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Structural evaluation of 6-(10-mercaptodecoyl) quinoline self-assembled monolayer on gold by reflectance absorption infrared spectroscopy

^aHao-Li Zhang, ^bHua Zhang, ^aJin Zhang, ^aHu-Lin Li, ^bZhong-Fan Liu*

^aCollege of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, China

^bCenter for Intelligent Materials Research (CIMR), College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

* Corresponding author. Tel.: + 86-10-6275-7157; fax: + 86-10-6275- 7157; E-mail: lzf@chemms.chem.pku.edu.cn

Abstract

Self-assembled monolayer (SAM) of 6-(10-mercaptodecaoxyl) quinoline (MDQ) on gold was characterized by reflectance absorption infrared spectroscopy (RA-IR). The molecular orientation of MDQ in the SAM was totally evaluated by comparing the RA-IR spectrum of the SAM with a transmission spectrum of a KBr pellet. It was found that the alkyl chain exhibit a tilting angle of $24 \pm 5^\circ$ and a twisting angle of $50 \pm 5^\circ$. The results suggested that the quinoline moieties in the SAM form an order layer upon the hydrocarbon chain and do not disturb the packing of the alkyl chains obviously.

Keywords: Quinoline derivative; Self-assembled monolayer (SAM.); Reflectance absorption infrared spectroscopy (RA-IR).

1. Introduction

The self-assembled monolayers (SAMs) of alkanethiol on metal surface have attracted considerable interest during recent years because of their promising application in interfacial chemical and material science research [1]. SAMs of long chain *n*-alkanethiols (usually contain more than 10 carbon atoms in chain) on gold have been studied extensively and they have been proved to be densely packed with the main part of the alkyl chain in an all-*trans* conformation. Modification to the end of *n*-alkanethiols to tailor the surface property widely expands the application of SAMs in various fields, such as adhesion, wetting and chemical catalysis. Functionalized SAMs are therefore important, and so far, amide groups [2, 3], azobenzene groups [4] or nitroanilino [5] containing SAMs have been investigated.

In the present work, we prepared the SAM of 6-(10-mercaptodecaoxyl) quinoline (MDQ) on gold and studied its structure by reflectance absorption infrared spectroscopy (RA-IR). Quinoline is known to be the basic skeleton of alkaloid widespread in the plant kingdom, and has been extensively studied in the fields of biochemistry and pharmacology. So that the quinoline group containing SAM is expected to be useful as a model system for investigating the wetting, catalysis and molecular recognition properties of alkaloid containing membranes.

2. Experiment

MDQ was synthesized and purified in our lab. Details of the synthesis will be reported elsewhere together with a series of analogues. The substrates employed in this study were prepared by evaporating a layer of 200 nm thick gold (99.99%) onto glass slide (7.5 cm × 2.5 cm) pre-coated with 10–15 nm chromium as an adhesion layer. SAMs were prepared by immersing the clean gold substrates into 1.0 mmol/l ethanol solution of thiols for over 24 h to reach a saturated coverage. Afterwards, the monolayer was washed with ethanol and dried in N₂ prior to the characterization.

A Perkin-Elmer System 2000 FTIR spectrometer equipped with a liquid-nitrogen-cooled MCT detector was adopted. The resolution was set to 4 cm⁻¹, and 500 interferograms were usually collected to achieve an acceptable signal-to-noise ratio. The sample chamber was purged with nitrogen to eliminate the interference of the absorption of water vapor in air. A SPECAC variable angle reflection accessory was used to perform the RA-IR measurement, in which the incident angle of the p-polarized infrared radiation was 86°.

3. Result and Discussion

The RA-IR spectrum of the MDQ SAM between 4000 and 800 cm⁻¹ is shown in Fig. 1. For comparison, the transmission spectrum of an isotropic sample of the same compound in a KBr pellet is also shown. Since the IR spectrum of MDQ has not been reported before, it is necessary to give the band assignments of the bulk spectrum firstly. The band positions and assignments [6] are listed in Table 1.

In the spectrum of the KBr pellet, a relative weak band around 3050 cm⁻¹ is assigned to the aromatic C–H stretching modes in the quinoline moiety. The band assigned to aromatic C–H stretching mode shows some shoulders. The splitting could be attributed to the stretching modes corresponding to various C–H bonds in the quinoline ring. The prominent modes between 2800 and 2950 cm⁻¹ are easily identified as the stretching vibrations of methylene group, they are symmetric stretching (ν_{sCH_2}) at 2851 cm⁻¹ and asymmetric stretching (ν_{asCH_2}) at 2923 cm⁻¹ bands, respectively. S–H stretching mode gives rise to a small peak at 2566 cm⁻¹. The bands fall in the middle frequency region of 1700–1400 cm⁻¹ show many benzene-like features, and are readily assigned to the aryl skeletal stretching vibrations of C=N and C=C bonds in quinoline ring. The band at 1469 cm⁻¹ is assigned to the in plane deformation (scissoring mode) of CH₂ groups. The most intense band in the region below 1000 cm⁻¹, at 842 cm⁻¹, is assigned to the aryl-H out-of-plane wagging [6,7].

Compared with the spectrum of the KBr pellet, RA-IR spectrum of MDQ SAM shows several important features. In the RA-IR spectrum, ν_{asCH_2} and ν_{sCH_2} are observed at 2921 and 2850 cm⁻¹, respectively. It is well known that the position, the intensity and the peak shape ν_{asCH_2} and ν_{sCH_2} modes are sensitive to the phase state of the poly-methylene chain [8, 9]. A disordered SAM is expected to give broader absorption bands and exhibit higher frequency than that in the crystalline state [10]. The positions of ν_{asCH_2} and ν_{sCH_2} in the RA-IR spectrum of the MDQ SAM are even lower than that in the transmission spectrum of the KBr pellet, suggesting that the molecules in the MDQ SAM are as densely packed as they are in solid state [8–10]. In order to find out the influence of quinoline group on the packing of alkyl chains, the SAM of decanethiol, which has same number of methylene groups as the MDQ molecule, has also been studied for

reference. In the spectrum of the decanethiol SAM, the ν_{asCH_2} and ν_{sCH_2} models are found around 2920 and 2850 cm^{-1} , respectively. The difference of ν_{asCH_2} and ν_{sCH_2} modes in the decanethiol SAM and the MDQ SAM is very little (within 1 cm^{-1}), suggesting that the quinoline ring in MDQ SAM does not introduce significant perturbation to the packing density of the alkyl chain. Therefore, it is reasonable to propose that the quinoline groups in the SAM are tightly packed and must adopt an orientation in which they have the smallest projection on the substrate. The most probable conformation is that the plane of quinoline group is perpendicular to the surface. And this guess is confirmed by the analysis of the vibration mode of aryl C–H out-of-plane wagging $\delta_{\text{Ph-H}}$. The $\delta_{\text{Ph-H}}$ at 842 cm^{-1} is the strongest band below 1000 cm^{-1} in the transmission spectrum, but is barely detected in the RA-IR spectrum. Since the direction of dipole moment transition of aryl-H out-of-plane wagging is perpendicular to quinoline plane, the weak intensity of this band in the RA-IR spectrum suggests that the plane of quinoline ring is roughly perpendicular to the substrate surface.

The stretching vibration of S–H bond is absent in the RA-IR spectrum of MDQ SAM, which is consistent with the formation of S–Au bond. The aromatic skeletal stretching vibrations of quinoline ring give prominent bands in the middle frequency region (1700–1400 cm^{-1}) of the RA-IR spectrum. Precise assignments to the quinoline ring stretching bands are not achieved yet but it can be agreed that these dipole moment transitions have most of their component in the plane of quinoline ring. Thus, the strong bands at 1625, 1598, 1504 and 1422 cm^{-1} in the RA-IR spectrum of MDQ SAM clearly indicate that the angle between quinoline plane and the surface normal is very small. In contrast with the medium absorption of methylene in plane deformation at 1469 cm^{-1} in the spectrum of the KBr pellet, the very weak band at 1464 cm^{-1} in the RA-IR spectrum of SAM indicates that the alkyl chain has a very small tilting angle with respect to the surface normal.

The two most characteristic bands of aromatic ether are the stretching vibrations of aryl C–O bond ($\nu_{\text{Ph-O}}$) and alkyl C–O bond ($\nu_{\text{C-O}}$). In the transmission spectrum, $\nu_{\text{Ph-O}}$ is observed as a strong band at 1228 cm^{-1} and $\nu_{\text{C-O}}$ as a medium strength band at 1030 cm^{-1} . For comparison, $\nu_{\text{Ph-O}}$ stretching exhibits the strongest band in the RA-IR spectrum of the MDQ SAM while $\nu_{\text{C-O}}$ stretching band is relatively weak. It is known that the dipole moment transition of $\nu_{\text{Ph-O}}$ is roughly parallel with the Ph–O bond. Therefore, the high intensity of $\nu_{\text{Ph-O}}$ in RA-IR spectrum suggests that the Ph–O bond is at a very small angle with respect to the surface normal. Analogous to the benzene and naphthalene derivatives, most medium intense bands fall in the region of 1400–1000 cm^{-1} involve deformation of aryl ring, rocking of methylene and Aryl-H in plane bending in quinoline group. Exact assignments for these deformation and bending bands are very complicate and not clear yet.

It is important to have an estimate to the orientation of MDQ molecules in the SAM. Molecular orientation in SAM could be estimated by comparing the transmission spectrum of an isotropic sample with a RA-IR spectrum of the SAM, which is based on the geometric analysis to the selected dipole moment transitions. According to the selection rule of grazing angle reflectance FTIR on metal surfaces, *only the transition having non-zero projection of its dipole moment in the direction of surface normal can bring about absorption, the intensity of a vibration mode for a molecule adsorbed on metal surfaces is given by*

$$I \propto |E \cdot \mu z|^2 \quad (1)$$

where E is the electric field at the metal surfaces and μz is the vertical projection of transition dipole moment.

Three vibration modes were used to evaluate the orientation of MDQ moiety at the gold surface, they are ν_{sCH_2} , ν_{asCH_2} and $\nu_{\text{Ph-O}}$. Expressions for μ_z for each mode used in our analysis of the MDQ SAM are presented in terms of the dynamic dipole moment for each mode and the tilting (α) and twisting (β) angles of the monolayer illustrated in Fig. 2 are given by [11].

$$(|\mu_{\nu_{\text{sCH}_2}}|)_z = |\mu_{\nu_{\text{sCH}_2}}| \sin \alpha \cos \beta \quad (2)$$

$$(|\mu_{\nu_{\text{asCH}_2}}|)_z = |\mu_{\nu_{\text{asCH}_2}}| \sin \alpha \cos \beta \quad (3)$$

$$(|\mu_{\nu_{\text{Ph-O}}}|)_z = |\mu_{\nu_{\text{Ph-O}}}| (\cos \alpha \cos \varphi + \sin \alpha \sin \beta \sin \varphi) \quad (4)$$

All the three bands are prominent in the transmission spectrum and exhibit strong enough integrated intensities in the RA-IR spectrum so that the errors in measuring integrated infrared bands intensities are small. The φ value in formula (4) was assumed to be 35° , which was obtained from the geometrical analysis of the MDQ molecule using the regular bond angle values.

Ratioing the infrared integrated band intensities for ν_{sCH_2} and ν_{asCH_2} gives the twisting angle β . Based on the correlation between the dynamic dipoles and the infrared intensity and using Eqs. (2) and (3), one gets

$$\beta = \arctan \left[\left(\frac{I_{\nu_{\text{asCH}_2}}}{I_{\nu_{\text{sCH}_2}}} \right)_R \left(\frac{I_{\nu_{\text{sCH}_2}}}{I_{\nu_{\text{asCH}_2}}} \right)_T \right]^{1/2} \quad (5)$$

Similar to the above process, the tilting angle α can be obtained from Eqs. (2) and (4).

$$\alpha = \arctan \left(\cos \varphi \cos^{-1} \beta \left[\left(\frac{I_{\nu_{\text{Ph-O}}}}{I_{\nu_{\text{sCH}_2}}} \right)_R \right]^{1/2} \times \left(\frac{I_{\nu_{\text{sCH}_2}}}{I_{\nu_{\text{Ph-O}}}} \right)_T \right)^{1/2} - \sin \varphi \right]^{-1} \quad (6)$$

By using the above formulae, we obtain from our experiment that the tilting and twisting angles are $24 \pm 5^\circ$ and $50 \pm 5^\circ$, respectively. The orientation of polyethylene chain in MDQ SAM is very similar to the previous reports on SAMs terminated with methyl and various small polar groups (e.g., CH_2OH , COOH , CO_2CH_3 , CN , etc.), in which the alkyl chain was found to prefer a tilting angle of about 30° [12,13]. Together with our previous result that the planes of quinoline moieties in monolayer are roughly perpendicular to the substrate surface, we describe the film structure as a tightly packed quinoline layer on a well-oriented polymethylene layer (Fig. 3).

Our previous investigations on molecular orientation in amide or azobenzene containing SAMs have demonstrated that the film structure is predominated by different inter-molecular interactions in SAMs and the optimum film structure should minimize the free enthalpy of the mono-layer [3, 4]. Understanding how the various molecular interactions influence molecular structure in SAM are important for setting up general route to designing functionalized surface. In the MDQ SAM, the hydrocarbon chain introduces interchain van der Waals attraction and the quinoline group introduces aromatic π - π interaction. In general, the head-head spacing (S - S spacing of 0.5 nm) in SAMs is usually greater than the van der Waals touching distance of alkyl chain (0.46 nm). Therefore, the alkyl chains incline in the MDQ SAM to have an optimum van der Waals contact. Meanwhile, the quinoline rings are roughly perpendicular to the substrate may be understood as a result of that the quinoline moieties pack near parallel so that the π - π interaction among aromatic rings could be optimized.

In conclusion, the structure of MDQ SAM has been evaluated by RA-IR spectroscopy. The orientation of MDQ in the monolayer are determined by the van der Waals interaction among the alkyl chains and the π - π interaction among the quinoline moieties. The MDQ SAM is expected to be used as a model for studying the aggregation of aromatic group in the film and the protonation of quinoline moiety at the solid/ liquid surface. Related investigations are being carried out in our group.

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Table 1 The assignments to the infrared bands s: strong; m: middle; w: weak; o.p.: out of plane

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- Fig.2. Definition of molecular tilting (α) and twisting (β) angle in the MDQ SAM and the related vibrational modes.
- Fig.3. The hypothesis film structure of the MDQ SAM on gold.

Vibration modes	KBr	SAM
ν_{asCH_2}	2922 s	2921 m
ν_{sCH_2}	2851 s	2850 m
$\nu_{\text{S-H}}$	2566 w	not observed
Aromatic skeleton	1622 m	1625 s
	1594 m	1598 m
	1500 m	1505 s
δ_{CH_2}	1469 m	1467 w
$\nu_{\text{Ph-O}}$	1228 s	1231 s
$\delta_{\text{Ph-H}}$ o.p.	843 s	842 w

Table 1

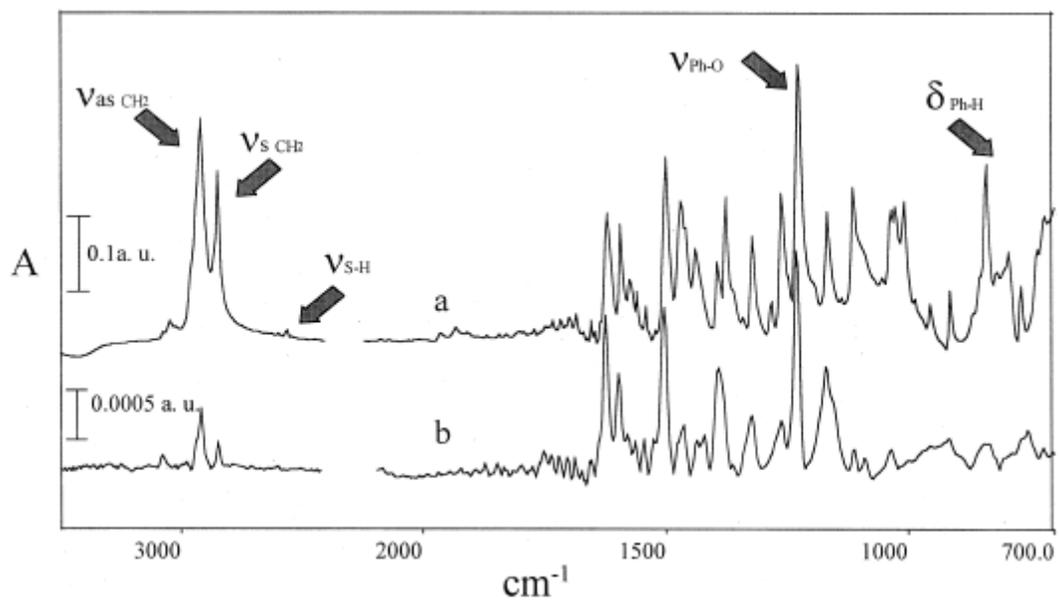


Fig. 1.

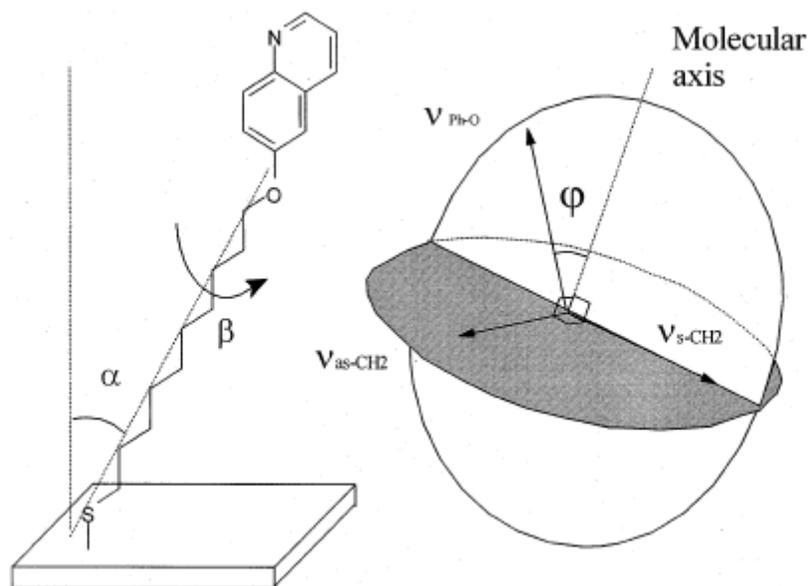


Fig. 2.

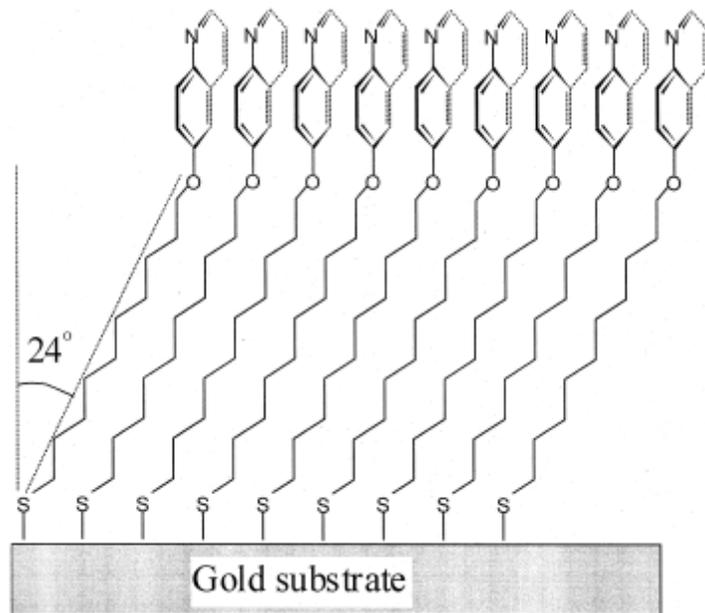


Fig. 3.