



# Sensing capability of molecularly imprinted self-assembled monolayer fabricated using dithiol compound



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## ABSTRACT

Synthesis of 3,5-di(6-mercaptohexyloxy)toluene (DMHT) was achieved starting from orcinol. A molecularly imprinted self-assembled monolayer (SAM) was fabricated by forming an SAM with both DMHT and the template molecule (cholesterol), followed by removal of the template molecules by solvent extraction. These imprinted SAMs were capable of discriminating the imprinted substrate. The stability of the imprinted SAMs was estimated precisely using a quartz crystal microbalance. In comparison to the results used monothiol compounds, the duration of the sensing capability of this imprinted SAM was improved greatly. The two thiol functional groups in DMHT clearly had a significant effect on the duration.

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## 1. Introduction

Recently, significant attention has been paid to the development of a molecular imprinting technique that allows for the preparation of polymers that mimic biological receptors. This technique is a very useful approach for the fabrication of a matrix with molecular recognition sites, which are formed by the addition of template molecules during the matrix formation, followed by the removal of the template molecules after matrix formation [1–5]. Molecularly imprinted matrices have been developed over the past decade in many fields including chromatography, catalysis, artificial antibodies, and sensing devices.

The detection of the binding molecules in the imprinted matrix can be achieved by electrochemical, impedance, and optical methods [6], with the former being the easiest and most economical method for the fabrication of commercial sensors [7,8]. The imprinting method in polymer science has been focused on 3D networks, but the creation of 2D, self-assembled monolayers (SAMs) on solid surfaces represents a significant difference from these materials and could be useful in technological and scientific applications. Therefore, SAMs have recently become very important owing to their potential applications to sensor nanotechnology and molecular electronics [9–17]. A sensitive electrochemical-sensing

protocol for detection by a surface molecular self-assembly formed by molecular imprinting at the electrode was reported [18]. Polymer nanowires, silica nanotubes, and silica nanoparticles could be used in the surface molecular self-assembly strategy [19–23].

SAMs are one of the most important systems for investigating the contributions of molecular structure and composition to the macroscopic properties of materials. They provide organic surfaces whose structures and properties can be varied. Control over dimensions and properties make SAMs excellent systems for understanding the fundamentals of many natural phenomena. Moreover, their end-group-dependent properties can be easily manipulated by various chemical reactions, thereby rendering them compatible for the desired applications. An SAM is a layer of molecular thickness formed by the self-organization of molecules in an ordered manner by chemisorption on a solid surface. It is the most elementary form of nanoscale organic thin-film material, and may be composed of three significant parts: a surface-active head group that bonds strongly to a substrate, an alkyl chain that imparts stability to the assembly by van der Waals interactions, and a functional end group that plays an important role in terms of coupling of a biomolecule to a monolayer.

Alkanethiols that spontaneously adsorb to gold surfaces have been used for SAM preparation. The self-assembly of alkanethiols on a gold surface occurs owing to the strong chemical interactions between the sulfur end-group and gold, which is believed to result in chemical adsorption of the molecules as thiolates [14]. The templating of SAMs is known as 2D molecular imprinting. When an

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SAM of alkanethiol is fabricated on a gold surface, the presence of foreign guest molecules and their removal results in cavities in the SAM. Since the cavities are complementary in size to the guest molecule, they lead to the formation of binding sites on the gold surface.

A molecular imprinting polymer–quartz crystal sensor based on 2-aminoethanethiol has been reported for the detection of terpene gases up to 1000 ppm [24]. The quartz crystal microbalance (QCM) is a simple, cost effective, and high-resolution mass sensing instrument that can measure nanogram levels of mass change loaded onto the surface of the QCM resonator. As mass sensors, QCMs have been widely used in biochemistry, environmental, food, and clinical analysis.

In our previous investigation, molecularly imprinted SAMs were formed using 1-hexadecanethiol and cholesterol [16]. These molecularly imprinted SAMs showed good cholesterol-sensing capability, but the duration of the sensing capability was poor. In addition, a terphenylthiol compound was synthesized and used to form a molecularly imprinted SAM, and this SAM showed improved sensing capability [17].

In this study, a dithiol compound was synthesized and used to form an SAM on a gold plate, and a molecularly imprinted matrix was produced using this monolayer. The sensing capability and sensor durability of the molecularly imprinted SAM were estimated using electrochemical and QCM studies.

## 2. Experimental

### 2.1. Materials and instruments

1-Dodecanethiol (DDT), 1-hexadecanethiol (HDT), [1,1':4',1''-terphenyl]-4-thiol (TPT), cholesterol, cholic acid, deoxycholic acid, potassium ferricyanide [ $K_3Fe(CN)_6$ ], sodium perchlorate, orcinol, 1,6-diiodohexane, 1,3-diaminoethane, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were purchased from Aldrich.

### 2.2. Synthesis of 3,5-di(6-mercaptohexyloxy)toluene (DMHT)

This dithiol compound was synthesized using the modified method from the reported results [25,26]. 5 M excess of 1,6-diiodohexane was used to prevent dimerization or polymerization during the synthetic reaction.

$^1H$  NMR (500 MHz,  $CDCl_3$ ) 1.35 (s, 2H, –SH), 1.43 (m, 8H, –CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>–), 1.63 (m, 4H, CH<sub>2</sub>–C–S), 1.74 (m, 4H, CH<sub>2</sub>–C–O), 2.20 (s, 3H, CH<sub>3</sub>–), 2.54 (t, 4H, –CH<sub>2</sub>–S–), 3.87 (t, 4H, –CH<sub>2</sub>–O–), 6.24–6.59 (m, 3H, aromatic).

### 2.3. Synthesis of [1,1':4',1''-terphenyl]-4-propanethiol (TPPT)

TPPT was synthesized using already reported methods [26].

$^1H$  NMR (500 MHz,  $CDCl_3$ ) 1.42 (t, 1H), 1.98 (m, 2H), 2.58 (m, 2H), 2.78 (t, 2H), 7.24–7.68 (m, 13H).

### 2.4. Molecular imprinting method using cholesterol

The round-shaped pure Au plate (surface area: 1.0 cm<sup>2</sup> × 2, thickness: 0.50 mm), which was connected with Au wire (2 cm), was manufactured by a goldsmith's shop. Before every experiment, the Au plates were cleaned with 'piranha' solution, which was made from 20 mL of 30 wt% H<sub>2</sub>O<sub>2</sub> and 60 mL of conc. H<sub>2</sub>SO<sub>4</sub>. The Au plate was placed in the 'piranha' solution for 10 min and then washed in 100 mL of distilled water for 1 h. To obtain a solution of 100 μM 1-hexadecanethiol and 1 wt% cholesterol in ethanol, 0.0026 g (3.1 μL, 10 μmol) of 1-hexadecanethiol and 0.79 g (2.04 mmol) of cholesterol was placed in 100 mL of ethanol. The cleaned Au plate was placed in this solution for 12 h for coating,

after which it was placed in 50 mL of ethanol for 40 min in order to remove the excessively overcoated materials and adsorbed cholesterol at the surface of Au plate. A cholesterol-shaped molecular cavity was formed by the removal of the cholesterol from the surface of the gold plate. This process was repeated three times using 50 mL of freshly prepared ethanol each time. Both sides of the Au plate were used in this experiment so the Au plate was hung down into the solution during all the processes.

### 2.5. Electrochemical measurement

Cyclic voltammograms were detected using an Ivium potentiostat (Ivium Technologies, Netherlands). The round pure Au plate (surface area: 1.0 cm<sup>2</sup> × 2, thickness: 0.50 mm) was used as a working electrode. All the electrochemical experiments were carried out using a standard, one-compartment, three-electrode cell. The reference electrode was Ag/AgCl (3 M KCl) and the counter electrode was a platinum wire (10 cm). All electrode potentials were referred to the reference electrode. These three electrodes were fixed accurately and tightly above the 50 mL reactor to ensure the identical condition for every experiment. In this electrochemical experiment, potassium ferricyanide was used as a background material for oxidation and reduction. The main solution was made by dissolving 0.0494 g (0.150 mmol) of potassium ferricyanide and 0.1837 g (1.50 mmol) of sodium perchlorate in 15 mL of water and 15 mL of ethanol. A cyclic voltammogram was conducted between –0.5 V and 0.5 V with a scan rate of 50 mV/s in 30 mL of 5 mM potassium ferricyanide and 50 mM sodium perchlorate of 50% aqueous ethanol solution. The maximum current of the oxidation step and the minimum current of the reduction step were recorded at every time by adding the substrates.

The cholesterol standard solution (1.0 mM) was prepared by dissolving 19.3 mg of cholesterol in 50 mL of ethanol, to which 150 μL of the standard cholesterol solution was added for cyclic voltammogram experiment, so that the cholesterol concentration of the main solution was increased 5 μM at every addition. The cholic acid standard solution was prepared by dissolving 20.4 mg of cholic acid in 50 mL of ethanol. The deoxycholic acid standard solution was prepared by dissolving 19.6 mg of deoxycholic acid in 50 mL of ethanol.

The sensing stability of the imprinted monolayer was determined by measuring the current gap between the results of adding 0.90 mL of 1 mM cholesterol and 0.90 mL of 1 mM cholic acid.

### 2.6. QCM experiment

It is very difficult to measure the change of the absorbed amount after every adsorption step and every cyclic voltammogram experiment using the Au plate directly, so a quartz resonator (USI System, Fukuoka, Japan) was used instead of the Au plate in the QCM technique. The resonator was immersed in a solution for 12 h, removed from the solution and dried with nitrogen, after which the change in frequency was measured. The quartz resonators were covered with gold electrodes on both faces and their resonance frequency was 9 MHz (AT-cut). The surface roughness factor of these electrodes was previously estimated to be 1.1 (±5%) by scanning electron microscopy. The reproducibility was ±2 Hz over 2 h [27].

The increase in mass [ $M$  (g)] for adsorption was estimated from the QCM frequency shift [ $\Delta F$  (Hz)] using the Sauerbrey equation [27]. The following equation was derived considering the resonator characteristics:

$$\Delta F = -1.832 \times 10^8 M/A$$

where  $A = 0.16 \pm 0.01$  cm<sup>2</sup>, which is the apparent area of the microbalance electrodes. A 1 Hz change in  $\Delta F$  corresponds to 0.87 ng.

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