Perdeuterated liquid crystals for near infrared applications

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Abstract

For majority of Liquid Crystalline compounds the absorption occurs at two spectral regions: ultraviolet UV (due to electronic excitations) and infrared IR (caused by molecular vibrations). Both cause the absorption which deteriorates electro-optical modulation abilities of LC. In the MWIR and LWIR regions, there are many fundamental molecular vibration bands. The most intense are the ones with high anharmonicity, which in the case of LCs corresponds to the C-H bonds, especially present in the aliphatic chains. In the NIR region, overtone molecular vibration bands derived from IR region begin to appear. In the case of C-H bond system, the first overtones are present at 1.6-1.7 microns. To reduce NIR absorptions, perdeuterated Liquid crystal has been proposed. In this paper, we report the physical and optical properties of liquid crystals based on polarimetry measurements method. We also provide a polar decomposition of experimentally measured Mueller matrix in order to determine polarization properties of the device such as depolarization and diattenuation which cannot be obtained from absorption spectra.

Key words: Liquid crystals, Infrared, Deuterium atom, Mueller matrix, Polar decomposition

1. Introduction

Liquid crystals (LC) whose optical properties are modulated by an electric field, exhibit interesting electro-optical properties which make them useful for photonic applications such as non-mechanical beam steerers [1], phase shifters and vortex generators [2]. For these applications, properties such as low absorption, wide nematic temperature range, high birefringence, low viscosity and large dielectric anisotropy are required. For the last 10 years there has been a substantial interest in the use of LCs for near infrared (NIR) applications [3]. However, strong absorption of light in nematic LCs has been observed at specific regions of

infrared which affects modulation performance, as well as physical properties. Minimizing absorption is important in order to maximize the optical efficiency and to preserve the light modulation capability of the device under study [4]. Many attempts have been made to improve the properties of nematic LCs for mid-wave infrared applications [5]. The absorption occurs when atoms in a LC molecule are in periodic motion. The molecular vibration bands depend on the spring constant and on the reduced mass of the diatomic group. As the reduced mass increases, the absorption band shifts toward a longer wavelength. Increasing the weight of one of the elements of the harmonic oscillator will cause frequency reduction of the fundamental vibration. Therefore, absorption bands can be moved toward longer wavelengths by shifting absorption peaks out of the electromagnetic spectrum of interest. By using a perdeuterated nematic LC, where hydrogen atoms in alkylchains and aromatic rings are replaced with deuterium atoms, one can increase the atomic mass of vibrating system causing vibration frequency to decrease and the absorption to shift toward longer wavelengths[6]. There are two synthetic methods to obtain deuterated LCs. The first approach is to adapt a synthetic scheme of non-deuterated isotopoanalogue and to use deuterated starting reagents. The second approach based on isotopic exchange where at chosen semi-product stage the exchange of C-H to C-D is performed usually on transition metal surface (Pt, Pd) in heavy water as a source of deuterium [6]. In this work we measure and compare polarimetric properties of perdeuterated and non-deuterated 5CB at NIR region in order to understand their electro-optical behavior and to optimize molecular design structure to be employed in spatial light modulators operating over entire telecommunication windows. Measuring Mueller matrix for a wavelength near absorption bands provides data on depolarization and diattenuation effects which limit performance of the LC modulator. Lu–Chipman decomposition of the Mueller matrix [7] will be applied to liquid crystals cells. Interesting but usually not considered information concerning depolarization and diattenuation will be reported to evaluate LCs for NIR applications.

Synthesis and preparation of the sample

Several approaches of shifting vibration bands outside the spectral region of interest can be considered. The change of reduced mass of the vibrating system by exchanging C-H to C-D is one possible approach. A bigger change of the reduced mass of the vibrating system attained by exchanging C-H to C-F can also be considered, but the mesomorphic properties are strongly affected by heavy fluorination for which a strong suppression of nematic phase is usually observed [8]. In this paper, we propose and investigate a complete deuteration at

terminal chain and aromatic rings starting the synthesis with deuterated chemicals of high purity (>99% of Deuterium atoms). There are two approaches to deuterated LC (5CB compound) which have been published in the literature. The first one is based on a synthesis of the conventional hydrocarbon skeleton (4-alkylbiphenyl) and forcing the hydrogen-deuterium exchange using Pd or/and Pt, and D₂O as a source of Deuterium: and finally introducing a fragile polar CN group. (Disadvantage of this method is that at some parts of molecule – usually in alkyl parts the exchange is poor <85-90%) [5]. The second one is to develop dedicated synthetic methods starting with already deuterated raw chemicals and synthesizing the LC molecule in conventional multistep synthesis. The advantage of the second approach is that isotopic purity is maintained at high level. The material measured in this paper has been synthesized according to modified literature procedure described in [8].

The mesogenic properties							
	Nematic Phase	//			K ₁₁	K ₃₃	K ₃₃ /K ₁₁
5CB	22.5-34.2	19.1	6.3	12.8	9.96	11.8	1.19
D5CB	21.6-32.9	18.1	6.4	11.7	7.1	8.5	1.19

Table. 1. Mesogenic properties of 5Cb and D5CB materials.

We have measured the mesogenic properties of D5CB and we compared the results with those obtained for nondeuterated 5CB [6] in order to find the relationships between those two different structures and their mesogenic properties. The results show that the melting and clearing temperatures of D5CB are about 1 and 2 °C lower than those for 5CB, respectively. D5CB has slightly lower dielectric anisotropy and optical anisotropy which might be attributed to stronger C-D bond vs. C-H systems and weaker intermolecular interaction as an effect of lower electronic polarizability of deuterated isotopoanalogue of 5CB. The same origins have differences of elastic constants, which are related to intermolecular interactions and are generally weaker for deuterated isotopoanalogues due to lower electronic polarizability.

2. Sample preparation and measurements

Test cells were prepared with ITO-coated polished glass plates. Homogeneous planar alignment was induced on the ITO by a spin-coated SE-130 polyimide followed by curing and antiparallel rubbing process steps. The cells' thickness was about 15 μm, thick enough to allow the LC to induce more than π retardation between the fast and the slow polarization of light in a transmission mode for the NIR. To provide full characterization of LC, it is highly

desirable that Mueller matrix of the LC cell is known in order to measure the three general polarization properties such as diattenuation, retardance and depolarization. Additionally, there were calculated total losses of the prepared samples.

Figure.1: Polarimetry setup

To provide the full characterization of LC, the cell was inserted into the polarimeter system (Fig.1). It consists of a source, polarization state generator (PSG) constituted by a linear polarizer followed by quarter-wave plate and a polarization state analyzer (PSA) consisting of the same elements but in reversed order and finally a detector. A quarter-wave retarder in (PSA) is continuously rotated followed by a fixed linear polarizer. One of the advantages of this configuration is that the polarization sensitivity of the detector will be eliminated because the orientation of the final polarizer is fixed, therefore, it only transmits the portion of light which is parallel to the transmission axis; in this case the analyzer transforms the polarization modulation into an amplitude modulation. The linear polarizer and quarter wave plate combination in PSG, enabled generation of the six required input polarization states. For each of the six different states of polarizations, the Stokes vector of transmitted light by an LC cell is determined. This polarimeter allows to measure output state of polarization (SOP) with accuracy of $\pm 2^\circ$ and degree of polarization (DOP) with accuracy of ± 0.02 .

The Mueller matrix in function of applied voltage was generated using standard relationships between its 16 elements and the measured output Stokes parameters for each of the six input polarization states for 5CB and D5CB [9]. In Figure 2 we present Mueller matrix elements for 5CB (dashed line) and D5CB (solid line) measured at a wavelength of 1550nm, for different voltages within the voltage range from 0V to 6V. Note that for each value of the applied

voltage, the Mueller matrix was normalized by m_{11} element. In both cases this matrix structure suggests that this type of optical element is defined as a retarder with apparent diattenuation [10] whose value had been significantly reduced in D5CB material.

Figure.2: Measurements of the sixteen Mueller matrix Coefficient versus voltage for 5CB (dashed line) and D5CB (solid line) at a wavelength of 1550nm

The Mueller matrix parameters presented in Figure 2 give full information about the optical polarization parameters of the liquid crystal cell. The difference between the transmissions for incident horizontal and vertical linearly polarized is shown in M_{01} , M_{10} elements. It indicates that the D5CB can be considered as a -diattenuator device. The variation of the elements M_{22} , M_{23} , M_{32} and M_{33} is caused by the changes in the retardation induced by LCs upon applied voltage. Additional information about losses of the prepared LC cells we extract directly from non-normalized M_{00} parameters with the following formula:

$$\alpha = -10 \log_{10} M_{00} \quad . \quad (1)$$

Taking into account the above relation, were calculated losses for all tested samples for three selected near infrared spectral region wavelengths, i.e. 1390nm, 1550nm and 1630nm shown in Figure 3.

Figure.3: Losses calculated from non-normalized M_{00} elements of Mueller matrices at wavelength of: (a) 1390nm, (b) 1550nm and (c) 1630nm for 5CB and D5CB

By analyzing these figures we can conclude that losses vary under applied voltages. For wavelengths of 1390nm and 1630nm losses measured in a cell filled with 5CB are higher than those measured in cell filled with D5CB. However, for a wavelength of 1550nm losses for D5CB increase because at this wavelength the absorption band is present in this material, being the second overtone of C-D vibrations, see Figure 4 previously published elsewhere by our group [12].

Figure.4: Comparison of absorption for 5CB and D5CB at NIR range with indication of characteristic C-H and C-D overtone bands.

Sixteen elements of the Mueller matrix from Figure 2 carry information about polarization properties of the LC cell considered in this work. These parameters can be efficiently extracted by decomposing the Mueller matrices into the “basic” Mueller matrices of retarder, diattenuator, and depolarizer performing the polar decomposition, described by Lu and Chipman [9]. This decomposition states that a general Mueller matrix M can be written as the product of three matrices: of diattenuation, retardance, and depolarization. The matrix can be decomposed as follows:

$$\mathbf{M} = \mathbf{M}_A \mathbf{M}_R \mathbf{M}_D \quad . \quad (2)$$

M is the depolarization matrix; M_R is the retardance matrix; M_D the diattenuation matrix. It is important to note that because the multiplication of Mueller matrices is not commutative, the results of this decomposition depend on the order in which the three elementary matrices are multiplied [11]. The proposed order leads to a physically realizable Mueller matrix. This order of decomposition has been adopted in this work. The phase shift of light introduced by the sample at any given voltage can be calculated from the retardance matrix. The retarder matrix provides a full specification of the cell’s retardance parameter that represents the combined effect of linear and circular birefringence. Linear retardance and its orientation angle can be used for the evaluation of the phase modulation and the circular retardance difference in phase between right and left circularly polarized light can be used for the evaluation of optical activity in the LC. The measured linear phase from polar decomposition is non-interferometric method; therefore, this technique is not sensitive to temperature and vibration.

Figure 5; plot the measured voltage dependent phase shift at three wavelengths in NIR region

Figure.5: Retardance performance calculated from Mueller matrix at wavelength of: (a) 1390nm, (b) 1550nm and (c) 1630nm for 5CB and D5CB.

for 5CB and D5CB. Note that the measured retardation is similar for both liquid crystals, since their mesogenic properties are comparable. Furthermore, this retardation is wavelength dependent, shorter wavelengths give rise to larger phase modulations depths.

The value of diattenuation is obtained from the first row of the of the Mueller matrix:

$$D = \sqrt{M_{01}^2 + M_{02}^2 + M_{03}^2} \quad (3)$$

Diattenuation measurements provide information about the dependence of the intensity transmittance of LC on? incident polarization state. This parameter is undesirable in an electro-optical modulator, because it causes some deviation from ideal retardance modulation achieved by LC upon switching. The techniques to determine the absorption spectrum proposed in the literature [4] do not measure the linear or circular diattenuation of the LC in NIR for 5CB and D5CB. To determine those parameters the Mueller matrix elements of LC under study should be considered. Mueller matrix which transforms the Stokes vector of incident light to the Stokes vector of transmitted light by a LC cell contains complete information about all the polarization properties of a given LC. Taking into account other important polarimetric parameters such as retardation and depolarization.

Figure.6: Diattenuation calculated from Mueller matrix at wavelength of: (a) 1390nm, (b) 1550nm and (c) 1630nm for 5CB and D5CB.

Figure 6 shows diattenuation variations with respect to the voltage for the operation wavelengths of 1390 nm, 1550 nm and 1690 nm. Furthermore, the diattenuation variation is different for each wavelength. Non-null values of diattenuation indicate that, depending on the incident polarization state, there are some differences in light transmittance. In the case of D5CB, the averaged diattenuation for all voltage values are lower than 0.1, which indicates that the intensity transmitted by these LCs weakly depends on the polarization state of the incident light. However, in the case of 5CB the diattenuation is higher within voltage range corresponding to 2π linear phase dynamic range. It is interesting to find that in the case of 5CB two maximas of diattenuation are located at 0.75 V and 1.25V, corresponding to 0.5π and 1.5π modulation deep which indicates that the diattenuation for 5CB varies within the phase modulation deep, of π in this range of voltage. This will induce an unfavorable effect, in the interest of using 5CB as half wave plate retarder. In this case the presence of linear

diattenuation avoids the device to switch exactly between two circular polarization states or between two orthogonal linearly polarized states. The larger the linear diattenuation, the further from orthogonal are the initial and final polarization states.

Figure.7: Depolarization coefficients calculated from Mueller matrix at wavelength of: (a) 1390nm, (b) 1550nm and (c) 1630nm for 5CB and D5CB.

Figure 7 shows the depolarization coefficients versus voltage. This parameter can be considered as a pure depolarizing transfer function of the medium. Since the six states of polarization used to generate the Mueller matrix are equally distributed along the Poincare sphere, this average shows the tendency of the cell to depolarize light. Depolarization coefficient measured in this work shows that at the shorter wavelength (1330nm) the lower is the depolarization effect. As the wavelength increases the depolarization effect increases up to 6% for an incident wavelength of 1550nm and 1630nm. This depolarization effect measured in LC was previously studied and demonstrated [13, 14]. In general, this depolarization effect in LC is related to scattering and time fluctuation of state of polarization of the transmitted light by a thick LC cell used in this work. Our results reveal that it is very desirable to operate with D5CB achieving linear phase retardation without coupled retardation or depolarization modulation. Hence phase only modulation device can be obtained in NIR using perdeuterated liquid crystals.

The accuracy in a Mueller matrix measurement has been verified according to the algorithm used in [15]. The uncertainty parameters, which determine accuracy of calculated elements of matrices from Figure 2 can come from the measured input and output elements of Stokes vectors. Based on the above, we have calculated uncertainties of Mueller matrices and optical parameters with accuracy of less than 5%.

3. Conclusions

We have described the preparation and physical properties of a new class of materials which offer low absorption at near infrared light. The synthetic approach undertaken in the preparation of the measured material gives precise control of high level of deuteration, what is clearly visible on 5CB and D5CB absorption comparison, exhibiting no absorption at the C-H first harmonic region for deuterated analogue. Polarization properties of cells under study have been efficiently extracted using polar decomposition of the experimental Mueller matrix. The intensity transmitted by deuterated liquid crystals weakly depends on the polarization state of the incident light in near infrared, therefore it leads to even further improvement in modulation properties of liquid crystals. Calculated optical parameters depend on applied voltage. For calculated loss, diattenuation and depolarization we observe oscillations in switching region and for retardance this effect is not present. This phenomenon will be studied in the next step of our project.

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