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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 μm. 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.

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 string 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.

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1.1. 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 D_2O 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 Ref. [8]. (Table 1).

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 deutrated 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 2π 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.

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 ±2° and degree of polarization (DOP) with accuracy of ±0.02.

Table 1
Mesogenic properties of 5CB and D5CB materials.

The mesogenic properties							
	Nematic Phase	$\varepsilon_{//}$	$\varepsilon_{\perp}$	$\Delta\varepsilon$	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

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 Fig. 2 we present Mueller matrix elements for 5CB (dashed line) and D5CB (solid line) measured at a wavelength of 1550 nm, for different voltages within the voltage range from 0 V to 6 V. Note that for each value of the applied voltage, the Mueller matrix was normalized by $\mathbf{M_{00}}$ 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.

The Mueller matrix parameters presented in Fig. 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 light is shown in $\mathbf{M_{01}}$, $\mathbf{M_{10}}$ elements. They indicate that the D5CB can be considered as a diattenuator device. The variation of the elements $\mathbf{M_{22}}$, $\mathbf{M_{23}}$, $\mathbf{M_{32}}$ and $\mathbf{M_{33}}$ 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:

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

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

By analyzing these figures we can conclude that losses vary under applied voltages. For wavelengths of 1390 nm and 1630 nm losses measured in a cell filled with 5CB are higher than those measured in cell filled with D5CB. However, for a wavelength of 1550 nm 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 Fig. 4 previously published elsewhere by our group [12].

Sixteen elements of the Mueller matrix from Fig. 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: