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ARTICLE TYPE

An Air-Supported Liquid Crystal System for Real-Time Reporting of Host-Guest Inclusion Events

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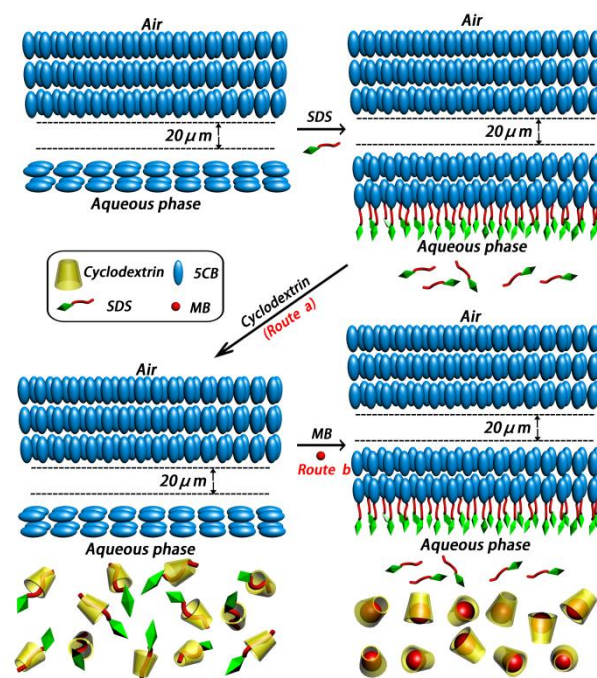
A new method for reporting host-guest inclusion phenomena by an air-supported liquid crystal (LC) system based on cyclodextrins (CDs) was developed. In this work inclusion complexation of β -CD with sodium dodecyl sulfate (SDS) or with methylene blue (MB) using SDS as the probe was visualized by the LC, according to the principle that the orientation of LC was coupled to the organization of SDS molecules.

Recent studies have revealed that a diverse range of dynamic and equilibrium phenomena can occur when molecular self assembly and specific bimolecular recognition events take place at interfaces formed between nematic liquid crystals (LCs) and immiscible aqueous phases [1-3]. For example, the self-assembly of surfactants [4], lipids [5], proteins [6] and synthetic polymers [7] adsorbed at these interfaces can strongly influence the orientational ordering of the LCs. Thus the interfacial events can be coupled to ordering transitions in LCs, which can be used as an imaging tool for sensing key molecular and nanoscopic events at the interfaces. Past studies have exploited this coupling to report enzymatic reactions [5, 8, 9], the interaction of cells with extracellular protein matrices [10], protein binding events [5, 11-13], DNA hybridization [14, 15] and reorganization of polymeric complexes [16]. In the present work, we report a new class of molecular interactions that can be coupled to ordering transitions in LCs: host-guest inclusion using cyclodextrins as the host molecules.

Cyclodextrins (CDs) are a group of naturally cyclic oligosaccharides, with six, seven, or eight glucose subunits linked by α -(1, 4) glycosidic bonds in a cylinder-shaped structure and are denominated as α -, β -, and γ -CD, respectively [17]. The outer surface of CDs is hydrophilic due to the hydroxyl groups. Conversely, the inner surface of their molecular cavity is hydrophobic, because it is lined with the glycosidic oxygen bridges [17]. This structure gives cyclodextrins their unique ability to form host-guest inclusion complexes with a wide range of suitably sized guest molecules [18]. In these complexes, the guest molecule is held within the cavity of the cyclodextrin host system [17, 18].

Formation of the host-guest complex can be easily monitored using techniques such as UV-visible spectroscopy (UV-vis) [19], nuclear magnetic resonance (NMR) [20], fluorescence spectroscopy [21], electrochemical approaches [22], among others. At present, the methods of investigation on inclusion interactions mainly include: (1) direct methods which are established based upon the remarkable changes of the observed signals (such as photochemistry, electrochemistry signals) when

the guest molecules are included into the CDs; (2) an indirect method, namely the competitive inclusion method [17-19] for other guests whose signals are not changed after being included by CDs.



Scheme 1. Reporting host-guest inclusion complexation using a liquid crystal sensor. Route a: Interaction between β -CD and SDS. Route b: interaction between β -CD and MB, using SDS as a probe.

Herein, we discuss a new air-supported LC system for analyzing host-guest inclusion phenomena based on CDs. To the best of our knowledge, LCs have never been used to report host-guest inclusion based on CDs. In the first part of this work, SDS was chosen as the guest molecule. The molecular-level interactions orienting molecules of 4-cyano-4'-pentylbiphenyl (5CB) in the presence of sodium dodecyl sulfate (SDS) occur primarily through interactions of 5CB with the surfactant tail [4]. Based on this study, we hypothesized that when β -cyclodextrin (β -CD) was introduced into this system, the hydrophobic tail of SDS was included by β -CD, thus inducing a reorientation of the LC from homeotropic to planar. Hence host-guest inclusion phenomena could be monitored *via* the macroscopic alignment of the LC (Scheme 1, Route a). In the second part of this work, using SDS as a probe, the inclusion of MB by β -CD was also

studied according to a competitive inclusion mechanism using SDS as a probe (Scheme 1, Route b). The overall approach was quite simple, and does not require complex instrumentation or laborious techniques.

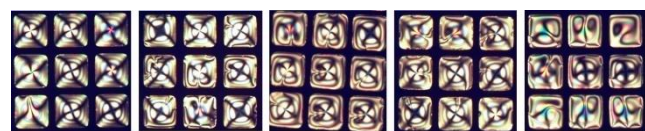


Figure 1. Cross-polarized optical images of 5CB confined within a copper grid when exposed to aqueous solutions of β -CD at various concentrations (mM): (a) 0, (b) 0.3, (c) 0.5, (d) 1.0, (e) 2.5.

Our first goal was to investigate whether β -CD could interact with 5CB and then affect its orientation. It was well known that bright images of LCs are caused by planar orientations of LCs at the aqueous/LC interface, while dark images of LCs are caused by homeotropic orientations. Figure 1 shows the optical appearance of 5CB when contacted with aqueous solution containing increasing concentrations of β -CD. A bright image associated with near-planar orientation of 5CB at the aqueous interface was observed in the presence of β -CD. But a small change in the color of the image was observed as the concentration of β -CD was increased. To understand whether this small change in color was due to the inclusion of 5CB by β -CD, the absorbance of UV-vis spectra of alcohol and water mixture solutions of 5CB in the presence of different concentrations of β -CD (Figure 1S) were measured. The inclusion constant was calculated to be 810 M^{-1} , which indicated that β -CD could interact with 5CB in solution. However, the experimental system that was central to the work discussed in this report involved an interface between an aqueous phase and a water-immiscible, thermotropic liquid crystal (5CB). Due to a competition between β -CD–5CB interaction and 5CB–5CB interaction at the aqueous/LC interface, the interaction between 5CB and β -CD perhaps was weaker than that in solution [23, 24]. When contacted with β -CD aqueous solution, a small number of 5CB molecules would be included in the cavity of β -CD, the resultant complexes were dissolved into aqueous solution and could not assemble at the aqueous/LC interface due to the hydrophilic nature of β -CD [25], which varied the thickness of the LC at the interface and thus induced the changes of the color of the LC [2]. The above result indicated that though β -CD could interact with 5CB in solution, it did not affect the orientation of LCs at the interface.

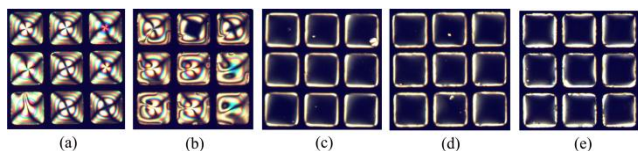


Figure 2. Cross-polarized optical images of 5CB confined within a copper grid when exposing to aqueous solutions of SDS at various concentrations (mM): (a) 0, (b) 0.1, (c) 0.25, (d) 1.0, (e) 2.5.

Next we tested the LC sensor to see whether it indicated a host-guest complex between β -CD and SDS. Past studies have shown that adsorption of surfactants at the aqueous/LC interface often leads to a planar-to-homeotropic transition in the orientation of the LCs when the density of a surfactant exceeds a critical value [4]. In this work, the effect of SDS on the orientation of 5CB was also investigated. It was shown that in the absence of SDS (Figure 2a), the optical appearance of 5CB reflected the in-plane birefringence associated with planar anchoring on the surface of

water. For SDS concentrations up to 0.1 mM (Figure 2b), the observed optical texture is similar to that seen in Figure 2a, indicating a strong in-plane birefringence at the aqueous-LC interface. At SDS concentrations of 0.25 mM and higher (Figure 2c-e), the optical appearance of LC within the grids was uniformly dark, consistent with homeotropic alignment of 5CB.

The introduction of β -CD at concentrations of 0.8 mM and higher to 0.25 mM SDS aqueous solutions caused the optical image of 5CB to change from dark to bright (Figure 3), which indicated that LCs transitioned from a homeotropic to planar state. As mentioned above, the hydrophobic interaction between the SDS tail and 5CB was responsible for the homeotropic ordering of LCs. A serial study demonstrated that β -CD molecules could disrupt the hydrophobic interaction because they could include the hydrophobic groups into their cavities [26, 27]. On the other hand, it was reported that β -CD could form an inclusion complex with SDS [28, 29]. These results suggested that the bright optical image observed in Figure 3d-f could be attributed to the host-guest inclusion of SDS by β -CD, which eliminated the 5CB-SDS hydrophobic interaction. Furthermore, we found that the inclusion of hexadecyl trimethyl ammonium bromide (CTAB) or alkyl glycosides (APG) by β -CD was also imaged by LCs (Figure 2S). These results confirmed that the host-guest inclusion phenomena could be reported and imaged by LCs.

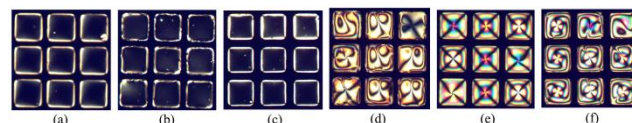


Figure 3. Cross-polarized optical images of 5CB confined within a copper grid after exposure to aqueous solutions of β -CD/SDS at various concentrations of β -CD (mM): (a) 0, (b) 0.1, (c) 0.25, (d) 0.8, (e) 1.0, (f) 2.5; [SDS]=0.25 mM.

The competitive method was based on the principle that the probe molecules and analyte guest molecules competed for the same cyclodextrin cavity which resulted in the related signal change [20-22]. In this part, we wanted to apply the liquid crystal sensor to prove the host-guest inclusion of methyl blue (MB) by β -CD using a competitive method.

In order to use LCs to image the host-guest inclusion of MB by β -CD, SDS was used as the probe. Figure 4 shows cross-polarized optical images of 5CB confined within a copper grid after exposure to aqueous solutions of various MB concentrations in the presence of SDS/ β -CD complex solution for various periods of time. It was found that addition of 0.05 mM MB or above to the SDS/ β -CD complex solution regenerated the dark image of LCs within 30 min. Figure 1S shows that when 5CB was combined with MB or SDS+MB solutions with MB concentrations from 0.01 to 0.5 mM, the images did not change. On the other hand, after addition of MB to an SDS solution the optical image remained dark. This result indicated that MB could not interact with 5CB and affect the interaction between SDS and 5CB. From these results, we could speculate that the bright to dark change of the image was due to the complexation of MB by β -CD which eliminated the interaction between the β -CD and SDS. The released SDS molecules interacted with 5CB again, which induced the change of the optical image. In this work, several other molecules including dopamine, methyl violet, alizarin red, phenolphthalein were also tested, however they did not change the image of LCs. From these results, we surmised that the bright to dark change of the image was due to the complexation of MB by β -CD which eliminated the interaction

between β -CD and SDS. The released SDS molecules interacted with 5CB again, which induced the change of the optical image. In addition, it was observed from Figure 4 that the bright-to-dark changes in the optical response were related with the exposure time and MB concentrations, which suggested that the interactions between MB and β -CD were concentration-dependent and time-dependent. Thus, we could conclude that using the competitive method, the host-guest interaction between β -CD and MB was successfully proved by LCs.

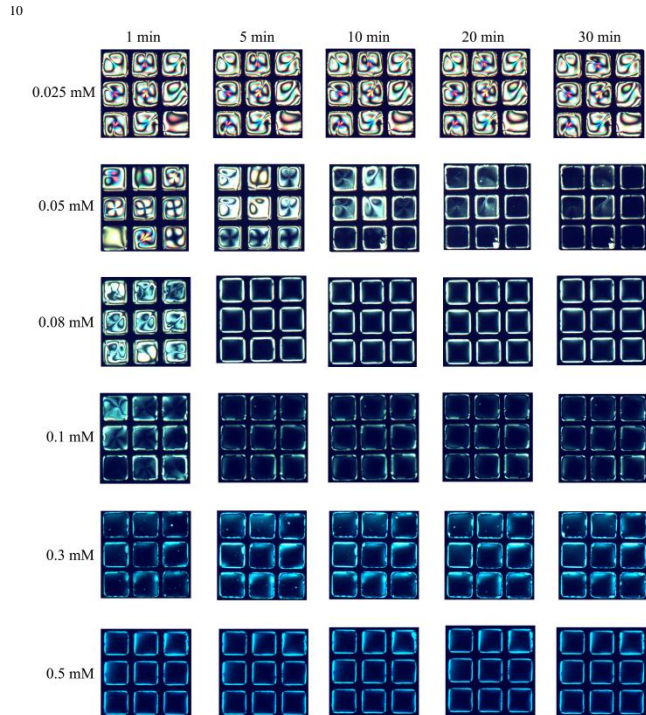


Figure 4. Cross-polarized optical images of 5CB confined within a copper grid after exposure to aqueous solutions of SDS/CD containing various concentrations of MB for periods of time from 1 to 30 min. The concentrations of SDS and CD were 0.25 and 0.9 mM respectively, while concentrations of MB varied from 0.01 to 0.5 mM.

In conclusion, we have designed a new air-supported LC system for reporting host-guest inclusion complexation using cyclodextrins as the host. Inclusion of SDS by β -CD disrupted the interaction between LCs and SDS, which allowed the LC to reorient to its bright planar alignment. On the other hand, when MB was added into the β -CD/SDS solution, the SDS released from the cavity of β -CD interacted with 5CB, which induced an orientational transition of the LCs from a planar to homeotropic state. Thus the host-guest inclusion of MB by β -CD was reported indirectly by using SDS as a probe. This method could be used to judge inclusion events directly for guest molecules that can induce a change in the orientation of LCs. Using the above mentioned molecules as the probe, the host-guest inclusion based on cyclodextrins could also be shown indirectly by LCs according to the competitive principle. This work demonstrates the development of a simple and cost-effective liquid crystal-based imaging tool for real-time reporting of host-guest inclusion complexation events. We are currently investigating the use of various LCs for reporting more host-guest inclusion events based on cyclodextrins, as well as determining the inclusion constant by designing new LC devices.

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