Adsorption of Azothiophene Dye Having an N-Bridging Bidentate Tail Group on Gold

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The novel azothiophene derivatives [AT-di(C₈Sac) (n = 6 and 12)], an azo linkage (N≡N) that bridges one phenyl ring with an N-bridging dialkylthioacetate tail and one thiophene ring, are synthesized and characterized. The azothiophene derivatives substituted with electron-withdrawing groups are blue in color, exhibit a bathochromic shift of a longer wavelength, and are electrochemically active. The formation and characterization of AT-di(C₈Sac) SAMs with a bidentate tail group of the N-bridging dialkylthioacetate have been studied by surface sensitive techniques such as grazing angle Fourier transform infrared (FT-IR), a quartz crystal microbalance (QCM), spectroscopic ellipsometry, X-ray photoelectron spectroscopy (XPS), and cyclic voltammetry (CV). It has been shown that the adsorption reaction of the thiophene group is almost spontaneous and the N-bridging dialkylthioacetate SAMs with longer methylene length have a packing density higher than that with a shorter methylene length. However, the sulfur tethers of the N-bridging dialkylthioacetate show incomplete binding of sulfur atoms in AT-di(C₈Sac) SAMs.

Introduction

Recently, in the fields of nanoscience and nanotechnology, functional molecular materials have been applied to magnetic storage media, electronic and optical devices, and bioanalytical devices using self-assembled monolayers (SAMs). Organic SAMs have been intensively studied as a powerful means of surface modification and functionalization with molecular-level control. Of particular note, the chemical functionality has a crucial influence on the surface properties, both structurally and electronically. It was already shown that organic SAMs can tune the electronic properties of the interface by modifying the adsorbate molecules with a dipole moment.† Furthermore, organic SAMs with electrical and optical properties are of great interest for device miniaturization, reduced cost, and lighter and more efficient devices.

Azo derivatives are photoactive isomers and are also electrochemically active. Because of their simple structure and reversible trans–cis isomerization under photoillumination,2,3 they have been widely studied as candidates for molecular switches or storage media. Thin films of these materials can be used for holographic and digital storage of information.4–8 The absorption characteristic of azobenzene derivatives can be easily controlled by the addition of polar groups on the azo molecule.4,9,10 It has been noted that azo dyes with one phenyl ring and a thiazole unit or electron donor and acceptor groups give lower excitation energy than azobenzene.10

In this work, we introduce azothiophene derivatives having a thiophene ring, including two nitro groups to the azo moiety for a lower excitation energy than azobenzene and a bridging amine group. Azothiophene chromophores with strong nonlinear optical (NLO) activity. It has been suggested on the basis of both experimental results and theoretical considerations that the azothiophene chromophores with strong electron donor and acceptor groups possess substantially large polarizabilities and a fairly large dipole moment.11 Multidentate SAMs are also a good choice because of their enhanced stability for exchange and desorption and better control of molecular orientation. It was reported that the stabilization (or tridentate) SAMs was superior to that of single dentate SAMs.12

These azothiophene derivatives, an azo linkage (N≡N) that bridges one phenyl ring with an N-bridging dialkylthioacetate tail and one thiophene ring, are synthesized by our previously reported method.13 We name these azothiophene derivatives \( \text{AT-di(C}_8\text{Sac)} \) (n = 6 and 12).

azothiophene-di(C$_2$SAc), AT-di(C$_2$SAc) ($n = 6$ or 12) (Figure 1). The azothiophene derivatives substituted with electron-withdrawing groups are blue in color, show a bathochromic shift$^{12}$ of a longer wavelength shift, and are electrochemically active. Furthermore, it was reported that the sulfur atom of the thiophene ring plays a decisive role by acting as an efficient electron sink, based on valence band theory.$^{9,14}$ These azothiophene derivatives give rise to intense optical absorption and may have potential applications in molecular-based information storage and electronic devices.$^{15}$ Thus, this bidentate structure with an N-bridging dialkylthioacetate tail and a single electro-active group has some advantages, including being thermally more robust than monodentate SAMs on gold.$^{16}$

Here, we report the formation and characterization of the AT-di(C$_n$SAc) SAMs with an N-bridging dialkylthioacetate by using surface sensitive techniques, including grazing angle Fourier transform infrared (FT-IR) spectroscopy, a quartz crystal microbalance (QCM), spectroscopic ellipsometry, X-ray photoelectron spectroscopy (XPS), and cyclic voltammetry (CV). The surface coverage, film thickness, and chemical composition of the molecular layer were determined by QCM and CV, spectroscopic ellipsometry, and XPS, respectively.

The SAMs of N-bridging dialkylthioacetate with two binding sites are expected to bind in a different manner and thus exhibit properties different from those of mono alkanethiols that have only one binding site. This lends insight into the interfacial structure and properties of N-bridging dialkylthioacetate groups on the structure of the SAMs and the electrochemical behaviors of the azothiophene redox center in the SAMs.

Experimental Section

Materials. The synthesis of azothiophene derivatives [AT-di(C$_n$SAc) ($n = 6$ and 12)] is reported in part 1 of the Supporting Information. AT-di(CH$_3$)SAc and AT-di([CH$_2$]$_n$)SAc are abbreviated AT-diHT and AT-diDT, respectively. Potassium ferrocyanide(III) [K$_3$[Fe(CN)$_6$], >99%, Aldrich], ethanol (99.5%, HPLC-grade, Aldrich), sulfuric acid (H$_2$SO$_4$, electronic-grade), hydrogen peroxide (H$_2$O$_2$, electronic-grade), and DMF (99.9%, HPLC-grade, Aldrich) were used without further purification.

Before chemisorption, the gold film was cleaned with piranha solution using a QCM. The QCM is very sensitive to mass changes and has some advantages, including being thermally more robust than monodentate SAMs on gold.$^{16}$

Preparation of AT-di(C$_n$SAc) Monolayers. Monolayers of AT-di(C$_n$SAc) were prepared by direct formation through the thiocarboxylic group functionalization containing a long bidentate tail group on a gold surface (Scheme 1). The AT-di(C$_n$SAc) monolayer was prepared by soaking the clean gold films in the solution containing only 3 mM AT-di(C$_n$SAc) without a catalyst of H$_2$SO$_4$ in DMF for 24 h. The films were removed from solution, via a thorough rinse with DMF and subsequent drying with a stream of nitrogen gas. The modified films were immediately used in all measurements.

Results and Discussion

Adsorption Kinetics. First, the tendencies of the self-assembling process of AT-di(C$_n$SAc) were observed in a pure DMF solution using a QCM. The QCM is very sensitive to mass changes as small as several nanograms.$^{18}$ The sensitivity to mass change is determined by the crystal resonant frequency, according to the Sauerbrey equation.$^{19}$ Figure 2 shows the QCM results (solid line) for the bonding dialkylthioacetate tail group to the gold surface as a thiolate$^{20}$ and the Langmuir fitting curve (dashed line) for the adsorption kinetics in a 0.1 mM AT-di(C$_n$SAc) solution. When the frequency change was stabilized within ±0.1 Hz with time for ca. 7 min, the AT-di(C$_n$SAc) solution was added and the frequency data were obtained. The frequency rapidly decreased immediately after the sample was added, followed by a gradual decrease. The adsorption kinetics was observed by monitoring the frequency decrease, which is equivalent to the increase in mass on the gold surface. From the frequency change (Δƒ), we estimate the surface density of AT-di(C$_n$SAc). The total frequency change was

Figure 1. Structure of AT-di(C$_n$SAc).


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Scheme 1. (A) Direct Immobilization through the N-Bridging Dialkylthioacetate Group of AT-di(CnSAc) on a Gold Surface and (B) Energy-Minimized Geometry

7.3 Hz for AT-diHT and 13.8 Hz for AT-diDT, which corresponds to $5.4 \times 10^{-11}$ and $9.6 \times 10^{-11}$ mol cm$^{-2}$, respectively. If the roughness factor of the gold surface was 1.2, the coverage would be $4.5 \times 10^{-11}$ and $8.0 \times 10^{-11}$ mol cm$^{-2}$ for AT-diHT and AT-diDT, respectively. The surface density of AT-diDT is higher than that of AT-diHT.

From the QCM results, the adsorption kinetics can also be fitted with the adsorption model of the Langmuir isotherm, which leads to

$$\theta = \frac{C[1 - \exp\left(-\frac{K}{N_0}(C+K)t\right)]}{C+K} \quad (1)$$

where $\theta$ is the fraction of the monolayer coverage and $C$ is the bulk concentration of the solution in molarity. The adsorption equilibrium constant $K = k_d/k_a$, where $k_d$ and $k_a$ are the desorption and adsorption rate constants, respectively. $N_0$ is the surface adsorbent concentration at full coverage, and $t$ is the adsorption time. Equation 1 can be simplified by the substitution $k_{obs} = (k_a/N_0)C + k_d$ and $K' = C/(C+K)$, giving

$$\theta = K'[1 - \exp\left(-k_{obs}t\right)] \quad (2)$$

The curves were fitted by an exponential decay function, and the dashed line in Figure 2 shows a fitting curve according to eq 2. We obtained the $k_{obs}$ values by fitting the raw data to eq 2. Then, by the linear regression fit of $k_{obs}$ versus the concentration of AT-di(CnSAc) (inset of Figure 2), the values of $k_a$ and $k_d$ were obtained. The free energy of adsorption of the AT-di(CnSAc) monolayer is obtained from $K (\Delta G = RT \ln K)$. Table 1 summarizes the resulting Langmuir fits and the Gibbs energies of adsorption. The adsorption of AT-di(CnSAc) on the gold surface is an equilibrium system since $k_d$ is greater than zero. This adsorption reaction is almost spontaneous according to $\Delta G$ values. This kinetic data are similar to the values obtained from monothiol compounds having a bulky terminal group. Our data provide direct evidence that the thioacetate-gold system is an equilibrium system.

Cyclic Voltammograms of AT-di(CnSAc) SAM. The AT-di(CnSAc) with an N-bridging bidentate dialkylthioacetate group spontaneously forms a self-assembled monolayer on gold, and it exhibits an electrochemically active reaction with unique reduction-oxidation behavior. The CVs of the AT-di(CnSAc) SAM are shown in Figure 3, and the electrochemical data are summarized in Table 2. The CVs shows a reversible redox peak at $\sim 0.24$ V. The ratio of the redox peak current is $1.0$, and the peak separation ($\Delta E_p = E_{pa} - E_{pc} = 20-30$ mV) is considerably smaller than the reported value of azobenzene SAM with a monoalkylthiol group. The small peak separation is a sign of reversibility of the faradaic process with fast electron transfer between the redox center and the electrode surface. The $\Delta E_p$ of AT-diDT SAM with a long alkyl chain is smaller than that of the AT-diHT SAM, which means packed and ordered SAMs for AT-diDT. The $\Delta E_{pwhm}$ provides information about the environments and interaction of the redox center in the AT-di(CnSAc) SAMs. The $\Delta E_{pwhm}$ value of AT-diHT SAMs is larger than those of AT-diDT SAMs and the theoretical value of 90.6/n mV, where $n$ is the mole number of electrons transferred. It is indicative of a higher degree of organization in the monolayer, whereas smaller values indicate attractive or stabilizing interactions. Thus, the broad wave of the AT-diHT SAM can be understood as a higher degree of organization, the change in structure, and the environment of the monolayer.

The peak currents increased quite linearly ($R^2 = 0.999$) with an increasing scan rate (inset of Figure 3 A,B), a typical characteristic curve of immobilized species. This strongly supports the possibility that the AT-di(CnSAc) compounds are immobilized on the

gold surface. The surface coverage of the AT-di(CₙSAc) SAM was then determined by integration of the reduction peak current of the CVs. Considering the roughness factor (1.1), the coverage value for AT-diHT SAM was 3.1 × 10⁻¹¹ mol/cm² and the value for AT-diDT was 1.3 × 10⁻¹⁰ mol/cm². The coverage of AT-diDT SAM shows a value higher than that of AT-diHT SAM. These coverage values correspond to the surface areas (602 and 129 Å²) for immobilized AT-diHT and AT-diDT, respectively. That is, AT-diDT has a more closely packed SAM structure than AT-diHT on gold. The surface coverage in QCM and CV results shows a slight difference, although absolute values of the CV and QCM results cannot be compared. The difference between the CV and QCM results can be understood by considering the sources of possible errors in the respective measurements. The CV technique is sensitive to only electroactive molecules bound to the metal surface to allow electron transfer. The QCM is used to monitor adhesion of molecules on the gold electrode surface in real time, and the QCM experiments are complicated by the unknown solvation state of the adsorbed species, density changes in the liquid phase, and the possibility of trapping of the solution in the adsorbed film.

The surface coverage of AT-diHT with N-bridging bidentate groups is substantially lower than the coverage observed for azobenzene hexanethiol with a monoalkylthiol group (1.7 × 10⁻¹⁰ mol/cm²).²⁵ This implies that the structure of AT-diHT is hindered for a closely packed SAM due to the N-bridging dialkylthioacetate group.

We next observed the response of Fe(CN₆)₃⁻/₄⁻ to obtain the blocking properties of these SAMs. Figure 3C shows the cyclic voltammogram for 0.4 mM Fe(CN₆)₃⁻/₄⁻ in 0.1 M phosphate buffer and (C) 0.5 mM Fe(CN)₆³⁻⁻ in 0.1 M phosphate buffer at 0.1 V/s.

Table 2. CV Data for AT-di(CₙSAc) SAM on Gold in 0.1 M Phosphate Buffer at 0.1 V/s

<table>
<thead>
<tr>
<th>SAM</th>
<th>Eᵖ (V)</th>
<th>ΔE (mV)</th>
<th>ΔEᶠʷˢʰᵐ (mV)</th>
<th>Γ (mol/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AT-diHT</td>
<td>−0.240</td>
<td>30</td>
<td>70</td>
<td>3.1 × 10⁻¹¹</td>
</tr>
<tr>
<td>AT-diDT</td>
<td>−0.240</td>
<td>20</td>
<td>56</td>
<td>1.3 × 10⁻¹⁰</td>
</tr>
</tbody>
</table>

modified electrode with AT-diHT SAM, the redox response of Fe(CN)₆³⁻/⁴⁻ was severely hindered and the current density was 5-fold smaller than that on the bare gold electrode. This indicates that the packing density of AT-diDT SAMs is higher than that of AT-diHT SAMs. From these results, it is found that the N-bridging dialkylthioacetate SAMs with a longer methylene length have a packing density higher than that with a shorter methylene length, and this is in agreement with the results of monoalkylthiol SAMs.²¹ In the monoalkylthiol SAM, the self-assembled molecule is defined by three parts, the headgroup, the space group of alkyl chain, and the terminal group.²² It was generally known that the interplay among the three parts within the monoalkylthiol molecule determines the order and packing density of SAM and the van der Waals forces between these methylene (-CH₂-) chains provide a driving force for the self-assembly.²³ It has been reported that a chain length of >10 tends to form more ordered SAMs.²⁶ In the case of AT-diHT and AT-diDT, the headgroup and the terminal group have the same structure as the N-bridging dialkylthioacetate group and thiophene ring with the NO₂ group. The only difference is the length based on the number of the methylenes. Therefore, the AT-diDT with a longer methylene length leads to higher ordered and packing density, which is in reasonable agreement with the surface coverage obtained with QCM and CV. A similar feature was previously observed for Fe(CO(CH₂)₅SH) and Fe[CO(CH₂)₅SH]₂ SAMs.²⁷

**Thickness and Wettability.** Spectroscopic ellipsometry is used to determine the thickness of the AT-di(C₆SAc) SAM. From the film thickness, the quality and the degree of surface coverage of the SAM can be estimated. The refractive index (n) value was between 1.0 and 1.5 over a wavelength range of 400–800 nm, and the absorption band near 640 nm in the extinction (k) curve was attributed to the maximum electronic transition of AT-di(C₆SAc) (part IV of the Supporting Information). The curve of extinction coefficient k is similar to the absorption spectrum, and the λmax of AT-di(C₆SAc) in THF is at 636 nm. This characteristic absorption band is mainly attributed to the π → π* transition of the conjugated chromophore containing an N=N group and a thiophene and benzene ring. The thicknesses were approximately 1.12 ± 0.08 and 2.61 ± 0.05 nm for AT-diHT and AT-diDT SAMs, respectively. The thickness value of AT-diHT SAM is ~1 nm lower than the estimated molecular length (Scheme 1B), and that of the AT-diDT SAM is similar to the estimated value. Molecular length was estimated using Cambridge Scientific Chem3D. On the basis of the molecular structure of the lowest-energy configuration, the molecular length is the distance from the terminal NO₂ group of the thiophene ring to the S plus the Au=S bond length (0.23 nm). The smaller thickness of the AT-diHT SAM would be expected for a loosely packed SAM. This also suggests that the AT-diDT SAM with a longer methylene length has a packing density higher than that with a shorter methylene length.

The wetting behavior is one of the monolayer properties and yields information about the ordering of the monolayer. The water contact angle (WCA) for bare gold was 53.7 ± 1.3°, and the angles for AT-diHT and AT-diDT SAM on gold were 72.5 ± 1.1° and 77.1 ± 0.2°, respectively. These values are quite similar to the value of the NO₂-terminated surface (θ = 75 ± 3°).²⁸

**Grazing Angle FT-IR.** The FT-IR spectra for the AT-di(C₆SAc) SAM on gold and bulk AT-di(C₆SAc) film (film on NaCl, transmission) are shown in Figure 4. Asymmetric and symmetric NO₂ stretching bands of the thiophene ring are observed at 1520 and 1327 cm⁻¹ for AT-diHT and AT-diDT SAMs, respectively. The aromatic C=C-C stretching bands (ν(C=C=) benzene and the thiophene ring are observed near 1602 and 1548 cm⁻¹ for AT-diHT SAM and 1602 and 1547 cm⁻¹ for AT-diDT SAM, respectively, and the benzene ring–N-dialkyl stretching is observed at 1126 cm⁻¹ for AT-diHT and AT-diDT SAM. The C=H stretching bands of the AT-diHT SAM are lower in intensity than that of the AT-diDT SAM. Two peaks in the C–H stretching region of the AT-diHT SAM, 2929 and 2857 cm⁻¹, are characteristic asymmetric and symmetric vibrations, respectively.

In general, the position and intensity of the C–H stretching bands (νasym-C=H and νsym-C=H) are sensitive to the phase state and packing density of the methylene chain in organic thin films.²⁹–³² In the AT-diHT SAM, the intensity of the C–H stretching bands is considerably lower than that of the AT-diDT SAM. The difference in this peak intensity could reflect different tilted orientations for the methylene chains or different amounts of the methylene chains on the gold surface. We infer hereby that the difference in the intensity of the C–H stretching bands indicates different amounts of methylene chains of AT-diHT and AT-diDT, and the AT-diHT molecule forms the more disordered SAM than the AT-diDT molecule. The frequencies of the antisymmetric and symmetric bands of methylene are known to be strongly influenced by the crystallinity and packing density of the organic monolayer.²¹,³² The wavenumber value for

![Figure 4](https://example.com/figure4.png)

**Figure 4.** Grazing angle FT-IR spectra of (A) the AT-diHT SAM and (B) the AT-diDT SAM on a gold surface.

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the C–H stretching of AT-diDT SAM is much higher than that of a well-packed monoalkanethiol monolayer (2920 and 2850 cm⁻¹). This observation shows disorder in the conformational structure of the methylene chains in the SAM. It is assumed that the N-bridging dialkylthioacetate group prevents the closest packing, and considerable space exists around the methylene chains of the AT-di(C₈SAc) SAM. Therefore, these results suggest that the AT-di(C₈SAc) SAM generates poorly ordered films.

In both AT-diHT and AT-diDT SAMs, the C=O peak is observed at 1695 cm⁻¹, which can be attributed to the carbonyl vibration (νC=O) of the unbound thioacetate group. This is a residual signal for the carbonyl vibration of S-acyl-protected molecules after monolayer formation. This band is a sign for unbound sulfurs of their unreacted thioacetate group and indicates that the unbound sulfur of the AT-di(C₈SAc) SAM was present after monolayer formation.

XPS Investigations. XPS can also provide important information about the quality and structure of SAMs. To characterize the bonding state of the AT-di(C₈SAc) SAM with an N-bridging dialkylthioacetate group on a gold surface in greater detail, XPS spectra of the AT-di(C₈SAc) SAMs were examined and the spectra of the N 1s and S 2p core levels are shown in Figure 5.

The N 1s spectrum shows two signals at 400 and 406 eV for N=N- and -N=C- parts of the benzene ring and the NO₂ part of the thioephene ring, respectively. The oxidized nitrogen occurs at a higher N 1s binding energy, and these values are in good agreement with the reported results for nitroazobenzene.

The S 2p region can provide evidence of bond formation between the sulfurs of the dialkylthioacetate tail group and the gold surface. From the reported data, the binding energy for bound sulfur on gold is known to be 162 and 163.2 eV with an intensity ratio of 2:1.35,36 and the binding energy for unbound sulfur on gold is known to be between 163 and 164 eV. Oxidized sulfur is known to appear above 165 eV. When the data are fit, the AT-di(C₈SAc) SAMs with an N-bridging dialkylthioacetate group contains two sulfur forms, bound and unbound, S 2p peaks were indicated at 162.2 and 163.1 eV for the AT-diHT SAM and 162.1 and 163.3 eV for the AT-diDT SAM. On the basis of the reported data, the peak at ~162 eV is assigned to typical S-Au species and the peak at ~163 eV is assigned to the unbound sulfur. SAMs on gold through disulfide and multipodal thiol have also reported the unbound sulfur peak at 163.5 or 164 eV.37 Thus, the unbound sulfur can likely be attributed to the unreacted thioacetate of the tail group.

From the clear XPS and FT-IR evidence, unbound thioacetate species are present in the AT-di(C₈SAc) SAM and the sulfur tethers of the N-bridging dialkylthioacetate show incomplete binding of sulfur atoms.

Conclusion

We have synthesized and described the preparation and characterization of a new azothiophene with an N-bridging dialkylthioacetate anchor group. These AT-di(C₈SAc) molecules form electrochemically detectable SAMs. The N-bridging bidentate SAM with a longer methylene length has a packing density higher than that with a shorter methylene length. As can be expected on the basis of the molecular structure of the bidentate, however, the surface coverage density is smaller than the reported data for a monoalkyl azobenzene SAM. The structure of AT-di(C₈SAc) molecules prevents close packing, and as a result, empty space exists around the methylene chains in their SAMs. In the AT-di(C₈SAc) SAMs, unbound thioacetate species are present and the sulfur tethers of the N-bridging dialkylthioacetate show incomplete binding of sulfur atoms.

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Supporting Information Available: Detailed syntheses of the new AT-di(C₈SAc) compounds, information about quartz crystals, and ellipsometric spectra of the AT-diDT SAM on gold. This material is available free of charge via the Internet at http://pubs.acs.org.