Liquid crystal nose based on chiral photonic bandgap materials: principles of selective response

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Abstract
Chiral liquid crystalline (LC) compositions with the selective reflection band (SRB) in a visible spectral range are suggested and studied as elements of LC-nose. This allows for optical detection of several volatile organic compounds (VOCs): SRB shifts and color of the sample changes under the action of VOCs. Ethanol, toluene, pyridine and acetic acid were detected by means of colorimetric and spectroscopic techniques during their diffusion inside chiral elements of LC-nose. Selectivity to different VOCs is enhanced by means of components of liquid crystal matrix with different viscosity, affinities to the solvents, and abilities to form hydrogen bonding.

Keywords
Cholesteric liquid crystals · Gases · Volatile organic compounds · Chirality · Detection · Liquid crystal nose

There is a continuous need for creating materials and devices (artificial noses) that can respond to different kinds of pollutants including volatile organic compounds (VOCs) [1]. A VOC is one of a group of carbon-containing compounds that evaporates readily at room temperature with adverse health effects. The VOCs of environmental concern are often organic solvents (for example, toluene, ethanol, pyridine, and acetic acid). Commercially available VOC sensors with a wide range of sensitivities are deployed for detection of VOCs in outdoor and indoor environment [2]. Most of the current compact and inexpensive gas and VOC sensors are based on metal oxides that can change their resistance in different gases [3]. There are different types of sensors, some work at low concentrations, others may work at relatively high concentrations from hundreds to thousands ppm [2, 4]. Most of these sensors and their assemblies in electronic noses [5, 6] designed to selectively distinguish volatile compounds (especially aromatic compounds) require electric power to operate. Organic solvents producing VOCs are used in industrial environment, and there are certain limits on the daily exposure of workers to harmful concentrations of these VOCs [7]. The requirements, established by governmental agencies, are different for different solvents and vary by countries. They typical require a detection range between tens to thousands ppm. However, there is also a need for sensors working in harsh environments at higher concentrations of VOCs. For example, in places where the explosive limits are by orders of magnitude higher than exposure limits [7], the sensors responding to VOCs should be installed in locations where the presence of electrical equipment is not desirable. In our view, the passive sensors based on polymers with different sensitivity to organic solvents is a promising way to address and solve this problem. The goal of this study is to design some VOCs discriminating liquid crystalline materials in a simple laboratory device (Liquid Crystal nose) based on selective optical response to VOCs.

Efforts were undertaken to create sensitive and selective sensors based on different types of polymers and polymer compositions, including crystalline polymers [8], nanoimprinted polymers [9], cholesteric polymers [10], wearable polymer compositions with liquid crystals [11, 12]. The recent review [13] discusses other applications and developments. Very often environmentally sensitive polymers are organized in an array with different sensitivities of elements to specific compounds [14]. This type of organization

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provides higher selectivity of the whole sensor and mimics sensors arrangements in electronic noses [5, 6]. Increased sensitivity can also be obtained using a stratified array of photonic bandgap materials [15]. Such a technique may provide both better selectivity and sensitivity to a number of VOCs.

Photonic bandgap materials in a form of chiral or cholesteric liquid crystals (CLCs) were used for detecting VOCs as a single composition material [16–20] for detecting amines [16], alcohols and aldehydes [17–19]. CLCs were also coupled with optical fibers [21] for mixed VOC sensing.

Ideally oriented CLCs can be imagined as a twisted structure of nematic planes with uniaxial molecular orientation within each plane. The given helical pitch defines a period of planes rotation inside the CLC. CLCs possess a photonic bandgap (selective reflection band, SRB) for circularly polarized light with the same sense of polarization as their rotation. If nematic planes are parallel to the substrate the whole structure displays the SRB centered at a wavelength [22] given by the product of average refractive index and helical pitch:

$$\lambda = n_{av} p.$$  \hspace{1cm} (1)

Oblique light incidence onto the planar cholesteric structure shifts SRB towards shorter wavelengths. As discussed in Refs. [20, 23], the general principles of a CLC gas detection are all based on recording responses in the spectral position of the SRB. In these studies, the composition of LC sensor was not tailored for detection of wide range of VOCs and the response was studied for just a few VOCs.

Recently [24], a promising approach, based on exploiting materials with different viscosities as the sensor elements, was employed for two types of VOCs, cyclohexane and ethanol. In the present publication, we propose a generalized approach describing a sensor (multielement array) with individual elements made of CLCs with compositions tailored for detecting specific VOCs (Fig. 1). This sensor displays a selective optical response to a number of VOCs of different polarities ranging from the acetic acid to toluene and essentially constitutes a peculiar type of sensor—liquid crystal nose (LC-nose). The sensor is passive, its response corresponds to color and/or spectral changes that makes it different from classical e-noses [5, 6]. Each element of the array is a droplet of CLC with a composition outlined in Fig. 1 (top panel). It is characterized by an individual response rate to a particular VOC, playing a role of the nose receptor. The whole array displays a characteristic response pattern or a fingerprint to a particular VOC.

The suggested formalism may be outlined as follows. We shall define the width of the SRB via the following band edges equations [22]:

$$n_o p \leq \lambda \leq n_e p.$$  \hspace{1cm} (2)
where \( n_e \) and \( n_o \) are ordinary and extraordinary refractive indices along the nematic planes. The diffusion of the VOC molecules inside the CLC matrix may result in changes of several parameters: (1) the order parameter \( S \) defining a degree of uniaxial molecular orientation in nematic planes; (2) the refractive indices \( n_e, n_o \) along with corresponding birefringence \( \delta n = n_e - n_o \); (3) the concentration of chiral molecules \( c \) producing a twisted structure; (4) the helical pitch \( p \) and twisting power for chiral solutes \( \beta = \frac{1}{p} \). Varying each of the parameters may result in a modified optical response. The induced shift of the stop band can be readily detected by means of spectroscopic or photographic techniques. These parameters are interdependent. For instance, the order parameter and birefringence are related via \( n_e = n_{nv} + \frac{2}{3} S \Delta n \), where \( S \Delta n \) is a birefringence in ideally oriented chiral planes \( (S = 1) \). Isotropic phase corresponds to \( S = 0 \) with no anisotropy inside nematic planes and no birefringence. In general, the precise order parameter \( S \) measurement for nematic planes in cholesteric liquid crystals is a complex task. It can be estimated by measuring birefringence and employing aforementioned equation for refractive indices. The value of \( S \sim 0.6 \) can serve as a good initial approximation.

The magnitude and rate of spectral response to the action of VOCs also depend on the diffusion rate of VOC molecules inside the matrix that in turn depends on the chemical nature of diffusant and viscosity of the matrix [24]. Taking these facts into consideration, we suggest an array-based sensor with elements consisting of multi-component CLCs responding to a particular VOC by changing predominantly either order parameter \( S \) or helical pitch \( p \). This is achieved by mixing components of CLCs capable to form specific physical bonds with the diffusant. More specifically, the wide range of affinities to the diffusant increase the response selectivity. The variable viscosities of some sensor elements affect the diffusion rate of specific VOCs thus contributing to improved response selectivity as well. The diffusant produced by a solvent effectively dissolving a specific CLC component has even greater effect on the whole composition provided that the concentration of that component gets higher. The proposed CLC compositions are based on the above outlined principles.

The chemical structures of the components are shown in Fig. 1. Compounds A and B are derivatives of chiral cholesterol, and their mixture (23:77 by weight) forms liquid crystal at room temperature with the selective reflection band at 620 nm. Both compounds are dissolved in toluene and should be sensitive to its vapor. Non-chiral compound E 4-methoxybenzylidene-4-butyilamine (MBBA) forms a nematic liquid crystal in its pure form. It is also capable to form hydrogen bonds with acids and alcohols through the nitrogen atom presented in its structure. Its pure form is dissolved in more polar solvents including ethanol and should be sensitive to its vapors. Compound D is methyladipic acid that exists in chiral and racemic forms and is not liquid crystalline. In its chiral form it twists the nematic phase forming left-handed chiral nematic phase. The presence of two acidic groups suggests that it can form strong hydrogen bonds with VOCs of acetic acid and pyridine and weak hydrogen bonds with ethanol. Such a complex of MAA with these compounds should have a different (presumably higher) twisting power than pure chiral MAA and, therefore, may affect the response by decreasing untwisting of cholesteric helix. Compound C is siloxane based oligomer forming a chiral glass at room temperature with the selective reflection band located at 550 nm. Dissolved in non-polar solvents, it provides sensitivity to their vapors, and it is also used here to vary the viscosity of the array elements, making them less sensitive to VOCs of non-polar solvents. The structure of the compounds suggests that their mixtures (compositions) presented in Fig. 1 (top panel) may respond to different VOCs through the aforementioned mechanisms involving specific inter-molecular interactions. The following four organic VOCs with different polarities and abilities to form hydrogen bonding were used in experiments: toluene, pyridine, ethanol, and acetic acid.

The sensor array comprised of eight elements shown in the top panel of Fig. 1 was placed on a glass plate. The plate was placed in a glassy Petri dish that was thoroughly sealed with the vacuum grease. The array then was exposed to a particular VOC freely evaporating at room temperature 21 °C from a solvent placed in a small open vessel at the bottom of the Petri dish. Concentration of VOC quickly reached saturation levels. VOCs diffused inside the droplets that resulted in (1) changes of droplets helical pitch and color, (2) decrease of order parameter \( S \) (see Eq. 3) and isotropization. The VOCs of four solvents ethanol, toluene, pyridine and acetic acid were used and identified by LC-nose in experiments. The care was taken of creating droplets of approximately the same mass. The color changes were continuously recorded by CCD camera during 30–40 min, followed by the analysis of color intensities in the red and green channels for different time intervals. The response function was then calculated for each element for the areas corresponding to c.a. 20% of the droplet surface near its edge as the ratio of intensity changes in the red and green channels. The negative response rate means that the changes of intensity in red or green channels happened in different directions. The responses related to color change and measured by CCD after 10 min of exposure time are shown in Fig. 2 (this corresponds to almost saturated vapors of VOCs). It can be seen that all responses are different and, therefore, all four VOCs can be selectively identified by this sensor at their high concentrations. Lower concentrations of VOCs can also be measured at shorter exposure times. The lowest concentrations measured by
CCD method correspond to c.a. 0.05 to detect even low concentrations. It is important to note that color changes (and a shift of the selective reflection band) happen first, followed by the isotropization of each droplet. It means that initially some diffusion of VOC molecules occurs inside liquid crystalline phase of the droplet, followed by isotropization. In terms of color loss (corresponding to isotropization), the sensor displays the fastest response to pyridine and toluene VOCs (isotropization occurs already after 3–4 min of exposure) and the slowest to ethanol for which isotropization starts in the thinnest part of the droplet 1 only after 40 min of exposure (Fig. 2a). However, all the compositions display some spectral and color changes within first 5 min of exposure (see Fig. 3). This should allow to lower the detection limit. The strongest response is displayed by first droplet (composition \(A_{0.73}B_{0.23}\)) to pyridine (Fig. 2b) and by second droplet to ethanol. Interestingly, the response of composition \((A_{0.73}B_{0.23})_{0.61}E_{0.49}\) (with MBBA) to ethanol is much faster than response of the pure composition \(A_{0.73}B_{0.23}\), confirming higher affinity between MBBA and ethanol. Composition

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**Fig. 2** Sensor response to different VOCs: a ethanol and acetic acid, b toluene and pyridine. The droplets are enumerated from droplet 1 (composition \(A_{0.73}B_{0.23}\)) counterclockwise as in the top panel of Fig. 1

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**Fig. 3** Spectral shift and narrowing of the selective reflection band under the action of the following compounds: a ethanol + composition \(A_{0.73}B_{0.23}\) (a.1) sample thickness 35 \(\mu m\) and (a.2) sample thickness is about 160 \(\mu m\); (b.1) toluene + composition \((A_{0.73}B_{0.23})_{0.9}C_{0.1}\) (more viscous than \(A_{0.73}B_{0.23}\)) sample thickness 180 \(\mu m\); (b.2) toluene + composition \((A_{0.73}B_{0.23})_{0.8}C_{0.2}\) (more viscous than composition \((A_{0.73}B_{0.23})_{0.9}C_{0.1}\). The call out numbers correspond to the expose time to ethanol in minutes.
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The character of spectral response also allows identifying the particular VOC. Various thin-film compositions were exposed to evaporating VOC. Recording the spectral changes (via Ocean Optics spectrometer) under the same experimental conditions allows detecting VOCs at much lower exposure times and calculating (see the supplementary materials for details) the shift of the selective reflection band and birefringence. This is illustrated in Fig. 3 (a.1) for the pair ethanol + composition \(A_{0.73}B_{0.23}\) and a film thickness of c.a. 35 \(\mu m\). The shift of the selective reflection band is already observed after 5 min of exposure and increases after 20 min; the width of the selective reflection band decreases as a function of exposure time. The refractive indices were measured by means of refractometry for composition \(A_{0.73}B_{0.23}\) and turned out to be 1.485 and 1.515 at 21°C. Eq. (1) were used to calculate helical pitch of the system \(p = 419\) nm by dividing a magnitude of the spectral position of the SRB center by the average refractive index \(n_{av} = 1.505\). It can be seen that the width of the selective reflection band determined from Eq. (2) is smaller than the width found in experiments. This can be explained in terms of non-planar structure of CLC films, slight fluctuations of helical pitch, and collimation of a light beam used in experiments. Thicker samples display much wider SRBs since disorientation of the domains and light scattering contribute significantly to SRB widening. This is seen in Fig. 3 (a.2) where spectral changes for a thicker film (c.a. 160 \(\mu m\)) of composition \(A_{0.73}B_{0.23}\) in ethanol atmosphere are presented. The smaller spectral shift of c.a. 25 nm of the whole SRB towards longer wavelength is seen in the thicker sample comparing to a shift of about 50 nm in the thinner sample (Fig. 3a). The similar spectroscopic changes occur for all other compositions and other VOCs. The spectral changes are all reversible, taking a shortest time for a pair composition \(A_{0.73}B_{0.23}\) + ethanol and much longer time for compositions \((A_{0.73}B_{0.23})_xC_{1-x}\) and toluene. The role of Wacker compound in increasing viscosity of compositions and decreasing diffusion rate of toluene is seen in Fig. 3. The transmission spectra of the two films with similar thicknesses (c.a. 180 \(\mu m\)) and increasing concentration of Wacker oligomer are presented. It can be seen that complete isotropization is achieved after 15 min in a film of composition \(A_{0.73}B_{0.23}\) (Fig. 3 (a.1)), it is not yet achieved in a film of composition \((A_{0.73}B_{0.23})_{0.9}C_{0.1}\), in which concentration of Wacker oligomer is close to 10% after 17 min of exposure (Fig. 3 (b.1)) and it is far from being achieved in a film of composition \((A_{0.73}B_{0.23})_{0.8}C_{0.2}\) after 25 min (Fig. 3 (b.2)).

Although the impressive selectivity of this sensor is demonstrated for the first time, the sensitivity of the sensor is somewhat depressed by non-planar structure of chiral droplets that increases with increasing the droplet’s size: it is well known that free cholesteric surface of large samples exposed to the air tend to adopt homeotropic orientation. This is seen in Fig. 3, where the transmission spectra show significant widening of the spectrum of composition \(A_{0.73}B_{0.23}\) due to the disorientation of the domains and increased light scattering when the thickness of the sample increases by a factor of ten. A similar spectral widening is observed for other samples. It is important to note that only some degree of widening can be explained in terms of domains disorientation. Indeed, the spectral position of the SRB depends on the angle of incidence of incoming light in accordance to Bragg’s equation. Thus, any disorientation of the planar CLC domains inside the droplet will result in spectral shift of the reflected (and transmitted) light. Thick CLC samples contain numerous domains along a light pass and the spectra of outcoming light will display the effect of disorientation by adding spectra centered at different wavelengths and widening the selective reflection band. The results of light transmission modeling conducted in accordance with Berreman method [25] for composition \(A_{0.73}B_{0.23}\) are the following. The refractive indices were measured to be \(n_p = 1.485\) and \(n_e = 1.515\), the birefringence of the sample then is \(\Delta n = 0.03\), the order parameter was assumed to be \(S = 0.6\). The calculations were performed for the samples of thickness 12 helical pitches and 48 helical pitches (the details of the calculations are presented in supplementary materials). Transmission spectra of thin samples can be well approximated by averaging over different orientations of the domains ranging from 0° (planar orientation) to 50.3°. Transmission spectra of thicker samples can be approximated by averaging over mentioned domain orientations. Thus, the disorientation inherently presented in the droplets can be suppressed by decreasing the size of the droplet that should also increase the overall sensitivity of the method.

In conclusion, the compositions of liquid crystals, liquid crystalline oligomers and non-mesogenic compound were designed and studied as the elements of LC-nose. The array of eight elements, liquid crystal compositions with varying viscosities and affinities to four VOCs (ethanol, acetic acid, toluene and pyridine), displayed a selective spectral response. The use of LC arrays for gas detection opens some opportunities in developing novel compact and wearable LC sensors.

The data that support the findings of this study are available from the corresponding author upon reasonable request.

See the supplementary material for a detailed description of transmission simulations used for describing some key theoretical calculations in the manuscript.
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