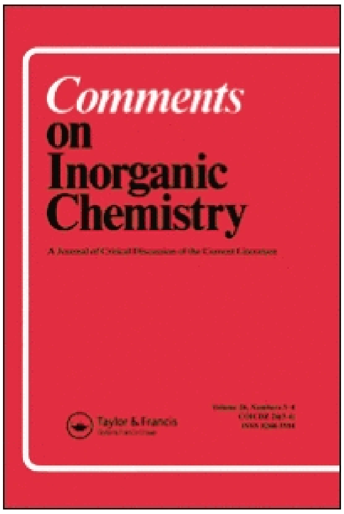

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Incorporating Inorganic Extended Lattice Structures into Langmuir—Blodgett Films: Comparing Metal Phosphonate LB Films to Their Solid-State Analogs

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Incorporating Inorganic Extended Lattice Structures into Langmuir–Blodgett Films: Comparing Metal Phosphonate LB Films to Their Solid-State Analogs

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Inorganic extended lattice structures can be incorporated into Langmuir–Blodgett (LB) films. The inorganic component not only adds lattice energy to the films, but also provides an opportunity to introduce electronic or magnetic ordering phenomena to the LB assemblies. In this Comment, LB films are described that are based on known divalent and tetravalent metal phosphonate inorganic layered solids. The LB film structures and properties are compared to the known solid-state metal phosphonates after which they are modeled. One of the films, manganese octadecylphosphonate, undergoes a magnetic ordering transition to a "weak ferromagnetic" state. It is the first example of a magnetic LB film, demonstrating how the extended lattice structure can be used to introduce new physical properties into LB films. Once the inorganic extended lattice structure is included, the possibility now exists for developing mixed organic/inorganic dual network LB films, where both the organic and inorganic networks add function.

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Key Words: *Langmuir–Blodgett films, metal phosphonates, layer structures, cooperative effects, magnetic ordering*

INTRODUCTION

The Langmuir–Blodgett (LB) method is normally considered as a technique that is used to prepare organic materials, generating organized monolayer or multilayer assemblies of molecules ranging from simple fatty acids to steroids to even polymers.[1,2] LB films sometimes contain inorganic ions, although they are usually passive elements that serve to crosslink and hold together the organic components.[1–3] Active inorganic species are generally in the form of discrete transition metal complexes and are organized in LB films the same way as organic molecules, such that interactions between metal ions are intermolecular. This constraint severely limits the types of physical phenomena that can be expected of LB assemblies. Many physical properties, such as superconductivity or magnetic order, require long-range structural order, and demonstration of cooperative phenomena in LB films has been elusive. While these effects have been observed in molecular solids,[4,5] they are more often seen in extended lattice solids. In this Comment, we explore the opportunity of using the unique LB deposition procedure for preparing extended lattice inorganic structures. We look at how the LB method can be used to learn about the inorganic monolayers and also at how the inorganic extended lattice structures might be used to control the organization of molecular components of mixed organic/inorganic LB films.

The LB technique (Fig. 1) organizes amphiphilic molecules at a water surface into a close-packed monolayer, which is then transferred to a solid support that is pushed or pulled through the film at the air/water interface.[1–3] The ability to organize molecules and to control the chemistry of interfaces is very powerful, and many fundamental areas of research have made use of the unique properties of organized LB films. Studies of membrane dynamics,[1] biomineralization at organic interfaces,[6] and electron and energy transfer processes in controlled geometries[7] are a few examples. Some practical applications of LB films include use in organic-based electronic devices,[8] organic non-linear optical devices,[9,10] and chemical and biochemical sensors.[1]

It has long been realized that metal ions added to the subphase under monolayer films of fatty acids can be incorporated into Langmuir–Blodgett

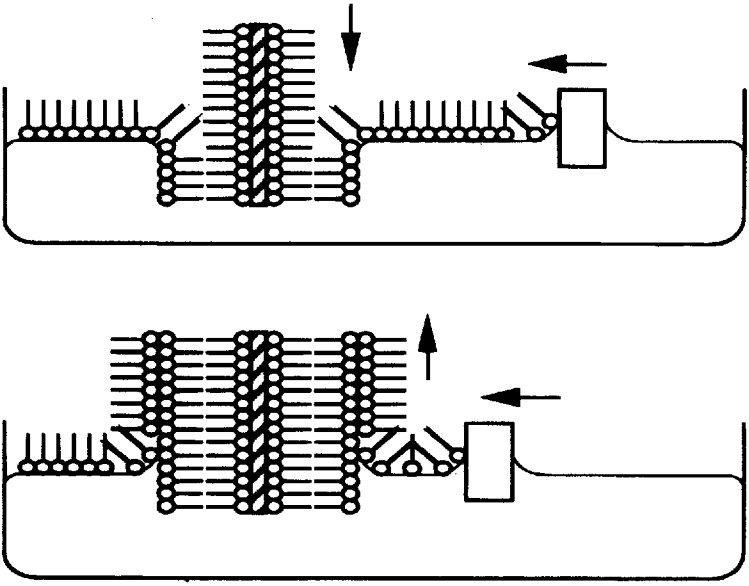


FIGURE 1 Langmuir–Blodgett deposition process. Amphiphilic molecules are organized into a close-packed monolayer at a water surface and then deposited onto a slide that is either pushed or pulled through the interface. Top, tail-to-tail deposition on the downstroke. Bottom, head-to-head deposition on the upstroke.

monolayer and multilayer films.[3,11] Divalent metal ions crosslink the carboxylate groups and are often used to enhance the stability of transferred films. The difference in solubility between a free acid and its metal salt was used by Blodgett[11] to produce films with a tunable refractive index through a process termed skeletonization. The free acid molecules of a partially ionized film were dissolved away with an organic solvent, leaving behind a skeletonized film of metal carboxylate with an enhanced porosity and a reduced refractive index.[11] The influence of metal ions on the film can be detected at the air/water interface by changes in pressure vs. area isotherms,[3] and pressure/pH phase diagrams clearly show changes in film structure as metal ions are incorporated.[12] As the film binds metal ions, headgroup–headgroup interactions change, which in turn lead to changes in the packing of the alkyl tails.

It has also become increasingly clear in recent years that the structure of the film at the air/water interface does not necessarily determine the structure of the transferred film.[1,13,14] For monolayer films, their structure may depend on the substrate onto which they are transferred.[1,14] Interaction of the polar headgroups with the substrate can determine the organization of the film. Different structures are observed as the identity of the metal ion changes. For multilayer Y-type (head-to-head) films, it is the polar interactions, specifically the ionic interactions between the polar headgroup and the metal ion, that determine the structure of the transferred films. For example, recent AFM studies on a series of divalent metal carboxylate LB films have revealed a complex assortment of structures that depend on the nature of the metal-ion/headgroup interaction.[14] In the transferred films, the alkyl chains vary their local packing, tilt angle and tilt direction to achieve close-packing in the film, but it is the metal-ion/headgroup lattice energy that dictates the molecular area.

While a picture has emerged suggesting that polar headgroup interactions can dictate the structure of LB films, historically little attention has been devoted to using ionic headgroup interactions to purposefully control monolayer structure. An approach that we are investigating is to utilize known solid-state layered structures to organize LB films, and in this way build up extended lattice structures.[15-17] There are several examples in the solid-state literature of mixed organic/inorganic layered compounds where polar ionic networks are separated by nonpolar organic networks.[18] Two examples are shown in Fig. 2. Transition metal organophosphonates frequently form layered structures where the binding within the metal phosphonate layer is ionic/covalent and the interaction between layers is van der Waals in nature.[19,20] The structure[21] of $Ca(HO_3PC_6H_{13})_2$ is shown in Fig. 2, but layered structures are known for many other organophosphonates with a variety of divalent, trivalent and tetravalent metal ions.[19,20,22,23] The alkylammonium layered perovskites, also pictured in Fig. 2, are another family of mixed organic/inorganic layered structures based on organic amphiphiles.[18] When comparing structures of this type it becomes clear that it is the inorganic lattice energy that determines these structures, as the same ionic lattices are found in examples without organic substituents. For example, the metal halide lattice in the alkylammonium layered perovskites is essentially isostructural with that in the purely inorganic K_2MnF_4. Since we can identify inorganic interactions that clearly favor layered structures, it is worthwhile to ask whether or not these inorganic structure types can be used to control, in a predictable way, the structures of mixed

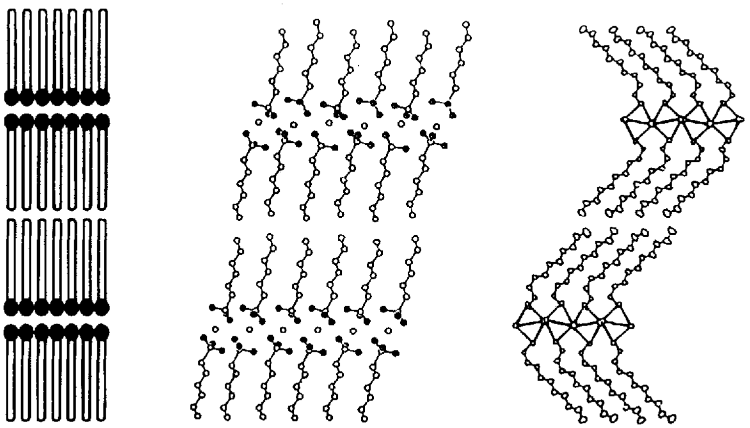


FIGURE 2 Left. Conventional schematic of a Y-type Langmuir–Blodgett Film. Center. Packing diagram of the layered metal phosphonate $Ca(HO_3PC_6H_{13})_2$ (Ref. 21). Right. The layered perovskite structure of $(C_{10}H_{21}NH_3)_2CdCl_4$ (Ref. 18). Note the similarity between these solid-state structures and Y-type LB films.

organic/inorganic LB films. We have now demonstrated this idea by characterizing several examples of transition metal phosphonate LB films.

ZIRCONIUM PHOSPHONATE LB FILMS

The prototype tetravalent metal phosphonate structure is $Zr(O_3PC_6H_5)_2$, whose structure (Fig. 3) was recently redetermined by Clearfield using Rietveld methods.[24] Zirconium ions within a sheet are bridged by phosphonate groups both above and below the metal ion plane. Each phosphonate bridges three zirconium ions, and the phenyl group projects nearly perpendicular to the metal ion plane, thereby separating zirconium layers. The result is an alternating organic/inorganic layered structure where the inorganic layer is an extended lattice. This is just the type of layered structure we were looking for to use as a model for mixed organic/inorganic LB films. In fact, the similarity between the layered nature of zirconium organophosphonates and that of conventional LB films was noted by Lee *et al.* when describing a layer-by-layer self-

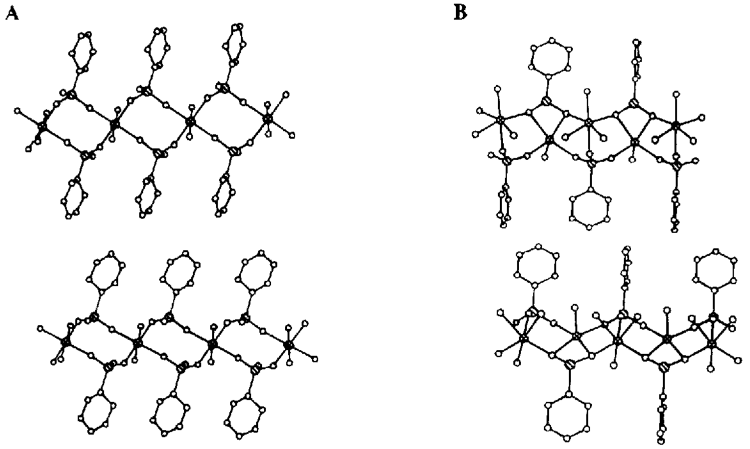


FIGURE 3 Examples of metal phosphonate layered solids. **A**. Two layers of $Zr(O_3PC_6H_5)_2$ viewed parallel to the zirconium layers (crystal data taken from Ref. 24). **B**. Two layers of $Mn(O_3PC_6H_5){\cdot}H_2O$ viewed parallel to the manganese layers (crystal data taken from Ref. 22). In both **A** and **B**, cross-hatched circles are the metal atoms, and diagonally shaded circles are phosphorus.

assembly procedure for forming thin films of zirconium phosphonates.[25] We attempted to incorporate the zirconium phosphonate extended lattice structure into LB films by replacing the phenylphosphonate in $Zr(O_3PC_6H_5)_2$ with an octadecylphosphonate Langmuir monolayer.

In order to prepare the zirconium phosphonate LB films it was necessary to develop an unusual three-step deposition procedure (Fig. 4)[17,26] because the strong affinity of Zr^{4+} ions for the phosphonic acid surface makes the Langmuir monolayers too rigid to process. In the first step of the deposition, an octadecylphosphonic acid (OPA) Langmuir monolayer is transferred in a tail-to-tail fashion onto a hydrophobic substrate. This creates an LB template, and Zr^{4+} ions are assembled to this surface outside the LB trough in step 2. The final step is to return the zirconated template to the trough and cap it with a second OPA monolayer, creating a Y-type zirconium octadecylphosphonate bilayer. Multiple layers can be achieved by repeating this three-step deposition process.[17,26]

Analysis shows that the zirconium phosphonate structure in the LB films must differ slightly from the known solid-state phases.[27,28] X-ray

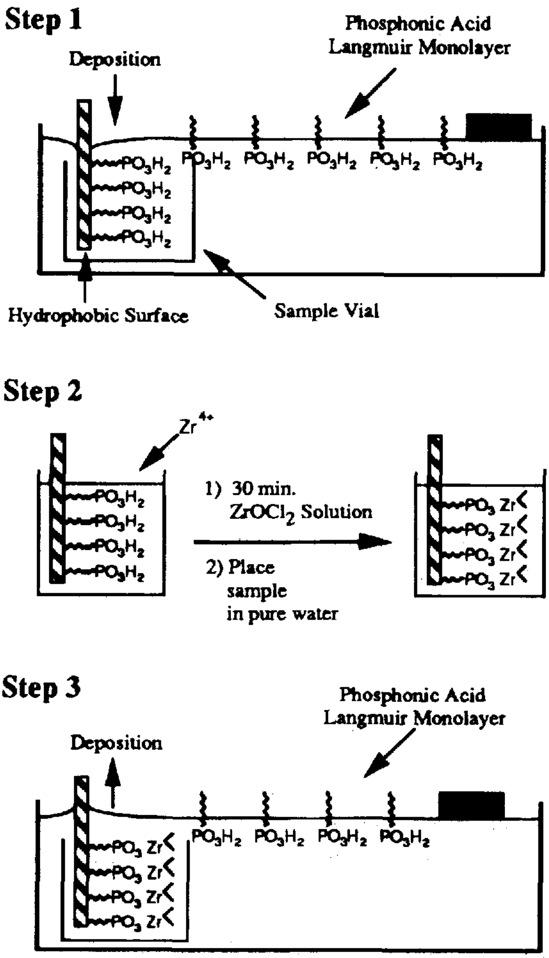


FIGURE 4 Stepwise procedure for depositing zirconium phosphonate LB films (adapted from Ref. 16).

diffraction demonstrates that the films are layered, and X-ray photoelectron spectroscopy (XPS) reveals a Zr:P chemical ratio of 1:2, just as expected from the bulk compounds.[17] However, polarized infrared analysis demonstrates that the LB template layer and the LB capping layer have two different orientations (Fig. 5).[27] The alkyl chain axis of molecules in the template layer is tilted at an angle of 31° with respect

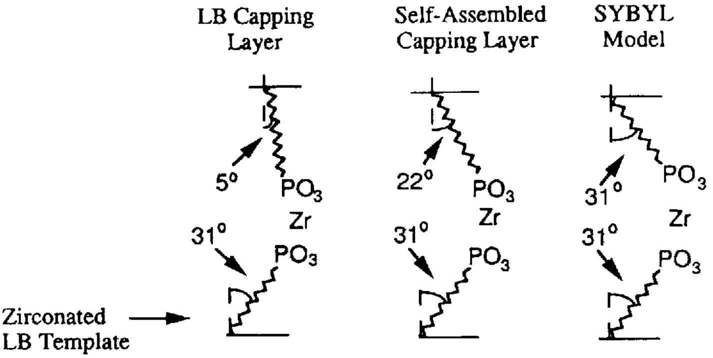


FIGURE 5 Tilt angles, determined by polarized ATR-FTIR, of the alkyl chains in zirconium octadecylphosphonate bilayers formed by LB and LB/SA procedures. The tilt angle predicted from a molecular model that assumes the zirconium/phosphonate binding is the same as in α-$ZrHPO_4$ is shown for comparison (adapted from Ref. 15).

to the substrate normal, while in the capping layer the alkyl chain tilt is 5°.[27] It appears that the alkylphosphonate molecules in the template layer relax upon transfer, from an essentially perpendicular orientation at the air/water interface to the tilted arrangement seen in the transferred film. The template layer is then held in place by the subsequent assembly of Zr^{4+} ions. When transferring the capping layer, the perpendicular arrangement of the floating monolayer is preserved because the strong binding to the zirconium layer does not allow the capping layer to relax. The difference in tilt angles suggests that the inorganic layer plays an important role in dictating the orientation of the organic assemblies. In an effort to compare this structure to one where the capping layer formed without the constraints of the LB compression, an alternative deposition procedure was developed.[27] The LB deposition procedure was carried out through step 2 in Fig. 4, the zirconation of the LB template layer. At this point, the zirconated template layer was placed into a solution of OPA in order to self-assemble (SA) a second OPA layer creating an LB-SA bilayer. Analysis of the LB-SA bilayer films by XPS showed the correct Zr:P ratio of 1:2, indicating complete coverage by the self-assembled layer.[15,27] This time, polarized FTIR studies demonstrated that the SA-capping layer has a tilt angle of 22° with respect to the normal. The tilt angle is clearly different from that of the LB capping layer, and the structure of the LB-SA bilayer more closely resembles the $Zr(O_3PR)_2$

analogs. Although no evidence for in-plane crystalline order has been observed in any of the zirconium phosphonate films, this is not unexpected given that the bulk zirconium phosphonates are also poorly crystalline.

An advantage of LB films possessing an extended lattice structure is increased stability due to enhanced lattice energy. LB films are often thermally unstable and readily soluble in organic solvents. However, solid zirconium phosphonates are highly insoluble in both water and organic solvents, and the zirconium phosphonate LB films are equally insoluble. Figure 6 compares the IR spectra of a ten-bilayer film before and after soaking in chloroform for 60 and 120 minutes. After 60 minutes approximately 20% of the film has been lost, but repeated washing shows no more loss of the film.[17] Also, there is no loss in crystallinity of the organic layers. We hypothesize that the original soaking washes away defect areas of the film, leaving behind the more crystalline zirconium phosphonate extended lattice domains.

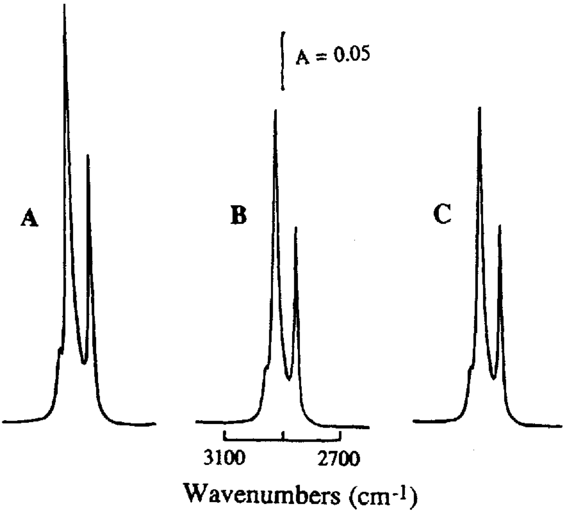


FIGURE 6 ATR-FTIR spectra monitoring film loss from 10 bilayers of zirconium octadecylphosphonate after soaking in chloroform: (**A**) before placing in chloroform; (**B**) after 60 min. in chloroform; (**C**) after 120 min. in chloroform. Additional washings with chloroform do not affect the film (adapted from Ref. 17).

We have also prepared LB films comprised of extended lattice layers of several different divalent metal phosphonates.[16,29,30] The solid-state analogs were first studied by Mallouk[22] who prepared alkylphosphonates of a series of divalent metals and showed them to form 1:1 metal:phosphonate phases isostructural with $Mn(O_3PC_6H_5)\cdot H_2O$, shown in Fig. 3. In this structure,[22] phosphonate groups bridge four metal ions, which are each coordinated by five phosphonate oxygens and a water of hydration. Other layered phases have also been observed with divalent metal ions, including a 1:2 calcium phosphonate phase.[21,22] A 1:1 calcium phosphonate phase, which is isostructural with the other $M(O_3PC_nH_{2n+1})\cdot H_2O$ salts, is seen for $n < 6$; while for longer alkyl chains a 1:2 phase (shown in Fig. 2) with formula $Ca(HO_3PC_nH_{2n+1})_2$ is observed.[21] Octadecylphosphonate LB films of Mg^{2+}, Co^{2+}, Mn^{2+}, Ca^{2+} and Cd^{2+} have all been prepared using normal LB deposition procedures.[31] Like the solids, different phases are observed, each consistent with known solid-state structures. In contrast to the zirconium films, a higher level of crystallinity is obtained for the divalent metal films because their greater solubility allows annealing of the extended lattice.[16,29] The deposited films are clearly layered, and several orders of the (001) Bragg reflection are seen in X-ray diffraction. Elemental ratios, determined by XPS, show a 1:1 metal:phosphorus ratio for the Mg^{2+}, Co^{2+}, Mn^{2+}, and Cd^{2+} films, which is consistent with the known $M(O_3PC_nH_{2n+1})\cdot H_2O$ solid-state phases. Interestingly, the metal:phosphorus ratio in the calcium octadecylphosphonate film is 1:2, indicating that the LB film forms the structure seen in the solid-state for the longer alkyl chain calcium phosphonates.

FTIR analysis confirms the similarity between the structures of the LB films and those of their solid-state analogs. FTIR also shows the differences between the two divalent metal phosphonate layered phases that we have observed in LB films. Spectra comparing the P–O stretching region of the Mn^{2+} and Ca^{2+} octadecylphosphonate LB films to their respective powdered alkylphosphonate solid-state analogs are shown in Fig. 7. For the manganese film, the asymmetric phosphonate stretch ($\nu_a(PO_3^{2-})$) at 1088 cm^{-1} and the symmetric phosphonate stretch ($\nu_s(PO_3^{2-})$) at 978 cm^{-1} are observed in the film, and the analogous bands appear at 1088 cm^{-1} and 968 cm^{-1} in the solids. The absence of a strong

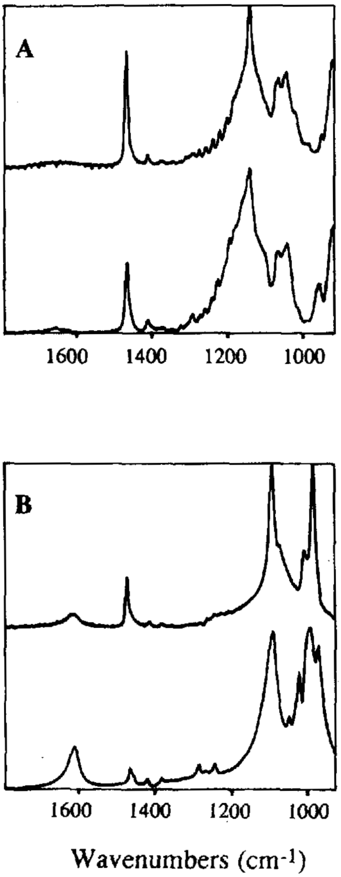


FIGURE 7 Comparison of the FTIR spectra of metal phosphonate LB films to known solid-state metal phosphonate analogs. **A**. Calcium octadecylphosphonate LB film (top) and calcium decylphosphonate powder with formula $Ca(HO_3PC_{10}H_{21})_2$ (bottom). **B**. Manganese octadecylphosphonate LB film (top) and manganese ethylphosphonate with formula $Mn(O_3PC_2H_5){\cdot}H_2O$ (bottom).

P=O stretch in the 1350–1250 cm^{-1} region or in the 1250–1110 cm^{-1} region for free and hydrogen bonded modes, respectively, indicates that all of the phosphonate groups are ionized. The appearance of the H–O–H bend at 1608 cm^{-1} is also common to both the film and the solid, and corresponds to the coordinated water molecule. The FTIR of the calcium film differs from the manganese film, but is clearly similar to the powdered calcium decylphosphonate. In these materials, the P–O stretches are broadened and shifted to higher energy because the phosphonate is monobasic in the $Ca(HO_3PC_nH_{2n+1})_2$ structure.

A Magnetic LB Film

An extended lattice structure allows the introduction of new physical properties into LB assemblies, and the manganese octadecylphosphonate LB film provides a good example. The manganese ions in the solid-state manganese phosphonates experience antiferromagnetic exchange, and several of the solids have been investigated as examples of layered antiferromagnets.[32,33] Carling *et al.*[32,33] have shown that the series $Mn(O_3PC_nH_{2n+1})\cdot H_2O$ ($n = 1$–4) are all canted antiferromagnets with ordering temperatures in the range 14.8–15.1 K. They are termed "canted antiferromagnets", sometimes called "weak ferromagnets", because the antiferromagnetically coupled moments do not exactly cancel in the ordered state, resulting in a net magnetization of the material. We have seen the same behavior in manganese octadecylphosphonate LB films.[16,29,34] The high-temperature (20–300 K) magnetic behavior was investigated using EPR which gives evidence for antiferromagnetic exchange in the LB films.[16,29] For example, the EPR intensity is proportional to the spin susceptibility, and a Curie–Weiss plot of 1/area vs. temperature (Fig. 8) gives a negative intercept, indicating antiferromagnetic exchange.[29] A plot of the area vs. temperature is also shown in Fig. 8, and the data are nicely fit by a numerical expression for Heisenberg antiferromagnetic exchange in a two-dimensional lattice.[16,29] The room-temperature EPR line width shows an angular dependence that is also characteristic of antiferromagnetic exchange in a two-dimensional lattice (Fig. 9), demonstrating the uniformity of the layered structure of the LB film.[29] The observed magnetic exchange arises from the crystalline extended-lattice structure of the LB layers and provides further evidence that the metal phosphonate extended lattice structures are formed during the Langmuir–Blodgett deposition procedure. In recent work, the low-temperature behavior has been studied by SQUID magnetometry where a magnetic ordering transition is seen at 12.5 K. Below this temperature a spontaneous magnetization develops in the film, which is consistent with a canted antiferromagnetic state.[34] This behavior is again analogous to the solid-state materials. We have also demonstrated magnetic memory effects in the films in plots of magnetization vs. applied field.[34]

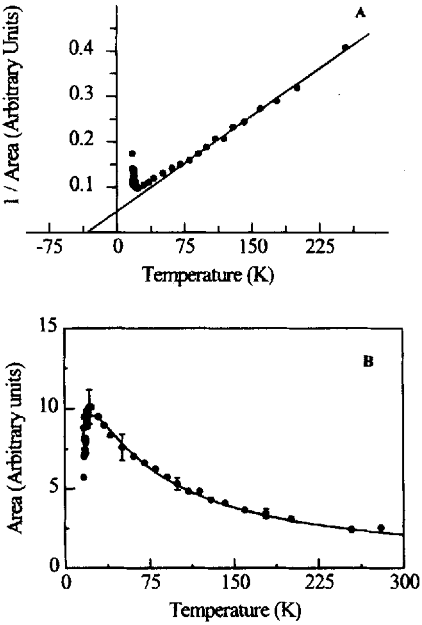


FIGURE 8 **A**. Temperature dependence of the inverse of the area (arbitrary units) of the EPR signal from a manganese octadecylphosphonate LB film. Extrapolation of the high temperature data yields a negative intercept of the temperature axis, indicating antiferromagnetic exchange. **B**. The data from **A**, now plotted as area vs. temperature. The solid line is a fit to the data using a numerical model for Heisenberg antiferromagnetic exchange in a two-dimensional lattice. The fit yields a value of the nearest-neighbor exchange constant, J, of $J/k = -2.8$ K, which is nearly identical to that observed for several isostructural solid-state analogs (adapted from Ref. 29).

FUNCTIONAL ORGANIC GROUPS: DUAL NETWORK ASSEMBLIES

The manganese phosphonate LB films provide the first example of magnetic order in an LB film, and demonstrate that cooperative phenomena are possible in LB assemblies. They also illustrate how the inorganic lattice can be used as an active component in LB films, thereby raising the possibility of using LB films as mixed organic/inorganic "dual-network" assemblies (Fig. 10). By "dual-network" we mean systems where the organic and inorganic networks contribute separate properties, either working independently, providing a material with composite properties, or working in synergy, potentially producing new phenomena. There is

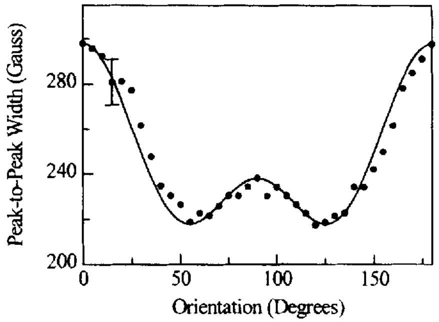


FIGURE 9 Room temperature EPR line width as a function of sample orientation. The solid line is a fit of the data to $\Delta H = A + B(3\cos^2\phi - 1)$ with $A = 218$ G and $B = 20$ G (ϕ is the angle between the static magnetic field and the film normal) which is characteristic of Heisenberg exchange in a two-dimensional lattice (adapted from Ref. 29).

precedence for incorporating functionalized organic groups into both solid-state and thin-film organophosphonate materials,[35] and we discuss below a few examples that highlight possible roles of the organic network.

Solid-State Examples

Solid-state transition metal phosphonates are known with a wide variety of organic groups, and most often they form as layered phases.[20,35] In many cases, the physical phenomena exhibited by the organic groups depend on their alignment and packing, which is dictated by the metal—phosphonate interaction. For example, Mallouk and co-workers[20] have prepared layered metal phosphonate phases from diacetylene functionalized α, ω-diphosphonic acid monomers and have attempted to topochemically polymerize the diacetylene groups. They observed that the degree of polymerization is affected by the choice of metal ion and that the optimal spacing between monomers is achieved only in structures with divalent metals.

There are other examples of layered metal phosphonates containing functionalized organic groups. In 1992, Thompson and co-workers reported a layered zirconium viologenphosphonate compound (ZrPV(X), where X = Cl, Br), which when exposed to UV radiation produced a charge separated state that was indefinitely stable in air.[36,37] The structure of the ZrPV(X) materials was determined to be layered, but it is very different from the α-$ZrHPO_4$ structure. The ZrPV(X) materials

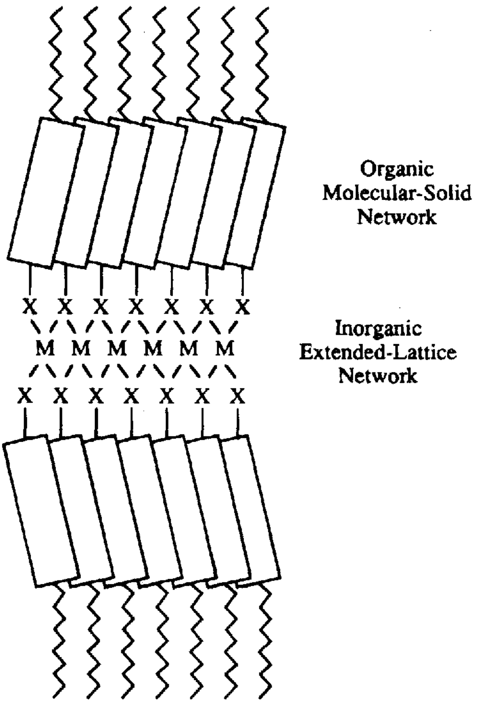


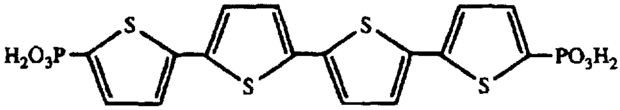
FIGURE 10 Schematic of a mixed organic/inorganic "dual network" Langmuir–Blodgett film.

are very dense, thereby inhibiting chemical use of the charge-separated state. In an attempt to take advantage of the charge-separated state, a new family of porous viologen-based compounds was prepared, where the viologen moieties act as pillars within the zirconium lattice, thereby creating open spaces in the organic region of the structure. Colloidal platinum particles can be incorporated into the porous structures, and these assemblies have been used to study the catalytic production of H_2O_2[38] and the photochemical generation of hydrogen gas.[39]

Thin Films

Mallouk and co-workers demonstrated the fabrication of thin films of zirconium phosphonates by first anchoring a layer of molecules bearing the phosphonate functionality followed by alternately adsorbing Zr^{4+}

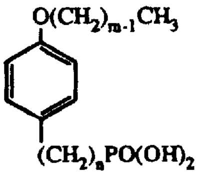
ions and α, ω-alkanediyldiphosphonic acid molecules from solution.[20,25] These alkane-based films showed promise as insulating layers in metal–insulator–metal and metal–insulator–semiconductor devices.[40] Howard Katz and co-workers used this method to prepare thin films of functionalized organic molecules possessing nonlinear optical,[41] conductive[42] and photoactive donor–acceptor properties.[43] In our own group, we have used highly organized LB films to produce a phosphonic acid template layer, and then following the Mallouk deposition scheme have shown that the organization of the template can affect the organization of the subsequently self-assembled layers.[27] Using a zirconated LB template (derived from step 2 in Fig. 4), we demonstrated that multilayer films of quaterthiophenediphosphonic acid (QDP, supplied by H. Katz)[42] can be self-assembled on a flat substrate in a sufficiently regular fashion that X-ray diffraction corresponding to the interlayer spacing is observed from a ten layer film.[27]



QDP

Thompson and co-workers have prepared thin film analogs of the solid state ZrPV(X) compounds by employing a viologen bisphosphonic acid in the Mallouk deposition process.[37] The viologen films, like their solid-state counterparts, access a charge separated state when irradiated with UV light and can also be used to photochemically produce hydrogen gas.[44] Recently, metal phosphonate films have been prepared that are composed of viologen-based acceptor layers and p-phenylenediamine donor layers.[45] These donor–acceptor films possess efficient photoinduced charge separation and directional electron transport, and they generate photocurrents when irradiated with ultraviolet and visible light.

We are currently attempting to incorporate functionalized organic groups into metal phosphonate LB films. The objective is to develop routes to thin film heterostructures with alternating organic and inorganic layers where the properties can be tuned by design of the organic and inorganic networks. Initial studies have been with simple organophosphonates in order to systematically study how the packing of the organic groups is affected by the metal-phosphonate lattice. Preliminary experiments are promising. Zirconium phosphonate LB films have been prepared from the phenyl and biphenyl functionalized phosphonic acids (**1–4**), using the three-step deposition procedure described in Fig. 4 for octadecylphosphonic acid. An interesting result is that mixed bilayers are easily prepared by alternating different organic groups in the template and capping layers. While alternating layer LB films have been achieved using more conventional molecules, the presence of the metal phosphonate inorganic extended lattice layer results in a significant increase in the stability of the alternating layer structure. Most LB films of functionalized molecules are metastable condensed phases, but metal phosphonate LB films represent preferred structures due to the lattice energy contributed by the inorganic extended lattice.



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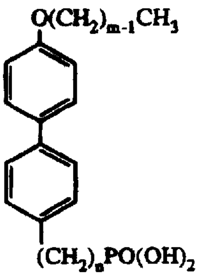

3 n=0, m=17
4 n=4, m=13

CONCLUSIONS

Continued investigation of mixed organic/inorganic LB films appears to hold great promise. We have developed a wet chemical method for layer-by-layer deposition of high-quality extended lattice structures. Using this approach, we have demonstrated spontaneous magnetization in an LB film, and examples exhibiting other physical properties requiring long-range structural order seem possible. Previously, the preparation of single layers of an inorganic solid was only achieved by CVD or electrochemical methods and was, therefore, limited to substrates whose surface structure is suitably matched to the depositing layer. LB films also provide an opportunity to prepare "dual-network" assemblies where function is assigned to both the organic and inorganic networks of the LB structure. There is the promise of being able to tune the properties of the thin films, but, perhaps more importantly, such geometries might also lead to new physical phenomena.

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