# Shaping Solid-State Supramolecular Cavities: Chemically Induced Accordionlike Movement of γ-Zirconium Phosphate Containing Polyethylenoxide Pillars**

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Layered zirconium phosphate derivatives containing organic pillars are very promising materials because the size, shape, and chemical function of free interpillar spaces may be designed by choosing the appropriate organic moieties and controlling the degree of pillaring.[1–3] Among the different zirconium phosphates, the α phase is less suitable for this purpose because, owing to the flexibility of the α layer, a random distribution of pillars in the interlayer region is not usually obtained, and special pillars (pillars with bases) must be used to create interpillar microporosity.[4] In contrast, the high rigidity of the lamellae of γ-zirconium phosphate ($[ZrPO_4\{O_2P(OH)_2\}] \cdot 2\,H_2O$; γ-ZrP) allowed us to prepare stable phases with a low extent of pillaring, making the use of pillars with bases no longer necessary.[5] The utilization of diphosphonic acid derivatives of crown ethers led to pillared materials with the ability to recognize cations.[6]

More recently, the behavior of γ-ZrP pillared with nonrigid alkyl chains was investigated. The presence or absence of solvent in the cavities of these pillared materials induced conformational changes of the alkyl chains and gave rise to an accordionlike movement of the layers.[7] This research led to the conclusion that appropriate functionalization of the pillars would allow the chemical control of this anisotropic movement.

With the aim of creating tailor-made supramolecular cavities in interlayer spaces, in which certain molecular species could be selectively inserted, a systematic study on the preparation and properties of γ-ZrP materials containing polyethylenoxide pillars of different length was initiated in our laboratories. This research showed that γ-ZrP derivatives containing these pillars in various densities in the interlayer space can be easily prepared by topochemical reactions, thus confirming that supramolecular interpillar cavities can indeed be tailored. In the course of this study it was also found that the oxygen atoms of the pillars played a decisive role in the chemically induced accordionlike movements of the layers.

Preparation procedures, compositions, model structures as well as the chemical and recognition properties of γ-ZrP containing a variety of polyethylenoxide chains at various interpillar distances will be reported elsewhere. Here our attention will be focused on the chemically induced accordionlike movement of these derivatives. Only compounds of general composition $ZrPO_4[O_2P(OH)_2]_{0.76}(O_2P(OH){-}R{-}(OH)PO_2)_{0.12} \cdot n\,H_2O$, where the pillar R can be diethylene glycol (DEG) or pentaethylene glycol (PEG), will be considered. This kind of pillaring can be seen as a process in which each diphosphonate molecule acts as a tetradentate ligand and replaces two bidentate $O_2P(OH)_2$ ligands belonging to two adjacent lamellae of the original γ-ZrP.[8]

The interlayer spaces of the DEG- and PEG-pillared derivatives after centrifugation from the mother liquors were 15.7 and 17.6 Å, respectively. When these samples were dehydrated at 80 °C, the interlayer distances decreased to 13.2 and 13.3 Å, respectively, with the loss of one mole of water per mole of zirconium. The initial hydrated phases were obtained again by rehydration in water, showing that the dehydration–rehydration process was reversible. The fact that the interlayer space of the anhydrous phases is independent of the chain length indicates that the pillars must lie almost parallel to the plane of the layer. Taking the average thickness of a γ layer and the polyethylenoxide chains as 9.3 and 4 Å, respectively, the experimental interlayer space agrees satisfactorily with the value expected when a stratum of heavily inclined pillars is interposed between layers (Figure 1).

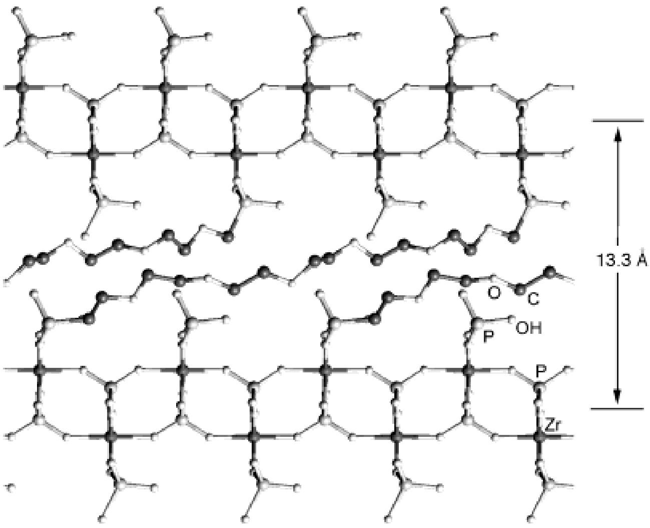

Figure 1. The structure of the anhydrous PEG-pillared derivative of γ-zirconium phosphate.

In derivatives with 25 % pillaring the total free area for each pillar is four times that of the free area available for each phosphorus atom (i.e., 4 × 33.3 = 133 Å$^2$). Therefore, the formation of a monolayer containing heavily inclined pillars is largely compatible with the total free area available in derivatives with 25 % pillaring, even in the case of very long pillars. For example, one PEG pillar should occupy an area approximately equal to the product of its cross section and its length (i.e., 4 × 27.5 = 110 Å$^2$). The differences between the interlayer spaces of the hydrated and anhydrous phases for

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DEG and PEG derivatives are 2.5 and 4.3 Å, respectively. Considering that DEG contains 11 chain atoms (8C and 3O), while PEG contains 20 chain atoms (14C and 6O), the average increment per chain atom is about the same for the two derivatives (0.23 and 0.22 Å, respectively). Thus, assuming that the chains are in their extended conformation, this small increment corresponds to an average inclination angle $\alpha$ of the chain to the plane of the hydrated $\gamma$-ZrP sheets of about 10°.

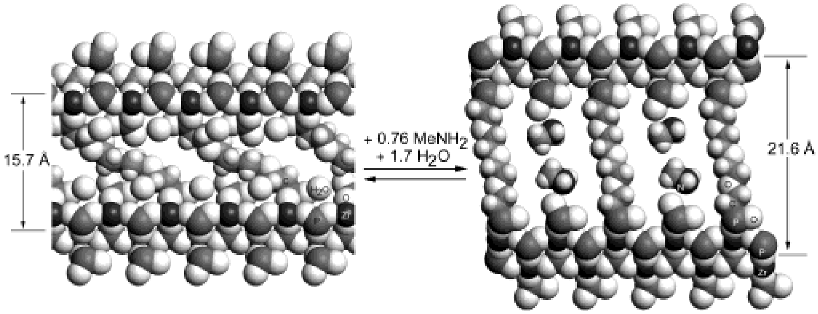

Figure 2. Schematic representation of the reversible enlargement – shortening of the interlayer space of the DEG-pillared derivative following intercalation – deintercalation of methylamine and additional water.

The pronounced inclination of the chains, even in the hydrated forms, suggests a low tendency of these derivatives to incorporate water in the interpillar region. This fact seems to be in contrast with the results previously obtained with alkyl pillars, where, despite their much lower hydrophilicity, several water molecules entered freely into the interpillar space, thus forcing the alkyl chains to assume a position almost perpendicular to the layers.[7] A reasonable explanation of this apparent contradiction is that the hydrophilic oxygens present in the pillars also have a strong affinity for the surface of the $\gamma$-ZrP lamellae, probably due to the formation of hydrogen bonds with the unexchanged $O_2P(OH)_2$ groups. The pillars could therefore be obliged to take a position almost parallel to the layers. Furthermore, the water molecules may be also well organized in the interlayer space. Composition data seem to indicate that one water molecule is present for each unexchanged $O_2P(OH)_2$ group, while the remaining water may be coordinated to the pillar chain (about one molecule per ethylenoxide monomer). On this assumption, molecular modeling reproduces reasonably well the water content and the increment of the interlayer distance when the DEG and PEG derivatives become hydrated.

To increase the number of water molecules in the interpillar space, we tried to break these hydrogen bonds between the pillars and the $O_2P(OH)_2$ groups by titrating the derivatives with various bases and checked whether the pillars could be forced to align perpendicular to the layers. The best results were obtained with methylamine (see Experimental Section). Elemental and thermogravimetric analysis as well as X-ray powder diffraction (XRD) patterns of samples titrated with methylamine showed that 0.76 – 0.78 moles of the amine (one molecule for each unexchanged $O_2P(OH)_2$ group) and additional 1.7 moles of water per mole of zirconium were taken up in the interlayer space. The interlayer distance of the DEG and PEG derivatives greatly increased to 21.6 and 26.7 Å, respectively.

We also tested whether the large variations in the interlayer spaces obtained with methylamine titration were reversible. After titration, the derivatives were suspended again in water and then 0.1 M HCl was added to pH 2.5. The compounds were centrifuged, and their XRD patterns recorded. The resulting interlayer distance had decreased to 15.7 and 17.6 Å, respectively. This clearly demonstrates the reversibility of the process schematically shown in Figure 2 for the DEG derivative. In the case of the titrated DEG derivative, the interlayer separation of 21.6 Å is almost the maximum possible because it corresponds to an $\alpha$ angle very close to 90°.

In the case of the PEG derivative a more spectacular variation of the interlayer space was observed (ca. 9 Å). However, this is still shorter than the maximum possible value predicted when the chains are in a completely extended conformation (ca. 33 Å). A plausible explanation could be that, owing to the interactions with water molecules, the long polyethylenoxide chains tend to assume a helicoidal conformation, as recently shown by IR measurements in solution.[9]

We also analyzed the stages of the methylamine titration of the DEG derivative. Detailed studies are in progress to determine the methylamine and water content of the above phases, but preliminary results clearly show that the passage from the initial to the final interlayer distance is reached through many intermediate steps; at least five different intermediate phases were identified. Thus, an almost continuous variation of the interlayer distance between 15.7 and 21.6 Å can be obtained by gradual addition of methylamine. We conclude that in the presence of methylamine, a progressive, reversible accordionlike movement of this pillared compound can be simply induced by a gradual change in the pH value of the solution. This is the first time, to the best of our knowledge, that the size and shape of the cavities of a pillared material can be finely tuned by chemical means.

Upon dehydration, the interlayer space of DEG and PEG derivatives loaded with methylamine decreased to 14.9 and 16.6 Å respectively. Since the original interlayer spaces are recovered when rehydrated, the phenomenon of the reversible elongation – shortening of the interlayer space induced by hydration – dehydration of the interlayer region seems to be similar to that already described for $\gamma$-derivatives pillared with alkyl chains.[7]

The possibility of engineering an accordionlike movement by simply controlling the pH value of the external solution is fascinating. The easy preparation of $\gamma$-ZrP derivatives containing polyethylenoxide phosphonates in which the length of the pillars, their conformation, and their distances to one another in the interlayer space can be modulated over a wide range is very promising for the realization of shaped interpillar spaces. The creation of these molecular vessels would allow the specific adsorption of different species with which selective reactions might be carried out. Additional studies are in progress to clarify the details of the conformational changes of the pillars when the corresponding derivatives are titrated with methylamine, other amines, or metal hydroxides and salts.

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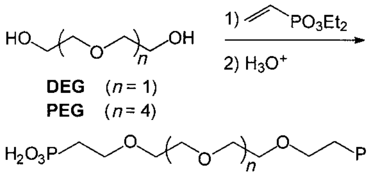
### Experimental Section

The DEG and PEG diphosphonic acids were prepared by Michael-type double addition of the corresponding diol to diethyl vinyl phosphonate and final acid hydrolysis of the resulting tetraethyl phosphonic diester [Eq. (1)].



(1)

The pillaring procedure was performed by first exfoliating $\gamma$-ZrP (0.5 g) in water/acetone (1/1, 60 mL) at 80 °C. This dispersion of exfoliated lamellae was then mixed with a 0.015 M solution (20 mL) of DEG or PEG bis-phosphonic acids in water/acetone (1/1) at 80 °C overnight.

Average values from elemental analysis and $^{31}$P NMR spectroscopy[10] were used to determine the composition of the solids. Water content was derived by thermogravimetry with a Stanton STA750 thermoanalyzer. The interlayer distances were taken from the first reflection in the XRD patterns.

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[1] G. Alberti in *Comprehensive Supramolecular Chemistry, Vol. 7* (Ed.: J. M. Lehn), Pergamon, **1996**, chap. 5.
[2] A. Clearfield in *Progress in Inorganic Chemistry, Vol. 47* (Ed.: K. D. Karlin), Wiley, **1998**, pp. 373–510.
[3] M. B. Dines, P. M. Di Giacomo, *Inorg. Chem.* **1981**, *20*, 92–97.
[4] G. Alberti, U. Costantino, R. Vivani, P. Zappelli, *Angew. Chem.* **1993**, *105*, 1396–1398; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1357–1359.
[5] G. Alberti, F. Marmottini, S. Murcia-Mascarós, R. Vivani, *Angew. Chem.* **1994**, *106*, 1655–1658; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1594–1597.
[6] E. Brunet, M. Huelva, R. Vázquez, O. Juanes, J. C. Rodríguez-Ubis, *Chem. Eur. J.* **1996**, *2*, 1578–1584.
[7] G. Alberti, S. Murcia-Mascarós, R. Vivani, *J. Am. Chem. Soc.* **1998**, *120*, 9291–9295.
[8] G. Alberti, E. Giontella, S. Murcia-Mascarós, R. Vivani, *Inorg. Chem.* **1998**, *37*, 4672–4676.
[9] R. Begum, H. Matsuura, *J. Chem. Soc. Faraday Trans.* **1997**, *93*, 3839–3848.
[10] $^{31}$P NMR (81 MHz, $D_2O$, 25 °C, 50 mg of sample dissolved in 1 mL of 2 M HF): $\delta = 28.7$ (m; $PCH_2R$), 0.6 (s; $PO_4$). Shifts are relative to 85 % $D_3PO_4$ in $D_2O$ as external reference.

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# Laser-Induced "Regeneration" of Colloidal Particles: The Effects of Thermal Inertia on the Chemical Reactivity of Laser-Heated Particles[**]

Thomas E. McGrath, Andrew C. Beveridge, and Gerald J. Diebold*

Colloidal suspensions of metal particles frequently display surprising colors,[1, 2] the most striking examples being perhaps the deep red of colloidal gold and the light yellow-green of colloidal silver. Irradiation of colloidal carbon[3, 4] or colloidal metal solutions[5, 6] by a high-power, pulsed laser causes a reduction in the diameters and the dispersion of the suspended particles, resulting in dramatic changes in their optical properties that are easily discernible by the unassisted eye. We show here that the mechanism of change in several colloidal metal solutions involves rapid production of ions as a result of laser heating, followed by diffusion and chemical reduction on a long time scale to form new small-diameter colloidal particles. A result of the experiments is that large particles are differentially consumed relative to small ones. The recently reported method[7, 8] of forming colloidal suspensions through irradiation of solid metal surfaces submerged in water is also shown here to involve formation of ionic species.

When an aqueous suspension of particulate carbon, known as "India ink", is irradiated with a high-power, pulsed laser it rapidly becomes transparent as a result of carbon consumption through the carbon–steam reaction: Heating of the carbon particles on absorption of the laser radiation[3, 4] converts carbon and water into hydrogen and carbon monoxide, gradually reducing both the diameter of the carbon particles and the total amount of carbon in suspension. The recently reported observation of the same effect of size reduction in colloidal silver and gold suspensions[5, 6] suggests examination of the possibility of chemical reactions, albeit of an altogether different character than in the case of carbon in water, as playing some role in the mechanism of change. The first experiments carried out here sought to determine if $Au^{3+}$ ions were generated by pulsed laser irradiation of a gold sol.

An aqueous suspension of gold particles of 100 nm diameter[9] has a surface plasmon resonance[1] at 566 nm, which is a result of collective oscillations of the electrons in small particles, giving the sol its distinctive color, as is evidenced by the absorption spectrum (inset of Figure 1). Irradiation of the suspension for 2 min at 10 Hz and 330 mJ per pulse with the unfocused output (532 nm, 15 ns) of a frequency-doubled Nd:YAG laser results in the formation of smaller gold particles, as is found from transmission electron microscope measurements[10] and as further evidenced in

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