

# Ordered Conducting Films of the Inorganic Polymer $(\text{LiMo}_3\text{Se}_3)_n$ Cast from Solution

Josh H. Golden,\* Francis J. DiSalvo, and Jean M. J. Fréchet

Cornell University, Department of Chemistry, Baker Laboratory, Ithaca, New York 14853-1301

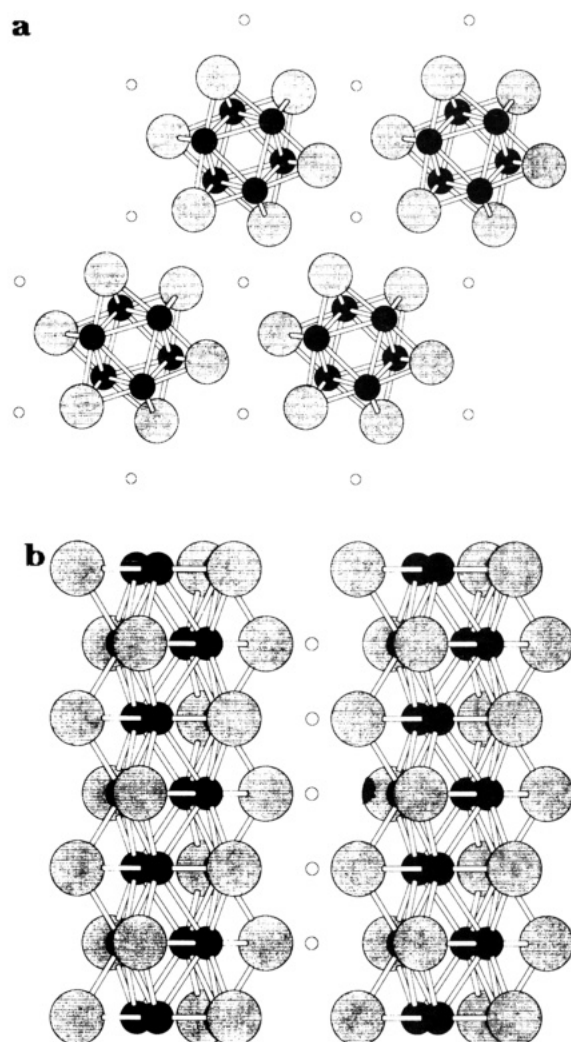
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Dimethyl sulfoxide (DMSO) solutions of the inorganic polymer  $(\text{LiMo}_3\text{Se}_3)_n$  are cast or spin coated to form lustrous metallic films after heating in vacuo. Transmission electron microscopy (TEM), ultrahigh-vacuum scanning TEM (UHV-STEM), X-ray diffraction, and SEM microprobe analysis confirm that the films consist of locally ordered linear chains and chain bundles of  $(\text{LiMo}_3\text{Se}_3)_n$ . Thick ( $\geq 1 \mu\text{m}$ ) free-standing foillike films display thermally activated conductivity and a low resistivity of  $5 \times 10^{-3} \Omega \text{ cm}^{-1}$  at 23 °C. Highly oriented thin films ( $< 1 \mu\text{m}$ ), prepared by the flowing of solutions, display order over 160  $\mu\text{m}$ , as confirmed by absorbance polarized light microscopy.

## Introduction

Interest in the rational design and synthesis of low-dimensional organic and inorganic solids has steadily increased over the past decade as part of a search for materials displaying novel physical properties. These properties include anisotropic conductivity, superconductivity, nonlinear optical phenomena, and piezoelectric behavior.<sup>1</sup> Recent reports have detailed progress in the fabrication of materials exhibiting “molecular wire” and “nanowire” morphologies.<sup>2</sup> Since our research interests include the synthesis and physical properties displayed by one-dimensional solids with similar structural characteristics,<sup>3</sup> we have investigated the properties exhibited by the inorganic polymer  $(\text{LiMo}_3\text{Se}_3)_n$ , a compound that is soluble in some polar organic solvents and water.

First described by Potel et al.,<sup>4</sup> the  $(\text{MMo}_3\text{X}_3)_n$  series of metallic linear chain compounds (M = an alkali or monovalent main-group metal, X = Se, S) are structurally related to the Chevrel phases,<sup>5</sup> with the stoichiometry  $\text{M}_x\text{Mo}_3\text{Se}_{3n+2}$  ( $n \geq 2$ ). As shown in Figure 1, when  $n = \infty$ , a hexagonal array of ca. 6 Å diameter  $(\text{Mo}_3\text{X}_3)_n$  inorganic polymers is formed, built from the polycondensation of octahedral clusters of molybdenum through



**Figure 1.** (a) Projection of the  $(\text{MMo}_3\text{Se}_3)_n$  structure (M = Li) onto the hexagonal (001) plane and (b) the (1120) plane (side view,  $n = 7$ ). Atoms in order of increasing size are: Li, Mo, Se.

trans faces, with the remaining faces capped by chalcogen atoms. Monovalent cations (M) reside in the interstitial spaces between the chains.

The  $(\text{MMo}_3\text{X}_3)_n$  compounds display a wide variety of physical and chemical properties depending on the

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identity of the M interstitial cation.<sup>6</sup> For example, when (LiMo<sub>3</sub>Se<sub>3</sub>)<sub>n</sub> is treated with the polar solvents propylene carbonate, *N*-methylformamide (NMF), DMSO, or water, it dissolves to form highly absorbing burgundy solutions that consist of solvated lithium cations and (Mo<sub>3</sub>Se<sub>3</sub>)<sub>n</sub> polyanionic chains.<sup>6e</sup> Solutions subjected to shear or flow have the ability to polarize light,<sup>6e</sup> an indication of (Mo<sub>3</sub>Se<sub>3</sub>)<sub>n</sub> alignment in the direction of the applied force. Recently, Davidson, Gabriel, and co-workers<sup>7</sup> have shown that 10<sup>-2</sup> M NMF solutions of (LiMo<sub>3</sub>Se<sub>3</sub>)<sub>n</sub> display nematic liquid-crystalline morphology,<sup>7</sup> one typical of aligned polymeric rigid rods in solution.

We now report that spin coated or cast DMSO solutions of (LiMo<sub>3</sub>Se<sub>3</sub>)<sub>n</sub> form lustrous metallic thin films after heating in vacuo to remove solvent. Conducting free-standing foils are obtained by peeling the films from the substrates. These materials display local order, as well as novel optical and electrical properties.

### Experimental Section

**Materials and Methods.** (LiMo<sub>3</sub>Se<sub>3</sub>)<sub>n</sub> was synthesized as previously described.<sup>6d</sup> Unless otherwise noted, all manipulations were carried out under a dry argon atmosphere in an inert-atmosphere box. Solutions were prepared by mixing predetermined amounts of (LiMo<sub>3</sub>Se<sub>3</sub>)<sub>n</sub> and anhydrous DMSO (Aldrich) for at least 2 h in a tightly capped vial by magnetic stirring. After dissolution appeared complete, the solution was centrifuged at 3000 rpm for 45 min to separate out any remaining undissolved particulate material. Following separation by careful decantation, the solution was kept in a tightly stoppered vial under argon until needed for further use.

In a typical preparation of a thick film (≥1 μm) of (LiMo<sub>3</sub>Se<sub>3</sub>)<sub>n</sub>, 5 mL of ca. 10<sup>-2</sup> M (LiMo<sub>3</sub>Se<sub>3</sub>)<sub>n</sub> in DMSO is poured into a 10 mL Petri dish and then placed in a desiccator fitted with a heating element. After slow evaporation of the DMSO (24 h, 23 °C, 10<sup>-4</sup> Torr), a silver mirrorlike film forms in place of the burgundy solution. Heating to ca. 200 °C at 10<sup>-4</sup> Torr for 24 h results in the formation of a lustrous foil material that can be peeled from the Petri dish. Thin films (<1 μm) are prepared by spin coating solutions onto KBr or sapphire disks under argon, followed by slow evaporation of DMSO by heating in vacuo. Less concentrated solutions lead to thinner films.

TEM, UHV-STEM, and SEM microprobe samples were prepared in an argon-filled inert-atmosphere box and loaded for analysis with a minimum of air exposure (<30 s). X-ray powder diffraction samples were prepared in a similar fashion and were protected from oxygen and moisture with a thin film of Mylar during the experiment.

UV-vis, IR, and optical spectroscopic analyses were conducted under an inert atmosphere with a minimum of air exposure during sample loading (<1 min).

**Analytical Methods.** TEM images were obtained using a JEOL 1200EX instrument at 120 keV. UHV-STEM images were obtained using a Vacuum Generators HB-501A STEM at 100 keV equipped with an analytical pole piece (C<sub>s</sub> = 3.3 mm) and a working vacuum of ca. 10<sup>-10</sup> Torr. The theoretical resolution limit is 2.7 Å. SEM analyses were conducted using a JEOL 733 microprobe at 15 keV. X-ray powder diffraction data were collected using a Scintag XDS 2000 diffractometer using Cu Kα radiation.

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The electrical resistivity of a 1 μm thick film of (LiMo<sub>3</sub>Se<sub>3</sub>)<sub>n</sub> cast onto a sapphire disk was obtained under dry inert conditions using the four-probe technique at 13 Hz by lock-in detection. A sealed holder with four spring-loaded gold pin contacts was used.

Infrared spectra were recorded on a Nicolet FT-IR/44 spectrophotometer under flowing N<sub>2</sub>. UV-vis spectra were recorded on a Nicolet 9430 instrument on sapphire disks under flowing N<sub>2</sub>. Optical microscopy was conducted under argon with a Olympus BH-2 microscope fitted with the Olympus PM-10-M Polaroid photomicrograph system.

### Results and Discussion

**Electron Microscopy.** Both TEM and UHV-STEM<sup>8</sup> were used to investigate the morphology of the foil material. The TEM images in Figures 2a and 2b show the wispy fibrous morphology that is typically seen along torn edges of the foil material. The UHV-STEM image in Figure 2c confirms that the foil material consists of sheets of ordered linear chains of (LiMo<sub>3</sub>Se<sub>3</sub>)<sub>n</sub>. Parallel ordering of the individual (LiMo<sub>3</sub>Se<sub>3</sub>)<sub>n</sub> fibers persists for lengths up to 300 nm, with the greatest degree of order observed at film edges subjected to shearing or tearing.

We attribute the highly anisotropic nature of these cast films to the lyotropic liquid crystalline behavior of precursor solutions at concentrations of ca. 10<sup>-2</sup> M.<sup>7</sup> Solvent removal in vacuo increases the concentration of the rigid rods, so it is likely that their nematic liquid crystalline order is retained or even enhanced. At high concentrations, a film of ordered (LiMo<sub>3</sub>Se<sub>3</sub>)<sub>n</sub> "wires" is produced.

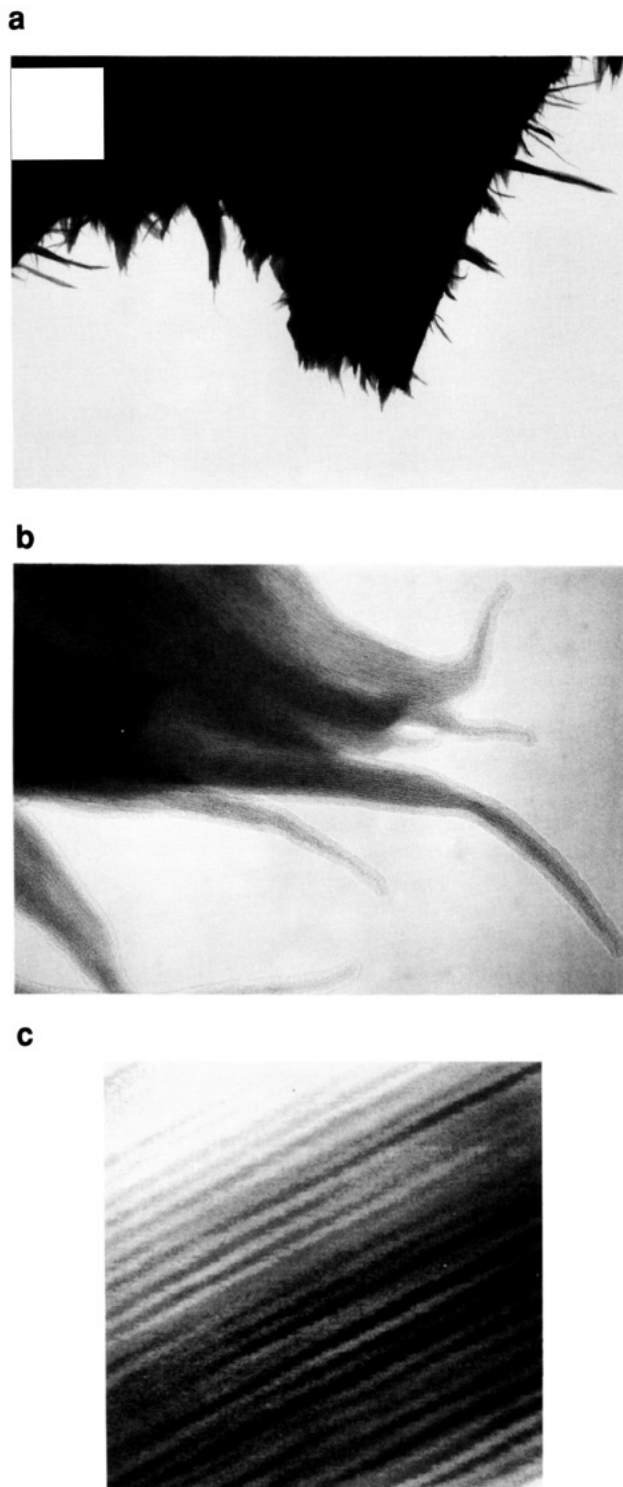
SEM microprobe analysis (Mo, Se, S) of the foil material is consistent with the stoichiometry (LiMo<sub>3</sub>Se<sub>3</sub>DMSO)<sub>n</sub>,<sup>9</sup> in which approximately one DMSO molecule is likely coordinated to the oxophilic lithium cation.<sup>10</sup> DMSO solvent inclusion between the (Mo<sub>3</sub>Se<sub>3</sub>)<sub>n</sub> chains is consistent with the findings of X-ray diffraction, in which an increase in interchain spacing is observed over that of polycrystalline (LiMo<sub>3</sub>Se<sub>3</sub>)<sub>n</sub>.

**X-ray Diffraction.** The X-ray powder diffraction pattern of 1 μm thick (LiMo<sub>3</sub>Se<sub>3</sub>)<sub>n</sub> foil (Figure 3a) differs from polycrystalline (LiMo<sub>3</sub>Se<sub>3</sub>)<sub>n</sub> (Figure 3b) by a ca. 2 Å increase in interchain spacing, and the almost complete absence of reflections other than the (100) peak at ca. 2θ = 12°. The absence of other peaks and the predominance of the (100) interchain reflection is consistent with the flat-sheet morphology observed by TEM and STEM, in which the inorganic polymer chains are ordered parallel to the flat diffraction substrate. Assuming that the chains are still hexagonally packed, the increase of interchain spacing from 7.42 to ca. 9.37 Å suggests that there is some DMSO solvent inclusion between the chains. The weak peak seen at ca. 2θ = 8° could be due to a portion of the film in which more than one DMSO molecule is included between the chains, thus resulting in greater chain separation.

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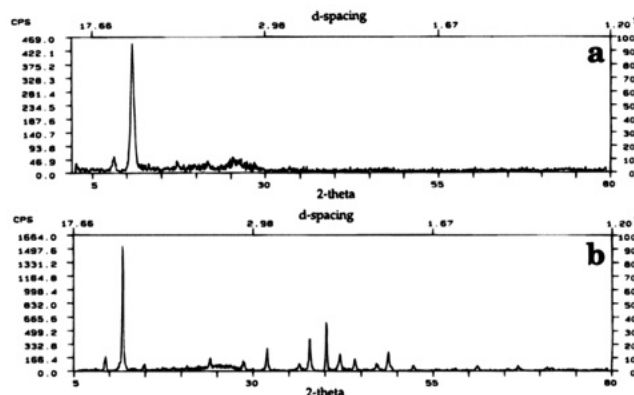
(9) Standardless microprobe analysis of (LiMo<sub>3</sub>Se<sub>3</sub>)<sub>n</sub> typically yields the following atomic percents: Li = 1.00 (fixed), Se, Mo = 42.0–42.5. The atomic ratios of Mo to Se can vary due to sample nonuniformity in thickness or density. Overlapping Mo Lα and S Kα lines were resolved via PET crystal spectrometer.

(10) For a comprehensive review on the coordination chemistry of the lithium ion see: Olsher, U.; Izatt, R. M.; Bradshaw, J. S.; Dalley, N. K. *Chem. Rev.* **1991**, *91*, 137.

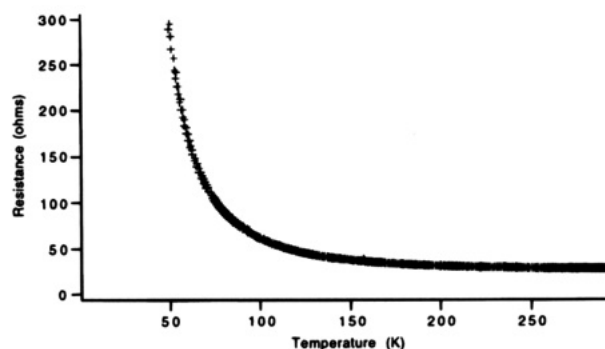


**Figure 2.** (a) Ca. 15000 $\times$  magnification TEM image of a sheared edge of the thick  $(\text{LiMo}_3\text{Se}_3)_n$  foil material. The horizontal field of view is ca. 7000 nm. The fibrous morphology is readily seen at torn edges of the foil material. (b) 330000 $\times$  magnification TEM image of  $(\text{LiMo}_3\text{Se}_3)_n$  tendrils pulled out from film edge. Horizontal field of view is 332 nm. Black striations are interpreted as individual  $(\text{LiMo}_3\text{Se}_3)_n$  fibers. Amorphous material around the film edges may be a result of brief air-exposure. (c) Brightfield UHV-STEM image of foil material at  $6 \times 10^6$  times magnification. Horizontal field of view is 170  $\text{\AA}$ . Black lines are interpreted as individual ca. 6  $\text{\AA}$  diameter  $(\text{LiMo}_3\text{Se}_3)_n$  fibers by calibration to a graphite standard.

**Four-Probe Resistivity Measurement.** As shown in Figure 4, a 1  $\mu\text{m}$  thick film of the foil material displays thermally activated conductivity. The four-



**Figure 3.** (a) X-ray powder diffraction pattern of  $(\text{LiMo}_3\text{Se}_3)_n$  foil material. Assuming hexagonal packing, the (100) peak at  $11^\circ$  ( $d = 9.37 \text{ \AA}$ ) has broadened and shifted ca. 2  $\text{\AA}$  in comparison to polycrystalline  $(\text{LiMo}_3\text{Se}_3)_n$ . (b) X-ray powder diffraction pattern of polycrystalline  $(\text{LiMo}_3\text{Se}_3)_n$ . The (100) peak at  $12^\circ$  ( $d = 7.42 \text{ \AA}$ ) is proportional to the interchain spacing  $d$ , where  $d = \sqrt{3}a/2$ .

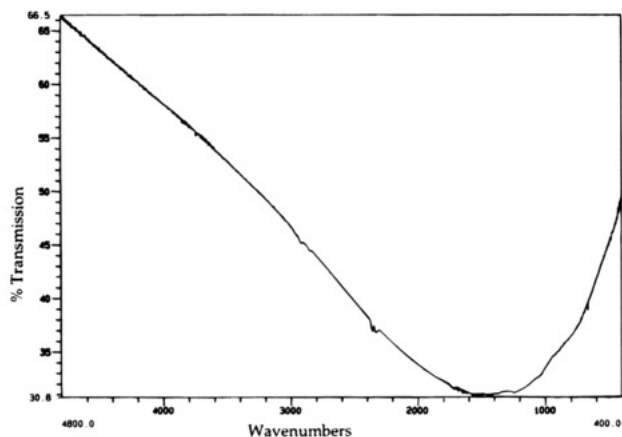


**Figure 4.** Four-probe temperature vs resistance plot of 1  $\mu\text{m}$  thick  $(\text{LiMo}_3\text{Se}_3)_n$  foil material cast onto a sapphire disk.

probe temperature vs resistance study yielded a resistivity value of  $5 \times 10^{-3} \Omega$  at  $23^\circ\text{C}$ , a factor of 50 greater than the  $10^{-4} \Omega \text{ cm}$  value observed for single crystals, where  $M \neq \text{Li}$ .<sup>6d</sup> The observed semiconducting-like behavior may be due to a one-dimensional Peierls's distortion, as previously suggested for this class of one-dimensional compounds.<sup>6d,11</sup> It is unclear what contribution interchain electron hopping may make to the observed resistivity behavior. However, due to the relatively short chain length and range of order in the foil material (hundreds of nanometers), it is likely that the contribution is substantial, since an electronic conduction pathway must be maintained over the area of the film being measured (0.5 cm between voltage contacts).

**Infrared Spectroscopy of Thin Films.** As shown in Figure 5, the IR spectrum of a KBr disc coated with  $(\text{LiMo}_3\text{Se}_3)_n$  displays a broad absorption centered at ca.  $1400 \text{ cm}^{-1}$  attributed to a plasma resonance. The plasma frequency is given by  $\omega_p = (4\pi e^2 n/m)^{1/2}$ , where  $n$  is the electron density, and  $m$  is the effective electron mass.<sup>3a,12</sup> In a previous IR study of  $(\text{LiMo}_3\text{Se}_3)_n$  suspended in a poly(ethylene oxide) film,<sup>3a</sup> a dc resistivity value for  $(\text{LiMo}_3\text{Se}_3)_n$  of  $10^{-2}$ – $10^{-3} \Omega \cdot \text{cm}$  was calculated from  $\rho = [\omega_p^2 \tau / 4\pi]^{-1}$ , where  $\tau$  is the carrier relaxation

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**Figure 5.** Infrared spectrum of ( $\text{LiMo}_3\text{Se}_3$ )<sub>n</sub> thin film spin-coated on a KBr disk shows broad absorption attributed to a plasma resonance.

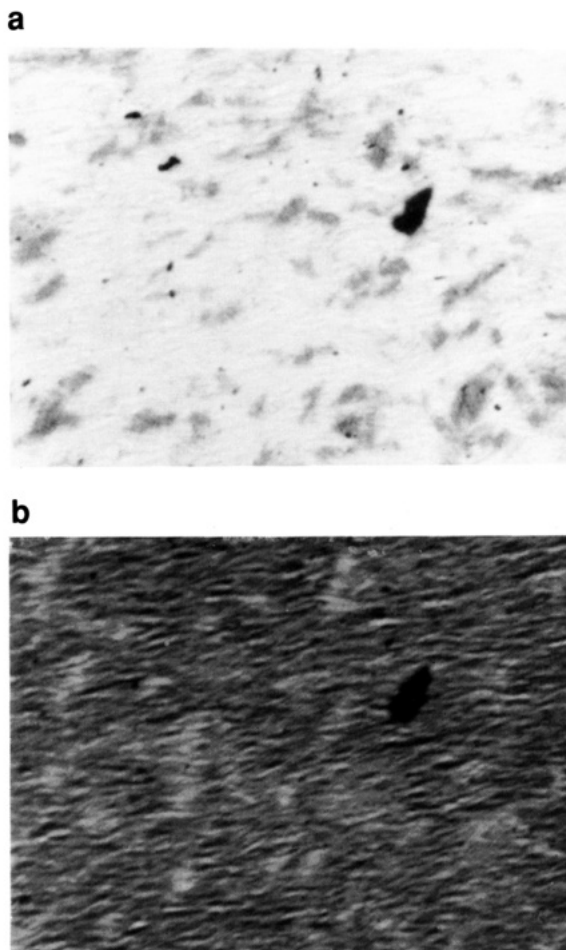
time. The experimental value of  $5 \times 10^{-3} \Omega\text{-cm}$  lies in the middle of the range calculated from  $\omega_p$ .

**UV-Vis Spectroscopy of Thin Films.** Thin films ( $<1 \mu\text{m}$ ) prepared by spin coating ca.  $10^{-2} \text{ M}$  DMSO solutions onto KBr disks under argon, are either transparent or reflective, depending on the viewing angle. When the coated disk is examined at a  $90^\circ$  angle, or perpendicular to its surface, the thin ( $\text{LiMo}_3\text{Se}_3$ )<sub>n</sub> coating appears transparent, and displays the burgundy color characteristic of intact ( $\text{Mo}_3\text{Se}_3^-$ )<sub>n</sub> chains in dilute solution(s).<sup>6e</sup> However, when the viewing angle is ca.  $45^\circ$  or less, a silver mirrorlike metallic luster is observed on the disk surface, similar to that observed for the thick foil material. The absorption behavior is consistent with the UV-vis spectrum (200–700 nm) obtained from a thin film cast onto a sapphire disk, in which a broad absorption maximum at 480 nm was observed.

**Oriented Thin Films and Optical Microscopy.** Highly anisotropic thin films of ( $\text{LiMo}_3\text{Se}_3$ )<sub>n</sub> are obtained by flowing ca.  $10^{-2} \text{ M}$  solutions down glass slides tilted at an angle of ca.  $30^\circ$  from vertical, and coated with a poly(tetrafluoroethylene) (PTFE) film in which the PTFE chains are oriented parallel to the direction of solution flow.<sup>13</sup> After slow removal of DMSO in vacuo, the lustrous thin films of ( $\text{LiMo}_3\text{Se}_3$ )<sub>n</sub> thus obtained were analyzed by absorbance polarized light microscopy.<sup>14a,b</sup> Figure 6 shows the extent of orientation of the ( $\text{Mo}_3\text{Se}_3^-$ ) fibers on the PTFE substrate. The templating effect of the PTFE substrate is evident in the absorbance-polarization phenomenon exhibited by the thin film of ( $\text{LiMo}_3\text{Se}_3$ )<sub>n</sub>. The oriented inorganic polymer film acts as a polarization grating, in that plane-polarized light parallel to ( $\text{Mo}_3\text{Se}_3^-$ ) chains shows a high degree of absorption (burgundy), while plane-polarized light perpendicular to the oriented chains is largely transmitted (white). This phenomenon is observed uninterrupted over areas that exceed the  $160 \mu\text{m}$  field of vision of the microscope. Thin films obtained from flowing solutions down glass slides without the PTFE template typically exhibit random domains of orientation ca.  $10\text{--}50 \mu\text{m}$  in length.

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**Figure 6.** (a) Polarized light perpendicular to orientation of ( $\text{LiMo}_3\text{Se}_3$ )<sub>n</sub> thin film on oriented PTFE shows almost no absorption. Dark spots are due to local film defects. (b) Polarized light parallel to the orientation of ( $\text{LiMo}_3\text{Se}_3$ )<sub>n</sub> chains on PTFE substrate shows large absorption anisotropy. The horizontal field of view for both samples is ca.  $160 \mu\text{m}$ .

## Conclusion

A new partially ordered form of ( $\text{LiMo}_3\text{Se}_3$ )<sub>n</sub> has been prepared by simple solution casting. The casting process and the liquid crystallinity of precursor solutions appears to provide a pathway for local parallel ordering of the inorganic polymer chains. Depending on film thickness and the degree of orientation, films of ( $\text{LiMo}_3\text{Se}_3$ )<sub>n</sub> films display a variety of desirable physical properties, including electrical conductivity and light absorption/polarization. Our ongoing research efforts will continue to focus on the demonstration of useful applications of this unique material.

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