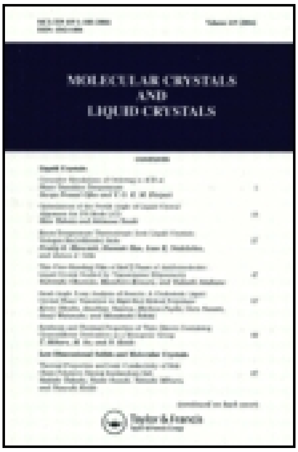

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INTERCALATION OF CATIONIC PORPHYRIN BEARING FOUR ω-AMMONIOALKYL SUBSUTITUENTS AT *MESO*-POSITIONS INTO CLAY MONTMORILLONITE, SAPONITE, AND HECTORITE

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Abstract A novel cationic porphyrin bearing flexible ω-ammonioalkyl side chains, **TMAP-Cl** was prepared in high yield by using the K10 method. It was found that **TMAP-Cl** can be quantitatively ion-exchanged into interlamellar spaces of Mont, Sapo, and Hecto without suffering any protonation to the porphine ring. Especially, in the **TMAP**-Mont intercalation compound, the interlamellar distance was expanded to 10 Å, which implies that a porphine ring in **TMAP** is installed upright rather than parallel to the clay surface.

INTRODUCTION

Montmorillonite and related smectite clays can accommodate a variety of cationic compounds as guest molecules between their negatively charged silicate sheets by ion-exchange. The clays including guest molecules, which are called intercalation compounds, are expected to be promising candidates for advanced materials based on molecular assembling. Two-dimensional interlamellar spaces of the clays are advantageous to assemble large guest molecules, compared with three-dimensional, small voids of zeolites. Particularly, cationic guest molecules are easily taken up, and arranged firmly in the interlamellar spaces of the smectite clays in subnano to nanometer dimensions.

We have been interested in assembling porphyrin molecules in nanometer-sized interlamellar spaces of smectite clays because the assembled porphyrins are expected to function as new photofunctional materials and efficient metal-chelating ligands in metal-catalyzed organic reactions.[1] Pinnavaia et al. first intercalated a neutral porphyrin molecule, *meso*-tetraphenylporphyrin (TPP) in VO^{2+}- or Fe^{3+}-montmorillonite, disclosing that the TPP molecule is staying parallel to the surface of the montmorillonite.[2] Later, Kameyama[3] and Carrado[4] used cationic porphyrins, *meso*-tetrakis(1-methyl-4-pyridiniumyl)porphyrin instead of neutral TPP in their intercalation in smectite clays.

In this study, we prepared a new type of cationic porphyrin, *meso*-tetrakis(5-trimethylammoniopentyl)porphyrin chloride salt (**TMAP-Cl**) which is composed of both a rigid porphine core and flexible side alkyl chains, and intercalated the **TMAP-Cl** into naturally occurring clay, montmorillonite, and synthetic smectites such as saponite and hectorite. We will discuss the difference in the intercalation states between the **TMAP-Cl** bearing flexible alkyl substituents on the porphine ring and already-known *meso*-tetrakis(1-methyl-4-pyridiniumyl)porphyrin iodide salt (**TMPyP-I**)[4] in which four rigid pyridinium rings are connected directly to the porphyrin periphery.

SYNTHESIS OF CATIONIC PORPHYRINS (TMAP-Cl, TMPyP-I)

We previously reported that montmorillonite K10 (commercially available sulfuric acid-treated montmorillonite) gave *meso*-tetraalkylporphyrins in high yields from aliphatic aldehydes and pyrrole because the nanometer-sized pores of K10 are suitable for the formation of a cyclic intermediate, porphyrinogen from a linear precursor, tetrapyrromethane.[5] We applied our K10 method to the preparation of **TMAP-Cl** as shown in Fig. 1: As expected, *meso*-tetrakis(5-chloropentyl)porphyrin was obtained in a gram scale in high yield of 46% from 6-chlorohexanal and pyrrole by use of K10. On treatment with a trimethylamine aqueous solution, the ω-chloroalkyl-substituted porphyrin was easily converted into **TMAP-Cl**, which is very soluble in water. Water-soluble **TMPyP-I** was also prepared by *N*-methylation of commercially available *meso*-tetra(4-pyridyl)porphyrin with iodomethane.

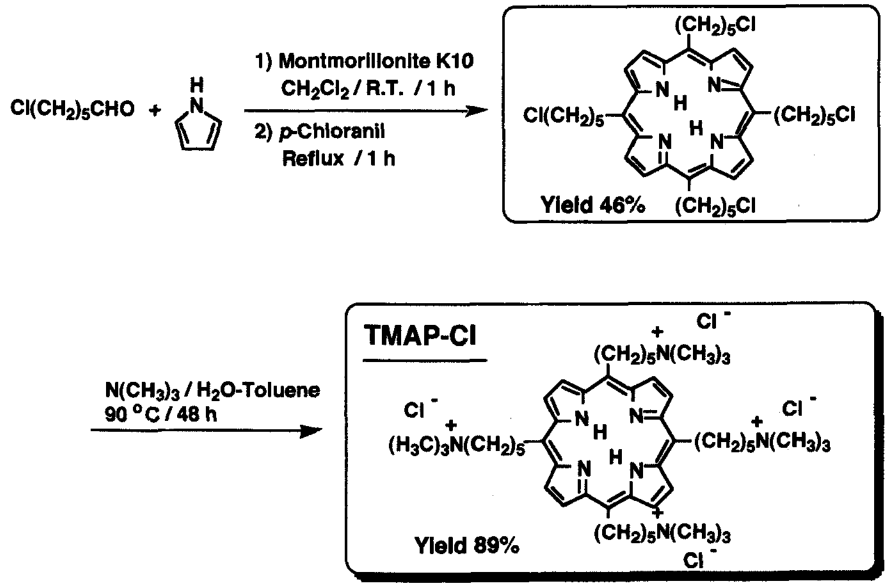

FIGURE 1. Synthetic route to **TMAP-Cl**.

INTERCALATION OF TMAP-Cl AND TMPyP-I INTO SMECTITE CLAYS

As hosts for the formation of intercalation compounds, we used three kinds of smectite clays (a family of complex layered oxides with 2:1 layer lattice structures) : montmorillonite (Mont), saponite (Sapo), hectorite (Hecto). A unit cell formula and cation exchange capacity (CEC) for each clay are provided in Table 1.

TABLE 1. Anhydrous unit cell formulas of smectite clays.[a)]

Mineral	Unit cell formula	Cation exchange capacity (meq/g)
Montmorillonite	$Na_{0.66}[Al_{3.34}Mg_{0.66}](Si_8)O_{20}(OH)_4$	1.12
Saponite	$Na_{0.66}\ [Mg_6](Al_{0.66}Si_{7.34})O_{20}(OH)_4$	1.12
Hectorite	$Na_{0.66}[Mg_{5.34}Li_{0.66}](Si_8)O_{20}(OH)_4$	1.04

a) Metals in square brackets occupy the octahedral sites in the clay sheets and metals in parentheses occupy the tetrahedral sites of the clay sheets.

TMAP-Cl and**TMPyP-I** have four ammonio groups per molecule, and hence can be theoretically exchanged for four sodium cations in parent clay to be installed in the clay interlamellar spaces as shown in Fig. 2. However, porphyrins are prone to be protonated under acidic circumstances to be in a dication form as shown in Fig. 3. If so, the porphyrin is considered to be a six-valent cation per molecule.

To an aqueous solution of **TMAP-Cl** (or **TMPyP-I**) was added a clay. The amount of **TMAP-Cl** (or **TMPyP-I**) used corresponds to 0.3 equivalents of the amount of sodium ions in the host clay. The suspended mixture was stirred at 80°C for 7 d. Heating the mixture at 80°C facilitated a smooth and complete exchange of the cationic porphyrin for sodium ions in the clay. Then, the clay was collected on a suction funnel,

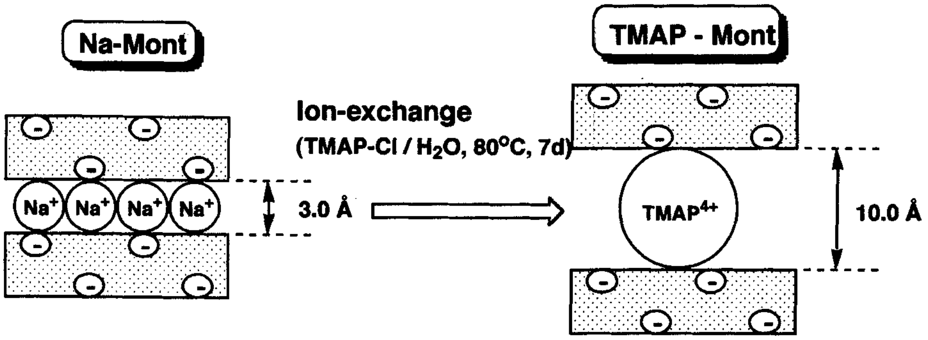

FIGURE 2. Intercalation of **TMAP** ions into Na-Mont.

and washed repeatedly with water until liberated **TMAP-Cl** (or **TMPyP-I**) was scarcely detected in the washings.

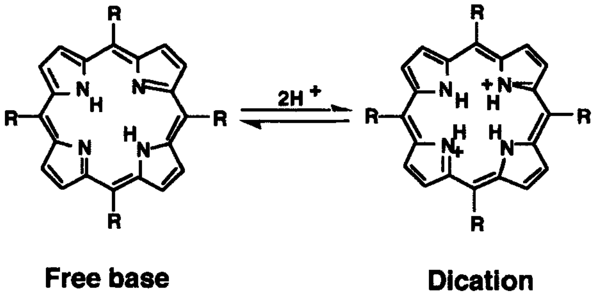

FIGURE 3. Interconversion between porphyrins in freebase and dication forms.

STATES OF TMAP AND TMPyP CATIONS INTERCALATED IN CLAYS

It is easy to confirm by UV-VIS spectrometry whether porphyrin molecules intercalated between clay sheets are in a free base or dication form.[4] Each intercalated sample was dried at 120°C/0.5 Torr for 24 h, and mounted on a UV-VIS diffuse reflectance spectrometer. Tables 2 and 4 summarize not only the spectra but also ion-exchange percentages and the colors of the porphyrin-clay intercalation compounds. As references, the spectra of free base and dication forms of **TMAP-Cl** and **TMPyP-I** were measured in aqueous solutions (Tables 3 and 5).

Tables 3 and 5 indicate that the clear difference in UV-VIS spectra between free base and dication forms of **TMAP-Cl** and **TMPyP-I** in solution is the color of the solution and the number of absorption bands in the Q band region: the free base porphyrin has reddish purple color and four bands, and the dication form has green color and only two

TABLE 2. Intercalation compounds of **TMAP** ions in smectite clays.

Clay	Color	Ion-exchange(%)[a]	UV-VIS spectra (nm)	State of a porphine ring
Mont	Maroon	117	396 518, 553, 596, 652	Free base
Sapo	Maroon	103	395, 437(s)[b] 521, 554, 596, 653	Free base
Hecto	Maroon	103	397, 483(s)[b]	Free base

a) Ion-exchange percentage of **TMAP-Cl** as a four-valent cation based on CEC of clay.
b) A shoulder peak.

TABLE 3. UV-VIS spectra of free base and dication forms of **TMAP-Cl** in water.

Form	Color of aq. solution	UV-VIS spectra (nm)
Free base	Reddish purple	412 (Soret bands) 521, 558, 591, 643 (Q bands)
Dication	Green	418 (Soret bands) 580, 627 (Q bands)

bands. Based on this diagnosis, it was found that the porphine ring in **TMAP** cation keeps a free base form in the interlamellar spaces of the smectite clays, while **TMPyP** ions between clay sheets adopt a dication form. Carrado has already reported that the porphine rings of **TMPyP** ions undergo protonation in the case of intercalation in montmorillonite and hectorite.[4] Consequently, the characteristic feature of **TMAP** ions we originally prepared is that one **TMAP** ion can stoichiometrically displace four sodium cations to stay in interlamellar spaces of clays without suffering any protonation to the porphine ring. As the protonated **TMPyP** ions were introduced as six-valent cations in

TABLE 4. Intercalation compounds of **TMPyP** ions in smectite clays.

Clay	Color	Ion-exchange(%)[a]	UV-VIS spectra (nm)	State of a porphine ring
Mont	Greyish green	93	421 605(br)[b]	Dication
Sapo	Greyish green	73	418 600(br)[b]	Dication
Hecto	Green	79	408 612(br)[b]	Dication

a) Ion-exchange percentage of **TMPyP-I** as a four-valent cation based on CEC of clay.
b) A broad peak.

TABLE 5. UV-VIS spectra of free base and dication forms of **TMPyP-I** in water.

Form	Color of aq. solution	UV-VIS spectra(nm)
Free base	Reddish purple	422 (Soret bands) 519, 554, 585, 648 (Q bands)
Dication	Green	445 (Soret bands) 591, 642 (Q bands)

clays, the ion-exchange percentage of **TMPyP** ions decreased, compared with that of **TMAP** ions in clays. The reason why a porphine ring bearing four ω-ammonioalkyl chains is less prone to undergo protonation than a porphine ring with four 4-pyridiniumyl groups such as **TMPyP** ions remains to be elucidated.

TABLE 6. Interlamellar distances of **TMAP**-clay and **TMPyP**-clay intercalation compounds.

Intercalation compound	Ion-exchange (%)[a)]	Interlamellar distance (Å)
TMAP-Mont	117	10.0
TMAP-Sapo	103	4.9
TMAP-Hecto	103	5.0
TMPyP-Mont	93	4.8
TMPyP-Sapo	73	4.0
TMPyP-Hecto	79	4.3

a) Ion-exchange percentage of **TMAP-Cl** or **TMPyP-I** as a four-valent cation based on CEC of each clay.

Table 6 shows the results of powder X-ray diffraction studies on the porphyrin-containing clays. Among the six intercalation compounds in Table 6, **TMAP**-Mont was found to have the largest interlamellar distance. It was reported that the interlamellar distance of **TMPyP**-Mont composites is 3.8~4.3 Å, indicating that the porphine ring of **TMPyP** is almost parallel to layered sheets of Mont and that the pyridinium rings are tilted.[3,4] In contrast, **TMAP** ions can expand the interlamellar distance in montmorillonite up to 10 Å as shown Fig. 2. The dimension of a porphine ring is almost 10 Å in diameter. Alkyl chains at the *meso*-positions adopt relatively flexible conformations. Therefore, it is assumed that porphine rings in the intercalated **TMAP** ions are firmly arranged standing up rather than lying on the surface of montmorillonite. Because the interlamellar distance of the**TMAP**-Mont scarcely changed (from 10.0 to 9.8 Å) after heat treatment at 120~160°C, the intercalation compound seems to have a tough structure. At 200°C, however, the **TMAP**-Mont gradually decomposed. Based on the rough calculation, the density of **TMAP** ions fixed in interlamellar spaces of Mont is one ion per 17 Å x 17 Å of surface area of the clay.

In contrast to **TMAP**-Mont, **TMAP** ions exchanged into Sapo and Hecto are likely to be parallel to the clay surface with interlamellar distances of around 5 Å.

EXPERIMENTAL

Material.

The commercially available K10 (Aldrich), Montmorillonite (Kunipia F, Kunimine Ind. Co.), Saponite (Sumecton SA, Kunimine Ind. Co.), and Hectorite (Laponite XLG, Laporte Ind. Co.) were used.

Synthesis of meso-tetrakis(5-chloropentyl)porphyrin.

Under nitrogen atmosphere, K10 (15 g), which was predried at 120°C/0.5 Torr for 3 h, was placed in a 2000 ml-flask. Then, CH_2Cl_2 (1450 ml, predried on molecular sieves 4A), a CH_2Cl_2 (50 ml) solution of 6-chlorohexanal (15 mmol), and neat pyrrole (15 mmol) were added successively. The suspended mixture was stirred at room temperature for 1 h until the aldehyde was completely consumed. After solid *p*-chloranil (11.5 mmol) was added, the mixture was gently refluxed at 50°C for 1 h. Solid materials including K10 were filtered off and washed well with AcOEt (400 ml). The combined filtrate was condensed, and adsorbed on Florisil (10 g). The adsorbate was placed on the top of an alumina column (Merck Aluminium Oxide 90, Activity II-III, 300 g), and developed with hexane-CH_2Cl_2 (1:1). The porphyrin fraction was collected, condensed, charged again on an alumina column (300 g), and developed with hexane-CH_2Cl_2 (1:1). The porphyrin fraction was condensed, giving pure porphyrin in 46% yield.

^1H NMR ($CDCl_3$): δ -2.71 (br s, 2H, NH), 1.94 (m, 16H), 2.51(m, 8H), 3.58 (t, J=6.2 Hz, 8H), 4.93 (t, J=7.6 Hz, 8H), 9.44 (s, 8H, Pyrr); ^{13}C NMR ($CDCl_3$) : δ 27.56, 32.52, 35.15, 37.56, 44.92, 118.02 (C-*meso*), 128.46 (br, C-β Pyrr); UV-VIS (C_6H_6) : λ 419, 521, 554, 602, 661 nm.

*Synthesis of meso-tetrakis(5-trimethylammoniopentyl)porphyrin tetrachloride (**TMAP-Cl**).*

In an autoclave, a mixture of *meso*-tetrakis(5-chloropentyl)porphyrin (1.1 mmol) in toluene (10 ml) and a 25% aqueous solution of Me_3N (15 ml) was stirred at 90°C for 2 d. Excess Me_3N was evaporated. The water phase including **TMAP-Cl** was washed with CH_2Cl_2 to remove the neutral porphyrin, and then condensed. After the crude **TMAP-Cl** was dissolved in MeOH (1 ml per 100 mg of the product), 15 ml of Et_2O (per 1 ml of MeOH) was added to precipitate. **TMAP-Cl** crystals. This procedure was repeated more than 10 times. After drying the crystals on KOH pellets in a desiccator at room temperature/0.5 Torr for over 24 h, purified **TMAP-Cl** was obtained in 89% yield.

Decomp. temp. >220°C. Anal. Calculated for $C_{52}H_{86}N_8Cl_4 \bullet 5.0H_2O$: C, 59.19; H, 9.17; N, 10.62; Cl, 13.44. Found: C, 58.91; H, 9.51; N; 10.57; Cl, 13.73. ^1H NMR (DMSO-d_6): δ -2.91 (br s, 2H, NH), 1.83 (m, 16H), 2.50 (m, 8H), 3.05 (s, 36H, NH_3) 3.35 (br, 8H), 5.05 (br, 8H), 9.78 (s, 8H, Pyrr); ^{13}C NMR (CD_3OD) : δ 22.75, 26.75, 34.67, 38.49, 52.92, 65.67, 120.32 (C-*meso*), 127.84 (br, C-β Pyrr); UV-VIS (H_2O) : λ 412 ($\varepsilon = 4.38 \times 10^5\ M^{-1} \bullet cm^{-1}$), 520, 558, 589, 643 nm.

*Synthesis of meso-tetrakis(1-methyl-4-pyridiniumyl)porphyrin iodide salt (**TMPyP-I**).*

Under nitrogen atmosphere a mixture of *meso*-tetra(4-pyridyl)porphyrin (0.645 mmol) in

DMF (100 ml) and iodomethane (19.2 mmol) was stirred at room temperature for 2 d. After the solution was evaporated for a short period to remove excess iodomethane, and allowed to stand at room temperature for 2 d, crude crystals of **TMPyP-I** were collected, and were dissolved in MeOH (50 ml) under reflux. After cooling the MeOH solution, EtOH was added to the solution to precipitate **TMPyP-I** crystals. Purified **TMPyP-I** was obtained in 80% yield after being dried at 80°C/0.5 Torr for 6 h.

Thermal gravimetric analysis revealed that **TMPyP-I** obtained contains 4.68 wt% of H_2O ($C_{44}H_{38}N_8I_4 \bullet 3.2H_2O$). Decomp. temp. >220°C. ^{1}H NMR (DMSO-d_6): δ −3.11 (br s, 2H, NH), 4.73 (s, 12H), 9.01 (d, J=6.8 Hz, 4H), 9.21 (s, 8H, Pyrr), 9.50 (d, J=6.8 Hz, 4H); UV-VIS (H_2O) : λ 422, 519, 554, 585, 648 nm.

*Intercalating **TMAP-Cl** and **TMPyP-I** into smectite clays.*

A procedure in intercalating **TMAP-Cl** into montmorillonite is shown as a representative example: to **TMAP-Cl** (0.080 mmol) in deionized and distilled water (30 ml) was added Mont (0.232 g) including 0.261 meq of exchangeable sodium cations. The mixture was stirred at 80°C for 7 d. The intercalation compound was collected on a suction funnel, and washed with water (50 ml) repeatedly until the concentration of the **TMAP** ions liberated in the washing was less than 5.0×10^{-6}M. The intercalation compound was dried at 120°C/0.5 Torr for 24 h prior to UV-VIS and powder X-ray diffraction analysis.

Analysis.

All the samples were characterized by powder X-ray diffraction on a Rigaku Geigerflex, and UV-VIS diffuse reflectance spectroscopy on a Jasco Ubest-55.

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