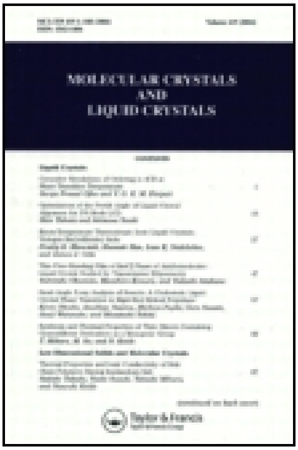

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Supramolecular Porphyrin Assemblies for Photosynthetic Antenna Mimics

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Version of record first published: 24 Sep 2006

To cite this article: Yoshiaki Kobuke & Naoto Nagata (2000): Supramolecular Porphyrin Assemblies for Photosynthetic Antenna Mimics, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 342:1, 51-56

To link to this article: http://dx.doi.org/10.1080/10587250008038243

Mol. Cryst. Liq. Cryst., 2000, Vol. 342, pp. 51-56
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Supramolecular Porphyrin Assemblies for Photosynthetic Antenna Mimics

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In order to construct artificial functional mimics of photosynthetic antenna complexes, two N-methylimidazole substituents were introduced at the facing meso positions of porphyrin and metalated by Mg^{2+} ion. In contrast to the specific dimer formation of pentacoordinating Zn atom, Mg metal center accepted the 6th ligation by imidazole and extended the slipped cofacial coordination to higher organized structures. FT Ion spray mass spectrum detected porphyrin oligomers up to a pentamer when the sample was prepared from a MeOH solution, and a heptamer from a $CHCl_3$-MeOH (1/1) solution. When imidazole instead of N-methylimidazole was employed as the porphyrin substituent, Zn^{2+}dimer, they further connected each other by hydrogen bonds to extend the supramolecular structure with a characteristic splitting and significant broadening of the Soret band.

Keywords: antenna complex; photosynthesis; imidazole; coordination; H-bonding

INTRODUCTION

Rapid advancements of supramolecular chemistry in recent years have enabled us to construct complex molecular systems from combinations of simple units if the original component parts are appropriately designed. We have been interested in constructing artificial photosynthetic systems by using intermolecular forces such as coordination or hydrogen bonds.

According to this line, we have already reported the construction of special pair type dimer formation by imidazole coordination at one of the meso positions of porphyrin to penta-coordinating Zn metal ion in another porphyrin having an imidazole substituent which in turn coordinates to the Zn center of the above porphyrin, affording a complementary coordinated dimer structure [1]. Antenna mimics have also been a fascinating target [2,3], since its structure determination [4]. Here, extension of the coordination structure by introducing hexa-coordinating Mg ion will be examined as well as supramolecular organization by use of the metal coordination and the H-bond formation.

RESULTS AND DISCUSSION

Supramolecule of Imidazolyl-substituted Mg Porphyrins

Since Mg^{2+} ion is known to accept the sixth coordination, 2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-5,15-bis(2-(1-methylimidazolyl))-porphyrin **1** was metalated by using $MgBr_2{\cdot}OEt_2$. NMR spectrum in a $CDCl_3$ solution showed actually a growth of the coordination structure by the continued network formation of complex pattern arising from the collapse of symmetric dimer structure showing the extension of the structure formation [2]. However, the mean assembly number was only 2.4, which corresponds roughly to the existence of 60 % dimer and 40 % trimer in a $CDCl_3$ solution.

Extension of the organized structure was thought to be limited by the relatively low solubility of the porphyrin aggregate. In order to obtain a proof of highly organized structure formation, the use of mass-spectrometry was attempted here. FT ion spray mass spectrum may be the best choice for detecting such structures organized by intermolecular forces. When the spectrum was obtained from MeOH solution, the trimer species was observed as the largest mass number along with monomer, dimer and dicationic trimer/2 peaks. Then the sample solution was changed to $MeOH/CHCl_3$(1/1) to favor the observation of larger aggregates. The positive ESI spectrum was illustrated in Figure 1.

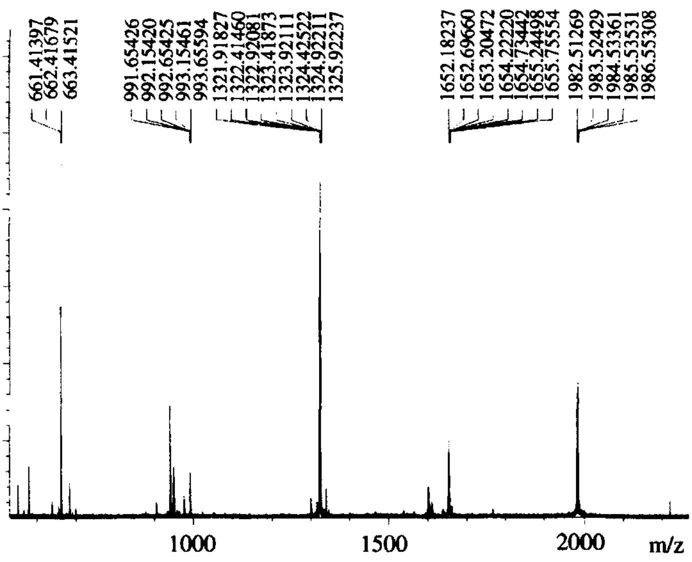

FIGURE 1 FT Ion spray mass spectrum of 5,15-bis(N-methylimidazolyl)porphyrin from a MeOH/CHCl$_3$(1/1) solution

There were observed a series of peaks up to pentamer. Tetramer and pentamer peaks were detected only at the corresponding half molecular weights with increments of 0.5 mass unit, indicating the ionization as dicationic species. The spectral areas affording trimer, tetramer and pentamer were enlarged in Figure 2. In the area of tetramer, dimer peaks with increments of one mass unit were overlapped with dicationic tetramer peaks having increments of 0.5 mass unit. Apparently, dimer peaks have larger intensities compared with tetramer dication peaks.

The spray voltage was then lowered to facilitate the observation of higher aggregates and monocationic tetramer peaks were observed at the area centered near at 2647-2648. It is notewothy to comment that dicationic heptamer peaks could be detected. Enlarged spectra of these two areas

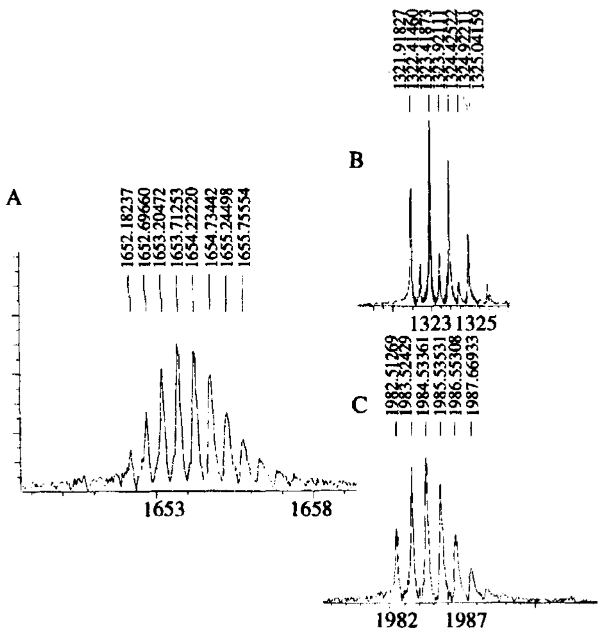

FIGURE 2 Mass spectra in the areas corresponding to A) trimer, B) tetramer with dimer and C) pentamer of 5,15-bis(N-methylimidazolyl)-porphyrin from a MeOH/$CHCl_3$ (1/1) solution.

were illustrated in Figure 3A.

These results conclude that magnesium metal center can accept the 6-th coordination from neutral imidazole ligand to be extended to really large oligomers. It may be illustrated as the extended coordination structure 2 with due consideration of dimer and oligomeric compounds as elucidated by NMR spectrum in $CDCl_3$ solutions (Figure 3B).

Organization of Bis(imidazolyl)porphyrinate Zn Complex by Coordination and Hydrogen Bond

We have also been interested in organizing porphyrin by using

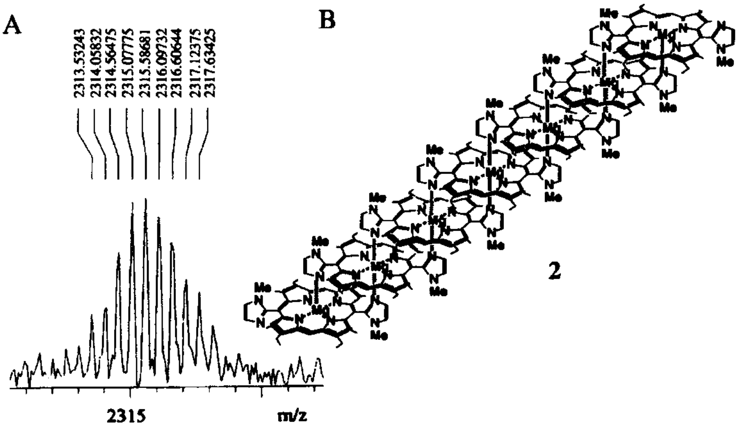

FIGURE 3. A) ESI Mass spectral corresponding to the dicationic heptamer species and B) the proposed heptameric coordination structure **2**.

hydrogen bonds as the next strong intermolecular forces giving stabilization energies of 5 kcal/mol per bond as the best Therefore, two imidazole substituents were introduced at the facing meso positions of porphyrin by the reaction of imidazol-4-caboxaldehyde and 5-(*p*-dodecanoxyphenyl)-dipyrromethane followed by oxidation to afford 5,15-bis(4-imidazolyl)-10,20-bis(*p*-dodecanoxyphenyl)-porphyrin **3**.

When bis(imidazolyl)porphyrin **3** was metalated by Zn^{2+} ion, significant broadening of the split Soret band, characteristic of the presence of two modes of exciton interactions by the complementary dimeric structure, was observed. The broadening of Soret band was more evident when UV spectra were measured in less polar solvents giving rise to the order: cyclohexane > chloroform > methanol. In Figure 4A, the spectrum obtained in cyclohexane was illustrated as an example. The complementary coordinated dimer is therefore expected to be further connected each other by hydrogen bond formation to extend the supramolecular structure as shown in **4** (Figure 4B) based on solvent dependent NMR spectral measurement (not shown).

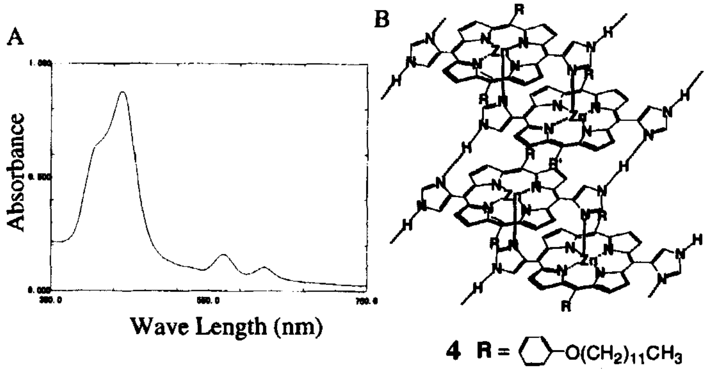

FIGURE 4 A) UV spectrum of bis(imidazolyl)-porphyrin-Zn complex in cyclohexane and B) the supramolecular structure by composite use of coordination and hydrogen bonds.

These results demonstrate that imidazole and its derivatives are excellent construction units leading to supramolecular porphyrin assemblies by using metal coordination as well as hydrogen bonding. Many structural variations are possible to develop unique structural mimics for photosynthetic reaction center and antenna functions. Acitve studies are under way.

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