

A new utilization of organic molecules for nanofabrication using the molecular ruler method

Takami Hino^a, Hirofumi Tanaka^{a,b,c,*}, Hiroaki Ozawa^{a,b}, Yuko Iida^{a,b}, Takuji Ogawa^{a,b,c,*}

^a Research Center for Molecular-Scale Nano Science, Institute for Molecular Science, Higashiyama 5-1, Myodaiji, Okazaki, Aichi 444-8787, Japan

^b The Graduate University for Advanced Studies, Higashiyama 5-1, Myodaiji, Okazaki, Aichi 444-8787, Japan

^c CREST, JST, Honcho 4-1-8, Kawaguchi, Saitama 332-0012, Japan

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Abstract

Oligothiophenes and porphyrin oligomers were exploited as new molecules for the “molecular ruler” (MR) method in the form of simple molecular monolayers. When handled in air, oligothiophenes yielded extremely homogeneous nanogaps about 30 nm wide, while handling under N₂ produced nanoscale gaps of around 10 nm between parent and daughter structures. The difference between these two results indicated that it was possible to control the width of this gap by varying the extent of oxidation of the oligothiophenes. Porphyrin oligomers also yielded nanogaps about 10 nm wide. Therefore, these two types of molecules are promising candidates for use in the MR methods.

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1. Introduction

The development of a convenient bottom-up technique for precise fabrication of nanostructures to allow downsizing of electronic devices has been aggressively pursued in recent years, because the commonly used top-down techniques such as electron-beam lithography [1,2] and scanning probe lithography [3–7] face several physical limits in fabricating continuous well-defined sub-nanometer scale structures. One of the most promising techniques is the combination of conventional lithography with the molecular ruler (MR) method, which utilizes multilayers composed of a chemical self-assembled monolayer (SAM) of organic molecules and metal ions grown on the parent metal structures [8–12]. This approach enables the fabrication of homogeneous 10–100 nm scale nanogaps between parent and daughter structures by controlling the number of these layers deposited [8–12]. However, defects are occasionally found in these structures when the method is used to make gaps of less than 10 nm. These defects indicate that the SAM did not grow densely and that the daughter metal penetrated through

the defects to the parent metal when the MR was less than 10 nm thick. Additionally, it is difficult in practice to use the MR method in industrial settings due to the time-consuming process of fabricating multilayers. It is desirable, therefore, to be able to form nanogaps using just a single layer, in order to minimize the number of steps in the process.

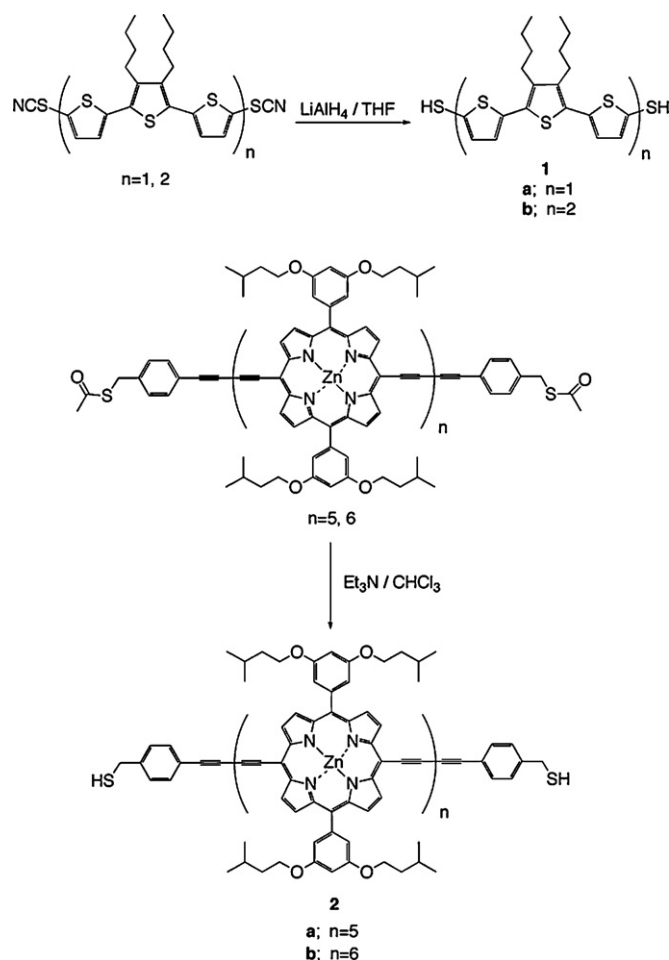
Accordingly, we explored the use of oligothiophenes **1** and porphyrins **2** as possible materials for the fabrication of defect-free SAMs on metal, because adjacent molecules of these species may be expected to adhere to one another due to intermolecular π – π stacking interactions (Scheme 1). Moreover, the use of these molecules should allow tuning of the gap size by varying the molecular length.

2. Experimental

All reagents and solvents were of analytical grade and were used without further purification. Thiocyanato derivatives of the oligothiophenes and *S*-acetylthio derivatives of the porphyrin oligomers used in the present study were prepared according to literature procedures [13,14]. Parent structures consisting of a 200 nm thick Au layer on a 10 nm Cr buffer layer were deposited onto a SiO₂ substrate using UV lithography. A SAM composed of organic molecules was then applied (see pro-

* Corresponding authors. Tel.: +81 564 5537; fax: +81 564 5537.

E-mail addresses: htanaka@ims.ac.jp (H. Tanaka), ogawat@ims.ac.jp (T. Ogawa).

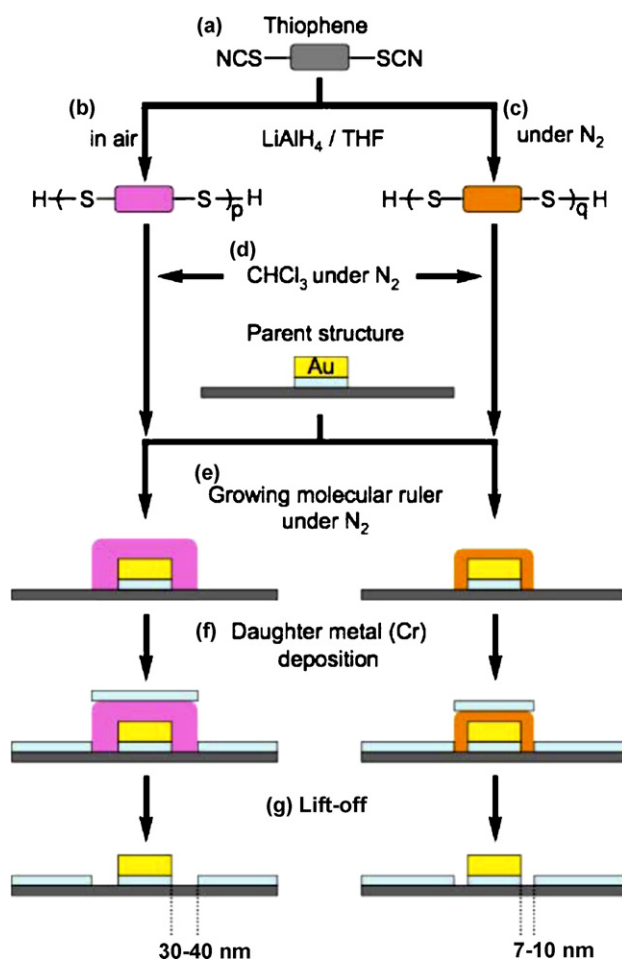


Scheme 1. Preparation of organic molecules used in the present study.

cedure below), and then a daughter structure consisting of a 10 nm thick Cr layer was evaporated onto the parent structure. The substrates were sonicated for 1 min in deionized water and then immersed in ACT935J (Nagase ChemteX Corporation) for 30 min at 70 °C to lift off the SAM resist. This lift-off process was repeated several times until the SAM was totally removed. Scanning electron microscopy (SEM) images were obtained with a JEOL JSM-6700F microscope at an acceleration voltage of 5–7 kV.

Scheme 2 shows the procedure for fabricating the MR nanostructure using oligothiophenes, and the results of the process. Oligothiophenes **1** were obtained from thiocyanato oligothiophenes by reaction with LiAlH_4 in air [13]. The SiO_2 substrate patterned with Au parent structures was washed with ACT935J before use, and then immersed in a CHCl_3 solution of **1** (1 mM) for 16 h under N_2 . The substrate was then washed with CHCl_3 and dried in a stream of N_2 . Separately, reduction of the thiocyanato oligothiophenes was performed under N_2 (Scheme 2) in order to avoid possible oxidative polymerization that would yield gaps wider than the original molecular length.

The other MR procedure was performed using porphyrin oligomers **2**. The Au-patterned SiO_2 substrates were immersed in CHCl_3 solutions of 4-(*S*-acetylthiomethyl)phenyl functionalized porphyrin (0.02 mM, 2 mL), to which was added 10 μL



Scheme 2. Schematic procedure for fabrication of nanogaps from oligothiophenes **1**, and results of the procedure. (a) Thiocyanato oligothiophenes. (b) Reduction by LiAlH_4 in air. (c) Reduction by LiAlH_4 under N_2 . (d) Preparation of CHCl_3 solutions of the oligothiophenes. (e) Immersion of SiO_2 substrates patterned with Au parent structures (with Cr buffer) in CHCl_3 solutions under N_2 . (f) Evaporative deposition of Cr daughter structures. (g) Lift-off of the molecular ruler.

Et_3N as a deprotecting agent, for 16 h under N_2 . They were then washed thoroughly with CHCl_3 and EtOH and dried in a stream of N_2 .

3. Results and discussion

3.1. Oligothiophenes

SEM images of the structures fabricated using oligothiophenes **1** prepared in air revealed very uniform nanogaps of about 38 and 24 nm for **1a** and **1b**, respectively (see Fig. 1). These results indicated that the SAM lift-off process proceeded smoothly and that these oligothiophene molecules were promising candidates for the fabrication of nanogaps. The widths of these gaps were, however, much larger than the molecular lengths (1.36 and 2.16 nm for **1** and **2**, respectively). There were two possible reasons for this: (i) the molecular lengths may have increased due to oxidative formation of disulfide bonds between the thiol groups or (ii) the oligothiophene molecules may have

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