Functional liquid crystal films selectively recognize amine vapours and simultaneously change their colour

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During recent years, cholesteric liquid crystals have found only a few applications, one of them being temperature detection; in this study, however, we intend to show that the combination of cholesteric liquid crystals and molecules with a trifluoroacetyl function can be applied to optically detect amine vapours.

Liquid crystalline materials have found widespread application in laptops, mobile phones, or PC games, and are now used to develop large flat screen television sets. Often they are composed of linear molecules with (a) medium length alkyl chains, (b) benzene or cyclohexane moieties and (c) nitrile, trifluoromethyl or fluoro substituents. These types of liquid crystals are called nematic liquid crystals.[1] Their transparency to polarized light depends on their alignment and orientation between two polarizers with a twist of 90 degrees.

A special form of the nematic liquid crystals are chiral nematic liquid crystals, also known as cholesteric liquid crystals.[2] In this phase the molecules are gradually twisted against each other, so that they form a helical structure. The length of a 360 degree rotation is called the pitch. If the length of the pitch corresponds to the wavelength of light, then this light is reflected with different efficiency. The colouration depends on ambient temperature as with an increase of temperature the length of the pitch rises and accordingly colour changes are observed. Consequently, the main application of cholesteric liquid crystals is temperature detection. The length of the pitch, however, may also be modified through the embedding of foreign molecules. This approach has already been used to detect vapours of organic solvents (*e.g.* acetone, benzene, methanol or chloroform) albeit without selectivity in the recognition process.[3] Here, we have evaluated an alternative procedure to selectively detect amine vapours.

Recently, different chromogenic and fluorogenic structures with trifluoroacetyl functions were developed to detect biogenic amines or alcohols.[4] While these trifluoroacetyl structures are generally sensitive to aliphatic and aromatic amines, the detection of alcohols requires the addition of the catalyst tridodecylmethylammonium chloride.[5] The trifluoroacetyl dyes have been modified in chemical structure so as to obtain absorbing and fluorescing chemosensors with tailored optical characteristics, sensitivity and selectivity. However, one inherent limitation is their photochemical stability. Generally speaking, long-wavelength absorbing and fluorescing structures are often photochemically decomposed and are no longer of use for optical evaluation.

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One reason for the success of liquid crystalline displays (LCDs) is their high operational stability. We wanted to combine the chemical stability of liquid crystalline materials with the chemosensor characteristics of our trifluoroacetyl receptors. Therefore, we synthesized cholesteryl benzoate with a trifluoroacetyl receptor attached to the benzene moiety, termed LCR-262.† This chemosensor was synthesized by converting 4-trifluoroacetylbenzoic acid with thionyl chloride into the corresponding benzoic chloride[6] and then was esterified with cholesterol in a mixture of pyridine and chloroform. LCR-262 was added to various mixtures of cholesteryl nonanoate (CN), cholesteryl oleyl carbonate (COC) and cholesteryl chloride (CC). The corresponding chemical structures are depicted in Fig. 1.

In the next step, the reflectance of the liquid crystal film (LCF) composed of the above components was investigated in the absence and presence of gaseous amines. White light in a spectral range 350–850 nm was directed onto a liquid crystal film at normal incidence using a fibre-optic diode-array photometer; then the reflected light was guided back to the detector of the photometer. In the course of the evaluation it became apparent that liquid crystal films composed of cholesteryl derivatives crystallized after several hours and were too liquid to remain stable on the substrate. Therefore, different amounts of structure-supporting polymers were added to raise mechanical stability and enhance the shelf lifetime. For this we used poly(methylmethacrylate) (PMMA) and polyurethane hydrogel (EG80A). Different compositions of the cholesteryl derivatives were finally used to prepare the LCFs, namely LCF1 composed of 12.2% CC, 32.4% COC, 32.4% CN, 15.4% PMMA and 7.6% LCR-262. LCF2 contained 12.7% CC, 29.9% COC, 29.9% CN, 20.3% PMMA and 7.2% LCR-262. LCF3 consisted of 15.3% CC, 33.4% COC, 36.1% CN, 6.8% EG80A and 8.4% LCR-262. Solutions of these cholesteryl derivatives in tetrahydrofuran were deposited onto planar

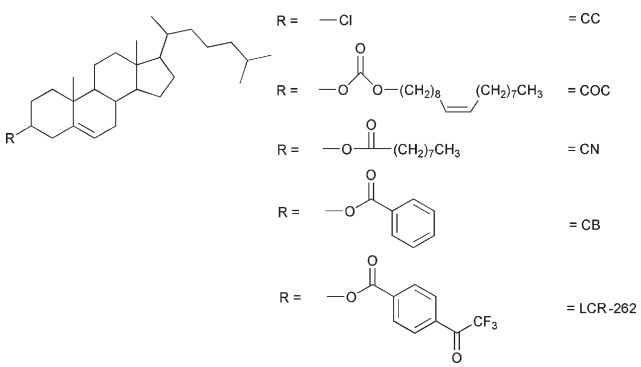

Fig. 1 Chemical structures of the cholesteryl derivatives and LCR-262.

substrates.‡ Films with a higher content of LCR-262 had a short shelf-time and crystallized within a few hours. Similarly, a higher content of polymer proved to be unsuitable because the film became inhomogeneous, as shown in Fig. 2. When the polymers were added to the cholesteryl derivatives, the films exhibited a significantly improved shelf lifetime, hydrophobic PMMA being superior over hydrophilic EG80A. Accordingly, LCF1 was stable for 52 days and LCF2 for 59 days, while LCF3 had a shelf life of 17 days only. During these periods the films were repeatedly used to detect amine vapours.

The following aliphatic amines were investigated as the analytes: 1-butylamine, diethylamine and triethylamine. The reflectance maximum of LCF1 was observed at around 477 nm. The interaction with 1-butylamine caused this maximum to shift to 503 nm when the concentration of 1-butylamine was as high as 3000 ppm. A similar behaviour was observed for LCF2 with a shift in the reflectance maximum from 473 nm to 523 nm and a concomitant change in colour from blue to green (Fig. 3). Fig. 4 illustrates the different stages of the visual colour change. In the case of LCF3, a shift from 474 nm to 520 nm was observed. When detecting diethylamine with a concentration as high as 8000 ppm, a comparable shift in the reflectance maximum was found. With LCF1, the shift was only 26 nm while it was 46 nm in the case of LCF2 and 49 nm in the case of LCF3. Only LCF1 did also react with triethylamine and showed a minor shift in the reflectance (6 nm), however, the reflectance decreased more strongly than in the case of 1-butylamine.

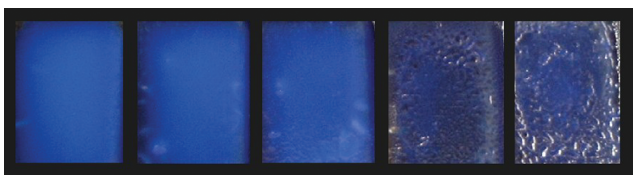

Fig. 2 Effect of increasing the polymer content on the homogeneity of the liquid crystal film LCF2 (from left to right: 6.8%, 15.4%, 20.3%, 26.7%, 35.3% PMMA).

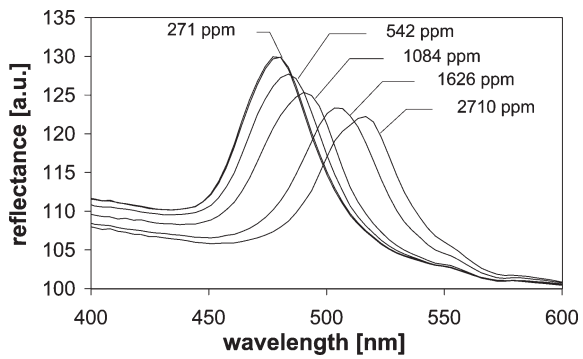

Fig. 3 Reflectance of LCF2 upon exposure to gaseous 1-butylamine.

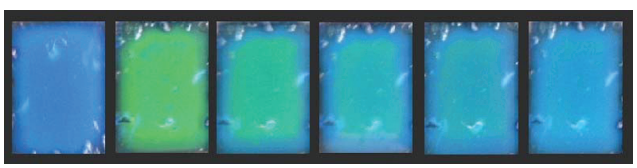

Fig. 4 Colour change of LCF2 (1st: initial colouration without analyte, 2nd: exposure to gaseous 1-butylamine, 3rd–6th: gradual recovery after removal of 1-butylamine).

In general, a higher sensitivity for 1-butylamine over diethylamine was observed (Fig. 5). This is due to the fact that primary amines such as 1-butylamine are less sterically hindered to interact with the trifluoroacetyl group of LCR-262 to form a hemiaminal than secondary amines such as diethylamine.[7]

In order to characterize the liquid crystal films with respect to forward and reverse response, time-course measurements at a defined wavelength were performed. The films generally showed longer forward and reverse response times in the presence of 1-butylamine than in the case of diethylamine (Table 1). The response behaviour of LCF2 upon exposure to diethylamine is given in Fig. 6. The regeneration time of the films was significantly longer for triethylamine (>24 h). We attribute this to the fact that 1-butylamine and diethylamine have a different reaction mechanism compared to triethylamine: both react with the trifluoroacetyl group to form a hemiaminal while triethylamine reacts with the trifluoroacetyl group to form a quarternary ammonium ion.[8]

The experiments were not only performed with films based on LCR-262 added but also with films having a similar amount of native cholesteryl benzoate (CB) to evaluate whether or not unspecific interactions would take place. None of these reference films showed colour changes with the amines under investigation.

In order to show that films based on LCR-262 were selective for gaseous amines, they were additionally exposed to gaseous acetone, methanol and ethyl acetate. No signal changes were observed with concentrations as high as 18 000 ppm of acetone, 8000 ppm of methanol and 7500 ppm of ethyl acetate.

Addition of polymers to liquid crystals usually leads to a so-called multi-domain polymer-dispersed liquid crystal, the individual domains of which are separated by thin polymer borders. If each domain is oriented perfectly with the helical axes normal to

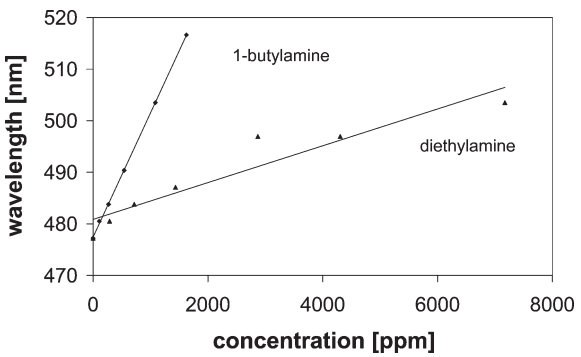

Fig. 5 Shift in the reflectance maximum of LCF2 upon exposure to 1-butylamine and diethylamine.

Table 1 Forward and reverse response times of the liquid crystal films[a]

	Forward response time/min			Reverse response time/min		
	BA	DEA	TEA	BA	DEA	TEA
LCF1	30 to 40	15 to 25	12 to 15	60	45 to 55	>24 h
LCF2	70 to 90	20 to 40	—	115	60	—
LCF3	15 to 30	12 to 15	—	30 to 40	30 to 40	—

[a] 1-Butylamine (BA), diethylamine (DEA), triethylamine (TEA).

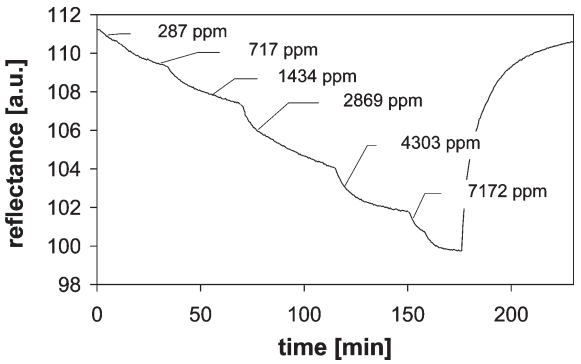

Fig. 6 Response behaviour of LCF2 upon exposure to different concentrations of diethylamine, measured at a wavelength of 477 nm.

the substrate surface (parallel to the *Z*-axis of the reference frame) the resulting state of helix orientation is called planar. In such a case, neither the reflected nor the transmitted part of linearly polarized light (incident along the normal of such a film) experiences depolarization.[9] Since we observed a non-zero cross-polarization (10% transmittance of the incident light through the liquid crystal film between crossed polarizers, independent of the wavelength), a purely planar alignment must be excluded.

In contrast to the planar alignment, there is also the possibility for a uniformly lying (quasi-planar) alignment, where the helical axes are oriented parallel to each other and parallel to the substrate surface. For such an alignment, the depolarization is a function of the relative orientation between the helical axes and the polarization vector. Therefore, any rotation around the *Z*-axis will lead to a change in the depolarization which was not observed in the present case. We therefore conclude that our films possess a focal conic alignment as is commonly observed for multi-domain polymer-dispersed liquid crystals.[9,10] Further investigation of this issue is in progress.

In conclusion, we have shown that by embedding selective cholesterol-based receptor molecules into liquid crystalline materials, we were capable of developing selective liquid crystal films for gaseous analytes such as aliphatic amines. We consider this approach to be generic in that by using other cholesteryl derivatives with appropriate receptor moieties, it will become possible to obtain liquid crystal sensor films for *e.g.* biogenic aldehydes, alcohols or volatile toxic agents.

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Notes and references

† Synthesis of LCR-262.

The amount of 0.4 g of 4-trifluoroacetylbenzoic acid was suspended in 2 ml of thionyl chloride and heated under reflux for 5 h. Then, the solution was evaporated to dryness and dissolved in 1 ml of toluene. This solution was carefully added to a solution of 0.71 g of cholesterol and 0.6 ml of pyridine in 2 ml of dry toluene cooled to 5 °C. The mixture was heated to 40 °C and stirred for 5 h. After evaporation to dryness, the residue was dissolved in 100 ml of dichloromethane, washed with 30 ml of 10% sodium carbonate solution and three times with water, evaporated to dryness and finally purified by flash-chromatography (60 g of silica gel 60) using dichloromethane : hexane = 1 : 1 as the solvent. λmax (chloroform) = 262 nm, λmax (hexane) = 258 nm, MS (*m*/*z*): 588, 370.

^{1}H-NMR ($CDCl_3$) δ: 0.62 (3H, s), 0.78 (3H, d), 0.79 (3H, d), 0.86 (3H, d), 1.00 (3H, s), 1.05–1.98 (28H, m), 4.82 (1H, m), 5.36 (1H, m), 8.05 (2H, d), 8.13 (2H, d).

‡ Preparation of liquid crystal films.

The glass substrates with a size of 9 × 14 mm were silanized prior to immobilisation of the liquid crystal films. They were cleaned in a mixture of concentrated sulfuric acid and 30% hydrogen peroxide (3 : 1 v/v) and silanized by exposing them to hexamethyldisilazane vapour for 15 h in an isolated container at room temperature and at ambient pressure. Finally, the lower side of the glass plates was blackened with matt black varnish.

For the preparation of the films 5.0% (w/v) stock solutions of CC, COC and CN in tetrahydrofuran were added to the respective polymer and LCR-262 to yield a 6.5% (w/v) solution of LCF1, a 6.9% solution of LCF2 and a 5.9% solution of LCF3. Then 50 µl of the respective solution was pipetted onto the silanized glass plate. After the evaporation of tetrahydrofuran a liquid crystal film was obtained.

The sensor film was fixed in contact with the optical fibre of the diode-array photometer and placed into a 100 ml flask closed with a septum, where different concentrations of gaseous amines were injected at 22 °C ± 1 °C.

Polarized transmittance spectra of samples lacking the black coating have been recorded on a Varian Cary 5000 instrument in the wavelength range 400–700 nm utilizing two Polaroid sheets, one acting as polarizer and the second as analyzer. For the measurements, the samples were oriented in a way that the substrate surface (*i.e.* the glass substrate which the liquid crystal solution was deposited on) was perpendicular to the ray direction (the *Z*-axis). A first series of measurements was carried out with the polarization direction of the polarizer and the analyzer being parallel and oriented either along the *X*- or the *Y*-axis. (*XX*- or *YY*-polarization), a second series of spectra was recorded with crossed polarization (*XY*- or *YX*-polarization).

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