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

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Version of record first published: 29 Oct 2010

To cite this article: Minsu Lee, Youngjune Hur, Jaeho Kim, Heungjin Choi & Kwangnak Koh (2002): Monosaccharides Sensing Characteristics of Phenylboronic Acid Monolayers, Molecular Crystals and Liquid Crystals, 377:1, 225-228

To link to this article: http://dx.doi.org/10.1080/713738555

Mol. Cryst. Liq. Cryst., Vol. 377, pp. 225-228

1058-725X/02 $12.00 + .00
DOI: 10.1080/10587250290088951

Monosaccharides Sensing Characteristics of Phenylboronic Acid Monolayers

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Abstract
To detect low concentrations of sugars, phenylboronic acid derivatives were synthesized and their self-assembled monolayers (SAM) were formed on a gold surface. Monosaccharides sensing with the constructed phenylboronic acid monolayers were evaluated through the surface plasmon resonance (SPR) technique. These phenylboronic acid monolayers showed good sensitivity and selectivity to detect fructose at low concentrations.

Keywords phenylboronic acid; monosaccharides; self-asssembled monolayer

INTRODUCTION

In the last few decades, many researchers have been interested in molecular recognition chemistry by synthetic receptors. Especially artificial receptors for biomolecules have been studied actively, but still remain unclear. Sugar is an important constituent of in living bodies. Therefore, recognition of sugar is essential in medicine, food industry, and biochemical science.

Boronic acids have been known to form covalently-bonded

complexes with diols.[1] In most cases of artificial receptors, hydrogen bonding interaction plays a central role. However, it is less effective in aqueous condition. Recently, covalent-bond formation between saccharide and boronic acid has been suggested as a solution to this problem.[2-3] Therefore, boronic acid derivatives can be used as a useful sensing material for monosaccharide detection.

In this paper, the formation of self-assembled phenylboronic acid monolayers and their monosaccharide sensing studies with SPR technique are described.

EXPERIMENTAL

SPR measurements were performed with a homemade Kretschmann configuration apparatus (Figure 1(a)). The gold surface was prepared using electron-beam evaporation of 3 nm of nikel-chrome as an adhesive layer and followed by 50 nm of gold layer. The gold substrate was cleaned with chloroform, methanol, acetone, and distilled extra pure water.

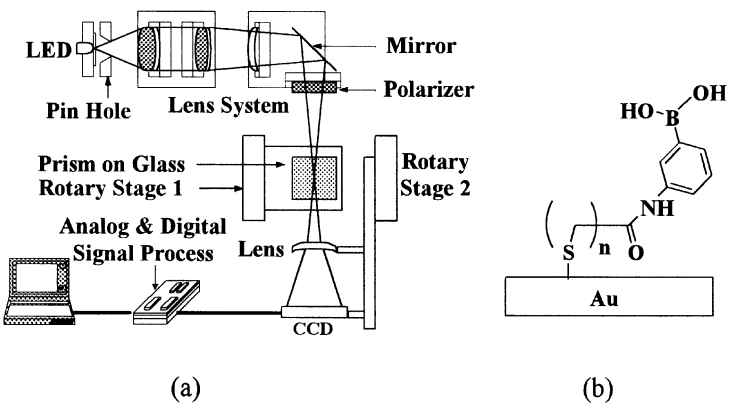


FIGURE 1 Schematic diagram of (a) sensor system and (b) phenylboronic acid monolayers (n = 1, 2, 3).

Phenylboronic acid derivatives (n = 1, 2, 3) were synthesized according to a previously reported method.[4] These phenylboronic acid derivatives have a thiol group that reacts with Au atoms. Therefore, immobilization process of phenylboronic acid derivatives on the Au

surface of a SPR sensor chip was spontaneous. Concentration of each phenylboronic acid solution was 0.1 mM in methanol. Gold-coated cover glass was immersed in a phenylboronic acid solution for 9hrs at room temperature. After rinsing with methanol, it was dried and prepared for measurement (Figure 1(b)). Monosaccharides sensing measurements for glucose and fructose ranged from 1.0×10^{-4} M to 1.0×10^{-12} M concentration (0.1 M Phosphate Buffer, pH = 7.0). All reagents were used analytical grade.

RESULTS AND DISCUSSION

Immobilization kinetics of phenylboronic acid derivatives were measured by SPR. The total SPR angle shift was 0.576° and this immobilization process was saturated in 6 hrs approximately (Figure 2).

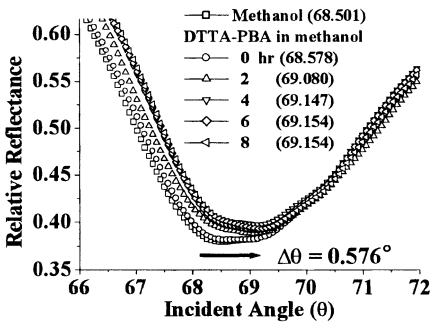
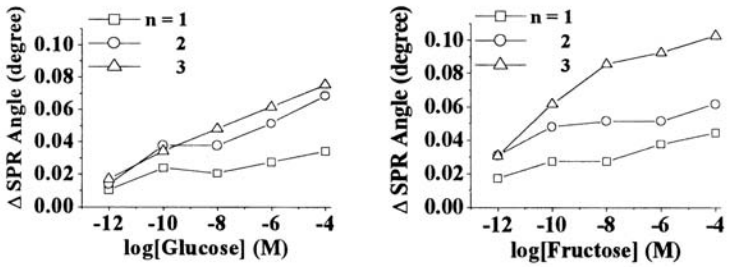


FIGURE 2 Imobilization kinetics of phenylboronic acid monolayers.

The results of sensing for glucose and fructose were compared with each other. In both cases, SPR angle shifts increased in accordance with the alkyl chain length (Figure 3). In each case of phenylboronic acid monolayers, fructose showed a larger SPR angle shift than that of glucose. These results agree with previous studies that constructed some phenylboronic acid monolayers on colloidal gold surface and investigated their sensing characteristics for mononsaccharides using FT-IR, Ramann scattering.[4] Based on these results, we are now perform more precise research for the phenyl boronic acid monolayer characteristics and its molecular recognition functions.

It is suggested that design and construction of self assembled phenylboronic acid monolayers such as those described in this report will be useful in many sensor systems for the efficient detection of monosaccharides.



(a) (b)

FIGURE 4 SPR angle shifts in accordance with phenylboronic acid monolayers with different alkyl chain length (n = 1, 2, 3) for (a) glucose and (b) fructose.

Acknowledgments

This work was supported by Korea Research Foundation Grant (KRF-2000-015-DP0247).

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