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A Self-Assembled Monolayer of a Thiophene Monomer

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ABSTRACT: Polymerizable thiophene containing a thiol group, (3-thienylethyl)-11-mercaptoundecanoate, was deposited on a gold surface. The thiophene monomer formed a self-assembled monolayer (SAM). By X-ray photoelectron spectroscopy, the structure of the SAM was characterized. The molecules were adsorbed at the thiol group with end-on configuration.

Keywords: a self-assembled monolayer; thiols; polythiophene; X-ray photoelectron spectroscopy

INTRODUCTION

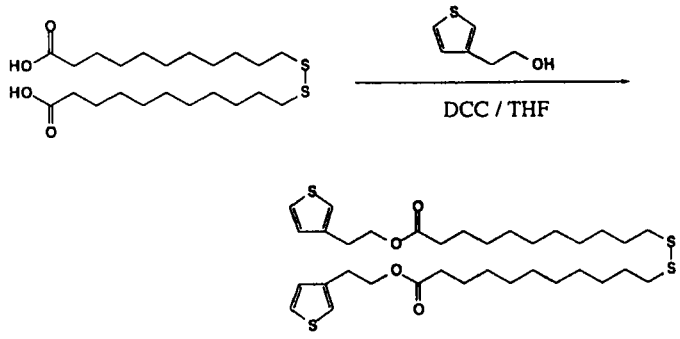
π-Conjugated polymers are very interesting materials of unique electrical and optical properties due to π-electrons delocalized along their main chains. These polymers can transport carriers and can potentially be applied for molecular devices as "molecular wires".[1] For these applications, fine polymerization without defects in their primary structures and controlling the orientation of the polymers are required. Molecular beam epitaxy (MBE) and the Langmuir Blodgett (LB) technique have been investigated to obtain ordered structure. Thiol derivatives form self-assembled monolayers (SAM's) on a gold surface. Their structure and the mechanism of the formation of SAM's have been investigated by atomic force microscopy (AFM), scanning tunneling microscopy (STM), and X-ray photoelectron spectroscopy (XPS). By oxidation, thiophene is polymerized to π-conjugated polymer, polythiophene with 2,5-linkages. It is promising to form SAM's of polythiophene by using thiol derivatives with thiophene rings as monomers. Tolbert *et al.* electropolymerized a thiophene thiol.[2] Nozoye *et al.* studied on the structure of α,ω-bis(mercaptomethylthiophene)alkane derivatives by

STM.[3] They observed two kinds of structures: one dimensional rows and a two dimensional honeycomb structure. As Whitesides *et al.* did[4], they also concluded that the molecules was adsorbed with end-on configuration in each structures. Garnier *et al.* fabricated SAM's of thiol-functionalized oligothiophenes on platinum electrodes.[5] They estimated the density of molecules by measuring charges for oxidation of the SAM's and proposed the structures of the SAM's.

However, these thiophene derivatives cannot be polymerized and cannot be applied to the molecular devices directly, because the derivatives have the substituents at the 3-positions of thiophene rings. Thus, in this study we synthesized a polymerizable thiophene monomer with a thiol group, and successfully fabricated an SAM. The structure of the SAM was characterized by XPS.

EXPERIMENTAL

Polycrystalline thin films of gold (300 nm) were prepared by thermal evaporation of gold on a glass substrate at the base pressure less than 10^{-6} Torr. As the thiophene monomer, a dithio derivative with a thiophene ring was synthesized by the coupling reaction of 11,11'-dithiodiundecanoic acid and 3-thienylethanol using *N,N'*-dicyclohexyldicarbodiimide (DCC) as shown in SCHEME I. The obtained crude product was purified by column chromatography (eluent: toluene) and recrystallization from hexane.



SCHEME I. Synthesis of the monomer.

The thiophene monomer was dissolved in ethanol at a concentration of 1 mmol. The gold substrate was exposed to the ethanol solution for 24 h. After the deposition of the SAM, the plates were rinsed with ethanol completely. As a reference, octadecanethiol (ODT) SAM was used. ODT purified by recrystallization was used. The characterization of the SAM was carried out by XPS (ESCALABB22Di), using a MgK_{α} line. More than 50 scans were averaged to increase the signal to noise (S/N) ratio.

RESULTS AND DISCUSSIONS

FIGUREs 1(a) and (b) show the XPS spectra in the C_{1s} region for the SAM's of ODT and the thiophene monomer, respectively. Both spectra have the main peak at around 287 eV and a shoulder at around 284 eV. Table I summarizes the positions and the intensity of the peaks. In the spectrum of the ODT SAM, the shoulder is assigned to the carbon atom attached to the thiol group and the main peak to other methylene and methyl carbons. In the monolayer of the thiophene monomer, the shoulder is stronger than that of the ODT spectrum. Usually, the peak position of the carbon attached to atoms with high electronegativity is shifted to higher energy.[6] In the spectrum thiophene monomer, the shoulder may include the signals of the -OCH_2- and C=O groups. The main peak is attributed to the other methylene and thiophene ring carbons.

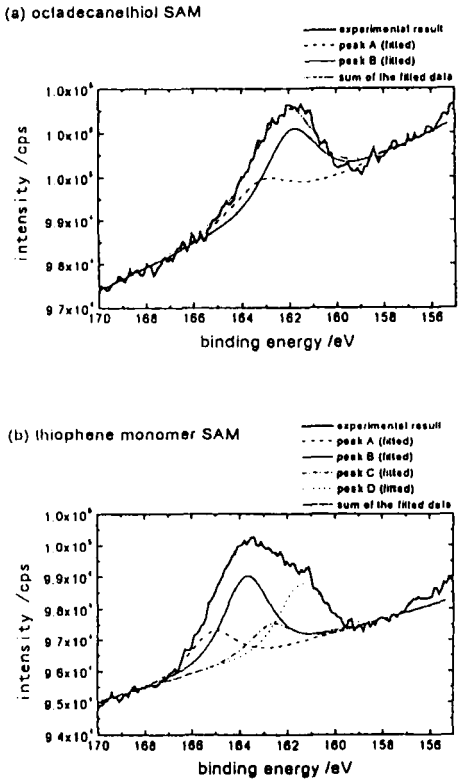


FIGURE 2. The XPS spectra in the S_{2p} region for the SAM's of ODT (a) and the thiophene monomer (b).

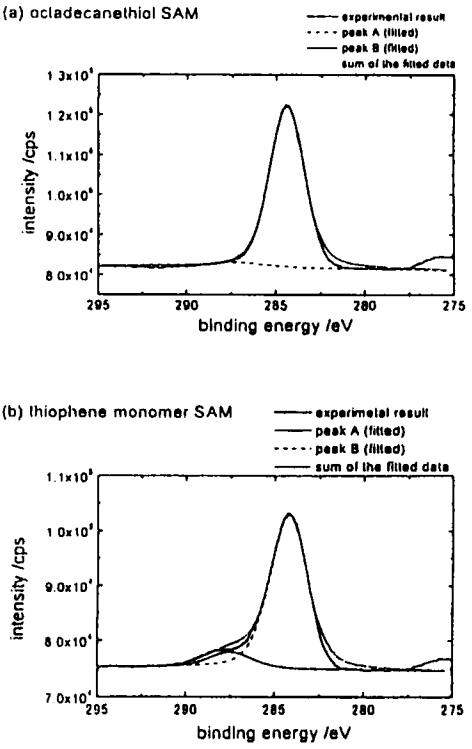


FIGURE 1. The XPS spectra in the C_{1s} region for the SAM's of ODT (a) and the thiophene monomer (b).

TABLE I. The intensity of the peaks in the C_{1s} XPS spectra. [a)]

peak	ODT	Thiophene Monomer
A	0.057	0.095
(chemical shift)	(284 eV)	(284 eV)
B	1.0	0.73
(chemical shift)	(287 eV)	(288 eV)

a) Normalized by the intensity of the main peak for ODT.

As the monomer has two kinds of sulfur atoms, both atoms have possibility to be adsorbed on the gold surface. FIGUREs 2 (a) and (b) show the XPS spectra in the S_{2p} region for the ODT and thiophene monomer SAM's, respectively. The obtained results are summarized in Tables II and III. The spectrum of ODT has two peaks, $S_{2p1/2}$ at 163.2 eV and $S_{2p3/2}$ at 161.9 eV, which are shifted to lower energy than those of the free thiophene.

TABLE II. The intensity of the peaks in the S_{2p} XPS spectrum for ODT.[a)]

peak	chemical shift (eV)	intensity	attribution
A	163.2	0.57	$S_{2p1/2}$
B	161.9	1.0	$S_{2p3/2}$

a) Normalized by the intensity of the peak B.

TABLE III. The intensity of the peaks in the S_{2p} XPS spectrum for the thiophene monomer[a)]

peak	chemical shift (eV)	intensity	attribution
A	165.0	0.78	$S_{2p1/2}$
B	163.7	1.62	$S_{2p3/2}$
C	162.6	0.50	$S_{2p1/2}$
D	161.4	1.0	$S_{2p3/2}$

a) Normalized by the intensity of the peak D.

These values agree with the reported ones.[7] In the monomer spectrum for the thiol group, the peaks , $S_{2p1/2}$ at 162.6 eV and $S_{2p3/2}$ at 161.4 eV, are also observed. The chemical shifts of these peaks are almost same as those of the ODT spectrum, suggesting that the thiol groups are attached to the gold surface in the monomer monolayer. The monomer spectrum has two other peaks, $S_{2p1/2}$ at 165.0 eV and $S_{2p3/2}$ at 163.7 eV, which is attributed to the sulfur atom in the thiophene ring. The intensity of these signals are smaller than those of the peaks for thiol because of the escape depth of the photoelectron due to the presence of the monolayer structure. In other words,

the sulfur atom of the thiol group is attached to the gold surface, while the sulfur of the thiophene is free at the opposite surface side.

CONCLUSION

We have synthesized a thiol terminated thiophene and deposited on the gold surface. Comparison of the XPS spectra of the monolayer with that of an ODT SAM lead to conclusion that the thiophene monomer was absorbed as a thiolate while the thiophene ring is located at the surface. However, the bulky thiophene rings and the flexible ester groups may prevent the monolayer from forming densely-packed structure, compared with the ODT SAM.

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REFERENCES

[1] *Molecular Electronic Devices II*; Carter, F. L., Ed.; Marcel Dekker: New York, 1987.
[2] Kowalik, J.; Tolbert, L.; Ding, Y.; Bottomley, L. A.; Vogt, K.; Kohl, P.; *Synth. Met.* **1993**, *55-57*, 1171.
[3] Nakamura, T.; Kondoh, H.; Matsumoto, M.; Nozoye, H. *Langmuir* **1996**, *12*, 5977.
[4] Tour, J. M.; Jones, L., II; Pearson , D. L.; Lamba, J. J. S.; Burgin, T. P.; Whitesides, G. M.; Allara, D. L.; Parikh, A. N.; Atre, S. V. *J. Am. Chem. Soc.* **1995**, *117*, 9529.
[5] Michalitsch, R.; Lang, P.; Yassar, A.; Nauer, G.; Garnier, F. Adv. Mater. **1997**, *9*, 321.
[6] *X-ray Photoelectron Spectroscopy* ; Holm, R.; (In *Analysis of Organic and Biological Surfaces*; Echlin, P. ed., Chapter 2 pp.37-72, John Wiley and Sons,
Inc. (1984) Toronto)
[7] Nuzzo, R. G.; Zegarski, B. R.; Dubois, L. H. *J. Am. Chem. Soc.* **1987**, *109*, 733.
Nuzzo, R. G.; Fusco, F. A.; Allara, D. L. *J. Am. Chem. Soc.* **1987**, *109* , 2358.