

More than a dozen SIFT apparatuses are being used in laboratories around the world, and the experiments are becoming more ambitious and sophisticated. For example, a major effort is being undertaken to discover how the larger molecules detected in interstellar clouds are synthesized. The larger the molecule the more isomeric forms are possible; both open-chain and cyclic isomeric ions are often energetically allowed products of some ion-molecule reactions which can be identified by their (often) very different reactivities with particular molecules, e.g., CO.^{22,23} Studies of interstellar molecules and interstellar ion chemistry also provide critical data from which the physical conditions and the

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chemical history of interstellar clouds can be deduced, and thus the laboratory studies of gas-phase ion chemistry outlined in this paper are a significant contribution to astrophysics as well as to astrochemistry.

Of course, the studies of the reactions of ions in the gas phase extend beyond the area of interstellar chemistry to include the ion chemistry of, for example, planetary atmospheres, laboratory etchant plasmas, and gaseous laser plasmas. Much thermochemical data are obtained from such studies, as well as a deeper insight into the mechanisms of ionic interactions (for this isotopic labeling is particularly profitable). No doubt research into gas-phase ions will continue for a very long time to come.

We are most grateful to Professor Michael Henchman for the continuous stimulus and insight he has provided and the interest he has shown in the isotope exchange work.

Layered Metal Phosphates and Phosphonates: From Crystals to Monolayers

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Although metal salts of phosphoric acid have been known for over a century, research on layered metal phosphates and their derivatives began only in the late 1950s, when it was recognized that some of these salts could be useful as cation exchangers in radioactive waste streams.¹ Because of the extremely low solubility product of the tetravalent metal phosphates, these materials were available at that time only in the form of amorphous gels, and it was not until Clearfield and Stynes² prepared the first crystalline compounds in 1964 that their structures and chemical reactivity began to be clearly understood. Layered solids of this type have since been studied extensively as inorganic ion exchangers.³ They have also enjoyed significant interest as catalysts and catalyst supports due in part to the success of one member of their family, (VO)₂P₂O₇,

in catalyzing the selective air oxidation of butane and butenes to maleic anhydride.⁴

Organic phosphates and phosphonates of the tetravalent metals, which were first made in the 1970s by Yamanaka⁵ and Alberti,⁶ have structures that are very closely related to their inorganic analogues. These compounds have two endearing properties that have stimulated an extensive exploration of their chemistry over the past several years. First, unlike many solid-state materials they are made at low temperatures, often from aqueous solutions. Most solid-state reactions require high temperatures for interdiffusion of ions and/or dissolution of precursor phases, and so the bond connectivity of the final product usually bears little resemblance to that of the starting materials. However, when the temperature of synthesis and crystal growth is low, it is possible to make well-ordered solid materials in which the bonding within the reactant molecules is

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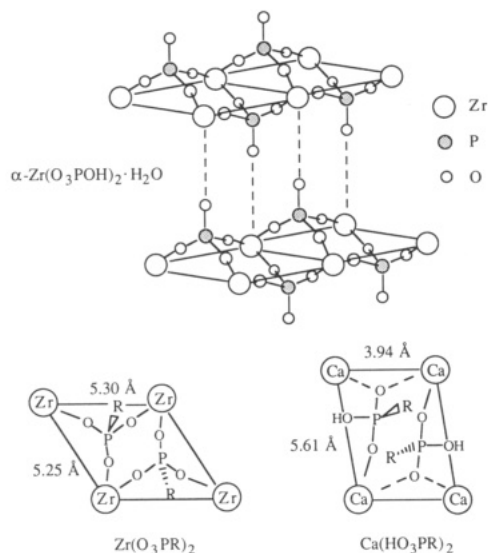


Figure 1. Idealized structure of α -zirconium phosphate, showing the pseudo-hexagonal unit cell, and schematic drawings of the related metal phosphonate structures $Zr(O_3PR)_2$ and $Ca(HO_3PR)_2$.

retained. Although this may not sound very special to an organic chemist, who is accustomed to using the reactivity of functional groups to bring together two halves of a molecule while retaining the integrity of each, to a solid-state chemist it is a rare luxury.

The second attractive feature of these materials that sets them apart from their inorganic analogues is their potential for *supramolecular* assembly. Since the structure of the layered solid is determined by strong ionic interactions between the metal ions and the phosphate groups, the organic groups that are "along for the ride" in the structure are geometrically disposed in predictable ways. This property allows one to design structures for purposes other than simple ion exchange or catalysis. For example, the organic groups can be juxtaposed in such a way as to facilitate an intralayer polymerization reaction or a molecular recognition event such as binding of a particular analyte. The lamellar structure of these materials also allows for supramolecular assembly in the third dimension, i.e., along the stacking axis, if one can design a synthesis whereby the solid is built up one layer at a time. This Account describes recent efforts we and others have made to develop these nontraditional applications of layered metal phosphate and phosphonate salts.

Structures and Synthesis

With very few exceptions,⁷ metal phosphonate salts form layered structures in which the metal ions and phosphonate oxygen atoms lie in puckered sheets. The bonding requirements of the metal determine the atomic arrangement within these layers, which is rather insensitive to the nature of the organic group. Figure 1 compares the structure of α -zirconium phosphate,⁸ $Zr(HOPO_3)_2 \cdot H_2O$, with those of the organic phosphonates $Zr(RPO_3)_2$ ($R = \text{alkyl, aryl}$) and $Ca(RPO_3)_2$. One can immediately see a common structural motif,

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Table I
Structural Relationships between Metal Phosphonates and Inorganic Phosphates

compound	space group	ref	inorganic relative	ref
$Zr(RPO_3)_2$	$C2/c$	9	α - $Zr(HOPO_3)_2 \cdot H_2O$	8
$Ca(RPO_3)_2$	$P1$	10	α - $Zr(HOPO_3)_2 \cdot H_2O$	8
$M(RPO_3)_2 \cdot H_2O$ ($M = Mg, Mn,$ Zn, Co, Ni)	$Pmn2_1$	11	$FeNH_4PO_4$	12
$VO(CH_3PO_3) \cdot 1.5H_2O$	$Pmmm$	13	$VO(HOPO_3) \cdot 0.5H_2O$	14
$VO(C_6H_5PO_3) \cdot 2H_2O$	orthorhombic	15	$MgHOPO_3 \cdot 3H_2O$	16
$VO(C_6H_5PO_3) \cdot H_2O$	$C2/c$	17	α - $VO(HOPO_3) \cdot 2H_2O$	14
$HfFe(C_6H_5PO_3)_2 \cdot H_2O$	monoclinic	18	α - $Zr(HOPO_3)_2 \cdot H_2O$	8
$Cu(RPO_3)_2 \cdot H_2O$	$P2_1/c$	19	unknown	
$Ca(RPO_3)_2 \cdot H_2O$	$P2_1/c$	10	unknown	
$Ln(RPO_3)_2(RPO_3)$	$P1$	10, 20	unknown	

namely, the planar network of tetra- or divalent metal ions^{9,10} knitted together by phosphonate oxygens above and below the layer plane. The tetravalent organic structure is simply derived from the inorganic one by the attachment of the R groups to the inorganic scaffolding. The calcium phosphonate structure is nearly the same, but is distorted slightly in order to accommodate two extra protons per formula unit that are needed for charge balance. Most of the known metal phosphonate structures are related in a similar manner to purely inorganic compounds,⁹⁻²⁰ and the correspondence is shown in Table I. Interestingly, the phosphonate salts of a particular metal are often structurally related to the inorganic phosphate of a different metal. For example, there are no known magnesium phosphonates that resemble the mineral newberyite, $MgHOPO_3 \cdot 3H_2O$. Rather, the magnesium phosphonates $Mg(RPO_3)_2 \cdot H_2O$ are structurally related to $FeNH_4PO_4$, and it is the vanadyl phosphonate $VO(C_6H_5PO_3)_2 \cdot 2H_2O$ that has a structure closely related to $MgHOPO_3 \cdot 3H_2O$.

Apart from the vanadyl phosphonates, which are made by alcohol reduction of V_2O_5 in the presence of

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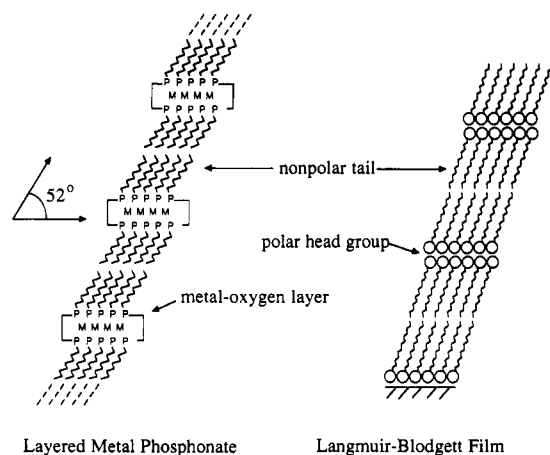


Figure 2. Structural analogy between metal phosphonate salts and Y-type Langmuir-Blodgett films. The tilt angle in the former is inferred from powder X-ray diffraction data for $Zr(O_3PC_nH_{2n}PO_3)_3$.³⁶

a phosphonic acid, layered compounds of this type are normally made by simple precipitation reactions in which a source of metal ions is mixed with a solution of the appropriate organic phosphoric or phosphonic acid. Since the precipitation of salts of M^{n+} involves the loss of n protons from weak acids, the reaction is pH-dependent. Diffraction-quality crystals can sometimes be obtained by slowly increasing the pH of an acidified metal phosphonate solution,^{10,11,19,20} although if the metal ion charge is high (3+ or greater) the compound may be too insoluble for this approach. Alternatively, the metal ion can be bound in solution by a complexing agent (usually F^-) that is slowly removed (as volatile HF).²¹ Often it is impossible to obtain single crystals for X-ray structure determination, but in these cases the unit cell dimensions can be determined from X-ray powder diffraction data and/or electron diffraction,²² allowing one to guess at the three-dimensional structure by analogy to inorganic models. Recently, Thompson and co-workers showed that solid-state NMR techniques can be very useful in determining the disposition of organic groups within the layers in the absence of single-crystal X-ray data.²³

Layer-by-Layer Growth of Metal Phosphonate Thin Films

One of the most striking features in all of the layered metal phosphonate structures is their similarity, in the "long wavelength view", to bilayer membranes, liposomes, and Langmuir-Blodgett (LB) films. Figure 2 shows this structural analogy. In Y-type LB multilayer films, amphiphilic molecules are stacked head-to-head and tail-to-tail to make layers of alternating polar and nonpolar groups. In the metal phosphonate structures the situation is similar, except that the polar part is held together by strong ionic bonds between the metal and phosphonate ions. LB films²⁴ have been quite exten-

sively studied since their discovery in the 1930s and are interesting as ultrathin photoresists,²⁵ electron tunneling spacers,²⁶ molecular diodes,²⁷ passive insulators for semiconductors,²⁸ chemical sensing elements,²⁹ and nonlinear optical devices,³⁰ to name a few possible applications. There are, however, two serious disadvantages to LB monolayers and multilayers that limit their practical utility. First, they are metastable structures and are therefore easily disrupted by, for example, a dust particle. Second, since they are grown by the transfer of preassembled monolayers from an air-water interface, they can generally be applied only to planar or nearly planar substrates.

In an attempt to overcome the shortcomings of the LB method, Jacob Sagiv and co-workers at the Weizmann Institute developed a technique for growing layered siloxane films, in which the head groups of one layer are bound covalently to the tails of the next.³¹ Multilayer films produced in this way are structurally analogous to Z-type (head-to-tail) LB films. Their work represented a conceptually novel strategy of sequential adsorption/chemical activation steps, which allowed them to grow mechanically robust films on planar as well as nonplanar surfaces. Unfortunately, the α -chlorosilane- ω -alkene molecules that they chose did not permit stacking of more than 2-3 layers before structural defects occurred in the film. More recently, Ulman and co-workers showed that one can make thicker and more well-ordered multilayer films, using a modification of Sagiv's technique in which interlayer bonds are formed from carboxylates rather than alcohols.³²

It occurred to us that, since metal phosphonates represent thermodynamically stable and extremely insoluble layer structures, they might form ordered inorganic analogues of LB films if a strategy could be developed for growing them one layer at a time on surfaces. This was accomplished by simply exposing a suitably prepared surface to solutions of the appropriate metal salt and α,ω -bis(phosphonic acid) alternately.³³ In this reaction scheme, an "anchoring" molecule, which bears a surface active group (thiol or silanol) at one end and a phosphonate group at the other, is first adsorbed. This molecule provides a binding site for metal ions, which are then adsorbed as a monolayer from aqueous solution. In the next step, one end of an α,ω -bis(phosphonic acid) binds to the adsorbed metal ion layer, and the other end is then free

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to bind the next layer. These adsorption steps are repeated as often as desired in order to produce multilayer films. The sequential dipping procedure can be automated, and films containing 100 or more layers can now be grown routinely.

The success of this approach to growing stable layered films derives from the exceptionally strong affinity of metal ions, particularly those of high charge, for the RPO_3^{2-} ($R = \text{alkyl, aryl, OH, OR}'$) group. Thus, the building blocks of the solid (e.g., zirconyl chloride and phosphonic acids) are individually soluble in water, but together they form salts that are quite insoluble even in strong mineral acids. This kind of "Velcro" interaction (strong attraction for each other, but not for themselves) between the two components ensures that only a single layer of either the metal or the phosphonic acid binds at a time. Time-resolved ellipsometry of the growing films³³ shows that most of the monolayer binds irreversibly to the surface within a few seconds of exposure to either component.

Since the structures of various metal salts of n -alkylphosphonic acids are quite similar, it is possible to prepare well-ordered films that contain different metal atoms in different layers. A triple-decker film containing Y^{3+} , Zr^{4+} , and Hf^{4+} in separate layers was used to illustrate this point. Angle-resolved XPS provides a sensitive means for depth profiling these films, since the escape depth of photoelectrons depends on the angle, relative to the surface normal, at which they are collected. This technique showed that the three different metals lay in approximately planar sheets that were separated by the length of the phosphonate spacer groups.³⁴ Together with other characterization techniques, particularly ellipsometry,^{33,35} reflectance-absorbance infrared spectroscopy,³⁶ electrochemistry,^{33,37} elemental analysis, and X-ray diffraction,³⁸ these measurements have allowed us to put together a composite picture of the structure of metal phosphonate thin films. Ellipsometric measurements show that $Zr-(O_3PC_nH_{2n}PO_3)$ films grow in stepwise fashion, with an increase in thickness per layer corresponding closely to the layer spacing in well-annealed bulk solids for $n = 6-10$. With shorter chain phosphonic acids the spacing is more irregular, possibly a consequence of weaker self-assembly (i.e., collective van der Waals) forces which help to order the alkyl chains. These films are quite impervious to solution species, and even a single monolayer will block $Fe(CN)_6^{4-}$ ions from transferring electrons to an underlying gold surface.^{33b,37} Somewhat thicker films (10–20 layers thick) are sufficiently impenetrable and pinhole-free to act as insulators in metal-insulator-semiconductor and metal-insulator-metal sandwich devices, in which the metal top contact is applied by thermal evaporation.³⁵

Infrared spectral line widths and frequencies of C–H stretching modes are particularly sensitive to the degree of order of polymethylene chains in self-assembled monolayers and pure n -alkanes.³⁹ Measurements of

line widths for the asymmetric and symmetric CH_2 stretching vibrations in $Zr(O_3PC_{10}H_{20}PO_3)$ multilayer films give values (FWHM = 39 and 22 cm^{-1}) that are intermediate between those of the well-crystallized²¹ bulk solids (27 and 12 cm^{-1}) and the poorly crystalline samples made by rapidly mixing zirconyl chloride and 1,10-decanediylbis(phosphonic acid) solutions (55 and 24 cm^{-1}). This result may be understood in terms of the size of tilt domains within the films, which are smaller than those typically found in well-ordered alkanethiol monolayers.³⁹ Most importantly, the infrared line widths remain constant as additional layers are grown, indicating that each new layer has the same degree of structural order as the preceding ones. X-ray diffraction line widths, which decrease with an increasing number of layers, corroborate the ellipsometric measurements of total film thicknesses.³⁸

The zirconium phosphonate structure is quite forgiving with respect to which organic groups it will accommodate, the only requirements being a cross-sectional area of 24 \AA^2 or less and sufficient conformational flexibility to allow the metal-oxygen-phosphorus network to adopt its usual geometry. This property has allowed us and others to build interesting chemical functionality into multilayer metal phosphonate films. It is well-known from the early work of Dines,⁴⁰ and later Clearfield et al.,⁴¹ that one can prepare solids that contain molecule-sized void spaces from mixtures of phosphonic acids. When they are Ostwald-ripened by refluxing in aqueous HF, these solid solutions form crystalline segregated phases and their microporosity is lost. However, since layer growth in the thin films is essentially complete within a few seconds, phase separation is inhibited and it is possible to obtain surface layers with interesting molecular sieving properties. For example, from a mixture of pillaring 1,10-decanediylbis(phosphonic acid) and inorganic phosphoric acid, one obtains microporous films that contain exchangeable protons (from the acidic phosphate OH group). Electroactive cations smaller than 10 \AA in diameter can be ion-exchanged into the film and seen electrochemically, whereas larger cations are excluded. The latter do intercalate into metal phosphonate films, but only when most or all of the pillaring groups have been removed, allowing the layers to separate.⁴²

Katz and co-workers at AT&T Bell Laboratories have recently given this method a new twist, aligning hyperpolarizable molecules into polar (i.e., noncentrosymmetric) multilayer films.⁴³ The key to their success in these experiments has been to design a three-step adsorption sequence involving molecules with a phosphonate group at one end and a hydroxyl at the other.

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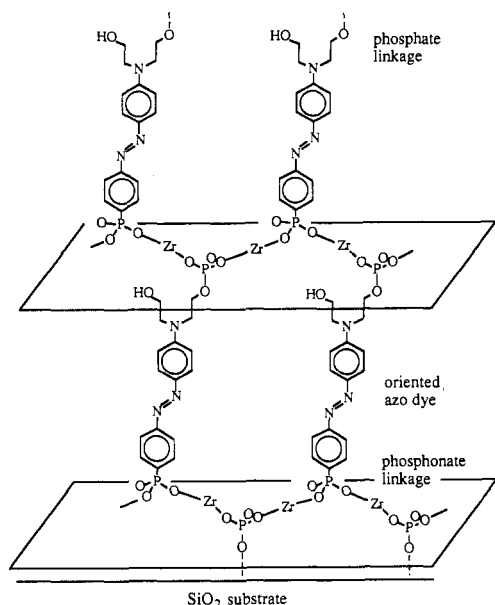


Figure 3. Polar zirconium phosphate/phosphonate multilayer film containing oriented azo dye molecules, prepared by a three-step adsorption sequence.^{43d}

The phosphonate end of the molecule is adsorbed onto a Zr^{4+} layer, and the exposed hydroxyl group is then converted to an organic phosphate with $POCl_3$. Zr^{4+} is adsorbed onto the phosphate layer, and the three-step sequence is then repeated to build up multilayer films. They have now made polar films (Figure 3) that show second-order nonlinear optical effects comparable to those of $LiNbO_3$, one of the most widely used inorganic nonlinear materials. Because the intensity of second harmonic generation increases with the square of film thickness up to ca. 30 layers, it may be inferred that all layers contain dye molecules with the same degree of polar orientation. Most significantly, the inorganic superstructure imparts orientational stability to the dye molecules up to at least 150 °C (at which temperature the azo dye itself begins to decompose). Other polar organic media, such as Z-type LB multilayers and poled polymers, undergo orientational randomization at much lower temperatures.

Topochemical Reactivity and Synthesis

The experiments of Katz et al., described above, provide an impressive demonstration of the role of inorganic superstructure in preserving the orientation of organic groups from layer to layer in metal phosphonate films. This structure-directing property can also be used to control the juxtaposition of reactive organic groups *within* layers, so as to align them for a topochemical reaction. We were particularly interested in intralayer diacetylene polymerization, a reaction which has been studied extensively in organic crystals⁴⁴ and layered cadmium halide/alkylammonium ("layer perovskite") salts.⁴⁵ Thin films of polydiacetylenes have shown significant potential for use in ultrafast signal processing because of their unusual nonlinear optical properties.⁴⁶ In principle, one might also use

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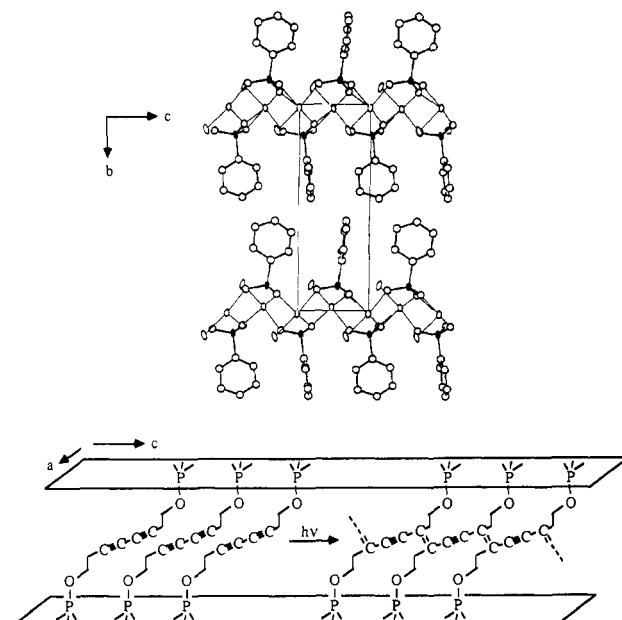


Figure 4. Top: Structure of $Mn(O_3PC_6H_5) \cdot H_2O$ viewed down the crystallographic a -axis; phosphorus and phenyl groups lie on mirror planes in the structure.¹¹ Bottom: Schematic representation of diacetylene polymerization along the c -axis in phosphate salts of the divalent metals Mn, Mg, and Zn.

this technique to grow ultrathin negative resists for X-ray or scanning probe (STM or SECM⁴⁷) microlithography, of which there have been a limited number of attempts⁴⁸ using diacetylene-containing LB films.

The solid-state polymerization of diacetylenes, shown schematically in Figure 4, is a radical addition reaction which yields high polymers only if the monomer units are aligned properly and if polymerization induces minimal strain in the host lattice. For these requirements to be met, the monomer chains must be essentially coplanar; simple geometric considerations also dictate that the optimal separation between monomer head groups must be between 4.7 and 5.2 Å. A glance at the structures shown in Figure 1 reveals that the head group separation distances are on the order of 5.3–5.6 Å, and the R groups are tilted in noncoplanar fashion. Consequently, only short chain oligomers are formed upon photolysis of La, Y, and Sm diacetylene diphosphate monomer salts, and the Ca and Cd salts have an even lower reactivity.⁴⁹ However, the phosphonate salts $M(O_3PR) \cdot H_2O$ of the smaller divalent metal ions (Mn, Mg, and Zn) crystallize in space group $Pmn2_1$. The special feature of this structure is that it contains a symmetry plane perpendicular to the crystallographic a -axis, which constrains all of the R groups to be coplanar. Fortunately, the head group separation (along the c -axis) is 4.8 Å, which is in the correct range for topochemical diacetylene polymerization. The diacetylene monomers are therefore prealigned for opti-

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mal reactivity in this structure, and a much higher degree of polymerization is found.

Another kind of interlayer reaction which takes special advantage of metal phosphonate symmetry and host-guest interactions is the epitaxial growth of semiconductor particles of nanometer dimensions. Interest in the transition from molecular to bulk electronic properties and, perhaps to a lesser extent, the prospects of practical applications in nonlinear optics⁵⁰ and photocatalysis⁵¹ has stimulated intensive research on semiconductor "quantum dots" over the past few years.⁵² In a more general sense, the epitaxial growth of inorganic materials at surfactant-liquid interfaces,⁵³ and within host media such as polymers⁵⁴ and zeolites,⁵⁵ is also a topic of much interest because of analogies to biomineralization processes.

The interlayer spaces of metal phosphonate crystals provide a well-ordered yet flexible matrix in which to carry out such reactions. By using phosphonic acids that terminate in either sulfonate⁵⁶ or carboxylate⁵⁷ groups, exchangeable protons are introduced into the structure. These protons can be easily replaced by Cd²⁺ ions to give salts such as $Zr[(O_3PCH_2CH_2COO^-)_2Cd^{2+}]$, in which the guest cadmium ions lie midway between the ionic zirconium-oxygen sheets of the host. Exposure of this solid to gas-phase H₂Se results in slow conversion to $Zr[(O_3PCH_2CH_2COOH)_2]/CdSe$. In the latter, cubic (zincblende-type) CdSe particles of 40–50 Å in diameter are dotted throughout the platelike crystallites of the host material. What is quite interesting in this case is that the semiconductor particles are not only monodisperse in size but are rotationally ordered with respect to each other. Electron diffraction from a single host microcrystal (which includes very many guest CdSe particles) gives rise to a 6-fold spot diffraction pattern, as if the reflections were from a single CdSe crystal; however, reflections from the host are absent following exposure to H₂Se. These observations may be rationalized as follows: the zirconium phosphonate crystal imposes rotational order on the guest nuclei, so that their 3-fold [111] zone axis is coincident with the pseudo 6-fold axis of the host. As these particles nucleate relatively far from each other and then grow to a size which greatly exceeds the original interlayer spacing, the flexible host layers buckle around them and lose long-range order. Apparently the particles grow sufficiently large, before the order of the host lattice is destroyed, that they cannot reorient.

Having grown from epitaxial nuclei, these particles thus retain the memory of their original orientation.

Molecular Recognition in Metal Phosphonates

The examples cited above of molecular-level control over guest intercalation, orientation, and reactivity in layered metal phosphonates suggest that it should be possible to engineer solids in which guest molecules bind according to their shape and chemical properties. Successful examples of both biological and non-biological molecular recognition generally involve multiple host-guest interactions, which act in concert to impart specificity to the process.^{58,59} In metal phosphonates this kind of cooperativity has been achieved using steric repulsion, in order to define the shape of the binding site, together with attractive interactions which serve to anchor the guest molecule. Two binding modes have been demonstrated so far: ligation of amines and alcohols at geometrically well-defined, coordinatively unsaturated metal sites and noncovalent binding of guest molecules at complementary hydrogen bonding/aromatic π -stacking sites.

Formation of a shape-selective pocket for ligand binding in layered metal phosphonates has, in the two examples studied to date, involved synthesis around a "template" molecule. The latter is a ligand, such as water or a primary alcohol, that occupies a metal coordination site. The interlayer volume is filled efficiently by the covalently bound organic groups and the weakly bound template. If the template can be removed topochemically (i.e., with retention of the remaining structure), a well-defined binding site for electron donor ligands is created. Johnson and co-workers first discovered this effect⁵⁹ in the vanadyl phosphonates $VO(O_3PR) \cdot H_2O \cdot R'OH$, where R is an *n*-alkyl group and R'OH is benzyl alcohol. The benzyl alcohol molecule occupies one of six vanadium coordination sites and can be thermally removed to yield $VO(O_3PR) \cdot H_2O$. This compound has the same unit cell dimensions as the parent compound in the plane of the V–O–P network, and one may thus reasonably conclude that loss of benzyl alcohol occurs topochemically. Primary alcohols bind at the open coordination site and cause expansion of the layers, but alcohols with branching at the α -position, such as *sec*- and *tert*-butyl alcohol, are sterically excluded.

The divalent metal phosphonates $M(O_3PR) \cdot H_2O$ ($M = Mg, Mn, Co, Zn$) undergo a similar reaction.⁶⁰ In this structure (Figure 4), the water molecule occupies one of six metal coordination sites and may be topochemically removed by heating. What is quite interesting about the anhydrous compounds in this series is that their intercalation reactions follow trends in the aqueous coordination chemistry of the metal ions, that is, the magnesium compounds are unreactive with amines and prefer oxygen-containing ligands, whereas the zinc compounds prefer amine ligands and will intercalate them even from aqueous solutions. With R = methyl, these compounds have shape selectivity similar to that observed by Johnson et al., namely, that only amines

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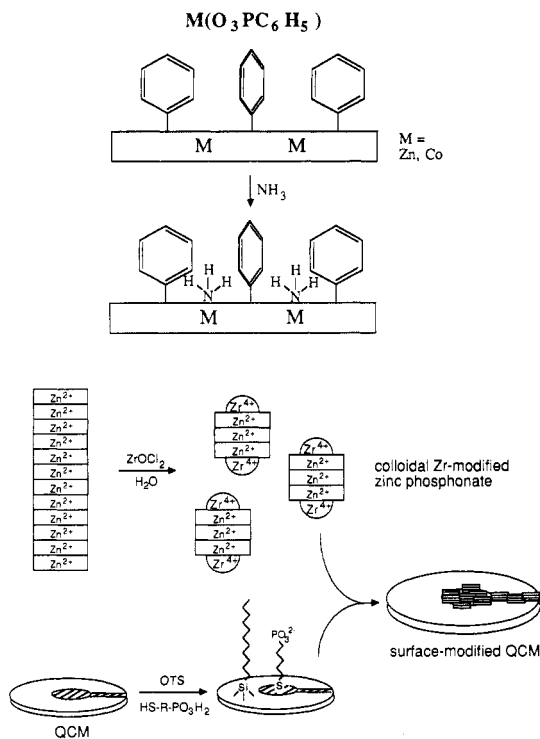


Figure 5. Top: Ammonia intercalation into $M(O_3PC_6H_5)$ ($M = Zn, Co$) prepared by topochemical dehydration of $M(O_3PC_6H_5) \cdot H_2O$. Bottom: Derivatization procedure for QCMs.

with no branching at the α -position are reactive. The $R =$ phenyl compounds provide a much more restrictive binding site, and in this case only ammonia will intercalate (Figure 5).

Recently, we developed shape-selective sensors for ammonia and primary amines on the basis of these reactions.⁶¹ A colloidal suspension of $Zn(O_3PR) \cdot H_2O$, in which individual particles are capped with Zr^{4+} , is prepared by reaction with aqueous $ZrOCl_2$. A quartz piezoelectric crystal with gold electrodes, functionalized with octadecyltrichlorosilane (OTS) and a thiol/phosphonate anchoring agent, is exposed to the colloidal particles, which then bind exclusively to the gold surface. Quartz crystal microbalance (QCM) sensors are extremely sensitive, responding to surface mass changes of as little as 1 ng. Upon thermal dehydration at 100 °C, the derivatized sensors react rapidly with gas-phase analytes, and large mass changes (hundreds of nanograms to micrograms) are seen within seconds of exposure to a few torr of ammonia or amines. The intercalation reaction may be thermally reversed at 165 °C, and these sensors have been cycled several times with no evidence of degradation.

An even more demanding form of molecular recognition is selective binding of a single enantiomer from a racemic solution. Such solid/analyte interactions form the chemical basis for enantiomer separation by high-performance liquid chromatography (HPLC).⁶² While an enormous body of literature representing tremendous collective effort on this subject already exists, there is a basic problem, namely, the limited capacity of conventional chromatographic support

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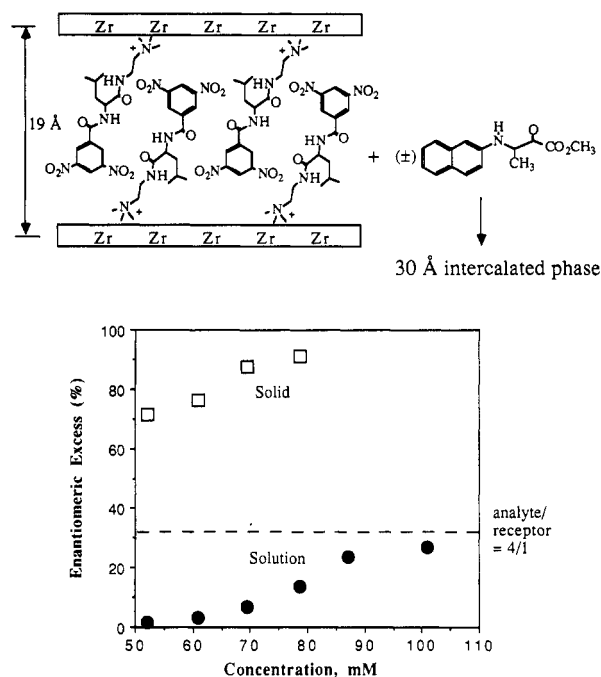


Figure 6. Top: Schematic structure of the cationic "Pirkle-phase" receptor intercalated into α -zirconium phosphate and structure of the racemic analyte. Bottom: Solution- and solid-phase enantiomeric excesses (ee) plotted against analyte concentration. The dotted line represents maximum theoretical solution ee, 33%, for molar composition 4/1 analyte/receptor.

materials such as silica for preparative-scale separations. An intercalated layer compound, being essentially 100% surface, represents a potential solution to this problem if it can be made to intercalate with chiral selectivity.

In approaching this problem, we selected a chiral receptor/analyte matched set from the Pirkle collection.⁶³ The receptor in this case is an enantiomerically pure amino acid derivative, which binds a chiral naphthylamine derivative through a three-point (two hydrogen bonds and one π -stacking interaction) recognition mechanism. A cationic derivative of the Pirkle receptor, ion-exchanged for protons in α -Zr-($HOPO_3$)₂· H_2O , expands the layer spacing of the latter from 7.6 to 19 Å. This material intercalates the analyte (Figure 6)⁶⁴ to form a 30-Å phase. Interestingly, very little intercalation of either enantiomer occurs at low analyte concentration, implying that a certain threshold must be reached in order to supply the driving force for separating the layers to 30 Å. Once that threshold is passed, however, the selectivity for the correct enantiomer is excellent, and the capacity is ca. 10^{-3} mol/g, an order of magnitude higher than that of conventional chiral stationary phases.

Summary and Conclusions

Layered salts of phosphoric and phosphonic acids are a versatile class of materials, amenable to structural design by modulation of both their ionic frameworks and organic constituents. Studied for many years as ion exchangers and catalysts, these solids now show promise of a much wider range of reactivity and device applications, which derive from their structural tunability, chemical and thermal stability, and morphological similarity to well-studied and useful phases such

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as LB films. This Account has described only those new reactions and applications that have been devised within the past few years, and it is certain that many more will be dreamed of in the years to follow.

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Account. We also thank our co-workers, past and present, who have taken this project in many creative directions. This work has been supported by grants from the National Institutes of Health (GM43844), the National Science Foundation (CHE-8657729), and the Robert A. Welch Foundation. T.E.M. also thanks the Camille and Henry Dreyfus Foundation for support in the form of a Teacher-Scholar award.

Vibrational Spectroscopy of High-Temperature, Dense Molecular Fluids by Coherent Anti-Stokes Raman Scattering

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The behavior of liquids and dense fluids has been the subject of several previous Accounts.¹⁻³ In a dense fluid the short-range repulsive interparticle (or intermolecular for our studies) forces dominate and determine the structure and thermodynamic behavior of the fluid.¹⁻⁴ This dominance is especially true in materials subjected to shock waves or explosive detonations in which the densities may be two or more times the initial densities and temperatures may be several thousand degrees. The structure, thermodynamics, energy transfer, and chemical reactions of dense fluids have been described theoretically in terms of intermolecular (and intramolecular, for interactions within the molecule) potential functions and statistical mechanical treatments.^{1,3-13} For liquids of not too high density, pairwise additive potential functions can be used. However, many-body effects necessitate corrections for the high-temperature dense fluids of interest in this Account.^{1,3,6}

Experimental confirmation of these theoretical descriptions, especially for high-temperature dense fluids, has been obtained in several ways. First, these descriptions have been compared with the results of hydrodynamic/thermodynamic experiments such as shock Hugoniot measurements^{4,9} or with numerical simulations, that is, computer experiments.^{5,8} A shock Hugoniot is the locus of all pressure-volume end states attainable by a shock wave propagating into a particular initial pressure-volume state. The problem is that

macroscopic experiments such as shock Hugoniot measurements average over the microscopic (that is, molecular) aspects of the fluid and are, therefore, inadequate for a complete understanding of dense fluid behavior. Consequently, present models of dense fluids have been verified only to the extent that they agree with such bulk property measurements. A complete verification of these models requires more experimental data,³ particularly from experiments that provide insight at the molecular level. In this Account, we describe an experiment, based on combining shock-compression techniques and nonlinear optical scattering methods, that was used to explore the microscopic aspects of dense fluid nitrogen, oxygen, and carbon monoxide. These simple diatomic molecules were chosen because initial results are easy to interpret and because these molecules are important in explosive applications.

The Experiment

Spectroscopic measurements, when possible, can provide the desired microscopic level information. Recently, we have been able to probe some of the microscopic phenomenology of high-temperature dense fluids^{14,15} using samples of liquid nitrogen, oxygen, and

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