

# Use of Layered Metal Phosphonates for the Design and Construction of Molecular Materials

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Layered metal phosphonate compounds can be used to prepare organic/inorganic materials with predetermined solid state structures. These phosphonate compounds can be prepared in three forms: microcrystalline solids, multilayer thin films, and porous solids. The syntheses of all three of these types of material will be described. The structures and optical properties of these materials will also be discussed. The emphasis of this review is in the use of tetravalent (particularly Zr) metal ions.

## Introduction

Our understanding of the physical properties of molecular inorganic and organic compounds is based largely on studies of these compounds in solution or in the gas phase. Chemists have developed the ability to tune the structural and electronic properties of molecular species very well. This ability to tune the electronic properties of these compounds could be very useful in designing new materials for a large number of different applications, ranging from heterogeneous catalysis to integrated electronics and optoelectronics. For many of these applications to be realized, the molecules must be aligned in the solid state so that the tailored electronic structure of the molecules constructively add to give the desired bulk property. Unfortunately, controlling the solid-state structure of molecular compounds is not straightforward. Many different techniques have been developed for encouraging molecular species to adopt predictable structures. Adding hydrogen-bonding groups to the periphery of a given molecule can lead to the formation of a predictable hydrogen-bonding network and structure.<sup>1</sup> A related approach involves the use of coordination polymerization to align inorganic complexes.<sup>2</sup> Incorporation of a molecule into a crystalline host lattice to form an inclusion<sup>3</sup> or intercalation<sup>4</sup> compound can lead to ordered materials. The application of an external field can lead to a net alignment of polar molecules dissolved in fluid medium.<sup>5,6</sup> This alignment can be frozen in at room temperature if the fluid medium is a molten polymer or glass. Langmuir-

Blodgett (LB)<sup>7</sup> and self-assembly (SA)<sup>8</sup> techniques have been successfully used to organize amphiphilic molecules into highly ordered lamellar structures. Langmuir-Blodgett relies on organization of the amphiphilic molecule at a liquid/air interface, to give an ordered monolayer. Multilayers are formed by transferring these monolayers onto a planar substrate. Self assembly involves a similar interfacial organization, but now at a solid/liquid interface. In contrast to LB films, most SA films have strong (often covalent) bonding within the hydrophilic layer. Both LB and SA techniques have been studied very extensively, and shown to lead to a high degree of alignment.

Metal phosphonates are useful for organizing molecules into lamellar structures. The structures formed in these metal phosphonates are very similar to those formed by LB and SA techniques but have better thermal stabilities than LB films. Metal phosphonates can be prepared as microcrystalline solids or as thin films on a variety of substrates. Adjacent lamellae can have a fixed orientation relative to each other, leading to solids which are ordered in three dimensions, or adjacent lamellae can be randomly oriented, leading to solid with good bulk order in only one dimension (the layer normal). This review will focus

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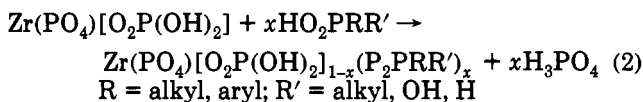
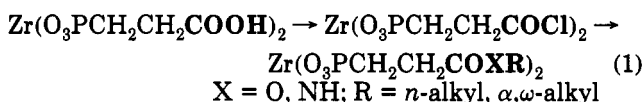
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principally on the use of tetravalent metal phosphonate compounds for the controlled organization of organic molecules in the solid state. The syntheses, structures and properties of layered compounds will be discussed. Both microcrystalline solids and multilayer thin films will be covered.

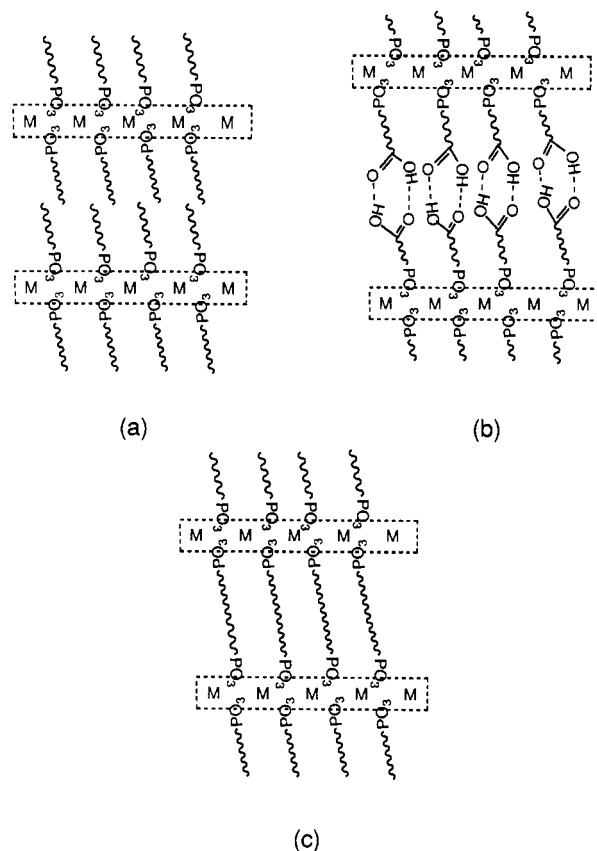
### Synthesis of Metal Phosphonates

Metal phosphonate compounds formed with di- and trivalent metal ions are more soluble than their tetravalent counterparts. As a result it is often possible to obtain crystals suitable for single-crystal X-ray diffraction of these materials by simple slow precipitation.<sup>9</sup> While crystals large enough for single-crystal X-ray diffraction cannot be typically obtained, microcrystalline samples of tetravalent metal phosphonates can be prepared by adding a strong complexing agent to solubilize the material. HF is the most common complexing agent, forming a soluble metalpolyfluoride (e.g.,  $ZrF_6^{2-}$ ). As the HF is removed from the system the metal polyfluoride decomposes, and the metal phosphonate crystallizes. This slow, HF-assisted, synthesis works well for preparing metal phosphonates from a wide range of different metal ions (i.e., Ti, Zr, Hf, Th, Sn, U, Ce) with phosphonates bearing a number of different functional groups [ $M(O_3P-R-X)_2$ ; R = alkyl, aryl; X = halide, pseudohalide, carboxyl, nitro, sulfonate, alcohol, amine, vinyl].<sup>10</sup> The only restrictions on the organic group are that it must be stable in hydrofluoric acid and that it can not be too large (vide infra). VO phosphonates are not prepared by slow precipitation with HF, but by reduction of  $V_2O_5$  in the presence of the desired phosphonic acid.<sup>11</sup>

It is also possible to form related materials by direct reaction of a preformed metal phosphonate with external reagents. For instance, it is possible to make highly crystalline samples of  $Zr(O_3PCH_2CH_2COOH)_2$  and in a two-step process convert this carboxylic acid derivative into well-ordered (layered) ester or amide compounds (eq 1).<sup>12</sup> The ester compound could



not be formed by the usual HF treatment, because the ester hydrolyzes under these conditions. Phosphonate derivatives can also be prepared directly from the zirconium



**Figure 1.** (a) Schematic representation of a layered metal phosphonate, viewed from the edge of the layers. (b) A metal phosphonate with interlayer hydrogen bonding. (c) A metal phosphonate with covalent interlayer bonding.

phosphate compounds by an exchange reaction. Two forms of zirconium hydrogen phosphate have been identified. One form is the  $\alpha$ -phase and consists of two hydrogen phosphate groups [i.e.,  $\alpha$ - $Zr(O_3POH)_2 \cdot H_2O$ ], while the  $\gamma$ -phase has two different types of phosphate [i.e.,  $\gamma$ - $Zr(PO_4)[O_2P(OH)_2]$ ]. In the  $\gamma$ -phase, the dihydrogen phosphate groups can be exchanged for alkyl and dialkyl phosphonates to give layered metal phosphonates (eq 2).<sup>13</sup> Similar exchange reactions have been reported for both the  $\alpha$ -phase and  $\gamma$ -phase phosphates with phosphate esters as well.<sup>14</sup>

### Structures of Metal Phosphonates

The most common structural motif for metal phosphonate compounds is a layered one. In these solids the phosphonate oxygens bond strongly to the metal ions, forming a tightly bound inorganic layer, with the organic groups lying between the inorganic lamellae (Figure 1). These inorganic layers can be built from planes of metal atoms, with the phosphonates lying above and below the plane. The phosphonates are bonded to two or three different metal atoms. This arrangement forces the P-C bond to be oriented away from the inorganic sheets,

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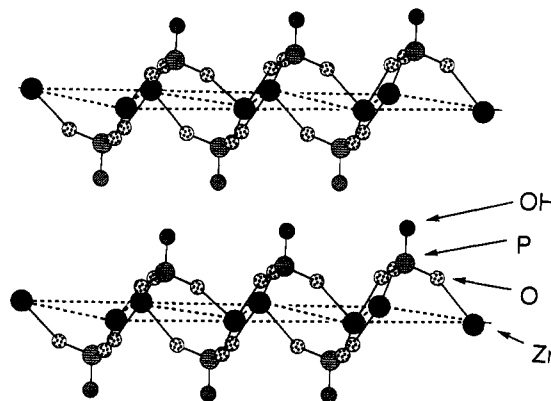
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forming the organic bilayer between the inorganic lamellae. In simple alkyl phosphonates, the bonding between adjacent layers is relatively weak, consisting of van der Waals bonding between the end groups of the alkyl chains of adjacent layers. Stronger interlayer bonding exists if hydrogen bonding groups are incorporated at the ends of the alkyl chains, e.g.,  $M(O_3PCH_2CH_2COOH)_2$  ( $M = Sn, Zr$ ; Figure 1).<sup>15</sup> Covalent bonding between adjacent layers is present in materials formed from bisphosphonic acids, e.g.,  $M(O_3P-R-PO_3)$  ( $R = \alpha, \omega$ -alkyl, aryl;  $M =$  tetravalent metal ion; Figure 1).<sup>10,16</sup>

This segregation of organic and inorganic groups into separate layers is a simple form of molecular engineering, and parallels the order seen in other systems. Layered metal phosphonates have structures reminiscent of lipid bilayers or multilayers prepared by LB or SA techniques, consisting of alternating hydrophilic and hydrophobic lamellar regions. In these materials the ionic head groups form a hydrophilic region, while the aliphatic chains form a hydrophobic region. In lipid bilayers, if the cross-sectional area of the organic group is significantly different from that of the head group, simple lamellar structures are not formed. Micelles and much more complicated structures are formed depending on the ratio of the size of the head group to the tail. For metal phosphonates, lamellar structures are formed for even the smallest organic groups [ $Zr(O_3PH)_2$  is a layered material<sup>17</sup>]. If the organic group has too large a cross-sectional area, simple lamellar structures are not formed. The reason for this size dependence is that the structures of these materials are dictated by the bonding in the inorganic network. The organic groups of metal phosphonate are forced to lie on a fixed scaffold, whose structure is dictated by the metal-phosphonate bonding. The lateral distance between organic groups can be altered by changing the metal ion used in forming the solid. For Zr compounds the organic groups must have the cross-sectional area equal to that of a phenyl group or less to give well-ordered layered structures. If the organic group has an area equal to or smaller than this critical size, a lamellar solid will be formed with the distance between neighboring organic groups being independent of the size of the organic group. The structure directing nature of these inorganic lamellae makes metal phosphonates very useful for organizing organic molecules.

The reasons that zirconium phosphonate compounds have been studied more than the other tetravalent metal compounds are that they are very stable and a large amount of information is known about the structure and properties of related metal phosphates of zirconium. The crystal structure of  $\alpha$ - $Zr(O_3POH)_2 \cdot H_2O$  was determined by Clearfield (Figure 2).<sup>10</sup> The phosphate groups are arranged in a hexagonal pattern above and below the sheets of zirconium ions, with 5.3 Å between adjacent hydroxyl groups. Interestingly, there is a strong intralayer hydrogen bonding network, involving the phosphate-OH groups and water molecules, but no interlayer hydrogen bonding in this compound. On the basis of spectroscopic and powder X-ray diffraction data, it has been proposed that the structures of tetravalent metal phosphonate compounds are closely related to  $\alpha$ - $Zr(O_3POH)_2 \cdot H_2O$ .<sup>10</sup> The inorganic sheets of these materials are thought to have the same



**Figure 2.** Structure of  $\alpha$ - $Zr(O_3POH)_2 \cdot H_2O$ . The water molecule and hydrogen atom have been left out for clarity.

bonding as is observed in the  $\alpha$  phase. Clearfield has recently determined the structure of  $Zr(O_3PC_6H_5)_2$  from a Rietveld analysis of powder X-ray diffraction data.<sup>18</sup> The structure of  $Zr(O_3PC_6H_5)_2$  is very similar to that of  $\alpha$ - $Zr(O_3POH)_2 \cdot H_2O$ . The principal difference between the two structures is that the tetrahedra of the phenyl phosphonate compound are tilted away from the layer normal slightly (i.e., P-C is not parallel to the layer normal). This tilting decreases the steric repulsions of the adjacent phenyl groups.

The structures of the organic portions of several of these layered metal phosphonates have been investigated as well. Both IR and powder X-ray diffraction data indicate that the alkyl chains of the simple alkyl phosphonate compounds are fully extended in an all transoid configuration in the interlamellar region. The dependence of the interlayer spacing on the identity of the R group is consistent with the P-C bonds being oriented perpendicular to the inorganic lamellae.<sup>10,12</sup>

The structure of the  $\gamma$ -phase of zirconium hydrogen phosphate [i.e.,  $Zr(PO_4)[O_2P(OH)_2]$ ] has not been determined crystallographically, but a good model for its structure has been put forth.<sup>19</sup> In this model each layer of the solid consists of two sheets of metal ions bridged by  $PO_4$  groups, with the dihydrogen phosphate groups bound with only two oxygens to the surfaces of these metal ion sheets. The result is that the two P-OH bonds are oriented toward the interlamellar region. Contrary to the situation found for the  $\alpha$ -phase, the P-OH bonds of the  $\gamma$ -phase are not orthogonal to the inorganic lamellae but lie nearly parallel to them. Phosphonate analogs of these compound have been prepared with both monoalkyl and dialkyl phosphonates. Interlayer spacings measured by powder X-ray diffraction of these organic materials are consistent with the structural model proposed for  $\gamma$ - $Zr(PO_4)[O_2P(OH)_2]$ .<sup>20</sup>

It has recently been shown that a more detailed picture of the arrangement of the organic groups in the interlamellar region can be obtained from orientational dependent NMR studies.<sup>21,22</sup> In this experiment NMR spectra are recorded with aligned thin films of the sample

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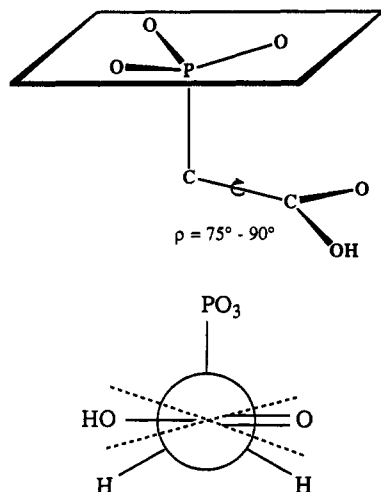
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(17) H is not an organic group, but what the heck, it is small.

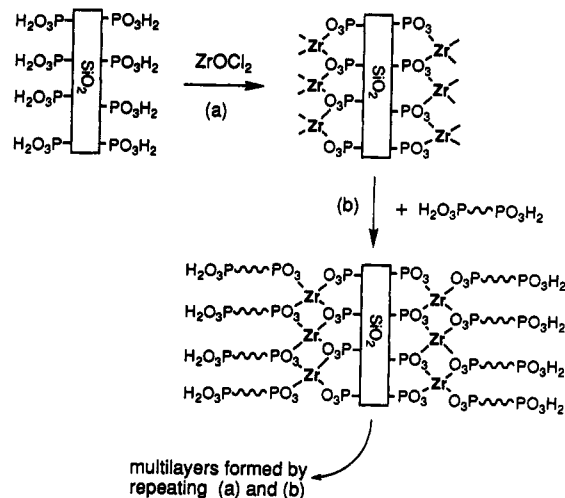


**Figure 3.** Orientations of the P-C bond and COOH plane relative to the inorganic layers that are consistent with the experimental data (top). Newman projection of a  $90^\circ$  P-C-C=O dihedral angle ( $\rho$ ) (bottom).

held at different orientations with respect to the applied magnetic field. By examining the dependence of the line shape on the orientation of the sample, it is possible to determine the arrangement of a given functional group relative to the layer normal. This technique was applied to  $\text{Zr}(\text{O}_3\text{PCH}_2\text{COOH})_2$ , and gave the structure shown in Figure 3. As expected, the P-C bond lies nearly orthogonal to the zirconium phosphonate lamellae. The carboxylic acid group has a P-C-C-O dihedral angle of  $90 \pm 15^\circ$ .<sup>22</sup> From this structure it is possible to rationalize a lower reactivity for  $n = \text{odd}$  relative to  $n = \text{even}$  for  $\text{Zr}[\text{O}_3\text{P}(\text{CH}_2)_n\text{COOH}]_2$  compounds.<sup>21</sup> For the  $n = \text{odd}$  compounds the steric constraints of the surface of the metal phosphonate lamellae act to retard the reactions of the carboxyl groups in these materials relative the  $n = \text{even}$  compounds, where the unfavorable steric interactions do not exist.

### Synthesis and Characterization of Thin Films

The materials described thus far are all microcrystalline solids. It is also possible to prepare many of these materials as thin films. The technique was first reported by Mallouk et al.<sup>23</sup> and involves several steps, outlined in Figure 4. The surface of the substrate is first derivatized with phosphonic acid groups; this treatment can be thought of as priming the surface. When this derivatized substrate is treated with an aqueous solution of the metal ion, the metal ions bind to the phosphonate groups on the surface, giving a metal-rich surface. The substrate is then removed from the solution, rinsed with water and treated with a solution of a bisphosphonic acid ( $\text{H}_2\text{O}_3\text{P}-\text{R}-\text{PO}_3\text{H}_2$ , R = alkyl, aryl, O). One of the phosphonate groups binds to the metal rich surface, while the other is left uncoordinated. The result is that the surface is now rich in phosphonate groups. The substrate is removed from the solution of the bisphosphonic acid, rinsed thoroughly, and treated with a solution of the metal ion again. Repeated sequential treatments with the bisphosphonic acid and metal solu-



**Figure 4.** Steps in the growth of multilayer metal phosphonate thin films.

tions leads to layer-by-layer growth of a metal phosphonate film. These metal phosphonate thin films are uniform and highly ordered (*vide infra*). Films can be grown on both planar and high surface area<sup>24</sup> supports. Film growth by this technique requires that the metal phosphonate compound to be grown as a thin film be very insoluble in the solvent that the growth is carried out in. If the metal phosphonate were even slightly soluble it would be dissolved in the growth solutions rather than deposited. Tetravalent metal phosphonate films are typically grown from aqueous solutions. Mallouk has shown recently that high quality thin films of divalent metal phosphonates can be grown from ethanol solutions.<sup>25</sup>

The structures and compositions of metal phosphonate thin films prepared by this method have been examined by a range of different techniques. Variable take off angle XPS studies are an excellent way to examine film uniformity and coverage. These studies indicate that metal phosphonate films cover the substrate well (very few defects)<sup>24a</sup> and that the metal atoms are confined to fairly thin layers between the alkylbisphosphonate groups.<sup>26</sup> Electrochemical and atomic force microscopy<sup>25</sup> measurements also show the uniformity of these films. Films as thin as one monolayer on a gold substrate are sufficient to completely block  $\text{Fe}(\text{CN})_6^{4-}$  oxidation by the gold electrode.<sup>24a,27</sup> Dielectric measurements also indicates that large ions such as ferrocyanide are blocked from the electrode, but show that somewhat smaller species (e.g.,  $\text{H}_2\text{O}$ ,  $\text{Cl}^-$ ) can reach the gold electrode.<sup>28</sup>

Interlayer spacings in these films have been measured ellipsometrically for many different films.<sup>23,29-32</sup> In every

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case the observed interlayer spacing for the films agrees with the value observed in a microcrystalline sample prepared from the same metal and bisphosphonate. Both ellipsometric and optical absorption<sup>24b,30,33</sup> data indicate that the same amount of material is being deposited in each cycle. For films of simple  $\alpha,\omega$ -alkylbisphosphonates, elemental analysis is consistent with the film having the same composition as the bulk materials [e.g.,  $\text{Zr}(\text{O}_3\text{P}-(\text{CH}_2)_n-\text{PO}_3)$ ]. XPS analysis of samples after each step of the deposition procedure give the compositions expected from Figure 4 (i.e., after step (a) of Figure 4, Zr:P 1:1; after step (b) Zr:P = 1:3).<sup>23,32</sup> IR analysis of the methylene CH stretching modes shows that the organic chains of these films are ordered, in a predominantly all trans configuration.<sup>25,32</sup>

Recently Talham et al., have shown that for specially primed substrates X-ray diffraction can also be used to measure the interlayer spacings of the metal phosphonate films. Most of the films that have been prepared have been grown onto substrates after a simple surface priming treatment. X-ray diffraction patterns are not observed for materials prepared this way on planar substrates. Talham demonstrated that it is possible to put down a much better ordered priming layer from a Langmuir-Blodgett (LB) trough.<sup>32</sup> Having a highly ordered priming layer leads to a much better ordered thin film. LB primed metal phosphonate thin films give good X-ray diffraction patterns after only 10–12 layers. The interlayer spacing calculated from X-ray diffraction data agrees well with the value obtained from ellipsometry (X-ray = 52 Å, ellipsometry = 51 Å).

The metal–phosphonate bonding in these materials has been proposed to be similar to that observed in  $\alpha\text{-Zr}(\text{O}_3\text{-POH})_2\cdot\text{H}_2\text{O}$ . For a phosphonate to have bonding similar to this inorganic phosphate compound the organic group must have a cross-sectional area  $\leq 24 \text{ \AA}^2$ , which is the area occupied by the hydroxyl groups of  $\alpha\text{-Zr}(\text{O}_3\text{POH})_2\cdot\text{H}_2\text{O}$ . This requirement is met easily by simple alkyl chains, but well-ordered thin films have been prepared for phosphonates with larger areas as well. Katz et al. have prepared films with tetraphosphonated-porphyrins whose cross sectional areas are significantly larger than  $24 \text{ \AA}^2$ .<sup>30</sup> Despite this poor size match, ellipsometric and optical absorption data show that thin films grow in a regular manner. Thin films can also be grown from quaterthiophenediphosphonic acid (QDP), whose cross-sectional area is also too large to make a perfect  $\alpha\text{-Zr}(\text{O}_3\text{POH})_2\cdot\text{H}_2\text{O}$  type of layer.<sup>31</sup> Again, ellipsometric and optical absorption data show that thin films grown with QDP increase in a regular manner. This system was also submitted to XPS analysis, which showed that these films are rich in zirconium.<sup>32</sup> The way that these materials appear to compensate for having a large organic group is to take up extra Zr. Further support for this hypothesis comes from the structure of a crystalline zirconium phosphonate compound, which has recently been solved from powder X-ray diffraction data.<sup>34</sup> In this material there are two zirconium ions per bisphosphonate molecule. The formula for this zirconium rich material is  $(\text{ZrF}_{3-n}\text{Cl}_n)_2(\text{O}_3\text{PCH}_2\text{CH}_2\text{-bipyridinium-CH}_2\text{CH}_2\text{PO}_3)\cdot 2\text{H}_2\text{O}$ ,  $n = 0\text{--}1$ . In this structure the Zr ions are octahedrally coordinated by three fluoride ions and three

phosphonate oxygens, in a meridional fashion. By adopting this structure the steric and electrostatic repulsions of adjacent bipyridinium groups are decreased relative to the  $\alpha$ -phase zirconium phosphate structure. We are currently investigating whether this phase is also formed in thin films of the same material.

### Optical Properties

A great deal of experimental and theoretical work has shown that controlling the rates of forward and back-electron-transfer reactions requires control of both the electronic and structural properties of the system. The electronic properties of organic and inorganic molecular species can be readily tuned, but the solid-state structures of these materials are harder to control. A number of different approaches have been used to control the spatial arrangements of donor and acceptor molecules with varying degrees of success. Metal phosphonates can be used to control the solid-state arrangement of the compounds of interest, and they are transparent in the visible portion of the spectrum, making them ideal for the study of electron-transfer reactions. The first report of electron-transfer reactions being studied in a metal phosphonate matrix involved the incorporation of  $\text{Ru}(\text{bipy})_3^{2+}$  and methylviologen ( $\text{MV}^{2+}$ ) into a zirconium phosphate sulfonophosphonate,  $\text{ZrPS} [\text{Zr}(\text{O}_3\text{POH})(\text{O}_3\text{PC}_6\text{H}_4\text{SO}_3\text{H})]$ .<sup>35</sup> Pronounced shifts are observed in both the absorption and emission spectra of  $\text{Ru}(\text{bipy})_3^{2+}$  when it is incorporated into this lattice, that are due to interactions of the aromatic groups of ZrPS with the bipy ligands of the Ru complex.<sup>35a</sup> When both  $\text{Ru}(\text{bipy})_3^{2+}$  and  $\text{MV}^{2+}$  are incorporated into ZrPS, emission from the Ru complex is significantly quenched. The microenvironment within ZrPS was found to restrict the movement of the cationic acceptor and donor molecules, presumably due to the high concentration of sulfonate groups. As a result, both dynamic and quasi static mechanisms are active in this quenching reaction.<sup>35b</sup>

Photophysical studies have also been carried out with metal phosphonates which have donors and acceptors covalently bound to the inorganic lamellae. These studies were aimed at investigating photoinduced electron-transfer reactions both within a given layer and between adjacent layers. Interlayer electron transfer was examined by studying a series of thin films formed with aliphatic and viologen bisphosphonates ( $\text{H}_2\text{O}_3\text{P}(\text{CH}_2)_3\text{-R-(CH}_2)_3\text{PO}_3\text{H}_2$ ,  $\text{R} = \text{C}_6\text{H}_{12}$  and bipyridinium, respectively) as well as a porphyrin tetraphosphonate.<sup>30</sup> The porphyrin molecules act as donors, the viologens as acceptors and the aliphatic layers as insulators. In this study the fluorescence of a film of the porphyrin alone was examined, as well as a sample which had the porphyrin layer grown on top of a viologen layer. The fluorescence observed for the viologen/porphyrin sample was dramatically less than that observed for the porphyrin alone. The quenching observed in the viologen/porphyrin system is due to interlayer electron transfer from the photoexcited porphyrin molecules to the viologens of the adjacent layer. To corroborate this hypothesis, a film was grown in which an aliphatic layer was placed between the viologen and porphyrin layers. The aliphatic layer acts as a good insulating layer in this case and no quenching of the porphyrin fluorescence is observed.

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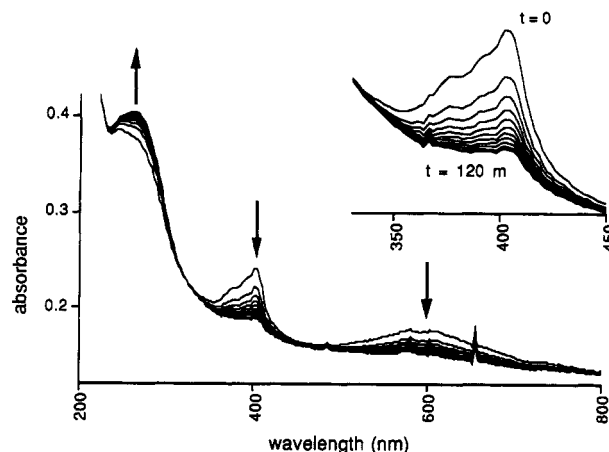
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Intralayer photoinduced electron transfer has also been observed in zirconium phosphonates. The zirconium phosphonates for this study were prepared as both thin films and bulk solids, from  $\text{H}_2\text{O}_3\text{PCH}_2\text{CH}_2(\text{bipyridinium})\text{-CH}_2\text{CH}_2\text{PO}_3\text{H}_2\text{X}_2$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) and will be abbreviated as  $\text{ZrPV}(\text{X})$ . These layered compounds show very efficient photoinduced charge transfer and form a charge separated state which is long-lived.<sup>36</sup> Spectroscopic studies indicate that the photoproduct is the dialkylviologen radical cation, produced in the interlamellar region of the zirconium phosphonate. The photochemistry was attributed to charge transfer from the halide counterions, followed by trapping of the halide radicals. The stability of this photoreduced state is believed to be due to structural features which allow for stabilization of the radicals due to delocalization and shielding from molecular oxygen.

Detailed mechanistic studies have been carried out on  $\text{ZrPV}(\text{X})$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ).<sup>24b</sup> Photoreduction of viologen in these thin film samples is very efficient (quantum yield = 0.15), showing simple isosbestic behavior in the electronic spectra. If the photolyzed films are protected from the air, the blue color persists indefinitely. The photoaction spectra for photoreduction of viologen in these materials shows no halide dependence, while the rates of photoreduction fall in the order  $\text{Cl} > \text{Br} > \text{I}$ . To account for these observations, a primary photoprocess involving a viologen-centered excitation was proposed, followed by oxidation of a halide anion to give  $\text{X}^\cdot$ . A similar process is observed for methylviologen in aqueous solution. Subsequent reactions of  $\text{X}^\cdot$  lead to the formation of a stable charge-separated state. The nature of these reactions depend strongly on the identity of  $\text{X}$ .<sup>24b</sup>  $\text{ZrPV}(\text{Cl})$  undergoes an irreversible series of reactions leading to the ultimate colored state. Contrary to the situation found for  $\text{ZrPV}(\text{Cl})$ , the bromide compound shows a high degree of reversibility in the photoreduction of its viologen groups. The photoprocess in this case is a photoinduced charge separation reaction. If a film of  $\text{ZrPV}(\text{Br})$  is photolyzed in a closed system to the point that >80% of the viologen groups are reduced and the UV light is removed, the characteristic blue color of reduced viologen gradually fades (Figure 5). After 2 h only 10% of the viologen is in a reduced state. The process can be repeated with the same outcome. If the same experiment is carried out with the sample under dynamic vacuum, the sample fades to a point where ca. 40% of the viologen is in a reduced state, and no further.<sup>37</sup> A likely explanation for these observations is that  $\text{Br}^\cdot$  atoms are formed, some of which form  $\text{Br}_2$  or  $\text{Br}_2^-$  before undergoing back electron transfer. Some of the  $\text{Br}_2$  may escape into the gas phase above the sample, giving a higher degree of "permanent" reduction for the samples irradiated under dynamic vacuum, relative to samples irradiated in a closed system. Both  $\text{Br}_2$  and  $\text{Br}_2^-$  may be too large to diffuse back to the reduced viologen readily after being formed, leading to a charge-separated state that gradually decays.

The photoreduction of the viologen compounds described above suggests they may act as catalysts for photochemical energy conversion. To carry this out, the energy stored in the charge-separated state must be coupled out of the solid. The approach that has been investigated for this is to incorporate colloidal platinum into the system to act as a catalyst for the photochemical reduction of external substrates (e.g., production of



**Figure 5.** Electronic spectra of a 10-layer film of  $\text{ZrPV}(\text{Br})$  (in vacuo), which was irradiated with a low-intensity UV lamp (254 nm). Spectra were recorded immediately on removing the lamp and then at 12-min intervals for 2 h. Up and down arrows indicate the bands which increase and decrease over time, respectively. The bands at ca. 400 and 600 nm are due to reduced viologen and the band at ca. 300 nm is due to oxidized viologen.

hydrogen from water).<sup>33</sup> To do this, the normal film growth procedure was altered by adding an ion-exchange step before treating the sample with the Zr solution. In this way it is possible to prepare thin films of  $\text{ZrPV}(\text{PtCl}_4)$ . Treatment of this film with hydrogen converts the  $\text{PtCl}_4^{2-}$  ions into colloidal platinum particles. If  $\text{H}_2$  is bubbled over the film, it turns from its pale gray color to deep purple, treatment of this reduced film with acid immediately bleaches the film back to its original gray color. The resulting film will equilibrate  $\text{H}^+$  and  $\text{H}_2$  very effectively. SEM studies show that the morphology of the thin film is the same before and after hydrogen reduction, suggesting that the colloidal particles are inside the film and have not migrated to the surface. If this platinized film is irradiated with a 200-W Hg/Xe lamp in the presence of a sacrificial reductant ( $\text{Na}_2\text{EDTA}$ ) hydrogen is produced (ca. 0.2 mL/h for 5 mg of catalyst). The photoreduction of hydrogen is decreased by more than an order of magnitude by filtering out the light below 330 nm, suggesting that the primary photoprocess here also involves a viologen centered transition, as proposed above. The measured quantum yield for hydrogen production in this system is ca. 0.01.

One area where control of the structure of a material will significantly effect the observed properties is in nonlinear optics. It is possible for a molecule to have a very large molecular second-order nonlinear optical (NLO) coefficient and show no second-order NLO response in the solid state. The reason for this is that the requirements for a material to show large second-order nonlinearities are that the individual chromophores have large molecular NLO coefficients and that those molecules be arranged in a polar fashion in the solid state.<sup>6</sup> A large number of organic molecules have been found to have large molecular NLO coefficients, but relatively few crystallize in polar space groups. To get around this problem, several approaches have been used to induce polar order in these molecular solids. Adding functional groups to the molecules can be used to make polar chains, but the adjacent chains often run antiparallel in the solid state, leading to a nonpolar solid. Langmuir-Blodgett and poled polymer techniques are more reliable but have the disadvantage that the alignment is usually not thermally stable.<sup>6</sup>

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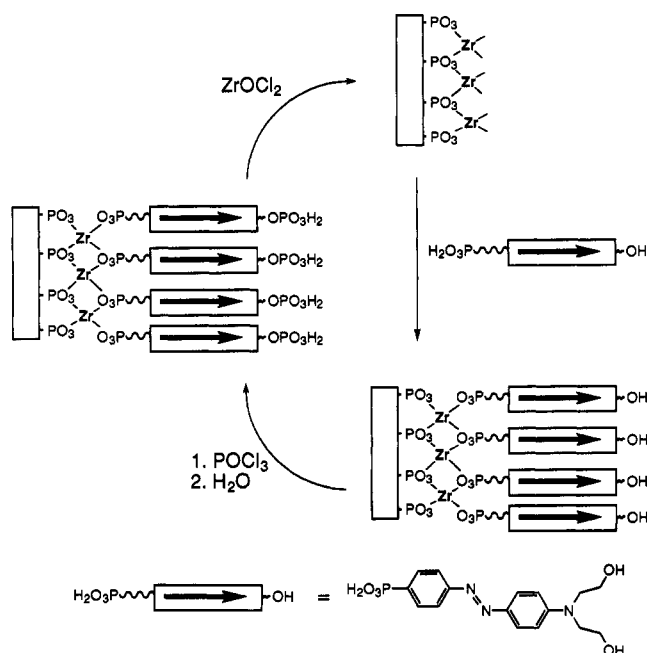
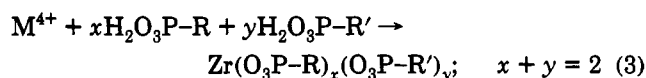


Figure 6. Steps in the growth of polar thin films.

Katz et al., have shown that zirconium phosphonate thin films can be very efficient at aligning organic chromophores in a polar manner.<sup>29</sup> The resulting films are quite stable and show good NLO response. The procedure for preparing these films is shown in Figure 6.<sup>38</sup> The trick here is to use an asymmetric monophosphonate that can be bound to a Zr-rich surface (step a). The hydroxyl group that is free at the surface of the films is then converted into a phosphate (step b) and a Zr solution is added to complete the cycle (step c). The end result is that each asymmetric monomer is bound to the surface in the same way, resulting in a polar film. A multilayer film grown this way, with the phosphate shown in Figure 6, gives an NLO response of the same order of magnitude as  $\text{LiNbO}_3$ .<sup>29</sup>  $\text{LiNbO}_3$  is one of the most widely used inorganic NLO materials (principally used for frequency multiplication and electrooptics). The stabilities of these films are excellent. The onset of randomization of the chromophores is observed above 150 °C. This temperature is far above that observed for Langmuir-Blodgett or poled polymer films.

### Porous Compounds

The materials described up to this point contain only a single type of phosphonate. If two different acids are mixed in the synthesis a very different type of layered material can be obtained (equation 3). The type of solid



one gets out of the reaction depends on how similar the two acids are. If the two groups are very different chemically, the two different acids tend to segregate into different layers in the solid state. For instance  $\text{Zr}(\text{O}_3\text{-POH})(\text{O}_3\text{PH})$  consists of layers of nearly pure phosphite alternating with layers of nearly pure phosphate.<sup>39</sup> If the

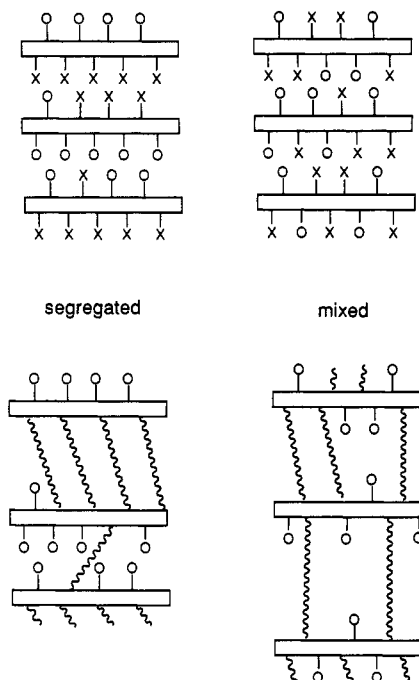


Figure 7. Several different structural possibilities for the mixed metal phosphonates and bisphosphonates. X and O represent two different types of phosphonate or a mixture of phosphonate and phosphate. The wiggly line represents a bisphosphonate. The structures to the left have the different groups segregated while those on the right have them intimately mixed.

two groups are very similar they will often mix intimately within the layers.<sup>10f,40</sup> Mixtures of  $\text{H}_2\text{O}_3\text{POH}$  and  $\text{H}_2\text{O}_3\text{-PCH}_2\text{CH}_2\text{COOH}$  lead to solids with the two acids completely mixed in the solid state.<sup>41</sup> Some of the different structural possibilities for the mixed metal phosphonates and bisphosphonates are shown schematically in Figure 7.  $\text{ZrPS}$  is a mixed phosphonate/phosphate of the type shown in upper right in Figure 7. Porous metal phosphonates are expected to have much higher surface areas than simple dense phosphonates [i.e.,  $\text{M}(\text{O}_3\text{P-R})_2$ ]. The measured surface areas for these solids can be very high,<sup>40,42</sup> consistent with their porous nature. The potential uses for these materials include catalysis, molecular sieving, and as ion-exchange materials. The catalytic reactions that have been examined involved using these mixed materials as acid catalysts.<sup>42b,43</sup> The catalytic activities of these solids are comparable to conventional solid acid catalysts.

The first porous solid of this type was prepared by first making a dense material, composed of a mixture of alkyl bisphosphonates and bisphosphates, i.e.,  $\text{Zr}[\text{O}_3\text{P}(\text{CH}_2)_8\text{-}$

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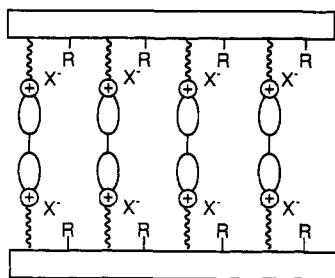
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**Figure 8.** Schematic representation of  $\text{Zr}(\text{O}_3\text{PR})(\text{O}_3\text{PCH}_2\text{CH}_2\text{-bipyridinium-CH}_2\text{CH}_2\text{PO}_3)\text{Cl}$  ( $\text{R} = \text{OH, H}$ ). The dicationic diellipse represents the bipyridinium molecule.

$\text{PO}_3]_{0.5}[\text{O}_3\text{PO}(\text{CH}_2)_6\text{OPO}_3]_{0.5}$ .<sup>40a</sup> Treatment of the solid with an aqueous solution of HBr hydrolyzed the phosphate groups to give  $\text{Zr}(\text{O}_3\text{P}(\text{CH}_2)_6\text{PO}_3)_{0.5}(\text{O}_3\text{POH})$ . This open solid has a measured surface area of  $209 \text{ m}^2/\text{g}$ . A more straightforward synthesis of mixed materials of this type was reported later, in which the reaction is carried exactly as described in eq 3. A mixture of two different acids is treated with the tetravalent metal ion. In these structures the organic groups act to pillar the layers apart, giving rise to the open space within the solid which leads to the porosity. Mixed phosphonates as well as mixed phosphate/phosphonate and phosphate/phosphite compounds have been prepared by this route.<sup>40b-g,41,44</sup> Alberti et al. have recently reported that pillared metal phosphonates can be prepared from  $\gamma$ -zirconium phosphate by exchanging the dihydrogen phosphate with an alkyl diphosphonate.<sup>13c</sup> While these synthetic techniques can lead to homogeneous, well-ordered mixed materials, it is also possible to obtain disordered solids. Varying degrees of microporosity can be found in a given mixed material, depending on its degree of structural disorder.

Most of the porous metal phosphonates prepared to date have organic pillars which are inert. The purpose of the organic pillar in these solids is only to hold the layers apart to allow ions (or substrates in the case of catalysis) to enter the solid. Thus the lattice is an inert one. A porous solid has recently been prepared, in which the pillars are quite reactive. This material is related to one of the photoactive materials described above. The materials have the formula  $\text{Zr}(\text{O}_3\text{PR})(\text{O}_3\text{PCH}_2\text{CH}_2(\text{bipyridinium})\text{CH}_2\text{-CH}_2\text{PO}_3)\text{Cl}$  ( $\text{R} = \text{OH, H}$ ).<sup>45</sup> A schematic representation of the material is shown in Figure 8. Exposure of these solids to UV light leads to an immediate reduction of the dicationic viologen pillars to their blue radical cation. Similar photochemistry is observed in the dense analog  $\text{ZrPV}(\text{Cl})$ . In the porous solid the pillar itself is being reduced, leading to a highly reactive lattice. This solid is immediately bleached on exposure to air, while the blue color photogenerated in  $\text{ZrPV}(\text{Cl})$  persists for days to months in the air. The porous nature of these materials and their photoreduction chemistry suggests that they may be good catalysts for shape-selective reductions.

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In many mixed phosphonate, phosphate/phosphonate and phosphite/phosphonate compounds the intimately mixed phase (Figure 7, right) is the kinetically favored phase, but on extended heating it converts to a material which is a mixture of the pure phases of each of the acids used to prepare it. In some cases, however, the intimately mixed phase can be the thermodynamically stable one. For the viologen–phosphonate materials described in the previous paragraph, crystalline samples of the intimately mixed phase are formed and do not separate into the pure phases of the individual acids on extended crystallization times or at elevated temperatures. Alberti et al. have reported a similar observation in the preparation of  $\text{Zr}(\text{O}_3\text{PH})_2(\text{O}_3\text{P-3,3',5,5'-tetramethylbiphenyl-PO}_3)_{1-x}$ .<sup>46</sup> The materials in which the intimately mixed phase is the stable one are composed of bulky bisphosphonates. The pure phase of the metal phosphonate for the bulky diphosphonate is not stable because to the steric repulsion of adjacent groups. By forming the mixed phase the bad steric interactions of the bisphosphonate are alleviated, since the smaller phosphite or phosphate groups require less than the  $24 \text{ \AA}^2$  available in the  $\alpha$ -phase type layers.<sup>47</sup>

### Conclusion

Chemists have focused a great deal of attention on synthesizing and studying compounds on a molecular level. The end result of this work is the ability to tailor both molecular structure and properties very efficiently. To extend this tailorability to bulk solids, one must be able to control the solid-state structure that the molecular species adopts. The use of metal phosphonates for organizing organic groups in the solid state has been explored and found to be particularly useful in this regard. Almost any organic molecule can be converted into a phosphonic acid derivative, and crystallized as a layered metal phosphonate. These layered materials can be used in a wide range of different applications, including chemical sensing, nonlinear optics, catalysis, dielectric coatings, ion exchangers, and materials for the study of photoinduced electron-transfer reactions. For many of these applications (particularly the optical ones) the degree of order and stability of the materials are critical, both of which are excellent for these layered solids.

An attractive feature of these layered metal phosphonates is the ability to prepare porous materials, by mixing a small phosphonic acid and a larger bisphosphonic acid in the solid. If the bisphosphonic acid is sufficiently rigid, it can act as a pillar, leading to open space in the solid. The resulting material is similar to a zeolite but is far less crystalline, often having good order in only the direction perpendicular to the layers. By choosing different organic groups in the bisphosphonate pillar or the smaller phosphonic acid, it may be possible to tailor the chemical properties or pore sizes of the resulting solids. Such materials could make an interesting new class of high surface area, shape-selective, heterogeneous catalysts or ion-exchange materials.

(47) The viologen–phosphonate is not actually too large to form a crystalline pure phase material, but electrostatic repulsion of the adjacent viologen groups can be minimized by forming an intimately mixed phase.