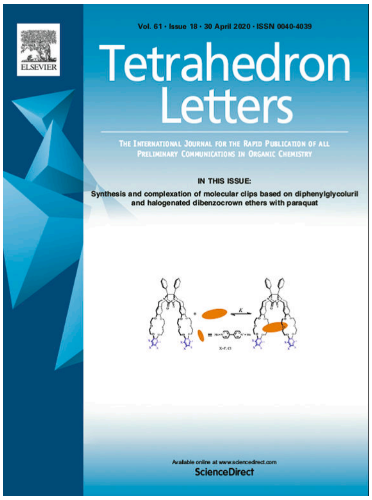

An Environmentally Friendly Lipophilic Coating of Metal Surface

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An Environmentally Friendly Lipophilic Coating of Metal Surface

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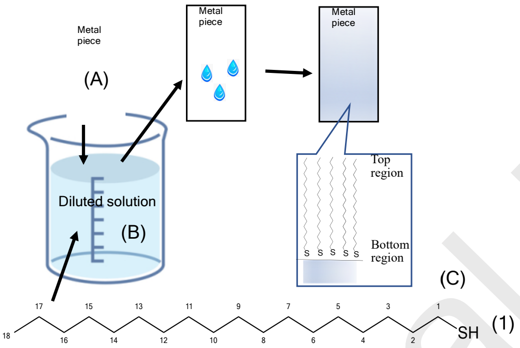
ABSTRACT
An environmentally friendly coating method of lipophilic thiols on metal surface is described. Lipophilic thiols were chemically modified to a water-soluble derivative, prepared from lipophilic thiol, succinic linker, and symmetrically branched oligoglycerol. Due to the chemical modification, water was used as a solute of coating reagent. The anticorrosive effect of metal piece with the water-soluble derivative in water was as high as with lipophilic thiol in organic solvent.

Keywords: Water-solubility, Environmentally Friendly, Symmetrically branched oligoglycerols, Anticorrosive

Introduction

Since Nuzzo *et al* found the disulfide adsorption on a gold surface [1], a lipophilic organothiol (RSH) has been often used as an anticorrosive for metal [2]. Among various RSH, octadecane-1-thiol (**1**) has been one of the most representative chemicals [3] (Scheme 1).



Scheme 1. Major coating procedure by using octadecane-1-thiol (**1**).

A target such as a piece of metal (**A**), is dipped into a diluted solution of **1** (**B**). During this operation, a strong coordination is generated between zero-valent metal surface and the thiolate generated from **1** to afford "self-assembled monolayers" (SAM) [3], as shown in (**C**). No further layers are assembled on the surface of metal after the SAM is created, because the top region shown in (**C**) is occupied with only chemically inert alkyl chains, which can generate no strong chemical bond such as covalent, ionic or dipole moment interaction. Accordingly, a very thin and stable coating completes via the simple procedure illustrated in Scheme 1. Due to such a thin layer, electroconductivity of the target metal is often retained after the coating procedure, in general. In contrast, required property of rust anticorrosive is often satisfied, in spite of such a thin layer [3].

Due to high lipophilicity of **1**, organic solvents*, a lipophilic and volatile liquid,* has been required for the coating procedure. If such an organic solvent could be displaced to water, it would be *environmentally friendly*. In addition, total cost, including purchased price and waste disposal costs, would be reduced, because the solute occupies major weight and volume of the commercial package such as (**B**). However, RSH possessing a long hydrocarbon chain is extremely insoluble in water. Although it has been reported that a large amount of surfactant was used to prepare a micellar solution [4], it means a top priority backwards since surfactant often facilitates rust.

Although a commercially available water-affinitive RSH such as oligoethyleneglycolated alkanethiols (**2**) [5,6,7] can be an alternative idea, property of the top region with **2** can be totally different from that with **1** (Fig 1). Accordingly, **2** can be incompatible to lipophilic thiol and use of organic solvent has been indispensable for lipophilic thiolate coating.

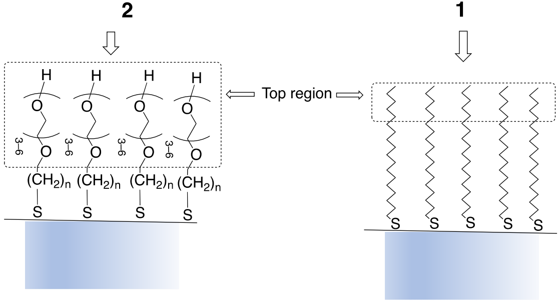
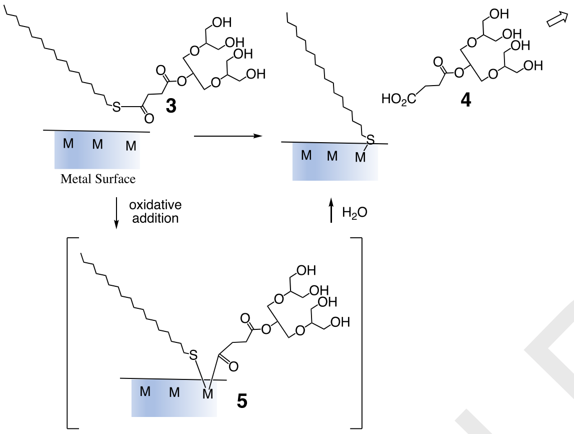


Figure 1. Comparison between **1** and a commercially available water-affinitive thiol **2** after coating procedure.

In this paper, we report a preparation method of lipophilic-thiolate-chemisorbed SAM on metal ((**C**) in Scheme 1) *in an aqueous solution*. In this method, original lipophilic thiol was modified to a water-soluble derivative such as **3** [8] (Scheme 2). Due to the result in a previous paper [9], it is anticipated that the thioester moiety of **3** is cleaved to afford the corresponding oxidative adduct **5**, followed by releasing the water-solubilizing fragment **4** into an aqueous solution. The fragment **4** can be finally converted to succinic acid [10] and BGL003 [11,12] (Fig 2), both of which are known to have extremely low toxicity. Accordingly, the released fragment **4** is also designed to be environmentally friendly.



Scheme 2. Proposed mechanism of metal surface coating with thioester **3**.

As a water-solubilizing fragment, our originally developed molecules, glycerol trimer BGL003 [13,14] and heptamer BGL007 [14] were used. Various functional groups X at apex have been used for the covalent bond formation with poorly water-soluble compounds [15,16,17] such as **1**. Primary hydroxy groups, four in BGL003 and eight in BGL007, respectively (terminal side of the dendric structure), have stronger water-affinitive property than another polyhydroxylated molecules such as cyclic carbohydrates, due to the high conformational flexibility and three-dimensional spread.

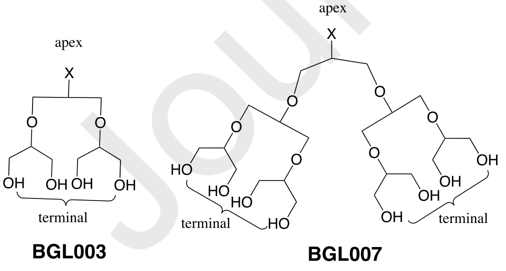
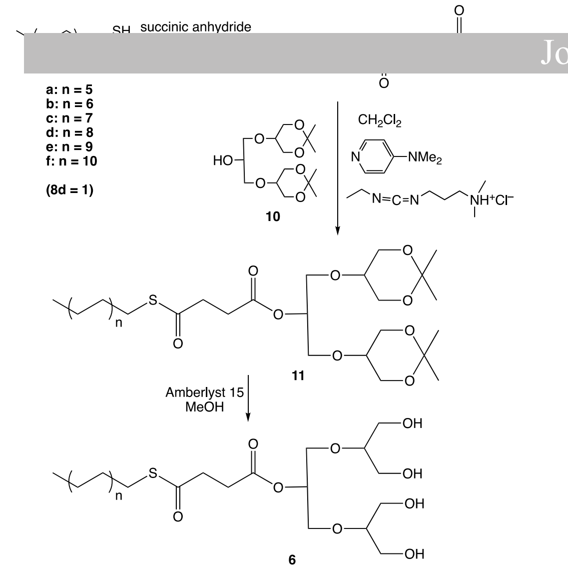


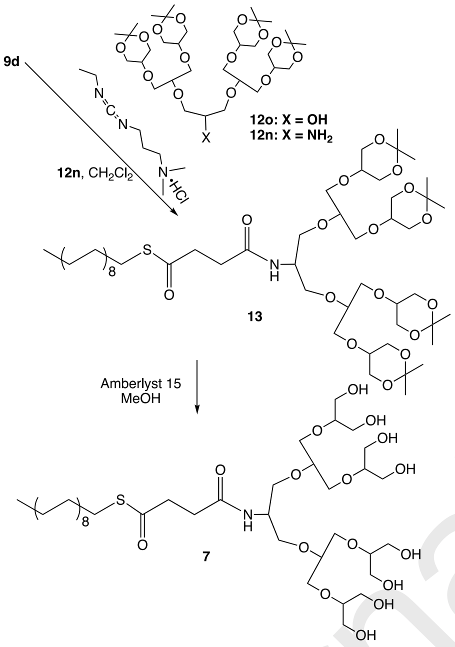
Figure 2. Our originally designed symmetrically branched glycerol trimer and heptamer.

Synthesis

In Scheme 3, the detail of the synthetic procedure of **3** (=**6d**) as well as the related derivatives **6a–6c**, **6e** and **6f** is illustrated. The reaction of **8** with succinic anhydride in pyridine afforded thioester **9** in a range of 87–96% chemical yield. Condensation between the alcohol **10**, and carboxylic acid **9** was carried out in dichloromethane with 3-(((ethylimino)methylene)amino)-*N*,*N*-dimethylpropan-1-aminium chloride (EDC•HCl) and 4-(N,N-dimethyl)pyridine (DMAP) to give the corresponding ester **11** in a range of 75–88% yield. Finally, **11** in anhydrous methanol was stirred for several hours in the presence of Amberlyst-15®, an acidic polystyrene polymer, to afford tetraol **6** in a range of 83–98% yield.



Scheme 3. Synthesis of various alkanethiol–BGL003 **6a–6f**.



Scheme 4. Synthesis of octadecane-1-thiol–BGL007 **7**

Next, instead of BGL trimer **10**, condensation of BGL heptamer **12o** [14] and **9d** was examined (Scheme 4). However, chemical yield of the corresponding ester was extremely low with almost quantitative recovery of both **12o** and **9d**. Therefore, more nucleophilic amine **12n** [14] was used instead to afford **13** in 25% yield. We did not optimize this step further, because water-solubility of smaller BGL derivative **6d** was high enough as mentioned later in this paper. Methanolic deprotection of **13** under acidic condition was carried out with Amberlyst-15® to afford octaol **7** in 93% yield.

Property and performance of a water-soluble thiol

Water-solubility of the final product was examined as follows. Water after distillation and deionization (50.09 g) and **6d** (0.320 g, 0.526 mmol) and was mixed. Although small drops of **6d** were visibly observed in the initial mixture, homogeneous solution was afforded after stirring for 6h at 60˚C. After the solution was cooled to room temperature, homogeneity of the solution was maintained. Accordingly, water-solubility of **6d** was recorded to be over 10.0 mmol/L with a large margin. ^{1}H NMR analysis indicated that pure **6d** was observed after the aqueous solution was stocked for three months at room temperature in a simple screw-capped plastic bottle.

For usual anticorrosive treatment in an organic solvent, less than 5.00 mmol/L of thiol has been usually reported [3,4]. Therefore, the prepared solution (10.0 mmol/L) was diluted with water again. By using the diluted aqueous solution of **6d**, various examinations such as observation by digital microscope, reflection of visible light (380–780 nm), measurement of the contact angle of small water-droplet, and resistance against hydrogen sulfide gas was carried out. Among these comparisons, the results with aqueous potassium sulfide solution (K_2Saq) were representatively [18] described (Fig 3).

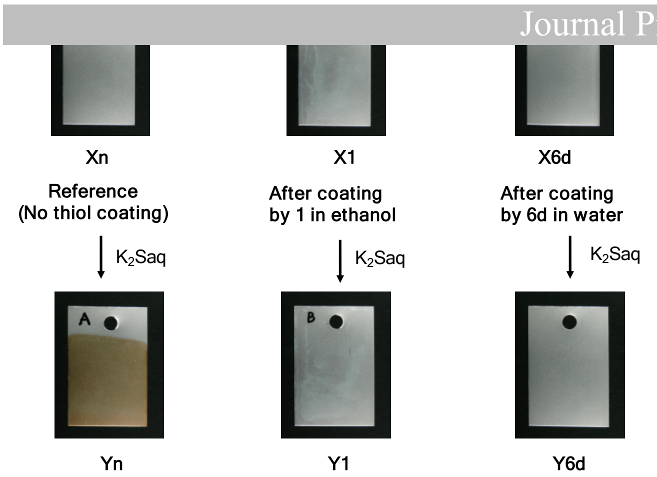


Figure 3. Color change of silver plates after aqueous K_2S (0.6 wt%) soaking

Three pieces of silver-plating metal (30 mm length) were prepared from commercially available long strings (20 mm width, 0.2 mm thickness). The three pieces were washed with deionized water, and dried at 100–120˚C for 5 sec to afford **Xn**, **X1** and **X6d**. The pieces **X1** and **X6d** were dipped into **1** in ethanol (0.1 wt% = 3.50 mmol/L) [19] and **6d** in water (0.2 wt% = 3.30 mmol/L) at 55˚C for 30 sec, respectively, and washed with deionized water, and dried at 100–120˚C. No pre-treatment was carried out for **Xn**. After being cooled to room temperature, all the three pieces **Xn**, **X1** and **X6d** were soaked with K_2Saq (0.6 wt%) at 22˚C for 1 min. Then, these surfaces were washed with deionized water at 22˚C and dried at 100–120˚C for 5 sec to afford **Yn**, **Y1** and **Y6d**, respectively.

The color of **Yn** was dark yellow, which indicated the direct effect from K_2Saq. In contrast, color change from **X1** to **Y1**, as well as from **X6d** to **Y6d**, was highly suppressed. It is noteworthy that mottled pattern was partially observed in **Y1** [20] but smooth surface was observed in all the area of **Y6d**.

Conclusion and perspective

In conclusion, synthesis of organothiol–BGL003 was successfully carried out within a few steps in high chemical yields. A thioester of each synthetic intermediate was stable during the following chemical reactions (carbodiimide condensation and methanolic solvolysis under acidic condition). In contrast, the thioester in the organothiol–BGL003 was probably cleaved to release original organothiol *in situ* at the metal surface. Accordingly, predictable result after coating with organothiol–BGL003 in water is as exactly same as with organothiol in organic solvent, due to the molecular design of organothiol–BGL003.

In fact, anticorrosive performance of organothiol–BGL003 in water was as high as, or slightly higher than, that of organothiol in organic solvent. We believe that the result reported in this paper will solve one of the environmental problems. To deploy this result for the practical use, the synthetic process in a large scale is under optimization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

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18. Water (10 mL) and 6d (1 mg) were mixed, and the resulting milky liquid was heated for 5h at 60˚C to convert to homogeneous solution. After evaporation of the solvent, ^{1}H NMR analysis of the residue indicated no hydrolysis.
19. Detail of other examinations are planning to be submitted to the more suitable journals such as *Surface & Coating Technology.*
20. At early period, lipophilic thiol was used as a solution of halogenated hydrocarbons such as 1,2-dichloroethane [3], which is negative impact on the environment. After the use of such a solvent was strictly prohibited under the law in various countries, ethanol has been used instead.
21. When the experiment reported in Figure 3 was carried out, the solution of **1** in ethanol was slightly cloudy. The solubility of **1** in ethanol was not as high as expected. Due to the inhomogeneity, the mottled pattern may be generated on the surface of **Y1**.

Supplementary Material

Supplementary material can be found online at https://doi.org/10.1016/j.tetlet.XXXX.XXXX.

Environmentally friendly anticorrosive

Symmetrically branched oligoglycerols

thioester

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Graphical Abstract

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