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Self-Assembled Alkanethiol Monolayers

Introduction

Highly stable molecular layers prepared by the self-assembling method have been applied for the development of various detection systems such as electrochemical detection, optical detection, and so on. Self-assembled monolayers (SAMs) are crystalline chemisorbed organic single layers formed on a solid substrate by spontaneous organization of molecules. Thiol compounds and gold is one of the well-established combinations[1)]. In addition, carboxylic acids, organosilicon derivatives and diphosphonates on the various metal oxide surfaces have been explored in recent years in an effort to find a good model for such adhesive processes (Fig. 1).

Since SAMs have high flexibility to be modified easily at the single molecular level and assembled levels, they should be very useful research models to promote our understanding of the self-organization mechanism of molecules, molecular structure and property relationships and phenomena at interface between different phases. Such high flexibility has allowed us to research for electron transfer mechanisms of proteins, molecular layers, and biosensors.

In this review, **i)** the self-assembly process of alkylthiols on gold, and **ii)** various applications and techniques in which self-assembled monolayers are applied.

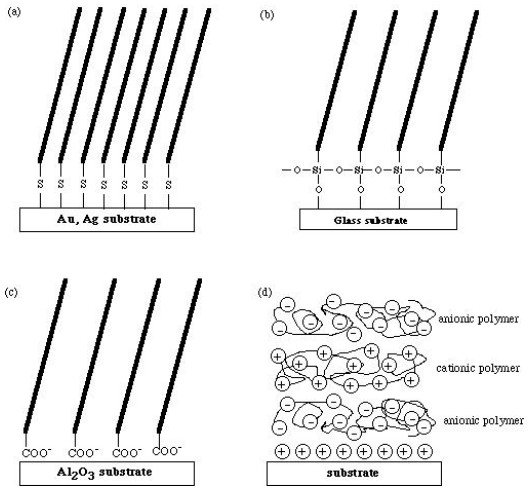

Fig. 1 Model of the surfaces of various SAMs

Self-assembling process of alkilthiols

Self-assembling process of alkylthiols on gold is initiated by the strong chemical interactions between the sulfur and gold surface. This interaction is considered a result of chemisorption that forced a thiorate molecule to adsorb commensurate with a gold lattice. Then, the tail-to-tail interaction of the molecules created by lateral interchain nonbonded interactions, such as by van der Waals, steric, repulsive and electrostatic forces, is strong enough to align the molecules parallel on the gold surface and create a crystalline film[1),2)]. In this technique, the solid substrate is simply dipped into a solution containing adsorbing molecules. Therefore, the packing and ordering of molecules is controlled by a chemisorption mechanism[3),4)]. In most cases, organic disulfides, thiols and sulfides have been utilized for the preparation of stable SAMs on the gold surfaces.

The mechanism of the self-assembling process of various alkylthiols and the orientation of the molecular layer on a gold surface have been investigated thoroughly by using Fourier transform infrared spectroscopy (FT-IR)[5),6)], scanning tunneling microscopy (STM)[1)], atomic force microscopy (AFM)[7)], X-ray photoelectron spectroscopy (XPS)[8),9)], electrochemistry[4),10)], Raman spectroscopy[11)], ellipsometry[12),13)] and quartz crystal microbalance (QCM)[14),15)] etc. Ulman extensively reviewed the self-assembly process[3),4)].

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Aminoalkanethiols

Aminoalkanethiols are utilized for the modification of a gold surface to introduce amino groups on it. The amino group is usually modified with amine-reactive materials, such as protein molecules or biomaterials, to functionalize the gold surface. Although several authors have been reported SAMs of short alkyl chain aminoalkanethiols, there are increasing number of reports on those of long alkyl chain compounds.

Takahara *et al.* formed 11-amino-1-undecanethiol monolayer on a gold electrode, and studied the effect of the terminal groups on the redox responses of ferrocene derivatives by voltammetric technique[16]. They also reported the relationship between the alkyl chain length of aminoalkanethiols and the redox behavior of 2,3-dichloro-1,4-naphtoquinone attached to the terminal amino group (Fig. 2)[17]. Tanahashi and co-workers modified a gold surface with SAMs of several kinds of functionalized alkanethiols. They reported the effect of their terminal functional groups on apatite formation in a simulated body fluid, by using X-ray photoelectron spectroscopic (XPS) measurement or quartz crystal microbalance (QCM) technique[18].

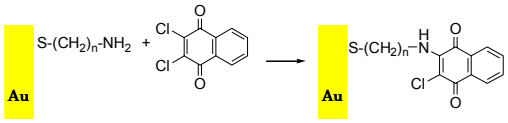


Fig. 2 The reaction scheme of 2,3-dichloro-1,4-naphtoquinone to the aminoalkanethiol SAMs on gold surface.

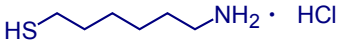
Related Products

unit: 10mg, 100mg

A423 11-Amino-1-undecanethiol, hydrochloride
A424 8-Amino-1-octanethiol, hydrochloride
A425 6-Amino-1-hexanethiol, hydrochloride

11-Amino-1-undecanethiol, hydrochloride
$C_{11}H_{26}ClNS$ = 239.85

8-Amino-1-octanethiol, hydrochloride
$C_8H_{20}ClNS$ = 197.77



6-Amino-1-hexanethiol, hydrochloride
$C_6H_{16}ClNS$ = 169.72

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N-Fmoc Aminoalkanethiols

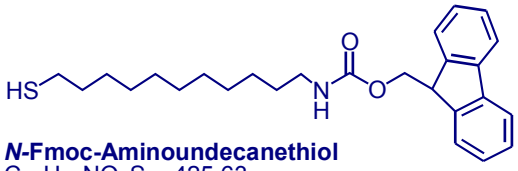
N-Fmoc Aminoalkanethiols are the compounds whose terminal amino group is protected by Fmoc-group. The Fmoc-group can be removed to reproduce the amino group under mild conditions, such as 30-minute immersion in 20% piperidine / acetonitrile, after the adsorption of *N*-Fmoc aminoalkanethiol on the gold surface.

Brockman and co-workers protected the amino group of 11-amino-1-undecanethiol with Fmoc group after making 11-amino-1-undecanethiol SAMs, in order to fabricate the DNA arrays with UV photopatterning and a multistep chemical modification procedure. They studied protein - DNA interactions by surface plasmon resonance (SPR) imaging (Fig. 3)[19]. *N*-Fmoc Aminoalkanethiols are expected to be used on similar techniques with short-steps, because these compounds have been originally protected (Fig.3A).

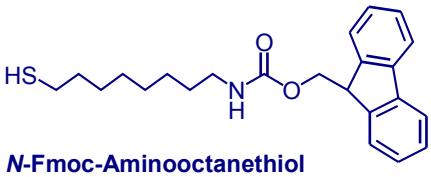
The modification of a gold substrate with SAMs of *N*-Fmoc aminoalkanethiols may be utilized to avoid amino group - gold surface interactions and to develop the sensor-chip highly regulated by photopatterning.

Related Products
unit: 10mg, 50mg

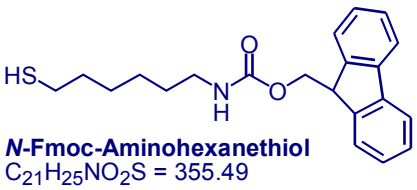
F287 *N*-Fmoc-Aminoundecanethiol
F288 *N*-Fmoc-Aminooctanethiol
F289 *N*-Fmoc-Aminohexanethiol



***N*-Fmoc-Aminoundecanethiol**
$C_{26}H_{35}NO_2S$ = 425.63



***N*-Fmoc-Aminooctanethiol**
$C_{23}H_{29}NO_2S$ = 383.55



***N*-Fmoc-Aminohexanethiol**
$C_{21}H_{25}NO_2S$ = 355.49

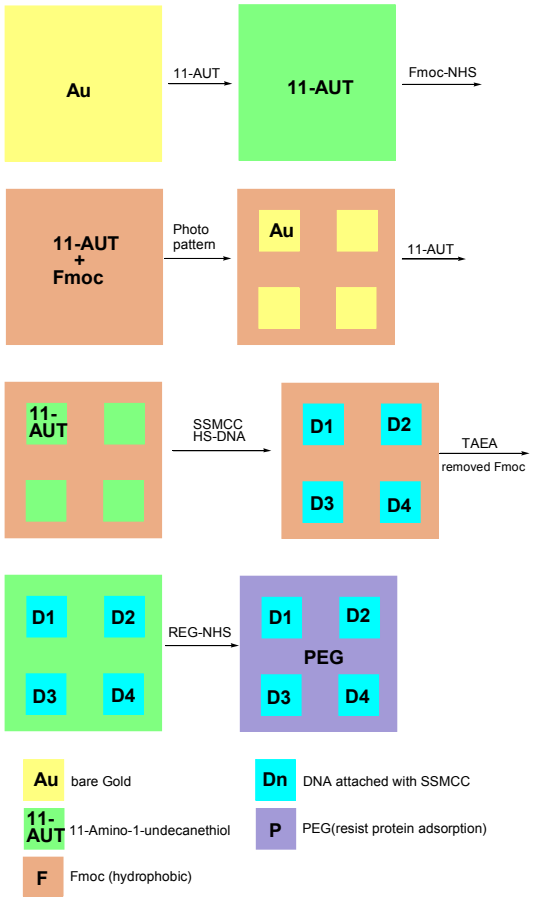


Fig. 3 The construction of multi-element DNA arrays.

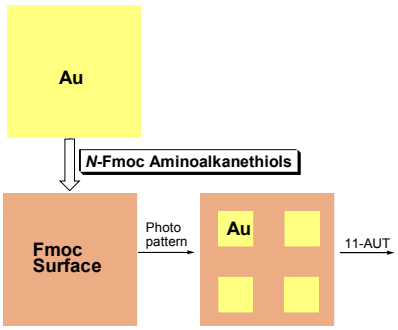


Fig. 3A The application of N-Fmoc Aminoalkanethiols to Fig.3.

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Carboxyalkanethiols

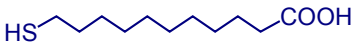
Carboxyalkanethiols are utilized for the modification of a gold surface to introduce carboxylic groups on it. The carboxylic group is often converted to activated *N*-hydroxysuccinimide ester, to conjugated to amines of biomaterials.

Glenn and co-workers used carboxyalkanethiol and poly-L-lysine to create cytochrome b5-immobilized multilayer electrode (Fig. 4)[20]. Mizutani *et al.* fabricated glucose oxidase-immobilized multilayer electrode in a similar manner[21]. Both of them reported the electron transfer from biomaterials to a gold surface. These kinds of multilayer film electrodes have been developed because those are well-suited for diffusion electron transfer studies.

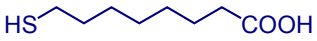
Frisbie and co-workers reported that atomic force microscopy (AFM) could be used to measure both the interactions and the spatial mapping of chemically distinct functional groups. They formed carboxyalkanethiols monolayer on the gold surfaces of AFM cantilever-tip. They used AFM to measure the adhesive and friction forces between molecularly modified probe tips and organic monolayers terminating in a lithographically defined pattern of distinct functional groups. They obtained the adhesive interactions and the friction image of the patterned sample surface and named their microscopy Chemical Force Microscopy (Fig. 5)[22].

Related Products
unit: 10mg, 100mg

C385 10-Carboxy-1-decanethiol
C386 7-Carboxy-1-heptanethiol
C387 5-Carboxy-1-pentanethiol



10-Carboxy-1-decanethiol
$C_{11}H_{22}O_2S$ = 218.36



7-Carboxy-1-heptanethiol
$C_8H_{16}O_2S$ = 176.28

5-Carboxy-1-pentanethiol
$C_6H_{12}O_2S$ = 148.22

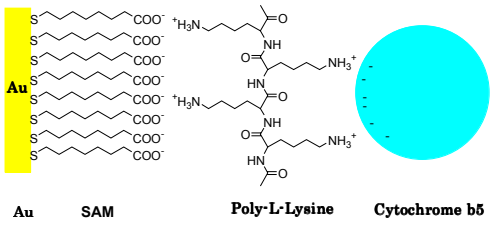


Fig. 4 The structure cytochrome b5/ PL / SAM gold immobilized ultilayer electrode

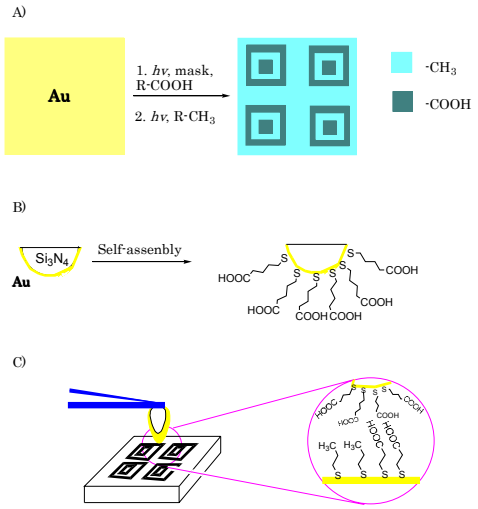


Fig. 5 Principle of Chemical Force Microscopy

A) The surface modification of sample pattern.
B) The Modification of the cantilever-tip surface with a specific functional group.
C) The detection of the interaction between the tip and the patterned sample.

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Carboxyalkyldisulfides

Carboxyalkyldisulfides are oxidized compounds of carboxyalkanethiols and are reported to form similar SAMs to those with carboxyalkanethiols. They are less stinking and more stable than thiols.

Kanayama *et al.* formed SAMs of 4,4'-dithiodibutyric acid on its gold colloids or gold electrodes, and introduced phenylboronic acid moieties to its terminus. They succeeded to recognize various sugars by surface-enhanced Raman spectroscopy (SERS) and cyclic voltammetry (CV) using these SAMs[23].

Takagi and co-workers fixed dinitrophenyl (DNP) group on carboxyalkyl-disulfide SAMs. They detected an anti-DNP antibody by electrical impedance measurement. The technique could be applied to impedimetric sensing of protein[24].

Delamarche and his fellows fabricated 10-carboxydecyl disulfide SAMs on the gold substrate, and introduced to photoactivatable benzophenone moiety to the termini. After conversion by the attachment of protein (IgG), it was tested by a variety of characterization techniques (ellipsometry, X-ray photoelectron spectroscopy, AFM and so on) (Fig. 6)[25].

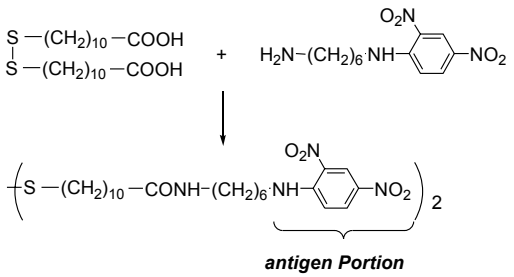
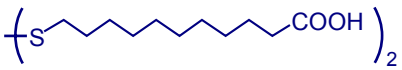


Fig. 6 The immobilization of the photoactivatable moiety to the 10-carboxydecyl disulfide SAMs.

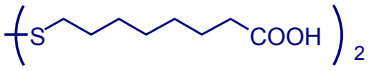
Related Products

unit: 10mg, 100mg

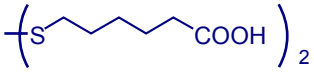
C404 10-Carboxydecyl disulfide
C405 7-Carboxyheptyl disulfide
C406 5-Carboxypentyl disulfide
D524 4,4'-Dithiodibutyric acid (unit: 500mg)



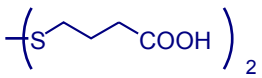
10-Carboxydecyl disulfide
$C_{22}H_{42}O_4S_2$ = 434.69



7-Carboxyheptyl disulfide
$C_{16}H_{30}O_4S_2$ = 350.53



5-Carboxypentyl disulfide
$C_{12}H_{22}O_4S_2$ = 294.42



4,4'-Dithiodibutyric acid
$C_8H_{14}O_4S_2$ = 238.32

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Succinimidylester-terminated alkyldisulfides

Succinimidyl ester-terminated alkyldisulfides are amine-reactive analogs of carboxyalkyldisulfide. They are utilized for the modification of a gold surface to introduce amine-reactive sites on the surface. It is possible to use this technique for the protein ctip or various sensors. There is no need to use coupling agents because these compounds have been already activated.

Wagner *et al.* characterized dithiobis(succinimidyl undecanoate) SAMs on a gold substrate by scanning tunneling microscopy (STM) and radiolabeling and *in situ* AFM imaging. The densely packed and highly reactive surfaces enabled authors to immobilize easily amino acids or proteins (Fig. 7)[26].

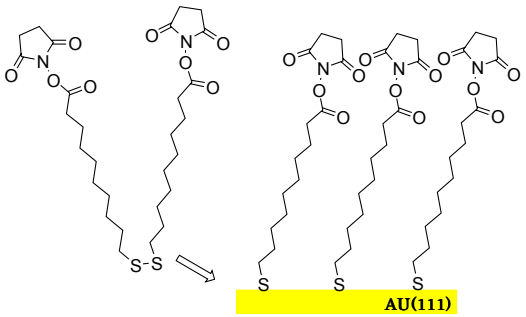
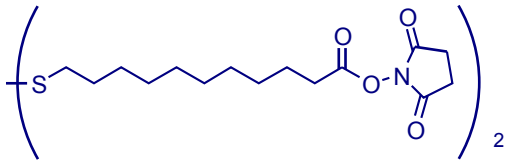


Fig. 7 Model of the surfaces of DSU SAMs.

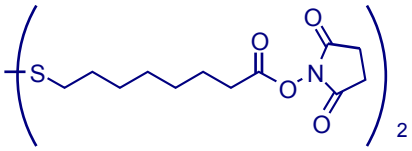
Related Products

unit: 10mg, 100mg

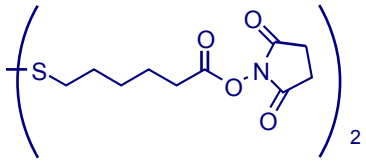
D537 Dithiobis (succinimidyl undecanoate)
D538 Dithiobis (succinimidyl octanoate)
D539 Dithiobis (succinimidyl hexanoate)



Dithiobis (succinimidyl undecanoate)
$C_{30}H_{48}N_2O_8S_2$ = 628.84



Dithiobis (succinimidyl octanoate)
$C_{24}H_{36}N_2O_8S_2$ = 544.68



Dithiobis (succinimidyl hexanoate)
$C_{20}H_{28}N_2O_8S_2$ = 488.58

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Ferrocenylalkanethiols

Ferrocenylalkanethiols are utilized for the modification of gold surface to introduce electrochemically active molecules on it. The modified gold surface can be utilized for the development of sensitive electrochemical analyses.

Rubin *et al.* fabricated mixed SAMs of aminoalkanethiols and ferrocenyl-alkanethiols with various chain lengths on a gold electrode surface. They immobilized glucose oxidase (GOx) on aminoalkanethiol sites and used ferrocenylalkanethiol sites as electron mediator. They reported the relationship between electrical response and chain-length of mixed SAMs (Fig. 8)[27].

Uosaki and co-workers reported the results of structural changes and the number of absorbed ferrocenylalkanethiols during redox reaction of 11-ferrocenyl-1-undecanethiol SAMs on a gold electrode by using of fourier transform infrared reflection adsorption spectroscopy (FT-IRRAS) and electrochemical quartz crystal microbalance (EQCM) system. They suggested the possibility of orientation change of the monolayer during the redox reaction of the ferrocene moiety[28,29,30]. They also estimated the change of it by using voltammograms[31] and ellipsometry[32].

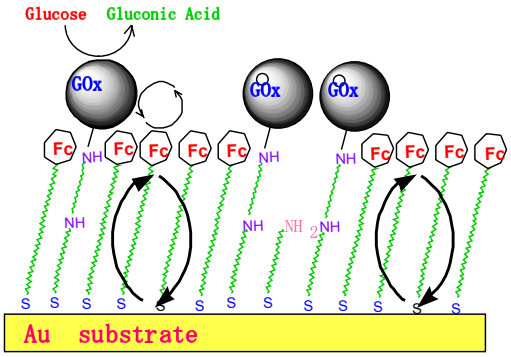
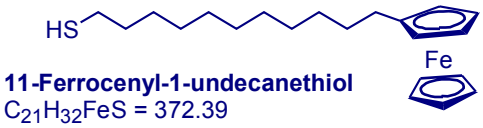


Fig. 8 The modification of the gold surface with the biosensor assembly.

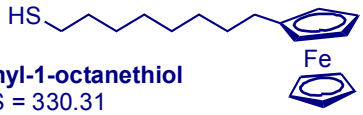
Related Products

unit: 10mg, 100mg

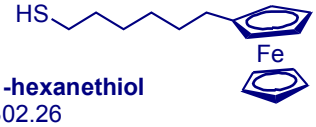
F246 11-Ferrocenyl-1-undecanethiol
F247 8-Ferrocenyl-1-octanethiol
F269 6-Ferrocenyl-1-hexanethiol



11-Ferrocenyl-1-undecanethiol
$C_{21}H_{32}FeS$ = 372.39



8-Ferrocenyl-1-octanethiol
$C_{18}H_{26}FeS$ = 330.31



6-Ferrocenyl-1-hexanethiol
$C_{16}H_{22}FeS$ = 302.26

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Hydroxyalkanethiols

Hydroxyalkanethiols are utilized as “dilution reagents” or “blocking reagents” on a gold surface to control the density of reactive groups on the surface or to prevent non-specific binding of analytes on the surface. Herne and her colleagues fabricated the mixed SAMs of thiol-derivatized single-stranded DNA (HS-ss-DN) and 6-hydroxy-1-hexanethiol on a gold surface. They prevented non-specific adsorption of HS-ss-DNA (Fig. 9)[33].

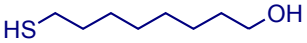
Perez-Luna *et al.* made the mixed SAMs of biotin-terminated thiol and 11-hydroxy-1-undecanethiol on a gold surface. They prevented non-specific adsorption of wild type streptavidin and streptavidin mutants[34].

Dubrovsky and his co-workers controlled the non-specific adsorption of protein on the surface of the gold-coated silicagel using 11-hydroxy-1-undecanethiol. They mentioned the usefulness of gold-coated silica gel for the preparation of well-defined and surface-functionalized supports for biological assay[35].

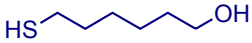
Related Products
unit: 10mg, 100mg

H337 11-Hydroxy-1-undecanethiol
H338 8-Hydroxy-1-octanethiol
H339 6-Hydroxy-1-hexanethiol

11-Hydroxy-1-undecanethiol
$C_{11}H_{24}OS$ = 204.37



8-Hydroxy-1-octanethiol
$C_8H_{18}OS$ = 162.29



11-Hydroxy-1-undecanethiol
$C_6H_{14}OS$ = 134.24

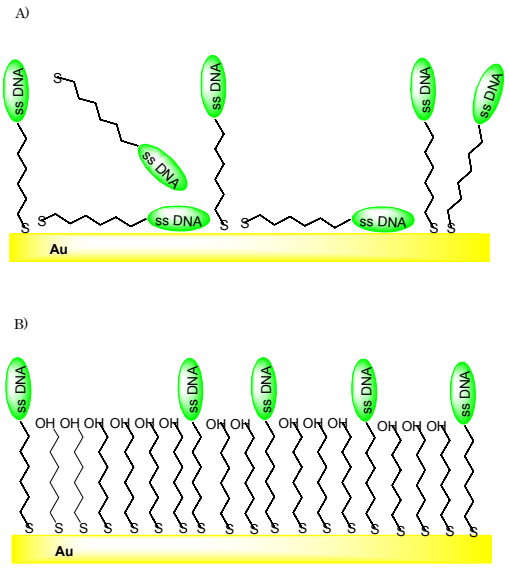


Fig. 9 The surface conditions of DNA sensor
A) HS-ss-DNA only
B) Coexistence of HS-ss-DNA and 6-hydroxy-1-hexanethiol

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Applications

Electrochemical sensing by SAMs-modified electrodes

One of the common applications of SAMs is in the creation of sensors with molecular recognition properties. Many groups have studied the electro-chemical characteristics of various alkylthiols for ion detection and molecular recognition. For example, SAMs prepared with ω-mercapto-carboxylic acids on mercury film and gold electrodes were utilized for the very sensitive and selective analysis of cadmium (II)[36]. Taniguchi *et al.* incorporated Meldola's Blue into self-assembled decanethiols monolayer-coated electrodes and demonstrated that this system could be a membrane model with molecular gating[37].

Katayama and Maeda reported an electrochemical detection of cyclic AMP by a 17-mer oligopeptide-coated Au electrode. Cyclic voltammograms of ferrocyanide/ferricyanide redox coupled with the electrode showed a response depending on the cyclic AMP concentration, but not ATP (Fig. 10)[38]. Wang *et al.* reviewed the behavior, utility and advantages of an amperometric flow detector coated with unsubstituted *n*-alkylthiols. They indicated that a hydrophilic alkylthiol monolayer can impart a high selectivity toward the lipophilic drugs such as chloropromazine and dipamine[39].

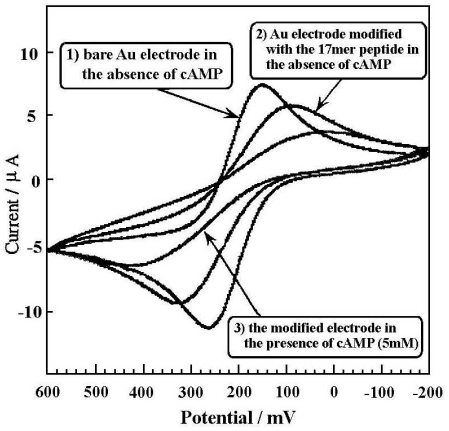

Fig. 10 Cyclic voltammogram of Au electrode modified with 17-mer peptide in the absence and presence of cAMP.

Detection of Histidine-tagged protein (His-tag Protein) using NTA-attached SAMs

The use of a short peptide as an affinity tag is one of the most common methods for the detection and purification of recombinant proteins. These tag proteins are mostly antibody epitopes and are detected with their antibodies[40].
Sigal *et al.* prepared a self-assembled monolayer that selectively binds a protein with a His-tag, a stretch of six histidines. They prepared two alkanethiols: one has a nitrilotriacetic acid (NTA) group which forms a tetravalent chelate with a nickel (II) ion. The other has a tri(ethyleneglycol) group which is capable of avoiding nonspecific adsorption of protein. This membrane can recognize only a His-tag protein through the nickel (II) ion chelated with NTA on the SAM. Therefore, this technique is useful for immobilization of His-tag proteins for study by using surface plasmon resonance (SPR)[41].

SPR is commonly used for measuring the kinetics of association and dissociation of ligands and proteins in aqueous solution. It is particularly powerful for the observation of the processes occurring at or near interfaces. The sensing element is a thin (40-50nm) gold or silver film deposited on a glass surface. *p*-Polarized light is irradiated from the opposite side of the gold-coated surface of the glass slide, and the reflection angle is controlled to minimize the intensity of the reflection. Since the value of this reflection angle linearly depends on the amount of protein adsorbed on the surface, the protein can be monitored by SPR (Fig. 11)[40-42].

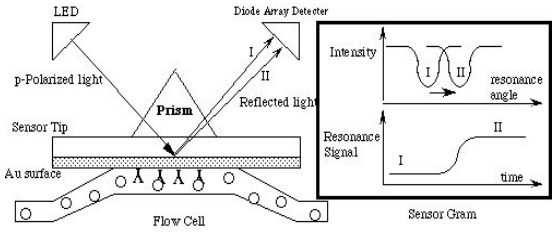

Fig. 11 Schimatic diagram of an experimental setup for SPR measurement

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Applications (cont.)

Sigal *et al.* used SPR to compare the immobilization techniques on their interaction capabilities with a protein in a solution. His-tag proteins were immobilized either by chelating to nickel (II) ion on an NTA-SAM or by conjugation on a carboxylated dextran surface with a coupling reagent, EDC [N-ethyl-N''-(3-dimethylaminopropyl)carbodiimide], in the presence of NHS [N-hydroxysuccinimide]. They used two different antibodies of scTCR [single-chain T-cell receptor] in order to determine their binding abilities. They indicated that the SPR signal from the carboxylated dextran-coated membrane was larger than that from NTA-SAM because of the larger immobilization capacity of the dextran surface. On the other hand, the Ni(II)-NTA surface membrane was more selective than the carboxylated dextran-coated membrane because of the three dimensional recognition by the antibodies in solution. They tested four other His-tag proteins, such as human TATA box binding protein (huTBP), the transcriptional activator Gal 4, and two components of the yeast RNA polymerase II holoenzyme-TFIIP and Gal 11 (Fig. 12)[41]. All the His-tag labeled proteins bound tightly onto Ni(II)-NTA-SAM surface. These results indicated that this molecule immobilization method may be useful for other bioanalytical techniques which require or are compatible with proteins immobilized on metal surfaces, for example: interometry, surface acoustic wave sensing (SAW), electrochemiluminescence.

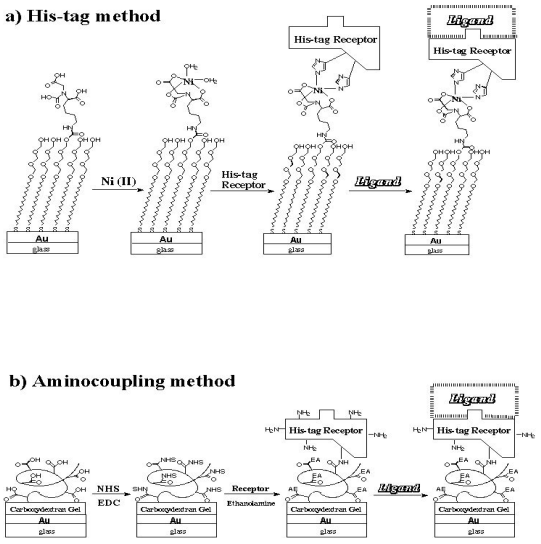

Fig. 12 Procedures for the immobilization of a receptor protein.
a) His-Tag method
b) covalent coupling with

Surface plasmon resonance (SPR) studies for interactions of SAMs and proteins

In this section, I will describe the surface plasmon resonance (SPR) studies for interactions of SAMs and proteins, except for His-tag methods.

Mrksich *et al.* studied the thermodynamic and kinetic mechanism between benzenesulfonamide-attached SAM and bovine carbonic anhydrase (EC 4.2.1.1) using the SPR technique (Fig. 13)[42),43)].

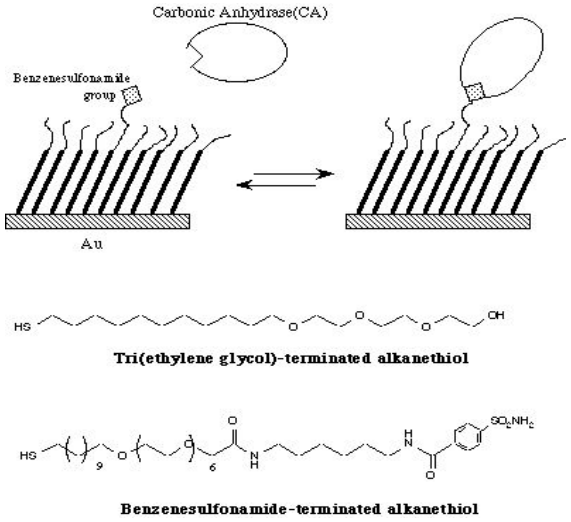

Fig. 13 Structure of benzene-sulfonamide-terminated SAM and interaction model between benzene-sulfonamide and carboxylic anhydrase

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Applications (cont.)

H. Ringsdorf *et al.* prepared triplet layers on biotin-attached SAMs on gold surface using streptavidin and anti-chorionic gonadotropin-Fab (anti-hCG-Fab) fragment. They investigated i) the hinge, or linkage region of the Fab fragment, and ii) the second layer formation (streptavidin, Fab fragment), iii) the third layer formation by antigen hCG, and iv) quantification of these processes (Fig. 14)[44].
SPR coupled with SAM is an excellent technique to determine surface phenomena. The SPR technique has been used in various studies and applications, for example, determination of epitopes of monoclonal antibodies, development of immuno-detection systems, research of signal transfer mechanism, and so on.

Electrochemical studies of proteins on SAMs-modified electrodes

Interfacial electron-transfer of proteins and bio-electrochemical studies will be described in this section.
Protein-coated electrodes provide us suitable systems not only for analyses of their properties by electrochemical and spectroscopic techniques but also for developments of applications such as constructions of devices in which protein layer interfaces are used[45], especially, cytochrome *c*, ferredoxins, and mioglobin, which are interesting proteins for interfacial electrochemical studies. For example, Niki's group has been studying diffusionless standard electron transfer rate constants of cytochrome *c* immobilized on a carboxyric acid-attached SAM with an electro-reflectance spectroscope[46].

Bowden, Mizutani and Jordan's groups individually applied electrochemical techniques for the characterization of the adsorption of poly (*L*-lysine)-coated SAMs. They fixed poly (*L-lysine*) on a carboxylic acid-attached SAM through an electrostatic binding between a negative charge of carboxylate and a positive charge of amine residue. They utilized the poly (*L-lysine*)-coated SAM for the development of the detection system of glucose or for the research of the electron transfer mechanism of cytochrome c[20),21),45),47]. Nakashima's group prepared polyethyleneglycol-attached SAM and reported that a supramolecular structure was formed by the interaction between poly(ethyleneglycol) and α-cyclodextrin[48].

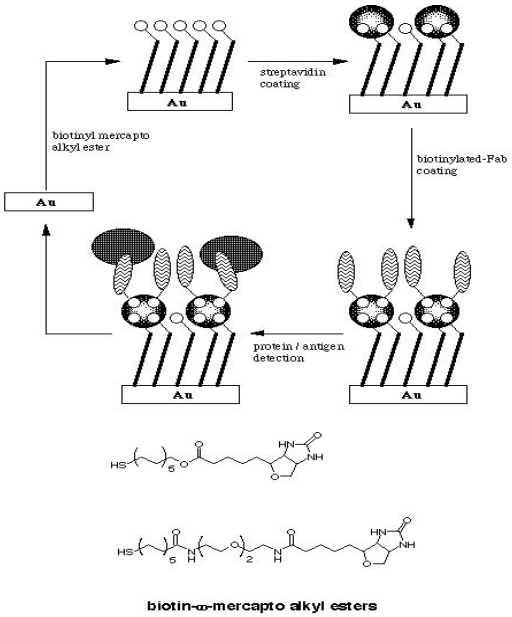

Fig. 14 Reversible formation of a protein triple layer on SAM using biotinvlated alkvlthiols.

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Applications (cont.)

DNA sensor by using electrochemical and QCM techniques

Electrochemical DNA sensors may be potentially useful devices for the sequence specific detection and quantification of DNA or RNA in solutions. The amount of DNA or RNA can be measured as an amperometric or voltammetric signal[45]. Katayama *et al*. prepared a calf thymus DNA-coated Au electrode to detect an anti-DNA antibody which recognizes DNA molecule. They demonstrated that this system could be useful for the development of biosensors for DNA binding proteins[49]. Okahata's group reported a new methodology to detect the one-to-one hybridization between the origonucleotide immobilized on Au electrodes of a quartz crystal microbalance (QCM) and target M13 phage DNAs in aqueous solution by the frequency changes of QCM. They prepared a 10-mer deoxynucleotide having a mercaptopropyl group at the 5'-phosphate end whose sequence was complementary with the *Eco*RI binding site of single-stranded M13 phage DNA (Fig. 15)[50),51]. The QCM technique is known to provide very sensitive mass measuring devices because its resonance frequency decreases upon the increase of the mass on the QCM at a nanogram level. This QCM method is useful for the study of molecular kinetics of base-pair hybridization in oligonucleotides and to detect various biological materials.

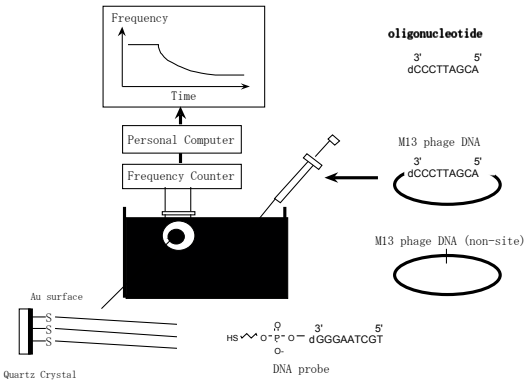

Fig. 15 The detection of the target DNA (M13 phage) by QCM immobilized with origonucleotide.

Conclusion

In this review, we have described various applications of the self-assembled monolayers. SAMs have been intensively studied in the recent few years because of their relevance to science and technology. Due to the ease of use and modification of the membranes, SAMs should be applied not only for biochemical studies but also for material science in electronics, photodissociation-photoionization processes, research of corrosion mechanisms, developments of lubrication materials, etc[4,11].

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Solubility Data

Product code	Product name
A423	11-Amino-1-undecanethiol, hydrochloride
A424	8-Amino-1-octanethiol, hydrochloride
A425	6-Amino-1-hexanethiol, hydrochloride
F287	N-Fmoc-Aminoundecanethiol
F288	N-Fmoc-Aminooctanethiol
F289	N-Fmoc-Aminohexanethiol
C385	10-Carboxy-1-decanethiol
C386	7-Carboxy-1-heptanethiol
C387	5-Carboxy-1-pentanethiol
C404	10-Carboxydecyl disulfide
C405	7-Carboxyheptyl disulfide

Product code	Product name
C406	5-Carboxypentyl disulfide
D524	4,4'-Dithiodibutyric acid
D537	Dithiobis(succinimidyl undecanate)
D538	Dithiobis(succinimidyl octanate)
D539	Dithiobis(succinimidyl hexanate)
F246	11-Ferrocenyl-1-undecanethiol
F247	8-Ferrocenyl-1-octanethiol
F269	6-Ferrocenyl-1-hexanethiol
H337	11-Hydroxy-1-undecanethiol
H338	8-Hydroxy-1-octanethiol
H339	6-Hydroxy-1-hexanethiol

	Methyl alchol (mol / l)				Chloroform (mol / l)				Ethyl alchol (mol / l)				Dichloromethane (mol / l)				Tetrahydrofuran (mol / l)				Acetonitrile (mol / l)			
	10m	1m	100µ	10µ	10m	1m	100µ	10µ	10m	1m	100µ	10µ	10m	1m	100µ	10µ	10m	1m	100µ	10µ	10m	1m	100µ	10µ
A423	○	○	○	○	○	○	○	○	○	○	○	○	×	×	○	○	×	×	×	○	×	×	×	×
A424	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	△	△	○	○	×	△	○	○
A425	○	○	○	○	×	○	○	○	○	○	○	○	×	○	○	○	×	△	△	○	×	×	×	×
F287	×	○	○	○	○	○	○	○	×	○	○	○	○	○	○	○	○	○	○	○	×	○	○	○
F288	×	○	○	○	○	○	○	○	×	○	○	○	○	○	○	○	○	○	○	○	×	○	○	○
F289	○	○	○	○	○	○	○	○	△	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○
C385	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	△	△	△	△
C386	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	△	△	△	△
C387	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	△	△	△	△
C404	△	○	○	○	×	○	○	○	△	○	○	○	×	○	○	○	×	○	○	○	×	△	○	○
C405	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	△	○	○	○
C406	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○
D524	○	○	○	○	○	○	○	○	○	○	○	○	×	○	○	○	○	○	○	○	×	△	○	○
D537	-	-	-	-	○	○	○	○	-	-	-	-	○	○	○	○	○	○	○	○	○	○	○	○
D538	-	-	-	-	○	○	○	○	-	-	-	-	○	○	○	○	○	○	○	○	○	○	○	○
D539	-	-	-	-	○	○	○	○	-	-	-	-	○	○	○	○	○	○	○	○	○	○	○	○
F246	×	○	○	○	○	○	○	○	△	○	○	○	○	○	○	○	○	○	○	○	△	△	△	△
F247	○	○	○	○	○	○	○	○	△	○	○	○	○	○	○	○	○	○	○	○	△	△	△	△
F269	×	○	○	○	○	○	○	○	△	○	○	○	○	○	○	○	△	△	○	○	○	○	○	○
H337	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	×	×	△	△
H338	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	△	○	○	○
H339	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	△	○	○	○

○: soluble, ×: insoluble, △: a little suspended, -: not available

	Ethyl acetate (mol / l)				Hexane (mol / l)				Dimethyl sulfoxide (mol/l)				Dimethylfomamide (mol/l)				Water (mol / l)			
	10m	1m	100µ	10µ	10m	1m	100µ	10µ	10m	1m	100µ	10µ	10m	1m	100µ	10µ	10m	1m	100µ	10µ
A423	×	×	×	×	×	×	×	×	○	○	○	○	○	○	○	○	×	○	○	○
A424	×	×	△	○	×	×	×	×	○	○	○	○	○	○	○	○	○	○	○	○
A425	×	×	×	×	×	×	×	×	○	○	○	○	○	○	○	○	×	○	○	○
F287	○	○	○	○	×	×	×	×	○	○	○	○	○	○	○	○	×	×	×	×
F288	○	○	○	○	×	×	×	×	○	○	○	○	○	○	○	○	×	×	×	×
F289	○	○	○	○	×	×	×	×	○	○	○	○	○	○	○	○	×	×	×	×
C385	△	△	△	△	○	○	○	○	○	○	○	○	○	○	○	○	×	×	×	×
C386	△	△	△	△	○	○	○	○	○	○	○	○	○	○	○	○	×	○	○	○
C387	△	△	△	△	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○
C404	×	○	○	○	×	×	×	×	○	○	○	○	○	○	○	○	×	×	×	×
C405	△	○	○	○	×	×	×	×	○	○	○	○	○	○	○	○	×	×	×	×
C406	○	○	○	○	×	×	×	×	○	○	○	○	○	○	○	○	×	×	×	×
D524	○	○	○	○	×	×	×	×	○	○	○	○	○	○	○	○	×	×	×	×
D537	○	○	○	○	×	×	×	×	○	○	○	○	○	○	○	○	-	-	-	-
D538	○	○	○	○	×	×	×	×	○	○	○	○	○	○	○	○	-	-	-	-
D539	○	○	○	○	×	×	×	×	○	○	○	○	○	○	○	○	-	-	-	-
F246	△	△	△	△	○	○	○	○	○	○	○	○	○	○	○	○	×	×	×	×
F247	△	△	△	△	○	○	○	○	○	○	○	○	○	○	○	○	×	×	×	×
F269	△	△	△	△	×	○	○	○	○	○	○	○	○	○	○	○	×	×	×	×
H337	△	△	△	△	×	○	○	○	○	○	○	○	○	○	○	○	×	×	×	×
H338	△	△	△	△	○	○	○	○	○	○	○	○	○	○	○	○	×	○	○	○
H339	△	△	△	△	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○

○: soluble, ×: insoluble, △: a little suspended, -: not available

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