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Liquid crystals-based sensor for the detection of lithocholic acid coupled with competitive host-guest inclusion

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ABSTRACT

A simple, low-cost and label-free strategy for detecting lithocholic acid (LCA) was designed at the liquid crystals (LCs)/aqueous interface via competitive host-guest inclusion. In this method, sodium dodecyl sulfate (SDS) was initially adsorbed on the fluid interface and induced LCs to adopt the homeotropic ordering. Inclusion complexation of SDS and β-cyclodextrin (β-CD) disturbed interaction between LCs and SDS and evoked LCs to keep a tilted alignment. When injecting LCA into the mixed solution of SDS and β-CD, SDS excluded from the cavity of β-CD by competitive host-guest inclusion and could be re-adsorbed at the LCs/aqueous interface, resulting in the orientational transition of LCs from tilted to homeotropic state. Correspondingly, a bright-to-dark optical response was observed under polarized optical microscope (POM). The as-prepared LCs-based sensor could detect LCA as low as about 2 μM in aqueous solution. Moreover, the practicability of the approach was validated by monitoring the known amount of LCA in human urine. This work offers an appealing approach for the detection of LCA which has a great potentiality in clinical diagnosis.

1. Introduction

Lithocholic acid (LCA), a secondary bile acid generating from the 7α-dehydroxylation of chenodeoxycholic acid, is known to be a toxic endobiotics [1,2]. Elevated level of LCA makes a significant contribution to carcinogenesis process [3,4]. Colon cancer is attributed to the accumulation of LCA reabsorbed poorly into enterohepatic circulation in the colon [5–7]. LCA concentration of 5 to 10 μM is also found in patients who suffer from chronic cholestatic liver disease [8]. Therefore, the establishment of LCA assay method provides useful clinical information for the diagnosis of relevant disease. However, just a few analytical methods were employed to achieve the determination of LCA, such as chromatography-mass spectrometry colorimetry [8,9] and fluorometry [10]. Although these existing methods can identify LCA with high sensitivity, they encounter some drawbacks, e.g. costly instrumentations, complex operation procedures and electric power, etc. Therefore, there is still a challenge to develop a novel, convenient and cost-effective strategy for determination of LCA.

β-CD is a cylinder-shaped host molecule with seven glucose subunits connected by α-(1, 4) glycosidic linkages [11,12]. The hydrophobic cavity of β-CD endows it with special capacity to form host-guest inclusion complexes with a variety of suitably-sized substrates in aqueous medium. As reported previously, LCA and β-CD could form inclusion complex [10,13], which exhibited much stronger affinity to the binding sites than other complexes formed by surfactants (e.g. SDS, DTAB) and β-CD. Hence, we attempted to construct an analytical platform for LCA detection on account of a competitive host-guest complexation.

LCs were considered as responsive materials. Some pioneering work of Abbot's group has successfully demonstrated the LCs are very sensitive to the presence of surfactants [14,15]. The adsorption of proteins [16,17], lipids [18,19], DNA [20–22] and polymers [23,24] at the LCs/aqueous interface also trigger the orientational transition of LCs, which are concomitantly transduced into alteration in the measurable optical signals. Brake et al. were the first to propose the use of LCs for reporting biological binding events [25]. Recent studies have reported that LCs can also respond to fundamental interactions between antibody-antigen [26–28], surfactant-protein [29,30] and host-guest [31–33], etc.

Herein a convenient, inexpensive and label-free LCs-based sensor was developed to detect LCA associated with competitive host-guest inclusion interactions. The adsorption of SDS at the LCs/aqueous interface was prevented due to its inclusion into β-CD. LCA could predominate SDS to enter into the cavity of β-CD. As a result, the extruded SDS from the cavity of β-CD was laden at the interface and induced LCs to undergo a tilted-to-homeotropic ordering transition, corresponding

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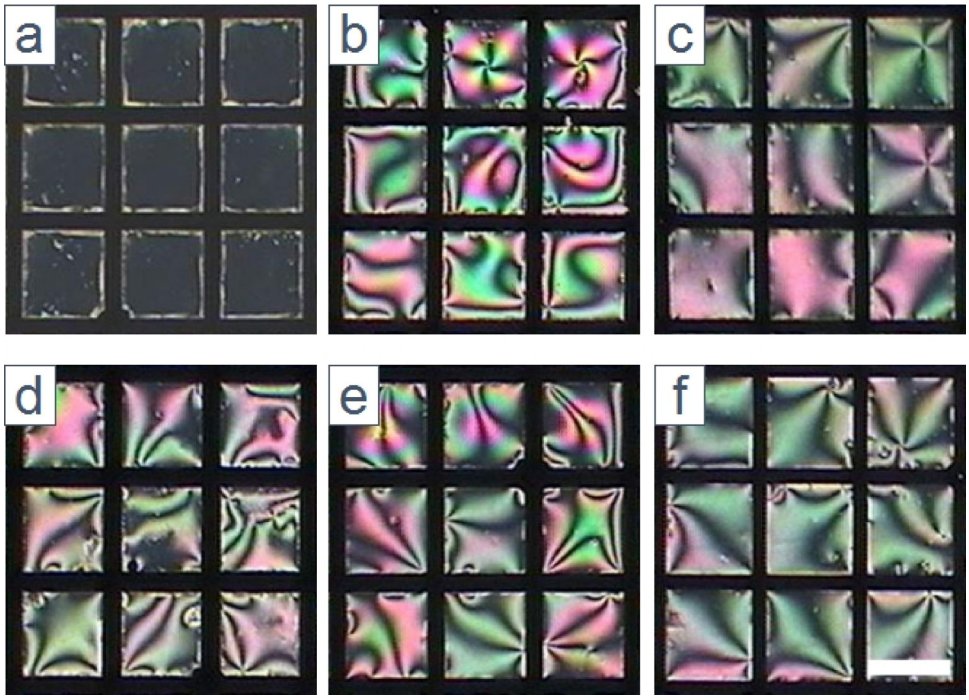

Fig. 1. POM images of LCs in contact with mixture solutions of SDS (0.50 mM) and β-CD at various concentrations (mM): (a) 0.25, (b) 0.50, (c) 0.80, (d) 1.00, (e) 1.50, (f) 2.00 for 2 h. Scale bar: 285 μm.

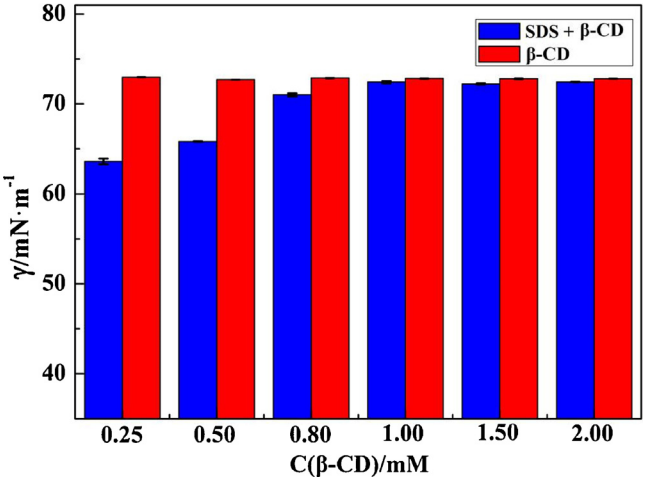

Fig. 2. A column diagram for the surface tension values of β-CD aqueous solutions, and SDS + β-CD mixtures with 0.50 mM SDS and various concentrations of β-CD at 25 ℃.

to a bright to dark shift in the optical images. Based on this mechanism, the detection limit of LCA is ~2 μM. The LCs sensor could also be used to identify LCA in human urine. This work opens a potential route for detection of LCA in practical application. Nematic liquid crystal, 4-cyano-4-pentylbi-phenyl (5CB), was utilized as LCs material. The chemical structures of main compounds employed are shown in Fig. S1.

2. Experimental

2.1. Materials

Octyltrichlorosilane (OTS, 95%), 5CB (99%), D-(+)-glucose (ACS Grade), L-ascorbic acid (99%), potassium carbonate (K_2CO_3, ≥99.5%), urea (99%) and uric acid (98%) were purchased from J&K Scientific Co., Ltd. SDS (99%) was provided by Alfa Aesar (China) chemicals Co., Ltd. β-CD (96%) was obtained from Aladdin Chemistry Co., Ltd. of China. Sodium hydroxide (NaOH, ≥96.0%) and sodium chloride (NaCl, ≥99.5%) were provided by Sinopharm Chemical Reagent Co., Ltd. LCA (> 98.0%) was produced by Tokyo Chemical Industry Co., Ltd. was dissolved in aqueous solutions at ~pH 8 (adjusted with NaOH aqueous solution). Sodium dihydrogen phosphate dihydrate ($NaH_2PO_4{\cdot}2H_2O$, ≥99.0%) and disodium hydrogen phosphate dodecahydrate ($Na_2HPO_4{\cdot}12H_2O$, ≥99.0%) were obtained from Tianjin Damao Chemical Reagent Company of China. Copper grids were bought from Zhongjingkeyi Technology Co., Ltd of China. All the chemicals were used without further purification. Ultrapure water (18.25 MΩ cm) was obtained with the Ulupure system and used in all the experiments.

2.2. Preparation of glass microscope slides

According to previous literature [34–36], glass microscope slides were cleaned in "piranha solution" (70% H_2SO_4/30% H_2O_2) for 30 min at 80 ℃ (Warning: do not store the lotion in closed containers; should be operated with extreme caution). After sequential rinsing with water, ethanol, and methanol, the slides were dried under inert atmosphere with N_2 and stoved overnight at 110 ℃. Then clean glass slides were soaked in the solution of heptane containing OTS for 30 min, followed by rinsing the slides using methylene chloride and drying under N_2.

2.3. Fabrication of LC cells

Copper specimen grids were placed onto the OTS-coated glass substrates. Initially 5CB was heated to isotropic phase (> 35 ℃) and then dispensed onto the grid. Capillary tube (20 μL) was employed to remove the excess LC to form a uniform thin film. Next, the 50 μL sample was introduced into the optical cell at ~25 ℃. Each assay was operated at least three times.

2.4. Optical observation of LCs appearances

The optical images of these samples were captured with POM (XPF-800C, Tianxing, Shanghai, China). Each image was obtained by a 2.5×