



Determination of self-exchange rate of alkanethiolates in self-assembled monolayers on gold using matrix-assisted laser desorption/ionization time-of-flight mass spectrometry



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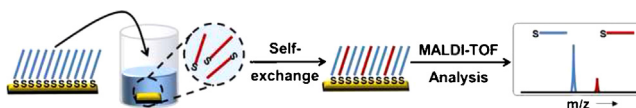
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HIGHLIGHTS

- Exchange rates of alkanethiolates in SAMs on gold were determined by MALDI-TOF MS.
- For the study of self-exchange, a deuterated alkanethiol was designed and prepared.
- It has the same molecular properties as the non-deuterated alkanethiol but a different molecular weight.
- The influences of various conditions on exchange rates were accessed.

GRAPHICAL ABSTRACT



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ABSTRACT

In this paper, we describe a new method for determining the exchange rates of alkanethiolates in self-assembled monolayers (SAMs) on gold using matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) to analyze the compositions of the alkanethiolate in SAMs rapidly and directly. In particular, to investigate the self-exchange of alkanethiols, we prepared a deuterated alkanethiol that has the same molecular properties as the non-deuterated alkanethiol but a different molecular weight. SAMs consisting of deuterated alkanethiolates were immersed in a solution of the non-deuterated alkanethiol, and the influences of the immersion time, temperature, concentration, and solvent on the self-exchange rates were investigated. Furthermore, we assessed the exchange rates among alkanethiols with different carbon chain lengths and different size of ethylene glycol units. In addition, we performed molecular dynamics simulations using a model SAM system in order to understand the molecular mechanism of the exchange process.

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1. Introduction

Self-assembled monolayers (SAMs) of alkanethiolates on gold would be ideal systems for a variety of applications such as sensors, chips, actuators, and molecular electronics because of their

multifarious advantages over other platforms [1–10]. For example, SAMs on gold can be easily prepared by immersing gold-coated materials in alkanethiol or disulfide solutions [11–14] and various conjugation chemistry can be grafted to immobilize essentially any (bio) molecule, including small organic molecules, peptides, oligonucleotides, sugars, and proteins [15–24]. In addition, SAMs on gold are compatible with many analytical and detection tools such as fluorescence microscopy, electron microscopy (EM), surface plasmon resonance (SPR) spectroscopy, electrochemistry,

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X-ray photoelectron spectroscopy (XPS), etc. [9,25–31]. Finally, SAMs on gold are biocompatible and can be made inert to prevent non-specific adsorption of proteins and cells, which is a strict requirement for many biological/biochemical applications [25,32–36].

In general, alkanethiols or disulfides are known to spontaneously form SAMs on gold through chemisorption via metal–sulfur interactions, with two distinct self-assembly steps: (i) fast chemisorption of more than 90% of the thiols onto the gold in a few minutes and (ii) stabilization of monolayer structures by van der Waals and dipole–dipole interactions, which takes several hours [9,14,37]. Although SAMs on gold are decently robust, sulfur–gold bond formation is not inherently irreversible because of the relatively weak bond energy ($\sim 40 \text{ kcal mol}^{-1}$) [14] compared to those of other chemical bonds such as sulfur–carbon ($\sim 75\text{--}90 \text{ kcal mol}^{-1}$) [38] and sulfur–hydrogen ($\sim 84 \text{ kcal mol}^{-1}$) [39] bonds. In fact, the structure of the SAMs on gold is dynamic rather than static in terms of the desorption of alkanethiolates from gold and the ensuing exchange with other alkanethiols in solution [40–42]. Whereas the growth process of SAMs on gold has been well studied [9,14], the desorption of alkanethiolates and exchange with other alkanethiols have not been actively explored due to a lack of effective methods for quantitative analysis. In most applications harnessing SAMs on gold, stability of SAMs should be secured so that the (bio) activity initially incorporated into the SAM is maintained during the experiment to provide reliable results. In this respect, acquisition of information on the stability of SAMs under various experimental conditions will be useful for many applications utilizing SAMs on gold systems. In addition, since the exchange of alkanethiolates in SAMs with other alkanethiols in solution would be an alternative tool for preparing mixed SAMs, the quantitative analysis of exchange rates would be informative and necessary.

Previously, the exchange of alkanethiolates on SAMs was investigated electrochemically by using electroactive ferrocenyl alkanethiols. Chidsey et al. reported the exchange of ferrocenyl alkanethiolates with *n*-alkanethiols in solution [40], and Collard et al. performed a kinetic study on the exchange using a similar system [41]. However, this strategy of using electroactive alkanethiols cannot be applied to alkanethiols without electroactive reporter groups. Therefore, this technique is not appropriate for observing the exchange between alkanethiols with different structures or even exchange between identical alkanethiols. Schlenoff et al. utilized a radiolabeled (^{35}S) alkanethiol to investigate self-exchange between identical alkanethiols on gold surfaces [43]. However, different radiolabel tagging for each alkanethiol would be required for the study of exchange between alkanethiols with different structures. For these reasons, we introduce a new strategy for general use so that the exchange not only between various alkanethiols with different structures but also between identical alkanethiols can be examined.

Our strategy harnesses the compatibility of SAMs on gold with MALDI-TOF MS, termed SAMDI MS, which determines the molecular weight of the constituents of the SAMs [24,44–46].

SAMDI has been used previously to detect products resulting from reactions on SAMs to verify various chemical/biochemical conversions on SAMs. Fig. 1 shows our strategy for the analysis of exchange of alkanethiolates in SAMs with other alkanethiols in solution using SAMDI [47]. A SAM consisting of one alkanethiolate is immersed into a solution of the other alkanethiol under various conditions to allow exchange between the two alkanethiols. The SAM is then directly analyzed by MALDI-TOF MS to determine the exchange rates of alkanethiols based on the relative surface coverage of the two alkanethiolates. In this study, two alkanethiols with the same molecular milieu were prepared for the analysis of self-exchange of alkanethiols in SAMs. We investigated the influences of immersion time, temperature, concentration, and solvent on the self-exchange rates of these two alkanethiols using SAMDI. Furthermore, we investigated the exchange rates between alkanethiols with different structures. Finally, we performed classical molecular dynamics (MD) simulations using a model SAM system to investigate the molecular mechanism of the exchange process. The MD simulations provided significant information about the role of solvents in the initial stage of the exchange process, insertion of alkanethiols into the SAM, in atomistic detail.

2. Experimental

2.1. Materials

Gold coated slides were prepared by vacuum deposition of titanium (10 nm) followed by gold (50 nm) onto #2 glass coverslips. 6-Bromohexane, di(ethylene glycol), carbontetrabromide (CBr_4), triphenylphosphine (Ph_3P), tetrahydrofuran (THF), sodium hydride (NaH), dimethylformamide (DMF), thioacetic acid, 2,2'-azobis(2-methylpropionamide) dihydrochloride (AMPA), 1,4-dioxane, hexane, and 2',4',6'-trihydroxyacetophenone monohydrate (THAP) were purchased from Sigma–Aldrich (St. Louis, MO, USA). Ethylene glycol- D_4 (isotope labeling percentage 98%) was purchased from Cambridge Isotope Laboratories, Inc. (Fr. Andover, MA, USA). Sodium hydroxide (NaOH), methanol (MeOH), and hydrochloric acid (HCl) were purchased from Dae Jung Chemical & Metals Co., Ltd. (Siheung, Korea). Acetonitrile (ACN) was purchased from Jun Sei Chemical Co., Ltd. (Tokyo, Japan). Ethanol (EtOH) was purchased from Merck (Darmstadt, Germany). All chemicals were used without further purification.

2.2. General

Gold chips were cleaned in piranha solution (sulfuric acid/hydrogen peroxide (30%) = 70:30; use caution, it is extremely hot and corrosive) before use. A gold chip was immersed into a solution of alkanethiol in EtOH (1 mM) for 12 h. The resulting SAM was rinsed with distilled water and EtOH and dried under a stream of nitrogen. After incubation under various conditions as described below, the SAMs were rinsed with distilled water and EtOH, dried under a stream of nitrogen, and then analyzed by MALDI-TOF MS.

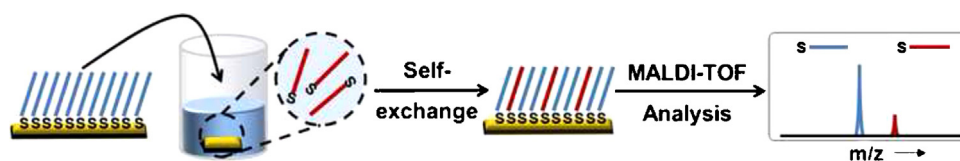


Fig. 1. Schematic diagram for the analysis of the exchange of alkanethiolates in SAMs with other alkanethiols in solution using MALDI-TOF MS. A SAM consisting of one alkanethiolate is immersed in a solution of the other alkanethiol under different temperatures, concentrations, or solvents for various time periods. The SAM is then directly analyzed by MALDI-TOF MS, which allows the exchange rates to be investigated by measuring the relative surface coverage of two alkanethiolates in the SAM.

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