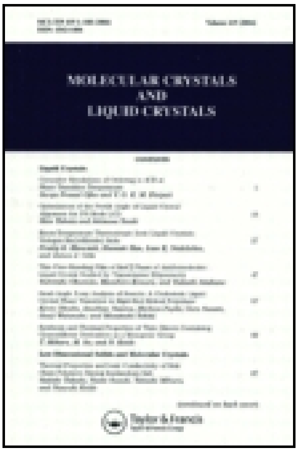

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A Magnetic Manganese Phosphonate Langmuir-Blodgett Film Containing a Tetrathiafulvalene Amphiphile

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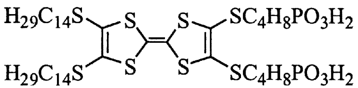
An amphiphilic tetrathiafulvalene derivative, with two alkylphosphonic acid substituents, has been prepared and used to form a mixed organic/inorganic Langmuir-Blodgett (LB) film containing a TTF-based organic network and a manganese phosphonate continuous lattice inorganic network. The inorganic network is isostructural with known manganese phosphonate layered solids, and undergoes magnetic ordering to a canted antiferromagnetic ground state. A model TTF derivative containing the alkylphosphonic acids, but without hydrophobic alkyl tails, was also synthesized and a manganese phosphonate solid, isostructural with the LB film, was prepared and characterized.

Keywords Langmuir-Blodgett, manganese phosphonate, canted antiferromagnet

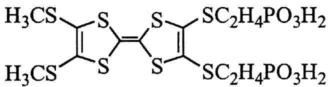
INTRODUCTION

The Langmuir-Blodgett (LB) film technique is one of the original methods of "supramolecular assembly." LB films are traditionally layered organic assemblies that are first formed at the air-water interface and then transferred to a solid support.[1] The process normally results in a two-dimensional crystalline or liquid crystalline array of organic amphiphiles. We have recently developed methods to incorporate inorganic networks into LB films to produce mixed organic/inorganic monolayers and multilayers.[2-5] The LB films incorporate two-dimensional metal phosphonate lattices and are modeled after known layered solid-state phases. An advantage of the mixed organic/inorganic LB films is that properties typical of the inorganic solid-state can now be included while retaining the elegance of LB deposition. For example, we have recently demonstrated that metal phosphonate LB films are significantly more stable than traditional LB films, because of the inorganic lattice.[4] We have also demonstrated magnetic order in manganese phosphonate LB films.[2]

A significant step will be to demonstrate "dual-network" assemblies where both the organic and inorganic networks contribute properties to the LB film. Working toward this goal, we have prepared manganese phosphonate LB films based on the tetrathiafulvalene (TTF) amphiphile 2T2, shown below. TTF cation radicals and related ions form conducting and superconducting networks in the solid state, and have in some cases been shown to form conducting LB films.[1] Manganese phosphonate LB films of 2T2 could produce "dual network" assemblies where the organic network is conducting and the inorganic network is magnetic. In this report, manganese phosphonate films of 2T2 are described. Structural and physical properties characterization are aided by comparing the LB films to analogous solid state compounds, including salts of the "model" compound m2T2, shown below.



2T2



m2T2

EXPERIMENTAL SECTION

All experimental procedures related to metal phosphonate LB film formation and characterization, including FTIR analysis and SQUID magnetometry, have been described in detail in previous publications.[2-4] The synthesis of the TTF phosphonic acids 2T2 and m2T2 are described in detail in the Ph.D. thesis of one of the authors.[5] The solid-state manganese phosphonate based on m2T2 was prepared according to the procedure of Cao *et al.*[6]

RESULTS AND DISCUSSION.

Preparation and Structural Analysis

Metal phosphonate LB films are prepared one bilayer at a time by depositing the first amphiphilic organophosphonate layer on the downstroke onto a hydrophobic support with the appropriate metal ion in the subphase, followed by depositing a second layer on the upstroke. The result is an organophosphonate bilayer sandwiching a layer of metal ions. If the dipping conditions and subphase pH are properly chosen, the metal ions crosslink the phosphonate groups to produce the extended networks known in solid-state metal phosphonates.[2-4] Several examples of metal phosphonate LB films are now known, and the different metal phosphonate structure types can be characterized by distinctive P-O stretching patterns observed in the IR.[2,3,6] For the $\mathrm{Mn(O_3PR)\cdot H_2O}$ structure type, exemplified by $\mathrm{Mn(O_3PC_4H_9)\cdot H_2O}$, strong $\nu_a(\mathrm{PO_3^{2-}})$ and $\nu_s(\mathrm{PO_3^{2-}})$ stretches appear at 1087 $\mathrm{cm^{-1}}$ and 984 $\mathrm{cm^{-1}}$, respectively. The phosphonate stretches of the manganese 2T2 LB film and the manganese m2T2 powdered solid are shown in Figure 1 where the distinctive $\nu_a(\mathrm{PO_3^{2-}})$ and $\nu_s(\mathrm{PO_3^{2-}})$ are observed. Their presence confirms the $\mathrm{Mn(O_3PR)\cdot H_2O}$ structure type for both the LB film and the powdered solid. With two phosphonate groups per molecule, this structure type requires a stoichiometry of $\mathrm{Mn_2(2T2)\cdot 2H_2O}$ and $\mathrm{Mn_2(m2T2)\cdot 2H_2O}$ for the LB film and powdered solid, respectively. Combustion analysis combined with TGA analysis confirms this stoichiometry for the $\mathrm{Mn_2(m2T2)\cdot 2H_2O}$ powdered solid.

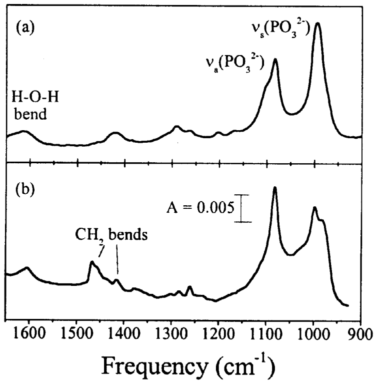


Figure 1. (a) FTIR spectrum of a $\mathrm{Mn_2(m2T2)2H_2O}$ powder, and (b) ATR-FTIR spectrum of a three-bilayer LB film of manganese 2T2. The frequencies of the P-O stretches are consistent with the $\mathrm{Mn(O_3PR)\cdot H_2O}$ structure type known for other manganese phosphonate solids and LB films.

Magnetic Properties

The manganese phosphonate layered solids are characterized by antiferromagnetic exchange and a transition to long-range order. The ordered state possesses a spontaneous magnetization as a result of spin canting, and such systems are called canted antiferromagnets, or sometimes, weak ferromagnets.[7] This ordering transition is observed near 12 K in the manganese phenylphosphonate, $Mn(O_3PC_6H_5){\cdot}H_2O$,[8] and we previously reported an analogous transition in an LB film of manganese octadecylphosphonate at 13.5 K.[2]

The TTF-containing manganese phosphonates also experience antiferromagnetic exchange and undergo magnetic ordering to a canted antiferromagnetic state. A plot of inverse susceptibility vs temperature for the $Mn_2(m2T2){\cdot}2H_2O$ powdered solid is shown in Figure 2. Extrapolation of the linear part of the plot to the temperature axis yields a negative intercept ($\theta = -47$ K), characteristic of antiferromagnetic exchange. A plot of susceptibility vs temperature can be fit with a series expansion for Heisenberg antiferromagnetic exchange in a quadratic lattice, yielding an exchange constant, $(J/k) = 2.5$ K, that is comparable to other manganese phosphonate layered solids.[7,8]

Evidence for magnetic ordering in both the manganese 2T2 LB film and the manganese m2T2 solid is shown in Figure 3. For magnetic measurements, a 100-bilayer LB film sample was deposited onto a mylar support and cut into small strips to fit into the magnetometer. Magnetization vs temperature was recorded for each sample by first cooling the sample in zero field and measuring upon warming with a 100 G measuring field. The sample was then cooled from 300 K in 100 G and measured again. The difference between the field cooled (FC) and zero-field cooled (ZFC) data is plotted in Figure 3. This presentation is an effective way to account for the large diamagnetic background present in the LB film,[2] where the amount of metal phosphonate sample is very small relative to the mylar support and sample container. The increase in $\Delta M_{FC\text{-}ZFC}$ indicates a transition to a magnetic ground state that, in analogy to other manganese phosphonates, can be assigned to a canted antiferromagnetic state. The transition temperature is nearly identical for both the powdered solid and the LB film, indicating that the two materials are isostructural. Also, the 11 K transition temperature is similar to the other layered manganese phosphonates,[8] lending additional evidence for the formation of the $Mn(O_3PR){\cdot}H_2O$ structure type in the TTF phosphonate solid and film.

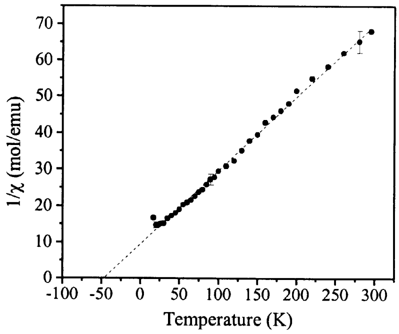


Figure 2. Plot of inverse susceptibility, determined from EPR intensity, vs temperature for the $Mn_2(m2T2)\cdot 2H_2O$ powdered solid. Extrapolation of the data to the temperature axis yields a Weiss constant of –47 K.

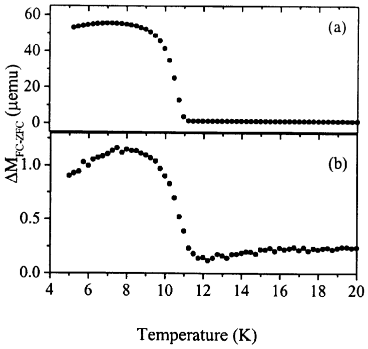


Figure 3. Plots of field-cooled minus zero-field-cooled magnetization for (**a**) the $Mn_2(m2T2)\cdot 2H_2O$ powdered solid, and (**b**) the $Mn_2(2T2)\cdot 2H_2O$ LB film. Transitions to a canted antiferromagnetic ground state are seen near 11.5 K for both materials.

Doping and Conductivity Measurements

Attempts to partially oxidize the films to form a conducting material were unsuccessful. The $Mn_2(2T2)\cdot 2H_2O$ LB films were exposed to I_2 vapor, and UV-vis spectroscopy showed evidence of TTF-oxidation. However, this phase was not stable, and quickly reverted back to the unoxidized form.

CONCLUSIONS

The new phosphonic acid derivatized TTF molecules, 2T2 and m2T2, described here form extended solid manganese phosphonate phases with the stoichiometry of $Mn_2(2T2)\cdot 2H_2O$ and $Mn_2(m2T2)\cdot 2H_2O$ as an LB film and powdered solid, respectively. Since there are two phosphonate groups on each molecule, the metal phosphonate networks are isostructural with the known $Mn(O_3PR)\cdot H_2O$ solid-state structure type. This conclusion is confirmed by the observation of a canted antiferromagnetic ground state in both materials, which is characteristic of the manganese phsophonate layered phase. The presence of the bulky TTF moiety does not inhibit formation of the metal phosphonate lattice, and these materials represent progress toward the goal of "dual network" LB films possessing conducting organic and magnetic inorganic networks.

ACKNOWLEDGEMENTS.

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