Molecular Assembly Recognition Process. Carbon Number Selective Intercalation of Amines by a Layered Zirconium Phosphonate

Tsuyoshi Kijima,* Shinichi Watanabe, Kaoru Ohe and Masato Machida

Department of Materials Science, Faculty of Engineering, Miyazaki University, Miyazaki 889-21, Japan

The reaction of *n*-alkylamines $C_nH_{2n+1}NH_2$ (*n* = 1–10) with a partially phosphated zirconium carboxyethylphosphonate shows that only heptylamine (*n* = 7) is preferentially intercalated to form a bilayer, demonstrating a new class of host–guest process based on molecular assembly recognition.

Much attention has been paid to various molecular selective processes, from ionic or molecular size-selective separations by crown compounds[1] and cyclodextrins,[2] and molecular shape-selective catalysis by zeolites[3] and intercalated clays,[4] to enantioselective sorption of molecules by chiral microporous solids.[5,6] Such chemical processes are characterized by the recognition of a substrate as a single molecule or ion through shape-selective binding pockets in macrocyclic host molecules[1,2,7] or those in framework or layered structures.[3–6] We have now found that the intercalation of *n*-alkylamines $C_nH_{2n+1}NH_2$ (*n* = 1–10) by a partially phosphated zirconium carboxyethylphosphonate occurs only for *n*-heptylamine (HpA, *n* = 7), leading to a new class of host–guest process based on molecular assembly recognition.

The zirconium carboxyethylphosphonate sample **1** was prepared in a manner similar to that of Alberti *et al.*,[8a] as described elsewhere.[9b] The composition of **1** was determined to be $Zr(O_3PC_2H_4CO_2H)_{1.67}(HPO_4)_{0.33}$ from thermogravimetric data combined with X-ray observation that the solid was totally converted into ZrP_2O_7 on heating at 1000 °C for 1 h. The phosphonate was mixed with an aqueous solution of alkylmonoamine, followed by stirring at 25 °C for 10 days. The resulting mixtures were centrifuged, fully washed with water, and freeze-dried. Sample characterization was made using powder X-ray diffraction (XRD), thermogravimetry (TG) and IR spectroscopy in the same manner as described previously.[9b]

A series of products with alkylamines, **2**(*n*), were obtained at an [amine/Zr] mixing ratio of 1.0 : 1. The XRD data for **2**(*n*) are shown in Fig. 1. The XRD pattern of **2**(**7**) shows a new diffraction peak at 2θ = *ca.* 2.9°, along with its second-order reflection, whereas only a few weak peaks are observed near 2θ = 23° for **2**(**1**). For the other solids, the diffraction peak at 2θ = *ca.* 6.8°, attributable to the (002) reflection observed for **1**, is markedly decreased in intensity, but the second major peaks at 2θ = *ca.* 19–28° remain little changed. The IR spectrum of **2**(**7**) shows a weak band attributable to the $-CO_2^-NH_3^+-$ group near 1680 cm⁻¹, whereas neither the 1680 cm⁻¹ band nor the 1710 cm⁻¹ peak associated with the $-CO_2H$ group are observed for **2**(**1**) and the other solids show nearly the same spectra as **1** (Fig. 2). The TG data (Fig. 3) show that the weight loss at above 100 °C for **2**(**7**), due to decomposition into ZrP_2O_7, is about 1.5 times the loss for **1**, while those for the other solids remain 1.1 times the latter loss [for **2**(**9**)] or below.

Additional XRD and IR data (Figs. 1 and 2) showed that the host phase is almost fully converted into an intercalated phase with *n*-heptylamine (HpA; *n* = 7), **2′**(**7**), at a [HpA]/[Zr] ratio as high as 2.0. Zirconium carboxyethylphosphonate has a structure similar to that of α-zirconium phosphate, $Zr(HOPO_3)_2{\cdot}H_2O$, with $-C_2H_4CO_2H$ groups replacing the OH ones, as suggested by several authors.[8b,10,11] It is thus most probable that the intercalation of HpA by the phosphonate **1** occurs in such a way that the heptylammonium cations replace the protons of the interlayer $-CO_2H$ groups to arrange as a bilayer, as shown in Fig. 4. The interlayer spacing of 30.5 Å for **2′**(**7**) is in good agreement with the 30.2 Å expected from those for the hexyl- and octyl-ammonium intercalates of fully carboxyethylated zirconium phosphonate.[11a] Combination of the TG data for **1** and **2′**(**7**) led to the composition $Zr(O_3PCH_2CH_2CO_2H)_{1.67}(HPO_4)_{0.33}(C_7H_{15}NH_2)_{1.80}{\cdot}1.5H_2O$ for **2′**(**7**). The additional uptake of HpA beyond the number of $-CO_2H$ groups in **1** would be due to binding to the residual P–OH sites. The condensation of the $-CO_2^-NH_3^+-$ group into a –CONH– form by heating to *ca.* 200 °C[9] also occurs for **2′**(**7**), accompanied by an appreciable reconversion of the ionic group into the initial $-CO_2H$ form (Fig. 2). XRD and TG analyses also showed that the uptake of nonylammonium ions is little promoted by increasing the [amine]/[Zr] ratio from 1.0 to 2.0. It is thus concluded that the host compound **1** (interlayer spacing 13.1 Å) forms an intercalated phase with HpA, whereas it is degraded into an amorphous dephosphonated phase such as $ZrO(OH)_2$ for *n* = 1 or become highly disordered in the stacking of phosphonate layers by taking up a trace amount of the amine guest with *n* = 2–6 or 8–10. This is in striking contrast to not only the indiscriminate uptake of *n*-alkylamines by fully carboxyethylated zirconium posphonate,[11a,12] but also those by many other layered compounds such as α-zirconium phosphate,[13] montmorillonite[14] and $Na_xWOP_2O_7{\cdot}nH_2O$.[15]

The remarkably preferential uptake of HpA by **1** can be explained as follows. The attractive interaction between intercalated alkylammonium cations would be enhanced with increasing chain length, but the interaction between any adjacent phosphonate layers would be lowered through the

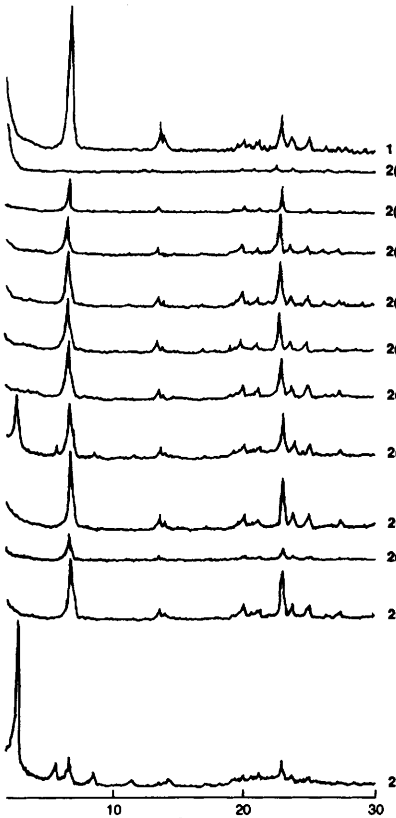

Fig. 1 X-ray diffraction patterns of **1**, **2**(*n*) and **2′**(**7**) (Cu-Kα radiation)

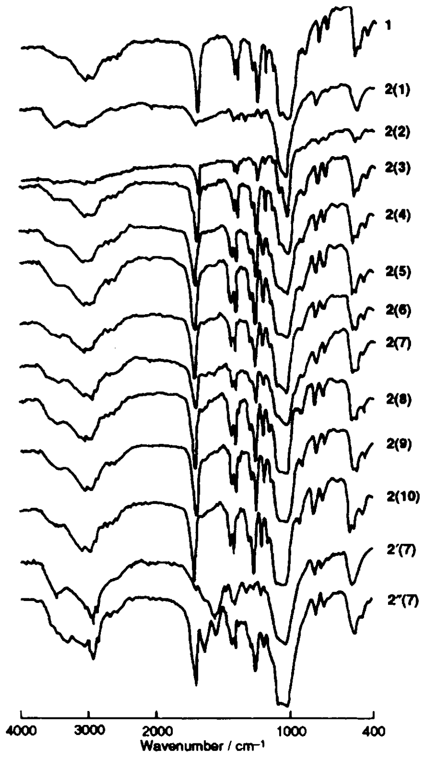

Fig. 2 IR spectra of **1**, **2**(*n*), **2'**(7) and **2"**(7); sample **2"**(7) is **2'**(7) heated at 210 °C for 1 h

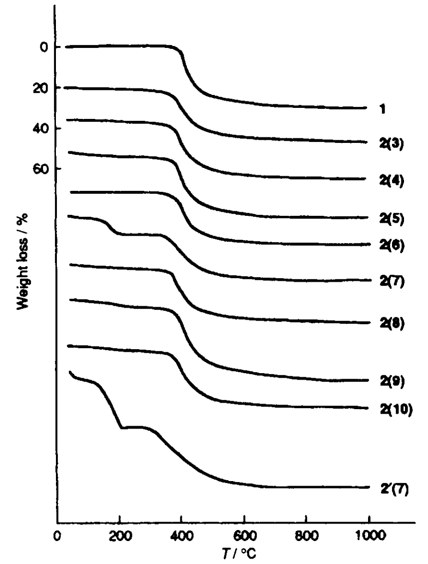

Fig. 3 TG curves for **1**, **2**(*n*) and **2'**(7) with a heating rate of 10 °C min^{-1} in air. The vertical scales for **2**(*n*) and **2'**(7) are shifted by an arbitrary percentage.

increase in interlayer spacing. Due to these two opposing effects, the free energy of the bilayered intercalates would be given by a downward curve as a function of carbon number *n*. Since the partially-substituted phosphate groups would serve as imperfections in the intercalated phase, the downward free energy curve may be positively biased so as to fall below the carbon number independent free energy of the dephosphonated or disordered phase for a limited range of *n*. The present observations means that the stability field of the alkylammonium-exchanged phase for **1** is minimized for $n = 7$. The uptakes of the other odd-numbered alkylamines ($n = 5$ and 9) appear to be a little greater than those of the odd-numbered but short or even-numbered ones (Fig. 3), but do not lead to the formation of any bilayered phase. It should be noted then that carbon number selectivity in the present system is highly amplified through the assembling of guest molecules. We can thus propose a new concept of molecular assembly recognition, in place of the molecular recognition usually used for the recognition of a single molecule or ion.

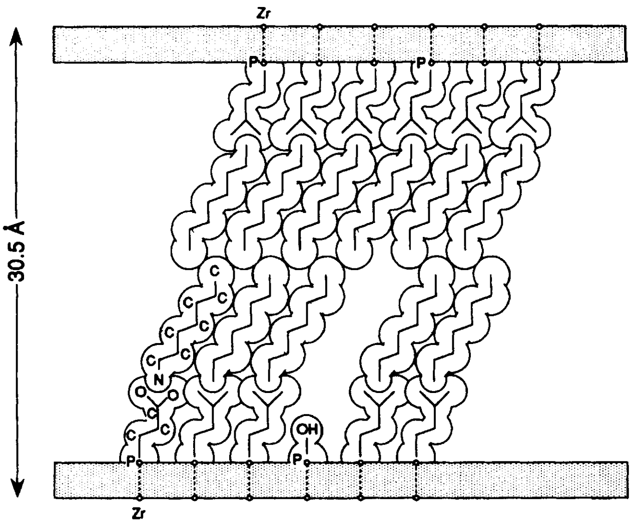

Fig. 4 Model proposed for the arrangement of heptylammonium cations in the interlayer space of **1**

The present work was supported by a Grant-in-Aid for General Scientific Research (05650843) from the Ministry of Education, Science, and Culture of Japan.

Received, 19th September 1994; Com. 4/05699J

References

1 *Synthetic Multidentate Macrocyclic Compounds*, ed. R. M. Izatt and J. J. Christensen, Academic, New York, 1978.
2 M. L. Bender and M. Komiyama, *Chemistry of Inclusion Compounds*, Tokyo-Kagaku-Dojin, Tokyo, 1969.
3 D. W. Breck, *Zeolite Molecular Sieves*, Wiley, New York, 1974.
4 T. J. Pinnavaia, *Science*, 1983, **220**, 365.
5 A. Yamagishi, *J. Phys. Chem.*, 1982, **86**, 2472.
6 G. Cao, M. E. Garcia, M. Alcaal, L. F. B.Burgess and T. E. Mallouk, *J. Am. Chem. Soc.*, 1992, **114**, 7574.
7 J. Jr. Rebeck, *Angew. Chem.*, 1990, **29**, 245.
8 (*a*) G. Alberti, U. Costantino, S. Alluilli and N. J. Tamassini, *J. Inorg. Nucl. Chem.*, 1976, **15**, 2811; (*b*) 1978, **40**, 1113.
9 (*a*) T. Kijima, Y. Kawagoe, K. Mihara and M. Machida, *J. Chem. Soc., Dalton Trans.*, 1993, 3827; (*b*) T.Kijima, S. Watanabe and M. Machida, *Inorg. Chem.*, 1994, **33**, 2586.
10 M. B. Dines and P. M. Di Giacomo, *Inorg. Chem.*, 1981, **20**, 92.
11 (*a*) D. A. Burwell and M. E. Thompson, *Chem. Mater.*, 1991, **3**, 730; (*b*) D. A. Burwell, K. G. Valentine, J. H. Timmermans and M. E. Thompson, *J. Am. Chem. Soc.*, 1992, **114**, 4144.
12 J. Kornyei, L. Szirtes and U. J. Costantino, *J. Radioanal. Nucl. Chem.*, 1985, **89**, 331.
13 A. Clearfield and B. M. Tndwa, *J. Inorg. Nucl. Chem.*, 1979, **41**, 871.
14 A. Weiss, *Angew. Chem.*, 1963, **2**, 134.
15 N. Kinomura, K. Onoda, M. Kobayashi, N. Kumada and F. Muto, *J. Mater. Sci.*, 1989, **24**, 1814.