Alcohol-Responsive, Hydrogen-Bonded, Cholesteric Liquid-Crystal Networks

Chin-Kai Chang, Cees M. W. Bastiaansen, Dirk J. Broer,* and Hui-Lung Kuo*

Hydrogen-bridged, cholesteric liquid-crystal (CLC) polymer networks are adopted as an optical sensor material to distinguish between ethanol and methanol. Fast uptake of the alcohols is facilitated by an incorporated porosity created by breaking the hydrogen bridges and by a previously removed non-reactive liquid-crystal agent. The discrimination between the alcohols is based on the diversity in molecular affinity of ethanol and methanol with the hydrogen-bridged CLC polymer networks. The CLC networks are molecular-helix-based, one-dimensional bandgap materials with a discrete reflection band in the visible part of the spectrum that depends on the pitch of the molecular helix. The changes in positions of the reflection bands of the CLC network accurately discriminate between the alcohol types and provide information on their ratio in case they are blended.

1. Introduction

With the development of new portable optical methodologies, even using the camera function of smart mobile phones, there is a need for new materials enabling simple optical detection of society-relevant species. Here we present a new material and method to detect alcohol molecules and to discriminate between methanol and ethanol. The latter is of importance to detect counterfeited alcoholic beverages containing, for instance, the toxic methanol. The method is based on a distinctive change in shift of the photonic bandgap of a cholesteric polymer in response to contact with different alcohols.

The methods generally used for distinguishing between ethanol and methanol include electrical[1,2] and optical[3,4] detection. Among these methods, the optical method of detection of alcohol molecules is more convenient because it offers battery-free operation and direct visualization.[5] The traditional optical detection method involves the oxidation of ethanol and methanol to acetic acid and formic acid, respectively, in an acid solution of potassium manganate. Through the addition of leucosulfonic acid the formic acid is converted to formaldehyde which subsequently reacts with leucosulfonic acid to give a purple-colored product. However, this method is complicated, and it has the difficulty of a difficult discrimination step between a deep and a light purple color depending on the methanol concentration in the alcoholic substances, respectively. The color-based distinction is here difficult because of the single color response.

Recently, liquid crystals (LCs) have been used as stimuli-responsive materials.[6–11] LCs have a long-range order and thereby exhibit unique optical properties, especially in terms of molecular orientation. The cholesteric liquid-crystal (CLC) phase exhibits helicoidal molecular order and the helical pitch can be tuned to reflect in the visible spectrum. The molecular structure of CLCs can be decorated with special functional groups to subsequently react with targeted analytes.[12] Accordingly, the color reflected by the CLC can be changed by absorbing specific chemical agents. Therefore, CLCs can act as stimuli-responsive materials for colorimetry.[13,14] Furthermore, CLC polymers are (inkjet) printable[15] and can be used in roll-to-roll (R2R) processing, which facilitates fabrication of large area at low cost.

Here, we propose porous hydrogen-bridged CLC networks as a new sensing material. The CLC networks have porosity on molecular length scales created by breaking the hydrogen bridges. In order to obtain fast response when brought into contact with an analyte we also aimed the creation of macroscopic pores. The macroscopic pores are formed by polymerizing the CLC in the presence of an inert (non-polymerizable) liquid crystal, which is acting as porogen that can be removed after the network has been formed. Previously it has been demonstrated that in smectic hydrogen-bridged LC networks[16] as well as in nematic LC networks[17–19] the hydrogen bridges of benzoic acid based dimers can be broken under alkaline conditions. The benzoic acid salts enable the formation of nanopores with sizes similar to those of small organic molecules. The polarity of the pores as determined by the ionic carboxylic groups provides discrimination on polarity and ionic strength.

As stated above, we enhanced the porosity of the hydrogen-bridged CLC networks further by a liquid crystal porogen added to the polymerized mixture. The cavities thus formed improve on the uptake of the analyte thereby enhancing the sensitivity

Dr. C. K. Chang, Prof. C. M. W. Bastiaansen, Prof. D. J. Broer
Functional Materials and Devices
Eindhoven University of Technology
P.O. Box 513, 5600 MB, Eindhoven, The Netherlands
E-mail: ChangCK@itri.org.tw; D.Broer@tue.nl
Dr. C. K. Chang, Dr. H. L. Kuo
Materials and Chemical Research Laboratory
Industrial Technology Research Institute
31040, Hsinchu, Taiwan
Prof. C. M. W. Bastiaansen
School of Engineering and Materials Science
Queen Mary University of London
Mile End Road, London E1 4NS, London, UK

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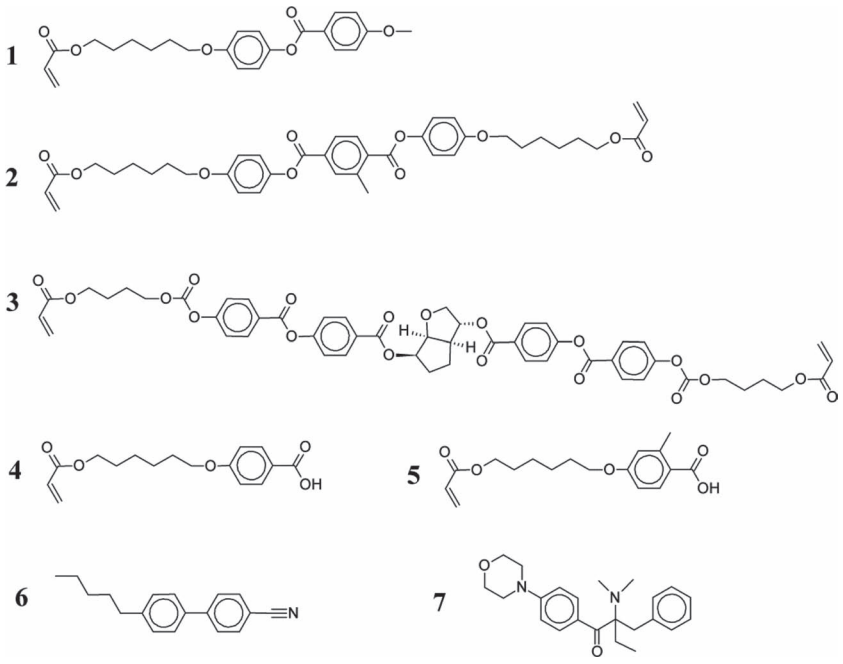

Scheme 1. Chemical structures of photopolymerizable CLC films.

of the sensing material. Here, we use a cyano biphenyl as the non-reactive mesogenic porogen. These molecules exhibit only non-covalent interactions within the polymer network and can be removed by extraction. In the idealized case, the cavities have a templated shape resembling the shape of the porogen with the presence of a large concentration of ionic entities. The sites where the analyte alcohol molecules will settle are therefore accurately characterized by size and balanced polar and ionic interactions. Given this, in combination with distinct differences in size and polarity of the alcohols, we anticipate a large difference in uptake of the two alcohols. The uptake of the alcohols will be recorded by the change of the reflection band of the cholesteric network as a consequence of the increase of the pitch of the molecular helix when the network swells by fast in-diffusion of the alcohols.

2. Materials

Scheme 1 shows the chemical compounds used in our photopolymerizable mixture. Monomers **1** and **2** are a mesogenic monoacrylate and diacrylate, respectively, and form a chemically crosslinked network upon polymerization. The chiral diacrylate **3** is added to the mixture to form the CLC phase. Monomers **4** and **5** are monoacrylates with a carboxylic acid unit, and they form hydrogen bridges to dimerize into a mesogenic entity that is preserved in the polymer network during polymerization. The non-reactive mesogen **6** is used to generate the porous organization. This mesogen is extracted by evaporation during a heat treatment after polymerization, which forms complementary cavities in the CLC networks. The photoinitiator **7** is used to initiate the photopolymerization process.

3. Results and Discussion

We used an inkjet printer to print the CLC mixture on rubbed films of triacetyl cellulose (TAC) and performed the photopolymerization process. **Figure 1** shows optical transmission spectra of the CLC films. Before the template molecule was extracted, the reflection band of the CLC films had a wavelength of around 563 nm. Upon extraction of the template molecule by heat treatment, the CLC films showed a blue shift to a reflection wavelength of around 470 nm caused by the shrinkage of helical pitch. The ratio of non-reactive mesogen is 18% in the CLC mixture, and the change in thickness of the CLC film is only 5.7% (from 7 μm to 6.6 μm) after extraction of the template molecule. It means that the CLC film will contain some free volume cavities after extraction of the template molecule.

For detecting ethanol and methanol using hydrogen-bridged CLC networks, the hydrogen bonds in the networks need to be broken and activated using an alkaline solution. This stimulates the absorption of analytes having hydrogen bonds. As shown in Figure 1, the color reflected by the CLC films showed a red shift after the activation in the alkaline solution, as a consequence of

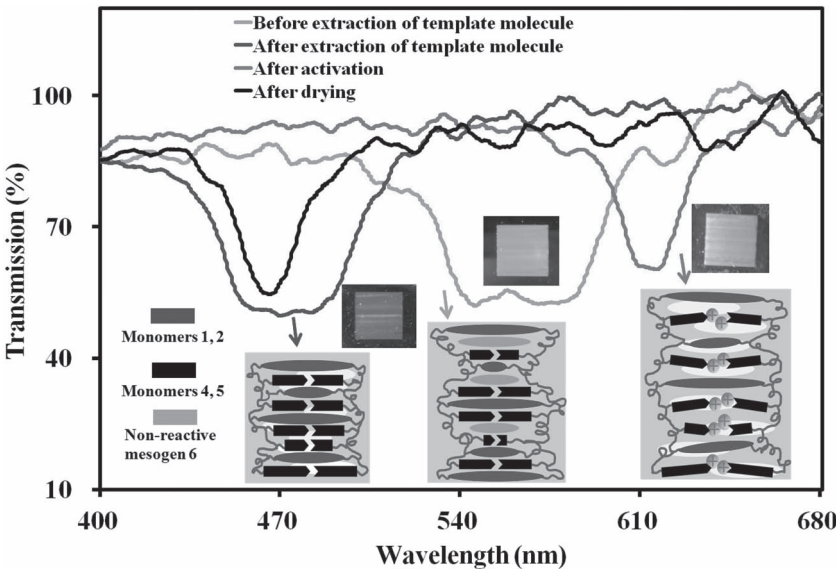

Figure 1. Optical transmission spectra of CLC films at different steps. Insets are the schematic drawings of different helical structures and the corresponding photographs of CLC films at different steps.

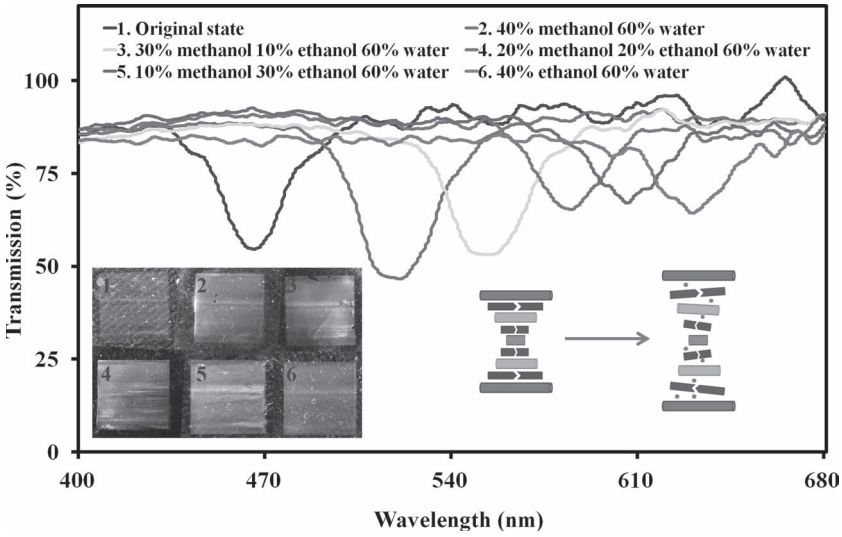

Figure 2. Changes in transmission spectra of CLC films as produced after removal of the porogen and breaking of the hydrogen bridges in alcohol solutions with different ethanol-methanol ratios. Right insets are schematic representations of different expansions of the hydrogen-bonded CLC with the absorption of ethanol and methanol. Left insets are the corresponding photographs of CLC films under uptakes of different ethanol-methanol ratios..

swelling of the helical structure of the CLC because of the broken hydrogen bonds in the CLC networks and the accompanying uptake of the alkaline buffer solution. However, when these CLC films were dried after activation, the color reflected by the CLC films showed a blue shift and reverted to reflecting a blue color.

After drying, the CLC films were placed in different solutions to assess their sensing ability for the alcohol molecules. **Figure 2** compares the sensing ability of the hydrogen-bonded CLC networks for ethanol and methanol. Blends were made of 60% water and 40% ethanol-methanol mixture of which the ethanol-methanol ratio was changed. Figure 2 shows that upon reaching equilibrium the CLC films reflect different colors in the alcohol solutions with different ethanol-methanol ratios. The hydroxyl group of alcohol molecules interacts with the carboxylic moieties that are activated during breaking of the hydrogen bridges. The molecular affinities of ethanol and methanol with hydrogen-bonded CLC are different, and hence, the extent of expansion of hydrogen-bridged CLC networks upon absorption of ethanol and methanol molecules is also different.

The Hildebrand solubility parameters are 29.6 and 26.5 $MPa^{0.5}$ for methanol and ethanol, respectively. The alcohol molecules interact with the carboxylic moities of the hydrogen-bridged CLC network. For reference, the Hildebrand solubility parameter of benzoic acid is 21.8 $MPa^{0.5}$ and is close to the value of ethanol. Therefore, ethanol will have higher molecular affinity with hydrogen-bridged CLC networks. Solutions containing more ethanol molecules caused the CLC films to exhibit a larger red shift. More specifically, the color reflected by the CLC films adjusted itself in accordance with the different swelling states of the helical structure. The absorption of the alcohol molecules with distinguishable molecular affinities to the helical structure result in different reflection colors. **Figure 3**a shows the influence of the porogen in distinguishing between methanol and ethanol. In this figure the variation in the transmission-valley wavelength, $\Delta\lambda$, for the CLC films at different ethanol-methanol ratios is shown. Figure 3a also demonstrates that the slope and $\Delta\lambda$ increase for the CLC films by the use of a porogen. In conclusion, by the use of porogens the CLC films definitely showed an enhanced sensitivity and selectivity for the detection of alcohol molecules.

Figure 3b also compares the sensing ability of the CLC films at different alcohol concentrations and different ethanol-methanol ratios. It was found that the application of the porogen the hydrogen-bridged CLC networks exhibit a good sensing ability for distinguishing between ethanol and methanol. Figure 3b shows that $\Delta\lambda$ of the CLC films increased with an increase in the alcohol concentration. This can be attributed to the interaction of the hydrogen bridge of the CLC films with the hydroxyl group of the alcohol molecule. An increase in the number of alcohol molecules absorbed causes the helical structure of a CLC to expand because of the swelling. Therefore, the color reflected by the CLC films showed a larger red shift with an increase in the alcohol concentration. Further, Figure 3b shows that the equilibrium $\Delta\lambda$ of the CLC films increased with an increase in the ethanol-methanol ratio. This was due to the expansion of the hydrogen-bridged helical structure with a larger number of ethanol molecules occupying the helical structure of the CLC films.

Next, we studied the reversibility of the hydrogen-bridged CLC networks for the detection of alcohol molecules. The CLC films were placed in solutions of pure water and in water with either methanol or ethanol for 10 min. Then, the CLC films were removed from these solutions, and they were exposed to the open air at room temperature (23 °C). The remnants of solutions around the CLC films were evaporated naturally with ambient air, and the optical transmission spectra of CLC films were obtained during the drying process. **Figure 4** shows that the hydrogen-bridged CLC networks have different reversibilities for the absorption of different solutions. For pure water, the color reflected by the CLC films reverted to the original one after drying. However, this was not the case for the absorption of alcohol molecules in the CLC films because they are highly polar molecules. Alcohols remained in the hydrogen-bridged helical structure even after drying. After drying of alcohol solutions (reaching equilibrium the CLC films), a comparison between the ethanol and methanol solutions showed that $\Delta\lambda$ was larger for the ethanol solution. Thus, we can conclude that the ethanol molecules showed stronger interaction than the methanol molecules with the hydrogen-bridged CLC networks.

Of relevance for practical use of this CLC sensor, it has only a limited reversibility for the detection of alcohol molecules. The molecular affinity of alcohol molecules to the carboxylic moieties makes it difficult to remove all alcohol molecules after the first time use, thus creating a new offset similar to the pristine sample. Therefore we propose to use the sensor a single time, making it disposable, which is acceptable because of the ease of fabrication of these sensors using inkjet technology.

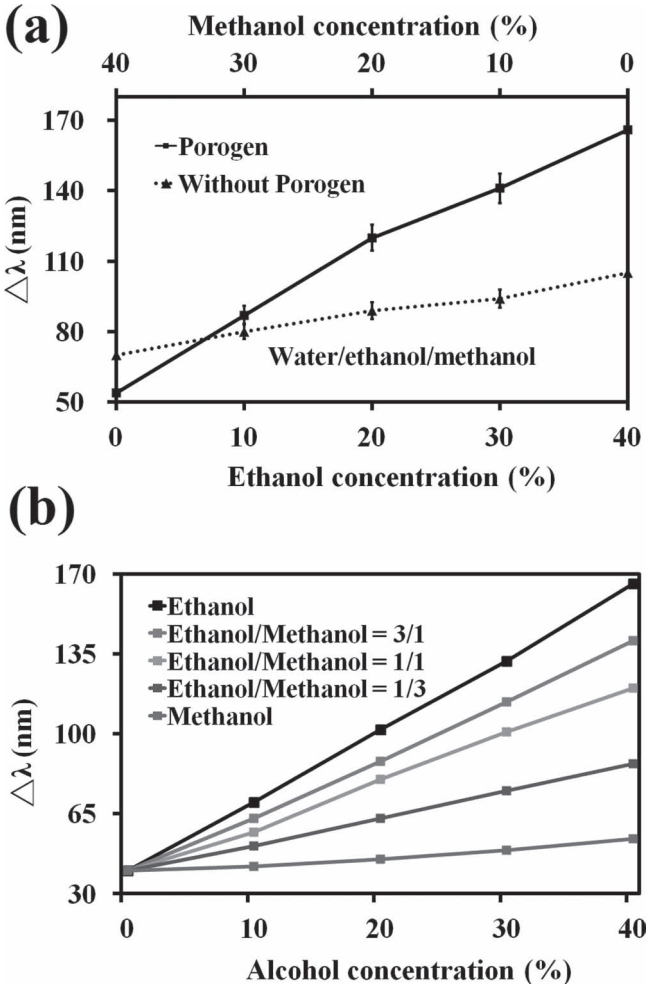

Figure 3. Variation in transmission-valley wavelength of CLC films: a) variation in transmission-valley wavelengths of CLCs with and without the use of a porogen in alcohol solutions (40%) with different ethanol-methanol ratios and b) variation in transmission-valley wavelength for CLCs made by using the porogen in solutions with different alcohol concentrations and different ethanol-methanol ratios.

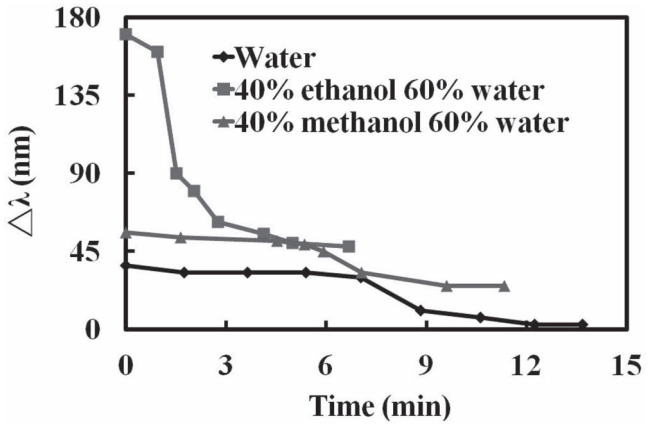

Figure 4. Reversibility of hydrogen-bridged CLC networks with the porous organization for absorption of pure water and different alcohol molecules.

4. Conclusions

In summary, hydrogen-bridged CLC networks can be used for distinguishing between ethanol and methanol. Alcohol molecules absorbed in the helical structure of hydrogen-bridged CLC networks reflect different colors owing to their different molecular affinity. Hydrogen-bridged CLC networks with ethanol molecules show a larger red shift than those with methanol molecules. This detection method based on the difference in molecular affinity can be extended to other types of alcohol molecules as well. Furthermore, hydrogen-bridged CLC networks that contain porogen-templated cavities have improved sensitivity and selectivity for the detection of alcohol molecules. Thus, these hydrogen-bridged CLC networks offer a promising method for distinguishing between alcohol molecules and can be potentially used to detect counterfeit wine.

5. Experimental Section

Materials: Monomers **1** and **2** and the non-reactive mesogen **6** were purchased from Merck. The chiral diacrylate **3** was purchased from BASF. Monomers **4** and **5** were obtained from Philips Research and Synthon, respectively. The photoinitiator **7** was purchased from Ciba. The CLC mixture used for the CLC films with enhanced cavities contained 26.4 wt% of monomer **1**, 14.4 wt% of monomer **2**, 18 wt% of monomer **4**, 18 wt% of monomer **5**, 18 wt% of non-reactive mesogen **6**, 4.5 wt% of chiral diacrylate **3**, and 0.7 wt% of photoinitiator **7**. Mesogen **6** is used here as porogen. The CLC mixture used for the CLC films without the porous organization contained 37.1 wt% of monomer **1**, 21.1 wt% of monomer **2**, 18 wt% of monomer **4**, 18 wt% of monomer **5**, 5.1 wt% of chiral diacrylate **3**, and 0.7 wt% of photoinitiator **7**. All the CLC mixtures were dissolved in tetrahydrofuran (THF) solution (1:1).

Film Preparation: We used an inkjet printer (Dimatix-Fujifilm) to print the CLC mixtures on TAC films that were pre-rubbed using a flannel sheet. The temperatures of the printing substrate and head were 53°C and 42°C, respectively. The printing area was 11 mm × 11 mm. The nozzle size was 10 picoliter drop volumes, and average diameter of droplet was 27 μm. The drop space was set to 25 μm, and the drops could be coalesced and a uniform print was obtained. After printing the CLC mixtures on the TAC films, photopolymerization was performed in a nitrogen atmosphere for 150 s. For the extraction of the template molecules, the CLC films were heated with the non-reactive mesogen on a hotplate at 105 °C for 1 h in the nitrogen-circulation atmosphere after photopolymerization. For activation, the CLC films were placed in an alkaline solution (NaOH, 0.05 M) for 20 min, and the films were dried on the hotplate at 75 °C for 1 h in the nitrogen-circulation atmosphere.

Transmission Measurement and Sensing Ability: A AvaSpec spectrometer (AvaSpec-USB2, version 7.3) was used to measure the transmission spectra of the CLC films after immersing them in different alcohol solutions for 10 min. Then, the CLC films were removed from the solutions and were placed between two glass sheets to prevent the solution from evaporating during the measurement of transmission spectra.

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