

Potassium-ion-selective sensing based on selective reflection of cholesteric liquid crystal membranes

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Abstract It is well-known that cholesteric liquid crystals have an optical property, selective reflection, due to changes in the pitch of their helical structure. This unique property of cholesteric liquid crystals can be used to attain a visual sensing system showing color changes as the detection signal. In this paper, we report a visual sensing membrane comprising cholesteric liquid crystals, in which a 15-crown-5 derivative was incorporated as ion recognizing sites, for K^+ in aqueous solution. The resulting CLC membrane showed a shift of the reflection peak sensitive to K^+ in water. We have also designed polymer-dispersed liquid crystal membranes that showed ion-selective reflection peak shifts with improved response time.

Keywords Cholesteric liquid crystal · Selective reflection · Structural color · Crown ether

Introduction

Cholesteric liquid crystal (CLC) is a type of the nematic liquid crystal, in which the LC molecules are aligned each other along with the longer molecular axis. In the CLC phase, the LC molecules twist to form self-organized structures with a helical ordering. It is well known that CLCs have a unique optical property, selective reflection, due to their helical structure. This light reflection is based on Bragg diffraction caused by the periodic molecular

ordering of the CLC molecules [1]. Reflection peak wavelength, λ , for the selective reflection band of CLCs membrane is given for normal incident light by

$$\lambda = nP$$

where n is the average refractive index of the cholesteric phase and P is the pitch of the helical structure. Thus, when the pitch of the helical structure in CLC is comparable to the wavelength corresponding to visible light, CLC shows iridescent colors by selective reflection. The value of P is dependent on the several factors including composition of the CLCs, temperature, pressure, electric field, and the nature and concentration of impurities in the CLC membrane. Therefore, variation in these factors can induce the changes in the wavelength of the light reflected by CLCs, resulting in their color changes.

The unique property of CLCs has been utilized for developing visual sensing materials showing the color change as a detection signal. CLC temperature sensor is one of well-known examples of such sensor applications. Recently, it has been reported that CLC membrane functionalized by incorporating a cholesteryl ester having a trifluoroacetyl receptor group, which forms an adduct with amine, can recognize amine vapors and show reflection peak shift owing to its selective reflection [2]. CLC membranes showing reflection peak shifts responsive to pH [3, 4] and amino acids [5] in aqueous solutions have been reported by Shibaev et al. In addition, an application of CLC to a color indicator of enantiomeric excess of chiral compounds has been also reported [6].

There have been some pioneering studies [7–10] on LC systems containing crown ethers and relatives for tuning the properties of LCs so far. Previously, we also reported specific ionic conduction in composite films of CLCs containing a crown ether moiety owing to ordering

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structure in the CLC phase and photoswitching of the ionic conductivity by an azobenzene compound [11]. It has been also reported that CLCs can be applied to liquid membrane used in ion-selective electrode [12]. The CLC membranes showed ion-selective responses based on the ordering of the LC molecules. In the present paper, we report CLC membranes showing changes in selective reflection band responsive to metal ion in aqueous media based on ion recognition by a crown ether derivative in the CLC phase.

Experimental section

Reagents

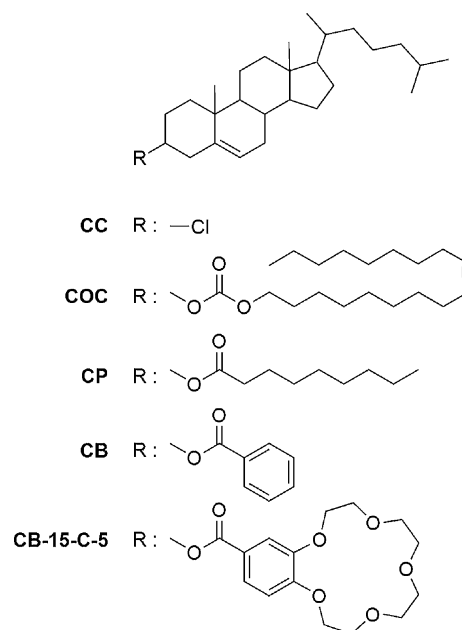
Cholesteryl chloride (CC), cholesteryl pelargonate (CP), cholesteryl oleyl carbonate (COC), and cholesteryl benzoate (CB) are commercially available and used as received. Cholesteryloxycarbonyl benzo-15-crown-5 (CB-15-C-5) was synthesized previously in our laboratory [12]. Tetrahydrofuran (THF) used as a solvent for preparing the CLCs membrane is reagent grade and used without any purification.

Poly(vinyl chloride) (PVC), and poly(2-hydroxyethyl methacrylate) (PHEMA) are commercially available and used as polymeric materials for preparing polymer-dispersed liquid crystals (PDLCs). Cellulose used for PDLC was obtained from a cellulose membrane filter (ADVANTEC).

Preparation of CLCs membrane

We used the cholesterol derivatives shown in Scheme 1 to prepare the CLCs membrane. The mixture of these compounds with appropriate contents was dissolved in THF. An aliquot of the THF solution was dropped onto glass substrate. Then, it was allowed to stand until the solvent was evaporated. Two of thus-obtained CLC membranes deposited on the different substrates were brought into contact with each other, and then these substrates were moved along with the surface. The resulting LC membranes show clear structural colors based on their selective reflection. The typical membranes were composed of 37.5 wt% COC, 37.5 wt% CP, 16 wt% CC, and 9 wt% CB-15-C-5, corresponding to the CB-15-C-5 concentration of 7.4 mol.%.

PDLC membranes were also prepared in a similar procedure to that described above except for that the THF solutions of CLCs contained a polymer. The polymers used for preparing PDLCs included PVC, PHEMA, and cellulose. The CLCs composition in the PDLCs was identical to the that of the CLCs membrane mentioned above. The



Scheme 1 Chemical structures of compounds used for preparing CLC membranes

ratios of the CLCs to the polymer in the PDLCs were 20:80 for PVC, 70:30 for PHEMA, and 20:80 for cellulose.

Reflection spectra measurements

The CLCs and PDLCs membranes were immersed into an aqueous solution containing an alkali metal ion. Then, the reflection spectra of the LC membranes were measured with a spectrophotometer (USB 4000, Ocean Optics Inc.) equipped with a light source (DH-2000, Ocean Optics Inc.) keeping the fiber probe with respect to the normal of the membranes. The responses of CLC membranes to metal ions were monitored during soaking them into aqueous solutions.

Results and discussion

Reflection-spectral changes of CLC membranes

It was already reported that CLCs containing a cholesteryl ester together with a trifluoroacetyl group showed color changes responsive to amine vapors [2]. We referred to this previous report [2] to decide to use a similar CLC membrane comprising of cholesteryl derivatives (Chart 1) for the preparation of an ion-sensing LC material allowing bare-eye sensing based on visible-light reflection. Previously, we reported that ion-selective electrodes, in which the CLC with a different composition was used as a liquid membrane, showed K^+ -selective electromotive force

responses based on the ion recognition of CB-15-C-5 ordered in the CLC phase [12].

Figure 1 shows reflection-spectral changes for the CLC membrane incorporating CB-15-C-5 soaked into an aqueous solution containing 0.1 M MSCN ($M = \text{Li}, \text{Na}, \text{K}$). The CLC membrane showed a distinct spectral change for K^+ (Fig. 1c) whereas no significant changes in the selective reflection band were observed for Li^+ and Na^+ (Fig. 1a, b). When the CLC membrane was immersed into an aqueous KCl solution, the selective reflection band did not change. Time-course changes of the reflection peak of the CLC membrane are given in Fig. 2. As can be seen from Fig. 2, the CLC membrane incorporating the 15-crown-5 derivative showed a gradual red-shift of the reflection peak by immersing the membrane into aqueous solution containing K^+ . It is clear that the reflection peak of the CLC membrane shifted to a longer wavelength being responsive to only K^+ ion. Moreover, in the control experiment conducted using a CLC membrane containing CB instead of CB-15-C-5, no significant shift of the reflection peak was observed in an aqueous solution containing KSCN. This observation indicates that the 15-crown-5 ring was essential for the response of the CLC to K^+ . These results clearly indicate that the K^+ -selective peak shifts of the CLC functionalized with CB-15-C-5 would be attributed to the complexation of K^+ ion with 15-crown-5 in the CLC membrane, which resulted in the increase in the helical pitch of the CLC phase. As shown in Fig. 2b, the reflection peak of the CLC increased with the increasing concentration of KSCN up to 0.1 M. The relationship between the reflection peak and K^+ concentration indicates that the CLC membrane can be used for a sensor material for detecting K^+ selectively in aqueous solution. The sensitivity of the LC membrane for K^+ in water can be estimated to be approximately 120 nm M^{-1} from the slope of the initial increase in the reflection peak shift.

The complex formation of the 15-crown-5 with K^+ in the CLC membrane would require the extraction of a metal ion and its counter anion from aqueous phase to the CLC phase. In order to examine the effect of K^+ ions on the selective reflection peak, we prepared the CLC membranes doped with different amount of KSCN and measured their reflection spectra. A similar study on the host–guest complexation of the crown ether cholesterols in the CLC phase was reported by Shinkai et al. [13]. Figure 3 depicts the reflection-peak shifts of the KSCN-doped CLC membrane as a function of the molar ratio of K^+ doped to CB-15-C-5 in the membrane. The KSCN-doped CLCs showed a similar red shift of the reflection peak depending on the ratio of KSCN to the crown ether in the membrane. Therefore, the peak red shift of the CLC membrane soaked into the K^+ solution can be explained by the complexation of the 15-crown-5 moiety with K^+ . It is well known that

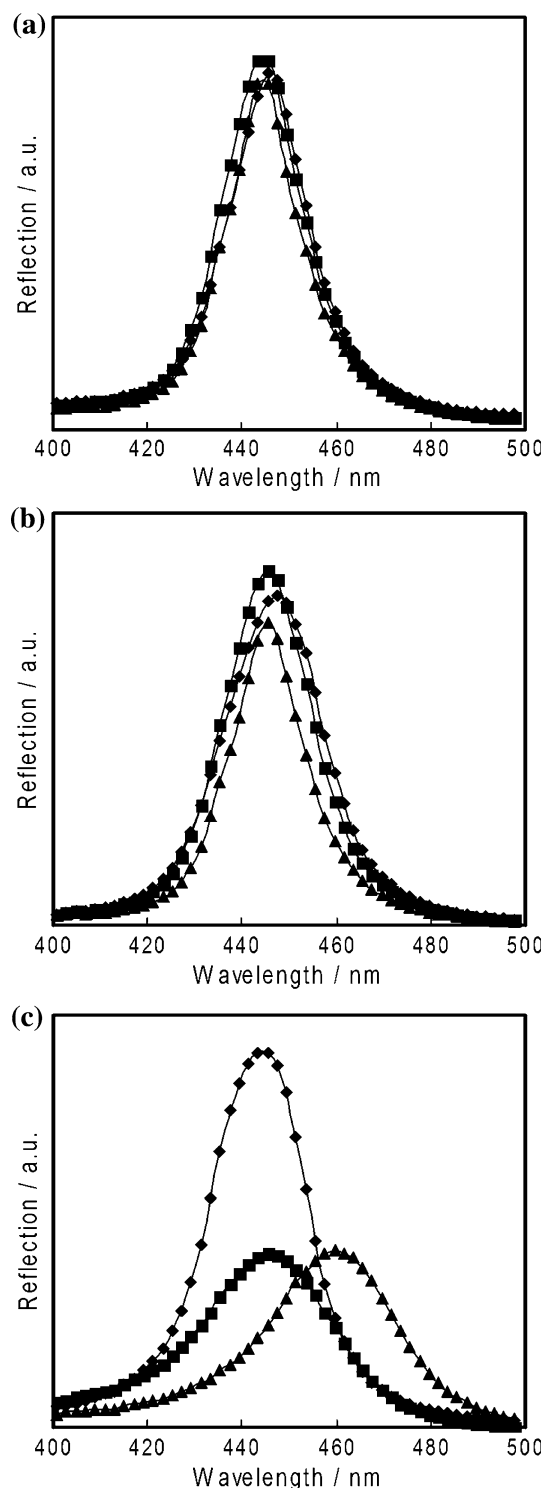


Fig. 1 Reflection-spectral changes of CLC membrane having CB-15-C-5 soaked into aqueous solutions containing **a** LiSCN, **b** NaSCN, and **c** KSCN. The concentration of the metal ions was 0.1 M. Soaking time: (*diamond*) 0 min; (*square*) 10 min; (*triangle*) 90 min

15-crown-5 ether derivatives can form sandwich complexes with K^+ at 2:1 stoichiometry. K^+ selectivity of our CLC membrane functionalized with CB-15-C-5 can be

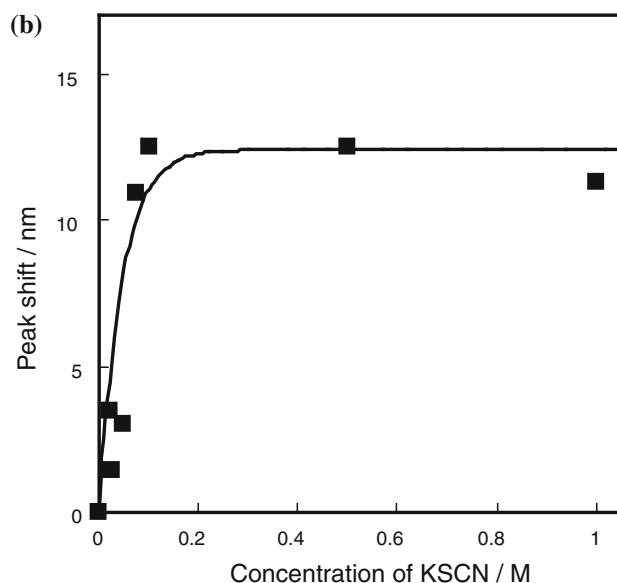
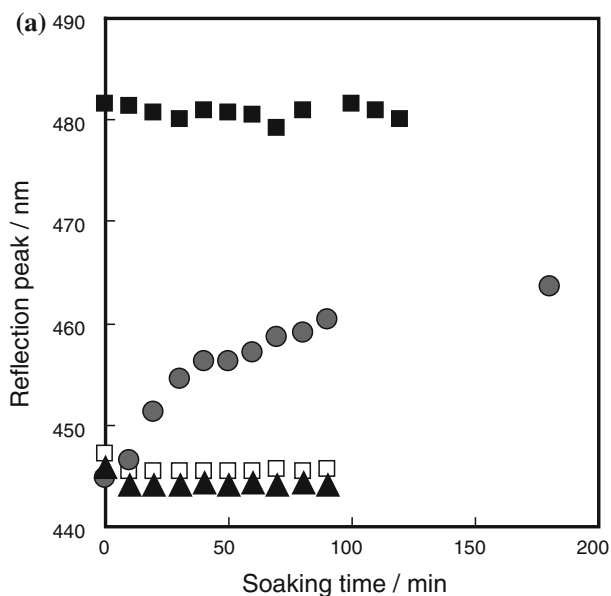


Fig. 2 **a** Reflection-peak shifts of CLC membrane incorporating CB-15-C-5 as a function of soaking time of the membrane into aqueous solutions containing (filled triangle) LiSCN, (open square) NaSCN, and (filled circle) KSCN. Filled squares indicate peak shifts for control CLC membrane containing CB instead of CB-15-C-5. The concentration of the metal ions was 0.1 M. **b** Reflection peak of the CLC membrane as a function of the concentration of KSCN

attributed to the sandwich complexation of CB-15-C-5 with K^+ in the CLC phase. Perturbation of asymmetry of the chiral component in the CLC usually results in a decrease in the helical twisting power of it, leading to the increase in helical pitch of the CLC and to the red-shift of the reflection peak. For our CLC membrane, the formation of sandwich complex of CB-15-C-5 would disturb the cholesteric helical structures owing to the decrease of the anisotropy of the chiral crown ether. Therefore, it is

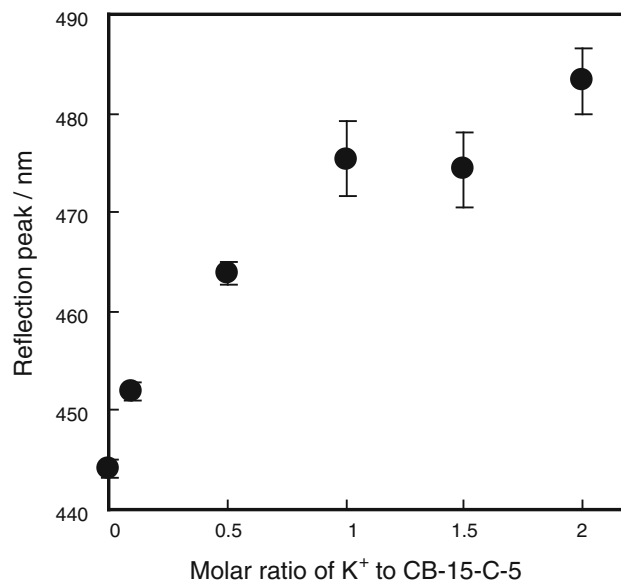
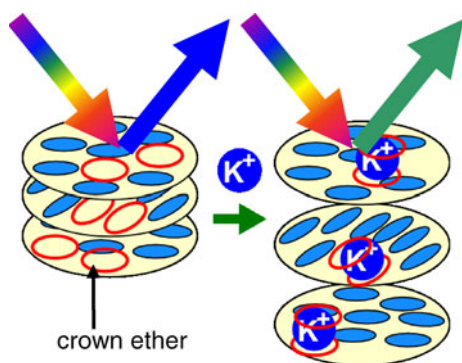


Fig. 3 Reflection-peak shifts of CLC membrane incorporating CB-15-C-5 as a function of molar ratio of KSCN to CB-15-C-5 in membrane

reasonable that the sandwich complexation is responsible for the K^+ -selective red shift of the reflection peak. From the comparison of the Figs. 2b and 3, the reflection-peak shift of the CLC soaked in a KSCN solution is almost equal to the peak shift of the KSCN-doped CLC at the K^+ /CB-15-C-5 molar ratio of 0.5. Thus, we conclude that the reflection-peak shift responsive to K^+ would be induced by favorable formation of the sandwich complex of CB-15-C-5 with K^+ in the CLC phase, as shown schematically in Scheme 2. We have already reported K^+ selectivity of an ion-selective electrode fabricated by using CLCs containing CB-15-C-5 as an ion sensing membrane [12].

PDLC membrane

Although a good ion selectivity of the CLCs was attained, the completion of the reflection-peak shift was time-consuming as shown in Fig. 2a. PDLC is a type of the LC membrane prepared by using polymeric materials as a matrix, which possesses LC domains dispersed in the polymer matrix. The PDLC membrane is very useful for reducing the amount of the LC parts in the membrane. It is expected that dispersed LC domains in the PDLC membrane are favorable to quick response of the reflection peak owing to the increase in the effective surface area of LC domains. Thus, we attempted to prepare the PDLC membrane based on the CLC molecules using different type of polymers to improve the response time of the CLCs sensor membrane. Figure 4 shows the time course of the reflection-peak shifts for the several PDLC membranes



Scheme 2 Schematic illustration for plausible mechanism of K^+ -selective reflection-peak shifts of CLC membrane incorporating CB-15-C-5

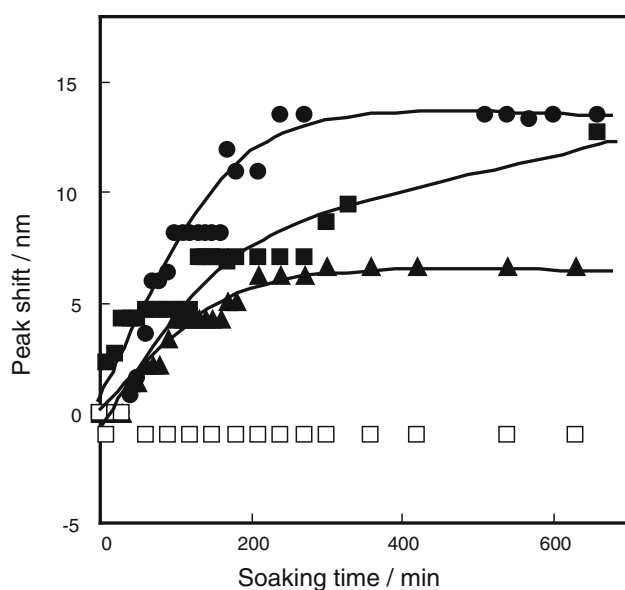


Fig. 4 Time course of reflection-peak shifts of PDLC membranes prepared using (filled triangle) PVC, (open square) PHEMA, and (filled circle) cellulose as polymer matrix and (filled square) CLC only (without polymer)

immersed into a K^+ aqueous solution. As a result, by the comparison of the initial slope of the plots in Fig. 4, the PDLC membrane prepared with cellulose derivatives clearly afforded K^+ -responsive peak shift much faster than the CLC-type membrane (without polymer). This finding indicates that the response time was effectively reduced by preparing the PDLC membrane with the use of the cellulose derivatives. Furthermore, the polymer matrix of the PDLC membrane had no effect on its K^+ selectivity of the CLCs domains. Thus, the response time of our K^+ -selective sensing CLC membrane was improved by preparing its PDLC membrane with the appropriate polymer as expected.

Conclusions

We have designed the ion-sensing membrane system consisting of cholesteric liquid crystals for metal ions in aqueous solution based on their optical property of selective reflection. The CLC membranes incorporating the 15-crown-5 derivative as an ion recognition site responded selectively to K^+ ion in aqueous solution and showed the red shift of the reflection peak with increasing concentrations of the metal ion. The ion selective peak shift would be attributable to formation of the sandwich complex of K^+ with the 15-crown-5 derivative in the CLC phase. Furthermore, we prepared the PDLC membrane with CLC domains with the 15-crown-5 derivative in order to improve the sensor response. The PDLC membrane prepared by using cellulose as a polymer matrix afforded the shortened response time to K^+ ion with a similar ion selectivity to that of the CLC membrane. The sensor performance may be further improved by modifying the membrane preparation process and more finely designing the membrane components and the host molecule. The CLC membranes presented in this report indicate that CLCs can be used to fabricate the visual sensor systems based on the selective reflection for detecting aqueous metal ions selectively.

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