

Communication

Adsorption of Amide-Containing Alkanethiols on Gold

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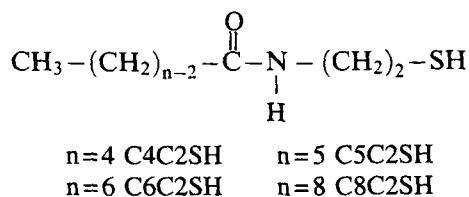
Monolayers of a new series of amide-containing alkanethiol compounds, $\text{CH}_3(\text{CH}_2)_{n-2}\text{C}(\text{O})\text{NHC}_2\text{H}_4\text{SH}$ (referred as $\text{C}_n\text{C}_2\text{SH}$, $n=4, 5, 6, 8$), were self-assembled from ethanol solutions onto gold and their structures have been characterized using the reflectance absorption infrared spectroscopy (RA-FTIR) and wettability measurement. It has been proved that the C=O and N-H bonds are parallel to the gold surface and the orientations of alkyl chain in these Self-Assembled Monolayers (SAMs) are perpendicular to the surface. The special orientation of the amide moiety and molecular axis are suggested to be attributed to the hydrogen-bonding formed between the amide moieties of neighbor molecules. Meanwhile, wettability measurement reveals that the packing degree of the SAMs depends on the length of the alkyl chains in the thiol molecules. These results demonstrate that both the hydrogen-bonding and the length of the alkyl chain exerts the tremendous influence on the orientation of amide-containing alkanethiol molecules. And also, it gives us a way to control the molecular orientation in SAMs in molecular level.

Introduction

Molecular self-assembly methods are commonly used to prepare organized molecular assemblies on surface, which can serve as excellent model system for studying a variety of interfacial process [1]. Recently, how to control the molecular orientation of Self-Assembled Monolayers (SAMs) has become a fundamental interest for the orientation of the dipole moments in the membrane in many fields such as Nonlinear Optical Materials [2]. In several important works, the effort of π - π interaction between aromatic groups, hydrogen-bonding, dipole interaction of polar moieties, and van der Waals interaction between alkyl chain on SAMs molecular packing, orientation have been studied [3–10], which give us a possibility to control the molecular orientation in SAMs by introducing various function groups. We have been paying particular attention to the fundamental problem to control the molecular orientation in assembly. We have designed and synthesized a new series of amide-containing alkanethiol compounds with the structure of $\text{CH}_3(\text{CH}_2)_{n-2}\text{C}(\text{O})\text{NHC}_2\text{H}_4\text{SH}$ (referred as $\text{C}_n\text{C}_2\text{SH}$, $n=4, 5, 6, 8$, shown in Scheme 1) [11], in which the hydrogen bond and different strength of van der Waals force are introduced by amide groups and the end groups

with different chain length. It should be noted that the preparation, the stability [12] and the electrochemistry properties [13] of amide-containing long alkanethiol monolayers have been discussed.

In this paper, the SAMs of these new series of amide-containing alkanethiols were studied by reflectance absorption infrared spectroscopy (RA-FTIR) and wettability measurement. The results illustrated that both well defined SAMs formed from these thiols and orientation of the SAMs were dominated by the amide moieties and the alkyl chain in the alkanethiol molecules, which provides us a way to control the molecular orientation of SAMs in molecular level.



Scheme 1

Experimental

Substrate Preparation: The substrate employed in this study were prepared by evaporating 200 nm gold (99.99%) onto a glass slide (7.5 cm×7.5 cm) pre-coated with 10–15 nm chromium. Monolayers of $\text{C}_n\text{C}_2\text{SH}$ were formed by immersing clean gold substrates into 1.0 mM $\text{C}_n\text{C}_2\text{SH}$ /ethanol solutions over 24 h to reach a saturated coverage [14]. Afterwards the monolayers were subsequently washed with ethanol and distilled water and dried in N_2 prior to the structure characterization.

Infrared Measurements: All infrared spectra were recorded on a Perkin Elmer System 2000 FT-IR spectrophotometer equipped with a liquid N_2 cooled MCT detector. The p-polarized infrared beam by Perkin Elmer wire-grid polarizer was incident on the sample plane at 86° (near grazing-angle) from the surface normal. The resolution was set to 4 cm^{-1} , and usually 500 interferograms were collected to achieve an acceptable signal-to-noise ratio. The sample chamber was purged with dry N_2 to eliminate the spectral influence from the water vapor in air.

Contact-Angle Measurements: Contact angle measurement were performed a JJC-II contact-angle goniometer under ambient conditions ($21\text{--}23^\circ\text{C}$, 50–60% relative humidity) using yellow light to illuminate the liquid droplet. At least four times reading in a same sample. The contact angle was obtained by expanding a droplet from a microsyringe until it advanced smoothly across the surface and then measured the angle 10–200 s after expansion.

Results and Discussion

The RA-FTIR spectra of $\text{C}_n\text{C}_2\text{SH}$ ($n=4, 5, 6, 8$) are presented in Fig. 1 corresponding to two regions, 3000–

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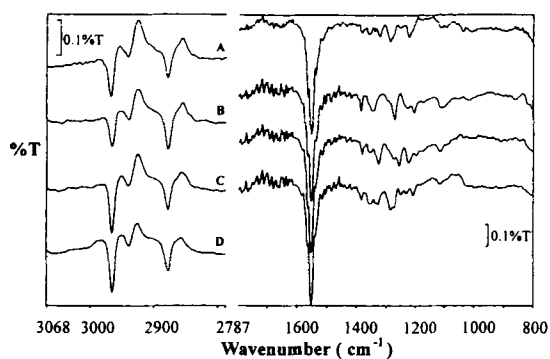


Fig. 1
RA-FTIR spectra of CnC2SH (A, n=4; B, n=5; C, n=6; D, n=8) SAMs on gold

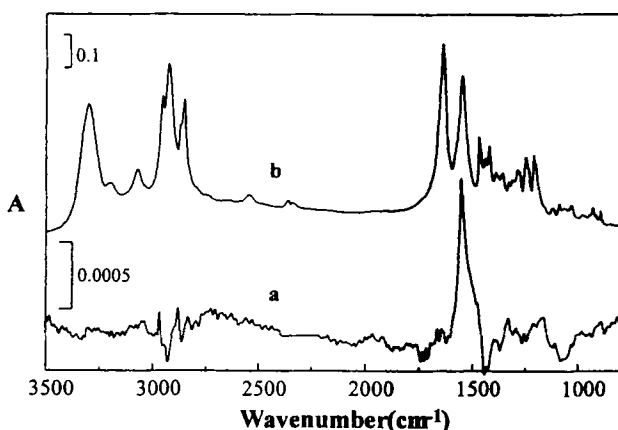


Fig. 2
Comparison of the reflectance absorption infrared spectrum of C8C2SH SAMs on gold (a) to a transmission spectrum of C8C2SH in a KBr pellet (b)

2400 cm^{-1} and 1700–800 cm^{-1} , respectively. For comparison, the spectrum of isotropic sample of C8C2SH in KBr pellet and its RA-FTIR spectrum of SAM are shown in Fig. 2. Based on previous studies [15–16], the band assignments and the peak position of CnC2SH in KBr pellet and in the SAMs are listed in the Table 1.

The first feature of these SAMs spectra is the absence of the absorption of the stretching vibration mode of the N-H group ($\nu_{\text{N-H}}$) and the C=O group ($\nu_{\text{C=O}}$) in the amide moieties. For an isotropic sample, these two modes give rise of strong bands around 3300 cm^{-1} and 1635 cm^{-1} , respectively. According to the selection rule of the RA-FTIR on the metal surface: only the transition having non-zero projection of its dipole moment in the direction of the surface normal can bring about absorption, above results indicate that the orientations of these two groups are parallel to the substrate surface plane. Another absorption concerning with the orientation of amide moiety is the position and the intensity of amide II band which has a large component of N-H in-plane bending motion and its dipole moment is parallel to the molecular axis. The position of the amide II is important to give insight to the degree of the hydrogen bonding among the amide groups.

For non bonded free amide groups, the amide II will appear at much lower frequency [15–16] (near 1510 cm^{-1}) contrasting with that in the bonded state (see Table 1). The amide II bands in the RA-FTIR spectra of these SAMs in our experiment are as high frequency as them in the KBr pellet (see in Table 1). The absence of the absorption of $\nu_{\text{C=O}}$ and $\nu_{\text{N-H}}$ in spectra of the SAMs and the high frequency of the amide II band strongly suggest that hydrogen bonding formed among the amide moieties.

In the high frequency region of RA-FTIR spectra of the CnC2SH (Fig. 1), only the absorption of asymmetric CH_3 and symmetric CH_3 stretching vibration modes are observed at 2966 cm^{-1} and 2878 cm^{-1} . The absence of the asymmetric and symmetric stretching vibration mode of CH_2 reveals that the plane defined by the CH_2 groups are parallel to the surface normal, which suggests that the molecular axis are perpendicular to the substrate surface. It is reasonable to consider this orientation is due to hydrogen bonding among the amide groups in the monolayers. The molecules have to adjust their orientations to fit in the spatial requirement for the formation of the intermolecular hydrogen bond.

Previously works [5] have illustrated that the SAMs of *n*-alkanethiol bear a tilting angle around 30° that is obviously different from our observation of CnC2SH in SAMs. This difference is due to the hydrogen bonding among the amide groups in the SAMs of CnC2SH. The molecules of CnC2SH have to adjust their orientations in order to meet the spatial demands of the hydrogen bonding among the amide groups.

The wettability of the CnC2SH SAMs has been investigated by measuring the advancing and receding contact angle of water and hexadecane (HD) on the monolayers. For comparison, the monolayer of octadecanethiol was also prepared and measured under the same condition as a reference [5]. The values of contact angles on the monolayers are shown in the Table 2. It is noticeable that the wettability of the series of the SAMs exhibits a strong dependence on the length of the hydrocarbon chain in CnC2SH. The contact angle of both the water and HD increased as the hydrocarbon chain is lengthened. For example, the advancing contact angle of water varied from 99° to 110° on the SAMs of C4C2SH to C8C2SH.

Bain [17] proposed that the water molecules were able to penetrate through the terminal alkyl chain, possibly by disordering the outermost part of the monolayer. Thus the order and packing degree of the hydrocarbon chain may play important role to the wettability of the monolayers. Consequently, the increasing of the contact angles of both water HD on the monolayers from C4C2SH to C8C2SH demonstrates that the alkanethiols containing long alkyl chain are more densely packed in the monolayers than those short molecules. The hysteresis between the advancing and receding contacting angles reflects the homogeneity of the monolayers. The SAM of C4C2SH, for example, showed an obviously larger hysteresis of either water and HD than SAMs of C8C2SH and octadecanethiol did. This also proves that there may be more de-

Table 1
Assignment of infrared bands

Vibration	Modes	C4C2SH		C5C2SH		C6C2SH		C8C2SH	
		KBr ^{a)}	SAM ^{b)}	KBr	SAM	KBr	SAM	KBr	SAM
CH ₃	va	2960	2965	2960	2965	2960	2965	2960	2965
	vs	^{c)}	2880	^{c)}	2880	^{c)}	2880	^{c)}	2880
CH ₂	va	2934	^{c)}	2933	^{c)}	2932	^{c)}	2927	^{c)}
	vs	2875	^{c)}	2857	^{c)}	2861	^{c)}	2852	^{c)}
ν_{N-H}		3292	^{c)}	3323	^{c)}	3285	^{c)}	3302	^{c)}
ν_{S-H}		2552	^{c)}	2554	^{c)}	2553	^{c)}	2554	^{c)}
$\nu_{C=O}$		1650	^{c)}	1651	^{c)}	1651	^{c)}	1639	^{c)}
Amide	II	1548	1550	1549	1550	1548	1550	1548	1550

^{a)} In KBr pallet.

^{b)} In the monolayer.

^{c)} Too weak to be observed.

Table 2
The contact angle of water and hexdecane (HD) on CnC2SH SAMs

Molecules for forming SAMs	Contact angle (deg)			
	Water		HD	
	θ_{adv}	θ_{re}	θ_{adv}	θ_{re}
C4C2SH	99±1	82±2	35±2	15±2.5
C5C2SH	106±1.5	86±1.5	37±1.5	24±2
C6C2SH	109±2	96±1	44±2	25±2
C8C2SH	110±1.5	98±2	47±1.5	35±1.5
Octadecanethiol	111±2	110±1	48±1	37±1.5

fects and disorder region in the SAM of C4C2SH than that in the SAMs of C8C2SH and octadecanethiol.

In a summary, we have designed, synthesized and prepared a series of novel amide-containing alkanethiols SAMs, in which the hydrogen bonding and different strength van der Waals force are introduced by amide groups and different length of terminated alkyl chain, respectively. RA-FTIR and wettability measurement demonstrated that the molecular orientation of these amide containing SAMs has been controlled by the presence of the hydrogen-bonding and the variation of van der Waals force.

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