Molecular Arrangement in an Azobenzene-Terminated Self-Assembled Monolayer Film

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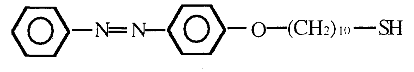
An azobenzene-functionalized material was used to perform comparative investigation of molecular arrangements in self-assembled monolayer film and in crystalline state. By the means of atomic force microscopy and absorption spectroscopy, a unique herringbone structure was revealed in the densely packed self-assembled monolayer film.

Self-assembly of monolayer films at solid surfaces provides a rational approach for fabricating interfaces with well-defined structure, long-term stability and desired surface property. The mostly investigated systems are alkane thiols chemisorbed onto gold substrates, which afford the essential understanding of the self-assembly system in various aspects. Considering the possibility for technological applications, surface functionalization of the self-assembled monolayer (SAM) film is of great importance. Azobenzene-based molecules are both photoactive and electrochemically active, and have been proved to be a potential medium for high-density recording elements and molecular switches.[1-5] In this work, a designed molecule by placing an azobenzene chromophore at the ω -end of the alkane thiol was used for self-assembling. As a frontier work of photoelectrochemical investigation, molecular alignment in the SAM film was examined by atomic force microscopy (AFM) as well as absorption spectroscopy.

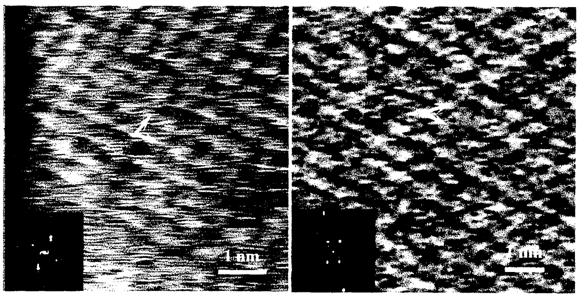
10-(4-(phenylazo)phenoxy)decyl-1-thiol (AzoC$_{10}$):



(AzoC$_{10}$)

was synthesized by Williamson ether formation from 4-hydroxyazobenzene, 1,10-dibromoalkane and one-pot thiol derivatization of ω-bromide group through isothiuronium salt.[6] A gold film with 15 nm of thickness was sputtered onto a quartz glass substrate. The gold deposited substrate was immersed into 1 mM AzoC$_{10}$ ethanol solution for 12 h to form uniform SAM. AzoC$_{10}$ microcrystals were obtained by spreading a drop of 1mM ethanol solution onto a quartz glass slide. After evaporation of ethanol solvent, rectangular microcrystals appeared under an optical microscope. High resolution AFM images were acquired on a commercial system (Seiko Instruments Inc., SPA300) using a Si_3N_4 cantilever with a 20 μm scanner in contact mode. Before each measurement, atomic resolution image of highly oriented pyrolytic graphite (HOPG) was obtained to check the system conditions. UV-visible spectra were taken on a Shimadzu UV-3101PC UV-visible spectrophotometer.

Morphology of the SAM film surface was directly observed by AFM. Highly ordered molecular assembly is presented in Figure 1(a). Two-dimensional fast Fourier transform (FFT) of the data (inset) displays a set of four spots, indicating an oblique[7] (or distorted hexagonal[8]) surface lattice which is typical for the azobenzene-containing film.[4,7-9] A unit cell with both of the in-plane vectors (arrow-pointed in Figure. 1(a)) of 4.36 ± 0.05 Å and the included angle of 85° is deduced from the FFT. For comparison, high resolution image of the AzoC$_{10}$ molecules on a microcrystal was also acquired to demonstrate the standard parameters based on the individual molecular arrangement in crystal state (Figure 1(b)). Its FFT (inset) shows a rectangular unit cell with the nearest neighbor spacings of 5.61 ± 0.05 Å and 5.05 ± 0.05 Å, respectively, and an angle of 57° between the two in-plane vectors. The AzoC$_{10}$ molecules in the SAM show shorter intermolecular spacings than in the microcrystal. It leads to an implausible conclusion that the molecules are more densely packed in the SAM than those in the crystal state. A reasonable interpretation is that the sufficient formation of the strong S-Au chemical bond forces the alkane chains densely packed, leaving limited intermolecular spacings to azobenzene moieties. Due to the larger cross section of the azobenzene moiety than that of the alkane chain, azobenzene moieties are supposed to form a herringbone structure (Figure 2(a)), in which the nearest neighbors are non-parallel, as the lowest energy configuration[9] in the SAM. On the contrary, the microcrystals were formed from a drop of ethanol solution. The spontaneous organization (Figure 2(b)) is achieved on the basis of only the nature of the AzoC$_{10}$ molecule. These may result in the different lattice parameters in the SAM and in the crystal state of the same molecule.



(a) (b)

Figure 1. Molecular resolution AFM images (5 nm × 5 nm) of AzoC$_{10}$ molecules in a SAM (a) and in a crystallite (b), respectively. Insets of both images show the corresponding Fourier transform patterns.

Another important feature for azobenzene containing materials is that, no matter in crystal state, SAM, or Langmuir-Blodgett film,[4] the molecularly resolved surface lattices show rectangular arrays independent of substrates. This implicates that the interaction among the azobenzene groups should govern the surface lattices of the self-organized systems.[7-9] As well known, the arrangement of the alkane thiols fairly relies on the substrate lattice due to the S-Au chemical bonding.[10] It was reported that the nearest neighbor spacing of octadecanethiol SAM onto a gold substrate is 5.1 Å,[8] which is even greater than the lattice parameter in the present azobenzene-containing SAM. These allow for a further inference that the arrangement of the terminal azobenzene moieties, i.e. the herringbone structure as presented in Figure 2(a), is hardly dependent on the arrangement of the alkane chains.

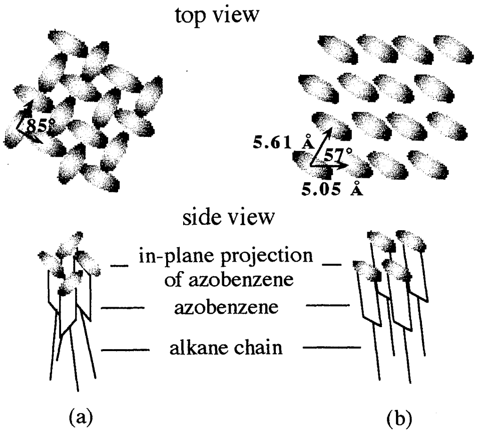


Figure 2. Schematic diagrams for the local packing of the $AzoC_{10}$ molecules in SAM (a) and in crystal state (b).

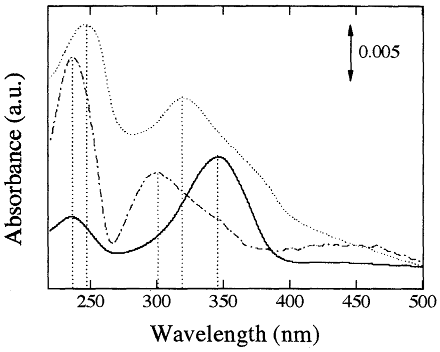


Figure 3. Absorption spectra of $AzoC_{10}$ molecules in 3×10^{-6} M ethanol solution (–), SAM (-·-), and microcrystals (···). The absorbance in ethanol solution shown here is 1/4 of the original.

As a further evidence of the herringbone structure, UV-visible spectroscopic study was accomplished to pursue the intermolecular interaction in the SAM. Figure 3 shows UV-visible spectra of $AzoC_{10}$ molecules in ethanol solution, microcrystals and SAM, respectively. The $AzoC_{10}$ molecules represent molecularly dispersed state in a dilute ethanol solution, exhibiting two intense bands at 236 nm and 347 nm, respectively. Little spectral shift was observed on the peak positions of both of the two bands in various solvents whose dielectric constants are ranged from 2 to 36. The 236 nm band and the 347 nm band are assigned to π-π^* transition with the electronic transition moment perpendicular and parallel to the long axis of the trans-azobenzene moiety, respectively.[11,12] The spectrum of $AzoC_{10}$ molecules in crystal state shows considerable shifts for both of the two bands. A 28 nm blue shift of the long wavelength band is observed, corresponding to an H aggregation, in which the long axes of the azobenzene chromophores are card-like packed with strong chromophoric interactions to enable these axes highly parallel to each other and oriented perpendicular to the film surface. The position of the short wavelength band also changed but red shifted by 12 nm relative to that in ethanol solution, revealing a J aggregation of the short axes of the azobenzene moieties. In the J aggregates, the short axes of the azobenzene moieties are suggested to be parallel to each other and oriented almost parallel to the film surface (brick-like packing).[11] The results coincide with the local packing model as shown in Figure 2(b).

In the SAM film, the long wavelength band shifts from 347 nm to 301 nm. Such a greater blue shift relative to the shift in the microcrystals is indicative of a closer chromophore packing, which is in good agreement with the shorter intermolecular spacings in the AFM image. No shift is observed for the short wavelength band, indicating that the short axes of the azobenzene moieties might be lack of order in the SAM. The lack of aggregation of the short axes of the azobenzene moieties confirms the non-parallel conformation of the neighboring short axes in the herringbone structure. According to the above observations, the azobenzene groups are intensively fixed in the SAM. The extraordinarily dense packing requires a herringbone arrangement, i.e. parallel packing of the long axes of the azobenzene chromophores and mutually non-parallel conformation of the short axes, to minimize the entire lattice energy.[9] As has been noted, the herringbone structure is in terms of the terminal azobenzene moieties and is uncorrelated to the alkane chains. The alkane chain, as a bridge between the azobenzene chromophore and the thiol, is to some extent disordered, as schematically illustrated in Figure 2(a). Fourier transform infrared (FTIR) spectroscopic study also suggests that the alkane chains involve twisted and bent conformations. When critical size of such assembly is reached, domain boundary should be formed.[8]

As a summary, a herringbone structure in the $AzoC_{10}$ SAM film was deduced from the experimental data of AFM and UV-visible spectra. In the film, the surface lattice was determined by the alignment of azobenzene terminal groups independent of both the alkane chains and the underlying substrate.

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References and Notes

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