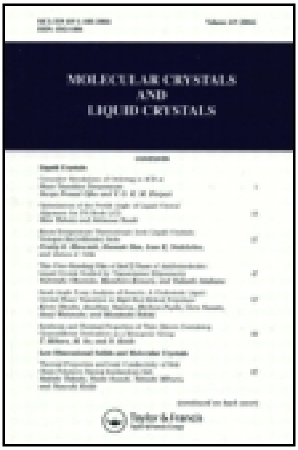

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CATIONIC SELF-ASSEMBLED MONOLAYERS COMPOSED OF GEMINI-STRUCTURED SULFUR COMPOUNDS ON GOLD: A NEW APPROACH TO CONTROL IONIC FUNCTIONS ON SURFACES

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CATIONIC SELF-ASSEMBLED MONOLAYERS COMPOSED OF GEMINI-STRUCTURED SULFUR COMPOUNDS ON GOLD: A NEW APPROACH TO CONTROL IONIC FUNCTIONS ON SURFACES

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Cationic self-assembled monolayers (SAMs) composed of quaternary ammonium (QA) sulfur derivatives have been synthesized to control a position and a distance between charged head groups on gold substrates. Three molecules bearing resembling molecular structures, "gemini"-structured didodecyl dithiol (HS-gQA-SH), didodecyl disulfide (QA-SS-QA), and gemini-structured didodecyl disulfide (gQA-SS-gQA), were utilized in this study, and the formation and structure of the SAMs were characterized by surface plasmon resonance spectroscopy (SPR).

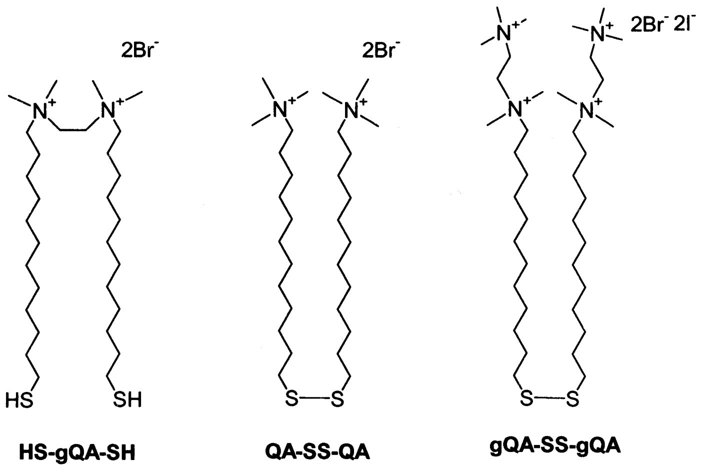
Keywords: gemini (dimeric) surfactant; quaternary ammonium group; self-assembled monolayer; surface plasmon resonance

INTRODUCTION

Self-assembled monolayers (SAMs) composed of organosulfur compounds on novel metals (e.g., gold and silver) have shown the great promise as a means of controlling two dimensional (2D) chemical structure on solid support [1]. A charged 2D surface as an analog of 3D aggregates composed of ionized surfactants can be easily created by self-assembling technique with thiol derivatives having ionized functional groups, such as carboxylate and quaternary ammonium (QA) [2–5]. Whitesides and co-workers fabricated the electrostatic SAMs having positive, negative and both charged terminal groups [5,6]. However, electric repulsion forces between charged groups prevent to form fully adsorbed SAMs, and the ellipsometric thickness of the SAMs estimated was much smaller than the molecular length.

Recently, we combined both the interests concerning the gemini surfactants [7] and the functional SAMs, and studied cationic SAMs composed of QA sulfur derivative with the gemini structure (HS-gQA-SH: Scheme 1, left) on gold [8]. The covalent bonding between QA groups in HS-gQA-SH resulted in the higher density of the SAM compared with that of a didodecyl disulfide derivative (QA-SS-QA: Scheme 1, center) SAM. We also observed the selective adsorption of L-tartaric acid on the SAMs. The strong affinity between the gemini surfactants and L-tartaric acids was interpreted by matching of the lengths between the charged functional groups controlled by ethylene spacer units.

In this paper, we synthesized a new QA sulfur derivative, gQA-SS-gQA (Scheme 1, right), that is a disulfide with gemini-structured QA functions



SCHEME 1 Molecular structures of HS-gQA-HS, QA-SS-QA and gQA-SS-gQA.

in both chains. The formation and structure of this cationic SAMs are characterized by surface plasmon resonance spectroscopy (SPR), and are compared with those of HS-gQA-SH and QA-SS-QA SAMs.

RESULTS AND DISCUSSION

In Figure 1, we compared the adsorption kinetics of gQA-SS-gQA on gold with these of HS-gQA-SH and QA-SS-QA. All the SAMs were formed in about 50 minutes from 0.1 mM methanol solutions, though the formation of QA-SS-QA SAM was a little slower than the other two. All the SAMs are stable against rinsing with absolute methanol as shown in Figure 1.

We determined both the refractive index (n) and the thickness (d) of the SAMs from SPR data taken in various solvents with different refractive indices (the contrast variation SPR measurement [9]). Figure 2 shows the simulation results of n and d estimated from the SPR peak shift by an angular scans in methanol, ethanol and air. If there is no solvent effect, such as swelling or adsorption of contaminants, the three simulated curves must have one intersection point which indicates the "real" n and d of the SAMs. The thickness values and refractive indices of the HS-gQA-SH, QA-SS-QA and gQA-SS-gQA SAMs estimated from Figure 2 were listed in Table 1. The thickness of the gQA-SS-gQA SAM was much smaller than HS-gQA-SH and QA-SS-QA SAMs ($d = 18.0 \pm 3$ Å). On the other hand, the estimated refractive index of gQA-SS-gQA is slightly higher than the other

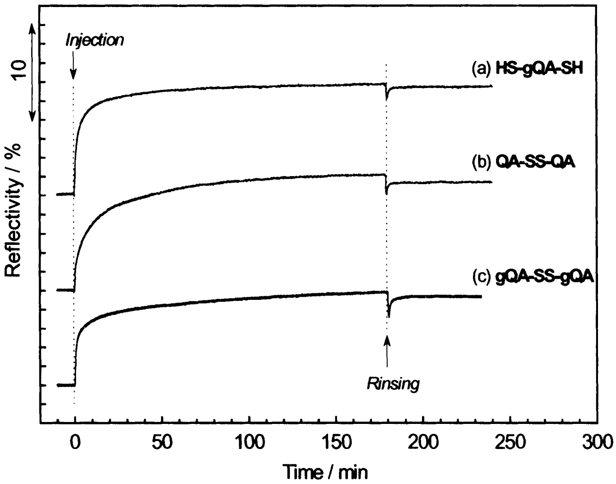


FIGURE 1 Adsorption kinetics of HS-gQA-HS (a), QA-SS-QA (b) and gQA-SS-gQA (c) on gold from 0.1 mM methanol solutions.

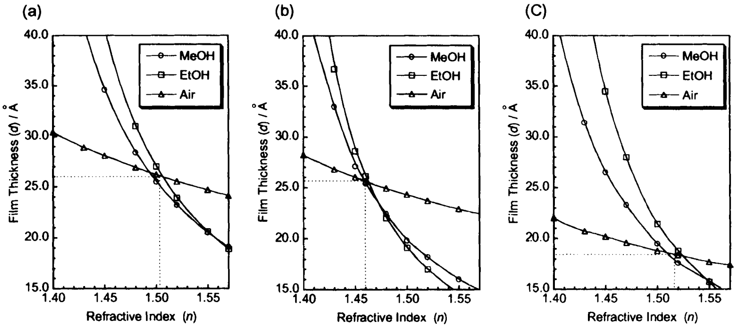


FIGURE 2 Film thickness (d) versus the refractive index (n) determined for HS-gQA-HS (a), QA-SS-QA (b) and gQA-SS-gQA (c) SAM, by a contrast variation SPR measurement.

SAMs. As shown in the data in air, there seems to be no doubt that the film density (the number of adsorbed molecules) of gQA-SS-gQA SAM is much less compared with the other two SAMs, where the influence of doubled cations in one chain must be suggested. The strong electrostatic repulsion between chains may result in less dense film formation. As the reason of relatively high refractive index estimated for gQA-SS-gQA SAM, the influence of the swelling of the SAM in polar solvents needs to be considered. It was known that the swelling of the SAM is not negligible for the case of less dense films. Since the swelling makes simulated curves in solvents deviate upward, the refractive index of less dense films tends to be overestimated in this analytical technique [10]. The real refractive index of the SAMs (estimated by the intersection point) must be lower than the value listed in Table 1 ($n = 1.52$), comparable to the other QA SAMs.

CONCLUSION

We investigated the formation and structure of the SAMs composed of QA sulfur derivatives by SPR measurements. It was found that each QA

TABLE 1 The Thickness and Refractive Indices of HS-gQA-SH, QA-SS-QA, and gQA-SS-gQA SAMs

SAM	SAM thickness (Å)	Refractive index
HS-gQA-SH	26 ± 2	1.50 ± 0.02
QA-SS-QA	26 ± 3	1.46 ± 0.01
gQA-SS-gQA	18 ± 3	1.52 ± 0.02

molecules formed unique SAM structures due to the design of charged head groups. A possibility to control the density and the distance between the charge groups on the surface is suggested from our result. These cationic SAMs with well-controlled structure can be used as affinity arrays for negatively charged materials, such as nanoparticles and proteins.

EXPERIMENTAL SECTION

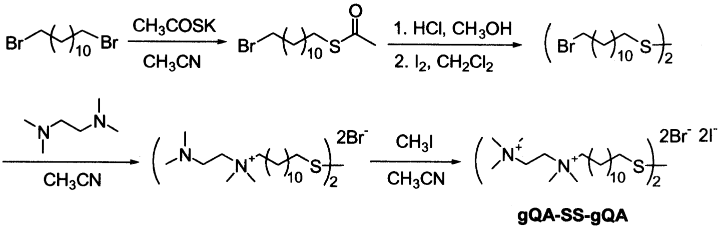
QA sulfur derivatives, HS-gQA-SH and QA-SS-QA, were synthesized as described in the literature [8]. The schematic procedure for the synthesis of gQA-SS-gQA is shown in Scheme 2.

Synthesis of Gemini-structured Didodecyl Disulfide (gQA-SS-gQA)

1-Bromo-12-(12-bromododecyl -disulfanyl)dodecane (0.10 g, 0.18 mmol) and tetramethylethylene diamine (TMEDA) (0.21 g, 1.8 mmol) were dissolved in acetonitrile (50 ml) and heated at 50°C for 48 hr. The reaction solution was evaporated under reduced pressure. To a solution of the white solid in methanol (100 ml), methyl iodide (0.13 g, 0.9 mmol) was added and the solution was stirred at room temperature for 48 hr. The reaction solution was evaporated under reduced pressure and was recrystallized from acetone/methanol (95:5) to give gQA-SS-gQA as a white solid (0.12 g, 62%).

^{1}H-NMR (300 MHz, DMSO)δ(ppm) 1.19-1.40 (m, 32H, CH_2), 1.54-1.75 (m, 8H, CH_2), 2.68 (t, 4H, J = 7.2 Hz, CH_2S), 3.11 (s, 12H, CH_3N$^+$), 3.17 (s, 18H, CH_3N$^+$), 3.27-3.31 (m, 4H, CH_2N$^+$), 3.77-3.93 (m, 8H, N$^+$CH_2CH_2N$^+$).

The SPR measurement setup was based on the configuration introduced by Kretschmann and Raether. The details of the experimental setup have been described elsewhere [11]. A 5 ml of solution with sulfur compounds was injected into the cell for SAM formation, and the adsorption process



SCHEME 2 Synthetic route of gQA-SS-gQA.

was monitored via the change of reflectivity by the kinetics-scan measurement (incident angle 55°). The SPR measurements were carried out in various polar solvents (methanol, ethanol, and water) to estimate both the thickness and the refractive indices of the SAMs, and these methods were named the contrast variation SPR measurements [9]. During this procedure, one solvent was successively replaced by another solvent, and the measurements with methanol were performed for several times in between to confirm that there is no damage or contamination on the SAM due to exposure to the new solvents: methanol (1st) → ethanol → methanol (2nd) → air → methanol (3rd).

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