and 50 mL distilled water containing 3 mmol ethylenediamine and 1 mmol $CdCl_2$ or $ZnCl_2$. The jars were sealed and kept static at room temperature in the dark for up to 7 days. Then the precipitates were filtered and washed with absolute alcohol and distilled water, then dried in vacuum at 20 °C.

After extracting the organic phase, post thermal treatments were performed by heating the water phase in a water bath at 60 °C for an hour with magnetic stirring.

X-ray powder diffraction (XRD) measurements of the as-prepared sample were carried on a Rigaku D/max-γA X-ray diffractometer with Cu Kα radiation (λ = 1.54178 Å). The TEM images and ED pattern were taken on a Hitachi H-800 transmission electron microscope with an accelerating voltage of 200 kV. HRTEM images were taken on a JEOL-2010 transmission electron microscope.

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Surfactant-Induced Mesoscopic Assemblies of Inorganic Molecular Chains**

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Yiying Wu, *Franklin Kim*, and *Peidong Yang**

Currently, there is an intensive research drive towards developing suitable one-dimensional (1D) conducting molecular wires because of their potential use as building blocks for molecular-scale electronic devices.[1–3] An interesting approach to obtaining molecular wires is the disassembly of quasi-1D crystals such as $LiMo_3Se_3$ into structurally and electronically identical molecular wires.[4–7] Previously, nematic liquid crystalline behavior has been observed in concentrated wire solutions.[5] These wires have also been successfully embedded into a polymer matrix to form an inorganic/organic composite.[6,7] No structural tunability, however, has been reported in these previous studies. These $[\mathrm{Mo_3Se_3^-}]_\infty$ chains, which can be viewed as a linear condensation of an infinite number of Mo_6Se_8 octahedra, are negatively charged and can be considered as inorganic polyelectrolytes in solution. Recently, they were found to be metallic over a wide temperature range,[8] and therefore they may represent an interesting system of 1D building blocks for molecular devices.

Herein we report the self-organization of these infinite $[\mathrm{Mo_3Se_3^-}]_\infty$ chains in the presence of oppositely charged surfactants. This mesoscopic organization is a direct result of complex formation induced by the electrostatic interactions between the inorganic polyelectrolytes and the surfactants. Low angle X-ray diffraction (XRD) and transmission electron microscopy (TEM) studies indicate that the spacing between these infinite inorganic chains can be varied from 20 to 40 Å by using surfactants with different alkane lengths, while the crystallinity along the individual inorganic chains is well maintained.

A red solution of $[\mathrm{Mo_3Se_3^-}]_\infty$ wires (10^{-4}–10^{-3} M) was obtained by dissolving fine $LiMo_3Se_3$ crystals in dimethyl sulfoxide (DMSO) or propylene carbonate (PC).[4] Proper amounts of the cationic surfactants alkylammonium bromide $(C_nH_{2n+1})N^+(CH_3)_3{\cdot}Br^-$, $12 \le n \le 18$, and $(C_{10}H_{2n+1})_2N^+(CH_3)_2{\cdot}Br^-$, $10 \le n \le 18$, and 12-crown-4 ether were added to this solution. After the solution had been shaken for 1–5 min, the red color disappeared and reddish products precipitated out. 12-Crown-4 ether helps to extract Li ions from the backbone of the wires and facilitates the formation of surfactant/wire complexes.

Cross-polarized optical microscopy studies indicate that the products consist of well-aligned microscopic fiber bundles or sheets. This is also clearly shown by field emission scanning electron microscopy (FESEM). Figure 1a shows one such image recorded on a sample prepared using the surfactant dihexadecyldimethylammonium bromide (DDAB). We found the molecular chains form bundles with uniform diameters of 10–200 nm. These molecular chain bundles were deposited on copper grids and examined by transmission electron microscopy (TEM). It was found that the individual molecular chains are aligned along the bundle axis and are evenly spaced. The spacing can be changed from 20 to 40 Å depending on the alkane length of the surfactant used. Surfactants with longer alkane chains generally yield assemblies with larger interchain spacing. Figure 1b shows a typical TEM image recorded on $[\mathrm{Mo_3Se_3^-}]_\infty$/DDAB fibrous products. The interchain spacing was considerably expanded upon the complex formation as compared with that of unmodified $LiMo_3Se_3$ crystal (d = 8.5 Å). Furthermore, the composition of the complexes was probed by energy-filtered elemental mapping in a Philips CM200 transmission electron microscope equipped with an electron energy loss spectrometer. It was found that carbon-rich regions and molybdenum-rich regions coincide

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with the alternating surfactant/$[Mo_3Se_3^-]_\infty$ stacking sequence, as seen in the bright-field image. This clearly indicates that the surfactants have been successfully incorporated between the infinite molecular chains.

It is also possible to modify the $[Mo_3Se_3^-]_\infty$ chains with polymerizable cationic surfactants. For example, we have successfully synthesized ω-undecenyltrimethylammonium bromide (ω-UTAB)/$[Mo_3Se_3^-]_\infty$ complexes and their mesostructures. Figures 1c and 1d show TEM images of the complexed ω-UTAB/$[Mo_3Se_3^-]_\infty$ molecular wires. In Figure 1d, individual wires can be readily seen with a diameter of ca. 6 Å and separation of 2.0 nm. The measured diameter is comparable with the diameter calculated from the crystal structure. Since ω-UTAB can be polymerized through either UV irradiation or free radical initiation, this may point out a possible route to form polymer-sheathed molecular wires.

The mesoscopic ordering of the complexes can be further confirmed using low angle XRD. Figure 2 shows the low angle and high angle XRD patterns for the unmodified $LiMo_3Se_3$ crystals and the $[Mo_3Se_3^-]_\infty$/hexadecyltrimethylammonium bromide (CTAB) and ω-UTAB complexes. Upon complexation, we observed that all high angle diffraction peaks disappear except for the (002) peak (Fig. 2a). Mesophase formation is unambiguously evidenced by the appearance of the low angle diffraction peaks between 2° and 10° (Fig. 2b,c). We observed both lamellar (Fig. 2b) and hexagonal (Fig. 2c) mesophases during this study, although complete phase diagrams still need to be mapped out. For example, the low angle peaks for $[Mo_3Se_3^-]_\infty$/ω-UTAB complexes can be indexed as (100), (110), and (200) diffractions of a hexagonal mesophase with $a = 23.2$ Å (Fig. 2c) while the low angle peaks for CTAB complexes can be indexed as (001) and (002) diffractions of a lamellar mesophase (Fig. 2b). It is interesting to notice that both ω-UTAB and CTAB exhibit lamellar mesostructures in their pure form (bottom traces in Fig. 2b,c). Compared with pure surfactants, all low angle diffraction peaks shift to lower angles upon complex formation, indicating the incorporation of the molecular wire units within the mesophases. The 002 diffraction peak at high angle for the complexes (Fig. 2a) confirms that these mesoscopic arrays are made of highly crystalline $[Mo_3Se_3^-]_\infty$ chains. This is consistent with the corresponding selected area diffraction (SAED) patterns recorded on the complexed wire arrays (Fig. 1b inset) and lattice fringe along the

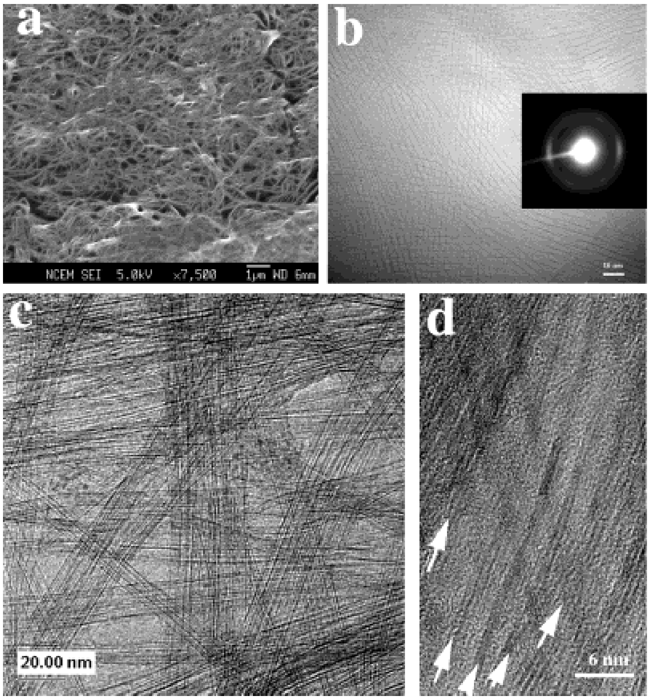

Fig. 1. a) FESEM image of $[Mo_3Se_3^-]_\infty$/DDAB complex nanofibers. b) TEM image of the molecular wire $[Mo_3Se_3^-]_\infty$/DDAB complex bundles deposited on a TEM grid. Each dark line represents one individual $[Mo_3Se_3^-]_\infty$ wire. The inset shows an SAED pattern recorded on the sample area to its left. c) TEM image of the $[Mo_3Se_3^-]_\infty$/ω-UTAB complex bundles. d) High resolution TEM image of several $[Mo_3Se_3^-]_\infty$/ω-UTAB complexed chains (indicated by arrows).

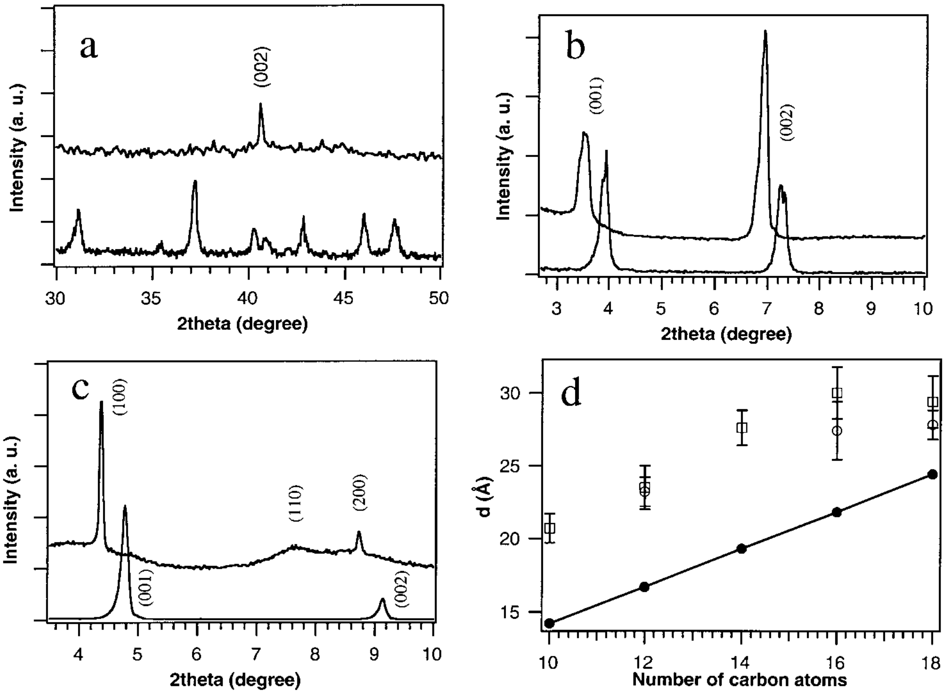

Fig. 2. a) High angle XRD for the complexes (upper trace) and $LiMo_3Se_3$ (bottom trace). b) Low angle XRD patterns for $[Mo_3Se_3^-]_\infty$/CTAB (upper trace) and CTAB itself (bottom trace). c) Low angle X-ray diffraction patterns for $[Mo_3Se_3^-]_\infty$/ω-UTAB mesophase (upper trace) and ω-UTAB itself (bottom trace). d) Values of *d*-spacing for the first peak in low angle XRD for the complexes. (○: double-chain surfactant complexes; ◇: single-chain surfactant complexes; ●: calculated fully extended alkane chain length.)

wire in high resolution TEM studies (d = 2.2 Å, Fig. 1d). In fact, this crystallinity of the $[Mo_3Se_3^-]_\infty$ molecular wires within the complexes was also reflected by the high conductivity measured on these complex fibers. Our preliminary measurements on strands of wire bundles yielded resistivity values between 10^{-1} and 5×10^{-3} Ω cm at room temperature.

Figure 2d shows the d spacing (for the first peak in the low angle XRD pattern) obtained from the low angle XRD for samples prepared using surfactants with different chain lengths. These values are consistent with the value obtained from the TEM studies. Similar interchain spacings were observed for samples prepared using either single-chain or double-chain surfactants. These values generally are larger than those expected for fully extended alkane chains ($l = 0.15 + 0.127n$ nm, where n is the number of carbon atoms)[9] by 3–10 Å. We postulate that the surfactant molecules are electrostatically attached to the surface of the $[Mo_3Se_3^-]_\infty$ wires (Fig. 3), and are partially interdigitated between the molecular wires. It should be mentioned that it was reported that these inorganic chains could be precipitated by adding salts or acids. No low angle diffraction peaks, however, were observed in that study except a broad peak at d = 12.2 Å, which was ascribed to the solvent intercalation.[4]

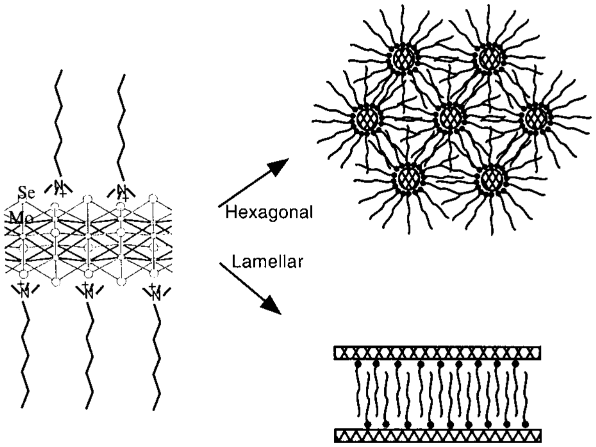

Fig. 3. Structural model for the ideal $[Mo_3Se_3^-]_\infty$/surfactant complex. The hexagonal and lamellar mesostructures are also illustrated.

We believe the mesoscopic organization of the $[Mo_3Se_3^-]_\infty$ molecular wires is a direct result of electrostatic interaction between the negatively charged inorganic polyelectrolytes and positively charged surfactant molecules (Fig. 3). The complex products can be considered as molecular cables with conducting $[Mo_3Se_3^-]_\infty$ cores sheathed by hydrophobic surfactant tails. The hydrophobic effect then drives the reassembly of these complexes into mesostructures. To a certain extent, this chemistry is similar to that of organic polyelectrolyte/surfactant complexes.[10,11] For example, both the chemistry and the resulting mesostructures in this study bear some similarity to the self-organization in a DNA–lipid system.[12,13]

In conclusion, we have demonstrated complex formation between negatively charged conducting $[Mo_3Se_3^-]_\infty$ chains and cationic surfactants through electrostatic interaction. This "disassembly–reassembly" strategy is general and can be readily applied to many other charged molecular systems.[14,15] It offers an easy approach to modifying the intermolecular wire spacing, hence provides a unique system to address the effect of wire–wire coupling strength on electron transport properties of molecular wires. It may prove to be useful for the chemical integration of molecular units into useful molecular devices.

Experimental

$LiMo_3Se_3$ crystals were prepared using the published procedure [4]. Briefly, $In_2Mo_6Se_6$ crystals were first made through solid-state reaction of an appropriate amount of In, Mo, and Se powders in an evacuated quartz tube. The In in $In_2Mo_6Se_6$ crystals was then exchanged for Li by reacting $In_2Mo_6Se_6$ with excess anhydrous LiI in an evacuated quartz tube. This quartz tube was placed in a temperature gradient, with one end close to room temperature and the other end at 560 °C.

Typically, 10 mg of the $LiMo_3Se_3$ crystals was dissolved in 10 mL of DMSO or PC. This solution was then used for the complexation with or without further dilution. Appropriate amounts of cationic surfactants alkylammonium bromide $(C_nH_{2n+1})N^+(CH_3)_3{\cdot}Br^-$, $12 \le n \le 18$, $(C_{10}H_{2n+1})_2N^+(CH_3)_2{\cdot}Br^-$, $10 \le n \le 18$, or ω-UTAB and 12-crown-4 were dissolved in DMSO or PC and mixed with the wire solution (surfactant:$[Mo_3Se_3]^-$ = (1–2):1, molar ratio). The precipitated products were collected and dried in an inert glove box. X-ray diffraction patterns were obtained on a Siemens D5000 powder diffractometer. Sample texture and microstructures were examined using a Nikon ME600 optical microscope and JEOL-JSM6430 field emission scanning electron microscope. Low-magnification and high-resolution transmission electron microscopy studies were carried out on either a Topcon 002B or a Philips CM-200 microscope.

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