

## Self-Assembled and Alternative Porphyrin-Phthalocyanine Array

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An alternative molecular porphyrin-phthalocyanine aggregate was prepared and characterized with UV-visible and X-ray absorption spectroscopies. UV-visible experiments evidence 1-dimensional porphyrin-phthalocyanine array formed by mixing SnTPPCL<sub>2</sub> ( $\lambda_{\max} = 429$ ,  $\epsilon = 2.4 \times 10^5/\text{M}\cdot\text{cm}$ ) and NiPc(OBu)<sub>8</sub> ( $\lambda_{\max} = 744$  nm,  $\epsilon = 2.0 \times 10^5/\text{M}\cdot\text{cm}$ ) in solution. In the UV-visible spectrum of the porphyrin-phthalocyanine array, (SnPNiPc)<sub>n</sub>, a new Q-band appeared at 844 nm with decrease of the Q-band peak of NiPc(OBu)<sub>8</sub> at 744 nm. The red-shift of Q-band evidences an alternative porphyrin-phthalocyanine array formed in solution through metal-halide interaction rather than  $\pi$ - $\pi$  facial interaction, in which nickel of NiPc(OBu)<sub>8</sub> coordinates with chloride of SnTPPCL<sub>2</sub> through self assembly. Ni K-edge XANES (X-ray absorption near edge structure) spectra also support the axial ligation of nickel to chloride. The square planar structure of NiPc(OBu)<sub>8</sub> turns to an octahedral structure in (SnPNiPcSnP) by axial ligation. A higher energy-shift (0.2 eV) of the preedge peak of (SnPNiPcSnP) indicates partial oxidation of nickel by charge transfer from NiPc(OBu)<sub>8</sub> to SnTPPCL<sub>2</sub>.

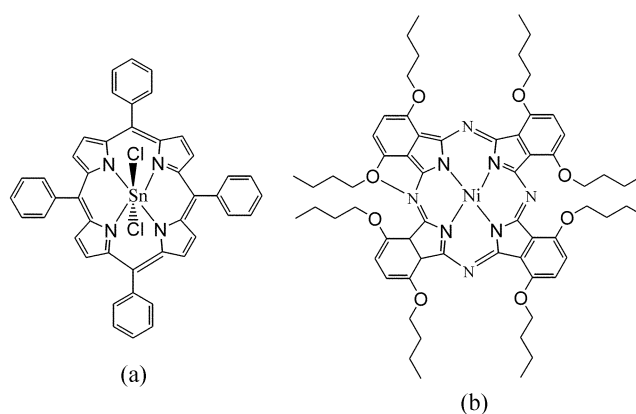
**Key Words :** 1-Dimensional porphyrin-phthalocyanine array, XANES

### Introduction

Molecular engineering of porphyrin (P) and phthalocyanine (tetraazaporphyrin, Pc) has become of great interest for use in molecular electronics, nonlinear optics, optical data storage, sensors, electrochromic devices, electrocatalytic systems and photodynamic therapy.<sup>1</sup> Intermolecular interactions as arrayed configuration are important biochemical processes in nature like light harvesting antenna or photosynthesis.<sup>2</sup> Such arrayed configurations have been modeled to develop artificial systems of molecular aggregates for device applications of optical, memory devices and gas sensors.<sup>1,3</sup> 1-Dimensional (1-D) and highly conductive nanowires have also been prepared by Kenney, Marks and Hannack groups such as [SiPcO]<sub>n</sub>, [GePcO]<sub>n</sub>, [SnPcO]<sub>n</sub>, [PcFe(py<sub>2</sub>)<sub>2</sub>]<sub>n</sub> (py<sub>2</sub> = pyrazine), [PcFe(CN-R-NC)]<sub>n</sub>, [PcRuL]<sub>n</sub> (L = *p*-phenylenediamine), and [FePcCN]<sub>n</sub> using metalloporphyrin derivatives.<sup>4</sup> However, the synthesis of alternative porphyrin-phthalocyanine arrays is a task of difficulty.<sup>5</sup> We have prepared an alternative porphyrin-phthalocyanine array in solution, and monitored 1-D array formed by self-assembly in solution with UV-visible and X-ray absorption spectroscopies.

### Results and Discussion

Among porphyrins and phthalocyanines used to make an 1-D array were tin tetraphenylporphyrin chloride (SnTPPCL<sub>2</sub> or SnP) and nickel octabutoxy phthalocyanine (NiPc(OBu)<sub>8</sub> or NiPc). Structures of SnTPPCL<sub>2</sub> and NiPc(OBu)<sub>8</sub> are shown in Figure 1, where SnP has an octahedral structure



**Figure 1.** Structures of SnTPPCL<sub>2</sub> and NiPc(OBu)<sub>8</sub>.

and NiPc has a square-planer structure. Electronic transition nature of porphyrin derivatives can be obtained in UV-visible spectroscopic experiments. The 1-D porphyrin-phthalocyanine array in solution was prepared by simply mixing of SnTPPCL<sub>2</sub> (14.0 mM) and NiPc(OBu)<sub>8</sub> (14.0 mM) solutions in CH<sub>2</sub>Cl<sub>2</sub>. In the absorption spectrum of SnTPPCL<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub>, an intense near-UV Soret band ( $\epsilon = 2.4 \times 10^5/\text{M}\cdot\text{cm}$ ) at 430 nm and a slight shoulder at higher energy at 409 nm are observed due to B(0,0) and B(0,1) electronic transitions. Four weak Q-bands in the visible spectral region are located at 525, 565, 605 and 629 nm, respectively. In the absorption spectrum of NiPc(OBu)<sub>8</sub> in CH<sub>2</sub>Cl<sub>2</sub>, the intense Q band ( $\epsilon = 2.0 \times 10^5/\text{M}\cdot\text{cm}$ ) at 744 nm and the slight shoulder at higher energy at 668 nm are observed. In the electronic spectrum of the porphyrin-phthalocyanine array (NiPcSnP)<sub>n</sub> formed by mixing of NiPc(OBu)<sub>8</sub> and SnTPPCL<sub>2</sub>, the most significant changes are (i) the loss in intensity of the Q-band at 744 nm, and (ii) the concurrent growth in intensity of

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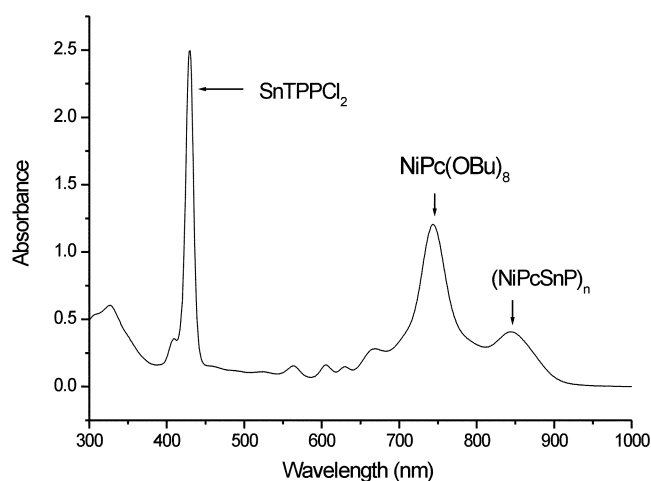


Figure 2. UV-visible spectrum of  $(\text{NiPcSnP})_n$ .

bands near 844 nm ( $\epsilon = 1.6 \times 10^5/\text{M}\cdot\text{cm}$ ), Figure 2. Generally in the oligomerization of phthalocyanine, Q-band shifts to blue due to exciton coupling depending on the distance between the macrocycles of a phthalocyanine oligomer.<sup>6</sup> The red shift of Q-band of the porphyrin-phthalocyanine array  $(\text{NiPcSnP})_n$  would be associated with charge-transfer interaction through metal-halide (Ni-Cl) bonding rather than with  $\pi$ - $\pi$  interaction by a face-to-face structure.<sup>7</sup> Orbital overlap of  $\pi$ -orbitals between the macrocycles is expected to be weak. Instead, a charge-transfer complex from  $\text{NiPc}(\text{OBu})_8$  to  $\text{SnTPPCL}_2$  through Ni-Cl bonding is proposed for a main interaction to make an alternative 1-D porphyrin-phthalocyanine array in solution by self-assembly. Steric bulkness and different electronic configuration would result in a weak facial interaction between the porphyrin and the phthalocyanine. No red shift or decrease of intensity of Q-band was observed at a low concentration, 0.0023 mM.

Ni K-edge XANES (X-ray absorption near edge structure) supports structural information of the porphyrin-phthalocyanine array in solution. In order to clarify the metal-halide interaction, a complex of  $(\text{SnPNiPcSnP})$  was prepared by mixing  $\text{NiPc}(\text{OBu})_8$  (0.02 mmol) and  $\text{SnTPPCL}_2$  (0.04 mmol) in  $\text{CH}_2\text{Cl}_2$ . The XANES spectrum of  $\text{NiPc}(\text{OBu})_8$  with an edge-absorption (at 8338.9 eV, 1s to 4p transition) and a shoulder peaks (at 8332.3 eV, 1s to 4p<sub>z</sub> transition) shows a typical square planar structure, in which the nickel coordinates with four nitrogens of planar phthalocyanine, Figure 3.<sup>8</sup> At the same positions of an edge-absorption (at 8338.8 eV, 1s to 4p transition) and a shoulder peaks (at 8332.4 eV, 1s to 4p<sub>z</sub> transition) of  $(\text{SnPNiPcSnP})$  are observed. A little difference in preedge positions of  $\text{NiPc}$  and  $(\text{SnPNiPcSnP})$ , due to dipole-forbidden but quadruple-allowed transition of 1s $\rightarrow$ 3d, are found at 8325.8 and 8326.0 eV, respectively, all indicating the +2 oxidation state of nickel. The little higher energy of  $(\text{SnPNiPcSnP})$  would evidence the nickel is partially oxidized by charge-transfer. The square planar structure turns to an octahedral structure in the mixture of  $\text{NiPc}(\text{OBu})_8$  and  $\text{SnTPPCL}_2$  solution. The XANES spectrum of  $(\text{SnPNiPcSnP})$  also showing an enhancement of the

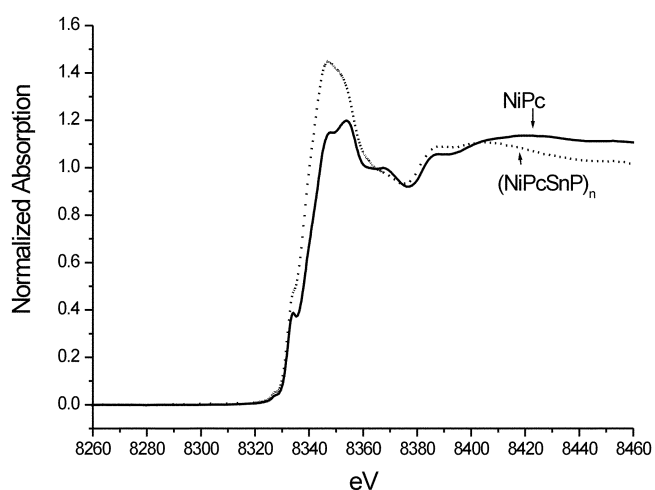


Figure 3. XANES spectra of  $\text{NiPc}(\text{OBu})_8$  and  $(\text{SnPNiPcSnP})$ .

edge-absorption peak evidences the axial ligation of the nickel to the chloride. The higher intensity of the edge absorption implies that nickel becomes surrounded by an octahedron environment, which would be four equatorial nitrogens and two halogen atoms, resulting in minimal orbital hybridization between nickel and ligand orbitals.<sup>9</sup> This result supports that halides of  $\text{SnTPPCL}_2$  coordinate to nickel of  $\text{NiPc}(\text{OBu})_8$  through metal-halide interaction.

In summary, we report the bond nature of a porphyrin-phthalocyanine array formed in solution, which mainly consists of metal-halide interaction rather than of facial  $\pi$ - $\pi$  interaction. This is an example of preparation of an alternative porphyrin-phthalocyanine. Future studies will focus on obtaining a 1-D alternative porphyrin-phthalocyanine array in solid state, and on the bond nature of metal-halide and electronic structure of an alternative porphyrin-phthalocyanine array using density functional calculations. Other metal-halide interaction in porphyrin-phthalocyanine array will be also studied.

## Experimental Section

**Materials.** Nickel(II) 1,4,8,11,15,18,22,25-octabutoxy-29*H*,31*H*-phthalocyanine ( $\text{NiPc}(\text{OBu})_8$ ) and 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine (TPP) were purchased from Aldrich.  $\text{SnTPPCL}_2$  was prepared according to the literature.<sup>10</sup>

**Spectroscopy.** JASCO V-570 and Varian Unit Inova 200 (200 MHz) were used to measure UV-visible and <sup>1</sup>H-NMR spectra, respectively.

**XAS measurement and Data Analysis.** Nickel K-edge XAS measurements were carried out using Beam Lines 3C1 at Pohang Light Source and 7C at Photon Factory, operating at 2.5 GeV with 100-140 mA and 200-400 mA beam current, respectively. A Si(111) double crystal was used as a monochromator. Under N<sub>2</sub> atmosphere, the 1-D porphyrin-phthalocyanine array sample in solution was prepared and placed in an air-tight XAS cell made of Teflon with two Mylar windows (1/2000 inch; window size, 20 mm  $\times$  8 mm; optical path length, 2 mm). The monochromator was

detuned by 20-30% in incident X-ray beam. All of data for nickel were internally calibrated using Ni foil (8333.0 eV), respectively. The near-edge region was scanned at equal energy step of 0.2 eV/point to resolve fine structures.

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