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Studies on the Structure of Self-Assembled Monolayer of Phenylazonaphthalene

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The structure of a self-assembled monolayer (SAM) of 1-mercapto-6-[1-(4-phenylazonaphthoxy)]hexane (**1**) has been investigated by UV-vis spectroscopy, atomic force microscopy and Grazing-Incidence Fourier Transform Infrared Spectroscopy. The results support the hypothesis that the molecules are firstly chemisorbed, and then oriented during a long period to achieve a good orientation. The morphology of SAM consists of large domains (ca. 100 nm wide by ca. 410 nm long) almost parallel to each other.

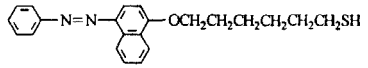
Keywords: phenylazonaphthalene; self-assembled monolayer; UV-vis spectroscopy; atomic force microscopy; Fourier transform infrared spectroscopy

INTRODUCTION

The self-assembled monolayers (SAMs) comprising aromatic azo group possesses many potential applications. The structure of SAMs is primarily important since it is relevant to its properties. For the SAM of n-alkanethiol, various surface analytical technologies including electron and X-ray diffraction, scanning tunneling microscopy (STM) and atomic force microscopy (AFM)[1] have been utilized to investigate the structures. Some results have demonstrated the structural crystallinity of SAMs is the main block of the chemical activities.

In our previous paper,[2] we have investigated the electrochemical properties of the SAM of a novel azo compound, thiol-terminated phenylazonaphthalene (Scheme 1) prepared by us,[3] and demonstrated the irreversibility of the electrode process. In this work, UV-vis spectrometry, AFM and GI-FTIR are employed to investigate the structure of the SAM.

SCHEME 1 The Structure of Thiol-Terminated Phenylazonaphthalene



(1)

EXPERIMENTAL

Gold films (5nm thick) were thermally evaporated onto polished quartz slides (for UV-vis spectroscopy measurement) and mica (for AFM observation) precoated with an evaporated titanium adhesion layer (2nm thick). The transmittance of the gold film on quartz was about 50% (200-900nm). The slides were immersed in 2 mL of the deposition solution (1mM of **1** in absolute ethanol) for an assigned time. Upon removal from the solution, the slides with SAM were rinsed with absolute ethanol, dried with nitrogen gas.

The UV-vis absorption spectra of the SAMs were recorded using Shimadzu UV-2201. The transmission spectrum of the gold film, taken prior to chemisorpton of the monolayer, was used as a background spectrum and subtracted from that of the phenylazonaphthalene monolayer chemisorbed on it.

The microscope was performed on a NanoscopIIIa Atomic force microscopy (Digital Instruments Inc., USA). AFM image of the SAM (Chemisorbing 12hours) was obtained in air in contact mode. The roughness of the gold films on mica was less than 0.6 nm.

Transmission FTIR spectra and Grazing-Incidence Fourier Transform Infrared Spectroscopy (GI-FTIR) experiments were performed on a Bruker Model RFS 100 FTIR spectrometer. The surface reflection spectra of the monolayer films were obtained at a grazing angle of 85°.

RESULTS AND DISCUSSION

The Self-Assembly Course of Thiol-derivatize Phenylazonaphthalene

Figure 1 shows the *ex situ* UV-visible absorption spectra of the SAM at different chemisorbing time. the absorption spectra exhibit two typical absorption peaks. The long axis π-π^* electron transition absorption (referred as A_L) locates at about 400nm which splits into two peaks (380 and 401 nm), comparing with that of **1** in solution. The short axis π-π^* electron transition absorption (referred as A_S) locates at about 230nm which almost maintain its position as that in solution. The peak splitting for the long axis π-π^* transition and the stability for the short π-π^* transition manifest that the interaction originates from intermolecular aromatic ring face-to-face interaction.

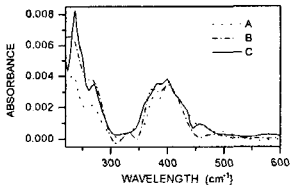


FIGURE 1 The UV-visible spectra of **1** at different chemisorbing time. a: 2 min; b: 30 min; c: 120 min

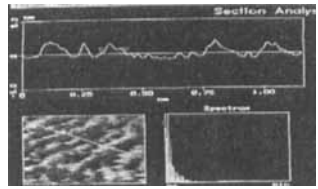


FIGURE 2 The AFM image of **1** SAM. (chemisorbing time: 12 hours). The substrate is 5 nm thick gold on mica.

On the other hand, the A_s value increases dramatically as self-assembly time increases. Xu et al have investigated the aggregated structures of azobenzene-containing amphiphiles at the air-water interface, and concluded the ratio of two absorbances of the azobenzene, A_S/A_L, was a good measure for the orientation of the azobenzene.[4] The smaller the tilt angle of long molecular axis was, the larger the A_S/A_L value was. Figure 1 shows that the chemisorbing course of **1** onto the gold film is almost completed within 2 minutes because there is no distinct increase of A_L value after 2 min. In addition, the A_S/A_L value changes from ca. 1 to ca. 2 and becomes stable. This suggests the orientation course is almost complete within 2 hours. The high ratio of A_S/A_L value demonstrates the molecules in the self-assembled monolayer are well oriented.

According to the A_L value 0.0037 and the extinction coefficient of **1** in chloroform (ε=19600), the coverage of **1** on the gold film is calculated to be about 1.89×10^{-10} mol/cm^2,[5] corresponding to the single molecular area 0.88 nm^2. The single molecular area is much larger than expected, Does this mean the molecules are loosely existed in the SAM?

Atomic Force Microscopy Observation

Figure 2 gives the AFM image of SAM of **1**. The domains and the domain boundaries form rows almost parallel to each other. The domain size is about 100nm wide by 410nm long. The coverage of SAM on gold substrate can be calculated to be about 50%. From the UV-vis spectra, the average single molecular area is 0.88nm^2, the actual single molecular area is 0.44nm^2, therefore, the molecules in SAM is still closely packed. The SAM structure do differ from that of long chain alkanethiols. Why do large domain boundaries exist in the SAM? It can be preliminarily explained by the existence of strong interaction between the bulky end moiety phenylazonaphthalenes which dominate the morphology of SAM.

Infrared Spectroscopy

The GI-FTIR spectrum of SAM of **1** is depicted in Figure 3. The peaks at 2926.0 and 2853.9 cm^{-1} are the typical absorption peaks of $\nu_a(CH_2)$ and $\nu_s(CH_2)$. Both of the methylene stretches are in close agreement with the values for a more liquid-like state in KBr, rather than the expected crystalline-like state. The aromatic ring stretches locate at 1576.2 and 1499.7 cm^{-1}. The strong peak of 1576.2 is attributed to the aromatic ring stretch related to the conjugated N and O atoms having lone pair electrons. The aromatic ring stretch absorption peaks 1576.2 and 1499.7 cm^{-1} red-shift 3.8 and 7.6 cm^{-1}, respectively, comparing with that of **1** in KBr. These data imply the phenylazonaphthalene components in the SAM are closely packed, and exhibit crystalline-like state. The peak at 1041.1 cm^{-1} is the absorption of Ar-O-C symmetric stretch, and this assignment reveals the phenylazonaphthalene moiety is not parallel to the gold surface, but tilted on the gold surface, although the exact orientation has not be depicted at present.

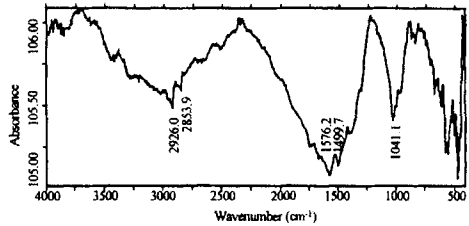


FIGURE 3 The GI-FTIR spectrum of the SAM (Chemisorbing for 12 hours)

Acknowledgements

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References

[1] R. H. Terill, T. A. Tanzer, P. W. Bohn, *Langmuir,* **14,** 845 (1998).
[2] A. Zhang, J. Qin, *SPIE,* **3562,** 168 (1998).
[3] To be published. Some spectral data of **1** used in this paper are: IR (KBr cm^{-1}) 2927.9, 2853.5, 1580.0, 1507.2; UV λ_{max} (nm, in $CHCl_3$): 234 (ε=20500), 394 (ε=19600).
[4] X. Xu, M. Era, T. Tsutsui, S. Saito, *Chem. Lett.,* 773 (1988).
[5] T. A. Postlethwaite, J. E. Hutchison, K. W. Hathcock, R. W. Murray, *Langmuir,* **11,** 4109 (1995).