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### COMMUNICATION

#### Irreversible visual sensing of humidity using a cholesteric liquid crystal<sup>†</sup><sup>‡</sup>

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Irreversible optical sensing of humidity by a doped cholesteric liquid crystal is achieved by using a thin film of nematic host E7 with a binaphthylorthosilicate ester as dopant (guest). The film changes its color from blue (to green to orange to red) to colorless when exposed to humidity as the dopant is hydrolyzed.

Monitoring the storage conditions of products such as food, pharmaceuticals and chemicals is important for extending shelf life, preserving freshness, improving quality, preventing spoilage and/or avoiding use after spoilage.<sup>1</sup> A convenient way to monitor products is by the use of optical disposable sensors built into packaging.<sup>2</sup> Using optical sensors is advantageous because color change is easily detected visually, obviating the use of any electronic circuit or instruments.<sup>3,4</sup> Moreover, with suitable technology, the sensors may be printed on the packaging in an economical process. Monitoring humidity in a way that records the complete exposure history of a product with so-called timeanalyte integrators is important for packaging of food, drugs, and chemicals and a range of other products. Several humidity sensors have been reported, among which are a sensor based on photonic ionic liquids,<sup>5,6</sup> a colorimetric humidity sensor based on encapsulation and dissolution of dye in urea,<sup>7</sup> as well as one based on amorphous Al<sub>2</sub>O<sub>3</sub> nanotubes.<sup>8</sup> However, these sensors are reversible and real-time humidity conditions are indicated.

Cholesteric liquid crystals (CLCs)<sup>9–14</sup> can be used as optical sensors as they exhibit a reflection band that can be tuned by appropriate chiral dopants. The helical structure of the cholesteric or chiral nematic (n\*) liquid crystals is induced by the interaction between the nematic liquid crystalline host molecules and the chiral guests (dopants).<sup>15–23</sup> Hence, the colour of such materials can be tuned either by proper selection of the helical twisting power of the chiral dopant or its concentration. Recently, we have demonstrated that optical sensors can be fabricated by dissolving reactive chiral dopants in nematic liquid crystals. A CLC optical sensor was obtained, for instance, in which the chiral dopant

reacted with the analyte, causing a change in helical twisting power of the dopant and hence the color. When a thin layer of CLC with the responsive dopant was exposed to an analyte  $(CO_2 \text{ or } O_2)$ ,<sup>19</sup> the initial color changed within minutes. In this communication, we describe an irreversible humidity sensor (a so-called time–humidity integrator) based on a doped cholesteric liquid crystal incorporating a chiral dopant that reacts with water.

Binaphthyl derivatives are known for their use as dopants due to their high capability to induce a helical pitch in nematic liquid crystals.<sup>24–27</sup> This capability is usually expressed as helical twisting power (HTP or  $\beta$ ). Covalently bridged 1,1-binaphthyl derivatives usually possess a higher HTP than open chain analogs.<sup>27,28</sup> This difference in HTP stimulated us to synthesize the hydrolytically labile orthosilicate ester **2** (Scheme 1), and to compare its HTP to that of R-BINOL (1) to establish the suitability of **2** as dopant for a CLC based humidity sensor.

Bis-[binaphthylen-(2.2')-dioxy]-silan (2) (Scheme 1) was synthesized from (R)-(+)-1,1'-bi(2-naphthol) (R-BINOL; 1) by stirring its solution in THF with SiCl<sub>4</sub> in an inert atmosphere at 0 °C.<sup>29</sup>

The hydrolytic lability of **2** was confirmed by exposing a CDCl<sub>3</sub> solution to humid air. A peak at  $\delta$  5.1 ppm corresponding to the phenolic proton of **1** was observed after 1 h exposure of the solution to humid air (Scheme 1 and ESI<sup>‡</sup>, Fig. S1). The favorable thermodynamics of the hydrolysis and the insolubility of the SiO<sub>2</sub> produced guarantee irreversibility of humidity sensors based on this reaction. Kinetics of hydrolysis



Scheme 1 Synthesis of bis-[binaphthylen-(2.2')-dioxy]-silan (2) from (*R*)-(+)-1,1'-bi(2-naphthol) (1) and reaction of bis-[binaphthylen-(2.2')-dioxy]-silan (2) with water to form (*R*)-(+)-1,1'-bi(2-naphthol) (1) and SiO<sub>2</sub>.

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of the dopant in THF was investigated by monitoring optical rotation with time using a polarimeter (Fig. S2, ESI‡). After addition of water, first a sharp increase in specific rotation from +52.12 at 1 min to +55.39 at 3.8 min was observed, then a gradual decrease was noticed to +25.09 at 195 min. This indicates that the dopant is hydrolysed in the presence of water.

The helical twisting power (HTP or  $\beta$ ) of a dopant is defined as  $\beta = (p \times ee \times c)^{-1}$ , where p is the pitch, ee the enantiomeric excess of the dopant, and c the concentration of the dopant. HTPs of 1 and 2 in E7 were determined from the position of the reflection band from the relationship  $\lambda = p \times n$ , where  $\lambda$  is the centered wavelength of reflection and n is the average in-plane refractive index. Assuming a refractive index of 1.6,  $\beta$  was calculated to be  $-34.9 \ \mu m^{-1}$  using a 10.1 wt% solution of 2 in E7, which has a reflection band at 454 nm and forms a blue film. Compound 1 has a much lower solubility than 2 in E7, and the HTP was determined by a modified Grandjean Cano method<sup>30</sup> on a 0.98% solution, which was prepared by dissolving the dopant above the clearing point of E7 and then measured at room temperature. The pitch was 3.22 µm and the HTP of the sample was found to be  $-31.7 \ \mu m^{-1}$  in E7. At higher concentrations, 1 was not soluble in E7 and precipitated. Hence, upon hydrolysis of 2 to 1, the helical pitch in films of E7 is expected to change significantly. However, this will only to a small extent be caused by the small change in HTP, but predominantly by the low solubility of 1, which results in precipitation of 1 from its host material.

In order to establish the use of the hydrolytic reaction as the basis for a CLC sensor, a blue colored CLC film was prepared by spreading E7 containing 10.1 wt% dopant (2) on a rubbed triacetyl cellulose (TAC) foil using a wire-bar coater because TAC foil is widely used in LCD as a protective layer<sup>31a</sup> and an optical sensor for nitrites in water and food based on the use of brilliant cresyl blue immobilized on a triacetyl cellulose membrane was also reported.<sup>31b</sup> This film was exposed to nitrogen (N<sub>2</sub>) with a 75% relative humidity (RH) (at 22 °C, 100% humid air contains 19.416 g m<sup>-3</sup> of water) and the change in the visible reflection band was continuously monitored. The initial blue reflection band (peak maximum at 454 nm) of the CLC film turned to orange-red and finally to colorless within a few minutes. After 1 h, the reflection band of the CLC had completely disappeared from the visible wavelength region *i.e.* the reflection shifted to the near infrared and its intensity decreased to some extent. When a CLC film was exposed to dry N2 (i.e., N2 with <0% RH) for 1 h, no change in the position or intensity of the reflection band was observed, indicating that the reaction requires an external source of moisture to proceed.

Next, the influence of relative humidity (RH) on response time of the CLC sensor was investigated. A CLC film with 10.1 wt% dopant was exposed to N<sub>2</sub> with RHs of 85, 75, 65, 47, 27 and 7%. This resulted in a continuous shift of the reflection band of the films and ultimately all films became colorless (Fig. 1). However, the rate of the shift is strongly dependent on the value of RH. At a relative humidity of 75%, the initial reflection peak at 454 nm (0 min) shifted to 821 nm within 10 minutes, whereas at RH = 7%, this took nearly 60 min. In Fig. 2, the reciprocal reflection peak maximum;  $1/\lambda_{max}$  is plotted against time, since this directly gives a measure of change in HTP ( $\beta$ ) with time. At higher RHs, a faster change of color was observed.



Fig. 1 (top) Photographs indicating color changes upon exposure to air (relative humidity of 75%) of a CLC film of E7 containing 10.1% of 2. (bottom) Reflection spectrum of this film as a function of time. The numbers in the graph are minutes of exposure time.

In order to establish whether diffusion of water through the film is a rate limiting factor, kinetics of the pitch change were also studied as a function of film thickness. Films with 10.1 wt% dopant in E7 and thicknesses of 6  $\mu$ m and 12  $\mu$ m were prepared. The position of the reflection band was monitored during exposure to N<sub>2</sub> with 75% RH. The time dependence of  $1/\lambda_{max}$  is plotted in Fig. 2b. Both films showed a similar response to exposure, which indicates that in this thickness range, the kinetics of response is not a diffusion limited process, such as the diffusion of water into the film.

The results indicate that thin films based on a nematic liquid crystal and a humidity responsive chiral dopant act as an irreversible humidity sensor with a limited cross-sensitivity. At room temperature, the thin films are in the chiral-nematic phase and, consequently, the films tend to exhibit flow and a limited mechanical coherence. Several routes were developed in the past to circumvent such issues by incorporating a network or gel *via* solvent, temperature or polymerization induced phase separation.<sup>32</sup>

In conclusion, we have demonstrated an optical humidity sensor based on a cholesteric liquid crystal with a dopant designed to hydrolyze irreversibly. Under humid conditions, hydrolysis of dopant **2** to the sparingly soluble product **1** leads to an increase in the pitch of the CLC. As a result, the color of the films changed from blue to colorless. It was also found that sensing behavior was independent of film thickness which



**Fig. 2** (a) Plot of the reciprocal reflection peak maximum  $(1/\lambda_{max}) vs.$  time for 10.1 wt% dopant in E7 upon exposure to six different RHs. (b) Plot of the reciprocal reflection peak maximum  $(1/\lambda_{max}) vs.$  time for films of 10.1 wt% dopant in E7 with two different thicknesses upon exposure to 75% RH.

indicates that the kinetics are chemistry controlled and not limited by diffusion of water vapor into the film.

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