Supramolecular Stacks of Bis(imidazolyl)porphyrin through Metal Coordination

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cis- and *trans*-bis(1-methyl-2-imidazolyl)tetraethyltetramethylporphyrin Mg complexes were prepared. ^{1}H NMR, absorption, and fluorescence spectra suggest that Mg has a high tendency toward dimer formation through coordination from imidazolyl to metal in a similar way to Zn, and accepts further the sixth coordination, which never occurred in Zn complexes. Propagation of the organization from a dimer to a trimer for *trans*-Mg complex starts at such a low concentration level as 10^{-5} M (1 M = 1 mol dm^{-3}) and a 2×10^{-3} M solution organized the system to a 2.34 mer on average.

The crystal structure of the light-harvesting antenna complex B850 from photosynthetic bacteria was identified recently at a 2.5 Å resolution.[1)] It had a supramolecular arrangement of eighteen bacteriochlorophyll a (Bchl a) molecules, which were sandwiched between apoprotein helices to constitute an efficient energy storage macroring. Each Bchl a molecule is partially overlapped with neighboring Bchl a's in a slipped, slightly tilted arrangement. This structural organization is provided by the coordination from imidazolyl residues extended from the helices embedded perpendicularly in the membrane. Figure 1 shows a schematic illustration of the arrangement. A similar, yet larger macroring arrangement is suggested for another light-harvesting complex I from bacteria.[2)] Trials for obtaining such molecular arrangements are fascinating problems in the field of biomimetic chemistry.

As a research program aimed at constructing efficient molecular systems of light-to- chemical energy conversion, we have been interested in designing molecules in which ligand-to-metal coordination creates well-defined supramolecular structures. In our previous report, we demonstrated self-organization of bis(1-methyl-2-imidazolyl)-substituted porphyrin Zn complex to a slipped cofacial dimer by mutual complementary coordination from the imidazolyl group to the Zn center in the counterpart porphyrin (Step A in Fig. 2).[3)] Several pyridylporphyrins have also been used as components for self-assembling units through coordination to central metals of metalated porphyrins[4)] or externally added metal ions.[5)] Now we have tried to introduce Mg instead of pentacoordinating Zn as the central metal ion of bis (*N*-methylimidazolyl)porphyrin in the hope that Mg may accept the sixth coordination[6)] and extend the structural organization further, from dimer to trimer (Step B) or to higher oligomers.

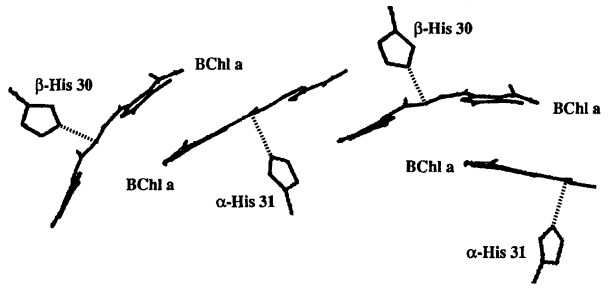


Fig. 1. Structural organization of bacteriochlorophylls in antenna complex B850 from photosynthetic bacteria. The original picture in Ref. 1[1)] was modified to illustrate the organization schematically.

Results and Discussion

Synthesis of Imidazolyl-Substituted Porphyrins. Bis-(3-ethyl-4-methyl-2-pyrrolyl)methane[7)] was stirred with 1-methylimidazole-2-carbaldehyde[8)] in the presence of *p*-toluenesulfonic acid in a methanol solution to afford porphyrinogen, which was then oxidized by DDQ in THF. The *cis*- and *trans*-5,15-bis(1-methyl-2-imidazolyl)porphyrins, *cis*- and *trans*-**1**, respectively, were isolated from the reaction products in 1.5 and 2% yields, respectively, through a column chromatograph packed with basic alumina (Chart 1). It was difficult to assign *cis* and *trans* atropisomers in the free base state, and their configurations were identified by the analysis of NMR spectra of their dimeric Zn complexes.[3)] The zinc complexes from *cis* and *trans* atropisomers appeared at R_f 0.78 and 0.50 (basic alumina, 15 : 1 (v/v) $CHCl_3$/EtOAc), respectively. Both gave almost the same UV-visible and fluorescence spectra.

The NMR spectrum from the *cis*-isomer retained the basic characteristics of the dimeric structure of the *trans*-isomer reported previously.[3)] The axis passing through two *meso* H's separated all other protons into two sets of equal intensity peaks at well separated higher and lower fields. The

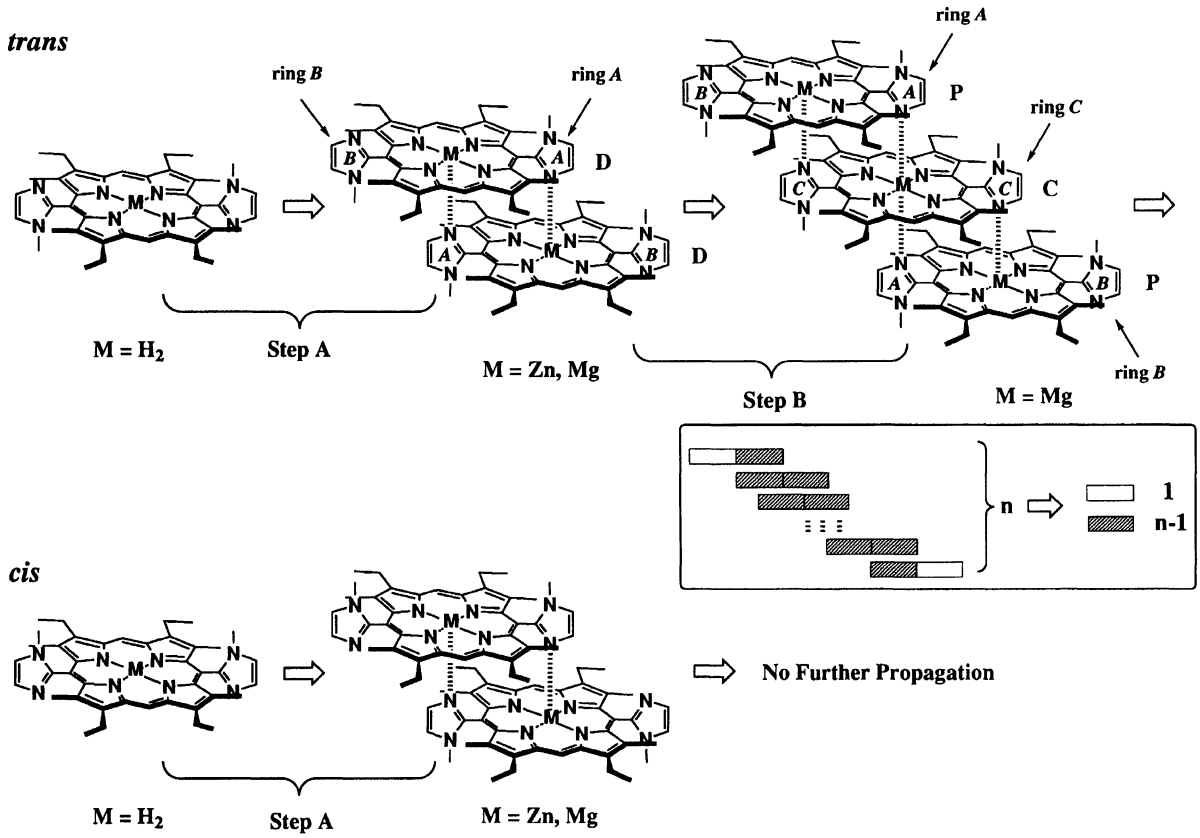
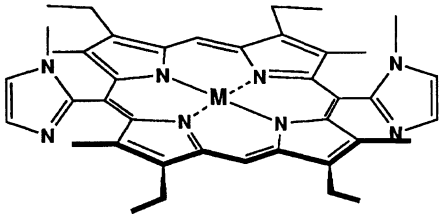
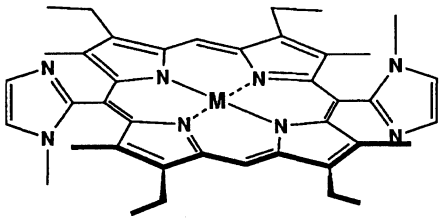


Fig. 2. Propagation of structure organization of bis(imidazolyl)-substituted porphyrin through ligand-to-metal coordination.



cis: 1(M=H_2), 2(M=Zn), 3(M=Mg)



trans: 1(M=H_2), 2(M=Zn), 3(M=Mg)

Chart 1.

NMR spectra of two geometrical isomers, however, also showed intriguing differences, which enabled us to assign their stereochemical configurations. In Fig. 3, a PNOESY spectrum of *cis*-Zn dimer, *cis*-**2**, is illustrated. The most characteristic difference in the NMR spectrum of the *cis* isomer from that of the *trans* was observed at the chemical shift of the *N*-methyl proton appearing at $\delta = 3.23$, which was correlated with the peak at $\delta = 1.54$ due to a chemical exchange process in the dimer.[3] The corresponding correlation peaks of the *N*-methyl protons appeared at $\delta = 4.07$ and 1.60 for *trans*-**2**. *N*-methyl peaks at $\delta = 1.54$ and 1.60 for *cis*- and *trans*-**2**, respectively, are assignable to the *N*-methyl of directly coordinating imidazolyl unit (ring *A* in Fig. 2 for the case of *trans*-Zn dimer), because these considerable up-field shifts are accounted for by the ring current effect of the facing porphyrin. The exchangeable counterparts, $\delta = 3.23$ and 4.07 for *cis*- and *trans*-**2**, respectively, are therefore assigned to the *N*-methyl of the free imidazolyl (ring *B* in Fig. 2 for *trans*-**2**) not incorporated into coordination. Coordination of an imidazolyl unit *A* in a porphyrin molecule to Zn in the counterpart porphyrin with a slipped cofacial arrangement places the free *N*-methyl unit *B* of the *trans* configuration into a paramagnetic deshielding area of the counterpart porphyrin and its imidazolyl substituent. On the other hand, the *N*-methyl units in the *cis* atropisomer are apart from the facing porphyrin plane and relatively insensitive toward such anisotropic deshielding effect. Therefore, the peak appearing at $\delta = 4.07$, which is shifted to a lower field by 0.7 ppm from the free base, is now assigned unequivocally to the *N*-methyl protons of the *trans*-configuration. In contrast, the peak at $\delta = 3.23$ assignable to *cis*-Zn complex was confirmed to appear at a position almost the same as the *cis*-free base porphyrin, $\delta = 3.26$.

Other correlations arising from chemical exchange processes in the dimer were also observed between peaks at $\delta = 2.64$ and -0.38 for CH_3, 1.90 and 1.43 for CH_2CH_3,

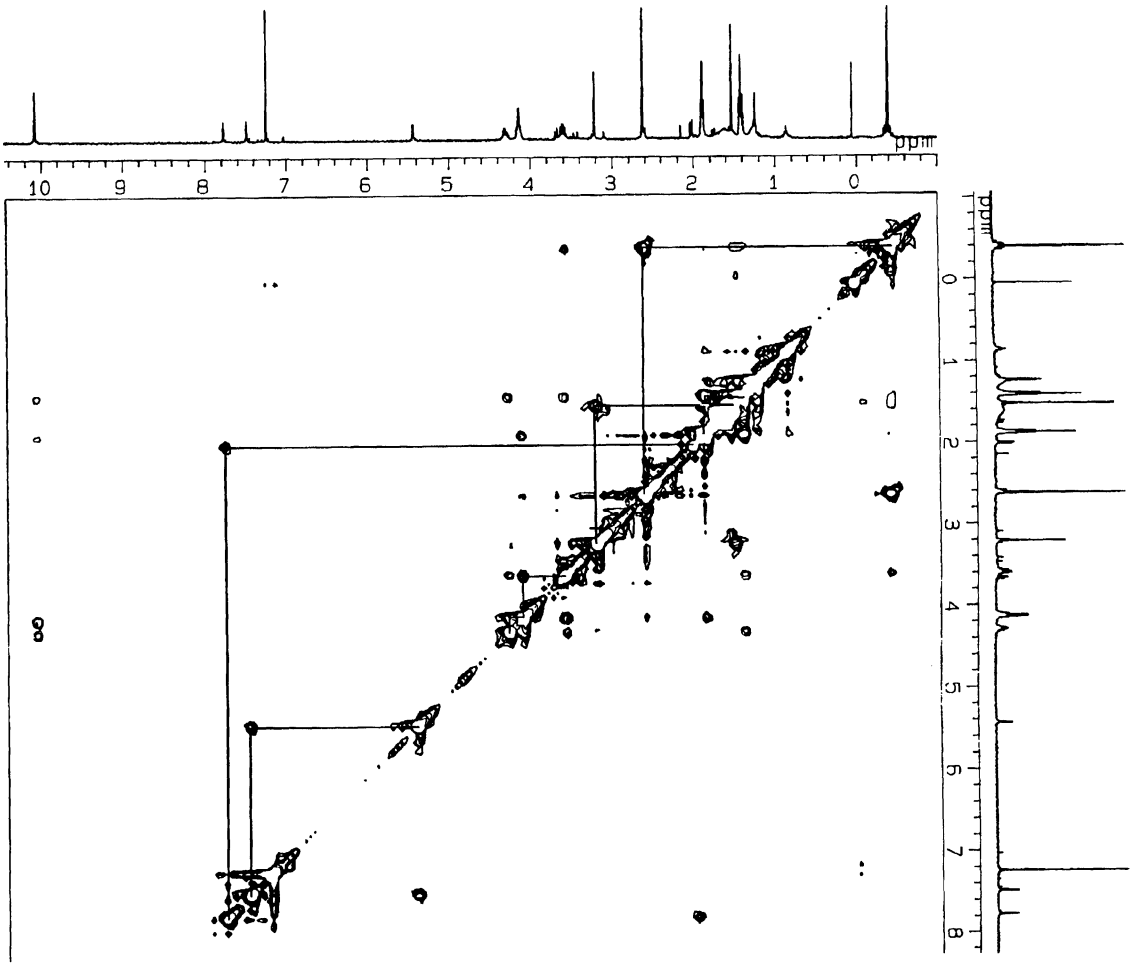


Fig. 3. PNOESY spectrum of *cis*-Zn porphyrin, *cis*-**2** (500 MHz). The chloroform-*d* solution was treated before the measurement with D_2O to eliminate water peak near $\delta = 1.60$, which partly overlapped with the *N*-methyl peak.

4.15 and 3.61, 4.15 and 4.32 for CH_2CH_3, 7.50 and 5.45, 7.79 and 2.03 for Imidazolyl. These correlations firmly established the assignment of all peaks in the slipped cofacial dimeric porphyrin.

Incorporation of Mg Metal and Molecular Organization. Insertion of Mg ion into the *trans* free base porphyrin was tried first by using $Mg(ClO_4)_2$ in pyridine (Method A) according to the conventional method.[9] However, the high reaction temperature (130 °C) induced *trans*-to-*cis* isomerization to a considerable extent. After eluting the isomerized Mg complex, *cis*-**3** at R_f 0.75 by using 15 : 1 (v/v) $CHCl_3$/EtOAc, the polar main fraction appearing at R_f 0.25—0 was eluted with methanol. Although the separation from the upper fraction was perfect, the ^{1}H NMR spectrum (in $CDCl_3$) of the isolated fraction suggested there was still contamination of as large as 30% *cis* isomer, based on the integration ratio of imidazolyl protons at 7.50 and 7.79 assignable to *cis* and those at 7.63 and 7.67 to *trans*. Therefore, the spot at R_f 0.75 must correspond to the *cis*–*cis* dimer and the lower spot a mixture of *cis*–*trans*, *trans*–*trans* dimers and/or higher oligomers. To suppress the isomerization, a lower reaction temperature (60 °C) was used to isolate the pure *cis*-complex, *cis*-**3**, starting from *cis*-**1** in a yield of 58% after a chromatographic separation. This method, however, turned out to be applicable only for the preparation of *cis*-**3**, because use of lower reaction temperature in the preparation of *trans*-**3** left a considerable amount of free base *trans*-**1** and a small amount of isomerized free base porphyrin, *cis*-**1**. The latter compound unfortunately had a similar R_f to that of the desired metalated product, *trans*-**3** and made it difficult to isolate pure *trans*-**3**. Another method using the Grignard reagent[10] was unsatisfactory because of a poor metal-incorporation yield. The difficulty in metalation of *trans*-**1** was overcome by adopting the method newly reported by Lindsey[11] during the course of this research. Thus, treatment of pure *trans*-**1** with $MgBr_2$·etherate in the presence of Et_3N at room temperature (Method B) afforded *trans*-Mg complex, *trans*-**3**, in a quantitative yield without *trans*–*cis* isomerization.

^{1}H NMR spectra of *cis*- and *trans*-**3** in a chloroform solution (2×10^{-3} M) are shown in Figs. 4A and 4B, respectively. The spectrum of *cis*-**3** is almost identical to that of the *cis*-Zn dimer, *cis*-**2**, as expected from the configuration where a further imidazolyl coordination is blocked. Therefore, the spectrum of *cis*-**3** was analyzed unequivocally as described in the experimental section. On the other hand, the spectrum of *trans*-**3** showed several characteristics different from those of the *trans*-bis(imidazolyl)porphyrin Zn dimer, *trans*-**2**. First, for example, the resonances at δ =

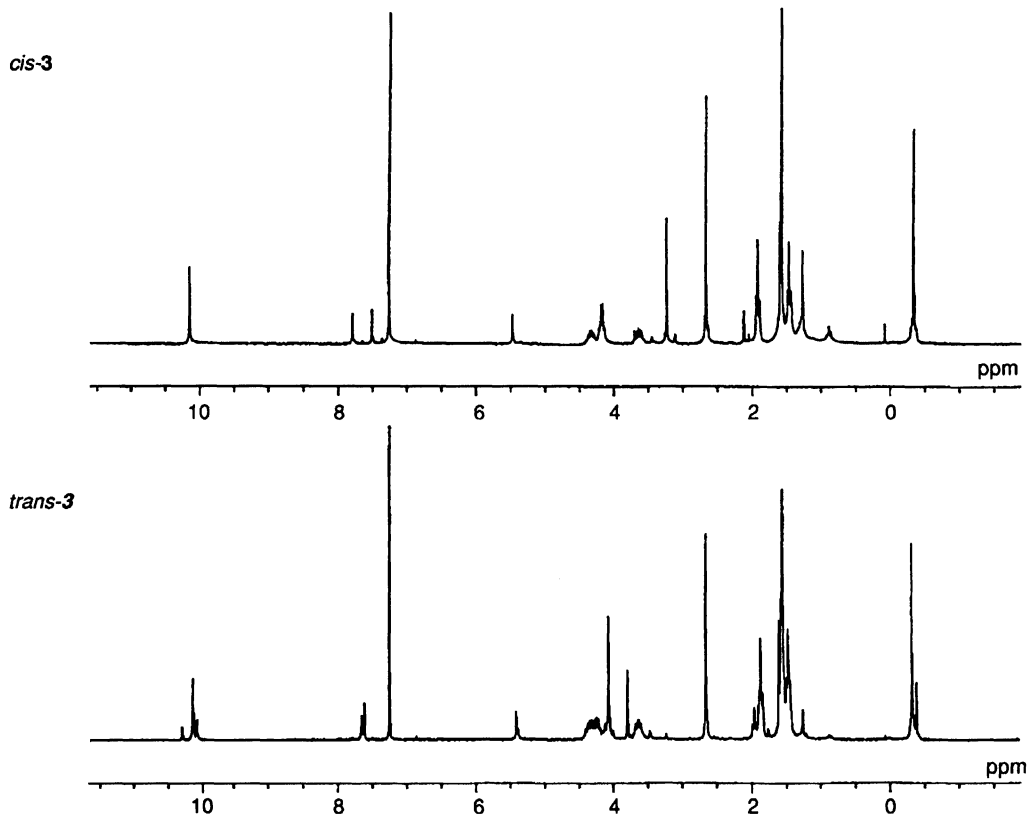


Fig. 4. 270 MHz ^{1}H NMR spectra of (A) *cis*- and (B) *trans*-Mg porphyrins **3**. Large peaks near $\delta = 1.6$ originate partly from water peaks at $\delta = 1.58$ and 1.56 for samples of *cis*- and *trans*-**3**, respectively. *N*-methyl peaks are slightly, but significantly separated from those on closer examination and assigned to the peak near $\delta = 1.56$ and 1.61 for *cis*- and *trans*-**3**, respectively, on the basis of peak correlations in 2D NMR measurements.

-0.34 and 2.63, corresponding to the stacked : nonstacked CH_3 groups, respectively, now appeared at $\delta = -0.32$, -0.35, and -0.39 for the former group and $\delta = 2.66$ for the latter with an integration ratio of 1.34 : 1 rather than 1 : 1 observed for *trans*-**2**. If we assume *n-mer* formation through coordination with a slipped cofacial arrangement, stacked and nonstacked areas correspond to $[(n-2)\times$ (central porphyrins) + $2\times$(terminal half porphyrins in the stacked area)] and [$2\times$(terminal half porphyrins in the non -stacked area)], i.e., $(n-1)$ and 1, respectively, as schematically illustrated by the inset in Fig. 2. Therefore the observed ratio implies a 2.34 *mer* formation on average. A further confident support for this assignment was obtained from *N*-methyl peaks, which appeared now at $\delta = 1.61$, 3.80, and 4.07 in relative integration ratios of 2.58H, 0.87H, and 2.58H, respectively. The peak at $\delta = 1.61$ and 4.07 correspond almost exactly to N–CH_3 of the dimeric *trans*-Zn complex, *trans*-**2**, and can easily be assigned to the peaks of directly coordinating (ring *A* in Fig. 2) and non-coordinating N–CH_3 (ring *B* in Fig. 2), respectively, of dimeric and of trimeric (and higher oligomeric) complexes in the peripheral positions. The peak at $\delta = 3.80$ should correspond to the central N–CH_3 (ring *C* in Fig. 2) in the trimeric (or higher oligomeric) complexes, which receive not only shielding but also deshielding effects from the facing porphyrins and their imidazolyl substituents, in a situation similar to the dimeric complex in the *trans* configuration. This integration ratio tells of exactly 2.34 *mer* formation, in a complete coincidence to that obtained from Me peaks directly attached to the porphyrin.

Since no monomeric unit exists even in far lower concentrations (10^{-6} M) as will be discussed below, the average 2.34 *mer* in this 2×10^{-3} M solution is calculated to contain 66% dimer and 34% trimer under the assumption that dimers and trimers are the sole species present in the equilibrium. Alternatively, it may mean that the solution contains 72% dimer, 21% trimer, and 6% tetramer in the equilibrium, if one assumes that tetramer is formed from trimer according to the same successive formation constant as trimer is formed from dimer. Considering the low solubility of *trans*-Mg complex, we rather prefer the former possibility. In any way, the step B organization proceeded significantly at this concentration level. Unfortunately, the solubility limit seems to hamper a further propagation of self-organization.

In agreement with this propagated organization, sharp singlets observed for the dimeric *cis* isomer at $\delta = 10.15$, 5.47, and -0.35, which correspond to meso, imidazolyl, and C(pyrrolyl)–methyl protons in the stacked area, respectively, split additionally in *trans*-**3**. These splittings are thought to reflect subtle differences of the environments among central and peripheral (C and P, respectively, in Fig. 2) porphyrins in trimeric and dimeric (D in Fig. 2) forms.

The degree of organization is expected to depend on

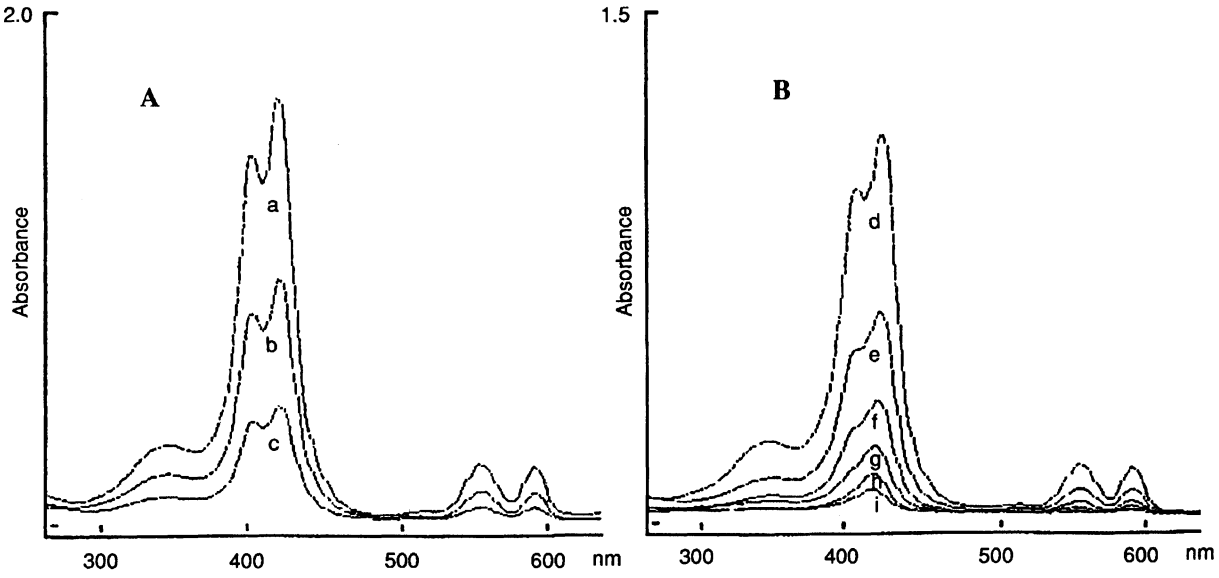


Fig. 5. Absorption spectra of *trans*-**3** at different concentrations in $CHCl_3$. The light path is 2 mm in A and 10 mm in B. a) 2.9×10^{-5} M, b) 1.5×10^{-5} M, c) 7.3×10^{-6} M, d) 3.6×10^{-6} M, e) 1.8×10^{-6} M, f) 9.1×10^{-7} M, g) 4.6×10^{-7} M, h) 2.3×10^{-7} M, i) 1.1×10^{-7} M.

the concentration used. Unfortunately, this concentration (2×10^{-3} M) seemed to be the maximum for *trans*-**3** in $CDCl_3$. The product from Method A, a mixture of 30% *cis* and 70% *trans* isomers, allowed a more concentrated solution of 5×10^{-3} M, indicating an increased solubility with the presence of *cis* isomer in the sample. However, the degree of organization, being a 2.40 *mer* on average, could not be increased because of the terminating effect of *cis* isomer on metal-organization.

To investigate the concentration effect on the molecular organization, spectroscopic studies were undertaken at more diluted solutions. The trimer content was decreased continuously down to 10% at 5.0×10^{-5} M, the lowest practical concentration possible for the NMR measurement. The behavior on further decrease of the concentration (2.9×10^{-5}—1.1×10^{-7} M) was then monitored by absorption spectroscopy (Fig. 5). At concentrations higher than 3.6×10^{-6} M, a clear splitting of the Soret band and red shifts of Q bands, arising from exciton interaction of porphyrins in the slipped cofacial dimeric arrangement, were observable.[12] These data, along with red shifts of the fluorescence maxima, suggest a high tendency of Mg porphyrins to be organized through coordination from imidazole to Mg in an order similar to Zn porphyrins.

At concentrations lower than 1.8×10^{-6} M, split Soret bands become difficult to discern and coalesced finally into a single broad band at concentrations lower than 4.6×10^{-7} M in the case of *trans*-**3**. This is a sign of the breakdown of the dimeric structure to the monomeric to some extent. A similar structural variation was also detected by blue shifts of the fluorescence maxima of *trans*-**3** (Table 1). In contrast, *cis*-**3** dimer tends to persist even at a lower concentration level of 10^{-7} M, judging from the fact that almost no variation of either absorption or fluorescence maxima was observed down to this concentration range. A further dilution effect lower than the 10^{-7} M range was traced now by fluorescence

Table 1. Concentration Dependence of Absorption and Fluorescence Maxima[a] of *cis*- and *trans*-Mg Complexes **3**

Concn	*trans*-**3**						*cis*-**3**					
	Abs. max.				Fluor. max.		Abs. max.				Fluor. max.	
M	Soret		Q-Bands				Soret		Q-Bands			
	nm		nm		nm		nm		nm		nm	
3.6×10^{-6}	405	422	557	592	595	647	404	424	557	593	596	647
1.8×10^{-6}	421		557	592	594	646	404	424	557	593	596	647
9.1×10^{-7}	420		557	592	594	646	404	424	557	593	596	647
4.6×10^{-7}	418		556	592	593	643	404	423	557	593	596	647
2.3×10^{-7}	417		555	591	592	643	404	424	556	593	596	647
1.1×10^{-7}	417		555	591	592	643	404	423	556	593	596	647
1.1×10^{-8}					592	643					594	646
1.1×10^{-9}					591	642					591	641

a) Solvent: chloroform.

spectra. First at the concentrations as low as 10^{-8}—10^{-9} M, *cis*-**3** showed significant blue shifts of the fluorescence maxima, suggesting the breakdown of the dimeric structure finally to the monomeric. The different behavior of the absorption and fluorescence spectra between *cis*- and *trans*-**3** indicates a higher stability constant for the *cis* dimer. The higher stability order of *cis* dimer was also observed for the series of Zn-porphyrin pairs, *cis*- and *trans*-**2** pairs. Some sort of stereoelectronic effect seems to be responsible for the different stabilities.

Combined observations of all these spectroscopies, ^{1}H NMR, absorption, and fluorescence, suggest that Mg complex **3** has a higher tendency of organization through an imidazole–metal coordination than the Zn Complex. The complex *cis*-**3** starts to dimerize even at such a low concentration level as 10^{-8} M, and exists predominantly as the dimer at the concentration level of 10^{-7} M. The *trans*-**3** needs a higher concentration by a factor of 10^1—10^2 for efficient dimerization and gets start to dimerize at a concentration range between 10^{-6}—10^{-7} M. However, the *cis* complex prohibits a further growth of self-organization, but *trans* Mg complex extends to be organized into a trimer at a higher concentration level like 10^{-5} M by accepting the sixth coordination. The maximum trimer content was 34% for the $CHCl_3$ solution of 2×10^{-3} M. This shows a contrast to the case of Zn complex, which never accepted the sixth coordination. Such the concentration dependence of Mg complex guarantees extended organization at more concentrated solutions. To avoid the solubility problems at the same time, crystal growth appropriate for the X-ray analysis may be the best to present a further growth of structural organization. Investigations are now under way for crystals obtained in the study.

Experimental

General: ^{1}H NMR spectra were recorded on either a JEOL JNM EX 270, or Alpha 500 spectrometer. Chemical shifts are reported on the δ scale with respect to δ (TMS, internal standard)=0 ppm. Coupling constants (J) are reported in hertz (Hz). Chloroform-*d* ($CDCl_3$, Aldrich) was dried and removed from acid contaminants before use by passing through a basic alumina column. UV-visible spectra were measured by an Otsuka Electronics MCPD-50S spectrometer. Fluorescence spectra were recorded on a Hitachi F-4500 spectrometer. Mass spectra were obtained with a JEOL JMS-DX300 spectrometer using positive-ion fast atom bombardment with 3-nitrobenzyl alcohol as a matrix. Thin layer chromatography (TLC) was done on glass plates coated with 0.25 mm aluminum oxide 60 F254 basic (E. Merck). Column chromatography was done with a column packed with aluminum oxide 90 basic (E. Merck, particle size 0.063—0.200 mm).

5,15-Bis(1-methyl-2-imidazolyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin 1: A solution of bis(3-ethyl-4-methyl-2-pyrrolyl)methane[7] (1.60 g, 6.96 mmol), 1-methylimidazole-2-carbaldehyde[8] (0.77 g, 6.96 mmol), and *p*-toluenesulfonic acid (0.35 g, 1.87 mmol) in methanol (90 ml) was stirred for 30 min and left at room temperature for 12 h in the dark. The solvent was removed by evaporation and the crude porphyrinogen was dissolved in THF (220 ml). The solution was treated with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 2.86 g, 12.58 mmol) in THF (40 ml). The resulting dark solution was stirred for 30 min at room temperature and left for 12 h more in the dark. The solvent was evaporated and the residual solid was washed with saturated $NaHCO_3$, then water, and then dried to yield bis(imidazolyl)porphyrin as a mixture of atropisomers. The product was chromatographed on basic alumina (activity stage II) using 15 : 1 (v/v) $CHCl_3$/EtOAc as the eluent to isolate atropisomers *cis*-**1** and *trans*-**1** as purple solids (*cis*-**1**: 33 mg, 1.5% and *trans*-**1**: 47 mg, 2%). The R_f of TLC on basis alumina with 15 : 1 (v/v) $CHCl_3$/EtOAc were 0.20 and 0.68 for *cis*-**1** and *trans*-**1**, respectively.

***cis*-1:** ^{1}H NMR (270 MHz, $CDCl_3$) δ_H = 10.20 (s, 2H, *meso*), 7.67 (s, 2H, imidazole), 7.48 (s, 2H, imidazole), 4.00 (q, J = 7.6 Hz, 8H, CH_2CH_3), 3.26 (s, 6H, N–CH_3), 2.52 (s, 12H, CH_3), 1.77 (t, J = 7.6 Hz, 12H, CH_2CH_3), −2.80 (s, 2H, NH). λ_{max} ($CHCl_3$)/nm 405, 507, 542, 575 and 628. λ_{em} ($CHCl_3$)/nm 628 and 692. MS *m/z* 639 (M^++1 ; 30%).

***trans*-1:** ^{1}H NMR (270 MHz, $CDCl_3$) δ_H = 10.26 (s, 2H, *meso*), 7.65 (s, 2H, imidazole), 7.48 (s, 2H, imidazole), 4.04 (q, J = 7.6 Hz, 8H, CH_2CH_3), 3.37 (s, 6H, N–CH_3), 2.54 (s, 12H, CH_3), 1.80 (t, J = 7.6 Hz, 12H, CH_2CH_3), −2.79 (s, 2H, NH). λ_{max} ($CHCl_3$)/nm 405, 507, 541, 577 and 627. λ_{em} ($CHCl_3$)/nm 628 and 692. MS *m/z* 639 (M^++1 ; 31%).

The configuration of two atropisomers was identified after converting these free bases to Zn complexes, separately.

[*cis*-5,15-Bis(1-methyl-2-imidazolyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrinato(2−)]zinc *cis*-2: Free base *cis*-**1** (25 mg, 0.039 mmol) was dissolved in $CHCl_3$ (40 ml) at reflux, a methanol solution of anhydrous zinc acetate (859 mg, 3.90 mmol) was added, and the mixture was heated at reflux. The reaction was monitored by TLC and UV-vis spectra. The main spot on alumina TLC (15 : 1 (v/v) $CHCl_3$/EtOAc) showed a change of the R_f from 0.20 (*cis*-**1**) to 0.78 (Zn complex, *cis*-**2**) together with a collapse of the four Q bands to two peaks. After refluxing for 2 h, the solvent was evaporated to dryness, washed with water, and dried. The crude product was chromatographed on a basic alumina (activity stage II) using 15/1 (v/v) $CHCl_3$/EtOAc as the eluent. The Zn complex *cis*-**2** was isolated as purple solids (23 mg, 84%): ^{1}H NMR (270 MHz, $CDCl_3$, *cis–cis* dimer) δ_H = 10.09 (s, 2H, *meso*), 7.79 (s, 1H, imidazole), 7.50 (s, 1H, imidazole), 5.45 (s, 1H, imidazole in stacking area), 4.32 (m, 2H, CH_2CH_3 in stacking area), 4.15 (m, 4H, CH_2CH_3), 3.61 (m, 2H, CH_2CH_3 in stacking area), 3.23 (s, 3H, N–CH_3), 2.64 (s, 6H, CH_3), 2.03 (s, 1H, imidazole in stacking area), 1.90 (t, J = 7.6 Hz, 6H, CH_2CH_3), 1.54 (s, 3H, N–CH_3 in stacking area), 1.43 (t, J = 7.6 Hz, 6H, CH_2CH_3 in stacking area), −0.38 (s, 6H, CH_3 in stacking area); λ_{max} ($CHCl_3$)/nm 409, 427, 558 and 592; λ_{em} ($CHCl_3$)/nm 596 and 647. MS *m/z* 701 (M^++1 ; 100%).

[*trans*-5,15-Bis(1-methyl-2-imidazolyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrinato(2−)]zinc *trans*-2: The Zn complex *trans*-**2** was obtained from free base *trans*-**1** by the procedure described above. The R_f on TLC (15/1 (v/v) $CHCl_3$/EtOAc) changed from 0.68 (*trans*-**1**) to 0.45 (*trans*-**2**). This complex was isolated through column chromatography in 74% yield. ^{1}H NMR (270 MHz, $CDCl_3$ *trans–trans* dimer) δ_H = 10.10 (s, 2H, *meso*), 7.65 (s, 1H, imidazole), 7.63 (s, 1H, imidazole), 5.41 (s, 1H, imidazole in stacking area), 4.36 (m, 2H, CH_2CH_3 in stacking area), 4.24 (m, 2H, CH_2CH_3), 4.07 (m, 2H, CH_2CH_3), 4.07 (s, 3H, N–CH_3), 3.63 (m, 2H, CH_2CH_3 in stacking area), 2.64 (s, 6H, CH_3), 1.86 (t, J = 7.6 Hz, 6H, CH_2CH_3), 1.79 (s, 1H, imidazole in stacking area), 1.60 (s, 3H, N–CH_3 in stacking area), 1.45 (t, J = 7.6 Hz, 6 H, CH_2CH_3 in stacking area), −0.35 (s, 6H, CH_3 in stacking area); λ_{max} ($CHCl_3$)/nm 408, 426, 556 and 591; λ_{em} ($CHCl_3$)/nm 594 and

647. MS *m/z* 701 ($M^+ + 1$; 3%).

[*cis*-5,15-Bis(1-methyl-2-imidazolyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrinato(2−)]magnesium *cis*-3: Free base porphyrin *cis*-**1** (5 mg, 0.0079 mmol) was dissolved in pyridine (1 ml) and $Mg(ClO_4)_2$ (25 mg, 0.11 mmol) was added. The solution was heated at 60 °C, since the use of higher reaction temperatures as usual induced significant *cis–trans* isomerization. The reaction was monitored by TLC and UV-vis spectra. The main spot appeared at R_f 0.75 on alumina TLC (15 : 1 (v/v) $CHCl_3$/EtOAc). A small amount of isomerized product(s) were observed at R_f 0.25 with a strong tailing down to R_f −0. Q-band patterns in the UV-vis spectra were sensitive to the metal insertion. After heating for 30 h, the solvent was evaporated to dryness, and the residue was washed successively with water, pH 3 buffer solution, saturated $NaHCO_3$ solution, and water, and dried. The crude product was chromatographed on an alumina (activity stage II) column using $CHCl_3$/EtOAc as the eluent. The Mg complex *cis*-**3** was isolated (3 mg, 58%). ^{1}H NMR (270 MHz, $CDCl_3$, *cis–cis* dimer) δ_H=10.15 (s, 2H, *meso*), 7.79 (s, 1H, imidazole), 7.50 (s, 1H, imidazole), 5.47 (s, 1H, imidazole in stacking area), 4.33 (m, 2H, CH_2CH_3 in stacking area), 4.17 (m, 4H, CH_2CH_3), 3.63 (m, 2H, CH_2CH_3 in stacking area), 3.23 (s, 3H, N–CH_3), 2.66 (s, 6H, CH_3), 2.12 (s, 1H, imidazole in stacking area), 1.91 (t, J=7.6 Hz, 6H, CH_2CH_3), 1.56(s, 3H, N–CH_3 in stacking area), 1.46 (t, J=7.6 Hz, 6H, CH_2CH_3 in stacking area), −0.35 (s, 6H, CH_3 in stacking area); λ_{max} ($CHCl_3$)/nm 404, 424, 557 and 593; λ_{em} ($CHCl_3$)/nm 596 and 646. MS *m/z* 661 ($M^+ + 1$; 18%).

[*trans*-5,15-Bis(1-methyl-2-imidazolyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrinato(2−)]magnesium *trans*-3: Method A: Free-base porphyrin *trans*-**1** (10 mg, 0.016 mmol) was dissolved in pyridine (2 ml) and $Mg(ClO_4)_2$ (50 mg, 0.22 mmol) was added, and the solution was heated at 130 °C. The R_f on TLC (15 : 1 (v/v) $CHCl_3$/EtOAc) changed from 0.68 (*trans*-**1**) to 0—0.25 (*trans*-**3**, oligomeric mixture). Isomerized product (R_f 0.75, *cis*-**3**) was also observed on TLC. After this was heated for 18 h, when no more free base porphyrins were detectable either by TLC or Q-bands, the solvent was evaporated to dryness, and the residue was washed successively with water, pH 3 buffer solution, saturated $NaHCO_3$ solution, and water, and dried under a vacuum. *Trans* Mg complex (*trans*-**3**) was adsorbed strongly on an alumina column and could not be isolated in the same manner as *cis*-**3** by the column chromatography. After eluting the product at R_f 0.75 (*cis*-**3**) by using $CHCl_3$/EtOAc eluent, the product at R_f 0—0.25 (*trans*-**3**, oligomeric mixture) was eluted with methanol. The solvent was evaporated and dried under a vacuum to afford *trans*-**3** (4 mg, 39%). MS *m/z* 661 ($M^+ + 1$; 25%).

Method B: Bis(imidazolyl)porphyrin *trans*-**1** (9 mg, 0.014 mmol) was dissolved in CH_2Cl_2 (1 ml) and triethylamine (0.16 ml, 1.13 mmol) and $MgBr_2 \cdot OEt_2$ (146 mg, 0.56 mmol) were added. The mixture was stirred magnetically at room temperature for 30 min, when the metalation appeared complete as judged from UV-vis spectroscopy. The reaction mixture was diluted with CH_2Cl_2 (15 ml), washed with 5% $NaHCO_3$ (2×15 ml), dried (Na_2SO_4), and filtered, and the filtrate was evaporated to dryness. Chromatography on an alumina column with CH_2Cl_2 elution eliminated the residual free-base *trans*-**1**. Further elution with methanol afforded *trans*-**3** after evaporation to dryness (9 mg, 98% yield): The R_f on alumina TLC (15/1 (v/v) $CHCl_3$/EtOAc) 0—0.25; ^{1}H NMR (270 MHz, $CDCl_3$, an average 2.34 *mer* solution at the saturated concentration: 2×10^{-3} M) δ_H = 10.31, 10.16 and 10.10 (s each, 2H, *meso*), 7.67 and 7.63 (s, 43% of 4H, imidazole), 5.42 and 5.40 (s each, 28.5% of 4H, imidazole in stacking area), 4.34 (m, 57% of 4H, CH_2CH_3 in stacking area), 4.24 (m, 43% of 4H, CH_2CH_3), 4.07 (m, 43% of 4H, CH_2CH_3), 4.07 (s, 43% of 6H, N–CH_3), 3.80 (s, 14.5% of 6H, N–CH_3 at central of trimer), 3.64 (m, 57% of 4 H, CH_2CH_3 in stacking area), 2.66 (s, 43% of 12 H, CH_3), 1.97 (s, 28.5% of 4 H, imidazole in stacking area), 1.87 (t, J = 7.6 Hz, 43% of 12 H, CH_2CH_3), 1.61 (s, 43% of 6 H, N–CH_3 in stacking area), 1.47 (t, J = 7.6 Hz, 57% of 12 H, CH_2CH_3 in stacking area), −0.32, −0.35 and −0.39 (s each, 57% of 12 H, CH_3 in stacking area); λ_{max} ($CHCl_3$)/nm 405, 422, 557 and 592; λ_{em} ($CHCl_3$)/nm 595 and 647. MS *m/z* 661 ($M^+ + 1$; 18%).

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