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Tris(porphyrinyl-oxinato)Ga Complexes as a Photosynthetic Antenna Miniature

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(Received 25 September 2001)

Two oxinylporphyrins, 5-(8-hydroxy-5-quinolinyl)-10,15,20-(*p*-tolyl)- porphyrin (1) and 5,15-bis(8-hydroxy-5-quinolinyl)-10,20-bis(*n*-heptyl)-porphyrin (2), were prepared and coordinated with Ga(III) to afford tris(oxinato) complex 3 and poly(oxinato) complex 4, respectively. The structure of 3 was analyzed by variable temperature NMR study with referring to tris(8-hydroxy-5-quinolinyl)Ga(III) complex 5 to be in a *meridional* form. Oxinato ligands of 3 and 5 were exchanged with one another, with keeping the *meridional* structure. UV–Vis and fluorescence spectra of tris(oxinato)complex 3 and poly(oxinato)complex 4 were compared with each monomeric compound 1 and 2. The absorption spectra showed only a slight broadening of the Soret band, suggesting trivial electronic and excitonic interactions. The fluorescence intensity was increased significantly compared with each monomeric compound 1 and 2. At the same time, efficient excitation energy transfer among three porphyrins has been observed.

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Keywords: Oxine; Complexation; Antenna; Porphyrins

INTRODUCTION

Successful elucidation of the crystallographic structure of antenna complexes from bacterial sources has given great impact on understanding the mechanism of how weak light energy is utilized efficiently in biology [1,2]. It has also provided clear and fascinating pictures toward construction of artificial light harvesting complexes. Recently, multi-porphyrin arrays have been synthesized by using supramolecular approaches [3] by using coordination to central [4–13] and external metal ions [14–22] or hydrogen bonding [23–25] as well as covalent approaches.

We have been interested in constructing artificial photosynthetic functions by using coordination bonds of imidazole to porphyrin metal centers and obtained analogues of special pair [26] and antenna complexes [27,28]. The proposal has been based on the coordination of imidazolyl substituent to the central metal ion of porphyrins. In this report, we wish to report the use of gallium-oxinato (8-hydroxyquinolinato) chelate bonds for assembling porphyrin units, because bidentate oxinato-ligands form rigid octahedral complex with gallium metal with extraordinary large stability constants [29,30]. Two kinds of oxinylporphyrins, mono(oxinyl)porphyrin **1** and 5,15-bis(oxinyl)porphyrin **2**, were prepared as precursors, and tris(porphyrin) assembly **3** and polyporphyrin assembly **4** were prepared by the introduction of gallium metal ion. The large stability constant of oxinato ligand may provide very stable porphyrin assemblies as well as huge structures for the case of dendritic growth of bis(oxinato)porphyrin **4**. These assemblies are expected to give useful information on energy/electron transfer reactions and be of significance in supramolecular chemistry.

RESULTS AND DISCUSSION

We have chosen 8-hydroxyquinoline (= oxine) as a ligand to assemble porphyrin units, since it forms stable, neutral, and rigid complexes with various metal ions, such as Al(III), Ga(III) [31,32]. Further, Al(III)- and Ga(III)-tris(8-hydroxyquinolinato) are

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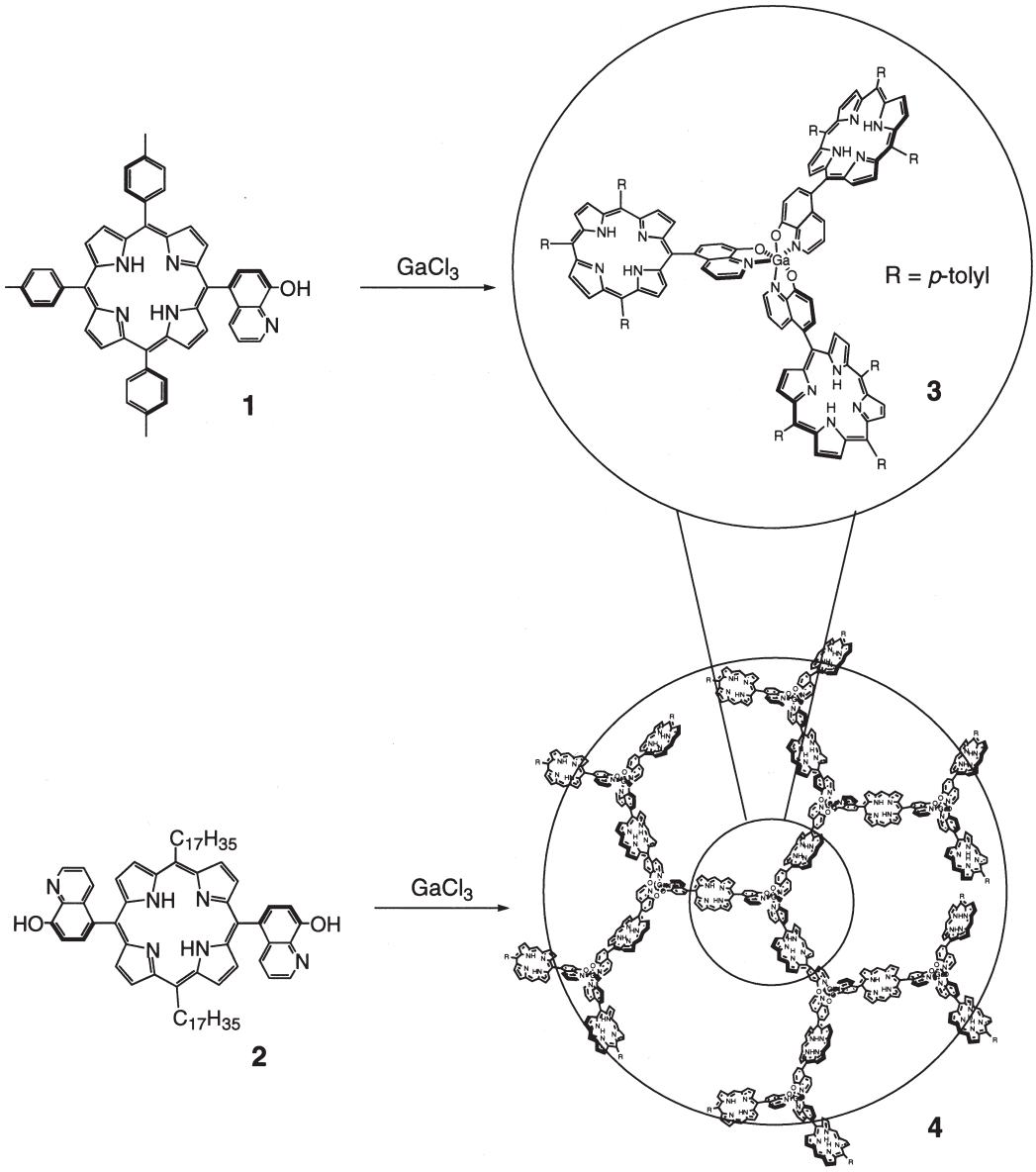
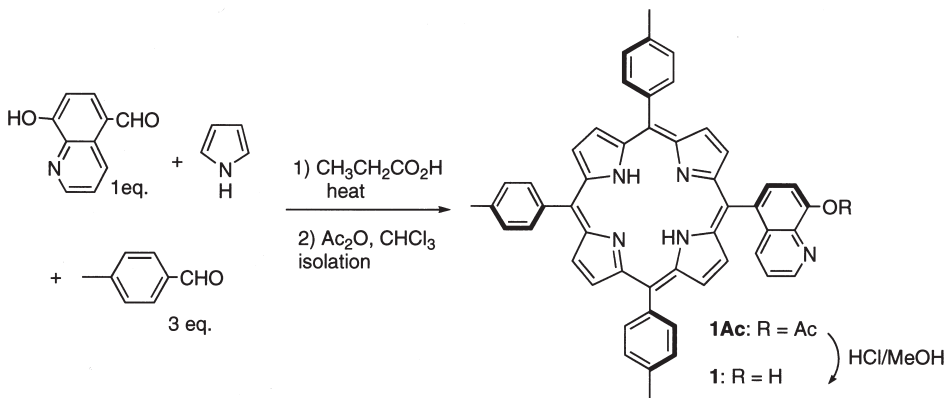
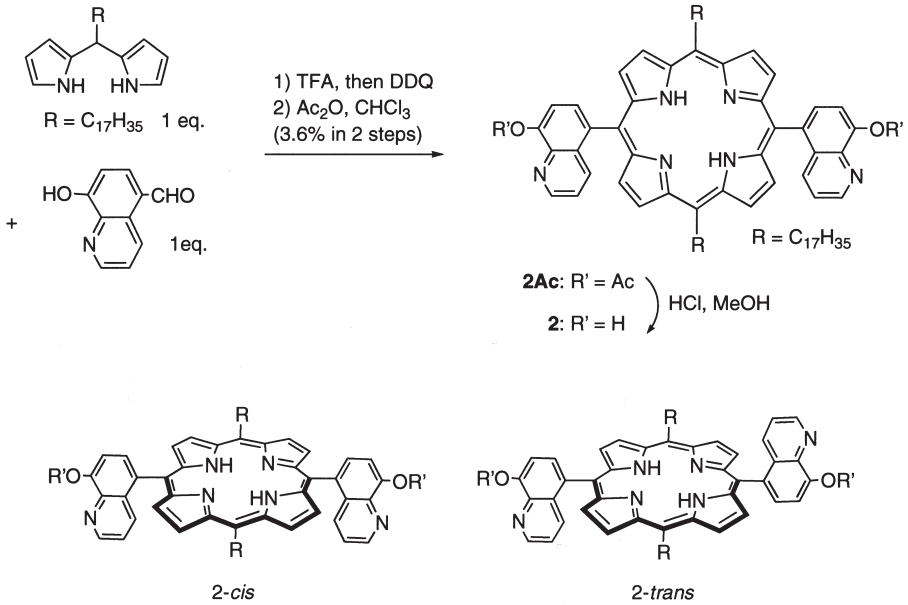


FIGURE 1 Mono(oxinyl)porphyrin **1**, bis(oxinyl)porphyrin **2**, and their tris(oxinato)Ga(III) complexes **3** and **4**.



SCHEME 1



SCHEME 2

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known as organic light-emitting diodes (OLED) [33,34], and therefore they are expected to assist efficient energy transfer. 5-(8-Hydroxy-5-quinolinyl)-porphyrin **1** and 5,10-bis(8-hydroxy-5-quinolinyl)-porphyrin **2** were designed as precursors for porphyrin assemblies. Porphyrin **1** whose oxinyl group was attached directly to the *meso* position was expected to afford rigid gallium-tris(porphyrin) complex **3** like a pinwheel as shown in Fig. 1. This minimum unit can be extended to a dendritic structure **4**, as shown in Fig. 1 by the introduction of another oxinyl group into porphyrin. Heptadecyl units in porphyrin **2** were employed to maintain high solubility in organic solvents even when large aggregates are formed.

Porphyrin **1** was synthesized by condensation of pyrrole, 8-hydroxyquinoline-5-carboxyaldehyde, and *p*-tolualdehyde in propionic acid for 1.5 h (Scheme 1). Desired product **1** was difficult to isolate at this stage because of strong tailing tendency on chromatography. Therefore, the crude product was once acetylated to isolate the product by column chromatography. Subsequent deacetylation in HCl–MeOH afforded porphyrin **1** in a total yield of 2%.

5,15-Bis(oxinyl)porphyrin **2** was synthesized by condensation of *meso*-(*n*-heptadecyl)dipyrromethane and 8-hydroxyquinoline-5-carboxyaldehyde in the presence of trifluoroacetic acid in $CHCl_3$, followed by oxidation with DDQ (Scheme 2). Desired compound **2** could not be separated from polymeric components in this case, too. After treatment with acetic anhydride in $CHCl_3$, acetylated compound **2Ac** was isolated as a mixture of two atropisomers (*cis* and *trans*) in a 3.6% yield. Two atropisomers of **2Ac** were observed as a 1:1 mixture in the ^{1}H NMR spectrum and TLC. Even atropisomers were isolated once, the product gave again a 1:1 mixture when dissolved in solution. These must exist as an equilibrium mixture in solution. Finally, 5,15-bis(oxinyl)porphyrin **2** was obtained by hydrolysis of acetyl groups as a 1:1 mixture of *cis* and *trans* atropisomers.

When an unsymmetrical bidentate ligand such as oxinato is used for octahedral metal complexation, two kinds of geometric isomers, *facial* (*fac*) and *meridional* (*mer*), can arise. Distances and spatial orientations among assembled porphyrin units are different for each geometric isomer. Schmidbaur *et al.* already established the *meridional* structure for Ga(III)-tris(8-hydroxyquinolinato) complex based on the NMR spectral and crystallographic studies [32]. However, porphyrin-bearing oxinato-Ga complex could not give crystals appropriate for X-ray crystallography, and the structural analysis must have been undertaken based only on the broad and less-resolved NMR spectrum with reference to the NMR analysis of simple Ga(III)-tris(oxinato) complex **5**. Therefore, the NMR spectral behavior of the simple reference compound **5** will first be briefly described.

Ga(III)-tris(oxinato) complex **5** was prepared according to the literature [31]. The absorption band from oxinyl moiety was shifted from 251 to 265 nm on complexation with Ga(III). The ^{1}H NMR spectra at various temperatures were shown in Fig. 2. The oxinato protons of the complex **5** split into a broad and complex pattern at 20°C (Fig. 2d), in accord with the assigned *meridional* structure. Broad signals at 20°C became sharp when it was measured at 0°C (Fig. 2f), while it was simplified by coalescence of isomeric peaks at temperatures higher than 50°C (Fig. 2c). The most remarkable behavior was observed for three protons appearing at 8.32 ppm

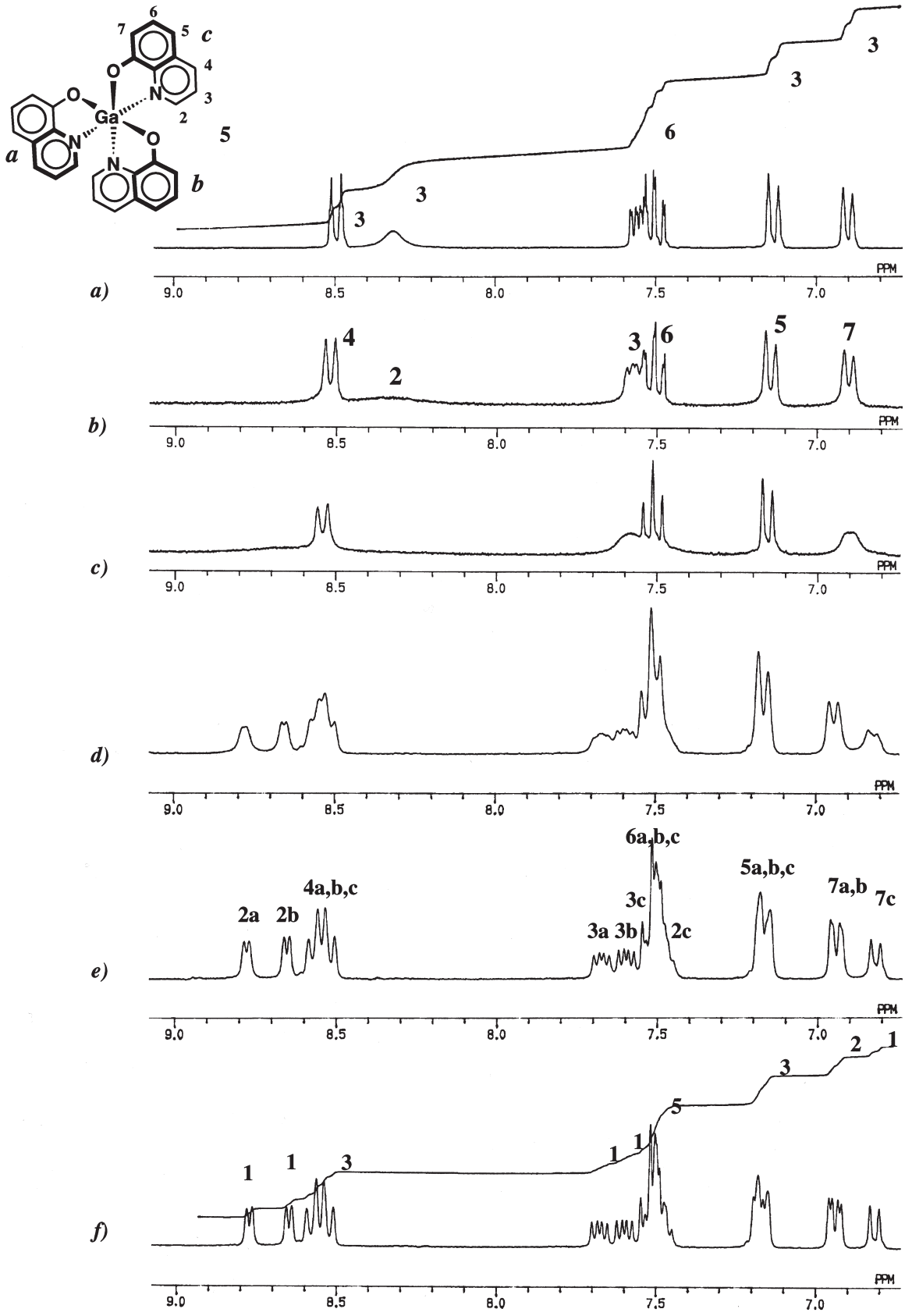

FIGURE 2 Temperature dependent NMR spectra of tris(oxinato)Ga complex **4** in DMSO-d_6 at (a) 110°C, (b) 80°C, (c) 50°C, and (d) 20°C. Spectra at (e) 10°C and (f) 0°C were measured in DMSO-d_6-CD_3OD (9/1).

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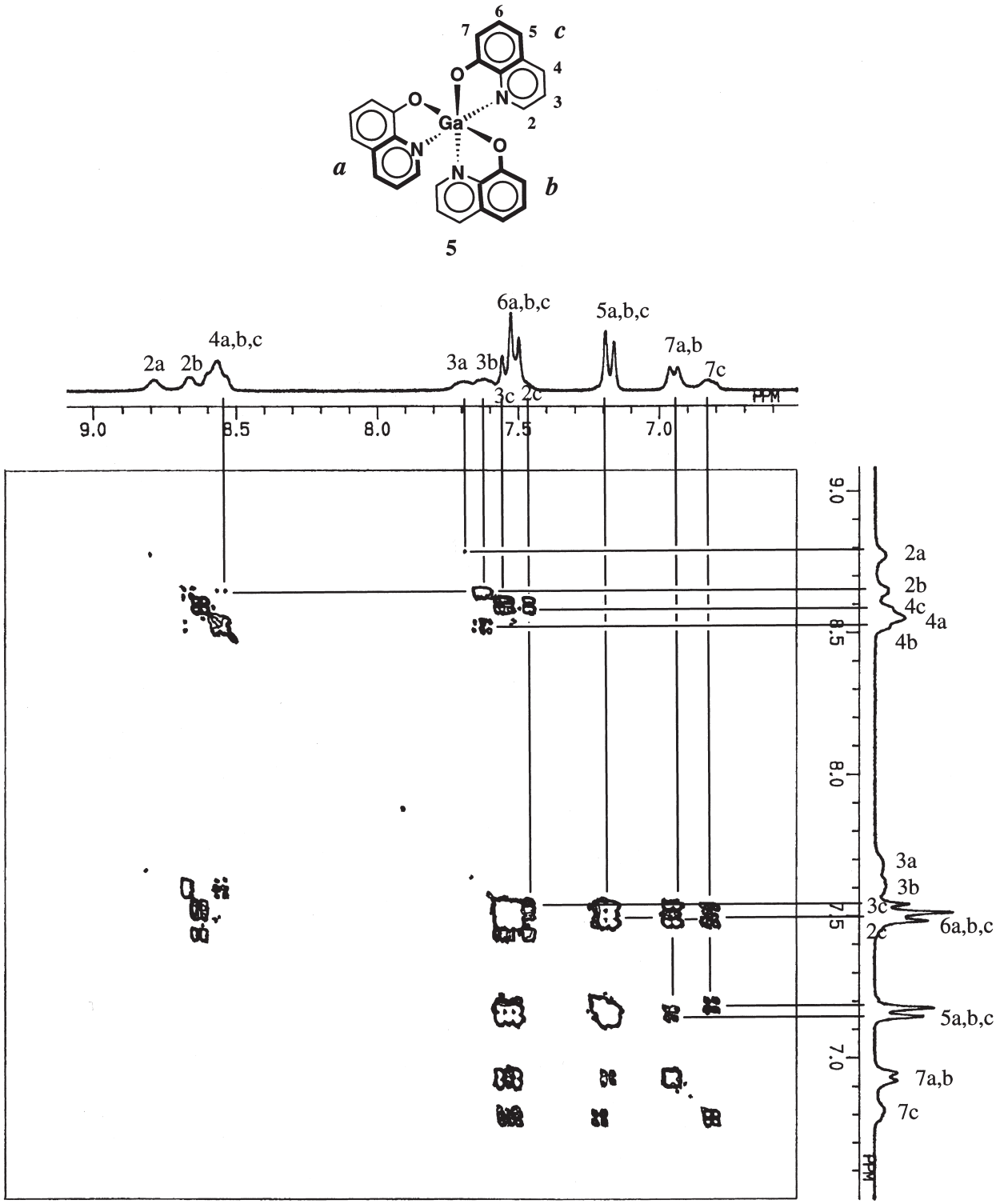

FIGURE 3 $^{1}H-^{1}H$ COSY NMR spectrum (270 MHz) of tris(oxinato)Ga complex **4** and its correlation analysis.

(2-H) at 110°C (Fig. 2a). At 0°C, two of them appeared at 8.64 and 8.77 ppm and the remaining one must be included in the multiplets near at 7.5 ppm based on the calculated chemical shift after the coalescence. This multiplets contain five protons, three of which correspond to triplet peaks at 7.52 ppm (6-H) in the spectrum at 110°C and one of the remaining proton belongs to a group of peaks appearing at 7.68 and 7.60 ppm as d of d assignable to 3-H. The one more remaining proton should be a family of peaks assigned to 2-H. Only the 2-H proton in the ring *c* is situated in a special stereochemical environment locating just above the aromatic ring of oxine *b* and receives the largest higher field shift from the facing

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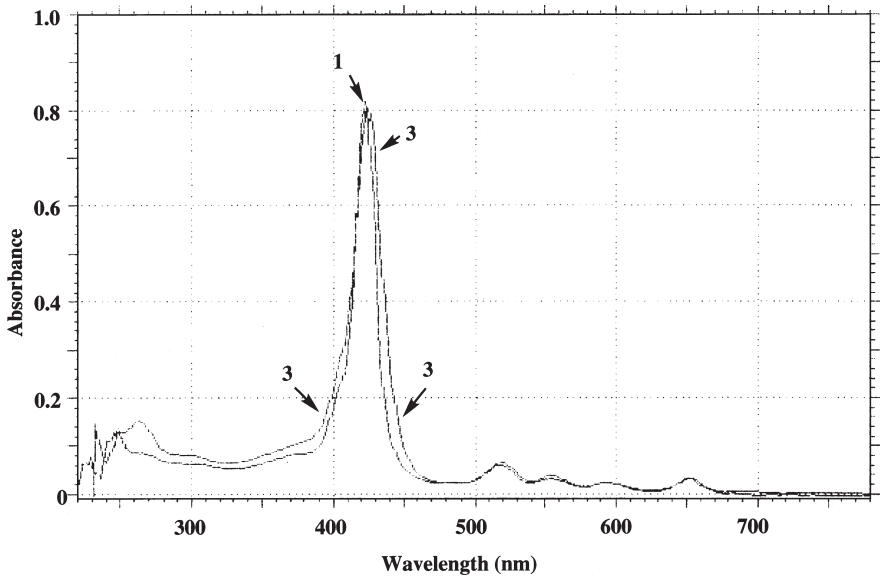

FIGURE 4 UV–Visible absorption spectra of oxinylporphyrin **1** and its Ga complex **3**. Absorption maxima appeared at 423 (Soret), 519, 555, 595, and 653 nm for **1** and 425 (Soret), 520, 555, 595, and 654 nm for **3**.

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ring *b*. This missing 2*c*-H proton appeared at 8.32 ppm after the coalescence (Fig. 2a). H–H COSY spectrum (Fig. 3) supported the above analysis by the observed correlations particularly between 2-H, 3-H, and 4-H protons for each ring *a*, *b*, and *c* and established the assignment. The temperature dependent behavior implies that the ligating atoms can exchange their locations with each other while keeping the *meridional* structure.

Next, tris(porphyrinyl-oxinato)Ga(III) complex **3** was synthesized from mono(oxinyl)porphyrin **1** (3 eq.) and $GaCl_3$ (1 eq.). UV–Vis spectra of the starting monomer **1** and its Ga-complex **3** were shown in Fig. 4. The absorption band from the oxinyl part appearing at 250 nm for the monomeric species **1** was shifted to 264 nm on Ga complexation in **3**. The Soret and Q-bands of **3** appeared at 425 nm and at 520, 555, 595, and 654 nm, respectively. These absorption bands were almost identical with those of monomeric species **1**, being 423 (Soret) and 519, 555, 595, and 653 nm (Q-bands). A small change was observed only for the half band widths of the Soret band, being 26 and 18 nm for **3** and **1**, respectively. The Q-bands were almost completely superimposed. The molecular weight of **3** was determined by vapor-pressure osmometry in $CHCl_3$ solution (8.9×10^{-4} M) as 2105 (Cald. 2235), the value corresponding to the tris(oxinato) complex considering the associated errors. The NMR spectrum of **3** at 20°C in $CDCl_3$ was rather broad and could not significantly be improved even measured at low temperatures (not shown). However, similar characteristics as **3** were maintained when measured at higher temperatures in $(CDCl_2)_2$ (Fig. 5). The doublet peaks at δ 9.33 and 9.27 ppm were assignable to 2*a*-H and 2*b*-H of the oxinato part as in **3**. These peaks almost disappeared at around 50°C, then appeared again at 110°C at δ 8.71 ppm after the coalescence with 2*c*-H, which originally appeared at 7.67 ppm at 20°C. From these behaviors, the interconvertible *meridional* structure with almost the identical coalescence temperature of 50°C was established. Fig. 6 shows the H–H COSY spectrum at 20°C with the peak assignment based on the correlation. Molecular mechanics calculation (with MM + force field) deduced the most stable configuration as shown in Fig. 7 and the center-to-center separation distances between three porphyrin units were estimated as 17, 15, and 18.5 Å for *a*–*b*, *b*–*c*, and *c*–*a*, respectively.

Fluorescence from the oxinato-Ga part appeared at 529 nm when excited at 398 nm, the longer absorption band of **5**, but no peak could be detected in this region for **3**. Efficient energy transfer from Ga(oxinato) to porphyrin parts of lower excited energy levels may account for this observation. The $0 \rightarrow 0$ and $0 \rightarrow 1$ emission bands from the porphyrin part appeared at 654 and 714 nm, respectively, for **3** and 652 and 712 nm, respectively, for **1** (Fig. 8). It is interesting to note that the fluorescence intensity of **3** is significantly larger than that of **1**, by a factor of 1.5. The fluorescence lifetime was estimated as 8.6 ns for **3** in CH_2Cl_2 solution. The value was almost the same, i.e. only slightly shorter than those of the monomeric species, 8.8 ns for **1** and 8.7 ns for tetra(tolyl)porphyrin as another reference porphyrin. Absorption and fluorescence spectral data suggest that the electronic state of porphyrin unit in the complex is not perturbed significantly either by intramolecular porphyrin–porphyrin interactions, Ga complexation or introduction of the oxinyl unit.

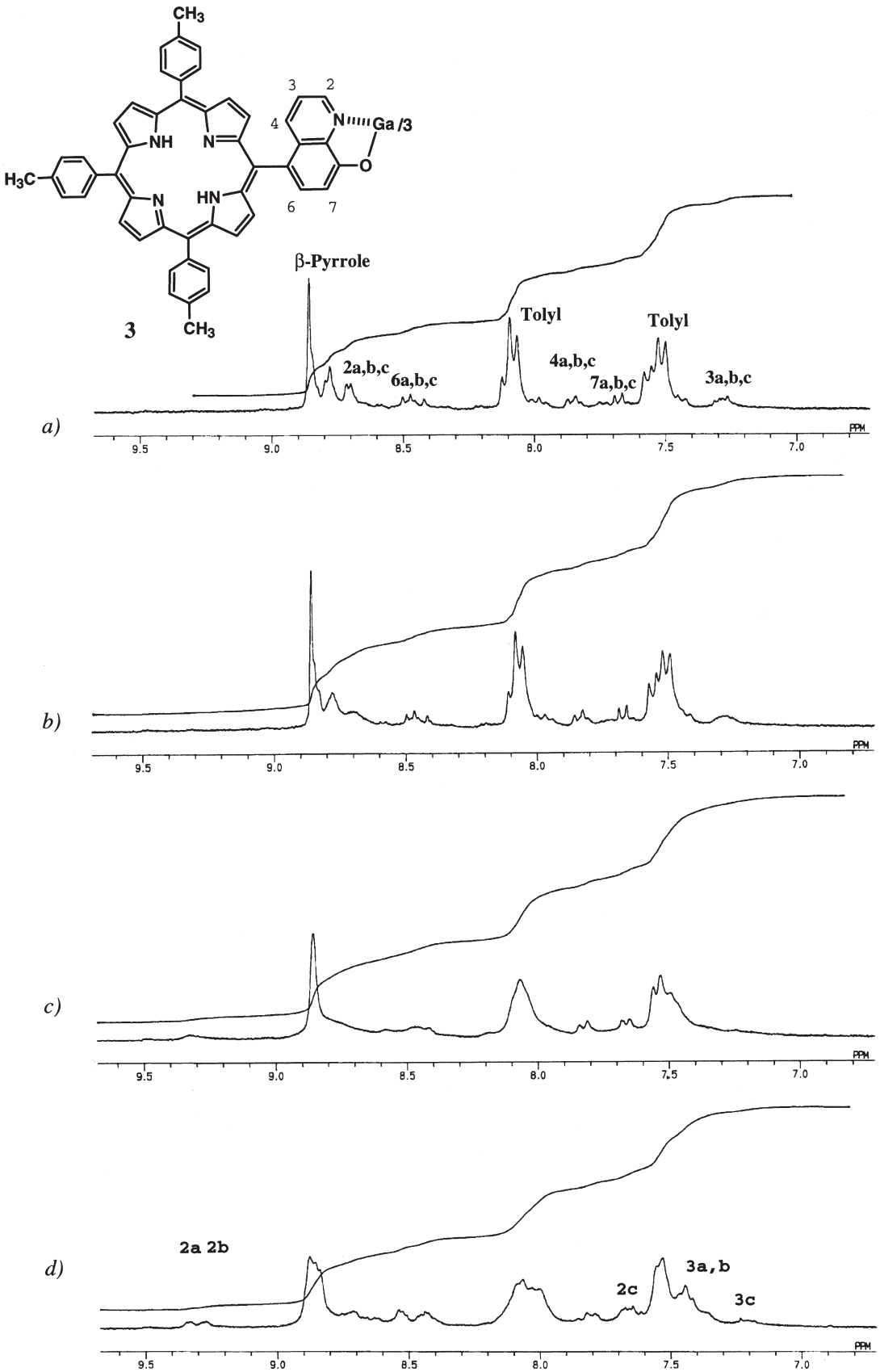

FIGURE 5 Temperature dependent NMR spectra of tris(porphyrinyl-oxinato)Ga complex **3** in $(CDCl_2)_2$ at (a) 110°C, (b) 80°C, (c) 50°C, and (d) 20°C.

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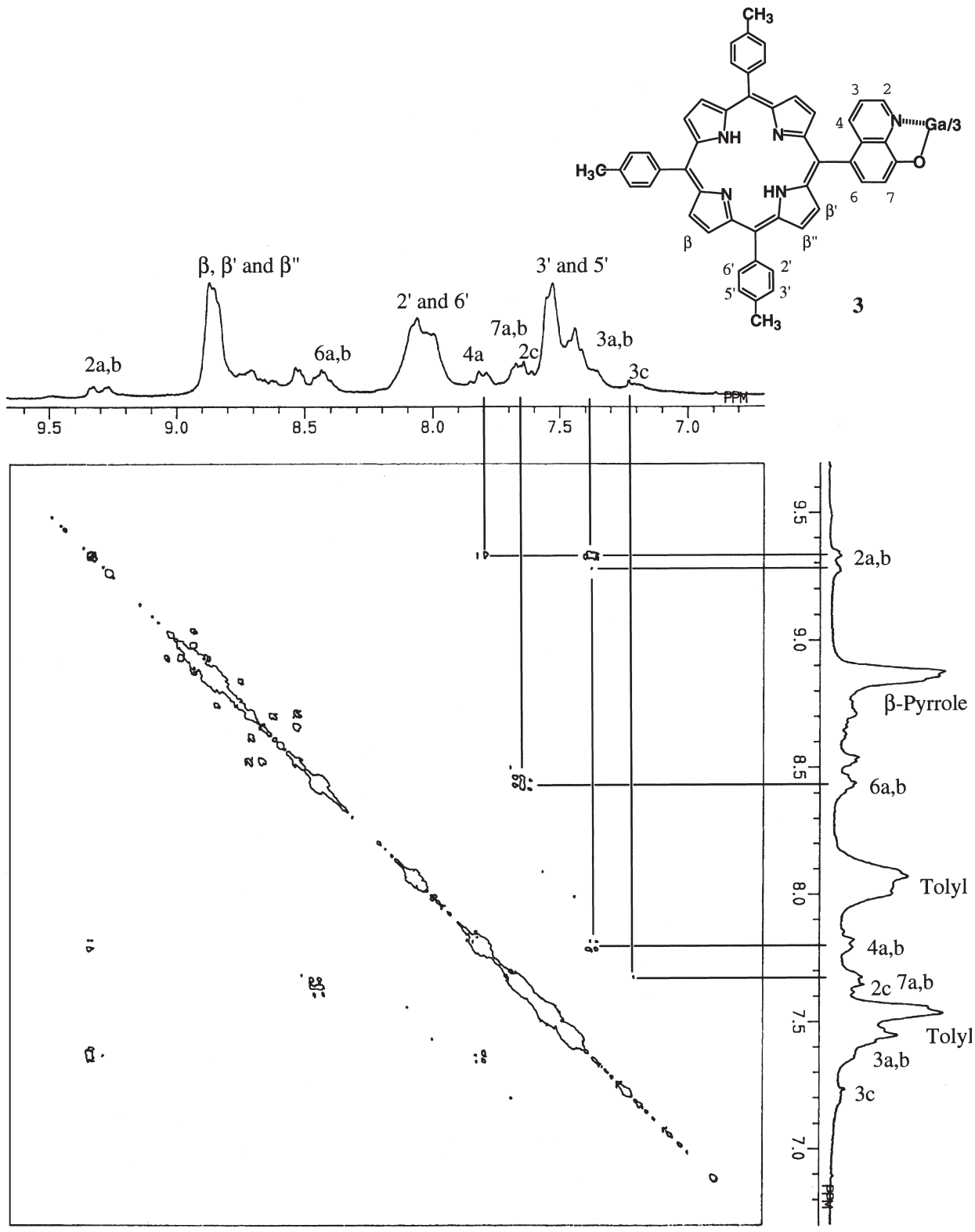

FIGURE 6 $^{1}H-^{1}H$ COSY NMR spectrum of tris(porphyrinyl-oxinato)Ga complex **3** and its correlation analysis.

Analysis of photophysical properties of **3**, especially of dynamic quenching experiment and rapid energy/electron transfer of pico-second time scale between porphyrin components have already been reported as a communication [35], where rapid delocalization of excitation energy has been testified to substantiate the complex as a photosynthetic antenna miniature.

Finally, dendritic oxinato-porphyrin complex **4** was synthesized according to a similar procedure as

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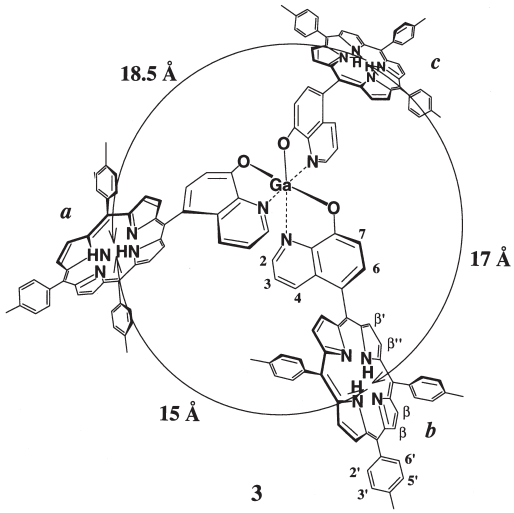

FIGURE 7 Center-to-center distances of three porphyrins estimated by molecular mechanics calculation by using an MM + force field.

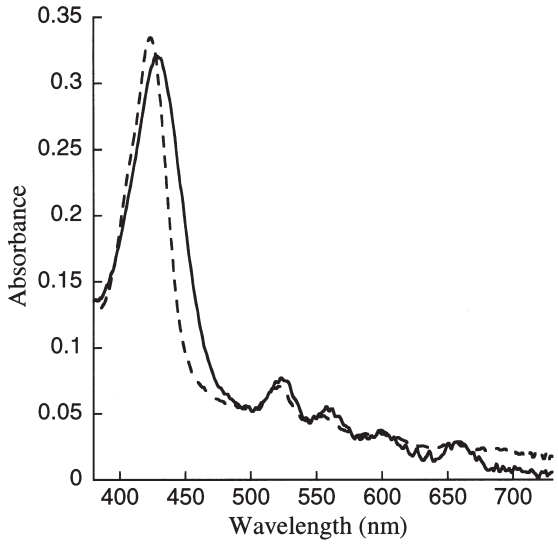

FIGURE 9 UV–Vis spectra of film-like samples of monomeric porphyrin **2** (broken line) and Ga-porphyrin assembly **4** (real line) on glass plate.

3. Gallium chloride in ethanol was added to **2** in chloroform, and the mixture was stirred for 30 min. After washing with a sodium bicarbonate solution and distilled water, methanol was allowed to diffuse slowly to the chloroform layer to give purple solid film. Since the film was insoluble in any organic solvents, absorption and fluorescence spectra of the intact film on glass plate were measured with optical microscope with a fluorescence microscope system. In this system, both absorption and fluorescence spectra at exactly the same area can be obtained. For comparison, a film-like sample of monomeric porphyrin **2** was prepared similarly on glass plate. UV–Vis spectra of film-like samples **2** and **4** were shown in Fig. 9. Uniform area ($0.2 \times 0.3\,mm^2$) of both samples were observed, and the sample from **2** was adjusted to be of similar absorbance of Soret band. The Soret band of **4** was slightly shifted to a longer wavelength, and the half band width of the Soret band of **4** spreads into 42 nm from 34 nm for the case of **2**. The Q-bands were almost identical with those of monomeric species **2**.

Fluorescence spectra at the same areas for the above two samples were also obtained, as shown in Fig. 10 by using an excitation band path filter, U-MWBV, which was transparent in the range 400–440 nm. Fluorescence from the oxinato-Ga part (529 nm) could not be observed also in this case. The fluorescence from porphyrin part seems to be increased significantly by complexation in this case too, when compared the fluorescence intensity of **4** and **2**. Since the excitation light has a broad band in this case, the intensity must be evaluated on the basis

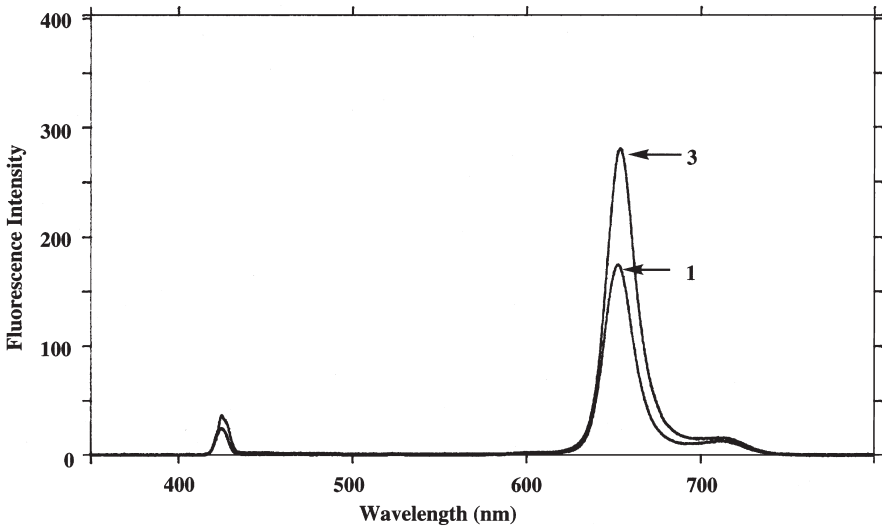

FIGURE 8 Fluorescence spectra of **1** and **3**, whose maxima appeared at 652 and 712 nm and 654 and 712 nm, respectively. Excitation at 423 and 425 nm for **1** and **3**, respectively.

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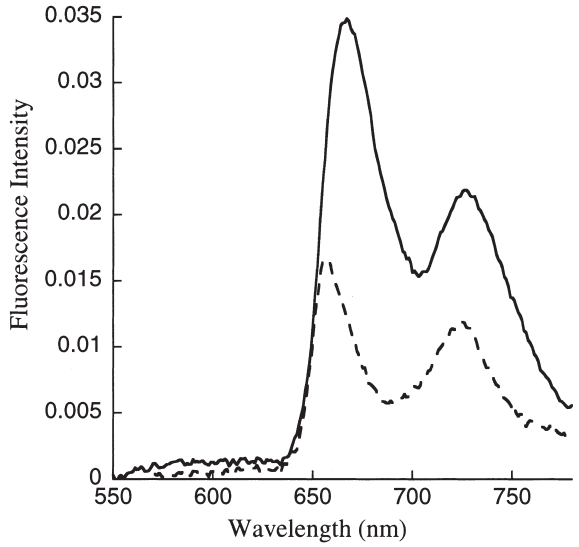

FIGURE 10 Fluorescence spectra of film-like samples of monomeric porphyrin **2** (broken line) and Ga-porphyrin assembly **4** (real line) on glass plate. The same areas of the above samples (Fig. 9) were measured. Excitation at 400–440 nm with a band-path filter.

of same absorption area. After correction of the absorption area, the increase factor was calculated to be 2.2 for **4**/**2**. Therefore, the fluorescence was even intensified by the formation of dendritic porphyrin structure rather than quenching, which was observed conventionally on assembly formation. The structure is interesting as a material to provide a large antenna complex of porphyrin aggregates.

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MATERIALS AND METHODS

General Procedure

^{1}H NMR spectra were recorded with JEOL EX270 (270 MHz) and JEOL ECP400 (400 MHz) spectrometers. Chemical shifts are reported as δ (ppm) downfield relative to tetramethylsilane (TMS). Coupling constants (J) are reported in hertz (Hz). UV–Vis spectra were obtained by Otsuka Denshi MCPD-50S and Shimadzu UV-3100PC spectrometers. Fluorescence spectra were measured by a Hitachi F-4500 spectrophotometer. Mass spectra were obtained on a JEOL JMS-DX-300 by either field desorption or electron impact ionization. MALDI-TOF mass spectra were measured with a Perseptive Biosystems Voyager DE-STR. Dithranol purchased from SIGMA was used as a matrix for MALDI-TOF mass spectrometric measurements. Molecular weight determination in solution was conducted by using a Kunauer vapor-pressure osmometry. Thin layer chromatography (TLC) was performed on glass plates coated with 0.25 mm silica gel 60 F254 (Merck). Column chromatography was performed with a column packed with 0.063–0.200 mm silica gel 60 (Merck).

5-(8-Hydroxy-5-quinolinyl)-10,15,20-(*p*-tolyl)-porphyrin (1)

Freshly distilled pyrrole (2.00 g, 29.9 mmol), 8-hydroxyquinoline-5-carboxyaldehyde (3.88 g, 22.4 mmol), and *p*-tolualdehyde (0.90 g, 7.4 mmol) were refluxed in propionic acid (100 ml) for 1.5 h. The solvent was concentrated under reduced pressure and the remaining solid was dissolved in chloroform (100 ml) and DDQ (55 mg, 0.242 mmol) dissolved in benzene (2 ml) was added, and the solution was refluxed for 2 h. The solution was concentrated and washed successively with saturated $NaHCO_3$, water and dried. Isolation of this product was difficult because of strong tailing tendency on chromatography. The crude product was then stirred with acetic anhydride in $CHCl_3$ and column-chromatographed ($CHCl_3$/MeOH = 15/1, $R_f = 0.4$) to isolate the corresponding acetylated mono(oxinyl)porphyrin. The isolated product was stirred in HCl–MeOH to generate the final product. Yield: 87 mg (2%). ^{1}H NMR ($CDCl_3$) δ 8.88–8.86 (m, 5H, 2-H and β-H), 8.80 (d, $J = 5$ Hz, 2H, β″-H), 8.58 (d, $J = 5$ Hz, 2H, β′-H), 8.29 (d, $J = 8$ Hz, 1H, 6-H), 8.11 (m, 6H, 2′- and 6′-H), 7.59 (d, $J = 8$ Hz, 1H, 7-H), 7.54 (m, 6H, 3′- and 5′-H), 7.49 (d of d, $J = 8$ and 2 Hz, 1H, 4-H), 7.10 (d of d, $J = 8$ and 4 Hz, 1H, 3-H), 2.72 and 2.69 (s, 9H, 4′-CH_3), −2.66 (s, 2H, NH). MS(FAB) m/z $(M + H)^+$ 724.

Ga Complex (3)

Gallium chloride (0.4 mg, 2.3 μmol) in 95% EtOH/HCl (4 ml) was added to porphyrin **1** (5 mg, 6.9 μmol) in 95% EtOH/HCl (30 ml), and the mixture was stirred for 30 min at 70°C. The mixture was neutralized by 0.85 N NH_3 in 95% EtOH to give purple precipitates. The precipitates were filtered off, washed with distilled water, and dissolved in $CHCl_3$/MeOH (1:1). The solution was concentrated and dried under reduced pressure to give gallium complex **3** (5 mg, 97%). ^{1}H NMR (270 MHz, $CDCl_3$) δ 9.39 (quinoline 2*a*,2*b*-H), 8.90–8.60 (pyrrole), 8.47 (quinoline 6*a*,6*b*-H), 8.12 (m, tolyl 2′, 6′-H), 7.83 (quinoline 4*a*,4*b*-H), 7.75 (quinoline 7*a*,7*b*-H) 7.57 (m, tolyl 3′,5′-H), 7.40 (quinoline 3*a*,3*b*-H), 2.66 (m, tolyl 4′-CH_3), −2.61 (m, NH).

5,15-Bis(8-acetyloxy-5-quinolinyl)-10,20-bis(*n*-heptadecyl)-porphyrin (2Ac)

Trifluoroacetic acid (16 μl, 0.2 mmol) was added to *meso*-(*n*-heptadecyl)dipyrromethane (76.9 mg, 0.2 mmol) and 8-hydroxyquinoline-5-carboxyaldehyde (34.6 mg, 0.2 mmol) in deoxygenated $CHCl_3$

(20 ml). The mixture was stirred for 22 h at room temperature. DDQ (136.2 mg, 0.6 mmol) in toluene (6 ml) was added to the mixture, and the mixture was stirred for 1 h. A NaOH solution (0.1N, 20 ml) was added to the mixture, and organic layer was extracted with $CHCl_3$. The organic layer was washed with water (50 ml × 2), dried over Mg_2SO_4, and concentrated under reduced pressure to give black paste solid containing **2**. Isolation of **2** was difficult because of strong tailing tendency on chromatography. The crude black solid was then dissolved in $CHCl_3$ (5 ml), and anhydrous acetic acid (1 ml, 10 mmol) was added to the solution. After 3 h, saturated $NaHCO_3$ solution was added to the mixture, and organic layer was extracted with $CHCl_3$, dried over anh. Mg_2SO_4, and concentrated under reduced pressure. Pure **2Ac** (8.4 mg, 3.6%) was obtained by column chromatography (SiO_2, EtOAc/$CHCl_3$ = 1/10) as a mixture of atropisomer (*cis* : *trans* = 1 : 1). ^{1}H NMR (270 MHz, $CDCl_3$) δ 9.35 (d, 8H (both *cis* and *trans*), J = 4.8 Hz, pyrrole), 9.00–8.92 (m, 8H (both *cis* and *trans*), quinoline 2-H), 8.60 (d, 4H, J = 4.8 Hz, pyrrole), 8.59 (d, 4H, J = 4.8 Hz, pyrrole), 8.38 (d, 2H, J = 7.6 Hz, quinoline 7-H), 8.34 (d, 2H, J = 7.6 Hz, quinoline 7-H), 7.87 (d, 2H, J = 7.6 Hz, quinoline 6-H), 7.86 (d, 2H, J = 7.6 Hz, quinoline 6-H), 7.46 (dd, 2H, J = 8.4, 1.2 Hz, quinoline 4-H), 7.40 (dd, 2H, J = 8.4, 1.2 Hz, quinoline 4-H), 7.08 (d, 2H, J = 8.4, 4.4 Hz, quinoline 3-H), 7.06 (d, 2H, J = 8.4, 4.4 Hz, quinoline 3-H), 4.95–4.85 (m, 8H, CH_2), 2.71 (s, 12H, Ac), 2.53–2.44 (m, 8H, CH_2), 1.86–1.73 (m, 8H, CH_2), 1.51–1.41 (m, 8H, CH_2), 1.40–1.15 (m, 48H, CH_2), 0.85 (t, 12H, J = 6.8 Hz, CH_3), −2.47 (s, 4H, NH). MALDI-TOF mass m/z 1157.7 $(M + H)^+$, Calcd. for $C_{76}H_{96}N_6O_4$ 1156.75.

5,15-Bis(8-hydroxy-5-quinolinyl)-10,20-bis(*n*-heptyl)-porphyrin (2)

Bis acetate **2Ac** (22.7 mg, 19.6 μmol) was dissolved in 20 ml of methanol/conc. HCl (10:1), and stirred for 4 h at room temperature. The solution was neutralized with aq. $NaHCO_3$ and then extracted with $CHCl_3$. The organic layer was washed with water and concentrated *in vacuo* to give **2** (19.4 mg, 18.0 μmol, 92%). UV–Vis, λ_{abs} (chloroform) 422, 519, 553, 594, 653 nm. ^{1}H NMR (270 MHz, $CDCl_3$) δ 9.35 (d, 8H, J = 4.8 Hz, pyrrole), 8.80–8.72 (m, 4H, quinoline 2-H), 8.60 (d, 8H, J = 4.8 Hz, pyrrole), 8.38–8.23 (m, 4H, quinoline 7-H), 7.63–7.51 (m, 4H, quinoline 6-H), 7.48–7.39 (m, 4H, quinoline 4-H),7.20–7.02 (m, 4H, quinoline 3-H), 4.95–4.85 (m, 8H, CH_2), 2.55–2.45 (m, 8H, CH_2), 1.80–1.70 (m, 8H, CH_2), 1.51–1.41 (m, 8H, CH_2), 1.40–1.15 (m, 48H, CH_2), 0.95–0.80 (m, 12H, CH_3), − 2.52 (s, 4H, NH). MALDI-TOF mass m/z 1073.7 $(M + H)^+$, Calcd. for $C_{72}H_{92}N_6O_2$ 1072.73.

Ga Complex (4)

Gallium chloride (2.1 mg, 12 μmol) in ethanol (0.5 ml) was added to a solution of **2** (19.4 mg, 18.0 μmol) in $CHCl_3$ (3 ml) under a nitrogen atmosphere. After stirring for 30 min at room temperature, the solution was washed with aq. $NaHCO_3$ and then water. Slow diffusion of methanol to this chloroform layer gave a purple solid film. Since the organized film was insoluble in any organic solvents, absorption and fluorescence spectra of the film on a glass plate were measured at the same point by using an optical microscope, OLYMPUS BX60, with a fluorescence microscope system, OLYMPUS BX-FLA (U-MWBV excitation filter with a transparent band path of 400–440 nm), and a HAMAMATSU Photonic Multi-Channel Analyzer C7473. For comparison, Ga free porphyrin **2** was prepared by slow evaporation on a glass plate from a chloroform solution, and its absorption and fluorescence spectra were also measured.

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