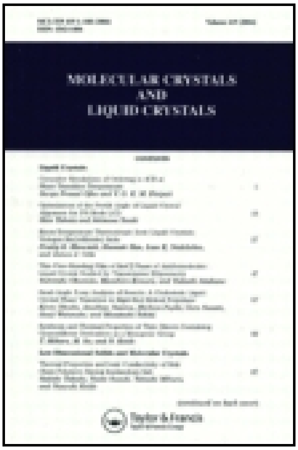

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Deep UV Photopatterning of Biphenyl Thiol Self-Assembled Monolayer and its Physical Properties

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Version of record first published: 12 Mar 2007

Mol. Cryst. Liq. Cryst., Vol. 463, pp. 229/[511]–236/[518], 2007

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400601027981

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Aromatic thiol such as a 4′-mercapto-biphenyl-4-carboxylic acid was synthesized, and then the self-assembled monolayer (SAM) was fabricated on a gold substrate. The pattern formation of biphenyl thiol and alkanethiol SAMs was obtained by oxidation reaction due to the irradiation of deep UV light. The resulting positive pattern image and current-voltage (I-V) characteristics of biphenyl thiol and alkanethiols were investigated through the measurements of Atomic Force Microscope (AFM) and Scanning Tunneling Microscope (STM). In addition, cytochrome c protein was immobilized onto the patterned gold substrate by self-assembly technique and electrochemical activity was studied with a cyclic voltammetry.

Keywords: biphenyl thiol; current-voltage characteristic; cytochrome c; electrochemical activity; self-assembled monolayer; UV photopatterning

INTRODUCTION

Over the past several years, self-assembled monolayers (SAMs) have attracted much attention because of their scientific interest in two-dimensional molecular assemblies and their potential applications in molecular device, sensor and surface engineering etc. [1–4]. The

This work was supported by the Korean Research Foundation Grant (KRF-2004-005-D00003).

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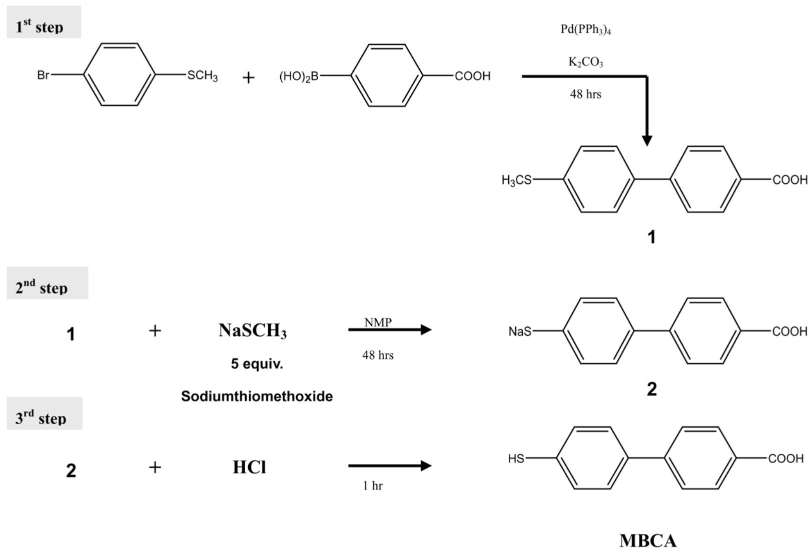
structure of SAMs can be finely controlled and modified by attaching a wide range of molecules that provide different functions to the SAMs. SAMs allow the formation of a variety of surfaces with specific interactions and fine structural control. Especially, modified SAMs have been used in studies of molecular recognition [5], biomolecular receptor [6], cell growth [7], crystallization [8], and many other systems [9].

In general, alkanethiols having carboxylic acid in the tail group have been used in the fabrication of self-assembled biomolecule monolayers [10–12]. However, the electroactivity and sensitivity of biosensor or bioelectronic device using the alkanethiol as biomolecular receptor were very low due to the flexible nature of carbon chains and poor electrical conductivity. The electrical conductivity of aromatic thiol is high due to the conjugated backbone system, and also aromatic thiol SAMs show good packing structure because of interchain interaction between benzene groups. In the present work, we have synthesized 4′-mercapto-biphenyl-4-carboxylic acid as biomolecular receptor, and then fabricated pattern of biphenyl thiol SAM by photochemical conversion of thiol to sulfonate with a deep UV light. In addition, cytochrome c protein was immobilized onto the patterned gold substrate. Also, we report the pattern image and the electrochemical activity of biphenyl thiol with a high electrical conductivity and conventional alkanethiols.

EXPERIMENTAL

4-carboxyphenylboronic acid, 4-bromothioanisole, tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$), sodiumthiomethoxide, 3-mercaptopropanoic acid (3-MPA), 11-mercaptoundecanoic acid (11-MUDA) and cytochrome c (extracted from horse heart muscle) were purchased from Aldrich Chemical Co., (USA). Au (111) substrate was purchased form INOSTEK Inc. (Korea). N,N-dimethylformamide (DMF), ethyleneglycoldimethylether (DME), N-methyl-2-pyrrolidinone (NMP), methanol and ethanol were distilled from first grade solvents purchased on the market.

Synthesis of 4′-mercapto-biphenyl-4-carboxylic acid (MBCA) was carried out according to the synthetic routes as shown in Scheme 1. 4′-methylsulfanyl-biphenyl-4-carboxylic acid (1) was synthesized by Suzuki coupling using approximately 6.12 g (0.03 mol) of 4-bromothioanisole and 5.0 g (0.03 mol) of 4-carboxyphenylboronic acid in the presence of 5 mol% of $Pd(PPh_3)_4$, 2 M K_2CO_3 aqueous solution and 100 mL DME solvent. The reaction was carried out under nitrogen atmosphere at 80°C for 18 hrs. The reaction mixture was filtered through a glass filter and washed with distilled water. The crude



SCHEME 1 Synthetic routes of MBCA.

product was recrystallized from methanol (yield: 94%). 4′-sodiummercapto-biphenyl-4-carboxylic acid (2) was synthesized by reaction of 1 and sodiumthiomethoxide (5 equiv.) in NMP solvent under nitrogen. The reaction ran at 100°C for 48 hrs and the NMP solvent was vacuum distilled. The final product, MBCA, was prepared by the reaction of 2 and hydrochloric acid in aqueous solution for 1 hr. The reaction mixture was filtered through a glass filter and washed with distilled water. The residual MBCA powder was dried under vacuum at 40°C for 24 hrs (yield: 25%). Elemental analysis; Calculated C: 67.80%; H: 4.38%; S:13.92%; Found C: 67.51%; H: 4.50%; S: 14.13%.

Gold substrate was immersed into 5 mM MBCA DMF solution for 48 hrs. The substrate was washed with DMF and ethanol, and then dried in nitrogen stream. Successful formation of MBCA SAM was identified by FT-IR analysis (Infiniti gold FT-IR 60AR, Thermo-mattson, USA).

Photopatterning of MBCA SAM was carried out with an exposure system of Spectral Energy Co., equipped with a 500 W high-pressure mercury lamp in conjunction with a narrow band pass filter for 254 nm. The self-assembled MBCA monolayer on a gold substrate was oxidized by deep UV light irradiation, and then developed with deionized water. The pattern image was investigated using an AFM (AutoProbe CP, Park Scientific Instruments, USA). Cytochrome c was adsorbed on the MBCA SAM by immersing the patterned gold substrate in a 30 μmol phosphate buffer solution (pH 7.2) containing 50 μmol cytochrome c for 12 hours, followed by thorough rinsing with the buffer solution and deionized water. Cyclic voltammetry measurement was carried out with a potentiostat measurement analyzer (IM6 system, Zahner Elektrik Co., Germany). The Ag/AgCl (3.0 M KCl) for reference electrode, a gold working electrode and a 1-cm^2 Pt-gauze counter electrode were used for the cyclic voltammetry measurements. The I-V characteristics of biphenyl thiol and alkanethiol SAMs were studied by a STM (BT00642, Nano Surf AG, Switzerland) technique. The set point for Au tip approaching was 0.5 nA and the scan range for conductivity measurement was $-1 \sim 1$ V. Cyclic voltammetry was also carried out for measuring electrochemical activities of the fabricated SAMs in potassium ferricyanide solution (0.01 M Phosphate buffered saline, 0.138 M NaCl, 0.0027 M KCl and 1 mM $K_3Fe(CN)_6$ in deionized water).

RESULTS AND DISCUSSION

The synthesized MBCA compound was identified through the measurements of elemental analysis and FT-IR. The FT-IR spectrum of MBCA was shown in Figure 1a. The spectrum of MBCA showed the absorption peaks corresponding to thiol and carboxylic groups, e.g., O–H stretching at 3000 cm^{-1}, S–H stretching at 2550 cm^{-1} and C=O stretching at 1700 cm^{-1}. The bands near 1650 cm^{-1} and 1450 cm^{-1} corresponded to C=C stretching of a benzene ring. Figure 1b showed the FT-IR spectrum of MBCA SAM fabricated on a gold substrate. The FT-IR measurement was carried out by attenuated total reflectance method. The spectrum of MBCA SAM was similar to the result of MBCA compound. It can be concluded that the successful preparation of MBCA SAM was confirmed through FT-IR analysis.

Photopatterning of MBCA SAM onto the gold substrate was carried out with a 7 μm positive mask by the irradiation of deep UV light. Sulfonates oxidized in the exposed regions were developed thoroughly with deionized water. The UV irradiation time for patterning of alkanethiol and biphenyl thiol SAMs was 2 hrs and 5 hrs, respectively. This result was obtained from the measurements of contact angle after UV irradiation. In order to explore the patterned image, the gold substrate was etched in an aqueous solution of KCN 0.1 M and KOH 1 M. Figure 2 showed the AFM image. The patterned MBCA SAM surface regions exhibited bright contrast while exposed regions exhibited dark contrast because of the difference in percolation rate of etching solution. It can be found that positive pattern of MBCA monolayer

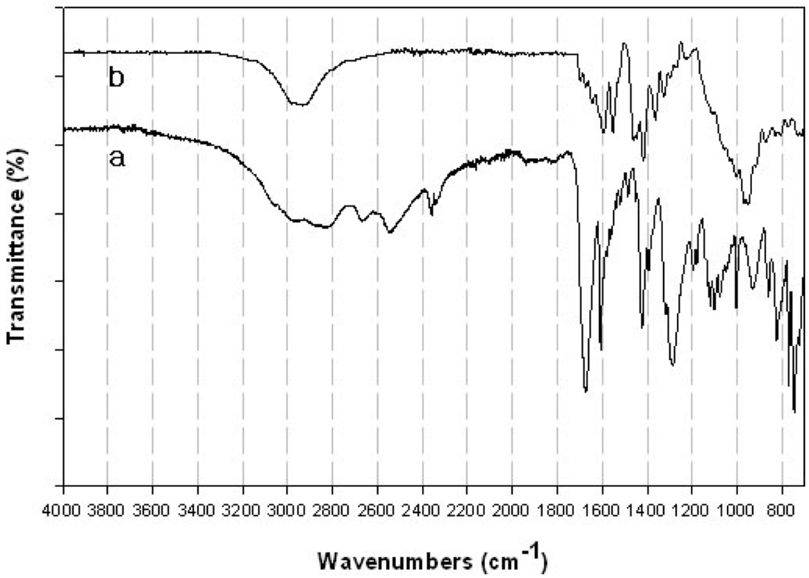


FIGURE 1 FT-IR spectra of MBCA and MBCA SAM. a) MBCA, b) MBCA SAM.

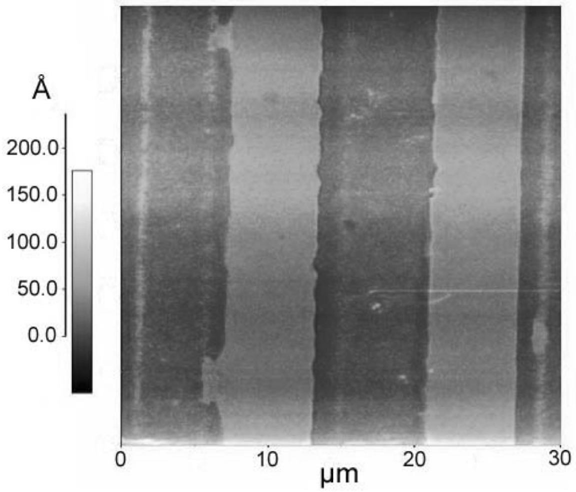


FIGURE 2 AFM image of photopatterned MBCA SAM.

with a 7 μm line was obtained by the photochemical conversion of thiols to sulfonates.

Figure 3 showed the I-V characteristics for an Au probe in contact with biphenyl thiol and alkanthiol SAMs. The electron transfer between the SAMs surface and STM probe has occurred, when a voltage was biased in the range $-1 \sim 1\,V$. The current of biphenyl thiol was higher than that of alkanethiol because of low gap resistance due to the conjugated backbone structure. Figure 4 showed the cyclic voltammograms of cytochrome c protein immobilized onto the each SAMs. The electrochemical activity of cytochrome c immobilized onto the biphenyl thiol SAM was higher than that of alkanethiol. In order to explore the effect of biphenyl thiol biomolecular receptor having high electrical conductivity on the performance of electoactivity of cytochrome c, cyclic voltammetry measurements of each SAMs and bare gold substrate in potassium ferricyanide solution was carried out. The biphenyl thiol SAM in potassium ferricyanide solution allowed high electrochemical activity compared to the alkanethiol SAMs as shown in Figure 5. Both results derived from cyclic voltammetry measurements indicated that high electrochemical activity of cytochrome c immobilized onto the biphenyl thiol SAM is mainly due to the difference in charge transport between cytochrome c and self-assembled molecular wire.

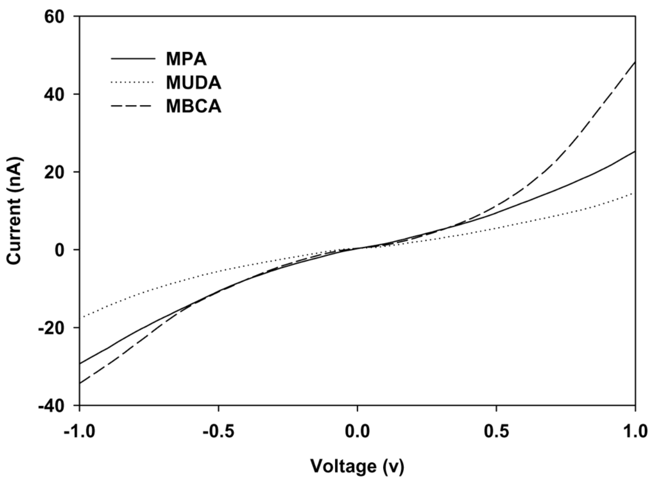


FIGURE 3 STM *I-V* characteristics of MPA, MUDA and MBCA monolayer junctions.

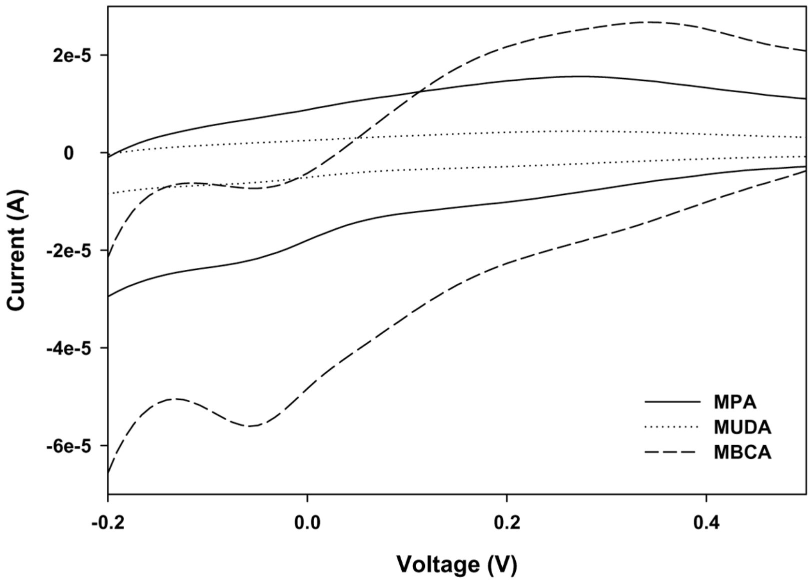


FIGURE 4 Cyclic voltammograms of cytochrome c immobilized onto the biphenyl thio and alkanethiol SAMs.

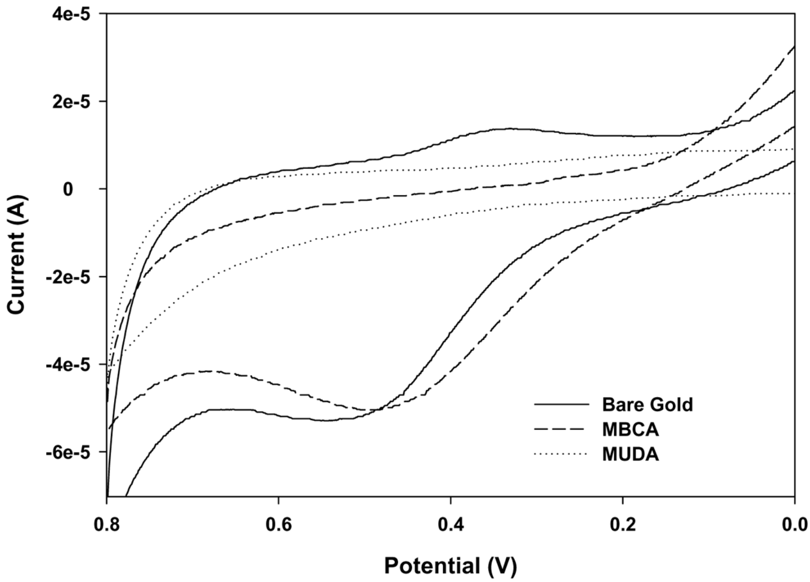


FIGURE 5 Cyclic voltammogram of Bare gold, MBCA SAM and MUDA SAM in potassium ferricyanide solution.

CONCLUSIONS

Micropattern of self-assembled biphenyl thiol monolayer on a gold substrate was obtained by photochemical oxidation using a 7 μm positive mask. Cytochrome c molecules were well self-assembled onto the positive patterned gold substrate. It can be found that cytochrome c protein immobilized onto the biphenyl thiol SAM was very effective in a view of electrochemical activity. Thus, it should be noted that aromatic thiol as a conducting bioreceptor exhibited the feasibility of application in biosensor or bioelectronic device using electrochemical activity.

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