



Luminescent columnar liquid crystals based on 1,3,4-oxadiazole



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ABSTRACT

In this study five new compounds, derivatives of 1,3,4-oxadiazole, were synthesized in order to achieve mesomorphic behavior and luminescence. Different types of aliphatic chains were used in order to investigate the influence of alkoxide groups in mesomorphic behavior. All of the compounds showed high thermal stability and strong blue photoluminescence in solution and in solid films. Furthermore, compounds **10a–d** presented hexagonal columnar mesomorphism, which was characterized by polarizing optical microscopy and X-ray diffraction, and strong π -stacking was observed. Notably, for two compounds (**10c,d**), the liquid crystal properties were preserved on cooling from the isotropic state to room temperature. These characteristics make these materials good candidates for application in organic electronics.

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1. Introduction

Since the first report of discotic liquid crystals (DLCs) by Chandrasekhar et al. in 1977,¹ the synthesis and study of these materials have been increasing exponentially, due to their great potential for application in organic devices.² DLCs are suitable for technological applications owing to the fact that these disc-shape compounds can self-assemble into molecular stacks, forming columns through π – π stacking interactions.³ The formation of these molecular columns leads to interesting properties, such as the formation of a semiconductor with unidimensional electrical properties, similar to a nanowire, where the aromatic rigid center acts as conducting core and the aliphatic chains function as an insulator around the semiconductor, increasing the efficiency of the charge-carrier mobility.⁴ This makes DLCs promising candidates for application in organic electronic devices, such as organic light-emitting diodes (OLEDs),^{2c,5} organic photovoltaic cells (OPVs),⁶ and organic field-effect transistors (OFETs).⁷

Liquid crystals offer many possibilities for their functionalization through hydrogen bonds leading to self-organized systems,⁸ arrangements with strong π -conjugation, which may promote luminescence, and the introduction of heterocyclic groups, which have a strong influence on their physical properties and mesomorphic behavior.⁹ Liquid crystals incorporating the

1,3,4-oxadiazole heterocycle have received significant attention since the first reports of their mesomorphic properties.¹⁰ They have become good candidates for application in organic electronics¹¹ due to high fluorescence quantum yields, charge-carrier mobility, and good chemical and thermal stability.¹² Thus, in recent years, various liquid crystals based on different molecular shapes, such as rod-like,¹³ dimers,¹⁴ polymers,¹⁵ 1,3,4-oxadiazole-based polycatenar,¹⁶ and star-shaped,¹⁷ and also bent-core LCs, have been reported.¹⁸ Oxadiazole molecules are among the most widely investigated as electroluminescent materials and as electron-transport materials in OLEDs,¹⁵ where a series of compounds containing the 1,3,4-oxadiazole ring, such as the compound 2,5-bis(4-naphthyl)-1,3,4-oxadiazole, has become one of the top organic electron conductors.¹⁶

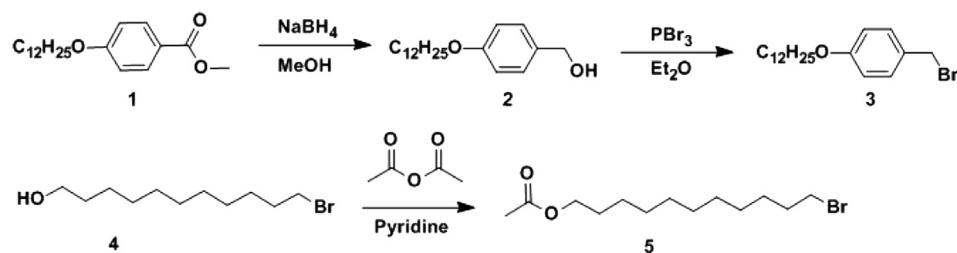
In this paper, we report the synthesis of new compounds, based on a 1,3,5-trisubstituted benzene core with threefold symmetry using three 1,3,4-oxadiazole arms, with a total of six peripheral aliphatic chains attached to the three terminal benzene rings. Their mesophase behavior was studied by differential scanning calorimetry, polarizing optical microscopy, and X-ray diffraction, which revealed mainly enantiotropic hexagonal columnar phases. However, the compounds containing six free hydroxyl groups at the end of the alkyl chain did not exhibit liquid crystalline properties. All compounds possess pronounced blue emission in solution and as thin films. For the films, the emission was also investigated as a function of the temperature, where a strong dependence with the mesophase was observed.

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2. Experimental section

2.1. Measurements and characterization

^1H and ^{13}C NMR spectra were obtained with a Varian Mercury Plus 400 MHz instrument using tetramethylsilane (TMS) as the internal standard. Infrared spectra were recorded on a Perkin–Elmer model 283 spectrometer using KBr disks or films. Mass spectra were recorded on a Bruker Autoflex III Smart beam with MALDI-TOF techniques, using α -cyano-4-hydroxycinnamic acid as the matrix, and high resolution mass spectra were recorded on a Bruker micrOTOF-Q II APCI-Qq-TOF mass spectrometer.



Scheme 1. Synthesis of bromide **3** and protection of compound **5**.

The textures of the mesophases were captured with polarizing optical microscopy (POM) using an Olympus BX50 microscope equipped with a Mettler Toledo FP-82 hot stage and a PM-30 exposure control unit. Thermal transitions and enthalpies were determined by differential scanning calorimetry (DSC) using the DSC-Q 2000 calorimeter. Thermogravimetric analysis (TGA) was carried out using a Shimadzu analyzer with the TGA-50 module. Elemental analysis was carried out using a Carlo Erba (model E-1110) instrument.

The X-ray diffraction (XRD) experiments were carried out on an X'Pert-PRO (PANalytical) diffractometer using the linear monochromatic Cu K α beam ($\lambda=1.5405$ Å), with an applied power of 1.2 kVA. The samples were prepared using procedures described in the literature¹⁹ with the heating and cooling of an amount of powder on glass plates. The scans were performed in continuous mode from 2° to 30° (2θ angle) with the samples in the mesophase, obtained by cooling from the isotropic state. The absorption spectra in solution were obtained with an HP UV–vis model 8453 spectrometer. The fluorescence spectra in solution were recorded on a Hitachi-F-4500.

The relative fluorescence quantum yields (Φ_{FI}) were determined according to a published method.²⁰ The absorption and fluorescence measurements for thin solid films were collected on an OceanOptics (USB4000) spectrophotometer.

For the absorption, spin-coated films were prepared on quartz glass plates with a concentration of 10 mg/ml, at 3000 rpm for 30 s. To investigate the photoluminescence as a function of the temperature the same samples used for the XRD were placed on a hot stage, illuminated with a UV lamp and the emission was captured with an optic fiber positioned close to the film.

Cyclic voltammetry analysis was performed to determine the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). A three-electrode cell was used, comprised of a glassy carbon electrode as the working electrode, a platinum wire as the counter electrode, an Ag^+/AgCl electrode as the reference, and the ferrocene/ferrocenium (Fc/Fc^+) redox couple as an internal standard. Before each measurement, the cell was deoxygenated by purging with nitrogen. Electrochemical measurements, using cyclic voltammetry, were

performed on an Autolab PGSTAT128N potentiostat/galvanostat (Eco Chemie, The Netherlands) connected to data processing software (GPES, software version 4.9.007, Eco Chemie).

The synthesis began with the preparation of two non-commercial bromides. The first compound was obtained starting from the methyl 4-(dodecyloxy)benzoate **1**, previously alkylated, which was reduced using NaBH_4 in dry methanol to give the benzyl alcohol **2**. This, in turn, was reacted with PBr_3 to obtain the 1-(bromomethyl)-4-(dodecyloxy)benzene **3**. In addition, the hydroxyl group of 11-bromoundecan-1-ol **4** was protected via the acetyl group by heating with acetic anhydride to give the bromide **5** (Scheme 1).

The synthetic route adopted for the preparation of the final compounds derived from 1,3,4-oxadiazole heterocyclic is shown in Scheme 2. Initially, with compound **6**, alkylation reactions were carried out using different bromides **3**, **5**, 1-bromoundecane, 3-(bromomethyl)heptane, and (*S*)-8-bromo-2,6-dimethyloct-2-ene and employing potassium carbonate and butanone under reflux.⁸ After obtaining the nitriles **7a–e**, these compounds were reacted with sodium azide and ammonium chloride in DMF to generate the corresponding tetrazoles **8a–e** through the Tiemann reaction.²¹ Following the synthetic route, the benzene-1,3,5-tricarboxylic acid was converted to its corresponding acid chloride with thionyl chloride and then immediately reacted with the tetrazoles **8a–e** in dry pyridine under reflux to afford the final compounds **10a–d**. The reaction applied to obtain the heterocyclic 1,3,4-oxadiazoles is followed by the intense liberation of nitrogen gas, which is characteristic of the Huisgen reaction.²² The **10e** molecule, with the acetyl group, was not isolated. After preparation, this compound was directly deprotected, remaining six free hydroxyl groups at the end of the alkyl chain. The hydrolysis reaction was carried out using sodium hydroxide in $\text{EtOH}/\text{H}_2\text{O}$ to obtain the respective compound **10f**. All compounds synthesized were characterized by ^1H and ^{13}C NMR and IR spectroscopy. Also, the final compounds were characterized by MALDI-MS (see Supplementary data).

3. Results and discussion

3.1. Mesomorphic properties

The phase transition temperatures of all of the compounds (**10a–d**, **f**) were initially established by POM and then accurately measured by DSC. The DSC results with their associated enthalpy changes are given in Table 1. The thermal parameters are taken from the first heating–cooling cycles of DSC scans. With the exception of **10f**, all compounds exhibited mesomorphic behavior, exclusively hexagonal columnar (Col_h), identified by the typical optical textures, where on cooling a dendritic growth from the isotropic liquid and a combination of mosaics with linear and fan shaped birefringent defects, together with homeotropic regions,

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