Engineering of crystals and solids is an active area of research that intertwines the concepts of supramolecular chemistry and materials science. The supramolecular construction of nanoporous solids with ample, open voids that can be freely accessed by other molecular species is quite a difficult task and pursued by a vast number of research groups. One common approach is the spontaneous aggregation of dissolved small-molecular building blocks. However, its success is rather limited because for the self-aggregation to render useful architectures, one should possess a profound predictive knowledge of the involved intermolecular forces, which implies the proposition and preparation of molecules (“aggregons”) with suitable geometries and functionalities. Yet, worse, once the crystal or solid is formed, there are few opportunities, if any, to further manipulate its structure.

Layered γ-zirconium phosphate (γ-ZP) is a versatile and well-known structure in which the phosphates that reside in the surfaces of the lamellae are topotactically replaceable by phosphonates and diphosphonates, the latter leading to pillared, porous solids. Layered γ-ZP can be thus used as a carving board in which appropriate organic molecules could be orderly grafted at a controlled, low density. Therefore, size and shape of interpillar spaces may be tuned by simply choosing organic moieties of appropriate length and flexibility and by controlling the degree of pillaring. Moreover, one may select a suitable chemical response of interpillar spaces by including sophisticated functionalities in the organic chain. These facts, together with the possibility of replacing all remaining superficial phosphates by other phosphorous functions of different polarity, make the prospects of this building-block combination to be limited only by the imagination of the researcher.

We report herein that the chemical response to a simple acid–base reaction induces fast, sharp porosity changes in the microcrystals of the inorganic–organic material created by stepwise, double topotactic exchange of γ-ZP by pentacycl oligo-derived diphasphonic acid and hypophosphite (see Scheme 1).

Treatment of exfoliated γ-ZP in 1:1 water/acetone at 80 °C with the diphasphonic acid in the appropriate molar ratio (step A) led to the pillared material I of empirical formula ZrPO4[O2P(OH)2]0.74[O2P(OH)-R-(OH)PO2]0.13·nH2O, R = CH2CH2(OCH2CH2)5OCH2CH2. Careful neutralization of I with methyamine followed by treatment with hypophosphorous acid (Scheme 1 step B; see Experimental Section) yielded a new material II. Elemental and thermogravimetric analyses for II gave the empirical formula Zr(P(O)2)(O2PH3)0.74(C6H5P2O3)0.13·0.8H2O, thus showing that all exchangeable phosphates of I were replaced by hypophosphite without appreciable loss of diphasphonate. A sample of material II, dissolved in HF/D2O, gave a 31P NMR spectrum with signals at 0.0, 8.9, and 25.3 ppm attributable to phosphoric, hypophosphorous, and phosphonic acids, respectively. Their relative intensity (3.97:2.91:1) was in excellent agreement with the calculated ratios (3.84:2.85:1) for the empirical formula obtained from the other techniques. FTIR of II showed the expected stretching P–H band at 2403 cm−1 while solid-state MAS 31P NMR revealed the presence of the nonexchangeable phosphates at −27.9 and the complete disappearance of the signal at −13.6 ppm arising from exchangeable phosphates of the starting material I. Both hypophosphite and phosphonate groups gave a broad signal at about 10 ppm, whose intensity heavily increased under cross-polarization conditions (contact time 2 ms).

The unexpectedly fast swelling of material II occurred when it reacted with a very small amount of methylamine. A comparative study of the titration of I and II with methylamine is depicted in Figure 1a. While I gradually increases its interlayer distance with increasing pH (see powder XRD patterns in Figure 1b), II shows a remarkable, sharp swelling from 1.28 nm to 2.14 nm in a very narrow pH range (ca. 4.2 to 5.0) corresponding to the addition of solely 0.2 equivalents of amine. It should be noted that II suffers extensive oxidation at pH > 7. Solid-state 31P NMR and elemental analysis indicate that phase II completely transforms into phase I at pH 9.

The forces governing the piling of γ-ZP and γ-ZP/hypophosphite (γ-ZPH) layers are very different. In γ-ZP the outer layer of exchangeable phosphates form a network of...
hydrogen bonding interactions between consecutive lamellae in which several molecules of interlayer water are involved.\cite{12}

In appropriate conditions of polarity and temperature, $\gamma$-ZP can be easily exfoliated, each lamella being surrounded by water molecules and thus effectively solvated. However, the $\gamma$-ZPH phase does not have polar exchangeable phosphates, the layer surfaces are carpeted by a grid of nonpolar PH$_2$ groups that glue the lamellae one another by sturdy hydrophobic, van der Waals forces. $\gamma$-ZPH phase lacks interlamellar water molecules and its interlayer distance is thus very short (0.88 nm) as compared to that of $\gamma$-ZP (1.22 nm). As a consequence, the $\gamma$-ZPH phase cannot be exfoliated in water or any other common organic solvent.\cite{13}

Besides, the very low acidic character of hypophosphite PH$_2$ bonds avoid phase swelling by the action of acid–base processes in the same way as those that take place in the $\gamma$-ZP intercalation of amines.

In material I, the acidity and polarity of the remaining superficial phosphoric groups and the relatively large initial interlayer distance (1.8 nm) allows for the methylammonium ions and the water molecules to move somewhat freely in the interlayer space, the hydrogen-bonding network is gradually disrupted and the material progressively swells.

In the case of II, the hydrophobic forces governing the behavior of the pure $\gamma$-ZPH phase are still much at work. The fact that the starting interlayer distance of II is very short (1.28 nm) and humidity independent should be manifestations of this behavior. Molecular modeling shows that at this interlayer distance, the organic chains have to lie parallel to the layers, somewhat compressed along the channels left along the hypophosphite grid. Yet in II every organic phosphonate still has an acidic OH and hence amine intercalation is now possible. In the highly nonpolar interlayer region of II there should be few opportunities for the ammonium ions to be stabilized but instead form tight ion pairs with phosphonates. Consequently, the bulky organic cations should rest very close to the organic chains and act as a wedge that makes the pillars stand up. The lamellae of $\gamma$-ZP and $\gamma$-ZPH phases are known to be very rigid. Once a few amine molecules have diffused into the interlayer region, the van der Waals forces are quickly disrupted and the material swells very abruptly. The interlayer distance is then almost doubled in the narrow gap of 0.2 equivalents of added amine.

To the best of our knowledge, this enormous sensitivity of microcrystalline porosity towards the intercalation of small molecules has no precedent.

This work shows that by selecting the appropriate functionality of both organic and inorganic moieties in $\gamma$-ZP pillared materials, shape, porosity, and functionality can be selected beforehand. But more interestingly, those properties can be remodeled afterwards in the solid state by processes as simple as small-molecule intercalation. Such reactions at the edges of the microcrystals can induce a cascade of conformational changes that remotely and sharply affect the entire structure, thus leading to a phenomenon that could be named supramolecular allostery.

**Experimental Section**

The synthesis of pentaethyleneglycol diphasophonic acid, and the pillaring procedure were previously described.\cite{14} Material I (0.3 g) was dispersed in a 0.1M water solution (30 mL) of methylammonium chloride. An aqueous solution of methylamine (0.1M) was then added by means of an automatic titroprocessor until the pH reached 7. The suspension was centrifuged, washed with water (25 × 3 mL) and dried at 100°C for 4 h. The resulting solid (0.3 g) was dispersed into a solution containing 3.8 g of 50%wt H$_3$PO$_2$ in water/acetone (1:1, 30 mL) and conditioned at 90% relative humidity (BaCl$_2$) for at least 24 h.

Received: August 25, 2003 [Z52711]

**Keywords:** crystal engineering · layered compounds · supramolecular chemistry · topochemistry · zirconium

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**Figure 1.** a) Variation of interlayer distance of materials I and II with pH (methylamine titration; see text). Relevant powder XRD patterns for I (b) and II (c).


