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Optical Monitoring of Gases with Cholesteric Liquid Crystals

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Abstract: A new approach to optical monitors for gases is introduced using cholesteric liquid crystals doped with reactive chiral compounds. The approach is based on cholesteric pitch length changes caused by a change in helical twisting power (HTP) of the chiral dopants upon reaction with the analyte. The concept is demonstrated for monitoring carbon dioxide via reversible carbamate formation and for oxygen using the irreversible oxidation of a chiral dithiol to a disulfide. Monitoring of CO_2 was achieved by doping a commercial cholesteric liquid crystalline mixture (E7) with 1.6% mol of the 1:1 complex of an optically pure diamine with a TADDOL derivative. Upon exposure to carbon dioxide, the reflection band of a thin film of the mixture shifted from 637 to 495 nm as a consequence of dissociation of the complex after carbamate formation of the diamine. An O_2 monitor was obtained by doping E7 with a chiral binaphthyl dithiol derivative and a nonresponsive codopant. The reflection band of the oxygen monitor film changed from 542 to 600 nm, due to the conformational change accompanying oxidation of the dithiol to disulfide. These monitoring mechanisms hold promise for application in smart packaging, where carbon dioxide and oxygen are of special interest because of their roles in food preservation.

Introduction

Cholesteric liquid crystals (CLCs), also known as chiral nematic liquid crystals, have been widely used as electro-optic materials in display devices and as responsive materials with a reflection band that can be tuned by stimuli such as temperature and light.[1−6] In comparison to nematic phases, cholesteric phases have additional helical organization along the orientation of the director. Cholesteric phases are characterized by a helical pitch (p), the distance corresponding to a 360° rotation of the mesogens along the helix director. If the length of the pitch is of the same order of magnitude as the wavelength of visible light, the cholesteric phase selectively reflects light and shows a color in the visible range. The wavelength of the selective reflection can be defined as $\lambda = np$, where n is the mean refractive index of the liquid crystal.[7] As the pitch changes in response to changes in the environment, color changes are observed, which enables use of CLCs as optical detectors for external stimuli. The widest application is temperature detection, as the color of the CLCs goes from blue to red, indicating an increase of pitch length with temperature.

Cholesteric phases occur only in optically active systems in which either the mesogen is chiral or the director is twisted by doping with a chiral dopant to generate the helical organization. The helical twisting power (HTP or β) of a dopant is defined as $\beta = (p \times \mathrm{ee} \times c)^{-1}$, where p is the pitch, ee the enantiomeric excess of the dopant, and c the concentration of the dopant. Doped CLCs have many favorable properties compared to those made up of chiral mesogens, one of which is the ease with which the pitch can be tuned by changing the concentration or nature of the dopant.[8] Chiral dopants can be shape persistent or switchable to the change of environment. Studies on shape-switchable chiral dopants in CLCs have been mainly focused on photo- or heat-responsive systems.[1b,2] An example of switchable dopant is the motor molecule designed by Feringa

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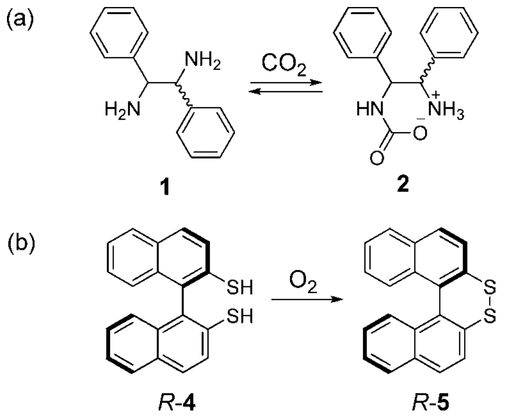
Scheme 1. Molecular Structures of (a) CO_2- and (b) O_2-Responsive Chiral Dopants and the Reactions with the Corresponding Gas



et al.,[3] which was dissolved in liquid crystals to drive the rotation of microscale objects. Upon UV irradiation a photochemical isomerization of the motor dopant resulted in a rotation of the fingerprint texture ascribed to the change of length and handedness of pitch induced by change of HTP and helicity of the dopant. Subsequent thermal isomerization induced rotation in the opposite direction. There are also examples of photoresponsive CLCs using chiral dopants carrying azobenzene moieties, which change color upon irradiation with light.[4] Other examples of CLC uses include chemical sensors for organic solvent detection using the swelling effect of the cholesteric pitch[5] and molecular recognition using cholesteryl mesogen based functional tectons.[6] The above-described optical sensors report the real-time conditions with respect to environmental parameters such as temperature, solvents, and light, and the sensors return to their original state upon removal of the stimuli. However, in many monitoring applications (food, medical, electronics, personal care products) it is essential to record the entire history of a product: i.e., the monitors should act as a so-called time-analyte integrator. CLCs with chiral dopants that change conformations and HTPs, and consequently induce color changes of the CLCs upon chemical monitoring of external compounds, have not been reported so far. In order to achieve effective monitoring, the chiral dopants should display a fast response and a large change in HTP in the presence of analytes, while for monitors that act as time analyte integrators, irreversible change is preferred. Here, we use the term "monitor" loosely to include reversible detection as well as dosimetric time analyte integration.

Herein we report an approach using responsive chiral compounds as dopants for CLCs to obtain monitors for gaseous carbon dioxide and oxygen. The presence of the analyte induces visible color changes in CLC thin films. As shown in Scheme 1, the design of carbon dioxide monitoring is based on the reversible reaction of an analyte with a chiral dopant containing diamine groups to form a carbamate, while the oxygen monitoring is based on the irreversible oxidation of a binaphthalene dithiol derivative to the corresponding disulfide by molecular oxygen. In either case, the chiral dopant was designed to undergo significant conformational change upon reaction with the analyte, resulting in a change in HTP with concomitant change in pitch of the CLC phase upon exposure to the gas. Importantly, carbon dioxide and oxygen monitoring is of strong interest in, for instance, food packaging applications to monitor the carbon dioxide atmosphere within the packaging or to monitor the diffusion of environmental oxygen into the packaging. The approach presented here may be implemented in an economical/high volume production process such as screen or inkjet printing to compete successfully with current monitoring techniques, which usually need expensive analytical instrumentation.[9]

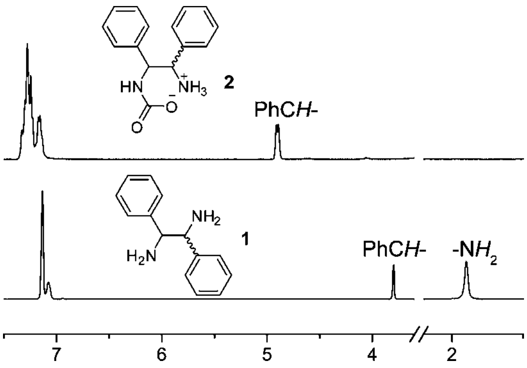
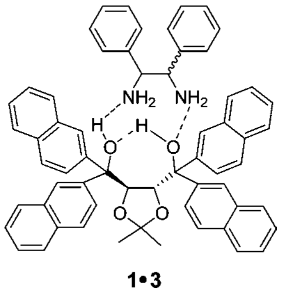


Figure 1. ^{1}H NMR spectra of **1** and carbamate **2** in *d*-DMSO.

Results and Discussion

Carbon Dioxide Monitoring. The principle for CO_2 monitoring is based on the reaction of CO_2 with amines to form carbamates. The mechanism of carbamate formation between CO_2 and amines and its implications to CO_2 monitoring was reviewed by Rudkevich et al.[10] The reaction of carbon dioxide with optically pure chiral diamines **1** ((*R*,*R*)-**1** or (*S*,*S*)-**1**) to form carbamate **2**, as shown in Scheme 1a, was investigated by ^{1}H NMR and IR. ^{1}H NMR spectra of **1** in *d*-DMSO solution before and after saturation with CO_2 showed changes which are typical for the transformation from amine to carbamate:[10] the peak of the amino protons at 1.91 ppm disappeared, the chemical shifts of aromatic protons moved downfield, and the peak for two benzyl protons shifted from 3.81 to 4.91 ppm and split into a doublet (Figure 1). In the IR spectra of **1** (Figure S2, Supporting Information), the N−H stretching vibrations of the amino group (3377 and 3355 cm^{-1}) disappeared after reaction with CO_2 and a broad N−H band (3314 cm^{-1}) of **2** appeared, while a carbonyl group stretching band was clearly observed at 1650 cm^{-1}.[11]

Because the helical twisting power (β_M) of (*R*,*R*)-**1** in liquid crystal host E7[12] was measured to be too low ($+10\ \mu m^{-1}$ using the Grandjean−Cano method[13]) to induce a cholesteric phase with a reflection band in the visible region at practical dopant concentrations, we introduced the TADDOL derivative (*R*,*R*)-**3**, with an extremely high HTP ($\beta_M = +250\ \mu m^{-1}$ in K15),[14] to form a complex with **1** through diamine/diol hydrogen bonding at a 1:1 molar ratio.



1•3

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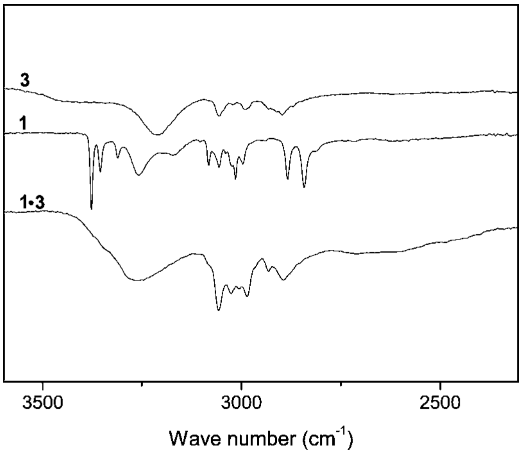

Figure 2. IR spectra of **1**, **3**, and the complex **1**•**3**. The complex sample was prepared by dissolving **1** and **3** in dichloromethane, and then the solvent was evaporated.

C$_2$-symmetrical diamines and diols are known to form supramolecular complexes with helical structures, known as supraminols, via weak hydrogen bonding between amines and alcohols, and these complexes were shown to be gradually carbonated by CO_2 in air.[15] The motif of dual dopant through hydrogen bonding and charge interactions has been used for chirality double amplification in liquid crystals.[16] The hydrogen bonding between **1** and **3** was reflected by the vibration band changes of amino and hydroxyl groups in IR spectra (Figure 2) after complexation. A sample for IR measurement was prepared by dissolving equimolar amounts of **1** and **3** in dichloromethane followed by evaporation of the solvent at room temperature. The bands at 3377 and 3355 cm^{-1} attributed to the amino groups of **1** disappeared, and the band for hydroxyl groups of **3** shifted from 3210 to 3262 cm^{-1} after complexation. The 1:1 binding stoichiometry of the (*R*,*R*)-**1**•**3** complex was confirmed by Job's plot analysis (Figure S5a, Supporting Information). ^{1}H NMR titration results fitted well with a 1:1 stoichiometry and the binding constant $K_a = 15.2 \pm 0.2$ M^{-1} (Figure S5b, Supporting Information). The complexation between (*S*,*S*)-**1** and **3** to give the diastereomeric complex (*S*,*S*)-**1**•**3** was similar to that between (*R*,*R*)-**1** and **3**. A Job's plot analysis showed a 1:1 binding stoichiometry for (*S*,*S*)-**1**•**3**, and ^{1}H NMR titration gave the binding constant $K_a = 18.3 \pm 0.2$ M^{-1} (Figure S6, Supporting Information).

In order to establish the response of the CLC monitor with the complex dopants to CO_2, a small amount of either (*R*,*R*)-**1** and **3** or (*S*,*S*)-**1** (typically 1.6% mol) was directly dissolved in E7 and thin CLC films were prepared by wire-bar coating. When (*R*,*R*)-**1** was used, a red CLC film was obtained with a maximum in the reflection band at 637 nm. This film was exposed to a pure gaseous CO_2 atmosphere, and the change in reflection band was monitored. The reflection band switched from red to green upon contact with CO_2 in seconds, which indicated shrinkage of the pitch length due to increasing HTP of the chiral dopant. The film was saturated with CO_2 in 40 min with a final color of greenish blue (Figure 3) and a maximum of the reflection at 495 nm, a change of 142 nm. Using the equations $\lambda = np$ and $\beta = (p \times \text{ee} \times c)^{-1}$, the HTP ($\beta_M$) value of the initial complex dopant and that after reaction with CO_2 in E7 were determined to be 157 and 202 μm^{-1}, respectively, corresponding to a 29% decrease in pitch. The formation of carbamate in the liquid crystals was confirmed by IR spectra (Figure 4), at a higher concentration of the complex dopant (10% mol) to increase the intensity of IR signals. The appearance of two vibration bands was in agreement with that of the product from free diamine **1** with CO_2: one broad band at 3314 cm^{-1} was attributed to N−H stretching of ammonium and carbamate groups, and the other sharp one at 1650 cm^{-1} was assigned to stretching of the carbamate carbonyl group.

When the complex (*S*,*S*)-**1**•**3**—a diastereomer of the complex of (*R*,*R*)-**1** and **3**—was used in the film of E7 at the same concentration (1.6% mol), the maximum of the reflection band was at 559 nm (Figure S7, Supporting Information), corresponding to a HTP of +179 μm^{-1}. After exposure to CO_2 for 1 h, the reflection band was at 536 nm, a shift of just 23 nm that was difficult to detect by eye. The HTP (β_M) of the complex dopant (*S*,*S*)-**1**•**3** after reaction with CO_2 was +187 μm^{-1}, corresponding to a decrease of the helical pitch of only 4%.

In a control experiment, a CLC film with **3** (1.2% mol) as the only dopant was exposed to a CO_2 atmosphere for 1 h. As shown in Figure 4, no shift of the reflection band or color change was observed, which indicated that **3** was not responsive to CO_2 and did not experience any chemical change in this system during the exposure. Therefore, the color change of the CLC monitor is ascribed to decomplexation of **1**•**3**, due to the reaction of **1** with CO_2 and not to any chemical change of **3**.

The HTPs of the chiral dopants relating to CO_2 monitoring both before and after exposure to CO_2 are summarized in Table 1. Due to low HTPs of (*R*,*R*)-**1** and the formed carbamate **2** and minimal change in HTP upon conversion of **1** to **2**, the diamine alone was not able to induce a significant color change in this CLC system. From the HTPs in Table 1, it can be concluded that the effects of carbamates **2** and **3** on pitch length are not additive, because the helical pitch of the system is larger than that calculated from the combined twisting powers of the separate components. For example, in the film prepared with 1.6% mol of (*R*,*R*)-**1** and **3** each, a pitch of 427 nm is calculated when (*R*,*R*)-**1** is fully converted to carbamate (*R*,*R*)-**2** if the carbamate does not interact with **3**, while the observed maximum of the reflection band is at 495 nm. On the basis of this observation we propose that carbamate **2** also interacts with **3**.

Although the HTP of (*S*,*S*)-**1**•**3** is sufficient to induce a reflection band in the visible range, the HTP change after CO_2 monitoring was too small to induce a visible color change. In comparison to (*S*,*S*)-**1**•**3**, (*R*,*R*)-**1**•**3** showed a much stronger HTP change after reaction with CO_2, which induced an unmistakable color change of the CLC film.

As mentioned above, the response of the CLC CO_2 monitor with (*R*,*R*)-**1**•**3** as chiral dopant was fast, as the reflection band of the sample shifted by 98 nm in 10 s. To investigate the

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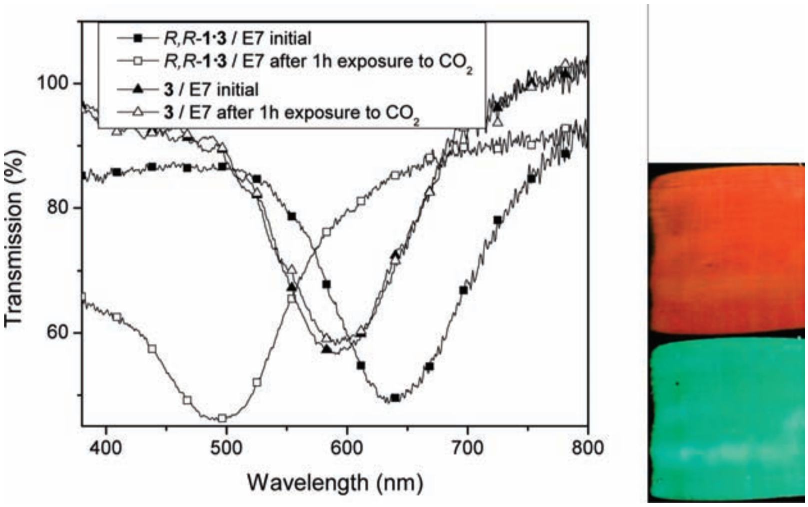

Figure 3. Transmission spectra of samples with the complex dopant ((R,R)-**1·3** (square) and **3** as dopant (triangle) in E7 before (solid symbols) and after (open symbols) exposure to CO_2. At the right are given images of the CLC film before (top) and after (bottom) exposure to CO_2 for 1 h.

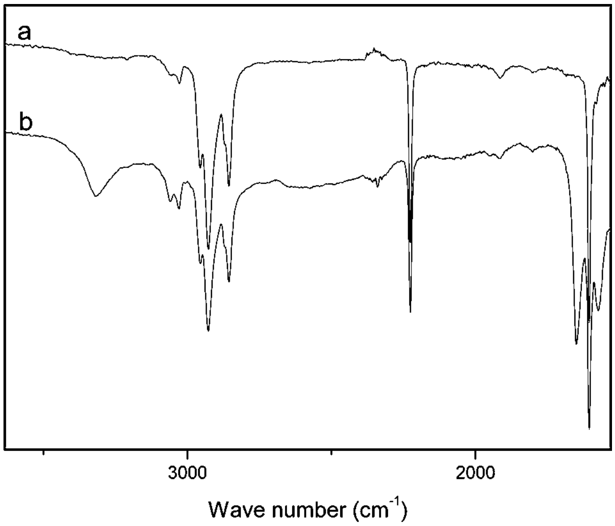

Figure 4. IR spectra of **1·3** in E7 before (a) and after (b) exposure to CO_2 for 1 h.

kinetics of the monitoring process, films with 1.6 mol % (R,R)-**1·3** in E7 were prepared at different thicknesses and the position of the reflection band was monitored during the exposure to CO_2. The time course is plotted in Figure 5a. The sample with a thickness of 9 μm showed a slightly faster decrease in pitch than did that of 4 μm, while for a diffusion-controlled process, saturation of the film with CO_2 is expected to be much slower for the thicker film. At the same time, if the monitoring process is diffusion controlled, a concentration gradient of carbamate will be present along the thickness of the monitor film, which results in different pitch lengths along the thickness. Accordingly, the reflection band will broaden during the carbamate formation reaction and narrow again when the pitch length is uniform because equilibrium has been reached throughout the film. The width of the reflection band was compared for films during exposure to CO_2, but no obvious increase in width was observed (Figure S8, Supporting Information). Therefore, we conclude that the monitoring process of the CLC CO_2 monitor is independent of film thickness and is not diffusion-controlled.

Since the monitoring process is not diffusion controlled, we assume that it is chemical reaction controlled. When the color shift is the result of a rate-limiting pseudo-first-order reaction, plotting $\ln(1 - X)$ (X = relative conversion) against time will result in a linear plot according to eq 1, in which k is the first-order rate constant.

$$\ln(1 - X) = -kt \tag{1}$$

The plot in Figure 5a is linear up to a conversion of at least 85%, which suggests that carbamate formation can be considered a pseudo-first-order reaction up to this stage, with a rate constant of 0.145 ± 0.023 s^{-1}.

Formation of ammonium carbamates is a reversible reaction, and the product can usually be converted to amines and CO_2 by elevating temperature or passing a stream of an inert gas such as nitrogen through a solution to remove CO_2.[10] Because the reverse reaction is unwanted in applications as time−analyte integrator monitors, the kinetics of decomplexation was also investigated. After complete saturation of the film with CO_2, the chamber containing the sample was continuously purged with nitrogen at room temperature. The reflection band slowly red-shifted, indicating a decrease of the HTP of the dopant due to dissociation of the formed carbamate. The decomplexation reaction of carbamate into amine and CO_2 is significantly slower than complexation. The reflection band shifted only 35 nm after 1 h. Plotting $\ln(1 - X)$ against time in Figure 5b is linear, with a first-order reaction rate constant for the reconverting process of 7.20×10^{-5} s^{-1}. Extrapolation of the reaction results in a time of 2.7 h for 50% decomplexation.

The response of the CO_2 monitor toward different analyte concentrations is shown in Figure S9 (Supporting Information). When the CO_2 concentration was decreased to 25%, complete conversion was observed, but with a longer time than that with pure CO_2. A further decrease of CO_2 concentration to 10% and 5% gave a much longer response time and incomplete conversion when the equilibrium was reached. A sample in air (0.03% CO_2) gave a conversion of 82% after 7 days.

The positions of the reflection band in both the bound and unbound CO_2 monitors is also dependent on temperature and is shown in Figure S10 (Supporting Information). As reported in the literature,[14] the helical twisting power of **3** decreases with temperature and a red shift by 14% in reflection band position was observed when the temperature was increased from 24 to 34 °C. The relatively large shift is probably due to breaking of the intramolecular hydrogen bonding between the hydroxyl

Table 1. Helical Twisting Powers ($\beta_M/\mu m^{-1}$) of Chiral Dopants Relating to CO_2 Monitoring

	dopant								
	(*R*,*R*)-**1**[a]	(*S*,*S*)-**1**[a]	(*R*,*R*)-**2**[a]	(*S*,*S*)-**2**[a]	**3**[b]	(*R*,*R*)-**1**·**3**[b]	(*R*,*R*)-**2**·**3**[b]	(*S*,*S*)-**1**·**3**[b]	(*S*,*S*)-**2**·**3**[b]
$\beta_M{}^c$, μm^{-1}	+10	−10	+9	−9	+225	+157	+202	+179	+187

[a] Measured by Grandjean−Cano method. [b] Determined using the equations $\lambda = np$ and $\beta = (p \times \text{ee} \times c)^{-1}$. [c] Not corrected for the optical purity; the sign of β_M was determined by contact method.

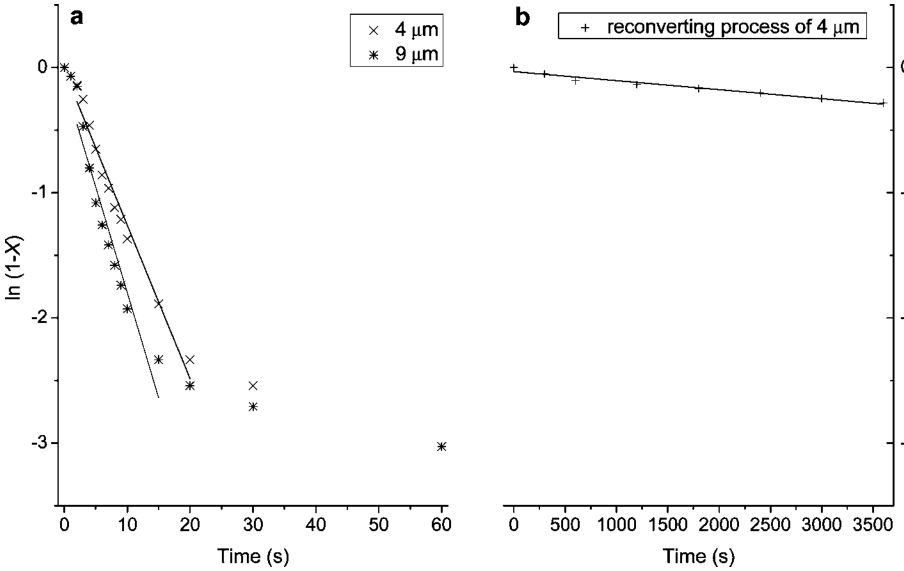

Figure 5. Time course for the monitoring and reconverting process of a CLC CO_2 monitor with 1.6% mol (*R*,*R*)-**1**·**3** as a chiral dopant in E7: (a) complexation under an atmosphere of pure CO_2, with *X* corresponding to the fraction of the maximum change of λ_{max}; (b) decomplexation under a nitrogen atmosphere, with *X* corresponding to the fraction of the total change back to the initial state of the monitoring process.

groups of **3** with increasing temperature. In our study, when the temperature was increased from 25 to 40 °C, the reflection band red-shifted by 11% and 12% for the unbound and bound CO_2 monitors, respectively, giving the same trend as in the literature report. If the temperature was lowered from 25 to 10 °C, the reflection band blue-shifted by 8% and 4% for the unbound and bound CO_2 monitors, respectively. The changes in position of the reflection band are therefore somewhat smaller than those induced by complexation with CO_2 but still large enough to necessitate measuring at constant temperature or comparing the color of a responsive area with that of a nonresponsive area (containing unreactive dopant).

Oxygen Monitoring. The design of an oxygen monitor was based on the oxidation of thiols with oxygen to give disulfides. Study of the oxidation chemistry of thiols has shown that aromatic thiols are more reactive than aliphatic ones and the reactivity of thiols with molecular oxygen can be increased by addition of metal complex catalysts[17] or bases such as amines[18,19] Axially chiral binaphthyl derivatives are widely used as chiral dopants in biphenyl host liquid crystals, because similarity of the biaryl structure to that of the host facilitates the chirality transfer.[7a] The HTP of optically pure 1,1-binaphthyl derivatives is highly dependent on the groups attached at the 2,2′-positions. With a covalent bridge or intramolecular hydrogen bonding, the dopants possess an HTP higher than that of open-chain derivatives.[20] Inspired by the above reports, we synthesized (*R*)-(+)-1,1′-binaphthalene-2,2′-dithiol (**4**)[21] and used it as a dopant in liquid crystals to fabricate a CLC optical oxygen monitor. We expected high monitoritivity of the aromatic dithiol groups toward molecular oxygen in the presence of catalyst and a strong HTP change from the conformational change from an open-chain structure of **4** to the bridged structure of disulfide **5** (Scheme 1b). Although some metal complexes accelerate the oxidation of thiols into disulfides, most of them are insoluble in liquid crystals. For the oxidation of **4** with molecular oxygen in air to give **5**, we found triethylamine to be an effective catalyst at room temperature without external activation. **4** was obtained as a white solid and was fairly stable in air and in solution in the absence of base catalyst. The neat compound turned slightly yellow after 1 month in air. The yellow color was attributed to the formation of **5**.

The oxidation of **4** with molecular oxygen was performed under ambient conditions by adding a catalytic amount of triethylamine to a DMF solution of **4**, which immediately turned yellow. Oxidation was monitored by TLC and was quantitative within 5 min. The HTP of **5** in E7 has been reported to be β_M

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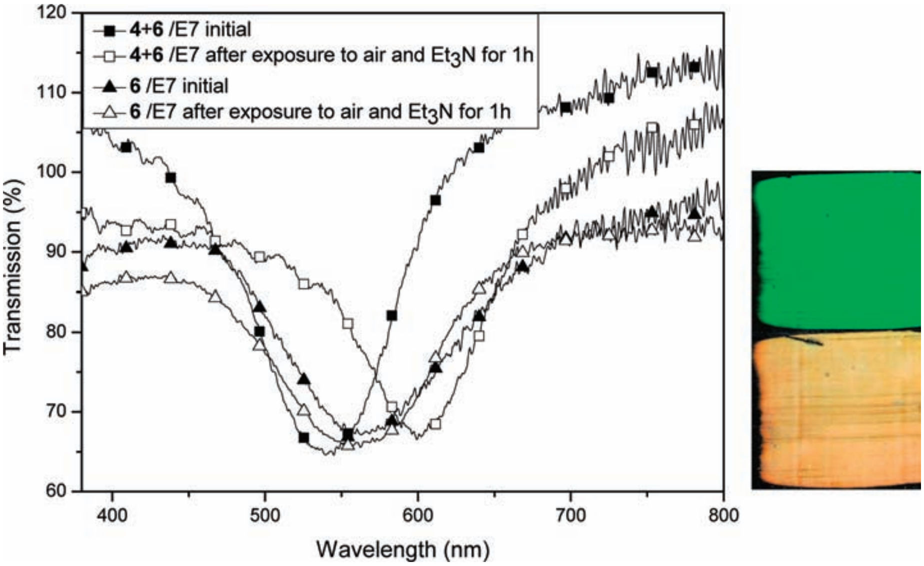
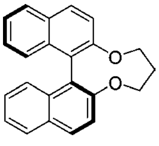


Figure 6. Transmission spectra of samples with **4** + **6** (squares) and **6** as dopant (triangles) in E7 before (solid symbols) and after (open symbols) exposure to air in the presence of triethylamine. At the right are given images of the CLC film before (top) and after (bottom) exposure to air for 1 h in the presence of triethylamine.

$= -65\ \mu\text{m}^{-1}$ both experimentally and theoretically,[22] while the HTP of **4** in E7 was measured to be $\beta_M = -13\ \mu\text{m}^{-1}$. The low HTP of **4** in combination with a limited solubility of oxidation product **5** in E7 (~1 mol %) precluded the use of **4** as the sole dopant in a CLC-based oxygen monitor, because it was practically impossible to obtain a CLC film containing **4** with a pitch length corresponding to the wavelength of visible light that would not give rise to precipitation of **5** after exposure to oxygen. In order to solve the solubility issues, the nonreactive chiral binaphthyl **6** of high HTP ($\beta_M = +79\ \mu\text{m}^{-1}$ in E7)[22] was used as codopant to bring the reflection band in a system with a low concentration of **4** to the visible region.[23]



S-**6**

For monitoring of O_2 with a CLC film, 0.9 mol % of **4** and 4.2 mol % of **6** were dissolved in E7 to form a homogeneous mixture. A thin film was prepared with a reflection band at 542 nm. After exposure to air in the presence of triethylamine vapor for 1 h, the reflection band had shifted to 600 nm, with an obvious color change from green to orange (Figure 6), reflecting a decrease of HTP. The oxygen monitoring rate was lower than that in DMF solution, which is probably due to the solvent effect on the rate of amine-catalyzed oxidation.[18] The result of a control experiment with **6** (3.9 mol %) as the only dopant component in E7 is also shown in Figure 6. After exposure to air in the presence of triethylamine vapor, the position of the reflection band remained unchanged. Another control experiment was performed in the presence of triethylamine vapor but under an inert nitrogen atmosphere. The position of the reflection band or color of the film showed no obvious change (Figure S11, Supporting Information). Therefore, the change in HTP induced by oxidation of the chiral dopant **4** is solely responsible for the monitoring of oxygen. It should be noted that the oxygen monitoring is irreversible under the monitoring conditions: that is, if the monitor is applied inside a packaging, it is favorable for the permanent recording of the oxygen contact history of the product.

The concentration-dependent response toward O_2 concentration is shown in Figure S12 (Supporting Information). When the O_2 concentration was decreased from 20% to 1%, the response time to reach complete conversion increased approximately 50% to approximately 60 min. The temperature dependence of both the unbound and bound O_2 monitor is shown in Figure S10 (Supporting Information). A sample with **6** in E7 was used as the reference. Both the bound and unbound states of the monitor gave the same trend as the reference, with a small shift of about 1.5% of the reflection band position in the temperature range from 10 to 35 °C, much smaller than the shift due to reaction with O_2.

Conclusions

In this report, we have introduced the use of changing the HTP of responsive chiral dopants in CLCs for chemical monitoring of gases by induction of color changes that can be detected by the naked eye. We demonstrate that the present approach can be applied in the monitoring of an analyte that interacts with chiral dopants in either a chemical or a supramolecular way. For CO_2 monitoring, a diamine/diol complex was utilized to undergo a reaction with CO_2 and a strong change in helical twisting power and color in the CLC system. CO_2 monitoring is reversible, on the basis of the equilibrium complexation of diamine with CO_2 to give carbamate, indicating a continuous response to the contact of CO_2, although the decomplexation of CO_2 is slow. Oxygen monitoring was realized by using a responsive binaphthyl dithiol derivative, which

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changed its conformation and twisting power upon oxidation with molecular oxygen in air to form disulfide in the presence of base catalyst. The oxygen monitoring process is irreversible and indicates the cumulative exposure to oxygen. The determination of the detection limits of the present CLC monitors in combination with new chiral dopants with functional groups which give faster response and the detection of other analytes are in progress.

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Supporting Information Available: Text and figures giving experimental procedures, full spectra of Figures 1−3, a Job's plot and proton NMR titration curve of **1·3**, and transmission spectra of control experiments for carbon dioxide and oxygen monitoring. This material is available free of charge via the Internet at http://pubs.acs.org.

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