hb ≈ Hβ' > Hβ" ≈ Hi ≈ Ho > Hi' > Ho' > Hβ

The largest shifts on lowering the temperature were observed for hydroquinonyl peaks Hc and Ha, showing the tendency similar to the concentration variation. The former peak was overlapped with Hb at 20 °C, but it was resolved at lower temperatures. Another important characteristic is broadening of all peaks, suggesting the complexation equilibria in solution. Hydroquinone protons were no more discernible each other at temperatures lower than -30 °C.

The growth of the degree of organization is favorable at higher concentrations and at lower temperatures, although no information is available for the aggregation number at present.

In conclution, compared to ^{1}H-NMR spectrum of the free base **1** in $CDCl_3$, the magnesium complex **2** showed an upfield shift of hydroquinonyl protons and β-pyrrolic ones next to the former substituent. The shift was more obvious at higher concentrations and at lower temperatures. The spectroscopic observations suggest the molecular organization of Mg porphyrin in a slipped cofacial arrangement, where each hydroquinonyl group in one porphyrin is coordinated to the Mg center in another porphyrin with a partial overlap of prophyrin π-orbitals. The method provides a possibility to construct an antenna chlorophyll model through a supramolecular approach.

References and Notes

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7 A mixture of pyrrole, 2,5-dimethoxybenzaldehyde, and *p*-tolualdehyde in a 5 : 2 : 3 molar ratio was heated to reflux in propionic acid. From porphyrin product mixtures of different meso substituents, mono(dimethoxyphenyl)tritolylporphyrin was isolated through silica gel column chromatography in a 5% yield. Demethylation with BBr_3 gave mono (hydroquinonyl)tritolylporphyrin **1**, which was purified under nitrogen by using silica gel column chromatography in a 82% yield.
^{1}H-NMR (270 MHz, $CDCl_3$, 8 mM, 20 °C) δ 8.93–8.86 (m, 8H, β-pyrrolic-H), 8.08 (d, *J* = 8 Hz, 6H, 2", 6"-H), 7.56 (d, *J* = 8 Hz, 6H, 3", 5"-H), 7.45 (d, *J* = 3 Hz, 1H, 6'-H), 7.21 (d, *J* = 8, 1H, 3'-H), 7.16 (d of d, *J* = 8, 3 Hz, 4'-H), 4.68 (s, 2H, OH), 2.71 (s, 9H, 4'-CH_3), -2.75 (s, 2H, NH). λ_{abs} ($CHCl_3$) 422, 518, 553, 592, 650 nm. λ_{em} ($CHCl_3$) 649, 711 nm.

8 Mg complex **2** was prepared by refluxing free base **1** with magnesium perchlorate in pyridine and purified under nitrogen by using silica gel column chromatography in a 30% yield.
^{1}H-NMR (270 MHz, $CDCl_3$, 8 mM, 20 °C) δ 8.86–8.81(m, 4H, β-pyrrolic-H), 8.68 (d, *J* = 4 Hz, 2H, β'-pyrrolic-H), 8.47 (d, *J* = 4 Hz, 2H, β"-pyrrolic-H), 8.07-7.92 (m, 6H, 2", 6"-H), 7.56-7.40 (m, 6H, 3", 5"-H), 6.70-6.50 (m, 2H, 4',6'-H), 6.50-6.30 (m, 1H, 3'-H), 2.69 (s, 3H, 4'"-CH_3), 2.64 (s, 6H, 4"-CH_3). λ_{abs} ($CHCl_3$) 428, 565, 606 nm. λ_{em} ($CHCl_3$) 611, 662 nm.