

## Molecular Wire by Supramolecular Array of Hexacoordinating Imidazolyl Porphyrin Ga Complex

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Attempt to construct supramolecular wire for efficient transport of electrons/holes and excitons by the use of non-covalent linkages of porphyrins is an interesting field of chemistry. We report here preparation of a novel coordination polymer of bis(imidazol-4-yl)porphyrin gallium complex **1Ga** by use of hexacoordinating gallium (III) as the central metal ion. The lattice constant  $d = 0.57\text{--}0.6\text{ nm}$  was obtained by X-ray diffraction in the solid state. Rough estimates of the specific resistances of multilayered films were about  $1.5 \times 10^6$  and  $1.8 \times 10^5 \Omega\text{ m}$  in the dark and under continuous light irradiation, respectively, assuming that the gap distance of  $100\ \mu\text{m}$  and  $25\text{ nm}$  depth of the cell were filled with the complex. The current level, still low mainly because of the presence of molecular boundaries, was increased by 800% upon light irradiation. This large enhancement of the conductivity by light irradiation is noteworthy and accounted for by facilitated electron/hole transfer in the porphyrin array.

Key words: porphyrin, Ga complex, supramolecular, molecular wire

### 1. INTRODUCTION

Photosynthetic organisms employ light harvesting complexes to catch dilute sunlight, and to concentrate the energy to the reaction center. These light-harvesting complexes have an ordered alignment of a pigment-protein complex and transport the excitation energy efficiently to the reaction center. Such natural photochemical function has received much attention in term of the development of molecular-scale photonic devices aimed at light energy conversion. Construction of noncovalent assemblies of pigments with excellent photochemical and electrochemical properties has been one of the important subjects in supramolecular chemistry. Molecular wire may be the first target to open the world of molecular-scale electronics.<sup>1</sup> Many works on constructing supramolecular wire for efficient

transport of electron/hole and excitons have been reported by the use of non-covalent<sup>2,4</sup> linkages of porphyrins. In our previous report, we demonstrated self-organization of bis(N-methylimidazolyl)porphyrin Zn complex to a slipped cofacial dimer by coordination from the imidazolyl group to the Zn center.<sup>3a</sup> In this paper, we will introduce bis(imidazolyl)porphyrin **1** for supramolecular assembly formation through hydrogen bonds between 4(5)-imidazoles substituted at two facing *meso* positions of the porphyrin ring. Novel coordination polymers of bis(imidazol-4-yl) porphyrin metal complex by the use of pentacoordinating zinc(II) and hexacoordinating gallium (III) will be reported (Fig. 1).

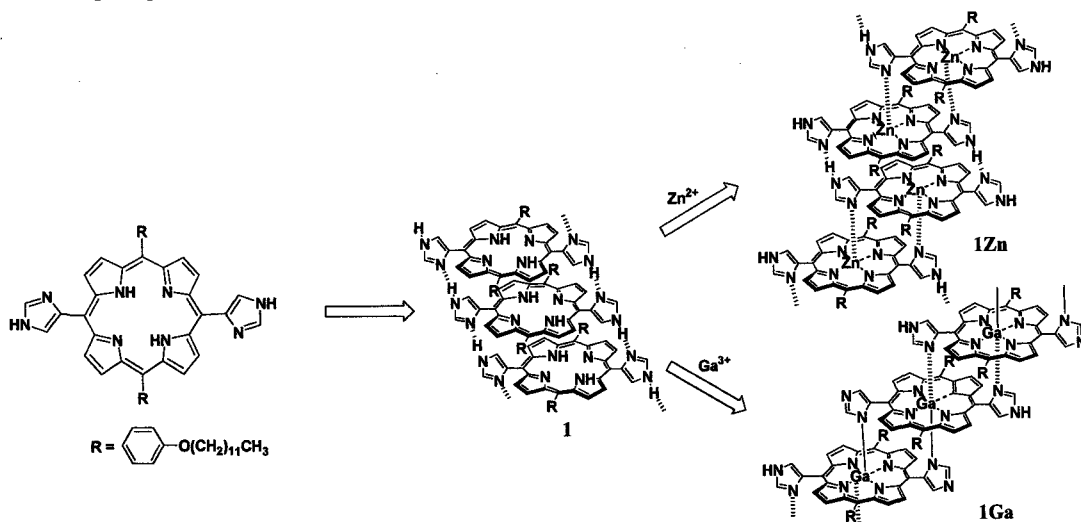


Fig. 1 Self-organization of bis(imidazolyl)porphyrin **1** and metal complexes.

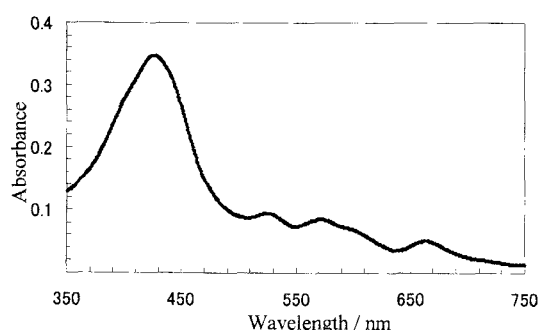


Fig. 2 UV-Vis spectrum of bis(imidazolyl)porphyrin **1** in cyclohexane.

## 2. RESULT AND DISCUSSION

### 2.1 Organization of Bis(imidazolyl)porphyrin **1** through Hydrogen Bonding.<sup>3e)</sup>

Free base porphyrin **1** was prepared by a Lindsey method. 4(5)-imidazolyl-2,2'-dipyrrylmethane was stirred with 4-dodecyloxybenzaldehyde in the presence of TFA in a  $\text{CHCl}_3$  solution to afford porphyrinogen, which was then oxidized by DDQ.  $^1\text{H-NMR}$  spectrum of **1** in  $\text{CDCl}_3$  gave broad peaks, which were sharpened gradually by the addition of  $\text{CD}_3\text{OD}$ . The characteristic up-field shift with decreasing  $\text{CD}_3\text{OD}$  concentration was observed most specifically at the 4(5)-imidazolyl proton, and less at one of the  $\beta$ -pyrrole protons. The shift behavior is accounted for by breakage of hydrogen bonds between imidazolyl substituents by the addition of  $\text{CD}_3\text{OD}$ . Selective shielding of the 4(5)-imidazolyl proton compared to the 2-imidazolyl proton in the assembly suggests that 4(5)-imidazolyl proton is brought above the porphyrin plane by hydrogen bond formation between imidazole substituents of different porphyrins. Therefore, slipped cofacial arrangement **1** is proposed as the structural unit of hydrogen bonded porphyrin rather than the head-to-tail one.

Such the porphyrin-porphyrin interaction reflected sensitively in their UV spectra. The half bandwidth of **1** was significantly broadened (84nm) in cyclohexane, as shown in Fig. 2. These behaviors are explained by exciton coupling of two porphyrin chromophores in a slipped cofacial orientation<sup>3,5</sup>, where two transition moments interact in face-to-face and parallel orientations to give rise to blue and red shifts, respectively. The peak splitting could not be observed in this case, but overall spectral maxima shifted to a longer wavelength. The very broad Soret bands of **1** in less polar solvents were compatible with the idea that they contain split absorption components.

### 2.2 Organization of Bis(imidazolyl)porphyrinatoZn Complex **1Zn** by Coordination and Hydrogen Bonding.<sup>3f)</sup>

Bis(imidazolyl)porphyrinatoZn complex, **1Zn**, was prepared from the corresponding free base porphyrin **1** and zinc acetate. The structure was confirmed by  $^1\text{H-NMR}$ , MALDI-TOF mass, and UV-Vis spectrum. The  $^1\text{H-NMR}$  spectrum of **1Zn** was broad in  $\text{CDCl}_3$  by the formation of hydrogen-bond networks. In a solution containing  $2.2 \text{ mol dm}^{-3}$   $\text{d}_4$ -methanol, peaks of  $^1\text{H-NMR}$  spectrum of **1Zn** were sharpened and identified as the zinc dimer complex by comparison of that of N-methyl-

Table. I Comparison of absorption spectral characteristics of **1Zn** in various solvent.

Compound	$\lambda_{\text{max}}$ (Half band width)/nm		
	MeOH	$\text{CHCl}_3^{\text{a}}$	Cyclohexane
<b>1Zn</b>	424(23)	430(47)	441(70)

a EtOH free,  $\text{CHCl}_3$  was used.

midazolylporphyrinatoZn complex.<sup>3a</sup> Like other imidazolylporphyrinatozinc complexes, **1Zn** has two split Soret bands at 418 and 430 nm in the UV-Vis spectrum in  $\text{CHCl}_3$ . These splittings are caused by exciton coupling of the corresponding B transitions of porphyrins in a slipped cofacial arrangement. 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 (Table. I). These results demonstrate that imidazole is excellent construction units leading to supramolecular porphyrin assemblies by combined use of metal coordination and hydrogen bonding.

### 2.3 Organization of Bis(imidazolyl)porphyrinatoGa Complex **1Ga** by Coordination.<sup>3g)</sup>

Bis(imidazol-4-yl)porphyrinatoGa complex **1Ga** was prepared by mixing the free base **1** with excess  $\text{GaCl}_3$  in  $\text{CHCl}_3$ -MeOH followed by washing the  $\text{CHCl}_3$  layer with saturated aqueous sodium bicarbonate in order to dissociate N-H proton from imidazole and to form the imidazolate anion. The insertion of Ga(III) ion was confirmed by MALDI-TOF mass, UV spectra. Significant line broadening in the  $^1\text{H NMR}$  spectrum of **1Ga** precluded unfortunately the use of NMR spectroscopy for structure determination. When the MALDI-TOF mass spectrum of bis(imidazolyl)porphyrinatoGa complex was measured by using dithranol as a matrix, peaks up to tetramer were detected.

Supramolecular array **1Ga** showed a larger splitting of Soret bands in  $\text{CHCl}_3$  (Fig. 3). The splitting energy of **1Ga** and **1Zn** are  $2550\text{cm}^{-1}$  and  $670\text{cm}^{-1}$ , respectively. Since splitting energies of Soret bands depend on the number of interacting porphyrins,<sup>6</sup> supramolecular array **1Ga** must have a larger degree of polymerization than **1Zn** complex.

The structure of supramolecular array **1Ga** was characterized by X-ray diffraction in the solid state.<sup>7</sup> X-ray diffraction data were obtained by Rigaku R-AXIS IV ( $\text{Cu } K_{\alpha}$  radiation:  $\lambda = 1.542 \text{ \AA}$ ). The distance

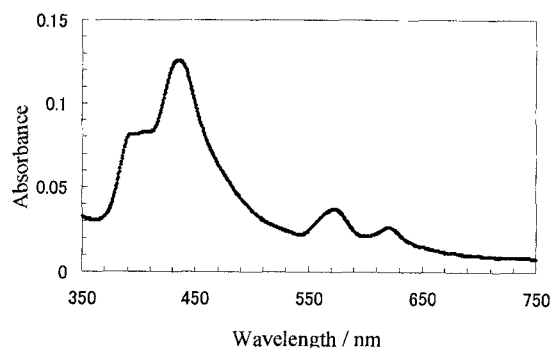


Fig. 3 UV-Vis spectrum of bis(imidazolyl)porphyrin Ga complex **1Ga** in  $\text{CHCl}_3$ .

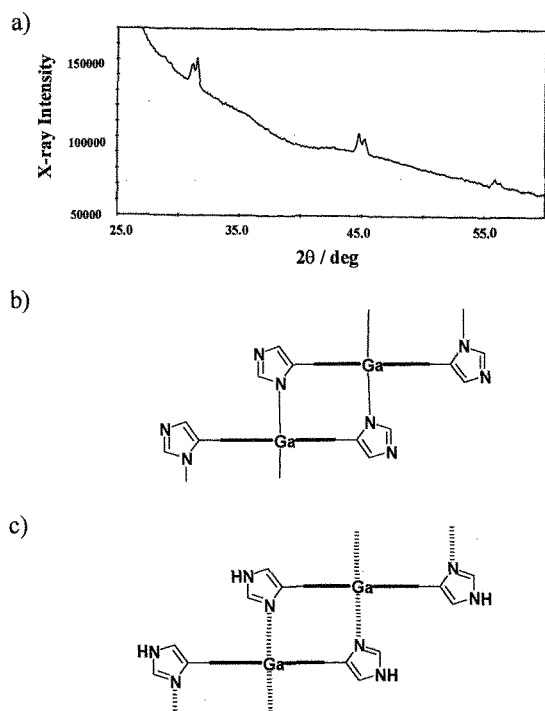


Fig. 4 a) X-ray diffraction pattern of **1Ga** self-assembly. b) Schematic drawing of **1Ga** assembly (Type A). c) Schematic drawing of **1Ga** assembly (Type B).

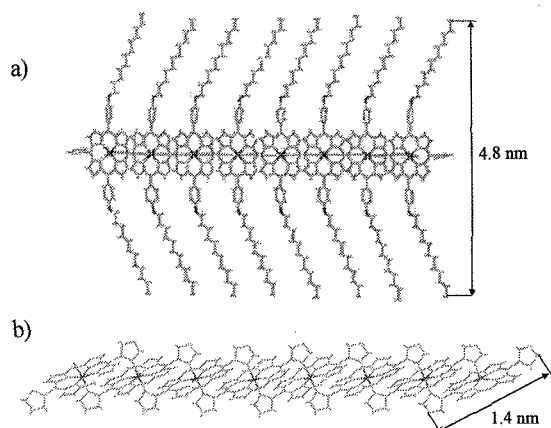


Fig. 5 Minimum energy structure of **1Ga** calculated by Cerius2 with universal force field. a) Top view and b) Side view with a stick model.

between CCD camera and the sample was 71 mm. As shown in Fig. 4, clear diffractions were observed as two peaks at around  $31.3^\circ$  and  $45.4^\circ$ . The lattice constant  $d = 0.57\text{--}0.6$  nm was obtained by using a Bragg's equation (1).<sup>7</sup>

$$n\lambda = 2d\sin\theta \quad (1)$$

The presence of two peaks indicates the presence of two different Ga-ligand coordination bonds in the structure (Type A, B, as shown in Fig. 4b), c)). Coordination of imidazolide anion to Gallium cation will be stronger than that of neutral imidazolyl nitrogen to Gallium ion. Therefore, this observation of two peaks was accounted for by the difference of the bond distance of imidazolide to Gallium (Type A) and that of the imidazole to

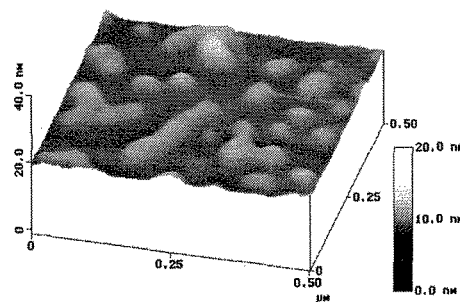


Fig. 6 AFM Image of **1Ga** deposited on HOPG with a Si cantilever, 56 mN/cm, tip curvature radius of 5-10 nm.

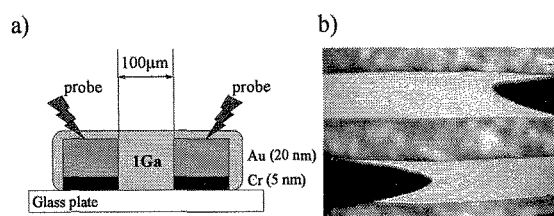


Fig. 7 a) Dimension of gold electrodes for photocurrent measurement and **1Ga** film. b) Top view of electrodes.

Gallium (Type B). In the corresponding free base **1** and Zn complex **1Zn**, such a diffraction pattern could not be observed. Coordination of Ga (III) to imidazolyl groups is assumed to be essential to form supramolecular array **1Ga**.

Supramolecular array structure **1Ga** was constructed using a molecular modeling program Cerius2 (Silicon Graphics, Inc), as shown Fig. 5. Geometry optimization was carried out by using the universal 1.02 force field. The calculated distance between porphyrin plane-plane was 0.35 nm. The distance of Ga-Ga is 0.6 nm, and the height (Im-Ga-Im) and the width ( $\omega\text{-CH}_3\text{-}\omega\text{-CH}_3$ ) of **1Ga** were 1.4, and 4.8 nm, respectively. Fig. 6 displays a tapping mode AFM image of the sample prepared from a solution of **1Ga** in  $\text{CHCl}_3$  (ca.  $5 \mu\text{mol dm}^{-3}$ ,  $1 \mu\text{L}$ ) on a fresh surface of HOPG substrate. Some long plates ( $150 \times 50$  nm) were observed on the substrate along with shorter plates ( $50 \times 60$  nm). The average height of **1Ga** in the topographic AFM image was 1.8-2.2 nm, a little higher than 1.4 nm and shorter than 4.8 nm. These results indicate that supramolecular assembly **1Ga** spreads their alkyl chains to the horizontal direction.

Current-voltage characteristics of **1Ga** supramolecular assembly was measured between the gold micro-gap electrodes with /without light irradiation. Gold electrodes were prepared by masking-lithographic technique. Glass plates were thermally deposited with chromium (50 Å) and gold (200 Å) at an evaporation rate of approximately 2-3 Å per second. The dimensions of the cell were shown in Fig. 7. The cast film of **1Ga** was obtained by casting  $\text{CHCl}_3$  (ca.  $0.1 \text{ mmol dm}^{-3}$ ,  $1 \mu\text{L}$ ) suspension on the gold electrodes. After the sample was dried under vacuum (0.1 Torr) at room temperature for 3 hrs, dark current between the electrodes was measured. The conductivity of the **1Ga** film was measured at  $25^\circ\text{C}$ . The temperature of the

sample was maintained at 25°C by Peltier effect device. Photocurrent of the **1Ga** film was measured under the irradiation with a YAG laser (532 nm, 160 mW/cm<sup>2</sup>). One scan from -20 V to 20 V took about 90 seconds. The photocurrent of **1Ga** did not change during the measurements with a continuous light irradiation for 5 min. Specific resistances of **1Ga** multilayered film in the dark and under the continuous light irradiation were about  $1.5 \times 10^6$  and  $1.8 \times 10^5$  Ωm, respectively, calculating not from the film thickness but from the cross section of electrodes (100 μm gap, 25 nm depth and 1000 μm width of the cell). The current level is still low mainly because of the presence of boundary between assemblies. Even so, the conductivity between the gap electrodes was increased by 800% on light irradiation. The light irradiation may have facilitated electron/hole transfers in **1Ga** array and the large enhancement of the conductivity is particularly noteworthy.

### 3. SUMMARY

In this paper, we have examined formation of porphyrin supramolecules by using ligand to central metal coordination and hydrogen bonding. Imidazolyl porphyrin **1** was found to be a useful component to obtain porphyrin supramolecules by combination of these intermolecular forces.

5,15-bis(imidazol-4-yl)porphyrinatogallium **1Ga** formed rigid supramolecular assemblies by axial coordination of two imidazolyl groups to Ga(III) in a staircase arrangement. When gap electrode was filled with **1Ga** supramolecules, electric currents were observed and enhanced dramatically by light irradiation. We believe that the imidazolylporphyrin arrays are one of the suitable candidates for constructing supramolecular electric wire with a photoswitch.

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(Received October 10, 2003; Accepted January 31, 2004)