A New Self-Assembled Porphyrin-Silver(I) Network

Mitsuru Kondo, Yu Kimura, Kenji Wada, Tadashi Mizutani, Yoshikatsu Ito, and Susumu Kitagawa*
Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University,
Yoshida, Sakyo-ku, Kyoto 606-8501

(Received April 13, 2000; CL-000346)

A new self-assembled porphyrin compound, [Ag(H_2TPyP)]·PF_6 (H_2TPyP = 5,10,15,20-tetrakis(4-pyridyl)porphyrin) (**1**), was synthesized and structurally characterized. Among four pyridyl groups of the H_2TPyP molecule, the two groups in the *trans* positions are coordinated to the silver atom, resulting in the formation of a linear one-dimensional network, in which the other two pyridyl moieties remain metal-free. Each of the chain is associated by a weak π–π interaction to afford a slipped-stack structure.

The synthesis and structural characterization of a coordination polymer with a porphyrin-ligand have attracted intense attention because such network compound could demonstrate the unique functions based on the porphyrin chromophore.[1] 5,10,15,20-Tetrakis(4-pyridyl)porphyrin (H_2TPyP) or the metal complexes, MTPyP (M = Cu, Zn, Pd), have recently been exploited for the syntheses of this type of network.[1] Nevertheless, the self-assembled chemistry is still in its infancy because of the limited examples of the well-characterized porphyrin–metal networks. We have succeeded in the synthesis and characterization of a new coordination polymer, [Ag(H_2TPyP)]·PF_6 (**1**), by the self-assembled reaction of H_2TPyP with $AgPF_6$. To the best of our knowledge, this is the first Ag(I) coordination network with a porphyrin moiety.

Compound **1** was synthesized by careful diffusion of a methanol solution (50 mL) of $AgPF_6$ (0.27 g, 1.1 mmol) into a 1,1,2,2-tetrachloroethane (TCE)/methanol (3:1) mixed solution (50 mL) of H_2TPyP (0.65 g, 1.1 mmol). The solution was allowed to stand at −10 °C for two weeks to yield deep purple columnar crystals. One of them was used for the single-crystal X-ray analysis. The residual crystals were collected by manual, washed with ethanol, and dried in vacuo (24% yield). Anal Calcd for $C_{40}H_{26}AgF_6N_8P$: C, 55.13; H, 3.01; N, 12.86%. Found: C, 55.83; H, 3.28; N, 12.82%.

This network material crystallizes as **1**·1.5TCE·MeOH·H_2O, and the crystal structure is shown in Figures 1 and 2.[2] Silver atom has a linear coordination circumstance with the two pyridine rings of the different H_2TPyP ligands; the Ag–N bond distances are about 2.13 Å, and the N–Ag–N bond angle is 178.4(2)°. The unique self-assembled process leads to the chain network by the connection between the two pyridine rings in the *trans* position via a silver(I) ion, with the remaining metal-free pyridine rings, providing a *fish-bone* type one-dimensional network along the (*a* - *c*) vector (Figure 2a).[3] The *fish-bone* structure of this compound is the first example in the series of the porphyrin–metal networks. This network has about 20 Å repetition, resulting from the large size of the porphyrin moiety. In the one-dimensional chain, each porphyrin plane arranges in the same plane without a rotation along the chain axis.

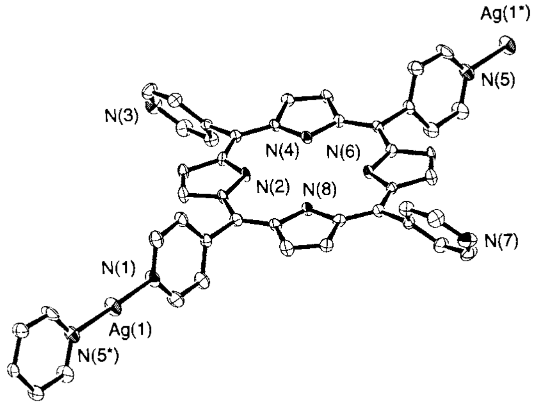


Figure 1. ORTEP drawing of the cationic part of the **1**·1.5TCE·MeOH·H_2O. (ellipsoids at 30% probability): Symmetry codes, *; -x, -y, -z. Selected bond distances [Å] and angles [°]: Ag(1)-N(1) 2.137(4), Ag(1)-N(5) 2.131(5). N(1)-Ag(1)-N(5) 178.4(2).

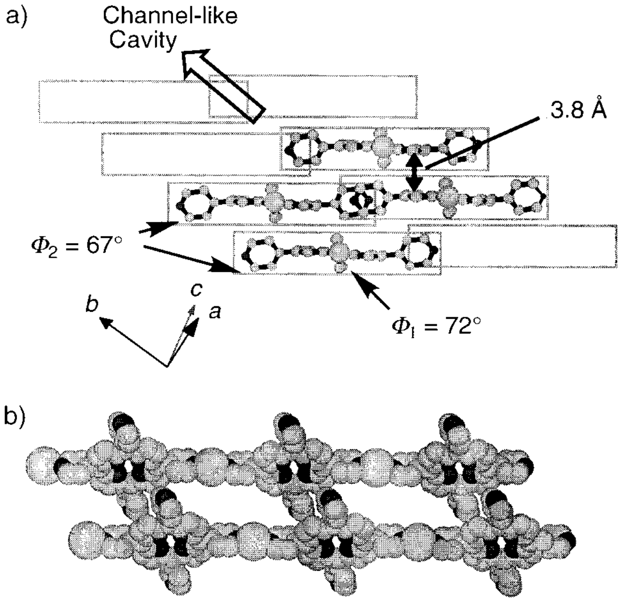
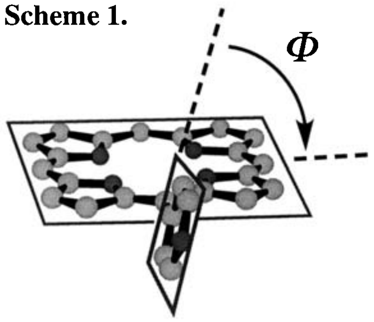


Figure 2. a) Stacking aspect of the one-dimensional chains of **1**·1.5TCE·MeOH·H_2O along the (*a*-*c*) vector. b) The channel-like cavities along the *b* axis, in which the counter anions and included guest molecules are omitted for clarity.

These one-dimensional chains assemble with the slipped-stack fashion as shown in Figure 2a. There is a weak π–π interaction (about 3.8 Å) between the porphyrin moieties in the adjacent chains. When the dihedral angle "Φ" between the pyridine ring and porphyrin plane is defined as Scheme 1, the Φ_2 value of the metal-free pyridine ring (about 67°) is smaller than that of the pyridine rings (about 72°) that bind to silver(I) atom

Scheme 1.



(Figure 2a). The larger deviation of Φ_2 from the 90° is a result of the steric repulsion between the metal-free pyridine rings and the porphyrin plane above or below the pyridine rings. This assembled structure forms the large channel-like cavities along the *b* axis. The dimension is about 13 × 5 Å, and is filled with counter anions and included TCE, methanol, and water molecules. The PF_6^- anion and water molecules are weakly associated with the silver(I) ion (Ag(1)–F(1) = 2.922(8) Å, Ag(1)–O(3) = 2.76(3) Å).

In order to characterize this one-dimensional coordination network, the absorption and fluorescence spectra and cyclic voltammogram (CV) (Figure 3) were measured in the solid state. **1** shows the intense absorption and fluorescence spectra, which are ascribed to the porphyrin chromophore.[4] Although some slight shifts are observed, the spectroscopic behavior of **1** is similar to that of H_2TPyP.

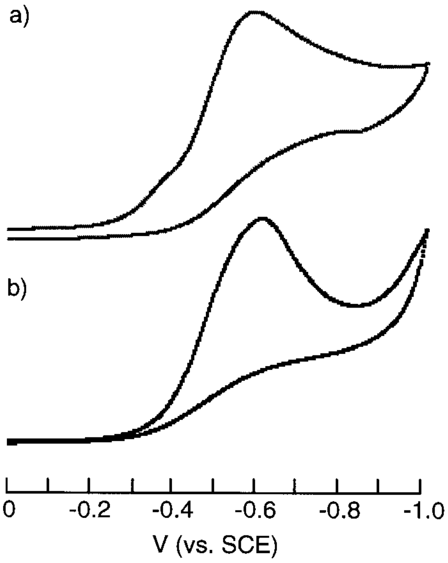


Figure 3. Cyclic voltammogram of H_2TPyP (a) and **1** (b) in the solid state.

CV of **1** was measured in the range from 1.2 V to –1.0 V (vs SCE) by using a carbon-paste electrode in aqueous media. A porphyrin moiety is known as a redox active macro-molecule, which is oxidized or reduced by a one-electron redox process.[5] **1** shows the irreversible reduction wave at about –0.6 V. Although this wave is sharper than that of the metal-free H_2TPyP, their reduction potentials are similar to each other, indicating that this network has a redox active property based on the porphyrin moiety. The oxidized wave was not observed in this measurement range that is limited to the narrow window in the aqueous media. This redox active property is contrast to that of the iron(II)-4,4'-azopyridine network of $[Fe(azpy)_2(NCS)_2]$ (azpy = 4,4'-azopyridine), which shows no redox activity ascribed to the azpy ligand.[6]

In summary, we demonstrate the new self-assembled coordination network, $[Ag(H_2TPyP)]\cdot PF_6$, which has unique spectral and redox properties. This study points out the utility of the porphyrin moiety for the synthesis of a new functional network compounds.

This work was supported by the Foundation of Advanced Technology Institute and a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan.

References and Notes

1 a) B. F. Abrahams, B. F. Hoskins, and R. Robson, *J. Am. Chem. Soc.*, **113**, 3606 (1991). b) B. F. Abrahams, B. F. Hoskins, D. M. Michail, and R. Robson, *Nature*, **369**, 727 (1994). c) C. V. K. Sharma, G. A. Broker, J. G. Huddleston, J. W. Baldwin, R. M. Metzger, and R. Rogers, *J. Am. Chem. Soc.*, **121**, 1137 (1999). d) D. Hagrman, P. J. Hagrman, and J. Zubieta, *Angew. Chem., Int. Ed. Engl.*, **38**, 3165 (1999). e) L. Pan, B. C. Noll, and X. Wang, *Chem. Commun.*, **1999**, 157.

2 General crystallographic information for $\mathbf{1}\cdot 1.5TCE\cdot MeOH\cdot H_2O$: Intensity data were collected on the Rigaku Mercury CCD system using graphite monochromated Mo Kα radiation (λ = 0.71069 Å). M = 1172.36 ($C_{44}H_{34}AgCl_6F_6N_8O_2P$), triclinic, space group $P\bar{1}$ (no. 2), a = 10.486(2), b = 13,399(4), c = 17.170(7) Å, α = 84.08(1), β = 87.18(1), γ = 76.320(5)°, V = 2330(1) Å^3, Z = 2, D_{calcd} = 1.670 g/cm^3, μ = 8.82 cm^{-1}, T = 213 K, 16124 reflections measured, 9498 independent (R_{int} = 0.023), 6176 [$I > 3.0\sigma(I)$] included in the refinement, anisotropic refinement for non-hydrogen atoms by full-matrix least-squares with a program package teXsan (MSC), R = 0.076, R_w = 0.097, GOF = 2.65 for 619 parameters.

3 Although we also attempted the synthesis of a network material formulated as $[Ag_2(H_2TPyP)]^{2+}$ by the reaction of H_2TPyP with two-equimolar $AgPF_6$, **1** was isolated as an only crystalline product from the reaction system.

4 Absortpion spectrum data [λ_{max}/nm] with KBr disk, **1** (H_2TPyP): 427 (431), 523 (522), 555 (555), 594 (594), 648 (648). Fluorescence spectrum data [λ_{max}/nm] with excitation at 420 nm, **1** (H_2TPyP): 580 (578), 657 (653), 716 (713), 753 (755).

5 "Porphyrins and Metalloporphyrins" ed. by K. M. Smith, Elsevier Scientific, Amsterdam (1995), Chap. 14.

6 S. Noro, M. Kondo, T. Ishii, S. Kitagawa, and H. Matsuzaka, *J. Chem. Soc., Dalton Trans.*, **1999**, 1569.