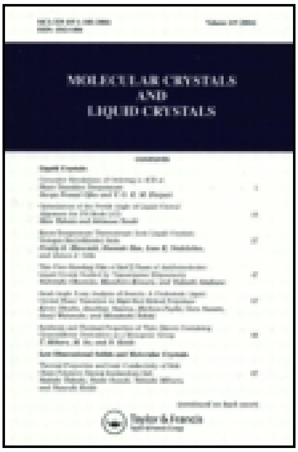

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Abstract

A self-assembled hydrophilic calix[6]arene monolayer was designed for uranyl ion detection. The uranyl ion recognition-function of the calix[6]arene monolayer was evaluated using surface plasmon resonance (SPR) at various concentrations of uranyl ions ($1.0 \times 10^{-4} \sim 1.0 \times 10^{-12}$ M) in 0.1 M Tris-HCl buffer solution (pH = 7.0). Calix[6]arene monolayer showed good sensitivity and selectivity to detect very low concentrations of uranyl ions.

Keywords calix[6]arene; self-asssembled monolayer; uranyl ion

INTRODUCTION

Calixarene, which is known as a cage compound, can recognize various ions and molecules with high selectivity.[1-3] Calixarene-based sensing devices are well known and have been used in many fields.[4-6] Shinkai et al. have shown that calix[6]arene derivatives exhibit remarkable selectivity of the order of $10^{-12} - 10^{-17}$ for uranyl ions from other alkali metals.[7-8] Therefore, calix[6]arene derivatives can be used to fabricate a uranyl ion sensing system exhibiting high selectivity. Especially, water soluble calix[6]arene derivatives not only have a good recognizing ability for uranyl ions, but also exhibit easy controlled properties in an aqueous solution.

In this paper, the application of a self-assembled water soluble calix[6]arene monolayer is reported for selective recognition of uranyl ions. In order to construct a sensing system, we used a self-assembled monolayer technology and surface plasmon resonance (SPR).

EXPERIMENTAL

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

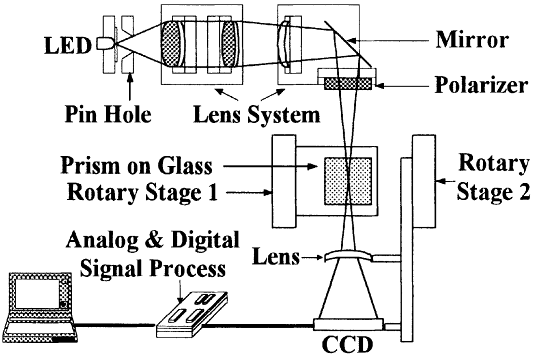


FIGURE 1 Schematic diagram of SPR sensor system.

After rinsing, the gold surface was modified using cystamine of 1.0 x 10^{-2} M in distilled water. Calix[6]arene *p*-hexasulfonylchloride was synthesized and prepared for self-assembled monolayer formation. THF was freshly distilled from Na/benzophenone before being used. All other reagents used in this work were spectroscopic grade.

A self-assembled Calix[6]arene monolayer was formed by covalent linkage of reaction between Calix[6]arene *p*-hexasulfonylchloride and a cystamine-modified gold surface (Figure 2). This reaction was achieved in freshly dried THF under N_2 gas for 18 hours. The concentration of

Calix[6]arne was 1.0 mM in THF and 2.0 Mm triethylamine was used to remove the side product, HCl. After drying, it was measured by SPR at various concentrations ($1.0 \times 10^{-4} \sim 1.0 \times 10^{-12}$ M) of uranyl ions and other metal cations in 0.1 M Tris-HCl Buffer solution (pH = 7.0), exceptionally 0.1 M Tis-H_2SO_4 Buffer (pH = 7.0) in case of Ag^+.

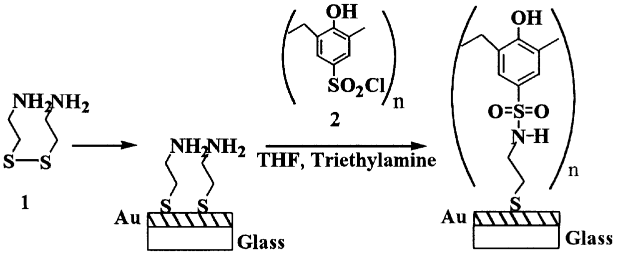
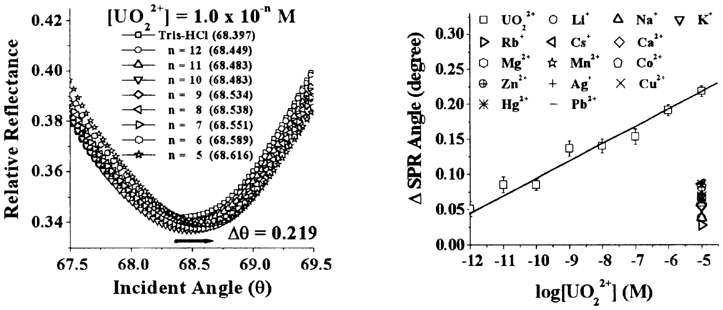


FIGURE 2 Schematic diagram of self-assembled calix[6]arene monolayer on Au layer (n = 6).

RESULTS AND DISCUSSION

SPR angle shifts which reflected recognition of calix[6]arene for uranyl ions was increased in accordance with uranyl ion concentrations (Figure 3(a)).



(a) (b)

FIGURE 3 SPR angle shifts (a) for various concentrations of uranyl ions and (b) comparing the sensing characteristics of uranyl ion with other metal ions.

SPR angle shifts by uranyl ion sensing with a calix[6]arene monolayer are linear and valuable at very low concentrations even in 1.0 × 10^{-12} M. However in the case of other metal cations, SPR angle shifts were very small, respectively (Figure 3(b)). A uranyl ion-sensing system using a self-assembled calix[6]arene monolayer as described in this paper has many advantages such as, simplixity, cost effectiveness, easy fabrication, and so on. Therefore, we believed that these experimental results will be useful to applications in various uranyl ion-related fields.

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