Chem. Mater. **1993,** *5,* 709–715

Inorganic Monolayers Formed at an Organic Template: A Langmuir–Blodgett Route to Monolayer and Multilayer Films of Zirconium Octadecylphosphonate

Houston Byrd, John K. Pike, and Daniel R. Talham*

Department of Chemistry, University of Florida, Gainesville, Florida 32611-2046

Received December 16, 1992

Single-layer and multilayer films of zirconium octadecylphosphonate have been prepared on silicon oxide surfaces and characterized by Langmuir–Blodgett (LB) transfer data, contact angle, ATR-FTIR, XPS, ellipsometry and X-ray diffraction. The deposition method uses a preformed, organized organic template for assembling the inorganic lattice by combining LB and self-assembly (SA) techniques. First, an LB template of octadecylphosphonic acid is formed on an octadecyltrichlorosilane-covered substrate, then Zr^{4+} ions are "self-assembled" from solution. A capping octadecylphosphonic acid LB monolayer is added to complete the bilayer. Transfer of the phosphonic acid is continuous with transfer ratios ranging between 1.1 and 1.2. Contact angle measurements on a completed bilayer give an advancing contact angle of 112 ± 1°. The asymmetric methylene ($\nu_a(CH_2)$) band of the template layer appears at 2918 cm^{-1} and possesses a fwhm of 20 cm^{-1} indicating that an all-trans, close-packed template is formed. The frequency and shape of the $\nu_a(CH_2)$ band remain unchanged in the progression from the template layer to bilayer to multilayers. XPS analysis of the zirconated LB template shows a 1:1 ratio of Zr:P, while bilayer and multilayer films possess a Zr:P ratio of 1:2 consistent with the stoichiometry observed in solid zirconium phosphonate. Ellipsometry shows a layer-by-layer increase in film thickness corresponding to a bilayer thickness of 51 Å, while X-ray diffraction reveals a *d* spacing of 52 Å and thus demonstrates the layered nature of the films. The zirconium phosphonate films are quite insoluble in both water and organic solvents.

Introduction

Current interest in layered inorganic materials ranges from applications in intercalation chemistry,[1] catalysis,[2] and separations[3] to the study of superconductivity and magnetism[1,4–6] where the quasi-two-dimensional structure of layered solids makes them attractive experimental models for investigating chemistry and physics in the limit of two-dimensions. A potentially better model for two-dimensions is a true monolayer, and recent advances in synthesis and characterization at surfaces have led to studies of single layers of atoms[7] or compounds,[8–10] prepared on surfaces by molecular beam epitaxy or chemical vapor deposition methods. Frequently, however, these monolayer films suffer as two-dimensional model systems because interactions with the substrate often dominate the physical properties of interest.[11] Another approach to inorganic monolayers is to incorporate two-dimensional arrays of inorganic ions or complexes into organic monolayers that have been formed by Langmuir–Blodgett[12–14] (LB) or organic self-assembly[15,16] (SA) techniques. This approach was first investigated by Pomerantz[17] in studies of magnetic ordering in LB bilayers of manganese stearate.

In this paper, we report the use of transferred LB films to form single layers, as well as multilayers, of layered

---

* Address correspondence to this author.

(1) Intercalation Chemistry; Whittingham, M. S., Jacobson, A. J., Eds.; Academic Press, Inc.: New York, 1982.

(2) (a) Alberti, G.; Constantino, U. *J. Mol. Catal.* **1984**, *27*, 235–250. (b) Clearfield, A. *J. Mol. Catal.* **1984**, *27*, 251–262.

(3) (a) Cao, G.; Garcia, M. E.; Alcalá, M.; Burgess, L. F.; Mallouk, T. E. *J. Am. Chem. Soc.* **1992**, *114*, 7574–7575. (b) Cao, G.; Hong, H.-G.; Mallouk, T. E. *Acc. Chem. Res.* **1992**, *25*, 420–427.

(4) (a) Schöllhorn, R. In *Inclusion Compounds*; Academic Press: London, 1984, and references therein. (b) Dresselhaus, M. S. *Mater. Sci. Eng., B1* **1988**, 259–277 and references therein. (c) Formstone, C. A.; Fitzgerald, E. T.; O'Hare, D.; Cox, P. A.; Kurmoo, M.; Hodby, J. W.; Lillicrap, D.; Goss-Custard, M. *J. Chem. Soc., Chem. Commun.* **1990**, 501–503.

(5) Day, P. *Philos. Trans. R. Soc. London, Ser. A* **1985**, *314*, 145–158.

(6) Day, P. *Chem. Br.* **1983**, 306–314.

(7) (a) Jonker, B. Y.; Walker, K.-H.; Kisker, E.; Prinz, G. A.; Carbone, C. *Phys. Rev. Lett.* **1986**, *57*, 142–145. (b) Krebs, J. J. *Appl. Phys. A* **1989**, *49*, 513–521. (c) Richter, R.; Gay, J. G.; Smith, J. R. *Phys. Rev. Lett.* **1985**, *54*, 2704. (d) Fu, C. L.; Freeman, A. J.; Oguchi, T. *Ibid.* 2700. (e) Qiu, Z. Q.; Pearson, J.; Bader, S. D. *Ibid.* **1991**, *67*, 1646–49. (f) Engel, B. N.; England, C. D.; Van Leeuwen, R. A.; Wiedmann, M. H.; Falco, C. M. *Ibid.* 1910–13. (g) Allenspach, R.; Stampanoni, M.; Bischof, A. *Ibid.* **1990**, *65*, 3344–47. (h) Beier, T.; Jahrreiss, H.; Pescia, D.; Woike, Th.; Gudat, W. *Phys. Rev. Lett.* **1988**, *61*, 1875–1877.

(8) Nakamura, O.; Fullerton, E. E.; Guimpel, J.; Schuller, I. K. *Appl. Phys. Lett.* **1992**, *60* (1), 120–122.

(9) Ihm, J.; Yu, B. D. *Phys. Rev. B* **1989**, *39*, 4760–4763.

(10) (a) Lowndes, D. H.; Norton, D. P.; Budai, J. D. *Phys. Rev. Lett.* **1990**, *65*, 1160–1163. (b) Triscone, J.-M.; Fischer, ø; Brunner, O.; Antognazza, L.; Kent, A. D. *Ibid* **1990**, *64*, 804–807. (c) Li, Q.; Xi, X. X.; Wu, X. D.; Inam, A.; Vadlamannati, S.; McLean, W. L. *Ibid.* 3086–3089.

(11) Falicov, L. M. *Thin Solid Films* **1992**, *216*, 169–173.

(12) Gaines, G. Jr. *Insoluble Monolayers at Liquid-Gas Interfaces*; Wiley-Interscience: New York, 1966.

(13) Roberts, G. G. *Adv. Phys.* **1985**, *34*, 475–512.

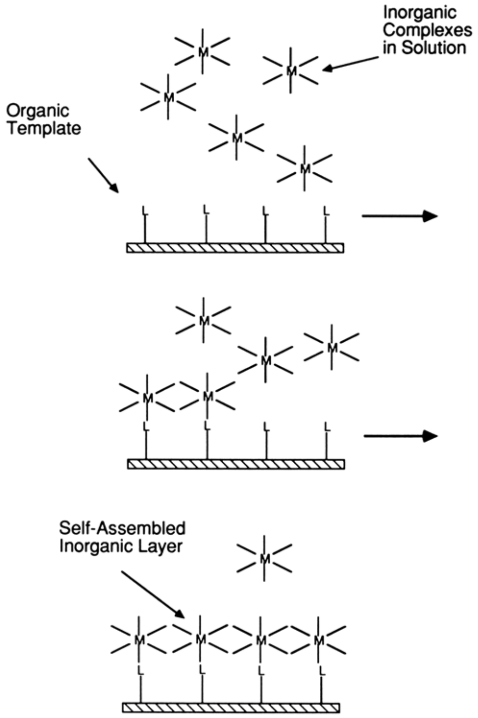
(14) (a) For summaries of recent work of LB films see: Proceedings of the Fourth International Conference on Langmuir-Blodgett Films. *Thin Solid Films* **1989**, 179–180. (b) Proceedings of the Fifth International Conference on Langmuir-Blodgett Films. *Thin Solid Films* **1991**, 210–211.

(15) (a) Sagiv, J. *Isr. J. Chem.* **1979**, *18*, 339. (b) Sagiv, J. *Ibid.* 346. (c) Maoz, R.; Sagiv, J. *J. Colloid Sci.* **1984**, *100*, 465. (d) Gun, J.; Iscovici, R.; Sagiv, J. *Ibid. 101*, 201. (e) Gun, J.; Sagiv, J. *Ibid.* **1986**, *112*, 457.

(16) (a) Holmes-Farley, S. R.; Reamey, R. H.; McCarthy, T. J.; Deutch, J.; Whitesides, G. M. *Langmuir* **1985**, *1*, 725. (b) Strong, L.; Whitesides, G. M. *Ibid.* **1988**, *110*, 3665. (c) Bain, C. D.; Whitesides, G. M. *Science* **1988**, *240*, 62. (d) Bain, C. D.; Whitesides, G. M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 506. (e) Singh, R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1990**, *112*, 1190. (f) Wilson, M. D.; Ferguson, G. S.; Whitesides, G. M. *Ibid.* 570. (g) Whitesides, G. M.; Laibinis, P. E. *Langmuir*, **1990**, *6*, 87. (h) Bain, C. D.; Troughton, E. B.; Tao, Y.-T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 321.

0897-4756/93/2805-0709$04.00/0

Scheme I. Assembly of an Inorganic Monolayer at an Organic Template



zirconium phosphonates. The method developed here demonstrates the idea of assembling an inorganic monolayer at a preformed, organized organic template (Scheme I) and should be useful when applied to other layered systems[5] including those that can be models for two-dimensional magnetism. A feature of these structures is that the inorganic lattice is isolated from the substrate by the organic template layer. When choosing inorganic systems for these studies, we draw on what is known about the structure of the three-dimensional solid-state analogs.[18–20] Our hypothesis is that the best chance to prepare a monolayer of an inorganic extended lattice is to investigate systems, such as the metal phosphonates,[18–22] that form layered structures in the bulk, crystalline phase.

Transition-metal alkylphosphonates belongs to the class of organic–inorganic layer compounds[5] in which layers of inorganic ions are separated by organized organic layers. Examples have been synthesized with divalent,[21] trivalent,[22] and tetravalent[18–20] metal ions. In the tetravalent Zr systems, $Zr(O_3PR)_2$, it is thought that the metal–phosphonate binding[19,20,23] is similar to the binding[18] observed in α-$Zr(HPO_4)\cdot H_2O$ where the metal ions are octahedrally coordinated by oxygen atoms, with the three oxygens of each phosphonate bound to three different

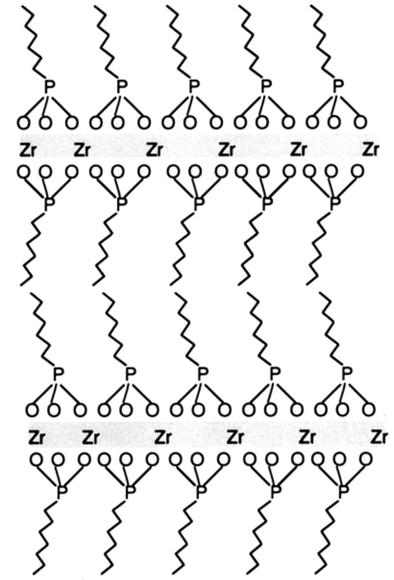


Figure 1. Schematic representation of a zirconium alkylphosphonate layered solid emphasizing the layered nature of the structure. The two-dimensional arrays of Zr^{4+} ions are linked together by layers of the organophosphonate above and below the zirconium ion plane.

zirconium ions.[18,23] Each layer consists of a plane of metal atoms linked together by layers of phosphonate groups above and below the metal ion plane (Figure 1).[18–20] The zirconium phosphonates are extremely insoluble, and Mallouk and co-workers[3b,24] have shown that thin films can be deposited onto surfaces by first anchoring a layer of molecules bearing the phosphonate functionality followed by alternately adsorbing Zr^{4+} ions and α,ω-alkanediyldiphosphonic acid layers from solution. Other groups[25] have used this method to prepare oriented assemblies of functionalized molecules one layer at a time for applications such as second harmonic generation.[25] To form an organized inorganic monolayer, we propose that the key is the first step where the array of phosphonate sites that form the template (Scheme I) must be close-packed. None of the published methods[24,25] or other SA schemes that we have attempted[26] have resulted in a close-packed template layer required to form an organized inorganic monolayer. We have, therefore, investigated the LB technique as a method to form suitable organic template systems for preparing inorganic monolayers.

Octadecylphosphonic acid forms a stable film at the air/water interface.[27,28] The surface pressure vs area (π–A) isotherms of octadecylphosphonic acid yields an extrapolated cross-sectional area of 24 Å^2/molecule, with collapse of the film occurring at a surface pressure of 60 mN/m.[28] Upon addition of Zr^{4+} ions to the water subphase, the octadecylphosphonic acid Langmuir monolayer be-

---

(17) (a) Pomerantz, M.; Dacol, F. H.; Segmuller, A. *Phys. Rev. Lett.* **1978**, *40*, 246. (b) Pomerantz, M. In NATO ASI Series "Phase Transitions in Surface Films". Dash, J. G., Ruvalds, J., Eds.; Plenum: New York, 1980; p 317. (c) Aviram, A.; Pomerantz, M. *Solid State Commun.* **1982**, *41*, 297. (d) Pomerantz, M. *Surf. Sci.* **1984**, *142*, 556.

(18) Clearfield, A.; Smith, G. D. *Inorg. Chem.* **1969**, *8*, 431–436.

(19) Alberti, G.; Constantino, U.; Allulli, S.; Tomassini, N. *J. Inorg. Nucl. Chem.* **1978**, *40*, 1113–1117.

(20) Dines, M. B.; Digiacomo, P. M. *Inorg. Chem.* **1981**, *20*, 92–97.

(21) (a) Cao, G.; Lee, H.; Lynch, V. M.; Mallouk, T. E. *Inorg. Chem.* **1988**, *27*, 2781–2785. (b) Cao, G.; Lee, H.; Lynch, V. M.; Mallouk, T. E. *Solid State Ionics* **1988**, *26*, 63–69. (c) Ortiz-Avila, C. Y.; Rudolf, P. R.; Clearfield, A. *Inorg. Chem.* **1989**, *28*, 2137–2141.

(22) (a) Cao, G.; Lynch, V. M.; Swinnea, J. S.; Mallouk, T. E. *Inorg. Chem.* **1990**, *29*, 2112–2117. (b) Bujoli, B.; Palvadeau, P.; Rouxel, J. *Chem. Mater.* **1990**, *2*, 582–589.

(23) Burwell, D. A.; Thompson, M. E. *Chem. Mater.* **1991**, *3*, 730–737.

(24) (a) Lee, H.; Kepley, L. J.; Hong, H.-G.; Akhter, S.; Mallouk, T. E. *J. Phys. Chem.* **1988**, *92*, 2597–2601. (b) Lee, H.; Kepley, L. J.; Hong, H.-G.; Mallouk, T. E. *J. Am. Chem. Soc.* **1988**, *110*, 618–620. (c) Kepley, L. J.; Sackett, D. D.; Bell, C. M.; Mallouk, T. E. *Thin Solid Films* **1992**, *208*, 132–136. (d) Akhter, S.; Lee, H.; Hong, H.-G.; Mallouk, T. E.; White, J. M. *J. Vac. Sci. Technol. A* **1989**, *7*, 1608–1613.

(25) (a) Putvinski, T. M.; Schilling, M. L.; Katz, H. E.; Chidsey, C. E. D.; Mujsce, A. M.; Emerson, A. B. *Langmuir* **1990**, *6*, 1567–1571. (b) Katz, H. E.; Scheller, G.; Putivinski, T. M.; Schilling, M. L.; Wilson, W. L.; Chidsey, C. E. D. *Science* **1991**, *254*, 1485. (c) Katz, H. E.; Schilling, M. L.; Chidsey, C. E. D.; Putvinski, T. M.; Hutton, R. S. *Chem. Mater.* **1991**, *3*, 699.

(26) Crews, M. L. M.S. Thesis, University of Florida, 1992.

(27) Riles, H. E.; Cook, H. D. *J. Colloid Sci.* **1954**, *9*, 535–546.

(28) Byrd, H.; Talham, D. R., unpublished results.

comes extremely rigid,[28] and conventional vertical LB deposition is not possible. Therefore, we have developed a new stepwise deposition procedure that involves a combination of LB and "inorganic self-assembly" methods to prepare monolayer and multilayer films of zirconium octadecylphosphonate. Characterization of bilayer and multilayer films shows that the structure of these films is similar to that observed for the bulk zirconium phosphonate solids.[18-20] In addition, the insolubility of the films suggests that the procedure might also be useful for forming stable films of oriented organic molecules.

Experimental Section

Materials. Octadecylphosphonic acid ($C_{18}H_{39}O_3P$) was synthesized from commercial octadecyl bromide (Aldrich Chemical Co.) by the Michaelis–Arbuzov[29] reaction, followed by acid hydrolysis. The acid was recrystallized from methanol and dried under vacuum. Zirconyl chloride, 98%, was used as purchased from Aldrich.

Substrate Preparation. Single-crystal (100) face silicon wafers, purchased from Semiconductor Processing Co. (Boston), were used as deposition substrates. Silicon attenuated total reflectance (ATR) crystals, 50 mm × 10 mm × 3 mm purchased from Wilmad Glass, were used as substrates for all infrared experiments. Silicon ATR crystals were parallelograms, with a 45° angle of incidence with respect to the parallel faces. The silicon substrates were cleaned using the RCA cleaning procedure[30] then dried under N_2. Octadecyltrichlorosilane (OTS)-coated surfaces were prepared by placing the cleaned substrates in a 2% solution of OTS in hexadecane for 30 min. Substrates were then rinsed in a chloroform Soxhlet extractor for 30 min. Upon removal from the Soxhlet, the substrates were hydrophobic.

Instrumentation. The Langmuir–Blodgett experiments were performed using KSV Instruments (Stratford, CT) Teflon-coated LB troughs with hydrophobic barriers. The surface pressure was measured by a platinum Wilhelmy plate. A Barnstead Nanopure purification system produced water with a resistivity of 18 MΩ cm for all experiments. Single-barrier pressure versus area (π–A) isotherms were recorded using a KSV 3000 Langmuir–Blodgett instrument, and all depositions were carried out using the KSV 3000 system. In all cases, films were compressed linearly at a rate of 5 mN/(m min) at room temperature. For the depositions, a target pressure of 20 mN/m was maintained with deposition speeds of 10 mm/min.

Advancing contact angle measurements were measured with a Ramé-Hart (Mountain Lakes, New Jersey) NRL Model 100-00 contact angle goniometer. A 250-μL syringe was used to dispense a fixed-volume water drop to the surface.

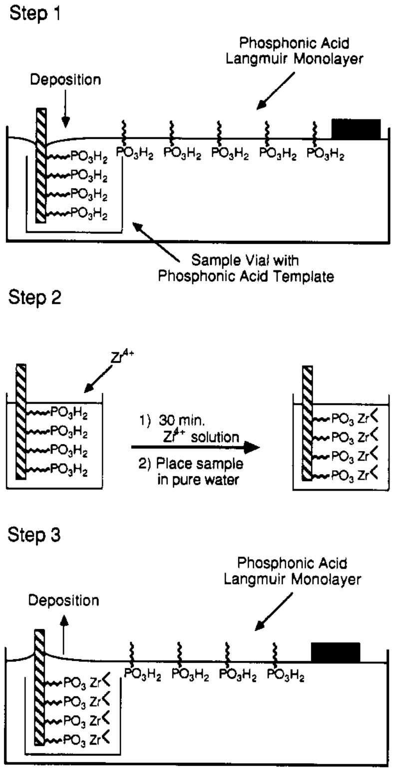
Infrared spectra were recorded with a Mattson Instruments (Madison, Wisconsin) Research Series-1 Fourier transform infrared (FTIR) spectrometer using a narrow-band mercury cadmium telluride detector. A Harrick (Ossining, NY) TMP stage was used for the ATR experiments. All spectra consist of 1000 scans at 4.0-cm^{-1} resolution and are ratioed to the OTS-covered substrates.

Film thickness was measured with a Gaertner (Chicago) Model L117 ellipsometer employing a 70° angle of incidence with a HeNe laser, λ = 632.8 nm, as the source. The refractive index and thickness of the films were calculated from Ψ and Δ using an in-house computer program.

Grazing-angle X-ray diffraction was performed on the films with a Rigaku 18-kW rotating anode diffractometer. The X-ray source was the Cu Kα line, λ = 1.54 Å, which was first passed through a graphite monochromator. The diffracted X-ray beam was passed through a graphite analyzer before hitting the detector to ensure monochromatic radiation.

Modeling of the zirconium octadecylphosphonate structure was performed using SYBYL (Tripos Associates) molecular modeling program. In SYBYL, the CRYSIN mode was used to import crystallographic coordinates[18] for α-$Zr(HPO_4)_2{\cdot}H_2O$. An octadecyl hydrocarbon chain, using the BUILD mode, was grafted onto the structure to simulate the zirconium octadecylphosphonate structure.

Scheme II. Deposition Procedure for the Preparation of Zirconium Octadecylphosphonate Bilayers



X-ray photoelectron spectra were obtained using a Perkin-Elmer PHI 5000 Series spectrometer. All spectra were taken using the Mg Kα line source at 1253.6 eV. The spectrometer has a typical resolution of 2.0 eV, with anode voltage and power settings of 15 kV and 300 W, respectively. Typical operating pressure was 5×10^{-9} atm. Survey scans were performed at a 45° takeoff angle with a pass energy of 89.45 eV. Multiplex scans, 140 scans at each peak, were run over a 20–40-eV range with a pass energy of 17.90 eV.

Results and Discussion

Deposition Procedure. The procedure developed for depositing zirconium phosphonate films is outlined in Scheme II. The method combines both LB and SA deposition techniques. The first step is to create an LB template of octadecylphosphonic acid suitable for binding Zr^{4+} ions. This is achieved by transferring a single LB layer of octadecylphosphonic acid from a pure water subphase onto an OTS-covered substrate. The substrate is dipped down through the film into a vial sitting in the subphase. The Langmuir monolayer is then decompressed, and the vial containing the octadecylphosphonic acid-coated slide, now immersed in the subphase, is removed from the trough. The second step is to "self-assemble" the Zr^{4+} ions at the organic template by adding enough $ZrOCl_2$ to the vial to produce a 5 mM zirconium solution. After 30 min, the substrate with the zirconated template layer is removed from the Zr^{4+} solution and placed into another vial containing pure water. The final step is to bind the capping layer to complete the bilayer assembly. The substrate, in pure water, is placed back into the LB trough, where a new octadecylphosphonic acid film is

---

[29] (a) Gilbert, A. R.; Precopio, F. M. *Abstracts of Papers Presented at the 125th Meeting, ACS* **1954**, 16N. (b) Bhattacharya, A. K.; Thyagarajan, G. *Chem. Rev.* **1981**, *81*, 415–430.

[30] Kern, W.; Puotinen, D. *RCA Rev.* **1970**, *31*, 187.

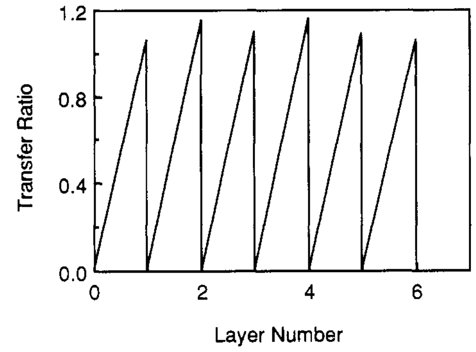


Figure 2. Transfer ratios for the transfer of six octadecylphosphonic acid layers during the formation of zirconium phosphonate bilayers. Odd layers are tail-to-tail depositions and even layers are deposited onto zirconated surfaces. The first layer is transferred onto an OTS-covered silicon substrate. Transfer ratios have not been corrected for creep of the Langmuir monolayer.

compressed over the vial, and is then transferred to the substrate creating a Y-type zirconium octadecylphosphonate bilayer. When the substrate is removed from the Zr^{4+} solution it is completely wetted, while after deposition of the capping layer the sample is dry. Contact angle measurements on bilayer and multilayer films result in an advancing contact angle of 112 ± 1°. Multilayers can be produced by repeating this three-step deposition procedure on the resulting hydrophobic surface.

Octadecylphosphonic acid was transferred at a constant surface pressure of 20 mN/m. The transfer ratios of the tail-to-tail (odd layers) and head-to-head (even layers) depositions are shown in Figure 2. Transfer ratios range between 1.1 and 1.2 and are high because they have not been corrected for slow creep of the phosphonic acid film on the subphase. We have determined by creep test[31] that the barrier moves forward at an average rate of 0.5 mm/min in order to maintain a surface pressure of 20 mN/m.

Infrared Spectroscopy. IR spectroscopy is useful to monitor and characterize transferred films.[15c,32,33] Figure 3 compares the FTIR spectrum, from 2600 to 3200 cm^{-1}, of the deposited LB monolayer template after binding of Zr^{4+} ions (after step 2 in Scheme II) to the spectrum of a zirconium phosphonate bilayer (after step 3 in Scheme II). Also shown in Figure 3 is the spectrum of a multilayer film (three bilayers) formed by repeating the deposition process. In each spectrum three bands are resolved:[15c,32] the asymmetric CH_3 stretch ($\nu_a(CH_3)$) at 2960 cm^{-1}, the asymmetric CH_2 stretch ($\nu_a(CH_2)$) at 2918 cm^{-1}, and the symmetric CH_2 stretch ($\nu_s(CH_2)$) at 2852 cm^{-1}. The $\nu_a(CH_2)$ band has been shown to be useful in understanding the order and packing of the aliphatic chains in monolayers.[32] The band frequency is indicative of the conformational order[15c,32] and ranges from 2918 cm^{-1} in an all-trans conformation to 2924 cm^{-1} in a "liquidlike" alkane that contains a large percentage of gauche bonds. The full width at half-maximum (fwhm) is a measure of the orientational order.[15c,33] For example, the fwhm of an OTS monolayer is 17 cm^{-1}, whereas a randomly oriented film[28] can result in a fwhm of greater than 35 cm^{-1}. For octadecylphosphonic acid, the $\nu_a(CH_2)$ band frequency ranges from 2918 cm^{-1} with a fwhm of 21 cm^{-1} in the crystalline solid to 2924 cm^{-1} with a fwhm of 35 cm^{-1} in solution.[28] In all three spectra presented in Figure 3, the frequency of the $\nu_a(CH_2)$ band is 2918 cm^{-1}, and the fwhm is 20 cm^{-1} indicating that the aliphatic chains are close-packed and possess an all-trans conformation. Progressing from template layer to bilayer, the intensities of the C–H bands double, but the position and appearance of the bands remain unchanged indicating that the structure of the film does not change during the deposition process. Figure 4 plots the intensity of the $\nu_a(CH_2)$ band versus the number of bilayers for multilayer films. The linear correlation is consistent with a layer-by-layer deposition as suggested by the transfer ratio data.

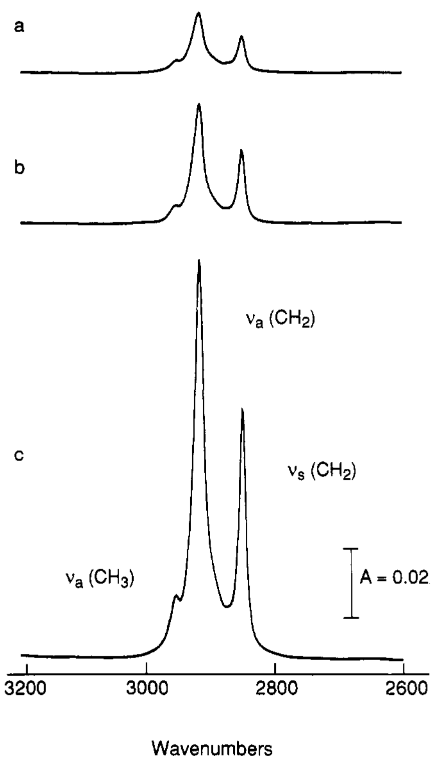


Figure 3. ATR-FTIR spectra monitoring the deposition of zirconium octadecylphosphonate: (a) a single octadecylphosphonic acid template layer after binding Zr^{4+}; (b) a single bilayer of zirconium octadecylphosphonate; (c) three bilayers of zirconium octadecylphosphonate. In each spectrum three bands are resolved: $\nu_a(CH_3)$ at 2960 cm^{-1}, $\nu_a(CH_2)$ at 2918 cm^{-1}, and $\nu_S(CH_2)$ at 2852 cm^{-1}. The full width at half maximum for each $\nu_a(CH_2)$ band is 20 cm^{-1}. All spectra are referenced to the OTS-covered silicon ATR crystal.

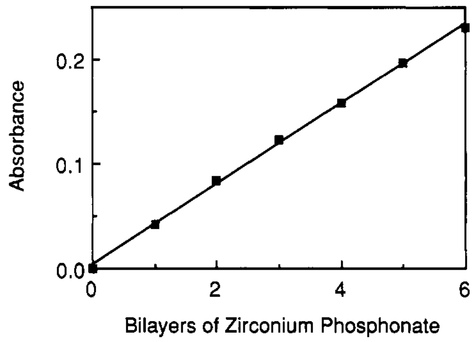


Figure 4. Plot of the intensity, measured as the absorbance, of the $\nu_a(CH_2)$ band at 2918 cm^{-1} versus the number of zirconium octadecylphosphonate bilayers. The fwhm is 20 cm^{-1} for each point. The solid line is a linear regression fit of the data.

---

[31] Biddle, M. B.; Rickert, S. E.; Lando, J. B. *Thin Solid Films* **1985**, *134*, 121.

[32] Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559–3568.

[33] Wood, K. A.; Snyder, R. G.; Strauss, H. L. *J. Chem. Phys.* **1989**, *91*, 5255–5267.

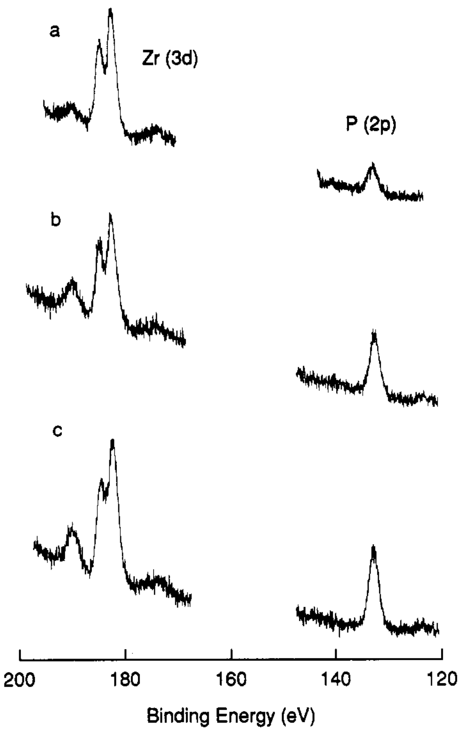


Figure 5. XPS spectra monitoring the deposition of zirconium octadecylphosphonate: (a) a single octadecylphosphonic acid template layer after binding Zr^{4+}; (b) a single bilayer of zirconium octadecylphosphonate; (c) three bilayers of zirconium octadecylphosphonate. The peaks are attributed to Zr ($3d_{3/2}$ at 183.6 eV; $3d_{5/2}$ at 185.9 eV) and P (2s at 191.5 eV; 2p at 134 eV). Elemental ratios are obtained from integrated signal intensities of the Zr 3d and P 2p peaks that have been corrected for instrument and atomic sensitivity factors.[34,35] The zirconium phosphorus ratios are 1:1 in (a), 1:2 in (b), and 1:2 in (c).

X-ray Photoelectron Spectroscopy. XPS analysis shows that C, Si, O, P, and Zr are the only elements present in the deposited films. Figure 5 shows XPS multiplex spectra of the Zr 3d and P 2p peaks for a template film capped with zirconium, a zirconium phosphonate bilayer, and three zirconium phosphonate bilayers all on OTS-covered silicon. Using the appropriate instrument and atomic sensitivity factors,[34,35] the ratio of the integrated signal intensities gives relative atomic concentrations accurate to within 10%.[36] According to the first spectrum in Figure 5, after zirconium ions bind to the octadecylphosphonic acid template layer, the P:Zr ratio is 1:1. This indicates that the molecules in the octadecylphosphonic acid film are spaced to allow one zirconium ion per phosphonate group and that the film is close-packed so that the molecules cannot rearrange to bind two phosphonates to a single zirconium ion. After capping the template with a second octadecylphosphonic acid LB layer (middle spectrum of Figure 5), the P:Zr ratio is 2:1 which is consistent with the stoichiometry observed in the bulk layered zirconium phosphonates.[18-20] Finally, the lower spectrum in Figure 5 shows a 2:1 P:Zr ratio in the film containing three bilayers, indicating that the chemical content of the film remains the same as multilayered films are deposited.

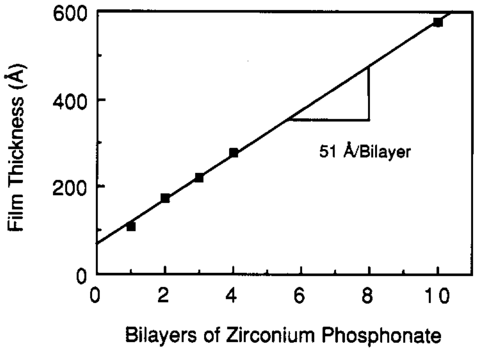


Figure 6. Ellipsometrically determined film thickness versus the number of bilayers of zirconium octadecylphosphonate deposited onto OTS-covered Si. The data are fit for a film refractive index of 1.49. The solid line is a linear regression fit of the data.

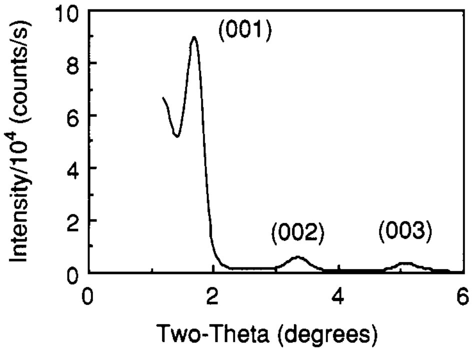


Figure 7. Grazing angle X-ray diffraction from 12 bilayers of zirconium octadecylphosphonate on OTS-covered Si. Three orders of the (00*l*) reflection are present and correspond to an interlayer spacing of 52 Å.

Ellipsometry and X-ray Diffraction. Reflection ellipsometry was used to determine the thickness of deposited films and to monitor the layer-to-layer deposition. Ellipsometric data (Figure 6) show a linear increase in film thickness with each successive bilayer. The data are fit using an index of refraction of 3.84 for the Si substrates and 1.49 for the zirconium alkylphosphonate films. From the slope of the regression line, a thickness of 51 ± 5 Å per bilayer is calculated. The fact that the regression line does not pass through the origin is expected. The template films are transferred onto an OTS-covered silicon wafer with an unknown oxide thickness. The combination of the oxide layer and OTS produces an initial film thickness which is constant throughout the experiment.

While ellipsometric results are consistent with layer-by-layer deposition, it should be remembered that ellipsometry yields an average film thickness,[37] but does not prove that the films indeed possess a layered structure. Ellipsometry should be used in conjunction with other experimental data, and here the ellipsometric results are confirmed by grazing angle X-ray diffraction. Figure 7 shows X-ray diffraction from 12 bilayers of zirconium octadecylphosphonate on a silicon substrate. Three orders of the (00*l*) reflection including the (001) reflection can be identified. The data correspond to a *d* spacing of 52 Å for the zirconium octadecylphosphonate films in excellent agreement with the ellipsometric data. More importantly,

---

(34) *Perkin-Elmer, PHI ESCA Operator's Manual.*

(35) Scofield, J. H. *J. Electron. Spectrosc.* **1976**, *8*, 129–137.

(36) Seah, M. P. *Practical Surface Analysis*, 2nd ed.; Briggs, D., Seah, M. P., Eds.; Auger and X-Ray Photoelectron Spectroscopy; John Wiley and Sons: Chichester, 1990; Vol. 2, p 240.

(37) Azzam, R. M. A.; Bashara, N. M. *Ellipsometry and Polarized Light*; North-Holland Publishing Co.: Amsterdam, 1977.

however, is that diffraction proves the layered nature of the films.

Structure of Monolayer and Multilayer Films. Steps 1 and 2 of the deposition method outlined in Scheme II represent an example of "inorganic self-assembly" at an organic template. The LB method is first used to arrange the octadecylphosphonic acid molecules into an organized assembly that is similar to the packing the alkylphosphonates assume in the three-dimensional solid-state structure. From structural data[18] of solid α-Zr-$(HPO_4)_2 \cdot H_2O$, the intermolecular distance between phosphonic acid molecules corresponds to a mean molecular area of 24.7 Å^2/molecule in the zirconium ion plane, while the mean molecular area of the octadecylphosphonic acid LB film is 24 Å^2/molecule.[28] This arrangement provides a surface that allows the binding from solution of one zirconium ion per phosphonate group at the surface as confirmed by the XPS data in Figure 5 and prohibits the phosphonate molecules from folding over to bind more than one phosphonate group per zirconium ion.

Addition of the capping phosphonic acid layer completes the metal phosphonate bilayer. The bilayer films, as well as the multilayer films, have structures similar to those observed for solid zirconium phosphonates. XPS shows that the films have the $Zr(O_3PR)_2$ stoichiometry, and X-ray diffraction proves that the films possess a layered structure. The complete analysis is in accord with a structure that consists of layers of zirconium ions bonded by phosphonate groups that extend above and below the plane, forming a layer of close-packed alkyl chains. We attempted to model the zirconium octadecylphosphonate bilayers with the SYBYL molecular modeling program. Using crystallographic coordinates for α-$Zr(HPO_4)_2 \cdot H_2O$[18] to model Zr–O_3P binding, a bilayer was generated by grafting on a $(CH_2)_{17}CH_3$ chain in place of the phosphate OH. In the generated structure, the all-trans hydrocarbon chain lies at a tilt angle of 31.3° with respect to the zirconium ion plane which is a consequence of the phosphonate P–C bond orienting nearly perpendicular to the plane of metal ions, just as the P–OH bond is oriented in the α-Zr-$(HPO_4)_2 \cdot H_2O$ structure.[18] The resulting Zr–Zr interplane spacing is 42.8 Å. If the alkyl chains are rotated such that the chain axes are oriented perpendicular to the zirconium ion plane, the maximum expected interlayer spacing is 53.7 Å. The experimentally determined interlayer spacing of 52 Å for the zirconium octadecylphosphonate films lies within the 42.8–53.7 Å range determined from modelling. The 52 Å spacing, however, requires the phosphonate alkyl chain to orient nearly perpendicular to the plane of metal ions, which would force the Zr–O_3P binding to differ from that observed for α-$Zr(HPO_4)_2 \cdot H_2O$.

In α-$Zr(HPO_4)_2 \cdot H_2O$ the phosphate group sits above an equilateral triangle of Zr^{4+} ions with phosphate oxygens binding three different metal ions in the triangle.[18] The phosphate groups are bridged by zirconium ions such that the oxygen atoms that form the octahedral coordination come from six different phosphates, three in the plane above and three in the plane below the zirconium ion plane.[18] In the zirconium octadecylphosphonate bilayers, the phosphonate alkyl chains can only orient perpendicular to the metal ion plane if the tetrahedral RPO_3 groups are tilted such that the three phosphonate oxygens no longer have equivalent orientations relative to the plane of zirconium ions. Such an arrangement has been observed in some γ-phase layered zirconium phosphates.[38] In the series γ-$Zr(HPO_4)(n\text{-}C_nH_{2n+1}PO_4) \cdot yH_2O$,[38b,c] the interlayer spacing increases with the alkyl chain length, and the slope of this increase is consistent with the phosphate groups orienting with their alkyl chain axes perpendicular to the zirconium ion plane. Because only every other phosphate is alkylated in the γ-phase materials, the alkyl chains fold over in the longer chain derivatives in order to maximize the van der Waals contact between the hydrocarbon chains.[38b,c] Upon intercalation with *n*-alcohols, however, the alkyl groups reorient themselves perpendicular to the zirconium plane, as the alcohol molecules fill the voids in the organic layer.[38b] Yamanaka and co-workers[38b,c] have prepared a number of intercalated derivatives, including the octadecyl analog,[38b] where X-ray diffraction shows the interlayer spacing to be 52 Å, which is exactly the thickness observed for the zirconium octadecylphosphonate films. It seems plausible that the zirconium phosphonate organization resulting from the layer-by-layer deposition developed here, most closely resembles the γ-phase materials. The assembly of the alkylphosphonate template by the Langmuir–Blodgett technique aligns the alkyl chains perpendicular to the substrate. This arrangement of the alkylphosphonate template is preserved by the zirconium bonding step, which suggests that the preformed LB template directs the bonding in the self-assembled inorganic layer.[39]

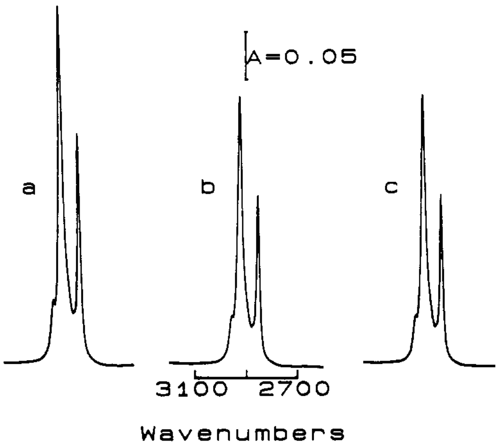


Figure 8. ATR-FTIR spectra monitoring film loss from 10 bilayers of zirconium octadecylphosphonate after soaking in chloroform: (a) before placing in chloroform; (b) after 60 min in chloroform; (c) after 120 min in chloroform. After initial washing 20% of the film is lost, however, the frequency and shape of the $\nu_a(CH_2)$ band remains unchanged. Additional washings with chloroform do not affect the film.

Solid zirconium phosphonates are highly insoluble in both water and organic solvents, and the zirconium phosphonate films described here are similarly insoluble. Figure 8 compares IR spectra of a 10-bilayer film before and after soaking in chloroform for 60 and 120 min. After 60 min, the $\nu_a(CH_2)$ is still at 2918 cm^{-1} with a fwhm of 20 cm^{-1}, but approximately 20% of the film has been lost. After this spectrum was taken, the film was placed back into chloroform for another 60 min and the spectrum recorded again. That the frequency and shape of the IR band remain constant after the first soaking in chloroform

---

[38] (a) Yamanaka, S.; Tanaka, M. *J. Inorg. Nucl. Chem.* **1979**, *41*, 45–48. (b) Yamanaka, S.; Matsunaga, M.; Hattori, M. *Ibid.* **1981**, *43*, 1343–1346. (c) Yamanaka, S.; Sakamoto, K.; Hattori, M. *J. Phys. Chem.* **1981**, *85*, 1930–1933.

[39] We wish to acknowledge helpful reviewers comments on this point.

indicates that the remaining film is still close-packed and does not rearrange. We hypothesize that the original soaking washes away defect areas of the film and that what remains is the insoluble zirconium phosphonate.

The approach of using an organic monolayer to organize the inorganic monolayer is similar to the concept of using Langmuir monolayers to influence nucleation and crystal growth of inorganic solids from an LB subphase.[40–48] Heywood and co-workers[40–44] have shown that crystals of the inorganic salts $CaCO_3$[40–42] and $BaSO_4$[43,44] can be grown from saturated solutions at Langmuir monolayers of surfactant molecules and that the choice of surfactant can influence the orientation and growth of specific faces or even regulate the selectivity of crystal polymorphs. Studies by Landau et al.[45,46] have demonstrated similar control on the growth of glycine crystals at Langmuir monolayers of resolved amino acids. In these studies, the Langmuir monolayer serves as a template for nucleation, where the intermolecular spacing of the template, as well as the stereochemical and electrostatic nature of the interface, can be controlled by choice of surfactant molecule. The work we present here is similar in that the organic layer is first organized in order to control the molecular spacing of the inorganic material, while in contrast, we restrict the growth of the inorganic lattice to a single layer. In addition, the template layer used here is not a floating monolayer, rather the template is placed onto a solid support.

The stability of these films in both aqueous and organic solvents suggests that zirconium phosphonate films could be useful in preparing materials that require organized assemblies of organic molecules analogous to other LB[49] and SA[25,50,51] work on preparing films with second-order nonlinear optical properties. While the LB method is ideally suited to orienting organic molecules, thin films are generally metastable and the desired physical effects decay with time. The films described here are modeled after a known layered solid-state structure, and the thermodynamic stability of the zirconium phosphonate structure greatly enhances the durability of these films, suggesting that the preparation procedure described herein should be considered for preparing materials that require organized organic assemblies. Other groups[25] have taken advantage of strong zirconium phosphonate binding in forming *self-assembling* multilayer films for nonlinear optical[25] applications. A feature of the LB deposition process, however, is that a close-packed phosphonic acid template is ensured, generating the optimum density of sites for binding zirconium ions. This should lead to a higher density of active organic molecules in the mixed organic/inorganic assembly as well as a higher degree of orientation. It is also possible[28] to use the LB method for depositing just the first template layer and then build up multilayer films using the alternate Zr^{4+} ion, α,ω-diphosphonic acid SA procedure developed by Mallouk and co-workers[3b,24] and used by other groups.[25] We are currently investigating how the order of the initial LB template film is transferred to successive SA layers.

Conclusions

In conclusion, we have demonstrated that an organized organic monolayer can be used as a template for assembling an extended lattice inorganic monolayer. A stepwise procedure has been developed for forming monolayer and multilayer films of zirconium octadecylphosphonate that uses an LB film of octadecylphosphonic acid to provide an organized surface for binding Zr^{4+} ions from solution. The zirconium phosphonate structure is completed by capping the surface with a second octadecylphosphonic acid LB film. Analysis of bilayer and multilayer films is consistent with forming layers on the surface whose structure is analogous to that of solid layered zirconium phosphonates. The approach of using organized monolayers for preparing inorganic monolayer films should be applicable to other layered organic/inorganic systems including systems that have been used to model two-dimensional conductors and magnets.

Acknowledgment. We thank Dr. Stephen E. Nagler for X-ray diffraction data, Dr. Joseph H. Simmons for use of the ellipsometer, the Major Analytical Instrumentation Center at the University of Florida for instrument time, and Mr. Eric Lambers for technical assistance. We also thank Professor Kirk S. Schanze for assistance with the SYBYL modeling program. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation [DMR-9205333], and the University of Florida Division of Sponsored Research for partial support of this Research.

---

(40) Mann, S.; Heywood, B. R.; Rajam, S.; Birchall, J. D. *Nature* 1988, *334*, 692–695.

(41) Rajam, S.; Heywood, B. R.; Walker, J. B. A.; Mann, S.; Davey, R. J.; Birchall, J. D. *J. Chem. Soc., Faraday Trans.* 1991, *87* (5), 727–734.

(42) Heywood, B. R.; Rajam, S.; Mann, S. Oriented Crystallization of $CaCO_3$ under Compressed Monolayers. Part 2. *Ibid.* 735–743.

(43) Heywood, B. R.; Mann, S. *Langmuir* 1992, *8*, 1492–1498.

(44) Heywood, B. R.; Mann, S. *J. Am. Chem. Soc.* 1992, *114*, 4681–4686.

(45) Landau, E. M.; Grayer-Wolf, S.; Levanon, M.; Leiserowitz, L.; Lahav, M.; Sagiv, J. *Mol. Cryst. Liq. Cryst.* **1986**, *134*, 323–325.

(46) Landau, E. M.; Popovitz-Bior, R.; Levanon, M.; Leiserowitz, L.; Lahav, M.; Sagiv, J. *J. Am. Chem. Soc.* **1989**, *111*, 1436–1439.

(47) Zaho, X. K.; Xu, S.; Fendler, J. H. *Langmuir* **1991**, *7*, 520–523.

(48) Gavish, M.; Popovitz-Bior, R.; Lahav, M.; Leiserowitz, L. *Science* **1990**, *250*, 973–974.

(49) (a) Bosshard, C.; Küpfer, M.; Günter, P.; Pasquier, C.; Zahir, S.; Siefert, M. *Appl. Phys. Lett.* **1990**, *56*, 1204–1206 and references therein. (b) Popovitz-Biro, R.; Hill, K.; Landau, E. M.; Lahav, M.; Leiserowitz, L.; Sagio, J.; Hsiung, H.; Meredith, G. R.; Vanherzeele, H. *J. Am. Chem. Soc.* **1988**, *110*, 2672–2674. (c) Cross, G. H.; Peterson, I. R.; Girling, I. R.; Cade, N. A.; Goodwin, M. J.; Carr, N.; Sethi, R. S.; Marsden, R.; Gray, G. W.; Lacey, D.; McRoberts, A. M.; Scrowston, R. M.; Toyne, K. J. *Thin Solid Films* **1988**, *156*, 39–52.

(50) Li, D.; Ratner, M. A.; Marks, T. J.; Zhang, C.; Yang, J.; Wong, G. K. *J. Am. Chem. Soc.* **1990**, *112*, 7389–7390.

(51) Ulman, A. *J. Phys. Chem.* **1988**, *92*, 2385.