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Assembly and Characterization of SAMs Formed by the Adsorption of Alkanethiols on Zinc Selenide Substrates

Alison R. Noble-Luginbuhl and Ralph G. Nuzzo

Alkanethiols $\text{HS}(\text{CH}_2)_n\text{CH}_3$ ($n = 7, 11, 15, 17$) and the hydroxy functional thiol $\text{HS}(\text{CH}_2)_{12}\text{OH}$ are shown to adsorb from solution onto zinc selenide crystals and form well-organized monolayers. The chemisorption of these organosulfur compounds has been studied using transmission Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and surface wetting properties. FTIR indicates that the longer chain alkanethiols ($n = 15, 17$) form well-defined SAMs with crystalline-like conformations of the chains within the monolayers. As the chain length decreases, there is less conformational order present in the monolayers. The orientation of the largely trans-zigzag alkyl chains on the surface is at a slight tilt off the surface normal direction, as indicated by the dichroism of the infrared spectra and the chain-length-dependent scaling of the mass coverage of the SAM. The structural data obtained by XPS and FTIR are compatible with the inferences derived from measurements of surface wetting properties. The thickness of the SAM layers calculated using XPS is found to be comparable to the thickness of alkanethiol SAMs formed on gold and other metal surfaces. Changes in the surface of the ZnSe crystal because of chemisorption of the thiols are illustrated by data from AFM imaging. The feasibility of forming cohesive patterned monolayers by microcontact printing is also demonstrated.

Introduction

The preparation and characterization of self-assembled monolayers (SAMs) on ZnSe is described herein. There have been many studies reported on the SAMs formed by alkanethiols and other functionalized thiols on metal surfaces.¹⁻⁹ A recent report has presented data characterizing the structures of very similar SAMs formed on an indium tin oxide (ITO) substrate.¹⁰ In this paper, we report a closely related example of SAM formation by thiol adsorbates on a nonmetallic substrate surface, namely, that of zinc selenide (ZnSe). ZnSe is a useful optical material. Its transparency in the mid-infrared region has engendered many applications, perhaps most notably in studies based on vibrational spectroscopy.¹¹⁻¹⁴ The ability to tailor the surface properties of this material via rational molecular design is thus of interest and potential utility

for the broad areas of interest impacted by SAMs. The formation of these monolayers on ZnSe is therefore of some importance because of the promise the system holds for spectroscopic studies of complex interfacial properties and processes.

As suggested above, modifying surfaces with thiols has provided a useful technique for studying the nature of processes occurring at molecular interfaces and surfaces. Notable examples include studies of the physicochemical basis of wetting,¹⁵ electron transfer,^{16,17} molecular recognition at interfaces,^{18,19} analysis of protein binding,²⁰⁻²³ modeling the biomolecular interactions of materials,²⁴ and the anchoring of liquid crystals.²⁵⁻²⁸

Understanding the interactions occurring between thiol adsorbates and ZnSe and the structures of the SAMs that result should enable the design of materials that directly enable new approaches to studying such areas of interest,

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notably in ways that can be analyzed via vibrational spectroscopy.^{14,29} In this paper, we present studies on the surface properties exhibited by ZnSe before and after exposure to thiol adsorbates, confirm the presence of adsorbed thiols, and characterize the SAMs formed by these adsorbates. The starting ZnSe samples are characterized using XPS and then compared to the surface after the adsorption of monolayers to better understand the physical and chemical changes caused by the formation of the SAM. The molecular structure and organization of the SAMs are investigated using transmission Fourier transform infrared (FTIR) spectroscopy, contact angle measurements, and X-ray photoelectron spectroscopy (XPS). Microcontact printing (μ CP) is then used to demonstrate the coherence of the films and the application of the system to experiments involving surface patterning.

Experimental Methods

Materials. Alkanethiols were purchased from Aldrich and used as received. A sample of 12-mercapto-1-dodecanol (12hdt) was provided by our frequent collaborator David L. Allara (Pennsylvania State University). The ZnSe samples were obtained from Wilmad Glass (Buena, NJ). Stamps used for microcontact printing were made from a poly(dimethylsiloxane) elastomer (PDMS) as described elsewhere in the literature.^{30–32}

Sample Preparation. The ZnSe substrates were cleaned prior to use by exposure in a UV/ozone chamber (low-pressure mercury lamp, $\lambda = 185$ and 254 nm) for ~ 10 min, rinsed with 2-propanol, and dried in a stream of nitrogen. The crystals were soaked overnight in a 1 mM alkanethiol solution in ethanol, rinsed with deionized water and 2-propanol, and then dried in a stream of nitrogen. For studies involving microcontact printing, a 1-hexa-decane thiol solution (1 mM in ethanol) was applied to the PDMS stamp by spin coating at 3000 rpm for 30 s. The thiol-coated PDMS stamp was dried for 30 s in a nitrogen stream and then applied to a cleaned sample (see above) for 2 min at room temperature. The sample was rinsed in 2-propanol and dried under a nitrogen flow.

X-ray Photoelectron Spectroscopy. Spectra were obtained using a Physical Electronics (PHI model 5400) photoelectron spectrometer using Mg K α radiation (15 kV, 400 W). The data were collected at a 45° takeoff angle. Survey scan spectra were obtained at a constant pass energy of 178.95 eV with a 1 \times 1.4 mm spot size. High-resolution data (used for film thickness calculations) were collected with the same spot size at a pass energy of 35.75 eV. Because ZnSe is a wide band gap semi-conductor, peaks appear at uncorrected binding energies higher than literature values due to a charging potential of approximately 8 eV. These shifts were corrected by referencing the C 1s core level binding energy to 285 eV. Curve fitting (using a Gaussian–Lorentzian line shape) was employed to determine the parameters used to calculate the thickness of the films.

Contact Angles. Static contact angles were measured on a home-built goniometer under ambient conditions. A sessile drop of 15 μ L of deionized water was delivered with a microsyringe. The contact angles were measured on three separate drops for each sample.

Atomic Force Microscopy (AFM). A Digital Instruments Dimension-3000 scanning probe microscope was used to image the ZnSe surface before and after exposure to the alkanethiol solution. A standard Si₃N₄ tip was used for contact mode imaging. The scan rate used for the unexposed ZnSe sample was 2 Hz; the scan rate for the ZnSe sample with a 1-hexadecanethiol SAM was 1 Hz.

Infrared Spectroscopy. All FTIR measurements were made in transmission mode using a Bio-Rad (Cambridge, MA) FTS

6000 spectrometer equipped with a KBr beam splitter and a high-temperature ceramic source. Bio-Rad Win-IR and Win-IR Pro software were used for the data acquisition and analysis. The experiments were carried out at an optical modulation of 20 kHz with a 5 kHz filter, an undersampling ratio of 2, and a spectral resolution of 4 cm⁻¹. All spectra were collected using a deuterated triglycine sulfate (DTGS) detector (Bio-Rad) and consist of 256 coadded scans.

Condensation Figures. Condensation figures were generated according to the method described by Whitesides and co-workers.³³

Results

General Observations. The films in this study were typically prepared by immersing the ZnSe sample into a 1 mM solution of thiol in ethanol and letting it soak overnight. It should be noted, though, that on occasion the ZnSe was left soaking for slightly longer times (24–48 h) with little (if any) difference being evidenced in the properties of SAMs obtained. After the samples were removed from the adsorbate solutions, they were rinsed with deionized water and isopropyl alcohol and dried in a stream of nitrogen. The surface properties were then qualitatively examined by applying drops of water to test for significant changes in wetting behavior. Untreated by thiols, the ZnSe surface is extremely hydrophilic; these same surfaces become hydrophobic upon exposure to an alkanethiol adsorbate solution. Such changes are suggestive of the formation of a SAM.³ To study this issue more quantitatively, we employed a variety of spectroscopic and physical characterization methods.

XPS Measurements. XPS data were obtained for a clean ZnSe substrate as well as for a series of samples modified by immersion in thiol adsorbate solutions. It is evident from the XPS data (Figure 1a, Table 1) that an oxide forms on the surface of ZnSe, as indicated by the large O 1s peak appearing at 531 eV. After a 24 h exposure to a 1 mM thiol solution, the intensity of the O 1s peak decreased markedly. The intensity of the C 1s peak for the chains, referenced to a binding energy of 285 eV, increases directly in proportion with the adsorbate chain length as illustrated by the data shown in Figure 1 and Table 2. The Zn 2p core levels (e.g., the Zn 2p_{3/2} core level at 1022 eV) are most intense in the survey spectrum measured for the untreated substrate. Because of the low kinetic energies (208 and 231 eV) of these photoelectrons and their relatively short mean free paths, these peaks are expected and found to be strongly attenuated by the presence of a SAM.^{34,35} The chain-length dependence of this attenuation is clearly evidenced in the data shown in Figure 1. For the structurally homologous series of the C₈, C₁₂, C₁₆, and C₁₈ alkanethiols, a direct correlation is seen between the Zn 2p_{3/2} core level intensity and that measured for the C 1s transition. The C 1s intensity and Zn 2p_{3/2} attenuation (as compared to the spectrum of untreated ZnSe) measured for the 12hdt-treated sample (intriguingly) is nearly indistinguishable from that seen for dodecanethiol. This suggests the adsorbate layers formed are tolerant of at least some degree of chain-end functionalization. Taken together, the data suggest that the thiols do indeed form a structurally self-similar series of SAMs on the ZnSe surface (see below).

The data do not allow us to establish the nature of the S binding involved in the formation of these SAMs with any confidence. The weak S 2p_{1/2} and 2p_{3/2} peaks for a

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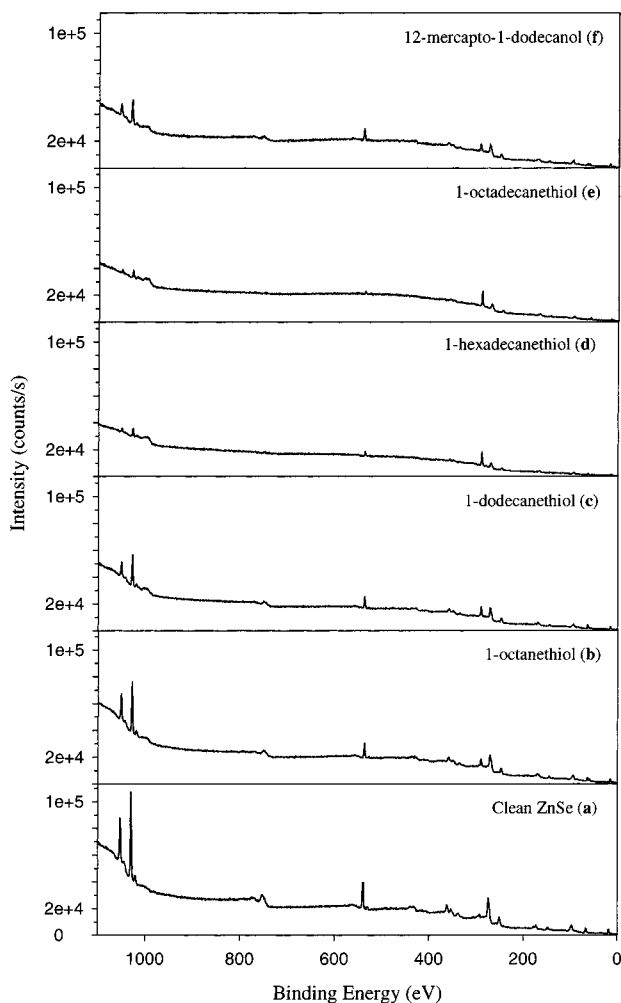


Figure 1. XPS spectra illustrating the changes that occur when alkanethiols and 12hdt are adsorbed onto a ZnSe surface. Shown are spectra of (a) ZnSe before exposure to adsorbate solution and (b–f) ZnSe with overlayers of (b) 1-octanethiol, (c) 1-dodecanethiol, (d) 1-hexadecanethiol, (e) 1-octadecanethiol, and (f) 12-mercapto-1-dodecanol.

thiolate structure are expected to appear at ~ 162 – 163 eV.⁴ Unfortunately, these peaks are obscured by the Se $3p_{1/2}$ and $3p_{3/2}$ core levels at 169 and 163 eV.³⁶

An O $1s$ core level peak is seen for all the spectra shown in Figure 1. The intensity of this peak varies sensitively with the nature of the SAM present. An attenuation of the O $1s$ core level intensity is expected for all the SAMs (with the possible exception of 12hdt, which contains a chain-end OH group). In fact for all the structures shown, such attenuations (and line shape changes) are seen. An examination of the Zn $2p_{3/2}$ core level data, however, reveals that the changes seen here are in fact more complex than is inferred from a mechanism based on the presence of an organic thin-film overlayer that attenuates the photoemission signals originating from an unvarying population of substrate atoms. In point of fact, thiols appear to be weak wet etchants of this substrate, removing some quantity of the Zn (presumably present initially as ZnO) in the form of soluble products. The quantities of O that remain are therefore expected to be sensitive to both the sample history and the solubility properties of the etching products. We therefore have not attempted to

Table 1. Peak Assignments for XPS Spectra

peak position (eV)	peak assignment
1045	Zn $2p_{1/2}$
1022	Zn $2p_{3/2}$
765	O KL_1L_{23}
744	O $KL_{23}L_{23}$
531	O $1s$
427	Zn $L_3M_{23}M_{23}/Zn L_2M_{23}M_{23}$
353	Zn $L_3M_{23}M_{45}$ (1P)
344	Zn $L_3M_{23}M_{45}$ (3P)
330	Zn $L_2M_{23}M_{45}$ (1P)
285	C $1s$
265	Zn $L_3M_{45}M_{45}$
242	Zn $L_2M_{45}M_{45}$
170	Se $3p_{1/2}$
165	Se $3p_{3/2}$
140	Zn $3s$
89	Zn $3p_{1/2}/Zn 3p_{3/2}$
59	Se $3d_{3/2}/Se 3d_{5/2}$
10	Zn $3d$

derive any quantitative understanding from the characteristics of the O $1s$ core level spectra. Rather, the character of the SAM is analyzed more self-consistently via an analysis of Zn $2p_{3/2}$ and C $1s$ core level intensities. It is to this analysis that we now turn our attention.

Film Thickness. An important metric for the quality of a SAM is given by a direct measurement of the mass coverage of the adsorbate on the surface. Ellipsometry is a useful method with which to make such measurements and has provided key insights into the structures of SAMs formed on a variety of metal substrates (e.g., Au, Ag, and Al).^{4,37} We were not able to make reliable measurements using this method on ZnSe, however.³⁸ For this reason, XPS measurements were used to determine the thickness of the thiol films on the surface. Toward this end, we used a method similar to one described elsewhere.³⁹ Because our system varies somewhat from the one reported previously, some revisions were made, and for the sake of clarity, we provide a description of the method used. On the basis of a two-layer model system that accounts only for inelastic scattering,³⁵ the following equation can be derived:

$$\ln\left(\frac{[C]}{[Zn]} + 1\right) = \frac{nd}{\lambda} \frac{1}{\sin \theta} \quad (1)$$

where n = the number of carbons in a long-chain adsorbate molecule, d = the thickness of one methylene group, θ is the takeoff angle (set at 45° in these experiments), and λ is the mean free path of the photoelectrons. The carbon and zinc atomic concentrations ($[C]$ and $[Zn]$) are determined by dividing the peak areas (obtained by curve fitting) by the sensitivity factors.³⁶ To estimate the mean free path for the Zn $2p$ photoelectrons through a thiol overlayer, we employed a method based on the so-called “universal” curve as described in eq 2.³⁵

$$\lambda = C_0(KE)^{1/2} \quad (2)$$

The mean free path for a gold $4f_{7/2}$ photoelectron through an attenuating thiol SAM is reported to be 32 Å (KE = 1402 eV).³⁴ This provides an estimate for C_0 of ~ 0.8 or a mean free path for a zinc $2p_{3/2}$ photoelectron (KE ~ 231 eV) of ~ 12 Å.

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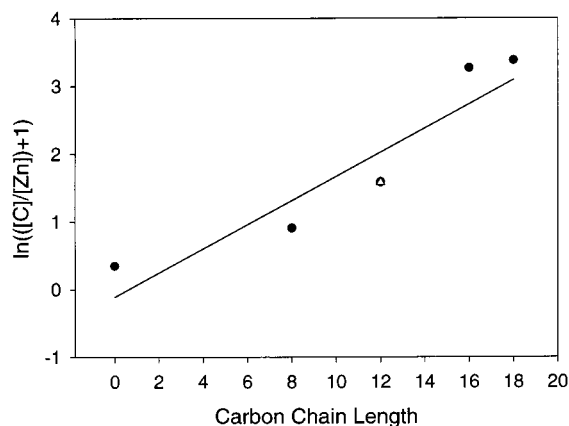


Figure 2. The ratio of carbon and zinc atomic concentrations determined via curve fitting of high-resolution spectra. The plot shows the $\ln([C]/[Zn] + 1)$ versus carbon chain length as well as the standard linear regression fit (solid line) used to calculate the thicknesses of the monolayers. Alkanethiols are represented by dark circles, and the 12hdt is marked with an open triangle.

Table 2. Thickness of Monolayers on ZnSe Calculated from XPS Data

thiol	carbons in chain	[C]/[Zn]	estimated thickness (Å)
clean ZnSe	0	0.4167	N/A
1-octanethiol	8	1.4792	12.08
1-dodecanethiol	12	3.8828	18.12
12-mercapto-1-dodecanol	12	3.8583	18.12
1-hexadecanethiol	16	25.2168	24.16
1-octadecanethiol	18	28.3401	27.18

Table 3. Static Contact Angles (15 μ L Drop Size)

thiol	contact angle (deg)
1-octanethiol	45 \pm 4
1-dodecanethiol	85 \pm 3
12-mercapto-1-dodecanol (12hdt)	49 \pm 4
1-hexadecanethiol	95 \pm 4
1-octadecanethiol	100 \pm 2

By rearranging eq 1, we can use the slope from Figure 2 to determine the thickness of the layer on the surface using eq 3:

$$\text{slope} = \frac{\ln\left(\frac{[C]}{[Zn]} + 1\right)}{n} = 1.414 \left(\frac{d}{\lambda}\right) \quad (3)$$

Figure 2 shows a plot of the measured peak areas from the XPS data for the various SAMs using this relationship. The slope measured in this way is 0.178. Because we believe the layers formed by thiols on the ZnSe substrate are a qualitatively self-similar structure, this implies a chain-length-dependent increment of the film thickness of 1.51 Å per CH₂ group. This closely matches the 1.5 Å expected for this group.⁹ Table 2 lists the experimentally derived [C]/[Zn] ratios and the thicknesses of the monolayers on ZnSe deduced from the XPS data.

Surface Wetting Properties. Static contact angles formed by water were measured on each of the adsorbate-derived films as well as on the untreated surface. These data (reported as the mean of three measurements) are presented in Table 3. The contact angles increase (as does the hydrophobicity of the SAMs) with increasing chain length for the alkanethiol series. Because of its hydrophilic terminal group, the 12-mercapto-1-dodecanol had an acute contact angle ($\sim 49^\circ$). Taken together, the data suggest

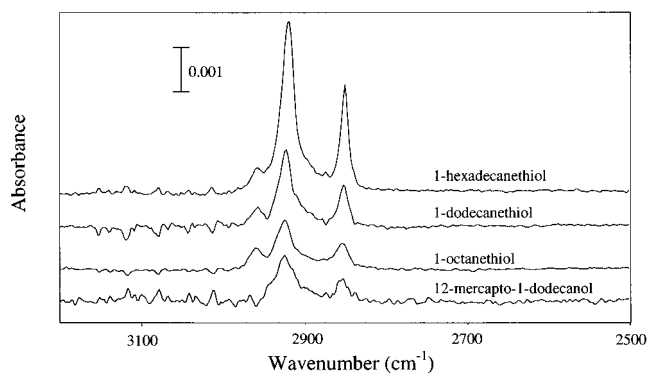


Figure 3. Transmission IR spectra for 1-hexadecanethiol, 1-dodecanethiol, 1-octanethiol, and 12-mercapto-1-dodecanol adsorbed on ZnSe. The figure shows the data measured in the C–H stretching region.

that the longer chain thiols form monolayers whose wetting properties closely resemble those seen in other SAM systems.^{3,4}

Investigation of Film Structure by IR Vibrational Spectroscopy. To understand the local molecular environments and organizational structures present in these films, transmission FTIR measurements were made. Figure 3 shows vibrational spectroscopy data measured in the C–H stretching region for 1-octanethiol, 1-dodecanethiol, 1-hexadecane thiol, and 12hdt. Table 4 lists the peak frequencies and mode assignments for the spectra shown in the figure.

It can be seen from the data in the figure that the line widths narrow and the bands for the methylene absorbances become more intense as the adsorbate chains increase in length. Both of these trends are signatures that the longer chains lead to a more defect-free organization in the SAM. The peak frequency of the methylene antisymmetric (d^-) mode measured for the longer, C₁₆ alkanethiol SAM (2919 cm⁻¹) is one associated with an organization of chains in the film containing a low density of gauche conformational defects. This strongly suggests that the longest chain thiol monolayers are densely packed, nearly all-trans crystalline-like structures.⁵ Similarly, the values of the d^- mode measured for the C₈ alkanethiol layer (2924 cm⁻¹) are indicative of a chain organization containing a significantly larger content of gauche conformers.³ We should also note that this same line of analysis suggests that the 12hdt-derived SAM is also likely to be less well organized than is the corresponding C₁₂ *n*-alkanethiol-derived SAM. Such distinctions have also been seen in the case of analogous SAMs on gold substrates.^{40–42}

The line widths and peak intensities of vibrational modes associated with the methyl groups of the *n*-alkanethiol SAMs provide significant insights into the structural organization adopted by these systems. To interpret the spectra properly, it is helpful to begin with a brief review of the experimental geometry and relevant selection rules. In a standard transmission measurement, the incident light projecting along the sample normal direction is characterized by a plane of polarization coincident with that of the surface. Any allowed vibrational mode with a transition moment projecting on this plane of polarization will, in principle, give rise to a measurable absorption at its characteristic frequency. With the geometry of this setup in mind, we analyze both the methyl

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Table 4. Peak Assignments for C–H Vibrational Modes of Thiols on ZnSe

mode description	C ₁₆ H ₃₃ S peak freq (cm ⁻¹)	C ₁₂ H ₂₅ S peak freq (cm ⁻¹)	C ₈ H ₁₇ S peak freq (cm ⁻¹)	12hdt peak freq (cm ⁻¹)	direction of transition dipole moment
CH ₃ asym (ip, r _a ⁻)/(op, r _b ⁻)	2958	2956	2960	N/A	ip of CCC backbone, ⊥ to C–CH ₃ bond/ ⊥ to CCC backbone
CH ₃ sym (r ⁺)	not distinguishable ^a	not distinguishable	not distinguishable	N/A	to C–CH ₃ bond
CH ₂ asym (d ⁻)	2919	2923	2924	2924	⊥ to CCC backbone plane
CH ₂ sym (d ⁺)	2851	2853	2854	2856	ip CCC backbone plane, ip HCH plane
CH ₂ scissors def (δ(CH ₂))	1468	1465	weak	not shown	ip of HCH, bisects HCH

^a The literature value for this stretch is at 2879 cm⁻¹ (ref 4).

and methylene stretching modes to determine the average molecular orientation of the adsorbates that compose the SAMs.

The organization of the alkanethiol SAMs is sensitively reported on by the vibrational modes of the chain-end methyl groups. Three main modes are of interest in this regard; these are the methyl symmetric (r⁺) and the two antisymmetric (r_{a/b}⁻) stretching vibrations. The frequency of the r⁺ stretch is typically found at or near 2879 cm⁻¹; the r⁻ mode has both an in-plane (ip) component (r_a⁻) at 2964 cm⁻¹ and an out-of-plane (op) component (r_b⁻) at 2954 cm⁻¹.^{3,4,43,44} We expect that both the methyl symmetric and antisymmetric modes will be weak in comparison to the methylene stretching modes discussed previously because, although there are many methylene groups per chain, there is only one methyl (terminal) group per molecule.

An examination of the data shown in Figure 3 reveals that, in fact, only the two antisymmetric methyl stretches appear with any significant intensity in the spectra (the component modes are unresolved bands appearing between 2956 and 2960 cm⁻¹ for the series of SAMs shown in the figure). It is significant that the methyl symmetric C–H stretching mode is a low-intensity band across the series. This suggests that there is no significant projection of the transition moment of this mode on the plane of polarization. This result is not compatible with a model based on an all-trans chain aligned perfectly along the surface normal direction. We therefore conclude that the axis defining the orientation of the adsorbate chains in the SAM is likely to be tilted slightly off the surface normal direction and in such a manner as to reduce the projection of the transition moment for this vibrational mode on the plane of polarization. Because of the geometry of the chain, this tilt could lead to larger projections of both the r_a⁻ and r_b⁻ transition moments on the surface plane and thus more intense bands in the spectra. Detailed calculations would be required to assess this tilt angle more quantitatively.⁴⁵

Perturbations related to structure are seen in the spectra of the methyl modes. For the series of spectra shown in Figure 3, the methyl antisymmetric stretch appears at a range of values between the expected peak locations for the in-plane (r_a⁻, 2964 cm⁻¹) and out-of-plane (r_b⁻, 2954 cm⁻¹) modes and thus suggests a varying unresolved combination of the two. The trends seen, though, are reasonably modest for at least the longest chain SAMs and appear to fall well within the quantitative limits that would easily result from chain-end conformational dynamics (see below).⁴

An examination of the spectra further reveals that, although shifting slightly, these modes do not exhibit any

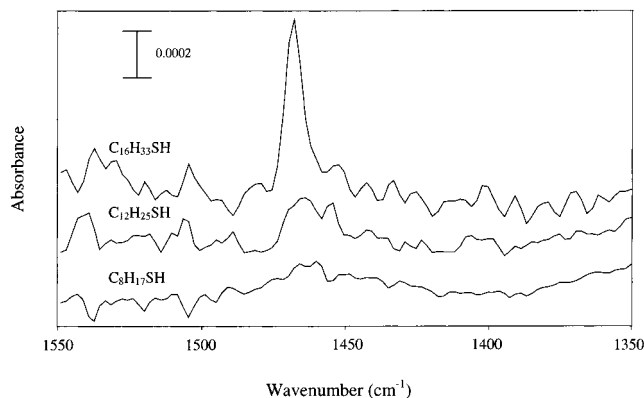


Figure 4. Infrared vibrational spectra measured in the region of the methylene C–H scissors deformation for 1-octanethiol, 1-dodecanethiol, and 1-hexadecanethiol adsorbed on ZnSe.

significant change in peak intensity for the C₈, C₁₂, and C₁₆ thiol adsorbates. We can thus conclude that the orientation of the C–CH₃ bond with respect to the plane of polarization (and ZnSe surface) does not vary with chain length in any significant way for SAMs formed from thiol adsorbates with an even number of carbons. The modest changes seen appear most consistent with a model based on a chain-length dependent population of conformational defects, as is discussed immediately below.

A predominant orientation of an all-trans zigzag alkyl chain along the surface normal direction (or very nearly so) results in strong projections of both the symmetric (d⁺) and antisymmetric (d⁻) CH₂ stretching on the plane of polarization sampled in the transmission infrared measurement. In fact, the data shown in Figure 3 reveal intense bands that dominate the features seen in the C–H stretching region for both of these modes. As noted above, the frequency of the d⁻ mode provides an instructive point of consideration with respect to developing a deeper understanding of the conformational states of the chains. For the longest chain SAM (C₁₆), the spectra suggest a structure with a relatively low density of gauche conformational defects. The question naturally arises as to whether other orderings beyond the evident orientational ordering are present in these SAMs. Infrared spectroscopy does not provide information about the nature of the translational order that may be present in a SAM. It can, however, give information about the local environments created by chain ordering, in particular, those adopting multichain unit cells.³

Further insights into this aspect of the organization were gleaned from an analysis of data measured for the methylene bending modes appearing near 1460–1470 cm⁻¹. Figure 4 shows the spectra measured for the C₈, C₁₂, and C₁₆ thiols; frequencies for these bands are given in Table 4. The methylene scissors deformation for the C₁₆ SAM (appearing as a single broad band centered at 1468 cm⁻¹) proves an enlightening point of consideration.

(43) Snyder, R. G.; Maroncelli, M.; Strauss, H. L.; Hallmark, V. M. *J. Chem. Phys.* **1986**, *90*, 5623.

(44) Snyder, R. G. *J. Chem. Phys.* **1979**, *71*, 3229.

(45) Parikh, A. N.; Allara, D. L. *J. Chem. Phys.* **1992**, *96*, 927–945.

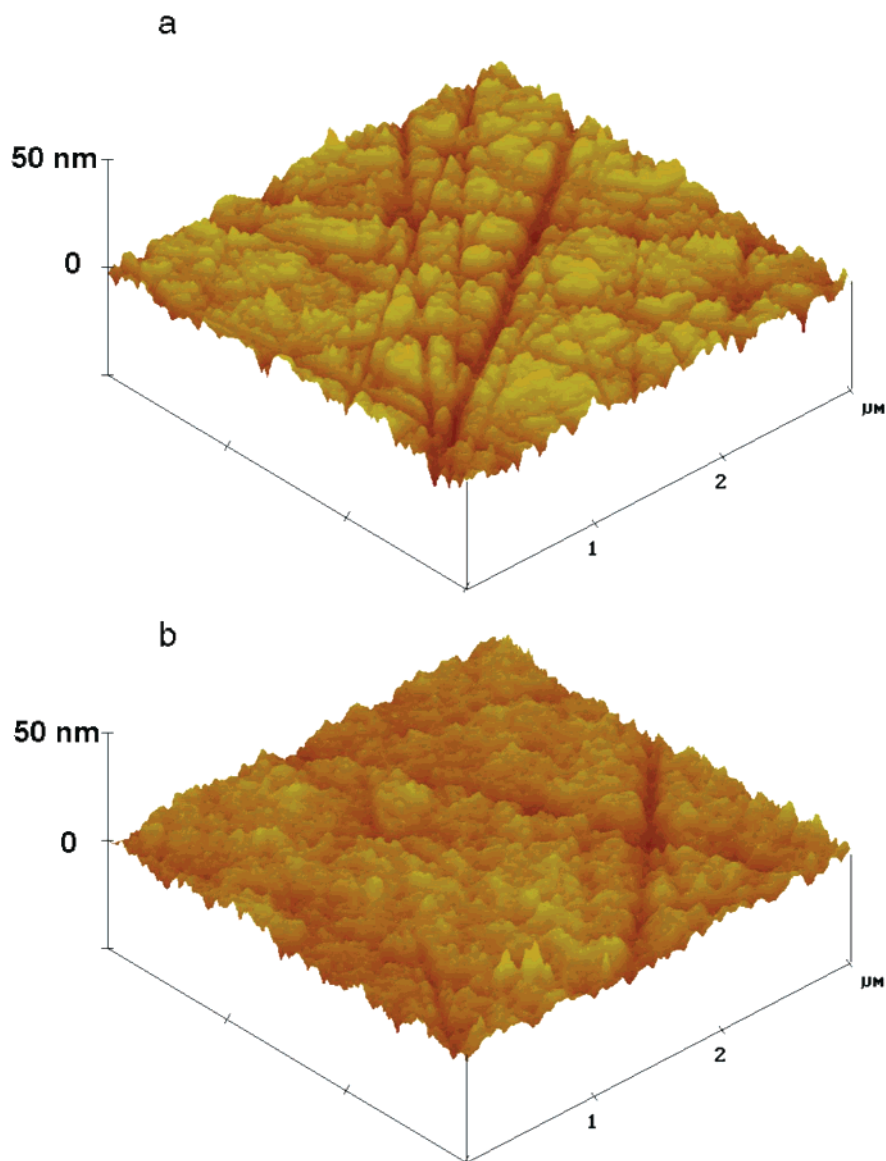


Figure 5. AFM images of (a) clean ZnSe (not exposed to adsorbate solution) and (b) the same sample after a 24 h exposure to a 1 mM solution of 1-hexadecanethiol in ethanol.

These data clearly suggest that the organization of the chains present in this structure does not involve a locally ordered lattice based on a multichain unit cell, such as is found, for example, in an orthorhombic crystal structure. Such packings give rise to factor group splittings of the $\delta(\text{CH}_2)$ mode that can be easily resolved.³ The absence of a multichain unit cell is not direct evidence that the structure is disordered, however, as a monoclinic *n*-alkane crystal would also show only a single peak for the $\delta(\text{CH}_2)$ mode. The heterogeneity introduced by small domain sizes, which might be expected to contain larger numbers of gross defects, could also make such splittings difficult to resolve. Data obtained from microscopy studies do in fact suggest that any ordered domains present in these SAMs should in fact be small.

Surface Morphology via AFM. The ZnSe surface was imaged both before and after exposure to the alkanethiol adsorbates in order to elucidate any changes in the surface caused by their adsorption. Figure 5a shows an image of the surface of the ZnSe crystal. Figure 5b shows the same piece of ZnSe after being exposed to a 1 mM solution of 1-hexadecanethiol in ethanol. As can be seen in Figure 5a, the surface of the mechanically polished ZnSe is heavily corrugated at the molecular size-scale, being characterized

by roughness on the order of about ± 100 Å. After exposure to the thiol adsorbate, the surface is measurably less corrugated (Figure 5b); notably, the grooves from mechanical polishing are shallower in comparison to the average surface height measured above. These data suggest that thiols etch the ZnSe surface, albeit slowly, during the formation of the SAM. From the XPS data, we believe it is likely that they are etching zinc oxide surfaces species (see above).

Application to Microcontact Printing. To further demonstrate the nature of the adsorbed monolayers as well as demonstrate the utility of this system for patterning studies, 1-hexadecanethiol was deposited onto a ZnSe surface via microcontact printing.^{6,7,31,32} The pattern used for this experiment was a grid array of circular holes (150 μm in diameter) and crosses (40 μm long); the 1-hexadecanethiol forms a negative image. The surface layer so obtained was then imaged via its condensation figure³³ using an optical microscope. A representative image is shown in Figure 6. The contrast between the hydrophilic (ZnSe) and hydrophobic (stamped thiol) areas can be seen clearly, and the feature resolution of the pattern obtained is very good on this scale.

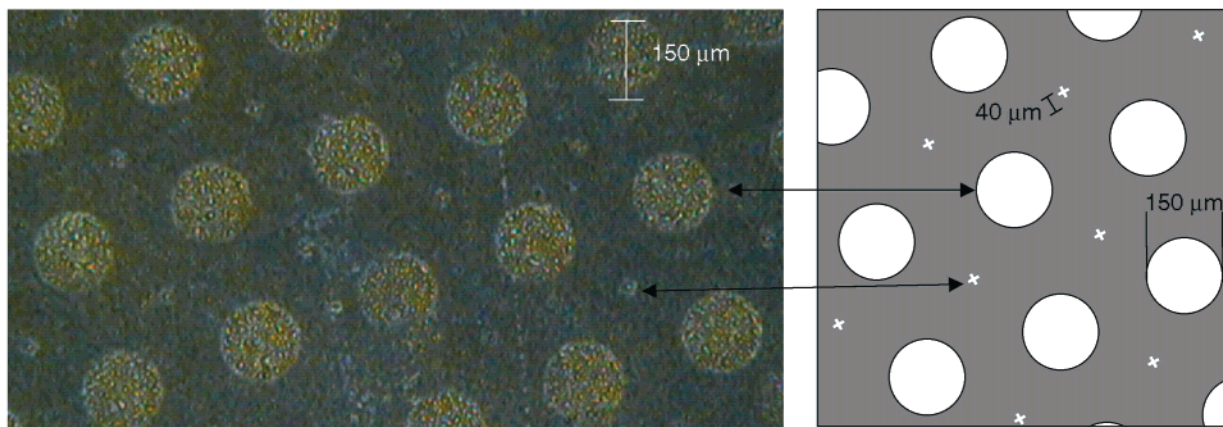


Figure 6. This condensation image of dots ($150\ \mu\text{m}$ diameter) and crosses ($40\ \mu\text{m}$ long) was patterned by microcontact printing. A stamp (inked with 1-hexadecanethiol) that covered all the area except where dots and small crosses are seen was applied to the ZnSe substrate for 2 min. The surface was then steam imaged to generate contrast between areas where the thiols adsorbed (darker gray area, hydrophobic) and where the ZnSe surface remained adsorbate-free (dots and crosses, hydrophilic). Shown on the right is a schematic of the stamp pattern.

Discussion

The data reported here form the basis for understanding the nature of the SAMs formed by alkanethiols on a novel substrate, ZnSe. The answer to the most fundamental question, “Do alkanethiol adsorbates form SAMs on ZnSe?”, is unequivocally, “yes”. It appears from our data that, although well-organized monolayers do form on the cubic ZnSe crystal substrate surfaces, there are differences between this system and the well-studied system of SAMs on Au(111). Some of the main differences (as well as the many similarities) have been elucidated by the data presented above and are discussed in somewhat more detail here. We will discuss how insights into the sulfur–ZnSe interaction, the structure of the polymethylene chains, the orientation of the terminal methyl groups of the *n*-alkane thiol SAMs, and the known properties of the SAMs help develop both an understanding of the adsorbate structures adopted in this system as well as its potential for applications in future research.

It is clear from the XPS data that the ZnSe substrates are significantly oxidized and that, most likely, there is a significant amount of oxide on the native surface (i.e., ZnO). The intensity of the O 1s peak measured on a ZnSe crystal that had not been exposed to a thiol adsorbate solution establishes that this layer is reasonably thick, although not so thick as to preclude the detection of Se in the bulk by XPS. Studies of other materials^{10,46} have shown that thiols can form well-organized SAMs even when surface oxygen is present. On metals such as Ag and Au, the thiols react with and ultimately strip these oxides in a fairly efficient way. Studies on oxidized copper substrates resulted in thiolate films that were widely varied in terms of their quality, however, indicating that the assembly chemistries are not uniformly forgiving of this surface contamination.⁴ The reproducible monolayers formed on ZnSe in this work indicate that the species present on this surface do not preclude SAM formation. The SAMs themselves appear to be robust and not vulnerable to rapid displacement via the sorption of environmental contaminants; ZnSe thus may be an ideal substrate for studies that cannot be (or need not be) carried out in UHV.

The nature of the substrate–sulfur bonding is not currently understood. This deficiency is due in large part to the close proximity of the Se $3p_{3/2}$, S $2p_{1/2}$, and $2p_{3/2}$ core level peaks. This overlap obscures important chemical state information for the sulfur atom of the adsorbate. This, and the fact that the substrate does retain some quantity of O at the interface, makes it difficult to exclude the possibility that the adsorption of the thiol may be accompanied by some degree of oxidation to the sulfonate. It is clear, however, that the O 1s peak seen on the cleaned substrate is strongly attenuated upon its exposure to thiol adsorbates. In addition to this attenuation, the AFM images discussed earlier indicate that the surface exposed to the thiol solution is in fact etched by the adsorbate. We believe it is likely that the thiol binds to Zn sites on the surface in the form of a thiolate species, but further studies will be needed to establish this point more definitively.

We have shown in the data presented that the thickness of the SAM increases linearly with the increasing chain length of the adsorbate and that the thickness change in the films per methylene group increment is approximately $1.51\ \text{\AA}$. This value is in excellent agreement with the thickness change measured per methylene group for SAMs formed on Au(111) and other metal surfaces. The low-frequency values of the d^- modes (especially for the C_{16} thiol derived SAM) and the narrow line width of this vibrational band suggest that, like analogous films on Au and Ag, the polymethylene chains are extended and reside in a crystalline-like environment. The organization found here, though, is chain length sensitive because line broadening and band shifts are seen in the vibrational spectra for the shorter chains, trends that are expected when increasing conformational defects are present. This again is reminiscent of the characteristic trends seen for shorter chain thiol SAMs on gold.

In densely packed monolayers, the chain-terminating functional group plays the largest role in mediating the interactions occurring between the SAM and a contacting phase. It is therefore useful for developing detailed structure–property correlations of interfacial processes to consider its packing and orientation as well as the effect of these properties on the overall characteristics of the monolayer surface. At the simplest level of analysis, one extracts from the data a relatively uncomplicated model for the organization of the average chain. The dense packing and near surface normal orientation of the chain suggest that the structures adopted by the groups on the ambient surface of the SAM should be relatively chain length insensitive. Odd–even effects, as are seen in

thiolate SAMs on Au (which have more significant chain cants), are not expected to be an important structural feature in this system. Rather, the near normal orientation of the chains should lead to structure–property correlations that follow more closely the trends seen in thiolate SAMs on Ag.⁴ The monolayers in the latter system have been characterized in considerable detail and adopt structures very similar to those believed to form here. This inference could be tested more explicitly by looking at the orientation adopted by the methyl group in SAMs derived from alkanethiols with an odd number of carbon atoms in the chain. We note, though, that the data presented above do in fact suggest that the analogy with the structures formed on Ag cannot be an explicit one. This is argued most persuasively by the trends seen in both the contact angle and AFM data.

The wettability of the monolayer provides insight into the structure of the film as well as its utility as an effective means of modifying the ZnSe surface. Defects, roughness, and contributions from the underlying ZnSe substrate are all factors that can affect the surface wetting properties. The contact angle studies done here show an increase in hydrophobicity with chain length. A similar trend (but one demonstrating changes of a lesser magnitude) has been observed in wetting studies of SAMs composed of alkanethiolates on metal surfaces.⁴ Because there is more disorder present in the SAMs derived from the shorter chain adsorbates, one expects their surfaces to be somewhat less hydrophobic. The magnitude of the changes seen in the wetting, though, is too large to be simply due to conformational defects. In this regard, the SAM formed by 1-octanethiol appears to be particularly defective, perhaps as a result of the higher solubility expected for the etching products in this case (which could lead to the loss of material on rinsing). The larger contact angles measured for the 1-hexadecanethiol and 1-octadecanethiol are on the same order as those measured for similar alkyl monolayers on other substrates.^{1,4,10} The monolayers of longer chain thiols are thus effective in forming a strongly adhering layer on the surface. The SAMs of the longer chain adsorbates appear to be useful model substrates and suitable to some degree for chain-end functionalization. This is demonstrated most directly by the drastic change in contact angle seen when an OH is substituted

for the CH₃ as the terminating functional group in a C₁₂ SAM. Although both SAMs have similar mass coverages, 1-dodecanethiol has a contact angle of 85° and 12hdt of only 49°.

These wetting studies, although demonstrating that the longer chain alkanethiols form SAMs that are similar in density and surface properties to those formed on gold and silver, remain differentiated in one very important way. The ZnSe crystals used in this study are polished during their processing. This in turn generates a roughness of finite scale that is still large compared to that found on the surfaces used to form thiolate SAMs on Ag or Au. This roughness must in turn affect the properties of the SAMs and should be considered in studies that use them.

Taken together, the data presented here indicate that alkanethiols and functionalized thiols adsorb onto ZnSe and self-assemble into well-organized dense monolayers. These layers provide an effective medium for manipulating the surface properties of this substrate. We have shown that SAMs with useful properties can be formed either by exposure to dilute adsorbate solutions or by microcontact printing. The formation of these monolayers, in combination with the utility of ZnSe as an IR-transparent crystal as well as its robust nature that enables it to undergo treatments involved in photolithography,^{14,29} makes it an ideal substrate for studying surface interactions at the molecular level. We will report on the application of these structures to studies of the effects of anchoring interactions on the electrooptical dynamics of thin liquid-crystalline assemblies in forthcoming publications.

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