Self-Assembled Monolayers of Azobenzene-Incorporated Alkanethiol on Silver

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Received December 14, 2004

In the past decade, self-assembled monolayers (SAMs) have received a great deal of attention for their fundamental importance in understanding interfacial properties as well as for their potential applications in molecular technologies.[1] SAMs have been used in the design of various interfaces for chemical sensors, nonlinear optical materials, optical switches, and high density memory devices.[2]

The principal ingredient for obtaining SAMs is a relatively strong interfacial binding asymmetry of the molecular constituents. For the most frequently studied alkanethiol SAMs on Au or Ag, this is obviously provided by the sulfur affinity for gold and silver and a comparatively strong lateral interaction arising from the van der Waals forces between the chains.[3] In this sense, a better understanding of the molecular details for various SAM systems is needed in order to engineer nanoscale surfaces.

Recently, azobenzene-based alkanethiol SAMs have attracted much attention not only from the structural point of view but also from that of the photo and electrochemical characteristics of the azobenzene group; azobenzene-based molecules have been proved to be a potential medium for high-density recording elements and molecular switches.[4] Simulations and infrared experiments suggested that such a bulky aromatic unit within an alkanethiol SAM could change the packing density as well as the lattice parameter.[5,6] For instance, Han *et al*. reported that azobenzene-incorporated alkanethiol SAMs on Au(111) should possess near hexagonal lattices on a Au(111) surface, with nearest spacing of *ca.* 5.5 Å.[7] The experimental data could be understood by bundle model. The azobenzene moieties condense to form small bundles, thereby causing the alkyl chains to be projected outward from the azobenzene moieties. This clearly indicates that the azobenzene group, although not completely independent from Au(111) surface influence, plays a significant role in dictating the overall monolayer structure regardless of its actual position in alkanethiols.

Herein we aim to report a study performed to further increase our understanding of the structure of azobenzene-based alkanethiol SAMs on Ag. Since most of the previous studies have dealt with SAMs on Au, we have investigated the effect of the azobenzene moiety on the structure and stability of SAMs on Ag surface with an azobenzene-based alkanethiol molecule, *i.e.*, 4-dodecoxy-4'-(6-mercaptohexoxy)azobenzene ($C_{12}AzoC_6SH$).

Experimental Section

A thiol-functionalized azobenzene ($C_{12}AzoC_6SH$) was synthesized following the procedure in the literature.[8] 1,2-Benzenedithiol and octadecanethiol were purchased from Aldrich. Unless otherwise stated, all chemicals and gases were analytical grade.

The silver substrates were prepared by resistive evaporation of titanium (Aldrich, >99.99%) and silver (Aldrich, >99.99%) at 1×10^{-6} Torr on batches of glass slides. Deposition of titanium prior to that of silver was performed to enhance adhesion to the substrate. After the deposition of approximately 200 nm of silver, the evaporator was back-filled with nitrogen. The silver substrates were immersed subsequently into 1 mM thiol solutions for a predetermined period of time. After the substrates were removed, they were rinsed with excess benzene and then ethanol, followed by drying in a N_2 gas stream.

The infrared spectra were obtained with a Bruker IFS 113v Fourier transform spectrometer equipped with a globar light source and a liquid N_2-cooled mercury cadmium telluride detector. The method for obtaining reflection-absorption infrared (RAIR) spectra has been reported previously.[9]

The ellipsometric thickness of the self-assembled $C_{12}AzoC_6SH$ film was estimated using a Rudolph Auto EL II optical ellipsometer. The measurement was performed using a He/Ne laser 632.8 nm line incident upon the sample at 70°. The ellipsometric parameters, Δ and Ψ, were determined for both the bare clean substrates and the self-assembled films. The so-called DafIBM program supplied by the Rudolph Technologies was employed to determine the thickness values. At least seven different sampling points were considered in order to obtain an averaged thickness value.

Results and Discussion

As one might expect, $C_{12}AzoC_6SH$ molecules chemisorbed on the silver surface very favorably. Figure 1a shows the RAIR spectrum of $C_{12}AzoC_6SH$ self-assembled on silver in 1 mM benzene solution for 7 hr. For reference, the transmission infrared (TIR) spectrum of neat $C_{12}AzoC_6SH$ in a KBr matrix is shown in Figure 1c. All the peaks in these spectra can be readily assigned by consulting the data in the
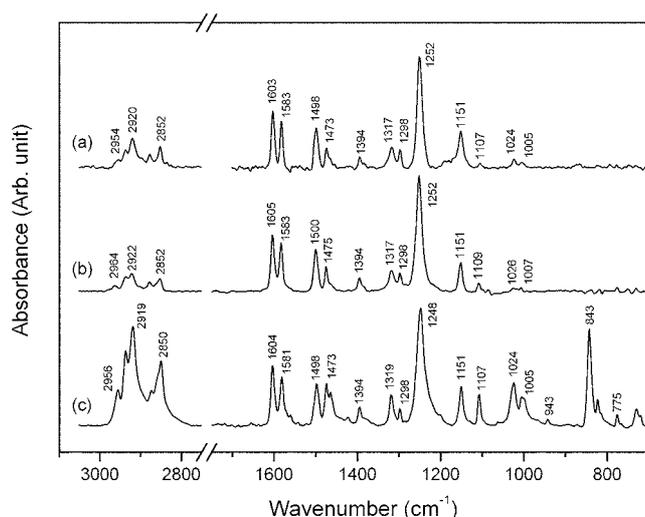
Figure 1. RAIR spectra of $C_{12}AzoC_6SH$ on (a) silver and (b) gold. (c) Neat (solid) TIR spectrum of $C_{12}AzoC_6SH$.

Table 1. Infrared spectral data and vibrational assignment of $C_{12}AzoC_6SH$ in neat solid and adsorbed states on silver

Neat $(cm^{-1})^a$	RAIR $(cm^{-1})^b$	Assignment^{c,d}
2956	2954	$\nu_{as}(CH_3)$
2937	2937	$\nu_s(CH_3)$, FR
2919	2920	$\nu_{as}(CH_2)$
2874	2877	$\nu_s(CH_3)$, FR
2850	2852	$\nu_s(CH_2)$
2560		$\nu(SH)$
1604	1603	8a/b
1581	1583	8a/b
1498	1498	19a
1473	1473	$\delta(CH_2)$
1394	1394	$\delta(CH_2)$
1319	1317	14
1298	1298	3
1248	1252	$\nu_{as}(COC)$
1151	1151	$\nu(C-N)$
1107	1107	18b
1024	1024	$\nu_s(COC)$
1005	1005	18a
999		12
943		17b(op)
843		10a(op)
775		11(op)

^{a}Taken in KBr matrix. ^{b}Reflection-absorption infrared spectrum on silver film. ^{c}Assigned based on references 4 and 10. ^{d}FR = Fermi resonance and op = out of plane.

literature,[4,10] and the results are summarized in Table 1. In the neat TIR spectrum, the S-H stretching peak appeared at 2560 cm^{-1}, but the counterpart was completely absent in the RAIR spectrum. This indicates that $C_{12}AzoC_6SH$ molecule should chemisorb on silver as thiolate.

The distinct peaks at 1603, 1583, and 1498 cm^{-1} in Figure 1a can be assigned, respectively, to the benzene ring, 8a/b, 8a/b, and 19a modes. Their transition dipoles are all aligned

parallel to the long axis of the trans azobenzene moiety. It is noteworthy that the out-of-plane benzene ring 10a mode appears very distinctly at 843 cm^{-1} in the TIR spectrum of neat $C_{12}AzoC_6SH$ (Figure 1c), but its counterpart is hardly seen in the RAIR spectrum (Figure 1a). Recalling the infrared surface selection rule that vibrational modes whose transition dipole moments are directed normal to the metal substrate are exclusively infrared active, the above observation dictates that the azobenzene moiety should assume a nearly perpendicular orientation with respect to the underlying silver substrate. The fact that peaks at low frequencies, *i.e.*, <~1000 cm^{-1}, are stronger in the TIR spectrum but their counterparts are only vaguely seen in the RAIR spectrum can be similarly understood by referring to such an orientation.

The upright orientation of adsorbates on silver was further confirmed from ellipsometry measurements. In the case when the alkyl chains of $C_{12}AzoC_6S^-$ on Ag are fully extended with trans zigzag conformations, the thickness of the full-coverage monolayer is then estimated to be 33.8 Å, using the known bond lengths, bond angles, van der Waals atomic radii, and the approximate distance between the sulfur atom and the Ag surface (1.5 Å[11]). From a three-phase optical model, the ellipsometry parameters corresponded to a thickness of 35.3 ± 0.9 Å for the SAMs of $C_{12}AzoC_6S^-$ on Ag. Although we could not rule out the growth of the oxide overlayer and other ambient contamination, the presently obtained value is wholly consistent with the structure assumed from the RAIR experiments.

It is well-known that the peak positions of the symmetric as well as the antisymmetric CH$_2$ stretching vibrations can be used as a sensitive indicator of the ordering of the alkyl chains[1,10]; for all-trans zigzag conformations, the $\nu_s(CH_2)$ and $\nu_{as}(CH_2)$ modes are usually observed below 2850 and 2920 cm^{-1}, respectively. For the case of $C_{12}AzoC_6SH$, the $\nu_s(CH_2)$ and $\nu_{as}(CH_2)$ modes in the SAM state are observed at higher frequencies than those in the neat solid state (Figure 1 and Table 1). This suggests that the alkyl chains of $C_{12}AzoC_6S^-$ on silver are disordered, *i.e.*, the alkyl chains have protruded away from the azobenzene moieties in nearly all directions. It is conceivable that such a structural feature should occur from the specific chemisorption mode of sulfur on Ag as well as from the rather stronger packing ability of azobenzene moieties compared to that of the alkyl chains.

Most of the earlier azobenzene-based SAM studies employed azobenzene-terminated alkanethiols. For ω-ended azobenzenealkanethiols, highly ordered SAMs were exclusively established on Au(111) regardless of the length of the alkyl chains.[8,12] These results suggest that the azobenzene group, although not completely independent from Au(111) surface influence, should play a major role in dictating the overall monolayer structure. This implies that the interaction between the azobenzene groups is much stronger than that between the alkyl chains. As mentioned briefly in the Introduction, even though the azobenzene moiety is situated at the intermediate position of an alkyl chain, the azobenzene groups are supposed to condense to form a
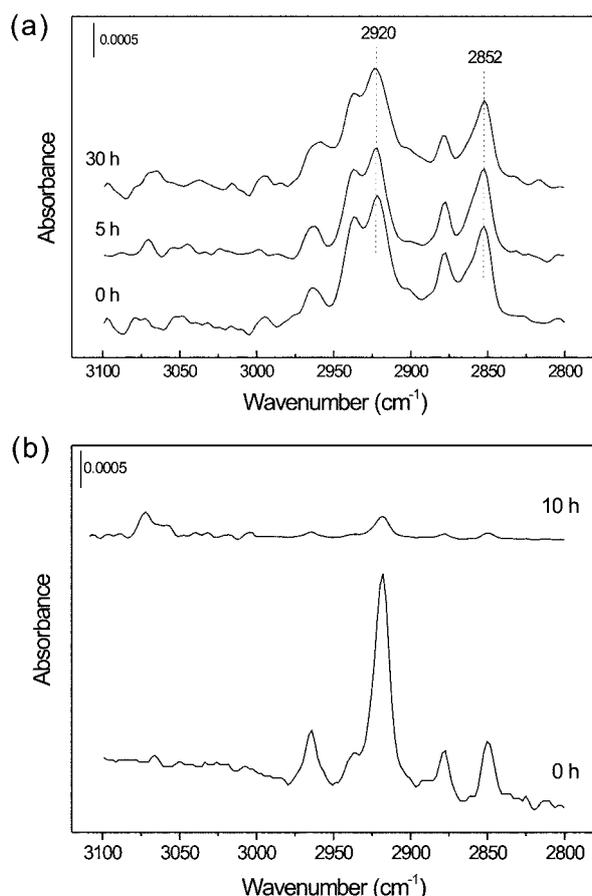
Figure 2. RAIR spectra of (a) $C_{12}AzoC_6SH$ and (b) ODT on silver. Spectra of each SAM were taken after dipping the monolayer films in 1 mM 1,2-BDT ethanol solution during the indicated times.

close-packed structure, with both the upper and lower alkyl chains tilting or bending to make this close approach possible. In the study of $C_{12}AzoC_6SH$ SAMs on Au(111), the AFM images actually observed showed that the dodecyl chains would be less closely packed than a pure alkanethiol SAM owing to a structural constraint imposed by the azobenzene moieties.[7] This is consistent with the RAIR spectral feature observed in the C-H stretching region. The RAIR spectrum of $C_{12}AzoC_6SH$ SAMs on Au(111) is reproduced in Figure 1b. The RAIR spectral data also dictated that the azobenzene moieties were directed to be normal with respect to the gold surface. As shown in Figures 1a and 1b, the overall spectral features of $C_{12}AzoC_6SH$ on Ag are almost same with those of $C_{12}AzoC_6SH$ on Au, indicating that the same structural model could also be adopted to explain the monolayer structure of $C_{12}AzoC_6SH$ on silver. This fact clearly shows that the packing of azobenzene moiety impose great structural constraint on SAMs regardless of type of substrates.

For assessing the stability of adsorbed $C_{12}AzoC_6SH$ on silver, a series of RAIR spectra were obtained after the immersion of monolayer film in an aromatic dithiol, *i.e.*, 1,2-benzenedithiol (1,2-BDT) ethanol solution. In general, thiol molecules in the SAMs are readily substituted with other

thiol molecules when the monolayer films are immersed in the solution of other thiol.[1] However, as shown in Figure 2a, the RAIR spectral features are hardly changed along the incubation time as indicated in the figure, indicating noticeable structural stability of the SAM. For comparison, same experiment has also been performed with simple alkanethiol monolayer on silver. Lower and upper spectra in Figure 2b are the RAIR spectra of octadecanethiol (ODT) SAM on Ag obtained before and after incubation in the 1,2-BDT solution for 10 h, respectively. In fact, when ODT monolayer was immersed in the 1,2-BDT solution, the RAIR spectral pattern varied enormously. For instance, as shown in Figure 2b, the intensity of RAIR peaks assignable to ODT was reduced by about 10 times and a new peak ascribed to 1,2-BDT distinctly appeared. Contrary to the case of $C_{12}AzoC_6SH$ SAMs, 1,2-BDT easily exchanged the ODT molecule because of its more favorable adsorption on silver surfaces. The enhanced stability of $C_{12}AzoC_6SH$ monolayer on Ag must be associated with the high inter-molecular forces between adsorbates arising from strong interactions between the azobenzene groups. The results of substitution experiments clearly indicate that the azobenzene moiety not only plays a dominant role in determining the monolayer structure but also greatly enhances the overall stability of SAMs on metal surfaces.

Conclusion

We have characterized the SAMs of $C_{12}AzoC_6SH$ on Ag surfaces by using RAIR spectroscopy and ellipsometry. The RAIR spectral data dictated that the molecule chemisorbed on silver very favorably as thiolate, with the azobenzene moiety being perpendicular to the silver surface. The alkyl chains were shown by RAIR spectroscopy to be disordered. These experimental data could be understood by the bundle model proposed previously for the SAMs on Au(111). The substitution experiment shows that the azobenzene moiety not only plays a crucial role in dictating the monolayer structure but also enormously enhances the structural stability. The stability is one of the key factors for the organic materials to be applied in the technologically relevant fields. From the application aspect, azobenzene group will thus be a promising organic moiety to be incorporated in self-assembled materials.

References

1. Ulman, A. *An Introduction to Ultrathin Organic Films from Langmuir-Blodgett to Self-Assembly*; Academic Press: San Diego, CA, 1991.
2. (a) Ulman, A. *Adv. Mater.* **1990**, *2*, 573. (b) Cha, S.-K. *Bull. Korean Chem. Soc.* **2004**, *25*, 786.
3. Ulman, A. *Chem. Rev.* **1996**, *96*, 1533.
4. (a) Liu, Z. F.; Hashimoto, K.; Fujishima, A. *Nature* **1990**, *347*,

658. (b) Wang, R.; Jiang, L.; Iyoda, T.; Tryk, D. A.; Hashimoto, K.; Fujishima, A. *Langmuir* **1996**, *12*, 2052. (c) Velez, M.; Mukhopadhyay, S.; Muzikante, I.; Matisova, G.; Vieira, S. *Langmuir* **1997**, *13*, 870.

5. Shnidman, Y.; Ulman, A.; Eilers, J. E. *Langmuir* **1993**, *9*, 1071.

6. Chang, S.-C.; Chai, I.; Tao, T.-T. *J. Am. Chem. Soc.* **1994**, *116*, 6792.

7. Han, S. W.; Kim, C. H.; Hong, S. H.; Chung, Y. K.; Kim, K. *Langmuir* **1999**, *15*, 1579.

8. Wolf, H.; Ringsdorf, H.; Delamarche, E.; Takami, T.; Kang, H.; Michel, B.; Gerber, C.; Jaschke, M.; Butt, H.-J.; Bamberg, E. *J. Phys. Chem.* **1995**, *99*, 7102.

9. Han, S. W.; Ha, T. H.; Kim, C. H.; Kim, K. *Langmuir* **1998**, *14*, 6113.

10. Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559.

11. Bain, C. D.; Troughton, E. B.; Tao, Y.-T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 321.

12. Caldwell, W. B.; Campbell, D. J.; Chen, K.; Herr, B. R.; Mirkin, C. A.; Malik, A.; Durbin, M. K.; Dutta, P.; Huang, K. G. *J. Am. Chem. Soc.* **1995**, *117*, 6071.