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# Study on the surface dissociation properties of 6-(10-mercaptodecaoxyl)quinoline self-assembled monolayer on gold by chemical force titration

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## Abstract

Chemical force microscopy (CFM) was used to measure the adhesion force between quinolyl group (–Q)-terminated Au-coated tip and gold substrate (abbreviated as –Q/–Q) modified with self-assembled monolayers (SAMs) of 6-(10-mercaptodecaoxyl) quinoline (MDQ) in pH buffer solution. From the plot of adhesion force vs. pH value, which is called force titration curve, the  $pK_{1/2}$  of surface –Q group of MDQ SAM can be estimated to be 5.3, which corresponds to the pH value at the peak. By using the –OH group as a general probe, the similar  $pK_{1/2}$  value, estimated from the force titration curve of –OH/–Q and –Q/–OH, which also corresponds to the pH at the peak, is 5.2 and 5.4, respectively. From the conventional contact angle titration,  $pK_{1/2} = 5.9$  was obtained. The difference of the obtained  $pK_{1/2}$  values arises from two different measurement methods and their measurement accuracies.

*Keywords:* Surface dissociation properties (surface  $pK_{1/2}$  value); Self-assembled monolayers (SAMs); Chemical force titration.

## 1. Introduction

In the field of surface and interfacial science, it is well-known that the acid–base interaction plays an important role. Many techniques have been employed to determine the  $pK$  value of surface or interface groups. For examples, Holmes-Farley et al. [1,2], Bain and Whitesides [3], Laibinis et al. [4] and Lee et al. [5] used the contact angle titration to obtain the surface  $pK$  values of acid/base groups and Creager and Clark [6] also did the similar work. Based on the interfacial capacitance of electrode surface, Bryant and Crooks [7] reported the titration results of 4-mercaptopyridine (4-MP) and 4-aminothiophenol (4-ATP) self-assembled monolayers (SAMs) on gold. Zhao et al. [8,9] developed second harmonic generation technique to estimate  $pK$  value of surface –NH<sub>2</sub> groups. Recently, a new method for the determination of surface  $pK$  value based on the combination of neutron reflection and surface measurements was proposed by Thomas and An [10]. As we know, all of the methods mentioned above only give the macroscopic and average dissociation properties of surface groups.

Chemical force titration, a new titration concept proposed by us [11,12] and

Vezenov et al. [13] independently in 1997, is a novel use of chemical force microscopy (CFM) [14–17] for characterizing the dissociation properties of surface functional groups like  $-\text{COOH}$ ,  $-\text{NH}_2$ , etc. Nearly at the same time, van der Vegte and Hadziioannou [18,19] and Werts et al. [20] also carried out the similar work. Using this force titration technique, we have obtained the  $\text{p}K_{1/2}$  values<sup>1</sup> of  $-\text{COOH}$  [11,12],  $-\text{NH}_2$  [21,22] and pyridyl [23] groups. In this paper, we report the force titration behavior of  $-\text{Q}$  groups of 6-(10-mercaptodecaoxyl)quinoline (MDQ) SAMs on gold, which is different either from that of conjugated basic group or from that of unconjugated one. The phenomenon can be explained by the interaction between the protonated  $-\text{Q}$  groups in low pH solution and that between the polarized  $-\text{Q}$  groups in high pH solution. The comparative studies using both force titration and contact angle titration were conducted on the surface  $-\text{Q}$  groups of MDQ SAMs on gold.

## 2. Experimental

MDQ [24] and 11-mercaptoundecanol was synthesized and purified in our laboratory. The other reagents were of analytical grade and used as received. Ultrapure water with a resistance of above 16.8 M $\Omega$  cm was used throughout the experiments. The ionic strength of phosphate buffer solution was maintained at 0.01 M.

The Si(111) substrate and commercial  $\text{Si}_3\text{N}_4$  tip (Digital Instruments (DI), Santa Barbara, CA) were sputter-coated sequentially with a 10-nm Ti adhesion layer and a 100-nm Au layer. The spring constant of such modified tip-cantilever was calibrated using the described method [25]. The Au-coated Si substrate and tip were cleaned by immersing into piranha solution ( $\text{V}(\text{H}_2\text{SO}_4):\text{V}(\text{H}_2\text{O}_2) = 70:30$ ) for about 5 min, then rinsed with ultrapure water and ethanol. After cleaning, they were immersed into 1 mM MDQ or 11-mercaptoundecanol ethanol solution for 24 h to form SAMs. Before use, the modified substrate and tip were rinsed with ethanol, ultrapure water, and dried with high-purity Ar gas sequentially. Adhesion measurements were conducted with a Nanoscope E System equipped with a fluid cell (DI). Contact angle measurements were carried out with a JJC-2 goniometer (The Fifth Optical Instrument Factory of Changchun, China).

## 3. Results and discussion

The adhesion interaction between  $-\text{Q}$  group-terminated tip and sample of MDQ SAMs was measured in a fluid cell filled with phosphate buffer solution. To ensure the comparativity of adhesion forces obtained at different pH solutions, one tip was used throughout one set of force titration experiments. By systematically changing the pH value of buffer solution, more than 400 force curves at each pH value were recorded. From the recorded force curve, the tip-cantilever deflection at pull-off point was obtained. The adhesion force can be derived from the tip-cantilever deflection by multiplying the tip-

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<sup>1</sup> The surface  $\text{p}K_{1/2}$  value we obtained from the force titration or contact angle titration is the apparent surface  $\text{p}K$  value, which is expressed by the corresponding bulk solution pH value at which the functional groups at the interface are half-ionized.

cantilever spring constant. Then a plot of adhesion force vs. pH value, which is called force titration curve where each adhesion force data was a statistical average value of the recorded adhesion forces using Gaussian fit [15], was obtained. Fig. 1a gives the force titration curve of surface  $-Q$  groups on gold by using  $-Q$  groups modified tip (abbreviated as  $-Q/-Q$ ). It shows that there is a peak at  $pH = 5.3$ , where the adhesion force reaches a maximum value. The adhesion force decreases either when  $pH > 5.3$  or when  $pH < 5.3$ . When  $pH < 3$  and  $pH > 8$ , the adhesion force reaches zero, suggesting the appearance of a repulsive interaction between tip and sample. When  $pH > 8$ , although  $-Q$  group keeps neutral, the strong polarization effect of  $-Q$  group results in an amount of negative charge in the surface of SAM of MDQ on gold. The repulsive interaction may originate from the polarization interaction of surface negative charge between the  $-Q$  group modified tip and substrate. This force titration behavior is similar to that of conjugated basic group-terminated SAMs, for example, 4-aminothiophenol (4-ATP) SAMs [22] and 4-mercaptopyridine (4-MP) SAMs [23] in high pH solution. The polarization effect of conjugated basic SAMs has been proved by quantum mechanics (ab initio calculation) [26]. When  $pH < 3$ , the repulsive interaction may arise from the long-range electrostatic interaction because the  $-Q$  groups have already been protonated. In low pH solution, the force titration behavior is different from that of conjugated basic group-terminated SAMs [22,23]. Towards the conjugated basic group-terminated SAMs, there are attractive interaction in low pH, which has also been proved by ab initio calculation [26]. Although in low pH, 4-ATP and 4-MP have been protonated, the conjugated structures may disperse the positive charges to whole molecules, which result in a low charge density in the surface of SAMs. The positive charge of  $-Q$  can disperse the positive charge to the quinolyl ring, but the positive charge is kept only in the quinolyl ring of SAM surface and it cannot be dispersed in the whole molecule of SAM. So in low pH, there is a repulsive interaction of  $-Q/-Q$ , which is like that of unconjugated basic group [13,21]. From Fig. 1a, we estimated the  $pK_{1/2}$  value of surface  $-Q$  groups of MDQ SAMs to be 5.3, which corresponds to the solution pH value at the peak of the force titration curve of  $-Q/-Q$  [27].

Using the general probe, the  $-OH$  group-terminated SAMs [13], we also titrated the MDQ SAMs. The force titration curves are given in Fig. 2. The force titration behaviors not only of  $-Q/OH$  but also of  $-OH/-Q$  are similar to that of  $-Q/-Q$ . From Fig. 2, the  $pK_{1/2}$  value of surface  $-Q$  groups of MDQ SAMs can be estimated to be 5.2 from the curve  $-Q/-OH$  and 5.4 from the curve of  $-OH/-Q$ , which also corresponds to the solution pH value at the peak of the force titration curves [27].

For comparison, we also titrated the MDQ SAMs on gold by contact angle measurement. The result is given in Fig. 1b, in which eight independent measurements were conducted for each pH value to get the average contact angle. From the contact angle titration curve, the  $pK_{1/2}$  value of surface  $-Q$  groups of MDQ SAMs was determined to be 5.9. The  $pK_{1/2}$  value estimated from force titration curve is 0.5–0.7 pH unit lower than that obtained from the contact angle titration curve. The difference may arise from the different experimental methods employed. Firstly, the methods have different spatial resolution. The contact angle measurement gave an average  $pK_{1/2}$  value of surface groups, while the force titration technique may reflect the local dissociation properties of the examined molecules because the CFM tip is very sharp and only a very small region of the sample surface beneath the tip is

characterized. Secondly, the difference arises from the accuracy of the methods. CFM can measure the  $10^{-14}$  N force [28], so the accuracy of measured adhesion force in each pH value will be satisfied. The error of the contact angle measurement can reach to several degrees. Throughout the pH range examined, the change of each average contact angle was only  $8^\circ$  and there is a large dispersion of the data points as seen from Fig. 1b, which apparently leads to a large error in determining the  $pK_{1/2}$  value, while the remarkable change in adhesion force allows a precise evaluation of surface  $pK_{1/2}$  value (see Fig. 1aFig. 2).

#### **4. Conclusion**

The surface dissociation properties of MDQ SAMs terminated with quinolyl groups was studied. Using chemical force titration technique, the surface  $pK_{1/2}$  value of quinolyl groups was estimated to be 5.3, 5.2 and 5.4 from force titration curves of  $-Q/-Q$ ,  $-Q/-OH$  and  $-OH/-Q$ , which is compared with the contact angle titration result ( $pK_{1/2} = 5.9$ ). The direct comparative study clearly shows that force titration is a sensitive and accurate method to estimate the  $pK_{1/2}$  value of surface acid/basic groups.

#### **5. Acknowledgements**

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## List of Figures

Figure 1 Force titration curve of  $-Q/-Q$  (a) and contact angle titration curve of MDQ SAM (b).

Figure 2 Force titration curves of  $-Q/-OH$  (a) and  $-OH/-Q$  (b).

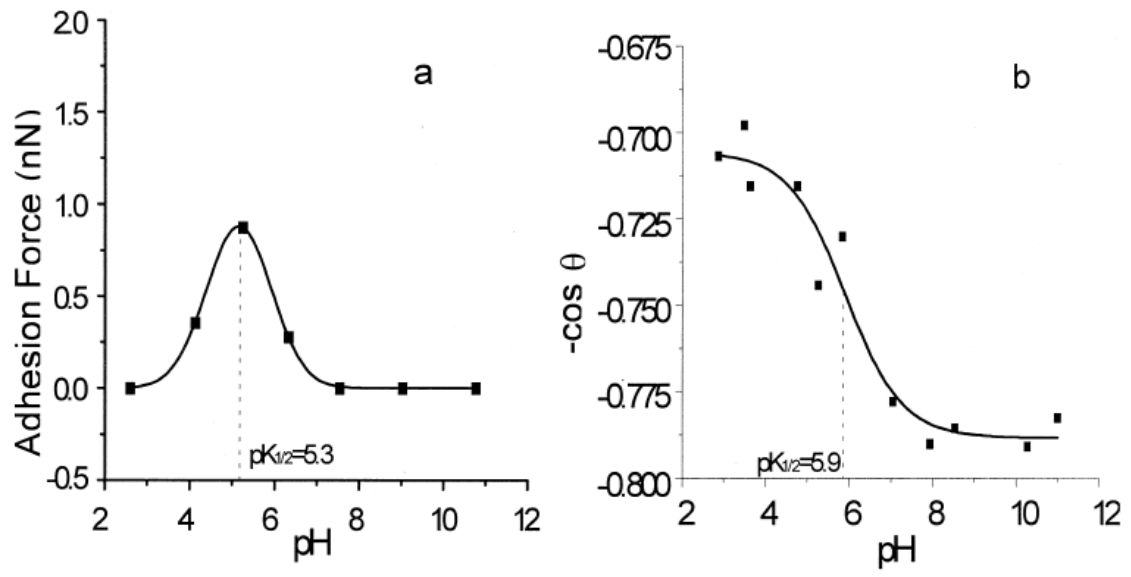


Figure 1



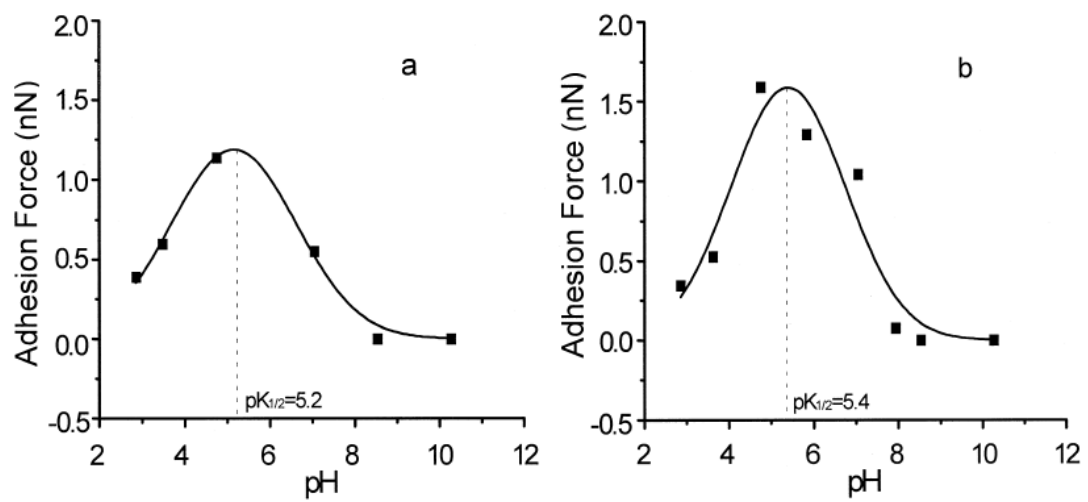


Figure 2