Structural evaluation of azobenzene-functionalized self-assembled monolayers on gold by reflectance FTIR spectroscopy

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Abstract

The end-group-dominated molecular orientation in azobenzene self-assembled monolayers (SAMs), $C_n AzoC_2 SH$ ($n = 1$–4), on gold was evaluated by grazing incidence reflection absorption FTIR spectroscopy. All these azobenzene SAMs form highly organized and closely packed structures, with the molecule tilting gradually away from the surface normal direction with increasing end group alkyl length.

The molecular self-assembling technique provides a rational approach for fabricating interfaces with a well defined structure [1]. We have been paying particular continuous attention to azobenzene-functionalized monolayer assemblies for both fundamental and technological perspectives. We have extensively studied the physicochemical properties of azobenzene self-assembled monolayers (SAMs) which covered photochromism [2], the long-range electron-transfer kinetics [3–6], pH-dependent electrochemical behaviour [7], ultrahigh density information storage [8], etc. Recently, we reported the end-group dominated electron-transfer kinetics of a novel series of azobenzene (SAMs) of $C_n AzoC_2 SH$ ($n = $ 1–4) (shown in Scheme 1) on gold [7], in which the unique change in the electron-transfer kinetic behavior was suggested to be closely related to the molecular orientational variation in this new class of monolayers. In this Letter, we report our grazing-an-

X=CH3 (C1AzoC2SH)

X=CH2CH3 (C2AzoC2SH)

X=CH2CH2CH3 (C3AzoC2SH)

x=CH2CH2CH2CH3 (C4AzoC2SH)
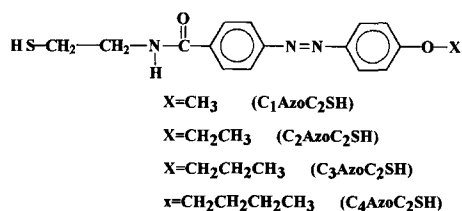
Scheme 1.

gle reflectance FTIR spectroscopic studies (RA-FTIR) on the SAMs of $C_n AzoC_2 SH$ ($n = $ 1–4).

The substrates employed in this study were prepared by evaporating 200 nm gold (99.99%) onto a glass slide (7.5 cm × 2.5 cm) pre-coated with 10–15 nm chromium. Self-assembled monolayers were prepared by immersing clean gold substrates into a 1.0 mM ethanol solution of $C_n AzoC_2 SH$ ($n = $ 1–4) over 24 h to reach a saturated coverage. Afterwards, the

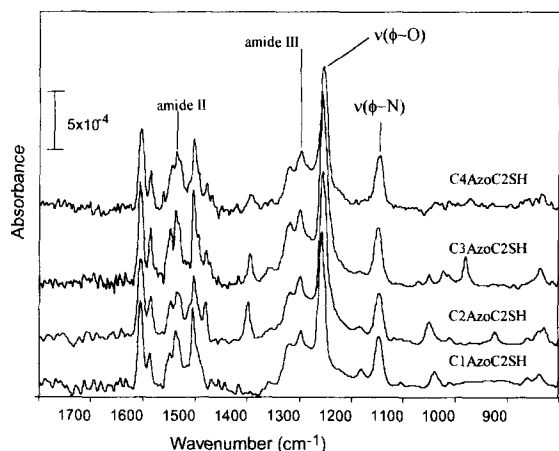Fig. 1. RA-FTIR spectra of $C_n AzoC_2 SH$ ($n = 1$–4) SAMs.

monolayers were washed with ethanol and dried in N_2 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 usually 500 interferograms were 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 vapour in air.

An accessory (a SPECAC variable angle reflection attachment) was used to perform the reflectance FTIR, in which the incident angle of the p-polarized infrared radiation was 86°.

The RA-FTIR spectra of $C_n AzoC_2 SH$ ($n = 1$–4) SAMs are shown in Fig. 1, in the frequency region 1800–800 cm^{-1}. For comparison, the spectrum of an isotropic sample of $C_3 AzoC_2 SH$ in KBr pellet and its SAMs spectrum are shown in Fig. 2.

The first feature of these SAMs spectra is the absence of absorption of the stretching vibration mode of the N–H group (ν(N–H)) and C=O group (ν(C=O)) in the amide group. For an isotropic sample (Fig. 2), the absorption of these two modes is at 3270 and 1635 cm^{-1}, respectively. According to the selection rule of grazing angle reflectance FTIR on a metal surface: *only the transition having a non-zero projection of its dipole moment in the direction of the surface normal can bring about absorption*, the above data indicate that the orientation of these two groups are orientated parallel to the substrate surface plane. This kind of parallel orientation of these two groups is attributed to the hydrogen bonds formed between the amide groups of different molecules, whose evidence can be found in the
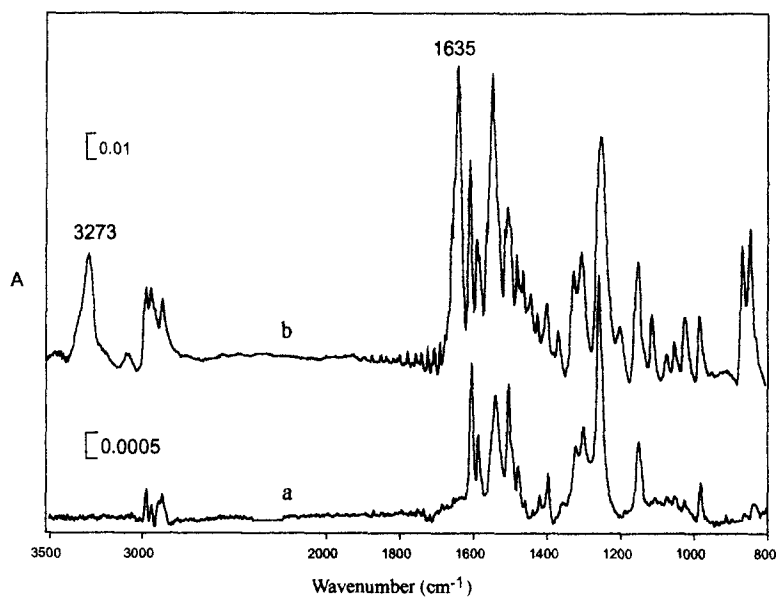

Fig. 2. Comparison of grazing incidence reflectance infrared spectrum of $C_2 AzoC_3 SH$ SAMs on gold (a) to a transmission spectrum of $C_2 AzoC_3 SH$ in a KBr pellet (b).
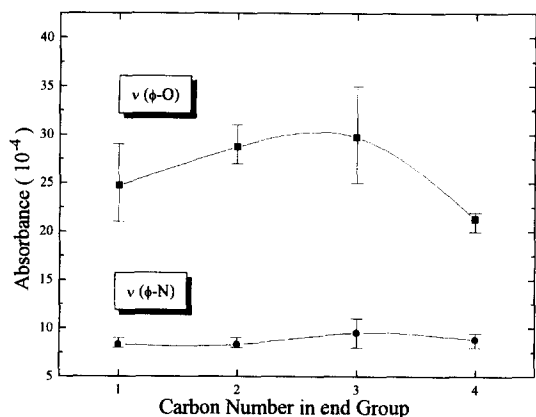
Fig. 3. The variation in absorbance of the $\nu(\phi-O)$ and $\nu(\phi-N)$ modes as a function of end group length.

frequency of the amide II band [9,10], which is ≈ 1537 cm^{-1} in SAMs and shifts to 1520 cm^{-1} in CCl$_4$ solutions.

It is interesting to know how the length of the end group alkyl chain affects the SAM structure, especially the molecular orientation. To do this, attention was paid to the absorption of the stretching vibration mode of benzene–O and benzene–N, i.e. $\nu(\phi-O)$

and $\nu(\phi-N)$, at 1255 cm^{-1} and 1147 cm^{-1}, respectively, whose transition dipole moments are parallel to the molecular axis of the azobenzene group. Fig. 3 is the absorbance of these two modes versus the length of the end group, in which the absorption intensity of $\nu(\phi-O)$ increases at first, and then decreases to a much lower level. The absorption intensity of the $\nu(\phi-N)$ mode has a similar behavior, although its absorbance change is much smaller than that of $\nu(\phi-O)$ mode because of its intrinsic low absorbance.

As reported in our previous publication [7], the surface concentration of the molecules was 3.02×10^{-10}, 4.26×10^{-10} and 5.03×10^{-10} mol/cm^2 for C$_1$AzoC$_2$SH, C$_2$AzoC$_2$SH, C$_3$AzoC$_2$SH SAMs, respectively, and even larger for C$_4$AzoC$_2$SH SAMs. An increase in packing density is expected to increase the absorption intensity of a certain vibration mode if the molecular orientation remains unchanged as the alkyl chain is lengthened. Our observation differs from this expectation. Therefore, there must exist another factor which brings about the decrease in absorbance, and it is the competition of these two factors that results in the maximum in absorbance of
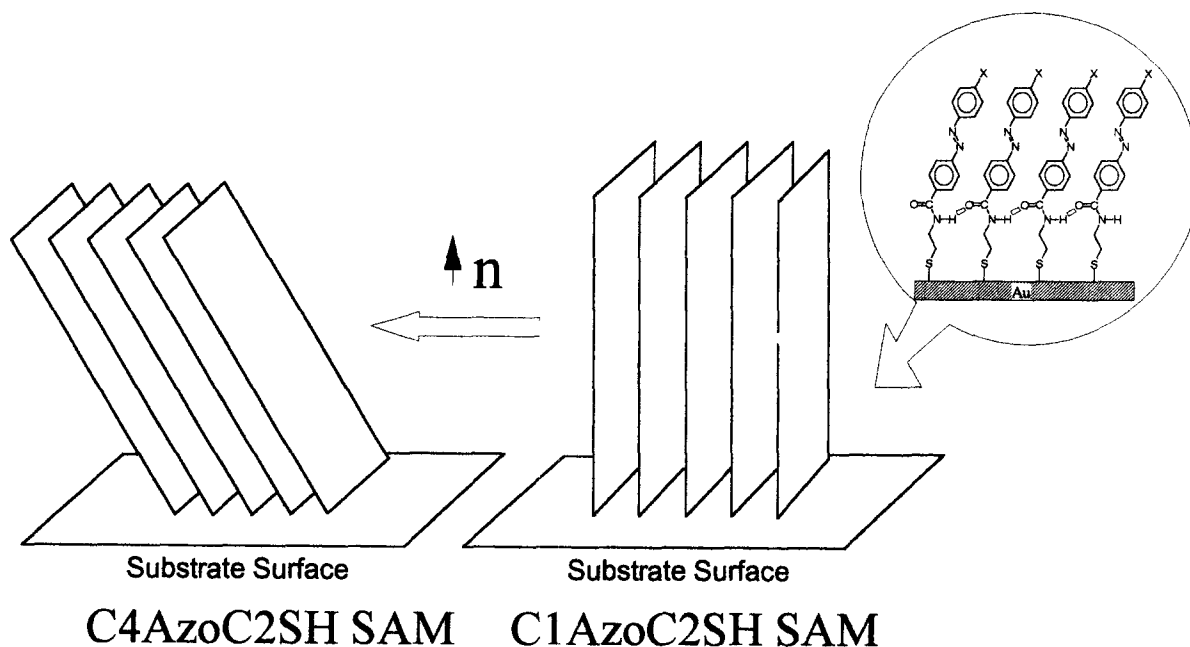

C4AzoC2SH SAM   C1AzoC2SH SAM

Fig. 4. Schematic representation of the molecular orientational changes in C$_n$AzoC$_2$SH SAMs with increasing end alkyl chain.

the $\nu(\phi-O)$ and $\nu(\phi-N)$ modes in Fig. 3. In the RA spectra, the decrease in absorbance of these vibration modes implies a smaller projection of its transition moment in the direction perpendicular to the surface, which indicates that the angle of the benzene–O and benzene–N bonds with respect to the surface normal increases from C_1AzoC_2SH to C_4AzoC_2SH SAMs, and this is also the same case for the molecular axis of the azobenzene molecule. The tilting behavior of the molecule can be illustrated by Fig. 4. For one C_nAzoC_2SH molecule, its amide group and azobenzene group lie in the same plane. In the SAMs, the adjacent molecules connect to each other in a side-by-side manner by hydrogen bonds through the N–H and C=O groups, which is represented by the insert in Fig. 3. As the end alkyl chain is lengthened, the molecular plane makes a larger angle to the normal of the substrate surface; in other words, the plane tilts to face down more to the surface.

It is important to have an estimation of the orientation angle of the molecules, which could be done by comparing the spectra of isotropic sample and those in SAMs. Measuring the IR spectra of the samples in a KBr pellet allows us to determine the absorbance per mole of molecules (A_i). The angle (θ) between the dipole moment of a certain vibration mode and the surface normal can be estimated by

$$\cos^2\theta = \eta\frac{A_r}{A_i}, \tag{1}$$

where A_r denotes the absorbance of per mole molecules in RA spectra, and η (≈ 1) is a constant regarding the difference in infrared intensities in measuring the isotropic sample and SAMs, taking into account the attenuation of the IR radiation intensity in the RA experiment and an enhancement of 4 on the gold surface in the case of grazing incident angle. The tilting angles which the molecular axis of the azobenzene group makes with the surface normal are estimated to be around 12°, 30° and 36°, for C_1AzoC_2SH, C_2AzoC_2SH and C_3AzoC_2SH SAM, respectively. The tilting angle of C_4AzoC_2SH is not determined, because of the lack of surface concentration data [7].

Previous studies show that the packing density and orientation of molecules in a monolayer of long-chain alkyl compounds are strongly related to the spacing between the adjacent head groups, and the van der Waals and dipole interactions between these molecules [11]. In general, in monolayer assemblies where the head–head spacing (S–S spacing of 0.5 nm) is greater than the van der Waals contact distance of the alkyl chains (0.46 nm), the alkanethiol molecules make a tilting angle to the surface normal, to minimize the free energy and to have an optimum van der Waals contact [11–13]. In the present case, hydrogen bonding and π–π interactions are also involved, which helps to organize the molecules into a highly ordered structure, along with van der Waals interactions of different strength. A stronger van der Waals force attracts molecules together more, resulting in a larger surface concentration. To minimize the free energy and to have an optimum van der Waals contact, a larger tilting angle in reference to the surface normal appears with increasing end alkyl chain length. A further investigation on these systems is being processed.

In conclusion, the introduction of a longer end alkyl chain of C_nAzoC_2SH ($n = 1$–4) affects the molecular orientation in SAMs, and, as a result, helps to form more closely packed molecular assemblies.

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