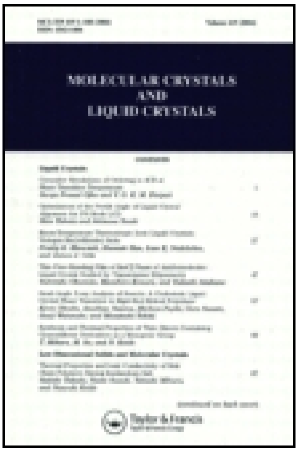

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MOLECULAR ORGANIZATION OF PORPHYRIN-METAL COMPLEXES

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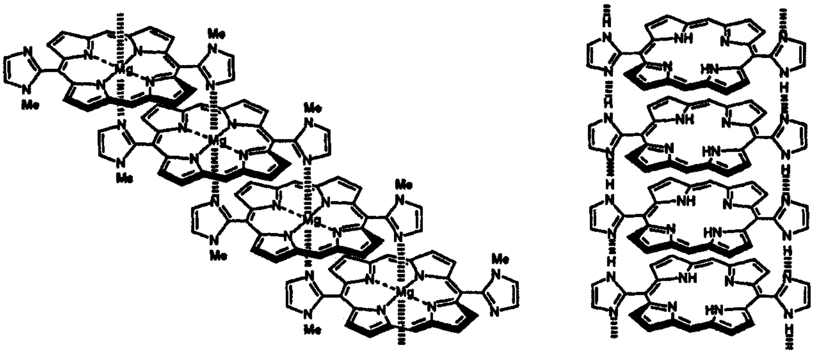
Abstract Tetraethyltetramethylporphyrin substituted at two facing meso positions by N-methylimidazolyl groupings and its metal complexes were prepared. The absorption spectra of Zn and Mg complexes showed a characteristic splitting of Soret band and red-shifts of Q-bands indicating the exciton interaction of porphyrins in a slipped cofacial arrangement, where each imidazolyl group in one metal porphyrin is coordinated to metals in the other porphyrin skeleton. Typical upfield shifts in the ^{1}H NMR spectra arising from such the stacking structure elucidated Zn and Mg complexes as a dimer and an oligomeric mixture, respectively. Bis(imidazolyl)substituted tetraethyltetramethyl-porphyrin was also prepared. It suggested the hydrogen bonded oligomer formation through imidazolyl-imidazolyl interactions in a columnar orientation.

Electric conductivities of films prepared from these compounds werecharacterized. In a same line with behaviors in solution, samples capable of π-stacking interaction with adjacent porphyrins via ligand-to-metal coordination or hydrogen bonding exhibited higher conductivities as well as lower activation energies for the thermal conduction. These behaviors are understood as due to the overlap of π-systems of one porphyrin with neighboring porphyrins.

INTRODUCTION

Macrocyclic compounds composed of conjugated polyenes, such as porphyrin or phthalocyanine, provide molecular systems exhibiting delocalized rich π-electrons in the molecule and strong absorptions of light energy in the visible as well as UV region. When these molecules are placed in the distance to allow intermolecular interactions in ground or exited states, high electric- or photoconducting materials are expected to result.[1] One of the beautiful examples in nature is a special pair dimer[2] or antenna oligomers[3] of chlorophylls in the photosynthetic pigments. In order to gain insights into the photosynthesis or valuable hints toward practical materials, a variety of dimer or oligomer models have hitherto been reported, where porphyrins are connected via chemical bonds in desired stereochemical dispositions.[4]

We have been interested in constructing artificial systems of biological function by using intermolecular forces rather than chemical bonds. Along this line, we have already reported a special pair type self-organization via imidazole-to-Zn metal coordination.[5] In this report, the central metal atom was replaced from penta-coordinating Zn[6] by Mg,[7] which may allow further growth of the slipped cofacial structure in solution as well as solid phases. Furthermore, non-N-alkylated imidazolyl substituent was introduced at the porphyrin[8] and the structural effects of these molecular organization on the electric conductivity in the solid phase were examined.



SCHEME 1 Self-organization of porphyrins through ligand-to-metal coordination or hydrogen bonding by imidazolyl substitutents

RESULTS AND DISCUSSION

Synthesis of Imidazolyl Substituted Porphyrins

We have prepared free bases, **1** and **2**, and their metal complexes **3** and **4** of tetraethyltetramethylporphyrins, which carry two imidazolyl or N-methylimidazolyl substituents at two facing meso positions. The synthetic pathway was illustrated in Figure 1.

Ethylmethyldipyrrylmethane was stirred with imidazole-2-carboxaldehyde or N-methyl-imidazole-2-carboxaldehyde in the presence of p-toluenesulfonic acid in a methanol solution to afford porphyrinogens, which were then oxidized by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in THF. Free base porphyrins **1** and **2** were obtained in yields of 6 and 2 %,[9] respectively. Zinc complex **3** was prepared by adding a methanolic solution of zinc acetate to a chloroform solution of **2** followed by refluxing in a 74 % yield.[10] Magnesium complex **4** was prepared by refluxing a mixture of magnesium perchlorate and **2** in pyridine in a yield of 66 %.[11]

Molecular Organization in Solution

^{1}H NMR spectra of Zn and Mg complexes, **3** and **4**, respectively, in a chloroform solution (5 x 10^{-3} M) were shown in Figure 2. In the case of **4**, the material shows low

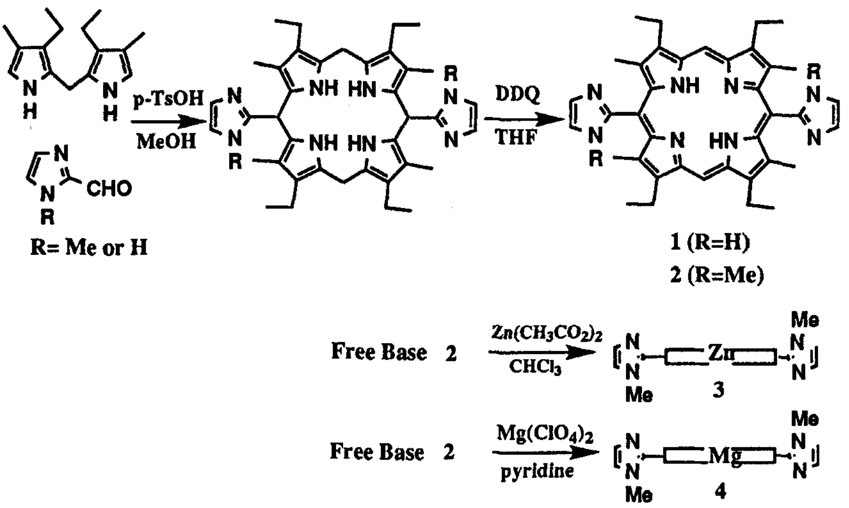


FIGURE 1 Synthetic pathway of imidazolyl- or N-methylimidazolyl-substituted porphyrins **1** and **2**, respectively and their metal complexes **3** and **4**.

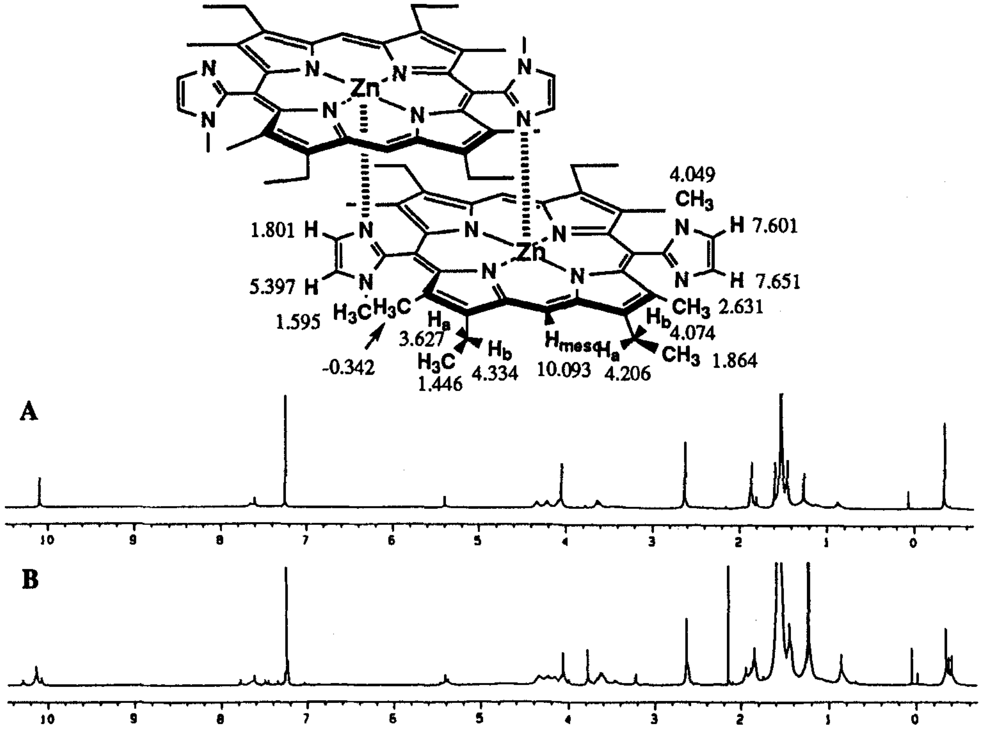


FIGURE 2 ^1H NMR spectra of Zn and Mg complexes, **3** and **4**, respectively, in a chloroform solution (5×10^{-3} M).

solubility in chloroform and this concentration is the saturated level.

It has already been shown that Zn complex **3** is of a dimeric structure as shown in Figure 2A, which contains the chemical shift data of all peaks assigned on the basis of COSY and PREOSY measurements.[5] The general outlook of the spectrum of **4**, 2B is quite similar to 2A. However, Figure 2B contains important differences from 2A. One is the integral ratio stacked to non-stacked regions. In 2A, the ratio, for example the methyl protons at stacked and non-stacked regions, i.e., δ -0.34 and 2.63 ppm, respectively, corresponds exactly to 1:1. In contrast, the ratio in **4** was found to be 1.4:1. If we assume n-mer formation through the metal coordination, the ratio corresponds to (n-1):1. Therefore the ratio observed for **4** corresponds to on average a 2.4-mer. Since no momomeric unit exists even in very low concentrations, dimer and trimer are thought to be the predominant species in equilibrium with a tiny contribution of higher oligomers. Therefore, the above observation means that the solution contains roughly 60 % dimer and 40 % trimer (Figure 3).

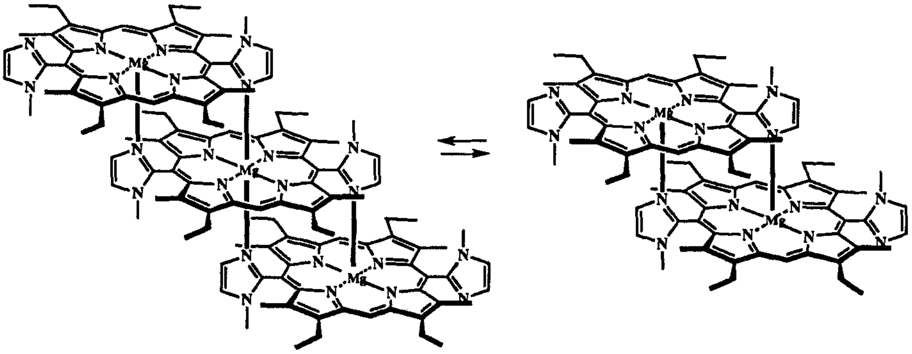


FIGURE 3 Dimer-trimer equilibrium structure for magnesium porphyrin **4**.

Another important difference in the NMR spectra of **3** and **4** exists in the peaks assigned to those at the stacking parts. Sharp singlets observed in 2A at δ 10.093, 5.397 and -0.342 ppm, which correspond to meso, imidazolyl and C(pyrryl)-methyl protons, respectively, in the stacking region, show additional splittings in 2B. Other parts of the peaks are also indicative of additional splittings, but not well-separated or overshadowed by other peaks. These splittings are explained by the idea that the central and peripheral porphyrins in the trimer are in slightly different environments and further that the environment of the peripheral in the trimer may also be different from that in the dimer.

The trimer contents were estimated at different concentrations by ^{1}H NMR spectra and found to decrease down to 10% at the lowest possible concentration (5.0×10^{-5} M) for the NMR measurement. The temperature dependence was also examined at the high concentration (5×10^{-3} M). No significant change of the trimer content was observable in the temperature range 20°C to -50°C.

Figure 4 shows the absorption spectrum of Mg complex **4** in a chloroform solution (1×10^{-6} M). In an analogy to the dimeric Zn complex **2**, splitting of the Soret band,[12] shift of Q bands to longer wave lengths[13] were observable, indicating the exciton interaction of porphyrins in a slipped cofacial arrangement. Red shifts of the fluorescence maxima of **4** were also detected.

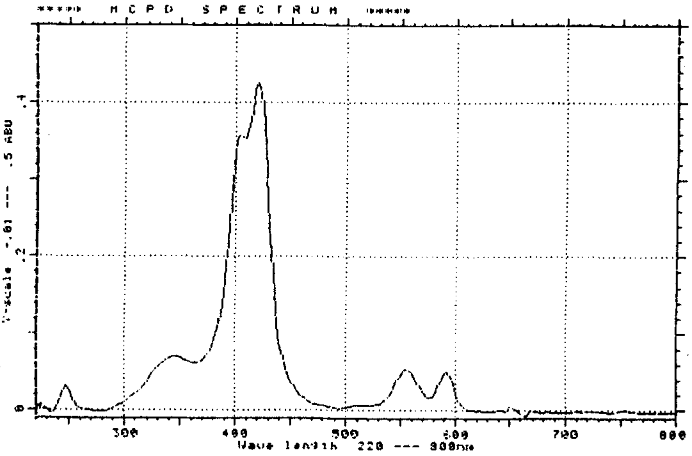


FIGURE 4 Absorption spectrum of Mg complex **4** in a chloroform solution (1×10^{-6} M).

Combined observations of all these spectroscopies, ^{1}H NMR, absorption and fluorescence, suggest that Mg complex **4** exists predominantly as a dimer at the concentration level for the absorption and fluorescence (10^{-6} M) spectral measurements and starts to be organized into a trimer through imidazole-to-metal coordination at a higher concentration level as 10^{-5} M for the ^{1}H NMR spectral measurement and its composition reaches 40% at the saturated concentration in chloroform (5×10^{-3} M).

Although N-methylimidazolyl-substituted porphyrin **2** was capable of affording ^{1}H NMR spectrum in chloroform, non-N-alkylated imidazolylporphyrin **1** was not soluble enough to give the spectrum. When a small amount of trifluoroacetic acid was added to chloroform, **1** gave satisfactorily the spectrum but of the protonated porphyrin. Polar solvents such as DMSO or methanol gave also a monomeric porphyrin. H-bond formation with the imidazole unit by use of H-N is assumed to make the compound sparingly soluble in chloroform and its breakdown in polar solvents or protonation seems to be required to be solubilized appreciably in chloroform. Absorption and fluorescence spectra of **1** were obtainable in chloroform at a low concentration (10^{-6} M) and compared with those of **2** in Table 1. No significant difference is observable between these two compounds. Therefore, the compound **1**, capable of H-bonding, can exist as a monomer only in the low concentration range 10^{-6} M, and starts to be organized into oligomer already in the range 10^{-5} M to make the compound sparingly soluble or insoluble.

TABLE 1 Comparison of absorption and fluorescence spectra of free base porphyrins **1** and **2**.

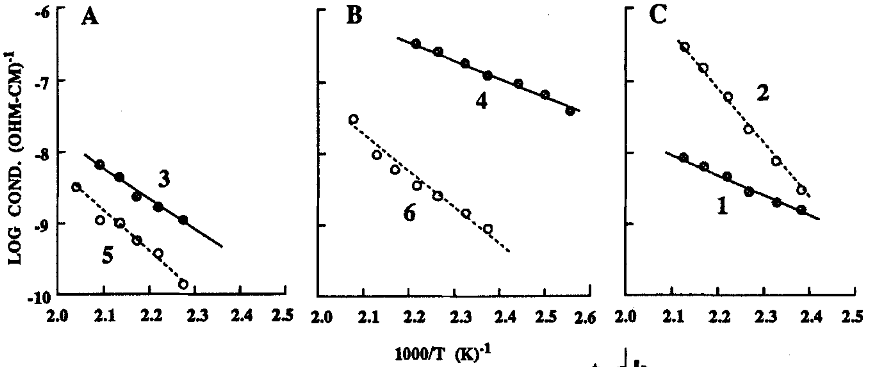
	Absorption maximum (nm)		Fluorescence maximum(nm)
	Soret(half width)	Q-bands	
1	404(41)	507, 541, 572, 624	629
2	405(41)	507, 541, 577, 627	628

Molecular Organization in the Solid

Samples of **1-4** and their reference compounds, Zn octaethylporphyrin(OEP) **5** or Mg(OEP) **6** were deposited from a chloroform solution between two gold electrodes (Distance $l = 0.01$ cm, Electrode surface area $S = 9 \times 10^{-6}$ cm^2), as illustrated in the inset of Figure 5. The sample was annealed at 130°C for 20 min in a high vacuum chamber (10^{-5} Torr) to remove solvent and moisture completely. The current I was measured by using a high-sensitivity ammeter under applying a constant voltage (E = 100V) in the presence of 1 Torr He gas.[14] The dc-electric conductivity of the sample σ was estimated by the equation $\sigma = l/RS$, where $R = E/I$ and plotted vs. 1/T (Figure 5).

As it is known that the electric conductivity of porphyrins generally lies in the semiconducting range, all of the samples showed the characteristics of semiconductor expressed by the equation: $\sigma = \sigma_0 \exp(-Ea/kT)$. Zn complex **3** showed a little bit higher conductivity and a smaller Ea compared to Zn(OEP) **5** (Figure 5A). However the difference was not very large. Zinc porphyrin cannot accept six-coordination and keeps its dimer structure even in the solid phase.

In contrast, magnesium porphyrin **4** can accept six-coordination and is capable of propagating the stacked structure in a slipped cofacial arrangement through ligand-to-metal coordination. The conductance of **4** is 2-3 orders of magnitude larger than that of Mg (OEP) **6** as the reference compound. The activation energy 0.5 eV is decreased by 0.44 eV from the reference (Figure 5B).



Activation Energy (eV)

Compd.	Zn	Mg	H_2
Im-P	(3) 0.73	(4) 0.50	(1) 0.55
Ref.	(5) 0.97	(6) 0.94	(2) 1.37

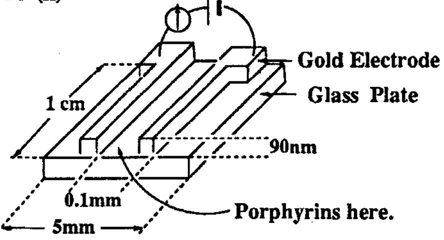


FIGURE 5 Conductivity and activation energy of imidazolyl **1** and N-methylimidazolyl substituted porphyrins **2**, and their Zn **3** and Mg complexes **4**, along with Zn and Mg octaethylporphyrins, **5** and **6**, respectively.

The activation energy of conductivity for free base porphyrin **1** was estimated to be 0.55 eV, exhibiting a large decrease compared to the value of N-methyl-substituted compound **2** 1.37 eV (Figure 5C). Compared to the latter N-alkylated compound, the former is capable of forming columnar stacks through N-H···N hydrogen bond in the condensed or solid phase.

All of these observations, the decrease of the activation energy and the variation of the conductivity, are compatible with the behavior in solution and are assumed to originate from the formation of oligomeric structure self-organized through ligand-to-metal coordination or hydrogen bonding.

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10. Zn metal was introduced into trans-pure free base porphyrin **2**. The product contained a small amount of the cis product (Rf = 0.78) and the trans (Rf = 0.45) was isolated pure through column chromatography.
11. Mg metal was introduced into trans-pure free base porphyrin **2**. See J. H. Fuhrhop and D. Mauzerall, J. Am. Chem. Soc., 91, 4174 (1969). The high reaction temperature induced isomerization to the cis product (Rf = 0.78). The trans (Rf = ≈0) was eluted by methanol, but the product still contained ca. 30% cis isomer.
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14. The conductivity lower than 10^{-10} S·cm^{-1} could not be estimated. Since the conductivity of the reference OEP's was low, the measurement was undertaken at high temperature range 112 to 227°C. He gas (1 Torr) was introduced into the chamber to assist thermal diffusion.