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Detection of heavy-metal ions using liquid crystal droplet patterns modulated by interaction between negatively charged carboxylate and heavy-metal cations



Gyeo-Re Han, Chang-Hyun Jang*

Department of Chemistry, Gachon University, Seongnam-Si, Gyeonggi-Do 461-701, Korea

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ABSTRACT

Herein, we demonstrated a simple, sensitive, and rapid label-free detection method for heavy-metal (HM) ions using liquid crystal (LC) droplet patterns on a solid surface. Stearic-acid-doped LC droplet patterns were spontaneously generated on an *n*-octyltrichlorosilane (OTS)-treated glass substrate by evaporating a solution of the nematic LC, 4-cyano-4'-pentylbiphenyl (5CB), dissolved in heptane. The optical appearance of the droplet patterns was a dark crossed texture when in contact with air, which represents the homeotropic orientation of the LC. This was caused by the steric interaction between the LC molecules and the alkyl chains of the OTS-treated surface. The dark crossed appearance of the acid-doped LC patterns was maintained after the addition of phosphate buffered saline (PBS) solution (pH 8.1 at 25 °C). The deprotonated stearic-acid molecules self-assembled through the LC/aqueous interface, thereby supporting the homeotropic anchoring of 5CB. However, the optical image of the acid-doped LC droplet patterns incubated with PBS containing HM ions appeared bright, indicating a planar orientation of 5CB at the aqueous/LC droplet interface. This dark to bright transition of the LC patterns was caused by HM ions attached to the deprotonated carboxylate moiety, followed by the sequential interruption of the self-assembly of the stearic acid at the LC/aqueous interface. The results showed that the acid-doped LC pattern system not only enabled the highly sensitive detection of HM ions at a sub-nanomolar concentration but it also facilitated rapid detection (< 10 min) with simple procedures.

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1. Introduction

In recent decades, the environmental problems caused by rapid and intensive industrialization and urbanization are receiving tremendous attention worldwide. Among these problems, heavy-metal (HM)-related environmental pollution is becoming a serious problem in many countries [1–3]. Recently, it has been revealed that smog or air pollutants such as fine dust (PM 10) and ultrafine particles (PM 2.5) containing high concentration of HM ions originating from the industrial regions of one country eventually lead to environmental problems in the adjacent countries [4,5]. An optimum level of HM ions is necessary for supporting living organisms, including humans [6]. However, excessive levels of HM ions destroy the ecosystem and eventually affect human health when these ions are accumulated in the body [6]. The toxic or carcinogenic effects of the HM ions accumulated in the body have been extensively reported [7,8].

In this context, many efforts have been made to monitor HM-ion concentrations by conventional analytical methods, i.e., atomic absorption/emission spectroscopy [9], inductively coupled plasma mass spectrometry [10], cold vapor atomic fluorescence spectroscopy [11], and electrochemical sensing [12]. Although these methods have contributed to the sensitive detection of HM ions, they have several limitations as well, such as the need for expensive and complex instrumentation and sophisticated and time-consuming chemical processes, which have imposed a restricted utility toward on-site HM-ion detection platforms that require portability, low cost, high sensitivity, and rapid detection [13–16].

Over the years, liquid crystals have been broadly studied as promising sensing materials that can replace conventional analytical methods for point-of-care detection [17–23]. Because of their anisotropic properties, orientation behavior, and molecular sensitivity, which enable the transduction of nanoscopic biochemical interactions into optical signals, various sensing strategies have been established for detecting parameters such as enzymatic activity [24–25], biomolecular interactions [17,18], and polymerization [19]. However, several limitations of previously explored LC-based sensing techniques, i.e., a relatively high detection limit,

* Corresponding author. Tel.: +82 31 750 8555.

E-mail address: chjang4u@gachon.ac.kr (C.-H. Jang).

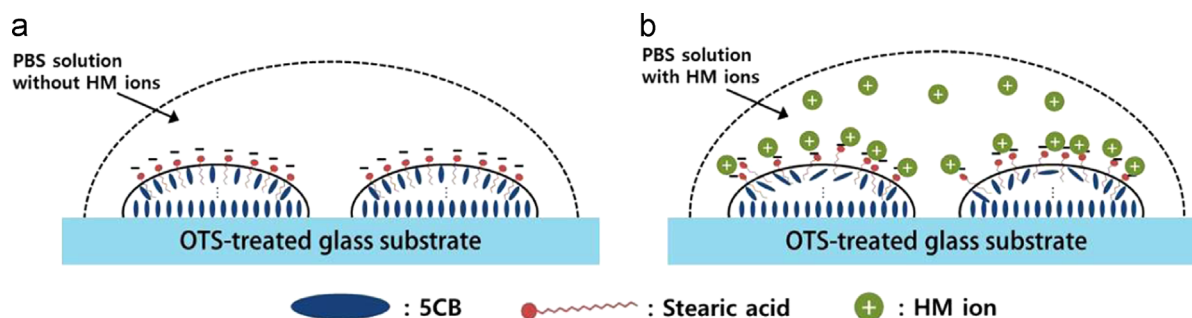


Fig. 1. Schematic illustration of orientation state of stearic-acid-doped 5CB at LC/aqueous solution interface: (a) without HM ions and (b) with HM ions.

instability of the LC/aqueous solution interface, large sample volumes, and long detection times, must be overcome. To this end, our group recently developed a new LC-based detection platform that uses surface-anchored LC droplet patterns spontaneously formed on solid surfaces [26]. Coupled with an improved stability and surface area, which should greatly improve both the sensitivity and the response time to analytes, two distinctive optical appearances, representing the orientation state of the LCs, have suggested the promising possibility of applying the LC droplet patterns as a biochemical sensing platform.

In this study, we demonstrated the sensing ability of the LC droplet patterns by investigating the orientation behavior of acid-doped LCs after the introduction of HM ions. A deprotonated stearic-acid moiety that self-assembled at the LC/aqueous solution interface was employed to induce a homeotropic anchoring of the LCs and to subsequently interact with HM ions. A dark crossed appearance, which represents the homeotropic orientation of the LCs, was observed after incubating with phosphate buffered saline (PBS) solution (pH 8.1 at 25 °C) (Fig. 1a). However, a bright, fan-shaped appearance, corresponding to a planar orientation of the LCs, was observed when the LC droplet patterns were incubated with PBS solution containing HM ions (Fig. 1b). The optical and orientation changes of the LC droplet patterns were attributed to the interaction of the HM ions with the deprotonated acid head groups and the consequent interruption of the self-assembly of the acid molecules at the LC/aqueous interface. The result of this study suggests that the LC droplet patterns can be used to build LC-based, real-time, label-free sensors that can sensitively detect HM ions with a simple method.

2. Experimental details

2.1. Materials

Glass microscope slides were obtained from Matunami (S-1215, Japan). Nematic liquid crystal 4-cyano-4'-pentylbiphenyl (5CB) was purchased from Tokyo Chemical Industry Co., Ltd. (C1555, Japan). Sulfuric acid, sodium hydroxide, hydrogen peroxide (30% v/v), and anhydrous *n*-heptane were purchased from Daejung Chemicals & Metals Co., Ltd. Octyltrichlorosilane (OTS), cobalt(II) chloride hexahydrate (60820), copper(II) chloride dihydrate (C3279), calcium chloride dehydrate (C3306), magnesium chloride hexahydrate (M2393) and phosphate buffered saline (PBS) (10^{-2} M phosphate, 1.38×10^{-3} M NaCl, 2.70×10^{-3} M KCl; pH=7.4 at 25 °C) were obtained from Sigma-Aldrich (St. Louis, MO, USA). All aqueous solutions were prepared with high-purity deionized water (18 M Ω cm) generated using a Milli-Q water purification system (Millipore, Bedford, MA, USA). Especially, as a standard solution, 10^{-4} M solutions of each metal ions were prepared using 10^{-3} M PBS (pH 8.1 at 25 °C), and they were

sequentially diluted with 10^{-3} M PBS solution (pH 8.1 at 25 °C) to make lower concentrations of the metal solutions.

2.2. Cleaning of substrates

Glass microscope slides and silicon wafers were cleaned using a piranha solution (70% H₂SO₄/30% H₂O₂) for 1 h at 80 °C. After removal from the cleaning solution, the substrates were rinsed with 500 mL of each deionized water, ethanol, and methanol, and dried under a stream of gaseous N₂. The cleaned substrates were then stored overnight in an oven at 120 °C.

2.3. Preparation of OTS-functionalized silica substrate

The piranha-cleaned glass slides and silicon wafers were immersed into an OTS/*n*-heptane solution for 30 min. The substrates were then rinsed with methylene chloride and dried under a stream of N₂. Next, the OTS-treated glass slides were tested to evaluate whether they could induce homeotropic alignment of 5CB. In order to observe optical images of 5CB in contact with the OTS-treated glass surface, 5CB optical cell was fabricated by spacing two OTS-treated glasses (facing each other) ~ 12 μ m apart using thin strips of plastic wrap. The edges of the optical cell were held together with clips, and were heated to 40 °C. Then, 5CB, heated to its isotropic phase, was spontaneously injected into vacant space of the optical cell by capillary force. The optical cell was cooled to 25 °C for inducing the phase transition of 5CB from isotropic to nematic. If the 5CB aligned homeotropic state, the optical image appears dark. Any slide that did not display the dark image (homeotropic alignment of 5CB) was discarded.

2.4. Preparation of stearic-acid-doped LC droplet patterns on solid surface

After mixing a solution of 1% (v/v) 5CB in heptane with 0.005% stearic acid dissolved in heptane, 3 μ L of the mixed solution was dispensed onto an OTS-treated glass slide. After evaporation of the organic solvent, a drop of HM-containing aqueous solution (4 μ L) was introduced onto the LC droplet patterns at 25 °C. During the incubation, a humidity of the enclosed reaction environment was controlled using wetted tissue to prevent the concentration change in HM solution, which could be triggered by the evaporation of solvent.

2.5. Imaging of LC textures

A polarized light microscope (ECLIPSE LV100POL, Nikon, Tokyo, Japan) was used to image the optical textures formed by light transmitted through the optical cells filled with nematic 5CB. All the images were obtained using a 10 \times objective lens under crossed polarizers. The images of the optical appearance of each liquid crystal cell were captured using a digital camera (DS-2Mv,

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