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Novel Synthetic Method for Metalloporphyrins with Inorganic Metal Salts in High-temperature Water

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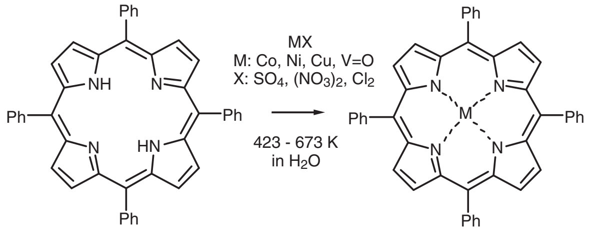
Cobalt, nickel, copper, and oxidovanadium(2+) could be incorporated into nonpolar tetraphenyl porphyrin by using feed materials as metal sulfate, nitrate, and chloride salts and reaction in high-temperature water (423 to 673 K). Yields of metalloporphyrins increased to 94% at 673 K, which indicates that the dissolution of porphyrin and reaction of the metal salts are enhanced in high-temperature water.

Porphyrins have received attention as advanced materials because they show strong absorption bands in the UV–visible region and work as a redox center. The incorporation of metal into the porphyrin structure changes their physical properties because the metal species affects structure and absorption band.[1] Nowadays, porphyrins are applied to solar batteries, catalysts, and drugs for photodynamic therapies. In particular, benzoporphyrins are used as an organic semiconductor for one of the key components in organic electroluminescence displays and organic transistors.[2]

There are several methods for incorporating metals into porphyrin structures. Organic acids or bases can be used as solvents. Rothemund et al.[3] reported that metalloporphyrin can be synthesized by using metal acetates in acetic acid under reflux or metal salts in hot pyridine. In these methods, the acid solvent shifts the reaction equilibrium to the reactant side, since the high proton concentration suppresses the exchange of hydrogens at the porphyrin center. On the contrary, basic solvents sometimes react with the metal ions. Further, the expensive metal organics are undesirable reagents. At present, the synthesis of metalloporphyrin in polar organic solvents such as dimethylformamide, dimethyl sulfoxide, tetrahydrofuran, or methanol has been addressed.[4–6] In particular, aprotic organic solvent is better. Both porphyrin and metal salts such as halides, hydroxides, and carbonates easily dissolve in polar organic solvents, and the solutions containing metal and porphyrin can be treated under reflux to give stoichiometric yield of metalloporphyrins.[4] However, aprotic organic solvents are difficult to remove, because they have high solubility for both the porphyrin and metal salt and high boiling points make the separation of the solvent a major problem. Microwave heating of metal organics in organic solvents enables the incorporation of group 10 metals into the porphyrin structure although the formation of byproducts occurs.[7]

On the other hand, water has been mostly overlooked probably due to solubility and reactivity. The exchange of metal for water-soluble porphyrin such as tetrakis(*N*-methyltetrapyridyl)porphyrin proceeds in water,[8] although most of porphyrins are insoluble in water. Synthesis of metalloporphyrin using water has the potential to become a green method for metal incorporation in organometallic chemistry.



Scheme 1. Incorporation of metals into TPP.

High-temperature water around 473–673 K is a low-density liquid or in the supercritical state, a high-density gas. The dielectric constant of high-temperature water at 573 K is around 20 compared with ambient water at 80, which makes high-temperature water have characteristics of a polar organic solvent.[9] High-temperature water dissolves organic compounds as well as metals salts. Further, the properties of high-temperature water can be manipulated with temperature so that the separation of organic products from water can be easily done by cooling to ambient conditions. In this study, we examined selective incorporation of metal into tetraphenylporphyrin using inorganic metal salts in high-temperature water as shown in Scheme 1. We also evaluated the effect of metals, counter ion, and temperature on incorporation kinetics.

Reactions were conducted with 6-cm^3 stainless 316 tube bomb reactors. 5,10,15,20-Tetraphenyl-21*H*,23*H*-porphyrin (TPP: Wako Pure Chemical Ltd.) was used as a porphyrin and had a purity of 96% by our analysis. An amount of 0.020 g of TPP, 0.032 g of sodium carbonate, and 3.0 g of metal salt aqueous solution were loaded into the reactors. The purity of reagents containing metal are described in Supporting Information.[16] Sodium carbonate was an additive used for the prevention of corrosion inside the reactor.[10] The air in the reactors was purged with argon gas and the reactor was sealed. The molar amounts of TPP and sodium carbonate were 3.3×10^{-5} and 3.0×10^{-4} mol, respectively. The concentration of aqueous cobalt, nickel, and copper solution was 0.10 mol L^{-1} corresponding to 3.0×10^{-4} mol of metal, which corresponded to 9.1 of the molar ratio of metal to TPP. The concentration of oxidovanadium(2+) was about 1.65×10^{-4} mol and the molar ratio of vanadium to TPP was 5.0.

After loading the reactor, it was submerged into a sand bath that was controlled at the reaction temperature. The heat-up time was about 4 min. After a reaction time of 60 min, the reactors were taken out of the sand bath and quenched in a water bath.

Table 1. Effect of metal on the incorporation of metals in TPP[a]

Metal	Counter ion	Yield/%		
		Metal–TPP	TPP	Others
Co	Sulfate	69.3	28.4	2.3
Ni	Sulfate	45.2	54.8	0
VO	Sulfate	45.1	49.8	5.1
Cu	Sulfate	83.3	12.5	4.2
Cu	Nitrate	18.9	41.7	39.4
Cu	Chloride	74.8	16.4	8.8

[a] 623 K; 60 min; $CoSO_4\cdot 7H_2O$, $NiSO_4\cdot 6H_2O$, $CuSO_4\cdot 5H_2O$, $CuNO_3\cdot 3H_2O$, and $CuCl_2\cdot 2H_2O$: 3.0×10^{-4} mol; $VOSO_4$: 1.65×10^{-4} mol; TPP: 3.3×10^{-5} mol; Na_2CO_3: 3.0×10^{-4} mol.

The inside of the reactor was rinsed with chloroform several times to recover sample. From the recovered sample, product and reactant were separated by column chromatography. A silica gel column was used, and the developing solvent was a mixture of chloroform and *n*-hexane in a weight ratio of about 1:1. The weight of product and reactant was weighed after the evaporation of the solvent. Qualitative analyses were conducted by UV–vis spectroscopy (V-560, JASCO Corporation) by comparing peaks to literature values[4,11] and by MALDI-TOF-MS (autoflex II, Bruker Daltonics Inc.) for checking the molecular weight. The product yield was on 96% purity of TPP loaded basis, defined as (mol of Metal–TPP or TPP)/(mol of TPP loaded) × 100.

We conducted the phase observation experiments on the dissolution of TPP to water by using a view cell (11.5 cm^3) for high pressure and high temperature conditions (Taiatsu Techno, Tokyo). The details of cell are explained in Supporting Information.[16] In this study, 5.0 g of water and 0.033 g of TPP were introduced into the view cell, which corresponded to almost the same ratio of TPP to water in the reaction experiments described above.

Table 1 shows the effect of metal and counter ion on the incorporation of metals in TPP. The incorporation of oxidovanadium(2+), cobalt, nickel, and copper to TPP structure proceeded in high-temperature water. We evaluated *Others* by using the sum of the yield of TPP and Metal–TPP and subtracting from 100%. For Co, Ni, VO, and Cu sulfate, the yield of *Others* was below 5.1%, and the reaction proceeded selectively regardless of the metals. The yield of Metal–TPP was in the order of Cu > Co > VO, and Ni. The yield of VO–TPP was lower than those of other metals because the initial amount of vanadium was about half that of the other metals. For copper sulfate, nitrate, and chloride, the yields of Cu–TPP obtained from copper sulfate and chloride were higher than that from copper nitrate. The higher yield of *Others* for copper nitrate indicates significant formation of by-products. It is reported that the copper ion incorporates to TPP structure in dimethyl sulfoxide through a rapid preequilibrium state, that is, Cu^{2+}–H_2TPP, and then the incorporation of metal to TPP structure occurs.[5] The reactivity was probably related to the stability of metalloporphyrins and intermediates, so that the form of metal ion may be important in reaction mechanism. The solubilities of metal salts to water in ambient conditions for $CoSO_4\cdot 7H_2O$, $NiSO_4\cdot 6H_2O$, $CuSO_4\cdot 5H_2O$, $Cu(NO_3)_2\cdot 3H_2O$, and $CuCl_2\cdot 2H_2O$ were 65, 150, 32, 138, and 73 g/100 mL aq, respectively.[12] The order in the yield of Metal–TPP does not follow this trend. In high-temperature water, the dissolution of species containing metal in water can be considered as not only as a cation but also as a salt itself, metal oxides, and metal hydroxide.[13] The dissolution form of metals in high-temperature water would probably depend on the metal species and counter ion, which probably affects the incorporation kinetics to change yield of Metal–TPP.

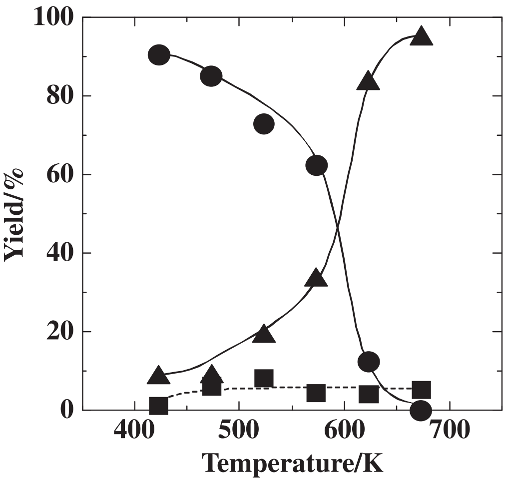


Figure 1. Yield of (●) TPP, (▲) Cu–TPP, and (■) others against reaction temperature for 60 min with copper(II) sulfate pentahydrate.

Figure 1 shows the effect of temperature on the incorporation of copper in TPP. The yield of Cu–TPP increased with temperature and significantly rose around 600 K while the yield of TPP decreased. The formation of Cu–TPP was enhanced at high temperature, and the maximum yield was 94.7% at 673 K. The yield of *Others* was always as low as 8%, which means that TPP structure was relatively stable in high-temperature water regardless of the temperature.

Figure 2 shows the observation of dissolution of TPP in water for the TPP–water system. At 323 K, TPP is seen as a solid phase above water. TPP was insoluble in water. The pressure in the cell was slightly different from the calculated values from saturated pressure and pressure in supercritical state of pure water but within 1.4 MPa.[14] At 573 and 648 K, there were two phases in the reactor, one liquid phase and one gas phase. The densities of the liquid phase and the gas phase were estimated at 573 and 623 K to be (0.71 and 0.05 $g\,cm^{-3}$) and (0.57 and 0.11 $g\,cm^{-3}$), respectively.[13] At 573 K, the color of liquid phase was dark while the color of gas phase was transparent, which means that TPP dissolved mainly in the liquid phase. At 623 K, the color of the gas phase became purple but the color in liquid phase was still dark. The dissolution of TPP into the gas phase was enhanced by increasing the density of the gas phase. At 648 K, the entire inside of cell became dark. Most TPP probably dissolved into the supercritical water phase. These observations clearly show that the dissolution of TPP into water occurred in the high-temperature region. The dissolution of both metals and TPP in water probably enhanced the reaction. The solubility of metal oxide such as CuO in water has a retrograde region in

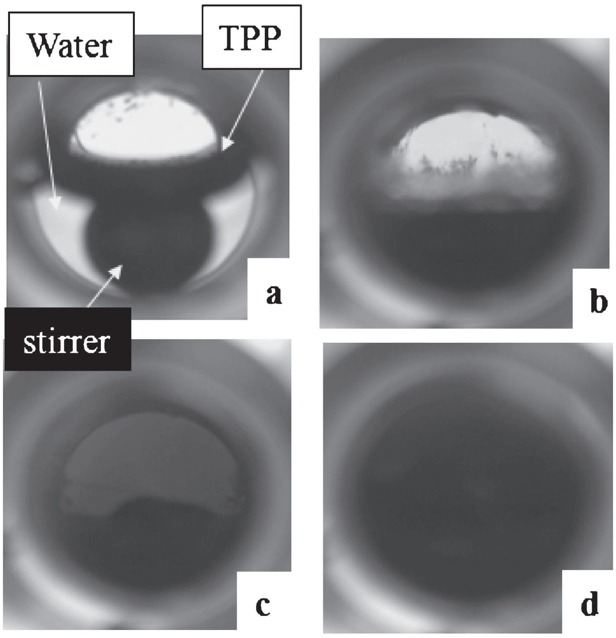


Figure 2. The observation of dissolution of TPP in water for water–TPP system (a: 323 K, 0.1 MPa; b: 573 K, 7.8 MPa; c: 623 K, 16.0 MPa; d: 648 K, 21.3 MPa).

which solubility increases with increasing temperature and then sharply decreases around the critical temperature of water.[15] The decrease in solubility of metals and metal oxides should inhibit metal incorporation by suppressing the formation of Cu^{2+}–H_2TPP from Cu^{2+} and TPP.[5] In the high-temperature region, the dissolution of TPP to water was enhanced, and the incorporation rate was accelerated. The Metal–TPP yields in the high-temperature region clearly show that the dissolution of TPP in water is an important factor for the reaction.

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